Binuclear Metal Complexes. IX.[1] Syntheses and Magnetic Properties of Copper(II) and Nickel(II) Complexes of Schiff Bases Derived from 3-Formylsalicylic Acid and Alkyl Amines

Mitsunori Tanaka, Hisashi Okawa,* Tomoko Tamura, and Sigeo Kida*

Faculty of Education, Kagawa University, Takamatsu, Kagawa 760

**Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812*

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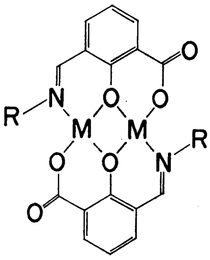
Copper(II) and nickel(II) complexes of H_2fsac-R have been synthesized, where H_2fsac-R denotes the Schiff bases prepared from 3-formylsalicylic acid and alkylamines (alkyl(R)=methyl, ethyl, hydroxyethyl, *n*-propyl, *n*-butyl, isobutyl, and *sec*-butyl). On the bases of elemental analyses, IR spectra, visible spectra and cryomagnetic measurements, it was found that the complexes have a binuclear structure connected by two phenolic oxygens; the complexes are abbreviated to M_2(fsac-R)$_2$. The nickel(II) complexes contain two, three or four molecules of coordinated water. The cryomagnetic data for Cu_2(fsac-R)$_2$ are interpreted in terms of the Bleaney-Bowers equation with large $-2J$ values (>700 cm^{-1}), indicating the presence of strong intramolecular antiferromagnetic spin-exchange interactions. The Ni_2(fsac-R)$_2 \cdot n$H$_2$O obey the Curie-Weiss law, the Weiss constants being estimated to -35—-41 K.

In the previous paper of this series,[2] it was shown that 3-formylsalicylic acid forms binuclear copper(II) and nickel(II) complexes bridged by the phenolic oxygens. This report relates to the syntheses and characterization of the copper(II) and nickel(II) complexes of the Schiff bases derived from 3-formylsalicylic acid and alkylamines (R-NH$_2$). The Schiff bases are abbreviated to H_2fsac-R, in which R is methyl, ethyl, hydroxyethyl, *n*-propyl, *n*-butyl, isobutyl, or *sec*-butyl. Based on elemental analyses, IR spectra, visible spectra, and cryomagnetic data, the complexes seem to possess the binuclear structure shown in Fig. 1. The complexes are denoted by M_2(fsac-R)$_2$.



R=alkyl
M=Cu(II), Ni(II)

Fig. 1.

The copper(II) complexes are similar in structure to dihalogenobis(N-alkylsalicylaldimino)dicopper(II) complexes,[3-7] whose magnetic properties have been well elucidated. The exchange integrals of Cu_2(fsac-R)$_2$ were discussed in comparison with those of the above complexes.

Experimental

Syntheses. 3-Formylsalicylic acid was prepared after the method of Duff and Bills.[8] The synthetic methods of the complexes are nearly the same. A typical procedure is as follows. To an aqueous solution (30 ml) of sodium carbonate (106 mg) containing 3-formylsalicylic acid (154 mg) and ethylamine (70% aqueous solution, 75 mg), was added an aqueous solution (30 ml) of copper(II) acetate monohydrate (200 mg). The mixture was heated at 60 °C on a water-bath for a while to give blue prisms, which were collected and thoroughly washed with hot water. The nickel(II) complexes were obtained as yellowish green prisms using nickel(II) acetate tetrahydrate as a metal source. The analytical data are given in Table 1.

Table 1. Elemental analyses of complexes

	Found (%)			Calcd (%)		
	C	H	N	C	H	N
Cu_2(fsac-Me)$_2$	44.56	2.93	5.45	44.91	2.93	5.82
Cu_2(fsac-Et)$_2 \cdot 1/2H_2O$	46.23	3.38	4.93	46.33	3.69	5.40
Cu_2(fsac-enOH)$_2$	44.03	3.34	5.04	44.37	3.35	5.17
Cu_2(fsac-Pr)$_2 \cdot H_2O$	47.96	4.02	4.56	47.57	4.35	5.04
Cu_2(fsac-*n*-Bt)$_2 \cdot 1/2H_2O$	49.82	4.70	4.71	50.17	4.74	4.88
Cu_2(fsac-*i*-Bt)$_2 \cdot 1/2H_2O$	49.85	4.48	4.51	50.17	4.74	4.88
Cu_2(fsac-*s*-Bt)$_2 \cdot 1/2H_2O$	50.26	4.58	4.77	50.17	4.74	4.88
Ni_2(fasc-Me)$_2 \cdot 2H_2O$	41.25	3.59	4.80	41.12	3.83	5.33
Ni_2(fsac-Et)$_2 \cdot 3H_2O$	43.03	4.12	4.55	43.37	4.37	5.06
Ni_2(fsac-enOH)$_2 \cdot 2H_2O$	41.44	3.78	4.54	41.65	3.84	4.86
Ni_2(fsac-*n*-Bt)$_2 \cdot 4H_2O$	46.28	5.10	4.15	45.91	5.45	4.46

Measurements. Magnetic susceptibilities of the comlexes were measured by the Faraday method from liquid nitrogen temperature to room temperature. The Pascal constants[9] were used for diamagnetic correction. The effective magnetic moments were determined by the equation, $\mu_{eff}=2.828\sqrt{(\chi_A-N\alpha)T}$, where the temperature-independent paramagnetism for nickel(II) ion is estimated at 193×10^{-6} e.s.u./mol.[10] The infrared spectra were measured with a Hitachi 215 grating infrared spectrophotometer in the region 4000—650 cm^{-1}. In some cases the hexachlorobutadiene-mull method was applied for the measurements in the region 4000—2000 cm^{-1}. Electronic spectra on solids and in pyridine solutions were obtained with a Hitachi EPS-3T spectrophotometer.

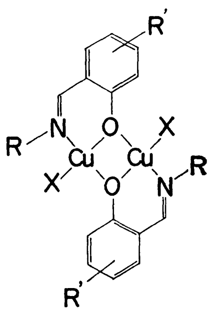
Results and Discussion

Copper(II) Complexes. Some IR bands, ligand field bands (powder and pyridine solution) and effective magnetic moments at room temperature are given in Table 2. The IR bands near 1640 and 1545 cm^{-1} were tentatively assigned to the azomethine and the

TABLE 2. PROPERTIES OF $Cu_2(fsac\text{-}R)_2$ COMPLEXES

	IR (cm^{-1})		d-d (kK)		μ_{eff} (K) (B.M.)
	C=N	COO^-	solid	py (ε)	
$Cu_2(fsac\text{-}Me)_2$	1645	1550	15.3	15.1 (124)	0.68 (297.7)
$Cu_2(fsac\text{-}Et)_2$	1640	1545	14.9	14.8 (118)	0.66 (291.6)
$Cu_2(fsac\text{-}enOH)_2$	1635	1540	15.4	15.1 (128)	0.54 (297.7)
$Cu_2(fsac\text{-}Pr)_2$	1635	1540	14.7	14.4 (114)	0.66 (294.2)
$Cu_2(fsac\text{-}n\text{-}Bt)_2$	1635	1545	14.8	14.6 (101)	0.71 (296.6)
$Cu_2(fsac\text{-}i\text{-}Bt)_2$	1630	1550	14.8	14.6 (119)	0.63 (294.1)
$Cu_2(fsac\text{-}s\text{-}Bt)_2$	1635	1545	14.7	14.4 (101)	0.63 (295.4)

carboxylate groups respectively. The skeletal vibration near 1550 cm^{-1} is useful to distinguish the binuclear structure bridged by phenolic oxygen.[3,11] In the present complexes, however, this band could not be well recognized owing to the strong absorption of the carboxylate group. The reflectance spectra of the complexes show a d-d band in the region 15.4—14.9 kK, that is higher in energy than that (14.1 kK) for bis-(3-formylsalicylato)dicopper(II)[2] (which is a $[CuO_4]$-chromophore). The spectral data are consistent with the binuclear structure of the $[CuO_3N]$-chromophore (Fig. 1), since most $[CuO_2N_2]$-chromophores containing bridging oxygen atoms exhibit a ligand field band in the region 15.4—18.5 kK.[12–15] The effective magnetic moments at room temperature are much lower than the spin-only value. From all of these facts, it is concluded that the complexes possess a binuclear structure given in Fig. 1. The oxygen of the hydroxyethyl substituent in $Cu_2(fsac\text{-}enOH)_2$ does not seem to coordinate to the copper(II) ion, since the O–H stretching vibration is found around 3400 cm^{-1}. This fact is in line with Tokii *et al.*'s finding[7] that dichlorobis(*N*-hydroxyethylsalicylaldimino)dicopper(II) has a binuclear structure as shown in Fig. 2 and the hydroxy group in the *N*-substituent is not concerned with coordination.



R=alkyl, aryl
R'=alkyl
X=Cl, Br

Fig. 2.

The ligand field band determined from pyridine solution spectrum of each complex is located to lower energy region than that from the corresponding powder spectrum. Since the shifts, however, are small (0.1—0.3 kK) and no splitting is found in each spectrum, the complexes seem to keep binuclear structure in pyridine, in which no coordination of pyridine to the metal is supposed. When the pyridine solution was concentrated, the pyridine-free complexes were recovered.

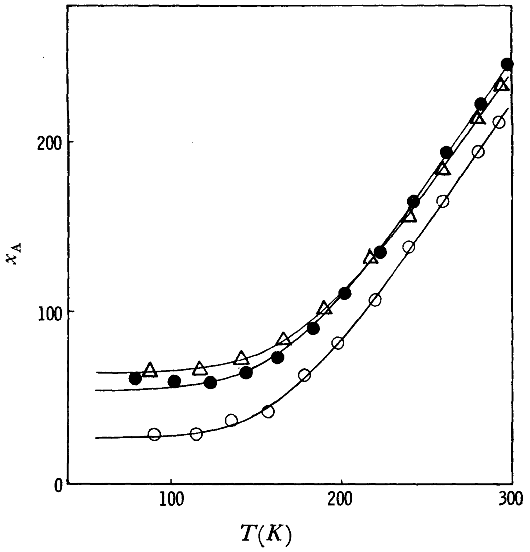


Fig. 3. Variation of molar susceptibility of $Cu_2(fsac\text{—}R)_2$ complexes; (●) R=Me, (○) R=Et, and (△) R=Pr.

The magnetic susceptibilities of the complexes were measured at various temperatures. The results were well interpreted on the basis of the Bleaney-Bowers equation,[16]

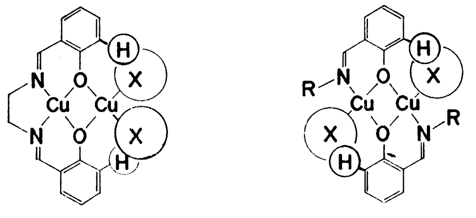
$$\chi_A = \frac{Ng^2\beta^2}{3kT}\left[1+\frac{1}{3}\exp\left(-2J/kT\right)\right]^{-1} + N\alpha,$$

where J is the exchange integral, k the Boltzmann constant, N the Avogadro number, β the Bohr magneton and g the Lange g-factor. The typical examples are shown in Fig. 3. The magnetic parameters, $-2J$, g and $N\alpha$, determined from the best fit of the data to the Bleaney-Bowers equation are given in Table 3. Judging from the $-2J$ values (which are energy separation between the singlet and triplet states) of the complexes presented here, it does not seem that the substituents attached to the imino-nitrogen exert any appreciable effect upon the spin-exchange interaction.

TABLE 3. MAGNETIC PARAMETERS OF $Cu_2(fsac\text{-}R)_2$ COMPLEXES

	$-2J$ (cm^{-1})	g	$N\alpha\times 10^6$ (e.s.u./mol)
$Cu_2(fsac\text{-}Me)_2$	720	2.20	55
$Cu_2(fsac\text{-}Et)_2$	715	2.20	27
$Cu_2(fsac\text{-}enOH)_2$	820	2.20	37
$Cu_2(fsac\text{-}Pr)_2$	725	2.20	55
$Cu_2(fsac\text{-}n\text{-}Bt)_2$	705	2.20	35
$Cu_2(fsac\text{-}i\text{-}Bt)_2$	735	2.17	65
$Cu_2(fsac\text{-}s\text{-}Bt)_2$	750	2.20	50

The magnetic properties of dihalogenobis(*N*-alkylsalicylaldimino(dicopper(II)complexes, which are similar to the present complexes, were explored by Kato *et al.*[6,7] and Harris *et al.*[3–5] The $-2J$ values of these complexes are in the range 194—580 cm^{-1}, depending upon the substituents attached to the aromatic ring and the



(a) (b)

Fig. 4.

imino-nitrogen. Therefore, it is evident that our complexes exhibit a very strong antiferromagnetic spin-exchange interaction compared to the dihalogenobis-(*N*-alkylsalicylaldimino)dicopper(II) complexes.

The difference in magnetic properties between the present complexes and dihalogenobis(*N*-alkylsalicylaldimino)dicopper(II) complexes can be explained in terms of the geometries of the complexes. It was demonstrated from X-ray investigation[17)] that the coplanarity of two tetragonal planes of the copper(II) ion in dichloro [*N*, *N'*-ethylenebis (salicylaldimino) copper (II)]-copper(II) is considerably distorted owing to the steric repulsions between the chloro group and the hydrogen attached to the 3-position of the salicylaldehyde moiety (Fig. 4a). From the same steric requirement (Fig. 4b), it is also expected that the $\substack{X\\N}{>}Cu{<}\substack{O\\O}{>}Cu{<}\substack{N\\X}$ plane in dihalogenobis (*N*-alkylsalicylaldimino) dicopper (II) complexes is distorted. In fact Sinn *et al.*[18)] have recently studied the structures of dichlorobis(*N*-methylsalicylaldimino) dicopper (II), dichlorobis (*N*-ethylsalicylaldimino)dicopper(II) and dibromobis(*N*-ethylsalicylaldimino)dicopper(II) and found that the dihedral angles between the planes formed by Cu_2O_2 and $Cu_2N_2Cl_2$ are appreciably large (39.3° for R=methyl and X=chloro, 33.1° for R=ethyl and X=chloro, and 35.7° for R=ethyl and X=bromo). On the other hand, such a steric hindrance is not anticipated for the present complexes, since the carboxyl group attached to 3-position is involved in coordination to the copper(II) ion. Accordingly our complexes seem to have a nearly coplanar structure in regard to the $\substack{N\\O}{>}Cu{<}\substack{O\\O}{>}Cu{<}\substack{O\\N}$ plane. In this case the overlapping of $d_\pi(Cu)$-$p_\pi(O)$-$d_\pi(Cu)$ orbitals is sufficiently large, thereby strengthening the spin-exchange interaction. An importance of π-superexchange pathway in spin-exchange interaction for binuclear copper(II) complexes has been reported.[13,19)] The present result is in line with the previous findings[20—22)] that the more coplanar the tetragonal planes of the copper(II) ions is, the larger the magnetic exchange interaction between the copper(II) ions becomes.

Nickel(II) Complexes. The nickel(II) complexes forms yellowish green prisms containing two, three or four water molecules. Some IR bands, d-d bands (powder and pyridine solution) and effective magnetic moments at room temperature and near liquid nitrogen temperature are given in Table 4. The IR bands near 1635 and 1565 cm^{-1} may be attributed to the azomethine and the carboxylate groups respectively. The broad band around 3300 cm^{-1} is assigned to the O–H vibration of coordinated water. The reflectance spectra of the complexes show two bands in visible region: 8.7—8.9 and 15.4—15.7 kK. This fact clearly indicates that the nickel(II) ion has a nearly octahedral geometry, although the complexes have only two or three molecules of water except Ni_2(fsac-*n*-Bt)$_2$·$4H_2O$. The solution spectrum of each complex in pyridine shows the first d-d band (which corresponds to 10 Dq) in the region 9.5—9.6 kK, which is higher by 0.7—0.9 kK than that from the corresponding powder spectrum. This fact implies that in pyridine solution the complexes are coordinated with solvents in apical positions.

The magnetic moments at room temperature are comparable to the values for common octahedral nickel(II) complexes. On the other hand, the values near liquid nitrogen temperature are lower than the spin-only value, 2.83 B.M. These facts imply an antiferromagnetic spin-exchange interaction between nickel-

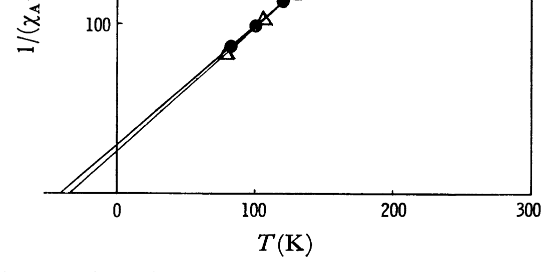


Fig. 5. Plots of inverse susceptibilities of (●) Ni_2(fsac—Et)$_2$·$3H_2O$ and (△) Ni_2(fsac–enOH)$_2$·$2H_2O$ per a nickel atom as a function of temperature.

Table 4. Properties of Ni_2(fsac-R)$_2$·nH_2O complexes

	IR (cm^{-1})			d-d (kK)				μ_{eff} (K) (B.M.)	
	O–H	C=N	COO$^-$	powder		py (ε)			
Ni_2(fsac-Me)$_2$·$2H_2O$	3300	1640	1560	8.8	15.4	9.6(42)	15.9(38)	3.14(197.8)	2.76(87.0)
Ni_2(fsac-Et)$_2$·$3H_2O$	3300	1640	1560	8.7	15.7	9.5(35)	15.7(33)	3.10(293.0)	2.64(77.5)
Ni_2(fsac-enOH)$_2$·$2H_2O$	3300	1630	1570	8.7	15.6	9.6(37)	16.0(35)	3.06(291.7)	2.74(83.5)
Ni_2(fsac-*n*-Bt)$_2$·$4H_2O$	3300	1635	1570	8.9	15.5	9.6(42)	16.1(40)	3.17(296.6)	2.72(87.1)

(II) ions. To elucidate the magnetic behaviors of the complexes, the magnetic susceptibilities were measured as a function of temperature. The results were well interpreted on the basis of the Curie-Weiss law, $\chi_A = C/(T-\theta)$. The representatives of the $1/(\chi_A - 193 \times 10^{-6})$ *versus* T plots are shown in Fig. 5. The Weiss constants obtained are −35 K for R=methyl, −41 K for R=ethyl, −35 K for R=hydroxyethyl, and −40 K for R=*n*-butyl.

There are a few binuclear nickel(II) complexes, in which two nickel(II) ions are connected by the phenolic oxygens.[2,23,24] These complexes show demagnetization by the spin-coupling *via* the phenolic oxygen bridges; the Weiss constants are estimated at −50—−125 °C. In general, the Weiss constants of the mononuclear nickel(II) complexes are small, say a few degrees at best. Therefore, judging from the magnitude of the Weiss constants it may be concluded that the demagnetization in $Ni_2(fsac\text{-}R)_2 \cdot nH_2O$ is caused by the intramolecular spin-exchange interaction through the oxygen bridges.

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