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Control of Intramolecular Ether-Oxygen Coordination in the Crystal Structure of Copper(II) Complexes With Dipicolylamine-Based Ligands

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Thirteen crystal structures of copper(II) complexes with a series of dipicolylamine (DPA)-derived ligands, *N*-(2-methoxyethyl)-*N*,*N*-bis(2-pyridylmethyl)amine (**L1**), *N*-[2-(2-hydroxyethyloxy)ethyl]-*N*,*N*-bis(2-pyridylmethyl)amine (**L2**) and *N*-(3-methoxypropyl)-*N*,*N*-bis(2-pyridylmethyl)amine (**L3**), have been determined and the factors that control the coordination of the ether-oxygen atom of these ligands to the copper centre are discussed. Complexes that have +1 or +2 charges exhibit coordination of the ether-oxygen atom, whereas neutral complexes in which two anions are bound to the copper(II) centre tend to lose the oxygen coordination. Upon chelation of the oxygen atom, **L3** forms a six-membered chelate ring with respect to the 3-aminopropyl ether moiety whereas **L1** and **L2** form a five-membered chelate. This difference, especially in the nitrate and bromide complexes, determines whether the ether-oxygen atom chelates to the metal centre to give a monocationic complex, or the second anion coordinates to the metal centre to form the ether-free, neutral complex. The terminal anchor hydroxy group of **L2** facilitates the ether-oxygen coordination via a hydrogen bond interaction to the donor atom located *trans* to the aliphatic nitrogen atom in the basal plane.
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Introduction

Weak interatomic interactions with noncovalent bonds, including hydrogen bonds and electrostatic and van der Waals interactions, are essential elements not only in life sciences but also in chemistry in general.[1–3] Cooperative binding by multipoint interactions, which are often called cluster effects in glycoscience, makes weak interactions strong and specific.[3–5] On/off switching of such noncovalent interactions is another important process, and triggers of such switching include conformational changes induced by remote sites as well as redox changes in the metal centre.[6] It is therefore important to regulate these weak interatomic interactions both in solution and in the solid state.

In this report, we will focus on the coordination of ether-oxygen atoms to metal ions. Although multipoint coordination of ether-oxygen atoms, such as those found in crown ethers, can exhibit strong metal-binding, an isolated oxygen atom has only a moderate to weak binding ability to the metal centre.[7–9] Sigel et al. have been extensively studying the solution chemistry of intramolecular ether-oxygen coordination to metal centres using phosphate-pendant alkyl ether derivatives.[10,11] Recently, by employing the sugar-pendant dipicolylamine (DPA) ligand, we reported that the oxygen atom in an asymmetric ether is capable of becoming a stereogenic centre upon coordination to a copper(II) ion.[12,13] Strong binding of the DPA unit to the copper(II)[14–19] assists the asymmetric coordination of the anomeric oxygen atom of the sugar unit to the metal centre in the crystal and in solution.

In this study, in order to gain general information about intramolecular ether-oxygen chelation, the factors that promote the oxygen atom coordination to the copper(II) centre in the solid state are investigated by means of X-ray crystallography with a series of DPA-derived ligands, namely *N*-(2-methoxyethyl)-*N*,*N*-bis(2-pyridylmethyl)amine (**L1**),[20–24] *N*-[2-(2-hydroxyethyloxy)ethyl]-*N*,*N*-bis(2-pyridylmethyl)amine (**L2**)[25] and *N*-(3-methoxypropyl)-*N*,*N*-bis(2-pyridylmethyl)amine (**L3**).[21] The anion of the metal salt as well as the ligand structure control the ether-oxygen coordination to the copper(II) centre in these complexes.

Results and Discussion

Preparation and Structure Determination of the Complexes

Single crystals of complexes of **L1** with $Cu(NO_3)_2$ {[Cu(**L1**)$(NO_3)_2$] (**1**) and [Cu(**L1**)(NO_3)](ClO_4) (**2**)}, **L3** with $Cu(NO_3)_2$ {[Cu(**L3**)$(NO_3)_2$] (**3**) and [Cu(**L3**)$(NO_3)$$(ClO_4)$] (**4**)}, **L1** with $Cu(ClO_4)_2$ {[Cu(**L1**)$(ClO_4)(CH_3OH)$](ClO_4) (**5**) and [Cu(**L1**)$(CH_3CN)(H_2O)$]$(ClO_4)_2$ (**6**)}, **L2** with $Cu(ClO_4)_2$ ([Cu(**L2**)$(ClO_4)(CH_3OH)$](ClO_4) (**7**)], **L1** with $CuCl_2$ {[Cu(**L1**)Cl](ClO_4) (**8**)}, **L2** with $CuCl_2$

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{[Cu(**L2**)Cl](ClO$_4$) (**9**)}, **L3** with CuCl$_2$ {[Cu(**L3**)Cl](ClO$_4$) (**10**)}, **L1** with CuBr$_2$ {[Cu(**L1**)Br](ClO$_4$) (**11**)}, **L2** with CuBr$_2$ {[Cu(**L2**)Br](ClO$_4$) (**12**)} and **L3** with CuBr$_2$ {[Cu(**L3**)Br$_2$] (**13**)} were prepared from methanol solutions of the ligand and metal salt by slow diffusion of diethyl ether into these solutions; in some cases sodium perchlorate was added. The complex numbers and metal salt/ligand combinations are summarised in Table 1. Complexes **3** and **10** afforded crystals from methanol/diethyl ether of insufficient quality for X-ray analysis and were therefore recrystallised from acetonitrile/diethyl ether, which resulted in good quality crystals. Complex **6** was prepared in acetonitrile and crystals were grown by ether diffusion. The crystallographic data and X-ray diffraction conditions for complexes **1**–**13** are summarised in Tables S1–S4 (see Supporting Information). ORTEP diagrams of these complexes with 50% probability ellipsoids are shown in Figures 1 (**1**), 2 (**2**), 3 (**3**), 4 (cation of **6**), 5 (cation of **7**), 6 (cation of **9**) and 7 (cation of **10**). The remainder are given as Supporting Information (Figures S1–S6). Selected bond lengths and the coordination geometries, including τ values,[26] ether oxygen atom coordination, complex charges and hydrogen-bond interactions, for the copper centres in complexes **1**–**13** are summarised in Tables 2 and 3.

The crystal structure for the complex of **L2** with Cu(NO$_3$)$_2$ has already been reported.[25] In spite of extensive crystallisation trials, the mixture of **L3** and Cu(ClO$_4$)$_2$ in methanol did not afford single crystals suitable for X-ray crystallography, although the formation of a metal–ligand complex was confirmed by UV/Vis spectral changes and ESI mass spectrometry (data not shown). All structures exhibit meridional coordination geometries for the DPA unit.[14–20,23–25] Among them, [Cu(**L1**)(NO$_3$)](ClO$_4$) (**2**),

Table 1. Preparation of copper(II) complexes **1**–**13**.[a]

		Ligand	
Metal salt	**L1**	**L2**	**L3**
Cu(NO$_3$)$_2$	**1**, **2**[b]	–[c]	**3***, **4**[b]
Cu(ClO$_4$)$_2$	**5**, **6***	**7**	–[d]
CuCl$_2$ + NaClO$_4$	**8***	**9**	**10**
CuBr$_2$ + NaClO$_4$	**11**	**12**	**13**

[a] Crystals were grown from the reaction mixture in methanol by diffusion of diethyl ether vapour except for those indicated with asterisks (*), which were obtained by recrystallisation from CH$_3$CN/diethyl ether. [b] In the presence of one equivalent of NaClO$_4$. [c] Reported in ref.[25] [d] No single crystals suitable for X-ray analysis were obtained.

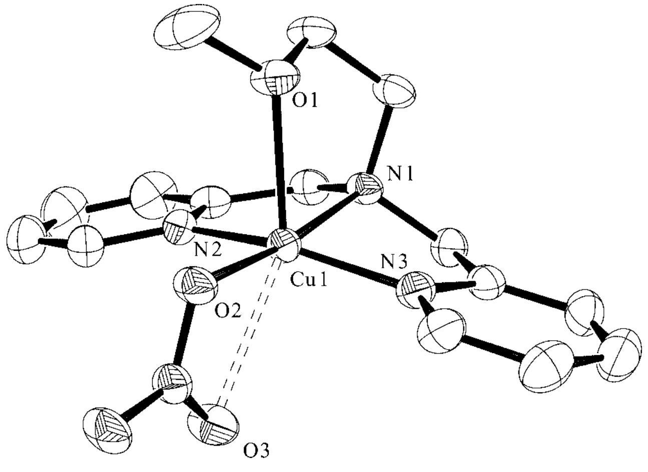

Figure 2. ORTEP plot of the cation of [Cu(**L1**)(NO$_3$)](ClO$_4$) (**2**).

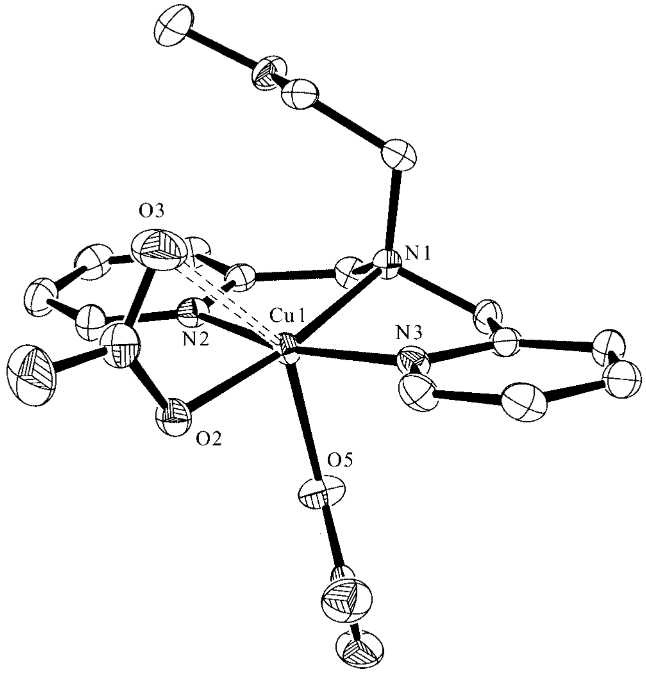

Figure 1. ORTEP plot of [Cu(**L1**)(NO$_3$)$_2$] (**1**).

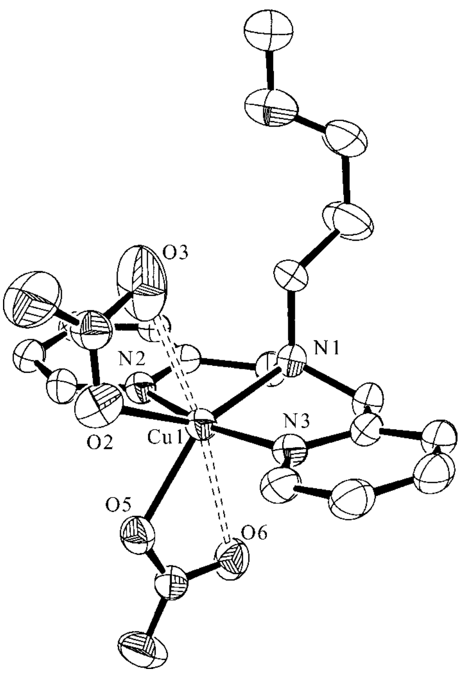

Figure 3. ORTEP plot of [Cu(**L3**)(NO$_3$)$_2$] (**3**).

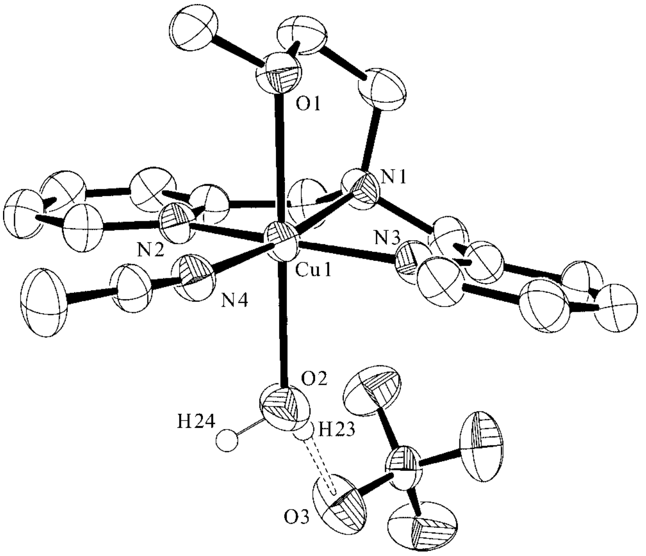

Figure 4. ORTEP plot of the cation of [Cu(**L1**)(CH_3CN)(H_2O)](ClO_4)$_2$ (**6**). Both hydrogen atoms of the coordinated water molecule (H23 and H24) are hydrogen bonded to the oxygen atoms of perchlorate ion (O3 and O4).

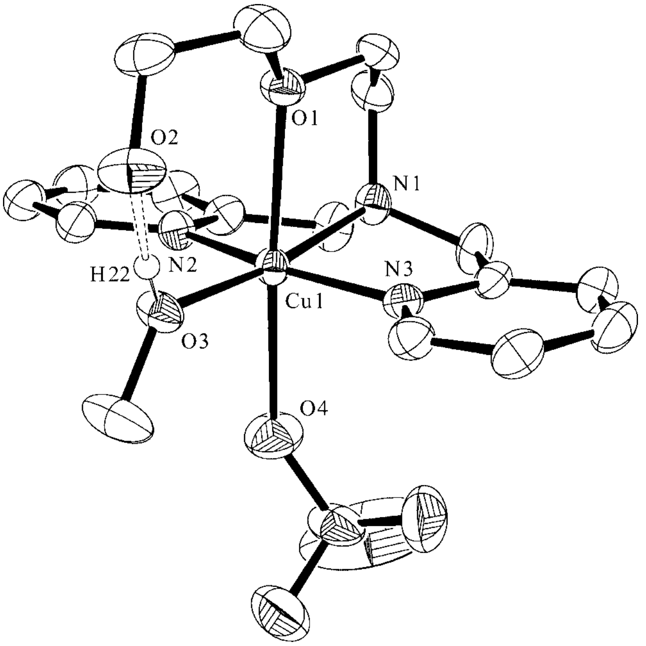

Figure 5. ORTEP plot of the cation of [Cu(**L2**)(ClO_4)(CH_3OH)](ClO_4) (**7**).

[Cu(**L1**)(ClO_4)(CH_3OH)](ClO_4) (**5**), [Cu(**L1**)(CH_3CN)(H_2O)](ClO_4)$_2$ (**6**), [Cu(**L2**)(ClO_4)(CH_3OH)](ClO_4) (**7**), [Cu(**L1**)Cl](ClO_4) (**8**), [Cu(**L2**)Cl](ClO_4) (**9**), [Cu(**L3**)Cl](ClO_4) (**10**), [Cu(**L1**)Br](ClO_4) (**11**) and [Cu(**L2**)Br](ClO_4) (**12**) are mono- or dicationic complexes with coordination of the ether-oxygen atom to the copper centre. The ether-oxygen atom in these structures occupies the apical position of a Jahn–Teller-distorted copper(II) centre with Cu–O bond lengths of between 2.329 and 2.453 Å.

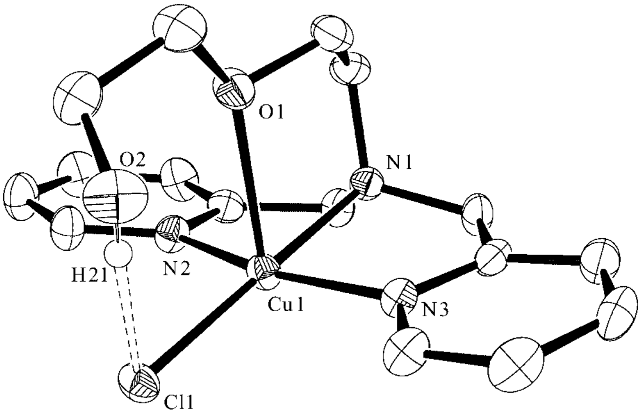

Figure 6. ORTEP plot of the cation of [Cu(**L2**)Cl](ClO_4) (**9**).

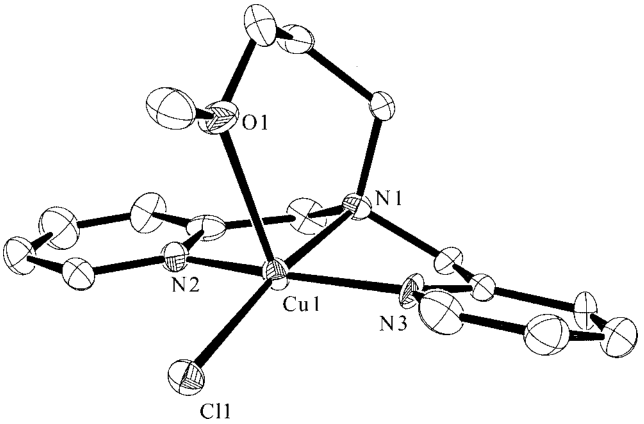

Figure 7. ORTEP plot of the cation of [Cu(**L3**)Cl](ClO_4) (**10**).

Nitrate Complexes

Metzler-Nolte and co-workers have already reported the structures of Ni^{II}, Cu^{II}, Co^{II} and Zn^{II} nitrate complexes of **L2**.[25] In all cases, the ether-oxygen atom in **L2** coordinates to the metal centre. In contrast to the Ni, Co and Zn complexes in which the hydroxy group of **L2** is directly coordinated to the metal centre, the hydroxy group in the Cu-**L2** complex no longer binds to the metal centre. This is due to the elongated Cu–O$_{ether}$ distance (2.562 Å) resulting from the Jahn–Teller effect of the d^9 copper(II) centre. As a consequence, the hydroxy group of **L2** in the complex is separated from the metal coordination sphere and hydrogen-bonded to the metal-coordinated water molecule located in the basal plane containing copper and three DPA nitrogen atoms.

The present study shows that the absence of the hydroxy anchor group results in the dissociation of the ether-oxygen atom from the copper(II) centre in the nitrate complexes (see Figures 1 and 3). Complex **1** adopts a five-coordinate, slightly distorted square-pyramidal geometry ($\tau = 0.11$) and is ligated by DPA and two nitrate anions. Weak chelation to the sixth site by the oxygen atom of the coordinated nitrate ion [Cu–O3 = 2.721(2) Å] is also observed. The coor-

Table 2. Bond lengths around the copper centre in complexes **1**–**13**.[a]

Complex	Cu–N1	Cu–N2	Cu–N3	Cu–X_{basal}	Cu–O1	Cu–X_{ap}	Figure
1 [Cu(**L1**)(NO$_3$)$_2$]	2.035(2)	1.991(2)	1.982(2)	1.983(1)[b]		2.237(2)[b] *2.721(2)*[b]	1
2 [Cu(**L1**)(NO$_3$)]ClO$_4$	2.026(2)	1.970(2)	1.968(2)	2.000(2)[b]	2.329(2)		2
3 [Cu(**L3**)(NO$_3$)$_2$]	2.077(3)	1.969(3)	1.967(3)	2.086(3)[b]		2.321(4)[b] *2.646(3)*[b] *2.805(6)*[b]	3
4 [Cu(**L3**)(NO$_3$)(ClO$_4$)]	2.042(6)	1.949(6)	1.957(6)	2.012(5)[b]		2.408(5)[b] *2.721(2)*[b]	S1
5 [Cu(**L1**)(ClO$_4$)(CH$_3$OH)](ClO$_4$)	1.997(5)	1.974(5)	1.991(5)	1.952(6)[c]	2.427(5)	*2.672(5)*[b]	S2
6 [Cu(**L1**)(CH$_3$CN)(H$_2$O)](ClO$_4$)$_2$	2.033(2)	1.997(2)	1.982(2)	1.999(2)[d]	2.367(2)	2.385(3)[c]	4
7 [Cu(**L2**)(ClO$_4$)(CH$_3$OH)](ClO$_4$)	2.013(3)	1.981(3)	1.985(3)	1.954(3)[c]	2.453(3)	2.478(3)[b]	5
8 [Cu(**L1**)Cl](ClO$_4$)	2.059(1)	1.988(1)	1.991(1)	2.2357(4)[e]	2.381(1)		S3
9 [Cu(**L2**)Cl](ClO$_4$)	2.026(3)	2.000(3)	2.013(3)	2.2471(8)[e]	2.451(2)		6
10 [Cu(**L3**)Cl](ClO$_4$)	2.029(7)	1.961(6)	1.989(6)	2.271(2)[e]	2.398(6)		7
11 [Cu(**L1**)Br](ClO$_4$)	2.061(2)	1.994(2)	1.982(2)	2.3900(4)[f]	2.452(2)		S4
12 [Cu(**L2**)Br](ClO$_4$)	2.051(2)	1.988(2)	2.007(2)	2.3725(4)[f]	2.4221(18)		S5
13 [Cu(**L3**)Br$_2$]	2.124(3)	1.986(4)	1.977(4)	2.5119(7)[f]		2.5282(6)[f]	S6

[a] Bond lengths in italics indicate semi-coordination (Cu–X = 2.5–2.9 Å). [b] X = O (anion: NO$_3^-$ or ClO$_4^-$). [c] X = O (solvent: H$_2$O or CH$_3$OH). [d] X = N. [e] X = Cl. [f] X = Br.

Table 3. Summary of the coordination geometries, ether-oxygen coordination, complex charges and hydrogen-bond interactions for complexes **1**–**13**.

Complex	Coordination[a] geometry	τ	O1-coordination	Complex charge	Hydrogen bond
[Cu(**L1**)(NO$_3$)$_2$] (**1**)	sqp	0.11	no	0	–
[Cu(**L1**)(NO$_3$)](ClO$_4$) (**2**)	sqp	0.18	yes	1	–
[Cu(**L3**)(NO$_3$)$_2$] (**3**)	sqp-tbp	0.28	no	0	–
[Cu(**L3**)(NO$_3$)(ClO$_4$)] (**4**)	sqp	0.08	no	0	–
[Cu(**L1**)(ClO$_4$)(CH$_3$OH)](ClO$_4$) (**5**)	sqp/oh	0.14	yes	1	–
[Cu(**L1**)(CH$_3$CN)(H$_2$O)](ClO$_4$)$_2$ (**6**)	oh	–	yes	2	coordinated water/perchlorate
[Cu(**L2**)(ClO$_4$)(CH$_3$OH)](ClO$_4$) (**7**)	oh	–	yes	1	O2-coordinated methanol
[Cu(**L1**)Cl](ClO$_4$) (**8**)	sqp	0.24	yes	1	–
[Cu(**L2**)Cl](ClO$_4$) (**9**)	sqp	0.22	yes	1	O2-coordinated chloride
[Cu(**L3**)Cl](ClO$_4$) (**10**)	sqp	0.14	yes	1	–
[Cu(**L1**)Br](ClO$_4$) (**11**)	sqp	0.19	yes	1	–
[Cu(**L2**)Br](ClO$_4$) (**12**)	sqp	0.28	yes	1	–
[Cu(**L3**)Br$_2$] (**13**)	tbp	0.59	no	0	–

[a] sqp: square pyramidal; oh: octahedral; tbp: trigonal bipyramidal.

dination geometry of pentacoordinate complex **3** is more distorted (τ = 0.28) and is close to a trigonal-bipyramidal geometry. For complex **3**, taking the weak intramolecular chelations [Cu–O6 = 2.646(3), Cu–O3 = 2.805(6) Å] into account, this structure can be regarded as seven-coordinate with a pentagonal bipyramidal geometry. This steric hindrance of chelated nitrate may remain during the crystallisation process, and, in combination with the neutral nature of the complexes, prevent the coordination of the ether side chain in **L1** and **L3** in the crystal structures.

In contrast, the addition of sodium perchlorate to the reaction solution of **L1** with Cu(NO$_3$)$_2$ affords the ether-bound complex **2** (Figure 2). Perchlorate ion is considered to promote crystallisation of monocationic complexes, giving rise to the oxygen-coordinated complex. On the other hand, for the **L3**/Cu(NO$_3$)$_2$/NaClO$_4$ system, a perchlorate anion coordinates to the copper centre together with a nitrate ion to give the neutral, ether-free complex **4** (Figure S1 in the Supporting Information). This difference could originate from the preferred formation of a five-membered chelate ring over a six-membered ring by the aminoalkyl ether system.

Perchlorate Complexes

Copper(II) perchlorate complexes were subsequently examined. Unfortunately, single crystals of the Cu/**L3** complex could not be obtained but the other two ligands afforded crystals suitable for X-ray analysis, resulting in the structures of the cationic portions of [Cu(**L1**)(ClO$_4$)(CH$_3$OH)](ClO$_4$) (**5**), [Cu(**L1**)(CH$_3$CN)(H$_2$O)](ClO$_4$)$_2$ (**6**) and [Cu(**L2**)(ClO$_4$)(CH$_3$OH)](ClO$_4$) (**7**) shown in Figures S2 (see Supporting Information), 4 and 5, respectively.

In complexes **5** and **7**, which were crystallised from methanol, the copper centre adopts an N$_3$O$_3$ hexacoordinate, slightly distorted octahedral geometry ligated by the tridentate DPA, methanol, perchlorate and the ether-oxygen atom in the ligand. Since the bond length for the sixth site of complex **5** occupied by the perchlorate oxygen atom is very long [Cu–O = 2.672(5) Å], the geometry of this complex could also be described as a distorted square-pyramid (τ = 0.14). The Cu–O_{ether} bond lengths of these two complexes are similar [2.427(5) Å for **5** and 2.453(3) Å for **7**] and are significantly different from that in the $Cu(NO_3)_2$/**L2** complex (2.562 Å).[25]

For complex **6**, which was crystallised from acetonitrile, the perchlorate anion is no longer coordinated to the copper centre; instead, acetonitrile and water molecules occupy the basal and apical positions, respectively. The weak coordination ability and superior crystallising ability of the perchlorate complex promotes the formation of a dicationic complex that facilitates the ether-oxygen coordination to the copper centre. The bond length between copper and the ether-oxygen atom (O1) in this six-coordinate complex is very short (2.367 Å) but slightly longer than that of the five-coordinate, monocationic complex **2** (2.329 Å). Both hydrogen atoms of the copper-bound water molecule in complex **6** are hydrogen-bonded to perchlorate anions, which increases the donor ability of this metal-coordinated water oxygen atom. Thus, the Cu–O_{water} bond length [2.385(3) Å] is very short and is close to those seen for anion coordination distances in the apical position [2.237(2) Å for **1**, 2.321(4) Å for **3** and 2.408(5) Å for **4**]. This strong water coordination to the copper centre makes the Cu–O1 bond relatively weak for dicationic complex **6** compared to that in monocationic complex **2**.

Chloride Complexes

Chloride anion, in combination with sodium perchlorate, is found to facilitate ether-oxygen coordination to the copper centre for all ligands (see Figure S3 in the Supporting Information and Figures 6 and 7). Complexes **8**–**10** comprise one copper(II) ion, one ligand molecule and one chloride ion in five-coordinate complexes with distorted square-pyramidal geometries (τ = 0.14–0.24). The copper-bound chloride ions occupy the site *trans* to the aliphatic nitrogen atom of DPA, which reduces the steric hindrance around the metal centre. For the perchlorate-bound, ether-coordinated complexes **5** and **7**, the weakly coordinating perchlorate anion occupies the Jahn–Teller-elongated apical position that allows solvent methanol to coordinate to the metal centre from the basal plane, which satisfies the steric requirements for ether-oxygen binding. For the ether-free neutral complexes **1**, **3** and **4**, the moderate coordination strength and steric hindrance of the nitrate anion located at the equatorial site prevent ether-oxygen binding to the metal centre. Chloride anion has enough coordination ability to occupy the equatorial ordinate and less steric bulk, which gives rise to ether-coordinated complexes for all ligands. In complex **9**, the hydroxy group is hydrogen-bonded to the metal-coordinated chloride atom.

In the absence of sodium perchlorate, the reaction mixture of **L1** and $CuCl_2$ afforded a complex formulated as $[Cu(\mathbf{L1})Cl]_2[CuCl_4]$ (data not shown). The structure of the cationic portion of this complex is almost the same as complex **8**. Ligands **L2** and **L3** did not afford any precipitates in the absence of sodium perchlorate.

Bromide Complexes

Bromide ion as the counterion also has an effect on the coordination sphere (see Figures S4–S6 in the Supporting Information). Complex **13** crystallises directly from the ligand/metal solution mixture, but addition of sodium perchlorate was found to be effective for crystallisation of complexes **11** and **12**. Even in the presence of perchlorate anion, the reaction mixture of **L3** with $CuBr_2$ in methanol affords the dibromide complex **13**. From these results, **L3** seems to exhibit weaker ether-oxygen coordination than **L1** and **L2**, thus forming an ether-free, neutral complex. This difference again highlights the preferred formation of a five-membered chelate over a six-membered ring, although the superior crystallising ability of complex **13** might be important. This complex adopts a distorted trigonal-bipyramidal geometry (τ = 0.59) due to the bulkiness of two copper-bound bromide ions. Complexes **11** and **12** exhibit five-coordinate, distorted square-pyramidal geometries (τ = 0.19 and 0.28) similar to the chloride complexes, but for **12**, the hydroxy group of the ligand is no longer hydrogen-bonded to the copper-bound bromide atom.

Solution Studies

The electronic absorption spectra, cyclic voltammetry and EPR spectra were examined for complexes **1**–**13** to investigate the solution structure. In methanol solution, all complexes exhibit a copper d–d transition band around 640–710 nm (ε = 80–200). No specific relationship between absorption maxima and ligand/complex structure was observed. For cyclic voltammetry in acetonitrile, the reduction potentials were significantly altered by ligand structure. Thus, the complexes ligated by **L3** exhibit positive-shifted reduction potentials that indicate a strong electron requirement for the copper centre. The EPR spectra in acetonitrile at room temperature exhibit well-resolved $^{63/65}$Cu hyperfine splitting in the range of 7–8 mT, except for complexes **7** and **13**, which show broad signals. $^{79/81}$Br hyperfine splitting in the range of 3 mT was also observed for complexes **11**–**13**, and this could be responsible for broadness of the signals for the dibromide complex **13**. Further studies of the solution structures of these complexes are in progress in our laboratory.

Conclusions

As summarised in Table 3, the ligand structure and the anion of the starting metal salt play crucial roles in the ether-oxygen coordination in metal complexes in the crystal structure. The difference in chelate ring size determines the ether-oxygen coordination to the metal centre. The steric bulk of the chelating nitrate ion prevents ether-oxygen coordination whereas chloride ion promotes it. As a consequence, complexes that have +1 or +2 charges exhibit coordination of the ether-oxygen atom, whereas neutral complexes in which two anions are bound to the copper(II) centre tend to dissociate the ether-oxygen atom. The strong electron-withdrawing character of the metal centre in cationic complexes requires ether-oxygen coordination. However, stronger electron demand would require more efficient coordination by anion binding. Compensating balance between enthalpy gain and entropy loss caused by the coordination of the external anion, as well as crystallising ability of the complex, controls the choice of formation of intramolecular ether-oxygen binding to afford cationic complexes or intermolecular anion binding leading to neutral complexes. The hydroxy group of **L2** does not coordinate to the copper centre but promotes the ether-oxygen coordination by hydrogen bonding to the oxygen or chloride atom located *trans* to the aliphatic nitrogen in the basal plane. The present information provides an important strategy to regulate the coordination of an oxygen atom to the metal centre in the solid state.

Experimental Section

Materials: *N*-(2-Methoxyethyl)-*N*,*N*-bis(2-pyridylmethyl)amine (**L1**),[21] *N*-[2-(2-hydroxyethyloxy)ethyl]-*N*,*N*-bis(2-pyridylmethyl)amine (**L2**)[25] and *N*-(3-methoxypropyl)-*N*,*N*-bis(2-pyridylmethyl)amine (**L3**)[21] were prepared from the corresponding amine by refluxing with two equivalents of 2-chloromethylpyridine hydrochloride in the presence of potassium carbonate in acetonitrile (75–84% yield). The spectroscopic data of **L1**–**L3** are in good agreement with those reported in the literature. Copper(II) nitrate trihydrate, copper(II) perchlorate hexahydrate (Wako Pure Chemical Industries, Ltd.), copper(II) chloride dihydrate, copper(II) bromide (Nacalai Tesque), sodium perchlorate monohydrate and all solvents (Wako Pure Chemical Industries, Ltd.) were used as received.

Preparation of Complexes: A methanolic solution of the ligands (0.03–0.25 mmol) was mixed with 1 equiv. of copper(II) salt in the same solvent at room temperature (total methanol volume: 0.4–2.0 mL), then diethyl ether vapour was introduced at 4 °C. In case crystallisation or precipitation did not occur, 1 equiv. of sodium perchlorate was added to the reaction mixture before ether diffusion. In most cases, single crystals suitable for X-ray crystallography were obtained directly from the reaction mixture. Complexes **3** and **8** precipitated from the reaction mixture and were recrystallised from acetonitrile/diethyl ether to obtain satisfactory single crystals. Single crystals of complex **6** were prepared from the ligand/metal mixture in acetonitrile under ether diffusion conditions. Table 1 summarises the preparation conditions, metal salt/ligand combinations and complex numbers.

CAUTION: *Perchlorate salts of metal complexes with organic ligands are potentially explosive. All due precautions should be taken.*

[Cu(L1)(NO$_3$)$_2$] (1): Starting from **L1** (64.3 mg, 0.25 mmol), 72.5 mg of complex was obtained (65% yield). $C_{15}H_{19}CuN_5O_7$ (**1**) (444.89): calcd. C 40.50, H 4.30, N 15.74; found C 40.52, H 4.40, N 15.66.

[Cu(L1)(NO$_3$)](ClO$_4$) (2): Starting from **L1** (12.9 mg, 0.05 mmol), 14.9 mg of complex **2** was obtained (62% yield). $C_{15}H_{19}ClCuN_4O_8$ (482.34): calcd. C 37.35, H 3.97, N 11.62; found C 37.57, H 4.07, N 11.66.

[Cu(L3)(NO$_3$)$_2$] (3): Starting from **L3** (40.7 mg, 0.15 mmol), 29.3 mg of complex **3** was obtained (41% yield). $C_{16}H_{23}CuN_5O_8$ (**3**·H_2O; 476.93): calcd. C 40.29, H 4.86, N 14.68; found C 40.48, H 4.77, N 14.83.

[Cu(L3)(NO$_3$)(ClO$_4$)] (4): Starting from **L3** (8.1 mg, 0.03 mmol), 10.3 mg of complex **4** was obtained (69% yield). $C_{16}H_{21}ClCuN_4O_8$ (496.36): calcd. C 38.72, H 4.26, N 11.29; found C 38.22, H 4.52, N 11.37.

[Cu(L1)(ClO$_4$)(CH$_3$OH)](ClO$_4$) (5): Starting from **L1** (18.0 mg, 0.07 mmol), 27.6 mg of complex **5** was obtained (69% yield). $C_{16}H_{25}Cl_2CuN_3O_{11}$ (**5**·H_2O; 569.84): calcd. C 33.72, H 4.42, N 7.37; found C 33.94, H 4.39, N 7.56.

[Cu(L1)(CH$_3$CN)(H$_2$O)](ClO$_4$)$_2$ (6): Starting from **L1** (12.9 mg, 0.05 mmol), 17.8 mg of complex **6** was obtained (62% yield). $C_{17}H_{24}Cl_2CuN_4O_{10}$ (578.85): calcd. C 35.27, H 4.18, N 9.68; found C 34.77, H 4.36, N 9.25.

[Cu(L2)(ClO$_4$)(CH$_3$OH)](ClO$_4$) (7): Starting from **L2** (14.4 mg, 0.05 mmol), 15.6 mg of complex **7** was obtained (52% yield). $C_{17}H_{27}Cl_2CuN_3O_{12}$ (**7**·H_2O; 599.87): calcd. C 34.04, H 4.54, N 7.00; found C 34.28, H 4.23, N 7.27.

[Cu(L1)Cl](ClO$_4$) (8): Starting from **L1** (7.7 mg, 0.03 mmol), 5.0 mg of complex **8** was obtained (34% yield). $C_{16}H_{23}Cl_2CuN_3O_6$ (**8**·CH_3OH; 487.83): calcd. C 39.39, H 4.75, N 8.61; found C 39.02, H 4.34, N 8.90.

[Cu(L2)Cl](ClO$_4$) (9): Starting from **L2** (14.4 mg, 0.05 mmol), 15.5 mg of complex **9** was obtained (62% yield). $C_{16}H_{23}Cl_2CuN_3O_7$ (**9**·H_2O; 503.83): calcd. C 38.14, H 4.60, N 8.34; found C 38.09, H 4.43, N 8.47.

[Cu(L3)Cl](ClO$_4$) (10): Starting from **L3** (21.7 mg, 0.08 mmol), 27.9 mg of complex **10** was obtained (71% yield). $C_{16}H_{23}Cl_2CuN_3O_6$ (**10**·H_2O; 487.83): calcd. C 39.39, H 4.75, N 8.61; found C 39.60, H 4.53, N 8.34.

[Cu(L1)Br](ClO$_4$) (11): Starting from **L1** (12.9 mg, 0.05 mmol), 17.9 mg of complex **11** was obtained (71% yield). $C_{15}H_{19}BrClCuN_3O_5$ (500.24): calcd. C 36.02, H 3.83, N 8.40; found C 36.04, H 3.78, N 8.34.

[Cu(L2)Br](ClO$_4$) (12): Starting from **L2** (8.6 mg, 0.03 mmol), 11.2 mg of complex **12** was obtained (71% yield). $C_{16}H_{21}BrClCuN_3O_6$ (530.26): calcd. C 36.24, H 3.99, N 7.92; found C 36.37, H 4.09, N 7.88.

[Cu(L3)Br$_2$] (13): Starting from **L3** (8.1 mg, 0.03 mmol), 10.3 mg of complex **13** was obtained (65% yield). $C_{17}H_{25}Br_2CuN_3O_2$ (**13**·CH_3OH; 526.76): calcd. C 38.76, H 4.78, N 7.98; found C 38.45, H 4.36, N 7.97.

X-ray Crystallography: Single crystals of **1**–**13** were covered by paraffin oil and mounted on a glass fibre. All data were collected at 173 K on a Rigaku Mercury CCD detector, with monochromatic Mo-K_α radiation, operating at 50 kV/40 mA. Data were processed with a PC using CrystalClear Software (Rigaku). Structures were solved by direct methods (SIR-97, SIR-92 or SHELXS-97) and refined by full-matrix least-squares methods on F^2 (SHELXS-97).

CCDC-612373 to -612385 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.request/cif.

Supporting Information (see also the footnote on the first page of this article): Crystallographic data for all complexes and ORTEP drawings for complexes **4**, **5**, **8**, **11**, **12** and **13**.

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