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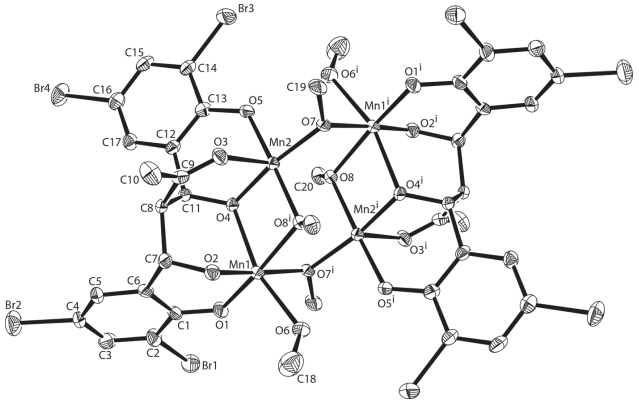
Synthesis and crystal structure of tetrakis (μ_2-methanolato)-dimethanol-bis(μ_2-2-acetyl-1,3-bis(3,5-dibromo-2-oxidophenyl)propane-1,3-bis(olato)-$\kappa^5O^1,O^2,O^3:O^3,O^4,O^5$)tetra-manganese(III), $C_{40}H_{40}Br_8Mn_4O_{16}$



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Abstract

$C_{40}H_{40}Br_8Mn_4O_{16}$, triclinic, $P\bar{1}$, $a = 9.3446(11)$ Å, $b = 11.6799(11)$ Å, $c = 12.5833(16)$ Å, $\alpha = 70.937(10)°$, $\beta = 76.049(11)°$, $\gamma = 80.984(9)°$, $V = 1255.2(3)$ Å^3, $Z = 1$, $R_{gt}(F) = 0.0641$, $wR_{ref}(F^2) = 0.1246$, $T = 293(2)$ K.

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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:	0.21 × 0.17 × 0.16 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	7.42 mm^{-1}
Diffractometer, scan mode:	SuperNova diffractometer, ω
θ_{max}, completeness:	26.0°, 99,77%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	8519, 4944, 0.055
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2869
$N(param)_{refined}$:	314
Programs:	CrysAlis^{PRO}, Agilent Technologies, Version 1.171.37.35 (release 13-08-2014 CrysAlis171 .NET) [17] SHELXL, SHELXS, SHELXTL [18]

Source of material

Synthesis of the ligand HL: 1-{4-[(3,5-dibromo-2-hydroxy benzylidene)amino]phenyl}ethanone O-methyl oxime: The chemicals used in the experiment were analytical pure. 1-(4-aminophenyl)ethanone used in the experiment were previously reported [1–3]. An ethanol solution (5 mL) of 4-amino acetophenone methoxy oxime (150.17 mg, 1 mmol) was added dropwise to an ethanol solution (5 mL) of 3,5-dibromosalicylaldehyde (279.91 mg, 1 mmol) at room temperature. The mixture was heated to reflux and kept refluxing for 12 h. Then the mixture was cooled down to room temperature and the yellow precipitates were filtered and washed successively with ethanol and *n*-hexane, respectively. The isolated compound was dried under reduced pressure and purified with recrystallization from ethanol to yield 293.7 mg of a yellow crystalline solid. Elemental analysis – Anal. calcd for $C_{16}H_{14}Br_2N_2O_2$: C, 45.10%; H, 3.31%; N, 6.57%; Found: C, 45.13%; H, 3.34%; N, 6.55%.

Synthesis of the Mn(III) complex: The solution of Manganese(II) acetate tetrahydrate (2.45 mg, 10 mmol) in ethanol

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.56805(10)	0.22317(8)	0.18224(9)	0.0514(3)
Br2	0.22280(12)	−0.05344(10)	0.06069(10)	0.0728(4)
Br3	−0.45158(12)	0.75297(9)	0.20027(10)	0.0647(3)
Br4	−0.26288(12)	0.46933(10)	−0.10156(9)	0.0649(3)
Mn1	0.14549(12)	0.29337(10)	0.46537(11)	0.0308(3)
Mn2	−0.13439(12)	0.48138(10)	0.44692(11)	0.0293(3)
O1	0.2925(5)	0.2408(4)	0.3561(5)	0.0387(14)
O2	0.0369(5)	0.1642(4)	0.4952(5)	0.0343(13)
O3	−0.2724(5)	0.3312(5)	0.4843(5)	0.0401(15)
O4	0.0036(5)	0.4113(4)	0.3475(4)	0.0292(12)
O5	−0.2354(6)	0.5774(4)	0.3304(5)	0.0378(14)
O6	0.2476(7)	0.2076(5)	0.6182(5)	0.0480(17)
H6	0.272(9)	0.2542(17)	0.650(4)	0.072*
O7	−0.2494(5)	0.5650(4)	0.5520(4)	0.0296(12)
O8	0.0163(5)	0.6204(4)	0.4375(4)	0.0268(12)
C1	0.2743(9)	0.1731(6)	0.2942(7)	0.033(2)
C2	0.3880(9)	0.1500(7)	0.2109(8)	0.042(2)
C3	0.3769(9)	0.0852(7)	0.1393(8)	0.047(2)
H3	0.4559	0.0746	0.0812	0.056*
C4	0.2448(10)	0.0370(7)	0.1568(8)	0.042(2)
C5	0.1286(9)	0.0530(7)	0.2417(8)	0.044(2)
H5	0.0414	0.0175	0.2537	0.052*
C6	0.1396(8)	0.1221(7)	0.3106(7)	0.033(2)
C7	0.0056(8)	0.1396(6)	0.4013(7)	0.032(2)
H7	−0.0400	0.0622	0.4325	0.039*
C8	−0.1144(8)	0.2376(6)	0.3495(7)	0.0318(19)
H8	−0.1483	0.2076	0.2964	0.038*
C9	−0.2444(8)	0.2454(7)	0.4436(7)	0.034(2)
C10	−0.3434(9)	0.1441(7)	0.4953(8)	0.057(3)
H10A	−0.3166	0.0918	0.5654	0.085*
H10B	−0.3331	0.0983	0.4425	0.085*
H10C	−0.4443	0.1770	0.5111	0.085*
C11	−0.0478(8)	0.3612(6)	0.2775(7)	0.0310(19)
H11	0.0396	0.3420	0.2230	0.037*
C12	−0.1521(8)	0.4481(7)	0.2057(7)	0.0306(19)
C13	−0.2384(8)	0.5473(7)	0.2360(7)	0.0319(19)
C14	−0.3330(9)	0.6200(7)	0.1633(7)	0.039(2)
C15	−0.3404(9)	0.5969(8)	0.0631(8)	0.045(2)
H15	−0.4034	0.6457	0.0160	0.054*
C16	−0.2514(9)	0.4992(7)	0.0348(7)	0.041(2)
C17	−0.1599(9)	0.4277(7)	0.1042(7)	0.036(2)
H17	−0.1009	0.3635	0.0833	0.044*
C18	0.2585(12)	0.0883(8)	0.6869(10)	0.084(4)
H18A	0.2223	0.0374	0.6544	0.126*
H18B	0.2005	0.0821	0.7624	0.126*
H18C	0.3601	0.0625	0.6915	0.126*
C19	−0.4033(8)	0.5562(7)	0.5954(8)	0.053(3)
H19A	−0.4339	0.5889	0.6589	0.079*
H19B	−0.4239	0.4724	0.6207	0.079*
H19C	−0.4564	0.6013	0.5360	0.079*
C20	0.0907(9)	0.6873(7)	0.3260(7)	0.040(2)
H20A	0.0218	0.7155	0.2754	0.060*
H20B	0.1696	0.6356	0.2964	0.060*
H20C	0.1306	0.7556	0.3314	0.060*

(3 mL) was added dropwise to the solution of HL (4.12 mg, 10 mmol) in acetone (3 mL) at room temperature. Immediately, the color of the solution turned brown. The mixture was filtered after being stirred for 2 h at room temperature, the filtrate was allowed to stand for several days at room temperature. Several clear dark brown crystals suitable for X-ray crystallographic analysis were obtained.

Experimental details

Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms.

Discussion

In recent years, transition metal complexes with Schiff base ligands have been extensively studied [4–6], and these compounds are an important class of compounds because of their applications in many fields. For example, optical and magnetic materials [7, 8], photophysical properties materials [9], supramolecular architectures [10–14] etc. But manganese complexes bearing oxime-type ligands have been reported rarely [15, 16]. So, we pay more attention to the complexes on the syntheses of oxime-type ligands with the transition metal.

The title complex is built up by the unexpected tetranuclear Mn(III) complex with a new ligand named 4-(3,5-dibromo-2-hydroxy-phenyl)-3-[(3,5-dibromo-2-hydroxy-phenyl)-hydroxy-methyl]-4-hydroxy-butan-2-one, which was obtained by acetone solvent participation. The complex consists of four Mn(III) ions, two new ligand $(L)^{4-}$ units, four methanolato ligands and two coordinated methanol molecules (*cf*. the figure). All bond lengths are in normal ranges. The four Mn(III) ions exhibit two different coordination environments. The Mn1 or $Mn1^i$ ion is hexa-coordinated by three oxygen atoms from one ligand $(L)^{4-}$ unit, two oxygen atoms of the two methanolato ligands and one oxygen atom of a coordinated methanol molecule, while Mn2 or $Mn2^i$ ion is penta-coordinated by three oxygen atoms from one ligand $(L)^{4-}$ unit, two oxygen atoms of the two methanolato ligands and one oxygen atom of a coordinated methanol molecule. The Mn1 or $Mn1^i$ ion displays a distorted octahedral geometry, and the Mn2 or $Mn2^i$ ion displays a distorted square-pyramidal geometry. The Mn1 and $Mn2^i$ (or Mn2 and $Mn1^i$) centers are bridged by one oxygen atom from μ_2-coordinated methanolato ligands (*cf*. the figure).

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