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Superexchange Interactions of Copper(II) Ions in some Binuclear Complexes Apically Bridged by Halogenide Ions

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*Binuclear copper(II) complexes [$Cu_2X_2(pyal)_2$=SPMN] Y_{2-4} (X = halogenide ion or H_2O; Y = nitrate or bromide ion) have been prepared from Schiff base ligands derived from pyridine-2-carbaldehyde (pyal) and spermine (SPMN). ESR spectra of these binuclear complexes in methanol glasses at 77 K exhibited seven hyperfine lines at the $g_\parallel$ region ($A_\parallel$ = 85–90 G). This is indicative of the existence of an interacting pair of Cu(II) atoms in the binuclear complexes. Magnetic susceptibilities were measured over the temperature range 4.2–300 K. The best fit values for g and 2J were 2.08 and –2.0 cm^{-1} for [$Cu_2Cl_2(pyal)_2$=SPMN(NO_3)$_2$, and 2.23 and –40.0 cm^{-1} for [$Cu_2Br_2(pyal)_2$=SPMN]Br_2 respectively. Redox behavior of these binuclear complexes were investigated by use of polarography and controlled-potential electrolysis. Reduction potentials for copper(II) ions of the binuclear complexes in DMF at 25 °C were not sufficiently high (*ca. –0.15 V *vs.* S.C.E.) as suitable models for type III coppers in biological systems.*

Introduction

A number of binuclear copper(II) complexes have hitherto been synthesized and characterized to mimic the protein binuclear copper sites as assumed for tyrosinase, laccase or hemocyanin [1–8]. In order to realize the function of these copper proteins it may be necessary to provide the complexes with several characteristics. Firstly the oxidized form of the binuclear sites must be strongly antiferromagnetically coupled as disclosed for the type III copper(II) ions [9, 10]. Secondly the donor set around the two coppers must consist of only nitrogen and/or oxygen in consideration of the very low possibility of containing thiol or thioether ligand in the active site of hemocyanin [11, 12]. Thirdly the redox potential of binuclear copper(II) complexes must be fairly high, for example, E^0 value for Cu^{II}/Cu^{I} has been known to be +0.54 V *vs.* N.H.E. for hemocyanin [13].

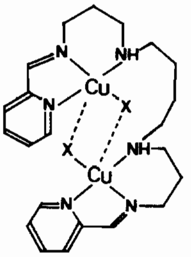

Fig. 1. Proposed structure of binuclear copper(II) complexes [$Cu_2X_2(pyal)_2$=SPMN] Y_{2-4} (X = Cl^-, Br^- or H_2O; Y = NO_3^- or Br^-).

We have been working toward the synthesis of model complexes for hemocyanin which satisfy most of the above necessary conditions. In this paper we report the preparation and properties of binuclear copper(II) complexes with a Schiff base derived from pyridine-2-carbaldehyde (pyal) and spermine (SPMN) as illustrated in Fig. 1.

Experimental

Materials

Copper(II) nitrate trihydrate, copper(II) perchlorate hexahydrate and trimethylenediamine were purchased from Nakarai Chemicals Ltd. and spermine from Sigma Chemical Co. Pyridine-2-carbaldehyde was obtained from Merck A.G. and distilled. All other reagents used were of the highest grade commercially available.

Preparation of Complexes

The binuclear complex [$Cu_2Cl_2(pyal)_2$=SPMN](NO_3)$_2$, where $(pyal)_2$=SPMN refers to the Schiff base derived from pyridine-2-carbaldehyde and spermine, was prepared as follows: 1.01 g (5 mmol) of spermine and 1.07 g (10 mmol) of pyridine-2-carbaldehyde were dissolved in 100 ml of methanol, and allowed to stand overnight at room temperature. In this solution was further dissolved 1.17 g (20 mmol) of NaCl. The methanol solution of the Schiff base thus obtained was added dropwise to a separately prepared 50 ml methanol solution containing 2.24 g (10 mmol) of $Cu(NO_3)_2 \cdot 3H_2O$ under vigorous stirring at room temperature, to give a precipitate of green solid. The precipitate was recrystallized from methanol and dried in vacuum over $CaCl_2$ for 24 hr. *Anal.* Found: C, 37.40; H, 4.80; N, 15.71; Cu, 17.8%. Calcd. for $[Cu_2Cl_2(C_{22}H_{32}N_6)](NO_3)_2$: C, 37.61; H, 4.59; N, 15.95; Cu, 18.1%.

$[Cu_2Br_2(pyal)_2{=}SPMN]Br_2$ and $[Cu_2(H_2O)_2(pyal)_2{=}SPMN](NO_3)_4$ were synthesized by the same method as that for $[Cu_2Cl_2(pyal)_2{=}SPMN](NO_3)_2$, using sodium bromide and a small amount of water respectively instead of sodium chloride. *Anal.* Found: C, 31.63; H, 3.83; N, 10.09; Cu, 16.3%. Calcd. for $[Cu_2Br_2(C_{22}H_{32}N_6)]$ Br_2: C, 31.94; H, 3.90; N, 10.16; Cu, 15.4%. *Anal.* Found: C, 33.96; H, 4.27; N, 17.63; Cu, 16.1%. Calcd. for $[Cu_2(H_2O)_2(C_{22}H_{32}N_6)](NO_3)_4$: C, 33.38; H, 4.58; N, 17.69; Cu, 16.1%.

The mononuclear complex $[Cu(pyal)_2{=}tn](ClO_4)_2$ was prepared as follows: 1.07 g (10 mmol) of pyridine-2-carbaldehyde and 1.85 g (5 mmol) of $Cu(ClO_4)_2 \cdot 6H_2O$ were dissolved in 25 ml of 50% aqueous methanol and stirred for 10 min at room temperature. To this was further added 0.37 g (5 mmol) of trimethylenediamine in 5 ml of 50% aqueous methanol, being heated for 90 min at 50 °C. The solution was then cooled at room temperature, to give a precipitate of blue-violet solid. The precipitate was recrystallized from water, washed with a small quantity of ice-cold water and methanol, and dried in vacuum over $CaCl_2$ for 24 hr. *Anal.* Found: C, 35.04; H, 3.26; N, 10.57; Cu, 12.8%. Calcd. for $[Cu(C_{15}H_{16}N_4)](ClO_4)_2$: C, 34.99; H, 3.14; N, 10.89; Cu, 12.4%.

Physical Measurements and Instruments

Infrared, far-infrared and electronic spectra were recorded on a Hitachi 260-10 infrared, a Hitachi EPI-L grating infrared and a Union Giken SM-401 High Sensitivity Spectrophotometer, respectively. Electron spin resonance spectra were recorded using a JEOL JES-FE1X at 77 K. Magnetic field was calibrated on a Mn(II) in MnO (ΔH_{3-4} = 86.9 G) and g values were calibrated based on Li·TNCQ (g = 2.0025). The Faraday method was applied for the measurement of magnetic susceptibility over the range from liquid helium temperature to room temperature. Redox behavior was examined by a Yanaco Voltammetric Analyzer Model P-1000 and a Yanaco Controlled-Potential Electrolyzer Model VE-8.

TABLE I. Electronic Spectra of Copper(II) Complexes in Methanol.

Complex	λ_{max}, nm (ϵ)
$[Cu_2Cl_2(pyal)_2{=}SPMN](NO_3)_2$	664 (243)
$[Cu_2Br_2(pyal)_2{=}SPMN]Br_2$	675 (314)
$[Cu_2(H_2O)_2(pyal)_2{=}SPMN](NO_3)_4$	662 (243)
$[Cu(pyal)_2{=}tn](ClO_4)_2$	640 (74)

Results and Discussion

Infrared and Far-infrared Spectra

The infrared spectra of Cl and aqua binuclear complexes exhibited a strong absorption at *ca.* 1400 cm^{-1}, indicating that these complexes are nitrate. The C=N stretching absorption band of azomethine group was found at 1640 cm^{-1}, indicating that all of these are Schiff base complexes. Their virtually identical infrared spectra imply that they are similar to each other in their structures.

The far-infrared spectra of the binuclear complexes exhibited a Cu–Cl stretching absorption band at 290 cm^{-1} and Cu–py at 260 cm^{-1} for Cl complex, Cu-Br at around 230 cm^{-1} and Cu–py at 270 cm^{-1} for Br complex and Cu–H_2O at around 305 cm^{-1} and Cu–py at around 245 cm^{-1} for aqua complex respectively. From these facts it is confirmed that chloro, bromo, aqua or pyridine are coordinated to the copper(II) ions of binuclear complexes [14].

Electronic Spectra

Numerical data for the visible absorption spectra are listed in Table I. Inspection of Table I reveals that the d–d bands of the binuclear complexes are observed at longer wavelengths than that of the mononuclear complex, which apparently has a $(N)_4$ donor set in the coordination sites, consistently supporting that the binuclear complexes have a $(N)_3X$ ($X = Cl^-$, Br^- or H_2O) donor set. Further, the considerably high intensity of the d–d band may indicate that these are five-coordinate complexes [15–19].

ESR Spectra

The ESR spectra of the binuclear complexes $[Cu_2X_2(pyal)_2{=}SPMN]Y_{2-4}$ in methanol glasses at 77 K are shown in Fig. 2 and the numerical data are listed in Table II. As is clear from Fig. 2, $[Cu_2X_2(pyal)_2{=}SPMN]Y_{2-4}$ exhibited seven hyperfine lines at the $g_\parallel$ region ($A_\parallel$ = 85–90 G), whereas the mononuclear complex $[Cu(pyal)_2{=}tn](ClO_4)_2$ presented

TABLE II. ESR Parameters of Copper(II) Complexes in Methanol Glasses at 77 K.

Complex	$g_{\parallel}$	$g_{\perp}$	$\lvert A_{\parallel}\rvert$(G)
$[Cu_2Cl_2(pyal)_2{=}SPMN](NO_3)_2$	2.30	2.08	91
$[Cu_2Br_2(pyal)_2{=}SPMN]Br_2$	2.23	2.08	87
$[Cu_2(H_2O)_2(pyal){=}SPMN](NO_3)_4$	2.26	2.08	85
$[Cu(pyal)_2{=}tn](ClO_4)_2$	2.23	2.07	182

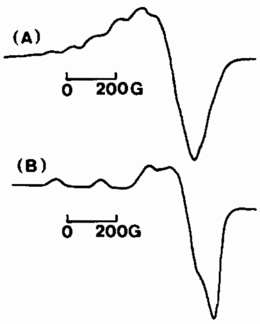

Fig. 2. ESR spectra of copper(II) complexes (A), $[Cu_2Br_2(pyal)_2{=}SPMN]Br_2$ and (B), $[Cu(pyal)_2{=}tn](ClO_4)_2$ in methanol glasses at 77 K.

TABLE III. Polycrystalline ESR Parameters of Copper(II) Complexes at 77 K.

Complex	$g_{\parallel}$ (g_{zz})	$g_{\perp}$ (g_{yy})	(g_{xx})
$[Cu_2Cl_2(pyal)_2{=}SPMN](NO_3)_2$	2.03	2.16	
$[Cu_2Br_2(pyal)_2{=}SPMN]Br_2$	2.03	2.11	2.19
$[Cu_2(H_2O)_2(pyal)_2{=}SPMN](NO_3)_4$	2.23	2.09	
$[Cu(pyal)_2{=}tn](ClO_4)_2$	2.22	2.06	

TABLE IV. Coupling Constants of Binuclear Copper(II) Complexes.

Complex	2J (cm^{-1})
$[Cu_2Cl_2(pyal)_2{=}SPMN](NO_3)_2$	–2.0
$[Cu_2Br_2(pyal)_2{=}SPMN]Br_2$	–4.0

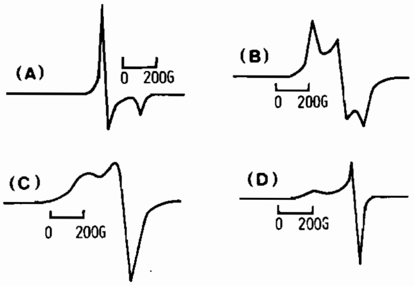

Fig. 3. Polycrystalline ESR spectra of copper(II) complexes (A), $[Cu_2Cl_2(pyal)_2{=}SPMN](NO_3)_2$, (B), $[Cu_2Br_2(pyal)_2{=}SPMN]Br_2$, (C), $[Cu_2(H_2O)_2(pyal)_2{=}SPMN](NO_3)_4$ and (D), $[Cu(pyal)_2{=}tn](ClO_4)_2$ at 77 K.

four lines at the $g_{\parallel}$ region ($A_{\parallel}$ = 182 G). These facts are indicative of the existence of an interacting pair of Cu(II) atoms in the binuclear complexes, providing evidence for an intramolecular coupling as an exchange pathway in these systems [20–23]. Although there would be expected some intermolecular interaction in a highly concentrated solution, the possibility is virtually neglected since no such trend was observed for the mononuclear complex $[Cu(pyal)_2{=}tn](ClO_4)_2$ at the same concentration.

The powder ESR spectrum of $[Cu_2(H_2O)_2(pyal)_2{=}SPMN](NO_3)_4$ at 77 K is shown in Fig. 3 and the numerical data are listed in Table III. The spectrum exhibited a considerably broader line shape than that of the mononuclear complex $[Cu(pyal)_2{=}tn](ClO_4)_2$, also suggesting the existence of Cu(II)–Cu(II) interaction [24–25]. The powder ESR spectrum of $[Cu_2Cl_2(pyal)_2{=}SPMN](NO_3)_2$ at 77 K indicated that the unpaired electron on copper(II) ion is in the d_{z^2} orbital. Therefore it is considered that the Cl^- ion coordinated to the one copper(II) ion in the equatorial plane apically bridges more strongly to the other copper(II) ion than in the case of H_2O in $[Cu_2(H_2O)_2(pyal)_2{=}SPMN](NO_3)_4$. In $[Cu_2Br_2(pyal)_2{=}SPMN]Br_2$ is obtained the rhombic ESR spectrum [26] of d_{z^2} base. It is also considered that Br^- ion apically bridges even more strongly to the one copper(II) ion whereas it is coordinated in the equatorial plane more weakly to the other copper(II) ion as compared with the case of Cl^- in $[Cu_2Cl_2(pyal)_2{=}SPMN](NO_3)_2$. In line with this, the magnetic susceptibility of $[Cu_2Br_2(pyal)_2{=}SPMN]Br_2$ revealed a stronger spin–spin superexchange interaction than that of $[Cu_2Cl_2(pyal)_2{=}SPMN](NO_3)_2$ (*vide infra*).

Magnetic Properties

Magnetic properties of the above described binuclear complexes were investigated in order to determine if the exchange coupling can occur *via* the bridging halogenide ions. For two binuclear complexes, magnetic susceptibilities were measured over the temperature range 4.2–300 K. The data fit the Bleany–Bowers equation using the Van Vleck temperature-independent paramagnetic constant $N\alpha = 60 \times 10^{-6}$ cm^3/mol. The best fit values for g and 2J were 2.08 and –2.0 cm^{-1} for $[Cu_2Cl_2(pyal)_2{=}$

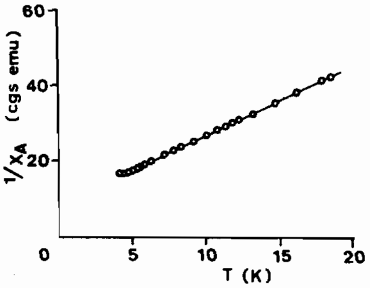

Fig. 4. Plot of the function $1/\chi_A$ *vs.* temperature for the binuclear copper(II) complex $[Cu_2Br_2(pyal)_2{=}SPMN]Br_2$. The solid line shows the theoretical inverse susceptibility calculated by the Bleany–Bowers equation with g = 2.23, 2J = –4.0 cm^{-1} and $N\alpha = 60 \times 10^{-6}$ cgs emu.

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

$SPMN](NO_3)_2$, and 2.23 and –4.0 cm^{-1} for $[Cu_2Br_2(pyal)_2{=}SPMN]Br_2$ respectively. In all the cases, plots of inverse susceptibilities, $1/\chi_A$, *versus* temperature yielded nearly straight lines as shown in Fig. 4. The magnetic behavior of all the compounds was very similar over the temperature range examined. No maximum susceptibility was observed above 4.2 K, suggesting small J values, as listed in Table IV, in these complexes. According to the so-called 90° angle rule [27–34], the exchange coupling in the case of a d^9 dimer is likely to be ferromagnetic if the bridging angle is nearly 90° and antiferromagnetic if it diverges considerably from 90°. The fact that antiferromagnetic interaction was observed, though very small, is supposed to result from slight off-axis bridging of the axial ligand to copper(II) ion. The empirical correlations of Hatfield [30, 31], which predict negative J values for a bridging angle of 97°, suggest that Cu(II)–bridge–Cu(II) angle for binuclear complexes is substantially larger than 90° (see Fig. 1).

Redox Behavior

A polarogram for $[Cu_2Br_2(pyal)_2{=}SPMN]Br_2$ in DMF solution at 25 °C gave three reduction waves and their half-wave potentials were 0.19, –0.13 and –0.55 V *vs.* S.C.E. The $[Cu_2Br_2(pyal)_2{=}SPMN]Br_2$ in DMF solution is green (λ_{max}: 758 nm) and the ESR spectrum in DMF glass at 77 K shows dimeric pattern of seven hyperfine lines at the $g_\parallel$ region ($A_\parallel$ = 87 G) as described above. By controlled-potential electrolysis at 0.05 V a slightly bluish green solution was obtained (λ_{max}: 716 nm) and the ESR spectrum at 77 K exhibited the monomeric pattern of four lines at the $g_\parallel$ region ($A_\parallel$ = 174 G). Further the electrolysis at –0.30 V resulted in a reddish brown solution (shoulder at 560 nm) which was ESR-silent. On exposing the solution to air for a few hours the same slightly bluish green solution was reproduced, whose ESR spectrum showed the monomeric pattern of the four lines at $g_\parallel$ region, as the solution reduced at 0.05 V. The controlled-potential electrolysis at –0.80 V gave a colorless solution, which was accompanied by a black deposit at the platinum cathode. These facts are interpreted as follows (see Scheme 1): the shift of absorption maxima of electronic spectra and the change of ESR spectra after the first electrolysis indicate that the reduction of the ligand, perhaps the azomethine group of the Schiff base, occurred and the accompanying conformational change made the intramolecular Cu(II)–Cu(II) interaction impossible. Disappearance of the d–d band in the electronic spectrum and of the ESR signal with the second reduction and their reappearance in contact with air reveal a reversible two-electron process: Cu(II)Cu(II) → Cu(I)–Cu(I). At the third reduction step, the black precipitate at the platinum cathode exhibits an irreversible two-electron process:Cu(I)–Cu(I) → 2Cu(0). Reduction potentials for copper(II) ions of some other complexes in DMF at 25 °C are listed in Table V.

TABLE V. Polarographic Data of Copper(II) Complexes in DMF at 25 °C.

Complex	$E_{1/2}$ *V vs.* S.C.E.
$[Cu_2Cl_2(pyal)_2{=}SPMN](NO_3)_2$	–0.15
$[Cu_2Br_2(pyal)_2{=}SPMN]Br_2$	–0.13
$[Cu(pyal)_2{=}tn](ClO_4)_2$	–0.16

Cu(II)Cu(II)L, dimeric (green soln.)
$\downarrow$ 0.05 V ($E_{1/2}$: 0.19 V)
Cu(II)Cu(II)L′, monomeric (slightly bluish green soln.)
$\uparrow\downarrow$ –0.30 V ($E_{1/2}$: –0.13 V)
Cu(I)Cu(I)L′, (reddish brown soln.)
$\downarrow$ –0.80 V ($E_{1/2}$: –0.55 V)
2Cu(0), L′, (black deposit)

Scheme 1. Redox behavior of the binuclear copper(II) complex $[Cu_2Br_2(pyal)_2{=}SPMN]Br_2$ in DMF at 25 °C.

Conclusion

ESR spectra and magnetic susceptibility data show that the binuclear complexes containing equatorial and axial bridges by halogenide or H_2O ligand have five-coordinate structures and the existence of antiferromagnetic spin–spin superexchange interaction between the two copper(II) ions. Because the binuclear complexes contain no soft donor atoms such as sulfur [35–38], they do not show high redox potentials.

However, the redox potentials are somewhat higher than those of ordinary mononuclear copper(II) complexes, probably because they contain many aromatic nitrogens as donor atoms [19]. It is very interesting whether the redox potentials of binuclear complexes which contain no sulfur (only nitrogen and oxygen) as donor atoms can be close to those of type III coppers, for example 0.54 V *vs.* N.H.E. for hemocyanin [13]. It is hoped that careful variation in ligand structure and bridging group of this kind will better delineate the copper environment in the enzymes than has hitherto been possible.

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