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Dinaionic Ligand Complexes, $K_2[CuL^n]$ and $K_2[NiL^n]$ ($n = 1, 2$; H_4L^1=1,2-Bis(2-hydroxybenzamido)ethane, H_4L^2 = 1,2-Bis(2-hydroxybenzamido)benzene), and Their Dinuclear Cu(II)–Cu(II) and Ni(II)–Cu(II) Complexes

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Copper(II) and nickel(II) complexes with tetraanionic quadridentate ligands, $K_2[CuL^n]$ and $K_2[NiL^n]$ ($n = 1, 2$), have been prepared. We examined whether or not they can function as "ligand complexes", where H_4L^1 = 1,2-bis(2-hydroxybenzamido)ethane and H_4L^2 = 1,2-bis(2-hydroxybenzamido)benzene. One of the ligand complexes, $K_2[NiL^1]\cdot 2dmf\cdot 2H_2O$, crystallizes in the monoclinic space group $P2_1/n$ with the cell dimensions of $a = 15.34(8)$, $b = 18.99(8)$, $c = 18.86(5)$ Å, $\beta = 100.2(3)$, $V = 5406$ Å^3, and $Z = 8$. The *ligand complex* assumes a unique one-dimensional structure consisting of $\{[KO_3][K(NiL^1)O]\}_n$ as the repeating unit, where each K^+ ion is surrounded octahedrally by six oxygen atoms with the distances of 2.672(2)—2.866(9) Å and all the oxygen atoms act as bridging group to K^+ ion. Each of the precursor complexes can function as an electrically dianionic bidentate "ligand complex" and reacts with Cu(II) ion and terminal capping ligand (cap) such as 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), ethylenediamine (en), and 1,3-diaminopropane (tn) to give di-μ-phenoxo-bridged dinuclear Cu(II)–Cu(II) and Ni(II)–Cu(II) complexes with the general formula of $[(Cu\ or\ Ni)L^nCu(cap)]$. The molar electrical conductivities of the dinuclear complexes measured in the DMF or DMSO solutions are essentially zero, indicating that the dinuclear structures are preserved in the solutions. The electrochemical measurements for a series of $[CuL^2Cu(cap)]$ (cap = bpy, phen, tn) demonstrated that the Cu(II/III) redox process of the $\{CuL^2\}$ site exhibits more positive potential (−0.04—−0.09 V) than that of the mononuclear precursor complex (−0.288 V). One of the dinuclear complexes, $[CuL^2Cu(phen)(DMSO)]$, crystallizes in the orthorhombic space group $Pna2_1$ with the cell dimensions of $a = 19.702(3)$, $b = 15.847(3)$, $c = 9.652(2)$ Å, $V = 3013$ Å^3, and $Z = 4$. The complex consists of a discrete di-μ-phenoxo-bridged dinuclear structure, in which two copper(II) ions assume a square planar and square pyramidal coordination geometry and the bridging core of Cu_2O_2 is unequivalent, as found in the distances of Cu(1)–O(1) = 1.924(4) Å, Cu(1)–O(2) = 1.908(4) Å, Cu(2)–O(2) = 1.964(4) Å and Cu(2)–O(1) = 2.249(4) Å. The magnetic susceptibility is well reproduced with the antiferromagnetic coupling parameter of $J = -82$ cm^{-1} by the Bleaney–Boweres equation.

Multinuclear metal complexes are of great interest not only in elucidating the magnetic coupling between metal ions[1)] but also in model compounds of the active sites of multi-metalloenzymes.[2)] For the synthesis of hetero-metal polynuclear complexes, two synthetic methods have been employed. One is the method which uses a polynucleating ligand exhibiting multi-unequivalent coordination sites.[3)] The another is the method which uses a "ligand complex" which involves coordination ability to other metal ions.[4)] The latter method has advantages for the syntheses of hetero-metal complexes with the systematic combination of metal ions and homo-metal complexes with unequivalent coordination geometries. From this viewpoint, an effective "ligand complex" should be developed, because only a limited number of "ligand complexes" have been known so far. E. Sinn et al. and others have reported that *N*,*N*′-ethylenebis(salicylideneaminato)copper(II) (hereafter abbreviated as [Cu(salen)]) and the derivatives can act as electrically neutral bidentate "ligand complexes".[5—8)] [Cu(salen)] reacts with a metal ion and an electrically negative ligand such as Cl^-, methoxide, or acetate to give di-, tri-, and tetra-nuclear complexes. Although the reaction of [Cu(salen)], the other metal ion, and ligand gives a variety of polynuclear complexes, the resulting polynuclear complexes can only be obtained together with an electrically negative ligand and they tend to dissociate easily in the solution state.

Ojima et al. reported the synthesis of mononuclear Cu(II) and Ni(II) complexes with 1,2-bis(2-hydroxybenzamido)ethane, $K_2[CuL^1]$ and $K_2[NiL^1]$.[9)] These complexes can be useful as "ligand complexes", because the phenoxo oxygen has a bridging ability. Further, the reaction of the anionic complex, cationic metal ion, and capping ligand would give much more stable polynuclear complexes than [Cu(salen)].

From the viewpoint, we synthesized and characterized dinuclear Cu(II)–Cu(II) and Ni(II)–Cu(II) complexes by the use of the dianionic ligand complexes[9)] and the analogoues $K_2[CuL^n]$ and $K_2[NiL^n]$. Further, since a series of the ligand complexes involves two amido nitrogen atoms which can stabilize high oxidation state owing to the strong σ donating ability,[10)] we have also studied how the electrochemical behavior is affected by the formation of dinuclear structure.

Experimental

General Procedures and Materials. All chemicals and solvents used for the synthesis were reagent grade. The solvents used for physical measurements were purified by the literature methods$^{11)}$ and stored under nitrogen atmosphere. The quadridentate ligands, H_4L^1 and H_4L^2, were prepared according to the literature.$^{9,10)}$ Precursor Cu(II) and Ni(II) complexes with H_4L^1 were prepared according to the procedure of Ojima.$^{9)}$ They were recrystallized from the mixed solution of DMF and methanol to give fine needle crystals containing DMF and water molecules as the crystal solvents.

K_2[NiL^1]·2DMF·2H_2O. Orange needles. Anal. Calcd for $C_{34}H_{30}N_4O_6Ni$: C, 42.94; H, 4.91; N, 9.10%. Found: C, 42.98; H, 4.94; N, 9.10%. IR 1666,1655 (ν_{CO}(DMF)), 1596 cm^{-1} (ν_{CO}(amido)). UV (log ε) 468 (2.50), 554 (1.96)sh nm. μ_{eff} (R.T.)/μ_B diamag.

K_2[CuL^1]·2DMF·2H_2O. Violet needles. Anal. Calcd for $C_{34}H_{30}N_4O_6Cu$: C, 42.60; H, 4.88; N, 9.03%. Found: C, 42.62; H, 4.91; N, 9.03%. IR 1668,1653 (ν_{CO}(DMF)), 1594 cm^{-1} (ν_{CO}(amido)). UV (log ε) 540 (2.40) nm. μ_{eff} (R.T.)/μ_B 1.74.

K_2[NiL^2]·3H_2O. Nickel(II) hydroxide Ni(OH)$_2$, H_4L^2, and KOH were mixed in water with the molar ratio of 1 : 1 : 4. The mixture was refluxed for 1h and then filtered. The filtrate was evaporated to dryness and the residue was dissolved in ethanol. The ethanolic solution was filtered and the filtrate was evaporated to dryness. This procedure was repeated twice and the crystallization was carried out from water. Red needles were obtained. Anal. Calcd for $C_{20}H_{18}N_2O_7Ni$: C, 44.88; H, 3.39; N, 5.23%. Found: C, 44.99; H, 3.15; N, 5.30%. IR 1597 (ν_{CO}(amido)) cm^{-1}. UV (log ε) 523 (2.70) nm. μ_{eff}(R.T.)/μ_B diamag.

K_2[CuL^2]·1.5H_2O. The complex was prepared by the method adapted for the Ni(II) complex. Dark violet needles. Anal. Calcd for $C_{20}H_{15}N_2O_{5.5}Cu$: C, 46.81; H, 2.95; N, 5.46%. Found: C, 46.67; H, 2.76; N, 5.44%. IR 1597 cm^{-1} (ν_{CO}(amido)). UV (log ε) 553 (2.23) nm. μ_{eff} (R.T.)/μ_B 1.78.

[NiL^{1}Cu(bpy)]·0.5H_2O·MeOH. To a solution of [Cu(bpy)(NO$_3$)$_2$]·3H_2O (397 mg, 1.0 mmol) in 25 cm^3 of methanol was added a solution of K_2[NiL^1]·2DMF·2H_2O (460 mg, 1.0 mmol) in 10 cm^3 of methanol. The resulting solution was stirred for 1 h at room temperature. The product which precipitated was collected by suction filtration, washed well with water, and dried. Black microcrystals. Anal. Calcd for $C_{27}H_{19}N_4O_{5.5}CuNi$: C, 52.67; H, 4.90; N, 9.10%. Found: C, 52.74; H, 4.23; N, 8.83%. Λ_M/S cm^2 mol^{-1} in DMSO, 3.0. IR 1597 cm^{-1} (ν_{CO}(amido)). μ_{eff} (R.T.)/NiCu/μ_B 2.00.

[NiL^{1}Cu(phen)]·0.5MeOH. The compound was prepared by the method adapted for [NiL^{1}Cu(bpy)]·0.5H_2O·MeOH. Black green microcrystals. Anal. Calcd for $C_{28.5}H_{18}N_4O_{4.5}CuNi$: C, 53.34; H, 3.92; N, 8.73%. Found: C, 53.63; H, 3.85; N, 8.58%. Λ_M/S cm^2 mol^{-1} in DMSO, 2.2. IR 1597 cm^{-1} (ν_{CO}(amido)). μ_{eff} (R.T.)/NiCu/μ_B 2.06.

[NiL^{2}Cu(bpy)]. The compound was prepared by the method adapted for [NiL^{1}Cu(bpy)]·0.5H_2O·MeOH. Black green microcrystals. Anal. Calcd for $C_{30}H_{20}N_4O_4CuNi$: C, 57.35; H, 3.47; N, 8.77%. Found: C, 57.30; H, 3.41; N, 8.45%. Λ_M/S cm^2 mol^{-1} in DMSO, 1.7. IR 1602 cm^{-1} (ν_{CO}(amido)). μ_{eff} (R.T.)/NiCu/μ_B 1.90.

[NiL^{2}Cu(phen)(DMSO)]. The compound was prepared by the method adapted for [NiL^{1}Cu(bpy)]·0.5H_2O·MeOH and recrystallized from dmso. Black prisms. Crystal data: orthorhombic, space group $Pna2_1$, $a=19.701(8)$, $b=15.809(8)$, $c=9.651(4)$ Å, $V=3006$ Å^3, $Z=4$. The X-ray diffraction study verified that [NiL^{2}Cu(phen)(DMSO)] is isostructural to [CuL^{2}Cu(phen)(DMSO)].

[CuL^{1}Cu(bpy)]·MeOH. All the dinuclear Cu(II)–Cu(II) compounds were prepared by mixing copper(II) acetate monohydrate, precursor mononuclear complex, and the capping ligand with the molar ratio of 1 : 1 : 1 in methanol. To the methanolic solution of copper(II) acetate monohydrate (200 mg, 1 mmol). in 25 cm^3 of methanol was added a solution of K_2[CuL^1]·2DMF·2H_2O (465 mg, 1 mmol). The mixture was stirred for 1 h and then a solution of 2, 2′-bipyridine (160 mg, 1 mmol) in 10 cm^3 of methanol was added to the mixture. The resulting solution was stirred for 1 h, the precipitates thus obtained were filtrated by suction filtration, washed with methanol, and dried. Dark brown microcrystals. Anal. Calcd for $C_{27}H_{24}N_4O_4Cu_2$: C, 53.02; H, 3.96; N, 9.16%. Found: C, 52.93; H, 3.94; N, 8.86%. Λ_M/S cm^2 mol^{-1} in DMF, 1.5. IR 1592 cm^{-1} (ν_{CO}(amido)). UV (log ε) 480 (2.97) nm. μ_{eff} (R.T.)/μ_B 1.71, $J=-22$ cm^{-1}, $g=2.02$.

[CuL^{1}Cu(bpy)(DMSO)]. [CuL^{1}Cu(bipy)]·MeOH is recrystallized from dmso to give black prisms. Anal. Calcd for $C_{28}H_{26}N_4O_5SCu_2$: C, 51.13; H, 3.98; N, 8.52%. Found: C, 51.13; H, 3.95; N, 8.72%. IR 946 (ν_{SO}(DMSO)), 1593 cm^{-1} (ν_{CO}(amido)). μ_{eff} (R.T.)/Cu/μ_B 1.56.

[CuL^{1}Cu(phen)]·2MeOH. The compound was prepared by the method adapted for [CuL^{1}Cu(bpy)]·MeOH. Dark brown microcrystals. Anal. Calcd for $C_{30}H_{28}N_4O_6Cu_2$: C, 53.97; H, 4.23; N, 8.39%. Found: C, 54.03; H, 3.93; N, 8.49%. IR 1592 cm^{-1} (ν_{CO}(amido)). μ_{eff} (R.T.)/Cu/μ_B 1.57.

[CuL^{1}Cu(en)]·H_2O. The compound was prepared by the method adapted for [CuL^{1}Cu(bpy)]·MeOH. Black green microcrystals. Anal. Calcd for $C_{18}H_{26}N_4O_5Cu_2$: C, 43.11; H, 4.42; N, 11.17%. Found: C, 43.10; H, 4.50; N, 10.95%. IR 1594 cm^{-1} (ν_{CO}(amido)). μ_{eff} (R.T.)/Cu/μ_B 1.74, $J=-17$ cm^{-1}, $g=2.01$.

[CuL^{1}Cu(tn)]·0.75H_2O. The compound was prepared by the method adapted for [CuL^{1}Cu(bpy)]·MeOH. Gray green microcrystals. Anal. Calcd for $C_{19}H_{26}N_4O_4Cu_2$·0.75H_2O: C, 44.66; H, 4.64; N, 10.96%. Found: C, 44.71; H, 4.62; N, 10.95%. IR 1593 cm^{-1} (ν_{CO}(amido)). μ_{eff} (R.T.)/Cu/μ_B 1.57.

[CuL^{2}Cu(bipy)]. The compound was prepared by the method adapted for [CuL^{1}Cu(bpy)]·MeOH. Black microcrystals. Anal. Calcd for $C_{30}H_{20}N_4O_4Cu_2$: C, 57.41; H, 3.21; N, 8.93%. Found: C, 57.22; H, 3.30; N, 8.83%. IR 1582 cm^{-1} (ν_{CO}(amido)). Λ_M/S cm^2 mol^{-1} in DMF, 3.2. μ_{eff} (R.T.)/Cu/μ_B 1.60.

[CuL^{2}Cu(phen)]·H_2O. The compound was prepared by the method adapted for [CuL^{1}Cu(bpy)]·MeOH. Black microcrystals. Anal. Calcd for $C_{32}H_{22}N_4O_5Cu_2$: C, 57.40; H, 3.31; N, 8.37%. Found: C, 57.43; H, 3.33; N, 8.24%. Λ_M/S cm^2 mol^{-1} in DMF, 3.5. IR 1582 cm^{-1} (ν_{CO}(amido)). UV (log ε) 411 (3.05), 492 (2.80) nm. μ_{eff} (R.T.)/Cu/μ_B 1.60.

[CuL^{2}Cu(phen)(DMSO)]. Crystals used for the X-ray diffraction study were obtained by a diffusion method, where the DMSO solution of [CuL^{2}Cu(phen)]·H_2O was diffused into methanol. Black prisms. Anal. Calcd for $C_{34}H_{26}N_4O_5SCu_2$: C, 55.56; H, 3.78; N, 7.51%. Found: C, 55.84; H, 3.67; N, 7.51%. IR 1594 (ν_{CO}(amido)), 963, 940 cm^{-1} (ν_{SO}(DMSO)). μ_{eff} (R.T.)/Cu/μ_B 1.57, $J=-82$ cm^{-1}, $g=2.02$.

[CuL^{2}Cu(en)]. The compound was prepared by the method adapted for [CuL^{1}Cu(bpy)]·MeOH. Black microcrystals. Anal. Calcd for $C_{22}H_{20}N_4O_4Cu_2$: C, 49.71; H, 3.79; N, 10.54%. Found: C, 49.49; H, 3.92; N, 10.29%. IR 1594 cm^{-1} (ν_{CO}(amido)). μ_{eff} (R.T.)/Cu/μ_B 1.62.

[CuL^{2}Cu(tn)]. The compound was prepared by the method adapted for [CuL^{1}Cu(bpy)]·MeOH. Anal. Calcd for

$C_{23}H_{22}N_4O_4Cu_2$: C, 44.66; H, 4.64; N, 10.96%. Found: C, 44.71; H, 4.62; N, 10.95%. Λ_M/S cm^2 mol^{-1} in DMF, 3.2. IR 1594 cm^{-1} (ν_{CO}(amido)). UV (log ε) 573 (2.44) nm. μ_{eff} (R.T.)/Cu/μ_B 1.34.

[CuL^{2}Cu(tn)]·MeOH. [CuL^{2}Cu(tn)] was dissolved in DMSO, then methanol was diffused into this solution. Deep green crystals were obtained. Anal. Calcd for $C_{24}H_{26}N_4O_5Cu_2$: C, 49.91; H, 4.53; N, 9.70%. Found: C, 50.23; H, 4.29; N, 9.89%. IR 1596 cm^{-1} (ν_{CO}(amido)). UV (log ε) 601 (2.35) nm. μ_{eff} (R.T.)/Cu/μ_B, 1.40, $J=-136$ cm^{-1}, $g=2.00$.

Physical Measurements. Elemental analyses for C, H, and N were performed at the Elemental Analysis Service Center of Kyushu University. Electrical conductivity measurements were carried out on a Horiba DS-14 conductivity meter in 10^{-3} mol dm^{-3} solution at room temperature. Infrared spectra were measured on KBr disks with JASCO A-102 spectrophotometers. Electronic spectra were measured on a Hitachi U-4000 spectrophotometer by the use of the 10^{-3} mol dm^{-3} solutions. Electrochemical measurements were carried out on a Yanagimoto P-1100 polarographic analyzer equipped with three electrodes of a glassy carbon working electrode, a platinum wire auxiliary electrode, and a saturated calomel electrode (SCE) as the reference, in which tetra-*n*-butylammonium perchlorate was employed as the supporting electrolyte. All the observed potentials were corrected by the Fc$^+$/Fc couple of ferrocene which was employed as an internal standard. The Fc$^+$/Fc couples in DMF were observed at ca. 0.44 V vs. SCE. Magnetic susceptibilities were measured with a Faraday balance in the temperature range 80—300 K, where the calibration was made with $[Ni(en)_3]S_2O_3$ (en = ethylenediamine).[12)] Corrections were applied for diamagnetism calculated from Pascal's constants.[13)] Effective magnetic moments were calculated by the equation $\mu_{eff}=2.828(\chi_A T)^{1/2}$, where χ_A is the magnetic susceptibility per formula unit.

X-Ray Data Collection, Reduction, and Structure Determination. All measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Mo $K\alpha$ radiation ($\lambda=0.71069$ Å) for $K_2[NiL^1]\cdot 2DMF\cdot 2H_2O$ and Cu $K\alpha$ radiation ($\lambda=1.54178$ Å) for [CuL^{2}Cu(phen)(DMSO)] and a 12 kW rotating anode generator. The peak profiles of the reflection data of $K_2[NiL^1]\cdot 2DMF\cdot 2H_2O$ showed a broad peak with ca. 0.95 degree in omega due to the fine needle habit of the crystal so that the standard deviations of the cell dimensions are substantially large. The data were collected at a temperature of 20±1°C using ω–2θ scan technique at a scan speed of 16.0 ° min^{-1} (in omega). The weak reflections ($I<10.0\sigma(I)$) were rescanned (maximum of 3 scans) and the counts were accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2 : 1. The intensities of three representative reflections were measured after every 150 reflections, showing a good stability of the intensities. An empirical absorption correction based on azimuthal scans of several reflections was applied. The data were corrected for Lorentz and polarization effects.

The structures were solved by direct methods[14)] and expanded using Fourier techniques.[15)] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculation. Full-matrix least-squares refinement based on the observed reflections ($I>3.00\sigma(I)$) were employed, where the unweighted and weighted agreement factors of $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$ and $R_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ are used. The weighting scheme was based on counting statistics. Neutral atomic scattering factors were taken from Cromer and Waber.[16)] Anomalous dispersion effects were included in F_{calcd}; the values $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[16)] All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation.[17)]

Crystal data and details of the structure determination for $K_2[NiL^1]\cdot 2DMF\cdot 2H_2O$ and [CuL^{2}Cu(phen)(DMSO)] are summarized in Table 1. Atomic coordinates for non-hydrogen atoms for $K_2[NiL^1]\cdot 2DMF\cdot 2H_2O$ and [CuL^{2}Cu(phen)(DMSO)] are given in Tables 2 and 3, respectively. The atomic coordinates, thermal parameters, bond distances and angles, and F_o-F_c tables were deposited as Document No. 70023 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

Synthesis and Characterization. Copper(II) and nickel(II) complexes with the quadridentate ligands, $K_2[CuL^n]$ and $K_2[NiL^n]$ ($n=1$, 2), act as a bidentate "ligand complexes". Each of the complexes reacts with Cu(II) ion and a terminal capping ligand such as bpy, phen, en, and tn with the 1 : 1 : 1 molar ratio in water/methanol solution to give electrically neutral dinuclear Cu(II)–Cu(II) and Ni(II)–Cu(II) complexes. The molar electrical conductance values measured in DMF or DMSO for the dinuclear complexes are nearly equal to zero, indicating that the dinuclear structures are preserved even in the 10^{-3} mol cm^{-3} DMF or DMSO solutions.[18)] This solution behavior is in contrast with that of the polynuclear complexes derived from Cu(salen) derivatives which dissociate easily in the solutions.[19)] The dinuclear complexes tend to crystallize as the solvate. When the compounds involving phen and bpy as the capping ligand obtained in water/methanol were recrystallized from the solution of DMF or DMSO, the crystals involving DMF or DMSO molecule were obtained. On the other hand, the compounds with tn and en gave the crystals involving methanol as the crystal solvent when the recrystallization was carried out in the mixed solution of DMSO and MeOH. The

Table 1. Crystallographic Data for $K_2[NiL^1]\cdot 2DMF\cdot 2H_2O$ and [CuL^{2}Cu(phen)(DMSO)]

Formula	$C_{22}H_{30}N_4O_8K_2Ni$	$C_{34}H_{26}N_4O_5SCu_2$
Formula weight	615.40	729.76
Crystal color	Orange	Dark brown
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$Pna2_1$
a/Å	15.34(8)	19.702(3)
b/Å	18.99(8)	15.847(3)
c/Å	18.86(5)	9.652(2)
α/deg	90	90
β/deg	100.2(3)	90
γ/deg	90	90
V/Å^3	5406(33)	3013(1)
Z	8	4
D_{calcd}/g cm^{-3}	1.512	1.608
Radiation	Mo$K\alpha$	Cu$K\alpha$
μ/cm^{-1}	10.78	15.32
No. of reflections	5563	3912
R	5.3	4.0
R_w	5.7	3.4

$R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$, $R_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, $w=1/[\sigma(F_o)^2]$.

Table 2. Atomic Coordinates and Equivalent Isotropic Thermal Parameters of Non-Hydrogen for $K_2[NiL^1]\cdot 2DMF\cdot 2H_2O$

Atom	x	y	z	$B_{eq}/Å^2$	Atom	x	y	z	$B_{eq}/Å^2$
Ni1	0.14765(6)	0.14872(5)	0.13374(5)	2.82(2)	C8	0.1107(6)	0.0858(5)	−0.0025(5)	5.1(2)
Ni2	0.65102(6)	0.15018(5)	0.12623(5)	2.68(2)	C9	0.1522(6)	0.0314(4)	0.0483(5)	5.2(3)
K1	0.0521(1)	0.26238(9)	0.25231(10)	3.68(4)	C10	0.1567(5)	0.0013(4)	0.1720(5)	3.7(2)
K2	0.3029(1)	0.23961(10)	0.26127(9)	3.67(4)	C11	0.1558(5)	0.0193(4)	0.2468(5)	3.5(2)
K3	0.5482(1)	0.25345(10)	0.2501(1)	4.19(5)	C12	0.1533(6)	−0.0348(5)	0.2965(6)	5.3(3)
K4	0.8004(1)	0.26158(9)	0.23437(9)	3.72(4)	C13	0.1520(6)	−0.0230(6)	0.3662(6)	6.1(3)
O1	0.1567(3)	0.2446(2)	0.1484(2)	3.2(1)	C14	0.1555(6)	0.0450(5)	0.3932(5)	5.5(3)
O2	0.1637(3)	0.1460(3)	0.2330(3)	3.3(1)	C15	0.1588(5)	0.1003(4)	0.3464(4)	4.2(2)
O3	0.0936(3)	0.2056(3)	−0.0769(3)	4.6(1)	C16	0.1591(5)	0.0887(4)	0.2739(4)	3.3(2)
O4	0.1655(4)	−0.0633(3)	0.1544(3)	5.2(2)	C17	0.5955(4)	0.2886(4)	0.0822(4)	2.8(2)
O5	0.6386(3)	0.2465(2)	0.1340(3)	3.4(1)	C18	0.5729(5)	0.3564(4)	0.1033(4)	3.8(2)
O6	0.6788(3)	0.1544(3)	0.2249(2)	3.2(1)	C19	0.5249(6)	0.4019(4)	0.0541(5)	4.5(2)
O7	0.5847(3)	0.1922(3)	−0.0871(3)	3.9(1)	C20	0.4980(6)	0.3823(5)	−0.0155(5)	4.7(2)
O8	0.6900(3)	−0.0595(3)	0.1606(3)	4.2(1)	C21	0.5219(5)	0.3173(5)	−0.0380(4)	3.9(2)
O9	−0.0875(4)	0.2964(4)	0.1406(3)	6.2(2)	C22	0.5704(4)	0.2688(4)	0.0100(4)	2.9(2)
O10	0.4420(5)	0.1449(3)	0.2879(4)	6.6(2)	C23	0.5940(5)	0.2002(4)	−0.0191(4)	3.1(2)
O11	0.3945(4)	0.2656(4)	0.1561(3)	6.0(2)	C24	0.6462(6)	0.0824(5)	−0.0031(4)	4.7(2)
O12	0.9310(4)	0.1626(3)	0.2623(3)	5.2(2)	C25	0.6373(6)	0.0255(4)	0.0494(5)	4.6(2)
O13	−0.0701(3)	0.3382(3)	0.3225(3)	4.1(1)	C26	0.6890(4)	0.0068(4)	0.1732(4)	3.0(2)
O14	0.2048(3)	0.3344(3)	0.3266(3)	4.4(1)	C27	0.7160(4)	0.0316(4)	0.2473(4)	3.0(2)
O15	0.4388(3)	0.3212(3)	0.3350(3)	4.3(1)	C28	0.7482(6)	−0.0172(5)	0.3016(5)	4.9(2)
O16	0.6936(3)	0.3291(3)	0.3208(2)	3.5(1)	C29	0.7727(6)	0.0001(6)	0.3717(5)	5.8(3)
N1	0.1253(4)	0.1555(3)	0.0339(3)	3.6(2)	C30	0.7663(6)	0.0691(6)	0.3926(5)	5.3(3)
N2	0.1483(4)	0.0519(3)	0.1223(4)	3.9(2)	C31	0.7351(5)	0.1186(4)	0.3415(4)	4.1(2)
N3	0.6234(4)	0.1492(3)	0.0273(3)	3.2(1)	C32	0.7097(5)	0.1017(4)	0.2697(4)	3.1(2)
N4	0.6649(4)	0.0531(3)	0.1214(3)	3.2(1)	C33	−0.0871(8)	0.315(1)	0.0837(7)	13.0(5)
N5	−0.1299(5)	0.3097(6)	0.0228(5)	7.2(3)	C34	−0.178(2)	0.256(2)	0.011(1)	34(1)
N6	0.4556(6)	0.0289(4)	0.2711(5)	5.8(2)	C35	−0.1230(10)	0.338(1)	−0.0444(7)	21.3(8)
N7	0.3648(4)	0.2123(4)	0.0484(4)	4.8(2)	C36	0.4839(7)	0.0899(7)	0.2962(6)	7.1(3)
N8	0.9261(4)	0.0582(4)	0.2010(4)	4.5(2)	C37	0.377(1)	0.0173(9)	0.228(1)	19.7(8)
C1	0.1424(5)	0.2946(4)	0.0972(4)	3.0(2)	C38	0.5136(9)	−0.0305(7)	0.2892(10)	15.5(6)
C2	0.1513(5)	0.3653(4)	0.1221(4)	4.0(2)	C39	0.3680(5)	0.2654(5)	0.0920(5)	4.5(2)
C3	0.1337(6)	0.4197(4)	0.0740(5)	5.5(3)	C40	0.3972(8)	0.1456(6)	0.0766(7)	9.1(4)
C4	0.1103(8)	0.4079(5)	0.0024(5)	6.5(3)	C41	0.3325(7)	0.2161(8)	−0.0266(5)	10.4(4)
C5	0.1036(7)	0.3400(5)	−0.0217(5)	5.9(3)	C42	0.9352(5)	0.0971(5)	0.2592(5)	4.4(2)
C6	0.1203(5)	0.2815(4)	0.0239(4)	3.4(2)	C43	0.9059(6)	0.0894(5)	0.1314(5)	6.5(3)
C7	0.1122(5)	0.2100(4)	−0.0088(4)	3.4(2)	C44	0.9309(6)	−0.0189(4)	0.2052(6)	6.7(3)

effective magnetic moments at room temperature for the precursor nickel(II) complexes and the dinuclear Ni(II)–Cu(II) complexes indicated that the nickel(II) ions for the complexes are all diamagnetic, suggesting that the coordination geometry around Ni(II) ion is square planar. The magnetic moments of the dinuclear Cu(II)–Cu(II) complexes obtained in water/methanol are different from those of the recrystallized compounds containing DMF or DMSO molecule as being exemplified in 1.71 μ_B of [CuL^{1}Cu(bpy)(MeOH)] and 1.56 μ_B of [CuL^{1}Cu(bpy)(DMSO)], suggesting that the coordination of the solvent molecules such as DMF, DMSO, and MeOH to Cu(II) ion in the outer site affects significantly the magnetic interaction between Cu(II) ions due to the distortion of the Cu_2O_2 core, etc., as decribed in [CuL^{2}Cu(phen)(DMSO)].

Structural Description of Ligand Complex, $K_2[NiL^1]\cdot 2DMF\cdot 2H_2O$. An ORTEP view of the unique molecule of $K_2[NiL^1]\cdot 2DMF\cdot 2H_2O$ with the atom numbering scheme is shown in Fig. 1, where there are two molecular units in the asymmetric unit. The one-dimensional structure running along the *a*-axis is given in Fig. 2. Selected bond distances and interatomic distances between K$^+$ and oxygens are reported in Table 4. The two molecular units are essentially the same both in the geometry and the dimensions. Each

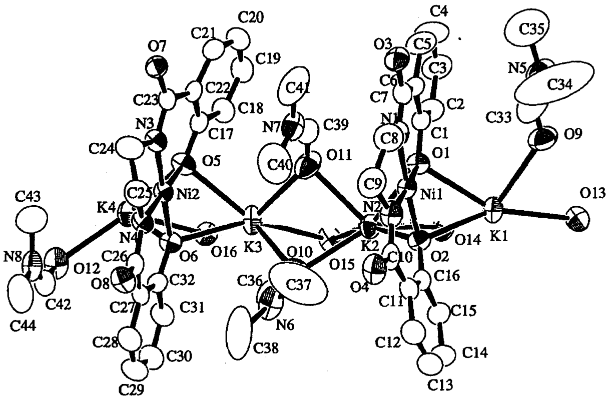

Fig. 1. An ORTEP drawing of $K_2[NiL^1]\cdot 2DMF\cdot 2H_2O$ with the atom numbering scheme, showing the asymmetric unit and 50% probability ellipsoids.

Table 3. Atomic Coordinates and Equivalent Isotropic Thermal Parameters of Non-Hydrogen for [CuL^{2}Cu(phen)(DMSO)]

Atom	x	y	z	$B_{eq}/Å^2$
Cu(1)	0.31902(4)	0.12577(5)	0.1934	2.15(1)
Cu(2)	0.21317(4)	0.22045(4)	0.0105	2.26(1)
S(1)	0.20744(10)	0.3223(1)	0.2862(2)	3.15(4)
O(1)	0.2279(2)	0.1015(2)	0.1339(5)	2.51(10)
O(2)	0.3050(2)	0.2265(3)	0.0889(5)	2.55(10)
O(3)	0.3257(3)	−0.1255(3)	0.2656(6)	5.3(1)
O(4)	0.4843(3)	0.2583(3)	0.3294(7)	6.8(2)
O(5)	0.1755(2)	0.2968(2)	0.1488(5)	3.5(1)
N(1)	0.3359(3)	0.0171(3)	0.2719(5)	1.7(1)
N(2)	0.4017(2)	0.1621(3)	0.2805(5)	2.2(1)
N(3)	0.1242(2)	0.2183(3)	−0.0896(6)	1.7(1)
N(4)	0.2453(3)	0.1743(3)	−0.1701(6)	2.0(1)
C(1)	0.2052(3)	0.0241(4)	0.1131(6)	1.5(1)
C(2)	0.1429(3)	0.0152(4)	0.0447(8)	3.3(2)
C(3)	0.1165(3)	−0.0630(4)	0.0114(10)	3.8(2)
C(4)	0.1525(4)	−0.1357(4)	0.0437(8)	3.6(2)
C(5)	0.2119(3)	−0.1272(4)	0.1137(7)	3.0(2)
C(6)	0.2411(3)	−0.0490(4)	0.1504(6)	2.0(1)
C(7)	0.3054(3)	−0.0537(4)	0.2337(6)	2.8(2)
C(8)	0.3912(3)	0.0205(4)	0.3657(7)	1.8(1)
C(9)	0.4101(3)	−0.0431(4)	0.4552(7)	3.3(2)
C(10)	0.4622(4)	−0.0313(5)	0.5508(8)	4.3(2)
C(11)	0.4953(4)	0.0436(5)	0.5594(8)	3.9(2)
C(12)	0.4771(3)	0.1084(5)	0.4698(7)	3.3(2)
C(13)	0.4257(3)	0.0983(4)	0.3718(7)	2.6(1)
C(14)	0.4340(3)	0.2369(4)	0.2645(7)	3.0(2)
C(15)	0.4048(3)	0.2985(4)	0.1576(7)	2.5(1)
C(16)	0.4478(3)	0.3711(4)	0.1371(8)	3.4(2)
C(17)	0.4345(4)	0.4299(4)	0.0388(9)	4.0(2)
C(18)	0.3793(4)	0.4198(4)	−0.0469(7)	3.9(2)
C(19)	0.3376(3)	0.3502(4)	−0.0301(6)	3.2(2)
C(20)	0.3502(3)	0.2903(4)	0.0737(6)	2.3(1)
C(21)	0.0644(4)	0.2426(4)	−0.0469(7)	3.4(2)
C(22)	0.0070(4)	0.2443(5)	−0.1356(10)	4.5(2)
C(23)	0.0134(4)	0.2174(5)	−0.2667(9)	4.4(2)
C(24)	0.0760(4)	0.1919(4)	−0.3149(9)	3.6(2)
C(25)	0.0892(4)	0.1638(5)	−0.4534(8)	4.4(2)
C(26)	0.1501(5)	0.1410(4)	−0.4944(9)	4.8(2)
C(27)	0.2059(4)	0.1432(4)	−0.4003(8)	3.4(2)
C(28)	0.2719(5)	0.1223(5)	−0.4372(8)	4.7(2)
C(29)	0.3326(4)	0.1255(5)	−0.3391(9)	4.7(2)
C(30)	0.3072(4)	0.1530(4)	−0.2071(8)	3.2(2)
C(31)	0.1960(4)	0.1691(4)	−0.2659(7)	1.8(1)
C(32)	0.1303(3)	0.1936(4)	−0.2203(7)	2.6(1)
C(33)	0.1380(4)	0.3549(5)	0.3817(8)	4.4(2)
C(34)	0.2430(4)	0.4219(5)	0.2568(8)	4.4(2)

$B_{eq} = (8\pi^2/3)(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha)$.

Table 4. Relevant Bond Distances (Å) and Interatomic Distances between K$^+$ and Oxygen Atoms with the Estimated Standard Deviations in Parentheses for $K_2[NiL^1]\cdot 2DMF\cdot 2H_2O$

(a) Bond distances			
Ni(1)–O(1)	1.842(7)	Ni(1)–O(2)	1.845(5)
Ni(1)–N(1)	1.858(6)	Ni(1)–N(2)	1.851(8)
Ni(2)–O(5)	1.847(7)	Ni(2)–O(6)	1.836(4)
Ni(2)–N(3)	1.840(6)	Ni(2)–N(4)	1.860(7)
(b) Interatomic distances between K$^+$ and oxygens			
K(1)–O(1)	2.763(8)	K(1)–O(2)	2.857(9)
K(1)–O(9)	2.803(10)	K(1)–O(12)	2.683(9)
K(1)–O(13)	2.866(9)	K(1)–O(14)	2.86(1)
K(2)–O(1)	2.808(9)	K(2)–O(2)	2.757(10)
K(2)–O(10)	2.77(1)	K(2)–O(11)	2.672(7)
K(2)–O(14)	2.771(8)	K(2)–O(15)	2.767(10)
K(3)–O(5)	2.794(7)	K(3)–O(6)	2.848(9)
K(3)–O(10)	2.796(10)	K(3)–O(11)	2.70(1)
K(3)–O(15)	2.826(9)	K(3)–O(16)	2.786(10)
K(4)–O(5)	2.86(1)	K(4)–O(6)	2.745(9)
K(4)–O(9)	2.756(9)	K(4)–O(12)	2.729(10)
K(4)–O(13)	2.768(9)	K(4)–O(16)	2.816(8)

nickel(II) ion assumes a square planar coordination geometry with two amido nitrogen atoms and two phenoxo oxygen atoms of quadridentate ligand. The average bond distances of ⟨Ni–O⟩ and ⟨Ni–N⟩ are 1.843(6) and 1.852(7) Å, respectively, which are both shorter than the corresponding distances of [Ni(salen)]. The most striking feature of the crystal structure is a one-dimensional rod-like structure, as shown in Fig. 2. The asymmetric unit contains four K$^+$ ions exhibiting essentially the same structural geometry. In the one-dimensional structure, each potassium ion is surrounded octahedrally by six oxygen atoms consisting of two phenoxo oxygens, two oxygens of two DMF molecules, and two oxygens of two water molecules to give a sandwich-like structure around K$^+$, similar to that seen in the potassium bis-crown ether complexes.[20] The K–O distances are in the range of 2.672(7)—2.866(9) Å and the values are compatible with those for the potassium bis-crown ether compounds.[20] All the six-oxygen atoms function as bridging ligands to K$^+$ to give a one-dimensional chain structure consisting of $\{[KO_3][K(NiL^1)O]\}_n$ as the repeating unit, where $[KO_3]$ and $[K(NiL^1)O]$ denote the adjacent units composing of (two DMF and one water) and (two phenoxo and one water), respectively. The adjacent one-dimensional chains are weakly bonded through a network of hydrogen bonding operating between water molecules of one-chain and amido oxygens of another chain, where each water molecule interacts with two amido oxygens, each amido oxygen interacts with two water oxygens, and the O–O distances are in the range of 2.70(1)—2.76(1) Å.

Electrochemical Property. Electrochemical measurements for a series of [CuL^{2}Cu(cap)] were carried out in the dmf solutions; the potentials are summarized in Table 5. The quasi-reversible process observed in −0.04—−0.09 V is assigned to Cu(II) to Cu(III) process of the {CuL^2} site. The corresponding process of the precursor mononuclear Cu(II) complex, $[Me_4N]_2[CuL^2]\cdot H_2O$, is observed at −0.288 V, indicating that the redox potential of the Cu(II) ion is substantially affected by the formation of dinuclear structure and the high oxidation state of Cu(III) is less stabilized by the formation of dinuclear structure.

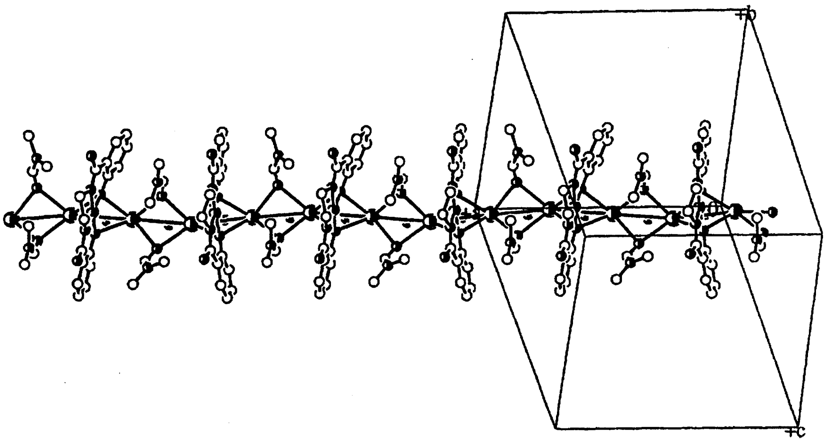

Fig. 2. One-dimensional structure of $K_2[NiL^1]\cdot 2DMF\cdot 2H_2O$ running along the *a*-axis. The one-dimensional rod-like structure is formed by potassium ions and oxygen atoms.

Table 5. Electrochemical Data of a Series of Dinuclear Complexes $[CuL^2Cu(cap)]$ and the Precursor Complex, Together with Their Molar Electrical Conductivities

Complex	$E_{1/2}/V$ $Cu_2(II,II)/Cu_2(III,II)$	$E_{1/2}/V$ $Cu_2(II,II)/Cu_2(II,I)$	$\Lambda_M/S\ cm^2\ mol^{-1}$
$[Me_4N]_2[CuL^2\cdot H_2O]$	−0.288	—	125
$[CuL^2Cu(bipy)]$	−0.053 (102)	−0.578	3
$[CuL^2Cu(phen)]\cdot 0.5H_2O$	−0.067 (130)	−0.585	3
$[CuL^2Cu(tn)]$	−0.084 (107)	—	3

All the observed potentials were corrected by the Fc^+/Fc couple of ferrocene which was employed as an internal standard. $\Delta E_p/mV$ is given in parenthesis; Tetrabutylammonium perchlorate was employed as supporting electrolyte. All the measurements were carried out in DMF.

The irreversible process observed at ca. −0.58 V of $[CuL^2Cu(cap)]$ is assigned to the Cu(II) to Cu(I) process of {Cu(cap)} site and the potential is compatible with those of $[Cu(bpy)](NO_3)_2\cdot 3H_2O$ (−0.520 V) and $[Cu(phen)](NO_3)_2\cdot 2H_2O$ (−0.499 V) under the same condition. It should be noted that the corresponding potential of $[CuL^2Cu(tn)]$ was not observed. A capping ligand such as bipy and phen has a ability to stabilize the low oxidation state Cu(I), but tn has no such ability.

Structural Description of $[CuL^2Cu(phen)(DMSO)]$. An ORTEP view of the dinuclear molecule with the numbering scheme is shown in Fig. 3, and the bond distances and angles are reported in Table 6.

The X-ray analysis confirmed a discrete dinuclear Cu(II)–Cu(II) structure bridged by two phenoxo oxygen atoms, in which Cu_2O_2 core assumes an unequivalent bridging mode as found in the distances of Cu(1)–O(1) = 1.924(4) Å, Cu(1)–O(2) = 1.908(4) Å, Cu(2)–O(2) = 1.964(4) Å, and Cu(2)–O(1) = 2.249(4) Å. One of the copper(II) ions, $\{CuL^2\}$ site, assumes a square planar four-coordination geometry, in which the planar coordination sites are occupied by two amido nitrogen atoms and two phenoxo oxygen atoms of a tetraanionic quadridentate ligand with the average bond distances of ⟨Cu–N⟩ = 1.916(5) Å and ⟨Cu–O⟩ = 1.916(4) Å. The average bond distances of the precursor mononuclear complex, $K_2[CuL^2]\cdot 5DMF$, are ⟨Cu–N⟩ = 1.960(8) Å and ⟨Cu–O⟩ = 1.896(7) Å.[21] The present Cu–O distances which participate in bridging are slightly longer than those of the precursor complex, while the Cu–N distances are substantially shorter than those of the precursor complex. The second copper(II) ion, {Cu(cap)} site, assumed a five-coordinated square pyramidal geometry, in which the equatorial sites are occupied by one phenoxo oxygen atom with the distance of Cu(2)–O(2) = 1.964(4) Å, oxygen atoms of a DMSO molecule with the distance of Cu(2)–O(5) = 1.948(4) Å, and

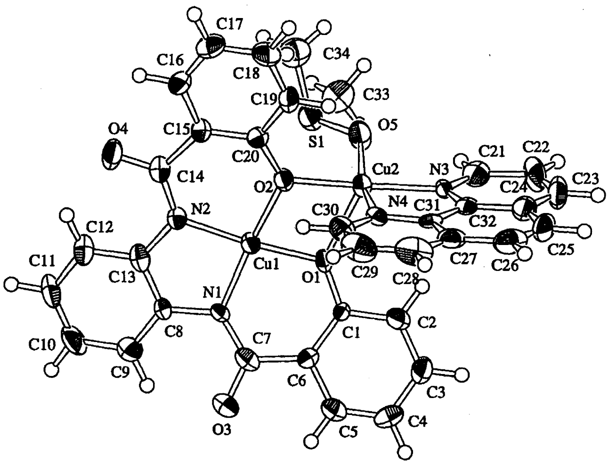

Fig. 3. An ORTEP drawing of $[CuL^2Cu(phen)(DMSO)]$ with the atom numbering scheme of the unique atoms, showing 50% probability ellipsoids.

Table 6. Relevant Bond Distances (Å) and Angles (°) with the Estimated Standard Deviations in Parentheses for [CuL^{2}Cu(phen)(DMSO)]

(a) Bond distances (Å)			
Cu(1)–O(1)	1.924(4)	Cu(2)–O(1)	2.249(4)
O(1)–C(1)	1.320(7)	Cu(1)–O(2)	1.908(4)
Cu(2)–O(2)	1.964(4)	Cu(2)–C(20)	1.356(7)
Cu(1)–N(1)	1.911(5)	Cu(2)–O(5)	1.948(4)
N(1)–C(7)	1.324(7)	Cu(1)–N(2)	1.921(5)
Cu(2)–N(3)	2.001(5)	N(1)–C(8)	1.418(7)
Cu(2)–N(4)	1.994(6)	N(2)–C(13)	1.421(8)
N(2)–C(14)	1.355(8)	Cu(1)–Cu(2)	3.1172(9)
(b) Bond angles (°)			
O(1)–Cu(1)–O(2)	82.8(2)	O(1)–Cu(2)–O(2)	73.6(2)
N(1)–Cu(1)–N(2)	87.1(2)	O(1)–Cu(2)–O(5)	102.0(2)
O(1)–Cu(1)–N(1)	95.8(2)	O(1)–Cu(2)–N(3)	110.8(2)
O(2)–Cu(1)–N(2)	95.9(2)	O(1)–Cu(2)–N(4)	96.6(2)
O(2)–Cu(2)–O(5)	93.3(2)	Cu(1)–O(1)–Cu(2)	96.3(2)
N(3)–Cu(2)–N(4)	81.4(2)	Cu(1)–O(2)–Cu(2)	107.2(2)
O(2)–Cu(2)–N(4)	93.5(2)	O(5)–Cu(2)–N(3)	90.4(2)

two nitrogen atoms of phen with the distances of Cu(2)–N(3), Cu(2)–N(4) = 2.001(5), 1.994(6) Å, and the apical site is occupied by one phenoxo-oxygen atom with the bond distance of Cu(2)–O(1) = 2.249(4) Å. Due to the unequivalent bridging mode, the significant bridging angles for the magnetic interaction, Cu(1)–O(1)–Cu(2) = 96.3(2)° and Cu(1)–O(1)–Cu(2) = 107.2(2)°, are unequivalent to each other and the dihedral angle between two basal coordination planes is 81.8°. Such a molecular structure can be caused by the steric repulsion between the benzene moieties of the quadridentate ligand and phen.

Magnetic Properties of [CuL^{2}Cu(phen)(DMSO)] and Other Dinuclear Cu(II) Complexes. The magnetic susceptibility values of the complexes were measured on a Faraday balance in the temperature range of 300—80 K. The χ_A vs. T plots of three representative complexes, [CuL^{2}Cu(phen)(DMSO)], are shown in Fig. 4. The magnetic behavior of the structurally confirmed compound, [CuL^{2}Cu(phen)(DMSO)], is described in detail. The μ_{eff}/per Cu at room temperature of 1.57 μ_B is smaller than the spin-only value (1.73 μ_B) expected for the d^9 system. On lowering the temperature, the μ_{eff} decreases from a subnormal value, indicating an antiferromagnetic spin-coupling between copper(II) ions. The magnetic behavior is well reproduced by the Bleaney–Boweres equation on the basis of the isotropic spin-Hamiltonian of dinuclear Cu(II)–Cu(II) structure $H = -2JS_1 \cdot S_2$ ($S_1 = S_2 = 1/2$) with the fitting parameter of $J = -82$ cm^{-1}. The relatively small J value is in accord with the fact that two basal coordination planes are nearly perpendicular, in which two magnetic orbitals of two Cu(II) ions can not overlap due to the nearly strict orthogonality.

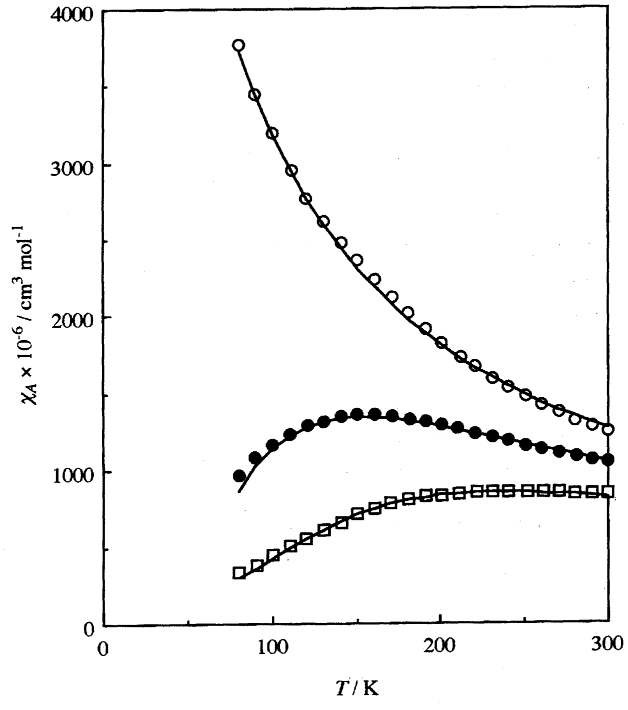

Fig. 4. Magnetic susceptibilities vs. T plots for [CuL^{1}Cu(bpy)(MeOH)] (○), [CuL^{2}Cu(phen)(DMSO)] (●), and [CuL^{2}Cu(tn)(MeOH)] (□). The solid lines represents the theoretical curves on the basis of the Bleaney–Boweres equation with the fitting parameters of (J, g, ρ) = (−22, 2.02, 0), (−82, 2.02, 0), (−135, 2.00, 0.02) cm^{-1} for [CuL^{1}Cu(bpy)(MeOH)], [CuL^{2}Cu(phen)(DMSO)], and [CuL^{2}Cu(tn)(MeOH)], respectively, where ρ denotes the paramagnetic impurity.

All other dinuclear Cu(II) complexes exhibit subnormal magnetic moments in the range of 1.3—1.7 μ_B, indicating an operation of weak antiferromagnetic interaction. The magnetic interaction for di-μ-hydroxo-, di-μ-phenoxo-, and di-μ-alkoxo-bridged dinuclear Cu(II) complexes exhibiting equivalent two coordination spheres has been extensively studied and the studies demonstrated that the coupling constants are determined by factors such as the Cu–O–Cu angle, the coplanarity of the two Cu(II) basal planes, and the axial coordination.[22] The wide-ranged distribution of the magnetic moments indicate that the present series of the dinuclear complexes supplies a good testing model to investigate the magnetic interaction of μ-phenoxo-bridged Cu(II)–Cu(II) dinuclear complexes exhibiting unequivalent two coordination spheres. The small reduction of magnetic moment for the dinuclear Cu(II) complexes may be related to (1) the fifth coordination of the solvent molecule to the second Cu(II) ion, (2) the distortion of Cu_2O_2 core from coplanarity due to the steric repulsion between the benzene moieties of the first Cu(II) site and the capping ligand around the second Cu(II) ion such as phen and bpy, (3) the coordination geometry around the second Cu(II) ion. Since the molecular structures are essential to overview and discuss the details of the magnetic interaction, only the experimental magnetic results are described here. On the basis of the magnetic moments at room temperature and the magnitude of the spin-coupling constants J, the complexes are further divided into two classes: class **1** involving [$CuL^1Cu(bpy)(MeOH)$] and [$CuL^1Cu(en)(H_2O)$] has the coupling constant of ca. 20 cm^{-1}; class **2** involving [$CuL^2Cu(phen)(DMSO)$] and [$CuL^2Cu(tn)(MeOH)$] has the J value around -80—-140 cm^{-1}.

Concluding Remarks. This study revealed that the dianionic copper(II) and nickel(II) complexes with 1,2-bis(2-hydroxybenzamido)ethane and 1,2-bis(2-hydroxybenzamido)benzene are new effective "ligand complexes" for the synthesis of homo-metal dinuclear complexes exhibiting two different coordination spheres and hetero-metal dinuclear complexes. It is expected that a series of hetero-metal dinuclear complexes with the systematic metal combinations can be obtained by the use of these and the analogous ligand complexes. Such study is now in progress in our laboratory.

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