Crystal structure of diaqua-*bis*-(1,10-phenanthroline)-manganese(II) thiophene-3,4-dicarboxylate heptahydrate, $[Mn(H_2O)_2(C_{12}H_8N_2)_2(C_6H_3O_4S)_2]\cdot 7H_2O$, $C_{36}H_{39}MnN_4O_{17}S_2$

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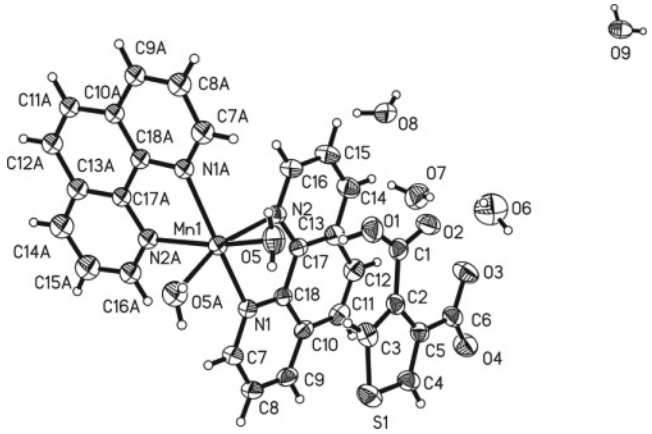
Received February 15, 2012, accepted June 12, 2012, available online September 28, 2012, CCDC no. 861483



Abstract

$C_{36}H_{39}MnN_4O_{17}S_2$, monoclinic, *C*2/*c* (no. 15), a = 16.793(3) Å, b = 22.949(2) Å, c = 13.044(2) Å, β = 125.122(7)°, V = 4111.7 Å^3, Z = 4, $R_{gt}(F)$ = 0.0610, $wR_{ref}(F^2)$ = 0.1642, T = 293 K.

Table 1. Data collection and handling.

Crystal:	yellow prisms, size 0.1×0.15×0.2 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	5.01 cm^{-1}
Diffractometer, scan mode:	CCD area detector, φ and ω
$2\theta_{max}$:	51°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	13779, 3785
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3344
$N(param)_{refined}$:	273
Programs:	SHELX [5]

Source of material

A mixture of $Mn(CH_3COO)_2\cdot 4H_2O$ (0.25mmol, 0.060 g), 1,10-phenanthroline (phen, 0.25mmol, 0.050 g), thiophene-3,4- dicarboxylic acid (0.25mmol, 0.043 g) and H_2O (7 mL) was heated in a 23 mL Teflon-lined autoclave under autogenous pressure at 413 K for five days. After cooling to room temperature, yellow crystals were collected by filtration and washed with distilled water in 56 % yield (based on Mn).

Elemental analysis calculated for $C_{36}H_{37}MnN_4O_{17}S_2$:
C 47.12, H 4.04, N 6.11%; found C 47.82, H 4.37, N 5.98%.

Discussion

In recent years, the design and synthesis of novel organic-inorganic hybrid materials have provoked significant interest owing to their fascinating properties and great potential applications [1-2]. Recently, the family of hybrid materials based on thiophene carboxylates have been synthesized under hydrothermal conditions [3-4]. Herein, we report hydrothermal synthesis and crystal structure of a new hybrid material. To the best of our knowledge, this is the first example of a hybrid material constructed from thiophene-3,4-dicarboxylic acid. The crystal structure, consists of a Mn^{2+} ion, two phen ligands, two coordinated water molecules, two free thiophene-3,4-di-carboxylate anions, and seven lattice water molecules. The Mn(II) ion is six-coordinated and exhibits an octahedral geometry, with four nitrogen atoms from phen ligands, and two oxygen atoms from coordinated water molecules. The Mn–N bond lengths range from 2.269(3) Å to 2.283(2) Å and the Mn–O bond length is 2.141(2) Å. The phen molecule acts as a typical chelating ligand, while the thiophene-3,4-dicarboxylate anion is non-bonded. Hydrogen bonding interactions are usually important in the supramolecular architectures. There is persistent O–H···O hydrogen bonding interactions between lattice water molecules, coordinated water molecules, hydroxyl group and carboxyl oxygen atoms with the distances in the range of 2.685(5) Å - 3.019(5) Å.

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

Atom	Site	Occ.	x	y	z	U_{iso}
H(8)	8*f*		0.7249	0.9038	0.2641	0.076
H(11)	8*f*		0.5778	0.7845	0.3994	0.072
H(7)	8*f*		0.8716	0.9278	0.4477	0.071
H(12)	8*f*		0.6217	0.7520	0.5889	0.073
H(14)	8*f*		0.7491	0.7454	0.8242	0.079
H(9)	8*f*		0.6174	0.8448	0.2700	0.072
H(16)	8*f*		1.0014	0.8270	0.9699	0.068
H(5A)	8*f*		0.9460	0.9980	0.7803	0.108
H(5B)	8*f*		1.0055	0.9738	0.8992	0.108
H(4)	8*f*		0.4775	0.9392	0.3561	0.071
H(3)	8*f*		0.7573	1.0038	0.6390	0.075
H(1)	8*f*		0.8398	0.9489	0.8134	0.114
H(7B)	8*f*		0.5871	0.6942	0.7378	0.160
H(7A)	8*f*		0.6450	0.6511	0.7378	0.160
H(6A)	8*f*	0.5	0.4579	0.7770	0.7110	0.206
H(6AA)	8*f*	0.5	0.5421	0.7770	0.7890	0.243
H(15)	8*f*		0.9016	0.7702	0.9962	0.082
H(9A)	8*f*		0.1006	0.0529	0.9703	0.147
H(9B)	8*f*		0.0067	0.0753	0.9026	0.147
H(8B)	8*f*		0.8032	0.6327	0.9347	0.177
H(8A)	8*f*		0.7507	0.6144	0.9809	0.177

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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)	4*e*	1	0.89927(3)	¾	0.0440(4)	0.0545(4)	0.0446(4)	0	0.0246(3)	0
S(1)	8*f*	0.61708(9)	0.99562(4)	0.4349(1)	0.0988(8)	0.0636(6)	0.0721(6)	0.0007(5)	0.0594(6)	0.0091(4)
C(17)	8*f*	0.8229(2)	0.8235(1)	0.6863(3)	0.046(2)	0.040(1)	0.043(2)	0.002(1)	0.025(1)	–0.003(1)
N(2)	8*f*	0.9133(2)	0.8374(1)	0.7879(2)	0.050(2)	0.050(1)	0.040(1)	0.002(1)	0.024(1)	–0.000(1)
N(1)	8*f*	0.8570(2)	0.8819(1)	0.5628(2)	0.046(2)	0.060(2)	0.042(1)	0.005(1)	0.025(1)	0.003(1)
C(18)	8*f*	0.7933(2)	0.8462(1)	0.5660(3)	0.047(2)	0.045(2)	0.042(2)	0.008(1)	0.026(1)	–0.001(1)
C(10)	8*f*	0.7017(2)	0.8313(1)	0.4588(3)	0.045(2)	0.051(2)	0.044(2)	0.008(1)	0.020(2)	–0.004(1)
C(13)	8*f*	0.7582(2)	0.7887(1)	0.6949(3)	0.057(2)	0.042(2)	0.057(2)	–0.001(1)	0.033(2)	–0.003(1)
C(8)	8*f*	0.7406(3)	0.8891(2)	0.3402(3)	0.063(2)	0.082(2)	0.041(2)	0.013(2)	0.027(2)	0.010(2)
C(11)	8*f*	0.6382(3)	0.7947(2)	0.4707(3)	0.050(2)	0.056(2)	0.062(2)	–0.005(2)	0.025(2)	–0.011(2)
C(7)	8*f*	0.8295(3)	0.9029(2)	0.4512(3)	0.062(2)	0.070(2)	0.049(2)	0.008(2)	0.034(2)	0.010(2)
C(12)	8*f*	0.6647(3)	0.7749(1)	0.5834(4)	0.056(2)	0.054(2)	0.069(2)	–0.009(2)	0.034(2)	–0.004(2)
C(14)	8*f*	0.7898(3)	0.7686(2)	0.8146(4)	0.076(3)	0.062(2)	0.065(2)	–0.009(2)	0.043(2)	0.007(2)
C(9)	8*f*	0.6771(3)	0.8539(2)	0.3437(3)	0.051(2)	0.073(2)	0.041(2)	0.009(2)	0.018(2)	–0.002(2)
C(16)	8*f*	0.9399(3)	0.8174(1)	0.8999(3)	0.060(2)	0.058(2)	0.045(2)	0.000(2)	0.026(2)	0.005(1)
O(5)	8*f*	0.9588(2)	0.9672(1)	0.8235(3)	0.074(2)	0.066(2)	0.090(2)	–0.009(1)	0.056(2)	–0.016(1)
C(1)	8*f*	0.7275(2)	0.9326(1)	0.7775(3)	0.052(2)	0.061(2)	0.054(2)	0.005(2)	0.032(2)	–0.009(2)
C(5)	8*f*	0.5703(2)	0.9243(1)	0.5428(3)	0.056(2)	0.047(2)	0.047(2)	0.005(1)	0.033(2)	–0.003(1)
C(2)	8*f*	0.6661(2)	0.9464(1)	0.6401(3)	0.057(2)	0.049(2)	0.053(2)	0.004(1)	0.037(2)	–0.002(1)
C(6)	8*f*	0.5055(3)	0.8822(2)	0.5493(3)	0.063(2)	0.065(2)	0.051(2)	–0.001(2)	0.035(2)	–0.003(2)
C(4)	8*f*	0.5377(3)	0.9482(2)	0.4294(3)	0.070(2)	0.059(2)	0.050(2)	0.004(2)	0.034(2)	–0.001(2)
C(3)	8*f*	0.6974(3)	0.9850(2)	0.5911(4)	0.071(2)	0.059(2)	0.070(2)	–0.004(2)	0.049(2)	–0.004(2)
O(4)	8*f*	0.4288(2)	0.8668(1)	0.4533(2)	0.066(2)	0.097(2)	0.055(2)	–0.020(1)	0.030(1)	–0.014(1)
O(3)	8*f*	0.5330(2)	0.8622(1)	0.6582(2)	0.082(2)	0.093(2)	0.059(2)	–0.023(2)	0.043(2)	0.002(1)
O(1)	8*f*	0.8104(2)	0.9540(1)	0.8456(2)	0.057(2)	0.109(2)	0.064(2)	–0.011(2)	0.036(1)	–0.015(2)
O(7)	8*f*	0.5874(2)	0.6601(2)	0.7128(3)	0.084(2)	0.130(3)	0.094(2)	0.005(2)	0.044(2)	–0.007(2)
O(6)	4*e*	½	0.7502(2)	¾	0.162(6)	0.089(3)	0.150(5)	0	0.084(5)	0
C(15)	8*f*	0.8803(3)	0.7831(2)	0.9167(3)	0.083(3)	0.066(2)	0.052(2)	–0.003(2)	0.037(2)	0.011(2)
O(2)	8*f*	0.6917(2)	0.9004(1)	0.8208(2)	0.071(2)	0.088(2)	0.050(1)	–0.005(1)	0.033(1)	0.004(1)
O(9)	8*f*	0.0565(3)	0.0693(1)	0.9021(3)	0.110(3)	0.090(2)	0.070(2)	–0.017(2)	0.037(2)	–0.010(2)
O(8)	8*f*	0.7586(2)	0.6420(2)	0.9440(3)	0.081(2)	0.196(4)	0.083(2)	0.042(2)	0.051(2)	0.060(2)

Acknowledgments. We thank the Foundation of the Education Department of Henan Province ((no.2011 A150021) for the financial support.

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