Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Sivý, J., Kettmann, V., Krätsmár-Šmogrovič, J., Švajlenová, O., Friebel, C. & Plesch, G. (1990). *Z. Anorg. Allg. Chem.* **583**, 55–66.
Ueki, T., Ashida, T., Sasada, Y. & Kakudo, M. (1967). *Acta Cryst.* **22**, 870–878.
Ueki, T., Ashida, T., Sasada, Y. & Kakudo, M. (1969). *Acta Cryst.* B**25**, 328–336.
Warda, S. A. (1994). In *Bioanorganische Kupfer(II) Komplexe mit dreizähnigen O,N,O-Chelat-Dianionen und additiven einzähnigen Donorliganden*. Aachen: Verlag Shaker.

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mer-Triaqua(chloranilato-*O*,*O'*)chloroiron(III) Pentahydrate

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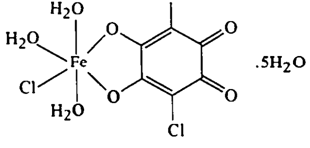
Abstract

The crystal structure of the title compound, $[FeCl(C_6Cl_2O_4)(H_2O)_3].5H_2O$, shows it to be a monomeric iron(III) complex with the metal ion chelated by the dianion of chloranilic acid (2,5-dichloro-3,6-dihydroxy-2,5-cyclohexadiene-1,4-dione). The octahedral coordination environment is completed by a chloride ion and three water molecules which are in a *mer* arrangement. Extensive hydrogen bonding occurs between the complex and lattice water molecules.

Comment

It has long been known that 2,5-dihydroxy-1,4-benzoquinone and its derivatives are capable of forming complexes with a variety of metals (Frank, Clark & Coker, 1950). As part of an examination of chelating ligands which have the potential to bridge metal centres, the reaction between ferric chloride and chloranilic acid in an aqueous ethanolic solution was investigated. Crystals of the title compound, (I), were obtained from this solution.



(I)

The ferric ion is octahedrally coordinated by two O atoms of a chloranilate dianion, three water molecules and a chloride ion (Fig. 1). The three aqua ligands adopt a *mer* configuration. The bite angle of the chloranilate anion and the size of the chloride ligand are largely responsible for the distortion from ideal octahedral geometry. A small degree of asymmetry is apparent in the chelation of the chloranilate ligand. The C—O atomic separations in the chloranilate dianion are significantly shorter for the non-coordinating O atoms. The variation in the ring C—C separations indicates that the canonical form of the ligand represented in the structural diagram is a major contributor to the structure. The geometry of the chelating ligand is very similar to

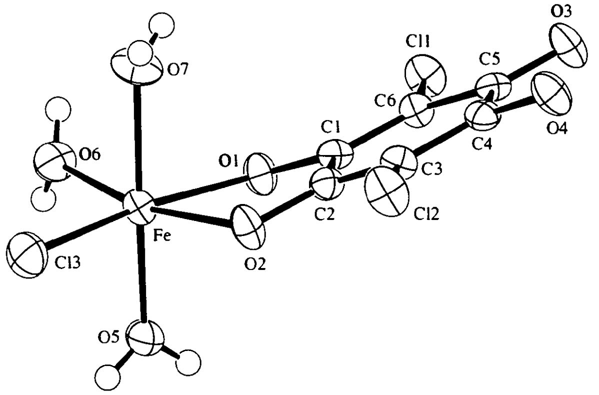


Fig. 1. An *ORTEP*II (Johnson, 1976) diagram of compound (I). Displacement ellipsoids are at the 50% probability level and H atoms are represented by spheres of arbitrary size. Solvate water molecules have been omitted for clarity.

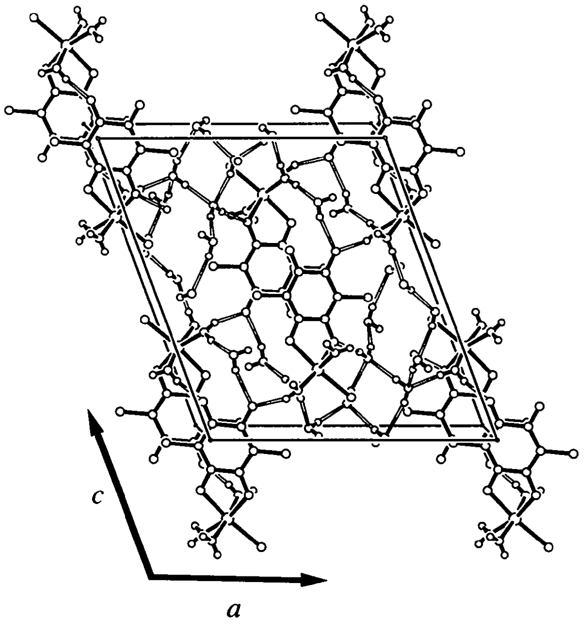


Fig. 2. An *ORTEP*II (Johnson, 1976) diagram of the unit cell of (I). Atoms are of arbitrary size and double lines represent hydrogen bonds.

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that of other metal complexes involving non-bridging chloranilate ligands (Johnston, Sen Gupta, Ossain, van der Helm, Jeong & Holwerda, 1990; Liu, Shaikh & Zubieta, 1989; Folgado, Ibáñez, Coronado, Beltrán, Savariault & Galy, 1988). Although the chloranilate dianion is planar, the iron(III) centre lies 0.584 (2) Å above the mean plane of the chelating ligand. Hydrogen bonding between the complex and lattice water molecules extends throughout the structure (Fig. 2).

Experimental

Crystals of (I) are deep red (almost black) in colour and were obtained by the slow evaporation of an aqueous ethanolic solution (10% water) containing ferric chloride and chloranilic acid mixed in a 1:1.5 molar ratio. Orange crystals of chloranilic acid were also obtained. The density D_m was measured by flotation in a chloroform/1,2-dibromoethane solution.

Crystal data

$[\mathrm{FeCl(C_6Cl_2O_4)(H_2O)_3}]$.-
$\mathrm{5H_2O}$
$M_r = 442.39$
Monoclinic
$P2_1/n$
$a = 14.880\,(5)$ Å
$b = 7.044\,(4)$ Å
$c = 16.836\,(8)$ Å
$\beta = 110.93\,(5)°$
$V = 1648.2\,(13)$ Å^3
$Z = 4$
$D_x = 1.783$ Mg m^{-3}
$D_m = 1.77\,(2)$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 6.2\text{–}16.2°$
$\mu = 1.454$ mm^{-1}
$T = 293\,(2)$ K
Flat needle
$0.47 \times 0.14 \times 0.04$ mm
Dark red

Data collection

Enraf–Nonius CAD-4*F* diffractometer
$\omega/2\theta$ scans
Absorption correction: analytical, indexed crystal faces
$T_{\min} = 0.8008$, $T_{\max} = 0.9490$
3833 measured reflections
2901 independent reflections

2207 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.0239$
$\theta_{\max} = 24.97°$
$h = -1 \rightarrow 17$
$k = -1 \rightarrow 8$
$l = -19 \rightarrow 19$
3 standard reflections
frequency: 120 min
intensity decay: 1%

Refinement

Refinement on F^2
$R(F) = 0.0345$
$wR(F^2) = 0.0740$
$S = 1.027$
2901 reflections
264 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0309P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.308$ e Å^{-3}
$\Delta\rho_{\min} = -0.269$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Fe	0.47044 (3)	0.15006 (7)	0.22442 (3)	0.02459 (14)
Cl1	0.35393 (5)	0.14030 (13)	0.47288 (5)	0.0309 (2)
Cl2	0.74748 (6)	0.44015 (15)	0.45119 (5)	0.0376 (2)
Cl3	0.54999 (6)	0.15857 (14)	0.13292 (5)	0.0394 (2)
O1	0.41106 (14)	0.1828 (3)	0.31871 (12)	0.0267 (5)
O2	0.56726 (15)	0.3169 (3)	0.30933 (12)	0.0301 (6)
O3	0.5313 (2)	0.2749 (4)	0.61509 (12)	0.0337 (6)
O4	0.69270 (15)	0.3984 (4)	0.60539 (12)	0.0333 (6)
O5	0.3804 (2)	0.3563 (4)	0.1623 (2)	0.0345 (6)
O6	0.3681 (2)	−0.0419 (4)	0.1663 (2)	0.0323 (6)
O7	0.5437 (2)	−0.0763 (4)	0.2902 (2)	0.0347 (6)
C1	0.4726 (2)	0.2362 (5)	0.3903 (2)	0.0227 (7)
C2	0.5655 (2)	0.3115 (4)	0.3850 (2)	0.0239 (7)
C3	0.6396 (2)	0.3649 (5)	0.4571 (2)	0.0245 (7)
C4	0.6297 (2)	0.3537 (5)	0.5371 (2)	0.0235 (7)
C5	0.5347 (2)	0.2818 (4)	0.5434 (2)	0.0225 (7)
C6	0.4602 (2)	0.2275 (5)	0.4672 (2)	0.0231 (7)
O8	0.6952 (2)	0.3583 (4)	0.77274 (15)	0.0349 (6)
O9	0.7308 (2)	−0.1001 (4)	0.3473 (2)	0.0415 (7)
O10	0.8742 (2)	−0.0032 (5)	0.5152 (2)	0.0439 (7)
O11	0.8282 (2)	0.0721 (5)	0.2587 (2)	0.0447 (7)
O12	0.9560 (3)	0.2089 (5)	0.4144 (2)	0.0544 (8)

Table 2. *Selected geometric parameters (Å, °)*

Fe—O5	2.000 (3)	O2—C2	1.284 (3)
Fe—O2	2.007 (2)	O3—C5	1.227 (3)
Fe—O6	2.010 (3)	O4—C4	1.237 (3)
Fe—O7	2.024 (3)	C1—C6	1.373 (4)
Fe—O1	2.087 (2)	C1—C2	1.513 (4)
Fe—Cl3	2.2540 (13)	C2—C3	1.369 (4)
Cl1—C6	1.731 (3)	C3—C4	1.407 (4)
Cl2—C3	1.727 (3)	C4—C5	1.541 (4)
O1—C1	1.282 (3)	C5—C6	1.415 (4)
O5—Fe—O2	97.08 (11)	O1—C1—C2	114.2 (3)
O5—Fe—O6	89.11 (12)	C6—C1—C2	120.3 (3)
O2—Fe—O6	165.20 (10)	O2—C2—C3	125.2 (3)
O5—Fe—O7	171.15 (11)	O2—C2—C1	114.3 (3)
O2—Fe—O7	87.84 (11)	C3—C2—C1	120.5 (3)
O6—Fe—O7	84.44 (12)	C2—C3—C4	120.4 (3)
O5—Fe—O1	86.03 (10)	C2—C3—Cl2	120.3 (2)
O2—Fe—O1	77.57 (9)	C4—C3—Cl2	119.3 (2)
O6—Fe—O1	89.51 (10)	O4—C4—C3	124.9 (3)
O7—Fe—O1	87.85 (10)	O4—C4—C5	115.4 (3)
O5—Fe—Cl3	92.34 (8)	C3—C4—C5	119.8 (3)
O2—Fe—Cl3	93.02 (7)	O3—C5—C6	125.9 (3)
O6—Fe—Cl3	100.18 (8)	O3—C5—C4	116.2 (3)
O7—Fe—Cl3	94.76 (8)	C6—C5—C4	117.9 (3)
O1—Fe—Cl3	170.15 (7)	C1—C6—C5	121.1 (3)
C1—O1—Fe	113.1 (2)	C1—C6—Cl1	120.1 (2)
C2—O2—Fe	115.2 (2)	C5—C6—Cl1	118.8 (2)
O1—C1—C6	125.6 (3)		

The structure was solved using the *PATT* routine in *SHELXS*86 (Sheldrick, 1990). Refinement was performed using *SHELXL*93 (Sheldrick, 1993). All non-H atoms were refined with anisotropic displacement parameters and H atoms were refined with isotropic displacement parameters. Water H atoms were refined with a common O—H separation. The figures were drawn using *ORTEP*II (Johnson, 1976) and the tables were prepared using *SHELXL*93. All calculations were carried out on a VAXstation 4000VLC computer system.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1074). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Folgado, J. V., Ibáñez, R., Coronado, E., Beltrán, J. R., Savariault, J. M. & Galy, J. (1988). *Inorg. Chem.* **27**, 19–26.
Frank, R. L., Clark, G. R. & Coker, J. N. (1950). *J. Am. Chem. Soc.* **72**, 1827–1829.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Johnston, R. F., Sen Gupta, P. K., Ossain, M. B., van der Helm, R., Jeong, W.-Y. & Holwerda, R. A. (1990). *Acta Cryst.* C**46**, 1796–1799.
Liu, S., Shaikh, S. N. & Zubieta, J. (1989). *Inorg. Chem.* **28**, 723–732.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

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Chloro[*N*,*N'*-ethylenebis(3-imino-1-phenyl-1-butanonato-*N*,*O*)]manganese(III), $[MnCl(C_{22}H_{22}N_2O_2)]$

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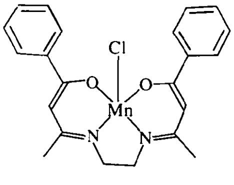
Abstract

The structure determination of chloro[1,1'-diphenyl-3,3'-(1,2-ethanediyldiimino)di-1-butanonato-*N*,*N'*,*O*,*O'*]-manganese(III), reveals a distorted square-pyramidal coordination at the Mn atom, with an N_2O_2 basal plane composed of atoms from the Schiff base ligand and a chlorine ligand in the axial position.

Comment

Mn^{III}-Schiff base complexes are among the simplest models for the active sites of manganoenzymes. Manganese complexes of the Schiff base ligand *N*,*N'*-ethylenebis(3-imino-1-phenyl-1-butanonato) (abbreviated to $bzacen^{2-}$) have been studied and shown to have three main structure types. Examples of these are mononuclear [Mn(bzacen)(pyrimidine)(NCS)] (Feng & Liu, 1996), bridged dinuclear $[Mn_2(bzacen)_2(MeOH)_2(\mu\text{-}4,4'\text{-bipy})](ClO_4)_2$ (where bipy is bipyridine; Liu & Feng, 1996) and the chain compound $[Mn(bzacen)(CH_3COO)]$ (Haider, Hashem, Khan, Malik & Hursthouse, 1985). The present work is part of a study of manganese complexes of the Schiff base ligand $bzacen^{2-}$ and reports the structure of [MnCl(bzacen)], (I).



(I)

The five-coordinate Mn atom is chelated through covalent bonds to the N(1), N(2), O(1) and O(2) atoms of the Schiff base ligand lying in the basal plane, the Cl atom being in the axial position (Fig. 1). The deviations of the four N or O atoms from the basal plane are less than 0.081 Å. The Mn—O and Mn—N bond distances agree with the average values found in similar complexes reported by us (Feng & Liu, 1996; Liu & Feng, 1996). The Mn^{III} ion is therefore in a distorted square-pyramidal configuration. The Mn(1)—Cl(1) bond length of 2.415 (2) Å is longer than the corresponding value of 2.381 (1) Å found in [MnCl(acen)] (Boucher & Day, 1977), but shorter than that of 2.461 (1) Å found in [MnCl(salen)] (Pecoraro & Butler, 1986) and that of 2.574 (9) Å found in $[Mn(C_{34}H_{38}ClN_2O_6)]$ (Nagata, Imagawa, Yamada & Mukaiyama, 1994). The Mn—Cl bonds in these complexes are significantly longer than the normal value of 2.32 Å, being approximately 2.34 Å (Pecoraro & Butler, 1986). The distance of the Mn atom from the basal plane is 0.304 (2) Å for the title complex, the corresponding distances being 0.344 Å for [MnCl(acen)] and 0.19 Å for [MnCl(salen)]. Because of the displacement of 0.304 Å, the Mn—Cl bond length in the title complex must be longer than 2.4 Å so that the Cl atom is just in contact with the imine N atom. In other words, the distance between N(2) and Cl(1) of 3.270 (3) Å agrees with the sum of the van der Waals radii for N—Cl of 3.20 Å (Pauling, 1960). This means that the distances of the Cl atom from the atoms of the basal plane are all about 2.7 Å due to van der Waals contacts within these complexes (Pecoraro & Butler, 1986). Delocalization of double bonds within the O(1)—C(1)—C(2)—C(3)—N(1) and O(2)—C(10)—C(9)—C(7)—N(2) chelate rings is observed in the title complex, as was also found in [Mn(acen)Cl] (Boucher & Day, 1977). The two six-membered Mn—O—C—C—C—N rings are respectively planar, the dihedral angle between them being 25.9 (3)°.

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