238. *The Crystal Structure of Black Nitrosylpentamminecobalt Dichloride.*

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Crystals of the black form of nitrosylpentamminecobalt dichloride are twins showing apparently tetragonal symmetry and an unusual pattern of absent X-ray reflections not required by any space group. The pattern can be interpreted in terms of a fundamental orthorhombic lattice with $a = 10\cdot445$, $b = 8\cdot70$, $c = 10\cdot445$ Å, $Z = 4$, space group $Cmcm$. Certain classes of reflections can be distinguished as belonging to individual crystals and used by Patterson and Fourier methods to define the atomic positions. The nitrosylpentamminecobalt ion is octahedral, and the bonds in the cobalt–nitrosyl group linear; the interatomic distances appear to be longer than usual within the nitrosyl group and in the Co–NH$_3$ bond *trans* to it; however, they cannot be given accurately owing to the twinning phenomenon.

So much controversy has surrounded the problem of the structure of black nitrosylpent-amminecobalt dichloride [1-11] that it seems worthwhile to give here a separate account of our investigation, carried out parallel with, and in ignorance of, that of Hall and Taggart, Our conclusions are essentially the same, namely, that the form of the cobalt-containing ion is octahedral, and the Co–nitrosyl group linear; we also find that the N–O separation and the Co–NH$_3$ bond *trans* to it are longer than expected. An outline of our evidence, with details only of procedures which differed from those of Hall and Taggart, is given here.

The crystals, small black bipyramids or plates, unstable in air, were prepared by Dr. B. F. Hoskins and given to us by Professor D. P. Mellor. Their molar susceptibility, measured by Dr. Hoskins, was $\chi_m = -11\cdot5 \times 10^{-6}$. X-Ray photographs, from a number of different specimens sealed in fine-walled glass capillaries, all showed essentially similar diffraction patterns, and apparently tetragonal symmetry, $4/mmm$. The reflections extended to the limit of the copper K_α sphere; they were often very sharp in low orders but tended to become diffuse at high angles.

The reflections were recorded from small crystals, $0\cdot1$ mm. across, on multiple-film Weissenberg photographs, and their intensities were estimated visually. A Wilson plot in the field of the $0kl$ reflections provided an overall B value of $\sim$2$\cdot$6, and an approximate absolute scale which was applied to the intensity data. The reflections showed a pattern of absences (Fig. 1) which does not conform with those required by any tetragonal space group. However, if the crystals are orthorhombic and multiply-twinned, with different crystallite regions, a and b, lying at 90° to one another owing to rotation around the pseudo-tetragonal axis (Fig. 1), the pattern can readily be explained. This explanation, first put to us by Dr. Beryl Rimmer, also accounts for the characteristics of the Patterson distributions, calculated from the observed F^2 values, which are described below.

Crystal Data.—CoN$_6$H$_{15}$Cl$_2$O, $M = 245\cdot0$, orthorhombic bipyramidal, $a = 10\cdot44_5$, $b = 8\cdot70$, $c = 10\cdot44_5$ Å, $U = 949\cdot1_5$ Å^3 (back reflection method), $D_m = 1\cdot70$ (by flotation in bromoform

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and carbon tetrachloride), $Z = 4$, $D_c = 1.71$, $F(000) = 4 \times 123.3$. Space group $Cmcm$ (D_{2h}^{17}, No. 63). Cu K_α-radiation ($\mu = 202$ cm.$^{-1}$), single-crystal oscillation and Weissenberg photographs; $h0l$—$h8l$ and $0kl$—$2kl$.

Structure Analysis.—Fig. 1 shows that the reflections, as indexed, fall into three main classes: (i) reflections which are superpositions of the two non-equivalent reflections of the separate twins a and b, *e.g.*, 200a coinciding with 002b; (ii) reflections of the type hkh in which

FIG. 1. Patterns of absences, showing the three main classes of reflections. Vertical strokes represent the a twin, and horizontal strokes the b twin.
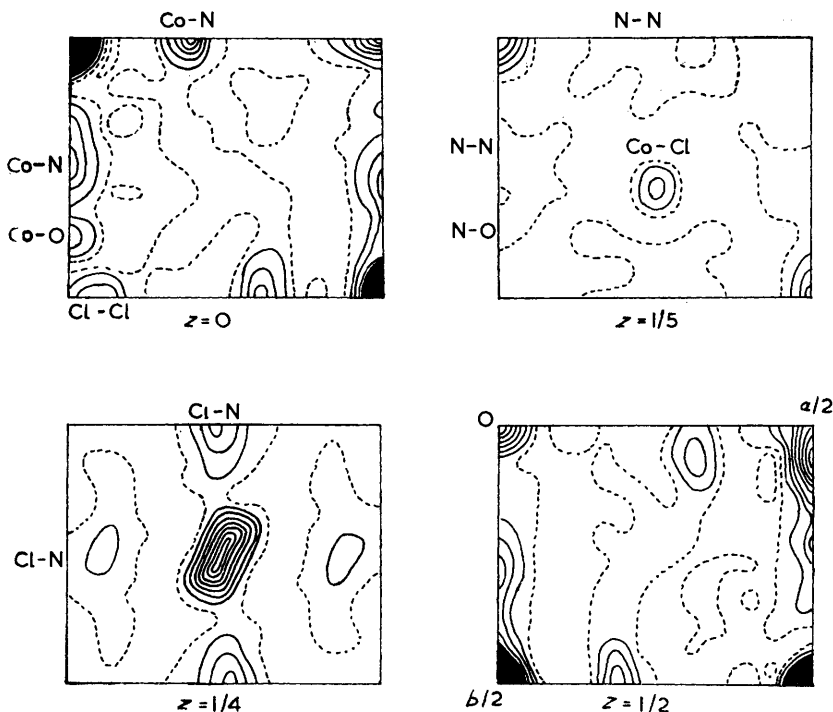
FIG. 2. Sections of the three-dimensional Patterson distribution for nitrosylpent-amminecobalt dichloride.

two equivalent reflections of the twins fall at the same position on the photograph, *e.g.*, $1k1$a = $1k1$b; (iii) reflections which correspond with a single-index type only; these occur twice, *e.g.*, 110a and 110b (which occurs at the position corresponding with the space-group extinguished reflection 011a). While reflections of type (i) constitute an experimentally inextricable mixture, those of types (ii) and (iii) can be sorted out and indexed as a unique set for one twin alone. 520 reflections in all were measured, of which about half could be indexed as the unique set.

The structure analysis began with the calculation of Patterson projections on (100) and (010). A three-dimensional Patterson distribution, using the F^2 values measured directly from the photographs, was also evaluated, and sections of this map are shown in Fig. 2. They show that

the idealised crystal structure is of the fluorite type. The cobalt ions form an approximately face-centred cubic close-packed array, and the chlorine ions lie between them along the unit-cell diagonals. The individual cobalt ions are clearly surrounded octahedrally by six atoms, probably nitrogen. These octahedra are arranged with the cobalt–nitrogen bonds parallel to the cell edges.

FIG. 3(a).

FIG. 3(b).
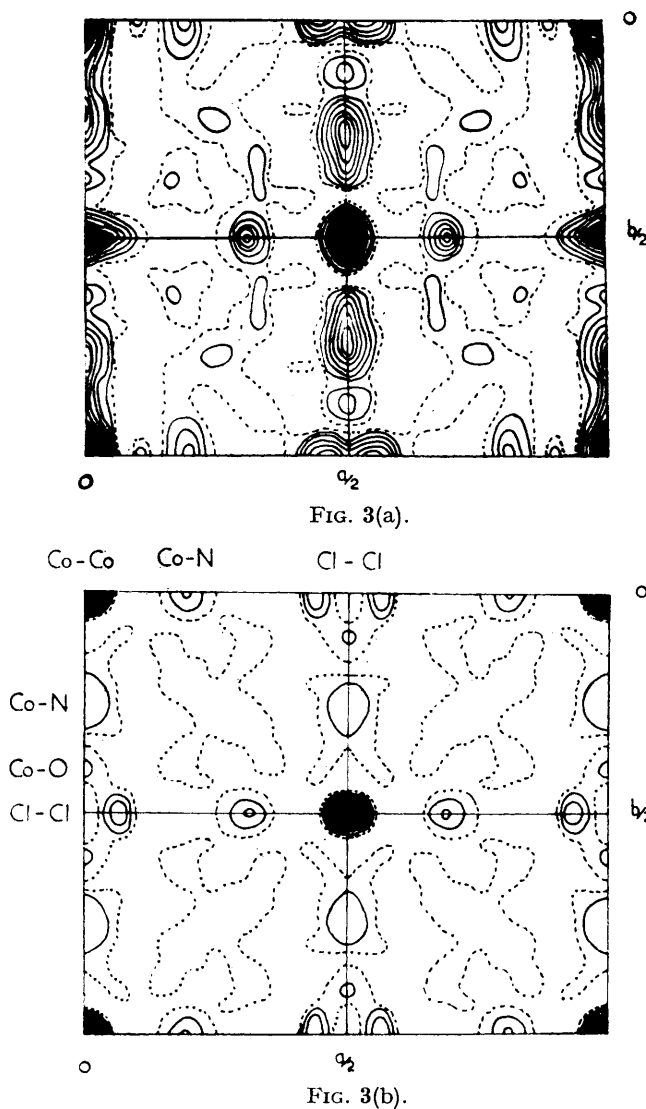
FIG. 3. Sections at $z = 0$, calculated (a) from the F^2 hkl terms as observed, and (b) from the unique terms given orthorhombic distribution.

While the four peaks, Co–N, are sharp in the plane $y = 0$ of the Patterson distribution, those parallel to the b-axis are drawn out and associated with smaller peaks, Co–O [Fig. 2], indicating that the nitrosyl group is linear and oriented parallel to b. The maps clearly show that the structure is distorted from the regular fluorite type; the Co–Co vectors in the section $z = \frac{1}{2}$ and the Cl–Cl vectors in the section $z = 0$ provide a measure of the actual relative cobalt and chlorine positional parameters. Possible distortions of the ideal structure maintaining tetragonal symmetry were examined but did not account for the observed absent reflections.

With the recognition of the underlying orthorhombic symmetry of the lattice it was realised that the Patterson distribution as calculated was confused by the superposition of non-crystallographically equivalent vectors from the twinned crystals. A second three-dimensional Patterson distribution was accordingly calculated, using only the unique terms of classes (ii) and (iii) above. This distribution is very similar to the first, given orthorhombic and not tetragonal symmetry. It is, of course, an incomplete representation of the vector density,
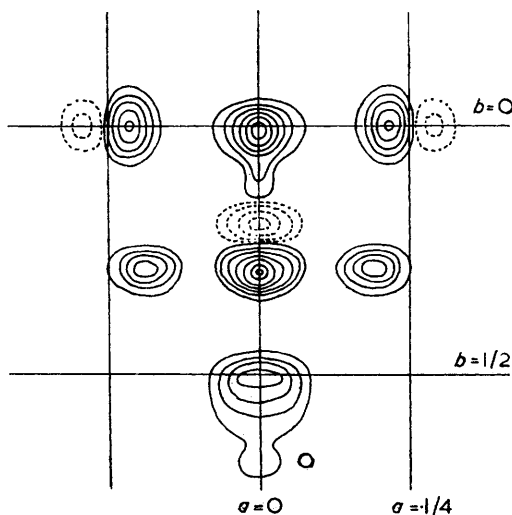
Fig. 4. Section, at $z = \frac{1}{4}$, of the electron-density distribution based on the unique terms. The chlorine atoms at $z = 0$ are shown superimposed. Contours at 1 e/Å³ except over the chlorine, cobalt, and negative peaks where they are at 4 e/Å³.

Fig. 5. Extracts from the three-dimensional electron-density distributions based on the full series. Contours at 1 e/Å³ except in the last section where they are at 0·5 e/Å³.

owing to the omission of the (i) group of reflections.   Corresponding sections, at $z = 0$, from the two distributions are shown in Figs. 3(a) and 3(b).

The parameters of the atoms derived directly from the Patterson maps were submitted to refinement by a least-squares calculation using the unique terms only.   The least-squares shifts ha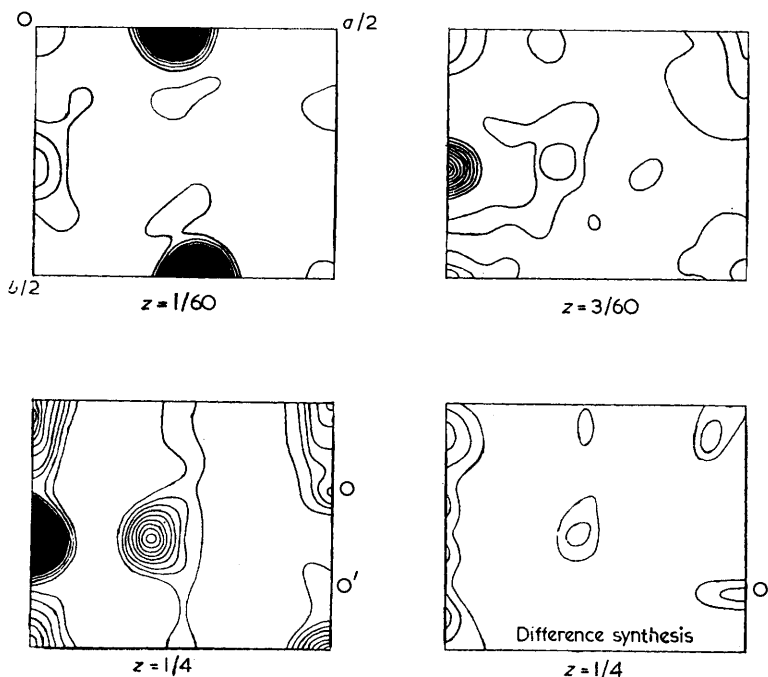d to be scrutinised and adjusted between successive cycles but some refinement occurred. The latest agreement factor, $R = 13.8\%$, was given by structure-factor calculations based on the atomic co-ordinates listed in Table 1.   The observed structure factors, together with the F

TABLE 1.

Atomic co-ordinates; derived from a least-squares and Fourier analysis of the unique terms.

Atom	Positional			Vibrational		
	x	y	z	B_{11}	B_{22}	B_{33}
Co	0·000	0·281	0·250	1·67	1·78	1·52
Cl	0·226	0·000	0·000	1·82	1·99	1·82
N(1)	0·188	0·276	0·250	2·28	3·99	1·37
N(2)	0·000	0·278	0·437	1·82	4·41	1·06
N(3)	0·000	0·017	0·250	1·82	6·29	1·06
N(4)	0·000	0·514	0·250	2·73	2·73	3·33
O	0·000	0·676	0·250	4·54	7·87	4·54

values calculated on these parameters, are listed in Table 2.   Corresponding observed and calculated structure factors for the twinned reflections are listed in Table 3.   The R value for this group is 13.5% and for all reflections is 13.6%.

An attempted refinement by Fourier methods suggests a more complex picture of the structure than that recorded in Table 1.   Two three-dimensional electron-density distributions were calculated, one based on the unique terms only, and the second on the full series; in the latter, values for terms of type (i) were introduced from the calculated F^2 values modified in the ratio of $I_{obs} : I_{calc}$ of Table 3.   Fig. 4 shows the section at $z = \frac{1}{4}$ in the first series on the unique terms, and Fig. 5 provides extracts from the full series.   Fig. 4 necessarily has certain false detail owing to the omission of terms of type (i); these include the extremely poor definition of the oxygen atom and the very large minima which are absent from Fig. 5.   Both distributions show the oxygen atom as a low ridge rather than as a peak, suggestive of atoms at more than one internuclear distance; they also both show a small peak, O′, at $x = 0$ and $y = 0.86$.   Peaks at the same position occur in the difference maps, together with other small maxima, some suggestive of hydrogen-atom positions around the ammine nitrogen atoms.   The ΔF map on the unique terms alone shows a small minimum at the oxygen site O.   Two further check structure-factor and difference calculations were made on the unique terms.   In one, a single oxygen was placed at O′; a minimum of -7.5 e/Å³ appeared here and a maximum of 7.4 at $y = 0.63$.   In the other, 60% O was placed at $y = 0.65$ and 40% at $y = 0.90$; small minima appeared at both positions.   These effects may partly be a consequence of difficulties in calculations based on limited data which tend to reproduce the point-group symmetry around the heavy atoms.   But they may also be a real reflection of disorder in the crystal, both within and between the single crystal domains.   (Compare the OD structures discussed by K. Downberger-Schiff.[16])

DISCUSSION

The crystal structure found and the distances corresponding with Table 1 co-ordinates are shown in Figs. 6 and 7.   These agree very well with those found by Hall and Taggart, with the exception of N–O which is longer here; however, as the oxygen atom is the atom most difficult to place precisely, it is unlikely that the difference is significant.   The angles in the cobalt octahedron are not significantly different from 90°.

The atomic arrangement found accounts very well for the easy twinning of the crystals. The closest contact between the octahedral ions is between NH_3 and O along the b-axis, 3.0 Å; the other two contacts, in the a- and c-planes, also NH_3–O, are very nearly the same, 3.2 and 3.3 Å, although the relative arrangements of the ions in these planes are

TABLE 2.

Observed and calculated structure factors for the unique reflections.*

0,2,l

l	F_o	F_c
0	9	−11
1	24	24
3	10	−10
5	26	24
7	16	−14

0,4,l

l	F_o	F_c
0	150	166
1	58	−58
3	46	35
5	54	−47
7	26	24
9	20	−19
11	15	15

0,6,l

l	F_o	F_c
0	27	27
1	33	39
3	32	−30
5	38	30
7	28	−23
9	10	13
11	12	−15

0,8,l

l	F_o	F_c
0	28	30
1	25	−28
3	21	22
5	30	−24
7	13	14
9	10	−13

0,10,l

l	F_o	F_c
0	28	20
1	15	11
3	13	−11
5	11	9

1,1,l

l	F_o	F_c
0	19	−21
1	91	−95
2	34	39
4	7	−5
6	21	20
8	11	4
10	13	6

1,3,l

l	F_o	F_c
0	56	81
1	76	74
2	17	−26
4	44	49
6	26	−28
8	23	21
10	13	−14
12	10	12

1,5,l

l	F_o	F_c
0	33	−49
1	30	−33
2	35	47

(continued)

l	F_o	F_c
4	31	−30
6	45	37
8	12	−11
10	19	18
12	5	−7

1,7,l

l	F_o	F_c
0	33	37
2	22	−20
4	31	28
6	25	−18
8	17	15
10	10	−10

1,9,l

l	F_o	F_c
0	18	−16
2	18	19
4	14	−13
6	16	15

1,11,l

l	F_o	F_c
1	9	−4
2	4	−5

0,2,l

l	F_o	F_c
2	154	−187

2,2,l

l	F_o	F_c
1	4	5
2	107	−89
5	17	14
9	8	5

2,4,l

l	F_o	F_c
1	42	−34
2	81	−92
3	24	20
5	36	−28
7	19	18
9	10	−9
11	11	13

2,6,l

l	F_o	F_c
1	23	26
2	37	−35
3	15	−16
5	27	24
7	10	−12
9	9	11

2,8,l

l	F_o	F_c
1	18	−21
2	22	−24
3	15	19
5	17	−16
7	12	14

2,10,l

l	F_o	F_c
1	11	10
2	20	−18
3	4	−8
5	7	9

3,1,l

l	F_o	F_c
0	59	−69
2	27	−31
3	15	−6
4	38	−40
6	14	−15
8	11	−14
10	12	−9
12	5	−5

3,3,l

l	F_o	F_c
0	7	9
2	43	−52
3	11	−9
6	40	−43
8	8	−3
10	22	−22

3,5,l

l	F_o	F_c
0	51	−62
2	8	5
3	11	9
4	41	−42
8	19	−20

3,7,l

l	F_o	F_c
0	12	10
2	31	−30
3	9	−3
4	10	6
6	29	−25
10	8	−14

3,9,l

l	F_o	F_c
0	21	−23
2	8	5

4,0,l

l	F_o	F_c
4	147	131

4,2,l

l	F_o	F_c
1	15	15
4	16	14
5	15	16

4,4,l

l	F_o	F_c
1	41	−38
3	26	23
4	62	68
5	35	−32
7	15	16
9	10	−13
11	9	11

4,6,l

l	F_o	F_c
1	24	27
3	19	−21
4	23	19
5	22	22
7	15	−16
9	8	9

4,8,l

l	F_o	F_c
1	20	−21
3	14	16

(continued)

l	F_o	F_c
4	17	16
5	18	−18

4,10,l

l	F_o	F_c
1	7	9

5,1,l

l	F_o	F_c
0	23	27
2	52	57
4	27	25
5	71	−63
6	32	35
8	20	18
10	11	15
12	5	8

5,3,l

l	F_o	F_c
0	74	83
2	10	6
4	63	60
5	47	44
6	8	−4
8	35	31

5,5,l

l	F_o	F_c
0	17	−15
2	56	56
5	34	−22
6	51	43
10	20	22

5,7,l

l	F_o	F_c
0	44	43
2	6	−3
4	37	35
6	10	−6
8	16	20

5,9,l

l	F_o	F_c
0	9	−5
2	22	24

6,0,l

l	F_o	F_c
6	77	−80

6,2,l

l	F_o	F_c
1	17	15
5	16	15
6	13	14
7	14	−7

6,4,l

l	F_o	F_c
1	33	−30
3	23	21
5	21	−24
9	6	−10

6,6,l

l	F_o	F_c
1	22	23
3	17	−17
5	24	20
6	7	−4
7	9	−12
9	8	10

6,8,l

l	F_o	F_c
1	18	−17
3	13	15
5	13	−14

6,10,l

l	F_o	F_c
1	5	8

7,1,l

l	F_o	F_c
0	42	−49
2	36	−35
4	40	−37
6	27	−23
7	22	16
8	21	−18
10	12	−13

7,3,l

l	F_o	F_c
0	13	−12
2	48	−47
4	12	−13
8	12	−10
10	21	−20

7,5,l

l	F_o	F_c
0	56	−49
2	13	−9
4	43	−38
7	4	9
8	18	−20

7,7,l

l	F_o	F_c
0	11	−2
2	28	−29
6	24	−23

7,9,l

l	F_o	F_c
0	17	−20

8,0,l

l	F_o	F_c
8	16	16

8,2,l

l	F_o	F_c
1	11	7
5	13	7
7	6	−4

8,4,l

l	F_o	F_c
1	17	−16
3	8	10
5	15	−14
8	9	11

8,6,l

l	F_o	F_c
1	12	13
3	8	−9
5	9	11
7	5	−7

8,8,l

l	F_o	F_c
1	10	−11

9,1,l

l	F_o	F_c
0	25	26
2	29	32
4	24	23
6	20	23
8	16	16
9	11	−8

9,3,l

l	F_o	F_c
0	46	44
2	16	15
4	42	34
8	18	19

9,5,l

l	F_o	F_c
2	32	32
4	8	6
6	22	25
8	4	5

9,7,l

l	F_o	F_c
0	24	26
2	8	4
4	20	21

10,2,l

l	F_o	F_c
7	13	−4

10,4,l

l	F_o	F_c
1	16	−15
3	11	11
5	13	−13
7	5	8

10,6,l

l	F_o	F_c
1	15	12
3	8	−9
5	10	10

11,1,l

l	F_o	F_c
0	22	−23
2	16	−18
4	18	−19
6	11	−12

11,3,l

l	F_o	F_c
0	9	−6
2	27	−25
6	19	−21

11,5,l

l	F_o	F_c
0	23	−26
2	6	−5
4	19	−20

12,2,l

l	F_o	F_c
1	7	4

12,4,l

l	F_o	F_c
1	7	−8

13,1,l

l	F_o	F_c
0	10	11
2	9	11

* The scattering factors employed were those of Thomas and Umeda [12] for cobalt, Freeman [13] for nitrogen, and Berghuis *et al.* [14] for carbon and oxygen. The cobalt scattering curve was corrected for anomalous absorption (cf. ref. 15).

dissimilar. The position of the chlorine ion, which makes a longer contact NO–Cl than NH₃–Cl, suggests that the NO group is negatively charged.

There is no decisive evidence that it is the nitrogen rather than the oxygen atom of the nitrosyl group that is attached to the cobalt atom. The poor definition of the peak O

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[16] K. Downberger-Schiff, *Abh. der Deutschen Akad. der Wissenschaften zu Berlin*, 1964, no. 3, 1.

TABLE 3.

Observed and calculated structure factors for the twinned reflections.

$l(h)$	$(1/\sqrt2)F_o$	F_c(r.m.s.)	$F_c(l)$	$F_c(h)$
0,0				
2	67	55	−52	58
4	205	229	238	219
6	55	67	−60	73
8	79	73	85	60
10	28	31	−23	38
12	27	32	42	16
0,2				
2	115	157	161	−154
4	13	7	10	−0
6	105	101	113	−87
8	13	12	14	−10
10	45	41	52	−28
12	12	12	0	−16
0,4				
2	10	5	4	−5
4	100	104	111	97
6	17	17	−9	22
8	46	43	52	31
10	17	13	−4	18
12	16	19	26	7
0,6				
2	46	48	51	−46
4	24	22	24	21
6	35	34	39	−27
8	17	11	15	3
10	14	15	20	−5
0,8				
2	28	22	22	−22
4	24	22	25	19
6	16	12	15	−8
8	10	11	15	5
0,10				
2	4	9	9	−8
4	19	16	17	15
1,1				
3	48	33	32	−53
5	88	78	−80	−75
7	38	36	36	−35
9	36	24	−24	−24
11	28	25	29	−21
13	9	8	−7	−9
1,3				
3	42	37	−38	35
5	57	56	58	55
7	26	28	−28	28
9	21	18	18	17
11	17	18	−20	16
1,5				
3	24	19	21	−17
5	38	26	−27	−25
7	18	15	15	−14
9	15	10	−11	−9
11	10	9	10	−8

$l(h)$	$(1/\sqrt2)F_o$	F_c(r.m.s.)	$F_c(l)$	$F_c(h)$
1,7				
3	7	6	−7	5
5	9	7	7	7
1,9				
3	9	4	−3	4
2,0				
4	19	15	9	−19
6	113	113	−125	−101
8	15	13	−11	−14
10	39	43	−54	−26
12	12	12	2	−18
2,2				
4	68	82	−87	77
6	17	11	−15	−1
8	30	27	−34	17
10	14	9	−6	11
12	13	14	−19	2
2,4				
4	15	11	−13	7
6	59	62	−68	−55
8	12	10	−14	−4
10	25	25	−33	−14
12	6	8	−3	−11
2,6				
4	33	34	−36	31
6	20	16	−20	−9
8	14	16	−20	8
10	7	7	−10	2
2,8				
4	21	18	−19	16
6	13	15	−17	−12
8	8	9	−12	4
3,1				
5	55	41	−43	40
7	25	16	15	16
9	20	11	−10	11
11	20	16	19	13
3,3				
5	35	34	34	−34
7	9	14	−13	−14
9	10	10	9	−10
11	10	11	−12	−10
3,5				
5	23	16	−15	17
7	10	9	9	10
9	8	5	−5	5
11	7	7	7	6
4,0				
6	37	37	−34	39
8	50	46	52	39
10	23	21	−15	26
12	20	21	28	10

$l(h)$	$(1/\sqrt2)F_o$	F_o(r.m.s.)	$F_c(l)$	$F_c(h)$
4,2				
6	60	63	68	−57
8	11	11	16	−0
10	24	26	33	−14
12	8	8	2	−11
4,4				
8	31	28	33	22
10	11	9	−2	13
4,6				
6	26	24	25	−22
8	10	9	12	4
10	9	10	13	−5
4,8				
6	10	10	12	−7
5,1				
7	37	33	32	−33
9	28	23	−23	−23
11	24	22	24	−19
5,3				
7	24	25	−25	25
9	16	16	16	15
11	14	16	−18	14
5,5				
7	13	12	12	−12
9	12	10	−10	−9
6,0				
8	17	16	11	−20
10	33	33	−40	−26
6,2				
8	24	24	−26	21
10	16	11	7	14
6,4				
10	17	19	−23	−13
6,6				
8	6	10	−12	7
7,1				
9	14	11	−10	11
11	13	13	15	11
7,3				
9	7	9	9	−9
7,5				
9	4	4	−4	3
8,0				
10	13	11	−11	11
8,2				
10	8	9	11	−5

might favour the idea of oxygen attachment were it not that the peak adjacent to O and directly linked to cobalt is very similar to those defining the other five nitrogen atoms. It seems more likely that the explanation of the character of the peak O is to be found in terms of the disorder effects discussed above, coupled with the presence of some hexamminecobalt(II) in the crystal. The existence of occasional lines of nitrosylpentamminecobalt(II) ions having reversed directions parallel to b, would account for the persistence of the low peak O'. The presence of hexamminecobalt(II) in small amounts, varying from crystal to crystal, would explain both the variable magnetic susceptibility of preparations of the black crystals and the relatively low oxygen peak. It might also lead to the disorder effects since the nitrosylpentamminecobalt ions would tend to change direction after a hexamminecobalt ion.

In view of the confused state shown to exist in the crystals it is very satisfactory that there is close agreement in the main conclusions on the structure reached by Hall and

Taggart and ourselves There are interesting differences in detail in our observations; the intensities we measured show greater fall-off with angle than do those of Hall and Taggart, the structure-factor ratio being proportioned to $\sin^2 \theta/\lambda^2$. This may be due to our use of smaller crystals, and possibly also to some decomposition of our crystals.

It is clearly desirable to study by X-rays some other members of the black nitrosylpentammine series, preferably containing a larger or less symmetrical anion than chloride.

FIG. 7. Bond lengths in the nitrosylpentamminecobalt ion.

FIG. 6. Atomic positions projected on (001).

Measurements at different temperatures might also be helpful in settling more precisely the state of the nitrosyl group.

We have made a preliminary examination of one member of the red series, nitrosylpentamminecobalt dibromide dihydrate. This is monoclinic, $a = 13.79$, $b = 7.06$, $c = 23.74$ Å, $\beta = 101.4°$, space group $A2/m$, $Z = 8$. From these data it is possible that the red compound is dimeric, having either a centre or two-fold axis of symmetry. But detailed three-dimensional analysis is necessary to settle the structure.