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Dinuclear Cobalt(II), Iron(II), and Manganese(II), and Trinuclear Manganese(II) Complexes with Tridentate Ligands of NNS-Donor Set Derived from 2-Aminoethanethiol

Makoto Handa, Hisashi Ōkawa,* and Sigeo Kida
Department of Chemistry, Faculty of Science, Kyushu University,
Hakozaki, Higashiku, Fukuoka 812
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Synopsis. Thiolate-bridged dinuclear cobalt(II), iron(II), and Manganese(II) complexes and trinuclear manganese(II) complexes of thiolic ligands, 2-[(2-aminoethyl)amino]ethanethiol, 2-[(3-aminopropyl)amino]ethanethiol, 2-[(2-pyridylmethyl)amino]ethanethiol, and 2-[[(2-pyridylethyl]amino]ethanethiol, were prepared and their magnetic properties were examined in the temperature range 80—300 K. The results indicated a significant antiferromagnetic spin-exchange interactions through the bridging sulfur atom for all the complexes.

Sulfur-bridged polynuclear metal complexes are of interest in view of magnetic spin-exchange interaction through the sulfur bridge. Some thiolate-bridged polynuclear metal complexes have been synthesized.[1] However, magnetic investigations on thiolate-bridged polynuclear metal complexes are still limited. In this study we have obtained two types of thiolate-bridged complexes of cobalt(II), iron(II), and manganese(II) ions using tridentate thiolic ligands with an NNS-donor set, 2-[(2-aminoethyl)amino]ethanethiol (HL^1), 2-[(3-aminopropyl)amino]ethanethiol (HL^2), 2-[(2-pyridylmethyl)amino]ethanethiol (HL^3), and 2-[[(2-pyridyl)ethyl]amino]ethanethiol (HL^4). This paper reports the magnetic study of dinuclear complexes $[M_2(L)_2X_2]$ ($M=Co^{2+}$, Fe^{2+}, Mn^{2+}; X=Cl, NO_3) and trinuclear complexes $[Mn_3(L)_4]X_2$ ($X=ClO_4$, NO_3).

Experimental

Preparations. The thiolic ligands were obtained by the methods described previously.[2]

$[M_2(L)_2X_2]$ (M=Co, Fe, Mn; $L=L^1—L^4$; X=Cl, NO_3). A methanolic solution of equimolar amounts of a metal salt and a ligand was stirred overnight at room temperature under nitrogen atmosphere. Microcrystals separated were collected by filter suction, washed with methanol, and dried in vacuo. The cobalt, iron, and manganese complexes are violet, yellow, and colorless, respectively.

$[Mn_3(L)_4]X_2$ ($L=L^1$, L^2; $X=ClO_4$, NO_3). The complexes were obtained as almost colorless microcrystals in nearly the same way as described above, except for the use of an excess of a ligand (about 1.5 times).

Elemental analyses of the complexes are given in Table 1.

Measurements. IR spectra were recorded on a JASCO IR-800 spectrometer on KBr disks or Nujol mulls. Electronic spectra were recorded on powder samples by the use of a Simadzu MPS-5000 spectrometer. Magnetic susceptibilities were determined by the Faraday method over the temperature range 80—300 K.

Results and Discussion

$[M_2(L)_2X_2]$. The complexes have the stoichiometry of M:L:X=1:1:1 and are presumed to be dinuclear bridged by the thiolate group, because such a dimeric structure has been shown for the nickel(II) complexes with HL^4 [3] and 3-[[(2-pyridyl)ethyl]amino]propanethiol (HL')[4] by single-crystal X-ray analysis. Further, similar alkoxo-bridged dinuclear structures are known for the copper(II) complexes of tridentate alcoholic ligands.[5]

In the case of $[Co_2(L^4)_2(NO_3)_2]$ the unidentate coordination of the nitrate ion to the metal was evidenced by the split NO_3^- vibrations (1460, 1380, 1290, and 1030 cm^{-1}).[6] Further, the diffuse reflectance

Table 1. Elemental Analyses of the Complexes

Complex	Found(%)			Calcd(%)		
	C	H	N	C	H	N
$[Co_2(L^3)_2Cl_2]$	36.31	4.13	10.54	36.73	4.24	10.71
$[Co_2(L^4)_2Cl_2]\frac{1}{2}H_2O$	38.48	4.80	9.74	38.58	4.86	10.00
$[Fe_2(L^1)_2Cl_2]$	23.20	5.56	13.23	22.82	5.56	13.31
$[Fe_2(L^3)_2Cl_2]$	36.96	4.32	10.72	37.16	4.29	10.83
$[Fe_2(L^4)_2Cl_2]\frac{1}{2}H_2O$	39.16	4.92	9.86	39.01	4.91	10.11
$[Mn_2(L^1)_2Cl_2]$	23.07	5.36	13.15	22.92	5.29	13.37
$[Mn_2(L^2)_2Cl_2]$	26.50	5.81	12.23	26.85	5.86	12.53
$[Mn_2(L^3)_2Cl_2]$	37.25	4.33	10.71	37.30	4.30	10.87
$[Mn_2(L^4)_2Cl_2]\frac{1}{2}H_2O$	39.16	5.00	10.10	39.14	4.93	10.14
$[Mn_2(L^4)_2(NO_3)_2]$	36.21	4.53	13.89	36.25	4.39	14.09
$[Mn_3(L^1)_4](ClO_4)_2$	22.72	5.26	13.25	22.86	5.28	13.33
$[Mn_3(L^2)_4](ClO_4)_2$	26.48	5.84	12.46	26.79	5.85	12.50
$[Mn_3(L^2)_4](NO_3)_2$	28.90	6.41	16.66	29.38	6.38	17.05

spectra of the cobalt(II) complexes showed three d-d bands in the region 10000—20000 cm^{-1} (e.g., [$Co_2(L^4)_2Cl_2$]: 13000, 15800, and 18200 cm^{-1}), indicating a pentacoordination around the metal.[7] The manganese(II) complexes showed no spin-allowed d-d transition and any reliable spectra could not be obtained for the iron(II) complexes because of their sensitivity toward dioxygen. However, we believe that in both the manganese(II) and iron(II) complexes the chloride ion coordinates to the metal ion to complete a penta-coordination around the metal.

The magnetic moment (per metal ion) of each complex is subnormal at room temperature for high-spin metal ion (Table 2), and the cryomagnetic susceptibility determined in the range 80—300 K did not obey the Curie-Weiss law below 150 K. This is probably due to an intramolecular antiferromagnetic spin-exchange interaction. Typical examples of the temperature-variation of magnetic susceptibility are given in Figs. 1 and 2.

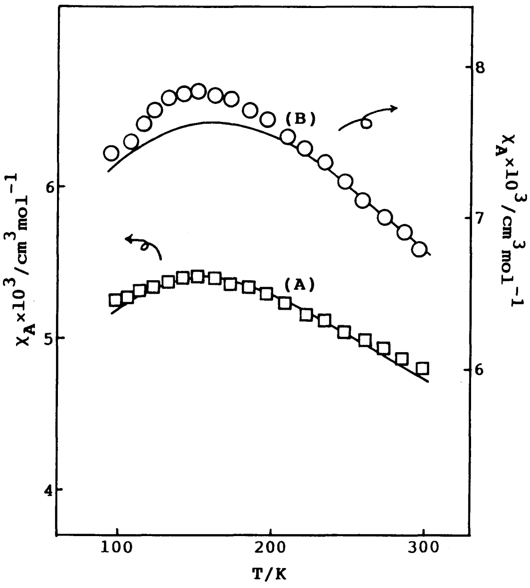

Fig. 1. Temperature variations of magnetic susceptibility of (A) [$Co_2(L^4)_2Cl_2$] and (B) [$Fe_2(L^4)_2Cl_2$]. The solid curves are drawn based on the susceptibility equations based on the Heisenberg model ($J=-35.1$ cm^{-1}, $g=2.20$, $N\alpha=220\times10^{-6}$ cm^{3}mol^{-1} for (A) and $J=-25.0$ cm^{-1}, $g=2.20$, $N\alpha=0$ for (B)). The discrepancy in the case (B) is presumed to be due to an orbital contribution to the susceptibility.

The χ_A vs. T curve of [$Co_2(L^3)_2Cl_2$] shows a maximum at 160 K. Based on the isotropic exchange Hamiltonian (Heisenberg model) for a dimer ($\mathscr{H}=-2J\hat{S}_1\cdot\hat{S}_2$), the maganetic susceptibility for the ($S_1=3/2$)—($S_2=3/2$) dimer is given by the equation,[8]

$$\chi_A=(Ng^2\beta^2/kT)[14+5\exp(-6J/kT)+\exp(-10J/kT)]/[7+3\exp(-10J/kT)+\exp(-12J/kT)]+N\alpha \qquad (1)$$

In this equation J is the exchange integral, N the Avogadro number, g the Lande g-factor, β the Bohr magneton, T absolute temperature, and $N\alpha$ the temperature-independent paramagnetism. As is seen

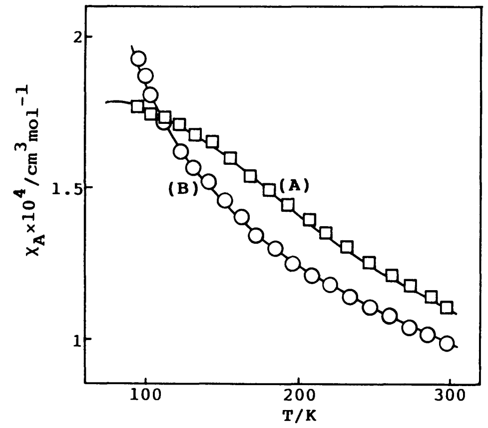

Fig. 2. Temperature variations of magnetic susceptibility of (A) [$Mn_2(L^4)_2Cl$] and (B) [$Mn_3(L^2)_4$](NO_3)$_2$. The solid curves are drawn in terms of the Heisenberg model (Eqs. 2 and 3, respectively) using the magnetic parameters given in Table 2.

Table 2. Magnetic Data of the Complexes

Complex	g	J/cm^{-1}	$N\alpha\times10^6$/cm^3 mol^{-1}	$\mu_{eff}/\mu_B(T/K)$
[$Co_2(L^3)_2Cl_2$]	2.20	−36.5	200	3.33(297.8)
[$Co_2(L^4)_2Cl_2$]$\frac{1}{2}H_2O$	2.20	−35.1	220	3.39(297.8)
[$Fe_2(L^1)_2Cl_2$]	—	—	—	3.58(299.0)
[$Fe_2(L^3)_2Cl_2$]	—	—	—	4.02(297.8)
[$Fe_2(L^4)_2Cl_2$]$\frac{1}{2}H_2O$	—	—	—	4.02(297.8)
[$Mn_2(L^1)_2Cl_2$]	2.00	−11.8	0	4.88(297.8)
[$Mn_2(L^2)_2Cl_2$]	2.00	−9.8	0	5.01(297.8)
[$Mn_2(L^3)_2Cl_2$]	2.00	−10.4	0	4.94(297.8)
[$Mn_2(L^4)_2Cl_2$]$\frac{1}{2}H_2O$	2.00	−9.0	0	5.14(297.8)
[$Mn_2(L^4)_2(NO_3)_2$]	2.00	−8.5	0	5.21(297.8)
[$Mn_3(L^1)_4$](ClO_4)$_2$	2.06	−14.7	0	4.71(297.8)
[$Mn_3(L^2)_4$](ClO_4)$_2$	2.05	−8.9	0	5.16(295.4)
[$Mn_3(L^2)_4$](NO_3)$_2$	2.03	−11.1	0	4.85(297.8)

in Fig. 1(A), the cryomagnetic behavior of this complex can be well simulated with the Eq. 1 using magnetic parameters given in Table 2, clearly demonstrating the dinuclear structure of this complex. Similarly, the magnetism of $[Co_2(L^4)_2Cl_2]$ obeyed the Eq. 1 in the temperature range 80—300 K.

The χ_A vs. T curves for the manganese(II) complexes show no maximum in the range 80—300 K but show an apparent decrease at lower temperature (Fig. 2(A)). The magnetic susceptibility for the $(S_1=5/2)$-$(S_2=5/2)$ system based on the Heisenberg model is given by the equation,[9]

$$\begin{aligned}\chi_A = (Ng^2\beta^2/kT)[55 &+ 30\exp(-10J/kT)\\ &+ 14\exp(-18J/kT) + 5\exp(-24J/kT)\\ &+ \exp(-28J/kT)]/[11 + 9\exp(-10J/kT)\\ &+ 7\exp(-18J/kT) + 5\exp(-24J/kT)\\ &+ 3\exp(-28J/kT) + \exp(-30J/kT)] + N\alpha, \qquad (2)\end{aligned}$$

where each simbol has the same meaning as in the Eq. 1. The magnetism of the manganese(II) complexes can be well explained with this equation, as exemplified in Fig. 2(A), using reasonable magnetic parameters given in Table 2. Thus, cryomagnetic investigations add a support for the dinuclear structure of the manganese(II) complexes.

Each χ_A vs. T curve of the iron(II) complexes shows a maximum near 120 K as seen in Fig. 1(B). Such a cryomagnetic behavior seemed to be characteristic of dimeric iron(II), but the exact magnetic simulation with the susceptibility equation for the $(S_1=2)$-$(S_2=2)$ system based on the Heisenberg model could not be attained as shown in Fig. 1(B). We believe that the complexes are indeed dinuclear but the magnetic simulation in terms of the Heisenberg model is not valid because of a significant orbital contribution, as suggested for related dinuclear iron(II) complexes.[10]

$[Mn_3(L)_4]X_2$. This type of complexes was obtained only with manganese(II) ions. The magnetic moment (per metal ion) of those complexes is also subnormal for high-spin manganese(II) ion and decreased with lowering of temperature. The most plausible structure for those complexes is trinuclear where each terminal metal is sixcoordinated with the two ligands, and the central metal is tetrahedrally coordinated with bridging thiolate sulfurs. Such a linear, trinuclear structure is known for nickel(II) complexes of amino thiolic ligands.[11] The évidence supporting this structure has been obtained by cryomagnetic investigations. The magnetic susceptibility equations for the $(S_1=5/2)$-$(S_2=5/2)$-$(S_3=5/2)$ system was derived Kambe's method[12] on assuming $J_{12}=J_{23}=J$ and $J_{13}=0$ and is expressed as follows:

$$\chi_A = (Ng^2\beta^2/36kT)[A/B] + N\alpha \qquad (4)$$

where $A=2040\exp(55J/kT)+1365\exp(50J/kT)+858\exp(45J/kT)+1860\exp(40J/kT)+858\exp(37J/kT)+252\exp(35J/kT)+495\exp(34J/kT)+252\exp(31J/kT)+105\exp(30J/kT)+105\exp(28J/kT)+858\exp(27J/kT)+495\exp(26J/kT)+252\exp(25J/kT)+105\exp(24J/kT)+30\exp(23J/kT)+30\exp(19J/kT)+105\exp(18J/kT)+252\exp(17J/kT)+498\exp(16J/kT)+30\exp(13J/kT)+108\exp(10J/kT)+252\exp(7J/kT)+30\exp(5J/kT)+105$
and $B=8\exp(55J/kT)+7\exp(50J/kT)+6\exp(45J/kT)+12\exp(40J/kT)+6\exp(37J/kT)+4\exp(35J/kT)+5\exp(34/kT)+4\exp(31J/kT)+3\exp(30J/kT)+3\exp(28J/kT)+6\exp(27J/kT)+5\exp(26J/kT)+4\exp(25J/kT)+3\exp(24J/kT)+2\exp(23J/kT)+2\exp(19J/kT)+3\exp(18J/kT)+4\exp(17J/kT)+6\exp(16J/kT)+2\exp(13J/kT)+4\exp(10J/kT)+4\exp(7J/kT)+2\exp(5J/kT)+3$.
As shown in Fig. 2(B) good agreements were obtained between the experimental and theoretical magnetic susceptibilities. To our knowledge these are the first example of linear trinuclear manganese(II) complexes bridged by thiolate sulfurs.

In conclusion it was revealed that the thiolate bridge mediates a significant antiferromagnetic spin-exchange interaction between cobalt(II), iron(II), or manganese(II) ions.

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