North, A. C. T., Philips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Pauling, L. (1948). *J. Chem. Soc.* pp. 1461–1467.
Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* University of Göttingen, Germany.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Steffen, W. L. & Palenik, J. (1978). *Inorg. Chem.* **17**, 1338–1340.
Tran Qui, D. & Palacios, E. (1990). *Acta Cryst.* C**46**, 1212–1215.
Vallarino, L. M., Goedken, V. L. & Quagliano, J. V. (1973). *Inorg. Chem.* **12**, 102–107.
Vanier, M. & Brisse, F. (1982). *Acta Cryst.* B**38**, 3060–3063.

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[*N*-Salicyl-*N*,*N*-bis(salicylidenenitriloethyl)amino]iron(III) acetonitrile solvate†

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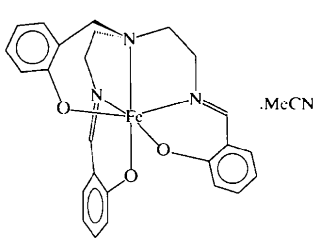
Abstract

The title complex, $[Fe(C_{25}H_{24}N_3O_3)]\cdot CH_3CN$, contains a tripodal ligand incorporating one phenolic group and two Schiff base moieties derived from salicylaldehyde and diethylenetriamine. The Fe^{III} centre is six-coordinate within an octahedral configuration. The bridgehead N atom lies 2.273 (2) Å from the metal; this is significantly longer than the other two Fe—N bond lengths of 2.122 (3) and 2.193 (2) Å.

Comment

Tripodal metal complexes have been widely investigated due to their special relevance to fields such as modelling metalloproteins (Sanyal *et al.*, 1995) and catalyzing the hydrolysis of activated phosphate esters (Young *et al.*, 1995), as well as their unique structural nature (Kichner *et al.*, 1987). We have previously reported several such compounds and studied their structural features (Gou *et al.*, 1991, 1992, 1993; Gong *et al.*, 1998). We have now directed our attention towards the preparation of novel tripodal ligands using diethylenetriamines as the amine precursors in order to synthesize new pendant-arm macrocyclic complexes *via* a sodium-template method (Gou & Fenton, 1994) and we report here an iron(III) complex, (I), of a new asymmetric tripodal ligand.



(I)

In the title complex, the Fe^{III} centre is coordinated by six donor atoms, namely three phenolic O atoms, two N atoms from C=N moieties and the bridgehead N atom. The differing lengths of the three pendant arms of the ligand result in a geometry about the metal which is significantly distorted from octahedral. Thus, the O2—Fe1—N1 angle is bent from linearity to 158.88 (9)°. The bond lengths Fe1—N2 and Fe1—N3 [2.122 (3) and 2.193 (2) Å, respectively] are clearly shorter than that between Fe1 and the bridgehead N1 atom [2.273 (2) Å]. The three Fe—O bond lengths [Fe1—O1 1.963 (2), Fe1—O2 1.924 (2) and Fe3—O3 1.900 (2) Å] are non-equivalent, presumably also as a consequence of the different pendant-arm lengths, but within the normal range.

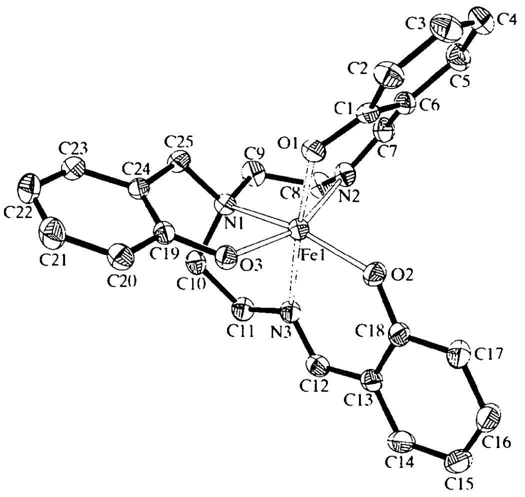


Fig. 1. The structure of the cation complex with the atom-numbering scheme. Displacement ellipsoids are shown at the 30% probability level, and H atoms and the acetonitrile solvate molecule have been omitted for clarity.

The structure of the title complex differs from that of a symmetric tripodal ligand derived from the condensation product of 2,2′,2″-triaminoethylamine and salicylaldehyde (Cook *et al.*, 1976), where the Fe centre has

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† Alternative name: {2,2′-[(salicylnitrilo)bis(ethylenenitrilomethylidene)]diphenolato-*N*,*N*′,*N*″,*O*,*O*′,*O*″}iron(III) acetonitrile solvate.

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a coordination polyhedron much closer to an ideal octahedron and lying on a threefold crystallographic axis; its bridgehead N atom does not coordinate to the metal, being located at a distance of 3.26 (2) Å, and the Fe—N and Fe—O distances are 2.186 (7) and 1.953 (6) Å, respectively. The corresponding symmetric tripodal ligands with 3-imine salicylaldehyde derivatives and their coordination chemistry with lanthanide metals have also been studied (Smith *et al.*, 1988; Liu *et al.*, 1992).

Experimental

2-Bromomethylphenyl acetate was added to an ethanolic solution in which diethylenetriamine and salicylaldehyde (molar ratio 1:2) had been condensing for 4 h. The reaction was carried out for a further 10 h, whereupon the yellow ligand ($C_{25}H_{27}N_3O_3$) was obtained. The reaction between equimolar $FeCl_3$ and the ligand in ethanol for 1 h resulted in a brown precipitate which was recrystallized from CH_3CN to give brown crystals.

Crystal data

$[Fe(C_{25}H_{24}N_3O_3)]\cdot C_2H_3N$
$M_r = 511.38$
Triclinic
$P\bar{1}$
$a = 9.969\,(4)$ Å
$b = 11.671\,(3)$ Å
$c = 12.706\,(2)$ Å
$\alpha = 63.859\,(13)°$
$\beta = 77.63\,(2)°$
$\gamma = 65.257\,(15)°$
$V = 1204.4\,(6)$ Å^3
$Z = 2$
$D_x = 1.410$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 35 reflections
$\theta = 4.99–8.36°$
$\mu = 0.663$ mm^{-1}
$T = 296\,(2)$ K
Square prism
0.50 × 0.45 × 0.35 mm
Brown

Data collection

Siemens *P*4 diffractometer
$2\theta/\omega$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.657$, $T_{max} = 0.793$
4362 measured reflections
4102 independent reflections
3405 reflections with $I > 2\sigma(I)$

$R_{int} = 0.067$
$\theta_{max} = 25°$
$h = 0 \rightarrow 11$
$k = -11 \rightarrow 12$
$l = -14 \rightarrow 15$
3 standard reflections every 97 reflections intensity decay: 14.66%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.121$
$S = 1.045$
4101 reflections
316 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0613P)^2 + 0.5425P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.001$
$\Delta\rho_{max} = 0.63$ e Å^{-3}
$\Delta\rho_{min} = -0.40$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Fe1—N1	2.273 (2)	Fe1—O1	1.963 (2)
Fe1—N2	2.122 (3)	Fe1—O2	1.924 (2)
Fe1—N3	2.193 (2)	Fe1—O3	1.900 (2)
N1—Fe1—N2	75.56 (9)	N2—Fe1—O3	156.28 (9)
N1—Fe1—N3	75.40 (9)	N3—Fe1—O1	176.01 (9)
N1—Fe1—O1	108.06 (9)	N3—Fe1—O2	85.14 (9)
N1—Fe1—O2	158.88 (9)	N3—Fe1—O3	91.77 (9)
N1—Fe1—O3	84.52 (9)	O1—Fe1—O2	91.14 (9)
N2—Fe1—N3	95.47 (10)	O1—Fe1—O3	90.55 (9)
N2—Fe1—O1	83.65 (9)	O2—Fe1—O3	104.50 (9)
N2—Fe1—O2	98.61 (10)		

A correction for linear isotropic decay was applied during data reduction (Siemens, 1994). The structure was solved by direct methods and refined by full-matrix least-squares techniques. All H atoms were introduced at calculated positions and refined using a riding model.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *SHELXTL* (Siemens, 1995). Program(s) used to solve structure: *SHELXTL*. Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1273). Services for accessing these data are described at the back of the journal.

References

Cook, D. F., Cummins, D. & McKenzie, E. D. (1976). *J. Chem. Soc. Dalton Trans.* pp. 1369–1376.
Gong, Y., Shi, Q.-F., He, L., Huang, X. & Gou, S.-H. (1998). *J. Inorg. Chem.* **14**, 241–243.
Gou, S.-H. & Fenton, D. E. (1994). *Inorg. Chim. Acta*, **233**, 169–172.
Gou, S.-H., Xu, Z., Lu, J.-P., You, X.-Z., Zhu, D.-L., Yu, Y.-P. & Alyea, E. C. (1992). *Acta Chim. Sin.* **50**, 1105–1110.
Gou, S.-H., You, X.-Z., Xu, Z., Liu, S.-X. & Lin, C.-C. (1991). *Acta Cryst.* C**47**, 708–711.
Gou, S.-H., You, X.-Z., Yu, K.-B. & Lu, J.-P. (1993). *Inorg. Chem.* **32**, 1883–1887.
Kichner, R. M., Mealli, C., Bailey, M., Howe, N., Torre, L. P., Wilson, L. J., Andrews, L. C., Rose, N. J. & Lingafelter, E. C. (1987). *Coord. Chem. Rev.* **77**, 89–163.
Liu, S., Gelmini, L., Rettig, S. J., Thompson, R. C. & Orvig, C. (1992). *J. Am. Chem. Soc.* **114**, 6081–6087.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sanyal, I., Ghosh, P. & Karlin, K. D. (1995). *Inorg. Chem.* **34**, 3050–3056.
Siemens (1994). *XSCANS User's Manual.* Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1995). *SHELXTL.* Version 5.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Smith, A., Rettig, S. J. & Orvig, C. (1988). *Inorg. Chem.* **27**, 3929–3934.
Young, M. J., Wahnon, D., Hynes, R. C. & Chin, J. (1995). *J. Am. Chem. Soc.* **117**, 9441–9447.