

agree well with those found in many comparable phosphates cited by Baur & Khan (1970) in which the short P–O distances range from 1.48 to 1.53 Å.

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## The Crystal Structure of Ammonium Monofluorophosphate: $(\text{NH}_4)_2\text{PO}_3\text{F}\cdot\text{H}_2\text{O}$

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The crystal structure of  $(\text{NH}_4)_2\text{PO}_3\text{F}\cdot\text{H}_2\text{O}$  has been determined by single-crystal X-ray methods using multiple-film equi-inclination Weissenberg data. The unit cell is monoclinic with  $a = 6.298 \pm 0.027$ ,  $b = 8.311 \pm 0.015$ ,  $c = 12.702 \pm 0.012$  Å,  $\beta = 98.58 \pm 0.13^\circ$ . The space group is  $P2_1/c$  and the density calculated for  $Z = 4$  is  $1.536 \text{ g.cm}^{-3}$ , experimental  $1.52 \text{ g.cm}^{-3}$ . The structure was refined by least-squares methods to a final value of  $R$  of 0.128. The data and results of this determination are compared with those of an independent determination by Perloff by the method of normal-probability plot analysis. Substitution of fluorine into the orthophosphate anion results in a decrease of the P–O distance and increase in the O–P–O angle.

### Introduction

The monofluorophosphate ion is used commercially as a toothpaste additive ('Colgate') as a decay inhibitor. A study of the crystal structure of  $(\text{NH}_4)_2\text{PO}_3\text{F}\cdot\text{H}_2\text{O}$  was undertaken, since, to understand the mechanism of decay inhibition, it is necessary to know the structure and reactivities of the monofluorophosphate ion.

### Experimental

Crystals of  $(\text{NH}_4)_2\text{PO}_3\text{F}\cdot\text{H}_2\text{O}$  were prepared by recrystallizing a sample of commercial diammonium monofluorophosphate (Alfa Inorganics, Inc.) from aqueous solution.

The crystal chosen for data collection was approximately cylindrical, 0.3 mm in diameter and 1.4 mm in length, and was mounted with the long dimension coincident with the axis of rotation. Multiple-film equi-inclination Weissenberg data were collected for layer lines  $0kl$  through  $3kl$  with Ni-filtered  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.54178$  Å). Intensities were estimated

visually using a calibrated intensity strip and were corrected for Lorentz and polarization effects.

The unit cell was found to be monoclinic with  $a = 6.298 \pm 0.027$ ,  $b = 8.311 \pm 0.015$ ,  $c = 12.702 \pm 0.012$  Å, and  $\beta = 98.58 \pm 0.13^\circ$ . The lattice constants were determined from a powder pattern indexed with the aid of the single-crystal data. Standard deviations in the lattice constants were estimated by a least-squares analysis.

The Laue symmetry is  $2/m$  and the space group was found to be  $P2_1/c$ . The density calculated for  $Z = 4$  was  $1.536 \text{ g.cm}^{-3}$ . The experimental density was determined by flotation to be  $1.52 \text{ g.cm}^{-3}$ .

### Structure determination

The structure was determined by standard techniques and was refined by least-squares methods using 593 observed reflections with weights assigned according to:

$$w = \frac{1}{\sigma} = \frac{A}{F_o} \quad \text{for } I_o \geq \sqrt{AI_{\min}}$$

$$1/w = \frac{1}{\sigma} = \frac{I_o^2}{I_{\min}^2 F_o} \quad \text{for } I_o \leq \sqrt{AI_{\min}}$$

where  $I_{\min}=1$  and  $A$  was chosen as 20. The least-squares calculations were performed using the *ORFLS* program (Busing, Martin & Levy, 1964) modified for an IBM 360-50 computer.

The final value of  $R$  was 0.128 and the largest atomic shift observed in the last least-squares cycle was  $0.06\sigma$ . Separate scale factors for each observed reciprocal layer were included as refinable parameters to minimize errors due to absorption ( $\mu R=0.55$  for the  $0kl$  reciprocal layer). The scattering factors were taken from *International Tables for X-ray Crystallography* (1962). No corrections were applied for anomalous dispersion, extinction or absorption. Unobserved reflections were not included in the refinements, nor were the hydrogen atoms.

The final atomic parameters and the temperature factors for each nonhydrogen atom are given in Table 1. [All atoms are in the general position  $(x, y, z; \bar{x}, \bar{y}, \bar{z}; \bar{x}, \frac{1}{2} + y, \frac{1}{2} - z; x, \frac{1}{2} - y, \frac{1}{2} + z)$  of the space group  $P2_1/c$ ].

Table 1. *Final atomic parameters*

	$x$	$y$	$z$	$B$
P	0.8035 (8)	0.4226 (4)	0.1434 (2)	1.80 (7)
F	0.2290 (18)	0.0720 (10)	0.4365 (6)	3.60 (18)
O(1)	0.6665 (18)	0.4623 (10)	0.2272 (6)	2.30 (19)
O(2)	0.7254 (15)	0.2773 (10)	0.0767 (6)	2.39 (18)
O(3)	0.0427 (20)	0.4258 (11)	0.1824 (7)	3.23 (20)
N(1)	0.6768 (21)	0.1744 (10)	0.3551 (7)	1.92 (18)
N(2)	0.2910 (22)	0.1850 (12)	0.0983 (8)	2.70 (21)
O(4)	0.1813 (26)	0.4598 (13)	0.3995 (9)	5.23 (30)

Table 2. *Distances and angles within the  $\text{PO}_3\text{F}^{2-}$  ion*

The standard deviations should be increased by a factor of 1.5 as indicated by the slope of Fig. 2.

P-O(1)	1.508 (17) Å	O(1)-P-O(2)	112.9 (10)°
P-O(2)	1.521 (16)	O(1)-P-O(3)	114.7 (11)
P-O(3)	1.511 (19)	O(2)-P-O(3)	114.6 (11)
P-F	1.592 (17)	O(1)-P-F	104.3 (11)
		O(2)-P-F	105.3 (10)
		O(3)-P-F	103.3 (11)

Table 3. *Effect of fluoride substitution on the structure of the phosphate ion*

Ion or Compound	Distances		Angles		References
	P-O	P-F	O-P-O	O-P-F	
Average $\text{PO}_4^{3-}$	1.546 Å		109.47°		Corbridge <i>et al.</i> (1966)
$(\text{NH}_4)_2\text{PO}_3\text{F} \cdot \text{H}_2\text{O}$	1.505	1.586 Å	114.02	104.41°	Perloff (1972)
$(\text{NH}_4)_2\text{PO}_3\text{F} \cdot \text{H}_2\text{O}$	1.513	1.592	114.10	104.32	This work
$\text{CaPO}_3\text{F} \cdot 2\text{H}_2\text{O}$	1.508	1.583	113.88	104.61	Perloff (1972)
Average $\text{PO}_3\text{F}^{2-}$	1.509	1.587	114.00	104.45	
$\text{NH}_4\text{PO}_2\text{F}_2$	1.457	1.541	118.7	109.4	Harrison & Trotter (1969)
$\text{KPO}_2\text{F}_2$	1.470	1.575	122.4	108.6	Harrison <i>et al.</i> (1966)
$\text{CsPO}_2\text{F}_2$	1.48	1.58	122.6	108.4	Trotter & Whitlow (1967)
Average $\text{PO}_2\text{F}_2^-$	1.469	1.565	121.2	108.8	
$\text{POF}_3$	1.45	1.52			Williams <i>et al.</i> (1952)
$\text{POF}_3$	1.48	1.52			Hawkins & Cohen (1952)
Average $\text{POF}_3$	1.465	1.52			

The numbers in parentheses are the standard deviations in the least significant figure as estimated from the least-squares analysis. Interatomic distances and angles within the  $\text{PO}_3\text{F}^{2-}$  ion are given in Table 2.

## Discussion

An independent study of the crystal structure of  $(\text{NH}_4)_2\text{PO}_3\text{F} \cdot \text{H}_2\text{O}$ , using automated diffractometer data is reported by Perloff (1972). The observed data and derived atomic positional parameters of his determination are compared with those of this work by the method of normal probability plot analysis (Abrahams & Keve, 1971).

Fig. 1 illustrates the normal probability plot of  $\delta m_i$  for 585 common reflections. The scale factor be-

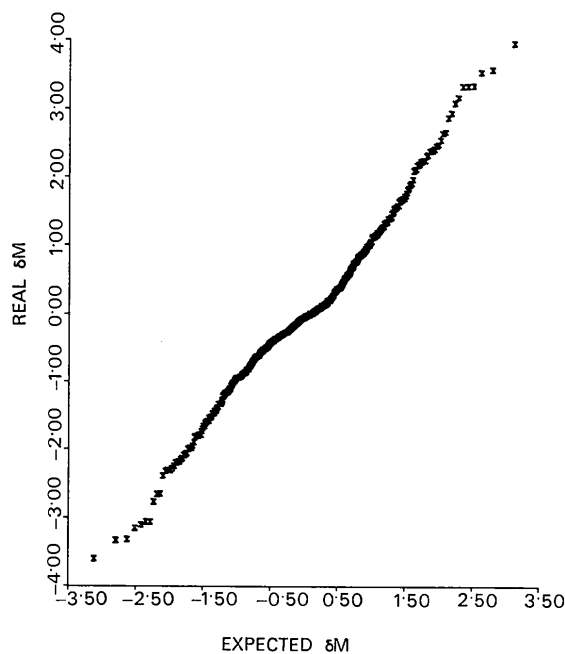


Fig. 1. Normal probability plot of 585  $\delta m_i$  based on the measurement of  $(\text{NH}_4)_2\text{PO}_3\text{F} \cdot \text{H}_2\text{O}$  structure factors by Perloff (1972) and in this work.

tween the two sets of observations was determined by minimizing  $\sum(\delta m_i)^2$ . Although the plot is not linear it is approximately so, suggesting that the two data sets are from the same normal population. The least-squares line through the points of Fig. 1 has slope 1.13 and intercept 0.01. Systematic differences between the two data sets and systematic misinterpretations of  $\sigma F$  are small, however, the standard deviations are underestimated by about 13%.

The half-normal probability plot of the 24  $\delta p_i$  for the nonhydrogen positional parameters calculated in the two determinations is illustrated in Fig. 2. The expected  $\delta p_i$  values were taken from Hamilton & Abrahams (1972). The linear portion of this plot has slope 1.5. The three points which depart from the linear plot correspond to (in decreasing order of  $\delta p$ ) O(3),  $y$ ; O(2),  $y$ ; F,  $x$ . The two sets of positional parameters agree but the estimated  $\sigma P_i$  are too small.

Figs. 1 and 2 taken together show that the systematic error is comparable with the random error with  $\sigma p > \sigma pR$ ,  $\Delta P > \Delta pR$ ,  $\sigma F \approx \sigma R$ , but  $\Delta F > \Delta R$  (Abrahams & Keve, 1971).

The effect, on the interatomic distances and angles, of the substitution of fluorine atoms into the orthophosphate anion is given in Table 3. The values for  $\text{POF}_3$  are from microwave data while the others are from X-ray data.

The P–O distance is seen to decrease with addition of fluorine. This is predicted by the classical pentavalent formulation of the orthophosphate anion as

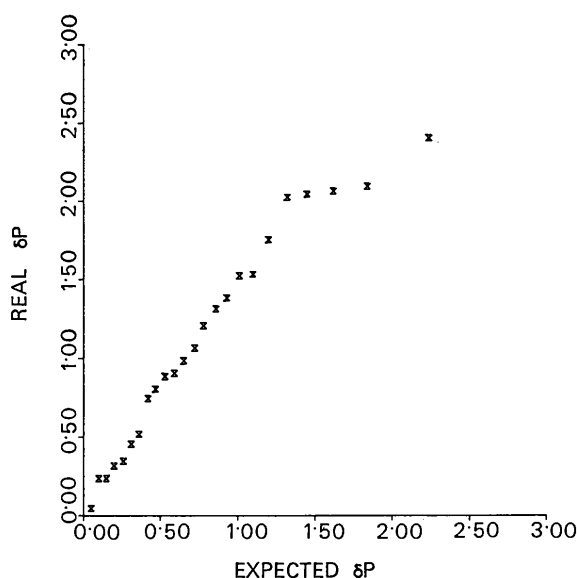
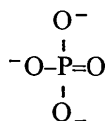
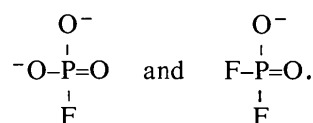


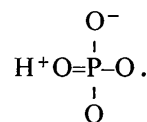
Fig. 2. Half-normal probability plot of 24  $\delta p_i$  derived from the atomic parameters of  $(\text{NH}_4)_2\text{PO}_3\text{F} \cdot \text{H}_2\text{O}$  as determined by Perloff (1972) and in this work.

and the fluorophosphate anions as



Resonance forms are implied by the equivalence of all P–O bonds. Since the fluorine atoms do not share in the double bond (this is approximately true, although not rigorously so, as evidenced by the small (0.022 Å) shortening of the P–F bond going from  $\text{PO}_3\text{F}^{2-}$  to  $\text{PO}_2\text{F}_2^-$ ) the addition of fluorine will increase the double bond character of the P–O bonds, thus decreasing their length.

This P–O bond shortening is also observed, but to a much lesser extent, upon substitution of OH (Baur & Khan, 1970). In the hydroxyl containing anions the increased double bond character of the P–O bond is diminished due to contributions such as



The calculated O–O distance increases from 2.525 Å in  $\text{PO}_4^{3-}$  to 2.531 Å in  $\text{PO}_3\text{F}^{2-}$  and to 2.560 Å in  $\text{PO}_2\text{F}_2^-$ , due to increased repulsion as a result of the increased electron density on the oxygen atoms.

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