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Binding of inorganic oxoanions to macrocyclic ligands: interactions of sulfate and dithionate with protonated forms of [18]aneN_6

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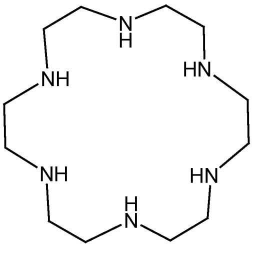
Received (in Durham, UK) 15th June 2004, Accepted 19th August 2004
First published as an Advance Article on the web 19th October 2004

Three sulfate-macrocycle adducts $[H_6\mathbf{L}(HSO_4)_4(SO_4)]\cdot H_2O$ (**1**), $[H_6\mathbf{L}(SO_4)_3]$ (**2**) and $[H_6\mathbf{L}(HSO_4)_2Cl_4]\cdot 2H_2O$ (**3**) (where L = [18]aneN_6) were crystallized from solutions containing the macrocycle and the appropriate inorganic acids, and $[H_4\mathbf{L}(S_2O_6)_2]\cdot 2H_2O$ (**4**) from an aqueous solution of the macrocycle and sodium dithionate. All four structures show that the polyammonium groups on the protonated macrocycle participate in 'co-ordination' or supramolecular interactions with one or more oxygen atoms from the polyoxoanions (*i.e.*, SO_4^{2-}, HSO_4^- or $S_2O_6^{2-}$). In **3**, the protonated macrocyclic cavity holds the two chloride anions in preference to the oxoanions. The sulfate anions show remarkable versatility in their interactions with the macrocycle. Of particular note is a unique η-5 N–H···O cluster involving the sole sulfate anion in **1**, but there are many common features throughout the structures, such as the inclusion of one anion on either side of the macrocycle and the participation of all ammonium protons in H-bonding interactions.

Introduction

Anion co-ordination, or recognition, is an area that has been receiving increased attention in the past two decades,[1,2] with particular emphasis on the thermodynamics of interactions between the anions and a wide variety of synthetic hosts. Interest in the co-ordination of biologically relevant oxoanions, such as sulfate and phosphate, has sparked efforts towards the elucidation of the features of the host that would result in strong affinity and high selectivity. The selectivity exhibited by proteins that bind these anions has provided a strong basis for the study of interactions between non-natural hosts and oxoanions. These efforts have resulted in the synthesis of a range of hosts including cyclic[3,4] and non-cyclic amides,[5] azacryptands,[6] mixed polyaza-ferrocene constructs,[7] porphyrins,[8] guanidinium compounds,[9] mixed oxo-aza macrocycles[10,11] and azamacrocycles.[12–14] The solution characterization of adducts formed by the receptors and oxoanions has involved the use of conductometric, potentiometric (pH titration) and NMR studies and on fewer occasions the solid state structures have been determined by X-ray crystallography. One system that has attracted interest is the hexaazamacrocycle, 1,4,7,10,13,16-hexaazacyclooctadecane ([18]aneN_6, **L**, sometimes referred to as hexacyclen or 18-azacrown-6).



[18]aneN_6, **L**

Until this year, however, only six structures of [18]aneN_6/anion adducts had been published: nitrate/chloride,[15,16] nitrate,[17] hexacyanocobaltate,[18] trifluoromethane sulfonate[19] and pyrophosphate[20] salts. We recently reported the structures of a series of adducts formed by the [18]aneN_6 macrocycle with the halide ions[21] and various protonated forms of the phosphate ions.[22] We herein have extended our investigation to adducts formed by tetra- and hexaprotonated forms of [18]aneN_6 and sulfate and dithionate. Four complexes, $[H_6\mathbf{L}(HSO_4)_4(SO_4)]\cdot H_2O$ (**1**), $[H_6\mathbf{L}(SO_4)_3]$ (**2**), $[H_6\mathbf{L}(HSO_4)_2Cl_4]\cdot 2H_2O$ (**3**) and $[H_4\mathbf{L}(S_2O_6)_2]\cdot 2H_2O$ (**4**), have been prepared and characterized and X-ray crystallography used to determine their structures and to elucidate the predominant anion–cation and anion–anion interactions and how these are influenced by pH.

Experimental methods

Reagents.

All reagents were purchased from commercial suppliers and used as supplied with the exception of 1,4,7,10,13,16-hexaazacyclooctadecane ([18]aneN_6), which was prepared *via* a previously reported method.[22]

Physical Measurements.

Microanalyses were performed by the Campbell Microanalytical Service of the University of Otago in New Zealand. Infrared spectra were recorded using KBr pellets on a Perkin-Elmer 1600 FTIR spectrometer at a resolution of 8 cm^{-1}.

Synthesis.

$[H_6\mathbf{L}(HSO_4)_4(SO_4)]\cdot H_2O$ (1). [18]aneN_6 (26 mg, 0.10 mmol) was dissolved in water (300 mg) and sulfuric acid (conc., 300 mg, 3.2 mmol) was added to the solution. The solution was left to slowly evaporate over a few days to produce clear crystals of **1**. Yield = 43 mg, 56%. Microanalysis (%) Found: C 18.9, H 6.0, N 11.6. Calc. for $C_{12}H_{42}N_6O_{21}S_5$: C 18.8, H 5.5, N 11.0. IR bands (ν, cm^{-1}) 3400 m, 3106 s, 3036 s, 2950 s, 2856 s, 2491 m,

DOI: 10.1039/b409088h

Table 1 Crystal structure and refinement data for **1–4**

	1	2	3	4
Empirical formula	$C_{12}H_{42}N_6O_{21}S_5$	$C_{12}H_{36}N_6O_{12}S_3$	$C_{12}H_{42}Cl_4N_6O_{10}S_2$	$C_{12}H_{38}N_6O_{14}S_4$
FW, g mol^{-1}	766.82	552.65	636.44	618.72
Crystal system	Orthorhomic	Monoclinic	Monoclinic	Monoclinic
Space group	*Pca*21	$P2_1/c$	$P2_1/n$	$C2/m$
a/Å	20.5271(4)	7.9597(2)	6.4044(2)	13.1554(3)
b/Å	8.3909(1)	11.2322(3)	20.6316(5)	11.4761(4)
c/Å	16.6116(2)	12.5897(4)	10.1970(4)	8.7203(3)
β/°		100.673(1)	94.455(1)	97.56(3)
Volume/Å^3	2861.20(7)	1106.11(5)	1343.29(7)	1305.07(7)
Z	4	2	2	2
ρ_{calcd}/g cm^{-3}	1.780	1.659	1.573	1.574
μ/mm^{-1}	0.507	0.409	0.653	0.439
θ range/°	2.43 to 28.28	2.45 to 28.28	2.23 to 28.29	3.48 to 28.31
Reflections collected	23302	9553	9801	4485
Independent reflections	6691	2718	3306	1684
Goodness-of-fit on F^2	0.98	1.032	1.043	1.086
R1^a, wR2^b [$I > 2\sigma(I)$]	0.0448, 0.0860	0.0428, 0.0972	0.0412, 0.0844	0.0509, 0.1389

^{a} $\Sigma||F_o|-|F_c||/\Sigma|F_o|$. ^{b} $[\Sigma w(F_o{}^2-F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$.

2444 m, 2365 m, 1588 m, 1544 w, 1494 m, 1464 m, 1418 m, 1322 s, 1289 s, 1236 s, 1205 s, 1167 s, 1133 s, 1057 s, 1021 s, 934 w, 885 s, 866 s, 763 m, 589 s, 571 s.

[$H_6L(SO_4)_3$] (2). [18]aneN_6 (26 mg, 0.10 mmol) was dissolved in water (300 mg) and sulfuric acid (conc., 300 mg, 3.2 mmol) was added. The pH was adjusted to 2 using sodium hydroxide solution (5 M) after which the solution was left to slowly evaporate. Clear crystals of **2** were produced after several days. Yield = 20 mg, 36%. Microanalysis (%) Found C 26.2, H 7.0, N 15.2. Calc. for $C_{12}H_{36}N_6O_{12}S_3$: C 26.1, H 6.6 N 15.2. IR bands (ν, cm^{-1}) 3501 m, 3036 m, 3008 m, 2855 m, 1619 m, 1605 m, 1522 m, 1495 w, 1464 w, 1430 w, 1418 w, 1322 m, 1300 m, 1150 s, 1087 s, 1058 s, 1030 s, 620 s.

[$H_6L(HSO_4)_2Cl_4$] · $2H_2O$ (3). Crystals of **3** were originally found to crystallize in the filtrate from the synthesis of 1,4,7-triazacyclononane trihydrochloride which was produced *via* the classic Richman-Atkins route.[23] A few crystals of **3** were separated from the mixture and used in X-ray structure determination. A clean synthetic route to **3** has not yet been devised.

[$H_4L(S_2O_6)_2$] · $2H_2O$ (4). [18]aneN_6 (18 mg, 0.06 mmol) was dissolved in water (2 ml). Sodium dithionate (100 mg, 0.48 mmol) added and the solution was left to slowly evaporate. Clear crystals of **4** were produced after several days. Yield = 10 mg, 38%. Microanalysis (%) Found C 22.9, H 5.9, N 13.2. Calc. for $C_{12}H_{38}N_6O_{14}S_4$: C 23.3, H 6.2, N 13.6. IR bands (ν, cm^{-1}) 3376 m, 3246 w, 3016 m, 2846 m, 1457 m, 1397 m, 1320 m, 1247 s, 1214 m, 1144 m, 1050 w, 1025 w, 997 s, 943 w, 914 w, 853 w, 790 m, 755 w, 577 s.

X-ray crystallography.

Single crystal X-ray data for **1–4** were collected on an Enraf-Nonius-Kappa CCD diffractometer with monochromated Mo Kα radiation (λ = 0.71073 Å) at 123(2) K using phi and/or omega scans. Data were corrected for Lorentz and polarization effects. The structures were solved by the direct methods and refined using the full matrix least-squares method of the programs SHELXS-97[24] and SHELXL-97,[25] respectively. The program X-Seed[26] was used as an interface to the SHELX programs, and to prepare the figures with thermal ellipsoids drawn at the 50% probability level where ORTEP representation is employed, and all hydrogen bonds drawn as dashed lines. In the discussion, hydrogen bond distances given are between donor and acceptor heteroatoms. A summary of the crystal data and structure refinement for **1–4** is given in Table 1. Across the series, all non-hydrogen atoms were refined anisotropically without restraint. In **1**, all hydrogen atoms were located on Fourier difference maps and refined isotropically without restraint with the exception of those on the water molecule, which were restrained to idealized geometries. In **2**, all hydrogen atoms were located on Fourier difference maps and refined without restraint. In **3**, all methylene and ammonium hydrogen atoms were assigned in calculated positions and refined isotropically with U(H) = 1.2 U_{eq} (C). The water and hydrogen sulfate protons were located on Fourier difference maps but were restrained to idealized geometries during refinement. In **4**, all macrocyclic hydrogen atoms were located on Fourier difference maps and refined isotropically without restraint. The water molecule ($\frac{1}{2}$ per symmetric unit) was modelled as two oxygen atoms each with $\frac{1}{4}$ occupancy. The minor component of the disordered pair was refined isotropically with its counterpart being refined anisotropically. The hydrogen atoms on the water molecule were unable to be located. CCDC reference numbers 246843–246846.†

Results and discussion

The crystallization of adducts **1**, **2** and **4** was achieved by slow evaporation of aqueous solutions containing [18]aneN_6 and an excess of the appropriate anion as the acid for **1** and **2**, and the sodium salt for **4**. Intergrowth of the crystals of **3** with other crystalline products in the reaction vessel made isolation and thorough analysis impractical. Further attempts to recreate the product also resulted in an intergrown mixture of crystals which included the known [H_6LCl_6] · $4H_2O$ species[21] and **1**. The IR spectra of the adducts showed absorbances that indicated the presence of the macrocycle and anions and microanalyses for **1**, **2** and **4** corresponded to calculated values based on the compositions elucidated from crystal structure determinations.

Structure determinations. [$H_6L(HSO_4)_4(SO_4)$] · H_2O (1).

The asymmetric unit in **1** consists of a hexaprotonated macrocycle whose charge is balanced by four hydrogen sulfate

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† See http://www.rsc.org/suppdata/nj/b4/b409088h/ for crystallographic data in .cif or other electronic format.

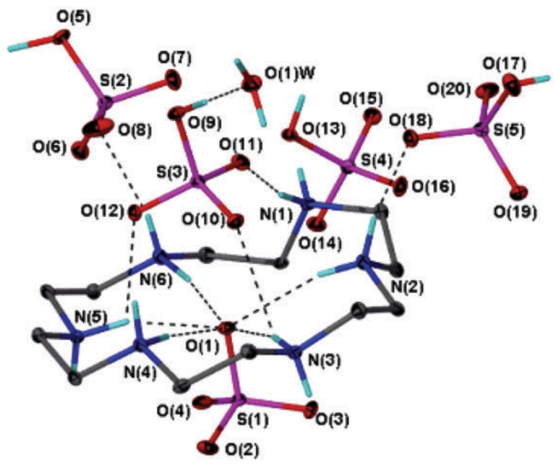

Fig. 1 ORTEP plot of the asymmetric unit in **1**. C–H hydrogen atoms have been removed for clarity.

anions, one sulfate anion and there is one water molecule of crystallization (Fig. 1). The ability to locate all hydrogen atoms gave unequivocal evidence for the degree of protonation of the macrocycle and the configuration of the oxoanions. Hydrogen bonding distances and close contacts are listed in Table 2 and discussed herein.

In **1**, [18]aneN_6 adopts the most asymmetrical conformation seen so far for this macrocycle. This arises from the interaction of five ammonium groups with a single oxygen atom of the SO_4^{2-} anion. The remaining ammonium group (N(1)) is pushed out of the plane of the other five, donating a hydrogen bond to an oxygen atom of a symmetry related SO_4^{2-} anion (N(1)–H(2)···O(2) 2.824(4) Å, 125(3)°) and an oxygen atom of a HSO_4^- anion bound on the opposite side of the ring to the sulfate anion (N(1)–H(1)···O(11) 2.705(4) Å, 168(3)°, see Fig. 1). The anions are hydrogen bonded to water, macrocyclic ammonium groups and each other in a variety of ways, the most notable of which is the η-5 coordinated sulfate anion (S(1)) mentioned above. The penta-coordinated O(1) lies just 0.668(3) Å from the least squares plane of the ring defined by the six nitrogen atoms and is reminiscent of a protonated sapphyrin–phosphate complex reported recently,[27] in which an oxygen atom of a phosphate anion interacts with all five ammonium groups of the sapphyrin ring. The S(3) HSO_4^- anion provides a unique example of co-operative C–H···O hydrogen bonding (Fig. 2) whose existence has been established for other systems.[28,29] Two of the oxygen atoms on this anion each interact with two N–H and one C–H donors, with the C–H···O contacts being particularly short but sacrificing some directionality by sharing the accepting oxygen atom. The remaining oxygen atoms on S(1), O(4) and O(2), are accepting H-bonds from an OH and a NH donor, respectively, while O(3) appears to be participating in a short C–H···O contact (C(7)–H(25)···O(3) 3.151(5) Å, 127(3)°) with a neighbouring macrocycle. Interestingly, the next-closest contact to this oxygen is another carbon atom on the host macrocycle (C(7)–H(15)···O(3) 3.237(5) Å, 134(3)). The HSO_4^- anion (S(3)) on the other side of the ring stands astride three of the macrocyclic

Table 2 Hydrogen bond lengths (Å) and angles (°) in **1** with esd's given in parentheses

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	< (DHA)
N(1)–H(1)···O(11)	0.93(4)	1.79(4)	2.705(4)	168(3)
O(1)W–H(2)W···O(6)#1	0.898(10)	1.92(2)	2.792(4)	163(6)
N(1)–H(2)···O(2)#2	0.82(4)	2.27(4)	2.824(4)	125(3)
N(1)–H(2)···O(13)	0.82(4)	2.54(4)	3.215(4)	141(3)
N(2)–H(3)···O(1)	0.88(5)	2.15(5)	3.011(4)	165(4)
N(2)–H(3)···O(10)	0.88(5)	2.58(5)	3.101(4)	118(4)
N(2)–H(4)···O(18)	0.91(5)	1.88(5)	2.785(4)	169(4)
N(3)–H(5)···O(1)	0.88(4)	2.08(4)	2.939(4)	165(3)
N(3)–H(5)···O(10)	0.88(4)	2.40(4)	2.870(4)	114(3)
N(3)–H(6)···O(20)#3	0.88(5)	1.95(5)	2.798(4)	163(4)
N(4)–H(7)···O(1)	1.00(5)	2.02(5)	3.020(4)	173(4)
N(4)–H(7)···O(2)	1.00(5)	2.62(5)	3.165(4)	114(3)
N(4)–H(8)···O(16)#4	0.90(5)	1.90(5)	2.763(4)	161(4)
N(5)–H(9)···O(1)	1.03(5)	1.98(4)	2.966(4)	159(3)
N(5)–H(9)···O(12)	1.03(5)	2.26(4)	2.818(4)	113(3)
N(5)–H(10)···O(7)#3	0.86(5)	1.88(5)	2.726(4)	170(4)
N(6)–H(11)···O(1)	1.09(5)	1.87(6)	2.950(4)	171(4)
N(6)–H(12)···O(8)	0.88(5)	2.02(5)	2.822(4)	151(5)
N(6)–H(12)···O(12)	0.88(5)	2.57(5)	3.020(4)	113(4)
O(13)–H(3)S···O(4)#2	0.84	1.67	2.503(3)	170.9
O(5)–H(1)S···O(14)#5	1.08(5)	1.51(6)	2.590(4)	177(5)
O(5)–H(1)S···O(15)#5	1.08(5)	2.65(5)	3.223(4)	113(3)
O(9)–H(2)S···O(1)W	1.003(10)	1.544(12)	2.546(4)	177(6)
O(17)–H(4)S···O(15)#6	0.73(6)	1.89(6)	2.615(4)	171(6)
O(1)W–H(1)W···O(19)#7	0.895(10)	1.972(19)	2.850(4)	166(6)
C(11)–H(33)···O(17)#8	0.87(4)	2.53(4)	3.384(5)	166(3)
C(1)–H(13)···O(16)	1.07(4)	2.38(4)	3.230(5)	135(3)
C(7)–H(25)···O(3)#9	1.00(3)	2.44(3)	3.151(5)	127(3)
C(4)–H(20)···O(6)#1	0.96(4)	2.40(4)	3.282(5)	153(3)
C(2)–H(16)···O(8)#10	1.04(4)	2.55(4)	3.384(5)	137(3)
C(2)–H(15)···O(3)	0.92(4)	2.53(4)	3.237(5)	134(3)
C(9)–H(30)···O(12)	1.03(4)	2.50(4)	3.017(5)	110(3)
C(8)–H(28)···O(12)	0.88(4)	2.57(3)	3.085(5)	119(3)
C(4)–H(20)···O(10)	0.96(4)	2.59(4)	3.065(5)	111(3)
C(5)–H(21)···O(10)	1.00(4)	2.54(4)	3.103(5)	115(3)

Symmetry transformations used to generate equivalent atoms: #1 $x + 1/2, -y + 1, z$ #2 $x, y + 1, z$ #3 $x, y - 1, z$ #4 $-x + 2, -y + 1, z + 1/2$ #5 $-x + 3/2, y, z + 1/2$ #6 $x + 1/2, -y + 2, z$ #7 $-x + 5/2, y, z + 1/2$ #8 $x - 1/2, -y + 1, z$ #9 $-x + 2, -y, z + 1/2$ #10 $-x + 2, -y + 1, z - 1/2$.

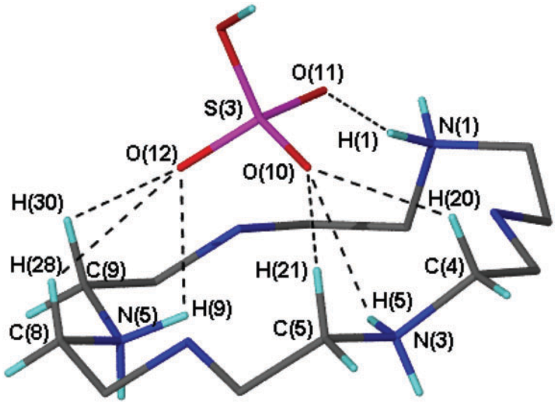

Fig. 2 Interactions between the S(3) HSO_4^- anion and the macrocycle in **1**. Only selected C–H hydrogen atoms are shown.

ammonium groups, each hydrogen bonded to one of the three non-protonated oxygen atoms. The OH group on this anion donates a hydrogen bond to a water molecule in a very short interaction (O(9)–H(2)S···O(1)W 2.546(4) Å, 177(6)°).

The other three HSO_4^- anions, S(2), S(4) and S(5) are similar to S(3) in that each of their three non-protonated oxygens are accepting just one hydrogen bond from NH_2^+ or OH functions, and the OH groups are donating solely to oxygen atoms. All five sulfate moieties and the water molecule assemble into 1D chains that run parallel to the *b* axis (Fig. 3), separated by macrocycles. The components all pack together to form a complex and quite dense H-bonded 3D network. There is a remarkable difference in the preferred interaction modes for the HSO_4^- anions compared to their isostructural but doubly charged HPO_4^{2-} when associating with the same macrocycle.[22] The phosphates tend to have more than one (often more than two) H-bonds to each of their non-protonated oxygen atoms whereas the sulfates in this structure have only one, most likely a result of the increased electrostatic attraction afforded by the extra negative charge on the phosphates. There is also a notable difference in the average O–H···O bonds involving the sulfate and phosphate anions, with the latter usually being around 0.1–0.2 Å shorter.

[$H_6L(SO_4)_3$] (2).

2 contains a hexaprotonated macrocycle lying around a two-fold axis of symmetry with three sulfate anions balancing the charge (Fig. 4). A list of hydrogen bonds and close contacts for **2** is presented in Table 3.

One of the sulfates (S(1)) present in the asymmetric unit has one half occupancy, with expansion of the asymmetric unit revealing the other half with perfectly superimposed sulfur atoms but with its oxygen atoms lying directly on the opposite side of the sulfur atom (*i.e.* O(1)–S(1)–O(1)* = 180°). Each has O(1) bridging neighbouring macrocycles through N(2)–H(4)···O(1)···H(6)–N(3). O(2) acts in a similar manner utilizing N(2) and N(3) on two separate macrocycles to those bridged by O(1) while O(3) bridges two macrocycles through N(2) and N(3), however the N(2)–H(4) donor is shared by O(1) and N(3)–H(6) by O(2). The remaining oxygen, O(4), is involved in three interactions: one sharing the N(2)–H(4) hydrogen bond to O(2) and the other two involving short C–H···O contacts (C(1)–H(7)···O(4) 3.119(4) Å, 164.2(18)°, C(5)–H(15)···O(4) 3.101(3) Å, 135(2)°). The other sulfate (S(2)) is bound to its host macrocycle by two interactions through two oxygen atoms (N(2)–H(3)···O(5) 2.880(3) Å, 164(2)°, N(1)–H(1)···O(7) 2.742(2) Å, 175(2)°), with an almost-linear third interaction with an adjacent macrocycle occupying a third oxygen (N(3)–H(5)···O(6) 2.694(3) Å, 179(2)°) in conjunction with a short C–H···O contact (C(2)–H(10)···O(6) 3.221(3) Å, 149(2)°). The fourth oxygen atom on S(2), O(8), does not participate in significant interactions with the possible exception of a weak C–H···O contact (C(3)–H(11)···O(8) 3.340(3) Å, 153(2)°).

The anions are all isolated from one another in the lattice, owing to their lack of H-bond donating groups, and in contrast to **1**, there are no solvent molecules in the lattice (Fig. 5). The macrocycle has all twelve of its ammonium protons involved in N–H···O interactions. The closest oxygen atom (O(7)) to the least squares plane of the macrocycle lies 0.876(3) Å above it.

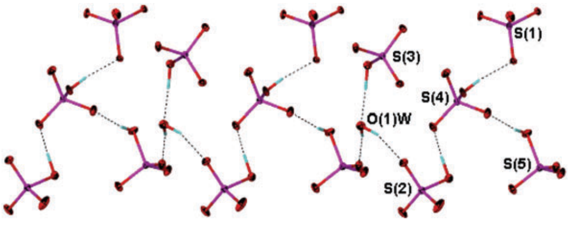

Fig. 3 ORTEP plot of the 1D chains formed by the HSO_4^- and SO_4^{2-} anions, and water in **1**. Macrocycles have been removed for clarity.

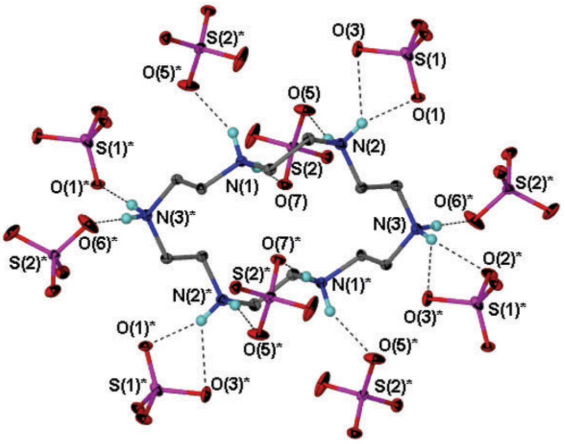

Fig. 4 ORTEP plot showing the hydrogen bonding environment around the macrocycle in **2**. Only one of the symmetry related half occupancy sulfate anions is shown. C–H hydrogen atoms have been removed for clarity.

Table 3 Hydrogen bond lengths (Å) and angles (°) in **2** with esd's given in parentheses

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	<(DHA)
N(1)–H(1)···O(7)	0.93(3)	1.81(3)	2.742(2)	175(2)
N(1)–H(2)···O(5)#3	0.91(2)	2.06(2)	2.892(2)	151(2)
N(1)–H(2)···O(6)#3	0.91(2)	2.52(2)	3.309(3)	145(2)
N(2)–H(3)···O(5)	0.86(3)	2.04(3)	2.880(3)	164(2)
N(2)–H(3)···O(7)	0.86(3)	2.55(3)	3.222(2)	135(2)
N(2)–H(4)···O(4)#1	0.92(3)	1.81(3)	2.643(3)	148(2)
N(2)–H(4)···O(1)	0.92(3)	1.94(3)	2.831(3)	160(2)
N(2)–H(4)···O(3)	0.92(3)	2.40(3)	3.090(3)	132(2)
N(2)–H(4)···O(2)#1	0.92(3)	2.41(3)	3.169(3)	140(2)
N(3)–H(5)···O(6)#4	0.93(3)	1.76(3)	2.694(3)	179(2)
N(3)–H(5)···O(8)#4	0.93(3)	2.60(3)	3.133(2)	117(2)
N(3)–H(6)···O(1)#5	0.91(3)	2.00(3)	2.906(3)	178(2)
N(3)–H(6)···O(2)#6	0.91(3)	2.08(3)	2.786(3)	133(2)
N(3)–H(6)···O(3)#6	0.91(3)	2.31(3)	3.039(4)	137(2)
C(1)–H(7)···O(4)#7	0.94(2)	2.20(2)	3.119(4)	164(2)
C(2)–H(10)···O(6)#3	0.97(2)	2.36(2)	3.221(3)	149(2)
C(3)–H(11)···O(8)#8	1.01(2)	2.41(2)	3.340(3)	153(2)
C(5)–H(15)···O(4)#5	0.98(2)	2.33(2)	3.101(3)	135(2)
C(5)–H(15)···O(5)#6	0.98(2)	2.42(2)	3.019(2)	119(2)

Symmetry transformations used to generate equivalent atoms: #1 $-x$, $-y$, $-z$ #3 $-x$, $-y+1$, $-z$ #4 $-x+1$, $y-1/2$, $-z+1/2$ #5 $-x+1$, $-y$, $-z$ #6 $x+1$, y, z #7 $-x$, $y+1/2$, $-z-1/2$ #8 x, $-y+1/2$, $z-1/2$.

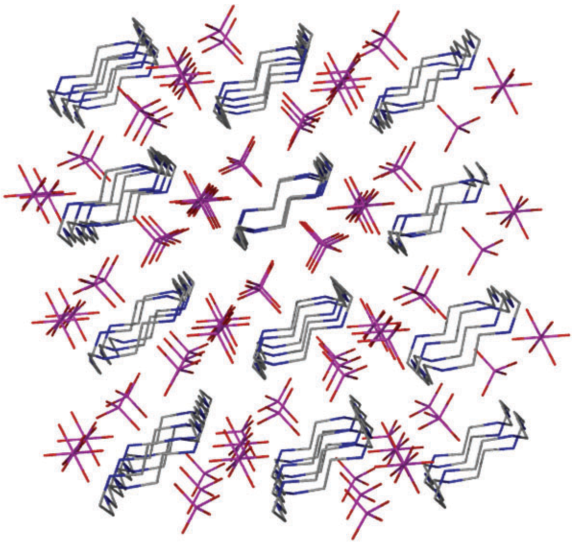

Fig. 5 Packing of the structure in **2** viewed down the *b* axis. Both parts of the $\frac{1}{2}$ occupancy sulfate are shown. Hydrogen atoms have been removed for clarity.

$[H_6L(HSO_4)_2Cl_4]\cdot 2H_2O$ (3)

The structure of **3** contains a hexaprotonated macrocycle, two hydrogen sulfate anions and four chlorides, with two waters of crystallization (Fig. 6). Table 4 contains a list of hydrogen bonds and close contacts in the structure.

The macrocycle lies around a two-fold crystallographic axis of symmetry, and is elongated along the axis defined by N(3) and N(3)*. Preference is given to chloride as a cavity guest, in spite of fact that a weak C–H···Cl contact (C(6)–H(17)···Cl(2) 3.605(2) Å, 160°) completes the trigonal co-ordination geometry often adopted by chlorides.[30] [18]aneN_6 was observed to chelate chloride anions in preference to nitrates in a structure reported by Cullinane *et al.*,[15] leaving the nitrates to form hydrogen bonded networks with water molecules much like those formed by sulfate and water in the present structure. Cl(2) lies 1.9221(6) Å from the least squares plane of the macrocycle, significantly further out than the chelated oxygen atoms in **1**, **2** and **4**, due to its larger van der Waals radius. The hydrogen sulfate and water moieties link up to form 1D chains (Fig. 7), which lie parallel to each other (but out of direct contact) to form 2D sheets that are separated by layers of macrocycle-bound chlorides. Cl(1) has the only interaction between the chloride anions and the water–sulfate chains (O(1)W–H(2)W···Cl(1) 3.2293(16) Å, 153(3)°). It also shows the trigonal pyramid motif, acting as a bridge between macrocycles (N(2)···Cl(1)···N(3)*). The distances from the planes of their H-bond donors are 1.279(1) Å and 1.731(2) Å for Cl(1) and Cl(2), respectively.

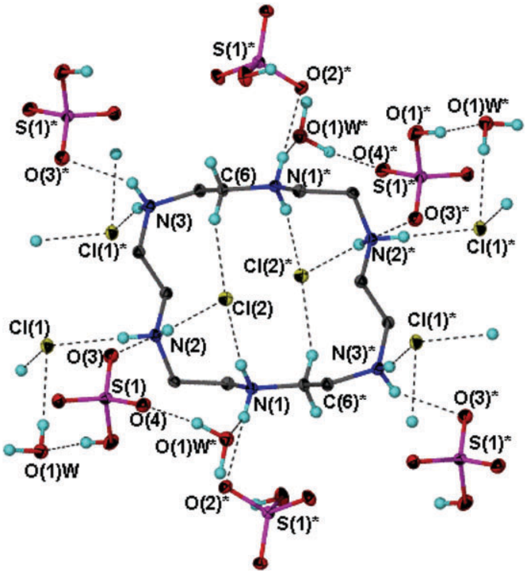

Fig. 6 ORTEP plot of the hydrogen bonding environment around the macrocycle in **2**. Non-interacting C–H hydrogen atoms have been removed for clarity. All hydrogen atoms participating in hydrogen bonds to chloride anions are included.

Table 4 Hydrogen bond lengths (Å) and angles (°) in **3** with esd's given in parentheses

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	>(DHA)
N(1)–H(1)···Cl(2)	0.92	2.16	3.0573(18)	165
N(1)–H(2)···O(2)#2	0.92	2.11	2.887(2)	141
N(1)–H(2)···O(1)W#3	0.92	2.29	2.982(2)	132
N(2)–H(4)···Cl(1)	0.92	2.24	3.1173(18)	160
N(2)–H(3)···Cl(2)	0.92	2.33	3.1658(18)	151
N(3)–H(6)···O(3)#4	0.92	2.11	2.842(2)	136
N(3)–H(6)···O(2)#4	0.92	2.52	3.000(2)	113
N(3)–H(5)···Cl(1)#5	0.92	2.19	3.0916(19)	165
O(1)W–H(1)W···O(4)#6	0.994(10)	1.746(11)	2.731(2)	170(3)
O(1)W–H(2)W···Cl(1)	0.991(10)	2.31(2)	3.2293(16)	153(3)
O(1)–H(19)···O(1)W	0.998(10)	1.573(14)	2.554(2)	166(4)
C(6)–H(17)···Cl(2)	0.99	2.66	3.605(2)	160

Symmetry transformations used to generate equivalent atoms: #2 $x - 1/2, -y + 1/2, z + 1/2$ #3 $x + 1/2, -y + 1/2, z + 1/2$ #4 $-x + 1, -y, -z + 1$ #5 $-x, -y, -z + 1$ #6 $x - 1/2, -y + 1/2, z - 1/2$.

The two O–H···O contacts between the water and HSO_4^- anions are very different, with the interaction involving hydrogen sulfate as donor being significantly shorter than its counterpart: 2.554(2) Å, 166(4)° for O(1)–H(19)···O(1)W compared to 2.731(2) Å, 170(3)° for O(1)W–H(1)W···O(4). The hydrogen sulfate itself shows a different overall co-ordination geometry to the four found in **1**, with one of its oxygen atoms, O(3), accepting two hydrogen bonds from adjacent macrocycles whereas the HSO_4^- anions in **1** only accept one H-bond to each of their three non-protonated oxygen atoms.

$[H_4L(S_2O_6)_2]\cdot 2H_2O$ (4).

The structure of **4** (Fig. 8) consists of a tetraprotonated macrocycle lying on a four-fold crystallographic axis of symmetry, two disordered waters and two dithionate anions which are involved in hydrogen bonding to the ammonium groups, one above and one below the ring. In the asymmetric unit, the dithionate is one half dithionate split along a plane defined by O(1)–S(2)–S(1)–O(3), with these atoms all having half occupancy. The water molecule is lying in the middle of a hydrophobic hole formed from the CH_2 groups of surrounding macrocycles, with its closest and only interaction being with

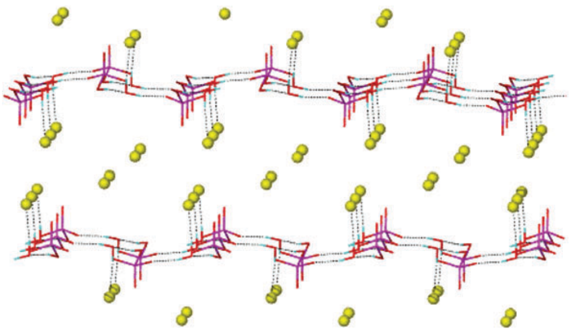

Fig. 7 Packing diagram of **3** highlighting the 2D sheets formed by sulfate anions and water.

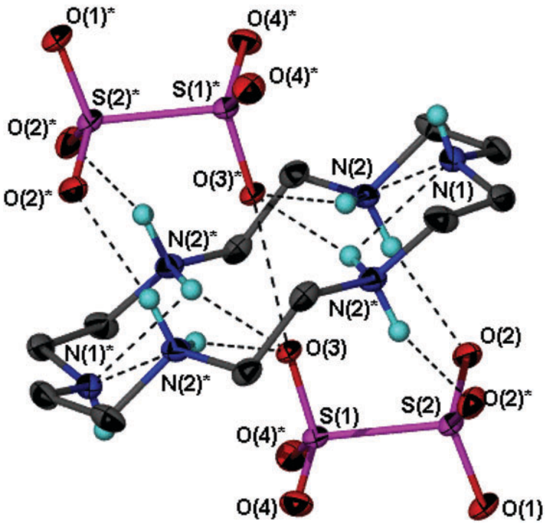

Fig. 8 ORTEP plot of the hydrogen bonding environment surrounding the macrocycle in **4**. The dashed line connecting O(3) and O(3)* through the macrocyclic cavity indicates a close contact rather than a hydrogen bond.

one of the dithionate oxygen atoms (O(1)W–O(1) 2.803(20) Å), with O(1) presumably acting as a hydrogen bond acceptor.

The dithionate anion sits above the macrocycle and is supported by four N–H···O interactions. The mode of interaction of the macrocycle with the dithionate anion is somewhat reminiscent of that seen in the analogous $CF_3SO_3^-$ adduct with [18]aneN$_6$ which had the anion bound to the cavity by a single oxygen atom as in **4**, with two separate N–H···F interactions at the other end of the macrocycle.[19] In that example, the shortness of the C–S bond compared to the S–S bond in the present structure allowed the two ammonium groups chelating the fluorines to use their other protons to provide two additional N–H···O interactions to the already doubly-bound oxygen atom (N–H···O ~2.9 Å). The same interactions are not possible in the present structure due to the two N(2)–H(3)···O(2) bonds stretching the macrocycle and leaving the N···O distance to the chelated oxygen atom at around 3.1 Å. Notably, the O(3)···O(3)* distance through the plane of the macrocycle is quite short, 2.652(5) Å, and suggestive of an O–H···O interaction, however there is no evidence supporting the presence of a proton between these two oxygen atoms. The anions and water molecules form 1D chains that run parallel to the *a–b–c* plane, threading through the macrocycle with the short O(3)···O(3)* contact (Fig. 9).

All four of the macrocyclic ammonium groups are involved in O–H···O interactions with dithionate groups with the macrocyclic amines finding no suitable acceptors. The macrocycle is elongated along its N(1)–N(1)* axis (which is also the S(1)–S(2) axis of the anions on either side of the ring) and in contrast to the hexaprotonated macrocycles in **2** and **3**, has all of its nitrogen atoms directed in towards the center of the macrocycle. This is not surprising as the positive charge of the macrocycle is neutralized solely by the two anions chelated within the ring, hence there is no requirement for charge distribution to an external negatively-charged component. There is a total of four internal N–H···N interactions (three symmetry generated, N(2)–H(2)···N(1) 2.823(3) Å, 110(2)°) which help to maintain the orientation of the amines, with the main driving force of the macrocyclic elongation being the two bridges (N–H···O···H–N and N–H···O–S–O···H–N) running perpendicular to its longest N–N axis. A list of the hydrogen bonds in **4** is given in Table 5. The packing of the structure (Fig. 10) shows the macrocycles all oriented in the same way within the lattice forming stacks of alternating macrocycle–dithionate moieties, separated by solvent water molecules.

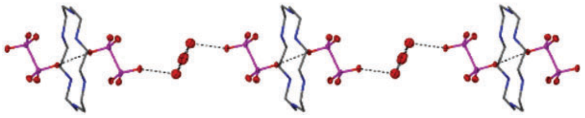

Fig. 9 1D chain formed by the disordered water molecules and dithionate.anions in **4** (ORTEP) threaded through the macrocycles (stick representation).

Table 5 Hydrogen bond lengths (Å) and angles (°) in **4** with esd's given in parentheses

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	<(DHA)
N(2)–H(3)···O(2)	0.94(4)	2.12(4)	2.966(3)	150(3)
N(2)–H(3)···O(2)#4	0.94(4)	2.64(4)	3.181(3)	117(3)
N(2)–H(2)···O(3)#5	0.87(3)	2.11(3)	2.911(3)	154(3)
N(2)–H(2)···O(3)	0.87(3)	2.58(3)	3.106(3)	120(2)
N(2)–H(2)···N(1)	0.87(3)	2.41(3)	2.823(3)	110(2)

Symmetry transformations used to generate equivalent atoms: #4 $-x + 1/2, -y + 1/2, -z + 2$ #5 $-x + 1, -y, -z + 2$.

Hydrogen bonding modes of sulfur oxoanions.

Fig. 11 shows the hydrogen bonding modes for the hydrogen sulfate anions found in **1** and **3**. For each HSO_4^- anion, each oxygen atom is accepting only one hydrogen bond with the notable exception of the tripodal hydrogen bonding involving C–H and N–H donors for the anion in **1**. The OH group of each anion invariably donates a hydrogen bond to an oxygen atom of either another anion or a water molecule.

The sulfate and dithionate anions behave differently to the hydrogen sulfate anions in that there is a tendency towards multiple hydrogen bonds to one oxygen atom (Fig. 12). Interestingly, three of the six dithionate oxygen atoms are not participating in any hydrogen bonds, and one oxygen atom on each sulfate anion is also completely free of H-bond interactions. In the case of the sulfate participating in the η-5 hydrogen bonding motif there are two oxygen atoms devoid of H-bond interactions, however, there is a particularly strong O–H···O interaction with a neighbouring HSO_4^- anion with an O···O distance of 2.503(3) Å. Whilst most of the N–H···O interactions have N···O distances of between 2.7 Å and 3.0 Å there are stronger interactions down to 2.64 Å. The C–H···O

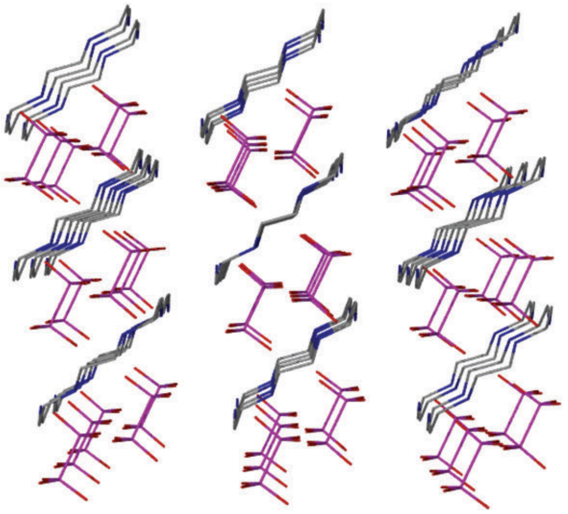

Fig. 10 Packed view of the macrocycles and dithionate anions in **4** viewed down the *b* axis. Water molecules are not shown for clarity.

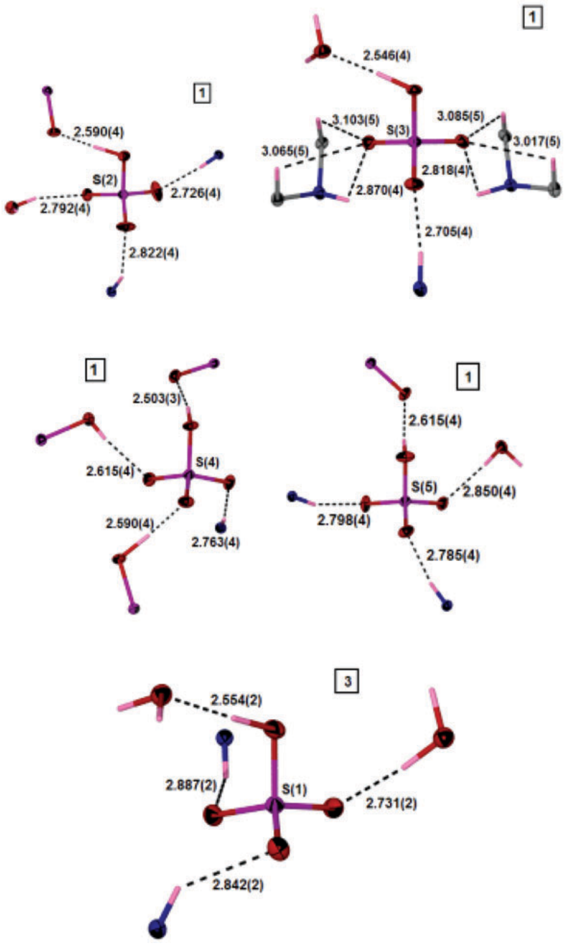

Fig. 11 Hydrogen bonding modes for the hydrogen sulfate anions in **1** and **3**. Distances between heteroatoms are given in Å. Compound numbers are given in insets.

interactions for both HSO_4^- and SO_4^{2-} anions are invariably weaker with C···O distances lying between 3.0 Å and 3.3 Å.

Conclusion

A number of unusual structural features have been elucidated in adducts formed by [18]aneN_6 and the sulfur oxoanions dithionate and sulfate, including an η-5 hydrogen bonding motif to a single sulfate oxygen atom with a unique asymmetric conformation of the macrocycle and a series of co-operative C–H···O hydrogen bonding interactions contributing to the tripodal binding of a hydrogen sulfate anion to the other side of the macrocyclic cavity. In the dithionate adduct there is a very close O···O contact between dithionate anions through a macrocyclic cavity with (surprisingly) no hydrogen bond directly connecting the two, highlighting the ability of [18]aneN_6 to bring two negatively charged atoms to within the sum of their van der Waals radii. When presented with the option of chelating to a chloride anion, the macrocycle binds it in preference to sulfate (and nitrate[15,16]), allowing anions with a greater number of hydrogen bonding possibilities to form networks beyond the macrocycle to stabilize the chloride binding motif in the solid state.

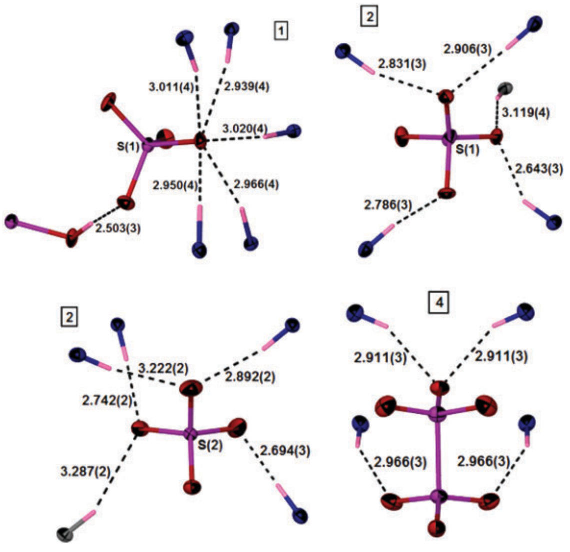

Fig. 12 Hydrogen bonding modes for the sulfate and dithionate anions in **1**, **2** and **4**. Distances between heteroatoms are given in Å. Compound numbers are given in insets.

Acknowledgements

This work was supported by the Australian Research Council. ACW gratefully acknowledges the award of a Teaching fellowship and Departmental Scholarship from Monash University.

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