

## NH<sub>4</sub>Ag<sub>3</sub>(PO<sub>3</sub>F)<sub>2</sub>, a layered monofluorophosphate(V) with seven different Ag sites

Matthias Weil

Institute for Chemical Technologies and Analytics, Division of Structural Chemistry, Vienna University of Technology, Getreidemarkt 9/164-SC, A-1060 Vienna, Austria  
Correspondence e-mail: mweil@mail.zserv.tuwien.ac.at

Received 29 January 2007

Accepted 22 February 2007

Online 14 April 2007

Single crystals of ammonium trisilver bis[fluorophosphate(V)], NH<sub>4</sub>Ag<sub>3</sub>(PO<sub>3</sub>F)<sub>2</sub>, were obtained from an aqueous solution and the structure was refined from a racemically twinned crystal. The asymmetric unit contains seven crystallographically distinct Ag atoms (two of which are located on twofold axes), four PO<sub>3</sub>F tetrahedra and two ammonium cations. The layered structure is composed of silver–monofluorophosphate sheets, [Ag<sub>3</sub>(PO<sub>3</sub>F)<sub>2</sub>]<sup>−</sup>, that extend parallel to (100). The F atoms of the PO<sub>3</sub>F tetrahedra point towards the ammonium cations, which are located in the interlayer space and stabilize the structure *via* moderate N–H···O and N–H···F hydrogen bonds.

### Comment

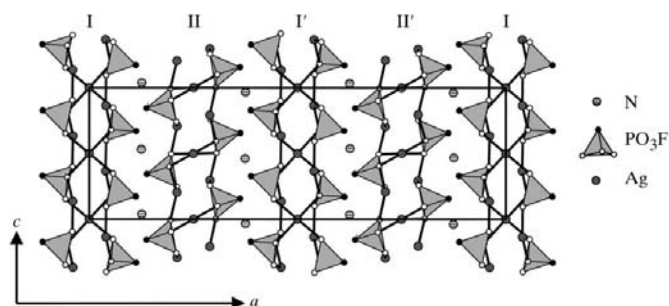
Monofluorophosphates M<sup>I</sup>PO<sub>3</sub>F·xH<sub>2</sub>O or M<sup>II</sup>PO<sub>3</sub>F·xH<sub>2</sub>O (M<sup>I</sup> = NH<sub>4</sub><sup>+</sup> or an alkali metal; M<sup>II</sup> = a transition or an alkaline earth metal; x can range from 0 to 5) are important materials that are used as pesticides, corrosion inhibitors, wood preservatives, toothpaste additives, solubility inhibitors for heavy metals, or as active agents against osteoporosis or caries during biomineralization of fluoroapatite. Preparation methods for monofluorophosphates include solid-state reactions between the corresponding metal fluorides and phosphates, flux reactions in fluoride melts, or conversion of the readily soluble (NH<sub>4</sub>)<sub>2</sub>PO<sub>3</sub>F with metal salts in aqueous solutions. One of the most convenient (but also most expensive) preparation routes for these materials is the metathesis reaction of Ag<sub>2</sub>PO<sub>3</sub>F and metal chlorides in aqueous solutions: Ag<sub>2</sub>PO<sub>3</sub>F + 2M<sup>I</sup>Cl/(M<sup>II</sup>Cl<sub>2</sub>) → M<sup>I</sup>PO<sub>3</sub>F/(M<sup>II</sup>PO<sub>3</sub>F) + 2AgCl. An advantage of this method is the separation of the phosphate anions, which are invariably present in aqueous solutions due to hydrolysis of the PO<sub>3</sub>F<sup>2−</sup> anion, by simultaneous precipitation as Ag<sub>3</sub>PO<sub>4</sub>. Crystallization from the remaining filtrate then leads to single-phase products. Although the preparation of Ag<sub>2</sub>PO<sub>3</sub>F was described a long time ago (Lange, 1929), its crystal structure was unknown until very recently (Weil *et al.*, 2007). During single-crystal growth

experiments aimed at Ag<sub>2</sub>PO<sub>3</sub>F from aqueous AgNO<sub>3</sub> and (NH<sub>4</sub>)<sub>2</sub>PO<sub>3</sub>F solutions, crystals of NH<sub>4</sub>Ag<sub>3</sub>(PO<sub>3</sub>F)<sub>2</sub> were obtained serendipitously, and the crystal structure of this new compound is reported here.

The asymmetric unit of the title compound contains seven crystallographically independent Ag<sup>+</sup> cations, four PO<sub>3</sub>F<sup>2−</sup> tetrahedra and two NH<sub>4</sub><sup>+</sup> cations. A characteristic feature of the crystal structure is the formation of two silver–monofluorophosphate sheets, each with an overall composition of [Ag<sub>3</sub>(PO<sub>3</sub>F)<sub>2</sub>]<sup>−</sup>, that extend parallel to (100) (Fig. 1). The first silver–monofluorophosphate sheet (labelled I) comprises atoms Ag1–Ag4/P3/P4 (Fig. 2a) and the second layer (labelled II) comprises atoms Ag5–Ag7/P1/P2 (Fig. 2b). Within such a sheet, the Ag and O atoms form a sublayer that is covered on the outside by the P and F atoms of the monofluorophosphate units, whereby the F atoms point towards the interlayer space. Sheets I and II are separated by interjacent ammonium cations, which stabilize the structure by means of moderate N–H···O and N–H···F hydrogen bonds.

As can be seen in Fig. 1, a superstructure seems to be present along *a*/2. However, on closer inspection it is apparent that in fact sheets II and II' show a superstructure relation with a translation of *a*/2, but such a translation is absent for sheets I and I' because the orientation of the PO<sub>3</sub>F tetrahedra in these layers is topologically different. Whereas in sheet I the vertices of the tetrahedra point alternately up (U) and down (D), in sheet I' the direction is reversed with an alternating D and U orientation of the respective tetrahedra.

The Ag<sup>+</sup> cations exhibit different coordination numbers (CN) with different AgO<sub>x</sub> coordination polyhedra. A review of the multifarious crystal chemistry of multinary silver oxides and silver–oxo compounds has been given recently by Müller-Buschbaum (2004). Atoms Ag1, Ag2, Ag5 and Ag6 are surrounded by four O atoms in a strongly distorted tetrahedral manner, with average Ag–O<sub>tetrahedral</sub> ≈ 2.39 Å (Table 1), which is in very good agreement with the sum of the ionic radii (Shannon, 1976) for Ag (CN = 4; 1.00 Å) and O (1.38 Å). Each of the AgO<sub>4</sub> polyhedra is surrounded by one additional F atom at distances ≈ 3.06 Å. However, the resulting Ag–F interactions are very weak [the contributions of the corresponding



**Figure 1**

A projection of the crystal structure along [010]. The two different silver–monofluorophosphate sheets are denoted I and II, with the symmetry-related sheets denoted I' and II', respectively. For clarity, only Ag–O bonds < 2.6 Å are drawn.

Ag–F bond valences are only 0.02 valence units (v.u.)] and therefore these contributions might be neglected. Atoms Ag3, Ag4 and Ag7 exhibit a distorted octahedral coordination, with average Ag–O<sub>octahedral</sub>  $\approx$  2.58 Å, likewise in good agreement with the sum of the ionic radii (2.54 Å). However, the variations of the bond lengths for these AgO<sub>6</sub> polyhedra are quite different. On the one hand, Ag3 and Ag4 are located on twofold axes and are better described as [2+2+2] coordinated, with two short ( $\approx$  2.36 Å), two medium ( $\approx$  2.51 Å) and two long ( $\approx$  2.91 Å) Ag–O bonds. On the other hand, Ag7 has a [4+2] coordination, with four similar equatorial Ag–O bonds ( $\approx$  2.45 Å) and two longer axial Ag–O bonds ( $\approx$  2.74 Å).

The four PO<sub>3</sub>F tetrahedra deviate slightly from the ideal C<sub>3v</sub> symmetry, with an average P–O distance of 1.507 Å and an average P–F distance of 1.590 Å (Table 1). In agreement with other monofluorophosphates (Weil *et al.*, 2007) or mono-substituted phosphates of the type PO<sub>3</sub>X (X = H, OH or OR), the P–O bond lengths are shorter than in a regular PO<sub>4</sub> tetrahedron (1.535 Å) and the P–X bond length is significantly increased. Likewise, the O–P–O angles, with an average of 114.4°, are widened and the corresponding O–P–F angles, with an average of 104.0°, are reduced. This behaviour is characteristic for all PO<sub>3</sub>X tetrahedra and has been attributed to the stronger  $\pi$ -character per P–O bond (Corbridge, 1974).

All O atoms have CN = 4 and are coordinated by one P atom and either by three Ag atoms or, when involved in hydrogen bonding, by two Ag atoms and one N atom, in a considerably distorted tetrahedral fashion.

The two interjacent ammonium cations show similar donor–acceptor distances, indicating medium-to-weak hydrogen bonds of types N–H...O and N–H...F (Table 2). Each N atom is surrounded by four O atoms [N1–O = 2.826 (9)–2.942 (10) Å and N2–O = 2.773 (8)–2.887 (9) Å] and by two

additional F atoms [N1–F = 3.002 (8) and 3.116 (11) Å, and N2–F = 3.056 (9) and 3.076 (11) Å]. The presence of six neighbouring atoms with similar donor–acceptor distances, and the fact that a refinement of H-atom positions was not successful, might be an indication of an orientational disorder of the ammonium H atoms. A verification of this assumption is planned for the future with high-resolution neutron data.

Results of bond-valence calculations (Brown, 2002), using the parameters of Brese & O’Keeffe (1991), are in accordance with expected values. The bond valence sums are (v.u.): Ag1 1.01, Ag2 0.94, Ag3 0.92, Ag4 0.93, Ag5 0.92, Ag6 0.95, Ag7 0.95, P1 5.13, P2 5.13, P3 5.19, P4 5.06, F1 1.09, F2 1.08, F3 1.07 and F4 1.10, and all O atoms (hydrogen bonds not considered) between 1.75 and 10.92.

## Experimental

(NH<sub>4</sub>)<sub>2</sub>PO<sub>3</sub>F was prepared according to the method of Schülke & Kayser (1991) from a stoichiometric mixture of (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> (Merck, p.A.) and NH<sub>4</sub>HF (Fluka, p.A.) in a urea melt at 443 K for 2 h. The product was then recrystallized from an acetone–water solution (3:1). X-ray powder diffraction revealed a single-phase product. Coarse crystalline (NH<sub>4</sub>)<sub>2</sub>PO<sub>3</sub>F (0.17 g) was added to an aqueous solution (10 ml) of AgNO<sub>3</sub> (0.43 g) (Merck, p.A.). Since phosphate anions were present in the solution owing to the hydrolysis of the monofluorophosphate anion, the precipitated yellow Ag<sub>3</sub>PO<sub>4</sub> was filtered off, and the remaining clear solution was allowed to stand in a dark room for 2 d. Besides minor quantities of plate-like crystals of Ag<sub>2</sub>PO<sub>3</sub>F (Weil *et al.*, 2007), crystals of the title compound with a block-like habit were obtained and separated mechanically under a microscope.

### Crystal data

(NH<sub>4</sub>)Ag<sub>3</sub>(PO<sub>3</sub>F)<sub>2</sub>  
*M<sub>r</sub>* = 537.59  
 Monoclinic, *I*2  
*a* = 30.895 (4) Å  
*b* = 5.5976 (7) Å  
*c* = 9.7522 (13) Å  
 $\beta$  = 90.027 (2)°

*V* = 1686.6 (4) Å<sup>3</sup>  
*Z* = 8  
 Mo *K* $\alpha$  radiation  
 $\mu$  = 7.31 mm<sup>−1</sup>  
*T* = 293 (2) K  
 0.14 × 0.08 × 0.03 mm

### Data collection

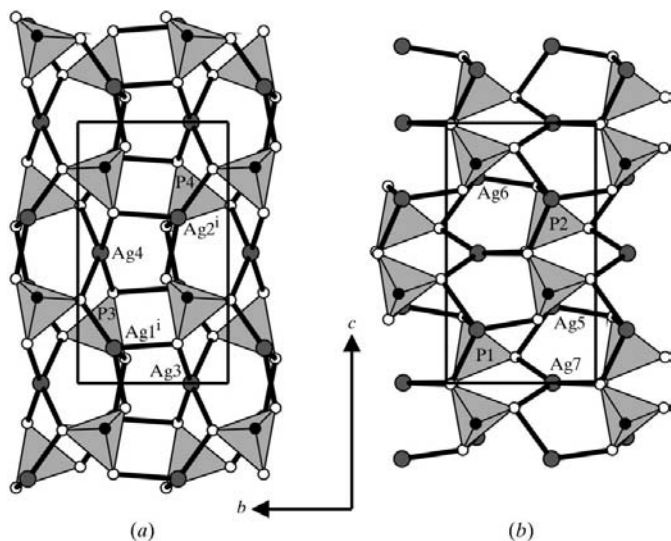
Bruker SMART APEX CCD area-detector diffractometer  
 Absorption correction: multi-scan (SADABS; Sheldrick, 2002)  
*T<sub>min</sub>* = 0.427, *T<sub>max</sub>* = 0.810

9818 measured reflections  
 4876 independent reflections  
 4262 reflections with *I* > 2 $\sigma$ (*I*)  
*R<sub>int</sub>* = 0.019

### Refinement

*R*[*F*<sup>2</sup> > 2 $\sigma$ (*F*<sup>2</sup>)] = 0.032  
*wR*(*F*<sup>2</sup>) = 0.076  
*S* = 1.07  
 4876 reflections  
 245 parameters  
 H-atom parameters not refined

$\Delta\rho_{\max}$  = 0.82 e Å<sup>−3</sup>  
 $\Delta\rho_{\min}$  = −0.95 e Å<sup>−3</sup>  
 Absolute structure: Flack (1983),  
 with 2094 Friedel pairs  
 Flack parameter: 0.48 (5)



**Figure 2**

Details of the silver–monofluorophosphate sheets, showing (a) sheet I and (b) sheet II. The atom shading is as in Fig. 1. [Symmetry code: (i)  $-x, y, 1 - z$ .]

The nonstandard setting *I*2 for space group No. 5 (standard setting *C*2) was chosen to emphasize the pseudo-orthorhombic metrics with  $\beta$  very close to 90°. The structure was refined from a racemically twinned crystal with an approximate twin ratio of 1:1 [Flack (1983) parameter 0.48 (5)]. Checking of the final model with the program *PLATON* (Spek, 2003) did not reveal any higher symmetry. As in many other silver–oxo compounds, the displacement parameters of

**Table 1**  
Selected geometric parameters (Å, °).

Ag1—O10	2.227 (6)	Ag6—O4	2.304 (5)
Ag1—O7 <sup>i</sup>	2.277 (6)	Ag6—O6 <sup>vii</sup>	2.409 (5)
Ag1—O12	2.434 (7)	Ag6—O4 <sup>viii</sup>	2.575 (5)
Ag1—O7 <sup>ii</sup>	2.545 (7)	Ag7—O6 <sup>ix</sup>	2.402 (5)
Ag2—O9	2.259 (7)	Ag7—O5	2.436 (5)
Ag2—O8	2.330 (6)	Ag7—O1 <sup>v</sup>	2.480 (5)
Ag2—O11	2.481 (9)	Ag7—O2 <sup>vi</sup>	2.480 (5)
Ag2—O8 <sup>ii</sup>	2.527 (6)	Ag7—O3 <sup>vi</sup>	2.741 (4)
Ag3—O12 <sup>iii</sup>	2.361 (5)	Ag7—O4 <sup>iii</sup>	2.743 (5)
Ag3—O12 <sup>iii</sup>	2.361 (5)	P1—O5	1.493 (5)
Ag3—O9 <sup>iv</sup>	2.501 (7)	P1—O3	1.504 (5)
Ag3—O9	2.501 (7)	P1—O1	1.523 (5)
Ag3—O7	2.906 (8)	P1—F1	1.587 (5)
Ag3—O7 <sup>iv</sup>	2.906 (8)	P2—O6	1.489 (5)
Ag4—O11 <sup>ii</sup>	2.361 (6)	P2—O4	1.508 (5)
Ag4—O11	2.361 (6)	P2—O2	1.522 (5)
Ag4—O10 <sup>ii</sup>	2.518 (6)	P2—F2	1.592 (5)
Ag4—O10	2.518 (6)	P3—O9 <sup>vii</sup>	1.485 (9)
Ag4—O8 <sup>ii</sup>	2.922 (7)	P3—O11	1.498 (6)
Ag4—O8	2.922 (7)	P3—O7	1.514 (7)
Ag5—O2	2.317 (5)	P3—F3	1.596 (5)
Ag5—O3 <sup>v</sup>	2.317 (5)	P4—O8	1.492 (7)
Ag5—O5	2.400 (5)	P4—O12	1.520 (6)
Ag5—O3 <sup>vi</sup>	2.553 (5)	P4—O10 <sup>v</sup>	1.532 (7)
Ag6—O1 <sup>i</sup>	2.279 (5)	P4—F4	1.585 (5)
O5—P1—O3	115.7 (3)	O9 <sup>vii</sup> —P3—O11	114.3 (5)
O5—P1—O1	114.7 (3)	O9 <sup>vii</sup> —P3—O7	113.2 (5)
O3—P1—O1	113.7 (3)	O11—P3—O7	116.1 (5)
O5—P1—F1	100.8 (4)	O9 <sup>vii</sup> —P3—F3	104.8 (4)
O3—P1—F1	104.9 (3)	O11—P3—F3	102.7 (3)
O1—P1—F1	104.8 (3)	O7—P3—F3	103.7 (4)
O6—P2—O4	114.6 (3)	O8—P4—O12	112.5 (4)
O6—P2—O2	114.4 (3)	O8—P4—O10 <sup>v</sup>	115.0 (4)
O4—P2—O2	113.8 (3)	O12—P4—O10 <sup>v</sup>	114.3 (4)
O6—P2—F2	101.4 (4)	O8—P4—F4	105.3 (3)
O4—P2—F2	105.4 (3)	O12—P4—F4	104.7 (3)
O2—P2—F2	105.5 (3)	O10 <sup>v</sup> —P4—F4	103.5 (4)

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

**Table 2**  
Hydrogen-bonding geometry.

$D \cdots A$	Distance (Å)	$D \cdots A$	Distance (Å)
N1...O12 <sup>i</sup>	2.826 (9)	N1...O6 <sup>ii</sup>	2.831 (9)
N1...O2 <sup>iii</sup>	2.919 (10)	N1...O9	2.942 (10)
N1...F1 <sup>iii</sup>	3.002 (8)	N1...F3 <sup>iv</sup>	3.116 (11)
N2...O11	2.773 (9)	N2...O5 <sup>ii</sup>	2.844 (9)
N2...O10	2.887 (9)	N2...O1 <sup>iii</sup>	2.887 (9)
N2...F2 <sup>v</sup>	3.056 (9)	N2...F4 <sup>vi</sup>	3.076 (11)

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

the Ag atoms are comparatively large. However, refinement of the site-occupation factors (s.o.f.) did not reveal any statistical population and all s.o.f. refined to full occupancy within the standard deviation. One of the ammonium N atoms had a physically meaningless displacement parameter when refined anisotropically, and therefore the displacement parameters of both ammonium N atoms were refined isotropically. The H atoms of the ammonium cations could not be located unambiguously from difference Fourier maps. When placed in calculated positions, the displacement parameters of the H atoms inflated to unreasonable values, also accompanied by slightly higher residuals. Thus, the H atoms were excluded from the refinement (for discussion of a possible disorder of the ammonium cations, see *Comment*). The highest remaining electron density in the final Fourier map was 0.78 Å from Ag<sub>3</sub> and the deepest hole was 0.67 Å from Ag<sub>1</sub>.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ATOMS* (Dowty, 2004); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC3036). Services for accessing these data are described at the back of the journal.

## References

- Brese, N. E. & O'Keeffe, M. (1991). *Acta Cryst.* **B47**, 192–197.
- Brown, I. D. (2002). *The Chemical Bond in Inorganic Chemistry*. Oxford University Press.
- Bruker (2003). *SMART* (Version 5.630) and *SAINT* (Version 6.45). Bruker AXS Inc., Madison, Wisconsin, USA.
- Corbridge, D. E. C. (1974). *The Structural Chemistry of Phosphorus*, pp. 261–266. Amsterdam: Elsevier.
- Dowty, E. (2004). *ATOMS for Windows*. Version 6.1. Shape Software, 521 Hidden Valley Road, Kingsport, Tennessee, USA. URL: <http://www.shape-software.com>.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Lange, W. (1929). *Ber. Dtsch. Chem. Ges. B*, **62**, 793–801.
- Müller-Buschbaum, Hk. (2004). *Z. Anorg. Allg. Chem.* **630**, 2125–2175.
- Schülke, U. & Kayser, R. (1991). *Z. Anorg. Allg. Chem.* **600**, 221–226.
- Shannon, R. D. (1976). *Acta Cryst.* **A32**, 751–767.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Sheldrick, G. M. (2002). *SADABS*. Version 2.06. Bruker AXS Inc., Madison, Wisconsin, USA.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- Weil, M., Puchberger, M., Füglein, E., Baran, E. J., Vannahme, J., Jakobsen, H. J. & Skibsted, J. (2007). *Inorg. Chem.* **46**, 801–808.