## A Family of Double-Bowl Pseudo Metallocalix[6]arene Discs

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#### Synthesis of (HL<sub>1</sub>)

To a solution of o-vanillin (4.00 g, 26.3 mmol) in MeOH (40 cm<sup>3</sup>) was added a 1:10 excess of MeNH<sub>2</sub> (20 cm<sup>3</sup> of a 40 % aqueous solution). The solution rapidly adopted an intense-yellow colour on addition of MeNH<sub>2</sub> and was then agitated for 10 h. A bright yellow crystalline solid of **HL**<sub>1</sub> was obtained solution via slow evaporation of the reaction mixture in a 62 % yield (2.69 g). The crystalline solid was then washed with n-hexane and dried under vacuum. Elemental analysis calcd (%) for C<sub>9</sub>H<sub>11</sub>N<sub>1</sub>O<sub>2</sub>: C 65.43, H 6.71, N 8.47; Found: C 64.95, H 6.27, N 8.33. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 3.47(s) (3H, N-CH<sub>3</sub>), 3.89(s) (3H, O-CH<sub>3</sub>), 6.75-6.90 (m, Ar-H), 8.30(s), (1H, N=CH). UV/vis (MeOH):  $\lambda_{max}$  [nm] ( $\varepsilon_{max}$  10<sup>3</sup> dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>): 202.0 (11.5), 221.0 (14.6), 242.0 (9.7), 258 (7.3), 290.0 (5.9), 328 (1.5), 415.1 (2.4). (MeCN):  $\lambda_{max}$  [nm] ( $\varepsilon_{max}$  10<sup>3</sup> dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>): 221.0 (18.3), 257.1 (7.9), 295 (1.6), 323.1 (2.0).



**Fig. SI1** UV-vis spectra obtained on a sample of HL<sub>1</sub> in MeOH (top) and MeCN (bottom) solutions respectively. For numerical data see experimental section.

#### Synthesis of (HL<sub>2</sub>)

To a solution of 5-bromo-2-hydroxy-3-methoxybenzaldehyde (2.50 g, 10.82 mmol) in MeOH (40 cm<sup>3</sup>) was added a 1:12 excess of MeNH<sub>2</sub> (10 cm<sup>3</sup> of a 40 % aqueous solution). The solution adopted an intense-yellow colour on addition of MeNH<sub>2</sub> and was left to stir for 10 h. The bright yellow needle-like crystalline product was obtained via slow evaporation of the reaction mixture and washed in n-Hexane to give **HL**<sub>2</sub> in 60 % yield (1.58 g). Elemental analysis calcd (%) for C<sub>9</sub>H<sub>10</sub>N<sub>1</sub>O<sub>2</sub>Br: C 44.28, H 4.10, N 5.74; Found: C 44.75, H 4.98, N 5.47. <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>):  $\delta = 3.47$ (s) (3H, N-CH<sub>3</sub>), 3.86(s) (3H, O-CH<sub>3</sub>), 6.93-6.95 (m, Ar-H), 8.19(s), (1H, N=CH). UV/vis (MeOH):  $\lambda_{max}$  [nm] ( $\varepsilon_{max}$  10<sup>3</sup> dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>): 203.1 (16.1), 228.0 (19.0), 244 (15.3), 288.0 (5.5), 334 (1.4), 422.0 (3.3). (MeCN):  $\lambda_{max}$  [nm] ( $\varepsilon_{max}$  10<sup>3</sup> dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>): 226.0 (26.4), 251 (sh), 291 (3.8), 332.0 (2.5), 421 (0.9).



Fig. SI2 UV-vis spectra obtained on a sample of  $HL_2$  in MeOH (top) and MeCN (bottom) solutions respectively. For numerical data see experimental section.

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Figure SI3 (A) Crystal packing observed in 1 as viewed down the *c* axis of the unit cell. Note that packing of 2 is identical to that of 1 minus disordered MeNO<sub>2</sub> guests. (B) View along *a* axis of the cell in 1. H-atoms omitted for clarity. Large spheres represent  $NO_3^-$  counter anions.



Fig. SI4: Infra-Red spectrum obtained from (top) a sample of  $[Ni_7(OH)_6(L_1)_6](NO_3)_2$ .2MeOH (2) and (bottom) the same sample of 2 dried under vacuum for 3 h prior to re-analysis.

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Fig. SI5 Infra-Red spectrum obtained from (top) a sample of  $[Ni_7(OH)_6(L_2)_6](NO_3)_2$ .2MeCN (4) and (bottom) the same sample of 4 dried under vacuum for 3 h prior to re-analysis.



Fig. SI6: Crystal structure observed in 5 (minus MeOH guest molecules) as viewed perpendicular (top) and parallel (bottom) to the [Zn<sub>7</sub>] plane.

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Fig. SI7 UV-vis spectra obtained from MeOH (top) and MeCN (bottom) solutions of  $[Ni_7(OH)_6(L_1)_6](NO_3)_2.2MeOH$  (2).



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**Fig. SI8** UV-vis spectra obtained on a sample of [Zn<sub>7</sub>(OH)<sub>6</sub>(L<sub>1</sub>)<sub>6</sub>](NO<sub>3</sub>)<sub>2</sub>.2MeOH.H<sub>2</sub>O (**5**) in MeOH (top) and MeCN (bottom) solutions respectively. For numerical data see experimental section.



Fig. SI9 Plots of  $1/\chi$  vs. T obtained from complexes 1 (top) and 4 (bottom) giving Curie-Weiss constants ( $\theta$ ) of +18.7 and +29.0 K respectively.



Fig. SI10 Plots of magnetisation (M/  $N\mu_B$ ) vs. H (G) obtained from complex 3 in the 2-7 K temperature range and fields of 0.5-7 T.



Fig. SI11 Microscope images of crystalline products of 2 (left) and 5 (right) clearly depicting the hexagonal single crystals obtained for all complexes in this work.

	5	6		
Formula	C56H66N8O27 Zn7	C57H66N11O30Zn7		
Formula Weight	1740.76	1842.80		
Crystal system	Trigonal	Trigonal		
Space group	P-3c1	P-3c1		
a / Å	13.902(2)	14.082(2)		
b / Å	13.902(2)	14.082(2)		
c / Å	23.353(5)	22.759(5)		
α, β, γ (°)	90, 90, 120	90, 90, 120		
$V / Å^3$	3908.9(11)	3908.2(11)		
Z	2	2		
$D_c (g cm^{-3})$	1.479	1.566		
$\mu (mm^{-1})$	2.187	2.196		
Reflections	2361	2338		
Unique reflections	1766	2059		
GOF on $F^2$	1.139	1.119		
R <sub>int</sub>	0.0628	0.0713		
R1 [I>2σ(I)]	0.0838	0.0769		
wR2 (all data)	0.1999	0.2035		

### Table SI1: Crystal refinement data obtained from [Ni7] complexes 5 and 6

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Table SI2: Dimensions of the unique intermolecular hydrogen bonds (distances in Å and angles in °) for complexes 1-6.

Complex	D <sup>a</sup> -H····A <sup>b</sup>	D <sup>a</sup> ····A <sup>b</sup>	H···A <sup>b</sup>	<d<sup>aHA<sup>b</sup></d<sup>
1	C(1)-H(1A)····O(4) [1-y, x-y, z]	3.543(2)	2.59	165
1	C(5)-H(5)····O(4) [y, x, 1/2-z]	3.391(1)	2.44	174
	C(1)-H(1A)O(4)	3.549(1)	2.58	168
2	C(8)-H(8)····O(4) [y, -1+x, 1/2-z]	3.417(1)	2.47	176
	O(10)…O(4) [x-y, -y, -z+1/2]	2.863(1)		
3	C(1)-H(1A)····O(4) [1-x, -x+y, 1/2-z]	3.519(9)	2.58	160
	C(2)-H(2)···O(4) [1-x, -x+y, 1/2-z]	3.471(8)	2.56	160
	C(5)-H(5)···O(4)	3.371(7)	2.43	171
	O(1)…O(5) [x, x-y, z+1/2]	3.08		
	O(1)…O(6) [-x+y, y, z+1/2]	3.25		
	$O(1)-H(1)\cdots Br(1) [x, -1+y, z]$	3.720(5)	2.82	153
	O(2)-H(2)···N(5)	3.161(1)	2.40	134
	O(3)-H(3A)…N(5) [1/2-x, 1/2-y, 1-z]	3.184(1)	2.36	141
4	C(17)-H(17)···O(10) [1-x, -y, 1-z]	3.438(1)	2.56	156
	C(18)-H(18B)-Br(3) [1/2-x, -1/2+y, 1/2-z]	3.821(1)	2.93	156
	C(24)-H(24)···O(12) [1-x, 1-y, 1-z]	3.484(1)	2.59	160
	C(27)-H(27B)-Br(2) [1-x, -y, 1-z]	3.604(1)	2.70	157
C(5) O(5 5 O(5' O(5)	C(5)-H(5)····O(4)	3.402(1)	2.46	175
	O(51)···O(4) [x-y, -y, -z-1/2]	2.95		
	O(57)···O(51) [y, 1-x+y, -z]	2.84		
	O(56)···O(57)	2.74		
6	O(1)-H(1)····O(5)	3.17(4)	2.29	146
	O(1)-H(1)····O(6) [-x+y, -x, z]	3.09(3)	2.12	164
	C(1)-H(1C)····O(4) [1-x, -x+y, -1/2-z]	3.467(1)	2.56	153
	O(2)-H(2)···O(4) [1-x, -x+y, -1/2-z]	3.460(1)	2.57	156
	O(7)-H(7)····O(4)	3.377(9)	2.43	171

<sup>a</sup> D = donor atom. <sup>b</sup> A = acceptor atom.

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#### X-ray diffraction details on the collection of 1-6

The structures of **1-6** were collected on an Xcalibur S single crystal diffractometer (Oxford Diffraction) using an enhanced Mo source. Each data reduction was carried out on the CrysAlisPro software package. The structures were solved by direct methods (SHELXS-97)<sup>1</sup> and refined by full matrix least squares using SHELXL-97.<sup>2</sup> SHELX operations were automated using the OSCAIL software package.<sup>3</sup> All hydrogen atoms were placed in calculated positions. The non hydrogen atoms were refined anisotropic except for the disordered guest solvent (MeNO<sub>2</sub>, MeCN and MeOH) molecules which were left isotropic. DFIX and restraints were required on the disordered MeNO<sub>2</sub> (in **3** and **6**), and MeOH (in **2** and **5**) guest molecules as a result of high isotropic thermal parameters upon refinement. The FLAT restraint was also imposed on the disordered MeNO<sub>2</sub> guests in complex **3** and **6**.

1. G. M. Sheldrick, Acta. Crystallogr., Sect. A: Found. Crystallogr., 1990, A46, 467.

2. G. M. Sheldrick, SHELXL-97, A computer programme for crystal structure determination, University of Gottingen, 1997.

3. P. McArdle, P. Daly and D. Cunningham, J. Appl. Crystallogr., 2002, 35, 378.