

SHORT STRUCTURAL PAPERS

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The Structure of μ -Amido-hexaammine-di- μ -hydroxo-dicobalt(III) Tribromide*

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Abstract. $[\text{Co}_2(\text{NH}_2)(\text{NH}_3)_6(\text{OH})_2]\text{Br}_3$, FW 509.80, orthorhombic, $Pmn2_1$, $a = 7.288$ (1), $b = 9.212$ (1), $c = 10.443$ (1) Å, $Z = 2$, $\rho_c = 2.41$, $\rho_o = 2.33$ (2) Mg m^{-3} , $F(000) = 492$, $\lambda(\text{Co } K\alpha) = 1.7902$ Å, $\mu = 19.31$ mm^{-1} . This triply bridged dicobalt compound forms completely ordered crystals. The two Co octahedra share one face, with a Co...Co separation of 2.570 (2) Å. The ions in the structure are held together by an extensive hydrogen-bonding network.

Introduction. The crystal structure of a triply bridged dicobalt compound, hexaammine-tri- μ -hydroxo-dicobalt(III) tribromide, was first reported by Anderson (1967). A study of the same cation crystallized as the chloride was subsequently published by Mandel, Mandel, Marsh & Schaefer (1977). Both these compounds crystallize with some disorder, leading to relatively high uncertainties in the bond lengths. In particular, although the cation would appear to be able to exhibit a threefold symmetry about the Co–Co axis, the two structures studied showed an unsymmetric cation, but with rather large e.s.d.'s in the bond lengths. In an attempt to produce a completely ordered, triply bridged dicobalt ion we synthesized the salt μ -amido-hexaammine-di- μ -hydroxo-dicobalt tribromide. The inherent symmetry of this cation is lower than that of the tri- μ -hydroxo salt and there are more opportunities for hydrogen bonding from the cation; thus we hoped that the ions in the structure would not be disordered and that we would be able to determine the structure more precisely than had been done previously. Although this cation does not have the high inherent symmetry of the tri- μ -hydroxo ion, we hoped that a more precise determination would indicate whether the

tri- μ -hydroxo compound is likely to be symmetric, or not.

The compound was prepared according to the directions given by Werner (1910), beginning with cobalt chloride and ammonia. The μ -amido-hexaammine-di- μ -hydroxo-dicobalt cation was first isolated as the nitrate. This material was dissolved in water and the solution was saturated with ammonium bromide; dark-red needles of the bromide salt formed overnight. Weissenberg photographs showed orthorhombic diffraction symmetry and systematic absences $h0l$ with $h + l = 2n + 1$, consistent with space group $Pmnm$ or $Pmn2_1$. Cell dimensions were obtained by a least-squares calculation using the diffractometer setting angles of 10 reflections within the 2θ limits of 80 and 123°.

Intensity data were collected on a Dtex-automated GE quarter-circle diffractometer using Fe-filtered Co $K\alpha$ radiation and a θ - 2θ scan technique; the crystal used measured $0.1 \times 0.09 \times 0.07$ mm. The scan speed was 1° min^{-1} and background was counted for 30 s at the ends of each scan. All reflections (or their Friedel equivalents) within the range $4^\circ < 2\theta < 155^\circ$ were surveyed. The three check reflections showed no systematic variations with time, but did exhibit differences over the four octants hkl , $\bar{h}kl$, $h\bar{k}l$ and $\bar{h}\bar{k}l$. Therefore an absorption correction, performed by the method of Gaussian quadrature (Busing & Levy, 1957), was applied; the transmission factors varied from 0.18 to 0.40.

Data from the four octants were averaged to yield 549 independent intensities after systematic absences were removed. The variances, $\sigma^2(I)$, were assigned on the basis of counting statistics plus an additional term, $(0.02S)^2$, where S is the scan count. The data were corrected for Lorentz and polarization effects and put on an approximately absolute scale using a Wilson plot.

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Table 1. Final positional parameters ($\times 10^4$)

	x	y	z
Br(1)	0	1544 (2)	224 (0)
Br(2)	0	2007 (2)	4647 (2)
Br(3)	$\frac{1}{2}$	3295 (2)	7569 (2)
Co(1)	$\frac{1}{2}$	1742 (3)	2393 (3)
Co(2)	$\frac{1}{2}$	4188 (2)	3576 (3)
O(1)	3339 (9)	3372 (6)	2371 (7)
N(1)	$\frac{1}{2}$	1611 (13)	534 (13)
N(2)	$\frac{1}{2}$	2224 (13)	4192 (12)
N(3)	$\frac{1}{2}$	6061 (14)	2702 (13)
N(4)	3102 (12)	4863 (8)	4748 (9)
N(5)	3102 (11)	261 (8)	2538 (10)

An ordered structure in the space group $Pmn2_1$ was derived from Patterson and electron density maps by standard heavy-atom techniques and refined to an R index ($= \sum |F_o - |F_c|| / \sum |F_o|$) of 0.029. In the final calculation, 76 parameters [positional and anisotropic thermal parameters of the nonhydrogen atoms, a scale factor, and a secondary-extinction parameter (Larson, 1967)] were refined in a single matrix. The H atom positions were obtained from difference maps and were not refined by least squares; the H atoms were assigned temperature factors of 4.0 \AA^2 . The form factors for H were taken from Stewart, Davidson & Simpson (1965), and those for Co, N, O and Br^- were from *International Tables for X-ray Crystallography* (1962). The values for Co and Br^- were adjusted to account for the real component of anomalous dispersion (Cromer, 1965). In the last cycle of least squares, no parameter shifted by more than 10% of its e.s.d. The secondary-extinction parameter had the value $g = 5.4 (5) \times 10^{-6}$. The final goodness of fit $\{= [\sum w(F_o^2 - F_c^2)^2 / (N - P)]^{1/2}$, where N = the number of reflections and P = the number of parameters} is 1.94. A final difference map showed no excursion greater than 0.5 e \AA^{-3} , with the largest deviations in the vicinity of the Br ions. The final positional parameters are given in Table 1.*

Discussion. The structure of the cation resembles that of the tri- μ -hydroxo-dicobalt cation (Anderson, 1967; Mandel *et al.*, 1977). Fig. 1 shows the cation with bond distances; the angles are given in Table 2. The Co atoms are approximately octahedrally coordinated, the two octahedra sharing one face. The $\text{Co}\cdots\text{Co}$ distance, $2.570 (2) \text{ \AA}$, agrees well with the $2.55 (2) \text{ \AA}$ found by Anderson (1967) and the $2.565 (1) \text{ \AA}$ found by Mandel *et al.* (1977). This distance is longer than

* Lists of structure factors, thermal parameters and H atom positional parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34631 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the 2.23 \AA calculated for a complex formed by sharing the faces of two undistorted octahedra. Undoubtedly there is a significant $\text{Co}\cdots\text{Co}$ repulsion which acts to increase the $\text{Co}\cdots\text{Co}$ distance, to increase the $\text{Co}-[\mu(\text{O}) \text{ or } \mu(\text{N})]-\text{Co}$ angles, and to decrease the $\mu(\text{O})-\text{Co}-[\mu(\text{O}) \text{ or } \mu(\text{N})]$ angles. The result of all this is a set of small ($<85^\circ$) angles at each Co atom to the bridging ligands, and three somewhat larger (but still small) angles at the bridging ligands. These bridging atoms are at about van der Waals distances apart and would resist being pulled any closer together, even though that would improve the $\text{Co}-[\mu(\text{O}) \text{ or } \mu(\text{N})]-\text{Co}$ angles. As is usual, these significant deviations from normal angles occur before any marked changes in bond distances; the $\text{Co}-\text{O}$ and $\text{Co}-\text{N}$ distances are all within normal limits. A stereoview of the cation is given in Fig. 2.

The Br ions are found in two planes in the unit cell with the cations between the planes. There is extensive hydrogen bonding between the cation and the Br ions; probable hydrogen bonds are listed in Table 3. This hydrogen bonding certainly helps to form an ordered

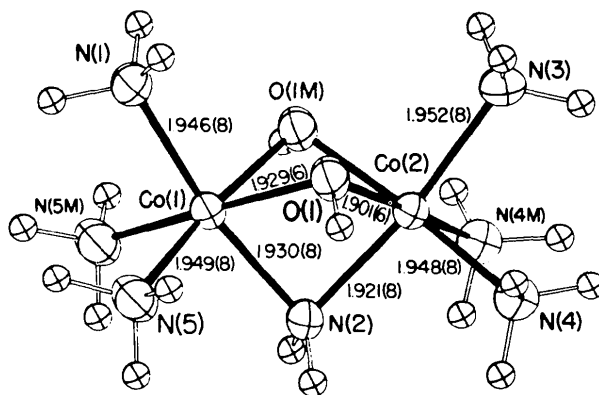


Fig. 1. An ORTEP drawing (Johnson, 1965) of the cation giving the labelling system and some bond distances (\AA).

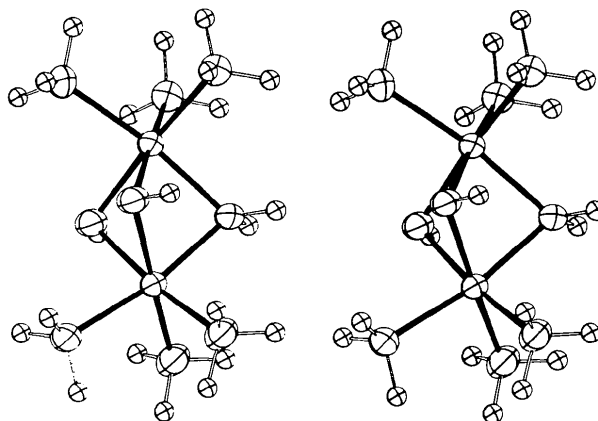


Fig. 2. A stereoview of the cation.

Table 2. Distances (Å) and angles (°) in the $[(\text{NH}_3)_3\text{Co}(\text{OH})_2\text{NH}_2\text{Co}(\text{NH}_3)_3]^{3+}$ cation

Co(1)···Co(2)	2.570 (2)	Co(1)—N(5)	1.949 (8)
Co(1)—O(1)	1.929 (6)	Co(2)—N(3)	1.952 (8)
Co(2)—O(1)	1.901 (6)	Co(2)—N(4)	1.948 (8)
Co(1)—N(2)	1.930 (8)	O(1)···O(1M)	2.421 (9)
Co(2)—N(2)	1.921 (8)	N(2)···O(1)	2.491 (10)
Co(1)—N(1)	1.946 (8)		
N(1)—Co(1)—O(1)	92.1 (3)	N(3)—Co(2)—O(1)	92.3 (3)
—N(5)	91.9 (4)	—N(4)	90.7 (4)
—N(2)	170.3 (4)	—N(2)	171.7 (4)
N(2)—Co(1)—O(1)	80.4 (3)	N(2)—Co(2)—O(1)	81.3 (3)
—N(5)	94.9 (4)	—N(4)	95.2 (4)
N(5)—Co(1)—O(1)	95.8 (3)	N(4)—Co(2)—O(1)	95.2 (3)
—N(5')	90.5 (4)	—N(4')	90.5 (4)
O(1)—Co(1)—O(1M)	77.7 (3)	O(1)—Co(2)—O(1M)	79.1 (3)
—N(5')	172.5 (3)	—N(4')	173.6 (3)
		Co(1)—O(1)—Co(2)	84.3 (3)
		Co(1)—N(2)—Co(2)	83.7 (3)

structure, but one in which the cation is still asymmetric. We suggest that the strains developed in the cation (evidenced by the highly abnormal bond angles) will lead to this observed asymmetry in any crystalline material; thus the asymmetry observed in the tri- μ -hydroxo-dicobalt cation is real and not a result of the disorder.

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Table 3. Hydrogen bonds

	Br···H	Br···A	Br···H—A	Symmetry*
Br(1)···H(O)	3.35 Å	3.71 (1) Å	104°	
H2(N5)	2.71	3.51 (1)	136	
H2(N1)	2.89	3.66 (1)	134	1
H3(N5)	3.55	3.51 (1)	125	2
H1(N3)	2.43	3.44 (1)	168	3
H(N2)	3.32	3.63 (1)	100	4
H1(N4)	2.67	3.62 (1)	158	5
H1(N5)	2.68	3.54 (1)	195	5
Br(2)···H(O)	2.75	3.63 (1)	198	
H2(N4)	3.02	3.47 (1)	108	
H3(N4)	3.11	3.47 (1)	103	
H2(N5)	3.00	3.54 (1)	114	
H2(N3)	3.19	3.65 (1)	110	
H(N2)	2.84	3.68 (1)	141	1
H1(N5)	3.28	4.01 (1)	131	2
H1(N1)	2.44	3.46 (1)	178	6
H3(N5)	2.98	3.92 (1)	156	7
Br(3)···H3(N4)	2.74	3.56 (1)	140	
H2(N3)	2.91	3.69 (1)	136	
H2(N1)	3.02	3.46 (1)	108	8
H2(N4)	2.82	3.63 (1)	139	7

* Symmetry code. The hydrogen bond is from H at x, y, z to the Br⁻ atom at:

- | | |
|---|---|
| (1) $x + 1, y, z$ | (5) $\bar{x} + \frac{1}{2}, \bar{y} + 1, z + \frac{1}{2}$ |
| (2) $x, y + 1, z$ | (6) $\bar{x} + \frac{1}{2}, \bar{y}, z - \frac{1}{2}$ |
| (3) $x, y, z + 1$ | (7) $\bar{x} + \frac{1}{2}, \bar{y} + 1, z - \frac{1}{2}$ |
| (4) $\bar{x} + \frac{1}{2}, \bar{y}, z + \frac{1}{2}$ | (8) $x, y, z - 1.$ |

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