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Binuclear Metal Complexes. XXI.[1] Copper(I)-Copper(II) Mixed-Valence Complexes with Quadridentate Schiff Bases

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Synopsis. Copper(I)–copper(II) mixed-valence complexes of the quadridentate Schiff bases were obtained and characterized. ESR and visible spectra showed no evidence for the delocalization of an unpaired electron between copper(I) and copper(II) ions.

It is well known[2] that *N,N'*-di(salicylidene)ethylenediaminatocopper(II) and its homologues react with bivalent metal ions to form binuclear and trinuclear metal complexes. In the previous paper[3] of this series it was shown that vanadium(V)–copper(I) hetero-metal complexes with *N,N'*-di(salicylidene)ethylenediamine and its derivatives are obtained by reacting oxovanadium(IV) complexes with the Schiff bases and copper(II) halides. This fact implies that the "outside" coordination site of these ligands is sterically suitable for a copper(I) ion which prefers tetrahedral or trigonal configuration to square-planar configuration. Thus, it seems possible to synthesize copper(I)–copper(II) mixed-valence complexes using the quadridentate Schiff bases. This report relates to the synthesis and characterization of the mixed-valence complexes, $[Cu_2(R_1,R_2\text{-en})an]ClO_4$, $[Cu_2(H,H\text{-ph})an]ClO_4$, and $[Cu_2(H,H\text{-tn})]ClO_4$ (R_1,R_2=H, CH_3; an=CH_3CN), where $H_2(R_1,R_2\text{-en})$ denotes *N,N'*-di(salicylidene)ethylenediamine with the substituents R_1 and R_2 at the 5- and α-positions respectively, and $H_2(H,H\text{-ph})$ and $H_2(H,H\text{-tn})$ indicate *N,N'*-di(salicylidene)-*o*-phenylenediamine and *N,N'*-di(salicylidene)trimethylenediamine respectively.

Experimental

Syntheses. The synthetic methods of the copper(I)–copper(II) mixed-valence complexes are practically the same. The synthesis of $[Cu_2(H,H\text{-en})an]ClO_4$ is exemplified. Nitrogen was bubbled through a suspension of Cu(H,H-en) (330 mg) in dry methanol (50 ml) for 10 min. Then $[Cu(an)_4]ClO_4$ (326 mg) was added and the mixture was stirred for 3 h under nitrogen atomosphere. Red-purple prisms which separated were collected, washed with dry methanol, and dried over P_2O_5 in vacuum. Elemental analyses are given in Table 1.

The compound used for the ESR study was prepared by a method similar to that described above except for using $Ni(R_1,R_2\text{-en})$ containing a slight amount of copper(II) ion instead of using $Cu(R_1,R_2\text{-en})$. $Cu(R_1,R_2\text{-en})ZnCl_2$ was obtained after the method described by Sinn *et al.*[4]

Measurements. IR spectra were measured with a Hitachi 215 Grating Spectrophotometer on a KBr disk. Reflectance spectra were measured with a Shimadzu Multipurpose Spectrophotometer Model MSP-5000. Magnetic susceptibilities were measured by the Faraday method. Effective magnetic moments were calculated by the expression, $\mu_{\text{eff}}=2.828\sqrt{(\chi_M-60\times10^{-6})T}$, where χ_M is molar magnetic susceptibility corrected by the use of Pascal's constants.

Results and Discussion

Selected IR bands, visible spectral bands and effective magnetic moments of the present complexes as well as $Cu(R_1,R_2\text{-en})ZnCl_2$ are given in Table 2. Magnetic moments clearly indicate that the present complexes contain one bivalent and one univalent copper ions in each molecule. One of the skeletal vibrations (near 1550 cm^{-1}) of the mixed-valence complexes is higher in frequency than that of the corresponding mononuclear complex. Furthermore, the frequency of this band is practically the same as that of $Cu(R_1,R_2\text{-en})ZnCl_2$, whose binuclear structure has been demonstrated.[4] These facts imply that the copper atoms in the mixed-valence complexes are bridged by the phenolic oxygens.

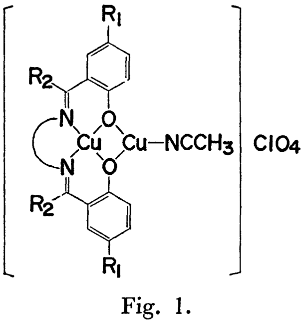

Fig. 1.

Table 1. Elemental analyses of mixed-valence complexes

	Found (%)				Calcd (%)			
	C	H	N	Cu	C	H	N	Cu
$[Cu_2(H,H\text{-en})an]ClO_4$	40.41	3.17	7.86	24.00	40.49	3.21	7.87	23.80
$[Cu_2(H,Me\text{-en})an]ClO_4$	42.54	3.75	7.43	22.60	42.75	3.77	7.48	22.62
$[Cu_2(Me,H\text{-en})an]ClO_4$	43.21	3.88	7.29	22.66	42.75	3.77	7.48	22.62
$[Cu_2(Me,Me\text{-en})an]ClO_4$	44.59	4.23	7.08	20.93	44.79	4.27	7.12	21.54
$[Cu_2(H,H\text{-ph})an]ClO_4$	45.28	2.94	7.29	21.66	45.41	2.94	7.22	21.86
$[Cu_2(H,H\text{-tn})]ClO_4$	40.09	3.47	6.02	25.13	40.36	3.19	5.54	25.12

TABLE 2. SELECTED IR BANDS, VISIBLE SPECTRAL BANDS, AND EFFECTIVE MAGNETIC MOMENTS OF COMPLEXES

	IR (cm^{-1})			Visible (cm^{-1})		μ_{eff} (B.M.)
	C≡N	skel.	ClO_4^-			
$[Cu_2(H,H\text{-en})an]ClO_4$	2290	1550	1090	17 500	19 500	1.82
$[Cu_2(H,Me\text{-en})an]ClO_4$	2300	1540	1080	18 000	19 600	1.80
$[Cu_2(Me,H\text{-en})an]ClO_4$	2290	1550	1100	17 000	19 600	1.88
$[Cu_2(Me,Me\text{-en})an]ClO_4$	2280	1540	1090	18 500	19 800	1.78
$[Cu_2(H,H\text{-ph})an]ClO_4$	2295	1525	1100	18 000		1.84
$[Cu_2(H,H\text{-tn})]ClO_4$		1550	1100	18 000		1.79
$Cu(H,H\text{-en})ZnCl_2$		1555		17 500	19 600	1.83
$Cu(H,Me\text{-en})ZnCl_2$		1540		18 000	19 800	1.82
$Cu(Me,H\text{-en})ZnCl_2$		1550		17 000	19 700	1.87
$Cu(Me,Me\text{-en})ZnCl_2$		1540		18 500	19 800	1.84

TABLE 3. TEMPERATURE VARIATIONS OF MAGNETIC MOMENT

$[Cu_2(H,H\text{-en})an]ClO_4$											
T(K)	83.5	103.5	125.1	146.3	168.5	190.0	211.3	234.2	256.1	276.1	297.4
μ_{eff}	1.79	1.80	1.81	1.81	1.82	1.81	1.82	1.81	1.82	1.81	1.82
$[Cu_2(H,Me\text{-en})an]ClO_4$											
T(K)	81.7	103.5	124.7	145.5	166.3	186.9	206.1	226.9	249.3	274.3	295.4
μ_{eff}	1.79	1.78	1.78	1.78	1.77	1.78	1.78	1.79	1.79	1.80	1.80
$[Cu_2(H,H\text{-tn})]ClO_4$											
T(K)	81.5	102.0	124.7	145.5	167.4	187.0	207.0	229.0	250.2	274.4	297.4
μ_{eff}	1.54	1.57	1.59	1.60	1.61	1.63	1.67	1.70	1.74	1.77	1.79

The IR spectra of $[Cu_2(R_1,R_2\text{-en})an]ClO_4$ and $Cu(R_1,R_2\text{-en})ZnCl_2$ resemble each other except the bands at 2300—2280 and 1100—1080 cm^{-1} of the former. They are assigned to coordinated acetonitrile and non-coordinated perchlorate ion respectively. Therefore, it is likely that $[Cu_2(R_1,R_2\text{-en})an]ClO_4$ and $[Cu_2(H,H\text{-en})an]ClO_4$ have a structure shown in Fig. 1.

On the other hand, $[Cu_2(H,H\text{-tn})]ClO_4$ differs from the other complexes in lacking acetonitrile in composition. It is likely that the "outside" copper(I) ion is coordinated by a donating atom of another molecule at the third (and forth) coordination position to form a polymeric structure. In fact, the magnetic moment of $[Cu_2(H,H\text{-tn})]ClO_4$ decreases with lowering of temperature, while the moments of $[Cu_2(H,H\text{-en})an]ClO_4$ and $[Cu_2(H,Me\text{-en})an]ClO_4$ are almost constant in the temperature range 78—300 K (Table 3).

The electronic spectra of $[Cu_2(H,H\text{-ph})an]ClO_4$ and $[Cu_2(H,H\text{-tn})]ClO_4$ are practically the same as those of Cu(H,H-ph) and Cu(H,H-tn), respectively. On the other hand, each spectrum of $[Cu_2(R_1,R_2\text{-en})an]ClO_4$ markedly differs from that of $Cu(R_1,R_2\text{-en})$, a new band being found around 19500 cm^{-1}. This band can not be an inter-valence transfer band, but should be one component of the d-d bands of the "inside" copper(II) ion, judging from the fact that the electronic spectra of $[Cu_2(R_1,R_2\text{-en})an]ClO_4$ and $Cu(R_1,R_2\text{-en})ZnCl_2$ resemble each other. It can be concluded that there is no appreciable delocalization of the unpaired electron over the binuclear unit, since the ESR spectra of $Ni(Cu)(R_1,R_2\text{-en})$ and $[Ni(Cu)Cu(R_1,R_2\text{-en})an]ClO_4$ show nearly the same $g_{\parallel}$ and $A_{\parallel}$, respectively.

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References

1) Part XX: H. Okawa *et al.*, *Mem. Faculty Sci., Kyushu Univ., Ser. C, Chem.*, in press.

2) E. Sinn and C. M. Harris, *Coord. Chem. Rev.*, **4**, 391 (1969).

3) H. Okawa and S. Kida, *Inorg. Chim. Acta*, **23**, 253 (1977).

4) S. J. Gruber, C. M. Harris, and E. Sinn, *J. Inorg. Nucl. Chem.*, **30**, 1805 (1968).