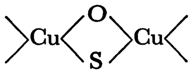
Binuclear Metal Complexes. XIII.[1] Syntheses and Magnetic Properties of Thiocyanato-Bridged Binuclear Copper(II) Complexes

Tomoko Ichinose, Yuzo Nishida, Hisashi Okawa,* and Sigeo Kida
Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812

(Received July 26, 1974)

Three binuclear copper(II) complexes, Cu_2(fsal-NMe_2)$(NCS)_3$, Cu_2(fsal-NEt_2)$(NCS)_3$ and Cu_2(fsal-pa)$(NCS)_3$, have been synthesized and characterized, where Hfsal-NMe_2, Hfsal-ENt_2 and Hfsal-pa denote the Schiff bases prepared by the condensation reaction of 2,6-diformyl-4-methylphenol with *N,N*-dimethylethylenediamine, *N,N*-diethylethylenediamine and 2-pyridylmethylamine, respectively. It was demonstrated that the complexes essentially consist of a binuclear unit of the thiocyanato-bridged skeleton,  . The cryomagnetic properties could be explained on the basis of the equation for the tetranuclear cluster formed with two binuclear units linked by the out-of-plane bonding. The magnetisms and structures of the complexes were discussed in comparison with those of the Cu_2(fsal–NR_2)X_3 (X=Cl, Br).

It is well known[2–7] that the Schiff bases of 2,6-diformyl-4-methylphenol form binuclear copper(II) complexes, in which copper(II) ions are connected by two different groups, *i.e.*, the phenolic oxygen and an anion, X^-, such as Cl^-, Br^-, OH^-, OR^-, N_3^-, and $C_3H_3N_2^-$ (the conjugate base of pyrazole). However, no binuclear copper(II) complexes possessing thiocyanato-bridging group has been obtained. In the preceeding paper of this series,[5] we reported the syntheses and magnetisms of some binuclear copper(II) complexes of the Schiff bases derived from 2,6-diformyl-4-methylphenol and *N,N*-dialkylethylenediamines (See Fig. 1). Their magnetic properties were well explained in terms of the Bleaney-Bowers equation and it was found that the magnitude of the spin-exchange integral, $-J$, decreased in the order X=OH>Br>Cl.

The object of this study is to synthesize the thiocyanato-bridged binuclear copper(II) complexes and to investigate their magnetic properties in comparison with those of the corresponding hydroxo-, chloro-, or bromo-bridged complexes.

The ligands used in this work are the Schiff bases derived from 2,6-diformyl-4-methylphenol and amines such as *N,N*-dimethylethylenediamine, *N,N*-diethylethylenediamine, and 2-pyridylmethylamine (the ligands are abbreviated to Hfsal-NMe_2, Hfsal-NEt_2, and Hfsal-pa respectively). On treating these ligands and diisothiocyanatodipyridinecopper(II) in acetonitrile, green prisms were obtained. Based on the results of elemental analyses, the complexes are formulated as Cu_2(fsal-NR_2)$(NCS)_3$ (R=Me and Et) and Cu_2(fsal-pa)$(NCS)_3$. The structures of these complexes were investigated on the basis of the infrared spectra, electronic spectra and magnetic measurements. The spin-exchange interactions between copper(II) ions were studied by measuring the temperature variation of magnetic susceptibility.

Experimental

Syntheses. The synthetic method of 2,6-diformyl-4-methylphenol was described elsewhere.[8] *N,N*-Dimethylethylenediamine, *N,N*-diethylethylenediamine and 2-pyridylmethylamine were of commercial origin.

Cu_2(fsal-NMe_2)$(NCS)_3$. 2,6-Diformyl-4-methylphenol (165 mg), and *N,N*-dimethylethylenediamine (176 mg) and diisothiocyanatodipyridinecopper(II) (675 mg) were mixed in acetonitrile (100 ml) and the mixture was stirred at room temperature for 20 hr. The green precipitate which separated was collected, recrystallized from dimethyl sulfoxide–methanol and dried over P_2O_5 under a reduced pressure.

Found: C, 39.62; H, 4.62; N, 16.00; Cu, 20.20%. Calcd. for $C_{22}H_{31}N_7OS_3Cu_2$: C, 39.72; H, 4.50; N, 16.21; Cu, 21.01%.

Cu_2(fsal-NEt_2)$(NCS)_3$. This complex was prepared by a method similar to that for Cu_2(fsal-NMe_2)$(NCS)_3$ except for using *N,N*-diethylethylenediamine (232 mg) instead of *N,N*-dimethylethylenediamine. The green product was recrystallized from acetonitrile and dried over P_2O_5 under a reduced pressure.

Found: C, 43.61; H, 5.24; N, 14.69; Cu, 18.93%. Calcd for $C_{24}H_{35}N_7OS_3Cu_2$: C, 43.62; H, 5.34; N, 14.84; Cu, 19.23%.

Cu_2(fsal-pa)$(NCS)_3$. This complex was synthesized by the reaction of 2,6-diformyl-4-methylphenol (165 mg), 2-pyridylmethylamine (216 mg) and diisothiocyanatodipyridinecopper(II). The green product was recrystallized from acetonitrile and dried over P_2O_5 under a reduced pressure.

Found: C, 44.28; H, 2.90; N, 14.92; Cu, 20.58%. Calcd for $C_{24}H_{19}N_7OS_3Cu_2$: C, 44.71; H, 2.97; N, 15.21; Cu, 19.71%.

Measurements. Infrared spectra were measured with a Hitachi 215 grating spectrophotometer on a KBr disk. Electronic spectra were measured with a Hitachi EPS-3T recording spectrophotometer. Magnetic susceptibilities were measured by the Faraday method over the range from liquid nitrogen temperature to room temperature. Effective magnetic moments were calculated from the equation, $\mu_{eff}=2.828\sqrt{(\chi_A-N\alpha)T}$, where χ_A is the atomic magnetic susceptibility corrected for diamagnetism and $N\alpha$ is the temperature-indepenent paramagnetism. Pascal's constants[9] were used for the correction of diamagnetism.

Results and Discussion

Infrared absorption bands, ligand-field bands (reflectance on solids) and effective magnetic moments at room temperature of the complexes are given in Table 1. The complexes obtained have the composition of L (organic ligand moiety) : Cu : NCS^-=1 ;

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* To whom correspondence should be addressed.

TABLE 1. IR BANDS, d-d BANDS, AND EFFECTIVE MAGNETIC MOMENTS OF COMPLEXES

	IR (cm^{-1})				Reflectance (kK)	μ_{eff} (K) (B.M.)
	C≡N	C-S	C=N	skeletal		
Cu_2(fsal-NMe_2)$(NCS)_3$	2080 2070	815 700	1635 1630	1550	15.2	1.57(298.0)
Cu_2(fsal-NEt_2)$(NCS)_3$	2080 2070	810 730	1640 1627	1550	14.3	1.62(297.0)
Cu_2(fsal-pa)$(NCS)_3$	2080 2060	820 720	1640	1550	14.3	1.57(296.0)

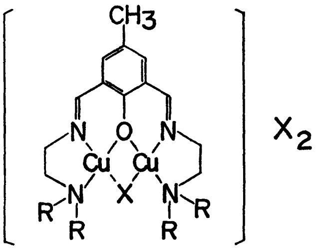
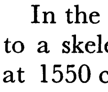
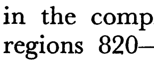
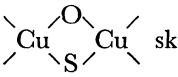


Fig. 1.

2 : 3. Therefore, the structures of the complexes are expected to be similar to those of the previously reported complexes given in Fig. 1. In fact the infrared spectra of Cu_2(fsal)-NR_2)$(NCS)_3$ are very similar to those of the corresponding Cu_2(fsal-NR_2)X_3[5] (X=Cl or Br, the halogenobridged complexes given in Fig. 1) in the region 4000—650 cm^{-1}, except some additional absorption bands observed for the present complexes. Hoskins *et al.*[7] studied the structure of the binuclear nickel(II) complex of 2,6-bis(thiosemicarbazonomethyl)-4-methylphenol and found that it has a skeleton  , *i.e.*, nickel(II) ions are connected by the phenolic oxygen and a $C_2H_5O^-$ group. Judging from this fact and from the infrared spectra of Cu_2(fsal-NR_2)$(NCS)_3$ similar to those of Cu_2(fsal-NR_2)X_3, it is likely that the present complexes have a skeleton  (Y=$^-$SCN or $^-$NCS).

In the infrared spectra of the complexes the band due to a skeletal vibration of the benzene ring is observed at 1550 cm^{-1}. This implies that the phenolic oxygen is concerned with bridging.[10] Two C-N stretching vibrations of thiocyanate group were found in the region 2080—2060 cm^{-1}, suggesting that there are two kinds of thiocyanate group of different bonding modes in the complexes. There are also two bands in the regions 820—810 and 730—700 cm^{-1}, which may be assigned to the C-S stretching vibrations of thiocyanate group. The band at 820—810 cm^{-1} may be due to the Cu-NCS bond, since this band is very close in frequency to the $\nu_{\mathrm{C-S}}$ band of [Cu(tren)NCS]NCS, whose copper(II)-NCS linkage was demonstrated from the X-ray investigation.[11] The band at 730—700 cm^{-1} is located at lower frequency side compared with the $\nu_{\mathrm{C-S}}$ band (745—750 cm^{-1}) of non-coordinated thiocyanate ion. In general the C-S stretching vibration of the soft metal complexes such as $(Et_4N)_2[Pd(SCN)_4]$ containing M-SCN bond are found in the region 720—690 cm^{-1}.[12] Therefore it is natural to assign this band to the C-S stretching vibration of the S-bonded thiocyanate group. It is well known that thiocyanate is always coordinated to a copper(II) ion with its N-atom. In addition to this the $\rangle$S-C≡N bridging mode is known,[13] whereas the $\rangle$N=C=S bridging have never been demonstrated. Thus it is very likely that two copper(II) ions are connected by the $\rangle$S-C≡N group and the N-bonded thiocyanates coordinate to copper(II) ions in the apical positions. It seems that the steric requirement of the ligands favors the formation of the binuclear copper(II) complex with the  skeleton.

All complexes show effective magnetic moments smaller than the spin-only value at room temperature. The magnetic susceptibilities were measured over a temperature range from liquid nitrogen temperature to room temperature. The magnetic parameters for Cu_2(fsal-NMe_2)$(NCS)_3$ can be estimated as g=1.99, $N\alpha$=60×10^{-6} c.g.s., e.m.u. and $-2J$=205 cm^{-1} from the best fit of the χ_A values to the Bleaney-Bowers equation,[14]

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

However, it seems unreasonable to assume the g value smaller than 2.0 for copper(II) complexes. When the $-2J$ value is chosen so as to fit the χ_A value calculated from the Bleaney-Bowers equation to the experimental χ_A value at room temperature, assuming g=2.15 and $N\alpha$=60×10^{-6} c.g.s., e.m.u. (which are very common values for copper(II) complexes), significant deviation is observed between the experimental and theoretical $\chi_A - T$ curves as shown in Fig. 3. Cu_2(fsal-NEt_2)$(NCS)_3$ and Cu_2(fsal-pa)$(NCS)_3$ displayed similar magnetic behaviors. The facts mentioned above imply that the present complexes are not binuclear.

Recently Hoskins *et al.*[15] reported that the cobalt(II)-cobalt(III) complex of the Schiff base derived from 2,6-diformyl-4-methylphenol and 2-aminophenol has a tetranuclear structure, in which the planar binuclear units are linked by out-of-plane bonds. Therefore, it is likely that the present complexes also have a similar structure and show a magnetic property of a tetranuclear cluster. Based on the tetranuclear structure given in Fig. 2, the spin Hamiltonian may be described as

$$\mathscr{H} = -2J_{13}S_1S_3 - 2J_{24}S_2S_4 - 2J_{12}S_1S_2 - 2J_{23}S_2S_3 - 2J_{14}S_1S_4 - 2J_{34}S_3S_4.$$

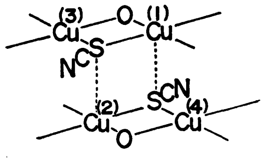


Fig. 2.

On assuming $J_{13}=J_{24}=J$, $J_{12}=J_{23}=J_{14}=J'$ and $J_{34}=0$, the magnetic susceptibility is expressed by the equation,

$$\chi_A = \frac{3g^2}{32T} \times \frac{\begin{array}{l} 10\exp[(J+3/2J')/kT]+2\exp[(-J-J'/2)/kT] \\ +2\exp[(-J'/2+\sqrt{2J'^2-2JJ'+J^2})/kT] \\ +2\exp[(-J'/2-\sqrt{2J'^2-2JJ'+J^2})/kT] \end{array}}{\begin{array}{l} 4\exp[(J+3/2J')/kT]+2\exp[(-J-J'/2)/kT] \\ +\exp[-Q(11)/kT]+\exp[-Q(22)/kT] \\ +\exp[-Q(33)/kT]+\exp[-Q(44)/kT] \\ +3\exp[(-J'/2+\sqrt{2J'^2-2JJ'+J^2})/kT] \\ +3\exp[(-J'/2-\sqrt{2J'^2-2JJ'+J^2})/kK] \end{array}} + N\alpha,$$

where $Q(11)$, $Q(22)$, $Q(33)$ and $Q(44)$ have the same meaning as was given by Hatfield *et al.*[16] As is shown in Fig. 3, the magnetic properties of the complexes can be well explained on the basis of the equation. The magnetic parameters, $-J$, $-J'$, g and $N\alpha$, obtained from the best fit of experimental χ_A values to the equation are listed in Table 2. Accordingly, it is evident that $Cu_2(fsal\text{-}NR_2)(SCN)_3$ and $Cu_2(fsal\text{-}pa)(NCS)_3$, which are essentially binuclear complexes with $\begin{smallmatrix}\diagdown & & O & & \diagup \\ & Cu & & Cu & \\ \diagup & & S & & \diagdown\end{smallmatrix}$ linkage, exhibit the magnetic behavior of a tetranuclear cluster, because of the out-of-plane linkage between two binuclear units. The most probable molecular structures of the complexes are given in Fig. 4.

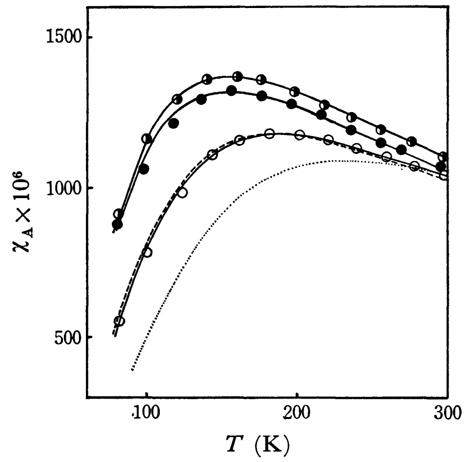


Fig. 3. Variation of molar suceptibilities per copper atom of (○) $Cu_2(fsal\text{-}NMe_2)(NCS)_3$, (◑) $Cu_2(fsal\text{-}NEt_2)(NCS)_3$ and (●) $Cu_2(fsal\text{-}pa)(NCS)_3$ as a function of temperature.
solid lines : theoretical curves based on the tetranuclear cluster using the parameters given in Table 2.
broken line : theoretical curve based on the Bleaney-Bowers equation using the parameters $g=1.99$, $N\alpha=60\times10^{-6}$ c.g.s. e.m.u. and $-2J=-205$ cm^{-1}.
dotted line : theoretical curve based on the Bleaney-Bowers equation assuming $g=2.15$, $N\alpha=60\times10^{-6}$ c.g.s. e.m.u. and $-2J=260$ cm^{-1}.

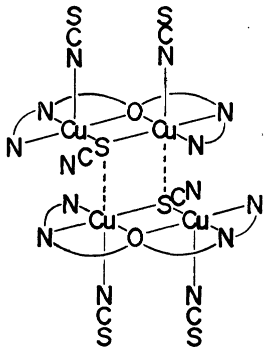


Fig. 4. Most probable structure of the complexes.

TABLE 2. MAGNETIC PARAMETERS OF COMPLEXES

	$-J$ (cm^{-1})	$-J'$ (cm^{-1})	g	$N\alpha\times10^6$ (c.g.s.e.m.u.)
$Cu_2(fsal\text{-}NMe_2)(NCS)_3$	105	15	2.18	43
$Cu_2(fsal\text{-}NEt_2)(NCS)_3$	87.5	20	2.17	50
$Cu_2(fsal\text{-}pa)(NCS)_3$	87.5	25	2.15	45

As is seen in Table 2, the $-J'$ values are of the order of 1/7∼1/4 of the $-J$ values. It is also seen that the $-J$ value is decreased when the $-J'$ value is increased. It is generally observed that the larger spin-exchange interaction operates between the copper(II) ions, the more coplanar the $\begin{smallmatrix}\diagdown & & O & & \diagup \\ & Cu & & Cu & \\ \diagup & & O & & \diagdown\end{smallmatrix}$ plane becomes.[17,18] It is compartible with this trend that the largest $-J$ value was observed for $Cu_2(fsal\text{-}NMe_2)(NCS)_3$ whose d-d band is highest in energy among those of the presently studied complexes. We were unsuccessful to obtain $Cu_2(fsal\text{-}N\text{-}i\text{-}Pr_2)(NCS)_3$. This fact implies that the bulky substituents attached to the nitrogen sterically hinder the complex formation of this type of structure.

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