Crystal structure of methanol[*N*,*N*′-*o*-phenylenebis(salicylaldiminato-*N*,*N*′,*O*,*O*′)](salicylaldehydato-*O*)manganese(III), $Mn(CH_3OH)(C_6H_4OCHO)[C_6H_4(C_6H_4OCHN)_2]_2$

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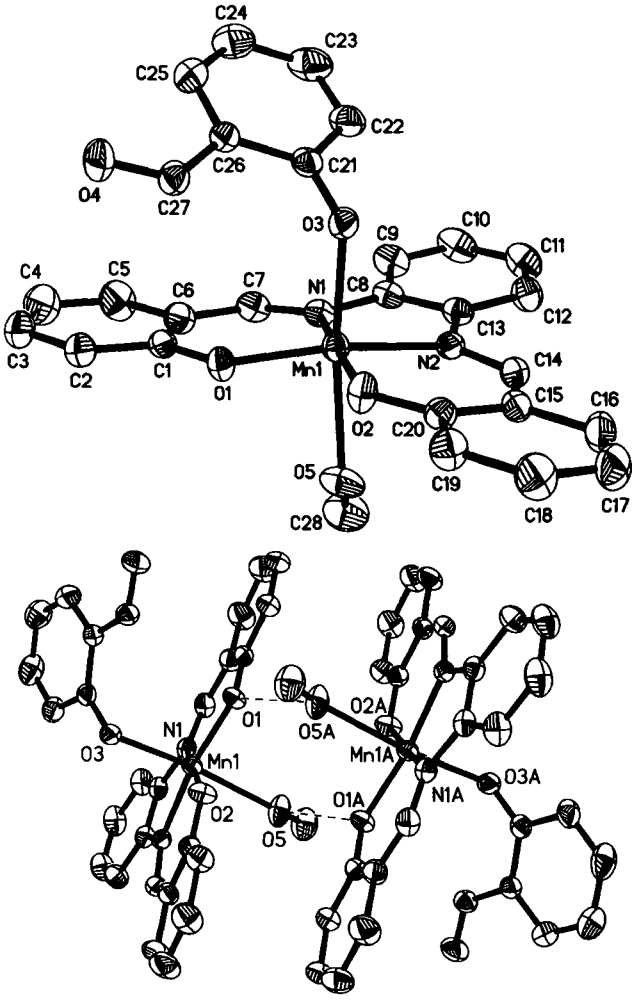

Abstract

$C_{28}H_{23}MnN_2O_5$, monoclinic, $P12_1/c1$ (no. 14), a = 10.321(1) Å, b = 13.503(2) Å, c = 17.390(2) Å, β = 93.950(2)°, V = 2417.7 Å^3, Z = 4, $R_{gt}(F)$ = 0.038, $wR_{ref}(F^2)$ = 0.103, T = 295 K.

Source of material

Bis(salicylidene)-*o*-phenylenediimine (salphen) was prepared as described previously [1]. The other reagents were of analytical grade from commercial sources and were used without any further purification. 2.0 g (6.3 mmol) salphen was dissolved in 50 mL methanol and 0.25 g (6.3 mmol) NaOH was added with stirring. After complete dissolution of NaOH, 1.3 g (6.5 mmol) $MnCl_2 \cdot 4H_2O$ was added under nitrogen atmosphere. The mixture were stirred for half an hour at room temperature. A yellow precipitate was obtained after filtration under the protecting of nitrogen. To the precipitate, methanol was added slowly, then oxygen passed into the solution. A deep-brown solution was obtained after the precipitate was solved in methanol. Dark-green block-like crystals were isolated after several days.

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Experimental details

While the H atoms bonded to C atoms were added geometrically and treated as riding, the coordinates of the hydroxyl H atom were found from Fourier difference map and refined. The methyl group was rotated to fit the electron density.

Discussion

Manganese complexes have attracted considerable interest in recent years because of their presence in various biosystems, especially in the oxygen-evolving complex (OEC) of photosystem II(PSII) [2]. A large number of manganese complexes with Schiff base ligands have been reported [1,3-5]. In the course of our studies on these compounds, the manganese salphen complex was synthesized and its crystal structure was determined.

In the title structure (figure, top), the Mn^{3+} ion is six-coordinated with four donor atoms of the salphen ligand (two N and two O atoms) located in the equatorial plane of a slightly distorted octahedron. In addition, one O atom from salicylaldehyde and another O from methanol molecule are bonded axially and occupy the fifth and sixth coordination positions. The Mn atom is displaced out of the N_2O_2 Schiff base plane toward the axial salicylaldehyde moiety. The Mn—O3 and Mn—O5 distances are consistent with the presence of a Jahn-Teller elongation of the coordination octahedron for a high-spin d^4 Mn^{3+} ion. Two molecules related by a crystallographic center of symmetry are linked to each other by two O1···O5 hydrogen bonds (2.823(2) Å, symmetry code: $-x+2,-y,-z$; figure, bottom).

Table 1. Data collection and handling.

Crystal:	dark-green block, size 0.12 × 0.20 × 0.25 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	5.89 cm^{-1}
Diffractometer, scan mode:	Bruker SMART APEX-II CCD, φ/ω
$2\theta_{max}$:	55.08°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	14620, 5544
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3890
$N(param)_{refined}$:	329
Programs:	SHELXS-97 [6], SHELXL-97 [7]

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

Atom	Site	x	y	z	U_{iso}
H(2)	4e	1.3426	–0.0075	0.0643	0.066
H(3)	4e	1.5020	–0.1155	0.1099	0.083
H(4)	4e	1.4623	–0.2287	0.2051	0.100
H(5)	4e	1.2635	–0.2357	0.2526	0.091
H(7)	4e	1.0527	–0.1793	0.2630	0.059
H(9)	4e	0.9125	–0.1754	0.3443	0.069
H(10)	4e	0.7287	–0.1701	0.4112	0.080
H(11)	4e	0.5575	–0.0691	0.3725	0.079
H(12)	4e	0.5705	0.0330	0.2663	0.067
H(14)	4e	0.5996	0.1026	0.1629	0.053
H(16)	4e	0.5109	0.2268	0.0835	0.073
H(17)	4e	0.5244	0.3453	–0.0092	0.089
H(18)	4e	0.7179	0.3714	–0.0644	0.082
H(19)	4e	0.8983	0.2796	–0.0284	0.066
H(22)	4e	0.9517	0.0962	0.3645	0.076
H(23)	4e	1.0845	0.0515	0.4696	0.090
H(24)	4e	1.3072	0.0523	0.4655	0.090
H(25)	4e	1.3977	0.0980	0.3547	0.073
H(27)	4e	1.2357	0.1632	0.1772	0.058
H(28A)	4e	0.8781	–0.2076	0.0439	0.127
H(28B)	4e	0.7421	–0.1700	0.0103	0.127
H(28C)	4e	0.7737	–0.1736	0.0997	0.127
H(29)	4e	0.874(3)	–0.056(2)	0.006(1)	0.080

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)	4e	0.95274(3)	0.04445(2)	0.14380(2)	0.0345(2)	0.0368(2)	0.0389(2)	0.0026(1)	0.0059(1)	0.0050(1)
N(1)	4e	0.9632(2)	–0.0679(1)	0.21837(9)	0.047(1)	0.0331(8)	0.0373(9)	–0.0007(7)	0.0030(7)	0.0004(6)
N(2)	4e	0.7721(2)	0.0515(1)	0.17662(8)	0.0362(8)	0.0419(9)	0.0345(8)	–0.0021(7)	0.0043(7)	–0.0004(7)
O(1)	4e	1.1156(1)	0.0126(1)	0.10561(7)	0.0400(8)	0.0469(8)	0.0483(8)	0.0107(6)	0.0096(6)	0.0059(6)
O(2)	4e	0.9233(1)	0.1430(1)	0.06898(8)	0.0380(7)	0.0540(8)	0.0549(9)	0.0065(6)	0.0096(6)	0.0205(7)
O(3)	4e	1.0167(1)	0.14317(9)	0.22942(8)	0.0392(7)	0.0439(8)	0.0579(9)	0.0014(6)	0.0006(6)	–0.0100(6)
O(4)	4e	1.4067(1)	0.1536(1)	0.21327(9)	0.0424(9)	0.085(1)	0.083(1)	–0.0076(8)	0.0202(8)	–0.0109(9)
O(5)	4e	0.8565(2)	–0.0663(1)	0.04928(9)	0.095(1)	0.068(1)	0.0418(9)	–0.0221(9)	0.0149(9)	–0.0071(8)
C(1)	4e	1.2031(2)	–0.0527(1)	0.1327(1)	0.042(1)	0.041(1)	0.046(1)	0.0093(8)	–0.0015(9)	–0.0084(9)
C(2)	4e	1.3253(2)	–0.0523(2)	0.1030(1)	0.046(1)	0.060(1)	0.059(1)	0.008(1)	0.004(1)	–0.007(1)
C(3)	4e	1.4209(2)	–0.1174(2)	0.1300(2)	0.046(1)	0.082(2)	0.080(2)	0.021(1)	–0.002(1)	–0.017(2)
C(4)	4e	1.3972(3)	–0.1854(2)	0.1868(2)	0.072(2)	0.093(2)	0.084(2)	0.044(2)	–0.010(2)	0.001(2)
C(5)	4e	1.2792(3)	–0.1885(2)	0.2154(2)	0.082(2)	0.075(2)	0.070(2)	0.035(2)	0.002(1)	0.015(1)
C(6)	4e	1.1784(2)	–0.1223(2)	0.1908(1)	0.055(1)	0.046(1)	0.049(1)	0.015(1)	–0.002(1)	0.001(1)
C(7)	4e	1.0606(2)	–0.1277(2)	0.2281(1)	0.065(1)	0.041(1)	0.042(1)	0.006(1)	0.002(1)	0.0051(9)
C(8)	4e	0.8532(2)	–0.0739(1)	0.2631(1)	0.054(1)	0.037(1)	0.039(1)	–0.0078(9)	0.0083(9)	–0.0018(8)
C(9)	4e	0.8443(2)	–0.1336(2)	0.3281(1)	0.081(2)	0.043(1)	0.050(1)	0.001(1)	0.009(1)	0.010(1)
C(10)	4e	0.7342(3)	–0.1303(2)	0.3679(1)	0.099(2)	0.056(1)	0.050(1)	–0.011(1)	0.028(1)	0.009(1)
C(11)	4e	0.6318(3)	–0.0694(2)	0.3451(1)	0.077(2)	0.064(2)	0.060(2)	–0.011(1)	0.031(1)	0.004(1)
C(12)	4e	0.6393(2)	–0.0087(2)	0.2816(1)	0.052(1)	0.062(1)	0.055(1)	–0.002(1)	0.018(1)	0.004(1)
C(13)	4e	0.7500(2)	–0.0105(1)	0.2408(1)	0.047(1)	0.043(1)	0.037(1)	–0.0084(9)	0.0080(9)	–0.0020(8)
C(14)	4e	0.6821(2)	0.1082(1)	0.1450(1)	0.037(1)	0.054(1)	0.042(1)	0.0004(9)	0.0070(8)	–0.0032(9)
C(15)	4e	0.6984(2)	0.1783(1)	0.0853(1)	0.043(1)	0.049(1)	0.038(1)	0.0086(9)	0.0051(9)	–0.0010(9)
C(16)	4e	0.5892(2)	0.2369(2)	0.0612(1)	0.049(1)	0.083(2)	0.052(1)	0.024(1)	0.009(1)	0.009(1)
C(17)	4e	0.5969(3)	0.3075(2)	0.0062(1)	0.073(2)	0.086(2)	0.063(2)	0.042(2)	0.002(1)	0.014(1)
C(18)	4e	0.7129(3)	0.3229(2)	–0.0268(1)	0.081(2)	0.062(2)	0.061(2)	0.023(1)	0.008(1)	0.019(1)
C(19)	4e	0.8212(2)	0.2678(2)	–0.0052(1)	0.058(1)	0.054(1)	0.055(1)	0.008(1)	0.007(1)	0.013(1)
C(20)	4e	0.8169(2)	0.1944(1)	0.0511(1)	0.043(1)	0.041(1)	0.039(1)	0.0025(8)	0.0013(8)	0.0019(8)
C(21)	4e	1.0933(2)	0.1215(1)	0.2907(1)	0.045(1)	0.037(1)	0.050(1)	–0.0066(9)	0.0078(9)	–0.0110(9)
C(22)	4e	1.0412(2)	0.0957(2)	0.3610(1)	0.057(1)	0.078(2)	0.056(2)	–0.024(1)	0.020(1)	–0.020(1)
C(23)	4e	1.1211(3)	0.0697(2)	0.4243(1)	0.096(2)	0.085(2)	0.046(1)	–0.030(2)	0.017(1)	–0.003(1)
C(24)	4e	1.2545(3)	0.0701(2)	0.4222(2)	0.087(2)	0.085(2)	0.052(2)	–0.005(2)	–0.005(1)	0.002(1)
C(25)	4e	1.3078(2)	0.0967(2)	0.3561(1)	0.052(1)	0.073(2)	0.057(2)	0.003(1)	–0.002(1)	–0.004(1)
C(26)	4e	1.2303(2)	0.1224(1)	0.2900(1)	0.041(1)	0.044(1)	0.046(1)	–0.0005(9)	0.0043(9)	–0.0065(9)
C(27)	4e	1.2905(2)	0.1487(1)	0.2204(1)	0.041(1)	0.046(1)	0.059(1)	–0.0049(9)	0.007(1)	–0.006(1)
C(28)	4e	0.8090(3)	–0.1616(2)	0.0509(2)	0.105(2)	0.068(2)	0.080(2)	–0.017(2)	0.010(2)	–0.006(1)

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