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Binuclear Metal Complexes. XXXI.[1] Synthesis and Magnetic Property of Binuclear Manganese(III) Complexes with 3-Salicylideneamino-1-propanol and Its Homologues[2]

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Binuclear manganese(III) complexes with 3-salicylideneamino-1-propanol and its homologues, MnL(ac) and MnLXH$_2$O (L=Schiff base dianion; ac=acetate ion; X$^-$=Cl$^-$, Br$^-$, N$_3^-$), were synthesized. It was shown that manganese(III) ions were bridged by the deprotonated alcoholic oxygen of the Schiff base in the equatorial plane and coordinated by bidentate acetate ion or X$^-$ and H$_2$O groups in apical positions to form six-coordination. Cryomagnetic measurements indicated that an antiferromagnetic spin-exchange interaction operates between a pair of manganese(III) ions; exchange integral being evaluated at -13.5—-20.4 cm^{-1}.

Binuclear manganese(III) complexes are of interest in studying spin-exchange interaction of d^4–d^4 system. Recently di-μ-oxo bridged binuclear manganese(III) complexes were found to be a model of photosystem-II in green plant photosynthesis, where manganese functions as a redox catalyst for the oxidation of water to molecular oxygen.[3] In spite of the growing interests in magnetism and in bioinorganic aspect, characterized binuclear manganese(III) complexes with di-μ-oxo bridging system are very few.[4–6]

Zelentsov *et al.*[5] prepared manganese(III) complexes with 2-(salicylideneamino)ethanol and its homologues. The magnetic moments of these complexes are higher at room temperature but lower near liquid nitrogen temperature than the spin-only value. They assumed that the complexes have a di-μ-oxo bridged binuclear structure, in which a ferromagnetic spin-exchange interaction is operating between the metal ions. In general binuclear metal complexes with 2-(salicylideneamino)ethanol markedly differ in magnetic property from those of 3-salicylideneamino-1-propanol. For example, copper(II) complex with 3-salicylideneamino-1-propanol forms a discrete binuclear structure which displays a very strong antiferromagnetic spin-exchange interaction.[7,8] On the other hand, the complex with 2-(salicylideneamino)ethanol shows a normal magnetic moment at room temperature and obeys the Curie-Weiss law with a positive Weiss constant.[7] The latter complex was considered to have a "cubane-type" tetranuclear structure, which has been confirmed for the copper(II) complex with the Schiff base derived from acetylacetone and 2-aminoethanol.[9] Thus, it was aimed in this study to prepare binuclear manganese(III) complexes with 3-salicylideneamino-1-propanol and its homologues and to investigate their magnetic property in comparison with the complexes obtained by Zelentsov *et al.*

The ligands used in this study are Schiff bases obtained by condensing salicylaldehyde, *o*-vaniline, 5-bromosalicylaldehyde, or 2-hydroxy-1-naphthaldehyde with 3-amino-1-propanol. They are abbreviated as H$_2$spa, H$_2$vpa, H$_2$brspa, and H$_2$npa respectively. Two types of binuclear complexes, MnL(ac) and MnLXH$_2$O (H$_2$L=Schiff base; X$^-$=Cl$^-$, Br$^-$, N$_3^-$), were synthesized in this study. Mononuclear complexes, Mn(Hspa)$_2$ClO$_4$ and Mn(Hspa)$_2$NCS, were also prepared.

Experimental

Syntheses. *Mn(Hspa)$_2$ClO$_4$*: A solution of salicylaldehyde (2.4 g), 3-amino-1-propanol (1.5 g) and manganese(II) perchlorate hexahydrate (14.4 g) in methanol (300 ml) were refluxed for 2 h. A deep black-green solution thus obtained was slowly concentrated at a temperature below 20 °C to give black prisms. They were collected by suction and dried under reduced pressure.

Found: C, 46.87; H, 4.67; N, 5.49%. Calcd for $C_{20}H_{24}N_2O_8ClMn$: C, 47.02; H, 4.74; N, 5.48%.

Mn(Hspa)$_2$NCS: Mn(Hspa)$_2$ClO$_4$ (1.0 g) was dissolved in methanol (50 ml) and to this solution was added NaNCS (0.8 g). The mixture was refluxed for 30 min, filtered while hot and allowed to stand over night. Black prisms which separated were collected and dried under reduced pressure.

Found: C, 53.53; H, 5.11; N, 9.01%. Calcd for $C_{21}H_{24}N_3O_4SMn$: C, 53.73; H, 5.15; N, 8.95%.

Mn(spa)(ac). To a solution of salicylaldehyde (2.4 g) and 3-amino-1-propanol (1.5 g) in methanol (300 ml) was added manganese(II) acetate tetrahydrate (9.8 g) to give a deep green solution. After refluxing for 5 h, the volume of the solution was concentrated to *ca.* 30 ml at a temperature lower than 20 °C to give black-green prisms. They were collected and recrystallized from methanol.

Found: C, 49.06; H, 4.79; N, 4.72%. Calcd for $C_{12}H_{14}NO_4Mn$: C, 49.50; H, 4.85; N, 4.81%.

Mn(vpa)(ac). This complex was obtained as black-green prisms in the same way as that of Mn(spa)(ac) except for using *o*-vaniline instead of salicylaldehyde.

Found: C, 48.67; H, 5.03; N, 4.20%. Calcd for $C_{13}H_{16}NO_5Mn$: C, 48.61; H, 5.02; N, 4.36%.

Mn(brspa)(ac)·MeOH. This complex was obtained as green prisms in the same way as that of Mn (spa) (ac) except for using 5-bromosalicylaldehyde instead of salicylaldehyde.

Found: C, 38.79; H, 4.25; N, 3.50%. Calcd for $C_{13}H_{17}NO_5BrMn$: C, 38.83; H, 4.26; N, 3.48%.

Mn(npa)(ac)·MeOH. This complex was obtained as black prisms by reacting 2-hydroxy-1-naphthaldehyde, 3-amino-1-propanol and manganese(II) acetate tetrahydrate in methanol.

Found: C, 54.72; H, 5.15; N, 3.77%. Calcd for $C_{17}H_{20}NO_5Mn$: C, 54.70; H, 5.13; N, 3.75%.

Mn(spa)ClH$_2$O. A solution of salicylaldehyde (2.4 g), 3-amino-1-propanol (1.5 g) and manganese(II) perchlorate hexahydrate (14.4 g) in methanol (300 ml) was refluxed for 2 h. To a black-green solution thus obtained was added sodium hydroxide (1.6 g) and the mixture was stirred for 5 d to give reddish black solution. When the solvent was evaporated, there remained an oily substance. It was dissolved in methanol (50 ml) to which lithium chloride (4.2 g) was added. The mixture was stirred under reflux for 30 min and filtered. The filtrate was allowed to stand over night to give deep green crystals, which were collected by suction and dried under reduced pressure.

Found: C, 41.96; H, 4.60; N, 4.90%. Calcd for $C_{10}H_{13}NO_3ClMn$: C, 42.05; H, 4.59; N, 4.90%.

Mn(spa)BrH$_2$O. This complex was obtained as deep green prisms in the same way as that of Mn(spa)ClH$_2$O except for using sodium bromide instead of lithium chloride.

Found: C, 36.10; H, 3.94; N, 4.31%. Calcd for $C_{10}H_{13}N_4O_3Mn$: C, 36.39; H, 3.97; N, 4.24%.

Mn(spa)N$_3$H$_2$O. This complex was obtained as deep green crystals in the same way as that of Mn(spa)ClH$_2$O except for using sodium azide instead of lithium chloride.

Found: C, 41.30; H, 4.49; N, 19.03%. Calcd for $C_{10}H_{13}N_4O_3Mn$: C, 41.11; H, 4.48; N, 19.18%.

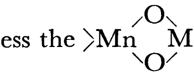
Measurements. Infrared spectra of the complexes were measured with a Hitachi infrared spectrophotometer Model 215 on a KBr disk and a nujol mull. Electronic spectra were measured with a Shimadzu multipurpose spectrophotometer Model MSP-5000 by a reflection on a powder sample. Magnetic susceptibilities were measured by Faraday method in a temperature range from liquid nitrogen temperature to room temperature. Magnetic moments were calcualted by the expression, $\mu_{\mathrm{eff}}=2.828\sqrt{\chi_A \times T}$, where χ_A is the magnetic susceptibility per one manganese ion corrected for diamagnetism using Pascal's constants.

Results and Discussion

In general manganese(II) complexes with Schiff bases are air-sensitive and easily oxidized to manganese(III) complexes by molecular oxygen. All complexes obtained in this study must be manganese(III) complexes judging from their elemental analyses and deep color.

Infrared spectrum of mononuclear Mn(Hspa)$_2$ClO$_4$ shows a strong band around 3400 cm^{-1}, which is attributed to the non-coordinated alcoholic OH group. This fact implies that Hspa$^-$ acts as a bidentate ligand. The Cl–O stretching frequency of perchlorate ion splits into three (1130, 1080, and 1040 cm^{-1}). This suggests that the perchlorate ion coordinates to manganese(III) ion as a bidentate ligand, because the splitting is quite similar to that (1130, 1093, and 1058 cm^{-1}) of blue form of Ni(en)$_2$(ClO$_4$)$_2$ in which perchlorate ion functions as a bidentate ligand.[10] On the other hand, two OH-stretching bands were found for Mn(Hspa)$_2$NCS at 3500 and 3250 cm^{-1}. It is likely that one Hspa$^-$ acts as a bidentate ligand and the other as a tridentate ligand. The C–N and C–S stretching bands of NCS$^-$ ion were observed at 2070 and 810 cm^{-1}, respectively, indicating the donation of NCS$^-$ ion to the metal at the nitrogen atom.[11] Thus, the infrared spectra and the compositions of the mononuclear complexes indicate that they possess structures of six-coordination.

Electronic spectrum of Mn(Hspa)$_2$ClO$_4$ shows bands at 15600 and 20600 cm^{-1}. The spectrum of Mn(Hspa)$_2$NCS shows bands at 12500, 15600, 20800, and 22200 cm^{-1}. The bands in the region 12000—16000 cm^{-1} are assigned to the d-d transitions. Although the correct intensities of the bands in the region 20000—23000 cm^{-1} are not known from reflectance spectrum, they are much weaker than the intra-ligand band near 28000 cm^{-1}. In addition to this, many manganese(III) complexes show d-d bands whose frequencies are higher than 20000 cm^{-1}. Thus, we tentatively assigned the bands in the region 20000—23000 cm^{-1} to d-d transitions. Since manganese(III) ion under O_h symmetry should show only one spin-allowed d-d band, it is likely that the geometry around the metal is much distorted from regular octahedron. Magnetic moments of Mn(Hspa)$_2$ClO$_4$ and Mn(Hspa)$_2$NCS at room temperature are 4.88 and 4.82 BM respectively, which are quite common for high-spin manganese(III) complexes.

Infrared spectra of the binuclear complexes do not show OH-stretching band of the alcoholic group. For the binuclear complexes with 3-salicylideneamino-1-propanol, alcoholic oxygen-bridged and phenolic oxygen-bridged binuclear structures are known.[12] The phenolic oxygen-bridged structure can be characterized by a skeletal band near 1550 cm^{-1},[12] which is higher in frequency than that of its related mononuclear complex. Although the skeletal band of MnL(ac) is concealed from a strong C–O band of carboxyl group, the band of MnLXH$_2$O is well resolved and observed at 1550 cm^{-1}. This frequency is almost the same as that of mononuclear Mn(Hspa)$_2$ClO$_4$ and Mn(Hspa)$_2$NCS. Thus, we may conclude that the complexes possess the  $>\mathrm{Mn}\langle{}^{\mathrm{O}}_{\mathrm{O}}\rangle\mathrm{Mn}<$ skeleton bridged by the alcoholic oxygen. This is compatible with the result of Miners and Sinn that the alcoholic oxygen-bridged binuclear structure is prefered to the phenolic oxygen-bridged structure when the complex is formed in alkaline media.[12]

The antisymmetric and the symmetric C–O stretching bands of acetate group in MnL(ac) were found at 1550 and 1400 cm^{-1} respectively. In general the antisymmetric and the symmetric C–O stretching bands of carboxylate ion coordinated to a metal as a unidentate ligand shifts to higher and to lower frequencies respectively, as the metal–O bond becomes strong.[13] On the other hand, both of the carbonyl bands shift in the same direction with a change of the metal–O bonding, when the carboxylate ion bridges metal ions.[13] The carboxyl bands of the present complexes seem to belong to the class of the latter type of bonding. Therefore, it is assumed that the acetate group in MnL(ac) functions as a bridge. Coordination of water molecule and azide ion to the metal for Mn(spa)N$_3$H$_2$O was confirmed by IR bands at 3250 and 2050 cm^{-1}. Coordination of chloride and bromide ions is supposed for Mn(spa)ClH$_2$O and Mn(spa)BrH$_2$O by the analogy of the above case. Based on these facts we assumed that two types of the binuclear complexes possess the structures given in Fig. 1.

Reflectance spectra of binuclear complexes of MnL(ac) and MnLXH$_2$O are similar to each other in that they have four absorption bands in the visible region. These bands are tentatively assigned to d-d

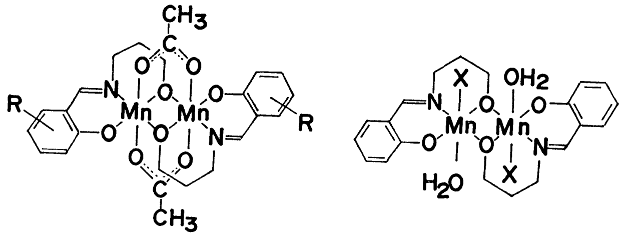


Fig. 1. Possible structures of binuclear complexes.

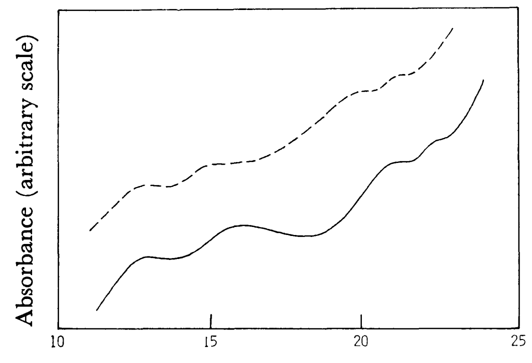


Fig. 2. Reflectance spectra of (------) Mn(spa)(ac) and (——) Mn(spa)ClH$_2$O.

Table 1. Magnetic parameters of complexes

	J/cm^{-1}	g
Mn(spa)(ac)	−19.1	1.99
Mn(vpa)(ac)	−20.4	2.00
Mn(brspa)(ac)·MeOH	−13.5	1.99
Mn(npa)(ac)·MeOH	−18.9	1.99
Mn(spa)ClH$_2$O	−16.0	2.00
Mn(spa)BrH$_2$O	−16.8	2.00
Mn(spa)N$_3$H$_2$O	−14.4	2.00

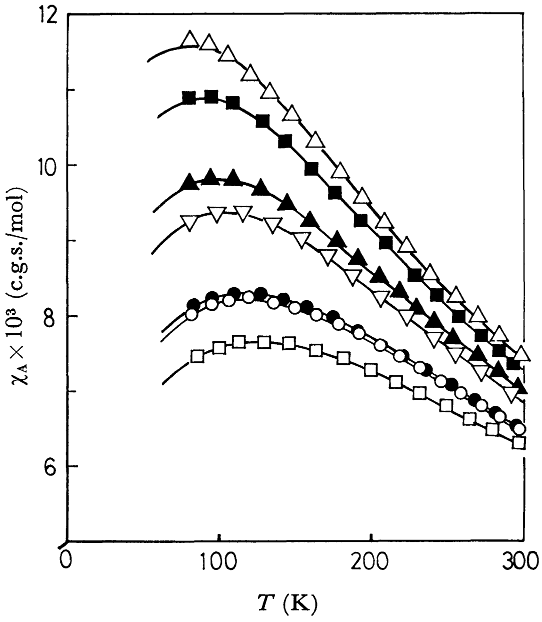


Fig. 3. Temperature variations of magnetic susceptibilities. (○) Mn(spa)(ac), (□) Mn(vpa)(ac), (△) Mn(brspa)(ac)·MeOH, (●) Mn(npa)(ac)·MeOH, (▲) Mn(spa)ClH$_2$O, (▽) Mn(spa)BrH$_2$O, and (■) Mn(spa)N$_3$H$_2$O.

transitions. Typical examples of electronic spectra are shown in Fig. 2. It is likely that the coordination geometry of the complexes is distorted from regular octahedron so that the ^5E_g and the $^5T_{2g}$ states of an octahedral manganese(III) ion split into five orbitally singlet states.

Effective magnetic moments of MnL(ac) and MnLXH$_2$O at room temperature fall in the range 3.84—4.22 BM, which are lower than the moments (4.8—5.0 BM) found for most high-spin manganese(III) complexes. The operation of antiferromagnetic spin-exchange interaction between a pair of manganese(III) ions appears to be the main reason for the subnormal magnetic moments. Cryomagnetic measurements have shown that the magnetic susceptibility of the complexes has a maximum around 100 K. These magnetic behaviors can be well interpreted in terms of the magnetic susceptibility expression for the high-spin d^4–d^4 system based on the isotropic spin-exchange model ($\mathscr{H}=-2J\sum\hat{s}_i\hat{s}_j-g\beta s_z'H$, total spin s_z' being calculated by Kambe's approach),

$$\chi_A = \frac{Ng^2\beta^2}{kT}\times\frac{30+14\exp(-8J/kT)+5\exp(-14J/kT)+\exp(-18J/kT)}{9+7\exp(-8J/kT)+5\exp(-14J/kT)+3\exp(-18J/kT)+\exp(-20J/kT)}+N\alpha,$$

where J is the exchange integral and other symbols have their usual meanings. Good agreements between the experimental and the theoretical susceptibilities are shown in Fig. 3. Magnetic parameters, g and J, determined from the best-fit technique, assuming $N\alpha$ at zero, are given in Table 1. Thus, it may be concluded that the manganese(III) complexes with 3-salicylideneamino-1-propanol and its homologues possess a discrete binuclear structure in which an appreciably strong antiferromagnetic spin-exchange interaction is operating between the metal ions.

In contrast to the above, the magnetisms of manganese(III) complexes with 2-(salicylideneamino)-ethanol and its homologues are quite strange. According to Zelentsov *et al.*,5) the complexes consist of binuclear units and their magnetisms can be interpreted in terms of intramolecular ferromagnetic spin-exchange interaction (J=20—30 cm^{-1}) and a large zero-field splitting (*ca.* 8 cm^{-1}). However, the presence of such a large zero-field splitting is unlikely, since magnetisms of most mononuclear manganese(III) complexes obey the Curie-Weiss law with a small Weiss constant (θ= 0—−25K).14) When we plotted the inverse magnetic susceptibilities measured by Zelentsov *et al.* against the temperature, nearly straight lines were drawn in the temperature range 80—300K and the Weiss constants were estimated at −40—−120K. Very large negative Weiss constants can most naturally be explained in terms of a predominantly operating antiferromagnetic spin-exchange interaction in the molecule.

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