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Triaqua(2,2′-bipyridine)(thiophene-2,5-dicarboxylato)manganese(II) 4,4′-bipyridine hemisolvate trihydrate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.048
wR factor = 0.139
Data-to-parameter ratio = 18.4

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

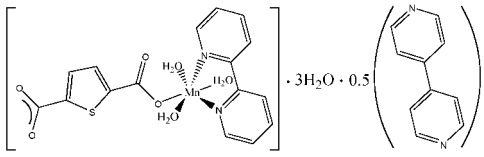
The title compound, $[Mn(C_6H_2O_4S)(C_{10}H_8N_2)(H_2O)_3]\cdot 0.5C_{10}H_8N_2\cdot 3H_2O$ or $[Mn(tdc)(bpy)(H_2O)_3]\cdot 3H_2O\cdot 0.5(bpyn)$ (tdc is thiophene-2,5-dicarboxylate, bpy is 2,2′-bipyridine and bpyn is 4,4′-bipyridine), crystallizes in space group $P\overline{1}$. Complex molecules are linked into one-dimensional chains, running along the b axis, by hydrogen bonds between the coordinated aqua ligands and uncoordinated carboxylate groups of tdc. Double-stranded chains consist of two of the one-dimensional chains and uncoordinated centrosymmetric bpyn molecules, connected by hydrogen bonds between N atoms of the bpyn molecules and coordinated aqua ligands. These double chains are further assembled into layers parallel to the ab plane, which extend into three-dimensional networks *via* hydrogen bonds between the coordinated and uncoordinated water molecules, and O atoms of tdc.

Comment

Supramolecular chemistry based on metal-ion-directed, hydrogen-bond and/or π–π-interaction assembly of organic molecular building blocks is receiving increasing attention owing to potential applications in the fields of catalysis, nonlinear optics, sensors, magnetism and molecular recognition (Lehn, 1995). The unique strength and direction of hydrogen bonding play a dominant role in the creation of a variety of molecular architectures for molecular self-assembly and molecular recognition in chemical, physical and biological sciences (Zheng *et al.*, 2004). In the construction of supramolecular frameworks, complexes based on carboxylates are of special interest. Many complexes with interesting structures have been designed and synthesized (Yaghi *et al.*, 1998). Chen *et al.* (1999) have recently reported the structural characterization of a coordination polymer with the thiophene-2,5-dicarboxylate ligand. Usually, coordination polymers are deposited from a mixture of dicarboxylic acid, bipyridine and transition metal salt in solution, especially under hydrothermal conditions. Metal-ion-directed coordination bonds play an important role in the assembly of coordination polymers.

We report here the crystal structure of a new complex, $[Mn(tdc)(bpy)(H_2O)_3]\cdot 3H_2O\cdot 0.5(bpyn)$ (tdc is thiophene-2,5-dicarboxylate, bpy is 2,2′-bipyridine and bpyn is 4,4′-bipyridine), (I). In (I), each Mn^{II} atom is coordinated by two N atoms from a chelating bpy ligand, one O atom from the monodentate carboxylate end of one tdc ligand and three O atoms from three aqua ligands to furnish a distorted octahedral geometry, in which atoms O3 and O7 are located at axial positions (Fig. 1). Complex molecules are linked into one-dimensional chains, running along the b axis, by hydrogen bonds between coordinated aqua ligands and uncoordinated

carboxylate groups of tdc (Fig. 2 and Table 1). Double-stranded chains consist of two of the one-dimensional chains and uncoordinated centrosymmetric bpyn molecules, connected by hydrogen bonds between N atoms of the bpyn molecules and coordinated aqua ligands (Fig. 3 and Table 1). These double chains are further assembled into layers parallel to the *ab* plane (Fig. 4), which extend into three-dimensional networks by hydrogen bonds between coordinated and uncoordinated water molecules, and O atoms of tdc (Fig. 5 and Table 1). To our knowledge, few complexes containing both bpy and bpyn have been reported previously. Moreover, bpyn generally links metal by coordination bonds, while in (I), bpyn links with coordinated aqua ligands by hydrogen bonds.



(I)

Experimental

$Mn(acetate)_2$(0.2 mmol), 2,2′-bipyridine (0.2 mmol), 4,4′-bipyridine (0.2 mmol) and thiophene-2,5-dicarboxylic acid (0.2 mmol) were dissolved in a water–alcohol (*v*/*v* 4:1) solution (20 ml), and an aqueous solution (5 ml) of NaOH (0.4 mmol) was added dropwise. The mixture was stirred for 1 h at 333 K and then filtered. The resulting solution was allowed to stand in air at room temperature for one week, yielding pale-green crystals.

Crystal data

$[Mn(C_6H_2O_4S)(C_{10}H_8N_2)(H_2O)_3]\cdot0.5C_{10}H_8N_2\cdot3H_2O$
$M_r = 567.45$
Triclinic, $P\overline{1}$
$a = 9.172\ (3)$ Å
$b = 12.014\ (7)$ Å
$c = 12.597\ (8)$ Å
$\alpha = 75.15\ (1)^\circ$
$\beta = 73.95\ (1)^\circ$
$\gamma = 86.79\ (1)^\circ$
$V = 1289.3\ (12)$ Å^3
$Z = 2$
$D_x = 1.462$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 2$–28°
$\mu = 0.65$ mm^{-1}
$T = 293\ (2)$ K
Block, pale green
0.51 × 0.43 × 0.36 mm

Data collection

Siemens R3m diffractometer
ω scans
Absorption correction: empirical (North *et al.*, 1968)
$T_{min} = 0.733$, $T_{max} = 0.800$
6573 measured reflections
6198 independent reflections
5369 reflections with $I > 2\sigma(I)$
$R_{int} = 0.053$
$\theta_{max} = 28.0^\circ$
$h = 0 \rightarrow 12$
$k = -15 \rightarrow 15$
$l = -15 \rightarrow 16$
2 standard reflections
every 200 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.139$
$S = 1.05$
6198 reflections
337 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.088P)^2 + 0.5664P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.30$ e Å^{-3}
$\Delta\rho_{min} = -0.42$ e Å^{-3}

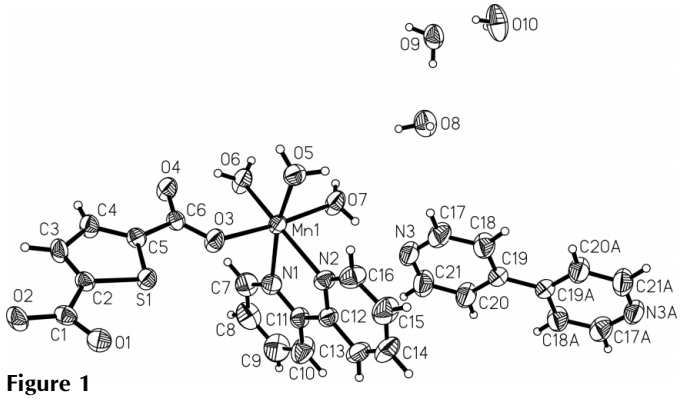


Figure 1
View of (I), with 50% probability displacement ellipsoids. [Symmetry code: (*A*) $2-x, 1-y, -z$.]

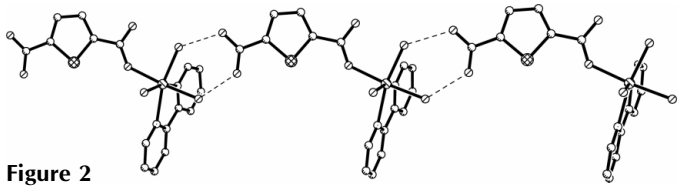


Figure 2
Perspective view of the one-dimensional chains. Hydrogen bonds are shown as dashed lines, and H atoms have been omitted.

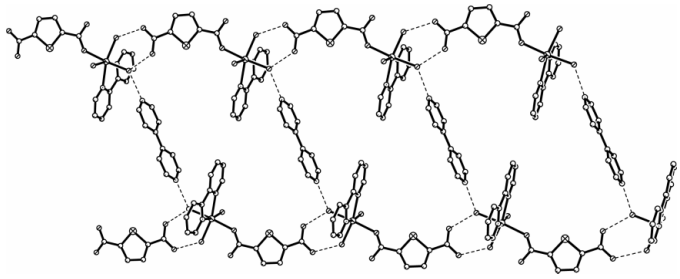


Figure 3
Perspective view of the one-dimensional double-stranded chains.

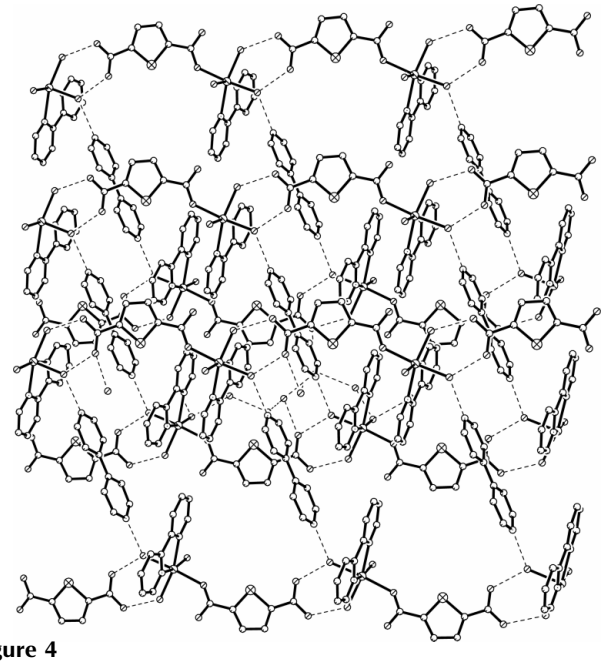


Figure 4
The layer consisting of double-stranded chains, viewed along the *c* axis.

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

D—H···A	D—H	H···A	D···A	D—H···A
O5—H5B···O4^{i}	0.85	1.84	2.679 (3)	170
O5—H5C···O10^{ii}	0.88	1.89	2.725 (3)	158
O6—H6B···O4	0.85	1.92	2.676 (3)	148
O6—H6C···O2^{iii}	0.85	1.86	2.699 (3)	170
O7—H7B···N3	0.85	1.95	2.778 (3)	166
O7—H7C···O1^{iii}	0.85	1.80	2.651 (3)	176
O8—H8B···O1^{iii}	0.85	1.96	2.810 (3)	176
O8—H8C···O9^{ii}	0.85	2.07	2.900 (3)	167
O9—H9B···O2^{i}	0.85	1.96	2.810 (3)	176
O9—H9C···O8	0.85	1.94	2.775 (3)	169
O10—H10B···O5^{iii}	0.85	2.08	2.872 (3)	154
O10—H10C···O9	0.85	1.95	2.740 (3)	155

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

C-bound H atoms were positioned geometrically (C—H = 0.93 Å), and water H atoms were located in Fourier difference maps (O—H = 0.85–0.88 Å). All H atoms were refined as riding on their parent atoms; U_{iso}(H) values were set at $1.2U_{eq}$(C) and $U_{iso}(H_{water})$ values were refined.

Data collection: *R*3*m Software* (Siemens, 1990); cell refinement: *R*3*m Software*; data reduction: *R*3*m Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1998); software used to prepare material for publication: *SHELXL*97.

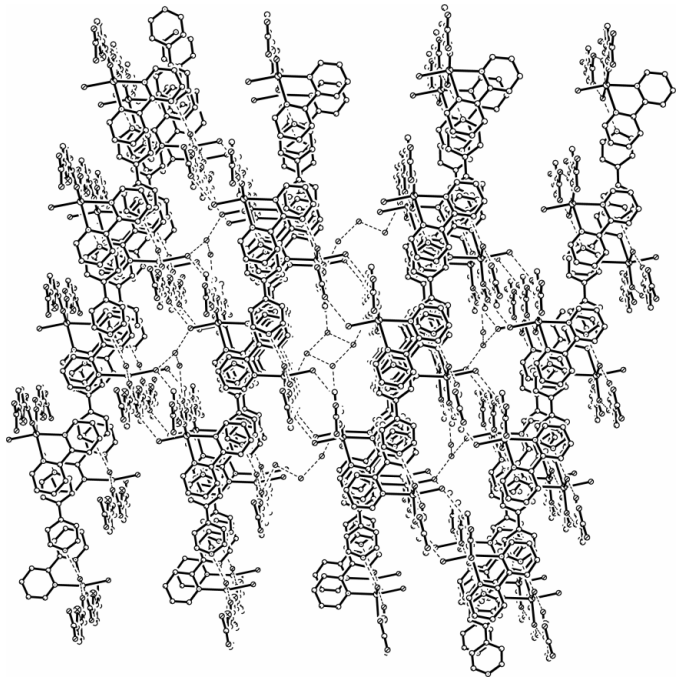


Figure 5
The three-dimensional hydrogen-bonded network in (I), viewed along the *b* axis.

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