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NOTE

Hydrothermal Synthesis and Crystal Structure of Thiophene-3,4-dicarboxylate Manganese(II)

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A new manganese complex with formula $C_{12}H_4O_8S_2Mn_2$ is formed by the reaction of $Mn(OAc)_2{\cdot}4H_2O$ and thiophene-3,4-dicarboxylic acid in presence of KOH. The compound has been characterized by X-ray single-crystal diffraction, compound shows a one-dimensional framework. The 3D supramolecular structure is formed *via* hydrogen bonding connection.

Keywords: Coordination polymer, Crystal structure, Manganese(II).

Metal organic frameworks (MOFs) have received much attention in the field of crystal engineering and supramolecular chemistry because of their diverse structures and promising applications in functional materials such as luminescent materials, gas adsorption and magnetism[1-4]. Hydrogen bonds are well suited for the design of polymeric arrangement and crystal engineering because of their important directional interactions and because they can interlink 1-D, or 3-D structures into higher-dimensionality systems[5,6].

All reagent and solvents employed were commercially available and used as received without further purification.

A mixture of $Mn(OAc)_2{\cdot}4H_2O$ (0.25 mmol), thiophene-3,4-dicarboxylic acid (0.75 mmol) and KOH (0.25 mmol) and distilled water (10 mL) was heated in a 25 mL stainless steel reactor with a Teflon liner 403 K for 36 h, followed by slow cooling to room temperature. Yellow crystals of the compound formed.

Detection method: Diffraction intensity data of the single crystal of the five compounds were collected on a Bruker SMART APEX-II CCD diffractometer equipped with a graphite monochromated MoK_α radiation ($\lambda = 0.71073$ Å) by using a ω-scan mode. All the structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 using the program SHEXL 97[7]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located by geometrically calculations and their positions and thermal parameters were fixed during the structure refinement. The crystallographic data and experimental details of structural analyses for coordination polymers are summarized in Table-1. Selected bond and angle parameters are listed in Table-2.

The molecular structure of $C_{12}H_4O_8S_2Mn_2$ is shown in Fig. 1.

X-ray diffraction analysis revealed that the fundamental building unit consists of metal manganese ion and thiophene-3,4-dicarboxylic acid as bridging ligands to construct a new coordination polymer. On the thiophene ring, the hydrogen atoms were assigned with Uiso(H) = 1.2Ueq(C) and included in the final refinement by using geometrical restraints, with

TABLE-1
CRYSTALLOGRAPHIC DATA AND STRUCTURE REFINEMENT SUMMARY

Empirical formula	$C_{12}H_4O_8S_2Mn_2$
Formula weight	450.15
Crystal system space group	Monoclinic, C2/c
Unit cell dimensions	a = 4.607(4) Å; b = 26.46(2) Å c = 6.124(5) Å
Volume (Å^3)	705.6(10)
θ range for data collection	3.08 -25.50
Final R indices [I > 2σ(I)]	R_1=0.0715; wR_2 = 0.2051
Z, calculated density (mg/m^3)	2, 2.119
Absorption coefficient (mm^{-1})	2.127
F(000)	444
Limiting indices	-5 ≤ h ≤ 5; - 32 ≤ k ≤ 31; -7 ≤ l ≤ 7
Largest diff. peak and hole (e/Å^3)	1.856 and -0.973
Goodness-of-fit on F^2	1.192
R indices (all data)	R_1 = 0.0791, wR_2 = 0.2173

TABLE-2
SELECTED BOND LENGTHS (Å) AND ANGLES (°)

Mn(1)-O(2)	2.171(4)	Mn(1)-O(2)#4	2.253(5)
Mn(1)-O(1)#1	2.128(4)	Mn(1)-O(1)#2	2.128(4)
O(2)#3-Mn(1)-O(2)#5	112.16(16)	O(2)#4-Mn(1)-O(2)#5	169.5(2)
O(2)#3-Mn(1)-O(2)	81.8(2)	O(1)#1-Mn(1)-O(2)#4	87.75(17)
O(1)#1-Mn(1)-O(2)	157.96(17)	O(2)#3-Mn(1)-O(2)#4	76.19(17)
O(1)#1-Mn(1)-O(2)#3	94.57(18)	O(1)#2-Mn(1)-O(2)#4	85.25(17)
O(1)#1-Mn(1)-O(1)#2	96.5(2)	O(1)#1-Mn(1)-O(2)#5	85.25(17)

Symmetry codes: #1 x+1/2,-y+1/2,z-1/2 #2 -x+3/2,-y+1/2,-z+1 #3 -x+2,y,-z+1/2#4 x-1/2,-y+1/2,z-1/2 #5 -x+5/2,-y+1/2,-z+1

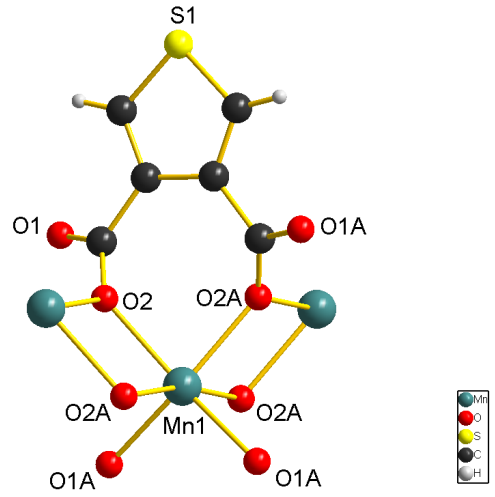

Fig. 1. Molecular structure of $C_{12}H_4O_8S_2Mn_2$ at 30 % probability displacement ellipsoids

d(C–H) = 0.93 Å, The C-C bonds within the thiophene are significantly shorter compared to tother C-C bonds. The manganese atom is six-coordinated [MnO_6] in a distorted octahedral manner and two oxygen atoms (O1 and O2) from thiophene-3,4- dicarboxylic acid ligands. The Mn-O bond lengths are 2.128(4) Å and 2.171(4) Å, respectively. The chains are further assembled by the intermolecular hydrogen bonding interaction leading to the formation of a 3D framework (Fig. 2).

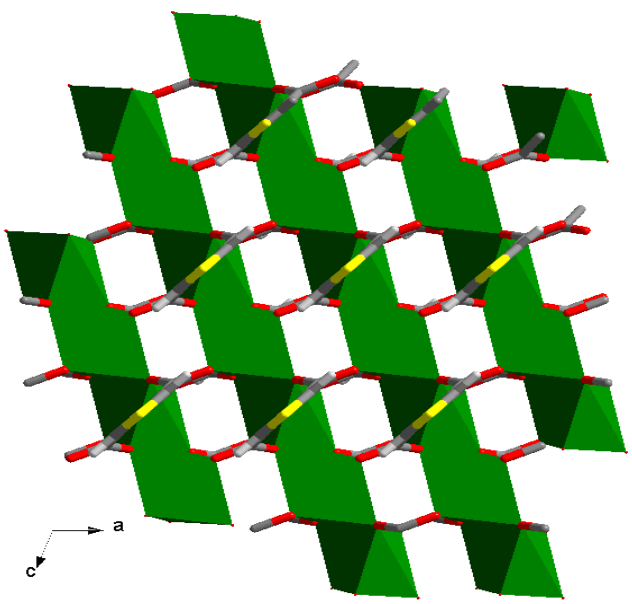

Fig. 2. 3D structure formed *via* hydrogen bonding interactions

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