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Tris(1,10-phenanthroline)manganese(II) bis(hexafluorophosphate)

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In the title complex, $[Mn(C_{12}H_8N_2)_3](PF_6)_2$, the Mn^{2+} ion is coordinated by three 1,10-phenanthroline molecules that define a distorted octahedral geometry. Each cation and anion lies on a twofold axis. In the crystal structure, there are intermolecular π–π interactions between adjacent phenanthroline ligands.

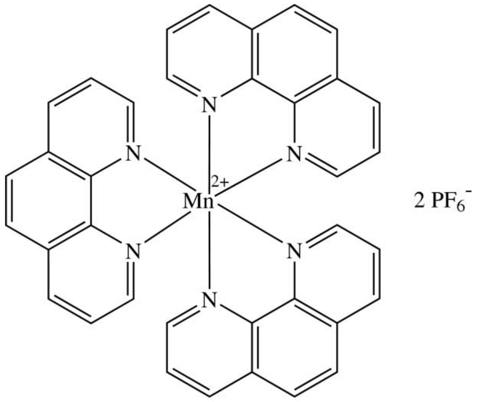
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.008 Å
Disorder in solvent or counterion
R factor = 0.077
wR factor = 0.185
Data-to-parameter ratio = 15.0

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

Comment

1,10-Phenanthroline (phen) is a widely utilized chelating ligand in coordination chemistry (Lee *et al.*, 1948). The lone pairs of electrons on the N atoms may act cooperatively in binding cations. Tris(1,10-phenanthroline) transition metal complexes have received considerable attention in biology and medicine (Barton *et al.*, 1984; Turro *et al.*, 1991), and in the mechanism of solid-state racemization (Fujiwara & Yamamoto, 1980). The $[Mn(phen)_3]^{2+}$ complex is of particular interest, owing to its antifungal (Shulman & Dwyer, 1964), and contraceptive and antivenereal properties (Shulman & Shulman, 1977). Several crystallographic structures containing $[Mn(phen)_3]^{2+}$ are known, *viz*. $[Mn(phen)_3][S_2P(OC_2H_5)_2]_2$ (Drew *et al.*, 1989), $[Mn(phen)_3](I_3)_2$ (Ramalakshmi *et al.*, 1999), $[Mn(phen)_3]I_7$ (Horn *et al.*, 2000), $[Mn(phen)_3]I_8$ (Horn *et al.*, 2001), $[Mn(phen)_3][Co(B_9C_2H_{11})_2]_2$ (Volkov *et al.*, 2003) and $[Mn(phen)_3](ClO_4)_2{\cdot}2CHCl_3$ (Cui & Li, 2005). The crystal packing and geometric properties of the $[Mn(phen)_3]^{2+}$ complex in these crystals are quite variable. Here, we report the structure of the title complex, $[Mn(phen)_3](PF_6)_2$, (I).



(I)

The analysis reveals that (I) is ionic, containing a monomeric Mn^{2+} complex with two PF_6^- counter anions (Fig. 1). Each ion is disposed about a twofold axis. The coordination geometry around the Mn^{2+} centre is distorted octahedral. The Mn—N bond lengths lie in the range 2.239 (3)–2.247 (3) Å

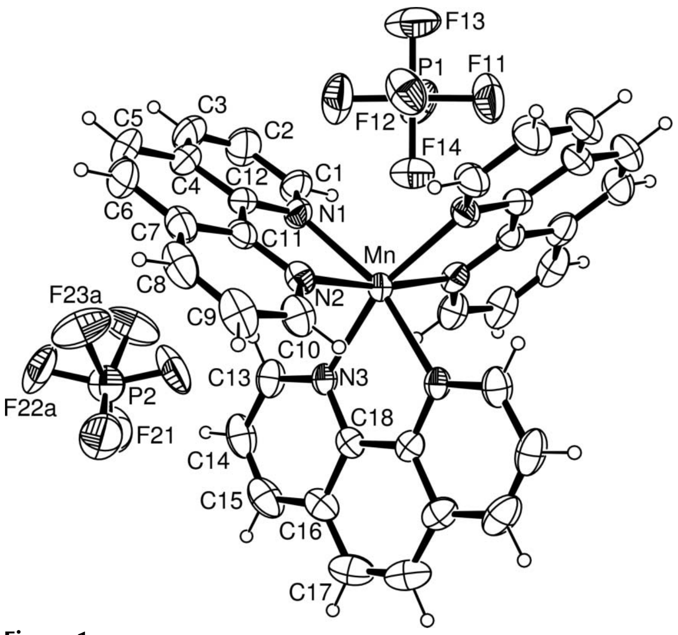


Figure 1
The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. For the sake of clarity, only the major component of the disordered atoms F22 and F23 is shown.

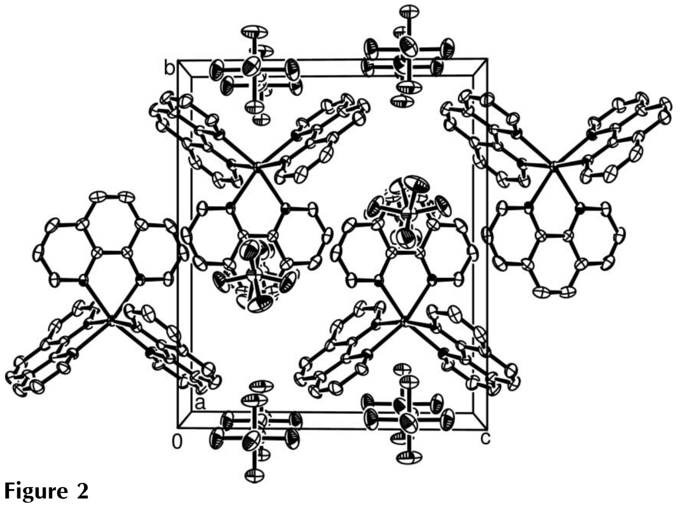


Figure 2
A packing diagram for (I). H atoms have been omitted. Only the major disorder component is shown.

(Table 1). The main contributions to the distortion are the tight N—Mn—N chelate angles [74.42 (13) and 74.57 (16)°], which result in non-linear *trans* N—Mn—N axes [163.43 (12) and 170.82 (18)°]. The PF_6^- ions are almost octahedral.

A packing diagram for (I) is shown in Fig. 2. There are intermolecular π–π interactions between centrosymmetrically related phen rings. The centroid–centroid distance between *Cg*1 (the centroid of the six-membered ring N3–C18) and *Cg*1^{i} [symmetry code: (i)$1 - x, 1 - y, 1 - z$] is 3.80 Å.

Experimental

Yellow crystals of (I) were isolated from an acetone solution of the dark-brown reaction product prepared by reacting $Mn(CH_3CO_2)_2\cdot4H_2O$ (0.49 g, 2 mmol) in MeOH (30 ml), CH_3COOH (99%, 3 ml), $KMnO_4$ (0.079 g, 0.5 mmol) in H_2O (2.5 ml), 1,10-phenanthroline (0.45 g, 2.5 mmol) and $NaPF_6$ (0.48 g, 2.86 mmol) in H_2O (2.5 ml).

Crystal data

$[Mn(C_{12}H_8N_2)_3](PF_6)_2$
M_r = 885.49
Monoclinic, $P2/c$
a = 9.3133 (7) Å
b = 15.2753 (11) Å
c = 12.8037 (9) Å
β = 94.263 (1)°
V = 1816.5 (2) Å^3
Z = 2
D_x = 1.619 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 48 reflections
θ = 2.1–28.3°
μ = 0.55 mm^{-1}
T = 293 (2) K
Needle, yellow
0.2 × 0.1 × 0.1 mm

Data collection

Bruker SMART 1000 area-detector CCD diffractometer
φ and ω scans
Absorption correction: none
11432 measured reflections
4178 independent reflections
2469 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.040
$\theta_{\max}$ = 28.3°
$h = -12 \rightarrow 12$
$k = -19 \rightarrow 17$
$l = -14 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.077
$wR(F^2)$ = 0.185
S = 1.06
4178 reflections
279 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0752P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 0.47 e Å^{-3}
$\Delta\rho_{\min}$ = −0.22 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mn—N1	2.239 (3)	Mn—N2	2.247 (3)
Mn—N3	2.242 (3)		
N1^{i}—Mn—N1	101.85 (18)	N1—Mn—N2^{i}	99.66 (12)
N1—Mn—N3^{i}	163.43 (12)	N1—Mn—N2	74.42 (13)
N1—Mn—N3	92.56 (12)	N3—Mn—N2	92.01 (11)
N3^{i}—Mn—N3	74.57 (16)	N2^{i}—Mn—N2	170.82 (18)

Symmetry code: (i) $-x + 1, y, -z + \frac{3}{2}$.

All H atoms were positioned geometrically and allowed to ride on their respective carrier atoms [C—H = 0.93 Å and $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(C)]. The F atoms (particularly F13, F22 and F23) displayed relatively large displacement factors so that the anions appear to be partially disordered. Atoms F22 and F23 were modelled anisotropically as disordered over two sites, with a site occupancy factor of 0.58 (3) for the major component.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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References

Barton, J. K., Danishefsky, A. T. & Goldberg, J. M. (1984). *J. Am. Chem. Soc.* **106**, 2172–2176.

Bruker (2000). *SMART* (Version 5.618) and *SAINT* (Version 6.02a). Bruker AXS Inc., Madison, Wisconsin, USA.

Cui, G.-H. & Li, J.-R. (2005). *Acta Cryst.* E**61**, m349–m350.

Drew, M. G. B., Hasan, M. & Hello, Y. (1989). *Polyhedron*, **8**, 1853–1854.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Fujiwara, T. & Yamamoto, Y. (1980). *Inorg. Chem.* **19**, 1903–1907.

Horn, C., Scudder, M. & Dance, I. (2000). *CrystEngComm*, **2**, 196–200.

Horn, C., Scudder, M. & Dance, I. (2001). *CrystEngComm*, **3**, 1–8.

Lee, T. S., Kolthoff, I. M. & Leussing, D. L. (1948). *J. Am. Chem. Soc.* **70**, 2348–2352.

Ramalakshmi, D., Reddy, K. R., Padmavathy, D., Rajasekharan, M. V., Arulsamy, N. & Hodgson, D. J. (1999). *Inorg. Chim. Acta*, **284**, 158–166.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.

Shulman, A. & Dwyer, F. P. (1964). *Chelating Agents and Metal Chelates*, edited by F. P. Dwyer & D. P. Mellor, p. 383. New York: Academic Press.

Shulman, A. & Shulman, G. M. (1977). US Patent 4 004 006.

Turro, N. J., Barton, J. K. & Tomalia, D. A. (1991). *Acc. Chem. Res.* **24**, 332–340.

Volkov, V. V., Ikorskii, V. N., Drozdova, M. K. & Lisoyvan, V. I. (2003). *J. Struct. Chem.* **44**, 821–826.