Structure of μ-Amido-μ-formato-bis[tetraamminecobalt(III)] Tetrachloride Tetrahydrate, [Co₂NH₂(CHO₂)(NH₃)₈]Cl₄.4H₂O

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Abstract. $M_r = 529.0$, orthorhombic, *Pnma*, $a = 11.661$ (1), $b = 19.811$ (2), $c = 9.105$ (1) Å, $V = 2103.4$ Å³, $Z = 4$, $D_x = 1.760$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 2.12$ mm⁻¹, $F(000) = 1096$, $T = 291$ K, $R = 0.033$ for 1627 observed reflections. As required by a crystallographic mirror plane, both bridging ligands are symmetrical, with Co–NH₂ 1.958 (2) and Co–O 1.912 (2) Å, Co–N–Co 127.8 (2)°. The mean Co–NH₃ of 1.963 (17) Å is essentially the same as the Co–NH₂ length. A three-dimensional network of hydrogen bonds links the cations, anions and water molecules.

Introduction. Carboxylate-bridged binuclear complexes are of current interest because of the presence of such a unit in the naturally occurring oxygen-carrier hemerythrin. In interpreting crystallographic (Sten-kamp, Sieker, Jensen & Sanders-Loehr, 1981) and EXAFS (Elam, Stern, McCallum & Sanders-Loehr, 1983) studies of this protein, simple model complexes are of value. A series of bridged binuclear complexes can be readily prepared and studied.

In previous crystallographic studies of dicobalt(III) complexes with bridging acetate ligands, an asymmetrically bonded acetate was reported for [{(NH₃)₃Co}₂(OH)₂(O₂CCH₃)]Br₃.3H₂O (Mandel, Marsh, Schaefer, Mandel & Wang, 1977), in contrast to an essentially symmetrical acetate bridge in NH₄[{(NH₃)₃Co}₂(OH)(NH₂)(O₂CCH₃)].(HSO₄)₄ (Schaefer, 1983). We report here the structure of a complex with a strictly symmetrical formate bridge. The preparation has already been described (Scott & Sykes, 1972).

Experimental. Crystals obtained from aqueous solution, mounted on glass fibres, $0.15 \times 0.27 \times 0.69$ mm. Stoe–Siemens AED diffractometer. Unit-cell parameters from 2θ values of 30 reflections ($20 < 2\theta < 25°$). Systematic absences: $0kl$ for $k+l$ odd, $hk0$ for h odd; space group *Pnma* or *Pn2₁a* (*Pna2₁* reoriented), *Pnma* confirmed by structure solution. 1899 non-extinguished reflections with $2\theta < 50°$, index ranges: $h \, 0 \to 13$, $k \, 0 \to 23$, $l \, 0 \to 10$. Profile analysis on-line (Clegg, 1981). No significant intensity variation for three standard reflections. Semi-empirical absorption corrections based on azimuthal scan data for equivalent reflections, transmission 0.298–0.413. 1627 reflections with $F > 4\sigma(F)$. Co atom from Patterson synthesis, others from difference syntheses. Blocked-cascade refinement on F, $w^{-1} = \sigma^2(F) + 0.00036F^2$. H atoms constrained to give N–H = O–H = 0.85 Å, C–H = 0.96 Å, H–N–H = 109.5° for NH₃, common isotropic U for H atoms attached to each N, O or C. Anisotropic thermal parameters for other atoms. No extinction correction. Scattering factors from *International Tables for X-ray Crystallography* (1974). 144 parameters, $R = 0.033$, $wR = 0.044$, slope of normal probability plot 1.41. Δ/σ max. = 0.008, mean = 0.001. Largest peak in final difference map 0.46 e Å⁻³, largest hole −0.58 e Å⁻³. Programs: *SHELXTL* (Sheldrick, 1978), diffractometer control program by WC.

Discussion. Atomic coordinates are given in Table 1, bond lengths and angles in Table 2.* The cation structure is shown in Fig. 1. A crystallographic mirror plane passes through both bridging ligands, which are, therefore, symmetrically bonded to the two Co atoms. The Co–NH₂ bond length of 1.958 (2) Å is essentially the same as the mean Co–NH₃ of 1.963 (17) Å; the shortest Co–NH₃ bond is *trans* to the Co–O bond, while the longest is *trans* to the Co–NH₂ bond, demonstrating the stronger *trans* influence of the bridging NH₂ group compared with formate.

The bridging formate ligand has Co–O 1.912 (2) Å, C–O 1.248 (3) Å, not significantly different from the essentially symmetrical bridging acetate ligand reported by Schaefer (1983). A symmetrical carboxylate bridge is expected in these complexes, not only because of the presumed equivalence of the metal atoms, but also on the basis of infrared spectroscopy (Scott & Sykes, 1972). The unsymmetrical bridging acetate reported by Mandel, Marsh, Schaefer, Mandel & Wang (1977)

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39614 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

must be regarded with some suspicion, as suggested by these authors. We have examined crystals of the same compound, and have found diffuse reflections with half-integral values of k for a unit cell otherwise indistinguishable from that reported (Clegg, 1983, unpublished). Whether this is an intrinsic property of the crystalline compound or only of the specific batch of crystals is unclear, and the bearing of this on the reported structure is under investigation (Marsh, 1984).

In contrast to the two acetate-bridged complexes, the present structure has only two bridging ligands. The Co—N—Co angle of 127·8 (2)° is rather greater than the 99·7° observed in $[\{(en)_2Co\}_2(OH)(NH_2)]^{4+}$ (en is ethylenediamine) (Thewalt & Marsh, 1971) and 113° in $[\{(NH_3)_4Co\}_2(NH_2)(Cl)]^{4+}$ (Barro, Marsh & Schaefer, 1970), reflecting the larger central ring size when the three-atom carboxylate bridge is present instead of a second single-atom bridge. Even larger angles are observed when NH_2 is the only bridge in the structures of $[\{(NH_3)_5Co\}_2(NH_2)]^{5+}$ (153°; Schaefer, Cordes & Marsh, 1968) and $[\{(en)_2(NH_3)Co\}_2(NH_2)]^{5+}$ (143·8°; Rotzinger & Marty, 1983). Here the NH_2 bridge is strained by the close approach of ligands attached to the two Co atoms.

The cations, anions and water molecules in the crystal structure are linked by an extensive three-dimensional network of hydrogen bonds.

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{Å}^2 \times 10^4$)

$U = \frac{1}{3}$(trace of the orthogonalized U_{ij} matrix).

	x	y	z	U
Co	1862 (1)	1613 (1)	5134 (1)	232 (1)
O(1)	1158 (2)	1927 (1)	6903 (2)	312 (6)
C	968 (3)	2500	7417 (4)	305 (12)
N(1)	2067 (3)	2500	4224 (3)	262 (10)
N(2)	3377 (2)	1676 (1)	6065 (3)	303 (7)
N(3)	331 (2)	1513 (1)	4276 (3)	347 (8)
N(4)	2545 (2)	1186 (1)	3427 (3)	400 (8)
N(5)	1647 (2)	718 (1)	6082 (3)	376 (8)
Cl(1)	6 (1)	2500	1353 (1)	400 (3)
Cl(2)	8317 (1)	2500	5684 (1)	461 (4)
Cl(3)	6144 (1)	−333 (1)	1676 (1)	511 (3)
O(2)	1945 (3)	1174 (2)	151 (4)	815 (14)
O(3)	9829 (3)	671 (2)	944 (5)	935 (15)

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

Co—O(1)	1·912 (2)	Co—N(1)	1·958 (2)
Co—N(2)	1·963 (2)	Co—N(3)	1·960 (3)
Co—N(4)	1·940 (3)	Co—N(5)	1·988 (3)
O(1)—C	1·248 (3)		

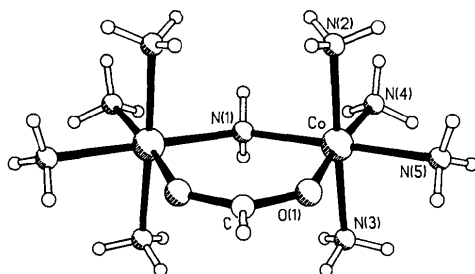| O(1)—Co—N(1)	96·7 (1)	O(1)—Co—N(2)	90·1 (1)
N(1)—Co—N(2)	90·9 (1)	O(1)—Co—N(3)	88·7 (1)
N(1)—Co—N(3)	91·9 (1)	N(2)—Co—N(3)	177·1 (1)
O(1)—Co—N(4)	173·1 (1)	N(1)—Co—N(4)	90·2 (1)
N(2)—Co—N(4)	90·3 (1)	N(3)—Co—N(4)	90·6 (1)
O(1)—Co—N(5)	82·6 (1)	N(1)—Co—N(5)	179·2 (1)
N(2)—Co—N(5)	89·0 (1)	N(3)—Co—N(5)	88·2 (1)
N(4)—Co—N(5)	90·6 (1)	Co—O(1)—C	133·5 (2)
O(1)—C—O(1a)	130·9 (4)	Co—N(1)—Co(a)	127·8 (2)

Fig. 1. Structure of the cation, showing the numbering scheme for the unique atoms.

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