

We acknowledge the support of the TCU Research Foundation and The Robert A. Welch Foundation (P-074). This is FASTBIOS contribution No. 98.

References

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
JOHNSON, C. K. (1971). *ORTEP II*. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee.

MAIN, P., LESSINGER, L., WOOLFSON, M. M., GERMAIN, G. & DECLERCQ, J. P. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
MUETTERTIES, E. L. & GUGGENBERGER, L. J. (1974). *J. Am. Chem. Soc.* **96**, 1748–1756.
STEWART, J. M., MACHIN, P. A., DICKINSON, C. W., AMMON, H. L., HECK, H. & FLACK, H. (1976). The XRAY system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.
VÖGTLE, F., SIEGER, H. & MÜLLER, W. M. (1981). *Top. Curr. Chem.* **98**, 107–161.
VÖGTLE, F. & WEBER, E. (1980). *The Chemistry of The Ether Linkage. Crown Ethers – Complexes and Selectivity*, edited by S. PATAI, pp. 59–156. London: John Wiley.
WEBER, E. & VÖGTLE, F. (1981). *Top. Curr. Chem.* **98**, 1–41.

Acta Cryst. (1983). **C39**, 723–725

Tris(3-hydroxy-4H-pyran-4-onato)iron(III), C₁₅H₉FeO₉

BY BRYAN F. ANDERSON,* DAVID A. BUCKINGHAM,† GLEN B. ROBERTSON‡ AND JOHN WEBB§

Research School of Chemistry, The Australian National University, PO Box 4, Canberra, ACT 2600, Australia

(Received 14 December 1982; accepted 9 February 1983)

Abstract. $M_r = 389.08$, rhombohedral, $R3c$, $a = 11.722(1) \text{ \AA}$, $\alpha = 47.77(1)^\circ$, $U = 808.6 \text{ \AA}^3$, $Z = 2$, $D_x = 1.598$, $D_m = 1.59(1) \text{ Mg m}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.71069 \text{ \AA}$, $\mu = 0.801 \text{ mm}^{-1}$, $F(000) = 394$, $T = 293(1) \text{ K}$. Final $R = 0.021$ for 746 observed diffractometer data. The molecule has exact C_3 symmetry with distorted octahedral coordination of the Fe atom.

Introduction. Recently we reported structural details of both a monomeric and a dimeric complex of iron(III) with 1,2-benzenediol (pyrocatechol) (Anderson, Buckingham, Robertson & Webb, 1982; Anderson, Webb, Buckingham & Robertson, 1982). Comparison of the chemical and spectroscopic properties of these compounds with those of the iron(III) enterochelin trianion permitted the identification of $[\text{FeO}_6]$ rather than $[\text{FeO}_3\text{N}_3]$ at the iron(III) coordination site in the siderophore (Anderson, Buckingham, Robertson, Webb, Murray & Clark, 1976). However, e.p.r. and Mössbauer data for both the pyrocatechol complexes

and the siderophores have resisted complete explanation, particularly as regards the symmetry of the coordination site relative to that of the spin Hamiltonian required to reproduce the spectral splitting (Oosterhuis & Spartalian, 1974; Oosterhuis, 1974). Unlike both the siderophore and the pyrocatechol complexes the title complex is uncharged, and might be expected to exhibit strict trigonal symmetry and be devoid of intermolecular hydrogen bonding.

Experimental. Prepared from 3-hydroxy-4-pyrone (pyromeconic acid) and basic ferric acetate by method of Garkusha (1946), recrystallized from dimethyl sulfoxide as small crimson rhombs, D_m measured by flotation, crystal used for data collection had dimensions $0.20 \times 0.18 \times 0.15 \text{ mm}$ parallel to \mathbf{a}^* , \mathbf{b}^* and \mathbf{c}^* respectively; reflection intensities for one complete reciprocal-space hemisphere ($3 < 2\theta < 50^\circ$) recorded on a Picker FACS-1 diffractometer, θ - 2θ scan mode, scan velocity 2° min^{-1} (2θ), two 10s background counts at extremes, Mo $K\alpha$, graphite-crystal monochromator, 2880 reflections excluding standards; quoted cell dimensions and standard errors derived from least-squares analysis of setting angles for 12 well centered reflections with $39 < 2\theta < 45$ (Mo $K\alpha$, radiation); intensities of three standard reflections (088, 808 and 880) did not vary significantly during data

* Present address: Department of Chemistry, Biochemistry and Biophysics, Massey University, Palmerston North, New Zealand.

† Present address: University of Otago, PO Box 56, Dunedin, New Zealand.

‡ To whom correspondence should be addressed.

§ Present address: School of Mathematical and Physical Sciences, Murdoch University, Murdoch, WA 6150, Australia.

collection, reflection intensities with $I \geq 2.5\sigma(I)$ and background imbalance $\Delta < 3\sigma(\Delta)$ accepted and reduced to $|F_o|$ and $\sigma(F_o)$ values with instrumental uncertainty constant $p = 0.045$ assumed (Busing & Levy, 1957; Corfield, Doedens & Ibers, 1967); data corrected for absorption (de Meulenaer & Tompa, 1965) and subsequently for extinction: transmission-factor range from 0.930 to 0.943; sorting and averaging of equivalent forms (3) yielded 746 unique data with $R_s = 0.006$ (Robertson & Whimp, 1975) and $R_{int} = 0.013$; with $Z = 2$ in $R3c$ Fe atoms are constrained to lie on the trigonal axis and were assigned coordinates $\frac{1}{3}, \frac{1}{3}, \frac{1}{3}$ and $\frac{2}{3}, \frac{2}{3}, \frac{2}{3}$; the remaining non-H atoms were located from an Fe-phased Fourier synthesis and H atoms were placed by calculation (see below); structure refined by full-matrix least-squares analysis, minimizing $\sum w(|F_o| - |F_c|)^2$ with $w = [\sigma(F_o)]^{-2}$; scattering factors, together with anomalous-dispersion corrections for Fe and O, taken from *International Tables for X-ray Crystallography* (1974); attempted H-atom refinement led to unrealistic out-of-plane deviations (0.2–0.4 Å) and, therefore, H-atom parameters constrained subsequently to calculated values (C–H = 0.95 Å, $B_H = 1.1B_C$); contributions from nine reflections, each with $\Delta/\sigma > 10$ and with $\sum w\Delta^2$ totalling 3000–4000 (cf. $\sum w\Delta^2 \approx 2000$ for 737 included reflections), excluded from final least-squares cycles; at convergence $R = 0.021$ (0.019) and $R_w = 0.045$ (0.026), values in parentheses those for included reflections only; extinction coefficient (Zachariasen, 1963) refined to $0.42(11) \times 10^{-5} \text{ mm}^{-1}$ and $[\sum w\Delta^2/(n-s)]^{1/2} = 1.7$; terminal shift/e.s.d. ratios uniformly < 0.1 and a final difference synthesis revealed no features exceeding $0.3 \text{ e } \text{Å}^{-3}$; stereopair drawn with *ORTEP* (Johnson, 1976).

For the enantiomeric packing arrangement convergence values of R and R_w were 0.021 (0.020) and 0.041 (0.027). R -factor ratios for all reflections and for least-squares-included reflections only are clearly contradictory. Each refinement excluded nine reflections ($\Delta/\sigma > 10$), seven of which were common. Because all excluded reflections were measured at least twice and showed excellent internal agreement, refinements were also attempted with all data included. However, for both enantiomers these refinements were ill-conditioned as regards convergence, gave unrealistic bond lengths, and failed to eliminate the poor F_o/F_c agreement for the previously excluded reflections ($\sum w\Delta^2 \sim 800$). The correct choice of space-group enantiomer remains ambiguous. That reported here and indicated by the R -factor ratio for included reflections (ratio = 1.035, probability < 0.005 ; Hamilton, 1965) is, we believe, to be preferred. In any case, significant coordinate differences occur only for O(3) $_x$ and O(2) $_y$ ($\Delta/\sigma = 3.0$) and bond-length/bond-angle differences only for Fe–O(3) (4.2 σ) and Fe–O(2) (3.9 σ). The large discrepancies in the nine rejected reflections ($\Delta/\sigma = 11.8$ –30.9) may be associated with slight disordering of O(1).

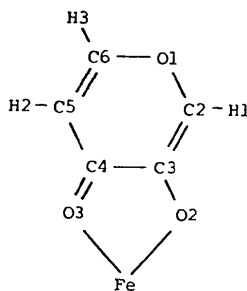


Fig. 1. Atomic-numbering scheme for the asymmetric unit of tris(3-hydroxy-4H-pyran-4-onato)iron(III).

Table 1. Atomic coordinates with e.s.d.'s in parentheses and equivalent isotropic thermal parameters for the non-H atoms

	x	y	z	B_{eq}^* (Å ²)
Fe	0.25	0.25	0.25	2.45
O(1)	−0.2794 (6)	0.7814 (6)	0.3078 (6)	6.56
O(2)	0.0891 (5)	0.4142 (5)	0.3595 (5)	3.05
O(3)	0.0800 (5)	0.4067 (5)	0.1490 (5)	2.89
C(2)	−0.1577 (9)	0.6671 (8)	0.3608 (8)	4.53
C(3)	−0.0382 (7)	0.5408 (7)	0.3074 (7)	2.94
C(4)	−0.0338 (6)	0.5251 (6)	0.1925 (6)	2.64
C(5)	−0.1709 (8)	0.6563 (9)	0.1432 (7)	4.21
C(6)	−0.2884 (7)	0.7864 (7)	0.1965 (8)	4.67

$$* B_{eq} = \frac{1}{3} \sum_i \sum_j B_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

Discussion. The atomic nomenclature is defined in Fig. 1 and the corresponding coordinates are listed in Table 1.*

Molecules of the title compound have exact trigonal symmetry with the Fe atom coordinated by two sets each of three equivalent O atoms. The trigonal twist angle is 39.4(2)° indicating substantially more trigonal-prismatic character in the present molecule than in the tris(pyrocatecholato)ferrate(III) ions, $\text{Fe}(\text{cat})_3^{3-}$ [K^+ salt, 44.7(10)° (Raymond, Isied, Brown, Fronczek & Nibert, 1976); piperidinium (py⁺) salt, 46.5(8)° (Anderson, Buckingham, Robertson & Webb, 1982)].

Bond distances and angles are given in Table 2. The metal–ligand distances are equivalent to within experimental error [2.019(4) and 2.024(4) Å]. The result is somewhat surprising given the chemical inequivalence of the ligating O atoms [C–O = 1.231(6) and 1.354(6) Å] and may be an artifact of the refinement as Fe–O values in the enantiomeric space group (see above) refine to significantly different values [1.995(4) and 2.046(4) Å respectively]. In either instance, however, the mean value agrees well with the average of the Fe–O distances observed in the

* Lists of structure amplitudes, anisotropic thermal parameters, H-atom coordinates and deviations from best planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38408 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

Fe—O(2)	2.024 (4)	O(3)—C(4)	1.231 (6)
Fe—O(3)	2.019 (4)	C(2)—C(3)	1.350 (9)
O(1)—C(2)	1.311 (9)	C(3)—C(4)	1.441 (3)
O(1)—C(6)	1.339 (4)	C(4)—C(5)	1.420 (7)
O(2)—C(3)	1.354 (6)	C(5)—C(6)	1.384 (9)
O(2)—Fe—O(3)	80.1 (1)	O(2)—C(3)—C(4)	113.3 (6)
O(2)—Fe—O(2)	90.0 (2)	C(2)—C(3)—C(4)	124.1 (6)
O(3)—Fe—O(3)	89.0 (2)	O(3)—C(4)—C(3)	120.3 (5)
C(2)—O(1)—C(6)	124.1 (6)	O(3)—C(4)—C(5)	127.3 (4)
Fe—O(2)—C(3)	112.6 (3)	C(3)—C(4)—C(5)	112.4 (6)
Fe—O(3)—C(4)	113.7 (3)	C(4)—C(5)—C(6)	122.0 (6)
O(1)—C(2)—C(3)	118.5 (6)	O(1)—C(6)—C(5)	118.8 (6)
O(2)—C(3)—C(2)	122.7 (5)		

Fe(cat)₃³⁻ salts [av. 2.017 Å; range 1.993 (2)–2.037 (2) Å]. Ligand bite angles for the present molecule [80.13 (5)°] and for the Fe(cat)₃³⁻ salts [80.3 (1)–82.1 (1)°] are also closely comparable. The ligand is planar to within experimental error ($\Delta_{\max} = 2.6\sigma$). The Fe atom is displaced 0.049 Å from the ligand plane corresponding to a bend of 1.9 (5)° about the O(2)···O(3) vector. Consistent with the tautomeric form shown in Fig. 1 the longer C—O(ligand) distance [1.354 (6) Å] agrees well with the ‘single-bond’ distances in Fe(cat)₃³⁻ [K⁺ salt, 1.338 (8) Å; py⁺ salt, 1.340 (3) Å] while the shorter distance [1.231 (6) Å] is close to the ‘double-bond’ distance in Fe(acac)₃ [1.258 (12) Å, acac = acetoacetate] (Iball & Morgan, 1967).

The formal double bonds C(2)—C(3) and C(5)—C(6) [equivalent within experimental error; mean value 1.367 (6) Å] are longer than their expected value (1.335 Å), while the two single bonds C(3)—C(4) and C(4)—C(5) [mean value 1.430 (5) Å] are shorter than expected (*ca* 1.48 Å), consistent with appreciable ring aromaticity such as is found, for instance, in naphthazarin (5,8-dihydroxy-1,4-naphthoquinone) (Cradwick & Hall, 1971). The C(2)—O(1) and C(6)—O(1) bonds [mean value 1.325 (7) Å] are also short, *vis-à-vis* both the C(3)—O(2) distance [1.354 (6) Å] and the lengths of the similar bonds [mean value 1.373 (11) Å] in the 5-methoxy-4,10-dioxo-4*H*,10*H*-benzo[1,2-*b*:4,3-*b'*]-dipyran 2,8-dicarboxylate dianion (Morris, Geddes, Sheldrick & Akrigg, 1979). The substantial amplitude of vibration for O(1) perpendicular to the ring plane (Fig. 2) and the large C(2)—O(1)—C(6) angle [124.1 (6)°] are both suggestive of ring strain with associated out-of-plane disordering of O(1). In contrast to the ligand as a whole the pyrone ring is just significantly aplanar ($\Delta_{\max} = 3.1\sigma$) due to ‘chair’-bending across C(5)···O(1) and C(2)···C(4).

As expected the crystal-packing arrangement is dominated by van der Waals interactions. In addition, however, three short, presumably attractive, C—H···O interactions to the ligating O atoms are present. All three H atoms are involved. O···H distances and O···H—C angles are as follows: O(3)···H(1)—C(2), 2.34 Å, 161°; O(3)···H(3)—C(6), 2.43 Å, 161°;

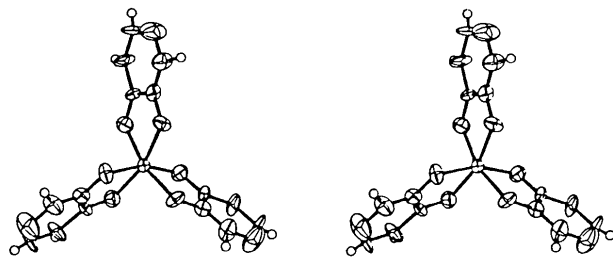


Fig. 2. Stereoscopic view down the trigonal axis. Thermal ellipsoids depict 50% probability surfaces. H atoms are shown as 0.1 Å radius spheres.

O(2)···H(2)—C(5), 2.43 Å, 153°. Molecular trigonal axes are equally disposed parallel and antiparallel to the crystallographic trigonal axis. The EPR spectrum of the crystalline solid consists of a broad resonance peak centered at $g = 4.3$ with a peak-to-peak width of 0.15 T. The extremely broad nature of the signal may well result from intermolecular spin–spin interaction facilitated by the parallel–antiparallel molecular alignment. Detailed analysis of this and related spectra is in progress (Boyd, 1982).

We thank Dr Roger Harris, Division of Plant Industry, CSIRO for a generous gift of pyromeconic acid and Mr G. M. McLaughlin and Dr T. Rauchfuss for helpful discussions.

References

- ANDERSON, B. F., BUCKINGHAM, D. A., ROBERTSON, G. B. & WEBB, J. (1982). *Acta Cryst.* B38, 1927–1931.
 ANDERSON, B. F., BUCKINGHAM, D. A., ROBERTSON, G. B., WEBB, J., MURRAY, K. S. & CLARK, P. E. (1976). *Nature (London)*, 262, 722–724.
 ANDERSON, B. F., WEBB, J., BUCKINGHAM, D. A. & ROBERTSON, G. B. (1982). *J. Inorg. Biochem.* 16, 21–32.
 BOYD, P. D. W. (1982). Private communication. Department of Chemistry, Univ. of Auckland, New Zealand.
 BUSING, W. R. & LEVY, H. A. (1957). *J. Chem. Phys.* 26, 563–568.
 CORFIELD, P. W. R., DOEDENS, R. J. & IBERS, J. A. (1967). *Inorg. Chem.* 6, 197–204.
 CRADWICK, P. D. & HALL, D. (1971). *Acta Cryst.* B27, 1990–1997.
 GARKUSHA, G. A. (1946). *J. Gen. Chem. USSR*, 16, 2025–2032.
 HAMILTON, W. C. (1965). *Acta Cryst.* 18, 502–510.
 IBALL, J. & MORGAN, H. C. (1967). *Acta Cryst.* 23, 239–244.
International Tables for X-ray Crystallography (1974). Vol. IV, pp. 99, 149. Birmingham: Kynoch Press.
 JOHNSON, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
 MEULENAER, J. DE & TOMPA, H. (1965). *Acta Cryst.* 19, 1014–1018.
 MORRIS, A. J., GEDDES, A. J., SHELDRICK, B. & AKRIGG, D. (1979). *Cryst. Struct. Commun.* 8, 237–242.
 OOSTERHUIS, W. T. (1974). *Struct. Bonding (Berlin)*, 20, 59–99.
 OOSTERHUIS, W. T. & SPARTALIAN, K. (1974). *J. Phys. (Paris), Colloq.* 35(6), 347–350.
 RAYMOND, K. N., ISIED, S. S., BROWN, L. D., FRONCZEK, F. R. & NIBERT, J. H. (1976). *J. Am. Chem. Soc.* 98, 1767–1773.
 ROBERTSON, G. B. & WHIMP, P. O. (1975). *J. Am. Chem. Soc.* 97, 1051–1059.
 ZACHARIASEN, W. H. (1963). *Acta Cryst.* 16, 1139–1144.