# Electronic Supplementary Information

# for

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

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### Synthesis and Characterization of [$Cu_2L_2Cl_2$]

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 $CuCl_2.2H_2O$ (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%). $C_{24}H_{18}N_4O_6S_2Cl_2Cu_2$ (721): Calcd. C, 40.01; H, 2.52; N, 7.78. Found: C, 40.35; H, 2.49; N, 7.71.

**Crystallographic Data**: Crystal system = monoclinic; Space group = $P2_1/c$; a = 6.757(3); b = 15.226(7); c = 12.246(4); α = γ = 90.00; β = 95.75(2); V = 1253.5(9); Z = 2.

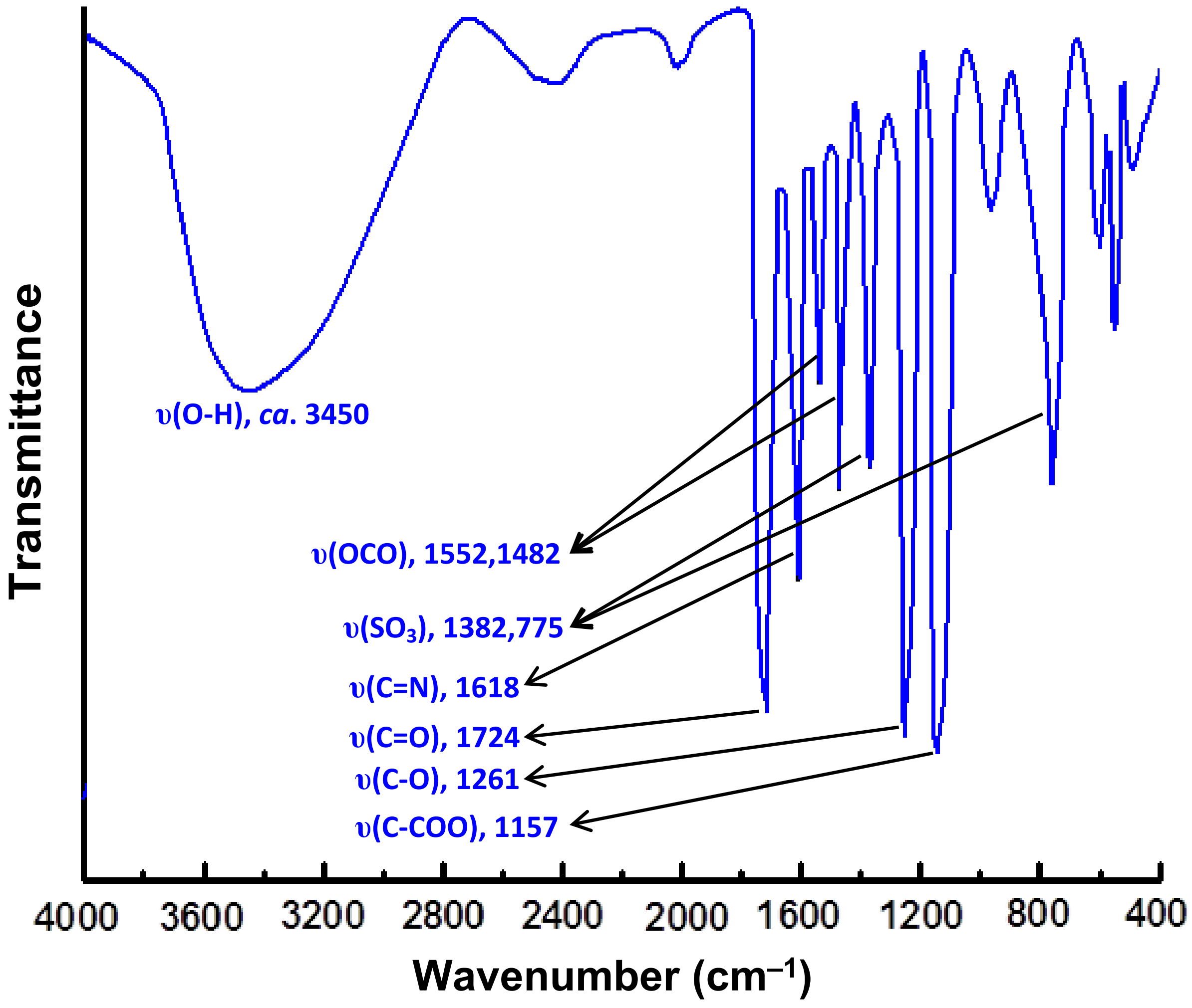


**Fig. S1.** FT-IR spectrum of $[(CuL)_2(\mu_4\text{-O,O',O'',O''''-CDC})]_2 \cdot 2H_2O$ (**1**) in the 4000–400 cm$^{-1}$ region.

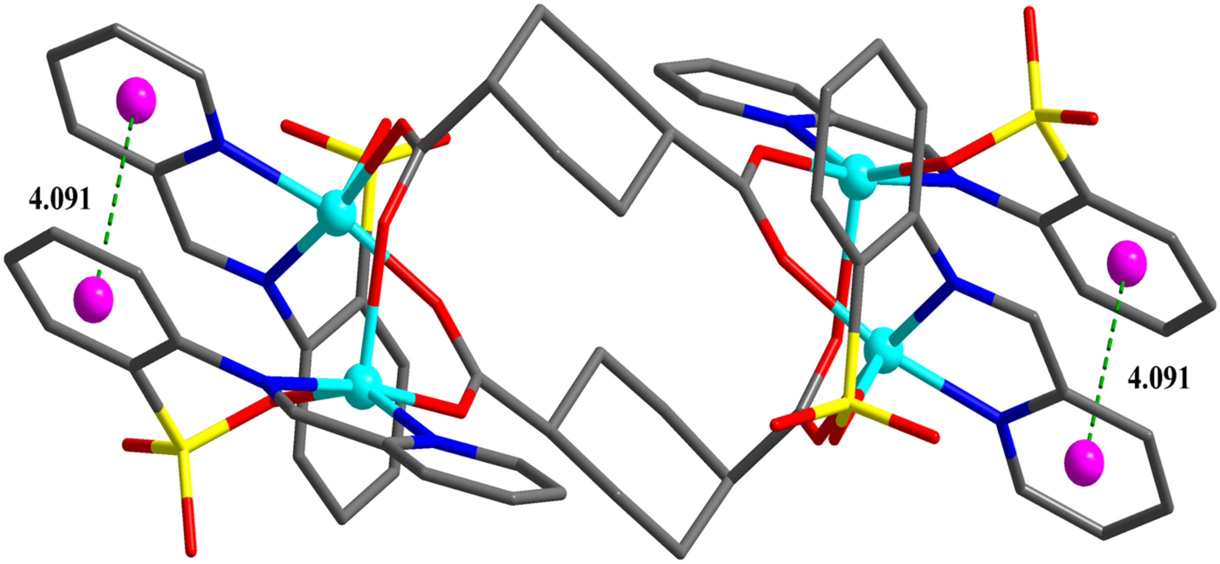


**Fig. S2**. π···π interactions (*centroid···centroid* distance of 4.091 Å) between C21-phenyl and N3-pyridyl rings in [(CuL)$_2$(μ$_4$-O,O',O'',O''''-CDC)]$_2$·2H$_2$O (**1**). Atom colors: carbon, ash; oxygen, red; sulfur, yellow; nitrogen, blue; hydrogen, green; copper, cyan; centroid, pink.

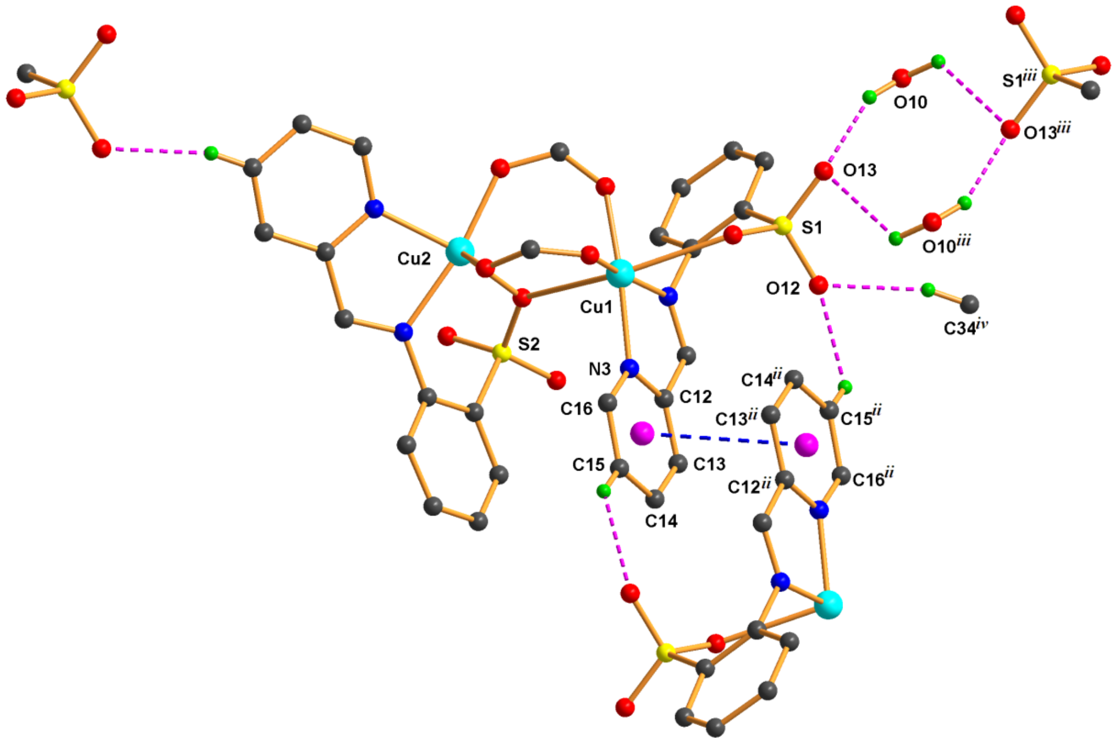


**Fig. S3**. Representation of the π···π interaction (*centroid···centroid* distance of 3.694 Å) between the N3-pyridyl rings and of the H-bond contacts in the structure of [(CuL)$_2$(μ$_4$-O,O',O'',O''''-CDC)]$_2$·2H$_2$O (**1**). Atom colors: carbon, ash; oxygen, red; sulfur, yellow;

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.

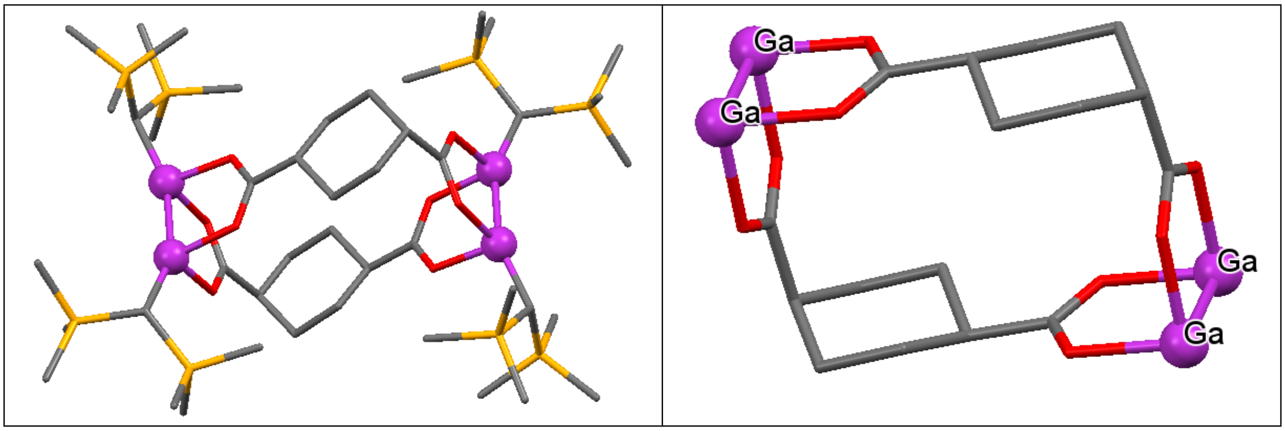


**Fig. S4**. Tetranuclear gallium complex[2] and the *cuboid* cage inside the molecule formed by doubly bridged cyclohexane dicarboxylate.

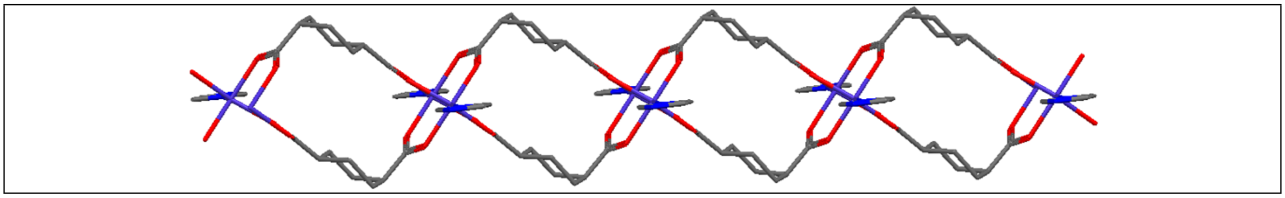
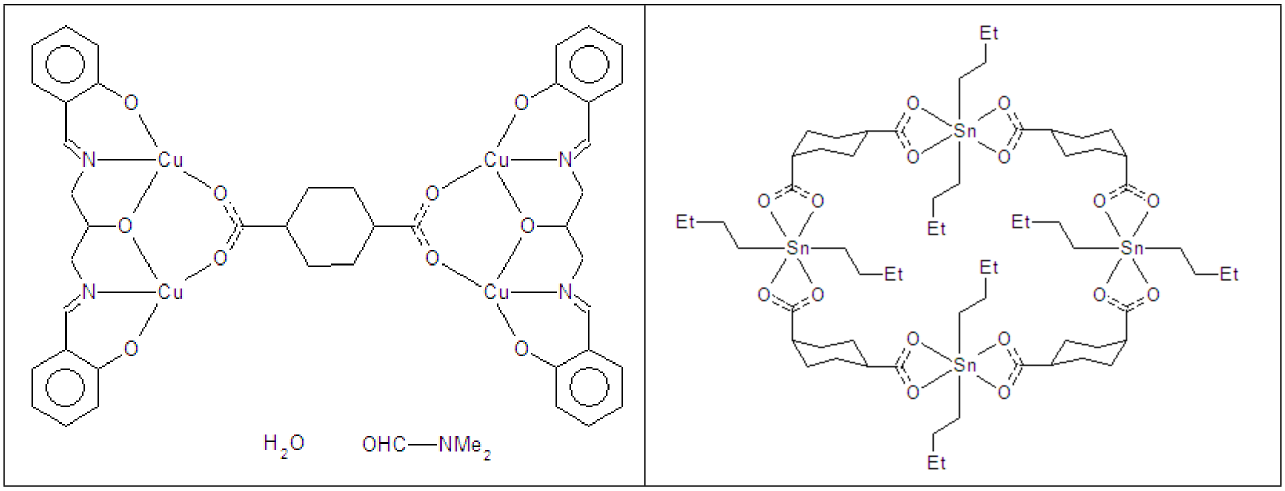
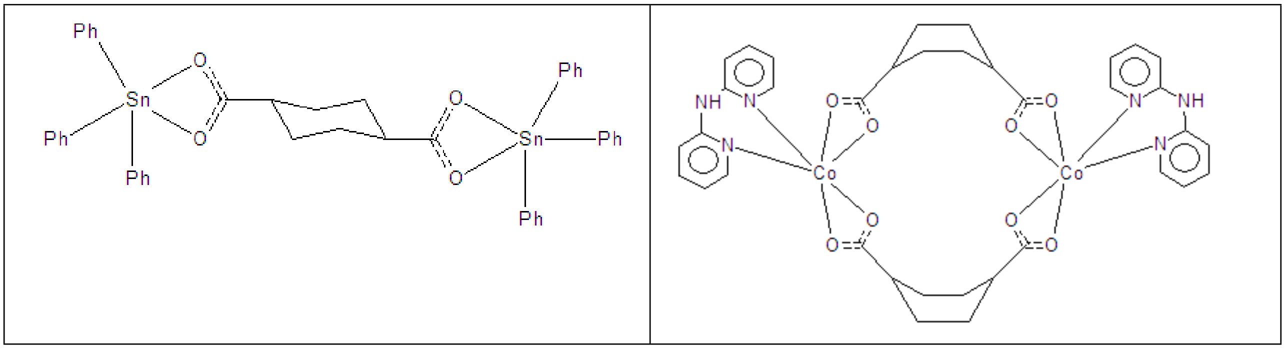


**Fig. S5**. Polymeric Co(II) compound[3] with inter-connected metal-CDC *cuboid* cages.



**Scheme S1**. Single bridged tetranuclear Cu(II) complex[4] and quadruple bridged tetranuclear Sn(IV) complex[5] with cyclohexane dicarboxylate bridge.



**Scheme S2**. **S**ingle CDC-bridged dinuclear Sn(IV) complex[5] and doubly CDC-bridged dinuclear Co(II) complex[6].

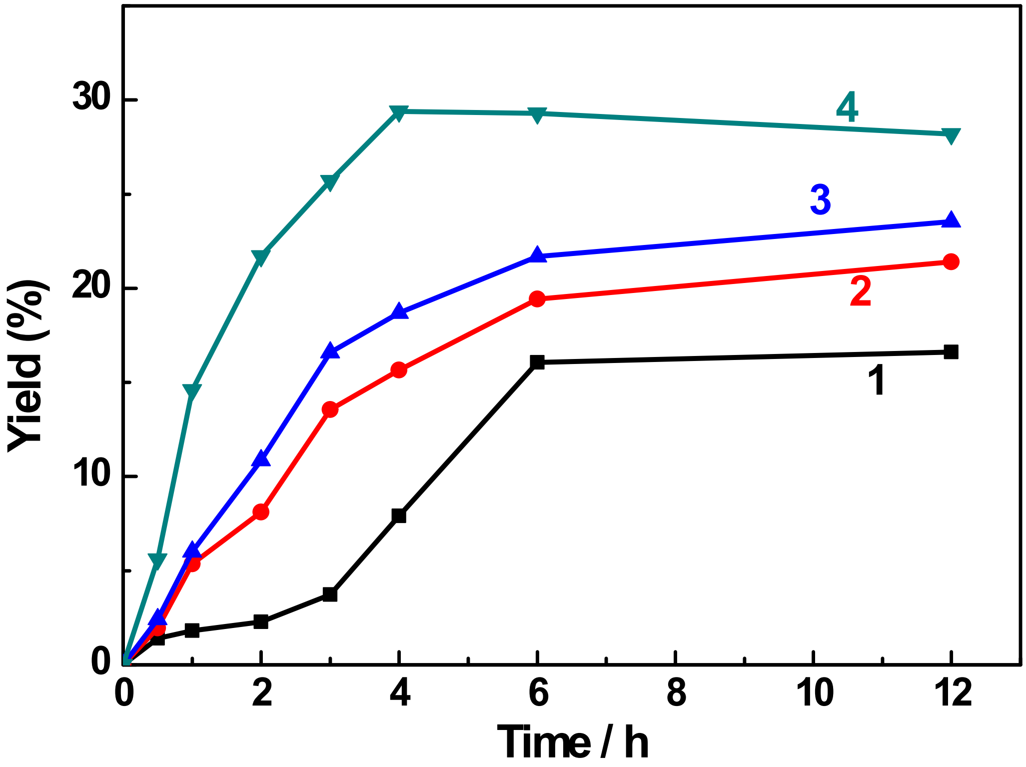


**Fig. S6**. Effect of $H_2O_2$ amount: accumulation of products (total of cyclohexanol and cyclohexanone, yield percentage) with time in the oxidation of cyclohexane (0.49 M) at 50 ºC in $CH_3CN$, catalyzed by complex **1** (0.6 x $10^{-3}$ M) in the presence of different concentrations of $H_2O_2$: 0.3 M (**curve 1**), 0.8 M (**curve 2**), 1.5 M (**curve 3**) and 2.0 M (**curve 4**).

### Thermal Properties of $[(CuL)_2(\mu_4\text{-}O,O',O'',O''''\text{-}CDC)]_2\cdot 2H_2O$ (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 $[(CuL)_2(\mu_4\text{-}O,O',O'',O''''\text{-}CDC)]_2\cdot 2H_2O$ (**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.

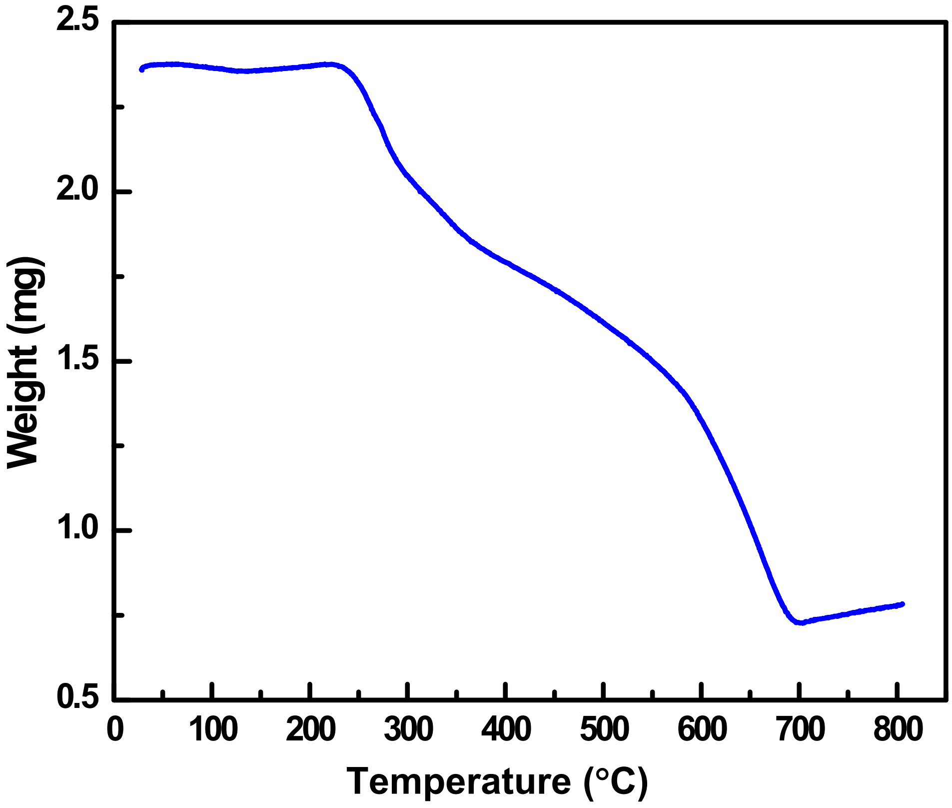


**Fig. S7**. Thermogravimetric analysis curve of [(CuL)$_2$($\mu_4$-O,O',O'',O''''-CDC)]$_2\cdot$2H$_2$O (**1**) under dinitrogen atmosphere. Heating rate: 5 °C/min. Weight of the sample: 2.353 mg.

**References:**

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