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Binuclear Metal Complexes. XLIII.[1] Magnetic, Spectroscopic, and Electrochemical Studies on Hetero-metal Binuclear Complexes of *N*,*N*′-Bis(3-carboxysalicylidene)-1,1-dibenzylethylenediamine

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Copper(II)–M(II) and copper(II)–iron(III) hetero-metal binuclear complexes of *N*,*N*′-bis(3-carboxysalicylidene)-1,1-dibenzylethylenediamine (H_4fsadb), CuM(fsadb)·$n$$H_2O$ (M=Co, Ni, Cu, Zn, Mg, Ca, Ba) and CuFe(fsadb)Cl·1.5H_2O, have been prepared and characterized. Cryomagnetic measurements (78—300 K) revealed that an antiferromagnetic spin-exchange interaction operates between the metal ions in the cases CuM(fsadb)·$n$$H_2O$ (M=Co, Ni, Cu) and CuFe(fsadb)Cl·1.5H_2O, exchange integrals being evaluated on the basis of the Heisenberg model. Ligand field bands due to the copper(II) ion bound at the N_2O_2-site of CuM(fsadb)·$n$$H_2O$ (M=Co, Ni, Cu, Zn, Mg) and CuFe(fsadb)Cl·1.5H_2O are in the range 1.9×10^3—21.4×10^3 cm^{-1}, while in the cases of CuCa(fsadb)·4H_2O and CuBa(fsadb)·3.5H_2O the frequencies of the bands are close to that (17.8×10^3 cm^{-1}) of the mononuclear complex Cu(H_2fsadb)·H_2O. This spectral feature has been explained in terms of the configuration of the second metal ion adjacent to the copper(II) ion: *trans*-octahedral in the cases of small metal ions (Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Mg(II)) and presumably *cis*-octahedral in the cases of large metal ions (Ca(II), Ba(II)). Copper(II/I) redox potentials of the hetero-metal complexes are much low compared with that of Cu(H_2fsadb)·H_2O. This shift has been discussed in terms of the electronic effect of the carboxylate group and the covalency in the bonding between the bridging phenolic oxygen and the second metal ion.

Recently there is a growing interest in chemistry of binuclear metal complexes in connection with metalloenzymes which involve two metal ions at their active sites.[2] Particularly, the recognition that superoxide dismutase[3] and cytochrome oxidase[4] contain two kinds of metal ions has stimulated an interest in hetero-metal binuclear complexes. Electrochemical technique is one of the essential tools for bioinorganic approach to metalloenzymes and several recent papers have been devoted to the analysis of the redox behavior of binuclear copper(II) complexes[5–9] in the hope to clarify the oxido-reductive function of copper proteins. On the other hand, electrochemical investigations on hetero-metal binuclear complexes are very limited,[10] because of the difficulty in preparation and the low stability in solvents.

Previously we reported the synthesis and the magnetic properties of copper(II)–M(II),[11–14] nickel(II)–M(II),[13] and cobalt(II)–M(II)[15,16] complexes of N,N′-bis(3-carboxysalicylidene)alkanediamines, which were demonstrated to be an excellent binucleating ligand possessing coordination selectivity. However, electrochemical properties of these complexes could not be examined because of their low solubility in solvents suitable for electrochemical measurements. In this study, we have prepared copper(II)–M(II) and copper(II)–iron(III) complexes of a new binucleating ligand, *N*,*N*′-bis(3-carboxysalicylidene)-1,1-dibenzylethylenediamine (abbreviated as H_4fsadb) which possesses hydrophobic benzyl groups in the ethylenediamine moiety (Fig. 1). These complexes, CuM(fsadb)·$n$$H_2O$ (M=Co, Ni, Cu, Zn, Mg, Ca, Ba) and CuFe(fsadb)Cl·1.5H_2O, are soluble in dichloromethane or *N*,*N*-dimethylformamide. Thus, we have examined the optical and electrochemical properties of the copper(II) ion bound at the N_2O_2-site varing the second metal ion at the O_4-site. We have also studied magnetic spin-exchange interaction in CuM(fsadb)·$n$$H_2O$ (M=Co, Ni, Cu) and CuFe(fsadb)Cl·1.5H_2O, comparing the results with those previously reported.[11–16]

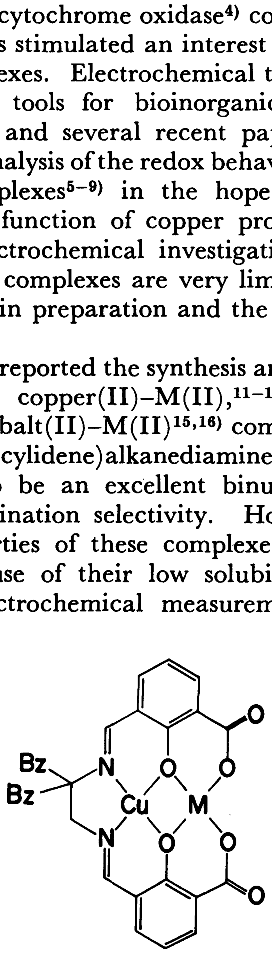

Fig. 1. The structure of hetero-metal binuclear complexes; M=Fe(III)Cl, Co(II), Ni(II), Cu(II), Zn(II), Mg(II), Ca(II), and Ba(II).

Experimental

Syntheses. 3-Formylsalicylic acid was prepared after the method of Duff and Bills.[17]

1,1-Dibenzylethylenediamine. An aqueous solution (20 cm^3) containing ammonium chloride (2.95 g), sodium cyanide (2.5 g) and ammonia water (28%, 7 cm^3) was placed in a round-bottomed flask, and to this was added an ethanolic solution (15 cm^3) of benzyl ketone (10.5 g). The flask was sealed with a rubber stopper and heated at 60 °C on a water bath for 5 hours to give an orange colored solution. The reaction mixture was shaken three times with 70 cm^3 portions of ether. The combined etherial solution was dried over sodium sulfate. Evaporation of the solvent left 2-amino-2-benzyl-3-phenylpropionitrile as pale orange solid. It was washed with a small amount of methanol and recrystallized from methanol to give colorless needles.

Found: C, 81.20; H, 7.02; N, 11.78%. Calcd for $C_{16}H_{16}N_2$: C, 81.32; H, 6.82; N, 11.85%.

This amino nitrile (15 g) was added to a suspension of $LiAlH_4$ (5 g) in absolute ether (250 cm^3). The mixture was stirred for 3 h at room temperature and then refluxed for 40 h on an oil bath. Unreacted $LiAlH_4$ was decomposed by addition of methanol–water (1:1, 40 cm^3), while the flask was cooled by means of ice-water. The reaction mixture was shaken with 150 cm^3 portions of ether four times and the combined etherial solution was dried over sodium sulfate. On evaporating the solvent, there remained 1,1-dibenzylethylenediamine as a hygroscopic, yellow solid. It was used for the preparation of the complexes without further purification.

Cu(H$_2$fsadb)·H$_2$O. 3-Formylsalicylic acid (310 mg) and 1,1-dibenzylethylenediamine (270 mg) were dissolved in absolute methanol (40 cm^3). To this solution was added a methanolic solution (20 cm^3) of copper(II) acetate monohydrate (220 mg), and the mixture was refluxed for several hours to give purple crystalline solid. It was collected, washed with methanol and recrystallized from a mixture of *N*,*N*-dimethylformamide and water.

Found: C, 62.77; H, 4.49; N, 4.74; Cu, 12.3%. Calcd for $C_{32}H_{26}N_2O_6Cu\cdot H_2O$: C, 62.38; H, 4.55; N, 4.55; Cu, 12.24%.

CuFe(fsadb)Cl·1.5H$_2$O. This complex was synthesized as purplish brown prisms by reacting Cu(H$_2$fsadb)·H$_2$O (50 mg) and iron(III) chloride (14 mg) in methanol (20 cm^3) in the presence of triethylamine.

Found: C, 53.68; H, 3.76; N, 3.80; Cu, 8.8; Fe, 8.2%. Calcd for $C_{32}H_{24}N_2O_6ClCuFe\cdot 1.5H_2O$: C, 53.79; H, 3.81; N, 3.92; Cu, 8.89; Fe, 7.82%.

CuCo(fsadb)·3H$_2$O. Cu(H$_2$fsadb)·H$_2$O (100 mg) was dissolved in a solution of lithium hydroxide monohydrate (16 mg) in methanol (40 cm^3). The solution was once filtered to separate insoluble materials. To the red-colored filtrate was added a methanolic solution (10 cm^3) of cobalt(II) acetate tetrahydrate (41 mg), and the mixture was heated at *ca.* 60 °C for a while. After the reaction mixture was left stand overnight, reddish orange needles which separated were collected, washed with water and dried under reduced pressure.

Found: C, 54.22; H, 4.12; N, 4.04; Co, 8.5; Cu, 8.8%. Calcd for $C_{32}H_{24}N_2O_6CoCu\cdot 3H_2O$: C, 54.20; H, 4.28; N, 3.95; Co, 8.31; Cu, 8.96%.

CuNi(fsadb)·6H$_2$O. This complex was obtained as reddish purple needles in the same way as that of CuCo(fsadb)·3H$_2$O except for using nickel(II) chloride hexahydrate (39.7 mg) instead of cobalt(II) acetate tetrahydrate.

Found: C, 50.28; H, 4.32; N, 3.59; Cu, 8.3; Ni, 8.0%. Calcd for $C_{32}H_{24}N_2O_6CuNi\cdot 6H_2O$: C, 50.38; H, 4.76; N, 3.67; Cu, 8.33; Ni, 7.69%.

CuCu(fsadb)·1.5H$_2$O. To a red solution of Cu(H$_2$fsadb)·H$_2$O (100 mg) and lithium hydroxide monohydrate (16 mg) in methanol (40 cm^3) was added a methanolic solution (10 cm^3) of copper(II) acetate monohydrate (37 mg). The mixture was heated at *ca.* 60 °C for 3 h to give pale green solid. It was collected and recrystallized from a mixture of *N*,*N*-dimethylformamide and water.

Found: C, 55.84; H, 4.01; N, 4.26; Cu, 18.6% Calcd for $C_{32}H_{24}N_2O_6Cu_2\cdot 1.5H_2O$: C, 55.97; H, 3.96; N, 4.08; Cu, 18.51%.

CuZn(fsadb)·3H$_2$O. This complex was obtained as reddish orange needles in the same way as that of CuCo(fsadb)·3H$_2$O using zinc(II) chloride (22.8 mg). It was recrystallized from a chloroform–ether mixture.

Found: C, 53.34; H, 4.20; N, 3.86; Cu, 8.9%. Calcd for $C_{32}H_{24}N_2O_6CuZn\cdot 3H_2O$: C, 53.72; H, 4.23; N, 3.92; Cu, 8.88%.

CuMg(fsadb)·4H$_2$O. This complex was obtained as reddish pink needles in the same way as that of CuCo(fsadb)–3H$_2$O using magnesium(II) acetate tetrahydrate (36 mg). It was recrystallized from a chloroform–ether mixture.

Found: C, 55.75; H, 4.32; N, 3.93; Cu, 9.1%. Calcd for $C_{32}H_{24}N_2O_6CuMg\cdot 4H_2O$: C, 55.51; H, 4.66; N, 4.05; Cu, 9.18%.

CuCa(fsadb)·4H$_2$O. This complex was obtained as reddish pink needles by the reaction of Cu(H$_2$fsadb)·H$_2$O (100 mg) and calcium(II) chloride dihydrate (24.4 mg) in methanol (50 cm^3) in the presence of lithium hydroxide monohydrate (16 mg).

Found: C, 54.34; H, 4.34; N, 4.01; Cu, 8.7%. Calcd for $C_{32}H_{24}N_2O_6CaCu\cdot 4H_2O$: C, 54.27; H, 4.55; N, 3.96; Cu, 8.97%.

CuBa(fsadb)·3.5H$_2$O. This complex was obtained as greenish purple needles by the reaction of Cu(H$_2$fsadb)·H$_2$O (100 mg) and barium(II) chloride dihydrate (41 mg) in the presence of lithium hydroxide monohydrate (16 mg).

Found: C, 48.20; H, 3.81; N, 3.59; Cu, 7.7%. Calcd for $C_{32}H_{24}N_2O_6BaCu\cdot 3.5H_2O$: C, 48.27; H, 3.92; N, 3.65; Cu, 7.98%.

Cu(saldb)·0.5H$_2$O. A mixture of salicylaldehyde (102 mg), 1,1-dibenzylethylenediamine (100 mg) and copper(II) acetate monohydrate (83 mg) in methanol (50 cm^3) was heated under stirring for 3 h. The reaction mixture was allowed to stand overnight to give purple prisms, which were collected and dried *in vacuo*.

Found: C, 68.91; H, 5.60; N, 5.25; Cu, 12.3%. Calcd for $C_{30}H_{26}N_2O_2Cu\cdot 0.5H_2O$: C, 69.41; H, 5.24; N, 5.40; Cu, 12.24%.

Measurements. Elemental analyses of carbon, hydrogen, and nitrogen were carried out at the Service Center of Elemental Analysis, Kyushu University. Analyses of copper, cobalt, iron, and nickel were made with a Shimadzu Atomic Absorption-Flame Spectrometer 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 or in *N*,*N*-dimethylformamide. Magnetic susceptibilities were measured by the Faraday method in the temperature range from liquid nitrogen temperature to room temperature. Diamagnetic correction was made using Pascal's constants.[18] Effective magnetic moments were calculated by the equation, $\mu_{eff}=2.828\times\sqrt{(\chi_M-N\alpha)T}$, where χ_M is the susceptibility per molecule. In the case of CuCu(fsadb)·1.5H$_2$O, the moment was calculated for one copper atom. Cyclic voltammograms were recorded with a Yanagimoto Voltammetric Analyzer Model P-1000 in dichloromethane or in *N*,*N*-dimethylformamide 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, the auxiliary electrode a platinum coil, and the reference electrode a saturated calomel electrode. All the redox potentials were corrected by the use of ferrocene as an internal standard,[19] where the ferrocenium/ferrocene redox potential is assumed to be 0.400 V *vs.* NHE.[20]

Results and Discussion

Hetero-metal binuclear complexes were prepared by reacting the mononuclear copper(II) complex Cu(H$_2$fsadb)·H$_2$O with a metal ion. The formation of the hetero-metal complexes can be diagnosed by the presence of a strong band at 1550 cm^{-1} attributable to the coordinated carboxylate group, while Cu(H$_2$fsadb)·H$_2$O exhibits a band at 1710 cm^{-1} due to the free carboxyl group.

Magnetic susceptibilities of the complexes were measured in the temperature range 78—300 K. Magnetic moments of CuM(fsadb)·nH$_2$O (M=Co, Ni, Cu) and CuFe(fsadb)Cl·1.5H_2O are temperature-dependent, indicating that a spin-exchange interaction operates between the metal ions. Magnetic properties of these complexes could be interpreted in terms of the magnetic susceptibility equations (1), (2), (3), and (4) for the (s=1/2)-(s=5/2),[21,22] (s=1/2)-(s=3/2),[13,14] (s=1/2)-(s=1),[10,13,14] and (s=1/2)-(s=1/2)[23] systems, respectively, on the basis of the Heisenberg model:

$$\chi_M = \frac{Ng^2\beta^2}{kT} \times \frac{5\exp(-6J/kT)+14}{5\exp(-6J/kT)+7} + N\alpha, \tag{1}$$

$$\chi_M = \frac{Ng^2\beta^2}{kT} \times \frac{2\exp(-4J/kT)+10}{3\exp(-4J/kT)+5} + N\alpha, \tag{2}$$

$$\chi_M = \frac{Ng^2\beta^2}{kT} \times \frac{\exp(-3J/kT)+2}{\exp(-3J/kT)+10} + N\alpha, \tag{3}$$

and

$$\chi_A = \frac{Ng^2\beta^2}{kT} \times \frac{1}{\exp(-2J/kT)+3} + N\alpha, \tag{4}$$

where χ_M and χ_A represent magnetic susceptibilities per molecule and per atom, respectively, and other symbols have their usual meanings. Best-fits of magnetic susceptibilities to the theoretical curves are shown in Figs. 2 and 3. Magnetic parameters thus determined are given in Table 1. The exchange integrals found for the present complexes are all negative, indicating antiferromagnetic spin-exchange interactions operating between the metal ions. Each integrals obtained is close to the value of corresponding hetero-metal complex of *N,N'*-bis(3-carboxysalicylidene)alkanediamine reported previously.[11-14,22] Magnetic moments of CuM(fsadb)·nH$_2$O (M=Zn, Mg, Ca, Ba) fall in the range 1.83—1.88 BM at room temperature, which indicates the presence of one unpaired electron per molecule.

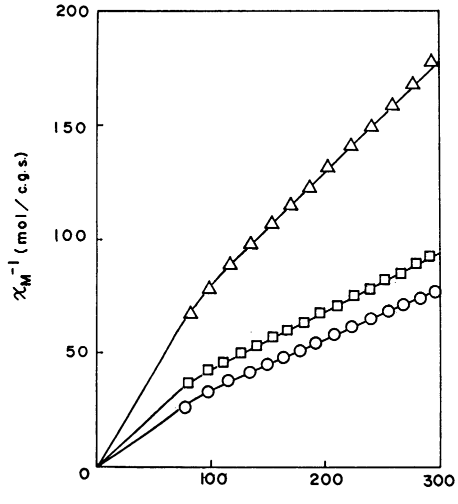

Fig. 2. Temperature variations of inverse magnetic susceptibilities for (○) CuFe(fsadb)Cl-1.5H_2O, (□) CuCo (fsadb)-3H_2O, and (△) CuNi (fsadb)-6H_2O.

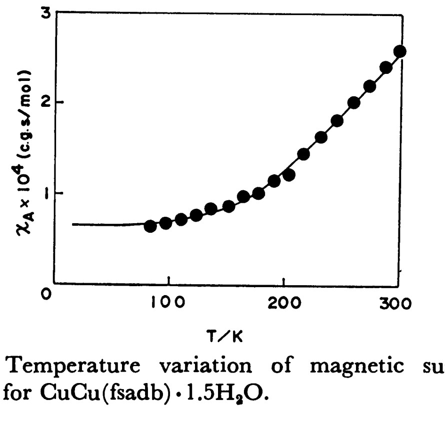

Fig. 3. Temperature variation of magnetic susceptibility for CuCu(fsadb)·1.5H_2O.

Conductance measurements revealed that the hetero-metal complexes are nonelectrolytes in *N,N*-dimethylformamide, suggesting the coordination of the second metal ion to the O_4-site.

Electronic spectra of the hetero-metal complexes were measured in dichloromethane. Because of the sparing solubility of CuCu(fsadb)·1.5H_2O in dichloromethane, the spectrum of this complex was measured in *N,N*-dimethylformamide. Some representatives of absorption spectra are shown in Fig. 4. Absorption maxima and

Table 1. Effective magnetic moments at room temperature and magnetic parameters, J, g, and $N\alpha$, of hetero-metal complexes

	μ_{eff}/BM(T/K)	J/cm^{-1}	g	$N\alpha\times10^6$/c.g.s. mol^{-1}
CuFe(fsadb)-Cl·1.5H_2O	5.57(297.4)	−48	2.00	60
CuCo(fsadb)·3H_2O	5.11(292.5)	−30	2.50	500
CuNi(fsadb)·6H_2O	3.67(295.5)	−22	2.24	200
CuCu(fsadb)·1.5H_2O	0.78(298.5)	−305	2.10	65[a)]
CuZn(fsadb)·3H_2O	1.86(295.7)			
CuMg(fsadb)·4H_2O	1.87(296.2)			
CuCa(fsadb)·4H_2O	1.88(295.4)			
CuBa(fsadb)·3.5H_2O	1.83(298.5)			

a) Data per copper atom.

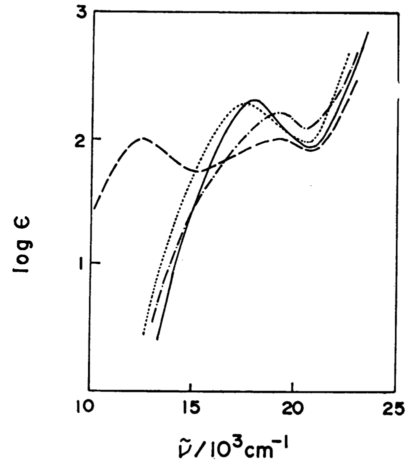

Fig. 4. Absorption spectra of (——) Cu(H_2fsadb)·H_2O (in CH_2Cl_2), (- - -) CuCu(fsadb)·1.5H_2O (in DMF), (—·—) CuMg(fsadb)·3H_2O (in CH_2Cl_2), and (······) CuBa(fsadb)·3.5H_2O (in CH_2Cl_2).

TABLE 2. FREQUENCIES AND EXTINCTION COEFFICIENTS OF THE LIGAND FIELD BANDS OF HETERO-METAL COMPLEXES IN DICHLOROMETHANE AND IONIC RADII OF THE SECOND METAL IONS

	$\tilde{\nu}/10^3$ cm^{-1} (ε)				Ionic radius$^{a)}$ / Å
Cu(H_2fsadb)·H_2O	17.8(211)				
CuFe(fsadb)Cl·1.5H_2O	21.4(1338)				0.63
CuCo(fsadb)·3H_2O	20.2(198)	18.0(151)	16.2(72)	7.5(9)	0.88
CuNi(fsadb)·6H_2O	19.0(164)	16.5(87)	7.8(4)		0.84
CuCu(fsadb)·1.5$H_2O^{b)}$	19.0(149)	12.6(97)			0.76
CuZn(fsadb)·3H_2O	20.5(385)				0.89
CuMg(fsadb)·4H_2O	19.1(168)				0.86
CuCa(fsadb)·4H_2O	18.2(210)				1.14
CuBa(fsadb)·3.5H_2O	17.5(197)				1.50

a) Radius for six-coordinate metal ion except for copper(II). b) Measured in *N*,*N*-dimethylformamide.

TABLE 3. CATHODIC AND ANODIC PEAKS (E_{pc} AND E_{pa}), PEAK SEPARATIONS (ΔE_p) AND REDOX POTENTIALS ($E_{1/2}$)

	E_{pc} / V	E_{pa} / V	ΔE_p / mV	$E_{1/2}$ / V
Cu(H_2fsadb)·H_2O	−0.91 (−0.93	−0.80 −0.79	110 140	−0.86 −0.86)$^{a)}$
CuFe(fsadb)Cl·1.5H_2O	−1.34 (−0.30	−1.23 −0.23	110 70	−1.29 −0.27
CuCo(fsadb)·3H_2O	−1.39	−1.14	250	−1.27
CuNi(fsadb)·6H_2O	−1.38	−1.18	200	−1.28
CuCu(fsadb)·1.5H_2O	(−0.84 (−1.29	−0.75 −1.18	90 110	−0.80)$^{a)}$ −1.24)
CuZn(fsadb)·3H_2O	−1.36	−1.20	160	−1.29
CuMg(fsadb)·4H_2O	−1.38	−1.23	150	−1.31
CuCa(fsadb)·4H_2O	−1.63	−1.21	420	−1.42
CuBa(fsadb)·3.5H_2O	−1.52	−1.37	150	−1.45

a) Data obtained by the measurements in *N*,*N*-dimethylformamide.

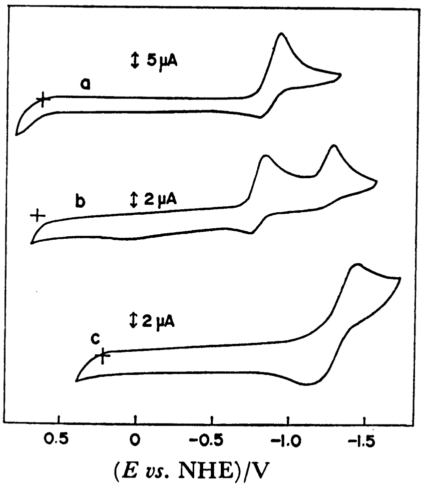

Fig. 5. Cyclic voltammograms of (a) Cu(H_2fsadb)·H_2O (in CH_2Cl_2), (b) CuCu(fsadb)·1.5H_2O (in DMF), and (c) CuMg(fsadb)·3H_2O (in CH_2Cl_2).

extinction coefficients of the ligand field bands are given in Table 2. The d-d band of Cu(H_2fsadb)·H_2O was observed at 17.8×10^3 cm^{-1} in dichloromethane and at 17.0×10^3 cm^{-1} in *N*,*N*-dimethylformamide. On the other hand, CuCu(fsadb)·1.5H_2O shows two bands at 12.6×10^3 and 19.0×10^3 cm^{-1}, which are assigned to the ligand field bands of the copper(II) ions bound at the O_4- and the N_2O_2-sites, respectively.[12] The spectrum of CuCo(fsadb)·3H_2O is composed of the bands at 7.5×10^3, 16.2×10^3, 18.0×10^3, and 20.2×10^3 cm^{-1}. The 20.2×10^3 cm^{-1} band is attributed to the [CuN_2O_2] chromophore. The remaining bands can be ascribed to the [CoO_6] chromophore,[14] which consists of four oxygen atoms of the ligand in the equatorial plane and of two water oxygens at apical positions. This is supported by the single-crystal X-ray analysis of CuCo(fsaen)·3H_2O.[24] Electronic spectrum of CuNi(fsadb)·6H_2O can also be explained by the superposition of the d-d bands of the planar [CuN_2O_2] and the [NiO_6] chromophores. This is also supported by the X-ray analysis for CuNi(fsaen)·3H_2O.[25] In the cases of CuFe(fsadb)Cl·1.5H_2O and CuM(fsadb)·$n$$H_2O$ (M=Zn, Mg, Ca, Ba), no absorption was found in the region less than 18.0×10^3 cm^{-1}. This is natural since high-spin iron(III) has no spin-allowed d-d transition and zinc(II), magnesium(II), calcium(II) and barium(II) ions have no ligand field band. It is likely that the second metal at the O_4-site takes a six-coordinate configuration with two water molecules.[26]

The d-d band due to the copper(II) ion in CuFe(fsadb)Cl·1.5H_2O and CuM(fsadb)·$n$$H_2O$ (M=Co, Ni, Cu, Zn, Mg) fall in the range 19.0×10^3—21.4×10^3 cm^{-1}, which is higher than 17.8×10^3 cm^{-1} of Cu(H_2fsadb)·H_2O. Such a blue shift of the d-d band may be attributed to the increased planarity of the [CuN_2O_2]

chromophore on forming a binuclear complex with a second metal bridged by the phenolic oxygens.[26,27] On the other hand, the frequencies of the d-d bands of CuCa(fsadb)·$4H_2O$ and CuBa(fsadb)·$3.5H_2O$ are close to that of Cu(H_2fsadb)·H_2O. It seems that this spectral feature is closely concerned with the configuration around the second metal ion at the O_4-site. Since iron(III), cobalt(II), nickel(II), copper(II), zinc(II) and magnesium(II) are small in size (ionic radii being less than 0.9 Å; Table 2), these metal ions can fit to the O_4-site to form a *trans*-octahedral configuration with water molecules at the apical positions.[24–26] On the other hand, calcium(II) and barium(II) are considerably large (radius being 1.14 and 1.50 Å respectively) so as to be forced to take a distorted structure such as *cis*-β-octahedral configuration when the metal ions bind at the O_4-site. This steric requirement may bring about the distortion of the CuN_2O_2 plane and hence the d-d bands of these complexes shift to a lower frequency compared with other hetero-metal binuclear complexes.

Electrochemical properties of the hetero-metal complexes were investigated by means of cyclic voltammetry in dichloromethane. In the case of CuCu(fsadb)·$1.5H_2O$ the measurement was carried out in *N*,*N*-dimethylformamide. Typical examples of cyclic voltammograms are shown in Fig. 5. Cathodic and anodic peaks, peak separations, and redox potentials ($E_{1/2}$) are given in Table 3. Cyclic voltammogram of Cu(H_2fsadb)·H_2O showed a Cu(II/I) redox wave at −0.86 V *vs.* NHE. Cyclic voltammogram of CuCu(fsadb)·$1.5H_2O$ (in *N*,*N*-dimethylformamide) was characterized by two redox waves at −0.80 and −1.24 V *vs.* NHE, indicating the difference in coordination environment between the two metal ions. Though the first redox potential is close to that of Cu(H_2fsadb)·H_2O, we attributed the −0.80 V wave to the Cu(II/I) redox process of the copper at the O_4-site and the −1.24 V wave to the copper at the N_2O_2-site, on the grounds described below. Cyclic voltammogram of CuFe(fsadb)Cl·$1.5H_2O$ also reveals two redox waves at −0.27 and −1.29 V *vs.* NHE, which are tentatively assigned to the Fe(III/II) and the Cu(II/I) redox processes respectively. Only one redox wave was observed for other hetero-metal complexes at −1.28—−1.45 V *vs.* NHE. This is unambiguously attributed to the redox of the copper(II) bound at the N_2O_2-site. This adds a strong support for the electrochemical interpretations for CuCu(fsadb)·$1.5H_2O$ and CuFe(fsadb)Cl·$1.5H_2O$ described above.

It is noteworthy that the Cu(II/I) redox potentials for the hetero-metal complexes are very lower than that of Cu(H_2fsadb)·H_2O. Recently, we have found that the reduction potential of the copper(II) ion of *N*,*N*′-disalicylidenealkanediaminatocopper(II) practically remains constant even when it forms a hetero-metal binuclear complex with a metal(II) halide, bridged by the phenolic oxygens.[28] Further, Gagne *et al.*[10] pointed out that the Cu(II)–M(II) complexes of a macrocycle (M=Mn, Fe, Co, Ni, Cu, Zn) show the Cu(II/I) redox at similar potentials, irrespective of second metal ions. Thus, the marked difference in the Cu(II/I) redox potential between the mononuclear and the hetero-metal binuclear complexes can not be attributed to the different coordination modes of the phenolic oxygen (simple coordination in the former and bridging in the latter). Since the peripheral substituents of the ligands are known to change the redox potential of the central metal in a striking manner,[29,30] it is likely that carboxyl and carboxylate groups differ in electronic effect on the redox potential of the copper(II) ion at the N_2O_2-site. In fact, *N*,*N*′-disalicylidene-1,1-dibenzylethylenediaminatocopper(II) Cu(saldb)·$0.5H_2O$, containing no carboxyl group on the ring, shows the Cu(II/I) redox wave at −1.36 V *vs.* NHE, which is more lower than that of Cu(H_2fsadb)·$1.5H_2O$ and comparable to those of the hetero-metal complexes. This implies that the electron-withdrawing effect of the carboxyl group diminishes the electron density on the phenolic oxygen and hence destabilizes the copper(II) oxidation state of Cu(H_2fsadb)·H_2O compared with Cu(saldb)·$0.5H_2O$. On the other hand, the electronic effect of the carboxyl group almost vanishes when it is deprotonated.[30] Thus, the substitution of a metal ion for the carboxyl protons of Cu(H_2fsadb)·H_2O may bring about the negative shift of the Cu(II/I) redox potential.

It is also noticed that the Cu(II/I) redox potential depends somewhat on the second metal ion. In the cases of CuM(fsadb)·nH_2O (M=Co, Ni, Zn, Mg) and CuFe(fsadb)Cl·$1.5H_2O$, the Cu(II/I) redox potentials fall in the range −1.27—−1.31 V *vs.* NHE, while the potentials of CuCa(fsadb)·$4H_2O$ and CuBa(fsadb)·$3.5H_2O$ are −1.42 and −1.45 V *vs.* NHE respectively. We presume that the bonding between the phenolic oxygen and calcium(II) or barium(II) ion is practically ionic. On the other hand, the bonding between the phenolic oxygen and the second metal ion of CuM(fsadb)·nH_2O (M=Co, Ni, Cu, Mg, Zn) and CuFe(fsadb)Cl·$1.5H_2O$ must contain some covalent character. This might result in the decrease in electron density on the phenolic oxygens and hence the positive shift of the Cu(II/I) redox potential compared with those of CuCa(fsadb)·$4H_2O$ and CuBa(fsadb)·$3.5H_2O$.

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