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Binuclear Metal Complexes. XXXIX.[1] Synthesis and Properties of Binuclear Copper(II) Complexes with [2-(2-Pyridyl)ethylamino]alkanols and [2-(2-Pyridyl)ethylthio]alkanols

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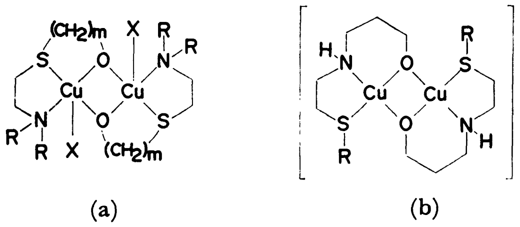
Di-μ-alkoxo-bridged binuclear copper(II) complexes, Cu(py-3-3-nno)X, Cu(py-3-2-nso)X, and Cu(py-3-3-nso)X (X=Cl, Br, ClO_4, NO_3, PF_6, BF_4), have been synthesized and characterized, where Hpy-3-3-nno, Hpy-3-2-nso, and Hpy-3-3-nso denote 3-[2-(2-pyridyl)ethylamino]-1-propanol, 2-[2-(2-pyridyl)ethylthio]ethanol, and 3-[2-(2-pyridyl)ethylthio]-1-propanol, respectively. It was found that 2-[2-(2-pyridyl)ethylamino]ethanol (Hpy-3-2-nno) cannot form di-μ-alkoxo-bridged binuclear copper(II) complexes owing to the high strain in the fused ring system. These complexes exhibited a band at 22000—27000 cm^{-1} characteristic of the di-μ-alkoxo-bridged structure, the bands for Cu(py-3-2-nso)X and Cu(py-3-3-nso)X being lower in frequency compared with those for Cu(py-3-3-nno)X. Antiferromagnetic interaction was stronger and reduction potential (Cu(II)–Cu(II)→Cu(I)–Cu(I)) was higher for Cu(py-3-3-nso)X than those for Cu(py-3-3-nno)X. Cu(py-3-3-nso)Cl and Cu(py-3-2-nso)Br showed two reduction waves at about +0.15 and −0.4 V *vs.* SCE. These results were discussed in terms of the structure in solution on the basis of conductivity measurements.

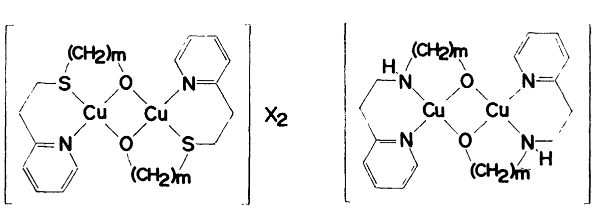
Di-μ-alkoxo-bridged binuclear copper(II) complexes containing a thioether sulfur as a donor atom are of interest as models of Type III copper proteins. In the preceding papers of this series,[2–6] we have reported preparations and properties of di-μ-alkoxo-bridged binuclear copper(II) complexes with the nso- and sno-type ligands (Fig. 1). Substitution of thioether sulfur for aliphatic amino nitrogen resulted in 1) a red shift of the characteristic band of di-μ-alkoxo-bridged binuclear copper(II) complexes in the near ultraviolet region (this band being assigned to the $\mathrm{p}_\pi(\mathrm{O})\rightarrow\mathrm{d}_\sigma(\mathrm{Cu})$ charge transfer band[7–9]), 2) an enhancement in antiferromagnetic spin-exchange interaction between the two copper(II) ions, 3) a positive shift of the copper(II)→copper(I) reduction potential, and 4) a strain relaxation in the fused ring system of the binuclear skeleton.



(a) (b)

Fig. 1. Complexes of (a) Cu(R-2-m-nso)X (m=2, 3) and (b) Cu(R-2-3-sno)X.

In order to further investigate the nature of binuclear copper(II) complexes with sulfur-containing ligands, new binuclear copper(II) complexes, Cu(py-3-m-nso)X (X=Cl, Br, ClO_4, NO_3, BF_4, PF_6; m=2, 3) (Fig. 2a), of 2-[2-(2-pyridyl)ethylthio]ethanol (abbreviated as Hpy-3-2-nso) and 3-[2-(2-pyridyl)ethylthio]-1-propanol (Hpy-3-3-nso) have been prepared and their spectral, magnetic, and electrochemical properties were compared with those of Cu(py-3-2-nno)X and Cu(py-3-3-nno)X (X=ClO_4, BF_4, PF_6), where Hpy-3-2-nno denotes 2-[2-(2-pyridyl)ethylamino]ethanol and Hpy-3-3-nno 3-[2-(2-pyridyl)ethylamino]-1-propanol (Fig. 2b).



(a) (b)

Fig. 2. Complexes of (a) Cu(py-3-m-nso)X (m=2, 3) and (b) Cu(py-3-m-nno)X (m=2,3).

Another purpose of this study is to examine the effect of substitution of pyridine-nitrogen for alkyl amine group in binuclear copper(II) complexes of diaminoalcohols.

Experimental

Preparation of the Ligands. Hpy-3-2-nno and Hpy-3-3-nno were prepared by the reaction of 2-vinylpyridine with 2-aminoethanol and 3-amino-1-propanol, respectively.[10] Similarly, Hpy-3-2-nso and Hpy-3-3-nso were prepared by the addition of 2-mercaptoethanol and 3-mercapto-1-propanol to 2-vinylpyridine, respectively.

Preparation of the Complexes. Cu(py-3-3-nno)X (X=ClO_4, BF_4). The preparation was exemplified by Cu(py-3-3-nno)ClO_4. To a solution of Hpy-3-3-nno (0.5 mmol) in absolute ethanol (10 cm^3) was added a solution of copper(II) perchlorate hexahydrate (0.5 mmol) in absolute ethanol (20 cm^3). To this mixture was added triethylamine to precipitate a blue solid. It was collected by filtration and recrystallized from methanol.

Cu(py-3-3-nno)PF_6. A mixture of Cu(py-3-3-nno)ClO_4 (0.5 mmol) and KPF_6 (0.5 mmol) in acetonitrile (20 cm^3) was stirred for 2 h at room temperature. The solvent was evaporated, and a remaining blue precipitate was collected by filtration and recrystallized from methanol twice to give deep blue needles.

Cu(py-3-2-nso)X and Cu(py-3-3-nso)X (X=ClO_4, Cl, Br, NO_3, BF_4). The compounds were prepared by a method similar to that for Cu(py-3-3-nno)ClO_4. They were recrystallized from methanol.

Cu(py-3-2-nso)PF_6 and Cu(py-3-3-nso)PF_6. These were prepared by the reaction of Cu(py-3-2-nso)ClO_4 and Cu(py-3-3-nso)ClO_4 with KPF_6 in acetonitrile, respectively.

TABLE 1. ELEMENTAL ANALYSES OF COMPLEXES

Complex	Found (%)			Calcd (%)		
	H	C	N	H	C	N
Cu(py-3-3-nno)ClO_4	4.39	34.90	8.14	4.42	35.10	8.18
Cu(py-3-3-nno)BF_4	4.61	36.42	8.49	4.59	36.44	8.50
Cu(py-3-3-nno)PF_6	4.02	30.99	7.29	3.90	30.98	7.22
Cu(py-3-3-nso)ClO_4	4.06	33.52	3.89	3.93	33.43	3.90
Cu(py-3-3-nso)PF_6	3.60	29.70	3.43	3.49	29.67	3.46
Cu(py-3-2-nso)Cl	4.40	38.22	4.90	4.30	38.43	4.98
Cu(py-3-2-nso)Br	3.77	32.81	4.21	3.71	33.19	4.30
Cu(py-3-2-nso)ClO_4	3.69	31.13	3.99	3.50	31.31	4.06
Cu(py-3-2-nso)$NO_3\cdot 1/2CH_3OH$	4.48	34.78	8.62	4.36	35.24	8.65
Cu(py-3-2-nso)$BF_4\cdot H_2O$	4.14	31.05	4.12	4.02	30.83	3.99
Cu(py-3-2-nso)$PF_6\cdot 1/2H_2O$	3.49	27.01	3.52	3.28	27.04	3.50

Carbon, hydrogen, and nitrogen analyses were carried out at the Service Center of Elemental Analysis, Kyushu University. The results are given in Table 1.

Measurements. Infrared spectra were measured with a Hitachi grating infrared spectrophotometer Model 215 in the region 4000—650 cm^{-1} on a KBr disk and on a nujol mull. Electronic spectra were measured with a Shimadzu multipurpose spectrophotometer Model MPS-5000 in methanol solutions and on solid samples. Magnetic susceptibilities were measured by the Faraday method in the temperature range from liquid nitrogen temperature to room temperature. The apparatus was calibrated by the use of $[Ni(en)_3]S_2O_3$.[11] All the susceptibilities were corrected for the diamagnetism of the constituting atoms by the use of Pascal's constants.[12] Effective magnetic moments were calculated by the equation, $\mu_{eff}=2.828\sqrt{(\chi_A-N\alpha)T}$, where χ_A is the atomic magnetic susceptibility and $N\alpha$ is the temperature-independent paramagnetism. Normal pulse polarography (NPP) and differential pulse polarography (DPP) were measured with a Yanagimoto voltammetric analyzer Model P-1000 in *N,N*-dimethylformamide (DMF) containing 0.1 mol dm^{-3} tetraethylammonium perchlorate at room temperature using a three-electrode cell. The saturated calomel electrode (SCE) was used as a reference, which was connected to a sample solution through a salt bridge. A dropping mercury electrode was used as a working electrode. The counter electrode was platinum coil. Conductivity was measured with a Yanagimoto conductivity outfit Model MY-8 for methanol and *N,N*-dimethylformamide solution. The cell constants were determined by the use of NaCl and KBr.[13,14]

Results and Discussion

Among the binucleating ligands utilized in this study, Hpy-3-3-nno, Hpy-3-3-nso, and Hpy-3-2-nso formed di-μ-alkoxo-bridged binuclear copper(II) complexes. On the other hand, we were unsuccessful in isolating Cu(py-3-2-nno)X using Hpy-3-2-nno. The product obtained by the reaction of Hpy-3-2-nno and copper(II) halide was supposed to be $Cu(H_2NCH_2CH_2O)X$ (X=halogenide ion)[9] on the basis of elemental analyses and cryomagnetic properties, and this was confirmed by comparing the infrared spectrum of the product with that of the authentic sample obtained from 2-aminoethanol and a copper(II) halide. Thus, it is evident that Hpy-3-2-nno cleaved into 2-aminoethanol and 2-vinylpyridine in this reaction. The complex, Cu(py-3-2-nno)X, should have a 6-5-(4)-5-6 fused ring system (Fig. 3) which is generally thought to be stable in the complexes with the fully saturated ligands, such as HR-3-2-nno.[7-9] However, the terminal six-membered chelate ring of Cu(py-3-2-nno)X must be small in size and may be comparable to the five-membered ring of a saturated ligand, because of short bond-distance in pyridine ring. So far, binuclear copper(II) complexes with a 5-5-(4)-5-5 fused ring system have not been obtained using diamino alcohols,[15-19] owing to a high strain in this system. A similar strain should exist in the 6-5-(4)-5-6 fused ring system of Cu(py-3-2-nno)X, and should be responsible for the cleavage of Hpy-3-2-nno and the formation of strain-free $Cu(H_2NCH_2CH_2O)X$.

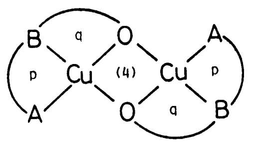


Fig. 3. Representation of the fused chelate-ring system, p-q-(4)-q-p, for binuclear complexes of alcoholic tridentate ligands.

On the other hand, we were successful in isolating Cu(py-3-2-nso)X, although it has the same 6-5-(4)-5-6 fused ring system as Cu(py-3-2-nno)X. It is to be noticed that the chelate ring system in Cu(py-3-2-nso)X contains a thioether group. Previously, we showed that the binuclear copper(II) complexes, Cu(R-2-2-nso)X (HR-2-2-nso=2-(2-dialkylaminoethylthio)ethanol), possessing a fully saturated 5-5-(4)-5-5 fused ring system can be isolated, because of a high flexibility in bond angle and large coordination bond distance of the thioether sulfur atom.[5] It is likely that a similar strain-releasing effect contributes to the formation of Cu(py-3-2-nso)X.

Since no band attributable to OH-stretching vibration was observed, the alcoholic oxygen should be deprotonated and coordinated to copper. The shift of the 990 cm^{-1} band of free pyridine to higher frequency showed the coordination of pyridine nitrogen. The bands due to ClO-stretching vibration in Cu(py-3-3-nno)ClO_4 and Cu(py-3-3-nso)ClO_4 were observed at 1070 cm^{-1}. Practically no splitting of the bands indicates

TABLE 2. BAND MAXIMA OF ELECTRONIC SPECTRA OF COMPLEXES ($\tilde{\nu}/10^3$ cm^{-1})

Complex	Reflectance		Methanol solution (log ε)	
Cu(py-3-3-nno)ClO_4	25.6	16.7	26.7(3.06)	15.7(1.89)
Cu(py-3-3-nno)BF_4	26.5	16.7	26.5(3.14)	16.3(1.95)
Cu(py-3-3-nno)PF_6	26.5	17.2	26.7(3.13)	16.0(1.94)
Cu(py-3-3-nso)ClO_4	23.3	17.4	25.0(2.95)	16.4(1.97)
Cu(py-3-3-nso)PF_6	23.5	17.2	24.8(3.02)	16.3(2.05)
Cu(py-3-2-nso)Cl	22.2	14.5	25.3(2.99)	16.3(2.09)
Cu(py-3-2-nso)Br	21.7	14.2	24.8(3.03)	15.3(2.19)
Cu(py-3-2-nso)ClO_4	23.1	16.1	24.6(3.02)	15.4(2.07)
Cu(py-3-2-nso)$NO_3\cdot 1/2CH_3OH$	23.8	15.4	24.7(3.15)	15.5(2.20)
Cu(py-3-2-nso)$BF_4\cdot H_2O$	24.1	15.9	24.5(3.11)	15.6(2.45)
Cu(py-3-2-nso)$PF_6\cdot 1/2H_2O$	23.3	16.3	24.4(3.16)	15.6(2.24)

that the perchlorate ion is free from coordination.[20] On the other hand, the ClO-stretching vibration of Cu(py-3-2-nso)ClO_4 splits into three components at 1120, 1030, and 930 cm^{-1}. This indicates the coordination of the perchlorate ion to the copper(II).[20] The NO-stretching band of the nitrate ion in Cu(py-3-2-nso)$NO_3\cdot 1/2CH_3OH$ was observed at 1320 and 1380 cm^{-1}, suggesting non-coordination of the nitrate ion to the metal.[21]

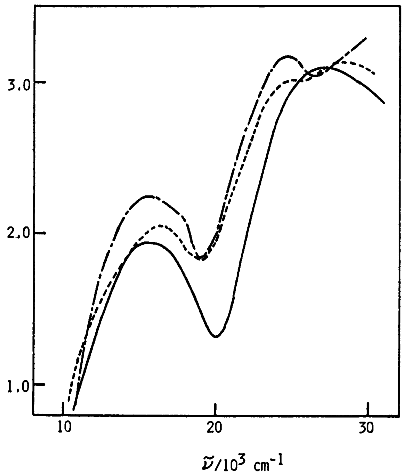


Fig. 4. Electronic absorption spectra of (——)Cu(py-3-3-nno)PF_6, (······) Cu (py-3-3-nso)PF_6, and (–·–) Cu (py-3-2-nso) PF_6 in methanol.

Electronic spectra of the complexes were measured in methanol and *N,N*-dimethylformamide solutions and on powder samples. Results are given in Table 2. Typical examples of absorption spectra are shown in Fig. 4. Spectra in solution and in solid state resemble each other, indicating essentially the same structure in solid and in solution. The band in the 14000—17000 cm^{-1} region can be assigned to d-d transition band. The d-d band of Cu(py-3-2-nso)X is slightly lower in frequency compared with those of Cu(py-3-3-nso)X and Cu(py-3-3-nno)X in solid state. This suggests that the coordination geometry around the copper ion in Cu(py-3-2-nso)X is distorted from square plane. Among these complexes, the d-d band of Cu(py-3-2-nso)Cl and Cu(py-3-2-nso)Br is notably low in energy. Recently, we determined the crystal structure of Cu(CH_3-2-2-nso)Br by the X-ray diffraction method.[5] The structure consists of alkoxo-bridged binuclear units, $Cu_2(CH_3\text{-}2\text{-}2\text{-nso})_2Br_2$, where bromide ions coordinate to copper(II) ions and the coordination geometry around each copper ion is a distorted square pyramid. As already mentioned, the strain in the fused ring system of Cu(py-3-2-nso)X is similar to that of Cu(R-2-2-nso)X. Hence, it is likely that Cu(py-3-2-nso)X (X=Cl, Br) takes a distorted square pyramidal structure similar to that of Cu(CH_3-2-2-nso)Br. The band with a relatively large intensity (ε=1000—2000) in the 24000—27000 cm^{-1} region is known to be characteristic of the di-μ-alkoxo-bridged binuclear copper(II) structure. Kida *et al.* have assigned this band to the $p_\pi(O)\rightarrow d_\sigma(Cu)$ charge transfer transition.[7—9] This is observed around 26000 cm^{-1} in the case of Cu(py-3-3-nno)X, while the CT band for Cu(py-3-3-nso)X and Cu(py-3-2-nso)X appeared in the region 22000—25000 cm^{-1}. Therefore, the $p_\pi(O)\rightarrow d_\sigma(Cu)$ charge transfer band shifts by 3000—4000 cm^{-1} to lower frequency when one of the amine nitrogen is replaced by a thioether sulfur. The present result is in line with our previous findings that the thioether substitution for amino group causes a red-shift of the charge-transfer band in di-μ-alkoxo-bridged binuclear copper(II) complexes.

The magnetic susceptibilities were measured over the temperature range 80—300 K. The magnetic moments per copper atom are all subnormal at room temperature and decrease with lowering of temperature, indicating the existence of an antiferromagnetic spin-exchange interaction between a pair of copper(II) ions. The temperature dependences of magnetic susceptibility for Cu(py-3-3-nso)ClO_4 and Cu(py-3-3-nno)BF_4 are shown in Fig. 5 as examples. These magnetic behaviors can be interpreted in terms of the Bleaney-Bowers equation,[22]

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

where χ_A is susceptibility per copper atom and other symbols have their usual meanings. The $-2J$ (the energy separation between the spin-singlet ground state and the spin-triplet excited state) and $N\alpha$ values were obtained by the best-fit of the experimental susceptibilities to the Eq. 1, assuming g at 2.10. The results are given in Table 3. Table 3 also includes the effective magnetic moments of the complexes at room tempera-

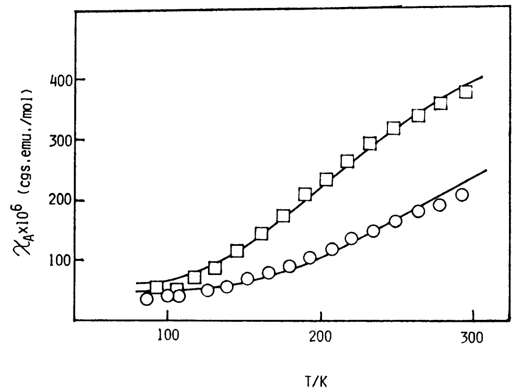


Fig. 5. Temperature-dependences of magnetic susceptibility of (○) Cu (py-3-3-nso) ClO_4 and (□) Cu (py-3-3-nno) BF_4.

TABLE 3. MAGNETIC DATA OF COMPLEXES

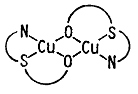
Complex	μ_{eff}[a)] BM	$-2J$ cm^{-1}	$N\alpha \times 10^6$ c.g.s. mol^{-1}
Cu(py-3-3-nno)ClO_4	0.88	510	60
Cu(py-3-3-nno)BF_4	0.87	540	60
Cu(py-3-3-nno)PF_6	0.67	700	40
Cu(py-3-3-nso)ClO_4	0.61	705	50
Cu(py-3-3-nso)PF_6	0.47	850	60
Cu(py-3-2-nso)Cl	1.63	170	90
Cu(py-3-2-nso)Br	1.48	225	60
Cu(py-3-2-nso)ClO_4	1.26	300	60
Cu(py-3-2-nso)$NO_3 \cdot 1/2CH_3OH$	0.83	550	60
Cu(py-3-2-nso)$BF_4 \cdot H_2O$	0.71	650	65
Cu(py-3-2-nso)$PF_6 \cdot 1/2H_2O$	0.48	850	60

a) Magnetic moment at room temperature.

TABLE 4. HALF-WAVE POTENTIALS OF NORMAL PULSE (NPP) AND DIFFERENTIAL PULSE (DPP) POLAROGRAPHIES (V *vs.* SCE)

Complex	NPP	DPP	
Cu(py-3-3-nno)ClO_4	−0.40		−0.43
Cu(py-3-3-nno)BF_4	−0.40	−0.39	−0.42
Cu(py-3-3-nno)PF_6	−0.42	−0.40	−0.42
Cu(py-3-3-nso)ClO_4		−0.09	
Cu(py-3-3-nso)PF_6		−0.09	
Cu(py-3-2-nso)Cl		+0.16	−0.56
Cu(py-3-2-nso)Br		+0.11	−0.56
Cu(py-3-2-nso)ClO_4		−0.06	
Cu(py-3-2-nso)$NO_3 \cdot 1/2CH_3OH$		−0.09	
Cu(py-3-2-nso)$BF_4 \cdot H_2O$		−0.08	
Cu(py-3-2-nso)$PF_6 \cdot 1/2H_2O$		−0.09	

ture. The $-2J$ values for Cu(py-3-3-nno)X (X=ClO_4, BF_4, PF_6) range from 510 to 700 cm^{-1}, which are comparable to the $-2J$ values for the binuclear copper(II) complexes with aliphatic diaminoalcohols.[9)] Therefore, we can not detect any marked effect of pyridine nitrogen donation on antiferromagnetic spin-exchange interaction in di-μ-alkoxo-bridged binuclear copper(II) complexes. It is to be noted that the $-2J$ values of Cu(py-3-3-nso)X (750—850 cm^{-1}) are much larger than the values of Cu(py-3-3-nno)X. Thus, antiferromagnetic spin-exchange interaction betweem the two copper(II) ions becomes stronger upon substitution of the sulfur donor atom for the nitrogen donor atom. A similar trend was already noticed in Cu(R-2-3-nso)X and Cu-(R-2-3-sno)X.[2–6)] The $-2J$ values of Cu(py-3-2-nso)X seem to depend on X. Namely, the complexes containing Cl, Br, or ClO_4 ion have smaller $-2J$ values compared with other complexes containing NO_3, BF_4, or PF_6 ion. Since the infrared and electronic reflectance spectral data evidenced the coordination of the anion X, the complexes Cu(py-3-2-nso)X (X=Cl, Br, ClO_4) should have a five-coordinate structure whose

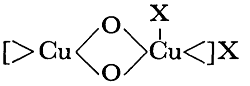


skeleton is much distorted from a coplane. Since spin-exchange interaction is known to be highly dependent on planarity around the metal, this distortion must be the main reason for the reduction in the exchange integral of Cu(py-3-2-nso)X (X=Cl, Br, ClO_4).

The results of normal pulse polarography (NPP) and differential pulse polarography (DPP) are listed in Table 4. The reduction from Cu(II)–Cu(II) to Cu(I)–Cu(I) for Cu(py-3-3-nno)X occured at −0.4 V *vs.* SCE. These reduction potentials are comparable to those of the binuclear complexes with the aliphatic diaminoalcohols.[4)] Therefore, it seems that the reduction potential from Cu(II)–Cu(II) to Cu(I)–Cu(I) is little affected by substitution of aromatic amine nitrogen for aliphatic amine nitrogen. The reduction of Cu(py-3-3-nso)X (X=ClO_4, PF_6) at −0.10 V *vs.* SCE positively shifted by *ca.* 300 mV relative to reduction potentials of Cu(py-3-3-nno)X. As was already pointed out in the preceding paper,[4)] the positive shift of the Cu(II)–Cu(II)→Cu(I)–Cu(I) reduction potential implies that the optical electronegativity[24)] of copper(II) ion increases when a sulfur atom is introduced as a donating atom. Electrochemical property of Cu(py-3-2-nso)X (X=ClO_4, NO_3, BF_4, and PF_6) resembles that of Cu(py-3-3-nso)X, showing a two-electron reduction at about −0.10 V. On the other hand, Cu(py-3-2-nso)Cl and Cu(py-3-2-nso)Br showed two reduction waves at +0.2 and −0.60 V, and +0.10 and −0.40 V, respectively. These complexes bear a marked electrochemical resemblance to Cu(R-2-2-nso)X (X=Cl, Br),[4)] which also showed two one-electron reductions at +0.15—+0.20 and −0.30——0.50 V *vs.* SCE. The controlled-potential electrolysis[4)] showed that Cu(R-2-2-nso)X (X=Cl, Br) was reduced stepwise as Cu(II)–Cu(II)→Cu(II)–Cu(I)→Cu(I)–Cu(I). Accordingly, it is assumed that Cu(py-3-2-nso)Cl and Cu(py-3-2-nso)Br are also stepwise reduced. In order to clarify the reasons for the difference in electrochemical behaviors between the two groups of the binuclear complexes, *i.e.*, those undergoing two one-electron reductions and those undergoing one two-electron reduction, conductivities were measured in methanol and *N*,*N*-dimethylformamide. The results are shown in Table 5. The conductivities of Cu(py-3-2-nso)ClO_4 and Cu(py-3-2-nso)PF_6 clearly indicate that they are 1 : 2 electrolyte in the solutions.[23)] Since two copper(II) ions in a molecule are equivalent in solution, we can reasonably understand

Table 5. Molar conductivity, Λ_M, of complexes at 10^{-3} mol dm^{-1} in methanol and *N,N*-dimethylformamide (Ω^{-1} cm^{-2} mol^{-1})

Complex	MeOH	DMF
$Cu(en)_2(ClO_4)_2$	204	146
Cu(py-3-2-nso)Cl	107	74
Cu(py-3-2-nso)Br	124	72
Cu(py-3-2-nso)ClO_4	195	
Cu(py-3-2-nso)$PF_6\cdot 1/2H_2O$	198	

the one two-electron reduction of these complexes. On the other hand, the conductivities of Cu(py-3-2-nso)Cl and Cu(py-3-2-nso)Br are about one half of those of Cu(py-3-2-nso)ClO_4 and Cu(py-3-2-nso)PF_6, implying that they are 1 : 1 electrolyte in methanol and *N,N*-dimethylformamide. This suggests that these complexes exist as  $[{>}\mathrm{Cu}\langle\begin{smallmatrix}O\\O\end{smallmatrix}\rangle\overset{X}{\mathrm{Cu}}{<}]X$ in solution, where two inequivalent copper(II) ions are reduced at different potentials. In general, copper(II) ions with a distorted coordination geometry have a high reduction potentials.[25] Therefore, it is likely that the reduction waves at $+0.1$—$+0.2$ V and -0.4—-0.6 V are due to the reduction of the five-coordinate copper(II) ion and the four-coordinate copper(II) ion, respectively. In relation to this result, conductivities of Cu(R-2-2-nso)X (X=Cl, Br) were also measured in *N,N*-dimethylformamide. The result again demonstrated the existence of 1 : 1 electrolyte in solution. Thus, we may conclude that Cu(py-3-2-nso)X (X=Cl, Br) as well as Cu(R-2-2-nso)X (X=Cl, Br) contains a five- and a four-coordinate copper(II) ions in solution, which are reduced at $\approx+0.15$ and ≈-0.5 V, respectively.

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