

A templating guest sorts out a molecular triangle from a dimer-trimer constitutional dynamic library.

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Electronic Supplementary Information

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1. Synthesis

Reagents were purchased from Aldrich and used as received. Single crystals of $[\text{Cu}(o\text{-L})]_2$ ^[1] and the ligand 1,2-bis-(3-acetylaceton)benzene (*o*-L)^[2] have been prepared as reported in literature.

$\{[\text{Cu}(o\text{-L})]_3\text{C}(\text{hmt})\} \cdot 3(\text{H}_2\text{O})$, guest induced self-sorting (path b). A chloroform solution (2 ml) of hmt (7 mg, 0.05 mmol) has been added to a $[\text{Cu}(o\text{-L})]_n$ ($n = 2, 3$) solution, prepared dissolving $[\text{Cu}(o\text{-L})]_2$ single crystals (50 mg, *i.e.* 0.15 mmol of Cu^{2+} ions) in 5 ml of CHCl_3 . The solution turned from olive green to blue-greenish. It has been left under stirring for few minutes, then toluene (4 ml) has been added. Single crystals have been obtained by slow evaporation after few days. Yield 94 % (based on the crystalline product). Before elemental analysis the compound has been redissolved in chloroform and dried in vacuum overnight: C 53.42%, N 4.59%, H 5.62% (exp.); C 53.97%, N 4.66%, H 5.54% (calc.).

$\{[\text{Cu}(o\text{-L})]_3\text{C}(\text{hmt})\} \cdot 3(\text{H}_2\text{O})$, templated self-assembly (path c). $\text{CuSO}_4 \cdot 5(\text{H}_2\text{O})$ (75 mg, 0.3 mmol) has been dissolved in 5 mL of water and converted to the $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ion by addition of a NH_3 solution (28 %) in excess (1-2 ml). This solution has been added to a chloroform solution (10 ml) of *o*-L (82 mg, 0.3 mmol) and hmt (14 mg, 0.1 mmol). Instantly, the organic phase became blue-greenish. The biphasic system has been stirred for 4 h. The two phases have been separated and the organic one has been evaporated under reduced pressure. The obtained green-blue solid has been dried in vacuum overnight. Single crystals (yield 95 %) have been obtained, after few days, by slow evaporation of a chloroform-toluene (5 ml + 2 ml) solution. The compound identity has been confirmed by X-ray analysis.

2. Absorption spectroscopy

Absorption spectra were recorded on a CARY5E double-beam spectrophotometer with a spectral bandwidth of 1 nm. The contribution due to the solvent was subtracted.

Titration with hmt. In a quartz cuvette, to 3.0 ml of a 3 mM chloroform solution of $[\text{Cu}(o\text{-L})]_n$ ($n = 2, 3$) a 50 mM hmt chloroform solution has been added in different aliquots according to Table S1. Under these conditions, absorbance variation due to dilution is negligible (starting volume 3.0 ml,

final volume 3.1 ml). After each addition the solution has been shaken a few seconds and the spectrum recorded. Spectra are shown in Figure 5 and in Figure S1. Data of Figure 6a are obtained from the absorbance at 625 nm and the hmt molar fraction is calculated considering the Cu^{2+} moles.

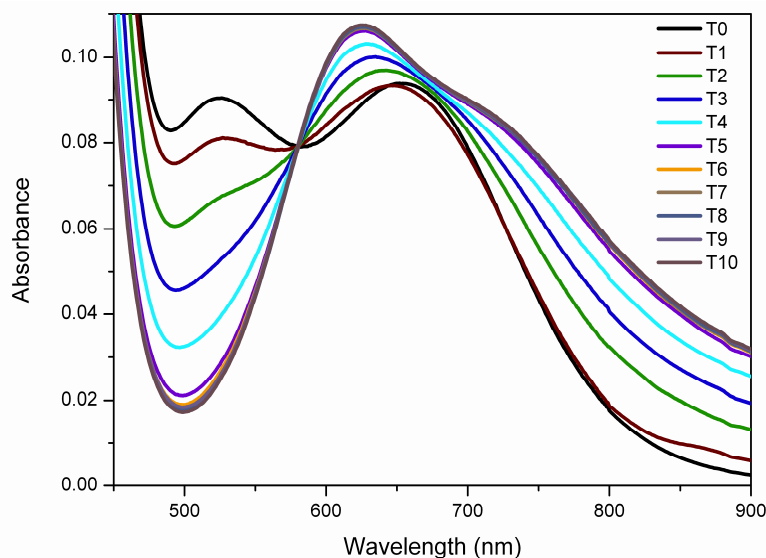


Figure S1

	Total hmt volume added (ml)
T0	0.00
T1	0.01
T2	0.02
T3	0.03
T4	0.04
T5	0.05
T6	0.06
T7	0.07
T8	0.08
T9	0.09
T10	0.10

Continuos variation method (Job plot). Job plot of Figure 6b has been determined by absorption spectroscopy considering the absorbance at 625 nm of the $\{[\text{Cu}(o\text{-L})]_3\text{C}(\text{hmt})\}$ species, using equimolar (3 mM) chloroform solutions of $[\text{Cu}(o\text{-L})]_n$ ($n = 2, 3$) and hmt. Spectra (Figure S2) have been recorded on $\{[\text{Cu}(o\text{-L})]_n + \text{hmt}\}$ solutions according to Table S2. To correctly estimate the absorbance at 625 nm, each spectrum (in the range 500-800 nm) has been fitted with a multi-peak routine (Origin 6.0 software) considering four peaks at 523, 625, 652 and 730 nm. The hmt molar fraction is calculated on the basis of the Cu^{2+} moles.

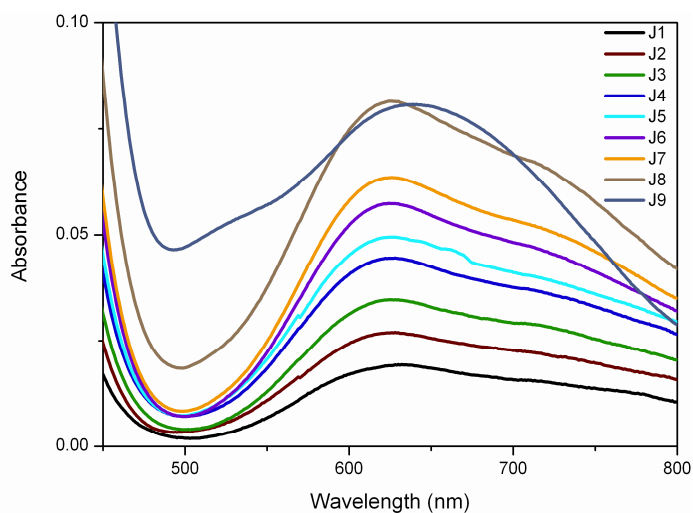


Figure S2

	$V_{[\text{Cu}(o\text{-L})]_n}$ (ml)	V_{hmt} (ml)
J1	0.1	0.9
J2	0.2	0.8
J3	0.3	0.7
J4	0.4	0.6
J5	0.5	0.5
J6	0.6	0.4
J7	0.7	0.3
J8	0.8	0.2
J9	0.9	0.1

3. X-Ray structure determination and refinement

A $\{[\text{Cu}(\text{o-L})]_3\text{C}(\text{hmt})\} \cdot 3(\text{H}_2\text{O})$ single crystal suitable for X-ray diffractometry studies was fastened on the top of a Lindemann glass capillary and centred on the head of the four-circle kappa goniometer of an Oxford Diffraction Gemini E diffractometer, equipped with a $2\text{K} \times 2\text{K}$ EOS CCD area detector and sealed-tube enhance (Mo) and (Cu) X-ray sources, at room temperature. Data were collected by means of the ω - scans technique, using graphite-monochromated radiation, in a 1024×1024 pixel mode, using 2×2 pixel binning. The diffraction intensities were corrected for Lorentz and polarization effects and were also optimized with respect to absorption. Empirical multi-scan absorption corrections using equivalent reflections were performed with the scaling algorithm *SCALE3 ABSPACK*. Data collection, data reduction and finalization were carried out through the CrysAlisPro software (CrysAlisPro, Oxford Diffraction Ltd., Version 1.171.34.36). Accurate unit cell parameters were determined during the whole data collection by least-squares refinement of all reflection positions. The structure was solved by means of heavy-atoms methods using SHELXS^[3] and refined by full-matrix least-squares methods based on F_o^2 with SHELXL-97^[3] in the framework of OLEX2^[4] software. In the last cycles of refinement, non-hydrogen atoms were refined anisotropically; hydrogen atoms were included in idealised positions and refined with a 'riding' model. The final difference Fourier map revealed a region with three non-negligible residual peaks, likely due to a crystallization solvent molecule, that could not be effectively modelled. The contribution of these peaks was removed by using the SQUEEZE routine of PLATON.^[5] The SQUEEZE routine highlighted the presence of two voids (548 \AA^3) in the unit cell large enough to host *ca.* 1.75 toluene molecules each, as estimated from the electron count (89 electrons per void). A summary of the main crystallographic data is given in Table S3. Selected bond lengths are reported in Table S4 and S5.

Comments on checkcif.

Checkcif routine highlighted two A alerts here reported and commented:

1) PLAT029_ALERT_3_A _diffrn_measured_fraction_theta_full Low 0.887

Several crystals have been checked, but all the specimens tested were unable to diffract the X radiation at high θ values (diffraction limit above 1 \AA *ca.*). The quality of the structural determination has been hampered by this limitation. Accordingly, we could not reach a data completeness greater than 88.7%. However, we also point out that, despite the above limitations, the structural and chemical identification of the studied species was not compromised.

2) PLAT601_ALERT_2_A Structure Contains Solvent Accessible VOIDS of . 548 A**3

With respect to the two large voids (548 \AA^3 *ca.*) identified during the PLATON check, they result inherently correlated to the crystal packing of the compound. This leaves enough

space to host *ca.* 1.75 toluene solvent crystallization molecules for each void (as estimated from the electron count). Unfortunately, every attempt to effectively model the residual peaks located in the voids did not provide a satisfactory solution. Accordingly, the contribution of these remnants peaks was removed by using the SQUEEZE routine of PLATON.

Table S3. {[Cu(*o*-L)]₃C(hmt)}·3(H₂O) crystal data and details of data collection.

Chemical formula	C ₅₄ H ₆₆ Cu ₃ N ₄ O ₁₅
Formula Mass	1201.73
Crystal system	monoclinic
<i>a</i> /Å	34.2239(10)
<i>b</i> /Å	23.4053(6)
<i>c</i> /Å	15.0341(4)
α /°	90.00
β /°	105.320(3)
γ /°	90.00
Unit cell volume/Å ³	11614.7(6)
Temperature/K	300.5
Space group	C2/c (no. 15)
<i>Z</i>	8
Radiation type	Mo K α
Crystal size/mm ³	0.30 × 0.25 × 0.20
Absorption coefficient, μ /mm ⁻¹	1.155
No. of reflections measured	52690
No. of independent reflections	8593
<i>R</i> _{int}	0.0430
Final R indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0391, <i>wR</i> ₂ = 0.0965
Final R indexes [all data]	<i>R</i> ₁ = 0.0558, <i>wR</i> ₂ = 0.1026
Goodness of fit on <i>F</i> ²	1.025
Largest diff. peak and hole/eÅ ⁻³	0.24/-0.23
CCDC number	856307

$R_1 = (\sum ||F_o| - |F_c|| / \sum |F_o|)$; $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$; GOF = $\{\sum [w(F_o^2 - F_c^2)^2] / (n - p)\}^{1/2}$ where *n* is the number of data and *p* is the number of parameters refined.

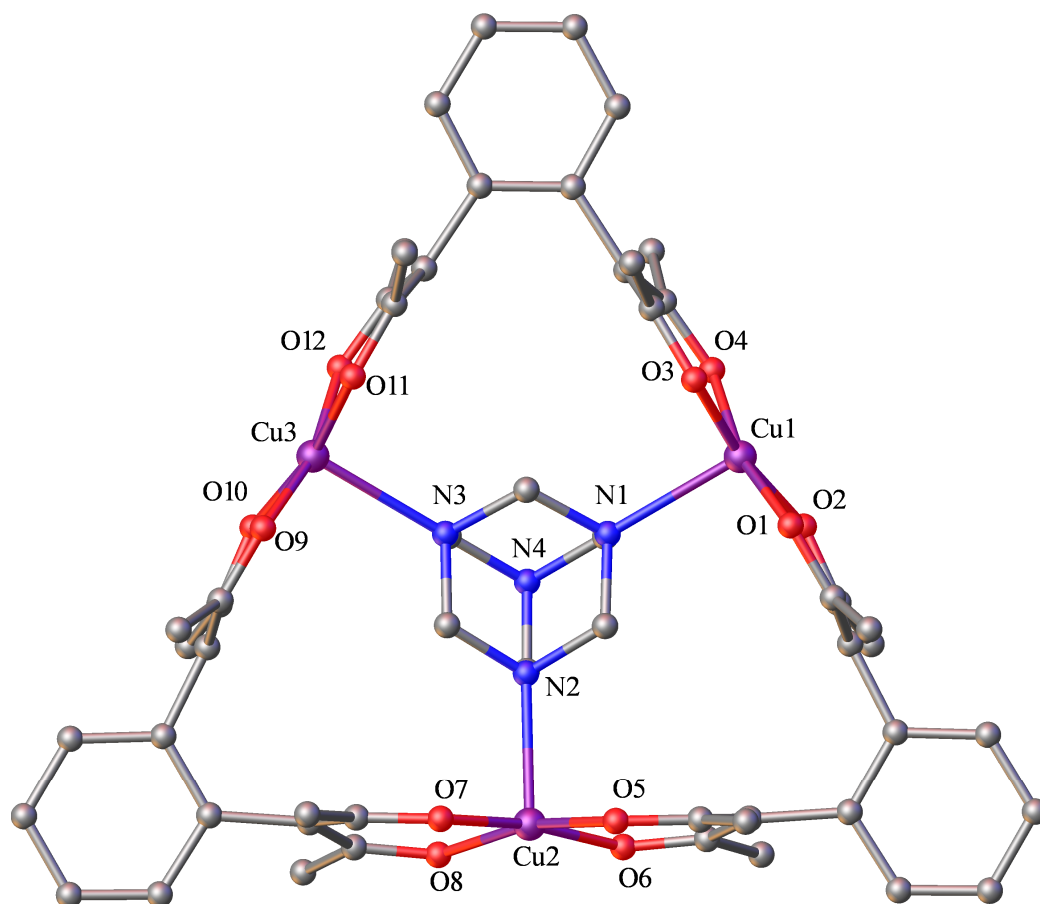


Figure S3. Structure of $\{[\text{Cu}(\text{o-L})]_3\text{C}(\text{hmt})\}$. Colour code: Cu purple, O red, N blue, C grey, H atoms and water molecules omitted.

Table S4. Selected bond distances in $\{[\text{Cu}(\text{o-L})]_3\text{C}(\text{hmt})\} \cdot 3(\text{H}_2\text{O})$

Atom 1	Atom 2	Distance (Å)
Cu1	O3	1.909(2)
Cu1	O2	1.912(2)
Cu1	O1	1.930(2)
Cu1	O4	1.939(2)
Cu1	N1	2.387(2)
Cu2	O5	1.910(2)
Cu2	O7	1.930(2)
Cu2	O6	1.934(2)
Cu2	O8	1.931(2)
Cu2	N2	2.367(2)
Cu3	O9	1.917(2)
Cu3	O12	1.926(2)
Cu3	O10	1.933(2)
Cu3	O11	1.931(2)
Cu3	N3	2.387(2)

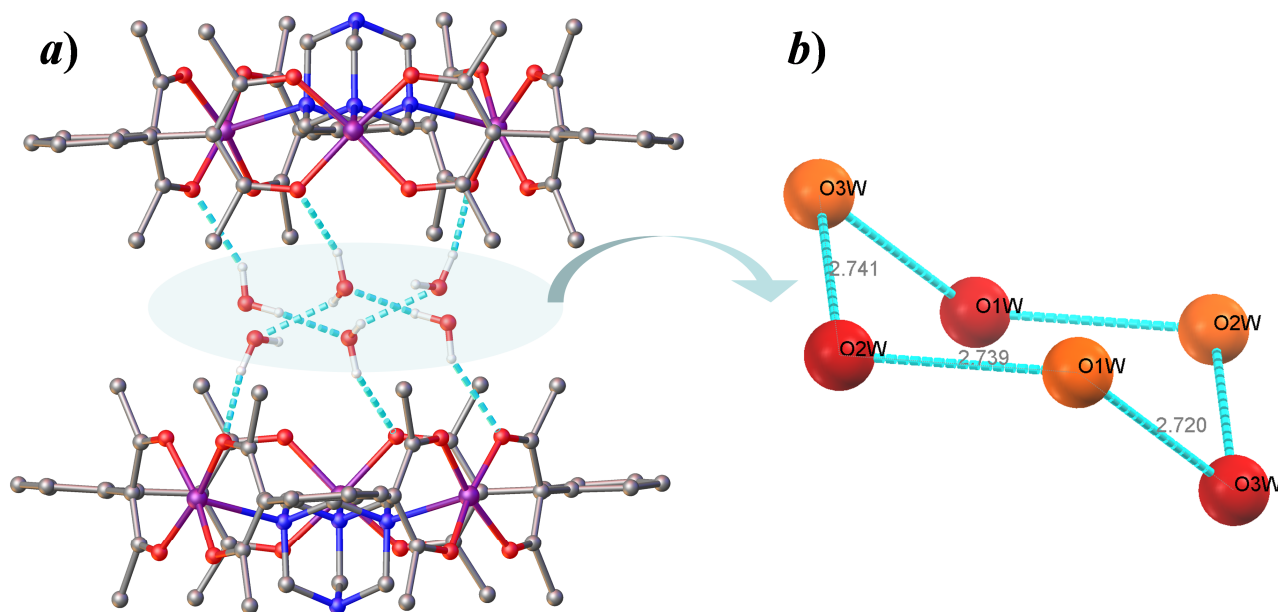


Figure S4. *a)* H-bond mediated supramolecular assembly $\{[\text{Cu}(\text{o-L})]_3\text{C}(\text{hmt})_2(\text{H}_2\text{O})_6\}$. *b)* The chair-like $\{\text{H}_2\text{O}\}_6$ cluster (symmetry operation for orange oxygen atoms: $3/2-x, 1/2-y, 1-z$). Colour code: Cu purple, O red (orange), N blue, C grey, H white (where not omitted). H-bonds cyan dotted line.

Table S5. H-bonds length in the $\{\text{H}_2\text{O}\}_6$ cluster.

Atom 1	Atom 2	Distance (Å)
O1W	O3W	2.720
O1W	O2W	2.739
O2W	O3W	2.741

4. Electrospray Mass Spectrometry

The ESI mass spectra were obtained using a LCQ DECA ion trap instrument (ThermoFisher Scientific, San José, CA, USA), operating in positive ion mode. The entrance capillary temperature was 280 °C and the capillary voltage was 4 kV. The compounds under study were firstly dissolved in tetrahydrofuran (THF) and then diluted in acetonitrile to obtain a 10^{-6} M concentration. The acetonitrile solutions of each compound were introduced into ESI ion source by direct infusion at a flow rate of 10 μ L/min. The He pressure inside the trap was kept constant. The pressure directly read by ion gauge (in the absence of the N₂ stream) was $2.8 \cdot 10^{-5}$ torr. MS/MS experiments were performed by resonant excitation of the ion of interest through a supplementary r.f. voltage in the range 30-35% of its maximum value (5 V peak-to-peak). The isolation width was set at 1 mass unit.

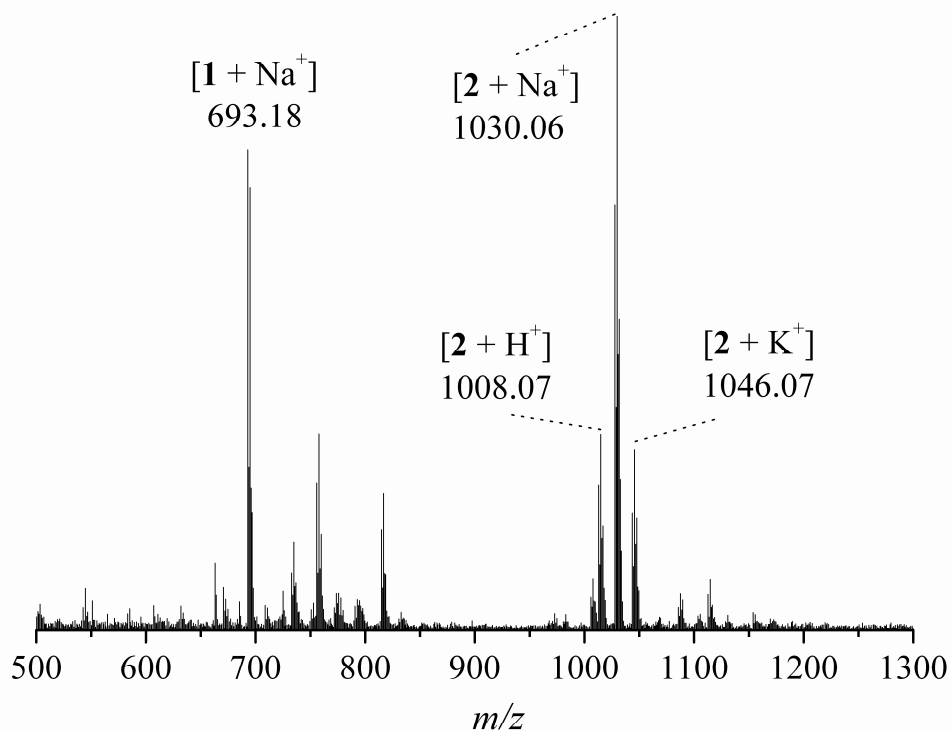


Figure S5. ESI-MS positive mode of a $[\text{Cu}(o\text{-L})]_n$ solution.

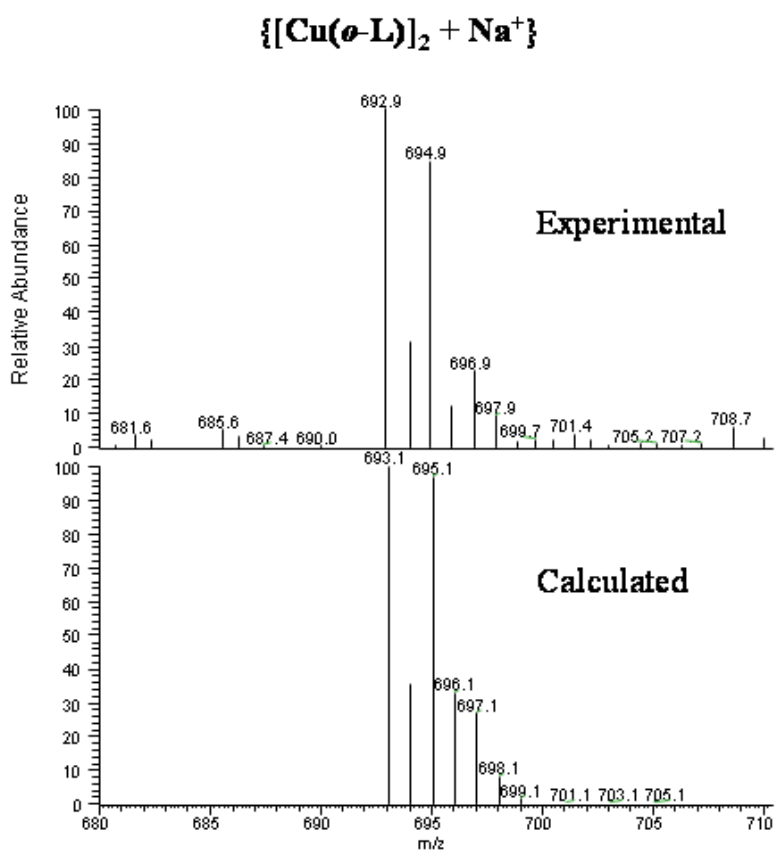


Figure S6. Experimental and calculated isotopic patterns for {[Cu(*o*-L)]₂ + Na⁺}.

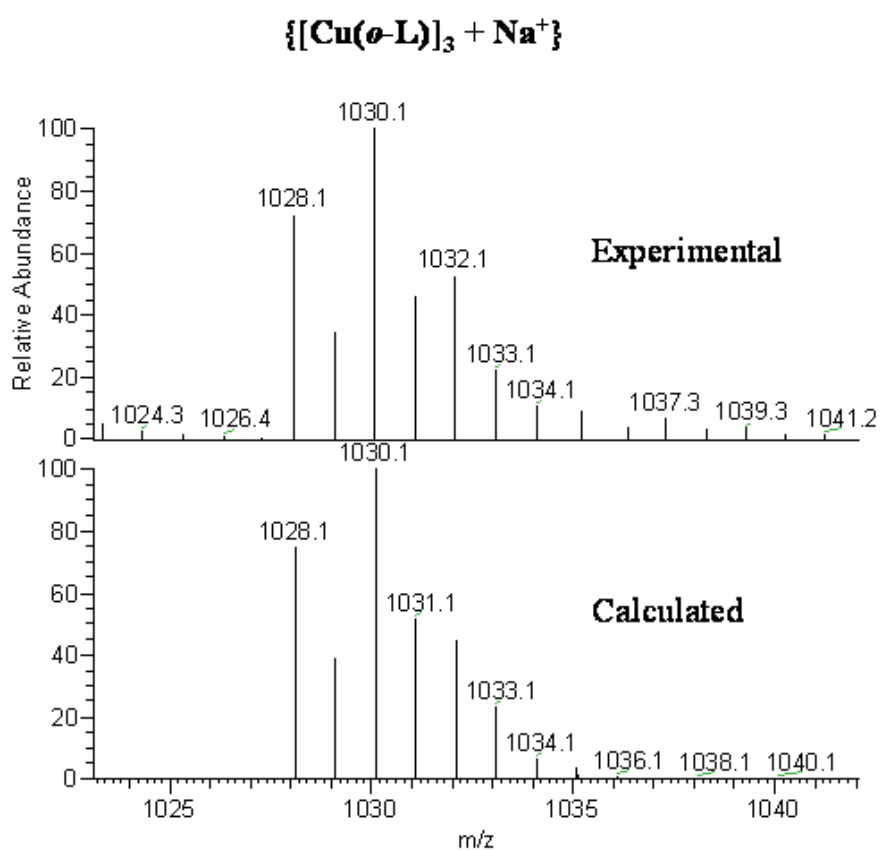


Figure S7. Experimental and calculated isotopic patterns for {[Cu(*o*-L)]₃ + Na⁺}.

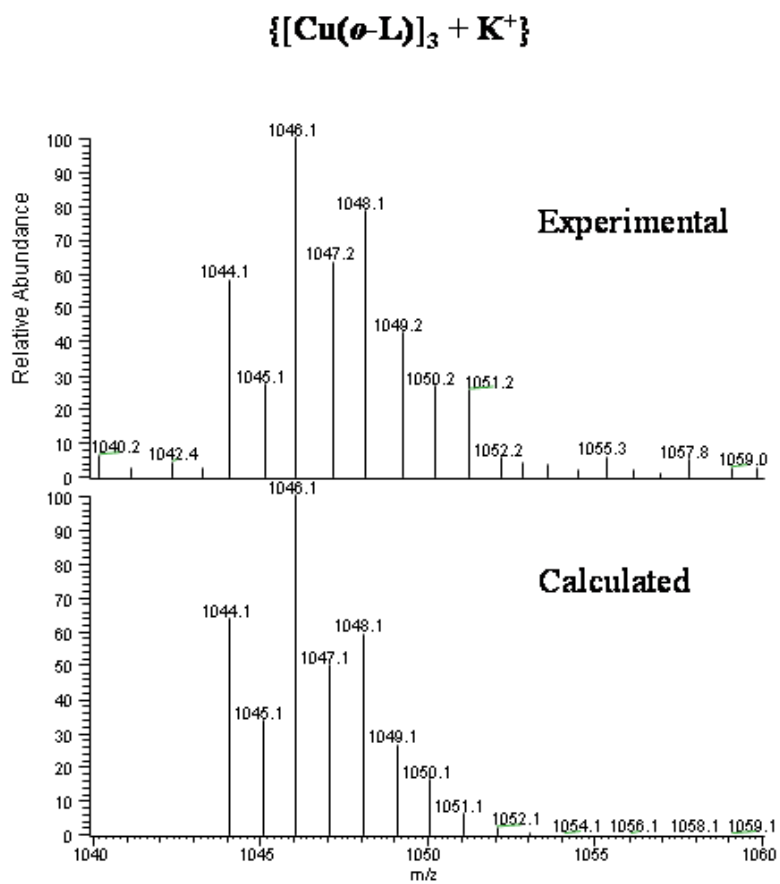


Figure S8. Experimental and calculated isotopic patterns for {[Cu(*o*-L)]₃ + K⁺}.

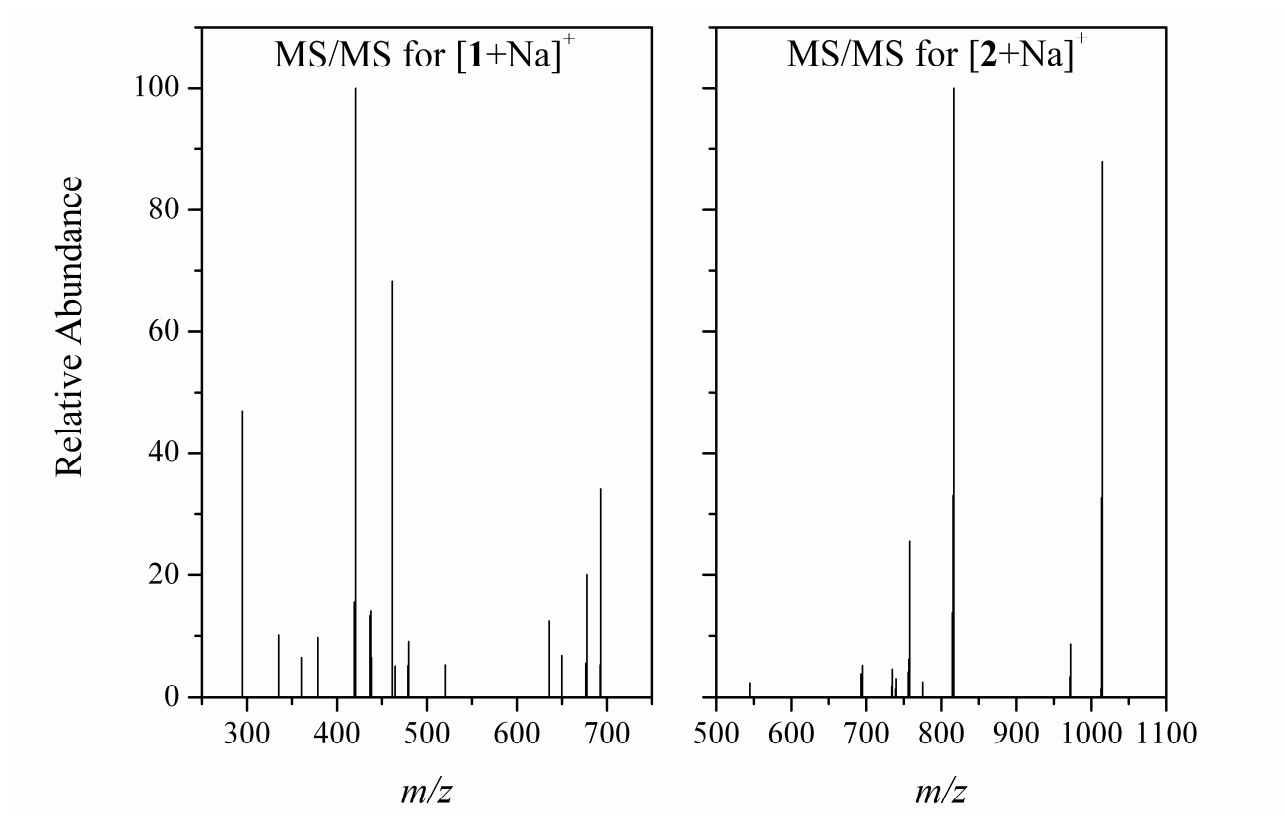


Figure S9. MS/MS fragmentation for the ions $[1+\text{Na}]^+$ and $[2+\text{Na}]^+$.

Table S6. MS/MS for $[1+\text{Na}]^+$, m/z 693

m/z	Loss
678	$-\text{CH}_3^\bullet$ (-15 Da)
650	$-\text{C}_2\text{H}_3\text{O}^\bullet$ (-43 Da)
636	$-\text{C}_3\text{H}_5\text{O}^\bullet$ (-57 Da)
520	$-\text{C}_{11}\text{H}_9\text{O}^\bullet$ (-173 Da)
480	$-\text{C}_{14}\text{H}_{13}\text{O}_2^\bullet$ (-213 Da)
461 [§]	$-\text{C}_{14}\text{H}_{16}\text{O}_3$ (-232 Da)
421 [§]	$-\text{C}_{16}\text{H}_{16}\text{O}_4$ (-272 Da)

Table S7. MS/MS for $[2+\text{Na}]^+$, m/z 1030

m/z	Loss
1015	$-\text{CH}_3^\bullet$ (-15 Da)
972	$-\text{C}_3\text{H}_5\text{O}^\bullet$ (-57 Da)
817	$-\text{C}_{14}\text{H}_{13}\text{O}_2^\bullet$ (-213 Da)
758 [§]	$-\text{C}_{16}\text{H}_{16}\text{O}_4$ (-272 Da)

[§] Peaks at 461 and 421 m/z are ascribed to species containing two Cu(I) ions, while the peak at 758 m/z is ascribed to a fragment with one Cu(II) and two Cu(I) ions. The reduction of Cu(II) to Cu(I) during the MS/MS fragmentation and in the ESI-MS analysis has been often reported in literature^[6].

5. References

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