The Crystal Structure of Trinitrotriammine-cobalt (III), $[Co(NH_3)_3(NO_2)_3]$

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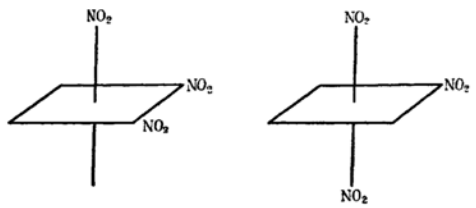
Introduction

According to Y. Shibata and R. Tsuchida,[1] the third absorption bands of co-ordinated compounds in aqueous solutions may be attributable to a pair or pairs of negative radicals co-ordinated in *trans*-positions and, from this point of view and because of the existence of the third absorption band at 120.4×10^{13} sec^{-1} ($\lambda=2492$ A.) with $\log\varepsilon=3.81$, it has been postulated that, to the trinitrotriammine-cobalt (III), $[Co(NH_3)_3(NO_2)_3]$, a *cis-trans*-configuration, instead of a *cis-cis* form, should be assigned (Fig. 1).



Cis-cis form *Cis-trans* form

Fig. 1.—Two possible forms of trinitrotriammine-cobalt (III).

In order to verify the above-mentioned conclusion by determining directly the configuration of the complex molecule, we have attempted to investigate the crystal structure of this compound.

Material

Trinitrotriammine-cobalt (III) was prepared by the method of Jörgensen.[2] Recrystallization from water containing a small amount of acetic acid yielded thin tabular crystals. The crystals belonging to the orthorhombic bisphenoidal class, are usually platy in habit with (010) extended.

According to Jaeger[3] the axial ratios are:

$$a:b:c=0.8682:1:0.6020\ ;$$

and the density is 1.992 g./cc. at 25°C.

Experimental

The X-ray work was carried out with Fe K_α radiation ($\lambda=1.937$ A.)

The crystals selected for the present study were $1\times1\times0.1$ mm. in effective dimensions. Only very thin platy crystals were available. Oscillation photographs about [100] and [001] gave the dimensions:

$$a=10.20\text{ A.},\ b=11.77\text{ A. and }c=6.99\text{ A.},$$

with the axial ratios

$$a:b:c=0.867:1:0.594$$

in agreement with the values obtained morphologically.

The space group is $D_2^4-P2_12_12_1$. There are four molecules in the unit cell, the calculated density being 1.972 g./cc. All the atoms are in the general positions: xyz; $1/2+x, 1/2-y, -z$; $1/2-x, 1/2+y, 1/2-z$; $-x, -y, 1/2+z$.

The reflections were estimated visually by comparison with a time calibrated scale of exposures, and they were converted into structure amplitudes by applying the appropriate correction factors, as shown in Fig. 2.

Analysis

At the outset of the analysis the following characteristics of intensity distribution were found:

(hkl); $h+l=2n$: strong
$(hk0)$; $h=2n$: strong
$(0kl)$; $k=2n$, $l=2n$: strong
and $(h0l)$; $h+l=2n$: strong.

This may indicate that the cobalt atoms are at $(x, 1/4, 1/4)$ etc., the arrangement of cobalt atoms alone thus having the symmetry D_{2h}^7-Bbmm. This was confirmed by synthesizing Patterson projections $I(xy)$ and $P(yz)$. These lead us to fix the positions of the cobalt atoms at 0.0686, 0.2500, 0.2500, etc.

Preliminary Fourier projections of electron density upon (001) and (100) were synthesized using $F(hk0)$'s with h even and $F(0kl)$'s with k, l

(1) Y. Shibata, *J. Chem. Soc. Japan*, **36**, 1243 (1915); R. Tsuchida, *J. Chem. Soc. Japan*, **59**, 586 (1938).
(2) S. M. Jörgensen, *Z. anorg. Ch.*, **17**, 463 (1898).
(3) F. M. Jaeger, *Z. Krist.*, **39**, 568 (1904).

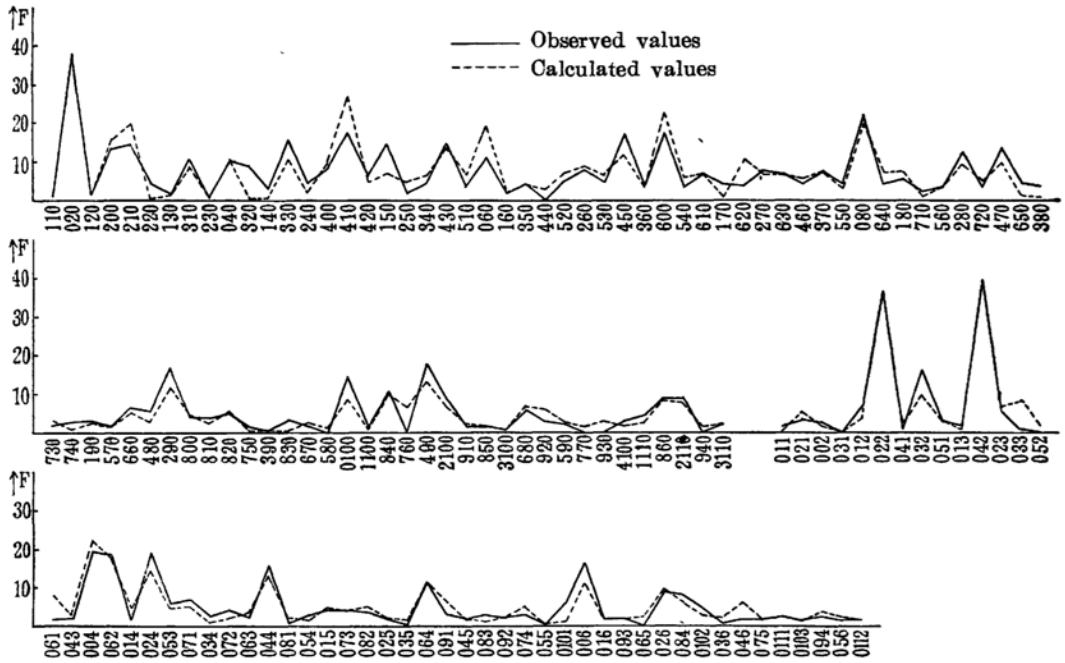


Fig. 2.—Observed and calculated F-values for trinitrotriammine-cobalt (III).

all even respectively, the signs of which were calculated from the parameter values of cobalt. From these projections we could assign approximate parameters for nitrogen atoms which form a distorted octahedron around each cobalt atom. These were in good accord with the conclusion drawn from Patterson projections $P(xy)$ and $P(yz)$. However, from the Fourier maps so obtained we could not locate the oxygen atoms unequivocally and we tried to determine the positions of these by trial and error. Bond angles and distances usual in nitro-compounds were used to locate oxygen atoms. Since the structure amplitudes $F(hk0)$ and $(F(0kl)$ could be accounted for only by one of the models having the *cis-trans* configuration, we regarded it as an approximate structure of trinitrotriammine cobalt (III) and started to determine the atomic parameters by successive approximations. The final parameters are listed in Table 1.

Table 1

Parameters of atoms in trinitrotriammine-cobalt (III)

	x/a	y/b	z/c
Co	0.0686	0.2500	0.2500
N(1)	−0.116	0.210	0.227
N(2)	0.020	0.360	0.450
N(3)	0.118	0.140	0.050
$NH_3(1)$	0.255	0.288	0.273
$NH_3(2)$	0.049	0.366	0.046
$NH_3(3)$	0.088	0.134	0.455
O(1)	−0.139	0.119	0.143
O(2)	−0.199	0.275	0.300
O(3)	0.135	0.393	0.472
O(4)	−0.068	0.401	0.558
O(5)	0.240	0.153	0.072
O(6)	0.076	0.054	−0.036

The values of $F(hk0)$ and $F(0kl)$ calculated from the parameter values in Table 1 are generally in good agreement with the observed values as shown in Fig. 2. In the calculation of the structure factors the atomic scattering curves in Internationale Tabellen (1935) were employed and corrected for temperature according to the Debye-Waller formula, the constant B being given the value 2.50×10^{-16} cm^2. For nitrogen belonging to the NH_3 group an appropriate correction,[4] due to the embedded hydrogen atoms, was made. A correction[5] for the anomalous dispersion for the Co atom ($\Delta f=2.2$) was also taken into account.

Description of the structure

The structure projected on the plane (001) is shown in Fig. 3 and the Fourier diagram in Fig. 4.

The cobalt atom occupies a general position. The arrangement of the cobalt atoms themselves has the symmetry D_{2h}^7—*Bbmm*. The proper symmetry of a cobalt atom is C_1-1 and this is surrounded by three nitrogen atoms of nitro-groups and three ammonia molecules, which form

(4) T. Watanabé, M. Atoji and C. Okazaki, *Acta Cryst.*, **3**, 405 (1950).

(5) H. Hönl, *Ann. Phys. Lpz.*, **18**, 625 (1935); R. W. James, "The Optical Principles of the Diffraction of X-rays" p. 609, G. Bell and Son, London, (1950).

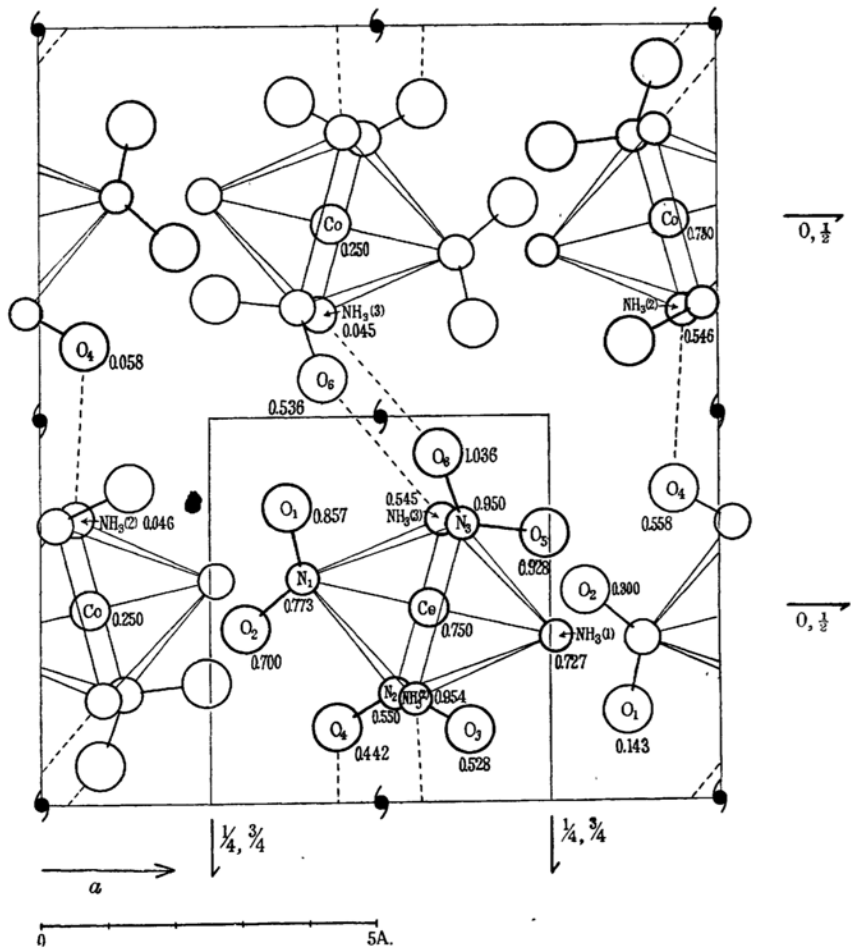


Fig. 3.—Projection of the structure upon (001) for trinitrotriammine-cobalt (III). Numbers give the height of atoms from (001) as fractions of the translation. N—H...O bonds are shown by dotted lines. The part of the cell corresponding to Fig. 4 is indicated.

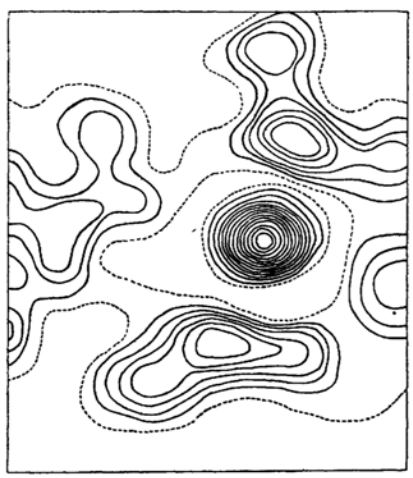


Fig. 4.—A Fourier projection of electron density of trinitrotriammine-cobalt(III). Contours at intervals of 2 e. A^{-2}., the first being broken.

a slightly distorted octahedron around the cobalt atom. Two of the nitro-groups are co-ordinated to a cobalt atom in *trans*-positions with respect to each other.

The interatomic distances as well as interbond angles are listed in Table 2.

Owing to the complexity of this crystal structure, involving the determination of 39 parameters and the overlapping of atomic peaks in both of the Fourier projections of electron density $\rho(xy)$ and $\rho(yz)$ it was not possible to determine the interatomic distances and interbond angles very accurately. The shape and size of the nitro-groups (N-O=1.25 A., $\angle$ONO=120°) may be compared with the values (N-O=1.25 A., $\angle$ONO=112°) for the Erdmann's salt,[6] or with the values recently obtained for aromatic nitro-compounds.[7]

(6) A. F. Wells, *Z. Krist.*, **94**, 74 (1935).
(7) For example, F. J. Llewellyn, *J. Chem. Soc.*, **1947**, 884.

Table 2

Interatomic distances and angles in trinitrotriammine-cobalt (III).

Within a complex radical			Between neighboring molecules		
		A.			A.
Co	N(1)	1.96	$NH_3(2)$	0(4)	2.74
	N(2)	1.97	$NH_3(3)$	0(6)	2.78
	N(3)	1.97	$NH_3(1)$	0(1)	3.29
Co	$NH_3(1)$	1.97	$NH_3(1)$	0(2)	3.10
	$NH_3(2)$	1.98	0(1)	0(6)	3.10
	$NH_3(3)$	1.99	0(2)	0(5)	2.76
N(1)	0(1)	1.24			
	0(2)	1.25			
	∠ONO	127°			
N(2)	0(3)	1.25			
	0(4)	1.27			
	∠ONO	119°			
N(3)	0(5)	1.27			
	0(6)	1.25			
	∠ONO	121°			
0(1)	0(6)	2.65			
0(2)	0(4)	2.69			
$NH_3(1)$	0(3)	2.23			
	0(5)	2.13			

The closest approach of the molecules is between O atom of NO_2 group of one molecule and NH_3 of another. It seems likely that the binding forces between the molecules are mainly due to the N-H...O bonds between ammonia and nitro-groups. This N-H...O bonds are evidenced by characteristic short NH_3-O distances (2.75 A., 2.80 A.). They are shown in Fig. 3 by dotted lines. Somewhat analogous hydrogen bridges have been recently reported in the case of ammonium tetrametaphosphate.[8] Such bridges of length 2.8 A. have also been reported in several other cases.

By these NH...O bonds the complex molecules form a spacial network parallel to the plane (010). The NH_3...O distances between the molecules in the adjacent (010) layers (3.10 A., 3.29 A.) are longer by far than those between the molecules in the (010) layers. This fact may suggest that the interactions which are responsible for uniting molecules in the (010) planes would be greater than those which exert between the molecules of adjacent (010) layers. It is to be noted here that the shorter N-H...O bonds are formed between the nitro-groups in *trans*-positions and the ammonia groups also in *trans*-coordination.

Unlike other complex salts consisting of neutral molecules, trinitrotriammine-cobalt (III) is fairly soluble in water (0.177 g. in 100 parts of water at 16.5°C.[9]) This fact may be related to the presence of hydrogen bonds between molecules in crystals and also between these molecules and water in solution.

Summary

The crystal structure of trinitrotriammine-cobalt (III) prepared accoding to the method of Jörgensen has been studied by X-rays, using rotation methods (Fe K_α, $\lambda=1.937$ A.). This structure belongs to the orthorhombic system and the dimensions of the unit cell which contains four molecules of $[Co(NH_3)_3(NO_2)_3]$ are $a=10.20$ A., $b=11.77$ A., and $c=6.99$ A. The space group is $D_2^4-P2_12_12_1$. The cobalt atom is surrounded by six nitrogen atoms approximately in octahedral coordination. The shape and size of the nitro-groups are like those in $Ag[Co(NH_3)_2(NO_2)_4]$. Two of the nitro-groups are found to be (coordinated to) the cobalt atom in the *trans*-positions with respect to each other in conformity with the conclusion drawn from spectroscopic investigations.

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(8) C. Romers, J. A. A. Ketelaar and C. H. MacGillavry, *Acta Cryst.*, **4**, 114 (1951).

(9) A. Werner, P. Larish and F. Ephraim., *Ber.*, **56**, 1532, (1923).