Supplementary Data

Rapid synthesis of cross-bridged cyclam chelators for copper(II) complex formation

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5. Alternative view of the X-ray crystal structure of [Cu**2**Cl_2]

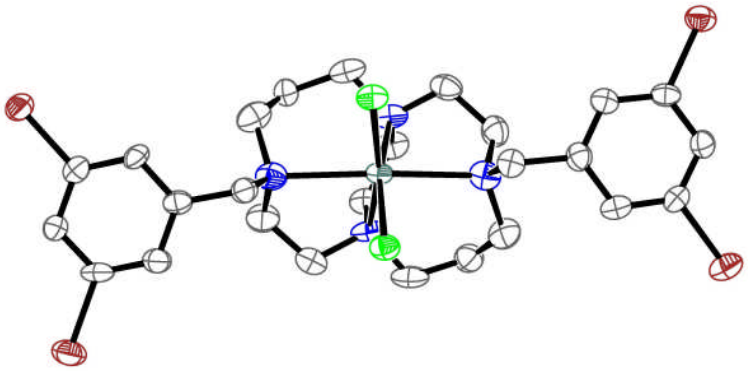

Figure S1. View of [Cu**2**Cl_2] showing the twist of Cl1-Cu1-Cl2 plane vs, N1-Cu1-N3 plane

2. Description of crystal packing

[Cu**1**NO_3]NO_3.CH_3OH has a cationic macrocyclic unit with an unbound nitrate counter anion. As the triclinic unit cell is centrosymmetric, there are two macrocyclic units and two nitrate residues per unit cell. Planes of macrocyclic units lie parallel to the diagonal of (010) and (001), see Figure S2. The cavities of the macrocycles in adjacent planes are oriented towards each other. As a result, the aryl groups of adjacent molecular units lie at an angle to each other. This reduces electrostatic repulsion between the two adjacent π-systems.[1]

The two chloride counterions coordinated to the metal centre in [Cu**2**Cl_2] result in the complex being a neutral species with no unbound ions in the crystal lattice. The extra symmetry of the molecule is reflected in the more symmetrical monoclinic unit cell. Planes of macrocyclic units run parallel to all three faces of the unit cell, showing regular packing of the macrocycles. In contrast to [Cu**1**NO_3]NO_3.CH_3OH, the cavities of the macrocycles are not oriented towards each other. The coplanar aryl groups run parallel to (001), with the π-systems arranged above each other, see Figure S3. The staggered nature of the aryl groups shows π-stacking between adjacent planes.[1] The distance between two adjacent aryl groups is approximately 3.6 Å, which is an appropriate distance for π-stacking.[1, 2]

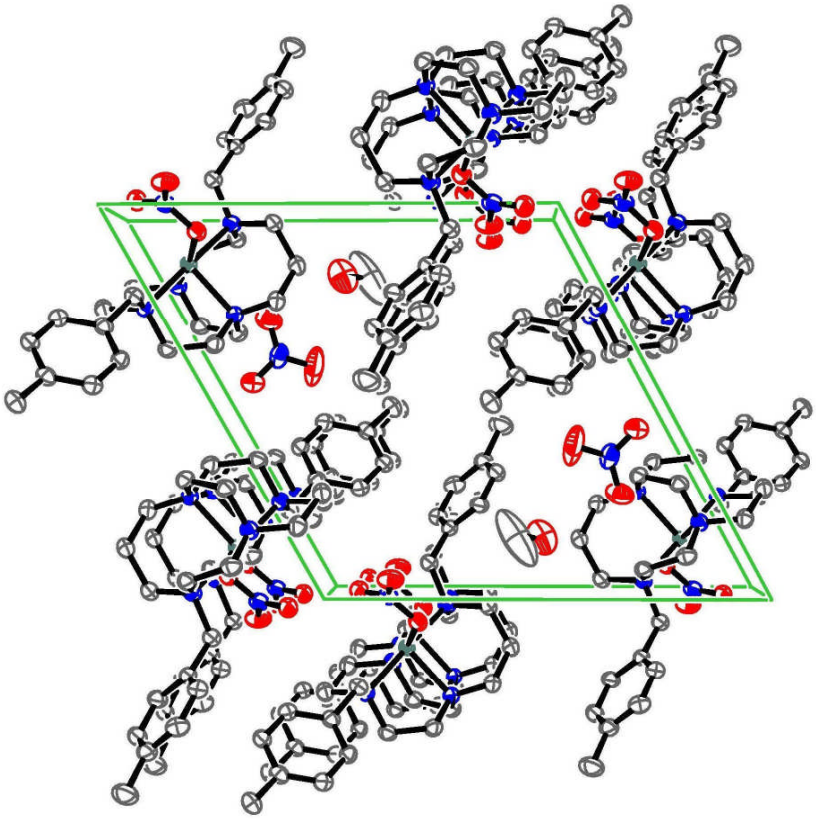

Figure S2. Unit cell of [Cu**1**NO_3]NO_3CH_3OH, shown normal to (100). Unit cell outline shown in green

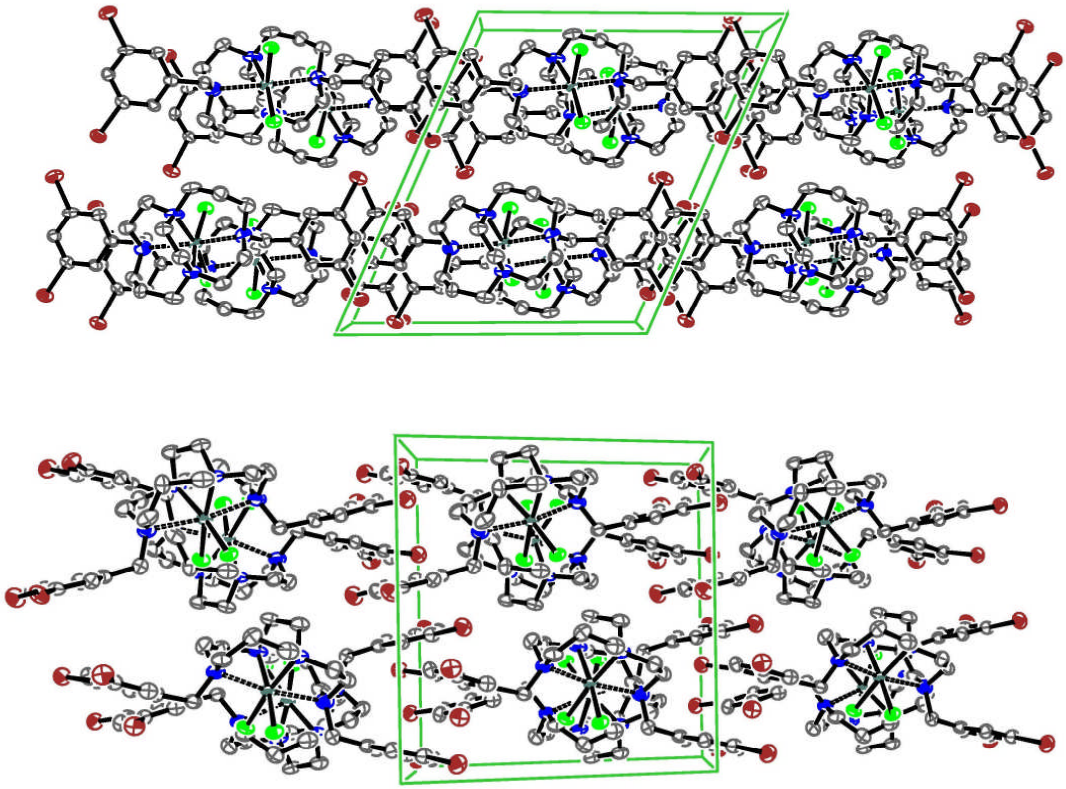

Figure S3. Unit cell of [Cu**2**Cl_2], viewed normal to (010) (above) and (001). Unit cell outline shown in green

3. Full tables of bond lengths and angles for X-ray crystal structures

Table S1. Bond lengths (Å) and angles (°) for [Cu**1**NO_3]NO_3.CH_3OH

C(2)-N(2)	1.477(5)	N(5)-O(2)	1.235(4)	O(1)-Cu(1)-N(1)	168.55(11)
C(2)-C(1)	1.500(5)	N(5)-O(3)	1.258(4)	O(1)-Cu(1)-N(2)	88.40(11)
C(1)-N(1)	1.493(5)	N(5)-O(1)	1.297(4)	N(1)-Cu(1)-N(2)	85.19(12)
C(10)-N(1)	1.495(4)	N(6)-O(6)	1.216(5)	O(1)-Cu(1)-N(4)	93.42(11)
C(10)-C(9)	1.501(5)	N(6)-O(4)	1.234(5)	N(1)-Cu(1)-N(4)	93.21(12)
C(9)-C(8)	1.516(5)	N(6)-O(5)	1.247(5)	N(2)-Cu(1)-N(4)	177.83(12)
C(8)-N(4)	1.489(4)			O(1)-Cu(1)-N(3)	102.99(11)
C(7)-N(4)	1.487(4)	N(2)-C(2)-C(1)	109.0(3)	N(1)-Cu(1)-N(3)	86.86(11)
C(7)-C(6)	1.510(5)	N(1)-C(1)-C(2)	109.9(3)	N(2)-Cu(1)-N(3)	93.18(11)
C(6)-N(3)	1.481(5)	N(1)-C(10)-C(9)	116.0(3)	N(4)-Cu(1)-N(3)	85.27(11)
C(5)-N(3)	1.481(4)	C(10)-C(9)-C(8)	116.7(3)	C(2)-N(2)-C(3)	111.7(3)
C(5)-C(4)	1.520(5)	N(4)-C(8)-C(9)	115.5(3)	C(2)-N(2)-C(13)	110.6(3)
C(4)-C(3)	1.513(5)	N(4)-C(7)-C(6)	110.2(3)	C(3)-N(2)-C(13)	108.6(3)
C(3)-N(2)	1.499(4)	N(3)-C(6)-C(7)	111.6(3)	C(2)-N(2)-Cu(1)	106.6(2)
C(11)-N(1)	1.503(4)	N(3)-C(5)-C(4)	115.2(3)	C(3)-N(2)-Cu(1)	111.2(2)
C(11)-C(12)	1.534(5)	C(3)-C(4)-C(5)	118.1(3)	C(13)-N(2)-Cu(1)	108.1(2)
C(12)-N(3)	1.473(5)	N(2)-C(3)-C(4)	116.7(3)	C(1)-N(1)-C(10)	107.8(3)
C(13)-N(2)	1.509(5)	N(1)-C(11)-C(12)	114.7(3)	C(1)-N(1)-C(11)	109.8(3)
C(13)-C(14)	1.509(5)	N(3)-C(12)-C(11)	114.7(3)	C(10)-N(1)-C(11)	110.7(3)
C(14)-C(15)	1.381(5)	N(2)-C(13)-C(14)	117.9(3)	C(1)-N(1)-Cu(1)	106.3(2)
C(14)-C(19)	1.387(5)	C(15)-C(14)-C(19)	117.6(3)	C(10)-N(1)-Cu(1)	113.0(2)
C(15)-C(16)	1.381(6)	C(15)-C(14)-C(13)	121.4(3)	C(11)-N(1)-Cu(1)	109.0(2)
C(16)-C(17)	1.389(6)	C(19)-C(14)-C(13)	120.8(3)	C(7)-N(4)-C(8)	111.6(3)
C(17)-C(18)	1.380(6)	C(14)-C(15)-C(16)	121.3(3)	C(7)-N(4)-C(21)	109.6(3)
C(17)-C(20)	1.506(6)	C(15)-C(16)-C(17)	121.3(4)	C(8)-N(4)-C(21)	107.0(3)
C(18)-C(19)	1.384(5)	C(18)-C(17)-C(16)	117.3(4)	C(7)-N(4)-Cu(1)	105.2(2)
C(21)-N(4)	1.509(4)	C(18)-C(17)-C(20)	120.4(4)	C(8)-N(4)-Cu(1)	112.3(2)
C(21)-C(22)	1.513(5)	C(16)-C(17)-C(20)	122.3(4)	C(21)-N(4)-Cu(1)	111.2(2)
C(22)-C(23)	1.383(5)	C(17)-C(18)-C(19)	121.5(3)	C(12)-N(3)-C(6)	112.2(3)
C(22)-C(27)	1.395(5)	C(18)-C(19)-C(14)	121.0(3)	C(12)-N(3)-C(5)	112.6(3)
C(23)-C(24)	1.380(5)	N(4)-C(21)-C(22)	117.4(3)	C(6)-N(3)-C(5)	109.4(3)
C(24)-C(25)	1.400(5)	C(23)-C(22)-C(27)	117.4(3)	C(12)-N(3)-Cu(1)	106.9(2)
C(25)-C(26)	1.395(5)	C(23)-C(22)-C(21)	121.8(3)	C(6)-N(3)-Cu(1)	102.77(19)
C(25)-C(28)	1.491(5)	C(27)-C(22)-C(21)	120.4(3)	C(5)-N(3)-Cu(1)	112.6(2)
C(26)-C(27)	1.374(5)	C(24)-C(23)-C(22)	121.5(3)	O(2)-N(5)-O(3)	124.6(3)
C(29)-O(7)	1.335(9)	C(23)-C(24)-C(25)	121.3(3)	O(2)-N(5)-O(1)	118.1(3)
Cu(1)-O(1)	1.989(3)	C(26)-C(25)-C(24)	116.8(3)	O(3)-N(5)-O(1)	117.3(3)
Cu(1)-N(1)	2.038(3)	C(26)-C(25)-C(28)	121.7(3)	O(6)-N(6)-O(4)	118.3(4)
Cu(1)-N(2)	2.096(3)	C(24)-C(25)-C(28)	121.5(3)	O(6)-N(6)-O(5)	121.9(5)
Cu(1)-N(4)	2.131(3)	C(27)-C(26)-C(25)	121.5(3)	O(4)-N(6)-O(5)	119.7(3)
Cu(1)-N(3)	2.154(3)	C(26)-C(27)-C(22)	121.4(3)	N(5)-O(1)-Cu(1)	112.5(2)

Table S2. Bond lengths (Å) and angles (°) for [Cu**2**Cl_2]

C(1)-N(1)	1.502(11)	Cu(1)-Cl(2)	2.302(2)	C(11)-N(1)-C(10)	110.6(7)
C(1)-C(2)	1.546(14)	Cu(1)-Cl(1)	2.322(2)	C(11)-N(1)-C(1)	108.0(7)
C(2)-N(2)	1.459(12)			C(10)-N(1)-C(1)	105.7(6)
C(3)-N(2)	1.507(11)	N(1)-C(1)-C(2)	110.6(6)	C(11)-N(1)-Cu(1)	112.4(5)
C(3)-C(4)	1.514(13)	N(2)-C(2)-C(1)	112.6(8)	C(10)-N(1)-Cu(1)	112.7(6)
C(4)-C(5)	1.487(13)	N(2)-C(3)-C(4)	115.6(8)	C(1)-N(1)-Cu(1)	107.0(5)
C(5)-N(3)	1.464(12)	C(5)-C(4)-C(3)	119.6(8)	C(2)-N(2)-C(13)	114.4(6)
C(6)-C(7)	1.537(14)	N(3)-C(5)-C(4)	114.6(7)	C(2)-N(2)-C(3)	112.4(7)
C(6)-N(3)	1.543(11)	C(7)-C(6)-N(3)	111.1(6)	C(13)-N(2)-C(3)	109.5(7)
C(7)-N(4)	1.426(11)	N(4)-C(7)-C(6)	115.1(8)	C(2)-N(2)-Cu(1)	103.9(5)
C(8)-C(9)	1.468(14)	C(9)-C(8)-N(4)	118.6(8)	C(13)-N(2)-Cu(1)	105.3(5)
C(8)-N(4)	1.515(12)	C(8)-C(9)-C(10)	119.6(8)	C(3)-N(2)-Cu(1)	111.0(5)
C(9)-C(10)	1.550(13)	N(1)-C(10)-C(9)	113.9(7)	C(5)-N(3)-C(12)	110.6(7)
C(10)-N(1)	1.488(12)	N(1)-C(11)-C(12)	113.1(7)	C(5)-N(3)-C(6)	104.5(6)
C(11)-N(1)	1.488(11)	N(3)-C(12)-C(11)	112.9(7)	C(12)-N(3)-C(6)	106.9(7)
C(11)-C(12)	1.505(11)	N(2)-C(13)-C(14)	114.2(7)	C(5)-N(3)-Cu(1)	115.5(6)
C(12)-N(3)	1.493(11)	C(19)-C(14)-C(15)	118.8(7)	C(12)-N(3)-Cu(1)	111.5(4)
C(13)-N(2)	1.472(11)	C(19)-C(14)-C(13)	120.3(7)	C(6)-N(3)-Cu(1)	107.2(5)
C(13)-C(14)	1.529(11)	C(15)-C(14)-C(13)	120.9(7)	C(7)-N(4)-C(20)	115.2(7)
C(14)-C(19)	1.378(10)	C(16)-C(15)-C(14)	118.4(7)	C(7)-N(4)-C(8)	111.7(8)
C(14)-C(15)	1.418(11)	C(17)-C(16)-C(15)	123.8(7)	C(20)-N(4)-C(8)	111.5(7)
C(15)-C(16)	1.371(12)	C(17)-C(16)-Br(1)	117.8(6)	C(7)-N(4)-Cu(1)	103.1(6)
C(16)-C(17)	1.368(10)	C(15)-C(16)-Br(1)	118.3(5)	C(20)-N(4)-Cu(1)	108.8(5)
C(16)-Br(1)	1.909(8)	C(16)-C(17)-C(18)	117.0(7)	C(8)-N(4)-Cu(1)	105.7(5)
C(17)-C(18)	1.394(11)	C(19)-C(18)-C(17)	121.3(6)	N(1)-Cu(1)-N(3)	83.2(3)
C(18)-C(19)	1.383(11)	C(19)-C(18)-Br(2)	120.2(6)	N(1)-Cu(1)-Cl(2)	168.5(2)
C(18)-Br(2)	1.880(7)	C(17)-C(18)-Br(2)	118.5(6)	N(3)-Cu(1)-Cl(2)	93.3(2)
C(20)-N(4)	1.477(11)	C(14)-C(19)-C(18)	120.6(7)	N(1)-Cu(1)-Cl(1)	92.47(18)
C(20)-C(21)	1.519(11)	N(4)-C(20)-C(21)	115.5(7)	N(3)-Cu(1)-Cl(1)	167.8(2)
C(21)-C(22)	1.386(11)	C(22)-C(21)-C(26)	118.2(7)	Cl(2)-Cu(1)-Cl(1)	93.12(8)
C(21)-C(26)	1.390(10)	C(22)-C(21)-C(20)	121.8(6)	N(1)-Cu(1)-N(2)	79.3(3)
C(22)-C(23)	1.380(11)	C(26)-C(21)-C(20)	119.9(7)	N(3)-Cu(1)-N(2)	92.0(3)
C(23)-C(24)	1.392(10)	C(23)-C(22)-C(21)	119.8(6)	Cl(2)-Cu(1)-N(2)	89.94(18)
C(23)-Br(3)	1.900(8)	C(22)-C(23)-C(24)	122.3(7)	Cl(1)-Cu(1)-N(2)	98.41(17)
C(24)-C(25)	1.378(11)	C(22)-C(23)-Br(3)	119.8(5)	N(1)-Cu(1)-N(4)	95.9(3)
C(25)-C(26)	1.367(12)	C(24)-C(23)-Br(3)	117.9(6)	N(3)-Cu(1)-N(4)	79.8(3)
C(25)-Br(4)	1.898(7)	C(25)-C(24)-C(23)	116.6(7)	Cl(2)-Cu(1)-N(4)	94.14(19)
N(1)-Cu(1)	2.071(7)	C(26)-C(25)-C(24)	122.1(6)	Cl(1)-Cu(1)-N(4)	89.43(17)
N(2)-Cu(1)	2.455(8)	C(26)-C(25)-Br(4)	120.4(6)	N(2)-Cu(1)-N(4)	171.0(2)
N(3)-Cu(1)	2.091(7)	C(24)-C(25)-Br(4)	117.3(6)		
N(4)-Cu(1)	2.495(8)	C(25)-C(26)-C(21)	120.9(7)		

4. References

[1] C.A. Hunter and J.K.M. Sanders, J. Am. Chem. Soc. 112 (1990) 5525.
[2] B.H. Ye, X.M. Chen, G.Q. Xue and L.N. Ji, Dalton Trans. (1998) 2827.