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Structures of *N*-(4-Cyanophenyl)acetohydroxamic Acid, $C_9H_8N_2O_2$ (I), and Tris[*N*-(4-cyanophenyl)acetohydroxamato]iron(III) Hydrate, $[Fe(C_9H_7N_2O_2)_3].0\cdot 1H_2O$ (II)

By Ramana R. Mocherla, Douglas R. Powell, Charles L. Barnes and Dick van der Helm

Department of Chemistry, University of Oklahoma, Norman, OK 73019, *USA*

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Abstract. (I) $M_r = 176\cdot 15$, orthorhombic, $Pna2_1$, $a = 7\cdot 176$ (3), $b = 12\cdot 549$ (2), $c = 9\cdot 410$ (3) Å, $V = 847\cdot 4$ Å, $Z = 4$, $D_m = 1\cdot 322$, $D_x = 1\cdot 341$ g cm^{-3}, $F(000) = 368$, Cu $K\overline{\alpha}$ radiation $\lambda = 1\cdot 5418$ Å, $\mu = 7\cdot 43$ cm^{-1}, $T = 138 \pm 2$K, $R = 0\cdot 041$ for 921 data, crystals from ethyl acetate equilibrated with hexane at 277 K. (II) $M_r = 583\cdot 15$, trigonal, $R\overline{3}$, $a = 13\cdot 118$ (6), $c = 26\cdot 728$ (19) Å, $V = 3983\cdot 2$ Å^3, $Z = 6$, $D_m = 1\cdot 396$, $D_x = 1\cdot 422$ g cm^{-3}, $F(000) = 1782$, Mo $K\overline{\alpha}$ radiation $\lambda = 0\cdot 70954$ Å, $\mu = 5\cdot 69$ cm^{-1}, $T = 138 \pm 2$K, $R = 0\cdot 076$ for 1839 data, crystals by evaporation from acetonitrile. In the free ligand the hydroxamate group is in a *trans* conformation. The Fe atom of the ferric complex, which lies on a crystallographic threefold axis, has a pseudo-octahedral coordination environment. Both *Λ-cis and Δ-cis* configurations of the ligand occur in the centrosymmetric crystal structure of the ferric complex.

Introduction. Hydroxamic acids, a group of weak organic acids, have wide applications as antifungal agents, food additives, inhibitors for copper corrosion in metallurgy and in nuclear fuel processing (Bauer & Exner, 1974). They form stable transition-metal complexes and therefore are used as analytical reagents (Agarwal, 1979; Agarwal & Roshania, 1980). They exhibit a high specificity for iron(III) over other biologically important metal ions, with formation constants for iron(III) as high as 10^{30}.

Under iron-limiting conditions microorganisms elaborate a variety of low-molecular-weight chelating agents (siderophores) that solubilize ferric iron in the environment and transport the iron into the cell. Many of these naturally occurring siderophores use hydroxamic acid functional groups for iron chelation and function as growth factors, antibiotics, antibiotic antagonists, tumor inhibitors, cell-division growth factors, *etc.* Some members of the ferrioxamine family of siderophores, which contain hydroxamic acid moieties, have been used as drugs for the treatment of iron overload in humans, which occurs as the result of transfusion therapy for the disease Cooley's anemia (Zaino & Roberts, 1977). There has been considerable interest in the development of synthetic and naturally occurring hydroxamic acids for use in such chelation therapy (Anderson & Hiller, 1977).

Despite widespread applications of hydroxamic acids, only few detailed structural studies have been made of transition-metal complexes of the monohydroxamic acids of the general formula *R*CON(*R*′)OH. The only X-ray diffraction study of a ferric complex of a monohydroxamic acid is that of Fe^{3+} benzohydroxamate trihydrate, which reported octahedral coordination of the Fe atom by the O atoms of the ligand (Lindner & Göttlicher, 1969). Although crystal structures of ferric complexes of several hydroxamate-type siderophores, ferrichrome (*Λ-cis*) (van der Helm, Baker, Eng-Wilmot, Hossain & Loghry, 1980), ferrichrome A (Zalkin, Forrester & Templeton, 1966), ferrichrysin (*Λ-cis*) (Norrestam, Stensland & Brändén, 1975), ferrimycobactin P (*Δ-cis*) (Hough & Rogers, 1974), tris(*N*-methylformothiohydroxamato)-iron(III) (Murray, Newman, Gatehouse & Taylor, 1978), ferric *N,N′,N′′*-triacetylfusarinine (Hossain, Eng-Wilmot, Loghry & van der Helm, 1980), have been determined, so far the only crystal structures of a free ligand and its ferric complex reported are those of desferriferrioxamine E (Hossain, van der Helm &

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Poling, 1983) and ferrioxamine E (van der Helm & Poling, 1976). We report here the crystal and molecular structures of the synthetic hydroxamic acid, *N*-(4-cyanophenyl)acetohydroxamic acid (Hcnpa), and its ferric complex [Fe(cnpa)$_3$] as a pair.

Experimental. (I) was a gift from Dr A. L. Crumbliss, P. M. Gross Chemical Laboratory, Dept. of Chemistry, Duke University, Durham, North Carolina. Crystal: 0·15 × 0·25 × 0·45 mm, room-temperature cell: $a = 7{\cdot}323\,(1)$, $b = 12{\cdot}522\,(1)$, $c = 9{\cdot}513\,(1)$ Å, $V = 872{\cdot}3$ Å^3; systematic absences $0kl$, $k + l = 2n + 1$, and $h0l$, $h = 2n + 1$, distribution of data $\langle E^2{-}1\rangle = 0{\cdot}796$ indicated noncentrosymmetric cell; $2\theta_{\max} = 150°$, hkl octant measured; three intensity monitors had a max. variation of 0·018 and $\sigma = 0{\cdot}004$; data measured 921, data observed 909 [$I > 2\sigma(I)$], unobserveds assigned $I = 1{\cdot}4$ (total count)$^{1/2}$; structure solved by *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), $wR = 0{\cdot}057$, $S = 2{\cdot}70$, $w = 1/\sigma^2(F)$, maximum and average ratio of |shift| to error = 0·094 and 0·017, maximum and minimum height in final difference Fourier maps = 0·20 and –0·26 e Å^{-3}.

(II) was prepared by neutralizing [10% NaHCO$_3$(aq)] a reaction mixture (3:1 mole ratio) of the ligand dissolved in ethanol and FeCl$_3$.6H$_2$O dissolved in water. Crystal: 0·10 × 0·25 × 0·35 mm, room-temperature cell: $a = 13{\cdot}271\,(1)$, $c = 26{\cdot}791\,(4)$ Å, $V = 4086{\cdot}5$ Å^3; systematic absences $-h + k + l \neq 3n$, distribution of data $\langle E^2{-}1\rangle = 0{\cdot}879$; refinement in $R3$ would not converge; $2\theta_{\max} = 53°$, unique data in hkl and $\bar{h}kl$ octants measured; three intensity monitors had a maximum variation of 0·017 and $\sigma = 0{\cdot}005$; data measured 1839, data observed 1299 [$I > 2\sigma(I)$], unobserveds assigned $I = 1{\cdot}4$(total count)$^{1/2}$; solved by Patterson methods. After refinement of all atoms in the molecule a peak of 1·3 e Å^{-3} appeared at $(0,0,\frac{1}{2})$. In the final structure factor calculations an oxygen (water) with an occupancy of 0·2 was included at this $\bar{3}$ symmetry site. $wR = 0{\cdot}048$, $S = 1{\cdot}38$, $w = 1/\sigma^2(F)$, maximum and average ratio of |shift| to error = 0·076 and 0·020, maximum and minimum height in final difference Fourier map = 0·70 e Å^{-3} (along Fe—O bonds) and –0·45 e Å^{-3}.

Both structures: densities by flotation using hexane and CCl$_4$, diffractometer: Enraf–Nonius CAD-4, $\pm\,2\theta$ values from 48 intensity maxima taken from all octants of reciprocal space used for lattice constants, no absorption corrections applied, $\sum w(|F_o| - |F_c|)^2$ minimized in the least-squares refinements, hydrogens located on difference Fourier maps, all independent or unrestricted positional parameters varied, the nonhydrogen thermal parameters varied anisotropically [except water O in Fe(cnpa)$_3$], hydrogens varied isotropically, scattering factors for the light atoms from Cromer & Mann (1968) with corrections for anomalous dispersion from Cromer & Liberman (1970), scattering factors for Fe^{3+} (including corrections for anomalous dispersion) from *International Tables for X-ray Crystallography* (1974), hydrogen scattering factors from Stewart, Davidson & Simpson (1965); structure factor, least-squares refinement and Fourier calculations were performed using the *SHELX*76 programs (Sheldrick, 1976).

Discussion. The final coordinates of the nonhydrogen atoms for Hcnpa and Fe(cnpa)$_3$ are given in Tables 1 and 2, respectively. The atom-numbering scheme for the hydroxamic acid is shown in Fig. 1. A stereoview of the ferric complex is presented in Fig. 2 (Johnson, 1965). In the ferric complex three ligand anions coordinate to the iron through their oxime and carbonyl oxygens. This bonding arrangement requires that the chelating hydroxamate groups have a *cis* conformation. Hcnpa crystallizes with its hydroxamate groups in a *trans* conformation. Bond distances, angles and selected torsion angles for both compounds are presented in Table 3.*

The bonding geometry of the hydroxamate group undergoes considerable change upon chelation with iron. The most notable changes occur around atom C(10). The C(10)—O(10) and N(9)—C(10) bonds change from 1·228 (5) and 1·365 (4) Å to 1·271 (4) and 1·328 (3) Å, respectively, upon chelation. The O(9)—N(9) bond shows much less change with chelation, decreasing from 1·393 (5) to 1·385 (3) Å. These changes are due primarily to a delocalization of the electron density gained from the loss of the hydroxamic proton.

Table 1. *Fractional atomic coordinates* (×10^4) *and equivalent isotropic thermal parameters* (×10^{4}Å^{-2}) *with e.s.d.'s in parentheses for the nonhydrogen atoms in* Hcnpa

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a^*_ia^*_j\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
C(1)	1491 (3)	3172 (2)	2694 (4)	243 (10)
C(2)	1762 (3)	2547 (2)	3903 (4)	300 (11)
C(3)	1647 (4)	1449 (2)	3803 (4)	326 (12)
C(4)	1308 (3)	974 (2)	2500	274 (11)
C(5)	1080 (4)	1590 (2)	1284 (4)	323 (12)
C(6)	1182 (4)	2691 (2)	1379 (4)	304 (11)
C(7)	1200 (4)	−170 (2)	2412 (5)	347 (13)
N(8)	1122 (4)	−1086 (2)	2350 (5)	477 (14)
N(9)	1578 (3)	4301 (2)	2860 (4)	267 (9)
O(9)	2386 (3)	4653 (1)	4122 (4)	363 (9)
C(10)	1008 (3)	5070 (2)	1930 (4)	265 (10)
O(10)	428 (3)	4833 (1)	744 (4)	348 (9)
C(11)	1151 (4)	6201 (2)	2447 (5)	327 (12)

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* Lists of structure factors, anisotropic thermal parameters for non-hydrogen atoms and thermal and positional parameters for hydrogen atoms for Hcnpa and Fe(cnpa)$_3$ have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38463 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Fractional atomic coordinates* (x *and* $y \times 10^4$, $z \times 10^5$) *and equivalent isotropic thermal parameters* ($\times 10^4$ Å^{-2}) *with e.s.d.'s in parentheses for the non-hydrogen atoms in* Fe(cnpa)$_3$

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Fe	0	0	12411 (3)	253 (3)
C(1)	3213 (3)	813 (2)	6656 (10)	246 (15)
C(2)	2888 (3)	558 (3)	1640 (11)	280 (16)
C(3)	3735 (3)	781 (3)	−1947 (11)	299 (17)
C(4)	4910 (3)	1253 (3)	−503 (11)	283 (16)
C(5)	5230 (3)	1518 (3)	4498 (12)	295 (16)
C(6)	4385 (3)	1314 (3)	8107 (11)	273 (16)
C(7)	5793 (3)	1467 (3)	−4241 (12)	326 (17)
N(8)	6487 (3)	1627 (2)	−7201 (11)	421 (17)
N(9)	2309 (2)	565 (2)	10233 (9)	255 (13)
O(9)	1448 (2)	792 (2)	8490 (7)	295 (11)
C(10)	2111 (3)	32 (2)	14641 (10)	256 (15)
O(10)	1165 (2)	−197 (2)	16878 (7)	280 (11)
C(11)	2947 (3)	−288 (3)	16940 (13)	355 (19)
O*W*	0	0	50000	1150 (161)†

† Isotropic value.

Table 3. *Bond distances* (Å), *angles* (°) *and selected conformational angles* (°) *with e.s.d.'s in parentheses for* Hcnpa *and* Fe(cnpa)$_3$

	Hcnpa	Fe(cnpa)$_3$
Fe—O(9)		1·952 (2)
Fe—O(10)		2·055 (2)
C(1)—C(2)	1·396 (5)	1·396 (4)
C(2)—C(3)	1·384 (3)	1·384 (4)
C(3)—C(4)	1·385 (4)	1·398 (4)
C(4)—C(5)	1·391 (4)	1·392 (4)
C(5)—C(6)	1·386 (4)	1·390 (4)
C(6)—C(1)	1·395 (5)	1·392 (4)
C(4)—C(7)	1·440 (3)	1·447 (4)
C(7)—N(8)	1·152 (3)	1·144 (4)
C(1)—N(9)	1·427 (3)	1·429 (4)
N(9)—O(9)	1·393 (5)	1·385 (3)
N(9)—C(10)	1·365 (4)	1·328 (3)
C(10)—O(10)	1·228 (5)	1·271 (4)
C(10)—C(11)	1·504 (3)	1·489 (4)
O(9)—Fe—O(10)		78·01 (7)
O(9)—Fe—O(9′)*		93·88 (8)
O(10)—Fe—O(10′)*		89·63 (8)
O(9)—Fe—O(10′)*		100·56 (7)
O(9)—Fe—O(10″)*		163·83 (7)
Fe—O(9)—N(9)		112·71 (14)
Fe—O(10)—C(10)		113·36 (16)
O(9)—N(9)—C(1)	115·2 (2)	113·5 (2)
C(10)—N(9)—C(1)	128·2 (3)	129·5 (2)
O(9)—N(9)—C(10)	116·6 (2)	116·5 (2)
N(9)—C(10)—O(10)	120·8 (2)	116·9 (2)
N(9)—C(10)—C(11)	116·1 (3)	122·5 (3)
O(10)—C(10)—C(11)	123·1 (3)	120·6 (2)
N(9)—C(1)—C(2)	117·6 (3)	118·0 (3)
N(9)—C(1)—C(6)	122·3 (3)	121·1 (2)
C(6)—C(1)—C(2)	120·2 (2)	120·9 (3)
C(1)—C(2)—C(3)	119·7 (3)	119·9 (3)
C(2)—C(3)—C(4)	120·0 (3)	119·6 (3)
C(3)—C(4)—C(5)	120·6 (2)	120·2 (3)
C(4)—C(5)—C(6)	119·7 (3)	120·4 (3)
C(5)—C(6)—C(1)	119·8 (3)	118·9 (3)
C(3)—C(4)—C(7)	119·3 (2)	119·6 (3)
C(5)—C(4)—C(7)	120·1 (2)	120·2 (3)
C(4)—C(7)—N(8)	179·5 (4)	179·4 (2)
ω_1 = C(1)—N(9)—C(10)—C(11)	175·7 (2)	7·8 (4)
ω_2 = O(9)—N(9)—C(10)—O(10)	173·8 (2)	−1·4 (3)
ω_3 = C(1)—N(9)—C(10)—O(10)	−4·6 (4)	−172·4 (2)
ω_4 = O(9)—N(9)—C(10)—C(11)	−5·9 (3)	178·8 (2)
$\chi_C = \pi + \omega_1 - \omega_3$	0·3 (4)	0·2 (4)
$\chi_N = \pi + \omega_2 - \omega_3$	−1·6 (4)	−9·0 (4)
$\tau = (\omega_1 + \omega_2)/2$	174·8 (2)	3·2 (4)

* Symmetry code: (′) $-y, x-y, z$; (″) $y-x, -x, z$.

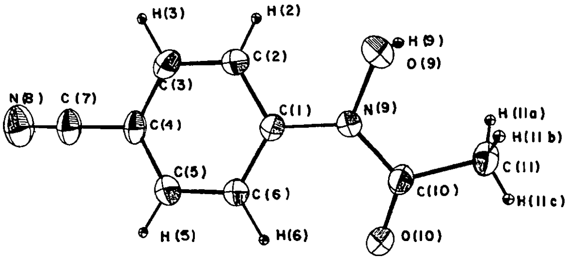

Fig. 1. Schematic drawing of the ligand molecule with 50% probability ellipsoids.

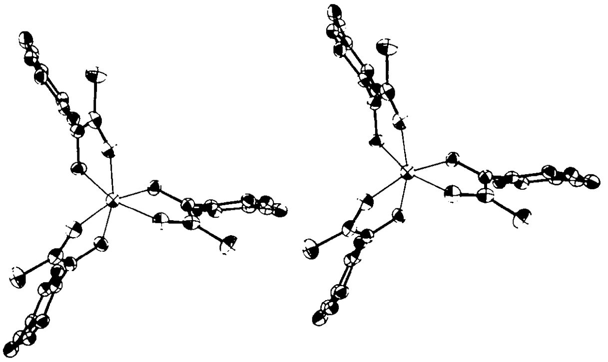

Fig. 2. A stereoview of a single molecule of ferric complex.

The torsion angle C(1)—N(9)—C(10)—C(11) changes from a *trans* conformation, 175·7 (2)°, to a *cis* conformation, 7·8 (4)°, upon chelation. Although the hydroxamate groups in both compounds are nearly planar, these torsion angles indicate significant out-of-plane deformations. Calculations described by Winkler & Dunitz (1971) suggest that these deformations are due principally to C—N twisting in Hcnpa and N out-of-plane bending in Fe(cnpa)$_3$ (see Table 3). Upon chelation, the torsion angles C(10)—N(9)—C(1)—C(6) and O(9)—N(9)—C(1)—C(2) changed from 15·3 (4) and 15·8 (3)° to −47·3 (3) and −37·5 (2)°, respectively, reflecting a change in the electron delocalization of the system and possible steric interactions between C(6) and C(11) in the ferric complex.

A comparison of the bond distances in the hydroxamate group of Hcnpa with similar groups reported in the literature reveals a lengthening of the N—C bond. Other *trans* hydroxamic acids have O—N, N—C and C—O lengths of 1·401 (5), 1·330 (5), and 1·239 (5) Å in desferriferrioxamine E (Hossain, van der Helm & Poling, 1983), 1·396 (2), 1·328 (2), and 1·241 (2) Å in *N*,*N*′-dihydroxy-*N*,*N*′-diisopropylhexanediamide (Smith & Raymond, 1980) and 1·390 (1), 1·347 (1) and 1·255 (1) Å in hydroxyurea (Thiessen, Levy & Flaig, 1978). The lengthening of the N—C bond in Hcnpa is due, at least in part, to the electron-withdrawing effects of the *N*-(4-cyanophenyl) group. The O—N, N—C and C—O distances in the ferric complex compare reasonably well with the 1·37 (1), 1·32 (1) and 1·28 (1) Å found in Fe^{3+} benzohydroxamate trihydrate (Lindner & Göttlicher, 1969).

The iron atom of the ferric complex has a pseudo-octahedral coordination sphere. The oxygens of each hydroxamate group form an O—Fe—O chelation angle of 78·01 (7)°. The twist angle of the chelating O atoms along the threefold axis has a magnitude of 40·81 (9)°. The Fe—O—(—N) and Fe—O—(—C) distances, 1·952 (2) and 2·055 (2) Å, compare reasonably well with the 1·98 (1) and 2·06 (1) Å found in Fe^{3+} benzohydroxamate trihydrate (Lindner & Göttlicher, 1969). The five-membered chelate ring has an envelope conformation with the iron atom sitting 0·3704 (4) Å from a least-squares plane through the O(9), N(9), C(10), and O(10) atoms.

The packing scheme (Motherwell, 1976) for the hydroxamic acid is shown in Fig. 3. The O(9)···O(10)($-x$, $1-y$, $\frac{1}{2}+z$) distance 2·612 (4) Å indicates a strong intermolecular hydrogen bond. There are no intermolecular hydrogen bonds in the ferric complex crystal structure. The closest atom to the water site in $Fe(cnpa)_3$ is 3·308 (5) Å.

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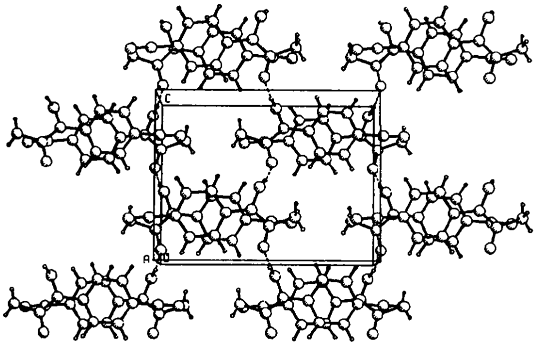

Fig. 3. Packing diagram of ligand molecule showing intermolecular hydrogen bonding (dashed lines).

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