

A Reinvestigation of the Structure of Pentaammine-nitritochromium(III) Dichloride at 245 K

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Abstract. $[\text{Cr}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$, $M_r = 254.06$, monoclinic, space group $P2_1/n$, $Z = 4$, $a = 10.486$ (1), $b = 13.392$ (2), $c = 7.013$ (1) Å, $\beta = 92.09$ (1)°, $V = 984.2$ (4) Å³, $F(000) = 524$, $D_m = 1.70$ (room temperature), $D_c = 1.71$ g cm⁻³, crystal volume = 3.13×10^{-3} mm³, $T = 245$ K. The structure consists of Cr complexes where the CrN_5O group has a symmetry close to O_h and Cl^- ions in a fluorite-like arrangement. The two N–O distances in the ONO^- ligand are equal, 1.190 (4) and 1.191 (4) Å; the O–N–O angle is 122.0 (3)°. The Cr–N_{NH₃} distances range from 2.053 to 2.063 Å.

Introduction. Since solid $[\text{Cr}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$ is a stable nitrito compound (Linhard, Siebert & Weigel, 1955; Nakamoto, Fujita & Murata, 1958; Basolo & Hammaker, 1962; Fee, Garner & Harrowfield, 1967) its structure and coordination geometry are of interest in comparison with those of the unstable $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$. The structure of the latter has been determined in order to study the $\text{ONO}^- \rightarrow \text{NO}_2^-$ linkage isomerization in the solid state (Grenthe & Nordin, 1978).

Hansson & Börtin (1968) gave a preliminary account of the Cr^{III} compound based on space group $Pnma$. Later the space group was revised to $P2_1/n$ (Börtin, 1971). Unfortunately, the accuracy of this determination does not permit a meaningful comparison with the Co^{III} compound. A redetermination of the structure of $[\text{Cr}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$ was thus undertaken.

Microcrystalline $[\text{Cr}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$ was prepared by dissolving the corresponding nitrate (Mori, 1957) in cold water and precipitating with solid ammonium chloride. The chloride was purified in the same manner until satisfactory elemental analyses were obtained. Single crystals were grown at 278 K from an aqueous solution by slow evaporation. This procedure gave

Table 1. *Collection and reduction of the intensity data, and the least-squares refinement*

$\lambda = 0.71073$ Å (graphite-monochromated Mo $K\alpha$)
 Take-off angle: 3°
 θ interval of the two data sets: (i) 3–20°, (ii) 20–27°
 $\Delta\omega$ interval,* ω – 2θ scan: (i) $0.75^\circ + 80^\circ \tan \theta$, (ii) $1.00^\circ + 1.00^\circ \times \tan \theta$
 $\mu(\text{Mo } K\alpha) = 17.2$ cm⁻¹
 Range of transmission factor: 0.778–0.810
 Minimum number of counts in a scan: 3000
 Maximum recording time: 180 s
 Number of reflexions used in the refinement, $m = 1999$
 Number of reflexions with zero weight ($I \leq 0$): 144
 Number of parameters refined, $n = 146$
 $R^\dagger = \sum |F_o| - |F_c| / \sum |F_o| = 0.045$
 $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.048$
 $S = [\sum w(|F_o| - |F_c|)^2 / (m - n)]^{1/2} = 1.5$
 a (weighting function): 0.0004

* The scan interval, $\Delta\omega$, was extended 25% at both ends for the background measurement.

† $R = 0.052$, including zero-weight data.

Table 2. *Positional parameters*

E.s.d.'s are given in parentheses in this and the following tables.

	<i>x</i>	<i>y</i>	<i>z</i>
Cr	0.24096 (4)	0.10799 (3)	0.18441 (5)
Cl(1)	–0.00489 (7)	0.36028 (6)	0.16921 (10)
Cl(2)	0.49836 (7)	0.35410 (6)	0.15538 (10)
O(1)	0.2589 (2)	–0.1094 (2)	–0.1956 (3)
O(2)	0.2184 (2)	–0.0132 (2)	0.0274 (3)
N(1)	0.2785 (3)	–0.0347 (2)	–0.1072 (5)
N(2)	0.2422 (3)	0.1999 (2)	–0.0512 (4)
N(3)	0.2506 (3)	0.2311 (2)	0.3610 (4)
N(4)	0.2425 (3)	0.0155 (2)	0.4197 (4)
N(5)	0.0442 (3)	0.1113 (3)	0.1827 (5)
N(6)	0.4365 (3)	0.1016 (3)	0.1836 (5)
H(12)*	0.179 (5)	0.181 (4)	–0.132 (8)
H(22)	0.235 (6)	0.248 (4)	–0.031 (9)
H(32)	0.313 (5)	0.192 (4)	–0.120 (8)
H(13)	0.184 (5)	0.263 (4)	0.352 (8)
H(23)	0.275 (5)	0.216 (5)	0.454 (9)
H(33)	0.302 (5)	0.274 (4)	0.321 (8)
H(14)	0.182 (5)	–0.028 (4)	0.422 (7)
H(24)	0.276 (6)	0.042 (5)	0.493 (8)
H(34)	0.296 (5)	–0.018 (4)	0.405 (8)
H(15)	0.017 (5)	0.060 (4)	0.213 (8)
H(25)	0.021 (5)	0.155 (4)	0.233 (9)
H(35)	0.030 (6)	0.107 (5)	0.095 (8)
H(16)	0.465 (5)	0.045 (4)	0.213 (8)
H(26)	0.462 (6)	0.132 (5)	0.249 (10)
H(36)	0.465 (5)	0.105 (5)	0.092 (9)

* H(12) denotes that the hydrogen atom is bonded to N(2) etc.

crystals with a slightly distorted octahedral habit. The same crystal was used for the cell determination and intensity collection. Cell parameters and their e.s.d.'s were obtained by least-squares refinement of 60 θ values measured on an Enraf-Nonius CAD-4 diffractometer with a low-temperature attachment (Danielsson, Grenthe & Oskarsson, 1976). Table 1 gives information concerning the intensity collection and reduction, and the least-squares refinement. Three standard reflexions were checked during the intensity collection. No systematic variations were observed. The values of I and $\sigma_c(I)$ [where $\sigma_c(I)$ is determined from counting statistics] were corrected for Lorentz, polarization and absorption effects. The polarization factor was calculated from $(\cos^2 2\theta + \cos^2 2\theta_M)/(1 + \cos^2 2\theta_M)$. θ_M ($= 6.08^\circ$) is the Bragg angle for the monochromator.

Preliminary atomic coordinates for the non-hydrogen atoms were taken from Börtin (1971). Full-matrix least-squares refinement minimized $\sum w(|F_o| - |F_c|)^2$ with weights $w = 1/[\sigma_c^2(|F_o|)^2/4|F_o|^2 + a|F_o|^2]$, where a was chosen to make the average value

$\langle w(|F_o| - |F_c|)^2 \rangle$ almost equal in different $|F_o|$ and $\sin \theta/\lambda$ intervals. A difference map with data with $\sin \theta/\lambda \leq 0.5 \text{ \AA}^{-1}$ gave the location of the H atoms which were given a fixed temperature coefficient, $B = 5.0 \text{ \AA}^2$. The final atomic coordinates are given in Table 2.* In the last cycle the shifts of the non-hydrogen parameters were less than one tenth of the e.s.d.'s, and less than one third for the H atoms. There was no evidence of extinction. A final difference map had its largest residual (1.1 e \AA^{-3}) in the vicinity of O(2) and N(1). A δR plot comparing the model with experiment is shown in Fig. 1 (Abrahams & Keve, 1971). The slope and intercept of the least-squares line fitted to all data are 1.32 and 0.12 respectively. The positive intercept may indicate a small overestimation of weak intensities (Svensson, 1975). Neglecting this systematic error in $|F_o|$, the value of the slope indicates that $\sigma(|F_o|)$ is underestimated by about 30%, but is still in acceptable agreement with the value of the e.s.d. of an observation of unit weight ($S = 1.5$, Table 1).

Scattering factors and corrections for anomalous scattering of Cr and Cl were taken from *International Tables for X-ray Crystallography* (1974).

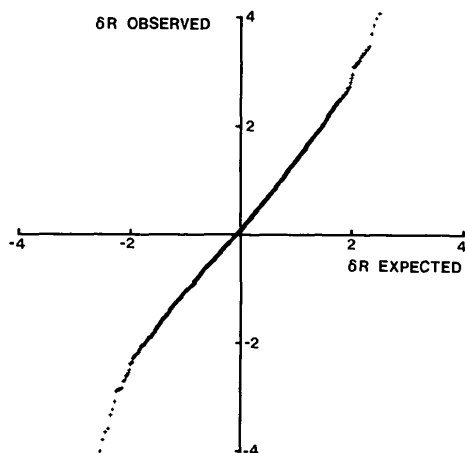


Fig. 1. δR normal probability plot. Only every other point is plotted.

Discussion. The structure is built up of nitropentamminechromium(III) ions in an approximately cubic close-packed manner with Cl^- ions in tetrahedral holes. The packing is similar to that found in fluorite-type structures. The anions and cations are held together by electrostatic forces and by a network of hydrogen bonds (Table 3 and Fig. 2). The symmetry of the CrN_5O group is close to O_h . The distortions are given by the tilt angle [the angle between the planes

* Lists of structure factors and anisotropic thermal parameters including r.m.s. components have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33466 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

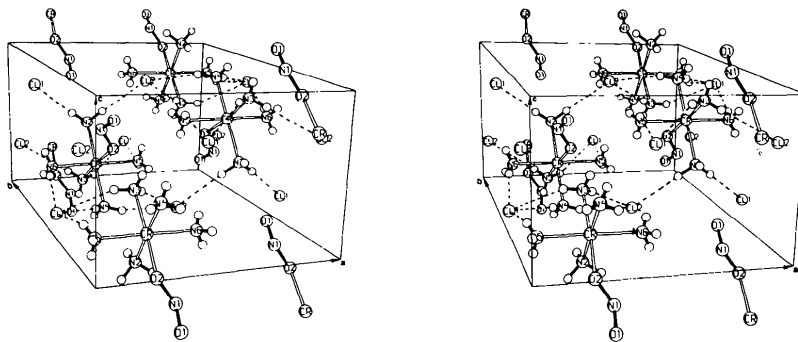


Fig. 2. The structure of $[\text{Cr}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$. Dashed lines represent hydrogen bonds.

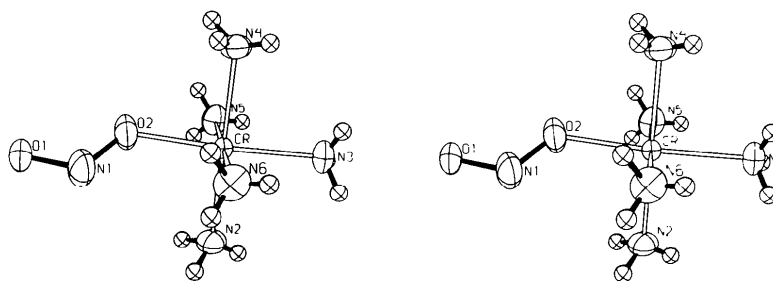


Fig. 3. The $[\text{Cr}(\text{NH}_3)_5\text{ONO}]^{2+}$ cation. The ellipsoids for the non-hydrogen atoms represent 50% of the probability distribution.

Table 3. Possible hydrogen bonds including $\text{Cl}\cdots\text{H}$ distances shorter than 2.8 Å

Distances are in Å and angles in degrees. Superscripts refer to the following transformations of the coordinates x, y, z : (i) $\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$; (ii) $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$; (iii) $-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$.

	N...Cl	N—H	H...Cl	N—H...Cl
N(2)—H(32)···Cl(1 ⁱ)	3.451 (3)	0.91 (5)	2.55 (5)	170 (5)
N(6)—H(16)···Cl(1 ⁱⁱ)	3.460 (4)	0.84 (6)	2.63 (6)	168 (5)
N(3)—H(13)···Cl(1)	3.423 (3)	0.82 (5)	2.66 (5)	156 (5)
N(4)—H(34)···Cl(1 ⁱⁱⁱ)	3.521 (3)	0.73 (6)	2.79 (6)	177 (6)
N(5)—H(25)···Cl(1)	3.375 (4)	0.73 (6)	2.80 (6)	138 (6)
N(2)—H(12)···Cl(2 ⁱⁱⁱ)	3.303 (3)	0.89 (6)	2.41 (6)	174 (5)
N(4)—H(14)···Cl(2 ⁱⁱ)	3.351 (3)	0.86 (6)	2.51 (6)	166 (5)
N(3)—H(33)···Cl(2)	3.437 (3)	0.84 (6)	2.64 (5)	161 (5)

Table 4. Dimensions of the cation $[\text{Cr}(\text{NH}_3)_5\text{ONO}]^{2+}$

Cr—O(2)	1.970 (3) Å	N(4)—H(14)	0.86 (6) Å
—N(2)	2.061 (3)	—H(24)	0.70 (6)
—N(3)	2.062 (3)	—H(34)	0.73 (6)
—N(4)	2.063 (3)	N(5)—H(15)	0.78 (6)
—N(5)	2.063 (3)	—H(25)	0.73 (6)
—N(6)	2.053 (3)	—H(35)	0.63 (6)
N(1)—O(1)	1.191 (4)	N(6)—H(16)	0.84 (6)
—O(2)	1.190 (4)	—H(26)	0.67 (6)
N(2)—H(12)	0.89 (5)	—H(36)	0.72 (6)
—H(22)	0.67 (6)		
—H(32)	0.91 (5)	Cr—O(2)—N(1)	125.9 (2)°
N(3)—H(13)	0.82 (5)	O(1)—N(1)—O(2)	122.0 (3)
—H(23)	0.72 (6)		
—H(33)	0.84 (6)		

defined by O(2), N(2), N(5) and N(3), N(4), N(6)], range of twist angles, range of edge lengths and the displacement of the Cr atom from the centroid of the polyhedron (Dymock & Palenik, 1975). The values calculated for O_h are given in parentheses: 1.2 (0.0)°, 55.8–63.9 (60.0)°, 2.73–2.94 (constant) Å and 0.028 (0.0) Å. No structural *trans*-effect is noticed. The Cr—N_{NH₃} distances are equal within the limits of error and are in agreement with those found in hexaamminechromium(III) complexes (Raymond, Meek & Ibers, 1968; Clegg, Greenhalgh & Straughan, 1975; Clegg, 1976).

In the nitrite ligand the two N—O distances are equal, 1.190 (4) and 1.191 (4) Å. This is in contrast to

some Cu^{II} complexes (Stephens, 1969; Camus, Marsich & Nardin, 1977; Klanderma, Hamilton & Bernal, 1977), where the N—O distances differ by about 0.06 (1) Å. In $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$ these distances are also unequal, but in this case the shortest distance is to the metal-coordinated O atom. This point will be discussed later (Grenthe & Nordin, 1978). The angle O—N—O, 122.0 (3)°, is significantly larger than the 114.9 (5)° found in sodium nitrite (Kay & Frazer, 1961). This angle is in most cases slightly altered on coordination. Bond distances and selected angles are given in Table 4. A view of the coordination polyhedron is shown in Fig. 3. The orientation of the ONO[−] ligand in relation to the rest of the polyhedron can be described by the torsion angle N(1)—O(2)—Cr—N(2), 48.3 (3)°. There is no evidence of hydrogen bonding of the nitrite ligand to any of the ammine ligands.

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Rubidium Hexabromobismuthate(III)

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Abstract. Rb_3BiBr_6 , orthorhombic, $Pnma$, $a = 13.311$ (8), $b = 26.63$ (1), $c = 8.603$ (4) Å; $D_o = 4.10$ (1) g cm⁻³, $Z = 8$, $D_c = 4.115$ g cm⁻³; $R = 0.079$ for 1240 reflexions [$I > 4\sigma(I)$]. The structure consists of isolated octahedral BiBr_6^{3-} anions and of Rb^+ cations with thoroughly irregular coordination polyhedra.

Introduction. This work is a new part of the systematic investigation of the stereochemical behaviour of the hexahalobismuthate(III) groups in the presence of various cations (Lazarini, 1977*a,b,c,d*). There are few known A_3BX_6 structures (Wells, 1975). Almost all of them can be derived from the cryolite structural type. Rb_3BiBr_6 seems to be unrelated to this structural family.

Yellow crystals of Rb_3BiBr_6 were grown by slow evaporation from an aqueous solution obtained by dissolving Bi(OH)_3 and Rb_2CO_3 (molar 2:3 ratio) in a dilute HBr solution. The formula was determined by standard chemical analytical methods (calculated: 22.12% Bi, 50.74% Br; found: 22.0% Bi, 51.2% Br). A well developed crystal, selected for the intensity measurements, was characterized by the following planes (in parentheses are the distances from the crystal faces to an arbitrary origin inside the crystal): (010) (0.316 mm), (0 $\bar{1}$ 0) (0.012 mm), \pm (011) (0.178 mm), \pm (0 $\bar{1}$ 1) (0.178 mm), (111) (0.234 mm), ($\bar{1}\bar{1}\bar{1}$) (0.222 mm), (1 $\bar{1}\bar{1}$) (0.225 mm), ($\bar{1}\bar{1}$ 1) (0.197 mm), ($\bar{1}$ 11) (0.233 mm), (1 $\bar{1}\bar{1}$) (0.190 mm) and ($\bar{1}$ 1 $\bar{1}$) (0.240 mm).

The intensity data were collected at 20 (1)°C with an Enraf–Nonius CAD-4 diffractometer. Experi-

mental conditions were: graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å), ω - 2θ scan, $\theta_{\min} = 1$, $\theta_{\max} = 25^\circ$, 2θ scan width ($^\circ$) = $0.9 + 0.2 \tan \theta$, aperture (mm) = $2.5 + 0.9 \tan \theta$, maximum scan time = 30 s, background: $\frac{1}{4}$ of the scan time at each of the scan limits. A set of 2722 independent reflexions were recorded. During the refinement procedure, it became apparent that the weaker reflexions were poorly measured. Therefore all reflexions with $I < 4\sigma(I)$ (calculations based on counting statistics) were rejected and only 1240 reflexions used in the refinement. Corrections were applied for Lorentz and polarization effects and for absorption [$\mu(\text{Mo } K\alpha) = 376.4$ cm⁻¹]. The absorption corrections A^* , calculated with the measured crystal dimensions (Gaussian-grid method), range from 34.9 to 206.3. The unit-cell parameters were obtained from a least-squares fit of the θ values of 15 reflexions measured on the diffractometer. The systematic absences ($Ok\bar{l}$: $k + l = 2n + 1$; $hk0$: $h = 2n + 1$) and the clearly centrosymmetric distribution of the normalized structure factors indicated the space group $Pnma$, which was subsequently confirmed by successful refinement.†

The positions of two Bi atoms of the asymmetrical set [on special 4(*b*) and 4(*c*) positions] were determined from the three-dimensional Patterson map, while the Br and Rb atoms were located from two successive

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33486 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.