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Anion-induced contraction of helical receptors.

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Synthesis of *N,N'*-dimethyl-N,N'-hexamethylenedi(3-hydroxyiminomethyl-2-hydroxy-5-*tert*-butylbenzylamine (L)

Hydroxylamine hydrochloride (117 mg, 1.68 mmol) and potassium hydroxide (94 mg, 1.68 mmol) were dissolved separately in hot ethanol (~20 mL) and the two solutions were cooled and combined to give a white precipitate (KCl) which was removed by filtration. *N,N'*-dimethyl-*N,N'*-hexamethylenedi(3-formyl-2-hydroxy-5-*tert*-butylbenzylamine) (400 mg, 0.762 mmol), prepared as described previously,[6] was added to the filtrate. The solution was refluxed overnight and set aside to cool. The precipitated product was collected and washed with cold ethanol (2 x 10 mL) to yield **L** (361 mg, 85%).

^{1}H NMR δ_H (500 MHz, d_6-DMSO): 8.28 (2H, s, C*H*=N), 7.46 (2H, s, Ar-*H*), 7.14 (2H, s, Ar-*H*), 3.65 (4H, s, Ar-CH_2-N), 2.40 (4H, t, N-CH_2-CH$_2$), 2.19 (6H, s, N-CH_3), 1.48 (4H, m, N-CH$_2$-CH_2), 1.26 (4H, m, N-CH$_2$-CH$_2$-CH_2) 1.23 (18H, s, C(CH_3)$_3$); ^{13}C NMR δ_H (400 MHz, d_6-DMSO) 153.6, 145.8, 140.8, 127.1, 122.8, 121.5, 117.7, 59.2, 56.1, 41.0, 33.7, 31.3, 26.4, 26.2; *m/z* (ESI) 555.72 M$^+$; Anal. Calc. for $C_{32}H_{50}N_4O_4 \cdot 0.5H_2O$ C 68.17, H 9.12, N 9.94, found: C 68.32, H 8.77, N 9.69 %; ν_{max} (KBr)/cm^{-1} 1637s (C=N).

Tab. S1: Bond lengths and angles of the H-bonds in $[Cu_2(\mathbf{L}\text{-}2H)_2] \cdot C_2H_4Cl_2$

D-H	A	D-H [Å]	H-A [Å]	D-A [Å]	D-H-A[°]
O21-H21	O12	0.82	2.21	2.818(8)	131
O21-H21	N622	0.82	2.13	2.770(9)	134
O22-H22	O11	0.82	2.06	2.692(10)	133
O22-H22	N621	0.82	2.21	2.866(11)	138
O23-H23	O14	0.82	2.12	2.725(9)	131
O23-H23	N624	0.82	2.21	2.899(9)	141
O24-H24	O13	0.82	2.16	2.777(8)	132
O24-H24	N623	0.82	2.18	2.801(10)	132
C613-H18A	O11^{i}	0.97	2.42	3.230(10)	141
C612-H51A	O14^{ii}	0.97	2.48	3.222(10)	133

Symmetry codes: i = -1/2+x,3/2-y,z; ii =1/2+x,3/2-y,z

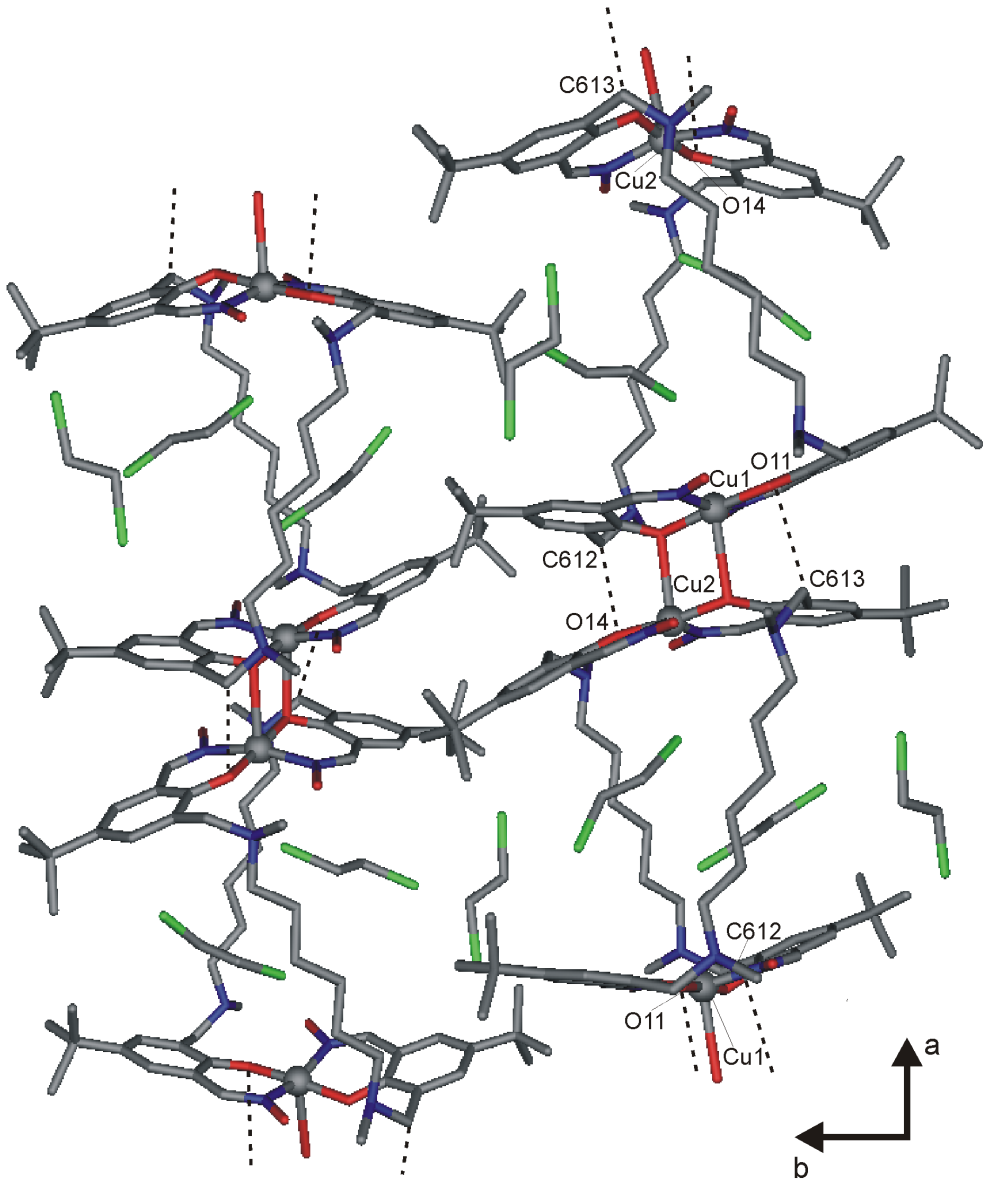

Fig S1: Cut-out of the crystal packing of $[Cu_2(\mathbf{L}\text{-}2H)_2]$ showing intermolecular interactions indicated as dotted lines and the incorporated 1,2-dichlorethane solvent molecules (major occupied species). Hydrogen atoms have been removed for clarity. Viewed along the crystallographic c-axis.

Tab. S2: Bond lengths and angles of weak interactions in $[BF_4 \subset Cu_2\mathbf{L}_2](BF_4)_3$

D-H	A	D-H [Å]	H-A [Å]	D-A [Å]	D-H-A[°]
O23- H23A	O1C	0.82	2.12	2.704(13)	128
O23A- H23B	O1B	0.82	2.06	2.688(13)	133
O23B- H23C	O1A	0.82	2.04	2.657(12)	132
O23C-H23D	O1	0.82	2.12	2.750(13)	133
N3-H3B	O1	0.91	2.28	2.920(14)	1.27
N3A-H3AB	O1A	0.91	2.33	2.957(15)	1.26
N3B-H3BB	O1B	0.91	2.33	2.982(17)	1.28
N3C-H3CB	O1C	0.91	2.53	3.115(17)	1.22
N3-H3B	F22	0.91	2.57	3.283(22)	135
N3A-H3AB	F22	0.91	2.62	3.348(22)	138
N3B-H3BB	F21	0.91	2.25	3.117(18)	159
N3C-H3CB	F24	0.91	2.53	3.112(25)	122

C64-H64A	F22	0.97	2.45	3.36(2)	155
C64A-H64D	F22	0.97	2.39	3.30(2)	155

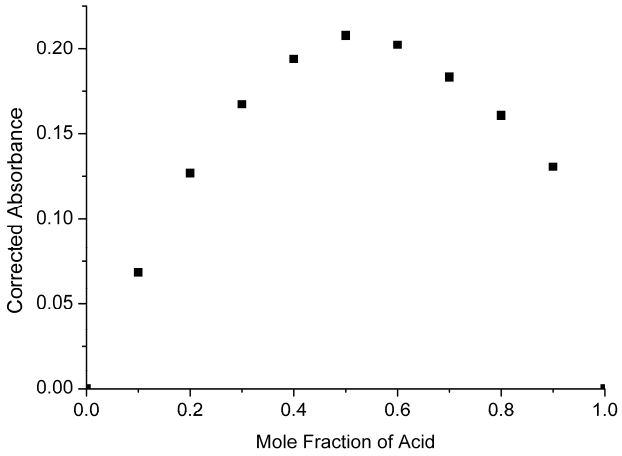

Fig. S2: Jobs plot of $[Cu_2(\mathbf{L}\text{-}2H)_2]$ and HBF_4 at 4.6×10^{-5} mol·L^{-1} in isopropanol / 1,2-dichloroethane, observed wave lengths 355 nm.