

*Acta Cryst.* (1975). B31, 914 **$\mu$ -Amido- $\mu$ -nitrito-bis[tetraamminecobalt(III)] Tetrachloride Dihydrate**

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**Abstract.**  $[\text{Co}_2(\text{NH}_3)_8(\text{NH}_2)(\text{NO}_2)]\text{Cl}_4 \cdot 2\text{H}_2\text{O}$ , orthorhombic  $Ccm2_1$ ,  $a = 11.221$  (1),  $b = 17.529$  (3),  $c = 9.729$  (1) Å, 296 (1) K,  $Z = 4$ ,  $D_m = 1722$ ,  $D_x = 1715 \text{ kg m}^{-3}$ . The mirror symmetry across the  $ac$  plane is associated with disorder involving the nitrito bridge polarity between the cobalt atoms. The geometry of the  $\mu$ -amido- $\mu$ -nitrito-bis[tetraamminecobalt(III)] moiety is similar to that found in the lower symmetry tetrahydrate form.

**Introduction.** The title compound was prepared by synthesizing  $\mu$ -amido- $\mu$ -superoxo-bis[tetraamminecobalt(III)] tetranitrate (Davies, Mori, Sykes & Weil, 1970), converting the superoxo bridge to the nitrito bridge (Werner, 1910) and then transforming the nitrate to the chloride. Crystals were grown from 6M aqueous hydrochloric acid at room temperature. Precession photographs showed  $mmm$  symmetry with systematic absences ( $hkl$ ,  $h+k=2n+1$ ;  $0kl$ ,  $l=2n+1$ ) indicating the space group to be  $Ccmm$ ,  $Ccm2_1$  or  $Cc2m$ . For  $Z=4$ , the first imposes  $2/m$  or  $mm$  point symmetry on the  $\mu$ -amido- $\mu$ -nitrito-bis[tetraamminecobalt(III)]<sup>2+</sup> ion. For  $Ccm2_1$ , the point symmetry imposed is  $m$ , whereas  $Cc2m$  demands  $m$  or 2. In the former case, however, the atomic packing required is not consistent with the expected dimensions of the cation.

A sample with the shape of a truncated tetragonal bipyramid and dimensions  $0.2 \times 0.2 \times 0.2$  mm was chosen for data collection. The integrated intensities of

1136 independent reflexions, between 0 and  $55^\circ$  in  $2\theta$ , were measured using a Picker automatic diffractometer equipped with a graphite monochromator. A  $\theta$ - $2\theta$  scan mode was used with a base width of  $2.5^\circ$ , a scan rate of  $2^\circ \text{ min}^{-1}$  and a 20 s background count at both limits of the scan. The data were reduced to observed structure factors by the usual methods. The crystal shape approximates a sphere with radius of 0.1 mm,  $\mu(\text{Mo K}\alpha) = 23.8 \text{ cm}^{-1}$ . Absorption corrections were therefore not applied to the data.

Initial attempts to solve the structure by Patterson methods in the space group  $Cc2m$  were not successful. Moreover, electron density maps generated from a partial solution of the Patterson function showed new peaks approximately related to the trial solution by a mirror normal to  $\mathbf{b}$ . A solution in the space group  $Ccm2_1$  was then attempted with a disordered  $\text{NO}_2$  bridge between the cobalt atoms (standard symbol  $Cmc2_1$ ). The averaged molecule thus shows a mirror plane between the cobalt atoms.

The cobalt and chlorine atoms were found from the Patterson map. The atoms Cl(2) and Cl(3) were in the special position 4(a) (*International Tables for X-ray Crystallography*, 1969). The other non-hydrogen atoms were then found from electron-density Fourier maps. All but two of the hydrogen atoms were found from difference Fourier maps. One of the missing hydrogen atoms [H(9) on N(3)] was placed to fit the geometry of  $\text{NH}_3$ . The other missing hydrogen atom [on the water molecule, O(3)] was left undetermined. Scattering fac-

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Table 1. Fractional coordinates and thermal parameters with estimated standard deviations for non-hydrogen atoms

All values have been multiplied by  $10^4$ . The origin is fixed by  $z/c$  for the cobalt atom.

The temperature-factor expression is  $\exp[-(\beta_{11}h^2 + \dots + 2\beta_{12}hk + \dots)]$ .

	$x/a$	$y/b$	$z/c$	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Co	2365.0 (0.4)	939.4 (0.3)	2500	23.8 (0.4)	9.4 (0.2)	42.5 (0.5)	0.9 (0.2)	0.1 (0.6)	-0.1 (0.4)
Cl(1)	428 (1)	2625 (1)	451 (2)	55 (1)	24 (1)	165 (2)	8 (1)	9 (1)	32 (1)
Cl(2)	3794 (2)	5000	3750 (2)	57 (1)	45 (1)	51 (2)	0	17 (1)	0
Cl(3)	648 (2)	5000	1066 (2)	52 (1)	29 (1)	78 (2)	0	30 (2)	0
O(1), N(6)	1859 (3)	373 (2)	4101 (4)	36 (4)	16 (1)	44 (4)	-1 (1)	2 (3)	1 (2)
O(2)	1488 (7)	626 (4)	5134 (8)	69 (7)	22 (2)	59 (8)	3 (3)	1 (6)	-12 (4)
O(3)	2349 (8)	3515 (5)	2507 (16)	192 (11)	57 (3)	429 (25)	-45 (5)	-115 (14)	94 (10)
N(1)	3993 (4)	993 (3)	3218 (5)	40 (3)	18 (1)	58 (5)	-2 (2)	-11 (3)	-11 (2)
N(2)	731 (4)	937 (3)	1815 (6)	30 (3)	16 (1)	80 (5)	-1 (2)	-2 (3)	6 (2)
N(3)	1991 (5)	1886 (3)	3560 (6)	59 (4)	14 (1)	96 (6)	3 (2)	2 (4)	-9 (2)
N(4)	2820 (5)	1529 (3)	905 (6)	43 (3)	19 (1)	78 (5)	-0.8 (2)	7 (4)	14 (3)
N(5)	2728 (5)	0	1579 (6)	31 (4)	11 (1)	39 (5)	0	-3 (4)	0

tors for the non-hydrogen atoms were from Cromer & Mann (1968) and the scattering factor for the hydrogen atoms were from Stewart, Davidson & Simpson (1965). The scattering factor for the disordered bridging atom was averaged from those for oxygen and nitrogen. The non-bridging nitrito oxygen atom, O(2), was given half weight. The temperature factors of the non-hydrogen atoms were varied anisotropically. The isotropic temperature factors of the hydrogen atoms were set equal to the isotropic temperature factors of the atom to which they were bonded and were not varied. The structure was refined by full-matrix least-squares calculations using the program *ORFLS* (Busing, Martin & Levy, 1962) to a least-squares residue,  $R = (\sum \omega |F_o| - |F_c|)^2 / \sum \omega |F_o|^2)^{1/2}$ , of 0.038.\* The weighting scheme used has been given elsewhere (Stone, Robertson & Stanley,

1971). 68 reflexions were excluded from the refinement either because they were weak or had been measured

Table 2. Fractional coordinates and thermal parameters with estimated standard deviations for hydrogen atoms

All fractional coordinates have been multiplied by  $10^3$ . The coordinates of atom H(9) were not varied. The isotropic temperature factors were taken from the atom bonded to the hydrogen atom.

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> (Å <sup>2</sup> )
H(1)	445 (4)	80 (3)	280 (5)	0.56
H(2)	419 (4)	143 (3)	349 (5)	0.56
H(3)	405 (4)	85 (3)	410 (6)	0.56
H(4)	50 (4)	71 (3)	130 (6)	0.54
H(5)	40 (4)	142 (3)	168 (5)	0.54
H(6)	17 (4)	81 (2)	271 (5)	0.54
H(7)	110 (4)	195 (3)	393 (5)	0.71
H(8)	250 (4)	216 (3)	387 (6)	0.71
H(9)	194	226	266	0.71
H(10)	295 (5)	129 (3)	28 (6)	0.65
H(11)	226 (4)	185 (3)	61 (6)	0.65
H(12)	341 (5)	174 (3)	91 (5)	0.65
H(13)	240 (6)	0	63 (8)	0.36
H(14)	363 (6)	0	127 (7)	0.36
H(15)	254 (6)	393 (4)	215 (8)	2.64

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30790 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. Bond distances (Å) and angles (°) for the cation

Co—Co	3.293 (1)	Co—N(5)	1.918 (3)
Co—N(1)	1.958 (5)	Co—[O(1), N(6)]	1.933 (4)
Co—N(2)	1.951 (4)	O(1)—N(6)	1.307 (7)
Co—N(3)	1.998 (5)	[O(1), N(6)]—O(2)	1.175 (8)
Co—N(4)	1.933 (5)		
N(1)—Co—N(3)	88.42 (2)	N(3)—Co—N(4)	91.49 (2)
N(1)—Co—N(4)	90.84 (2)	N(3)—Co—[O(1), N(6)]	87.08 (3)
N(1)—Co—N(5)	90.52 (2)	N(4)—Co—N(5)	91.60 (2)
N(1)—Co—[O(1), N(6)]	90.64 (2)	N(5)—Co—[O(1), N(6)]	89.86 (3)
N(2)—Co—N(3)	88.93 (2)	Co—N(5)—Co	118.28 (1)
N(2)—Co—N(4)	88.60 (2)	Co—O(1)—N(6)	120.93 (4)
N(2)—Co—N(5)	92.17 (2)	Co—[O(1), N(6)]—O(2)	126.78 (4)
N(2)—Co—[O(1), N(6)]	89.86 (3)	O(1)—N(6)—O(2)	112.24 (4)

Table 4. Hydrogen-bond lengths (Å) and angles (°)

Symmetry-related sites generated from *xyz*

i	<i>x</i>	<i>y</i>	<i>z</i>	iv	$\frac{1}{2} + x$	$\frac{1}{2} - y$	<i>z</i>
ii	$\frac{1}{2} + x$	$\frac{1}{2} + y$	<i>z</i>	v	$-x$	<i>y</i>	$\frac{1}{2} + z$
iii	$\frac{1}{2} - x$	$\frac{1}{2} - y$	$\frac{1}{2} + z$				

<i>D—H—A</i>	<i>D—H</i> (Å)	<i>D—A</i> (Å)	<i>H—A</i> (Å)	<i>D—H—A</i> (Å)
N(1)—H(1)···Cl(3 <sup>ii</sup> )	0.73 (5)	3.295 (5)	2.58 (5)	167 (3)
N(1)—H(2)···Cl(1 <sup>iii</sup> )	0.84 (5)	3.318 (5)	2.56 (6)	150 (3)
N(1)—H(3)···Cl(3 <sup>iii</sup> )	0.90 (5)	3.296 (5)	2.44 (5)	158 (3)
N(2)—H(4)···Cl(2 <sup>iii</sup> )	0.69 (5)	3.445 (6)	2.88 (5)	141 (3)
···O(2 <sup>v</sup> )		3.029 (9)	2.51 (5)	134 (5)
N(2)—H(5)···Cl(1 <sup>i</sup> )	0.93 (5)	3.262 (5)	2.43 (5)	148 (3)
N(2)—H(6)···Cl(2 <sup>ii</sup> )	1.09 (5)	3.311 (5)	2.34 (4)	147 (3)
N(3)—H(7)···Cl(1 <sup>v</sup> )	1.07 (5)	3.527 (5)	2.55 (5)	151 (3)
N(3)—H(8)···Cl(1 <sup>iii</sup> )	0.81 (5)	3.536 (5)	2.82 (5)	150 (3)
N(3)—H(9)···O(3 <sup>i</sup> )	1.10	3.061 (11)	2.25	129
N(4)—H(10)···O(3 <sup>iii</sup> )	0.75 (6)	3.312 (7)	2.74	135 (5)
N(4)—H(11)···Cl(1 <sup>i</sup> )	0.90 (5)	3.331 (5)	2.46 (5)	163 (3)
N(4)—H(12)···Cl(1 <sup>iv</sup> )	0.76 (6)	3.310 (5)	2.57 (6)	169 (3)
N(5)—H(13)···Cl(2 <sup>iii</sup> )	0.99 (4)	3.239 (6)	2.27 (7)	166 (3)
N(5)—H(14)···Cl(3 <sup>ii</sup> )	1.05 (4)	3.314 (6)	2.28 (6)	168 (3)
O(3)—H(15)···Cl(2 <sup>i</sup> )	0.83 (8)	3.296 (10)	2.82 (7)	118 (3)
···O(2 <sup>iii</sup> )		3.049 (15)	2.37 (8)	139 (5)

during a machine malfunction. Positional and thermal parameters are given in Tables 1 and 2.

**Discussion.** The atom labelling sequence is given in Fig. 1. The bond distances and angles for the cation are given in Table 3. The intermolecular connectivity consists primarily of hydrogen bonding through the chloride ions, linking ammine (and amido) nitrogen atoms. Information relating to the hydrogen-bonding network is given in Table 4. The hydrogen atom H(4) on N(2) and the water hydrogen atom H(15) appear to form weak bifurcated hydrogen bonds. However, both bifurcated bonds involve the disordered nitrito oxygen atom O(2) and the possibility remains that N(2) and the water are bonded to O(2) when the O(2) site is occupied and to Cl(2) when it is not. The hydrogen bonds formed by H(8) and H(16) are also weak. The anisotropic temperature factors of the water oxygen atom, O(3), are large. The observed and calculated densities using the stoichiometry  $[\text{Co}_2(\text{NH}_3)_8(\text{NH}_2)(\text{NO}_2)]\text{Cl}_4 \cdot 2\text{H}_2\text{O}$  are consistent and partial occupancy of the O(3) site is not indicated. Rather, we suspect that the disorder associated with the atom O(2) is transferred to the O(3) atom through the hydrogen atom H(15) and that the missing hydrogen atom is also disordered.

The structure of monoclinic  $\mu$ -amido- $\mu$ -nitrito-bis[tetraamminecobalt(III)] tetrachloride tetrahydrate has been reported earlier (Thewalt & Marsh, 1970). The geometry of the cation in the tetrahydrate is not significantly different from that in the dihydrate. It is possible that the latter is the orthorhombic form reported by Werner (1910) to be a monohydrate. The dihydrate is presently being used to study the electron paramagnetic resonance of  $\mu$ -amido- $\mu$ -superoxo-bis[tetraamminecobalt(III)]<sup>4+</sup> in solid solution.

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### Tris-(1,3-propanedionato)chromium(III)

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**Abstract.** Tris-(1,3-propanedionato)chromium(III), the simplest transition-metal 1,3-diketonate chelate, is monoclinic,  $P2_1/c$ ,  $a = 10.803$  (8),  $b = 8.121$  (5),  $c = 14.583$  (9) Å,  $\beta = 120.24$  (3)°,  $\rho_{\text{calc}} = 1.60$  g cm<sup>-3</sup>,  $\rho_{\text{meas}} = 1.58$  g cm<sup>-3</sup>. The molecule has crystallographic symmetry 2 and idealized symmetry 32.

**Introduction.** The chelates of 1,3-diketonates have been studied extensively for a variety of reasons. One reason

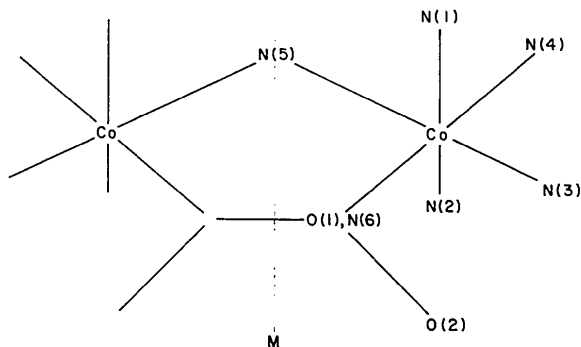


Fig. 1. Atom labelling scheme for the cation. Oxygen atom O(2) is assumed to be bonded to nitrogen atom N(6).

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for continuing interest in these systems is the ease with which the ring substituents may be varied, resulting in dramatic changes in the chelate's physical properties. Spectral transitions in the visible region, for example, are affected by the nature of the substituent groups. Spectral shifts brought about by substituent group changes are generally explained in terms of the groups' electronic effects. Although a large number of 1,3-diketonate chelate structures have been reported, no