Crystal Structures of the Imidazole and the 1,4-Di(1-imidazolyl)butane Adducts of *N,N'*-Ethylenebis[salicylideneaminato]-manganese(III) Perchlorate

Naohide MATSUMOTO,* Naohiko TAKEMOTO, Akira OHYOSI, and Hisashi ŌKAWA†
Department of Applied Chemistry, Faculty of Engineering, Kumamoto University, Kurokami 2-39-1, Kumamoto 860
†Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812
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Synopsis. Crystal structures of the titled compounds [Mn(Him)(salen)][ClO_4]CH_3OH (**1**) and [Mn(biim)(salen)][ClO_4] (**2**), have been determined by the single-crystal X-ray diffraction method. The molecular structure of the imidazole adduct (**1**) is a binuclear structure bridged by phenoxy oxygen atoms of salen ligand, while that of the 1,4-di(1-imidazolyl)butane adduct (**2**) is a polynuclear structure bridged by imidazole nitrogen atoms of 1,4-di(1-imidazolyl)-butane.

It is well-known that metal complexes with N,N'-ethylenebis[salicylideneamine] (well-known salen ligand) tend to assume a dimeric structure bridged by phenoxy oxygen atoms.[1] In this study the imidazole adduct and the 1,4-di(1-imidazolyl)butane adduct of [Mn(salen)][ClO_4] were prepared and their crystal structures were determined by a single-crystal X-ray diffraction technique in order to investigate their molecular structures.

Experimental

Synthesis. [Mn(Him)(salen)][ClO_4]CH_3OH (**1**). To a solution of [Mn(salen)][ClO_4]$2H_2O$ (2 mmol) in 30 cm^3 of methanol was added a solution of imidazole (3 mmol) in 10 cm^3 of methanol. The solution was gently warmed on a water bath for 10 min and cooled to room temperature. The solution was kept standing overnight. The dark-brown crystals precipitated were collected by suction filtration and dried. Found: C, 45.72; H, 4.31; N, 10.78%. Calcd for $MnClO_7N_4C_{20}H_{22}$: C, 46.13; H, 4.26; N, 10.76%. Mp >300 °C, Λ_M 88 S mol^{-1} cm^2 (methanol).

[Mn(biim)(salen)][ClO_4] (**2**). The complex (**2**) was prepared by a method similar to that of **1**, where 1,4-di(1-imidazoyl)butane instead of imidazole was used. Found: C, 51.07; H, 4.62; N, 13.75%. Calcd for $MnClO_6N_6C_{26}H_{28}$: C, 51.12; H, 4.62; N, 13.76%. Mp 253—257 °C, Λ_M 65 S mol^{-1} cm^2 (DMF).

Physical Measurements. Elemental analyses were performed by Mr. Shinichi Miyazaki at the Technical Service Center of Kumamoto University. Melting points were measured on a Yanagimoto micro-melting points apparatus and were uncorrected. Molar electrical conductivities were measured on a Denki Kagaku Keiki AOC-10 digital conductometer.

X-Ray Diffraction Study. Diffraction data for complexes **1** and **2** were obtained on a Rigaku Denki AFC-5 four-circle diffractometer at the Faculty of Science, Kyushu University, using graphite monochromatized Mo$K\alpha$ radiation at ambient temperature (20±1 °C). Pertinent crystallographic parameters are summarized below:

[Mn(Him)(salen)][ClO_4]CH_3OH (**1**). Formula=$MnClO_7N_4C_{20}H_{22}$, FW=520.8, triclinic, space group $P\bar{1}$, a=11.203(2) Å, b=11.565(2) Å, c=9.832(1) Å, α=112.25(1)°, β=107.50(1)°, γ=86.64(1)°, V=1119.9 Å^3, D_x=1.544 g cm^{-3} (Z=2), D_m=1.52 g cm^{-3}, crystal size 0.2×0.3×0.4 mm, scan mode θ-2θ, scan rate 6° min^{-1}, 2θ range 2.5°<2θ<48°, no. unique data used 2182, R=4.93%, R_w=5.16%.

[Mn(biim)(salen)][ClO_4] (**2**). Formula=$MnClO_6N_6C_{26}H_{28}$, FW=610.9, monoclinic, space group $P2_1/a$, a=16.566 (9) Å, b=16.141(4) Å, c=10.527(2) Å. β=102.81(2)°, V=2759.7 Å^3, D_x=1.470 g cm^{-3} (Z=4), D_m=1.46 g cm^{-3}, crystal size 0.2×0.2×0.4 mm, scan mode θ-2θ, scan rate 6° min^{-1}, 2θ range 2.5°<2θ<48°, no. unique data used 3204, R=5.62%, R_w=5.68%. One of two imidazole moieties of biim has been subjected to disorder. The occupancy factors for C(17) and C(18) atoms were assigned on the basis of the peak heights of the difference Fourier synthesis.

Reflection data were corrected for Lorentz-polarization effects but not for absorption. The structures were solved by the standard heavy-atom method and refined by a block-diagonal least-squares method using the Universal Crystallographic Computation Program System UNICS III.[2]

Table 1. Atomic Parameters of Non-Hydrogen Atoms for [Mn(Him)(salen)][ClO_4]MeOH (×10^4)

Atom	x	y	z	B_{eqv}
Mn	1418(1)	851(1)	659(1)	2.6
O(1)	1569(3)	324(3)	−1338(4)	2.6
O(2)	−252(3)	1315(3)	79(4)	2.6
N(1)	2962(4)	60(4)	1388(5)	2.5
N(2)	1297(4)	1154(4)	2735(5)	2.3
N(3)	2391(4)	2715(4)	1395(5)	2.7
N(4)	3564(5)	4128(5)	1302(6)	4.3
C(1)	2375(5)	−427(5)	−1927(6)	2.5
C(2)	2219(6)	−785(5)	−3509(6)	3.3
C(3)	3006(6)	−1581(6)	−4200(7)	4.0
C(4)	3990(6)	−2062(6)	−3362(7)	4.2
C(5)	4156(6)	−1715(6)	−1802(7)	3.9
C(6)	3381(5)	−900(5)	−1060(6)	2.7
C(7)	3632(5)	−618(5)	574(6)	2.8
C(8)	3323(5)	325(5)	3063(6)	3.2
C(9)	2133(6)	404(5)	3494(6)	2.9
C(10)	575(5)	1928(5)	3379(6)	2.7
C(11)	−323(5)	2613(5)	2646(6)	2.6
C(12)	−901(6)	3567(5)	3538(7)	3.8
C(13)	−1811(6)	4213(5)	2894(8)	4.4
C(14)	−2157(6)	3898(5)	1312(8)	4.1
C(15)	−1622(5)	2948(5)	381(7)	3.2
C(16)	−702(5)	2286(5)	1025(6)	2.5
C(17)	2728(7)	3690(6)	2798(7)	4.8
C(18)	3438(8)	4555(6)	2736(8)	5.6
C(19)	2917(6)	3019(5)	539(7)	3.3
Cl	4397(2)	2902(1)	−2726(2)	3.5
O(3)	4624(5)	3951(4)	−1340(5)	6.2
O(4)	5568(7)	2600(6)	−3010(9)	9.8
O(5)	3950(5)	1844(5)	−2621(6)	6.7
O(6)	3641(8)	3179(6)	−3938(6)	10.7
OS	194(6)	1837(7)	−3097(7)	9.7
CS	135(9)	3134(9)	−2292(10)	8.2

Table 2. Atomic Parameters of Non-Hydrogen Atoms for [Mn(biim)(salen)][ClO_4] ($\times 10^4$)

Atom	x	y	z	B_{eqv}
Mn	517(0)	1693(0)	2013(1)	3.2
O(1)	704(2)	1705(2)	315(3)	3.6
O(2)	−543(2)	1231(2)	1513(3)	3.7
N(1)	1670(2)	2220(2)	2738(4)	3.0
N(2)	456(2)	1708(3)	3879(4)	3.4
N(3)	43(3)	3023(3)	1730(5)	4.2
N(4)	−407(4)	4262(3)	1976(8)	8.2
N(5)	−3003(3)	5623(3)	2615(4)	3.4
N(6)	−3877(3)	4589(3)	2305(4)	3.5
C(1)	1418(3)	1765(3)	−19(5)	3.2
C(2)	1460(4)	1543(3)	−1289(5)	4.0
C(3)	2176(4)	1610(4)	−1707(5)	4.5
C(4)	2895(4)	1910(4)	−894(6)	4.4
C(5)	2877(3)	2139(3)	351(5)	3.8
C(6)	2148(3)	2060(3)	820(5)	3.1
C(7)	2185(3)	2316(3)	2135(5)	3.2
C(8)	1667(3)	2561(4)	4048(5)	4.0
C(9)	1226(3)	1972(4)	4770(5)	4.5
C(10)	−147(3)	1452(4)	4352(5)	4.0
C(11)	−904(3)	1111(3)	3594(5)	3.7
C(12)	−1491(4)	843(4)	4275(6)	5.3
C(13)	−2222(4)	500(4)	3631(7)	5.7
C(14)	−2378(4)	408(4)	2299(7)	5.0
C(15)	−1815(3)	664(3)	1590(6)	4.2
C(16)	−1059(3)	1012(3)	2225(5)	3.3
C(17A)[a]	81(15)	4385(13)	1233(23)	5.9
C(17B)[a]	−411(6)	4098(7)	395(11)	3.8
C(17C)[a]	287(13)	4426(14)	1629(21)	2.5
C(18A)[a]	444(13)	3625(12)	1126(22)	5.0
C(18B)[a]	−86(6)	3322(7)	356(11)	4.1
C(18C)[a]	−328(22)	3601(20)	1088(34)	6.3
C(19)	−296(3)	3518(3)	2440(5)	4.0
C(20)	−775(4)	4973(4)	2503(9)	7.1
C(21)	−1457(4)	5352(4)	1508(7)	5.1
C(22)	−1764(4)	6168(3)	1958(7)	4.7
C(23)	−2227(4)	6084(3)	3034(6)	4.4
C(24)	−3725(4)	5923(3)	1872(6)	4.3
C(25)	−4260(3)	5282(3)	1696(5)	4.1
C(26)	−3123(3)	4816(3)	2844(5)	3.4
Cl	3915(1)	1591(1)	5841(2)	5.4
O(3)	4722(3)	1697(4)	5685(5)	8.5
O(4)	3900(4)	995(5)	6780(8)	12.0
O(5)	3422(4)	1373(5)	4647(6)	12.0
O(6)	3580(4)	2339(4)	6237(7)	10.8

a) Occupancy factors: A 0.3; B 0.2; C 0.5.

The positions of hydrogen atoms were calculated. The hydrogen atoms were included in the structure factor calculation but not refined. The calculations were carried out on a FACOM M 200 computer at the Computer Center of Kyushu University. Positional parameters of non-hydrogen atoms for the complexes **1** and **2** are given in Tables 1 and 2, respectively. Tables of the anisotropic thermal parameters for non-hydrogen atoms, atomic parameters for hydrogen atoms, and F_o-F_c tables are given as supplementary data at the office of the Chemical Society of Japan as Document No. 8815.

Results and Discussion

Bond distances and angles with their estimated standard deviaitons of **1** and **2** are given in tables, which are deposited as supplementary data. Perspective drawings of the cations of **1** and **2** with the atom numbering scheme are shown in Figs. 1 and 2, respectively.

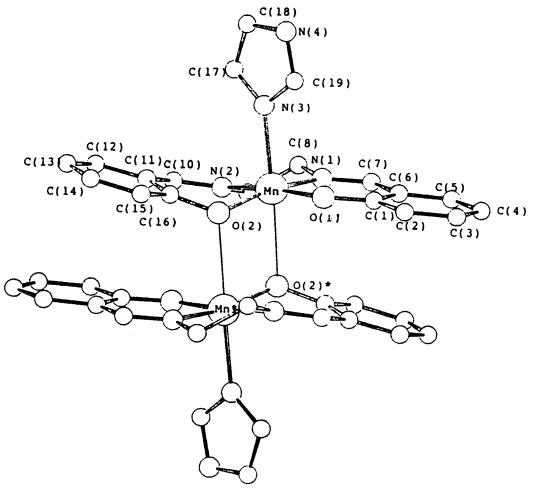

Fig. 1. Perspective drawing of **1** with the atom numbering scheme.

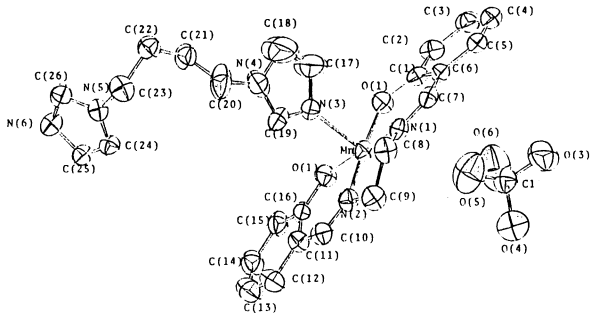

Fig. 2. Perspective drawing of unique molecule of [Mn(biim)(salen)][ClO_4] **2** with the atom numbering scheme.

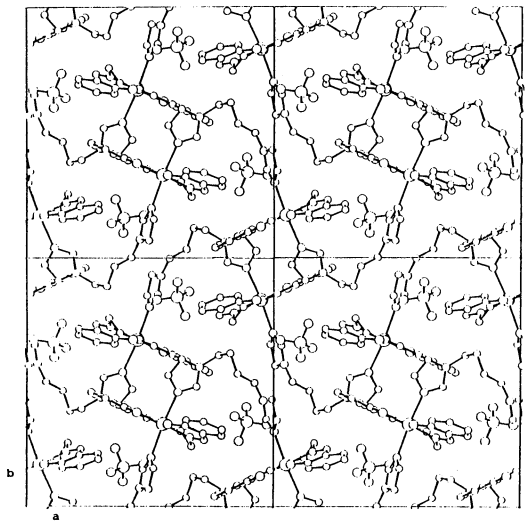

Fig. 3. Polynuclear structure of **2**.

Structural Description of [Mn(Him)(salen)][ClO_4] CH_3OH (1). As shown in Fig. 1, the structure of **1** is a binuclear structure bridged by phenoxy oxygen atoms

of salen ligands, in which two $[Mn(Him)(salen)]^+$ cations are related by an inversion center. The manganese(III) ion has a tetragonal bipyramidal coordination geometry, in which the basal coordination plane comprises N_2O_2 donors of quadridentate salen ligand; the two elongated axial positions are occupied by an imidazole nitrogen atom N(3) (Mn-N(3) 2.231(4) Å) and a phenoxy oxygen atom O(2)* of symmetry related salen ligand ($-x$, $-y$, $-z$) (Mn-O(2)* 2.635(3) Å). The imidazole plane lies on the Mn-O(1) and Mn-N(2) bonds.

Structural Description of [Mn(biim)(salen)][ClO_4] (2). The structure of **2** is a polymeric chain structure bridged by imidazole nitrogen atoms of 1,4-di(1-imidazolyl)-butane, as shown in Fig. 3. The manganese(III) ion has a tetragonal bipyramidal coordination geometry, in which the basl plane comprises N_2O_2 donors of the salen ligand; the two elongated axial positions are occupied by imidazole nitrogen atoms N(3) and N(6)* ($x+1$, $-y+1/2$, $z+1/2$) of biim ligands with the bond distances Mn-N(3) (2.278(5) Å) and Mn-N(6)* (2.283(4) Å).

References

1) M. Gerloch and F. E. Mabbs, *J. Chem. Soc. A*, **1967**, 1900; M. Calligaris, G. Nardin, and L. Randaccio, *Coord. Chem. Rev.*, **7**, 385 (1972).

2) T. Sakurai and K. Kobayashi, *Rikagaku Kenkyusho Houkoku*, **55**, 69 (1979); S. Kawano, *Rep. Compuut. Cent. Kyushu Univ.*, **13**, 39 (1980).