

Supplementary Information

A unique 1-amino-1-cyclopropane carboxylate cupric-cryptate hosting sodium

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All reagents were purchased and used without further purification. *Caution: Perchlorate salts Perchlorate salts including those of metal complexes with organic ligands are potentially explosive and should be handled with care.*

Synthesis: 1 equivalent of Sodium perchlorate (0.056 g, 0.4 mmol), 6 equivalent of copper perchlorate (0.89 g, 2.4 mmol) and 8 equivalent of 1-aminocyclopropane carboxylate (0.323 g, 3.2 mmol) were stirred for one hour in 50 mL methanol in a 250 mL Erlenmeyer flask. Subsequently, the resulting methanolic solution was left standing at 8°C and vapors of diethyl ether were allowed to slowly diffuse in it. Blue crystals formed, they were collected by filtration and dried yielding complex **1** quantitatively.

Elemental Analysis: Analysis was performed on a PerkinElmer 2400 II series CHNS/O Analyzer. C, H and N calculated for $C_{32}H_{60}Cl_5Cu_6N_8NaO_{42}$ are C: 21.23; H: 3.34 and N: 6.19 % the experimental values obtained from crystals of **1** were: C: 21.22; H: 3.35 and N: 6.17 %.

Electrospray ionization mass spectrometry: Experiments were carried on a MicrOTOF-Q Bruker instrument using a source acceleration voltage (i.e. In-Source Collision-Induced Dissociation ISCID on this particular instrument) of 130 eV and transfer capillary temperature (i.e. Dry heater on this particular instrument) of 180°C. 1 pM solutions of complex **1** in acetonitrile were injected without addition of charge carriers. Data was calibrated internally with ESI-L Low Concentration Tuning Mix (Agilent-Technologies).

UV-Vis spectrophotometry: Measurements were performed on a varian Cary 300 Bio UV-Vis spectrometer using a 88 mM solution of **1**, Figure S1. The obtained spectrum is shown in Figure S1, $\lambda_1 = 270$ nm and $\lambda_2 = 666$ nm with corresponding $\varepsilon_1 = 220$ mol⁻¹.cm⁻¹ and $\varepsilon_2 = 6$ mol⁻¹.cm⁻¹. On the one hand the absorption at λ_1 may be assigned to the $n \rightarrow \pi^*$ excitation of the unshared electron on the oxygen of the C=O of the carboxylate functions. On the other hand the absorption at λ_2 may be assigned to the d-d transition of the copper cations.

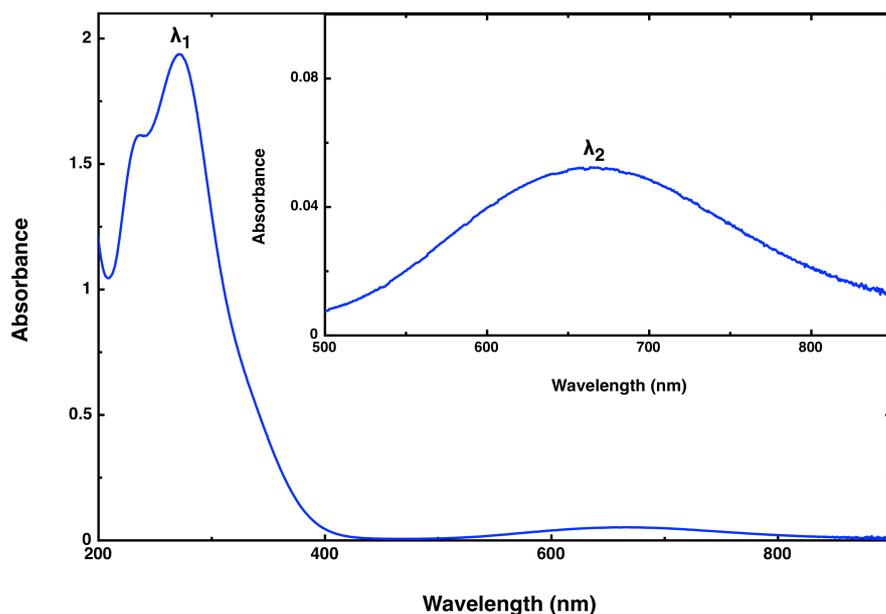


Figure S1: UV-Visible spectrum of complex **1** in acetonitrile.

Crystal structure: Crystals were mounted on a CryoLoop (Hampton Research) with Paratone-N (Hampton Research) as cryoprotectant and flashfrozen in a nitrogen-gas stream at 100 K. The temperature was maintained throughout the experiment to within an accuracy of ± 1 K by means of a 700 series Cryostream cooling device. X-ray diffraction data were collected using a Kappa X8 APPEX II Bruker diffractometer with graphite-monochromated MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) and corrected for Lorentz polarization, and absorption effects. The structure was solved by direct methods using SHELXS-97¹ and refined against F^2 by full-matrix least-squares techniques using SHELXL-97² with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms of acc were added from the difference Fourier map, and refined by the riding model. Hydrogen atoms of water molecules were subsequently included in the refinement in geometrically idealized positions with O—H = 0.96(3) \AA and H---H = 1.52(3) \AA and refined using the riding model with isotropic displacement parameters of Uiso(H) = 1.3 Ueq (parent atom). One ligand was disordered and was modeled in two orientations with occupancies of 0.5 and 0.5. Two of the three perchlorate anions are disordered over two sets of sites with a 0.5/0.5 and 0.6/0.4 occupancy ratios. Restraints on the positional and displacement parameters of the disordered atoms were required. All calculations were performed using the crystal structure crystallographic software package WINGX.³ The crystal data collection and refinement parameters are given in Table S1. Cambridge Crystallographic Data Centre CCDC 978249 and the attached .CIF file contain further crystallographic data.

Compound	1
Empirical Formula	C ₃₂ H ₅₂ Cl ₄ Cu ₆ N ₈ Na O ₃₄ , Cl O ₄ , 4(H ₂ O)
M_r	1810.36
Crystal size, mm ³	0.11 x 0.05 x 0.01
Crystal system	triclinic
Space group	$P - 1$
a, \AA	11.226(4)
b, \AA	11.865(4)
c, \AA	12.792(5)

α , °	88.050(9)
β , °	79.235(9)
γ , °	68.272(8)
Cell volume, Å ³	1553.7(10)
Z	1
T, K	100(1)
F ₀₀₀	914
μ , mm ⁻¹	2.350
θ range, °	1.62 – 26.56
Collected reflection	23370
Unique reflections	8632
R _{int}	0.0672
GOF	1.052
Observed reflections ($I > 2\sigma(I)$)	4135
Parameters	464
wR ₂ (all data)	0.2469
R value ($I > 2\sigma(I)$)	0.0792
Largest diff. peak and hole (e-Å ⁻³)	-1.183 ; 1.305

Table S1: Crystallographic data and structure refinement details.

Magnetism: The magnetic properties of **1** were studied on a SQUID Quantum Design MPMS 5 spectrometer using a microcrystalline sample placed in a gelatin capsule. Experimental molar magnetic susceptibility (χ_m) measurements were performed in a 2 to 300 K temperature (T) range in an applied constant magnetic field of $5 \cdot 10^3$ Oe. Isothermal magnetization (M) measurements were performed at 10, 6, 4 and 2 K in a magnetic field (H) range of 0 to $5 \cdot 10^4$ Oe.

Electrochemistry: The electrochemical characterization of **1** was performed in a three-electrode cell from BASi under argon on a 0.3 mM solution of **1** in acetonitrile containing 0.5 M NaClO₄ using an Autolab PGSTAT 12 potentiostat-galvanostat controlled by Nova Software version 1.8. The three electrodes used were a platinum mesh counter electrode, a glassy carbon disk (surface 2.01×10^{-2} cm²) working electrode and an Ag/AgCl reference electrode calibrated internally at the end of the measurements using the Fc⁺/Fc redox couple ($E_{1/2} = 0.37$ V).⁵ Cyclic voltammetry (CV) was performed by cycling the potential from the resting value of 1.1 V to -0.2 V at scan rates of 50, 200, 500 and 1000 mV.s⁻¹. Square wave voltammetry (SWV) was performed in a range of potential close to that the observed CV wave (1.1 V to -0.5 V) with 30 s conditioning time at the solution equilibrium potential (1.1 V), a modulation amplitude of 20 mV and a frequency of 25 Hz.

References:

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