Monofluorophosphates—New Examples and a Survey of the \( \text{PO}_3\text{F}^{2-} \) Anion

Matthias Weil

Abstract: During a systematic study of monofluorophosphates, i.e., compounds comprising the tetrahedral anion \( \text{PO}_3\text{F}^{2-} \), twelve, for the most part new, compounds were obtained from aqueous solutions. Crystal structure refinements based on single crystal X-ray diffraction data revealed the previously unknown crystal structures of \( \text{CdPO}_3\text{F} \), \( \text{Cr}_2(\text{PO}_3\text{F})_3 \), \( \text{Cr}_2(\text{PO}_3\text{F})_3 \), \( \text{Mn}_2(\text{PO}_3\text{F})_2(\text{H}_2\text{O})_2 \), \( \text{NH}_4\text{Cr}(\text{PO}_3\text{F})_2(\text{H}_2\text{O})_3 \), \( \text{NH}_4\text{Cu}_2(\text{H}_2\text{O})_2(\text{PO}_3\text{F})_2 \), \( \text{NH}_4\text{Zn}(\text{PO}_3\text{F})_2(\text{H}_2\text{O})_2 \), and \( \text{NH}_4\text{Zn}_3(\text{PO}_3\text{F})_4(\text{H}_2\text{O})_2 \), as well as redeterminations of \( \text{ZnPO}_3\text{F} \) and \( \text{Ni(PO}_3\text{F})_2(\text{H}_2\text{O})_2 \). From the previously unknown crystal structures, \( \text{CdPO}_3\text{F} \) (space group \( \text{Pt} \)), \( \text{Cr}_2(\text{PO}_3\text{F})_3 \) (space group \( \text{Pt} \)), \( \text{Pb}_2(\text{PO}_3\text{F})_2(\text{H}_2\text{O})_3(\text{K} \text{S} \text{m}) \), \( \text{NH}_4\text{Cr}(\text{PO}_3\text{F})_2(\text{H}_2\text{O})_3(\text{P} \text{m} \text{a}) \), \( \text{NH}_4\text{Cu}_2(\text{H}_2\text{O})_2(\text{PO}_3\text{F})_2(\text{C} \text{2} \text{m}) \), and \( \text{NH}_4\text{Zn}_3(\text{PO}_3\text{F})_4(\text{H}_2\text{O})_2(\text{I} \text{T} \text{d} \text{d}) \) each crystallizes in an unique crystal structure, whereas compounds \( \text{NH}_4\text{Zn}(\text{PO}_3\text{F})_2(\text{H}_2\text{O})_2(\text{M} \text{g}, \text{Co}) \) crystallize in the \( \text{NH}_4\text{Cu}_2(\text{PO}_3\text{F})_2(\text{H}_2\text{O})_2 \) type of structure \( (\text{C} \text{2} \text{m}) \) and \( \text{NH}_4\text{Zn}_3(\text{PO}_3\text{F})_4(\text{H}_2\text{O})_2 \) in a subgroup thereof \( (\text{P} \text{2} \text{1} / \text{n}) \). Database entries of all inorganic compounds comprising this group, revealed mean bond lengths of \( \text{P} \text{–} \text{O} = 1.506(13) \text{ Å} \), \( \text{P} \text{–} \text{F} = 1.578(20) \text{ Å} \), and angles of \( \text{O} \text{–} \text{P} \text{–} \text{O} = 113.7(1.7) ° \) and \( \text{O} \text{–} \text{P} \text{–} \text{F} = 104.8(1.7) ° \), using a dataset of 88 independent \( \text{PO}_3\text{F}^{2-} \) anions or entities. For those crystal structures of monofluorophosphates where hydrogen bonding is present, in the vast majority of cases, hydrogen bonds of the type \( \text{D} \text{–} \text{H} \cdots \text{F} \) \( \text{P} \text{–} \text{O} \text{–} \text{N} \) are not developed.

Keywords: monofluorophosphate; crystal growth; mean bond lengths and angles; structure determination; relationship monofluorophosphate and sulfate; \( \text{D} \text{–} \text{H} \cdots \text{F} \) hydrogen bonds

1. Introduction

The family of monofluorophosphates comprising the \( \text{PO}_3\text{F}^{2-} \) anion was introduced by Lange more than 90 years ago [1]. In the \( \text{PO}_3\text{F}^{2-} \) anion, the fluorine atom is directly bound to the phosphorus atom. However, in the literature, compounds with discrete \( \text{PO}_3^{3-} \) and \( \text{F}^- \) anions are also sometimes incorrectly described as “fluorophosphates”, e.g., \( \text{Mn}_2\text{PO}_3\text{F} \) [2] or \( \text{Na}_2\text{FePO}_4\text{F} \) [3]. These compounds correctly belong to the family of ‘phosphate fluorides’. Various preparation methods for monofluorophosphates as well as applications of this family of compounds as additives in toothpastes, wood preservatives, corrosion inhibitors, solubility inhibitors for lead in potable water sources, or as active agents against osteoporosis or caries during biomineralization of fluoroapatite were summarized some time ago [4]. More recently, some monofluorophosphates were also shown to exhibit excellent nonlinear optical (NLO) behaviour [5].

In his seminal paper, Lange emphasized the chemical relationships between monofluorophosphates and sulfates in terms of solubilities and reaction behaviours. In fact, the \( \text{PO}_3\text{F}^{2-} \) anion is isoelectronic with the \( \text{SO}_4^{2-} \) anion, and both anions have a tetrahedral shape, as later evidenced by the very first structure determination of a monofluorophosphate [6]. Prior to this first experimental proof about the structure and shape of the \( \text{PO}_3\text{F}^{2-} \) anion, it was assumed that monofluorophosphates are isomorphic with corresponding...
sulfates [7]. It should be noted that also the terms isomorph/isonomorphism still are found in literature to express structural relationships, but their use is not recommended any longer [8]. More appropriate terms are isostructural/isostructurality or synonymous isotypic/isotypism. Meanwhile, numerous other monofluorophosphates were synthesized and structurally determined, but not for all reported monofluorophosphates corresponding sulfates even exist or show isotypism with existing sulfates.

The current study was undertaken to add more examples of structurally determined monofluorophosphates with inorganic cations to the already existing list of this family of compounds. Although some of the monofluorophosphates investigated during this study have previously been reported and their powder diffraction data deposited in the International Centre for Diffraction Data’s (ICDD) powder diffraction file (PDF) [9], structural details of corresponding phases are still missing up to now. As it turned out, some of the data compiled in the PDF at that time are incorrect (wrong space groups, wrong unit cell volume) and were revised during the current study. Moreover, results of the present crystal structure analyses were used under special emphasis to review structural characteristics (bond lengths and angles, point group symmetries) and hydrogen-bonding features of the PO$_3^{2-}$ anions as well as their structural relationships to corresponding sulfates. O and F atoms differ only in one electron and thus have very similar atomic form factors for X-rays. Consequently, a distinction of the two atom types on the basis of X-ray diffraction methods alone is not free from ambiguity, as was recently shown for minerals that were claimed to comprise monofluorophosphate groups [10]. Nevertheless, the result of the current structure evaluation for the PO$_3^{2-}$ anion is a useful tool to correctly assign F and O atoms in monofluorophosphates, as exemplified by using structure data of a published crystal structure with incorrectly assigned F and O atoms.

2. Materials and Methods

2.1. Syntheses and Single Crystal Growth

For syntheses of NH$_4^+$-containing monofluorophosphates, the starting compound (NH$_4$)$_2$PO$_3$F(H$_2$O) was prepared according to Schülke and Kayser [11] and its purity checked with X-ray powder diffraction (XRPD). One gram of this material was dissolved in 10 mL of a methanol/water mixture (1:1 v:v). Then, 80 mg solid AgNO$_3$ were added to this solution to precipitate the phosphate anions present due to incomplete conversion or partial hydrolysis of the PO$_3^{2-}$ anion. The yellow Ag$_3$PO$_4$ was filtered off, and the filtrate was repeatedly checked for PO$_3^{3-}$ anions by adding a few drops of an AgNO$_3$ solution until no more clouding was observed in the filtrate, ensuring that all PO$_3^{3-}$ anions were removed. Then, 10 mL of a solution consisting of 500 mg of the respective metal chloride in methanol/water (1:1 v:v) were added to the monofluorophosphate solution. The excessive Ag$^+$ ions were precipitated as AgCl and filtered off. To the remaining clear filtrate 100 mL of an acetone/methanol solution (2:1 v:v) were slowly added, resulting in flocculent precipitates in all cases. The respective suspensions were stirred for one hour and then were filtered. The obtained solids were washed with methanol and acetone and then dried in an exsiccator overnight. XRPD revealed an amorphous state for the obtained samples, except for (NH$_4$)$_2$Mg(PO$_3$F)$_2$(H$_2$O)$_2$ that was obtained as a pure polycrystalline phase (cf. PDF entry #00-059-0045).

For single crystal growth of NH$_4^+$-containing monofluorophosphates, 100 mg of the as-precipitated solids were dissolved in 10 mL of a methanol/water mixture (1:1 v:v), to some extent under mild warming. The clear solutions were allowed to evaporate for 2–4 days until full dryness. In all cases, the majority of material was still amorphous, and only few single crystals were found to be suitable for X-ray analysis. This way, single crystals of (NH$_4$)$_2$M(PO$_3$F)$_2$(H$_2$O)$_2$ (M = Mg, Co, Mn), (NH$_4$)$_2$Ni(PO$_3$F)$_2$(H$_2$O)$_2$, NH$_4$Cr(PO$_3$F)$_2$(H$_2$O)$_4$, and NH$_4$Cu$_2$(H$_2$O)$_5$(PO$_3$F)$_2$ could be obtained from the respective metal salt solution. Single crystals of Cr$_2$(PO$_3$F)$_3$(H$_2$O)$_{18.8}$ were likewise harvested from the batch containing the ammonium-chromium monofluorophosphate solution. From the original ammonium zinc monofluorophosphate solution, three different types
of single crystals were isolated, *viz.* ZnPO$_3$F(H$_2$O)$_{2.5}$, (NH$_4$)$_2$Zn(PO$_3$F)$_2$(H$_2$O)$_{0.2}$ and (NH$_4$)$_2$Zn$_3$(PO$_3$F)$_4$(H$_2$O).

Single crystals of CdPO$_3$F(H$_2$O)$_2$ and Pb$_2$(PO$_3$F)Cl$_2$(H$_2$O) were obtained from metathesis reactions. For this purpose, 200 mg Ag$_2$PO$_3$F (prepared according to [4]) were dissolved in 10 mL of water; equimolar amounts of CdCl$_2$ and PbCl$_2$, respectively, were added to the solution, resulting in an immediate precipitation of AgCl. The suspension was stirred for two hours, AgCl filtered off, and the filtrate allowed to evaporate until complete dryness. CdPO$_3$F(H$_2$O)$_2$ was obtained as a single phase material, whereas only few single crystals of Pb$_2$(PO$_3$F)Cl$_2$(H$_2$O) could be isolated. In the latter batch, polycrystalline 2PbCO$_3$·Pb(OH)$_2$ was also determined by XRPD next to a dark-brown to metallic film deposited at the surface of the glass. The formation of the film points to silver that apparently was also present in the filtrate and was reduced to its metallic form during evaporation.

2.2. Single Crystal Diffraction and Structure Analysis

Single crystals were optically preselected under a polarising microscope, embedded in perfluorinated polyether for protection from air and humidity and mounted on MiTeGen MicroLoops™ for the diffraction studies. Experimental details of the data collections and refinements are collated in Table 1.

All crystal structures were initially solved with SHELXS [12] and refined with SHELXL [13]. For the renewed refinement of ZnPO$_3$F(H$_2$O)$_{2.5}$ and (NH$_4$)$_2$Ni(PO$_3$F)$_2$(H$_2$O)$_6$, the original atom labelling and atomic coordinates (as starting parameters) were resumed from the original structure reports [14,15]. For NH$_4$Cu$_2$(H$_3$O$_2$)(PO$_3$F)$_2$, atom labelling and coordinates were adopted from isotypic KCu$_2$(H$_3$O$_2$)$_3$(SO$_4$)$_2$ [16]. In cases where H atom positions were clearly discernible from difference Fourier maps, the corresponding sites were refined with soft restraints on N–H or O–H bond lengths. In cases where H atom positions could not be unambiguously located, H atoms were not considered in the final model, but are part of the chemical formula, X-ray density, etc. These cases apply to Pb$_2$(PO$_3$F)Cl$_2$(H$_2$O), Cr$_2$(PO$_3$F)$_3$(H$_2$O)$_{18.8}$ and (NH$_4$)$_2$Zn(PO$_3$F)$_2$(H$_2$O)$_{0.2}$. In the crystal structure model of the chromium compound severe disorder of the free water molecules (i.e., the non-coordinating or structural water molecules) is observed, both in terms of occupational and positional disorder; the same applies for the partly hydrated zinc compound.

Site occupation factors (s.o.f.) for these O sites were refined freely without restraints or constrains. Disorder was also observed for NH$_4$Cr(PO$_3$F)$_2$(H$_2$O)$_6$ and NH$_4$Cu$_2$(H$_3$O$_2$)(PO$_3$F)$_2$ where the N atom of the ammonium cation is situated on a position with site symmetry 3$m$ and 2$/m$, respectively, which results in a symmetry-restricted disorder of the corresponding ammonium H atoms. Finally, in the crystal structure of (NH$_4$)$_2$Zn$_3$(PO$_3$F)$_4$(H$_2$O)$_4$, the N site of the ammonium cation and the O site of the water molecule share the same fully occupied site with a 2/3 occupation by N and a 1/3 occupation by O.

Further details of the crystal structure investigations may be obtained from The Cambridge Crystallographic Data Centre (CCDC) on quoting the depository numbers listed at the end of Table 1. The data can be obtained free of charge via www.ccdc.cam.ac.uk/structures.

Table 2 lists selected bond lengths and angles for all crystal structures, and Table 3 gives numerical details of hydrogen bonding.
Table 1. Details of data collections and structure refinements.

| Compound | CdPO$_3$F(H$_2$O)$_2$ | Cr$_2$(PO$_3$F)$_2$(H$_2$O)$_{18.8}$ | Pb$_2$(PO$_3$F)Cl$_2$(H$_2$O) | ZnPO$_3$F(H$_2$O)$_{2.5}$ | (NH$_4$)$_2$Co(PO$_3$F)$_2$(H$_2$O)$_2$ | (NH$_4$)$_2$Mg(PO$_3$F)$_2$(H$_2$O)$_2$ |
|----------|------------------------|-----------------------------------|-----------------------------|-------------------------------|----------------------------------|-----------------------------------|
| Formula weight | 246.40 | 736.88 | 601.27 | 208.38 | 326.99 | 292.37 |
| Temperature/°C | 23 | -173 | 23 | -173 | 23 | 23 |
| Radiation; $\lambda$/Å | Mo K$\alpha$, 0.71073 | Mo K$\alpha$, 0.71073 | Mo K$\alpha$, 0.71073 | Mo K$\alpha$, 0.71073 | Mo K$\alpha$, 0.71073 | Mo K$\alpha$, 0.71073 |
| Diffractometer | SMART CCD | SMART CCD | SMART CCD | SMART CCD | SMART CCD | SMART CCD |
| Crystal dimensions / mm | 0.14 × 0.10 × 0.04 | 0.10 × 0.10 × 0.01 | 0.35 × 0.05 × 0.04 | 0.12 × 0.02 × 0.02 | violet; plate | colourless; plate |
| Crystal colour; shape | colourless; fragment | green; plate | colourless; needle | colourless; rod | | |
| Space group, no. | $P\overline{1}$, 2 | $P\overline{1}$, 2 | $Pnma$, 62 | $P\overline{1}$, 2 | C$2/m$, 12 | C$2/m$, 12 |
| Formula units | 2 | 4 | 2 | 4 | 2 | 2 |
| $a$/Å | 5.27680(10) | 11.5937(16) | 7.6020(2) | 9.4671(3) | 7.390(2) | 7.390(2) |
| $b$/Å | 6.66970(10) | 15.292(2) | 8.633(2) | 5.3476(9) | 5.3476(9) | 5.3476(9) |
| $c$/Å | 7.7037(2) | 15.360(2) | 8.888(2) | 7.390(2) | 7.390(2) | 7.390(2) |
| $\alpha$/° | 65.5060(10) | 83.804(6) | 88.633(2) | 90 | 90 | 90 |
| $\beta$/° | 85.9190(10) | 84.203(6) | 88.888(2) | 90 | 90 | 90 |
| $\gamma$/° | 75.3940(10) | 6.9722(5) | 87.182(2) | 90 | 90 | 90 |
| $V$/Å$^3$ | 3238.584(9) | 2674.1(6) | 549.58(3) | 484.01(13) | 484.01(13) | 484.01(13) |
| $\mu$/mm$^{-1}$ | 4.867 | 1.188 | 4.733 | 1.169 | 1.169 | 1.169 |
| X-ray density/g·cm$^{-3}$ | 3.430 | 1.830 | 3.247 | 1.806 | 1.806 | 1.806 |
| Absorption correction | multi-scan; SADABS | multi-scan; SADABS | multi-scan; SADABS | numerical; HABITUS | multi-scan; SADABS | multi-scan; SADABS |
| Trans. coeff. $T_{min}$; $T_{max}$ | 0.0549; 0.829 | 0.0778; 0.972 | 0.0549; 0.749 | 0.884; 0.934 | 0.884; 0.934 | 0.884; 0.934 |
| Range $h_{max}$–$h_{min}$ | 2.91–35.51 | 1.34–26.00 | 3.99–43.26 | 3.02–29.96 | 3.02–29.96 | 3.02–29.96 |
| $k_{max}$–$k_{min}$ | 2.91–35.51 | 1.34–26.00 | 3.99–43.26 | 3.02–29.96 | 3.02–29.96 | 3.02–29.96 |
| $l_{max}$–$l_{min}$ | 2.91–35.51 | 1.34–26.00 | 3.99–43.26 | 3.02–29.96 | 3.02–29.96 | 3.02–29.96 |
| Measured reflections | 20950 | 80926 | 77904 | 77904 | 77904 | 77904 |
| Independent reflections | 2055 | 10504 | 8539 | 7722 | 540 | 540 |
| Obs.reflections [$I > 2\sigma(I)$] | - | - | - | - | - | - |
| $R_1$ | 0.0235 | 0.0731 | 0.0390 | 0.0329 | 0.0686 | 0.0525 |
| Number of parameters | 87 | 681 | 198 | 55 | 55 | 55 |
| Ext. coef. (SHELXL) | 0.0173(9) | - | 0.00298(15) | - | - | - |
| Diff. elec. dens. max; min | 0.51 (0.70, Cd1); -0.56 (0.65, Cd1) | 1.24 (0.94, O6W); -0.97 (0.43, O14W) | 2.33 (0.80, Pb1); -1.51 (0.26, Pb2) | 1.34 (1.52, O8); -0.48 (0.48, O4) | 0.44 (0.49, O1); -0.34 (0.51, H2) | 0.57 (0.71, O2); -0.34 (1.23, H2) |
| $wR_2$ [all] | 0.0297 | 0.0210 | 0.0554 | 0.0523 | 0.0662 | 0.1153 |
| Goof | 1.081 | 1.036 | 1.062 | 1.225 | 0.989 | 1.031 |
| CSD number | 2,048,140 | 2,048,141 | 2,048,144 | 2,048,145 | 2,048,134 | 2,048,135 |
| Compound | (NH₄)₂Mn(PO₄)F₂(H₂O) | (NH₄)₂Ni(PO₄)F₂(H₂O)ₖ | NH₄Cr(PO₄)F₂(H₂O)ₖ | NH₄Cu₂(H₂O)₂(PO₄)F₂ | NH₄Zn₂(PO₄)F₂(H₂O)ₖ₂ | NH₄Zn₃(PO₄)F₄(H₂O)₂ |
|----------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Formula weight | 323.00 | 398.83 | 374.08 | 376.09 | 301.10 | 642.09 |
| Temperature/°C | -173 | -173 | -173 | -173 | 23 | -173 |
| Radiation; λ/Å | Mo Kα, 0.71073 | Mo Kα, 0.71073 | Mo Kα, 0.71073 | Mo Kα, 0.71073 | Mo Kα, 0.71073 | Mo Kα, 0.71073 |
| Diffractometer | APEX-II CCD | APEX-II CCD | APEX-II CCD | APEX-II CCD | APEX-II CCD | APEX-II CCD |
| Crystal dimensions/mm | 0.08 × 0.06 × 0.01 | 0.44 × 0.32 × 0.15 | 0.15 × 0.15 × 0.08 | 0.20 × 0.10 × 0.08 | 0.10 × 0.10 × 0.01 | 0.08 × 0.08 × 0.08 |
| Crystal colour; shape | light-pink; plate | blue; fragment | green; plate | light-blue; parallelepiped | colourless; plate | colourless; octahedron |
| Space group, no. | P2₁/n, 14 | P2₁/c, 14 | R₃̅m, 166 | C2/m, 12 | C2/c, 15 | I₃̅d, 220 |
| Formula units Z | 2 | 2 | 3 | 2 | 12 | 4 |
| a/Å | 12.558(3) | 6.2700(3) | 6.5491(2) | 9.1012(8) | 18.9363(17) | 11.3693(4) |
| b/Å | 5.4559(19) | 12.2845(6) | 6.5491(2) | 6.4121(5) | 7.6955(7) | 11.3693(4) |
| c/Å | 7.4215(18) | 9.1894(4) | 25.4381(14) | 7.8506(7) | 20.5276(18) | 11.3693(4) |
| α/° | 90 | 90 | 90 | 90 | 90 | 90 |
| β/° | 99.9185(8) | 106.033(2) | 90 | 116.277(3) | 108.641(2) | 90 |
| γ/° | 90 | 90 | 120 | 90 | 90 | 90 |
| V/Å³ | 500.9(2) | 680.27(6) | 944.88(8) | 410.80(6) | 2834.4(4) | 1469.61(16) |
| µ/mm⁻¹ | 1.697 | 1.745 | 1.245 | 5.631 | 2.976 | 5.415 |
| X-ray density/g·cm⁻³ | 2.142 | 1.947 | 1.972 | 3.040 | 2.117 | 2.902 |
| Absorption correction | multi-scan; SADABS | multi-scan; SADABS | multi-scan; SADABS | multi-scan; SADABS | multi-scan; SADABS | multi-scan; SADABS |
| Trans. corr. Tₘᵢₙₐᵢₙ; Tₘᵃₓ | 0.663; 0.747 | 0.662; 0.749 | 0.661; 0.747 | 0.631; 0.748 | 0.889; 0.995 | 0.656; 0.746 |
| Range θ₂₃₀⁻θ₃₄₀ | 2.98–32.99 | 2.34–45.97 | 2.40–34.71 | 2.89–39.98 | 2.88–31.00 | 4.39–30.00 |
| Range h | −18–19 | −12–12 | −10–10 | −16–16 | −15–15 | −15–15 |
| k | −8–8 | −24–24 | −9–10 | −11–11 | −15–15 | −15–15 |
| l | −11–11 | −18–18 | −40–40 | −14–13 | −23–29 | −16–16 |
| Measured reflections | 10.452 | 105.648 | 6844 | 7619 | 11.828 | 6077 |
| Independent reflections | 1886 | 5910 | 557 | 1356 | 4382 | 362 |
| Obs. reflections [I > 2σ(I)] | 1059 | 5659 | 461 | 1183 | 3079 | 328 |
| R₁ | 0.0881 | 0.0227 | 0.0526 | 0.0336 | 0.0392 | 0.0516 |
| Number of parameters | 94 | 129 | 30 | 57 | 234 | 33 |
| Ext. corr. (SHELXL) | - | 0.0022(9) | - | - | - | - |
| Flack parameter | - | - | - | - | - | 0.026(15) |
| Diff. elec. dens. max, min | 0.56 (0.63, O1) | 0.53 (0.56, Ni1); | 0.51 (0.77, Cr1); | 1.07 (1.52, H1W); | 0.78 (0.75, O1); | 0.34 (0.78, O1); |
| [e⁻·Å⁻³] (dist. /Å, atom) | −0.63 (0.72, P1) | −0.79 (0.55, Ni1) | −0.51 (0.60, Cu1) | −0.83 (1.36, Zn2) | −0.45 (1.36, Zn1A) | −0.33 (0.41, Zn1A) |
| R₁[2] > 2σ(R₁²) | 0.0404 | 0.0142 | 0.0232 | 0.0299 | 0.0467 | 0.0265 |
| wR₂[2] (all) | 0.1009 | 0.0400 | 0.0621 | 0.0575 | 0.1133 | 0.0533 |
| Good | 1.012 | 1.160 | 1.140 | 1.109 | 1.009 | 1.114 |
| CSD number | 2,048,136 | 2,048,137 | 2,048,142 | 2,048,143 | 2,048,138 | 2,048,139 |
Table 2. Selected interatomic distances Å and angles/°.

| Substance | CdPO2F(H2O)2 | Cr2(PO3F3)(H2O)2.5 | Pb3(PO3F3)(H2O)2 | ZnPO2F(H2O)2.5 |
|-----------|---------------|-------------------|------------------|-----------------|
| Cd1 OW1   | 2.2474(10)    | Cr1 O1            | Pb1 O1           | Zn1 O10         |
| Cd1 O2    | 2.2505(9)     | Cr1 O2            | Pb1 O1W          | Zn1 O18         |
| Cd1 O1    | 2.2545(9)     | Cr1 O3            | Pb1 Cl1          | Zn1 O19         |
| Cd1 O3    | 2.2867(9)     | Cr2 O4            | Pb1 Cl2          | Zn1 O3          |
| Cd1 O3    | 2.3310(9)     | Cr2 O5            | Pb1 Cl2          | Zn1 O9          |
| Cd1 OW2   | 2.3665(10)    | Cr2 O6            | Pb2 O2           | Zn1 O9          |
| P1 O1     | 1.5086(9)     | Cr3 O7            | Pb2 O1           | Zn2 O2          |
| P1 O2     | 1.5073(9)     | Cr3 O8            | Pb2 Cl1          | Zn2 O2          |
| P1 O3     | 1.5155(9)     | Cr3 O9            | Pb2 Cl2          | Zn2 O1          |
| P1 F1     | 1.5747(8)     | Cr3 O10           | Pb2 Cl2          | Zn2 O1          |
| O–P1–O   | 113.89(5)–114.93(5) | Cr3 O12         | Pb2 Cl2          | Zn2 O1          |
| O–P1–F1  | 103.37(5)–104.33(5) | Cr4 O13         | Pb2 Cl2          | Zn2 O1          |
| ZnPO2F(H2O)2.5 | Zn1 O10 | Cr4 O17          | Pb2 Cl2          | Zn2 O1          |
| Zn1 O8    | 1.9614(8)     | Cr4 O18           | Pb2 Cl2          | Zn2 O1          |
| Zn1 O7    | 1.9647(7)     | Cr5 O19           | Pb2 Cl2          | Zn2 O1          |
| Zn1 O5    | 1.9915(7)     | Cr5 O20           | Pb2 Cl2          | Zn2 O1          |
| Zn1 P2    | 2.9235(3)     | Cr5 O21           | Pb2 Cl2          | Zn2 O1          |
| Zn2 O9    | 2.0199(8)     | Cr5 O22           | Pb2 Cl2          | Zn2 O1          |
| Zn2 O9    | 2.0199(8)     | Cr5 O24           | Pb2 Cl2          | Zn2 O1          |
| Zn2 O6    | 2.0941(8)     | Cr5 O23           | Pb2 Cl2          | Zn2 O1          |
| Zn2 O4    | 2.1306(8)     | Cr5 O23           | Pb2 Cl2          | Zn2 O1          |
| Zn3 O3    | 1.9979(8)     | Cr5 O12P          | Pb2 Cl2          | Zn2 O1          |
| Zn3 O11   | 2.1130(9)     | Cr5 O13P          | Pb2 Cl2          | Zn2 O1          |
| Zn3 O1    | 2.1308(8)     | P1 F1             | Pb2 Cl2          | Zn2 O1          |
| P1 O3     | 1.4866(8)     | P2 O21P           | Pb2 Cl2          | Zn2 O1          |
| P1 O8     | 1.5123(8)     | P2 O22P           | Pb2 Cl2          | Zn2 O1          |
| P1 O7     | 1.5342(7)     | P2 O23P           | Pb2 Cl2          | Zn2 O1          |
| P1 F2     | 1.5604(7)     | P2 F2             | Pb2 Cl2          | Zn2 O1          |
| P2 O9     | 1.4906(8)     | P3 O31P           | Pb2 Cl2          | Zn2 O1          |
| P2 O10    | 1.5167(8)     | P3 O32P           | Pb2 Cl2          | Zn2 O1          |
| P2 O5     | 1.5302(7)     | P3 O33P           | Pb2 Cl2          | Zn2 O1          |
| P2 F1     | 1.5595(7)     | P4 F3             | Pb2 Cl2          | Zn2 O1          |
| O–P–O    | 109.98(5)–115.78(5) | P4 O42P         | Pb2 Cl2          | Zn2 O1          |
| O–P–F    | 103.61(4)–108.61(4) | P4 O43P         | Pb2 Cl2          | Zn2 O1          |
| NH4Cr(PO3F3)(H2O)4 | Cr1 O2W      | 1.9622(10)         | P5 O53P          | NiO O4          |
| P1 F1     | 1.5160(10)   | P5 O53P           | NiO O4           | NiO O4          |
| O1-P-O1   | 113.44(4)    | P6 F6B            | NiO O4           | NiO O4          |
| O1-P-F1   | 105.13(4)    | P6 F6A            | NiO O4           | NiO O4          |
| (NH4)2Mn(PO3F3)(H2O)2 | Mn1 O3   | 2.151(2)           | O–P–O            | (NH4)2Zn(PO3F3)(H2O)2 | Zn1 A O1 |
| Mn1 O1    | 2.1650(19)   | O–P–F             | 90.4(4)–118.9(4) | Zn1 B O1 |
| Mn1 O1W   | 2.240(2)     | O–P–F             | 90.4(4)–118.9(4) | Zn1 B O1 |
| P1 O1     | 1.512(2)     | (NH4)2Zn(PO3F3)(H2O)2 | Zn1 B O1 | Zn1 B O1 |
| P1 O2     | 1.5140(19)   | Zn1 O9            | O–P–O            | Zn1 B O1 |
| P1 O3     | 1.517(2)     | Zn1 O5            | O–P–O            | Zn1 B O1 |
| P1 F1     | 1.5944(19)   | Zn1 O3            | O–P–O            | Zn1 B O1 |
| O–P–O    | 112.73(12)–114.98(12) | Zn1 O2         | O–P–F             | O–P–F |
| O–P–F1   | 103.15(10)–105.12(10) | Zn2 O8B        | O–P–F             | O–P–F |
| NH4Cu2(H2O)(PO3F3)2 | Cu1 O2 | 1.9493(10)         | Zn2 O4A          | O–P–O            | Zn1 A O1 |
| Cu1 O1H   | 2.0217(8)    | Zn2 O4A           | O–P–O            | Zn1 B O1 |
| Cu1 O1    | 2.3642(10)   | Zn2 O8A           | O–P–O            | Zn1 B O1 |
|                  | CdPO₃F(H₂O)₂ | Cr₂(PO₃F)₃(H₂O)₁₈.₈ | Pb₁(PO₃F)Cl₂(H₂O) |
|------------------|--------------|----------------------|------------------|
| P₁ O₁            | 1.5052(14)   | Zn₂ O₄B              | 1.988(12)        |
| P₁ O₂            | 1.5138(10)   | P₁ O₁                | 1.484(3)         |
| P₁ F₁            | 1.5934(12)   | P₁ O₂                | 1.512(2)         |
| P₁ O₃            |              | P₁ O₃                | 1.512(2)         |
| O—P₁—O          | 114.36(8)—114.85(5) | P₁ O₃                | 1.575(2)         |
| O—P₁—F₁         | 103.15(5)—104.34(7) | P₁ F₁                | 1.575(2)         |
| P₂ O₅            |              | P₂ O₅                | 1.488(3)         |
| P₂ O₆            |              | P₂ O₆                | 1.489(3)         |
| P₂ O₄A           |              | P₂ O₄A               | 1.532(7)         |
| P₂ O₇            |              | P₂ O₇                | 1.472(3)         |
| P₃ O₈A           |              | P₃ O₈A               | 1.485(6)         |
| P₃ O₉            |              | P₃ O₉                | 1.498(3)         |
| P₃ F₃            |              | P₃ F₃                | 1.556(3)         |
| P₃ O₈B           |              | P₃ O₈B               | 1.597(13)        |
| O—P—O           | 101.6(4)—127.3(10) | O—P—O               | 101.6(4)—127.3(10) |
| O—P—F           | 86.8(9)—116.2(6)  | O—P—F               | 86.8(9)—116.2(6)  |
Table 3. Details of hydrogen bonding/Å, °.

| Compound | D H A | D–H | H···A | D···A | D–H···A | D H A | D–H | H···A | D···A | D–H···A |
|----------|-------|------|-------|-------|---------|-------|------|-------|-------|---------|
| CdPO₃F(H₂O)₂ | OW1 H1 OW2 | 0.83(2) | 1.99(2) | 2.7983(15) | 164(2) | O1 H1 O10 | 0.819(9) | 1.960(9) | 2.7778(11) | 177(2) |
|           | OW1 H2 O2 | 0.81(2) | 2.34(3) | 2.9231(14) | 129(2) | O1 H2 O5 | 0.819(10) | 2.004(10) | 2.8212(11) | 175(3) |
|           | OW1 H2 O1 | 0.81(2) | 2.36(3) | 2.9635(14) | 133(2) | O2 H3 O1 | 0.818(10) | 2.25(2) | 2.9854(14) | 149(3) |
|           | OW2 H3 O2 | 0.90(2) | 2.00(2) | 2.8740(15) | 162(2) | O2 H4 O4 | 0.814(10) | 2.496(15) | 3.2526(14) | 155(3) |
|           | OW2 H3 F1 | 0.90(2) | 2.57(3) | 3.1411(14) | 121(2) | O2 H4 O6 | 0.814(10) | 2.52(2) | 3.1410(13) | 134(2) |
|           | OW2 H4 O1 | 0.84(2) | 2.18(2) | 3.0032(15) | 167(2) | O4 H5 O2 | 0.823(9) | 1.992(11) | 2.8053(13) | 170(3) |
|           | OW2 H4 F1 | 0.84(2) | 2.60(2) | 3.0887(13) | 118(2) | O4 H6 O5 | 0.828(9) | 2.047(10) | 2.8707(11) | 173(2) |
|           | (NH₄)₂Co(PO₃F)₂(H₂O)₂ | N1 H1 O1 | 0.92(4) | 1.88(4) | 2.800(4) | 180(5) | O1 H9 O7 | 0.819(10) | 2.059(11) | 2.8641(11) | 175(2) |
|           | N1 H2 O2 | 0.86(4) | 2.22(3) | 2.924(3) | 139(9) | O11 H10 O2 | 0.822(10) | 2.059(10) | 2.8742(13) | 171(3) |
|           | N1 H3 O2 | 0.85(3) | 2.32(3) | 3.031(4) | 143(4) | (NH₄)₂Ni(PO₃F)₂(OH₂)₆ | N1 H1N O3 | 0.849(12) | 2.159(12) | 2.9613(5) | 157.6(11) |
|           | O1W H4 O1 | 0.81(3) | 2.14(3) | 2.8702(14) | 149(3) | N1 H2N O3 | 0.917(11) | 1.921(11) | 2.8283(4) | 169.8(10) |
|           | (NH₄)₂Mg(PO₃F)₂(H₂O)₂ | N1 H1 O1 | 0.90(4) | 1.90(4) | 2.801(5) | 175(5) | N1 H3N O1 | 0.896(12) | 1.921(12) | 2.8134(5) | 173.7(10) |
|           | N1 H2 O2 | 0.88(4) | 2.21(3) | 2.933(4) | 139(9) | N1 H4N O2 | 0.849(11) | 2.115(11) | 2.9053(5) | 154.7(10) |
|           | N1 H3 O2 | 0.82(3) | 2.34(4) | 3.040(4) | 143(4) | N1 H5W O3 | 0.834(10) | 1.866(10) | 2.6969(4) | 174.0(11) |
|           | O1W H4 O1 | 0.76(3) | 2.15(3) | 2.8732(16) | 160(4) | O1 H5W O1 | 0.826(11) | 1.938(11) | 2.7489(4) | 167.0(10) |
|           | (NH₄)₂Mn(PO₃F)₂(H₂O)₂ | N1 H1W O2 | 0.850(10) | 1.93(14) | 2.748(3) | 161(3) | N1 H7W O2 | 0.799(11) | 1.883(11) | 2.6792(4) | 173.7(11) |
|           | O1W H2W O2 | 0.849(10) | 2.44(3) | 3.103(3) | 136(4) | N5 H8W F1 | 0.804(11) | 2.010(11) | 2.8146(3) | 178.6(12) |
|           | N1 H1N O1 | 0.889(10) | 2.131(19) | 2.945(3) | 150(3) | N5 H9W O1 | 0.805(12) | 1.956(12) | 2.7589(4) | 175.3(11) |
|           | N1 H2N F1 | 0.897(10) | 2.50(3) | 3.041(3) | 119(3) | O6 H10W O2 | 0.789(10) | 2.001(11) | 2.7874(4) | 174.1(11) |
|           | N1 H2N O1 | 0.897(10) | 2.59(3) | 3.209(3) | 127(3) | (NH₄)₂Cu₂(H₂O₃)(PO₃F)₂ | O1H H1O O1H | 0.837(10) | 2.344(10) | 3.1797(18) | 177(4) |
|           | N1 H3N O2 | 0.902(10) | 1.909(11) | 2.810(3) | 176(3) | O1H H2O O1H | 0.999(10) | 1.50(4) | 2.489(3) | 169.2(10) |
|           | N1 H4N O3 | 0.900(10) | 1.912(12) | 2.803(3) | 170(3) | N1 H1N O2 | 0.899(10) | 2.021(18) | 2.8448(10) | 152(3) |
|           | N1 H2N F1 | 0.900(10) | 2.03(4) | 3.041(3) | 119(3) | N1 H2N O1 | 0.900(10) | 2.24(6) | 2.9730(13) | 139(8) |
|           | (NH₄)Cr(PO₃F)₂(H₂O)₆ | O2W H1 O1 | 0.864(16) | 1.753(16) | 2.6124(9) | 173.1(16) | N1H/O1W H1 F1 | 1.02(8) | 2.31(8) | 3.1703(11) | 141(6) |
|           | N1H H2 O1 | 0.95(4) | 2.00(4) | 2.9493(10) | 176(3) | N1H/O1W H1 O1 | 1.02(8) | 2.40(8) | 3.007(3) | 117(6) |
| D   | H   | A   | D–H | H···A | D···A | D–H···A | D   | H   | A   | D–H | H···A | D···A | D–H···A |
|-----|-----|-----|-----|-------|-------|---------|-----|-----|-----|-----|-------|-------|---------|
| (NH₄)₂Zn(PO₃F)₂(H₂O)₀.₂   | N1H/O1W | H1  | O1  | 1.02(8) | 2.38(9) | 3.190(4) | 136(7) |
| N1  | H1  | O7  | 0.897(10) | 1.874(16) | 2.756(5) | 167(5) |
| N1  | H2  | O1  | 0.891(10) | 2.173(3) | 2.955(5) | 147(5) |
| N1  | H3  | O3  | 0.898(10) | 2.130(18) | 3.000(4) | 163(5) |
| N1  | H4  | O6  | 0.894(10) | 1.992(14) | 2.878(5) | 171(5) |
| N2  | H5  | O6  | 0.897(10) | 2.015(18) | 2.890(4) | 164(5) |
| N2  | H6  | O2  | 0.896(10) | 2.162(2) | 3.000(4) | 156(4) |
| N2  | H6  | O9  | 0.896(10) | 2.744(4) | 3.321(5) | 123(4) |
| N2  | H7  | O6  | 0.899(10) | 1.925(13) | 2.817(5) | 172(5) |
| N2  | H8  | O8A | 0.897(10) | 1.962(2) | 2.811(8) | 158(5) |
| N2  | H8  | O8B | 0.897(10) | 2.494(4) | 3.283(3) | 148(5) |
| N3  | H11 | O1  | 0.894(10) | 2.083(3) | 2.869(5) | 146(4) |
| N3  | H9  | O7  | 0.899(10) | 1.989(2) | 2.743(5) | 158(5) |
| N3  | H10 | O4A | 0.897(10) | 2.165(16) | 3.055(9) | 171(4) |
| N3  | H10 | O8B | 0.897(10) | 2.555(5) | 3.03(2)  | 114(4) |
| N3  | H12 | O1  | 0.892(10) | 1.949(13) | 2.837(5) | 173(5) |
2.3. Vibrational Spectroscopy

The infrared (IR) spectrum of a powdered CdPO3F(H2O)2 sample was recorded as a KBr pellet in the spectral range between 4000 and 400 cm\(^{-1}\) employing a Bruker-EQUINOX-55 FTIR-instrument (Billerica, MA, USA). Raman spectra down to 100 cm\(^{-1}\), were measured using the FRA 106 Raman accessory of an IF66 Bruker spectrophotometer (Billerica, MA, USA). Radiation from a Nd:YAG solid-state laser (1064 nm) was used for excitation. The spectral resolution was ± 4 cm\(^{-1}\) in both measurements.

2.4. Thermogravimetry (TG)

A Netzsch TG209 F1 thermobalance (Selb, Germany) was used for measurement using a corundum crucible in flowing nitrogen atmosphere and a heating rate of 20 °C/min.

3. Results

In the current study, only (NH\(_4\))\(_2\)Mg(PO\(_3\)F\(_2\)) and CdPO3F(H2O)\(_2\) were obtained as pure and crystalline phases and in amounts sufficient for the application of other current analytical methods (vibrational spectroscopy, thermogravimetry). All other monofluorophosphates either were obtained in form of multi-phase material or in form of only few single crystals next to amorphous material. This allowed in all cases the determination of the crystal structure but prevented further analytical measurements.

3.1. CdPO3F(H2O)\(_2\)

All atoms in the crystal structure of CdPO3F(H2O)\(_2\) are located on general sites. The cadmium cation exhibits a distorted octahedral coordination sphere defined by two cis-aligned water molecules (OW1, OW2) and four O atoms from four PO\(_3\)F\(_2\)\(^{-}\) anions. Two [CdO\(_4\)(OH\(_2\))\(_2\)] octahedra share an edge to form a dimer [Cd\(_2\)O\(_8\)(OH\(_2\))\(_4\)]; adjacent dimers are linked by corner-sharing with PO\(_3\)F\(_2\)\(^{-}\) groups into layers extending parallel (001). An intralayer hydrogen bond between two water molecules (OW1 and OW2) consolidates this arrangement. Neighbouring layers are held together by medium-strong to weak and partly bifurcated hydrogen bonds between both water molecules and O1 and O2 atoms of the monofluorophosphate anions (Figure 1).

Figure 1. The crystal structure of CdPO3F(H2O)\(_2\) in a projection along [\(\bar{1}00\)]. PO\(_3\)F tetrahedra are given in red (O atoms as colourless, F atoms as green spheres), [CdO\(_6\)] octahedra are given in blue, and H atoms are given as grey spheres. O–H···O hydrogen bonding is indicated by yellow lines.
On the basis of the known structural data, it is possible to perform an analysis of the vibrational-spectroscopic behaviour of the PO$_3$F$_2$$^-$ anion present in the CdPO$_3$F(H$_2$O)$_2$ crystal structure, using the simple site-symmetry approximation [17–20]. Since the monofluorophosphate anion is located on a general C$_1$ position, the symmetry of the “free” PO$_3$F$_2$$^-$ anion (C$_{3v}$) was correlated with its site symmetry (C$_1$), as shown in Table 4. From these results, it becomes evident that, under site symmetry conditions, the three double degenerated E modes are split, and all vibrations present IR and Raman activity. The FTIR spectrum of CdPO$_3$F(H$_2$O)$_2$ is quite simple (Figure 2a) and can be clearly correlated with the results of this analysis. In the Raman spectrum, a more reduced number of bands was observed which, notwithstanding, was useful to additionally support the performed assignments, which are shown in Table 4 and briefly commented on as follows:

- Regarding the vibrations of the water molecules, the O–H stretchings are seen as a relatively broad and clearly splitted band due to the presence of two crystallographically different water molecules. The positions of these bands are characteristic for the presence of hydrogen bridges of medium strength [20], in agreement with the results of the structure analysis. Interestingly, the corresponding deformational mode, $\delta$(H$_2$O), shows also splitting signals.

- The antisymmetric $\nu$(PO$_3$) vibration was not observed in the Raman spectrum, whereas in the IR spectrum it is very strong and broad. In accord with the predictions of the site-symmetry analysis two components can be seen. The corresponding symmetric stretching vibration is the strongest Raman band in both compounds and is also relatively strong in the IR spectrum.

- The $\nu$(P–F) vibration can be clearly identified in the spectra, lying at somewhat higher energy than that observed in the solution Raman spectrum (795 cm$^{-1}$) [20].

- For the deformational modes only $\delta$(PO$_3$) could be identified, clearly split in the IR spectra as predicted (cf. Table 4), whereas no signals for the $\delta$(FPO$_3$) mode could be found. In the Raman spectrum of a PO$_3$F$^-$ solution, both vibrations are reported at the same energy (520 cm$^{-1}$) [20], although in the case of crystalline Hg$_2$PO$_3$F, both vibrations were identified at slightly different wavenumbers, with $\nu_5 > \nu_3$ [21].

- The corresponding $\nu_6$-PO$_3$-rocking mode was only identified in the Raman spectrum, as a very weak band.

Table 4. Site symmetry analysis of the PO$_3$F$_2$$^-$ vibrations in the lattice of CdPO$_3$F(H$_2$O)$_2$ and assignment of IR and Raman bands (band positions in cm$^{-1}$).

| Vibrational Mode | Free Anion (C$_{3v}$) | Site Symmetry (C$_1$) | IR | Raman |
|------------------|---------------------|----------------------|----|-------|
| $\gamma_1$ | $\nu$(P–F) | A$_1$ | A | 825 vs | 826 m |
| $\gamma_2$ | $\gamma$(PO$_3$) | A$_1$ | A | 1006 vs | 1022 vs |
| $\gamma_3$ | $\delta$(FPO$_3$) | A$_1$ | A | — | — |
| $\gamma_4$ | $\gamma$(PO$_3$) | E | 2A | 1142 vs, 1106 vs | — |
| $\gamma_5$ | $\delta$(PO$_3$) | E | 2A | 560 sh, 541 s | 540 w |
| $\gamma_6$ | $\gamma$(PO$_3$) | E | 2A | 3496 vs, | 395 w |
| $\nu$(OH) | — | — | 3393 vs, | — |
| $\delta$(H$_2$O) | — | — | 3223 sh, | — |
| — | — | — | 1648 sh, | — |
| — | — | — | 1626 m, | — |

Activity: A$_1$: IR and Raman; A: IR and Raman. Intensity: vs: very strong; s: strong; m: medium; w: weak; sh: shoulder.
The crystal structure of Cr$_2$(PO$_3$F)$_3$(H$_2$O)$_{18.8}$ is rather complex, with five Cr sites (two of which (Cr1, Cr2) are situated on inversion centres on Wyckoff positions 1a and 1h, respectively), with six PO$_3$F$^2$- anions (one of which (P6) shows positional disorder of the F6 atom over two set of sites), with 24 O atoms associated with aqua ligands of the Cr(III) atoms, and with 14 crystal water molecules (five of which (O1W–O5W) are positionally disordered over multiple sites). The five chromium(III) atoms are solely ligated by water molecules in an octahedral manner and are isolated in the crystal structure. The corresponding Cr–O$_{\text{water}}$ distances are normal and agree with other [Cr(OH)$_2$$_6$] octahedra, e.g., like those found in alums [25].
[Cr(OH$_2$)$_6$] octahedra associated with Cr3, Cr4, and Cr5 are arranged in (011) layers that are sandwiched by the six monofluorophosphate anions, giving an overall composition of [[Cr(OH$_2$)$_6$]$\text{3}$(PO$_3$F)$_6$]$\text{3}$$. Interestingly, all F atoms of the monofluorophosphate tetrahedra point away from the intermediate cationic layer. The two remaining [Cr(OH$_2$)$_6$] octahedra, associated with the two chromium sites Cr1 and Cr2, lie in-between adjacent [[Cr(OH$_2$)$_6$]$\text{3}$(PO$_3$F)$_6$]$\text{3}$ layers. Together with the partly disordered water molecules O1W-O5W they define an own layer with composition [[Cr(OH$_2$)$_6$]$(\text{H}_2\text{O})_{13.6}$]$\text{3}$+. Both types of layers alternate and stack along [011] (Figure 3). Although H atoms could not be located for the water molecules, it is evident that hydrogen bonding is the crucial force for stabilising the stacking arrangement in this crystal structure. Within an anionic [[Cr(OH$_2$)$_6$]$\text{3}$(PO$_3$F)$_6$]$\text{3}$− layer the aqua ligands most probably are involved in hydrogen bonding to the monofluorophosphate O atoms and also among each other; in the intermediate [[Cr(OH$_2$)$_6$]$(\text{H}_2\text{O})_{13.6}$]$\text{3}$+ layer hydrogen bonds might occur between aqua ligands and crystal water molecules. From the same orientation of all monofluorophosphate F atoms towards the [[Cr(OH$_2$)$_6$]$(\text{H}_2\text{O})_{13.6}$]$\text{3}$+ layers one might expect also O–H···F hydrogen bonds in this crystal structure. However, a clear localisation of (disordered) H atoms will be possible only by the application of neutron diffraction, provided that crystals large enough for this diffraction technique can be grown.

![Figure 3. The crystal structure of Cr$_2$(PO$_3$F)$_3$(H$_2$O)$_{18.8}$ in a projection along [001]. Colour code of PO$_3$F tetrahedra as in Figure 1; [CrO$_6$] octahedra are given in blue, O atoms of crystal water molecules with full occupation are given as colourless spheres and those of disordered crystal water molecules as yellow spheres. For clarity, disorder of one of the PO$_3$F groups is not shown.](image)

The formula of this compound can also be written as [Cr(H$_2$O)$_{10}$]$\text{2}$(PO$_3$F)$_3$·6.8$H_2$O. Considering full occupancy of the positionally and occupationally disordered five crystal water sites, this would result in a ’19-hydrate’, i.e., [[Cr(H$_2$O)$_{10}$]$\text{2}$(PO$_3$F)$_3$·7$H_2$O. This amount of water is close to that reported for highly hydrated violet chromium(III) sulfates that are described to contain about 18 water molecules [26]. However, crystal structure determinations of corresponding chromium(III) sulfate hydrates have not been performed up to now.
3.3. \( \text{Pb}_2(\text{PO}_3\text{F})\text{Cl}_2(\text{H}_2\text{O}) \)

The crystal structure of \( \text{Pb}_2(\text{PO}_3\text{F})\text{Cl}_2(\text{H}_2\text{O}) \) comprises two unique lead(II) atoms, two chloride anions, one monofluorophosphate anion and one water molecule of an aqua ligand. Except one oxygen atom of the latter (O2; H atom(s) could not be determined), all other atoms are situated on a mirror plane (Wyckoff position 4c). The two lead(II) atoms exhibit different coordination environments whereby in each case the F atom of the monofluorophosphate anion is not part of the first coordination sphere (shortest Pb–F distances are 3.624(3) Å for Pb1 and 3.912(3) Å for Pb2). Pb1 has a coordination number of 7 (considering distances less than 3.5 Å) and is bonded to two monofluorophosphate O atoms, the O atom of the aqua ligand and four chloride anions. Pb2 has a coordination number of 9, with one very short and two short distances to monofluorophosphate O atoms, two bonds to chloride anions and two pairs of long bonds to monofluorophosphates O atoms. The corresponding \([\text{Pb}_1\text{O}_2(\text{H}_2\text{O})\text{Cl}_4]\) and \([\text{Pb}_2\text{O}_7\text{Cl}_2]\) polyhedra are irregular and share vertices and edges to build up a three-dimensional framework structure (Figure 4). The water molecules protrude into the interstices present in this framework. The monofluorophosphate tetrahedron shares all its O atoms with the framework, whereby the P and F atoms are also oriented towards the interstices of the framework. The next nearest distance between two water molecules in this section of the structure amounts to 3.102(7) Å; three shorter distances to the monofluorophosphate F atom (2.848(8) Å and twice 3.007(4) Å) are also present, making O–H⋯O and also O–H⋯F hydrogen bonding interactions possible. Since H atoms could not be determined, detailed hydrogen bonding interactions cannot be provided.

\[ \text{Figure 4.} \text{ The crystal structure of Pb}_2(\text{PO}_3\text{F})\text{Cl}_2(\text{H}_2\text{O}) \text{ in a projection along [010]. Colour code of PO}_3\text{F tetrahedra as in Figure 1; Pb atoms are represented by dark-blue spheres, Cl atoms as turquoise spheres and O atoms of the water molecules as yellow spheres.} \]
3.4. ZnPO3F(H2O)2.5

The crystal structure of ZnPO3F(H2O)2.5 has been determined previously from a single crystal X-ray data set at room temperature, using a CAD-4 four-circle diffractometer equipped with a point detector. Since only parts of the water hydrogen atoms could be located at that time [14], the crystal structure model remained incomplete, in particular in terms of hydrogen-bonding interactions. The current re-refinement unambiguously revealed all hydrogen atoms, making a complete assignment of hydrogen-bonding interactions possible.

Two of the three unique zinc cations (Zn2, Wyckoff position 1h and Zn3, Wyckoff position 1i) are located on inversion centres; all other atoms are in general sites. Zn1 has a tetrahedral coordination environment and is bonded to the O atoms of four monofluorophosphate tetrahedra. Two such units dimerise into an inversion-symmetric \( \{\text{Zn}_1\text{2(PO}_3\text{F)}_6\} \) unit. Both Zn2 and Zn3 atoms have an octahedral coordination environment, being bound to two monofluorophosphate O and four water O atoms. The corresponding \( \{\text{ZnO}_2\text{(OH)}_2\text{)}_4\} \) octahedra share the non-water O atoms with the \( \{\text{Zn}_1\text{2(PO}_3\text{F)}_6\} \) units to define a three-dimensional framework structure. O–H···O hydrogen bonding of medium strengths between the coordinating water molecules and the monofluorophosphate O atoms reinforces this arrangement. There is an additional crystal water molecule (O2) present in the structure acting both as a donor and an acceptor group. O2 donates weak hydrogen bonds (partly bifurcated) to two ligand water O and one monofluorophosphate O atoms, and accepts medium-strong hydrogen bonds of two coordinating water molecules (Figure 5).

![Figure 5](image_url)

Figure 5. The crystal structure of ZnPO3F(H2O)2.5 in a projection along [010]. Colour code of PO3F tetrahedra and H atoms as in Figure 1; \( \{\text{ZnO}_6\} \) octahedra are given in dark-blue, \( \{\text{ZnO}_4\} \) tetrahedra in turquoise and the O atom of the crystal water molecule as an orange sphere. O–H···O hydrogen bonding with the aqua ligands as donor groups is given as yellow lines, and involving the crystal water molecules as donor groups as orange lines.
3.5. \((NH_4)_2M(PO_3F)_2(H_2O)_2\) \((M = Co, Mg)\)

\((NH_4)_2Co(PO_3F)_2(H_2O)_2\) and \((NH_4)_2Mg(PO_3F)_2(H_2O)_2\) crystallize isotopically with the copper member \((NH_4)_2Cu(PO_3F)_2(H_2O)_2\) in space group \(C2/m\) \([27]\). Instead of the \(C\)-centred unit cell for this structure type, PDF entry #00-045-0355 for \((NH_4)_2Co(PO_3F)_2(H_2O)_2\) reports a primitive unit cell (without further assignment of possible space groups) with lattice parameters of \(a = 12.3817(1)\), \(b = 5.3449(5)\), \(c = 7.3894(6)\) \(\text{Å}\), \(\beta = 98.930(8)^\circ\), \(V = 483.10\) \(\text{Å}^3\). Comparison with the current single crystal X-ray study (Table 1) revealed virtually the same lengths of the \(b\) and \(c\) axes and the same unit cell volume. Preparation, chemical analysis as well as infra-red spectroscopic measurements and thermal behaviour of \((NH_4)_2Mg(PO_3F)_2(H_2O)_2\) were already reported some time ago, without determination of the crystal structure. The originally given lattice parameters \((a = 15.476(4), b = 5.372(1), c = 13.416(3)\) \(\text{Å}\), \(\beta = 118.76(1)^\circ\); determined from polycrystalline material using a Guinier camera) and two possible space groups (\(Cc\) or \(C2/c\) \([23]\) do not match with the current single crystal data with a halved unit cell volume (978 \(\text{Å}^3\) for \([23]\) versus 484 \(\text{Å}^3\) in the current single crystal study) and space group \(C2/m\). Nevertheless, the deposited X-ray powder diffraction data (PDF entry #00-039-029) can be indexed with the actual halved cell. Rietveld refinement of \((NH_4)_2Mg(PO_3F)_2(H_2O)_2\) unambiguously showed the correctness of the halved cell in space group \(C2/m\) (PDF entry #00-059-0045; no structure data given).

The metal cation in the \((NH_4)_2M(PO_3F)_2(H_2O)_2\) \((M = Co, Cu, Mg)\) structure is situated on Wyckoff position 2\(c\) with site symmetry 2\(/m\) and thus has four equal \(M-O\) bonds to the O2 atoms of four \(PO_3F^2^-\) anions and two equal bonds to two \(trans\)-aligned water molecules (O1W). The monofluorophosphate anion is located about a mirror plane, just like the ammonium cation. Adjacent \([MO_4(OH_2)]_2\) octahedra are linked by corner-sharing with the \(PO_3F^2^-\) anions into \([Mg(OH_2)(PO_3F)_2]^2-\) strands running along [010]. Adjacent strands are aligned in parallel and are arranged into layers along [001]. Within a strand, medium-strong hydrogen bonds between the water molecules and the non-coordinating O1 atom of the \(PO_3F^2^-\) anion are established. The ammonium cations are situated between the strands and are hydrogen-bonded to the O1 and O2 atoms of the anions into a three-dimensional network (Figure 6).

**Figure 6.** The crystal structure of \((NH_4)_2M(PO_3F)_2(H_2O)_2\) \((M = Mg, Co; data used from the Mg-compound)\) in a projection along [001]. Colour code of \(PO_3F\) tetrahedra, H atoms and O–H⋯O hydrogen bonding as in Figure 1; \([MO_4]_2\) octahedra are given in blue, N atoms of the ammonium groups as magenta spheres. N–H⋯O hydrogen bonding is indicated by orange lines.
3.6. (NH₄)₂Mn(PO₃F)₂(H₂O)₂

Although manganese is part of the first-row transition metals, (NH₄)₂Mn(PO₃F)₂(H₂O)₂ does not adopt the (NH₄)₂Cu(PO₃F)₂(H₂O)₂ structure type in space group C2/m described above for the transition metals cobalt and copper. The manganese compound shows a group-subgroup relation with the (NH₄)₂Cu(PO₃F)₂(H₂O)₂ structure type, crystallizing in space group P2₁/n that is a klassengleiche subgroup of index 2 [28]. Hence, some of the sites and/or groups in the higher-symmetric space group C2/m have a reduced symmetry or split into two positions in the P2₁/n structure. The divalent metal position (Wyckoff position 2c) now shows site symmetry 1, and all other atoms are located on general sites (Wyckoff positions 4e). The general features of the (NH₄)₂Mn(PO₃F)₂(H₂O)₂ crystal structure (Figure 7) are the same as for the (NH₄)₂Cu(PO₃F)₂(H₂O)₂ structure type. [Mn(OH₂)(PO₃F)₂]ₙ strands run along [010] with the water molecule hydrogen-bonded to the non-coordinating O atom of the monofluorophosphate anions; adjacent strands are organised into layers parallel (101). The ammonium cations again are hydrogen-bonded to the strands by weak hydrogen bonds. As expected, the Mn–O bond lengths are the longest in all four (NH₄)₂M(PO₃F)₂(H₂O)₂ structures because Mn has the largest ionic radius of all divalent transition metal cations. Most probably, the large ionic radius of Mn³⁺ is the driving force for the symmetry reduction from C2/m to P2₁/n.

![Figure 7](image.png)

**Figure 7.** The crystal structure of (NH₄)₂Mn(PO₃F)₂(H₂O)₂ in a projection along [001]. Colour code as in Figure 6.

3.7. (NH₄)₂Ni(PO₃F)₂(H₂O)₆

In contrast to the ammonium transition metal monofluorophosphate dihydrates (NH₄)₂M(PO₃F)₂(H₂O)₆ (M = Mg, Mn, Co, Cu) described in the preceding sections, the nickel compound crystallizes with six water molecules. (NH₄)₂Ni(PO₃F)₂(H₂O)₆ is a member of the vast family of Tutton salts with general formula M₁₂M⁴⁺(XO₄)₁₂(H₂O)₆. Typical crystal-chemical features of Tutton salts have been reviewed in various reports, e.g., ([29], and references therein). In short, the unit cell of a Tutton salt comprises two formula units and is made up of one M⁴⁺ site (here Ni) located on a centre of inversion (Wyckoff position 2n) and surrounded by six water molecules in the form of a slightly distorted octahedron, one XO₄ tetrahedron (here PO₄³⁻), and one ammonium cation (for cases with other M⁺ cations distorted M⁺O₆ polyhedron are present). Hydrogen bonds of medium strengths between the building units of the type O–H···O and, as a peculiarity in the case
of (NH₄)₂Ni(PO₃F)₂(H₂O)₆, also of the type O–H···F generate a three-dimensional network structure. The crystal structure of (NH₄)₂Ni(PO₃F)₂(H₂O)₆ has previously been determined based on a X-ray diffraction data set recorded at room temperature using a CAD-4 four-circle diffractometer and a point detector. Since the crystal intensities dropped by up to 73% of their initial values during the long-lasting data collection [15], it was decided to re-refine the crystal structure with CCD data at 100 K for an improved model. In principle, the current low-temperature data confirm the previous room-temperature data, however with much higher precision as indicated by standard uncertainties for bond lengths and angles about three to five times smaller. The crystal structure of (NH₄)₂Ni(PO₃F)₂(H₂O)₆ is depicted in Figure 8.

Figure 8. The crystal structure of (NH₄)₂Ni(PO₃F)₂(H₂O)₆ in a projection along [100]. Colour code as in Figure 6; O–H···F hydrogen bonding is indicated by green lines.

3.8. NH₄Cr(PO₃F)₂(H₂O)₆

PDF entry #00-044-0535 reports the same R-centred cell for NH₄Cr(PO₃F)₂(H₂O)₆ but with space group R̅3 instead of R̅3̅m determined from the present single crystal X-ray data. In the crystal structure, isolated [Cr(OH₂)₆] octahedra (point group symmetry 3̅m) are organised in layers parallel (001) and are sandwiched by double layers of PO₃F²⁻ anions (point group symmetry 3m) along the [001] stacking direction. The disordered ammonium cations (site symmetry 3̅m) are situated between the PO₃F²⁻ anions in the middle of the monofluorophosphate double layer. Strong hydrogen bonds between the [Cr(OH₂)₆] octahedra and the O atoms of the monofluorophosphate groups link the chromium and monofluorophosphate layers together. Ammonium cations additionally hydrogen-bond to the O atoms within a monofluorophosphate double layer (Figure 9).
Figure 9. The crystal structure of NH$_4$Cr(PO$_3$F)$_2$(H$_2$O)$_6$ in a projection along [110]. Colour code as in Figure 6.

3.9. NH$_4$Cu$_2$(H$_3$O)$_2$(PO$_3$F)$_2$

The ammonium copper compound crystallizes isotypically with KCu$_2$(H$_3$O)$_2$(PO$_3$F)$_2$ [30] in the natrochalcite structure type [16]. The copper cation (site symmetry 2/m; Wyckoff position 4e) is surrounded by six O atoms and shows its characteristic tetragonally distorted octahedral coordination owing to the Jahn-Teller effect. Neighbouring [CuO$_6$] polyhedra share common edges to form chains parallel to [010]. Adjacent chains are bridged by the monofluorophosphate tetrahedra (site symmetry m), sharing exclusively the O atoms into (001) layers. The disordered ammonium cation (with the N atom situated on Wyckoff position 2d with site symmetry 2/m) is located between adjacent layers and links them through hydrogen bonding to the monofluorophosphate O atoms. Additional hydrogen bonds, albeit of weak nature, develop between the non-disordered part of the {H$_3$O$_2$}$^-$ group and the F atom of the monofluorophosphate anion. The crystal structure is shown in Figure 10. It is well known that natrochalcite-type compounds contain such {H$_3$O$_2$}$^-$ groups where a positionally disordered H atom with half-occupation (here H$_2$O) sits between two OH$^-$ groups. Since the features of the resulting hydrogen bonding system, including a clear location of hydrogen atoms by neutron diffraction, was reported for isotypic KCu$_2$(H$_3$O)$_2$(SO$_4$)$_2$, we refer to the original description [16] for further details.
3.10. \((\text{NH}_4)_2\text{Zn}(\text{PO}_3\text{F})_2(\text{H}_2\text{O})_{0.2}\)

Three ammonium cations, two zinc cations, three monofluorophosphate anions and one positionally and occupationally disordered water molecule are present in the asymmetric unit. Except one Zn site (Zn2) located on a twofold rotation axis (Wyckoff position 4e), all other atoms in this structure are located on general positions (Wyckoff position 8f). The O atoms of four monofluorophosphate anions tetrahedrally surround both zinc cations. The latter do not share common atoms but are bridged by the monofluorophosphate units into \((10\bar{1})\) layers. Within a layer disorder of the four O atoms around Zn2 over two sets of sites is observed, with atoms O4 and O8 having an occupational ratio of 0.65(3):0.35(3) for the split pair A:B. This disorder also affects the monofluorophosphate anions associated with P2 and P3 that share these O atoms with Zn2. Additionally, the water molecule (O1W) shows positional and occupational disorder. It is disordered over an inversion centre and shows an occupancy of 0.309(12); full occupation of this site would result in a value of 0.5, leading to a formula of \((\text{NH}_4)_2\text{Zn}(\text{PO}_3\text{F})_2(\text{H}_2\text{O})_{0.33}\). Neighbouring layers are linked through intermediate ammonium cations by medium to weak hydrogen bonds to the monofluorophosphate O atoms. The crystal structure of \((\text{NH}_4)_2\text{Zn}(\text{PO}_3\text{F})_2(\text{H}_2\text{O})_{0.2}\) is displayed in Figure 11.
The site symmetry of the PO$_3$F tetrahedron is $4_{1}$ with the P atom situated on Wyckoff position $16f$. Due to disorder around this axis, the remaining Zn cations split into four equivalent sites (ZnB) with an occupancy of 0.0625 each. The N atom of the ammonium cation (N1H) and the O atom of a water molecule (O1W) simultaneously occupy Wyckoff position 12b with $4$ site symmetry. Due to disorder around this axis, the remaining Zn cations split into four equivalent sites (ZnB) with an occupancy of 0.0625 each. The N atom of the ammonium cation (N1H) and the O atom of a water molecule (O1W) simultaneously occupy Wyckoff position 12b (located on a $4$ axis) in a ratio of 0.67/0.33. The site symmetry of the PO$_3$F tetrahedron is $3$ with the P atom situated on Wyckoff position $12a$. The remaining Zn cations split into four equivalent sites (ZnB) with an occupancy of 0.0625 each. The N atom of the ammonium cation (N1H) and the O atom of a water molecule (O1W) simultaneously occupy Wyckoff position 12b with $4$ site symmetry. Due to disorder around this axis, the remaining Zn cations split into four equivalent sites (ZnB) with an occupancy of 0.0625 each. The N atom of the ammonium cation (N1H) and the O atom of a water molecule (O1W) simultaneously occupy Wyckoff position 12b (located on a $4$ axis) in a ratio of 0.67/0.33. The site symmetry of the PO$_3$F tetrahedron is $3$ with the P atom situated on Wyckoff position $12c$. The disordered part of the crystal structure is shown in Figure 12.

Whereas ZnA is exclusively bonded to four O atoms (O1) of symmetry-related monofluorophosphate anions with an equal bond length of 1.934(3) Å, ZnB is coordinated by only three monofluorophosphate O atoms at two shorter and one longer Zn–O distances. The fourth coordination site, completing a distorted tetrahedron, is occupied by the water molecule at the longest distance of 2.204(14) Å. Again, the F atom of the monofluorophosphate tetrahedron does not take part in constructing the framework structure because it is not part of the coordination spheres around the two zinc sites (Figure 13). However, it is involved in weak hydrogen bonding interactions as the acceptor atom with the disordered (N1H/O1W) donor group. Two more hydrogen bonding interactions of similar strength are present between the donor group and the monofluorophosphate O atoms.
Figure 12. Disorder in the crystal structure of (NH₄)₂Zn₃(PO₃F)₄(H₂O). Colour code of the PO₃F tetrahedra as in Figure 1. The major part of the disordered Zn site (ZnA) is given as a blue sphere, the minor part (ZnB) as a turquoise sphere. The statistically occupied (NH₄/H₂O) site is given in magenta. For clarity, H atoms are not shown.

Figure 13. The crystal structure of (NH₄)₂Zn₃(PO₃F)₄(H₂O) in a projection along [−100] giving only the major part of the disordered Zn site. Colour code of PO₃F tetrahedra as in Figure 1; [ZnO₄] tetrahedra are given in blue and (N,O)–H···F hydrogen bonding is indicated by green lines. For clarity, (N,O)–H···O hydrogen bonding is not shown.

3.12. Survey on the PO₃F²⁻ Group
• Mean bond lengths and angles in the PO₃F tetrahedron

For the statistical analysis of bond lengths and angles within a PO₃F tetrahedron in inorganic monofluorophosphates that are compiled in the most recent version of the Inorganic Structure Database (ICSD, [31]), reliability factors $R1 \leq 0.08$ for the structure
model and only ordered PO$_3$F groups were considered as criteria, disregarding different measurement temperatures or redeterminations. HPO$_2$F$^-$ tetrahedra present in hydrogen-monofluorophosphates were not taken into account. In summary, 88 independent PO$_3$F tetrahedra from 63 different monofluorophosphate phases (including the examples of the current study) were used (Table 5). As a result, the P–F bond of 1.578(20) Å is significantly longer than the three P–O bonds with 1.506(13) Å, and relative to the ideal tetrahedral angle of 109.47°, the three O–P–O angles of 117.3(1.7)° are enlarged by about 4° and the O–P–F angle of 104.8(1.7)° reduced by about the same value. The averaged values for bond lengths and angles in the monofluorophosphate PO$_3$F tetrahedron differ markedly from those of the difluorophosphate PO$_2$F$_2$ tetrahedron. Here, the two P–O and the two P–F bonds are shortened with mean values of 1.459 (27) and 1.530 (21) Å, respectively, and the O–P–O angle once more is widened to 121.2 (2.9)°, whereas the O–P–F angle of 108.7 (6)° now is closer to the ideal value (the F–P–F angle is the smallest in the PO$_2$F$_2$ tetrahedron with 98.5 (2.6)°) [32].

The computed mean values of the monofluorophosphate tetrahedron can be used as a simple tool for evaluation of crystal structures with this entity. In one case (Table 5), a significant deviation in terms of bond lengths and angles was observed for the crystal structure of (NH$_4$)$_2$Fe(PO$_3$F)$_2$ [33] where one of the two distinct monofluorophosphate anions has one of the P–O bonds as the longest in the tetrahedron, a very short P–F bond, anions has one of the P–O bonds as the longest in the tetrahedron, a very short P–F bond, and with O–P–O and O–P–F angles unexpected: P2–O1 = 1.562(5) Å, P2–F4 = 1.498(5) Å, P2–O4 = 1.485(6) Å (2x), O1–P2–F4 = 106.7(3)°, O1–P2–O4 = 102.7(2)° (2x), F4–P2–O4 = 115.0(2)° (2x), O4–P2–O4 = 112.8(3)°. Based on the current averaged data for a PO$_3$F tetrahedron, it is clear that atoms O1 and F4 were wrongly assigned and must be interchanged.

- **Symmetry of the PO$_3$F group in crystal structures**

Possible point group symmetries of a PO$_3$F group in a crystal structure are 1, 3, m and 3m, the latter being the highest possible point group symmetry for this tetrahedron in the crystalline state. The vast majority of monofluorophosphate groups exhibits point group symmetry 1 (70 examples), followed by point group symmetry m (15 examples), 3m (two examples) and 3 (one example). The reported point group symmetry of 42m for the PO$_3$F group in K$_3$(PO$_3$F)$_3$ [34] is incompatible with its molecular symmetry and consequently, this group is disordered.

- **Isotypism with sulfates**

From the numerous phases compiled in Table 5, only nine show isotypism with the corresponding sulfate, *viz.* Na$_3$PO$_3$F(H$_2$O)$_{10}$, NaK$_3$(PO$_3$F)$_2$, K$_5$(PO$_3$F)$_5$, M$_2$PO$_3$F ($M = K, Rb, Cs, NH$_4$), (NH$_4$)$_2$Ni(PO$_3$F)(H$_2$O)$_6$ and CuK(OH)(PO$_3$F)(H$_2$O). Eleven monofluorophosphate phases have equivalent sulfate phases but with different crystal structures, *viz.* Li(NH$_4$)$_2$PO$_3$F, Na$_2$PO$_3$F, CaPO$_3$F(H$_2$O)$_2$, SrPO$_3$F, BaPO$_3$F, (NH$_4$)$_2$Mn(PO$_3$F)$_2$F$_2$, Fe$_2$(PO$_3$F)$_3$, NaFe(PO$_3$F)$_2$, SnPO$_3$F, Ag$_2$PO$_3$F and Hg$_2$PO$_3$F, but the majority of monofluorophosphate phases has no sulfate counterpart.

- **Hydrogen bonding with the monofluorophosphate F atom as an acceptor**

As discussed briefly for appropriate structures above and detailed in Table 3, hydrogen bonding involving the F atom of the monofluorophosphate anion occurs only occasionally and then only as a comparatively weak interaction. A review of the crystal structures where hydrogen bonding is possible and where all H atoms were determined revealed that this situation holds also for most other monofluorophosphates. Considering a D···F distance (D = donor atom: N, O) less than 3.2 Å and D–H···F angles greater than 130°, as relevant for a significant hydrogen bonding interaction [35], then only for Li(NH$_4$)$_2$PO$_3$F, Na$_2$PO$_3$F(H$_2$O)$_{10}$, CaPO$_3$F(H$_2$O)$_2$, Cu$_2$K(OH)(H$_2$O)(PO$_3$F)$_2$, K$_2$Mn$_3$(HPO$_4$)$_2$(PO$_3$F)$_5$ and (NH$_4$)$_2$Ni(PO$_3$F)$_3$(H$_2$O)$_6$ is this kind of interaction realized, albeit of weak nature (Table 5). In all other monofluorophosphates capable of hydrogen-bonding interactions either the D···F–P distances are much greater than the threshold of 3.2 Å, or the D–H···F angles are much smaller than 140°. In these structures, D–H···O hydrogen bonds dominate or are the only hydrogen-bonding interactions.
Table 5. Structural details of monofluorophosphates, site symmetries of corresponding PO$_3$F tetrahedra, relation to the sulfate analogues and details of D–H···P–F hydrogen bonding.

| Monofluorophosphate (Reference) | Space Group, Z | Site Symmetry PO$_3$F Group(s) | D–H···F–P Hydrogen Bonding with D–F/A and D–H···F$^\dagger$ | Corresponding Sulfate | Relationship | Remark |
|-------------------------------|---------------|---------------------------------|-------------------------------------------------|------------------------|-------------|--------|
| LiKPO$_3$(H$_2$O) [36]       | P2$_1$/c, 4   | 1                              | 3.15; 120                                      | Li(NH$_4$)$_2$(SO$_4$) | -           | -      |
| Li(NH$_4$)$_2$PO$_3$F [37]   | P2$_1$/c, 4   | 1                              | 2.98; 147                                      | P$_2$1cn, Z = 4; P$_2$1/c Z = 8; Pmcn, Z = 8. Na$_2$SO$_4$ | -           | Sulfate shows poly-morphism. |
| Na$_2$PO$_3$F [38]           | P2$_1$2$_1$2$_1$, 8 | 1, 1                           | -                                              | Fdd, Z = 8; P6$_3$/mmc, Z = 2. Na$_2$PO$_3$F $^{[39]}$ | -           | Sulfate shows dimorphism. |
| Na$_2$PO$_3$(H$_2$O)$_{10}$ [39] | P2$_1$/c, 4   | 1                              | 2.83, 149                                      | Na$_2$SO$_4$(H$_2$O)$_{10}$ (Glauber salt) NaK$_3$(SO$_4$)$_2$ (glauserite) | Isotypic     | -      |
| NaK$_3$(PO$_3$F)$_2$ [40]    | P3m1, 1       | 3m                            | -                                              | NaK$_3$(SO$_4$)$_2$ (glauserite) | Isotypic     | -      |
| (NH$_4$)$_2$(PO$_3$F)(H$_2$O) [41] | Pn, 2       | 1                              | -                                              | K$_2$SO$_4$ (arcanite); high-temperature form: P6$_3$/mmc; Z = 2. | Isotypic     | Isotypic with low-temperature form; PO$_3$F disordered. Phase transition reported for the sulfate. |
| K$_2$PO$_3$F [6,42]          | Pnam, 4       | m                              | -                                              | K$_3$(PO$_3$F)$_2$F | Isotypic     | -      |
| K$_3$(PO$_3$F)$_2$F [34]     | I4/mcm, 4     | Z2m                           | -                                              | K$_3$(PO$_3$F)$_2$F | Isotypic     | -      |
| Rb$_2$PO$_3$F [43]           | Pnma, 4       | m                              | -                                              | Rb$_2$SO$_4$ | Isotypic     | -      |
| Cs$_2$PO$_3$F [43]           | Pnma, 4       | m                              | -                                              | Cs$_2$SO$_4$ | Isotypic     | -      |
| Cs$_3$(NH$_4$)$_2$(HPO$_3$F)$_2$(PO$_3$F) [44] | P2$_1$/c, 8 | 1,1,1,1                      | -                                              | Cs$_3$(NH$_4$)$_2$(HPO$_3$F)$_2$(PO$_3$F) | Isotypic     | -      |
| (NH$_4$)$_2$(PO$_3$F)(H$_2$O) [46–48] | P2$_1$/c, 4 | 1                              | -                                              | (NH$_4$)$_2$(PO$_3$F)(H$_2$O) | Isotypic     | -      |
| (NH$_4$)$_2$Mg(PO$_3$F)$_2$(H$_2$O)$_2$ [this work] | C2/m, 2 | m                              | -                                              | (NH$_4$)$_2$Mg(PO$_3$F)$_2$(H$_2$O)$_2$ | Isotypic     | -      |
| CaPO$_3$F(H$_2$O)$_2$ [46]   | PT, 2         | 1                              | 3.12, 147                                      | CaPO$_3$(H$_2$O)$_2$ (gypsum) C2/m, Z = 4. | -           | -      |
| SrPO$_3$F [49]               | P2$_1$/c, 4   | 1                              | -                                              | Barite-type SrSO$_4$; Pnma, Z = 4; | SrPO$_3$F adopts the monazite structure type. | X-ray powder data. |
| SrPO$_3$(H$_2$O)$_2$ [49]    | P2$_1$/c, 4   | 1                              | 2.77, 108                                      | -                                              | -           | -      |
| BaPO$_3$ [50]                | P2$_1$/c, 8   | 1, 1                          | 2.95, 110                                      | BaSO$_4$ (barite), Pnma, Z = 4; F$\bar{4}$3m, Z = 4 (HT) | -           | Sulfate shows dimorphism. |
| Cs$_2$Te$_2$(PO$_3$F)$_2$(PO$_3$F)$_2$ [51] | P2$_1$/c, 2 | 1                              | -                                              | Cs$_2$Te$_2$(PO$_3$F)$_2$(PO$_3$F)$_2$ | Isotypic     | -      |
| Cr$_5$(PO$_3$F)$_2$(H$_2$O)$_{18,8}$ [this work] | PT, 4 | 1, 1, 1, 1, 1, 1               | ?                                              | -                                              | -           | -      |
| NH$_4$Cr(PO$_3$F)$_2$(H$_2$O)$_8$ [this work] | R3m, 3  | 3m                            | 2.91, 111                                      | -                                              | -           | -      |
| MnPO$_3$F(H$_2$O)$_2$ [52]   | PT, 2         | 1                              | 3.11, 128                                      | -                                              | -           | -      |
| Li$_2$Mn(PO$_3$F)$_2$F$_2$ [53] | P2$_1$/c, 2 | 1                              | 3.18, 127                                      | -                                              | -           | -      |
| K$_3$Mn$_2$(PO$_3$F)$_2$F$_2$ [53] | P2$_1$/c, 4 | 1                              | -                                              | -                                              | -           | -      |
| K$_2$Mn$_2$(PO$_3$F)$_2$(PO$_3$F)F [54] | P2$_1$/c, 4 | 1                              | 3.09, 142                                      | -                                              | -           | -      |
|                              |               |                                | 2.93, 122                                      | -                                              | -           | -      |
| Monofluorophosphate (Reference) | Space Group, Z | Site Symmetry PO3F Group(s) | D–H···F–P Hydrogen Bonding with D···F/Å and D–H···F/° | Corresponding Sulfate | Relationship | Remark |
|-------------------------------|---------------|-----------------------------|-----------------------------------------------|----------------------|--------------|--------|
| Rh3Mn2(PO3F)2F5 [53]          | Cc, 4         | 1, 1                        | -                                             | -                    | -            | -      |
| Cs2MnF3(PO3)2F2 [53]         | P21/n, 2      | 1, 1                        | -                                             | -                    | -            | -      |
| (NH4)2Mn(PO3)2F2(H2O)2 [this work] | P21/n, 4   | 1                          | -                                             | NH4Mn(SO4)2F2, Pnma, Z = 8 | -            | -      |
| (NH4)2Mn(PO3)2F2 [53,55] | P21/c, 4       | 1                          | N–H 3.11, 160                                 | O–H 2.87, 104        | -            | -      |
| (NH4)2Mn2(HPO4)2(PO3)F2F2 [54] | C2/c, 4       | 1                          | O–H 2.97, 128                                 | -                    | -            | -      |
| (NH4)2Mn3(PO3)2F2(PO3)F2 [54] | C2/c, 4       | 1                          | -                                             | -                    | -            | -      |
| Ba2Mn2(PO3)F4 [57]            | P21/c, 4       | 1                          | -                                             | -                    | -            | -      |
| Fe2(PO3)2F2 [33]             | P6/m, 6        | m, m, m                     | -                                             | Fe2(SO4)2,           | -            | Sulfate shows dimorphism. |
| NaFe(PO3)2F2 [33]            | P21/c, 4       | 1, 1                        | -                                             | NaFe(SO4)2, C2/m, Z = 2 | -            | -      |
| KFe(PO3)F2 [54]              | P21/c, 4       | 1, 1                        | -                                             | -                    | -            | -      |
| KFe2(PO3)F2(PO3)F2F2 [33]    | P4/m, 2        | 1, 1                        | -                                             | -                    | -            | -      |
| RbFe(PO3)2[(PO3)2F2(Fe3O)3]2F2 [33] | C2/c, 4 | 1                          | -                                             | -                    | -            | -      |
| Cs2Fe2F3(PO3)2(PO3)F2 [33]   | Aa2, 4         | 1                          | -                                             | -                    | -            | -      |
| (NH4)2Fe(PO3)2F2Cl2 [33]     | Pa21/n, 4      | 1, 1                        | -                                             | -                    | -            | -      |
| (NH4)2Fe(PO3)2F2 [33]        | P21/m, 4       | m, m                        | -                                             | -                    | -            | -      |
| CoPO3(PO2)F2(H2O)2 [56]      | P4/n, 2        | 1                          | 2.98, 118                                      | -                    | -            | -      |
| (NH4)2CO(PO3)3(PO2)F2 [56]   | C2/m, 2        | m                          | -                                             | -                    | -            | -      |
| Ba2CO(PO3F)3 [55]            | P21/c, 4       | 1                          | 2.96, 115                                      | -                    | -            | -      |
| (NH4)2(NH2O6)2(PO2)F2 [15]   | P21/c, 2       | 1                          | 2.84, 176                                      | (NH4)2(NH2O6)2(SO4)2 Isotypic | Picromerite structure type. |
| (NH4)2(NH2O6)2(PO2)F2 [15]   | P21/c, 2       | 1                          | 2.81, 179                                      | (NH4)2(NH2O6)2(SO4)2 Isotypic | -            | -      |
| Ba2N2(PO3F)3 [57]             | P21/c, 4       | 1                          | -                                             | -                    | -            | -      |
| CuPO(PO2)F2(H2O)2 [59]       | P21/c, 4       | 1                          | -                                             | -                    | -            | -      |
| Cu2K(HO)(PO3)3(PO3)H2O [30]  | C2/m, 2        | m                          | 3.00, 174                                      | Cu2K(H2O)2(SO4)2 Isotypic | -            | -      |
| KCu3(PO3)2F2(PO3)F2F2 [55]   | C2/c, 4        | 1                          | -                                             | -                    | -            | -      |
| RbCu3(PO3)2F2(PO3)F2F2 [55]  | C2/c, 4        | 1                          | -                                             | -                    | -            | -      |
| NH4Cu2(H2O)2(PO3)F2 [this work] | C2/m, 2       | m                          | O–H 3.18, 177                                 | -                    | -            | -      |
| (NH4)2Cu(H2O)2(PO3)F2 [27]   | C2/m, 2        | m                          | N–H 2.97, 139                                 | -                    | -            | -      |
| Ba2Cu2(PO3F)3 [57]           | P21/c, 4       | 1                          | -                                             | -                    | -            | -      |
Table 5. Cont.

| Monofluorophosphate (Reference) | Space Group, Z | Site Symmetry PO₃F Group(s) | \( D-H-\cdot-F-P \) Hydrogen Bonding with \( D-\cdot-F/\AA \) and \( D-H-\cdot-F/^\circ \) | Corresponding Sulfate | Relationship | Remark |
|--------------------------------|---------------|----------------------------|---------------------------------|----------------------|-------------|--------|
| ZnPO₃F(H₂O)$_{2.5}$ [14]      | \( \text{P}T, 4 \) | 1, 1                       | -                              | -                    | -           | H atoms not reliably determined. |
| ZnPO₃F(H₂O)$_{2.5}$ [this work] | \( \text{P}T, 4 \) | 1, 1                       | -                              | -                    | -           | -      |
| (NH₄)$_2$Zn(PO₃F)$_2$(H₂O)$_{0.2}$ [this work] | \( C2/c, 12 \) | 1, 1, 1                     | ?                              | -                    | -           | H atoms of water not determined. |
| (NH₄)$_2$Zn(PO₃F)$_4$(H₂O) [this work] | \( \text{I}3d, 4 \) | 3                          | (N,O)-- 3.17, 141               | Barite-type SnSO₄, \( Pnma, Z = 4 \) | -           | -      |
| SnPO₃F [60]                    | \( P2_1/c, 4 \) | 1                          | -                              | -                    | -           | -      |
| Ag$_2$PO₃F [4]                | \( C2/c, 8 \)  | 1                          | -                              | Fddd, \( Z = 8; P6_3/mmc, Z = 2 \) | -           | Sulfate shows dimorphism. |
| (NH₄)$_2$Ag$_3$(PO₃F)$_2$ [61] | \( I2, 8 \)    | 1, 1, 1, 1                  | ?                              | -                    | -           | H atoms not determined |
| CdPO₃F(H₂O)$_2$ [this work]    | \( P\text{T}, 2 \) | 3.14, 121                   | 3.09, 118                      | -                    | -           | -      |
| Hg$_2$PO₃F [21]               | \( \text{Ibam}, 8 \) | \( m \)                     | -                              | Hg$_2$SO₄           | -           | -      |
| Pb₂PO₃Cl₃(H₂O) [this work]     | \( P\text{nma}, 4 \) | \( m \)                     | ?                              | \( P2/c, Z = 2 \)   | -           | -      |

* It is most unlikely that (NH₄)$_2$Mn$_3$(PO₃F)$_2$(PO₂F$_2$)$_2$ and (NH₄)$_2$Mn$_3$(PO₃F)$_2$(H₂PO₄)F$_2$ crystallize in the same type of structure with virtually the same unit cell and the same space group symmetry and differ only in one of the anions, i.e., PO₂F$_2$- and PO₂(OH)$_2$- . In all likelihood, one of the crystal structure models (and the respective composition) is incorrect. Based on the available data, an evaluation was, however, not possible.
4. Conclusions

Single crystals of twelve and partly unknown monofluorophosphate phases were grown from aqueous solutions. Crystal structure refinements of these compounds extend our knowledge about the PO$_3$F$_2^-$ anion. Based on the present crystal structure data and a complete literature search addressing monofluorophosphate structures of inorganic compounds, the following structural characteristics for the tetrahedral PO$_3$F group were obtained: The P—F bond has a mean value of 1.578(20) Å and is considerably longer than the mean of the three P—O bonds of 1.506(13) Å, and the mean O–P–O angles of 113.7(1.7)$^\circ$ are considerably larger than the mean O–P–F angle of 104.8(1.7)$^\circ$. The point group symmetry of the “free” PO$_3$F group (C$_{3v}$ in Schoenflies or 3$m$ in Hermann–Maugin notation) is found with this symmetry in the solid state only in two examples. In most cases (70 examples) the point group symmetry is reduced to C$_1$ (1) followed by point group symmetry C$_s$ (m) with 15 examples and C$_3$ (3) with one example. The monofluorophosphate F atom is characterized by its isolated state in the crystal structure. In the vast majority of cases, it is not part of the coordination sphere of the cation and/or is not engaged in hydrogen bonding as an acceptor atom. Only in exceptional cases are weak interactions realized, i.e., for large cations with high coordination numbers in form of long metal–F bonds or as hydrogen bonds with long donor···F distances between 2.8 and 3.2 Å.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available in The Cambridge Crystallographic Data Centre (CCDC) and can be obtained free of charge via www.ccdc.cam.ac.uk/structures.

Acknowledgments: The author thanks Enrique J. Baran (Consejo Nacional de Investigaciones Científicas y Técnicas de la República Argentina (CONICET) and the Universidad Nacional de La Plata, Argentina) for recording and interpreting the vibrational spectra of CdPO$_3$F(H$_2$O)$_2$, and Ekkehard Füglein (Netzsch GmbH, Selb, Germany) for recording the TG of CdPO$_3$F(H$_2$O)$_2$.

Conflicts of Interest: The author declares no conflict of interest.

References

1. Lange, W. Über die Monofluorphosphorsäure und die Ähnlichkeit ihrer Salze mit den Sulfaten. Ber. Dtsch. Chem. Ges. 1929, 62B, 793–801. [CrossRef]
2. Rea, J.R.; Kostiner, E. The crystal structure of manganese fluorophosphate, Mn$_2$(PO$_4$)F. Acta Crystallogr. 1972, B28, 2525–2529. [CrossRef]
3. Jin, D.; Qiu, H.; Du, F.; Wei, Y.; Meng, X. Co-doped Na$_2$FePO$_4$F fluorophosphates as a promising cathode material for rechargeable sodium-ion batteries. Solid State Sci. 2019, 93, 62–69. [CrossRef]
4. Weil, M.; Puchberger, M.; Füglein, E.; Baran, E.J.; Vannahme, J.; Jakobsen, H.J.; Skibsted, J. Single-Crystal Growth and Characterization of Disilver(I) Monofluorophosphate(V), Ag$_2$PO$_3$F: Crystal Structure, Thermal Behavior, Vibrational Spectroscopy, and Solid-State $^{19}$F, $^{31}$P, and $^{109}$Ag MAS NMR Spectroscopy. Inorg. Chem. 2007, 46, 801–808. [CrossRef]
5. Xiong, L.; Chen, J.; Lu, J.; Pan, C.-Y.; Wu, L.-M. Monofluorophosphates: A New Source of Deep-Ultraviolet Nonlinear Optical Materials. Chem. Mater. 2018, 30, 7823–7830. [CrossRef]
6. Robinson, M.T. The crystal structures of β-K$_2$SO$_4$ and β-K$_3$PO$_3$F. J. Phys. Chem. 1958, 62, 925–928. [CrossRef]
7. Râyi, R.C. Isomorphism and Chemical Homology. Nature 1930, 126, 310–311. [CrossRef]
8. Lima-de-Faria, J.; Hellner, E.; Liebau, F.; Makovicky, E.; Parthé, E. Nomenclature of Inorganic Structure Types—Report of the International Union of Crystallography Commission on Crystallographic Nomenclature Subcommittee on the Nomenclature of Inorganic Structure Types. Acta Crystallogr. 1990, A46, 1–11. [CrossRef]
9. Gates-Rector, S.D.; Blanton, T.N. The Powder Diffraction File: A Quality Materials Characterization Database. Powder Diffr. 2019, 34, 352–360. [CrossRef]
10. McCubbin, F.M.; Phillips, B.L.; Adcock, C.T.; Tait, K.T.; Steele, A.; Vaughn, J.S.; Fries, M.D.; Atudorei, V.; Vander Kaaden, K.E.; Hausrath, E.M. Discreditation of bobdownsite and the establishment of criteria for the identification of minerals with essential monofluorophosphate (PO$_3$F$_2^-$). Am. Mineral. 2018, 103, 1319–1328. [CrossRef]
11. Schülke, U.; Kayser, R. Herstellung von Fluorophosphaten, Difluorophosphaten, Fluorophosphonaten und Fluorophosphiten in floridhaltigen Harnstoffschmelzen. Z. Anorg. Allg. Chem. 1991, 600, 221–226. [CrossRef]
12. Sheldrick, G.M. A short history of SHEXL. Acta Crystallogr. 2008, 64, 112–122. [CrossRef]
13. Sheldrick, G.M. Crystal structure refinement with SHELXL. Acta Crystallogr. 2015, 71, 3–8.
14. Durand, J.; Larbot, A.; Cot, L.; Duprat, M.; Dabosi, F. Etude Structurale de ZnPO3F-2H2O, Nouvel Inhibiteur de Corrosion. Z. Anorg. Allg. Chem. 1983, 504, 163–172. [CrossRef]
15. Berraho, M.; R’kha, C.; Vegas, A.; Rafiq, M. Structure of Ni(H2O)6(NH4)2(PO3F2). Acta Crystallogr. 1992, C48, 1350–1352. [CrossRef]
16. Chevrier, G.; Giester, G.; Jarosch, D.; Zemann, J. Neutron Diffraction Study of the Hydrogen-Bond System in Cu2K(H2O)(SO4)2. Acta Crystallogr. 1990, C46, 175–177. [CrossRef]
17. Ross, S.D. Inorganic Infrared and Raman Spectra; McGraw Hill: London, UK, 1972.
18. Müller, A.; Baran, E.J.; Carter, R.O. Vibrational spectra of oxo-, thiо-, and selenometallates of transition elements in the solid state. Struct. Bond. 1976, 26, 81–139.
19. Fadini, A.; Schnebel, F.M. Vibrational Spectroscopy: Methods and Applications; Ellis Horwood: Chichester, UK, 1989.
20. Siebert, H. Crystal structure of Cs(HPO4)2. Acta Crystallogr. 1971, B27, 204–209. [CrossRef][PubMed]
21. Weil, M.; Puchberger, M.; Baran, E.J. Preparation and characterization of dimercury(I) mononitrophosphate(V), Hg2PO3F2: Crystal structure, thermal behavior, vibrational spectra, and solid state 31P and 35F NMR spectra. Inorg. Chem. 2004, 43, 8330–8335. [CrossRef]
22. Calvo, C.; Au, P.K.L. Crystal structure of Cd3P2Oy. Can. J. Chem. 1969, 47, 3409–3416. [CrossRef]
23. Menz, D.-H.; Kolditz, L. Synthese und thermisches Verhalten von Mg(NH4)2(PO3F2)2·2H2O. Z. Chem. 1985, 25, 189–190. [CrossRef]
24. Menz, D.-H.; Kolditz, L.; Heide, K.; Kunert, C.; Mensing, C. Zur Thermischen Zersetzung von SrPO3F2·H2O. Z. Anorg. Allg. Chem. 1986, 540, 191–197. [CrossRef]
25. Nyburg, S.C.; Steed, J.W.; Aleksovska, S.; Petrovič, V.M. Structure of the alums. I. On the sulfate group disorder in the α-alums. Acta Crystallogr. 2000, B56, 204–209. [CrossRef][PubMed]
26. Gmelin Handbook of Inorganic Chemistry. Cr-Chrom (Systemnummer 52); Springer-Verlag: Berlin/Heidelberg, Germany, 1962; Teil B; p. 306ff.
27. Berraho, M.; Vegas, A.; Martinez-Ripoll, M.; Rafiq, M. A copper monofluorophosphate, Cu(H2O)2(NH4)2(PO3F2). Acta Crystallogr. 1994, C50, 666–668. [CrossRef]
28. Muller, U. Symmetry Relationships between Crystal Structures; IUCr/Oxford Science Publications: Oxford, UK, 2013.
29. Weil, M. On the (non)existence of Tutton salts with formula types [M(H2O)6][ClO4]2(H2O)2 and Na2M(SO4)2(H2O)6 (M is a first-row transition metal). Acta Crystallogr. 2013, C69, 990–994. [CrossRef]
30. Moewius, F.; Ziemer, B.; Reck, G.; Meisel, M.; Gronze, H. Darstellung und Kristallstruktur von Kalium-dikupferhydroxid-14. Durand, J.; Larbot, A.; Cot, L.; Duprat, M.; Dabosi, F. Etude Structurale de ZnPO3F-2H2O, Nouvel Inhibiteur de Corrosion. Z. Anorg. Allg. Chem. 1983, 504, 163–172. [CrossRef]
31. Zagorac, D.; Müller, H.; Ruehl, S.; Zagorac, J.; Rehme, S. Recent developments in the Inorganic Crystal Structure Database: Theoretical crystal structure data and related features. J. Appl. Crystallogr. 2019, 52, 918–925. [CrossRef]
32. Weil, M.; Fürst, M. Crystal structure of (1,4-diphenyl-4H-1,2,4-triazol-3-yl)phenylamine difluorophosphate, and a survey of the difluorophosphate ion (PO2F−2). Acta Crystallogr. 2020, E76, 1003–1006. [CrossRef]
33. Keates, A.C.; Armstrong, I.A.; Weller, M.T. Iron fluorophosphates. Dalton Trans. 2013, 42, 10715–10724. [CrossRef]
34. Skakle, J.M.S.; Fletcher, J.G.; West, A.R. The crystal structures of potassium oxyfluorides, K2SeO4F and K3PO3F2. An. Quim. Int. Ed. 1996, 92, 358–361.
35. Steiner, T. The Hydrogen bond in the Solid State. Angew. Chem. Int. Ed. 2002, 41, 48–76. [CrossRef]
36. Galigé, J.L.; Durand, J.; le Côt, L. Etudes structurales de composes oxyfluorés du P(V). I. Structure cristalline de LiKPO3F2H2 O. Acta Crystallogr. 1974, B30, 697–701. [CrossRef]
37. Durand, J.; le Côt, L.; Galigé, J.L. Etudes structurales de composes oxyfluorés du P(V). V. Structure cristalline de LiNH4PO3F2. Acta Crystallogr. 1978, B34, 388–391. [CrossRef]
38. Galigé, J.L.; Durand, J.; le Côt, L.; Galigé, J.L. Etudes structurales de composes oxyfluorés du P(V) II. Structure cristalline de Na2PO3F beta. Acta Crystallogr. 1974, B30, 1565–1569. [CrossRef]
39. Prescott, H.A.; Troyanov, S.I.; Kemnitz, E. The synthesis and crystal structures of two new hydrated sodium monofluorophosphates: NaPO3F·2.5H2O (I) and Na2PO3F·10H2O (II). J. Solid State Chem. 2001, 156, 415–421. [CrossRef]
40. Durand, J.; Granier, W.; le Côt, L.; Galigé, J.L. Etudes structurales de composes oxyfluorés du P(V). III. Structure cristalline de NaK3PO3F2. Acta Crystallogr. 1975, B31, 1533–1535. [CrossRef]
41. Fabry, J.; Dušek, M.; Krupkova, R. Ammonium sodium fluorotrioxophosphate monohydrate. Acta Crystallogr. 2007, E63, i92–i94. [CrossRef]
42. Payen, J.; Durand, J.; le Côt, L.; Galigé, J.L. Etude structurale du monofluorophosphate de potassium K2PO3F. Can. J. Chem. 1979, 57, 886–889. [CrossRef]
43. Fabry, J.; Dušek, M.; Fejarová, K.; Krupkova, R.; Vanek, P.; Cisarova, I. Dirubidum fluorotrioxophosphate, Rb2PO3F2at 290 and 130 K, and dicesium fluorotrioxophosphate, Cs2PO3F2 at 240 and 100 K. Acta Crystallogr. 2006, C62, i49–i52. [CrossRef]
44. Prescott, H.; Troyanov, S.; Kemnitz, E. The crystal structures of two hydrogen monofluorophosphates: CsHPO3F and Cs3(NH4)2(HPO3F2)(PO3F). Z. Kristallogr. 2000, 215, 240–245. [CrossRef]
45. Krupkova, R.; Fabry, J.; Cisarova, I.; Vanek, P. Bis(ammonium) fluorophosphate at room temperature. Acta Crystallogr. 2002, C58, i66–i68. [CrossRef]
46. Perloff, A. The crystal structures of hydrated calcium and ammonium monofluorophosphates: CaPO$_3$(H$_2$O)$_2$ and (NH$_4$)$_2$PO$_3$F(H$_2$O). Acta Crystallogr. 1972, B28, 2183–2191. [CrossRef]
47. Berndt, A.F.; Sylvester, J.M. The crystal structure of ammonium monofluorophosphate: (NH$_4$)$_2$PO$_3$F(H$_2$O). Acta Crystallogr. 1972, B28, 2191–2193. [CrossRef]
48. Durand, J.; Beys, L.; Hillaire, P.; Aleonard, S.; le Cot, L. Etude structurale de (NH$_4$)$_2$PO$_3$F, H$_2$O a 120 K par diffraction des rayons X et spectroscopie Raman entre 293 et 83 K. Spectrochim. Acta 1978, A34, 123–127. [CrossRef]
49. Jantz, S.G.; van Wuellen, L.; Fischer, A.; Libowitzky, E.; Baran, E.J.; Weil, M.; Höppe, H.A. Syntheses, crystal structures, NMR spectroscopy, and vibrational spectroscopy of Sr(PO$_3$F)$_2$.H$_2$O and Sr(PO$_3$F). Eur. J. Inorg. Chem. 2016, 7, 1121–1128. [CrossRef]
50. Stöger, B.; Weil, M.; Skibsted, J. The crystal structure of BaPO$_3$F revisited—A combined X-ray diffraction and solid-state $^{19}$F, $^{31}$P MAS NMR study. Dalton Trans. 2013, 42, 11672–11682. [CrossRef]
51. Marshall, K.L.; Weller, M.T. Synthesis of titanium fluorophosphates and fluorosulfates from hexafluorotitanic acid. Z. Anorg. Allg. Chem. 2014, 640, 2766–2770. [CrossRef]
52. Weil, M.; Baran, E.J.; Kremer, R.K.; Libowitzky, E. Synthesis, crystal structure, and properties of Mn(PO$_3$F)(H$_2$O)$_2$. Z. Anorg. Allg. Chem. 2015, 641, 184–191. [CrossRef]
53. Armstrong, J.A.; Williams, E.R.; Weller, M.T. Manganese(III) fluorophosphate frameworks. Dalton Trans. 2013, 42, 2302–2308. [CrossRef]
54. Wang, G.; Valldor, M.; Dorn, K.V.; Wilk-Kozubek, M.; Smetana, V.; Mudring, A.-V. Ionothermal Synthesis Enables Access to 3D Open Framework Manganese Phosphates Containing Extra-Large 18-Ring Channels. Chem. Mater. 2019, 31, 7329–7339. [CrossRef]
55. Armstrong, J.A.; Williams, E.R.; Weller, M.T. Fluoride-rich, hydrofluorothermal routes to functional transition metal (Mn, Fe, Co, Cu) fluorophosphates. J. Am. Chem. Soc. 2011, 133, 8252–8263. [CrossRef]
56. Jiang, J.; Zhu, B.; Zhu, T.; Yang, H.; Jin, Y.; Lü, M. Open-framework ammonium transition metal fluorophosphates with a Kagomé lattice network: Synthesis, structure and magnetic properties. Dalton Trans. 2020, 49, 841–849. [CrossRef] [PubMed]
57. Zhu, B.; Jiang, J.; Zhu, T.; Yang, H.; Jin, Y.; Choi, K.-Y.; Lü, M. Transition-Metal Monofluorophosphate Ba$_2$M$_2$(PO$_3$F)$_6$ (M = Mn, Co, and Ni): Varied One-Dimensional Transition-Metal Chains and Antiferromagnetism. Inorg. Chem. 2020, 59, 3794–3804. [CrossRef] [PubMed]
58. Durand, J.; le Cot, L.; Berraho, M.; Rafiq, M. Structure du monofluorophosphate de cobalt trihydrate. Acta Crystallogr. 1987, C43, 611–613.
59. Zeibig, M.; Wallis, B.; Moewius, F.; Meisel, M. Darstellung und Kristallstruktur von Kupfer(II)-monofluorophosphat-Dihydrat CuPO$_3$F.2H$_2$O. Z. Anorg. Allg. Chem. 1991, 600, 231–238. [CrossRef]
60. Berndt, A.F. The crystal structure of SnPO$_3$F. Acta Crystallogr. 1974, B30, 529–530. [CrossRef]
61. Weil, M. NH$_4$Ag$_3$(PO$_3$F)$_2$, a layered monofluorophosphate(V) with seven different Ag sites. Acta Crystallogr. 2007, C63, i31–i33.