The Crystal Structure of Chlorodinitro-triammine-cobalt. III.

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Introduction

In the absorption spectra of aqueous solution of chlorodinitrotriammine-cobalt III, $[Co(NH_3)_3 (NO_2)_2 Cl]$, the third absorption band was found at $\lambda = 2500$Å with log $\varepsilon = 4.4$[1], and therefore, it has been postulated that two of the negative radicals are co-ordinated in trans-positions with respect to each other. Since there are three negative ligands in the molecule, there remain the following two possibilities about the configuration of this molecule as shown in Fig. 1.

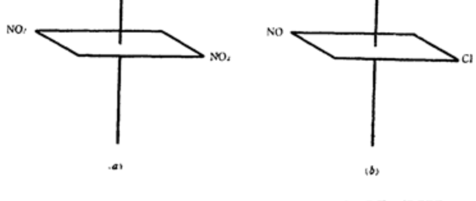

Fig. 1 Two possible forms of $[Co(NH_3)_3 (NO_2)_2 Cl]$, having two negative radicals in *trans* positions.

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[1] M. Kobayashi, A. Hagitani, and I. Mita: *J. Chem. Soc. Japan*, **58** (1937) 391.

In order to decide between (a) and (b) we have attempted to investigate the crystal structure of this compound by means of X-rays.

Unit Cell and Space Group

Chlorodinitro-triammine-cobalt (III) was prepared from trinitro-triammine-cobalt (III) and hydrochloric acid according to the method described by Jörgensen.[2] The crystals for this work were grown by slow evaporation of saturated aqueous solution containing a small amount of acetic acid at about 20° C. in a dessicator containing calcium chloride.

They are dark red tetragonal bipyramids, the effective dimensions of which are 0.4 mm. in each dimensions.

Making use of these crystals, oscillation photographs were taken around the [110] and [001] axes.

The unit cell dimensions were found from high order reflections. They are:

$$a=9.87\pm0.02\ \text{Å},\quad c=16.51\pm0.05\ \text{Å}.$$

The unit cell contains eight formula units. The calculated density is 1.961 g./cc., whereas the observed value was 1.952 g./cc. determined at 10°C. by the pyknometer method.

The Laue symmetry was found to be C_{4h}-$4/m$.

The systematic absences are: (hkl) present only with $h+k+l=$even, $(hk0)$ present only with $h=2n$, $k=2n$, and $h+k=4n$, and $(00l)$ present only with $l=4n$, so that the space group is C_{4h}^6-$I4_1/a$. The intensities of the diffraction maxima were estimated visually by comparison with a time-exposure calibrated standard and converted into structure amplitudes in the usual way, which were later placed on an absolute scale by comparison with the calculated values.

Analysis

The space group $I4_1/a$ possesses sixteen general positions, and since the unit cell contains eight units of $[Co(NH_3)_3\ (NO_2)_2\ Cl]$, it may be concluded that 16 N (nitro), 16 N (ammonia), and 32 O probably lie in general positions, while the other 8 Co, 8 Cl and 8 N ammonia) must occupy special positions.

The possible eight fold special positions for these Co, Cl and N atoms are: $(00z)$, etc., which lie on two fold axes, sets of symmetry centres at (0, 1/4, 1/8), etc., or (0, 1/4, 5/8) etc., or otherwise, two sets of four fold positions at (000), (00½), etc., in the four fold inversion axes.

It is quite natural to assume an octahedral co-ordination around a cobalt atom as shown in Fig. 1.

Since the symmetry $\bar{1}$ and also $\bar{4}$ cannot be achieved by any octahedral arrangement of the ligands around a central atom, it may be concluded that the cobalt atom lies on a two-fold axis, having two NO_2 and two NH_3 groups in trans-positions with respect to each other, and a Cl atom and one NH_3 group being on the two-fold axis (Fig. 1 (a)).

A trial model of a molecule was derived from the knowledge of interatomic distances and bond angles found in our previous works on cobaltic complexes.[3][4][5] The approximate coordinates for those atoms which lie on the symmetry axis were easily deduced from packing considerations.

A Patterson projection P (xy) was synthesized, from which the azimuthal orientation of the complex molecule could be readily deduced.

Approximate coordinates for all the atoms were then written down, and the structure amplitudes for about 60 planes $(hk0)$ and $(h0l)$ were calculated. The agreement was reasonably good, and enabled a start to be made with the process of refinement by means of Fourier syntheses. These parameter values were used for a calculation of the signs of the $F(hkl)$ values, the origin of coordinates being shifted on a center of symmetry at (0, 1/4, 1/8).

Successive refinement of these parameter values was made by two dimensional Fourier syntheses $\rho(xy)$ and $\rho(xz)$. Then Fourie syntheses along lines parallel to the c-crystal axis were made at the values of x and y obtained from the two-dimensional projection. It was found that the maxima on these lines were sharp, and by taking these new maxima as new z-coordinates and then repeating the process of structure amplitude calculation and Fourier syntheses, refinement was achieved fairly rapidly. After five stages of these refinement processes all the $F(hkl)$ values were involved in a final set of line syntheses. One of the results is shown in Fig. 2. Finally, all the structure amplitudes were inserted as terms of a three-dimensional Fourier syntheses which was computed in sections perpendicular to c axis at the values obtained in the line syntheses for Co, $O_{(1)}$ and $O_{(2)}$. The result is shown in Fig. 3. The final parameter values obtained from these Fourier syntheses are listed in Table 1.

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[2] S. M. Jörgensen: *Z. anorg. Ch.* **7**. 310 (1894); **13**, 180 (1897).

[3] Y. Tanito, Y. Saito and H. Kuroya: This Bulletin, **25**, 188 (1952).

[4] Y. Tanito, Y. Saito and H. Kuroya: This Bulletin, **25**, 328 (1952).

[5] A. Nakahara, Y. Saito and H. Kuroya: This Bulletin, **25**, 331 (1952).

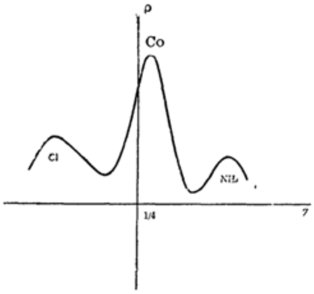

Fig. 2 Electron density along a two-fold axis, showing positions of Cl, Co and NH_3

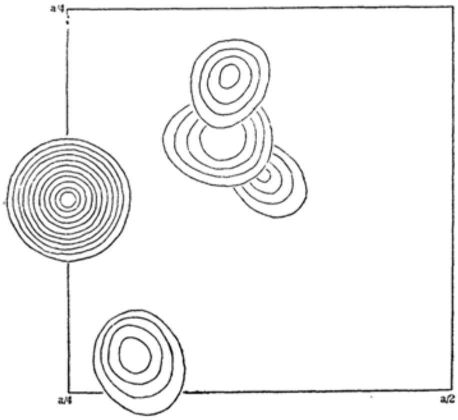

Fig. 3 Superposition of three-dimensional Fourier sections for [Co $(NH_3)_3$ $(NO_2)_2$ Cl]. Those for Cl and NH_3 (1) are not shown, which lie above and below Co respectively. The electron-density contours are drawn to an arbitrary scale.

Table 1.
Parameter Values Found for [Co $(NH_3)_3$ $(NO_2)_2$ Cl] (Values in fractions of the cell dimensions)

	x	y	z
Co	0	0	0.267
Cl	0	0	0.128
N (1) (ammonia)	0	0	0.382
N (2) (ammonia)	0.077	−0.186	0.267
N	0.187	0.075	0.267
O (1)	0.215	0.180	0.304
O (2)	0.275	0.015	0.230

The atomic scattering factors used in computing the structure amplitudes were those given in the International Tables. The value of B in the temperature factor was given the value 2.5 Å^2.

The figure of merits $\Sigma||F_o|-|F_c||/\Sigma|F_o|$ is 0.26 for all the (hkl) data, for which only observed 330 reflections up to sin $\theta/\lambda=0.49$ have been included. Fig. 4 gives a general indication of the agreement between the calculated and experimental F values.

Description of the structure

The crystal consists of [Co $(NH_3)_3$ $(NO_2)_2$ Cl] molecules and Fig. 5 gives a perspective drawing of the structure. Interatomic distances and interbond angles are listed in Table 2.

A molecule of [Co $(NH_3)_3$ $(No_2)_2$ Cl] is illustrated in Fig. 6. It has a two fold axis of symmetry. Two nitro-groups and two ammonia molecules, NH_3 (2), are co-ordinated to a cobalt atom in trans-positions respectively.

These four nitrogen atoms form a square around a cobalt atom within experimental

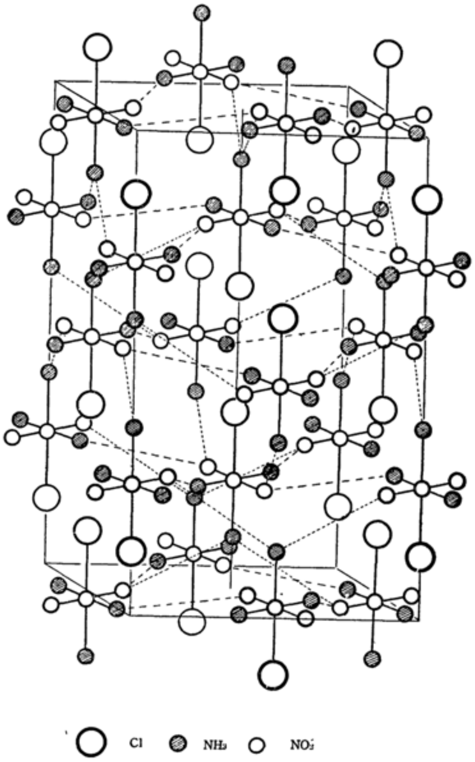

Fig. 5 A perspective drawing, showing the packing of the molecules in [Co $(NH_3)_3$ $(NO_2)_2$ Cl]. Circles are not drawn strictly to scale. Oxygen atoms are omitted.

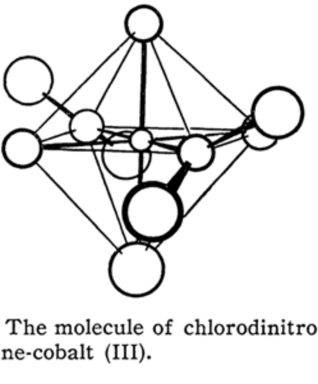

Fig. 6 The molecule of chlorodinitro-triammine-cobalt (III).

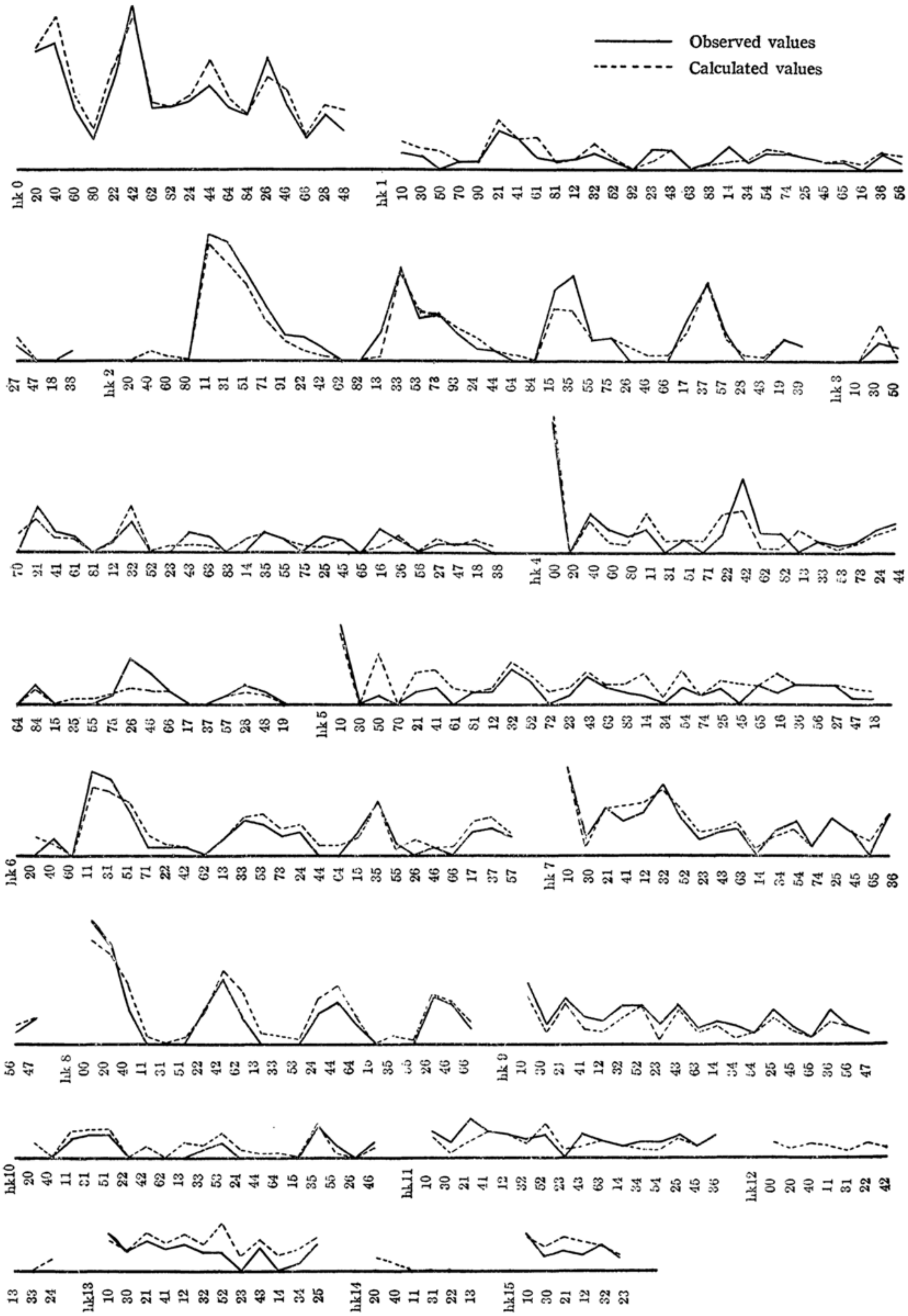

Fig. 4 Observed and calculated *F*'s

Table 2

Calculated Interatomic Distances and Bond Angles (Values in A Maximum errors about ±0.05 A and ±4°.)

within a molecule				between molecules	
Co	N (1) (ammonia)	1.90	O (1)	N (2) (ammonia)	2.84
	Cl	2.30	O (2)	N (1) (ammonia)	2.75
	N (2) (ammonia)	1.99	N (1) (ammonia)	Cl	3.68
	N	1.99		Cl	3.99
N	O (1)	1.24	Cl	Cl	4.24
	O (2)	1.22			
O (1)	O (2)	2.12			
∠ONO		119°			

errors, being 1.99 Å apart from it. On a line through a cobalt atom and perpendicular to the plane of four nitrogen atoms are a Cl atom and a NH_3 (1) group at 2.30 Å and 1.90 Å respectively, thus forming a distorted octahedron around a metal atom. These interatomic distances are in good agreement with those found in the structures of [Co $(NH_3)_3$ $(NO_2)_3$], [Coen$_2$ Cl_2] Cl · HCl · $2H_2O$ and [Co $(NH_3)_3$ H_2OCl_2] Cl.[3)4)5)]

The shape and size of the nitro-groups (N . . . O = 1.24, 1.22 Å and ∠ONO = 119°) are also in agreement with our previous results as well as with those in the case of KNO_2 recently determined very accurately.[6)] The plane containing a nitro-group is inclined at an angle of about 34.8° with the plane of four nitrogen atoms. Thus there exist two kinds of molecules in the crystal, each being the mirror image of the other.

The closest approach of molecules is between NH_3 of one molecule and O of a nitro-group of the other. The unusual short NH_3 . . . O distances of 2.75 and 2.85 Å suggest probable hydrogen bonding between molecules.

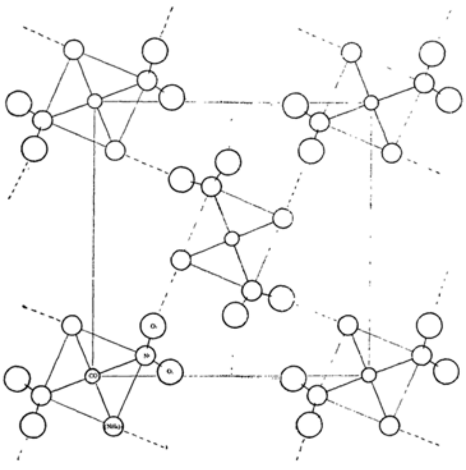

Fig. 7 Portion of the structure projected upon a plane perpendicular to [001], showing NH_3 . . . O linkages. Broken lines represent linkages in the layer, and dotted lines indicate those between layers.

Such hydrogen bonds were also found in the structure of trinitrotriammine-cobalt (III).[3)] Molecules are arranged approximately in a layer parallel to (001) which is shown in Figs. 5 and 7. Each layer comprises equal numbers of two kinds of molecules above-mentioned.

The main forces acting between molecules in the layer seem to be NH_3(2) . . . O(1) interactions which are indicated in the figure by broken lines. These (001) layers are held together by hrdrogen bonds between NH_3 (1) of one layer and O (2) of a nitro-group of the molecule belonging to the adjacent layer. These bonds are also shown by dotted lines in Figs. 5 and 7.

Thus each molecules are bound together by these two kinds of hydrogen bonds, forming a three-dimensional net work.

Summary

The crystal structure of [Co $(NH_3)_3$ $(NO_2)_2$ Cl] is tetragonal, with eight formula units in a cell of dimensions $a = 9.87$ Å and $c = 16.51$ Å.

The space group is C_{4h}^6-$I4_1/a$. The determination of atomic parameters was made by three dimensional Fourier syntheses. The configuration of the complex molecule is described.

Two nitro-groups are found to be in trans-positions with respect to each other. The main forces acting between these molecules in the crystal seem to be O . . . H-N bonds between the oxygen atoms of the nitro-group and the ammonia of the other. Molecules are linked together by these hydrogen bonds, forming a compact three-dimensional network in the crystal.

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6) G. B. Carpenter: *Acta Cryst.* **5**, 132 (1952).