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THE NEW TRINUCLEAR COPPER(II) COMPLEXES WITH N,N-DIALKYL DIAMINOALCOHOLS

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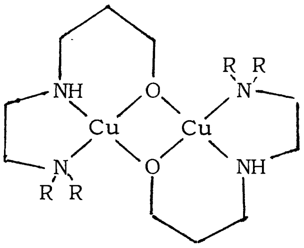
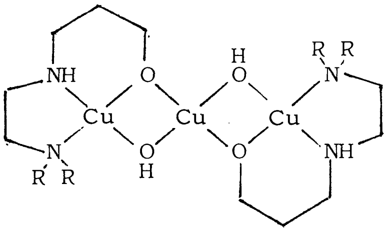
New trinuclear copper(II) complexes, $\left[Cu_3[R_2N(CH_2)_2NH(CH_2)_3O]_2(OH)_2\right](ClO_4)_2$ (R = CH_3 , C_2H_5) were prepared and characterized by elemental analyses, IR-, UV- and ESR spectra, and magnetic susceptibilities (80 ~ 295 K). In the trinuclear complex the three copper atoms are linearly arrayed and bridged with two alkoxo- and two hydroxo-groups. Under a little different experimental condition the same ligands and copper perchlorate form different crystals which were characterized as a complex of a binuclear structure.

In the previous paper[1)] we reported the preparation of the binuclear copper(II) complexes of the skeltal structure(A), using various aliphatic diaminoalcohols as ligands. In the present study, using N,N-disubstituted diaminoalcohol, $R_2N(CH_2)_2NH(CH_2)_3OH$ (R = CH_3 , C_2H_5), copper perchlorate and sodium hydroxide, we obtained two kinds of crystals, the green and the blue ones. Whereas only a single kind of crystals was obtained in the previous study using $H_2N(CH_2)_2NH(CH_2)_3OH$ as a ligand under a similar condition[1)]. The green crystals were found to be similar in various properties to the previously reported binuclear complexes. On the other hand, the blue ones appeared to be complexes of a novel type, and were subjected to the present investigation.



[A]



[B]

Preparations

$[Cu_3(R_2N(CH_2)_2NH(CH_2)_3O)_2(OH)_2](ClO_4)_2$. A methanol solution (10 ml) containing the N,N-disubstituted diaminoalcohol (0.006 mole) and sodium hydroxide (0.012 mole) was added to a hot ethanol solution (50 ml) of copper perchlorate hexahydrate (0.006 mole). The green solution was allowed to stand at room temperature for one night. Blue crystals were separated from the solution, which were recrystallized from hot methanol. In this procedure excess sodium hydroxide was used in order to prevent the formation of green crystals.

$[Cu_2(R_2N(CH_2)_2NH(CH_2)_3O)_2](ClO_4)_2$. The procedure is similar to that for the blue compound except for mixing the diaminoalcohol, copper perchlorate and sodium hydroxide with the mole ratio 1 : 1.2 : 1 insted of 1 : 1 : 2. The green crystals were recrystallized from a hot methanol. The elemental analyses were tabulated in Table I.

Table I Elemental analyses

Complex type	R	Calcd* C	H	N	Cu	Found C	H	N	Cu
green	CH_3	28.23	6.22	8.23	19.60	27.83	6.38	8.30	19.28
green	C_2H_5	30.69	6.01	7.95	18.04	30.44	5.95	8.12	17.94
blue	CH_3	23.55	5.08	7.85	26.70	23.25	4.86	7.75	26.81
blue	C_2H_5	28.06	5.76	7.27	24.76	28.03	5.75	7.24	24.14

* Calculated for $[Cu_2(R_2N(CH_2)_2NH(CH_2)_3O)_2](ClO_4)_2$ for the green complexes. Calculated for $[Cu_3(R_2N(CH_2)_2NH(CH_2)_3O)_2(OH)_2](ClO_4)_2$ for the blue complexes.

Results and Discussion

The results of elemental analyses of the green and the blue crystals show a good agreement with the calculated values for the binuclear structure[A] and the trinuclear structure[B], respectively. In the IR spectra of the blue complexes a sharp absorption was observed at 3620 cm^{-1} which is absent in the case of green complexes as shown in fig. 1. This absorption is attributable to the stretching vibration of the bridging OH group, since Okawa et al. have demonstrated that the binuclear copper(II) complexes containing bridging OH groups always show such a characteristic sharp absorption in that region$^{2)}$.

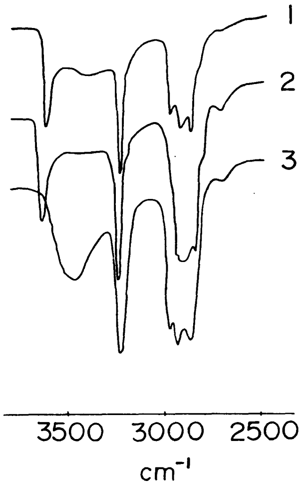


Fig. 1. IR spectra (in KBr) of the blue (1: R = C_2H_5, 2: R = CH_3) and the green complexes (3: R = C_2H_5)

The ESR spectra of the green complexes show very broad bands and are essentially similar in general feature to those of the previously reported binuclear complexes$^{1)}$.

The blue complexes show only one broad band ($g \approx 2.10$), which becomes sharp at lower temperature.

The electronic spectra are shown in fig's. 2 and 3. Both types of the complexes show bands at $26 \sim 28 \times 10^3$ cm^{-1}. On the basis of the discussion of the previous papers,[1,3] these bands are undoubtedly assigned to the characteristic bands of alkoxo- or hydroxo-bridged bi(or poly)nuclear copper(II) complexes.

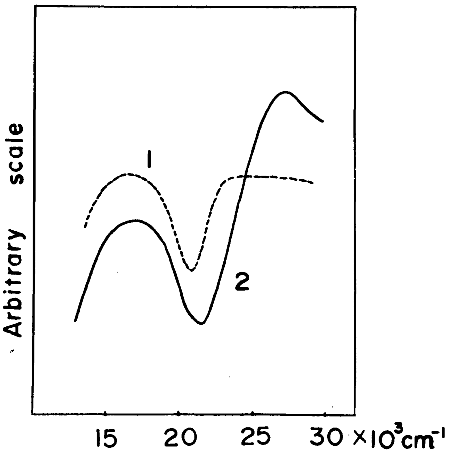


Fig. 2. Reflectance spectra of the green complexes (1: R = CH_3, 2: R = C_2H_5)

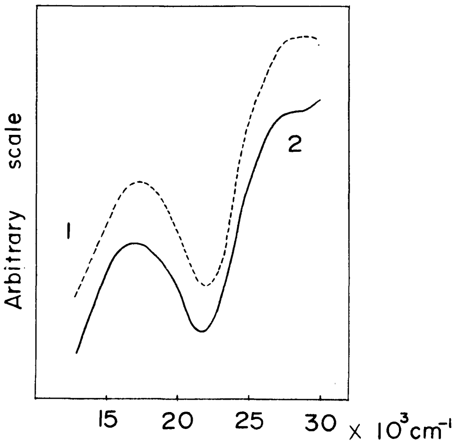


Fig. 3. Reflectance spectra of the blue complexes (1: R = CH_3, 2: R = C_2H_5)

Magnetic susceptibilities were measured over the temperature range 300 ~ 80 K by the Faraday method. The results are shown in fig's. 4 and 5. As seen in the diagram, the curve for the green complexes is well interpreted in terms of the Bleany-Bowers equation[4] formulated for binuclear copper(II) complexes

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

if $g = 2.10$, $-2J = 580$ cm^{-1} and $N\alpha = 35 \times 10^{-6}$ are assumed. On the other hand, as expected the results for blue complexes are best interpreted by the equation

$$\chi_A = \frac{Ng^2\beta^2}{12kT}\,\frac{10\exp(J_{12} + \frac{1}{2}J_{13}) + \exp(-\frac{3}{2}J_{13}) + \exp(-2J_{12} + \frac{1}{2}J_{13})}{2\exp(J_{12} + \frac{1}{2}J_{13}) + \exp(-\frac{3}{2}J_{13}) + \exp(-2J_{12} + \frac{1}{2}J_{13})} + N\alpha \qquad (2)$$

which is based on the spin Hamiltonian for a trinuclear complex,[5]

$$\mathcal{H} = -2J_{12}S_1\cdot S_2 - 2J_{13}S_1\cdot S_3 - 2J_{23}S_2\cdot S_3 \qquad (3)$$

where J_{ij} denotes the exchange integral between i'th and j'th copper ions. The parameters, g, J_{12}, J_{23}, J_{13} and $N\alpha$ were determined by the best fit of the theoretical χ-T curve to the experimentally obtained one, and were tabulated in Table 2. The experimental results are interpretable by equation (3) only on setting $J_{13} = 0$. This indicates that the three copper ions are linearly arrayed in the complex.

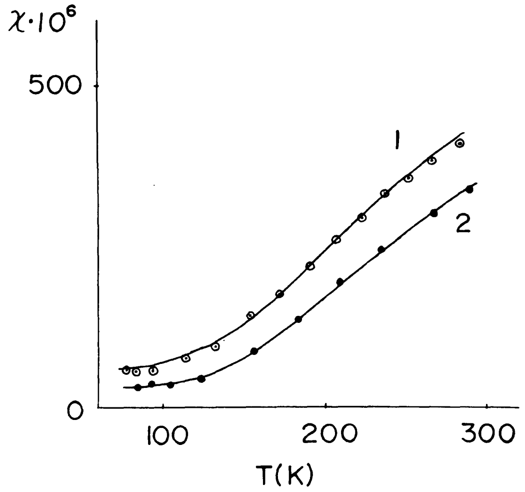


Fig. 4 Magnetic susceptibilities of the green complexes (1: R = CH_3, 2: R = C_2H_5)

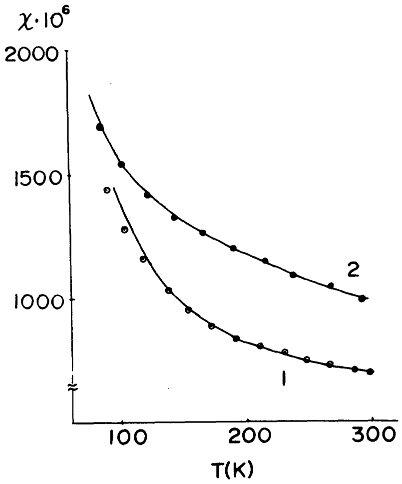


Fig. 5 Magnetic susceptibilities of the blue complexes (1: R = CH_3, 2: R = C_2H_5)

Table II The best fit values of g, J (cm^{-1}) and Nα (c.g.s)

Complex type	R	g	$J_{12}(=J_{23})$	J_{13}	$N\alpha \times 10^6$
green	CH_3	2.08	-265	—	60
green	C_2H_5	2.10	-290	—	35
blue	CH_3	2.07	-190	0	65
blue	C_2H_5	2.10	-100	0	55

Thus, from the all experimental results described above, we may conclude that the green complexes are binuclear with the skeltal structure[A] and the blue ones are of the trinuclear structure[B].

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