AgPO₂F₂ and Ag₉(PO₂F₂)₁₄: the first Ag(I) and Ag(I)/Ag(II) difluorophosphates with complex crystal structures.

Electronic Supplementary Information

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1. Crystal structure determination details

The first step of the crystal structure determination was indexing of the obtained powder patterns with the use of X-Cell¹ programme implemented in Accelrys Materials Studio 5.0 package. The data have been further processed with the use of Jana 2006 software.² The description of the powder profiles has been done using 30 Legendre polynomials to describe background and pseudo-Voigt peak profiles. The number of Legendre polynomials was necessary to describe the background correctly, but it has not disturbed the reflections' intensities. The peak asymmetry for Ag₉(PO₂F₂)₁₄ was treated using Bérar-Baldinozzi model,³ while for AgPO₂F₂ a model of asymmetry resulting from axial divergence was applied.⁴ Absorption correction was applied for the model of cylindrical sample with μ ·r equal 0.3 and 1 for Ag₉(PO₂F₂)₁₄ has not been known at the moment of the structure solution and had to be determined in the course of the structure refinement. Atomic displacement parameters were treated only as isotropic with U_{iso} restricted to be equal for all atoms within one structure.

The structure solution was realized through localization of Ag atoms positions, which was possible due to their scattering power much stronger than for other atoms present in the unit cell. In the next step the phosphorous atoms have been introduced and upon finding their positions in reasonable distances from the silver atoms (3-3.5 Å) the O and F atoms were introduced with proper restraints on P-O (1.47–1.49 Å) and P-F (1.51 Å) distances as well as O-P-O (ca. 117°), O-P-F (ca. 109°) and F-P-F (ca. 100°) angles. P-O distance varied depending on the type of silver atoms bound to the oxygen. In case it was a strong bond to Ag(II) the P-O was restrained to 1.49 Å. The weaker the coordination to silver the shorter the restricted P-O bond length was. The relatively short O-F and F-F distances in $PO_2F_2^-$ generate

alerts while validation of the CIF files, which seems to be unavoidable due to nature of the anion studied. The issue is addressed in Validation Response Form in corresponding CIF filed deposited in ICSD database.

Ag-O restraints:

Due to inability to determine exact bond lengths from the best set of powder diffraction data it was necessary to impose restraints on some of the Ag(II)-O bonds. Based on the known Ag(II) oxo compounds, the Ag(II)-O distance for apical oxygen atoms is in the region 2.05-2.16 Å, while for equatorial it is above 2.48 Å. Distances deviating significantly from these values were restricted in the course of the structure refinement. Helpful were the results of the DFT optimization which confirmed elongated octahedron coordination of Ag4 and rhombic distortion of [Ag4^{II}O₆], which on the basis of the available crystallographic data was not clear. Hence the two Ag4-O distances were restrained at 2.25 Å. The restricted Ag(II)-O distances are marked with red color in the S-Table 1 below.

Ag5 is coordinated by 5 oxygen atoms forming square pyramid, which is the first example of such coordination of Ag(II) in inorganic salt. The Ag5-O distances at its base (2.08–2.17 Å) are typical for equatorial bonds in $[Ag(II)O_6]$ elongated octahedron, while the peak of the pyramid is 2.49 Å away from Ag5, which is a typical value for apical oxygen atoms in Ag(II) oxo-salts.



S-Figure 1. Powder diffractogram of Ag₉(PO₂F₂)₁₄ (blue line) together with differential (obs.-calc.) diffractogram from the structure solution (green line). Yellow line is the background and black lines mark the positions of the observed reflections. The region above 45° has been magnified threefold.



S-Figure 2. Powder diffractogram of AgPO₂F₂ (blue line) together with differential (obs.-calc.) diffractogram from the structure solution (green line). Yellow line is the background and black lines mark the positions of the observed reflections. The insert shows the region above 45° in 6.5-fold magnification.

2. List of relevant Ag(II)-O-O-Ag(II) angles in Ag₉(PO₂F₂)₁₄

	Ag4	Ag5
Δ σ3	$162 1(4)^{\circ} \cdot 110 6(3)^{\circ}$	115,0(3)°; 142,6(4)°
Ago	102.1(4), 119.0(5)	164.7(5)°; 140.4(5)°
	164.7(4)°; 114.5(3)°	162.2(4)°; 103.3(4)°
Ag4		104.7(4)°; 160.4(5)°
		165.1(5)°; 108.3(4)°

S-Table 1. Tabulated data for the angles observed in Ag(II)-O-O-Ag(II) fragments in $Ag_9(PO_2F_2)_{14}$. The first angle is Ag(II)-O-O referring the Ag(II) atom specified on the left while the second is O-O-Ag(II) angle referring to the silver atom in the top row.

3. Data of the DFT optimized structures of $AgPO_2F_2$ and $Ag_9(PO_2F_2)_{14}$

$AgPO_2F_2 \\$

Unit cell parameters:

 $\begin{array}{ll} a = 11.2610 \ \text{\AA} \\ b = 24.2768 \ \text{\AA} \\ c = 6.19381 \ \text{\AA} \\ \end{array} \begin{array}{ll} \beta = 115.0820^{\circ} \\ V = 1533.6 \ \text{\AA}^{3} \end{array}$

Atomic coordinates:

Ag1	0.08257	0.05998	0.05945
Ag2	0.84107	0.18915	0.63376
P1	0.74819	0.43327	0.19653

P2	0.00000	0.68268	0.25000
РЗ	0.00000	0.18975	0.25000
F1	0.87098	0.47176	0.30400
F2	0.80304	0.38683	0.08747
F3	0.48760	0.14063	0.43166
F4	0.88307	0.23185	0.15200
01	0.64127	0.46297	-0.00867
02	0.72071	0.40897	0.39284
03	0.37446	0.21415	0.13063
04	0.00400	0.15856	0.04386

 $Ag_9(PO_2F_2)_{14}$ Unit cell parameters:

a = 9.90720 Å	
b = 10.18790 Å	$\beta = 105.1132^{\circ}$
c = 24.14700 Å	$V = 2352.94 \text{ Å}^3$

Atomic coordinates:

Ag1	0.33482	0.05145	0.77786
Ag2	-0.06683	3 0.18556	-0.0793
Ag3	0.00000	0.00000	0.50000
Ag4	0.66714	0.21508	0.78264
Ag5	0.25662	0.05158	-0.0852
Ρ1	0.37186	0.78794	0.86580
P2	0.73381	0.64116	0.03776
РЗ	0.23843	0.51874	0.12912
P4	0.63947	0.88752	0.74591
Ρ5	0.58649	0.13642	-0.07853
Рб	-0.00186	0.14992	0.06752
P7	0.00578	0.83385	0.22109
F1	0.35668	0.63782	0.87492
F2	0.53470	0.79641	0.87536
F3	0.63413	0.70141	-0.01754
F4	0.62342	0.59020	0.06800
F5	0.22923	0.36659	0.13509
F6	0.36941	0.52729	0.10463
F7	0.69464	-0.09007	0.69179
F8	0.78036	0.85806	0.79085
F9	0.63048	0.01243	-0.03912
F10	0.59991	0.24217	-0.03077
F11	0.15845	0.11755	0.08735
F12	-0.02320	0.21453	0.12342
F13	-0.00627	0.68469	0.23406
F14	0.05937	0.88751	0.28371
01	0.33288	0.85631	-0.08531
02	0.30358	0.82410	0.80501
03	0.80765	0.52441	0.02241
04	0.81723	0.75127	0.07225
05	0.11025	0.56755	0.08611
06	0.27242	0.57635	0.18829
07	0.57599	0.01161	0.76103
08	0.55555	0.76221	0.73791
09	0.43522	0.12216	0.88839
010	0.68861	0.16228	0.88731
011	-0.07499	0.01770	0.05932
012	-0.02870	0.24743	0.02019
013	0.86679	0.89054	0.19271
014	0.11986	0.85118	0.19022

4. Comparison of Ag-O bond lengths (in Å) in $AgPO_2F_2$ and $Ag_9(PO_2F_2)_{14}$ obtained from Rietveld refinement and DFT optimization.

Red colour indicates Ag-O bonds that had their distances restrained.

AgPO ₂	F ₂				
Ag1	XRDP	DFT	Ag2	XRDP	DFT
01	2.337(15)	2.327	O2	2.437(12)	2.467
O2	2.299(11)	2.468	03	2.313(7)	2.379
O2	2.592(13)	2.529	03	2.389(11)	2.360
O2	2.645(11)	2.531	O4	2.451(15)	2.536
O4	2.478(12)	2.539	O4	2.742(9)	2.534

$Ag_9(PO_2F_2)_{14}$

Ag(l)			Ag(II)		
Ag1	XRDP	DFT	Ag3	XRDP	DFT
O2	2.44(2)	2.449	O3	2.080(11)	2.127
O6	2.517(10)	2.461	05	2.084(11)	2.192
O7	2.63(2)	2.558	O12	2.648(17)	2.648
O8	2.677(15)	2.480			
O9	2.76(2)	2.692	Ag4		
O13	2.435(19)	2.363	02	2.506(19)	2.473
			O6	2.250(10)	2.269
Ag2			07	2.252(13)	2.267
O4	2.515(16)	2.517	08	2.099(13)	2.185
O5	2.66(2)	2.550	O10	2.451(13)	2.538
O10	2.400(18)	2.357	O14	2.103(16)	2.149
011	2.679(17)	2.478			
012	2.41(2)	2.418	Ag5		
O14	2.74(2)	2.617	01	2.099(17)	2.128
			O4	2.094(12)	2.188
			09	2.09(2)	2.154
			O11	2.10(2)	2.172
			O13	2.49(2)	2.631
			F9	3.21(3)	2.991

5. The FT-IR spectra of $AgPO_2F_2$ and $Ag_9(PO_2F_2)_{14}$



S-Figure 3. IR spectra of AgPO₂F₂ and Ag₉(PO₂F₂)₁₄.

References

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