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BINUCLEAR METAL COMPLEXES. XXII.[1] ANTIFERROMAGNETIC SPIN-EXCHANGE INTERACTION IN COPPER(II)-MANGANESE(II) HETERO-METAL COMPLEXES

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Copper(II)-manganese(II) hetero-metal binuclear complexes with 3-formylsalicylic acid-diamine Schiff bases were synthesized and characterized. The cryomagnetic measurements demonstrated that an antiferromagnetic spin-exchange interaction operates between the metal ions, the exchange integral, J, being estimated at $-22\sim-44$ cm^{-1}.

It is known[1-6] that 3-formylsalicylic acid-diamine Schiff bases are binucleating ligands with coordination selectivity. They form binuclear nickel(II)[2] and cobalt(II)[3] complexes in mixed-spin state and hetero-metal (Cu(II)-Ni(II) and Cu(II)-Co(II)) binuclear complexes.[4-6] In this study we have synthesized the copper(II)-manganese(II) hetero-metal complexes with 3-formylsalicylic acid-diamine Schiff bases and investigated spin-spin exchange between the metal ions.

3-Formylsalicylic acid-diamine Schiff bases with ethylenediamine, propylenediamine, 2,3-butanediamine, 1,2-cyclohexanediamine, and o-phenylenediamine are abbreviated as H_4fsaen, H_4fsapn, H_4fsabn, H_4fsach, and H_4fsaph, respectively. The copper(II)-manganese(II) hetero-metal complexes are denoted as CuMn(fsaen) and so on. This abbreviation represents that the first and the second metal ions are coordinated to the "inside"(N_2O_2-) and the "outside"(O_4-) coordination sites, respectively. Synthesis of CuMn(fsaen)H_2O has been described.[4) Other complexes were obtained in the same way as that of CuMn(fsaen)H_2O. Elemental analyses of the complexes are given in Table 1. Infrared spectra of the complexes show a strong band near 1540 cm^{-1} attributable to the coordinated carboxylate group. Based on the above facts it may be concluded that the complexes have a binuclear skeleton shown in Fig. 1.

Powder reflectance spectra of the complexes exhibit a strong band at 19000-20000 cm^{-1} and a shoulder at 17000-18000 cm^{-1}, the latter corresponding to the

Table 1. Elemental analyses of copper(II)-manganese(II) complexes

	Found(%)					Calcd(%)				
	C	H	N	Cu	Mn	C	H	N	Cu	Mn
CuMn(fsaen)H_2O	44.69	2.64	5.73	12.5	11.5	44.23	2.89	5.73	13.0	11.2
CuMn(fsapn)H_2O	45.91	2.72	5.76	12.7	10.2	45.39	3.21	5.57	12.6	10.9
CuMn(fsabn)H_2O	46.89	3.20	5.40	11.9	11.2	46.48	3.51	5.42	12.3	10.6
CuMn(fsach)H_2O	48.38	3.46	5.16	11.2	10.5	48.68	3.71	5.16	11.7	10.1
CuMn(fsaph)	50.38	2.37	5.34	11.8	10.0	50.74	2.32	5.38	12.2	10.5

d-d band for the mononuclear copper(II) complexes of the present ligands. For the origin of the former band it is difficult to draw a definite conclusion from the available data, but it can not be due to the manganese(II) ion, because 1) the manganese(II) ion is in high-spin state judged from the molar magnetic moments (5.76-6.03 BM), so that no spin-allowed d-d transition is expected, and 2) the spectra of the present complexes closely resemble those of the Cu(II)-Cu(I) and Cu(II)-Zn(II) binuclear complexes[7,8] with N,N'-bis(salicylidene)ethylenediamine and its homologues. Therefore, the band at 19000-20000 cm^{-1} is tentatively attributed to the charge-transfer band from the bridging phenolic oxygen to the copper(II) ion.

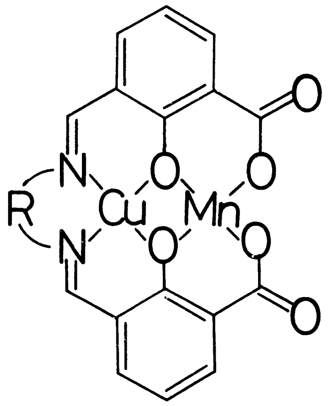

Fig. 1.

If we assume that there is no magnetic interaction between copper(II) and manganese(II) ions, the magnetic moments of the complexes will be 6.3 BM on estimating the individual atom magnetic moment at 1.8 and 6.0 BM respectively. The experimental values for the present complexes are a little lower than 6.3 BM, and decrease with lowering of temperature. This fact is indicative of an antiferromagneticspin-pairing between the metal ions. Based on the Heisenberg model the molar magnetic susceptibility for the copper(II)-manganese(II) complex is expressed by the expression,

$$\chi_M = \frac{Ng^2\beta^2}{kT} \cdot \frac{28 + 10\exp(-6J/kT)}{7 + 5\exp(-6J/kT)} + N\alpha \qquad (1),$$

where each symbol has its general meaning. The energy separation between the supposed spin-quintet ground state and the spin-heptet excited state is -6J (J is the exchange integral). It seems that the susceptibilities of the complexes can be practically explained by the expression (1), but the agreements between the empirical and theoretical susceptibilities were poor at lower temperatures than 150K. As is shown in Fig. 2, the magnetic properties of the complexes, on the other hand, could be satisfactorilly interpreted by the expression,

$$\chi_M = \frac{Ng^2\beta^2}{K(T-\theta)} \cdot \frac{28 + 10\exp(-6J/kT)}{7 + 5\exp(-6J/kT)} + N\alpha \qquad (2),$$

where θ is regarded as the measure of inter-cluster interaction. Magnetic parameters obtained are tabulated in Table 2. Thus, it is clear that an antiferromagnetic spin-exchange interaction occurs between the metal ions. It was also suggested that a considerable magnetic interaction operates among the binuclear clusters.

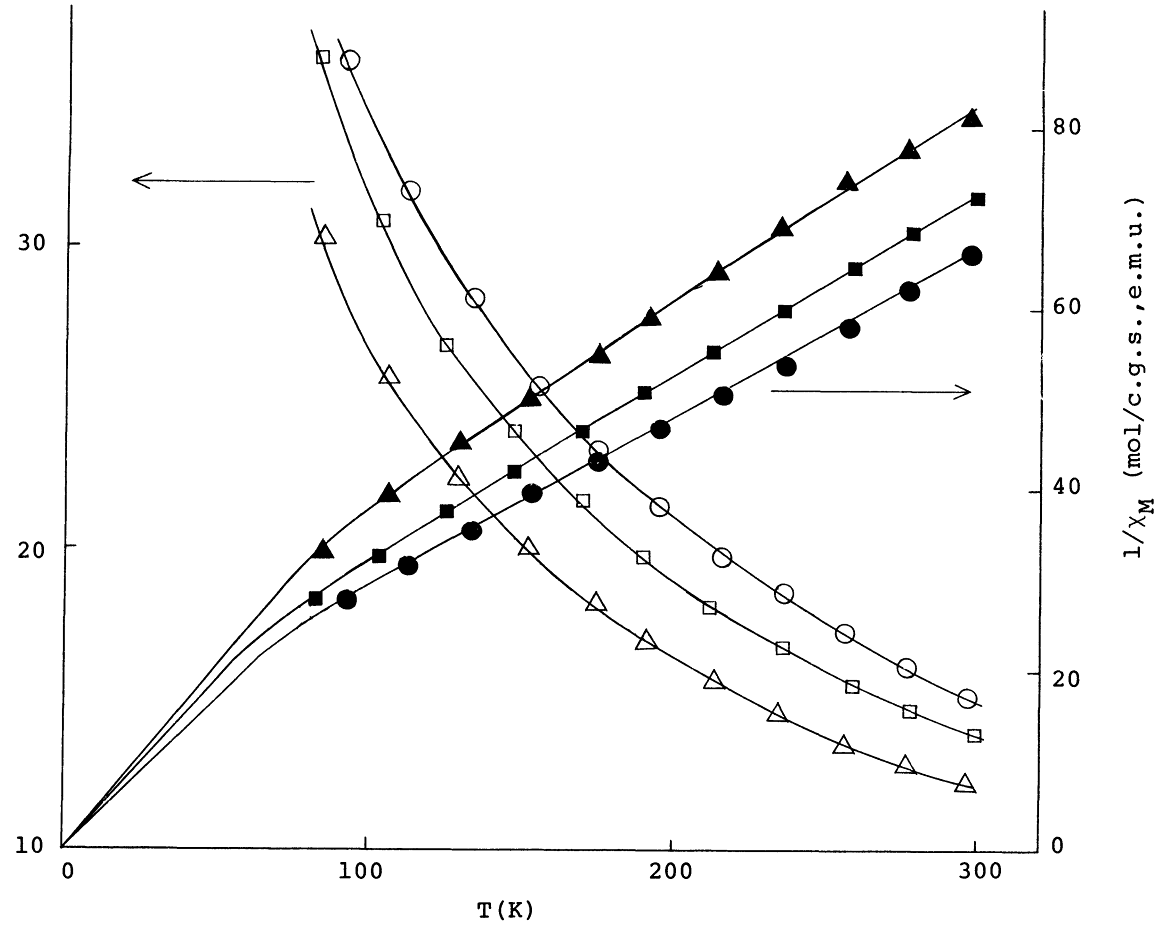

Fig. 2. Temperature variations of magnetic susceptibilities and inverse susceptibilities of (○) CuMn(fsaen)H_2O, (□) CuMn(fsapn)H_2O and (△) CuMn(fsaph). Solid lines are drawn on the basis of the expression (1) using parameters given in Table 2. The magnetic property of CuMn(fsabn) is almost same as that of CuMn(fsaen)H_2O.

In Table 3 the exchange integrals of the copper(II)-M(II) (M(II)=Cu(II), Ni(II), Co(II) and Mn(II)) binuclear complexes with H_4fsaen and H_4fsapn are shown. As is generally known, the -J value for the binuclear copper(II) complexes are very large, while the -J value for the copper(II)-nickel(II), copper(II)-cobalt(II) and copper(II)-manganese(II) complexes are very small. Although the -J value, in general, decreases in the order Cu(II)-Ni(II), Cu(II)-Co(II) and Cu(II)-Mn(II), it seems that there is no substantial change in the exchange integral among these complexes.

Table 2. Magnetic parameters for Cu(II)-Mn(II) complexes.

	-J (cm^{-1})	θ(K)	g
CuMn(fsaen)H_2O	22	-14	2.10
CuMn(fsapn)H_2O	26	-6	2.00
CuMn(fsabn)H_2O	22	-14	2.10
CuMn(fsach)H_2O	22	-10	2.00
CuMn(fsaph)	44	-15	2.00

Parameters were obtained on estimating Nα at zero.

Table 3. Exchange integral, -J(cm^{-1}) for binuclear complexes with H_4fsaen and H_4fsapn.

	H_4fsaen	H_4fsapn
Cu(II)-Cu(II)	330	328
Cu(II)-Ni(II)	75	34
Cu(II)-Co(II)	35	36
Cu(II)-Mn(II)	22	26

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