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Compounds Containing Layers of Composition [($Sb^{III}F$)XO_4] (X = P, As). Crystal Structures of $Na(SbF)PO_4 \cdot 1.5H_2O$, $Na(SbF)AsO_4$, $NH_4(SbF)PO_4 \cdot H_2O$, and $NH_4(SbF)AsO_4 \cdot 3H_2O$

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The title compounds have been prepared in water by reaction of SbF_3 with dihydrogen phosphates or arsenates and characterized by single crystal X-ray work, IR, Raman, and Mössbauer spectroscopy. They have identical layer structures. Layers of composition $[(SbF)XO_4]^-$ (X = P, As) were formed by sharing four corners between XO_4 tetrahedra and $SbFO_4$ pseudooctahedra. The lengths of the terminal Sb–F bond (with the lone pair in a *trans*-position) and the Sb–O bonds are 192 and 219 pm, respectively. The stacking of the layers and the interlayer distance depend on the cations and the number of intercalated water molecules. In $Na(SbF)AsO_4$ the Na^+ ion is coordinated by only two oxygen atoms within 300 pm. Crystal data: $Na(SbF)PO_4 \cdot 5H_2O$, monoclinic, $P2_1/m$, $a = 656.2(5)$, $b = 654.1(5)$, $c = 867.9(3)$ pm, $\beta = 92.43(1)°$, 889 reflections, 81 parameters, $R = 0.044$, $R_w = 0.046$. $NH_4(SbF)PO_4 \cdot H_2O$, tetragonal, $I4/m$, $a = 656.6(3)$, $c = 1439.8(5)$ pm, 680 reflections, 31 parameters, $R = 0.023$, $R_w = 0.021$. $Na(SbF)AsO_4$, tetragonal, $P4/ncc$, $a = 671.8(1)$, $c = 1756.4(4)$ pm, 1056 reflections, 28 parameters, $R = 0.052$, $R_w = 0.065$. $NH_4(SbF)AsO_4 \cdot 3H_2O$, tetragonal, $P4/ncc$, $a = 683.8(2)$, $c = 1873.0(7)$ pm, 1194 reflections, 30 parameters, $R = 0.042$, $R_w = 0.050$.

Introduction

SbF_3 is a strong Lewis acid and forms addition compounds with many metal fluorides, sulfates, and nitrates. Their structures have been intensively discussed with respect to the stereochemical activity of the lone pair of Sb(III) (*1–6*). In reactions with hydrogen and dihydrogen phosphates compounds with the formula $M^I(SbF_2)HPO_4$, or $M^I(SbF)PO_4$ (M^I = Na, K, NH_4) are formed, depending on the reaction conditions. Reactions with hydrogen and dihydrogen arsenates yield similar products. The compounds $M^I(SbF_2)HXO_4$ with X = P, As and M^I = K, NH_4 show complicated layer structures with pentacoordinated Sb(III) atoms (*4, 5*). In this paper we report the closely related structures of a series of compounds containing the hitherto unknown SbF^{2+} unit. A short communication of part of this work has already been published (*6*).

Experimental

Preparation of the Compounds

All preparations were performed in PVC or Teflon vessels.

The following instruments were used in this work: IR, Perkin-Elmer 457 infrared spectrometer and Bruker IFS 113 FTIR-

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spectrometer; Raman spectra, Coderg T-800 spectrometer, Ar^+ laser (514.5 nm); X-ray crystallography, Syntex $P2_1$ or Siemens $R3m/V$ diffractometer (MoK_α radiation, λ = 0.71073 Å; graphite monochromator).

$Na(SbF)PO_4 \cdot 1.5H_2O$ and $NH_4(SbF)PO_4 \cdot H_2O$. To a stirred saturated aqueous solution of SbF_3 was added a concentrated solution of $M^1H_2PO_4$ (M^1 = Na, NH_4) in the molar ratio 1 : 2. The solution was warmed up to 40–50°C and the precipitate immediately formed was filtered off. After cooling to room temperature the products crystallized as very thin plates. Larger crystals for structural work were obtained within 2 days.

$Na(SbF)AsO_4$. To a stirred saturated solution of SbF_3 was added a saturated solution of Na_2HAsO_4 in the molar ratio 1 : 1. After heating up to 60°C for 1–2 min the precipitate formed was filtered off. The product crystallizes within 3–4 hr from the filtrate.

$NH_4(SbF)AsO_4 \cdot 3H_2O$. To a 6 *M* SbF_3 solution was added a 3 *M* $(NH_4)_2HAsO_4$ solution. A microcrystalline product precipitated. It changed within a few hours to small platelet like crystals. Crystals of X-ray quality were obtained by recrystallization in a temperature gradient (7), using mother liquor as solvent.

$Ag(SbF)PO_4$. Freshly precipitated Ag_3PO_4 was dissolved as AgH_2PO_4 in the stoichometric amount of H_3PO_4 (85%). To this solution was added a saturated solution of SbF_3 in the molar ratio 1 : 1. Within several hours $Ag(SbF)PO_4$ crystallized from the viscous solution as microcrystalline product.

Analyses. Sb was analyzed volumetrically with BrO_3^-, P, or As as 12-molybdatophosphate(arsenate), F potentiometrically by using an ion-sensitive electrode (Orion Model 407 ion analyser), N with the Kjeldahl method, and Na by flame photometry. All compounds gave satisfactory elemental analyses.

Structural Determinations

Crystal data and details of data collection are summarized in Table I. Crystal quality, unit cells, and systematic extinctions were checked by using rotation and Weissenberg photography. An improved empirical absorption correction (fitting of azimuthal data to a thin plate, program XEMP of SHELXTL) was applied to all data sets but $Na(SbF)PO_4 \cdot 1.5H_2O$, where only the usual empirical correction was applied. No variations were observed for the intensity check reflections. The structures were solved by Patterson methods and refined by standard least squares methods by using the SHELXTL and SHELXTL PLUS program systems. Nonhydrogen atoms were refined with anisotropic thermal parameters; for $NH_4(SbF)PO_4 \cdot H_2O$ hydrogen atoms were located in difference maps and refined isotropically. The weighting scheme $w^{-1} = \sigma(F_0) + (g \cdot F_0)^2$ was used throughout (for *g* see Table I). In two cases an extinction parameter *x* was refined ($F' = F_c/1.0 + 0.002 \cdot x \cdot F_c^2/\sin 2\theta)0.25$. Tables II and III contain the final parameters. Some special features of the structure solutions are outlined below.

$Na(SbF)PO_4 \cdot 1.5H_2O$. Refinement in space group $P2_1$ yielded $R = 0.046$, but the tetrahedral PO_4^{3-} group was unreasonably distorted with OPO angles ranging from 89 to 136°. A disordered structure model was then chosen with Sb and P on the mirror plane of space group $P2_1/m$ and the remaining atoms half-filling the general positions. The refinement converged rapidly to R = 0.044.

$NH_4(SbF)PO_4 \cdot H_2O$. Refinement in space group $I\bar{4}$ was tried first, yielding R = 0.025 with 46 parameters; but many parameters were strongly correlated. The correct space group was found to be $I4/m$.

TABLE I

CRYSTAL DATA AND DATA COLLECTION

	$Na[SbF]PO_4 \cdot 1.5H_2O$	$NH_4[SbF]PO_4 \cdot H_2O$	$Na[SbF]AsO_4$	$NH_4[SbF]AsO_4 \cdot 3H_2O$
Lattice type	Monoclinic	Tetragonal	Tetragonal	Tetragonal
Space group	$P2_1/m$	$I4/m$	$P4/ncc$	$P4/ncc$
a(pm)	656.2(5)	656.6(3)	671.8(1)	683.8(2)
b(pm)	654.1(5)			
c(pm)	867.9(3)	1439.8(5)	1756.4(4)	1873.0(7)
β(deg)	92.43(1)			
$V(pm^3 10^6)$	372.2	620.7	792.7	876.3
X	2	4	4	4
$d_{obs.}(d_{cal.})(g \cdot cm^{-3})$	(2.55)	2.87(2.91)	2.48(2.54)	2.66(2.67)
Crystal dimensions, (mm)	0.40 · 0.30 · 0.15	0.35 · 0.35 · 0.10	0.38 · 0.36 · 0.05	0.40 · 0.40 · 0.13
Abs.coeff.$(MoK_\alpha)(mm^{-1})$	4.02	4.71	7.64	6.92
Temperature (K)	298	298	200	140
Scan type	$\theta/2\theta$	$\theta/2\theta$	$\theta/2\theta$	$\theta/2\theta$
Range, 2θ(deg)	4-54	4-54	4-54	4-54
Data collected	965($+h$, $+k$, $+l$)	680($+h$, $+k$, $+l$)	1056($+h$, $+k$, $+l$)	1194($+h$, $+k$, $+l$)
Unique data	959	354	443	475
$R_{int.}$	—	0.042	0.072	0.050
Observed data ($I > 2\sigma(I)$)	889	343	380	434
No. of variables	81	31	28	30
g in weighting scheme	0.02	0.014	0.02	0.016
Extinction parameter	—	—	0.0008(3)	0.0031(4)
$R(R_w)$	0.044(0.046)	0.023(0.021)	0.052(0.065)	0.042(0.050)
Residual electron density in final map($e \cdot pm^{-3} \times 10^{-6}$)	3.8; - 2.0	0.6; - 1.5	2.4; - 1.0	1.4; - 2.0

TABLE II

ATOMIC PARAMETERS OF $NH_4(SbF)PO_4 \cdot H_2O$ (FIRST LINE), $Na(SbF)AsO_4$ (SECOND LINE) AND $NH_4(SbF)AsO_4 \cdot 3H_2O$ (THIRD LINE)

Atom	Site	$x \times 10^4$	$y \times 10^4$	$z \times 10^4$	$U_{eq} \times 10^3$
Sb	4e	0000	0000	7782.9(3)	118(1)
	4c	2500	2500	0307.3(6)	131(4)
	4c	2500	2500	0297.1(3)	92(2)
P/As	4d	0000	5000	2500	127(4)
	4b	7500	2500	0000	140(5)
	4b	7500	2500	0000	87(3)
F	4e	0000	0000	9119(3)	186(9)
	4c	2500	2500	1406(6)	192(22)
	4c	2500	2500	1325(3)	150(13)
O	16i	1809(4)	4430(4)	3128(2)	190(7)
	16g	1838(10)	-0603(9)	0571(3)	193(16)
	16g	1986(5)	-0591(5)	0542(2)	145(8)
Na/N/O	16i	6469(9)	7746(9)	0000	363(16)
	16g[a]	6100(60)	0335(41)	1854(6)	908(123)
	16g	6357(6)	0151(5)	1825(2)	291(12)

[a] Site occupation factor 0.25.

TABLE III

ATOMIC PARAMETERS OF $Na[SbF]PO_4 \cdot 1.5H_2O$

	$x \times 10^4$	$y \times 10^4$	$z \times 10^4$	$U_{eq} \times 10^2$
Sb	2573(1)	2500	518(1)	7(1)
P	2454(3)	7500	0(3)	8(1)
O(1)	5824(11)	3149(12)	1071(9)	14(2)
O(2)	9419(10)	3096(11)	1032(8)	11(2)
O(3)	8057(15)	666(11)	8944(9)	12(2)
O(4)	6861(13)	766(12)	8928(8)	10(2)
F	2741(6)	2500	2748(5)	8(28)
O(5)	8909(12)	5386(14)	3636(7)	71(3)
O(6)	4869(16)	7122(63)	3892(10)	52(12)
Na	5842(9)	4191(11)	3633(6)	36(2)

Note. Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

$NH_4(SbF)AsO_4 \cdot 3H_2O$ and $Na(SbF)AsO_4$. These crystallize in space group *P4/ncc*. In the former compound four NH_4^+ ions and twelve H_2O molecules occupy together a sixteenfold site (16g); in the latter compound 4 Na^+ ions are statistically distributed over this site.

Results and Discussion

All four compounds crystallize in highly symmetrical and, considering the individual layers, identical structures. In three dimensions the structures differ in the stacking of the layers and/or in the interlayer distances. One layer consists of a net of corner-shared $:SbFO_4$ pseudooctahedra and XO_4 (X = P, As) tetrahedra (see Fig. 1) with the oxygen atoms of the XO_4^{3-} ions connected to four different SbF^{2+} units. So puckered layers of tetragonal symmetry are formed, in which the Sb–F bonds show alternatively up and down. The lone pair at Sb(III) is stereochemically active and in a *trans*-position to the Sb–F bond. Similar structures are formed by $VOPO_4 \cdot 2H_2O$ and $NbOPO_4 \cdot 3H_2O$, which gained recent interest as host compounds in intercalation reactions (*8*). $Na(SbF)AsO_4$ and $NH_4(SbF)AsO_4 \cdot 3H_2O$ are isotypic and crystallize in the tetragonal space group *P4/ncc*.

$NH_4(SbF)PO_4 \cdot H_2O$, space group *I4/m*, forms a body-centered structure. $Na(SbF)PO_4 \cdot 1.5H_2O$ crystallizes monoclinic in a disordered structure. The identity periods within the layers are between 656 and 684 pm for all four compounds. In the *c* direction, the identity periods depend on the cations involved and the mode of stacking.

Tables IV and V list some relevant bond distances and angles in these structures. As can be seen, the individual bond distances vary little. The single Sb–F distance, in the range 192–193 pm, is rather short and close to the (mean) Sb–F distance in SbF_3 (192 pm) (*9*). The mean Sb–O distance is 219 pm and again comparatively short. Besides the five primary bonds no secondary interactions can occur due to the unique structure. The bond strength of the dative Sb–O bonds approaches the strength of Sb–O single bonds, because the SbF^{2+} group acts as a very strong Lewis acid. The $SbFO_4$ poly-

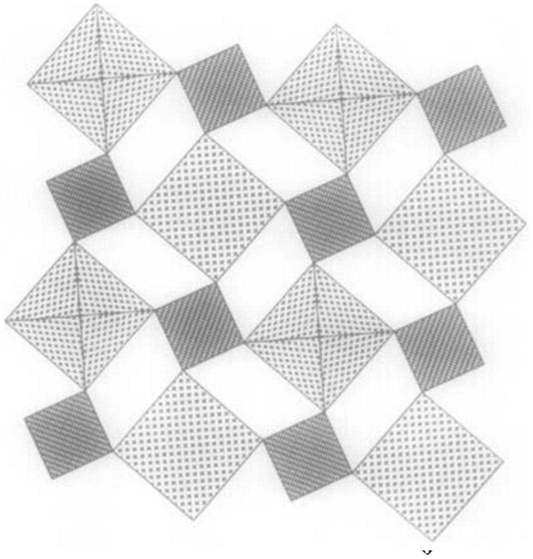

FIG. 1. Top view of a layer consisting of cornerlinked $SbFO_4$ pseudooctahedra and XO_4 tetrahedra.

TABLE IV

SELECTED BOND DISTANCES (PM) AND ANGLES (DEG)

	$NH_4(SbF)PO_4 \cdot H_2O$	$Na(SbF)AsO_4$	$NH_4(SbF)AsO_4 \cdot 3H_2O$	
Sb–F	192.4(5)	193.0(10)	192.5(6)	
Sb–O	218.5(3)	218.1(6)	219.2(3)	
X–O	153.9(3)	168.2(6)	169.1(3)	
Na–O	—	249.2(16)	—	
Na–F	—	293.0(36)	—	
N/O . . . O	292.2(4)	—	276.2(5)	
N/O . . . N/O	289.3(5)	—	276.2(5)	
			278.4(7)	
			279.3(5)	
O–X–O	108.0(2)	106.8(4)	106.2(2)	2×
F–Sb–O	110.2(1)	110.8(2)	111.1(1)	4×
	76.9(1)	77.7(1)	77.9(1)	
O–Sb–O	87.0(0)	87.4(1)	87.5(0)	4×
	153.7(2)	155.5(3)	155.9(2)	2×
X–O–Sb	124.4(2)	122.9(3)	125.9(2)	

hedra are distorted due to the stereochemical activity of the lone pair. All bonds are on the same side of the central atom (see Fig. 2). The F–Sb–O angles are in the range 77–78°, the O–Sb–O angles of adjacent bonds in the range 87–88°. The PO_4^{3-} and AsO_4^{3-} tetrahedra are slightly distorted. The P–O bond length is intermediate between the terminal (150 pm) and the bridging (161 pm) P–O distances in the $P_3O_{10}^{5-}$ ion (*10*).

The individual features of the compounds in this study can be described as follows: In $Na(SbF)PO_4 \cdot 1.5H_2O$ the interlayer distance (876.9 pm) is identical with the c-axis length. The structure is disordered with respect to the layer sequence. Two types of layers, formally created by a mirror plane through Sb, P, and F are stacked along c in a statistical sequence, yielding the overall diffraction symmetry $P2_1/m$. Due to the lack of strong periodicity all reflections along (001) are diffuse. The sodium ions and one third of the H_2O molecules occupy half-filled fourfold positions. Na^+ is surrounded within 260 pm by six oxygen atoms.

TABLE V

BOND DISTANCES (PM) AND BOND ANGLES IN $Na(SbF)PO_4 \cdot 1.5H_2O$

Sb–O(1)	220.8(7)	P–O(1)	155.2(8)
Sb–O(2)	217.1(7)	P–O(2)	154.0(7)
Sb–O(3)	216.6(8)	P–O(3)	155.5(8)
Sb–O(4)	221.8(8)	P–O(4)	152.3(8)
Sb–F	193.4(4)	Na–F	241.3(7)
Na–O(1)	232.5(9)	Na–O(6)	203.6(40)
Na–O(5)	215.9(10)		237.8(18)
			250.8(41)
			259.8(24)
O–P–O	106.2(4)–112.0(4), mean 109.5		
F–Sb–O	76.6(2)– 79.0(2)		
P–O–Sb	122.6(4)–125.4(4), mean 123.8		

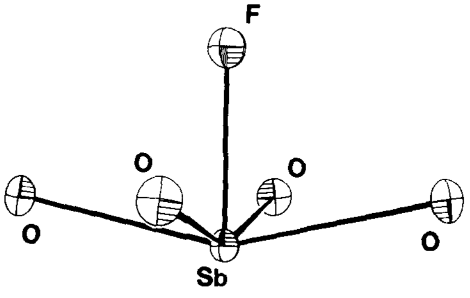

FIG. 2. Coordination of Sb(III).

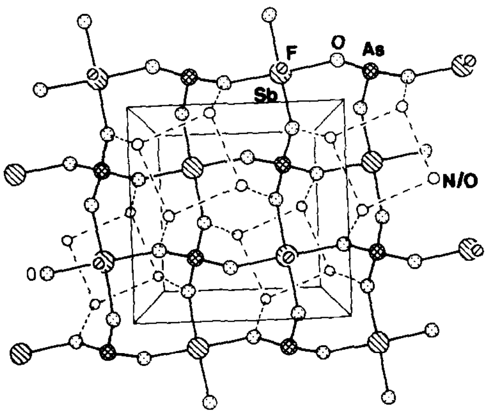

FIG. 3. Projection of the structure of $NH_4(SbF)AsO_4$ $3H_2O$ along *c*. In $Na(SbF)AsO_4$ N/O sites are partially occupied by Na.

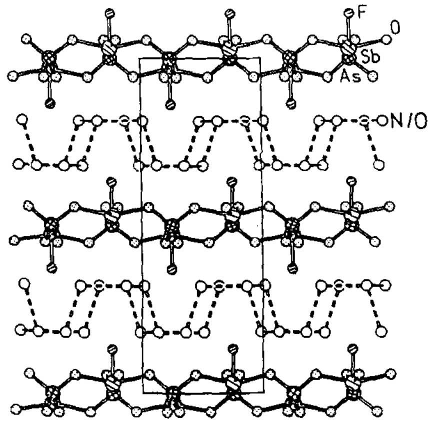

FIG. 4. Projection of the structure of $NH_4(SbF)AsO_4$ $3H_2O$ along *a*. H-bonds within the $NH_4^+(H_2O)_3$ units are shown as dashed lines. In $Na(SbF)AsO_4$ one quarter of the N/O sites is statistically occupied by Na.

The two arsenates $Na(SbF)AsO_4$ and $NH_4(SbF)AsO_4 \cdot 3H_2O$ (see Figs. 3 and 4) are isostructural. Sb and F are situated on 4-fold axes of the space group, As on a $\bar{4}$ site. In $NH_4(SbF)AsO_4 \cdot 3H_2O$ four NH_4^+ and twelve H_2O molecules occupy together a 16-fold general site. As an interesting feature of the structure, one NH_4^+ ion and three H_2O molecules form squares via hydrogen bonds; further hydrogen bonds connect these squares with four oxygen atoms in the layer above and with four other $NH_4^+(H_2O)_3$ units below. So each N/O position is involved in four hydrogen bonds with N/O . . . N/O distances from 276 to 279 pm; 10 hydrogen atoms are necessary to build up this framework, as much as are available.

In $Na(SbF)AsO_4$ for Na^+ ions are distributed over a 16-fold site. The coordination number of Na^+ is very low. Within a distance of 300 pm only one fluorine (at 293 pm) and one oxygen atom (at 249 pm) are located. The Na^+ ions are very probably highly mobile as indicated by the large anisotropy of the thermal parameters. So $Na(SbF)AsO_4$ is expected to be an ionic conductor. Along *c* the layers are stacked with the Sb (and P) on top of each other, the Sb–F vectors being in the same directions. The identity period is twice this distance, because neighboring layers differ in the positions of the bridging oxygen atoms. Due to the lack of hydrogen bonds, the layers in $Na(SbF)AsO_4$ are packed more densely and are slightly less expanded (see Table I).

A different stacking of the layers and also a different hydrogen bond network is ob-

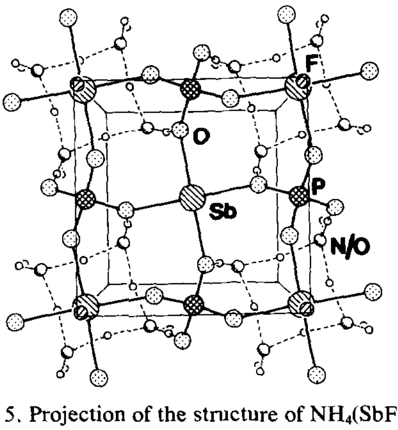

FIG. 5. Projection of the structure of $NH_4(SbF)PO_4 \cdot H_2O$ along *c*. Hydrogen bond network.

served for $NH_4(SbF)PO_4 \cdot H_2O$ (see Fig. 5). Sb and P again occopy sites of symmetry 4 and $\bar{4}$, respectively. Due to the centering of the unit cell, the Sb–F vectors in neighboring layers oppose each other directly, giving a very short nonbonding F . . . F distance of 253.6 pm. Four NH_4^+ ions and four H_2O molecules occupy together an eightfold site on the mirror plane of the space group. They form squares through hydrogen bonds. Further hydrogen bonds connect these squares up and down to oxygen atoms within the layers. Again each N/O position is involved in four hydrogen bonds with N/O . . . N/O distances from 289 to 292 pm. Twelve hydrogen atoms, as much as are available, are necessary for this network. In $NH_4(SbF)PO_4 \cdot H_2O$ the number of ions or molecules between the layers is one half the number in $NH_4(SbF)AsO_4 \cdot 3H_2O$. Consequently, the interlayer distance is much smaller in the former compound. Both structures are symmetry related. Their respective space groups, $I4/m$ and $P4/ncc$, are subgroups of space group $I4/mcm$. Driving force for the differentiation in individual structures may be the smaller overall volume of the PO_4^{3-} ion compared to the AsO_4^{3-} ion.

Infrared and Raman Spectra

The wavenumbers of the vibrational spectra in the range 1100–300 cm^{-1} are collected in Table VI. The spectra look very similar due to the close structural relationship of the compounds. On the basis of the spectra of PO_4^{3-} and AsO_4^{3-} the assignment is straightforward. According to group theoretical considerations, one expects for $\nu_1 XO_4$ one Ra-active mode only, and for $\nu_3 XO_4$ two IR-active and two Ra-active modes. All modes but the second Raman mode of $\nu_3 XO_4$ are observed. This mode may be weak or accidently degenerate with $\nu_1 XO_4$. A band, observed for all compounds at 540–560 cm^{-1}, is assigned to νSb–F; it is shifted to higher energy by approximately 60 cm^{-1} compared to SbF_3. The remaining bands have to be assigned to deformation frequencies of the XO_4 groups and Sb–O stretching vibrations.

Mössbauer Spectra

Table VII contains the Mössbauer parameters of the compounds under discussion and of some related compounds. The observed values are correlated with the Sb(III) coordination (*11*), the presence of hydrogen bonds (*12*), and the electronegativity of the ligands (*13*). The highest isomer shifts are observed for compounds with symmetrical AX_5E coordination. This enables a stronger participation of the *s* obital of Sb(III) in the bonding (*14*), with a maximum in K_2SbF_5 due to the number of most electronegative ligands. A second factor for

TABLE VI

VIBRATIONAL SPECTRA

$Na[SbF]PO_4 \cdot 1.5H_2O$		$NH_4[SbF]PO_4 \cdot H_2O$		$Ag[SbF]PO_4$		$Na[SbF]AsO_4$		$NH_4[SbF]AsO_4 \cdot 3H_2O$		
IR	Ra	IR	Ra	IR	Ra	IR	Ra	IR	Ra	
1060 s,sh		1050 s,sh		1063 s		859 s,sh		860 s		ν_3 XO_4
1008 vs	1004 vs	1008 vs	1008 vs	988 vs	1011 vs	815 vs	812 vs	807 vs	814 vs	ν_3 XO_4
	958 s		955 vs		955 vs		840 vs		848 vs	ν_1 XO_4
645 m	640 w	646 m	605 vs		647 m		445 w		445 w	ν_4 XO_4
555 s	540 vs	552 s	560 m		545 s	552 s	540 s	565 m	560 m	ν Sb-F
450 m	480 w	450 w	489 s		450 w	375 vs	390 w	385 s	384 w	ν_2, ν_4 XO_4
	420 w		410 w		420 w	325 w		325 w		ν Sb-O

TABLE VII

MÖSSBAUER PARAMETERS

Compound	δ(mm/sec)	eQV_{zz}(mm/sec)	Sb-coordination	Refs.
$Na(SbF)PO_4 \cdot 1.5H_2O$	−5.8	14.4	AX_5E	This work
$NH_4(SbF)PO_4 \cdot H_2O$	−4.9	18.0 (?)	AX_5E	This work
$Na(SbF)AsO_4$	−4.5	14.4	AX_5E	This work
$NH_4(SbF)AsO_4 \cdot 3H_2O$	−5.1	16.0	AX_5E	This work
$K(SbF_2)HPO_4$	−5.2	18.4	AX_5E distorted	(*15*)
$K(SbF_2)HAsO_4$	−5.8	15.8	AX_5E distorted	(*15*)
$NH_4(SbF_2)HAsO_4$	−5.3	17.7	AX_5E distorted	(*15*)
K_2SbF_5	−4.1	14.3	AX_5E	(*16*)
SbF_3	−6.3	19.1	AX_6E	(*16*)

this observation is the increased shielding of the *s* electrons from the nuclear charge by the presence of at least four primary bonds. Hydrogen bonds generally induce larger isomer shifts (*12*). The quadruple coupling constant depends on the homogeneity of the ligand field at the nucleus. Therefore, this value is generally larger in compounds with SbF^{2+} groups than in compounds with a more symmetrical coordination of Sb. Hydrogen bonds tend to increase this value as well.

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