

The binary adduct of 3,6,9,16,19,22-hexaazatricyclo[22.2.2.2^{11,14}]triaconta-11,13,24,26(1),27,29-hexaene and benzene-1,2,4,5-tetracarboxylic acid

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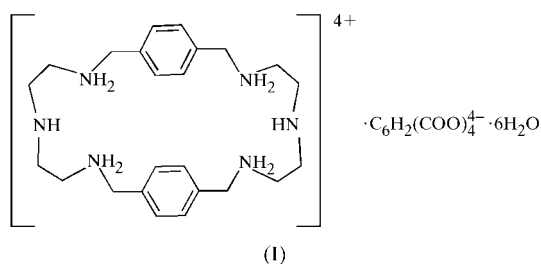
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The crystals of the title salt, 6,21-diaza-3,9,18,24-tetraazoniatricyclo[22.2.2.2^{11,14}]triaconta-11,13,24,26(1),27,29-hexaene benzene-1,2,4,5-tetracarboxylate(4⁻) hexahydrate, C₂₄H₄₂N₆⁴⁺·C₁₀H₂O₈⁴⁻·6H₂O, are formed by the intermolecular interaction of a macrocyclic hexamine with a molecule of C₆H₂(COOH)₄ in aqueous solution. Both the cation and the anion are on inversion centres. Hydrogen bonds are formed between the four ammonium cations in the hexamine and the four carboxylate anions in the aromatic acid. Stacks exist along the crystallographic *a* axis in the solid state. The water molecules also take part in a hydrogen-bonding network which joins these stacks together.

Comment

Macrocyclic compounds may form supramolecules if the stereochemistry of the donor atoms and the size and shape of the central cavity are suitable (Lehn, 1985, 1988). We are interested in the interplay of the covalent, ionic and hydrogen-bonding interactions that hold these supramolecules together, and in the dependence of these interactions on the conformation.



The inclusion properties of macrocyclic compounds can be adjusted by controlling the ring size. In the macrocyclic hexamine compound 3,6,9,16,19,22-hexaazatricyclo[22.2.2.2^{11,14}]triaconta-11,13,24,26(1),27,29-hexaene, designated *L*, the two identical diethylenetriamine moieties can be considered as

two arms of the molecule, which can coordinate to transition metal ions to form binuclear (Zhu *et al.*, 1998; Jurek & Martell, 1999) and tetranuclear (He *et al.*, 2001) metal complexes. This macrocyclic hexamine also creates a supramolecule, through intermolecular hydrogen bonding between water molecules and both the hexamine and other water molecules (He *et al.*, 2000). However, when metal ions are absent from the central cavity, the amino groups (as ammonium cations) become available for electrostatic interactions with carboxylic acid

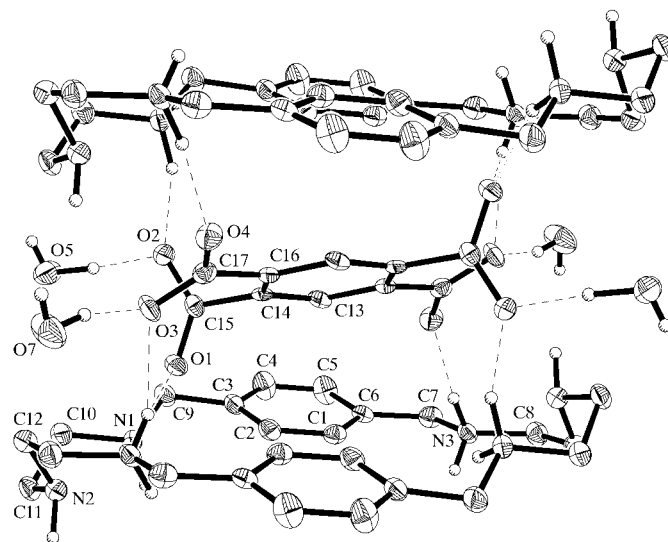


Figure 1

A view of the crystal structure of (I) showing the intermolecular interactions within a stack. Displacement ellipsoids are drawn at the 50% probability level. One of the water molecules, and the H atoms not participating in these interactions, have been omitted for clarity.

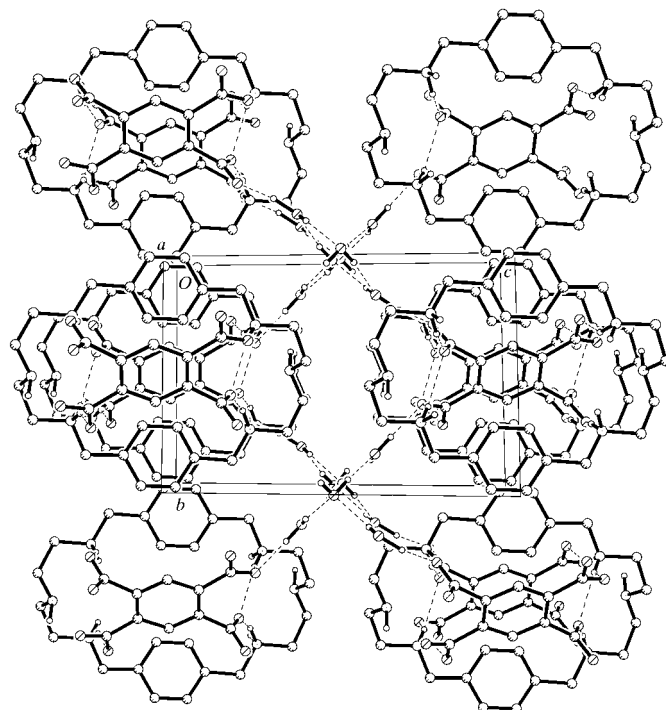


Figure 2

The packing diagram for (I) viewed along the *a* axis. Only hydrogen bonds with H...A distances shorter than 2.40 Å are shown.

groups (as carboxylate anions). Here, we show that the centrosymmetric hexamine *L* and C₆H₂(COOH)₄ form a salt, (I).

The asymmetric unit of the triclinic cell of (I) contains one half of the tetraprotonated LH₄⁴⁺ cation, one half of the C₆H₂(COO)₄⁴⁻ anion and three water molecules. The cations adopt a chair-like conformation, with one diethylenetriamine moiety flipped down and the other flipped up. The hydrogen bonding, involving the H atoms at N1 and N3 in LH₄⁴⁺, and the O atoms in C₆H₂(COO)₄⁴⁻, gives rise to aggregated stacks along the *a* axis (Fig. 1). The water molecules form hydrogen bonds that join the C₆H₂(COO)₄⁴⁻ ions of different stacks, yielding a three-dimensional network (Fig. 2). All bond lengths and angles in (I) agree well with the corresponding dimensions of the isolated macrocycle (He *et al.*, 2000). The observed differences from the standard values can be attributed to the participation of some atoms in hydrogen bonding.

The structure of (I) shows that the LH₄⁴⁺ macrocycle adjusts its conformation in order to optimize ionic interactions with C₆H₂(COO)₄⁴⁻.

Experimental

The macrocyclic hexamine *L* was synthesized according to the procedure of Chen & Martell (1991). Needle-shaped single crystals of the title salt were obtained by mixing a 10 mM aqueous solution of *L* (1.44 ml) with a 20 mM aqueous solution of C₆H₂(COOH)₄ (0.36 ml) (molar ratio 2:1), 2.00 M NaOH (3.6 μl) and 5.6 ml H₂O. The total volume was 7.40 ml. Similar crystals were also obtained using the binuclear Mg^{II} complex [LMg₂(OH)₂](ClO₄)₂ instead of *L*, and mixing a 20 mM aqueous solution of [LMg₂(OH)₂](ClO₄)₂ (300 μl) and a 20 mM aqueous solution of C₆H₂(COOH)₄ (150 μl) and water (250 μl). Spectroscopic analysis for (I): ¹H NMR (D₂O, δ, p.p.m.): 7.28 (*s*, 8H, ArH in LH₄⁴⁺), 4.11 (*s*, 8H, ArCH₂ in LH₄⁴⁺), 3.25 (*t*, 8H, NHCH₂ in LH₄⁴⁺), 3.03 (*t*, 8H, NHCH₂ in LH₄⁴⁺), 7.16 [*s*, 2H, ArCH in C₆H₂(COO)₄⁴⁻].

Crystal data

C₂₄H₄₂N₆⁴⁺·C₁₀H₂O₈⁴⁻·6H₂O

M_r = 772.85

Triclinic, P $\bar{1}$

a = 7.0983 (11) Å

b = 9.3947 (15) Å

c = 13.880 (2) Å

α = 87.686 (3)°

β = 79.635 (3)°

γ = 79.498 (3)°

V = 895.2 (2) Å³

Z = 1

D_x = 1.434 Mg m⁻³

Mo Kα radiation

Cell parameters from 3621 reflections

θ = 7–21°

μ = 0.11 mm⁻¹

T = 298 (2) K

Prism, black

0.2 × 0.2 × 0.1 mm

θ_{max} = 24.7°

h = –8 → 8

k = –10 → 11

l = –16 → 15

50 standard reflections

every 1085 reflections

intensity decay: none

Data collection

Bruker SMART 1000

diffractometer

φ and ω scans

4531 measured reflections

3011 independent reflections

1669 reflections with *I* > 2σ(*I*)

R_{int} = 0.034

Table 1

Hydrogen-bonding geometry (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
N1–H11N...O2	0.96 (3)	1.85 (3)	2.759 (4)	157 (2)
N1–H12N...O1 ⁱⁱⁱ	1.03 (3)	1.95 (3)	2.891 (3)	151 (3)
N3–H31N...O3 ⁱ	0.88 (3)	2.17 (4)	2.837 (4)	132 (3)
N3–H31N...O1 ⁱ	0.88 (3)	2.23 (3)	2.942 (3)	138 (3)
N3–H32N...O4 ⁱⁱ	1.16 (5)	1.69 (5)	2.726 (3)	146 (4)
O5–H11W...O2	1.08 (5)	1.66 (5)	2.727 (3)	170 (5)
O5–H12W...O6 ^{iv}	0.73 (3)	2.12 (3)	2.835 (4)	163 (3)
O6–H21W...O5 ^v	0.85 (3)	1.91 (4)	2.753 (3)	169 (3)
O6–H22W...O7	0.92 (4)	1.80 (4)	2.722 (4)	174 (3)
O7–H31W...O3	0.91 (4)	1.83 (4)	2.730 (3)	166 (4)
O7–H31W...O4	0.91 (4)	2.64 (4)	3.337 (3)	134 (3)
O7–H32W...O6 ^{vi}	0.84 (3)	2.03 (3)	2.801 (4)	151 (3)

Symmetry codes: (i) 1 – *x*, 1 – *y*, –*z*; (ii) 2 – *x*, 1 – *y*, –*z*; (iii) 1 + *x*, *y*, *z*; (iv) *x*, 1 + *y*, *z*; (v) –*x*, 1 – *y*, 1 – *z*; (vi) 1 – *x*, –*y*, 1 – *z*.

Refinement

Refinement on *F*²

R[*F*² > 2σ(*F*²)] = 0.047

wR(*F*²) = 0.104

S = 0.90

3011 reflections

293 parameters

H atoms: see below

w = 1/[σ²(*F_o*²) + (0.039*P*)²]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} < 0.001

Δρ_{max} = 0.22 e Å⁻³

Δρ_{min} = –0.22 e Å⁻³

Extinction correction: *SHELXL97*

Extinction coefficient: 0.010 (2)

H atoms involved in hydrogen bonding were located from a difference Fourier map, and their positions and isotropic displacement parameters were refined. All other H atoms were introduced at calculated positions and refined riding on their carrier atoms (C–H = 0.93 and 0.97 Å).

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1508). Services for accessing these data are described at the back of the journal.

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