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A Manganese(III) Complex with 1-[(2-Hydroxyethyl)amino]-2-(salicylideneamino)ethane

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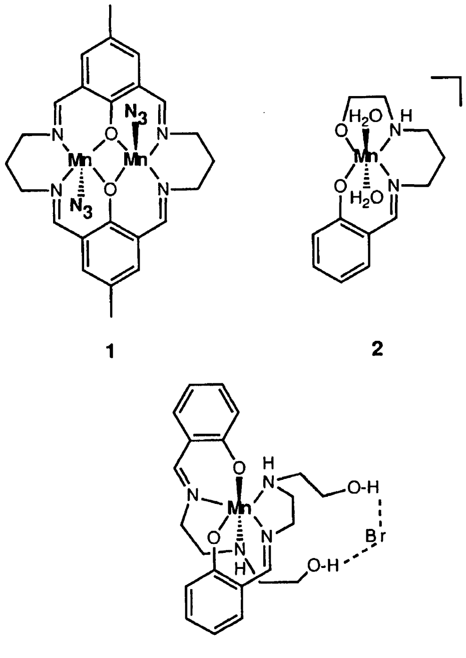
Synopsis. A meridional manganese(III) complex with tridentate 1-[(2-hydroxyethyl)amino]-2-(salicylideneamino)ethane ($H_2L_{6\text{-}5\text{-}5}$), $[Mn(HL_{6\text{-}5\text{-}5})_2]Br$, has been synthesized and characterized by X-ray crystal structure analysis, electronic absorption spectroscopy, and variable temperature magnetic susceptibility. The manganese atom is coordinated in an elongated octahedral environment.

Manganese complexes are of current interest because of the significant involvement of manganese in various biological systems.[1] We have previously reported the syntheses and characterization of mononuclear,[2] dinuclear,[3—6] trinuclear,[7] and tetranuclear[3] manganese complexes with some Schiff-base ligands. We have shown that reactions of 2,6-diformyl-4-methylphenol and 2-[(3-aminopropyl)amino]ethanol in the presence of Mn(II) template ion lead to the formation of a dinuclear manganese(II) complex with a Robson-type macrocyclic ligand $[Mn_2(L_{macro})(N_3)_2]$ (**1**).[6] This indicates that an elimination reaction of the 2-hydroxyethyl group in 2-[(3-aminopropyl)amino]ethanol occurs during the template reaction of the Schiff-base. However, such an elimination reaction does not occur in the template reaction of salicylaldehyde and 2-[(3-aminopropyl)amino]ethanol that yields the manganese(III) complex of 1-[(2-hydroxyethyl)amino]-3-(salicylideneamino)propane ($H_2L_{6\text{-}6\text{-}5}$), $[Mn(L_{6\text{-}6\text{-}5})(H_2O)_2]Br$ (**2**). The formation of the stable 6-6-5 fused chelate ring probably prevents the 2-hydroxyethyl group from being eliminated in the reaction. Hence, it is interesting to study the effect of the fused chelate ring size on the types of manganese complexes formed (Chart 1).



1

2

3

Chart 1.

In this study, in order to examine the 6-5-5 fused chelate ring system, salicylaldehyde was reacted with 2-[(2-aminoethyl)amino]ethanol in the presence of Mn(II) ion. As observed in the synthesis of **2**, the mononuclear manganese(III) complex, $Mn(HL_{6\text{-}5\text{-}5})_2Br$ (**3**) [$H_2L_{6\text{-}5\text{-}5}$ = 1-[(2-hydroxyethyl)amino]-2-(salicylideneamino)ethane] was produced without elimination of the 2-hydroxyethyl group. However, structural analysis has proved conclusively that complexes **2** and **3** differ markedly from each other. The molecular structure of **3** has been determined by X-ray crystallography; the result is shown in Fig. 1. The manganese atom adopts an elongated octahedral geometry with two phenolic oxygen atoms, two imine nitrogen atoms, and two amine nitrogen atoms of the two Schiff-base ligands, $HL_{6\text{-}5\text{-}5}$, each of which acts as a meridional tridentate chelate forming a fused 6-5 chelate ring. Both 2-hydroxyethyl groups of the Schiff-base ligands are uncoordinated and are positioned *cis* to each other, forming hydrogen bonds with the bromide ion, as implied by the distances O3···Br 3.308(6) Å and O4···Br 3.707(7) Å. The atoms O1, N1, N2, and N3 form an approximately square plane. The Mn–O1 [1.895(5) Å], Mn–N1 [1.996(5) Å], Mn–N2 [2.114(6) Å], Mn–N3 [2.027(5) Å] distances fall in the range of the corresponding bonds in manganese(III) complexes with similar Schiff-base ligands.[3,4] The axial Mn–O2 (phenolate) [2.034(5) Å] and Mn–N4 (amine) [2.341(6) Å] bonds are considerably longer than the in-plane Mn–O (phenolate) and Mn–N (amine) distances, respectively. This tetragonal elongation is a consequence of the Jahn–Teller effect expected for a high-spin d^4 ion. The high-spin d^4 electronic configuration was confirmed by the magnetic susceptibility measurements. The effective magnetic moment (5.00 B.M.) is close to the spin-only value for a high-spin d^4 system and the magnetic data obey the Curie–Weiss law with $\theta = 3.9$ K, in harmony with the monomeric nature of the complex. The electronic spectrum of **3** is consistent with the elongated octahedral manganese(III) ion, showing three absorption bands in the visible region.

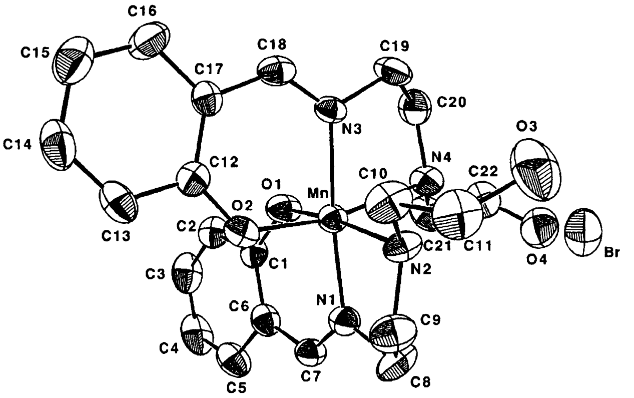


Fig. 1. A perspective view of **3**. Selected bond distances (l/Å) and angles (ϕ/°) are: Mn–O1 1.895(5), Mn–O2 2.034(5), Mn–N1 1.996(5), Mn–N2 2.114(6), Mn–N3 2.027(5), Mn–N4 2.341(6), O1–Mn–O2 94.5(2), O1–Mn–N1 90.4(2), O1–Mn–N2 172.1(2), O1–Mn–N3 93.3(2), O1–Mn–N4 88.4(2), O2–Mn–N1 95.8(2), O2–Mn–N2 88.6(2), O2–Mn–N3 88.2(2), O2–Mn–N4 167.3(2), N1–Mn–N2 82.0(2), N1–Mn–N3 174.4(2), N1–Mn–N4 96.6(2), N2–Mn–N3 94.1(2), N2–Mn–N4 90.2(2), N3–Mn–N4 79.3(2).

The complexes **2** and **3** have a similarity in retaining the 2-hydroxyethyl group. However, their mononuclear structures are different. In **2**, the Schiff-base ligand, $L_{6\text{-}6\text{-}5}{}^{2-}$, acts as a tetradentate chelate in *trans* configuration and forms the 1 : 1 complex, whereas the $HL_{6\text{-}5\text{-}5}{}^{-}$ ligand of **3** binds the manganese ion tridentately to form the bis-chelate 2 : 1 complex. This difference seems to be the result of the shortening of the aliphatic chain in the fused chelate ring.

Experimental

Synthesis of $[Mn(HL_{6\text{-}5\text{-}5})_2]Br$ (3). Salicylaldehyde (90 mg, 0.73 mmol) and 2-[(2-aminoethyl)amino]ethanol (87 mg, 0.83 mmol) were dissolved in ethanol (10 ml), then manganese(II) bromide terahydrate (50 mg, 0.17 mmol) was added. The solution was allowed to stand overnight to give dark brown crystals. These were collected by filtration, washed and dried in vacuo over P_2O_5 (yield 72 mg, 75%). Anal. Found: C, 48.18; H, 5.54; N, 10.15%. Calcd for $C_{22}H_{30}BrMnN_4O_4$: C, 48.10; H, 5.51; N, 10.20%. IR (KBr) ν/cm^{-1} ν(C=N) 1616. Diffuse reflectance spectrum λ_{max}/nm 395, 520sh, 650sh, 1311. μ_{eff} (297 K)/B.M. 5.00.

Measurements. Carbon, hydrogen, and nitrogen analyses were carried out using a Perkin-Elmer 2400 Series II CHNS/O Analyzer. Infrared spectra were measured with a JASCO Infrared Spectrophotometer Model IR700 in the region 4000—400 cm^{-1} on a KBr disk. Electronic spectra were measured with a Shimadzu UV-vis-NIR Recording Spcetrophotometer Model UV-3100. Magnetic susceptibilities were measured by the Faraday method over the temperature range 80—300 K. The susceptibility apparatus was calibrated with $[Ni(H_2NCH_2CH_2NH_2)_3]S_2O_3$.[8] The susceptibilities were corrected for diamagnetism of the constituent atoms by employing Pascal's constants.[9] Effective magnetic moments were calculated from the equation, $\mu_{\mathrm{eff}}=2.828\sqrt{\chi_A T}$, where χ_A is the atomic magnetic susceptibility.

Table 1. Fractional Positional Parameters and Thermal Parameters of Non-Hydrogen Atoms with Their Estimated Standard Deviations in Parentheses

Atom	x	y	z	B_{eq}/Å^2 a)
Br	0.5098(1)	0.01295(4)	0.20414(9)	4.73(2)
Mn	0.7697(1)	−0.13997(4)	0.3922(1)	2.47(2)
O1	0.9337(5)	−0.1759(2)	0.3839(5)	3.5(1)
O2	0.7497(5)	−0.1908(2)	0.5325(5)	3.5(1)
O3	0.2673(6)	−0.0571(3)	0.2730(6)	5.8(2)
O4	0.8242(6)	0.0137(2)	0.1003(6)	5.7(2)
N1	0.9126(6)	−0.0914(2)	0.5385(5)	2.9(1)
N2	0.6082(5)	−0.0914(2)	0.4154(5)	2.7(1)
N3	0.6133(5)	−0.1830(2)	0.2332(5)	2.4(1)
N4	0.7459(6)	−0.0914(2)	0.1939(5)	3.0(1)
C1	1.0760(7)	−0.1779(3)	0.4790(7)	2.7(2)
C2	1.1697(7)	−0.2174(3)	0.4681(7)	3.4(2)
C3	1.3190(8)	−0.2205(3)	0.5634(9)	4.5(2)
C4	1.3819(8)	−0.1844(4)	0.6715(9)	4.9(2)
C5	1.2948(8)	−0.1459(4)	0.6869(8)	4.1(2)
C6	1.1388(7)	−0.1411(3)	0.5895(7)	3.1(2)
C7	1.0572(7)	−0.0987(3)	0.6116(7)	3.1(2)
C8	0.8385(8)	−0.0467(3)	0.5705(9)	4.3(2)
C9	0.6908(8)	−0.0668(3)	0.5579(8)	4.0(2)
C10	0.4688(7)	−0.1185(3)	0.4024(8)	3.6(2)
C11	0.3450(7)	−0.0833(3)	0.4000(8)	4.0(2)
C12	0.6882(7)	−0.2373(3)	0.5103(7)	2.7(2)
C13	0.7021(7)	−0.2686(3)	0.6266(7)	3.4(2)
C14	0.6418(8)	−0.3175(3)	0.6083(8)	4.1(2)
C15	0.5629(8)	−0.3386(3)	0.4730(8)	4.5(2)
C16	0.5442(8)	−0.3088(3)	0.3585(8)	3.9(2)
C17	0.6040(7)	−0.2584(3)	0.3735(6)	2.5(2)
C18	0.5707(7)	−0.2294(3)	0.2446(7)	2.8(2)
C19	0.5528(8)	−0.1584(3)	0.0926(7)	3.5(2)
C20	0.6756(8)	−0.1291(3)	0.0754(7)	3.6(2)
C21	0.8933(8)	−0.0721(3)	0.2049(8)	4.0(2)
C22	0.8849(8)	−0.0351(3)	0.0899(8)	4.3(2)

a) Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameters defined as $4/3[a^2B(1,1)+b^2B(2,2)+c^2B(3,3)+ab(\cos\gamma)B(1,2)+ac(\cos\beta)B(1,3)+bc(\cos\alpha)B(2,3)]$.

X-Ray Crystal Structure Analysis. The unit-cell parameters and intensities were measured on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ=0.71073 Å). The intensity data were collected by the ω–2θ scan technique and were corrected for Lorentz-polarization effects, but not for absorption.

Crystal Data for 3: $C_{22}H_{30}BrMnN_4O_4$, F.W.=549.3, monoclinic, $P2_1/n$; $a=9.858(2)$, $b=25.530(5)$, $c=10.474(2)$ Å, $\beta=115.97(9)$°, $V=2369.8(8)$ Å^3, $D_{\mathrm{m}}=1.51$, $D_{\mathrm{c}}=1.53$ g cm^{-3}, $Z=4$, μ(Mo $K\alpha$)=22.39 cm^{-1}, R=0.041, R_{w}=0.046. 3820 Reflections were measured in the range $2<2\theta<48$°; 1984 with $I>3\sigma(I)$ were assumed as observed. The structure was solved by direct methods and refined by the full-matrix least-squares method. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed and fixed at their calculated positions. The weighting scheme $w=1/[\sigma^2(|F_o|)+(0.02|F_o|)^2+1.0]$ was employed.

All the calculations were carried out on a Micro VAXII computer using a MolEN program package.[10] Atomic coordinates and thermal parameters of non-hydrogen atoms are listed in Table 1. The anisotropic thermal parameters of non-hydrogen atoms, and the F_o-F_c tables have been deposited as Document No. 67062 at the Office of the Editor of Bull. Chem. Soc. Jpn.

References

1) K. Wieghardt, *Angew. Chem., Int. Ed. Engl.*, **28**, 1153 (1989).

2) M. Mikuriya, S. Shigematsu, K. Kawano, T. Tokii, and H. Oshio, *Chem. Lett.*, **1990**, 729; M. Mikuriya, D. Jie, Y. Kakuta, and T. Tokii, *Bull. Chem. Soc. Jpn.*, **66**, 1132 (1993).

3) M. Mikuriya, S. Kida, and I. Murase, *Chem. Lett.*, **1988**, 35; M. Mikuriya, Y. Yamato, and T. Tokii, *Inorg. Chim. Acta*, **181**, 1 (1991); M. Mikuriya, Y. Yamato, and T. Tokii, *Chem. Lett.*, **1991**, 1429; M. Mikuriya, Y. Yamato, and T. Tokii, *Bull. Chem. Soc. Jpn.*, **65**, 2624 (1992).

4) M. Mikuriya, Y. Kawasaki, T. Tokii, S. Yanai, and A. Kawamori, *Inorg. Chim. Acta*, **156**, 21 (1989); M. Mikuriya, T. Fujii, S. Kamisawa, Y. Kawasaki, T. Tokii, and H. Oshio, *Chem. Lett.*, **1990**, 1181; M. Mikuriya, T. Fujii, T. Tokii, and A. Kawamori, *Bull. Chem. Soc. Jpn.*, **66**, 1675 (1993).

5) M. Mikuriya, Y. Yamato, and T. Tokii, *Chem. Lett.*, **1992**, 1571.

6) M. Mikuriya, K. Nakadera, and T. Tokii, *Inorg. Chim. Acta*, **194**, 129 (1992).

7) M. Mikuriya, K. Majima, and Y. Yamato, *Chem. Lett.*, **1992**, 1929.

8) N. F. Curtis, *J. Chem. Soc.*, **1961**, 3147.

9) P. W. Selwood, "Magnetochemistry," Interscience Publishers, New York (1956), pp. 78 and 91.

10) C. K. Fair, "MolEN Structure Determination System," Delft Instruments, Delft, The Netherlands (1990).