Binuclear Metal Complexes. XXXVII.[1] Crystal and Molecular Structure of a Binuclear Manganese(III) Complex Bridged by Two Alkoxo Oxygens and Two Bidentate Acetate Ions

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The crystal structure of binuclear manganese(III) complex, Mn(spa)(ac) (H_2spa=3-salicylideneamino-1-propanol, ac=acetate), was determined by the single-crystal X-ray diffraction method. The crystals are triclinic, space group $P\bar{1}$, a=8.804(3), b=9.376(3), c=8.671(3) Å, α=111.24(3), β=101.34(3), γ=65.00(3)°, and Z=1. The structure was solved by the heavy atom method and refined by the block-diagonal least-squares method to an R factor of 0.034. The crystal structure consists of discrete binuclear clusters, where the two manganese atoms are bridged by two alkoxo oxygens of the spa ligands and two bidentate acetate ions. The structural detail is in conformity with the magnetic and spectral properties previously reported.

The chemistry of binuclear manganese(III) and manganese(IV) complexes is of importance in connection with the metalloenzymes in biological systems.[2,3] However, X-ray structural investigations on binuclear manganese complexes are very limited.[4-6]

In the previous paper of this series, we reported the synthesis and magnetic property of binuclear manganese(III) complexes with 3-salicylideneamino-1-propanol and its homologues, MnL(ac) and MnLX·H_2O (L= Schiff base dianion; ac=acetate ion; X=Cl, Br, N_3).[7] The temperature dependence of their magnetic susceptibilities (80—300 K) could be well interpreted in terms of the Van Vleck equation for the high-spin d^4-d^4 system based on the Heisenberg model, $\mathcal{H}=-2JS_1\cdot S_2$ (J=−13.5——20.4 cm^{-1}). Thus, it was thought that they possess a discrete binuclear structure in which an antiferromagnetic spin-exchange interaction is operating between a pair of manganese(III) ions. Based on the infrared and electronic spectral data, it was proposed that the binuclear complexes, MnL(ac) and MnLX·H_2O, are both bridged by an alcoholic oxygen. The antisymmetric and symmetric C–O stretching frequencies of the acetate group in the MnL(ac) led us to the conclusion that the acetate groups also bridge the two manganese(III) ions (Fig. 1). The binuclear structure consisting of two monatomic and two triatomic bridges as supposed for MnL(ac) is quite rare. Although such a mode of bridging has been observed for α-di-μ-hydroxo-bis[2-(2-dimethylaminoethyl)pyridine]dicopper(II) perchlorate,[8] to our knowledge it has not yet been documented in carboxylate chemistry. In order to confirm the bridging mode we have determined the crystal structure of Mn(spa)(ac) (H_2spa=3-salicylideneamino-1-propanol) by the single-crystal X-ray diffraction method.

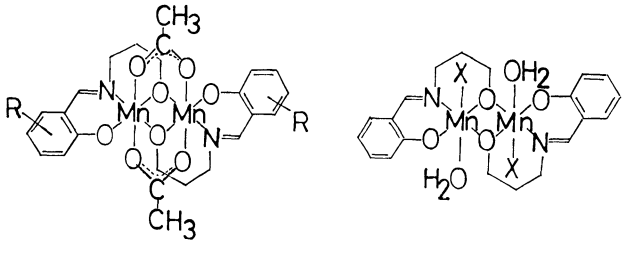

Fig. 1. Structures of MnL(ac) and MnLX·H_2O.

Experimental

Greenish black crystals of Mn(spa)(ac) were prepared by the method previously reported.[7] A crystal with dimensions of 0.23×0.25×0.50 mm was used for the X-ray analysis. Preliminary Weissenberg photographs revealed no systematic absences and showed the triclinic symmetry. The cell parameters and intensities were measured on a Rigaku AFC-5 automated four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ=0.71069 Å).

Crystal data: $C_{24}H_{28}N_2O_8Mn_2$, F.W.=582.37, triclinic, $P\bar{1}$, a=8.804 (3), b=9.376 (3), c=8.671 (3) Å, α=111.24 (3), β=101.34 (3), γ=65.00 (3)°, D_m=1.59 (by floatation in n-C_6H_{14}–CCl_4), D_c=1.60 gcm^{-3}, Z=1, μ(Mo $K\alpha$)=10.5 cm^{-1}.

Intensity data were collected by the 2θ-ω scan technique with a scan rate of 8 °min^{-1}. For weak reflections the peak scan was repeated up to four times depending on their intensities. The intensities of three standard reflections monitored every 100 reflections showed a good stability. A total of 2784 reflections with 2θ<55° were collected. The intensity data were corrected for the Lorentz and the polarization effects, but not for absorption. 2614 Independent reflections with $|F_o|>3\sigma(|F_o|)$ were considered as "observed" and were used for the structure analysis.

Structure Determination and Refinement

The structure was solved by the heavy atom method. Of the two possible space groups, the centrosymmetric space group $P\bar{1}$ was assumed. Successful solution and refinement support this choice. The position of the manganese atom was obtained from a three-dimensional Patterson synthesis. Successive Fourier synthesis revealed all the nonhydrogen atoms. Refinement was carried out by the block-diagonal least-squares method. Anisotropic thermal parameters being introduced, the least-squares refinement yielded discrepancy factors $R_1=\sum||F_o|-|F_c||/\sum|F_o|=0.047$ and $R_2=[\sum\omega(|F_o|-|F_c|)^2/\sum\omega|F_o|^2]^{1/2}=0.075$. All the hydrogen atoms were located from the subsequent difference Fourier map. Further refinement with anisotropic thermal parameters for nonhydrogen atoms and isotropic temperature factors for hydrogen atoms gave final values of 0.034 and 0.052 for R_1 and R_2, respectively. In the least-squares refinement the function minimized was $\sum w(|F_o|-k|F_c|)^2$, where $w=(2.0+|F_o|+$

$0.016|F_o|^2)^{-1}$.[9] The final shifts in the atomic parameters of the nonhydrogen atoms were less than 0.13σ. The final difference Fourier synthesis showed no peaks higher than 0.77 e/Å^3.

The atomic scattering factors for Mn, O, N, C_{val}, and H and the anomalous dispersion corrections, $\Delta f'$ and $\Delta f''$ for Mn, were taken from the International Tables for X-Ray Crystallography.[10] All the calculations were carried out on the FACOM M-200 computer in the Computer Center of Kyushu University by the use of a local version[11] of the UNICS-II[12] and the ORTEP[13] programs.

The final positional and thermal parameters with their estimated standard deviations are given in Tables 1 and 2.***

TABLE 1. FRACTIONAL POSITIONAL PARAMETERS ($\times 10^4$) AND THERMAL PARAMETERS OF NON-HYDROGEN ATOMS WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	x	y	z	B_{eq}/Å^2
Mn	671.1(3)	412.8(3)	1675.5(3)	2.3
O(1)	397(2)	−1472(2)	37(2)	2.5
O(2)	951(2)	2320(2)	3083(2)	3.3
O(3)	3034(2)	− 564(2)	437(2)	3.1
O(4)	2015(2)	−1184(2)	−2206(2)	3.1
N	1675(2)	− 748(2)	3392(2)	2.6
C(1)	166(3)	−2769(3)	295(3)	3.2
C(2)	1527(3)	−3448(3)	1494(3)	3.9
C(3)	1453(4)	−2284(3)	3221(3)	4.0
C(4)	2510(3)	− 208(3)	4709(2)	2.9
C(5)	2725(2)	1341(3)	5262(2)	2.8
C(6)	1923(2)	2538(2)	4441(2)	2.7
C(7)	2119(3)	4061(3)	5129(3)	3.5
C(8)	3063(3)	4379(3)	6583(3)	4.1
C(9)	3871(3)	3185(4)	7387(3)	4.3
C(10)	3702(3)	1698(3)	6741(3)	3.7
C(11)	3195(2)	−1243(2)	−1102(3)	2.8
C(12)	4961(3)	−2209(3)	−1666(3)	3.9

TABLE 2. FRACTIONAL POSITIONAL PARAMETERS ($\times 10^3$) AND ISOTROPIC TEMPERATURE FACTORS OF HYDROGEN ATOMS WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	x	y	z	B/Å^2
H(C1A)	−99(3)	−245(3)	67(3)	3.7(5)
H(C1B)	20(3)	−365(3)	− 77(3)	3.5(5)
H(C2A)	137(3)	−440(3)	161(3)	3.5(5)
H(C2B)	275(3)	−380(3)	113(3)	3.8(5)
H(C3A)	14(3)	−185(3)	357(3)	3.8(5)
H(C3B)	224(3)	−279(3)	398(3)	3.5(5)
H(C4)	295(3)	− 88(3)	543(3)	3.0(5)
H(C7)	158(3)	487(3)	461(3)	3.3(5)
H(C8)	318(3)	541(3)	700(3)	3.7(5)
H(C9)	461(3)	344(3)	840(3)	3.6(5)
H(C10)	429(3)	86(3)	729(3)	3.5(5)
H(C12A)	500(3)	−261(3)	−280(3)	3.8(5)
H(C12B)	550(3)	−301(3)	−129(3)	4.0(6)
H(C12C)	547(3)	−166(3)	−158(3)	4.1(6)

*** Lists of structure factors and anisotropic thermal parameters have been deposited with the Chemical Society of Japan as a Document No. 8123.

Results and Discussion

The molecular structure is shown in Fig. 2. The bond distances and angles with their estimated standard deviations are listed in Table 3. Some least-squares planes with the deviations of atoms from the planes are given in Table 4.

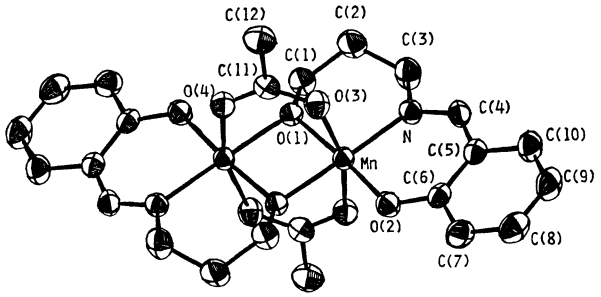

Fig. 2. Molecular Structure of Mn(spa)(ac) with thermal ellipsoids (50% probability level).

The crystal structure consists of discrete binuclear clusters, the closest intercluster contact being O(4)–C(9) (3.279(3) Å). Therefore, the binuclear clusters must be considered to be magnetically isolated. This is in harmony with the result of our magnetic investigation of MnL(ac).[7] The manganese atoms are bridged by the alcoholic oxygens. For the binuclear complexes with 3-salicylideneamino-1-propanol, alcoholic oxygen-bridged and phenolic oxygen-bridged binuclear structures are known.[14–27] As stated above, the infrared spectra of MnL(ac) and $MnLX\cdot H_2O$ suggest the alcoholic oxygen-bridged binuclear structures,[7] and this has been confirmed by the present X-ray structure analysis.

The coordination geometry around the manganese atom is an elongated octahedron. The approximate square plane involving the manganese atom at its center is formed by two alcoholic oxygen, imino nitrogen and phenolic oxygen atoms of the spa ligands (Table 4). The Mn–O(1) (1.899(2) Å), Mn–O(1)^i (1.951(2) Å), Mn–O(2) (1.849(2) Å) and Mn–N (2.006(2) Å) distances are normal for the in-plane bonds of manganese(III) complex.[4,6,28] The bond angles around the manganese atom vary from 82 to 97°. The axial Mn–O distances (2.208(2), 2.251(2) Å) are considerably longer than the in-plane Mn–O distances. Thus the coordination geometry around the manganese atom evidently deviates from a regular octahedron and this tetragonal elongation is attributable to the Jahn-Teller effect. Therefore, the ground ^5E_g and the excited $^5T_{2g}$ states for octahedral manganese(III) should split into sublevels. In fact, the diffuse reflectance spectrum of Mn(spa)(ac) shows d-d bands at 13000, 16400, 21200, and 22200 cm^{-1}.[7]

The four-membered Mn_2O_2 ring is exactly planar owing to the presence of an inversion center. The carbon atom, C(1), attatched to the bridging oxygen, O(1), deviates significantly from the plane of the four-membered Mn_2O_2 ring (Table 4). Each bond length in the spa ligand has a normal value.[29] The spa moiety

TABLE 3. INTERATOMIC DISTANCES (l/Å) AND BOND ANGLES (φ/°) WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Symmetry code
Superscript
None x y z
i $-x$ $-y$ $-z$

(a) Manganese coordination spheres			
Mn···Mn^{i}	2.869(1)	Mn–O(3)	2.208(2)
Mn–O(1)	1.899(2)	Mn–O(4)	2.251(2)
Mn–O(1)^{i}	1.951(2)	Mn–N	2.006(2)
Mn–O(2)	1.849(2)		
O(1)–Mn–O^{i}(1)	83.66(7)	O(1)^{i}–Mn–N	176.57(8)
O(1)–Mn–O(2)	173.76(8)	O(2)–Mn–O(3)	94.28(8)
O(1)–Mn–O(3)	82.43(8)	O(2)–Mn–O(4)^{i}	97.07(8)
O(1)–Mn–O(4)^{i}	85.17(7)	O(2)–Mn–N	91.93(8)
O(1)–Mn–N	93.66(8)	O(3)–Mn–O(4)^{i}	164.00(5)
O(1)^{i}–Mn–O(2)	90.86(8)	O(3)–Mn–N	95.36(8)
O(1)^{i}–Mn–O(3)	86.42(7)	O(4)^{i}–Mn–N	95.49(8)
O(1)^{i}–Mn–O(4)^{i}	82.19(7)	Mn–O(1)–Mn^{i}	96.34(8)
(b) Spa moiety			
O(1)–C(1)	1.412(4)	C(10)–C(5)	1.412(3)
O(2)–C(6)	1.319(2)	C(1)–H(C1A)	1.02(3)
N–C(3)	1.485(4)	C(1)–H(C1B)	0.99(2)
N–C(4)	1.290(3)	C(2)–H(C2A)	1.00(3)
C(1)–C(2)	1.505(3)	C(2)–H(C2B)	1.06(3)
C(2)–C(3)	1.494(3)	C(3)–H(C3A)	1.11(3)
C(4)–C(5)	1.438(4)	C(3)–H(C3B)	0.95(3)
C(5)–C(6)	1.405(3)	C(4)–H(C4)	0.96(3)
C(6)–C(7)	1.406(4)	C(7)–H(C7)	0.93(3)
C(7)–C(8)	1.377(3)	C(8)–H(C8)	0.94(3)
C(8)–C(9)	1.393(4)	C(9)–H(C9)	1.01(3)
C(9)–C(10)	1.363(4)	C(10)–H(C10)	0.97(3)
Mn–O(1)–C(1)	127.4(1)	C(2)–C(1)–H(C1B)	110(1)
Mn^{i}–O(1)–C(1)	128.2(1)	H(C1A)–C(1)–H(C1B)	102(2)
Mn–O(2)–C(6)	129.9(1)	C(1)–C(2)–H(C2A)	108(1)
Mn–N–C(3)	120.8(1)	C(1)–C(2)–H(C2B)	113(2)
Mn–N–C(4)	123.1(2)	C(3)–C(2)–H(C2A)	104(1)
C(3)–N–C(4)	116.1(2)	C(3)–C(2)–H(C2B)	105(1)
O(1)–C(1)–C(2)	109.2(2)	H(C2A)–C(2)–H(C2B)	111(2)
C(1)–C(2)–C(3)	115.0(2)	N–C(3)–H(C3A)	105(2)
N–C(3)–C(2)	115.0(3)	N–C(3)–H(C3B)	108(2)
N–C(4)–C(5)	126.9(2)	C(2)–C(3)–H(C3A)	105(1)
C(4)–C(5)–C(6)	122.4(2)	C(2)–C(3)–H(C3B)	113(1)
C(4)–C(5)–C(10)	118.1(2)	H(C3A)–C(3)–H(C3B)	111(2)
C(6)–C(5)–C(10)	119.4(2)	N–C(4)–H(C4)	116(2)
O(2)–C(6)–C(5)	123.1(2)	C(5)–C(4)–H(C4)	117(2)
O(2)–C(6)–C(7)	118.3(2)	C(6)–C(7)–H(C7)	119(2)
C(5)–C(6)–C(7)	118.6(2)	C(8)–C(7)–H(C7)	120(2)
C(6)–C(7)–C(8)	120.7(2)	C(7)–C(8)–H(C8)	118(2)
C(7)–C(8)–C(9)	120.7(3)	C(9)–C(8)–H(C8)	121(2)
C(8)–C(9)–C(10)	119.7(2)	C(8)–C(9)–H(C9)	118(2)
C(5)–C(10)–C(9)	121.0(3)	C(10)–C(9)–H(C9)	122(2)
O(1)–C(1)–H(C1A)	114(2)	C(5)–C(10)–H(C10)	120(2)
O(1)–C(1)–H(C1B)	110(2)	C(9)–C(10)–H(C10)	119(2)
C(2)–C(1)–H(C1A)	111(2)		
(c) Acetate group			
O(3)–C(11)	1.261(3)	C(12)–H(C12A)	0.92(3)
O(4)–C(11)	1.263(3)	C(12)–H(C12B)	0.84(3)
C(11)–C(12)	1.505(3)	C(12)–H(C12C)	0.80(4)
Mn–O(3)–C(11)	124.6(1)	C(11)–C(12)–H(C12B)	113(2)
Mn^{i}–O(4)–C(11)	123.6(2)	C(11)–C(12)–H(C12C)	115(2)
O(3)–C(11)–O(4)	126.1(2)	H(C12A)–C(12)–H(C12B)	108(2)
O(3)–C(11)–C(12)	116.5(2)	H(C12A)–C(12)–H(C12C)	92(3)
O(4)–C(11)–C(12)	117.4(2)	H(C12B)–C(12)–H(C12C)	114(3)
C(11)–C(12)–H(C12A)	113(2)		

TABLE 4. DEVIATIONS OF THE ATOMS FROM LEAST-SQUARES PLANES (l/Å) AND DIHEDRAL ANGLES BETWEEN THE PLANES (φ/°)

(I) Plane through Mn, Mn^i, O(1), $O(1)^i$
$0.9246X+0.2240Y-0.4357Z=0$[a)]
[Mn 0.000, Mn^i 0.000, O(1) 0.000, $O(1)^i$ 0.000, O(2) 0.097, N −0.075, C(1) −0.558, C(2) −0.046, C(3) −0.513, C(4) 0.220, C(5) 0.512, C(6) 0.421, C(7) 0.640, C(8) 0.926, C(9) 1.029, C(10) 0.823][b)]

(II) Plane through O(1), $O(1)^i$, O(2), N
$0.9164X+0.1911Y-0.4269Z=0.0010$
[O(1) 0.042, $O(1)^i$ −0.044, O(2) 0.041, N −0.039, Mn −0.006, C(1) −0.472, C(2) 0.060, C(3) −0.430, C(4) 0.244, C(5) 0.490, C(6) 0.361, C(7) 0.538, C(8) 0.818, C(9) 0.959, C(10) 0.795]

(III) Plane through O(1), N, C(1), C(3)
$0.7956X-0.1269Y-0.3020Z=0.4082$
[O(1) 0.035, N −0.034, C(1) −0.040, C(3) 0.038, Mn −0.426, C(2) 0.680]

(IV) Plane through Mn, O(2), N, C(4), C(5), C(6)
$0.8399X+0.1269Y-0.5353Z=-0.3449$
[Mn 0.113, O(2) −0.107, N −0.080, C(4) −0.010, C(5) 0.077, C(6) 0.007]

(V) Plane through C(5), C(6), C(7), C(8), C(9), C(10)
$0.8207X+0.1485Y-0.5852Z=-0.5109$
[C(5) −0.003, C(6) 0.000, C(7) 0.005, C(8) −0.007, C(9) 0.003, C(10) 0.002]

(VI) Plane through Mn, Mn^i, O(3), O(4), C(11)
$0.2624X+0.9853Y-0.3629Z=0.0090$
[Mn 0.000, Mn^i −0.018, O(3) 0.033, O(4) 0.057, C(11) −0.072, $O(3)^i$ −0.052, $O(4)^i$ −0.075, $C(11)^i$ 0.054, C(12) −0.380, $C(12)^i$ 0.362]

(VII) Plane through O(3), O(4), C(11), C(12)
$0.4469X+0.9971Y-0.4280Z=0.5044$
[O(3) 0.000, O(4) 0.000, C(11) 0.000, C(12) 0.000, Mn −0.476, Mn^i −0.533, $O(3)^i$ −1.009, $O(4)^i$ −1.009, $C(11)^i$ −1.009, $C(12)^i$ −1.009]

Dihedral angles between the planes (φ/°)

(I) and (II)	1.9	(II) and (IV)	9.6
(I) and (III)	20.2	(II) and (V)	12.3
(I) and (IV)	10.5	(II) and (VI)	87.9
(I) and (V)	12.8	(III) and (IV)	17.6
(I) and (VI)	86.0	(IV) and (V)	3.4
(II) and (III)	18.3	(VI) and (VII)	11.8

a) The equation of the plane is expressed as $LX+MY+NZ=D$, where X, Y, and Z are in Å units referred to the crystallographic axes.
b) Deviations (l/Å) of atoms from the planes are listed in square brackets. Superscript (i) refers to the equivalent position $(-x, -y, -z)$.

forms two six-membered chelate rings with the manganese atom. The Mn–O(1)–C(1)–C(2)–C(3)–N chelate ring has a chair conformation, and Mn and C(2) are located 0.426 Å below and 0.680 Å above the plane defined by O(1), C(1), C(3) and N, respectively. On the other hand, the Mn–N–C(4)–C(5)–C(6)–O(2) chelate ring is nearly planar, the maximum deviation from the least-squares plane being 0.113 Å.

As was predicted,[7] the acetate groups are involved in the bridges in a syn-syn configuration. The acetate group is positioned above or below the Schiff base dimeric unit. The only example of two-acetate bridging in a similar fashion is found in di-μ-acetato-bis(diphenyltin), $Sn(Ph)_2(ac)$.[30] However, this complex is different from Mn(spa)(ac) in having a direct Sn–Sn bond and no monatomic bridging. Thus, the present complex, Mn(spa)(ac), including two monatomic and two triatomic bridges is unique in this regard. The manganese-carboxyl oxygen bonds deviate in several degrees from the axis perpendicular to the equatorial plane (Fig. 2), the O(3)–Mn–$O(4)^i$ bond angle being 164.00(5)°. This is due to the fact that the acetate bite (the O(3)–O(4) distance, 2.250(2) Å) is much less than the manganese-manganese distance (2.869(1) Å). The C(11)–O(3) and C(11)–O(4) distances are equal within experimental error. The $\begin{matrix}O\\O\end{matrix}\!>\!C\!-\!C$ plane retains its planarity (Table 4). Such planarity was also observed for dimeric copper(II) carboxylates.[31–36]

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