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Crystal structure of bis(μ_3 -methanolato- $\kappa^3O:O:O$)-bis(μ_2 -methanolato- $\kappa^2O:O$)-dimethanol-bis{6,6'-(1,3-dihydroxyl-2-acetylpropane-1,3-diyl)bis(2-chloro-4-bromophenolato)}tetramanganese(III) $C_{40}H_{40}Br_4Cl_4Mn_4O_{16}$

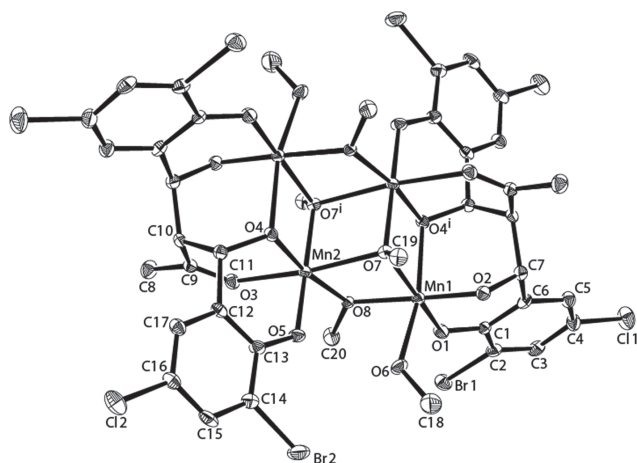


Table 1: Data collection and handling.

Crystal:	clear dark brown block
Size:	0.2 × 0.15 × 0.14 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	4.47 mm ⁻¹
Diffractometer, scan mode:	SuperNova, ω
$\theta_{\max}$, completeness:	26.0°, 99.6%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	8276, 4908, 0.052
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2854
$N(\text{param})_{\text{refined}}$:	314
Programs:	SHELX [19], CrysAlis PRO [20]

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Abstract

$C_{40}H_{40}Br_4Cl_4Mn_4O_{16}$, triclinic, $P\bar{1}$, $a = 9.3724(9)$ Å, $b = 11.7867(16)$ Å, $c = 12.3994(18)$ Å, $\alpha = 70.650(13)^\circ$, $\beta = 75.462(10)^\circ$, $\gamma = 81.085(10)^\circ$, $V = 1247.1(3)$ Å³, $Z = 1$, $R_{\text{gt}}(F) = 0.0618$, $wR_{\text{ref}}(F^2) = 0.1201$, $T = 294$ K.

CCDC no.: 1514252

The title 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.

Source of material

Synthesis of the ligand HL: All chemicals were used without further purification. 4-amino acetophenone methoxy oxime was prepared by an similar method reported earlier [1–3]. 3-Bromo-5-chloro salicylaldehyde (353.2 mg, 1.5 mmol) in ethanol (5 mL) was added slowly to a solution of 4-amino acetophenone methoxy oxime (246.0 mg, 1.5 mmol) in ethanol

(5 mL) at 338 K, and the solution was stirred for 10 h at the same temperature. The precipitate was filtered off and washed successively with ethanol and ethanol/hexane (1:4). The product was dried under vacuum and obtained yellow solid (yield 80.2%, m.p. 390–392 K). Elemental analysis: Anal. Calcd. For $C_{16}H_{14}BrClN_2O_2$: C, 50.35%; H, 3.70%; N, 7.34%. Found: C, 50.38%; H, 3.71%; N, 7.32%.

Synthesis of the Mn(II) complex: The solution of manganese(II) acetate tetrahydrate (2.0 mg, 10 mmol) in ethanol (3 mL) was added dropwise to the solution of HL (7.6 mg, 20 mmol) in trichloromethane (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 and the filtrate was allowed to stand for 10 days at room temperature. The solvent was partially evaporated and we obtained several clear dark brown crystals suitable for X-ray crystallographic analysis. Anal. Calcd. for $C_{40}H_{40}Br_4Cl_4Mn_4O_{16}$: C, 32.95%; H, 2.77%; Mn, 15.07%. Found: C, 32.84%; H, 2.71%; Mn, 15.32%.

Experimental details

Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms.

Discussion

Schiff base ligands with transition metal complexes have been studied for many decades [4–8], which have been attracted research interests for their magnetic properties [9–11], and their supramolecular architectures [12–16] and so on. Noticeably, manganese complexes bearing oxime-type ligands have been reported rarely [17, 18].

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
Br1	0.42881(8)	1.27872(7)	0.81835(7)	0.0538(3)
Br2	0.55329(9)	1.24957(8)	0.19518(8)	0.0685(3)
Mn1	0.85603(10)	1.20494(9)	0.53396(9)	0.0312(3)
Mn2	0.86696(10)	0.98154(9)	0.44563(9)	0.0301(3)
Cl1	0.7659(2)	1.5527(2)	0.9289(2)	0.0784(7)
Cl2	0.7381(2)	0.9678(2)	−0.09658(18)	0.0697(7)
O1	0.7084(4)	1.2578(4)	0.6439(4)	0.0417(12)
O2	0.9641(4)	1.3339(4)	0.5031(4)	0.0343(11)
O3	0.7287(4)	0.8326(4)	0.4843(4)	0.0394(12)
O4	1.0054(4)	0.9122(4)	0.3442(3)	0.0299(11)
O5	0.7696(4)	1.0767(4)	0.3257(4)	0.0398(12)
O6	0.7561(6)	1.2907(4)	0.3792(5)	0.0511(14)
H6	0.738(7)	1.2450(16)	0.344(4)	0.077*
O7	1.0173(4)	1.1186(4)	0.4354(3)	0.0294(11)
O8	0.7518(4)	1.0642(4)	0.5523(4)	0.0283(10)
C1	0.7250(7)	1.3254(6)	0.7047(6)	0.0321(16)
C2	0.6095(7)	1.3511(6)	0.7892(6)	0.0404(19)
C3	0.6167(8)	1.4206(6)	0.8581(7)	0.049(2)
H3	0.5349	1.4355	0.9136	0.059*
C4	0.7503(8)	1.4672(7)	0.8414(7)	0.049(2)
C5	0.8681(7)	1.4468(6)	0.7574(6)	0.0426(19)
H5	0.9563	1.4803	0.7459	0.051*
C6	0.8588(7)	1.3776(6)	0.6894(6)	0.0370(18)
C7	0.9965(7)	1.3581(6)	0.5987(6)	0.0374(18)
H7	1.0442	1.4341	0.5664	0.045*
C8	0.6590(7)	0.6457(6)	0.4955(7)	0.055(2)
H8A	0.5913	0.6557	0.5646	0.082*
H8B	0.7180	0.5707	0.5155	0.082*
H8C	0.6044	0.6453	0.4396	0.082*
C9	0.7567(7)	0.7470(6)	0.4438(6)	0.0336(17)
C10	0.8877(6)	0.7405(5)	0.3468(6)	0.0299(16)
H10	0.8542	0.7107	0.2930	0.036*
C11	0.9523(7)	0.8610(6)	0.2745(6)	0.0335(17)
H11	1.0396	0.8420	0.2188	0.040*
C12	0.8504(6)	0.9478(6)	0.2007(6)	0.0338(17)
C13	0.7663(7)	1.0469(6)	0.2319(6)	0.0365(17)
C14	0.6728(7)	1.1162(6)	0.1570(6)	0.0427(19)
C15	0.6630(7)	1.0927(7)	0.0578(6)	0.049(2)
H15	0.5993	1.1406	0.0109	0.059*
C16	0.7487(7)	0.9975(7)	0.0292(6)	0.0408(18)
C17	0.8404(7)	0.9273(7)	0.0988(6)	0.0399(18)
H17	0.8984	0.8634	0.0775	0.048*
C18	0.7433(10)	1.4116(7)	0.3092(8)	0.085(3)
H18A	0.8115	1.4217	0.2351	0.128*
H18B	0.7654	1.4631	0.3478	0.128*
H18C	0.6443	1.4325	0.2968	0.128*
C19	1.0964(7)	1.1858(6)	0.3207(6)	0.0445(19)
H19A	1.1837	1.1381	0.2964	0.067*
H19B	1.1239	1.2593	0.3244	0.067*
H19C	1.0339	1.2043	0.2656	0.067*
C20	0.5987(7)	1.0561(7)	0.5973(7)	0.056(2)
H20A	0.5469	1.0924	0.5350	0.084*
H20B	0.5664	1.0974	0.6552	0.084*
H20C	0.5786	0.9728	0.6324	0.084*

However, the manganese and the reaction conditions caused the original ligand to break, a new ligand and an unexpected tetranuclear Mn(III) complex were synthesized with four Mn(III), two complex organic ligands and methanol as well as methanol ligands (*cf.* the figure). The coordination environment of the four manganese atoms is more or less identical, so we only study one of them. Mn1 atom is six-coordinated with the complex organic ligand in which the three O atoms (O1, O2 and O4i), and three other O atoms (O6, O7 and O8) from methanol/methanolate. The bond angles around the metal range from 98.2(2)° (O1–Mn1–O6) to 97.86(17)° (O1–Mn1–O4ⁱ) and from 93.5(2)° (O1–Mn1–O8) to 170.11(19)° (O7–Mn1–O1). Hence, with regard to a regular octahedron, the angles show a certain distortion [18].

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