THE CRYSTAL STRUCTURE OF

OCTAMMINE μ-AMIDO μ-PEROXO DICOBALT TETRANITRATE

A Thesis

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ABSTRACT

Octammine μ-amido μ-peroxo dicobalt tetranitrate,

$$\left[(NH_3)_4Co\begin{matrix} O_2 \\ NH_2 \end{matrix}Co(NH_3)_4 \right](NO_3)_4 ,$$

forms green-black plate-like crystals with space group $P2_1/c$ and unit cell dimensions

$$\underline{a} = 8.451,\ \underline{b} = 13.196,\ \underline{c} = 17.304\ \text{Å},\quad \beta = 103.90^\circ$$

There are four molecules per unit cell. The crystal structure was determined and refined using three dimensional Fourier and least-squares techniques.

The coordinating ligands form nearly regular octahedra about the cobalt atoms with Co-N and Co-O distances of 1.96 and 1.87 Å. The five-membered ring formed by the two cobalt atoms and the peroxo and amido bridges is very nearly planar. The Co-Co distance is 3.24 Å, the O-O distance is 1.32 Å, and the Co-N-Co and Co-O-O angles are 115° and 120° respectively. The extensive system of hydrogen bonds in the crystal appears to involve nearly all of the ammine hydrogens and all of the oxygen acceptors with the exception of the oxygen atoms in the peroxo bridge. The present value of the residual R index is 0.053 for all 2078 observed reflections.

INTRODUCTION

Dinuclear cobalt complexes have been known for some time; the major analytical, preparative and constitutional work was done by Alfred Werner at about the turn of the century.[1]

These compounds may be prepared with one, two, or three bridging groups which can be one or more of the following: OH^-, NH_2^-, $O_2^=$, CH_3COO^-, NO_2^-, $SO_4^=$, $RCOO^-$, $C_2O_4^=$. The compounds of particular interest here are those containing a peroxo bridge, as they possess interesting oxidation-reduction behavior and also exist in paramagnetic as well as diamagnetic forms.

The first of such compounds was prepared and isolated as a bright red salt by Fremy in 1852[2]. He completely and correctly analyzed the salt and found it to contain the cation

$$[(NH_3)_5Co\text{-}O_2\text{-}Co(NH_3)_5]^{+4}$$

in which both cobalt atoms are formally in the +III oxidation state. Vortman[3], and later, Werner, prepared a number of green salts and derivatives from this red series, one of which contains the cation

$$[(NH_3)_5Co\text{-}O_2\text{-}Co(NH_3)_5]^{+5}$$

On the basis of chemical information Werner and Mylius concluded that in these green compounds one of the cobalt atoms had to be in the +IV valency state and the other in the +III state.[4] Werner also found this to be true in the analogous μ-amido μ-peroxo dinuclear cobalt complex[5], which could similarly be obtained in red and green forms.

The major consequence of Werner's conclusions regarding these green complexes is that they both possess one unpaired electron and are consequently paramagnetic.

The controversy which has up to now surrounded these

compounds has centered primarily upon where this unpaired electron resides, and thus upon what the configuration of the cation should be. This information whould be quite useful in interpreting the body of data on the general chemical properties and kinetics and redox mechanisms that has accumulated on these compounds. Because of ~~its~~ the greater relative stability of the dibridged μ-amido μ-peroxo complex over the singly bridged peroxo complex, it has been the most intensively studied of these compounds. Detailed knowledge of its structure should therefore be especially valuable.

Electron spin resonance studies by Bernal, Ebsworth and Weil[6] and Ebsworth and Weil[7] have demonstrated that the unpaired electron spends an equal amount of time on each of the two cobalt atoms. This suggests that Werner's scheme cannot be wholly true and that either a resonance effect is present which gives each cobalt a valency between +III and +IV, or that the electron resides primarily upon the peroxo bridge, giving it more the character of a superoxide group.[8]

Vlček proposed on the basis of steric effects and probable bond lengths and angles that the O_2 bridge would be oriented perpendicular to the Co-Co axis, the bridging bonding involving interaction of the oxygen pi electrons with the cobalt d-orbitals.[9]

From their ESR measurements Goodman, Hecht and Weil proposed another alternative wherein the O_2 bridge is rotated approximately forty-five degrees from the Co-Co axis.[10]

Schaefer and Marsh have recently reported the x-ray diffraction structure determination of the cation of decammine

μ-peroxo dicobalt monosulfate tris(bisulfate) in which the peroxo bridge is centered between the cobalt atoms, but is skewed to the Co-Co axis.[11] They further state that the bonding is definitely not of the type proposed by Vlcek, and that the O-O distance is 1.31 Å, close to the value 1.28 Å reported for alkali metal superoxides. Their results suggest that the cation of the μ-amido μ-peroxo dicobalt cation should be planar, which this investigation has indeed shown to be the case.

EXPERIMENTAL

Vortman's Sulfate was prepared by the method given by Werner,[12] and from it samples of octammine μ-amido μ-peroxo dicobalt tetranitrate were extracted with concentrated nitric acid. The samples obtained were washed with a little dilute nitric acid, then with alcohol, and then dried. Crystals of the compound were prepared by allowing a test tube of hot, saturated nitrate solution about 2 F. in nitric acid to cool slowly overnight in a thermos of hot water.

The dark green-black crystals grown in this fashion were generally extremely thin blades which appeared to be hollow. A number of smaller, slightly stockier blades were also formed from which the crystals used in this structure analysis were chosen.

The compound was also crystallized in a second modification from more acidic nitric acid solutions (ca. 8 to 10 F.) than used above. These crystals were obtained in the form of small "stars" consisting of about a dozen needle-like crystals radiating from a central point. Weissenberg photographs of single needles of these crystals mounted about the needle axis indicated that they were all twinned. The crystals were monoclinic with approximate unit cell dimensions: a = 8.0, b = 18.6, c = 12.4 A. The monoclinic angle was not determined, but it is probably quite close to 90°.

The space group of the first modification was determined from the systematic absences observed on Weissenberg photographs:

$h0\ell$ with ℓ odd absent

$0k0$ with k odd absent

This information fixed the space group as $P2_1/c$.

The cell constants were determined by a least-squares fit of comparator measurements of 67 reflections on photographs made using the C.I.T. Precision Weissenberg camera. Wavelengths for Cu $K\alpha_1$ and Cu $K\alpha_2$ radiation of 1.5405 Å and 1.5443 Å were used in this calculation, which gave the following values and standard deviations for the cell constants:

$$\underline{a} = 8.451 \pm 0.001 \text{ Å}$$
$$\underline{b} = 13.196 \pm 0.002 \text{ Å}$$
$$\underline{c} = 17.304 \pm 0.001 \text{ Å}$$
$$\beta = 103.90 \pm 0.03^\circ$$

The calculated unit cell volume and density using these parameters and assuming four formula units of $Co_2(\mu\text{-}NH_2, \mu\text{-}O_2)(NH_3)_8(NO_3)_4$ per unit cell are 1873.1 $Å^3$ and 1.947 ± 0.001 g-cm^{-3}. The density determined by flotation in a carbon tetrachloride-1,2 dibromoethane solution is 1.947 ± 0.001 g-cm^{-3}.

A nearly rectangular prism of the first crystal modification about 0.05 x 0.07 x 0.04 mm was used in the collection of the three dimensional data. A total of 2078 reflections with $2\theta \leq 154^\circ$ were measured with a Datex-automated General Electric XRD-5 diffractometer employing a proportional counter. The intensities were measured using a $\theta - 2\theta$ scan at a scanning speed of 1°/minute. Background was counted for 100 seconds at each end of the scan. The scan range was adjusted to account

for α_1-α_2 splitting.

A moderately strong reflection, 225, was chosen as a "check" reflection. The diffractometer automatically returned to, and recollected background and scan counts for this reflection after each fifteen reflections. This served as a check on long term fluctuations or changes in beam intensity, crystal stability, and crystal orientation. There were no significant deviations in the ckeck reflection measurements from the average of the first five measurements during the collection of the data, which required approximately twelve days of twenty-four hour operation.

Iron radiation, K_α = 1.9373 Å, was used for the data collection instead of the more commonly used copper radiation because of the significantly lower linear absorption coefficient of this compound, 59 cm^{-1}, for iron radiation relative to that for copper radiation, 144 cm^{-1}. The average value of μr calculated for the crystal that was used in the data collection was 0.36.

A single thickness of Du Pont manganese dioxide x-ray filter* was used to filter out the Fe $K\beta$ radiation.

The temperature in the laboratory containing the diffractometer was fairly constant at 27°C. throughout the data collection.

* General Electric Part No. 257.

TREATMENT OF THE DATA

The values for the observed intensities, $I_{obs.}$, were derived from the scaler counts using the following formula:

$$I_{obs.} = \left[S - \frac{B_1 + B_2}{2} \cdot \frac{t}{100} \right]$$

where S is the scan count, B_1 and B_2 are the two background counts, and t is the time in seconds required for the diffractometer to scan the 2θ scan range through the reflection. Negative values of $I_{obs.}$ calculated from this formula were set to zero.

The standard deviation for each reflection was calculated using

$$\sigma^2(I_{obs.}) = S + \frac{B_1 + B_2}{2} \cdot \frac{t}{100} + (0.03\,S)^2$$

where the symbols have the same meanings as defined above. The last term in this equation corrected for the possible "dead time" in the electronics and the counter. Only very strong reflections were affected by this term. The standard deviations calculated in this way were the basis for the weights used in the least-squares refinement.

Lorentz and polarization factors were applied for each reflection. No absorption correction was applied in view of the small size of μr.

DETERMINATION AND REFINEMENT OF THE STRUCTURE

A three dimensional Patterson synthesis was calculated and from it the approximate positional parameters for the cobalt atoms were found.

A three dimensional Fourier synthesis was then computed using the phases calculated on the basis of the two cobalt atoms. All the non-hydrogen atoms in the asymmetric unit were apparent in this synthesis. The R index based only on the cobalt positions was 0.44.

The positional parameters deduced from this Fourier map were used as the starting parameters in the least-squares refinement of the structure. Two cycles of full matrix least-squares calculations reduced the R index to 0.11. Introducing anisotropic temperature factors for the cobalt atoms further reduced the R index to 0.10. At this point difference maps were calculated in the planes perpendicular to each Co-N vector 0.3 Å from the nitrogen atoms in an attempt to determine the locations of the ammine hydrogens. Nearly all of the hydrogen atoms were well resolved, and their positions could be immediately determined. Only in the case of one ammine group was it necessary to use the three-fold symmetry of the group to fix the positions of two of the hydrogen atoms of the group.

Four additional cycles of least squares, in which a cobalt dispersion correction was added and the positional parameters and anisotropic temperature factors for all of the heavy atoms were refined, resulted in an R index of 0.068.

The limited amount of core storage available in the computer made it necessary to switch from full matrix refinement to block matrix refinement in order to refine the increased number of parameters.

The "goodness of fit, " $\frac{\sum w\left(k^2|F_{obs}|^2-|F_{calc}|^2\right)^2}{n-p}$, where w is the weight $\left(=\frac{1}{\sigma^2(I_{obs})}\right)$, k is a scaling factor, n is the number of observed reflections, and p is the number of parameters refined, was, at this stage of refinement, equal to 2.51.

Additional least-squares cycles, in which all but the hydrogen isotropic temperature factors were refined, were made until the full shifts in the parameters of all the "heavy" atoms were less than or equal to their standard deviations. The hydrogen atoms were all assigned isotropic temperature factors with $B = 3.5$. The 020 and $\bar{1}02$ reflections were given zero weight in the last stages of the refinement because they appeared to be suffering from secondary extinction. The resultant R factor was 0.053 and the "goodness of fit" was 1.63.

All calculations were carried out on an IBM 7094 computer using subprograms operating under the CRYRM crystallographic computing system.[13] The quantity minimized in the least-squares calculations was $\sum w\left(F_{obs}^2-F_{calc}^2\right)^2$, w being the weight as defined above. Atomic form factors for cobalt, nitrogen and oxygen were taken from the International Tables for X-Ray Crystallography (1962)[14] and the form factor for hydrogen was that calculated by Stewart, Davidson and Simpson.[15]

A total of nine least-squares refinement cycles were

necessary to reduce the R index to its present value of 0.053. A total of 340 parameters were varied in 89 matrices in the final least-squares cycles; this included three positional and six anisotropic temperature parameters for each of the twenty-nine heavy atoms and three positional parameters for each of the twenty-six hydrogen atoms. The most recent set of parameters for these atoms is listed in Table 1. An electron density projection down the a axis, calculated from these parameters, is given as Figure 1.

The estimated standard deviations in the positions of the cobalt atoms are approximately 0.001 Å, while the esd's for the ammine nitrogens and the bridge oxygens are about 0.004 Å. The estimated standard deviations in the positions of the nitrate group atoms are roughly 0.008 Å, but these appear not to be expecially meaningful because the vibration amplitudes for several of the nitrate oxygens are on the order of 0.3 Å.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

Contrary to the predictions of Vlček[9] and Goodman, Hecht, and Weil,[10] the oxygens of the peroxo bridge are very nearly coplanar with the cobalt atoms, the sum of the angles in the ring formed by the cobalt atoms and the bridges being 539.6°, only 0.4° from the total expected for a planar, five-membered ring. This small distortion is probably due to a combination of angle strain and enhanced possibilities for hydrogen bonding and more favorable crystal packing. The distortion results from the peroxo bridge being very slightly twisted out of the plane of the two cobalts and the amido nitrogen; the oxygen atoms are only 0.045 A from this plane and are located on opposite sides of it. Since these distances are roughly ten times the estimated standard deviations in the oxygen coordinates, the distortion is real and cannot be accounted for by experimental error.

The ring structure of the cation is indicated in Figure 2. Each of the cobalt atoms is bonded to one of the bridging oxygen atoms and to the bridging nitrogen, the remaining four octahedral positions about each cobalt atom being filled by the ammine nitrogens. The Co-N-Co angle is 115° and the distances between the two cobalt atoms and the bridging nitrogen are 1.92 Å and 1.93 Å. The N(amide)-Co-O angles are both 91°, extremely close to the 90° required for perfect octahedral coordination about the cobalt atoms. The Co-O distances and the Co-O-O angles are 1.87 Å and 120° and 121°.

The Co-N(ammine) distances average 1.96 Å and the non-bonded Co-Co distance is 3.24 Å.

The O-O distance is 1.32 Å, exactly that which would be expected for a superoxide ion and close to the value found for the O-O distance in the analogous single bridged peroxo complex.[11]

Pauling (1960) considers the superoxide oxygen-oxygen bond as a combination of a single bond and a three electron bond.[15] This may be interpreted as requiring the electrons in the superoxide ion to have the configuration:

$$\text{(filled levels)}\ (\sigma_g^2)\ (\pi_u)^4\ (\pi_g)^3.$$

The important aspect of this in relation to the peroxo bridged compounds is that two orbitals are involved in the oxygen to oxygen bond, thus making it impossible for the anion to form any type of bridged molecule other than a planar one. Furthermore, interpreting the peroxo bridge in this compound as a superoxo bridge satisfactorily accounts for the observed ESR spectra since the unpaired electron can be expected to be delocalized over the bridge such that it can interact equally with the nuclear spins of both cobalt atoms. Recent ESR measurements by Weil and Kinnaird (1967) on O^{17} labeled octammine μ-amido μ-peroxo dicobalt tetranitrate indicate that this is indeed the case.[16]

The planarity of the ring in this compound, together with the ESR data and particularly the O-O distance of 1.32 Å seems to be conclusive enough proof that the O_2 bridge is actually a superoxo bridge and not a peroxo bridge.

This and analogous compounds would consequently be more properly termed μ-superoxo dicobalt salts to indicate the true nature of their constitution.

The overall symmetry of the cation is C_2, however, because the oxygen atoms are only slightly out of plane with respect to the cobalts, the symmetry is very close to being the maximum possible for the molecule, C_{2v}. Bond distances and angles for the cation are summarized in Table 2.

There are four nitrate groups per asymmetric unit. The average N-O distance for all the nitrates is 1.24 Å, a value slightly higher than expected, but not significantly so in view of the relatively higher standard deviations of the atomic positions compared with those of the cation atoms.

Three of the nitrate groups are planar well within experimental error. The nitrate group containing N(26), however, appears to be significantly non-planar, the nitrogen atom being located nearly 0.1 Å above the plane of the oxygens. The large thermal vibration amplitudes for the atoms of this group , all nearly 0.4 Å and perpendicular to the "plane" of the group, and the possibilities for the formation of several alternative hydrogen bonds seem to suggest that this nitrate group is either partially disordered, or that it is confined in a very wide and shallow potential well which permits it to freely vibrate with such large amplitudes. Attempts to refine a disordered, static model were unsuccessful as the parameters in the least-squares refused to converge. Further attempts will be made to ascertain whether the static or the dynamic model presents the correct

solution to this problem, or whether a solution can be found at all.

Bond distances and angles for the nitrate groups appear in Table 3.

The ions are held together in the crystal by a very extensive network of hydrogen bonds. The lengths of the majority of these bonds stand in relatively good agreement with the average tabulated value of 3.04 ± 0.13 A reported by Pimentel and McClellan[17] for bonds of the type

N---H·····O

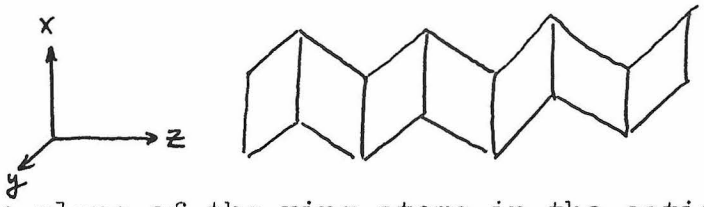
Table 4 lists the most probable hydrogen bonding scheme, while Table 5 lists other N---H····O distances which may be considered as hydrogen bonds, but which appear to be either excessively long or contain angles which would make the interactions at best very weak.

The hydrogen positions were allowed to vary in the least-squares refinement. In general, most of the hydrogen atoms have been located in chemically reasonable positions. Several of them, however, are clearly in error, such as H(52), which is located only 0.66 A from the center of the nitrogen to which it is bonded. For this reason, not too much reliance should be placed on the hydrogen bonding scheme as it is given here as it is still relatively tentative. Figure 3 illustrates the hydrogen bonding according to this scheme in a projection onto the yz plane.

The oxygen atoms in the superoxo bridge appear to be the only oxygen atoms in the crystal that are not involved in

hydrogen bonding. This is understandable in view of the steric problem of arranging the ions so that interaction with the bridge oxygens is possible for ammine donors from other cations, without at the same time creating any direct hydrogen-hydrogen interactions. The cations carry a formal charge of +4 and their coulomb repulsions would be a formidible barrier to such an arrangement.

The hydrogen bond network appears to link the cations together in sheets nearly parallel to the yz plane at about $x = \frac{1}{2}$, and these sheets are linked in stacks by hydrogen bonds to the nitrate groups containing N(18) and N(22). The planes containing these nitrate groups are nearly perpendicular to the yz plane and follow the c glide plane in a zig-zag pattern in the sense of the diagram below.



The plane of the ring atoms in the cation is oriented approximately 45° to the yz plane.

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FOOTNOTES

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TABLE 1.

Positional Parameters

Coordinates in fractions of a unit cell x 10^6

	No.	Atm.	X	Y	Z
COORD	1	CO	656429	259852	097361
COORD	2	CO	949164	185474	244018
COORD	3	O	831195	345219	141934
COORD	4	O	944703	317524	204926
COORD	5	N	746952	152676	169325
COORD	6	N	767872	211444	018399
COORD	7	N	579152	378053	027800
COORD	8	N	467766	176556	049606
COORD	9	N	536880	316210	170617
COORD	10	N	834693	230508	323377
COORD	11	N	964718	048872	290421
COORD	12	N	1153086	226613	318381
COORD	13	N	1074870	143264	168503
COORD	14	N	1099007	078008	-058703
COORD	15	O	1098738	162941	-028643
COORD	16	O	1165986	006516	-017662
COORD	17	O	1030701	065268	-129450
COORD	18	N	468549	076623	303790
COORD	19	O	351849	031514	319044
COORD	20	O	605882	068701	349007
COORD	21	O	447025	131660	243275
COORD	22	N	1125334	124359	509839
COORD	23	O	974766	120878	478617
COORD	24	O	1176667	155730	578359
COORD	25	O	1221107	099135	468422
COORD	26	N	460852	395204	351353
COORD	27	O	473713	455730	405539
COORD	28	O	513656	308634	364616
COORD	29	O	362078	418522	287570
COORD	30	HS	665697	128861	191201
COORD	31	HS	756462	096528	143254
COORD	32	HS	853497	254146	013509
COORD	33	HS	701811	212320	-027610
COORD	34	HS	805855	158879	023531
COORD	35	HS	651551	429339	030480
COORD	36	HS	497261	400992	028962
COORD	37	HS	587847	373421	-013800
COORD	38	HS	449905	126314	077109
COORD	39	HS	480917	140419	010886
COORD	40	HS	377418	201807	047383
COORD	41	HS	594637	380372	199589
COORD	42	HS	508098	274184	201642
COORD	43	HS	445105	336335	148657
COORD	44	HS	853274	292908	333194
COORD	45	HS	733031	215788	321337
COORD	46	HS	876694	206671	373125
COORD	47	HS	1071232	008727	288516
COORD	48	HS	994316	053127	336338
COORD	49	HS	907692	011532	275758
COORD	50	HS	1141284	274168	339117
COORD	51	HS	1206748	170059	354640
COORD	52	HS	1207066	246601	302924
COORD	53	HS	1087865	182669	147225
COORD	54	HS	1188445	121782	196454
COORD	55	HS	1052815	091153	142310

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Anisotropic Temperature Factors x 10^9

	ATM No.	B11	B22	B33	B12	B13	B23
ANISO	1	005931791	002294397	000997996	-000162530	000888849	000089157
ANISO	2	006103196	002428726	001103783	000452548	000657463	-000033326
ANISO	3	007127436	002825141	001515094	-001314464	-000265679	000234209
ANISO	4	008314811	003173479	001506044	-002064399	-000804342	000316310
ANISO	5	006120653	002123785	001216711	-000057423	000498349	000816228
ANISO	6	010642556	004251398	001526820	001654255	002669601	-000226281
ANISO	7	010111064	004640798	002273487	002270026	002139698	002381856
ANISO	8	007887097	003824549	002134450	-000980511	001388128	-000598038
ANISO	9	009434602	002494350	001774749	001283372	002858765	000098382
ANISO	10	008612018	004874104	001384475	000201164	001817532	-000433839
ANISO	11	012130760	002982056	002582923	000991286	000596070	001068941
ANISO	12	007646161	004239013	002272830	000843103	-000098256	-000715152
ANISO	13	008656814	004246867	002082474	-000303529	002309395	-001033363
ANISO	14	012775189	003643589	004101838	-000335503	004963147	000785996
ANISO	15	017175998	002891629	003618441	-001217690	002979114	-001904998
ANISO	16	024362853	005568093	010494250	006445800	004139970	005072321
ANISO	17	047078478	007076821	002757550	-014099898	007012801	-002353802
ANISO	18	011461800	003332912	003366406	000835629	006190655	-000245904
ANISO	19	014712289	005634422	008395482	005160505	014817241	007446429
ANISO	20	013690798	009082558	003480356	002882672	000128302	000508620
ANISO	21	014983624	004750990	003059635	000250702	005981108	002920118
ANISO	22	009836887	003575638	002646985	-000018596	001165108	001615414
ANISO	23	009786961	005013433	002983214	001597082	000797014	000506428
ANISO	24	016087683	007257799	001784187	000334900	-000383322	-000788759
ANISO	25	011805157	008004867	002621597	005141346	005554069	000536021
ANISO	26	023164917	005264849	001471670	002143363	001108051	-000308674
ANISO	27	048349848	006422958	004838568	003496694	-000162270	-001744999
ANISO	28	018439502	005268152	003911561	008808427	-003399531	-001591189
ANISO	29	027065076	008756030	004214995	008235395	002580380	001427677

TABLE 2.

BOND DISTANCES AND ANGLES FOR THE $Co_2(\mu\text{-}O_2\,\mu\text{-}NH_2)(NH_3)_8(NO_3)$ cation

ATOM	ATOM	DISTANCE (Å)
Co1	Co2	3.241
Co1	O3	1.870
Co1	N5	1.918
Co1	N6	1.944
Co1	N7	1.982
Co1	N8	1.949
Co1	N9	1.948
Co2	N10	1.953
Co2	N11	1.965
Co2	N12	1.963
Co2	N13	1.953
Co2	O4	1.866
Co2	N5	1.928

ATOM	ATOM	ATOM	ANGLE
3	1	5	91.38°
3	1	6	91.14
3	1	7	83.62
3	1	8	177.28
3	1	9	89.04
5	1	6	91.66
5	1	7	174.99
5	1	8	91.00
5	1	9	92.71
6	1	7	88.64
6	1	8	90.10
6	1	9	175.61
7	1	8	93.99
7	1	9	87.02
8	1	9	89.54

ATOM	ATOM	ATOM	ANGLE
4	2	5	91.67°
4	2	10	90.03
4	2	11	176.59
4	2	12	85.27
4	2	13	89.46
5	2	10	91.76
5	2	11	91.69
5	2	12	176.89
5	2	13	91.40
10	2	11	89.29
10	2	12	87.71
10	2	13	176.81
11	2	12	91.36
11	2	13	91.03
12	2	13	89.11
4	3	1	121.29
2	4	3	120.37

TABLE 3.

BOND DISTANCES AND ANGLES FOR THE NITRATE GROUPS

ATOM	ATOM	DISTANCE
N 14	O 15	1.236 Å
	O 16	1.233
	O 17	1.233
N 18	O 19	1.234
	O 20	1.238
	O 21	1.251
N 22	O 23	1.258
	O 24	1.232
	O 25	1.248
N 26	O 27	1.216
	O 28	1.228
	O 29	1.252

ATOM	ATOM	ATOM	ANGLE	
O 15	N14	016	119.88°	
O 15	N14	017	119.59	$\sum \Delta s = 359.996°$
O 16	N14	017	120.52	
O 19	N18	020	120.01	
O 19	N18	021	119.75	$\sum \Delta s = 359.988°$
O 20	N18	021	120.23	
O 23	N22	024	120.76	
O 23	N22	025	118.17	$\sum \Delta s = 359.936°$
O 24	N22	025	121.01	
O 27	N26	028	120.37	
O 27	N26	O 29	115.81	$\sum \Delta s = 358.113°$
O 28	N26	O 29	121.93	

TABLE 4

HYDROGEN BONDING SCHEME

X—H····Y

ATOM X	H ATOM	ATOM Y	DIST X-H	DIST H-Y	DIST X-Y
O27	H 39	N8	0.85 Å	2.21 Å	3.05 Å
O27	H 38	N8	0.85	2.34	3.02
O28	H 33	N6	0.86	2.16	3.00
O21	H 42	N9	0.85	2.12	2.92
O23	H 46	N10	0.96	2.14	3.03
O21	H 30	N5	0.92	2.24	3.11
O25	H 51	N12	1.01	2.16	3.03
O23	H 32	N6	0.94	2.11	3.00
O19	H 41	N9	1.04	2.09	2.98
O21	H 54	N13	1.00	2.14	3.10
O24	H 43	N9	0.82	2.30	3.10
O25	H 36	N7	0.76	2.32	2.97
O24	H 40	N8	0.83	2.67	3.43
O17	H 55	N13	0.82	2.17	2.92
O16	H 34	N6	0.76	2.20	2.93

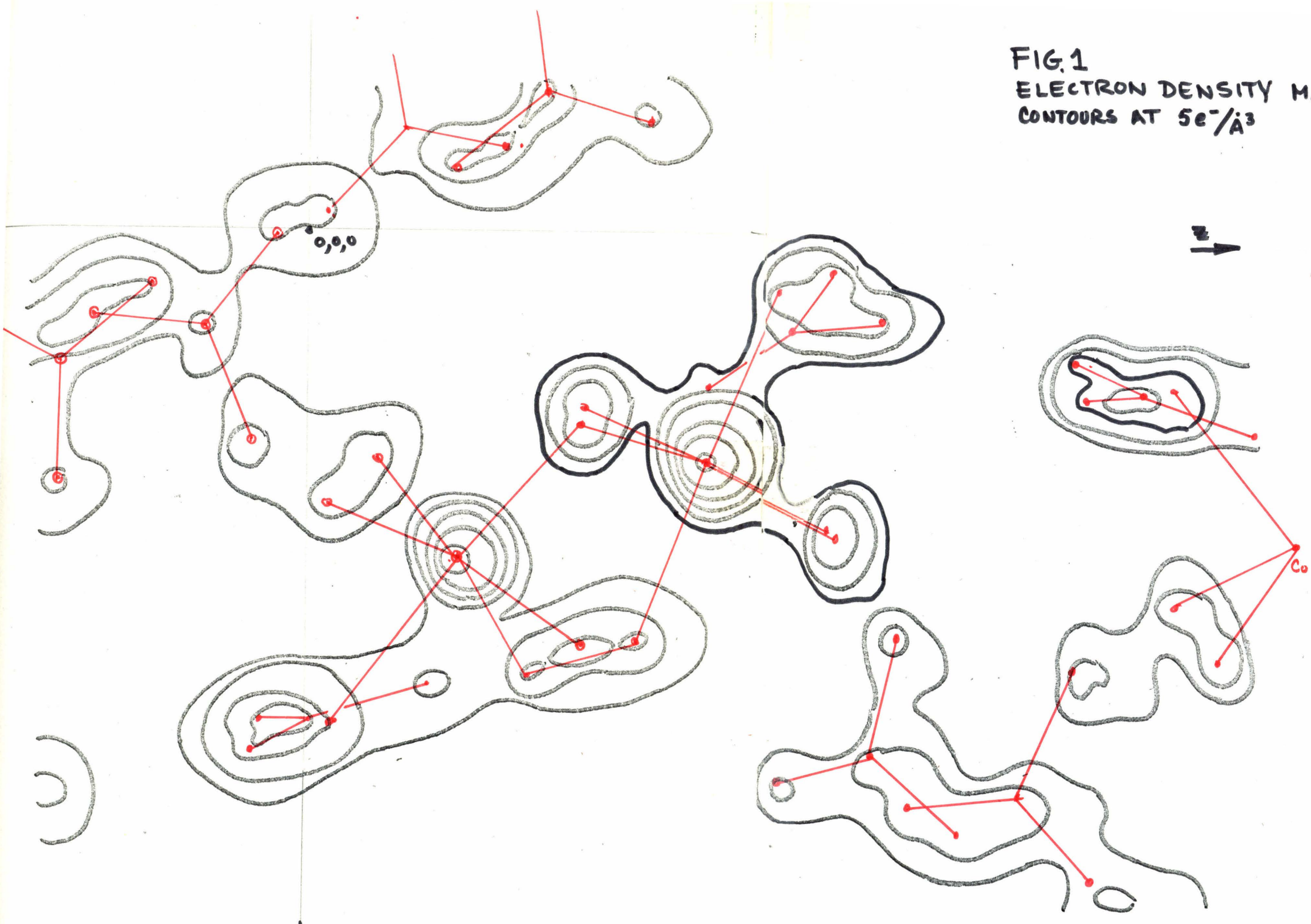
TABLE 5

POSSIBLE HYDROGEN BONDS

X — H . . . . Y

ATOM X	H ATOM	ATOM Y	DIST H-Y	DIST X-Y	ANGLE ∠XHY
O25	H35	N7	2.48 Å	3.36 Å	162°
O27	H31	N5	2.68	3.28	127
O28	H52	N12	2.68	3.15	132
O28	H45	N10	2.48	3.14	133
O20	H45	N10	2.32	2.98	133
O20	H37	N7	2.53	3.23	158
O29	H49	N11	2.59	3.26	165
O17	H44	N10	2.39	3.17	152
O17	H50	N12	2.43	3.14	162
O19	H47	N11	2.32	3.20	141
O19	H51	N12	2.36	3.07	127
O24	H53	N13	2.64	3.29	168
O15	H50	N12	2.54	3.15	142
O19	H54	N13	2.53	?	
O15	H40	N8	2.46	3.09	134
O29	H52	N12	2.66	3.20	145

FIG. 1
ELECTRON DENSITY MAP
CONTOURS AT $5e^-/Å^3$



(0,0)

Z

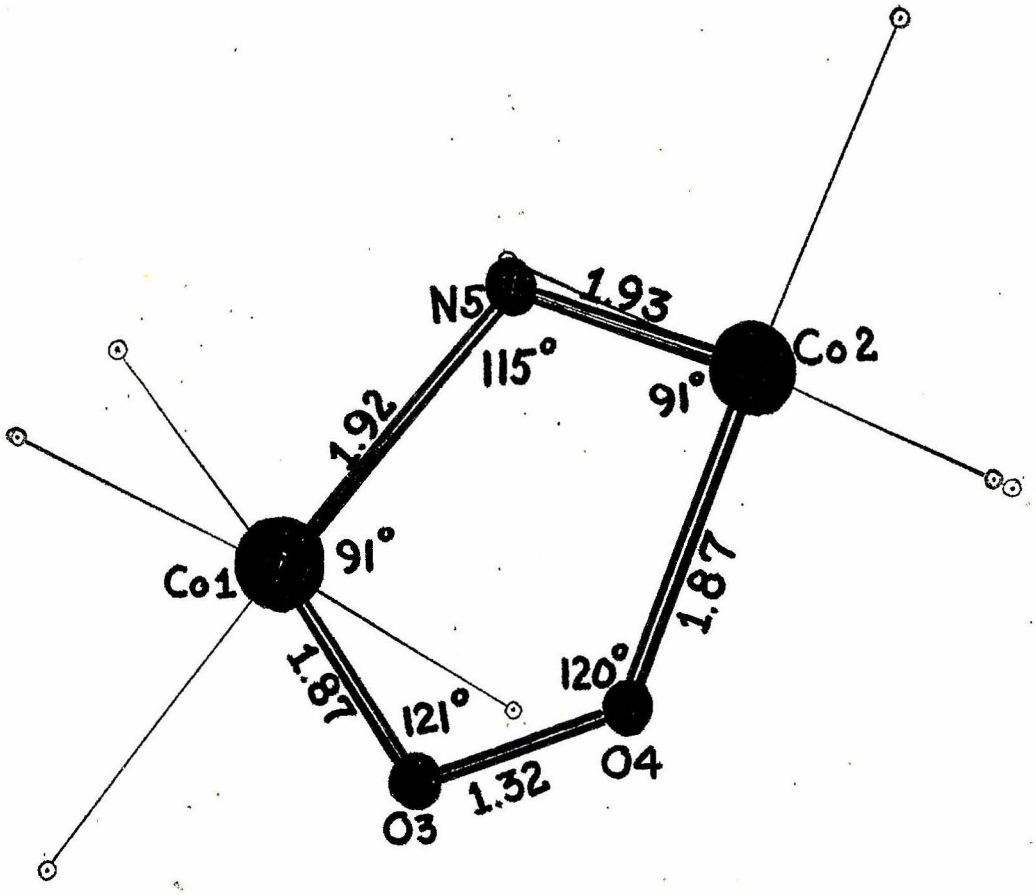


Fig. 2 Ring Structure

Projection onto yz plane

scale = 1" = 1 Å

Y Y

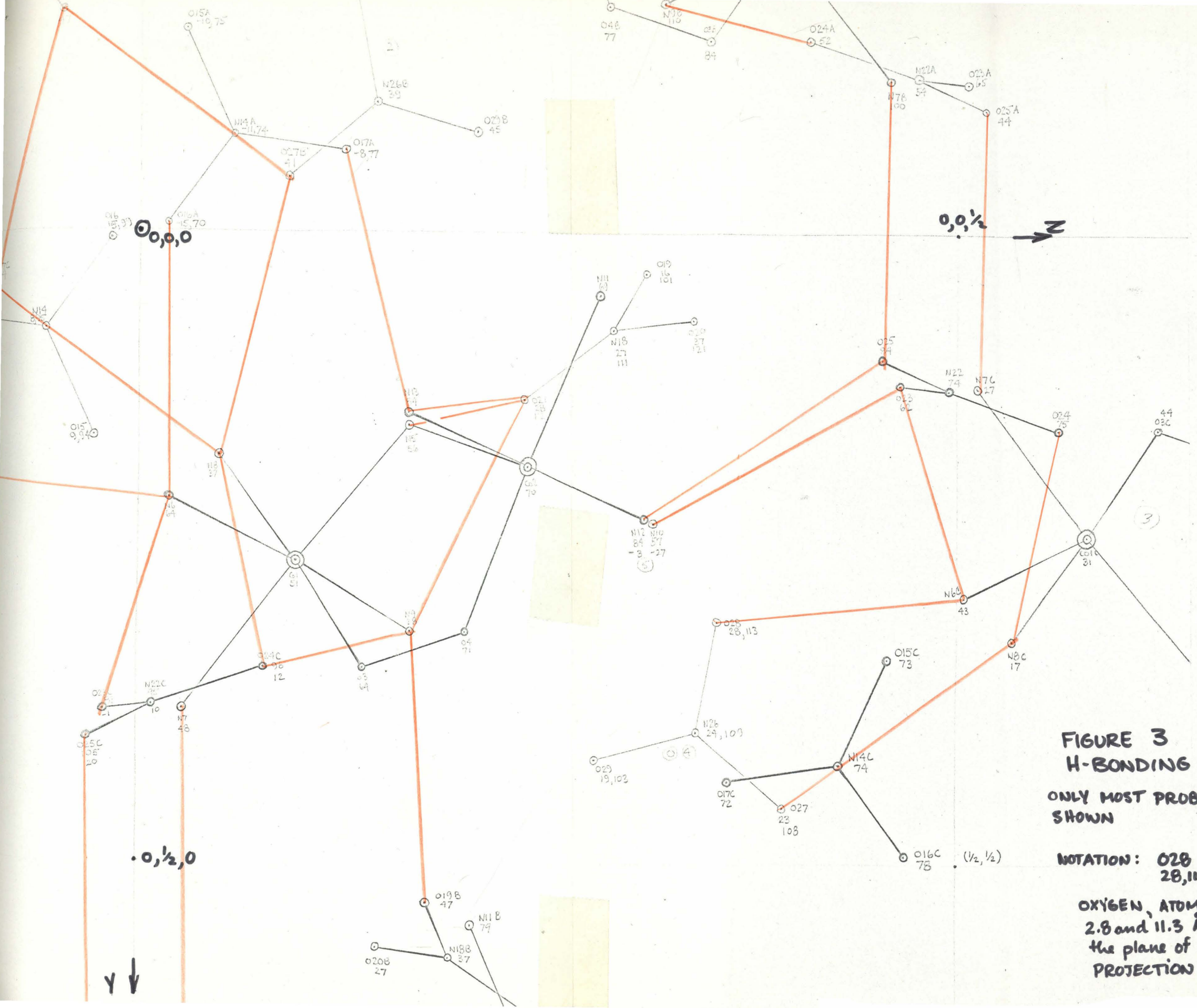


FIGURE 3
H-BONDING DIAGRAM

ONLY MOST PROBABLE H-BONDS SHOWN

NOTATION: 028 28,113 MEANS

OXYGEN, ATOM NO. 28
2.8 and 11.3 Å above
the plane of paper (=0.00Å)
PROJECTION ONTO YZ PLANE