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1,4,8,11-Tetraazoniacyclotetradecane tetrakis(phenylphosphonate) dihydrate forms hydrogen-bonded sheets

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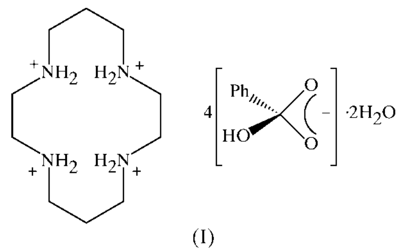
In the title compound, $C_{10}H_{28}N_4^{4+}\cdot4C_6H_6O_3P^-\cdot2H_2O$, the cation lies across a centre of inversion in space group $P2_1/n$. The two independent anions and the water molecule are linked by four O—H···O hydrogen bonds [H···O = 1.74–2.15 (3) Å, O···O = 2.5482 (14)–3.0438 (16) Å and O—H···O = 160–176 (2)°] into sheets containing equal numbers of centrosymmetric $R_6^6(16)$ and $R_{10}^{10}(36)$ rings. The cation lies at the centre of the $R_{10}^{10}(36)$ ring and is linked to it by eight N—H···O hydrogen bonds [H···O = 1.77–1.98 Å, N···O = 2.6756 (15)–2.8168 (16) Å and N—H···O = 151–169°].

Comment

We reported recently (Gregson *et al.*, 2000) the molecular and supramolecular structure of the adduct formed between *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane ($C_{16}H_{36}N_4$, tet-a) and phenylphosphonic acid [PhP(O)(OH)$_2$]. This adduct crystallizes from methanol solution as a hydrated 1:4 salt, $[\{(\text{tet-a})H_4\}^{4+}]\cdot[\{PhP(O)_2OH\}^-]_4\cdot2H_2O$, containing a centrosymmetric tetracation. The anions and the water molecules form chains of edge-fused $R_4^4(12)$ and $R_6^6(20)$ rings, and these chains are linked into sheets by the cations.

As part of a detailed structural comparison of the supramolecular behaviour of tet-a and its simpler analogue 1,4,8,11-tetraazacyclotetradecane ($C_{10}H_{24}N_4$, cyclam), we have now prepared and structurally characterized the 1:4 adduct formed between cyclam and phenylphosphonic acid. This adduct is also a hydrated salt, $[\{(\text{cyclam})H_4\}^{4+}]\cdot[\{PhP(O)_2OH\}^-]_4\cdot2H_2O$, (I), with a composition similar to that of the adduct formed by tet-a. However, the supramolecular structure of (I) is entirely different from that of the tet-a analogues. Moreover, although both salts crystallize in monoclinic space group No. 14 ($P2_1/c$ and $P2_1/n$ for the adducts from tet-a and cyclam, respectively) with $Z' = 0.5$, and hence with unit cells of comparable volume, the shapes of these cells are very different. In particular, the *b* repeat vector in the tet-a adduct is three times the *b* vector in the cyclam adduct.



(I)

The cation in (I) (Fig. 1) lies across a centre of inversion, selected as that at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$), and there are two anions and one water molecule in general positions. All H atoms are fully ordered, corresponding to complete transfer of one H atom from each phenylphosphonic acid unit to the cyclam group. The N—C distances in the cation and the P—O distances in the anions (Table 1) are fully consistent with the H-atom locations deduced from difference maps. In the cation, there is almost perfect staggering about all of the C—C and C—N bonds (Table 1); the synclinal torsion angles are all within 5° of ±60° and the antiperiplanar torsion angles are all within 10° of 180°. The overall conformation of the $[(\text{cyclam})H_4]^{4+}$ cation is very similar to that of the $[(\text{tet-a})H_4]^{4+}$ cation in the corresponding phenylphosphonate salt.

The independent components are linked into continuous sheets by an extensive series of hydrogen bonds (Table 2) amplified by the inversion symmetry of the cation. The supramolecular structure is, however, readily analysed and

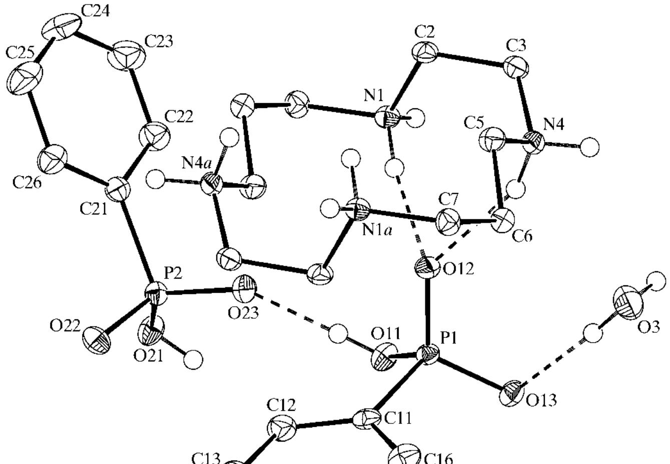


Figure 1
The independent components of (I), showing the atom-labelling scheme. Atoms with the suffix '*a*' are at the symmetry position (1 − *x*, 1 − *y*, 1 − *z*), and displacement ellipsoids have been drawn at the 50% probability level.

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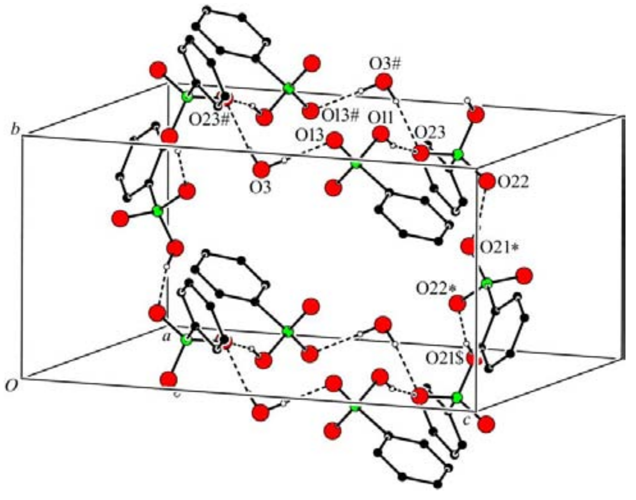

Figure 2
Part of the crystal structure of (I), showing the formation of the $R^{6}_{6}(16)$ and $R^{10}_{10}(36)$ rings in the anion–water substructure. For clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*), hash (#) or dollar sign ($) are at the symmetry positions ($\frac{3}{2} - x$, $-\frac{1}{2} + y$, $\frac{3}{2} - z$), ($1 - x$, $2 - y$, $1 - z$) and (x, $-1 + y$, z), respectively.

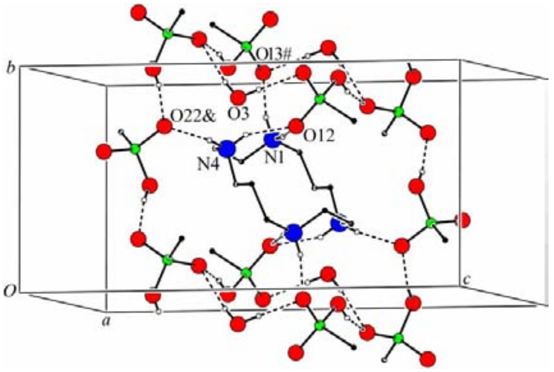

Figure 3
Part of the crystal structure of (I), showing the linking of the cation to the anion–water substructure. For clarity, atoms C12–C16 and C22–C26 in the anions have been omitted, as have all H atoms bonded to C atoms. Atoms marked with a hash (#) or ampersand (&) are at the symmetry positions ($1 - x$, $2 - y$, $1 - z$) and ($-\frac{1}{2} + x$, $\frac{3}{2} - y$, $-\frac{1}{2} + z$), respectively.

described in terms of the substructures generated first by the anions alone, and then by the anions and water molecules combined. Atom O21 in the type 2 anion (containing P2) at (x, y, z) acts as a hydrogen-bond donor to atom O22 in the type 2 anion at ($\frac{3}{2} - x$, $\frac{1}{2} + y$, $\frac{3}{2} - z$), so producing a $C(4)$ chain running parallel to the [010] direction and generated by the 2_1 screw axis along ($\frac{3}{4}$, y, $\frac{3}{4}$) (Fig. 2). A second antiparallel $C(4)$ chain, related to the first by inversion, is generated by the 2_1 screw axis along ($\frac{1}{4}$, $-y$, $\frac{1}{4}$). In the corresponding salt derived from tet-a, by contrast, the two anions and the water molecule combine to form $C^{3}_{3}(10)$ chains generated by translation, and no simple $C(4)$ motif can be identified (Gregson *et al.*, 2000).

The $C(4)$ chains in (I), containing only type 2 anions, are linked into $(10\bar{1})$ sheets by the type 1 anions (containing P1) and the water molecules. Water atom O3 at (x, y, z) acts as a hydrogen-bond donor, *via* atom H31, to the type 1 anion, also at (x, y, z). This type 1 anion is in turn hydrogen bonded to the type 2 anion at (x, y, z), which forms part of the ($\frac{3}{4}$, y, $\frac{3}{4}$) chain. Atom O3 at (x, y, z) also acts as a hydrogen-bond donor, this time *via* atom H32, to atom O23 in the type 2 anion at ($1 - x$, $2 - y$, $1 - z$), which lies in the $C(4)$ chain along ($\frac{1}{4}$, $-y$, $\frac{1}{4}$). In this manner, an $R^{6}_{6}(16)$ ring is formed, centred at ($\frac{1}{2}$, 1, $\frac{1}{2}$) (Fig. 2). At the same time, water atom O3 at ($\frac{3}{2} - x$, $\frac{1}{2} + y$, $\frac{3}{2} - z$) acts as a donor to atom O23 in the type 2 anion at ($\frac{1}{2} + x$, $\frac{5}{2} - y$, $\frac{1}{2} + z$), which lies in the $C(4)$ chain along ($\frac{5}{4}$, $-y$, $\frac{5}{4}$). Propagation of these hydrogen bonds by the space group thus generates a $(10\bar{1})$ sheet containing centrosymmetric $R^{6}_{6}(16)$ and $R^{10}_{10}(36)$ rings alternating in a checkerboard fashion (Fig. 2). Hence, the anion–water substructure in (I) is two-dimensional, in contrast to the one-dimensional anion–water substructure in the corresponding salt formed by tet-a.

The cations lie at the centre of the $R^{10}_{10}(36)$ rings in the anion–water substructure, linked to the anion–water sheet by eight N—H$\cdots$O hydrogen bonds (Table 2). In the reference cation centred at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$), atom N1 at (x, y, z) is linked to atom O12 in the type 1 anion at (x, y, z) and to atom O13 in the type 1 anion at ($1 - x$, $2 - y$, $1 - z$), while atom N4 at (x, y, z) is linked to atom O12 at (x, y, z) and to atom O22 in the type 2 anion at ($-\frac{1}{2} + x$, $\frac{3}{2} - y$, $-\frac{1}{2} + z$). These interactions are all duplicated by inversion (Fig. 3). There are no direction-specific interactions between adjacent $(10\bar{1})$ sheets. In particular, there are neither C—H$\cdots\pi$(arene) hydrogen bonds nor aromatic π–π-stacking interactions.

Experimental

Stoichiometric quantities of cyclam and phenylphosphonic acid (both purchased from Aldrich) were dissolved separately in methanol. The solutions were mixed and the mixture was then set aside to crystallize, exposed to the laboratory atmosphere, providing analytically pure (I). Analysis found: C 47.8, H 6.5, N 6.4%; $C_{34}H_{56}N_4O_{14}P_4$ requires: C 47.0, H 6.5, N 6.5%. Crystals suitable for single-crystal X-ray diffraction were selected directly from the analytical sample.

Crystal data

$C_{10}H_{28}N_4^{4+}\cdot 4C_6H_6O_3P^{-}\cdot 2H_2O$
M_r = 868.71
Monoclinic, $P2_1/n$
a = 13.0678 (3) Å
b = 8.7475 (2) Å
c = 17.6106 (5) Å
β = 90.5130 (11)°
V = 2013.00 (9) Å^3
Z = 2
D_x = 1.433 Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 4536 reflections
θ = 2.6–27.4°
μ = 0.26 mm^{-1}
T = 150 (1) K
Needle, colourless
0.24 × 0.14 × 0.08 mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO-SMN*; Otwinowski & Minor, 1997)
T_{min} = 0.936, T_{max} = 0.978
14 531 measured reflections
4536 independent reflections

3866 reflections with $I > 2\sigma(I)$
R_{int} = 0.042
θ_{max} = 27.4°
$h = -16 \rightarrow 16$
$k = -11 \rightarrow 11$
$l = -21 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.085$
$S = 1.04$
4536 reflections
265 parameters
H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.0223P)^2 + 0.9176P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.28$ e Å^{-3}
$\Delta\rho_{\min} = -0.38$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0054 (9)

Table 1
Selected geometric parameters (Å, °).

N1—C2	1.4931 (17)	N4—C3	1.5036 (19)
N1—C7^{i}	1.4971 (17)	N4—C5	1.4927 (18)
P1—O11	1.5731 (10)	P2—O21	1.5702 (10)
P1—O12	1.5132 (10)	P2—O22	1.5156 (10)
P1—O13	1.5045 (10)	P2—O23	1.5017 (10)
P1—C11	1.8076 (15)	P2—C21	1.8071 (15)
C7^{i}—N1—C2—C3	177.99 (12)	N4—C5—C6—C7	−170.20 (11)
N1—C2—C3—N4	−66.63 (16)	C5—C6—C7—N1^{i}	56.80 (16)
C2—C3—N4—C5	−59.50 (15)	C6—C7—N1^{i}—C2^{i}	61.48 (15)
C3—N4—C5—C6	173.38 (11)		

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

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O12	0.92	1.81	2.7240 (15)	169
N1—H1B···O13^{ii}	0.92	1.77	2.6756 (15)	166
N4—H4A···O12	0.92	1.98	2.8168 (16)	151
N4—H4B···O22^{iii}	0.92	1.90	2.7806 (16)	160
O11—H11···O23	0.84	1.75	2.5555 (15)	160
O21—H21···O22^{iv}	0.84	1.74	2.5482 (14)	161
O3—H31···O13	0.88 (2)	1.93 (2)	2.8025 (16)	176 (2)
O3—H32···O23^{i}	0.90 (2)	2.15 (3)	3.0438 (16)	171 (2)

Symmetry codes: (ii) $1-x, 2-y, 1-z$; (iii) $x-\frac{1}{2}, \frac{3}{2}-y, z-\frac{1}{2}$; (iv) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$.

Crystals of (I) are monoclinic and the space group $P2_1/n$ was assigned uniquely from the systematic absences. All H atoms were located from difference maps, and those of the water molecule were refined using a DFIX restraint, leading to O—H distances of 0.88 (2) and 0.90 (2) Å. All other H atoms were treated as riding atoms, with C—H distances of 0.95 (aromatic) or 0.99 Å (CH_2), N—H distances of 0.92 Å and O—H distances of 0.84 Å.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

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

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1643). Services for accessing these data are described at the back of the journal.

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