Bis(2,2':6',2''-terpyridine-κ³N)manganese(II) tetrathionate trihydrate

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The structure of the title compound, $[Mn(tpy)_2](S_4O_6)\cdot 3H_2O$ (tpy is 2,2':6',2''-terpyridine, $C_{15}H_{11}N_3$), consists of monomeric $[Mn(tpy)_2]^{2+}$ units embedded in a complex anionic network made up of tetrathionate ions and hydration water molecules connected *via* a complex hydrogen-bonding scheme.

Comment

In our studies of transition metal complexes with the thiosulfate ion and polydentate nitrogenated organic bases, we have quite frequently found the occurrence of oxidation processes of the anion giving rise to complexes containing polythionate groups [*e.g.* with copper (Freire *et al.*, 1998), manganese (Freire, Baggio, Baggio & Mombru, 2001) and nickel (Freire, Baggio & Baggio, 2001)]. In the case of manganese, this process seems to be highly favored due to the different oxidation states the element is able to exhibit. In particular, the structure described by Freire, Baggio & Baggio (2001) of bis(2,2'-bipyridyl-*N*,*N*')(tetrathionato-*O*,*O*')manganese(II) presents the only occurrence in the literature of a complex with a tetrathionate anion (generated 'in situ' during the synthesis binding) acting in a bidentate fashion. In light of these quite interesting results, we decided to explore further

(I)
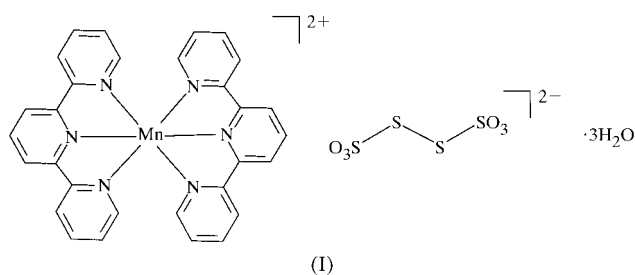
the possibility of generating polythionate anions during the synthesis process and investigate their eventual coordinating capacity. In the present paper, we report the structure of bis(2,2':6',2''-terpyridine-κ³N)manganese(II) tetrathionate trihydrate, (I), a partially successful attempt in which a tetra-

thionate group was indeed generated, though here it acts as a counter-ion.

Compound (I) (Fig. 1) consists of $[Mn(tpy)_2]^{2+}$ cations embedded in the empty spaces of an anionic matrix built up of $(S_4O_6)^{2-}$ ions and three independent hydration water molecules.

The MnN_6 chromophore shows a significant deformation, due to the presence of two highly constrained tridentate ligands (labeled *A* and *B* in Fig. 1), with expected coordination angles of 90° ranging between 71.57 (16) and 116.01 (12)°, and expected coordination angles of 180° ranging between 144.33 (14) and 168.07 (13)°. The two tpy molecules present a significant degree of 'out-of-plane' deformation, resulting in a concave shape; this departure from planarity is greater for unit *A*, where the normals of the planar pyridine rings subtend angles as large as 15.8° with one another. Unit *B* is less deformed, with a maximum deviation of around 4.1°. In spite of these deformations, the two mean tpy planes are almost perpendicular to one another (92°), as expected.

The cationic $[Mn(tpy)_2]^{2+}$ group has been reported only once before, *i.e.* in bis(2,2':6',2''-terpyridine-*N*,*N*',*N*'')manganese(II) bis(triiodide), (II) (Bhula & Weatherburn, 1991), and a comparison of the structures of (I) and (II) shows them to be very similar, with an r.m.s. deviation for the least-squares fit of homologous atoms of 0.23 Å [as calculated with *XP* in *SHELXTL/PC* (Sheldrick, 1994)]. The similarities are also revealed in the values of the homologous coordination distances, and can be appreciated from the following mean values, reported in the order (I)/(II): outer Mn—N 2.249 (11)/2.249 (7) Å and central Mn—N 2.192 (6)/2.186 (6) Å.

The tetrathionate anion is not disordered [as found in some of the structures where it does not coordinate to the cation,
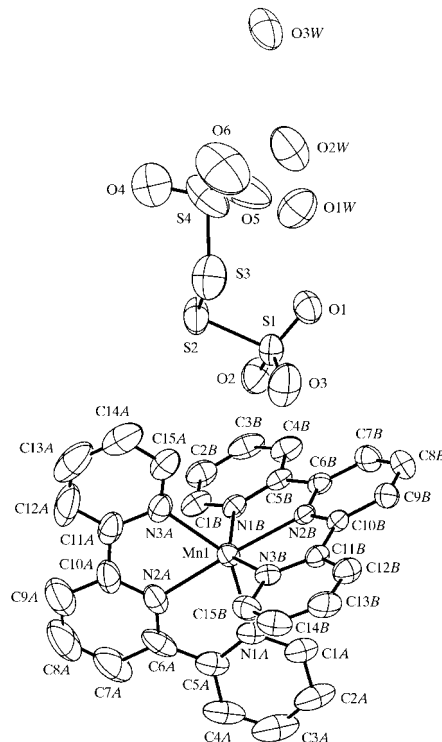

Figure 1
A view of the asymmetric unit of (I), showing the atom-numbering scheme. For clarity, H atoms are not shown. Displacement ellipsoids are drawn at the 40% probability level.

e.g. Freire *et al.* (1998)] and does not present any unusual features with regard to bond distances and angles. This includes the fact (present also in other anionic tetrathionates) that among the three terminal O—S—S angles at each end,
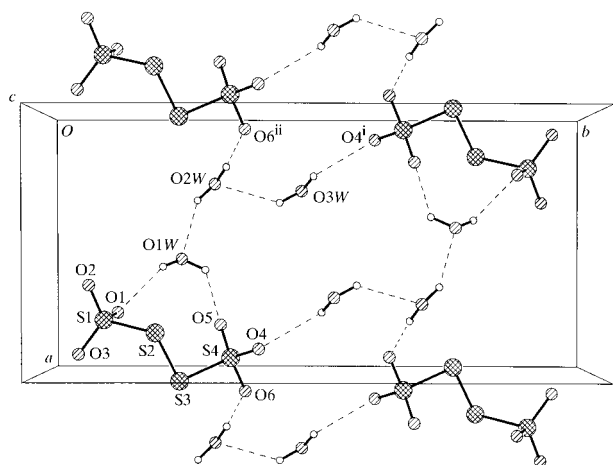

Figure 2
Schematic packing view showing the intricate hydrogen-bonding network leading to the anionic matrix. [Mn(tpy)₂]²⁺ cations (omitted from the drawing) occupy the matrix voids. [Symmetry codes: (i) $1 - x$, $3 - y$, $1 - z$; (ii) $-1 + x$, y, z.]

that associated with the O—S—S—S torsion angle nearer 180° is significantly smaller than the other two; in this case, 107.47 (16)° against 114.6 (2) and 113.5 (2)°, and 110.1 (3)° against 113.6 (5) and 114.5 (3)°. This behavior has been observed in other O₃—S—X—X (X = S or O) groups and is discussed elsewhere (Harvey *et al.*, 2001).

The ionic network is profusely interlinked by hydrogen bonding (Fig. 2 and Table 1), in which all the water H atoms and four of the six tetrathionate O atoms take part. The embedded cations interact with the matrix *via* weaker C—H···O contacts.

Experimental

The title compound was obtained by diffusion of an aqueous solution of manganese chloride and sodium thiosulfate into a methanolic solution of terpyridine (1:3:1 ratio). A few days after mixing, yellow plates, badly formed but suitable for X-ray diffraction, were obtained.

Crystal data

[Mn(C₁₅H₁₁N₃)₂](S₄O₆)·3H₂O
$M_r = 799.76$
Monoclinic, $P2_1/c$
$a = 8.783$ (3) Å
$b = 18.594$ (7) Å
$c = 21.556$ (12) Å
$\beta = 94.05$ (4)°
$V = 3512$ (3) Å³
$Z = 4$

$D_x = 1.513$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 7.5$–15°
$\mu = 0.67$ mm⁻¹
$T = 293$ (2) K
Plate, yellow
$0.48 \times 0.32 \times 0.12$ mm

Data collection

Siemens $R3m$ diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.77$, $T_{\max} = 0.92$
6852 measured reflections
6187 independent reflections
3567 reflections with $I > 2\sigma(I)$

$R_{\mathrm{int}} = 0.058$
$\theta_{\max} = 25.0°$
$h = -10 \rightarrow 10$
$k = 0 \rightarrow 22$
$l = 0 \rightarrow 25$
2 standard reflections
every 98 reflections
intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.124$
$S = 1.00$
6187 reflections
469 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.050P)^2 + 0.672P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.01$
$\Delta\rho_{\max} = 0.27$ e Å⁻³
$\Delta\rho_{\min} = -0.25$ e Å⁻³

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1WA···O1	0.90 (2)	2.17 (3)	2.955 (6)	144 (2)
O1W—H1WB···O5	0.90 (2)	2.04 (3)	2.722 (7)	131 (2)
O2W—H2WA···O1W	0.90 (3)	2.04 (3)	2.859 (7)	152 (3)
O2W—H2WB···O6ⁱ	0.90 (3)	2.05 (3)	2.928 (8)	165 (2)
O3W—H3WA···O2W	0.90 (2)	2.40 (2)	3.090 (11)	134 (1)
O3W—H3WB···O4ⁱⁱ	0.91 (4)	2.43 (5)	3.156 (11)	137 (3)

Symmetry codes: (i) $x - 1$, y, z; (ii) $1 - x$, $3 - y$, $1 - z$.

H atoms attached to C atoms were added at expected positions and refined as riding (C—H = 0.93 Å). Water H atoms were found in a difference Fourier map and were refined with restraints (O—H = 0.90 Å and H···H = 1.50 Å). Their isotropic displacement parameters were taken as 1.2 times those of the water O atom to which they were attached.

Data collection: *P3/P4-PC* (Siemens, 1991); cell refinement: *P3/P4-PC*; data reduction: *XDISK* in *SHELXTL/PC* (Sheldrick, 1994); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL/PC*; software used to prepare material for publication: *PARST* (Nardelli, 1983).

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