Determination of the Structure of Decammine-μ-peroxodicobalt (III) Tetrathiocyanate.

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A Thesis Describing Chemical Research Undertaken in Ch 80

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ABSTRACT

Crystals of $[(NH_3)_5Co\text{-}O_2\text{-}Co(NH_3)_5](SCN)_4$ were prepared, and three-dimensional crystallographic data taken around one axis. Space group Pnnm, No. 58 was determined for the crystal with a unit cell in close agreement with previous work on the compound by Vannerberg. The structure was redetermined to the extent that the data justified, and reasonable agreement with Vannerberg's findings was obtained.

EXPERIMENTAL

The crystals were prepared by Dr. Ulf Thewalt by oxygenating a solution of 20 gm of $CoO_2 \cdot 6H_2O$ in 100 ml of water for about an hour, then letting the oxygenated solution sit over solid NH_4SCN for another hour. The fine, dark red, needlelike crystals were then filtered from the solution, washed with acetone and preserved under mineral oil.

A crystal was mounted with the needle (c) axis along the direction of rotation in a sealed capillary tube. The crystal was first aligned by means of an optical goniometer, and the alignment was checked by taking several oscillation photographs.

A rotation photograph of the crystal was then taken, and used to calculate camera position for equi-inclination Weissenberg photographs that were taken next. Weissenberg photographs were taken of the layer lines for **L**=0,1,2,3 and 4, all that could be reached with the Fe Kα (λ = 1.934 Å) radiation used. From inspection of the Weissenberg photographs an orthorhombic unit cell was deduced, and measurements of the rotation photograph and of the 0-layer Weissenberg gave the periodicities along the three axes as: a = 13.28 A, b = 10.57 A, and c = 7.88 A.

These are in good agreement with those of the previous work on decammine-μ-peroxodicobalt tetrathiocyanate by Vannerberg. His values were: a = 13.22, b = 10.58, and c = 7.88 Angstroms. (The latter values were used in all our calculations, as the former were merely estimated from the intensity films, and there was no time to take precision photographs from the crystal.)

Systematic absences in the reflections were noted for 0KL, K+L odd, and for HOL for H+L odd. This indicated either space group number 58, Pnnm or space group number 34, Pnn2. The former space group was arbitrarily assumed for the purposes of data reduction and structure factor calculations in the absence of indicative data to the contrary.

In exposing the Weissenberg photographs, a multiple film technique was used with three films in the camera for each exposure. Both a long (60 hr.) and a short (18 hr.) exposure was taken of each layer line. All films were developed a standard length of time.

Relative intensities of maxima on the films were measured with a standard intensity strip provided by Dr. R.E. Marsh. This data was punched onto cards, and films in the same layer were scaled together, average intensities and standard deviations were calculated using the CRYRM system programs for that purpose. A data tape was prepared from the converted intensities. The computer program then applied Wilson statistics to the data and applied a scale factor of 8.0009 to the observed intensities. A Wilson temperature factor of 4.20 was printed out and used as an isotropic temperature factor for all atoms in the cell in the later determinations of trial F values.

Intensity data from the 0-layer Weissenberg photographs was used to prepare a Patterson projection onto (001). A unit cell with two formula units per cell was assumed at this point in accordance with the results of Vannerberg. The positions of the cobalt atoms were easily deduced from the Patterson projection, and structure factors were calculated using just the cobalts. Assigning the derived signs to the observed intensities, an electron density map was then calculated. A dispersion correction of -1.74 electrons was applied to the cobalt atom for the use of iron radiation.

Succeeding structure factor calculations were made and further electron density maps as more and more of the atoms were located. At the time of writing approximate positions for all of the atoms except the hydrogens have been determined.(See Table I and Figure I.). No least squares determination of positions was done because it was felt that the accuracy of the data would not justify it (See below.).

DISCUSSION

Data Collection

It was found that the crystals of decammine-μ-peroxodicobalt tetrathiocyanate suffered from severe internal disordering if exposed to atmospheric moisture. The disordering was so severe that no reflections could be observed on a crystal that had been exposed to the air for as short a time as a week. The crystals thus had to be kept under oil to preserve them and mounted in sealed capillary tubes for photographing.

Some difficulty was encountered in collecting and analysing

the data because of the shift of the x-ray facilities from the basement of Crellin Laboratory to the basement of the new Noyes Laboratory. In the month immediately preceeding the move, the developer in the darkroom was not changed, despite being almost completely exhausted, and lost strength rapidly with time. As a result, the films for the 3rd and 4th layer Weissenberg photographs were badly underdeveloped and the relative intensities of maxima on these films were much lower than they ought to have been and many reflections were too faint to be read properly. As a result of this high order terms in the Fourier series for electron densities will be too small in many cases, and thus the mapping and structure factor fit will be less accurate than they might be.

Additional data would have been gathered both around the c axis and around either the a or b axis, but the x-ray tubes were disconnected for almost a month an a half during the move and by the time they were reconnected and ready for use there was no time to mount another crystal and gather more data before the deadline for this report. (The crystal used for the data used here was destroyed inadvertantly during the move.)

Results

The gradual synthesis of the electron density maps as the positions of more and more of the atoms were discovered lead to the placement of disordered SCN groups at $0\frac{1}{2}0$ and at $\frac{1}{2}\frac{1}{2}0$, as was proposed by Vannerberg. In Figure 1 this means that in half of the unit cells the SCN group at $\frac{1}{2}\frac{1}{2}0$ is in the position S(2),C(2),N(5) represented by the circles, and in the other half of the unit cells is in the position S(2)',C(2)',N(5)',

represented by the crosses and related to the first positions by the twofold axis in the c direction at $\frac{1}{2}\frac{1}{2}$. (Vannerberg also tried unsuccessfully to construct a completely ordered structure. Due to the incomplete and inaccurate data it was not felt that any sort of attempt at comparison of the two possibilities was feasible at the present time.)

The final positions of the atoms are presented in Table I. As can be seen from the table, the results of this work agree quite well with the results of Vannerberg's work, though we did not assume as he did that the sulfur and the nitrogen in the disordered SCN's occupy the same crystallographic positions. It was felt that the difference in the sulfur-nitrogen distance between the ordered and the disordered SCN groups was enough to make this possibility unlikely, and placed the alternate positions of the atoms in such a way that the average electron density of the two atoms as estimated from a superimposed map of one of the ordered SCN groups would most closely approximate the observed electron density function.

The column labled "Mult. of position" is the crystallographic multiplicity of the position indicated in the table, and the column immediately following is the number of atoms in the unit cell that are used to fill that position. For all ordered atoms the last column will be equal to the multiplicity, but for the atoms in the disordered groups it is only equal to half of the multiplicity, since the group is centered on a position of half the multiplicity of the positions of the atoms and the group multiplicity determines the number of atoms. Another way of

looking at it is that the position that, say, the carbon is in is a four-fold position, but the carbon is only there half of the time, so there are only two carbon atoms needed to fill the crystallographic equivalence.

An electron density map of the basal plane of the unit cell (z = 0.0) is presented in Figure 1. Contours are drawn at every 1 electron/ $Å^3$ starting at 1 electron/ $Å^3$, except for the cobalt atom where the contours are every 2 electron/ $Å^3$ starting at 1 electron/ $Å^3$. The atoms presented in Table I are labled, and the labling also shows the two positions possible for the disordered SCN groups. There is a second plane at z = $\frac{1}{2}$ which is related to the basal plane by the two net glide planes at y = $\frac{1}{4}$ and perpendicular to y, and at x = $\frac{1}{4}$ and perpendicular to x. The net effect is to form the mirror image of the basal plane and translate it so the Co-O-O-Co group is centered on $\frac{1}{2}\frac{1}{2}\frac{1}{2}$.

Table II shows the Observed and calculated sturcture factors as of this las electron density map. The calculated structure factors are computed from the positions of the atoms as given in Table I. What is mainly of interest here is the fact that for the 3rd and 4th layer line data (L = 3,4) the observed structure factor is systematically lower than the calculated structure factor, showing the effect of the underdeveloping noted above. At the present time the R index of goodness of fit is equal to 29.5%, another indication of the problem with the data.

I would like in conclusion to express my sincere thanks to Dr. R.E. Marsh and Dr. Ulf Thewalt for their continuing patience and assitance and to Miss Lillian Casler for inking and preparing for photoreduction the electron density map of Figure 1.

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TABLE I.

Coordinates of non-symmetry related atoms in the unit cell of decammine-μ-peroxodicobalt tetrathiocyanate. a = 13.22 A, b = 10.58 A, c = 7.88 A. Space group no. 58, Pnnm.

ATOM	X (observed)	Y (observed)	Z (observed)	X (Vannerberg)	Y (Vannerberg)	Z (Vannerberg)	Mult. of position	No. of atoms
Co	0.1087	0.1626	0.0	0.1103	0.1636	0.0	4	4
O	-0.010	0.064	0.0	-0.009	0.077	0.0	4	4
N(1)	0.234	0.267	0.0	0.232	0.267	0.0	4	4
N(2)	0.050	0.274	0.160	0.048	0.277	0.171	8	8
N(3)	0.162	0.052	0.155	0.163	0.047	0.173	8	8
S(1)	0.248	0.752	0.0	0.245	0.751	0.0	4	4
C(1)	0.182	0.626	0.0	0.187	0.623	0.0	4	4
N(4)	0.138	0.528	0.0	0.130	0.526	0.0	4	4
S(2)	0.466	0.400	0.0	0.463*	0.387*	0.0	4	2
C(2)	0.532	0.542	0.0	0.519	0.525	0.0	4	2
N(5)'	0.451	0.356	0.0	0.463*	0.387*	0.0	4	2
S(3)'	0.415	0.018	0.0	0.405**	0.017**	0.0	4	2
C(3)	0.464	0.007	0.0	0.464	0.004	0.0	4	2
N(6)	0.375	0.027	0.0	0.405**	0.017**	0.0	4	2

TABLE II. Listing of observed and calculated structure factors. (Unobserved reflections are not listed.) Entries are K, F_{obs}, F_{calc}.

0 K 0		
0	---*	5057
2	294	-229
4	726	599
6	101	-30
8	297	156
10	398	-290

1 K 0		
1	536	583
2	702	-829
3	614	-720
4	247	-184
5	401	-446
6	124	-71
7	159	37
8	472	-418
9	480	-361
10	123	57

2 K 0		
0	347	357
1	789	-864
2	525	628
3	319	328
4	416	-400
5	379	332
6	380	273
7	399	-207
8	259	-181
9	71	56
10	167	152

3 K 0		
1	119	190
2	400	-401
3	247	262
4	383	284
5	396	-323
6	150	-113
7	138	-3
8	495	-393
9	260	131
10	177	44

4 K 0		
0	94	-97
1	447	-359
2	723	-626
3	698	591
4	605	483
5	359	321
6	949	-847
7	139	63
8	360	241
9	-77	-12
10	-55	18

5 K 0		
1	360	233
2	839	828
3	948	920
4	-68	85
5	185	-124
6	227	241
7	361	-240
8	-79	-29
9	175	123
10	90	71

6 K 0		
0	464	-412
1	375	322
2	894	864
3	408	465
4	355	-322
5	572	-458
6	163	-110
7	193	110
8	274	-241
9	-65	-23

7 K 0		
1	404	279
2	602	543
3	-74	22
4	399	-290
5	162	46
6	-79	-16
7	150	-121
8	255	136
9	-51	-1

8 K 0		
0	576	447
1	326	276
2	274	-212
3	195	135
4	140	102
5	458	-317
6	125	4
7	-78	16
8	-63	7

9 K 0		
1	161	90
2	293	217
3	486	-396
4	-79	-15
5	153	123
6	-78	-23
7	165	83
8	-42	-55

10 K 0		
0	-80	-155
1	162	-81
2	232	141
3	192	148
4	375	-338
5	307	207
6	355	326

11 K 0		
1	-79	27
2	210	-78
3	98	-42
4	377	309
5	119	113
6	89	52

12 K 0		
0	-77	57
1	110	-50
2	106	10
3	-69	33
4	189	158
5	123	168

13 K 0		
1	-57	-69
2	101	-79
3	123	121

0 K 1		
1	491	657
3	47	-12
5	356	377
7	292	252
9	479	-373

1 K 1		
0	713	752
1	318	-247
2	513	-638
3	330	-346
4	262	-164
5	424	335
6	175	137
7	494	-398
8	294	-210
9	101	76
10	272	-201

2 K 1		
1	241	219
2	771	1034
3	-50	114
4	366	304
5	105	157
6	237	172

2 K 1		
7	-79	108
8	381	-273
9	134	-75
10	173	145

3 K 1		
0	780	-982
1	905	1279
2	185	-118
3	153	100
4	275	274
5	304	131
6	366	-211
7	80	-70
8	158	-55
9	287	-218
10	97	39

4 K 1		
1	436	-443
2	155	-133
3	666	639
4	354	278
5	344	-191
6	287	224
7	377	-188
8	-78	-9
9	203	192
10	117	117

5 K 1		
0	212	-176
1	114	55
2	420	409
3	264	-219
4	459	422
5	107	79
6	556	-344
7	-79	5
8	-79	86
9	101	49

6 K 1		
1	287	-209
2	374	249
3	271	230
4	394	-350
5	246	-135
6	210	157
7	366	-269
8	265	157
9	-62	-3

7 K 1		
0	301	244
1	223	71

TABLE II (2)

7 K 1		
2	401	409
3	241	179
4	111	4
5	566	-508
6	-79	108
7	385	340
8	111	-65
9	66	-15

8 K 1		
1	308	211
2	151	44
3	476	-380
4	376	-345
5	-79	-9
6	-79	-64
7	130	43
8	134	71

9 K 1		
0	484	379
1	159	103
2	301	-173
3	134	-179
4	286	-179
5	239	161
6	206	155
7	94	34

10 K 1		
1	327	266
2	193	-127
3	313	-199
4	181	62
5	114	94
6	-68	25
7	83	57

11 K 1		
0	-79	59
1	333	-297
2	-79	44
3	152	92
4	273	-239
5	211	94
6	-44	29

12 K 1		
1	107	131
2	203	-177
3	123	99
4	204	161

13 K 1		
0	101	-11
1	-54	53
2	67	70
3	-27	-123

0 K 2		
2	132	-121
4	171	69
6	243	216
8	204	215
10	168	-175

1 K 2		
1	179	274
2	249	-446
3	420	-943
4	259	241
5	158	-169
6	126	67
7	-77	-55
8	235	-273
9	194	-169
10	67	17

2 K 2		
0	99	85
1	192	-242
2	492	1065
3	220	359
4	359	-548
5	423	685
6	306	319
7	232	-118
8	244	-253
9	-79	83
10	96	109

3 K 2		
1	392	655
2	323	-438
3	263	351
4	309	440
5	202	-191
6	200	-217
7	230	-196
8	239	-250
9	116	79
10	40	-24

4 K 2		
0	48	36
1	113	0
2	182	-199
3	191	-42
4	318	395
5	215	258
6	481	-760
7	174	-108
8	201	144
9	-71	-7

5 K 2		
1	98	60
2	304	397
3	467	737
4	70	-18
5	149	-105
6	177	-79
7	199	-180
8	-80	23
9	132	140

6 K 2		
0	403	-587
1	414	566
2	327	420
3	130	136
4	224	-286
5	268	-309
6	-77	-70
7	-81	21
8	115	-124
9	-52	-9

7 K 2		
1	156	53
2	408	531
3	-74	-4
4	144	-35
5	-77	-16
6	-80	-9
7	-80	-2
8	221	221
9	-17	6

8 K 2		
0	461	630
1	319	432
2	251	-309
3	144	172
4	164	210
5	162	-97
6	-81	-70
7	102	55
8	-51	13

9 K 2		
1	211	212
2	177	209
3	240	-212
4	-80	47
5	-81	29
6	-74	-18
7	108	92

10 K 2		
0	233	106
1	140	-102
2	105	82
3	-81	68
4	155	-193
5	142	122
6	187	223

11 K 2		
1	-80	-13
2	162	-123
3	-76	-6
4	162	176
5	-55	51

12 K 2		
0	-69	42
1	136	-110
2	-64	-123
3	-57	49
4	105	176

13 K 2		
1	63	-125

0 K 3		
1	-27	87
3	361	-449
5	305	503
7	128	169
9	170	-102

1 K 3		
0	137	-191
1	76	89
2	179	-224
3	101	-98
4	334	-432
5	416	559
6	234	283
7	226	-242
8	184	-155
9	98	90
10	82	-121

2 K 3		
1	300	394
2	392	-582
3	-52	38
4	405	622
5	201	260
6	211	211
7	128	-68
8	151	-89
9	55	-26

3 K 3		
0	390	-489
1	414	-570
2	358	456
3	105	-142
4	129	146
5	248	256
6	205	-164
7	103	-180
8	199	-174
9	148	-164

TABLE II (3)

4 K 3		
1	144	-106
2	318	-380
3	410	546
4	136	150
5	159	-109
6	74	-84
7	270	-243
8	-77	52
9	109	56

5 K 3		
0	296	-276
1	289	287
2	207	227
3	441	-634
4	233	314
5	-74	28
6	320	-248
7	137	-157
8	101	104
9	55	45

6 K 3		
1	339	-438
2	194	90
3	-70	83
4	190	-208
5	175	-135
6	-82	-6
7	122	-111
8	191	203

7 K 3		
0	164	164
1	294	286
2	-72	71
3	149	122
4	-75	59
5	221	-217
6	-83	77
7	224	297
8	-51	14

8 K 3		
1	219	186
2	133	109
3	232	-220
4	102	-94
5	97	-82
6	-74	-5
7	84	83

9 K 3		
0	446	606
1	130	148
2	184	-161
3	123	-156
4	116	-15

9 K 3		
5	167	192
6	-62	37
7	-37	33

10 K 3		
1	238	287
2	156	-154
3	115	-61
4	-71	-19
5	-60	10
6	-40	-28

11 K 3		
0	100	130
1	234	-312
2	57	-70
3	-64	27
4	108	-135

12 K 3		
1	-54	24
2	110	-150
3	50	69

0 K 4		
2	130	-105
4	83	4
6	97	167
8	98	178

1 K 4		
1	149	175
2	189	-271
3	261	-639
4	140	201
5	-66	-98
6	-78	57
7	-81	-48
8	130	-190
9	93	-106

2 K 4		
0	94	43
1	190	-157
2	273	688
3	103	224
4	185	-386
5	245	503
6	163	237
7	110	-79
8	133	-199
9	-47	67

3 K 4		
1	226	412
2	214	-307
3	155	241
4	203	317

3 K 4		
5	68	-129
6	68	-163
7	111	-160
8	150	-174
9	66	55

4 K 4		
0	52	10
1	54	12
2	81	-100
3	-62	-60
4	223	277
5	116	179
6	297	-547
7	-75	-93
8	83	103

5 K 4		
1	-60	20
2	204	237
3	313	499
4	-73	-23
5	-81	-73
6	65	-90
7	97	-125
8	-53	19

6 K 4		
0	255	-437
1	288	414
2	211	258
3	68	72
4	116	-210
5	187	-208
6	-76	-42
7	-63	2

7 K 4		
1	68	26
2	250	379
3	-81	0
4	-82	-4
5	-77	-14
6	-68	-6
7	-53	12

8 K 4		
0	288	463
1	191	319
2	142	-242
3	66	130
4	63	170
5	98	-52
6	-57	-65

9 K 4		
1	153	163
2	90	157
3	111	-139
4	-68	44
5	-58	13
6	-37	-13

10 K 4		
0	107	94
1	58	-75
2	-68	63
3	-62	42
4	75	-132
5	-32	83

11 K 4		
1	-55	-18
2	72	-94
3	-41	-2
4	-35	120

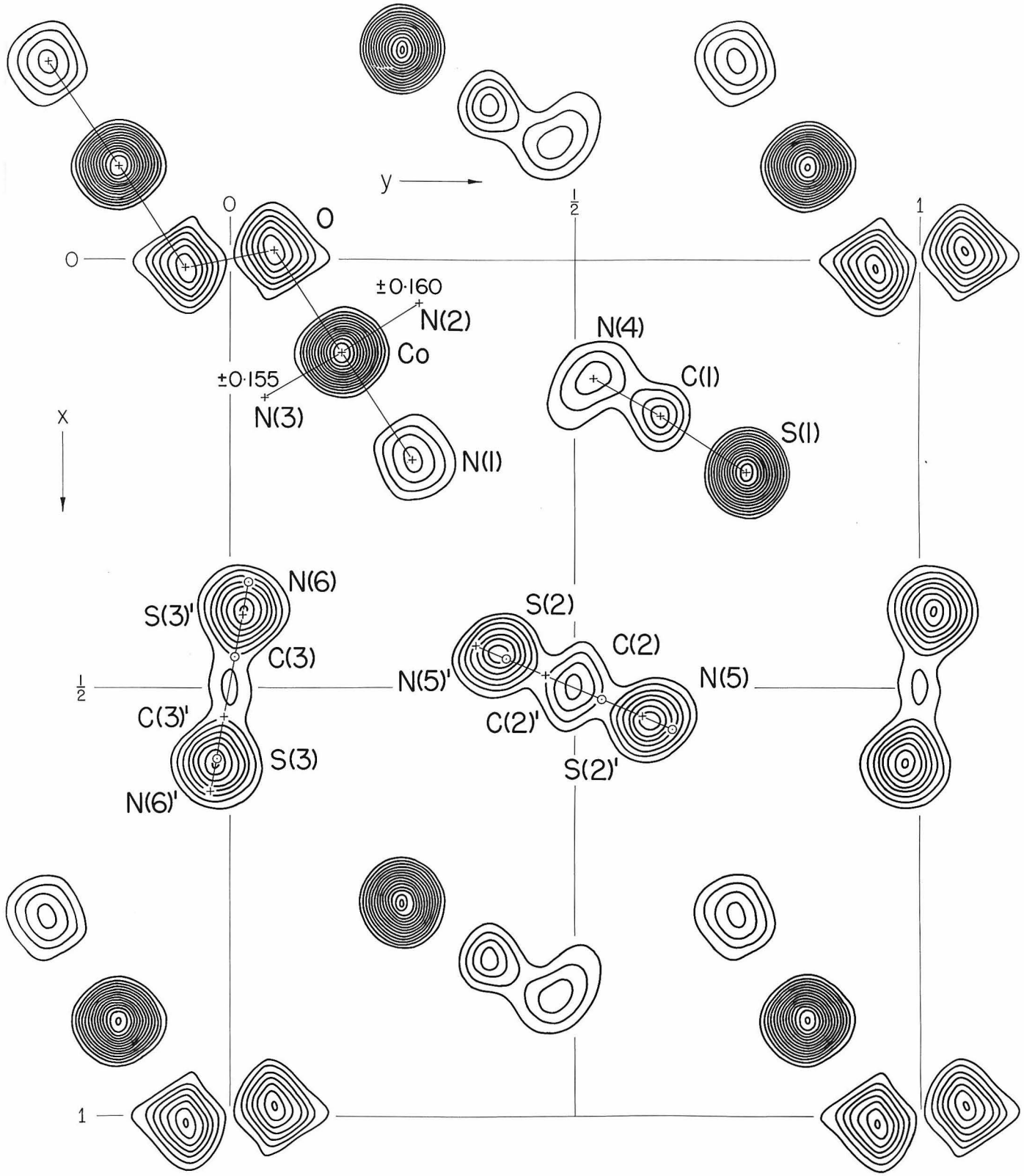

Figure 1 - Electron density map of basal plane (z=0) of a unit cell. (See text for discussion.)