3,6,9,16,19,22-Hexaazatricyclo[22.2.2.2^{11,14}]triconta-1(26),11(29),12,14(30),24,27-hexaene, C$_{24}$H$_{38}$N$_6$, as a building block in supramolecular chemistry: structures in two and three dimensions

Christopher Glidewell,[a]* George Ferguson,[a]† Richard M. Gregson[a] and Alan J. Lough[b]

[a]School of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, Scotland, and [b]Lash Miller Chemical Laboratories, University of Toronto, Toronto, Ontario, Canada M5S 3H6

† On leave from: Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1.

Correspondence e-mail: cg@st-andrews.ac.uk

The adduct (1) formed between the hexaaza macrocycle 3,6,9,16,19,22-hexaazatricyclo[22.2.2.2^{11,14}]triconta-1(26),-11(29),12,14(30),24,27-hexaene, C$_{24}$H$_{38}$N$_6$, and 4,4′-sulfonyldiphenol, O$_2$S(C$_6$H$_4$OH)$_2$, is a salt [(C$_{24}$H$_{40}$N$_6$)$^{2+}$]·2[(HOC$_6$H$_4$SO$_2$C$_6$H$_4$O)$^-$], and the adduct (2) formed by the same macrocyclic amine with 4,4′-biphenol is an aquated salt which also contains neutral biphenol molecules, [(C$_{24}$H$_{40}$N$_6$)$^{2+}$]·2[(HOC$_6$H$_4$C$_6$H$_4$O)$^-$]·(HOC$_6$H$_4$C$_6$H$_4$OH).2H$_2$O. In both compounds the cations lie across centres of inversion: there are two crystallographically distinct cation sites in (1) and the conformations of the cations occupying them are quite different. In (2) the single type of cation site is occupied by a conformationally disordered cation: the major and minor components represent two further distinct conformers. In (1) the anions are linked by O—H···O hydrogen bonds into chains, and each cation is linked by a total of six N—H···O hydrogen bonds to anions in four different chains, so linking the chains into continuous sheets. In (2) the anions and the water molecules are linked into sheets, which are further linked into a continuous three-dimensional framework by both the cations and the neutral biphenol units.

1. Introduction

The tetraaza macrocycle cyclam (1,4,8,11-tetraazacyclotetradecane, C$_{10}$H$_{24}$N$_4$, I) readily forms hydrogen-bonded adducts with bisphenols (Ferguson *et al.*, 1998; Ferguson, Gregson & Glidewell, 1999). In these adducts the macrocyclic tetraamine captures two protons which are held within the N$_4$ cavity of the [(cyclam)H$_2$]$^{2+}$ cation, forming intramolecular N—H···N hydrogen bonds, while the axial N—H bonds normal to the plane of the macrocycle form hydrogen bonds with the anionic components, generating elaborate multidimensional supramolecular structures.

Developing this theme, we have now commenced a new investigation into the use of the hexaaza macrocycle 3,6,9,16,19,22-hexaazatricyclo[22.2.2.2^{11,14}]triconta-1(26),11-(29),12,14(30),24,27-hexaene, C$_{24}$H$_{38}$N$_6$ (II), as a building block in supramolecular chemistry, and here we report the synthesis and structures of its adducts (1) and (2) formed with 4,4′-sulfonyldiphenol, O$_2$S(C$_6$H$_4$OH)$_2$, and 4,4′-biphenol (HOC$_6$H$_4$—C$_6$H$_4$OH), respectively.

Co-crystallization of the macrocyclic hexaamine (II) and the bisphenols from solutions in methanol yields with 4,4′-sulfonyldiphenol a 1:2 adduct (1), which proves to be the salt [(C$_{24}$H$_{40}$N$_6$)$^{2+}$]·2[(HOC$_6$H$_4$SO$_2$C$_6$H$_4$O)$^-$], and with 4,4′-biphenol an aquated 1:3 adduct (2), also a salt, [(C$_{24}$H$_{40}$N$_6$)$^{2+}$]·-

2[(HOC$_6$H$_4$C$_6$H$_4$O)$^-$]·(HOC$_6$H$_4$C$_6$H$_4$OH).2H$_2$O, in which both anionic and neutral biphenol units are present.

(I)   (II)
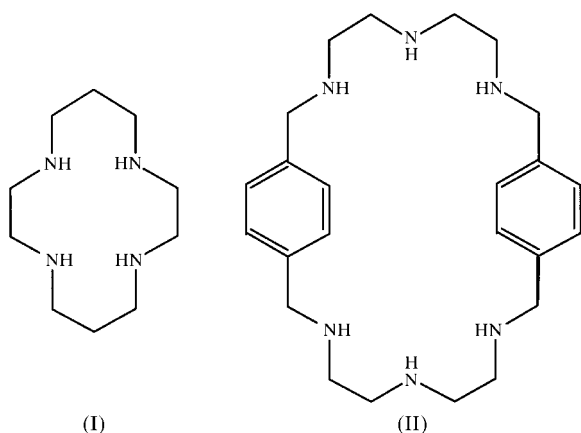
2. Experimental

2.1. Syntheses

The macrocycle (II) was prepared using published methods (Chen & Martell, 1991; Comba *et al.*, 1996). Co-crystallization of equimolar quantities of (II) and 4,4′-sulfonyldiphenol from a solution in methanol yielded crystals of the adduct (1) which were suitable for single-crystal X-ray diffraction. Analysis for (1): found C 63.3, H 6.7, N 9.4%; C$_{48}$H$_{58}$N$_6$O$_8$S$_2$ requires C 63.3, H 6.4, N 9.2%. The same product was formed when molar ratios of amine to phenol in the range 2:1 to 1:2 were employed, and also when ethanol was used as the solvent rather than methanol. Co-crystallization of (II) and 4,4′-biphenol always gave mixtures of the adduct (2) along with free 4,4′-biphenol, and hence the elemental analyses were inconsistent.

2.2. Data collection, structure solution and refinement

Diffraction data were collected at 100 (1) K using a Nonius Kappa-CCD diffractometer, with graphite-monochromated Mo *Kα* radiation (λ = 0.71073 Å). Other details of cell data, data collection and refinement are summarized in Table 1. For (1) and (2) the space groups $P2_1/n$ and $P2_1/c$, respectively, were uniquely determined from the systematic absences. The structures were solved by direct methods using *SHELXS*97

(a)

(b)

(c)

(d)
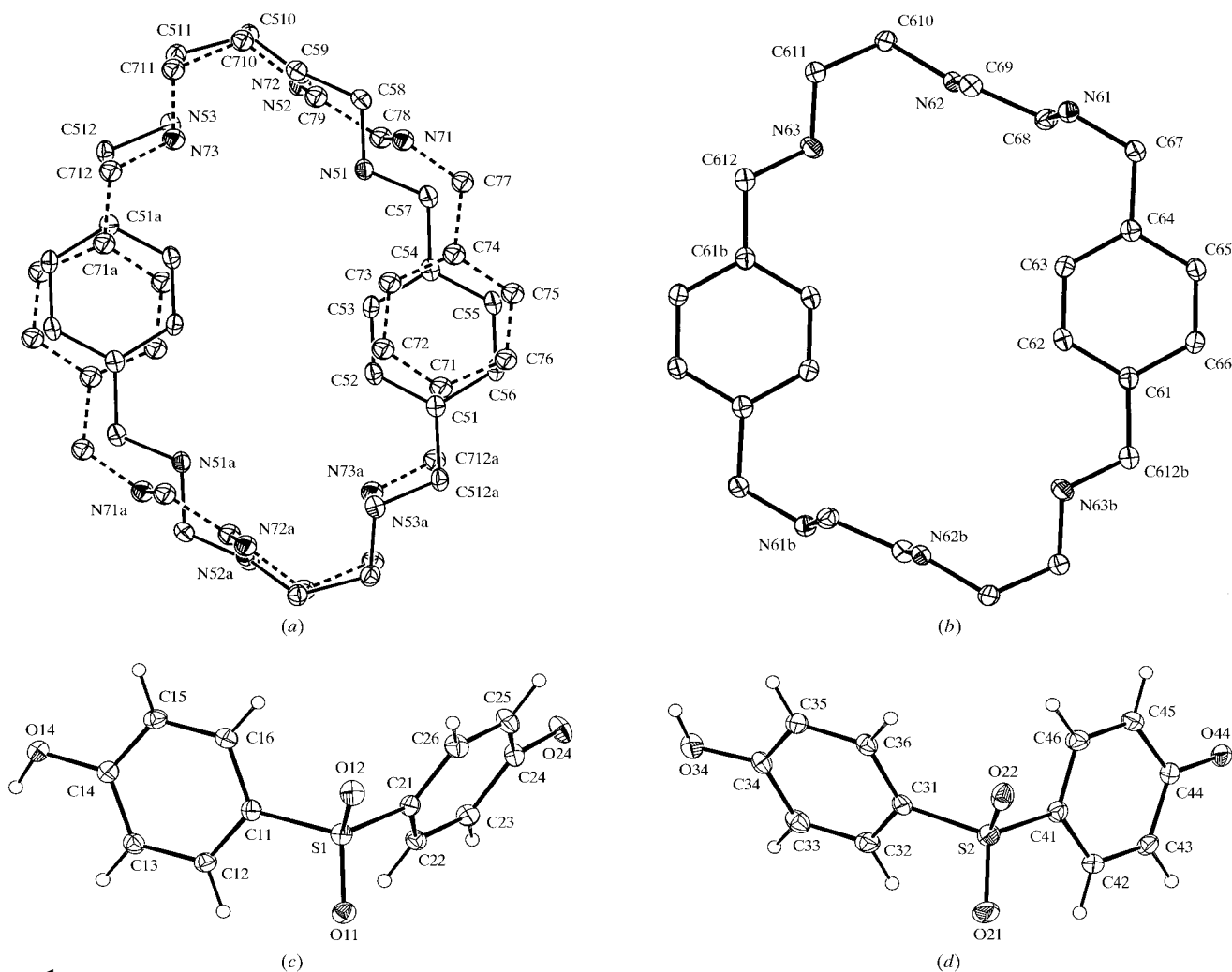
Figure 1
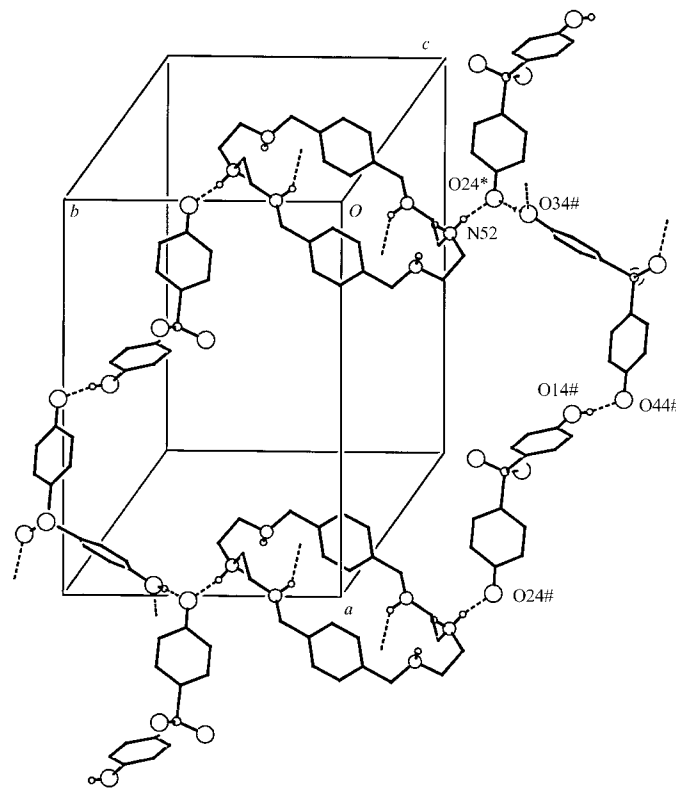The molecular components of (1), showing the atom-labelling scheme. For the cationic components, the two conformers at site 1 are shown superimposed; the major component is drawn with solid bonds, the minor components with dashed bonds. For all cations, H atoms are omitted for the sake of clarity. Displacement ellipsoids are drawn at the 30% probability level: the minor conformer at site 1 was refined isotropically.
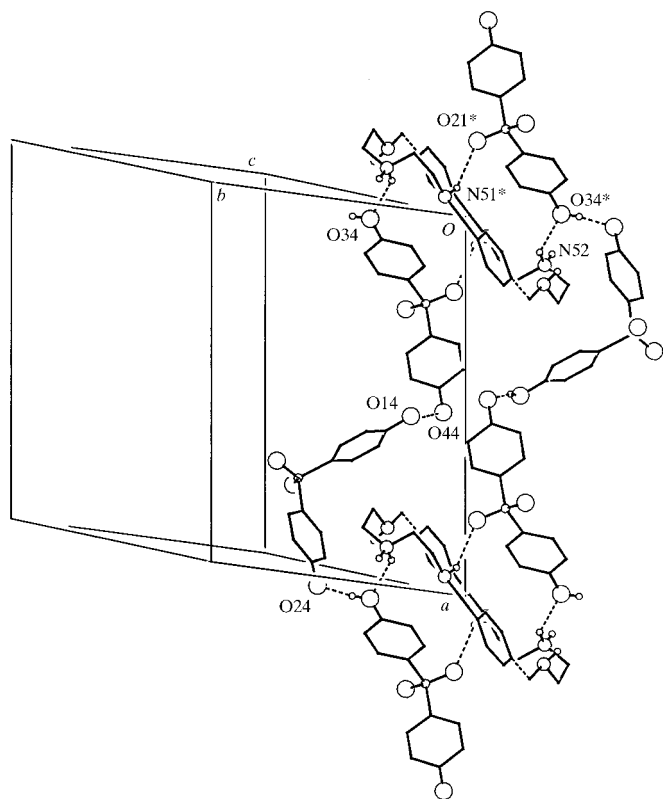
Figure 2
Part of the crystal structure of (1) showing the pair of [100] chains containing phenolate anions at (x, y, z) and $(-x, -y, -z)$, linked by a site 1 cation. For the sake of clarity, H atoms bonded to C are omitted, and only the major conformer of the cation is shown; atoms marked with a star (*) are at the symmetry position $(-x, -y, -z)$.

Figure 3
Part of the crystal structure of (1) showing the pair of [100] chains containing phenolate anions at $(x, -1 + y, z)$ and $(-x, 1 - y, -z)$, linked by a site 1 cation. For the sake of clarity, H atoms bonded to C are omitted, and only the major conformer of the cation is shown; atoms marked with a star (*) or a hash (#) are at the symmetry positions $(-1 + x, -1 + y, z)$ and $(x, -1 + y, z)$, respectively.

(Sheldrick, 1997a) and refined with all data on F^2 using *SHELXL*97 (Sheldrick, 1997b). A weighting scheme based upon $P = [F_o^2 + 2F_c^2]/3$ was employed in order to reduce statistical bias (Wilson, 1976). No absorption corrections were necessary. In both structures the cations lie across centres of inversion, but it was apparent from an early stage that in each of (1) and (2) there was some disorder in the cation skeletons. In (1), where there are two independent cations, that centred at $(\frac{1}{2}, \frac{1}{2}, 0)$ is fully ordered, but the cation centred at the origin is disordered over two sets of sites with major and minor occupancies 0.920 (3) and 0.080 (3); in adduct (2) there is only one site, but again the cation is disordered over two sets of sites with occupancies 0.789 (4) and 0.211 (4). In both compounds the minor conformer was refined isotropically, initially with soft restraints applied to the bond lengths. All H atoms were located from difference maps, and all were fully ordered relative to the occupancies of the non-H-atom sites to which they are bonded: all were included in the refinements as riding atoms. The diagrams were prepared with the aid of *PLATON* (Spek, 1999). Figs. 1 and 5 show the molecular components of compounds (1) and (2), and Figs. 2–4 and 6–9 show aspects of their crystal structures. Hydrogen-bond dimensions are presented in Table 2 and other selected dimensions in Table 3.[1]

---

[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA0100). Services for accessing these data are described at the back of the journal.

2.3. Molecular modelling

Conformational optimizations were carried out by molecular mechanics using the MM2+ force field, followed by simulated annealing using the *HyperChem* package (Hypercube Inc., 1999): the molecular dynamics calculations ran from 100 to 1300 K in 1 ps, followed by 5 ps at 1300 K, and final cooling to 0 K in 3 ps. Finally, single-point calculations of molecular energy were made using the AM1 method (Dewar *et al.*, 1985).

3. Results and discussion

3.1. Co-crystallization behaviour

Compound (1) was readily obtained in analytically pure form from mixtures of a wide range of compositions of the hexaamine (II) and 4,4′-sulfonyldiphenol, in methanol or ethanol as the solvent: as with other adducts of this general type, the constant composition of the crystalline product, compared with the variation in the composition of the initial solution, suggests that (1) represents a rather deep minimum on the overall potential energy surface for this system. Unlike the analogous adduct formed by the tetraaza macrocycle *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (tet-a), $C_{16}H_{36}N_4$ (III), which crystallizes as a

Table 1
Experimental details.

	(1)	(2)
Crystal data		
Chemical formula	$C_{24}H_{40}N_6 \cdot 2(C_{12}H_9O_4S)$	$C_{24}H_{40}N_6 \cdot C_{12}H_{10}O_2 \cdot 2(C_{12}H_9O_2) \cdot 2(H_2O)$
Chemical formula weight	911.12	1005.23
Cell setting	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
a (Å)	18.0527 (5)	12.3442 (4)
b (Å)	13.1074 (2)	7.6496 (3)
c (Å)	20.5723 (5)	29.1745 (9)
β (°)	108.2524 (11)	110.686 (2)
V (Å^3)	4622.97 (18)	2577.29 (15)
Z	4	2
D_x (Mg m^{-3})	1.309	1.295
Radiation type	Mo $K\alpha$	Mo $K\alpha$
Wavelength (Å)	0.71073	0.71073
No. of reflections for cell parameters	9421	4832
θ range (°)	4.10–26.32	4.20–25.63
μ (mm^{-1})	0.176	0.086
Temperature (K)	100 (1)	100 (1)
Crystal form	Block	Plate
Crystal size (mm)	$0.35 \times 0.34 \times 0.31$	$0.25 \times 0.20 \times 0.04$
Crystal colour	Colourless	Colourless
Data collection		
Diffractometer	Kappa-CCD	Kappa-CCD
Data collection method	φ scans and ω scans with κ offsets	φ scans and ω scans with κ offsets
Absorption correction	Multi-scan	Multi-scan
$T_{\min}$	0.9574	0.9787
$T_{\max}$	0.9657	0.9966
No. of measured reflections	40273	19716
No. of independent reflections	9421	4832
No. of observed reflections	6549	2686
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.059	0.070
θ_{max} (°)	26.32	25.63
Range of h, k, l	$0 \rightarrow h \rightarrow 22$	$0 \rightarrow h \rightarrow 15$
	$0 \rightarrow k \rightarrow 16$	$-9 \rightarrow k \rightarrow 0$
	$-25 \rightarrow l \rightarrow 24$	$-35 \rightarrow l \rightarrow 32$
Refinement		
Refinement on	F^2	F^2
$R[F^2>2\sigma(F^2)]$	0.0495	0.0443
$wR(F^2)$	0.1337	0.1048
S	1.038	0.844
No. of reflections used in refinement	9421	4832
No. of parameters used	626	362
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0642P)^2 + 1.8417P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0568P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.016	0.001
$\Delta\rho_{max}$ (e Å^{-3})	0.400	0.157
$\Delta\rho_{min}$ (e Å^{-3})	−0.564	−0.237
Extinction method	None	None
Source of atomic scattering factors	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Computer programs		
Data collection	*KappaCCD Software* (Nonius, 1997)	*KappaCCD Software* (Nonius, 1997)
Cell refinement	*DENZO–SMN* (Otwinowski & Minor, 1997)	*DENZO–SMN* (Otwinowski & Minor, 1997)
Data reduction	*DENZO–SMN* (Otwinowski & Minor, 1997)	*DENZO–SMN* (Otwinowski & Minor, 1997)
Structure solution	*SHELXS*97 (Sheldrick, 1997a)	*SHELXS*97 (Sheldrick, 1997a)
Structure refinement	*NRCVAX*96 (Gabe *et al.*, 1989) and *SHELXL*97 (Sheldrick, 1997b)	*NRCVAX*96 (Gabe *et al.*, 1989) and *SHELXL*97 (Sheldrick, 1997b)
Preparation of material for publication	*NRCVAX*96, *SHELXL*97 and *WordPerfect* macro *PRPKAPPA* (Ferguson, 1999)	*NRCVAX*96, *SHELXL*97 and *WordPerfect* macro *PRPKAPPA* (Ferguson, 1999)

Table 2
Hydrogen-bond dimensions (Å, °).

Compound (1)

O14···O44	2.496 (2)	H14···O44	1.68	O14—H14···O44	165	
O34···O24^i	2.501 (2)	H34···O44^i	1.67	O34—H34···O44^i	171	
N51···O21	3.092 (3)	H51A···O21	2.38	N51—H51A···O21	134	
N52···O34^{ii}	2.914 (3)	H52A···O34^{ii}	2.20	N52—H52A···O34^{ii}	134	
N52···O24^{iii}	2.612 (3)	H52B···O24^{iii}	1.71	N52—H52B···O24^{iii}	167	
N61···O12^{iv}	3.134 (3)	H61A···O12^{iv}	2.33	N61—H61A···O12^{iv}	145	
N62···O14	2.898 (2)	H62A···O14	2.10	N62—H62A···O14	144	
N62···O44^v	2.652 (2)	H62B···O44^v	1.75	N62—H62B···O44^v	168	

Compound (2)

O6···O24	2.667 (2)	H61···O24	1.81 (2)	O6—H61···O24	178 (2)	
O6···O34^{vi}	2.923 (2)	H62···O34^{vi}	2.07 (2)	O6—H62···O34^{vi}	173 (2)	
O14···O24	2.604 (2)	H14···O24	1.77	O14—H14···O24	172	
O34···O6^i	2.649 (2)	H34···O6^i	1.81	O34—H34···O6^i	175	
N52···O24	2.662 (2)	H52B···O24	1.76	N52—H52B···O24	165	

Symmetry codes: (i) $-1+x, y, z$; (ii) $-x, -y, -z$; (iii) $-1+x, -1+y, z$; (iv) $1-x, 1-y, -z$; (v) $1-x, -y, -z$; (vi) $-1-x, \frac{1}{2}+y, \frac{1}{2}-z$.

methanol solvate (Gregson *et al.*, 2000), compound (1) contains neither methanol nor water molecules. Co-crystallization of mixtures of (II) and the simpler 4,4′-biphenol was always characterized by at least some phase separation, regardless of input stoichiometry and regardless of whether the solvent was methanol, ethanol or isopropanol. The crystalline products obtained always consisted of mixtures of (2) with 4,4′-biphenol, but manual separation provided sufficient

Figure 4
Part of the crystal structure of (1) showing an [010] chain linking pairs of site 1 cations. For the sake of clarity, H atoms bonded to C are omitted, and only the major conformer of the cation is shown; atoms marked with a star (*) or a hash (#) are at the symmetry positions $(-1+x, y, z)$ and $(x, 1+y, z)$, respectively.
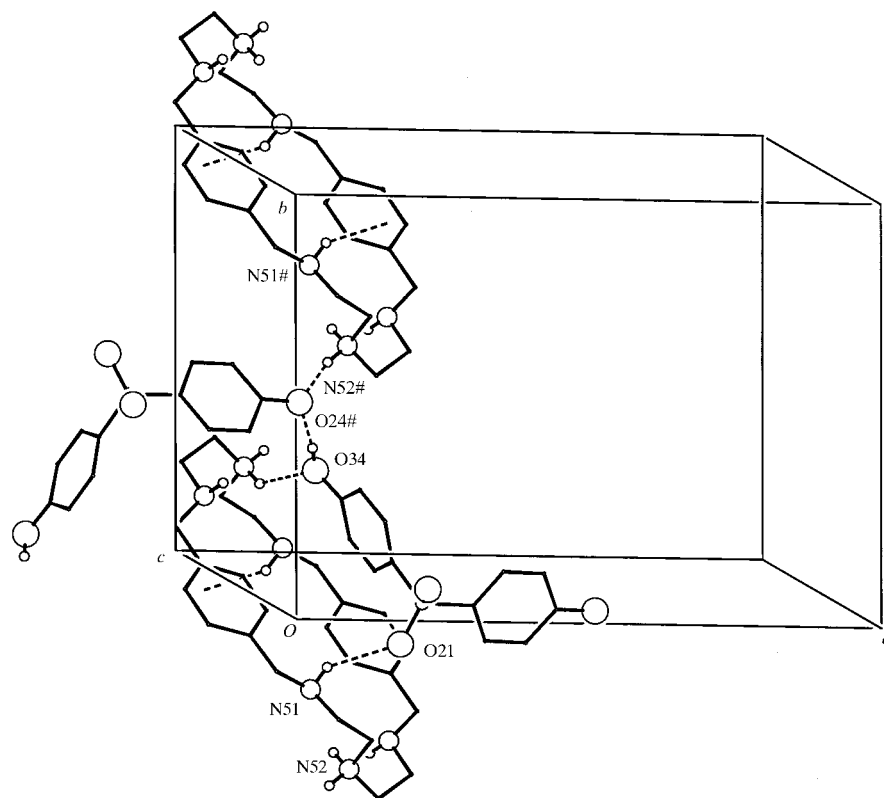
quantities of pure (2) for structure analysis. In contrast to where the ratio of amine to bisphenol is 1:2, in (2) this ratio is 1:3 and there are moreover two molecules of water per amine. Since the solvents employed were not rigorously dried, the water could be derived either from the solvent or from the laboratory atmosphere. The structure analysis for (2) demonstrates, however, the integral role of the water molecules in the overall supramolecular architecture.

3.2. Constitution of the compounds

In compound (1) the bisphenol component is present as the mono-anion [(HOC$_6$H$_4$SO$_2$C$_6$H$_4$O)$^-$], as commonly found in combinations of this bisphenol with aliphatic amines (Coupar *et al.*, 1996; Ferguson *et al.*, 1998; Ferguson, Glidewell, Gregson & Lavender, 1999). The crystal structure is built from two independent phenolate anions, and two independent centrosymmetric cations [(C$_{24}$H$_{40}$N$_6$)$^{2+}$], so that the asymmetric unit contains two anions and two half-cations (Fig. 1), confirming the 1:2 molar ratio of macrocycle to bisphenol deduced from the elemental analysis. Careful examination of difference maps showed first of all that the H atoms show no disorder additional to that imposed by the skeletal disorder; secondly, that the protonation of the hexaaza macrocycle occurs exclusively at the central N atoms, N52 and N62, in the aliphatic chains; and finally that there are no intramolecular N—H···N hydrogen bonds.

The independent molecular components of (2) (Fig. 5) comprise a doubly protonated cation [(C$_{24}$H$_{40}$N$_6$)$^{2+}$], lying across a centre of inversion; a neutral 4,4′-biphenol molecule, also lying across a centre of inversion; and a biphenolate anion [(HOC$_6$H$_4$C$_6$H$_4$O)$^-$] and a water molecule, both lying in general positions. The overall stoichiometry of amine:biphenol:water is thus 1:3:2. These components are linked into a continuous framework by O—H···O and N—H···O hydrogen bonds, but it is possible to identify a cation-free framework built simply from the biphenol and water units: within this three-dimensional and cation-free substructure it is possible to identify a two-dimensional substructure containing only the biphenolate anions and the water molecules. It is convenient to build up the structural description from this two-dimensional fragment, which in turn can be most simply described in terms of two sets of one-dimensional chains.

For both (1) and (2) the site of protonation of the hexaaza macrocycle (II) is in
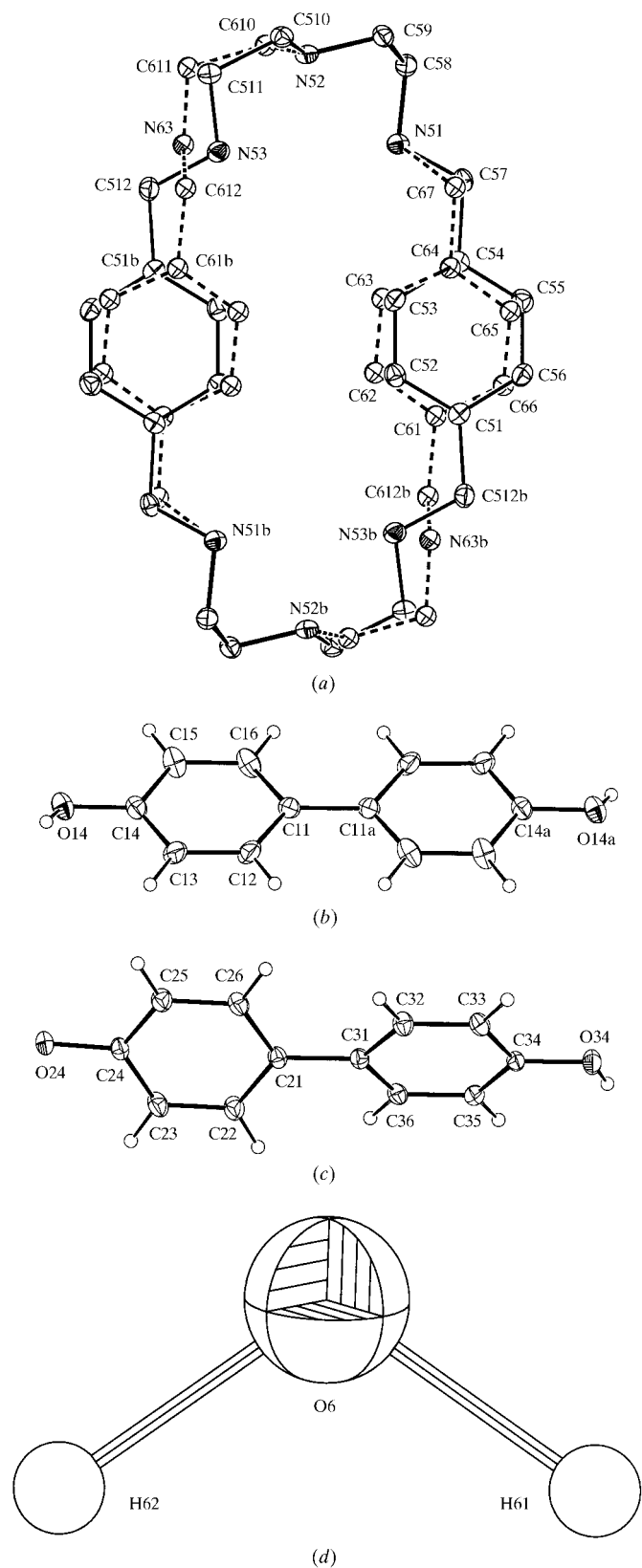
Figure 5
The molecular components of (2), showing the atom-labelling scheme. For the cationic components, the two conformers are shown super-imposed; the major component is drawn with solid bonds, the minor components with dashed bonds: for both cations, H atoms are omitted for the sake of clarity. Displacement ellipsoids are drawn at the 30% probability level: the minor conformer was refined isotropically.
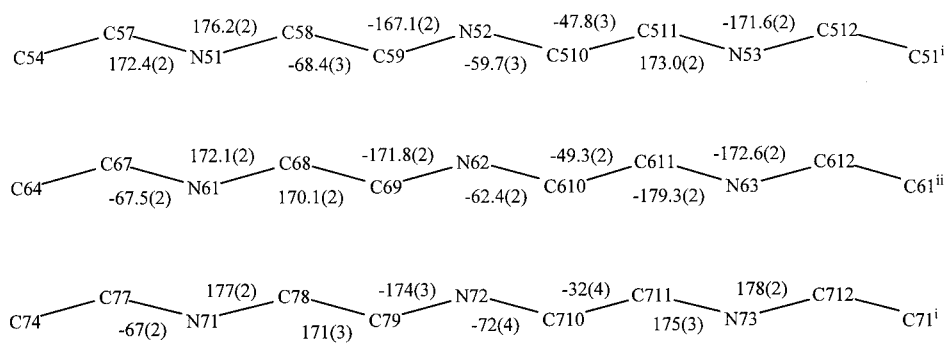
sharp contrast to the behaviour of this macrocycle in aqueous solution. In those conditions the macrocycle exhibits four protonation constants in the range $7.9 < \log K < 8.7$, with two others in the range $2.9 < \log K < 3.9$: the two weakly basic N atoms were assigned as the central pair in the aliphatic chains, and this assignment was supported by studies of the ^{13}C chemical shifts as a function of pH (Clifford, 1997). In an entirely similar way, the isomeric hexaaza macrocycle 3,6,9,17,20,23-hexaazatricyclo[23.3.1.1^{11,15}]triconta-1(29),11-(30),12,14,25,27-hexaene, (L) (IV), exhibits in aqueous solution four protonation constants in the range $7.1 < \log K < 9.5$ and two in the range $3.2 < \log K < 3.8$, and it has been reported that in the crystal structure of $[(LH_4)^{4+}]\cdot 2(Br^-)\cdot[(H_2P_2O_7)^{2-}]\cdot 5.2H_2O$, grown from aqueous solution, the four N atoms adjacent to the m-xylenyl units are protonated, while the two central N atoms are not (Nation et al., 1996).
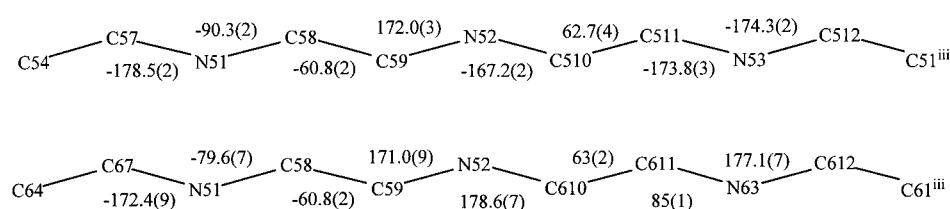

(III) (IV)
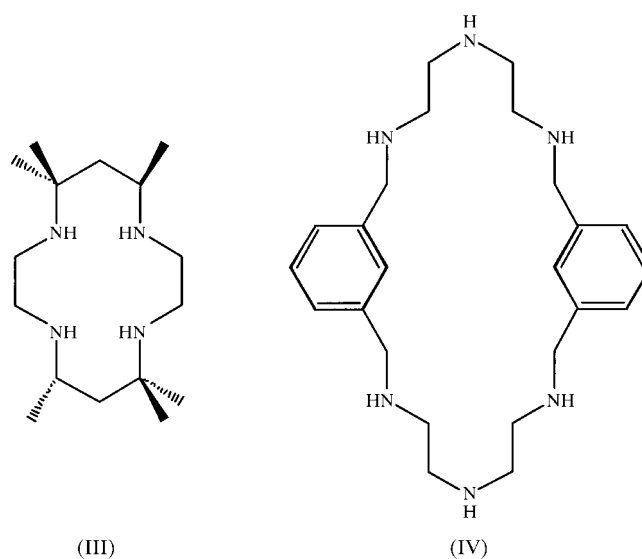
3.3. Conformation of the cations

3.3.1. Compound (1). In (1) there are two crystal-lographically independent cations present: the cations containing N51–N53 are centred at the vertices of the cell and at the cell centre (sites 1), so forming a pseudo body-centred arrangement, while those centred at $(0, 0, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2}, 0)$ (sites 2) and containing N61–N63 form a similar type of array, offset from the first by c/2. The second unexpected feature of the cation structure, after the sites of protonation, is that the cations in the different sites adopt entirely different confor-mations. The non-H atoms in the aliphatic parts of these cations show almost perfect staggering about all of the C—C and C—N bonds, with the antiperiplanar (ap) torsional angles all within 13° of 180°, and the synclinal (sc) torsional angles all within 13° of ±60° (Scheme 3). The overall conformation of the aliphatic chains between Cn7 and Cn12 (n = 5 or 6, see Fig. 1) is, in each cation, defined by eight independent torsional angles and, in both of the conformations observed in (1), five of these are ap and three are sc. It is the ordering of the ap and sc torsional angles which determines the different conformations of the two independent cations. In the first conformation (conformation A) the order from C57 to C512 is

Compound (1)

C54 — C57 — 176.2(2) — C58 — -167.1(2) — N52 — -47.8(3) — C511 — -171.6(2) — C512 — C51^i
172.4(2) N51 -68.4(3) C59 -59.7(3) C510 173.0(2) N53

C64 — C67 — 172.1(2) — C68 — -171.8(2) — N62 — -49.3(2) — C611 — -172.6(2) — C612 — C61^{ii}
-67.5(2) N61 170.1(2) C69 -62.4(2) C610 -179.3(2) N63

C74 — C77 — 177(2) — C78 — -174(3) — N72 — -32(4) — C711 — 178(2) — C712 — C71^i
-67(2) N71 171(3) C79 -72(4) C710 175(3) N73

Compound (2)

C54 — C57 — -90.3(2) — C58 — 172.0(3) — N52 — 62.7(4) — C511 — -174.3(2) — C512 — C51^{iii}
-178.5(2) N51 -60.8(2) C59 -167.2(2) C510 -173.8(3) N53

C64 — C67 — -79.6(7) — C58 — 171.0(9) — N52 — 63(2) — C611 — 177.1(7) — C612 — C61^{iii}
-172.4(9) N51 -60.8(2) C59 178.6(7) C610 85(1) N63

ap, ap, sc, ap, sc, sc, ap, ap, and in the second conformation (*B*) the order, from C67 to C612 is *sc, ap, ap, ap, sc, sc, ap, ap*. The exchange of just the first and third members of these series serves to switch the cations from one conformation to the other.

The co-existence of two cation conformations in the same crystal structure suggests that these two conformations have rather similar energies, and this in turn opens up the possibility that the mapping of the two conformations into the two independent cation sites may not be perfect. Extensive exploration of difference maps in the vicinity of the cation sites showed, in fact, that the $(0, 0, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2}, 0)$ sites are occupied exclusively by cations having conformation *B* (*sc*, 3*ap*, 2*sc*, 2*ap*), but that the $(0, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ sites are occupied mainly by conformation *A* (2*ap, sc, ap*, 2*sc*, 2*ap*) with a minor component having conformation *B*. The site-occupation factors for the major and minor conformers at these sites refined to 0.920 (3) and 0.080 (3), respectively, representing roughly an 11:1 ratio of conformers.

Each of the centrosymmetric conformers contains eight N—H bonds: in each conformer only six of these bonds participate in the hydrogen bonding. The cationic N atoms N52 and N62 both act as double donors, the neutral N51 and N61 both act as donors but not as acceptors, while the neutral N53 and N63 act neither as donors nor as acceptors. There are thus only two types of hydrogen bond present in (1), O—H···O and N—H···O, as only the O atoms act as hydrogen-bond acceptors. The hydrogen-bonding behaviour of the two conformers at the $(0, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ sites turns out to be identical, so that for the sake of convenience only the contribution of the major conformer will be discussed (see §3.5.1).

3.3.2. Compound (2). There is only one independent cation in (2), centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ with a symmetry-equivalent cation centred at $(\frac{1}{2}, 0, 0)$; as in (1), this cation exhibits conformational

disorder (Fig. 5). The major conformer, site-occupation factor 0.789 (4), exhibits a conformation different from either of those found in (1). Of the eight independent torsional angles defining the conformation of the aliphatic chain between C57 and C512 (Fig. 5), five are *ap* with torsional angles within 13° of 180° (Scheme 3), two are *sc* and are within 3° of ±60°, but the last, δ(C57—N51—C58—C59), has the value −90.3 (2)°, exactly at the boundary between *ap* and *sc*. In the minor cation conformer, site-occupation factor 0.211 (4) (Fig. 5 and Scheme 3), there are in fact two such torsional angles, δ(C57—N51—C58—C59) as in the major conformer and δ(C610—C611—N63—C612) where the value is 85.1 (2)°. This minor component thus has a conformation close to C_{2h} ($2/m$) point symmetry (Fig. 5 and Scheme 3). Although the N51 and N52 sites are common to both cation conformers in (2), the sites N53 and N63 are distinct (Fig. 5). In contrast to the hydrogen-bonding behaviour of both the cations in (1), in (2) only the protonated N52 participates in the hydrogen bonding: hence, in this respect only the contribution of the major conformer need be considered explicitly (see §3.5.2).

In addition to the torsional angles in the saturated parts of the cations (Scheme 3), there are two other parameters which provide a simple measure of the differences between the different cation conformations present in (1) and (2): the distance between the ring centroids within a given cation is a measure of the 'openness' of the conformation, while the perpendicular distance between the two ring planes (parameter defined as 'Step' in Table 3) provides a measure of the twist of the aryl rings relative to the saturated framework.

3.3.3. Modelling the cation conformations. Compounds (1) and (2) between them contain four distinct centrosymmetric conformers of the di-cation $(C_{24}H_{40}N_6)^{2+}$, and we have attempted to model the conformational behaviour with a combination of molecular mechanics, molecular dynamics and semi-empirical SCF calculations. Extensive exploration of the conformational hypersurface for the cation doubly protonated on the central N atoms only, both with and without constraints on the permitted ranges for the independent torsional angles, indicated that this surface was extremely flat and featureless: this means that a very wide range of molecular conformations are accessible, both because they are all of similar energy, and because the barriers between different conformers are generally low. However, it was noticeable that the conformations observed experimentally were at the lower extreme of the range of individual conformational energies. It must, of course, be emphasized that calculations of this type are strictly applicable only to isolated gas-phase species, free from inter-

Table 3
Selected molecular dimensions (Å, °).

(a) Cation geometries
Compound (1)

N51—C57	1.463 (3)	N51—C58	1.461 (3)
N52—C59	1.483 (3)	N52—C510	1.488 (3)
N53—C511	1.445 (3)	N53—C512	1.461 (3)
N61—C67	1.459 (3)	N61—C68	1.452 (3)
N62—C69	1.482 (3)	N62—C610	1.484 (3)
N63—C611	1.464 (3)	N63—C612	1.458 (3)
N71—C77	1.46 (2)	N71—C78	1.46 (3)
N72—C79	1.49 (4)	N72—C710	1.48 (4)
N73—C711	1.46 (4)	N73—C712	1.46 (3)
N51—C57—C54—C53	−24.2 (3)	N53^i—C512^i—C51—C52	−20.1 (3)
N61—C67—C64—C63	−14.9 (3)	N63^{ii}—C612^{ii}—C61—C62	−30.3 (3)
N71—C77—C74—C73	−16 (2)	N73^i—C712^i—C71—C72	−23 (3)
Cg(A)···Cg(A)^i	6.706 (4)	Step	2.122 (4)
Cg(B)···Cg(B)^{ii}	7.592 (4)	Step	2.782 (4)
Cg(C)···Cg(C)^i	7.36 (5)	Step	2.98 (5)

Compound (2)

N51—C57	1.457 (3)	N51—C58	1.459 (2)
N52—C59	1.483 (2)	N52—C510	1.494 (3)
N53—C511	1.455 (3)	N53—C512	1.467 (3)
N51—C67	1.476 (14)	N52—C610	1.485 (17)
N63—C611	1.457 (8)	N63—C612	1.446 (8)
N51—C57—C54—C53	−26.6 (3)	N53^{iii}—C512^{iii}—C51—C52	4.7 (4)
N51—C67—C64—C63	−37 (2)	N63^{iii}—C612^{iii}—C61—C62	−92 (1)
Cg(A)···Cg(A)^{iii}	6.280 (5)	Step	2.158 (5)
Cg(B)···Cg(B)^{iii}	5.88 (2)	Step	2.72 (2)

(b) Anion geometries
Compound (1)

S1—O11	1.443 (2)	S2—O21	1.443 (2)
S1—O12	1.445 (2)	S2—O22	1.434 (2)
S1—C11	1.761 (2)	S2—C31	1.754 (2)
S1—C21	1.746 (2)	S2—C41	1.746 (2)
C14—O14	1.348 (2)	C34—O34	1.353 (3)
C24—O24	1.315 (3)	C44—O44	1.320 (3)
O11—S1—O12	118.4 (1)	O21—S2—O22	118.8 (1)
C11—S1—C21	106.0 (1)	C31—S2—C41	106.3 (1)
C13—C14—O14	122.0 (2)	C33—C34—O34	117.3 (2)
C15—C14—O14	118.2 (2)	C35—C34—O34	122.2 (2)
C23—C24—O24	121.0 (2)	C43—C44—O44	121.0 (2)
C25—C24—O24	121.3 (2)	C45—C44—O44	121.2 (2)
O11—S1—C11—C12	−14.0 (2)	O21—S2—C41—C42	5.7 (2)
O12—S1—C21—C26	−7.3 (2)	O22—S2—C31—C36	10.8 (2)
(C11—S1—C21)^(C11—C16)	77.6 (1)		
(C11—S1—C21)^(C21—C26)	70.5 (1)		
(C31—S2—C41)^(C31—C36)	75.4 (1)		
(C31—S2—C41)^(C41—C46)	71.2 (1)		
(C51—C56)^(C71—C76)	11 (1)		

Compound (2)

C14—O14	1.370 (2)		
C24—O24	1.356 (2)	C34—O34	1.378 (2)
C13—C14—O14	122.8 (2)	C15—C14—O14	119.1 (2)
C23—C24—O24	121.5 (2)	C25—C24—O24	121.5 (2)
C33—C34—O34	117.9 (2)	C35—C34—O34	122.9 (2)
(C21—C26)^(C31—C36)	20.2 (1)		

Cg(A), Cg(B) and Cg(C) are the centroids of rings (C51–C56), (C61–C66) and (C71–C76), respectively. 'Step' is the perpendicular distance between the two ring planes. Symmetry codes: (i) −x, −y, −z; (ii) 1 − x, 1 − y, −z; (iii) 1 − x, 1 − y, 1 − z.

molecular perturbations. However, the deduction of extreme conformational flexibility is probably valid, despite the above caveat. We conclude that the energy differences between the individual conformers is sufficiently small that the actual conformer, or conformers, observed in any given system will in fact be more influenced by the effect of the intermolecular forces than by the intra-cation forces. Of the intermolecular

forces, two stand out as important: the largely non-directional interactions between the charged centres (N^+ and O^-) in the ionic components, and the highly directional hydrogen bonds.

3.4. Conformation of the anions

In each of the two independent phenolate anions present in (1) the heavy-atom skeletons adopt conformations very close to C_2 symmetry, as commonly observed for both neutral $O_2S(C_6H_4OH)_2$ and its mono-anion (Ferguson, Glidewell, Gregson & Lavender, 1999). This conformation (Table 3) appears, in general, to be largely determined by the formation of almost planar five-membered $S(5)···O{=}S-C-C-H···$ rings, resulting from the strong electrostatic attraction between acidic aryl C—H bonds, polarized $C^{\delta-}-H^{\delta+}$, and sulfone S=O bonds, polarized $S^{\delta+}-O^{\delta-}$. The four independent C···O distances lie in the range 2.889 (3)–2.915 (3) Å, with corresponding H···O distances between 2.50 and 2.54 Å and C—H···O angles between 103 and 105°; clearly these interactions cannot be regarded as conventional C—H···O hydrogen bonds. In the C_2 conformation, both of the sulfone O atoms participate, each interacting with a different ring: in the alternative, but less common, conformation (Ferguson, Glidewell, Gregson & Lavender, 1999), one sulfone O atom only is involved interacting with two $C^{\delta-}-H^{\delta+}$ bonds in different rings.

The dihedral angle between the ring planes in the phenolate anion in (2) is 20.2 (1)°, while in the neutral centrosymmetric biphenol molecule the aromatic ring planes are necessarily parallel.

3.5. Supramolecular structures

3.5.1. Compound (1). The phenolate anions are linked into chains by means of strong ionic O—H···O$^-$ hydrogen bonds (Table 2). Within the asymmetric unit (Fig. 1), O14 in one phenolate anion acts as a donor to the deprotonated O44 in the other anion: in addition, O34 at (x, y, z) acts as a donor to the deprotonated O24 at $(−1 + x, y, z)$, so generating by translation a $C_2^2(24)$ chain running parallel to the [100] direction (Figs. 2 and 3). Four of these chains run through each unit cell: one pair of antiparallel chains, related to one another by the centre of inversion at the origin, lies in the domain $−0.25 < z < +0.25$, while a second pair of antiparallel chains, related by the centre of inversion at the centre of the unit cell, lies in the domain $0.25 < z < 0.75$. Within each of these domains the anionic chains are linked by the cations

to give two-dimensional networks parallel to (001): two such nets, related to one another by the action of the 2_1 screw axes, are required completely to define the unit-cell contents, and hence the overall crystal structure.
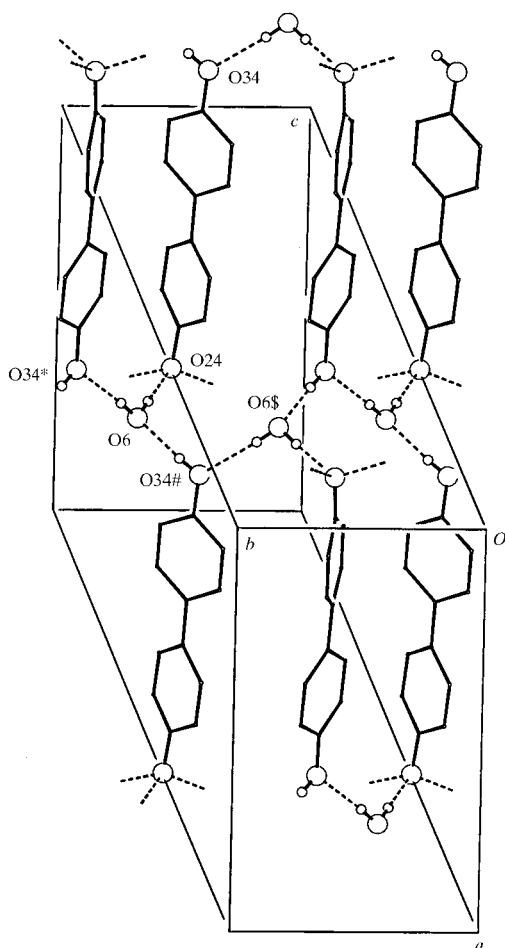
Each cation uses six of its eight N—H bonds in the formation of N—H⋯O hydrogen bonds: moreover, each cation forms hydrogen bonds to four distinct chains, all in the same domain of z. Thus the cation centred at the origin forms two N—H⋯O hydrogen bonds to each of the chains containing the phenolate anions at (x, y, z) and $(-x, -y, -z)$ (Fig. 2), and one hydrogen bond to each of the chains containing the phenolate anions at $(x, -1 + y, z)$ and $(-x, 1 - y, -z)$ (Fig. 3): the neighbouring cation centred at $(0, 1, 0)$ similarly forms two hydrogen bonds to each of the chains containing phenolates at $(x, 1 + y, z)$ and $(-x, 1 - y, -z)$ and one each to those at (x, y, z) and $(-x, 2 - y, -z)$. In this manner, all of the phenolate chains in the domain $-0.25 < z < +0.25$ are continuously linked by the site 1 cations at $(0, n, 0)$ (n = zero or integer) (Fig. 4). In an entirely similar way, the site 2 cation centred at $(\frac{1}{2}, \frac{1}{2}, 0)$ forms two N—H⋯O hydrogen

Figure 6
Part of the crystal structure of (2), showing an (001) net of $R_6^6(30)$ rings built from phenolate anion and water molecules only. For the sake of clarity, H atoms bonded to C are omitted. Atoms marked with a star (*), a hash (#) or a dollar sign ($) are at the symmetry positions $(-1 - x, \frac{1}{2} + y, \frac{1}{2} - z)$, $(1 + x, y, z)$ and $(-x, -\frac{1}{2} + y, \frac{1}{2} - z)$, respectively.

bonds to each of the chains containing the phenolate anions at (x, y, z) and $(1 - x, 1 - y, 1 - z)$ and one to each of the chains containing the phenolates at $(x, 1 + y, z)$ and $(1 - x, -y, -z)$, and so on.

3.5.2. Compound (2). In (2) the phenolate anions and the water molecules form two-dimensional nets, and these nets are linked into a three-dimensional framework by the action of the neutral biphenol units, and also by means of the cations: thus it is possible to define a cation-free three-dimensional framework. Within the asymmetric unit the water molecule acts as hydrogen-bond donor, via H61, to the deprotonated O24 of the biphenolate anion (Table 2 and Fig. 5), and the hydroxyl group O34—H34 in the same anion at (x, y, z) acts as donor to O6 in the water molecule at $(-1 + x, y, z)$: thus a $C_2^2(13)$ chain, running parallel to the [100] direction, is generated by translation (Fig. 6). O6 at (x, y, z) also acts as a donor, via H62, to O34 in the anion at $(-1 - x, \frac{1}{2} + y, \frac{1}{2} - z)$: this O34 acts as a donor to O6 at $(-x, \frac{1}{2} + y, \frac{1}{2} - z)$, and this latter O6 in turn acts as a donor to O34 at $(1 + x, 1 + y, z)$, which itself acts as a donor to O6 at $(x, 1 + y, z)$. Hence a $C_2^2(4)$ chain, running parallel to the [010] direction, is generated by the action of the 2_1 screw axis along $(-\frac{1}{2}, y, \frac{1}{4}$, see Fig. 6).
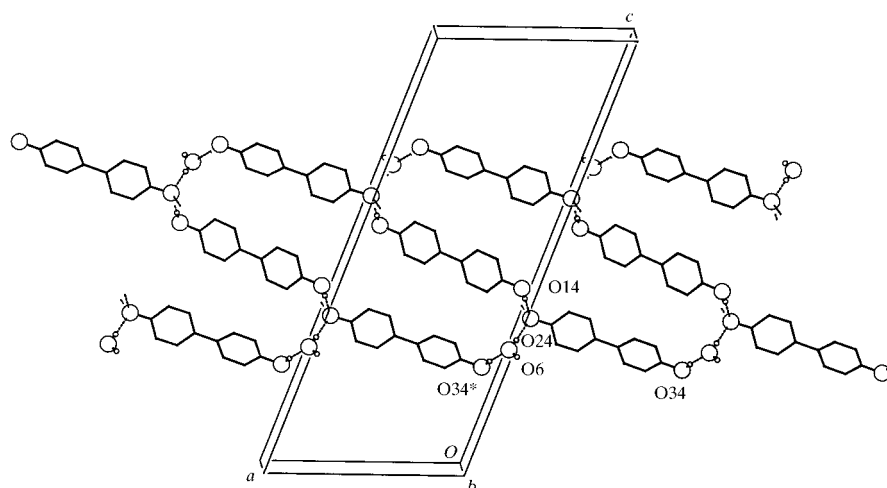
These two chain motifs combine to generate a deeply puckered two-dimensional net, parallel to (001) and built from a single type of $R_6^6(30)$ ring (Fig. 6). Within this net there are polar oxygen-rich strips at $x = 0, \pm 1, \pm 2$ etc., separated by broad non-polar strips consisting of biphenyl ($-C_6H_4-C_6H_4-$) units only. The (001) net containing the biphenolate anion and the water molecule, both at (x, y, z), lies wholly within the domain $0.11 < z < 0.39$, and there is a second net within the unit cell, related to the first by the action of the inversion centres at $z = 0.5$ and lying in the domain $0.61 < z < 0.89$. These two nets thus occupy thick slices of the unit cell, but there are substantial spaces between them: these spaces are occupied by the neutral biphenol molecules and by the cations.

Neighbouring (001) nets are linked by the neutral biphenol molecules to form a single three-dimensional framework (Fig. 7): O14 at (x, y, z) acts as a hydrogen-bond donor to the anionic O24, also at (x, y, z), which forms part of the net lying in the domain $0.11 < z < 0.39$: the symmetry-related O14 in the same neutral biphenol molecule, centred at $(\frac{1}{2}, 1, \frac{1}{2})$, is at $(1 - x, 2 - y, 1 - z)$ and acts as a donor to O24 at $(1 - x, 2 - y, 1 - z)$, which is a component of the net lying in the domain $0.61 < z < 0.89$ (Fig. 7). The two nets in the domains $0.11 < z < 0.39$ and $0.61 < z < 0.89$ are, in fact, linked by a series of neutral biphenol molecules centred at $(n + \frac{1}{2}, 1, \frac{1}{2})$ (n = zero or integer), forming $R_8^6(52)$ rings centred at $(n, 1, \frac{1}{2})$ (n = zero or integer) (Fig. 7). Similarly, the neutral biphenol molecule centred at $(\frac{1}{2}, \frac{1}{2}, 0)$ acts as a hydrogen-bond donor to the O24 sites at $(x, -\frac{1}{2} + y, \frac{1}{2} - z)$ in the domain $0.11 < z < 0.39$, and at $(1 - x, \frac{3}{2} - y, -\frac{1}{2} + z)$ in the domain $-0.39 < z < -0.11$: hence neutral biphenol molecules serve to link each of the (001) nets to its two neighbouring nets, so generating a continuous three-dimensional framework, built from just the biphenol units (neutral and anionic) and the water molecules.

The cations are linked into this framework by means of just two N—H···O hydrogen bonds: this behaviour may be contrasted with the multi-point linking of the cations to the anion chains in (1). In (2) only the central protonated N52 participates in the hydrogen bonding. The reference cation lies across the centre of inversion at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and N52 at (x, y, z) acts as a hydrogen-bond donor to O24, also at (x, y, z), which is thus a triple acceptor of hydrogen bonds (Fig. 2 and Table 2): the symmetry-related N52 at $(1 - x, 1 - y, 1 - z)$ similarly acts as a donor to O24 at $(1 - x, 1 - y, 1 - z)$. Hence the cations, like the neutral biphenol molecules, link together the two (001) nets within the unit cell (Fig. 8). Thus, along the [010] direction cations at $(\frac{1}{2}, n + \frac{1}{2}, \frac{1}{2}; n$ = zero or integer) alternate with neutral biphenol molecules centred at $(\frac{1}{2}, n, \frac{1}{2}; n$ = zero or integer, see Fig. 9). Despite the modest b dimension of the unit cell, there are no hydrogen bonds formed directly between the cations and the neutral biphenol molecules: the most direct connection between these units is *via* O24, towards which both O14 and N52 act as hydrogen-bond donors within the asymmetric unit (Fig. 5).
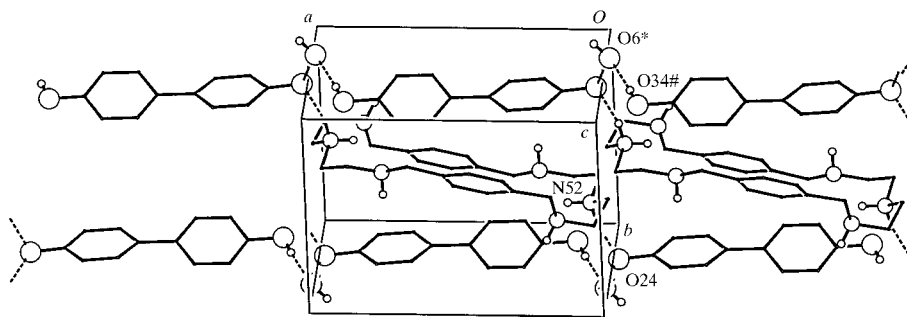
3.5.3. General comments on the structures. Possibly the most striking feature of the supramolecular structures of (1) and (2) is the difference in the hydrogen-bond behaviour of the $(C_{24}H_{40}N_6)^{2+}$ cations: in (1) each cation forms six intermolecular N—H···O hydrogen bonds, while in (2) only two such bonds are formed per cation, although in neither compound are there any relevant intramolecular N—H···N interactions.

It is thus of interest to compare the behaviour of the cations in (1) and (2) with that of the cations $[(\mathrm{cyclam})H_2]^{2+}$ and $[(\mathrm{tet\text{-}a})H_2]^{2+}$, derived from the tetraaza macrocycles (I) and (III), respectively, in the compounds formed by (I) and (III) with bisphenols (Ferguson *et al.*, 1998; Ferguson, Glidewell, Gregson & Lavender, 1999; Gregson *et al.*, 2000). In all cases the $[(\mathrm{cyclam})H_2]^{2+}$ and $[(\mathrm{tet\text{-}a})H_2]^{2+}$ cations, which like the cations in (1) and (2) are always centrosymmetric, contain paired intramolecular N—H···N hydrogen bonds and carry four axial N—H bonds approximately normal to the plane of the macrocycle. In general, $[(\mathrm{cyclam})H_2]^{2+}$ utilizes all four axial N—H bonds, whereas $[(\mathrm{tet\text{-}a})H_2]^{2+}$ generally uses only the two which are less sterically shielded: the axial N—H bonds adjacent to the gem-dimethyl groups are not usually active in hydrogen-bond formation. The dominant mode of supramolecular aggregation between these cations and bisphenolate anions, in adducts of (I) or (III) with bisphenols, is the formation of molecular ladders, where the uprights are formed by chains of anions and the treads by the cations (Ferguson *et al.*, 1998; Ferguson, Glidewell, Gregson & Lavender, 1999; Gregson *et al.*, 2000). The inactivity in hydrogen bonding of many of the N—H bonds in the $(C_{24}H_{40}N_6)^{2+}$ cations, particularly in (2), cannot readily be ascribed to steric factors, as in the $[(\mathrm{tet\text{-}a})H_2]^{2+}$ cation: rather, there is in (2) a very large excess of hydrogen-bond donors over acceptors. In (1), on the other hand, the number of hydroxyl groups per cation is smaller and there are also sulfone O atoms available as additional acceptors. Finally, in the comparison of (1) and (2) with salts of $[(\mathrm{tet\text{-}a})H_2]^{2+}$ it is interesting to note that in the adduct of tet-a with 4,4-biphenol there are both anions $(\mathrm{HOC_6H_4C_6H_4O})^-$ and neutral centrosymmetric $(\mathrm{HOC_6H_4})_2$ molecules (Gregson *et al.*, 2000), just as there are in (2) reported here: this combination of neutral and anionic units has not so far been observed with any other bisphenol.

Figure 7
Part of the crystal structure of (2) showing the action of the centrosymmetric neutral biphenol molecules in linking pairs of (001) nets *via* the formation of centrosymmetric $R_8^6(52)$ rings. For the sake of clarity, H atoms bonded to C are omitted. The atom marked with a star (*) is at the symmetry position $(1 + x, y, z)$.

Figure 8
Part of the crystal structure of (2) showing the action of the cations in linking pairs of (001) nets. For the sake of clarity, H atoms bonded to C are omitted, and only the major conformer of the cation is shown; atoms marked with a star (*) or a hash (#) are at the symmetry positions $(-x, 1 - y, 1 - z)$ and $(-1 - x, 1 - y, 1 - z)$, respectively.

There are no examples of any cations derived from the hexamine (II) recorded in the Cambridge Structural Database (CSD; Allen & Kennard, 1993): hence no comparisons of the cations $(C_{24}H_{40}N_6)^{2+}$ in (1) and (2) can be made with previous examples. There are, however, two examples in the CSD of cations derived from the isomeric hexamine L (IV) (see §3.2). In $[(LH_4)^{4+}] \cdot 2(Br^-) \cdot [(H_2P_2O_7)^{2-}] \cdot 5.2H_2O$ (TODRAF: Nation *et al.*, 1996) the cation contains ten N—H bonds, and all ten are engaged in the formation of hydrogen bonds: five form N—H$\cdots$O hydrogen bonds to an encapsulated $(H_2P_2O_7)^{2-}$ anion, three form similar bonds to $(H_2P_2O_7)^{2-}$ anions within two other cation cavities, and the remaining two form hydrogen bonds to a bromide ion and a water molecule, respectively. Unfortunately, the H atoms of water molecules and the $[(H_2P_2O_7)^{2-}]$ anion were not located, so that the overall supramolecular structure cannot be analysed completely, but it is certainly three-dimensional. For the salt $[(LH_6)^{6+}] \cdot 6(Br^-)] \cdot 7H_2O$ derived from the same hexamine (TODQUY: Nation *et al.*, 1996), the coordinates deposited in the CSD do not generate a recognizable structure. Indeed, the CSD entry carries the comment 'some atoms are not bonding correctly: many H atoms are unbonded'. Hence no analysis is currently possible for this potentially interesting supramolecular structure. Plainly, there is considerable scope for further structural investigations of organic salts derived from the hexamines (II) and (IV).

3.6. Hydrogen-bond dimensions

The hydrogen-bond dimensions (Table 2) show clearly the significant shortening of the $D\cdots A$ and H$\cdots A$ distances when one or both of the donor and acceptor species carries a charge adjacent to the hydrogen-bonding sites (Gilli *et al.*, 1994;

Aakeröy, 1997). Of the O—H$\cdots$O hydrogen bonds, the shortest O$\cdots$O distances are those formed in (1) between neutral OH donors and the anionic O24 and O44 as acceptors: these distances approach those where symmetrically centred H is often found (Ellison & Levy, 1965; Emsley, 1980), but careful inspection of difference maps showed that, for both (1) and (2), there was no evidence whatsoever for any symmetrical O$\cdots$H$\cdots$O hydrogen bonds. The longest O$\cdots$O distance, 2.923 (2) Å, is found in (2) between the neutral water molecule as a hydrogen-bond donor and the neutral phenolic O34 as an acceptor; by contrast, when O34 acts as a donor to a symmetry-related water molecule, the O$\cdots$O distance, 2.649 (2) Å, is significantly shorter. The difference in these two O$\cdots$O distances may be a consequence of the continuous two-dimensional sheet formed in (2), where the water molecules act both as double donors as well as acceptors of hydrogen bonds and thus are independently linked to three other species: in such circumstances, some of the individual inter-molecular dimensions may be at values which are less than ideal, as it is the energy of the entire ensemble which seeks a minimum.

The N—H$\cdots$O hydrogen bonds exhibit a similar pattern, with the $D\cdots A$ distances strongly dependent on the exact nature of the components. In (1) the protonated N atoms N52 and N62 are the sole donors to phenolic O, whether neutral or anionic, and the hydrogen bonds formed to the anionic O24 and O44 as acceptors are very much shorter than those involving the neutral O14 and O34 as acceptors (Table 2); the N—H$\cdots$O angles are also much larger in the hydrogen bonds to the anionic O24 and O44. The unprotonated N51 and N61, however, form hydrogen bonds only to sulfone oxygen, which is one of the strongest neutral acceptors commonly encountered, while the unprotonated N53 and N63 participate in no significant interactions at all. In (2) the sole hydrogen bond involving the cation (Table 2) is formed between the protonated N52 and the anionic O24.

In the pairing-off of hydrogen-bond donors with hydrogen-bond acceptors in systems containing several types of donors and acceptors, a broad general principle (Etter, 1990) is that, of the donors and acceptors available, the strongest donor pairs off with the strongest acceptor. All the donors in a given system can in principle be ranked, as can the acceptors, so that in the absence of any other constraints a hierarchy of D—H$\cdots A$ interactions can be predicted. In (1) and (2) the hydrogen bonding actually observed is a compromise between the application of Etter's (1990) principle and the constraints imposed by the presence of multiple donors, of different rank, within the same molecular unit, the cation, while the anions also contain
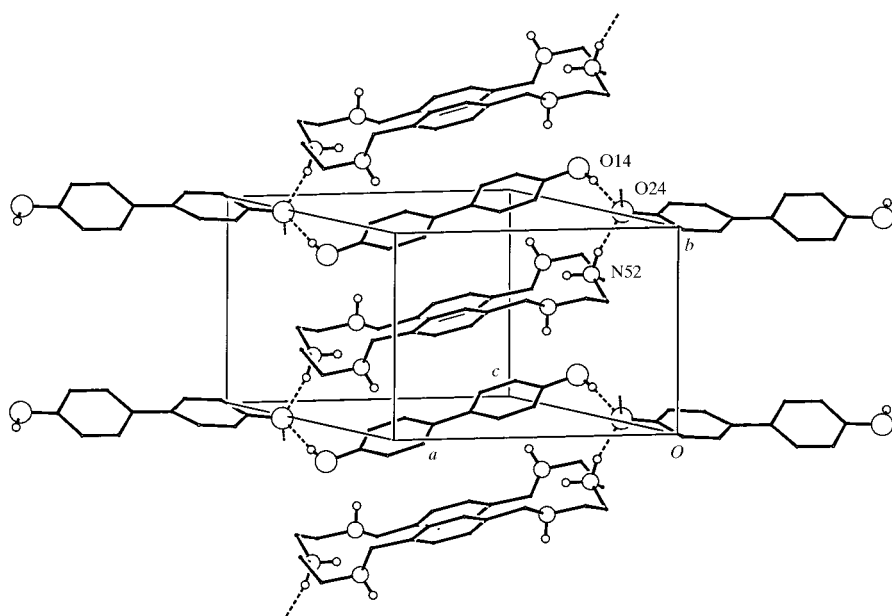
Figure 9
Part of the crystal structure of (2) showing the stacking along the [010] direction of alternating cations and neutral biphenol molecules. For the sake of clarity, H atoms bonded to C are omitted, and only the major conformer of the cation is shown.

multiple acceptor sites of different rank. In the presence of such geometric constraints, the maximization of the overall hydrogen-bond binding energy will take precedence over the ranking of particular pairwise $D—H\cdots A$ interactions.

3.7. Molecular dimensions

The C—N bonded distances in both (1) and (2) show a clear difference between bonds to neutral N and bonds to protonated N (Table 3). Taking just the major conformers in both compounds (the minor conformer was in each case refined isotropically), the C—N bonds with neutral N have lengths in the range 1.445 (3)–1.467 (3) Å, while bonds to protonated N have lengths in the range 1.482 (4)–1.494 (3) Å. For comparison, the mean values for C—N bonds of the general types $(C^*)_2—NH$ and $(C^*)_2—NH_2^+$ are 1.469 and 1.494 Å, respectively (Allen *et al.*, 1987). Similarly, in the phenolic components, there is clear distinction between C—O(H) and C—O$^-$ bond lengths (Table 3): these components also show the usual dependence of the exocyclic C—C—O angles on the orientation of the O—H bonds. Other bond lengths and angles are typical of their types.

4. Concluding comments

At the outset of our structural investigations of the adducts of the hexaaza macrocycle (II) with bisphenols, our expectation was that the principal features of interest in these adducts would be centred firstly on the patterns of the intermolecular hydrogen bonding and the role of this bonding in the generation of the supramolecular architecture, and secondly on the comparison of these architectures with those generated from the simpler macrocycle (I) (Ferguson *et al.*, 1998; Ferguson, Gregson & Glidewell, 1999) and its hexa-C-methyl analogue tet-a (Gregson *et al.*, 2000; Lough *et al.*, 2000). However, the structure analyses described here have revealed a number of other features which at the outset were not expected. First, the sites of protonation of the macrocycle (II) are entirely different from those expected on the basis of solution NMR studies (Clifford, 1997): in this instance, since the solid-state structure is a reflection of the totality of the intermolecular forces dominated by inter-ionic forces and hydrogen bonds, the different cation constitutions in the two phases may be rationalized even if not predicted. Secondly, there is no intramolecular N—H···N hydrogen bonding, probably as a non-predictable consequence of the larger ring size in (II) as compared with tetraaza macrocycles such as (I). Thirdly, and probably a consequence of the absence of intramolecular N—H···N hydrogen bonds, a wide range of cation conformations is observed. Each of (1) and (2) contains two distinct centrosymmetric cation conformations, and it is plausible to suggest that in adducts of the macrocycle (II) with other hydrogen-bond donors yet further conformations may be observed.

References

Aakeröy, C. B. (1997). *Acta Cryst.* B**53**, 569–586.
Allen, F. H. & Kennard O. (1993). *Chem. Des. Autom. News*, **8**, 1; 31–37.
Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–S19.
Chen, D. & Martell, A. E. (1991). *Tetrahedron*, **47**, 6895–6902.
Clifford, T. (1997). PhD thesis, University of St Andrews, St Andrews, Scotland.
Comba, P., Hambley, T. W., Hilfenhaus, P. & Richens, D. T. (1996). *J. Chem. Soc. Dalton Trans.* pp. 533–539.
Coupar, P. I., Ferguson, G. & Glidewell, C. (1996). *Acta Cryst.* C**52**, 3052–3055.
Dewar, M. J. S., Zoebisch, E. G., Healy, E. F. & Stewart, J. J. P. (1985). *J. Am. Chem. Soc.* **107**, 3902–3909.
Ellison, R. D. & Levy, H. A. (1965). *Acta Cryst.* **19**, 260–268.
Emsley, J. (1980). *Chem. Soc. Rev.* **9**, 91–124.
Etter, M. C. (1990). *Acc. Chem. Res.* **23**, 120–126.
Ferguson, G. (1999). *PRPKAPPA. A WordPerfect-5.1 Macro to Formulate and Polish CIF Format Files from the SHELXL97 Refinement of KappaCCD Data.* University of Guelph, Canada.
Ferguson, G., Glidewell, C., Gregson, R. M. & Lavender, E. S. (1999). *Acta Cryst.* B**55**, 573–590.
Ferguson, G., Glidewell, C., Gregson, R. M. & Meehan, P. R. (1998). *Acta Cryst.* B**54**, 139–150.
Ferguson, G., Gregson, R. M. & Glidewell, C. (1999). *Acta Cryst.* C**55**, 815–817.
Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
Gilli, P., Bertolasi, V., Ferretti, V. & Gilli, G. (1994). *J. Am. Chem. Soc.* **116**, 909–915.
Gregson, R. M., Glidewell, C., Ferguson, G. & Lough, A. J. (2000). *Acta Cryst.* B**56**, 39–57.
Hypercube Inc. (1999). *HyperChem Molecular Modelling System.* Hypercube Inc., Gainsville, Florida, USA.
Lough, A. J., Gregson, R. M., Ferguson, G. & Glidewell, C. (2000). *Acta Cryst.* B**56**, 85–93.
Nation, D. A., Reibenspies, J. & Martell, A. E. (1996). *Inorg. Chem.* **35**, 4597–4603.
Nonius (1997). *KappaCCD Software.* Nonius, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods Enzymol.* **276**, 307–326.
Sheldrick, G. M. (1997a). *SHELXS*97. University of Göttingen, Germany.
Sheldrick, G. M. (1997b). *SHELXL*97. University of Göttingen, Germany.
Spek, A. L. (1999). *PLATON.* January 1999 version. University of Utrecht, The Netherlands.
Wilson, A. J. C. (1976). *Acta Cryst.* A**32**, 994–996.