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Zwitterionic dicopper helicates: Anion encapsulation and binding studies.

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Ligand Synthesis

N,N'-dimethyl-N,N'-hexamethylenedi(3-formyl-2-hydroxy-5-tert-butylbenzylamine) (L^1)

Prepared via the method of *Plieger et al.*[1], analytical data are in agreement to reported data [1] MS(ESI) *m*/*z* 525.5 [M + H]$^+$,^{1}H NMR in $CDCl_3$ δ_H [ppm] 10.36 (2H, s, C*H*O), 7.63 (2H, s, Ar*H*), 7.27 (2H, s, Ar*H*), 3.73 (4H, s, ArCH_2N), 2.50 (4H, t, NC$H_2$$CH_2$), 2.30 (6H, s, NC$H_3$), 1.60 (4H, m, NCH_2CH_2), 1.36 (4H, m, NCH_2CH_2CH_2), 1.29 (18H, s, t-Bu).

2,2'[1,6-hexanediylbis[(metylimino)methylene]]bis[4-tert-buthyl-6-(phenylazomethinyl)phenol (L)

The final ligand **L** was synthesised by the Schiff base condensation of **L^1** (250 mg, 0.476 mmol) and aniline (89 mg, 0.953 mmol) in acetonitrile at 60°C overnight. The solvent was removed, the yellow residue taken up in $CHCl_3$ and washed twice with H_2O. The organic layer was dried over $MgSO_4$ and evaporated to dryness; yield 96%; MS(ESI) m/z 675 [M + H]$^+$; Anal. Calc. for $C_{44}H_{58}N_4O_2 \cdot 2H_2O$: C 74.33, H 8.79, N 7.88; found: C 74.53, H 8.54, N 7.86%; ^{1}H NMR in $CDCl_3$ δ_H [ppm] 8.69 (2H, s, C*H*N), 7.38 (2H, m, Ar*H*), 7.27 (2H, s, Ar*H*), 7.25 (2H, s, Ar*H*), 3.63 (4H, s, ArCH_2N), 2.44 (4H, t, NC$H_2$$CH_2$), 2.27 (6H, s, NC$H_3$), 1.58 (4H, m, NCH_2CH_2), 1.33 (9H, s, t-Bu), 1.29 (4H, m, NCH_2CH_2CH_2); ^{13}C NMR in $CDCl_3$ δ_H [ppm] 162.1 (C14), 157.5 (C15), 149.7 (C13), 141.3 (C8), 131.5 (C7), 129.4 (C17), 126.5 (C11), 125.6 (C18), 121.3 (C16), 119.1 (C6), 115.2 (C12), 57.81 (C5), 56.9 (C3), 42.4 (C9), 34.2 (C4), 31.6 (C10), 27.7, (C2), 27.4 (C1); IR ν_{max}(KBr)/cm^{-1} 1607 s (C=N).

Description of Metal binding in ***1***

N,O-chelating units of any one ligand face two different Cu(II) centres and are connected by the 2,9-diazadecane strap. The overall coordination number of the Cu(II) atoms is five where in addition to the N,O-donor sets of the two salicyaldimine-subunits, coordination of an oxygen atom of the encapsulated anion (ClO_4^-) occurs. The coordination geometry can be described as disorder square pyramidal with a geometric parameter of τ = 0.15 and τ = 0.11 for Cu1 and Cu2, respectively.[2] The observed Cu-O-bond lengths are between 1.89 and 1.90 Å, where the bond distance of the N_{im}-donor atoms towards the Cu(II) centres are 1.99 Å in all cases (see Table S1). The Cu-O-bond lengths to the ClO_4^- anion are significantly longer (2.67 and 2.72 Å), but comparable to reported Cu-O-ClO_3^- interactions.[3-7]

Table S1 Bond lengths (Å) and angles (°) of the Cu(II) coordination environment in **1**.

bond	length [Å]	angle	[°]	angle	[°]
Cu1-O1	1.8959(18)	O1-Cu1-O1C	154.45(8)	O1A-Cu2-O1B	155.60(9)
Cu1-O1C	1.8973(18)	O1-Cu1-O32	79.52(9)	O1A-Cu2-O31	75.26(13)
Cu1-O32	2.721(3)	O1-Cu1-N2	94.13(9)	O1A-Cu2-N2A	93.35(10)
Cu1-N2	1.993(2)	O1-Cu1-N2C	92.92(9)	O1A-Cu2-N2B	93.42(10)
Cu1-N2C	1.993(2)	O1C-Cu1-O32	77.15(8)	O1B-Cu2-O31	83.33(13)
Cu2-O1A	1.886(2)	O1C-Cu1-N2	93.60(9)	O1B-Cu2-N2A	91.43(10)
Cu2-O1B	1.887(2)	O1C-Cu1-N2C	94.48(9)	O1B-Cu2-N2B	94.63(10)
Cu2-O31	2.668(4)	O32-Cu1-N2	131.62(9)	O31-Cu2-N2A	129.79(12)
Cu2-N2A	1.989(2)	O32-Cu1-N2C	83.10(9)	O31-Cu2-N2B	80.94(12)
Cu2-N2B	1.987(2)	N2-Cu1-N2C	145.29(9)	N2A-Cu2-N2B	149.21(9)

Description of the Hydrogen Bonding in ***1***

Numerous intramolecular H-bonds in the metallo-macrocycle stabilise the structure. Two moderate and two weak interactions from all four protonated tertiary amines to the nearest deprotonated phenol with N-H···O bond lengths between 2.08 and 2.35 Å (N-H-O angle between 123 and 132° and C-O-H angle between 88 and 95°) (see Table S2) support the twisted arrangement of the ligand molecules.[8] The N-H-function, namely N3B - H3BB and N3C - H3CB, with the significant longer NH-O-distances of 2.35 and 2.34 Å, respectively, are involved in the formation of bifurcated hydrogen bonds towards the encapsulated ClO_4^- anion. In addition to the intramolecular N-H···O-phenol, an intramolecular CH-π short contact between C31C-H31K and the centroid of an salicyaldimine aromatic ring Cg1 (Fig. 1) exists further locking the metallo-macrocycle in the present helical arrangement. The CH-Cg distance is 2.91 Å with a CH-Cg-angle of 121° (C-Cg1 distance 3.502(4) Å).

In order to balance the +3 charge of $[ClO_4\subset Cu_2\mathbf{L}_2]^{3+}$, three ClO_4^- anions are placed outside of the metallo-macrocycle. Two of these anions are connected to the complex by weak $CH\cdots O\text{-}ClO_3^-$ interactions with CH-O-distances between 2.30 and 2.50 Å and C-H-O angles between 130 and 170° (Table S2).

In the crystal packing arrangement the complex molecules stack in alternating columns with intermolecular interactions between them. The molecules in adjacent columns are linked by one of the ClO_4^- counterions. The H-bonds between O23 and C21-H21C (CH-O distance: 2.46 Å) and C28-H28B (CH-O distance: 2.30 Å) to one neighbouring complex molecule (1 + x, y, z symmetry) leads to the formation of H-bonded chains along the crystallographic a-axis throughout the crystal (Fig. S1).

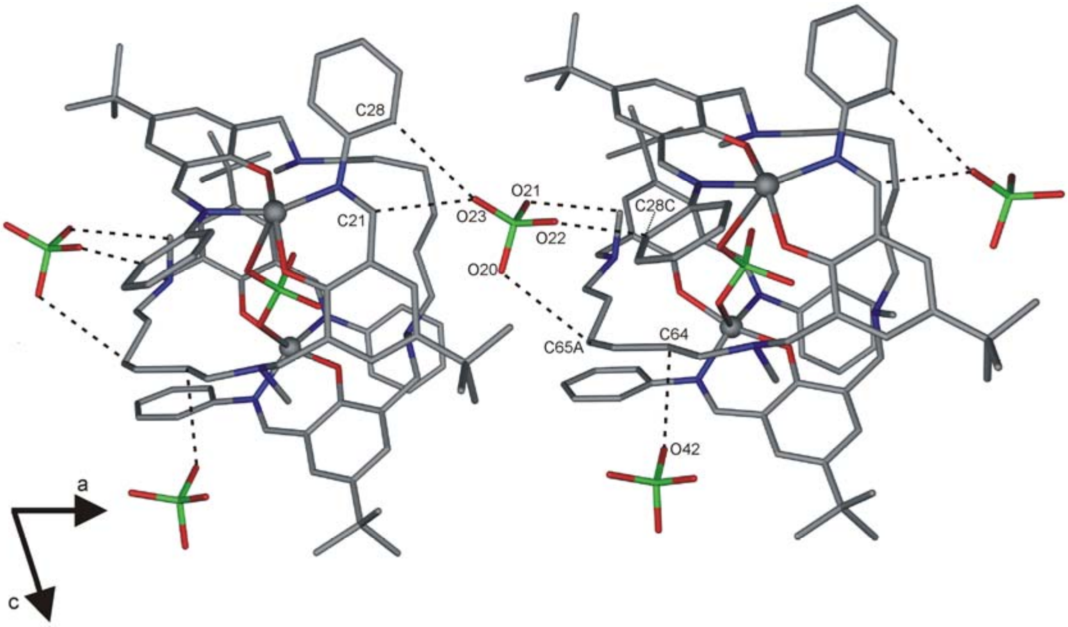

Fig. S1 Schematic drawing of the intermolecular H-bond chain in [$ClO_4 \subset Cu_2\mathbf{L}_2$]($ClO_4$)$_3$ - (**1**) as dotted lines with selected atom labels, non interacting ClO_4^- anions and H-atoms have been removed for clarity. Note: the central perchlorate is disordered in the ratio 0.66 : 0.33 and are restrained to be equal to one another.

Table S2 Bond lengths and angles of the H-bonds in **1**.

D-H	A	D-H [Å]	H-A [Å]	D-A [Å]	D-H-A[°]
N3-H3B	O1	0.91	2.17	2.826(3)	128
N3A-H3AB	O1A	0.91	2.08	2.772(4)	132
N3B-H3BB	O1B	0.91	2.35	2.939(3)	123
N3C-H3CB	O1C	0.91	2.34	2.942(3)	123
N3B-H3BB	O30	0.91	2.21	2.926(5)	135
N3C-H3CB	O33	0.91	2.17	2.910(4)	138
C64-H64D	O32	0.97	2.51	3.452(5)	165
C64A-H64B	O31	0.97	2.42	3.362(7)	165
C21-H21C	O23 ^{i}	0.93	2.46	3.143(5)	130
C28C-H28A	O22	0.93	2.49	3.378(5)	161
C28-H28B	O23 ^{i}	0.93	2.30	3.220(5)	170
C31A-H31F	O21	0.96	2.43	3.188(5)	135
C64-H64C	O42	0.97	2.45	3.300(5)	147
C65A-H65A	O20	0.97	2.50	3.252(5)	134

Symmetry codes: i = 1+x,y,z

Description of Metal binding in **2**

The Cu-O-distances are 1.90 Å (Cu1-O1 and Cu1-O11), whereas the Cu-N-donor atom distances are considerable longer (Cu1-N1 2.01 Å and Cu1-N11 1.98 Å). The trans angles O1-Cu1-O11 and N1-Cu1-N11 are 148° and 145°, respectively and the cis angles are between 93° and 97° (see Table S3). These angles are in agreement to previously reported values for geometrically similar unconnected salicyaldimine N,O-chelate units.[9-13]

Table S3 Selected bond lengths (Å) and angles (°) for **2**.

bond	length [Å]	angle	[°]
Cu1-O1	1.8959(18)	O1-Cu1-O11	148.17(12)
Cu1-O11	1.8973(18)	O1-Cu1-N1	93.36(11)
Cu1-N1	2.721(3)	O1-Cu1-N11	93.03(11)
Cu1-N11	1.993(2)	O11-Cu1-N1	97.00(11)
		O11-Cu1-N11	95.33(11)
		N1-Cu1-N11	145.21(13)

Hydrogen bonding description in ***2***

Both NH-functional groups are involved in the formation of bifurcated hydrogen bonds towards the encapsulated NO_3^- anion. Again two significant different NH-O bond lengths are observed. A strong interaction between the anion (NH-O distance 2.10 Å) and the ammonium groups is present with a weaker interaction to the deprotonated phenol O-atom, namely N12-H12J (see Table S4). The observed distance between N2-H2B and O201 is 2.49 Å (N-O distance 3.19 Å). Thus each of these protons are involved in both a moderate and a weak H-bond with an O-atom.

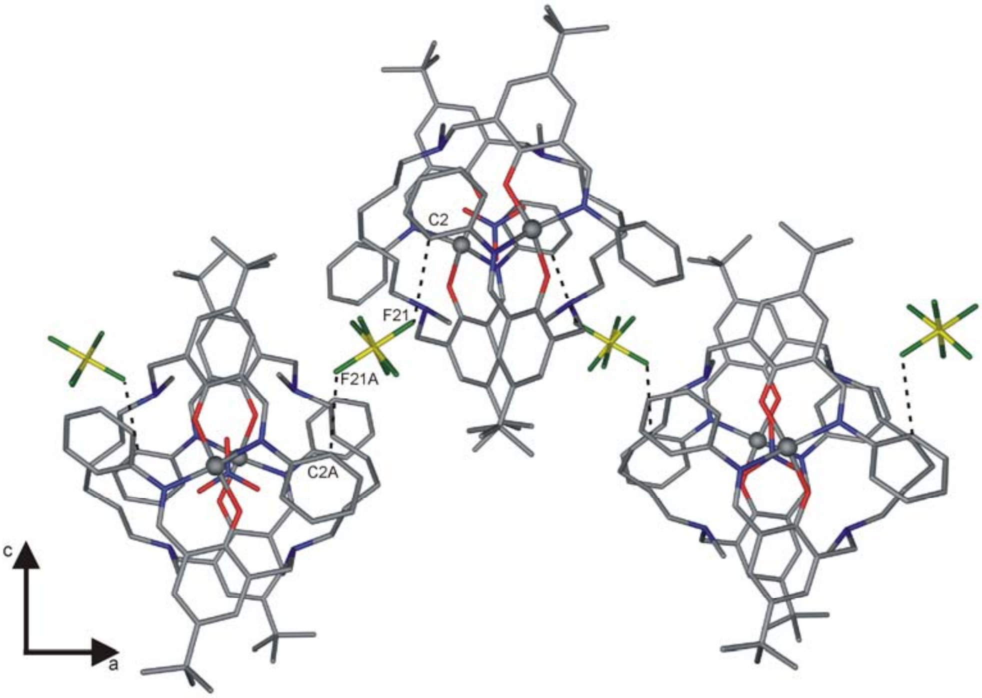

Fig. S2 Schematic drawing of the intermolecular H-bond chain in $[NO_3\subset Cu_2\mathbf{L}_2](NO_3)(PF_6)_2$ - (**2**) as dotted lines with selected atom labels. Non H-bonded NO_3^- and PF_6^- anions and H-atoms have been removed for clarity.

Two PF_6^- and one NO_3^- anion are placed outside the cation core of **2**. A weak CH-F interaction (CH-F distance 2.44 Å, see Table S4) is formed between the ligand and one of the PF_6^- anions. This CH-F interaction continues in a sinuous shaped H-bond chain along the crystallographic a-axis (Fig. S2).

Table S4 Bond lengths and angles of the H-bonds in **2**.

D-H	A	D-H [Å]	H-A [Å]	D-A [Å]	D-H-A[°]
N2-H2B	O1	0.91	2.07	2.750(4)	131
N12-H12J	O11	0.91	2.46	3.044(4)	123
N2-H2B	O201	0.91	2.49	3.190(4)	134
N12-H12J	O200 ^{i}	0.91	2.10	2.876(4)	142
C21-H21A	O200	0.97	2.50	3.469(5)	172
C2-H2A	F21 ^{i}	0.93	2.44	3.348(5)	165

Symmetry codes: i = 1-x,1/2-y,z

In addition the discussed weak CH-anion interactions, there exists an unusually close placement of the remaining NO_3^- and PF_6^- anions. This results in a distance of 2.48 Å between O300 and F6 (NO-F angle 132°, PF-O angle 134°), which is significant shorter than the sum of the van der Waals radii (O 1.52 Å, F 1.47 Å).[12] A search of the Cambridge Structural Database (CSD) (version May, 06th, 2009) revealed two examples of a similar arrangement of a NO_3^--PF_6^--anion pairing, that show comparable short O-F distances of 2.34 Å[13] and 2.58 Å.[14]

*Iodide complex **3***

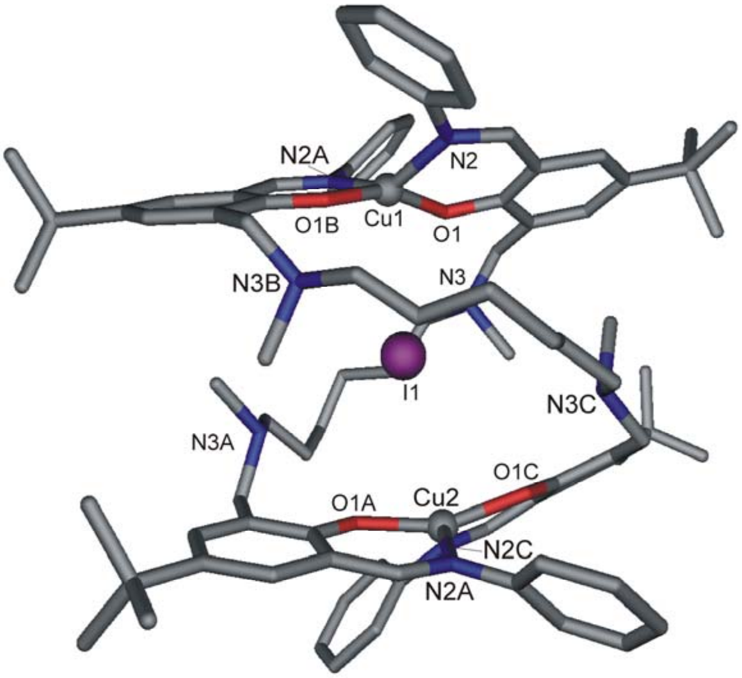

Fig. S3 Schematic drawing of the iodide encapsulated metallo-macrocycle in the $[\mathrm{I}\subset\mathrm{Cu}_2\mathbf{L}_2]^{3+}$ cation of (**3**) with hetero atoms labelled. Non encapsulated anions, co-crystallised solvent molecules and H-atoms have been removed for clarity.

The formula below is considered to consist of an unsymmetrical mix of anions, i.e. 9.17 x BF_4^- and 6.83 x I^- per four complex cages. Each cage has one fully occupied iodine atom at its centre with the remaining 2.83 spread among four cages partially interchanged with the tetrafluoroborate anions. Within the crystal lattice of the large and weakly diffracting crystal there was also found one ether molecule and 1.5 x water molecules. Hydrogen atoms were not modelled for the water molecules. The tetrafluoroborate anions have been restrained to be equal and a number of carbon – carbon bond lengths have also been geometrically restrained to be reasonable.

$C_{352}H_{464}B_{9.17}Cu_8F_{36.68}I_{6.83}N_{32}O_{16}\cdot 2C_4O\cdot 3O$, M = 7746.63, green plate, 0.39 x 0.24 x 0.05 mm, monoclinic, $P21/c$, a = 26.986(5) Å, b = 24.260(5) Å, c = 29.252(6) Å, β = 95.28(3), V =19069(7) Å^3, Z = 2, μ(MoKα) = 1.069 mm^{-1}, F(000) = 7974, T =153(2) K. A total of 101654 reflections were collected in the range 8.2° < 2θ < 47.6°. The 28487 independent reflections [R(int) = 0.231] were used after absorption correction (T_{min} = 0.572, T_{max} = 0.951). Refinement of 2177 parameters converged to R_1 = 0.1169 [for 8970 reflections having I > 2σ(I)], wR_2 = 0.3937 and goodness-of-fit of 1.01 (for all 28487 F^2 data). Peak/hole 2.69/-1.19 e Å^{-3}.

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