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Syntheses, Structures, and Properties of the Dinuclear Copper(II) and Nickel(II) Complexes Bridged by an Alkoxide and a Pyridazine or a Phthalazine

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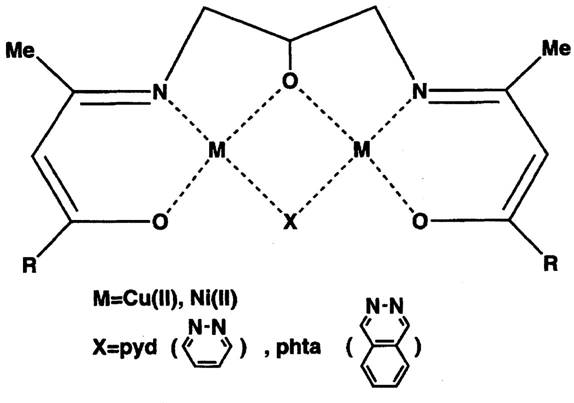
In this paper we report our recent research on the dinuclear copper(II) and nickel(II) complexes **1**—**10** (Chart 1) containing Schiff bases, derived from acetylacetone, benzoylacetone, or trifluoroacetylacetone, and 1,3-diaminopropane-2-ol. These complexes are bridged by an alkoxide and a pyridazine (pyd) or phthalazine (phta). The magnetic susceptibilities, visible absorption spectra, conductivities, and redox properties of the complexes were investigated and the molecular structures of **2**, **4**, and **5** are described. The Cu–O–Cu angles found in these complexes indicate a role of the alkoxo-bridge as one of the principal antiferromagnetic exchange pathways. At the same time, the coplanarity of two coordination planes of copper(II) ions is also shown to relate to the exchange process.



M=Cu(II), Ni(II)
X=pyd ( ) , phta ( )

L_1: R=CH_3 L_2: R=C_6H_5 L_3: R=CF_3

1 $[Cu_2(L_1)(pyd)]ClO_4 \cdot 0.5H_2O$
2 $[Cu_2(L_1)(pyd)]BF_4 \cdot H_2O$
3 $[Cu_2(L_2)(pyd)]ClO_4$
4 $[Cu_2(L_3)(pyd)]ClO_4$
5 $[Cu_2(L_1)(phta)]ClO_4 \cdot 0.5C_2H_5OH$
6 $[Cu_2(L_2)(phta)]ClO_4 \cdot H_2O$
7 $[Ni_2(L_1)(pyd)]ClO_4$
8 $[Ni_2(L_2)(pyd)]ClO_4$
9 $[Ni_2(L_1)(phta)]ClO_4 \cdot 1.5H_2O$
10 $[Ni_2(L_2)(phta)]ClO_4 \cdot 0.5MeCN$

Chart 1.

There has been considerable interest among inorganic chemists in studying the structures, magnetic properties, and redox properties of dinuclear multibridged copper(II) and nickel(II) complexes.[1—17] Their investigations are carried out as attempts to understand the structure-magnetism relationships, behavior of the reduction process, and the structural characteristics of the active site in type 3 copper proteins such as hemocyanin. Both single-atom and multi-atom bridges are known to propagate antiferromagnetic exchange with the magnitude of the exchange interaction being dependent upon the bridge identity, metal–metal distance, the angle subtended at the bridge, the metal ion stereochemistry, etc. Mc'Kee et al. have reported a diamagnetic dinuclear copper(II) complex $[Cu_2(L\text{-}Et)X](BF_4)_2$, where X is an alkoxo or an μ-1,3-azido bridge and HL-Et represents *N*,*N*,*N*′,*N*′-tetrakis-[(1-ethyl-2-benzimidazolyl)methyl]-2-hydroxy-1,3-diaminopropane. Both copper ions in the complex have a square pyramidal geometry. The alkoxide and μ-1,3-azide bridge these coordination planes. They concluded that the diamagnetism of the complex resulted from the coplanarity of these coordinational basal planes.[4] Thompson et al. reported that the dinuclear hydroxo-bridged copper(II) complexes containing tetradentate (N_4) phthalazine and pyridazine derivatives, such as 1,4-bis((6-methylpyrid-2-yl)amino)phthalazine, have copper–copper separations in the range 3.0—3.5 Å and Cu–O(H)–Cu bridge angles in the range 100—127°.[5,6,14] The magnitude of the antiferromagnetic exchange varied in a linear manner with hydroxide bridge angle for a related series of complexes in which the $N_4Cu_2(OH)$ dinuclear fragment remains intact and the copper ions have $d_{x^2-y^2}$ ground states. The phthalazine and pyridazine moieties have been suggested to provide a roughly constant contribution to the total exchange. Electrochemical studies revealed that the multibridged dinuclear copper(II) complexes tend to be relatively kinetically labile. However, nickel(II) analogues may be more inert in their redox behavior.[8,17] In this paper we report our recent research on the dinuclear copper(II) and nickel(II) complexes **1**—**10** (Chart 1) containing Schiff bases derived from acetylacetone, benzoylacetone, or trifluoroacetylacetone, and 1,3-diaminopropane-2-ol. These complexes are bridged by an alkoxide and a pyridazine (pyd) or a phthalazine (phta). The magnetic susceptibilities, visible absorption spectra, conductivities, and redox properties of the complexes were investigated and the molecular structures of **2**, **4**, and **5** were determined by the X-ray diffraction method. The results revealed that these complexes mimic the active site in metazidohemocyanin. Furthermore, the half-wave potentials of these complexes are compared with those of the similar complexes bridged by an alkoxo and a pyrazolato (pz) groups.

Experimental

Preparation of Schiff Bases. H_3L_1 and H_3L_2 were derived from acetylacetone or benzoylacetone and 1,3-diaminopropane-2-ol according to the method described in the literature.[8] H_3L_3 was derived from trifluoroacetylacetone and 1,3-diaminopropane-2-ol by the method similar to that described for H_3L_1 and H_3L_2.

Preparation of Copper(II) Complexes. $[Cu_2(L_1)(pyd)]ClO_4\cdot 0.5H_2O$ (1). H_3L_1 (0.64 g, 2.5 mmol) was dissolved in ethanol (30 cm^3). Then copper(II) perchlorate hexahydrate (1.85 g, 5.0 mmol), pyridazine (0.20 g, 2.5 mmol), and sodium hydroxide (0.30 g, 7.5 mmol) were added successively into the solution. After being stirred at room temperature for several hours, the reaction mixture was filtered. The obtained dark-purple products were recrystallized from acetone. Found: C, 36.00; H, 4.17; N, 9.91%. Calcd for $C_{17}H_{23}N_4O_7ClCu_2\cdot 0.5H_2O$: C, 36.01; H, 4.28; N, 9.88%.

$[Cu_2(L_1)(pyd)]BF_4\cdot H_2O$ (2). H_3L_1 (0.64 g, 2.5 mmol) was dissolved in ethanol (20 cm^3). Then 45% copper(II) borofluoride water solution (2.64 g, 5.0 mmol), pyridazine (0.20 g, 2.5 mmol), and sodium hydroxide (0.30 g, 7.5 mmol) were added successively into the solution. After being stirred at room temperature for several hours, the reaction mixture was filtered.The obtained red-brown products were recrystallized from acetone. Found: C, 36.33; H, 4.58; N, 10.30%. Calcd for $C_{17}H_{23}N_4O_3BF_4Cu_2\cdot H_2O$: C, 36.25; H, 4.47; N, 9.94%.

$[Cu_2(L_2)(pyd)]ClO_4$ (3). H_3L_2 (0.95 g, 2.5 mmol) was dissolved in ethanol (50 cm^3). Then copper(II) perchlorate hexahydrate (1.85 g, 5.0 mmol), pyridazine (0.20 g, 2.5 mmol), and sodium hydroxide (0.30 g, 7.5 mmol) were added successively into the solution. After being stirred at room temperature for several hours, the reaction mixture was filtered. The obtained purple products were recrystallized from acetonitrile. Found: C, 47.30; H, 4.01; N, 8.23%. Calcd for $C_{27}H_{27}N_4O_7ClCu_2$: C, 47.54; H, 4.00; N, 8.22%.

$[Cu_2(L_3)(pyd)]ClO_4$ (4). H_3L_3 (0.91 g, 2.5 mmol) was dissolved in ethanol (20 cm^3). Then copper(II) perchlorate hexahydrate (1.85 g, 5.0 mmol), pyridazine (0.20 g, 2.5 mmol), and sodium hydroxide (0.30 g, 7.5 mmol) were added successively into the solution. After being stirred at room temperature for overnight, the reaction mixture was filtered. The obtained violet products were recrystallized from acetone. Found: C, 30.52; H, 2.56; N, 8.43%. Calcd for $C_{17}H_{17}N_4O_7F_6ClCu_2$: C, 30.66; H, 2.58; N, 8.42%.

$[Cu_2(L_1)(phta)]ClO_4\cdot 0.5C_2H_5OH$ (5). H_3L_1 (0.64 g, 2.5 mmol) was dissolved in ethanol (30 cm^3). Then copper(II) perchlorate hexahydrate (1.85 g, 5.0 mmol), phthalazine (0.33 g, 2.5 mmol), and sodium hydroxide (0.30 g, 7.5 mmol) were added successively into the solution. After being stirred at room temperature for several hours, the reaction mixture was filtered. The obtained violet products were recrystallized from acetone. Found: C, 42.10; H, 4.37; N, 8.77%. Calcd for $C_{21}H_{25}N_4O_7ClCu_2\cdot 0.5C_2H_5OH$: C, 41.87; H, 4.48; N, 8.88%.

$[Cu_2(L_2)(phta)]ClO_4\cdot H_2O$ (6). H_3L_2 (0.95 g, 2.5 mmol) was dissolved in ethanol (30 cm^3). Then copper(II) perchlorate hexahydrate (1.85 g, 5.0 mmol), phthalazine (0.33 g, 2.5 mmol), and sodium hydroxide (0.30 g, 7.5 mmol) were added successively into the solution. After being stirred at room temperature for several hours, the reaction mixture was filtered. The obtained dark-blue products were recrystallized from acetonitrile. Found: C, 49.40; H, 4.22; N, 7.94%. Calcd for $C_{31}H_{29}N_4O_7ClCu_2\cdot H_2O$: C, 49.63; H, 4.17; N, 7.47%.

$[Ni_2(L_1)(pyd)]ClO_4$ (7). H_3L_1 (0.51 g, 2.0 mmol) was dissolved in ethanol (30 cm^3). Then nickel(II) perchlorate hexahydrate (1.46 g, 4.0 mmol), pyridazine (0.24 g, 3.0 mmol), and sodium hydroxide (0.24 g, 6.0 mmol) were added successively into the solution. After being stirred at room temperature for overnight, the reaction mixture was filtered. The obtained products were recrystallized from *N*,*N*-dimethylformamide (DMF) to give the red-brown needle crystals. Found: C, 37.07; H, 4.13; N, 10.27%. Calcd for $C_{17}H_{23}N_4O_7ClNi_2$: C, 37.24; H, 4.23; N, 10.22%.

$[Ni_2(L_2)(pyd)]ClO_4$ (8). H_3L_2 (1.89 g, 5.0 mmol) was dissolved in ethanol (50 cm^3). Then nickel(II) perchlorate hexahydrate (3.66 g, 10.0 mmol), pyridazine (0.40 g, 5.0 mmol), and sodium hydroxide (0.60 g, 15.0 mmol) were added successively into the solution. After being stirred at room temperature for overnight, the reaction mixture was filtered. The obtained products were recrystallized from acetonitrile to give the dark-yellow needle crystals. Found: C, 48.17; H, 4.00; N, 8.38%. Calcd for $C_{27}H_{27}N_4O_7ClNi_2$: C, 48.23; H, 4.06; N, 8.33%.

$[Ni_2(L_1)(phta)]ClO_4\cdot 1.5H_2O$ (9). H_3L_1 (0.51 g, 2.0 mmol) was dissolved in ethanol (55 cm^3). Then nickel(II) perchlorate hexahydrate (1.46 g, 4.0 mmol), phthalazine (0.26 g, 2.0 mmol), and sodium hydroxide (0.24 g, 6.0 mmol) were added successively into the solution. After being stirred at room temperature for overnight, the reaction mixture was filtered. The obtained products were recrystallized from acetonitrile to give the dark-yellow micro-needle crystals. Found: C, 40.40; H, 4.25; N, 9.09%. Calcd for $C_{21}H_{25}N_4O_7ClNi_2\cdot 1.5H_2O$: C, 40.33; H, 4.52; N, 8.96%.

$[Ni_2(L_2)(phta)]ClO_4\cdot 0.5MeCN$ (10). H_3L_2 (0.76 g, 2.0 mmol) was dissolved in ethanol (20 cm^3). Then nickel(II) perchlorate hexahydrate (1.46 g, 4.0 mmol), phthalazine (0.26 g, 2.0 mmol), and sodium hydroxide (0.24 g, 6.0 mmol) were added successively into the solution. After being stirred at room temperature for overnight, the reaction mixture was filtered. The obtained products were recrystallized from acetonitrile to give the yellow-brown micro-needle crystals. Found: C, 51.89; H, 4.25; N, 8.53%. Calcd for $C_{31}H_{29}N_4O_7ClNi_2\cdot 0.5CH_3CN$: C, 51.72; H, 4.15; N, 8.49%.

Measurement of the Physical Properties. The visible absorption spectra were recorded by Hitachi U-3410 spectrophotometer and conductivity by Toa Conduct Meter Model CM-7B. The magnetic susceptibility at room temperature was obtained by Gouy method. Temperature-dependence of magnetic susceptibility over the range of liquid helium to room temperature was determined by a SQUID magnetometer (Quantum design MPMS-5S). The electrochemical experiments were performed at 25 °C in DMF, using an assembly comprising a Huso HECS-972 microelectrode Potentiostat, a Hokuto Denko function generator (HB-104), and a Yokogawa Denki Type 3086 X–Y recorder. A three-electrode system was used in which the working electrode was a glassy carbon disk electrode (B. A. S. 11-2012), and the counter electrode was platinum, with a silver–silver chloride electrode as a reference. The supporting electrolyte was tetrabutylammonium hexafluorophosphate (n-Bu_4NPF_6, 0.1 mol dm^{-3}).

X-Ray Structure Determination. Crystal structure analyses were carried out only for **2**, **4**, and **5** because of the low quality of the crystals of all the other compounds. X-Ray diffraction data were collected on a Rigaku AFC-5R diffractometer using ω-2θ scan technique at room temperature. Complexes **2** and **5** were unstable in the air so the crystals were sealed in the glass capillary tubes for the data collection. Lorentz, polarization and absorption effects were corrected for all the three crystals. The crystal structures were solved by the heavy-atom method and were expanded by the successive Fourier syntheses. The non-hydrogen atoms were refined anisotropically by the full-matrix least-squares techniques, while the hydrogen atoms were fixed at their standard geometries and were not refined. In complex **2**, the thermal parameters of hydrogen atoms were refined isotropically. All calculations were performed by the use of teXsan crystallographic software package.[18] The crystallographic data and the experimental details for X-ray structure analyses are given in Table 1.

Results and Discussion

Physical Properties. The magnetic moments (μ_{eff}), visible absorption spectra ($\lambda_{\max}$), and electric conductivity (Λ) for complexes **1**—**10** are given in Table 2. Cyclic voltammetry (CV) data of complexes **1**—**10** are listed in Table 3.

Table 2. Physical Properties of the Complexes **1**—**10**

Complex	μ_{eff} / BM	$\lambda_{\max}$ (ε/Cu or Ni[a]) / nm	Λ[b] / S cm^2 mol^{-1}
1	0.94	582 (236)	82
2	0.75	579 (235)	70
3	0.71	588 (268)	63
4	0.91	603 (151)	73
5	0.74	576 (244)	68
6	0.84	581 (253)	66
7	0.31	560 (77)[c]	78
8	0.22	564 (104)[c]	80
9	0.42	567 (71)[c]	75
10	Diamag.	567 (101)[c]	83

a) mol^{-1} dm^3 cm^{-1}. b) DMF solution. c) Shoulder.

Table 3. CV Data for Complexes **1**—**10** (mV)[a]

Complex	$E^{\mathrm{I}}_{\mathrm{pc}}$	$E^{\mathrm{I}}_{\mathrm{pa}}$	$E^{\mathrm{I}}_{1/2}$	$E^{\mathrm{II}}_{\mathrm{pc}}$	$E^{\mathrm{II}}_{\mathrm{pa}}$	$E^{\mathrm{II}}_{1/2}$
1	−810	−520	−665	−1290	−1100	−1195
2	−790	−580	−685	−1290	−1100	−1195
3	−740	—	—	−1160	—	—
4	−630	—	—	−1030	—	—
5	−820	—	—	−1280	—	—
6	−780	—	—	−1170	−1030	−1100
7	−940	−860	−900	−1720	−1630	−1675
8	−1040	−790	−915	−1810	−1500	−1655
9	−1070	−700	−885	−1660	−1580	−1620
10	−1100	—	—	−1700	−1520	1610

a) DMF; Scan rate: 200 mV s^{-1}.

Magnetism. The magnetic moments of all the copper(II) complexes **1**—**6** at room temperature were below 1 BM (Table 2), indicating a very strong antiferromagnetic interaction within each dinuclear complex. In addition, the magnetic susceptibilities of the complexes **1**, **2**, **4**, and **5** were measured over the temperature range from the liquid helium to room temperatures. The temperature dependence of all the four complexes obeys the modified Bleaney–Bowers

Table 1. Crystal Data and Experimental Conditions for X-Ray Analyses of **2**, **4**, and **5**

Compound	**2**	**4**	**5**
Formula	$C_{17}H_{25}N_4O_4BF_4Cu_2$	$C_{17}H_{17}N_4O_7F_6ClCu_2$	$C_{21}H_{25}N_4O_7ClCu_2 \cdot 0.5CH_3OH$
Mol wt	563.30	665.88	624.02
Space group	$P\bar{1}$	$P2_1/m$	$P\bar{1}$
a/Å	11.081(2)	7.954(2)	10.472(1)
b/Å	11.232(1)	16.426(3)	15.143(2)
c/Å	10.1533(6)	9.277(1)	10.412(1)
α/°	113.546(6)		105.63(1)
β/°	96.97(1)	97.71(1)	112.409(7)
γ/°	71.26(1)		97.34(1)
V/Å^3	1090.8(3)	1201.1(3)	1419.8(4)
Z	2	2	2
D_c/g cm^{-3}	1.715	1.841	1.464
Radiation	Cu $K\alpha$	Mo $K\alpha$	Cu $K\alpha$
λ/Å	1.54178	0.71069	1.54178
μ/cm^{-1}	30.12	19.75	31.14
No. unique reflections	3251	2863	4223
No. observed reflections [$I > 3\sigma(I)$]	2491	1963	3225
No. variables	312	175	352
F(000)	572	664	638
R	0.054	0.052	0.065
R_{W}	0.056	0.064	0.069

equation (Eq. 1).[19)]

$$\chi_A = \frac{Ng^2\beta^2}{kT}\frac{1}{3+\exp(-2J/kT)}(1-p)+\frac{Ng^2\beta^2}{4kT}\cdot p+N\alpha. \quad (1)$$

In this expression, g is the g factor, J is the exchange integral, p is the percentage of paramagnetic impure species, $N\alpha$ is T. I. P., and other symbols have their usual meaning. The magnetic parameters estimated from the best fit of the χ_A values to the Bleaney–Bowers equation for complexes **1**, **2**, **4**, and **5** are listed in Table 4. A typical example of the data is shown in Fig. 1. The exchange integral $-J$ for complexes **1**, **2**, **4**, and **5** (293, 391, 313, and 366 cm^{-1}, respectively) indicates very strong antiferromagnetic exchange interaction between the copper(II) centers for these complexes.

Dinuclear copper(II) complexes bridged by an alkoxo group of Schiff bases (L_1 and L_2) and an exogenous bridging ligand X (N_3^-, OH^-, CH_3COO^-, pyrazolate, and so on) have been intensively studied and their two copper(II) centers are usually found to show antiferromagnetic coupling.[7,9,11,16)] Compared with these complexes (except azido-bridged copper(II) complexes), **1**—**6** have smaller magnetic moments and larger $-J$ values,[15,16)] implying the stronger antiferromagnetic coupling between the metal centers. So it may be concluded that pyridazine or phthalazine as the exogenous bridging ligand X is a better superexchange medium than those reported before.[7,9,11,16)]

The magnetic moments for the corresponding nickel(II) complexes **7**—**10** are small positive values (Table 2), which show that these complexes are diamagnetic or nearly so. It is likely, therefore, that the four coordination bonds, a ketimine nitrogen and two alkoxo oxygens of Schiff base L_1 or L_2, and a nitrogen of pyridazine or phthalazine are arranged in a square-planar around each nickel(II) ion. This stereochemistry made up of Schiff base and pyridazine or phthalazine is the same as those of copper(II) complexes **1**—**6**, which is supported by the results of the X-ray structure analyses of complexes **2**, **4**, and **5** to be mentioned later.

Table 4. The Magnetic Parameters of Complexes **1**, **2**, **4**, and **5**

Complex	g	J / cm^{-1}	p / %	$N\alpha\times10^{-6}$ / $\mathrm{S\,cm^2\,mol^{-1}}$
1	2.20	−293	1.4	60
2	2.00	−391	3.0	60
4	2.20	−313	2.6	60
5	2.07	−366	2.3	60

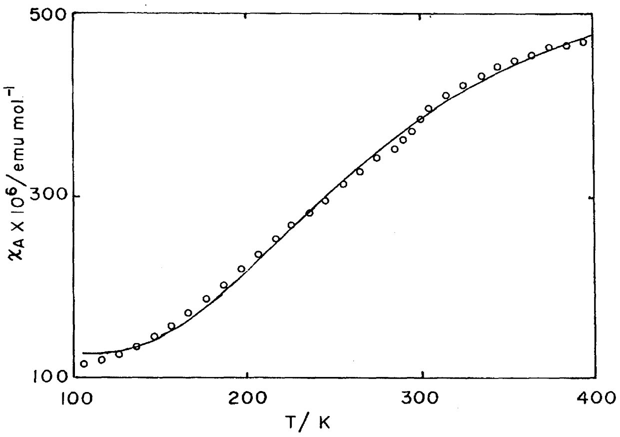


Fig. 1. The temperature-dependence of magnetic susceptibility for complexes **4** (4—300 K). The open circles indicate observed susceptibility. The solid line shows the theoretical susceptibility calculated by the modified Bleaney–Bowers equation.[19)]

Visible Absorption Spectra. The $\lambda_{\max}$ values of the d–d absorption bands of these copper complexes **1**—**6** were observed in the region of 576—603 nm (Table 2), which is similar to the corresponding pyrazolate-bridged dinuclear complexes $[\mathrm{Cu_2(L_1)(pz)}]$ and $[\mathrm{Cu_2(L_2)(pz)}]$.[16)] On the other hand, all nickel(II) compounds **7**—**10** have an absorption in the region 560—567 nm (Table 2), which is characteristic for square-planar nickel(II) complexes.[20,21)] This agrees with the conclusion obtained from the data of magnetic moments described above.

Conductivity and Electrochemistry. Table 2 shows that the electric conductivities (Λ) for complexes **1**—**10** are around 70—80 S $\mathrm{cm^2\,mol^{-1}}$, which imply they are 1 : 1 electrolytes in DMF solution. Therefore, the molecular structures in the crystalline state are supposed to be maintained in DMF. As indicated in Table 3, the dinuclear copper(II) and nickel(II) complexes display a two-step reduction consisting of one-electron transfer at each step as indicated by the separation in reduction and oxidation potentials. This behavior agrees with the electrochemical data for the pyrazolato-bridged copper(II) and nickel(II) complexes.[8)] Both two reduction and two reoxidation potential peaks were observed for copper(II) complexes **1** and **2**. Compared with the reoxidation potential peaks, their reduction potential peaks were a little more negative, implying a quasi-reversible two-step reduction processes for these complexes. In the cases of **3**, **4**, and **5**, only two reduction potential peaks were observed. On the reverse scan no appreciable reoxidation potential peak corresponding to the anodic peak appeared, so the two-step reduction processes of these complexes are chemically irreversible. The reduction processes of **6** are more complicated. Two reduction potential peaks are observed. However, on the reverse scan, only the second oxidation peak was observed at a more positive potential (+140 mV). So the first-step reduction process of **6** is chemically irreversible and the second-step reduction process is quasi-reversible. For the same reason we mentioned above, only the first-step reduction process of nickel(II) complex **10** can be considered chemically irreversible. The reduction processes of all the other remained nickel(II) complexes are quasi-reversible. The half-wave or reduction potentials are more positive with these copper(II) complexes **1**—**6** than with the corresponding pyrazolate-bridged complexes.[8)] A similar result is seen in the nickel(II) complexes **7** and $[\mathrm{Ni_2(L_1)(pz)}]$ ($E^{\mathrm{I}}_{\mathrm{pc}}=-1810$ mV, $E^{\mathrm{I}}_{\mathrm{pa}}=-1730$ mV, $E_{1/2}=-1770$ mV; $E^{\mathrm{II}}_{\mathrm{pc}}=-2400$ mV, $E^{\mathrm{II}}_{\mathrm{pa}}=-2250$ mV, $E_{1/2}=-2325$ mV). These results are available for modeling of the active site of diamagnetic type 3 copper protein which have high oxidation-reduction potential.[22] In addition, the $E^{\mathrm{I}}_{\mathrm{pc}}$ and $E^{\mathrm{II}}_{\mathrm{pc}}$ values of **4** in the copper(II) complexes **1**—**6** are observed in the most positive potential. It is considered that this is due to the presence of electrophylic trifluoromethyl groups in **4**.

Molecular and Crystal Structures. The final atomic parameters and equivalent isotropic thermal parameters for **2**, **4**, and **5** are listed in Tables 5, 6, and 7, respectively. The molecular structures of these complexes are shown in Fig. 2. The interatomic distances and angles relevant to the copper coordination spheres are given in Table 8.

Description of the Crystal Structure of 2. The molecular structure of **2** consists of a pair of copper(II) centers bound simultaneously to the tetradentate Schiff base ligand L_1 and bridged by two groups, the pyridazine N–N moiety and an alkoxo group. The molecule is almost planar. The atomic mean deviation from the least-squares plane, which comprises the main skeleton of the molecule, is 0.154 Å. As indicated in Table 8, each copper center has an essentially square planar geometry. Cu(1) lies 0.039 Å below its coordination plane, while Cu(2) lies 0.079 Å above the plane. The dihedral angle between these two coordination planes is 6.2°. The copper–copper separation is 3.367(2) Å with an angle of 129.1(2)° at the bridging oxygen. The counter anion BF_4^- was found far from the two copper centers and one water molecule was located.

Description of the Crystal Structure of 4. Two possible structural formulae of 1,11-di(trifluoromethyl)-3,9-dimethyl-1,6,11-trihydroxy-4,8-diazaundeca-1,3,8,10-tetraene (**A**) and 4,10-di(trifluoromethyl)-2,7,12-trihydroxy-5,9-diazatrideca-2,4,9,11-tetraene (**B**) are considered for H_3L_3. From the result of the crystal structure analysis of **4**, it has become apparent that H_3L_3 is **A**. The molecular structure of **4** has an higher symmetry when it is compared with those of **2** and **5**. A crystallographic mirror plane is in the molecule so the asymmetric unit contains only half of the molecule. The molecule is almost planar with atomic mean deviation from the least-square plane of 0.085 Å. Two oxygen atoms in the counter anion ClO_4^- were found axially coordinated to each copper center with an identical distance of 2.574(6) Å. The similar perchlorate bridged structure has been reported before.[23—25] As a result, the stereochemistry at each copper center in **4** can be approximately described as distorted square pyramidal geometry. The copper atoms deviate 0.119 Å above their coordination planes toward the axial oxygen atoms of ClO_4^- anion. The dihedral angle between the coordination planes is 12.55°. The copper–copper separation is 3.331(2) Å with an angle of 126.5(4)° at the bridging oxygen. Usually, the magnetic exchange interaction between the two copper(II) ions occurs via the hydroxo and the diazine bridges. Any interaction between axial bridges is regarded as "nonmagnetic".[14] The relatively large values of μ and J of **4** compared with those of **2** and **5** show that the perchlorate bridge in **4** makes no contribution to the magnetic exchange interaction of the copper(II) ions.

Table 5. The Final Atomic Coordinates and Equivalent Isotropic Thermal Parameters for **2**

Atom	x	y	z	$B_{\mathrm{eq}}/\mathrm{Å}^2$
Cu(1)	0.10941(9)	0.1143(1)	0.0847(1)	4.19(3)
Cu(2)	0.04154(9)	0.3182(1)	0.4322(1)	4.28(3)
F(1)	0.6230(8)	0.3622(8)	0.6054(10)	16.3(4)
F(2)	0.5981(6)	0.1719(8)	0.5683(8)	12.9(3)
F(3)	0.5595(6)	0.3292(10)	0.7785(7)	17.7(3)
F(4)	0.7561(5)	0.2328(6)	0.7082(6)	9.0(2)
O(1)	0.0681(4)	0.0500(5)	−0.1112(5)	5.1(1)
O(2)	−0.0689(4)	0.4515(5)	0.5840(5)	4.7(1)
O(3)	0.1475(4)	0.1832(5)	0.2787(4)	4.5(1)
O(4)	0.4310(10)	0.394(1)	0.421(1)	8.6(4)
N(1)	0.2815(5)	−0.0066(6)	0.0651(6)	4.1(1)
N(2)	0.1743(5)	0.2545(6)	0.5506(6)	4.4(1)
N(3)	−0.0633(5)	0.2647(5)	0.1368(6)	3.9(1)
N(4)	−0.0941(5)	0.3390(5)	0.2783(6)	4.0(1)
C(1)	0.2520(9)	0.095(1)	0.3182(9)	8.8(3)
C(2)	0.3463(7)	0.0114(8)	0.2032(8)	4.9(2)
C(3)	0.3379(7)	−0.0924(7)	−0.0574(8)	4.4(2)
C(4)	0.2749(7)	−0.1039(7)	−0.1905(8)	4.6(2)
C(5)	0.1516(8)	−0.0358(8)	−0.2120(8)	4.7(2)
C(6)	−0.1472(7)	0.2867(7)	0.0388(8)	4.4(2)
C(7)	−0.2667(7)	0.3814(8)	0.0738(9)	5.1(2)
C(8)	−0.2988(7)	0.4514(8)	0.2123(9)	5.1(2)
C(9)	−0.2087(7)	0.4272(7)	0.3133(8)	4.5(2)
C(10)	−0.0570(7)	0.4519(7)	0.7131(8)	4.7(2)
C(11)	0.0491(8)	0.3775(8)	0.7645(8)	5.1(2)
C(12)	0.1633(7)	0.2848(7)	0.6872(8)	4.5(2)
C(13)	0.2890(7)	0.1565(8)	0.4666(8)	5.3(2)
C(14)	0.4740(7)	−0.1836(8)	−0.0605(9)	5.2(2)
C(15)	0.0997(8)	−0.0557(9)	−0.3605(8)	5.7(2)
C(16)	−0.1701(8)	0.5470(10)	0.8113(9)	6.2(3)
C(17)	0.2683(9)	0.2222(9)	0.7714(9)	6.0(3)
B(1)	0.633(1)	0.278(1)	0.669(2)	7.9(4)
H(1)	0.2157	0.0298	0.3229	18(3)
H(4)	0.3248	−0.1700	−0.2768	4(1)
H(6)	−0.1245	0.2328	−0.0635	5(1)
H(7)	−0.3265	0.3966	−0.0028	4(1)
H(8)	−0.3844	0.5174	0.2411	4(1)
H(9)	−0.2302	0.4774	0.4141	4(1)
H(11)	0.0459	0.3911	0.8662	8(2)
H(21)	0.4125	0.0550	0.2115	6(1)
H(22)	0.3914	−0.0760	0.2089	6(1)
H(131)	0.3518	0.2017	0.4719	6(2)
H(132)	0.3281	0.0884	0.5066	7(2)
H(141)	0.5056	−0.2405	−0.1540	6(1)
H(142)	0.4786	−0.2417	−0.0081	3(1)
H(143)	0.5328	−0.1313	−0.0112	6(1)
H(151)	0.0274	−0.0889	−0.3759	9(2)
H(152)	0.1624	−0.1181	−0.4336	9(2)
H(153)	0.0718	−0.0300	−0.3729	7(2)
H(161)	−0.1576	0.5433	0.9056	9(2)
H(162)	−0.1853	0.6411	0.8251	9(2)
H(163)	−0.2490	0.5255	0.7749	7(1)
H(171)	0.2458	0.2531	0.8699	7(1)
H(172)	0.2887	0.1222	0.7325	6(2)
H(173)	0.3482	0.2393	0.7682	6(2)

Description of the Crystal structure of 5. As we can see from Table 8, **5** and **2** are isostructural, with quite similar overall geometries and dimensions involving the ligands and the copper centers. This molecule is also planar, with atomic mean deviation from the least-square plane of 0.163 Å, which

Table 6. The Final Atomic Coordinates and Equivalent Isotropic Thermal Parameters for **4**

Atom	*x*	*y*	*z*	$B_{eq}/Å^2$
Cu(1)	0.0507(1)	0.14861(5)	0.22457(9)	3.26(2)
Cl(1)	0.3230(3)	0.2500	0.5133(3)	3.75(5)
F(1)	0.0926(8)	−0.1639(3)	0.1890(10)	11.4(2)
F(2)	0.1999(9)	−0.0912(4)	0.0414(6)	9.7(2)
F(3)	0.3166(6)	−0.1008(3)	0.2542(6)	7.7(2)
O(1)	0.1428(6)	0.0459(3)	0.1859(5)	4.1(1)
O(3)	−0.0477(8)	0.2500	0.2477(7)	3.6(1)
O(4)	0.2989(8)	0.1791(3)	0.4251(7)	7.1(2)
O(5)	0.202(1)	0.2500	0.611(1)	9.5(3)
O(6)	0.4879(9)	0.2500	0.5947(8)	5.2(2)
N(1)	−0.1348(6)	0.1068(3)	0.3180(6)	3.3(1)
N(3)	0.2061(6)	0.2090(3)	0.0994(5)	3.0(1)
C(1)	−0.168(1)	0.2500	0.345(2)	5.9(3)
C(2)	−0.2432(9)	0.1726(4)	0.3623(9)	4.6(2)
C(3)	−0.1733(8)	0.0306(4)	0.3328(8)	3.6(1)
C(4)	−0.0693(9)	−0.0317(4)	0.2841(8)	4.0(2)
C(5)	0.0706(9)	−0.0203(4)	0.2193(8)	3.8(2)
C(6)	0.3030(9)	0.1690(4)	0.0171(8)	4.3(2)
C(7)	0.4063(9)	0.2094(5)	−0.0702(8)	4.9(2)
C(8)	−0.327(1)	0.0038(5)	0.3945(9)	5.5(2)
C(9)	0.171(1)	−0.0942(4)	0.176(1)	4.9(2)
H(1)	−0.0844	0.2500	0.4406	5.7
H(4)	−0.1032	−0.0866	0.3000	4.6
H(6)	0.2985	0.1099	0.0163	5.7
H(7)	0.4778	0.1803	−0.1298	5.7
H(21)	−0.2676	0.1631	0.4595	5.7
H(22)	−0.3513	0.1723	0.2994	5.1
H(81)	−0.3274	0.0247	0.4909	6.0
H(82)	−0.4291	0.0251	0.3360	6.0
H(83)	−0.3369	−0.0535	0.3963	4.9

is slightly bigger than those of **2** and **4**. Cu(1) lies 0.058 Å below its coordination plane, while Cu(2) lies 0.074 Å above its coordination plane. The dihedral angle between the coordination planes is 1.40°. The copper–copper separation is 3.368(2) Å with an angle of 128.8(4)° at the bridging oxygen. The counter anion ClO_4^- was found far from the two copper centers and one water molecule was located.

The molecular structures of **2**, **4**, and **5** can be compared with those of dinuclear, alkoxo-bridged copper(II) complexes of tetradentate (N_4) phthalazine and pyridazine ligands reported by Thompson et al. and Mazurek et al.[1,5—8,14] Their copper–copper separations and Cu–O(H)–Cu bridge angles are in the same range. Although the magnitude of the antiferromagnetic exchange did not vary in a linear manner with the alkoxo-bridge angle, the increase of the antiferromagnetic exchange interaction is coherent with the increase of the Cu–O–Cu bridge angles, indicating the role of the alkoxo-bridge as one of the principal exchange pathways. At the same time, the coplanarity of two coordination planes of copper(II) ions is also shown to correlate with the antiferromagnetic exchange. The other reason for the relatively weak antiferromagnetic exchange in **4** compared with those of **2** and **5** may be the relatively great dihedral angle between the two copper coordination planes in the complexes. As it is considered that the ground state of each copper-

Table 7. The Final Atomic Coordinates and Equivalent Isotropic Thermal Parameters for **5**

Atom	*x*	*y*	*z*	$B_{eq}/Å^2$
Cu(1)	0.4207(2)	−0.0274(1)	0.3143(2)	4.78(5)
Cu(2)	0.0658(2)	−0.0583(1)	0.1305(2)	4.33(5)
Cl(1)	0.7126(4)	0.3116(3)	0.2979(5)	7.1(1)
O(1)	0.6086(7)	0.0476(6)	0.4455(9)	5.7(2)
O(2)	−0.1019(7)	−0.0159(5)	0.0862(8)	4.6(2)
O(3)	0.2347(7)	−0.0987(6)	0.1850(9)	4.9(2)
O(4)	0.705(2)	0.322(1)	0.428(2)	18.6(7)
O(5)	0.611(2)	0.343(1)	0.210(2)	23.5(8)
O(6)	0.846(1)	0.364(1)	0.331(2)	20.0(8)
O(7)	0.697(2)	0.218(1)	0.221(2)	20.6(8)
O(8)	0.979(6)	0.477(3)	0.758(7)	18(3)
N(1)	0.470(1)	−0.1418(7)	0.246(1)	4.7(3)
N(2)	−0.0265(9)	−0.1894(7)	0.018(1)	4.1(2)
N(3)	0.3371(9)	0.0879(7)	0.343(1)	3.8(2)
N(4)	0.1894(8)	0.0718(7)	0.281(1)	3.7(2)
C(1)	0.219(2)	−0.192(1)	0.117(2)	11.4(6)
C(2)	0.347(1)	−0.223(1)	0.151(2)	6.5(4)
C(3)	0.602(1)	−0.149(1)	0.268(1)	4.9(4)
C(4)	0.721(1)	−0.068(1)	0.343(1)	5.1(4)
C(5)	0.720(1)	0.019(1)	0.429(2)	5.5(4)
C(6)	0.417(1)	0.1750(9)	0.421(1)	4.1(3)
C(7)	0.366(1)	0.2532(9)	0.451(1)	4.0(3)
C(8)	0.453(1)	0.347(1)	0.537(2)	5.8(4)
C(9)	0.392(2)	0.422(1)	0.568(2)	6.7(4)
C(10)	0.243(2)	0.403(1)	0.522(2)	6.3(4)
C(11)	0.158(1)	0.312(1)	0.436(1)	5.4(4)
C(12)	0.216(1)	0.2368(9)	0.401(1)	4.6(3)
C(13)	0.137(1)	0.143(1)	0.313(1)	4.4(3)
C(14)	−0.228(1)	−0.071(1)	0.022(1)	5.1(4)
C(15)	−0.261(1)	−0.170(1)	−0.046(1)	4.2(3)
C(16)	−0.165(1)	−0.2276(9)	−0.048(1)	4.4(3)
C(17)	0.075(1)	−0.2503(9)	0.018(2)	6.2(4)
C(18)	0.628(1)	−0.242(1)	0.200(2)	6.3(4)
C(19)	0.856(1)	0.100(1)	0.513(2)	7.3(5)
C(20)	−0.346(1)	−0.0238(9)	0.017(1)	5.2(3)
C(21)	−0.228(1)	−0.3336(9)	−0.125(2)	6.6(4)
H(1)	0.2283	−0.1763	0.0175	5.0
H(4)	0.8063	−0.0745	0.3344	6.1
H(6)	0.5170	0.1837	0.4599	6.2
H(8)	0.5542	0.3592	0.5717	6.9
H(9)	0.4504	0.4851	0.6193	8.0
H(10)	0.2018	0.4532	0.5480	7.7
H(11)	0.0568	0.3001	0.3982	6.5
H(13)	0.0317	0.1290	0.2699	5.2
H(15)	−0.3600	−0.2012	−0.0985	5.0
H(21)	0.3364	−0.2626	0.2051	14.8
H(22)	0.3604	−0.2586	0.0684	7.6
H(81)	0.9990	0.5394	0.7583	4.0
H(82)	0.8940	0.4696	0.7674	4.0
H(171)	0.0565	−0.2843	−0.0820	5.0
H(172)	0.0618	−0.2949	0.0639	7.5
H(181)	0.7271	−0.2332	0.2887	7.6
H(182)	0.5767	−0.2621	0.0970	7.6
H(183)	0.5958	−0.2868	0.2374	7.6
H(191)	0.9319	0.0761	0.4983	8.5
H(192)	0.8426	0.1495	0.4746	8.5
H(193)	0.8784	0.1210	0.6143	8.5
H(201)	−0.4347	−0.0708	−0.0333	6.1
H(202)	−0.3472	0.0188	−0.0361	6.1
H(203)	−0.3316	0.0102	0.1140	6.1
H(211)	−0.1944	−0.3645	−0.0550	7.9
H(212)	−0.2004	−0.3557	−0.2020	7.9
H(213)	−0.3293	−0.3469	−0.1649	7.9

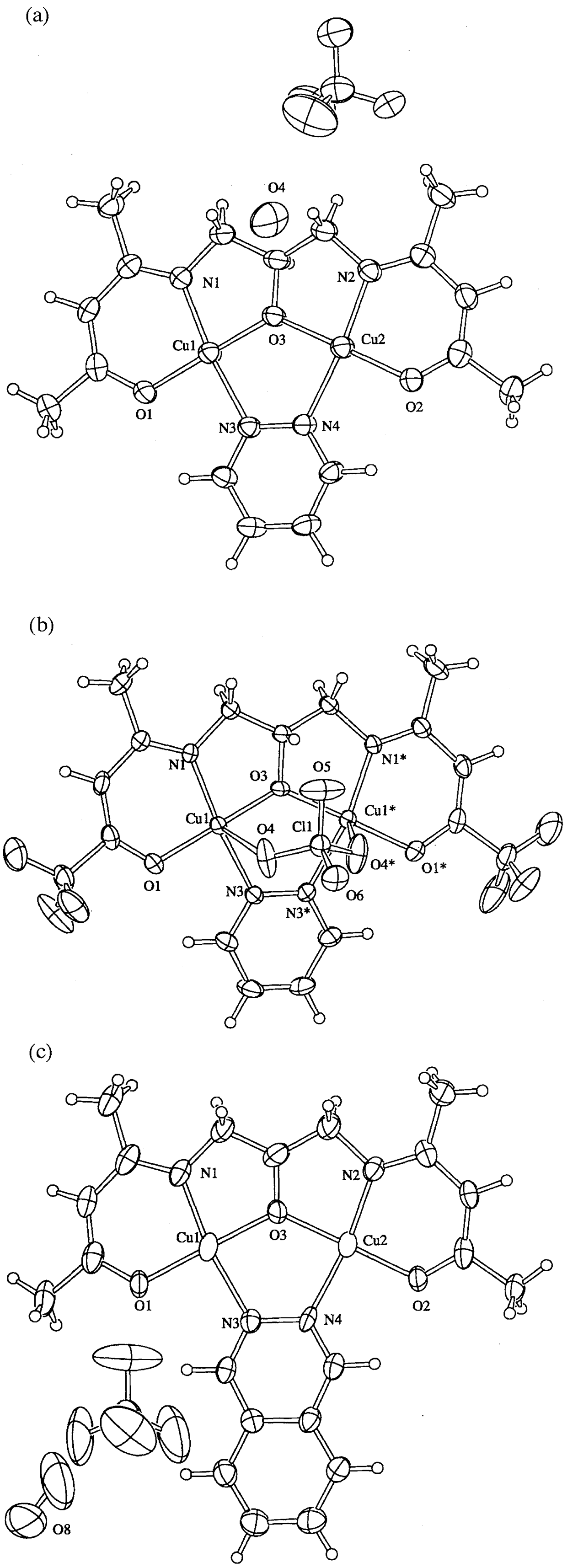
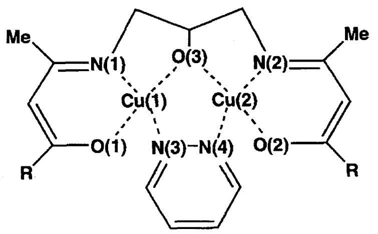


Fig. 2. Molecular structures of complexes **2**, **4**, and **5** shown by the 30% probability thermal ellipsoids for non-hydrogen atoms. (a) **2**; (b) **4**; (c) **5**.

Table 8. Selected Bond Distances(Å) and Angles(deg) in **2**, **4**, and **5**



	2	**4**	**5**
Bond distances			
Cu(1)–O(1)	1.878(4)	1.892(4)	1.890(6)
Cu(1)–O(3)	1.857(4)	1.865(3)	1.857(6)
Cu(1)–N(1)	1.924(5)	1.935(5)	1.90(1)
Cu(1)–N(3)	2.054(5)	2.060(5)	2.05(1)
Cu(2)–O(2)	1.882(4)		1.881(8)
Cu(2)–O(3)	1.873(4)		1.877(8)
Cu(2)–N(2)	1.920(6)		1.908(9)
Cu(2)–N(4)	2.057(6)		2.036(8)
Cu(1)–N(2)	3.367(2)	3.331(2)	3.368(2)
Bond angles			
O(1)–Cu(1)–O(3)	178.2(2)	175.6(2)	178.7(4)
O(1)–Cu(1)–N(1)	96.7(2)	96.1(2)	97.0(4)
O(1)–Cu(1)–N(3)	92.2(2)	92.6(2)	92.2(3)
O(3)–Cu(1)–N(1)	84.7(2)	84.7(2)	84.2(4)
O(3)–Cu(1)–N(3)	86.4(2)	85.9(2)	86.6(3)
N(1)–Cu(1)–N(3)	170.2(2)	167.1(2)	168.2(4)
O(2)–Cu(2)–O(3)	178.3(2)		177.0(4)
O(2)–Cu(2)–N(2)	96.2(2)		96.4(4)
O(2)–Cu(2)–N(4)	93.1(2)		92.2(3)
O(3)–Cu(2)–N(2)	84.8(2)		84.8(4)
O(3)–Cu(2)–N(4)	85.7(2)		86.2(3)
N(2)–Cu(2)–N(4)	166.7(2)		168.8(4)
Cu(1)–O(3)–Cu(2)	129.1(2)	126.5(4)	128.8(4)

(II) has a $d_{x^2-y^2}$ configuration, the stronger antiferromagnetic interaction in **2** and **5** is due to the facts that the coordination geometry around each copper(II) is planar and two nitrogens of pyridazine and an alkoxo oxygen bridge the two coordination planes resulting in their coplanarity. The EPR-nondetectable metazidohemocyanin was prepared for the molluscs by ligand displacement of peroxide from oxyhemocyanin with sodium azide.[26] The strong antiferromagnetic coupling exists in the metazidohemocyanin. From the magnet-structural relationship in dinuclear copper(II) complexes described above, one may considered that in the active site of the metazidohemocyanin two basal planes around copper(II) ions are nearly coplanar and two magnetic orbitals are strongly antiferromagnetically coupled through the bridging ligands to give an EPR-nondetectable property.

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