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A New Bis-amidinium Calix[4]arene-difluorophosphinate Network: An Unexpected but not Unwelcome Guest

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A complex hydrogen bonded network is formed between a mono-deprotonated bis-amidinium calix[4]arene 1 and difluorophosphinate in the presence of methanol. The compound crystallises in the triclinic space group $P\bar{1}$ with $a = 12.0665(5)$, $b = 12.5737(6)$, $c = 20.0201(15)$ Å, $\alpha = 86.4098(18)$, $\beta = 79.747(2)$, $\gamma = 66.816(4)°$, and $D_c = 1.159\,\mathrm{Mgm^{-3}}$ for $Z = 4.7824$ independent reflections were collected and the final $R1$ $[F^2 > 2\alpha(F^2)]$ was 0.1243.

Keywords: Crystalengineering; Calix[4]arene; Salt bridge

INTRODUCTION

The coordination chemistry of anionic species by hydrogen bond donating receptors is an area of supramolecular chemistry that continues to attract the attention of coordination chemists [1]. Amidinium containing species have been utilised in a variety of supramolecular systems including crystal engineered tapes [2], self-replicating molecules [3] and ordered three-dimensional aggregates [4]. Recently we reported the synthesis of bis-amidinium lower-rim substituted calix[4]arene derivatives such as **1** [5] and have shown that they form a variety of solution and solid state complexes with various bis-carboxylates including lower rim bridged complexes [5b]. During this work, we discovered serendipitously that the bis-amidinium calix[4]arene **1** forms a complex with difluorophosphinate anions (a hydrolysis product of hexafluorophosphate), that in the presence of methanol forms an interesting pseudo one-dimensional hydrogen bonded network **2**.

On one occasion during the preparation of the hexaflurophosphate salt of **1** by metathesis of the chloride salt with silver hexafluorophosphate, an old batch (ca. three years old) of $AgPF_6$ was used. It was subsequently found by ^{31}P NMR that the $AgPF_6$ was contaminated with difluorophosphinate ($PF_2O_2^-$) anions, a known hydrolysis product of PF_6^- (Fig. 1). After passing the supposed calix[4]arene 'hexafluorophosphate' salt through a Sephadex® LH-20 gel filtration column in methanol, the sample was found to contain a mixture of PF_6^- and $PF_2O_2^-$ counter anions. These

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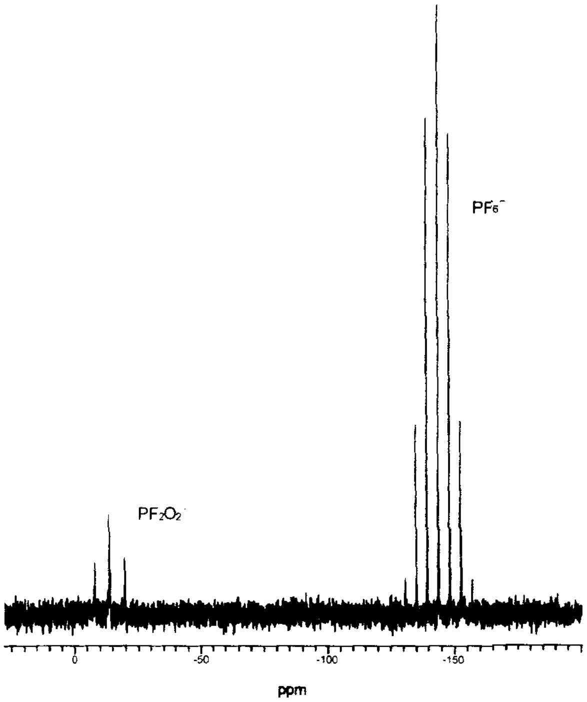

FIGURE 1 ^{31}P NMR of the silver hexafluorophosphate salt used to prepare 2 showing difluorophosphinate impurity.

could be observed by ^{31}P NMR, however interestingly negative electrospray mass spectrometry failed to detect the $PF_2O_2^-$ impurity, and PF_6^- was the only assignable peak observed.

EXPERIMENTAL

X-ray Structure

Single crystals of the difluorophosphinate salt of 1 suitable for X-ray diffraction were obtained from a CD_3OD solution of the calixarene. Cell dimensions and intensity data were recorded at 150 K, using a Nonius KappaCCD area detector diffractometer mounted at the window of a rotating molybdenum anode (50 KV, 90 mA, $\lambda = 0.71073$ Å). The crystal-to-detector distance was 30 mm and ϕ and Ω scans (1° increments, 100 s exposure time) were carried out to fill the Ewald sphere. Data collection and processing were carried out using the programs COLLECT [6], DENZO [7] and maXus [8] and an empirical absorption correction was applied using SORTAV [9, 10].

The structure was solved *via* direct methods [11] and refined by full matrix least squares [11] on F^2. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealised positions and refined using a riding model, with the exception of the hydroxyl hydrogens on O3, O7, O8 and O9 whose positions were located from the difference map and later restrained. One of the four *t*-butyl groups was disordered and modelled in the staggered position with occupancies of 0.54 and 0.46 respectively. The high $R1$ and R_{merge} values are a direct result of the week diffraction from a small crystal (0.05 x 0.02 x 0.01 mm^3).

Crystal Data for 2

$C_{51}H_{77}N_4F_2O_9P$ – [$C_{48}H_{65}N_4O_4 \cdot 3CH_3OH \cdot PF_2O_2$], Mr = 959.14, T = 150(2) K, triclinic, space group $P\bar{1}$, $a = 12.0665(5)$, $b = 12.5737(6)$, $c = 20.0201(15)$ Å, $\alpha = 86.4098(18)$, $\beta = 79.747(2)$, $\gamma = 66.816(4)$°, $V = 2747.5(3)$ Å^3, $D_c = 1.159$ Mgm^{-3}, $\mu = 0.111$ mm^{-1}, Z = 2, reflections collected: 31416, independent reflections: 7824 ($R_{int} = 0.2447$), final R indices [$I > 2\sigma I$]: $R1 = 0.1243$, $wR2 = 0.2996$, R indices (all data): $R1 = 0.2668$. $wR2 = 0.3794$. Full Crystallographic data (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 156575. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Solid State Structure

The calixarene adopts the cone conformation with an intramolecular hydrogen bond

(O3—H3A···O4) between the phenolic oxygens at the lower rim. In addition each amidinium moiety forms a hydrogen bond (N4—H4B···O1, N2—H2B···O3) to the lower rim as previously observed [5b]. This results in the amidinium arms being twisted round into an offset parallel configuration (Fig. 2). The difluorophosphinate anion is bound to the amidinium group by two near identical N—H···O hydrogen bonds (N4—H4A···O5^{i}, N3—H3B···O6^{i}) to one arm and a single N—H···F hydrogen bond (N3—H3C···F2^{iii}) to the other. These units form into chains *via* a second hydrogen bond (N1—H1B···O5^{ii}) to an amidinium group of an adjacent molecule (Fig. 3). This leaves one amidinium hydrogen and a difluorophosphinate fluorine free to coordinate to a methanol molecule by two further hydrogen bonds (N1—H1A···O7^{i}, O7—H7···F1). Table I contains details of the hydrogen bonds and their symmetry codes. The two remaining methanol molecules are not involved in hydrogen bonding; one sits in the cavity of the calixarene whilst the other lies between the chains. These chains are arranged in a square grid pattern when viewed looking down the *a* axis, see Figure 4, with individual calixes being titled at an angle of ca. 45° to the *c* axis

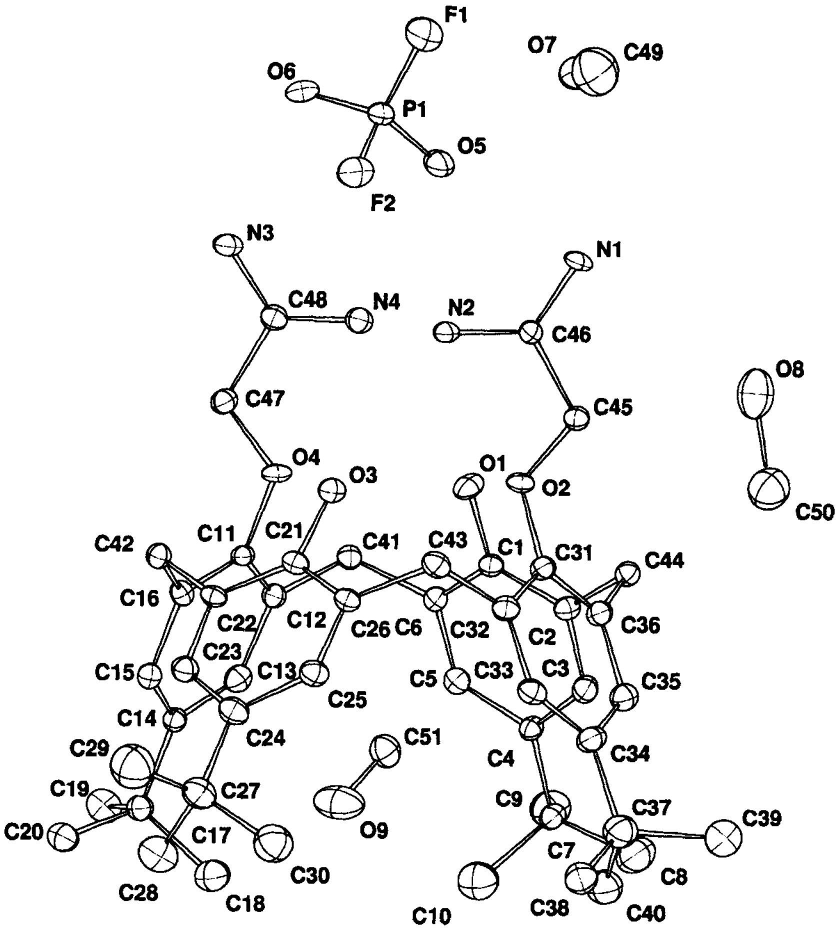

FIGURE 2 ORTEP view of 2. Only one orientation of the disordered *t*-butyl group has been shown and the ellipsoids are drawn at the 30% probability level.

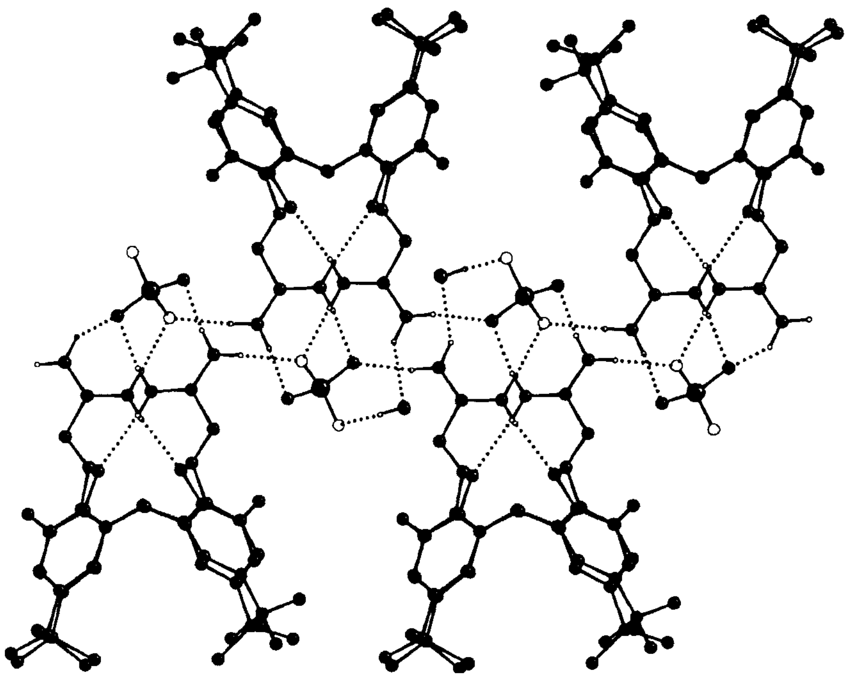

FIGURE 3 Pseudo one-dimensional hydrogen bonding network of 2. The two non-interacting methanol molecules have been omitted for clarity. (See Color Plate I).

TABLE I Hydrogen bonds [Å and °]

D—H···A	$d(D$—H)	d(H···A)	$d(D$···A)	∠(DHA)
O3—H3A···O4	0.84	1.93	2.751(9)	163.8
N1—H1A···O7^{i}	0.88	2.15	2.906(11)	144.3
N1—H1B···O5^{ii}	0.88	1.88	2.727(10)	160.0
N2—H2A···F2^{i}	0.88	1.93	2.800(10)	169.2
N2—H2B···O3	0.88	2.12	2.990(10)	171.1
N3—H3B···O6^{i}	0.88	1.94	2.799(11)	165.8
N3—H3C···F2^{iii}	0.88	1.93	2.791(11)	164.6
N4—H4A···O5^{i}	0.88	1.97	2.839(11)	167.2
N4—H4B···O1	0.88	2.17	3.047(10)	172.5
O7—H7···F1	0.84	1.97	2.747(12)	152.4

Symmetry transformations used to generate equivalent atoms: (i) x, y, z + 1 (ii) −x + 1, −y + 1, −z + 1 (iii) −x + 2, −y + 1, −z + 1.

to allow closer approach of the upper ring *t*-butyl groups. The twist of the amidinium group-phenolic oxygen hydrogen bonding network relative to the calixarene ring gives rise to enantiomers related by a centre of inversion. The hydrogen-bonded chains are formed by alternating enantiomers such that one side of the chain consists of one enantiomer and the other side the other (top and bottom in Fig. 3).

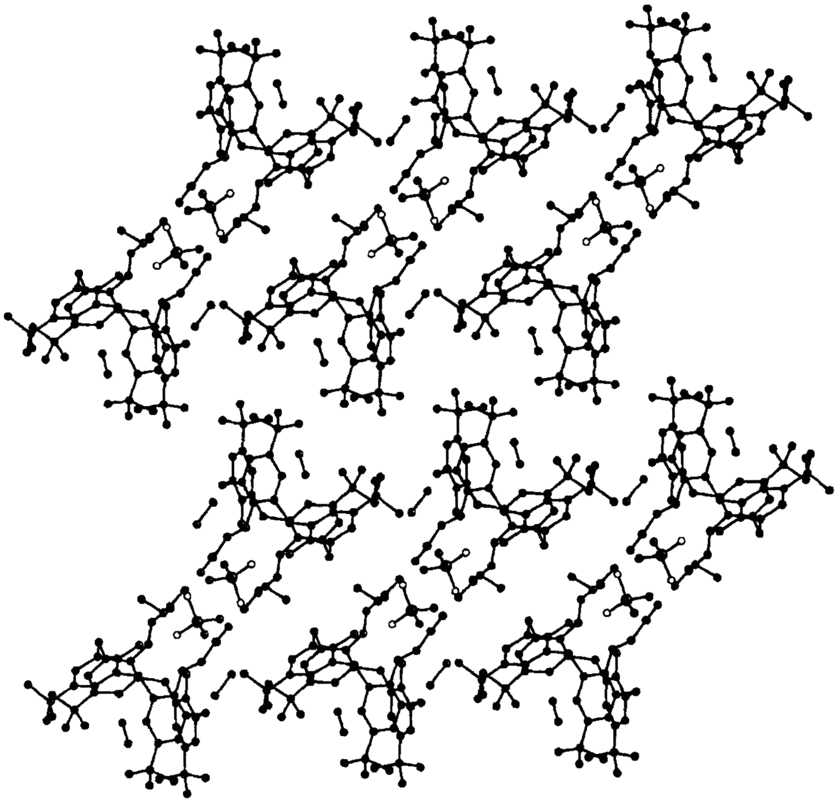

FIGURE 4 Packing diagram of **2** viewed down the *a* axis. (See Color Plate II).

CONCLUSIONS

A search of the Cambridge crystallographic database (version 1.1 2000) [12] for $PF_2O_2^-$ produces twenty nine hits, of which over two thirds involve one or both oxygens coordinating directly to a metal centre [13]. There are nine occurrences of the free anion but only two [14, 15] are involved in hydrogen bonding *via* a monodentate N—H···O bond. Thus, to the best of our knowledge, the title compound is the first occurrence of $PF_2O_2^-$ in a complex hydrogen bonding network and suggests that this anion may be a useful synthon in the production of anion-directed assemblies in the solid state.

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