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Binuclear Metal Complexes. IL.[1] Synthesis, ESR, and Electrochemical Properties of Strati-bis Copper(II)-Nickel(II) Complexes

Hisashi Ōkawa,* Miyuki Kakimoto, Tatuo Izumitani,
Masaaki Nakamura, and Sigeo Kida
Department of Chemistry, Faculty of Science, Kyushu University 33,
Hakozaki, Higashi-ku, Fukuoka 812

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Strati-bis copper(II)–nickel(II) complexes, CuNi(R-sata) and CuNi(R-sacta) (R=H, 5-Me, 5-Br), have been prepared, where H_4(R-sata) and H_4(R-sacta) denote 1,2,3,4-tetrakis(R-salicylideneamino)-2,3-dimethylbutane and 1,2-bis(R-salicylideneamino)-1,2-bis(R-salicylideneaminomethyl)cyclohexane, respectively. ESR spectra of the complexes (frozen chloroform solution at liquid nitrogen temperature) showed a tetragonal pattern with a hyperfine coupling constant $A_{//}$ smaller than that of the relevant mononuclear copper(II) complex. Based on cyclic voltammetry and differential pulse polarography, it was shown that the Cu(II)→Cu(I) reduction occurs at a higher potential than that of the mononuclear reference complex. The ESR and electrochemical properties have been interpreted in terms of the stacking of the CuN_2O_2 and NiN_2O_2 planes and hence the electron delocalization over the whole molecule through the ligand π-system.

So far many binucleating ligands have been devised for the studies of magnetic spin-exchange interaction, redox properties and catalytic functions of binuclear metal complexes.[2,3] In almost all of these complexes, metal ions are linked with bridging groups so that two equatorial planes are kept coplanar. On the other hand, there have been obtained few binucleating ligands capable of forming "strati-bis" metal complexes.[4–9]

In the previous paper of this series,[4] we have reported the synthesis and characterization of strati-bis copper(II) complexes of 1,2,3,4-tetrakis(R-salicylideneamino)-2,3-dimethylbutane (H_4(R-sata)) and 1,2-bis(R-salicylideneamino)-1,2-bis(R-salicylideneaminomethyl)cyclohexane (H_4(R-sacta)). By comparing the properties of Cu_2(R-sata) and Cu_2(R-sacta) with Cu(R-salpn) (H_2(R-salpn) = *N,N'*-bis(R-salicylideneamino)-1,2-propanediamine) and Cu(R-sacda) (H_2(R-sacda) = 1-(R-salicylideneamino)-1-(R-salicylideneaminomethyl)cyclohexane), respectively, the following characteristics have been recognized for the strati-bis copper(II) complexes: (1) seven-lined hyperfine structure with a small hyperfine coupling constant ($A_{//}\approx 85$ G ($1\ \mathrm{G}=1\times10^{-4}$ T)) in ESR spectrum, (2) red shift of the π-π^* transition band involving azomethine π-character, and (3) one-electron transfer process, Cu(II,II)$\rightleftharpoons$Cu(II,I), occuring at a high potential compared with the corresponding mononuclear copper(II) complex. These characteristics can be explained in terms of the assumption that the two CuN_2O_2 planes are stacked in a face-to-face manner and interact with each other through the ligand π-system.

As the extension of this study, the strati-bis complexes, CuNi(R-sata) and CuNi(R-sacta), were prepared in the present study and their properties were examined in comparison with those of Cu(R-salpn) and Cu(R-sacda), respectively. Chemical structures of CuNi(R-sata), CuNi(R-sacta), Cu(R-salpn), and Cu(R-sacda) are shown in Fig. 1.

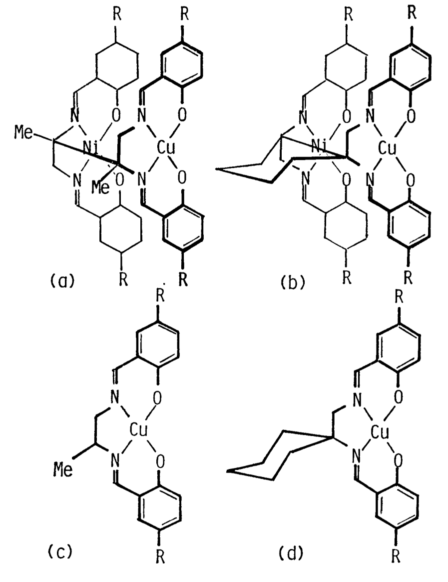

Fig. 1. Chemical structures of (a) CuNi(R-sata), (b) CuNi(R-sacta), (c) Cu(R-salpn), and (d) Cu(R-sacda); R (substituent on the ring)=H, 5-Me, or 5-Br.

Experimental

Syntheses. Synthetic methods for 2,3-dimethyl-1,2,3,4-butanetetramine and 1,2-bis(aminomethyl)-1,2-cyclohexanediamine have been described in the previous paper.[4] Syntheses of Cu(R-salpn)[10] and Cu(R-sacda)[4] were performed by the methods in the literatures.

CuNi(sata). 2,3-Dimethyl-1,2,3,4-butanetetramine (0.30 g) and salicylaldehyde (1.0 g) were dissolved in ethanol (50 cm^3), and the mixture was refluxed with stirring. To this was added an ethanolic solution (30 cm^3) of copper(II) acetate monohydrate (0.41 g) and the mixture was stirred at 60 °C for 10 min. Then, an ethanolic solution (30 cm^3) of nickel(II) acetate tetrahydrate (0.51 g) was added, and the mixture was stirred at 60 °C for 10 min. The reaction mixture was filtered, concentrated to *ca.* 30 cm^3 and allowed to stand in a refrigerator to give brown crystals. They were recrystallized from a chloroform–ethanol mixture.

Found: C, 58.81; H, 4.90; N, 7.91; Cu, 9.37%. Calcd for $C_{34}H_{30}N_4O_4CuNi\cdot H_2O$: C, 58.43; H, 4.62; N, 8.02; Cu, 9.09%.

CuNi(5-Me-sata). This complex was obtained as brown crystals in the same way as that of CuNi(sata), except for using 5-methylsalicylaldehyde instead of salicylaldehyde. It was recrystallized from a chloroform–ethanol mixture.

Found: C, 60.90; H, 5.40; N, 7.34; Cu, 8.26%. Calcd for $C_{38}H_{38}N_4O_4CuNi\cdot 1/2\,H_2O$: C, 61.18; H, 5.27; N, 7.51;

Cu, 8.52%.

CuNi(5-Br-sata). The synthetic method for this complex is the same as that for CuNi(sata), except for using 5-bromosalicylaldehyde instead of salicylaldehyde. It forms brown crystals when crystallized from a chloroform–ethanol mixture.

Found: C, 40.58; H, 3.01; N, 5.33; Cu, 6.52%. Calcd for $C_{34}H_{26}N_4O_4Br_4CuNi \cdot 1/2\,H_2O$: C, 40.61; H, 2.71; N, 5.57; Cu, 6.32%.

CuNi(sacta). An ethanolic solution (50 cm^3) of 1,2-bis(aminomethyl)-1,2-cyclohexanediamine (0.30 g) and salicylaldehyde (0.85 g) was refluxed for 20 min. To this was added copper(II) acetate monohydrate (0.35 g), and the mixture was heated at *ca.* 60 °C for 10 min. To this solution was added nickel(II) acetate tetrahydrate (0.44 g), and the mixture was heated at 60 °C for 10 min. The reaction mixture was filtered and allowed to stand in a refrigerator. A brown precipitate was filtered and recrystallized from a chloroform–ethanol mixture to form brown prisms.

Found: C, 58.44; H, 4.77; N, 7.53; Cu, 8.10%. Calcd for $C_{36}H_{32}N_4O_4CuNi \cdot 2H_2O$: C, 58.20; H, 4.88; N, 7.54; Cu, 8.55%.

CuNi(5-Me-sacta). This complex was obtained as brown prisms in the same way as that of CuNi(sacta), except for using 5-methylsalicylaldehyde in place of salicylaldehyde. It was recrystallized from a chloroform–ethanol mixture.

Found: C, 62.67; H, 5.66; N, 6.80; Cu, 7.74%. Calcd for $C_{40}H_{40}N_4O_4CuNi \cdot C_2H_5OH$: C, 62.35; H, 5.73; N, 6.92; Cu, 7.85%.

CuNi(5-Br-sacta). This complex was obtained as brown prisms in the same way as that of CuNi(sacta), except for using 5-bromosalicylaldehyde instead of salicylaldehyde.

Found: C, 42.73; H, 3.12; N, 5.21; Cu, 6.24%. Calcd for $C_{36}H_{28}N_4O_4Br_4CuNi \cdot C_2H_5OH$: C, 42.71; H, 3.12; N, 5.24; Cu, 5.95%.

Measurements. Electronic spectra were recorded on a Shimadzu MPS-5000 spectrophotometer. Magnetic susceptibilities were measured by the Faraday method at room temperature. Effective magnetic moments were calculated by the equation, $\mu_{\mathrm{eff}}=2.828\ (\chi_{\mathrm{M}} \times T)^{1/2}$, where χ_{M} is the magnetic susceptibility per molecule corrected for diamagnetism by the use of Pascal's constants.[11)] ESR spectra were recorded on a JES-FE3X instrument in frozen chloroform solutions near liquid nitrogen temperature. Cyclic voltammograms were recorded on a Yanagimoto P-1000 voltammetric analyzer in dichloromethane containing 0.1 M (1 M = 1 mol dm^{-3}) tetrabutylammonium perchlorate as the supporting electrolyte. The measurements were carried out in a three-electrode cell equipped with a glassy carbon working electrode, a platinum coil auxiliary electrode, and a saturated calomel reference electrode. The potentials were corrected for liquid junction potential by the use of ferrocene as an internal standard.[12,13)] Differential pulse polarograms were recorded on the same instrument by the use of dropping mercury electrode instead of glassy carbon electrode.

Results and Discussion

The magnetic moments of CuNi(R-sata) and CuNi(R-sacta) fall in the range 1.80—1.96 BM (Table 1), indicating the presence of one unpaired electron per molecule. Since *N,N'*-disalicylideneethylenediaminatonickel(II) and its congeners are diamagnetic, the magnetic moments in Table 1 clearly indicate that the complexes contain one copper(II) and one nickel(II) ions.

Table 1. Magnetic moments of CuNi(R-sata) and CuNi(R-sacta)

Complex	μ_{eff}/BM
CuNi(sata)·H_2O	1.96
CuNi(5-Me-sata)·1/2 H_2O	1.80
CuNi(5-Br-sata)·1/2 H_2O	1.94
CuNi(sacta)·$2H_2O$	1.80
CuNi(5-Me-sacta)·C_2H_5OH	1.85
CuNi(5-Br-sacta)·C_2H_5OH	1·89

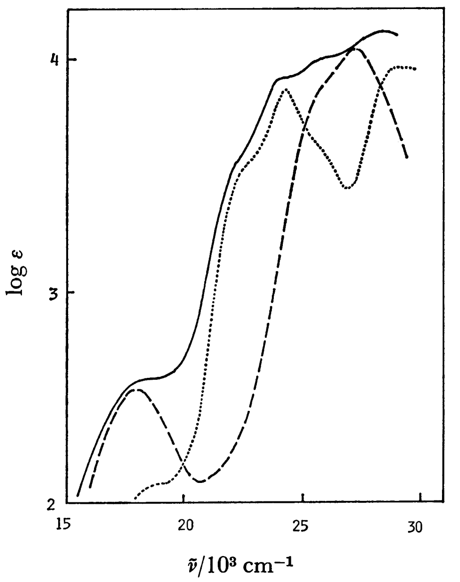

Fig. 2. Electronic spectra of (——) CuNi(sata), (——)-Cu(salpn), and (----)Ni(salpn).

With respect to two asymmetric carbon atoms in the tetramine moieties, two geometrical isomers (*meso*- and *dl*-) are considered for CuNi(R-sata) and CuNi(R-sacta). It has been shown that 1,2-bis(aminomethyl)-1,2-cyclohexanediamine is of the *dl*-form (*trans*-form), since 1,2-dicyano-1,2-cyclohexanediamine (the precursor of 1,2-bis(aminomethyl)-1,2-cyclohexanediamine) forms a *trans*-octahedral nickel(II) complex.[14)] The geometrical structure of H_4(R-sacta) has not yet been determined.

Electronic spectra of the CuNi-complexes were well explained by the superposition of the [CuN_2O_2] and [NiN_2O_2] chromophores. The spectrum of CuNi(sata) is shown as an example in Fig. 2, together with the spectra of Cu(salpn) and Ni(salpn) as the references.

ESR spectra of the CuNi-complexes were measured in frozen chloroform solutions (at liquid nitrogen temperature). All the complexes showed a tetragonal pattern. ESR spectrum of CuNi(sata) is shown as an example in Fig. 3. Figure 3 also includes the spectra of Cu_2(sata) and Cu(salpn) for comparison. The spectrum of CuNi(sata) markedly differs from that of Cu_2(sata) and resembles that of Cu(salpn). This clearly indicates that CuNi(sata) is not an equimolar mixture of Cu_2(sata) and Ni_2(sata) but a discrete hetero-metal complex.

The ESR parameters, $A_{/\!/}$ and $g_{/\!/}$, for the CuNi-complexes and their relevant reference complexes are

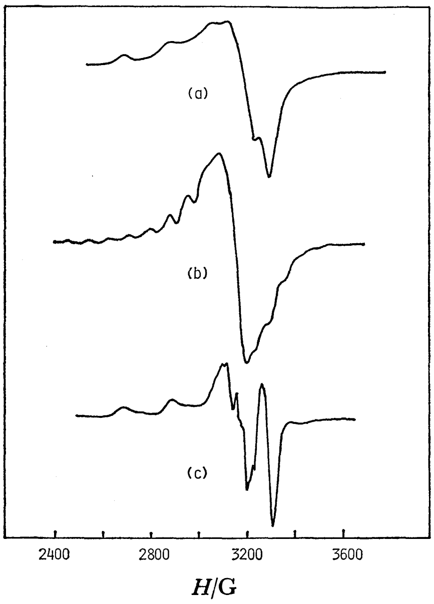

Fig. 3. ESR spectra of (a) CuNi(sata), (b) Cu_2(sata), and (c) Cu(salpn).

TABLE 2. ESR PARAMETERS OF THE CuNi-COMPLEXES AND THEIR REFERENCE COMPLEXES

	$A_{//}$/G	$g_{//}$		$A_{//}$/G	$g_{//}$
CuNi(sata)	183	2.22	Cu(salpn)	193	2.18
CuNi(5-Me-sata)	185	2.22	Cu(5-Me-salpn)	198	2.20
CuNi(sacta)	178	2.24	Cu(sacda)	206	2.18
CuNi(5-Me-sacta)	185	2.25	Cu(5-Me-sacda)	209	2.16

given in Table 2. ESR spectra of CuNi(5-Br-sata) and CuNi(5-Br-sacta) were not well resolved and hence their ESR parameters were not evaluated. Detailed examination of the ESR spectra of the CuNi-complexes revealed that the hyperfine coupling constant $A_{//}$ is smaller than that of the corresponding reference complex. Smaller $A_{//}$ values, compared with the reference complexes, of the CuNi-complexes can be interpreted in terms of the spin-delocalization over the molecule. As was shown for the binuclear copper(II) complexes,4) it is likely that the CuN_2O_2 and NiN_2O_2 planes are stacked each other and interact through the ligand π-system.

It is to be noted that the $g_{//}$ values for the CuNi-complexes are larger than those of the corresponding reference mononuclear copper(II) complexes. The frequency of the d-d band due to the copper for the CuNi-complexes is practically the same as that of the reference complexes. Therefore, the large $g_{//}$ values of the CuNi-complexes may be attributed to the increase of λ due to the stacked configuration, based on the simple equation $g=2.0-8\lambda/(d_{x^2-y^2}-d_{xy})$.15)

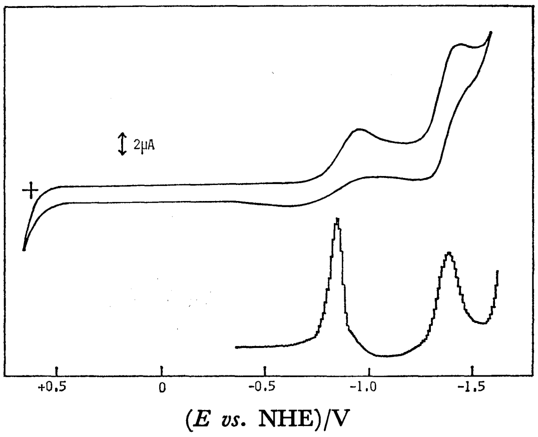

Fig. 4. Cyclic voltammogram and differential pulse polarogram of CuNi(sata).

Both of the cyclic voltammograms and differential pulse polarograms of CuNi(R-sata) and CuNi(R-sacta) showed two reduction waves. Typical examples are given in Fig. 4. The processes are irreversible or quasi-reversible judging from the separation ΔE_p between the cathodic and anodic peaks, E_{pc} and E_{pa}, of the cyclic voltammograms. Electrochemical data for the CuNi-complexes are given in Table 3. Approximate redox potentials $E^f_{1/2}$, which were determined by the arithmetic mean of E_{pa} and E_{pc} of cyclic voltammogram, substantially accord with the half-wave potentials determined from the differential pulse polarogram.

Reduction of Ni(R-salpn) and Ni(R-sacda) did not occur in the accessible range. Thus, all the reduction processes observed for the CuNi-complexes can be attributed to the reduction of copper(II) ion. Appearance of two reduction waves suggests the presence of two species, the stacked and non-stacked species, in solution. Two reduction waves have also been observed for Cu_2(sata), Cu_2(sacta), and Cu_2(5-Me-sacta).4) For these complexes, the first and second reduction processes can be attributed to the one-electron transfer of the stacked species (Cu(II,II)$\rightleftharpoons$Cu(II,I)) and two electron transfer of the non-stacked species (Cu(II,

TABLE 3. ELECTROCHEMICAL DATA OF THE CuNi-COMPLEXES

	1st				2nd			
	CV			DPP	CV			DPP
	E_{pc}	E_{pa}	$E^f_{1/2}$	$E_{1/2}$	E_{pc}	E_{pa}	$E^f_{1/2}$	$E_{1/2}$
CuNi(sata)	−0.95	−0.77	−0.86	−0.86	−1.44	−1.30	−1.37	−1.38
CuNi(5-Me-sata)	−1.00	−0.83	−0.92	−0.91	−1.49	−1.33	−1.41	−1.45
CuNi(5-Br-sata)	−0.89	−0.69	−0.79	−0.87	−1.32	−1.15	−1.24	−1.27
CuNi(sacta)	−1.06	−0.96	−1.01	−0.89	−1.44	−1.32	−1.38	−1.42
CuNi(5-Me-sacta)	−1.06	−0.81	−0.94	−0.94	−1.47	−1.36	−1.42	−1.41
CuNi(5-Br-sacta)	−0.89	−0.67	−0.78	−0.90	−1.30	−1.14	−1.22	−1.26

$E^f_{1/2}=1/2(E_{pa}+E_{pc})$.

II)⇌Cu(I,I)), respectively, based on the controlled-potential electrolysis.[16] Further, the second reduction potentials of the CuNi-complexes well correspond to the potentials of the reference copper(II) complexes, respectively. Thus, it is natural to assign the first and the second processes to the reductions of copper of the stacked and non-stacked species, respectively.

The redox potential of the stacked species is higher by 0.4—0.5 V than that of the non-stacked species. Therefore, the copper ion of the stacked species must be stabilized by $(3—4)\times 10^3\ \mathrm{cm}^{-1}$ (9—12 kcal/mol) compared with that of the non-stacked species or of the reference mononuclear complex. It is likely that such a stabilization is effected by the electron-delocalization over the CuN_2O_2 and NiN_2O_2 coordination units through the ligand π-system. It is also to be noted that the Cu(II)→Cu(I) reduction occurs more easily in the cases of the CuNi-complexes compared with the Cu_2-complexes.[4]

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16) Controlled-potential electrolysis of Cu_2(sacta) (which shows two redox waves at −1.09 and −1.40 V *vs.* SCE) at −1.2 V revealed an electron transfer of *ca.* 0.7. ESR spectrum of the reduced solution showed a tetragonal pattern with the parameters $A_{//}=188$ G and $g_{//}=2.25$. These parameters differ from those ($A_{//}=206$ G and $g_{//}=2.18$) of Cu(sacda) but are similar to those ($A_{//}=178$ G and $g_{//}=2.22$) of CuNi(sacta). Thus, this process can be attributed to a one-electron transfer, Cu(II,II)→Cu(II,I), of the stacked species. Electron number transfered by the further electrolysis at −1.6 V could not be determined because of the concomitant reduction of the ligand with the reduction of the non-stacked species. However, the process at −1.40 V should involve a two-electron transfer, since the controlled-potential electrolysis at −1.60 V of Cu_2(5-Me-sata) (which exists only as the non-stacked species and shows one redox wave at −1.42 V) revealed the transfer of two electrons.