

trans-Aquafluorobis(1,3-propanediamine)chromium(III) Diperchlorate

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Abstract. $[\text{Cr}(\text{C}_3\text{H}_{10}\text{N}_2)_2\text{F}(\text{H}_2\text{O})](\text{ClO}_4)_2$, $M_r = 415.90$, monoclinic, $P2_1/n$, $a = 17.406$ (3), $b = 9.506$ (2), $c = 10.216$ (2) Å, $\beta = 94.26$ (2)°, $V = 1686$ (1) Å³, $Z = 4$, $D_x = 1.64$ Mg m⁻³. The structure was solved with *MULTAN* and *DIRDIF* computer programs and refined by the full-matrix least-squares method. The final R value is 0.051 for 3279 observed reflections. The Cr atom displays an octahedral coordination, and the two six-membered rings have chair conformations.

Introduction. In connection with a systematic study of magnetic properties of compounds with the fluoro-bis(1,3-propanediamine)chromium moiety, the crystal structure of the title compound has been solved.

A red crystal $0.09 \times 0.09 \times 0.11$ mm was selected for measurements on a Philips PW 1100 four-circle diffractometer. The unit cell was measured by centring 25 independent reflections and refining the orientation matrix and unit-cell parameters by least-squares calculations. Intensities were collected with Mo $K\alpha$ radiation, monochromatized by reflection from a graphite crystal. 3351 independent reflections were measured in the range $2\theta \leq 60^\circ$; 3279 of these were considered as observed with $I \geq 2.5(I)$.

The location of the Cr atom was determined using the *MULTAN* system of computer programs (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); the remaining non-hydrogen atoms were found by means of the program *DIRDIF* (Beurskens, Bosman, Doesburg, Gould, Van den Hark & Prick, 1980). The structure was refined isotropically and anisotropically by the least-squares method using the program *SHELX* (Sheldrick, 1976). The function minimized was $w||F_o| - |F_c||^2$, where $w = [\sigma^2(F_o) + 0.0203|F_o|^2]^{-1}$. A difference synthesis revealed the positions of 18 H atoms; these were refined isotropically and the remaining atoms anisotropically. The refinement was terminated at $R = 0.051$ for all

Table 1. Atomic coordinates ($\times 10^4$, for Cr $\times 10^5$, for H $\times 10^3$) and equivalent isotropic thermal parameters (Å²)

$$B_{\text{eq}} = 8\pi^2/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j. \text{ For H atoms } U_{\text{iso}} = 0.066 \text{ (4) \AA}^2.$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq}
Cr	15553 (3)	22126 (4)	69935 (4)	1.8 (1)
O	934 (2)	427 (3)	6854 (3)	3.5 (4)
N(2)	692 (2)	3048 (3)	8042 (3)	2.7 (4)
C(3)	502 (3)	2437 (6)	9307 (5)	3.9 (4)
C(4)	1220 (3)	2282 (6)	10242 (4)	4.2 (4)
C(5)	1745 (3)	1089 (5)	9861 (4)	3.8 (4)
N(6)	2153 (2)	1435 (3)	8684 (3)	2.3 (3)
N(7)	980 (2)	2945 (4)	5280 (3)	2.9 (3)
C(8)	1462 (3)	3621 (4)	4304 (4)	3.3 (3)
C(9)	2030 (3)	2619 (5)	4788 (4)	3.9 (3)
C(10)	7664 (3)	2869 (5)	-216 (4)	3.4 (3)
N(11)	2367 (2)	1284 (3)	5860 (3)	2.6 (3)
F	2099 (1)	3899 (2)	7197 (2)	2.5 (3)
Cl(1)	-633 (1)	3149 (1)	2674 (1)	2.5 (1)
O(11)	-8 (2)	2178 (3)	2687 (4)	3.8 (3)
O(12)	-484 (2)	4158 (3)	3694 (3)	4.3 (3)
O(13)	-745 (2)	3853 (3)	1435 (3)	4.4 (3)
O(14)	-1330 (2)	2380 (3)	2864 (4)	4.4 (3)
Cl(2)	3832 (1)	3478 (1)	1510 (1)	3.1 (1)
O(21)	3137 (2)	3617 (4)	689 (4)	4.9 (3)
O(22)	4449 (2)	4101 (6)	850 (4)	6.3 (3)
O(23)	3774 (3)	4177 (5)	2717 (4)	6.7 (3)
O(24)	4016 (3)	2047 (4)	11733 (6)	8.0 (4)
H(O)	108 (3)	-22 (6)	703 (5)	
H(N2)	75 (3)	395 (6)	818 (5)	
H(N2)'	29 (4)	294 (6)	751 (6)	
H(C3)	24 (3)	152 (6)	900 (5)	
H(C3)'	11 (3)	288 (6)	975 (6)	
H(C4)	167 (3)	320 (6)	1009 (6)	
H(C4)'	115 (3)	212 (5)	1114 (6)	
H(C5)	212 (3)	104 (6)	1054 (6)	
H(N6)	239 (4)	154 (7)	844 (7)	
H(N6)'	260 (4)	230 (7)	891 (6)	
H(N7)	63 (3)	192 (6)	504 (6)	
H(N7)'	57 (4)	335 (6)	540 (6)	
H(C8)	123 (4)	307 (7)	481 (7)	
H(C9)	191 (3)	153 (6)	337 (5)	
H(C9)'	226 (3)	283 (6)	305 (7)	
H(C10)	306 (3)	300 (5)	520 (6)	
H(C10)'	292 (3)	158 (6)	437 (6)	

Table 2. Bond angles (°) for the cation

N(2)—Cr—O	87.3 (1)	N(7)—Cr—O	90.0 (1)
N(6)—Cr—O	89.6 (1)	N(11)—Cr—O	89.2 (1)
N(2)—Cr—F	89.7 (1)	N(7)—Cr—F	90.9 (1)
N(6)—Cr—F	89.7 (1)	N(11)—Cr—F	93.8 (1)
N(2)—Cr—N(6)	92.5 (1)	N(7)—Cr—N(11)	88.7 (1)
N(2)—Cr—N(7)	89.1 (1)	N(6)—Cr—N(11)	89.6 (1)
C(3)—N(2)—Cr	121.4 (2)	C(8)—N(7)—Cr	116.6 (2)
C(4)—C(3)—N(2)	111.1 (4)	C(9)—C(8)—N(7)	112.3 (3)
C(5)—C(4)—C(3)	113.0 (4)	C(10)—C(9)—C(8)	115.1 (4)
N(6)—C(5)—C(4)	112.1 (3)	N(11)—C(10)—C(9)	112.8 (3)
Cr—N(6)—C(5)	120.8 (2)	Cr—N(11)—C(10)	117.9 (2)

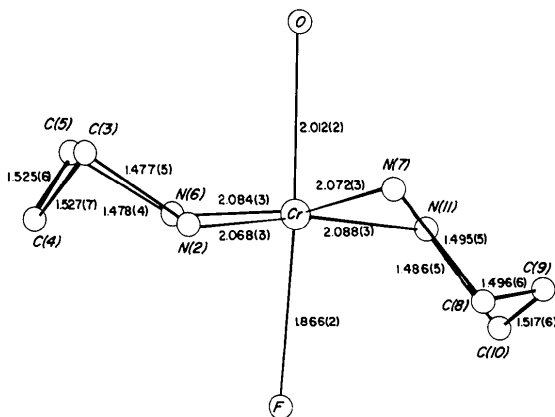
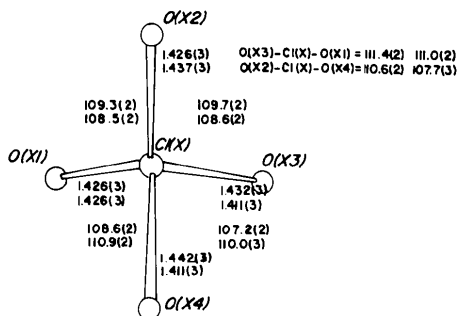


Fig. 1. A view of the cation, with the numbering of the atoms and bond distances (Å).

Fig. 2. A view of the perchlorate ion, with the numbering of atoms ($X = 1$ or 2), and bond distances (Å) and angles (°).

observed reflections.* Table 1 shows final atomic coordinates and equivalent isotropic temperature coefficients. Fig. 1 shows the cation with the atom-numbering scheme and bond distances. Fig. 2 shows the bond distances and angles for the anion. Bond angles for the cation are in Table 2.

Discussion. The Cr atom displays an octahedral coordination, with the N atoms of the 1,3-propane-

diamine ligands in the equatorial plane and the fluoro and aqua ligands in *trans* positions. The Cr—N distances [mean 2.08 (1) Å, range 2.068 (3)—2.088 (3) Å] are similar to those observed in Cr complexes with ethylenediamine or 1,3-propanediamine ligands (mean 2.08 Å, range 2.01–2.09 Å) (Alcock, de Meester & Kemp, 1978; Brouty, Spinat & Whuler, 1977; Brouty, Spinat, Whuler & Herpin, 1977; Brouty, Whuler, Spinat & Herpin, 1977; Duesler & Raymond, 1978; Journak & Raymond, 1974; Whuler, Brouty, Spinat & Herpin, 1977; Whuler, Spinat & Brouty, 1978). The angles between the Cr—O and F—Cr bonds and the equatorial mean plane are 90.0 (1)°.

The two six-membered rings have chair conformations (Fig. 1). A comparative study of these two rings shows differences in the values of the torsion angles (Table 3) and the bond distances and angles. Thus, the mean N—C (1.490 Å) and C—C (1.506 Å) distances and the N—Cr—N angle (88.7°) of ring B are similar to those observed in the literature (1.49, 1.50 Å, and 89°, respectively) (Duesler & Raymond, 1978; Journak & Raymond, 1974), while ring A shows a shorter mean N—C distance (1.477 Å), a larger mean C—C distance (1.526 Å) and a larger N—Cr—N angle (92.5°).

Table 3. Selected torsion angles (°)

N(6)—Cr—N(2)—C(3)	-27.4 (3)	N(11)—Cr—N(7)—C(8)	-46.6 (3)
N(2)—Cr—N(6)—C(5)	26.1 (3)	N(7)—Cr—N(11)—C(10)	45.0 (3)
Cr—N(2)—C(3)—C(4)	51.6 (3)	Cr—N(7)—C(8)—C(9)	62.9 (3)
C(4)—C(5)—N(6)—Cr	-49.6 (3)	C(9)—C(10)—N(11)—Cr	-58.4 (3)
N(2)—C(3)—C(4)—C(5)	-73.1 (4)	N(7)—C(8)—C(9)—C(10)	-67.2 (4)
C(3)—C(4)—C(5)—N(6)	72.5 (4)	C(8)—C(9)—C(10)—N(11)	64.8 (4)

Table 4. Hydrogen-bond distances and other short intramolecular distances

A	H	B	d_{AB}	d_{HB}
N(2)—H(N2)...		O(12 ^v)	3.200 (3) Å	2.64 (5) Å
N(2)—H(N2)...		O(13 ^b)	2.994 (3)	2.12 (5)
N(2)—H(N2)...		O(24 ^{ll})	3.119 (3)	2.30 (6)
N(6)—H(N6)...		O(14 ^{lll})	3.045 (3)	2.23 (6)
N(6)—H(N6)...		O(21 ^{lv})	3.302 (3)	2.34 (6)
N(7)—H...		O(11 ^v)	3.135 (3)	
N(7)—H...		O(12 ^v)	3.136 (3)	
N(7)—H(N7)...		O(12 ^l)	3.093 (3)	2.55 (6)
N(11)—H...		O(14 ^{lll})	3.203 (3)	
N(11)—H...		O(21 ^{lv})	3.082 (3)	
O—H(O)...		O(11 ^{vll})	3.010 (3)	3.67 (5)
O—H(O)...		O(14 ^{vll})	2.765 (3)	2.10 (5)
O—H(O)...		O(22 ^{vll})	3.064 (3)	
O—H(O)...		O(22 ^{vlll})	2.747 (3)	

Symmetry code

(i)	$\bar{x}, 1 - y, 1 - z$	(v)	x, y, z
(ii)	$x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} - z$	(vi)	$\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$
(iii)	$\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$	(vii)	$\bar{x}, \bar{y}, 1 - z$
(iv)	$x, y, z + 1$	(viii)	$x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36961 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The perchlorate ion has standard geometry [mean Cl—O distance 1.42 (2) Å, range: 1.411 (3)–1.442 (3) Å; mean O—Cl—O angle 109 (2)°, range 107.2 (2)–111.4 (2)°].

The molecular packing is due to ionic forces and weak hydrogen bonds (Table 4). Other short intermolecular distances are also shown in Table 4.

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Hexaaquacobalt(II) Bis[dibromobis(ethanedial dioximato)cobaltate(III)] Acetone Solvate

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Abstract. [Co(H₂O)₆][CoBr₂(C₂H₃N₂O₂)₂]₂·2C₃H₆O, 2C₄H₆Br₂CoN₄O₄·CoH₁₂O₆²⁺·2C₃H₆O, *M_r* = 1068.89, monoclinic, *P*2₁/*n*, *a* = 7.005 (3), *b* = 12.964 (5), *c* = 20.134 (10) Å, β = 92.91 (4)°, *V* = 1826 Å³, *Z* = 2, *D_x* = 1.94 Mg m⁻³. Final *R* = 0.036 for 1876 observed diffractometer data. The compound, which decomposes rapidly in the air by loss of acetone, contains cobalt complexes in two different oxidation states: hexaaquacobalt(II) and *trans*-dibromobis(ethanedial dioximato)cobaltate(III). The crystal structure is held together by an extended network of hydrogen bridges.

Introduction. The title compound was prepared in the course of our efforts to synthesize and study sys-

tematically complexes of α,β-dione dioxime ligands with divalent metal halides, *MX*₂ (Andoseh, Douglas, Egharevba & Mégnamisi-Bélobbé, 1982; Mégnamisi-Bélobbé, 1981*a,b*). So far our interest has mainly focused on the dimeric adducts of Cu^{II} halides, in search of a better understanding of their magnetic properties (Mégnamisi-Bélobbé, 1979; Mégnamisi-Bélobbé & Novotny, 1980). Some of these Cu^{II} dimers have been analyzed by X-ray diffraction (Svedung, 1969; Endres, 1978; Endres, Andoseh & Mégnamisi-Bélobbé, 1981). Although complexes of NiCl₂, NiBr₂, and CoCl₂ with ethanedial dioxime (glyoxime, gH₂) have not been structurally characterized so far, their 1:1 composition *MX*₂(gH₂) is confirmed by analytical and IR data (Mégnamisi-Bélobbé, 1981*a*). By contrast, unclear data were obtained for the reaction product of CoBr₂ with gH₂. Hence we performed the X-ray structure determination described below.

* Correspondence about preparation and properties should be addressed to M. Mégnamisi-Bélobbé, about the structure to H. Endres.