Electronic Supplementary Information (ESI)

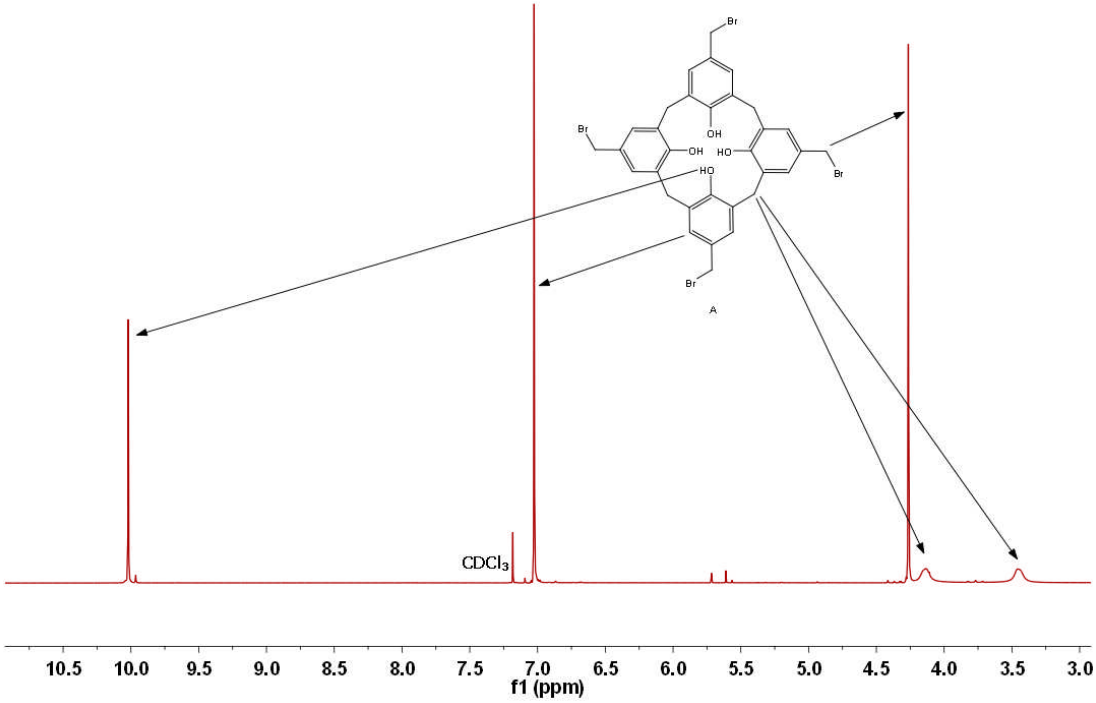
Tetrakis(methylimidazole) and tetrakis(methylimidazolium) calix[4]arenes: competitive anion binding and deprotonation

Emma K. Bullough,[a] Colin A. Kilner[a] Marc A. Little[a] and Charlotte E. Willans*[a]

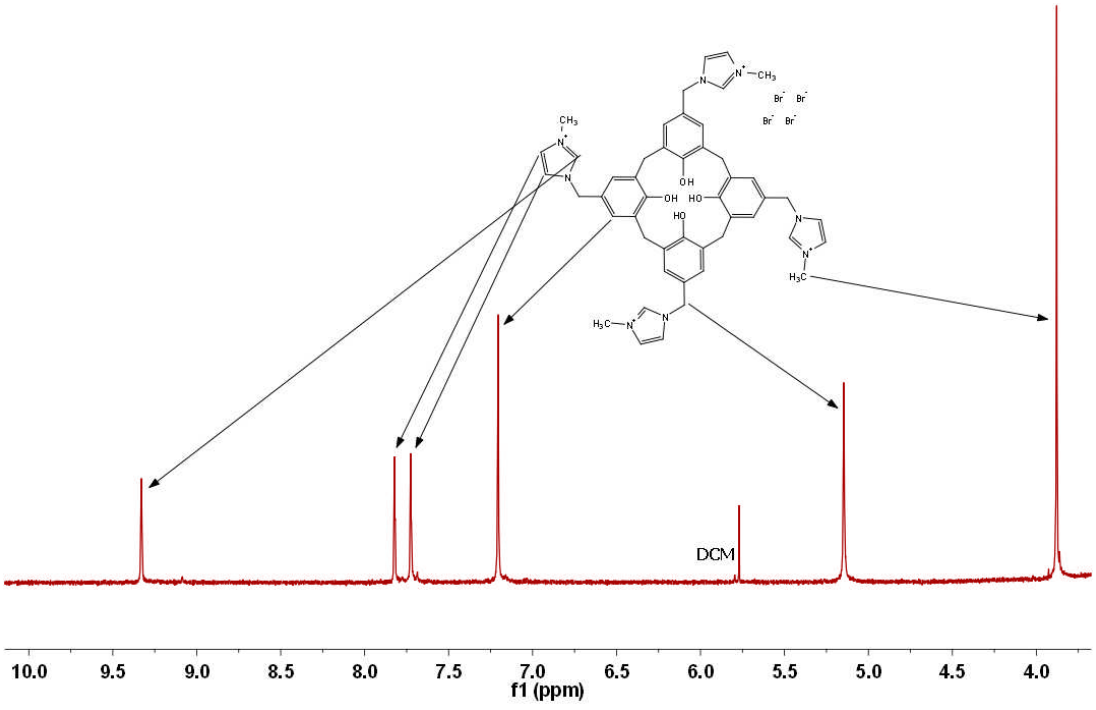
[a]*Department of Chemistry, University of Leeds, Woodhouse Lane, Leeds LS2 9JT, U.K..*
E-mail: c.e.willans@leeds.ac.uk

Contents

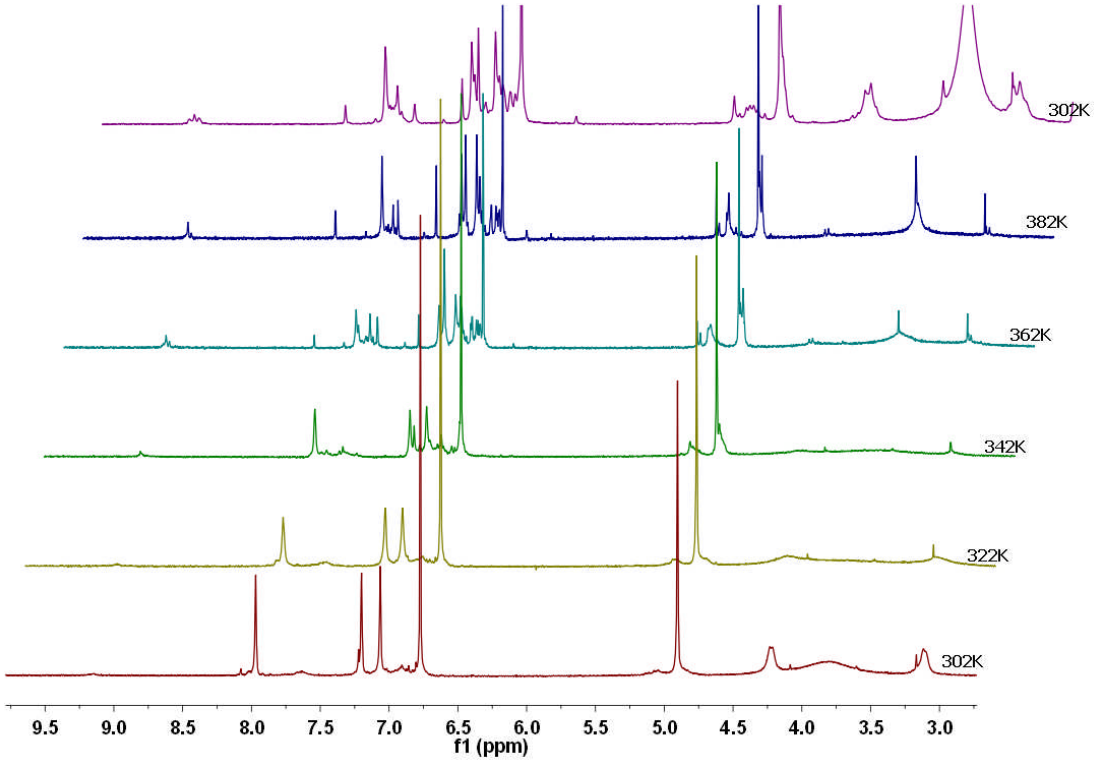
1. ^{1}H NMR spectrum for compound A



2. ^{1}H NMR spectrum for compound 2Br



3. Variable temperature ^{1}H NMR spectra for compound 1



4. Crystallographic details for 1

Crystals were mounted under oil on glass fiber and X-ray diffraction data collected at 150(1)K with Mo-K_α radiation (λ = 0.71073 Å) using Bruker Nonius X-8 diffractometer with ApexII detector and FR591 rotating anode generator. Data sets were corrected for absorption using a multiscan method, and structures were solved by direct methods using SHELXS-97[1] and refined by full-matrix least-squares on F2 by SHELXL-97,[1] interfaced through the program X-Seed.[2] Compound **1** crystallises in the monoclinic space group $P2_1/c$ with one molecule of C_{44} H_{40} N_8 O_4, one molecule of $CHCl_3$ and one-and-a-half molecules of H_2O in the asymmetric unit.

Two of the four imidazolyl groups (N25 > C29 and N35 > C39) are disordered over two equally occupied positions. Hydrogen bonded with the N25 > C29 imidazolyl is a water (H5-O2-H4) modelled with an SOF of 0.5. To maintain sensible N…H-O bond lengths it is assumed that the water is only present when the N25A > C29A component of the imidazolyl is present and not when the B component is present.

Another of the imidazolyl groups (N55 > C59) is protonated at N57 and charge is balanced in the molecule by deprotonation of O7. Dimers are formed by two complimentary N57-H57…N47 hydrogen bonds.

All non-hydrogen atoms were refined anisotropically.

All hydrogen atoms could be located in a difference Fourier map but, in the final stages of the refinement, all H atoms bonded to carbon were placed in calculated positions and refined using a riding model.

C-H distances: C-H distances: CH3, 0.98\A; CH2, 0.99\A; CH, 1.00\A; aromatic, 0.95\A, olefinic and ethylinic, 0.95\A.

Those hydrogen atoms bonded to nitrogen and oxygen could be located in a difference Fourier map. N-H distances were subsequently restrained to be 0.88\A and O-H distances were restrained to be 0.84\A.

All Uiso(H) values were constrained to be 1.2 times (1.5 for methyl and hydroxyl) Ueq of the parent atom.

The HTAB instruction in SHELXL-97 was applied to analyse the hydrogen bonds present in the structure.

Chemical formula	$C_{45}H_{44}Cl_3N_8O_{5.50}$
Formula mass	891.23
Crystal system	Monoclinic
Crystal size (mm)	0.18 x 0.11 x 0.09
a/Å	10.0579(8)
b/Å	40.788(3)
c/Å	10.7646(9)
α/°	90.00
β/°	101.688(4)
γ/°	90.00
Unit cell volume/Å^3	4324.5(6)
Temperature/K	150(2)
Space group	$P2_1/c$
No. of formula units per unit cell, Z	4
Radiation type	MoKα
Absorption coefficient, μ/mm^{-1}	0.270
No. of reflections measured	61030
No. of independent reflections	9587
R_{int}	0.0443
Final R_1 values ($I > 2\sigma(I)$)	0.0492
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1009
Final R_1 values (all data)	0.0799
Final $wR(F^2)$ values (all data)	0.1133
Goodness of fit on F^2	1.031

5. Crystallographic details for 2Br

Crystals were mounted under oil on glass fiber and X-ray diffraction data collected at 150(1)K with Mo-K_α radiation (λ = 0.71073 Å) using Bruker Nonius X-8 diffractometer with ApexII detector and FR591 rotating anode generator. Data sets were corrected for absorption using a multiscan method, and structures were solved by direct methods using SHELXS-97[1] and refined by full-matrix least-squares on F2 by SHELXL-97,[1] interfaced through the program X-Seed.[2] Compound **2Br** crystallises in the monoclinic space group *C*2/*m* with one half of the molecule, four bromide anions at 50% occupancy, one complete methanol solvent molecule and two methanol solvent molecules at 50% occupancy.

One methanol solvent molecule was disordered over two positions located on symmetry operation x, 1-y, z. C27A O5 was refined at 28.5% occupancy, C27B O6 was refined at 21.5% occupancy. C27A and C27B were refined with equivalent x, y and z parameters and anisotropic displacement parameters. Another methanol solvent molecule, C26 O4, was refined at 50% occupancy and was located on a symmetry operation 1-x, y, 1-z.

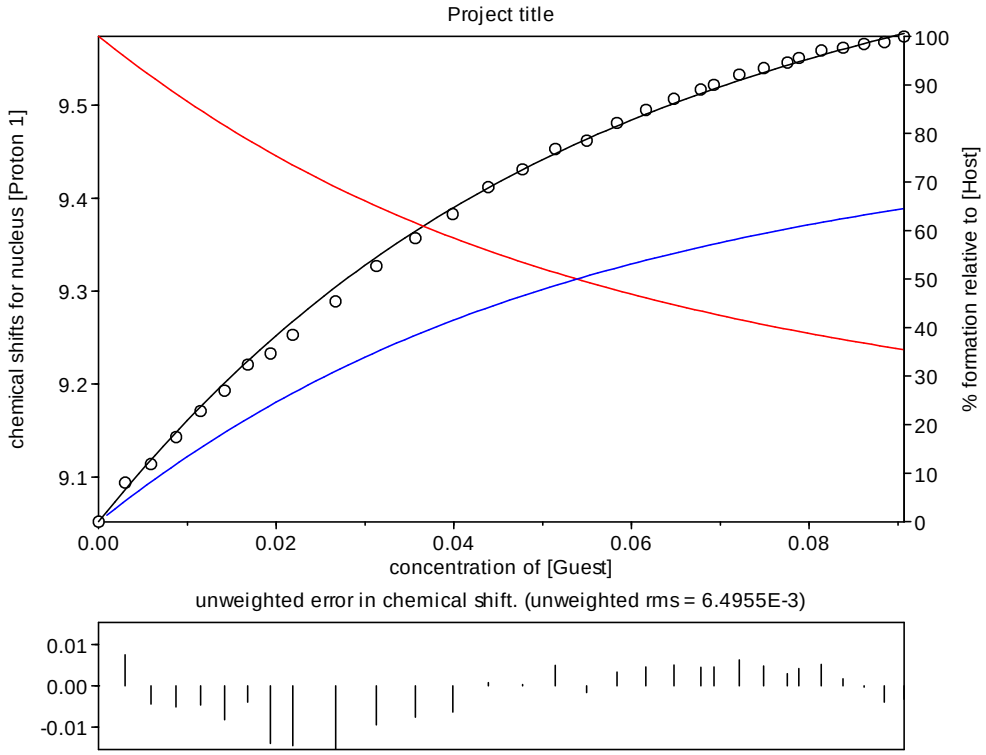
All non hydrogen atoms were refined anisotropically.

H4, H6, H27D, H27E and H27F were located in the difference map and fixed in position during refinement. All other H atoms were placed in calculated positions and refined using a riding model. All other H atoms were placed in calculated positions and refined using a riding model.

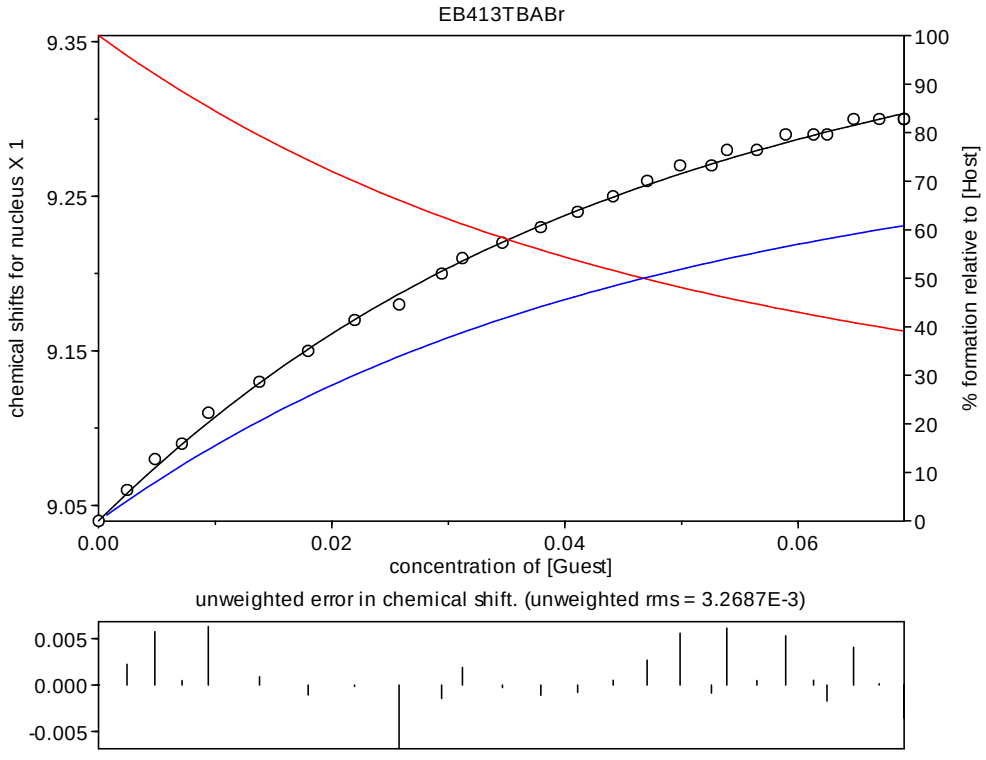
C-H distances: CH3, 0.98\A, CH2 0.99\A, aromatic, 0.95\A. All Uiso(H) values were constrained to be 1.2 times (1.5 for methyl) Ueq of the parent atom. N-H distance: 0.88\A. The Uiso(H) value was constrained to be 1.2 times Ueq of the parent atom.

Chemical formula	$C_{26}H_{37.50}Br_2N_4O_4$
Formula mass	629.92
Crystal system	Monoclinic
Crystal size (mm)	0.46 x 0.37 x 0.15
a/Å	17.580(2)
b/Å	39.483(5)
c/Å	11.7189(15)
α/°	90.00
β/°	130.147(4)
γ/°	90.00
Unit cell volume/Å^3	6217.9(14)
Temperature/K	150(2)
Space group	*C*2/*m*
No. of formula units per unit cell, *Z*	8
Radiation type	MoKα
Absorption coefficient, μ/mm^{-1}	2.642
No. of reflections measured	36400
No. of independent reflections	6240
R_{int}	0.0669
Final R_1 values ($I > 2\sigma(I)$)	0.0628
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1780
Final R_1 values (all data)	0.1115
Final $wR(F^2)$ values (all data)	0.2041
Goodness of fit on F^2	1.061

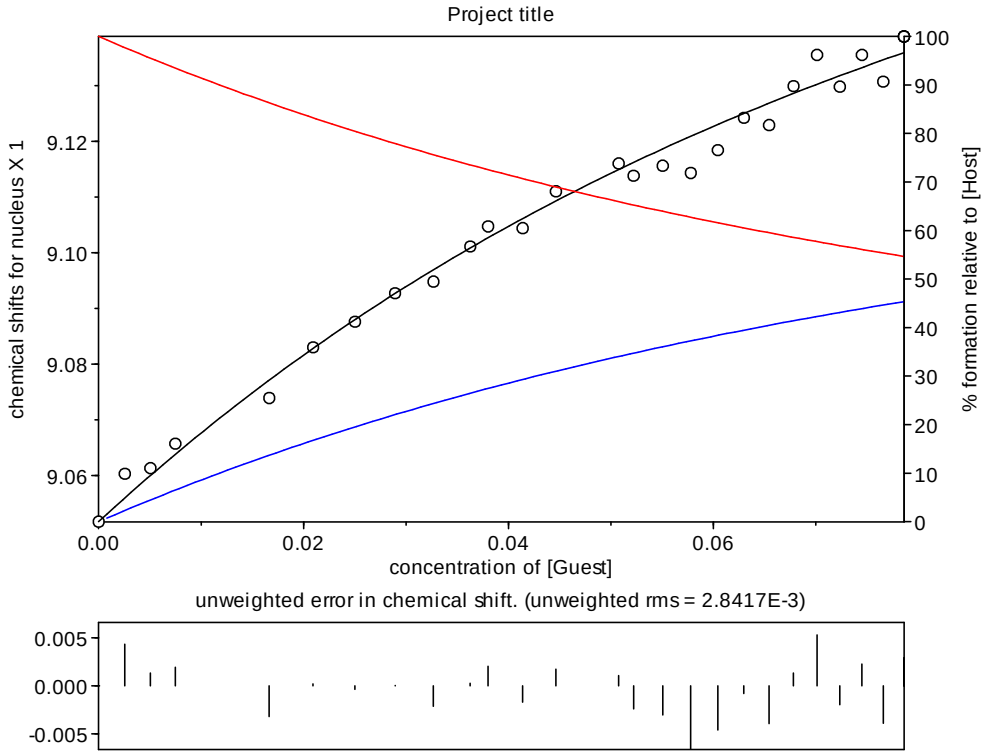
6. HypNMR data



HypNMR fitting data for Cl^- binding by **2**.



HypNMR fitting data for Br^- binding by **2**.



HypNMR fitting data for NO_3^- binding by **2**.

7. References

(1) Sheldrick, G. M. SHELXS-97; *Acta Crystallogr*. 2008, **A64**, 112.

(2) Barbour, L. J. J. *Supramol. Chem*. 2003, **1**, 189.