

STUDIES ON THE CONSEQUENCES
OF METAL-METAL
INTERACTIONS

Thesis by
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Abstract

A series of binuclear complexes $M_A(II)M_B(II)L^{+2}$ have been synthesized and characterized. The binucleating macrocyclic ligand, $L^=$, is a symmetric Schiff base composed of two 2,6-diformyl, 4-methylphenol units condensed with two 1,3-diaminopropane groups, resulting in two identical N_2O_2 coordination sites. The stepwise synthesis is described in detail. In all cases, $M_A(II) = Cu(II)$ while M_B was varied across the series $M_B(II) = Mn(II), Fe(II), Co(II), Ni(II), Cu(II),$ and $Zn(II)$.

The electrochemical properties of these species were examined by cyclic voltammetry, differential pulse polarography, sampled DC polarography, and coulometry. In each case reversible to quasi-reversible $Cu(II/I)$ electrochemistry was observed. The $Cu(II/I)$ reduction potential was, within experimental error, invariant with respect to the remote metal, M_B ; $E_f(Cu II/I) = -1.068$ V vs. ferrocene/ferricinium⁺. The one exception is the homobinuclear complex, $M_A(II)=M_B(II)=Cu(II)$; the homobinuclear complex was more readily reduced, $E^f = -0.925$ V vs. Fc/Fc^+ , than the heteronuclear species. The difference between the heteronuclear and homonuclear reduction potentials, 143 mv=3.3 kcal/mole, has been ascribed, after a correction due to magnetic stabilization,

to a special stability associated with the mixed valent Cu(II)Cu(I)L^+ species, where some electronic delocalization has been previously demonstrated. In addition, the electrochemical properties of homonuclear complexes ($M_A = M_B$) are reported.

The ligand binding properties of the species $\text{Cu(I)M}_B(\text{II})\text{L}^+$, $M_B(\text{II}) = \text{Mn(II)}, \text{Fe(II)}, \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)},$ and Zn(II) , have been examined. Cu(I) shows an affinity for axial based carbon monoxide, ethylene, tris (o-methoxyphenyl) phosphine, and 4-ethylpyridine. In contrast to the Cu(II/I) reduction potentials, the binding of axial bases to Cu(I) does seem to depend on the nature of the remote metal, M_B .

The magnetic properties of these square pyramidal 5-coordinate heteronuclear species were explored via variable temperature susceptibility measurements. Antiferromagnetism was observed in all cases. A trend toward increased coupling in traversing the series $\text{Cu(II)Mn(II)L}^{+2}$ ($J = -22.5 \text{ cm}^{-1}$), $\text{Cu(II)Fe(II)L}^{+2}$ ($J = -70.5 \text{ cm}^{-1}$), $\text{Cu(II)Co(II)L}^{+2}$ ($J = -81.0 \text{ cm}^{-1}$), $\text{Cu(II)Ni(II)L}^{+2}$ ($J = -103.0 \text{ cm}^{-1}$), and $\text{Cu(II)Cu(II)L}^{+2}$ ($J = -294 \text{ cm}^{-1}$) was observed. This same trend had been previously reported for isostructural square-pyramidal 5-coordinate homonuclear complexes. An effort to understand whether this trend was dominated by structural changes or electronic changes was

undertaken. New homonuclear complexes of $L^=$ were prepared in a pseudo-octahedral environment with pyridyl and imidazole bases occupying trans-axial positions. A crystal and molecular structure confirmed this geometry. Since little change in magnetic coupling was observed in comparing 6-coordinate to 5-coordinate species, the variation in exchange coupling constants in traversing the first transition series has been primarily ascribed to the changing number and symmetry of the d-electrons.

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PART I.

Introductory Remarks.

Introduction

What happens when two metal atoms coexist in the same discrete molecule? What types of interactions take place between them? Can the properties of these molecules be represented as the simple sum of their mononuclear constituents, or does something special occur when two metals communicate? Can we design multimetallic systems which possess unusual physical, chemical, redox, or catalytic properties by manipulating the metals and their concomitant coupling? Can we generalize our understanding of simple, controlled polynuclear molecules to account for the more complex behavior exhibited by multimetallic catalysts and enzymes?

These are some of the key questions this thesis will address. Research into these problems is neither new nor has it been left fallow.

The study of multinuclear species, dating back to 1704, and Prussian blue,¹ has undergone continual growth, blossoming in recent years through novel theoretical approaches accompanied by fresh experimental data. Nonetheless, hopefully the reader will find the experimental approach described herein efficacious, and the results provocative.

Significance of Metal-Metal Interactions

Multimetallic enzymes are ubiquitous in Nature, playing a vital role in biosynthetic and metabolic pathways. They are studied in vivo,² in vitro as pure cell extracts,³ as isolable prosthetics,⁴ and as synthetic biomimetic entities.⁵

One example of such a system is cytochrome c oxidase. This mitochondrial membrane-bound protein contains two iron atoms and two copper atoms per 200,000 molecular weight unit.⁶ It functions in the terminal stages of oxidative phosphorylation, coupling the four-electron reduction of oxygen to water with the production of ATP. Because of the critical role of this enzyme in all aerobic eukaryotes,⁷ its biocatalytic mechanism is the subject of extensive, current research programs throughout the world. These studies reveal that the metals are coupled in a manner that is still not completely understood, though presumably they represent both a potential binding site and a source of electrons for the oxygen molecule. Active sites have been postulated⁸ and model complexes have been prepared and studied.⁹ Current hypotheses on the resting state of cytochrome oxidase include an isolated, low spin heme iron (III), and isolated copper (II) center, with the other O₂ active site being a heme iron (III) strongly coupled to a copper (II) via an oxo bridge.⁸ This structural unit is suggested by the magnetic coupling in the native protein, greater than 200 cm⁻¹.^{10,11}

Other examples of multimetallic enzymes are the high potential iron proteins (HiPIP), such as the ferredoxins. These electron transfer proteins exist in almost all forms of life,¹² playing a vital role in metabolic and photosynthetic processes. The active site contains Fe_4S_4 units, with iron and sulfur occupying alternate corners of a cube.¹³ The ability to achieve multiple oxidation states over a broad range of potentials allows this prosthetic group to function in a wide variety of enzymes. These systems have been the subject of a series of elegant studies centered in Dr. R. H. Holm's laboratories.

Nitrogenase is another protein which utilizes a multimetallic moiety to accomplish a key chemical and redox transformation, the six electron reduction of dinitrogen to ammonia.¹⁴ The active site is believed to contain cubane-like iron clusters coupled in some manner to a molybdenum species, though this is the subject of much speculation.¹⁵ Recently, mixed metal molybdenum and iron clusters have been characterized, and may play an important role in better understanding this catalysis.¹⁶

There are many other examples of multimetallic biosystems which accomplish a wide variety of important chemical and redox transformations. One is tyrosinase, a binuclear copper enzyme which activates oxygen for selective hydroxylations.¹⁷ Hemocyanin¹⁸ and hemerythrin¹⁹ are involved in O_2 transport and contain binuclear

copper and iron sites respectively. Superoxide dismutase contains copper and zinc atoms bridged by an imidazolate group,²⁰ catalyzing the disproportionation of toxic superoxide to oxygen and peroxide.

These several examples illustrate the utility of multimetallic enzymes in accomplishing variegated chemical and redox phenomena including oxygen transport, oxygen reduction, oxygen activation, redox disproportionations, and multi-electron transfers. If we can understand metal-metal interactions in general, and specifically their role in biocatalyses, not only will we gain intrinsic knowledge in understanding our complex biochemical nature, but we may also develop economically viable reagents and catalysts as byproducts.

Already we can see exploration of multimetallic catalysts for utilization in industrial processes. The water gas shift reaction currently employs a mixed nickel-iron catalyst.²¹ A rhodium carbonyl cluster catalyzes carbon-carbon bond formation to yield ethylene glycol from synthesis gas ($\text{CO} + \text{H}_2$).²² A rhodium isocyanide binuclear acts as a reagent for the conversion of solar energy to chemical energy via the water splitting reaction.²³ Utilization of multielectron multimetal catalysts as fuel cell cathodes has been demonstrated in principle.²⁴

From these and other examples, it should be evident that something special occurs when two or more metals are communicating within a given molecule. It is the nature and extent of these

communications, along with their various chemical, physical, and redox manifestations which are the subject of this thesis.

Previous Studies

The approach that has been taken in examining these questions has centered around understanding the pathway for intramolecular communication. In particular, molecules have been designed and synthesized which contain two metals, each accompanied by their appropriate complement of ligands, but with one or more ligands in common. This bridging entity can be an atom, an ion, or even a polyfunctional molecule such as pyrazine or cyanogen. Many studies have shown that metal-metal communications depend strongly on the nature of the bridging group.

One example is in the magnetic exchange interaction where Hoffmann²⁵ theoretically determined that the extent of superexchange coupling in $L-Cu(OH)_2Cu-L$ groups depends very strongly on the Cu-O-Cu angle. He predicted that when the bridging angle became greater than 96° , the net exchange would be antiferromagnetic. For angles less than 96° , ferromagnetism was predicted, with the triplet representing the ground state. Hatfield and coworkers verified this trend in combined X-ray structural and magnetic susceptibility studies,²⁶ and found that a single degree change in the Cu-O-Cu angle constitutes a 77 cm^{-1} change in coupling energy.

Another example involves the electronic consequences of the metal-metal coupling, especially in species where the metals are in mixed oxidation states. Robin and Day have classified these species into

three categories depending on the extent of communication.²⁷

According to their scheme, Class I species are those species which are most accurately represented as the simple sums of their mononuclear constituents. Class II ions are best described by perturbation methods where the pure oxidation states represent zero order approximations accompanied by incremental corrections due to fractional oxidation states. Class III systems bear little resemblance to their mononuclear components and are categorized as completely delocalized molecular systems. Hush²⁸ has taken this approach one step further by combining Marcus' harmonic potential treatment of electron transfers with Mulliken's²⁹ perturbation method for electronic spectra. The result has been a quantitative theory relating molecular parameters to observable spectral and thermal characteristics. Hush's theories have been modified to include vibronic³⁰ and superexchange coupling.³¹

Numerous experimental studies have accompanied theoretical developments. It is not out of place to mention Henry Taube and his school for an extensive series of elegant synthetic and quantitative approaches toward a better understanding of the relationship between metal-metal interactions, electron transfer, and charge delocalization.³²⁻⁴⁰ Their method has been to systematically vary the bridging group between the metals, usually bifunctional heterocycles, and see how this alters the metal-metal communication. Among other

things, they have found that the longer bridging groups tend to favor formation of Class II (weak coupling) or even Class I (no coupling) systems.³² In addition, extended π systems favor stronger metal-metal interactions over saturated bridges.³³ Small units such as μ -oxo⁴¹ or μ -dinitrogen bridges³⁴ favor Class III behavior (strong coupling). Often their results corroborate Hush's theory,³² though extensive delocalization renders the perturbation treatment ineffective. In any case, the results demonstrate the utility of systematically varying the bridge while holding the metals constant.

In contrast, the approach taken in this work is based on retaining the same bridging entity while systematically varying the metals. Not only has the bridging moiety been vigorously maintained, but the entire liganding environment about the metals has been controlled. These complexes are pictured in Figure 1. The ligand, 11,23-dimethyl-3,7,15,19-tetraazatricyclo (19.3.1.1^{9,13}) hexacosa 2,7,9,11,13(26), 14,19,21(25), 22,24-decaene-25,26-diol, referred to as LH₂ throughout, provides a unique opportunity to study metal-metal interactions. It holds two metals in close proximity (ca. 3.15 ± 0.05 Å)^{42,43,44} ensuring some intramolecular communication between the metals. It is a macrocycle and thus provides the necessary rigidity for maximizing structural control. Being a macrocycle, it is also a polydentate chelate. This enables us to circumvent the inherent substitution lability⁴⁵ of the first

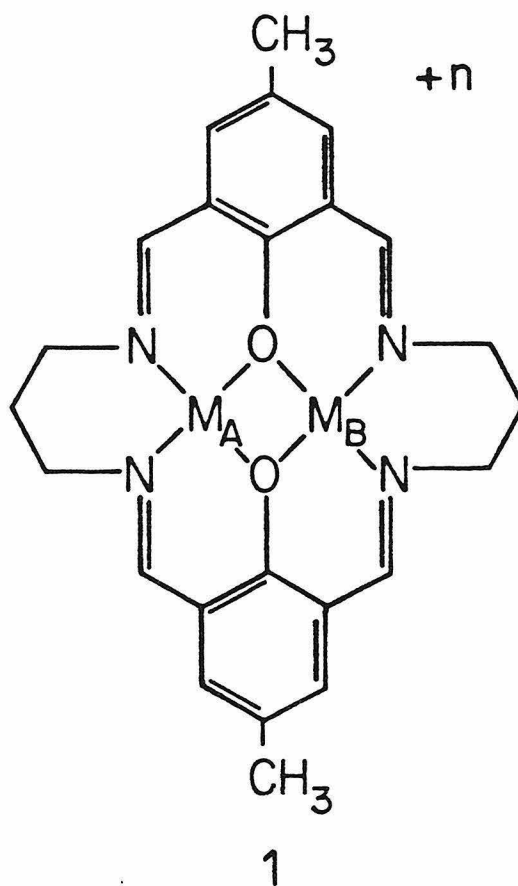


Figure 1. $M_A M_B L^{+n}$, the binuclear macrocyclic species which are the subject of this thesis.

transition series. Therefore, the complexes we put in solution remain reasonably intact throughout the course of chemical, physical, and redox studies (vide infra). In addition, these compounds have a high degree of symmetry. In the case of homonuclears, ($M_A = M_B$), originally prepared by Robson,⁴⁶ the high degree of symmetry and structural rigidity ensures that the environment about one metal be identical to its adjacent counterpart. The electrochemical properties of these species are discussed in Part II, and help provide the basis for comparison to isostructural heteronuclear species.

The synthesis and isolation of pure mixed-metal complexes was less than straightforward due to the high symmetry and the propensity of these complexes to disproportionate, or 'scramble', yielding intractable mixtures of homo- and heteronuclear species. Part III is a description of several unsuccessful synthetic approaches to this problem, along with the ultimately successful scheme.

Part IV is a communication which recently appeared in J. Am. Chem. Soc.,⁴⁷ and reports the Cu(II/I) reduction potential in $Cu(II)M_B(II)L^{+2}$ where $M_B(II)$ was varied across the series $M_B(II) = Mn(II), Fe(II), Co(II), Ni(II), Cu(II),$ and $Zn(II)$. By controlling the charge on the remote metal M_B , it was possible to probe the effects of other forms of metal-metal interactions on the Cu(II/I) redox couple.

Part V⁴⁸ is a full paper being submitted to J. Am. Chem. Soc..

The article, which comprises the bulk of this thesis, not only includes the preliminary results described in Parts III and IV, but also a detailed synthesis and characterization of the heterobinuclear complexes. The characterization includes spectral and magnetic properties, a thorough examination of the electrochemical properties, and a study on the chemical manifestations of metal-metal interactions. An interpretation of these studies is offered in the discussion section. A detailed experimental section including syntheses and microanalytical data appears at the end of Part V.

Part VI⁴⁹ compares in detail the magnetic properties of homo- and heterobinuclear complexes of $L^=$ in an effort to better understand the role of electronic vs molecular structure in magnetic exchange coupling. This section includes the magnetic properties of these species, Part VIa, as the coordination environment is held constant and the metals are varied; and Part VIb, as the coordination environment is varied and the metals are held constant.

References

-13-

1. J. Woodward, Phil. Trans., 33, 15 (1724).
2. W. E. Donaldson and J. P. Thaxton, Poultry Science, 54, 1613 (1975).
3. R. H. Holm, Endeavour, 34, 38 (1975).
4. A. L. Lehninger, Biochemistry, 2nd ed., 1976, Worth Publishers, Inc., New York, p. 606.
5. R. R. Gagné, R. P. Kreh, and J. Dodge, J. Am. Chem. Soc., 101, 6917 (1979).
6. A. L. Lehninger, Biochemistry, 2nd ed., 1976, Worth Publishers, Inc., New York, p. 493.
7. G. Palmer, G. T. Babcock, and L. E. Vickery, Proc. Natl. Acad. Sci., 73, 2206 (1976).
8. G. Brudvig, T. Stevens, and S. I. Chan, Biochemistry, in press.
9. J. T. Landrum, C. A. Reed, K. Hatano, W. R. Scheidt, J. Am. Chem. Soc., 100, 3232 (1978).
10. M. F. Tweedle, L. J. Wilson, L. Garcia-Iniguez, G. T. Babcock, and G. Palmer, J. Biol. Chem., 253, 8065 (1978).
11. T. H. Moss, E. Shapiro, T. E. King, H. Beinert, and C. Hartzell, J. Biol. Chem., 253, 8072 (1968).
12. A. L. Lehninger, Biochemistry, 2nd ed., 1976, Worth Publishers, Inc., New York, p. 488-489.

13. T. Herskovitz, B. A. Averill, R. H. Holm, J. A. Ibers, W. D. Phillips, and J. F. Weiner, Proc. Nat. Acad. Sci., 72, 2437 (1969).
14. A. L. Lehninger, Biochemistry, 2nd ed., 1976, Worth Publishers, Inc., New York, p. 722.
15. S. P. Cramer, W. O. Gillum, K. O. Hodgson, L. E. Mortenson, E. I. Steifel, J. R. Chisnell, W. J. Brill, and V. K. Shah, J. Am. Chem. Soc., 100, 3814 (1978).
16. T. E. Wolff, J. M. Berg, K. O. Hodgson, R. B. Frankel, and R. H. Holm, J. Am. Chem. Soc., 101, 4140 (1979).
17. H. S. Mason, Annu. Rev. Biochem., 35, 595 (1965).
18. R. Lontic, Inorg. Biochem., G. I. Eichorn, ed., Elsevier, 1973, p. 344.
19. I. R. Klotz, Biol. Macromol., 5, 105 (1971).
20. R. J. Carrico and H. F. Deutsh, J. Biol. Chem., 245, 723 (1970).
21. H. Koebel and H. Giehring, German Patent 1, 245, 028, (1967).
22. R. L. Pruett and W. E. Walker, U. S. Patent 3,833,634 (1974).
23. K. Mann, R. Bell, and H. B. Gray, Inorg. Chem., 18, 2671 (1979).
24. J. P. Collman, M. Marocco, P. Denisovich, F. C. Anson, and C. A. Koval, J. Electroanal. Chem., 101, 117 (1979).
25. P. J. Hay, J. C. Thibeault, and R. Hoffmann, J. Am. Chem. Soc., 97, 4884 (1975).

26. K. T. McGregor, N. T. Watkins, O. L. Lewis, R. F. Drake, D. J. Hodgson, and W. E. Hatfield, Inorg. Nucl. Chem. Lett., 9, 423, (1973) and refernces contained therein.
27. M. B. Robin and P. Day, Advan. Inorg. Chem. Radiochem., 10, 247 (1967).
28. N. S. Hush, Prog. Inorg. Chem., 8, 391 (1967).
29. R. S. Mulliken and W. P. Person, Molecular Complexes, Wiley, New York, (1969).
30. P. N. Schatz, S. B. Piepho, E. R. Krausz, Chem. Phys. Lett. 65, 539 (1978).
31. P. A. Cox, Chem. Phys. Lett., 69, 340 (1980).
32. J. E. Sutton, Doctoral Dissertation, Stanford Univ., Stanford, Ca. (1978).
33. H. Krentzian, Doctoral Dissertation, Stanford Univ., Stanford, Ca. (1978).
34. R. H. Magnuson and H. Taube, J. Am. Chem. Soc., 94, 7213 (1972).
35. G. M. Tom, C. Creutz, and H. Taube, J. Am. Chem. Soc., 96, 7827 (1974).
36. C. Creutz and H. Taube, J. Am. Chem. Soc., 91, 3988(1969).
37. A. von Kameke, G. M. Tom, and H. Taube, Inorg. Chem., 17, 1790 (1978).

38. C. A. Stein and H. Taube, Inorg. Chem., 18, 2212 (1979).
39. H. Fischer, G. Tom, and H. Taube, J. Am. Chem. Soc., 98, 5512 (1976).
40. S. Isied and H. Taube, Inorg. Chem., 15, 3070 (1976).
41. T. R. Weaver, T. J. Meyer, S. Adeyemi, G. M. Brown, R. P. Eckberg, E. C. Johnson, R. W. Murray, and D. Untereker, J. Am. Chem. Soc., 97, 3039 (1975).
42. R. R. Gagné, L. M. Henling, and J. J. Kistenmacher, Inorg. Chem., 19, 1226 (1980).
43. B. F. Hoskins, N. J. McLeod, and H. A. Schaap, Aust. J. Chem., 29, 515 (1976).
44. B. F. Hoskins and G. A. Williams, Aust. J. Chem., 28, 2607 (1975).
45. F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 3rd ed., 1972, p. 656-657, Wiley and Sons, New York.
46. N. H. Pilkington and R. Robson, Aust. J. Chem. 23, 225 (1970).
47. R. R. Gagné and C. L. Spiro, J. Am. Chem. Soc., 102, 1443 (1980).
48. Parts of this chapter will appear in the following two articles:
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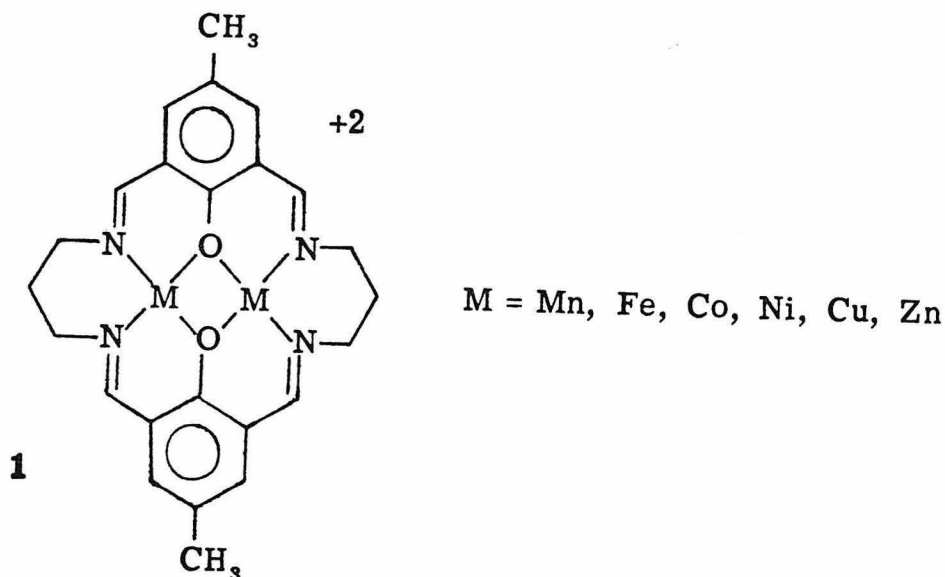
49. C. L. Spiro, S. M. Lambert, E. Deuřlar, T. J. Smith, R. R. Gagné, and D. N. Hendrickson, manuscript in preparation.
- C. L. Spiro, S. M. Lambert, R. R. Gagné, and D. N. Hendrickson, manuscript in preparation.

PART II

Electrochemical Properties of a
Series of Homobinuclear Macrocyclic
Complexes

R. R. Gagné and C. L. Spiro

In order to study periodic trends in metal-metal interactions, we first electrochemically characterized a series of binuclear macrocyclic complexes, **1**, of the first transition series.



These complexes, a slight variation on those reported by Pilkington and Robson,¹ are of considerable theoretical interest because they house two metals in close proximity (ca. $3.15 \text{ \AA}$)^{2,3} in a symmetric ligand environment. Detailed studies of these and related systems have already provided a wealth of information with regard to intramolecular electron transfer,⁴ multi-electron charge transfer,⁵ magnetic coupling phenomena,^{1,6} and electronic spectral properties.¹ These data and those reported herein also provide a basis for comparison to isostructural heterobinuclear species to be discussed in later

chapters. The symmetry and isostructurality of these homo- and heterobinuclear complexes may facilitate isolation of metal-metal coupling phenomena from metal-ligand and metal-solvent interactions. We ultimately hope to further elucidate the relationships among magnetic coupling, redox potential, comproportionation equilibria, intramolecular electron transfer, and intervalence spectral properties. These studies also potentially have both biological and electrocatalytic ramifications since many natural⁷ and proposed industrial⁸ systems incorporate multimetal interactions to accomplish chemical and redox transformations.

Results and Discussion

Initial attempts to study the redox properties of the chloride salts of 1 were thwarted by low solubility in most organic solvents. The corresponding bromide salts afforded adequate concentrations for differential pulse polarography, and in some cases, cyclic voltammetry. Methanol was the solvent of choice because it provided sufficient solubility and potential range to obtain data on most of the compounds. Neither anodic nor cathodic waves for the binuclear nickel complex were observed in methanol, though two nickel (II/III) redox couples were present in aqueous solution, the second oxidation appearing as a shoulder on the water oxidation wave. No anodic waves for the dicopper complex were observed in any solvent including propylene carbonate and acetonitrile whose anodic ranges far surpass both water

and methanol. Only the first reduction wave of the binuclear copper complex was within the cathodic range of methanol, while in N,N-dimethylformamide, both waves were observed.

Figure 1 shows a representative cyclic voltammogram, this one of the binuclear iron complex, Fe_2LBr_2 , where L is the metal free diphenoxide macrocycle. The first two waves at +0.330 V and +0.590 V vs. the normal hydrogen electrode (nhe) are metal based, representing the Fe(II/III) redox couples. The large irreversible wave at +0.900 V is assigned to a bromide/bromine oxidation since it is present in all species at roughly the same potential including the non-electroactive dizinc complex, but is absent in the chloro-complexes. The 0.900 V wave integrates to two electrons and is enhanced by the addition of tetraalkylammonium bromide.

Electrochemical data are summarized in Table I. In each case a small amount (ca. 10^{-4} M) of ferrocene was added to each non-aqueous solution as an internal solvent independent redox couple. The metallo-based formal potentials were measured versus the normal hydrogen electrode using a ferrocene potential of +0.400 vs. nhe.⁹ The reader is cautioned against placing too much emphasis on the absolute potentials since the Fc/Fc^+ couple is known to be unstable in methanol.¹⁰ In aqueous solution the $\text{Ru}(\text{NH}_3)_6^{+3/2}$ couple was chosen as the calibrant.

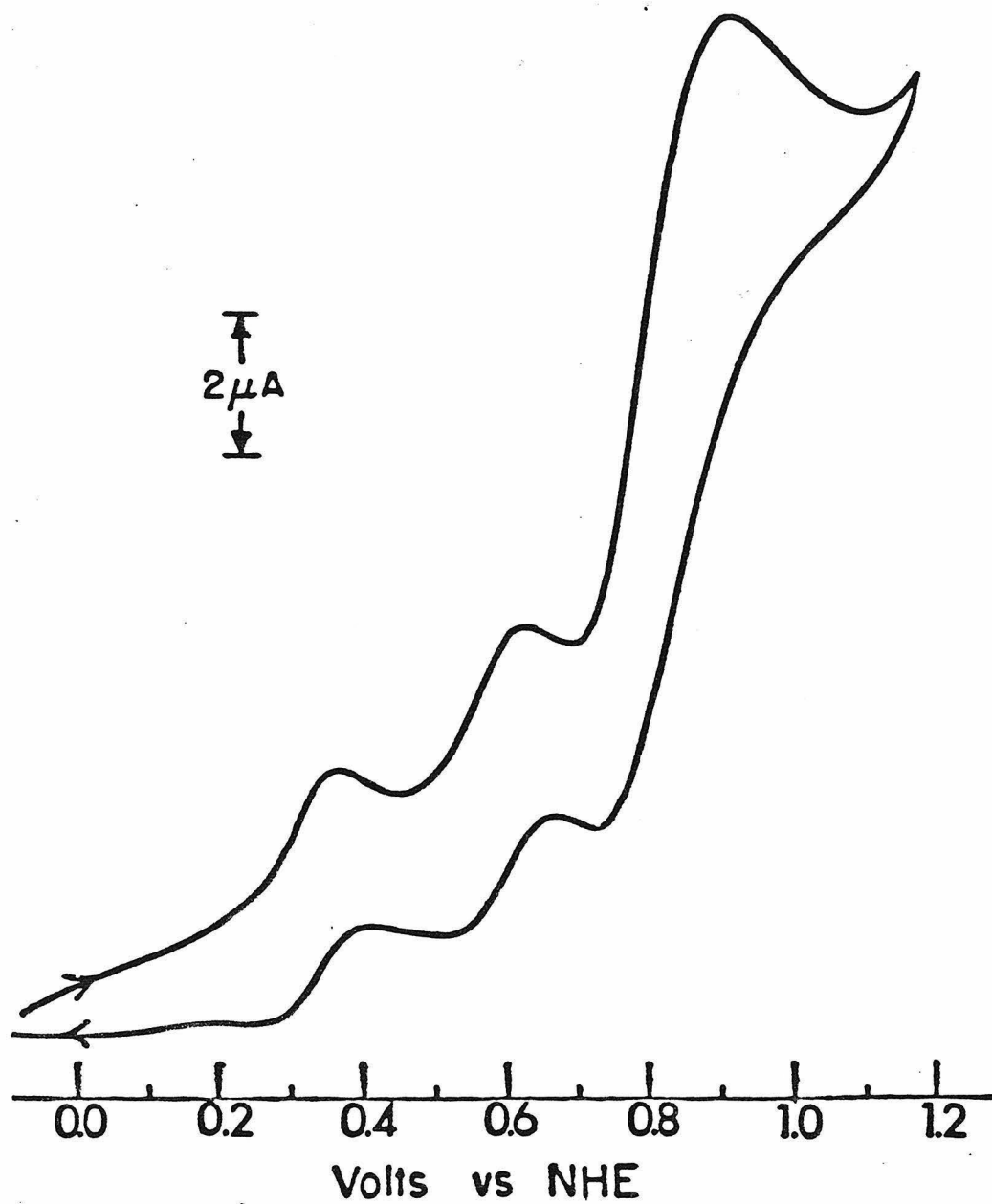
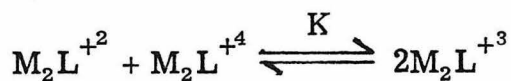


Figure 1. Cyclic voltammogram of Fe(II)Fe(II)LBr_2 in methanol.

The criterion for electrochemical reversibility in differential pulse polarography is that the peak width at half height of the redox wave be 0.090 V wide.¹¹ In this sense, only the dicopper couples are truly Nernstian. It is, however, unreasonable to believe that all redox couples are irreversible since even the ferrocene/ferricinium⁺ system failed to show 0.090 V peak widths. For cyclic voltammetry, one criterion for electrochemical reversibility is that the difference between the cathodic and anodic peak potentials be 0.058 V.¹² At scan rates of 0.200 V per second the complexes studied showed peak separations of 0.100 V, though in the limit that scan rates approach zero, peak separations approached the required 58 millivolts. The other requirement for electrochemical reversibility is that plots of current versus [scan rate]^{1/2} be linear with zero intercept,¹³ a criterion which is met by the complexes we examined by cyclic voltammetry. Uncompensated solution resistance may be primarily responsible for the apparent quasi-reversibility rather than an inherently slow electron transfer within the complexes.

The usual periodic trends in absolute potential¹⁴ with Mn(III) most accessible and Cu(III) least accessible was observed. In addition, it appears that for the series manganese to copper, a trend toward increased comproportionation constants for the following reaction is observed:

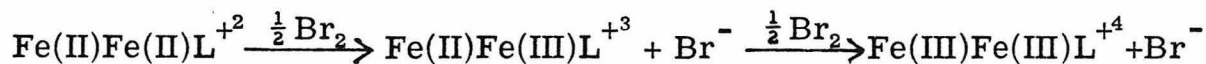


Comproportionation constants were determined from the following relation:

$$\ln K = \frac{nF}{RT} [E_2 - E_1]$$

Only the dicobalt ion prevents this series of equilibrium constants from being completely monotonically increasing with atomic number. It is possible that the spin change that accompanies oxidation in the complex, going from an $S = 3/2$, $S' = 3/2$ to an $S = 3/2$, $S' = 0$ system upon initial oxidation,² is responsible for the apparent disorder in periodicity. Spin changes have been shown to cause shifts upward of 0.200 volts in spin equilibrium systems.¹⁵ The near periodic order may be fortuitous as comproportionation constants represent the relative stability of three different molecules, each with energetics being a complicated function of electronic structure, metal-ligand distances, coordination number, and geometry.

One such complication in interpreting the relative importance of the several factors involved in comproportionation equilibria is illustrated in Figure 2. The reaction sequence below,



was carried out using aliquots of bromine. The conductivity was monitored throughout the course of the titration. In the figure, the dashed line represents the expected conductivity for the solution in progressing stepwise from a 2:1 to a 4:1 ideal electrolyte. The sharp break in the solid line, the actual experimental results, demonstrates

Figure Caption. Figure 2 is a conductometric titration of $\text{Fe(II)Fe(II)L}^{+2}$ with bromine in N,N-dimethylformamide. Initially the anions are completely dissociated with the species acting as a 2:1 electrolyte. As bromine is added, it oxidizes the iron centers and associates with the metal ions to the extent shown by the solid line. The dashed line is the ideal behavior that would be expected for complete dissociation ultimately resulting in a 4:1 electrolyte.

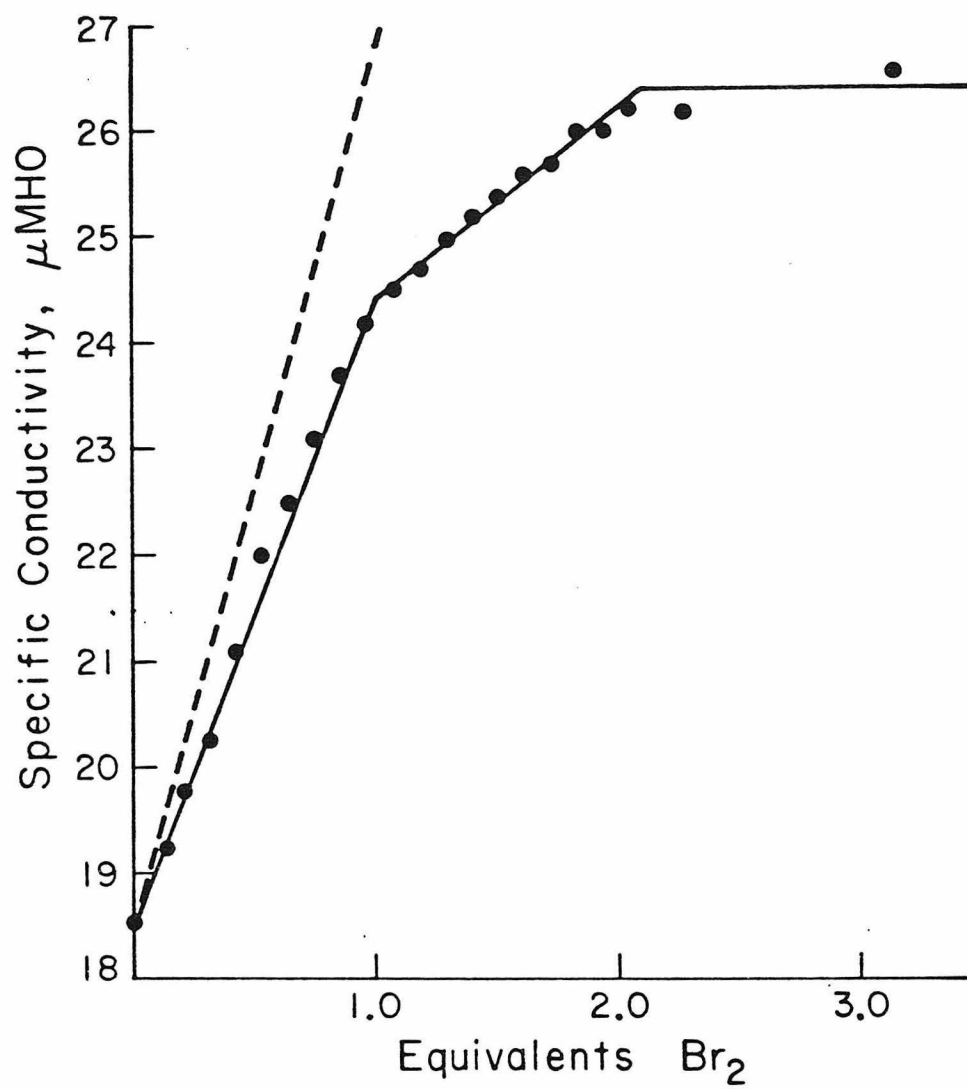


Figure 2.

that $\text{Fe(III)Fe(III)L}^{+4}$ coordinates or strongly associates with the bromide anions which were released upon oxidation of the complex. Similar complicating behavior was observed in the dinuclear manganese and cobalt species. The fact that the anion coordinates to a varying extent and lowers the charge of the fully oxidized species makes it extremely difficult to compare the potentials and extent of comproportionation equilibria in this series.

Fortunately no such complications occur in the two copper reductions, where the anion remains dissociated throughout the course of redox transformations, and has no effect on the electrochemical properties of the copper ion. For this reason, a series of complexes $\text{Cu(II)M}_B\text{(II)L}$, $\text{M}_B = \text{Mn(II), Fe(II), Co(II), Ni(II), Cu(II),}$ and Zn(II) was explored, the details to be described in upcoming chapters.

Experimental

Electrochemical measurements were made with a Princeton Applied Research polarographic analyzer, model 174A, in the cyclic voltammetric and differential pulse polarographic modes. The experimental setup consisted of a two compartment cell separated by a medium glass frit, with one compartment containing a platinum auxiliary electrode, and the other compartment containing a working (platinum) and reference (Ag/Ag^+ (0.01 N in MeCN)) electrode. Measurements were taken at the ambient temperature under an

inert atmosphere. Since diffusion of methanol into the reference electrode could not be avoided all potentials were referenced to a well characterized internal reference couple, usually ferrocene/ferricinium⁺, and in aqueous solution, $\text{Ru}(\text{NH}_3)_6^{+3/+2}$. The potentials which appear in Table I were then calculated using a value of $E^f = +0.400 \text{ V}^9$ and $+0.051 \text{ V}^{16}$ vs. nhe for ferrocene and ruthenium hexammine, respectively. For differential pulse polarography, the modulation amplitude was 10 and the scan rates ranged from 1 to 10 millivolts per second, with potentials independent of scan rate. For cyclic voltammetry, scan rates were 200 millivolts per second. In all non-aqueous solutions, 0.1 M tetrabutylammonium perchlorate was the supporting electrolyte. In water, 0.1 M sodium bromide was the electrolyte.

Conductivity titrations were carried out using a YSI model 31 conductivity bridge. Bromine stock solutions were prepared and calibrated by electronic absorption spectroscopy, and kept in the dark prior to use.

Magnetic measurements were made at 294° K on a Cahn Faraday balance, calibrated with $\text{HgCo}[\text{SCN}]_4$. Molar susceptibilities were corrected via Pascal's method.¹⁷ Magnetic moments are reported in Table II on a per metal basis.

All compounds were prepared according to the method of Robson¹ with the single isomolar substitution of $\text{MBr}_2 \cdot x\text{H}_2\text{O}$ for $\text{MCl}_2 \cdot x\text{H}_2\text{O}$ in

the initial work. All $MBr_2 \cdot xH_2O$ reagents were purchased from Alfa Chemicals with the exceptions of hydrated zinc bromide and hydrated ferrous bromide. Hydrated zinc bromide was prepared by heating zinc powder with concentrated HBr under an argon flow, followed by rotary evaporation, yielding white crystalline $ZnBr_2 \cdot xH_2O$. Ferrous bromide proved to be exceedingly air-sensitive, and was prepared via Schlenk techniques. Hydrogen reduced iron powder was heated in argon saturated concentrated HBr until the evolution of hydrogen ceased. The pale blue solution was filtered and a steady stream of argon was passed over the boiling solution. When crystalline hydrated ferrous bromide first appeared in the flask, the flask was cooled to room temperature. Pale blue crystals of $FeBr_2 \cdot 4H_2O$ were collected and immediately removed to an inert atmosphere glovebox where the crystals were dried under vacuum and used without further purification.

Elemental analyses were performed by the California Institute of Technology microanalytical facility and, along with magnetic moments, are reported in Table II.

References and Notes

1. N. H. Pilkington and R. Robson, Aust. J. Chem., 23, 2225 (1970).
2. B. F. Hoskins, R. Robson, and G. A. Williams, Inorg. Chim. Acta, 16, 121 (1976).
3. B. F. Hoskins, P. M. Johnson, N. J. McLeod, and H. A. Schaap, Ninth Meeting of Australian Crystallographers, La Trobe University, February 1973.
4. R. R. Gagné, C. A. Koval, and T. J. Smith, J. Amer. Chem. Soc., 99, 1367 (1977).
5. D. E. Fenton, R. R. Schroeder, and R. I. Lintvedt, J. Amer. Chem. Soc., 100, 1931 (1978).
6. D. N. Hendrickson, private communication.
7. For example cytochrome c oxidase, laccase, nitrogenase and numerous others.
8. Air battery cathodes and water-gas shift catalysts, for example.
9. H. Strehlow et al., Zeit. Electrochim., 64, 483 (1960).
10. V. P. Nikol'skii, A. A. Pendin, and O. M. Susareva, Vzaimodeistviya Rastvorakh Okislitel'no-Vosstanov. Sist., 124 (1977).
11. E. A. Parry and R. A. Osteryoung, Anal. Chem., 37, 1634 (1965).
12. D. S. Polcyn and I. Shain, Anal. Chem., 37, 1634 (1965).
13. R. S. Nicholson and I. Shain, Anal. Chem., 36, 706 (1964).

14. E. P. Rillema, J. F. Endicott, and E. Papconstantinou,
Inorg. Chem., 10, 1739 (1971).
15. M. Hoselton, L. Wilson, and R. Drago, J. Amer. Chem. Soc.,
97, 1722 (1975).
L. Wilson, manuscript in preparation (1979).
16. H. S. Lim, D. J. Barclay, and F. C. Anson, Inorg. Chem., 11,
1461 (1972).
17. A. Earnshaw, Introduction to Magnetochemistry, Academic
Press, London, 1968, pp. 9-12.

Table I. Electrochemical Data^(a)

Compound	Solvent ^(b)	Mode ^(c)	E_1^f (d)	E_2^f (d)	Δ_2 (e)	Δ_2 (e)	Δ Standard ^(f)	$\log K$ (g)
Mn_2LBr_3	CH_3OH	DPP	+0.350	+0.465	0.120	0.120	0.110	1.95
Fe_2LBr_3	CH_3OH	CV	+0.380	+0.640	0.120	0.120	0.100	4.40
Co_2LBr_3	CH_3OH	DPP	+0.410	+0.640	0.120	h	0.120	3.90
Ni_2LBr_3	HOH	DPP	+0.480	+0.825	0.100	0.100	0.180	5.85
Cu_2LBr_3	CH_3OH	DPP	-0.540	--	0.090	--	0.100	--
Cu_3LBr_3	DMF	DPP	-0.540	-0.910	0.100	0.090	0.110	6.27
Zn_2LBr_3	CH_3OH	DPP	--	--	--	--	--	--

^a All potentials are reported in volts versus the normal hydrogen electrode (nhe).^b DMF = N, N-dimethylformamide.^c CV - cyclic voltammetry; DPP - differential pulse polarography.^d With the exception of the binuclear copper ion, all formal potentials are for the $M^{+3/4+}$ couples, Cu is $2^+/1^+$ couple.^e Δ is defined as the peak width at half height in DPP mode, and the difference between the cathodic and anodic potentials in CV mode.^f Standards are ferrocene for organic solvents and $Ru(NH_3)_6^{+3}$ in aqueous solution.^g $\log K \equiv \frac{RT}{nF} [E_2^f - E_1^f]$.^h Shoulder on bromide oxidation.

Table II. Analytical and Magnetic Data

<u>Compound</u>	%C calcd (obsd)	%H calcd (obsd)	%N calcd (obsd)	μ_{eff} (Bohrs) ^(a) literature ^(b) (obsd)
Mn ₂ LBr ₂ · 2MeOH	42.64 (42.5)	4.29 (4.4)	7.96 (8.4)	5.97 (5.98)
Fe ₂ LBr ₂ · MeOH	42.49 (42.05)	4.25 (4.3)	7.93 (8.1)	5.10 (5.10)
Co ₂ LBr ₂ · 2MeOH	41.93 (41.6)	4.56 (4.4)	7.52 (7.7)	4.61 (4.61)
Ni ₂ LBr ₂ · 2H ₂ O	40.28 (40.55)	4.19 (4.35)	7.83 (7.95)	3.15 (2.86)
CuLBr ₂ · 2H ₂ O	39.78 (40.1)	4.12 (3.9)	7.73 (7.9)	0.65 (0.59)
Zn ₂ LBr ₂ · 2H ₂ O	39.56 (39.45)	4.12 (4.1)	7.69 (7.4)	0.00 (0.02) ^(c)

^aCorrected magnetic moments reported on a per metal basis at 294°K.

^bLiterature values are for the chloride salts.⁽¹⁾

^cCalculated using Pascal's method.

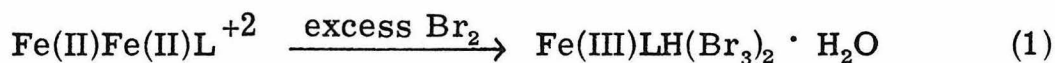
PART III.

Early Attempts to Synthesize
Pure Mixed-Metal Binuclear
Complexes.

Early Attempts Toward Heteronuclear Complexes

Several unsuccessful methods were attempted in an effort to isolate pure heteronuclear complexes of L^- , and will be discussed here. The details of the ultimately successful syntheses are covered in the next chapters, which consist of a communication which appeared in J. Am. Chem. Soc.¹ and the full paper which is being submitted to the same journal.

Initial attempts to obtain pure heteronuclear species stemmed from reaction (1) which was, in actuality, an attempt to prepare the dinuclear $Fe(III)Fe(III)L^{+4}$ species, but resulted in the isolation of a mononuclear $Fe(III)$ complex of LH^- , as a bis-tribromide⁻ salt.



The formulation of this species as a bis-tribromide⁻ mononuclear complex is reasonable for several reasons. It is consistent with microanalysis. The complex slowly evolves molecular bromine even after recrystallization, a result of the tribromide⁻ to bromide⁻/bromine disproportionation. In addition, Robson et al² had reported an analogous reaction which occurs when $Co(II)Co(II)L^{+2}$ is oxidized by molecular bromine. These complexes are all black due to the intense absorption of the anion. The iron complex has a room temperature magnetic moment of 5.99 Bohr magnetons, consistent only with magnetically dilute high-spin $Fe(III)$. It shows a

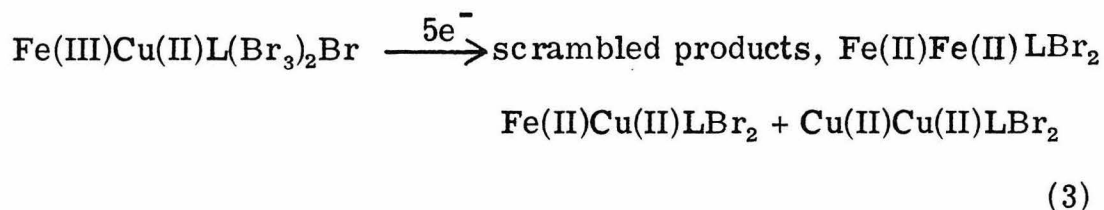
single one-electron Nerstian wave ($E_{pc} - E_{pa} = 60$ mv when measured by cyclic voltammetry in methanol containing 0.1M tetrabutylammonium perchlorate) corresponding to the Fe(III/II) couple at -0.130V. vs ferrocene/ferricinium⁺, (Fc/Fc⁺), as well as a much larger peak at ca. +0.6 V. vs Fc/Fc⁺ due to Br⁻ oxidation. The location of this wave is substantially negative of the Fe(III/II) wave in Fe(II)Fe(II)L⁺², -0.020V. vs Fc/Fc⁺, consistent with the lowered charge on the mono-nuclear ion. In addition, the rest potential of solutions containing Fe(III)LH(Br₃)₂·H₂O implicates Fe(III). The infrared spectrum reveals a splitting in the $\nu_{C=N}$ region which does not occur in binuclear complexes of L⁼. Most significant is the observation that this species exhibits the reactivity expected based on its formulation. Addition of CuBr₂ to this species, reaction (2), apparently incorporates Cu(II) to the vacant N₂O₂ site based on elemental analysis which revealed a Cu:Fe ratio of 1:1. In addition, infrared spectroscopy showed a coalescence in the $\nu_{C=N}$ region.



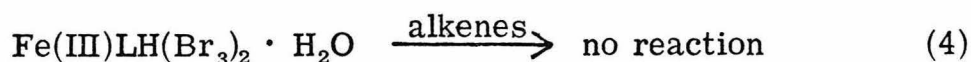
The presence of Br₃⁻ anions in these heteronuclear species was not desirable, as the anion is both spectrally and electrochemically active, and could compete with observations of metal-based phenomena. In addition, the slow decomposition of tribromide⁻ to bromide⁻ and bromine would militate against any studies which might require

quantitative molar determinations. For these reasons it was desirable to reduce, exchange, or avoid this anion.

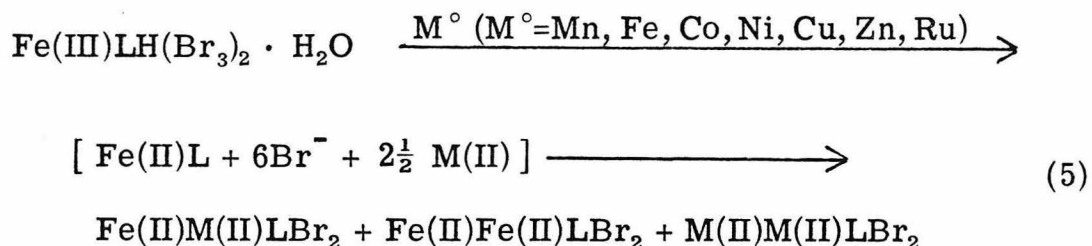
A five-electron reduction by controlled potential electrolysis of $\text{Fe(III)Cu(II)L(Br}_3)_2\text{Br}$, reaction (3), did result in a bromide⁻ product, but of a highly scrambled nature, containing mixtures of heteronuclear and homonuclear species.



Attempts to use alkenes as chemical reagents, (4), to reduce the tribromide anions were unsuccessful.

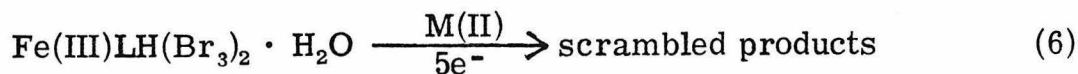


A sequence of reactions utilizing zero-valent metals as reducing agents for tribromide⁻ were attempted, as outlined in reaction (5).

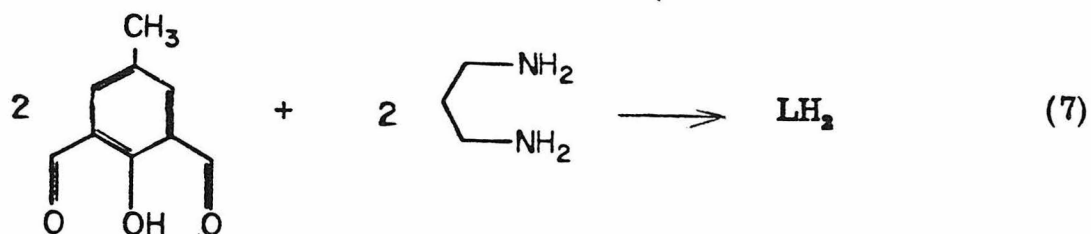


No mechanism is implied by this sequence. The zerovalent metal not only reduces the tribromide⁻ to bromide⁻, but also releases M(II) ions into solution which can substitute into the ferrous complex, resulting in lovely orange and red monoclinic single crystals of binuclear species. Unfortunately, each one starting mononuclear complex releases $2\frac{1}{2}$ M(II) ions from the Fe(III) and two Br₃⁻ reductions, and this excess of M(II) apparently drives the equilibrium toward homonuclear formation. Though numerous reactions with manganese chips, iron wire, cobalt chunks, nickel shot, copper and zinc foil, and ruthenium flakes repeatedly resulted in substantial homonuclear contamination, they represented several days amusement around the chemical laboratory.

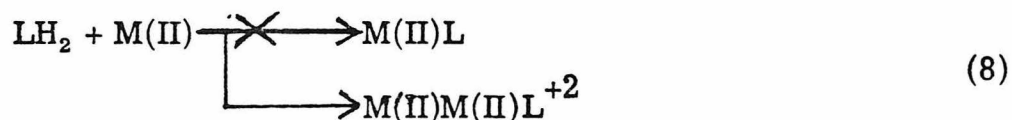
A series of electrochemical reductions of the tribromide⁻ anion in the presence of M(II) salts at the outset, reaction (6), also resulted in impure products. At this stage, use of Fe(III)LH(Br₃)₂ · H₂O as a starting material was abandoned.



The metal-free macrocyclic ligand, LH₂, was synthesized and characterized in spite of accounts in the literature³ which reported difficulties here, reaction (7).

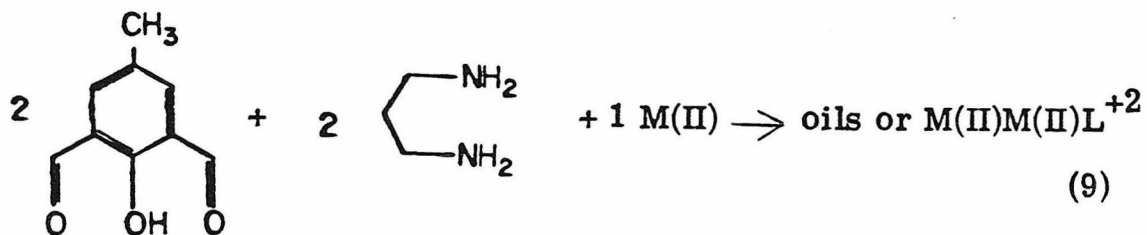


This largely insoluble organic compound was reacted in 1:1 stoichiometries with M(II) salts in an effort to isolate pure mononuclear complexes M(II)L, but consistently resulted in the isolation of homobinuclear products, reaction (8).

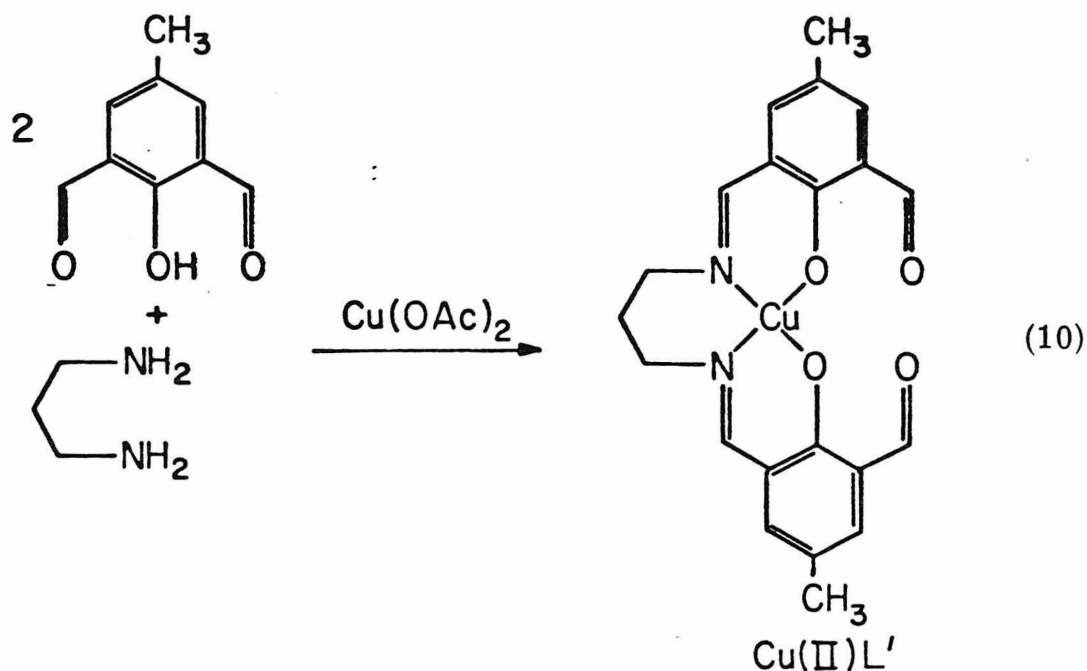


The homobinuclear ions may be preferred over mononuclear species based on solubility and crystal packing considerations.

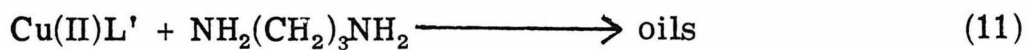
Further attempts to prepare mononuclear species by a template reaction (9) also failed, yielding either oils or homobinuclear species.



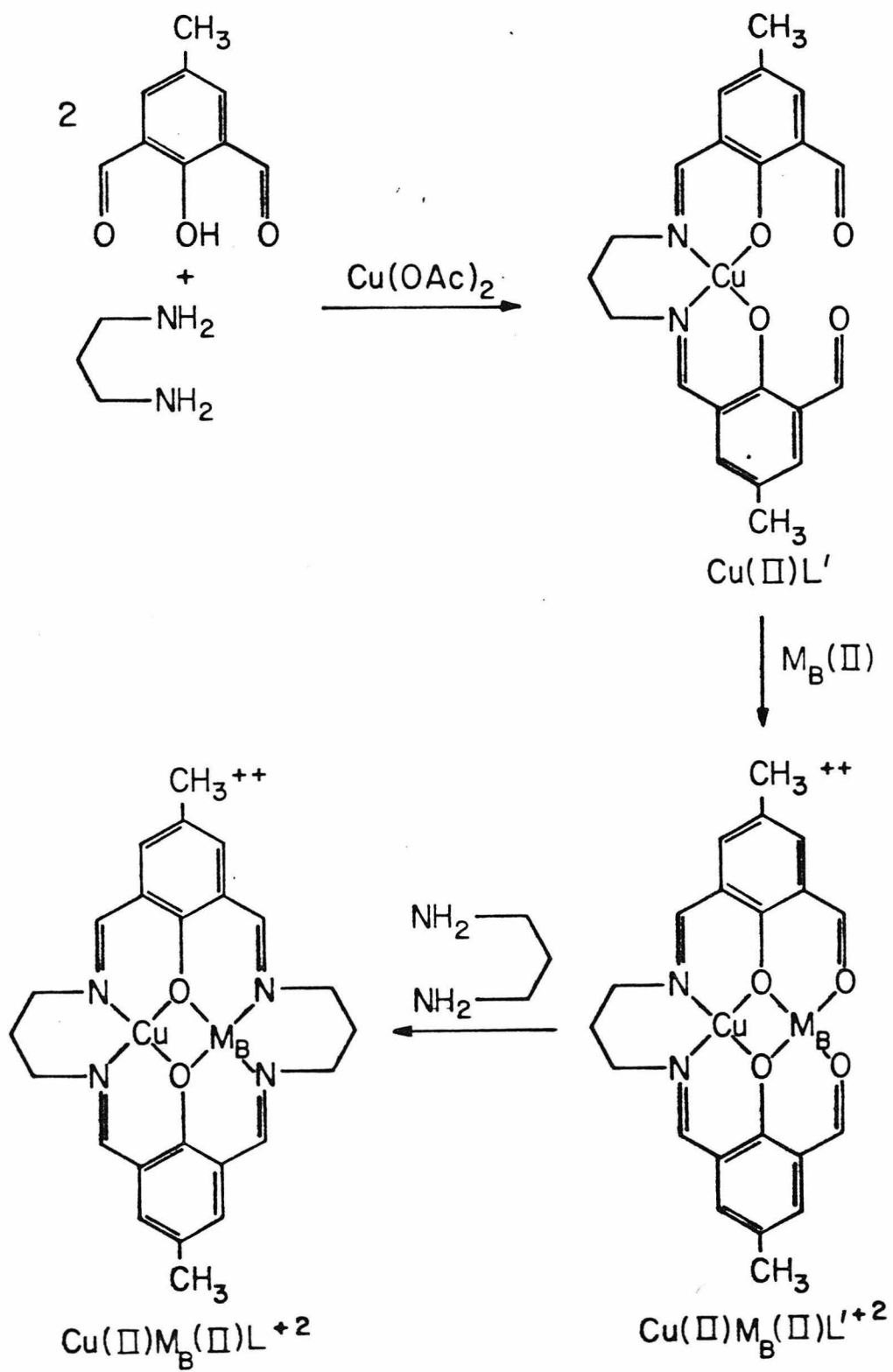
Okawa et al⁴ had reported the preparation of Cu(II)L' , reaction (10).



Addition of a second equivalent of 1,3-diaminopropane to this species, reaction (11), yielded a highly soluble product which oiled in all attempts to isolate this species.



At this stage, the ultimately successful synthetic pathway to pure heteronuclear complexes of $\text{L}^=$ was developed as shown on the following page.



Experimental

Preparation, $\text{FeLH}(\text{Br}_3)_2 \cdot \text{H}_2\text{O}$. Molecular bromine (~ 1.0 g) was added dropwise with stirring to Fe(II)Fe(II)LBr_2 (0.3 g) which was slurried in methanol (25 ml) in air at the ambient temperature. After 30 sec., black crystals began pouring out of solution. These were collected and washed with ether.

Anal. Calc: C, 29.51%; H, 3.28%; N, 5.73%.

Obsd: C, 29.18%; H, 3.21%; N, 5.63%.

Preparation, LH_2 . 2,6-Diformyl, 4-methylphenol (0.164 g) was dissolved in methanol (100 ml) at 40°C in air. 1,3-Diaminopropane (0.74 g) was added slowly with stirring. The yellow solution was allowed to cool and slowly evaporate to near-dryness. Yellow crystalline LH_2 crystallized on the beaker and was collected by vacuum filtration. Insufficient solubility for NMR was realized. Mass spectrum revealed a parent ion at 404 ± 1 mass units.

Anal. Calc: C, 71.29%; H, 6.93%; N, 13.86%.

Obsd: C, 70.82%; H, 7.00%; N, 13.29%.

References and Notes

1. R. R. Gagné and C. L. Spiro, J. Am. Chem. Soc., 102, 1443 (1980).
2. B. F. Hoskins, R. Robson, and G. A. Williams, Inorg. Chim. Acta., 16, 121 (1976).
3. N. H. Pilkington and R. Robson, Aust. J. Chem., 23, 2225 (1970).
4. H. Okawa and S. Kida, Bull. Chem. Soc. Japan, 45, 1759 (1972).

PART IV.

An Electrochemical Method for
Measuring Electronic Delocalization
in Mixed-Valent Species

R. R. Gagné and C. L. Spiro

An Electrochemical Method for Measuring Electronic
Delocalization in Mixed-Valent Species.

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Contribution No. 5917 from the Division of Chemistry and
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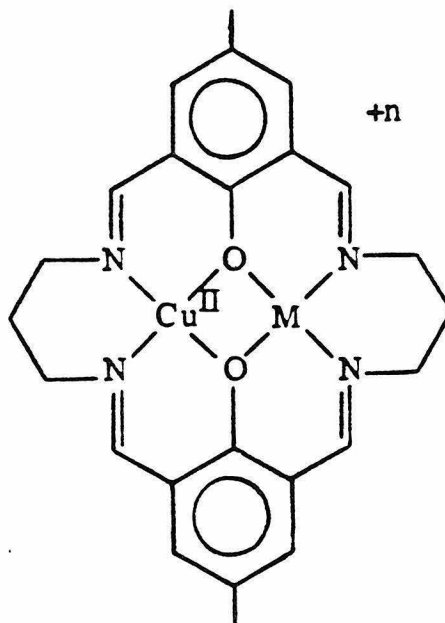
Abstract:

Homobinuclear and heterobinuclear complexes derived from 2-hydroxy-5-methylisophthalaldehyde and 1,3-diaminopropane provide an opportunity to study intramolecular electron transfer and metal-metal interactions in a series of complexes having comparable ligand environments including that of the bridging ligands. Electrochemical measurements of the Cu(II/I) reduction potential in a series of complexes Cu(II)M(II)L^{+2} reveal that the potential is essentially invariant at -1.07 V vs. the ferrocene/ferricinium couple. The sole exception is the dicopper complex with a potential of -0.93 V . Since charges and ligand types are held constant the difference of $140 \pm 30 \text{ mV}$, $3.2 \pm 0.8 \text{ kcal/mole}$, is ascribed to the electronic delocalization in the mixed-valent Cu(I)Cu(II)L^+ ion.

An Electrochemical Method for Measuring Electronic Delocalization
in Mixed-Valent Species.

Sir:

Binucleating macrocyclic ligands offer attractive opportunities to study electron transfer processes and metal-metal interactions. For example, the mixed-valent complex, Cu(I)Cu(II)L^+ , 2, apparently

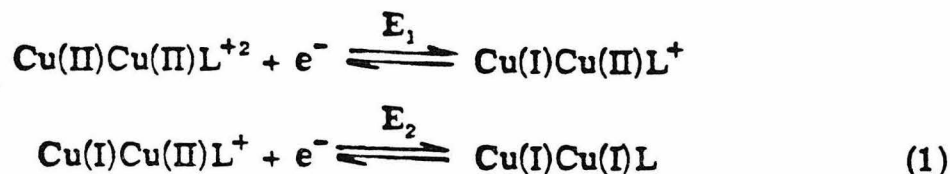


- 1 $\text{M} = \text{Cu(II)}, n = 2$
- 2 $\text{M} = \text{Cu(I)}, n = 1$
- 3 $\text{M} = \text{Mn(II)}, n = 2$
- 4 $\text{M} = \text{Fe(II)}, n = 2$
- 5 $\text{M} = \text{Co(II)}, n = 2$
- 6 $\text{M} = \text{Ni(II)}, n = 2$
- 7 $\text{M} = \text{Zn(II)}, n = 2$

exhibits temperature dependent intramolecular electron transfer ($\sim 10^{10} \text{ sec}^{-1}$ at 25°C).^{1, 2} The macrocyclic ligand in 2 also permits study of a series of complexes in which the ligand environment, including that of the bridging ligands, remains essentially constant while the metals are varied. Capitalizing on this feature, we report here an electrochemical method for directly measuring the electronic delocalization energy in the mixed-valent complex, 2, and in related materials.

The $\text{Cu(II)Cu(II)L}^{+2}$ complex, 1,³ was prepared by the method of Robson.⁴ All of the new heterobinuclear complexes, Cu(II)M(II)L^{+2} , 3-7, were prepared by a stepwise synthesis, under mild conditions, as follows. Condensation of two equivalents of 2-hydroxy-5-methylisophthalaldehyde with one equivalent each of 1, 3-diaminopropane and Cu(II) led to isolation of a mononuclear copper(II) complex.⁵ Further reaction with one equivalent of the appropriate divalent metal ion gave a complex with Cu(II) presumably in an N_2O_2 site and the second metal in an O_4 site. Subsequent reaction with one more equivalent of 1, 3-diaminopropane gave the heterobinuclear complexes, 3-7.⁶ All of the complexes gave satisfactory C, H, N, and M analyses and have been further characterized by X-ray fluorescence spectroscopy, electronic and infrared absorption spectroscopy, and variable temperature magnetic susceptibility.⁷ All complexes also exhibit cyclic voltammograms and differential pulse polarograms, which help to provide further evidence that the new complexes are uniformly

heterobinuclear and not mixtures of homobinuclear species. For example, the $\text{Cu(II)Cu(II)L}^{+2}$ complex, 1, exhibits two one-electron redox processes at $E_1 = -0.94$ V and $E_2 = -1.31$ V, eq 1.^{3, 8, 9}



In contrast, only a single reduction of Cu(II) to Cu(I) is observed in the CuM(II)L^{+n} series, 3-7, as shown in Figure 1 for the complex $\text{Cu(II)Mn(II)L}^{+2}$, 3.

Mixed-valent ion stabilization energies can be extracted from the magnitude of the separation of the two one-electron redox processes, $E_1 - E_2$, observed for the homobinuclear complexes. The separation actually reflects several phenomena, which can be considered for any binuclear complex, in the absence of significant coordination geometry changes, as follows: 1) Non-interacting metal sites will have $E_1 - E_2 = 36$ mV, attributable to the simple statistical factor, $\frac{RT}{F} \ln 4$.¹¹ 2) Electrostatic interactions become important as the metals come closer together yielding $E_1 - E_2 > 36$ mV. If $E_1 - E_2$ is large enough (~ 100 mV) two one-electron waves can often be resolved.¹² 3) Superexchange interactions may occur in one or more oxidation states, which can either increase or decrease the magnitude of $E_1 - E_2$. 4) Electronic delocalization can stabilize mixed-valent species which will be reflected as an increased separation, $E_1 - E_2$.

The electrochemical behavior of the $\text{Cu(II)Cu(II)L}^{+2}$ species, 1, can be analyzed in this context. The measured separation $E_1 - E_2 = 370$ mV is corrected for the statistical factor, 36 mV, to give $E_1 - E_2 = 334$ mV.

The measured superexchange stabilization in the $\text{Cu(II)Cu(II)L}^{+2}$ species ($-3/4 J = 217 \text{ cm}^{-1} = 27 \text{ mV}$)¹³ is used to correct $E_1 - E_2$ to 361 mV. No correction need be applied due to the diamagnetic Cu(I)Cu(I)L species. The separation $E_1 - E_2 = 361 \text{ mV}$ then reflects electrostatic interactions, and covalent stabilization of the mixed-valent Cu(I)Cu(II) species relative to the Cu(II)Cu(II) and Cu(I)Cu(I) species. Previous attempts to separate these contributions have relied on estimating the electrostatic component.¹⁴ In the present case the heterobinuclear complexes, 3-6, permit the covalent factor to be isolated since the electrostatic factor is constant.

Copper(II/I) reduction potentials as a function of the divalent metal ion in the second site, eq 2, are listed in Table 1.



Reduction potentials have been corrected for superexchange stabilization in the Cu(II)M(II)L^{+2} species as described above, and as estimated from magnetic susceptibility measurements in the solid state.¹⁵ These corrections increase in value to a maximum for the $\text{Cu(II)Cu(II)L}^{+2}$ species, 1, but in all cases represent only a small perturbation on the overall reduction potentials. Notice that in all cases the observed Cu(II/I) reduction potentials are identical within error limits at -1.07 V, with the sole exception of the dicopper ion at -0.93 V.

Since charges and ligand types are held constant in all complexes we propose that the observed 140 mV difference (3.2 ± 0.8 kcal/mole) can be ascribed to the stabilization of the mixed-valent Cu(I)Cu(II)L^+ ion, 2, relative to the Cu(I)M(II)L^+ , ions due to electronic delocalization. That no significant electronic delocalization occurs in the mixed-valent heterobinuclear species, Cu(I)M(II)L^+ , 3-7, ($\text{M(II)} \neq \text{Cu(I)}$) is suggested by the consistent Cu(II)/I reduction potentials obtained for this series of complexes.

Acknowledgment. We thank T. J. Smith for providing a sample of $\text{Cu(II)Zn(II)L(ClO}_4)_2$ and for synthetic advice and the National Science Foundation (Grant No. CHE76-82124) for financial assistance.

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Table I. Copper (II/I) reduction potentials as a function of the adjacent metal.⁷ Potentials are given vs. the ferrocene/ferricinium⁺ ion.⁷

Complex	Adjacent Metal	E^f , measured	E^f , corrected ^a
<u>3</u>	Mn(II)	-1.07 ± 0.01	-1.07 ± 0.01
<u>4</u>	Fe(II)	-1.07 ± 0.01	-1.06 ± 0.01
<u>5</u>	Co(II)	-1.08 ± 0.01	-1.07 ± 0.01
<u>6</u>	Ni(II)	-1.10 ± 0.01	-1.09 ± 0.01
<u>1</u>	Cu(II)	-0.94 ± 0.01	-0.93 ± 0.02^b
<u>7</u>	Zn(II)	-1.06 ± 0.01	-1.06 ± 0.01

^aCorrected for estimated antiferromagnetic coupling as described in the text.^{12,14} ^bThe reduction potential, E^f , for the dicopper complex, 1, has also been corrected for the statistical factor of 18 mV, as explained in the text.

References and Notes

- (1) Gagné, R. R.; Koval, C. A.; Smith, T. J. J. Amer. Chem. Soc. 1977, 99, 8367.
- (2) Gagné, R. R.; Cimolino, M. C.; Koval, C. A.; Smith, T. J. J. Amer. Chem. Soc. 1979, 101, 4571.
- (3) All complexes were studied as chloride salts, except for 7, $\text{Cu(II)Zn(II)L}^{+2}$, which was prepared as a perchlorate salt. The anion does not appear to affect the redox behavior of copper, as digestion of the halides with silver perchlorate left the reduction potential invariant in all complexes.
- (4) Pilkington, N. H.; Robson, R. Aust. J. Chem. 1970, 23, 225.
- (5) Okawa, H.; Kida, S. Bull. Chem. Soc. Jpn. 1972, 45, 1759.
- (6) Details of preparation and characterization will be reported in a subsequent paper. For $\text{Cu(II)Ni(II)L}^{+2}$, 6, the mononuclear Ni(II) complex was made first, followed by complexation of Cu(II).
- (7) Gagné, R. R.; Spiro, C. L.; Lambert, S. M.; Hendrickson, D. N. manuscript in preparation.
- (8) Note that preliminary electrochemical measurements on the perchlorate salt of 1 gave $E_1 = -0.92 \text{ V}$ and $E_2 = -1.31 \text{ V}$ vs. the ferrocene/ ferrocenium^+ couple, as reported in references 1 and 2.
- (9) All electrochemical measurements were made using N,N-dimethylformamide containing 0.1 M tetrabutylammonium perchlorate as solvent. Cyclic voltammetry and differential pulse polarography were performed using a platinum button electrode and

a Ag/Ag^+ reference electrode with ferrocene as an internal standard, as described elsewhere.^{2, 10}

(10) Gagné, R. R.; Koval, C. A.; Lisensky, G. A. manuscript in preparation.

(11) The statistical factor, $E_1 - E_2 = 36 \text{ mV}$, holds for the case in which the two metal ions have identical inherent reduction potentials. This value rapidly decreases in magnitude as the inherent reduction potentials of the two metal centers differ: Flanagan, J. B. Ph.D. Dissertation, California Institute of Technology, Pasadena, Ca., 1978. In the present study the statistical factor correction need be applied only to the dicopper complex, 1.

(12) (a) Ammar, F.; Savéant, J. M. Electroanal. Chem. Interfacial Electrochem. 1973, 47, 115; 1973, 47, 215; (b) Polcyn, D. S.; Shain, I. Anal. Chem. 1966, 38, 370; (c) Myers, R. L.; Shain, I. Anal. Chem. 1969, 41, 980; (d) Flanagan, J. B.; Margel, S.; Bard, A. J.; Anson, F. C. J. Amer. Chem. Soc. 1978, 100, 4248; (e) Phelps, J.; Bard, A. J. J. Electroanal. Chem. 1976, 68, 313.

(13) Lambert, S. M.; Hendrickson, D. N., Inorg. Chem. 1979, 18, 2683.

(14) Sutton, J. E.; Sutton, P. M.; Taube, H. Inorg. Chem. 1979, 18, 1017.

(15) Magnetic susceptibilities of Cu(II)M(II)LCl_2 were measured in the solid state⁷ but these should be reasonable estimates of solution

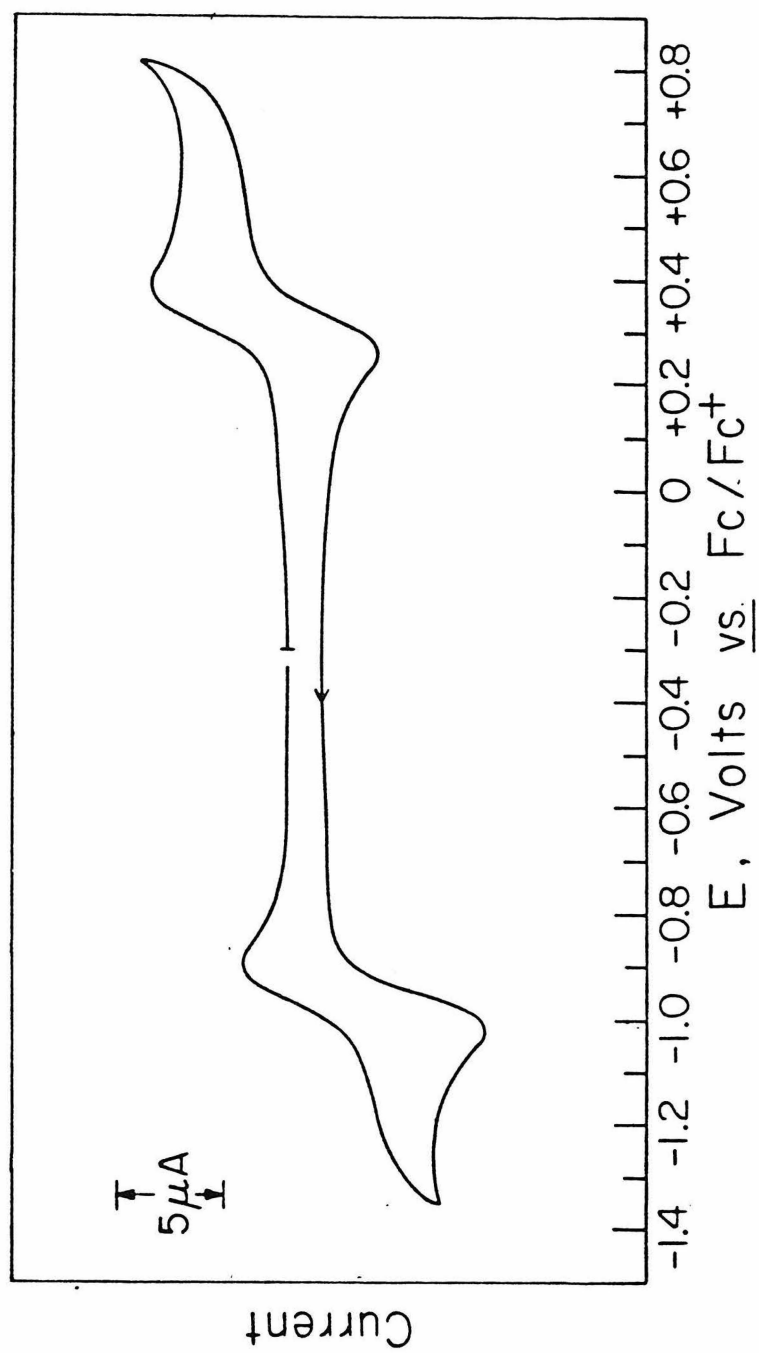
values since solid state intermolecular interactions are small and the macrocycle maintains the essential coordination features in both states. This conclusion is supported by susceptibility measurements of $M(II)_2LCl_2$ (five-coordinate metals) and $M(II)_2L(pyridine)_4Cl_2$ (six-coordinate metals) which give comparable results despite changes in the number and types of axial ligands.^{7, 16}

(16) Spiro, C. L.; Lambert, S.; Smith, T.; Gagné, R. R.; Hendrickson, D., manuscript in preparation.

Figure 1. The cyclic voltammogram of CuMnL^{+n} , 3, in methanol.

The wave at +0.3 V corresponds to the Mn(III/II) couple.

At -1.0 V is the Cu(II/I) wave. The absence of shoulders on each wave indicates little contamination by homonuclear impurities.



PART V.

The Synthesis, Redox Properties, and
Ligand Binding of Heterobinuclear Transition
Metal Macrocyclic Ligand Complexes.

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Abstract

A series of binuclear complexes $M_A(II)M_B(II)L^{+2}$ have been synthesized and characterized. The binucleating macrocyclic ligand, $L^=$, is a symmetric Schiff base composed of two 2,6-diformyl, 4-methylphenol units condensed with two 1,3-diaminopropane groups, resulting in two identical N_2O_2 coordination sites. The stepwise synthesis is described in detail. In all cases, $M_A(II) = Cu(II)$ while M_B was varied across the series $M_B(II) = Mn(II), Fe(II), Co(II), Ni(II), Cu(II),$ and $Zn(II)$.

The electrochemical properties of these species were examined by cyclic voltammetry, differential pulse polarography, sampled DC polarography, and coulometry. In each case reversible to quasi-reversible $Cu(II/I)$ electrochemistry was observed. The $Cu(II/I)$ reduction potential was, within experimental error, invariant with respect to the remote metal, M_B ; $E_f(Cu II/I) = -1.068 V$ vs. ferrocene/ferricinium⁺. The one exception is the homobinuclear complex, $M_A(II)=M_B(II)=Cu(II)$; the homobinuclear complex was more readily reduced, $E^f = -0.925 V$ vs. Fc/Fc^+ , than the heteronuclear species. The difference between the heteronuclear and homonuclear reduction potentials, $143\text{ mv}=3.3\text{ kcal/mole}$, has been ascribed, after a correction due to magnetic stabilization,

to a special stability associated with the mixed valent Cu(II)Cu(I)L^+ species, where some electronic delocalization has been previously demonstrated. In addition, the electrochemical properties of homonuclear complexes ($M_A = M_B$) are reported.

The ligand binding properties of the species $\text{Cu(I)M}_B(\text{II})\text{L}^+$, $M_B(\text{II}) = \text{Mn(II)}, \text{Fe(II)}, \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)},$ and Zn(II) , have been examined. Cu(I) shows an affinity for axial bases carbon monoxide, ethylene, tris (o-methoxyphenyl) phosphine, and 4-ethylpyridine. In contrast to the Cu(II/I) reduction potentials, the binding of axial bases to Cu(I) does seem to depend on the nature of the remote metal, M_B .

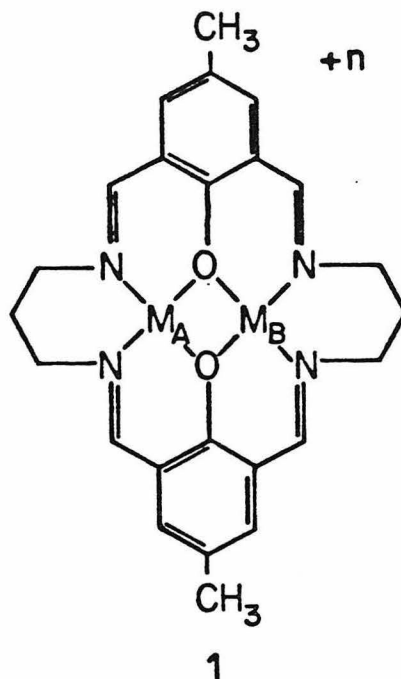
Introduction

Multimetallic species occupy an important position in modern inorganic chemistry. They are ubiquitous in nature as active sites in a variety of metalloenzymes, and are playing a significant and expanding role in industrial chemical catalysis.

The importance of multimetallic species has prompted a wide range of theoretical treatments concerning their properties. These include orbital models for magnetic exchange coupling,³ potential energy surface treatments of thermal intramolecular electron transfer,⁴ and perturbation calculations for optically induced intra-system charge transfer⁴ including vibronic⁵ and superexchange⁶ coupling contributions.

The experimental study of multimetallic complexes, dating back to 1704 and the discovery of Prussian blue⁷ is neither new nor has it been left fallow. The traditional approach to work in this area has been to synthesize complexes which contain two or more metal ions each with their appropriate complement of external ligands and one or more shared entities referred to as bridging groups. Metal-metal interactions are usually propagated through orbitals on the bridging group in an inner sphere fashion⁸ though outer sphere through-space coupling is also known.⁹ By systematically varying the bridging group, holding the metals and nonbridging ligands constant, the nature and extent of metal-metal communication has been studied.

In contrast, our approach has been not to vary the ligands, but rather to control as rigorously as possible both the external and bridging groups, while systematically varying the metal ions. This has been accomplished utilizing complexes of the type 1, $M_A M_B L^{+n}$.



The complexes 1 provide a good opportunity to study metal-metal interactions. By virtue of the close proximity of the metal ions (ca. 3.15 Å)¹⁰⁻¹³ the ligand ensures that some intramolecular coupling is likely. In the case of homonuclear species ($M_A = M_B$), originally prepared by Robson and co-workers,¹⁴ the high degree of symmetry requires that the fields and potentials about one metal ion be identical to its adjacent counterpart. This is especially important when comparisons are made to a series of heteronuclear ($M_A \neq M_B$) ions. Our hypothesis is that many differences in the physical, chemical, or redox properties of these complexes can then be ascribed to metal-

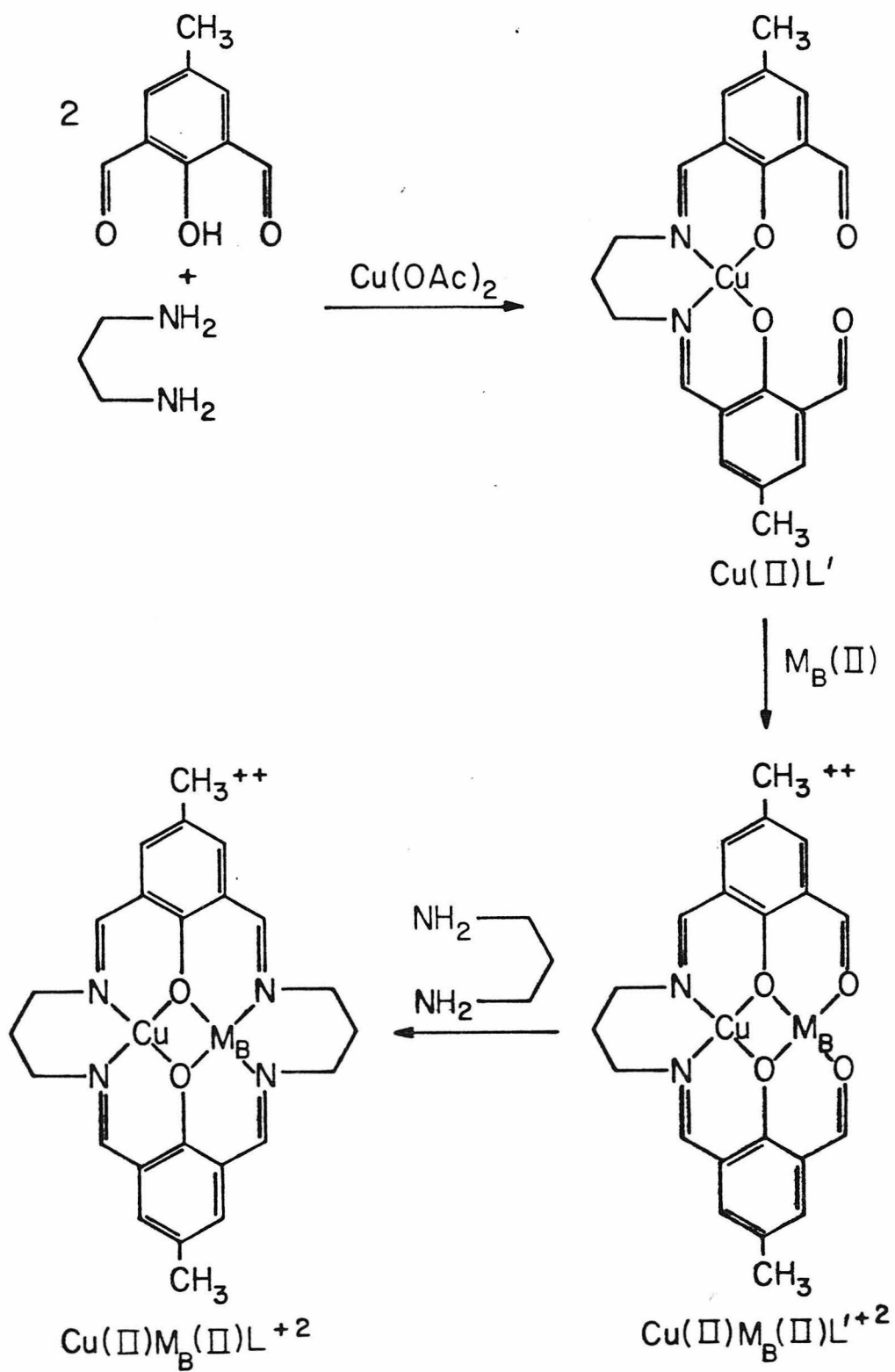
metal interactions since the liganding environment is held constant. In an earlier communication¹⁵ we reported the redox properties of 1 with copper in the M_A site while varying M_B across the series $M_B = \text{Mn(II)}, \text{Fe(II)}, \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)}, \text{and Zn(II)}$. Since the ligand remains constant, the observed changes in the electrochemical properties at the M_A site have been ascribed to some form of metal-metal communication with the remote metal M_B (vide infra). Reported herein are the detailed syntheses and characterization of these complexes, along with some of the physical, chemical, and redox consequences of these metal-metal interactions.

Results

Synthesis. Homonuclear complexes ($M_A = M_B$) were prepared by a slight variation of the method of Robson,¹⁴ utilizing a template synthesis. Since we did not succeed in separating mixtures of homo- and heteronuclear species, an alternate pathway to pure mixed metal binuclear complexes was developed, as outlined in Scheme 1. This route was chosen for several reasons. Mononuclear compounds $M_A(\text{II})L'$ and related systems were prepared and characterized by Okawa and co-workers,¹⁷ who found that the metal ion binds preferentially to the N_2O_2 site. We found that addition of $M_B(\text{II})$ salts to a suspension of $\text{Cu(II)}L'$ in methanol resulted in the rapid complexation of $M_B(\text{II})$ to what is likely the vacant O_4 site. Within ten minutes at the ambient temperature formation of crystalline salts of $\text{Cu(II)}M_B(\text{II})L'^{+2}$ appeared complete. Since the time in solution was short and the temperature apparently too low to surmount the

Scheme 1.

-64-



activation barrier to dissociation, little scrambling

$(2M_A M_B L'^{+2} \rightleftharpoons M_A M_A L'^{+2} + M_B M_B L'^{+2})$ was observed

(vide infra). Subsequent addition of one equivalent of

1,3-diaminopropane to a solution containing redissolved

$Cu(II)M_B(II)L'^{+2}$ resulted in the formation¹⁶ of salts of

$Cu(II)M_B(II)L'^{+2}$, 1. It was necessary to isolate the intermediates

$Cu(II)L'$ and $Cu(II)M_B(II)L'^{+2}$, as failure to do so resulted in

scrambled products. Several attempts at alternate syntheses¹⁸

either by performing reaction sequences in situ or by altering the

order of reactants consistently resulted in considerable quantities

of homonuclear impurities.

Characterization

Spectroscopy. The infrared spectra of all binuclear complexes of L are virtually indistinguishable, and have been discussed previously.¹⁴ Examination of IR spectra was useful in showing that the formation of complexes of L and its various intermediates was complete, but failed to distinguish which metals and in what ratios were present. Figure 1 shows the most diagnostic changes which occur in the various synthetic stages observed in the $\nu_{C=O}$ and $\nu_{C=N}$ stretch region for the compounds $M_A(II)L'$, $M_A(II)M_B(II)L'^{+2}$, and $M_A(II)M_B(II)L'^{+2}$.

The solid state electronic absorption spectra of these complexes,

Table 1, reveals little in the way of metal-metal coupling. It appears that the absorption maxima can be approximated by their homonuclear analogues.¹⁴ The low solubility of these complexes and the presence of intense charge transfer bands due to the ligand prevented detailed analysis of molar absorptions.

One technique that was useful in characterizing these complexes was X-ray fluorescence spectroscopy. By integrating back-scattered X-rays using a scanning electron microscope, metal ratios were approximated and sample homogeneity was confirmed. Though atomic absorption spectroscopy was ultimately utilized in the quantitative determination of metal content in these species, X-ray fluorescence spectroscopy enabled us to discard a large number of impure sample preparations without resorting to more time consuming and expensive analytical procedures.

Magnetic Properties. Room temperature magnetic moments, Table II, show that each metal is high spin in the solid state. Variable temperature susceptibility studies¹⁹ indicated some degree of magnetic exchange coupling in the homonuclear complexes. Similar studies on the heteronuclear species are in progress and will be reported elsewhere.²⁰

Electrochemistry. Electrochemical methods have been most effective in characterizing these complexes. The techniques utilized include cyclic voltammetry, differential pulse polarography, coulometry, and sampled DC polarography.

The first problem that electrochemical methods helped resolve was the establishment of purity of the heteronuclear complexes. For the homonuclear complexes, $M_A(II)M_A(II)L^{+2}$, two sequential redox processes were observed as shown in Table III. For example, for the dinuclear copper complex of L, the two sequential reductions from $Cu(II)Cu(II)L^{+2}$ first to $Cu(II)Cu(I)L^{+1}$ and then to $Cu(I)Cu(I)L$ were observed²¹ at -0.93 and -1.32 V negative of an internal reference standard,²² the ferrocene/ferricinium⁺ couple, (Fc/Fc^+) . In contrast, as shown in Figure II, only a single $Cu(II/I)$ wave is observed in the mixed metal copper-manganese species at -1.0 V. This indicates that only a single type of copper ion is present. The absence of shoulders at the potentials observed for the homonuclear species (Table III) indicates a less than ~5% homonuclear contaminant. The wave at ~+0.3 V (Figure 2.) is the $Mn(III)/(II)$ couple, and again appears without contamination. When compounds were prepared by alternate synthetic schemes to that shown in Scheme 1, shoulders on the principal waves were evident to varying degrees, reaching a maximum when isomolar mixtures of pure $Fe(II)Fe(II)L^{+2}$ and $Cu(II)Cu(II)L^{+2}$ were heated at reflux for 72 hours. In the latter case electrochemical

analysis of products revealed an approximately statistical distribution of homo- and heteronuclear species.

The reduction potential of the Cu(II/I) couple was determined as a function of the nature of the remote metal, M_B , in $Cu(II)M_B(II)L^{+2}$, 1. The results are shown in Table IV. Potentials are, within experimental error, independent of anion, the electrode (Hg or Pt), and the scan rate.

To ensure that the anion was innocent in these redox processes, a variety of experiments were undertaken. All complexes with halide anions were digested with $AgClO_4$; the Cu(II/I) reduction potentials determined in both the absence and presence of halide were identical. Addition of hundred-fold excesses of tetraethylammonium chloride and bromide also confirmed the spectator role of the anion for Cu(II/I) redox behavior. This is clearly not the case for oxidations at the M_B site. Figure 3 shows a conductometric titration of $Fe(II)Fe(II)L^{+2}$ with molecular bromine. After the first equivalent of bromine was added, enough to completely form $Fe(II)Fe(III)L^{+3}$, a sharp drop in conductivity relative to the ideal conductivity was observed in subsequent additions of bromine. The most reasonable interpretation of this behavior is that not only does bromine serve as an oxidant for Fe(II), but also, when the charge reaches a maximum in $Fe(III)Fe(III)L^{+4}$, the resultant bromide acts as a ligand and coordinates to one of the axial sites at the metal, resulting in the formation

of appreciable amounts of $\text{Fe(III)Fe(III)LBr}^{+3}$. Similar behavior was observed for Mn(III) and Co(III) .¹² For this reason, only the Cu(II/I) couple was explored, fixing the remote metal at the divalent oxidation state where complications due to the anion can be avoided.

When measured by cyclic voltammetry, the Cu(II/I) redox processes were quasi-reversible to reversible. $E_{p_c} - E_{p_a}$ exceeds the Nernstian requirement of 59 millivolts by up to 60 millivolts.²³

The deviation from 59 millivolts is highly scan rate dependent, with slower scan rates approaching the reversibility criterion. In addition, at scan rates less than 0.1 V/sec, anodic to cathodic peak currents are not equal, disproportionate loss of anodic current being observed.

The reason for this is not well understood, but could be due to a slow chemical reaction or rearrangement subsequent to charge transfer.

Measurements of reduction potentials by differential pulse polarography yielded similar results, where potentials agreed with those measured by other techniques and are independent of scan rate. Quasi-reversible behavior was observed with this technique as well, with full widths at half maxima (FWHM, Table IV) ranging from 92 to 120 millivolts. The criterion for reversibility is a 90 millivolt FWHM.²⁴

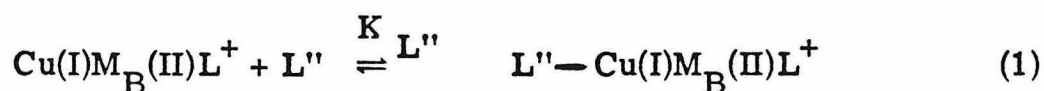
When measured by sampled DC polarography, reversible waves were observed, showing linear plots of $\ln(i_d/i_d - i)$ with slopes of 59 ± 3 millivolts.²⁵ The values for the formal Cu(II/I) reduction potential in Table IV represent an equally weighted average of each determination

of E^f by the various techniques. Standard deviations were determined in the usual fashion. Sampled DC polarographic slopes, differential pulse peak widths, and cyclic voltammetric determinations of $E_{p_c} - E_{p_a}$ are all consistent with one electron redox processes. Controlled potential electrolyses yielded coulometric n -values of unity in the cases examined, Table IV.

The electrochemistry occurring at the second metal ion, M_B in $Cu(II)M_B(II)L^{+2}$, is well out of the range of redox activity at the copper site. In the case of the manganese-copper complex, a broad $Mn(III/II)$ wave ($E_{p_c} - E_{p_a} = 160\text{mv}$) is observed at $\sim +0.150\text{ V vs. }Fc/Fc^+$ in DMF. In methanol, Figure 2, the wave occurs at $+0.300\text{ vs. }Fc/Fc^+$, and is quasi-reversible ($E_{p_c} - E_{p_a} = 80\text{mv}$). In N,N -dimethylformamide, the iron-copper binuclear complex shows a nearly reversible ($E_{p_c} - E_{p_a} = 80\text{mv}$) wave at $-0.15\text{ V vs. }Fc/Fc^+$ (Figure 4) corresponding to the $Fe(III/II)$ couple. In methanol, a reversible wave ($E_{p_c} - E_{p_a} = 60\text{mv}$) is present at $+0.110\text{ V vs. }Fc/Fc^+$. Current is observed for the cobalt-copper complex in the region around $+0.25\text{ V vs. }Fc/Fc^+$, but the wave is so broad as to offer no reasonable approximation to the $Co(III/II)$ formal potential. The nickel-copper species $Cu(II)Ni(II)L^{+2}$, shows two differential pulse polarographic waves (Figure 5) at -1.075 and $-1.560\text{ V vs. }Fc/Fc^+$. The $Ni(II/I)$ couple, the more negative wave, has a 70 millivolt peak to peak separation via cyclic voltammetry. No nickel (III/II) couple is present prior to

solvent oxidation at ca. +1.0 V. Zinc is electroinactive in the zinc-copper ion.

Chemical Studies. Ligand binding to Cu(I) as a function of the remote metal ion, M_B in $Cu(I)M_B(II)L^{+1}$, 1, eq. 1, was examined.



$$K_{L''} = \frac{[L'' - Cu(I)M_B(II)L^{+}]}{[Cu(I)M_B(II)L^{+}] [L'']} \quad (2)$$

Again, the remote metal, M_B was varied across the series $M_B = Mn(II), Fe(II), Co(II), Ni(II), Cu(II),$ and $Zn(II)$. The results are shown in Table V. Equilibrium constants, $K_{L''}$ in eq. 2 were determined via an electrochemical method which does not require the isolation of $Cu(I)M_B(II)L^{+}$ complexes. This method has been described in detail elsewhere,^{26, 27} and is based on the principle that binding of the axial base L'' in eq. 1 depletes the concentration of $Cu(I)M_B(II)L^{+}$. Since $Cu(I)M_B(II)L^{+}$ appears in the Nernst equation, eq. 3, this decrease in the concentration of $Cu(I)M_B(II)L^{+}$ due to binding causes a shift in the measured potential for the $Cu(II/I)$ couple.

$$E_{\text{measured}} = E^{\circ} - \frac{RT}{nF} \ln \frac{[Cu(I)M_B(II)L^{+}]}{[Cu(II)M_B(II)L^{+2}]} \quad (3)$$

For example, as can be seen in Figure 6, addition of $5 \times 10^{-3} \text{ M}$ of $\text{L}'' = \text{tris (o-methoxyphenyl) phosphine}$, to the nickel-copper heterobinuclear complex, $\text{Cu(II)Ni(II)L}^{+2}$, shifts the polarographic wave due to Cu(II/I) positive by 30 millivolts. By applying the Nernst expression, eq. 3, to the equilibrium binding equation, this 30 mv shift in potential can be quantitatively related to the equilibrium binding constant by the use of eq. 4,

$$K_{\text{L}''} = \frac{e^{nF(\Delta E)/RT} - 1}{[\text{L}'']} \quad (4)$$

in which $\Delta E = E_{\text{blank}}^{\frac{1}{2}} - E_{\text{L}''}^{\frac{1}{2}}$

$E_{\text{blank}}^{\frac{1}{2}}$ is the half wave potential measured polarographically in the absence of L'' (Table IV), while $E_{\text{L}''}^{\frac{1}{2}}$ is the measured potential at a given concentration of L'' . The other symbols have their usual meanings, with $n=1$ in all cases and $K_{\text{L}''}$ representing the equilibrium constant in eq. 2. In the example above for Cu(I)Ni(II)L^+ , $E_{\text{blank}}^{\frac{1}{2}} = -1.055 \text{ V}$, $E_{\text{PR}_3}^{\frac{1}{2}} = -1.025 \text{ V}$ where $[\text{PR}_3] = 5 \times 10^{-3} \text{ M}$, and $K_{\text{PR}_3} = 4.4 \times 10^2 \text{ M}^{-1}$.

Use of this expression requires the usual assumption that little change in the diffusion constants take place upon charge transfer. In addition, it requires that equilibrium be established rapidly relative to the electrochemical time scale, that the electrode surface concentration of L'' is maintained, and that no other conflicting equilibria be present.

For each substrate L'' studied, (L'' = carbon monoxide, ethylene, 4-ethylpyridine, and tris(o-methoxyphenyl) phosphine) quasi-reversible to reversible sampled DC polarograms were obtained, indicating that fast on-off equilibria had been established. All other phosphines and phosphites examined showed irreversible electrochemistry. These included triphenyl phosphine, tris-tolyl phosphines, tris-cyclohexyl phosphine, tris(p-methoxyphenyl) phosphine, and a wide variety of substituted aromatic phosphites. Molecular models indicate extensive steric hindrance in the tris(o-methoxyphenyl) phosphine, which may play an important role in facilitating rapid establishment of equilibrium with L'' .

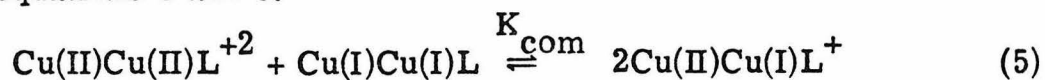
The criterion that no other equilibria are present requires some further discussion, since these substrates may potentially bind to Cu(II) or the other $M_B(II)$ centers in the mixed metal species. For $L'' = PR_3$ and 4-ethylpyridine, a broad range of concentrations of L'' were utilized, yielding results consistent with only a single equilibrium. In addition, no shifts in the remote metal ion's wave, the $M_B(III/II)$ couple, were observed.²⁸ No spectral changes were observed in these species upon addition of bases to the oxidized form, $Cu(II)M_B(II)L^{+2}$, also consistent with negligible competing equilibria. Still, due to the spectral and/or electroinactivity of some of these species (i.e. Zn(II) in $CuZn(II)L^{+n}$) contributions to the data due to binding to the oxidized form cannot be completely ruled out. In the

cases where $L'' = \text{CO}$ or ethylene (1Atm), binding to the high spin $M(\text{II})$ ions would be most unusual;²⁹ all evidence is consistent with the oxidized form being inert to these bases.

The assumption that the surface concentration of L'' at the electrode was maintained during and subsequent to charge transfer is reasonable for several reasons. A minimum ten-fold excess of L'' over $\text{Cu(I)M}_B(\text{II})L^+$ was utilized in all experiments, the equilibrium constants are quite small (Table V), and the equilibrium constants do not vary appreciably nor consistently over a wide range of concentrations of L'' .

Discussion and Conclusions

Delocalization Energy. The binuclear copper complex, $\text{Cu(II)Cu(II)L}^{+2}$, like many homobinuclear species, shows two sequential reductions, E_1 and E_2 separated by an amount $\Delta E = E_1 - E_2 = 0.390 \text{ V}$.^{21, 22} The thermodynamic significance of ΔE can be illustrated by the comproportionation equilibrium shown in equations 5 and 6.



$$\Delta E = \frac{RT}{nF} \ln (K_{\text{com}}) \quad (6)$$

A large value of ΔE indicates a considerable stability of the mixed valent Cu(II)Cu(I)L^+ ion relative to its constituents, the equilibrium lying far to the right in equation 5.

In general K_{com} reflects a number of microscopic phenomena.

I) Major structural changes such as bond making and breaking, changes in coordination number, and severe changes in coordination geometry upon charge transfer can shift comproportionation equilibria.³⁰ II) If no interaction takes place between the metal ions, $K=4$ based on statistical distribution of charges, resulting in a ΔE value of 0.036 V and a single voltammetric wave.³¹ III) If the metal ions are in close proximity, a through space coulombic interaction may be important. A $+n$ ion will be more readily reduced than a $+n-1$ ion based on electrostatic considerations alone. This will increase ΔE and hence K_{com} . IV) Magnetic superexchange effects between two metals may stabilize one or more oxidation states in species which contain multiple paramagnetic centers, also resulting in a change in ΔE . V) Electronic delocalization in mixed oxidation states will enhance the stability of these species with resulting increases in ΔE .

The heteronuclear complexes $M_A(II)M_B(II)L^{+2}$, 1, were examined to help quantitatively define some of these effects. The complexes were designed to I) minimize structural effects accompanying redox changes, II) keep coulombic interactions constant and cancellable, and III) permit superexchange effects to be measured separately. It was expected that electrochemical measurements would then permit a determination of electronic delocalization energies in mixed valent

species. In fact, this approach worked well for the complexes $\text{Cu(II)}M_B(\text{II})L^{+2}$, 1, for which the Cu(II/I) reduction potential was determined as a function of the remote metal ion, $M_B(\text{II})$. The results, summarized in Table IV, are unequivocal. Within experimental error, the Cu(II/I) reduction potentials are independent of the remote metal ion M_B , unless M_B is copper (II). For $M_A = M_B = \text{Cu(II)}$, it is easier to add an electron by an average of 143 (14) mv or 3.3 (3) kcal/mole. We ascribe this difference in $\text{Cu(I)Cu(II)}L^+$ vs $\text{Cu(I)}M_B(\text{II})L^+$ ($M_B \neq \text{Cu}$) to the fact that only the $\text{Cu(I)Cu(II)}L^+$ species can exist, to any extent, as a resonance stabilized, delocalized ion. The electronic delocalization energy in $\text{Cu(I)Cu(II)}L^+$ is the major contribution to the 3.3 (3) kcal/mole value, as can be shown by more detailed analysis of the experimental data and the factors affecting the redox properties of these particular complexes, as follows.

Although the macrocyclic ligand in $\text{Cu}M_B(\text{II})L^{+n}$ can accommodate a range of coordination geometries,¹⁰⁻¹³ it is likely that only negligible structural changes accompany one electron reduction of $\text{Cu(II)}M_B(\text{II})L^{+2}$. While conductivity studies along with electrochemical experiments cited in the Results section clearly demonstrate that the anion exhibits the potentiality to bind to higher oxidation states of metals complexed with L, they also indicate the spectator role of the anion in Cu(II/I) redox behavior. Indeed for this reason, the decision

to study Cu(II/I) electrochemistry as a function of the remote metal was made. It is possible, however, that the solvent may be involved in some fluxional manner with the copper center. While it is unreasonable to suggest that there will be no changes in the coordination geometry at copper upon charge transfer, it is likely that whatever changes occur in the reduced form (e.g. a distortion toward tetrahedrality) do so in such a uniform fashion across the series $M_B(II) = Mn(II), Fe(II), Co(II), Ni(II), Cu(II),$ and $Zn(II)$ as to obviate the need for concern here. The concordance of the data supports our interpretation. While the geometry at the $M_B(II)$ site in solution is unknown, it is unlikely that significant changes in coordination occur at $M_B(II)$ upon charge transfer to Cu(II).

The statistical contribution to ΔE of 36 mv ($K_{com} = 4$) holds for identical, non-interacting metal ions. As metal-metal interaction increases, the statistical contribution is expected to decrease. For $Cu(I)Cu(II)L^+$, in which significant interaction is apparent (vide infra), only a very small (< 5 mv), essentially negligible, statistical contribution is expected.³¹

Coulombic contributions to the Cu(II/I) reduction potential in $CuM_B(II)L^{+n}$ are essentially constant since the +2 charge on M_B and, most likely, the Cu to $M_B(II)$ distance ($\sim 3.15 \text{ \AA}$)¹⁰⁻¹³ are maintained for all $M_B(II)$. This hypothesis is supported by the data in Table IV. Although the Cu(II/I) reduction potentials are surely dependent on the

charge of the remote metal, M_B ,⁻⁷⁸⁻ constant values of $E^f_{Cu(II/I)}$ were observed for all $M_B(II) \neq Cu(II)$, within experimental error.

The contribution to ΔE due to magnetic superexchange is more complex. In the dicopper ion, $Cu(II)Cu(II)L^{+2}$, $J = -293 \text{ cm}^{-1}$,¹⁹ where $2J$ represents the singlet-triplet splitting. The coupling drops off rapidly for the other heteronuclear species.²⁰ Since only a slight excess of the dinuclear copper ions are in the singlet state (59%) relative to the triplet state (41%) at ambient temperatures, and since spin equilibria are likely to be established rapidly,³² only a very slight difference between the observed potential and the potential corrected under the assumption the $J=0$, is expected.

The correction has been calculated as follows. The uncorrected potential was measured as described previously ($E^f = -0.925 \text{ V vs. Fc/Fc}^+$). It was assumed that the distribution of spin states was maintained at the electrode throughout the course of charge transfer and $E^{\frac{1}{2}}$ was then calculated under the assumption that 100% (rather than 59%) of the species were in the triplet form ($E^{\frac{1}{2}} = -0.902 \text{ V vs. Fc/Fc}^+$). Since the singlet-triplet separation is $588 \text{ cm}^{-1} = 73 \text{ millivolts}$, $E^{\frac{1}{2}}_{\text{singlet}}$ was calculated to be $[-0.902 - 0.073 \text{ V}] = -0.975 \text{ V vs. Fc/Fc}^+$. Solution of the isotropic Heisenburg Hamiltonian, $H = J \hat{S}_1 \cdot \hat{S}_2$, yields the result $E_S = J(S(S+1) - s_1(s_1+1) - s_2(s_2+1))$. For the dinuclear copper centers, s_1 and s_2 are $\frac{1}{2}$, and $S=1$ or 0 for the triplet and singlet respectively; $E_{\text{singlet}} = -\frac{1}{2}J$, while

$E_{\text{triplet}} = +3/2 \text{ J}$. If we assume $J=0$, the calculated potential will lie three-fourths of the way between the triplet potential (0.902 V) and singlet potential (0.975 V) so $E_{\text{corr}} = -0.955 \text{ V}$, where E_{corr} is the reduction potential corrected for superexchange stabilization. No such correction need be applied to the other species since these corrections drop off rapidly with J , and are quite small.³³

Having determined the entropic and magnetic contributions to the reduction potentials, and having held the coulombic factor constant, leaves 113 mv, or 2.6 kcal/mole, of special stability associated with the dinuclear Cu(I)Cu(II)L^+ ion due entirely to the delocalization phenomenon.

That the mixed-valent Cu(I)Cu(II)L^+ ion experiences significant delocalization is supported by previous studies of this molecule²¹ which demonstrated the presence of a delocalized 7-line hyperfine pattern in the esr spectrum, as well as an intervalence, or metal-to-metal charge transfer band in the electronic spectrum. It is unlikely that electron transfer from Cu(I) to $M_B(\text{II})$ will occur for any other metal, since the transfer of charge from Cu(I) to $M_B(\text{II})$ would require surmounting a minimum barrier of 10 kcal/mole in the case where $M_B = \text{Ni(II)}$, and may reach several hundred kcal/mole where $M_B = \text{Zn(II)}$.

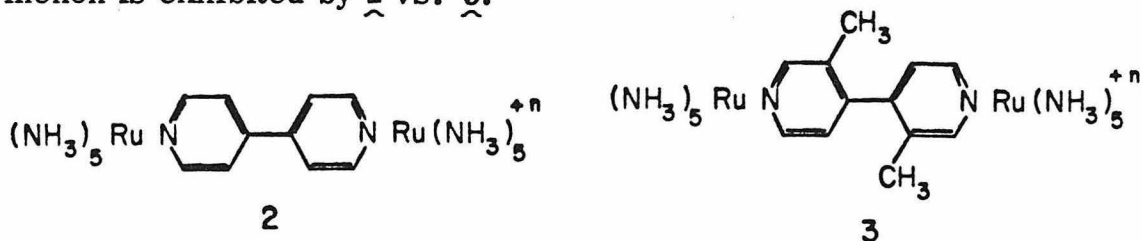
The data also reveal a consistent pattern when examining the $M_B(\text{III/II})$ redox couples in $\text{Cu(II)M}_B(\text{II})\text{L}^{+2}$. It appears easier to

oxidize $M_B(II)$ in the homonuclear complexes $M_B(II)M_B(II)L^{+2}$ (Table III) than in $Cu(II)M_B(II)L^{+2}$. In light of the $Cu(II/I)$ data, a special stability might be expected for $M_B(II)M_B(III)L^{+3}$. In particular, the $Mn(III/II)$ couple in the dinuclear manganese ion occurs at -0.05 V vs. ferrocene compared to $+0.300$ V in $Mn(II)Cu(II)L^{+2}$, though in the former the manganese (III/II) couple is strongly anion dependent ranging from -0.05 V ($X=Br^-$) to -0.02 V ($X-OAc^-$) to $+0.03$ V (ClO_4^-). In any case, it does appear to always be negative of the heteronuclear (III/II) couple ($X=Cl^-$) consistent with the copper(II/I) trend. In addition, comparison of the $Fe(III/II)$ couple in $Fe(II)Fe(II)L^{+2}$ vs. that in $Cu(II)Fe(II)L^{+2}$, Figure 7, reveals that the mixed valent $Fe(II)Fe(III)L^{+3}$ is more accessible (by 130 mv = 3.3 kcal/mole) than $Cu(II)Fe(III)L^{+3}$. While no clean cobalt (III/II) electrochemical processes were observed in $Cu(II)Co(II)L^{+2}$, current was observed approximately 250 millivolts positive of the $Co(III/II)$ couple in $Co(II)Co(II)L^{+2}$, again consistent with the observed trend in the dinuclear copper ion. In each case, the species which exhibits the structural potentiality for delocalization is the most thermodynamically accessible. It cannot be overemphasized, however, that these latter results may be fortuitous and artifactual since structural controls have been relaxed, based on the known propensity of trivalent metals bound to L coordinate anions to varying degrees (Figure 3). In addition, no extensive study such as that for the mixed metal series $Cu(II)-M_B(II)$

has been undertaken as a control, nor has any evidence for delocalization in the $M_B(II)M_B(III)L^{+3}$ series been demonstrated.

Our interpretation of these results may shed some light on previously reported electrochemical data in other systems which show a propensity toward electronic delocalization. In mixed valent systems which have a completely delocalized ground state, Class III in the Robin and Day scheme,³⁴ unusually large values of K_{com} and ΔE have been observed. For example, the oxo bridged binuclear ruthenium complexes, $(NH_3)_5 Ru-O-Ru(NH_3)_5^{+5}$ ³⁵ and $(bipy)_2 Cl-Ru-O-Ru(bipy)_2 Cl^{+3}$ ³⁶ exhibit ΔE values of 2.0 V ($K_{com} = 10^{34}$) and 2.2 V ($K_{com} = 10^{38}$) respectively. We suggest that such extraordinarily large values of K_{com} are primarily due to the special stability of delocalized ions. Another system which exhibits delocalization is the mixed valent $(NH_3)_5 Ru-pyrazine-Ru(NH_3)_5^{+5}$ ³⁷ ion reported by Creutz and Taube.³⁸ The reported $Ru(III/II)$ reduction potentials for $Ru(III)Ru(III) \rightarrow Ru(II)Ru(III) \rightarrow Ru(II)Ru(II)$ are $E_1 = +0.700$ V and $E_2 = +0.310$ V, giving $\Delta E = 0.39$ V and $K_{com} = 4 \times 10^6$. The $Ru(III/II)$ reduction potential in the Ru-Rh analogue, $(NH_3)_5 Ru-pyrazine-Rh(NH_3)_5^{+6/+5}$, was also reported ($E_1 = 0.650$ V). We propose that the difference of 50 mv = 1.2 kcal/mole between E_1 for the Ru-Ru vs. the Ru-Rh complex is another manifestation of the delocalization phenomenon where the $Ru(III)-Ru(II)$ species can have a delocalized ground state,

while the electron is clearly trapped at ruthenium in the Ru(II)-Rh(III) dimer. Additional supportive evidence for the generality of this phenomenon is exhibited by 2 vs. 3.

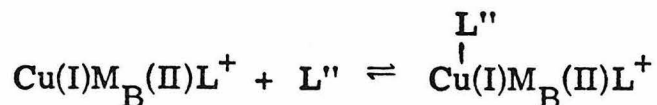


For 2, $K_{\text{com}} = 20$ while complex 3 has $K_{\text{com}} = 10$; ³⁹ in 3 the dimethyl substitution probably results in a dihedral twist between the pyridyl planes, a steric effect which may block the conjugated pathway, and hence delocalization between the metals.

In seeking to understand polymetallic enzymes and catalysts, especially those involved in redox transformations, it is important to recognize that mixed-valent moieties may represent special pockets of stability. In some cases Nature may have utilized these thermodynamic sinks to adjust reduction potentials. For example, in high potential iron proteins with cubane type Fe_4S_4 groups extensive delocalization in the mixed valent species has been demonstrated⁴⁰ and is likely to be one reason these clusters have such positive potentials as well as a large range of potentials in subsequent reductions. Elsewhere, such as in electrocatalysts to be utilized for multielectron reactions, this delocalization energy could cause sequential rather than concerted charge transfers, resulting in

significant overpotentials and loss of catalyst efficiencies.

Ligand Binding. In addition to redox coupling between metals, the chemical manifestations of metal-metal interactions have been probed by studying the equilibria:



In light of the electrochemical data summarized in Table IV which indicated that the heterometal ion $\text{M}_{\text{B}}(\text{II})$, has little effect on the electron density at the copper site, the results on the chemical consequences (Table V) of metal-metal interactions are somewhat surprising. No obvious trends are present in this limited study, but some predictions are clearly not borne out. First, the chemical binding of axial bases, L'' , to Cu(I) is not independent of the heterometal, as the redox potentials might imply. Second, we might have expected that the axial bases would bind more poorly to the dinuclear copper species relative to the others, since this would likely result in some loss of electronic delocalization by introducing an inequivalence to the metals. This was also not observed. In any case, it is apparent that the chemical manifestations of metal-metal interactions do not represent a simple reflection of their redox properties, but are a complicated function of several as yet undetermined factors. Though these results are poorly understood, it is both encouraging and exciting that some chemical manifestation that is dependent on the

nature of the heterometal ion has been discovered. Obviously, more extensive experimental studies accompanied by a firm theoretical basis are needed to determine the generality and significance of this observation.

Experimental

Physical Measurements. Infrared spectra were taken as Nujol mulls, using a Beckmann IR4240 model grating infrared spectrophotometer. Electronic absorption spectra were measured using a Cary 14 model UV/visible spectrophotometer. Magnetic measurements were made via the Faraday method, at the ambient temperature using a Cahn electrobalance, or by a vibrating magnetometer as described elsewhere.⁴¹ Magnetic moments were corrected for diamagnetism using Pascal's constants.⁴² Elemental analyses were performed by the California Institute of Technology analytical facility along with Galbraeth Microanalytical Laboratories, Knoxville, Tenn. Absolute metal percentages were determined by atomic absorption. Metal ratios were conveniently determined by the integral counting of back scattered X-ray fluorescence radiation from an International Scientific Instruments SMS 2-2 model scanning electron microscope, equipped with a Tracor Northern model TN-1700 data processor.

Electrochemical data were taken with a Princeton Applied Research model 174A Polarographic Analyzer in the cyclic voltammetric (CV),

differential pulse polarographic (DPP), and sampled DC (SDC) polarographic modes. Platinum button electrodes were used in the CV and DPP modes, with the dropping mercury electrode used in the SDC mode. In the latter case, drop times were restricted to 5 seconds, though scan rates varied from 0.2 to 1.0 millivolts/second. Coulometric measurements were performed on a Princeton Applied Research model 173 digital coulometer using a platinum gauze electrode for oxidations, and a mercury pool electrode for reductive electrolyses. The cell components consisted of a standard two compartment cell with the chambers separated by a medium porosity sintered glass. One compartment housed the working electrode, the auxiliary electrode (Pt wire) and the electroactive solution. The other chamber contained a Ag/Ag^+ reference electrode (Ag wire/ AgNO_3 , 0.01 N in acetonitrile) to complete the circuit. In actuality, the reference electrode was not used to determine reduction potentials. Rather, an internal standard, the ferrocene/ferricinium⁺ couple was utilized. In each case, a small amount of ferrocene was added to the electroactive solution for comparison to the measured potentials. This method, described in detail elsewhere,²² enables us to circumvent any temporal variations in junction potentials or ohmic drop due to uncompensated solution resistance. All solutions were saturated with an inert gas for at least 15 minutes prior to analysis.

Synthesis of Compounds. All solutions and reagents were purchased from commercial sources and utilized without further purification. One exception is the N,N-dimethylformamide (DMF) used as an electrochemical solvent, which was distilled over molecular sieves and anhydrous MgSO_4 prior to use.

2,6-diformyl, 5-methylphenol.⁴³ Para-cresol (216 g) was added to a solution of NaOH (100 g) in water (400 ml). Following full development of a gold color, 37% formaldehyde (430 g) was added. The mixture was stirred for 20 min., and allowed to stand overnight at the ambient temperature. The yellow granular 2,6-dimethylol, 5-methylphenol product was collected by vacuum filtration and washed with water saturated with sodium chloride (2 X 400 ml). This product was transferred to a 3-neck, 5 liter round-bottom flask fitted to an overhead stirrer. Water (1300 ml) and a 33% sodium hydroxide solution (130 ml) were added. The mixture was stirred for ~0.5 hr. Para-toluenesulfonyl chloride (494 g) dissolved in toluene (520 ml) was added and the solution was allowed to stir for 20 hours, at which time an aqueous and emulsified phase was present. The mixture was cooled in an ice-water bath and toluene (200 ml) was added with stirring. After 10 min., additional toluene (300 ml) was added at which point solids were evident. After an hour, a final amount of toluene (100 ml) was added. This slurry was stirred for 15 min. at which time the white solid tosylated derivative was collected by vacuum filtration,

washed with toluene (400 ml), and dried in a vacuum for 12 hrs, or until the drying was judged complete. The white solids were weighed and transferred to a 5 liter, 3-neck round bottom flask equipped with an overhead stirrer, a water-cooled reflux condensor, and a 125 ml addition funnel. Acetic acid (14 moles per mole of tosylated phenol) and sodium dichromate (one mole per mole of the tosylated phenol, FW = 338 g/mole) were required for the oxidation, as follows.

Approximately 1/4 of the acetic acid was added to the tosylated phenol in the 5 liter flask. The mixture was heated to reflux with stirring (110-116°C). The remaining acetic acid was added to the dichromate in a 2 liter beaker, with dissolution accomplished by heating on a steam bath. The dichromate/acid solution was added dropwise with stirring to the tosylated phenol over 35 min. CAUTION: strong oxidant. After addition was complete, stirring at reflux was continued for 10 min. The solution was then allowed to cool slowly (~3 hr.) to the ambient temperature. The crystals which had formed were collected with vacuum filtration, and washed with water until most of the green color was gone, leaving a pale green solid. The product was vacuum dried overnight. The dry tosylated dialdehyde (~285 g) was added slowly to concentrated sulfuric acid (900 ml) in a 4 liter beaker, and stirred for 1 hr. The beaker was placed in an ice bath. An ice-water slurry was added slowly to the acid solution until the total volume reached 3800 ml. After all the ice melted, the

precipitate was collected by vacuum filtration, washed with water (3 X 250 ml) and dried overnight. The crude product was recrystallized from toluene, yielding pale brown needles (95 g, 29% overall yield) which were used without further purification. A more pure product can be obtained by sublimation. CAUTION: Skin contact with 2,6-diformyl, 4-methylphenol leaves a deep yellow stain which will persist for several days. Melting point 129-130° C, literature 133.5° C. The nmr spectrum, showing singlets at 11.4 ppm (phenolic), 10.2 ppm (aldehydic), 7.8 ppm (aromatic), and 2.4 ppm (methyl), is consistent with the assigned structure.

Cu(II)L'¹⁷ To warm N,N-dimethylformamide (40° C, 50 ml) containing 2,6-diformyl, 4-methylphenol (1.950 g), 1,3-diaminopropane (0.5 ml) was added dropwise, with stirring, followed by the addition of solid cupric acetate (1.183 g Cu(OAc)₂ · 2H₂O). The warm solution was allowed to stir until all the turquoise crystals of copper acetate had dissolved. At this point, deep olive green needles of CuL' had formed. These were collected within 0.5 hr., washed with diethyl ether, and vacuum dried.

Anal. Calc: C, 58.74%; H, 4.66%; N, 6.52%

Obsd: C, 58.5%; H, 4.7%; N, 6.75%

Ni(II)L'. The preparation is identical to that of Cu(II)L', excepting that nickel acetate (1.475 g of Ni(OAc)₂ · 4H₂O) was substituted for cupric acetate. The resulting crystals were yellow-brown.

Anal. Calc: C, 59.43%; H, 4.71%; N, 6.60%

Obsd: C, 59.75%; H, 4.9%; N, 6.7%

Cu(II)Mn(II)L'Cl₂. To methanol (30 ml) under helium atmosphere at the ambient temperature was added manganous chloride (2.0 g MnCl₂ · 6H₂O). To this solution was added solid Cu(II)L' (2.09 g). This was stirred until the resulting green solids appeared homogeneous, but in no case for more than 10 min. The product was collected by vacuum filtration, washed with diethyl ether, and vacuum dried.

Cu(II)Mn(II)LCl₂ · H₂O. To methanol (30 ml) at the ambient temperature under a helium atmosphere was added Cu(II)Mn(II)L'Cl₂ (2.32 g). 1,3-Diaminopropane (0.33 ml) was added dropwise with stirring. Within 5 min. brownish green crystals had formed and were collected. washed with diethyl ether, and vacuum dried.

Anal. Calc: C, 47.2%; H, 4.6%; N, 9.2%; Cu, 10.3%; Mn, 9.1%.

Obsd: C, 46.8%; H, 4.4%; N, 8.7%; Cu, 9.8%; Mn, 9.5%.

$\text{Cu(II)Fe(II)L'Cl}_2 \cdot 2\text{H}_2\text{O}$. To methanol (30 ml) at the ambient temperature under a helium atmosphere was added Cu(II)L' (0.5 g). Ferrous chloride (0.233 g $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) was added to this solution with stirring until the formation of deep purple crystals was judged complete, ~ 10 min. These were collected, washed with diethyl ether, and vacuum dried. Addition of diethyl ether to the filtrate resulted in the formation of additional product.

Anal. Calc: C, 42.71%; H, 4.06%; N, 4.74%.

Obsd: C, 43.1%; H, 3.9%; N, 4.45%.

$\text{Cu(II)Fe(II)LCl}_2 \cdot \text{H}_2\text{O}$. To methanol (20 ml) at the ambient temperature under a helium atmosphere was added $\text{Cu(II)Fe(II)L'Cl}_2 \cdot \text{H}_2\text{O}$ (0.576 g). 1,3-Diaminopropane (0.068 ml in 1.0 ml methanol) was added dropwise with stirring. Within 5 min. orange crystals had formed, and were collected, washed with diethyl ether, and vacuum dried.

Anal. Calc: C, 47.2%; H, 4.6%; N, 9.2%; Fe, 9.2%; Cu, 10.3%.

Obsd: C, 47.6%; H, 4.6%; N, 9.3%; Fe, 9.1%; Cu, 10.4%.

$\text{Cu(II)Co(II)L'Cl}_2 \cdot 2\text{H}_2\text{O}$. To methanol (20 ml) at the ambient temperature under a helium atmosphere was added cobaltous chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 2.0 g recrystallized from H_2O). To this was added Cu(II)L' (2.0 g) as a solid. After stirring for ~10 min., emerald green microcrystalline solid had formed, and was collected, washed with diethyl ether, and vacuum dried.

Anal. Calc: C, 43.8%; H, 3.8%; N, 4.9%.

Obsd: C, 43.3%; H, 4.3%; N, 4.6%.

$\text{Cu(II)Co(II)LCl}_2 \cdot \text{H}_2\text{O}$. To methanol (15 ml) at the ambient temperature under a helium atmosphere was added $\text{Cu(II)Co(II)L'Cl}_2 \cdot \text{H}_2\text{O}$ (1.0 g). 1,3-Diaminopropane (0.13 ml in 1.0 ml methanol) was added dropwise with stirring. Within 10 min. olive green crystals had formed, and were collected, washed with diethyl ether, and vacuum dried. The copper-cobalt binuclear seems much more soluble than the other hetero-binuclear species reported herein. For this reason, considerable care should be exercised in keeping solution volumes to a minimum in this synthesis.

Anal. Calc: C, 47.0%; H, 4.6%; N, 9.1%; Co, 9.6%; Cu, 10.3%.

Obsd: C, 47.0%; H, 5.0%; N, 9.0%; Co, 9.2%; Cu, 10.4%.

Ni(II)Cu(II)L'Cl₂ · 3H₂O . Hydrated cupric chloride (2.0 g CuCl₂ · 4H₂O) was dissolved in methanol (40 ml) at the ambient temperature in air. Solid Ni(II)L' (1.7 g) was added with stirring. Within 10 min. a golden brown microcrystalline solid was collected, washed with diethylether and vacuum dried.

Anal. Calc: C, 40.00%; H, 4.45%; N, 4.45%.

Obsd: C, 40.35%; H, 4.25%; N, 4.25%.

Cu(II)Ni(II)LCl₂ · 2H₂O . In methanol (30 ml) in air at the ambient temperature was added Ni(II)Cu(II)L'Cl₂ · 3H₂O (1.0 g). A solution of methanol (1.0 ml) containing 1,3-diaminopropane (0.13 ml) was added dropwise with stirring. The solution first turned greenish yellow, and within ca. 5 min., an emerald green solid had formed. This was collected, washed with diethyl ether, and vacuum dried.

Anal. Calc: C, 45.6%; H, 4.8%; N, 8.9%; Cu, 10.0%; Ni, 9.4%.

Obsd: C, 45.8%; H, 4.7%; N, 8.8%; Cu, 10.0%; Ni, 10.0%

Cu(II)Zn(II)L'(ClO₄)₂ · 2H₂O . To methylene chloride (10 ml) at the ambient temperature in air was added CuL' (0.1 g). A solution of tetrahydrofuran (6 ml) containing Zn (ClO₄)₂ · 6H₂O (0.18 g) was added to the CH₂Cl₂ solution slowly with stirring. Within 20 min., light green solids were present. After cooling on an ice bath for ~0.5 hr., the powder was collected, washed with THF (15 ml) and vacuum dried.

Anal. Calc: C, 34.64%; H, 3.32%; Cu, 8.73%.

Obsd: C, 34.77%; H, 3.43%; Cu, 8.53%.

Cu(II)Zn(II)L (ClO₄)₂ · 2H₂O. To tetrahydrofuran (8 ml) at the ambient temperature in air was added Cu(II)Zn(II)L'(ClO₄)₂ · 2H₂O.

1,3-Diaminopropane (0.01 ml) was added dropwise with stirring to the green suspension. Stirring was continued for 20 min., at which time the solution was cooled on an ice bath. The green powder was collected by vacuum filtration, washed with THF (2 X 10 ml) and vacuum dried.

Anal. Calc: C, 37.61%; H, 3.95%; Cu, 8.29%.

Obsd: C, 38.88%; H, 4.35%; Cu, 7.92%.

References and Notes

1. California Institute of Technology.
2. Kalamazoo College.
3. P. J. Hay, J. C. Thibeault, and R. Hoffmann, J. Am. Chem. Soc., 97, 4884 (1975).
4. N. S. Hush, Prog. Inorg. Chem., 8, 391 (1967).
5. P. N. Schatz, S. B. Piepho, E. R. Krausz, Chem. Phys. Lett., 65, 539 (1978).
6. P. A. Cox, Chem. Phys. Lett., 69, 340 (1980).
7. J. Woodward, Phil. Trans., 33, 15 (1724).
8. H. Taube, Ann. N. Y. Acad. Sci., 313, 481 (1978).
9. B. P. Sullivan and T. J. Meyer, Inorg. Chem., 19, 752 (1980).
10. B. F. Hoskins, R. Robson, and G. A. Williams, Inorg. Chim. Acta., 16, 121 (1976).
11. R. R. Gagné, L. M. Henling, and T. J. Kistenmacher, Inorg. Chem., 19, 1226 (1980).
12. B. F. Hoskins, N. J. McLeod, H. A. Schaap, Aust. J. Chem., 29, 515 (1976).
13. C. L. Spiro, S. L. Lambert, T. J. Smith, E. N. Duesler, R. R. Gagné, and D. N. Hendrickson, submitted for publication. Fe-Fe distance is 3.11Å with both metals constrained to lie in ligand plane.

14. N. H. Pilkington and R. Robson, Aust. J. Chem., 23, 225, (1970).
15. R. R. Gagné and C. L. Spiro, J. Am. Chem. Soc., 102, 1443 (1980).
16. It is noteworthy that this method fails for only one case thus far examined. Addition of 1,3-diaminopropane to $\text{Cu(II)Ni(II)L}^{+2}$ does not result in the formation of $\text{Cu(II)Ni(II)L}^{+2}$, but rather wrests the Ni(II) from the O_4 site, resulting in the reisolation of neutral $\text{Cu(II)L}'$. If the reaction sequence is first carried out by forming $\text{Ni(II)L}'$ with nickel in the N_2O_2 site, with subsequent addition of Cu(II) to form $\text{Ni(II)Cu(II)L}'^{+2}$, addition of 1,3-diaminopropane does result in the desired product.
17. H. Okawa and S. Kida, Bull. Chem. Soc. Japan, 45, 1759 (1972).
18. C. Spiro, Doctoral Dissertation, California Institute of Technology, Pasadena, Ca. (1981).
19. S. M. Lambert and D. N. Hendrickson, Inorg. Chem., 18, 2683 (1979).
20. S. M. Lambert, C. L. Spiro, R. R. Gagné, and D. N. Hendrickson, Manuscript in preparation. The J values for the heteronuclear complexes Cu(II)Mn(II)LCl_2 , Cu(II)Fe(II)LCl_2 , and Cu(II)Ni(II)LCl_2 are -22.5 cm^{-1} , -81 cm^{-1} , and -103 cm^{-1} respectively. These values enable us to estimate a magnetic contribution to redox parameters as described in the text.

21. R. R. Gagné, C. A. Koval, T. J. Smith, and M. C. Cimolino, J. Am. Chem. Soc., 101, 4571 (1979).
C. A. Koval, Doctoral Dissertation, California Institute of Technology, Pasadena, Ca. (1978).
22. R. R. Gagné, C. A. Koval, and G. C. Lisensky, Inorg. Chem., 0000.
23. R. S. Nicholson and I. Shain, Anal. Chem., 36, 706 (1964).
24. E. P. Parry and R. A. Osteryoung, Anal. Chem., 37, 1634 (1964).
25. L. Meites, Polarographic Techniques, John Wiley and Sons, Inc., New York (1965), p. 218.
26. J. L. Allison, Doctoral Dissertation, California Institute of Technology, Pasadena, Ca. (1978).
27. R. R. Gagné, J. L. Allison, and D. M. Ingle, Inorg. Chem., 18, 2767 (1979).
28. One exception is the Mn(III/II) wave in the presence of high concentrations (>0.1 M) of ethylpyridine, when the wave is obliterated. At low concentrations of ethylpyridine, the Mn(III/II) wave is unchanged. Equilibrium constants, $K_{L''}$, were determined at low concentrations where only a slight error may be introduced due to K(II), the binding to Mn(II).
29. The lack of affinity for CO by Fe(II) may appear somewhat surprising, but all attempts to prepare complexes of this type were unsuccessful.

30. J. Phelps and A. J. Bard, J. Electroanal. Chem., 68, 313 (1976).

R. E. Dessy, P. M. Weissman, and R. L. Pohl, J. Am. Chem. Soc., 88, 5117 (1966).

N. H. Furman and G. Stone, J. Am. Chem. Soc., 70, 3055 (1948).
31. Michael Flanagan, Doctoral Dissertation, California Institute of Technology, Pasadena, Ca. (1978).
32. E. V. Dose, M. A. Hoselton, N. Sutin, M. F. Tweedle, and L. J. Wilson, submitted for publication (1979).
33. This is in contrast to a previously reported calculation of E_{corr} due to magnetic exchange.¹⁵ The authors are grateful to Dr. Charles Dismukes, Princeton University, for pointing this out.
34. M. B. Robin and P. Day, Advan. Inorg. Chem. Radiochem., 10, 247 (1967).
35. J. A. Bauman and T. J. Meyer, Inorg. Chem., 19, 345 (1980).
36. T. R. Weaver, T. J. Meyer, S. Adeyemi, G. M. Brown, R. P. Eckberg, E. C. Johnson, R. W. Murray, and D. Untereker, J. Am. Chem. Soc., 97, 3039 (1975).
37. J. H. Elias and R. S. Drago, Inorg. Chem., 11, 415 (1972).
38. C. Creutz and H. Taube, J. Am. Chem. Soc., 95, 1086 (1973).
39. James P. Sutton, Doctoral Dissertation, Stanford University, Stanford, Ca. (1979).

40. C. Y. Yang, K. H. Johnson, R. H. Holm, and J. B. Norman, Jr.,
J. Am. Chem. Soc., 97, 6596 (1975).
41. See, for example, reference 19.
42. A. Earnshaw, Introduction to Magnetochemistry, Academic
Press, London (1968), pp. 9-12.
43. F. Ullmann and K. Brittner, Chim. Ber., 42, 2539 (1909).

Table I. Absorption maxima of the binuclear macrocyclic complexes $M_A(II)M_B(II)L^{+2}$. Spectra were taken in the solid state as Nujol mulls.

Complex	$\lambda_{\max}$ (nm)
$Cu(II)Mn(II)L^{+2}$	650
$Cu(II)Fe(II)L^{+2}$	600, 1200
$Cu(II)Co(II)L^{+2}$	600, 900
$Cu(II)Ni(II)L^{+2}$	625, 775, 1200, 1500
$Cu(II)Cu(II)L^{+2}$	620 ¹⁴
$Cu(II)Zn(II)L^{+2}$	610

Table II. Room temperature magnetic moments of binuclear complexes. All data were taken in the solid state and are corrected for diamagnetism by Pascal's constants. Results are reported on a per-metal basis in Bohr magnetons.

<u>Complex</u>	<u>μ_{eff} (β; 285°K)</u>
$\text{Cu(II)Mn(II)L}^{+2}$	4.12
$\text{Cu(II)Fe(II)L}^{+2}$	3.02
$\text{Cu(II)Co(II)L}^{+2}$	2.89
$\text{Cu(II)Ni(II)L}^{+2}$	1.88
$\text{Cu(II)Cu(II)L}^{+2}$	0.70^{14}
$\text{Cu(II)Zn(II)L}^{+2}$	1.74

Table III. Electrochemical data for homonuclear complexes.

Measurements were made by differential pulse polarography using a platinum button electrode. Tetrabutylammonium perchlorate (0.1 M) acted as supporting electrolyte in nonaqueous solutions, with sodium bromide (0.1 M) used in water. All redox processes involve (III/II) couples excepting the dicopper species, where reductions were observed.

Compound	Solvent	$E_1(\text{V vs Fc})^a$	$E_2(\text{V vs Fc})^a$
$\text{Mn(II)Mn(II)L}^{+2}$	methanol	-0.050	+0.065
$\text{Fe(II)Fe(II)L}^{+2}$	methanol	-0.020	+0.240
$\text{Co(II)Co(II)L}^{+2}$	methanol	+0.010	+0.240
$\text{Ni(II)Ni(II)L}^{+2}$	water	+0.080	+0.425
$\text{Cu(II)Cu(II)L}^{+2}$	methanol	-0.940	--- ^b
$\text{Cu(II)Cu(II)L}^{+2}$	DMF ^c	-0.925	-1.310

^aAn internal reference, the ferrocene/ferricinium⁺ couple was utilized in all nonaqueous measurements. An internal reference couple, $\text{Ru(NH}_3)_6^{+3/2}$ was utilized in water, and calculated versus ferrocene using an aqueous ferrocene potential of +0.400 V vs nhe.²²

^bSolvent reduction occurs prior to Cu(II)Cu(I)L^+ reduction.

^cN, N-dimethylformamide.

Table IV. Reduction potentials for the Cu(II/I) couple as a function of the remote metal, M_B (II). All measurements were taken with N, N-dimethylformamide as solvent and 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte. Data are reported in Volts versus an internal reference, the ferrocene/ferrocinium⁺ redox couple. Formal reduction potentials, $E^f(\sigma)$, represent weighted average values of measured potentials by the various techniques.

Starting Compound	Cyclic Voltammetry ^a		Differential Pulse Polarography		Sampled DC ^c Polarography		Coulometric ^d n value	$E^f(\sigma)^e$ (V)
	E^f (V)	$E_{p_a} - E_{p_c}$ (V)	E^p (V)	FWHM (V)	$E^{\frac{1}{2}}$ (V)	slope (V)		
Cu(II)Mn(II)L ⁺²	-1.080	0.120	-1.070	0.095	-1.052	0.062		-1.070(10)
Cu(II)Fe(II)L ⁺²	-1.058	0.060	-1.050	0.095	-1.068	0.062	0.98	-1.063(12)
Cu(II)Co(II)L ⁺²	-1.070	0.070	-1.060	0.120	-1.067	0.061		-1.066(6)
Cu(II)Ni(II)L ⁺²	-1.090	0.080	-1.092	0.100	-1.055	0.060		-1.074(29)
Cu(II)Cu(II)L ⁺² 21, 22	-0.930	0.070	-0.923	0.092	-0.917	0.058	1.0	-0.925(8)
Cu(II)Zn(II)L ⁺²	-1.060	0.070	-1.060	0.100	-1.076	0.058	0.95	-1.067(15)

^a Formal potentials reported are $(E_{p_a} - E_{p_c})/2$. Scan rates are 0.5 V/sec. Platinum button electrode was utilized as working electrodes.

^b Peak potentials measured with platinum button electrode at scan rates of 1-10 mV/sec. ^c Half wave potentials measured using dropping mercury electrode at a scan rate of 1 mV/sec. Drop time was 5 sec. ^d Coulometric n-values measured by electrolysis using a platinum gauze electrode. ^e Average formal potentials with one standard deviation in parentheses.

Table V. Equilibrium constants, $K(L'')$, for the binding of axial bases. Measurements were taken as a function of the remote metal ion, $M_B(II)$. Substrates (L'') studied include carbon monoxide (CO), ethylene (CH_2CH_2), tris (o-methoxyphenyl) phosphine (PR_3) and 4-ethylpyridine (etpy). Binding constants were determined by an electrochemical method as described in the text. Standard deviations appear in parentheses. In all cases, N, N-dimethylformamide containing 0.1 M tetrabutylammonium perchlorate was the solvent.

Complex	$K(CO) M^{-1}$	$K(CH_2CH_2), Atm^{-1}$	$K(PR_3) M^{-1}$	$K(etpy) M^{-1}$
$Cu(I)Mn(II)L^+$	$0.9(3) \times 10^4$	0.3(3)	0	22.5(0.7)
$Cu(I)Fe(II)L^+$	$1.5(4) \times 10^4$	0.9(4)	0	28(6)
$Cu(I)Co(II)L^+$	$0.9(5) \times 10^4$	0.3(3)	0	10.2(0.6)
$Cu(I)Ni(II)L^+$	$1.5(4) \times 10^4$	0.4(3)	$4.1(0.4) \times 10^2$	30(4)
$Cu(I)Cu(II)L^+$	$3.1(3) \times 10^4$	1.5(3)	$1.2(0.2) \times 10^3$	38(14)
$Cu(I)Zn(II)L^+$	$1.1(4) \times 10^4$	1.6(3)	0	9.7(1.7)

Figure Captions

Figure 1. Infrared spectra showing the $\nu_{\text{C=N}}$ and $\nu_{\text{C=O}}$ stretching frequencies for Cu(II)L' , $\text{Cu(II)M}_\text{B}\text{(II)L'}$, and $\text{Cu(II)M}_\text{B}\text{(II)L}$.

Figure 2. Cyclic voltammogram of $\text{Cu(II)Mn(II)L}^{+2}$ in methanol. The wave at ~ -1 V is the Cu(II/I) wave, while the Mn(III/II) couple appears at $\sim +0.3$ V. Notice the absence of shoulders which would correspond to homonuclear impurities.

Figure 3. Conductometric titration of $\text{Fe(II)Fe(II)L}^{+2}$ with bromine in N,N-dimethylformamide. Initially the anions are completely dissociated with the species acting as a 2:1 electrolyte.¹⁴ As bromine is added, it oxidizes the iron centers and associates with the metal ions to the extent shown by the solid line. The dashed line is the ideal behavior that would be expected for complete dissociation ultimately resulting in a 4:1 electrolyte. That the break occurs at the 1-equivalent point implies the bromide coordinates primarily with $\text{Fe(III)Fe(III)L}^{+4}$, forming appreciable quantities of $\text{Fe(III)Fe(III)LBr}^{+3}$.

Figure 4. Cyclic voltammogram of $\text{Cu(II)Fe(II)L}^{+2}$. The peak at -1.058 V negative of ferrocene corresponds to the Cu(II/I) couple in N,N-dimethylformamide.

Figure 5. Differential pulse polarogram for $\text{Cu(II)Ni(II)L}^{+2}$. The more positive wave is the Cu(II/I) couple, the peak at -1.5 V is the Ni(II/I) wave.

Figure 6. Polarographic determination of equilibrium binding constant for Cu(I) with tris (o-methoxyphenyl)phosphine in the complex Cu(I)Ni(II)L^{+} . The most negative wave, curve A, is the blank, while curves B and C are polarograms of $\text{Cu(II)Ni(II)L}^{+2}$ in the presence of 5×10^{-3} M and 1×10^{-2} M phosphine respectively. Note the positive shifts in the waves (+0.030 V for A, +0.040 V for B) indicate binding to the reduced species.

Figure 7. Cyclic voltammograms of $\text{Cu(II)Fe(II)L}^{+2}$ (solid line) and $\text{Fe(II)Fe(II)L}^{+2}$ in methanol. Note that the Fe(III/II) couple occurs at a more positive potential in $\text{Cu(II)Fe(II)L}^{+2}$ than in $\text{Fe(II)Fe(II)L}^{+2}$.

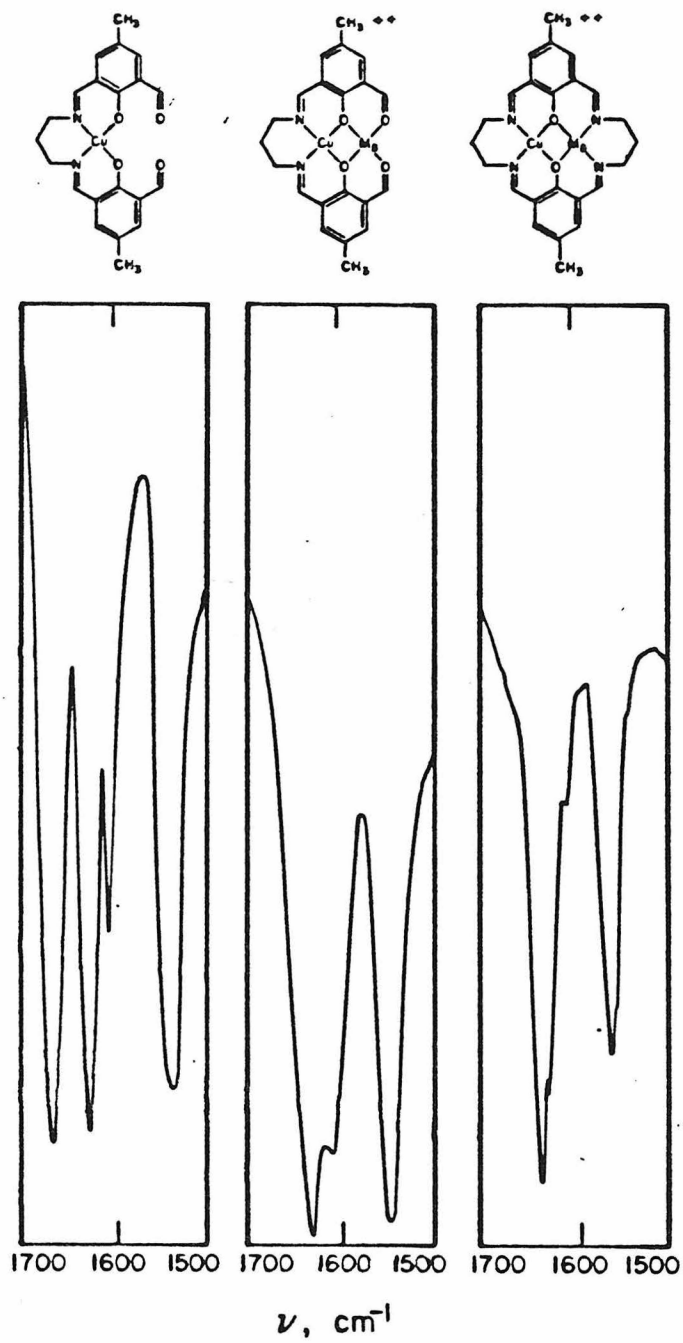


Figure 1.

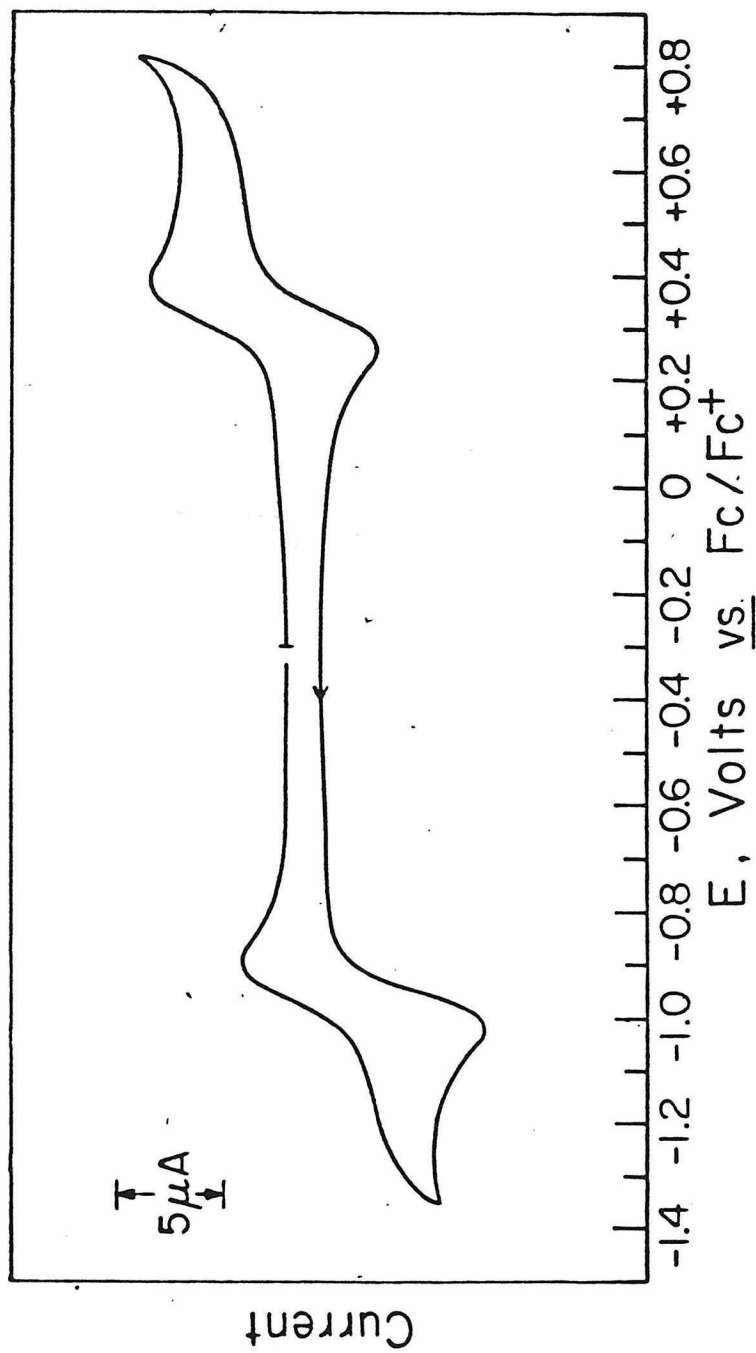


Figure 2.

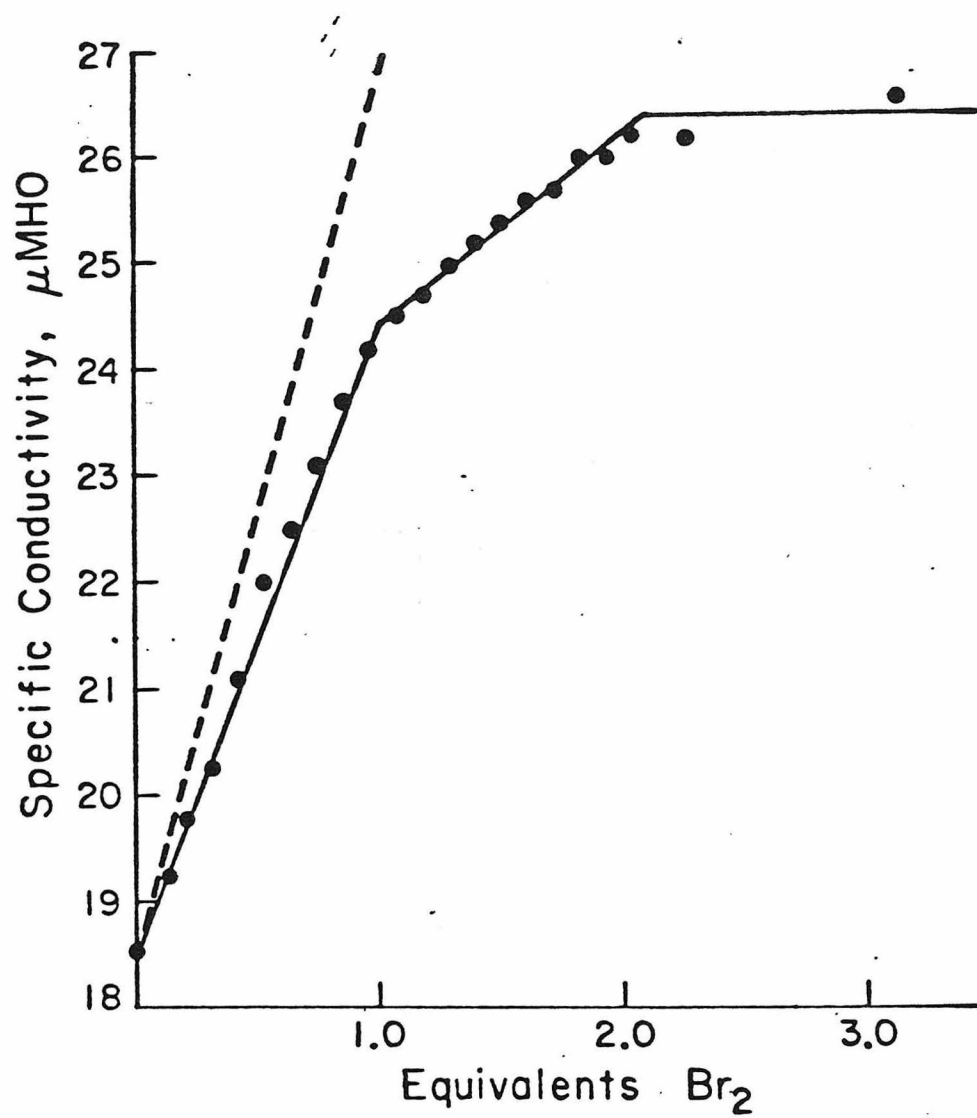


Figure 3.

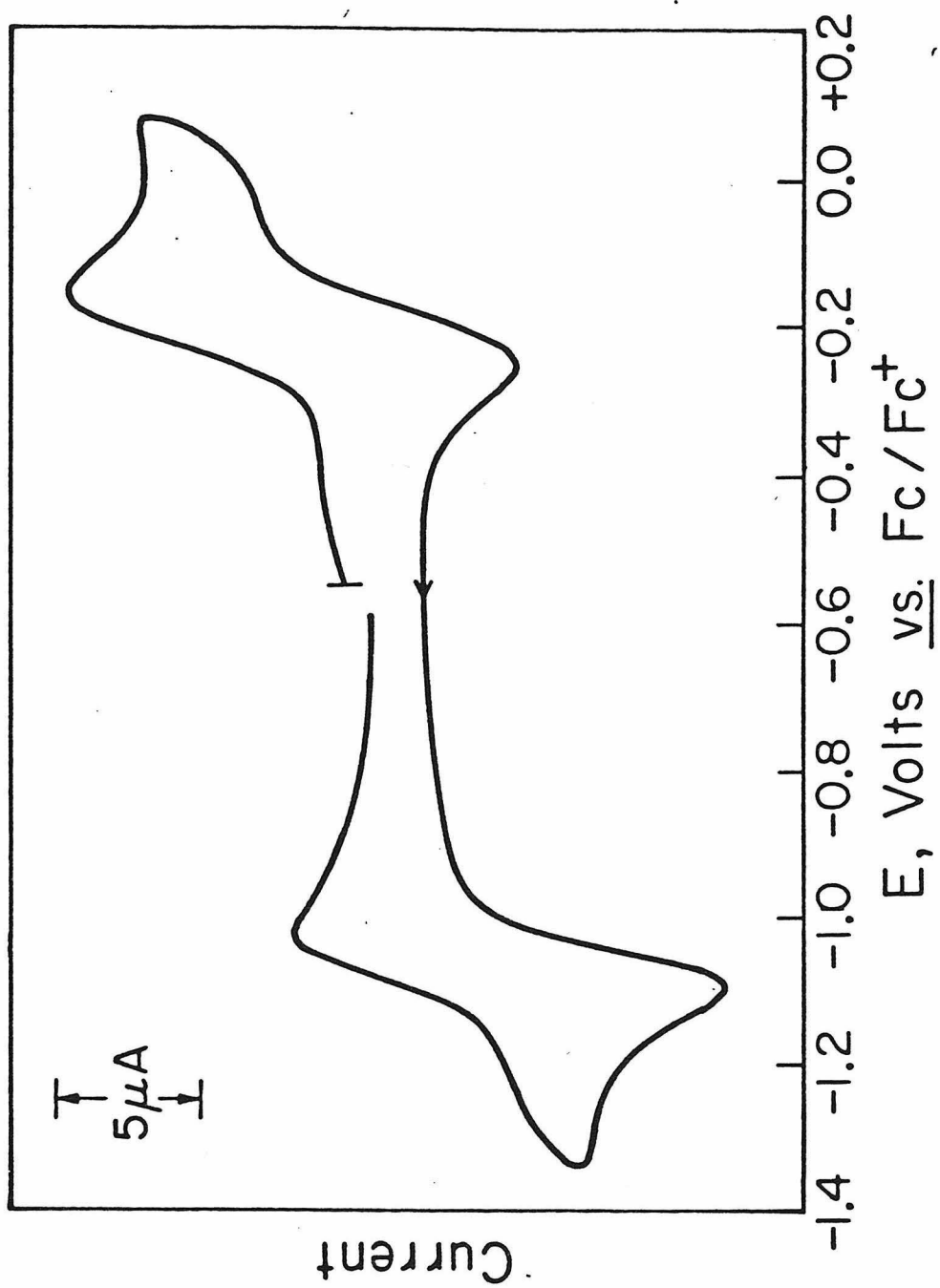


Figure 4.

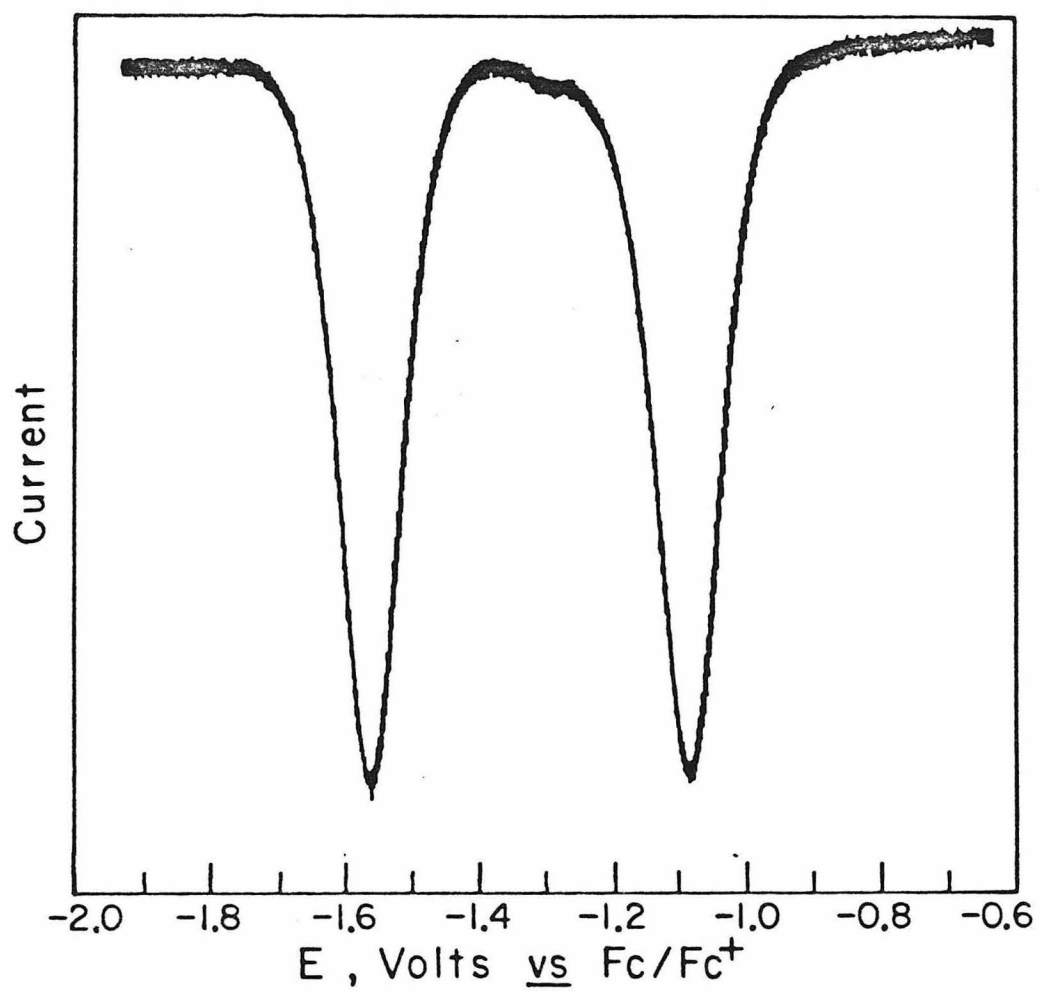


Figure 5.

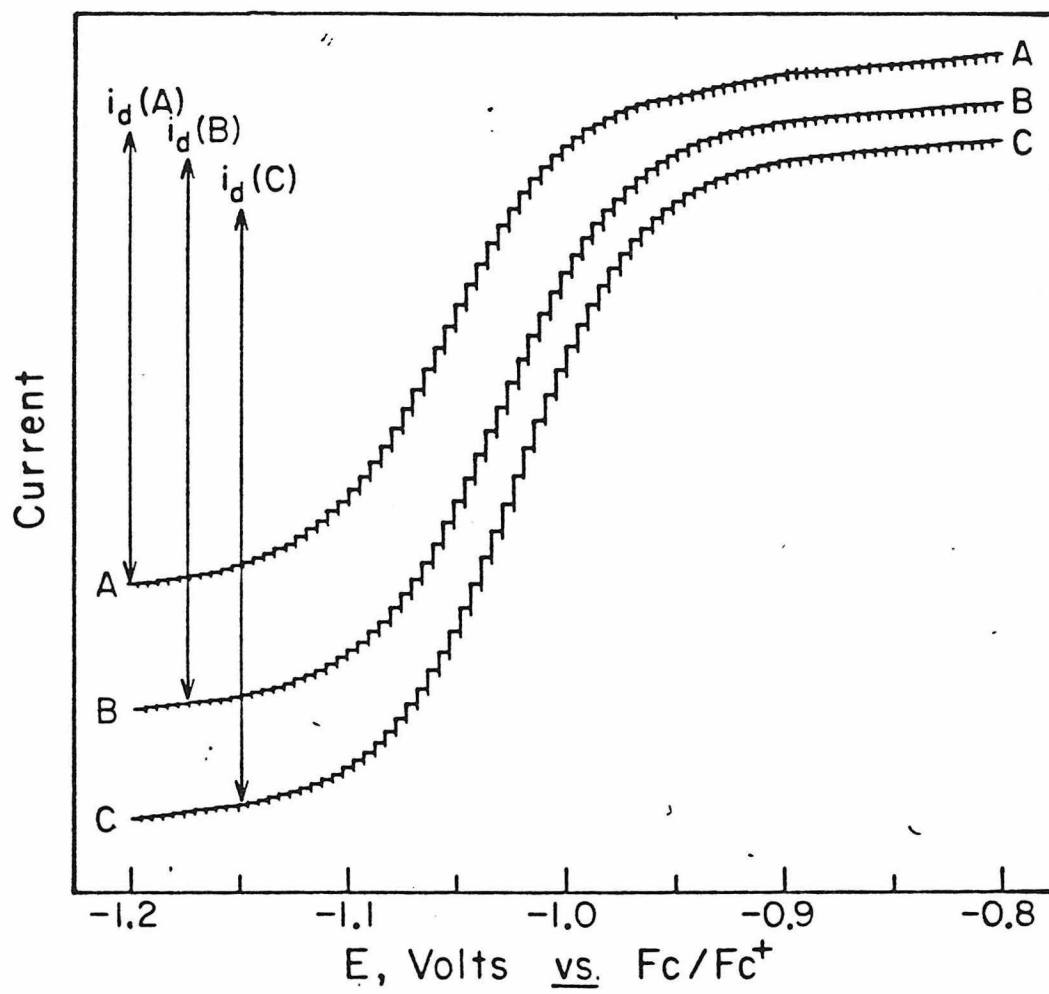


Figure 6.

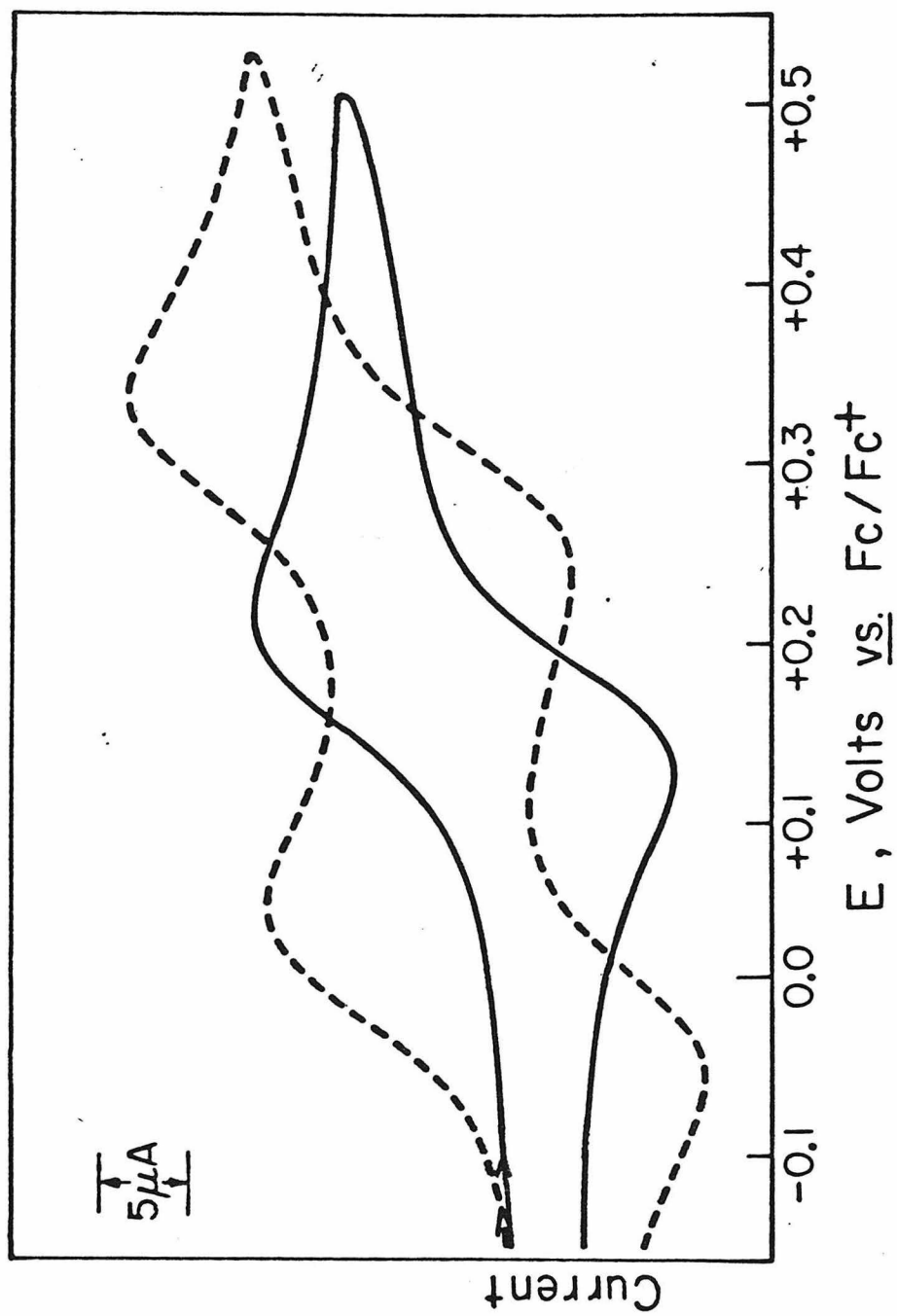


Figure 7.

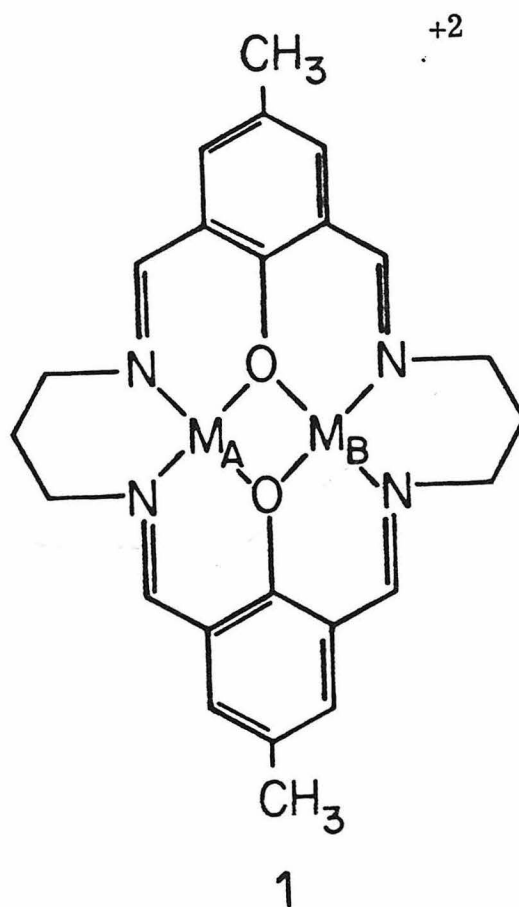
PART VI.

Magnetic Properties of
Binuclear Macrocyclic Transition Metal
Complexes

Introduction

When two paramagnetic metal centers, M_1 and M_2 , coexist in the same discrete molecule, exchange coupling is often observed. The spin operators associated with each metal, $\hat{S}_1$ and $\hat{S}_2$, can couple and cause a splitting in the energy levels associated with the spin states $S_1 + S_2, S_1 + S_2 - 1, \dots, S_1 - S_2$. In the simpler cases, this splitting can be made quantitative by the use of the Hamiltonian $\hat{H} = J \hat{S}_1 \cdot \hat{S}_2$, where J is the exchange coupling constant. Couplings are on the order of kT , and are usually expressed in cm^{-1} . If $J < 0$, an antiferromagnetic interaction is observed, with the lowest spin system representing the ground state. If $J > 0$, ferromagnetism results, with the high spin ($S_1 + S_2$) system representing the ground state.¹

Our aim in general is to gain a fundamental understanding of the physical and chemical properties of multimetallic species, and in particular, the magnetic exchange interaction between the metals. The complexes, 1, provide an excellent opportunity to study these effects. The macrocyclic ligand houses two high spin metals in close proximity ($\sim 3.15\text{\AA}$)² which are coupled to various degrees. In the case of the square pyramidal homonuclear species, $M_A = M_B$, originally prepared by Robson et al,³ an interesting trend was observed.⁴



The exchange coupling constant, Table 1, Part VIa, revealed a feebly ferromagnetic system for Mn(II)Mn(II)LCl_2 , and a monotonically increasing antiferromagnetic behavior in traversing the series Fe(II)Fe(II)LCl_2 , Co(II)Co(II)LCl_2 , Ni(II)Ni(II)LCl_2 , and Cu(II)Cu(II)LCl_2 . This trend was ascribed to one of two factors. 1) The decreasing number of unpaired electrons in traversing this series may result in the increased exchange coupling. 2) The change in coupling may reflect variations in metal to ligand-plane distances.

In order to better understand the generality and relative importance of these factors, two studies were undertaken, and are described in the following sections. First, coupling in the square pyramidal heteronuclear series $\text{Cu(II)}\text{M}_{\text{B}}(\text{II})\text{LCl}_2$, $\text{M}_{\text{B}}(\text{II}) = \text{Mn(II)}, \text{Fe(II)}, \text{Co(II)}, \text{and Ni(II)}$ was examined. These data are reported in Part VIa. Part VIb, an article submitted to Inorg. Chem.,⁵ describes a comparison between the Robson five-coordinate square pyramidal system and a new series of homonuclear complexes $\text{M(II)}\text{M(II)}\text{L}^{+2}$. In the latter species, the metals are constrained to lie in the ligand plane, occupying a six-coordinate pseudo-octahedral coordination environment.

The author is grateful to Dr. D. N. Hendrickson and his group for the use of their equipment, computing facilities, and especially for deriving and diagonalizing the non-trivial spin Hamiltonians associated with orbital and zero-field contributions, as well as the solution of the X-ray crystal and molecular structure described in Part VIb.

References and Notes

1. A. Earnshaw, Introduction to Magnetochemistry, Academic Press, London (1968).
2. B. F. Hoskins, R. Robson, and G. A. Williams, Inorg. Chim. Acta., 16, 121 (1976).
3. N. H. Pilkington and R. Robson, Aust. J. Chem., 23, 225 (1970).
4. S. M. Lambert and D. N. Hendrickson, Inorg. Chem., 18, 2683 (1979).
5. C. L. Spiro, S. M. Lambert, T. J. Smith, E. N. Duesler, R. R. Gagné, and D. N. Hendrickson, Manuscript in preparation.

PART VIa.

Magnetic Exchange Coupling in
Heterobinuclear Macrocyclic Ligand
Transition Metal Complexes

C. L. Spiro, S. M. Lambert,
R. R. Gagné, and D. N. Hendrickson

Part VIa

Introduction. Hendrickson¹ reported regular changes in magnetic coupling for the square-pyramidal five-coordinate complexes Mn(II)Mn(II)LCl_2 , Fe(II)Fe(II)LCl_2 , Co(II)Co(II)LCl_2 , Ni(II)Ni(II)LCl_2 . These data are summarized in Table 1. He ascribed these changes to one of two factors. 1) The decreasing number of unpaired electrons in traversing this series may result in increased exchange coupling. 2) The change in coupling may reflect variations in metal to ligand-plane distances.

To confirm the generality of this trend, the square pyramidal complexes $\text{Cu(II)M}_B\text{(II)LCl}_2$, $\text{M}_B\text{(II)} = \text{Mn(II), Fe(II), Co(II), and Ni(II)}$, were explored. Herein is a preliminary account of these data which are being incorporated into an article for subsequent publication.²

Experimental. All compounds were prepared and characterized as described in Part V. Physical measurements are reported in Part VII.

Results. Variable temperature (4.2 - 285°K) magnetic susceptibility data were collected for the compounds $\text{Cu(II)M}_B\text{(II)LCl}_2$, $\text{M}_B\text{(II)} = \text{Mn(II), Fe(II), Co(II), and Ni(II)}$. These data are given in Appendix I.

The data for Cu(II)Mn(II)LCl_2 is illustrated in Figure 1. A moderate antiferromagnetic exchange interaction is seen to be present; the magnetic moment drops from a high temperature value associated with six

Table 1. Magnetic exchange coupling constants for a series of homobinuclear macrocyclic complexes, $M(II)M(II)LCl_2$.
Data from reference 1.

<u>Compound</u>	<u>$J, \text{ cm}^{-1}$</u>
$Mn(II)Mn(II)LCl_2$	+0.20
$Fe(II)Fe(II)LCl_2$	-4.2
$Co(II)Co(II)LCl_2$	-6.0
$Ni(II)Ni(II)LCl_2$	-27.
$Cu(II)Cu(II)LCl_2$	-294.

unpaired electrons to a value consistent with four unpaired electrons at 30°K. The additional drop in μ_{eff} below 30°K arises from orbital contributions and zero field effects normally encountered with manganese ions. The data were initially fit to the susceptibility expression derived from the isotropic spin Hamiltonian, $H = -2J\hat{S}_1 \cdot \hat{S}_2$.

A least squares fitting of the data yields values of $J = -29.6 \text{ cm}^{-1}$ and $g = 2.03$, but the data below 30°K could not be satisfactorily fit. In order to include zero field effects in the calculation, an equation was derived using $H = -2J\hat{S}_1 \cdot \hat{S}_2 + D\hat{S}_{z_1}^2 - g\beta H\hat{S}_z$. The parameters obtained from a least square fit of the data, illustrated in Figure 1, are $J = -22.5 \text{ cm}^{-1}$, $g = 2.07$, and $D = 0.59 \text{ cm}^{-1}$.

The magnetic susceptibility data for Cu(II)Fe(II)LCl₂ are illustrated in Figure 2. The data reveal an already-depressed magnetic moment at room temperature, indicating a sizable exchange interaction. Using the same Hamiltonian as for the copper-manganese species, a least squares fit of the data obtained $J = -70.5 \text{ cm}^{-1}$, $g = 2.01$, and $D = 1.13 \text{ cm}^{-1}$.

Figure 3 illustrates the susceptibility data for Cu(II)Co(II)LCl₂. The appearance of the susceptibility vs. temperature curve is qualitatively different from the other cases. This is due to the presence of extensive spin-orbit coupling associated with high spin d^7 systems. The data for Cu(II)Co(II)LCl₂ were fit to a Hamiltonian derived by O. Kahn and coworkers.³ A least squares fitting gave $J = -81.0 \text{ cm}^{-1}$,

$g = 2.05$, and $D = 1289 \text{ cm}^{-1}$ with λ , the spin orbit coupling constant, fixed at 160 cm^{-1} .

The magnetic susceptibility data for Cu(II)Ni(II)LCl_2 are illustrated in Figure 4. The magnetic moment at room temperature is considerably depressed from the moment expected for three unpaired electrons on two metal centers ($1.9 \mu_B$ vs expected $2.3 \mu_B$). Since no zero-field effects were observed below 30°K , the data were fit to the simple Hamiltonian, $H = -J\hat{S}_1 \cdot \hat{S}_2$. A least squares fit yield, $J = -103 \text{ cm}^{-1}$ and $g = 2.17$.

These data are summarized in Table 2.

Table 2. Exchange coupling parameters for a series of heterobinuclear complexes obtained by least squares fitting of magnetic susceptibility vs temperature data.

<u>Compound</u>	<u>g</u>	<u>J (cm⁻¹)</u>
Cu(II)Mn(II)LCl_2	2.07	-22.5
Cu(II)Fe(II)LCl_2	2.01	-70.5
Cu(II)Co(II)LCl_2	2.05	-81.0
Cu(II)Ni(II)LCl_2	2.17	-103.0
Cu(II)Cu(II)LCl_2	2.06	-294.

Discussion

The data reported in the Results section, Table 2, reveal the same trend as that in Table 1. An increased antiferromagnetic exchange coupling was observed in traversing the first transition series from manganese to copper. The effect appears general in this series, as well as in a related asymmetric series reported by Kahn et al.³

While changes in the copper to ligand-plane distance may be invariant in the mixed metal series, it is likely that variations in the remote metal (M_B) to ligand-plane distance can still occur. Therefore, no clear delineation between whether the coupling reflects changes in electronic structure (i.e. the d-orbital symmetries and populations) or the molecular structure (i.e. metal to ligand-plane distance) can be made. For this reason, homonuclear complexes $Fe(II)Fe(II)L^{+2}$, $Co(II)Co(II)L^{+2}$, and $Ni(II)Ni(II)L^{+2}$ were prepared with the metals constrained to lie within the ligand-plane in a six-coordinate pseudo-octahedral environment. If molecular structural effects are predominant in determining magnetic coupling, then major changes in J values would be expected in going from five-coordinate square-pyramidal geometries to six-coordinate pseudo-octahedral geometries. On the other hand, if electron effects predominate, little changes in J would be expected. These results are reported in Part VIb.

References and Notes

1. S. M. Lambert and D. N. Hendrickson, Inorg. Chem., 18, 2683 (1979).
2. C. L. Spiro, S. M. Lambert, R. R. Gagné, and D. N. Hendrickson, Manuscript in preparation.
3. O. Kahn, P. Tola, and H. Coudanne, Chem. Phys., 42, 355 (1979).

Figure Captions

Figure 1. Illustration of magnetic data for Cu(II)Mn(II)LCI_2 .

Figure 2. Illustration of magnetic data for Cu(II)Fe(II)LCI_2 .

Figure 3. Illustration of magnetic data for Cu(II)Co(II)LCI_2 .

Figure 4. Illustration of magnetic data for Cu(II)Ni(II)LCI_2 .

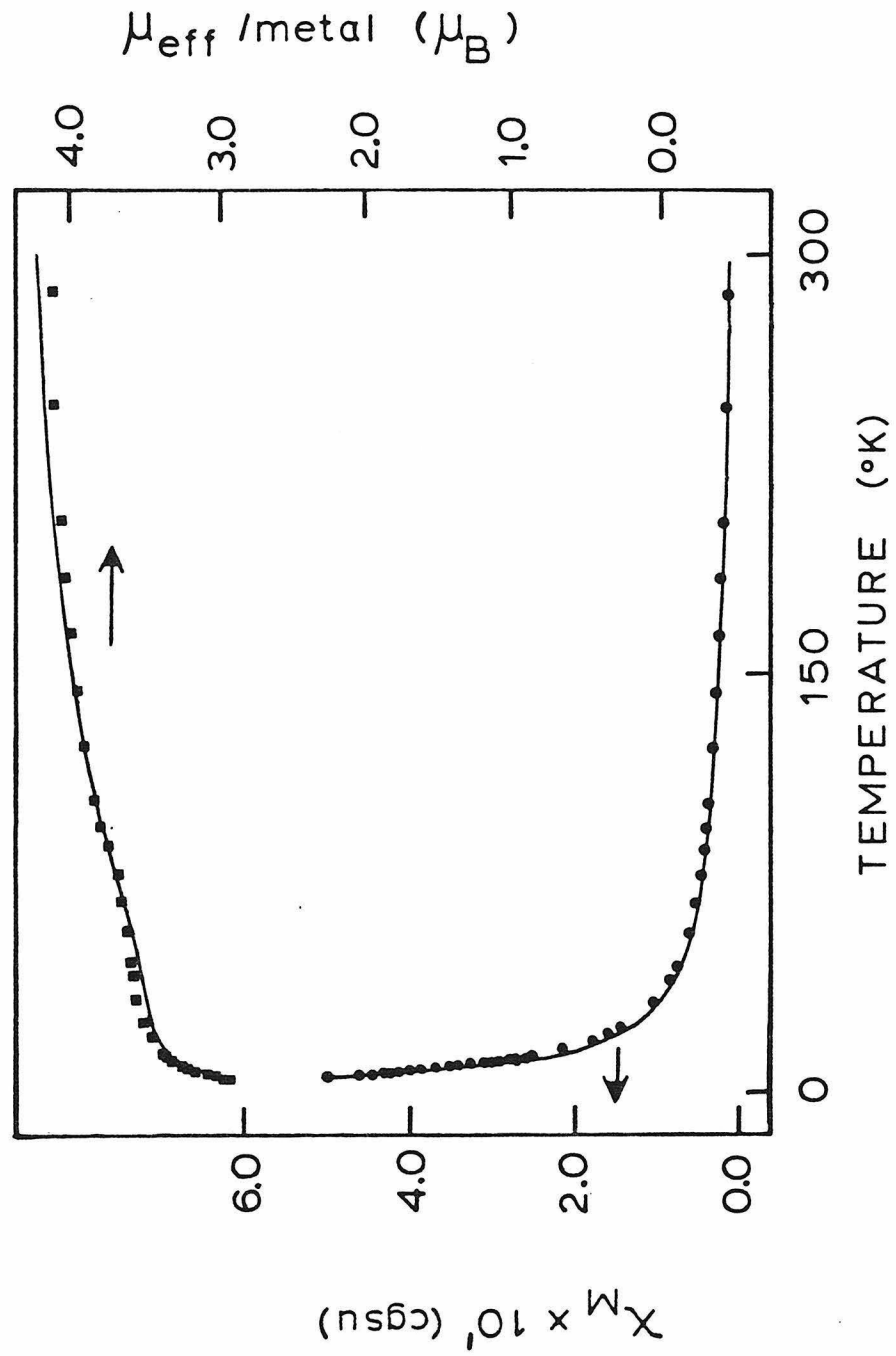


Figure 1.

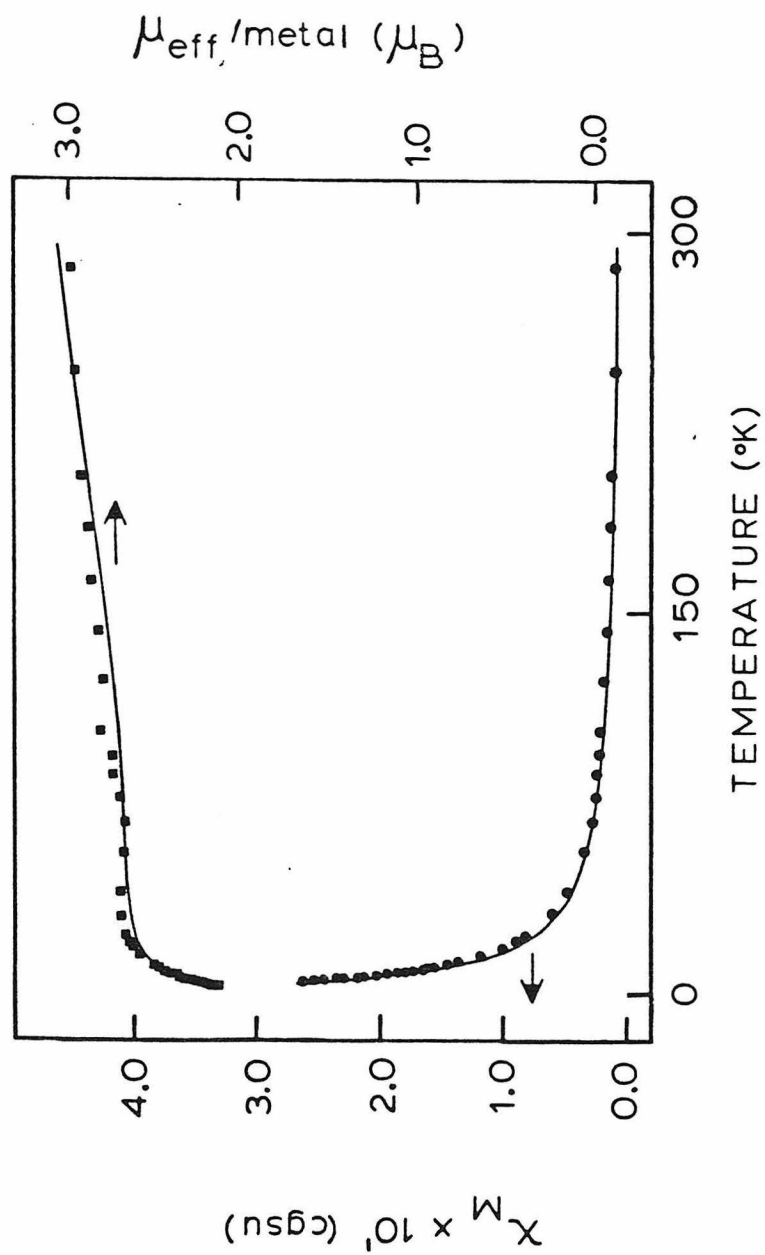


Figure 2.

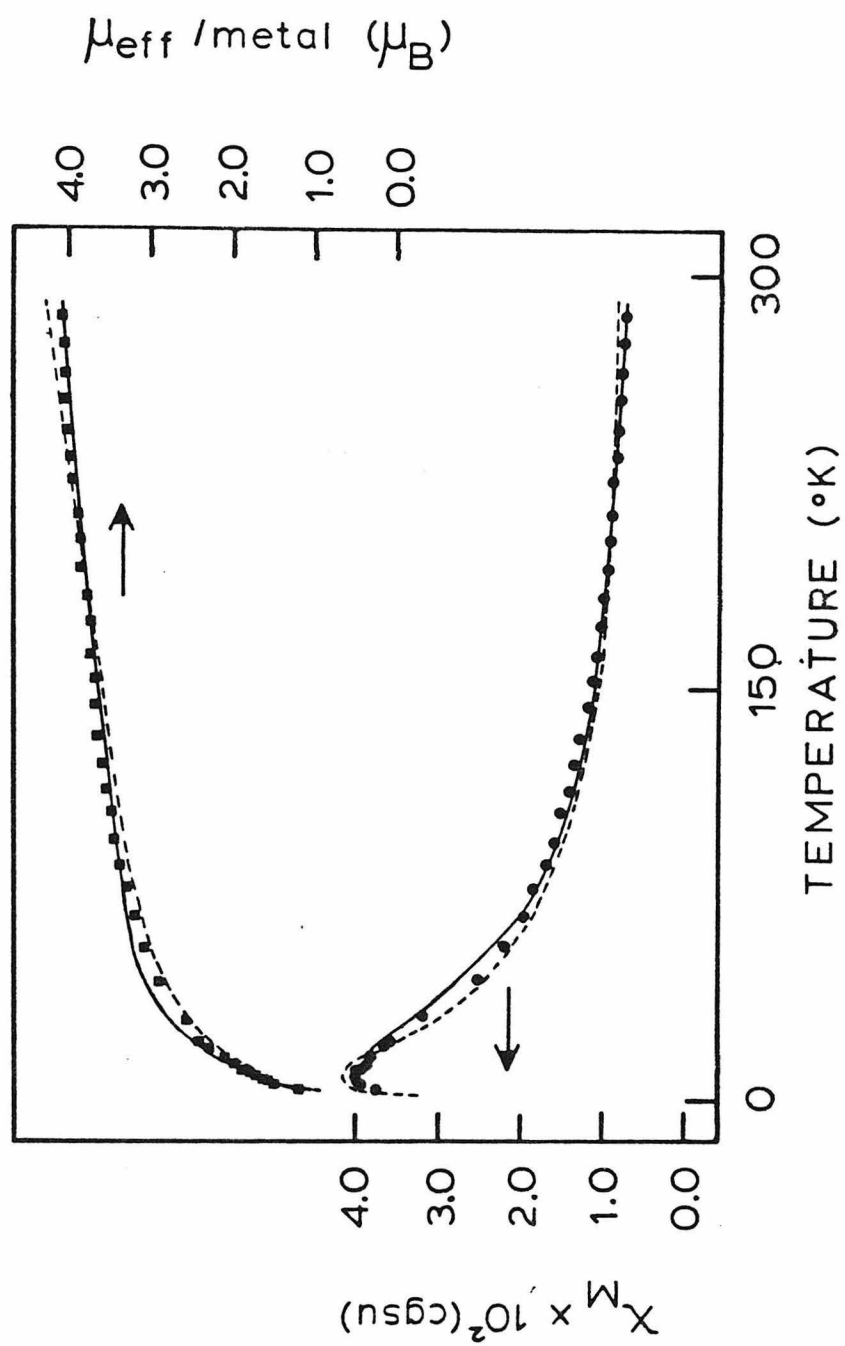


Figure 3.

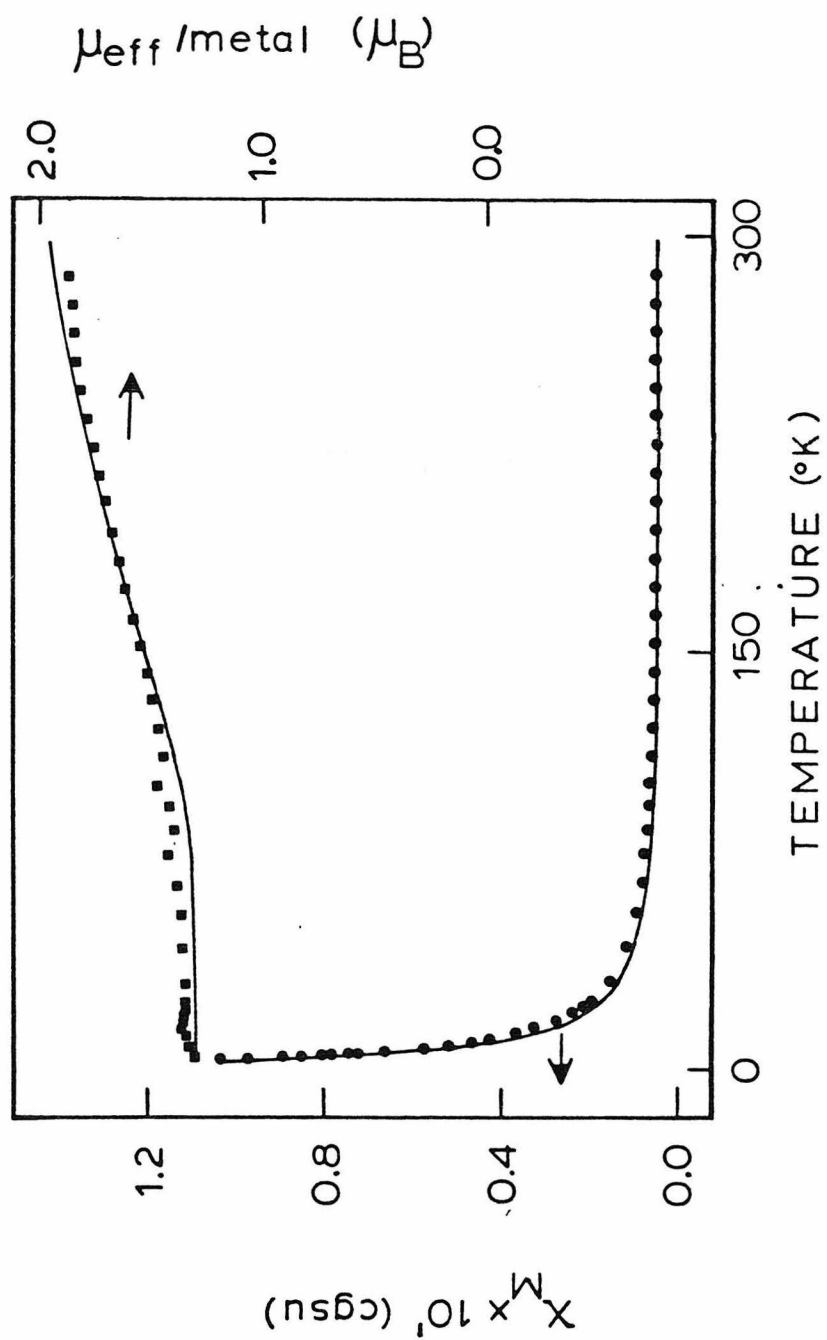


Figure 4.

PART VIb.

Binuclear Complexes of Macrocyclic Ligands:
Variation of Magnetic Exchange Interaction in a Series
of Six-Coordinate Iron(II), Cobalt(II), and Nickel(II)
Complexes, and the X-Ray Structure of a Binuclear
Iron(II) Macrocyclic Ligand Complex.

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E. N. Duesler, R. R. Gagné, and D. N. Hendrickson.

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Binuclear Complexes of Macrocyclic Ligands: Variation of Magnetic
Exchange Interaction in a Series of Six-Coordinate Iron(II), Cobalt(II),
and Nickel(II) Complexes and the X-ray Structure of a Binuclear Iron(II)-
Macrocyclic Ligand Complex.

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EILEEN N. DUESLER,² ROBERT R. GAGNÉ,^{*1} and
DAVID N. HENDRICKSON^{*2}

Received

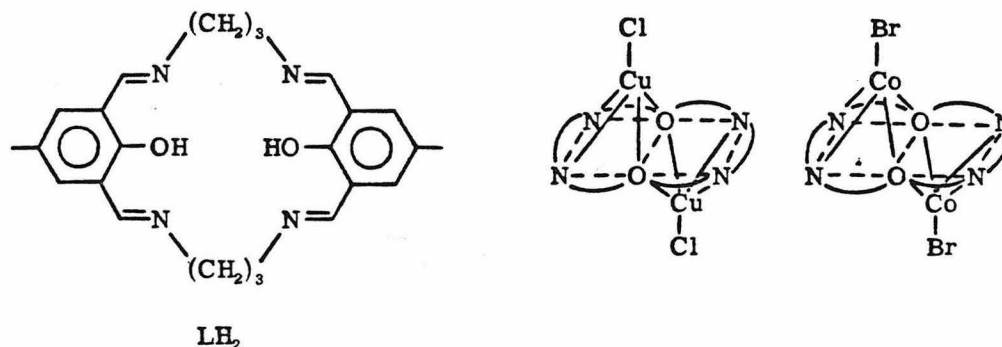
The X-ray crystal and molecular structure of $[\text{LFe}_2(\text{Im})_4](\text{BF}_4)_2$, where Im is imidazole and L is the dianion of the binucleating ligand 11, 23-dimethyl-3, 7, 15, 19-tetraazatricyclo[19.3.1.1^{9,13}]-hexacos-2, 7, 9, 11, 13(26), 14, 19, 21(25), 22, 24-decaene-25, 26-diol, has been determined on a Syntex P2₁ diffractometer. A total of 2468 reflections at the 1.5 σ (I) significance level were used to give final discrepancy indices of $R_1 = 0.082$ and $R_2 = 0.083$. The complex crystallizes in the monoclinic space group C2/c in a cell having the dimensions $a = 21.060(5)$ Å, $b = 17.138(4)$ Å, $c = 12.172(2)$ Å, and $\beta = 108.82(2)^\circ$. The observed and calculated densities are 1.53 and 1.52 g/cm³, respectively. Four formula units comprise the unit cell with half of the binuclear complex in the asymmetric unit. Discrete $[\text{LFe}_2(\text{Im})_4]^{2+}$

cations and BF_4^- anions were found. The binuclear cations are centrosymmetric with each iron(II) ion being six-coordinate by virtue of interactions with two nitrogen and two oxygen atoms of the binucleating ligand L and two nitrogen atoms each from the imidazole ligands. The ligand L is planar except for the two trimethylene bridges. The two iron ions are only 0.011(1) Å out of this ligand plane with an Fe-Fe distance of 3.117(2) Å and Fe-N(imidazole) distances of 2.218 Å. Variable-temperature (4.2-286 K) magnetic susceptibility data are given for the binuclear high-spin six-coordinate complexes $[\text{LNi}_2(\text{py})_4](\text{BF}_4)_2$, $[\text{LCo}_2(\text{py})_4](\text{BF}_4)_2$, $[\text{LFe}_2(\text{py})_4](\text{BF}_4)_2$, $[\text{LFe}_2(\text{Im})_4](\text{BF}_4)_2$, $[\text{LFe}_2(\text{MeIm})_4](\text{BF}_4)_2$, and $[\text{LFe}_2(\text{MeNic})_4](\text{BF}_4)_2$, where py is pyridine, Im is imidazole, MeIm is 1-methylimidazole and MeNic is the methyl ester of isonicotinic acid. In each case an antiferromagnetic exchange interaction is present. The data were least-squares fit to the susceptibility equations resultant from the Hamiltonian $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$ to give exchange parameters (J) of -23 cm^{-1} (Ni^{2+}), -4.1 cm^{-1} (Co^{2+}) and -7.5 cm^{-1} (Fe^{2+}) for the three pyridine complexes. Values of $J = -6.8 \text{ cm}^{-1}$, -4.5 cm^{-1} , and -1.5 cm^{-1} were obtained for the other three high-spin iron(II) complexes with MeNic, MeIm, and Im axial ligands, respectively. It was found that there is little difference in the magnitude of magnetic exchange interaction between LM_2Cl_2 (M = Fe(II), Co(II), and Ni(II)) with five-coordinate

metal ions and the corresponding complex in the $[LM_2(py)_4]-(BF_4)_2$ series with six-coordinate metal ions. An increase in antiferromagnetic exchange interaction was expected for a six-coordinate complex compared to the analogous five-coordinate complex as a consequence of improved orbital overlap from the metal ion being in the plane of the binucleating ligand for the six-coordinate complex. This was not realized, possibly because the increased ligand field splitting in the six-coordinate complex attenuated the increased antiferromagnetic interaction.

Introduction

Complexes of the binucleating ligand LH_2 can be formed from the condensation of 2 moles of 2,6-diformyl-4-methylphenol with 2 moles of 1,3-diaminopropane in the presence of divalent transition metal ions.³ X-ray structural work^{4,5} on $LCu_2Cl_2 \cdot 6H_2O$ and



$LCo_2Br_2 \cdot CH_3OH$ has shown that the metal ion coordination geometry is square pyramidal with one halide ion bonded to each metal ion in an axial site. The cobalt(II) ion is further out of the L ligand plane ($0.30 \text{ \AA}$) than is the copper(II) ion ($0.21 \text{ \AA}$).

In a recent paper⁶ we reported variable-temperature magnetic susceptibility data for a series of complexes of L including $LCu_2Cl_2 \cdot 6H_2O$, $LNi_2Cl_2 \cdot 2H_2O$, $LCo_2Br_2 \cdot CH_3OH$, LMn_2Cl_2 , and LFe_2Cl_2 . The magnetic exchange interaction observed for each complex was assessed with the isotropic spin Hamiltonian, $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$. A strong antiferromagnetic interaction is seen for the copper complex where $J = -294 \text{ cm}^{-1}$. The net antiferromagnetic interaction decreases monotonically in the series copper, nickel ($J = -27 \text{ cm}^{-1}$), cobalt ($J = -9.3 \text{ cm}^{-1}$), and iron ($J = 4.2 \text{ cm}^{-1}$), to finally become a net ferromagnetic exchange interaction in the

manganese complex ($J = +0.2 \text{ cm}^{-1}$). The variation in J-value across this series was attributed to an increasing number of unpaired electrons and also to an increasing metal-ligand-plane distance in going from copper(II) to manganese(II).

In this paper the preparation and physical properties of a series of binuclear complexes of ligand L with six-coordinate metal ions are reported. The new complexes are $[\text{LNi}_2(\text{py})_4](\text{BF}_4)_2$, $[\text{LCo}_2(\text{py})_4](\text{BF}_4)_2$, $[\text{LFe}_2(\text{py})_4](\text{BF}_4)_2$, $[\text{LFe}_2(\text{Im})_4](\text{BF}_4)_2$, $[\text{LFe}_2(\text{MeIm})_4](\text{BF}_4)_2$ and $[\text{LFe}_2(\text{MeNic})_4](\text{BF}_4)_2$, where py is pyridine, Im is imidazole, MeIm is 1-methylimidazole, and MeNic is the methyl ester of isonicotinic acid. The single-crystal X-ray structure of $[\text{LFe}_2(\text{Im})_4](\text{BF}_4)_2$ is also reported. The point of enquiry of the present paper is whether the magnetic exchange interaction is responsive to a change in the metal ion coordination geometry from five-coordinate to six-coordinate.

Experimental Section

Compound Preparation. All reagents and solvents were purchased from commercial sources and used without further purification unless otherwise described. 2,6-Diformyl-4-methylphenol was prepared according to literature methods.⁷ Ferrous tetrafluoroborate hexahydrate was prepared by heating iron filings with 50% fluoroboric acid under an inert atmosphere. Caution: rapid hydrogen evolution. The pale green solution was evaporated under vacuum, leaving pale blue crystals of $\text{Fe}(\text{BF}_4)_2 \cdot 6 \text{H}_2\text{O}$ which were removed by filtration, vacuum dried, and stored under an inert atmosphere.

Binuclear Iron Complexes $\text{LFe}_2(\text{base})_4(\text{BF}_4)_2$. Under an inert atmosphere 1,3-diaminopropane (1.0 ml) was added dropwise to a hot (50°) solution (30 ml) of base (base = pyridine, 1-methylimidazole, or methyl isonicotinate) containing ferrous tetrafluoroborate (1.8 g). A solution (20 ml) of hot base containing 2,6-diformyl-4-methylphenol (0.82 g) was added with stirring. Slow addition of an equal volume of distilled water afforded purple crystals of $\text{LFe}_2(\text{base})_4(\text{BF}_4)_2$. These were collected and stirred with petroleum ether (30°-60°) overnight to remove excess base, and vacuum dried. Where base = pyridine, slow evolution of pyridine from the solid resulted in continual weight loss. Anal. Calcd for $[\text{LFe}_2(\text{MeIm})_4](\text{BF}_4)_2$, $\text{C}_{36}\text{H}_{42}\text{N}_{12}\text{O}_2\text{Fe}_2\text{B}_2\text{F}_8$: C, 45.00; H, 4.37; N, 17.50; Fe, 11.7. Found: C, 45.15; H, 4.50; N, 17.05; Fe, 12.0. Anal. Calcd for $[\text{LFe}_2(\text{MeNic})_4](\text{BF}_4)_2$, $\text{C}_{52}\text{H}_{52}\text{N}_8\text{O}_2\text{Fe}_2\text{B}_2\text{F}_8$: C, 50.89; H, 4.40; N, 9.13. Found: C, 50.65;

H, 4.30; N, 9.15. Anal. Calcd for $\text{LFe}_2(\text{py})_{3.5}(\text{BF}_4)_2$, C, 51.60; H, 4.51; N, 10.90; Fe, 10.90. Found: C, 50.95; H, 4.8; N, 10.69; Fe, 10.8. Note loss of pyridine in analysis.

Preparation of $[\text{LFe}_2(\text{Im})_4](\text{BF}_4)_2$. All manipulations leading to this compound were carried out either in a Vacuum Atmospheres glove box or in a Schlenk apparatus under an atmosphere of argon gas. The methanol used was distilled under argon and stored over 4 Å molecular sieves. Ferrous tetrafluoroborate tetrahydrate (2.09 g) was dissolved in methanol (10 ml). Equal-molar quantities of 1,3-diaminopropane and 2,6-diformyl-4-methylphenol, dissolved in minimum quantities of methanol, were added sequentially. The solution was refluxed 45 min before imidazole (2.29 g) in methanol (10 ml) were added and the refluxing was continued for an additional 80 min. A small volume of solvent was removed and the purple microcrystalline solid which formed was filtered off. Anal. Calcd. C, 45.03; H, 4.41; N, 17.51; Fe, 11.63. Found: C, 45.00; H, 4.35; N, 17.35; Fe, 11.3. The crystals used in the structure determination were grown from the filtrate of the above reaction on standing at ca. -10°C for two weeks under argon. The analysis of the crystals is given below: Calcd. C, 45.03; H, 4.41; N, 17.51; Fe, 11.63. Found: C, 45.00; H, 4.30; N, 18.05; Fe, 11.05.

Binuclear Co and Ni Complexes. The following procedure is typical of the methods used to prepare the binuclear cobalt and nickel complexes. Into a pyridine solution (20 ml) of 2,6-diformyl-4-methylphenol (0.20 g, 1.22 mmol), 1,3-diaminopropane (0.1 ml, 1.20 mmol) was pipetted with stirring and mild heating. Previously dried $\text{Co}(\text{BF}_4)_2 \cdot 6 \text{H}_2\text{O}$ (0.43 g, 1.85 mmol) in methanol (5 ml) was added to the pyridine solution which became deep red-brown. Heating was continued as the solution volume was reduced to a few ml while orange crystals formed. After the mixture was cooled, the precipitate was collected by filtration, washed with a small amount of pyridine followed by a larger quantity of diethyl ether and vacuum dried. Anal. Calcd. for $\text{C}_{44}\text{H}_{46}\text{N}_8\text{O}_2\text{B}_2\text{Co}_2\text{F}_8$: C, 52.3; H, 4.6; N, 11.1. Found: C, 51.9; H, 4.6; N, 11.0.

Identical procedures afforded orange crystals of $[\text{LCo}_2(\text{py})_4]-(\text{ClO}_4)_2$ and dull gold-brown microcrystalline samples of $[\text{LNi}_2(\text{py})_4]-(\text{BF}_4)_2$ and $[\text{LNi}_2(\text{py})_4](\text{ClO}_4)_2$. Anal. Calcd. for $\text{C}_{44}\text{H}_{46}\text{N}_8\text{O}_{10}\text{Cl}_2\text{Co}_2$: C, 51.0; H, 4.5; N, 10.8. Found: C, 50.7; H, 4.5; N, 10.8. Calcd. for $\text{C}_{44}\text{H}_{46}\text{N}_8\text{O}_2\text{B}_2\text{F}_8\text{Ni}_2$: C, 52.3; H, 4.6; N, 11.1. Found: C, 52.2; H, 4.7; N, 11.7. Calcd. for $\text{C}_{44}\text{H}_{46}\text{N}_8\text{O}_{10}\text{Cl}_2\text{Ni}_2$: C, 51.0; H, 4.5; N, 10.8. Found: C, 51.1; H, 4.7; N, 10.8.

The cobalt compounds appear to be reactive toward oxygen in solution but not in the solid state. All the complexes are soluble in polar organic solvents, and loss of pyridine in the solids appears to be negligible.

Physical Measurements. Infrared spectra were recorded on a Beckman 4240 infrared spectrophotometer as nujol mulls between NaCl plates. Electronic absorption spectra were obtained with a Cary 14 spectrophotometer with 1 cm quartz cells for solution studies and as mulls on filter paper for solids with the solvent in both cases in the reference compartment. Faraday magnetic susceptibility measurements were accomplished using a Cahn Instruments Faraday balance with powdered samples at room temperature with $\text{HgCo}-(\text{SCN})_4$ as a calibrant. Diamagnetic corrections were made using Pascal's constants. A PAR model 150A vibrating-sample magnetometer operated at 13.5 kG, was used to obtain the magnetic susceptibility data. Data for various samples of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ were periodically run in the range of 4.2 - 286° K and were used to standardize the system.⁸ In addition, two samples of $[\text{Ni}(\text{qnqn})\text{Cl}_2]_2$, where qnqn is trans-2-(2'-quinolyl)methylene-3-quinuclidinone, were run at different times to ensure that data obtained in this study are in agreement with those obtained previously for this same compound.⁹ A calibrated GaAs diode was employed for determination of the sample temperature.

A correction for the diamagnetism of the sample container and the background was made at all temperatures to the data for all compounds. The data were also corrected for the diamagnetism of each compound with estimated values from Pascal's constants.¹⁰ The resulting molar paramagnetic susceptibilities were least-squares fit to the appropriate theoretical susceptibility expressions by means

of a computer program.¹¹ Mössbauer data were collected on a previously described instrument.¹²

Crystal Measurements. A deep maroon crystal of $[\text{LFe}_2(\text{Im})_4](\text{BF}_4)_2$ with dimensions $0.18 \times 0.25 \times 0.38$ mm was used for data collection. Preliminary examination of the crystal and data collection were performed on a Syntex P2₁ four-circle automatic diffractometer equipped with a graphite monochromator. The unit cell parameters, listed in Table I, were obtained by a least-squares fit to the automatically centered settings for 15 reflections.¹³ The space group used was C2/c. All subsequent refinements were done in this space group. After averaging symmetry-equivalent reflections, a total of 4717 reflections were obtained; of these 2468 were considered above zero at the $1.5\sigma(I)$ significance level. A calculation of the transmission range (0.82-0.86) indicated that no absorption correction was necessary. There was no evidence for crystal decomposition. Lorentz and polarization corrections were applied but no corrections were deemed necessary for either absorption or extinction.

Structure Solution and Refinement. The structure was solved by the usual heavy atom techniques using Patterson and Fourier maps in the space group C2/c. The center of the cation is at the inversion center $\frac{1}{4}, \frac{1}{4}, \frac{1}{2}$. There is disorder at the methylene bridge of the cation at C(7) and at the BF_4^- anion at B(2). The disorder at the latter is a 2-fold rotation about the B(2)-F(3) bond. The disorder at C(7) showed up initially as a highly anisotropic ellipsoid at C(7). When the atom C(7) was removed, there were two peaks in the difference maps which

were near atom C(7). The heights of these peaks were in the approximate ratio 2:1. Refinement, holding all parameters fixed except the occupancies and positions of the major and minor sites of C(7), converged to $gC(7)/gC(7'')$ of 0.70/0.30. In subsequent refinements the positional and anisotropic thermal parameters for all non-hydrogen atoms were allowed to vary. Hydrogen atom positions were calculated according to standard criteria and were not allowed to vary. The hydrogen atoms were assigned a fixed isotropic thermal parameter of 7.0. Final, full matrix, least-squares refinements converged to agreement factors of $R_1 = 0.082$, $R_2 = 0.083$, and $E = 1.25$ where $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $R_2 = \sum w ||F_o| - |F_c||^2 / \sum w |F_o|^2$ and $E = [\sum w ||F_o| - |F_c||^2 / (m-n)]^{1/2}$ where m is the number of observations and n is the number of variables. The scattering curves used for Fe^{2+} , O^- and neutral atoms were taken from the analytical expression used in the International Tables for X-ray Crystallography.¹⁴ The anomalous dispersion effects for iron were included in the structure factor calculations.¹⁵ A final difference map showed the highest peak (height = $0.72 \text{ e}/\text{\AA}^3$) on the two fold axis at (0.50, 0.12, 0.25) which is $\sim 1.8 \text{ \AA}$ from B(1) and $1.5 \text{ \AA}$ from F(2). The next six peaks are $0.58 - 0.48 \text{ e}/\text{\AA}^3$ in height and are within one angstrom of Fe^{2+} and F(2). These residual peaks do not fit any disorder model for the BF_4^- group situated about B(1). The final positional and thermal parameters are given in Tables II and III, respectively.

Results

Compound Synthesis and Characterization. The formation of binuclear macrocyclic complexes of Fe^{II} , Co^{II} , and Ni^{II} of the type $[\text{LM}_2(\text{py})_4]\text{X}_2$ ($\text{X} = \text{BF}_4^-$ or ClO_4^-) from the condensation of 2, 6-diformyl-4-methylphenol and 1, 3-diaminopropane proceeds readily in pyridine solution. The isolation of binuclear compounds of these metals with non-coordinating anions is in contrast to the results obtained in other solvents. For example, the principal material recovered from the reaction employing $\text{Ni}(\text{ClO}_4)_2 \cdot 6 \text{H}_2\text{O}$ in methanol was reported to be a mononuclear complex, $\text{LH}_2\text{Ni}(\text{ClO}_4)_2 \cdot 2 \text{H}_2\text{O}$.³ When the anion is chloride or bromide, the incorporation of two metal ions occurs in methanol.

The initial concern with these species was to ascertain the coordination geometry about the metal atoms. Previous structure determinations have shown that the macrocycle L is capable of accommodating several metal stereochemistries including square pyramidal, octahedral and square planar.^{4, 16} Though it would probably involve severe distortion of the ligand, a tetrahedral arrangement may also be possible. In the absence of structural information the distinction among ligand geometries must be based on the interpretation of available spectral and magnetic data.

Certain mononuclear complexes of Co^{II} and Ni^{II} with Schiff bases and β -ketoenolates when dissolved in pyridine manifest changes in spectral and magnetic behavior consistent with the formation of

octahedral and occasionally five-coordinate species. In several cases bis(pyridine) complexes have been isolated and a few characterized crystallographically. More recently pyridine adducts of binuclear Co^{II} and Ni^{II} complexes of the 1,5-diphenyl-1,3,5-pentantrionato anion were prepared and their octahedral geometries confirmed by structure determinations.^{17,18}

The infrared spectra of the four Co^{II} and Ni^{II} complexes are virtually indistinguishable, the only difference being the positions of the bands due to BF_4^- and ClO_4^- , e. g., $\nu_3(\text{T}_2)$ occurs at 1050 cm^{-1} for BF_4^- and at 1090 cm^{-1} for ClO_4^- . All other bands are attributable to L or py.³ It appears likely that these materials are isostructural in the solid state.

The magnetic and electronic spectral properties of Co^{II} and Ni^{II} are often diagnostic of metal stereochemistry. The Faraday magnetic moments (Table IV) indicate that the complexes are all high spin which is confirmed by the variable temperature results (vide infra). This effectively eliminates a square planar arrangement for either metal since Co^{II} species are invariably low spin and those of Ni^{II} are diamagnetic. The magnetic moments for both complexes lie within their usual ranges for octahedral geometries. However, these values are also consistent with five-coordinate structures.

Electronic spectra were recorded for both solution and solid phases (Table V). High intensity absorptions of intraligand and/or charge transfer origin which occur in the UV region may obscure higher energy ligand field bands. Indeed shoulders are observed

on these bands in solid state spectra. The spectra are qualitatively similar in all media although there is some variation in the location of band maxima particularly with the nickel materials.

For the cobalt complexes the spectra closely resemble previously reported results for bis(pyridine) adducts of mononuclear species in the appropriate N_2O_2 and O_4 environments and are consistent with octahedral coordination.¹⁹ Only one well-defined absorption is observed at 10.4 kK although in solution there appears to be a weak feature at 8.3 kK which causes the tail of the former band to fall off less rapidly. The square pyramidal geometry would be expected to give rise to several bands in the near IR region. Moreover the low intensity of this band seems to preclude a tetrahedral structure. In idealized octahedral symmetry the 10.4 kK band would probably correspond to ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}$, and transitions to higher excited states (including spin-forbidden processes) occur as the observed shoulders or are obscured by the high intensity bands.

Based on similar comparison of the spectra of $[LNi_2(py)_4]X_2$ species with those of well established pyridine adducts of analogous mononuclear Ni^{II} complexes, octahedral geometry again appears most reasonable.¹⁹ The position of the lowest energy band is dependent on the medium which may reflect replacement of pyridine by solvent molecules. For the square pyramidal environment several bands are again anticipated in the near IR at lower frequency than is usually found with octahedral structures. Indeed the spectrum of $LNi_2Cl_2 \cdot 2H_2O$ displays five bands in solution and in the solid state

and is believed to be five-coordinate.³ By analogy with the cobalt system the low intensities of the observed bands also militate against tetrahedral geometry. According to an octahedral model a tentative assignment of the lowest energy band is ${}^3A_{1g} \leftarrow {}^3T_{2g}$. The next band of increasing energy is quite weak and could arise from a spin forbidden transition such as ${}^3A_{1g} \rightarrow {}^1E_g$ which is occasionally observed in Ni^{II} spectra. The 17.7 kK band is then due to ${}^3A_{1g} \rightarrow {}^3T_{1g}(F)$ and the shoulder at ~ 21.7 kK is attributable to ${}^3A_{1g} \rightarrow {}^3T_{1g}(P)$.

The spectra of the high spin Fe^{II} complexes are dominated by charge transfer bands. Significant by its absence is the low energy d-d band observed in the square pyramidal Fe_2LCl_2 species at 7.9 kK. It is also noteworthy that little differences exist in comparing solution and solid state spectra. Weak features at 11.1 kK in the pyridine adducts are tentatively assigned to ${}^5T_{2g} \rightarrow {}^5E_g$. The corresponding $Fe(H_2O)_6^{2+}$ complex shows this transition at 10.0 kK, consistent with the weaker field aquo ion.²⁰

Molecular Structure of $[LFe_2(Im)_4](BF_4)_2$. The single-crystal X-ray structure of this compound was solved using standard heavy-atom techniques. The structure consists of discrete binuclear $[LFe_2(Im)_4]^{2+}$ cations and BF_4^- anions. Bond distances and angles are given in Table VI and are also indicated in Figure 1. The binuclear cation is located about a crystallographic center of inversion. Each iron ion is coordinated to four atoms of the ligand L as well as two axial imidazole ligands. Least-squares fit planes were calculated

for the cation and, as can be seen by the results given in Table VII, the ligand L in $[\text{LFe}_2(\text{Im})_4](\text{BF}_4)_2$ is planar except for the disorder at the C(7) carbon atom of the trimethylene bridge. The stereoscopic view of $\text{LFe}_2(\text{Im})_4^{2+}$ given in Figure 2 illustrates the planarity of L. Disorder in the trimethylene bridge of the L ligand was also noted for the two five-coordinate complexes.^{4, 5} This disorder at C(7) is, of course, merely the reflection of two possible sites for the C(7) atom. There is a decided preference for the C(7) site over the C(7^{''}) site apparently due to steric interactions between atom C(7^{''}) and the array B(2)-F(4).

Of primary importance to the present study of magnetic exchange interactions is the finding that the two iron ions are only 0.011(1) Å out the plane of the ligand L. By way of comparison it is to be noted that the metal ions in the five-coordinate complexes of L are considerably removed from the ligand plane. The copper(II) ion is 0.21 Å out of the ligand plane in $\text{LCu}_2\text{Cl}_2 \cdot 6\text{H}_2\text{O}$,⁴ whereas the high-spin cobalt(II) ion is 0.298 Å out of the ligand plane in $\text{LCo}_2\text{Br}_2 \cdot \text{CH}_3\text{OH}$.⁵

The $\text{LFe}_2(\text{Im})_4^{2+}$ cation possesses two high-spin iron(II) ions with an Fe-Fe distance of 3.117(2) Å. The overall charge on the cation, Mössbauer effect data, and magnetic susceptibility data (vide infra) clearly indicate high-spin iron(II) ions. The 4.2°K ⁵⁷Fe Mössbauer spectrum obtained for the sample of $[\text{LFe}_2(\text{Im})_4](\text{BF}_4)_2$ used for the crystal structure is shown in Figure 3. There is only one quadrupole-split doublet; least-squares fitting gives

a quadrupole splitting of $\Delta E_Q = 2.0797(14)$ mm/sec and an isomer shift of $\delta = 0.7387(7)$ mm/sec vs. iron metal. Values of ΔE_Q for six-coordinate, high-spin iron(II) complexes have been found to be in the range of 2.0 - 3.0 mm/sec.²¹ There is no evidence in the spectrum for the presence of iron(III) in the sample. The room-temperature Mössbauer spectrum for $[\text{LFe}_2(\text{MeIm})_4](\text{BF}_4)_2$ also shows only one doublet with $\Delta E_Q = 2.22(2)$ mm/sec and $\delta = 0.94(2)$ mm/sec. In contrast, the high-spin iron(II) ions in LFe_2Cl_2 give a Mössbauer spectrum (ambient temperature) consisting of one doublet with an appreciably larger quadrupole splitting: $\Delta E_Q = 3.600(10)$ mm/sec and $\delta = 0.941(5)$ mm/sec.

Figure 4 gives a stereoscopic view of the unit cell for $[\text{LFe}_2(\text{Im})_4](\text{BF}_4)_2$, where it can be seen that the binuclear cations are reasonably well isolated from each other. Not shown is the disorder present in the BF_4^- ion, which consists of a two-fold rotation about B(2)-F(3) and appears only at B(2). There are no strong intermolecular hydrogen bonds. The range of normal hydrogen bonds of the type $\text{N}-\text{H}\cdots\text{F}$ is 2.61 to 2.82 Å²² and it can be seen in Table VIII²² that one of the intermolecular contacts in $[\text{LFe}_2(\text{Im})_4](\text{BF}_4)_2$ are within this range.

Magnetic Susceptibility. Variable-temperature (4.2 - 285° K) magnetic susceptibility data were collected for $[\text{LFe}_2(\text{py})_4](\text{BF}_4)_2$, $[\text{LFe}_2(\text{MeIm})_4](\text{BF}_4)_2$, $[\text{LFe}_2(\text{Im})_4](\text{BF}_4)_2$, $[\text{LFe}_2(\text{MeNic})_4](\text{BF}_4)_2$, $[\text{LCo}_2(\text{py})_4](\text{BF}_4)_2$, and $[\text{LNi}_2(\text{py})_4](\text{BF}_4)_2$. The data are given in Tables IX-XV²² and are illustrated in Figures 5-10.

There is a maximum at ca. 70° K in the χ vs. T curve for

$[\text{LNi}_2(\text{py})_4](\text{BF}_4)_2$ (see Figure 5). The effective magnetic moment per nickel ion, $\mu_{\text{eff}}/\text{Ni}$, varies from $2.83 \mu_{\text{B}}$ at 285°K to $0.21 \mu_{\text{B}}$ at 4.2°K . An antiferromagnetic exchange interaction is present. In order to compare the interactions present in these six-coordinate complexes with those reported⁶ for the analogous five-coordinate complexes, it was decided to fit the data to theoretical susceptibility expressions that result from the spin Hamiltonian for an isotropic magnetic exchange, $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$. In the case of a binuclear nickel(II) complex, $S_1 = S_2 = 1$ and the molar paramagnetic susceptibility for the binuclear complex is given by eq (1), where the symbols have the usual meanings.

$$\chi_M = \frac{Ng^2\beta^2}{kT} \left[\frac{10 + 2 \exp(-4J/kT)}{5 + 3 \exp(-4J/kT) + \exp(-6J/kT)} \right] \quad (1)$$

Least-squares fitting the data for $[\text{LNi}_2(\text{py})_4](\text{BF}_4)_2$ to eq (1) gives $J = -23 \text{ cm}^{-1}$ and $g = 2.13$. As can be seen in Figure 5, the fit (solid lines) is good.

The compound $[\text{LCo}_2(\text{py})_4](\text{BF}_4)_2$ also exhibits a χ vs. T curve with a maximum, in this case at ca. 16°K (see Figure 6). The values of $\mu_{\text{eff}}/\text{Co}$ vary from $4.55 \mu_{\text{B}}$ at 285°K to $0.69 \mu_{\text{B}}$ at 4.2°K . Each cobalt(II) ion is high-spin. The molar paramagnetic susceptibility for an $S_1 = S_2 = \frac{3}{2}$ binuclear complex is given by eq (2).

$$\chi_M = \frac{Ng^2\beta^2}{kT} \left[\frac{28 + 10 \exp(-6J/kT) + 2 \exp(-10J/kT)}{7 + 5 \exp(-6J/kT) + 3 \exp(-10J/kT) + \exp(-12J/kT)} \right] \quad (2)$$

Fitting the data to this equation gives the solid lines in Figure 2, which are characterized by $J = -4.1 \text{ cm}^{-1}$ and $g = 2.41$.

The axial ligands for two of the iron(II) compounds are pyridines. Figure 7 shows the data for $[\text{LFe}_2(\text{py})_4](\text{BF}_4)_2$. The data obtained for $[\text{LFe}_2(\text{MeNic})_4](\text{BF}_4)_2$ are very similar in appearance. As can be seen in Figure 7, there is an increase in χ_M at low temperatures following the maximum at ca. 44°K . This increase in χ_M at temperatures less than ca. 17°K is most likely attributable to a small amount of a paramagnetic impurity. The impurity could, for instance, be either a binucleating ligand L with only one Fe^{II} or Fe^{III} ion coordinated or some other ferric containing impurity. The susceptibility equation for an $S_1 = S_2 = 2$ binuclear complex can be easily derived. A second term accounting for the paramagnetic impurity was added to this equation to give eq (3).

$$\chi_M = \frac{N g^2 \beta^2}{kT} \left[\frac{60 + 28 \exp(-8J/kT) + 10 \exp(-14J/kT) + 2 \exp(-18J/kT)}{9 + 7 \exp(-8J/kT) + 5 \exp(-14J/kT) + 3 \exp(-18J/kT) + \exp(-20J/kT)} \right] + \frac{4.2}{T} (\text{PARA}) \quad (3)$$

In eq (3), PARA is the molar paramagnetic susceptibility of the impurity at 4.2°K .

Least-squares fitting the data for $[\text{LFe}_2(\text{py})_4](\text{BF}_4)_2$ to eq (3) gives $J = -7.5 \text{ cm}^{-1}$, $g = 2.10$ and $\text{PARA} = 0.0564 \text{ cgsu}$. The value of PARA corresponds to ca. 6% by weight of $[\text{LFe}(\text{py})_2]\text{BF}_4$. Fitting the data for $[\text{LFe}_2(\text{MeNic})_4](\text{BF}_4)_2$ gave $J = -6.8 \text{ cm}^{-1}$, $g = 1.98$, and

PARA = 0.0581 cgsu, where the PARA value corresponds to ca. 7% by weight of $[\text{LFe}(\text{MeNic})_2]\text{BF}_4$. There is no evidence of paramagnetic impurity in the susceptibility data for $[\text{LFe}_2(\text{MeIm})_4](\text{BF}_4)_2$, as can be seen in Figure 8. Fitting the data for this compound to eq (3) with PARA fixed at zero gave $J = -4.5 \text{ cm}^{-1}$ and $g = 2.25$. The magnetic susceptibility data for $[\text{LFe}_2(\text{Im})_4](\text{BF}_4)_2$ are illustrated in Figure 9. In this case the best fitting parameters were found to be $J = -1.5 \text{ cm}^{-1}$ and $g = 2.17$.

Discussion

The magnetic exchange parameters for the six-coordinate $[\text{LM}_2(\text{base})_4](\text{BF}_4)_2$ complexes studied in this paper are summarized in Table XVI, together with the J-values reported⁶ previously for the analogous five-coordinate complexes. The variation in magnetic exchange parameter across the series of five-coordinate LM_2Cl_2 complexes was attributed to two factors. The structural work on $\text{LCo}_2\text{Br}_2 \cdot \text{CH}_3\text{OH}$ ⁴ and $\text{Cu}_2\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ ⁵ demonstrates the variation in metal-ligand plane distance. The second important factor that varies across the series is the number (and spatial distribution) of unpaired electrons.

Because the ligand L is expected to be relatively rigid, the first of these factors could be eliminated, or at least minimized, by constraining the metal ions to lie in the plane of the ligand L. This was accomplished by preparing six-coordinate complexes of the binucleating ligand L. In the Results section it was shown via electronic absorption spectroscopy that the nickel(II) and cobalt(II) complexes with composition $[\text{LM}_2(\text{py})_4](\text{BF}_4)_2$ have six-coordinate metal ions. The X-ray crystal structure of $[\text{LFe}_2(\text{Im})_4](\text{BF}_4)_2$ confirms six-coordination for iron. With the metal ion constrained to lie in the plane of the ligand L the variation in geometry as the metal ion radius changes should be minimized. It should be possible then to study the effect of the variation of the number and distribution of unpaired electrons on the magnetic exchange interaction.

Examination of Table XVI shows that there are only relatively small differences in J-values between the five-coordinate and six-coordinate complexes of a given metal ion. This could result from two opposing factors. By moving the metal ion into the plane, overlap between the metal based $d_{x^2-y^2}$ orbitals and the oxygen based sp^2 hybrid orbitals has been increased. Since this sigma framework represents the dominant pathway for the superexchange mechanism, the enhanced overlap should result in an increase in the antiferromagnetic interaction. On the other hand, these structural changes will result in a stronger ligand field about the metal ions, leading to an enhanced difference between the energies of the metal based and bridging oxygen atom orbitals. This will decrease the exchange interaction. As is evident from the data, these two effects apparently cancel.

The magnetic susceptibility data for the four $[LFe_2(\text{base})_4](BF_4)_2$ complexes substantiate the statement that an increased ligand-field splitting would affect the net antiferromagnetic interaction. The two iron(II) complexes with pyridine bases (py and MeNic) as the axial ligands exhibit approximately the same magnitude of interaction, whereas the two iron(II) complexes with the stronger axial bases (Im and MeIm) exhibit the weaker net antiferromagnetic interaction.

In summary, the two offsetting factors of improved orbital overlap and increased ligand field splitting for the six-coordinate complexes lead to only a small difference in the J-values between the five- and six-coordinate complexes of a given metal ion. What is of

greater significance is that the exchange parameter does vary appreciably across the $[\text{LM}_2(\text{py})_4](\text{BF}_4)_2$ [$\text{M} = \text{Fe}(\text{II})$, $\text{Co}(\text{II})$, and $\text{Ni}(\text{II})$] series. It is likely that this variation reflects the changing number of unpaired electrons from one complex to another. In this regard it is important to note that an antiferromagnetic exchange interaction has been noted²³ for MnO , FeO , CoO , and NiO , where the Néel temperatures increase regularly from 116 to 523 K in going from MnO to NiO . Each of these compounds has a rock salt structure and the exchange interaction occurs through linear M-O-M units. Presumably both the M-O distances and the number of unpaired electrons are important. In contrast, Sinn *et al.*²⁴ very recently came to a different conclusion. Magnetic susceptibility data were collected for a series of heterobinuclear complexes. It was concluded that the differences in J -values could be entirely accounted for by changes in structure differences in the compounds, and did not depend on the number of unpaired electrons. It is clear that additional work is needed.

Acknowledgment. We are grateful for support from NIH grant HL 13652 (to D. N. H.) and NSF grant CHE79-27141 (to R. R. G.).

Registry No.

Supplementary Material Available: Tables VIII-XIV (non-bonding contacts, calculated and observed magnetic susceptibility data) and listings of observed and calculated structure factors (40 pages). Ordering information is given on any current masthead page.

References and Notes

- (1) California Institute of Technology.
- (2) University of Illinois.
- (3) Pilkington, N. H.; Robson, R. Aust. J. Chem. 1970, 23, 2225.
- (4) Hoskins, B. F.; Williams, G. A. Aust. J. Chem. 1975, 28, 2607.
- (5) Hoskins, B. F.; McLeod, N. J.; Schaap, H. A. Aust. J. Chem. 1976, 29, 515.
- (6) Lambert, S. L.; Hendrickson, D. N. Inorg. Chem. 1979, 18, 2683.
- (7) Ullmann, F.; Brittner, K. Chim Ber. 1909, 42, 2539.
- (8) Reekie, J. Proc. Royal Soc. (London), 1939, 173, 367.
- (9) Laskowski, E. J.; Felthouse, T. R.; Hendrickson, D. N.; Long, G. J. Inorg. Chem. 1976, 15, 2908.
- (10) Figgis, B. N.; Lewis, J. in "Modern Coordination Chemistry", Lewis, J.; Wilkins, R. G., Eds., Interscience: New York, N. Y., 1960, p. 403.
- (11) Chandler, J. P. Program 66, Quantum Chemistry Program Exchange; Indiana University: Bloomington, Ind.
- (12) Munck, E.; Debrunner, P. G.; Tsibris, J. C. M.; Gunsalvs, I. C. Biochemistry, 1972, 11, 855.
- (13) All crystallographic calculations were carried out on the Syntex EXTL X-ray crystallographic package, based on the Data Genereal ECLIPSE computer.

- (14) "International Tables for X-ray Crystallography", Vol. IV, Ibers, J. A.; Hamilton, W. C., Ed., Kynoch Press, Birmingham, England, 1974, p. 99, 102.
- (15) Ibid., p. 148, 150.
- (16) Gagné, R. R.; Henling, L. M.; Kistenmacher, T. J. Inorg. Chem. 1980, 19, 1905.
- (17) Kuszaj, J. M.; Tomlonovic, B.; Lintvedt, R. L.; Glick, M. D. Inorg. Chem. 1973, 12, 1297.
- (18) Lintvedt, R. L.; Borer, L. L.; Murtha, D. P.; Kuszaj, J. M.; Glick, M. D. Inorg. Chem. 1974, 13, 18.
- (19) (a) Yamada, S. Coord. Chem. Rev. 1966, 1, 415.;
(b) Holm, R. H.; Everett, G. W.; Chakravorty, A. Prog. Inorg. Chem. 1966, 7, 83.
- (20) Dunn, T. M. in "Modern Coordination Chemistry", Lewis, J.; Wilkins, R. G., Eds., Interscience: New York, N. Y., 1960, p. 290.
- (21) Merrill, P. H.; Goedken, V. I.; Busch, D. H.; Stone, J. A. J. Am. Chem. Soc. 1975, 92, 7590.
- (22) Supplementary material.
- (23) Nesbet, R. K. Phys. Rev., 1960, 119, 658.
- (24) O'Connor, C. J.; Freyberg, D. P.; Sinn, E. Inorg. Chem. 1979, 18, 1077.

Figure Captions

- Figure 1. ORTEP plot of the ligand L and coordinated ferrous ions.
- Figure 2. Stereoscopic view of the cation $[\text{LFe}_2(\text{Im})_4]^{2+}$.
- Figure 3. Room-temperature ^{57}Fe Mössbauer spectrum of $[\text{LFe}_2(\text{Im})_4](\text{BF}_4)_2$.
- Figure 4. Stereoscopic view of the unit cell for $[\text{LFe}_2(\text{Im})_4](\text{BF}_4)_2$.
- Figure 5. Molar paramagnetic susceptibility, χ_M , and effective magnetic moment, $\mu_{\text{eff}}/\text{Ni}$, vs. temperature curves for $[\text{LNi}_2(\text{py})_4](\text{BF}_4)_2$. The solid lines represent the least-squares fit of the data to the theoretical equation given in the text.
- Figure 6. Molar paramagnetic susceptibility, χ_M , and effective magnetic moment, $\mu_{\text{eff}}/\text{Co}$, vs. temperature curves for $[\text{LCo}_2(\text{py})_4](\text{BF}_4)_2$. The solid lines represent the least-squares fit of the data to the theoretical equation given in the text.
- Figure 7. Molar paramagnetic susceptibility, χ_M , and effective magnetic moment, $\mu_{\text{eff}}/\text{Fe}$, vs. temperature curves for $[\text{LFe}_2(\text{py})_4](\text{BF}_4)_2$. The solid lines represent the least-squares fit of the data to the theoretical equation given in the text.
- Figure 8. Molar paramagnetic susceptibility, χ_M , and effective magnetic moment, $\mu_{\text{eff}}/\text{Fe}$, vs. temperature curves for $[\text{LFe}_2(\text{MeIm})_4](\text{BF}_4)_2$. The solid lines represent the

least squares fit of the data to the theoretical equation given in the text.

Figure 9. Molar paramagnetic susceptibility, χ_M , and effective magnetic moment, $\mu_{\text{eff}}/\text{Fe}$, vs. temperature curves for $[\text{LFe}_2(\text{Im})_4](\text{BF}_4)_2$. The solid lines represent the least-squares fit of the data to the theoretical equation given in the text.

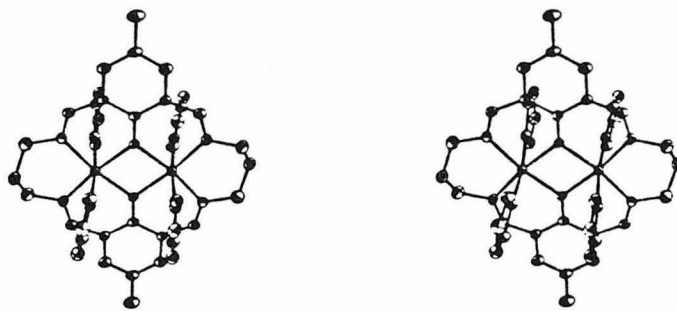


Figure 2.

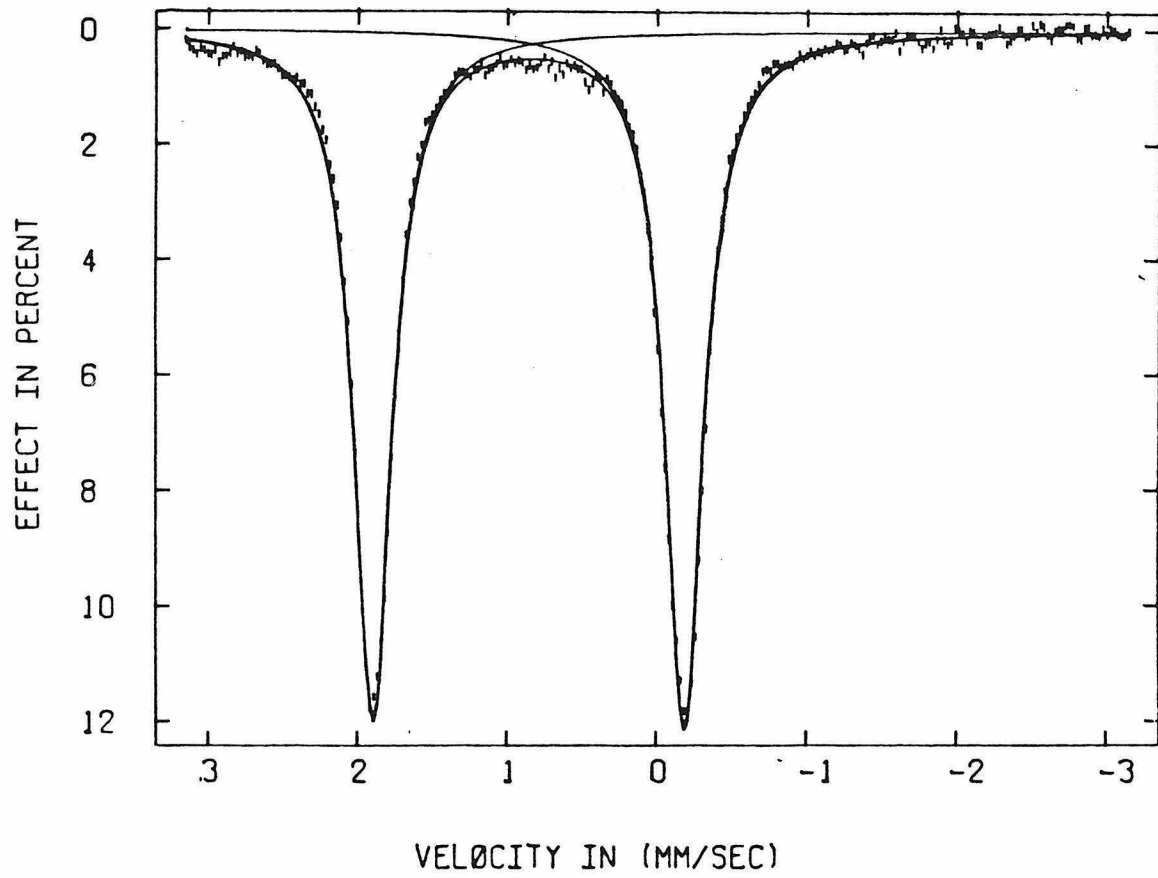


Figure 3.

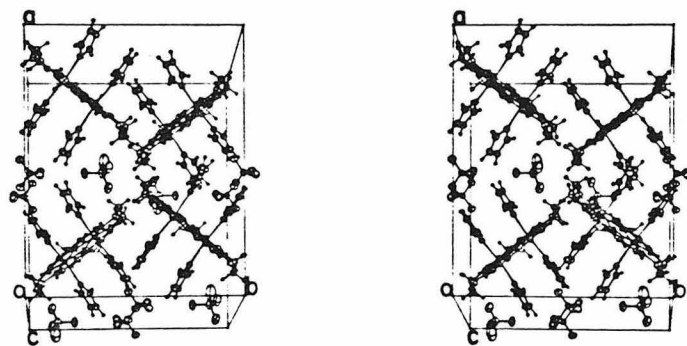


Figure 4.

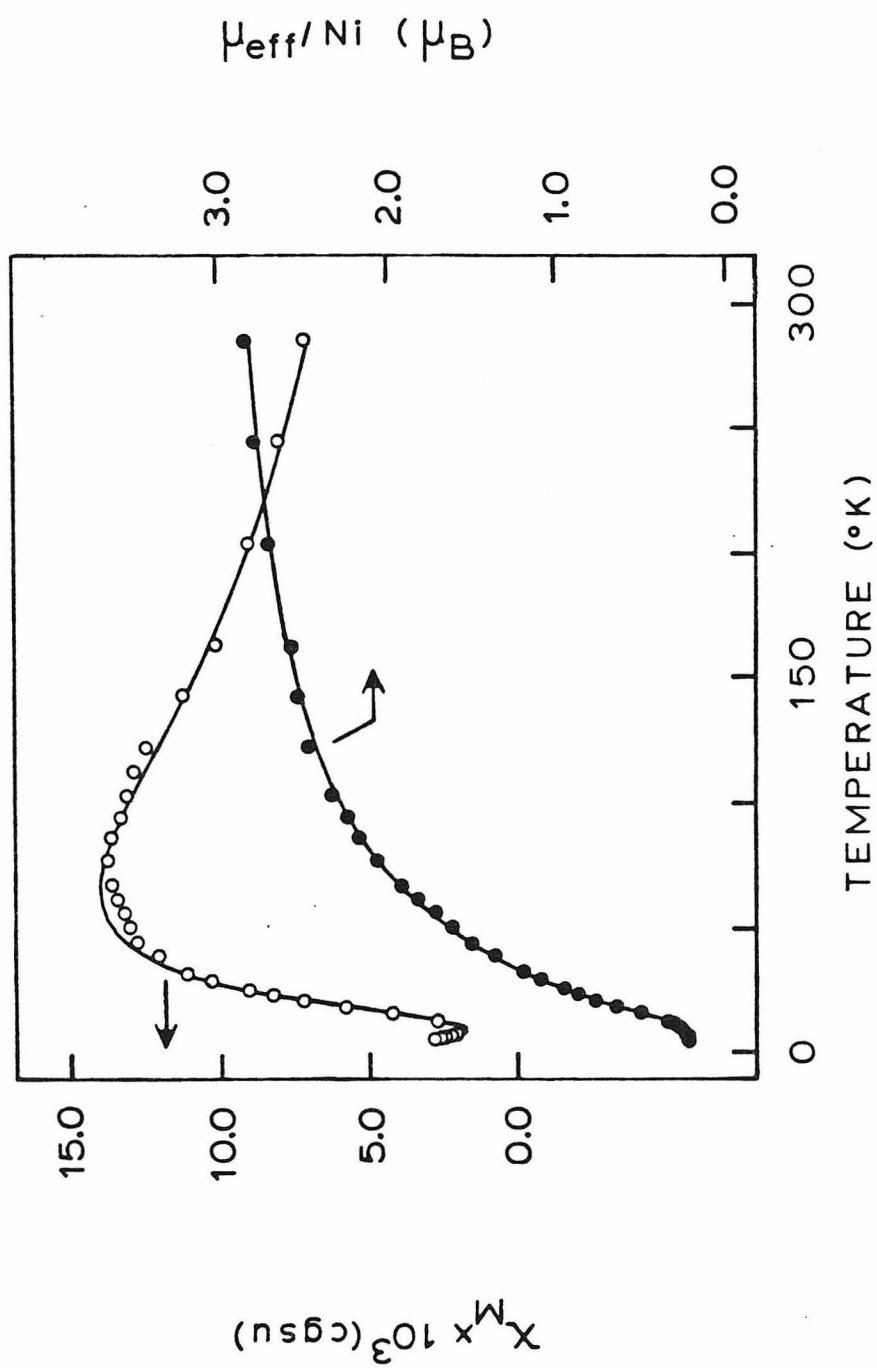


Figure 5.

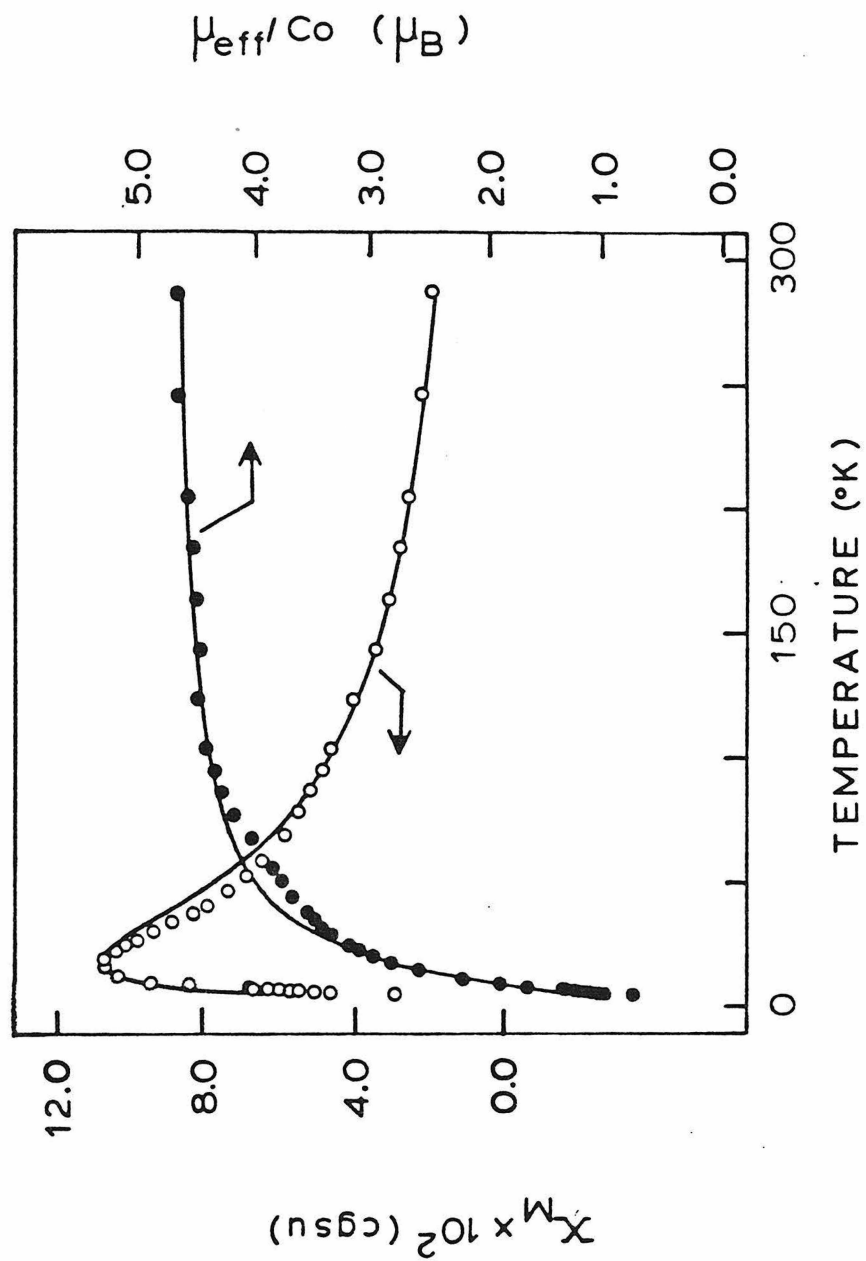


Figure 6.

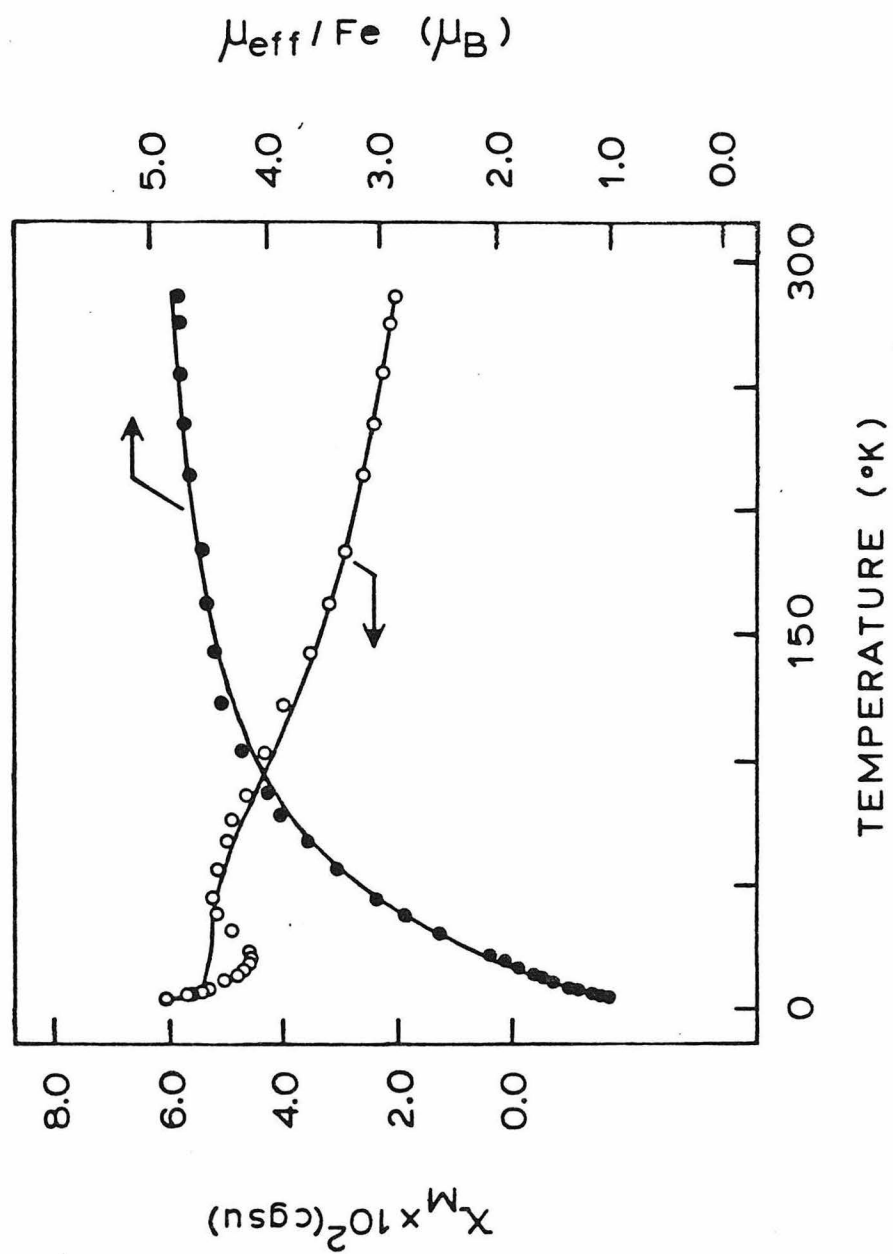


Figure 7.

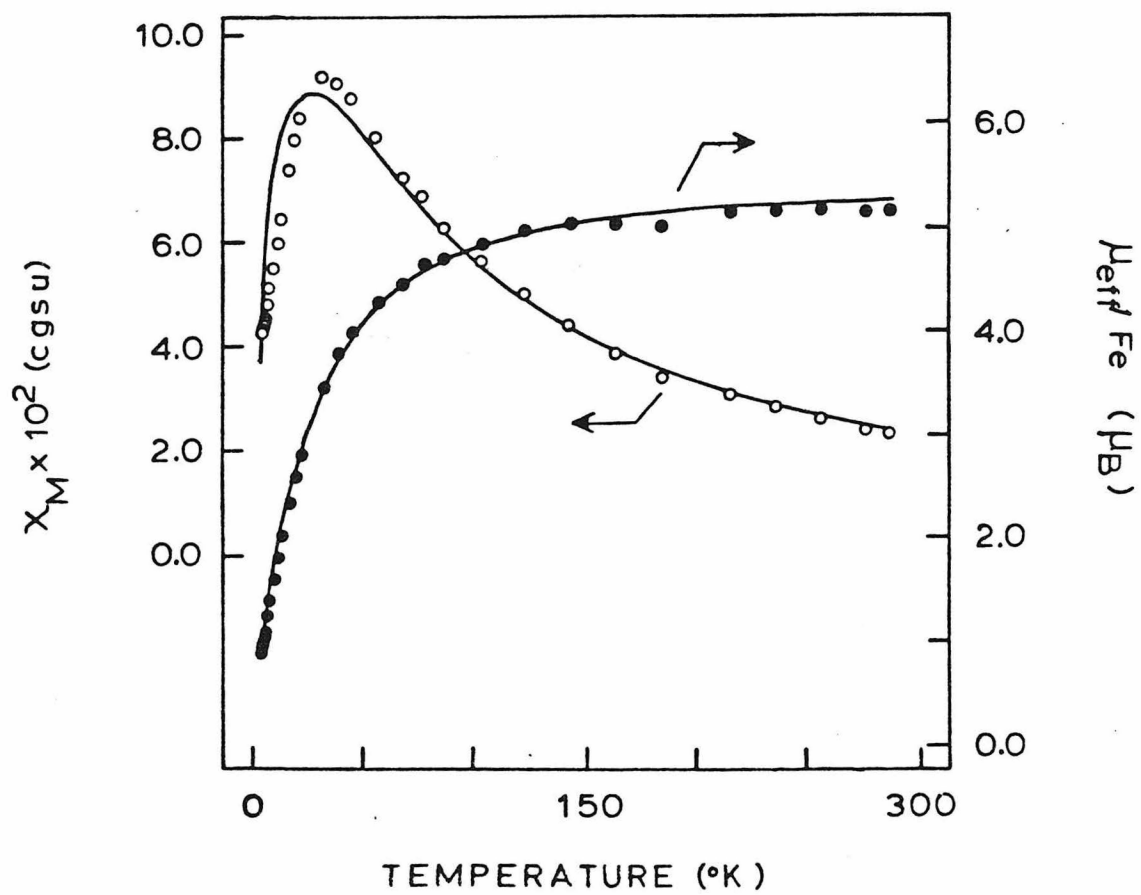


Figure 8.

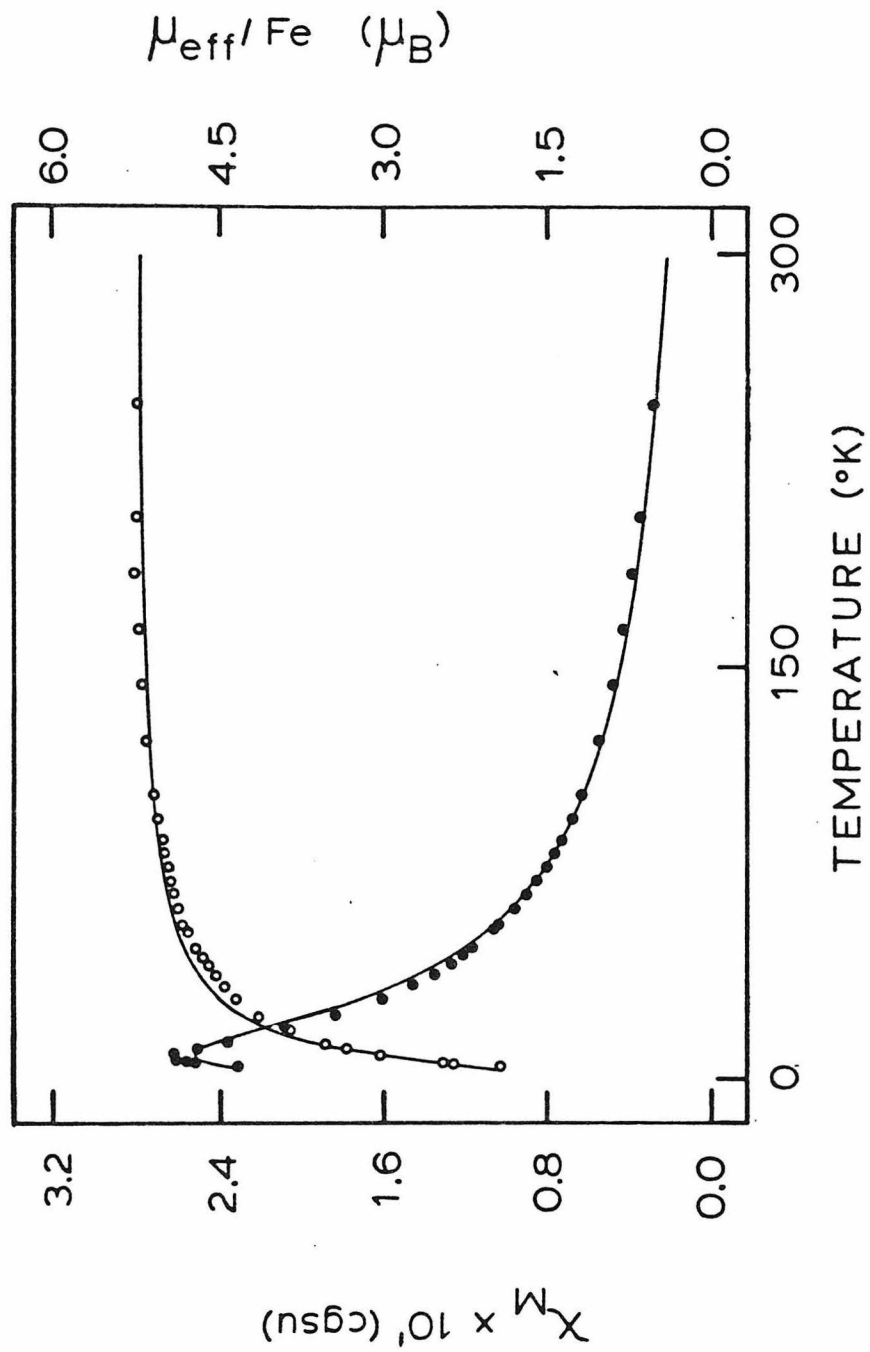


Figure 9.

Tables I - XVI.

Table I. Experimental Data for the X-ray Diffraction Study of
 $[\text{LFe}_2(\text{Im})_4](\text{BF}_4)_2$

Crystal Parameters

$a = 21.060 (5) \text{ \AA}$	Space group = $C2/C$
$b = 17.138 (4) \text{ \AA}$	$Z = 4$ (binuclear units)
$c = 12.172 (2) \text{ \AA}$	Mol. wt. = 956.09
$\beta = 108.82 (2)^\circ$	ρ calcd. = 1.52 gm/cm^3
monoclinic	ρ exptl. = 1.53 gm/cm^3
	(flotation in bromoform- methylene chloride)
	$V = 4158.3 \text{ \AA}^3$

Measurement of Intensity Data

Radiation: $\text{MoK}\alpha$, $\lambda 0.71069 \text{ \AA}$

Monochromator: graphite crystal

Monochromator angle: 6.2°

X-ray beam collimator diameter: 1.0mm

Crystal orientation: random

Reflections measured: (h, k, l) and $(-h, -k, -l)$

Maximum 2θ : 55°

Scan type: $0-2\theta$ scan technique

Scan speed: $3 - 29.3^\circ / \text{min.}$

Base width: 2.25°

Background measurement: background counting/total scan time = 0.5

Table II. Final Positional Parameters^a for [LFe₂(Im)₄](BF₄)₂
Including Hydrogen Atoms^b

Atom	X	Y	Z
Fe	0.19877(5)	0.18140(6)	0.47625(8)
O	0.2293(2)	0.2672(3)	0.3817(4)
C(2)	0.2129(4)	0.2799(4)	0.2698(6)
C(3)	0.1636(3)	0.2326(4)	0.1875(6)
C(4)	0.1271(4)	0.1678(5)	0.2173(6)
N(5)	0.1344(3)	0.1403(4)	0.3180(5)
C(6)	0.0949(5)	0.0710(6)	0.3254(8)
C(7)	0.0758(7)	0.0585(8)	0.4295(11)
C(7 ^u)	0.1236(15)	0.0222(16)	0.4268(27)
C(8)	0.1298(5)	0.0415(5)	0.5437(8)
N(9)	0.1797(3)	0.1032(4)	0.5926(5)
C(10)	0.2055(4)	0.1052(5)	0.7037(6)
C(11)	0.2435(4)	0.3399(4)	0.2260(6)
C(12)	0.2269(4)	0.3516(5)	0.1054(7)
C(13)	0.1796(4)	0.3053(5)	0.0258(6)
C(14)	0.1487(4)	0.2467(5)	0.0686(6)
C(15)	0.1637(5)	0.3187(6)	-0.1037(7)
N(16)	0.2746(3)	0.0992(4)	0.4522(5)
C(17)	0.3188(4)	0.0581(5)	0.5324(7)
N(18)	0.3626(3)	0.0220(4)	0.4924(7)
C(19)	0.3452(4)	0.0382(5)	0.3787(9)

Table II con' t.

C(20)	0.2914(4)	0.0855(5)	0.3552(7)
N(21)	0.1144(3)	0.2538(4)	0.4903(5)
C(22)	0.0910(4)	0.2574(5)	0.5778(6)
N(23)	0.0359(3)	0.3012(4)	0.5539(6)
C(24)	0.0220(4)	0.3268(6)	0.4455(8)
C(25)	0.0692(5)	0.2973(5)	0.4057(7)
B(1)	0.0000(0)	0.5200(9)	0.2500(0)
F(1)	-0.0517(3)	0.4744(3)	0.2544(5)
F(2)	-0.0230(3)	0.5659(4)	0.1516(6)
B(2)	0.0000(0)	0.1450(14)	-0.2500(0)
F(3)	0.0000(0)	0.2259(5)	-0.2500(0)
F(4)	-0.0042(22)	0.1163(19)	-0.1545(44)
F(5)	0.0530(20)	0.2254(18)	-0.2638(44)
F(6)	-0.0563(36)	0.1324(18)	-0.3382(54)
H(4)	0.092(0)	0.142(0)	0.151(0)
H(6A)	0.122(0)	0.024(0)	0.317(0)
H(6B)	0.052(0)	0.073(0)	0.258(0)
H(6A')	0.089(0)	0.038(0)	0.255(0)
H(6B')	0.050(0)	0.089(0)	0.326(0)
H(7A)	0.044(0)	0.013(0)	0.413(0)
H(7B)	0.052(0)	0.107(0)	0.441(0)
H(7A')	0.170(0)	0.011(0)	0.428(0)
H(7B')	0.096(0)	-0.027(0)	0.410(0)

Table II con' t.

H(8A)	0.155(0)	-0.006(0)	0.532(0)
H(8B)	0.107(0)	0.030(0)	0.602(0)
H(8A')	0.143(0)	-0.006(0)	0.592(0)
H(8B')	0.085(0)	0.060(0)	0.546(0)
H(10)	0.189(0)	0.064(0)	0.748(0)
H(12)	0.250(0)	0.394(0)	0.076(0)
H(14)	0.114(0)	0.213(0)	0.012(0)
H(15A)	0.194(0)	0.333(0)	-0.139(0)
H(15B)	0.128(0)	0.360(0)	-0.125(0)
H(15C)	0.144(0)	0.268(0)	-0.141(0)
H(17)	0.319(0)	0.054(0)	0.615(0)
H(18)	0.401(0)	-0.011(0)	0.538(0)
H(19)	0.368(0)	0.019(0)	0.323(0)
H(20)	0.268(0)	0.108(0)	0.277(0)
H(22)	0.113(0)	0.230(0)	0.654(0)
H(23)	0.009(0)	0.313(0)	0.608(0)
H(24)	-0.016(0)	0.361(0)	0.402(0)
H(25)	0.071(0)	0.306(0)	0.326(0)

^a Standard deviations of the least significant figures are given in parentheses and are given in this fashion in succeeding tables.

^b The hydrogen atom positions were calculated with fixed bond lengths of 1.0Å.

Table III. Anisotropic Thermal Parameters^a for [LFe₂(Im)₄](BF₄)₂

Atom	B ₁₁	B ₂₂	B ₃₃	B ₁₂	B ₁₃	B ₂₃
FE	0.00176(3)	0.00303(4)	0.00415(7)	-0.00011(3)	0.00110(3)	0.00002(6)
O	0.0023(1)	0.0030(2)	0.0027(3)	-0.0002(1)	0.0007(2)	-0.00
C(2)	0.0022(2)	0.0033(3)	0.0039(5)	0.0008(2)	0.0012(7)	0.0003(3)
C(3)	0.0019(2)	0.0030(3)	0.0037(5)	0.0006(2)	0.0008(3)	-0.0002(3)
C(4)	0.0021(2)	0.0046(4)	0.0037(5)	0.0003(2)	0.0005(3)	-0.0004(4)
N(5)	0.0017(2)	0.0036(3)	0.0061(5)	-0.0003(2)	0.0013(2)	-0.0005(3)
C(6)	0.0032(3)	0.0064(5)	0.0079(8)	-0.0018(3)	0.0014(4)	-0.0014(6)
C(7)	0.0030(4)	0.0043(6)	0.0072(11)	-0.0007(4)	-0.0012(6)	-0.0006(7)
C(7")	0.0027(9)	0.0026(12)	0.0116(33)	-0.0012(8)	0.0028(14)	-0.0035(16)
C(8)	0.0041(3)	0.0037(4)	0.0081(8)	-0.0006(3)	0.0024(4)	0.0006(5)
N(9)	0.0025(2)	0.0027(3)	0.0063(6)	-0.0004(2)	0.0018(3)	0.0002(3)
C(10)	0.0029(2)	0.0036(4)	0.0048(6)	0.0008(2)	0.0016(3)	0.0014(4)
C(11)	0.0023(2)	0.0030(3)	0.0043(5)	0.0002(2)	0.0011(3)	-0.0000(3)
C(12)	0.0035(3)	0.0036(3)	0.0053(7)	0.0011(3)	0.0017(4)	0.0014(4)
C(13)	0.0033(3)	0.0046(4)	0.0035(5)	0.0013(3)	0.0013(3)	0.0002(4)

Table III con't

C(14)	0.0025(2)	0.0045(4)	0.0053(6)	0.0007(3)	0.0012(3)	-0.0003(4)
C(15)	0.0049(4)	0.0065(5)	0.0046(6)	0.0013(4)	0.0019(4)	0.0014(4)
N(16)	0.0020(2)	0.0039(3)	0.0061(6)	0.0001(2)	0.0012(3)	0.0004(3)
C(17)	0.0026(3)	0.0045(4)	0.0078(8)	0.0001(3)	0.0013(4)	-0.0001(5)
N(18)	0.0026(2)	0.0042(4)	0.0104(8)	0.0009(2)	0.0012(3)	-0.0017(4)
C(19)	0.0028(3)	0.0042(4)	0.0116(10)	-0.0000(3)	0.0032(4)	-0.0017(5)
C(20)	0.0032(3)	0.0042(4)	0.0072(7)	0.0002(3)	0.0027(4)	-0.0002(4)
N(21)	0.0022(2)	0.0035(3)	0.0048(5)	-0.0000(2)	0.0014(2)	-0.0000(3)
C(22)	0.0030(3)	0.0039(4)	0.0055(6)	0.0006(3)	0.0016(3)	-0.0002(4)
N(23)	0.0028(2)	0.0043(4)	0.0100(7)	0.0005(2)	0.0028(3)	-0.0002(4)
C(24)	0.0032(3)	0.0042(4)	0.0110(9)	0.0014(3)	0.0021(4)	0.0020(5)
C(25)	0.0034(3)	0.0044(4)	0.0068(7)	0.0012(3)	0.0018(4)	0.0007(4)
B(1)	0.0022(4)	0.0039(7)	0.0127(17)	0.0000(0)	0.0026(7)	0.0000(0)
F(1)	0.0034(2)	0.0068(3)	0.0132(6)	-0.0008(2)	0.0033(3)	-0.0004(3)
F(2)	0.0044(2)	0.0074(3)	0.0216(9)	-0.0011(2)	0.0009(4)	0.0066(5)
B(2)	0.0066(12)	0.0051(11 _o)	0.0127(23)	0.0000(0)	0.0042(14)	0.0000(0)

Table III con't

F(3)	0.0076(4)	0.0041(4)	0.0171(11)	0.0000(0)	0.0078(6)	0.0000(0)
F(4)	0.0095(13)	0.0088(15)	0.0441(56)	0.0052(13)	0.0173(26)	0.0141(27)
F(5)	0.0083(11 _o)	0.0060(12)	0.0490(68)	0.0039(11)	0.0178(28)	0.0063(23)
F(6)	0.0181(27)	0.0094(14)	0.0487(69)	-0.0007(20)	-0.0157(37)	0.0060(32)

Table III con't

Atom	B	Atom	B	Atom	B
H(4)	7(0)	H(8A)	7(0)	H(15C)	7(0)
H(6A)	7(0)	H(8B)	7(0)	H(17)	7(0)
H(6B)	7(0)	H(8A')	7(0)	H(18)	7(0)
H(6A')	7(0)	H(8B')	7(0)	H(19)	7(0)
H(6B')	7(0)	H(10)	7(0)	H(20)	7(0)
H(7A)	7(0)	H(12)	7(0)	H(22)	7(0)
H(7B)	7(0)	H(14)	7(0)	H(23)	7(0)
H(7A')	7(0)	H(15A)	7(0)	H(24)	7(0)
H(7B')	7(0)	H(15B)	7(0)	H(25)	7(0)

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^a The form of the anisotropic thermal ellipsoids is given by $\exp[-B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{13}hl + 2B_{23}kl]$.
All hydrogen atoms were assigned the same isotropic thermal parameters.

Table IV. Faraday Magnetic Moments

	$\mu_{\text{eff}}/M^{2+} \text{ (298K)}$
$[\text{LCo}_2(\text{py})_4](\text{BF}_4)_2$	$4.84 \pm 0.05 \mu_B$
$[\text{LCo}_2(\text{py})_4](\text{ClO}_4)_2$	4.88
$[\text{LNi}_2(\text{py})_4](\text{BF}_4)_2$	2.88
$[\text{LNi}_2(\text{py})_4](\text{ClO}_4)_2$	2.87
$[\text{LFe}_2(\text{py})_{3.5}](\text{BF}_4)_2$	4.81
$[\text{LFe}_2(\text{MeIm})_4](\text{BF}_4)_2$	4.71
$[\text{LFe}_2(\text{MeNic})_4](\text{BF}_4)_2$	5.16

Table V. Electronic Absorption Spectra

	<u>medium^a</u>	<u>$\bar{\nu}$ (kKx10⁻³)^b</u>
[LCo ₂ (py) ₄](BF ₄) ₂	solid	19.4 sh, 18.4 sh, 10.3
	CH ₃ CN	10.4 (20), 8.3 sh
	DMF	10.4 (15), 8.3 sh
[LCo ₂ (py) ₄](ClO ₄) ₂	solid	19.4 sh, 18.4 sh, 10.3
	CH ₃ CH	10.4 8.3 sh
[LNi ₂ (py) ₄](BF ₄) ₂	solid	21.7 sh, 18.2, 12.1, 10.2
	CH ₃ CN	17.7, 12.4, 10.1
	DMF	17.7, 12.6, 9.4
[LNi ₂ (py) ₄](ClO ₄) ₂	solid	21.5 sh, 18.2, 12.5, 10.0
	CH ₃ CN	17.7 (30), 12.4 (5), 10.2 (15)
	DMF	17.7, 12.6, 9.4
[LFe ₂ (py) ₄](BF ₄) ₂	solid	19.8, 11.1
	pyridine	30.0 (8000), 2.22 (3100), 19.8 (3100), 11.0 (24)
[LFe ₂ (Melm) ₄](BF ₄) ₂	solid	18.0
	Melm	310.0 (8000), 22.2 (1800) 18.0 (1800)
[LFe ₂ (MeNic) ₄](BF ₄) ₂	solid	20.0
	MeNic	30.0 (8000), 27.0 (2400) 22.2 (2400), 11.3 (17)

^a Solid spectra recorded as nujol mulls

^b Extinction coefficient given in parentheses (M⁻¹ cm⁻¹)

Table VI. Principal Interatomic Distances (Å) and Angles (deg.)
for $[\text{LFe}_2(\text{Im})_4](\text{BF}_4)_2$

Distances Within $[\text{LFe}_2(\text{Im})_4]^{2+}$			
Fe-N(16)	2.218(7)	N(9)-C(10)	1.285(10)
Fe-N(21)	2.218(7)	C(10)-C(11)	1.475(11)
Fe-O'	2.091(4)	C(11)-C(12)	1.410(10)
Fe-O	2.092(5)	C(12)-C(13)	1.392(12)
Fe-N(5)	2.088(6)	C(13)-C(14)	1.386(12)
Fe-N(9)	2.081(6)	C(13)-C(15)	1.519(10)
O' -C(2)	1.311(8)	C(14)-C(3)	1.399(10)
C(2)-C(3)	1.439(10)	N(16)-C(17)	1.317(11)
C(2)-C(11)	1.407(11)	C(17)-N(18)	1.326(12)
C(3)-C(4)	1.462(11)	N(18)-C(19)	1.341(13)
C(4)-N(5)	1.275(9)	C(19)-C(20)	1.347(13)
N(5)-C(6)	1.468(12)	C(20)-N(16)	1.358(11)
C(6)-C(7)	1.463(16)	N(21)-C(22)	1.312(10)
C(6)-C(7'')	1.451(31)	C(22)-N(23)	1.333(12)
C(7)-C(8)	1.513(16)	N(23)-C(24)	1.329(12)
C(7'')-C(8)	1.426(32)	C(24)-C(25)	1.339(14)
C(8)-N(9)	1.475(11)	C(25)-N(21)	1.374(11)
N(5)-Fe-N(16)	86.8(2)	O' -Fe-N(21)	92.6(2)
O-Fe-N(21)	94.9(2)	O' -Fe-N(16)	90.7(2)
O-Fe-N(16)	92.9(2)	O' -Fe-O	83.7(2)

Table VI con't.

Angles Within $[\text{LFe}_2(\text{Im})_4]^{2+}$			
O - Fe-N(5)	87.3(2)	C(2)-C(11)-C(12)	120.6(7)
O - Fe-N(9)	171.2(2)	C(11)-C(12)-C(13)	121.7(8)
O' Fe-N(5)	171.0(2)	C(12)-C(13)-C(14)	117.9(8)
O' Fe-N(9)	87.5(2)	C(12)-C(13)-C(15)	120.3(8)
N(5)-Fe-N(9)	101.5(3)	C(14)-C(13)-C(15)	121.8(8)
Fe-O - Fe'	96.3(2)	C(13)-C(14)-C(3)	122.6(8)
C(2)-O - Fe	131.6(5)	C(20)-N(16)-C(17)	103.4(7)
C(2)-O - Fe	131.5(5)	N(16)-C(17)-N(18)	112.7(8)
O - C(2)-C(3)	121.3(7)	C(17)-N(18)-C(19)	107.0(8)
O - C(2)-C(11)	121.1(7)	N(18)-C(19)-C(20)	106.0(8)
C(3)-C(2)-C(11)	117.7(7)	C(19)-C(20)-N(16)	110.9(8)
C(2)-C(3)-C(14)	119.6(7)	C(25)-N(21)-C(22)	103.4(7)
C(2)-C(3)-C(4)	125.1(7)	N(21)-C(22)-N(23)	112.2(7)
C(4)-C(3)-C(14)	115.4(7)	C(22)-N(23)-C(24)	107.4(8)
C(3)-C(4)-N(5)	127.5(7)	C(24)-C(25)-N(21)	110.4(8)
C(4)-N(5)-Fe	127.1(5)	Fe-N(16)-C(17)	127.5(6)
C(16)-N(5)-Fe	115.4(5)	Fe-N(16)-C(20)	128.7(5)
C(4)-N(5)-C(16)	117.5(7)	Fe-N(21)-C(22)	127.5(3)
N(5)-C(6)-C(7)	119.4(9)	Fe-N(21)-C(25)	128.6(5)
N(5)-C(6)-C(7'')	115.4(14)	N(5)-Fe-N(21)	87.8(2)
C(6)-C(7)-C(8)	119.3(10)	N(9)-Fe-N(21)	89.2(2)
C(6)-C(7'')-C(8)	126. (2)	N(9)-Fe-N(21)	88.4(2)

Table VI con' t.

C(7)-C(8)-N(9)	117.3(8)	N(16)-Fe-N(21)	173.6(2)
C(7'')-C(18)-N(9)	113.1(14)		
C(10)-N(9)-Fe	117.1(5)	C(10)-N(9)-Fe	126.2(5)
C(8)-N(9)-C(10)	116.6(7)	N(9)-C(10)-C(11)	127.5(7)
C(10)-C(11)-C(12)	113.7(7)	C(10)-C(11)-C(2)	125.7(7)

Table VI con' t.

Distances Within the Tetrafluoroborate Anion			
B(1)- F(1)	1. 355(11)	B(1)- F(2)	1. 382(12)
B(2)- F(3)	1. 39(3)	B(2)- F(4)	1. 29(5)
B(2)- F(5)	1. 29(4)	B(2)- F(6)	1. 34(7)

Table VI con't.

Angles Within the Tetrafluoroborate Anion			
F(1)-B(1)-F(1)'	109.5(7)	F(4)'-B(2)-F(6)'	111. (3)
F(1)-B(1)-F(2)	107.5(7)	F(5)-B(2)-F(6)	114. (3)
F(1)-B(1)-F(2)'	110.8(8)	F(5)'-B(2)-F(6)'	114. (3)
F(2)-B(1)-F(2)'	110.8(7)	F(4)-B(2)-F(4)'	135. (3)
F(3)-B(2)-F(4)	112. (2)	F(5)-B(2)-F(5)'	133. (3)
F(3)-B(2)-F(4)'	112. (2)	F(6)-B(2)-F(6)'	161. (4)
F(3)-B(2)-F(5)	113. (2)	F(4)-B(2)-F(5)'	54. (3)
F(3)-B(2)-F(5)'	113. (2)	F(4)'-B(2)-F(5)	54. (3)
F(3)-B(2)-F(6)	99. (3)	F(4)-B(2)-F(6)'	61. (3)
F(3)-B(2)-F(6)'	99. (3)	F(4)'-B(2)-F(6)	61. (3)
F(4)-B(2)-F(5)	106. (3)	F(5)-B(2)-F(6)'	57. (3)
F(4)'-B(2)-F(5)'	106. (3)	F(5)'-B(2)-F(6)	57. (3)
F(4)-B(2)-F(6)	111. (3)		

Table VII. Least-Squares Planes for $[\text{LFe}_2(\text{Im})_4](\text{BF}_4)_2$

Atom	Distance, Å	Atom	Distance, Å
Ligand Plane ^a , Plane 1, $\chi^2 = 4979$			
O	-0.065(5), 0.065(5) ^b	C(8)	0.098(10), -0.098(10)
C(2)	-0.035(8), 0.035(8)	N(9)	0.064(6), -0.064(6)
C(3)	-0.017(7), 0.017(7)	C(10)	0.035(9), -0.035(9)
C(4)	-0.035(8), 0.035(8)	C(11)	-0.009(8), 0.009(8)
N(5)	-0.010(6), 0.010(6)	C(12)	0.061(9), -0.061(9)
C(6)	0.056(10), -0.056(10)	C(13)	0.092(9), -0.092(9)
C(7)	-0.525(14), 0.525(14)	C(14)	0.049(9), -0.049(9)
C(7 ^u)	0.656(31), -0.656(31)		
Imidazole "A" Plane, Plane 2, $\chi^2 = 8.62$			
N(16)	-0.005(7)		
C(17)	0.013(9)		
N(18)	-0.007(8)		
C(19)	0.004(9)		
C(20)	0.004(9)		
Imidazole "B" Plane, Plane 3, $\chi^2 = 2.94$			
N(21)	-0.005(6)		
C(22)	0.007(8)		
N(23)	-0.002(7)		
C(24)	-0.005(10)		
C(25)	0.010(9)		

Table VII con' t

Ligand Plane^c, Plane 4, $\chi^2 = 1652$

O	-0.072(5), 0.072(5) ^b	N(9)	0.046(6), -0.046(6)
C(2)	-0.049(8), 0.049(8)	C(10)	0.026(9), -0.026(9)
C(3)	-0.046(7), 0.046(7)	C(11)	-0.015(8), 0.015(8)
C(4)	-0.074(8), 0.074(8)	C(12)	0.047(9), -0.047(9)
N(5)	-0.045(6), 0.045(6)	C(13)	0.064(9), -0.064(9)
C(6)	0.010(10), -0.010(10)	C(14)	0.013(9), -0.013(9)
C(8)	0.064(10), -0.064(10)	C(15)	0.155(11), -0.155(11)

Table VII con' t.

Atom	Distance, Å	Atom	Distance, Å		
Benzene Ring Plane, Plane 5, $\chi^2 = 1.75$					
C(2)	0.007(8)	C(12)	0.000(9)		
C(3)	-0.003(7)	C(13)	0.004(9)		
C(1)	-0.005(8)	C(14)	-0.002(9)		
Angles between Planes (deg.)					
Plane	Plane	Angle	Plane	Plane	Angle
1	2	85.8	2	4	86.3
1	3	80.7	2	5	85.6
1	4	0.6	3	4	81.3
1	5	2.6	3	5	80.9
2	3	8.7	4	5	2.5

^a The ferrous ions are located = 0.011(1)Å out of this plane.

^b The second column denotes the out-of-plane distance for those atoms related to the listed atom by inversion.

^c The ferrous ions are located = 0.026(1)Å out of this plane.

Table VIII. Non-bonding Contacts^a (Å) for [LFe₂(Im)₄](BF₄)₂

		Translations
Fe-Fe'	3.117(2)	1/2-x, 1/2-y, 1-z
O-O'	2.790(6)	1/2-x, 1/2-y, 1-z
F(1)-C(17)	3.207(11)	-1/2+x, 1/2-y, -1/2+z
F(2)-N(18)	3.118(9)	-1/2+x, 1/2-y, -1/2+z
F(2)-N(18)	2.970(10)	-1/2+x, 1/2-y, -1/2+z
F(3)-N(23)	3.017(8)	x, y, -1+z
F(3)-C(22)	3.309(7)	x, y, -1+z
F(5)-C(18)	3.485(46)	x, y, -1+z
F(5)-C(22)	3.358(41)	x, y, -1+z
F(5)-C(10)	3.364(42)	x, y, -1+z
F(6)-C(14)	3.460(65)	-x, y, -1/2-z
F(4)-C(22)	3.341(40)	-x, y, 1/2-z
F(6)-C(7)	3.437(39)	-x, -y, -z
F(6)-C(7')	3.034(54)	-x, -y, -z
F(2)-C(15)	3.454(12)	-x, 1-y, -z
F(4)-C(7)	3.428(41)	x, -y, -1/2+z
F(4)-C(7')	3.485(51)	x, -y, -1/2+z
F(5)-C(7')	3.306(52)	x, -y, -1/2+z
F(2)-N(23)	3.016(10)	x, 1-y, -1/2+z
F(2)-C(24)	3.480(12)	x, 1-y, -1/2+z
F(2)-C(19)	3.213(11)	-1/2+x, 1/2+y, z
F(5)-C(6)	3.398(36)	x, -y, -1/2+z

^aOnly contacts less than 3.5 Å are listed.

Table IX. Experimental and Calculated Magnetic Susceptibility Data for
 $\text{LNi}_2(\text{py})_4(\text{BF}_4)_2^a$

T, °K	$\chi_M \times 10^2$, cgsu		$\mu_{\text{eff}}/\text{Ni}$, μ_B	
	obsd	calcd	obsd	calcd
285.	0.7001	0.6909	2.83	2.81
245.	0.7876	0.7782	2.77	2.76
204.	0.8901	0.8889	2.69	2.69
163.	0.997	1.030	2.55	2.59
143.	1.114	1.113	2.52	2.52
123.	1.247	1.203	2.47	2.43
113.	1.289	1.249	2.41	2.37
103.	1.313	1.293	2.32	2.31
94.2	1.326	1.330	2.23	2.24
86.1	1.357	1.360	2.16	2.16
76.9	1.364	1.387	2.05	2.07
67.0	1.346	1.401	1.90	1.94
61.6	1.322	1.400	1.80	1.85
55.9	1.299	1.386	1.70	1.76
50.2	1.282	1.360	1.60	1.65
44.1	1.262	1.313	1.49	1.52
38.2	1.192	1.242	1.35	1.38
31.5	1.102	1.113	1.18	1.18
28.4	1.020	1.027	1.08	1.08
24.7	0.8933	0.8928	0.94	0.94
22.6	0.8088	0.7991	0.85	0.85

Table IX con^t

20.3	0.7089	0.6814	0.76	0.74
17.7	0.5686	0.5338	0.63	0.61
14.9	0.4074	0.3731	0.49	0.47
11.1	0.2572	0.2088	0.34	0.30
8.80	0.2107	0.1740	0.27	0.25
7.60	0.1945	0.1792	0.24	0.23
6.50	0.1983	0.1993	0.23	0.23
6.00	0.2129	0.2117	0.23	0.23
5.60	0.2213	0.2267	0.22	0.22
5.10	0.2307	0.2450	0.22	0.22
4.70	0.2371	0.2670	0.21	0.22
4.20	0.2667	0.2940	0.21	0.22

^aThe diamagnetic correction used is $-516. \times 10^{-6}$, cgsu.

Table X. Experimental and Calculated Magnetic Susceptibility Data
for $\text{LCO}_2(\text{py})_4(\text{BF}_4)_2^{\text{a}}$

T, °K	$\chi_M \times 10^1$ cgsu		$\mu_{\text{eff}}/\text{Co}, \mu_B$	
	obsd	calcd	obsd	calcd
285.	0.1812	0.1817	4.55	4.55
245.	0.2108	0.2101	4.54	4.53
204.	0.2437	0.2491	4.45	4.50
183.	0.2665	0.2744	4.42	4.48
163.	0.2943	0.3055	4.38	4.46
143.	0.3326	0.3437	4.35	4.43
123.	0.3951	0.3926	4.40	4.39
103.	0.4538	0.4556	4.32	4.33
94.2	0.4733	0.4896	4.22	4.29
86.1	0.5031	0.5263	4.16	4.26
76.9	0.5363	0.5749	4.06	4.20
67.0	0.5687	0.6372	3.90	4.13
55.9	0.6258	0.7228	3.74	4.02
50.2	0.6696	0.7744	3.67	3.94
44.1	0.7223	0.8359	3.57	3.84
38.2	0.7799	0.9009	3.45	3.71
35.0	0.8195	0.9377	3.39	3.62
31.5	0.8775	0.9780	3.32	3.51
28.4	0.9262	1.012	3.24	3.39

Table X con't

24.7	0.9741	1.049	3.10	3.22
22.6	1.005	1.065	3.01	3.10
20.3	1.035	1.077	2.90	2.96
17.7	1.066	1.082	2.75	2.77
14.9	1.066	1.072	2.52	2.53
11.1	1.025	1.021	2.13	2.13
8.80	0.9407	0.9577	1.82	1.83
7.60	0.8319	0.9088	1.59	1.67
6.50	0.6826	0.8389	1.33	1.48
6.30	0.6648	0.8212	1.29	1.43
6.00	0.6262	0.8018	1.23	1.39
5.80	0.6002	0.7805	1.18	1.35
5.60	0.5681	0.7572	1.13	1.30
5.30	0.5442	0.7314	1.08	1.25
5.10	0.5009	0.7031	1.01	1.20
4.90	0.4561	0.6717	0.94	1.15
4.20	0.2826	0.5571	0.69	0.97

^aThe diamagnetic correction used is $-512. \times 10^{-6}$ cgsu.

Table XI. Experimental and Calculated Magnetic Susceptibility Data
for $\text{LFe}_2(\text{py})_4(\text{BF}_4)_2^{\text{a}}$

T°K	$\chi_{\text{M}} \times 10^2$, cgsu		$\mu_{\text{eff}}/\text{Fe}$, μ_{B}	
	obsd	calcd	obsd	calcd
286.	1.944	2.048	4.71	4.83
275.	2.018	2.107	4.17	4.82
255.	2.181	2.244	4.71	4.78
234.	2.333	2.399	4.68	4.74
214.	2.498	2.576	4.62	4.69
183.	2.811	2.891	4.54	4.60
163.	3.111	3.141	4.50	4.52
143.	3.465	3.427	4.45	4.42
123.	3.967	3.756	4.41	4.29
103.	4.317	4.119	4.21	4.11
86.1	4.637	4.451	3.99	3.91
76.9	4.926	4.635	3.89	3.77
67.0	4.894	4.823	3.62	3.59
55.9	5.085	5.009	3.37	3.35
44.1	5.162	5.154	3.02	3.01
38.2	5.026	5.204	2.77	2.82
31.5	4.826	5.247	2.47	2.57
22.6	4.471	5.303	2.01	2.19
20.3	4.43	5.321	1.90	2.08

Table XI con't

17.7	4.64	5.343	1.78	1.94
14.9	4.529	5.370	1.64	1.79
13.0	4.683	5.384	1.56	1.67
11.1	4.907	5.385	1.47	1.55
8.80	5.278	5.346	1.36	1.37
7.60	5.288	5.313	1.27	1.27
6.50	5.338	5.310	1.18	1.17
6.30	5.333	5.322	1.16	1.15
6.00	5.463	5.342	1.15	1.13
5.80	5.511	5.371	1.13	1.12
5.60	5.583	5.411	1.12	1.10
5.30	5.611	5.466	1.09	1.08
4.20	5.944	6.093	1.00	1.01

^aThe diamagnetic correction used is $-500. \times 10^{-6}$ cgsu.

Table XII. Experimental and Calculated Magnetic Susceptibility
Data for $\text{LFe}_2(\text{MeIm})_4(\text{BF}_4)_2^a$

T, °K	$\chi_M \times 10^2$, cgsu		$\mu_{\text{eff}}/\text{Fe}$, μ_B	
	obsd.	calcd.	obsd.	calcd.
286.	2.252	2.418	5.07	5.25
275.	2.323	2.499	5.06	5.24
255.	2.531	2.677	5.08	5.20
234.	2.737	2.882	5.06	5.20
214.	2.976	3.119	5.05	5.17
183.	3.287	3.558	4.91	5.11
163.	3.751	3.923	4.94	5.05
143.	4.360	4.359	4.99	4.99
123.	4.974	4.900	4.94	4.90
103.	5.583	5.551	4.79	4.78
86.1	6.225	6.231	4.63	4.63
76.9	6.866	6.663	4.59	4.53
67.0	7.188	7.171	4.39	4.38
55.9	8.011	7.777	4.23	4.17
44.1	8.825	8.399	3.95	3.85
38.2	9.096	8.652	3.73	3.63
31.5	9.222	8.834	3.41	3.33
22.6	8.341	8.783	2.75	2.82
20.3	7.915	8.694	2.53	2.66
17.7	7.312	8.546	2.27	2.46

Table XII con't

14.9	6.383	8.311	1.95	2.23
13.0	5.932	8.087	1.76	2.05
11.1	5.449	7.779	1.55	1.86
8.80	5.066	7.205	1.34	1.59
7.60	4.752	6.765	1.21	1.44
6.50	4.450	6.131	1.07	1.26
6.00	4.455	5.795	1.04	1.18
5.80	4.445	5.604	1.02	1.14
5.60	4.389	5.394	0.99	1.10
4.10	4.342	4.915	0.94	1.00
4.90	4.310	4.643	0.92	0.95
4.20	4.204	3.680	0.84	0.79

^a The diamagnetic correction used is $-506. \times 10^{-6}$ cgsu

Table XIII. Experimental and Calculated Magnetic Susceptibility
Data for $\text{LFe}_2(\text{Me-isn})_4(\text{BF}_4)_2^a$

T, °K	$\chi_M \times 10^2$, cgsu		$\mu^{\text{eff}}/\text{Fe}$, μ_B	
	obsd.	calcd.	obsd.	calcd.
285.	1.773	1.862	4.50	4.61
275.	1.889	1.920	4.56	4.60
255.	2.042	2.048	4.56	4.57
234.	2.229	2.194	4.57	4.53
214.	2.385	2.361	4.52	4.49
183.	2.747	2.661	4.49	4.41
163.	3.027	2.903	4.44	4.35
143.	3.410	3.182	4.41	4.26
123.	3.813	3.510	4.32	4.15
103.	4.140	3.884	4.13	4.00
86.1	4.353	4.238	3.87	3.82
76.9	4.573	4.443	3.75	3.70
67.0	4.553	4.663	3.49	3.53
55.9	4.718	4.893	3.25	3.31
44.1	4.761	5.094	2.90	3.00
38.2	4.709	5.171	2.68	2.81
31.5	4.619	5.244	2.41	2.57
22.6	4.383	5.343	1.99	2.20
20.3	4.406	5.377	1.89	2.09
17.7	4.460	5.423	1.78	1.96

Table XIII con't

14.9	4.582	5.486	1.65	1.81
13.0	4.798	5.537	1.58	1.70
11.1	5.049	5.593	1.50	1.57
8.80	5.525	5.653	1.39	1.41
7.60	5.583	5.677	1.31	1.32
6.50	5.665	5.722	1.21	1.22
6.30	5.782	5.739	1.20	1.20
6.00	5.898	5.763	1.19	1.18
5.80	5.988	5.793	1.18	1.16
5.60	6.015	5.833	1.16	1.14
5.30	6.072	5.884	1.14	1.12
4.20	6.237	6.457	1.02	1.04

^a The diamagnetic correction used is $-668. \times 10^{-6}$ cgsu

Table XIV. Experimental and Calculated Magnetic Susceptibility
Data for $\text{LCo}_2\text{Cl}_2 \cdot 2\text{CH}_3\text{OH}^a$

T, °K	$\chi_M \times 10^2$, cgsu		$\mu_{\text{eff}}/\text{Co}$, μ_B	
	obsd.	calcd.	obsd.	calcd.
286.	1.761	1.663	4.48	4.36
245.	2.009	1.914	4.43	4.33
224.	2.217	2.070	4.46	4.31
204.	2.309	2.253	4.34	4.28
183.	2.524	2.471	4.30	4.25
163.	2.756	2.733	4.24	4.22
143.	3.084	3.051	4.19	4.17
122.	3.626	3.448	4.21	4.11
103.	4.060	3.941	4.09	4.03
94.2	4.160	4.198	3.96	3.98
86.1	4.449	4.468	3.91	3.92
81.5	4.567	4.635	3.86	3.89
76.9	4.696	4.812	3.80	3.85
71.5	4.812	5.033	3.71	3.79
67.0	4.902	5.229	3.62	3.74
61.61	5.022	5.476	3.52	3.67
55.9	5.304	5.750	3.44	3.59
50.2	5.528	6.031	3.33	3.48
44.1	5.761	6.329	3.19	3.34
38.2	6.036	6.591	3.04	3.17

Table XIV con't

31.5	6.367	6.809	2.83	2.93
28.4	6.514	6.859	2.72	2.79
24.7	6.583	6.856	2.55	2.60
22.6	6.595	68.16	2.44	2.48
21.4	6.631	6.780	2.38	2.41
20.3	6.523	6.733	2.30	2.34
19.0	6.485	6.665	2.22	2.25
17.7	6.422	6.580	2.13	2.16
16.3	6.269	6.466	2.02	2.05
14.9	6.063	6.323	1.90	1.94
13.0	5.867	6.071	1.75	1.78
11.1	5.583	5.715	1.57	1.59
8.80	5.162	5.030	1.35	1.33
6.50	4.554	3.753	1.09	0.99
6.00	4.426	3.383	1.03	0.90
5.60	4.417	2.968	0.99	0.81
5.10	4.413	2.512	0.95	0.72
4.70	4.496	2.027	0.91	0.61
4.20	4.596	1.531	0.88	0.51

^a The diamagnetic correction used is $-328. \times 10^{-6}$ cgsu

Table XV. Experimental and Calculated Magnetic Susceptibility

Data for $[\text{LFe}_2(\text{Im})_4](\text{BF}_4)_2^{\text{a}}$

T, °K	$X_M \times 10^1$, cgsu		$\mu_{\text{eff}}/\text{Fe}; \mu_B$	
	Obsd	Calcd	Obsd	Calcd
245.	0.2773	0.2789	5.21	5.22
204.	0.3357	0.3325	5.23	5.20
183.	0.3756	0.3678	5.25	5.19
163.	0.4155	0.4115	5.20	5.17
143.	0.4690	0.4659	5.17	5.17
123.	0.5368	0.5369	5.13	5.13
103.	0.6232	0.6307	5.06	5.09
94.2	0.6643	0.6826	5.00	5.07
86.6	0.7139	0.7360	4.97	5.05
81.8	0.7512	0.7747	4.95	5.03
76.9	0.7873	0.8175	4.92	5.01
71.5	0.8379	0.8710	4.89	4.99
67.0	0.8881	0.9212	4.88	4.96
61.6	0.9471	0.9893	4.83	4.94
55.9	1.026	1.073	4.79	4.90
53.6	1.048	1.111	4.74	4.88
47.3	1.149	1.228	4.66	4.82
44.2	1.196	1.293	4.60	4.78
41.2	1.254	1.364	4.55	4.74

Table XV continued

T, °K	$X_M \times 10^1$, cgsu		$\mu_{\text{eff}}/\text{Fe}; \mu_B$	
	Obsd	Calcd	Obsd	Calcd
37.4	1.337	1.466	4.47	4.68
33.5	1.440	1.583	4.39	4.61
28.9	1.590	1.744	4.29	4.49
23.0	1.821	1.994	4.09	4.28
18.4	2.037	2.207	3.88	4.03
13.1	2.340	2.446	3.50	3.58
11.0	2.492	2.508	3.30	3.31
8.6	2.615	2.526	3.00	2.95
6.0	2.610	2.452	2.51	2.43
5.7	2.537	2.434	2.41	2.36
5.4	2.526	2.413	2.33	2.28
4.2	2.100	2.302	1.88	1.97

^aThe diamagnetic correction used is -0.000415.

Table XVI. Magnetic Exchange Parameters

Compound Type ^a	J, cm ⁻¹				
	Mn ₂ ⁺	Fe ₂ ⁺	Co ₂ ⁺	Ni ₂ ⁺	Cu ₂ ⁺
LM ₂ Cl ₂ · nH ₂ O ^b (five-coordinate)	+0.20	-4.2	-6.0	-27	-294
[LM ₂ (py) ₄](BF ₄) ₂		-7.5	-4.1	-23	.
[LM ₂ (MeNic) ₄](BF ₄) ₂		-6.8			
[LM ₂ (MeIm) ₄](BF ₄) ₂		-4.5			
[LM ₂ (Im) ₄](BF ₄) ₂		-1.5			

^a L is the binucleating ligand formed from the condensation of 2 moles of 2, 6-diformyl-4-methylphenol with 2 moles of 1, 3-diaminopropane.

^b All of these data, except the J-value for the Co-Cl case, are from ref. 6. The J-value for LCo₂Cl₂ · 2CH₃OH was determined in this study.

Appendix I.

Magnetic Data,

Cu(II)Mn(II)LC1_2 , Cu(II)Fe(II)LC1_2 ,

Cu(II)Co(II)LC1_2 , Cu(II)Ni(II)LC1_2 .

Table I. Experimental and Calculated Magnetic Susceptibility Data
for $\text{LCuMnCl}_2 \cdot \text{H}_2\text{O}^a$.

T, °K	$\chi_M \times 10^1$, cgsu		$\mu_{\text{eff}}/\text{Metal}$, μ_B	
	Obsd	Calcd	Obsd	Calcd
285.5	0.1487	0.1584	4.12	4.25
244.6	0.1740	0.1811	4.13	4.21
203.7	0.2040	0.2114	4.08	4.15
183.3	0.2233	0.2307	4.05	4.11
162.8	0.2469	0.2538	4.01	4.06
142.6	0.2760	0.2817	3.97	4.01
122.5	0.3136	0.3167	3.92	3.94
102.8	0.3621	0.3617	3.86	3.85
94.0	0.3853	0.3868	3.81	3.81
86.0	0.4062	0.4137	3.74	3.77
76.9	0.4412	0.4507	3.68	3.72
67.0	0.5026	0.5020	3.67	3.67
55.9	0.5865	0.5820	3.62	3.61
44.6	0.7303	0.7081	3.61	3.55
39.5	0.8153	0.7891	3.59	3.53
31.3	1.019	0.9790	3.57	3.50
22.3	1.401	1.343	3.53	3.46
19.9	1.563	1.489	3.51	3.44
17.3	1.739	1.688	3.47	3.42
14.3	2.112	2.009	2.47	3.38
11.6	2.485	2.399	3.40	3.34
11.1	2.549	2.487	3.37	3.33
10.7	2.649	2.581	3.36	3.32
10.2	2.745	2.673	3.35	3.31
9.8	2.851	2.772	3.34	3.29
9.3	2.964	2.878	3.33	3.28

Table I continued

T, °K	$\chi_M \times 10^1$, cgsu		$\mu_{\text{eff}}/\text{Metal}, \mu_B$	
	Obsd	Calcd	Obsd	Calcd
8.9	3.078	2.993	3.31	3.26
8.5	3.208	3.117	3.29	3.25
8.0	3.370	3.251	3.29	3.23
7.6	3.478	3.399	3.24	3.21
7.1	3.644	3.557	3.22	3.18
6.7	3.810	3.730	3.19	3.16
6.3	3.954	3.919	3.14	3.13
6.1	4.075	4.005	3.14	3.11
5.8	4.037	4.110	3.07	3.09
5.6	4.267	4.251	3.08	3.07
5.5	4.179	4.303	3.02	3.07
5.1	4.405	4.479	3.01	3.03
4.8	4.561	4.660	2.97	3.00
4.2	4.955	5.066	2.88	2.92

^aThe diamagnetic correction used was -0.000298.

Table II. Experimental and Calculated Magnetic Susceptibility Data
for $\text{LCuFeCl}_2 \cdot 2\text{N}_2\text{O}^a$.

T, °K	$\chi_M \times 10^1$, cgsu		$\mu_{\text{eff}}/\text{Metal}, \mu_B$	
	Obsd	Calcd	Obsd	Calcd
285.5	0.0799	0.0840	3.02	3.10
244.6	0.0909	0.0935	2.98	3.02
203.7	0.1072	0.1061	2.95	2.94
183.3	0.1163	0.1145	2.92	2.90
162.8	0.1294	0.1251	2.90	2.85
142.6	0.1438	0.1388	2.86	2.81
122.5	0.1637	0.1577	2.83	2.78
102.8	0.1958	0.1843	2.84	2.75
94.0	0.2053	0.2001	2.78	2.74
86.0	0.2234	0.2176	2.77	2.73
76.9	0.2385	0.2421	2.71	2.73
67.0	0.2670	0.2764	2.67	2.72
55.9	0.3245	0.3292	2.69	2.71
39.5	0.4714	0.4591	2.73	2.69
31.3	0.5889	0.5727	2.71	2.68
22.3	0.8118	0.7845	2.69	2.64
19.9	0.8927	0.8688	2.66	2.63
17.3	1.007	0.9825	2.64	2.61
14.3	1.188	1.164	2.60	2.58
11.6	1.371	1.383	2.52	2.53
10.7	1.460	1.483	2.49	2.51
9.8	1.558	1.589	2.47	2.49
9.3	1.614	1.646	2.45	2.48
8.9	1.669	1.708	2.44	2.47
8.5	1.734	1.775	2.42	2.45
8.0	1.811	1.846	2.41	2.43

Table II continued

T, °K	$\chi_M \times 10^1$, cgsu		$\mu_{\text{eff}}/\text{Metal}, \mu_B$	
	Obsd	Calcd	Obsd	Calcd
7.6	1.878	1.925	2.38	2.41
7.1	1.969	2.007	2.37	2.39
6.7	2.054	2.096	2.34	2.37
6.3	2.145	2.192	2.31	2.34
6.1	2.221	2.236	2.32	2.33
5.8	2.166	2.288	2.25	2.31
5.6	2.328	2.357	2.27	2.29
5.5	2.311	2.383	2.25	2.28
5.1	2.388	2.467	2.21	2.25
4.8	2.485	2.552	2.19	2.22
4.5	2.574	2.640	2.16	2.18
4.2	2.665	2.734	2.11	2.14

^aThe diamagnetic correction used was -0.000298.

Table III. Experimental and Calculated Magnetic Susceptibility Data
for $\text{LCuCoCl}_2 \cdot \text{H}_2\text{O}^{\text{a}}$.

T, °K	$\chi_{\text{M}} \times 10^2, \text{ cgsu}$			$\mu_{\text{eff}}/\text{Metal}, \mu_{\text{B}}$		
	Obsd	Calcd ^d	Calcd ^c	Obsd	Calcd ^b	Calcd ^c
285.5	0.7354	0.7904	0.7317	2.90	3.00	2.89
275.3	0.7570	0.8043	0.7481	2.89	2.97	2.87
265.0	0.7747	0.8187	0.7653	2.87	2.94	2.85
254.8	0.7960	0.8339	0.7835	2.85	2.91	2.83
244.6	0.8212	0.8499	0.8027	2.83	2.88	2.80
234.4	0.8441	0.8668	0.8230	2.81	2.85	2.78
224.1	0.8831	0.8849	0.8448	2.81	2.82	2.75
213.9	0.9045	0.9043	0.8681	2.78	2.78	2.72
203.7	0.9213	0.9255	0.8934	2.74	2.75	2.69
193.5	0.9561	0.9488	0.9208	2.72	2.71	2.67
183.3	0.9893	0.9747	0.9510	2.69	2.67	2.64
173.0	1.021	1.004	0.9846	2.66	2.63	2.61
162.8	1.066	1.037	1.022	2.63	2.60	2.58
152.7	1.130	1.075	1.065	2.63	2.56	2.55
142.6	1.192	1.119	1.113	2.61	2.53	2.52
132.6	1.269	1.171	1.117	2.59	2.49	2.49
122.5	1.351	1.232	1.239	2.57	2.46	2.46
112.6	1.404	1.304	1.319	2.51	2.42	2.44
102.8	1.509	1.390	1.415	2.49	2.39	2.41
94.2	1.581	1.479	1.518	2.44	2.36	2.39

Table III continued

T, °K	$\chi_M \times 10^2, \text{ cgsu}$			$\mu_{\text{eff}}/\text{Metal}, \mu_B$		
	Obsd	Calcd ^d	Calcd ^c	Obsd	Calcd ^b	Calcd ^c
86.1	1.697	1.579	1.635	2.42	2.33	2.37
76.9	1.836	1.712	1.796	2.38	2.29	2.35
67.0	1.962	1.888	2.014	2.29	2.25	2.32
55.9	2.204	2.136	2.328	2.22	2.18	2.28
44.4	2.544	2.471	2.753	2.13	2.09	2.21
31.4	3.172	2.991	3.342	1.99	1.94	2.05
21.7	3.604	3.517	3.746	1.77	1.75	1.80
19.3	3.705	3.665	3.814	1.69	1.68	1.71
16.2	3.817	3.860	3.875	1.57	1.58	1.58
13.2	3.843	4.036	3.905	1.42	1.46	1.43
12.1	3.920	4.091	3.909	1.38	1.41	1.37
11.0	3.995	4.133	3.912	1.33	1.35	1.31
9.7	4.010	4.162	3.914	1.25	1.27	1.23
9.3	4.041	4.163	3.914	1.23	1.24	1.21
8.3	4.027	4.146	3.941	1.16	1.17	1.14
7.9	4.019	4.129	3.914	1.13	1.14	1.11
7.0	3.942	4.057	3.914	1.05	1.07	1.05
6.8	3.954	4.034	3.914	1.04	1.05	1.03
6.6	3.960	4.008	3.914	1.02	1.03	1.02
4.2	3.773	3.278	3.914	0.80	0.74	0.81

Table III continued

^aThe diamagnetic correction used is -0.000296.

^bFrom fitting to the equation derived from the spin Hamiltonian including zero field effects.

^cFrom fitting to the equation derived from the real Hamiltonian including zero field and spin orbit effects.

Table IV. Experimental and Calculated Magnetic Susceptibility Data
for $\text{LCuNiCl}_2 \cdot 2\text{H}_2\text{O}^a$.

T, °K	$\chi_M \times 10^2$, cgsu		$\mu_{\text{eff}}/\text{Metal}$, μ_B	
	Obsd	Calcd	Obsd	Calcd
285.5	0.3108	0.3396	1.88	1.96
275.3	0.3166	0.3446	1.87	1.94
265.0	0.3271	0.3495	1.86	1.92
254.8	0.3370	0.3544	1.85	1.90
244.6	0.3410	0.3593	1.83	1.87
234.4	0.3474	0.3641	1.80	1.85
224.1	0.3510	0.3688	1.77	1.82
213.9	0.3562	0.3735	1.75	1.79
203.7	0.3615	0.3782	1.72	1.75
193.5	0.3679	0.3829	1.69	1.72
183.3	0.3745	0.3877	1.66	1.69
173.0	0.3879	0.3927	1.64	1.65
162.8	0.3934	0.3983	1.60	1.61
152.7	0.4044	0.4046	1.57	1.57
142.6	0.4174	0.4123	1.54	1.53
132.6	0.4375	0.4221	1.52	1.49
122.5	0.4565	0.4351	1.49	1.46
112.6	0.4744	0.4524	1.46	1.43
102.8	0.5440	0.4758	1.49	1.40
94.2	0.5541	0.5036	1.44	1.38
86.1	0.5894	0.5381	1.42	1.36
76.9	0.6817	0.5904	1.45	1.35
67.0	0.7366	0.6683	1.40	1.34
55.9	0.8593	0.7948	1.39	1.33
44.1	1.093	1.005	1.39	1.33
31.5	1.498	1.407	1.37	1.33
24.7	1.922	1.794	1.38	1.33

Table IV continued

T, °K	$\chi_M \times 10^2$, cgsu		$\mu_{\text{eff}}/\text{Metal}, \mu_B$	
	Obsd	Calcd	Obsd	Calcd
22.6	2.090	1.960	1.37	1.33
20.3	2.342	2.182	1.38	1.33
17.7	2.703	2.503	1.38	1.33
14.9	3.187	2.973	1.38	1.33
13.0	3.632	3.408	1.37	1.33
11.1	4.223	3.991	1.37	1.33
9.9	4.649	4.457	1.36	1.33
8.8	5.201	5.035	1.35	1.33
7.6	5.750	5.791	1.33	1.33
6.5	6.652	6.816	1.31	1.33
6.0	7.247	7.335	1.32	1.33
5.8	7.464	7.625	1.32	1.33
5.6	7.873	7.940	1.33	1.33
5.3	8.109	8.281	1.32	1.33
5.1	8.565	8.653	1.32	1.33
4.8	8.997	9.154	1.32	1.33
4.7	9.797	9.507	1.35	1.33
4.2	10.44	10.55	1.32	1.33

^aThe diamagnetic correction used was -0.000309.

PROPOSITIONS- Clifford L. Spiro

Abstract.

Proposition 1. A method for electrochemically determining microscopic phenomena is proposed. These include coulombic forces, metal-metal overlaps, and off-diagonal coupling elements.

Proposition 2. A method for degrading, solubilizing, and better characterizing coal is proposed. Enzymes secreted from or contained within biologically active materials will be utilized.

Proposition 3. A study on macromolecular species containing redox active prosthetic groups is proposed.

Proposition 4. A new general synthesis of ruthenium, osmium, and platinum macrocyclic complexes is proposed.

Proposition 5. A study on the effects of variations in d-orbital energetics on magnetic exchange coupling is proposed.

PROPOSITION 1

A method for electrochemically determining microscopic phenomena is proposed. These include coulombic forces, metal-metal overlaps, and off-diagonal coupling elements.

A number of industrial and biological processes take advantage of several transition metal centers, acting in concert to accomplish important chemical and redox transformations. Some examples include oxygen activation,¹ nitrogen fixation,² water-gas shift reactions,³ carbon-carbon bond formation,⁴ water splitting,⁵ and multi-electron charge transfers.⁶ It is evident that the properties of multimetal systems are more than the simple sum of their parts. For these reasons, numerous studies of metal-metal interactions have been initiated in recent years. 7-15

One of the most sensitive properties of multimetal complexes is the reduction potential of each metal center, and in particular, how one metal influences the reduction potential of another. These relative potentials represent a complex composite of entropic, coulombic, magnetic, solvent, electronic-delocalization, metal-metal mixing and overlap effects. Previous attempts to quantify these factors have relied on estimation by spectroscopic¹⁶ or dielectric¹⁷ models, or by holding one parameter constant and systematically varying others.⁷ While each of these methods has proven fruitful, a far from complete picture exists. My contribution to this field will be to address the following questions:

1. What are the effects of charge on reduction potentials?
2. What is the influence of the outer coordination shell?
3. What is the role of intramolecular electron transfer?
4. How are thermal and kinetic barriers related to thermally and optically induced electron transfer?

5. Can we use electrochemical techniques to isolate the quantum mechanical parameters H_{12} and S_{12} , the metal-metal mixing and overlap integrals? Will these be identical to spectroscopically determined values based on Mulliken approximations? (vide infra.)

Specifically, I will prepare and electrochemically characterize a number of ruthenium and mixed ruthenium/rhodium complexes. The choice of these systems is an obvious one since many of these species have already been prepared and characterized, and synthetic methods for new species exist. In addition, I have spent several years working with ruthenium, mixed ruthenium/rhodium, and mixed ruthenium/cobalt complexes, and am familiar with synthesis and characterization of these species.

Though charge effects are the most conspicuous consequences of polynucleation, little systematically has been done to quantitatively elucidate this contribution to reduction potentials. Intuitively, one would expect a $+n$ ion to be more readily reduced than a $+n-1$ ion. For example, Anson¹⁸ has shown that $\text{Ru}(\text{NH}_3)_5\text{Cl}^{+2}$ and $\text{Ru}(\text{NH}_3)_5\text{OH}^{+2}$ reduce at a potential 270 millivolts negative of $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{+3}$ in agreement with intuition. In addition, pentammine pyrazine ruthenium reduces 200 millivolts negative of the protonated pentammine pyrasinium ion. Taube has estimated⁸ that charge effects are negligible (<20 mv) in ligand bridged ruthenium binuclears. The disparity between Anson's results and Taube's indicates the state of confusion in this area. The following complexes should help elucidate the extent of coulombic interactions:

- 217-
1. $(\text{NH}_3)_5\text{Ru}-\text{L}-\text{RuCl}_n(\text{NH}_3)_{5-n}^{+6-n}$ $n = 0, 1, 2, 3, 4, 5$
 2. $(\text{bipy})_2\text{Cl}-\text{Ru}-\text{L}-\text{RuCl}_n(\text{NH}_3)_{5-n}^{+5-n}$
 3. $(\text{NH}_3)_5\text{-Ru-L-Rh}(\text{NH}_3)_5^{+6}$
 4. $\text{cis}-(\text{NH}_3)_5\text{-Ru-L-Rh}(\text{NH}_3)_4\text{Cl}^{+5}$
 5. $\text{trans}-(\text{NH}_3)_5\text{-Ru-L-Rh}(\text{NH}_3)_4\text{Cl}^{+5}$

L is a bifunctional bridging group.

For complexes of type 1 and 2, reduction will most easily occur at the non-halogenated site. By examining this potential as a function of the charge at the remote metal, $\frac{\partial(\ln E)}{\partial q}$ can be determined. If only coulombic effects are important, plots of $\ln E$ vs. q should be linear (Figure 1).

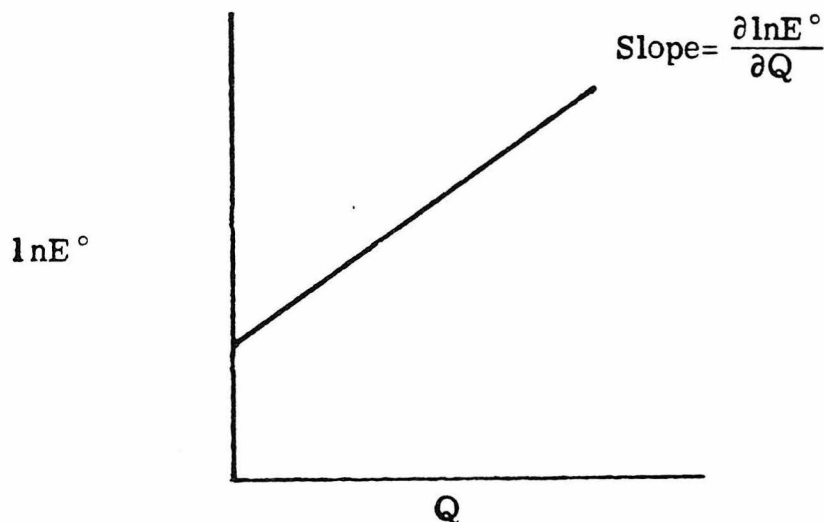
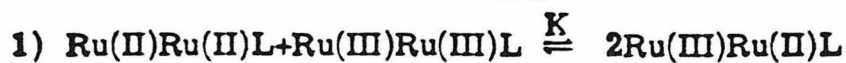


Figure 1. Potential as function of charge.

Deviations due to other affects could be important, but some regions of the curve should be linear. The necessity to examine both the pentammine

and bis-bipy, chloro centers is obvious as a control. It will be interesting to see whether only metal-metal distance is important, or whether coulombic effects are preferentially transmitted by a particular bridge. Some complications may arise in comparing cis versus trans substitution of halide on the remote metal. For this reason complexes 3, 4, and 5 should prove interesting.

The role of the outer sphere coordination shell, the solvent, has been implicated as a major contributor toward the facility of electron transfer reactions. Hush¹⁷ has proposed a dielectric continuum model relating solvent properties to intervalence electron transfer energetics. In some instances, theory agrees quite well with experiment. In others, the approximations break down. Much has been done in the way of solvent dependent spectroscopy of mixed valent systems, and since electrochemical measurements elucidate much about electron transfer in mixed valent systems, it seems logical that solvent dependent electrochemistry will further elucidate outer sphere contributions to intramolecular electron transfer. While comparison of absolute formal potentials in different solvents is usually meaningless, relative peak potentials should prove interesting. Typically what is observed in these systems are two well resolved cyclic voltammetric waves separated by an amount ΔE (Figure 2). ΔE can be related to the relative stability of the mixed valent ion by the following two equations:



$$2) K = e^{-nF\Delta E/RT}$$

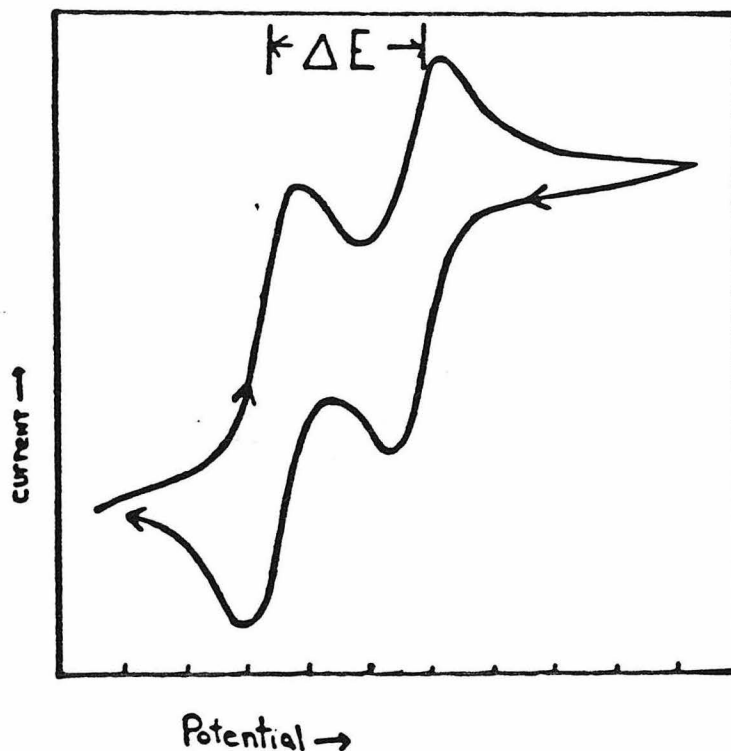
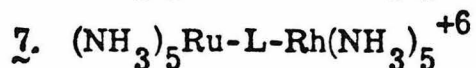
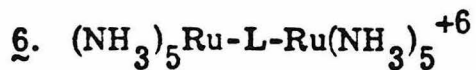


Figure 2. Typical cyclic voltammogram of binuclear complex.

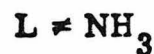
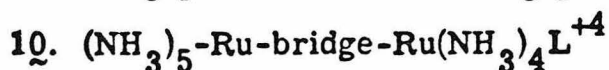
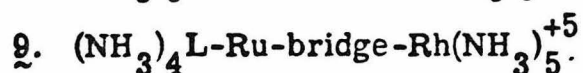
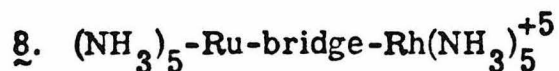
By examining ΔE as a function of solvent, interesting trends should be observed. For example, Hush's model implies that $\ln \Delta E$ should be linearly related to $\frac{1}{n^2} - \frac{1}{D}$, where n is the index of refraction and D is the static dielectric constant. If specific solvent interactions are present, as Meyer suggests in aqueous $(\text{NH}_3)_5\text{Ru-pyrazine-Ru}(\text{NH}_3)_5^{+5}$, normal solvent dependence will break down. In order to eliminate the possibility of specific solvent interactions in the fully oxidized species,

controls can be done through comparing the Ru 2/3 couple in the following two complexes:

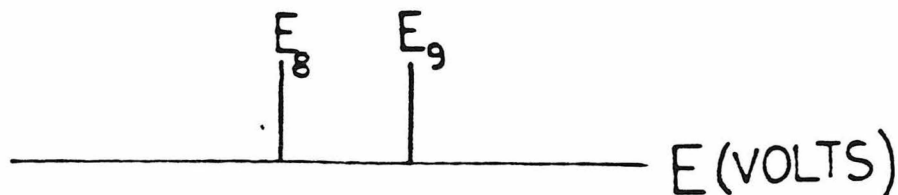


Similar controls can be developed for the fully reduced species. This study should also have implications for intermolecular electron transfer as well.

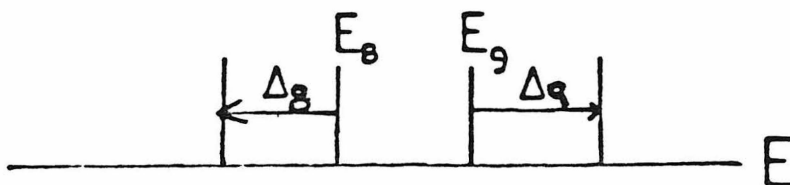
Taube⁸ has applied the Mulliken spectroscopic model¹⁶ for two weakly interacting charge transfer states to estimate the quantum mechanical parameter, H_{12} . This is the off diagonal matrix element in the first order perturbation secular determinant, corresponding to covalent stabilizations in the mixed valent ions. He has assumed overlap integrals, S_{12} , to be negligible. I propose an alternate method for determining both H_{12} and S_{12} quantitatively from electrochemical measurements. Not only are these numbers intrinsically interesting, representing a direct measure of quantum mechanical parameters from electrochemical measurements, but will also provide a basis for comparison to spectroscopically determined values. This will be an important test of the Mulliken model and its associated approximations. Consider the following three complexes:



We observe a single wave corresponding to the ruthenium 3/2 couple in both complexes 8 and 9 schematically pictured below:



The difference, $E_9 - E_8$ can be varied depending on the extent of asymmetry introduced by L. In comparing the reduction potentials of 8 and 9 with the two waves in complex 10, we expect the waves to further split due to the special stability of the mixed valent ion due to electron delocalization:



This delocalization stabilization is unlikely in the mixed ruthenium/rhodium system based on symmetry and energetics. Using the parameters $E_9 - E_8$, Δ_8 , Δ_9 , and a coulombic correction, a perturbation matrix can be solved as follows:

$$\text{DET} \begin{vmatrix} -\Delta_i & H_{1,9} - \Delta_i S_{1,9} \\ H_{9,1} - \Delta_i S_{9,1} & E_9 - E_1 + Q_{corr} - \Delta_i \end{vmatrix} = 0$$

From this determinant and the experimentally measured roots Δ_i , one can calculate $H_{1,9}$ and $S_{1,9}$. These parameters can be determined as a function of bridging group and L, the asymmetry group. From this we can determine the effects of thermodynamic barriers ($E_9 - E_1$) on electron transfer properties. By comparing H_{ij} measured here with the spectroscopically determined H_{ij} , the Mulliken model can be evaluated. In addition, Hush's model for asymmetric systems can be applied to the optical electron transfer process in a similar manner, where extensive testing has not yet been applied.

In summary, though extensive redox and spectroscopic studies of ruthenium ammines and related systems exist, a far from complete understanding has emerged. Specifically, the roles of charge, solvent, thermodynamic barriers, kinetic barriers, and intramolecular electron transfer are not yet quantitatively understood. Their influences on each other will be explored. Theoretical models will be tested. Molecular

parameters will be determined. What is proposed is a series of systematic attempts to quantitatively elucidate each of these factors and their concomitant effects on metal-metal interactions.

References

1. Mason, H.S., Ann. Rev. Biochem., 35, 595 (1965).
2. P. J. Stevens et al, Proc. Natl. Acad. Sci., 76, 2585 (1979).
3. H. Cohen, C. Ungerman, H. Walker, and P. Ford, ACS Pacific Conference, Pasadena, California, October 1979.
4. E. L. Muertterties, Science, 196, 839 (1977).
E. L. Muertterties, T. Rhodin, E. Band, C. Brucker, and
W. R. Pirtzer, Chem. Rev., 79, 91 (1979).
R. L. Pruet and W. E. Walker (Union Carbide), German offen,
2 262 318 (1973); U.S. Appl. 210 538 (1971).
5. K. Mann, R. Bell, and H.B. Gray, Inorg. Chem., 18, 2671 (1979).
6. J. P. Collman, M. Marocco, P. Denisovich, F. C. Anson, and
C. Koval, J. Electroanal. Chem., 101, 117 (1979).
7. R. R. Gagne and C. L. Spiro, J. Am. Chem. Soc., 102, 1443 (1980).
8. J. Sutton, P. Sutton, and H. Taube, Inorg. Chem., 18, 1017 (1979).
9. C. Creutz and H. Taube, J. Am. Chem. Soc., 95, 1086 (1973).
10. D. Brown, J. Donner, J. Hall, S. Wilson, R. Wilson, D. Hodgson,
and W. Hatfield, Inorg. Chem., 18, 2635 (1979).
11. J. Darriet, M. Haddad, E. Duesler, and D. N. Hendrickson,
Inorg. Chem., 18, 2679 (1979).
12. R. E. Dessy and L. A. Bares, Accts. of Chem. Rsrch., 5, 415 (1972).
13. P. Hay, J. Thibeault, and R. Hoffman, J. Am. Chem. Soc., 97,
4884 (1975).
14. N. H. Pilkington and R. Robson, Aust. J. Chem., 23, 2225 (1970).
15. T. J. Meyer, Accts. Chem. Rsrch., 11, 94 (1978).
16. R. S. Mulliken and W. P. Person, "Molecular Complexes", Wiley,
New York, 1969.

17. N. S. Hush, Prog. Inorg. Chem., 8, 391 (1967).
18. H. S. Lim, D. J. Barclay, and F. C. Anson, Inorg. Chem., 11, 1460 (1972).

PROPOSITION 2

A method for degrading, solubilizing, and better characterizing coal is proposed.

Enzymes secreted from or contained within biologically active materials will be utilized.

Proposed Enzymatic Degradation of Coal

There is little doubt that, for economic and political reasons, coal will be playing a growing role as a fuel and chemical feedstock in America's immediate future. For environmental and technological reasons, raw coal is not very suitable as a direct source of energy and chemicals, but must be refined to more basic chemicals. The most valuable chemical species from coal would be low molecular weight hydrocarbons which have been liberated from sulfur and mineral contaminants. While a number of technologies exist for coal gasification¹ to synthesis gas (CO and H₂), sulfur² and ash removal,³ and subsequent recombination of syn-gas to hydrocarbons by Fischer-Tropsch catalysis⁴ or to H₂ and CO₂ by the shift reaction,⁵ all of these methods are expensive and energy intensive. Ambient temperature processes would be highly desired for coal solubilization, decontamination, and conversion.

Since coal represents a complex composite of metamorphosed biological materials, I propose a biodegradative study on coal. Some basic questions include the following:

- 1) Will microorganisms, cell secretions, or free enzymes be able to penetrate the highly polymerized organic sub-structure⁶ of coal (see Figure 1)?
- 2) Which species, under what conditions, might react, functionalize, decontaminate, or otherwise dissolve coal?

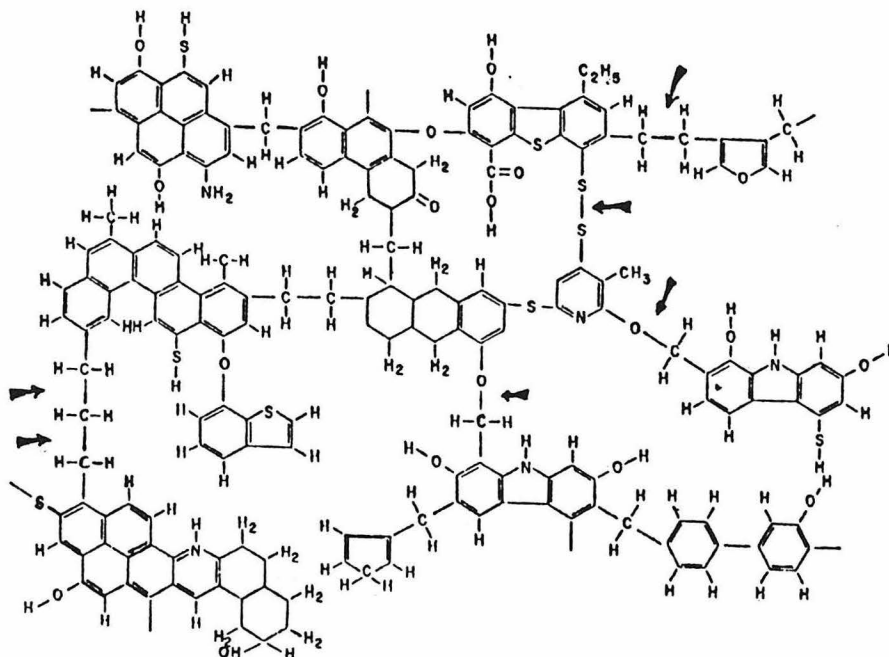


Figure 1. Model for coal.⁶ Arrows indicate potential sites for biodegradation.

Only recently has the first question been addressed with some highly encouraging results. Dugan and Apel⁷ have reacted coal slurries with 5% microbial *thiobacillus ferrooxidans* in the presence of nutrients for several days. They found that the bacteria did indeed release inorganic sulfate from the coal, resulting in the removal of 55% of the sulfur by weight from coal samples initially containing 4% sulfur. In addition, they reported the surprising result that the microbial activity increased with coal particle size, rather than the converse, though no explanation for this was offered. In addition, Kucher et al⁸ grew the yeast fungi, *candida tropicalis* on coal substrates, resulting in a 2 gram yield of low molecular weight product (primarily amino acids)

from 600 ml of an aqueous coal slurry. Indeed, it appears that coal should be reasonably penetrable by high molecular weight enzymes.

The choice of species to study will be in part dictated by the initial success of Kucher et al⁸ with *C. tropicalis*, a yeast whose activity on a wide range of hydrocarbons is well characterized.⁹ It is possible that, rather than a specific enzyme contained in the yeast showing activity, an enzyme secretion is involved in the degradation of coal. A simple series of experiments might yield some highly useful information in this regard. I suggest first growing the yeast on a coal slurry, followed by removal of the yeast and the coal by ultracentrifuge techniques. Reacting the resulting solution with coal after removal of the yeast should reveal whether a secretion is involved in coal degradation, or whether enzymes contained within the microorganism are the active species. If the former is implicated, the secreted enzyme will be characterized, with conditions for coal degradation optimized. In the latter case, if no secretions are located from *C. tropicalis*, the specific enzymes already isolated from the organism can be systematically explored for coal activity. Studies of this fungi¹⁰ revealed the presence of malate dehydrogenase, isocitrate lyase, fumarase, malate synthetase, NADPH cytochrome c reductase, cytochrome c peroxidase, catalase, succinic dehydrogenase, hydroxylase, alcohol dehydrogenase, aldehyde dehydrogenase, cytochrome oxidase, and cytochrome P450. These are likely candidates for initial

studies on coal. In addition to these enzymes, a wide range of sulfur metabolites are known and can be explored. Digestive enzymes such as trypsin can be included in this study. Some promise for success may exist in the functional group specific enzymes such as etherases and esterases.

Even if these prove unsuccessful in completely degrading coal, some byproducts from this study may prove fruitful. For example, suppose an esterase exhibits some activity, though insufficient to completely dissolve coal. The extent of activity can be monitored by quantifying the swelling of coals in solvents as described elsewhere;¹⁰ and may reveal, for example, that for each gram of a particular coal sample, 500 ester linkages exist in the organic substructure. By repeating these types of experiments, not unlike earlier biodegradative studies on protein sequencing, we may be able to piece together a detailed functional mapping of the polymeric nature of coals. This will further our understanding of the chemical structure of coal and may enable others to utilize this information in their studies.

References and Notes

1. N. P. Cochran, Sci. Am., 234, 24 (1976).
2. S-C. Sun and M-J. Wu, Earth Miner Sci., 44, 57 (1975).
3. I. Liebman, J. Corry, and K. Richmond, U. S. Pat. Appl. 446, 972 (1974).
4. C. Masters, Advances in Organometallic Chemistry, 11, 61 (1979), Academic Press, Inc.
5. J. R. Muenger, U. S. Patent 3,825, 501 (1974).
6. J. W. Larsen ed., The Organic Chemistry of Coal, ACS Symposium Series, 71, 29 (1978).
7. P. R. Ougen and W. A. Apel, Pap. Symp. Coal Prop., 3, 10(1977).
8. R. V. Kucher, A. A. Turovskii, O. V. Bazarova, O. N. V. Ozumedzei, M. I. Pavlyvk, and U. L. Khmel'nitskaya, Mikrobiologiya, 46, 583 (1977).
9. A. H. Cook, ed., The Chemistry and Biology of Yeasts, Academic Press, New York (1958).
10. M. Gallo, B. Roche, L. Aubert, and E. Azoulay, Biochemie, 55, 195 (1973).
11. L. R. G. Treloar, The Physics of Rubber Elasticity, Clarendon Press, Oxford (1975).

PROPOSITION 3

A study on macromolecular species
containing redox active prosthetic
groups is proposed.

By interfacing polymers with redox active transition metal prosthetics, a number of significant questions can be addressed. For example:

1. How will the tertiary structure of polymers change as a function of added charge and applied potentials? Will the macromolecule unfold as it gets charged? Will the transitions be smooth or will critical charge/mass ratios be observed?
2. Can polymers be made to crystallize reversibly at an electrode by stepping the voltage on a potentiostat?
3. Can reversible crosslinking be accomplished by using applied potentials to change coordination environments at the metals or induce metal-metal bond formation?
4. Can we use the metals as a probe to determine which polymers absorb on electrodes? In what fashion will they absorb? Will electrons be able to penetrate this membrane-like structure? How will homo- and heterogeneous electron transfer rates be affected by the hydrophobic environment?
5. Will hydrophobic environments about the metals affect their reduction potentials?
6. Can we use metal containing redox polymers as electrocatalysts?
By heterometal copolymerization, can substrate specific guest/host catalyses be accomplished?

I propose to start very simply by examining polyvinyl ferrocene and vinyl-ferrocene/styrene copolymers in various ratios. The polymers

will be characterized in the usual fashion with emphasis on molecular weight distribution, average length and radius of gyration, viscosity and solubility. In addition, their redox properties will be explored by a number of electrochemical techniques. The polymers will be electrolyzed in small increments all the way to the fully oxidized macromolecule, if possible. The electrolysis will be accompanied by detailed determinations of changes in physical properties as a function of added charge. Light scattering and viscometry will be the main techniques involved in these studies. By judicious choice of counter ions in the electrolyte, one may accomplish reversible crystallizations as shown in Figure 1.

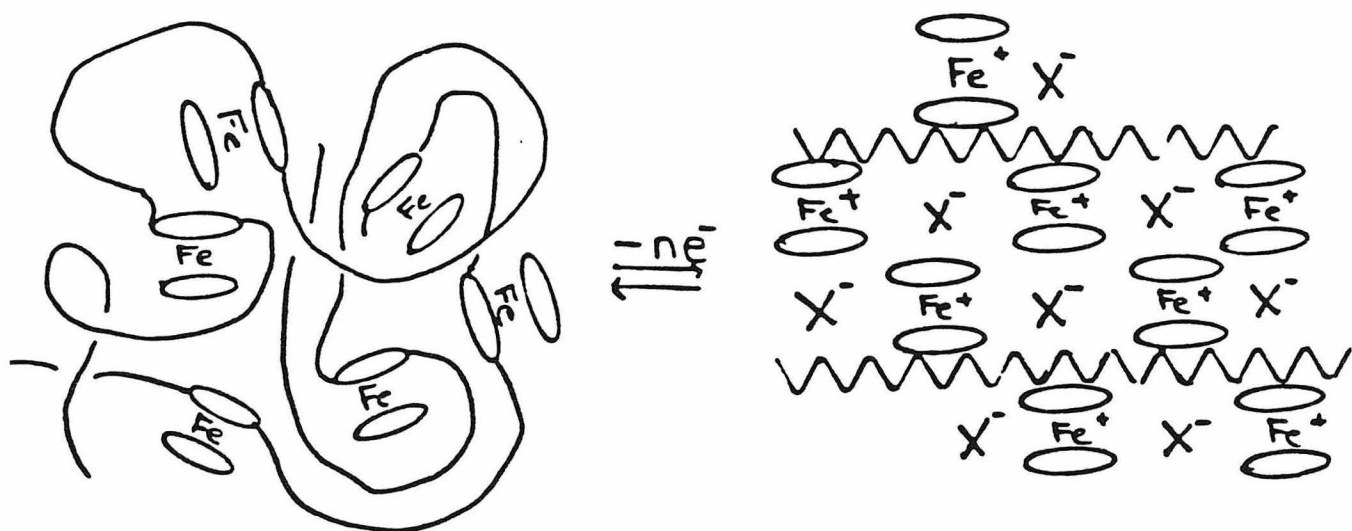


Figure 1. Reversible crystallization of redox polymers.

Will changes be abrupt or smooth? Consider the possibilities as in Figure 2.

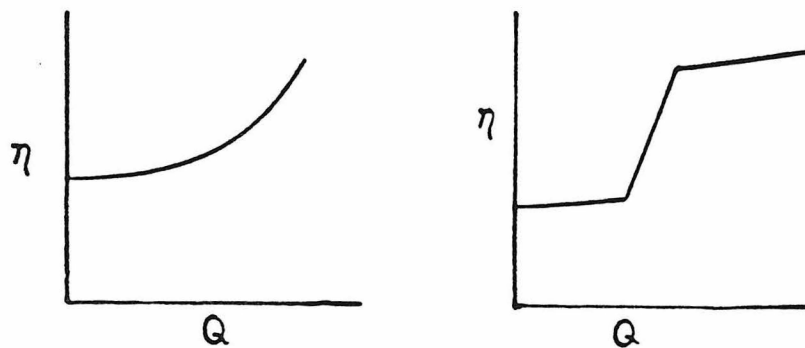


Figure 2. Possibilities for viscosity (η) as a function of added charge (Q).

How will these changes be affected by extent of metalation?

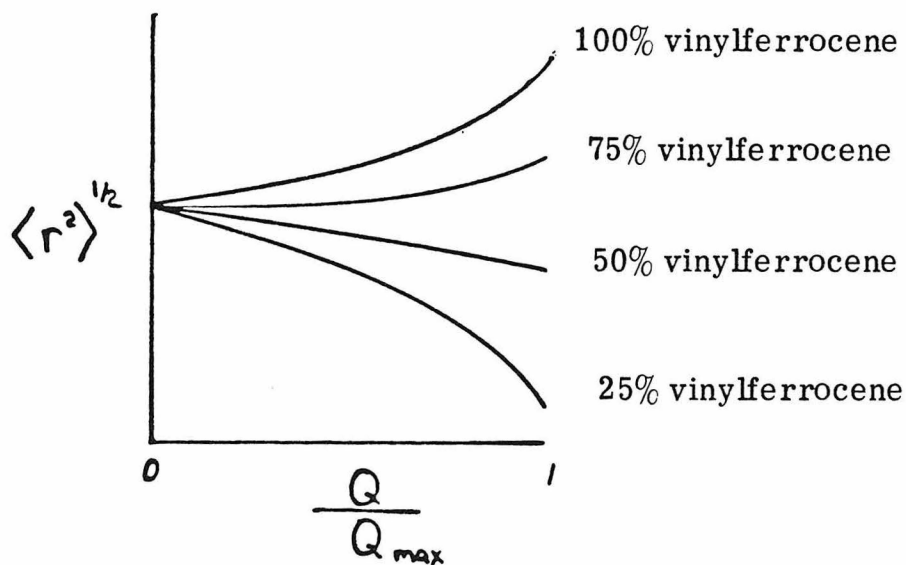


Figure 3. Suggested mean radius of redox polymer as a function of charge and metal content.

Studies of this nature may have bearing on biological processes where a number of metalloenzymes show changes in tertiary structure accompanying charge transfer, possibly implicated in cooperativity.

After these studies are underway, more exotic copolymers can be explored, with emphasis on metals whose coordination environment is reversibly affected by charge transfer. If one oxidation state is labile, with another inert, can we accomplish reversible crosslinking via electrolysis (Figure 4)?

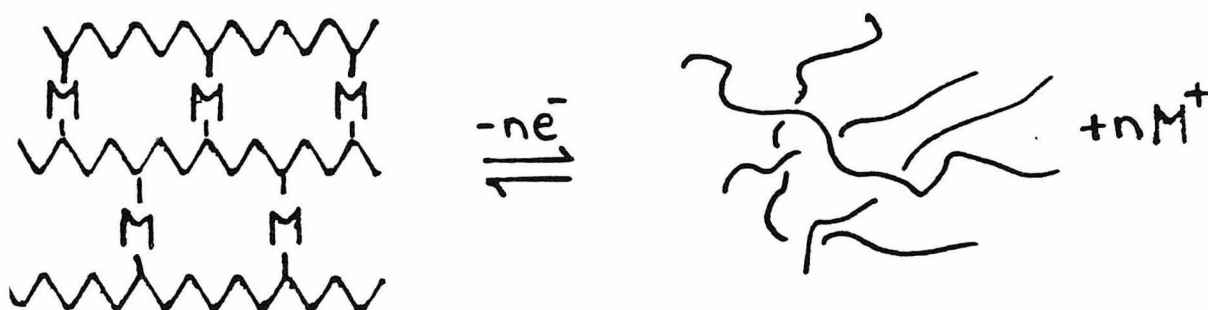


Figure 4. Reversible redox crosslinking, metals labilized in oxidized form.

Can we reductively form metal-metal bonded crosslinkages?

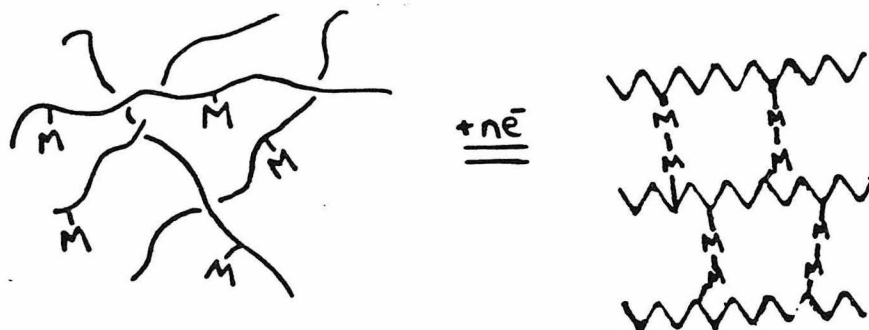


Figure 5. Reversible crosslinking via reductive metal-metal bond formation.

Since polymers often absorb on certain electrodes, ^{1, 2, 3, 4, 5} useful electrocatalysts may be developed, with several layers of catalytic sites (Figure 6).

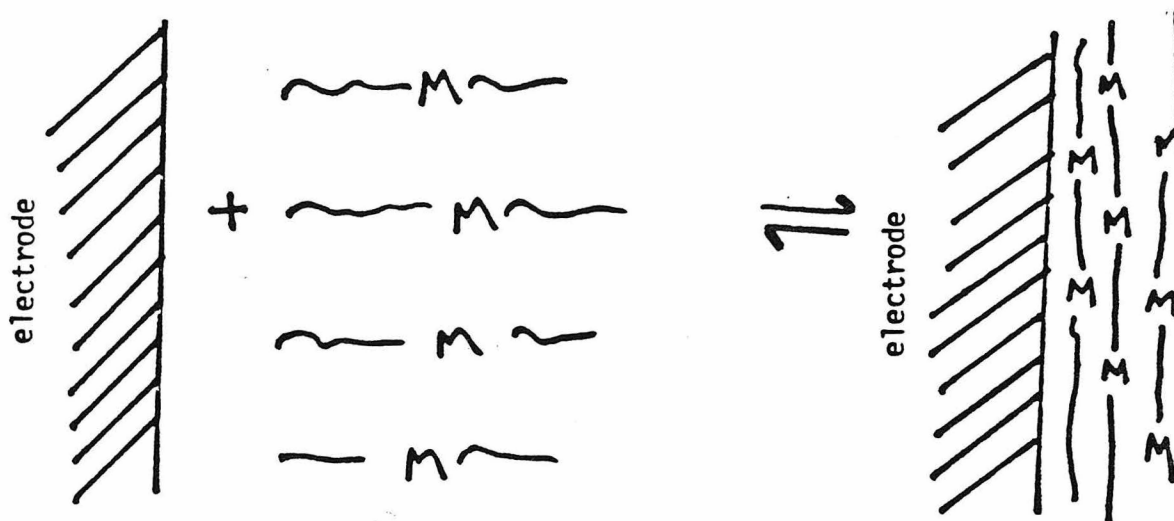


Figure 6. Absorbed redox polymers as potential electrocatalysts.

Useful information with regard to electron transfer rates through membrane-like environments, a subject of much current interest, may be discovered here.

By using even more elaborate copolymers, several types of metals can be put into the same macromolecule. These may be of significant catalytic interest in combining various substrates. One metal may activate one substrate while a second binds another reagent, the two combining on charge transfer. For example, consider the following reaction scheme (Figure 7).

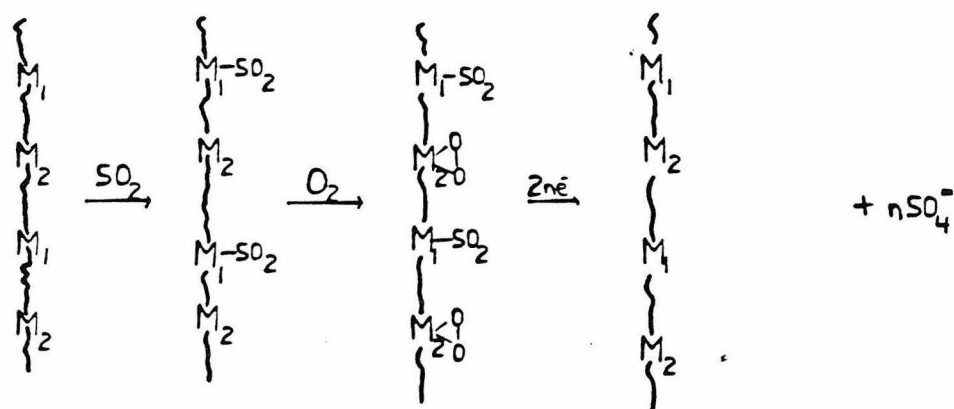


Figure 7. Guest-host redox catalysis.

In summary, I propose to synthesize and characterize a number of redox active polymers containing transition metal sites as electron acceptors. Physical, chemical, and interfacial properties will be explored as a function of added charge and applied potential.

REFERENCES

1. L. L. Miller and M. R. Van de Mark, J. Am. Chem. Soc., 100, 639 (1978).
2. A. Merz and A. J. Bard, J. Am. Chem. Soc., 100, 3222 (1978).
3. M. R. Van de Mark, J. Am. Chem. Soc., 100, 3224 (1978).
4. J. B. Kerr and L. L. Miller, J. Electroanal. Chem., 101, 263 (1979).
5. M. C. Pham, J. E. Dubois, and P. C. Lacaze, J. Electroanal. Chem., 99, 331 (1979).
6. N. Oyama and F. C. Anson, private communication.

PROPOSITION 4.

A new general synthesis of ruthenium, osmium,
and platinum macrocyclic complexes is proposed.

Proposed General Synthesis of Ruthenium, Osmium, and Platinum
Macrocyclic Ligand Complexes

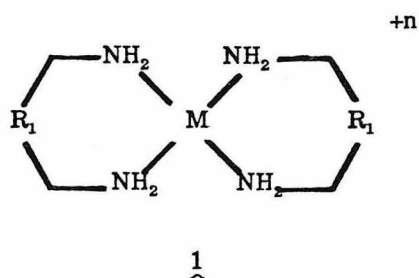
While a primary reason for studying macrocyclic ligand complexes is to circumvent substitution lability problems of the first transition series, the utility of these ligands in affording both structural control and the opportunity for systematic variation in the physical, chemical, and redox properties of coordination complexes is well documented.¹ Complexes of macrocyclic ligands exhibit the potentiality for absorption on surfaces based on the extended planarity of the species,² making them attractive as heterogeneous catalysts. When the metal exhibits appropriate redox properties, these species can be utilized as electrocatalysts.

While macrocyclic ligand complexes of substitution labile transition metals are readily prepared via template syntheses,¹ only rarely have macrocyclic complexes of second and third row transition metals appeared in the literature. These include only the porphyrins,³ phthalocyanines,^{4, 5, 6} and a few scattered saturated tetra-aza species.⁷ The syntheses of these complexes are difficult, requiring the preparation of metal-free ligands, followed by substitution of the metal into the ligand at elevated temperatures and prolonged reaction periods.

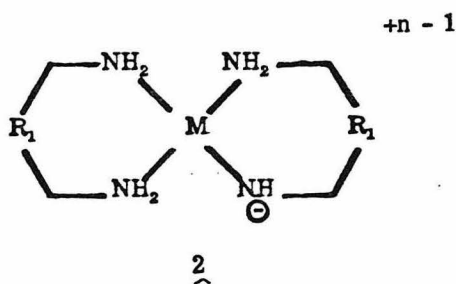
Decomposition, polymerization, and intractable reaction mixtures are often the result.⁷ This is most unfortunate from a catalytic or electrocatalytic standpoint, since it is often these metals which

exhibit the most profound chemical and redox properties. Therefore, I propose a new and general route to mononuclear tetra-aza macrocyclic ligand complexes of ruthenium, osmium, and platinum.

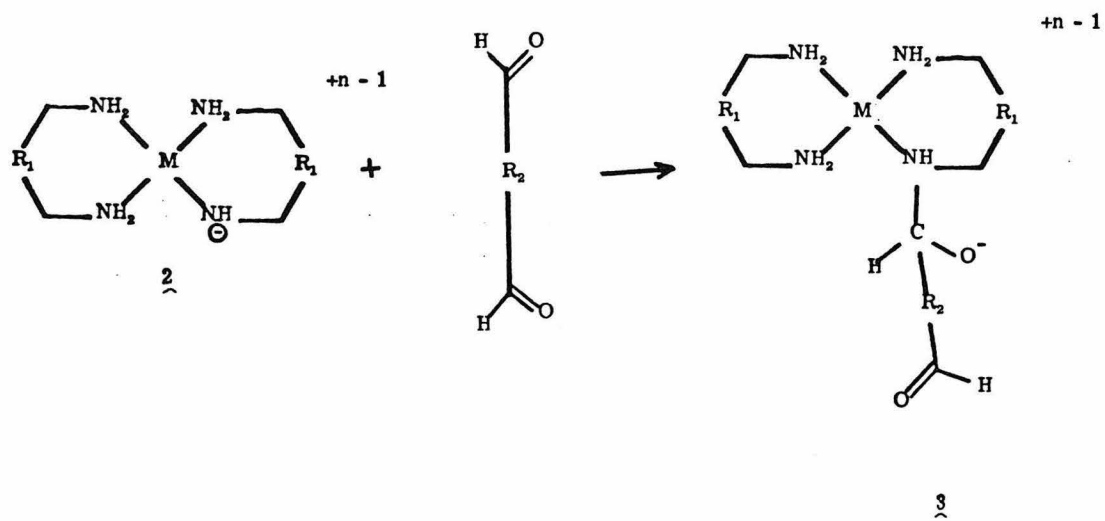
The synthesis I propose should require relatively gentle conditions. It begins with well known trans-bis-diammine complexes, ⁸ 1. Trans-axial anions have been left off the figures to eliminate confusion.



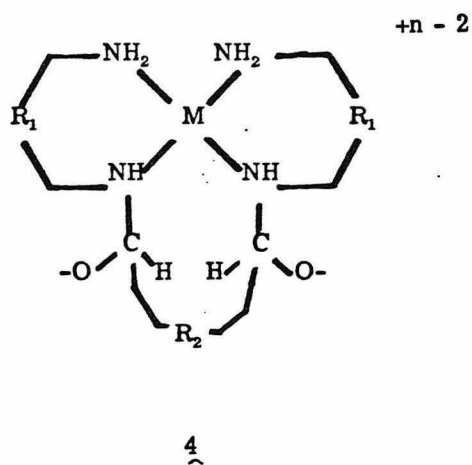
In strong base these will undergo deprotonation to 2.



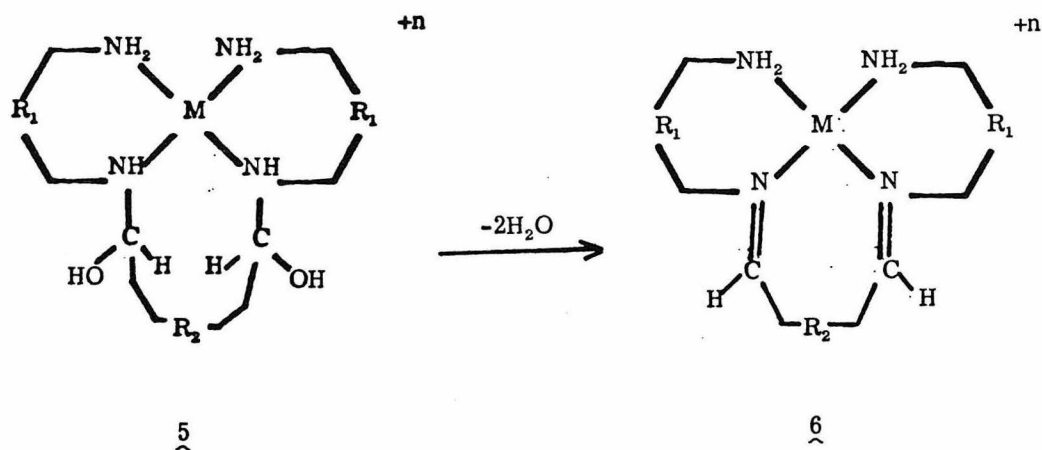
This will condense with a variety of dialdehydes to form 3.



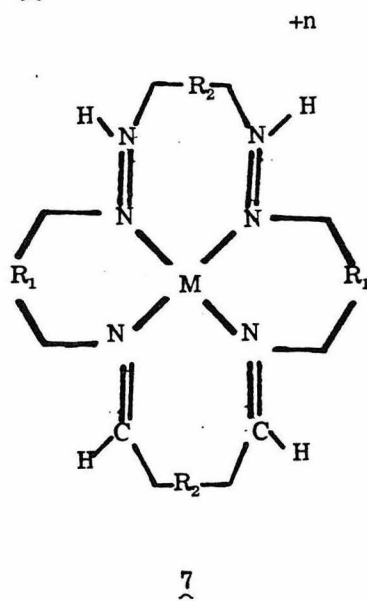
After a second deprotonation and condensation, 4 will be formed.



Protonation, 5, followed by dehydration, will result in the formation of 6.



Repeating the process on the other amine sites will yield the macrocyclic complex, 7.



This should readily be reduced to the desired degree of saturation with a variety of chemical reagents. These syntheses seem reasonable in light of results reported by Sargeson *et al*⁹ on the reactions of $\text{Ru}(\text{NH}_3)_6^{+3}$, $\text{Os}(\text{NH}_3)_6^{+3}$, and $\text{Pt}(\text{NH}_3)_6^{+4}$ with bi-acetyl in 1M NaOH. A condensation to form diimines was observed in all cases, and for the osmium amine, a bis-diimine was formed. By resorting to non-aqueous solvents and stronger bases such as alkoxides, the latter two protons should be easily removed with a second condensation occurring in all cases. While the various R- groups will certainly affect the pK_a of the primary amine protons, it is reasonable to expect that conditions for these condensations could be developed.

The generality and versatility of this synthesis is dependent on the availability of dialdehydes and starting trans-diammine complexes. The former compounds can be purchased from commercial sources, while the latter species should be accessible by substituting various diaminoalkanes for 1,2-ethylenediamine in otherwise well characterized preparative procedures.

The most serious complication with this synthetic scheme may lie in the prevention of aldol condensations,¹⁰ polymerization, and self condensations. Since the aldol reaction usually requires high temperatures, and prolonged reaction periods, and since the amine condensation occurs rapidly under ambient conditions,⁹ this may not be a problem.

Nonetheless, high dilution techniques and chromatography may be necessary.

References and Notes

1. D. H. Busch, K. Farmery, V. Goedkem, V. Katovic, A. C. Melnyk, C. Sperati, and N. Tokel, Adv. Chem. Ser., 100, 44 (1971).
2. J. Zagal, R. K. Sen, and E. Yeager, J. Electroanal. Chem., 83, 207 (1977), for example.
3. C. P. Wong, Doctoral Dissertation, Penn. State University, State College, Pa. (1976).
4. A. N. Shlyapova and B. D. Perezin, Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol., 14, 1810 (1971).
5. O. I. Kafman, N. G. Zemlyanaya, M. I. Al'yanov, and V. R. Larionov, Izv. Vyssh. Uchebn. Zaved., Khim Khim Tekhnol., 18, 1644 (1975).
6. P. E. Fielding and G. A. Mackay, Aust. J. Chem., 28, 1445 (1975).
7. C. K. Poon, Submitted for publication (1979).
D. Walker, Unpublished results.
8. A. L. Coelho and J. M. Malin, Inorg. Chim. Acta., 14, L41(1975).
N. N. Zheligovskaya, N. Kamalov, and V. I. Spitsyn, Izv. Akad. Nauk. SSR, Ser. Khim., 2, 264 (1975).
J. A. Broomhead, L. Kane-Maguire, and D. Wilson, Inorg. Chem., 14, 2575 (1975).

9. I. P. Evans, G. W. Everett, and A. M. Sargeson, J. Am. Chem. Soc., 98, 8041 (1976).
10. A. Stretwieser Jr. and C. H. Heathcock, Introduction to Organic Chemistry (1976), MacMillan Publishing Co., New York, p. 385.

PROPOSITION 5

A study on the effects of variations in d-orbital energetics on magnetic exchange coupling is proposed.

The Role of Ligand Field Splittings in Magnetic Exchange Coupling

When two paramagnetic centers exist in a discrete molecule, exchange coupling between the metals can occur. This exchange interaction has been quantitatively parameterized by the use of the Heisenberg Hamiltonian, $\hat{H} = -J(\hat{S}_1 \cdot \hat{S}_2)$. Here $\hat{S}_1$ and $\hat{S}_2$ are the spin operators associated with each unperturbed center, and J is the exchange coupling parameter. Couplings are on the order of kT , and are usually expressed in wavenumbers (cm^{-1}).

A number of theoretical¹⁻⁵ and experimental⁶⁻¹⁰ efforts have given some insight into the various contributions to J . Typically, systems have been designed which contain two high spin centers that are connected by a bridge. This bridge may be an atom, ion, or polyfunctional heterocycle. Most studies have implicated the bridging moiety as dominant with respect to the quantitative aspects of these superexchange interactions. In particular, both the geometry^{1,6} and the electron density¹ at the bridging group play critical roles in the coupling.

By holding the geometry of the metals and the bridging group constant, it has been demonstrated that other effects may be crucial in stabilizing one spin state over another. These include 1) overlap between the bridging group and the paramagnetic centers, and 2) energetic differences between these entities.¹¹ What I propose is to probe these effects one step further by holding the geometry about the metals,

geometry about the bridging orbitals, and, therefore, the overlap between the orbitals constant. Then, the energy levels of the metal-based orbitals will be manipulated quantitatively. The result should be a better understanding of which factor, the overlap or the energy differences between the bridging orbital and the metals, dominates the exchange interaction.

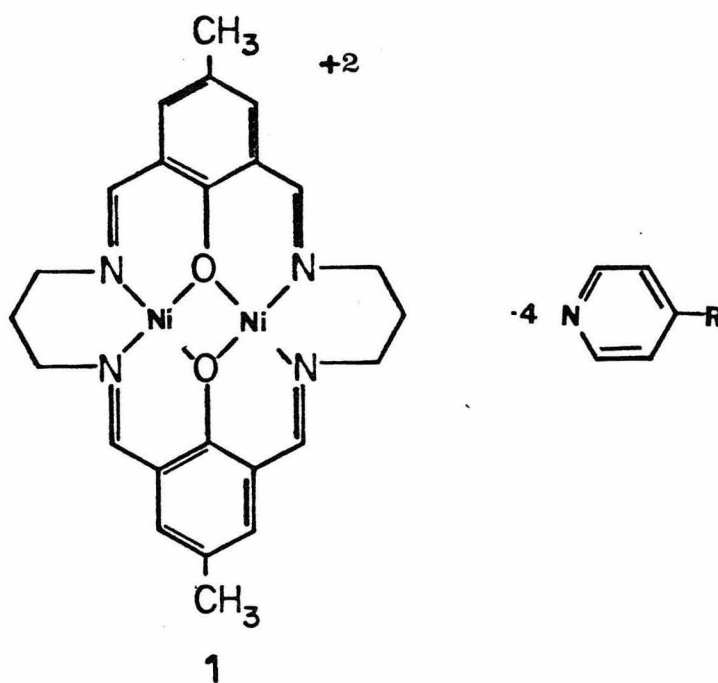


Figure 1.

The system that best lends itself to this study is shown in Figure 1. These high spin Ni(II) species should all be isostructural, with the macrocyclic ligand constraining the metals to lie within the plane at

a Ni-Ni distance of roughly $3.15\text{\AA}$.¹¹⁻¹⁴ The trans-axial pyridines complete the pseudo-octahedral coordination environment about the metal centers. Where L=pyridine, J was found to be -23cm^{-1} , large enough to be sensitive to subtle electronic effects.¹¹ In addition, this species shows four ligand field bands which have been assigned to a pseudo-octahedral ligand field.¹¹ These also should be sensitive to changes in the trans-axial ligands. While substitution in the trans-axial position may affect ligand field parameters, the coordination geometry about the metals should remain constant. Therefore, little variation in metal-bridge overlap is expected. By varying R- in the para position (e.g. R=H-, CH₃-, NO₂-, CH₃O-, Cl, etc.), it will be possible to truly isolate the role of energy differences in magnetic exchange.

Experimentally, I can foresee few problems. The synthesis of these species is limited only by the availability of p-substituted pyridines, and is very straightforward.¹¹ Measurement of the electronic spectra is a simple affair, as is the determination of the magnetic exchange coupling parameter, J, through variable temperature susceptibility studies.

In summary, the preparation, spectral characterization, and parameterization of magnetic exchange coupling for a series of iso-structural high spin dinuclear Ni(II) complexes is proposed. In this way, it will be possible to directly determine the significance of the

energy difference between the metals and the bridging orbitals on the exchange coupling constant. Studies of this nature may shed further light on the relationship between molecular, electronic, and magnetic parameters.

References and Notes

1. P. J. Hay, J. C. Thibeault, and R. C. Hoffmann, J. Am. Chem. Soc., 97, 4884 (1975).
2. R. L. Martin, New Pathways in Inorganic Chemistry, E. A. V. Ebsworth, A. G. Maddock, and A. G. Sharpe, ed., Cambridge University Press, London (1968), Ch. 9.
3. A. E. Hansen and C. J. Ballhausen, Trans. Farad. Soc., 61, 631 (1955).
4. I. G. Dance, Inorg. Chim. Acta, 9, 77 (1974).
5. L. Salem and C. Rouland, Agnew Chem., 84, 86 (1972).
6. K. T. McGregor, N. T. Watkins, D. L. Lewis, R. F. Drake, O. J. Hodgson, and W. E. Hatfield, Inorg. Nucl. Chem. Lett., 9, 423 (1973).
7. D. L. Lewis, W. E. Hatfield, and D. J. Hodgson, Inorg. Chem., 11, 2216 (1972).
8. D. L. Lewis, K. T. McGregor, W. E. Hatfield, and D. J. Hodgson, Inorg. Chem., 13, 1013 (1974).
9. S. L. Lambert and D. N. Hendrickson, Inorg. Chem., 18, 2683 (1979).
10. E. D. Estes, W. E. Hatfield, and D. J. Hodgson, Inorg. Chem., 13, 1054 (1974).
11. C. L. Spiro, S. M. Lambert, T. J. Smith, E. N. Duesler, R. R. Gagné, and D. N. Hendrickson, Manuscript in preparation.