Crystal Structure and Magnetic Property of the Binuclear Manganese(III) Complex $[Mn(L)H_2O]_2(ClO_4)_2$ (L = *N*-(acetylacetonylidene)-*N'*-(α-methylsalicylidene)-ethylenediamine)

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Abstract

The crystal structure and magnetic property of the title compound $[Mn(L)H_2O]_2(ClO_4)_2$ are described. The complex crystallizes in the triclinic space group $P\bar{1}$ with formula = $MnClO_7N_2C_{15}H_{20}$, $a = 11.615(4)$, $b = 11.955(4)$, $c = 7.753(2)$ Å, $\alpha = 104.65(2)$, $\beta = 111.84(3)$, $\gamma = 63.64(2)°$, $V = 890.5(6)$ Å^3 and $Z = 2$. The complex consists of a binuclear structure bridged by two phenoxo oxygen atoms O(1) and O(1)* of the quadridentate ligands in an out-of-plane mode, where the binuclear structure has a crystallographical center of symmetry, and the bond distances of Mn–Mn* and Mn–O(1)* are 3.318(1) and 2.305(2) Å, respectively. The magnetic susceptibility data (4.2–300 K) showed a maximum at 11 K and were closely reproduced by the spin-Hamiltonian $\mathcal{H} = 2JS_1 \cdot S_2$ with $J = -1.68$ cm^{-1} and $g = 2.01$. The deviation of the observed values from the theoretical curve in the lower temperature region is due to the zerofield splitting term. The X-band ESR spectrum in frozen dichloromethane solution at 20 K showed a broad signal at 900 G and a multiline signal at 3300 G.

Introduction

Polynuclear manganese complexes are of increasing interest because such multinuclear systems are known to exist at the active center of some Mn-containing enzymes, such as the photosystem II of green plants [1] and pseudo-catalase from *Lactobacillus planatrum* [2]. However, few well characterized dinuclear manganese(II) [3] and manganese(III) [4, 5] complexes have been reported.

In this study, a new dinuclear manganese(III) complex $[Mn(L)H_2O]_2(ClO_4)_2$ of *N*-(acetylacetonylidene)-*N'*-(α-methylsalicylidene)ethylenediamine (H_2L) has been prepared and studied by magnetic susceptibility in the 4.2–300 K temperature range, X-band ESR spectrum at 20 K, and the single-crystal X-ray diffraction technique.

Experimental

Synthesis

[H_2L]

The unsymmetrical quadridentate ligand [H_2L] was prepared according to the literature method [6, 7] and identified by melting point (130 °C) and elemental analysis.

[$Mn(L)H_2O]_2(ClO_4)_2$

To a methanol solution (20 cm^3) of the ligand (1 mmol) was added a methanol solution (50 cm^3) of manganese(III) acetate dihydrate (1 mmol). The solution was stirred at room temperature for several hours and filtered. To the filtrate was added a methanol solution (20 cm^3) of sodium perchlorate (3 mmol). The solution was left to stand overnight and the black prisms precipitated were collected. They were recrystallized from a methanol/water mixture. *Anal.* Found: C, 41.36; H, 4.64; N, 6.42. Calc. for $MnClO_7N_2C_{15}H_{20}$: C, 41.83; H, 4.68; N, 6.50%. Λ_M 87 S mol^{-1} cm^2 (methanol).

Physical Measurements

Elemental analyses were performed at the Elemental Analysis Service Center of Kyushu University. Melting points were measured on a Yanagimoto micro-melting points apparatus and were uncorrected. Electrical conductivity was measured on a Denki Kagaku Keiki AOL-10 digital conductometer in *c.* 10^{-3} mol dm^{-3} methanol solution of the complex. Magnetic susceptibilities were obtained at 4–100 K by use of a HOXAN HSM-2000 SQUID magnetometer in the magnetic field 0.5 T and at 80–300 K by the Faraday method. Data were corrected for magnetization of the sample holder and for the diamagnetism of the component atoms by use of Pascal's constants. The X-band ESR spectrum was measured on a JEOL JES-FE-2XG ESR spectrometer.

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X-ray Crystallography

Reflection data were measured on a Rigaku Denki AFC-5 automated four-circle diffractometer with graphite monochromatized Mo Kα radiation at 20 ± 1 °C. The crystal was stable during the X-ray diffraction measurement and the standard reflections monitored showed no decay. The diffraction data were corrected for Lorentz–polarization effects but not for absorption. Information concerning conditions for crystallographic data collection and structure refinement is as follows: formula = $MnClO_7N_2C_{15}H_{20}$, formula weight = 430.68, triclinic, space group $P\bar{1}$, $a = 11.615(4)$, $b = 11.955(4)$, $c = 7.753(2)$ Å, $\alpha = 104.65(2)$, $\beta = 111.84(3)$, $\gamma = 63.64(2)°$, $V = 890.5(6)$ Å^3, $D_m = 1.58$ g cm^{-3}, $D_x = 1.606$ g cm^{-3} ($Z = 2$), crystal size 0.4 × 0.3 × 0.3 mm, μ(Mo Kα) = 5.61 cm^{-1}, scan mode θ–2θ, scan range 2.5–55°, scan width $(1.2 + 0.35 \tan\theta)°$, octant measured $+h$, $\pm k$, $\pm l$, number of observed reflections $|F_o| > 3\sigma(|F_o|)$ 3680, $R = 5.43\%$, $R_w = 5.77\%$, function minimized in least-squares calculation $\Sigma w(|F_o| - |F_c|)^2$, $w = 1$, heighest peak on the final D-Fourier map 0.4 e Å^{-3}.

The structure was solved by the heavy-atom method and refined by the block-diagonal least-squares method using the UNICS III program system [8] on a FACOM M 780 computer at the Computer Center of Kyushu University. The oxygen atoms of perchlorate anion have been subjected to disorder and the occupancy factors evaluated by the peak heights on the Fourier map were assigned for six possible positions. Hydrogen atoms were located by the difference Fourier synthesis and were refined with the isotropic thermal parameters. Final difference Fourier synthesis is featureless, where the residual peaks are less than 0.4 e Å^3. Final positional parameters of non-hydrogen atoms are given in Table 1. See also 'Supplementary Material'.

Results and Discussion

Structural Description

The crystal structure consists of a binuclear cation $[Mn(L)H_2O]_2$ containing a crystallographical center of symmetry and two perchlorate anions ClO_4^-. The molecular structure of the crystallographical unique unit with the atom numbering scheme is shown in Fig. 1. Bond distances and angles with their estimated standard deviations in parentheses

TABLE 1. Positional parameters of non-hydrogen atoms (×10^4)

Atom	x	y	z	B_{EQ}
Mn	514.6(0.6)	1165.0(0.5)	1018.4(0.8)	2.38(1)
OW	506(3)	2379(3)	3786(4)	3.85(11)
O1	−358(3)	311(2)	1534(3)	2.23(7)
O2	2309(3)	68(2)	2076(4)	2.67(8)
N1	−1296(3)	2387(3)	−192(4)	2.55(10)
N2	1154(3)	2126(3)	125(4)	2.64(10)
C1	−1435(4)	931(3)	2160(5)	2.23(10)
C2	−1593(4)	376(4)	3385(6)	3.06(13)
C3	−2668(5)	971(5)	4088(6)	3.99(17)
C4	−3625(5)	2135(5)	3585(7)	4.13(17)
C5	−3509(4)	2678(4)	2341(6)	3.57(14)
C6	−2438(4)	2106(3)	1563(5)	2.65(11)
C7	−2396(4)	2696(3)	156(5)	2.66(11)
C8	−3685(5)	3674(4)	−879(7)	4.10(15)
C9	−1197(5)	2940(4)	−1610(6)	3.62(15)
C10	29(5)	3216(4)	−795(7)	3.96(17)
C11	2705(6)	2880(5)	−132(8)	5.02(22)
C12	2386(4)	1968(4)	452(6)	3.03(14)
C13	3507(4)	937(4)	1331(6)	3.30(14)
C14	3411(4)	65(4)	2049(5)	2.71(12)
C15	4673(4)	−999(4)	2896(7)	3.87(15)
CL	2427(1)	4464(1)	5253(2)	4.24(4)
O3	3544(6)	4497(5)	5003(10)	8.96(29)
O4	2581(6)	3202(4)	5218(9)	8.80(27)
O5	2001(10)	5206(7)	6783(12)	8.74(41)
O6	1312(10)	4717(9)	3621(11)	8.70(42)
O7	1366(13)	5502(13)	4683(18)	10.04(60)
O8	2978(16)	4537(13)	7179(17)	9.45(65)

Occupancy factors: 0.9 for O(3), O(4); 0.6 for O(5), O(6); 0.4 for O(7), O(8).

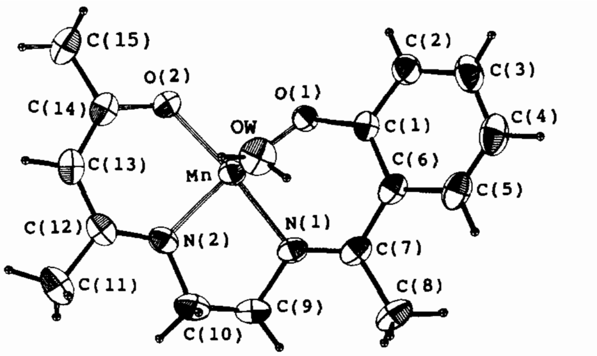

Fig. 1. ORTEP drawing of the cation $[Mn(L)H_2O]^+$ with the atom numbering scheme.

are given in Table 2. As seen in Fig. 2, two crystallographical unique units related by a crystallographical center of inversion form a binuclear structure in which two metal ions are bridged by two phenoxo oxygen atoms O(1) and O(1)* of the *o*-hydroxyacetophenone residue of the unsymmetrical quadridentate ligand in an out-of-plane fashion, where the bond distances of Mn–Mn* and Mn–O(1)* are 3.318(1) and 2.305(2) Å, respectively.

The manganese(III) ion has a tetragonal bipyramidal coordination geometry, in which the basal coordination plane is composed of the N_2O_2 donor atoms of the quadridentate ligand and two axial positions are occupied by a water molecule with the bond distance of Mn–OW = 2.266(3) Å and a phenoxo oxygen atom of the neighboring quadridentate ligand with the bond distance of Mn–O(1)* = 2.305(2) Å. In the equatorial coordination plane, the bond distances Mn–O(2) (1.892(2) Å) and Mn–N(2) (1.973(4) Å) of the acetylacetone residue are apparently shorter than the Mn–O(1) (1.912(3) Å) and Mn–N(1) (1.983(2) Å) distances of the *o*-hydroxyacetophenone residue, respectively. The

TABLE 2. Bond distances and angles

(a) Bond distances (Å)			
Mn–Mn*	3.318(1)	Mn–OW	2.266(3)
Mn–O(1)	1.912(3)	Mn–O(2)	1.892(2)
Mn–O(1)*	2.305(2)	Mn–N(1)	1.983(2)
Mn–N(2)	1.973(4)	O(1)–C(1)	1.339(5)
C(1)–C(2)	1.389(7)	C(1)–C(6)	1.421(4)
C(2)–C(3)	1.373(7)	C(3)–C(4)	1.364(9)
C(5)–C(6)	1.404(7)	C(6)–C(7)	1.465(7)
C(7)–C(8)	1.509(5)	N(1)–C(7)	1.276(6)
N(1)–C(9)	1.480(7)	C(9)–C(10)	1.475(8)
N(2)–C(10)	1.476(5)	N(2)–C(12)	1.289(6)
C(11)–C(12)	1.504(10)	C(12)–C(13)	1.420(5)
C(13)–C(14)	1.362(8)	O(2)–C(14)	1.285(6)
C(14)–C(15)	1.499(5)		
Cl–O(3)	1.400(8)	Cl–O(4)	1.431(5)
Cl–O(5)	1.397(9)	Cl–O(6)	1.412(7)
Cl–O(7)	1.329(11)	Cl–O(8)	1.385(11)
(b) Bond angles (°)			
O(1)–Mn–O(2)	88.8(1)	O(1)–Mn–N(1)	88.0(1)
N(1)–Mn–N(2)	83.8(1)	O(2)–Mn–N(2)	90.8(1)
OW–Mn–O(1)	90.5(1)	OW–Mn–O(2)	90.8(1)
OW–Mn–N(1)	90.1(1)	OW–Mn–N(2)	94.0(1)
Mn–O(1)–C(1)	122.0(2)	O(1)–C(1)–C(2)	118.3(3)
O(1)–C(1)–C(6)	122.3(4)	C(2)–C(1)–C(6)	119.2(4)
C(1)–C(2)–C(3)	121.0(4)	C(2)–C(3)–C(4)	120.6(6)
C(3)–C(4)–C(5)	119.1(5)	C(4)–C(5)–C(6)	122.5(3)
C(5)–C(6)–C(1)	117.2(4)	C(5)–C(6)–C(7)	120.4(3)
C(1)–C(6)–C(7)	122.2(4)	C(6)–C(7)–N(1)	120.7(3)
C(6)–C(7)–C(8)	118.5(4)	N(1)–C(7)–C(8)	120.6(4)
Mn–N(1)–C(7)	127.8(3)	Mn–N(1)–C(9)	108.9(2)
C(7)–N(1)–C(9)	123.1(3)	N(1)–C(9)–C(10)	107.7(3)
C(9)–C(10)–N(2)	109.1(4)	Mn–N(2)–C(10)	111.7(3)
Mn–N(2)–C(12)	126.9(3)	C(10)–M(2)–C(12)	120.7(4)
N(2)–C(12)–C(11)	120.5(3)	N(2)–C(12)–C(13)	123.1(5)
C(11)–C(12)–C(13)	116.2(4)	C(12)–C(13)–C(14)	124.2(4)
C(13)–C(14)–O(2)	125.3(3)	C(13)–C(14)–C(15)	118.9(4)
O(2)–C(14)–C(15)	115.7(4)	Mn–O(2)–C(14)	128.8(2)

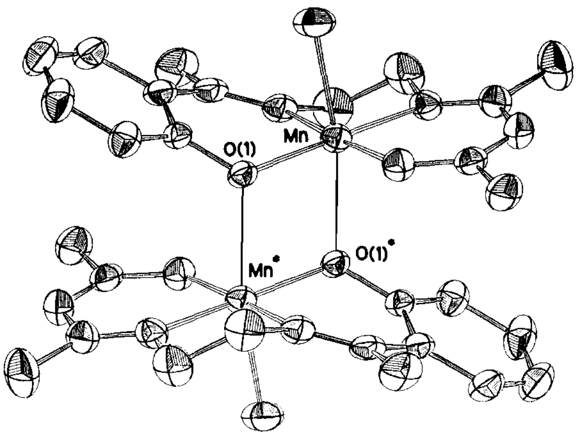

Fig. 2. Binuclear structure.

longer axial bond distances relative to the equatrial ones should be due to the Jahn–Teller effect in the high-spin d^4 system.

Magnetic Property

The temperature dependences of the magnetic susceptibility (χ_A) per copper atom, the reciprocal susceptibility ($1/\chi_A$), and the effective magnetic moment (μ_{eff}) per manganese atom are shown in Fig. 3. See also 'Supplementary Material'. The $1/\chi_A$ versus T plot is nearly linear above 20 K and follows the Curie–Weiss law ($\chi_A = C(T + \theta)$) with the Weiss constant of 17 K. This suggests that there operates intra- or/and intermolecular antiferromagnetic interaction. The effective magnetic moment at room temperature is 4.84 BM which is very close to the spin-only value expected for high-spin manganese(III) ion ($S = 2$; 4.90 BM). Upon cooling down, the magnetic moment decreases from 4.84 BM at 298 K to 1.70 BM at 4.4 K, showing the existence of antiferromagnetic interaction and/or zerofield splitting of the ground state. The χ_A versus T plot shows a maximum at 11 K, which is indicative of antiferromagnetic interaction between two manganese(III) ions. To interpret the magnetic susceptibility data quantitatively, the spin-only expression deduced from the spin-Hamiltonian $\mathcal{H} = -2JS_1 \cdot S_2$ ($S_1 = S_2 = 2$) was employed. The observed susceptibility data was closely reproduced by the spin-only expression with the parameters of $J = -1.68$ cm^{-1} and $g = 2.01$, although in the lower temperature region the observed magnetic susceptibilities deviate slightly from the calculated ones. The theoretical curve using the parameters is represented as a solid line in Fig. 3. The disagreement in the lower temperature region implies that the zerofield splitting term is not negligible.

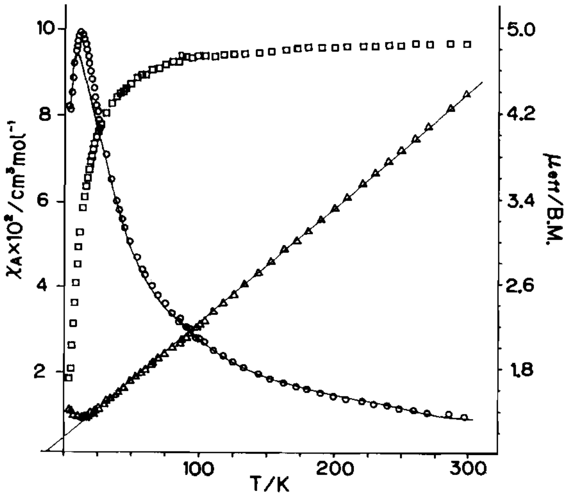

Fig. 3. Temperature dependence of the magnetic susceptibilities, the reciprocal magnetic susceptibilities, and the effective magnetic moments, where the solid line represents the theoretical curve with the best-fit parameters $J = -1.68$ cm^{-1} and $g = 2.01$.

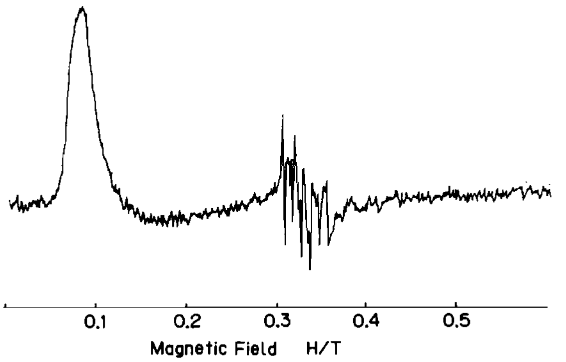

Fig. 4. X-band ESR spectrum of frozen dichloromethane solution at 20 K.

The spin-exchange interaction in the present complex is weakly antiferromagnetic and its magnitude is similar to those reported for [Mn(salen)X]$_2$ which takes a dimeric structure similar to that of the present complex [9]. Thus, we note that the spin-exchange in the binuclear manganese(III) complexes bridged in an out-of-plane mode shows a weak antiferromagnetic spin-exchange compared with those bridged in an in-plane mode [5].

The X-band ESR spectrum of the complex measured in frozen dichloromethane solution at 20 K is shown in Fig. 4. The spectrum showed a broad signal at 900 G and a signal with multiplet at 3300 G. Their assignments are not feasible at present.

Supplementary Material

Tables of observed and calculated structure factors, listings of atomic parameters of hydrogen atoms and thermal parameters of non-hydrogen atoms, and magnetic susceptibility data are available from the authors on request.

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