Study of isomorphism in fluorine-containing antimony(III) complexes

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The mutual influence of the atoms on the composition of solid fluorine-containing antimony(III) complexes formed in aqueous solutions in the $(MF)_x$—$(M'F)_{n-x}$—SbF_3 (M, M′ = Na, K, Rb, Cs, and NH_4; $n = 1, 2$; $x = 0$ to 2), $(KNO_2)_n$—$(KY)_n$—SbF_3 (Y = F, Cl, SO_4; $n = 0.5, 1$), and K_2SbF_5—K_2SbCl_5 systems was investigated by elemental, X-ray, and thermogravimetric analyses and by IR and ^{121,123}Sb NQR spectroscopy. The isomorphism conditions for fluorine-containing antimony(III) compounds resulting in the formation of complexes $NaM'SbF_5 \cdot 1.5H_2O$ (M′ = K and Rb), $K_2SbF_5 \cdot 1.5H_2O$, $NaCs_3Sb_4F_{16} \cdot H_2O$, $KSbF_3Cl$, $K_2SbF_2Cl_3$ with constant compositions, continuous $M_xM'_{2-x}SbF_5$ ($0 < x < 2$) and limited $M_xM'_{1-x}SbF_4$ ($0.25 < x < 0.75$; M, M′ = K, Rb, Cs, and NH_4) solid solutions or LiF+$MSbF_4$ (M = Na, K, Rb, and Cs), M_2SbF_5+Cs_2SbF_5 (M = Na and K) and $MSbF_4$+$NaSbF_4$ (M = Rb and NH_4) mechanical mixtures were determined.

Key words: antimony(III), fluoride complexes, isomorphism, fluoroantimonates(III), continuous and limited solid solutions; IR spectra, ^{121,123}Sb NQR spectra.

Isomorphous substitution of atoms in the crystals is a well known phenomenon[1–3] that opens up great possibilities for the synthesis of new complexes of constant or variable chemical composition and for modification of their properties. The character of the interaction between the components of a system at the same temperature is dependent on a number of factors and, first of all, on the chemical composition and concentration of the components.

Information on mutual isomorphous substitution of atoms in the crystals of antimony(III) complexes is restricted to that obtained in the studies of solid solutions in the binary $Cs_3Sb_2Br_9$—$Cs_3Sb_2I_9$, $Cs_3Sb_2Br_9$—$Rb_3Sb_2Br_9$, $Cs_3Sb_2I_9$—$Rb_3Sb_2I_9$, and $Rb_3Sb_2Br_9$—$Rb_3Sb_2I_9$ systems[4] and mixed pentafluoroantimonates(III) $M_xM'_{2-x}SbF_5$ (M, M′ = Na, K, Rb, Cs, and NH_4; $x = 0$ to 2).[5,6] The aim of this work was to investigate the mutual influence of atoms on the chemical composition and properties of fluorine-containing antimony(III) compounds formed as solid products from aqueous solutions in the systems $(MF)_x$—$(M'F)_{n-x}$—SbF_3 (M, M′ = Na, K, Rb, Cs, and NH_4; $n = 1, 2$; $x = 0$ to 2), $(KNO_2)_n$—$(KY)_n$—SbF_3 (Y = F, Cl, and SO_4; $n = 0.5, 1$), and K_2SbF_5—K_2SbCl_5.

Experimental

Antimony trifluoride and trichloride, alkali metal and ammonium fluorides and chlorides, and potassium nitrite were used as starting substances for the syntheses. The interaction between the components of reaction mixtures for different compositions of the systems and concentrations of the reagents was studied in aqueous solutions following a procedure analogous to that described previously.[6] The composition of solid phases that formed was determined by elemental, X-ray phase, and thermogravimetric analyses following standard procedures, and by IR and ^{121,123}Sb NQR spectroscopy. The unit cell parameters and volumes were calculated from the data of X-ray phase analysis and the asymmetry parameters of the electric field gradient (EFG) η at the nuclei of Sb atoms were calculated from the NQR spectra. The thermogravimetric study was carried on a derivatograph (a system of F. Paulik, J. Paulik, and L. Erdey) in a dry air stream (at a heating rate of 10 deg min^{-1}).

Results and Discussion

It is known that perfect isovalent isomorphism is unattainable if the components are not isostructural, whereas no structural limitations are known for a limited isomorphism. If the initial components have different structures, one can expect to obtain either new compounds or mixed crystals in which some of the basis atoms are replaced by impurity atoms.[1,2] Below we present the results of our study of solid fluorine-containing antimony(III) compounds formed from aqueous systems of different chemical composition and concentration of components.

Systems $(MF)_x$—$(M'F)_{2-x}$—SbF_3—H_2O (M, M′ = Na, K, Rb, Cs, and NH_4)

The interaction of MF compounds (M = Na, K, Rb, Cs, and NH_4) with SbF_3 in aqueous solutions at a molar ratio of the reagents of 2 : 1 results in the formation of crystalline isostructural pentafluoroantimonates(III) M_2SbF_5 (M = K, Rb, Cs, and NH_4) and the compound

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Na_2SbF_5 with different structure.[7,8] All pentafluoroantimonates(III) are ionic conductors.[9] The composition of the solid phases of analogous mixed cation systems has been studied previously.[5,6] It has been found that two new chemical compounds of constant composition, $NaM'SbF_5 \cdot 1.5H_2O$ (M′ = K and Rb), and several series of $M_xM'_{2-x}SbF_5$ continuous solid solutions (M = K, Rb, Cs, and NH_4; $x = 0$ to 2) are formed. The study of the structure of the former two compounds is currently in progress. It has been shown that in all pentafluoroantimonates(III) with both monoelemental and mixed cations, the coordination polyhedra of antimony atoms have the same configuration of a slightly distorted $[SbF_5E]^{2-}$ octahedron (E is the lone electron pair of Sb^{3+}).

In addition to the substances mentioned above, cationic pairs whose participation in the reactions results in the formation of mechanical mixtures of antimony(III) compounds with monoelemental cations were found in the system under consideration. Detailed information on the interaction between the components in the $(MF)_x-(M'F)_{2-x}-SbF_3-H_2O$ system is given in Table 1, where the compositions of the solid phases that formed are compared with the differences of the ionic radii of the cations in corresponding pairs.

Analysis of the results obtained shows that the interaction of antimony trifluoride with alkali metal and ammonium fluorides in this system obeys the basic empirical Goldschmidt rule,[1,2] according to which solid isomorphous mixtures are formed if the difference of the radii (Δ*r*) of mutually substituting structural units is not more than 15% relative to the smaller radius. Thus, continuous solid solutions of composition $M_xM'_{2-x}SbF_5$ were obtained from the $(MF)_x-(M'F)_{2-x}-SbF_3-H_2O$ system with cationic pairs for which the difference of ionic radii lies within the limits 4.2 to 15.4% (see Table 1). In the case of the Na^+-K^+ and K^+-Rb^+ cationic pairs, for which the difference of the ionic radii is much larger than 15% (35.7 and 52.0%, respectively), the formation of the compounds of constant composition occurs involving water molecules. The absence of isomorphism for the K^+-Cs^+, $Na^+-NH_4^+$, Na^+-Cs^+, and $Li^+-M'^+$ (M′ = Na, K, Rb, Cs, and NH_4) cationic pairs corresponds to the Goldschmidt criterion (see Table 1). However, $LiNaR_2F_8$ complexes (R = Ho—Lu, Y) were obtained[10] from the melt for the Li^+-Na^+ pair.

Table 1. Cationic pairs and the composition of the solid phases formed in $(MF)_x-(M'F)_{2-x}-SbF_3-H_2O$ systems

Cationic pair in solution	Δ*r** Å	Δ*r** %	Composition of solid phase
Li—Na	0.20	25.6	LiF+$NaSbF_4$
Li—K	0.55	70.5	LiF+$KSbF_4$
Li—NH_4	0.65	83.3	LiF+NH_4SbF_4
Li—Rb	0.71	91.0	LiF+$RbSbF_4$
Li—Cs	0.87	111.5	LiF+$CsSbF_4$
Rb—NH_4	0.06	4.2	$Rb_{2-x}(NH_4)_xSbF_5$
K—NH_4	0.10	7.0	$K_{2-x}(NH_4)_xSbF_5$
Rb—Cs	0.16	10.7	$Rb_{2-x}Cs_xSbF_5$
K—Rb	0.16	12.0	$K_{2-x}Rb_xSbF_5$
Cs—NH_4	0.22	15.4	$Cs_{2-x}(NH_4)_xSbF_5$
K—Cs	0.32	24.0	$K_2SbF_5+Cs_2SbF_5$
Na—K	0.35	35.7	$NaKSbF_5 \cdot 1.5H_2O$
Na—NH_4	0.45	45.9	$Na_2SbF_5+(NH_4)_2SbF_5$
Na—Rb	0.51	52.0	$NaRbSbF_5 \cdot 1.5H_2O$
Na—Cs	0.67	68.3	$Na_2SbF_5+Cs_2SbF_5$

* Data taken from Ref. 1.

In addition to the results of our study[6] it should be noted that, according to the data of elemental analysis, the *x* values for the same cationic pair determined in the initial components and in $M_xM'_{2-x}SbF_5$ solid solutions that formed are, as a rule, different (Table 2). Most likely, this fact can be explained taking into account another empirical Goldschmidt rule, *viz.*, the polarity rule, according to which the ion with smaller radius will enter into the common crystal structure more easily than that with larger radius. According to the data in Table 2, this rule is obeyed by solid solutions with the K^+-Rb^+ and Rb^+-Cs^+ cationic pairs. When the NH_4^+ cation is one of the two cations in a cationic pair, it can be seen that despite its smaller radius, the isomorphous substitution with participation of this cation occurs in the crystal structure more difficultly.

Investigation of IR absorption spectra of the $M_xM'_{2-x}SbF_5$ solid solutions for which characteristic vibrations of Sb—F bonds in the SbF_5^{2-} anions are

Table 2. Change in the composition of the $M_xM'_{2-x}SbF_5$ solid products depending on the molar ratio of cations in solution

Cationic pair	Molar ratio of cations *x*	Molar ratio of cations 2 − *x*	Sb (%), found / calculated	Composition of solid phase
K—Rb	1.75	0.25	39.8 / 39.72	$K_{1.75}Rb_{0.25}SbF_5$
K—Rb	1.50	0.50	38.6 / 38.27	$K_{1.5}Rb_{0.5}SbF_5$
K—Rb	1	1	36.6 / 36.66	$K_{1.2}Rb_{0.8}SbF_5$
K—Rb	0.50	1.50	34.7 / 34.73	$K_{0.8}Rb_{1.2}SbF_5$
K—Rb	0.25	1.75	32.7 / 32.37	$K_{0.25}Rb_{1.75}SbF_5$
Rb—Cs	1	1	30.4 / 29.94	$Rb_{1.6}Cs_{0.4}SbF_5$
Rb—NH_4	1.50	0.50	32.1 / 32.53	$Rb_{1.8}(NH_4)_{0.2}SbF_5$
Rb—NH_4	1	1	34.4 / 34.40	$Rb_{1.5}(NH_4)_{0.5}SbF_5$
Rb—NH_4	0.50	1.50	38.8 / 38.84	$Rb_{0.9}(NH_4)_{1.1}SbF_5$
Cs—NH_4	1.75	0.25	25.9 / 25.84	$Cs_{1.9}(NH_4)_{0.1}SbF_5$
Cs—NH_4	1	1	33.4 / 33.11	$CsNH_4SbF_5$

observed[11] in the region 400—500 cm^{-1} shows that substitution of the atoms in the cationic sublattice causes a shift of the maximum of the Sb—F stretching band ($\nu_1 A_1$) towards the long-wave region as compared to the position of the corresponding maximum in the spectra of M_2SbF_5 compounds with the same cations. The shift magnitude lies in the range from 1 to 42 cm^{-1} and is dependent on the composition of the cationic pair (Table 3). In this case the frequency of the Sb—F bond vibration decreases, as a rule, for $x = 0.25$ and 1.75, whereas in the range $0.25 < x < 1.75$ the position of the maximum of the Sb—F absorption band remains unchanged. This indicates that the IR spectra of isostructural $M_xM'_{2-x}SbF_5$ pentafluoroantimonates(III) are poorly sensitive to isomorphous substitution.

In $M_xM'_{2-x}SbF_5$ systems, the Sb content in the solid phase, the crystal lattice parameters, and the ^{121}Sb NQR spectra are more sensitive to changes in the cationic component. The dependences of the Sb content, the unit cell volume, and the ^{121}Sb NQR frequency (the $\pm 1/2 \rightleftharpoons \pm 3/2$ transition, at 77 K) on the x value in the system for the $Rb_xK_{2-x}SbF_5$ and $Cs_x(NH_4)_{2-x}SbF_5$ solid solutions are shown in Fig. 1. The results obtained show that nonlinear changes are observed for all the parameters studied on going from M_2SbF_5 to $M_xM'_{2-x}SbF_5$, whereas the magnitude of the deviation from linearity depends on the composition and concentration of cations in solution.

The sharp decrease in the integrated intensities of the signals and their broadening from 180 to 1450 kHz (and even more) in the range $0.25 < x < 1.75$ is a characteristic feature of the ^{121,123}Sb NQR spectra of $M_xM'_{2-x}SbF_5$ solid solutions as compared to those of M_2SbF_5 compounds (see Ref. 12). The dependence of the shape of the ^{121}Sb NQR line for $Cs_x(NH_4)_{2-x}SbF_5$ on x is shown in Fig. 2. Narrow intense ^{121,123}Sb NQR signals correspond to the pure components of the Cs_2SbF_5 and $(NH_4)_2SbF_5$ solid solutions in which the Sb atoms occupy definite positions in the crystal lattice. Broadening of the NQR lines in the $Cs_x(NH_4)_{2-x}SbF_5$ solid solutions indicates the EFG scatter over all resonance antimony atoms in the $[SbF_5]^{2-}$ anions upon introducing cations of another sort into the crystal lattice. It should be noted that the magnitude of the EFG scatter over Sb atoms depends on the composition of the cationic pair. For instance, weak broad ^{121,123}Sb NQR lines are observed[6] at all x for the K^+—Rb^+ and Rb^+—Cs^+ cationic pairs, whereas for the M^+—NH_4^+ pairs (M = K^+, Rb^+, and Cs^+) they are observed only at $x = 0.25$

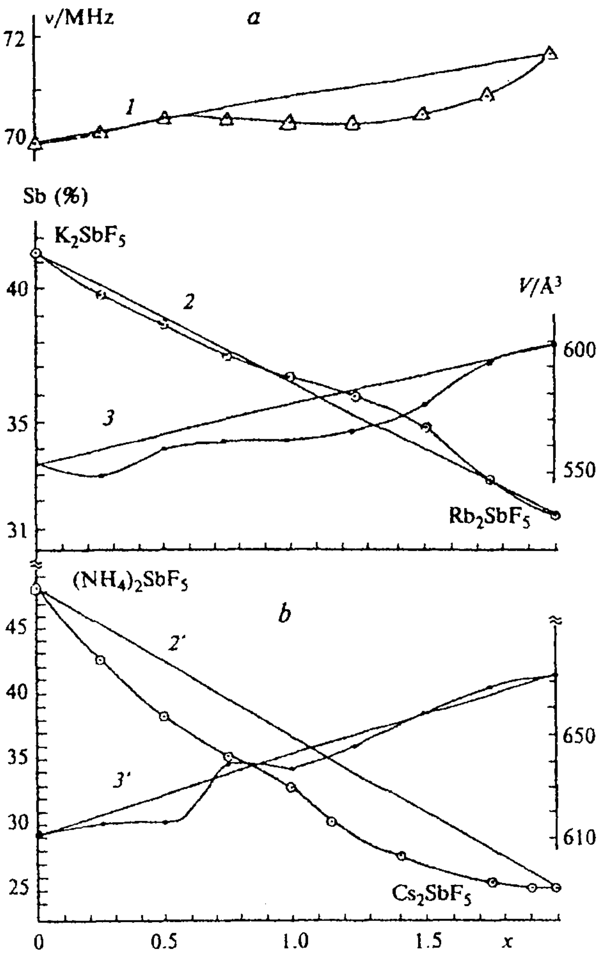

Fig. 1. Dependence of the ^{121}Sb NQR frequency (the $\pm 1/2 \rightleftharpoons \pm 3/2$ transition) at 77 K (*1*), Sb content in the solid phase (*2*, *2'*), and the unit cell volume (*3*, *3'*) on the composition of the cationic pair for $Rb_xK_{2-x}SbF_5$ (*a*) and $Cs_x(NH_4)_{2-x}SbF_5$ (*b*).

Table 3. Shifts of the maxima of bands of the Sb—F stretching vibrations in the IR spectra of pentafluoroantimonates(III) with univalent cations

Cationic pair	Compound	Δν/cm^{-1}	
		*A**	*B***
Rb—NH$_4$	Rb_2SbF_5, $(NH_4)_2SbF_5$, $Rb_{2-x}(NH_4)_xSbF_5$	8	12; 20
K—NH$_4$	K_2SbF_5, $(NH_4)_2SbF_5$, $K_{2-x}(NH_4)_xSbF_5$	4	11; 20
Rb—Cs	Rb_2SbF_5, Cs_2SbF_5, $Rb_{2-x}Cs_xSbF_5$	10	12; 2
K—Rb	K_2SbF_5, Rb_2SbF_5, $K_{2-x}Rb_xSbF_5$	4	11; 7
Cs—NH$_4$	Cs_2SbF_5, $(NH_4)_2SbF_5$, $Cs_{2-x}(NH_4)_xSbF_5$	18	4; 22
K—Cs	K_2SbF_5, Cs_2SbF_5	14	
Na—K	Na_2SbF_5, K_2SbF_5, $NaKSbF_5 \cdot 1.5H_2O$	29	1; 28
Na—NH$_4$	Na_2SbF_5, $(NH_4)_2SbF_5$	33	
Na—Rb	Na_2SbF_5, Rb_2SbF_5, $NaRbSbF_5 \cdot 1.5H_2O$	25	17; 42
Na—Cs	Na_2SbF_5, Cs_2SbF_5	15	

* *A*: $\Delta\nu = \nu(M_2SbF_5) - \nu(M'_2SbF_5)$. ** *B*: $\Delta\nu = \nu(M_2SbF_5; M'_2SbF_5) - \nu(M_xM'_{2-x}SbF_5)$.

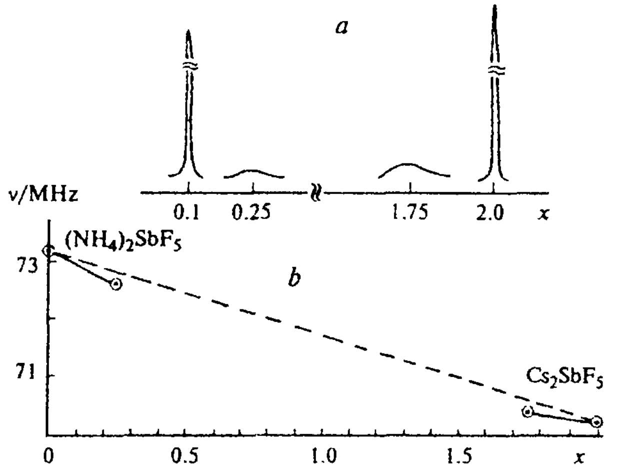

Fig. 2. Dependence of the shape (*a*) and frequency (*b*) of the ^{121}Sb NQR line (the ±1/2 $\rightleftharpoons$ ±3/2 transition) at 77 K on the composition of the cationic pair for $Cs_x(NH_4)_{2-x}SbF_5$: $x = 0.25$ and 1.75. No NQR signals are observed in the range $0.25 < x < 1.75$.

and 1.75. No NQR signals of the $M_x(NH_4)_{2-x}SbF_5$ (M = K, Rb, and Cs) solid solutions are observed in the concentration range $0.25 < x < 1.75$ because of appreciable line broadening (see Fig. 2).

Calculations of the EFG asymmetry parameters η at the nuclei of Sb atoms using the experimental NQR frequencies carried out in this work and previously[6] indicate that the EFG symmetry at the antimony atoms in the $[SbF_5]^{2-}$ anions in both the $M_xM'_{2-x}SbF_5$ solid solutions and the $NaM'SbF_5 \cdot 1.5H_2O$ compounds (M' = K and Rb) is higher than in individual pentafluoroantimonates(III)[11] (Table 4).

Another peculiarity of the ^{121,123}Sb NQR spectra of pentafluoroantimonates(III) studied is their higher sensitivity to temperature changes: the intensities of all NQR signals detected at 77 K strongly decreases as the temperature increases. No NQR signals are detected for $M_xM'_{2-x}SbF_5$ compounds at $T > 120$ K and for $NaM'SbF_5 \cdot 1.5H_2O$ at $T > 254$ K,[6] whereas the ^{121,123}Sb NQR spectra of M_2SbF_5 compounds are observed in the temperature range from 77 to 290—400 K depending on the cation.[13—15]

Table 4. The EFG asymmetry parameters (η) at the nuclei of Sb atoms in pentafluoroantimonates(III) with univalent cations at 77 K

Compound	*x*	η (%)	Compound	*x*	η (%)
K_2SbF_5		8.8	Na_2SbF_5		17.5
$Rb_xK_{2-x}SbF_5$	0.25	5.1	$NaKSbF_5 \cdot 1.5H_2O$	1.0	4.7
$Rb_xK_{2-x}SbF_5$	0.50	6.2	$NaRbSbF_5 \cdot 1.5H_2O$	1.0	7.2
$Rb_xK_{2-x}SbF_5$	0.80	6.6	$(NH_4)_2SbF_5$		8.4
$Rb_xK_{2-x}SbF_5$	1.20	6.3	$Rb_{1.8}(NH_4)_{0.2}SbF_5$	1.8	5.9
$Rb_xK_{2-x}SbF_5$	1.50	6.2	$Rb_{1.6}Cs_{0.4}SbF_5$		4.7
$Rb_xK_{2-x}SbF_5$	1.75	6.0	Cs_2SbF_5		6.5
Rb_2SbF_5		6.8			

System K_2SbF_5—K_2SbCl_5—H_2O

Isolated $[SbX_5E]^{2-}$ anions and $K(1)^+$, and $K(2)^+$ cations are structural units of K_2SbX_5 (X = F, Cl) compounds.[7] In these compounds, the coordination polyhedra of Sb^{III} atoms have a square pyramidal configuration completed with the lone pair of the $5s^2$ electrons to SbX_5E octahedra. These octahedra are arranged pairwise in the structure so that the bases of the SbX_5E semioctahedra are directed towards each other.

Anionic isomorphism in the K_2SbF_5—K_2SbCl_5—H_2O system was studied only at the equimolar ratio of the components. To prevent hydrolysis of potassium pentachloroantimonate(III), its crystals were introduced into an aqueous solution of K_2SbF_5. The compound $KSbF_3Cl$ studied previously[16] is formed on slow crystallization of such a solution. The structure of $KSbF_3Cl$ is built of $[SbF_3Cl]_n^{n-}$ corrugated anionic sheets with K^+ cations between them. Hence, the anionic isomorphism in this system is responsible for the increase in the coordination number of the Sb^{III} atom in the solid product from 5 in K_2SbX_5 to 6 in $KSbF_3Cl$ and the formation of polymeric $[SbF_3Cl]_n^{n-}$ mixed ligand anion.

Systems $(MF)_x$—$(M'F)_{1-x}$—SbF_3—H_2O (M, M' = Na, K, Rb, Cs, and NH_4)

The interaction of MF (M = Na, K, Rb, Cs, and NH_4) compounds and SbF_3 in aqueous solutions at a molar ratio of the reagents of 1 : 1 results in the formation of non-isostructural individual compounds of composition $MSbF_4$.[8] The crystal structures of tetrafluoroantimonates(III) with Na^+ and K^+,[7] Cs^+,[17] and NH_4^+ [18] cations have been studied.

Previously,[19] the compositions of the solid phases formed in the $(MF)_x$—$(M'F)_{1-x}$—SbF_3—H_2O systems (M, M' = Na, K, Rb, Cs, and NH_4) were determined and their ^{121,123}Sb NQR spectra at 77 K were studied. Below we present the results of our study of isomorphism in these systems.

In Table 5, the compositions of the solid phases formed in the systems studied are compared with the difference of the ionic radii of the cations in the pairs. The analysis of the data obtained shows that the range of miscibility of the compounds with the same cationic pair changes on going from one class of antimony(III) fluoride compounds (pentafluoroantimonates, see Table 1) to another class (tetrafluoroantimonates, see Table 5). Thus, it was found that the $M_xM'_{1-x}SbF_4$ (M, M' = K, Rb, Cs, and NH_4) mixed crystals are also formed in the $(MF)_x$—$(M'F)_{1-x}$—SbF_3—H_2O system. In contrast to the $M_xM'_{2-x}SbF_5$ crystals, the former crystals exist in a more narrow range of concentrations of the initial components ($0.20 < x < 0.80$); however, the range of corresponding Δr values in this case is wider (from 4.2 to 24.0%). The results of elemental analysis of

Table 5. Cationic pairs and composition of the solid phases formed in the $(MF)_x$—$(M'F)_{1-x}$—SbF_3—H_2O systems

Cationic pair in solution	Δr* (%)	Composition of solid phases successively formed in the range $0.20 < x < 0.80$	Range in which solid solutions are formed
Rb—NH_4	4.2	NH_4SbF_4, $Rb_x(NH_4)_{1-x}SbF_4$, $RbSbF_4$	$0.25 < x < 0.50$
K—NH_4	7.0	$K_x(NH_4)_{1-x}SbF_4$, $KSbF_4$	$0.25 < x < 0.75$
Rb—Cs	10.7	$CsSbF_4$, $Rb_xCs_{1-x}SbF_4$, $RbSbF_4$	$0.25 < x < 0.50$
K—Rb	12.0	$RbSbF_4$, $K_xRb_{1-x}SbF_4$, $KSbF_4$	$0.25 < x < 0.50$
Cs—NH_4	15.4	$Cs_x(NH_4)_{1-x}SbF_4$, $CsSbF_4$	$0.25 < x < 0.75$
K—Cs	24.0	$CsSbF_4$, $K_xCs_{1-x}SbF_4$, $KSbF_4$, KSb_2F_7	$0.25 < x < 0.50$
Na—K	35.7	KSb_2F_7, $NaKSbF_5 \cdot 1.5H_2O$, $NaSbF_4$	
Na—NH_4	45.9	NH_4SbF_4, $NaSbF_4$	
Na—Rb	52.0	$RbSbF_4$, $NaSbF_4$	
Na—Cs	68.3	$CsSbF_4$, $NaCs_3Sb_4F_{16} \cdot H_2O$	

* Relative difference of the ionic radii.

Table 6. Change in the composition of the $M_xM'_{1-x}SbF_4$ solid products depending on the molar ratio of cations in solution

Cationic pair	Molar ratio of cations		Sb (%), $\frac{\text{found}}{\text{calculated}}$	Composition of solid phase
	x	$1-x$		
Rb—NH_4	0.5	0.5	$\frac{44.0}{44.03}$	$Rb_{0.9}(NH_4)_{0.1}SbF_4$
K—NH_4	0.25	0.75	$\frac{51.7}{51.86}$	$K_{0.9}(NH_4)_{0.1}SbF_4$
K—NH_4	0.5	0.5	$\frac{52.4}{52.33}$	$K_{0.8}(NH_4)_{0.2}SbF_4$
K—NH_4	0.75	0.25	$\frac{54.0}{53.80}$	$K_{0.5}(NH_4)_{0.5}SbF_4$
Rb—Cs	0.5	0.5	$\frac{42.4}{42.28}$	$Rb_{0.9}Cs_{0.1}SbF_4$
K—Rb	0.5	0.5	$\frac{48.7}{48.55}$	$K_{0.7}Rb_{0.3}SbF_4$
Cs—NH_4	0.5	0.5	$\frac{44.2}{44.56}$	$Cs_{0.5}(NH_4)_{0.5}SbF_4$
Cs—NH_4	0.75	0.25	$\frac{50.1}{49.83}$	$Cs_{0.25}(NH_4)_{0.75}SbF_4$
K—Cs	0.5	0.5	$\frac{45.8}{45.94}$	$K_{0.7}Cs_{0.3}SbF_4$

Table 7. Temperatures of endothermic effects (T_{endo}) and melting (T_{melt}) of the solid phases formed in the $(MF)_x$—$(M'F)_{1-x}$—SbF_3—H_2O systems

Composition	T_{endo}	T_{melt}
	°C	
$NaSbF_4$		270,* 250
$KSbF_4$	210,* 195, 270	315,* 285
$RbSbF_4$		275,* 255
$CsSbF_4$	220*	245,* 225
NH_4SbF_4		180
$Rb_{0.9}(NH_4)_{0.1}SbF_4$	220	255
$K_{0.8}(NH_4)_{0.2}SbF_4$	195, 215	275
$Rb_{0.9}Cs_{0.1}SbF_4$	195	240
$K_{0.7}Rb_{0.3}SbF_4$	240	255
$Cs_{0.5}(NH_4)_{0.5}SbF_4$		165
$NaKSbF_5 \cdot 1.5H_2O$ [6]	100, 190	320
$NaCs_3Sb_4F_{16} \cdot H_2O$	147, 168	195

* Measured in helium stream.[8]

$M_xM'_{1-x}SbF_4$ solid solutions (Table 6) indicate that the regularities of changes in the phase composition depending on x in the solution are the same as those discussed above for $M_xM'_{2-x}SbF_5$ compounds (see Table 2). The $^{121,123}Sb$ NQR spectra of isomorphous $M_xM'_{1-x}SbF_4$ mixtures considered previously[19] indicate a drastic reduction of the EFG symmetry at the nuclei of Sb atoms as compared to that of corresponding tetrafluoroantimonates(III) with monoelemental cations, which is most likely due to a disordering in the mutual arrangement of the cations.

The study of the IR spectra of the $M_xM'_{1-x}SbF_4$ phases in the region of frequencies of the Sb—F stretching vibrations shows that at $x = 0.7$ to 0.9 their structure remains virtually unchanged as compared to that of the spectra of $MSbF_4$ compounds (see Ref. 11), where M is the cation with a higher content in this isomorphous mixture. At $x = 0.5$, absorption bands of two $MSbF_4$ complexes with monoelemental cations are observed in the IR spectra of mixed cation compounds.

The individual compound $NaKSbF_5 \cdot 1.5H_2O$ was obtained in the $(MF)_x$—$(M'F)_{1-x}$—SbF_3—H_2O system (M = Na, M' = K) (*cf.* Table 1). It was surprising that, contrary to the Goldschmidt criterion, the second compound, $NaCs_3Sb_4F_{16} \cdot H_2O$ (the Na^+—Cs^+ cationic pair), is formed in this system, though the difference of the ionic radii Δr for this pair is 68.3%. The chemical composition of this compound and its $^{121,123}Sb$ NQR spectrum have been reported previously,[19] and the study of its crystal structure is currently in progress. For two cationic pairs, Na^+—NH_4^+ and Na^+—Rb^+, no isomorphism is observed (see Table 5).

The cationic isomorphous substitution occurring in antimony(III) complexes affects the thermal properties of mixed cation substances, *viz.*, the melting temperature decreases and the number of endothermic effects changes (Table 7).

Systems $(KNO_2)_n$—$(KY)_n$—SbF_3—H_2O (Y = F, Cl, and SO_4; $n = 0.5, 1$)

Previously,[20] it has been shown that complex $K_2SbF_5 \cdot 1.5H_2O$ is formed by the reaction of aqueous solutions of KNO_2 with antimony trifluoride in the range of the molar ratios of the reagents varied from 0.5 : 1.0 to 5 : 1. Under the same conditions, fluoride (KSb_2F_7 and $KSbF_4$),[8] chlorofluoride ($KSbF_3Cl$),[16] or sulfatofluoride ($K_2Sb_2F_6SO_4$ and $K_2SbF_3SO_4$)[21] compounds have been obtained at the KY : SbF_3 (Y = F, Cl, and SO_4) molar ratios varied in the range (0.5—1) : 1.

The interaction between the components in the $(KNO_2)_n$—$(KY)_n$—SbF_3—H_2O systems (Y = F, Cl, and SO_4) at $n = 0.5$ and 1 was studied. All reactions resulted in the formation of the complex $K_2SbF_5 \cdot 1.5H_2O$ as the end product. Some of the properties of this complex have been described previously.[20] It should be noted that its recrystallization from water results in the formation of Sb_2O_3. Most likely, the reaction occurs following the scheme shown below:

$$2\ K_2SbF_5 \cdot 1.5H_2O \xrightarrow{H_2O} Sb_2O_3 + 4\ KF + 6\ HF.$$

Complex $K_2SbF_2Cl_3$ obtained previously[22] by interaction of KF with $SbCl_3$ in HCl is formed in a hydrochloric solution of the KNO_2—KCl—SbF_3 system at a molar ratio of the components of 1 : 1 : 1. It should be noted that, in contrast to the reaction[22] where KCl coprecipitates simultaneously with $K_2SbF_2Cl_3$, in this case potassium chlorofluoroantimonate(III) crystallizes in pure form.

Thus, the phenomenon of isomorphism in crystalline fluorine-containing antimony(III) complexes formed from aqueous solutions in the $(MF)_{n-x}$—$(M'F)_x$—SbF_3 (M, M' = Na, K, Rb, Cs, and NH_4; n = 1, 2; x = 0 to 2), $(KNO_2)_n$—$(KY)_n$—SbF_3 (Y = F, Cl, and SO_4; n = 0.5, 1), and K_2SbF_5—K_2SbCl_5 systems was studied. The conditions of the formation of the adducts of constant composition, continuous and limited solid solutions, and mechanical mixtures of antimony(III) compounds were established.

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