

A hydrogen-bonded adduct containing seven-component supramolecular aggregates

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Received 14 September 2000

Accepted 5 October 2000

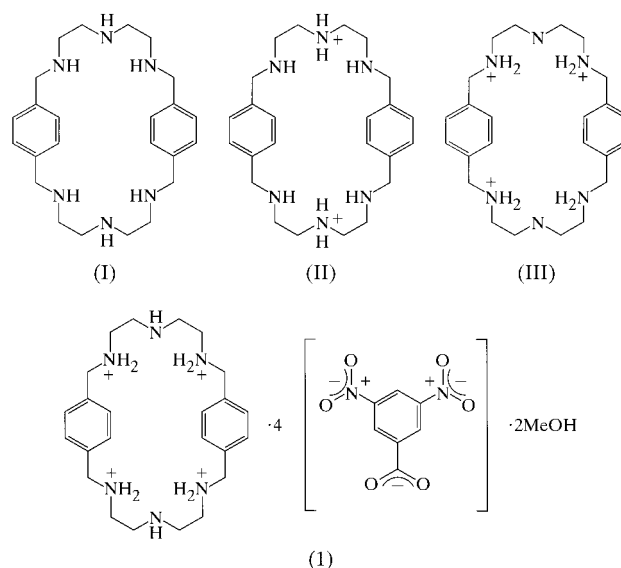
The title compound is a salt, 3,6,9,16,19,22-hexaazatri-cyclo[22.2.2.2^{11,14}]triaconta-1(26),11(29),12,14(30),24,27-hexa-ene-3,5-dinitrobenzoic acid-methanol (1/4/2), C₂₄H₄₂N₆⁴⁺·4C₇H₃N₂O₆⁻·2CH₃O, in which the cation lies across a centre of inversion and one of the two independent anions is positionally disordered over two sets of atom sites having equal occupancy. The components are linked by four types of N—H···O hydrogen bond [N···O 2.674 (2)–2.815 (2) Å; N—H···O 149–163°] and one type of O—H···O hydrogen bond in which the acceptor is disordered over two closely adjacent sites [O···O 2.67 (4) and 2.75 (4) Å; O—H···O 172 and 173°], forming centrosymmetric seven-component aggregates.

Comment

The salt-type adducts formed between the hexaaza macrocycle (I) (C₂₄H₃₈N₆) and the bis-phenols 4,4'-sulfonyldiphenol and 4,4'-biphenol are characterized by three salient features: (i) proton transfer leads to formation of the dication (II), C₂₄H₄₀N₆²⁺, in which only the central N atoms of the aliphatic chain are protonated; (ii) the cation (II) is centrosymmetric, but can adopt a range of widely different conformations having rather similar energies and, indeed, two different cation conformations co-exist in each of these adducts, giving a total of four distinct conformers overall; (iii) extensive hydrogen bonding links the components into continuous arrays, which are two-dimensional in the 4,4'-sulfonyldiphenol adduct and three-dimensional in the adduct with 4,4'-biphenol (Glidewell *et al.*, 2000).

Extending our study of the macrocycle (I), we have now characterized a methanol-solvated adduct (1) formed with 3,5-dinitrobenzoic acid, which differs from the bis-phenol adducts in all material respects. The title compound is a salt, C₂₄H₄₂N₆⁴⁺·4(O₂N)₂C₆H₃COO⁻·2CH₃OH, with the cation

lying across a centre of inversion in *C*2/*c*, chosen for the sake of convenience as that at ($\frac{1}{4}, \frac{1}{4}, 0$). The two independent anions lie in general positions, and one of them is positionally disordered over two sets of sites having equal occupancy (see *Experimental*); the unique methanol also lies in a general position. Because the coordinates of corresponding atoms in the two sets of sites defining the disordered anion are extremely similar, apart from one of the nitro groups (containing N35/N45), only one orientation of the anion need be considered in the structure description; in particular, the hydrogen-bonding characteristics of the alternative atom sites O31/O41 and O32/O42 are very similar (Table 2). The H atoms are all ordered such that the cation is protonated at the four N atoms adjacent to the *p*-xylenyl units (III); this pattern of protonation differs from that observed previously in bis-phenol adducts, but it is entirely consistent with the behaviour of the macrocycle (I) 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 ¹³C chemical shifts as a function of pH (Clifford, 1997).



In the aliphatic portion of the centrosymmetric cation C₂₄H₄₂N₆⁴⁺, there is almost perfect staggering about all of the C—C and C—N bonds, with the antiperiplanar (*ap*) torsional angles all within 18° of 180°, and the synclinal (*sc*) torsional angles both within 6° of ±60° (Table 1, Fig. 1). However, this conformation differs markedly from the four conformers previously observed for the cation C₂₄H₄₀N₆²⁺; in particular, the eight torsional angles in the aliphatic chain from C7 to C15 exhibit the pattern *ap, ap, sc, ap, ap, sc, ap, ap*, so that the overall conformation is close to *C*_{2h} (*2/m*) symmetry. Most of the observed conformers of (II) have only *C*_i symmetry; the one conformer which is close to *C*_{2h} symmetry exhibits a pattern of torsional angles in the aliphatic chain different from that observed here, namely *ap, sc, sc, ap, ap, sc, sc, ap*. A necessary condition for near *C*_{2h} symmetry is that the pattern

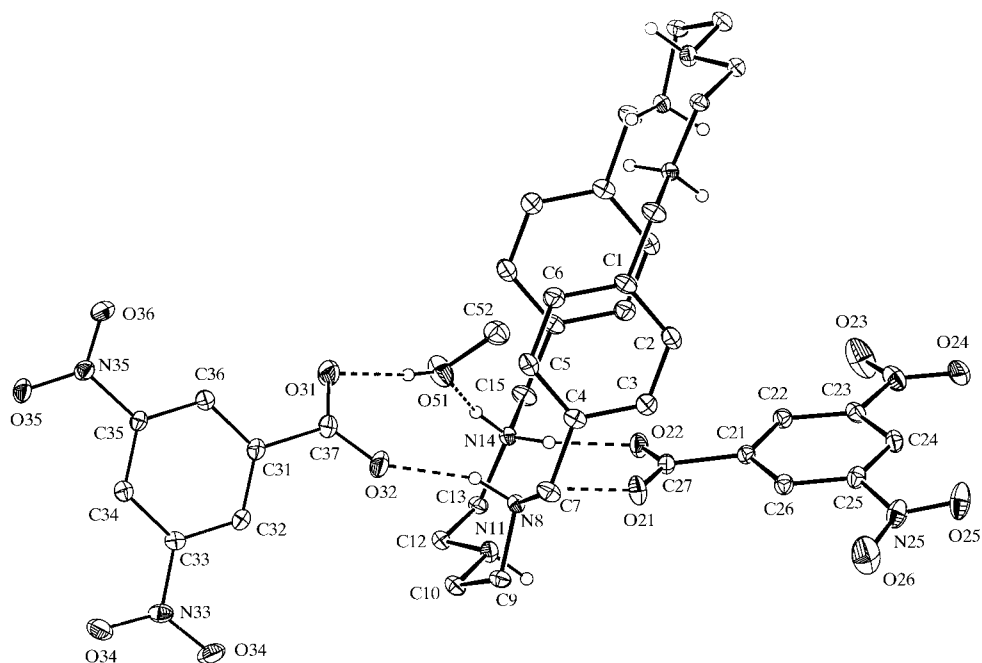


Figure 1

The independent molecular components of (1) showing the atom-labelling scheme. One anion is equally disordered over two closely related sites (O31–C37 and O41–C47); for clarity, only one of these sites (O31–C37) is shown. Displacement ellipsoids are drawn at the 30% probability level.

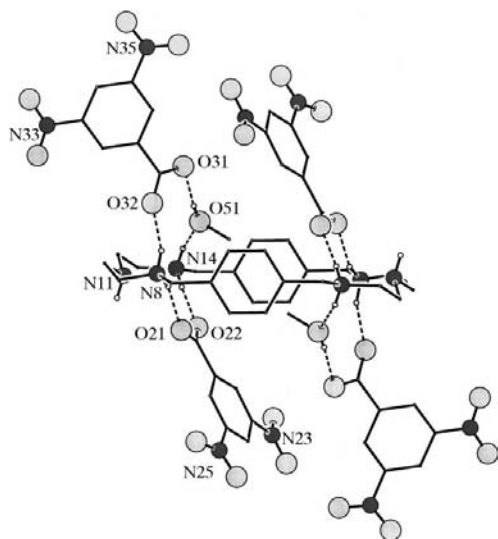


Figure 2

The seven-component hydrogen-bonded aggregate in (1). For the sake of clarity, H atoms bonded to C atoms have been omitted.

of torsional angles from C7 to N11 is repeated from C15 to N11 but with opposite signs for the corresponding angles in the two domains.

Within the cation, there is a clear difference between the C–N bond lengths involving protonated and unprotonated N atoms (Table 1); the observed ranges here are very similar to those for the corresponding types of bond in cation (II). 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). The trigonally trisubstituted anion carries three formally similar substituents; however, there is no orientation disorder resulting from this, and the two types of $-XO_2$ substituent ($X = C, N$) are readily distinguished in terms of the $X-O$ and exocyclic C–X distances (Table 1). It is noteworthy that for the anion without positional disorder, the interior C–C–C angles *ipso* to the substituents provide clear evidence for the strong electron-withdrawing behaviour of the NO_2 substituent, while CO_2^- appears to be neither an electron donor nor an electron acceptor (Domenicano & Murray-Rust, 1979). Also noteworthy is the fact that only the carboxylate O atoms are effective acceptors in $N-H \cdots O$ hydrogen bonds. The degree of twist of the substituents

out of the plane of the adjacent aryl ring varies between near planarity for the N43 nitro group to $35(4)^\circ$ for the C37 carboxylate group; no clear pattern is evident.

The tetraprotonated cation (III) contains ten N–H bonds, and its skeletal conformation means that there are no intramolecular N–H \cdots N hydrogen bonds. Rather, there are five N–H bonds on each face potentially available for intermolecular hydrogen-bond formation (Table 2 and Fig. 2), but the unprotonated N11 acts neither as hydrogen-bond donor nor as hydrogen-bond acceptor. On one face of the macrocycle, N8 and N14 act as donors (*via* H8B and H14A) to O21 and O22, respectively, forming paired N–H \cdots O hydrogen bonds reminiscent of those formed between the dication of the tetraaza macrocycle *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (tet-a) and aromatic carboxylate anions (Lough *et al.*, 2000). On the opposite face, N8 (*via* H8A) again acts as a donor to a carboxylate O atom, in this case, O32 in the second independent anion, but N14 is a donor (*via* H14B) to the methanol O51, which in turn acts as a donor (*via* H51) to O31, the other carboxylate O in the same anion. Thus, on one face, an $R_2^2(12)$ motif is formed, while on the other, an $R_3^3(14)$ ring is present. By means of these two cyclic motifs, four molecular components are linked together; since the cation lies across a centre of inversion, the entire molecular aggregate contains no fewer than seven components: one cation, four anions, and two neutral methanol molecules. The composition of one aggregate thus provides a precise microcosm of the overall stoichiometry of adduct (1). The only significant C–H \cdots O hydrogen bond in the structure (Table 2) lies within this aggregate: C36 in one of the anions acts as

donor to nitro-group O24 in the other anion on the same face of the macrocycle.

The isomeric cation (IV) in the salt $C_{24}H_{42}N_6^{4+} \cdot H_2P_2O_7^{2-} \cdot 2Br^- \cdot 5.2H_2O$ has neither crystallographic nor even approximate symmetry, but all ten of the N—H bonds participate in the hydrogen bonding: seven N—H...O hydrogen bonds are formed to three different diphosphate cations, two N—H...O hydrogen bonds are formed to water molecules, and there is an N—H...Br hydrogen bond (Nation *et al.*, 1996).

There are four of the seven-component aggregates in each unit cell, but there are no significant hydrogen bonds between them. There are, however, weak $\pi \cdots \pi$ stacking interactions leading to linking of the aggregates along the [010] direction. Anions containing O21 at (x, y, z) and $(\frac{1}{2} - x, \frac{3}{2} - y, -z)$ are components of the supramolecular aggregate centred at (0.25, 1.25, 0) and these anions exhibit aromatic $\pi \cdots \pi$ stacking interactions: the perpendicular distance between the ring planes is 3.291 (4) Å and the centroid offset is 1.257 (4) Å. Four of these [010] stacks run through each unit cell.

Experimental

The macrocycle (I) was prepared using published procedures (Chen & Martell, 1991; Comba *et al.*, 1996). The macrocycle and 3,5-dinitrobenzoic acid were separately dissolved in methanol, and then these solutions were mixed to give a molar ratio of macrocycle to acid of 1:2; the mixture was then set aside to crystallize, producing analytically pure (1). Analysis: found C 49.0, H 4.7, N 15.0%; $C_{54}H_{62}N_{14}O_{26}$ requires C 49.0, H 4.7, N 14.8%. Crystals suitable for single-crystal X-ray diffraction were selected directly from the analytical sample.

Crystal data

$C_{24}H_{42}N_6^{4+} \cdot 4C_7H_3N_2O_6^- \cdot 2CH_4O$	$D_x = 1.446 \text{ Mg m}^{-3}$
$M_r = 1323.18$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 19757 reflections
$a = 24.6342 (7) \text{ \AA}$	$\theta = 2.60\text{--}30.01^\circ$
$b = 11.7501 (2) \text{ \AA}$	$\mu = 0.117 \text{ mm}^{-1}$
$c = 21.4967 (7) \text{ \AA}$	$T = 150 (2) \text{ K}$
$\beta = 102.3970 (10)^\circ$	Block, colourless
$V = 6077.2 (3) \text{ \AA}^3$	$0.27 \times 0.25 \times 0.16 \text{ mm}$
$Z = 4$	

Data collection

KappaCCD diffractometer	5934 reflections with $I > 2\sigma(I)$
φ and ω scans with κ offsets	$R_{\text{int}} = 0.026$
Absorption correction: multi-scan (DENZO-SMN; Otwinowski & Minor, 1997)	$\theta_{\text{max}} = 30.01^\circ$
$T_{\text{min}} = 0.969, T_{\text{max}} = 0.982$	$h = 0 \rightarrow 34$
19757 measured reflections	$k = 0 \rightarrow 16$
8760 independent reflections	$l = -30 \rightarrow 29$
	Intensity decay: negligible

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0486P)^2 + 5.3065P]$
$R[F^2 > 2\sigma(F^2)] = 0.058$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.137$	$(\Delta/\sigma)_{\text{max}} = 0.002$
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.53 \text{ e \AA}^{-3}$
8760 reflections	$\Delta\rho_{\text{min}} = -0.43 \text{ e \AA}^{-3}$
448 parameters	Extinction correction: SHELXL97 (Sheldrick, 1997)
H-atom parameters constrained	Extinction coefficient: 0.00067 (17)

Table 1

Selected geometric parameters (Å, °).

N8—C7	1.492 (2)	O23—N23	1.215 (2)
N8—C9	1.492 (2)	O24—N23	1.228 (2)
N11—C10	1.455 (2)	O25—N25	1.219 (2)
N11—C12	1.452 (2)	O26—N25	1.210 (2)
N14—C13	1.492 (2)	N23—C23	1.466 (2)
N14—C15	1.496 (2)	N25—C25	1.476 (2)
O21—C27	1.242 (2)	O51—C52	1.404 (2)
O22—C27	1.255 (2)		
O21—C27—O22	128.32 (15)	C22—C21—C26	119.64 (14)
O23—N23—O24	123.89 (17)	C22—C23—C24	122.81 (15)
O25—N25—O26	123.88 (17)	C24—C25—C26	123.13 (16)
C3—C4—C7—N8	−100.88 (18)	C22—C21—C27—O21	−172.4 (2)
C4—C7—N8—C9	171.03 (14)	C22—C21—C27—O22	8.8 (2)
C7—N8—C9—C10	169.19 (13)	O33—N33—C33—C34	−162 (3)
N8—C9—C10—N11	54.38 (17)	O34—N33—C33—C34	14 (3)
C9—C10—N11—C12	−164.64 (13)	O35—N35—C35—C34	−19 (2)
C10—N11—C12—C13	−179.92 (13)	O36—N35—C35—C34	161.3 (3)
N11—C12—C13—N14	−59.59 (17)	C32—C31—C37—O31	145 (4)
C12—C13—N14—C15	−163.25 (13)	C32—C31—C37—O32	−35 (4)
C13—N14—C15—C1 ⁱ	178.45 (14)	O43—N43—C43—C44	177 (3)
N14—C15—C1 ⁱ —C2 ⁱ	−81.8 (2)	O44—N43—C43—C44	−2 (3)
O23—N23—C23—C24	173.9 (2)	O45—N45—C45—C44	9 (2)
O24—N23—C23—C24	−5.1 (2)	O46—N45—C45—C44	−170.4 (3)
O25—N25—C25—C24	11.4 (2)	C42—C41—C47—O41	163 (4)
O26—N25—C25—C24	−167.7 (2)	C42—C41—C47—O42	−17 (4)

Symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} - y, -z$.

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N8—H8A...O32	0.92	1.89	2.72 (5)	149
N8—H8A...O42	0.92	1.86	2.69 (5)	150
N8—H8B...O21	0.92	1.88	2.716 (2)	149
N14—H14A...O22	0.92	1.78	2.674 (2)	163
N14—H14B...O51	0.92	1.96	2.815 (2)	155
O51—H51...O31	0.84	1.91	2.75 (4)	173
O51—H51...O41	0.84	1.84	2.67 (4)	172
C36—H36...O24 ⁱ	0.95	2.30	3.234 (6)	169

Symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} - y, -z$.

Compound (1) crystallized in the monoclinic system; space group $C2/c$ or Cc from the systematic absences and $C2/c$ was assumed. It soon became apparent from peaks in difference maps and ellipsoid shapes that one of the dinitrobenzoic acid molecules was either slightly disordered in its volume element, or that the space group should be Cc and not $C2/c$. As subsequent refinement in Cc led to unsatisfactory ellipsoid shapes and geometry details for many of the atoms, this approach was abandoned and refinement continued in $C2/c$. The disorder was carefully modelled using planar hexagons for the benzene rings and using the *SAME* command in the *SHELXL97* refinement to ensure that both components of the disorder had similar geometries; the atoms of the disordered molecule are O31—C37 and O41—C47. Refining the disordered model with tied occupancy factors led to values of 0.54 (3) and 0.46 (3), not significantly different from equal occupancy; in the final cycles, the occupancies of the disordered atoms were fixed at 0.5. All H atoms involved in hydrogen bonding were clearly revealed in difference maps; all H atoms were treated as riding atoms with C—H distances ranging from 0.95 to 0.99 Å, N—H = 0.92 Å and O—H = 0.84 Å. Examination of

the structure with *PLATON* (Spek, 2000) showed that there were no solvent-accessible voids in the crystal lattice.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *NRCVAX96* (Gabe *et al.*, 1989) and *SHELXL97* (Sheldrick, 1997); molecular graphics: *NRCVAX96*, *ORTEPII* (Johnson, 1976) and *PLATON* (Spek, 2000); software used to prepare material for publication: *NRCVAX96*, *SHELXL97* and *WordPerfect* macro *PRPKAPPA* (Ferguson, 1999).

X-ray data were collected at the University of Toronto using a Nonius KappaCCD diffractometer purchased with funds from NSERC (Canada).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1023). Services for accessing these data are described at the back of the journal.

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