DOI: 10.1002/ejic.200600917

[Cu^{II}_4] Clusters From the Self-Assembly of Two Imidazolidinyl 2-Phenolate-Bridged [Cu^{II}_2] Units: The Role of the Chloride Bridge

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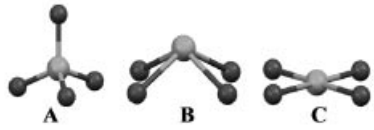
Keywords: Template synthesis / Self-assembly / Cluster compounds / Copper / Magnetic properties

A new family of tetracopper clusters [$Cu_4(\mu_4$-X)L_2]ClO_4·nH_2O (**1a**–**c**) [X = Cl, Br, I; n = 12, 2, 2; H_3L = 2-(2′-hydroxyphenyl)-1,3-bis[4-(2-hydroxyphenyl)-3-azabut-3-enyl]-1,3-imidazolidine] have been synthesised and characterised. The X-ray crystal structure of **1a** reveals that the template action of the spherical Cl^- anion (μ_4-Cl^-), which features a unique rectangular planar bridging mode, is responsible for the self-assembly of two $[Cu_2L]^+$ units in complex **1a**. In this family of complexes the spherical halides serve as templates to assemble the dimeric unit into tetrameric complexes, which gives an insight into the role of the halide bridge in tetranuclear complex formation. The capacity of this bridge to mediate magnetic coupling has been examined by bulk magnetic measurements for complex **1a**.

Introduction

Cluster-like metal-organic assemblies can be obtained from cation-[1] and anion-templated[2] syntheses, and several recent reports have demonstrated that anions can be successfully employed as a template for the formation of a wide range of organic[3] and metal-organic[4] assemblies. The anionic species in these syntheses plays a templating role by using its directing properties and determines the geometry and connectivity of the final structure. The spherically symmetrical Cl^- ion has recently been shown to direct the self-assembly of four trimethylphosphane-stabilised diphenylstibenium ions.[5] Anion-templated synthesis is expected to yield novel structures with properties of chemical significance. Single-atom-nucleated paramagnetic M_4 assemblies can generate interesting structures depending upon the number and nature of the coordination bonds they form in space.[6] The size, charge and nature of the nucleating atom also control the geometry and stability of the cluster. The μ_4-Cl^- coordination mode is rare for Cu_4 clusters of polydentate ligands and can have either tetrahedral (A)[7] or square-pyramidal (B)[2b,2c,8] geometries (Scheme 1). In these two coordination modes, the {$Cu^{II}_4(\mu_4$-Cl)} core is further supported by either phosphate or halide auxiliary bridges. The presence of auxiliary bridging ligands helps the nucleation around the chloride anion in a particular mode of binding.



Scheme 1. Left: tetrahedral μ_4-Cl (ref.[7]); middle: pyramidal μ_4-Cl (ref.[2b]); right: part of complex **1a**; grey: Cl; black: Cu. Structures generated with the Mercury X-ray crystallography software package (version 1.4).

On the other hand the rectangular planar structure (C), which has C_{2h} symmetry and long M–Cl bonds, is not known in the literature for complexes of polydentate ligands. Recently, we have shown that the spherical O^{2-} anion can function as a nucleating group that allows isolation of the tetrahedral {$Cu^{II}_4(\mu_4$-O)} core of two different non-bridging hexadentate ligands.[9] No analogous μ_4-Cl-templated tetranuclear complex of a 3d element is known with similar Schiff-base ligand systems. Currently, efforts are be-

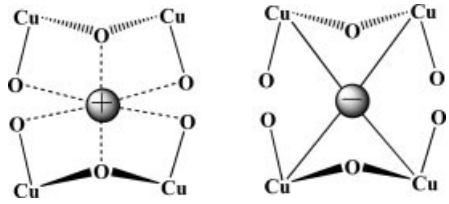


Figure 1. Schematic presentation of a cation-centred assembly around octahedral Na^+ (left, ref.[11]) and the anion-centred assembly around spherical Cl^- in complex **1a** (right).

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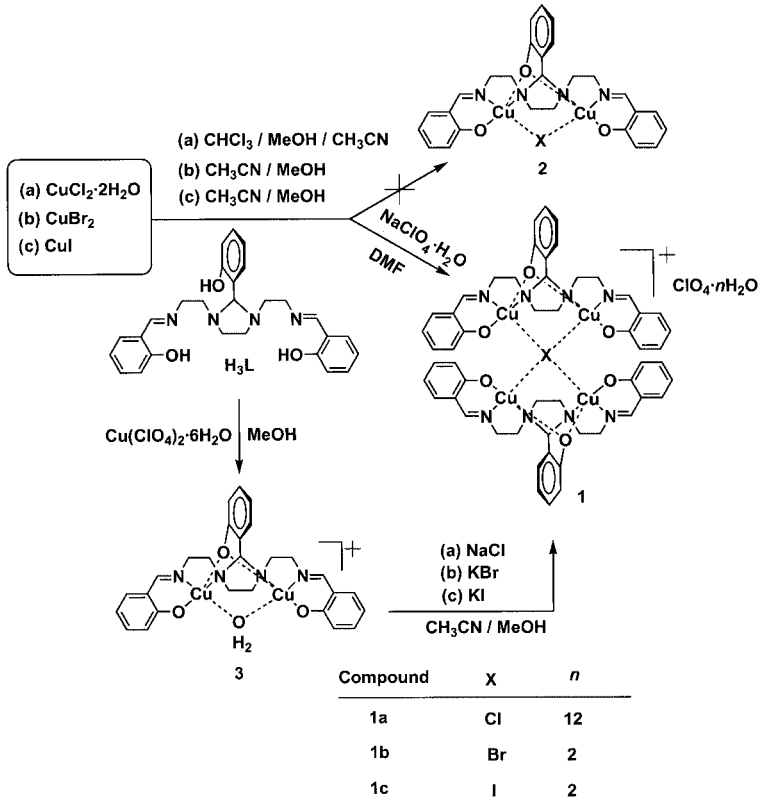


Scheme 2.

ing made to rationalize the role of the Cu_4 cluster based catalytic site, which has never before been found in biology, for the reduction of N_2O to N_2.[10] The ligand H_3L [2-(2′-hydroxyphenyl)-1,3-bis[4-(2-hydroxyphenyl)-3-azabut-3-enyl]-1,3-imidazolidine] has recently been shown to undergo the cation (sodium)-centred assembly of two $[Cu_2L]^+$ units upon octahedral coordination of Na^+ to the terminal phenolate oxygen atoms of two ligands[11] (Figure 1, left).

Here, we report the preferential formation of a rectangular {$Cu^{II}_4(\mu_4\text{-Cl})$} core in **1a**, where two Cu_2 units assemble around the meridian of the spherical chloride anion (Figure 1, right). The centrosymmetric geometry reduces the ligand's steric crowding. The anion (chloride)-centred assembly of two $[Cu_2L]^+$ units is responsible for its entrapment in the final complex and coordination in a μ_4 mode (**1**) instead of bridging (**2**) or terminal monodentate (**6** in Scheme 3) coordination in dinuclear complex formation (Scheme 2).

Results and Discussion

Syntheses and Spectroscopic Characterisation

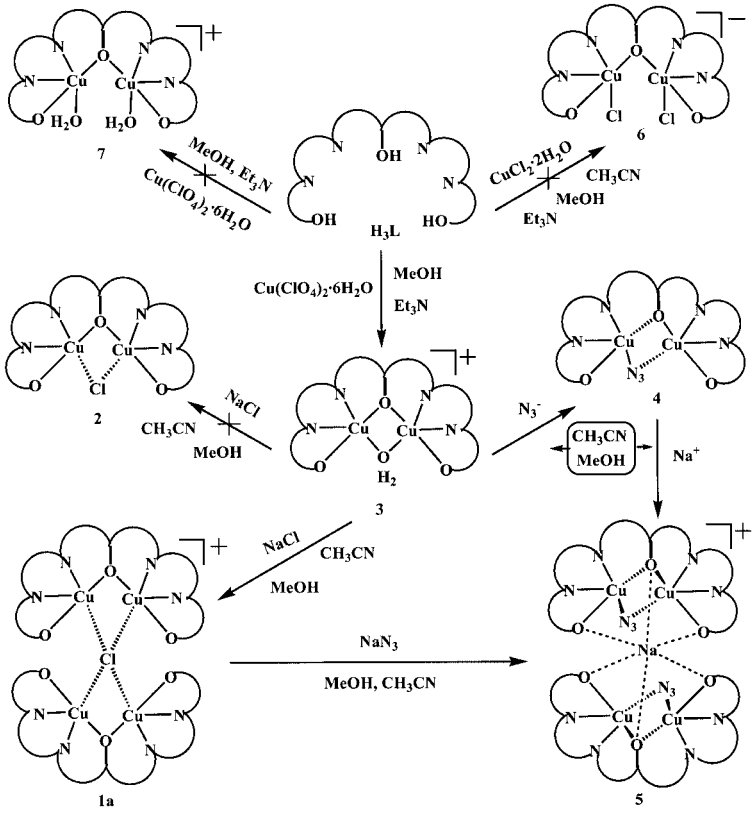
The μ-bis(tetradentate) ligand H_3L [2-(2′-hydroxyphenyl)-1,3-bis[4-(2-hydroxyphenyl)-3-azabut-3-enyl]-1,3-imidazolidine] was prepared according to a literature procedure,[12] and a general procedure was followed for the synthesis of complexes **1a**–**c**. The reaction of H_3L in a CH_2Cl_2/MeOH (1:1) solvent mixture with an CH_3CN/MeOH (1:1) solution of $CuCl_2·2H_2O$ in air followed by addition of $N(C_2H_5)_3$ (1:2:3 molar ratio) at room temperature afforded a green precipitate of $[Cu_4(\mu_4\text{-Cl})L_2]Cl·2H_2O$. Addition of a saturated solution of $NaClO_4·H_2O$ in MeOH to the above precipitate in dmf produced a green solution, which yielded green crystalline **1a** upon slow evaporation in air for six days. The elemental analysis and solution electrical conductivity data in dmf are consistent with the formula $[Cu_4(\mu_4\text{-Cl})L_2]ClO_4·12H_2O$ (**1a**); the yield was found to be 80%. Complexes $[Cu_4(\mu_4\text{-Br})L_2]ClO_4·2H_2O$ (**1b**) and $[Cu_4(\mu_4\text{-I})L_2]ClO_4·2H_2O$ (**1c**) were synthesised in a similar manner but with $CuBr_2$ and CuI, respectively, in CH_3CN/MeOH (1:1). During the synthesis of **1c** the light-yellow colour of the reaction mixture changed to green after 10 min.

All the compounds are insoluble in water and separate immediately from the reaction mixture. Elemental analysis, metal estimation, solution electrical conductivity and FT-IR and UV/Vis studies confirmed the formation of **1a**–**c**. Based on tetranuclear formulations, the molar conductivity values (Λ_M) in dmf are 90, 95 and 92 $\Omega^{-1}cm^2mol^{-1}$ (28 °C) for **1a**, **1b** and **1c**, respectively. These values correspond to the 1:1 electrolyte behaviours of **1a**–**c** in dmf and indicate the stability of the Cu_4 clusters in solution.[13] In the strong donor solvent dmf solvolysis of the clusters to $[Cu_2(dmf)_2L]X$ (X = Cl, Br and I) is not observed. The sharp peaks in the IR spectra of complexes **1a**–**c** at 1633, 1636 and 1632 cm^{-1}, respectively, are characteristic of the C=N functionality of the ligand and the broad/medium bands at

3388, 3427 and 3392 cm^{-1}, respectively, are observed for $\nu(OH)_{H_2O}$ of the lattice water molecules. Compounds **1a–c** show broad electronic absorption bands at 660 (ε = 440), 620 (ε = 510) and 635 nm (ε = 745 $M^{-1}cm^{-1}$), respectively, for the d–d transitions. In dmf solution the $L \rightarrow Cu^{II}$ charge-transfer (CT) transitions are observed around 377 (ε = 7810, 15425 and 16305 $M^{-1}cm^{-1}$). The intra-ligand CT transitions are seen around 280 nm (ε = 20150, 21800 and 22425 $M^{-1}cm^{-1}$). Similarly, peaks at 1627 and 3388 cm^{-1} in the IR spectrum of complex **3** are characteristic of the C=N functionality of the ligand and the $\nu(OH)_{H_2O}$ stretch of the water molecules. Compound **3** shows a broad electronic absorption band at 640 nm (ε = 440 $M^{-1}cm^{-1}$) for the d–d transition and bands at 402 (ε = 2770 $M^{-1}cm^{-1}$) and 273 nm (ε = 22041 $M^{-1}cm^{-1}$) are observed for the charge-transfer transitions.

The nature of the final reaction product is greatly influenced by the ligand, solvent system and sequence of addition of the reactants. For example, under similar reaction conditions H_3L and a substituted analogue of H_3L (H_3mhbai in ref.[14])[15] react differently with NaN_3 to give the cation- and anion-centred tetranuclear copper complexes $[NaCu_4L_2(N_3)_2]ClO_4 \cdot H_2O$[11] and $[Cu_4L_2(N_3)]Cl \cdot 16H_2O$,[15] respectively. Following several synthetic trials with NaN_3, we failed to obtain same products (μ_2-N_3^- or μ_4-N_3^-) for either of these two ligands in varying solvent systems and reaction conditions. Thus, the ligands play the deciding role for final product formation and act independently of the nature of the solvent and sequence of addition of reagents. It is an inherent property of the ligand systems that they show different self-assembly behaviours for cluster formation. Likewise, for ligand H_3L reported in this paper, the dinuclear complex **2** was not obtained (Scheme 3) when a methanolic solution of the ligand was added to $CuCl_2 \cdot 2H_2O$ in MeOH/H_2O (2:1) in a 1:2 molar ratio.

Complexes **1a–c** can also be obtained by an indirect route via the exogenous aqua-bridged dinuclear complex $[Cu_2L(H_2O)]ClO_4 \cdot 2H_2O$ (**3**). Complex **3** is obtained from the reaction of $Cu(ClO_4)_2 \cdot 6H_2O$ with H_3L in the presence of Et_3N in MeOH in a 2:1:3 molar ratio (Scheme 3). Complex **3** reacts further with NaCl, KBr or KI in a 2:1 molar ratio to give complexes **1a–c** (Scheme 2). In a two-step reaction, complex **3** initially reacts with N_3^- to form the dicopper species **4** in solution. The basal-apical mode of azide coordination and face-to-face orientation of two such species provides a cavity to accommodate a Na^+ ion and give tetrameric complex **5**.[11] In this work, we have shown that the larger halide anions prefer metal coordination in an apical-apical mode to produce **1a–c**. The μ_4-X centred Cu_4 complexes **1a–c**, which have four Cu–X apical bonds, also react with NaN_3 in MeOH/CH_3CN (1:1) to produce **5**, which contains two apical and two basal Cu–N(azide) bonds. These reactions also demonstrate the successful replacement of halide groups with weaker apical-apical coordination by strong azide coordination in a basal-apical mode. So far, we have been unable to synthesise complexes **6** and **7** by varying the solvents and reaction conditions (Scheme 3).



Scheme 3.

X-ray Structure of $[Cu_4(\mu_4\text{-}Cl)L_2]ClO_4\cdot 12H_2O$ (1a)

Single crystals of **1a** suitable for X-ray diffraction were obtained by slow evaporation of a dmf solution of the compound. It consists of a tetracopper cluster cation $[Cu_4(\mu_4\text{-}Cl)L_2]^+$ along with a disordered ClO_4^- anion and twelve water molecules. An ORTEP view of $[Cu_4(\mu_4\text{-}Cl)L_2]^+$ is shown in Figure 2, and selected bond lengths and bond angles are listed in Table 1.

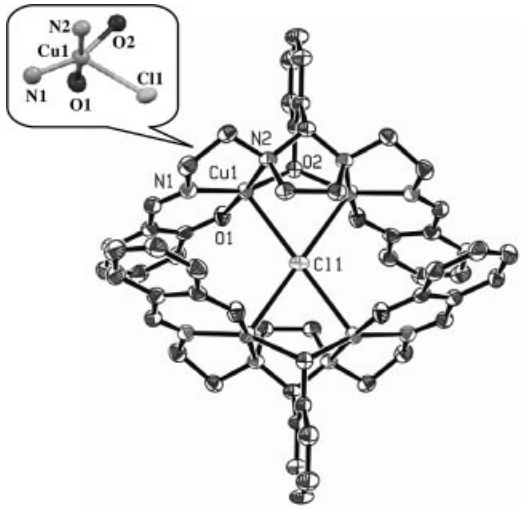
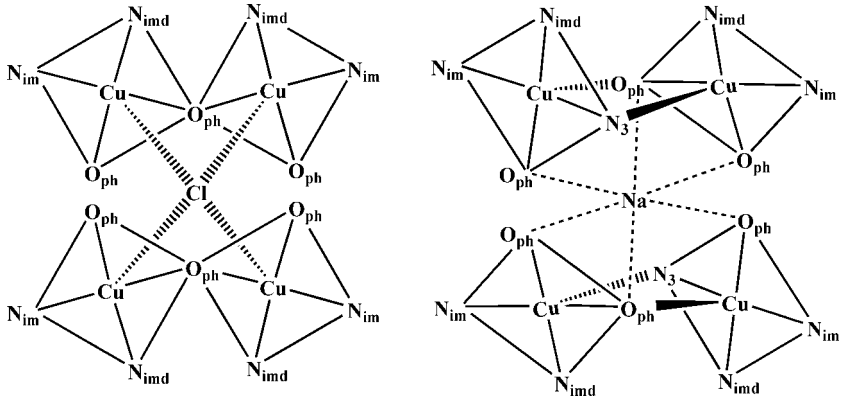


Figure 2. ORTEP representation of $[Cu_4(\mu_4\text{-}Cl)L_2]^+$ (**1a**) with ellipsoids at the 40% probability level. Hydrogen atoms have been omitted for clarity. Only independent non-carbon atoms are labelled.

Table 1. Selected bond lengths [Å] and bond angles [°] in complex **1a**.

Bond lengths [Å]	
Cu1–O1	1.906(3)
Cu1–N1	1.935(3)
Cu1–N2	2.070(3)
Cu1–O2	1.971(2)
Cu1–Cl1	2.776(5)
Bond angles [°]	
O1–Cu1–N1	93.50(14)
N1–Cu1–N2	83.94(14)
N2–Cu1–O2	91.16(13)
O1–Cu1–O2	89.92(13)
N1–Cu1–O2	157.70(14)
O1–Cu1–N2	175.66(12)
Cu1–O2–Cu1	110.63(17)
Cu1–Cl1–Cu1	71.44(13)

A rectangular arrangement of four crystallographically equivalent Cu^{II} ions as two pairs of metal ions is seen in $[Cu_4(\mu_4\text{-}Cl)L_2]^+$. The cationic tetramer has crystallographic 2/*m* symmetry, with the central Cl atom at the 2/*m* centre. The metal ions within each $[Cu_2]$ pair are bridged and chelated by one $\mu\text{-}L^{3-}$ ligand. These dinuclear units are in turn linked exclusively by one unsupported Cl^- ligand in a μ_4-bridging mode. The polydentate ligand L^{3-} within each dinuclear unit bridges the metal ions through one imidazolidine and one phenoxide moiety while further coordinating the copper ions through two terminal phenoxide and imine groups. The four copper atoms are placed at the vertices of a regular rectangle, with the chloride ligand lying at the centre of the rectangle. Each $[Cu_2]$ pair, spanning the short axis of the $[Cu_4Cl]$ rectangle is also bridged by one end of the $\mu_4\text{-}Cl^-$ ligand. The Cl^- ligand fills the fifth apical coordination site of each copper. Within the $[Cu_2L]^+$ units, the bridging Cl^- ions show an apical-apical coordination mode, which is different from the apical-basal binding mode of the azide ions in $[NaCu_4L_2(N_3)_2]ClO_4$.[11] At the same time, this mode of bridging also forces the imidazolidinyl phenolate oxygens to exhibit a complementary basal-apical coordination. This apical-basal and basal-apical combination is responsible for the formation of an interdimer cavity that nicely accommodates Na^+ ion in **5**. Contrary to this, the apical-apical halide bridging within $[Cu_2L]^+$ in **1a**–**c** retains the basal-basal coordination mode of the imidazolidinyl phenolate oxygens (Scheme 4). The four Cu^{II} ions in **1a** are pentacoordinate and feature a distorted square-pyramidal N_2O_2Cl environment (τ = 0.30).[16] The polyhedra around copper share the chlorine atom Cl(1) as a common apical vertex and the ligand phenolate oxygen atoms O(2) and O(2)$^{\#}$ as the shared basal donors. The sum of the angles around the oxygen atom of the central phenolate bridge is 330.61° in all basal coordinations and shows a pyramidal distortion arising from a folding of the ligand around the imidazolidine backbone, while the chlorine



Scheme 4.

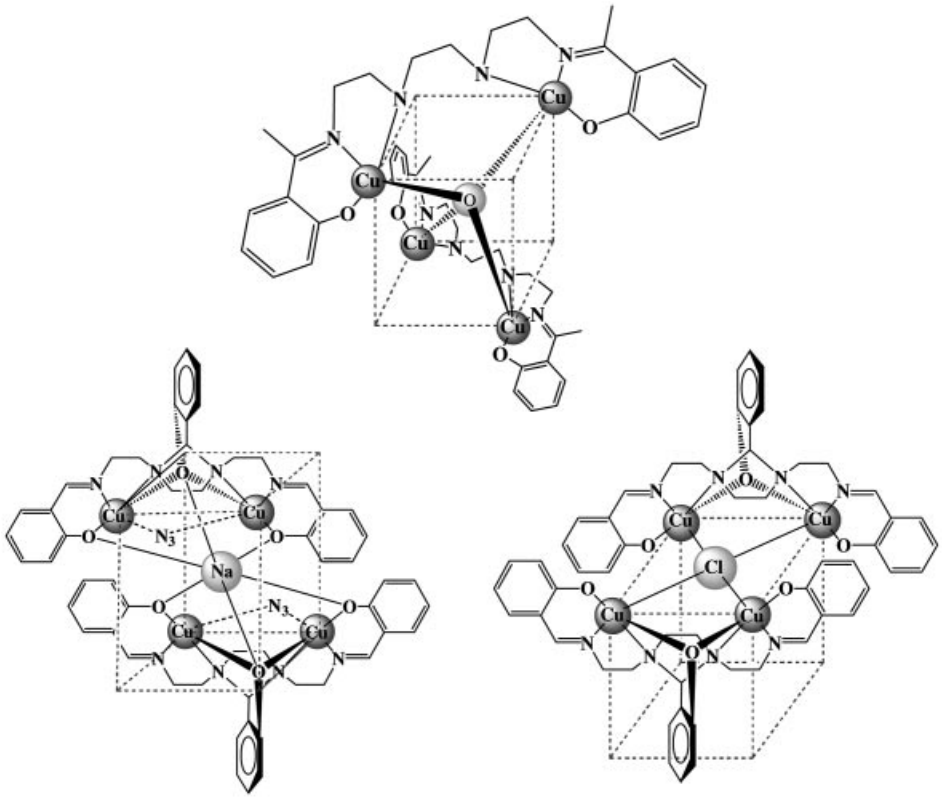


Figure 3. Three single atom nucleating self-assemblies with different polyhedral geometries: a tetrahedral μ_4-O^{2-}-directed self-assembly (top, ref.[9]), an octahedral Na^+-templated self-assembly (bottom left, ref.[11]) and a planar μ_4-Cl^--templated self-assembly (bottom right, **1a**).

atom for apical coordination to Cu^{II} presents a perfect planar geometry (sum of angles is 360°). The angle between the basal planes of the pyramids is 139.78°, thereby highlighting the non-coplanarity induced by the folded ligand system.

Each copper centre lies 0.220 Å above the mean N_2O_2 basal plane and is shifted towards Cl^-. To the best of our knowledge, this is the first μ_4-chloride copper cluster of any multidentate ligand. The conformation of the μ_4-Cl^- moiety in **1a** is different from the two previously reported cases with respect to its symmetry (Scheme 1).[2b,7] The Cu···Cu distances within the [Cu_4] rectangle of **1a** are 3.241(8) Å within each [Cu_2] pair and 4.507(6) Å when spanned by only the μ_4-Cl^- ligand. The first distance is longer and the second distance is shorter than the values (3.040 and 6.009 Å, respectively) for a Na^+-templated tetramer of the same ligand with a rectangular disposition of the Cu^{II} ions.[11] These differences are due to basal-apical coordination of the imidazolidinyl phenolic oxygen in the case of [$NaCu_4$] compared to basal-basal coordination in the present case. In the case of the [$NaCu_4$][11] cluster, the azide apical-basal coordinations provide space for Na^+, which controls the positions of the phenolate donors, whereas in the [Cu_4Cl] cluster the chloride ion with four apical bonds controls the Cu^{II} positions in the cluster (Figure 3).

The Cu(1)–Cl(1) bond is inclined towards O(2), as indicated by the O(2)–Cu(1)–Cl(1) angle of 84.01° (inset of Figure 2). The C=N and C–O distances of the salicylaldimine fragments are 1.280(5) and 1.316(5) Å, respectively, consistent with the coordination of the deprotonated form of the salicylaldimine functionalities.[11] The single chloride anion binds all four Cu ions sitting at the corners of the rectangle with an average Cu···Cl distance of 2.775(5) Å, which is slightly longer than complexes containing tetrahedral and pyramidal μ_4-Cl.[2b,2f,7] The C–C distance within the imid-

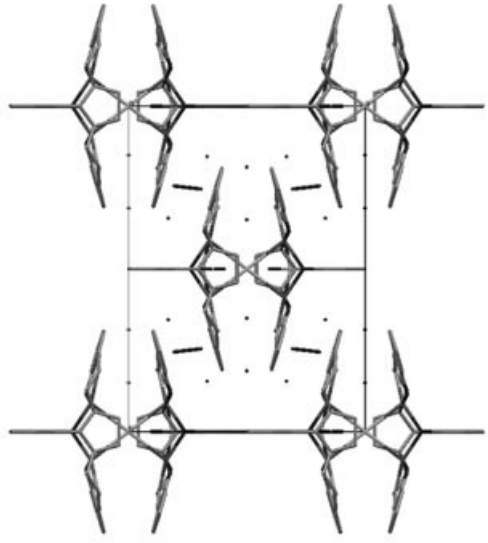


Figure 4. Packing diagram of **1a** along the crystallographic *c* axis.

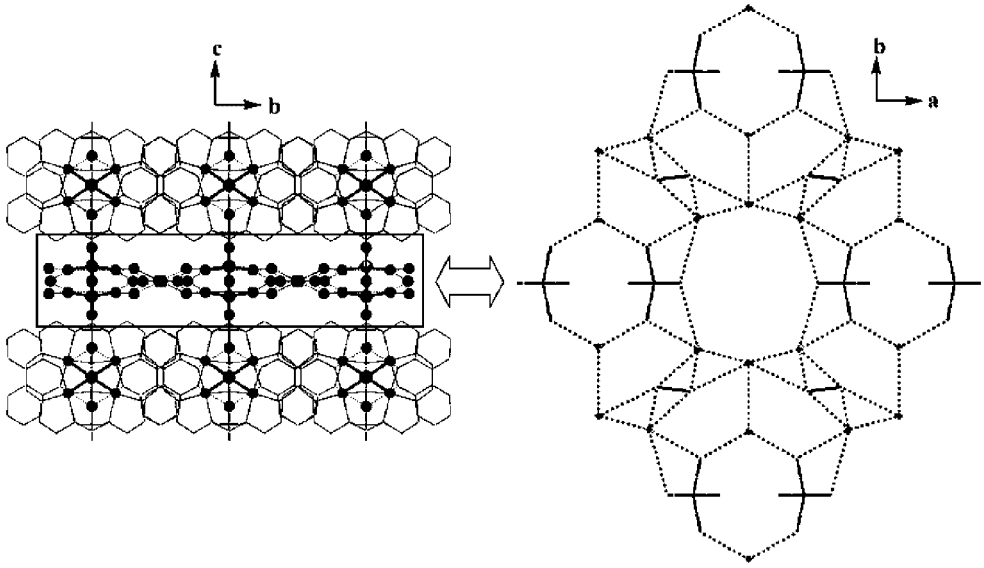


Figure 5. Packing diagram of **1a** along the crystallographic *a* axis (left) and the water–anion net inside the channel viewed along the crystallographic *c* axis (right).

azolidine ring is longer [1.527(8) Å] than the distance in the ethylenediamine backbone [1.46(2) Å].[9] The Cu–N_{imine} [1.935(3) Å] and Cu–N_{amine} [2.070(3) Å] distances are clearly different. The terminal Cu–$O_{phenolate}$ distance [1.906(3) Å] is shorter than the distance involving the central bridging phenolate arm [1.971(2) Å], and the intradimer Cu–Cl–Cu angle [71.44(2)°] is much smaller than the Cu–O–Cu angle [88.2(3)°] in a previously reported Cu_2 complex of the same ligand.[17] The Cl^- ligand serves as a template and assembles two Cu_2 units in an inverted configuration, which reduces the steric crowding of the central imidazolidinyl phenolate parts of the ligands. Convex molecules of **1a** pack nicely along the crystallographic *c* axis (Figure 4).

The crystal packing diagram along the *a* axis clearly shows the formation of a novel water-anion net within the intercluster space (Figure 5). This net forms hydrogen bonds with the terminal phenolate oxygens (O1) that are held tight in the intercluster space. The presence of these water molecules is crucial for cluster stability and crystal growth.

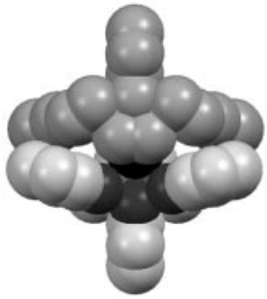


Figure 6. Two inverted crown $[Cu_2L]^+$ motifs sandwiching the chloride anion in a space filling model (ligand carbon atoms are shown in light grey and grey; black: oxygen; deep black: chlorine).

A space filling view of **1a** shows that two Cu_2 units sit over each other in an inverted fashion and the spherical chloride anion is trapped inside the complex (Figure 6).

Magnetochemistry of $[Cu^{II}_4(\mu_4\text{-}Cl)L_2]ClO_4\cdot 12H_2O$ (1a)

To determine the effect of a planar μ_4-Cl-bridging mode on the magnetic exchange within the cluster, bulk magnetisation measurements were carried out under a constant magnetic field of 5000 G between 1.8 and 300 K. The magnetic susceptibility data, corrected for the diamagnetic contribution of the complex and the sample holder, and TIP (temperature-independent paramagnetism) of 0.0016 cm^3 mol^{-1}, are shown in Figure 7.

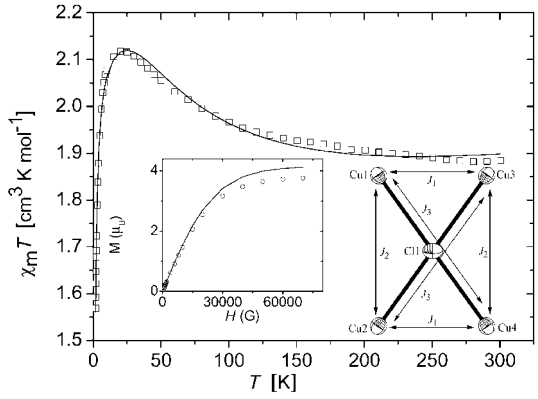


Figure 7. Plot of $\chi_m T$ vs. T in a magnetic field of 5000 G. The solid lines represent the best fit. The left inset shows the field-dependence of the magnetisation at T = 1.8 K. The solid line denotes the Brillouin curve calculated from two independent S = 1 spin system. The right inset shows the Cu_4Cl topology of the complex.

At 300 K, the $\chi_m T$ value of 1.88 $cm^3 K mol^{-1}$ is slightly higher than the expected value for four uncoupled copper(II) ions. $\chi_m T$ increases on lowering the temperature, reaching a maximum of 2.12 $cm^3 K mol^{-1}$ at 20 K and then decreasing rapidly. The initial rise in $\chi_m T$ on cooling implies the existence of dominant ferromagnetic interactions within the cluster. Based on the structural parameters, there are three possible magnetic exchange pathways, as illustrated in the inset of Figure 7. One is through the phenoxide bridge and the Cu–*N*–C–*N*–Cu route (J_1), in which the main magnetic contribution would arise from the former because of the longer pathway of the latter; the other two occur via the central Cl atom (J_2 and J_3). The magnetic data were properly fitted using the isotropic exchange Hamiltonian $H = -2J_1(S_1 \cdot S_3 + S_2 \cdot S_4) - 2J_2(S_1 \cdot S_2 + S_3 \cdot S_4) - 2J_3(S_1 \cdot S_4 + S_2 \cdot S_3)$.[18] A best fit gives magnetic parameters of $g = 2.08$, $J_1 = 33.4$, $J_2 = -0.25$ and $J_3 = -0.25$ cm^{-1}. These magnetic results are reliable as the bond length between Cu and the apical Cl atom is significantly longer (2.775 Å) than the $Cu–O_{phenoxide}$ distance (1.980 Å). It is reasonable to suppose that the magnetic exchange coupling for J_1 is strong whereas J_2 and J_3 are very weak. The ferromagnetic nature through the J_1 pathway can arise from the counter complementary effect between the phenoxide ligand and an NCN link from the Schiff base.[19] Accurate values of J_2 and J_3 could not be determined, although overall weak antiferromagnetic interactions through pathways J_2 and J_3 are still evident. The μ_4-Cl bridge mediates the magnetic coupling ineffectively because of the longer metal–chloride distance. This can be compared with the μ_4-O unit, which can transmit a stronger antiferromagnetic interaction.[9] The magnetic strength through the J_1 pathway is stronger than in the [$NaCu_4$] cluster ($J = 5.43$ cm^{-1})[11] and the tetranuclear carbonate complex ($2J = 39.44$ cm^{-1}).[20] From a magnetostructural point of view the magnetic orbital $d_{x^2-y^2}$ lies in the basal plane.[21] The pronounced exchange coupling (J_1) through the phenoxide route, compared with the [$NaCu_4$], can be understood by taking into account that the phenoxide ligand bridges two adjacent Cu centres in basal positions. This leads to effective overlap of the magnetic orbitals residing on the two Cu ions. In contrast, the apical-basal bridging mode of the phenoxide that operates in the [$NaCu_4$] cluster gives rise to a weaker overlap.[11] The field dependence of the magnetisation is plotted in the inset of Figure 7. The experimental data lie below the theoretical values derived from two uncoupled $S = 1$ spin systems. This result indicates that there are weak antiferromagnetic interactions between two pairs with an $S = 1$ ground state created by the intradimer ferromagnetic couplings at 1.8 K, which is consistent with the $\chi_m T$ vs. T plot.

Electrochemistry of $[Cu^{II}_4(\mu_4\text{-}Cl)L_2]ClO_4 \cdot 12H_2O$ (1a)

The electron-transfer behaviour of $[Cu^{II}_4(\mu_4\text{-}Cl)L_2]ClO_4 \cdot 12H_2O$ (**1a**) in dmf was studied by cyclic voltammetry at room temperature. A glassy-carbon working electrode with tetrabutylammonium perchlorate (TBAP) as supporting electrolyte at 298 K was used. The cyclic voltammogram was recorded in the potential range between –1.0 and +1.0 V vs. an Ag/AgCl reference electrode at a scan rate of 100 mV s^{-1}. Complexes **1b** and **1c** do not display any characteristic cyclic voltammetric response within the above-mentioned potential window, and only the μ_4-chlorido-bridged complex **1a** exhibits a quasi-reversible ($i_{pc}/i_{pa} = 0.8$) response at $E_{1/2} = 0.515$ V ($\Delta Ep = 156$ mV; Figure 8). The formal potential value for the copper(II) to copper(III) oxidation is similar to other complexes containing phenoxido donor ligands.[22] No characteristic voltammetric wave was observed on the negative side (vs. Ag/AgCl) of the potential window. The observed quasi-reversible peak is assigned to a one-electron transfer process [Equation (1)] for a metal-centred oxidation. The present electrochemical redox reaction in dmf is consistent with a quasi-reversible one-electron transfer process.[23]

$$[Cu^{III}Cu^{II}_3(\mu_4\text{-}Cl)L_2]^{2+}\ (\mathbf{1a^{2+}}) + e^- \leftrightarrow [Cu^{II}_4(\mu_4\text{-}Cl)L_2]^{+}\ (\mathbf{1a^{+}}) \quad (1)$$

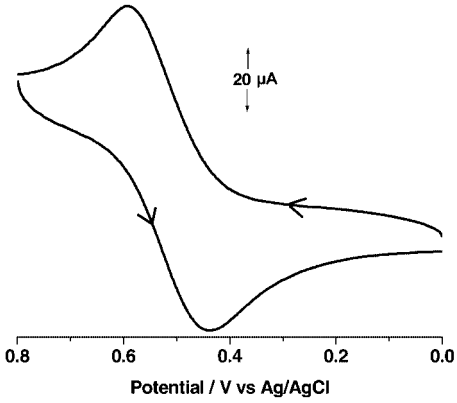


Figure 8. Cyclic voltammogram (scan rate 100 mV s^{-1}) of 10^{-3} M solutions of **1a** in dimethylformamide at a glassy-carbon electrode ($T = 298$ K).

The quasi-reversible nature of the voltammogram indicates the formation of a copper(III) centre within the cluster that is still coordinated to the μ_4-Cl^-. The absence of any voltammetric response in the analogous bromido- and iodido-bridged complexes **1b** and **1c** indicates that the trivalent state is only stable in solution when coordinated to chloride. At 298 K the oxidized species is only stable on the voltammetric timescale.

Concluding Remarks

We have shown that entrapment of a chloride ion by four copper ions is possible by isolating a {$Cu_4(\mu_4$-Cl)} core within a tetranuclear cluster. Two [Cu_2] units can be assembled around the spherical chloride ion, which serves as an anion template to give a rectangular planar geometry. The new supramolecular chlorido complex is formed in a discrete centrosymmetrical structure. The in-plane single atom nucleating coordination mode of Cl^- is the first example of its kind and exclusively binds four copper(II) centres without any auxiliary bridging units. The templating role of

Cl^- has been demonstrated with the help of the reaction of $[Cu_2L(H_2O)]ClO_4{\cdot}2H_2O$ (**3**) with NaCl. In **1a**, a weak antiferromagnetic interaction is observed between two [Cu^{II}_2] units with an $S = 1$ ground state that is created by an intradimer ferromagnetic coupling mediated by the basal-basal bridging mode of the phenoxido groups.

Experimental Section

Materials and Physical Measurements: Triethylenetetramine was obtained from S.D. Fine Chem. (India) and 2-hydroxybenzaldehyde from SRL (India). Cupric perchlorate hexahydrate was prepared by treating copper(II) carbonate with $HClO_4$ in a 1:1 ratio and crystallised after concentration in a water bath. All other chemicals and solvents were reagent-grade materials and were used as received without further purification. The elemental analyses (C, H, N) were performed with a Perkin–Elmer model 240 C elemental analyzer. IR spectra were recorded with a Perkin–Elmer 883 spectrophotometer. The solution electrical conductivity and electronic spectra were obtained with a Unitech type U131C digital conductivity meter with a solute concentration of about 10^{-3} M and a Shimadzu UV 3100 UV/Vis/NIR spectrophotometer, respectively. The room-temperature magnetic susceptibilities in the solid state were measured using a home built Gouy balance fitted with a Polytronic d.c. power supply. The experimental magnetic susceptibilities were corrected for the diamagnetic response using Pascal's constants. Magnetic measurements were carried out on polycrystalline samples (ca. 30 mg) using a Quantum Design MPMS-7 SQUID magnetometer operating at a constant magnetic field of 5000 G between 1.8 and 300 K. The experimental magnetic moment was corrected for the diamagnetic contribution from the sample holder and the diamagnetic response from the sample, which was evaluated from Pascal's constants. Electrochemical measurements were made using a PAR model 173 potentiostat/galvanostat, 175 universal programmer, 178 electrometer, and 377-cell system. A glassy carbon working electrode, a platinum-wire auxiliary electrode, and an Ag/AgCl reference electrode were used in a three-electrode configuration. A digital series 2000 Omni Graphic recorder was used to trace the voltammograms. Electrochemical measurements were performed under nitrogen in dry dmf.

All experimental procedures were performed in air at room temperature. The ligand H_3L [2-(2′-hydroxyphenyl)-1,3-bis[4-(2-hydroxyphenyl)-3-azabut-3-enyl]-1,3-imidazolidine) was prepared according to a literature procedure.[12]

Synthesis of Complexes: Two methods were followed for the synthesis and isolation of tetranuclear complexes **1a**–**c**. Method **1** is a direct method where the complexes were synthesised from the ligand and the corresponding copper salts. Method **2** is an indirect synthetic pathway from complex **3**. Details are given below for the representative cases.

$[Cu^{II}_2(\mu\text{-}H_2O)L]{\cdot}ClO_4{\cdot}2H_2O$ (3): A methanolic solution of triethylamine (0.55 mL, 4 mmol) was added to a solution of the ligand (0.50 g, 1.09 mmol) in 15 mL of dichloromethane followed by a methanolic solution of $Cu(ClO_4)_2{\cdot}6H_2O$ (0.80 g, 2.18 mmol) and the mixture was stirred at ambient temperature for one hour. The solvent was then evaporated in air, and the deep green precipitate obtained was filtered and washed with water, ethanol and finally dried in vacuo over P_4O_{10}. Yield: 0.60 g (75%). $C_{27}H_{33}ClCu_2N_4O_{10}$ (736.12): calcd. C 44.05, H 4.51, Cu 17.26, N 7.61; found C 43.82, H 4.94, Cu 16.90, N 7.37. IR (KBr disk): $\tilde{\nu}$ = 3388 cm^{-1} br, 2936 m, 1627 s, 1595 s, 1537 s, 1447 s, 1312 s, 1094 s, 914 s, 722 s. Molar conductance (MeCN solution): Λ_M = 130 $\Omega^{-1}cm^2mol^{-1}$. UV/Vis (dmf): λ_{max} (ε) = 640 nm (290 $M^{-1}cm^{-1}$), 402 (2770), 273 (22041).

$[Cu_4(\mu_4\text{-}Cl)L_2]ClO_4{\cdot}12H_2O$ (1a)

Method 1: A solution of H_3L (0.5 g, 1.09 mmol) in CH_2Cl_2/MeOH (1:1) (15 mL) was added to a solution of $CuCl_2{\cdot}2H_2O$ (0.371 g, 2.18 mmol) in CH_3CN/MeOH (1:1; 20 mL) then Et_3N (0.5 mL, 3.58 mmol) was added dropwise. The mixture was stirred for 1 h and $[Cu_4(\mu_4\text{-}Cl)L_2]Cl$ precipitated as a green solid in about 80% yield. This solid was isolated, washed with cold methanol, and dried under vacuum over P_4O_{10}. It was then dissolved in dmf and a stoichiometric amount of $NaClO_4$ was added. Single crystals suitable for X-ray analysis were obtained from the above mixture after 6 d. $C_{54}H_{78}Cl_2Cu_4N_8O_{22}$ (1516.3): calcd. C 42.77, H 5.18, Cu 16.76, N 7.39; found C 42.48, H 5.46, Cu 16.42, N 6.98. Molar conductance (dmf): Λ_M = 90 $\Omega^{-1}cm^2mol^{-1}$. UV/Vis spectrum (dmf): λ_{max} (ε) = 660 nm (440 $M^{-1}cm^{-1}$), 377 (7810), 280 (20150). Selected IR bands (KBr) $\tilde{\nu}$ = 3388 cm^{-1} vs, 1633 vs, 1445 m, 1304 m, 1120 w, 1091 m, 770 w, 667 m.

Caution! *Perchlorates are potentially explosive and should be handled only in very small quantities.*

Method 2: A methanolic solution of NaCl (0.016 g, 0.27 mmol) was added dropwise to an acetonitrile solution (50 mL) of complex **3** (0.4 g, 0.54 mmol) and stirring was continued for 1 h to give a greenish crystalline product. This solid was isolated, washed with cold methanol/water and dried under vacuum over P_4O_{10}. Analytical and spectroscopic data indicated the formation of complex **1a**.

$[Cu_4(\mu_4\text{-}Br)L_2]ClO_4{\cdot}2H_2O$ (1b)

Method 1: A solution of H_3L (0.5 g, 1.09 mmol) in methanol (15 mL) was added to an acetonitrile solution (30 mL) of $CuBr_2$ (0.486 g, 2.18 mmol) and then Et_3N (0.5 mL, 3.58 mmol) was added dropwise. The mixture was stirred for 1 h, whereupon the complex precipitated as a green solid (ca. 74% yield). This solid was isolated, washed with cold methanol, and dried under vacuum over P_4O_{10}. It was then dissolved in dmf and a stoichiometric amount of $NaClO_4$ was added. After one week the resulting crystals of **1b** were isolated and dried under vacuum over P_4O_{10}. $C_{54}H_{58}BrClCu_4N_8O_{12}$ (1380.6): calcd. C 46.97, H 4.23, Cu 16.76, N 8.11; found C 46.88, H 4.44, Cu 16.62, N 7.86. Molar conductance (dmf): Λ_M = 95 $\Omega^{-1}cm^2mol^{-1}$. UV/Vis (CH_3CN): λ_{max} (ε) = 620 nm (510 $M^{-1}cm^{-1}$), 377 (15426), 280 (21800). Selected IR data (KBr): $\tilde{\nu}$ = 3427 cm^{-1} vs, 1636 vs, 1458 s, 1307 m, 1130 m, 1088 s, 762 s.

Method 2: A methanolic solution of KBr (0.032 g, 0.27 mmol), was added dropwise to an acetonitrile solution (30 mL) of complex **3** (0.4 g, 0.54 mmol) and stirring was continued for 1 h to give a greenish crystalline product. This solid was isolated, washed with cold methanol/water and dried under vacuum over P_4O_{10}. All analytical and spectroscopic data indicated formation of complex **1b**. All attempts to obtain crystals of **1b** suitable for an X-ray structure determination were unsuccessful.

$[Cu_4(\mu_4\text{-}I)L_2]ClO_4{\cdot}2H_2O$ (1c)

Method 1: A solution of H_3L (0.5 g, 1.09 mmol) in methanol (15 mL) was added to an acetonitrile solution (50 mL) of CuI (0.415 g, 2.18 mmol) and then Et_3N (0.5 mL, 3.58 mmol) was added dropwise. The mixture was stirred for 1 h, and the complex precipitated as a green solid (ca. 69% yield). This solid was isolated, washed with cold methanol, and dried under vacuum over P_4O_{10}. It was then dissolved in dmf and a stoichiometric amount of $NaClO_4$ was added. After one week crystals of **1c** were isolated and dried under vacuum over P_4O_{10}. $C_{54}H_{58}ClCu_4IN_8O_{12}$ (1427.6):

calcd. C 45.43, H 4.09, Cu 17.80, N 7.84; found C 45.28, H 4.34, Cu 17.70, N 7.52. Molar conductance (dmf): Λ_M = 92 $\Omega^{-1}cm^2mol^{-1}$. UV/Vis (CH_3CN): λ_{max} (ε) 635 nm (747 $M^{-1}cm^{-1}$), 377 (16305), 280 (22426). Selected IR bands (KBr): $\tilde{\nu}$ = 3392 cm^{-1} vs, 1632 vs, 1536 m, 1448 s, 1311 m, 1196 m, 1090 s, 766 s.

Method 2: A methanolic solution of KI (0.044 g, 0.27 mmol) was added dropwise to an acetonitrile solution (50 mL) of complex **3** (0.4 g, 0.54 mmol) and stirring was continued for 2 h to give a greenish crystalline solid. This solid was isolated, washed with cold methanol/water and dried under vacuum over P_4O_{10}. All analytical and spectroscopic data indicated formation of complex **1c**. All attempts to obtain crystals of **1c** suitable for X-ray structure determination were unsuccessful.

$[NaCu_4L_2(N_3)_2]ClO_4\cdot H_2O$ (5)

Method 1: A methanolic solution of $Cu(ClO_4)_2\cdot 6H_2O$ (0.80 g, 2.18 mmol) was added to a dichloromethane solution (10 mL) of the ligand (0.50 g, 1.09 mmol) and then a methanolic solution of NaN_3 (0.07 g, 1.09 mmol) was added dropwise whilst stirring at ambient temperature in air. After 15 min, a dilute methanolic solution of Et_3N (0.45 mL ,3.27 mmol) was added and the reaction mixture was stirred for 1 h more. The complex precipitated as a green solid (ca. 85% yield), which was isolated, washed with water, and dried under vacuum over P_4O_{10}. Single crystals suitable for X-ray analysis were obtained from MeOH/MeCN (1:1) after five days. $C_{54}H_{56}ClCu_4N_{14}NaO_{11}$ (1389.8): calcd. C 46.66, H 4.06, Cu 18.28, N 14.10; found C 46.64, H 4.25, Cu 18.50, N 13.88. Molar conductance (dmf): Λ_M = 73 $\Omega^{-1}cm^2mol^{-1}$. UV/Vis (dmf): λ_{max} (ε) = 650 nm (150 $M^{-1}cm^{-1}$), 398 (2660), 271 (16062). IR (KBr disk): $\tilde{\nu}$ = 3425 cm^{-1} br, 2926 m, 2076 s, 1633 s, 1595 s, 1537 s, 1447 s, 1312 s, 1274 s, 1081 s, 747 s, 625 s.

Caution! *Azide derivatives are potentially explosive and should be handled only in very small quantities.*

Method 2: A methanolic solution of NaN_3 (0.035 g, 0.54 mmol) was added dropwise to an acetonitrile solution (50 mL) of complex **3** (0.4 g, 0.54 mmol) and stirring was continued for 2 h to give a greenish crystalline product, which was isolated, washed with cold methanol/water and dried under vacuum over P_4O_{10}. All analytical and spectroscopic data indicated the formation of complex **5**.

Method 3: A methanolic solution of NaN_3 (0.025 g, 0.395 mmol) was added dropwise to an acetonitrile solution (50 mL) of complex **1a** (0.3 g, 0.197 mmol) and stirring was continued for 1 h to give a greenish crystalline product, which was isolated, washed with cold methanol/water and dried under vacuum over P_4O_{10}. All analytical and spectroscopic data indicated the formation of complex **5**.

X-ray Crystallographic Study of $[Cu_4(\mu_4\text{-}Cl)L_2]ClO_4\cdot 12H_2O$ (1a): Green block-shaped single crystals of $[Cu_4(\mu_4\text{-}Cl)L_2]ClO_4\cdot 12H_2O$ suitable for X-ray analysis were grown by the slow evaporation of a dmf solution of the complex. The intensity data for the complex were collected on a CAD-4 single-crystal X-ray diffractometer equipped with a graphite-monochromated Mo-K_α radiation source (λ = 0.71073 Å) by the ω-scan method for a single crystal with dimensions 0.14 × 0.12 × 0.11 mm^3. Precise unit cell dimensions were determined by least-squares refinement of 25 strong reflections having 2θ values between 1.57 and 24.97 °. Data were collected at 298 K. A total of 3127 reflections were recorded with Miller indices h_{min} = 0, h_{max} = 16, k_{min} = 0, k_{max} = 22 and l_{min} = –15, l_{max} = 15. In the final cycles of full-matrix least-squares refinement on F^2 all non-hydrogen atoms were assigned anisotropic thermal parameters and refinement converged at R = 0.0473. The residual electron density was in the range +0.491 to –0.541 e $Å^{-3}$. The structure was solved with the SHELX-97 programme system[24] and refined using full-matrix least-squares with all non-hydrogen atoms treated anisotropically and hydrogens included at calculated positions as riding on their carrier atoms. H-atoms on water molecules could not be located. The ClO_4^- anion and some solvent water molecules were found to be disordered. Further information concerning X-ray data collection and structure refinement of the compound is summarised in Table 2.

Table 2. Crystallographic data for compound $[Cu_4(\mu_4\text{-}Cl)L_2]ClO_4\cdot 12H_2O$ (**1a**).

Molecular formula	$C_{54}H_{78}N_8O_{22}Cl_2Cu_4$
Molecular weight	1516.33
Crystal system	monoclinic
Space group	*C*2/*m*
a [Å]	13.643(3)
b [Å]	18.619(8)
c [Å]	13.139(2)
β [°]	100.25(2)
V [$Å^3$]	3284.3(17)
D_c [$g\,cm^{-3}$]	1.541
Z	2
F(000)	1552
λ [Å]	0.71073
T [K]	298(1)
Crystal size [mm]	0.14 × 0.12 × 0.11
μ [mm^{-1}]	1.441
R,[a] R_w[b] [$I > 2\sigma(I)$]	0.0473, 0.1190
GOF	1.047
Max., min. residual electron density [e $Å^{-3}$]	0.491, –0.541

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$; $w = 0.75/[\sigma^2(F_o) + 0.001F_o^2]$.

CCDC-611922 contains 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.

Acknowledgments

We are grateful to the Council of Scientific and Industrial Research, New Delhi, for financial support. C. S. H. acknowledges financial support from the Korean Government (MOEHRD, Basic Research Promotion Fund) (KRF-2005-070-C00068) and H. C. K. acknowledges financial support from the Korean Government.

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Received: September 28, 2006
Published Online: March 13, 2007

