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Binuclear Metal Complexes.
XLVI[1]. Electronic and Electrochemical Properties of Copper(II)M(II) Binuclear Complexes of N,N'-Bis(5-t-butylsalicylidene)alkanediamines

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Copper(II)–M(II) binuclear complexes, Cu(bstc)-MX_2 (M = Cu, Co, Cd, Hg; X = Cl, Br, I) have been prepared and characterized, where H_2bstc represents N,N'-bis (5-t–butylsalicylidene)-trans-1,2-diaminocyclohexane. Ligand field bands due to the copper(II) ion bound at the N_2O_2–coordinating site in Cu(bstc)-MX_2 are blue-shifted relative to the mononuclear complex Cu(bstc). This suggests that the CuN_2O_2 moiety becomes more planar when Cu(bstc) coordinates to MX_2 with the phenolic oxygens. The copper(II/I) redox potentials of Cu(bstc)MX_2 were determined by cyclic voltammetry in dichloromethane. The redox potentials were around −1.4 V vs. NHE, which was almost the same as the redox potential of Cu(bstc). The similar redox potential in Cu(bstc) and Cu(bstc)MX_2 has been discussed in terms of structural and electronic effects.

Introduction

There is growing interest in electrochemical properties of complexes in connection with metalloenzymes incorporating two metal ions in close proximity at the active site. In the last half decade, electrochemical studies on binuclear copper(II) complexes were carried out in a hope to gain an insight into the function of bimetallic copper proteins [1–14]. These studies have revealed some important factors in the determination of the redox potential and the redox process for binuclear copper(II) complexes. However, they have invoked more problems than those elucidated. Thus, more systematic and detailed investigations on the redox properties of binuclear complexes are desired.

In this study we have prepared and characterized a series of binuclear metal complexes, Cu(bstc)MX_2 (M = Co, Cu, Zn, Cd, Hg; X = Cl, Br, I), where H_2bstc represents N,N'-bis(5-t-butylsalicylidene)-*trans*-1,2-diaminocyclohexane. These complexes are soluble and stable in organic solvents such as dichloromethane. This enabled us to make electrochemical measurements of these complexes. The results were discussed in comparison with those of the mononuclear complex Cu(bstc), in order to elucidate the effect of the M(II) ion on the redox potential of the copper(II) ion at the N_2O_2-donating site. The d–d band of Cu(bstc) showed a considerable blue shift when Cu(bstc) bound to MX_2. This was also discussed in relation to the structural and electronic effects.

Experimental

Preparation

5-t-Butylsalicylaldehyde was prepared by the formylation (Duff's reaction) of *p*-t-butylphenol [15]. *Trans*-1,2-diaminocyclohexane was separated and purified by a literature method [16]. N,N'-Bis(5-t-butylsalicylidene)-*trans*-1,2,-diaminocyclohexane (H_2bstc) was prepared by the condensation of 5-t-butylsalicylaldehyde and *trans*-1,2-diaminocyclohexane in methanol in a 2:1 mole ratio.

Cu(bstc)·1/2H_2O

Copper(II) acetate monohydrate (10 mmol) and H_2bstc (10 mmol) were dissolved in methanol (50 ml), and the solution was refluxed for several minutes. The reaction mixture was allowed to stand overnight, to give purple fine crystals which were collected and dried *in vacuo.*

Cu(bstc)MX_2 (M = Co, Cu, Zn, Cd, Hg; X = Cl, Br, I)

The synthetic methods for these complexes are similar to those for Cu(bstc)$CuCl_2$. A suspension of Cu(bstc)·1/2H_2O (10 mmol) in absolute ethanol (40 ml) containing $CuCl_2$ (13 mmol) was refluxed for six hours, and then the reaction mixture was allowed to stand overnight. Pale purple, fine crystals precipitated, were collected by suction, washed with absolute ethanol, and dried *in vacuo.* For preparation

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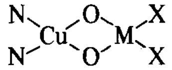
of Cu(bstc)$CoCl_2$, anhydrous $CoCl_2$ prepared by heating $CoCl_2 \cdot 6H_2O$ in an oven was used.

Elemental analyses of Cu(bstc) and Cu(bstc)MX_2 are given in Table I.

Physical Measurements

Elemental analyses of carbon, hydrogen and nitrogen were carried out at the Service Center of Elemental Analysis, Kyushu University. Analysis of copper and cobalt were made with a Shimadzu Atomic Absorption-Flame Spectrophotometer Model AA-610S. Infrared spectra were measured with a Hitachi Infrared Spectrometer Model 215 on a KBr disk. Electronic spectra were recorded on a Shimadzu Multipurpose Spectrophotometer Model MPS-5000 in dichloromethane. Magnetic susceptibilities were measured by the Faraday method, from liquid nitrogen temperature to room temperature. Diamagnetic correction was made using Pascal's constants [17]. Effective magnetic moments were calculated by the equation, $\mu_{eff} = 2.828[(\chi_M - 60 \times 10^{-6})T]^{1/2}$, where χ_M is the susceptibility per molecule. In the case of Cu(bstc)$CuCl_2$, the moment was calculated for one copper atom. Cyclic voltammograms were recorded on a Yanagimoto Voltammetric Analyzer Model P-1000 in dichloromethane containing 0.1 *M* tetrabutylammonium perchlorate as the supporting electrolyte. A three-electrode cell was used for measurements, in which the working electrode is a glassy carbon and the auxiliary electrode a platinum coil. A saturated calomel electrode (SCE) was used as the reference, separated from the bulk electrolyte solution by a salt bridge prepared with benzylidene-D-glucitols [18]. All the redox potentials were corrected by the use of ferrocene as an internal standard [19], where the ferrocenium/ferrocene redox potential is estimated at 0.40 V *vs.* NHE [20].

Results and Discussion

It is known that N,N′-disalicylideneethylenediaminatocopper(II) and its congeners, Cu(SB), react with a metal halide MX_2 to form binuclear metal complexes Cu(SB)MX_2 [21–24]. X-ray structural analyses for some of the Cu(SB)MX_2 complexes have demonstrated that the copper and M ions are bridged by the phenolic oxygens to form the  skeleton [25–27]. A characteristic in the infrared spectra of Cu(SB)MX_2 is a skeletal vibration of the aromatic ring around 1550 cm^{-1}, which is always higher (by 10–20 cm^{-1}) than that of the corresponding mononuclear complex Cu(SB). A similar trend in the frequency of the skeletal vibration was observed for the present complexes: 1530 cm^{-1} for Cu(bstc) and 1540–1550 cm^{-1} for Cu(bstc)MX_2. The magnetic susceptibility of Cu(bstc)$CuCl_2 \cdot 1/2H_2O$ obeyed the Bleaney-Bowers equation in the temperature range 100–300 K, with the magnetic parameters, g = 2.10, J = −125 cm^{-1} (−2J corresponds to the separation between the lowest singlet and triplet states) and $N\alpha = 60 \times 10^{-6}$ c.g.s./mol. Such magnetic behavior resembles that of Cu(salen)$CuCl_2$ [22], whose binuclear structure has been demonstrated by X-ray analysis [25]. Based on these facts we may conclude that Cu(bstc)MX_2 possesses the structure shown in Fig. 1.

The effective magnetic moments of the complexes are given in Table I. The magnetic moment per copper atom of Cu(bstc)$CuCl_2 \cdot 1/2H_2O$ is subnormal at room temperature because of an intramolecular antiferromagnetic spin-exchange interaction. The magnetic moment of Cu(bstc)$CoCl_2$ is 4.92 BM,

TABLE I. Elemental Analyses and Magnetic Moments at Room Temperature.

Complexes	Found (%)					Calcd (%)					μ_{eff} (BM)
	C	H	N	Cu	Co	C	H	N	Cu	Co	
Cu(bstc)·$1/2H_2O$	66.55	7.27	5.66	12.3		66.59	7.19	5.55	12.6		1.84
Cu(bstc)$CuCl_2 \cdot 1/2H_2O$	52.41	6.15	4.20	19.5		52.58	5.83	4.38	19.9		1.65[a]
Cu(bstc)$CoCl_2$	53.38	5.97	4.37	10.4	9.5	53.72	5.80	4.47	10.2	9.4	4.92
Cu(bstc)$HgCl_2$[b]				8.0					8.3		1.85
Cu(bstc)HgI_2[b]				6.8					6.7		1.85
Cu(bstc)$CdBr_2$	43.84	4.84	3.65	8.1		43.77	4.72	3.65	7.8		1.86
Cu(bstc)CdI_2	39.06	4.35	3.14	7.3		39.00	4.21	3.25	7.4		1.84
Cu(bstc)$ZnCl_2$	52.75	5.90	4.34	10.2		53.17	5.74	4.43	10.1		1.86
Cu(bstc)$ZnBr_2$	46.66	5.17	3.89	8.9		46.62	5.03	3.88	8.8		1.86
Cu(bstc)ZnI_2	41.43	4.48	3.43	7.8		41.25	4.45	3.44	7.8		1.79

[a] Moment per copper atom. [b] C, H, and N analyses were not carried out because of the presence of Hg.

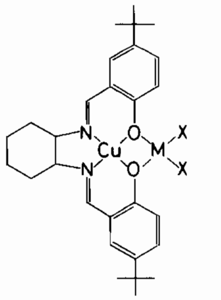


Fig. 1. Chemical structure of $Cu(bstc)MX_2$ (M = Co, Cu, Zn, Cd, Hg; X = Cl, Br, I).

which is a normal value for complexes containing copper(II) and a tetrahedral cobalt(II) ions [24]. Magnetic moments of other $Cu(bstc)MX_2$ complexes (M = Zn, Cd, Hg; X = Cl, Br, I) fall in the range 1.79–1.86 BM at room temperature. These values are quite reasonable since the second metal ion has no unpaired electron.

The ligand H_2bstc has large hydrophobic groups on the aromatic rings and in the diamine moiety, hence the complexes $Cu(bstc)MX_2$ are fairly soluble in organic solvents. Thus, we could obtain the electronic spectra of $Cu(bstc)MX_2$ in solution. Some examples of the absorption spectra in dichloromethane are shown in Fig. 2. Absorption maxima and extinction coefficients of the d–d bands are given in Table II. The mononuclear complex $Cu(bstc)\cdot 1/2H_2O$ showed a d–d band centered at 18,000 cm^{-1}. On the other hand, $Cu(bstc)CuCl_2\cdot 1/2H_2O$ showed two d–d bands at 18,690 and 10,690 cm^{-1}, which are assigned to the d–d bands of the copper(II) ions bound at the N_2O_2- and O_2Cl_2-sites, respectively. The low frequency of the latter band implies the distorted configuration of the $[CuO_2Cl_2]$-chromophore from square-plane, as was evidenced by X-ray analysis for $Cu(salen)CuCl_2$ [25] and its homolog [27]. The spectrum of $Cu(bstc)CoCl_2$ showed the bands at 15,380 and 14,810 cm^{-1}, in addition to the band at 18,080 cm^{-1} attributable to the copper(II) ion at the N_2O_2-site. The 15,380 and 14,810 cm^{-1} bands are certainly due to the cobalt(II) ion, and judging from the band positions and intensities the configuration around the cobalt(II) is nearly tetrahedral. Other $Cu(bstc)MX_2$ (M = Hg, Cd, Zn; X = Cl, Br, I) show the d–d bands of copper ion in the region 18,000–19,500 cm^{-1}. The band maximum shifts to higher frequency and its intensity decreases compared with the corresponding mononuclear complex (Table II). Such a blue shift of the copper d–d band was first observed by Sinn *et al.* when they prepared $Cu(salen)MX_2$ from Cu(salen) and MX_2 [24]. However, they mentioned nothing about the intensity of the bands since their data were based on the powder reflectance spectra. As seen in Table II, the blue shift and the intensity loss of the d–d band of $Cu(bstc)MX_2$ (M = Zn, Cd, Hg; X = Cl, Br, I) are promoted in the order Zn > Cd > Hg, which is the reverse of the order of ionic radius (Hg^{2+} 1.10, Cd^{2+} 0.98 and Zn^{2+} 0.78 Å [28]). This trend can be well explained by the assumption that the $[CuN_2O_2]$-chromophore becomes more planar when Cu(bstc) is linked with MX_2. Thus, it is quite understandable that this effect becomes large as the size of M^{2+} decreases.

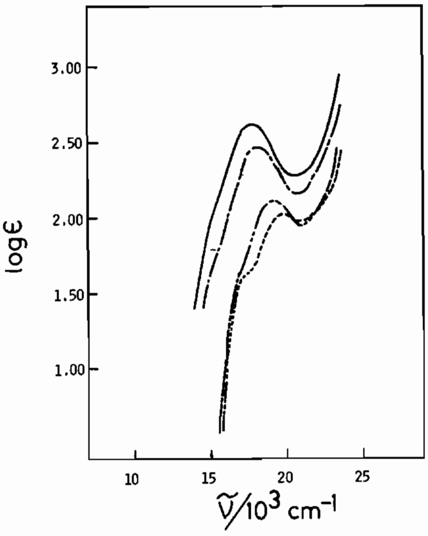


Fig. 2. Electronic spectra of $Cu(bstc)\cdot 1/2H_2O$ (——), $Cu(bstc)HgCl_2$ (– – –), $Cu(bstc)CdBr_2$ (— ·· —), and $Cu(bstc)ZnCl_2$ (- - - -) in dichloromethane.

Electrochemical properties of the complexes were investigated by means of cyclic voltammetry in dichloromethane. Cathodic and anodic peaks (E_{pc} and E_{pa}), peak separations (ΔE_p) and redox potentials ($E_{1/2}$) approximated by the arithmetic mean of E_{pc} and E_{pa} are given in Table III. The cyclic voltammogram of $Cu(bstc)\cdot 1/2H_2O$ showed only one Cu(II/I) redox wave at −1.45 V *vs.* NHE. On the other hand, the cyclic voltammograms of the binuclear complexes are rather complicated. The cyclic voltammogram of $Cu(bstc)CoCl_2$ could not be analyzed because of overlapping of the redox waves due to the cobalt and copper ions. Cyclic voltammograms of $Cu(bstc)CuCl_2\cdot 1/2H_2O$ showed two redox waves, at +0.76 and −1.46 V *vs.* NHE, which were assigned to the Cu(II/I) redox processes of the copper(II) ions at the O_2Cl_2- and the N_2O_2-sites, respectively. The high reduction potential of the copper(II) ion at the O_2Cl_2-site may be attributed to the pseudotetrahedral configuration around the metal ion. Cyclic voltammograms of $Cu(bstc)HgX_2$ showed a redox wave around −1.4 V *vs.* NHE, attributable to the Cu(II/I) process. In addition to this, another redox wave was observed at −0.20— −0.34 V *vs.* NHE. This may be ascribed to the redox process of mercury.

TABLE II. Electronic Spectral Data of Complexes.

Complexes	$\tilde{\nu}_{max}/10^3$ cm^{-1}	(logϵ)	
$Cu(bstc)\cdot 1/2H_2O$	17.70 (2.62)		
$Cu(bstc)CuCl_2\cdot 1/2H_2O$	18.69 (3.00)	10.69 (2.18)	
$Cu(bstc)CoCl_2$	18.08 (2.54)	15.38 (2.50)sh[a]	14.81 (2.59)
$Cu(bstc)HgCl_2$	18.21 (2.46)		
$Cu(bstc)HgI_2$	17.86 (2.55)		
$Cu(bstc)CdBr_2$	19.08 (2.11)		
$Cu(bstc)CdI_2$	19.08 (2.24)		
$Cu(bstc)ZnCl_2$	19.80 (2.03)	17.24 (1.62)sh[a]	
$Cu(bstc)ZnBr_2$	19.69 (1.98)	17.24 (1.55)sh[a]	
$Cu(bstc)ZnI_2$	19.65 (2.16)	17.24 (1.81)sh[a]	

[a]sh = shoulder.

TABLE III. Cyclic Voltammetric Data of Complexes.

Complexes	E_{pc}[a] (V)	E_{pa}[a] (V)	ΔE_p (mV)	$E'_{1/2}$[b] (V)
$Cu(bstc)\cdot 1/2H_2O$	−1.57	−1.35	220	−1.46
$Cu(bstc)CuCl_2\cdot 1/2H_2O$	−1.60	−1.20	400	−1.40
	+0.67	+0.84	170	+0.76[c]
$Cu(bstc)HgCl_2$	−1.53	−1.32	210	−1.43
	−0.34	−0.08	260	−0.20[d]
$Cu(bstc)HgI_2$	−1.56	−1.38	180	−1.47
	−0.42	−0.26	160	−0.34[d]
$Cu(bstc)CdBr_2$	−1.57	−1.31	260	−1.44
$Cu(bstc)CdI_2$	−1.54	−1.34	200	−1.44
$Cu(bstc)ZnCl_2$	−1.53	−1.32	210	−1.43
$Cu(bstc)ZnBr_2$	−1.53	−1.30	230	−1.42
$Cu(bstc)ZnI_2$	−1.51	−1.26	250	−1.39

[a]E_{pc} and E_{pa} are corrected by the use of E_{Fc/Fc^+} [19] and given in V *vs.* NHE. [b]$E_{1/2}$ is approximated by $E'_{1/2} = 1/2(E_{pc} + E_{pa})$. [c]Assigned to the Cu(II)/Cu(I) process of the $[CuO_2Cl_2]$-chromophore. [d]Assigned to the redox process of mercury.

Inspection of the redox potentials of $Cu(bstc)MX_2$ and Cu(bstc) has revealed that the redox of the copper ion at the N_2O_2-site always occurs around −1.4 V *vs.* NHE. This appeared strange, because there is a considerable structural difference between the mononuclear and the binuclear complexes, and this is reflected by the electronic spectra. Why were only minor differences observed between $Cu(bstc)MX_2$ and Cu(bstc)? Indeed, Patterson and Holm showed that redox potentials of copper(II) complexes shift to the negative side when their configurations become more planar [29]. Thus, factors other than the steric effect must contribute to the redox potential of $Cu(bstc)MX_2$. The most marked difference between the mononuclear and the binuclear complexes is the bonding mode of the phenolic oxygen: the simple coordination in the former and the bridging in the latter. Thus, we may assume that the electron donation from the phenolic oxygen to the copper(II) ion is diminished relative to that for Cu(bstc) when each oxygen coordinates to two metal ions, as in the case of $Cu(bstc)MX_2$. This may result in the decrease in electron density at the copper(II) ion, and hence the positive shift in the redox potential in binuclear complexes. This electronic effect on the redox potential is quite opposed to the structural effect. Therefore, both the structural and the electronic effects may operate in the present complexes in nearly the same extent.

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