Crystal structure of acetato[*N*,*N*′-bis(3-ethoxysalicylidene)propane-1,3-diiminato]manganese(III) — acetonitrile (1:1), $Mn(C_{21}H_{24}N_2O_4)(CH_3COO) \cdot CH_3CN$

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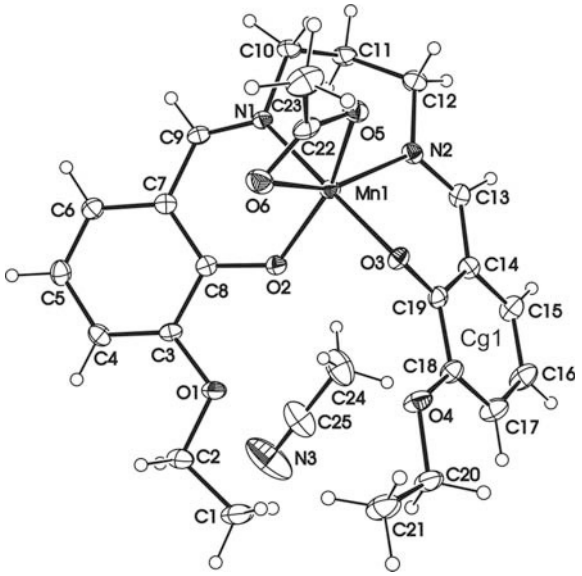

Abstract

$C_{25}H_{30}MnN_3O_6$, monoclinic, $P2_1/n$ (no. 14), a = 9.8702(6) Å, b = 12.0550(7) Å, c = 22.083(1) Å, β = 102.628(1)°, V = 2564.0 Å^3, Z = 4, $R_{gt}(F)$ = 0.050, $wR_{ref}(F^2)$ = 0.140, T = 200 K.

Source of material

$Mn(CH_3COO)_3 \cdot 2H_2O$ (0.50 g, 1.86 mmol), NaCl (0.11 g, 1.88 mmol) and *N*,*N*′-bis(3-ethoxysalicylidene)-1,3-diiminopropane (0.70 g, 1.89 mmol) in EtOH (70 ml) and H_2O (5 ml) were stirred for 3 h at room temparature and then filtered. The solvent was evaporated in vacuo, the residue washed with acetone/H_2O and dried, to give a dark brown powder (0.93 g). Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation from a CH_3CN solution.

Experimental details

Hydrogen atoms were positioned geometrically and allowed to ride on their respective carrier atoms [d(C—H) = 0.95 Å (CH), 0.99 Å (CH_2) or 0.98 Å (CH_3) and U_{iso}(H) = 1.2 U_{eq}(CH, CH_2) or 1.5 U_{eq}(CH_3)].

Discussion

The crystal structure of the title compound consists of a neutral complex [$Mn(C_{21}H_{24}N_2O_4)(CH_3COO)$] and an acetonitrile solvent molecule. Mn(III) ion is six-coordinated by two N and two O atoms from the *N*,*N*′-bis(3-ethoxysalicylidene)-1,3-diiminopropane dianionic ligand and two O atoms of the acetate anion in a considerably distorted octahedral environment. In the octahedral structures of metal complexes of salen or salen-like ligands (where salen is dianion of *N*,*N*′-bis(salicylidene)ethylenediimine), the equatorial planes were generally defined by the two N and two O atoms of the dianion [1,2]. However, in this complex, the four atoms (N1, N2, O2 and O3) are not coplanar, with the torsion angle ∠N1–N2–O3–O2 = 40.80(8)°. The N2, O2, O5 and O6 atoms lie on the equatorial plane (∠O5–O6–O2–N2 = 0.70(9)°). Within the plane, the ∠O5–Mn1–O6 chelate angle is 58.21(8)°, which results in the distortion of the octahedral structure. The apical bond angle ∠N1–Mn1–O3 is 176.09(9)°. While the Mn—N and Mn—$O_{phenoxo}$ bond lengths are nearly equivalent, respectively (d(Mn—N) = 1.998(2) Å and 2.160(2) Å; d(Mn—O) = 1.891(2) Å and 1.889(2) Å), the two Mn—$O_{acetato}$ bond lengths are somewhat different (2.043(2) Å and 2.402(2) Å). The compound displays the intermolecular C–H···O hydrogen bonds with d(C···O) = 3.266(4) Å - 3.411(3) Å. Moreover, there are weak intermolecular π-π interactions between the adjacent benzene rings. For Cg1 (the centroid of 6-membered ring C14-C19) and Cg1[i] (symmetry code i: –x,1–y,–z), the centroid-centroid distance is 5.254(2) Å and the ring planes are parallel and shifted for 3.902 Å.

Table 1. Data collection and handling.

Crystal:	brown rod, size 0.17 × 0.25 × 0.26 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	5.59 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 1000 CCD, φ/ω
$2\theta_{max}$:	56.64°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	18767, 6349
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3746
$N(param)_{refined}$:	320
Programs:	SHELXS-97 [3], SHELXL-97 [4], ORTEP [5], PLATON [6]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1A)	4*e*	0.5884	0.3449	0.0580	0.075
H(1B)	4*e*	0.7152	0.4237	0.0889	0.075
H(1C)	4*e*	0.5649	0.4437	0.1030	0.075
H(2A)	4*e*	0.7290	0.2511	0.1418	0.043
H(2B)	4*e*	0.7130	0.3519	0.1874	0.043
H(4)	4*e*	0.7531	0.1934	0.2434	0.034

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Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(5)	4*e*	0.7478	0.0741	0.3269	0.038
H(6)	4*e*	0.5401	0.0023	0.3409	0.035
H(9)	4*e*	0.2969	–0.0285	0.3040	0.029
H(10A)	4*e*	–0.0206	0.0313	0.2709	0.038
H(10B)	4*e*	0.0857	–0.0701	0.2884	0.038
H(11A)	4*e*	0.0558	–0.1037	0.1774	0.039
H(11B)	4*e*	–0.0753	–0.1338	0.2058	0.039
H(12A)	4*e*	–0.1535	–0.0416	0.1127	0.042
H(12B)	4*e*	–0.1821	0.0353	0.1676	0.042
H(13)	4*e*	–0.1166	0.0670	0.0432	0.035
H(15)	4*e*	–0.0540	0.1380	–0.0466	0.042
H(16)	4*e*	0.0388	0.2758	–0.0980	0.051

Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(17)	4*e*	0.1535	0.4255	–0.0430	0.047
H(20A)	4*e*	0.1785	0.5857	0.0135	0.046
H(20B)	4*e*	0.3209	0.5166	0.0246	0.046
H(21A)	4*e*	0.2510	0.6638	0.1139	0.076
H(21B)	4*e*	0.3571	0.6942	0.0710	0.076
H(21C)	4*e*	0.3951	0.5986	0.1222	0.076
H(23A)	4*e*	0.0681	0.3868	0.3622	0.074
H(23B)	4*e*	–0.0715	0.3161	0.3412	0.074
H(23C)	4*e*	–0.0537	0.4308	0.3073	0.074
H(24A)	4*e*	0.2973	0.1612	–0.0001	0.098
H(24B)	4*e*	0.3582	0.1779	0.0727	0.098
H(24C)	4*e*	0.3300	0.0556	0.0446	0.098

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mn(1)	4*e*	0.12211(5)	0.19081(4)	0.19214(2)	0.0235(3)	0.0214(3)	0.0264(3)	–0.0012(2)	0.0072(2)	0.0028(2)
O(1)	4*e*	0.5380(2)	0.2640(2)	0.15879(9)	0.031(1)	0.034(1)	0.035(1)	–0.005(1)	0.014(1)	0.006(1)
O(2)	4*e*	0.3018(2)	0.1817(2)	0.17550(9)	0.025(1)	0.035(1)	0.027(1)	0.0016(9)	0.0078(9)	0.007(1)
O(3)	4*e*	0.0804(2)	0.3091(2)	0.13505(9)	0.033(1)	0.024(1)	0.020(1)	0.0003(9)	0.0039(9)	0.0002(9)
O(4)	4*e*	0.1913(2)	0.4654(2)	0.07715(9)	0.053(2)	0.026(1)	0.027(1)	–0.010(1)	0.011(1)	0.002(1)
O(5)	4*e*	–0.0199(2)	0.2416(2)	0.24112(9)	0.028(1)	0.032(1)	0.036(1)	0.003(1)	0.014(1)	–0.001(1)
O(6)	4*e*	0.1845(2)	0.3118(2)	0.2803(1)	0.035(1)	0.032(1)	0.046(1)	–0.007(1)	0.009(1)	0.002(1)
N(1)	4*e*	0.1651(2)	0.0586(2)	0.2476(1)	0.024(1)	0.021(1)	0.025(1)	–0.002(1)	0.006(1)	0.004(1)
N(2)	4*e*	–0.0291(2)	0.0939(2)	0.1282(1)	0.025(1)	0.021(1)	0.034(2)	–0.003(1)	0.005(1)	0.000(1)
C(1)	4*e*	0.6305(4)	0.3874(3)	0.0952(2)	0.065(3)	0.048(2)	0.040(2)	–0.024(2)	0.019(2)	0.004(2)
C(2)	4*e*	0.6661(3)	0.3106(3)	0.1499(2)	0.036(2)	0.038(2)	0.038(2)	–0.008(2)	0.017(2)	0.001(2)
C(3)	4*e*	0.5463(3)	0.1937(2)	0.2085(1)	0.031(2)	0.013(1)	0.026(2)	–0.002(1)	0.011(1)	–0.001(1)
C(4)	4*e*	0.6670(3)	0.1650(2)	0.2490(1)	0.022(2)	0.028(2)	0.037(2)	0.001(1)	0.009(1)	–0.004(1)
C(5)	4*e*	0.6637(3)	0.0936(2)	0.2989(1)	0.030(2)	0.028(2)	0.035(2)	0.006(1)	0.000(1)	0.000(2)
C(6)	4*e*	0.5409(3)	0.0519(2)	0.3075(1)	0.032(2)	0.026(2)	0.029(2)	0.001(1)	0.007(1)	0.002(1)
C(7)	4*e*	0.4153(3)	0.0821(2)	0.2671(1)	0.028(2)	0.022(2)	0.027(2)	0.002(1)	0.010(1)	–0.003(1)
C(8)	4*e*	0.4156(3)	0.1535(2)	0.2163(1)	0.027(2)	0.021(2)	0.026(2)	0.004(1)	0.009(1)	–0.001(1)
C(9)	4*e*	0.2882(3)	0.0311(2)	0.2753(1)	0.032(2)	0.020(2)	0.024(2)	0.001(1)	0.012(1)	–0.000(1)
C(10)	4*e*	0.0497(3)	–0.0139(2)	0.2563(1)	0.031(2)	0.027(2)	0.037(2)	–0.007(1)	0.010(1)	0.008(1)
C(11)	4*e*	–0.0179(3)	–0.0717(2)	0.1962(1)	0.037(2)	0.023(2)	0.040(2)	–0.009(1)	0.011(2)	0.005(1)
C(12)	4*e*	–0.1082(3)	0.0032(2)	0.1491(2)	0.034(2)	0.031(2)	0.040(2)	–0.009(1)	0.007(2)	0.001(2)
C(13)	4*e*	–0.0532(3)	0.1145(2)	0.0698(1)	0.033(2)	0.024(2)	0.028(2)	–0.001(1)	0.002(1)	–0.004(1)
C(14)	4*e*	0.0073(3)	0.2034(2)	0.0408(1)	0.029(2)	0.023(2)	0.031(2)	0.001(1)	0.006(1)	–0.001(1)
C(15)	4*e*	–0.0065(3)	0.1987(3)	–0.0239(1)	0.048(2)	0.026(2)	0.028(2)	–0.002(2)	0.003(2)	–0.004(2)
C(16)	4*e*	0.0475(4)	0.2802(3)	–0.0544(2)	0.068(3)	0.037(2)	0.021(2)	–0.004(2)	0.008(2)	–0.003(2)
C(17)	4*e*	0.1150(4)	0.3695(3)	–0.0216(1)	0.058(2)	0.036(2)	0.026(2)	–0.006(2)	0.013(2)	0.001(2)
C(18)	4*e*	0.1272(3)	0.3786(2)	0.0416(1)	0.039(2)	0.022(2)	0.026(2)	0.001(1)	0.006(1)	0.001(1)
C(19)	4*e*	0.0732(3)	0.2953(2)	0.0748(1)	0.024(2)	0.023(2)	0.028(2)	0.006(1)	0.005(1)	0.003(1)
C(20)	4*e*	0.2515(4)	0.5498(3)	0.0454(2)	0.050(2)	0.032(2)	0.035(2)	–0.010(2)	0.011(2)	0.009(2)
C(21)	4*e*	0.3196(4)	0.6338(3)	0.0922(2)	0.075(3)	0.036(2)	0.039(2)	–0.022(2)	0.009(2)	0.003(2)
C(22)	4*e*	0.0579(4)	0.3035(2)	0.2803(2)	0.042(2)	0.020(2)	0.034(2)	0.005(2)	0.014(2)	0.010(2)
C(23)	4*e*	–0.0053(4)	0.3647(3)	0.3268(2)	0.073(3)	0.041(2)	0.042(2)	0.010(2)	0.029(2)	–0.002(2)
N(3)	4*e*	0.6087(5)	0.1237(4)	0.0183(3)	0.061(3)	0.084(3)	0.202(5)	–0.015(2)	0.049(3)	–0.062(3)
C(24)	4*e*	0.3601(4)	0.1307(4)	0.0367(2)	0.045(3)	0.078(3)	0.070(3)	0.003(2)	0.006(2)	–0.030(2)
C(25)	4*e*	0.4995(5)	0.1267(3)	0.0265(2)	0.046(3)	0.052(3)	0.094(4)	–0.001(2)	0.011(3)	–0.034(2)

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