Crystal structure of hexaquamanganese(II) (4-carboxythiophene-3-carboxylate hemihydrate, $C_{12}H_{16}MnO_{16}S_2$

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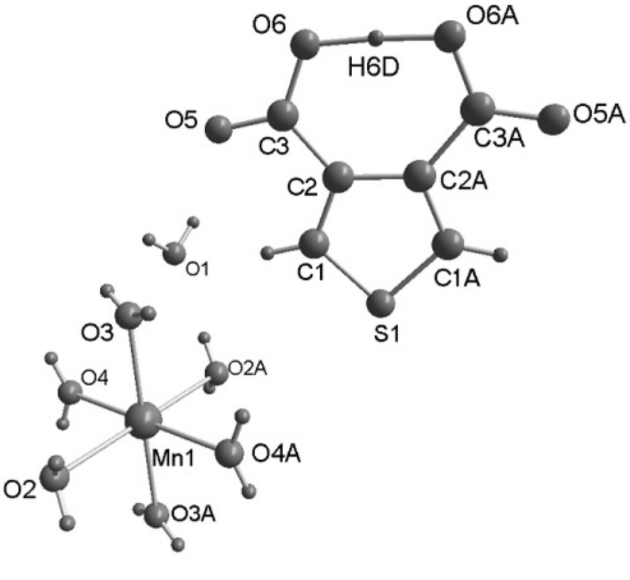

Abstract

$C_{12}H_{16}MnO_{16}S_2$, monoclinic, $C2/m$ (no. 12), $a = 6.991(2)$ Å, $b = 17.518(6)$ Å, $c = 9.440(3)$ Å, $\beta = 108.750(4)°$, $V = 1094.7$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0469$, $wR_{ref}(F^2) = 0.1431$, $T = 296$ K.

Table 1. Data collection and handling.

Crystal:	pink blocks, size 0.16×0.28×0.39 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	8.68 cm^{-1}
Diffractometer, scan mode:	CCD area detector, φ and ω
$2\theta_{max}$:	51°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3114, 1037
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 995
$N(param)_{refined}$:	80
Programs:	SHELX [13]

Source of material

A mixture of $Mn(CH_3COO)_2 \cdot 4H_2O$ (0.25 mmol, 0.006 g) and thiophene-3,4-dicarboxylic acid (0.50 mmol, 0.086 g) were dissolved in 10 mL H_2O. The solution was heated in a 23 mL Teflon lined autoclave under autogenous pressure at 403K for three days. After cooling to room temperature, pink block-shaped crystals that formed were collected. The pink crystals suitable for X-ray diffraction analysis were collected.

Experimental details

On the thiophene ring, the hydrogen atoms were assigned with $U_{iso}(H) = 1.2\ U_{eq}(C)$, and included in the final refinement by using geometrical restraints, with d(C–H) = 0.93 Å. A data completeness of only 97.2 % was achieved.

Discussion

The study and design of new metal complexes is of current interest in inorganic chemistry as well as in materials science. In recent years, the synthetic efforts have been particularly directed towards the preparation of molecular-based magnetic materials [1], conducting compounds with extended structures and of materials with zeolite-like structures [2–4]. The design and evaluation of coordination compounds which are able to build extended chain, layer or three-dimensional structures has many interesting aspects. One goal in this field is the development of synthetic routes for the molecular engineering. A second goal is to develop molecular ferromagnets on the basis of three-dimensional structures [5]. Among the reported studies about the construction of such complexes, versatile multicarboxylate ligands such as benzenepolycarboxylates, pyridinecarboxylates, and imidazolecarboxylates have been extensively employed to construct new complexes owing to their rich coordination modes and strong coordination ability [6–8]. A significant number of reports have been contributed to the use of thiophene and thiophene derivatives as ligands. These are useful and important organic moieties for the synthesis of electronic and optical materials owing to their good electron-transferring ability and structural rigidity [9–12]. However, new complexes constructed from thiophene-based compounds are rather limited and most of the work has been devoted on complexes built from commercially available thiophene-2,5-dicarboxylic acid. Considering structural rigidity, thiophene-3,4-dicarboxylic acid (H_2*tdc*) and its deprotonated analoga are good bridging ligands for constructing new complexes. The title structure consists of discrete ionic entities. A labeled diagram of the strucutre is shown in the figure. In the cations, the metal atom is surrounded by six aqua ligands, exhibiting a slightly distorted octahedral geometry. The Mn–O bonding distances are Mn1–O2 = 2.235(4), Mn1–O3 = 2.172(3), Mn1–O4 = 2.157(3) Å. The intramolecular hydrogen bond produces a short O···O distance: O6···O6#2 = 2.429(5) Å. The intermolecular hydrogen bonds result in a three-dimensional polymer.

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Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(1W)	8*j*		0.4346	0.3487	0.5393	0.074
H(2)	8*j*	0.5	0.3141	0.4660	0.4172	0.075
H(3)	8*j*	0.5	–0.1046	0.3604	0.4387	0.064
H(4)	8*j*	0.5	0.2640	0.5436	0.7423	0.087
H(6D)	4*g*		0	0.1255	0	0.089
H(1)	8*j*		0.1287	0.3444	0.2376	0.051

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mn(1)	2*d*	0	½	½	0.0374(5)	0.0286(5)	0.0286(5)	0	0.0011(3)	0
O(1)	4*h*	½	0.3782(2)	½	0.058(2)	0.039(2)	0.056(2)	0	0.028(2)	0
O(2)	4*i*	0.2316(5)	½	0.3829(4)	0.049(2)	0.047(2)	0.053(2)	0	0.015(2)	0
O(3)	4*h*	0	0.3760(2)	½	0.044(2)	0.030(2)	0.044(2)	0	–0.002(1)	0
O(4)	4*i*	0.2448(6)	½	0.7091(4)	0.071(2)	0.030(2)	0.045(2)	0	–0.020(2)	0
O(5)	8*j*	0.1783(4)	0.2083(2)	0.3226(3)	0.059(1)	0.051(1)	0.031(1)	0.004(1)	0.003(1)	0.006(1)
O(6)	8*j*	0.0745(4)	0.1277(1)	0.1348(3)	0.084(2)	0.027(1)	0.048(2)	0.002(1)	–0.006(1)	0.007(1)
S(1)	4*g*	0	0.40079(7)	0	0.107(1)	0.0224(6)	0.0594(9)	0	0.0223(8)	0
C(1)	8*j*	0.0739(5)	0.3332(2)	0.1362(4)	0.057(2)	0.033(2)	0.036(2)	–0.002(1)	0.013(1)	–0.005(1)
C(2)	8*j*	0.0440(4)	0.2611(2)	0.0805(3)	0.029(1)	0.028(1)	0.031(2)	–0.001(1)	0.009(1)	–0.002(1)
C(3)	8*j*	0.1034(4)	0.1960(2)	0.1869(3)	0.035(1)	0.036(2)	0.038(2)	0.001(1)	0.006(1)	0.005(1)

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