Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Tris(2,2′-bipyridyl-*N*,*N*′)iron(II) bis[tetrachloroferrate(III)]

L. Mihiri D. Ariyananda and Richard E. Norman*

Chemistry Department, CNSB-210, University of Louisiana at Monroe, Monroe, LA 71209, USA

Correspondence e-mail: rnorman@ulm.edu

Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.004 Å
R factor = 0.043
wR factor = 0.072
Data-to-parameter ratio = 14.4

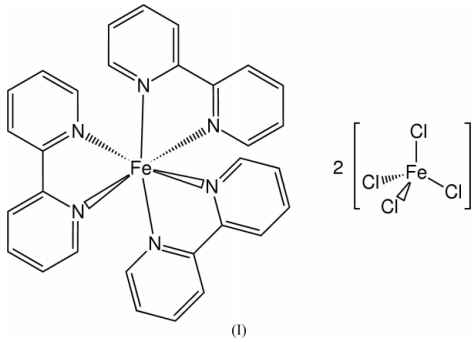
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 25 October 2002
Accepted 25 November 2002
Online 30 November 2002

The title compound, $[Fe(C_{10}H_8N_2)_3][FeCl_4]_2$, consists of a pseudo-octahedral tris(2,2′-bipyridyl)iron(II) cation and two pseudo-tetrahedral tetrachloroferrate(III) anions.

Comment

We are currently interested in the relationship between the structure of paramagnetic metal complexes and the paramagnetically shifted nuclear magnetic resonance spectra of these complexes (Ariyananda & Norman, 2002). During an attempt to synthesize a bis(2,2′-bipyridyl)dichloroiron(III) complex as an example of a d^5 cationic species, the title complex, (I), was produced.



(I)

The title complex consists of a pseudo-octahedral low-spin iron(II) complex and two tetrachloroferrate(III) anions. Given the eight chlorides, charge neutrality requires the presence of one iron(II) and two iron(III) centers. The metrical parameters within the tris(2,2′-bipyridyl)iron(II) cation are typical for iron(II), with an average Fe—N distance of 1.964 (1) Å and an average 'bite' angle of 81.75 (5)° (Batten *et al.*, 2000; Decurtins *et al.*, 1993). The metrical parameters within the 2,2′-bipyridyl units are unremarkable. The identity as iron(II) is confirmed by the Fe—N distances and by the NMR spectrum (see *Experimental*), since the resonances, while broadened, are not paramagnetically shifted. The metrical parameters within the approximately tetrahedral tetrachloroferrate(III) ions are also typical, with an average Fe—Cl distance of 2.1946 (3) Å; the reported average for 97 structures is 2.18 (1) Å (Cotton *et al.*, 1998, and references therein). Fe—Cl distances for $[FeCl_4]^{2-}$ anions are typically longer than 2.3 Å (Alcock *et al.*, 1999).

Experimental

2,2′-Bipyridyl (0.0625 g, 0.400 mmol) was dissolved in 10 ml of methanol. $FeCl_3{\cdot}6H_2O$ (0.0915 g, 0.202 mmol) was dissolved in another 10 ml of methanol. The iron solution was slowly added to the bipyridyl solution. The resultant solution was deep red, and was allowed to stand for one week before the volume was reduced by half

via rotoevaporation. This solution was then placed in an ethyl acetate bath, yielding dark red crystals after five days. ^{1}H NMR on a D_2O solution of the crystals gave four broadened peaks at 7.11, 7.26, 7.85 and 8.31 p.p.m..

Crystal data

$[Fe(C_{10}H_8N_2)_3][FeCl_4]_2$	D_x = 1.668 Mg m^{-3}
M_r = 919.72	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 13 360 reflections
a = 18.6108 (4) Å	θ = 2.5–30.0°
b = 10.7729 (2) Å	μ = 1.79 mm^{-1}
c = 18.5661 (6) Å	T = 100 K
β = 100.381 (2)°	Prism, dark red
V = 3661.43 (14) Å^3	0.35 × 0.22 × 0.20 mm
Z = 4	

Data collection

Nonius KappaCCD diffractometer (with Oxford Cryosystems Cryostream cooler)	50 254 measured reflections
	10 556 independent reflections
	6113 reflections with $I > 3\sigma(I)$
ω scans with κ offsets	R_{int} = 0.054
Absorption correction: multi-scan (*HKL SCALEPACK*; Otwinowski & Minor, 1997)	θ_{max} = 30.0°
	$h = -23 \rightarrow 26$
	$k = -13 \rightarrow 15$
T_{min} = 0.600, T_{max} = 0.699	$l = -23 \rightarrow 26$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.043	$w = 1/[\sigma^2(F_o) + 0.0004\|F_o\|^2]$
$wR(F^2)$ = 0.072	$(\Delta/\sigma)_{max} < 0.001$
S = 1.02	$\Delta\rho_{max}$ = 0.72 e Å^{-3}
6113 reflections	$\Delta\rho_{min}$ = −0.55 e Å^{-3}
424 parameters	

Table 1
Selected geometric parameters (Å, °).

Fe1—N1	1.960 (2)	Fe2—Cl2	2.1978 (8)
Fe1—N2	1.966 (2)	Fe2—Cl3	2.2109 (8)
Fe1—N3	1.964 (2)	Fe2—Cl4	2.1847 (7)
Fe1—N4	1.975 (2)	Fe3—Cl5	2.1793 (8)
Fe1—N5	1.950 (2)	Fe3—Cl6	2.1962 (8)
Fe1—N6	1.971 (2)	Fe3—Cl7	2.2116 (8)
Fe2—Cl1	2.1880 (8)	Fe3—Cl8	2.1884 (9)
N1—Fe1—N2	81.53 (8)	N2—Fe1—N6	96.14 (8)
N1—Fe1—N3	88.31 (9)	N3—Fe1—N4	81.76 (9)
N1—Fe1—N4	95.82 (8)	N3—Fe1—N5	174.21 (9)
N1—Fe1—N5	94.98 (9)	N3—Fe1—N6	94.92 (9)
N1—Fe1—N6	176.24 (9)	N4—Fe1—N5	93.16 (9)
N2—Fe1—N3	97.13 (9)	N4—Fe1—N6	86.55 (8)
N2—Fe1—N4	177.18 (9)	N5—Fe1—N6	81.95 (9)
N2—Fe1—N5	88.07 (9)		

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *TEXSAN for Windows* (Molecular Structure Corporation, 1997–1999); molecular graphics: *TEXSAN for Windows*; software used to prepare material for publication: *TEXSAN for Windows*.

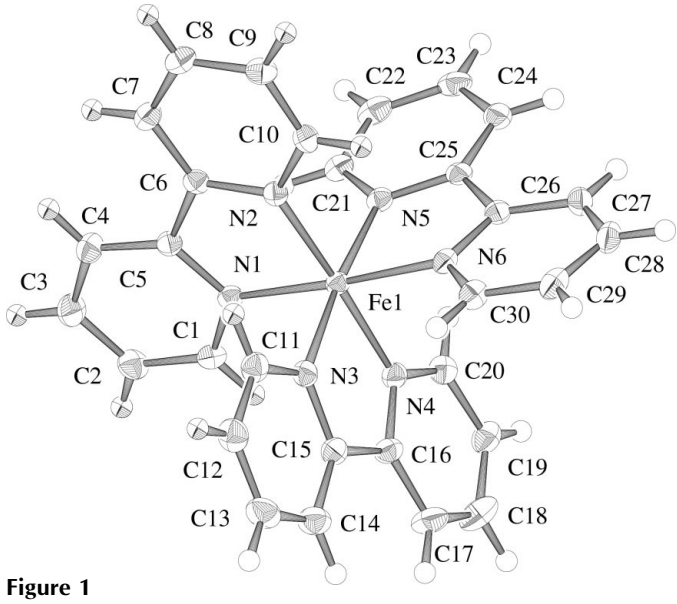


Figure 1
Displacement ellipsoid plot of the tris-(2,2′-bipyridyl)iron(II) cation, with ellipsoids at the 50% probability level.

We thank Frank Fronczek for data collection and the Louisiana Board of Regents Support Fund for financial support.

References

Alcock, N. W., Zhang, D. & Busch, D. H. (1999). *Acta Cryst.* C**55**, 886–889.
Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.
Ariyananda, L. M. D. & Norman, R. E. (2002). Unpublished results.
Batten, S. R., Murray, K. S. & Sinclair, N. J. (2000). *Acta Cryst.* C**56**, e320.
Cotton, F. A., Daniels, L. M. & Pascual, I. (1998). *Acta Cryst.* C**54**, 1575–1578.
Decurtins, S., Schmalle, H. W., Schneuwly, P. & Oswald, H. R. (1993). *Inorg. Chem.* **32**, 1888–1892.
Molecular Structure Corporation (1997–1999). *TEXSAN for Windows*. Version 1.06. MSC, 9009 New Trails Drive, The Woodlands, TX 77381, USA.
Nonius (2000). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.