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Adducts of *meso* and racemic 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane with trigonally trisubstituted benzene carboxylic acids: supramolecular structures in one and two dimensions

Colin J. Burchell,[a] George Ferguson,[b] Alan J. Lough[c] and Christopher Glidewell[a]*

[a]School of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, Scotland, [b]Department of Chemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1, and [c]Lash Miller Chemical Laboratories, University of Toronto, Toronto, Ontario, Canada M5S 3H6

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

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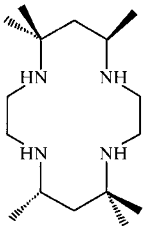
The *meso* and racemic forms of 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, $C_{16}H_{36}N_4$ (tet-a and tet-b, respectively), form adducts with trigonally trisubstituted benzene carboxylic acids; tet-a–3,5-dinitrobenzoic acid (1/2) (1), tet-a–5-hydroxyisophthalic acid–water (1/1/1) (3) and tet-b–5-hydroxyisophthalic acid–water (1/1/1) (4) are all salts, $[C_{16}H_{38}N_4]^{2+}\cdot 2[C_7H_3N_2O_6]^-$ (1) and $[C_{16}H_{38}N_4]^{2+}\cdot[C_8H_4O_5]^{2-}\cdot H_2O$ (3) and (4). The conformations of the $[(\text{tet-a})H_2]^{2+}$ and $[(\text{tet-b})H_2]^{2+}$ cations are entirely different: $[(\text{tet-a})H_2]^{2+}$ is precisely centrosymmetric in (1) and approximately so in (3), while $[(\text{tet-b})H_2]^{2+}$ has approximate C_2 symmetry in (4). In each salt the cation forms two intramolecular N—H···N and four intermolecular N—H···O hydrogen bonds. In (1) the supramolecular structure is one-dimensional, a $C_2^2(13)[R_2^4(16)]$ chain of rings. Compounds (3) and (4) crystallize in space groups $P2_12_12_1$ and $P2_1/c$, respectively, but the supramolecular structures are very similar: in each, the anions and the water molecules form a $C(7)[R_3^3(13)]$ chain of rings, generated in (3) by a 2_1 axis and in (4) by a glide plane. These chains are linked, in both (3) and (4), by cations to form sheets. Adjacent *meso* cations in (3) are related by a 2_1 axis and adjacent chiral cations in (4) are related by a glide plane.

1. Introduction

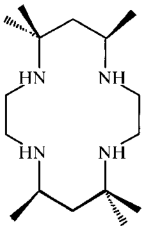
The tetra-aza macrocycle 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, $C_{16}H_{36}N_4$, exists in two isomeric forms: the *meso* compound [(I), tet-a] and the racemic form [(II), tet-b]. The *meso* form has been shown to be a versatile building block in supramolecular chemistry (Gregson *et al.*, 2000; Lough *et al.*, 2000), where it generally captures two protons from acidic species to form a dication $[C_{16}H_{38}N_4]^{2+}$ in which two H atoms are held in the interior N_4 cavity of the ring, forming a pair of intramolecular N—H···N hydrogen bonds. There are four external N—H bonds roughly normal to the ring and hence this dication could, in principle, act as a fourfold donor in hydrogen-bond formation in which the geometric arrangement of the hydrogen bonds is pre-determined.

The major difference between the cations derived from tet-a and tet-b lies in their molecular symmetry: whereas $[(\text{tet-a})H_2]^{2+}$ can, and generally does, lie across a centre of inversion, $[(\text{tet-b})H_2]^{2+}$ can instead lie across a twofold rotation axis. In both cations, it may be expected that there are two N—H bonds on each face of the macrocycle available for hydrogen-bond formation. It has previously been shown (Lough *et al.*, 2000) that with dicarboxylic acids such as terephthalic acid, the $[(\text{tet-a})H_2]^{2+}$ cation can form paired $N—H\cdots O$ hydrogen bonds with carboxylate anions, thus giving rise to chain formation.

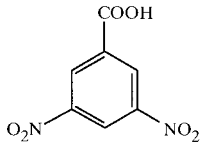
Extending this idea, we have now investigated the salt-type adducts formed between this macrocycle and the trigonally trisubstituted benzene carboxylic acids (III)–(VI), and we report here the synthesis of six such compounds, together with the structure analyses of three of them. The compounds formed are: tet-a–3,5-dinitrobenzoic acid (1/2) (1), tet-a–5-nitroisophthalic acid (1/2) (2), tet-a–5-hydroxyisophthalic acid–water (1/1/1) (3), tet-b–5-hydroxyisophthalic acid–water (1/1/1) (4), tet-a–1,3,5-benzenetricarboxylic acid–methanol (1/1/2) (5) and tet-b–1,3,5-benzenetricarboxylic acid–methanol (1/1/2) (6). Structure analyses are reported here for (1), (3) and (4): (3) and (4) illustrate the configurational and conformational differences between the isomeric forms of the tetra-aza macrocyclic cations $[(\text{tet-a})H_2]^{2+}$ and $[(\text{tet-b})H_2]^{2+}$. The structure of the 1:2 adduct formed between tet-a and 3,5-dihydroxybenzoic acid (VII) has been described previously (Gregson *et al.*, 2000).



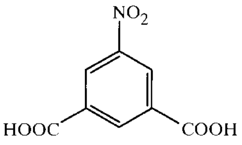
(I)



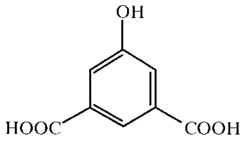
(II)



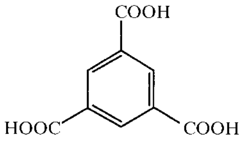
(III)



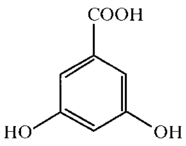
(IV)



(V)



(VI)



(VII)

2. Experimental

2.1. Synthesis

Samples of tet-a and tet-b were prepared as the dihydrate and monohydrate, respectively, by the literature method (Hay *et al.*, 1975). The acids (III)–(VI) were purchased from Aldrich and were all used as received. For all adducts, stoichiometric quantities of the macrocyclic amine and the appropriate acid were separately dissolved in methanol: these solutions were mixed and the mixtures were set aside to crystallize, exposed to the laboratory atmosphere, yielding analytically pure samples of the adducts (1)–(6). Analyses: (1) found C 50.8, H 5.9, N 15.8%; $C_{30}H_{44}N_8O_{12}$ requires C 50.8, H 6.3, N 15.8%; (2) found C 53.8, H 7.1, N 11.8%; $C_{32}H_{46}N_6O_{12}$ requires C 54.4, H 6.6, N 11.9%; (3) found C 59.1, H 9.8, N 11.5%; (4) found C 59.0, H 10.1, N 11.5%; $C_{24}H_{44}N_4O_6$ requires C 59.5, H 9.2, N 11.6%; (5) found C 57.9, H 9.1, N 10.0%; (6) found C 58.0, H 9.5, N 10.4%; $C_{27}H_{50}N_4O_8$ requires C 58.0, H 9.0, N 10.0%. Crystals of (1), (3) and (4) suitable for single-crystal X-ray diffraction were selected directly from the analytical samples: no suitable crystals of (2), (5) or (6) have yet been obtained.

2.2. Data collection, structure solution and refinement

Diffraction data for (1), (3) and (4) were collected, at 150 (2) K for (1) and 100 (2) K for (3) and (4), using a Nonius KappaCCD diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å). Other details of cell data, data collection and refinement are summarized in Table 1, together with details of the software employed (Ferguson, 1999; Gabe *et al.*, 1989; Johnson, 1976; Nonius, 1997; Otwinowski & Minor, 1997; Sheldrick, 1997*a*,*b*; Spek, 2000). Compound (1) is triclinic: the space group $P\bar{1}$ was assumed and confirmed by the structure analysis. For (3) and (4) the space groups $P2_12_12_1$ and $P2_1/c$, respectively, were uniquely determined from the systematic absences. The structures were solved by direct methods and refined with all data on F^2. A weighting scheme based upon $P = [F_o^2 + 2F_c^2]/3$ was employed in order to reduce statistical bias (Wilson, 1976). All H atoms were located from difference maps and those in the organic components were included in the refinements as riding atoms with O—H 0.84, N—H 0.92, C—H 0.95 (aromatic), 0.98 (CH_3), 0.99 (CH_2), 1.00 Å (aliphatic CH); for H atoms in water molecules, the O—H bond lengths were originally refined as a single variable to a value of 0.84 Å, but in the final cycles they were constrained to 0.840 (3) Å by the use of a *DFIX* command. It was apparent at an early stage in the refinements that two H atoms had been transferred from the acid units to the tet-a or tet-b units. In (3) it was apparent that there was some orientational disorder in the cation, consistent with an end-over-end rotation which led to partial disorder of the axial methyl groups. The site occupation factors for the two orientations refined to 0.856 (3) and 0.143 (3). The absolute configuration of (3) could not be determined by Flack refinement and for the final refinements the Friedel equivalents were merged.

The diagrams were prepared with the aid of *PLATON* (Spek, 2000). Hydrogen-bond dimensions are presented in Table 2 and other selected dimensions in Tables 3 and 4.[1]

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[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA0108). Services for accessing these data are described at the back of the journal.

Figs. 1–3 show the molecular components, with the atom-labelling schemes; in each case the atom-numbering in the macrocycles corresponds to the chemical (IUPAC) numbering scheme. Figs. 4–6 illustrate aspects of the supramolecular structures.

3. Results and discussion

3.1. Co-crystallization behaviour and molecular constitutions

Based upon previous observations that tet-a in general captures two protons from phenols and carboxylic acids to form the di-cation $[(\text{tet-a})H_2]^{2+}$ (Gregson *et al.*, 2000; Lough *et al.*, 2000), all co-crystallization experiments in the present study were designed to provide two carboxyl groups per tetra-aza macrocycle. Consistent with expectation, (1) is a 1:2 adduct, while (3) and (4) are both 1:1 adducts, although both are monohydrates. Since both tet-a and tet-b are normally prepared and crystallized as hydrates (Hay *et al.*, 1975), the formation of (3) and (4) as monohydrates is not exceptional: as the structure analyses described below (§3.3.2 and §3.3.3) demonstrate, the water molecules are intimately bound into the hydrogen-bonded crystal structure.

In the absence of structure analyses no definitive comments can be made on the constitutions of (2), (5) and (6), but it may be noted that in each of these compounds the ratio of tetra-aza macrocycle-to-acid is unexpected. It is possible that in (2), tet-a has formed the tetra-positive cation $[(\text{tet-a})H_4]^{4+}$, which has previously been observed in an adduct with phenylphosphonic acid (Gregson *et al.*, 2000); the formation of $[(\text{tet-a})H_2]^{2+}$ in (5) and (6) requires that the anion retains unionized carboxyl groups, possibly involved in the formation of the usual carboxylic acid dimer $R_2^2(8)$ motif.

The constitutions of (1), (3) and (4) are all those of salts, $[C_{16}H_{38}N_4]^{2+}\cdot2[C_7H_3N_2O_6]^-$ (1) and $[C_{16}H_{38}N_4]^{2+}\cdot[C_8H_4O_5]^{2-}\cdot H_2O$ (3) and (4): in each, the cation is characterized by the presence within the N_4 cavity of two protons held by intramolecular hydrogen bonds (Table 2). The internal H atoms are fully ordered in each compound, but the site of protonation varies: in (1), the N atoms adjacent to the gem-dimethyl groups are protonated (N4), while in (3) and (4) it is the N atoms, remote from these groups, N1 and N8, which are protonated.

3.2. Cation conformations

In (1) the $[(\text{tet-a})H_2]^{2+}$ cation lies across a centre of inversion, in the usual *trans*-III conformation (Barefield *et al.*, 1986), with almost perfect staggering about all the C—C and C—N bonds. In this conformation, the four N atoms are strictly coplanar and there are four axial N—H bonds, two on each face of the macrocycle; these are essentially normal to the plane of the macrocycle and all are potentially available for intermolecular hydrogen-bond formation. Although the $[(\text{tet-a})H_2]^{2+}$ cation in (3) lies in a general position, its conformation is virtually identical to that of the centrosymmetric cation in (1), and it is itself very close to being centrosymmetric, with again the four N atoms almost coplanar.

By contrast, in the $[(\text{tet-b})H_2]^{2+}$ cation of (4), where the maximum possible symmetry is C_2, the four N atoms are by no means coplanar, but instead the conformation is such that the N4 group approaches tetrahedral (Fig. 3). Nevertheless, there are still two N—H bonds on each face available for hydrogen-bond formation, but the staggering about the C—N bonds, in particular about N4—C5 and N11—C12, is far from ideal (Table 3). The overall conformation of this cation is close to C_2 symmetry and it closely resembles the exactly C_2-symmetric

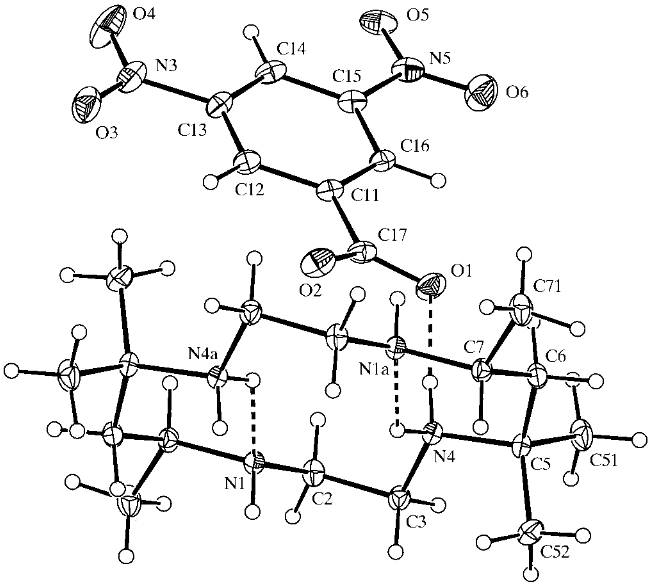

Figure 1
The molecular components of (1), showing the atom-labelling scheme: atoms labelled with an 'a' are at the symmetry position $(1-x, 1-y, 1-z)$. Displacement ellipsoids are drawn at the 30% probability level.

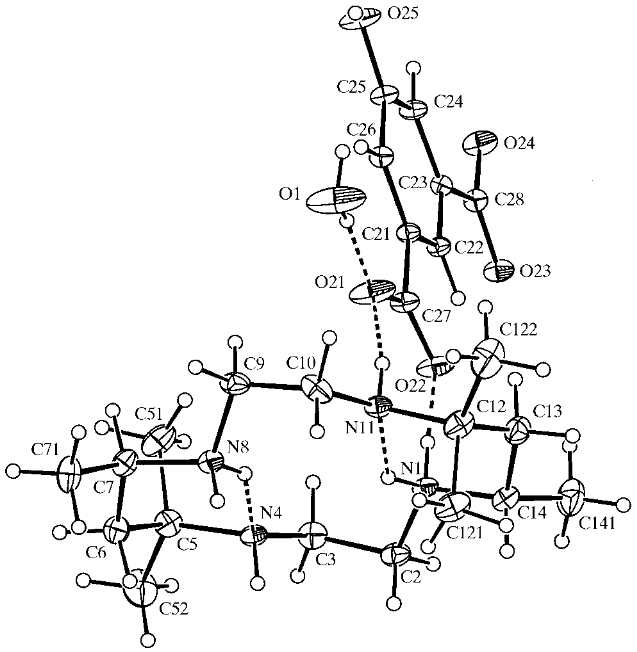

Figure 2
The asymmetric unit of (3), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

cation in $[(\text{tet-b})H_2]^{2+}\cdot(Cl^-)_2\cdot3H_2O$ (Simonov *et al.*, 1998). In (3) the corresponding torsional angles for the two halves of the molecule, counting from N1 and N8, respectively, have similar magnitudes but opposite signs, whereas in (4) they have similar magnitudes with the same signs. This reflects the approximate C_i and C_2 symmetry of the cations in (3) and (4), respectively. The other principal difference between the conformations of the $[(\text{tet-a})H_2]^{2+}$ and $[(\text{tet-b})H_2]^{2+}$ cations lies in the distribution of antiperiplanar (*ap*) and synclinal (*sc*) torsional angles: each half of a $[(\text{tet-a})H_2]^{2+}$ cation in (1) or (3) contains 4 *ap* and 3 *sc* torsional angles, while in the $[(\text{tet-b})H_2]^{2+}$ cation there are 3 *ap* and 4 *sc* torsional angles. Such a simple change leading to a wholly different molecular conformation has been observed previously in adducts of hexa-aza macrocycles (Glidewell *et al.*, 2000).

The other important difference consequent upon the different conformations of the cations, and their approximate symmetries, lies in the disposition of the axial N—H bonds. In $[(\text{tet-a})H_2]^{2+}$, the axial bonds associated with N1 and N11 lie on one face of the macrocycle, and those associated with N4 and N8 lie on the other face: in $[(\text{tet-b})H_2]^{2+}$, by contrast, the pairings are N1 and N8 on one face and N4 and N11 on the other. Thus, in $[(\text{tet-a})H_2]^{2+}$, the near-parallel N—H bonds on a given face are separated by a C_3 bridge, while in $[(\text{tet-b})H_2]^{2+}$ the space unit is C_3—N(H)—C_3.

3.3. Supramolecular structures

In each of (1), (3) and (4) the individual molecular components, ionic and neutral, are linked by an extensive series of hydrogen bonds, of both N—H···O and, in (3) and (4), O—H···O types. The overall supramolecular aggregation is one-dimensional in (1) and two-dimensional in (3) and (4).

3.3.1. Compound (1). In (1) the cation lies across a centre of inversion, chosen for convenience as (0.5, 0.5, 0.5), with an anion in a general position, consistent with the 1:2 stoichiometry deduced from microanalytical data. The structure is best described in terms of centrosymmetric, three-component aggregates, anion–cation–anion. The axial N—H bonds on each face of the cation form paired N—H···O hydrogen bonds to the anions (Table 2; Fig. 1), in a motif which may be described as either $R_2^2(10)$ counting round the C12—C13—C14 bridge of the macrocycle, or $R_3^3(8)$ counting across one of the intramolecular N—H···N hydrogen bonds. This motif of paired N—H···O hydrogen bonds between $[(\text{tet-a})H_2]^{2+}$ and a carboxylate anion is identical to one found in the hydrated adducts of tet-a with terephthalic acid (Lough *et al.*, 2000), and hence the three-component aggregate in (1) is most simply regarded as containing three $R_2^2(10)$ motifs. Atom N4 at (x, y, z) acts as a hydrogen-bond donor to O1 within the same asymmetric unit, while N1 at ($1-x$, $1-y$, $1-z$) acts as a donor to O2 in the same anion; similarly, N1 at (x, y, z) and N4 at ($1-x$, $1-y$, $1-z$), whose axial N–H bonds project from the

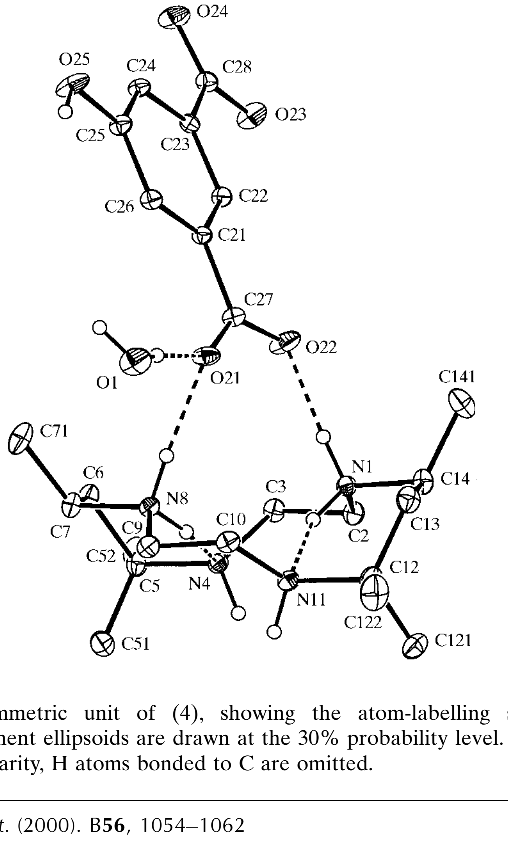

Figure 3
The asymmetric unit of (4), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. For the sake of clarity, H atoms bonded to C are omitted.

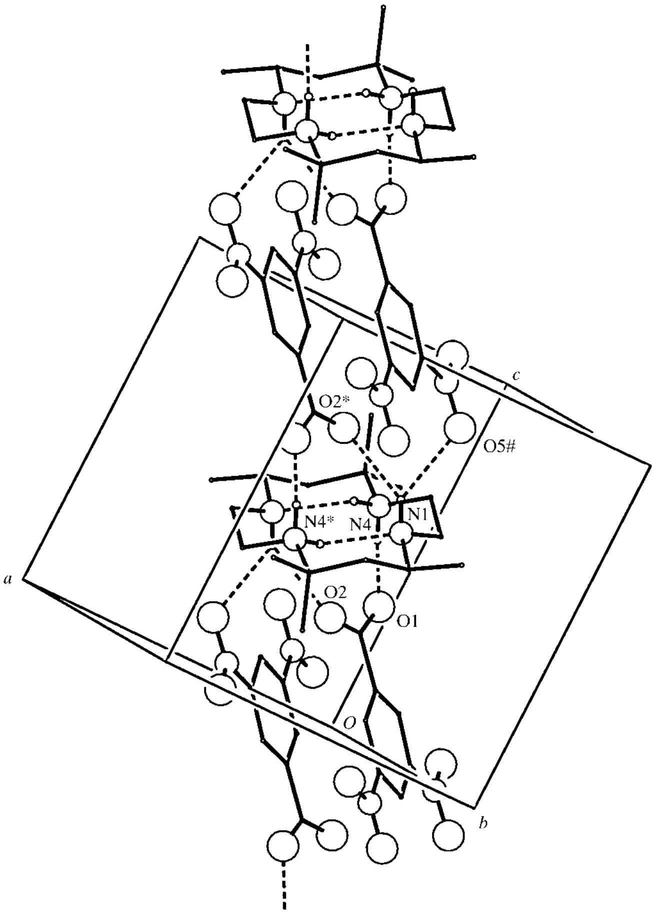

Figure 4
Part of the crystal structure of (1), showing the formation of a [111] chain. For the sake of clarity, H atoms bonded to C are omitted. Atoms marked with a star (*) or hash (#) are at the symmetry positions ($1-x$, $1-y$, $1-z$) and ($1+x$, $1+y$, $1+z$), respectively.

Table 1
Experimental details.

Computer programs used: for data collection: *KappaCCD Software* (Nonius, 1997); for cell refinement and data reduction: *DENZO-SMN* (Otwinowski & Minor, 1997); for structure solution: *SHELXS*97 (Sheldrick, 1997*a*); for structure refinement: *NRCVAX*96 and *SHELXL*97 (Sheldrick, 1997*b*); preparation of material for publication: *NRCVAX*96, *SHELXL*97 and *WordPerfect* macro PRPKAPPA (Ferguson, 1999).

	(1)	(3)	(4)
Crystal data			
Chemical formula	$C_{16}H_{38}N_4 \cdot 2C_7H_3N_2O_6$	$C_{16}H_{38}N_4 \cdot C_8H_4O_5 \cdot H_2O$	$C_{16}H_{38}N_4 \cdot C_8H_4O_5 \cdot H_2O$
Chemical formula weight	708.73	484.63	484.63
Cell setting	Triclinic	Orthorhombic	Monoclinic
Space group	$P\bar{1}$	$P2_12_12_1$	$P2_1/c$
a (Å)	8.7336 (3)	11.8760 (5)	16.0262 (4)
b (Å)	10.9388 (3)	13.8395 (6)	11.6461 (3)
c (Å)	11.0284 (3)	15.8571 (7)	15.7907 (3)
α (°)	114.5800 (17)	90	90
β (°)	91.9660 (18)	90	118.6520 (12)
γ (°)	111.6740 (18)	90	90
V (Å^3)	868.09 (4)	2606.2 (2)	2586.33 (10)
Z	1	4	4
D_x (Mg m^{-3})	1.356	1.235	1.245
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
Wavelength (Å)	0.71073	0.71073	0.71073
No. of reflections for cell parameters	12 749	4203	5899
θ range (°)	3.03–30.0	2.60–30.04	2.58–27.45
μ (mm^{-1})	0.106	0.089	0.089
Temperature (K)	150 (2)	100 (2)	100 (2)
Crystal form	Block	Block	Block
Crystal size (mm)	0.26 × 0.16 × 0.14	0.24 × 0.24 × 0.16	0.32 × 0.26 × 0.20
Crystal colour	Colourless	Colourless	Colourless
Data collection			
Diffractometer	KappaCCD	KappaCCD	KappaCCD
Data collection method	φ scans and ω scans with κ offsets	φ scans and ω scans with κ offsets	φ scans and ω scans with κ offsets
Absorption correction	Multi-scan	Multi-scan	Multi-scan
$T_{\min}$	0.9730	0.9791	0.9720
$T_{\max}$	0.9853	0.9860	0.9824
No. of measured reflections	12 749	30 326	23 221
No. of independent reflections	5013	4203	5899
No. of observed reflections	3651	3479	4676
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.023	0.033	0.035
$\theta_{\max}$ (°)	30.00	30.04	27.45
Range of *h*, *k*, *l*	$0 \rightarrow h \rightarrow 12$	$0 \rightarrow h \rightarrow 16$	$-20 \rightarrow h \rightarrow 18$
	$-15 \rightarrow k \rightarrow 14$	$0 \rightarrow k \rightarrow 19$	$-15 \rightarrow k \rightarrow 0$
	$-15 \rightarrow l \rightarrow 15$	$0 \rightarrow l \rightarrow 22$	$0 \rightarrow l \rightarrow 20$
Refinement			
Refinement on	F^2	F^2	F^2
$R[F^2>2\sigma(F^2)]$	0.0490	0.0579	0.0485
$wR(F^2)$	0.1329	0.1243	0.1257
S	1.071	1.044	1.017
No. of reflections used in refinement	5013	4203	5899
No. of parameters used	229	323	321
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0542P)^2 + 0.1566P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0480P)^2 + 0.8417P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0515P)^2 + 1.3466P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	0.001	0.008	0.000
$\Delta\rho_{\max}$ (e Å^{-3})	0.243	0.299	0.283
$\Delta\rho_{\min}$ (e Å^{-3})	−0.268	−0.272	−0.240
Extinction method	None	None	*SHELXL* (Sheldrick, 1997*b*)
Extinction coefficient	–	–	0.0051 (10)
Source of atomic scattering factors	*International Tables for X-ray Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	*International Tables for X-ray Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	*International Tables for X-ray Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

opposite face of the macrocycle (Fig. 1), are donors to the anion at $(1 - x, 1 - y, 1 - z)$.

The axial N1—H1 bond is bonded not only to a carboxylate O, but also to a nitro O atom in a three-centre N—H···(O)$_2$ system (Table 2). On one face of the reference cation centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, N1 at (x, y, z) acts as a hydrogen-bond donor to O5 at $(1 + x, 1 + y, 1 + z)$, which is a component of the tripartite aggregate centred at $(\frac{3}{2}, \frac{3}{2}, \frac{3}{2})$; on the opposite face of the reference cation, the symmetry-related N1 at $(1-x, 1-y, 1-z)$ is a donor to O5 at $(-x, -y, -z)$, which is a component of the aggregate centred at $(-\frac{1}{2}, -\frac{1}{2}, -\frac{1}{2})$. Propagation of this interaction by translation generates a $C_2^2(13)[R_2^4(16)]$ chain of rings running parallel to the [111] direction (Fig. 4). Along this chain, cations centred at $(n+\frac{1}{2}, n+\frac{1}{2}, n+\frac{1}{2})$ (n = zero or integer) alternate with $R_2^4(16)$ rings centred at (n, n, n) (n = zero or integer). It is noteworthy that only one of the nitro O atoms participates in the hydrogen bonding: in the absence of the hydrogen bond to O5, the structure would consist of finite (zero-dimensional) centrosymmetric aggregates. The successive centres of inversion along the [111] chain mean that the aryl ring planes of the anions are all parallel and adjacent anions can engage in $\pi\cdots\pi$ stacking interactions (Fig. 4): the perpendicular separation between adjacent planes is 3.317 (3) Å, with a centroid offset of 1.939 (3) Å. These $\pi\cdots\pi$ interactions, albeit weak, serve to reinforce the supramolecular aggregation along the [111] direction.

3.3.2. Compound (3). In (3) the component ions (Fig. 2) are linked by a total of seven hydrogen bonds, four of the N—H···O type and three of O—H···O type (Table 2). Each of the axial N—H bonds of the cation and each of the O—H bonds of the water molecule, as well as the hydroxyl group of the anion, acts as a hydrogen-bond donor. All four O atoms in the carboxylate groups act as hydrogen-bond acceptors, O21 and O23 as double acceptors, and O22 and O24 as single acceptors. In addition, the hydroxyl O atom acts as a single acceptor, although the water O atom does not. Despite this apparent complexity, the supramolecular structure is, in fact, rather straightforward and is best described using the substructure approach (Gregson *et al.*, 2000). The anions and the water molecules form isolated cation-free chains and these chains are then linked into sheets by the cations (Fig. 5).

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

D	H	A	H···A	D···A	D—H···A
(1)					
N4	H4A	N1^{i}	2.12	2.808 (2)	131
N4	H4B	O1	1.81	2.730 (2)	175
N1	H1	O2^{i}	2.46	3.107 (2)	127†
N1	H1	O5^{ii}	2.42	3.169 (2)	139†
(3)					
N1	H1A	N11	2.02	2.767 (3)	138
N8	H8B	N4	1.97	2.762 (3)	144
N1	H1B	O22	1.71	2.622 (3)	173
N4	H4A	O25^{iii}	2.03	2.952 (3)	175
N8	H8A	O23^{iv}	1.91	2.795 (3)	160
N11	H11A	O21	2.25	3.122 (3)	159
O1	H41	O21	1.90	2.720 (2)	165
O1	H42	O24^{v}	1.95	2.761 (3)	160
O25	H25	O23^{v}	1.93	2.655 (2)	144
(4)					
N1	H1A	N11	1.93	2.762 (2)	150
N8	H8A	N4	1.92	2.742 (2)	148
N1	H1B	O22	1.81	2.702 (2)	162
N4	H4A	O25^{vi}	2.01	2.913 (2)	165
N8	H8B	O21	1.85	2.765 (2)	176
N11	H11A	O23^{vii}	2.11	3.023 (2)	170
O1	H41	O21	1.92 (2)	2.752 (2)	172 (2)
O1	H42	O24^{viii}	1.91 (2)	2.748 (2)	172 (2)
O25	H25	O23^{viii}	1.82	2.565 (2)	147

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $1+x, 1+y, 1+z$; (iii) $1+x, y, z$; (iv) $\frac{1}{2}-x, 1-y, \frac{1}{2}+z$; (v) $-\frac{1}{2}-x, 1-y, \frac{1}{2}+z$; (vi) $x, 1-y, z$; (vii) $x, \frac{3}{2}-y, -\frac{1}{2}+z$; (viii) $x, \frac{1}{2}-y, -\frac{1}{2}+z$. † N1—H1···O2^{i}/O5^{ii} is a three-centre hydrogen bond; the sum of angles at H1 is 347°.

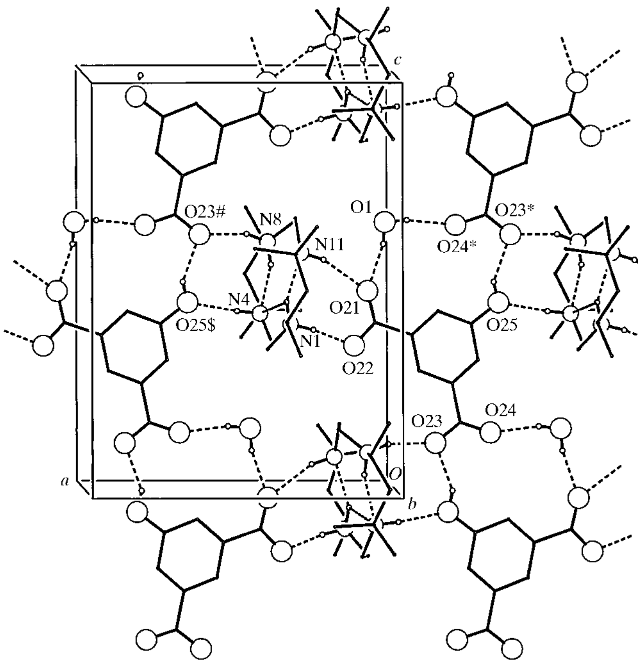

Figure 5
Part of the crystal structure of (3), showing a sheet parallel to (010) formed by linking parallel $C(7)[R_3^3(13)]$ chains of rings. For the sake of clarity, H atoms bonded to C are omitted. Atoms marked with a star (*), hash (#) or dollar ($) sign are at the symmetry positions $(-\frac{1}{2}-x, 1-y, \frac{1}{2}+z)$, $(\frac{1}{2}-x, 1-y, \frac{1}{2}+z)$ and $(1+x, y, z)$, respectively.

The anions themselves are assembled into C(7) chains running parallel to [001]: hydroxyl O25 at (x, y, z) acts as a hydrogen-bond donor to carboxylate O23 at $(-\frac{1}{2}-x, 1-y, \frac{1}{2}+z)$, while O25 at $(-\frac{1}{2}-x, 1-y, \frac{1}{2}+z)$ in turn acts as a donor to O23 at $(x, y, 1+z)$, thus generating a spiral around the 2_1 axis along $(-\frac{1}{4}, \frac{1}{2}, z)$. Each water molecule is linked to two adjacent anions within a single chain: the water O1 at (x, y, z) is linked, *via* H41 to O21 also at (x, y, z) and *via* H42 to O24 at $(-\frac{1}{2}-x, 1-y, \frac{1}{2}+z)$. Hence, the [001] motif is a $C(7)[R_3^3(13)]$ chain of rings (Fig. 5). Two such chains run through each unit cell.

Adjacent parallel [001] chains, offset by translations along [100], are linked by the cations. On one face of the cation at (x, y, z), N1 and N11 act as donors to O22 and O21 in the anion at (x, y, z) forming paired and essentially parallel N—H···O hydrogen bonds analogous to those in (1). On the opposite face of the cation at (x, y, z), N4 and N8 act as donors to, respectively, hydroxyl O25 at $(1+x, y, z)$ and carboxylate O23 at $(\frac{1}{2}-x, 1-y, \frac{1}{2}+z)$, both of which are components of the [001] chain around the 2_1 axis along $(\frac{3}{4}, \frac{1}{2}, z)$. The cations thus serve to link adjacent chains of anions and water molecules into a continuous sheet (Fig. 5). Two such sheets pass through each unit cell, one in the domain $\frac{1}{4} < y < \frac{3}{4}$ and the other in the domain $-\frac{1}{4} < y < \frac{1}{4}$. There are no bonding interactions between

Table 3
Selected torsional angles (°).

	(1)	(3)	(4)
N1—C2—C3—N4	−59.6 (2)	−69.4 (3)	−62.2 (2)
C2—C3—N4—C5	−175.2 (2)	−175.6 (2)	178.5 (2)
C3—N4—C5—C6	−174.6 (2)	177.0 (2)	−85.6 (2)
N4—C5—C6—C7	60.7 (2)	68.5 (3)	−66.3 (2)
C5—C6—C7—N8	−67.1 (12)†	−61.4 (3)	61.3 (2)
C6—C7—N8—C9	−177.8 (2)‡	158.0 (2)	−155.6 (2)
C7—N8—C9—C10	−178.79 (9)§	173.2 (2)	−177.3 (2)
N8—C9—C10—N11		63.8 (3)	−60.7 (2)
C9—C10—N11—C12		−171.5 (2)	178.9 (2)
C10—N11—C12—C13		−172.5 (2)	−80.7 (2)
N11—C12—C13—C14		−64.9 (3)	−66.5 (2)
C12—C13—C14—N1		62.2 (3)	57.8 (2)
C13—C14—N1—C2		−169.3 (2)	−148.1 (2)
C14—N1—C2—C3		177.7 (2)	−176.1 (2)

Symmetry code: (i) $1-x, 1-y, 1-z$. † C5—C6—C7—N1^{i}. ‡ C6—C7—N1^{i}—C2^{i}. § C7^{i}—N1—C2—C3.

neighbouring sheets: in particular, there are neither hydrogen bonds nor $\pi\cdots\pi$ stacking interactions between sheets.

3.3.3. Compound (4). Despite different configurations at C14, and different conformations of the $[(\text{tet-a})H_2]^{2+}$ and $[(\text{tet-b})H_2]^{2+}$ cations (§3.2), and the different space groups for (3) and (4) ($P2_12_12_1$and $P2_1/c$, respectively), the supramolecular structures of these two compounds are remarkably similar (compare Figs. 5 and 6). The differences between them are nonetheless important in terms of the stereochemistry of the cations.

In (4) the anion/water chains are parallel to [001] (Fig. 6) generated by the glide planes and the sheets are parallel to (010), whereas in (3) the chains are generated by a 2_1 axis and the sheets lie parallel to (100). Similarly, whereas the neighbouring cations in (3) are related by a 2_1 axis, in (4) they are related by a glide plane. Thus, in (3) all the cations have the same chirality, but in (4) equal numbers of the two enantiomorphic forms are present. Since the cations in (3) all have the *meso* configuration and are thus in principal achiral, they are indifferent to the nature of the symmetry operation relating them: each individual cation in (4), on the other hand, is chiral and in a racemic mixture, as utilized here, there are equal numbers of the two enantiomorphs, so that the space group must contain improper operators. Hence, the apparent paradox that the salt containing $[(\text{tet-a})H_2]^{2+}$, where the highest intrinsic symmetry of the cation is C_i, crystallizes in a non-centrosymmetric space group, while the corresponding salt of $[(\text{tet-b})H_2]^{2+}$, where the highest possible symmetry of the cation is C_2, crystallizes in a centrosymmetric space group.

3.3.4. General comments on the crystal structures. In both (1) and (3) all four of the axial N—H bonds of the $[(\text{tet-a})H_2]^{2+}$ cations are engaged in the formation of N—H$\cdots$O hydrogen bonds: this is also the case in the salt-like adducts formed by tet-a with terephthalic acid (Lough *et al.*, 2000) and with the trigonally substituted 3,5-dihydroxybenzoic acid (VII), itself very closely related to (V) (Gregson *et al.*, 2000). However, in the corresponding adducts formed with bisphenols, or with 3- or 4-hydroxybenzoic acids, only two of the axial N—H bonds of the $[(\text{tet-a})H_2]^{2+}$ cation are so engaged, but in the salt formed between the $[(\text{tet-a})H_4]^{4+}$ cation and the phenylphosphonate anion, $[PhP(O)_2OH]^-$, all eight N—H bonds of the cations are involved in intermolecular hydrogen bonding (Gregson *et al.*, 2000). It is not yet clear what factors are important in determining, in any given system, how many of the axial N—H bonds in the $[(\text{tet-a})H_2]^{2+}$ cation will be active in intermolecular hydrogen bonding.

It is of interest to compare the two-dimensional structure observed in (3) and (4) with the three-dimensional structure observed in the analogous 1:2 adduct formed between tet-a and (VII). In this adduct, the anions $[(HO)_2C_6H_3COO]^-$ form a two-dimensional sub-structure in the form of a (4,4) net (Batten & Robson, 1998) containing $R_2^2(14)$ and $R_6^4(30)$ rings: these nets are linked by the usual $[(\text{tet-a})H_2]^{2+}$ cations to form a three-dimensional framework. The $[(\text{tet-a})H_2]^{2+}$ salt formed by the simpler analogue 3-hydroxybenzoic acid, where one of the hydroxyl groups of (VII) has been notionally excized, has a much simpler one-dimensional structure: chains of anions are linked in pairs by $[(\text{tet-a})H_2]^{2+}$ cations to form a molecular ladder (Gregson *et al.*, 2000). The motif of paired N—H$\cdots$O hydrogen bonds to a single carboxylate anion observed in (1), (3) and (4) and in a tet-a adduct with terephthalic acid is not found in the tet-a adducts formed either with (VII) or with 3- and 4-hydroxybenzoic acids.

3.4. Hydrogen-bond dimensions

With the exception of the intramolecular N—H$\cdots$N hydrogen bonds within the cations, all the hydrogen bonds (Table 2) are of N—H$\cdots$O or O—H$\cdots$O types: neither intermolecular N—H$\cdots$N nor O—H$\cdots$O types are present. In the two-centre hydrogen bonds the N—H$\cdots$O angles range

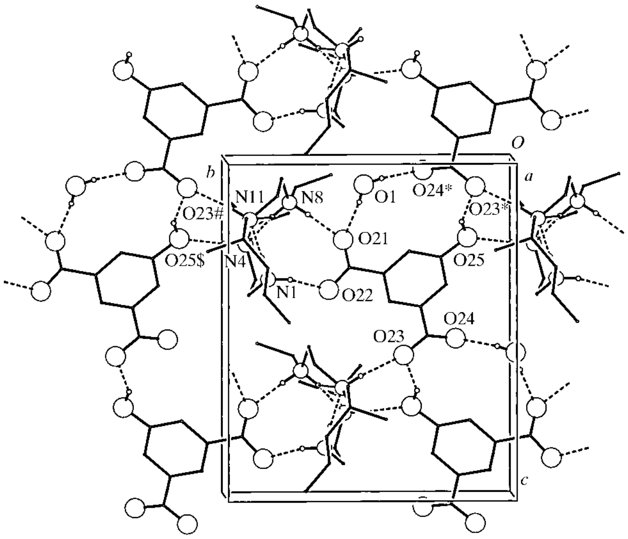

Figure 6
Part of the crystal structure of (4), showing a sheet parallel to (100) formed by linking parallel $C(7)[R_3^3(13)]$ chains of rings. For the sake of clarity, H atoms bonded to C are omitted. Atoms marked with a star (*), hash (#) or dollar ($) sign are at the symmetry positions $(x, \frac{1}{2}-y, -\frac{1}{2}+z)$, $(x, \frac{3}{2}-y, -\frac{1}{2}+z)$ and $(x, 1+y, z)$, respectively.

Table 4
Selected bond lengths and angles (Å, °).

(1)			
N1—C7^{i}	1.477 (2)	N1—C2	1.461 (2)
N4—C3	1.490 (2)	N4—C5	1.518 (2)
O1—C17	1.258 (2)	O2—C17	1.244 (2)
C2—N1—C7^{i}	114.71 (9)	C3—N4—C5	117.10 (9)
O1—C17—O2	127.1 (2)		

	(3)	(4)
N1—C14	1.501 (3)	1.506 (2)
N1—C2	1.481 (3)	1.487 (2)
N4—C3	1.470 (3)	1.467 (2)
N4—C5	1.495 (3)	1.496 (2)
N8—C7	1.509 (3)	1.511 (2)
N8—C9	1.485 (3)	1.487 (2)
N11—C10	1.463 (3)	1.470 (2)
N11—C12	1.478 (3)	1.497 (2)
O21—C27	1.241 (3)	1.264 (2)
O22—C27	1.258 (3)	1.249 (2)
O23—C28	1.267 (3)	1.258 (2)
O24—C28	1.238 (3)	1.248 (2)
C2—N1—C14	116.7 (2)	114.9 (2)
C3—N4—C5	115.3 (2)	116.1 (2)
C7—N8—C9	113.6 (2)	115.3 (2)
C10—N11—C12	115.0 (2)	116.3 (2)
O21—C27—O22	124.4 (2)	123.7 (2)
O23—C28—O24	123.9 (2)	124.4 (2)

Symmetry code: (i) $1-x, 1-y, 1-z$.

from 159 to 176° with mean value 168°, while the O—H···O angles range from 144 to 172° with mean value 160°. The O—H···O hydrogen bonds are all reasonably short for their type, with O···O distances ranging from 2.565 (2) in (4) to 2.761 (3) Å in (3) and H···O distances in the range 1.82 Å in (4) to 1.95 Å in (3).

The N···O distances in the paired N—H···O hydrogen bonds show some significant and interesting variations. In each of (1), (3) and (4) there is a unique pair of N—H···O hydrogen bonds involving a single carboxylate group: in both (3) and (4) the second pair of N—H···O hydrogen bonds involves one carboxylate and one hydroxyl acceptor. The two N···O distances in the bonds to the carboxylate anion are very different for both (1) and (3), with a difference of well over 0.40 Å, while in (4) the corresponding difference is only *ca* 0.06 Å (Table 2). In the tetrahydrated salt formed between tet-a and terephthalic acid, where the $[(\text{tet-a})H_2]^{2+}$ cations lie in general positions, the differences between the paired N···O distances are 0.546 (2) Å on one face of the macrocyclic cation and 0.277 (2) Å on the other (Lough *et al.*, 2000). Evidently, the interaction of a carboxylate anion with the $[C_{16}H_{38}N_4]^{2+}$ cation allows a considerable degree of orientational freedom, consequent upon the sum total of all the inter-ionic interactions, one result of which is the rather wide range of the observed N···O distances in the N—H···O hydrogen bonds. In the two-centre N—H···O hydrogen bonds the variation of the H···O distances closely mirrors that of the N···O distances, as the angles N—H···O are all close to 180°; in the three-centre system the H···O distances are much longer, as expected.

3.5. Molecular geometries

In the cations of each compound, the C—N distances (Table 4) show systematic variation depending upon whether the N atom involved is, or is not, protonated. As observed previously, C—N bonds involving protonated N are somewhat longer than those involving unprotonated N. There is however, no systematic variation of the corresponding C—N—C angles. In the carboxylate groups the C—O distances observed here range from 1.238 (3) to 1.267 (3) Å: within each carboxylate group, the difference between the two independent C—O distances is always significant, but there is no systematic variation with the number of hydrogen bonds a given O atom accepts. The O—C—O angles are all substantially greater than the ideal trigonal value of 120°.

4. Conclusions

In each of the compounds studies here, the macrocyclic amine has captured two protons, forming the dipositive cation $[C_{16}H_{38}N_4]^{2+}$, and in each salt, all four of the axial N—H bonds are active in intermolecular hydrogen bonding. While in (3) and (4) it might reasonably be expected that the cations lie across inversion centres and twofold rotation axes, respectively, in the event the cations lie in general positions, although they have approximate C_i and C_2 symmetry. The striking feature of the structures of (3) and (4) is the close similarity of their supramolecular organization, despite the major differences in cation configurations and conformations. It is possible that the supramolecular behaviour of $[(\text{tet-b})H_2]^{2+}$ will be found to mimic rather closely that of $[(\text{tet-a})H_2]^{2+}$.

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

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