

Synthesis and structure of $[18\text{-MC}_{\text{Cu}^{\text{II}}(\text{N})_{\text{pko}}\text{-6}]^{6+}$: A new member of anion encapsulating metallamacrocycles

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Abstract

The reaction of copper(II) perchlorate with di-2-pyridyl ketone oxime yields the first 18-MC-6 complex with M–N–O connectivity, $[\text{Cu}_6(\text{pko})_6\text{ClO}_4(\text{CH}_3\text{CN})_6] [\text{Cu}_6(\text{pko})_6(\text{ClO}_4)_3(\text{CH}_3\text{CN})_4] \cdot 8\text{ClO}_4 \cdot 14\text{CH}_3\text{CN} \cdot \text{H}_2\text{O}$ **1**. In the solid state the cationic complex encapsulates a perchlorate anion within the central cavity. Magnetic susceptibility measurements reveal that the complex is diamagnetic. EPR measurements indicate that the complex dissociates in DMF.

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Metallamacrocycles have been intensively studied over the past decade. Already these molecules have been used in applications as diverse as catalysts [1], sensor [2], or chiral building blocks for two- and three-dimensional solids [3]. Metallacrowns (MC) were one of the first examples of this molecular class, exhibiting selective recognition of cations and anions, displaying interesting intramolecular magnetic exchange interactions, and being used as building blocks for chiral layered solids [4–6]. The simplest metallacrowns exhibit a cyclic structure analogous to crown ethers [7,8], with transition metal ions and a nitrogen atom replacing the methylene carbons. The vast majority of reported metallacrowns have been prepared using hydroxamic acids and/or ketonoximic acids as constructing ligands. Di-2-pyridyl ketone oxime (Hpko) is a bifunctional ligand binding metals simultaneously in five and six membered

chelate rings (Scheme 1). Each pko^- provides a single negative charge to the metallacrown. The ketonoxime oxygen (O_K) and one pyridyl nitrogen (N) bind to one metal ion while the other pyridyl nitrogen (N) plus the ketonoxime nitrogen (N_K) chelate an adjacent metal ion. These juxtaposed 5- and 6-membered chelate rings form the basis of the metallacrown ring through the $[\text{M–N–O}]_n$ linkage. Simple metallacrown structure types include [9-MC-3] [9], [12-MC-4] [4], [12-MC-6] [10], [15-MC-5] [5], [18-MC-6] [11], [24-MC-6] [12], [24-MC-8] [13], and [30-MC-10] [14]. Stacking metallacrowns [15,16], dimers and fused metallacrowns [17], metallacryptates [18], and metallahelicates [19] have all been reported. A series of organometallic metallacrowns [20], metallacalixarenes [21], and other metallamacrocycles can also act as inorganic molecular hosts capable of selectively binding cationic, anionic, and neutral guests [22–24]. Herein we report the synthesis and characterization of a new topology for 18-MC-6 complexes, $[\text{Cu}_6(\text{pko})_6\text{ClO}_4(\text{CH}_3\text{CN})_6] [\text{Cu}_6(\text{pko})_6(\text{ClO}_4)_3(\text{CH}_3\text{CN})_4] \cdot 8\text{ClO}_4 \cdot 14\text{CH}_3\text{CN} \cdot \text{H}_2\text{O}$ **1**, with an $[18\text{-MC}_{\text{Cu}^{\text{II}}(\text{N})_{\text{pko}}\text{-6}]^{6+}$ ring that forms a “band” similar to a wedding ring, which encapsulates the poorly coordinating perchlorate anion.

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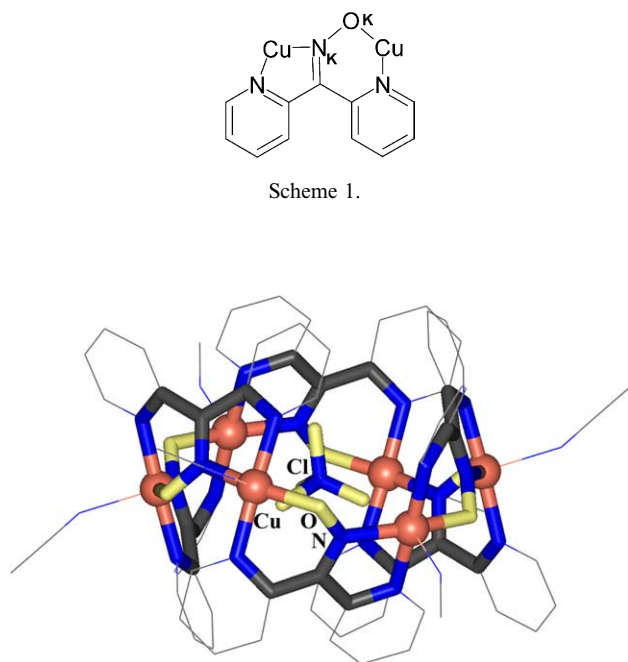


Fig. 1. X-ray crystal structure of **1a** with the chelate rings highlighted. Scheme: Spheres – Cu^{II}; dark tubes – nitrogen; light tubes – oxygen; medium tubes – carbon. Hydrogen atoms, lattice solvent, and lattice perchlorate anions removed for clarity.

Complex **1** is the first 18-MC-6 to consist of [M–N–O] connectivity.

The title compound is prepared by the reaction of 10 mmol of the sodium salt of di-2-pyridyl ketone oxime with 10 mmol of Cu(ClO₄)₄ · 6 H₂O in 50 mL of acetonitrile. A dark green solution results whose volume was reduced to 20 mL after 5 h of stirring. After slow evaporation for three days without stirring, dark green crystals of **1** were deposited from the mother liquor in 60% yield.³ [Perchlorate salts are potentially explosive and should be handled with utmost care.]

The crystal structure consists of two crystallographically distinct [18-MC_{Cu^{II}(N)_{pkO}-6]⁶⁺ metallacrown cations. Both structures contain one encapsulated perchlorate ion, which is disordered in the cavity over two tetrahedral geometries. The only difference between the metallacrowns is the ligands bound to the copper ions on the outside of the ring. In the first molecule, **1a** (Figs. 1 and 2), there are six bound acetonitrile solvent molecules. In the second molecule, **1b**,}

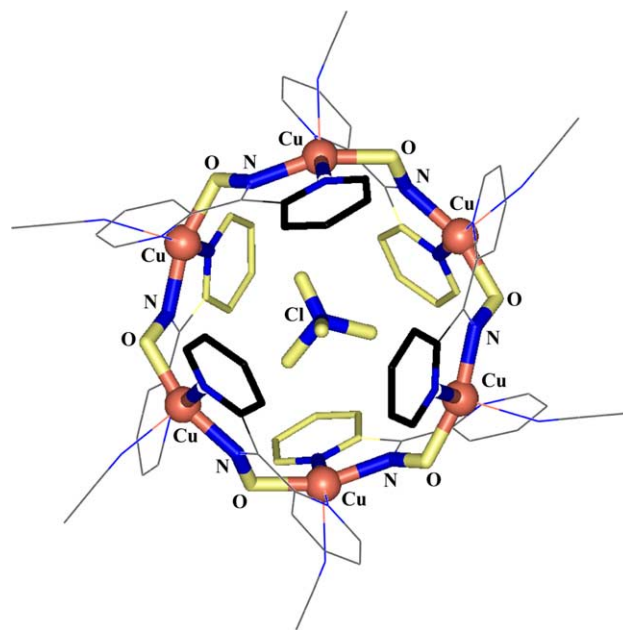


Fig. 2. View of **1a** down the pseudo-six-fold axis with highlighted pyridyl rings forming a hexagonal channel. Dark rings are above the plane of the paper, while light rings are below the plane of the paper.

there are four bound acetonitrile molecules and two bound perchlorate ions (Fig. 3).

In both molecules, six Cu^{II} ions and six pko[−] ligands form the 18-MC-6 ring. The coordination environment for a typical Cu^{II} ion is shown in Fig. 4. Each Cu^{II} ion is in a distorted square pyramidal geometry with angles around Cu^{II} ions varying between 80.37° and 105.30°. For **1a** each Cu^{II} is bound to a ketonoximato nitrogen and a pyridyl nitrogen of a pko[−] ligand and to a ketonoximato oxygen and pyridyl nitrogen of a second pko[−] ligand in five- and six-membered chelate rings, respectively. The fifth axial ligand is an acetonitrile, which coordinates through the nitrogen atom. The pko[−] ligands are bound to copper ions in a *trans*-orientation with an average Cu^{II}–N_{pko}/O_{pko} bond distance of 1.98 Å. The average Cu^{II}–N_{MeCN} is 2.25 Å representing the Jahn–Teller axis. For **1b** the Cu^{II} ions are again bound by a ketonoximato nitrogen and a pyridyl nitrogen of a pko[−] ligand and by a ketonoximato oxygen and pyridyl nitrogen of a second pko[−] ligand in five- and six-membered chelate rings, respectively. The average pko[−] ligand Cu^{II}–N_{pko}/O_{pko} bond distance is 1.97 Å. In **1b**, however, only four of the Cu^{II} ions are bound to acetonitrile, and the other two Cu^{II} ions (Cu5 and Cu5a) are bound to perchlorate ions on the metallacrown exterior. The average Cu–N_{MeCN} bond distance is 2.28 Å, and the average Cu–O_{perchlorate} bond distance is 2.38 Å. Both bonds form along the Jahn–Teller axis. For both **1a** and **1b** the juxtaposed 5- and 6-membered chelate rings form the basis of the metallacrown core through the [Cu–N–O]₆ linkage. The 18-membered metallacrown ring of the type [18-MC_{Cu^{II}(N)_{pkO}-6]⁶⁺ is formed by the following specific connectivity of atoms of **1a**:}

³ Crystals of **1** have been structurally characterized with the formula Cu₁₂C₁₈₀H₁₇₀Cl₁₂N₆₀O₆₁. Analytical data for **1**: Found C, 40.85; H, 3.30; N, 15.40; (*F*_w = 5337.64) requires C, 40.46; H, 3.18; N, 15.73. Crystal data for **1**: *M*_r = 5337.64, triclinic, space group *P*1, *a* = 14.8833(8) Å, *b* = 15.7709(9) Å, *c* = 23.9609(13) Å, α = 94.337(2)°, β = 97.714(2)°, γ = 97.147(2)°, *V* = 5505.5(5) Å³, *Z* = 1; *d*_{calc} = 1.610 mg/m³; 2.75° < θ < 24.94°; crystal dimensions (mm), 0.18 × 0.12 × 0.09; μ = 1.374 mm^{−1}; *T* = 118(2) K; 18814 used of 42675 reflections collected. 18814 reflections and 1519 parameters were used for the full-matrix, least-squares refinement of *F*², *R*₁ = 0.0511 [*I* > 2σ(*I*)], *R*₁ = 0.1111 (all data); *wR*₂ = 0.1191 [*I* > 2σ(*I*)], *wR*₂ = 0.1473 (all data). All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions.

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