

## Tris{bis[hydrotris(1-pyrazolyl)borato- $\kappa^3N^2,N^2',N^2''$ ]iron(III)} hexaisothiocyanatoiron(III)

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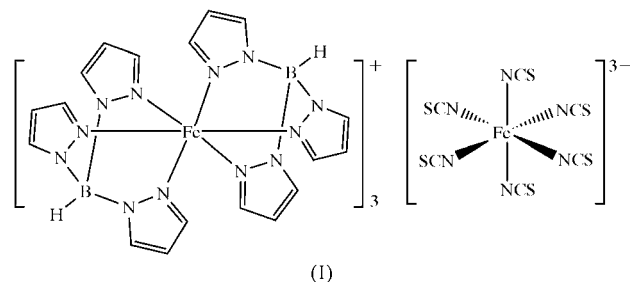
The title compound,  $[\text{Fe}(\text{C}_9\text{H}_{10}\text{BN}_6)_2]_3[\text{Fe}(\text{NCS})_6]$  or  $[\text{Fe}^{\text{III}}(\text{Tp})_2]_3[\text{Fe}^{\text{III}}(\text{NCS})_6]$  [Tp is hydrotris(1-pyrazolyl)borate], crystallizes in space group  $R\bar{3}$ ; the asymmetric unit comprises one-half of an  $[\text{Fe}(\text{Tp})_2]^+$  cation, with its Fe atom on a crystallographic inversion centre, and one-sixth of an  $[\text{Fe}(\text{NCS})_6]^{3-}$  anion, on a site of  $\bar{3}$  symmetry. The anions and cations are stacked into a three-dimensional supramolecular aggregate *via* two distinct types of weak C—H... $\pi$  interactions.

### Comment

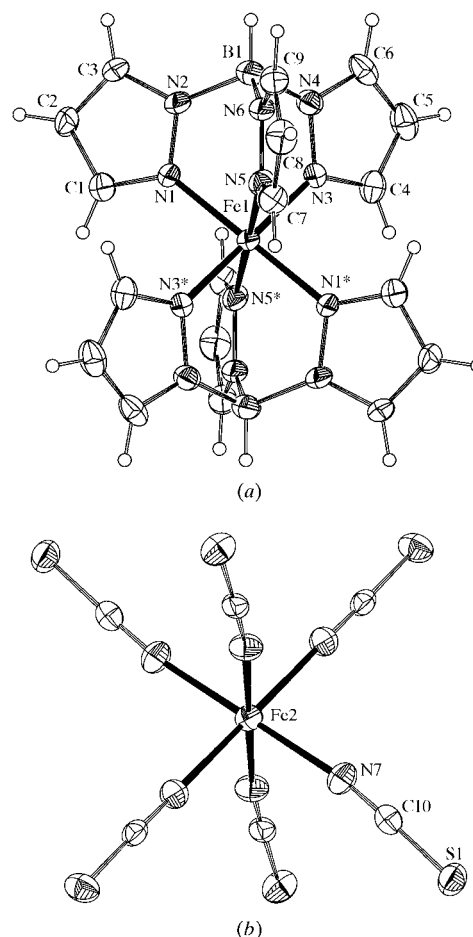
Poly(1-pyrazolyl)borate ligands  $[\text{BH}_n\text{Pz}_{4-n}]^-$  (Pz is 1-pyrazolyl) have become one of the most popular families of ligands in coordination chemistry since their introduction. When present in a tridentate coordination mode they are often considered as analogues to  $\pi$ -cyclopentadienyl groups, in that both kinds of ligands effectively occupy three facial coordination sites around a metal ion and are six-electron donors with one negative charge (Trofimenko, 1993). A large number of poly(pyrazolyl)borate complexes of main-group and transition metals have been prepared, and these complexes have attracted much interest in organometallic, coordination and bioinorganic chemistry. For example, the  $[\text{Cu}(\text{Tp})_2]$  dimer [Tp is hydrotris(pyrazolyl)borate] has been found to be useful as a starting material for bioinorganic modelling studies (Carrier *et al.*, 1993).

Iron(III) complexes with these ligands are of interest, especially from the bioinorganic point of view, because the  $\kappa^3N$  coordination mimics the multiimidazole coordination often found at the active sites of non-heme iron proteins (Lippard, 1988). The synthesis and characterization of a binuclear iron complex, namely  $[\text{Fe}_2^{\text{III}}\text{O}(\text{O}_2\text{CCH}_3)_2(\text{Tp})_2]$ , as a synthetic analogue for methemerythrin is a good example (Armstrong, 1983; Armstrong *et al.*, 1984). Iron(II) complexes with this kind of ligand are of special interest because of their

unusual magnetic properties (Weldon *et al.*, 2001). The  $\text{Fe}[\text{HB}(\text{Pz})_3]_2$ ,  $\text{Fe}[\text{HB}(3,5\text{-Me}_2\text{Pz})_3]_2$  and  $\text{Fe}[\text{HB}(3,4,5\text{-Me}_3\text{-Pz})_3]_2$  complexes have been the subject of several variable-temperature Mössbauer spectral studies in investigating spin-state transitions (Jesson *et al.*, 1967; Long & Hutchinson, 1987; Grandjean *et al.*, 1989).

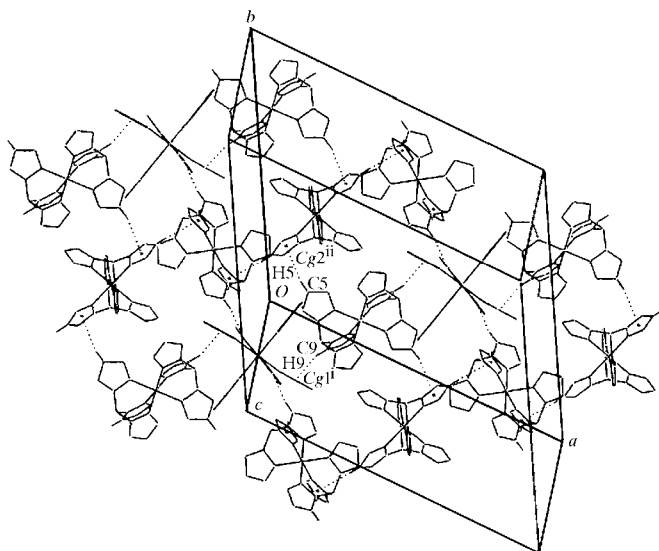


We report here the synthesis and structure of the title complex,  $3[\text{Fe}^{\text{III}}(\text{Tp})_2]^+ \cdot [\text{Fe}^{\text{III}}(\text{NCS})_6]^{3-}$ , (I) (Fig. 1), in the  $R\bar{3}$  space group. The asymmetric unit comprises one-half of an



**Figure 1**

The structures of (a) the  $[\text{Fe}(\text{Tp})_2]^+$  cation [atom Fe1 is on an inversion centre and atoms marked with an asterisk (\*) are at the symmetry position  $(\frac{2}{3} - x, \frac{1}{3} - y, \frac{1}{3} - z)$ ] and (b) the  $[\text{Fe}(\text{NCS})_6]^{3-}$  anion (atom Fe2 is at a site with  $\bar{3}$  symmetry). Displacement ellipsoids are drawn at the 30% probability level.


**Figure 2**

A view of a layer in (I) parallel to the  $(10\bar{1})$  plane. The broken lines show weak C—H $\cdots\pi$  interactions, as detailed in Table 1 [C9—H9 $\cdots$ Cg1<sup>i</sup> and C5—H5 $\cdots$ Cg2<sup>ii</sup>; symmetry codes: (i)  $y, -x + y, 1 - z$ ; (ii)  $x - y, x, -z$ ].

[Fe(Tp)<sub>2</sub>]<sup>+</sup> cation, with its Fe atom on a crystallographic inversion centre, and one-sixth of an [Fe(NCS)<sub>6</sub>]<sup>3-</sup> anion, on a site of  $\bar{3}$  symmetry. The structure of the [Fe(Tp)<sub>2</sub>]<sup>+</sup> cation is very similar to that of Fe(Tp)<sub>2</sub> (Oliver *et al.*, 1980). The Fe atom is octahedrally coordinated to six N atoms of the two Tp ligands. The Fe—N<sub>Tp</sub> bond distances lie in the narrow range 1.941 (3)–1.953 (3) Å. The *cis* intraligand N—Fe—N bond angles are in the range 88.30 (9)–88.59 (9)°. The parameters in the anion compare favourably with those found for (NMe<sub>4</sub>)<sub>3</sub>[Fe(NCS)<sub>6</sub>] [values for the NMe<sub>4</sub><sup>+</sup> salt (Müller, 1977) are given in square brackets; Fe2—N7 = 2.063 (2) Å [2.03–2.06 Å], Fe2—N7—C10 = 172.1 (2)° [170–179°], N7—C10—S1 = 178.3 (3)° [178–179°], N7—C10 = 1.161 (4) Å [1.11–1.15 Å] and C10—S1 = 1.621 (3) Å [1.57–1.66 Å]]. A search of the Cambridge Structural Database (Allen, 2002) for compounds that contain the hexaisothiocyanatoiron(III) anion yielded only four hits. Of these, only one involved a metal complex as its cation (Coleman *et al.*, 1988).

There has been increased interest recently in hydrogen bonds and other non-covalent interactions involving  $\pi$  acceptors (Ni *et al.*, 2003; Li *et al.*, 2003). Jeffrey (1997) mentions this possibility and classifies these interactions as weak hydrogen bonds. There are two types of weak C—H $\cdots\pi$  interactions in (I), which play an important role in the extended structure [Cg1 is the centre of gravity of the isothiocyanate group (type I) and Cg2 is the centroid of the N3/N4/C4—C6 pyrazole ring (type II); Table 1] Each [Fe(NCS)<sub>6</sub>]<sup>3-</sup> ion is connected to six [Fe(Tp)<sub>2</sub>]<sup>+</sup> units *via* weak C—H $\cdots$ Cg1 interactions, while each [Fe(Tp)<sub>2</sub>]<sup>+</sup> ion is connected to four neighbouring [Fe(Tp)<sub>2</sub>]<sup>+</sup> moieties *via* C—H $\cdots$ Cg2 interactions and to two [Fe(NCS)<sub>6</sub>]<sup>3-</sup> units *via* weak C—H $\cdots$ Cg1 interactions. Thus, the alternating cations and anions are stacked together into an extended three-dimensional network.

In order to describe this structure in detail, we chose one layer parallel to the  $(10\bar{1})$  plane. As shown in Fig. 2, there are two types of environment for the [Fe(Tp)<sub>2</sub>]<sup>+</sup> ion. In one, each [Fe(Tp)<sub>2</sub>]<sup>+</sup> ion is connected to two [Fe(Tp)<sub>2</sub>]<sup>+</sup> ions *via* type II interactions and to two [Fe(NCS)<sub>6</sub>]<sup>3-</sup> ions *via* type I interactions; in the other, each [Fe(Tp)<sub>2</sub>]<sup>+</sup> ion is connected to four [Fe(Tp)<sub>2</sub>]<sup>+</sup> ions *via* type II interactions. Each [Fe(NCS)<sub>6</sub>]<sup>3-</sup> ion is connected to four [Fe(Tp)<sub>2</sub>]<sup>+</sup> ions *via* type I interactions. Thus, type II interactions exist only between the [Fe(Tp)<sub>2</sub>]<sup>+</sup> units, and type I interactions occur between the [Fe(Tp)<sub>2</sub>]<sup>+</sup> and [Fe(NCS)<sub>6</sub>]<sup>3-</sup> ions. The layers are connected by the two types of weak C—H $\cdots\pi$  interactions, thus forming a three-dimensional network.

## Experimental

A solution of KTp (25.2 mg, 0.1 mmol) in acetonitrile (3 ml) was added dropwise to a solution of (Et<sub>4</sub>N)[FeCl<sub>4</sub>] (32.5 mg, 0.1 mmol) in acetonitrile (2 ml). The mixture was stirred at room temperature for 15 h. Solid KSCN (48.6 mg, 0.5 mmol) was added to the mixture, which was stirred for another 15 h and then filtered. Red crystals of (I) suitable for X-ray analysis were obtained by slow diffusion of ether into the filtrate. IR (KBr pellet): 2508 (BH), 2069, 2029 cm<sup>-1</sup> (CN).

### Crystal data

[Fe(C<sub>9</sub>H<sub>10</sub>BN<sub>6</sub>)<sub>2</sub>]<sub>3</sub>[Fe(NCS)<sub>6</sub>]  
 $M_r = 1850.12$   
 Trigonal,  $R\bar{3}$   
 $a = 22.676$  (2) Å  
 $b = 22.676$  (2) Å  
 $c = 13.5195$  (18) Å  
 $\alpha = 90.00^\circ$   
 $V = 6020.3$  (12) Å<sup>3</sup>  
 $Z = 3$   
 $D_x = 1.531$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation  
 Cell parameters from 531 reflections  
 $\theta = 2.1$ – $19.0^\circ$   
 $\mu = 0.93$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 Block, red  
 0.30 × 0.25 × 0.25 mm

### Data collection

Bruker SMART APEX CCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Bruker, 2000)  
 $T_{\min} = 0.76$ ,  $T_{\max} = 0.79$   
 11 418 measured reflections

2638 independent reflections  
 1915 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.044$   
 $\theta_{\text{max}} = 26.0^\circ$   
 $h = -27 \rightarrow 25$   
 $k = -25 \rightarrow 27$   
 $l = -9 \rightarrow 16$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.044$   
 $wR(F^2) = 0.104$   
 $S = 1.11$   
 2638 reflections  
 181 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0526P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.002$   
 $\Delta\rho_{\text{max}} = 0.25$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.38$  e Å<sup>-3</sup>  
 Extinction correction: SHELXL97  
 Extinction coefficient: 0.00035 (9)

**Table 1**

Hydrogen-bonding geometry (Å, °).

Cg1 is the centroid of the isothiocyanate group and Cg2 is the centroid of the N3/N4/C4—C6 pyrazole ring.

$D$ —H $\cdots$ A	$D$ —H	H $\cdots$ A	$D\cdots A$	$D$ —H $\cdots$ A
C9—H9 $\cdots$ Cg1 <sup>i</sup>	0.93	2.54	3.399	153
C5—H5 $\cdots$ Cg2 <sup>ii</sup>	0.93	2.75	3.654	164

Symmetry codes: (i)  $y, -x + y, 1 - z$ ; (ii)  $x - y, x, -z$ .

All H atoms were identified in difference maps and were included in the refinement in the riding-motion approximation [C—H = 0.93 Å, B—H = 0.98 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier atom})$ ].

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINTE* (Bruker, 2000); program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1750). Services for accessing these data are described at the back of the journal.

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## References

Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.

Armstrong, W. H. (1983). *J. Am. Chem. Soc.* **105**, 4837–4838.

Armstrong, W. H., Spool, A., Papaefthymiou, G. C., Frankel, R. B. & Lippard, S. J. (1984). *J. Am. Chem. Soc.* **106**, 3653–3667.

Bruker (2000). *SMART, SAINTE, SHELXTL* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Carrier, S. M., Ruggiero, C. E., Houser, R. P. & Tolman, W. B. (1993). *Inorg. Chem.* **32**, 4889–4899.

Coleman, A. W., Baskar, A. J., Bott, S. G. & Atwood, J. L. (1988). *J. Coord. Chem.* **17**, 339–345.

Grandjean, F., Long, G. T., Hutchinson, B. B., Ohlhausen, L., Neill, P. & Holcomb, J. D. (1989). *Inorg. Chem.* **28**, 4406–4414.

Jeffrey, G. A. (1997). In *An Introduction to Hydrogen Bonding*. New York: Oxford University Press.

Jesson, J. P., Trofimenko, S. & Eaton, D. R. (1967). *J. Am. Chem. Soc.* **89**, 3158–3164.

Li, Y.-Z., Liu, W.-W., Li, Y.-J., Pan, G.-J. & Hu, H.-W. (2003). *Acta Cryst.* **C59**, o611–o612.

Lippard, S. J. (1988). *Angew. Chem. Int. Ed. Engl.* **27**, 344–361.

Long, G. J. & Hutchinson, B. B. (1987). *Inorg. Chem.* **26**, 608–613.

Müller, U. (1977). *Acta Cryst.* **B33**, 2197–2201.

Ni, J., Li, Y.-Z., Qi, W.-B., Liu, Y.-J., Chen, H.-L. & Wang, Z.-L. (2003). *Acta Cryst.* **C59**, o470–o472.

Oliver, J. D., Mullica, D. F., Hutchinson, B. B. & Milligan, W. O. (1980). *Inorg. Chem.* **19**, 165–169.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

Trofimenko, S. (1993). *Chem. Rev.* **93**, 943–980.

Weldon, B. T., Wheeler, D. E., Kirby, J. P. & McCusker, J. K. (2001). *Inorg. Chem.* **40**, 6802–6812.