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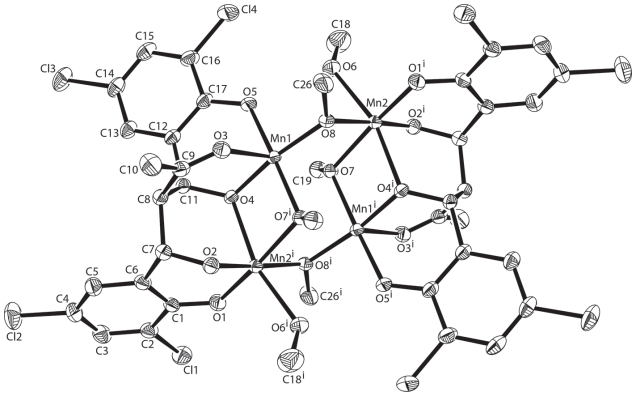
Synthesis and crystal structure tetrakis(μ_2-methanolato)-dimethanol-bis(μ_2-2-acetyl-1,3-bis(3,5-dichloro-2-oxidophenyl)propane-1,3-bis(olato)-$\kappa^5O^1,O^2,O^3:O^3,O^4,O^5$), tetramanganese(III), $C_{40}H_{40}Cl_8Mn_4O_{16}$



DOI 10.1515/ncrs-2017-0013
Received April 3, 2017; accepted August 12, 2017; available online September 16, 2017

Abstract

$C_{40}H_{40}Cl_8Mn_4O_{16}$, triclinic, $P\bar{1}$, $a = 9.2586(5)$ Å, $b = 11.6798(10)$ Å, $c = 12.3267(8)$ Å, $\alpha = 70.237(7)°$, $\beta = 75.557(5)°$, $\gamma = 81.358(6)°$, $V = 1211.65(16)$ Å^3, $Z = 1$, $R_{gt}(F) = 0.0333$, $wR_{ref}(F^2) = 0.0906$, $T = 294$ K.

CCDC no.: 1514251

The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

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Table 1: Data collection and handling.

Crystal:	Clear dark brown block
Size:	0.16 × 0.13 × 0.12 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	12.94 mm^{-1}
Diffractometer, scan mode:	SuperNova, diffractometer, ω
θ_{max}, completeness:	69.8°, 99.75%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	7765, 4474, 0.020
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3912
$N(param)_{refined}$:	314
Programs:	CrysAlis^{PRO} [20], SHELX [21]

Source of material

Synthesis of the ligand HL: 1-{4-[(3,5-Dichloro-2-hydroxy benzylidene)amino]phenyl}ethanone O-methyl oxime: All chemicals were used without further purification. 4-Amino acetophenone methoxy oxime was prepared by an similar method reported earlier [1–3]. 3,5-Dibromosalicylaldehyde (279.91 mg, 1 mmol) in EtOH (5 mL) was added slowly to a solution of 4-amino acetophenone methoxy oxime (164.09 mg, 1 mmol) in EtOH (5 mL) at 338 K. The precipitate was heated, stirred and kept refluxing for 12 h at the same temperature. Then the mixture was cooled down to room temperature and the yellow precipitates were filtered and washed successively. The isolated raw product was dried under reduced pressure and purified (yield 71.3%, m.p.: 410–411 K). Elemental analysis – Anal. calcd for $C_{16}H_{14}Cl_2N_2O_2$: C, 56.99%; H, 4.18%; N, 8.31%; Found: C, 57.02%; H, 4.20%; N, 8.25%.

Synthesis of the Mn(III) complex: A solution of $Mn(CH_3COO)_2{\cdot}4H_2O$ (2.45 mg, 0.01 mol) in EtOH (3 mL) was added slowly to a solution of HL (6.72 mg, 0.02 mmol) in acetone (3 mL) at room temperature. The color of the mixture turned to brown immediately. The mixture was filtered after being stirred for 2 h at room temperature and the filtrate was allowed to stand for 10 days at room temperature, the solvent

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Mn1	0.36606(4)	0.48082(4)	0.94574(4)	0.03059(11)
Mn2	0.35414(4)	0.70558(4)	1.03418(4)	0.03199(12)
Cl1	1.06407(8)	0.21488(8)	0.68449(8)	0.0559(2)
Cl2	0.73700(12)	−0.05362(11)	0.56923(10)	0.0789(3)
Cl3	0.22791(12)	0.47114(10)	0.40178(7)	0.0716(3)
Cl4	0.06451(11)	0.74558(9)	0.69039(9)	0.0701(3)
O1	0.7950(2)	0.24301(19)	0.85533(19)	0.0435(5)
O2	0.5355(2)	0.16468(17)	0.99672(16)	0.0371(4)
O3	0.2260(2)	0.32958(19)	0.98456(18)	0.0416(5)
O4	0.50529(19)	0.41261(16)	0.84309(15)	0.0321(4)
O5	0.2682(2)	0.57860(18)	0.82508(17)	0.0418(5)
O6	0.2506(3)	0.79227(19)	0.8775(2)	0.0527(6)
H6	0.241(4)	0.7438(15)	0.841(2)	0.079*
O7	0.51667(19)	0.62132(16)	0.93474(15)	0.0313(4)
O8	0.25043(19)	0.56266(17)	1.05403(16)	0.0339(4)
C1	0.7765(3)	0.1743(2)	0.7944(2)	0.0370(6)
C2	0.8970(3)	0.1499(3)	0.7086(3)	0.0423(7)
C3	0.8875(4)	0.0807(3)	0.6392(3)	0.0509(8)
H3	0.9695	0.0669	0.5826	0.061*
C4	0.7542(4)	0.0332(3)	0.6559(3)	0.0514(8)
C5	0.6321(4)	0.0520(3)	0.7410(3)	0.0469(7)
H5	0.5434	0.0171	0.7523	0.056*
C6	0.6413(3)	0.1228(3)	0.8096(2)	0.0380(6)
C7	0.5032(3)	0.1408(3)	0.9013(2)	0.0368(6)
H7	0.4553	0.0635	0.9341	0.044*
C8	0.3863(3)	0.2398(2)	0.8439(2)	0.0354(6)
H8	0.3532	0.2095	0.7897	0.043*
C9	0.2526(3)	0.2455(3)	0.9427(3)	0.0380(6)
C10	0.1517(4)	0.1431(3)	0.9931(3)	0.0582(9)
H10A	0.0911	0.1485	0.9385	0.087*
H10B	0.0884	0.1484	1.0662	0.087*
H10C	0.2108	0.0667	1.0071	0.087*
C11	0.4529(3)	0.3624(2)	0.7713(2)	0.0342(6)
H11	0.5411	0.3447	0.7147	0.041*
C12	0.3480(3)	0.4498(3)	0.6991(2)	0.0349(6)
C13	0.3365(3)	0.4284(3)	0.5970(2)	0.0426(7)
H13	0.3941	0.3640	0.5754	0.051*
C14	0.2412(4)	0.5014(3)	0.5279(3)	0.0481(7)
C15	0.1576(4)	0.5990(3)	0.5554(3)	0.0541(8)
H15	0.0937	0.6485	0.5082	0.065*
C16	0.1708(3)	0.6218(3)	0.6551(3)	0.0467(7)
C17	0.2645(3)	0.5493(3)	0.7295(2)	0.0385(6)
C18	0.2421(6)	0.9118(4)	0.8019(4)	0.0868(14)
H18A	0.3077	0.9170	0.7268	0.130*
H18B	0.2716	0.9656	0.8354	0.130*
H18C	0.1413	0.9351	0.7915	0.130*
C19	0.5957(3)	0.6897(3)	0.8195(2)	0.0443(7)
H19A	0.6861	0.6435	0.7964	0.066*
H19B	0.6200	0.7657	0.8220	0.066*
H19C	0.5338	0.7053	0.7634	0.066*
C26	0.0946(3)	0.5519(3)	1.1016(4)	0.0578(9)
H26A	0.0401	0.5943	1.0409	0.087*
H26B	0.0641	0.5868	1.1647	0.087*
H26C	0.0744	0.4673	1.1312	0.087*

was partially evaporated and we obtained several clear dark brown crystals suitable for X-ray crystallographic analysis. Anal. calcd. for $C_{40}H_{40}Cl_8Mn_4O_{16}$: C, 37.53%; H, 3.15%; Mn, 17.17%. Found: C, 37.49%; H, 3.12%; Mn, 17.26%.

Experimental details

Molecular structure was refined using the SHELX-14/7 package. Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms.

Discussion

Oxime-type compounds with a general formula of $R_1R_2C=N\text{-}OR_3$ are synthesized by condensation reaction of aldehydes or ketones with hydroxylamine. These compounds can be used as potential chelating agents and excellent coordination abilities with many metals [4–9]. Oxime-type compounds and their complexes could be applied in many fields, such as magnetic materials [10–12], optical materials [13–15] etc. Herein we report on a new Mn(III) complexes, which may be related to literature known manganese complexes [16–19].

The title complex consists of four Mn(III) atoms, two 4-(3,5-dichloro-2-hydroxy-phenyl)-3-[(3,5-dichloro-2-hydroxy-phenyl)-hydroxy-methyl]-4-hydroxy-butan-2-one ligands as well as methanolato and methanol ligands (*cf.* the figure). Mn1 and Mn1^i atoms are five-coordinated, but Mn2 and Mn2^i atoms are six-coordinated. Mn1/Mn1^i has a distorted square-pyramidal coordination environment with three oxygen atoms from $(L)^{4-}$ and two oxygen atoms provided by two methanolato ligands. Mn2/Mn2^i has a distorted octahedral coordination environment with three oxygen atoms from $(L)^{4-}$ and three oxygen atoms provided by two methanolato ligands and one oxygen atom of a coordinated methanol molecule. Bond lengths and angles are all in the expected ranges.

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