1,3-Bis(salicylideneamino)-2-propanol as the Ligand for Manganese(III) Ions

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Synopsis. Reaction of 1,3-bis(salicylideneamino)-2-propanol (H_3L) with manganese(II) acetate tetrahydrate in the presence of ethylenediamine and sodium thiocyanate give a salen complex [Mn(salen)(NCS)] (H_2salen=*N*,*N*′-disalicylidene-ethylenediamine), while that in the presence of water and triethylamine gives a binuclear manganese(III) complex $[Mn_2(L)_2(H_2O)]\cdot 3CH_3OH$. Both complexes have been characterized by X-ray crystal structure analyses, electronic spectra, and magnetic susceptibilities.

Binuclear manganese complexes are of current interest because of the increased recognition of their role in biological systems.[1] As part of continuing project on binuclear manganese complexes, we have recently reported preparation and characterization of several manganese complexes with the pentadentate Schiff base ligand, 1,5-bis(salicylideneamino)-3-pentanol. This binucleating ligand affords interesting binuclear manganese(III) complexes which contain a variety of counter anions or solvent molecules.[2-4] Concerning this, we have also studied manganese complexes with related binucleating ligand, 1,3-bis(salicylideneamino)-2-propanol (H_3L); however, some part of our study coincided with vigorous studies which have been recently reported by Pecoraro and Murray et al.[5-7] Thus, we report some aspects of 1,3-bis(salicylideneamino)-2-propanol as the ligand for manganese ions which have not been convered by them.

Mazurek et al. reported the synthesis, structure and magnetic properties of several unsymmetric doubly bridged binuclear copper(II) and nickel(II) complexes with 1,3-bis(salicylideneamino)-2-propanol. These complexes incorporate 1,3-diamino-2-propanol moiety where the two metal ions are bridged by the deprotonated alkoxide oxygen atom and by another bridging ligand X^- such as pyrazolate anion. We tried to prepare a similar alkoxo-bridged manganese complex containing a pyrazolate exogenous bridge, e.g., $Mn_2(L)(pz)$ (Hpz= pyrazole). Thus far we have not been able to isolate such species despite many attempts. Then we changed the exogenous bridge for ethylenediamine to accomodate the larger size of manganese(II) ion (ionic radii of Mn^{2+} and Cu^{2+} are 0.97 and 0.87 Å, respectively).[8] Addition of ethylenediamine to the manganese solution containing 1,3-bis(salicylideneamino)-2-propanol resulted in isolation of an unexpected product, [Mn(salen)NCS] (H_2salen=*N*,*N*′-disalicylideneethylenediamine) (**1**). (The NCS ion comes from sodium thiocyanate which was used as precipitant for the complex.) The molecular structure of **1** is illustrated in Fig. 1. The coordination geometry can be described as a square pyramid with the manganese(III) ion being displaced from the O1, N1, N2, O2 plane by a 0.20 Å toward an axially coordinated thiocyanate ion. The Mn–N and Mn–O bond lengths are normal for a high-spin Mn(III) ion. The manganese ions of adjacent molecules are separated by 7.406(2) Å. Thus, we may expect that the ions do not exhibit appreciable magnetic interaction. The magnetic moment of **1** is 4.81 B.M. at 300 K, which is slightly lower than the spin-only value for a high-spin d^4 ion. Kennedy and Murray assumed that the complex **1** had a binuclear structure based on the temperature dependence of magnetic susceptibilities ($J=-0.44\ cm^{-1}$).[9] Diffuse reflectane spectrum of **1** shows three absorption bands at 363, 450(shoulder), and 575(shoulder) nm, probably being d–d transitions. The isolation of **1** means that a subsitution reaction of 1,3-diamino-2-propanol moiety with ethylenediamine occurs during the complex formation.

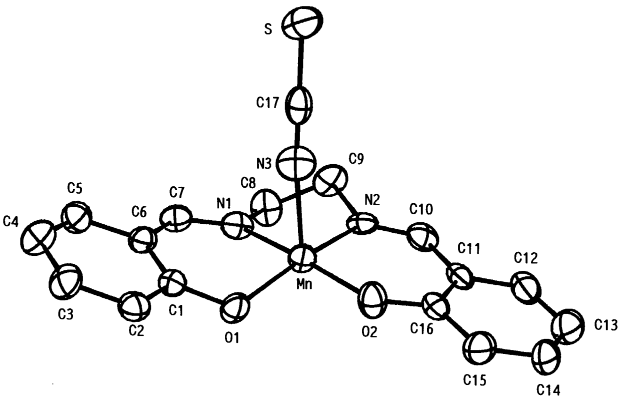

Fig. 1. A perspective view of [Mn(salen)(NCS)]. Selected bond distances (l/Å) and angles (ϕ/°) are: Mn–O1 1.880(6), Mn–O2 1.875(5), Mn–N1 1.989(6), Mn–N2 1.964(6), Mn–N3 2.162(7), O1–Mn–O2 93.5(2), O1–Mn–N1 89.4(2), O1–Mn–N3 100.4(3), O2–Mn–N2 91.7(2), O2–Mn–N3 100.4(3), N1–Mn–N2 83.0(3), N1–Mn–N3 88.9(3), N2–Mn–N3 93.3(3).

In 1,5-bis(salicylideneamino)-3-pentanolato complexes system, we have obtained a novel tetranuclear manganese(III) complex by adding water to the reaction solution.[4] Following this pocedure, we tried to prepare a tetranuclear species with 1,3-bis(salicylideneamino)-2-propanol. However, isolated complex was a binuclear complex $[Mn_2(L)_2(H_2O)]\cdot 3CH_3OH$ (**2**) similar to manganese(III) complexes reported by Pecoraro and Murray et al., $[Mn_2(L)_2(THF)]$ (**3**) and $[Mn_2(L')_2(CH_3OH)]\cdot CH_3OH$ (**4**) (H_3L'=1,3-bis(5-chlorosalicylideneamino)-2-propanol).[5,7] The crystal structure of **2** shows the same monoalkoxo-bridged binuclear structure as in **3** and **4** except for the H_2O molecule, which occupies the THF or CH_3OH site (Fig. 2). The coordination modes of the two ligands L are different: One acts as a symmetrical binucleating ligand with O1 and N1 atoms coordinated to Mn1 atom, O3 and N2 atoms coordinated

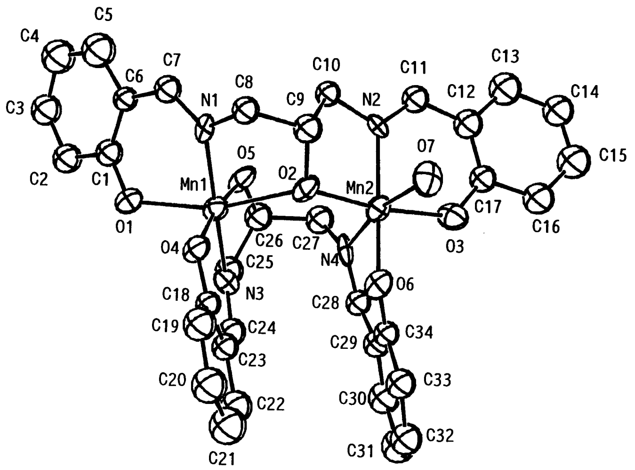

Fig. 2. A perspective view of the $[Mn_2(L)_2(H_2O)]$ molecule. Selected bond distances (l/Å) and angles (ϕ/°) are: Mn1-O1 2.143(10), Mn2-O2 1.912(10), Mn1-O2 2.367(10), Mn2-O3 1.911(11), Mn1-O4 1.878(10), Mn2-O6 1.912(11), Mn1-O5 1.911(10), Mn2-O7 2.420(11), Mn1-N1 2.038(12), Mn2-N2 1.997(12), Mn1-N3 1.965(12), Mn2-N4 2.226(12), Mn1-Mn2 3.818(3), Mn1-O2-Mn2 126.0(5), O1-Mn1-N1 84.8(4), O2-Mn2-N2 82.6(5), O2-Mn1-N1 76.2(4), O3-Mn2-N2 90.1(5), O4-Mn1-N3 89.7(5), O6-Mn2-N4 87.6(4), O5-Mn1-N3 83.6(5).

to Mn2 atom, and O2 bridge between the two metals. The other acts as a tridentate chelate for Mn1 with O4, O5, and N3 atoms and a bidentate chelate for Mn2 with O6 and N4 atoms. The sixth position of the Mn2 coordination sphere is occupied by a water molecule. Both manganese ions have severely distorted octahedral geometries as expected for high-spin Mn(III).[2-4] The Jahn–Teller distortion occurs along the O1-Mn1-O2 and O7-Mn2-N4 axes for Mn1 and Mn2, respectively. The Mn1-Mn2 separation is 3.818(3) Å and the Mn1-O2-Mn2 angle is 126.0(5)°. Diffuse reflectance spectrum of **2** shows three absorption bands at 372, 525 (shoulder), and 725 (shoulder) nm. These bands may be due to the splitting of the ground ^5E_g and the excited $^5T_{2g}$ states of octahedral Mn(III) ion. The magnetic moment (4.53 B.M./Mn at 293 K) is significantly lower than the spin-only value for a high-spin d^4 ion. The magnetic susceptibility data (80—300 K) were analyzed with the van Vleck equation based on the Heisenberg model ($\mathscr{H}=-2JS_1\cdot S_2$ ($S_1=S_2=2$)) and the best fitting parameters are $J=-5.8$ cm^{-1} and $g=2.00$. The J value is comparable to those found in **3** and **4**.[5,7] Structural and magnetic data for **2**, **3**, and **4** are listed in Table 1. Comparison of these data suggests that the largest Mn–O–Mn angle and the smallest $-J$ value in **4** probably come from the different substituent on the salicylideneamino moiety. In these complexes magnetic exchange interaction via the bridging alkoxo oxygen would be negligible for the d_{z^2}(Mn1)—$d_{x^2-y^2}$(Mn2) pathway, since the $d_{x^2-y^2}$ orbital is unoccupied owing to the elongated octahedral structure. As pointed out by Pecoraro and Hatfield et al.,[5] the superexchange promoting the weak antiferromagnetism may due to a mixing of d_{z^2} and $d_{x^2-y^2}$ caused by considerable distortions of the metal environments.

Experimental

Preparation of Complexes. [Mn(salen)(NCS)] (**1**) Ethylenediamine (15 mg, 0.25 mmol) was added to a stirred suspension of 1,3-bis(salicylideneamino)-2-propanol (75 mg, 0.25 mmol) and manganese(II) acetate tetrahydrate (123 mg, 0.5 mmol) in acetonitrile (20 ml) to give a dark brown solution. Insoluble material was filtered off, and an acetonitrile solution (3 ml) of sodium thiocyanate (81 mg, 1.0 mmol) was added to the filtrate. Brown crystals were deposited and filtered. Yield 46 mg. Anal. Found: C, 53.64; H, 3.75; N, 11.02%. Calcd for $C_{17}H_{14}MnN_3O_2S$: C, 53.83; H, 3.72; N, 11.08%.

$[Mn_2(L)_2(H_2O)]\cdot 3CH_3OH$ (2). To a mixture solution of manganese(II) acetate tetrahydrate (492 mg, 2 mmol) and 1,3-bis(salicylideneamino)-2-propanol (600 mg, 2 mmol) in methanol (15 ml) were added 6 ml of water and 600 mg of triethylamine to give a black precipitate, which was collected by filtration. Yield 692 mg. They were recrystallized from methanol to give dark green crystals. Anal. Found: C, 54.45; H, 5.36; N, 6.82%. Calcd for $C_{37}H_{44}Mn_2N_4O_{10}$: C, 54.55; H, 5.44; N, 6.88%.

Measurements. Carbon, hydrogen, and nitrogen analyses were carried out at the Service center of Elemental Analysis, Kyushu University. Infrared spectra were measured with a JASCO Infrared Spectrometer Model IR700 in the region 4000—400 cm^{-1} on a KBr disk. Electronic spectra were measured with a Shimadzu UV-vis-NIR Recording Spectrophotometer Model UV-3100. Magnetic susceptibilities were measured by the Faraday method over the temperature range 80—300 K. The susceptibilities were corrected for the diamagnetism of the constituent atoms by the use of Pascal's constants.[10]

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 ($\lambda=0.71073$ Å). The intensity data were collected by the ω–2θ scan technique and corrected for Lorentz-polarization effects, but not for absorption.

Crystal Data for **1**: $C_{17}H_{14}MnN_3O_2S$, F.W.=379.3, orthorhombic, $Pbca$ (No. 61); $a=13.744(6)$, $b=18.766(5)$, $c=12.449(2)$ Å, $V=3210.9(18)$ Å^3, $D_m=1.56$, $D_c=1.57$ g cm^{-3}, $Z=8$, μ(Mo-$K\alpha$)=9.29 cm^{-1}, $R=0.056$, $R_w=0.064$. 5658 Reflections were measured in the range $1\leq 2\theta\leq 62°$; 1665 with $I\geq 3\sigma(I)$ were

Table 1. Structural and Magnetic Data for the Monoalkoxo-Bridged Binuclear Manganese(III) Complexes

Complex	Mn···Mn/Å	Mn-O-Mn/°	J/cm^{-1}	Ref.
2	3.818(3)	126.0(5)	−5.8	This work
3	3.756(2)	124.5(1)	−5.5	7
4	3.808(1)	128.9(2)	−3.55	5

assumed as observed. For **2**: $C_{37}H_{44}Mn_2N_4O_{10}$, F.W.=814.7, orthorhombic, *Pbca* (No. 61); a=16.613(4), b=32.287(5), c=14.004(4) Å, V=7511.8(29) Å^3, D_m=1.44, D_c=1.44 g cm^{-3}, Z=8, μ(Mo-$K\alpha$)=7.04 cm^{-1}, R=0.075, R_w=0.085. 6509 reflections were measured in the range $1 \leq 2\theta \leq 48°$; 1608 with $I \geq 3\sigma(I)$ were assumed as observed.

The structure was solved by the direct methods and refined by the full-matrix least-squares method. All the non-hydrogen atoms of **1** and the Mn, O, and N atoms of **2** were refined with anisotropic thermal parameters. Hydrogen atoms were inserted at their calculated positions and fixed at their 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 the Micro VAXII computer using a SDP program package.[11] The atomic coordinates and thermal parameters of non-hydrogen atoms, and the F_o-F_c tables have been deposited as a Document No. 8992 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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References

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

2) M. Mikuriya, S. Kida, and I. Murase, *Chem. Lett.,* **1988**, 35.

3) M. Mikuriya, Y. Yamato, and T. Tokii, *Inorg. Chim. Acta,* **181**, 1 (1991).

4) M. Mikuriya, Y. Yamato, and T. Tokii, *Chem. Lett.,* **1991**, 1429.

5) J. A. Bonadies, M. L. Kirk, M. S. Lah, D. P. Kessissoglou, W. E. Hatfield, and V. L. Pecoraro, *Inorg. Chem.,* **28**, 2037 (1989).

6) J. A. Bonadies, M. J. Maroney, and V. L. Pecoraro, *Inorg. Chem.,* **28**, 2044 (1989).

7) K. Bertoncello, G. D. Fallon, K. S. Murray, and E. R. T. Tiekink, *Inorg. Chem.,* **30**, 3562 (1991).

8) R. D. Shannon, *Acta Crystallogr., Sect. A,* **32**, 751 (1976).

9) B. J. Kennedy and K. S. Murray, *Inorg. Chem.,* **24**, 1552 (1985).

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

11) B. A. Frenz, "The SDP-User's Guide," Enraf-Nonius, Delft, The Netherlands (1985).