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Bis(4-dimethylaminopyridinium) 1,2-difluorodiphosphate

Radek Sluka, Marek Nečas* and Miloš Černík

Department of Inorganic Chemistry, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic

Correspondence e-mail: man@chemi.muni.cz

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The title compound, $2DMAPH^+\cdot P_2O_5F_2^{2-}$, where DMAP is $[(CH_3)_2NC_5H_4N]$ or $C_7H_{10}N_2$ (4-dimethylaminopyridine), belongs to the class of *catena*-difluoropolyphosphates of general formula $[P_nO_{3n-1}F_2]^{n-}$ (n = 2,3,...), and is the second representative of this series characterized by single-crystal X-ray diffraction. Compared to $K_2[P_2O_5F_2]$, the anion adopts a different conformation, enforced by its N—H···O bridging to the cation.

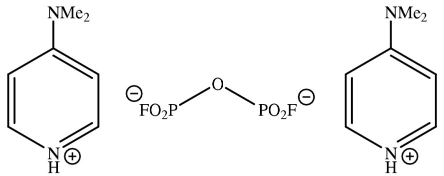
Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.005 Å
R factor = 0.045
wR factor = 0.142
Data-to-parameter ratio = 12.9

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

Comment

Phosphorus forms two extensive series of polyphosphoric acids: the cyclic metaphosphoric and the *catena*-polyphosphoric acids. Replacing one or more OH groups of chain polyphosphoric acids by fluorine gives fluoropolyphosphoric acids, some of which known in the form of their salts. The following fluoropolyphosphates have been reported: monofluorodiphosphate, $[P_2O_6F]^{3-}$ (Schülke, 1968), 1-monofluorotriphosphate, $[P_3O_9F]^{4-}$ (Feldmann, 1965), 1,2-difluorodiphosphate, $[P_2O_5F_2]^{2-}$ (Falius, 1968; Neels & Grunze, 1979) and α,ω-difluorotri(tetra,penta)phosphates, $[P_nO_{3n-1}F_2]^{n-}$ (n = 3–5) (Grunze *et al.*, 1973). Their preparations are mostly based on a nucleophilic degradation of appropriate P—O—P bridged precursors by the fluoride ion, which proceeds in aqueous solutions ($[P_3O_9]^{3-}$) (Feldmann, 1965) or in melts (P_4O_{10}) (Falius, 1968; Grunze *et al.*, 1973). The potassium difluorodiphosphate, $K_2[P_2O_5F_2]$, was first isolated by Falius (1968) from fluorophosphate melt and its crystal structure has been determined by Durand *et al.* (1978).



(I)

The bond lengths and angles in the difluorodiphosphate anion in $[DMAPH]_2[P_2O_5F_2]$, (I), are very similar to those already observed by Durand *et al.* (1978). The phosphorus environment is approximately tetrahedral, with the O5—P1—F1 and O5—P2—F2 angles being the most compressed [99.0 (1) and 98.7 (1)°]. The P1—O5—P2 angle is 130.7 (1)°.

The σ-bonds of the P—O—P bridge allow rotation of the –PO_2F groups but, unlike $K_2[P_2O_5F_2]$, they are not related by crystallographic symmetry, thus taking arbitrary relative orientations. Nevertheless, the anion shows approximate internal symmetry $C2$ and its conformation with respect to the mutual orientation of –PO_2F moieties can be described as

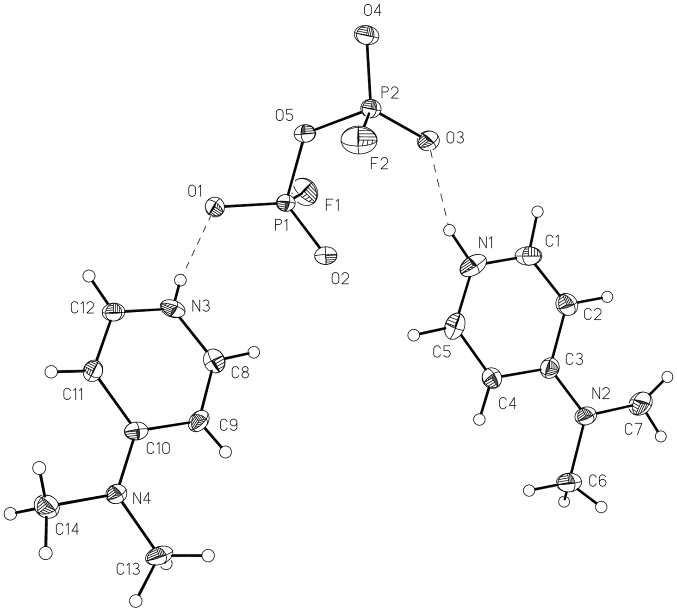
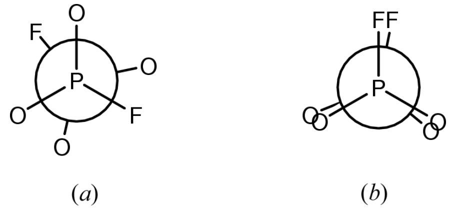


Figure 1
The molecular structure of bis(4-dimethylaminopyridinium) 1,2-difluorodiphosphate, showing the atom-numbering scheme and the hydrogen bonding (as dashed lines). Ellipsoids are drawn at the 50% probability level.

staggered, while in $K_2[P_2O_5F_2]$ the substituents in both groups are nearly eclipsed (Fig. 2). This is also reflected in the dihedral angles F1—P1—O5—P2 [−98.2 (2)°] and F2—P2—O5—P1 [−74.4 (2)°]. Considering the 'dihedral angle' F1—P1···P2—F2, both –PO$_2$F groups are staggered by 166.0 (1)°. Analogous values calculated for $K_2[P_2O_5F_2]$ are 178.2 (2)° for both symmetry-equivalent F—P—O—P dihedral angles, and 4.4 (3)° for the F—P···P—F 'dihedral angle'. The staggered conformation of the anion in (I) also results in the central O2—P1—O5—P2—O4 chain being nearly planar, with the r.m.s. deviation of atoms being 0.0505 Å. Corresponding dihedral angles O4—P2—O5—P1 and O2—P1—O5—P2 are 173.3 (2) and 16.2 (3)°, respectively.

Different conformations have been observed previously for disulfuryl difluoride, $S_2O_5F_2$, which is isoelectronic with the difluorodiphosphate anion. The –SO$_2$F groups in the crystalline state at 100 K (Blake & Žák, 1993), and in the gas phase determined by electron diffraction (Hencher & Bauer, 1973), are staggered differently, with an angular difference of 25.9°. The conformational flexibility of $S_2O_5F_2$ was further confirmed by Toužín & Černík (1993) by Raman and IR spectroscopy of its liquid phase. Unfortunately, there are no relevant *ab initio* conformational studies on either $S_2O_5F_2$ or $[P_2O_5F_2]^{2-}$ to afford a deeper insight into their conformation transitions and corresponding torsional barriers.

The dimethylaminopyridinium cations are almost perfectly planar and are comparable in their bond parameters to other examples found in the Cambridge Structural Database (Allen, 2002). The aromatic rings are inclined by 17.7 (1)° to each other. Each of the cations is involved in N—H···O hydrogen bonding with the terminal O atoms in the anion (Fig. 1 and Table 1). A similar donor–acceptor distance [2.723 (3) Å] was found for the N—H···O hydrogen bond in 4-dimethylaminopyridinium trifluoroacetate (Dega-Szafran *et al.*, 1992). Nearly perpendicular to the *c* axis, the structure consists of layers of dimethylaminopyridinium cations. The perpendicular distances between the ring centroids and parallel aromatic planes vary from 3.319 to 3.571 Å, indicating π–π-stacking interactions between pyridine rings, as previously observed by Choi & Angelici (2000).



(*a*) (*b*)

Figure 2
The schematic Newman projections of the $[P_2O_5F_2]^{2-}$ anions, viewed along the P···P vector in (*a*) $[DMAPH]_2[P_2O_5F_2]$ and (*b*) $K_2[P_2O_5F_2]$.

Obviously the different conformations in the difluorodiphosphate anion are closely related to the different cationic counterparts in the crystal structures of $[DMAPH]_2[P_2O_5F_2]$ and $K_2[P_2O_5F_2]$. We assume the following three factors may be of importance: (*a*) DMAPH π–π stacking, which is the main driving force of the observed packing arrangement; (*b*) easy rotation of –PO$_2$F pendants connected to the bridging O atom; (*c*) directionality of the N—H···O bridge bonding (in contrast to non-directional attractive forces around K^+ ions in $K_2[P_2O_5F_2]$), which controls the extent of rotation of the –PO$_2$F groups in the anion. However, reliable structural data of higher fluoropolyphosphates with longer chains are needed for a better understanding of all the relevant factors.

Experimental

The title compound was prepared by the reaction of betaine DMAP.PO$_2$F (Černík, 2000) (2 mmol) and water (2 mmol) in acetonitrile (4 ml) at room temperature. A white powder was formed in the course of the reaction (yield 0.2 g). Recrystallization from hot acetonitrile produced uniform colourless crystals of $[DMAPH]_2[P_2O_5F_2]$.

Crystal data

$2C_7H_{11}N_2^+\cdot F_2O_5P_2^{2-}$
$M_r = 426.30$
Monoclinic, $P2_1/c$
$a = 8.386$ (2) Å
$b = 31.076$ (6) Å
$c = 7.072$ (1) Å
$\beta = 92.13$ (3)°
$V = 1841.7$ (6) Å^3
$Z = 4$

$D_x = 1.537$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 100 reflections
$\theta = 5.2$–25.4°
$\mu = 0.29$ mm^{-1}
$T = 120$ (2) K
Prism, colourless
0.10 × 0.10 × 0.05 mm

Data collection

Kuma KM-4 CCD diffractometer
ω scans
Absorption correction: none
9769 measured reflections
3200 independent reflections
2625 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.046$
$\theta_{\rm max} = 25.0°$
$h = -9 \rightarrow 7$
$k = -36 \rightarrow 36$
$l = -8 \rightarrow 8$

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Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.142$
$S = 1.28$
3200 reflections
249 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0728P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.59$ e Å^{-3}
$\Delta\rho_{\min} = -0.58$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.024 (3)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3···O1	0.88	1.85	2.724 (3)	170
N1—H1···O3	0.88	1.92	2.735 (3)	153

Data collection: *Xcalibur* (Oxford Diffraction, 2001); cell refinement: *Xcalibur*; data reduction: *Xcalibur*; program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *PLATON* (Spek, 1990).

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