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Tris(2,2'-bipyridyl)iron(II) dibromide 4.5-hydrate

Received 30 May 2006
Accepted 1 June 2006

The title compound, $[\text{Fe}(\text{C}_{10}\text{H}_8\text{N}_2)_3]\text{Br}_2 \cdot 4.5\text{H}_2\text{O}$, contains discrete tris(2,2'-bipyridyl)iron(II) cations, bromide anions and water molecules. The Fe atom (site symmetry 3) is octahedrally coordinated by six N atoms of the three bidentate bipyridyl ligands. One bromide ion occupies a site of symmetry m ; the other one is located on a site of symmetry 32. All the water O atoms are also located on special positions of site symmetries 3, m ($\times 2$) and $\bar{6}$.

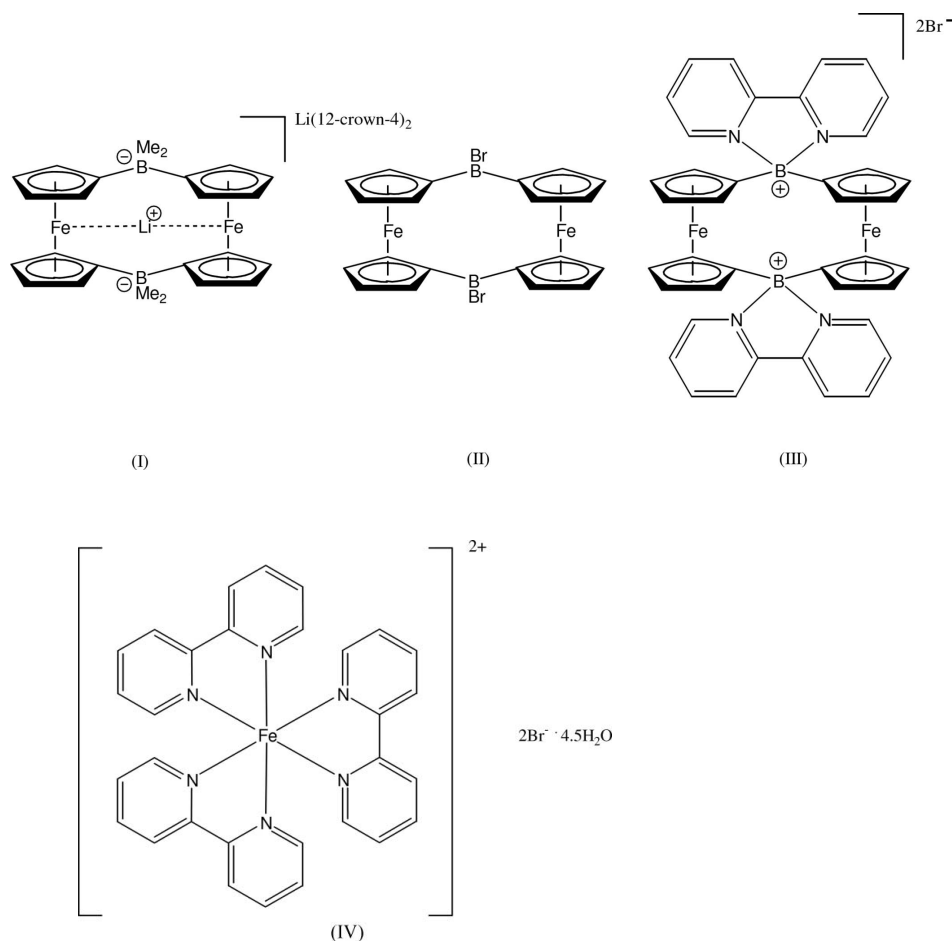
Key indicators

Single-crystal X-ray study
 $T = 173\text{ K}$
 Mean $\sigma(\text{C}-\text{C}) = 0.017\text{ \AA}$
 H-atom completeness 73%
 Disorder in solvent or counterion
 R factor = 0.101
 wR factor = 0.283
 Data-to-parameter ratio = 14.9

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

Comment

Recently, we have synthesized the anionic [1,1]diborataferrocenophane (I), which represents a highly efficient Li^+ scavenger (Scheibitz *et al.*, 2003). Now we are attempting to prepare the cationic [1,1]diborataferrocenophane, (III). In attempting to synthesize (III)· Br_2 from (II) and 2,2'-bipyridine, we have obtained the title compound, (IV), as a side-product.



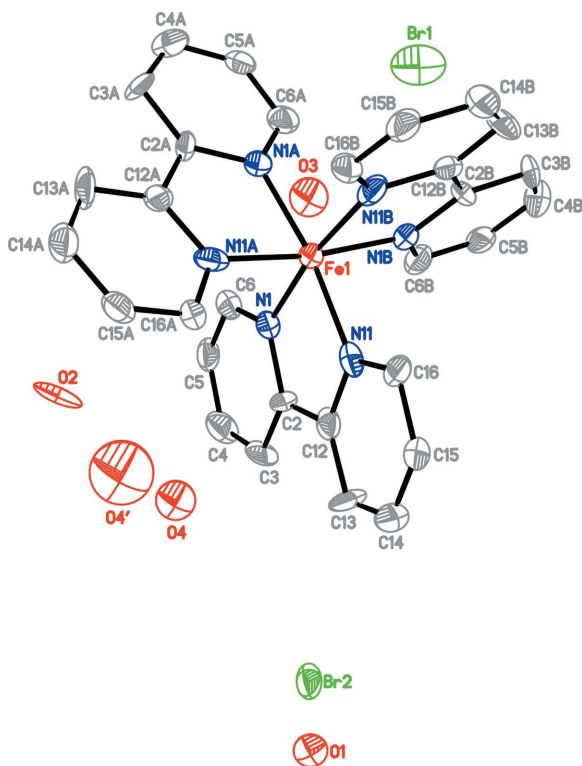


Figure 1
 Perspective view of (I), showing 50% probability displacement ellipsoids (H atoms omitted for clarity). [Symmetry codes: (A) $1 - y, 1 + x - y, z$, (B) $-x + y, 1 - x, z$.]

Compound (IV) crystallizes in the uncommon high-symmetry space group $P\bar{6}2c$ and contains discrete tris(2,2'-bipyridyl)iron(II) cations accompanied by charge-balancing bromide anions and uncoordinated water molecules. The Fe atom is located on a crystallographic threefold axis parallel to c , with just one-third of a complex molecule in the asymmetric unit. The Fe atom is octahedrally coordinated by six N atoms of the bipyridyl ligands. The bipyridyl group is slightly bent; the dihedral angle between the two aromatic rings is $5.4(6)^\circ$. The two unique bromide ions have site symmetries m (Br1) and 32 (Br2). The water O atoms also lie on special positions with the following site symmetries: O1 3 , O2 m , O3 $\bar{6}$, O4 and O4' m (the latter atom is disordered over two sites). The water molecule H atoms could not be found but $O \cdots Br$ distances in the range $3.0\text{--}3.2$ Å suggest that $O\text{--}H \cdots Br$ hydrogen bonds may be present.

A search in the Cambridge Structural Database (Version 5.27 including two updates, May 2006; Allen, 2002) yielded 25 entries containing the $[Fe(C_{10}H_8N_2)_3]^{2+}$ fragment, with a mean Fe–N bond length of $1.976(12)$ Å, a value that agrees well with that found for (IV) (Table 1).

Experimental

In an attempt to synthesize complex (III)·Br₂ from the reaction of (II) (0.066 g, 0.120 mmol) with 2,2'-bipyridine (0.047 g, 0.301 mmol) in acetonitrile (30 ml), we obtained $[Fe(2,2'\text{-bipy})_3]Br_2$ as a side-product. X-ray quality crystals of (IV) were grown from CD₃CN in an NMR tube at ambient temperature over a period of several months.

Crystal data

$[Fe(C_{10}H_8N_2)_3]Br_2 \cdot 4.5H_2O$
 $M_r = 765.29$
 Hexagonal, $P\bar{6}2c$
 $a = 13.1386(12)$ Å
 $c = 21.630(3)$ Å
 $V = 3233.6(6)$ Å³
 $Z = 4$

$D_x = 1.572$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 2.98$ mm⁻¹
 $T = 173(2)$ K
 Plate, red
 $0.26 \times 0.24 \times 0.08$ mm

Data collection

Stoe IPDSII two-circle diffractometer
 ω scans
 Absorption correction: multi-scan (MULABS; Spek, 2003; Blessing, 1995)
 $T_{\min} = 0.511$, $T_{\max} = 0.796$

25866 measured reflections
 2071 independent reflections
 1569 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.097$
 $\theta_{\max} = 25.6^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.101$
 $wR(F^2) = 0.283$
 $S = 1.15$
 2071 reflections
 139 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.188P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.033$
 $\Delta\rho_{\max} = 2.19$ e Å⁻³
 $\Delta\rho_{\min} = -1.17$ e Å⁻³
 Absolute structure: Flack (1983),
 892 Friedel pairs
 Flack parameter: 0.56 (5)

Table 1

Selected bond lengths (Å).

| Bond | Length (Å) | Bond | Length (Å) |
|--------|------------|---------|------------|
| Fe1–N1 | 1.973 (9) | Fe1–N11 | 1.989 (10) |

H atoms were placed in idealized locations ($C\text{--}H = 0.95$ Å) and refined as riding with $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$; the water H atoms could not be found. One water molecule (O4), which is located on a crystallographic mirror plane, is disordered over two sites in a $0.61(5):0.39(5)$ ratio (occupancy sum constrained to unity). The crystal used for data collection was an inversion twin: the volume fractions of the twin components refined to $0.56(5):0.44(5)$. The highest peak is located 0.24 Å from Fe1 and the deepest hole is located 0.71 Å from Br1.

Data collection: *X-Area* (Stoe & Cie, 2001); cell refinement: *X-Area*; data reduction: *X-Area*; program(s) used to solve structure: *SIR2002* (Burla *et al.*, 2003); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

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