

Binuclear Metal Complexes. XLV.¹⁾ Synthesis and Magnetic, Spectral, and Electrochemical Studies of Strati-bis Copper(II) Complexes of Some Schiff Bases Derived from Primary Tetraamines and Salicylaldehydes

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New Schiff base ligands, 1,2,3,4-tetrakis(R-salicylideneamino)-2,3-dimethylbutane (abbreviated as $H_4(R-sata)$; R (substituent on the ring)=H, 5-Me, 5-Bu^t) and 1,2-bis(R-salicylideneamino)-1,2-bis(salicylideneaminomethyl)cyclohexane ($H_4(R-sacta)$), which are capable of forming "strati-bis" type binuclear copper(II) complexes, $Cu_2(R-sata)$ and $Cu_2(R-sacta)$, were investigated in comparison with those of mononuclear copper(II) complexes $Cu(R-salpn)$ and $Cu(R-sacda)$, where $H_2(R-salpn)$ is *N,N'*-bis(R-salicylidene)-1,2-propanediamine and $H_2(R-sacda)$ 1-(R-salicylideneamino)-1-(R-salicylideneaminomethyl)cyclohexane. ESR spectra of $Cu_2(sata)$, $Cu_2(sacta)$ and $Cu_2(5-Me-sacta)$ showed a seven-lined hyperfine structure whose hyperfine coupling constant ($A_{||} \approx 85$ G, 1 G = 10^{-4} T) was about one half of that of the corresponding mononuclear copper(II) complex. Each electronic spectrum of these binuclear complexes showed the $\pi-\pi^*$ transition originated from the azomethine group at a low frequency compared with that of the corresponding mononuclear complex. Cyclic voltammograms of these three complexes involved two redox couples. The first redox couple attributable to the Cu(II, II)/Cu(II, I) process is higher in potential than the Cu(II)/Cu(I) process of the corresponding mononuclear complex. These characteristics were discussed in terms of the electron-delocalization through the $\pi-\pi$ interaction between the two $[CuN_2O_2]$ -chromophores.

Recently, much attention has been devoted to electrochemical investigations of copper complexes in which two metal ions are bound in close proximity, in the hope to clarify the redox function of copper proteins.^{2–6)} Reduction of binuclear copper(II) complexes into the corresponding copper(I) complexes occurs *via* two mono-electronic steps^{2,5)} or one dielectronic step.^{3,4,6)} In most of these complexes two equatorial planes of the metal ions are linked so as to be coplanar with oxygen-bridges^{2–5)} and there are very few electrochemical investigations on binuclear copper(II) complexes whose coordination planes face to each other.

In the preliminary report⁷⁾ we have suggested that the binuclear copper(II) complex, $Cu_2(sata)$ ($H_4(sata)$ denotes 1,2,3,4-tetrakis(salicylideneamino)-2,3-dimethylbutane), takes a unique configuration in which two CuN_2O_2 planes are stacked in a face-to-face manner. In this study we have prepared the binuclear copper(II) complexes, $Cu_2(R-sata)$ (R=5-Me, 5-Bu^t), which are the homologs of $Cu_2(sata)$ containing methyl or *t*-butyl group at the 5-position of the aromatic ring. We have also prepared the copper(II) complexes, $Cu_2(R-sacta)$, where $H_4(R-sacta)$ denotes 1,2-bis(R-salicylideneamino)-1,2-bis(R-salicylideneaminomethyl)cyclohexane. Magnetic, spectral and electrochemical properties of $Cu_2(R-sata)$ and $Cu_2(R-sacta)$ were investigated in comparison with those of the mononuclear copper(II) complexes, $Cu(R-salpn)$ and $Cu(R-sacda)$ ($H_2(R-salpn)$ = *N,N'*-bis(R-salicylidene)-1,2-propanediamine; $H_2(R-sacda)$ = 1-(R-salicylideneamino)-1-(R-salicylideneaminomethyl)cyclohexane), respectively, in the hope to elucidate the characteristics of the binuclear copper(II) complexes stacked in the face-to-face manner.

Experimental

Syntheses. 1-Aminomethyl-1-cyclohexanamine was

prepared by the method in the literature.⁸⁾ Synthesis of $Cu(R-salpn)$ (R=H, 5-Me, 5-Bu^t) was carried out by the method of Holm.⁹⁾

2,3-Dicyano-2,3-butanediamine. A solution of 2,3-dicyano-2,3-butanediol¹⁰⁾ (40 g) in methanol (300 cm³) was chilled by means of ice-water and to this was introduced a stream of dry ammonia. After the mixture was allowed to stand overnight, the solvent and ammonia were evaporated to give 2,3-dicyano-2,3-butanediamine as white crystals. They were recrystallized from ethanol as colorless needles melting at 138–141 °C. The yield was ca. 15 g.

Found: C, 52.25; H, 7.42; N, 40.23%. Calcd for $C_6H_{10}N_4$: C, 52.16; H, 7.30; N, 40.55%.

1,2-Dicyano-1,2-cyclohexanediol. This was prepared by the reaction of 1,2-dicyano-1,2-cyclohexanediol¹⁰⁾ and ammonia in the same way as described above. It forms colorless needles melting at 169–171 °C. The yield was ca. 30%.

Found: C, 58.49; H, 7.42; N, 33.93%. Calcd for $C_8H_{12}N_4$: C, 58.52; H, 7.37; N, 34.12%.

2,3-Dimethyl-1,2,3,4-butanetetramine. A suspension of $LiAlH_4$ (25 g) in dry dioxane (500 cm³) was stirred at 70 °C, and to this was added dropwise a solution of 2,3-dicyano-2,3-butanediamine (15 g) in dry dioxane (200 cm³) and the mixture was refluxed for three hours. The reaction mixture was cooled by ice-water and decomposed by the addition of 50 cm³ of water and then 50 cm³ of a 15% sodium hydroxide solution. Inorganic substances that precipitated were filtered and washed with three 50 cm³ portions of dioxane. The filtrate and the washings were combined and to this was added hydrobromic acid (60%, 20 cm³). On evaporating the solvent there remained 2,3-dimethyl-1,2,3,4-butanetetramine tetrahydrobromide as a yellow mass. It was dissolved in water (10 cm³) and to this solution was added potassium hydroxide (pellets 20 g). The free tetramine thus liberated was extracted with three 100 cm³ portions of ether, and the combined ethereal solution was dried with KOH. Evaporation of the solvent left 2,3-dimethyl-1,2,3,4-butanetetramine as pale yellow, oily substance (3 g). It was used for preparation of complexes without further puri-

TABLE 1. ELEMENTAL ANALYSES OF $\text{Cu}_2(\text{R-sata})$, $\text{Cu}_2(\text{R-sacta})$, AND $\text{Cu}(\text{R-sacda})$

	Found(%)				Calcd(%)			
	C	H	N	Cu	C	H	N	Cu
$\text{Cu}_2(\text{sata}) \cdot \frac{5}{2}\text{H}_2\text{O}$	55.70	4.61	7.54	17.52	55.88	4.83	7.67	17.39
$\text{Cu}_2(5\text{-Me-sata}) \cdot \frac{1}{2}\text{EtOH}$	61.18	5.73	7.13	15.93	61.24	5.40	7.33	16.13
$\text{Cu}_2(5\text{-Bu}^t\text{-sata}) \cdot 2\text{H}_2\text{O}$	63.70	6.94	5.81	13.02	63.47	7.03	5.92	13.43
$\text{Cu}_2(\text{sacta}) \cdot \text{H}_2\text{O}$	59.54	4.57	7.68	17.62	59.25	4.70	7.68	17.42
$\text{Cu}_2(5\text{-Me-sacta}) \cdot \text{H}_2\text{O}$	61.43	5.31	7.19	16.34	61.13	5.31	7.19	16.17
$\text{Cu}_2(5\text{-Bu}^t\text{-sacta}) \cdot \frac{3}{2}\text{H}_2\text{O}$	64.98	7.00	5.80	12.94	64.84	7.01	5.81	13.19
$\text{Cu}(\text{sacda}) \cdot \frac{1}{4}\text{H}_2\text{O}$	62.69	5.52	6.89	16.08	62.67	5.57	6.96	15.80
$\text{Cu}(5\text{-Me-sacda}) \cdot \frac{1}{4}\text{H}_2\text{O}$	64.17	6.17	6.41	15.98	64.16	6.15	6.51	16.13
$\text{Cu}(5\text{-Bu}^t\text{-sacda}) \cdot \text{H}_2\text{O}$	66.27	7.86	4.99	13.02	65.94	7.63	5.30	13.43

fication.

1,2-Bis(aminomethyl)-1,2-cyclohexanediamine. This was prepared as yellow, oily substance by the reduction of 1,2-dicyano-1,2-cyclohexanediamine in a way similar to that described above.

$\text{Cu}_2(\text{R-sata})$ ($R=H, 5\text{-Me}, 5\text{-Bu}^t$). Synthetic methods for these complexes are practically the same. The methods were exemplified by that for $\text{Cu}_2(\text{sata})$ as follows. 2,3-Dimethyl-1,2,3,4-butanetetramine (0.5 g) and salicylaldehyde (1.7 g) were dissolved in ethanol (30 cm^3), and the mixture was heated at *ca.* 70 °C for 10 min. To this solution was added powdered copper(II) acetate monohydrate (1.4 g), and the mixture was stirred at 60 °C for 30 min and then allowed to stand in a refrigerator to give brown to dark green crystals. They were collected and recrystallized from a chloroform-ethanol mixture.

$\text{Cu}_2(\text{R-sacta})$ ($R=H, 5\text{-Me}, 5\text{-Bu}^t$). These complexes were obtained by a method similar to that of $\text{Cu}_2(\text{R-sata})$.

$\text{Cu}(\text{R-sacda})$ ($R=H, 5\text{-Me}, 5\text{-Bu}^t$). These complexes were prepared by the reaction of 1-aminomethyl-1-cyclohexanamine, salicylaldehyde, and copper(II) acetate monohydrate in a 1:2:1 mole ratio in ethanol.

Elemental analyses of $\text{Cu}_2(\text{R-sata})$, $\text{Cu}_2(\text{R-sacta})$, and $\text{Cu}(\text{R-sacda})$ are given in Table 1.

Measurements. Electronic spectra were measured in chloroform by a Shimadzu MPS-5000 spectrophotometer. Magnetic susceptibilities were measured by the Faraday method in the temperature range 80–300 K. The apparatus was calibrated by the use of $[\text{Ni}(\text{en})_3]\text{S}_2\text{O}_3$.¹¹ Effective magnetic moments were calculated by the equation, $\mu_{\text{eff}} = 2.828(\chi_A \times T)^{1/2}$, where χ_A is the magnetic susceptibility per copper atom corrected for the diamagnetism of the constituting atoms by the use of Pascal's constants.¹² ESR spectra were measured in chloroform at liquid nitrogen temperature (frozen solution) with a JES-FE3X ESR instrument. Cyclic voltammograms were recorded on a Yanagimoto P-1000 voltammetric analyzer in dichloromethane containing 0.1 M[†] tetrabutylammonium perchlorate as the supporting electrolyte. A three-electrode cell with a glassy carbon as the working electrode, a platinum coil as the auxiliary electrode, and a saturated calomel as the reference electrode was used for the measurements. All the potentials were corrected for liquid junction potential by the use of ferrocene as an internal standard.^{13,14}

Results and Discussion

By the reaction of 2,3-dicyano-2,3-butanediol and ammonia two isomers of 2,3-dicyano-2,3-butanediamine were obtained; one is liquid and the other is solid.

[†] 1 M = 1 mol dm⁻³.

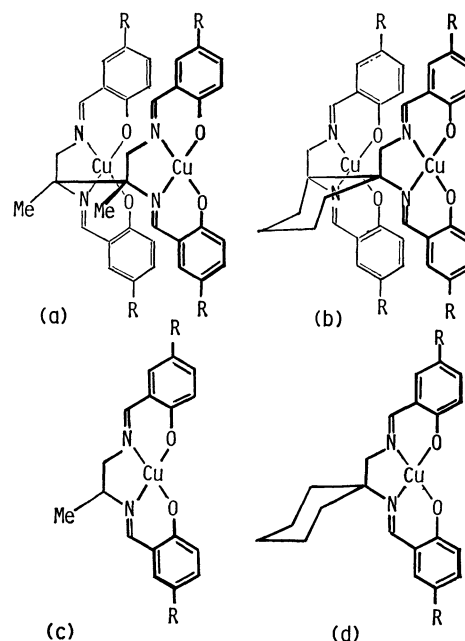


Fig. 1. Chemical structures of (a) $\text{Cu}_2(\text{R-sata})$, (b) $\text{Cu}_2(\text{R-sacta})$, (c) $\text{Cu}(\text{R-salpn})$, and (d) $\text{Cu}(\text{R-sacda})$.

Similarly ammonolysis of 1,2-dicyano-1,2-cyclohexanediol gave two isomers (liquid and solid) of 1,2-dicyano-1,2-cyclohexanediamine. The presence of two isomers can be attributed to the fact that these diamino dinitriles are diastereomeric and exist as a mixture of *dl*- and *meso*-isomers. In this study, the solid diamino dinitriles were reduced to prepare 2,3-dimethyl-1,2,3,4-butanetetramine and 1,2-bis(aminomethyl)-1,2-cyclohexanediamine. However, we have not yet determined whether the tetramines are the *meso*- or the *dl*-isomer. In Fig. 1 the structures of $\text{Cu}_2(\text{R-sata})$ and $\text{Cu}_2(\text{R-sacta})$ of the *meso*-tetramines are shown.

The half of $\text{Cu}_2(\text{R-sata})$ corresponds to *N,N'*-bis(*R*-salicylidene)-1,2-propanediaminatocopper(II), $\text{Cu}(\text{R-salpn})$, which is hence adopted as the reference complex to $\text{Cu}_2(\text{R-sata})$. As the reference complex to $\text{Cu}_2(\text{R-sacta})$, we adopted the complexes $\text{Cu}(\text{R-sacda})$ of 1-(*R*-salicylideneamino)-1-(*R*-salicylideneamino-methyl)cyclohexane ($\text{H}_2(\text{R-sacda})$), taking into account the steric characteristics of cyclohexane ring. The structures of $\text{Cu}(\text{R-salpn})$ and $\text{Cu}(\text{R-sacda})$ are also given in Fig. 1.

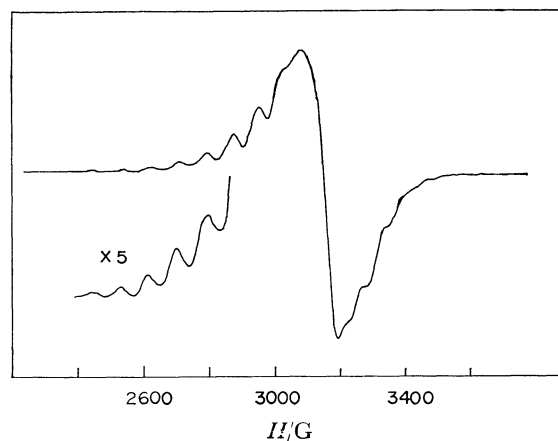
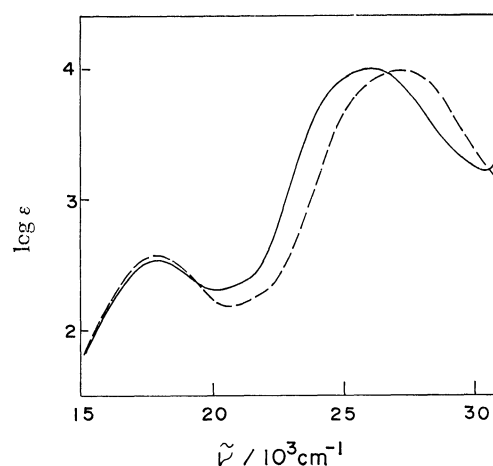
TABLE 2. EFFECTIVE MAGNETIC MOMENTS AND WEISS CONSTANTS OF COMPLEXES

	$\mu_{\text{eff}}/\text{BM}(T/\text{K})$		θ/K
$\text{Cu}_2(\text{sata})$	1.94 (86.3)	1.87 (295.6)	8
$\text{Cu}_2(5\text{-Me-sata})$	1.90 (87.4)	1.85 (293.2)	3
$\text{Cu}_2(5\text{-Bu}^t\text{-sata})$	1.86 (86.9)	1.84 (297.8)	≈ 0
$\text{Cu}_2(\text{sacta})$	2.02 (87.4)	1.87 (296.1)	17
$\text{Cu}_2(5\text{-Me-sacta})$	1.94 (86.3)	1.84 (295.4)	10
$\text{Cu}_2(5\text{-Bu}^t\text{-sacta})$	1.88 (88.5)	1.86 (295.6)	≈ 0

Magnetic susceptibilities of $\text{Cu}_2(\text{R-sata})$ and $\text{Cu}_2(\text{R-sacta})$ were measured on solid samples in the temperature range from liquid nitrogen temperature to room temperature. The effective magnetic moments at room temperature and near liquid nitrogen temperature are given in Table 2. Magnetic moments of $\text{Cu}_2(5\text{-Bu}^t\text{-sata})$ and $\text{Cu}_2(5\text{-Bu}^t\text{-sacta})$ are almost independent of temperature. On the other hand, the moments of $\text{Cu}_2(\text{sata})$, $\text{Cu}_2(5\text{-Me-sata})$, $\text{Cu}_2(\text{sacta})$, and $\text{Cu}_2(5\text{-Me-sacta})$ increase with lowering of temperature. The χ_A vs. T^{-1} plots for these complexes revealed that they obey the Curie-Weiss law, $\chi_A = C/(T - \theta)$. The Weiss constants thus determined are given in Table 2. Positive Weiss constants for $\text{Cu}_2(\text{R-sata})$ ($\text{R}=\text{H}$, 5-Me) and $\text{Cu}_2(\text{R-sacta})$ ($\text{R}=\text{H}$, 5-Me) imply the operation of an intramolecular, ferromagnetic spin-exchange interaction. This magnetic behavior resembles that of dimeric N,N' -disalicylideneethylenediaminacopper(II), $[\text{Cu}(\text{salen})]_2$.¹⁵⁾ Weiss constants for $\text{Cu}_2(\text{R-sacta})$ are larger than those of the corresponding $\text{Cu}_2(\text{R-sata})$. It is likely that two copper(II) ions are held in close distance in $\text{Cu}_2(\text{sacta})$ and $\text{Cu}_2(5\text{-Me-sacta})$ because of the steric requirement of cyclohexane ring, while two CuN_2O_2 planes of $\text{Cu}_2(\text{R-sata})$ can rotate about the C(2)–C(3) axis of the tetramine moiety. The temperature-independence of the magnetic moments of $\text{Cu}_2(5\text{-Bu}^t\text{-sata})$ and $\text{Cu}_2(5\text{-Bu}^t\text{-sacta})$ suggests that access of the copper(II) ions is sterically hindered by the bulky *t*-butyl group.

ESR spectra of $\text{Cu}_2(\text{R-sata})$ and $\text{Cu}_2(\text{R-sacta})$ were measured on frozen solutions in chloroform at liquid nitrogen temperature. The spectra of $\text{Cu}_2(5\text{-Me-sata})$, $\text{Cu}_2(5\text{-Bu}^t\text{-sata})$ and $\text{Cu}_2(5\text{-Bu}^t\text{-sacta})$ showed a tetragonal pattern with $A_{\parallel} \approx 190\text{G}$ ($1\text{G} = 1 \times 10^{-4}\text{T}$) and resemble the spectra of $\text{Cu}(\text{R-salpn})$ and $\text{Cu}(\text{R-sacda})$. This implies that metal-metal interaction is very weak in these complexes in chloroform solution. On the other hand, ESR spectra of $\text{Cu}_2(\text{sata})$, $\text{Cu}_2(\text{sacta})$, and $\text{Cu}_2(5\text{-Me-sacta})$ were characterized by a seven-lined hyperfine structure ($A_{\parallel} \approx 85\text{G}$) centered around 3200 G. In Fig. 2 the ESR spectrum of $\text{Cu}_2(\text{sata})$ is shown as an example. It is evident that in these three complexes two copper(II) ions ferromagnetically couple to produce the $s=1$ ground state. The ESR spectral features of $\text{Cu}_2(\text{sata})$, $\text{Cu}_2(\text{sacta})$, and $\text{Cu}_2(5\text{-Me-sacta})$ resemble that of dimeric $\text{Cu}(\text{salen})$, which has been demonstrated to have a face-to-face structure¹⁶⁾ and displays a seven-lined hyperfine structure in ESR spectrum based on the $s=1$ ground state.¹⁵⁾

Electronic spectra of $\text{Cu}_2(\text{R-sata})$ and $\text{Cu}_2(\text{R-sacta})$ were measured in chloroform. Electronic spectra of

Fig. 2. ESR spectrum of $\text{Cu}_2(\text{sata})$ in chloroform at liquid nitrogen temperature.Fig. 3. Electronic spectra of (—) $\text{Cu}_2(\text{sata})$ and (---) $\text{Cu}(\text{salpn})$ in chloroform.

$\text{Cu}_2(\text{sata})$ and $\text{Cu}(\text{salpn})$ are given in Fig. 3. Absorption bands near $18 \times 10^3\text{cm}^{-1}$ is assigned to the d-d transition,¹⁷⁻¹⁹⁾ while the band around $26 \times 10^3\text{cm}^{-1}$ has been assigned to the $\pi\text{-}\pi^*$ transition which involves the π -orbital functions of the azomethine group.^{17,18)} Table 3 includes the wavenumbers and the extinction coefficients of the d-d and the $\pi\text{-}\pi^*$ transition bands of the binuclear complexes together with those of the mononuclear complexes as the reference. There is no substantial change in the frequency and the intensity of the d-d band between the binuclear and the corresponding mononuclear complexes. This clearly indicates that the configurations around the metal in $\text{Cu}_2(\text{R-sata})$ and $\text{Cu}_2(\text{R-sacta})$ are practically the same as those of $\text{Cu}(\text{R-salpn})$ and $\text{Cu}(\text{R-sacda})$, respectively. We presume that the configuration around the metal for $\text{Cu}_2(\text{R-sata})$ and $\text{Cu}_2(\text{R-sacta})$ is of planar, four-coordination as demonstrated for $\text{Cu}(\text{salen})$.²⁰⁾

The $\pi\text{-}\pi^*$ transition frequencies of $\text{H}_4(\text{R-sata})$, $\text{H}_4(\text{R-sacta})$, $\text{H}_2(\text{R-salpn})$, and $\text{H}_2(\text{R-sacda})$ are almost the same and appear near $31 \times 10^3\text{cm}^{-1}$ (e.g., 31.1×10^3 for $\text{H}_4(\text{sata})$, 31.0×10^3 for $\text{H}_4(\text{sacta})$, 31.3×10^3 for $\text{H}_2(\text{salpn})$, and $31.1 \times 10^3\text{cm}^{-1}$ for $\text{H}_2(\text{sacda})$). The $\pi\text{-}\pi^*$ band shifts to lower wavenumber when the

TABLE 3. ABSORPTION SPECTRAL DATA OF COMPLEXES IN CHLOROFORM ($\bar{\nu}/10^3 \text{ cm}^{-1}$)

Binuclear complexes	d-d(log ϵ)	π - π^* (log ϵ)	Mononuclear complexes	d-d(log ϵ)	π - π^* (log ϵ)
Cu ₂ (sata)	17.92 (358)	26.11 (10400)	Cu(salpn)	17.89 (389)	27.25 (11100)
Cu ₂ (5-Me-sata)	17.61 (380)	26.31 (9470)	Cu(5-Me-salpn)	17.61 (416)	26.18 (10000)
Cu ₂ (5-Bu ^t -sata)	17.99 (305)	26.11 (8970)	Cu(5-Bu ^t -salpn)	17.54 (421)	26.46 (9520)
Cu ₂ (sacta)	17.73 (321)	25.45 (8730)	Cu(sacda)	17.67 (358)	27.10 (11700)
Cu ₂ (5-Me-sacta)	17.54 (324)	25.19 (8710)	Cu(5-Me-sacda)	17.79 (372)	26.39 (11200)
Cu ₂ (5-Bu ^t -sacta)	17.86 (288)	25.97 (9120)	Cu(5-Bu ^t -sacda)	17.86 (389)	26.60 (12000)

TABLE 4. CYCLIC VOLTAMMETRIC DATA OF COMPLEXES

Binuclear complexes	E_{pc}/V	E_{pa}/V	$\Delta E/mV$	$E'_{1/2}$	Mononuclear complexes	E_{pc}/V	E_{pa}/V	$\Delta E/mV$	$E'_{1/2}$
Cu ₂ (sata)	$\begin{cases} -1.28 \\ -1.42 \end{cases}$	$\begin{cases} -0.95 \\ -1.16 \end{cases}$	$\begin{cases} 330 \\ 260 \end{cases}$	$\begin{cases} -1.12 \\ -1.29 \end{cases}$	Cu(salpn)	-1.36	-1.25	110	-1.31
Cu ₂ (5-Me-sata)	-1.48	-1.36	120	-1.42	Cu(5-Me-salpn)	-1.44	-1.30	140	-1.37
Cu ₂ (5-Bu ^t -sata)	-1.55	-1.35	200	-1.45	Cu(5-Bu ^t -salpn)	-1.47	-1.35	120	-1.41
Cu ₂ (sacta)	$\begin{cases} -1.23 \\ -1.45 \end{cases}$	$\begin{cases} -0.94 \\ -1.34 \end{cases}$	$\begin{cases} 290 \\ 110 \end{cases}$	$\begin{cases} -1.09 \\ -1.40 \end{cases}$	Cu(sacda)	-1.48	-1.34	140	-1.41
Cu ₂ (5-Me-sacta)	$\begin{cases} -1.30 \\ -1.51 \end{cases}$	$\begin{cases} -0.97 \\ -1.28 \end{cases}$	$\begin{cases} 290 \\ 230 \end{cases}$	$\begin{cases} -1.09 \\ -1.40 \end{cases}$	Cu(5-Me-sacda)	-1.49	-1.37	120	-1.43
Cu ₂ (5-Bu ^t -sacta)	-1.52	-1.28	240	-1.40	Cu(5-Bu ^t -sacda)	-1.52	-1.38	160	-1.44

All potentials are corrected by the use of ferrocene as an internal standard and given in V (or mV) *vs.* NHE. Approximate redox potentials ($E'_{1/2}$) are given by the mean of E_{pc} and E_{pa} .

ligand coordinates to copper(II) ion. It is noteworthy that the band frequency for Cu₂(sata), Cu₂(sacta), and Cu₂(5-Me-sacta) are lower than those of Cu(salpn), Cu(sacda), and Cu(5-Me-sacda), respectively. The shift is more than $1,100 \text{ cm}^{-1}$ (see Table 2). The red shift of the π - π^* transition for these complexes suggests the stacking of the two CuN₂O₂ chromophores interacting through the π -bonding systems of the ligand. The π - π^* transitions for Cu₂(5-Me-sata), Cu₂(5-Bu^t-sata), and Cu₂(5-Bu^t-sacta) are practically the same in wavenumber as that of the corresponding mononuclear complexes.

Electrochemical properties of Cu₂(R-sata), Cu₂(R-sacta), Cu(R-salpn), and Cu(R-sacda) were studied by means of cyclic voltammetry. Cathodic peak (E_{pc}), anodic peak (E_{pa}), peak separation (ΔE_p), and approximate redox potential ($E'_{1/2}$) given by the mean of the E_{pc} and E_{pa} are shown in Table 4. All waves observed are quasi-reversible or irreversible judging from the peak separations and the wave shapes. Each cyclic voltammogram of Cu₂(5-Me-sata), Cu₂(5-Bu^t-sata), and Cu₂(5-Bu^t-sacta) involves only one redox couple attributable to the process Cu(II,II)/Cu(I,I). Each redox potential is essentially the same as that of the corresponding mononuclear copper(II) complex. There is no interaction between the CuN₂O₂ chromophores of these complexes as demonstrated on the basis of ESR and visible spectra, and hence the two metal ions are reduced at an identical potential to copper(I) ion.

Cyclic voltammograms of Cu₂(sata), Cu₂(sacta), and Cu₂(5-Me-sacta) were characterized by two redox couples, a typical example being shown in Fig. 4. This separation is much larger than 0.036 V expected from the statistical effect.²¹ The electrochemical behavior

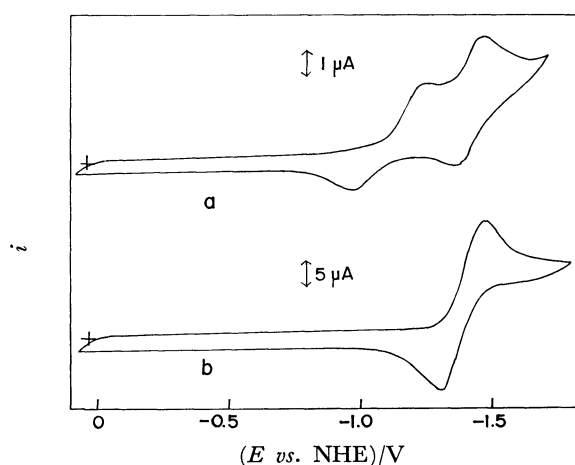


Fig. 4. Cyclic voltammograms of (a) Cu₂(sata) and (b) Cu(salpn) in dichloromethane (scan rate: 40 mV/s).

of this kind has usually been interpreted in terms of the stepwise redox-process, Cu(II,II) \rightleftharpoons Cu(II,I) \rightleftharpoons Cu(I,I).^{2,5} Each of the first redox potentials for Cu₂(sata), Cu₂(sacta), and Cu₂(5-Me-sacta) is higher than that of the corresponding mononuclear complex. This may be ascribed to the stabilization of the Cu(II, I) state effected by the electron-delocalization over the molecule through the ligand π -system.

The second potential for these complexes well corresponds to the potential of the corresponding mononuclear complex. Thus, we tentatively assigned the second redox wave to the two-electron transfer from Cu(II,II) to Cu(I,I), although theoretical analysis²² is impossible because of the irreversible process. Occurrence of the Cu(II,II)/Cu(I,I) and the Cu(II,II)/

Cu(II, I) processes is not clear at present. One plausible explanation is that an equilibrium exists between the stacked and the non-stacked forms at ambient temperature, and the latter form is reduced to the Cu(I, I) species at practically the same potential as that of the reference mononuclear complex.

The difference between the first and the second redox potentials, $E'_{1/2}$, is 0.17 V for Cu₂(sata), 0.31 V for Cu₂(sacta), and 0.26 V for Cu₂(5-Me-sacta). It is likely that the geometrical fixation of the CuN₂O₂ planes in the cases of Cu₂(sacta) and Cu₂(5-Me-sacta) owing to the cyclohexane ring brings about a considerable stabilization of the Cu(II,I) state compared with the case of Cu₂(sata), whose two chromophores can be remote from each other because of the free rotation around the C(2)–C(3) bond of the tetramine. Further, it seems that the stacking of the CuN₂O₂ planes may be sterically hindered by the substituent on the ring, since $E'_{1/2}$ decreases in the general trend R=H>5-Me>5-Bu^t and any indications of the stabilization of the Cu(II,I) state were not recognized in the cases of Cu₂(5-Bu^t-sata) and Cu₂(5-Bu^t-sacta).

The magnetic, spectral, and electrochemical characteristics found for the present complexes are particularly interesting in connection with the "dimeric bacteriochlorophyll", whose cation radical shows an ESR spectrum of a narrow line-width²³⁾ and is reduced at a high potential compared with monomeric bacteriochlorophyll *in vitro*.²⁴⁾

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