Electronic Supplementary Information

for

A Cyclic Tetranuclear Cuboid Type Copper(II) Complex Doubly Supported by Cyclohexane-1,4-Dicarboxylate: Molecular and Supramolecular Structure and Cyclohexane Oxidation Activity

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Synthesis and Characterization of [Cu$_2$L$_2$Cl$_2$]

The dichlorobridged dicopper(II) was synthesized in a procedure which is slightly different to the reported one$^1$. To a hot and stirring water solution (10 mL) of 2-aminobenzenesulfonic acid (0.173 g, 1.00 mmol) was added a methanol solution (5 mL) of pyridine-2-carboxyaldehyde (0.107 g, 1.00 mmol) dropwise and the solution was stirred for 4 h. To the resulting orange solution was added dropwise a methanol solution (5 mL) of CuCl$_2$.2H$_2$O (0.170 g, 1.00 mmol) to produce a dark green solution. After stirring for one more hour, the solution was filtered and kept for slow evaporation. After 2 days, a green crystalline compound containing diffractable crystals that deposited was collected by filtration and washed with methanol. Yield: 0.306 g (85%).

C$_{24}$H$_{18}$N$_4$O$_6$S$_2$Cl$_2$Cu$_2$ (721): Calcd. C, 40.01; H, 2.52; N, 7.78. Found: C, 40.35; H, 2.49; N, 7.71.

Crystalllographic Data: Crystal system = monoclinic; Space group = P2$_1$/c; a = 6.757(3); b = 15.226(7); c = 12.246(4); $\alpha = \gamma = 90.00$; $\beta = 95.75(2)$; V = 1253.5(9); Z = 2.
Fig. S1. FT-IR spectrum of [(CuL)₂(μ₄-O,O',O''',O''''-CDC)]₂·2H₂O (1) in the 4000–400 cm⁻¹ region.
Fig. S2. \( \pi \cdots \pi \) interactions (centroid···centroid distance of 4.091 Å) between C21-phenyl and N3-pyridyl rings in \([\text{CuL}]_2(\mu_4-O,O',O'',O'''\text{-CDC})\)\(_2\)·2H\(_2\)O (1). Atom colors: carbon, ash; oxygen, red; sulfur, yellow; nitrogen, blue; hydrogen, green; copper, cyan; centroid, pink.

Fig. S3. Representation of the \( \pi \cdots \pi \) interaction (centroid···centroid distance of 3.694 Å) between the N3-pyridyl rings and of the H-bond contacts in the structure of \([\text{CuL}]_2(\mu_4-O,O',O'',O'''\text{-CDC})\)\(_2\)·2H\(_2\)O (1). Atom colors: carbon, ash; oxygen, red; sulfur, yellow;
nitrogen, blue; hydrogen, green; copper, cyan; centroid, pink. Symmetry, \(ii\), 1-x, -y, 1-z; \(iii\), 1-x, 1-y, 1-z; \(iv\) x, y, -1+z.

**Fig. S4.** Tetranuclear gallium complex\(^2\) and the *cuboid* cage inside the molecule formed by doubly bridged cyclohexane dicarboxylate.

**Fig. S5.** Polymeric Co(II) compound\(^3\) with inter-connected metal-CDC *cuboid* cages.
Scheme S1. Single bridged tetranuclear Cu(II) complex\textsuperscript{4} and quadruple bridged tetranuclear Sn(IV) complex\textsuperscript{5} with cyclohexane dicarboxylate bridge.

Scheme S2. Single CDC-bridged dinuclear Sn(IV) complex\textsuperscript{5} and doubly CDC-bridged dinuclear Co(II) complex\textsuperscript{6}.
Fig. S6. Effect of H_2O_2 amount: accumulation of products (total of cyclohexanol and cyclohexanone, yield percentage) with time in the oxidation of cyclohexane (0.49 M) at 50 °C in CH_3CN, catalyzed by complex 1 (0.6 x 10^{-3} M) in the presence of different concentrations of H_2O_2: 0.3 M (curve 1), 0.8 M (curve 2), 1.5 M (curve 3) and 2.0 M (curve 4).

Thermal Properties of [(CuL)_2(μ_4-O,O',O'',O''''-CDC)]_2·2H_2O (1)

Thermogravimetric analysis was carried out under dinitrogen atmosphere in the range of the room temperature (30 °C) to 800°C at an applied heating rate of 5 °C min^{-1}. Features of the thermal stability of the complex [(CuL)_2(μ_4-O,O',O'',O''''-CDC)]_2·2H_2O (1) are illustrated in Fig. S7. The compound is stable up to the temperature of 230 °C, beyond which it gradually degrades, the weight loss ceasing at 700 °C. The weight loss of 69.0 % along this temperature range may be accounted for the total removal of the organic ligand (L−) from the coordination sphere of the metal. It is slightly less than the calculated one (71.6 %) if the final product is assumed to be a mixture of CuSO_4 and CuO in a molar ratio of 1:1.
**Fig. S7.** Thermogravimetric analysis curve of \([\text{(CuL)}_2(\mu_4-O,O',O''',O''''-CDC)]_2\cdot2\text{H}_2\text{O}\) (1) under dinitrogen atmosphere. Heating rate: 5 °C/min. Weight of the sample: 2.353 mg.

**References:**


