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SYNTHESIS AND MAGNETIC PROPERTY OF COBALT(II)-MANGANESE(II) AND COBALT(II)-IRON(II) HETERO-METAL COMPLEXES WITH N,N'-BIS(3-CARBOXYSALICYLIDENE)ALKANEDIAMINES[1)]

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CoMn(fsaen)(py)$_3$, CoMn(fsapn)(py)$_3$ and CoFe(fsapn)(py)$_3$ (H_4fsaen=N,N'-bis(3-carboxysalicylidene)ethylenediamine, H_4fsapn=N,N'-bis(3-carboxysalicylidene)propylenediamine) were synthesized and characterized. Cryomagnetic measurements indicated no spin-exchange interaction operating between the low-spin cobalt(II) and high-spin manganese(II) or iron(II) ions.

Hetero-metal and mixed-spin polynuclear complexes are useful in investigating spin-exchange mechanism between the metal ions. Since a low-spin cobalt(II) ion has an unpaired electron on either d_{z^2} or d_{yz} orbital, spin-exchange interaction of polynuclear metal complexes containing a low-spin cobalt(II) ion may be closely associated with the electronic configuration of the cobalt(II) ion. Recently, mixed-spin polynuclear cobalt(II) complexes containing low-spin and high-spin cobalt(II) ions in one molecule were first synthesized in our laboratory and their magnetic properties were investigated.[2,3)] However, hetero-metal polynuclear complexes composed of low-spin cobalt(II) and other metal ions have not yet been obtained. Thus, this study relates to the syntheses and the magnetic investigations of cobalt(II)-manganese(II) and cobalt(II)-iron(II) complexes with N,N'-bis(3-carboxysalicylidene)ethylenediamine (H_4fsaen) and N,N'-bis(3-carboxysalicylidene)-propylenediamine (H_4fsapn).

A solution of H_4fsaen (3.5 g) and cobalt(II) acetate tetrahydrate (2.5 g) in pyridine (100 ml) was stirred at ca. 100°C in an atmosphere of nitrogen. The reaction mixture was allowed to stand over night to give Co(H_2fsaen)(py)$_2$ as orange prisms. In a similar way Co(H_2fsapn)(py)$_2$ was obtained as yellowish brown needles. Then, Co(H_2fsaen)(py)$_2$ (570 mg) and manganese(II) acetate tetrahydrate (245 mg) were dissolved in pyridine (30 ml) under nitrogen atmosphere and the mixture was refluxed for 2 h to give CoMn(fsaen)(py)$_3$ as orange prisms. In a similar way CoMn(fsapn)(py)$_3$ was obtained as red-purple prisms. When Co(H_2fsapn)(py)$_2$ (584 mg) and iron(II) acetate (175 mg) were reacted in pyridine (25 ml) in an atmosphere of nitrogen, CoFe(fsapn)(py)$_3$ was obtained as dark reddish brown prisms. The Co(II)-Fe(II) complex with H_4fsaen, obtained by the same procedure as that of CoFe(fsaen)-(py)$_3$, was air-sensitive.

Elemental analyses of Co(H_2fsaR)(py)$_2$ and CoM(fsaR)(py)$_3$ (R=en, pn; M(II)=Mn(II), Fe(II)) are given in Table 1.

Table 1. ELEMENTAL ANALYSES OF COMPLEXES

	Found(%)			Calcd(%)		
	C	H	N	C	H	N
Co(H_2fsaen)(py)$_2$	58.84	4.23	9.84	58.85	4.23	9.80
Co(H_2fsapn)(py)$_2$	59.02	4.53	9.56	59.49	4.48	9.57
CoMn(fsaen)(py)$_3$	56.36	3.99	10.30	56.34	3.87	9.96
CoMn(fsapn)(py)$_3$	56.67	3.99	9.77	56.92	4.07	9.76
CoFe(fsapn)(py)$_3$	56.48	3.94	9.87	56.84	4.07	9.75

IR spectra of Co(H_2fsaen)(py)$_2$ and Co(H_2fsapn)(py)$_2$ display a band near 1690 cm^{-1} due to the free carboxyl group and a band at 700 cm^{-1} attributable to the pyridine C-H deformation. The latter band is much lower in frequency compared with the band (750 cm^{-1}) for free pyridine,[4)] thence the coordination of pyridine in the present complexes being supposed. Electronic spectra of these complexes show d-d bands at 12,100 and 18,000 cm^{-1}, indicating an octahedral configuration around the cobalt(II) ion. It is likely that the cobalt(II) is bound at the N_2O_2-donating site with two molecules of pyridine at the apical positions.

IR spectra of CoMn(fsaen)(py)$_3$, CoMn(fsapn)(py)$_3$ and CoFe(fsapn)(py)$_3$ resemble those of Co_2(fsaR)(py)$_3$[2)] and show the C=O stretching band of coordinated carboxylato group at 1550 cm^{-1} and the C-H deformation band of coordinated pyridine at 700 cm^{-1}. Powder reflectance spectra of the Co(II)-Mn(II) complexes show d-d bands at 5,900, 9,100 and 14,000 cm^{-1}(Fig. 1). The spectra are essentially the same as that of Co(salen)py.[5)] Since high-spin manganese(II) show no spin-allowed d-d band,

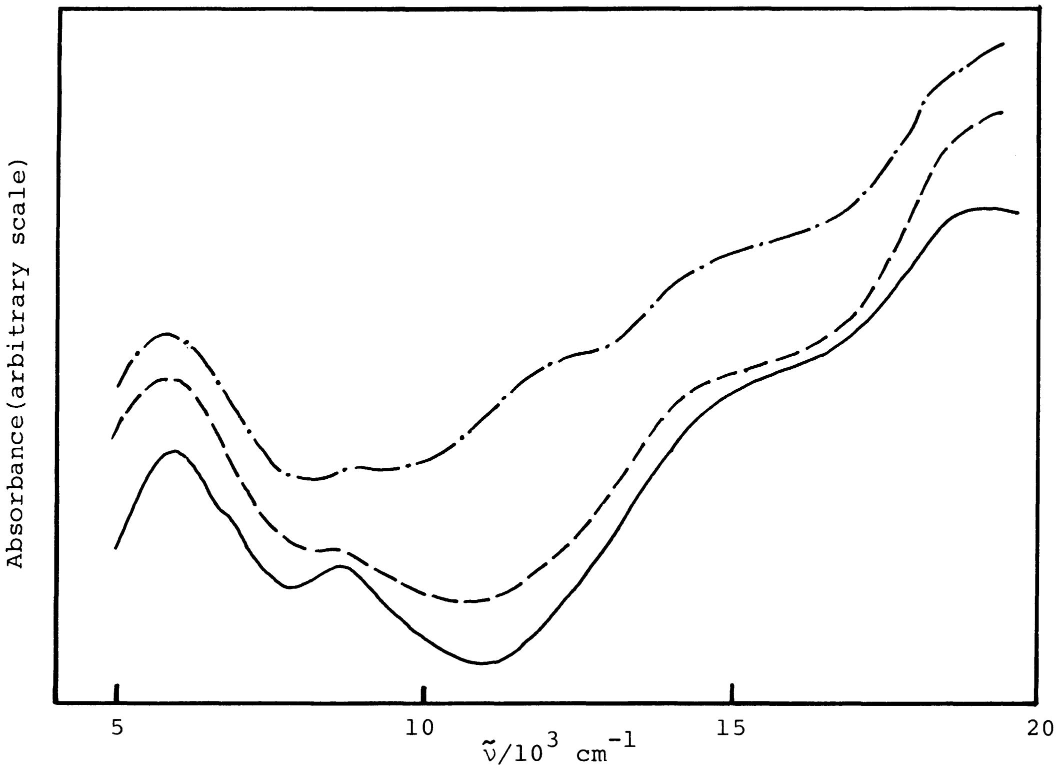

Fig. 1. Reflectance spectra of (———)CoMn(fsaen)(py)$_3$, (— — —) CoMn(fsapn)(py)$_3$ and (—·—)CoFe(fsapn)(py)$_3$.

electronic spectra of the Co(II)-Mn(II) complexes strongly suggest that the geometry around the cobalt(II) ion is square-pyramidally coordinated by the imino-nitrogen and phenolic oxygen atoms in equatorial plane and by pyridine at the apex. Reflectance spectrum of CoFe(fsapn)(py)$_3$ is substantially the same as those of the Co(II)-Mn(II) complexes but characterized by an additional band near 12,000 cm^{-1}, which can be assigned to the $^5E_g \leftarrow {}^5T_{2g}$ transition of six-coordinate iron(II). Thus, electronic spectra as well as the molecular compositions of the present complexes are compatible with the structure given in Fig. 2.

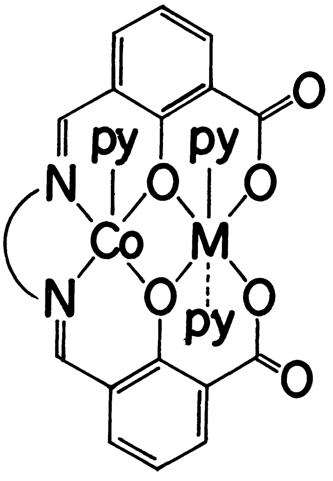

Fig. 2.

Magnetic susceptibilities of the Co(II)-Mn(II) and Co(II)-Fe(II) complexes were measured from liquid nitrogen temperature to room temperature. In Fig. 3 magnetic

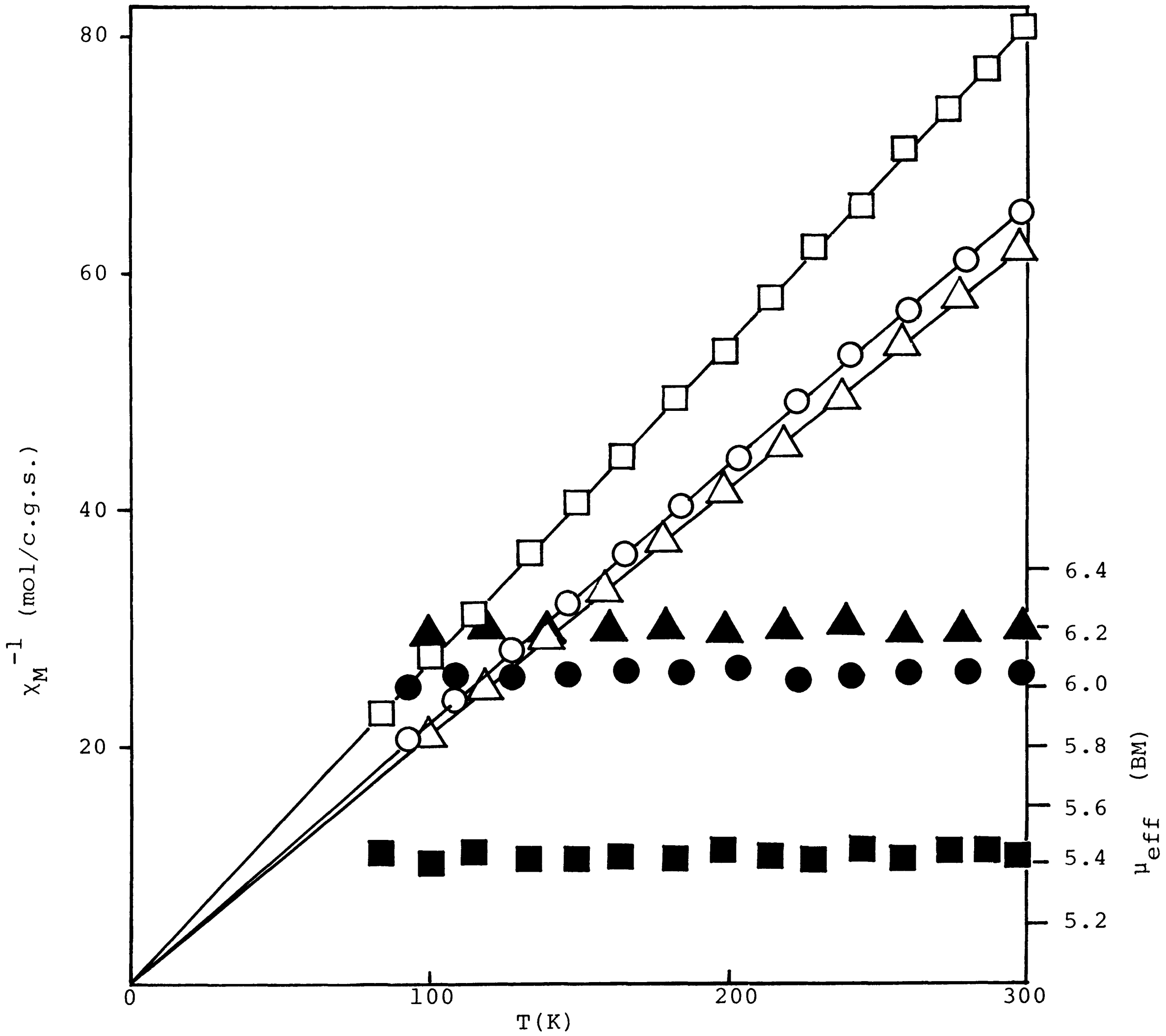

Fig. 3. Temperature variation of magnetic moments and inverse magnetic susceptibilities of (●,○)CoMn(fsaen)(py)$_3$, (▲,△) CoMn(fsapn)(py)$_3$ and (■,□)CoFe(fsapn)(py)$_3$.

moments and inverse magnetic susceptibilities are plotted against the temperature. Magnetic moments are almost independent of temperature, and magnetic susceptibilities obey the Curie-Weiss law with a very small Weiss constant. These facts indicate that the spin-state of the Mn(II) and Fe(II) ions is high-spin and spin-exchange interaction is very little between the metal ions. Magnetic properties of the present complexes are in line with the magnetism of $Co_2(fsaR)(py)_3$[2)] showing no spin-exchange interaction between the metal ions.

Previously we reported mixed-spin trinuclear cobalt(II) complexes of Co(II)(s=1/2)-Co(II)(s=3/2)-Co(II)(s=1/2) system with N,N'-disalicylideneethylenediamine and its homologues,[3)] where a considerably strong antiferromagnetic spin-exchange interaction operates between the low-spin and high-spin cobalt(II) ions. Furthermore, antiferromagnetic spin-exchange interaction is observed for the Co(II)(s=1/2)-Mn(II)(s=5/2)-Co(II)(s=1/2) complexes with the same ligands.[6)] Since an unpaired electron of the low-spin cobalt(II) in these trinuclear complexes occupies d_{yz} orbital, the d_π(low-spin Co)-p_π(O)-d_π(high-spin Co or Mn) super pathway plays an important role in antiferromagnetic spin-exchange interaction.

On the other hand, the absence of magnetic interaction in $CoM(fsaR)(py)_3$ (M(II)=Mn(II), Fe(II), Co(II)) must be associated with the spin-state of the low-spin cobalt(II) ion and it is reasonable to assume that the cobalt(II) ion possesses an unpaired electron on its d_{z^2} orbital judging from the ESR spectrum of $CoMg(fsaen)(py)_3$.[2)] Thus, we may conclude that very little spin-exchange interaction between the low-spin cobalt(II) and high-spin manganese(II) or iron(II) is attributed to little overlapping between the cobalt d_{z^2} orbital and the bridging oxygen orbital.

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References

1) Binuclear Metal Complexes. Part XXIX. Part XXVIII: Ref. 3.
2) N. Torihara, H. Okawa, and S. Kida, Bull. Chem. Soc. Jpn., 51, 3236(1978).
3) V. Kasempimolporn, H. Okawa, and S. Kida, Bull. Chem. Soc. Jpn., in press.
4) C. G. Cannon and G. B. B. M. Sutherland, Spectrochim. Acta, 4, 373(1951).
5) M. A. Hitchman, Inorg. Chem. 16, 1985(1977).
6) V. Kasempimolporn, H. Okawa, and S. Kida, Presented at the Meeting of Chugoku-Shikoku and Kyushu Branches of Chemical Society of Japan, Tokushima, November, 1978.

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