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The crystal structure of *catena*-poly [(1,10-phenanthroline- k^2N,N')-(μ_3 -tetraoxido-moybdate(VI)- $k^3O:O':O''$) manganese(II)] $C_{12}H_8N_2O_4MoMn$

Table 1: Data collection and handling.

Crystal:	Yellow cube
Size:	0.40 × 0.31 × 0.22 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	2.07 mm ⁻¹
Diffraction, scan mode:	New Xcalibur, ω
θ_{max} , completeness:	29.3°, 99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	2729, 1520, 0.029
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 1342
$N(param)_{refined}$:	118
Programs:	CrysAlis ^{PRO} , Olex2 [1], SHELX [2, 3]

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A part of the polymeric title crystal structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

A mixture containing $MnSO_4 \cdot 4H_2O$ (0.480 g), 1,10-phenanthroline monohydrate (0.460 g), $(NH_4)_2MoO_4 \cdot 4H_2O$ (0.740 g), and deionized water (H_2O) (15.0 mL), with pH value 7.5, was prepared by mixing these components and sealed in a 25 mL Teflon-lined stainless steel autoclave (70% of the total volume of the autoclave). Then, the resulting slurry was heated to 463 K in an oven and kept at the temperature for a week. Then dark yellow purity-phase crystals of the title compound (about 45% yield based on Mn) were obtained.

Experimental details

The hydrogen atoms were placed at calculated positions with the SHELX program.

Comment

Manganese complexes have been attracting attention for a long time due to the intriguing structures, deriving from its

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Abstract

$C_{12}H_8N_2O_4MoMn$, monoclinic, $P2_1/m$ (no. 11), $a = 8.9812(5)$ Å, $b = 6.5212(3)$ Å, $c = 10.6167(6)$ Å, $\beta = 100.120(6)^\circ$, $V = 612.13(6)$ Å³, $Z = 2$, $R_{gt}(F) = 0.0391$, $wR_{ref}(F^2) = 0.0783$, $T = 293(2)$ K.

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	U _{iso} [*] /U _{eq}
Mn1	0.19766 (9)	0.7500	0.16874 (8)	0.0209 (2)
Mo1	−0.00443 (5)	0.2500	0.17991 (4)	0.01716 (14)
C1	0.4663 (7)	0.7500	0.0065 (6)	0.0307 (14)
H1	0.3891	0.7500	−0.0646	0.037*
C2	0.6170 (8)	0.7500	−0.0123 (6)	0.0371 (16)
H2	0.6377	0.7500	−0.0952	0.044*
C3	0.7336 (8)	0.7500	0.0888 (6)	0.0356 (15)
H3	0.8334	0.7500	0.0760	0.043*
C4	0.6992 (6)	0.7500	0.2142 (6)	0.0266 (13)
C5	0.8112 (7)	0.7500	0.3289 (6)	0.0365 (16)
H5	0.9129	0.7500	0.3217	0.044*
C6	0.7752 (7)	0.7500	0.4441 (6)	0.0332 (15)
H6	0.8513	0.7500	0.5159	0.040*
C7	0.6176 (6)	0.7500	0.4599 (6)	0.0228 (12)
C8	0.5726 (7)	0.7500	0.5803 (6)	0.0249 (12)
H8	0.6447	0.7500	0.6548	0.030*
C9	0.4236 (7)	0.7500	0.5868 (6)	0.0302 (14)
H9	0.3922	0.7500	0.6657	0.036*
C10	0.3172 (7)	0.7500	0.4731 (6)	0.0269 (13)
H10	0.2150	0.7500	0.4788	0.032*
C11	0.5042 (6)	0.7500	0.3515 (5)	0.0202 (11)
C12	0.5446 (6)	0.7500	0.2258 (5)	0.0202 (11)
N1	0.4303 (5)	0.7500	0.1223 (4)	0.0226 (10)
N2	0.3546 (5)	0.7500	0.3588 (5)	0.0212 (10)
O1	0.1094 (3)	0.4728 (4)	0.2096 (3)	0.0303 (5)
O2	−0.1344 (6)	0.2500	0.2788 (5)	0.0580 (16)
O3	−0.1010 (6)	0.2500	0.0217 (4)	0.0483 (13)

multi-form of oxidation states and multi-coordination modes [4, 5], and the outstanding physicochemical properties, including optical, electric, magnetic, and catalytic performances [6–8]. Therefore, the preparation of a new manganese compound has become an important research orientation [9–11]. The hydrothermal synthesis is known as one of the most efficient methods to obtain new manganese-organic compounds [12, 13]. Nevertheless, the synthetic features of “black box” and “one-pot” lead to the preparation processes being hardly controlled. Some subtle factors, including temperature, pH-value, solvent, ratio of reactants, structure direct-agent, counterion, and so on, will greatly affect reaction processes and experimental results [14]. Based on our previous work, on [Mn(phen)(H₂O)MoO₄·H₂O]_n (phen = 1′10-phenanthroline) [15], we obtained the analogous title compound [Mn(phen)MoO₄]_n, by virtue of somewhat changing the hydrothermal synthesis conditions. By contrast, the requirement of the title compound is under conditions of higher temperature and pH-value of reaction, without CH₃COOH (aqueous solution) as pH-value conditioning agent.

Outwardly, the title compound shows the deeper color (yellow) than [Mn(phen)(H₂O)MoO₄·H₂O]_n. The single-crystal X-ray diffraction structure analyses indicate that the title compound shows the same one-dimensional configuration. The asymmetric unit contains one half of the empirical formula (Table 2). The [Mn(phen)]²⁺ moieties are connected by molybdates, MoO₄^{2−}. By contrast, the chemical composition of title compound has one crystal water molecule and one coordination water molecule less than [Mn(phen)(H₂O)MoO₄·H₂O]_n. Meanwhile, Mn-organic coordination ions [Mn(phen)]²⁺, and molybdates, MoO₄^{2−}, in title compound shows a zigzag arrangement, instead of straight line arrangement, in [Mn(phen)(H₂O)MoO₄·H₂O]_n. In [Mn(phen)]²⁺, the five-coordinated Mn²⁺ shows bond lengths of 2.230(5) and 2.249(5) Å for Mn–N, bond lengths of 2.051(3) and 2.055(4) Å for Mn–O_b. The O/N–Mn–O/N bond angles are within the normal range of 74.60(17)–166.5(2)°. The four-coordinated Mo atom show bond distances of 1.750(4) and 1.773(3) Å for two-bridging oxygen atoms (Mo–O_b) and the bond distance of 1.701(4) Å for terminal oxygen atoms (Mo–O_t). The O–Mo–O bond angles are in the range of 108.3(3)–110.11(13)°. Bond valence sum calculations on the Mo and Mn sites afford values of 6.1 and 2.2.

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