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Formation of a four-bladed waterwheel-type chloro-bridged dicopper(II) complex with dithiamacrocycle *via* double *exo*-coordination[†]

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A combination of O_3S_2 -macrocycles incorporating different sulfurto-sulfur separations (S-(CH₂)_n-S, L¹: n = 2, L²: n = 3) and copper(II) nitrate afforded new types of both monocopper(II) and dicopper(II) complexes, respectively. L¹ gave a 1D coordination polymer [Cu₂(L¹)₂(NO₃)₄]_n (1) based on a convergent *exo*-coordination mode while L² resulted in the formation of a divergent *exo*/*exo*-coordinated dicopper(II) complex, [Cu₂(L²_{ox})₄(μ -Cl)](NO₃)₄ (2), whose shape resembles a four-bladed waterwheel in which *in situ* oxidized macrocycles (L²_{ox}) act as the blades and a Cu^{II}-(μ -Cl)-Cu^{II} entity corresponds to the axle shaft. The chloro-bridging ligand is derived from the dichloromethane solvent and its arrangement is held together by C-H····Cl⁻ H-bonds. Compound 2 shows a weak antiferromagnetic property *via* the Cu^{II}-(μ -Cl)-Cu^{II} entity.

Dinuclear complexes are of special interest across diverse areas that include biomimetic catalysts, allosteric behaviours and magnetic materials.¹ Thus, various approaches have been devoted to the development of ligating systems capable of binding two metal ions in defined sites. In particular, the dinucleating process is well exemplified by the formation of dinuclear macrocyclic complexes *via* self-assembly and/or molecular recognition.^{2–5}

Common motifs in the design of dinucleating macrocycles involve, as shown in Fig. 1, a large macrocycle capable of binding two metal ions in its cavity (type A),^{1c,d,2} two linked macrocycles sharing a spiro-centre (type B)³ and two linked macrocycles connected by a spacer unit (type C).⁴ Unlike types A–C that give rise to endocyclic metal coordination, type D can

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Gyeongsang National University, Jinju 52828, South Korea. E-mail: sslee@gnu.ac.kr ^bDepartment of Chemistry, National University of Singapore, Singapore 117543, Singapore. E-mail: pihghost@nate.com undergo both endocyclic and exocyclic coordination in which the single-ring macrocycle binds to two metal ions in different ways.⁵ In this study, we report an example of another macrocyclic ligand coordination mode that differs from types A–D which gives rise to a new type of dinuclear complex involving "double" *exo*-coordination.

Although *exo*-coordination occurs less frequently in macrocyclic complexes, it quite often occurs in thiamacrocycles upon binding soft metal ions.⁵ Furthermore, *exo*-coordination is a promising tool for linking macrocycles in diverse ways for the construction of highly ordered discrete metallosupramolecules^{5b,6} and coordination polymers.^{5a,7} The incorporation of a specific binding subunit into a ligand design provides an approach toward the development of new supramolecular coordination compounds and metal-organic nanomaterials.⁸ Recently, we have reported the use of bis-O₂S₂macrocycle isomers that incorporate U-shaped and W-shaped *exo*-coordination binding sites, respectively, for the controlled formation of Cu_nI_n (n = 2 or 4) clusters.^{3a}

In this work, we propose a rational approach for constructing *exo/exo*-type dinuclear copper(π) complexes (Fig. 2b) that represent a new dinuclear type that is different from types A–D. In particular, unlike paramagnetic mononuclear copper(π) complexes, the dinuclear copper(π) complexes bridged by small ligands tend to exhibit antiferromagnetic coupling.⁹



Fig. 1 Four types of dinuclear macrocyclic complexes.



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Fig. 2 Two copper(II) complexes 1 and 2 isolated in this work showing (a) convergent *exo*-mode and (b) divergent *exo/exo*-modes, respectively, depending on the size of $(-CH_2-)_n$ chain linking the sulfur donors.

Toward this goal, we employed two macrocycles incorporating different $-S-(CH_2)_n-S-$ segments, L¹: n = 2 and L²: n = 3, because the alteration of such binding sites might induce the formation of *exo*-coordination-based complexes exhibiting either a convergent mode or a divergent mode.¹⁰

Indeed, L^1 resulted in the formation of a one-dimensional (1D) coordination polymer involving convergent *exo*-coordination (Fig. 2a). Surprisingly, the resulting product 2 upon using the L^2 ligand was a waterwheel-like dicopper(II) complex based on divergent *exo/exo*-coordination which has Cu^{II} - $O_{sulfoxide}$ bonds by the oxidation of L^2 to L^2_{ox} (Fig. 2b and c). Furthermore, the chlorido ligand in the mono-chloro-bridged dicopper(II) complex 2 showing an antiferromagnetic superexchange⁹ is derived from the decomposition of the dichloromethane solvent. Both isolated products appear to be the first examples of such species yet reported. The details of our investigation are described below.

The macrocyclic ligands L^1 and L^2 were each synthesized using a coupling reaction between dichloride 5 and the required dithiols in the presence of cesium carbonate under high dilution conditions (Scheme S1†). The intermediate compounds 3–5 were prepared using known procedures.¹¹ Single crystals of L^1 and L^2 were obtained by slow evaporation from dichloromethane and their solid structures were determined by single crystal X-ray analysis (Table S1,† see later).

The crystalline copper(II) complexes **1** and **2** were obtained by the reaction of one equivalent of $Cu(NO_3)_2 \cdot 3H_2O$ with L^1 and L^2 in dichloromethane/acetonitrile, respectively. In obtaining **1**, slow evaporation of the reaction mixture afforded the product as dark blue crystals in 40% yield. In the case of **2**, slow evaporation of the reaction mixture over 3 weeks afforded a small number of blue crystals (yield ~2%). A comparison of the PXRD patterns for **1** and **2** with the corresponding simulated data confirmed the phase purity of each product (Fig. S7†).

Product 1 crystallizes in the monoclinic space group C2/c with the formula $[Cu_2(L^1)_2(NO_3)_4]_n$ by adopting a 1D polymeric structure (Fig. 3a). The asymmetric unit for 1 contains half of the formula unit. In 1, the two crystallographically different



Fig. 3 Copper(II) nitrate complex of L¹, $[Cu_2(L^1)_2(NO_3)_4]_n$ (1): (a) 1D polymeric structure, (b) local coordination environments of the Cu1 and Cu2 atoms and (c) comparison of the S1...S2 distances (Å) in free and bound L¹.

copper atoms (Cu1 and Cu2) have different coordination environments. The Cu1 atom is six-coordinate, being bound to four sulfur donors from two different L¹ ligands to form a square plane. The two axial sites are occupied by the bridging nitrate ions, linking the Cu1 atom and Cu2 atoms. The Cu2 atom is four-coordinate, trans square planar, being bound to two bridging nitrate ions and two terminal monodentate nitrate ions. The preferred formation of 1 accords well with L¹ incorporating a shorter sulfur-to-sulfur distance to form a stable 5-membered chelate ring involving a convergent exocoordination mode (Fig. 2a), leading to a bis(macrocycle) monocopper(II) complex unit. The open sites in the copper coordination sphere of the Cu1 atom allow nitrate coordination which also links another copper atom (Cu2) to ultimately afford the 1D chain. The S1...S2 distance in 1 (3.2380(8) Å) is shorter than that in the free ligand L^1 (4.3857(1) Å) due to the twisting of the torsion angle between the two S atoms from a trans to a gauche arrangement upon complexation (Fig. 2c).

Product 2 crystallizes in the monoclinic space group I4/m with the formula $[Cu_2(\mu-Cl)(L^2_{ox})_4]Cl(NO_3)_2$ showing a 2:4 (metal-to-ligand) stoichiometry (Fig. 4a). As mentioned, the overall structure of 2 resembles a four-bladed waterwheel (Fig. 4b). Furthermore, the double *exo*-coordinated dicopper(π) system coupled with the multiple events arising from the ligand oxidation (L^2_{ox}) (Fig. 2c) and the solvent decomposition provides a pathway to this unique complex. Thus, 2 incorporates two copper(π) centres linked by one chloride ion (μ -Cl⁻) to form a central shaft or axle of type Cu^{II}-(μ -Cl)-Cu^{II}. The centrosymmetric complex has a C_4 rotation axis, with an inversion centre at the chloro-bridge. The chloro-bridged dicopper(π) shaft and four L^2_{ox} ligands are linked by Cu1–O3 bonds (1.945(3) Å) in the divergent *exo/exo*-coordination mode to form the four-bladed waterwheel-like structure.



Fig. 4 Crystal structure of $[Cu_2(\mu-Cl)(L^2_{ox})_4]Cl(NO_3)_2$ (2): (a) view of the 2:4 (metal-to-ligand) stoichiometric complex, (b) schematic presentation of the four-bladed waterwheel complex, (c) chloro-shared double square pyramidal geometry and (d) comparison of the interatomic distances (Å) before and after complexation.

Each copper(II) centre in 2 is five-coordinate being bound to four oxygen atoms (Cu1–O3 1.945(3) Å) from S=O groups arising from four different \mathbf{L}^2_{ox} ligands together with a μ -Cl⁻ group (Cu1–Cl1 2.4699(19) Å) to yield a square pyramidal geometry for each centre, with the apical position occupied by the bridging chloride ligand (Fig. 4c); the τ value is 0.11 (where $\tau =$ 0 corresponds to a perfect square pyramid, while $\tau = 1$ corresponds to a perfect trigonal bipyramid).¹² The conformation of the S1–C–C–C–S2 linkage in the free \mathbf{L}^2 shows a *g*-*t*-*g* (*g* = *gauche*; *t* = *trans*) arrangement which is then changed to a *g*-*g*-*g* arrangement upon complexation (Fig. 4d). In 2, the S=O···O=S distance (5.3491(29) Å) is larger than that of the S···S distance (3.8463(21) Å) (Fig. 4d).

Meanwhile, the formation of 2 raises the following questions. (i) How is the *in situ* oxidized macrocycle (L^2_{ox}) formed? (ii) What is the source of the chloro-bridge? (iii) What is the mechanism for the assembly of this highly ordered suprastructure from its individual components? Each of these aspects will now be discussed.

First, in forming the waterwheel structure from the reaction mixture of $Cu(NO_3)_2 \cdot 3H_2O$ and L^2 , clear sulfoxidation of L^2 has occurred *in situ* to afford L^2_{ox} . The observed sulfoxidation of L^2 was initially confirmed by the IR spectrum of 2 which shows a new peak at 1009 cm⁻¹ assigned to the $\nu_{S=O}$ stretching mode (Fig. S6†).¹³ It appears that the sulfoxidation might occur *via* one of the two routes: oxidation by copper(II) or by air. In this respect, it is noted that, on standing in air, the reaction mixture maintained its blue colour over about 3 weeks; during this time a few blue single crystals of 2 grew in the mixture. It is relevant to the above that we have previously reported the

reaction of copper(π) nitrate with 1,10-dithia-18-crown-6, forming a polymeric product in which the air-oxidation of sulfur donors to disulfoxides had taken place.^{13b} Since in this past example and in the present case we found no evidence for the reduction of copper(π), we conclude that L^2_{ox} was generated by air-oxidation. Among the 380 hits found for -S=O-Cu^{II} in the Cambridge Structural Database,¹⁴ almost all correspond to solvato complexes of dimethylsulfoxide (DMSO), with complexes related to other sulfoxide ligands being rare.

Second, we were puzzled by the origins of the chloride ion that bridges the two copper(π) centres in **2**. In other reactions of the present general type, species arising from decomposed solvent molecules have been shown to sometimes participate in product formation as auxiliary ligating components.¹⁵ For example, we recently reported isostructural dichloro-bridged dicopper(π) bis(macrocycle) complexes of the type [LCu-(μ -Cl)₂-CuL]X₂ (L: N₃O₂-macrocycle, X: NO₃ or ClO₄) whose chlorido ligands are derived from the decomposition of the dichloromethane solvent.^{15b} Similarly, this appears to be the source of the chloro-bridge in **2**. Compared with the di-chloro-bridged dicopper(π) entity, mono-chloro-bridged dicopper(π) entities as found in **2** are less common.¹⁶ The preferred formation of this linear mono-chloro-bridged dicopper(π) entity in **2** may reflect the confined environment in which it resides.

Third is the question of how such a supra-structure could be formed. If it is supposed that four L^2 ligands were to coordinate to the copper(II) centres directly via Cu-S bonds to form such a highly ordered structure, then difficulties would almost certainly be encountered in overcoming the steric hindrance between adjacent bulky macrocycles. Instead, L²_{ox} binds via Cu–O=S bonds^{13b} and this will ameliorate any such steric hindrance, allowing the waterwheel product to form. Furthermore, the chloro-bridge in 2 was found to interact with four CH₂ groups from four different ligands via C-H…Cl⁻ bonds, with the C…Cl⁻ distances and C-H…Cl⁻ angles being 2.9684(15) Å and 150.04°, respectively (dashed lines in Fig. S8a[†]).¹⁷ Considering that synthetic hosts for halide ions normally employ between 2 and 6 binding interactions, the octahedral geometry of the chloride ion in 2 (Fig. S8a[†]) represents a good example of the use of the highest coordination number to achieve maximum stabilization.

Our attempts to prepare analogous products incorporating other (larger) halide ions by addition of the corresponding sodium(1) salts were not effective, probably because this would lead to the formation of less favourable H-bonds and, also, because of the limited space available to occupy the larger halide ions. Weaker H-bonds, including C–H…N and C–H…O interactions, quite often play an important role in stabilizing supramolecular structures when large numbers may act in concert.^{17*a*,18} In **2**, the presence of three C–H…O interligand H-bonds were confirmed [C–H11b…O2F 2.7433(14) Å (144.70°), C–H11bE…O2B 2.7433(14) Å (144.70°), C–H12b…O1F 2.464(1) Å (171.98°)] (Fig. S8b†). The linking of four macrocycles *via* twelve H-bonds stabilizes the overall structure to yield a pseudo-cage, with all these H-bonds being geometrically and electronically well matched to satisfy the mutual complementary conditions required for the pseudo-cage formation.

Although the procedure for 2 was reproducible, the low yield (~2%) was probably due to the chloride being the limiting reagent; it appeared to be present from the decomposition of the dichloromethane solvent,^{15*a,b*} since no chloride was added to the reaction solution. When an excess amount of NaCl was added to the same reaction mixture, it resulted in the formation of crystalline 2 in higher yield (~10%) after one week. However, an attempt for the sulfoxidation of L^2 to L^2_{ox} by H_2O_2 was ineffective in increasing the yield.¹⁹

As mentioned, dinuclear ligand-bridged paramagnetic metal complexes often exhibit weak antiferromagnetic coupling, sometimes giving them a diamagnetic nature.¹⁰ Magnetic susceptibility (χ_M) measurements for **1** and **2** were carried out (Fig. 5). The $\chi_{\rm M}T$ values for 1 slightly decrease with decreasing temperature over 20-300 K and then increase below 20 K, indicating the presence of weak ferromagnetic coupling, with a coupling constant (J) of +1.12 cm⁻¹. The experimental data were fitted by using the PHI²⁰ program by means of an isotropic spin Hamiltonian (SH) accounting for the exchange coupling (Heisenberg-Dirac-van Vleck Hamiltonian) and zero-field splitting (ZFC) for the two interacting S = 1/2 centers. The bestfitting for experimental data leads to the parameters: J =+1.12 cm⁻¹, TIP = 5×10^{-4} cm³ mol⁻¹ and g = 2.03. The solid line in Fig. 5 corresponds to the best theoretical fit. The corresponding plot for 2 shows that the $\chi_{M}T$ values are nearly constant over 25-300 K but sharply decrease below 25 K, indicating the presence of weak antiferromagnetic coupling (J = -0.64 cm^{-1}) between the two copper(II) atoms *via* the linear chloro-bridge.

The ¹H-NMR spectrum of 2 using DMSO- d_6 was observed to occur in the normal (diamagnetic) region due to the antiferromagnetic coupling (Fig. S9†), indicating that the waterwheel structure remains intact and is in keeping with complexation occurring through both sulfoxides of L^2_{ox} . However, the 1D polymeric structure of 1 was found to dissociate in DMSO- d_6 to yield free L^1 in accord with the DMSO- d_6 sulfoxide group showing higher affinity towards copper(π) relative to that of the thioether sulfurs in L^1 .



Fig. 5 Temperature dependence of $\chi_M T$ for **1** and **2**.

Conclusions

In summary, our approach toward the development of an exo/ exo-type dinuclear macrocyclic complex led to the formation of an unusual waterwheel-like tetra(macrocycle) dicopper(II) complex. In this aspect, the supra-structured product isolated was much more interesting than initially expected. Furthermore, the formation of the waterwheel structure highlights the decisive roles of the individual components in determining the final structural outcome. For example, the chloride ion is bound by two copper(II) to form a linear Cu^{II}-(µ-Cl)-Cu^{II} axis and the supramolecular arrangement is held together by Cu-O=S coordination bonds in addition to strategically positioned CH…Cl⁻ interactions. Furthermore, the "opening up" that occurs with the use of four disulfoxide ligands of type L^2_{ox} minimizes the steric repulsion between macrocyclic units by the Cu–O=S bonding in forming the waterwheel-like dicopper(n)complex 2. In this, each component is precisely matched to satisfy the divergent exo/exo-coordination mode required for the generation of the observed highly ordered assembly. The restricted structural conformation of the waterwheel-like dicopper(II) complex by its ¹H-NMR spectrum has proved possible due to the presence of antiferromagnetic coupling between two copper(II) centres. The present work not only represents a step forward in achieving the construction and characterization of a new exo/exo-type dinuclear macrocyclic complex but may also serve as an inspiration and guide for the design and development of new sulfur-extended supramolecular materials in the future.

Conflicts of interest

There are no conflicts to declare.

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