

Structure of  $\mu$ -Amido- $\mu$ -bromo-bis[tetraamminecobalt(III)] Tetrabromide Dihydrate

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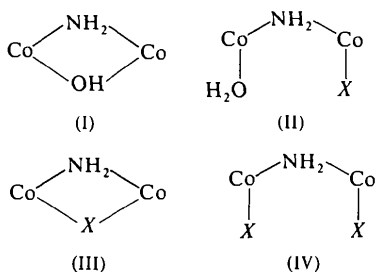
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**Abstract.**  $[\text{Co}_2\text{Br}(\text{NH}_2)(\text{NH}_3)_8]\text{Br}_4 \cdot 2\text{H}_2\text{O}$ ,  $M_r = 705.7$ , monoclinic,  $C2/c$ ,  $a = 10.090$  (3),  $b = 13.734$  (4),  $c = 13.815$  Å,  $\beta = 90.22$  (2)°,  $D_m = 2.43$ ,  $D_c = 2.45$  Mg  $\text{m}^{-3}$ ,  $Z = 4$ . The structure was solved by heavy-atom methods and refined by full-matrix least squares to a final  $R$  of 0.073 and  $R_w$  of 0.071 for 1457 reflections with  $F > 2\sigma(F)$  measured on a Syntex  $P2_1$  diffractometer using Mo  $K\alpha$  radiation. The analysis confirms the  $\mu$ -amido- $\mu$ -bromo structure [ $\text{Co}-\text{N}_{\text{br}} = 1.916$  (2),  $\text{Co}-\text{Br}_{\text{br}} = 2.461$  (1) Å,  $\angle\text{Co}-\text{N}-\text{Co} = 112.30$  (4) and  $\angle\text{Co}-\text{Br}-\text{Co} = 80.56$  (4)°] and the presence of two water molecules in the compound.

**Introduction.** The structure of binuclear ammine-cobalt(III) complexes has been the subject of numerous spectroscopic, kinetic and X-ray studies. However, there are some problems not yet solved, concerning the structure in the solid state of the compounds containing halogen atoms in the cation. The kinetic studies of Foong, Mast, Stevenson & Sykes (1971) show that depending on the halogen (Cl, Br) concentration the following structures exist in solution.



Werner (1910) originally assigned the aqua-halogeno structure (II) to the complexes prepared by reaction of the  $\mu$ -amido- $\mu$ -hydroxo sulfate with concentrated HCl and HBr. His analytical data have shown that the chloride and bromide crystallize as

tetrahydrate and dihydrate respectively. An X-ray structure analysis carried out on the chloro complex (Barro, Marsh & Schaefer, 1970) confirmed the  $\mu$ -chloro structure (III). A similar structure (III) was proposed (Foong & Sykes, 1974) for the bromo complex, obtained in the reaction of  $(\text{NH}_3)_4\text{Co}[\mu-(\text{NH}_2, \text{OH})]\text{Co}(\text{NH}_3)_4^{4+}$  bromide with concentrated HBr. The product obtained by these authors is anhydrous.

Recent IR studies (Kubicki, Kowal & Wojciechowski, 1977) suggest structure (III) and the presence of lattice water for the bromo complex. The purpose of the present study was to establish the crystal and molecular structure of this complex.

Samples of the  $\mu$ -amido- $\mu$ -bromo complex were obtained by reaction of concentrated HBr with (1)  $\mu$ - $(\text{NH}_2, \text{OH})$  chloride, bromide, nitrate, sulfate and selenate; (2)  $\mu$ - $(\text{NH}_2, \text{SO}_4)$  nitrate [manifest reaction until no  $\nu_3(\text{SO}_4)$  bands were observed in the IR spectra]; and (3)  $\mu$ - $(\text{NH}_2, \text{PO}_4)$  bromide. The products of all reactions are reddish-brown and differ somewhat in shape as well as in the quality of crystals, but their IR spectra are very similar. However, the densities of different samples measured by flotation in a bromoform-ethylene bromide mixture were found to be in the range 2.36–2.43 Mg  $\text{m}^{-3}$ . The well formed crystals were obtained by slow crystallization (6 weeks) from the water solution of equal amounts of concentrated HBr and 0.01 M  $\mu$ -amido- $\mu$ -hydroxo nitrate. A crystal  $0.20 \times 0.15 \times 0.10$  mm was chosen for X-ray analysis ( $D_m = 2.43$  Mg  $\text{m}^{-3}$ ).

Rotation and Weissenberg photographs indicated that the crystals were monoclinic, space group  $C2/c$  or  $Cc$  (systematic absences:  $h + k = 2n + 1$ ,  $l = 2n + 1$ ). All measurements were carried out on a Syntex  $P2_1$  diffractometer at room temperature. The cell parameters were determined by least-squares refinement of the setting angles of 15 reflections given by the automatic centering program [ $\lambda(\text{Mo } K\alpha) = 0.71069$  Å]. Intensities of 1704 reflections were measured up to  $2\theta = 50^\circ$  by the  $2\theta-\theta$  scan technique. 1457 reflections with  $F > 2\sigma(F)$  were regarded as observed. The scan

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rate varied from 2.0 to 20.0° min<sup>-1</sup>, depending on the intensity. After each group of 15 reflections the intensity of a standard was remeasured; no significant or regular change was observed. The intensities were corrected for Lorentz and polarization factors, but not for absorption.

The distribution of intensities, Hamilton's test and the analysis of the Patterson function indicate the centrosymmetric space group *C2/c*, so the binuclear cation must be located on the twofold axes. A bridging and one of the anionic bromines were located from a sharpened three-dimensional Patterson map. The remaining Br, Co and N atoms were found in subsequent electron density calculations. The last map clearly shows one maximum which is slightly higher than those of the N atoms, so the O atom of the water molecule was located there (*R* = 0.145).

Two cycles of full-matrix least-squares refinement with isotropic temperature factors reduced *R* to 0.089. The function minimized was  $\sum w||F_o| - |F_c||^2$  with  $w = 1/\sigma^2(F)$ . Two cycles of anisotropic refinement gave *R* = 0.073. A difference Fourier synthesis showed the maxima located near the heavy atoms. One further cycle of anisotropic refinement with dispersion correction for Br and Co changed neither *R* nor the positional parameters of the atoms. Because no absorption correction was applied, location of the H atoms was unsuccessful. The final *R* = 0.073 and *R<sub>w</sub>* = 0.071 for 1457 observed reflections.\* The atomic form factors of all atoms and anomalous-dispersion corrections for Br and Co atoms were taken from *International Tables for X-ray Crystallography* (1974). All calculations were performed with the XRAY 70 system (Stewart, Kundell & Baldwin, 1970) on the Riad 32 computer.

**Discussion.** The final positional parameters are listed in Table 1 and the interatomic distances and angles in Table 2. Fig. 1 shows the arrangement of the molecules

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34401 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final positional parameters with *e.s.d.*'s in parentheses ( $\times 10^5$  for Co and Br,  $\times 10^4$  for N and O)

	<i>x</i>	<i>y</i>	<i>z</i>
Co	34311 (16)	30325 (13)	26138 (13)
Br(1)	50000	16652 (14)	25000
Br(2)	9746 (16)	7386 (11)	8715 (11)
Br(3)	287 (14)	35793 (11)	43570 (11)
N(1)	5000	3810 (1)	2500
N(2)	3565 (1)	3103 (8)	4039 (7)
N(3)	3161 (1)	2925 (9)	1206 (8)
N(4)	2314 (1)	4203 (8)	2639 (9)
N(5)	1884 (1)	2128 (9)	2804 (8)
O	2638 (1)	465 (8)	4117 (8)

Table 2. Bond lengths (Å) and angles (°)

Co...Co <sup>I</sup>	3.183 (1)	N(1)-Co-N(2)	90.07 (4)
Br...N(1)	2.945 (1)	N(1)-Co-N(3)	94.13 (4)
Co-Br(1)	2.461 (1)	N(1)-Co-N(4)	91.1 (6)
Co-N(1)	1.916 (2)	N(1)-Co-N(5)	174.7 (5)
Co-N(2)	1.976 (3)	Br(1)-Co-N(2)	93.40 (4)
Co-N(3)	1.968 (3)	Br(1)-Co-N(3)	88.1 (5)
Co-N(4)	1.964 (5)	Br(1)-Co-N(4)	174.3 (5)
Co-N(5)	2.013 (5)	Br(1)-Co-N(5)	92.1 (5)
		N(2)-Co-N(3)	175.69 (5)
		N(2)-Co-N(4)	88.8 (5)
		N(2)-Co-N(5)	87.1 (3)
Co-N(1)-Co <sup>I</sup>	112.30 (4)	N(3)-Co-N(4)	90.1 (6)
Co-Br(1)-Co <sup>I</sup>	80.56 (4)	N(3)-Co-N(5)	88.8 (3)
N(1)-Co-Br(1)	83.57 (4)	N(4)-Co-N(5)	93.3 (6)

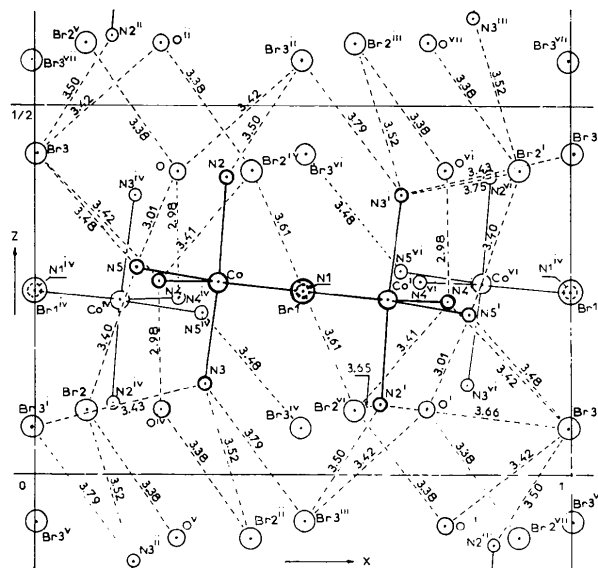


Fig. 1. A projection of the unit cell down the *y* axis. Hydrogen bonds are indicated by dashed lines; the distances given are between the heavy atoms involved in the hydrogen bond. Symmetry code: (i)  $\bar{x}, y, \frac{1}{2} - y$ ; (ii)  $\frac{1}{2} - x, \frac{1}{2} - y, \bar{z}$ ; (iii)  $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$ ; (iv)  $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$ ; (v)  $x, \bar{y}, \frac{1}{2} + z$ ; (vi)  $\frac{1}{2} + x, \frac{1}{2} + y, z$ ; (vii)  $\bar{x}, \bar{y}, \bar{z}$ ; unprimed atoms have the coordinates  $x, y, z$ .

in half the unit cell. The geometry of the cation is typical for doubly bridged binuclear Co<sup>III</sup> complexes (Fig. 2). The Co-N distances vary from 1.916 to 2.013 Å. The bridging bond length [Co-N(1)] is significantly smaller, and that *trans* to it [Co-N(5)] is longer than the mean value for all Co-N bonds (1.967 Å). The mean value of the Co-N(1) and Co-N(5) bonds is equal to the overall mean. This could indicate the existence of a *trans* effect in the cation. This is rather surprising because of the absence, in the coordination sphere of Co<sup>III</sup>, of the ligands capable of forming  $\pi$  bonds with the central atom. However, the strong Co-N(1) bridging  $\sigma$  bond as well as the presence of a large Br atom *cis* to N(5) could influence the elongation of Co-N(5).

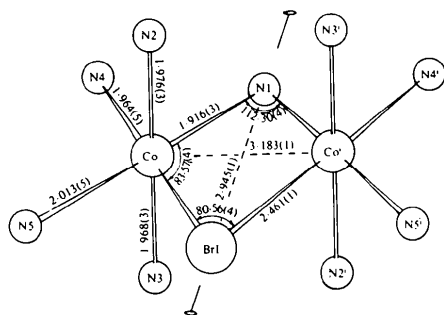


Fig. 2. Geometry of the  $\mu$ -amido- $\mu$ -bromo-bis[tetraamminecobalt(III)] cation.

The bridging N(1) and Br(1) atoms, both Co atoms and the N atoms *trans* to the bridges are approximately coplanar. The angle between this plane and the plane defined by N(2), N(3), N(2') and N(3') is  $90^\circ$ .

Although the H atoms were not located, some of the intermolecular distances indicate a well developed system of hydrogen bonds (Fig. 1). The N(1)···Br(2<sup>iv</sup>) [and Br(2<sup>iv</sup>)] distance of 3.61 Å suggests that the amido bridge is involved in hydrogen bonding. A corresponding distance of 3.59 Å was found in

$\mu$ -amido- $\mu$ -sulfato-bis[bis(ethylenediamine)cobalt(III)] bromide (Thewalt, 1971).

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