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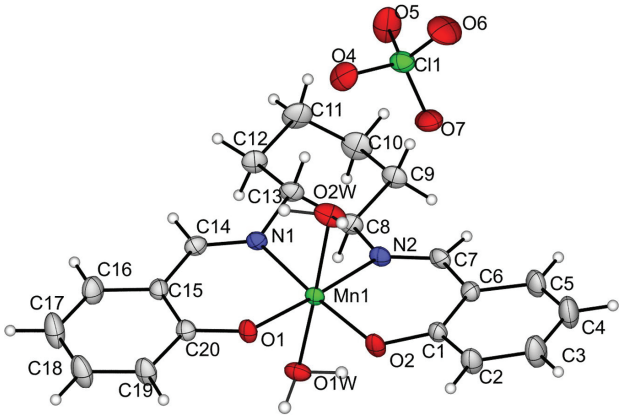
The crystal structure of diaqua-2,2′-((cyclohexane-1,2-diylbis (azanylylidene))bis(methanylylidene))diphenolato-κ^4*N*,*N*′,*O*,*O*′) manganese(III) perchlorate, $C_{20}H_{24}MnClN_2O_4$



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Abstract

$C_{20}H_{24}MnClN_2O_4$, triclinic, $P\bar{1}$ (no. 2), $a = 7.9912(8)$ Å, $b = 11.8174(9)$ Å, $c = 12.7781(15)$ Å, $\alpha = 112.855(9)°$, $\beta = 97.649(9)°$, $\gamma = 91.215(7)°$, $V = 1098.6(2)$ Å^3, $Z = 2$; $R_{gt}(F) = 0.0491$, $wR_{ref}(F^2) = 0.1319$, $T = 250(2)$ K.

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A part of the title crystal structure is shown in the figure. Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

A mixture of salicylaldehyde (0.045 g, 0.2 mmol), (+−)1.2-cyclohexanediamine (0.011 g, 0.1 mmol) and triethylamine (0.005 g, 0.01 mmol) were dissolved in ethanol (2 mL), forming a yellow solution. A second solution made by dissolving 0.361 g (1.0 mmol) of $Mn(ClO_4)_2{\cdot}6H_2O$ (0.072 g, 0.2 mmol) in 20 mL of water was added dropwise to the aforementioned

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Table 1: Data collection and handling.

Crystal:	Block, brown
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.77 mm^{-1}
Diffractometer, scan mode:	Xcalibur, ω-scans
$2\theta_{max}$, completeness:	25°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	7226, 3855, 0.033
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3038
$N(param)_{refined}$:	305
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], DIAMOND [4]

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.78794(13)	0.29436(9)	0.27489(9)	0.0503(3)
Mn1	0.24919(7)	0.38384(4)	0.04312(4)	0.03245(18)
O1	0.2438(3)	0.3987(2)	−0.09764(19)	0.0395(6)
H1WA	−0.096(7)	0.373(5)	−0.034(5)	0.10(2)*
H1WB	−0.005(5)	0.411(4)	0.077(4)	0.044(11)*
O1W	−0.0367(4)	0.3427(3)	0.0041(3)	0.0498(7)
O2	0.2364(4)	0.5532(2)	0.1210(2)	0.0501(7)
H2WA	0.523(4)	0.344(3)	0.006(3)	0.021(8)*
H2WB	0.592(6)	0.482(4)	0.091(4)	0.078(15)*
O2W	0.5332(4)	0.4092(3)	0.0828(3)	0.0612(8)
O4	0.8001(5)	0.2809(3)	0.1598(3)	0.0884(12)
O5	0.7699(7)	0.1771(3)	0.2743(3)	0.1138(16)
O6	0.9284(5)	0.3615(4)	0.3502(4)	0.1182(16)
O7	0.6434(4)	0.3576(4)	0.3044(3)	0.0854(11)
N1	0.2647(4)	0.2043(2)	−0.0261(2)	0.0348(7)
N2	0.2509(4)	0.3535(3)	0.1848(2)	0.0383(7)
C1	0.2879(5)	0.6196(3)	0.2330(3)	0.0412(9)
C2	0.3174(6)	0.7447(3)	0.2704(3)	0.0589(12)
H2A	0.3059	0.7811	0.2165	0.071*
C3	0.3631(8)	0.8176(4)	0.3844(4)	0.0806(17)
H3A	0.3833	0.9032	0.4077	0.097*
C4	0.3798(8)	0.7672(4)	0.4657(4)	0.0827(17)
H4A	0.4116	0.8174	0.5440	0.099*
C5	0.3495(6)	0.6436(4)	0.4303(3)	0.0619(12)
H5A	0.3588	0.6090	0.4856	0.074*
C6	0.3052(5)	0.5661(3)	0.3147(3)	0.0406(9)
C7	0.2784(5)	0.4374(3)	0.2861(3)	0.0414(9)
H7A	0.2813	0.4120	0.3474	0.050*
C8	0.2161(5)	0.2212(3)	0.1592(3)	0.0457(9)
H8A	0.0933	0.1998	0.1314	0.055*
C9	0.2615(6)	0.1833(3)	0.2603(3)	0.0510(10)
H9A	0.3818	0.2061	0.2920	0.061*

Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
H9B	0.1946	0.2261	0.3210	0.061*
C10	0.2248(7)	0.0450(4)	0.2189(4)	0.0722(14)
H10A	0.2616	0.0199	0.2824	0.087*
H10B	0.1023	0.0247	0.1966	0.087*
C11	0.3102(7)	−0.0252(4)	0.1205(4)	0.0718(14)
H11A	0.2754	−0.1131	0.0943	0.086*
H11B	0.4330	−0.0139	0.1457	0.086*
C12	0.2695(6)	0.0144(3)	0.0206(3)	0.0499(10)
H12A	0.3366	−0.0292	−0.0397	0.060*
H12B	0.1493	−0.0071	−0.0119	0.060*
C13	0.3088(5)	0.1517(3)	0.0614(3)	0.0459(10)
H13A	0.4319	0.1702	0.0897	0.055*
C14	0.2410(5)	0.1389(3)	−0.1346(3)	0.0395(8)
H14A	0.2454	0.0533	−0.1577	0.047*
C15	0.2084(5)	0.1840(3)	−0.2239(3)	0.0382(8)
C16	0.1768(6)	0.0987(4)	−0.3372(3)	0.0588(12)
H16A	0.1790	0.0144	−0.3522	0.071*
C17	0.1429(7)	0.1337(4)	−0.4267(4)	0.0768(16)
H17A	0.1212	0.0744	−0.5026	0.092*
C18	0.1408(7)	0.2581(4)	−0.4045(4)	0.0725(15)
H18A	0.1170	0.2830	−0.4660	0.087*
C19	0.1726(6)	0.3445(4)	−0.2952(3)	0.0557(11)
H19A	0.1703	0.4284	−0.2820	0.067*
C20	0.2086(5)	0.3101(3)	−0.2022(3)	0.0375(8)

solution. After left to stir overnight in a conical flask at 40 °C, a brown solution was obtained. After filtration, the filtrate was sealed with parafilm containing tiny pores for slow evaporation. Dark-brown crystals of the title compound were isolated after 2 weeks. In 69.7% yield by filtration, washed with metanol, and dried in air.

Experimental details

H atoms were generated geometrically and refined as riding atoms with C—H = 0.93 Å and $U_{iso}(H) = 1.2$ times $U_{eq}(C)$ for benzene H atoms, with C—H = 0.98 Åand $U_{iso}(H) = 1.2$ times, $U_{eq}(C)$ for cyclohexane H atoms.

Discussion

The design and synthesis of manganese tetradentate Schiff-base ligands (salen) complexes have provoked wide interest for their specific magnetic and catalytic behaviors [5, 6]. So far, although, dozens of Mn-salen type complexes have been isolated [7–10], the isolation of new salen based Mn complexes remains a highly rewarding research area, since the Mn-salen family is a well researched field, systematically explore the relationship between reaction conditions and the structures may provide more clues for further understanding the formation mechanisms of complexes or crystalline materials [11–13].

The title compound crystallizes in the triclinic space group $P\bar{1}$, which is constructed by one mononuclear Mn-salcy cation as well as one perchlorate. The central manganese atom is chelated with one salcy ligand via N_2O_2 in the equatorial plane. The bond lengths of Mn(1)—N(1), Mn(1)—N(2), Mn(1)—O(1) and Mn(1)—O(1) are 1.9759(32), 1.9702(22), 1.8689(27) and 1.8695(22) Å, respectively. In the apical position, Mn^{III} is coordinated by two oxygen atoms from water ligands. The bond lengths of Mn1—O1W and Mn1—O2W are 2.273(3) Å and 2.246(3) Å, respectively. ClO_4^- act as counter-anion. It is noteworthy that the unit cell of the title compound contains two racemic units $[Mn((+)\text{-salcy})(H_2O)_2]^+$ and $[Mn((+)\text{-salcy})(H_2O)_2]^+$and overall exhibiting centrosymmetry.

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