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Single-Crystal Growth and Characterization of Disilver(I) Monofluorophosphate(V), Ag_2PO_3F: Crystal Structure, Thermal Behavior, Vibrational Spectroscopy, and Solid-State ^{19}F, ^{31}P, and ^{109}Ag MAS NMR Spectroscopy

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Single crystals of disilver(I) monofluorophosphate(V), Ag_2PO_3F (**1**), were obtained by slow evaporation of a diluted aqueous Ag_2PO_3F solution. Compound **1** adopts a new structure type and crystallizes in the monoclinic space group $C2/c$ with eight formula units and lattice parameters of $a = 9.2456(8)$ Å, $b = 5.5854(5)$ Å, $c = 14.7840(13)$ Å, and $\beta = 90.178(2)°$. The crystal structure of **1** [$R(F^2 > 2\sigma(F^2)) = 0.0268$, $wR(F^2\ \text{all}) = 0.0665$] is composed of three crystallographically independent Ag^+ cations and PO_3F^{2-} anions as single building units. The oxygen environment around each of the Ag^+ cations is different, with one Ag^+ in distorted octahedral ($\bar{d}$(Ag–O) = 2.553 Å), one in nearly rectangular ($\bar{d}$(Ag–O) = 2.445 Å), and one in distorted tetrahedral ($\bar{d}$(Ag–O) = 2.399 Å) coordination. Additional Ag–F contacts to more remote F atoms located at distances >2.80 Å augment the coordination polyhedra for the two latter Ag^+ cations. The monofluorophosphate anion deviates slightly from C_{3v} symmetry and exhibits the characteristic differences in bond lengths, with a mean of 1.510 Å for the P–O bonds and one considerably longer P–F bond of 1.575(2) Å. Compound **1** was further characterized by vibrational spectroscopy (Raman and IR) and solid-state ^{19}F, ^{31}P, and ^{109}Ag MAS NMR spectroscopy. The value for the isotropic one-bond P–F coupling constant in **1** is $^1J_{PF} = -1045$ Hz. Thermal analysis (TG, DSC) revealed a reversible phase transition at 308 °C, which is very close to the decomposition range of **1**. Under release of POF_3, $Ag_4P_2O_7$ and Ag_3PO_4 are the thermal decomposition products at temperatures above 450 °C.