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The Goldilocks Principle in action: synthesis and structural characterization of a novel $\{Cu_4(\mu_3\text{-}OH)_4\}$ cubane stabilized by monodentate ligands

Electronic Supplementary Information

G. Attilio Ardizzoia,[a] Stefano Brenna,[a] Sara Durini,[a] Bruno Therrien[b] and Ivan Trentin[a,c]

[a] Department of Science and High Technology, University of Insubria, via Valleggio 11, 22100 Como, Italy

[b] Institute of Chemistry, University of Neuchatel, Avenue de Bellevaux 51, CH-2000 Neuchâtel, Switzerland

[c] Institut für Biochemie, Ernst-Moritz-Arndt-Universität, Felix-Hausdorff-Strasse 4, 17487 Greifswald, Germany

Contents

Experimental section

General Procedures and Materials: Caution! *Although we have experienced no difficulties, perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled with care even in small quantities*. All reactions were carried out under nitrogen (Schlenk technique) to prevent hydrolysis induced by moisture. Solvents were dried and distilled according to standard procedures prior to use. NMR spectra were recorded with an AVANCE 400 Bruker spectrometer at 400 MHz for ^{1}H NMR. Chemical shifts are given as δ values in ppm relative to residual solvent peaks as the internal reference. UV-vis spectra were recorded on a Beckman DU 640 Spectrophotometer. Elemental analyses were obtained with a Perkin-Elmer CHN Analyzer 2400 Series II. IR spectra were recorded with a Shimadzu Prestige-21 spectrophotometer with a 1 cm^{-1} resolution. $[Cu(Hdmpz)_4(ClO_4)_2]$ was prepared according to literature.[i] All other chemicals were of reagent grade quality, were purchased commercially and used as received.

3,4,5-trimethyl-*1H*-pyrazole. Step a) To a solution of acetylacetone (5.13 mL, d = 0.975 g/mL, 50 mmol) in acetone, K_2CO_3 (previously oven-dried at 120°C for 12 h) was added (7.6 g, 55 mmol) and the suspension was kept under stirring at room temperature for 30 minutes. Then methyl iodide (3.74 mL, d = 2.28 g/mL, 60 mmol) was added in small portions and the suspension was stirred at room temperature for 5 days. The solvent was removed under reduced pressure and the residue was treated with diethyl ether. The precipitate was collected by filtration and the filtrate was brought to dryness under reduced pressure affording a light yellow oil (3-methylpentane-2,4-dione), which was used in the following step without further purification. Step b) 3-methylpentane-2,4-dione was dissolved in water (50 mL) and 2-3 drops of glacial acetic acid were added. After cooling the mixture at 0°C, hydrazine (1.96 mL 80% aqueous solution, 50 mmol) was dropped and the suspension was stirred for 12 hours at room temperature affording a white precipitate which was filtered, washed thoroughly with water and dried under vacuum to give 3,4,5-trimethyl-*1H*-pyrazole (3.19 g, 58%). Elemental analysis (%) found: C, 65.38; H, 9.42; N, 25.19; calc. for $C_6H_{10}N_2$: C, 65.42; H, 9.15; N, 25.43.

$[Cu(Htmpz)_4(ClO_4)_2]$ (1). Copper (II) perchlorate hexahydrate (1 g, 2.70 mmol) was dissolved in THF (15 mL) and 3,4,5-trimethyl-1*H*-pyrazole (1.49 g, 13.5 mmol) was added. Rapidly the color changed to dark green. The solution was allowed to stir for 30 minutes. The solvent was removed under reduced pressure leaving a violet solid which was suspended in diethyl ether. Filtering and drying *in vacuo* gave **1** (1.80 g, 95%). IR (hexachlorobutadiene) $\tilde{\upsilon}$ = 3326 (N-H), 1148 (ClO_4^-) cm^{-1}; elemental analysis (%) found: C, 41.35; H, 5.71; N, 15.74; calc. for $C_{24}H_{40}Cl_2CuN_8O_8$: C, 41.00; H, 5.73; N, 15.94. Single crystals suitable for X-ray determination were obtained by slow diffusion of diethyl ether into a saturated solution of compound **1** in dichloromethane. Complex **1** can also be obtained carrying out the reaction in other solvents as H_2O, ethanol, *iso*-propanol, *n*-propanol.

$[Cu(\mu\text{-}OCH_3)(Htmpz)_2(ClO_4)]_2$ (2). Complex **1** (1 g, 1.4 mmol) was dissolved in methanol (15 mL). In few minutes a blue precipitate formed from the solution. The resulting suspension was stirred at room temperature for 30 minutes, filtered and the solid washed with diethyl ether, giving **2** (354 mg, 60%). IR (hexachlorobutadiene) $\tilde{\upsilon}$ = 3343 (N-H), 2913 (C-H), 2804 (C-H in μ-OCH_3), 1091 (ClO_4^-) cm^{-1}; elemental analysis (%) found: C, 37.75; H, 5.62; N, 13.48; calc. for $C_{26}H_{46}Cl_2Cu_2N_8O_{10}$: C, 37.68; H, 5.60; N, 13.52. Single crystals suitable for X-ray determination were obtained by slow evaporation of solvent from a concentrated solution of compound **2** in methanol.

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[i] G. A. van Albada, M. G. van der Horst, I. Mutikainen, U. Turpeinen, J. Reedijk, *Inorg. Chim. Acta* 2008, **361**, 3380-3387.

[Cu$_4$(μ$_3$-OH)$_4$(Htmpz)$_8$(ClO$_4$)$_4$] · 1.5 Et$_2$O (3 · 1.5 Et$_2$O). Complex **2** (300 mg, 0.36 mmol) was dissolved in dichloromethane (3 mL) and stirred for 6 hours at room temperature in the presence of 50 μL of H_2O. Then, the solvent was removed under reduced pressure and the crude precipitate was purified by diethyl ether obtaining a light-blue crystalline solid (275 mg, 95%). IR (hexachlorobutadiene) $\tilde{\upsilon}$ = 3552 (O-H), 3291 (N-H), 2926 (C-H), 1091 (ClO_4^-); elemental analysis (%) found: C, 37.06; H, 5.41; N, 13.37; calc. for $C_{54}H_{99}Cl_4Cu_4N_{16}O_{21.5}$: C, 37.87; H, 5.83; N, 13.09. Single crystals suitable for X-ray determination were obtained by layering diethyl ether over a concentrated solution of compound **3** · 1.5 Et$_2$O in dichloromethane.

[Cu$_4$(μ$_3$-OH)$_4$(Htmpz)$_8$(ClO$_4$)$_4$] (3). Complex **3** · 1.5 Et$_2$O was heated in vacuum for 3 h. During this time the color of the solid turned into green. Elemental analysis revealed that complex **3** · 1.5 Et$_2$O was converted into the corresponding cubane **3** after quantitative loss of diethylether. IR (hexachlorobutadiene) $\tilde{\upsilon}$ = 3547 (O-H), 3291 (N-H), 2926, 2860 (C-H), 1147 (ClO_4^-); elemental analysis (%) found: C, 36.70; H, 5.56; N, 13.52; calc. for $C_{48}H_{84}Cl_4Cu_4N_{16}O_{20}$: C, 36.00; H, 5.29; N, 14.00.

[Cu(μ-OH)(Htmpz)$_2$(ClO$_4$)]$_2$ · RCN (R = CH$_3$, 5; R = Ph, 6). Compound [Cu(μ-OCH$_3$)(Htmpz)$_2$(ClO$_4$)]$_2$ (**2**) (300 mg, 0.36 mmol) was dissolved in the nitrile (3 mL) and stirred for 6 hours at room temperature in the presence of 50 μL of H_2O. Then, the dark green compound formed was filtered, washed with the nitrile, diethylether and dried *in vacuo*. **5** (240 mg, 79%). IR (hexachlorobutadiene) $\tilde{\upsilon}$ = 3551 (broad, O-H), 3303 (N-H), 2925, 2863 (C-H), 2265 (CN), 1103 (ClO_4^-); elemental analysis (%) found: C, 37.31; H, 5.64; N, 15.09; calc. for $C_{26}H_{45}Cl_2Cu_2N_9O_{10}$: C, 37.10; H, 5.39; N, 14.98. **6** (280 mg, 86%). IR (hexachlorobutadiene) $\tilde{\upsilon}$ = 3550 (broad, O-H), 3298 (N-H), 2925, 2863 (C-H), 2266 (CN), 1103 (ClO_4^-); elemental analysis (%) found: C, 41.52; H, 5.69; N, 14.11; calc. for $C_{31}H_{47}Cl_2Cu_2N_9O_{10}$: C, 41.20; H, 5.24; N, 13.95.

[Cu(Htmpz)$_4$(NO$_3$)$_2$] (7). Copper (II) nitrate tetrahydrate (0.652 g, 2.70 mmol) was dissolved in THF (15 mL) and 3,4,5-trimethyl-1*H*-pyrazole (1.49 g, 13.5 mmol) was added and the solution was allowed to stir for 30 minutes. The solvent was removed under reduced pressure leaving a violet solid which was suspended in diethyl ether, filtered and dried *in vacuo* to get **7** (1.41 g, 83%). IR (hexachlorobutadiene) $\tilde{\upsilon}$ = 3272 (N-H), 2927, 2865 (C-H), 1347, 1362 (NO_3^-); elemental analysis (%) found: C, 45.42; H, 6.61; N, 22.18; calc. for $C_{24}H_{40}CuO_6N_{10}$: C, 45.89; H, 6.42; N, 22.30.

[Cu(Htmpz)$_4$(BF$_4$)$_2$] (8). Copper (II) tetrafluoborate hydrate (0.640 g, 2.70 mmol anhydrous basis) was dissolved in triethylorthoformate[1] (3 mL) and 3,4,5-trimethyl-1*H*-pyrazole (1.49 g, 13.5 mmol) in THF (15 mL) was added. The resulting solution was allowed to stir for 30 minutes, then the solvent was removed under reduced pressure leaving a violet solid which was suspended in diethyl ether, filtered and dried *in vacuo* to get **8** (1.26 g, 69%). IR (hexachlorobutadiene) $\tilde{\upsilon}$ = 3285 (N-H), 2926, 2863 (C-H), 1168 (BF_4^-); elemental analysis (%) found C, 42.20; H, 6.01; N, 16.32; calc. for $C_{24}H_{40}B_2CuF_8N_8$: C, 42.53; H, 5.95; N, 16.53.

[Cu(μ-OCH$_3$)(Hdmpz)$_2$(ClO$_4$)]$_2$ (9). Complex [Cu(Hdmpz)$_4$(ClO$_4$)$_2$] (1 g, 1.55 mmol) was suspended in methanol (15 mL). Suddenly, a blue precipitate formed. The resulting suspension was stirred at room temperature for 30 minutes, filtered and the solid washed with diethyl ether, obtaining **9** (442 mg, 74%). IR (hexachlorobutadiene) $\tilde{\upsilon}$ = 3345 (N-H), 2926 (C-H), 2819 (C-H in μ-OCH$_3$), 1094 (ClO_4^-); elemental analysis (%) found C, 34.29; H, 4.72; N, 14.39; calc. for $C_{22}H_{38}Cl_2Cu_2N_8O_{10}$: C, 34.20; H, 4.96; N, 14.50.

Hydrolysis of 9. Complex **9** (630 mg, 0.81 mmol) was dissolved in dichloromethane (10 mL) and stirred for 6 hours at room temperature in the presence of 50 μL of H_2O. A violet solution formed, and a light blue precipitate grafted to the walls of the flask. Then, the solution was separated from the solid, the solvent removed under reduced pressure and the crude precipitate was purified by diethylether, obtaining a violet crystalline product, identified as $[Cu(Hdmpz)_4(ClO_4)_2]$ (537 mg, 49%, based on copper). The light blue solid was washed with diethylether, and subsequently identified as $Cu(OH)_2$ (108 mg, 48%, based on copper).

X-ray crystallography

Crystals of complexes **1**, **2** and **3** were mounted on a Stoe Image Plate Diffraction system equipped with a ϕ circle goniometer, using Mo-Kα graphite monochromated radiation (λ = 0.71073 Å) with ϕ range 0–200°. The structures were solved by direct methods using the program SHELXS–97, while refinement and all further calculations were carried out using SHELXL–97.[ii] The H-atoms were included in calculated positions and treated as riding atoms using the SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-square on F^2. Despite using multiple crystals from different batches, collecting data at different temperatures, unfortunately only poor quality data were obtained for **3**. Nevertheless, the best data collection was resolved and the structure is presented here. Upon examination of the crystal packing of **3** with PLATON,[iii] two large solvent accessible voids were observed. These solvent accessible voids occupy an area of approximately 1240 Å^3. Chemical evidence suggests that diethylether molecules sit in these regions, however, the electron densities in these areas are quite low and it was not possible to define crystallographically the solvent molecules. Therefore, a data set corresponding to omission of the missing solvent was generated using the SQUEEZE[iv] algorithm from PLATON and the structure was refined to convergence. Crystallographic details are summarized in Table S1.

CCDC-930623 (**1**), 930624 (**2**) and 930625 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

[ii] G. M. Sheldrick, *Acta Crystallogr., Sect. A* 2008, **64**, 112-122.

[iii] A. L. Spek, *J. Appl. Cryst.* 2003, **36**, 7-13.

[iv] P. van der Sluis, A. L. Spek, *Acta Cryst., Sect. A* 1990, **46**, 194-201.

Table S1. Crystallographic and structure refinement parameters for complexes **1**, **2** and **3**.

	1	**2**	**3**
Chemical formula	$C_{24}H_{40}Cl_2CuN_8O_8$	$C_{26}H_{46}Cl_2Cu_2N_8O_{10}$	$C_{48}H_{84}Cl_4Cu_4N_{16}O_{20}$
Formula weight	703.08	828.69	1601.27
Crystal system	tetragonal	triclinic	monoclinic
Space group	*I* 4_1*cd* (no. 110)	*P* -1 (no. 2)	*P* 2_1/*c* (no. 14)
Crystal color & shape	violet cube	blue block	blue block
Crystal size	0.18 x 0.16 x 0.16	0.21 x 0.19 x 0.18	0.18 x 0.16 x 0.13
a (Å)	15.795(2)	8.7851(17)	15.9451(6)
b (Å)	15.795(2)	10.375(2)	30.6995(8)
c (Å)	27.870(6)	10.915(2)	20.6734(9)
α (°)	90	85.01(2)	90.00
β (°)	90	76.37(2)	122.694(3)
γ (°)	90	72.47(2)	90.00
V (Å^3)	6953.1(19)	921.8(3)	8516.5(5)
Z	8	2	4
T (K)	173(2)	173(2)	173(2)
D_c (g.cm^{-3})	1.343	1.493	1.249
μ (mm^{-1})	0.835	1.359	1.174
Scan range (°)	$2.58 < \theta < 26.05$	$2.65 < \theta < 25.75$	$1.48 < \theta < 29.35$
Unique reflections	3050	3380	23126
Reflections used [I>2σ(I)]	1799	1881	13196
R_{int}	0.0508	0.1051	0.1237
Final R indices [I>2σ(I)]*	0.0356, wR_2 0.0784	0.0672, wR_2 0.1590	0.1020, $wR_2$0.1925
R indices (all data)	0.0714, wR_2 0.0896	0.1075, wR_2 0.1768	0.1880, $wR_2$0.2306
Goodness-of-fit	0.855	0.849	1.101
Max, Min $\Delta\rho$/e (Å^{-3})	0.271, -0.459	0.677, -1.170	1.737, -1.021

* Structures were refined on F_0^2: $wR_2 = [\Sigma[w(F_0^2 - F_c^2)^2] / \Sigma w(F_0^2)^2]^{1/2}$, where $w^{-1} = [\Sigma(F_0^2) + (aP)^2 + bP]$ and $P = [\max(F_0^2, 0) + 2F_c^2]$

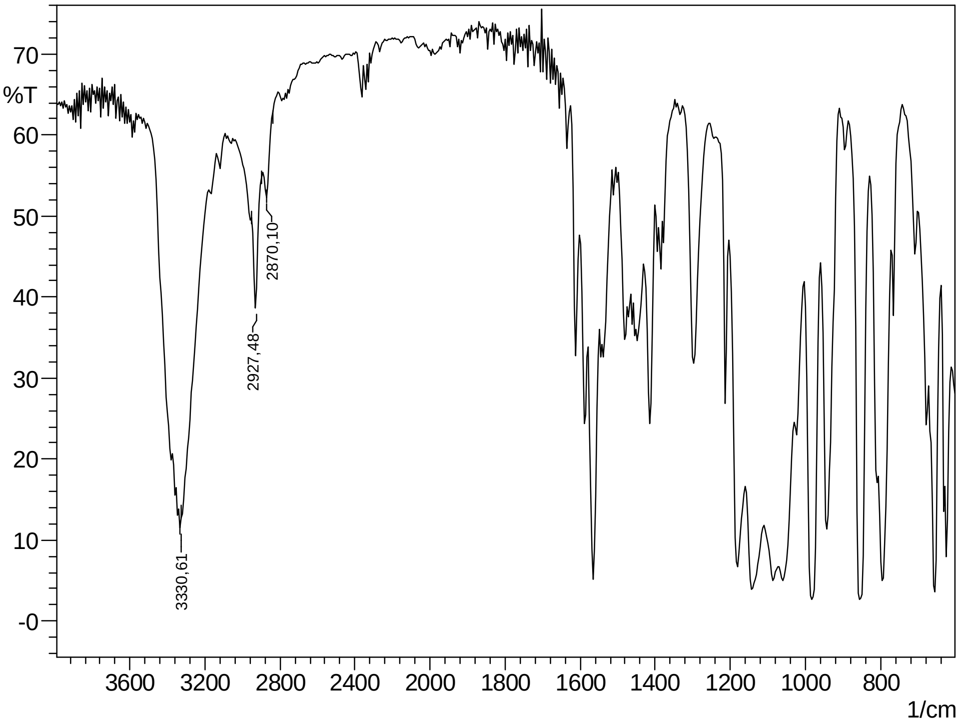


Figure S1. Infrared spectrum (hexachlorobutadiene) of [Cu(Htmpz)$_4$(ClO$_4$)$_2$] (**1**).

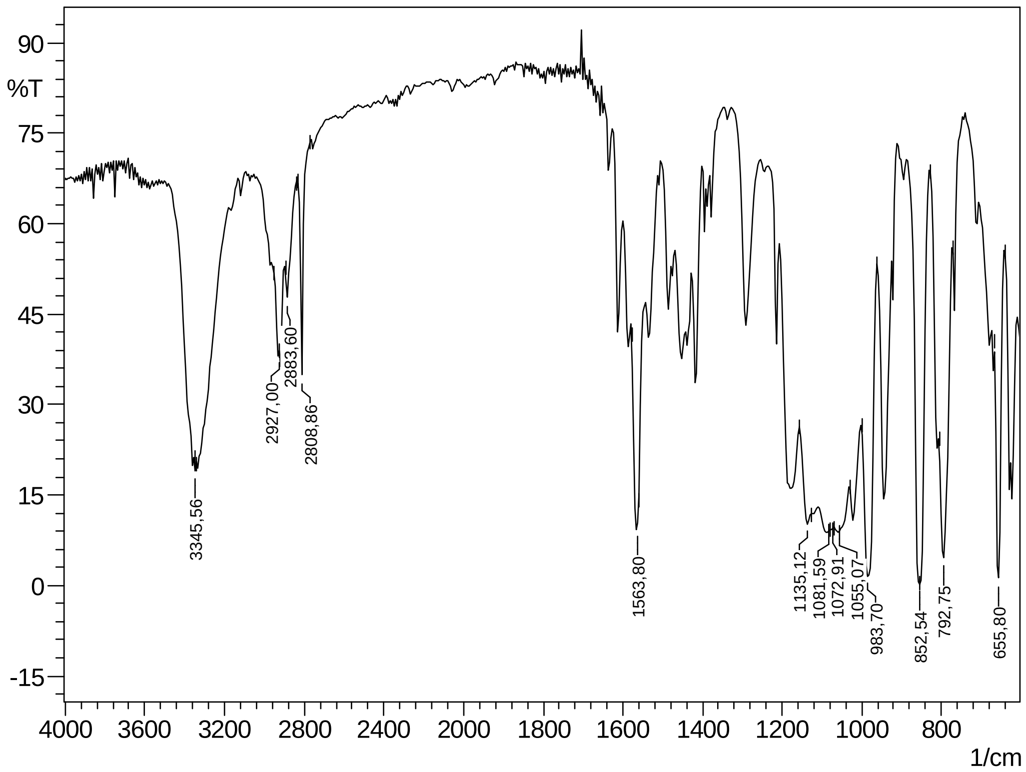


Figure S2. Infrared spectrum (hexachlorobutadiene) of [Cu(μ-OCH_3)(Htmpz)$_2$(ClO_4)$_2$] (**2**).

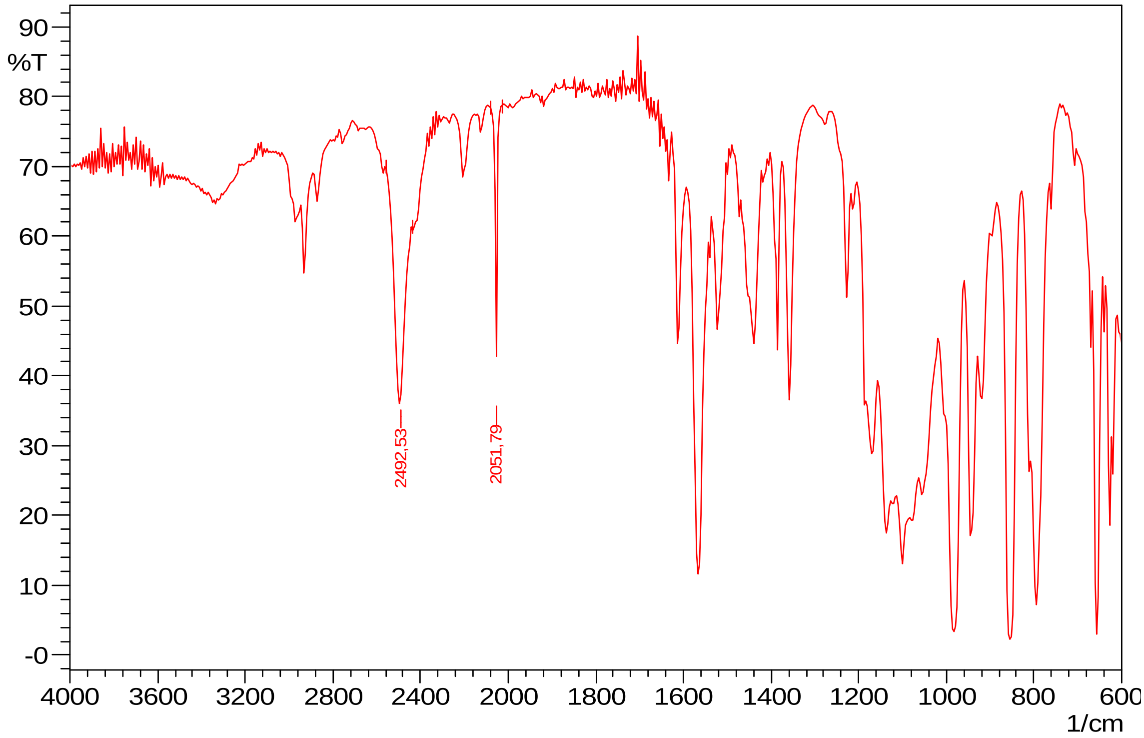


Figure S3. Infrared spectrum (hexachlorobutadiene) of [Cu(μ-OCD_3)(Dtmpz)$_2$(ClO_4)$_2$] (**2-D$_4$**).

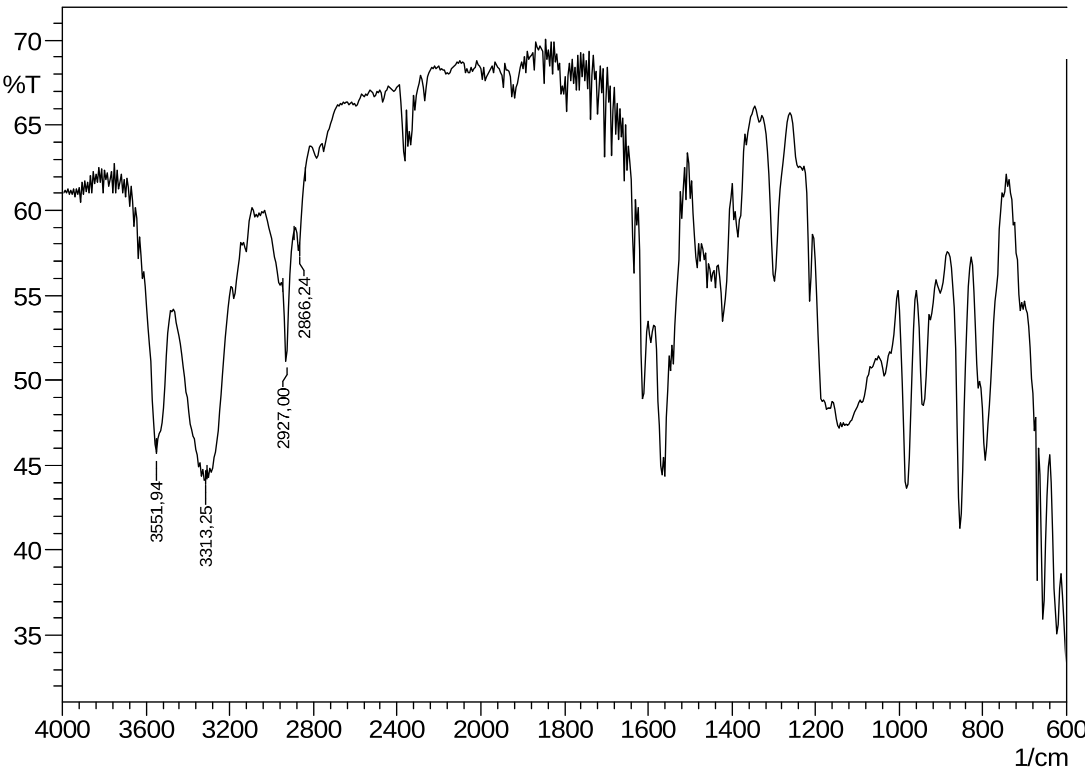


Figure S4. Infrared spectrum (hexachlorobutadiene) of $[Cu_4(\mu_3\text{-}OH)_4(Htmpz)_8](ClO_4)_4 \cdot 1.5\ Et_2O$ (**3** · 1.5 Et_2O).

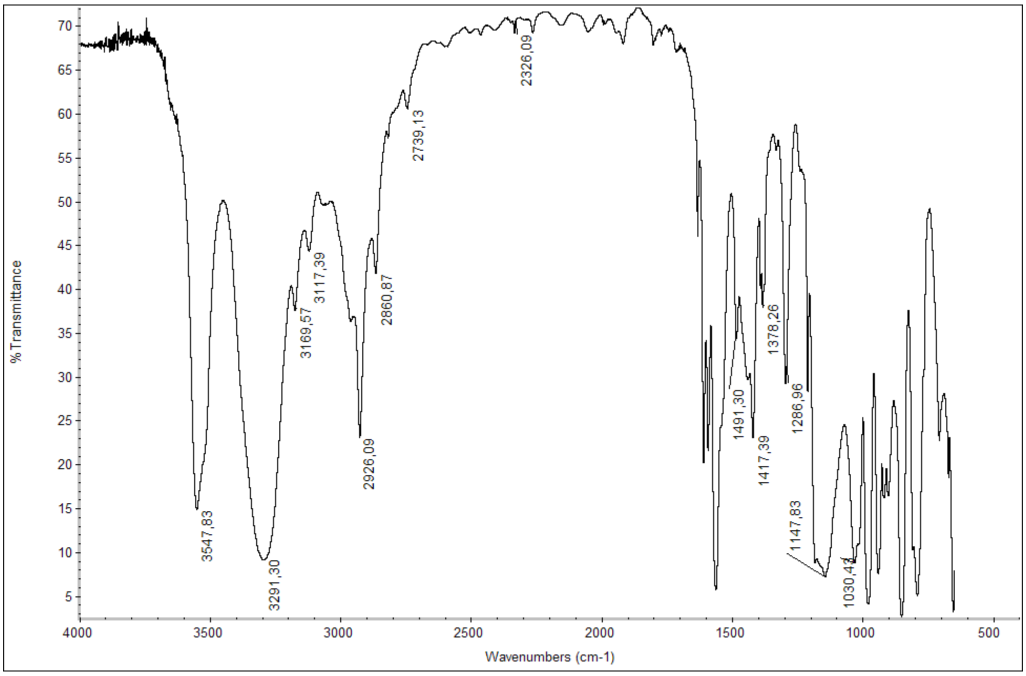
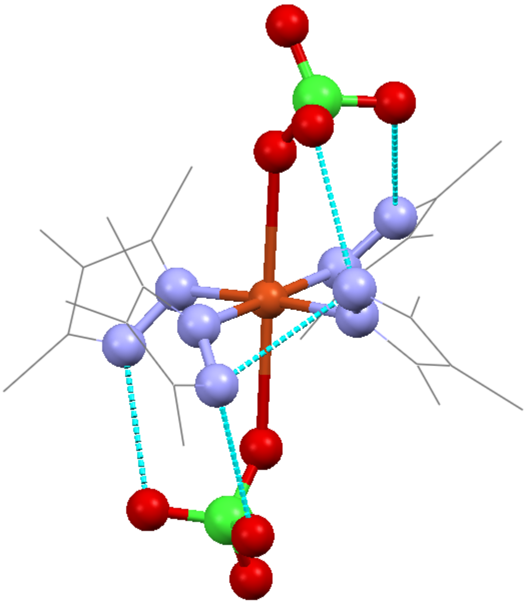


Figure S5. Infrared spectrum (hexachlorobutadiene) of $[Cu_4(\mu_3\text{-}OH)_4(Htmpz)_8](ClO_4)_4$ (**3**).



FigureS6. H-bonding interactions in **1.**

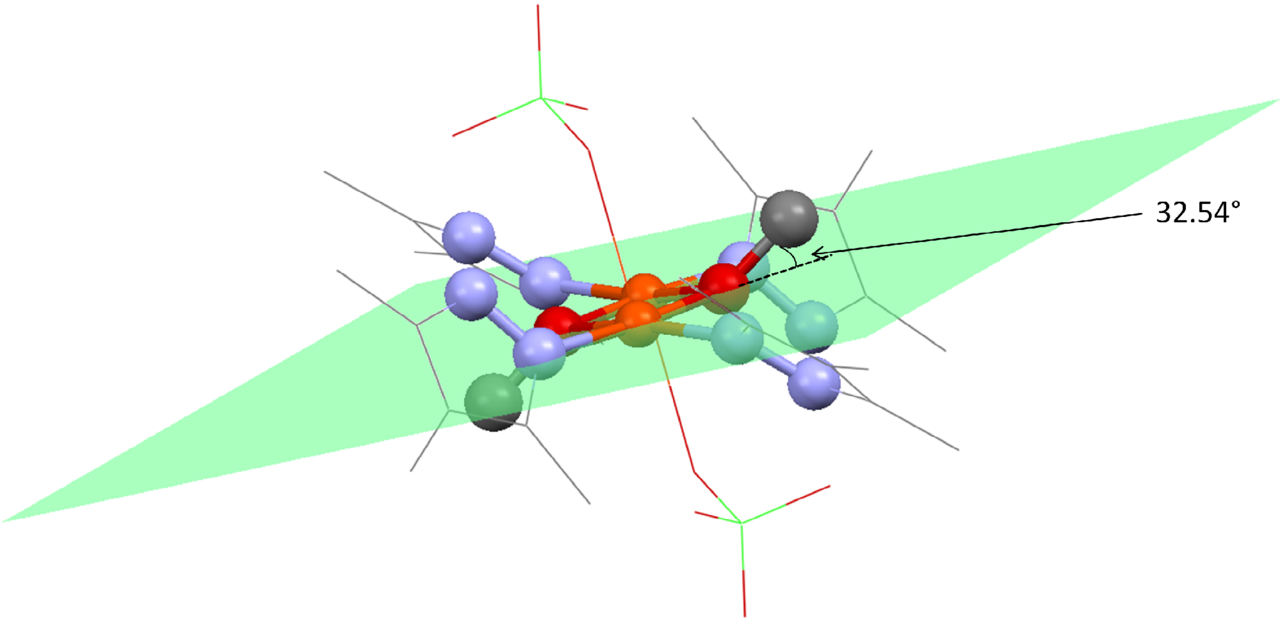


Figure S7. Out-of-plane angle of CH_3 substituents on bridging oxygens in **2**.

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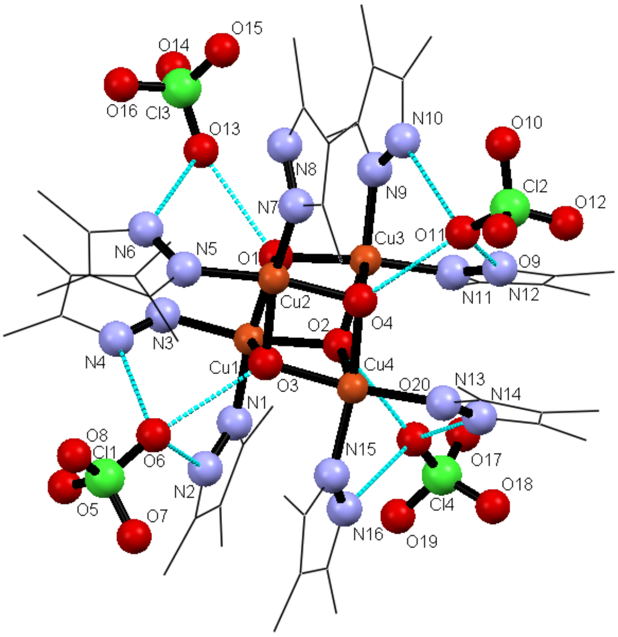

Figure S8. H-bonding interactions involving ClO_4^-, Htmpz and bridging OH groups in **3**.

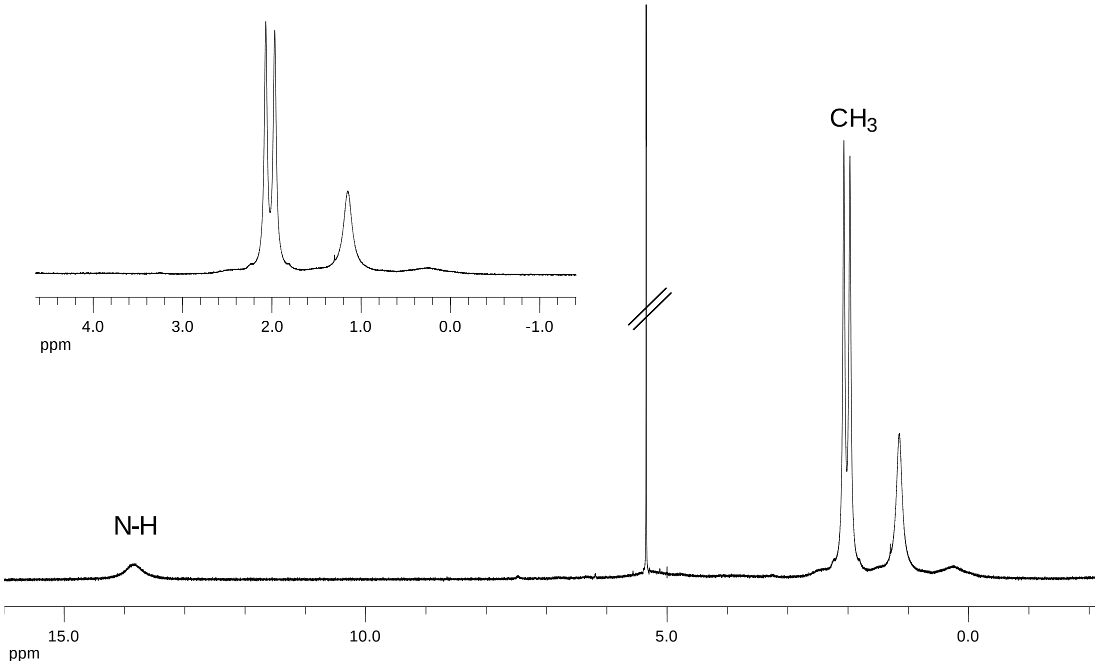

Figure S9. ^{1}H NMR (CD_2Cl_2, 25°C) of [Cu(μ-OCH_3)(Htmpz)$_2$(ClO_4)$_2$] (**2**). Inset: expansion of the methyl region.

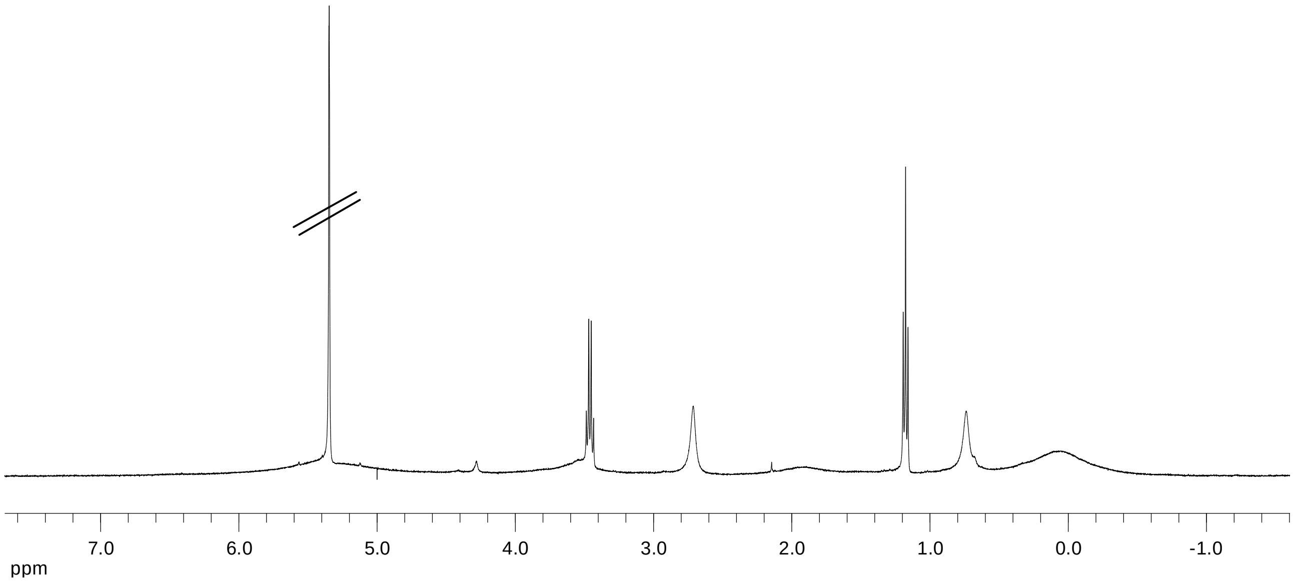

Figure S10. ^{1}H NMR (CD_2Cl_2, 25°C) of $[Cu_4(\mu\text{-}OH)_4(Htmpz)_8(ClO_4)]\cdot Et_2O$ (**3**·Et_2O).

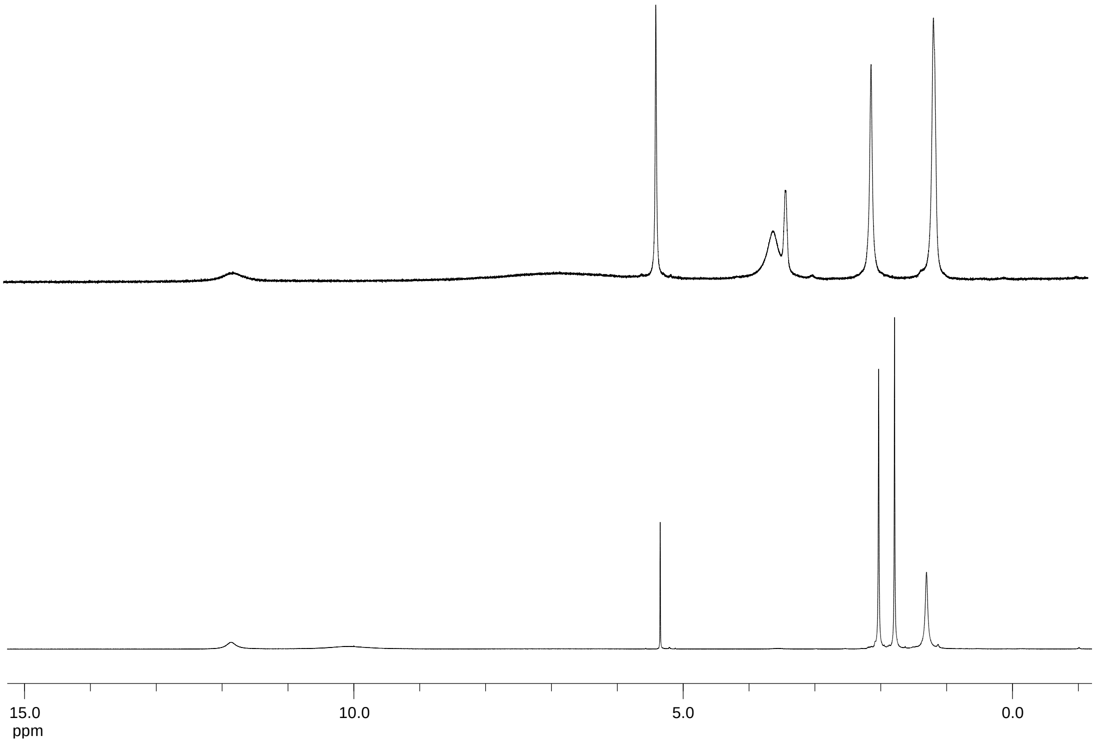

Figure S11. ^{1}H NMR (CD_2Cl_2, -60°C) of **2** (bottom) and **3**·Et_2O (up).

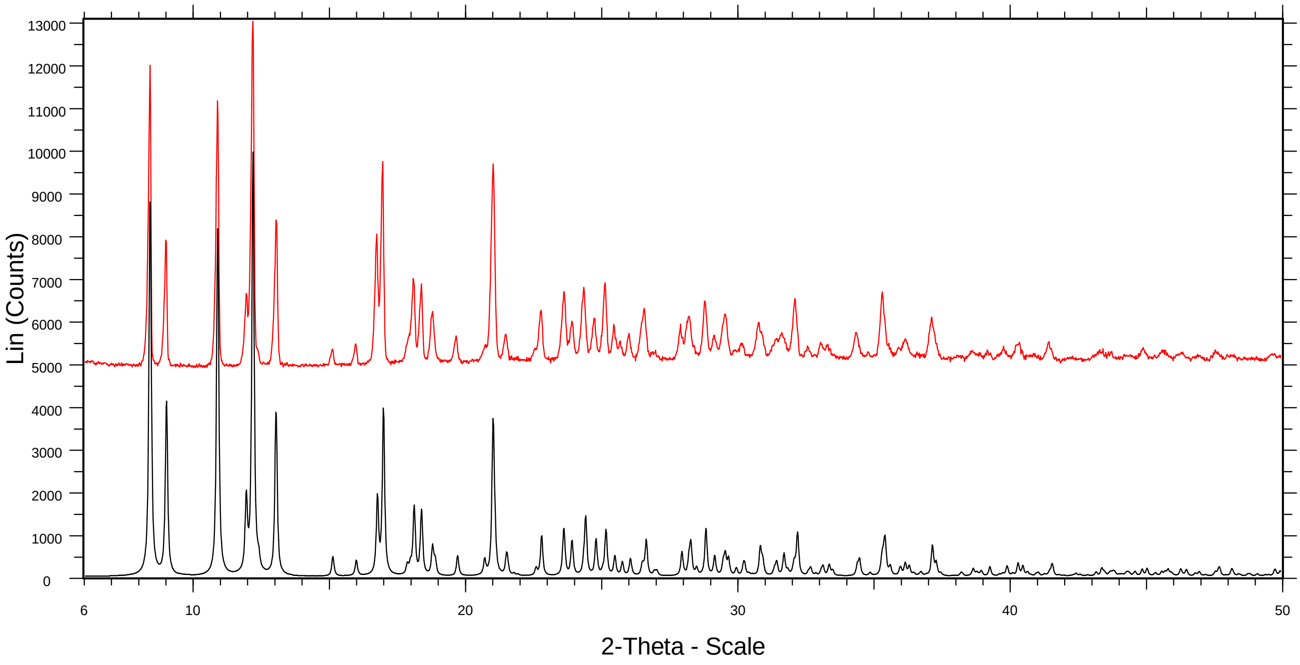

Figure S12. XRPD traces of **3**·Et$_2$O (grinded crystals, bottom) and of [Cu$_4$(μ_3-OH)$_4$(Htmpz)$_8$](ClO$_4$)$_4$ intercept during hydrolysis of **2**.

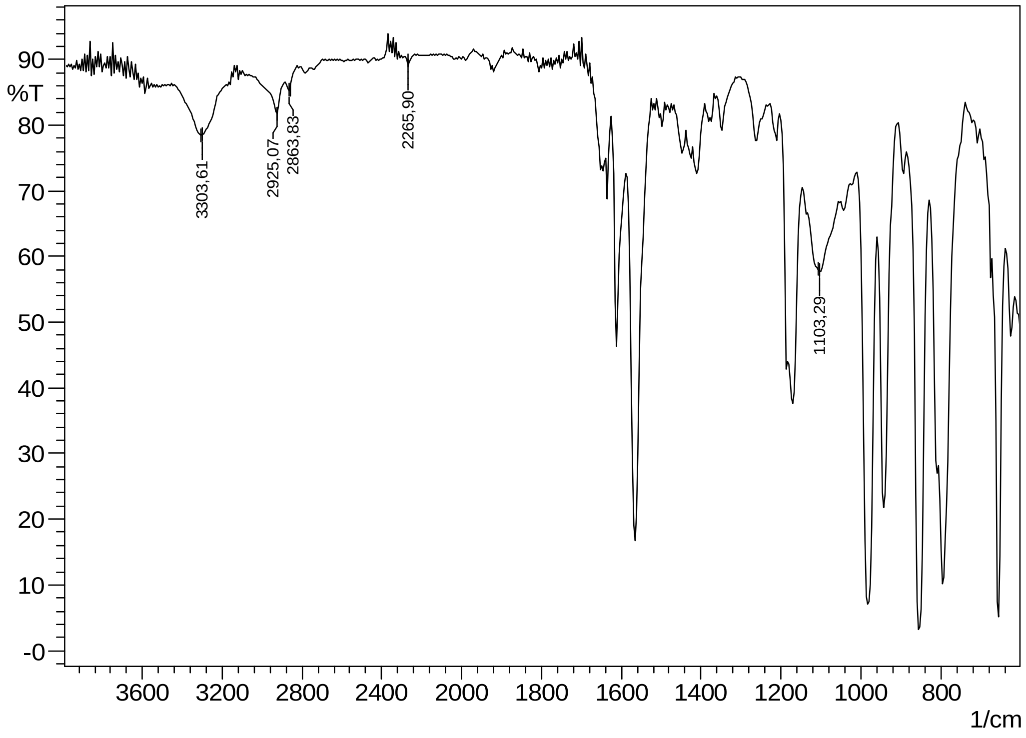

Figure S13. Infrared spectrum (hexachlorobutadiene) of [Cu(μ-OH)(Htmpz)$_2$(ClO$_4$)]$_2$·CH$_3$CN (**5**) (the IR spectrum of compound **6** is substantially the same, and is not reported).

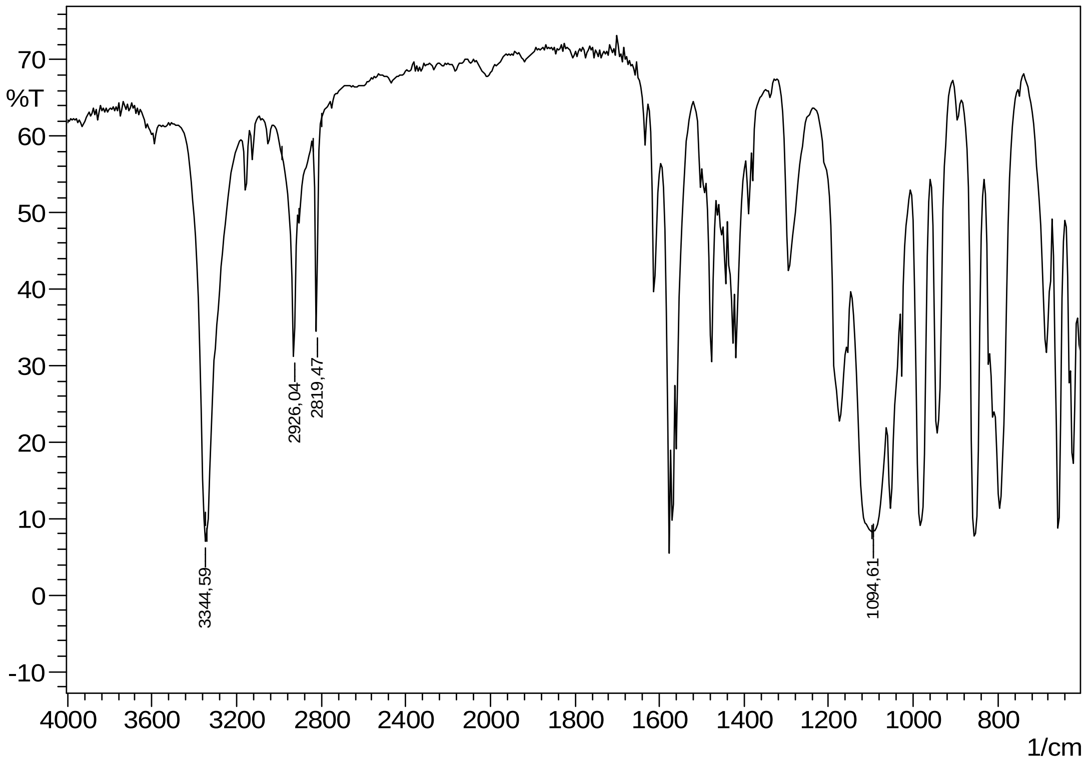

Figure S14. Infrared spectrum (hexachlorobutadiene) of [Cu(μ-OCH$_3$)(Hdmpz)$_2$(ClO$_4$)]$_2$ (**9**).