Vibrational spectra of the layered monofluorophosphate (V), NH₄Ag₃(PO₃F)₂

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The powder Fourier-transform (FT) infrared (IR) and Raman spectra of the recently characterized $NH_4Ag_3(PO_3F)_2$ were recorded and are discussed with a site-symmetry analysis based on its known structural data. Some comparisons are made with the solution spectra of the PO_3F^{2-} anion and with those of crystalline Ag_2PO_3F. Copyright © 2009 John Wiley & Sons, Ltd.

Introduction

Monofluorophosphoric acid, H_2PO_3F, can be obtained by the reaction of metaphosphoric acid with anhydrous hydrogen fluoride, and an important number of its salts have been isolated and characterized.[1] Preparation methods of these salts include flux reactions in fluoride melts, solid-state reactions between corresponding metal fluorides and phosphates, or conversion of the readily soluble $(NH_4)_2PO_3F$ or Na_2PO_3F with metal salts in aqueous solution, a process usually employed for the preparation of insoluble fluorophosphates. Water-soluble salts are appropriately obtained by metathesis reaction of Ag_2PO_3F with corresponding metal chlorides.[1,2]

Although the synthesis of Ag_2PO_3F has been already described,[2] its crystal structure was unknown until very recently.[3] During the experiments performed to grow Ag_2PO_3F single crystals from aqueous $AgNO_3$ and $(NH_4)_2PO_3F$ solutions, the generation of another, unknown, phase was established. Crystals of the new compound, finally identified as $NH_4Ag_3(PO_3F)_2$, could be obtained and its structure was eventually determined by single-crystal x-ray diffractometry after adjusting the experimental conditions.[4] To complement the characterization of this interesting new fluorophosphate, we have now performed an analysis of its vibrational spectra.

Experimental

The starting material for the synthesis was $(NH_4)_2PO_3F$, prepared according to the method of Schülke and Kayser.[5] This compound (0.17 g) was added to a 10-ml aqueous solution of 0.43-g $AgNO_3$. Because phosphate anions were present in the solution, owing to the hydrolysis of the monofluorophosphate anion, the precipitated yellow Ag_3PO_4 was rapidly filtered off, and the remaining clear solution was allowed to stand in a dark room for 2 days. Besides minor amounts of plate-like crystals of Ag_2PO_3F, crystals of $NH_4Ag_3(PO_3F)_2$ presenting a block-like habit were obtained and separated mechanically under a microscope.[4]

The infrared (IR) spectra were recorded as Nujol mulls between KBr plates in the spectral range between 4000 and 400 cm⁻¹ employing a Bruker-EQUINOX-55 FTIR-instrument. The spectra had to be recorded immediately after sample preparation, as the mulls were relatively unstable and a dark coloration appeared after a few minutes. Black coloration and rapid changes in band positions and intensities with time were also observed using KBr disks in the usual way. This is a well-known behavior for silver salts which originate from interchange processes that occur in the alkali halide matrix.[6] Raman spectra in the same spectral range were measured on powdered samples using the FRA 106 Raman accessory of an IF66 Bruker spectrophotometer. Radiation from an Nd : YAG solid-state laser (1064 nm) was used for excitation. The spectral resolution was ±4 cm⁻¹ in both measurements.

Results and Discussion

Structure of the compound

The new double monofluorophosphate salt, $NH_4Ag_3(PO_3F)_2$, crystallizes in the monoclinic crystal system with $Z = 8$. To emphasize its pseudo-orthorhombic structure, with the unit cell angle β very close to 90°, the structure was refined in the nonstandard setting $I2$ for space group No. 5 (standard setting $C2$).[4] It presents an interesting layered structure, built up by silver monofluorophosphate sheets $[Ag_3(PO_3F)_2]^-$ that extend parallel to (100). The F atoms of the PO_3F^{2-} units point toward the empty space of the structure where the interjacent NH_4^+ cations are located. These cations stabilize the structure by moderate $N-H\cdots O$ and $N\cdots F$ hydrogen bonds.[4]

Vibrational spectra

On the basis of the known structural characteristics, it is possible to perform an analysis pf the vibrational spectroscopic behavior of the PO_3F^{2-} anion present in the $NH_4Ag_3(PO_3F)_2$ lattice. The obtained IR and Raman spectra, shown in Fig. 1, are rather simple presenting only a reduced number of bands, without clear signs

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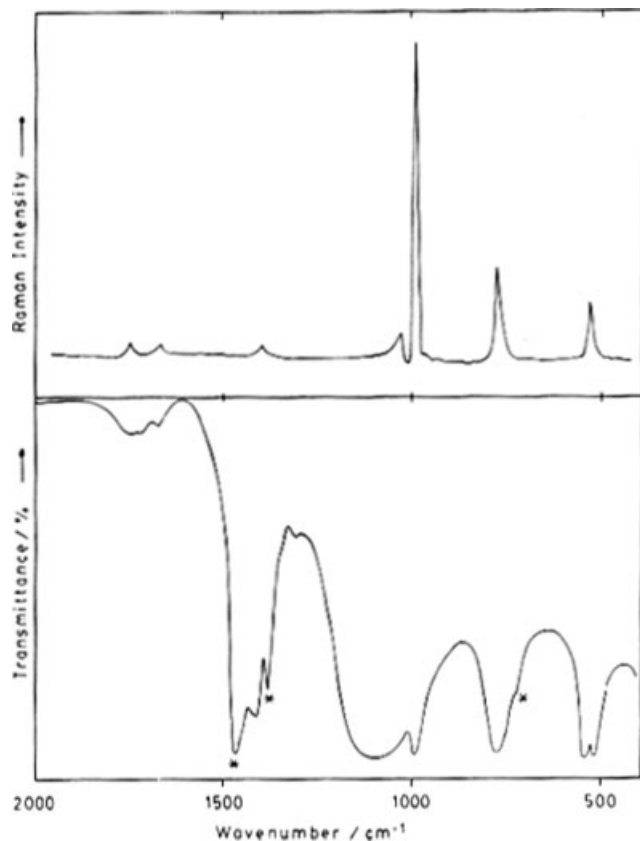
Figure 1. FT-Raman spectrum (a) and FTIR spectrum of $NH_4Ag_3(PO_3F)_2$ (b) in the spectral range 2000–400 cm^{-1} (asterisks indicate Nujol bands).

Table 1. Site-symmetry analysis of the PO_3F^{2-} vibrations in the $NH_4Ag_3(PO_3F)_2$ lattice

	Vibrational mode	Free anion (C_{3v})	Site symmetry (C_1)
ν_1	$\nu(P-F)$	A_1	A
ν_2	$\nu_s(PO_3)$	A_1	A
ν_3	$\delta(FPO_3)$	A_1	A
ν_4	$\nu_{as}(PO_3)$	E	$2A$
ν_5	$\delta(PO_3)$	E	$2A$
ν_6	$\rho(PO_3)$	E	$2A$

Activity: A_1; E, IR and Raman; A, IR and Raman.

of splitting and suggesting that correlation field effects may be neglected. Therefore, it seems sufficient to analyze these spectra on the basis of the simple site-symmetry approximation, correlating the symmetry of the 'free' PO_3F^{2-} anion (C_{3v}) with that of its site symmetry (C_1), as shown in Table 1.[7–9] 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 activities.

The proposed assignments are presented in Table 2 and are briefly commented as follows:

- Regarding the $\nu(PO_3)$ vibrations, the antisymmetric mode is only seen as a very weak Raman band, whereas in the IR spectrum it is very strong and broad, presenting a shoulder on the lower energy side of the main band, in agreement

Table 2. Wavenumbers (in cm^{-1}) and assignment of the vibrational spectra of crystalline $NH_4Ag_3(PO_3F)_2$[a]

Infrared	Raman	Assignment
1745/1717 w	1747 vw	$\nu_4 + \nu_6$ (NH_4^+), see text
1669 vw	1667 vw	$\delta_s(NH_4^+)$
1410 s	1405 vw	$\delta_{as}(NH_4^+)$
1108 vs, 1085 sh	1040 w	$\nu_4, \nu_{as}(PO_3)$
991 s	997 vs	$\nu_2, \nu_s(PO_3)$
776 vs	776 s	$\nu_1, \nu(P-F)$
542 vs, 516 vs	540 m	$\nu_5, \delta(PO_3)$
–	380 vw	$\nu_6, \rho(PO_3)$

[a] s, strong; w, weak; sh, shoulder; v, very.

with the splitting predicted by the site-symmetry analysis. The corresponding symmetric stretching vibration is the strongest Raman band and is also relatively strong in the IR spectrum.

- The $\nu(P-F)$ vibration can be clearly identified in both spectra, lying at the same energy in both of them, and at somewhat lower energy than that observed in the solution Raman spectrum (795 cm^{-1}).[10]

- For the deformational modes only $\delta(PO_3)$ could be identified, clearly split as predicted (cf Table 1), whereas no signals for the $\delta(FPO_3)$ mode could be found. In the Raman spectrum of a PO_3F^{2-} solution, both vibrations are reported at the same wavenumber (520 cm^{-1}),[10] although in the case of crystalline Hg_2PO_3F, both vibrations were identified at slightly different wavenumbers, with $\nu_5 > \nu_3$.[11]

- The corresponding ν_6-PO_3 rocking mode was only identified in the Raman spectrum, as a very weak band.

- A comparison of corresponding IR and Raman bands shows only slight energy differences. These differences are considered as a valuable criterion for the evaluation of the strength of coupling effects in the unit cell[12,13] and confirm, additionally, that these effects are relatively weak in the present case.

- The spectroscopic behavior of the NH_4^+ vibrations can usually be correlated with the structural behavior of this moiety in the crystal lattice.[14–16] Unfortunately, in the present case, it was not possible to analyze the behavior of all the NH_4^+ vibrations in detail, as they are partially overlapped by strong bands originating from the Nujol matrix. Only the position of the antisymmetric deformational mode, $\nu_4(NH_4^+)$, could be identified with certainty, whereas the corresponding symmetric mode is seen only as a very weak IR signal. Besides, close to this last-mentioned vibration, the IR spectrum shows another weak doublet located at 1745/1717 cm^{-1} which can be assigned to a combinational mode involving ν_4 and an external (lattice) mode located at about 340 cm^{-1} ($\nu_4 + \nu_6$ in Waddington's nomenclature[14]). The activation of this combination may be regarded as a proof that the NH_4^+ cation does not rotate freely in the lattice.[14–16]

Finally, a comparison with the spectroscopic behavior of the simple silver monofluorophosphate, Ag_2PO_3F, also seems interesting. The P–O stretching vibrations are found at somewhat higher energies in the present case, whereas the $\nu(P-F)$ vibration is found at lower energy. These findings are in a good agreement with the structural peculiarities of both compounds, as the average P–O bond distance in $NH_4Ag_3(PO_3F)_2$ (1.507 Å) is somewhat shorter than in Ag_2PO_3F (1.510 Å), whereas the reverse situation is found

for the P−F bonds (1.590 Å in $NH_4Ag_3(PO_3F)_2$ and 1,575 Å in Ag_2PO_3F). The lengthening of this bond in $NH_4Ag_3(PO_3F)_2$ must surely be related to the participation of the F atoms in the formation of hydrogen bonds with the NH_4^+ cations, as mentioned above.

Acknowledgements

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