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Copper(II) Complexes with Some Aliphatic Diaminealcohols

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Copper(II) complexes were prepared with a series of tridentate ligands, $NH_2(CH_2)_mCHRNH(CH_2)_nOH$ (R=H or CH_3; $m=1$ or 2; $n=2$ or 3). Compounds obtained can be classified into three groups: (1) $CuLCl_2$, (2) $CuL'(ClO_4)$ and (3) CuL_2X_2, (L and L′ represent the neutral and the anionic ligands, respectively, and X denotes Cl or ClO_4). (1) and (3) were found to be mononuclear in which L functions as a bidentate ligand donating with the two nitrogen atoms. (2), except for the complex with $L'=NH_2(CH_2)_3NH(CH_2)_2O^-$, have the binuclear structure with alkoxo bridges. The absorption bands at about 350 nm are characteristic of the binuclear structure with alkoxo or hydroxo bridges.

Since it was found that the band at 370 nm in copper(II) alkanoates is diagnostic of the binuclear structure,[1-4] a number of spectral studies of copper(II) alkanoates have been reported.[5-10] However, the origin of the band has been a subject of controversy.[8,9] It seems desirable to see whether binuclear copper(II) complexes of other types show similar bands to those copper(II) alkanoates. Recently Yamada and Ojima[11] observed the bands at about 355 nm in a series of the binuclear copper(II) complexes such as bis(μ-*N*-oxo-propyl-*N*′-methylglycinamido)dicopper(II), and assumed the bands to be characteristic of the μ-dioxo structure of the complexes. However, further evidences seem to be necessary for establishing general relationship between the binuclear structure and the appearance of the band at about 350—360 nm in copper(II) complexes. In most dimeric copper(II) complexes so far reported, the ultraviolet region is masked by absorptions resulting from ligands. We therefore, attempted to prepare a series of ligands such as $NH_2(CH_2)_mCHRNH(CH_2)_nOH$ (R=H or CH_3, $m=1$ or 2, and $n=2$ or 3), which are capable of forming five- and/or six-membered chelate rings and, under some conditions, of forming binuclear complexes. They are new compounds except for the one with R=H, $m=1$ and $n=2$. Since these ligands have no double

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[1] R. Tsuchida and S. Yamada, *Nature*, **176**, 1171 (1955).

[2] R. Tsuchida, H. Nakamura, and S. Yamada, *ibid.*, **178**, 1192 (1956).

[3] S. Yamada, H. Nakamura, and R. Tsuchida, This Bulletin, **30**, 953 (1957).

[4] S. Yamada, H. Nakamura, and R. Tsuchida, *ibid.*, **31**, 303 (1958).

[5] B. N. Figgis and R. L. Martin, *J. Chem. Soc.*, **1957**, 3837.

[6] R. L. Martin and A. Whithey, *ibid.*, **1958**, 1394.

[7] S. Kida, Y. Nakashima, Y. Morimoto, K. Niimi, and S. Yamada, This Bulletin, **37**, 549 (1964).

[8] A. E. Hansen and C. J. Ballhausen, *Trans. Faraday Soc.*, **61**, 631 (1965).

[9] L. Dubicki and R. L. Martin, *Inorg. Chem.*, **5**, 2203 (1966).

[10] L. Dubicki, XIIIth ICCC, Poland, (1970). Proceedings, I, 129.

[11] K. Yamada and H. Ojima, 24th Annual Meeting of Chemical Society of Japan, Osaka, (1971) Proceedings, 2, p. 729.

bond, and consequently no absorption in visible and near-ultraviolet region, their complexes were considered to be suitable for the present investigation.

The relationship of the structure of a tridentate chelate ring system to the stability and magnetic properties of the binuclear copper(II) complexes was discussed by Ueda *et al.*,[12] but the ligands studied were limited to the condensed Schiff bases. Thus, in addition to the spectral study, we have investigated the effects of size and structure of chelate rings on the stability and magnetic properties of the binuclear copper(II) complexes, using the series of tridentate ligands of saturated chains.

Experimental

Preparation of Ligands. N-*(β-hydroxyethyl)ethylenediamine,* $NH_2(CH_2)_2NH(CH_2)_2OH$*=en-etol*: This compound was prepared by the method of Knorr and Brownsden.[13]

N-*(γ-hydroxypropyl)ethylenediamine,* $NH_2(CH_2)_2NH(CH_2)_3OH$ *=en-prol*: This compound was prepared by the method of Keller and Edwards,[14] except for the use of trimethylene chlorohydrin instead of trimethylene bromohydrin.

N-*(β-hydroxyethyl)trimethylenediamine,* $NH_2(CH_2)_3NH(CH_2)_2OH$*=tn-etol*: Gaseous ethylene oxide produced by dropwise addition of 24 g (0.3 mol) ethylene chlorohydrin to 32 g (0.6 mol) potassium hydroxide was introduced with stirring into a solution of 74 g (1.0 mol) trimethylenediamine. The unreacted trimethylenediamine was distilled off, and the remaining mixture was distilled under reduced pressure. Bp. 133—134 °C/7 mmHg.

N-*(γ-hydroxypropyl)trimethylenediamine,* $H_2N(CH_2)_3NH(CH_2)_3OH$*=tn-prol*: To a well-stirred solution of 74 g (1.0 mol) trimethylenediamine in 80 ml of isopropyl alcohol was added 28.4 g (0.3 mol) of trimethylene chlorohydrin, the reaction mixture being maintained at about 50 °C. The mixture was refluxed for 3 hr. 8 g (0.2 mol) of sodium hydroxide was added to the solution, yielding white precipitates which were filtered off. The filtrate was evaporated to remove isopropyl alcohol and the unreacted trimethylenediamine, and then, distilled under reduced pressure. Fractionation of the distillate yielded 11.5 g (43.5% yield based on the trimethylene chlorohydrin) of the final product. Bp. 130—131 °C/3 mmHg.

N-*(γ-hydroxypropyl)-(−)-1,2-propanediamine,* $NH_2CH(CH_3)CH_2NH(CH_2)_3OH$ *= pn-prol*: This compound was prepared in a similar way to that for $H_2N(CH_2)_3NH(CH_2)_3OH$, except for the use of (−)-1,2-propanediamine instead of trimethylenediamine.

Table 1. Abbreviation of ligands

en-etol	$NH_2CH_2CH_2NHCH_2CH_2OH$
en-prol	$NH_2CH_2CH_2NHCH_2CH_2CH_2OH$
tn-etol	$NH_2CH_2CH_2CH_2NHCH_2CH_2OH$
tn-prol	$NH_2CH_2CH_2CH_2NHCH_2CH_2CH_2OH$
pn-prol	$NH_2CH_2CH(CH_3)NHCH_2CH_2CH_2OH$

The primed abbreviation, such as en-prol′ *etc.*, denotes the anion of the ligand, such as $NH_2CH_2CH_2NHCH_2CH_2CH_2O^-$ *etc.*

Preparation of the Complexes. *Cu en-etol* Cl_2 *(A)* (For abbreviation of ligands, see Table 1): A solution of 1.1 g of en-etol (0.01 mol) in 40 ml of ethanol was added dropwise to a solution of 1.7 g of copper(II) chloride dihydrate (0.01 mol) in 40 ml of ethanol with stirring. The blue powder immediately formed was filtered off, washed with cold ethanol and dried over phosphoric anhydride.

Cu en-prol Cl_2 *(B), Cu tn-etol* Cl_2 *(C) and Cu pn-prol* Cl_2 *(D)* were prepared in a similar way to that for A.

Cu en-prol′ ClO_4 *(E)*: Six tenth grams of potassium hydroxide (0.01 mol) and 1.2 g of en-prol (0.01 mol) were dissolved in 50 ml of methanol. To this was added dropwise a solution of 3.7 g of copper(II) perchlorate hexahydrate (0.01 mol) in 30 ml of methanol. The mixture was stirred for two hours at room temperature. The white precipitate ($KClO_4$) formed was removed by filtration. The filtrate was kept in a refrigerator for a few hours to complete the precipitation of potassium perchlorate, which was removed by centrifugation. The bluish violet solution was evaporated and a dark blue oily substance was obtained. This was dissolved in a small amount of hot ethanol and kept in a refrigerator overnight. Dark blue-violet crystals were obtained. These were recrystallized from ethanol. The compound obtained was hygroscopic in the atmosphere, and was found by elemental analysis to contain one molecule of ethanol for one copper ion. The ethanol was removed by keeping the crystals ***in vacuo*** at 100 °C for 1 hr.

Cu tn-prol′ClO_4 *(F), Cu tn-prol′*NO_3 *(G), Cu pn-prol′*ClO_4 *(H), Cu tn-etol′*$ClO_4\cdot H_2O$ *(I) and Cu tn-etol′Cl–*H_2O *(J)* were prepared in a similar way to that for E. The crystals of F and H obtained from the ethanol solution were found to contain a certain amount of ethanol (1.0 mol for F and 0.7—0.8 mol for H) which was easily removed as in the case of E.

Compounds F, G, I, and J can also be prepared by mixing copper(II) salt and the ligand with the 1 : 2 mol-ratio in hot ethanol.

Cu(en-etol)$_2$*Cl*$_2$*, (K)*: A hot solution of 1.7 g of copper(II) chloride dihydrate (0.01 mol) in 30 ml methanol was added dropwise to a well-stirred solution of 2.2 g of en-etol (0.02 mol) dissolved in 40 ml methanol. The solution was kept overnight in a refrigerator. The violet crystals separated were filtered off, washed with cold ethanol and dried over phosphoric anhydride.

Cu(tn-etol)$_2$*Cl*$_2$ *(L)* was prepared in a similar way to that for K.

Cu(en-etol)$_2$*(ClO*$_4$*)*$_2$ *(M) and Cu(en-prol)*$_2$*(ClO*$_4$*)*$_2$ *(N)* were prepared in a similar way to that for the chloride analogues except for the use of copper(II) perchlorate hexahydrate instead of copper(II) chloride dihydrate.

Measurements. Electronic spectra were measured with a Hitachi EPS-3T recording spectrophotometer equipped with a reflectance attachment.

Magnetic susceptibility was determined by the Gouy method at room temperature, diamagnetic corrections being made with Pascal's constants.

ESR spectra were measured using X-band with a JES-ME-3 ESR spectrometer.

Results and Discussion

The analytical, magnetic and spectral data of the fourteen copper(II) complexes obtained are summarized in Tables 2 and 3.

The complexes are classified into three types with the general formulas $CuLCl_2$, $CuL'ClO_4$ and CuL_2X_2, where $X=Cl$ or ClO_4 and L and L′ denote the ligands

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[12] H. Ueda, K. Mori, M, Kishita, and S. Nakahara. 24th Annual Meeting of Chemical Society of Japan, Osaka (1971). Proceedings, 2, p. 761.

[13] L. Knorr and H. W. Brownsdon, *Ber.*, **35**, 4470 (1902).

[14] R. N. Keller and L. J. Edwards, *J. Amer. Chem. Soc.*, **74**, 215 (1952).

TABLE 2. ELEMENTAL ANALYSES

Compd	Formula	C (%) Found	C (%) Calcd	H (%) Found	H (%) Calcd	N (%) Found	N (%) Calcd
A	$CuC_4H_{12}N_2Cl_2O$	20.23	20.13	4.97	5.08	11.78	11.32
B	$CuC_5H_{14}N_2Cl_2O$	23.57	23.77	5.45	5.59	11.04	11.09
C	$CuC_5H_{14}N_2Cl_2O$	23.76	23.77	5.70	5.59	10.61	11.09
D	$CuC_6H_{16}N_2Cl_2O$	27.10	27.02	6.13	6.02	10.41	10.51
E	$CuC_5H_{13}N_2ClO_5$	21.11	21.43	4.78	4.69	9.86	10.00
F	$CuC_6H_{15}N_2ClO_5$	24.28	24.49	5.31	5.14	9.46	9.52
G	$CuC_6H_{15}N_3O_4$	28.22	28.06	5.82	5.90	16.54	16.37
H	$CuC_6H_{15}N_2ClO_5$	23.81	24.49	5.28	5.14	9.23	9.52
I	$CuC_5H_{13}N_2ClO_5$	21.19	21.43	4.68	4.69	9.77	10.00
J	$CuC_5H_{15}N_2ClO_2$	25.44	25.64	6.51	6.46	11.56	11.96
K	$CuC_8H_{24}N_4Cl_2O_2$	28.16	28.03	7.01	7.07	16.30	16.35
L	$CuC_{10}H_{28}N_4Cl_2O_2$	32.26	32.38	7.61	7.63	15.07	15.11
M	$CuC_8H_{24}N_4Cl_2O_{10}$	20.30	20.19	5.02	5.15	11.96	11.90
N	$CuC_{10}H_{28}N_4Cl_2O_{10}$	23.83	24.05	5.60	5.67	11.29	11.23

TABLE 3. OPTICAL AND MAGNETIC DATA

Compd	Formula	μ_{eff} (BM)	Refl (nm)	Abs (ε) (nm)		
A	[Cu Cl_2(en-etol)]	1.79	700	710 (90.0)		met[a)]
B	[Cu Cl_2(en-prol)]	1.81	660	670 (85.8)		met
C	[Cu Cl_2(tn-etol)	1.92	700	655 (88.2)		met
D	[Cu Cl_2(pn-prol)]	1.92	700	660 (88.1)		met
E	Cu(en-prol')ClO_4	0.90	590, 360	570 (70.5)	358 (1310)	et[a)]
F	Cu(tn-prol')ClO_4	0.62	590, 360	580 (84.4)	358 (2820)	et
G	Cu(tn-prol')NO_3	0.69	580, 360	585 (86.1)	354 (2360)	et
H	Cu(pn-prol')ClO_4	0.83	570, 360	565 (66.1)	360 (1170)	et
I	Cu(tn-etol')$ClO_4\cdot H_2O$	1.79	610	610 (76.3)	363 (128)	et
J	Cu(tn-etol')$Cl\cdot H_2O$	1.79	600	610 (76.2)	360 (422)	met
K	Cu(en-etol)$_2Cl_2$	1.95	570	595 (100)		met
L	Cu(en-prol)$_2Cl_2$	1.84	590	585 (107)	350 (295)	met
M	Cu(en-etol)$_2(ClO_4)_2$	1.77	600	590 (95.0)		met
N	Cu(en-prol)$_2(ClO_4)_2$	1.92	590	570 (88.0)	354 (553)	met

a) met and et denote "in methanol" and "in ethanol", respectively.

$NH_2(CH_2)_mCHRNH(CH_2)_nOH$ and $NH_2(CH_2)_mCHRNH(CH_2)_nO^-$, respectively.

(1) Cu L Cl_2: Compounds A, B, C, and D (where L=en-etol, en-prol, tn-etol and pn-prol; *cf.* Table 3) belong to this group. The tn-prol complex of this type could not be isolated in spite of repeated attempts.

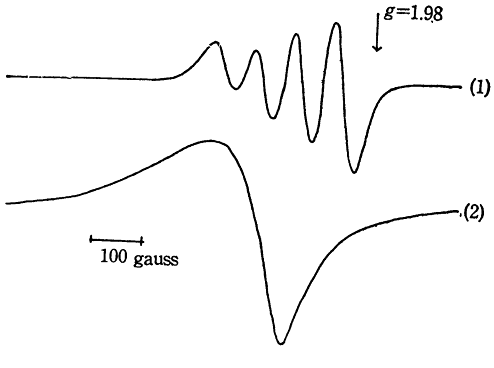

Fig. 1. ESR spectra of Cu en-prol Cl_2
(a) methanol solution at room temperature.
(b) powder at 150 °C (gain 1×1).

The compounds show normal magnetic moments for ordinary mononuclear copper (II) complexes (Table 3). ESR measurements in methanol solution and in powder provide further evidences for the mononuclear structure (Fig. 1).

Their reflectance spectra are similar to that of [Cu-en Cl_2] (en=ethylenediamine), known as a dichloro complex.[15] Thus, the structure of this group is essentially square planar, a copper ion being coordinated with two chloride ions and two amine nitrogen atoms. The alcoholic hydroxyl group is not likely to form a distinct bond with the metal ion, as judged from the visible spectrum (Table 3).

(2) CuL'ClO_4: Compounds E, F, H, and I (where L'=en-prol', tn-prol', pn-prol' and tn-etol'; *cf.* Table 3) belong to this group. Compounds G(=Cu tn-prol'NO_3) and J (=Cu tn-etol'$Cl\cdot H_2O$) appear to be similar to the above compounds and will be discussed here. All attempts to prepare the homologue with en-etol were unsuccessful. The compounds show

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[15] D. E. Billing and B. J. Hathway, *J. Chem. Soc., A*, **1969**, 312.

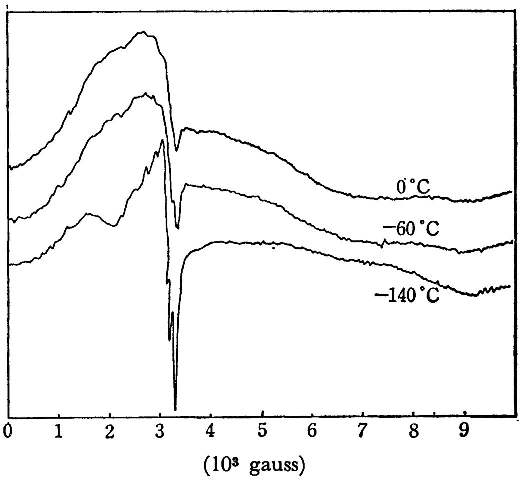

Fig. 2. Powder ESR spectra of Cu en-prol' ClO$_4$ (gain 2.8×100).

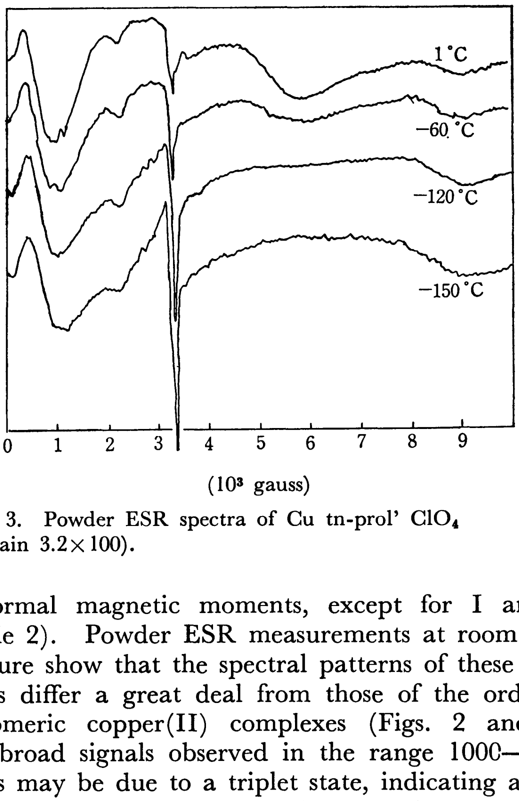

Fig. 3. Powder ESR spectra of Cu tn-prol' ClO$_4$ (gain 3.2×100).

subnormal magnetic moments, except for I and J (Table 2). Powder ESR measurements at room temperature show that the spectral patterns of these complexes differ a great deal from those of the ordinary monomeric copper(II) complexes (Figs. 2 and 3). The broad signals observed in the range 1000—8000 Gauss may be due to a triplet state, indicating a considerable magnetic interaction between the two copper ions. Therefore, we may conclude that E, F, G, and H have a binuclear structure bridged with alcoholate oxygen (Fig. 5).

On the other hand, both I and J show a normal magnetic moment, 1.79 BM, at room temperature. However, their ESR spectra, which are very similar to each other, differ entirely from those of ordinary mononuclear copper(II) complexes, especially at low temperature (Fig. 4, and also Fig. 1). It should be noted that the intensities of the ESR signals remarkably increase with the lowering of temperature (Fig. 4), whereas in the other complexes E, F, G, and H, the spectra except for the band at about 3000 Gauss do not increase in intensity but gradually decline with the lowering of temperature (Figs. 2 and 3).

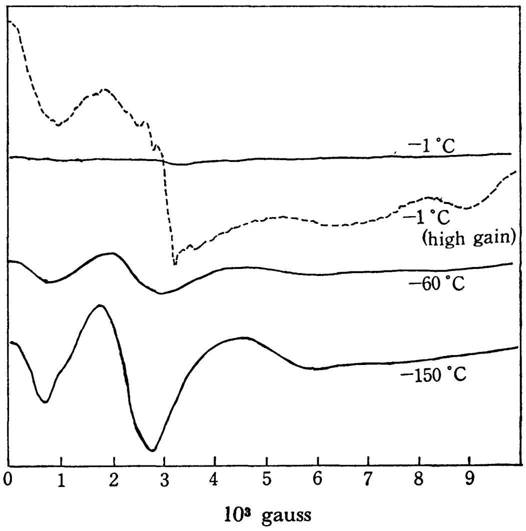

Fig. 4. Powder ESR spectra of Cu tn-etol' ClO$_4$·H$_2$O (gain 1×10 for solid line, 3.2×100 for broken line).

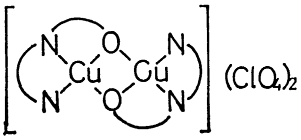

Fig. 5. The structure of CuL'ClO$_4$.

This suggests that ferromagnetic interaction takes place in I and J, where the ground state is triplet (or multiplet) and an upper singlet state is thermally populated at room temperature. As is well-kown in magnetically dilute solid, an ESR signal generally increases in intensity with lowering of temperature due to an increase of the difference of thermal population between the split Zeeman levels.[16] In addition to this effect, in the case of compounds I and J, the ground triplet or multiplet state becomes more populated with the lowering of temperature to increase the ESR intensity. On the other hand, in the antiferromagnetic compounds where the ground state is singlet such as E, F, G, and H, the near-lying upper triplet state becomes less populated with lowering of temperature. The effect acts on ESR to reduce its intensity at low temperature. Thus, the observed ESR intensities of these compounds are nearly counterbalanced by the two opposite temperature effects in a certain temperature range (Figs. 2 and 3). In contrast to this, the signal at about 3000 gauss, which is attributable to a trace of mononuclear impurity, remarkably increases in intensity with the lowering of temperature.

The structures of compounds I and J are likely to be similar to those of Cu aca-etol'[17] and Cu sal-etol'[18] (where aca-etol' and sal-etol' denote $^-$OC(CH$_3$)=CHC(CH$_3$)=NCH$_2$CH$_2$O$^-$ and *o*-O$^-$(C$_6$H$_4$)CH=NCH$_2$CH$_2$O$^-$, respectively), since tn-etol is similar to these

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[16] M. Bersohn and J. C. Baird "An Introduction to Electron Paramagnetic Resonance," Chapt. 1 Benjamin, New York (1966).

[17] J. A. Bertland and J. A. Kelley, *Inorg. Chim. Acta*, **4**, 203 (1970).

[18] K. Mori, H. Ueda, A. Nakahara, and M. Kishita, 24th Annual Meeting of Chem. Soc. Japan, Osaka (1971). Proceedings, 2, p. 762.

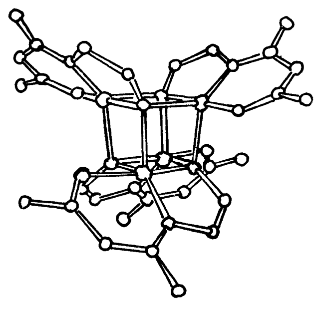
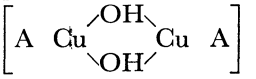


Fig. 6. The structure of Cu aca-etol'[17]

ligands in forming 5- and 6-membered chelate rings upon coordination, and in their magnetic behavior, *i.e.* ferromagnetic interaction takes place though they all show normal magnetic moments at room temperature. The X-ray analysis[17] shows that Cu aca-etol' is tetrameric (Fig. 6), where alcoholate oxygens coordinate to three copper ions and, consequently, are tetrahedrally bonded.

Since no stable binuclear complexes were obtained by using en-etol, pn-etol and tn-etol, we may conclude that for the formation of the binuclear complex the favorable member of the chelate ring involving bridging oxygen is six. The 5- and 6-membered chelate ring system such as Cu tn-prol'ClO_4 seems to be slightly more favorable for the formation of the binuclear complex than the 5- and 6-membered chelate ring system such as Cu en-prol'ClO_4, judging from the easier formation of the former than the latter.

Compounds E, F, G, and H show similar electronic spectra to each other in both solid and ethanolic solutions, giving two bands in the 10—33 kK region (Fig. 7). The numerical data are summarized in Table 3. The bands around 600 nm are undoubtedly assigned to d–d transitions, and the more intense bands around 350 nm can be attributed to charge-transfer transitions from ligands to a metal ion. The latter bands seem to be characteristic of the binuclear structure in which two copper ions are bridged by oxo anions. This assumption well coincides with Yamada and Ojima's observation[11] on some binuclear copper(II) complexes bridged with two alcoholate oxygens. In order to confirm this assumption we have measured powder reflectance spectrum of the binuclear complex,  $\left[A\ Cu\overset{OH}{\underset{OH}{\rightleftarrows}}Cu\ A\right](ClO_4)_2$ (where A=*N,N,N',N'*-tetramethylethylenediamine or *N,N,N',N'*-tetraethylethylenediamine), and have observed similar bands at about 360 nm (Fig. 10). Their aqueous solutions show shoulders at the same position at pH 8 where the binuclear species dominates in the equilibrium.[19]

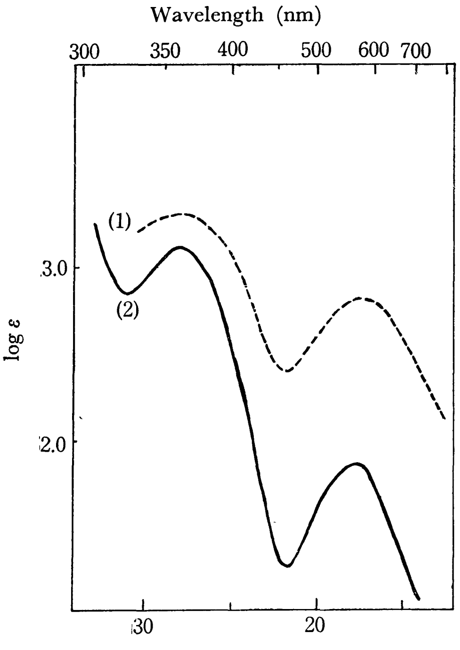


Fig. 7. Electronic spectra of Cu en-prol' ClO_4. (1) powder, (2) ethanol solution.

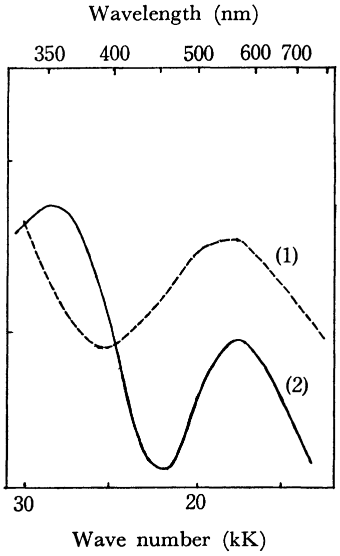


Fig. 8. Electronic spectra of $Cu(en\text{-}prol)_2(ClO_4)_2$. (1) powder reflectance, (2) methanol solution.

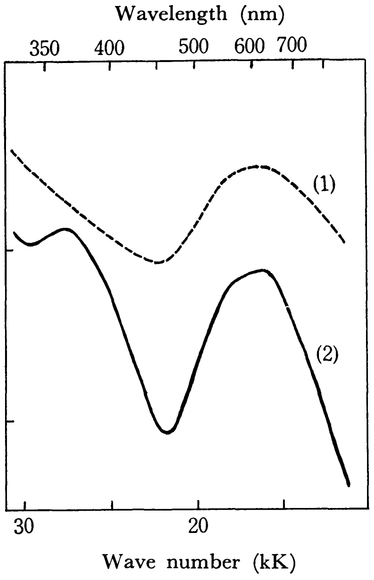


Fig. 9. Electronic spectra of Cu tn-etol' $ClO_4 \cdot H_2O$. (1) powder reflectance, (2) aqueous solution.

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[19] We have studied the equilibria of this solution by ESR (unpublished). A detailed study was recently reported on the equilibria of this system: E. Arenare, P. Paoletti, A. Dei, and Vacca, *J. Chem. Soc., Dalton*, **1972**, 736.

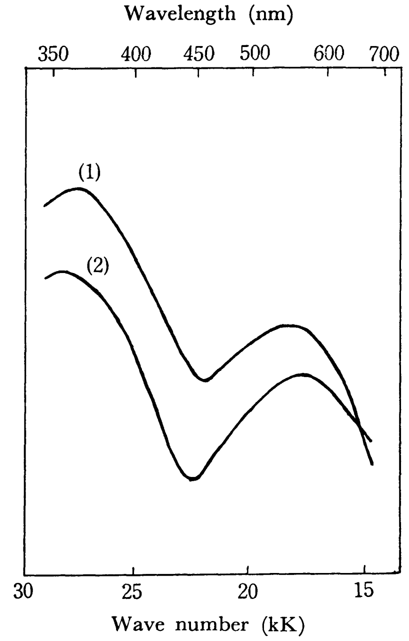

Fig. 10. Power reflectance spectra of $\left[\mathrm{A\ Cu}\left\langle{}^{\mathrm{OH}}_{\mathrm{OH}}\right\rangle\mathrm{Cu\ A}\right](ClO_4)_2$.
(1) A=*N,N,N',N'*-tetraethylethylenediamine,
(2) A=*N,N,N',N'*-tetramethylethylenediamine.

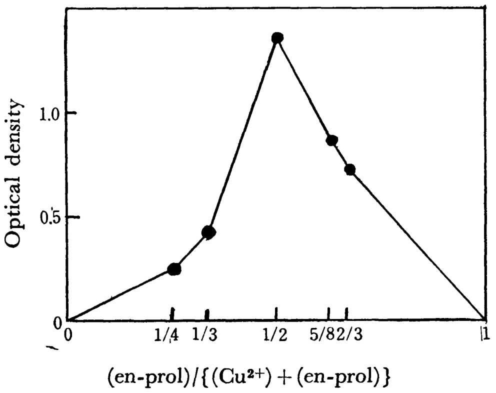

Fig. 11. The continuous variation method at 354 nm applied to the system Cu^{2+}/en-prol in basic solution.
The total concentration of Cu^{2+} and en-etol was 2×10^{-3} mol/l in each solution containing *t*-butylamine with the same molar concentration as that of en-etol.

However, in the low (<6) and the high (>9) pH regions, where the concentration of the binuclear species is negligible, neither a peak nor a shoulder was observed around 360 nm. We also investigated the powder reflectance spectrum of [Cu eta eta']ClO_4[20] (where eta and eta' denote $NH_2CH_2CH_2OH$ and $NH_2CH_2CH_2O^-$, respectively), in order to see whether the band around 360 nm is brought about by coordination of an alkoxo or a hydroxo group to copper(II) ion regardless of bridged or simple coordination. Neither peak nor shoulder has been found in the near-ultraviolet region, indicating that coordination of the alkoxo group to copper(II) ion itself does not cause the characteristic band in the near-ultraviolet region.

In conclusion, all experimental results so far obtained support the rule that the binuclear copper(II) complex bridged by alkoxo or hydroxo groups always show the characteristic band in the near-ultraviolet region (<29 kK), unless there are other intense absorptions to mask the region.

Compounds I and J show no characteristic band in the near-ultraviolet region in the powder reflectance spectrum (Fig. 9). This is undoubtedly due to the tetrameric structure, where bridging alcoholate oxygens are tetrahedrally bonded, and accordingly have no π-electrons to cause the absorption around 360 nm. In an aqueous or methanolic solution, however, the band was observed at 350 nm, though its intensity is very low as compared to that of the binuclear complexes in this group. Thus, a binuclear complex similar to E, F, G, and H might be partially formed in the solutions of I and J.

(3) CuL_2X_2: Compounds K, L (where L=en-etol, and en-prol; X=Cl), M and N (where L=en-etol and en-prol; X=ClO_4), belong to this group. It should be noted that the same preparative procedure as for the above compounds, *viz.*, mixing the copper(II) salt and the ligand in a 1 : 2 mole-ratio in methanolic solution, did not give rise to the formation of Cu(tn-etol)$_2$(ClO_4)$_2$ and Cu(tn-prol)$_2$(ClO_4)$_2$, but gave Cu tn-etol'$ClO_4\cdot H_2O$ and Cu tn-prol'ClO_4.

The compounds show normal magnetic moments at room temperature, and d-d bands at 560—600 nm (Table 3). The solution and the powder ESR spectra are very close to those of the compounds of group (1), showing characteristic patterns of a mononuclear copper(II) complex. We can thus conclude that complexes of this group are similar to [Cu en$_2$]X_2 in various properties, and that they are of essentially square-planar structure coordinated with four amine nitrogens. The red shift in 10—50 nm relative to [Cu en$_2$](ClO_4)$_2$ implies that there is some perturbation along the tetragonal axis, but not strong enough to be called a coordination bond.

It is remarkable that the solution spectra in the near-ultraviolet region differ from the powder spectra (Fig. 8). The bands observed at about 360 nm are similar in contour and in position to those of the oxo-bridged complexes. Therefore, $[Cu\ L_2]^{2+}$ is very likely to dissociate partially in solution to form a binuclear species similar to compounds E, F, G, and H, giving rise to the equilibrium

$$2[CuL_2]^{2+} \rightleftarrows [Cu_2L'_2]^{2+} + 2LH^+. \qquad (a)$$

In fact, the intensities of the bands are much lower than those of the binuclear complexes of group (2), and the spectra do not follow Beer's law in the near-ultraviolet region. The formation of a 1 : 1 complex was verified spectrophotometrically by the use of a continuous variation method (Fig. 11). It should be noted that the addition of some proton acceptor such as trimethylamine to the methanolic solution of a complex of this group gives rise to a distinct promotion of the intensity of the band at about 360 nm. This also supports assumption based on equilibrium (a).

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[20] S. Kida, *Nippon Kagaku Zasshi*, **85**, 428 (1964).