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Structure of Bis(L-histidinato-*O*,*N*,*N'*)chromium(III) Nitrate, $[Cr(C_6H_8N_3O_2)_2]NO_3$

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Abstract. $M_r = 422{\cdot}3$, monoclinic, $P2_1$, $a = 7{\cdot}404$ (2), $b = 7{\cdot}209$ (3), $c = 15{\cdot}663$ (5) Å, $\beta = 100{\cdot}68$ (2)°, $V = 821{\cdot}5$ (9) Å^3, $Z = 2$, $D_x = 1{\cdot}707$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 7{\cdot}32$ cm^{-1}, $F(000) = 434$, $T = 294$ K, final $R = 0{\cdot}036$ for 1812 observed reflections. The L-histidinate anions function as tridentate ligands, with the two imidazole rings in the *trans* orientation. The imidazole rings are planar with the Cr atom out of these planes. Hydrogen bonding occurs between amine groups and nitrate oxygen atoms and also between amine and carboxylate groups.

Introduction. Histidine is frequently found to be a metal-binding site in metalloproteins (Ibers & Holm, 1980) and metal complexes of the histidine anion are important for metal-ion transport in blood plasma (Lau & Sarkar, 1971). The L-histidine anion generally functions as either a bidentate or a tridentate ligand (Martin, 1979); several isomers have been reported for octahedral complexes involving two tridentate histidine ligands around Co^{III} (Bagger, Gibson & Sorensen, 1972) and Cr^{III} (Hoggard, 1981). We report here the structure of the bis(L-histidinato)chromium(III) isomer with *trans* imidazole rings, which was determined in order to verify the spectroscopic structural assignment for this most dominant product of the Cr^{III}–histidine reaction and also to provide structural data for comparisons with future structural work on binuclear chromium complexes with histidine.

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Experimental. Title compound prepared by general method reported by Hoggard (1981); orange-red crystal used for data collection, dimensions $0{\cdot}2 \times 0{\cdot}2 \times 0{\cdot}3$ mm, mounted with epoxy on a glass fiber; all data collected using Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation; 25 reflections with 2θ between 17 and 32° used for least-squares determination of cell constants. 2753 reflections measured, ω–2θ scans, 2θ from 4 to 60° ($h = 0$ to 10, $k = \overline{10}$ to 0, $l = \overline{22}$ to 22). $R_{\rm int} = 0{\cdot}028$. Scan range $(1{\cdot}00 + 0{\cdot}35\tan\theta)$°, scan speeds 4–20° min^{-1}. Intensities of three reflections ($\overline{1}3\overline{2}$, $03\overline{6}$ and $\overline{1}1\overline{6}$) measured periodically during 30·0 h of data collection varied by 1·9%, indicating crystal and electronic stability; 801 reflections with $I \le 3\sigma(I)$ considered unobserved; systematic absences of $0k0$ for k odd indicate space group $P2_1$ or $P2_1/m$; however, statistical tests of intensity distribution of data set and chemical composition of the cation which precludes crystallographically imposed symmetry (a necessary condition for $P2_1/m$, $Z = 2$) confirmed space group $P2_1$. Structure solved by Patterson methods and refined by full-matrix least squares based on $(|F_o| - |F_c|)^2$. H atoms constrained to idealized positions (C—H = 0·95 Å, N—H = 0·90 Å). Anisotropic refinement of non-hydrogen atoms gave 243 parameters for parameter/reflection ratio 1:7·5. No absorption or secondary-extinction corrections; $1\overline{1}\overline{2}$ and 103 reflections given zero weight due to evidence of extinction problems. Final $R = 0{\cdot}036$, $R_w = 0{\cdot}044$, $S = 0{\cdot}98$; weighting scheme based on counting statistics $\{\sigma(F^2)$

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$= [\sigma_I^2 + (0{\cdot}06\,I)^2]^{1/2}\}$ gave no systematic variation of $\Delta F/\sigma$ as a function of either F or $\sin\theta$; in final cycle of refinement max. Δ/σ 0·03; final difference map had min. and max. values of −0·33 and 0·35 e Å^{-3}. Atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974); computer programs were those of Enraf–Nonius (1979) *SDP* program package. The L conformation was verified by Hamilton's *R* ratio test (Hamilton, 1965) which rejected the D isomer at the 0·005 level and by three out of four Friedel pairs measured during crystal alignment.

Discussion. Table 1 gives atom coordinates and Table 2 derived distances and angles. Fig. 1 gives a general view of the cation and anion and shows the atom numbering scheme used.*

The L conformation and required facial coordination of each histidine tridentate ligand determines that there will be one and only one ligating group *trans* to the same group on the other ligand, *i.e.* possible isomers are limited to those with *trans* imidazole, *trans* amine, or *trans* carboxylate units. The complex reported here has *trans* imidazole units, as shown by Fig. 1 and as predicted by spectroscopic analysis (Hoggard, 1981). The deviations from octahedral angles at the chromium, caused by the 'bite' of the chelate rings, are all within 10°; the largest deviations are for the O—Cr—N_{am} angles, as has been found for other complexes of histidine (Candlin & Harding, 1970; Fraser & Harding, 1967; Harding & Long, 1968). The angles subtended by the chelate rings at the Cr atom increase with increasing ring size, as previously noted for histidine complexes (de Meester & Hodgson, 1977). The imidazole rings are planar within 0·007 (4) Å [N(2) ring] and 0·006 (5) Å [N(5) ring], and the Cr atom is displaced 0·184 (1) and 0·299 (1) Å from these planes. These latter displacements are not unusual for octahedral complexes of histidine: displacements of up to 0·74 Å have been reported (Candlin & Harding, 1970). The N(2) imidazole ring is twisted 18·0 (1)° with respect to the nearest plane of the octahedron [Cr–N(1)–N(2)–O(3)–N(5)], the N(5) imidazole ring is twisted 23·0 (1)° with respect to the Cr—O(1)—N(2)—N(4)–N(5) plane, and the planes of the two imidazole rings form a dihedral angle of 44·6 (1)°. The Cr—N_{im} distances are, as expected, slightly shorter than the Cr—N_{am} distances.

* Lists of intramolecular distances and angles, anisotropic thermal parameters, H-atom coordinates, best-planes' data and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39381 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates and B_{eq} (Å^2) values with e.s.d.'s in parentheses*

	x	*y*	*z*	B_{eq}*
Cr	0·37232 (7)	0·529	0·21245 (3)	1·596 (8)
O(1)	0·6204 (3)	0·5384 (5)	0·1836 (2)	2·16 (5)
O(2)	0·8118 (4)	0·3717 (5)	0·1203 (2)	2·70 (6)
O(3)	0·2985 (4)	0·7891 (4)	0·1882 (2)	2·27 (5)
O(4)	0·1113 (4)	1·0100 (5)	0·2181 (2)	2·73 (5)
N(1)	0·4438 (4)	0·2547 (5)	0·2294 (2)	2·07 (6)
N(2)	0·2683 (4)	0·4637 (5)	0·0846 (2)	1·91 (6)
N(3)	0·1314 (4)	0·4969 (6)	−0·0511 (2)	2·15 (6)
N(4)	0·1177 (4)	0·5191 (6)	0·2450 (2)	2·06 (5)
N(5)	0·4688 (4)	0·6034 (5)	0·3390 (2)	2·20 (6)
N(6)	0·6608 (5)	0·6877 (7)	0·4559 (3)	3·65 (9)
C(1)	0·6740 (5)	0·3832 (6)	0·1541 (3)	2·11 (7)
C(2)	0·5586 (5)	0·2126 (6)	0·1632 (3)	1·99 (7)
C(3)	0·4356 (5)	0·1596 (6)	0·0770 (3)	2·11 (7)
C(4)	0·3120 (5)	0·3149 (6)	0·0377 (2)	1·81 (7)
C(5)	0·2279 (5)	0·3341 (7)	−0·0472 (2)	2·25 (7)
C(6)	0·1598 (5)	0·5722 (6)	0·0282 (3)	2·15 (8)
C(7)	0·1675 (5)	0·8485 (6)	0·2243 (2)	2·06 (7)
C(8)	0·0821 (5)	0·7055 (7)	0·2767 (2)	2·12 (7)
C(9)	0·1666 (6)	0·7246 (7)	0·3730 (3)	2·76 (8)
C(10)	0·3706 (6)	0·6963 (6)	0·3938 (3)	2·37 (8)
C(11)	0·4911 (7)	0·7475 (8)	0·4656 (3)	3·7 (1)
C(12)	0·6442 (6)	0·6031 (7)	0·3791 (3)	2·91 (9)
N(7)	0·9357 (6)	0·1890 (6)	0·3875 (3)	3·66 (9)
O(5)	0·9309 (6)	0·0669 (7)	0·4424 (3)	6·4 (1)
O(6)	1·0891 (6)	0·2683 (7)	0·3917 (3)	5·8 (1)
O(7)	0·8117 (6)	0·2360 (9)	0·3317 (3)	8·1 (1)

* $B_{eq} = \frac{4}{3}(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{13}ac\cos\beta)$.

Table 2. *Selected bond distances* (Å) *and angles* (°) *for* $Cr(L\text{-}His)_2^+NO_3^-$

Cr—O(1)	1·972 (3)	O(1)—Cr—O(3)	99·2 (2)
Cr—O(3)	1·970 (3)	O(1)—Cr—N(1)	80·4 (2)
Cr—N(1)	2·052 (4)	O(1)—Cr—N(2)	89·0 (1)
Cr—N(2)	2·062 (3)	O(1)—Cr—N(4)	178·8 (1)
Cr—N(4)	2·043 (3)	O(1)—Cr—N(5)	92·3 (1)
Cr—N(5)	2·050 (3)	O(3)—Cr—N(1)	176·3 (1)
N(3)—O(2)	2·970 (5)	O(3)—Cr—N(2)	89·4 (1)
N(4)—O(2)	2·904 (4)	O(3)—Cr—N(4)	81·1 (2)
N(1)—O(4)	3·007 (5)	O(3)—Cr—N(5)	88·4 (2)
N(3)—O(4)	2·888 (4)	N(1)—Cr—N(2)	86·9 (1)
N(1)—O(7)	2·897 (5)	N(1)—Cr—N(4)	99·3 (2)
N(4)—O(6)	2·963 (6)	N(1)—Cr—N(5)	95·3 (2)
		N(2)—Cr—N(4)	92·2 (1)
		N(2)—Cr—N(5)	177·6 (2)
		N(4)—Cr—N(5)	86·6 (1)

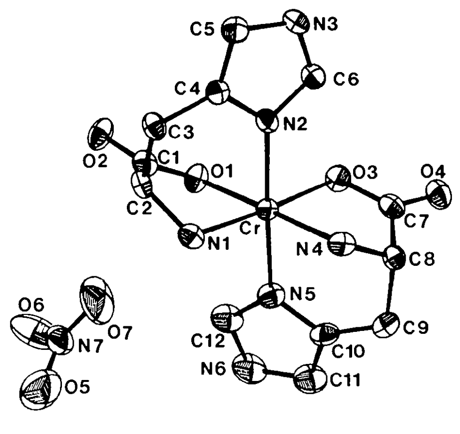

Fig. 1. A general view of the cation and anion (50% probability ellipsoids) showing the atom numbering scheme.

The solid-state packing involves cation–anion H-bonding between amine groups and nitrate oxygen atoms [N(1)—O(7^{i}) = 2·897 (5); N(4)—O(6^{ii}) = 2·963 (6) Å]* to form zigzag chains of cations and anions which are related by translation along x. The cations of this chain are also directly related by H-bonding between an amine group and a carboxyl oxygen atom [N(4)—O(2^{iii}) = 2·904 (4) Å]. Another set of amine–carboxyl H-bonds [N(1)—O(4^{iv}) = 3·007 (5) Å] occurs between cations related by y translation. A bifurcated H-bond occurs between an imidazole NH group of one cation and carboxyl oxygen atoms of two different cations [N(3)—O(2^{v}) = 2·970 (5); N(3)—O(4^{vi}) = 2·888 (4) Å], which are related to the first by space-group symmetry coupled with x and y translations, respectively.

* Symmetry code: (i) O(7) at x, y, z; (ii) O(6) at $x-1, y, z$; (iii) O(2) at $x-1, y, z$; (iv) O(4) at $x, y-1, z$; (v) O(2) at $1-x, \frac{1}{2}+y, -z$; (vi) O(4) at $-x, y-\frac{1}{2}, -z$.

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Structure of (Benzenethiolato)(2,3,7,8,12,13,17,18-octaethylporphinato)iron(III), $[Fe(C_{36}H_{44}N_4)(C_6H_5S)]$

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Abstract. $M_r = 697·78$, triclinic, $P\bar{1}$, $a = 10·246$ (4), $b = 13·040$ (4), $c = 14·900$ (5) Å, $\alpha = 107·82$ (4), $\beta = 73·00$ (4), $\gamma = 101·98$ (5)°, $V = 1797·12$ Å^3, $Z = 2$, $D_m = 1·30$ (1), $D_x = 1·29$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 0·508$ mm^{-1}, $F(000) = 742$, $T = 117$ K, $R = 0·069$, $R_w = 0·076$ for 4676 unique reflections. In the five-coordinate complex Fe(oep)(C_6H_5S) the Fe atom is displaced 0·466 (1) Å from the plane of the four N atoms and 0·512 (1) Å from the plane of the 24-atom porphyrin core. The Fe—S distance is 2·299 (3) Å and the average Fe—N distance is 2·057 (6) Å.

Introduction. Studies of the hemoprotein, cytochrome P-450, and of small-molecule analogues of the heme active site have suggested that a thiolate ligand is coordinated to the heme center of the enzyme (Blumberg & Peisach, 1971; Collman & Groh, 1982; Dolphin, 1979). Accurate and unambiguous structural parameters have been reported for only two thiolate-ligated ferric porphyrin complexes, Fe(ppixdme)(p-$NO_2C_6H_4S$) (Tang, Koch, Papaefthymiou, Foner, Frankel, Ibers & Holm, 1976) and $[Fe(tpp)(C_6H_5S)_2]^-$ (Byrn & Strouse, 1981) (ppixdme is protoporphyrin IX dimethyl ester and tpp is tetraphenylporphinato). Herein is reported the structure of a third iron porphyrin thiolate complex, Fe(oep)(C_6H_5S).

Experimental. A solution of 50 mg $[Fe(oep)]_2O$ in 20 ml benzene was stirred under dinitrogen with 12·5 ml 15% H_2SO_4(v/v). After one hour, 2·5 ml benzenethiol was added with rapid stirring. The organic phase was separated, and crystallization was achieved by slow evaporation under a stream of dinitrogen. Purple, rectangular parallelepiped single crystal. 0·20 × 0·25 × 0·28 mm. D_m by flotation in KI/water. Picker diffractometer equipped with a variable temperature device (Strouse, 1976), Zr filter. Unit-cell parameters by least-squares refinement of 10 reflections

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