Structures and Magnetic Properties of Dinuclear Copper(II) Complexes Containing a Bulky Diamine Ligand, 1,2-Dipiperidinoethane

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A reaction of copper(II) perchlorate with a sterically hindered diamine, 1,2-dipiperidinoethane (dipe), yields two dinuclear complexes: di-μ-hydroxo dinuclear complex [{Cu(ClO$_4$)(dipe)(μ-OH)}$_2$] (**1**) and di-μ-alkoxo dinuclear complex [{Cu(ClO$_4$)(dipe-O)}$_2$] (**2**) (dipe-O$^-$ is 1-(2-piperidinoethyl)piperidin-3-olate which was newly obtained in this work). The structures of complexes **1** and **2** were confirmed by X-ray crystallography. Complex **2** is meso form containing (*R*)- and (*S*)-dipe-O$^-$. Dipe-O$^-$ acts as a tridentate ligand with an N,N,O-donor set and bridges two copper(II) ions through the oxygen atom. The oxygen atom is incorporated into dipe from atmospheric molecular oxygen during the reaction of dipe with copper ion. The temperature dependences of $\chi_m T$ values were different between **1** and **2** depending on the bridging structures. Complex **1** shows ferromagnetic interaction and the value of $2J = 117\,\mathrm{cm^{-1}}$ is in agreement with that predicted from the ∠Cu–O–Cu bridging angle of 96.9°. Complex **2**, the bridging angle of which is 100.59°, shows a strong antiferromagnetic interaction ($-2J > 400\,\mathrm{cm^{-1}}$). The singlet–triplet energy gap for complex **2** was estimated from DFT calculation.

In the designing of multi-nuclear complexes, steric repulsion of bulky ligands often plays an important role to form a multinuclear complex in the presence of small co-ligands. For example, a small copper(II) ion forms a mono-nuclear complex [Cu(en)$_2$]$^{2+}$ with small en ligands (en denotes ethylenediamine), while it easily forms a di-μ-hydroxo dinuclear complex [(diam)Cu(OH)$_2$Cu(diam)]$^{2+}$ with a sterically hindered N-alkylated diamine (diam): [{Cu(tmen)(μ-OH)}$_2$](ClO$_4$)$_2$ and [{Cu(teen)(μ-OH)}$_2$](ClO$_4$)$_2$ where tmen is *N*,*N*,*N*′,*N*′-tetramethylethylenediamine[1] and teen is *N*,*N*,*N*′,*N*′-tetraethylethylenediamine,[2] respectively. We have used these di-μ-hydroxo dinuclear copper(II) complexes as the starting compounds in synthesizing the mixed ligand complexes. This synthetic method is rather convenient because no by-product is produced as shown in eq 1, where HL is a mono-protonated bidentate ligand such as 1,3-diketone (Hdike) and amino acid, and X is a mono-anion.[3,4]

$$[\{\mathrm{Cu(diam)}(\mu\text{-OH})\}_2]\mathrm{X}_2 + 2\mathrm{HL} \rightarrow 2[\mathrm{Cu(diam)L}]\mathrm{X} + 2\mathrm{H_2O} \quad (1)$$

A number of studies have been reported on magnetic properties of di-μ-hydroxo dinuclear copper(II) complexes and di-μ-alkoxo dinuclear copper(II) complexes since the 1970s.[1,2,5–10] These studies revealed that the magnetic interaction between two copper(II) ions is rather sensitive to the geometry of the Cu$_2$O$_2$ moiety and that the value of exchange integral (*J*) exhibits a negative linear relationship with the Cu–O–Cu bridging angle (ϕ). The authors interpreted their results in terms of superexchange interaction between the two copper(II) ions via the Cu–O–Cu bridges. Theoretical approaches have been also performed toward understanding the magnetic interaction in this system.[7–10] Some complexes exhibit deviation from the linear relationship described above, suggesting the presence of other structural factors which affects the *J* value. The counter anion may also influence the magnetic interaction. To clarify the relationship between structures and magnetic behaviors in this series of dinuclear copper(II) complexes, further experimental research with new complexes is important.

In the present study, we focused on the di-μ-hydroxo dinuclear copper(II) complex containing 1,2-dipiperidinoethane (dipe, Figure 1) in order to understand the steric effect of dipe on the structure and the magnetic properties of the complex. Dipe is a bulky and rigid ligand due to two piperidine rings and a unique steric effect is observed in some complexes.[11,12] The structure and the magnetic properties of purple complex **1**, [{Cu(ClO$_4$)(dipe)(μ-OH)}$_2$] are reported in comparison to analogous di-μ-hydroxo dinuclear copper(II) complexes. Interestingly, a green compound was obtained as a minor product in the synthesis of complex **1**. The compound was identified to be complex **2**, [{Cu(ClO$_4$)(dipe-O)}$_2$] (dipe-O$^-$ = 1-(2-piperidinoethyl)piperidin-3-olate, Figure 1) by sin-

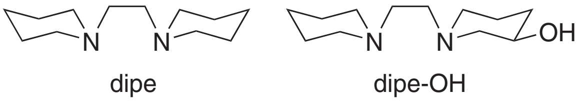

Figure 1. Dipe and dipe-OH ligands.

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gle-crystal X-ray structural analysis. The magnetic properties of **2** were also investigated. In addition, we mention the formation pathway of **2**, which involves novel copper-mediated oxygenation of the ligand.

Experimental

Materials. Copper(II) perchlorate, dipe ligand, and other chemicals were purchased from Wako Pure Chemical Industries, Ltd., KANTO CHEMICAL Co., and Sigma-Aldrich Co., and were used without further purification. Stable isotope $^{18}O_2$ gas (99% isotopic purity) was obtained from ISOTEC, Sigma-Aldrich Co.

Physical Measurements. Elemental analyses (C, H, N) were measured on a Perkin-Elmer 2400 II CHN analyzer. IR spectra were obtained as KBr pellets on a Perkin-Elmer FT-IR SPECTRUM 2000. Mass spectra were obtained on a JEOL JMS-700 Mstation in the Fast Atom Bombardment (FAB) mode using ultramark as standard and 3-nitrobenzyl alcohol (NBA) as matrix. Thermal analyses (TG-DTA) were carried out using a Shimadzu thermal analyzer (DTG-50). Magnetic data were measured on a Shimadzu Torsion Magnetometer MB-100 at room temperature and a Quantum Design MPMS 5S for temperature variation measurement under 1 T. ^{1}H (400 MHz) and ^{13}C (100.4 MHz) NMR spectra were obtained on a JEOL JNM-AL400 spectrometer. Diffuse reflectance spectra were obtained on a Shimadzu UV-3600PC Spectrophotometer at room temperature.

Synthesis of Complexes. Complex **1** was prepared according to the method reported for a similar tmen complex.[1] $Cu(ClO_4)_2\cdot 6H_2O$ (7.448 g, 20 mmol) was dehydrated with 12 mL of 2,2-dimethoxypropane. Dipe (7.487 g, 40 mmol) and ethanol (40 mL) were added to the solution while stirring. The blue-violet precipitate was filtered and recrystallized from acetonitrile–benzene. The crystal contained benzene molecules which were lost immediately in the air. The sample was dried in vacuo and then used in all measurements other than X-ray structure analysis. Yield 88% (complex **1**). From the concentrated filtrate, green crystals were obtained. Yield 6% (complex **2**).

$[\{Cu(ClO_4)(dipe)(\mu\text{-}OH)\}_2]$ (**1**). Anal. Found: C, 38.47; H, 6.76; N, 7.42%. Calcd for $C_{24}H_{50}Cl_2Cu_2N_4O_{10}$: C, 38.30; H, 6.70; N, 7.44%. λ_{max}(solid): 567 nm. FAB$^+$ MS: m/z 276, $[Cu_2(dipe)_2(OH)_2]^{2+}$; 197, $[dipe + H]^+$; 195, $[dipe - H]^+$. μ_{eff} at 293 K: 1.88 BM.

$[\{Cu(ClO_4)(dipe\text{-}O)\}_2]$ (**2**). Anal. Found: C, 38.51; H, 6.30; N, 7.44%. Calcd for $C_{24}H_{46}Cl_2Cu_2N_4O_{10}$: C, 38.50; H, 6.19; N, 7.48%. λ_{max}(solid): 682, 381 nm. FAB$^+$ MS: m/z 649, $[Cu_2(dipe\text{-}O)_2ClO_4]^+$; 548, $[Cu_2(dipe\text{-}O)_2]^+$; 275, $[Cu_2(dipe\text{-}O)_2]^{2+}$; 213, $[dipe\text{-}OH + H]^+$; 211, $[dipe\text{-}OH - H]^+$. μ_{eff} at 293 K: 1.00 BM.

Isolation of the Ligand Molecule Dipe-OH from Complex 2. Aqueous ammonia was added to a water suspension of **2**, then copper(II) ions dissolved in water as deep blue-colored $[Cu(NH_3)_4]^{2+}$. From the solution, dipe-OH was extracted with chloroform and dried with magnesium sulfate. After removing the solvent, yellow oil was obtained. FAB$^+$ MS: m/z 213, $[dipe\text{-}OH + H]^+$; 211, $[dipe\text{-}OH - H]^+$. Spectra of ^{1}H NMR in CD_3OD and ^{13}C NMR in $CDCl_3$ are shown in Figures S1 and S2, respectively, in Supporting Information.

Labeling Experiment. A flask containing $Cu(ClO_4)_2\cdot 6H_2O$ (0.372 g, 1 mmol) and 5 mL of 2,2-dimethoxypropane was flushed with $^{18}O_2$ gas. The green solution and purple precipitate were formed after addition of dipe (0.392 g, 2 mmol). The purple precipitate was filtered, and the green powder was obtained by concentration of the filtrate under reduced pressure. FAB$^+$ MS spectra were measured for both of two products. Purple powder: m/z 276, $[Cu_2(dipe)_2(OH)_2]^{2+}$; 197, $[dipe + H]^+$; 195, $[dipe - H]^+$. Green powder: m/z 277, $[Cu_2(dipe\text{-}^{18}O)_2]^{2+}$; 215, $[dipe\text{-}^{18}OH + H]^+$; 213, $[dipe\text{-}^{18}OH - H]^+$.

X-ray Crystallography. X-ray data of complex **1** were collected on a Mac Science M03XHF four-circle diffractometer with graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) at 298 K. The structure was solved by the direct method using SIR92,[13] and refined by full-matrix least-square techniques with SHELXL97.[14] All non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters. All calculations were performed using maXus[15] and WinGX.[16]

X-ray data of complex **2** were collected on a Bruker Smart APEX CCD diffractometer with graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) at 100 K. The structure was solved by the direct method using SHELXS97[17] and refined using least-squares methods on F^2 with SHELXL97.[14] All non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters. All calculations were performed using Bruker SMART.[18]

Crystallographic data and refinement parameters are listed in Table 1. Crystal data have been submitted to CCDC; the document numbers are 711121 (**1**) and 711122 (**2**). Copies of this information may be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing: data_request@ccdc.cam.ac.uk, or contacting CCDC, 12, Union Road, Cambridge, CB2 1EZ, U.K. [Fax: +44 1223 336033].

DFT Calculation. The 2J value of complex **2** was estimated in the structure obtained by X-ray analysis. The energies of triplet state and broken-symmetry singlet state were calculated by UB3LYP method. 6-31G* basis set was used for carbon and hydrogen atoms, 6-311+G* for nitrogen and oxygen atoms and TZVP for copper atom. All calculations were carried out by the Gaussian 03 program (Research Center for Computational Science, Okazaki, Japan).[19]

Table 1. Crystallographic Data

Complex	$1\cdot 2C_6H_6$	2
Crystal color	Purple	Green
Formula	$C_{36}H_{62}Cl_2Cu_2N_4O_{10}$	$C_{24}H_{46}Cl_2Cu_2N_4O_{10}$
Formula weight	908.88	748.63
Cystal dimensions/mm^3	0.25 × 0.25 × 0.15	0.25 × 0.20 × 0.15
Crystal system	Monoclinic	Monoclinic
Space group	$C2/m$	$P2_1/c$
a/Å	12.645(6)	9.5343(14)
b/Å	14.619(7)	10.7150(15)
c/Å	11.690(5)	14.678(2)
β/°	107.80(3)	107.150(15)
V/Å^3	2057.5(16)	1468.7(4)
Z	2	2
D_{calcd}/Mg m^{-3}	1.467	1.693
F(000)	956	780
μ/mm^{-1}	1.222	1.692
No. of observations	1750	4273
Parameters	140	190
R_1 ($I > 2\sigma(I)$)	0.0794	0.0415
R_w (all data)	0.1823	0.0877
S	1.054	0.882

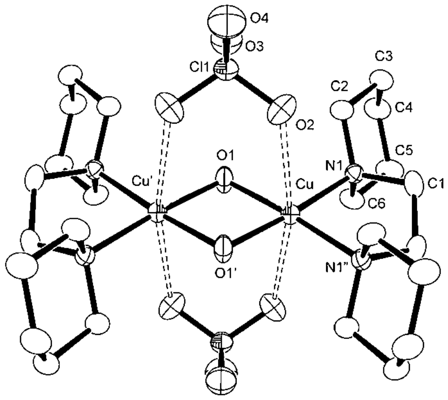

Figure 2. ORTEP drawing (30% probability) of **1**. Hydrogen atoms and two benzene molecules are omitted for clarity.

Results and Discussion

Identification of Green Crystals. The reaction of copper(II) perchlorate with dipe gave a green-colored complex as a minor product in addition to the major product, $[\{Cu(ClO_4)(dipe)(\mu\text{-}OH)\}_2]$ (**1**). The formation of the green complex was reproducible in several synthetic experiments, although the yield was low. This complex was identified to be $[\{Cu(ClO_4)(dipe\text{-}O)\}_2]$ (**2**) where dipe-O^- denotes 1-(2-piperidinoethyl)piperidin-3-olate by the X-ray structure analysis (vide infra). The formation of a C–O bond at the 3-position in one piperidine ring of the dipe ligand was further confirmed by isolation of dipe-OH, which was identified by ^1H and ^{13}C NMR spectra (see Experimental).

In order to clarify the mechanism of formation of complex **2**, particularly for the oxygen source of the ligand oxygenation, we carried out the following experiments. A similar reaction under N_2 produced only **1**, not **2**. The reaction under $^{18}O_2$ produced ^{18}O-incorporated complex **2**, $[\{Cu(ClO_4)(dipe\text{-}^{18}O)\}_2]$. Stirring a solution of dipe itself in 2,2-dimethoxypropane under air (without copper(II) salt) did not produce dipe-OH. These results reveal that the origin of the oxygen atom is molecular oxygen O_2 from the atmosphere, neither H_2O nor OH^- and that the presence of copper ion is necessary for oxygenation of dipe. In TG-DTA, no reaction was observed other than the decomposition at 202 °C for **1** and 222 °C for **2**. So the interconversion between **1** and **2** does not occur in the solid state. When a solution of isolated complex **1** in 2,2-dimethoxypropane was kept under air at room temperature, no formation of **2** was observed. These suggest that **2** may be formed by reaction of an intermediate leading to **1** with oxygen. The formation of dipe-OH is a novel type of oxygen-atom insertion into a C–H bond involving a copper complex. The reaction may be applicable to other diamines such as 1-(2-dimethylaminoethyl)piperidine (dmaepip).[20]

X-ray Crystal Structures. Complex 1: Figure 2 shows the molecular structure of **1**. Selected bond lengths and angles are listed in Table 2. Complex **1** possesses a crystallographic mirror plane, on which O1, Cl1, O3, and O4 are located, and a two-fold axis passing through the Cu···Cu axis. Each copper atom is coordinated by two oxygen atoms of bridging hydroxo ions (coordination distance is 1.942(5) Å) and two nitrogen atoms of dipe ligand (2.039(5) Å), and weakly coordinated by two oxygen atoms of perchlorate ions at axial sites (2.896(6) Å) to give an elongated octahedral structure. All four piperidine rings adopt a chair form. The perchlorate ion bridges the two copper atoms as a bidentate ligand, however the bond distance was much longer than the reported Cu–$OClO_3$ distances in analogous di-μ-hydroxo dinuclear copper(II) complexes (Table 3 in the section of magnetic properties). As a result, the four Cl–O distances are similar. Other bond lengths around the copper centers and the Cu···Cu separation are similar to analogs listed in Table 3. Among the N-alkylated ethylenediamine (tmen, teen, and dipe) complexes, complex **1** has the longest Cu–N bond distances due to the steric repulsion of piperidine rings.

Table 2. Selected Bond Lengths/Å and Angles/°

1[a)]			
Cu–O1	1.942(5)	Cu–O1–Cu′	96.9(3)
Cu–N1	2.039(5)	N1–Cu–N1″	87.3(3)
Cu–O2	2.896(6)	O1–Cu–O1′	83.1(3)
Cl1–O2	1.428(6)	O1–Cu–N1	95.0(2)
Cl1–O3	1.436(8)	O1–Cu–N1″	175.4(3)
Cl1–O4	1.416(8)		
Cu···Cu′	2.907(3)		
2[b)]			
Cu–O1	1.9440(16)	Cu–O1–Cu′	100.59(8)
Cu–O1′	1.9279(17)	O1–Cu–N2	84.03(7)
Cu–N1	2.037(2)	N1–Cu–N2	87.70(8)
Cu–N2	2.015(2)	N1–Cu–O1′	104.31(8)
Cu–O3	2.4751(17)	O1–Cu–O1′	79.41(8)
Cl1–O2	1.4399(17)	O1–Cu–N1	161.73(7)
Cl1–O3	1.4616(18)	N2–Cu–O1′	159.10(8)
Cl1–O4	1.4396(19)		
Cl1–O5	1.4367(17)		
Cu···Cu′	2.9788(7)		

a) Prime and double prime refer to the equivalent positions, operating $-x$, $-y$, $-z$ and $-x$, y, $-z$, respectively. b) Prime refers to the equivalent position, operating $-x + 1$, $-y$, $-z$.

Complex 2: Figure 3 shows the molecular structure of **2**. Selected bond lengths and angles are listed in Table 2. Complex **2** consists of two asymmetric units which were related by the inversion center at the midpoint of Cu···Cu. The two nitrogen atoms of dipe-O^- coordinate to each copper center (Cu–N1 = 2.037(2) Å, Cu–N2 = 2.015(2) Å). The carbon atom at the 3-position of one piperidine (C9) was oxygenated and this oxygen atom bridges the two copper atoms (Cu–O1 = 1.9440(16) Å, Cu–O1′ = 1.9279(17) Å). C9 is a chiral carbon and complex **2** contains one (*R*)-dipe-O^- and one (*S*)-dipe-O^-. Monodentate perchlorate ion occupies the axial site of the copper atom (Cu–O3 = 2.4751(17) Å), and consequently, the copper is in a square-pyramidal coordination. The copper atom is located 0.2779(7) Å above the N_2O_2 mean plane toward the perchlorate oxygen atom. All the copper–donor bond lengths are in the region of the values observed in similar tridentate diaminoalcoholate (N,N,O-donor set) dinuclear complexes.[29] The Cu···Cu separation of 2.9788(7) Å is also similar to analogs (2.939–3.045 Å).[29,30] The μ-alkoxo dinuclear com-

Table 3. Comparison of the Structural and Magnetic Parameters in $Cu_2(L)_2(\mu\text{-}OH)_2X_2$

L–X	Cu coord. no.	Cu–X/Å	Cu···Cu/Å	$\phi/°$ a)	$2J/cm^{-1}$	Ref. no.
dipe-ClO_4 (**1**)	6	2.896(6)	2.907(3)	96.9(3)	+117(2)	this work
bipy-ClO_4	6	2.797(4)	2.871(1)	96.6(2)	+99	21,22
eaep-ClO_4 b)	5	2.562(10) 2.618(9)	2.917(5)	98.8(3) 99.5(4)	−130	23
α-dmaep-ClO_4	6	2.716(3) 2.782(2)	2.938(1)	98.35(9)	−4.8	24
β-dmaep-ClO_4	5	2.721(4)	2.935(1)	100.4(1)	−201	25
tmen-ClO_4	4	—	2.966(3)	102.3(4)	−360	1, 5
teen-ClO_4	4	—	2.978(2)	103.0(2)	−410	2
bipy-NO_3	5	2.379(2)	2.847	95.6(1)	+172	26
bipy-1/2SO_4	5	2.207(5) 2.244(5)	2.893(2)	95.9(2) 97.1(2)	+47	22,27
tmen-Br	4	—	3.000(4)	104.08(17)	−509	28

a) O–Cu–O bridging angle. b) eaep = 2-(2-ethylaminoethyl)pyridine.

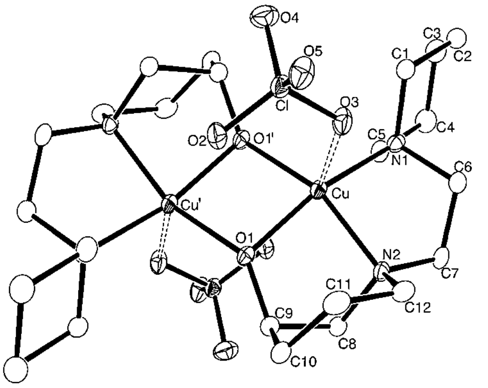

Figure 3. ORTEP drawing (50% probability) of **2**. Hydrogen atoms are omitted for clarity.

plexes with N,N-dialkylated diaminoalcoholate reported by Kida et al. contain at least one six-membered ring,[29] whereas in complex **2**, two five-membered rings neighbor each other with sharing a Cu–N2 bond. This rigidity of the chelating skeleton made the Cu–O1 bond length longer than Cu–O1′. In addition, three carbon atoms in the oxygenated piperidine ring, i.e., C10, C11, and C12 protrude from the Cu_2O_2 plane and the perchlorate ion coordinates from this side in spite of crowding. A hydrogen bond is formed between O3 and H–C11 (2.506 Å) and the hydrogen bond may also stabilize this structure.

Spectroscopic Properties. The solid reflectance spectrum of **1** has an absorption band at 567 nm attributed to d–d transition, which is similar to those of analogous di-μ-hydroxo dinuclear copper(II) complexes.[1,2] Complex **2** showed a charge-transfer band from bridging oxygen to copper at 381 nm in addition to the d–d band at 682 nm. Compared with analogous di-μ-alkoxo dinuclear copper(II) complexes summarized by Kida et al.,[29] the CT absorption band of **2** lies at a similar position, but its λ_{max} of d–d absorption is shifted toward lower energy. In Kida's complexes, N,N-dialkylated diaminoalcoholate ligands, $R_2N(CH_2)_nNH(CH_2)_mO^-$, contain one secondary nitrogen and one tertiary nitrogen, whereas dipe-O^- ligand in **2** contains two tertiary nitrogen atoms in a bulky piperidine ring which might have weaker donor abilities than the secondary nitrogen donor atom. As a result, the ligand field strength of **2** was weakened more than those in other analogs.

Spectral features of IR absorption for each complex can be accounted for in the structure determined by X-ray analyses. A broad ν_{OH} band of the bridging O–H was observed at 3542 cm^{-1} for **1**, which indicates the absence of intramolecular hydrogen bonding. No O–H stretching absorption was observed for **2**. The coordination mode of perchlorate anion can generally be determined by splitting of ν_{ClO_4} appearing around 1100 cm^{-1},[31] since the band is broad in the case of free ion and it splits into multiplets in the case of mono- or bidentate coordination due to the deformation from T_d symmetry. The spectrum of **1** shows a strong and broad band around 1100 cm^{-1}, suggesting that the perchlorate ion exists as a free ion. The four Cl–O bond distances were found to be almost the same due to weak coordination of perchlorate ion from X-ray analysis. Therefore ν_{ClO_4} in **1** is broad like a free ion. The corresponding band in **2** splits into two (1058 and 1108 cm^{-1}), indicating the coordination of perchlorate ion in a monodentate fashion.

Magnetic Properties. Complex 1: The magnetic susceptibility of **1** was measured at various temperatures from 300 to 2 K. The χ_mT–T plot is shown in Figure 4. The susceptibilities were fitted to the Bleaney–Bowers eq 2, where T.I.P. is the temperature-independent paramagnetism and fixed at 0.00012 emu mol^{-1} for two copper(II) ions.[32]

$$\chi_m T = \frac{Ng^2\beta^2}{3k}[1 + 1/3\exp(-2J/kT)]^{-1} + \text{T.I.P.} \quad (2)$$

The best fit values for the parameters are $g = 2.07(2)$ and $2J = 117(2)$ cm^{-1}, indicating a presence of a ferromagnetic interaction between the copper(II) ions. The magnetic parameters of **1** and analogous complexes are listed in Table 3 together with structural parameters. The $2J$ values are plotted against the Cu–O–Cu bridging angle (ϕ) in Figure 5. The $2J$ value of **1** roughly follows the linear tendency of the other di-μ-hydroxo dinuclear copper(II) complexes, however it is slightly larger than the expected value from the Cu–O–Cu bridging angle of $\phi = 96.9(3)°$ using eq 3 proposed by Hatfield et al.[5]

$$2J = -74.53\phi + 7270 \quad (3)$$

Ruiz et al. reported additionally that the $2J$ value is also influenced by the planarity of bridging oxygen atoms (τ,

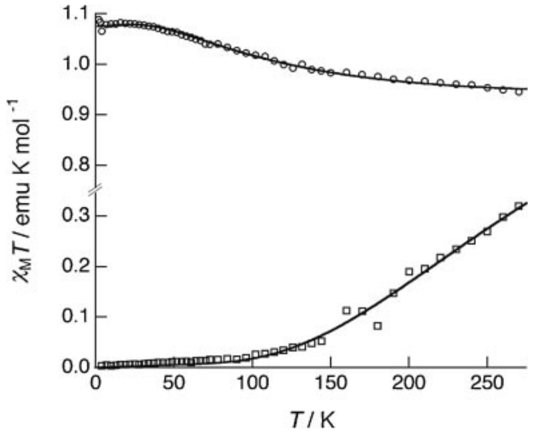

Figure 4. $\chi_m T$–T plots for **1** (○) and for **2** (□). The solid lines are the theoretical curves using the $2J$ values of 117 cm^{-1} for **1** and −400 cm^{-1} for **2**, respectively.

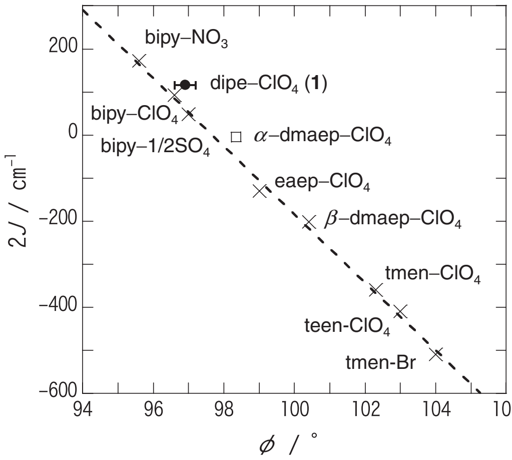

Figure 5. $2J$–ϕ plots of analogous complexes $Cu_2(diam)_2(OH)_2X_2$: diam-X. The dashed regression line was calculated by using × marked value.

defined in Figure 6), the deviation of the copper atom from the least-square plane of N_2O_2 donor atoms (b) and the bending of the Cu_2O_2 plane (γ, defined in Figure 6).[7,8] These parameters for **1** are $\tau = 1.03°$, $b = 0.07$ Å and $\gamma = 0°$, indicating the high planarity around both of the copper and bridging oxygen. These structural parameters, therefore, cannot account for the slightly larger $2J$ value. Hatfield et al. reported that $[\{Cu(ClO_4)(dmaep)(\mu\text{-}OH)\}_2]$ (dmaep = 2-(2-dimethylaminoethyl)pyridine) is dimorphic: α-form, in which two perchlorate ions are bidentate and bridge two copper atoms, and β-form, in which each perchlorate ion coordinates as a monodentate to each copper.[23,24] The magnetic properties of α-form and β-form show slight difference, and the authors focused on the number of bridges between two copper atoms suggesting that the additional bridges enhance the superexchange interaction.[5,23,24] The same explanation can be applied to **1**. We tried to synthesize another form of **1** in which two perchlorate ions were non-coordinated or monodentate by recrystallization from different solvents, but no such crystals have been obtained yet.

Complex 2: The $\chi_m T$–T plot in Figure 4 indicates that complex **2** is strongly antiferromagnetic ($-2J > 400$ cm^{-1}). Analysis was attempted according to eq 2, but accurate parameters could not be obtained from the data in the temperature range investigated. The $2J$ value was estimated from DFT calculation as the difference in energy between the broken-symmetry singlet and the triplet states with the structure obtained by X-ray analysis. The J values were calculated with eq 4 proposed by Yamaguchi et al.[33] and Kida et al.[7]

$$J = -(E_t - E_s)/(\langle S^2\rangle_t - \langle S^2\rangle_s) \tag{4}$$

In this equation, E_t and E_s are energies for the triplet and singlet states, respectively, and $\langle S^2\rangle_t$ and $\langle S^2\rangle_s$ are the spin eigenvalues of $\hat{S}^2$ for the triplet and singlet states, respectively. The results obtained are: $E_t - E_s = 315$ cm^{-1}, $\langle S^2\rangle_t = 2.0057$, and $\langle S^2\rangle_s = 0.9535$, consequently $-2J = 559$ cm^{-1}. This value lies in the range of the parameters found in earlier study of di-μ-alkoxo copper(II) dinuclear complexes, $-2J = 430$–860 cm^{-1}, $\phi = 98.4$–$104.8°$.[7–9,20] In addition, the relationship between the calculated $2J$ value and the Cu–O–Cu angle determined by X-ray analysis ($\phi = 100.59(8)°$) follows the tendency of μ-alkoxo copper(II) dinuclear complexes studied by Merz and Haase.[6]

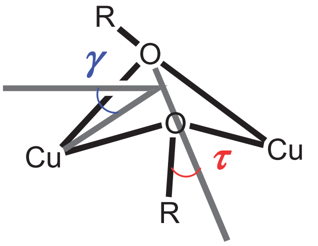

Figure 6. Definition of structural parameters employed by Ruiz et al.

Conclusion

The reaction of bulky 1,2-dipiperidinoethane (dipe) and copper(II) perchlorate produced the di-μ-hydroxo complex, $[\{Cu(ClO_4)(dipe)(\mu\text{-}OH)\}_2]$ as the main product and the di-μ-alkoxo complex, $[\{Cu(ClO_4)(dipe\text{-}O)\}_2]$ as the minor product. The di-μ-hydroxo complex presents ferromagnetic interaction and the $2J$ value is in rather good agreement with the value predicted from the relationship between $2J$ and the Cu–O–Cu bridging angle reported before. In contrast, di-μ-alkoxo complex shows antiferromagnetic interaction as analogous di-μ-alkoxo dinuclear copper(II) complexes. Dipe-OH ligand in the di-μ-alkoxo complex was produced by the oxygenation of only one piperidine ring under mild conditions through the copper complex by uptaking oxygen from air.

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Supporting Information

^{1}H and ^{13}C NMR spectra of free dipe-OH are shown in Figures S1 and S2. These materials are available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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20 Unpublished preliminary experiment. The reaction of $Cu(ClO_4)_2 \cdot 6H_2O$ with dmaepip gave a green complex as a minor product in addition to the purple major product $Cu_2(ClO_4)_2(dmaepip)_2(OH)_2$. FAB$^+$ MS spectra were measured for both of two products. Purple powder: m/z 475, $[Cu_2(dmaepip)_2(OH)_2]^+$; 157, $[dmaepip + H]^+$; 155, $[dmaepip - H]^+$. Green powder: m/z 173, this peak is equal to the m/z value of $[dmaepip\text{-}OH + H]^+$.

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