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Binuclear Metal Complexes. XVI.¹⁾ Hetero Metal Binuclear Complexes with *N,N'*-Bis(3-carboxysalicylidene)ethylenediamine²⁾

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Hetero metal binuclear complexes, MM' (fsaen)·nH$_2$O (M=Cu(II) and Ni(II); M'=Cu(II), Ni(II), Co(II), Fe(II), and Mn(II); n=1—3), with *N,N'*-bis(3-carboxysalicylidene)ethylenediamine (H$_4$fsaen) have been synthesized and characterized, where M and M' denote the metal ion coordinated by the N$_2$O$_2$-coordinating atoms and the O$_4$-coordinating atoms, respectively. The magnetism of CuNi(fsean)·3H$_2$O and CuCo(fsaen)·3H$_2$O is explained in terms of the Heisenberg model. The magnetism of NiCu(fsaen)·H$_2$O, NiCo(fsaen)·2H$_2$O, and NiMn(fsaen)·2H$_2$O obeys the Curie-Weiss law, demonstrating the binuclear structure to be composed of one diamagnetic nickel(II) and one paramagnetic M'(II) ions. CuFe(fsaen)·2H$_2$O, NiFe(fsaen)·2H$_2$O, and CuMn(fsaen)·H$_2$O each shows unusual magnetic property.

Binuclear metal complexes containing two different metal ions are of interest in connection with spin-exchange and charge-transfer between metal ions and in the domain of metalloenzymes and homogeneous catalysis. One method for the synthesis of hetero metal binuclear and polynuclear complexes is to use the reaction of a simple metal salt with a metal chelate ligand such as a quadridentate Schiff base complex³⁻⁵⁾ or a sulfur-ligand complex.⁶,⁷⁾ Binuclear and polynuclear complexes such as V(IV)O–Cu(II)³,⁴⁾ and Cu(II)–M(II)–Cu(II)⁵⁾ have been obtained by this method. The success in synthesizing hetero metal binuclear complexes depends on the stability of the starting metal chelate and the solubility of the hetero metal complex. Thus, application of this method to other hetero metal polynuclear complexes is limited.

Another method for obtaining hetero metal binuclear complexes is to use a step-wise reaction of two different metal ions with a coordinatively selective binucleating ligand, in which two coordinating sites differ from each other in the ligand field strength or in the stereochemistry of coordination. A few such ligands have recently been reported.¹,⁸,⁹⁾

In previous papers of this series,¹,⁸⁾ it was shown that the Schiff bases derived from 3-formylsalicylic acid and diamines are binucleating ligands with coordinative selectivity. They formed a hetero metal complex of Cu(II)–Ni(II)⁸⁾ and binuclear nickel(II) complexes with one diamagnetic and one paramagnetic nickel(II) ions.¹⁾ This report deals with the synthesis and characterization of hetero metal binuclear complexes with *N,N'*-bis(3-carboxysalicylidene)ethylenediamine (abbreviated to H$_4$ fsaen). The complexes are represented by MM'(fsaen)·nH$_2$O (M(II)=Cu(II) and Ni(II); M'=Cu(II), Ni(II), Co(II), Fe(II), and Mn(II); n=1—3), where M is an "inside" metal ion coordinated by the N$_2$O$_2$-coordinating atoms and M' is an "outside" metal ion coordinated by the O$_4$-coordinating atoms (Fig. 1). A part of this work has been reported,⁸⁾ which is the first report on hetero metal binuclear complexes with H$_4$ fsaen. Recently some hetero metal binuclear complexes such as Cu(II)–U(VI)O$_2$ and Ni(II)–Th(IV) were obtained using H$_4$ fsaen.¹⁰⁾ However, no hetero metal binuclear complexes with first transition metal ions have been obtained.

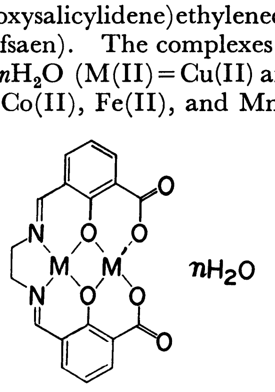

Fig. 1.

Experimental

Syntheses. The syntheses of mononuclear complexes, Cu(H$_2$fsaen)·0.5H$_2$O and Ni(H$_2$fsaen)·0.5H$_2$O, have been described in the previous paper.¹⁾

CuNi(fsaen)·3H$_2$O. Cu(H$_2$fsaen)·0.5H$_2$O (107 mg) was dissolved in an aqueous solution (50 ml) of lithium hydroxide monohydrate (21 mg) by warming. A small amount of insoluble particles was separated by filtration. To this solution was added an aqueous solution (10 ml) of nickel(II) chloride hexahydrate (60 mg) and the resulting red-purple solution was left to stand overnight at room temperature to give reddish purple prisms, which were collected, washed with water, and dried over P$_2$O$_5$ in a vacuum desiccator.

Found: C, 40.65; H, 3.45; N, 5.27; Cu, 12.27; Ni, 10.74%. Calcd for C$_{18}$H$_{12}$N$_2$O$_6$CuNi·3H$_2$O: C, 40.90; H, 3.43; N, 5.30; Cu, 12.02; Ni, 11.10%.

CuCo(fsaen)·3H$_2$O. To an aqueous solution prepared from Cu(H$_2$fsaen)·0.5H$_2$O (107 mg) and lithium hydroxide monohydrate (21 mg), was added an aqueous solution (10 ml) of cobalt(II) chloride hexahydrate (80 mg) to give a red-purple solution. After the reaction mixture was left to stand overnight at room temperature, purple prisms separated were collected, washed with water, and dried over P$_2$O$_5$ *in vacuo*.

Found: C, 40.94; H, 3.58; N, 5.32; Co, 11.41; Cu, 12.28%. Calcd for C$_{18}$H$_{12}$N$_2$O$_6$CoCu·3H$_2$O: C, 40.88; H, 3.43; N, 5.30; Co., 11.14; Cu, 12.02%.

CuFe(fsaen)·2H$_2$O. This complex was obtained as yellowish brown prisms by reacting Cu(H$_2$fsaen)·0.5H$_2$O (107 mg) with iron(II) sulfate heptahydrate (70 mg) in the presence of lithium hydroxide monohydrate (21 mg).

Found: C, 42.25; H, 3.18; N, 5.50; Cu, 12.60; Fe, 10.65%. Calcd for C$_{18}$H$_{12}$N$_2$O$_6$CuFe·2H$_2$O: C, 42.58; H, 3.18; N, 5.52; Cu, 12.52; Fe, 11.00%.

CuMn(fsaen)·H$_2$O. This complex was obtained as pink-purple prisms by reacting Cu(H$_2$fsaen)·0.5H$_2$O (107 mg) with manganese(II) sulfate hexahydrate (65 mg) in the presence of lithium hydroxide monohydrate (21 mg).

Found: C, 44.06; H, 2.63; N, 5.72; Cu, 12.52; Mn, 11.51%. Calcd for $C_{18}H_{12}N_2O_6CuMn\cdot H_2O$: C, 44.23; H, 2.89; N, 5.73; Cu, 13.00; Mn, 11.24%.

NiCu(fsaen)·H_2O. Ni(H_2fsaen)·0.5H_2O (106 mg) was dissolved in an aqueous solution (60 ml) of lithium hydroxide monohydrate (21 mg) by warming. To the resulting red solution was added an aqueous solution (10 ml) of copper(II) chloride dihydrate (34 mg). Immediately pinkish orange prisms separated. After the reaction mixture had been warmed at 50 °C for 10 min, the product was isolated, washed with water, and dried over P_2O_5 *in vacuo*.

Found: C, 43.53; H, 2.52; N, 5.62; Cu, 12.72; Ni, 12.30%. Calcd for $C_{18}H_{12}N_2O_6CuNi\cdot H_2O$: C, 43.89; H, 2.86; N, 5.69; Cu, 12.90; Ni, 11.92%.

NiCo(fsaen)·2H_2O. This complex was obtained as yellowish brown micro-crystals from Ni(H_2fsaen)·0.5H_2O (106 mg), cobalt(II) chloride hexahydrate (65 mg) and lithium hydroxide monohydrate (21 mg).

Found: C, 43.13; H, 2.92; N, 5.67; Co, 11.98; Ni, 12.16%. Calcd for $C_{18}H_{12}N_2O_6CoNi\cdot 2H_2O$: C, 42.73; H, 3.19; N, 5.54; Co, 11.65; Ni, 11.60%.

NiFe(fsaen)·2H_2O. This complex was obtained as reddish orange micro-crystals from Ni(H_2fsaen)·0.5H_2O (106 mg) and iron(II) sulfate heptahydrate (70 mg) in the presence of lithium hydroxide monohydrate (21 mg).

Found: C, 43.24; H, 2.75; N, 5.49; Fe, 11.46; Ni, 12.02%. Calcd for $C_{18}H_{12}N_2O_6FeNi\cdot 2H_2O$: C, 42.99; H, 3.21; N, 5.57; Fe, 11.11; Ni, 11.67%.

NiMn(fsaen)·2H_2O. This complex was obtained as yellow needles from Ni(H_2fsaen)·0.5H_2O (106 mg), manganese(II) sulfate hexahydrate (65 mg) and lithium hydroxide monohydrate (21 mg).

Found: C, 42.74; H, 2.82; N, 5.45; Mn, 10.91; Ni, 11.31%. Calcd for $C_{18}H_{12}N_2O_6MnNi\cdot 2H_2O$: C, 43.07; H, 3.22; N, 5.58; Mn, 10.95; Ni, 11.70%.

Measurements. C, H, and N elemental analyses were carried out at the Service Center of Elemental Analysis, Kyushu University. Metal analyses were carried out with a Shimadzu Atomic Absorption-Flame Spectrophotometer Model AA-610S. The aqueous solution for the measurement was prepared by thermally decomposing a complex in the presence of sulfuric acid and dissolving the resulting metal sulfate in dilute hydrochloric acid or sulfuric acid. Infrared spectra were measured with a Hitachi Infrared Spectrophotometer Model 215 on a KBr disk. Electronic spectra were measured with a Shimadzu Multipurpose Spectrophotometer Model MSP-5000 by the reflection on a powder sample. Magnetic susceptivility was measured by the Faraday method, where diamagnetic correction was carried out by means of Pascal's constants.

Results and Discussion

Infrared spectra of the complexes resemble each other and are similar to those of Cu_2(fsaen)·3H_2O and Ni_2(fsaen)·3H_2O, whose binuclear structures have been characterized.[1] No band was found in the region 1750—1650 cm^{-1}. Instead a broad and strong band was found around 1550 cm^{-1}, which is attributable to the coordinated carboxylate group.

Because of the low solubility of the complexes in most solvents, the electronic spectra were measured by reflection on a solid sample. The electronic spectra are given in Figs. 2 and 3. The room temperature magnetic moments of the complexes are given in Table 1.

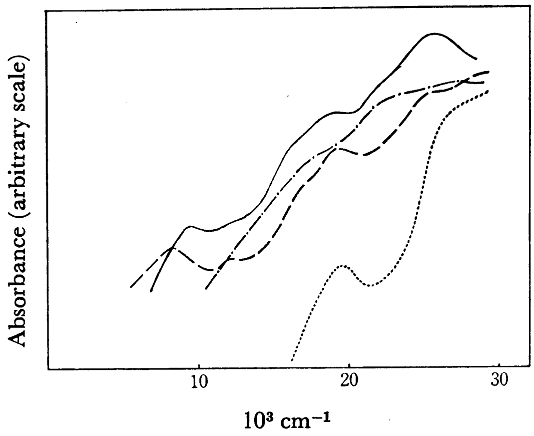

Fig. 2. Electronic spectra of (——)CuNi(fsaen)·3H_2O, (— —)CuCo(fsaen)·3H_2O, (—·—)CuFe(fsaen)·2H_2O, and (······)CuMn(fsaen)·H_2O.

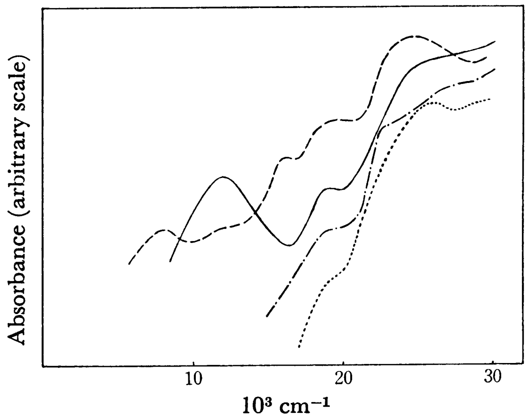

Fig. 3. Electronic spectra of (——)NiCu(fsaen)·H_2O, (— —)NiCo(fsaen)·2H_2O, (—·—)NiFe(fsaen)·2H_2O, and (······)NiMn(fsaen)·2H_2O.

TABLE 1. MAGNETIC MOMENTS OF COMPLEXES AT ROOM TEMPERATURE

	μ_{eff} (T(K)) (Bohr magneton)	
CuNi(fsaen)·3H_2O	3.05$^{a)}$(292.6)	$N\alpha=200\times10^{-6}$ e.m.u.
CuCo(fsaen)·3H_2O	4.76$^{a)}$(295.4)	$N\alpha=450\times10^{-6}$ e.m.u.
CuFe(fsaen)·2H_2O	2.76$^{b)}$(297.8)	
CuMn(fsaen)·H_2O	5.17$^{b)}$(293.2)	
NiCu(fsaen)·H_2O	1.87$^{a)}$(294.7)	$N\alpha=60\times10^{-6}$ e.m.u.
NiCo(fsaen)·2H_2O	5.15$^{a)}$(293.1)	$N\alpha=400\times10^{-6}$ e.m.u.
NiFe(fsaen)·2H_2O	2.29$^{b)}$(297.8)	
NiMn(fsaen)·2H_2O	5.71$^{b)}$(293.0)	

a) Magnetic moment was calculated by the equation $\mu_{eff}=2.828\sqrt{(\chi_M-N\alpha)T}$ using the estimated $N\alpha$ given in the Table. b) Calculated by the equation $\mu_{eff}=2.828\sqrt{\chi_M T}$.

The electronic spectrum of CuNi(fsaen)·3H_2O possesses ligand field bands (9500, 16000, and 19000 cm^{-1}) in the visible region. The band at 19000 cm^{-1} seems substantially the same as the band found for Cu(H_2fsaen)·0.5H_2O and tentatively assigned to the "inside" copper(II). The bands at 9500 and 16000 cm^{-1}, on the other hand, may be assigned to the nickel(II) in an octahedral environment. The molar magnetic moment of this complex is subnormal (3.05 Bohr magnetons (μ_B)). It has been shown¹⁾ that this magnetic behavior can be explained on the basis of the Heisenberg model by the equation,

$$\chi_M = \frac{Ng^2\beta^2}{4kT} \cdot \frac{10+\exp(-3J/kT)}{2+\exp(-3J/kT)} + N\alpha \qquad (1)$$

where J is the exchange integral, k the Boltzmann constant, N the Avogadro number, β the Bohr magneton and g the Lande g-factor. The magnetic parameters, J, g_{ave}, and $N\alpha$(temperature-independent paramagnetism), determined from the best fit of the experimental χ_M values to the Eq. 1 are $-75\ \text{cm}^{-1}$, 2.19 and 200×10^{-6} e.m.u./mol, respectively.¹⁾

The electronic spectrum of CuCo(fsaen)$\cdot 3H_2O$ shows the ligand field bands at 8300, 11000, 17000, and 19200 cm^{-1}. The band at 19200 cm^{-1} is attributed to the copper(II) in the "inside" coordination site. The remaining bands may be assigned to the cobalt(II) ion. The spectrum resembles that of hexaaquacobalt(II). Therefore, coordination of water molecule to the cobalt(II) from an apical direction is presumed. On assuming an octahedral configuration around the cobalt(II), the band at 8300, 11000, and 17000 cm^{-1} are assigned to the ${}^4T_{2g} \leftarrow {}^4T_{1g}$, ${}^2E_g \leftarrow {}^4T_{1g}$, and ${}^4A_{2g} \leftarrow {}^4T_{1g}$ transitions, respectively. The transition ${}^4T_{1g}$ (P)$\leftarrow {}^4T_{1g}$ (F) can be superposed by the band of the copper(II) ion.

The magnetic moment for a cobalt(II) ion under octahedral symmetry is, in general, larger than the spin-only value because of the contribution from an orbital angular momentum, and is in the range 4.3—5.2 μ_B. The magnetic moment of CuCo(fsaen)$\cdot 3H_2O$ is 4.76 μ_B which seems common to a magnetically noninteracting Cu(II)–Co(II) system if we take into account the 1.85 μ_B of Cu(H_2fsaen)$\cdot 0.5H_2O$. However, the magnetic moment of this complex markedly depends on temperature, indicating the spin-spin exchange interaction between the metal ions (Fig. 4). Based on the Heisenberg model, spin-spin coupling between copper(II) ($s_1=1/2$) and cobalt(II) ($s_2=3/2$) would result in two spin states, $s=1$ and $s=2$. The spin-quintet state is separated by $-4J$ from the supposed spin-triplet ground state, where J is the exchange integral. The molar magnetic susceptibility for this system is expressed by the equation,

$$\chi_M = \frac{Ng^2\beta^2}{kT} \cdot \frac{10+2\exp(-4J/kT)}{5+3\exp(-4J/kT)} + N\alpha \qquad (2)$$

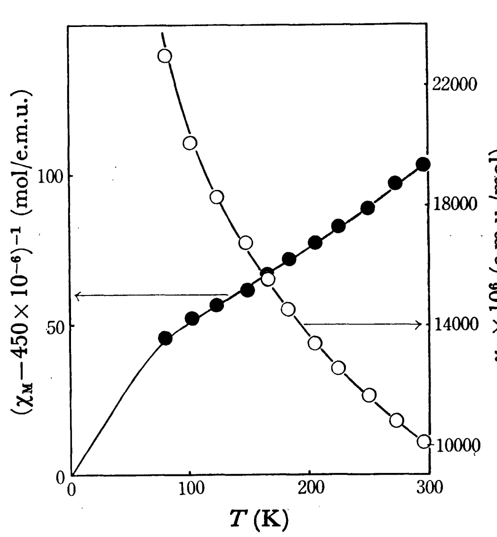

Fig. 4. Variations of molar susceptibility and inverse molar susceptibility for CuCo(fsaen)$\cdot 3H_2O$ as a function of temperature.

As is seen in Fig. 4, the magnetic susceptibility (and the inverse magnetic susceptibility) is in accordance with the theoretical value when average g-value, J and $N\alpha$ are estimated at 2.45, $-35\ \text{cm}^{-1}$ and 450×10^{-6} e.m.u./mol, respectively. It is likely that the orbital contribution from the cobalt(II) to the total magnetic susceptibility is small. This implies that the geometry around the cobalt(II) is not exactly octahedral. The ${}^4T_{1g}$ ground state of cobalt(II) in an octahedral environment should split into two or three states under a low symmetry. If the first excited state were thermally accessible, the temperature dependence of magnetic susceptibility would become much complicated, and could not be interpreted in terms of Eq. 2. Thus, the ground state for the cobalt(II) in CuCo(fsaen)$\cdot 3H_2O$ is orbitally singlet and the first excited state is above the ground state more than 1000 cm^{-1}. According to Sinn¹¹⁾ the orbital contribution to magnetic susceptibility of a poly-nuclear cluster, in general, can be ignored. Thus the geometry around the cobalt in CuCo(fsaen)$\cdot 3H_2O$ is pseudo-octahedral; it is supposed that the water molecules in the apical positions are elongated.

Electronic spectrum of CuFe(fsaen)$\cdot 2H_2O$ shows a band at 22000 cm^{-1} in addition to the band (19000 cm^{-1}) attributable to the "inside" copper(II). In general, high-spin iron(II) in an octahedral crystal field should show the spin-allowed transition ${}^5E_g \leftarrow {}^5T_{2g}$ around 11000 cm^{-1}. However, such a band could not be found for CuFe(fsaen)$\cdot 2H_2O$. The molar magnetic moment decreases with lowering of temperature from 2.76 μ_B at 297.8 K to 1.90 μ_B at 79.9 K (Table 2). This behavior can not be explained in terms of the spin-exchange interaction between a copper(II) and a high-spin iron(II). It might be possible to explain the magnetism in terms of a spin-equilibrium between high-spin (or intermediate-spin) and low-spin states of iron(II). Based on this assumption, the band at 22000 cm^{-1} is attributable to a low-spin iron(II). However, most iron(II) cross-over complexes are restricted to those containing imine-nitrogen ligands¹²⁻¹⁸⁾ and no iron(II) cross-over complex with only oxygen-ligands has yet been obtained.

In the spectrum of CuMn(fsaen)$\cdot H_2O$ no characteristic band was found except the band at 19400 cm^{-1}, which is attributable to the "inside" copper(II). This seems natural since a high-spin manganese(II) shows no spin-allowed d-d transition. The molar magnetic moment is 5.17 μ_B which is much lower than the value expected for only high-spin manganese(II). This indicates an antiferromagnetic spin-exchange interaction between copper(II) and manganese(II).

In composition, color, infrared spectrum, electronic spectrum and magnetic property NiCu(fsaen)$\cdot H_2O$ differs from CuNi(fsaen)$\cdot 3H_2O$. The reflectance spec-

TABLE 2. TEMPERATURE DEPENDENCE OF MOLAR SUSCEPTIBILITY(e.m.u./mol) AND EFFECTIVE MAGNETIC MOMENT (μ_B) FOR CuFe(fsaen)·$2H_2O$ AND NiFe(fsaen)·$2H_2O$

CuFe(fsaen)·$2H_2O$												
T(K)	79.7	102.2	122.3	146.4	167.2	188.1	207.6	226.0	246.1	265.2	284.1	297.8
$\chi_M \cdot 10^6$	5678	5202	4780	4455	4221	4018	3821	3660	3510	3401	3304	3203
μ_{eff}	1.90	2.06	2.16	2.28	2.38	2.46	2.52	2.57	2.63	2.69	2.74	2.76
NiFe(fsaen)·$2H_2O$												
T(K)	80.6	100.1	119.2	128.9	147.2	167.9	188.3	208.1	227.7	247.8	268.0	297.8
$\chi_M \cdot 10^6$	3384	3048	2810	2684	2606	2547	2483	2401	2349	2295	2256	2198
μ_{eff}	1.48	1.56	1.64	1.66	1.75	1.85	1.93	2.00	2.07	2.13	2.20	2.29

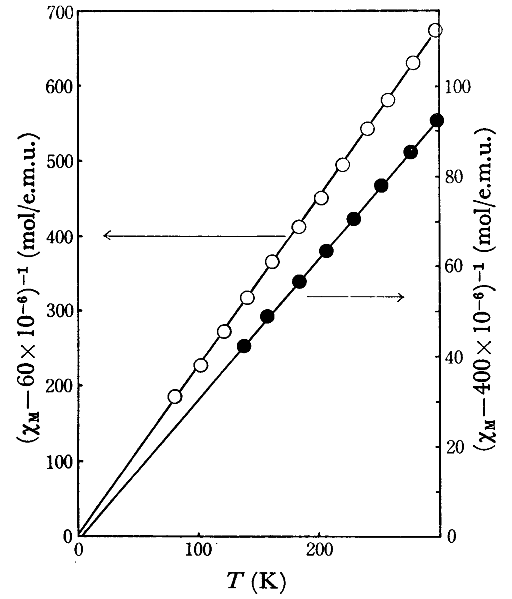

Fig. 5. The inverse magnetic susceptibilities for (○) NiCu(fsaen)·H_2O and (●) NiCo(fsaen)·$2H_2O$.

trum of NiCu(fsaen)·H_2O possesses two ligand field bands at 12000 and 19000 cm^{-1}. The first band seems to be essentially the same as the band (13400 cm^{-1}) found for Cu_2(fsaen)·$2H_2O$. The bands at 12000 and 19100 cm^{-1} are tentatively assigned to the "outside" copper(II) and the "inside" nickel(II), respectively. The molar magnetic moment at room temperature is 1.87 μ_B and the inverse magnetic susceptibility obeys the Curie-Weiss law in the temperature range 78—300 K. Spectral and magnetic properties indicate that NiCu(fsaen)·H_2O is composed of one diamagnetic nickel(II) and one copper(II) ions.

The electronic spectrum of NiCo(fsaen)·$2H_2O$ resembles that of CuCo(fsaen)·$3H_2O$. Therefore, the assignment of the ligand field bands was tentatively done by an assumption of a pseudo-octahedral configuration around the cobalt(II); 8100 ($^4T_{2g}\leftarrow{}^4T_{1g}$), 12000 ($^2E_g\leftarrow{}^4T_{1g}$), 16200 ($^4A_{2g}\leftarrow{}^4T_{1g}$), and 19500 cm^{-1} ($^4T_{1g}(P)\leftarrow{}^4T_{1g}(F)$). The band at 19500 cm^{-1} may be overlapped by the band due to the "inside" nickel(II). The supposed structure of planar nickel(II)-octahedral cobalt(II) is supported by magnetic measurements. The magnetic moment at room temperature is 5.15 μ_B, which is common to high-spin cobalt(II) complexes. The plot of the inverse magnetic susceptibility against temperature obeys the Curie-Weiss law as is shown in Fig. 5.

NiFe(fsaen)·$2H_2O$ resembles CuFe(fsaen)·$2H_2O$ in spectral and magnetic properties. The magnetic susceptibility and magnetic moments at various temperature are given in Table 2. Since the electronic spectrum indicates that the nickel(II) has a planar configuration, unusual magnetic property of this complex is attributed to the iron(II).

From the electronic spectrum it is apparent that the configuration around the nickel(II) in NiMn(fsaen)·$2H_2O$ is also planar. The fact that the room temperature magnetic moment is 5.71 μ_B which is common to high-spin manganese(II) supports the binuclear structure composed of planar nickel(II) and high-spin manganese(II).

Consequently the nickel(II) in NiM'(fsaen)·nH_2O is always planar. This finding is compatible with the fact that the "inside" nickel(II) is always diamagnetic in Ni_2(fsaen)·$3H_2O$ and its homologues. The ligand field band due to the "inside" metal ion in the present complexes shifts to higher energy as compared with the band of the corresponding monomeric complex. This implies that the binuclear complex formation enhances the coplanarity of the "inside" metal plane.[19]

References

1) Part XV. M. Tanaka, M. Kitaoka, H. Okawa, and S. Kida, *Bull. Chem. Soc. Jpn.*, **49**, 2469 (1976).

2) This work was presented at 24th Symposium of Coordination Chemistry, Kanazawa, October 9, 1974.

3) J. Selbin and L. Ganguly, *Inorg. Nucl. Chem. Lett.*, **5**, 815 (1969).

4) H. Okawa and S. Kida, unpublished data.

5) S. J. Gruber, C. M. Harris, and E. Sinn, *J. Inorg. Nucl. Chem.*, **30**, 1805 (1968).

6) D. C. Jicha and D. H. Busch, *Inorg. Chem.*, **1**, 872, 878, 884 (1962).

7) D. Coucouvanis and D. Piltingsrud, *J. Am. Chem. Soc.*, **95**, 5556 (1973).

8) H. Okawa, M. Tanaka, and S. Kida, *Chem. Lett.*, **1974**, 987.

9) B. Tomlonovic, R. L. Hough, M. D. Glick, and R. L. Lintvedt, *J. Am. Chem. Soc.*, **97**, 2925 (1975).

10) M. Vidali, P. A. Vigato, and U. Gasellato, *Inorg. Chim. Acta*, **17**, L5 (1976).

11) E. Sinn, *Coord. Chem. Rev.*, **5**, 313 (1970).

12) Y. Nishida, S. Oshio, and S. Kida, *Chem. Lett.*, **1975**, 79.

13) E. König, G. Ritter, H. Spiering, S. Kremer, K. Madeja, and A. Rosenkrauz, *J. Chem. Phys.*, **56**, 3139 (1972).

14) G. Ritter and H. A. Goodwin, *Chem. Phys.*, **1**, 17 (1973).

15) E. König and K. Madeja, *Inorg. Chem.*, **6**, 48 (1968).

16) E. König, K. Madeja, and K. J. Watson, *J. Am. Chem. Soc.*, **90**, 1146 (1968).

17) C. M. Harris and E. Sinn, *Inorg. Chim. Acta.*, **2**, 296 (1968).

18) A. J. Cunningham, J. E. Fergusson, H. K. J. Powell, E. Sinn, and H. Wong, *J. Chem. Soc., Dalton*, **1972**, 2155.

19) S. J. Gruber, C. M. Harris, and E. Sinn, *J. Inorg. Nucl. Chem.*, **30**, 1805 (1968); *Inorg. Nucl. Chem. Lett.*, **4**, 107 (1968).