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Syntheses and characterization of $ANi(AsF_6)_3$ ($A = H_3O^+$, O_2^+, NO^+, NH_4^+, K^+, Rb^+, and Cs^+) compounds

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ABSTRACT

$ANi(AsF_6)_3$ ($A = O_2^+$, NO^+, NH_4^+) compounds could be prepared by reaction between corresponding $AAsF_6$ salts and $Ni(AsF_6)_2$. When mixtures of AF (A = Li, Na, K, Rb, Cs) and NiF_2 are dissolved in aHF acidified with an excess of AsF_5 the corresponding $AAsF_6$ and $Ni(AsF_6)_2$ were formed in situ. For A = Li and Na only mixtures of $AAsF_6$ and $Ni(AsF_6)_2$ were obtained, while for A = K, Rb and Cs, the final products were $ANi(AsF_6)_3$ (A = K–Cs) compounds contaminated with $AAsF_6$ (A = K–Cs) and $Ni(AsF_6)_2$.

$ANi(AsF_6)_3$ ($A = H_3O^+$, O_2^+, NO^+, NH_4^+ and K^+) compounds are structurally related to previously known $H_3OCo(AsF_6)_3$. The main features of the structure of these compounds are rings of NiF_6 octahedra sharing apexes with AsF_6 octahedra connected into infinite tri-dimensional network. In this arrangement cavities are formed where single charged cations are placed.

In $O_2Ni(AsF_6)_3$ the vibrational band belonging to O_2^+ vibration is found at $1866\ cm^{-1}$, which is according to the literature data one of the highest known values, and it is only $10\ cm^{-1}$ lower than the value for free O_2^+.

1. Introduction

$H_3OM(AsF_6)_3$ (M = Mn, Co, Ni) compounds are prepared by reactions between H_3OAsF_6 and $M(AsF_6)_2$ (M = Mn, Co, Ni) in anhydrous hydrogen fluoride (aHF) [1]. When MF_2 is used instead of $M(AsF_6)_2$ then aHF must be acidified with AsF_5 in order to prepare $M(AsF_6)_2$ in situ. Beside H_3OAsF_6, water or transition metal oxide can be used as source of the oxonium cation [1]. Crystal structure determination of $H_3OCo(AsF_6)_3$ [1] showed that the main feature of the structure is a ring of four AsF_6 octahedra connected by four cobalt atoms. This ring system is further extended infinitely in the plane and also perpendicular to the plane, forming on that way cavities in which oxonium ions are situated.

In the following study it was investigated if it is possible to replace H_3O^+ by other single charged cations which are smaller, bigger or of similar size as H_3O^+ (i.e. O_2^+, NO^+, NH_4^+, Li^+, Na^+, K^+, Rb^+ and Cs^+) and to preserve the basic structure motif, i.e. infinite tri-dimensional network consisting from rings of NiF_6 octahedra sharing apexes with AsF_6 octahedra. Results of this study are given in the present work.

2. Results and discussion

2.1. Syntheses

As already mentioned in the introduction, $H_3OM(AsF_6)_3$ (M = Mn, Co, Ni) compounds could be prepared by different ways (i.e. H_3OAsF_6 and $M(AsF_6)_2$ in aHF; H_3OAsF_6 and MF_2 in HF acidified with AsF_5; MO and AsF_5 in aHF) [1].

With corresponding starting materials it is possible to prepare other types of $ANi(AsF_6)_3$ compounds where H_3O^+ moieties are replaced by other single charged cations, i.e. $A = O_2^+$, NO^+, NH_4^+ (Eq. (1)):

$$AAsF_6 + Ni(AsF_6)_2 \xrightarrow[298K]{aHF} ANi(AsF_6)_3 \quad A = O_2^+,\ NO^+, NH_4^+ \tag{1}$$

As reported before [2] and observed also in this study, O_2AsF_6 partly decomposes when it is dissolved in aHF. Final mass of the product of reaction between O_2AsF_6 and $Ni(AsF_6)$ was lower than the sum of mass of reactants. A consequence of a deficiency of O_2AsF_6 was, that the isolated $O_2Ni(AsF_6)_3$ was most likely contaminated with a small amount of $Ni(AsF_6)_2$.

In the case of reactions between $AAsF_6$ (A = Li, Na) and $Ni(AsF_6)_2$ in aHF no corresponding $ANi(AsF_6)_3$ compounds could be detected. Final products were mixtures of $AAsF_6$ and $Ni(AsF_6)_2$ compounds. It seems that the cavities in the lattice of the tri-dimensional network of $ANi(AsF_6)_3$ are too large to be filled by small Li^+ and Na^+ cations.

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Table 1
Summary of crystal data and refinement results for $ANi(AsF_6)_3$ (A = H_3O^+, K^+, O_2^+, NO^+, NH_4^+).

Formula	$H_3ONi(AsF_6)_3$	$KNi(AsF_6)_3$	$O_2Ni(AsF_6)_3$	$NONi(AsF_6)_3$	$NH_4Ni(AsF_6)_3$[a]
Fw	644.47	664.55	657.47	655.48	643.51
T (K)	200	200	200	200	200
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
a (pm)	1023.99(7)	1027.70(7)	1032.4(2)	1030.1(8)	1036.8(2)
b (pm)	1380.3(1)	1377.8(1)	1378.9(3)	1383(1)	1395.3(6)
c (pm)	943.51(6)	941.77(8)	929.2(2)	941.3(1)	947.5(3)
V (nm^3)	1.3336(2)	1.3336(2)	1.3228(4)	1.341(2)	1.3707(7)
Space group	*Pnma* (No. 62)	*Pnma* (No. 62)	*Pnma* (No. 62)	*Pnma* (No. 62)	
Z	4	4	4	4	–
D_{calcd} (g/cm^3)	3.21	3.31	3.301	3.247	–
λ (pm)	0.7107	0.7107	0.7107	0.7107	0.7107
μ (mm^{-1})	9.056	9.361	9.139	9.012	–
GOF indicator[b]	1.178	1.195	1.202	1.233	–
R_1[c]	0.055	0.056	0.0546	0.1186	–
wR_2 [d]	0.1556	0.1167	0.1353	0.2361	–

[a] Because of the poor quality of obtained crystals and consequently poor quality of collected data only lattice parameters are given.

[b] GOF = $[\Sigma w(F_o^2 - F_c^2)^2/(N_o - N_p)]^{1/2}$, where N_o = no. of reflections and N_p = no. of refined parameters.

[c] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[d] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(w(F_o^2)^2]^{1/2}$.

Additionally, due to the high lattice energies of $AAsF_6$ (A = Li, Na), the formation of $AAsF_6$ and $Ni(AsF_6)_2$ (A = Li, Na) mixtures is more preferable than the formation of $ANi(AsF_6)_3$ (A = Li, Na) compounds. In the case of reactions of $Ni(AsF_6)_2$ with $KAsF_6$, $RbAsF_6$ or $CsAsF_6$, Raman spectra of isolated products show also the vibrational bands which could be related to that found in Raman spectra of $ANi(AsF_6)_3$ (A = H_3O^+, O_2^+, NO^+, NH_4^+) compounds, indicating that $ANi(AsF_6)_3$ phases were formed also for A = K^+, Rb^+ and Cs^+. However, isolated solids were not pure $ANi(AsF_6)_3$ compounds, but contaminated with $AAsF_6$ (A = K–Cs) and $Ni(AsF_6)_2$.

2.2. Crystal structures of $ANi(AsF_6)_3$ (A = H_3O^+, O_2^+, NO^+, NH_4^+, K^+)

Crystal and structure refinement data of $ANi(AsF_6)_3$ (A = H_3O^+, K^+, O_2^+, NO^+, NH_4^+) are given in Table 1.

Crystal structures of $ANi(AsF_6)_3$ (A = H_3O^+, O_2^+, NO^+, NH_4^+ and K^+) compounds are structurally related to previously known crystal structure of $H_3OCo(AsF_6)_3$ [1]. The main features of the structure are rings of NiF_6 octahedra sharing apexes with AsF_6 octahedra connected into infinite tri-dimensional network (Fig. 1). In this arrangement cavities are formed where single charged cations are placed. The neighbouring cavities are connected by apertures resulting in infinite goffered channels along *b*. Their size could be roughly determined from the shortest F···F distances. They are larger along the *b* direction (350–370 pm) as compared with 300 pm along other perpendicular directions (*a*- and *c*-axes). Considering the size of single charged cations used in this study, the aperture's sizes seem to be insufficient to promote cation mobility or cation exchange, and to justify that the cavities are forming open channels.

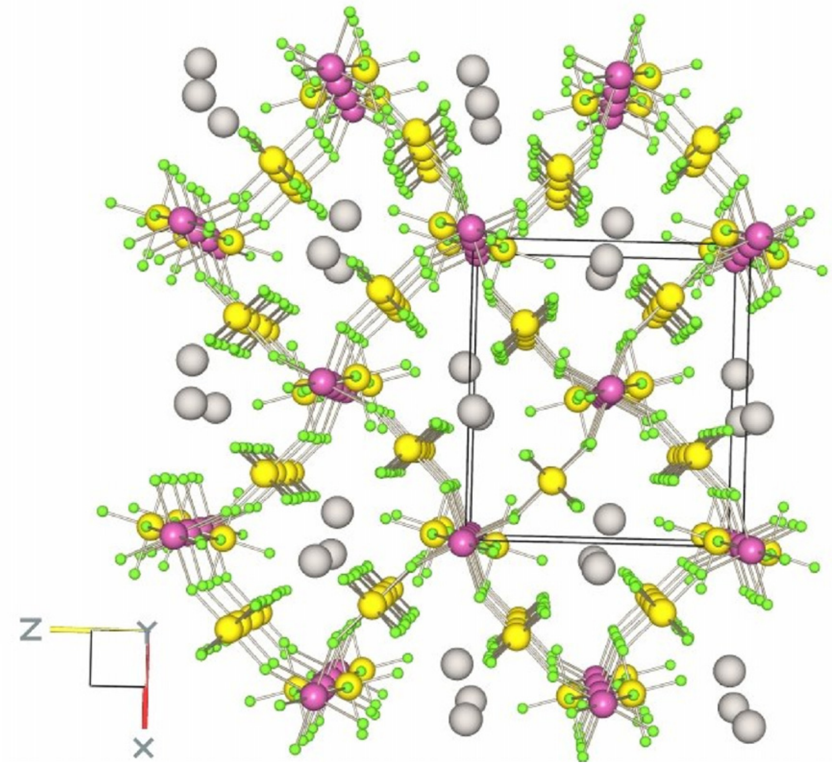

Fig. 1. Formation of cavities in tri-dimensional network consisted from NiF_6 octahedra sharing apexes with AsF_6 octahedra in the crystal structure of $KNi(AsF_6)_3$.

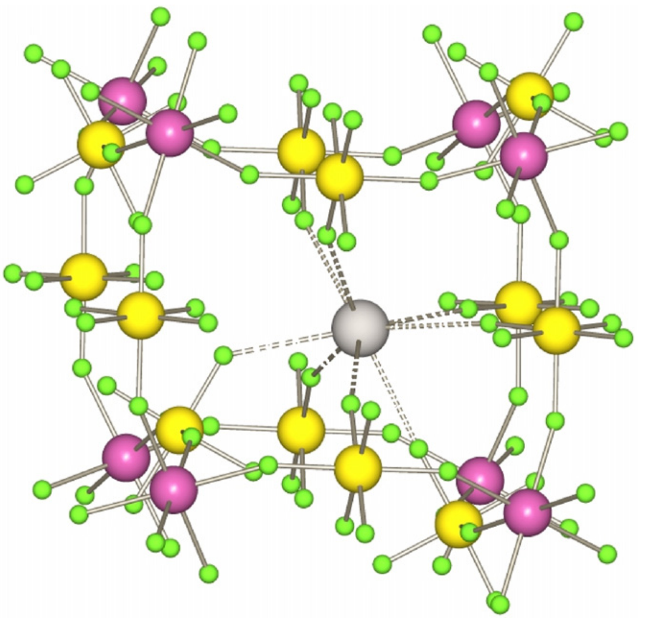

Fig. 2. Part of the crystal structure of $KNi(AsF_6)_3$ showing eight K· · ·F contacts in the 262.8(7)–319.3(5) pm range.

The crystal structure of $ANi(AsF_6)_3$ can alternatively be described as a pseudo-cubic array of NiF_6 octahedra linked to the opposite corners of AsF_6 octahedra, located at the middle of the cubic cell edges. Single charged cations (A^+) are slightly shifted from the center of the cubic cell cavities (Fig. 2). Cell parameter relations between the pseudo-cubic and the orthorhombic cell are given by the expression: $a_{cub} = 1/2{\cdot}2^{1/2}{\cdot}a_{ort} = 1/2{\cdot}2^{1/2}{\cdot}c_{ort} = 1/2{\cdot}b_{ort} \approx 700$ pm).

In all three completely determined crystal structures of $ANi(AsF_6)_3$ ($A = H_3O^+$, K^+, O_2^+) quite regular NiF_6 octahedra are present with Ni–F bond lengths from 197.6 to 200.3 pm and F–Ni–F angles between 87.4° and 92.6°. The As–F distances are in the range 165.1 – 170.9 pm for terminal and 176.5–177.7 pm for the bridging F atoms.

In the crystal structure of $H_3ONi(AsF_6)_3$, like in the case of $H_3OCo(AsF_6)_3$ [1], the hydrogen atoms were not localized from Fourier maps. That is why calculated positions of H atoms were used in final refinement. The shortest distances between oxygen and terminal fluorine atoms belonging to AsF_6 groups are 264(1) pm, 2× 267.7(9), 274(1) and 2× 281.1(9) pm. Next shortest O· · ·F distance is much longer (324.2 pm). The most appropriate model for H_3O^+ moiety in such environment (six fluorine atoms around oxygen) it seems, it is the model, where each hydrogen atom of H_3O^+ cation forms two hydrogen bonds (i.e. two O–H· · ·F bonds). The H· · ·F distances of 208.7–228.4 pm in such a model seem reasonable.

K^+ cations are found in an irregular coordination of eight fluorine atoms with six short (262.8(7) pm, 2× 270.6(5) pm, 273.4(8) pm, 2× 279.3(5) pm) and two long (2× 319.3(5) pm) K· · ·F contacts. For comparison, in the crystal structure of $KSbF_6$ eight fluorine atoms surround K atoms at distances between 261.8(7) and 320.4(7) pm [3].

In $KNi(AsF_6)_3$, the total bond valence [4–6] around K^+ arising from fluorine contacts gives the total bond valence of 0.914 vu (bond valence units) which is less than 1. The next shortest test K· · ·F distances (2× 347.8 pm) are too long to be considered as significant contacts (the corresponding bond valences are 0.018).

Because of the oriental disorder of O_2^+ cations, the O–O bond distance (101.7 pm) in $O_2Ni(AsF_6)_3$ seems little short in comparison with distances found in β-O_2AuF_6 (106.8(30) pm) [7], α-O_2AuF_6 (107.9(27) pm at 104 K) [8], $[O_2][Mn_2F_9]$ (110 pm) [9], O_2PtF_6 (121(17) pm) [10], O_2RuF_6 (112.5(17) pm at 146 K; 112(4) pm at 293 K) [11] with three-fold model for disordered cation. Anomalously short O–O bond lengths were reported for $[O_2]_2[Ti_7F_{30}]$ (96 pm) [12] and for O_2MF_6 (M = Sb, Ru, Pt) [13].

Rather unusual disordering of NO^+ moiety has been found in the structure of $NONi(AsF_6)_3$. The nitrogen atom is located on special position on the mirror plane, whereas the position of oxygen is split on two positions with the occupancy 1/2. Low quality of obtained crystals makes senseless further discussion of this structure.

2.3. Vibrational spectra of ANi(AsF6)3 (A = H_3O^+, O_2^+, NO^+, NH_4^+, K^+–Cs^+) compounds

The Raman spectra of $ANi(AsF_6)_3$ ($A = H_3O^+$, O_2^+, NO^+, NH_4^+) are shown in Fig. 3 and given in Table 2. In the 100–900 cm^{-1} range only the bands belonging to the vibrations of octahedral $[AsF_6]^-$ groups could be found. Since $[AsF_6]^-$ is well studied it will not be further discussed. The similarity of all Raman spectra is in agreement with crystallographic results where it was found that the basic tri-dimensional network is not significantly affected by the presence of different single charged cations.

Raman spectra of products of reactions of $AAsF_6$ (A = Li, Na) with $Ni(AsF_6)_2$ show only the presence of $AAsF_6/Ni(AsF_6)_2$ mixtures. Neglecting the vibrational bands belonging to $AAsF_6$ (A = K, Rb, Cs), Raman spectra of the products of reactions between $AAsF_6$ (A = K–Cs) and $Ni(AsF_6)_2$ in aHF (Table 2, Fig. 4) are very similar to previously mentioned Raman spectra of $ANi(AsF_6)_3$ ($A = H_3O^+$, O_2^+, NO^+, NH_4^+) compounds (Table 2, Fig. 3). They could be assigned to the presence of $ANi(AsF_6)_3$ (A = K–Cs) phases. In Raman spectra of all three products of reactions between $AAsF_6$ and $Ni(AsF_6)_2$ the vibrational bands belonging to $AAsF_6$ (A = K–Cs) could be easily observed, while $Ni(AsF_6)_2$ could not be detected,

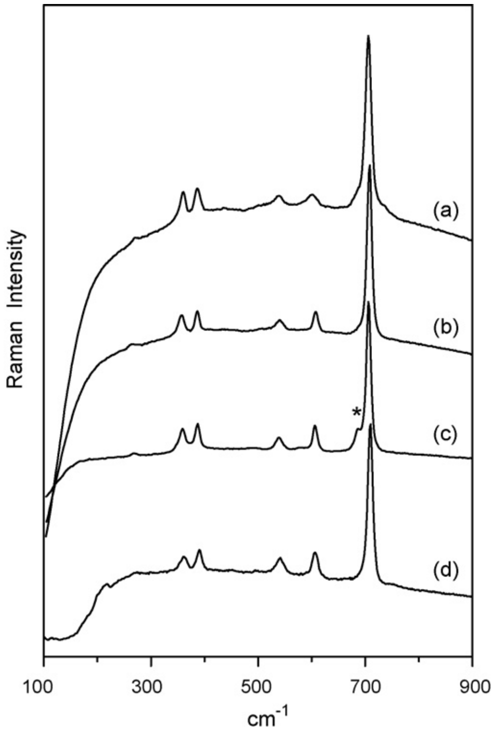

Fig. 3. Raman spectra of $H_3ONi(AsF_6)_3$ (a), $NH_4Ni(AsF_6)_3$ (b), $NONi(AsF_6)_3$ (c), and $O_2Ni(AsF_6)_3$ (d) in the 100–900 cm^{-1} range where vibrations belonging to anionic part, i.e. $[AsF_6]^-$, are found. The asterisk (*) denotes band that could be assigned to $NOAsF_6$.

Table 2
Raman spectra of $ANi(AsF_6)_3$ compounds ($A = H_3O^+, K^+, O_2^+, NO^+, NH_4^+, Rb^+, Cs^+$).

$H_3ONi(AsF_6)_3$	$KNi(AsF_6)_3$	$O_2Ni(AsF_6)_3$	$NONi(AsF_6)_3$	$NH_4Ni(AsF_6)_3$	$RbNi(AsF_6)_3$	$CsNi(AsF_6)_3$	Assig.[a]
				3244(3)			$\nu(NH_4^+)$
			2338(40)				$\nu(NO^+)$
		1866(40)					$\nu(O_2^+)$
707(100)	707(100)	709(100)	706(100)	708(100)	705(100)	707(100)	ν_1
601(10)	609(12)	607(10)	607(10)	608(10)	610(10)	606(18)	ν_2
540(5)	543(8)	542(5)	540(5)	541(5)	540(9)	548(10)	ν(As–F–Ni)
386(7)	388(25)	391(10)	387(10)	387(10)	385(25)	387(22)	ν_5
359(10)	359(20)	362(5)	359(5)	357(8)	356(23)	355(15)	ν_5
	272(1)			264(1)	263(0.2)		
215(5)		216(5)					
207(5)							

[a] Assignments are made for octahedral symmetry although in the solid state the actual symmetry is lower.

due to the overlap of its vibrational bands with that of $ANi(AsF_6)_3$ compounds. The second reason is that $Ni(AsF_6)_2$ usually gives very poor Raman spectra.

As previously found for other H_3O^+ salts [34], the bands due to the H_3O^+ were not observed in Raman spectra owing to their low intensity and broadness. For $NH_4Ni(AsF_6)_3$ only medium weak band at 3243 cm^{-1} was observed. It belongs to cationic part, i.e. to tetrahedral NH_4^+ and it could be assigned to symmetrical stretching ν_1' [14]. Other three Raman active vibrations could not be detected.

For $NONi(AsF_6)_3$ and $O_2Ni(AsF_6)_3$, strong bands at 2338 and 1866 cm^{-1}, respectively, were observed. They are characteristic for NO^+ and O_2^+ cations, respectively (Tables 3 and 4).

In the Neil Bartlett's paper about the nature of O_2RhF_6 [11] it was already pointed out that, on the basis of vibrational frequency of O_2^+, is possible to judge about the nature of interactions between O_2^+ cation and the anionic part of the compound. For example, in O_2RhF_6 and O_2SbF_6 the vibrational bands belonging to O_2^+ are found at 1825 and 1861 cm^{-1}, respectively, whereas the value for gaseous O_2^+ is equal to 1876.4 cm^{-1} and for neutral O_2 to 1580 cm^{-1}. This data hints that O_2SbF_6 is fully ionic, while the decrease of 36 cm^{-1} in O_2RhF_6 could mean that more than 10% of the O_2 species could be neutral at any instant [11]. In $O_2Ni(AsF_6)_3$, the value of $\nu(O_2^+)$ is found at 1866 cm^{-1} which is according to the literature data (Table 3) one of the highest known values, which is only 10 cm^{-1} lower than value for free O_2^+. That confirms that character of interactions between O_2^+ and the rest of the crystal lattice is completely ionic.

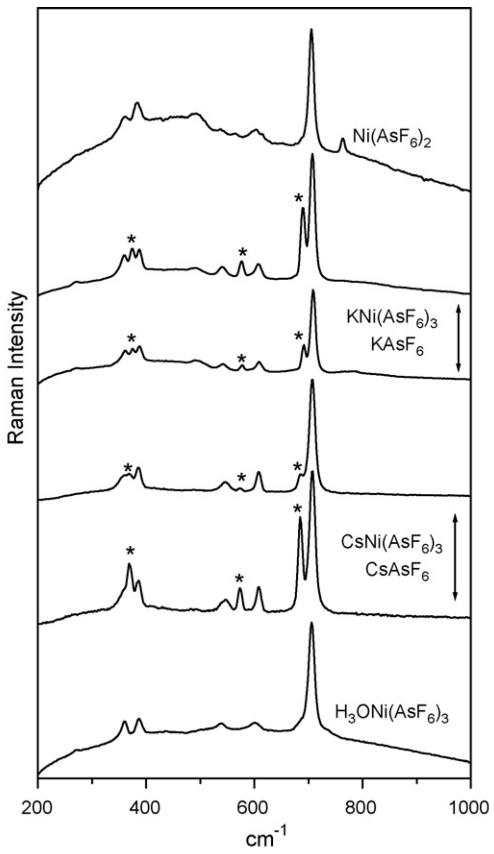

Fig. 4. Raman spectra of the powdered products of reactions between $AAsF_6$ (A = K, Cs) and $Ni(AsF_6)_2$ recorded on different spots of the same sample and the Raman spectra of pure $Ni(AsF_6)_2$ and $H_3ONi(AsF_6)_3$. The asterisk (*) denotes bands that could be assigned to $KAsF_6$ or $CsAsF_6$, respectively.

Table 3
Vibrational data for $\nu(O_2^+)$ for different dioxygenyl fluoro-salts together with values for free O_2^+ and for free neutral O_2.

O_2^+–salt[a]	$\nu(O_2^+)$	Ref.
Free O_2	1580	[11]
$(O_2)_2NiF_6$	1801	[15]
$(O_2)_2MnF_6$	1805	[15]
$(O_2)_2PdF_6$	1820	[2]
O_2RhF_6	1825	[16]
O_2AuF_6	1837	[7]
$O_2Mn_2F_9$	1838	[9]
O_2RuF_6	1838	[16]
O_2PtF_6	1838	[16]
$O_2V_2F_{11}$	1839	[17]
O_2BiF_6	1849	[16]
O_2GeF_5	1849	[18]
$O_2Bi_2F_{11}$	1853	[19]
O_2NbF_6	1853	[19]
$(O_{2)2}Ti_7F_{30}$	1857	[12]
O_2AsF_6	1858	[16]
$O_2Nb_2F_{11}$	1858	[16]
$O_2Ta_2F_{11}$	1858	[16]
O_2BF_4	1860	[b]
O_2SbF_6	1861	[16]
$(O_2)_2Hg_2F(SbF_6)_5$	1863	[20]
$O_2Sb_2F_{11}$	1864	[16]
$O_2Ni(AsF_6)_3$	1866	[c]
Free O_2^+	1876.4	[11]

[a] Data are from Raman spectra.
[b] Raman data are from this work. Infrared data (1863/1865 cm^{-1}) were reported in Ref. [21].
[c] This work.

The relationship between O_2^+ stretching frequency and the ionic nature of the salt (i.e. the influence of Lewis basicity of the anion) can be treated in terms of molecular orbital theory. In the case of diatomic oxygen species (O_2^+, O_2, O_2^-, O_2^{2-}) it is known that, as the bond order decreases, the bond distances increases, the bond energy decreases, and the vibrational frequency decreases, i.e. $\nu(O_2^+) > \nu(O_2) > \nu(O_2^-) > \nu(O_2^{2-})$ [27]. The lengthening of the O–O bond (and decreasing of $\nu(O_2^+)$) in O_2^+ salts is caused by donation of electron density from the HOMO of the anion to the

Table 4
Vibrational data for $\nu(NO^+)$ for different nitrosyl fluoro-salts.

NO^+–salt[a]	$\nu(NO^+)$	Ref.
$(NO)_3CrF_6$	2290	[22]
$(NO)_2RuF_6$	2311	[22]
$(NO)_2RhF_6$	2312	[22]
$(NO)_2PdF_6$	2312	[22]
$(NO)_2CrF_6$	2312	[22]
$(NO)_2IrF_6$	2315	[22]
$(NO)_2PtF_6$	2316	[22]
$NOUF_7$	2318/2320	[23]
$(NO)_2NbF_7$	2322	[22]
$(NO)_2TaF_7$	2324	[22]
$(NO)_2WF_8$	2324	[22]
$NOAuF_6$	2326	[22]
$NOReOF_6$	2327	[24]
$NORhF_6$	2328	[22]
$NOReF_8$	2328	[24]
$NOMoF_7$	2328	[22]
	2330/2325	[23]
$NOWF_7$	2327/2330	[22]
$NOMoF_6$	2330	[22]
$NOReF_6$	2330	[22]
$NORuF_6$	2330	[22]
$NOPtF_6$	2332	[22]
$NOIrF_6$	2334	[22]
$NOOsF_6$	2334	[22]
$NO[B(CF_3)_4]$	2337	[25]
$NONi(AsF_6)_3$	2338	[b]
$NOTaF_6$	2339	[22]
$NOPF_6$	2339	[22]
$NOAsF_6$	2339	[22]
$NOBiF_6$	2339	[22]
$NONbF_6$	2340	[22]
$NOBF_4$	2340	[26]
$NOSbF_6$	2342	[16]

[a] Data are from Raman spectra.
[b] This work.

LUMO and/or related low lying orbitals of cation. Although, due to his smaller volume, the $[BF_4]^-$ anion is much better Lewis base than many of the $[MF_6]^-$ anions [28], its O_2^+ salt has one the highest value for O–O stretch (Table 3). The same behaviour is evident also for NO^+ salts (Table 4). The satisfying explanation for high values for $\nu(O_2^+)$ and $\nu(NO^+)$ found in O_2BF_4 and $NOBF_4$, respectively, is still missing.

3. Conclusions

The size of the H_3O^+ is roughly comparable to that of K^+, while O_2^+ and NO^+ are slightly bigger. For the NH_4^+ cation it was reported that its size is close to Rb^+ [29–31,34]. On the basis of these facts it is not surprising that beside $H_3ONi(AsF_6)_3$ also other $ANi(AsF_6)_3$ compounds with different single charged cations ($A = O_2^+$, NO^+, NH_4^+, K^+, Rb^+, Cs^+) can be prepared without destroying the basic structure motif of $H_3ONi(AsF_6)_3$. Additionally, it was found that alkaline cations smaller than K^+ (i.e. Li^+ and Na^+) cannot stabilize the tri-dimensional network of $ANi(AsF_6)_3$ compounds, which consists from rings of NiF_6 octahedra sharing apexes with AsF_6 octahedra.

4. Experimental

4.1. Apparatus and reagents

Volatile materials (anhydrous HF, F_2) were handled in a nickel vacuum line and an all PTFE vacuum system equipped with PTFE valves as previously described [32]. The manipulation of the non-volatile materials was done in a dry box (M. Braun, Germany). The residual water in the atmosphere within the dry-box never exceeded 2 ppm. The reactions were carried out in FEP (tetrafluoroethylene-hexafluoropropylene; Polytetra GmbH, Germany) reaction vessels (height 250–300 mm with inner diameter 15.5 mm and outer diameter 18.75 mm) equipped with PTFE valves [33] and PTFE coated stirring bars. Prior to their use all reaction vessels were passivated with elemental fluorine (Solvay Fluor and Derivate GmbH, Germany). BF_3 (Union Carbide Austria, 99.5%), NiO (Ventron, 99%), NiF_2 (Ventron), NH_4F (Merck), LiF (Merck, 99.9%), NaF (Merck, 99%), KF (Ventron, 99.9%), RbF (Aldrich, 99%), CsF (Aldrich, 99.9%) were used as supplied. H_3OAsF_6 [34], O_2AsF_6 [35], and $Ni(AsF_6)_2$ [36] were prepared as described previously. $NOAsF_6$ and NH_4AsF_6 have been synthesized using NOF or NH_4F, respectively, with the excess of AsF_5 [37] in anhydrous hydrogen fluoride. Anhydrous HF (Fluka, Purum) was treated with K_2NiF_6 (Ozark Mahoning) for several hours prior to use.

O_2BF_4 was prepared by photochemical reaction [38,39] between O_2, BF_3 and F_2 (~1.2 mmol each) in aHF as a solvent. After 12 h of intense stirring, the volatiles were pumped off at 253 K. Colorless solid precipitate from colorless transparent solution. The Raman spectrum of isolated solid (O_2BF_4: 1860(100), 1048(5), 1008(5), 767(100), 727(3), 354(90) cm^{-1}), recorded at ambient temperature, was in agreement with the formation of $[BF_4]^-$ salt [40].

4.2. Raman spectroscopy

Raman spectra were recorded (10–20 scans) on a Renishaw Raman Imaging Microscope System 1000, with the 632.8 nm exciting line of a He–Ne laser (50 mW) with a resolution of 2 cm^{-1}.

4.3. Powder X-ray diffraction photographs

X-ray powder diffraction photographs were obtained using the Debye-Scherrer technique with Ni-filtered Cu Kα radiation. Samples were loaded into quartz capillaries (0.3 mm) in a dry-box. Intensities were estimated visually.

4.4. Synthesis of $H_3ONi(AsF_6)_3$

NiO 0.097 g (1.30 mmol) was loaded in a reaction vessel in a glove-box. aHF (3 ml) and 1 g (5.88 mmol) AsF_5 were condensed onto the reaction mixture and the reaction vessel was brought to room temperature. NiO dissolved in aHF to give a yellow solution. The reaction mixtures were left stirring for few hours at room temperature. Volatiles were slowly pumped off at room temperature for few hours, leaving yellow solid (final mass of $H_3ONi(AsF_6)_3$: 0.818 g; expected on the basis of NiO: 0.840 g). Raman spectrum was recorded and X-ray powder diffraction pattern was taken. Chemical analysis of $H_3ONi(AsF_6)_3$ was done (Found: %Ni = 9.7, %F = 51.6, %As = 34.8; Calculated: %Ni = 9.11 %F = 53.07, %As = 34.88).

4.5. Synthesis of $O_2Ni(AsF_6)_3$

A mixture of $Ni(AsF_6)_2$ 0.666 g (1.53 mmol) and O_2AsF_6 0.338 g (1.53 mmol) was loaded in a reaction vessel in a glove-box. aHF (5 ml) was condensed onto the reaction mixture and the reaction vessel was brought to room temperature. Clear yellow solution was obtained. Reaction vessel was cooled down to 77 K in liquid nitrogen. Beside yellow frozen solution, two rings (orange and blue-violet) formed on the inner walls of reaction vessel. When reaction was warmed again to ambient temperature, rings disappeared and only clear yellow solution was visible. Volatiles were slowly pumped off at room temperature for few hours, leaving yellow solid (final mass of isolated product: 0.831 g. Raman spectrum was recorded and X-ray powder diffraction pattern was taken.

4.6. Syntheses of $NONi(AsF_6)_3$

A mixture of $Ni(AsF_6)_2$ 0.665 g (1.52 mmol) and $NOAsF_6$ 0.333 g (1.52 mmol) was loaded in a reaction vessel in a glove-box. aHF (5 ml) was condensed onto the reaction mixture and the reaction vessel was brought to room temperature. A clear yellow solution was obtained. The reaction mixture was left stirring for few hours at room temperature. Volatiles were slowly pumped off at room temperature, leaving behind yellow solid (final mass of $NONi(AsF_6)_3$: 0.999 g. Raman spectrum was recorded and X-ray powder diffraction pattern was taken. Chemical analysis of $NONi(AsF_6)_3$ was done (Found: %Ni = 9.4, %F = 51.6, %As = 33.4; Calculated: %Ni = 8.96 %F = 52.18, %As = 34.29).

4.7. Syntheses of $NH_4Ni(AsF_6)_3$

$Ni(AsF_6)_2$ 0.207 (1.00 mmol) and NH_4AsF_6 0.437 g (1.00 mmol) were loaded in a separate arms of double T-shaped apparatus. After aHF (5 ml) was condensed onto the $Ni(AsF_6)_2$ and the reaction vessel was brought to room temperature clear yellow solution was obtained. The later was poured onto NH_4AsF_6. After 6 days, clear yellow solution was present above insoluble solid. Solution was poured away and aHF condensed back. This time all remaining stuff dissolved. Volatiles were slowly pumped off at room temperature, leaving behind yellow solid (final mass: 0.581 g). X-ray powder diffractions pattern was taken. Attempts to record Raman spectra of powdered material have been unsuccessful due to the strong fluorescence of measured sample. Chemical analysis of was done (Found: %Ni = 9.0, %F = 52.5, %As = 36.8(8); Calculated: %Ni = 9.12 %F = 53.15, %As = 34.93).

4.8. Reactions between $AAsF_6$ and $Ni(AsF_6)_2$ (A = Li, Na, K, Rb, Cs)

Appropriate mixtures of AF (A = Li, Na, K, Rb, Cs) and NiF_2 were loaded in a reaction vessel in a glove-box (Table 5). aHF (5–8 ml) and AsF_5 (3–5 mmol) were condensed onto the reaction mixture and the reaction vessel was brought to room temperature. With the presence of AsF_5 the corresponding $AAsF_6$ and $Ni(AsF_6)_2$ were formed in situ.

In all cases insoluble material was observed beside clear yellow solution. After 4 days volatiles were slowly pumped off at room temperature, leaving behind yellow solids. Raman spectra were recorded and X-ray powder diffractions pattern were taken.

4.9. Crystal growth of $ANi(AsF_6)_3$ (A = H_3O^+, O_2^+, NO^+, NH_4^+ and K^+)

In a general procedure, single crystals growth was carried out in a double T-shaped apparatus consisting of two FEP tubes (19 mm o.d., and 6 mm o.d.). Starting $ANi(AsF_6)_3$ (A = H_3O^+, O_2^+, NO^+, NH_4^+) compounds (approximately 200–400 mg for H_3O^+, O_2^+, NO^+, and 70 mg for NH_4^+) and products of reactions between AF (A = Li–Cs) and NiF_2 in aHF/AsF_5 (200–300 mg) were loaded into the wider arm of the crystallization vessel in a dry-box. aHF (~4–8 ml) was then condensed onto the starting material at 77 K. The crystallization mixtures were brought up to ambient temperature and the clear solutions, which had developed, were decanted into the narrower arm. The evaporation of the solvent from these solutions was carried out by maintaining a temperature gradient corresponding to about 10 K between both tubes for 2–4 weeks. The effect of this treatment was to enable aHF to be slowly evaporated from narrower into wider tube leaving the crystals. Yellow-orange single crystals of $ANi(AsF_6)_3$ (A = H_3O^+, O_2^+, NO^+, NH_4^+) were grown from clear yellow solutions of corresponding $ANi(AsF_6)_3$ compounds. In the case of products of reactions between AF (A = Li, Na, Rb and Cs) and NiF_2 in aHF acidified with AsF_5, only colorless crystals of $AAsF_6$ and yellow powdered material were obtained. In the case of potassium, large (to 3 cm long) needle shaped $KAsF_6$ crystals were formed. Additionally, small yellow single crystals of $KNi(AsF_6)_3$ were found among polycrystalline material. Selected single crystals of $ANi(AsF_6)_3$ (A = H_3O^+, O_2^+, NO^+, NH_4^+, K^+) were placed inside 0.3 mm quartz capillaries in a dry-box and their Raman spectra recorded.

Crystallization products were immersed in a perfluorinated oil (ABCR, FO5960, melting point 263 K) in a dry-box. Single crystals were then selected from the crystallization products under the microscope (at temperatures between 265 and 273 K) outside the dry-box and then transferred into the cold nitrogen stream of the diffractometer.

4.10. X-ray structure determinations

Single-crystal data were collected on a Mercury CCD area detector coupled to a Rigaku AFC7S diffractometer using monochromatized Mo Kα radiation. Data were corrected for Lorentz, polarization, and absorption effects and processed using Rigaku CrystalClear software suite program package [41]. All structures were solved by direct methods using SIR-92 [42] program and refined with SHELXL-97 [43] software, implemented in program package TexSan [44].All attempts to localize the positions of hydrogen atoms in the crystal structure of $H_3ONi(AsF_6)_3$ from difference Fourier maps were unsuccessful. Taking into account the geometry of H_3O^+ cation, and the presence of six fluorine atoms around oxygen at short distances (2.64(1)–281.1(9) pm), the most probable positions (each hydrogen participates in the formation of two hydrogen bonds) of H atoms were calculated. Before the final refinement geometrical and thermal parameters of H atoms were fixed (isotropical thermal parameters of hydrogen atoms were set as 1.2 equiv. thermal parameter of O).

In the case of $O_2Ni(AsF_6)_3$ compound, the ordered model of O_2^+ unit located on an mirror symmetry plane, was found by direct methods. Refinement of this model led to extremely short O–O distance and enormously high thermal parameters. Splitting of each oxygen positions on two positions (on both sides of mirror plane) with the occupancy 1/2 improved the refinement results, resulting in more adequate O–O distance and lower thermal parameters of oxygen atoms.

Table 5
Experimental conditions for the reactions between $AAsF_6$ (A = Li–Cs) and $Ni(AsF_6)_2$ in aHF.

	Starting compounds				Mass balance		Final product
	AF		NiF_2		Calculated (g)	Obtained (g)	
	g	mmol	g	mmol			
Li	0.021	0.83	0.08	0.83	0.522	0.517	$LiAsF_6/Ni(AsF_6)_2$
Na	0.028	0.67	0.065	0.67	0.435	0.368	$NaAsF_6/Ni(AsF_6)_2$
K	0.049	0.83	0.081	0.83	0.554	0.572	$KAsF_6/Ni(AsF_6)_2/KNi(AsF_6)_3$
Rb	0.073	0.70	0.068	0.70	0.498	0.470	$RbAsF_6/Ni(AsF_6)_2/RbNi(AsF_6)_3$
Cs	0.100	0.66	0.064	0.66	0.500	0.518	$CsAsF_6/Ni(AsF_6)_2/CsNi(AsF_6)_3$

In the structure of $NONi(AsF_6)_3$ the NO moiety appeared to be disordered. The nitrogen atom was located on a special position on a mirror plane, and O atom was split on two positions with the 1/2 occupancy.

Because of poor quality of $NH_4Ni(AsF_6)_3$ crystals only lattice parameters were determined.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jfluchem.2009.01.003.

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