Double Template Effect in (4+4) Schiff Base Macrocycle Formation; an ESI-MS Study

Julia Barreira-Fontecha, Rafal Kulmaczewski, Xiaomai Ma and Vickie McKee

SUPPLEMENTARY DATA

A. Mass spectrometry

Electrospray ionisation mass spectrometry experimental.

Electrospray ionisation mass spectrometry experiments were performed on a Thermo Fisher Exactive Orbitrap mass spectrometer coupled to Advion TriVersa Nanomate injection system. The instrument was used in positive ion mode and samples were delivered to the ESI source using nanomate chip base system. The spray voltage was set to 1478 V and the capillary voltage to 92.5 V. The temperatures were set as follows, 191 °C at capillary, 27 °C at analyser and 46 °C at the ESI source. No nebulizer or sheet gas flows were employed. The data were processed using Thermo Xcalibur software version 2.1.0.1139 provided by Thermo Scientific. The isotope pattern calculations were carried on the Thermo Xcalibur Qual Browser. The differences observed ion the relative intensities between experimental and calculated signals for some of the isotope clusters is a consequence of the (over?) optimisation of the mass accuracy on the departmental Orbitrap instrument. Test data collected on the Waters Synapt in Professor Creaser's lab did not show this problem. An example from the Synapt has been included in Figure S5 (page13).

Samples acquired on the Thermo Fisher Exactive Orbitrap instrument were prepared as follows. 100 µL of the reaction mixtures was extracted from the refluxing reaction mixtures, and diluted up to 500 µL with methanol. A test reaction showed that this procedure effectively quenched the reaction.

Next samples were carried to the departmental mass spectrometry service. Then 1 drop of that prepared solution (approx 25 µL) was diluted with 1 mL of MeOH (final conc ~10^{-6} M) and this was placed on the well plate from which sample was injected. Data were acquired at various times, measured from the moment of extraction.

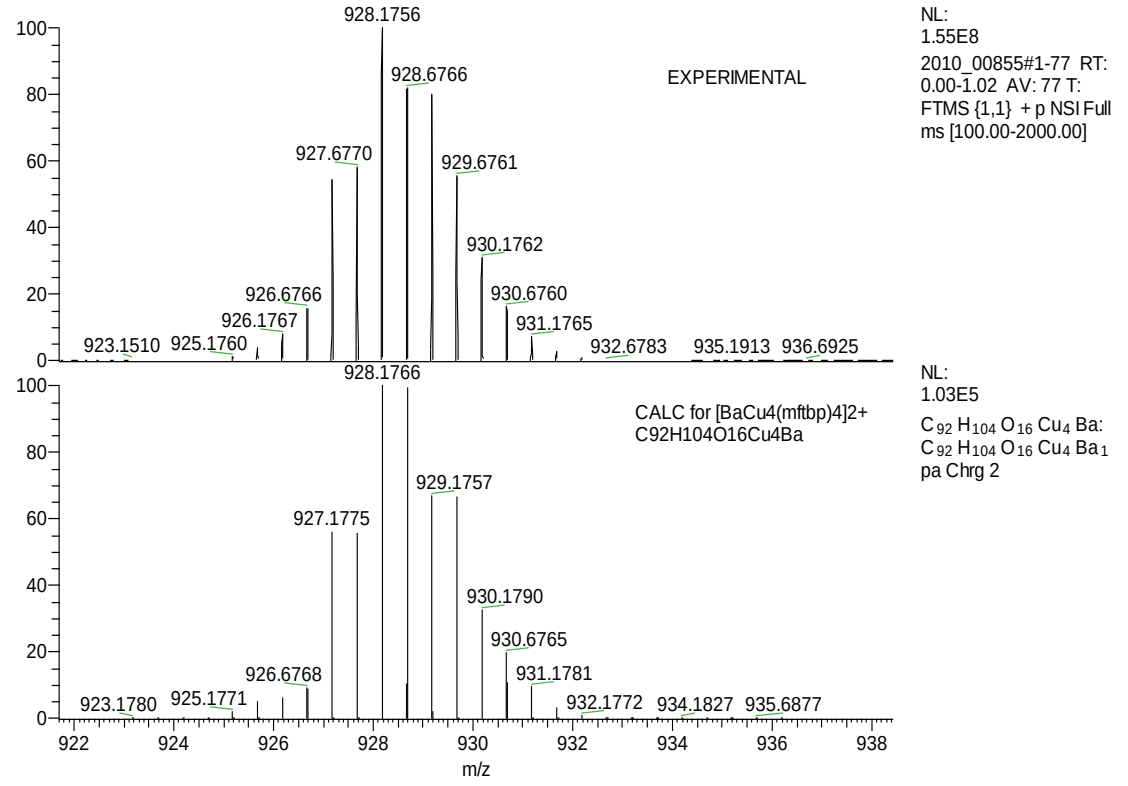
B. Complex 1 $[BaCu_4(dthmb)_4(EtOH)(MeOH)_3](ClO_4)_2 \cdot 4EtOH \cdot 3H_2O$

(i) Synthesis

H_2dhtmb, (0.100 g, 0.270 mmol), $Cu(ClO_4)_2 \cdot 6H_2O$ (0.100 g, 0.270 mmol) and $Ba(ClO_4)_2 \cdot 6H_2O$ (0.026 g, 0.067 mmol) were dissolved in 60 mL of EtOH (IMS) and brought to reflux. After 30 min. 1 mL of triethylamine was introduced to the reaction mixture and reflux was continued for further 30 min. Samples for ESI-MS were extracted one minute after addition of base and 30 minutes after addition (no change). Crystals of the complex suitable for X-ray crystallography were obtained by evaporation of the solvent; bulk samples were contaminated bu NEt_3 and $[HNEt_3]^+$ salts and satisfactory CHN analysis was not obtained.

(ii) ESI-MS

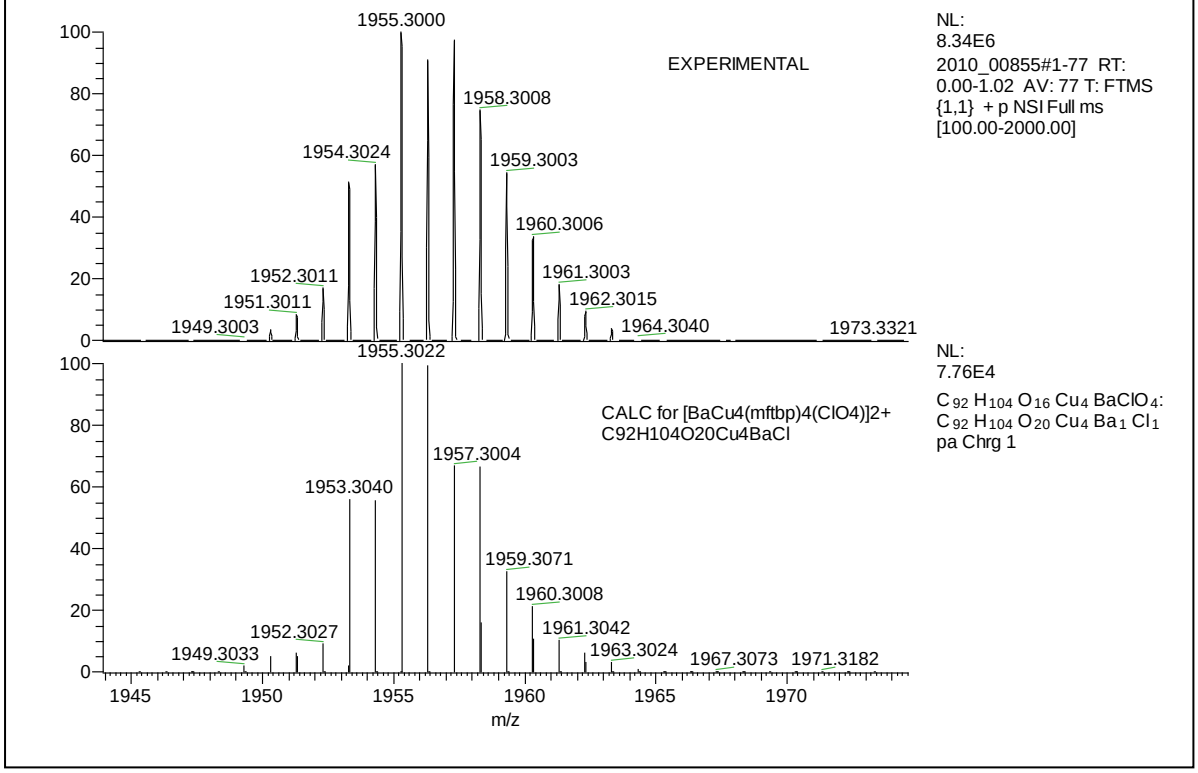
Fig S1



Figures S1 and S2 show the measured and calculated isotope patterns for the only significant peaks in the ESI spectrum of a sample of the reaction mixture extracted one minure after addition of the NEt_3 (the full spectrum is Fig 1 in the main text).

Fig S1 corresponds to $[BaCu_4(dthmb)_4]^{2+}$ and Fig S2 matches $\{[BaCu_4(dthmb)_4](ClO_4)\}^+$

Fig S2


1955.3000
1958.3008
1954.3024
1959.3003
1960.3006
1952.3011
1961.3003
1951.3011
1962.3015
1949.3003
1964.3040
1973.3321
EXPERIMENTAL
NL:
8.34E6
2010_00855#1-77 RT:
0.00-1.02 AV: 77 T: FTMS
{1,1} + p NSI Full ms
[100.00-2000.00]
1955.3022
1957.3004
1953.3040
1959.3071
1960.3008
1961.3042
1952.3027
1963.3024
1949.3033
1967.3073
1971.3182
CALC for [BaCu4(mftbp)4(ClO4)]2+
C92H104O20Cu4BaCl
NL:
7.76E4
C92 H104 O16 Cu4 BaClO4:
C92 H104 O20 Cu4 Ba1 Cl1
pa Chrg 1
100
80
60
40
20
0
1945
1950
1955
1960
1965
1970
m/z

(iii) Crystallography

The data were collected at 150(2)K on a Bruker Apex II CCD diffractometer using Mo*K*□ radiation (λ = 0.71073Å). The structure was solved by direct methods and refined on F^2 using all the reflections. All the non-hydrogen atoms were refined using anisotropic atomic displacement parameters and hydrogen atoms bonded to carbon were inserted at calculated positions using a riding model. Hydrogen atoms bonded to the alcohol oxygen atoms were not included. Two of the coordinated alcohol molecules were disordered and refined as 50% methanol/ethanol.

Disordered, non-coordinated solvent molecules were treated using SQUEEZE:

```
# SQUEEZE RESULTS (APPEND TO CIF)
# Note: Data are Listed for all Voids in the P1 Unit Cell
# i.e. Centre of Gravity, Solvent Accessible Volume,
# Recovered number of Electrons in the Void and
# Details about the Squeezed Material
loop_
  _platon_squeeze_void_nr
  _platon_squeeze_void_average_x
  _platon_squeeze_void_average_y
  _platon_squeeze_void_average_z
  _platon_squeeze_void_volume
  _platon_squeeze_void_count_electrons
  _platon_squeeze_void_content
   1  0.500  0.500  0.000       966       266 ' '
   2  0.000  0.000  0.500       966       266 ' '
_platon_squeeze_details
```

This was modelled as 4EtOH and $3H_2O$ per formula unit (134 electrons) but other combinations of EtOH/MeOH and H_2O are also possible.

The checkcif report raises level A alerts because these solvate molecules are not in the atom list but have been included in the formula.

Other alerts refer to the ellipsoids of the tert-butyl groups, some rotational disorder here has not been modelled.

Parameters for data collection and refinement are summarised in Table S1.

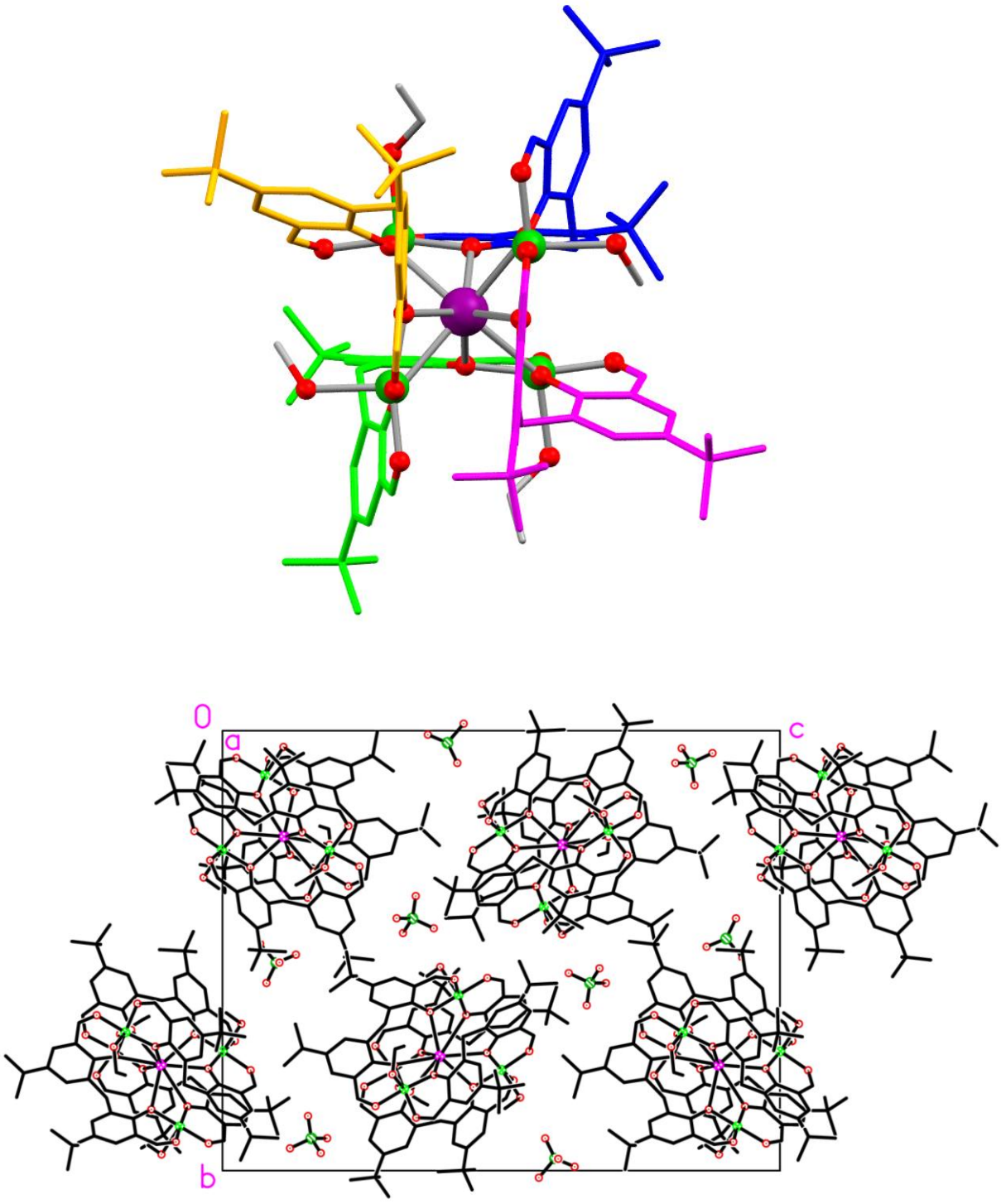


Fig S3. Top: Alternate view of the cation 1; Bottom; packing diagram – projection down a axis.

Table S1. Crystal data and structure refinement for Complex 1.

Identification code	raf13sq	
Empirical formula	C105 H154 Ba Cl2 Cu4 O35	
Formula weight	2438.68	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 14.1493(7) Å	α= 90°.
	b = 25.3525(12) Å	β= 101.8360(10)°.
	c = 32.8654(15) Å	γ = 90°.
Volume	11538.8(9) $Å^3$	
Z	4	
Density (calculated)	1.404 Mg/m^3	
Absorption coefficient	1.184 mm^{-1}	
F(000)	5080	
Crystal size	0.36 x 0.19 x 0.10 mm^3	
Crystal description	green block	
Theta range for data collection	1.48 to 25.00°.	
Index ranges	-16<=h<=16, -30<=k<=30, -39<=l<=38	
Reflections collected	90748	
Independent reflections	20325 [R(int) = 0.0592]	
Completeness to theta = 25.00°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8907 and 0.6751	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	20325 / 106 / 1198	
Goodness-of-fit on F^2	1.042	
Final R indices [I>2sigma(I)]	R1 = 0.0602, wR2 = 0.1655	
R indices (all data)	R1 = 0.0883, wR2 = 0.1791	
Largest diff. peak and hole	1.875 and -0.894 e.$Å^{-3}$	

Table S2. Bond lengths [Å] and angles [°] for Complex1.

Ba(1)-O(2)	2.706(4)	Ba(1)-Cu(3)	3.7000(8)
Ba(1)-O(10)	2.723(4)	Ba(1)-Cu(4)	3.7026(8)
Ba(1)-O(15)	2.730(4)	Ba(1)-Cu(2)	3.7033(8)
Ba(1)-O(7)	2.743(3)	Ba(1)-Cu(1)	3.7604(7)
Ba(1)-O(3)	2.875(3)	Cu(1)-Cu(3)	5.1177(9)
Ba(1)-O(6)	2.932(4)	Cu(2)-Cu(4)	5.0343(12)
Ba(1)-O(11)	2.934(4)		
Ba(1)-O(14)	2.974(3)		
Cu(1)-O(14)	1.925(4)	Cu(3)-O(10)	1.921(3)
Cu(1)-O(13)	1.926(4)	Cu(3)-O(4)	1.931(4)
Cu(1)-O(7)	1.931(3)	Cu(3)-O(3)	1.937(4)
Cu(1)-O(8)	1.970(4)	Cu(3)-O(9)	1.963(4)
Cu(1)-O(300)	2.260(4)	Cu(3)-O(200)	2.236(5)
Cu(2)-O(2)	1.913(4)	Cu(4)-O(11)	1.916(4)
Cu(2)-O(5)	1.926(4)	Cu(4)-O(15)	1.922(4)
Cu(2)-O(6)	1.933(4)	Cu(4)-O(12)	1.931(4)
Cu(2)-O(1)	1.970(4)	Cu(4)-O(16)	1.982(4)
Cu(2)-O(100)	2.250(6)	Cu(4)-O(400)	2.239(5)
O(2)-Ba(1)-O(10)	95.01(11)	O(10)-Ba(1)-O(11)	81.62(10)
O(2)-Ba(1)-O(15)	145.58(11)	O(15)-Ba(1)-O(11)	55.93(11)
O(10)-Ba(1)-O(15)	94.38(11)	O(7)-Ba(1)-O(11)	130.41(10)
O(2)-Ba(1)-O(7)	94.25(11)	O(3)-Ba(1)-O(11)	137.56(10)
O(10)-Ba(1)-O(7)	146.02(10)	O(6)-Ba(1)-O(11)	62.84(12)
O(15)-Ba(1)-O(7)	96.20(10)	O(2)-Ba(1)-O(14)	130.32(10)
O(2)-Ba(1)-O(3)	82.35(11)	O(10)-Ba(1)-O(14)	94.22(10)
O(10)-Ba(1)-O(3)	57.07(10)	O(15)-Ba(1)-O(14)	81.74(10)
O(15)-Ba(1)-O(3)	129.78(11)	O(7)-Ba(1)-O(14)	55.77(10)
O(7)-Ba(1)-O(3)	92.03(10)	O(3)-Ba(1)-O(14)	62.83(10)
O(2)-Ba(1)-O(6)	56.24(11)	O(6)-Ba(1)-O(14)	135.59(10)
O(10)-Ba(1)-O(6)	130.19(10)	O(11)-Ba(1)-O(14)	136.71(11)
O(15)-Ba(1)-O(6)	93.14(12)	O(14)-Cu(1)-O(13)	95.64(17)
O(7)-Ba(1)-O(6)	81.34(11)	O(14)-Cu(1)-O(7)	88.12(15)
O(3)-Ba(1)-O(6)	137.08(11)	O(13)-Cu(1)-O(7)	174.94(18)
O(2)-Ba(1)-O(11)	92.94(11)	O(14)-Cu(1)-O(8)	167.56(16)

O(13)-Cu(1)-O(8)	83.44(18)	O(5)-Cu(2)-O(100)	88.9(2)
O(7)-Cu(1)-O(8)	92.16(17)	O(6)-Cu(2)-O(100)	101.3(2)
O(14)-Cu(1)-O(300)	97.66(17)	O(1)-Cu(2)-O(100)	93.0(2)
O(13)-Cu(1)-O(300)	92.04(15)	O(10)-Cu(3)-O(4)	172.45(17)
O(7)-Cu(1)-O(300)	90.81(15)	O(10)-Cu(3)-O(3)	87.90(15)
O(8)-Cu(1)-O(300)	94.77(17)	O(4)-Cu(3)-O(3)	95.08(16)
O(14)-Cu(1)-Ba(1)	51.57(11)	O(10)-Cu(3)-O(9)	92.99(16)
O(13)-Cu(1)-Ba(1)	136.66(13)	O(4)-Cu(3)-O(9)	82.32(17)
O(7)-Cu(1)-Ba(1)	44.56(10)	O(3)-Cu(3)-O(9)	164.78(16)
O(8)-Cu(1)-Ba(1)	122.14(12)	O(10)-Cu(3)-O(200)	95.37(17)
O(300)-Cu(1)-Ba(1)	116.92(11)	O(4)-Cu(3)-O(200)	90.89(18)
O(14)-Cu(1)-Cu(3)	37.88(10)	O(3)-Cu(3)-O(200)	100.7(2)
O(13)-Cu(1)-Cu(3)	90.48(12)	O(9)-Cu(3)-O(200)	94.4(2)
O(7)-Cu(1)-Cu(3)	90.42(10)	O(11)-Cu(4)-O(15)	87.85(15)
O(8)-Cu(1)-Cu(3)	129.69(11)	O(11)-Cu(4)-O(12)	95.58(17)
O(300)-Cu(1)-Cu(3)	135.44(13)	O(15)-Cu(4)-O(12)	173.06(19)
Ba(1)-Cu(1)-Cu(3)	46.197(11)	O(11)-Cu(4)-O(16)	166.2(2)
O(2)-Cu(2)-O(5)	174.40(19)	O(15)-Cu(4)-O(16)	91.61(16)
O(2)-Cu(2)-O(6)	87.70(16)	O(12)-Cu(4)-O(16)	83.62(18)
O(5)-Cu(2)-O(6)	95.26(18)	O(11)-Cu(4)-O(400)	104.18(19)
O(2)-Cu(2)-O(1)	91.80(17)	O(15)-Cu(4)-O(400)	96.00(19)
O(5)-Cu(2)-O(1)	84.16(19)	O(12)-Cu(4)-O(400)	89.0(2)
O(6)-Cu(2)-O(1)	165.7(2)	O(16)-Cu(4)-O(400)	89.6(2)
O(2)-Cu(2)-O(100)	95.19(19)		

CuO_4 Mean Plane Calculations Geometry (Complex 1)

Least-squares planes (x,y,z in crystal coordinates) and deviations from them
(* indicates atom used to define plane)

7.6840 (0.0163) x - 17.8908 (0.0234) y + 10.9776 (0.0426) z = 3.0601 (0.0098)

* 0.1055 (0.0015) Cu1
* 0.0536 (0.0018) O7
* -0.1079 (0.0019) O8
* 0.0552 (0.0019) O13
* -0.1065 (0.0018) O14

Rms deviation of fitted atoms = 0.0895

12.0095 (0.0129) x + 11.4624 (0.0384) y - 14.5414 (0.0530) z = 6.6436 (0.0155)

Angle to previous plane (with approximate esd) = 89.02 (0.10)

* -0.1252 (0.0020) Cu2
* 0.1153 (0.0024) O1
* -0.0524 (0.0024) O2
* -0.0522 (0.0024) O5
* 0.1145 (0.0023) O6

Rms deviation of fitted atoms = 0.0975

- 7.9672 (0.0172) x + 17.9380 (0.0262) y - 9.9389 (0.0430) z = 0.0892 (0.0159)

Angle to previous plane (with approximate esd) = 87.65 (0.11)

* 0.1451 (0.0016) Cu3
* -0.1085 (0.0019) O3
* 0.0384 (0.0020) O4
* -0.1100 (0.0020) O9
* 0.0350 (0.0019) O10

Rms deviation of fitted atoms = 0.0976

11.9864 (0.0130) x + 12.0569 (0.0394) y - 13.3356 (0.0493) z = 10.2879 (0.0145)

Angle to previous plane (with approximate esd) = 87.75 (0.11)

* 0.1298 (0.0019) Cu4
* -0.1026 (0.0023) O11
* 0.0375 (0.0024) O12
* 0.0372 (0.0023) O15
* -0.1019 (0.0024) O16

Rms deviation of fitted atoms = 0.0901

B. Complex 2.

(i) Synthesis

For the ESI-MS experiments, the precursor, complex 1 was prepared as described above. 4 equivalents of 1.3-diaminopropan-2-ol were added and refluxing continued for 8.5 hours. Samples for ESI-MS analysis were removed at intervals as described above.

A clean, bulk sample of complex **2** was obtained as follows: $Cu(ClO_4)_2{\cdot}6H_2O$ (0.2 g, 0.543 mmol), $Ba(ClO_4)_2{\cdot}3H_2O$ (0.1 g, 0.27 mmol) and H_2dhtmb (0.2 g, 0.543mmol) were dissolved in hot ethanol (IMS) (*ca.* 80 mL). The solution was refluxed for 15 minutes, then a solution of 1,3-diaminopropan-2-ol (0.052 g, 0.543 mmol) in *ca.* 10 mL of ethanol was added dropwise to the refluxing solution. The colour changed from yellow-brown to dark green. After 15 more minutes refluxing few drops of triethylamine were added and mixture was refluxed for 24 hours. The green-brownish solution was cooled and concentrated under vacuum to dryness and was washed with water and with dichloromethane. The chloroform-soluble part of the crude product was evaporated to dryness then dissolved in methanol and crystallised by slow diffusion of diethylether to give $[BaCu_4(4+4)](ClO_4)_2{\cdot}4H_2O$. (Yield: 0.44g; 69%). CHN: Found (Calc for $[BaCu_4(4+4)](ClO_4)_2{\cdot}4H_2O$): %C 53.40 (53.28); %H 5.75 (5.85); %N 5.04 (4.78). FAB: m/z, (rel intensity), assignment: 1036 (65%) $[BaCu_4(4+4)]^{2+}$, 2073 (95%) $[BaCu_4(4+4)+H^+]^+$; 2171 (100%) $[BaCu_4(4+4)(ClO_4]^+$. Selected infrared absorptions (KBr)/ cm^{-1}: 3446 bs; 2957 m; 1628 s; 1559 (m); 1540 m; 1457 m; 1263 m; 1122, 1108 and 1088 s; 668 m. Although crystals can be obtained by this route they were invariably very poorly diffracting and rather unstable.

Marginally better quality, rather unstable green plates suitable for X-ray crystallography were obtained by diethylether diffusion into the reaction solution obtained at the end of the reflux. Possibly due to the basic nature of the mother liquor, these crystals contained no perchlorate anions, the charge being (presumably) balanced by hydroxide ions within the disordered solvate of alcohol groups (see section (iii)).

(ii) ESI-MS

Figures S3, S4 and S5 show the measured and calculated isotope patterns for the significant peaks in the ESI spectrum at m/z 982.23, 1009.26 and 1036.29 (see Fig 3 in the main text). The first two correspond to intermediates in which 2 and 3 molecules of 1,3-diaminopropan-2-ol have condensed with complex **2**,and the signal at m/z 1036.29 corresponds to the product $[BaCu_4(4+4)]^{2+}$

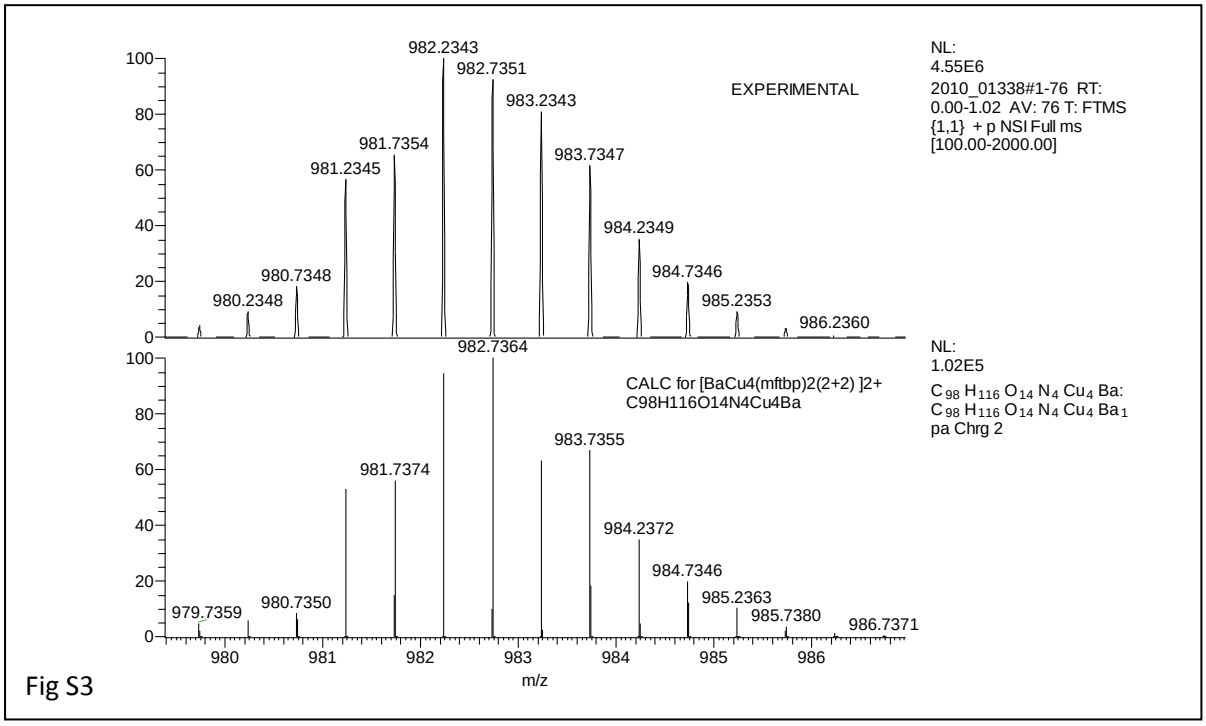
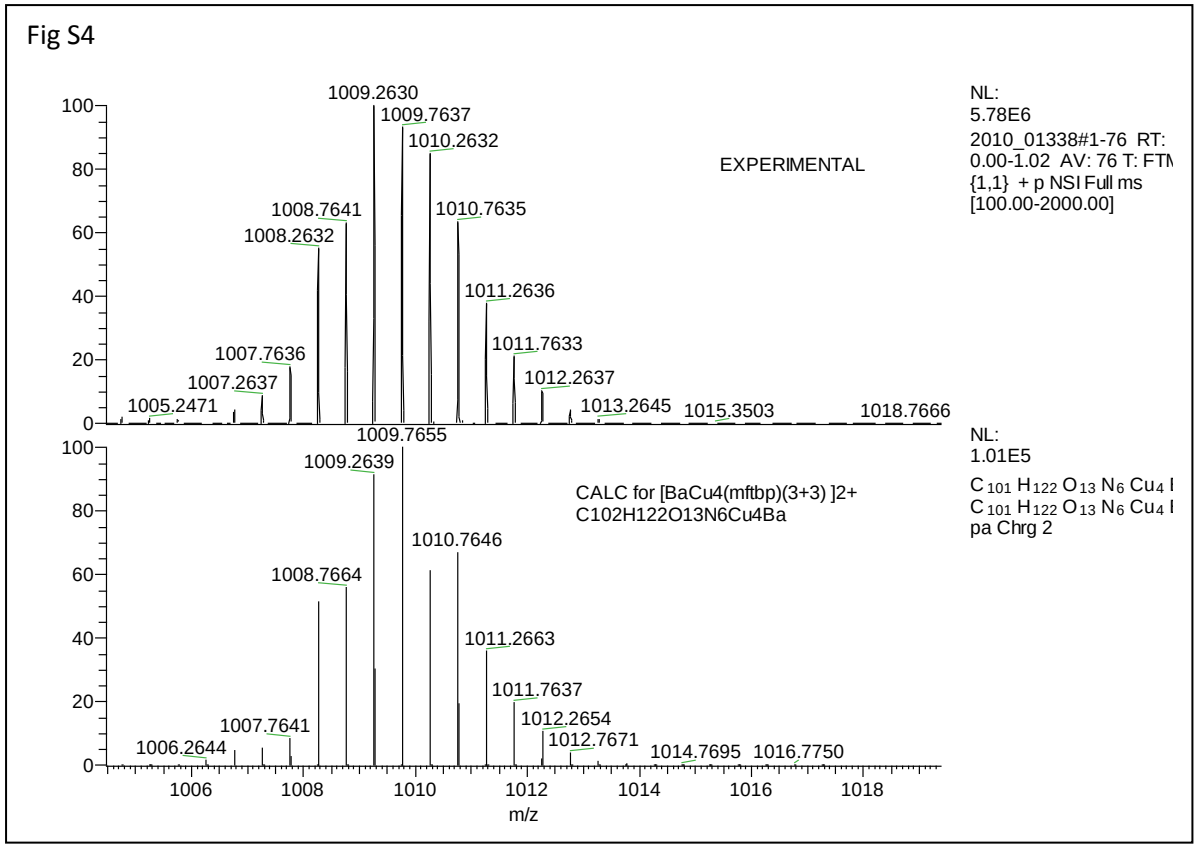
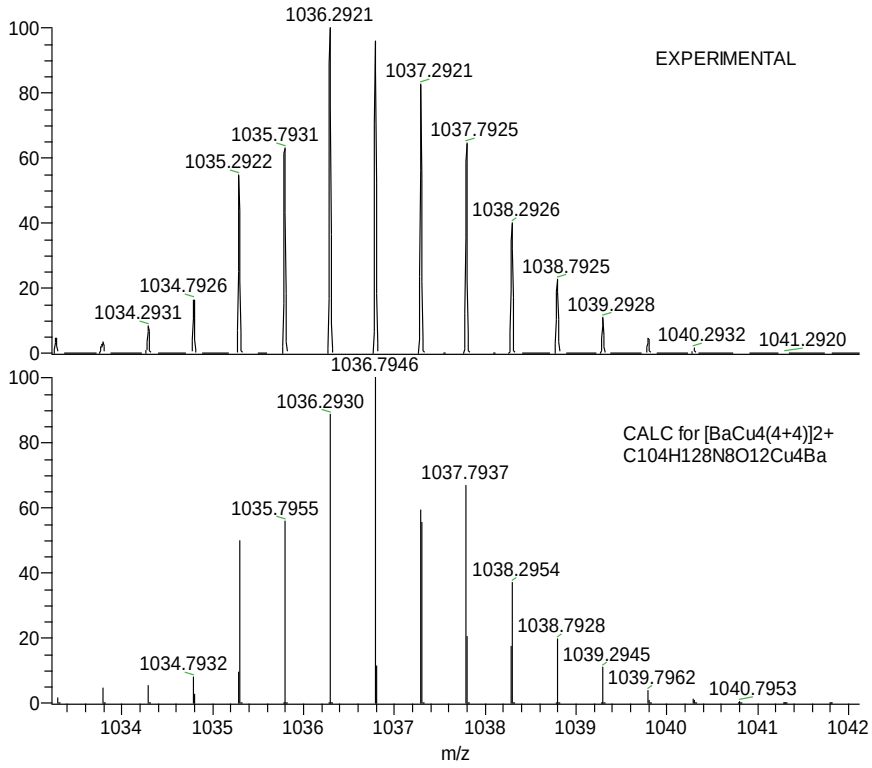


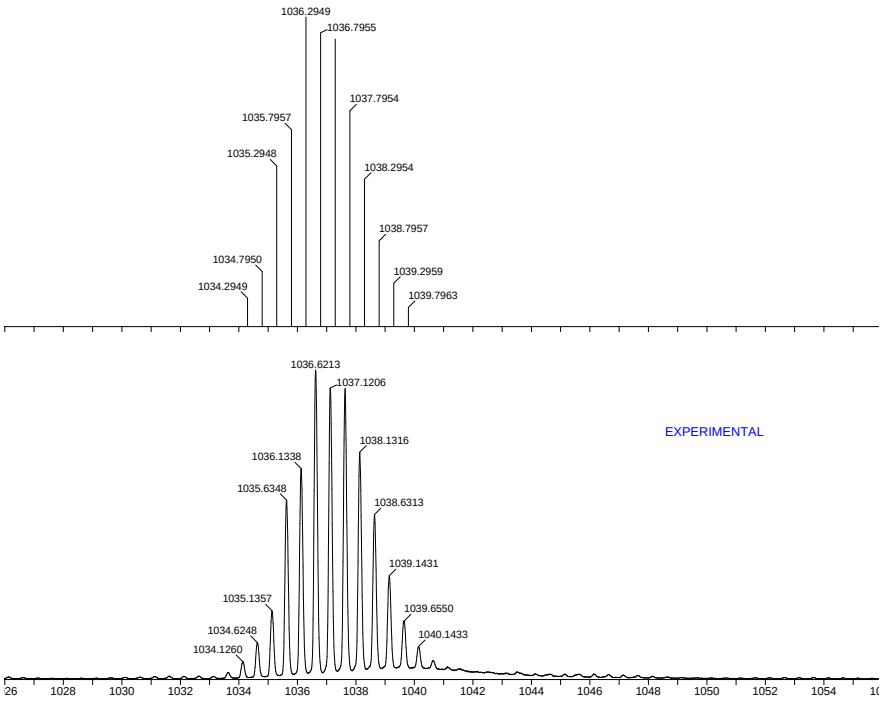
Fig S3



Note. For comparison the measured and calculated isotope patterns for $[BaCu_4(4+4)]^{2+}$ are shown for the Orbitrap instrument (top) and the Waters Synapt machine (below)

Fig S5





(iii) Crystallography

The data were collected at 150(2)K at station 16.2SMX of the Synchrotron Radiation Source, Daresbury using radiation of wavelength 0.84640 Å. The structure was solved by direct methods and refined on F^2 using all the reflections. All the non-hydrogen atoms were refined using anisotropic atomic displacement parameters and hydrogen atoms bonded to carbon were inserted at calculated positions using a riding model. Hydrogen atoms bonded to the alcohol oxygen atoms were not included.

The asymmetric unit contains one complete cation (shown in Fig 4) and two independent half cations lying on C_2 axes. The three cations do not show any very significant differences. There anions were not located, suggesting that they are unlikely to be perchlorate, and there was significant diffuse electron density in the lattice. This was treated using SQUEEZE as follows:

```
# SQUEEZE RESULTS (APPEND TO CIF)
# Note: Data are Listed for all Voids in the P1 Unit Cell
# i.e. Centre of Gravity, Solvent Accessible Volume,
# Recovered number of Electrons in the Void and
# Details about the Squeezed Material
loop_
   _platon_squeeze_void_nr
   _platon_squeeze_void_average_x
   _platon_squeeze_void_average_y
   _platon_squeeze_void_average_z
   _platon_squeeze_void_volume
   _platon_squeeze_void_count_electrons
   _platon_squeeze_void_content
    1 -0.005 -0.001 -0.004      7567      1652 ' '
    2  0.000  0.500  0.500       136        32 ' '
    3  0.000  0.500  1.000       136        33 ' '
    4  0.098  0.312  0.487        32         4 ' '
    5  0.098  0.688 -0.013        32         4 ' '
    6  0.127  0.446  0.890        28         5 ' '
    7  0.127  0.554  0.390        28         5 ' '
    8  0.134  0.451  0.538        28         2 ' '
    9  0.134  0.549  0.038        28         2 ' '
   10  0.251  0.250  0.500       174        31 ' '
   11  0.251  0.750  1.000       174        32 ' '
   12  0.244  0.500  1.044       658       113 ' '
   13  0.255  0.000  0.676       658       115 ' '
   14  0.373  0.054  0.110        28         5 ' '
   15  0.367  0.049  0.462        28         3 ' '
   16  0.367  0.951  0.962        28         3 ' '
   17  0.373  0.946  0.610        28         5 ' '
   18  0.404  0.186  0.513        31         5 ' '
   19  0.404  0.814  0.013        32         5 ' '
   20  0.500  0.000  0.500       136        32 ' '
   21  0.500  1.000  1.000       136        33 ' '
   22  0.598  0.188 -0.013        32         4 ' '
   23  0.598  0.812  0.487        32         4 ' '
   24  0.627  0.054  0.390        28         5 ' '
   25  0.627  0.946  0.890        28         5 ' '
   26  0.634  0.049  0.038        28         2 ' '
   27  0.634  0.951  0.538        28         2 ' '
   28  0.751  0.250  1.000       174        32 ' '
   29  0.751  0.750  0.500       174        31 ' '
   30  0.745  0.000  0.682       658       113 ' '
```

```
  31   0.755   0.500   0.173       658       115 ' '
  32   0.866   0.451   0.962        27         3 ' '
  33   0.873   0.446   0.610        28         5 ' '
  34   0.873   0.554   0.110        28         5 ' '
  35   0.866   0.549   0.462        27         3 ' '
  36   0.904   0.314   0.013        32         5 ' '
  37   0.904   0.686   0.513        31         5 ' '
_platon_squeeze_details
;
```

_platon_squeeze_details

;

Electron counts >10 in voids of >100 A^3 were considered = 2364 e/cell

= 296/asymmetric unit, or 148/formula unit.

This was modelled as $2Et_2O$, 2OH-, H_2O, 2MeOH per formula unit (148e)

The Et_2O is likely in view of the instability of the crystals out of solvent

The 2OH- is needed for charge balance since no other anions have been located and it seems unlikley that perchlorate anions would not have been located if they were present

other H_2O/MeOH were already observed in non-disordered sites.

;

The checkcif report raises level A alerts because these solvate molecules/anions are not in the atom list but have been included in the formula.

Other alerts refer to the ellipsoids of the tert-butyl groups, some rotational disorder here has not been modelled.

Parameters for data collection and refinement are summarised in Table S3.

Figure S6 shows an alternate view of the cation $[BaCu_4(4+4)]^{2+}$.

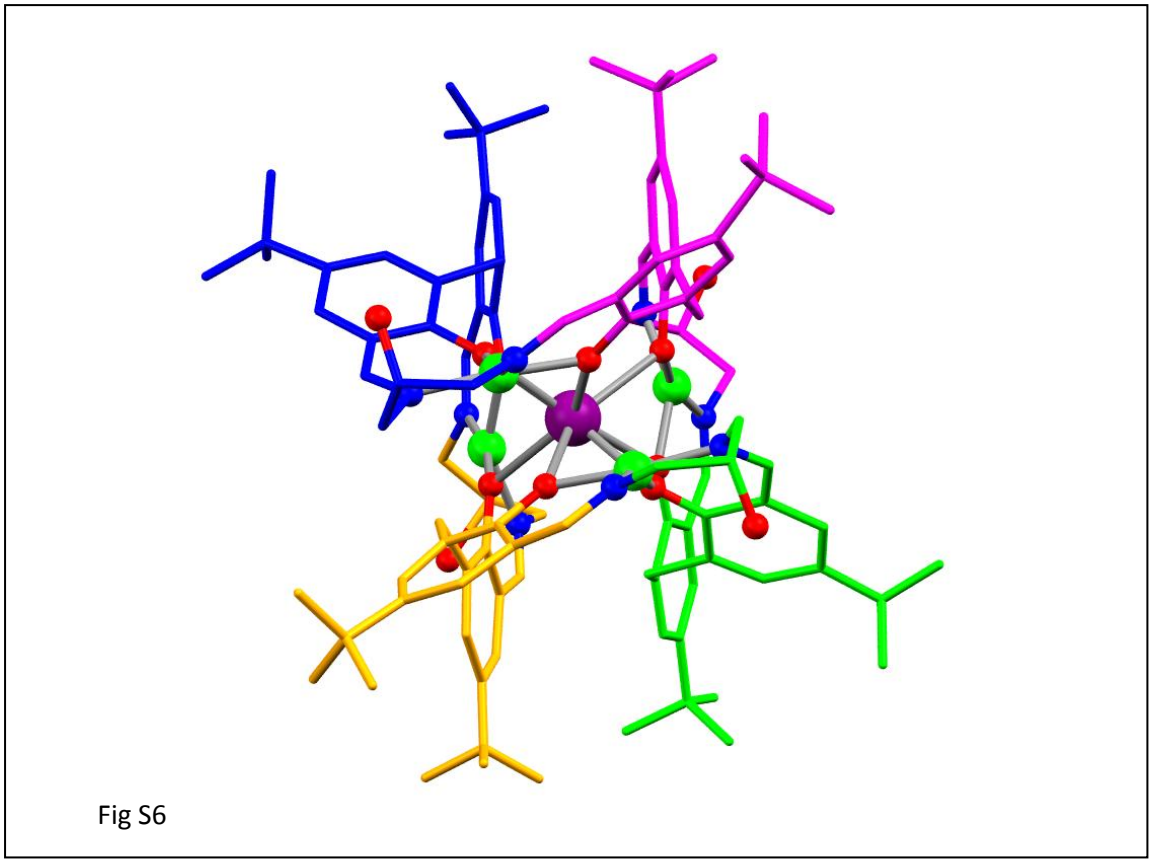


Fig S6

Figure S7 shows a packing diagram for complex **2** showing H-bonding (dashed lines) linking the cations into 2D sheets. Different colours represent the three independent cations in the cell.

Fig S7

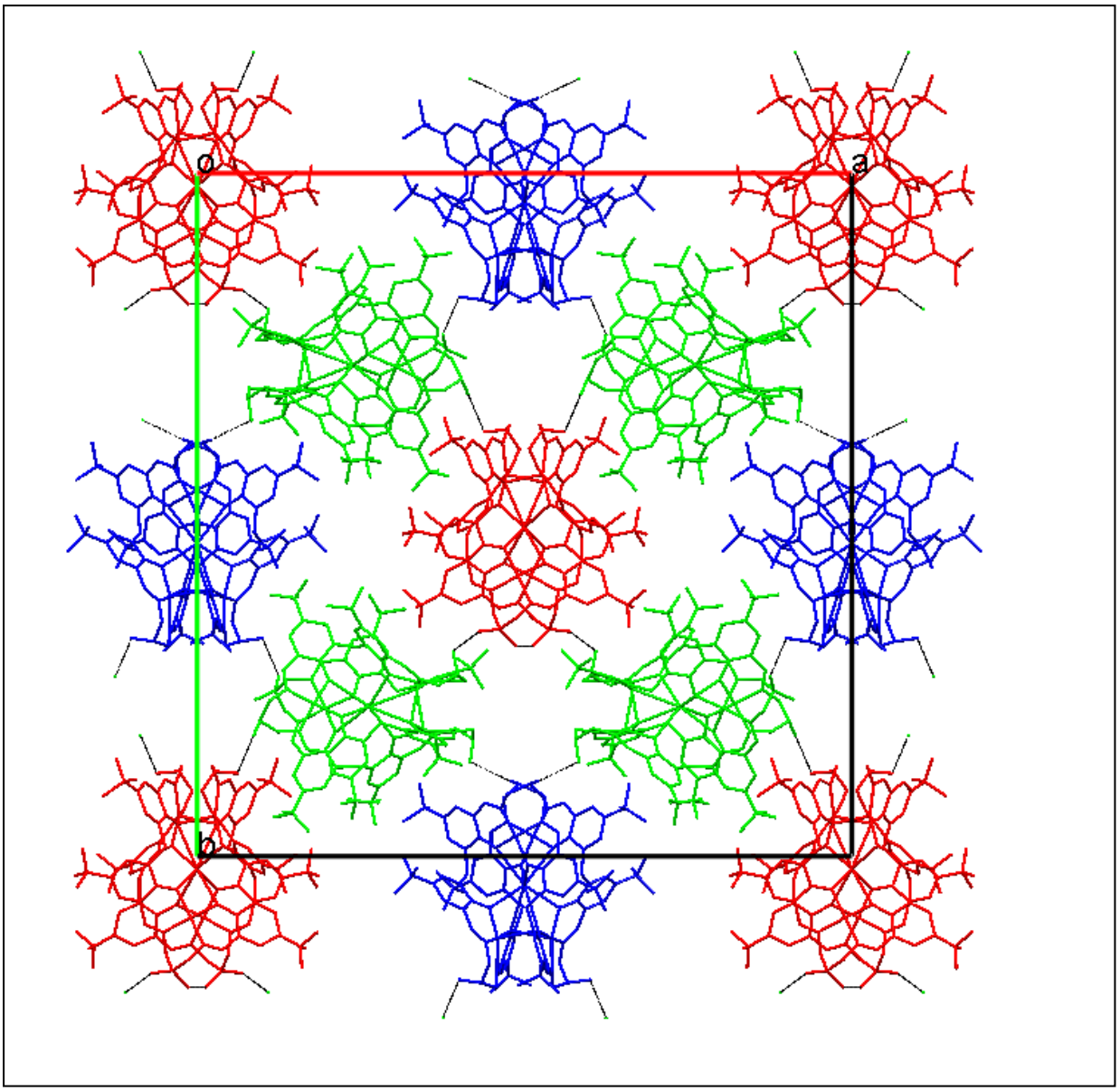


Table S3. Crystal data and structure refinement for Complex **2**.

Identification code	4msq	
Empirical formula	C115 H163 Ba Cu4 N8 O22	
Formula weight	2401.03	
Temperature	150(2) K	
Wavelength	0.84640 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 41.415(9) Å	α= 90°.
	b = 42.163(9) Å	β= 101.949(3)°.
	c = 28.256(6) Å	γ = 90°.
Volume	48271(18) $Å^3$	
Z	16	
Density (calculated)	1.322 Mg/m^3	
Absorption coefficient	1.083 mm^{-1}	
F(000)	20112	
Crystal size	0.23 x 0.16 x 0.03 mm^3	
Crystal description	green plate	
Theta range for data collection	3.65 to 25.00°.	
Index ranges	-41<=h<=41, -42<=k<=42, -28<=l<=28	
Reflections collected	103961	
Independent reflections	25090 [R(int) = 0.1529]	
Completeness to theta = 25.00°	99.6 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	25090 / 3305 / 2395	
Goodness-of-fit on F^2	0.908	
Final R indices [I>2sigma(I)]	R1 = 0.0970, wR2 = 0.2658	
R indices (all data)	R1 = 0.1665, wR2 = 0.2936	
Largest diff. peak and hole	1.213 and -1.123 $e.Å^{-3}$	

Table S4. Selected Bond lengths [Å] and angles [°] for Complex **2**.

Ba(1)-O(10)	2.651(10)	Ba(1A)-O(5A)#1	3.079(9)
Ba(1)-O(7)	2.659(10)	Ba(1A)-O(5A)	3.079(9)
Ba(1)-O(4)	2.667(9)	Ba(1A)-Cu(2A)#1	3.679(2)
Ba(1)-O(1)	2.702(11)	Ba(1A)-Cu(2A)	3.679(2)
Ba(1)-O(5)	2.960(9)	Ba(1A)-Cu(1A)#1	3.705(2)
Ba(1)-O(2)	3.074(9)	Ba(1A)-Cu(1A)	3.705(2)
Ba(1)-O(11)	3.101(10)	Ba(1B)-O(1B)#2	2.648(9)
Ba(1)-O(8)	3.159(10)	Ba(1B)-O(1B)	2.648(9)
Ba(1)-Cu(2)	3.690(2)	Ba(1B)-O(4B)#2	2.673(10)
Ba(1)-Cu(3)	3.693(2)	Ba(1B)-O(4B)	2.673(10)
Ba(1)-Cu(1)	3.712(2)	Ba(1B)-O(2B)#2	2.982(9)
Ba(1)-Cu(4)	3.765(2)	Ba(1B)-O(2B)	2.982(9)
Ba(1A)-O(1A)#1	2.669(9)	Ba(1B)-O(5B)	3.142(9)
Ba(1A)-O(1A)	2.669(9)	Ba(1B)-O(5B)#2	3.142(9)
Ba(1A)-O(4A)#1	2.695(12)	Ba(1B)-Cu(1B)	3.711(2)
Ba(1A)-O(4A)	2.696(12)	Ba(1B)-Cu(1B)#2	3.711(2)
Ba(1A)-O(2A)	3.019(9)	Ba(1B)-Cu(2B)	3.715(2)
Ba(1A)-O(2A)#1	3.019(9)	Ba(1B)-Cu(2B)#2	3.715(2)
Cu(1)-N(2)	1.909(16)	Cu(4)-N(8)	1.967(12)
Cu(1)-O(4)	1.919(8)	Cu(1A)-O(4A)	1.927(10)
Cu(1)-O(2)	1.937(12)	Cu(1A)-O(2A)	1.927(10)
Cu(1)-N(1)	1.983(13)	Cu(1A)-N(1A)	1.935(13)
Cu(1)-Cu(3)	3.464(3)	Cu(1A)-N(2A)	1.942(12)
Cu(2)-O(7)	1.904(9)	Cu(2A)-N(4A)	1.918(14)
Cu(2)-N(3)	1.937(11)	Cu(2A)-O(5A)	1.919(11)
Cu(2)-O(5)	1.953(9)	Cu(2A)-O(1A)#1	1.943(8)
Cu(2)-N(4)	1.971(11)	Cu(2A)-N(3A)	1.991(12)
Cu(2)-O(1S)	2.392(15)	Cu(1B)-O(4B)	1.919(9)
Cu(2)-Cu(4)	4.241(4)	Cu(1B)-N(1B)	1.927(11)
Cu(3)-O(10)	1.925(9)	Cu(1B)-O(2B)	1.944(8)
Cu(3)-O(8)	1.931(14)	Cu(1B)-N(2B)	1.947(12)
Cu(3)-N(5)	1.932(16)	Cu(2B)-N(4B)	1.919(14)
Cu(3)-N(6)	1.95(2)	Cu(2B)-O(5B)	1.927(11)
Cu(4)-O(1)	1.932(9)	Cu(2B)-O(1B)#2	1.933(8)
Cu(4)-O(11)	1.934(10)	Cu(2B)-N(3B)	1.977(12)
Cu(4)-N(7)	1.943(12)		

O(10)-Ba(1)-O(7)	114.2(3)	N(2)-Cu(1)-O(4)	92.0(5)
O(10)-Ba(1)-O(4)	115.3(3)	N(2)-Cu(1)-O(2)	173.5(5)
O(7)-Ba(1)-O(4)	94.9(3)	O(4)-Cu(1)-O(2)	84.0(4)
O(10)-Ba(1)-O(1)	95.7(3)	N(2)-Cu(1)-N(1)	94.0(6)
O(7)-Ba(1)-O(1)	121.0(3)	O(4)-Cu(1)-N(1)	159.8(5)
O(4)-Ba(1)-O(1)	117.2(3)	O(2)-Cu(1)-N(1)	91.4(5)
O(10)-Ba(1)-O(5)	161.9(3)	O(7)-Cu(2)-N(3)	170.7(6)
O(7)-Ba(1)-O(5)	57.0(3)	O(7)-Cu(2)-O(5)	88.7(4)
O(4)-Ba(1)-O(5)	82.2(3)	N(3)-Cu(2)-O(5)	93.9(4)
O(1)-Ba(1)-O(5)	78.7(3)	O(7)-Cu(2)-N(4)	92.6(4)
O(10)-Ba(1)-O(2)	69.6(3)	N(3)-Cu(2)-N(4)	89.6(5)
O(7)-Ba(1)-O(2)	139.1(3)	O(5)-Cu(2)-N(4)	149.9(6)
O(4)-Ba(1)-O(2)	52.8(3)	O(7)-Cu(2)-O(1S)	85.1(5)
O(1)-Ba(1)-O(2)	98.0(3)	N(3)-Cu(2)-O(1S)	85.6(6)
O(5)-Ba(1)-O(2)	127.9(2)	O(5)-Cu(2)-O(1S)	104.9(5)
O(10)-Ba(1)-O(11)	80.7(3)	N(4)-Cu(2)-O(1S)	105.1(6)
O(7)-Ba(1)-O(11)	80.0(3)	O(10)-Cu(3)-O(8)	85.7(5)
O(4)-Ba(1)-O(11)	163.7(3)	O(10)-Cu(3)-N(5)	159.2(6)
O(1)-Ba(1)-O(11)	55.2(3)	O(8)-Cu(3)-N(5)	91.5(7)
O(5)-Ba(1)-O(11)	82.0(3)	O(10)-Cu(3)-N(6)	91.3(6)
O(2)-Ba(1)-O(11)	138.0(3)	O(8)-Cu(3)-N(6)	172.6(6)
O(10)-Ba(1)-O(8)	52.8(3)	N(5)-Cu(3)-N(6)	93.7(8)
O(7)-Ba(1)-O(8)	95.4(3)	O(1)-Cu(4)-O(11)	89.1(4)
O(4)-Ba(1)-O(8)	68.9(3)	O(1)-Cu(4)-N(7)	164.7(6)
O(1)-Ba(1)-O(8)	140.8(3)	O(11)-Cu(4)-N(7)	94.2(5)
O(5)-Ba(1)-O(8)	138.5(3)	O(1)-Cu(4)-N(8)	93.9(4)
O(2)-Ba(1)-O(8)	52.7(3)	O(11)-Cu(4)-N(8)	152.2(6)
O(11)-Ba(1)-O(8)	126.7(2)	N(7)-Cu(4)-N(8)	90.1(5)

O(1A)#1-Ba(1A)-O(1A)	116.6(4)	O(4A)-Ba(1A)-O(2A)	56.6(3)
O(1A)#1-Ba(1A)-O(4A)#1	94.0(3)	O(1A)#1-Ba(1A)-O(2A)#1	79.3(3)
O(1A)-Ba(1A)-O(4A)#1	115.5(3)	O(1A)-Ba(1A)-O(2A)#1	163.7(3)
O(1A)#1-Ba(1A)-O(4A)	115.5(3)	O(4A)#1-Ba(1A)-O(2A)#1	56.6(3)
O(1A)-Ba(1A)-O(4A)	94.0(3)	O(4A)-Ba(1A)-O(2A)#1	81.3(3)
O(4A)#1-Ba(1A)-O(4A)	123.1(5)	O(2A)-Ba(1A)-O(2A)#1	85.0(4)
O(1A)#1-Ba(1A)-O(2A)	163.7(3)	O(1A)#1-Ba(1A)-O(5A)#1	69.5(3)
O(1A)-Ba(1A)-O(2A)	79.3(3)	O(1A)-Ba(1A)-O(5A)#1	53.3(3)
O(4A)#1-Ba(1A)-O(2A)	81.3(3)	O(4A)#1-Ba(1A)-O(5A)#1	96.4(3)

O(4A)-Ba(1A)-O(5A)#1	138.3(3)	O(4B)-Ba(1B)-O(2B)#2	79.3(3)
O(2A)-Ba(1A)-O(5A)#1	126.4(2)	O(1B)#2-Ba(1B)-O(2B)	161.1(2)
O(2A)#1-Ba(1A)-O(5A)#1	137.3(3)	O(1B)-Ba(1B)-O(2B)	82.5(3)
O(1A)#1-Ba(1A)-O(5A)	53.3(3)	O(4B)#2-Ba(1B)-O(2B)	79.3(3)
O(1A)-Ba(1A)-O(5A)	69.6(3)	O(4B)-Ba(1B)-O(2B)	57.2(2)
O(4A)#1-Ba(1A)-O(5A)	138.3(3)	O(2B)#2-Ba(1B)-O(2B)	79.6(4)
O(4A)-Ba(1A)-O(5A)	96.4(3)	O(1B)#2-Ba(1B)-O(5B)	52.2(3)
O(2A)-Ba(1A)-O(5A)	137.3(3)	O(1B)-Ba(1B)-O(5B)	70.4(2)
O(2A)#1-Ba(1A)-O(5A)	126.4(2)	O(4B)#2-Ba(1B)-O(5B)	139.5(3)
O(5A)#1-Ba(1A)-O(5A)	51.4(3)	O(4B)-Ba(1B)-O(5B)	94.9(3)
O(4A)-Cu(1A)-O(2A)	90.0(4)	O(2B)#2-Ba(1B)-O(5B)	128.0(2)
O(4A)-Cu(1A)-N(1A)	166.8(7)	O(2B)-Ba(1B)-O(5B)	138.9(3)
O(2A)-Cu(1A)-N(1A)	93.9(5)	O(1B)#2-Ba(1B)-O(5B)#2	70.4(2)
O(4A)-Cu(1A)-N(2A)	91.8(5)	O(1B)-Ba(1B)-O(5B)#2	52.2(3)
O(2A)-Cu(1A)-N(2A)	149.8(7)	O(4B)#2-Ba(1B)-O(5B)#2	94.9(3)
N(1A)-Cu(1A)-N(2A)	91.1(5)	O(4B)-Ba(1B)-O(5B)#2	139.5(3)
N(4A)-Cu(2A)-O(5A)	173.5(4)	O(2B)#2-Ba(1B)-O(5B)#2	138.9(3)
N(4A)-Cu(2A)-O(1A)#1	91.5(5)	O(2B)-Ba(1B)-O(5B)#2	128.0(2)
O(5A)-Cu(2A)-O(1A)#1	84.9(4)	O(5B)-Ba(1B)-O(5B)#2	53.8(3)
N(4A)-Cu(2A)-N(3A)	92.9(5)	O(4B)-Cu(1B)-N(1B)	167.5(6)
O(5A)-Cu(2A)-N(3A)	92.4(5)	O(4B)-Cu(1B)-O(2B)	89.4(4)
O(1A)#1-Cu(2A)-N(3A)	159.1(5)	N(1B)-Cu(1B)-O(2B)	94.6(4)
O(1B)#2-Ba(1B)-O(1B)	115.8(4)	O(4B)-Cu(1B)-N(2B)	93.0(4)
O(1B)#2-Ba(1B)-O(4B)#2	96.3(3)	N(1B)-Cu(1B)-N(2B)	88.8(5)
O(1B)-Ba(1B)-O(4B)#2	113.2(3)	O(2B)-Cu(1B)-N(2B)	152.9(6)
O(1B)#2-Ba(1B)-O(4B)	113.2(3)	N(4B)-Cu(2B)-O(5B)	173.1(4)
O(1B)-Ba(1B)-O(4B)	96.3(3)	N(4B)-Cu(2B)-O(1B)#2	91.1(5)
O(4B)#2-Ba(1B)-O(4B)	123.4(4)	O(5B)-Cu(2B)-O(1B)#2	84.2(4)
O(1B)#2-Ba(1B)-O(2B)#2	82.5(3)	N(4B)-Cu(2B)-N(3B)	94.2(6)
O(1B)-Ba(1B)-O(2B)#2	161.1(2)	O(5B)-Cu(2B)-N(3B)	91.9(5)
O(4B)#2-Ba(1B)-O(2B)#2	57.2(2)	O(1B)#2-Cu(2B)-N(3B)	160.8(5)

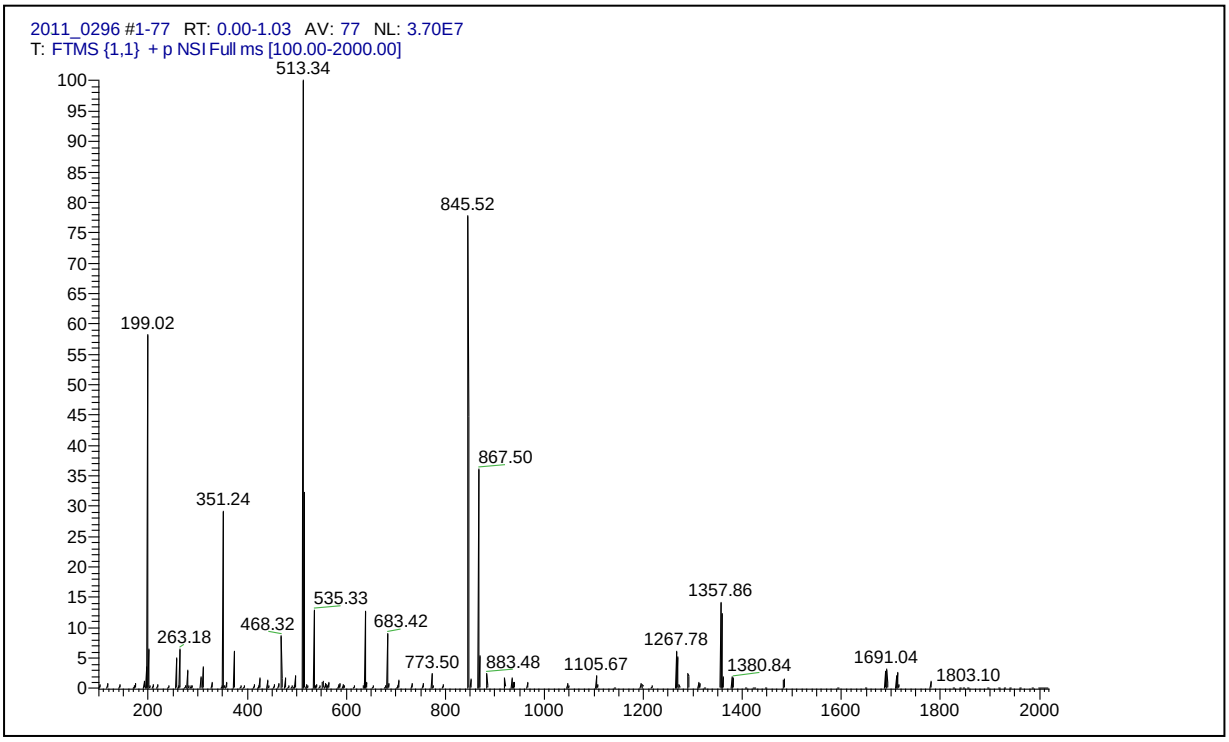
Symmetry transformations used to generate equivalent atoms: #1 -x,y,-z+3/2 #2 -x+1,y,-z+3/2

CuO_2N_2 Mean Plane Calculations Geometry (Complex 2)

```
Least-squares planes (x,y,z in crystal coordinates) and deviations from
them
 (* indicates atom used to define plane)

 - 2.5720 (0.1708) x + 41.2087 (0.0381) y + 5.9543 (0.1140) z = 16.9139
(0.0677)

 *    -0.1042 (0.0045)  Cu1
 *     0.2161 (0.0050)  N1
 *    -0.1854 (0.0059)  O2
 *    -0.1664 (0.0052)  N2
 *     0.2399 (0.0059)  O4

 Rms deviation of fitted atoms =   0.1882


  3.3120 (0.2245) x - 10.4097 (0.2350) y + 26.2285 (0.0587) z = 15.9708
(0.1019)

 Angle to previous plane (with approximate esd) = 87.08 ( 0.39 )

 *    -0.1424 (0.0059)  Cu2
 *     0.3662 (0.0075)  O5
 *    -0.3003 (0.0075)  O7
 *    -0.2865 (0.0072)  N3
 *     0.3631 (0.0073)  N4

 Rms deviation of fitted atoms =   0.3028


  1.5686 (0.2243) x + 41.5078 (0.0407) y + 4.5193 (0.1435) z = 13.8501
(0.1019)

 Angle to previous plane (with approximate esd) = 85.73 ( 0.43 )

 *     0.0951 (0.0057)  Cu3
 *     0.2121 (0.0077)  O8
 *    -0.2418 (0.0065)  N5
 *     0.1940 (0.0062)  N6
 *    -0.2593 (0.0076)  O10

 Rms deviation of fitted atoms =   0.2085


 - 9.2838 (0.2343) x - 8.0289 (0.2504) y + 27.7321 (0.0332) z = 17.7413
(0.1182)

 Angle to previous plane (with approximate esd) = 88.16 ( 0.45 )

 *     0.0863 (0.0062)  Cu4
 *     0.3462 (0.0080)  O1
 *    -0.3922 (0.0078)  O11
 *     0.3390 (0.0075)  N7
 *    -0.3793 (0.0077)  N8

 Rms deviation of fitted atoms =   0.3286
```

D. Additional ESI-MS data

(i) Fig S8 ESI of reaction of H_2dhtmb and 1,3-diaminopropan-2-ol in absence of metal templates (5 hr reflux)



(ii) Fig S9 ESI of reaction mixture Ba/H_2dhtmb/1,3-diaminopropan-2-ol /NEt_3 (overnight reflux)