Synthesis and Properties of Novel Type Binuclear Copper(II) Complexes Whose Coordination Units Are Linked by a Flexible Polyatomic Chain

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Synopsis. Binuclear copper(II) complexes with two bis(2-benzimidazolylmethyl)amine moieties linked by a flexible polyatomic chain were prepared. Their ESR spectral properties were highly dependent on the bridging chains linking two coordination units.

In the preceding paper,[1] we reported that the reactivities of binuclear copper(I) complexes with (L-px), (L-mx), and (L-cy) (for the abbreviations of the ligands, see Fig. 1) towards molecular oxygen are highly dependent on the bridging chains (R in Fig. 1) linking two coordination units. The above facts are suggesting that the steric arrangements of the two copper ions in these binuclear complexes are controlled by the bridging chain, making the reactivity of the copper(I) complexes towards O_2 molecule different from each other. In order to obtain additional support for the above view, in this study, we have investigated the ESR spectra of the copper(II) complexes with the binucleating ligands shown in Fig. 1.

Experimental

The ligands cited in Fig. 1 were prepared according to the method described in the literature.[1] The analytical data of the new compounds are summarized in the Table 1. The copper(II) complexes were obtained as blue or bluish-green crystals by mixing the methanol solution of the ligand and the stoichiometric amount of $Cu(NO_3)_2 \cdot 3H_2O$, and recrystallized from a *N*,*N*-dimethylformamide–methanol solution. The analytical data of the copper(II) complexes are listed in the Table 1.

ESR spectra of the complexes ($[Cu^{2+}] = 1 \times 10^{-3}$ mol dm^{-3}) were obtained with a JEOL ESR apparatus model JES FE3X by the use of an X-band at 77 and 291 K.

Results and Discussion

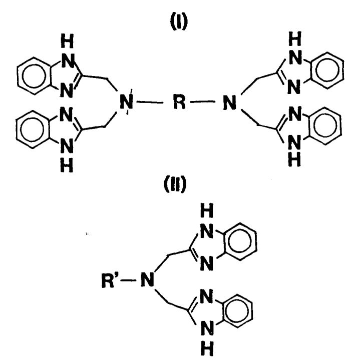
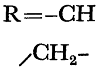
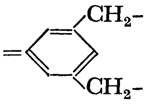
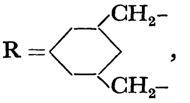
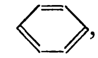


Fig. 1. Chemical structures of the ligands cited in this study and their abbreviations.
(I) Binucleating ligands, R=$-CH_2CH_2-$, (L-2); R=$-(CH_2)_3-$, (L-3); R=$-(CH_2)_4-$, (L-4); R=$-(CH_2)_6-$, (L-6); R=$-CH_2-$$-CH_2-$, (L-px); R= (L-mx); R=, (L-cy) (II) mononucleating ligand, R'=H, (ibz); R'=$-CH_2-$, (babz).

ESR spectra of $Cu_2(L\text{-}2)(NO_3)_4$[2] and $Cu_2(L\text{-}3)(NO_3)_4$ in *N*,*N*-dimethylforamide, obtained at 291 K are shown in Fig. 2. The spectrum of mononuclear complex, $Cu(babz)(NO_3)_2$ is similar to that of $Cu_2(L\text{-}2)(NO_3)_4$, showing four hyperfine splittings due to the nuclear spin(I=3/2) of copper atom. In the spectrum of other binuclear copper(II) complexes, only a broad peak was observed, as exemplified by $Cu_2(L\text{-}3)(NO_3)_4$ in Fig. 2.

ESR spectra of the binuclear copper(II) complexes obtained at 77 K are shown in Fig. 3. Mononuclear complex, $Cu(babz)(NO_3)_2$ exhibits the spectrum characteristic of the tetragonal copper(II) complexes[3] ($g_{//}$= 2.27, $g_{\perp}$=2.05, $|A_{//}|$=145 G, 1 G=1×10^{-4} T). In the spectrum of $Cu_2(L\text{-}4)(NO_3)_4$, six hyperfine peaks (the seventh peak may be overlapped with the $g_{\perp}$

TABLE 1. ANALYTICAL DATA OF THE NEW COMPOUNDS

Compound	C (%) Found(Calcd)	H (%) Found(Calcd)	N (%) Found(Calcd)	Cu(%) Found(Calcd)
(L-3)	70.17(70.69)	5.75(5.76)	23.36(23.55)	
(L-4)·H_2O	69.24(68.99)	6.08(6.11)	22.23(22.35)	
(L-6)·H_2O	70.20(69.70)	6.42(6.47)	21.56(21.39)	
(L-mx)·H_2O	70.89(71.19)	5.75(5.68)	20.43(20.76)	
(L-px)·1/2 H_2O	72.43(72.16)	5.63(5.60)	20.99(21.04)	
Cu_2(L-3)$(NO_3)_4 \cdot 3H_2O$	40.97(41.06)	3.87(3.94)	18.98(19.15)	12.4(11.9)
Cu_2(L-4)$(NO_3)_4 \cdot 2H_2O$	42.12(42.40)	3.84(3.95)	18.97(19.23)	12.7(12.5)
Cu_2(L-6)$(NO_3)_4 \cdot H_2O$	44.35(44.32)	4.02(4.11)	18.94(19.04)	12.5(12.3)
Cu_2(L-mx)$(NO_3)_4 \cdot H_2O$	45.72(45.70)	3.58(3.64)	18.36(18.65)	12.4(12.1)
Cu_2(L-px)$(NO_3)_4 \cdot H_2O \cdot CH_3OH$	45.51(45.70)	3.94(3.64)	18.65(18.12)	11.7(11.7)
Cu_2(L-cy)$(NO_3)_4 \cdot 4H_2O$	43.37(43.28)	4.37(4.54)	17.67(17.67)	11.5(11.4)

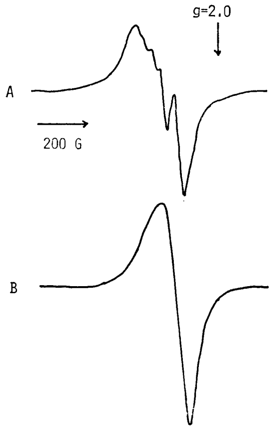


Fig. 2. ESR spectra of A: $Cu_2(L\text{-}2)(NO_3)_4$ and B: $Cu_2(L\text{-}3)(NO_3)_4$ (dmf, 291 K).

peak) are observed; hyperfine splitting ($|A|=71$ G) is as half as that of $Cu(babz)(NO_3)_2$. The spectra of $Cu_2(L\text{-}px)(NO_3)_4$ and $Cu_2(L\text{-}cy)(NO_3)_4$ were similar to that of $Cu_2(L\text{-}4)(NO_3)_4$.

The spectrum of $Cu_2(L\text{-}6)(NO_3)_4$ (and also $Cu_2(L\text{-}mx)(NO_3)_4$) is different from that of $Cu_2(L\text{-}4)(NO_3)_4$, and similar to those of $Cu_2(L\text{-}2)(NO_3)_4$ and $Cu(babz)(NO_3)_2$. The spectrum of $Cu_2(L\text{-}3)(NO_3)_4$ is rather complicated, different from either of $Cu_2(L\text{-}4)(NO_3)_4$ and also $Cu_2(L\text{-}6)(NO_3)_4$. In the case of $Cu_2(L\text{-}2)(NO_3)_4$, the ESR spectra at 291 and 77 K closely resemble those of mononuclear complex, $Cu(babz)(NO_3)_2$. Thus, it has became apparant that the ESR spectral properties of the binuclear copper(II) complexes obtained in this study are dependent on the bridging chains linking two coordination units. These facts may be due to the difference in the weak interaction between two copper(II) ions, controlled by the flexible polyatomic chain used.

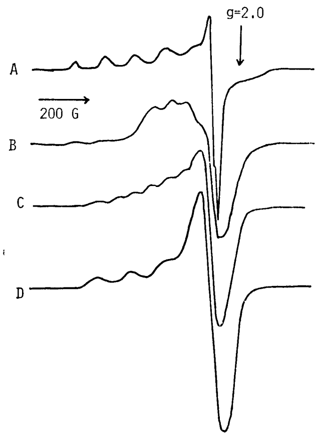


Fig. 3. ESR spectra of binuclear copper(II) complexes (dmf, 77 K).
A: $Cu_2(L\text{-}2)(NO_3)_4$, B: $Cu_2(L\text{-}3)(NO_3)_4$, C: $Cu_2(L\text{-}4)(NO_3)_4$, D: $Cu_2(L\text{-}6)(NO_3)_4$.

References

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