

Structure of μ -(Terephthalato)-bis[N,N' -ethylenebis(salicylaldiminato)iron(III)]

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Abstract. μ -(1,4-Benzenedicarboxylato- $O,O':O'',O'''$)-bis{2,2'-[1,2-ethanediylbis(iminomethyl)]diphenolato- N,N',O,O' }diiron(III), $[\text{Fe}_2(\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_2)_2(\text{C}_8\text{H}_4\text{O}_4)]$, $M_r = 808.41$, monoclinic, $P2_1/c$, $a = 6.954(1)$, $b = 17.196(3)$, $c = 15.333(2)$ Å, $\beta = 99.53(1)^\circ$, $V = 1808.2(5)$ Å³, $Z = 2$, $D_m = 1.51$, $D_x = 1.48$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu = 68.48$ cm⁻¹, $F(000) = 832$, $T = 293$ K, $R = 0.072$ for 2432 observed reflections. The crystal used for the structure determination was a twin with partially coinciding reflections and the twin ratio $\alpha = 0.4936(3)$. The molecule $[\text{Fe}(\text{salen})_2]_{\text{ter}}$, where $\text{salen} = N,N'$ -ethylenebis(salicylaldiminato) and $\text{ter} = \mu$ -(terephthalato), consists of two $\text{Fe}(\text{salen})$ complexes connected by the μ -(terephthalato) bridge. Each Fe atom is six coordinated by two donor atoms of the bridge and four donor atoms of the salen. Its properties are compared with those of the closely related $[\text{Fe}(\text{salen})\text{Cl}]_2$, $[\text{Fe}(\text{salen})_2\text{O}]$ and $[\text{Fe}(\text{saloph})_2]_{\text{ter}}$, where $\text{saloph} = N,N'$ -*o*-phenylenebis(salicylaldiminato).

Introduction. Schiff-base complexes of transition-metal ions continue to be of wide interest with respect to studies of stereochemistry and conformation. Their magnetic properties are closely related to their structures and in many cases enable prediction of dimerization of the molecule.

The aim of the present work was to prove the existence of the bridge structure of $[\text{Fe}(\text{salen})_2]_{\text{ter}}$ by means of X-rays and to compare measured magnetic properties with the structural data.

Experimental. 1 g (1.5 mmol) of $[\text{Fe}(\text{salen})_2\text{O}]$ (Gerloch, McKenzie & Towl, 1969) was suspended in 40 cm³ of ethanol and heated to boiling point. 0.25 g (0.75 mmol) of terephthalic acid was added and the mixture was heated for 2 h under reflux. The crystalline black product was separated, washed with ethanol and diethyl ether and dried at room temperature. Small brown needle-like crystals were obtained

by recrystallization from a mixture of ethanol and pyridine.

Analysis: calculated for $\text{Fe}_2\text{C}_{40}\text{H}_{32}\text{N}_4\text{O}_8$, C 59.42, H 3.99, N 6.93, Fe 13.82%; found, C 59.19, H 3.56, N 6.57, Fe 14.00%.

Magnetic susceptibilities were measured at 80–300 K using the Gouy method, with $\text{HgCo}(\text{SCN})_4$ as the standard (Šindelář, 1987). The density was measured by pycnometry.

Oscillation and Weissenberg photographs were taken about the principal axes, using $\text{Cu } K\alpha$ radiation. The unit-cell dimensions given in the *Abstract* were obtained from Weissenberg photographs, but for indexing of Weissenberg photographs for layers $1kl$ – $3kl$ c axes needed to be multiplied by four. Only Weissenberg photographs for the layer lines zero and four could be indexed with the original parameters. The new cell parameters, however, led to unusual systematic extinctions.

For these reasons the hypothesis was examined that the crystal is a twin with twinning matrix

$$M_1 = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ \frac{3}{4} & 0 & 1 \end{pmatrix}$$

and with cell parameters as calculated from the Weissenberg photographs. This assumption made it possible to index all diffraction spots with normal extinctions. The matrix M_1 transforms indices of the first individual to those of the second. Thus for $h = 0,4,8\dots$ coincidences occur, contributions of the individuals cannot be separated and the spots on the Weissenberg photograph are located as for a non-twinned crystal.

In order to confirm the hypothesis, the needle-like crystal ($0.1 \times 0.1 \times 0.3$ mm) was mounted on a Hilger & Watts four-circle diffractometer with Ni-filtered $\text{Cu } K\alpha$ radiation. Indexing of 36 reflections ($3.8 < \theta < 27^\circ$) led to two orientation matrices and confirmed twinning of the crystal. After refinement of the first orientation matrix the unique reflections

of the first individual and coinciding reflections were measured by the learnt-profile method (Clegg, 1981) in the range $\theta < 57^\circ$, $0 \leq h \leq 7$, $0 \leq k \leq 18$, $-16 \leq l \leq 15$, with standards (102, 013 and 040) monitored every 30 reflections showing no significant variations, with a θ - 2θ scan technique with the scan speed varied from 1 to 4° min^{-1} on the basis of a rapid prescan, and with a 2° scanning interval. Then the second orientation matrix was refined and unique reflections of the second individual were measured in the same range of θ and hkl with the standards 102, 013 and 040. Thus three types of reflection were obtained:

Type (I): 1854 unique reflections (1154 observed, 700 unobserved) for the first individual.

Type (II): 1847 unique reflections (1095 observed, 752 unobserved) for the second individual.

Type (III): 621 inseparable reflections (454 observed, 167 unobserved).

The twinning matrix calculated from the orientation matrices was

$$M_2 = \begin{pmatrix} -1.00 & 0.00 & 0.00 \\ 0.00 & -1.00 & 0.00 \\ 0.73 & 0.00 & 1.00 \end{pmatrix}$$

with the e.s.d.'s in the third significant figure.

Reflections with $I < 3\sigma(I)$ were classified as unobserved. The resulting number of reflections was 2703 observed and 1619 unobserved. The parameters obtained by least squares (Shoemaker, 1970) were $a = 6.958$ (1), $b = 17.204$ (2), $c = 15.338$ (1) Å, $\beta = 99.52$ (1) $^\circ$ and $a = 6.950$ (1), $b = 17.188$ (3), $c = 15.328$ (2) Å, $\beta = 99.53$ (1) $^\circ$ for the first and for the second individual, respectively. The average from these values was used in the refinement.

The structure was solved by the heavy-atom method. The general position (*e*) of the Fe atom was determined from a three-dimensional Patterson synthesis. The remaining non-H atoms were located by a Fourier synthesis based on the structure factors corrected for the twinning (*i.e.* recalculated as if they had been from only one individual) (Petříček, Císařová & Šubrtová, 1983).

All calculations were performed by our system of programs for solution and refinement of crystal structures (Petříček & Malý, 1990) using *F* magnitudes. Scattering factors including anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The input reflections were indexed on the first individual basis with *h* multiplied by 4. For each reflection a decision between the types (I), (II) and (III) was made by transformation of indices to the first and the second individual basis. The matrix M_1 was used for this transformation.

In the case of coincidence, two individuals contribute independently to the same measured intensity

(Catti & Ferrari, 1976). Thus $I_{h_1} = (1 - \alpha)J_{h_1} + \alpha J_{h_2}$, where J_{h_1} and J_{h_2} are the intensities of the individuals which an untwinned crystal of the same total volume would give, α is the fraction of the second individual, and h_1 and h_2 are the reciprocal vectors in the first and the second crystal basis.

The program enables us to refine directly the twin fractions and all positional and vibrational parameters. The function minimized was $\sum [w(|F_o| - |F_c|)^2]$, with $w^{-1} = \sigma^2(F_o) + (0.03F_o)^2$.

Refinement with all non-H atoms and with isotropic temperature factors converged to $R = 0.134$. After refinement with anisotropic temperature factors the *R* value was 0.104. At this stage of the refinement systematically large $|F_o| - |F_c|$ differences for $h = 4$ (see Table 1) suggested that the approximate form of the matrix M_1 as given by equation (1) was too inaccurate. The comparison of the diffractometer angles for the pairs $4kl$ and $-4, -k, l + 3$ showed that the pairs are only in partial coincidence but inseparable by means of our experimental equipment. For these reasons this class of reflection (269 observed, 95 unobserved) was excluded from the calculation. After three cycles of refinement the resulting *R* was 0.084.

All 16 H atoms were found from the difference Fourier synthesis with the structure factors corrected for the twinning (Petříček, Císařová & Šubrtová, 1983). The final refinement, with non-H atoms anisotropic and with a mean isotropic temperature factor for H atoms, converged to $R = 0.072$, $wR = 0.091$, $S = 1.821$. The initial ratio factor α was chosen as 0.5 and the refined value was 0.4936 (3). The ratio of maximum least-squares shift to e.s.d., $(\Delta/\sigma)_{\text{max}}$, was 0.31 for the *z* coordinate of H17. The maximum and minimum electron densities in the final difference Fourier synthesis were $(\Delta\rho)_{\text{max}} = 0.71$ and $(\Delta\rho)_{\text{min}} = -0.63 \text{ e \AA}^{-3}$, respectively.

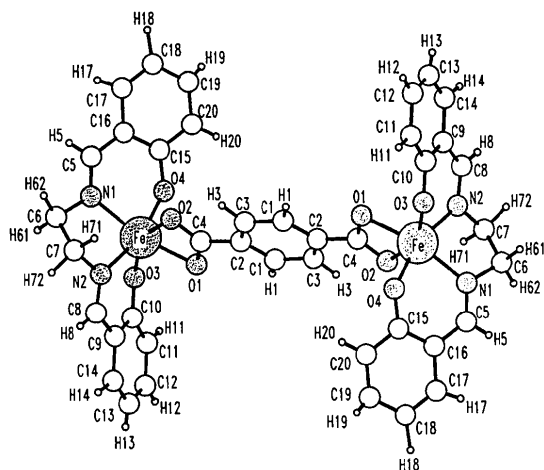
Discussion. The crystallographic asymmetric unit comprises one half of the dimer, the second being related to the first by the centre of symmetry. The connection of the Fe(salen) moieties is achieved *via* the terephthalato bridge which completes the six coordination of each metal atom.

The molecule is shown in Fig. 1. The final positional parameters and equivalent isotropic thermal parameters are given in Table 2, the interatomic distances in Table 3.*

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, and bond distances involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55074 (24 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL0515]

Table 1. Values of the *R* factors as a function of *h* index

<i>h</i>	<i>R</i>	<i>h</i>	<i>R</i>
0	0.059	4	0.269
1	0.062	5	0.091
2	0.067	6	0.108
3	0.074	7	0.147

Fig. 1. The molecular structure of $[\text{Fe}(\text{salen})_2\text{ter}]$. The centre of symmetry is at the centre of the bridge ligand. The Fe atoms and coordinated atoms are shaded.

Stereochemistry. The $[\text{Fe}(\text{salen})_2\text{ter}]$ is related to two similar molecules, $[\text{Fe}(\text{salen})\text{Cl}]_2$ (Gerloch & Mabbs, 1967) and $[\text{Fe}(\text{salen})_2\text{O}]$ (Gerloch, McKenzie & Towl, 1969). In these molecules the salen ligand adopts geometries in which each salicylaldehyde group is approximately planar but the angle between them depends on the arrangement round the Fe atoms.

In the $[\text{Fe}(\text{salen})_2\text{O}]$ the Fe atoms are five coordinate and a square-pyramidal description with the bridging O atom at a common apex can be used. The donor atoms of the salen are arranged in a distorted square around the Fe atom. The salicylaldehyde groups are twisted approximately along their O–N lines.

In $[\text{Fe}(\text{salen})\text{Cl}]_2$ the Fe atoms are six coordinate. The coordination can be approximately described as an octahedron with two shared apexes. The bridging atoms are the O atoms of the salen ligands. The arrangement of donor salen atoms is similar to that in $[\text{Fe}(\text{salen})_2\text{O}]$.

In the present molecule the Fe atoms are six coordinate and the square arrangement of the donor salen atoms is distorted because the salicylaldehyde groups are twisted not along but across their O–N line. The coordination around the Fe atoms is an irregular octahedron.

The coordinations of donor salen atoms in the present molecule, $[\text{Fe}(\text{salen})_2\text{O}]$ and $[\text{Fe}(\text{salen})\text{Cl}]_2$ are compared in Table 4.

Table 2. Atomic coordinates and equivalent isotropic thermal parameters (\AA^2)
$$B_{\text{eq}} = \frac{1}{3} \sum_i \beta_i a_i \cdot b_i \text{ (Hamilton, 1959).}$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq}
Fe	0.1517 (1)	0.53965 (6)	0.66621 (6)	3.60 (3)
O1	0.3545 (7)	0.5721 (3)	0.7745 (3)	4.6 (1)
O2	0.1225 (7)	0.4943 (3)	0.8004 (3)	4.6 (1)
O3	0.2509 (6)	0.6172 (3)	0.5976 (3)	4.0 (1)
O4	0.2896 (7)	0.4500 (3)	0.6375 (3)	5.0 (1)
N1	-0.1052 (8)	0.4793 (3)	0.6132 (3)	3.9 (1)
N2	-0.0701 (8)	0.6175 (3)	0.6787 (3)	4.0 (1)
C1	0.583 (1)	0.5384 (4)	0.9377 (4)	4.0 (2)
C2	0.392 (1)	0.5137 (3)	0.9168 (4)	3.7 (2)
C3	0.307 (1)	0.4762 (4)	0.9798 (4)	3.8 (2)
C4	0.281 (1)	0.5271 (4)	0.8279 (4)	4.3 (2)
C5	-0.117 (1)	0.4061 (5)	0.5974 (4)	4.8 (2)
C6	-0.285 (1)	0.5259 (5)	0.6064 (5)	4.9 (2)
C7	-0.258 (1)	0.5800 (5)	0.6831 (5)	4.9 (2)
C8	-0.056 (1)	0.6916 (5)	0.6754 (5)	5.3 (3)
C9	0.111 (1)	0.7314 (5)	0.6523 (4)	5.2 (2)
C10	0.253 (1)	0.6932 (4)	0.6138 (4)	4.3 (2)
C11	0.402 (1)	0.7373 (5)	0.5872 (6)	6.0 (3)
C12	0.411 (2)	0.8155 (8)	0.5999 (8)	8.4 (4)
C13	0.275 (3)	0.8520 (6)	0.6387 (9)	9.4 (5)
C14	0.122 (2)	0.8133 (5)	0.6649 (6)	6.7 (3)
C15	0.237 (1)	0.3751 (4)	0.6293 (5)	4.8 (2)
C16	0.042 (1)	0.3525 (4)	0.6063 (4)	4.6 (2)
C17	0.003 (1)	0.2708 (5)	0.5975 (5)	5.9 (3)
C18	0.147 (2)	0.2181 (5)	0.6092 (6)	6.6 (3)
C19	0.338 (2)	0.2414 (5)	0.6361 (8)	7.5 (4)
C20	0.385 (1)	0.3188 (5)	0.6451 (6)	5.9 (3)

Table 3. Interatomic distances (\AA)

Fe—O1	2.069 (4)	C2—C4	1.469 (8)
Fe—O2	2.241 (5)	C5—C16	1.43 (1)
Fe—O3	1.898 (5)	C6—C7	1.49 (1)
Fe—O4	1.905 (5)	C8—C9	1.44 (1)
Fe—N1	2.109 (5)	C9—C10	1.40 (1)
Fe—N2	2.075 (6)	C9—C14	1.42 (1)
O1—C4	1.292 (9)	C10—C11	1.40 (1)
O2—C4	1.248 (9)	C11—C12	1.36 (2)
O3—C10	1.330 (9)	C12—C13	1.35 (2)
O4—C15	1.339 (9)	C13—C14	1.37 (2)
N1—C5	1.28 (1)	C15—C16	1.40 (1)
N1—C6	1.474 (9)	C15—C20	1.40 (1)
N2—C7	1.469 (9)	C16—C17	1.43 (1)
N2—C8	1.28 (1)	C17—C18	1.34 (1)
C1—C2	1.38 (1)	C18—C19	1.38 (2)
C1—C3	1.388 (8)	C19—C20	1.37 (1)
C2—C3	1.374 (9)		

Table 4. Comparison of the arrangement of the donor salen atoms in $[\text{Fe}(\text{salen})_2\text{ter}]$, $[\text{Fe}(\text{salen})_2\text{O}]$ and $[\text{Fe}(\text{salen})\text{Cl}]_2$ (bonds, \AA ; angles, $^\circ$)

	$[\text{Fe}(\text{salen})_2\text{ter}]$	$[\text{Fe}(\text{salen})_2\text{O}]$	$[\text{Fe}(\text{salen})\text{Cl}]_2$
Fe—O	1.898 (5)	1.91 (2)	1.90 (2)
Fe—N	1.905 (5)	1.95 (2)	1.98 (3)
	2.075 (6)	2.09 (2)	2.09 (2)
	2.109 (5)	2.11 (2)	2.10 (2)
O—Fe—O	101.4 (2)	94.0 (1)	108.7 (3)
N—Fe—N	76.0 (2)	76.6 (7)	77.9 (4)

Magnetism. Wollman & Hendrickson (1978) have shown that compounds of composition $[\text{Fe}(\text{salen})X]_2$, where *X* is trichloroacetic, trifluoroacetic or salicylic acid, exhibit antiferromagnetic exchange interactions typical of dimeric compounds. The compound $[\text{Fe}(\text{salen})\text{Cl}]_2$ (discussed above) is a weak antiferromagnet with dipolar exchange coupling integral *J* ca 7.5 cm^{-1} , while the $[\text{Fe}(\text{salen})_2\text{O}]$ is a medium antiferromagnet with *J* ca 90 cm^{-1} (Gerloch, McKenzie & Towl, 1969). The dimerization of $[\text{Fe}(\text{salen})_2\text{ter}]$ has been proved by the present study, but an antifer-

romagnetic exchange interaction has not been found between 80 and 300 K (Šindelář, 1987). On the other hand the similar compound [Fe(saloph)]₂ter exhibits the expected exchange interaction.

The donor atoms of the saloph in [Fe(saloph)]₂ter are expected to be equatorial (square coordination) because of the inflexibility of the saloph ligand, with the bridge donor atoms completing an arrangement similar to that in [Fe(salen)]₂O. Six coordination in [Fe(salen)Cl]₂ leads to a significant distortion of the salen ligands and, simultaneously, to weaker exchange interaction. The further distortion of the salen ligands in [Fe(salen)]₂ter corresponds to the fact that an exchange interaction has not been found for this compound.

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A Platinum Chloro (Fluoroaryl)phosphine Complex

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Abstract. *trans*-Dichlorobis[tris(pentafluorophenyl)phosphine]platinum(II), [PtCl₂{P(C₆F₅)₃}₂], *M_r* = 1330.29, triclinic, *P* $\bar{1}$, *a* = 9.536 (4), *b* = 11.221 (2), *c* = 11.613 (1) Å, α = 62.55 (1), β = 65.81 (2), γ = 73.05 (2)°, *V* = 997.8 (4) Å³, *Z* = 1, *D_x* = 2.21 g cm⁻³, $\lambda(\text{Mo } K\alpha)$ = 0.71073 Å, μ = 39.27 cm⁻¹, *F*(000) = 628, room temperature, *R* = 0.034 for 3497 reflections with *F_o*² > 0. The molecule is centrosymmetric, with Pt—Cl distance 2.304 (2) and Pt—P 2.280 (1) Å, and P—Pt—Cl angle 94.8 (1)°. The C—P distances average 1.824 (4) Å, slightly longer than normal, and the pentafluorophenyl groups all have small [116.3 (3)°] angles at the c atom bonded to P.

Introduction. Platinum(II) halide complexes of the sterically demanding ligand tris(pentafluorophenyl)phosphine [cone angles = 184° (Tolman, 1977)] have received cursory examination in the literature owing to the presence of rotational isomers in solution at reduced temperature (Kemmitt, Nichols & Peacock, 1967; Docherty, Rycroft, Sharp & Webb, 1979). An X-ray crystal-structure analysis of *trans*-[PtI₂{P(C₆F₅)₃}₂] has been reported demonstrating that the complex does not contain substantial distortion

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of the metal coordination sphere despite the steric demands of the bulky phosphine and iodide ligands (Hunter, Muir & Sharp, 1986). Our interest in the title compound arose as a result of our continuing studies into electrophilic alkane activation and functionalization by platinum chloride solutions (Labinger, Herring & Bercau, 1990*a,b*; Herring, Henling, Labinger & Bercau, 1991) and recent reports noting the novel reactivity demonstrated by organometallic complexes containing fluoroalkylphosphines (Ernst & Roddick, 1989, 1990*a,b*; Koola & Roddick, 1991). The previously unreported synthesis of *trans*-[PtCl₂{P(C₆F₅)₃}₂] was performed analogously to routes described in the literature for triphenylphosphine complexes of [PtX₂] (Haake & Mastin, 1971; Gillard & Pilbrow, 1974) and gave the complex in good yield (73%).

Experimental. Synthesis of *trans*-[PtCl₂{P(C₆F₅)₃}₂]: PtCl₂ (266.0 mg, 1.0 mmol) and P(C₆F₅)₃ (1067.2 mg, 2.0 mmol) were placed in a 100 mL round-bottom flask equipped with a condenser. The apparatus was connected to a vacuum line with a 180° needle-valve and evacuated for *ca* 3 h. Toluene (50 mL) was vacuum-transferred onto the solids and the slurry was refluxed for 48 h under an argon atmosphere. The toluene was then removed under vacuum and

* Contribution No. 8515.