

Two novel compartmental macrocyclic dinuclear copper(II) complexes with μ_2 -Cl and μ_2 -OAc bridges

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ARTICLE INFO

Article history:

Received 23 May 2008

Accepted 23 June 2008

Available online 27 June 2008

Keywords:

Dinuclear copper(II) complex

Macrocyclic compounds

Schiff base

Structural elucidation

ABSTRACT

Two novel compartmental macrocyclic dinuclear copper(II) complexes with different bridging ligands, formulated as $[\text{Cu}_2^{\text{II}}(\text{L})(\mu_2\text{-Cl})] \cdot 1.5(\text{H}_2\text{O})$ (**1**) and $[\text{Cu}_2^{\text{II}}(\text{L})(\mu_2\text{-OAc})] \cdot (\text{DMF})$ (**2**), are characterized by X-ray single-crystal diffraction where LH_3 is a pentadentate ligand obtained from the Schiff base condensation between 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde and 2,6-bis(aminomethyl)-4-chlorophenol in a molar ratio of 2:1. Due to the use of different bridges and bulky *t*-bu groups, different molecular conformation and dimeric packing structures are observed.

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The growing interest in the macrocyclic chemistry lies in designing new synthetic approach, asymmetric and chiral macrocyclic complexes, theoretical calculations and their possible applications in a number of fields, especially for those having photoluminescent and non-linear optical properties, or having robust and thermally stable open-framework structures giving rise to permanent porosity which is a prerequisite for sorption or selective inclusion of guest molecules [1–5]. Till now, many [2+2] and [3+3] macrocyclic complexes and [1+2] compartmental macrocyclic complexes have been obtained from the Schiff base condensation between 2,6-diformyl-4-methylphenol or salicylaldehyde and 2,6-bis(aminomethyl)-4-methylphenol have been studied, especially the contributions from Mikuriya's and Robson's research groups. They are [2+2] tetranuclear Ni(II) and Zn(II) macrocyclic complexes [6–8], one [3+3] hexanuclear Cu(II) complex [9], [1+2] hexanuclear Cu(II) [10], pentanuclear Fe(III) [11], tetranuclear Mn(III), and Zn(II) [12,13] and dinuclear Fe(III) and V(IV) complexes [14,15], and [1+2] pyrazole bridged tetranuclear Zn(II) [16] and Ni(II) [17–19], dinuclear Ni(II) [17] and Cu(II) complexes [20]. All the above-mentioned metal complexes with different nuclearities used 2,6-bis(salicylideneaminomethyl)-4-methylphenolato ligand, but alkyl-substituted salicylaldehyde and 4-chlorophenol related double Schiff base structures are seldom.

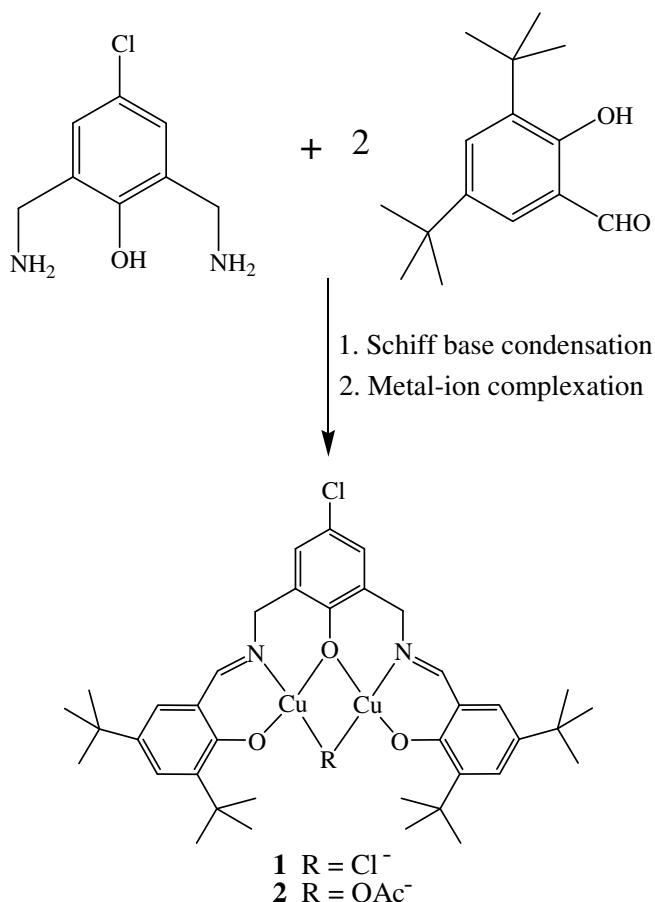
In our systematic work, a variety of chiral and achiral metallo-macrocyclic complexes have been synthesized by sodium(I) template condensation [21–28]. We have newly acquired [2+2], [2+1], [1+2] kinds of ring-contraction metal complexes from chiral

or racemic [3+3] macrocyclic ligands [29,30]. In this paper, we present two novel compartmental macrocyclic dinuclear copper(II) complexes, formulated as $[\text{Cu}_2^{\text{II}}(\text{L})(\mu_2\text{-Cl})] \cdot 1.5(\text{H}_2\text{O})$ (**1**) and $[\text{Cu}_2^{\text{II}}(\text{L})(\mu_2\text{-OAc})] \cdot (\text{DMF})$ (**2**), where LH_3 is a pentadentate ligand obtained from the Schiff base condensation between 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde and 2,6-bis(aminomethyl)-4-chlorophenol in a molar ratio of 2:1.

Compartmental macrocyclic dinuclear copper(II) complexes of **1** and **2** were synthesized via a conventional sodium template [1+2] Schiff base condensation (Scheme 1) [31,32] between 2,6-bis(aminomethyl)-4-chlorophenol dihydrochloride and 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde [33]. The elemental analyses and spectral characterizations of **1** and **2** are consistent with their molecular structures. Two analogous UV–Vis absorption peaks were found at 279 and 381 nm for **1** and 275 and 379 nm for **2**, respectively, corresponding to the $\Pi\text{-}\Pi^*$ transition of the phenolic rings and the $\Pi\text{-}\Pi^*$ transition of the azomethine chromophore (see Fig. 1). Electrospray ionization mass spectra (ESI-MS) in methanol gave the same dimeric peak at $m/z = 1545$ for both dinuclear copper(II) complexes, which can be assigned as $[2\text{M}\text{-Cl}]^+$ in **1** and $[2\text{M}\text{-OAc}]^+$ species in **2**.

The X-ray determination result of **1** [34] reveals that it crystallizes in the monoclinic space group $C2/c$ and each Cu(II) center displays very distorted four-coordinate square planar configuration (Fig. 2) where one nitrogen and two oxygen donors on the compartmental macrocyclic framework as well as a μ_2 -bridged chlorine atom constitute the basal plane. The basal coordination planes for each copper(II) center are essentially planar with the mean deviations from plane of 0.3426 Å (least-squares plane comprised of atoms Cl1, N2, O1 and O3) and 0.2975 Å (least-squares

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Scheme 1. Schematic illustration for the preparation of **1** and **2** in the present study.

plane comprised of atoms Cl1, N1, O1 and O2), respectively. The dihedral angle between the two planes is 26.3°. The distances between the central copper(II) ions and the least-squares coordination planes are 0.0214 Å for Cu1 and 0.0561 Å for Cu2, respectively. Three phenyl rings in the molecular structure of **1** are not coplanar mainly due to the presence of multiple bulky *t*-bu groups and the restriction of the coordination geometry of central copper(II) ions.

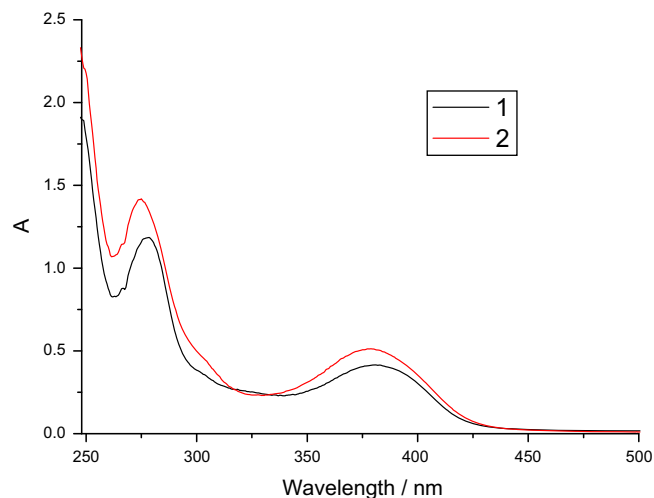


Fig. 1. UV-Vis absorption spectra of **1** and **2** in ethanol.

The dihedral angles between the middle phenyl ring (defined by C1 ~ C6) and the two side phenyl rings (defined by C9 ~ C14 and C25 ~ C30) are 122.8 and 128.0°, respectively, and that between the latter two is 121.0°.

The geometry of each copper(II) center in **2** is similar to that of **1** except that an oxygen atom from acetate anion replaces the chlorine atom (Fig. 3). The basal coordination plane is also essentially planar in **2** with the mean deviations from plane of 0.2263 Å (least-squares plane comprised of atoms N1, O1, O2 and O4) and 0.2236 Å (least-squares plane comprised of atoms N2, O1, O3 and O4), respectively and the dihedral angle between them is 23.6°. The distances between the central copper(II) ions and the least-squares coordination planes are 0.0206 Å for Cu1 and 0.0140 Å for Cu2, respectively. The dihedral angles between the middle phenyl ring (defined by C1 ~ C6) and the two side phenyl rings (defined by C9 ~ C14 and C25 ~ C30) are 137.4 and 134.7°, respectively, and that between the latter two is 131.8°. It is found that the geometry of molecular structure of **2** is less distorted compared with that of **1**.

It is interesting to mention that the geometric difference of Cl⁻ and OAc⁻ in the coordination planes of **1** and **2** results in different dimeric packing structures. In complex **1**, offset π - π stacking inter-

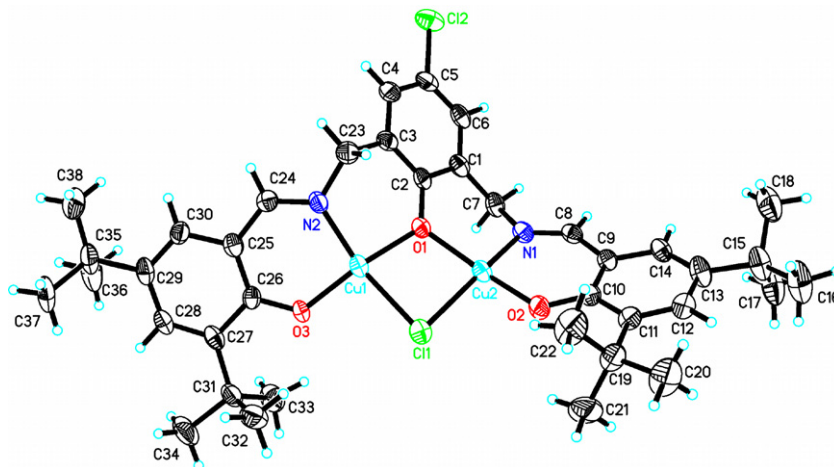


Fig. 2. ORTEP diagram of molecular structure of **1** with the atom-numbering scheme (thermal ellipsoids at the 30% probability level). The lattice water molecules have been omitted for clarity. Selected bond lengths and bond angles: Cu1–O1, 1.948(4), Cu1–O3, 1.854(4), Cu1–N2, 1.904(4), Cu2–Cl1, 2.283(2), Cu2–O1, 1.929(4), Cu2–O2, 1.847(4), Cu2–N1, 1.927(4) Å; Cl1–Cu1–O1, 82.8(1), Cl1–Cu1–O3, 95.4(1), Cl1–Cu1–N2, 158.3(1), O1–Cu1–O3, 160.0(2), O1–Cu1–N2, 93.0(2), O3–Cu1–N2, 95.6(2), Cl1–Cu2–O1, 83.6(1), Cl1–Cu2–O2, 93.7(1), Cl1–Cu2–N1, 159.5(1), O1–Cu2–O2, 164.5(2), O1–Cu2–N1, 93.0(2), O2–Cu2–N1, 94.7(2)°.

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