metal-organic compounds

Bis[S-6-(2,2:6′,2″-terpyridin-4′-yl-oxy)hexyl thioacetate]manganese(II) bis(hexafluorophosphate)

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The structure of a manganese(II) complex of terpyridine functionalized with acetylsulfanyl-terminated hexyloxy chains, $[Mn(C_{23}H_{25}N_3O_2S)_2](PF_6)_2$, is described. This type of complex is of interest in the study of single-molecule transport properties in open-shell systems. The manganese coordination environment is distorted octahedral but, importantly, with no larger deviations from the idealized geometry than those observed for other metal–terpyridine complexes. The Mn—N bond lengths range from 2.192 (2) to 2.272 (3) Å. The title compound crystallizes with the cation and anions all on general positions, with the hexafluorophosphate anions exhibiting orientational disorder. When compared with other bis-terpyridine complexes, this structure demonstrates that manganese(II) is no more prone to undergo low-symmetry distortions than systems with ligand field stabilization energy contributions.
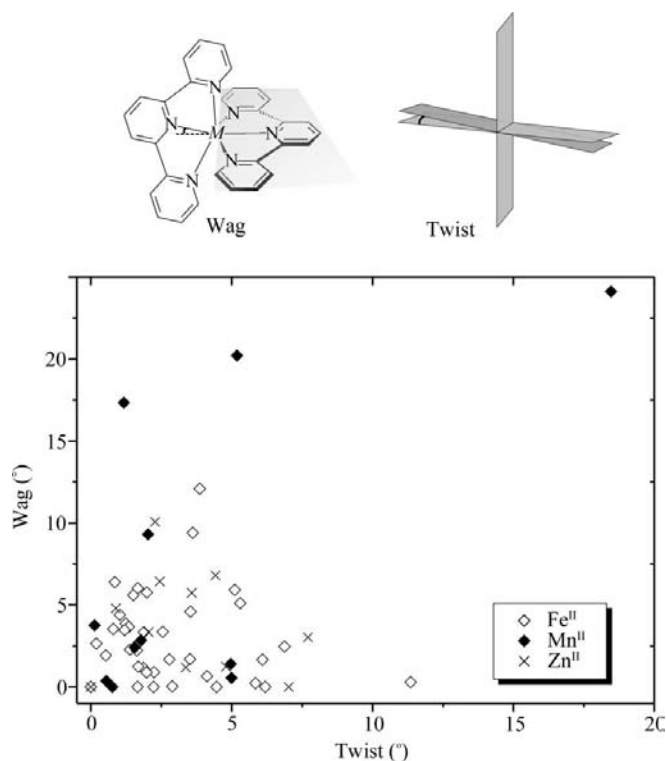
Comment

Transition metal complexes of terpyridine have recently attracted attention as robust and geometrically well defined systems for the study of electron transport at the single-molecule level (Park, 2002; Albrecht, Moth-Poulsen, Guckian et al., 2006; Albrecht, Moth-Poulsen, Christensen et al., 2006). The title compound, (I), was functionalized with an acetyl-protected thiol via a 6-(acetylsulfanyl)hexyloxy ether linkage to the 4-position of the central pyridine ring to facilitate attachment to gold surfaces and leads. The acetyl-protected thiol has been shown to be stable at room temperature and permits the formation of self-assembled monolayers of the compound on a gold surface (Albrecht, Moth-Poulsen, Guckian et al., 2006; Albrecht, Moth-Poulsen, Christensen et al., 2006). The coordination around the manganese(II) centre is distorted octahedral, governed by the steric requirements of the terpyridine units (Fig. 1). The terpyridine ligands are quite rigid and, accordingly, the Mn—N bond lengths (Table 1) deviate only slightly from the values reported for the dithionate, (II), and triiodide, (III), salts of the parent bis(2,2′:6′,2″-terpyridine-N,N′,N″)manganese(II) ion (Bhula & Weatherburn, 1991; Freire et al., 2001). In (II) and (III), the outer

(I)
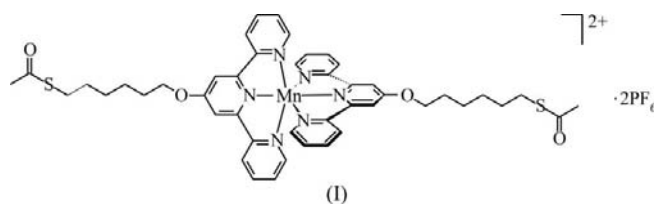
Mn—N bond lengths are 2.249 (11) and 2.249 (7) Å, respectively, while the central Mn—N bond lengths are 2.192 (6) and 2.186 (6) Å. While the bond lengths are effectively fixed in terpyridine complexes of a given central metal ion, angular distortions are frequently observed. For example, the angles between trans-situated donor atoms in (I) include some significant distortions [N42—Mn1—N44 = 145.03 (10)° and N24—Mn1—N26 = 144.13 (9)°].
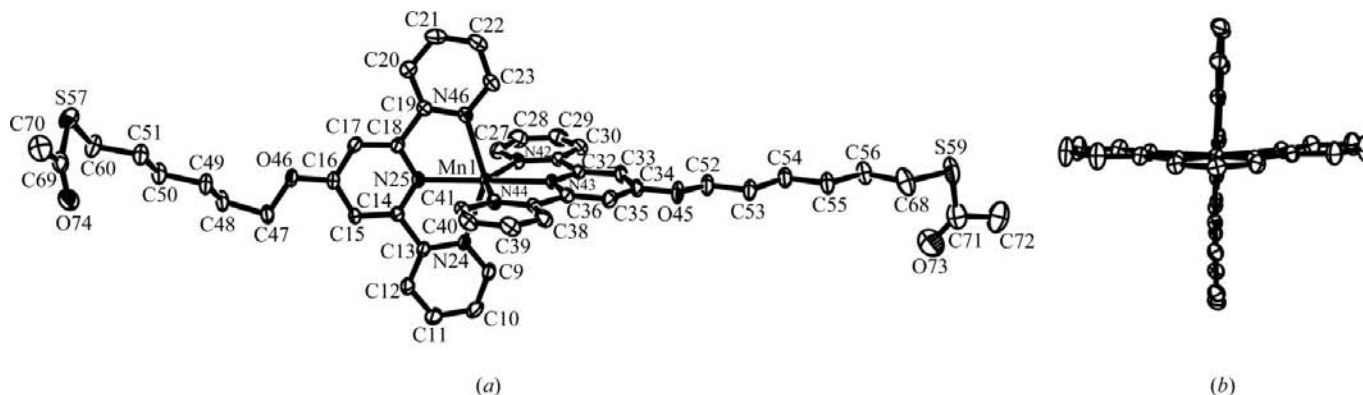
Figure 1
(a) The molecular structure of the cation in the title compound, including labelling of the atoms. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity. (b) A view along the N25···N43 axis, illustrating the regular coordination around the manganese centre. The atoms of the pendant arms of the ligands and the H atoms have been omitted for clarity.
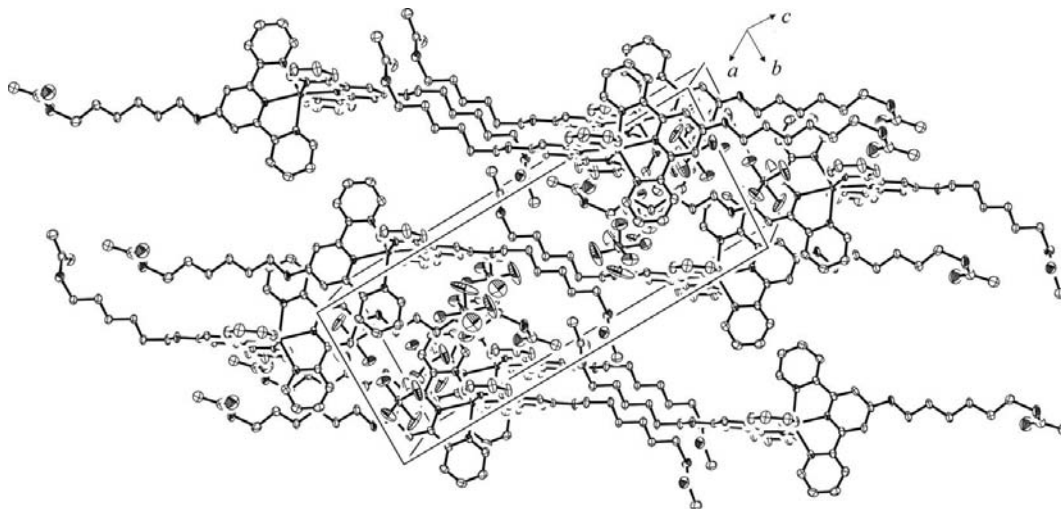
Figure 2
Top: illustrations of the wag and twist modes of distortion from idealized D_{2d} symmetry. Bottom: a plot of the twist and wag angles for all monomeric Mn^{II}, Zn^{II} and Fe^{II} bis-terpyridine complexes in the CSD (only systems without *ortho* substituents on the terpyridine rings are included in the plot).

been included to isolate the importance of the electronic structure of the metal in determining its coordination geometry. Mn^{II} and Zn^{II} have spherical d-electron density and no ligand field stabilization energy (LFSE), while Fe^{II} has maximal LFSE among the divalent transition metals. The plot illustrates that the two distortion modes have a mutually quenching relationship, with relatively few systems falling on the diagonal. It also shows, most importantly, that all three metal centres deliver examples of systems with nearly idealized D_{2d} symmetry as well as significantly distorted complexes. For manganese(II), a couple of systems that contain 4′-substituted terpyridines with wag angles of more than 15° particularly stand out (Jeitler *et al.*, 2003).

In the title compound, the aromatic part of each terpyridine ligand is close to being planar. The r.m.s. deviation from planarity in the C9–C23/N24–N26 ring system is 0.0480 Å, with a largest deviation (for atom C11) of 0.098 (4) Å, while the C27–C41/N42–N44 system has an r.m.s. deviation from planarity of 0.0392 Å and a largest deviation (C30) of 0.078 (3) Å. The two ligand planes are almost perpendicular [88.06 (3)°], amounting to a twist angle of 1.94°. In this respect, the present complex differs significantly from the analogue bis(4′-methylthio-2,2′:6′,2″-terpyridine)manganese(II) perchlorate (Jeitler *et al.*, 2003), which is significantly more distorted, with twist angles of 23.8 and 15.1° for the two independent molecules. The wag angle in the present system is relatively large at 10.6°, but is exceeded by that in at least one Fe^{II} system with a similar substitution pattern (Constable *et al.*, 2000). In the study by Jeitler *et al.* (2003), structures were determined for the Mn^{II}, Fe^{II} and Ni^{II} complexes, and it was found that the absolute differences in bond lengths between the outer and inner pyridine rings were 0.06–0.12 Å, with the manganese complex having the smallest bond-length difference. If one considers systems with substituents in the *ortho* positions to the nitrogen ligators, larger distortions are also found for Fe^{II} systems (Constable *et al.*, 1999; Pelascini *et al.*, 2004) than for Mn^{II}, albeit with different substituents.

In Fig. 2, the magnitudes of the two most common low-symmetry distortions of bis-terpyridine complexes, the wag and the twist, are shown for all monomeric Mn^{II}, Fe^{II} and Zn^{II} bis-terpyridine complexes in the Cambridge Structural Database (CSD; Version 5.29, update of 2 August 2008; Allen, 2002). Only systems without bulky *ortho* substituents have

Figure 3
The crystal packing in the title compound. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

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Contrary to the common assumption that the large ionic radius of the manganese(II) ion and the lack of ligand field stabilization in high-spin d^5 systems result in pronounced deviations from idealized geometries (Erre *et al.*, 2000; Figgins & Busch 1961), the crystallographically characterized bis-terpyridine manganese(II) complexes do not constitute a structurally distinct class, but span the full range from undistorted to highly distorted. The title compound differs significantly from other 4′-substituted bis-terpyridine manganese(II) complexes by its low twist angle. It may be speculated that the fairly dense packing (*cf.* Fig. 3) of the long side chains in the present system suppresses this degree of freedom and thus contributes to the quite symmetrical coordination of the manganese(II) centre.

In conclusion, comparison between bis-terpyridine complexes of different divalent transition metal centres need not treat manganese(II) as a special case owing to the lack of LFSE.

Experimental

Synthesis of the title compound was accomplished by combining the ligand 4′-[6-(acetylsulfanyl)hexyloxy]-2,2′:6′,2″-terpyridine (204 mg, 0.5 mmol, in 20 ml acetone) (Albrecht, Moth-Poulsen, Guckian *et al.*, 2006) and manganese(II) acetate (61 mg, 0.025 mmol, in 5 ml water). The reaction mixture was heated to 323 K for 1 h and the compound was precipitated as a white powder by the addition of a 0.2 *M* aqueous solution of potassium hexafluorophosphate (100 ml). Crystals suitable for X-ray study were obtained by slow diffusion of water into an acetonitrile solution of the compound.

Crystal data

$[Mn(C_{23}H_{25}N_3O_2S)_2](PF_6)_2$	$\gamma = 105.312\ (14)^\circ$
$M_r = 1159.94$	$V = 2561.2\ (8)\ \text{Å}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 9.1270\ (16)\ \text{Å}$	Mo $K\alpha$ radiation
$b = 11.403\ (3)\ \text{Å}$	$\mu = 0.50\ \text{mm}^{-1}$
$c = 25.822\ (2)\ \text{Å}$	$T = 122\ (2)\ \text{K}$
$\alpha = 96.302\ (12)^\circ$	$0.63 \times 0.14 \times 0.03\ \text{mm}$
$\beta = 94.287\ (11)^\circ$	

Data collection

Nonius KappaCCD diffractometer	55194 measured reflections
Absorption correction: Gaussian (Coppens, 1970)	12876 independent reflections
	9290 reflections with $I > 2\sigma(I)$
$T_{min} = 0.717$, $T_{max} = 0.979$	$R_{int} = 0.102$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.068$	12 restraints
$wR(F^2) = 0.185$	H atom parameters constrained
$S = 1.04$	$\Delta\rho_{max} = 1.93\ \text{e Å}^{-3}$
12876 reflections	$\Delta\rho_{min} = -0.99\ \text{e Å}^{-3}$
692 parameters	

Most H atoms were identified in a difference Fourier map. All H atoms were subsequently placed in idealized positions and treated as riding, with U_{iso}(H) parameters constrained to $1.2U_{eq}$ of the connected non-H atom in all cases. Disorder of the hexafluorophosphate ions was modelled with two different orientations but identical structures for each of the sites. The major populations were refined to 0.814 (7) and 0.842 (7). Short F12*A*···F12*A* inter-cell distances of 2.23 Å indicate that the disorder modelling could be further optimized and that long-range correlations between the

Table 1
Selected geometric parameters (Å, °).

Mn1—N25	2.192 (2)	Mn1—N24	2.266 (3)
Mn1—N43	2.193 (2)	Mn1—N26	2.270 (3)
Mn1—N42	2.226 (3)	Mn1—N44	2.272 (3)
N25—Mn1—N43	169.40 (10)	N43—Mn1—N24	110.53 (9)
N43—Mn1—N42	72.83 (10)	N42—Mn1—N24	97.74 (10)
N25—Mn1—N24	72.45 (9)		

orientations of the anions could be relevant. Similarity restraints with a default s.u. value of 0.03 Å were applied to the F···F distances within each unique set of F atoms defined for the rotationally disordered hexafluorophosphate counter-ions. The largest residual peak is located near one of the S atoms (S59).

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DIRAX/LSQ* (Duisenberg, 1992); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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