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Ammonium 2,5,8,11,21,24,27-octaoxatricyclo-[26.4.0.0^{12,17}]dotriaconta-1(32),12(17),13,15,28,30-hexaene hexafluorophosphate

Gary D. Fallon,* Vei-Lin Lau and Steven J. Langford

School of Chemistry, PO Box 23, Monash University, Victoria 3800, Australia

Correspondence e-mail: g.fallon@sci.monash.edu.au

Key indicators

Single-crystal X-ray study
T = 123 K
Mean σ(C–C) = 0.003 Å
R factor = 0.051
wR factor = 0.132
Data-to-parameter ratio = 17.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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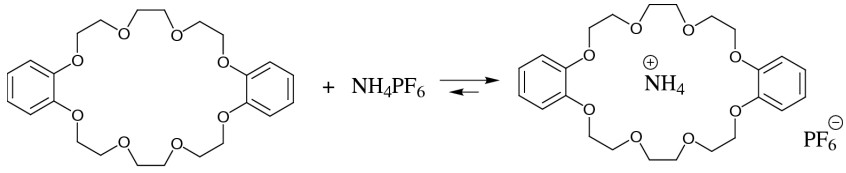
Dibenzo-24-crown-8 crystallizes with ammonium hexafluorophosphate to produce a complex in which the ammonium ion is encapsulated by the crown ether, $NH_4^+ \cdot C_{24}H_{32}O_8 \cdot PF_6^-$.

Comment

The host–guest relationship between crown ethers and ammonium-based cationic components is an important concept in the generation of a number of supramolecular assemblies. From our perspective, this relationship may be useful in providing electronic and structural roles towards the self-assembly of supramolecular photosynthetic mimics (Duggan *et al.*, 2001). Here, we report on the solid-state structure obtained for the complex between ammonium hexafluorophosphate and dibenzo-24-crown-8 (DB24C8), (I).



(I)

The molecular structure of $[(I)\cdot NH_4]PF_6$ is shown in Figs. 1 and 2. The ammonium cation lies within the cavity of the crown ether (Fig. 1) and is stabilized by a series of single (N1—H1*D*···O6 = 1.90 Å and N1—H1*A*···O2 = 1.91 Å) and bifurcated (N1—H1*B*···O8 and N1—H1*B*···O1 2.11 and 2.48 Å, respectively; N1—H1*C*···O4 and N1—H1*C*···O5 = 2.08 and 2.48 Å, respectively) hydrogen-bonding interactions (Table 1). The difference in size complementarity between the radius of the ammonium cation and the 24-crown-8 cavity causes the macrocycle to adopt a folded and twisted conformation, effectively encapsulating the ammonium cation (Fig. 2). This encapsulation is similar to that observed for Na^+ with DB24C8 (Dapporto *et al.*, 1998), but differs from the large volume of work now published on the interactions of DB24C8 with dialkylammonium salts (Ashton, Fyfe *et al.*, 1997; Ashton, Ballardini *et al.*, 1997; Ashton, Baxter *et al.*, 1998), or other alkali metal ions (Gallagher *et al.*, 1991), in which relatively flat conformations are observed.

Experimental

Colourless crystals of $[(I).NH_4]PF_6$ suitable for X-ray analysis were grown by slow evaporation from a CD_3COCD_3 solution of ammonium hexafluorophosphate (1.6 mg, 9.82 mmol) and dibenzo-24-crown-8 (4.2 mg, 9.36 mmol).

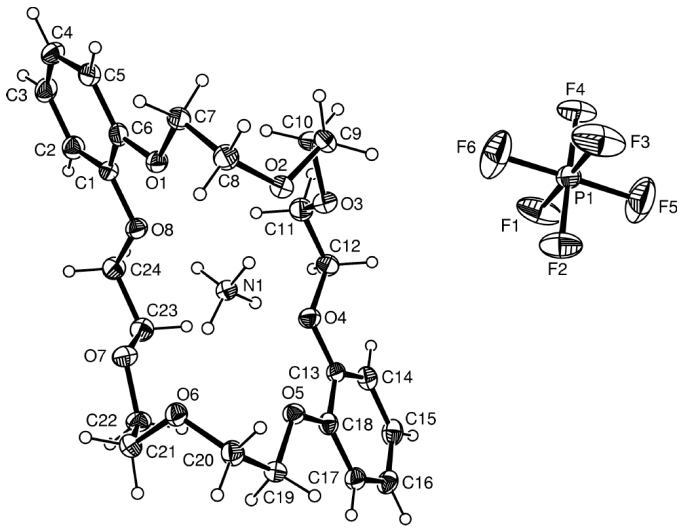


Figure 1
View of $[(I).NH_4]PF_6$ (50% probability displacement ellipsoids)

Crystal data

$NH_4^+ \cdot C_{24}H_{32}O_8 \cdot PF_6^-$
$M_r = 611.51$
Triclinic, $P\overline{1}$
$a = 10.1950\ (2)$ Å
$b = 10.6379\ (2)$ Å
$c = 14.5447\ (3)$ Å
$\alpha = 69.371\ (1)^\circ$
$\beta = 71.536\ (1)^\circ$
$\gamma = 89.670\ (1)^\circ$
$V = 1390.30\ (5)$ Å^3
$Z = 2$
$D_x = 1.461$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 16366 reflections
$\theta = 0.4$–28.3°
$\mu = 0.19$ mm^{-1}
$T = 123\ (2)$ K
Tabular, colourless
0.20 × 0.12 × 0.08 mm

Data collection

KappaCCD diffractometer
CCD rotation images, thick slices, φ and ω scans
Absorption correction: none
16366 measured reflections
6721 independent reflections
3813 reflections with $I > 2\sigma(I)$
$R_{int} = 0.044$
$\theta_{max} = 28.3^\circ$
$h = -12 \rightarrow 13$
$k = -13 \rightarrow 14$
$l = -18 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.133$
$S = 0.97$
6721 reflections
377 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0619P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.009$
$\Delta\rho_{max} = 0.64$ e Å^{-3}
$\Delta\rho_{min} = -0.55$ e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1B···O1	0.88 (3)	2.48 (3)	3.038 (2)	122 (2)
N1—H1A···O2	0.97 (3)	1.91 (3)	2.848 (2)	163 (2)
N1—H1C···O4	0.90 (3)	2.08 (3)	2.973 (2)	168 (3)
N1—H1C···O5	0.90 (3)	2.48 (3)	3.035 (2)	120 (2)
N1—H1D···O6	0.97 (3)	1.90 (3)	2.862 (2)	168 (2)
N1—H1B···O8	0.88 (3)	2.11 (3)	2.977 (3)	168 (2)

The H atoms were included in the riding-model approximation, except those of the ammonium ion which were located in difference Fourier syntheses and refined.

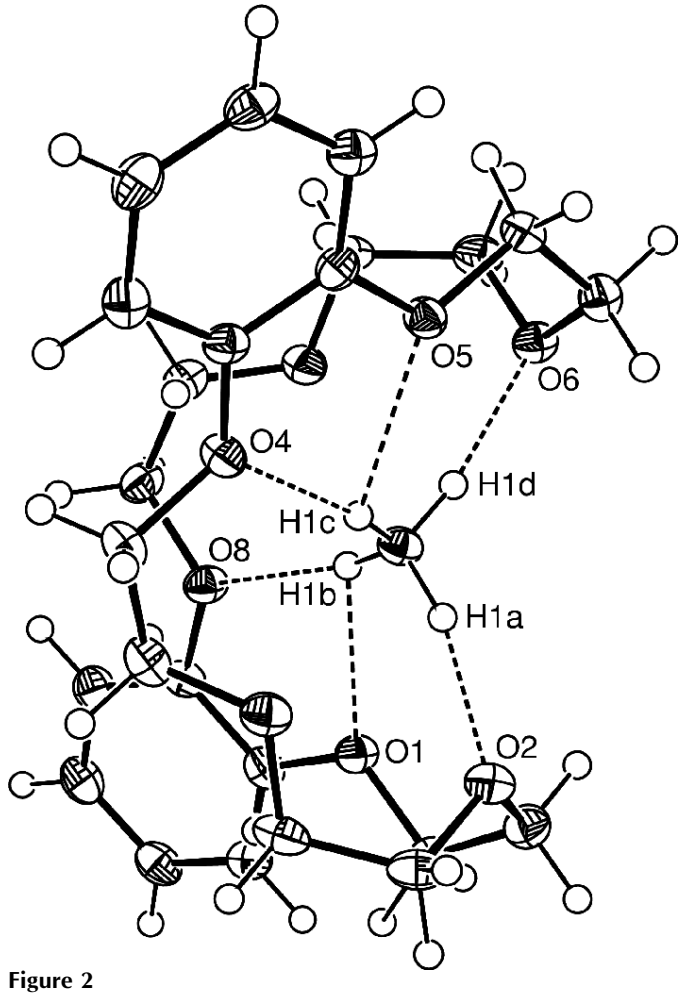


Figure 2
Side view illustrating the encapsulating nature of the crown ether around the ammonium guest.

Data collection: *COLLECT* (Nonius, 1997–2000); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 for Windows (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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