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Binuclear Metal Complexes. XXXV.[1] Synthesis and Magnetism of Binuclear Copper(II) Complexes with 3-[2-(Dialkylamino)ethylthio]-1-propanols

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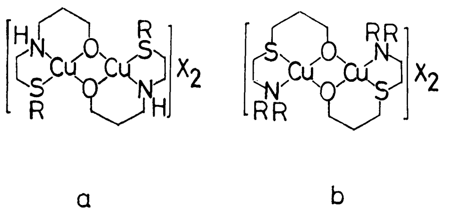
Synopsis. Binuclear copper(II) complexes with 3-[2-(dialkylamino)ethylthio]-1-propanols, $Cu[R_2N(CH_2)_2S(CH_2)_3O]X$ ($R=CH_3$, C_2H_5; $X=NO_3^-$, ClO_4^-), were prepared and their magnetic properties were investigated in the temperature range 80—300K. The magnetisms were interpreted in terms of the Bleaney-Bowers equation with exchange integral $-J=450$—$495\ cm^{-1}$, which is much larger than the values ($-J=\approx 250\ cm^{-1}$) for $Cu[R_2N(CH_2)_2NH(CH_2)_3O]X$.

As a part of the continuing study on binuclear copper(II) complexes mimic to type III copper,[2] we recently reported the synthesis and spectral and magnetic properties of the binuclear copper(II) complexes with *N*-[2-(alkylthio)ethyl]-3-amino-1-propanols, $Cu[RS(CH_2)_2NH(CH_2)_3O]X$ (abbreviated as Cu(R-sno)X, where R=alkyl, X=anion) (Fig. 1a).[3,4] It was shown that these complexes reveal a stronger antiferromagnetic spin-exchange interaction than the complexes with *N*-[2-(dialkylamino)ethyl]-3-amino-1-propanols (abbreviated as Cu(R-nno)X).[5,6] This suggests that the spin-spin coupling between the copper(II) ions is facilitated by substituting a sulfur donor atom for a nitrogen donor atom.[3,4] In order to examine further the sulfur donation effect on the spin-exchange interaction, we synthesized binuclear copper(II) complexes with 3-[2-(dialkylamino)ethylthio]-1-propanols, $Cu[R_2N(CH_2)_2S(CH_2)_3O]X$ (abbreviated as Cu(R-nso)X, where $R=CH_3$, C_2H_5; $X=ClO_4^-$, NO_3^-) (Fig. 1b) and investigated their magnetic properties in comparison with those of the Cu(R-sno)X and Cu(R-nno)X complexes.



a b

Fig. 1. Structures of complexes.
(a) Cu(R-sno)X and (b) Cu(R-nso)X.

Experimental

Preparation of the Complexes. The ligands, $R_2N(CH_2)_2S(CH_2)_3OH$ ($R=CH_3$, C_2H_5) were prepared after the method described by Clinton *et al.*[7] Preparation of the complexes is exemplified by $Cu(CH_3\text{-nso})ClO_4$. Copper(II) perchlorate hexahydrate (186 mg) and 2,2-dimethoxypropane (2 cm^3) were mixed in absolute ethanol (4 cm^3) and allowed to stand at room temperature for one night in order to decompose water in the solution. This solution was added to a solution of CH_3-nsoH (163 mg) in absolute ethanol (5 cm^3). The mixture was allowed to stand for several days at room temperature to give black needles, which were collected and dried *in vacuo* over P_2O_5. Yield: 75 mg. The $Cu(R\text{-nso})NO_3$ complexes were prepared by a method similar to that for $Cu(R\text{-nso})ClO_4$. Analytical data of the complexes are given in Table 1.

Measurements. Infrared spectra were measured with a Hitachi Grating Infrared Spectrophotometer Model 215 on a KBr disk. Diffuse reflectance spectra were measured with a Shimadzu Multipurpose Spectrophotometer Model MSP-5000. Magnetic susceptibilities were measured by the Faraday method in the temperature range 80—300 K. All the susceptibilities were corrected for the diamagnetism of the constituting atoms by the use of Pascal's constants.[8] 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 and $N\alpha$ is the temperature-independent paramagnetism.

Results and Discussion

The complexes obtained were sparingly soluble in any conventional solvents. Hence, the electronic spectra of the complexes were measured by reflection on powder samples. The spectra display a fairly broad band centered around $15\times10^3\ cm^{-1}$ which is attributable to d-d transition bands. In addition, the spectra show a band at 22—$24\times10^3\ cm^{-1}$ characteristic of alkoxo-bridged structure.

The infrared spectra of $Cu(R\text{-nso})ClO_4$ showed a strong broad band at 1080—1140 cm^{-1}. Because of little splitting of this band, no coordination of the perchlorate ion to the copper is supposed.[9] The infrared spectra of $Cu(R\text{-nso})NO_3$ show a strong broad band at 1380 cm^{-1} and a sharp band at 820 cm^{-1}. Hence it is assumed that the nitrate ion does not coordinate to the metal.[10] Thus, it is likely that the present complexes possess a binuclear structure with a nearly planar $^{S}_{N}\!\rangle Cu\langle^{O}_{O}\rangle Cu\langle^{N}_{S}$ skeleton.

Table 1. Analytical data

Complex	C(%) Found (Calcd)	H(%) Found (Calcd)	N(%) Found (Calcd)
$Cu(CH_3\text{-nso})ClO_4$	25.66 (25.85)	4.96 (4.96)	4.29 (4.31)
$Cu(C_2H_5\text{-nso})ClO_4$	30.34 (30.60)	5.80 (5.71)	3.92 (3.96)
$Cu(CH_3\text{-nso})NO_3$	28.90 (29.21)	5.57 (5.60)	9.57 (9.73)
$Cu(C_2H_5\text{-nso})NO_3\cdot 1/2H_2O$	32.99 (33.27)	6.31 (6.51)	8.53 (8.62)

TABLE 2. MAGNETIC DATA OF Cu(R-nso)X[a)]

Complex	μ_{eff}/BM (293K)	$2J/cm^{-1}$	$N\alpha$/cgs emu	P
$Cu(CH_3\text{-nso})ClO_4$	0.48	−930	57×10^{-6}	2.2×10^{-2}
$Cu(C_2H_5\text{-nso})ClO_4$	0.58	−900	63×10^{-6}	4.5×10^{-2}
$Cu(CH_3\text{-nso})NO_3$	0.53	−910	59×10^{-6}	3.0×10^{-2}
$Cu(C_2H_5\text{-nso})NO_3\cdot1/2H_2O$	0.72	−990	66×10^{-6}	11.7×10^{-2}

a) For all the complexes $g=2.10$ is assumed.

Magnetic moments per copper atom are very low at room temperature, indicating that a fairly strong antiferromagnetic interaction is operating between copper(II) ions (Table 2). The magnetic susceptibility decreases with lowering of temperature but increases again below 150 K. This feature is most likely due to the binuclear structure and a small amount of mononuclear paramagnetic impurity. Accordingly, the impurity term was added to the Bleaney-Bowers equation[11)] giving,

$$\chi_A = \frac{Ng^2\beta^2}{3kT}\left[1+\frac{1}{3}\exp(-2J/kT)\right]^{-1}(1-P) + \frac{0.45P}{T} + N\alpha \qquad (1)$$

where χ_A is susceptibility per copper atom, P is the ratio of mononuclear copper(II) ions to total copper(II) ions, and other symbols have the usual meanings.[12)] The magnetic data evaluated from the best fit of the experimental data to Eq. 1 are listed in Table 2. The results suggest that these complexes contain an appreciable amount of paramagnetic impurity. Since $Cu(C_2H_5\text{-nso})X$ ($X=ClO_4^-$, NO_3^-) are hygroscopic in the open atmosphere, partial decomposition might take place in these complexes. It is clear that the $-2J$ values for Cu(R-nso)X are more than 900 cm^{-1}. This magnetic behavior is essentially the same as that of Cu(R-sno)X ($-2J=$*ca.* 800 cm^{-1}).[3,4)] On the other hand, the binuclear copper(II) complexes with *N*-[2-(dialkylamino)ethyl]-3-amino-1-propanols, Cu(R-nno)X, show a weaker spin-exchange interaction; $-2J$ values being evaluated at 500 cm^{-1}.[5,6)] Thus, it may be concluded that the binuclear copper(II) complexes with *SNO*- and *NSO*-donor sets exhibit a stronger antiferromagnetic spin-exchange interaction compared with the complexes with *NNO*-donor set.

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