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Binuclear Metal Complexes. XX [1]. Antiferromagnetic Spin-Exchange Interaction in Copper(II)–Nickel(II) and Copper(II)–Cobalt(II) Hetero-Metal Complexes with 3-Formylsalicylic Acid-Diamine Schiff Bases [2]

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Copper(II)–nickel(II) hetero-metal binuclear complexes, CuNi(fsapn)·2H$_2$O, CuNi(fsach)·2H$_2$O and CuNi(fsaph)·5H$_2$O, and copper(II)–cobalt(II) complexes, CuCo(fsapn)·2H$_2$O, CuCo(fsabn)·2H$_2$O and CuCo(fsaph)·2H$_2$O, have been synthesized and characterized, where H$_4$fsapn, H$_4$fsabn, H$_4$fsach and H$_4$fsaph denote Schiff bases obtained by condensing 3-formylsalicylic acid with propylenediamine, 2,3-butanediamine, 1,2-cyclohexanediamine and o-phenylenediamine, respectively. Based on cryomagnetic measurements, it was found that a considerable antiferromagnetic spin-exchange interaction is operating between the metal ions except for CuNi(fsaph)·5H$_2$O and CuCo(fsaph)·2H$_2$O, the magnetisms being interpreted in terms of the Heisenberg model. The magnetisms of CuNi(fsaph)·5H$_2$O and CuCo(fsaph)·2H$_2$O obeyed the Curie law and the Curie–Weiss law respectively.

Introduction

Recently hetero-metal polynuclear complexes are of great interest in connection with spin-exchange and electron-transfer between metal ions. In line with this, some hetero-metal binuclear complexes have been synthesized using binucleating ligands which can stepwise combine two metal ions [3–8]. In the previous papers of this series [3, 4], the Cu(II)–M(II) and Ni(II)–M(II) hetero-metal complexes (M(II)=Cu(II), Ni(II), Co(II), Fe(II) and Mn(II)) have been obtained using the Schiff base, H$_4$fsaen, formed from 3-formylsalicylic acid and ethylenediamine in the 2:1 mol ratio. Among these complexes, the copper(II)–nickel(II) and the copper(II)–cobalt(II) complexes exhibited a considerable antiferromagnetic spin-exchange interaction between the metal ions [3, 4].

The object of this study is synthesizing the copper(II)–nickel(II) and the copper(II)–cobalt(II) complexes with Schiff bases derived from 3-formylsalicylic acid and diamines (Fig. 1), and investigating the magnetic spin-exchange interaction between the metal ions. The Schiff bases derived from propylenediamine, 2,3-butanediamine, 1,2-cyclohexanediamine and *o*-phenylenediamine are abbreviated as H$_4$fsapn, H$_4$fsabn, H$_4$fsach and H$_4$fsaph, respectively. The mononuclear copper(II) complexes with these ligands are represented by, *e.g.*, Cu(H$_2$fsapn). By reacting a mononuclear copper(II) complex with a nickel(II) or a cobalt(II) ion, the copper(II)–nickel(II) and the copper(II)–cobalt(II) hetero-metal binuclear complexes have been obtained. The hetero-metal binuclear complexes are represented by, *e.g.*, CuNi(fsapn)·2H$_2$O, where the first metal is bonding to the N$_2$O$_2$-site (the inner coordination site) and the second metal to the O$_4$-site (the outer coordination site) (Fig. 1).

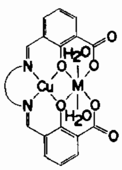

Figure 1. The hetero-metal binuclear complexes.

Experimental

Syntheses

3-Formylsalicylic acid [9] and 2,3-butanediamine [10] were prepared after the method in the literature. The synthesis of Cu(H$_2$fsapn)·1/2H$_2$O has been described previously [11].

Cu(H$_2$fsabn)

To a solution of 3-formylsalicylic acid (220 mg) and 2,3-butanediamine (100 mg) in 50% methanol (100 ml) was added an aqueous solution (30 ml) of copper acetate monohydrate (120 mg) to give purple needles. To this mixture was added acetic acid (10 ml) and the reaction mixture was kept at *ca.* 60 °C for 30 minutes, in order to convert trace amounts of Cu_2(fsabn) to Cu(H_2fsabn). The complex was isolated, washed with water and dried under reduced pressure. *Anal.* Found: C, 53.75; H, 3.98; N, 6.00%. Calcd for $C_{20}H_{18}N_2O_6Cu$: C, 53.87; H, 4.07; N, 6.28%.

Cu(H₂fsach)·½H₂O

The complex was obtained in the same way as Cu(H_2fsabn) from 3-formylsalicylic acid (220 mg), 1,2-cyclohexanediamine (68 mg) and copper(II) acetate monohydrate (120 mg). *Anal.* Found: C, 54.65; H, 4.36; N, 5.82%. Calcd for $C_{22}H_{20}N_2O_6Cu\cdot\frac{1}{2}H_2O$: C, 54.72; H, 4.38; N, 5.80%.

Cu(H₂fsaph)

The complex was obtained from 3-formylsalicylic acid (220 mg), *o*-phenylenediamine (72 mg) and copper(II) acetate monohydrate (120 mg). The product was collected and recrystallized from DMF to give greenish brown crystals. *Anal.* Found: C, 56.51; H, 3.00; N, 6.11%. Calcd for $C_{22}H_{14}N_2O_6Cu$: C, 56.48; H, 3.02; N, 5.99%.

CuNi(fsapn)·2H₂O

Cu(H_2fsapn)·½H_2O (220 mg) was dissolved in an aqueous solution (200 ml) of lithium hydroxide monohydrate (42 mg). A deep red solution obtained was once filtered in order to separate insoluble material. To this filtrate was added an aqueous solution (20 ml) of nickel(II) acetate tetrahydrate (125 mg). When the reaction mixture was concentrated to *ca.* 100 ml and left stand for 3 days reddish purple prisms separated. They were collected, washed with water and dried under vacuum. *Anal.* Found: C, 43.23; H, 3.42; N, 5.35; Cu, 12.36; Ni, 11.01%. Calcd for $C_{19}H_{18}N_2O_8CuNi$: C, 43.50; H, 3.46; N, 5.34; Cu, 12.11; Ni, 11.19%.

CuNi(fsach)·2H₂O

The complex was synthesized in the same way as CuNi(fsapn)·2H_2O from Cu(H_2fsach)·½H_2O (240 mg) and nickel(II) acetate tetrahydrate (125 mg). *Anal.* Found: C, 46.34; H, 3.91; N, 4.88; Cu, 10.97; Ni, 10.89%. Calcd for $C_{22}H_{22}N_2O_8CuNi$: C, 46.86; H, 3.93; N, 4.96; Cu, 11.25; Ni, 10.40%.

CuNi(fsaph)·5H₂O

The complex was obtained as brown micro-crystals from Cu(H_2fsaph) (240 mg) and nickel(II) acetate tetrahydrate (125 mg). *Anal.* Found: C, 43.02; H, 3.47; N, 4.80; Cu, 10.27; Ni, 9.35%. Calcd for $C_{22}H_{22}N_2O_{11}CuNi$: C, 42.99; H, 3.61; N, 4.56; Cu, 10.34; Ni, 9.55%.

CuCo(fsapn)·2H₂O

The complex was synthesized as red–purple prisms in the same way as CuNi(fsapn)·2H_2O using cobalt(II) acetate tetrahydrate except for nickel(II) acetate tetrahydrate. *Anal.* Found: C, 43.32; H, 3.49; N, 5.55; Co, 10.85; Cu, 12.56%. Calcd for $C_{19}H_{18}N_2O_8CoCu$: C, 43.48; H, 3.46; N, 5.34; Co, 11.23; Cu, 12.11%.

CuCo(fsabn)·2H₂O

The complex was obtained as blue–violet prisms from Cu(H_2fsabn) (240 mg) and cobalt(II) acetate tetrahydrate (125 mg). *Anal.* Found: C, 40.48; H, 4.25; N, 4.81; Co, 11.07; Cu, 12.24%. Calcd for $C_{20}H_{20}N_2O_8CoCu$: C, 40.52; H, 4.42; N, 4.72; Co, 10.94; Cu, 11.79%.

CuCo(fsaph)·2H₂O

The complex was obtained as red–purple micro-crystals from Cu(H_2fsaph) (240 mg) and cobalt(II) acetate tetrahydrate (125 mg). *Anal.* Found: C, 46.78; H, 2.86; N, 5.02; Co, 10.12; Cu, 11.17%. Calcd for $C_{22}H_{16}N_2O_8CoCu$: C, 47.12; H, 2.88; N, 5.00; Co, 10.51; Cu, 11.33%.

Measurements

Carbon, hydrogen and nitrogen analyses were carried out at the Service Center of Elemental Analysis, Kyushu University. Metal analyses were carried out with a Shimazu Atomic Absorption-Flama Spectrophotometer Model AA-610. Infrared spectra were measured with a Hitachi Infrared Spectrophotometer Model 215 on a KBr pellet. Electronic spectra were measured with a Shimazu Multipurpose Spectrophotometer Model MSP-5000 by reflection on a powder sample. Magnetic susceptibilities were determined by the Faraday method from the liquid nitrogen temperature to room temperature, the apparatus being calibrated using $HgCo(NCS)_4$ [12]. Diamagnetic corrections were carried out using Pascal's constants [13].

Results and Discussion

Color, selected infrared absorption bands and effective magnetic moments of the mononuclear and the hetero-metal binuclear complexes are given in Table I. The electronic spectra of the copper(II)–nickel(II) and the copper(II)–cobalt(II) complexes are shown in Figs. 2 and 3, respectively.

One of the characteristics in the infrared spectra of the complexes is the C=O stretching vibration found at 1700–1710 cm^{-1} for the mononuclear copper(II) complexes and at ~1550 cm^{-1} for the hetero-metal binuclear complexes. The C=N stretching vibration for mononuclear copper(II) complexes with Schiff bases derived from aliphatic diamines is

TABLE I. Color, Selected IR Bands and Effective Magnetic Moment of Complexes.

	Color	IR (cm^{-1})		μ_{eff}(T) (B.M.)
		C=O	C=N	
$Cu(H_2fsapn)\cdot½H_2O$	Purple	1705	1640	1.85 (294.3)
$Cu(H_2fsabn)$	Purple	1705	1645	1.84 (297.3)
$Cu(H_2fsach)\cdot½H_2O$	Purple	1705	1640	1.88 (297.5)
$Cu(H_2fsaph)$	Blue–Green	1710	1615	1.85 (297.6)
$CuNi(fsapn)\cdot2H_2O$	Red–Purple	1555	1625	3.36 (297.8)
$CuNi(fsach)\cdot2H_2O$	Red–Purple	1550	1635	3.48 (290.5)
$CuNi(fsaph)\cdot5H_2O$	Brown	1545	1610	3.78 (297.8)
$CuCo(fsapn)\cdot2H_2O$	Red–Purple	1560	1630	4.75 (297.8)
$CuCo(fsabn)\cdot2H_2O$	Blue–Violet	1555	1635	4.86 (297.7)
$CuCo(fsaph)\cdot2H_2O$	Brown	1550	1610	5.29 (294.2)

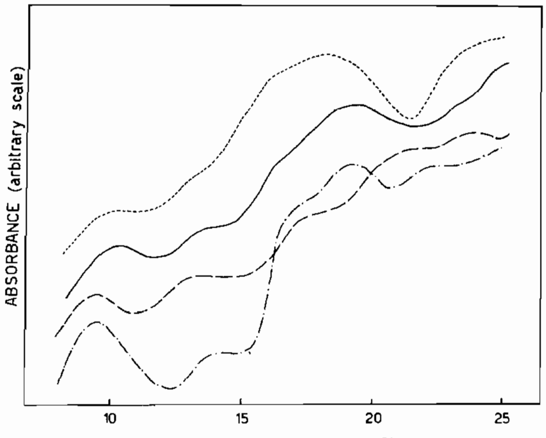

Figure 2. Electronic spectra of (——) $CuNi(fsapn)\cdot2H_2O$, (– – – –) $CuNi(fsach)\cdot2H_2O$, (------) $CuNi(fsaph)\cdot5H_2O$, and (–·–·–) $CuNi(fsaen)\cdot3H_2O$.

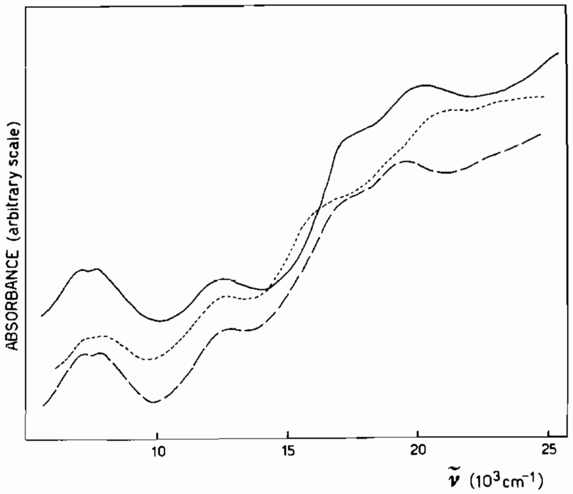

Figure 3. Electronic spectra of (——) $CuCo(fsapn)\cdot2H_2O$, (– – – –) $CuCo(fsabn)\cdot2H_2O$, and (------) $CuCo(fsaph)\cdot2H_2O$.

found at 1640–1645 cm^{-1}, while the C=N band for $Cu(H_2fsaph)$ is found at 1615 cm^{-1}. When the hetero-metal binuclear complexes are formed the C=N stretching vibration shifts to lower frequency by 5–20 cm^{-1}. Electronic spectra of mononuclear copper(II) complexes show a d–d band near 18 × 10^3 cm^{-1}. This band is practically the same in energy as that of N,N′-bis(salicylidene)ethylenediaminatocopper(II) [14]. Thus, it is evident from infrared and electronic spectral data that in the mononuclear copper(II) complexes the metal ion is in the inner coordination site.

Electronic spectra of the copper(II)–nickel(II) hetero-metal complexes display d–d bands at 9–10 and 13–14 × 10^3 cm^{-1} and complicated bands in the region 17–22 × 10^3 cm^{-1}. The d–d band due to the copper(II) ion in the copper(II)–nickel(II) hetero-metal complexes should appear near 18 × 10^3 cm^{-1}, since in comparison between $Cu(H_2fsaen)\cdot½H_2O$ and $Cu_2(fsaen)\cdot2H_2O$ (and their homologues) [11] the d–d band attributable to the copper(II) ion in the inner coordination site remains almost unaltered. Thus the remaining bands are attributed to the nickel(II) ion. In the previous paper [4] the electronic spectrum of $CuNi(fsaen)\cdot3H_2O$ was explained in terms of nickel(II) under O_h-symmetry. Judging from the fact that the electronic spectra of the present complexes resemble the spectrum of $CuNi(fsaen)\cdot3H_2O$ and that each complex contains at least two molecules of water, it is likely that the configuration around the nickel(II) ion is pseudo-octahedral with the phenolic and carboxylate oxygens at the equatorial coordinating positions and with water molecules at the apical positions.

The electronic spectra of the copper(II)–cobalt(II) hetero-metal binuclear complexes are also interpreted in terms of the planar copper(II) in the inner coordination site and the octahedral cobalt(II) in the outer coordination site. By assuming O_h-symmetry around the cobalt(II) ion, the bands at

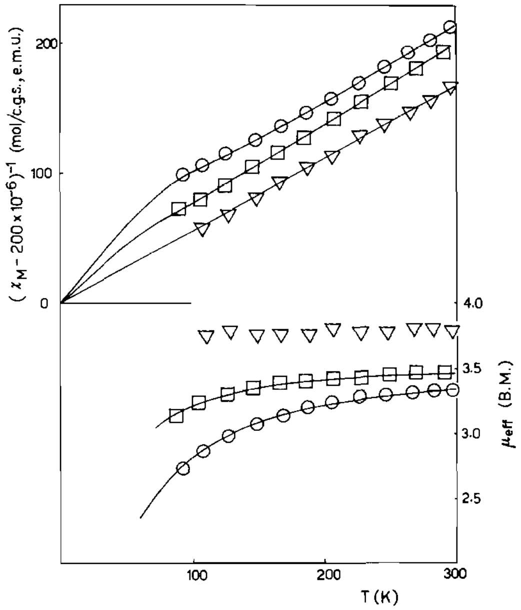

Figure 4. Temperature variations of inverse magnetic susceptibilities and magnetic moments for (○) CuNi(fsapn)•$2H_2O$, (□) CuNi(fsach)•$2H_2O$, and (△) CuNi(fsaph)•$5H_2O$.

TABLE II. Magnetic Parameters for Hetero-metal Binuclear Complexes.

	–J (cm^{-1})	g	Nα × 10^6 (c.g.s., e.m.u./mol)
CuNi(fsaen)•$3H_2O$[a]	75	2.19	200
CuNi(fsapn)•$2H_2O$	34	2.20	200
CuNi(fsach)•$2H_2O$	18	2.20	200
CuNi(fsaph)•$5H_2O$[b]			
CuCo(fsaen)•$3H_2O$	35	2.45	450
CuCo(fsapn)•$2H_2O$	36	2.44	450
CuCo(fsabn)•$2H_2O$	50	2.55	450
CuCo(fsaph)•$2H_2O$[c]			

[a]Data from Ref. 4. [b]Obeying the Curie law. [c]Obeying the Curie–Weiss law with Weiss constant of –40 °K.

7–8, 13.5 and 17–18 × 10^3 cm^{-1} may be assigned to the $^4T_{2g} \leftarrow {}^4T_{1g}$, $^2E_g \leftarrow {}^4T_{1g}$ and $^4A_{2g} \leftarrow {}^4T_{1g}$ transitions, respectively. Thus, water molecules are coordinated to the cobalt(II) ion at the fifth and sixth coordinating positions. However, the geometry around the cobalt(II) should not be regular octahedron, since the band around 7–8 × 10^3 cm^{-1} splits into two components in each spectrum, the splitting being estimated at *ca.* 1 × 10^3 cm^{-1}. This is plausible, since even in cobalt(II) Tutton salts, $(NH_4)_2Co(SO_4)_2 \cdot 6H_2O$ and $K_2Co(SO_4)_2 \cdot 6H_2O$, the ground $^4T_{1g}$ under O_h-symmetry splits into two states [15].

Magnetic susceptibility for copper(II)–nickel(II) hetero-metal complexes were determined by the Faraday method in the temperature range 78–300 K (Fig. 4). It was shown that in CuNi(fsaph)•$5H_2O$ there is little spin–spin coupling between the metal ions, the molar effective magnetic moment being almost constant and inverse magnetic susceptibilities obeying the Curie law in the temperature range 78–300 K. On the other hand, antiferromagnetic spin-exchange interaction is operating between metal ions in CuNi(fsapn)•$2H_2O$ and CuNi(fsach)•$2H_2O$, where the molar magnetic moment decreases with lowering of temperature to 2.71 B.M. at 93.0 K for CuNi(fsapn)•$2H_2O$ and to 3.13 B.M. at 87.4 K for CuNi(fsach)•$2H_2O$. The molar magnetic susceptibility for a magnetically interacting copper(II)–nickel(II) (s = 1) cluster is expressed by the expression [3, 4, 16],

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

where N is the Avogadro constant, β the Bohr magneton, k the Boltzmann constant, T the temperature, J the exchange integral and Nα the temperature-independent paramagnetism. The spin-quartet state is separated from the spin-doublet ground state by –3J. In the derivation of equation (1) it is assumed that the g-values for the spin-doublet and the spin-quartet states are the same. In spite of the obscurity in the physical meaning of g-value, the deviation of g from the free-spin value serves to evaluate the contribution from orbital angular momentum. Using equation (1) and the magnetic parameters listed in Table II, the magnetic susceptibilities and magnetic moments of CuNi(fsapn)•$2H_2O$ and CuNi(fsach)•$2H_2O$ were well explained (Fig. 4). The temperature-independent paramagnetism is assumed at 200 × 10^{-6}c.g.s., e.m.u./mol, which has been obtained with good accuracy for CuNi(fsaen)•$2H_2O$ [3]. The temperature-independent paramagnetism for a copper(II) ion is empirically known to be *ca.* 60 × 10^{-6} c.g.s., e.m.u./mol. On the other hand Nα for a nickel(II) in high-spin state is not well known. Gruber *et al.* [17] estimated the Nα value for a nickel(II) in the Cu(II)–Ni(II)–Cu(II) trinuclear complexes at 80 × 10^{-6} c.g.s., e.m.u./mol, while the Nα for $Ni(NH_3)_6Br_2$ is calculated to be 193 × 10^{-6} c.g.s., e.m.u./mol [18]. Considered from these facts the Nα value assumed for the present complexes seems quite reasonable.

Cobalt(II) ion under O_h-symmetry possesses the $^4T_{1g}$ ground state whose magnetic moment is temperature-dependent. Therefore, the magnetic susceptibility for a spin-coupled copper(II)–cobalt(II) (s = 3/2) cluster with cobalt(II) under O_h-symmetry is difficult to explain. Based on the electronic spectra in Fig. 3, however, the configuration around the cobalt(II) ion is somewhat distorted from O_h-symmetry. According to Sinn [19], the magnetic susceptibility for a polynuclear cluster can be interpreted by considering only spin–spin coupling between metal

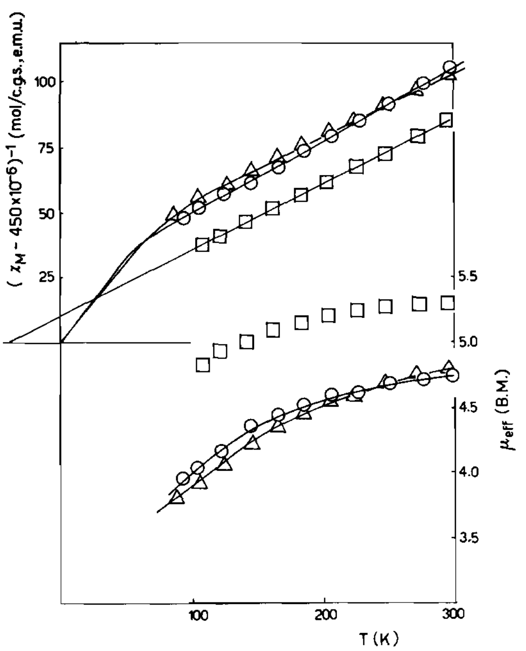

Figure 5. Temperature variation of inverse magnetic susceptibilities and magnetic moments for (○) CuCo(fsapn)$\cdot$2H_2O, (△) CuCo(fsabn)$\cdot$2H_2O, and (□) CuCo(fsaph)$\cdot$2H_2O.

ions, because the symmetry around the metal is in general lower than regular octahedron. Judging from these facts, it is likely that the Heisenberg model is applicable to the explanation for the magnetism of the present copper(II)–cobalt(II) complexes. Based on this model, the molar magnetic susceptibility for a copper(II)–cobalt(II) (s = 3/2) cluster is represented by the expression [4],

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

where each symbol has the same meaning as in expression (1). The contribution from orbital angular momentum is included in the variable g. The energy separation between the supposed spin-triplet ground state and the spin-quintet excited state is –4J. In Fig. 5 the good agreements between the experimental and the theoretical effective magnetic moments and inverse magnetic susceptibilities are shown, where theoretical curves were drawn on the basis of expression (2) using parameters given in Table II. The temperature-independent paramagnetism (450 X 10^{-6} c.g.s., e.m.u./mol) assumed for the present complexes is quite reasonable judging from the Nα value for cobalt(II) ion appeared in the literature [17]. The magnetic susceptibility for CuCo(fsaph)$\cdot$2H_2O was explained in terms of the Curie–Weiss law, $\chi_M = C/(T - \theta)$, with a Weiss constant of –40 °K. It is likely that a weak antiferromagnetic spin-exchange interaction is operating between the metal ions.

In Table II the magnetic parameters obtained for the hetero-metal binuclear complexes with 3-formylsalicylic acid-diamine Schiff bases are tabulated. It is noticed that no spin-exchange interaction was recognized in CuNi(fsaph)$\cdot$5H_2O and a weak interaction was found in CuCo(fsaph)$\cdot$2H_2O. Other hetero-metal complexes are the first examples displaying a considerable antiferromagnetic spin-spin exchange between copper(II) and high-spin nickel(II) ions and between copper(II) and high-spin cobalt(II) ions. It is worthy of remark that the exchange integrals for these complexes are comparable to those found for the Cu(II)–M(II)–Cu(II) trinuclear complexes (M(II)=Ni(II) and Co(II)) with N,N′-bis(salicylidene)ethylenediamine and its homologues [17].

References

1 Part XIX: H. Okawa, T. Tokii, M. Nakashima, Y. Muto, and S. Kida, *Mem. Fac. Sci., Kyushu Univ., Ser. C,* in press.
2 Presented at *36th Annual Meeting of the Chemical Society of Japan,* Oosaka, April 3 (1977).
3 H. Okawa, M. Tanaka, and S. Kida, *Chem. Lett.,* 987 (1974).
4 H. Okawa, Y. Nishida, M. Tanaka and S. Kida, *Bull. Chem. Soc. Jpn., 50,* 127 (1977).
5 M. Vidali, U. Casellato, P. A. Vigato and R. Graziani, *J. Inorg. Nucl. Chem., 38,* 1455 (1976).
6 R. L. Lintwedt, M. D. Glick, B. K. Tomlonovic and D. P. Gavel, *Inorg. Chem., 15,* 1646 (1976).
7 D. E. Fenton, S. E. Gayda, U. Casellato, M. Vidali and P. A. Vigato, *Inorg. Chim. Acta, 21* L29 (1977).
8 M. Vidali, P. A. Vigato, and U. Casellato, *Inorg. Chim. Acta, 17,* L5 (1976).
9 J. C. Duff and E. J. Bills, *J. Chem. Soc.,* 1987 (1932).
10 F. H. Dickey, W. Fickett, and H. J. Lucas, *J. Am. Chem. Soc., 74,* 944 (1952).
11 M. Tanaka, M. Kitaoka, H. Okawa, and S. Kida, *Bull. Chem. Soc. Jpn., 49,* 2469 (1976).
12 B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.,* 331 (1959).
13 P. W. Selwood, "Magnetochemistry", Interscience, New York (1956), pp. 78, 91.
14 R. H. Holm, *J. Am. Chem. Soc., 82,* 5632 (1960).
15 A. Bose, A. S. Chakravarty, and R. Chatterki, *Proc. Roy. Soc. (London), A261,* 207 (1961).
16 J. S. Griffith, *Mol. Phys., 21,* 141 (1971).
17 S. J. Gruber, C. M. Harris, and E. Sinn, *J. Chem. Phys., 49,* 2183 (1968).
18 Ballhausen, "Introduction to Ligand Field Theory", McGraw-Hill, New York (1962), p. 142.
19 E. Sinn, *Coord. Chem. Rev., 5,* 313 (1970).