Crystal structure of acetato-aqua-[*N*,*N*′-bis(4-methoxy-salicylidene)ethane-1,2-diaminato]-manganese(III) hydrate, $C_{20}H_{23}MnN_2O_7 \cdot H_2O$

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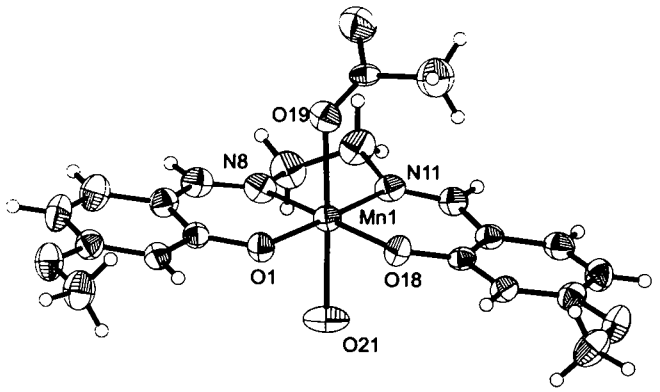
Received April 24, 2001, CCDC-No. 1267-653



Abstract

$C_{20}H_{25}MnN_2O_8$, orthorhombic, *Pbca* (No. 61), $a = 12.158(4)$ Å, $b = 13.915(4)$ Å, $c = 24.747(5)$ Å, $V = 4186.7$ Å^3, $Z = 8$, $R_{gt}(F) = 0.057$, $wR_{all}(F^2) = 0.126$, $T = 293(2)$ K.

Source of material

N,*N*′-bis(4-methoxy-salicylidene)ethane-1,2-diamine was prepared according to [1]. The title compound was obtained by adding one equivalent of the ligand to a solution of manganese(III)-acetate in absolute ethanol. Mass spectrometry (observation of M^+) and elemental analyses (correct values for C,H,N) confirmed the formation of the title compound. Cyclic voltammetric measurements (in absolute methanol, 298 K) exhibited quasi reversible redox behavior with a redox potential of –0.28 V versus the Ag/AgCl reference. Single crystals were grown from an aqueous solution by slow evaporation at room temperature.

Experimental details

The water of crystallization proved to be disordered and was refined with two positions for the oxygen atom and four positions for the hydrogen atoms with site occupancies of 63(7)% and 37(7)%, respectively. The hydrogen atoms of the coordinated water ligand could not be located and were not considered. The H positions of the two methyl groups and of the water of crystallization were refined with fixed isotropic displacement parameters. All other hydrogen atoms were placed at calculated positions using a riding model.

Discussion

Mn(III)-salen complexes received considerable attention recently due to their potential as catalyst for peroxide activation in laundry bleaching [2]. A variety of such complexes with different substituents at the aromatic rings have already been crystalized and structurally characterized [3]. However, a corresponding complex with the 4-methoxy derivative has not yet been reported. The structure of the title compound exhibited the well known Jahn-Teller distorted octahedral geometry where the coordinating water molecule and the acetato-ligand adopt a trans orientation with comparably long Mn—O bonds of 230.9(4) pm and 223.5(4) pm, respectively. The four donor atoms of the salen ligand form a slightly distorted trapezium (deviation from mean plane: 2.1 pm – 2.2 pm, Mn—O distances: 188.7(3) pm and 189.1(3) pm, Mn—N distances: 197.4(4) pm and 197.5(4) pm). The entire structure can be described as layers oriented parallel to the *ac*-plane. These layers are held together by hydrogen bonds. The disordered water of crystallization donates its hydrogen atoms to an acetato-ligand and a methoxy group. Short O···O distances of 278 pm indicate additional interlayer hydrogen bonding between the coordinated water ligands and the acetato ligands, forming chains along axis b. The phenyl rings of the salen ligands have a roughly parallel orientation, however, the interlayer C···C distances of 340 pm – 350 pm indicate only some minor π stacking.

Table 1. Data collection and handling.

Crystal:	dark brown prism, size 0.34 × 0.58 × 0.64 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	6.81 cm^{-1}
Diffractometer, scan mode:	Siemens P4, ω
$2\theta_{max}$:	47.42°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2764, 2764
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1907
$N(param)_{refined}$:	306
Programs:	SHELXS-87 [4], SHELXL-93 [5]

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

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(2)	8*c*		–0.2369(4)	0.9325(4)	0.0984(2)	0.061
H(32A)	8*c*		–0.4858(9)	0.974(3)	0.1629(3)	0.127
H(32B)	8*c*		–0.416(3)	0.899(1)	0.130(1)	0.127
H(32C)	8*c*		–0.393(2)	1.009(2)	0.124(1)	0.127
H(4)	8*c*		–0.1854(6)	0.9326(5)	0.2583(2)	0.091

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Table 2. Continued.

Atom	Site	Occ.	x	y	z	U_{iso}
H(5)	8c		-0.0077(6)	0.8942(5)	0.2446(2)	0.09
H(7)	8c		0.1451(5)	0.8678(4)	0.1908(2)	0.075
H(9A)	8c		0.3147(5)	0.9110(5)	0.1115(3)	0.094
H(9B)	8c		0.3040(5)	0.8193(5)	0.1482(3)	0.094
H(10A)	8c		0.3051(5)	0.7205(5)	0.0785(3)	0.094
H(10B)	8c		0.3896(5)	0.7994(5)	0.0600(3)	0.094
H(12)	8c		0.3543(4)	0.7898(4)	-0.0309(2)	0.064
H(14)	8c		0.3478(5)	0.7986(4)	-0.1241(2)	0.072
H(15)	8c		0.2550(5)	0.8094(4)	-0.2042(3)	0.079
H(16A)	8c		-0.0779(8)	0.861(3)	-0.2629(3)	0.125

Table 2. Continued.

Atom	Site	Occ.	x	y	z	U_{iso}
H(16B)	8c		-0.0741(7)	0.915(2)	-0.207(2)	0.125
H(16C)	8c		-0.0969(5)	0.804(2)	-0.209(2)	0.125
H(17)	8c		-0.0264(4)	0.8578(4)	-0.1253(2)	0.062
H(20A)	8c		0.135(4)	0.539(2)	-0.0157(6)	0.154
H(20B)	8c		0.116(4)	0.645(2)	-0.0352(3)	0.154
H(20C)	8c		0.0151(9)	0.580(4)	-0.0209(7)	0.154
H(221)	8c	0.37(7)	0.18(4)	0.57(1)	0.19(2)	0.139
H(222)	8c	0.37	0.21(2)	0.59(2)	0.145(9)	0.139
H(223)	8c	0.63	0.14(1)	0.61(1)	0.150(6)	0.175
H(224)	8c	0.63	0.13(1)	0.62(1)	0.212(5)	0.175

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

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mn(1)	8c		0.09212(6)	0.84995(6)	0.04224(3)	0.0355(4)	0.0519(4)	0.0516(5)	0.0033(4)	-0.0066(4)	0.0021(4)
O(1)	8c		-0.0465(3)	0.8914(3)	0.0679(1)	0.043(2)	0.067(2)	0.050(2)	0.012(2)	-0.004(2)	-0.003(2)
C(1)	8c		-0.0794(4)	0.9014(4)	0.1184(2)	0.049(3)	0.044(3)	0.049(3)	-0.005(3)	0.003(3)	-0.002(3)
C(2)	8c		-0.1898(4)	0.9242(4)	0.1276(2)	0.050(3)	0.051(3)	0.052(3)	-0.002(3)	0.002(3)	-0.002(3)
C(3)	8c		-0.2297(5)	0.9347(4)	0.1794(2)	0.064(4)	0.059(4)	0.061(4)	-0.007(3)	0.009(3)	-0.002(3)
O(31)	8c		-0.3368(4)	0.9546(3)	0.1919(2)	0.060(3)	0.100(4)	0.073(3)	-0.003(3)	0.020(2)	-0.008(3)
C(32)	8c		-0.4141(5)	0.9593(5)	0.1487(3)	0.061(4)	0.111(6)	0.082(5)	-0.001(4)	0.012(4)	-0.004(4)
C(4)	8c		-0.1592(6)	0.9242(5)	0.2233(2)	0.084(5)	0.096(5)	0.047(4)	-0.017(4)	0.008(4)	-0.007(4)
C(5)	8c		-0.0534(6)	0.9018(5)	0.2148(2)	0.071(4)	0.097(5)	0.056(4)	-0.009(4)	-0.008(3)	-0.005(4)
C(6)	8c		-0.0084(5)	0.8894(4)	0.1631(2)	0.059(4)	0.060(4)	0.054(4)	-0.002(3)	-0.005(3)	-0.002(3)
C(7)	8c		0.1056(5)	0.8713(4)	0.1587(2)	0.064(4)	0.064(4)	0.059(4)	-0.002(3)	-0.021(3)	-0.002(3)
N(8)	8c		0.1602(4)	0.8590(3)	0.1145(2)	0.041(3)	0.063(3)	0.067(3)	0.002(3)	-0.016(2)	-0.003(3)
C(9)	8c		0.2802(5)	0.8484(5)	0.1145(3)	0.052(4)	0.103(5)	0.081(4)	0.014(4)	-0.028(3)	-0.010(4)
C(10)	8c		0.3131(5)	0.7877(5)	0.0689(3)	0.044(3)	0.115(6)	0.077(4)	0.022(4)	-0.016(3)	0.019(4)
N(11)	8c		0.2424(3)	0.8105(3)	0.0217(2)	0.032(2)	0.058(3)	0.064(3)	0.006(2)	-0.005(2)	0.010(2)
C(12)	8c		0.2803(4)	0.8049(4)	-0.0267(2)	0.035(3)	0.059(4)	0.067(4)	0.002(3)	0.008(3)	0.005(3)
C(13)	8c		0.2174(4)	0.8201(4)	-0.0742(2)	0.044(3)	0.045(3)	0.057(3)	0.000(3)	0.001(3)	0.005(3)
C(14)	8c		0.2724(5)	0.8099(4)	-0.1239(2)	0.048(4)	0.054(4)	0.079(4)	0.004(3)	0.012(3)	0.006(3)
C(15)	8c		0.2172(5)	0.8162(4)	-0.1718(3)	0.058(4)	0.074(4)	0.065(4)	-0.003(3)	0.017(3)	-0.001(3)
C(16)	8c		0.1051(5)	0.8329(4)	-0.1721(2)	0.057(4)	0.054(4)	0.056(4)	-0.012(3)	0.003(3)	0.004(3)
O(161)	8c		0.0582(4)	0.8374(3)	-0.2220(2)	0.071(3)	0.107(4)	0.047(2)	-0.013(3)	0.000(2)	0.002(2)
C(162)	8c		-0.0571(5)	0.8557(5)	-0.2256(2)	0.077(5)	0.114(6)	0.060(4)	-0.021(5)	-0.021(3)	0.017(4)
C(17)	8c		0.0486(4)	0.8448(4)	-0.1245(2)	0.049(3)	0.053(3)	0.052(3)	0.000(3)	0.001(3)	0.008(3)
C(18)	8c		0.1028(4)	0.8376(3)	-0.0748(2)	0.039(3)	0.040(3)	0.054(3)	-0.003(3)	0.002(3)	0.008(3)
O(18)	8c		0.0434(3)	0.8461(3)	-0.0301(1)	0.037(2)	0.075(2)	0.045(2)	0.003(2)	-0.002(2)	0.004(2)
O(19)	8c		0.0481(3)	0.6978(3)	0.0616(2)	0.044(2)	0.064(3)	0.082(3)	0.000(2)	0.004(2)	-0.002(2)
O(20)	8c		0.1601(4)	0.5789(4)	0.0744(2)	0.110(4)	0.099(4)	0.099(4)	0.027(3)	0.000(3)	0.001(3)
C(19)	8c		0.0949(4)	0.6295(3)	0.0466(2)	0.042(3)	0.041(3)	0.057(3)	0.001(3)	-0.015(3)	0.011(3)
C(20)	8c		0.0898(6)	0.5949(5)	-0.0117(3)	0.121(6)	0.102(6)	0.087(5)	-0.004(5)	-0.010(5)	-0.008(4)
O(21)	8c		0.1500(3)	1.0059(3)	0.0276(2)	0.064(3)	0.054(2)	0.134(4)	-0.008(2)	-0.027(3)	0.025(3)
O(22)	8c	0.37(7)	0.196(3)	0.651(3)	0.178(2)	0.10(2)	0.15(2)	0.10(2)	-0.03(2)	-0.05(2)	0.05(2)
O(22')	8c	0.63	0.204(2)	0.602(4)	0.1832(8)	0.13(2)	0.24(3)	0.060(8)	0.05(2)	0.022(9)	0.03(1)

Acknowledgments. We thank the Fonds der Chemischen Industrie for financial support and Prof. W. S. Sheldrick for helpfull suggestions and discussion.

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