

Electronic Supplementary Information

Ditopic binding of perchlorate anion to hexaazamacrocyclic hosts

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Synthesis

L1. Diethylenetriamine (1.00 g, 9.70 mmol) and 2,5-thiophenedicarboxaldehyde (1.35 g, 9.70 mmol) were separately dissolved in CH₃OH (200 cm³). Both solutions were added simultaneously dropwise over 4 h to a stirred CH₃OH (400 cm³) at 0° C. The mixture was kept at room temperature under stirring for another 24 h, after which the solvent was evaporated. The resulting Schiff base was reduced to amine with NaBH₄ (1.73 g, 45.7 mmol) in CH₃OH (100 cm³) at room temperature for 12 h. The solvent was evaporated under reduced pressure and the residue was dissolved in water ((100 cm³). The aqueous phase was extracted by CH₂Cl₂ (3x100 cm³). The organic layers were combined and dried with MgSO₄. The product was purified by column chromatography on neutral Al₂O₃ using an eluent of CH₂Cl₂ containing 2% CH₃OH to give the hexaazamacrocycle **L1** as a white powder. Yield 1.23 g, 65%. Found: C, 56.6; H, 8.2; N, 20.1. C₂₀H₃₄N₆S₂ requires C, 56.8; H, 8.1; N, 19.9. ¹H NMR (300 MHz, CDCl₃, TMS): δ 6.73 (s, 4H, ArH), 3.87 (s, 8H, ArCH₂), 3.77 (t, 8H, CH₂), 2.72 (t, 8H, CH₂).

[H₆L1]⁶⁺·6TsO⁻. The tosylate salt of **L1** was obtained by titrating the macrocycle **L1** (0.05 g, 0.118 mmol) dissolved in CH₃OH (2 cm³) with TsOH. The addition of diethyl

ether (2 cm³) yielded a white precipitate that was filtered and dried. Yield 0.135 g, 80%. Found: C, 51.6; H, 5.8; N, 5.7. C₆₂H₈₂N₆O₁₈S₈ requires C, 51.1; H, 5.7; N, 5.8. ¹H NMR (300 MHz, D₂O, TSP): δ 7.69 (d, 12H, ArH), 7.38 (d, 12H, ArH), 7.22 (s, 4H, ArH), 4.48 (s, 8H, ArCH₂), 3.51 (t, 8H, CH₂), 2.99 (t, 8H, CH₂), 2.42 (s, 12H, CH₃).

[H₆L1]⁶⁺·6ClO₄⁻. To a solution of L1 (50 mg, 0.118 mmol) in CH₃OH (2 cm³) was added perchloric acid (ca. 0.05 cm³). The white precipitate formed immediately was filtered and washed with diethyl ether. Yield 0.05 g, 80%. Found: C, 23.1; H, 4.0; N, 8.1. C₂₀H₄₀Cl₆N₆O₂₄S₂ requires C, 23.4; H, 3.9; N, 8.2). ¹H NMR (300 MHz, D₂O, TSP): δ 7.23 (s, 4H, ArH), 4.46 (t, 8H, CH₂), 3.32 (t, 8H, CH₂), 2.95 (s, 12H, CH₃).

L2. This ligand was prepared from the reaction of diethylenetriamine (1.00 g, 9.70 mmol) and terephthalaldehyde (1.30 g, 9.70 mmol) following the similar method as described for L1. Yield 1.20 g, 60%. Found: C, 69.7; H, 9.1; N, 20.7. C₂₄H₃₈N₆ requires C, 70.2; H, 9.3; N, 20.5. ¹H NMR (300 MHz, CDCl₃, TMS): δ 7.29 (s, 8H, ArH), 3.80 (s, 8H, ArCH₂), 2.85 (t, 8H, CH₂), 2.83 (t, 8H, CH₂).

[H₆L2]⁶⁺·6TsO⁻. The salt was prepared from the reaction of L2 (50 mg, 0.122 mmol) with TsOH in CH₃OH (2 cm³). A white precipitate was obtained on the addition of diethyl ether (2 cm³). Yield 0.140 g, 80%. Found: C, 54.2; H, 5.8; N, 5.6. C₆₆H₈₆N₆O₁₈S₆ requires C, 54.9; H, 6.0; N, 5.8. ¹H NMR (300 MHz, D₂O, TSP): δ 7.70 (d, 12H, ArH), 7.42 (d, 12H, ArH), 7.26 (s, 8H, ArH), 4.21 (s, 8H, ArCH₂), 3.27 (t, 8H, CH₂), 3.01 (t, 8H, CH₂), 2.43 (s, 12H, CH₃).

[H₄L2]⁴⁺·4ClO₄⁻. To a solution of L2 (50 mg, 0.122 mmol) in CH₃OH (2 cm³) was added perchloric acid (ca. 0.05 cm³). The white precipitate formed immediately was filtered and washed with diethyl ether. The white precipitate formed, was filtered and washed with diethyl ether. Yield 0.07 g, 75%. Found: C, 35.8; H, 5.4; N, 10.2. C₂₄H₄₂Cl₄N₆O₁₆ requires C, 35.5; H, 5.2; N, 10.3. ¹H NMR (300 MHz, D₂O, TSP): δ 7.43 (s, 8H, ArCH₂), 3.30 (t, 8H, CH₂), 2.99(t, 8H, CH₂).

NMR titration studies

Binding studies were carried out by ^1H NMR titrations of $[\text{H}_6\text{L1}]^{6+}\cdot 6\text{TsO}^-$ or $[\text{H}_6\text{L2}]^{6+}\cdot 6\text{TsO}^-$ with NaClO_4 in D_2O at pH 4.0 at room temperature, performed on a 300 MHz Bruker NMR spectrophotometer. Initial concentrations were used as 2 mM and 20 mM for the ligand and anion, respectively, and the pH of the solution was adjusted with a concentrated solution of TsOH and NaOH in D_2O . Sodium salt of 3-(trimethylsilyl)propionic-2,2,3,3,- d_4 acid (TSP) in D_2O was used as an external reference in a sealed capillary tube. Each titration was performed by 12 measurements in the range of R ($[\text{perchlorate}]_0/[\text{ligand}]_0$) = 0 to 10. The association constant K was calculated from the non-linear regression analysis of the NMR shifts of aliphatic protons with a 1:1 association model using Sigma Plot software, from the equations, $\Delta\delta = ([\text{A}]^0 + [\text{L}]^0 + 1/K - (([\text{A}]_0 + [\text{L}]_0 + 1/K)^2 - 4[\text{L}]_0[\text{A}]_0)^{1/2}) \Delta\delta_{\text{max}} / 2[\text{L}]_0$ (where L is ligand and A is anion). Error limit in K was less than 15%.

Job plot

Binding stoichiometry was determined by Job plot analysis of the ^1H NMR spectra of $[\text{H}_6\text{L1}]^{6+}\cdot 6\text{TsO}^-$ or $[\text{H}_6\text{L2}]^{6+}\cdot 6\text{TsO}^-$ with varying amount of perchlorate anion in D_2O at pH 4.0 to match what was used in the NMR binding studies described above. Stock solutions (10 mM) of ligands and perchlorate anion were prepared separately in D_2O and the solution pH was adjusted with a concentrated solution of TsOH and NaOH in D_2O . Ten NMR samples were prepared with different proportions of the ligand and anion solution so that the final concentration ($[\text{L}] + [\text{ClO}_4^-]$) of each sample became 10 mM. Sodium salt of 3-(trimethylsilyl)propionic-2,2,3,3,- d_4 acid (TSP) in D_2O was used as an external reference in a sealed capillary tube. The Job plots were obtained plotting $\Delta\delta$ ($[\text{L}]/([\text{L}] + [\text{ClO}_4^-])$) with $(\text{L})/([\text{L}] + [\text{ClO}_4^-])$ as shown in **Figure S1** and **Figure S2**.

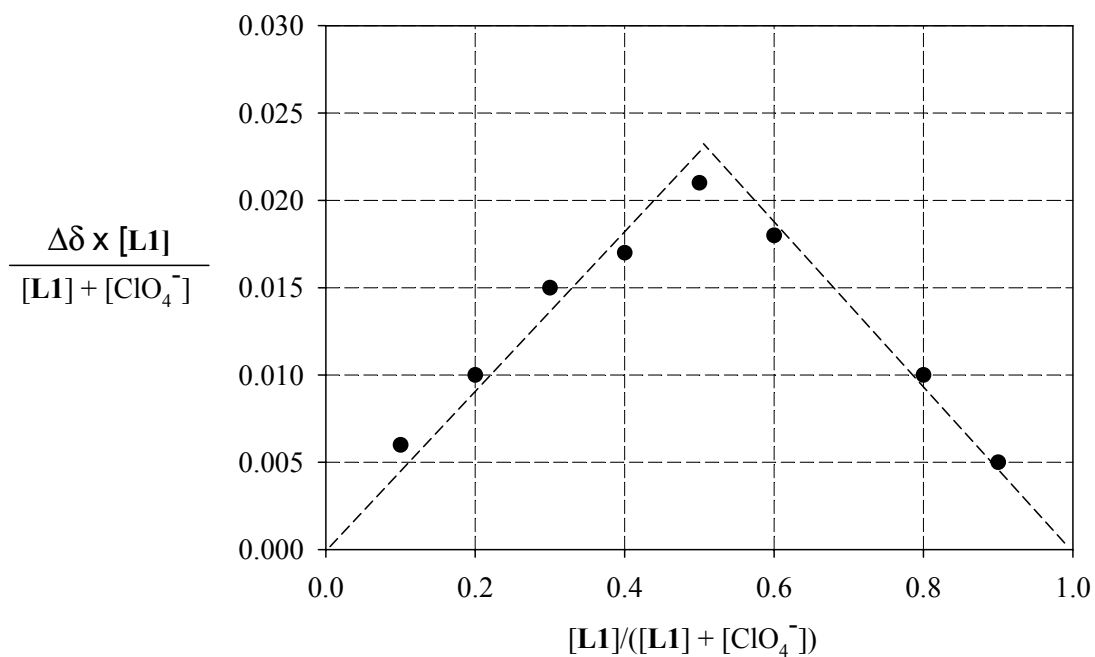


Figure S1. Job plot of **L1** with NaClO₄ in D₂O at pH 4.0 showing a maximum at 0.5 mole fraction of **L1**.

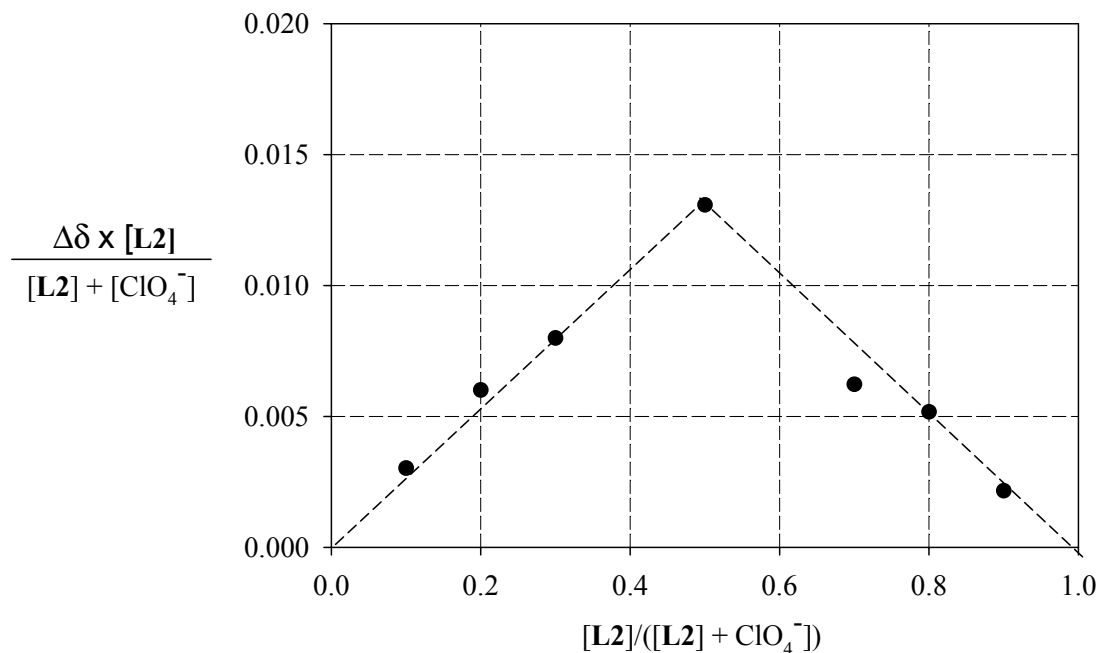


Figure S2. Job plot of **L2** with NaClO₄ in D₂O at pH 4.0 showing a maximum at 0.5 mole fraction of **L2**.

Crystallographic details

Crystallographic data for $[\text{H}_6\text{L1}(\text{ClO}_4)_2](\text{ClO}_4)_4 \cdot 4\text{H}_2\text{O}$

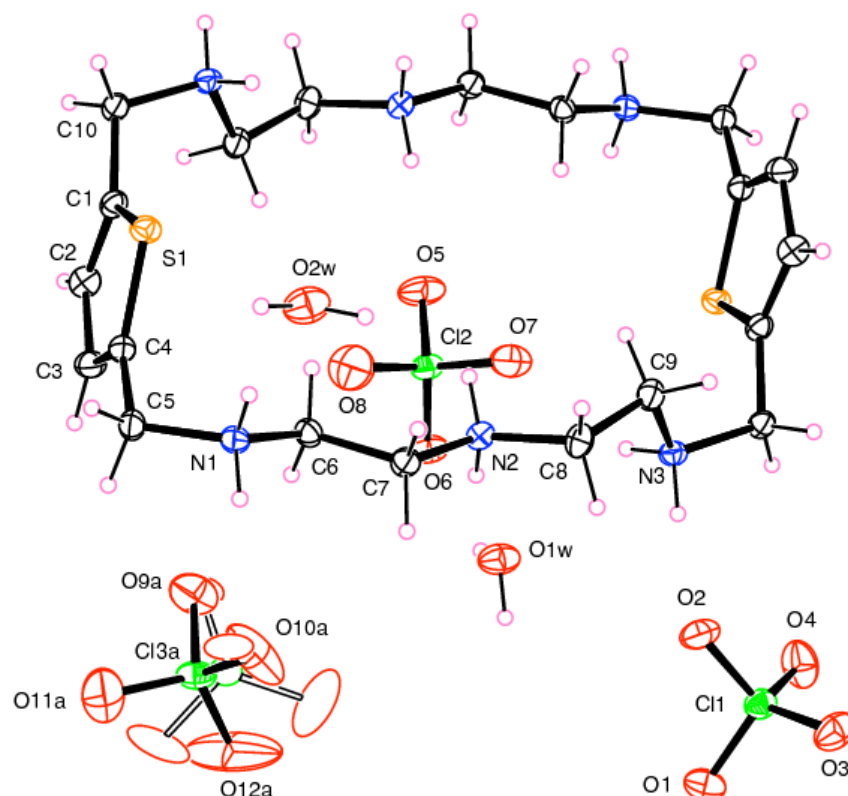


Figure S3. The molecular structure of $[\text{H}_6\text{L1}(\text{ClO}_4)_2](\text{ClO}_4)_4 \cdot 4\text{H}_2\text{O}$ showing the atom-numbering scheme

Instrumentation and software

Data collection: Bruker Apex2; cell refinement: Bruker Apex2; data reduction: Bruker Apex2; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: Bruker *SHELXTL*.

Data collection

Bruker Kappa Apex-II CCD area detector diffractometer	3690 independent reflections
Radiation source: fine-focus sealed tube	3561 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.030$
$T = 90$ K	$\theta_{\text{max}} = 68.7^\circ$
phi and ω scans	$\theta_{\text{min}} = 3.6^\circ$
Absorption correction: multi-scan	
SADABS (Sheldrick, 2002)	$h = -9 \rightarrow 9$
$T_{\text{min}} = 0.314$, $T_{\text{max}} = 0.605$	$k = -12 \rightarrow 12$
10176 measured reflections	$l = -13 \rightarrow 14$

Refinement

Refinement on F^2 map	Secondary atom site location: difference Fourier
Least-squares matrix: full sites	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.032$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.087$	$w = 1/[\sigma^2(F_o^2) + (0.0406P)^2 + 1.0629P]$
where $P = (F_o^2 + 2F_c^2)/3$	
$S = 1.05$	$(\Delta/\sigma)_{\text{max}} = 0.002$
3690 reflections	$\Delta\rho_{\text{max}} = 0.45 \text{ e } \text{\AA}^{-3}$
345 parameters	$\Delta\rho_{\text{min}} = -0.37 \text{ e } \text{\AA}^{-3}$
103 restraints	Extinction correction: SHELXL,
$F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$	
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0022 (3)

Crystallographic data for $[H_4L2(ClO_4)_2(H_2O)](ClO_4)_2$:

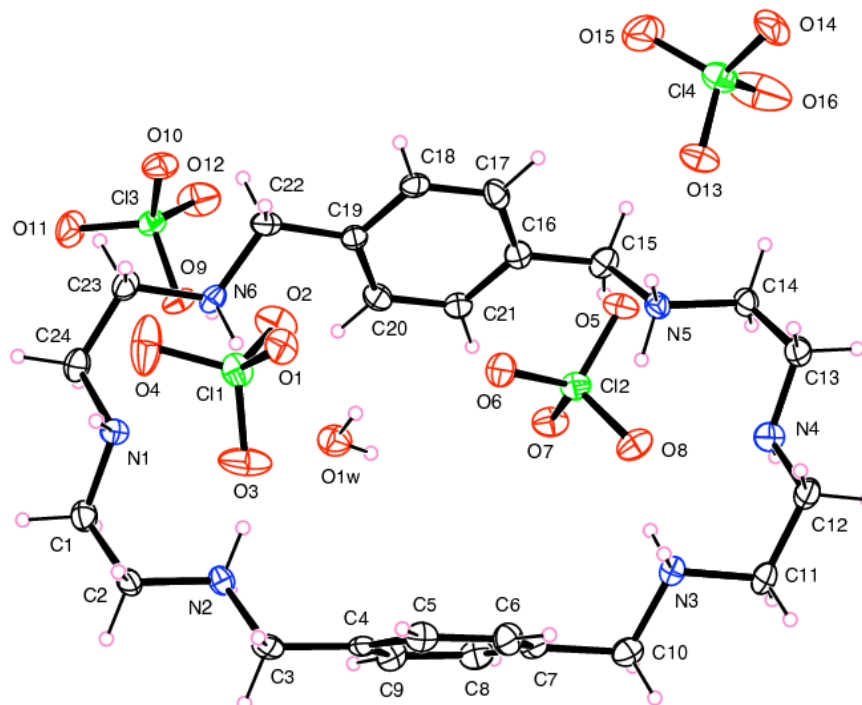


Figure S4. The molecular structure of $[H_4L2(ClO_4)_2(H_2O)](ClO_4)_2$: showing the atom-numbering scheme

Instrumentation and software

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor 1997); data reduction: *HKL DENZO* and *SCALEPACK* (Otwinowski & Minor 1997); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008).

Data collection

KappaCCD (with Oxford Cryostream) diffractometer	7932 independent reflections
Radiation source: fine-focus sealed tube	5349 reflections with $I > 2\sigma(I)$

Monochromator: graphite	$R_{\text{int}} = 0.097$
$T = 90$ K	$\theta_{\text{max}} = 27.1^\circ$
ω and ϕ scans	$\theta_{\text{min}} = 2.6^\circ$
Absorption correction: multi-scan	
HKL Scalepack (Otwinowski & Minor 1997)	$h = -15 \rightarrow 15$
$T_{\text{min}} = 0.910$, $T_{\text{max}} = 0.968$	$k = -18 \rightarrow 18$
61377 measured reflections	$l = -26 \rightarrow 26$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full independent and constrained refinement	H atoms treated by a mixture of
$R[F^2 > 2\sigma(F^2)] = 0.051$	$w = 1/[\sigma^2(F_o^2) + (0.042P)^2 + 1.0851P]$
where $P = (F_o^2 + 2F_c^2)/3$	
$wR(F^2) = 0.105$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.03$	$\Delta\rho_{\text{max}} = 0.55 \text{ e } \text{\AA}^{-3}$
7932 reflections	$\Delta\rho_{\text{min}} = -0.41 \text{ e } \text{\AA}^{-3}$
474 parameters	Extinction correction: SHELXL,
$F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$	
2 restraints	Extinction coefficient: 0.0008 (2)
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983)
Secondary atom site location: difference Fourier map	Flack parameter: 0.28 (5)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to

zero for negative $F2$. The threshold expression of $F2 > \sigma(F2)$ is used only for calculating R -factors (gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on $F2$ are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

References:

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