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**OXIDATION OF FIRST ROW TRANSITION ELEMENTS WITH
AsF₅ IN AsF₃ AT AMBIENT TEMPERATURE: SYNTHESSES AND
STRUCTURES OF M(AsF₆)₂·2AsF₃, M = Fe, Co, Ni[†]**

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Abstract

A novel synthetic approach *via* reactions between pure metals (Cr, Mn, Fe, Co, Ni, Cu) and AsF₅ in AsF₃ as a solvent has been investigated. AsF₅ proved to oxidize these metals to their (+2) oxidation state. In the case of Cr, Mn or Cu the same compounds as those in the superacidic systems MF₂-AsF₅-aHF (anhydrous hydrogen fluoride) were obtained: CrFAsF₆, Mn(AsF₆)₂, and CuFAsF₆, respectively. In the case of Fe, Co and Ni a new type of fluoroarsenates has been isolated: M(AsF₆)₂·2AsF₃. The latter compounds are isostructural and crystallize in the monoclinic space group P2₁/n (no. 14) with Z=2. Unit cell dimensions of Fe(AsF₆)₂·2AsF₃ are: a = 733.8(4) pm, b = 1303.0(8) pm, c = 735.4(5) pm, β = 91.43(7)° at 292 K, and for Co(AsF₆)₂·2AsF₃: a = 725.9(4) pm, b = 1292.9(7) pm, c = 727.6(5) pm, β = 91.64(5)° at 288 K. The structure is characterized by layers formed through transcoordinating AsF₆ units in the basal plane of the octahedron about the transition metal. Both apical positions of this octahedron are occupied by AsF₃ molecules. A main feature of the layers are characteristic rings resulting from the apex-sharing connectivity of AsF₆ and MF₆ octahedra. As AsF₃ molecules of neighbouring layers are localized above and below the center of a particular ring, a stacking sequence ABAB... results.

Introduction

The most common method for the synthesis of metal(II)hexafluoroarsenates are reactions between MF₂ and excess of AsF₅ in aHF [1,2]. AsF₅ proved to be a strong enough fluorinating agent to bring about the *in-situ* synthesis of some metal(II)fluorides *via* the reaction between the respective metal and AsF₅ in aHF. As by-product AsF₃ is produced by these reactions. In order to have as clean a system as possible it was

[†] Dedicated to the memory of Prof. Dr. Jože Šiftar

decided to investigate aforementioned reactions between first row transition metals and AsF_5 in AsF_3 as a solvent. In the past AsF_3 has rarely been used as solvent in respective reactions, most characteristic examples are reactions of sulphur, selenium or tellurium with fluoro acids like AsF_5 or SbF_5 in AsF_3 [3-7]. In the current paper first results on reactions between some metals of the first transition series and AsF_5 in AsF_3 at ambient temperature are described.

Experimental

1. Apparatus, reagents and techniques. The reactions were carried out in PFA reaction vessels (16 mm i.d. x 19 mm o.d.) equipped with Teflon valves and Teflon coated stirring bars. The part of the vacuum line used for manipulation of volatile materials was made entirely from Teflon, FEP or PFA and equipped with a Monel Helicoid pressure gauge (0-1500 torr ($\pm 0.3\%$), Bristol Babcock). Nonvolatile materials were handled in the argon atmosphere of a drybox with maximum content of water vapours of 0.1 ppm (MBraun). Metals in all cases were fine powders and were used as supplied: chromium (BDH), manganese (Hopkin and Williams), iron (99.5%, Fluka), cobalt (-325 mesh, Alfa-Ventron), nickel (1 Φ m, Alfa-Ventron), and copper (BDH). AsF_5 was prepared by the reaction of As_2O_3 with elemental fluorine as described for the synthesis of PF_5 [8]. AsF_3 was prepared according to a modified literature procedure [9] by the reaction of As_2O_3 with aHF in a nickel reaction vessel at 120°C. The purity of AsF_5 and AsF_3 was checked by IR spectroscopy. FeF_2 and CoF_2 were prepared from respective chlorides in a flow of aHF at elevated temperatures [10]. SbF_3 was prepared from Sb_2O_3 and aqueous HF [11]. The purity of FeF_2 , CoF_2 and SbF_3 was checked by chemical analysis and X-ray powder diffraction patterns. SO_2 (Merck) was purified according to standard procedures. Fluorine (99.8%, Solvay) was used as supplied. Anhydrous HF (99.9%, Praxair) was treated with K_2NiF_6 for several days prior to use. Infrared spectra were taken in a 10 cm nickel cell with AgCl windows on an FTIR spectrometer (Perkin Elmer 1710). X-ray powder diffraction patterns were obtained with a General Electric camera with Straumanis loading using Cu-K_α radiation, and where high resolution was required on an image plate based Guinier camera (Huber) applying $\text{Co-K}_{\alpha 1}$ radiation.

2. Chemical analysis. After complete decomposition of the sample in an alkaline melt total fluoride ion content was determined with an ion selective electrode using ORION 960 Autochemistry System Analyser. The amount of free fluoride ions was measured

directly by selective electrode after hydrolysis of the sample in distilled water. Arsenic present as AsF_6^- species was determined gravimetrically as insoluble tetraphenylarsonium salt. Total amount of arsenic was determined by the ICP method. Transition metals were determined by complexometric titrations.

3. Reactions of Cr, Mn, Fe, Co, Ni and Cu with AsF_5 in AsF_3 . In a typical experiment few mmols of the particular metal were loaded into a PFA reaction vessel within the drybox. Then about 3-5 ml of AsF_3 and an excess of AsF_5 were added by condensation at 77 K on the vacuum system. Starting reaction conditions are shown in Table 1. All reactions were carried out at ambient temperature. Reactions are exothermic and all metals slowly start to dissolve. Reactions were finished in about twelve hours with the products being not completely dissolved. The colour of chromium reaction product was white with greenish tint. In the case of manganese the dense solution for several hours showed a red colour which later disappeared. The colour of the isolated compound was a very faint beige. In the case of iron the colour of solution was dark while the precipitate was grey. In the case of cobalt both the colour of solution and precipitate were a dark pink, while for nickel both phases showed a yellow-green. The colour of the copper compound was white. Finally volatiles were pumped away at room temperature, the pumping in dynamic vacuum being stopped when the change of weight was less than 5-10 mg/mmol?h. The largest vapour pressure created by decomposition was observed for the iron compound. The weight of reaction products is depicted in Table 1.

In the case of Cr, Mn and Cu the mass balance corresponded to CrFAsF_6 , $\text{Mn}(\text{AsF}_6)_2$ and CuFAsF_6 compounds, and X-ray powder diffraction patterns showed only the lines of these compounds [2,12]. The mass balances of iron (white beige), cobalt (pink) and nickel (light yellow) products corresponded to composition $\text{M}(\text{AsF}_6)_2 \cong 2\text{AsF}_3$. Data of chemical analyses for these compounds are shown in Table 2.

4. Reaction of $\text{Co}(\text{AsF}_6)_2$ with AsF_3 . $\text{Co}(\text{AsF}_6)_2$ was prepared by literature method [1] from CoF_2 and excess AsF_5 in aHF, and its purity was checked by X-ray powder diffraction pattern. Onto 1.3540 g (3.10 mmol) $\text{Co}(\text{AsF}_6)_2$ in a PFA reaction vessel excess of AsF_3 (15 mmol) was condensed at 77 K. Reaction was carried out at ambient temperature for five hours before excess of AsF_3 was pumped away till constant weight of the sample was reached (2.1040 g). Theoretical increase of the weight for the composition $\text{Co}(\text{AsF}_6)_2 \cdot 2\text{AsF}_3$ is 0.8179 g (obtained increase was 0.7500 g). X-ray powder diffraction pattern of the obtained reaction product showed only lines of $\text{Co}(\text{AsF}_6)_2 \cong 2\text{AsF}_3$.

Table 1. Starting Conditions for Reactions between M (M = Cr, Mn, Fe, Co, Ni, Cu) and AsF₅ in AsF₃, and Weights of Products

M	M		AsF ₅	AsF ₃	Weight of product (g)					
	g	mmol	mmol	ml	MFAsF ₆		M(AsF ₆) ₂		M(AsF ₆) ₂ ≅2AsF ₃	
					Calcd.	Found	Calcd.	Found	Calcd.	Found
Cr	0.2188	4.21	20	5	1.0937	1.1074				
Mn	0.1608	2.93	20	3			1.2667	1.2631		
Fe	0.1905	3.41	20	3					2.3790	2.3694
Co	0.2395	4.06	20	5					2.8468	2.8377
Ni	0.1410	2.40	20	3					1.6824	1.6801
Cu	0.2415	3.80	20	4	1.0315	1.1302				

Table 2. Chemical Analyses for M(AsF₆)₂≅2AsF₃ (M = Fe, Co, Ni)

	Calcd. (%)					Found (%)				
	M	AsF ₆	F _t	F _f	As	M	AsF ₆	F _t	F _f	As
Fe(AsF ₆) ₂ ≅2AsF ₃	8.00	54.17	49.03	16.34	42.96	8.8	57.0	48.8	15.0	39.9
Co(AsF ₆) ₂ ≅2AsF ₃	8.41	53.93	48.81	16.27	42.78	8.4	53.9	48.5	16.3	42.7
Ni(AsF ₆) ₂ ≅2AsF ₃	8.38	53.95	48.83	16.28	42.79	8.7	54.3	48.7	15.5	43.1

M = Fe, Co, Ni; F_t = total fluoride ion content; F_f = free fluoride ion content

5. Substitution reactions of M(AsF₆)₂·2AsF₃ (M = Co, Ni) with SbF₃ and SO₂. Onto the mixture of Co(AsF₆)₂·2AsF₃ (1.2069 g, 1.72 mmol) and SbF₃ (0.6113 g, 3.42 mmol) about 3 ml of AsF₃ were condensed at 77 K. The reaction was carried out at room temperature for one day. Then volatiles were pumped out and the weight of the obtained solid compound was 1.4324 g (calcd. weight for Co(AsF₆)₂·2SbF₃ is 1.3682 g). Chemical analysis showed: calcd. for Co(AsF₆)₂·2SbF₃: Co, 7.42; AsF₆, 47.57; Sb, 30.66; F_t, 14.35%; found: Co, 7.3; AsF₆, 43.0; Sb, 32.5; F_t, 16.4%. The weight of the obtained product from the analogous reaction between Ni(AsF₆)₂·2AsF₃ (1.9451 g, 2.78 mmol) and SbF₃ (1.0100 g, 5.65 mmol) in AsF₃ was 2.4388 g (calcd. weight for Ni(AsF₆)₂·2SbF₃ is 2.2278 g). Chemical analysis of this product showed: calcd. for Ni(AsF₆)₂·2SbF₃: Ni, 7.39; AsF₆, 47.58; Sb, 30.66; F_t, 14.36%; found: Ni, 7.1; AsF₆, 45.6; Sb, 30.0; F_t, 15.5%.

In respective reactions SO₂ acted both as reagent and as solvent. Onto 0.5417 g of Co(AsF₆)₂·2AsF₃ (0.77 mmol) about 5 ml of SO₂ were condensed at 77 K. At room temperature a red solution was obtained and reaction mixture was left for one day. Volatiles were separated by fractional condensation and eliminated AsF₃ was identified

by IR spectroscopy. The weight of the obtained solid compound was 0.4650 g (calcd. weight for $\text{Co}(\text{AsF}_6)_2 \cdot 2\text{SO}_2$ is 0.4350 g). The reaction between $\text{Ni}(\text{AsF}_6)_2 \cdot 2\text{AsF}_3$ (0.7663g, 1.09 mmol) and about 5 ml of SO_2 gave green-yellow solution. Again the release of AsF_3 was shown by IR spectra of volatiles. The weight of obtained solid compound was 0.6528 g (calcd. weight for $\text{Ni}(\text{AsF}_6)_2 \cdot 2\text{SO}_2$ is 0.6145 g). The IR spectra of $\text{M}(\text{AsF}_6)_2 \cdot 2\text{SO}_2$ ($\text{M} = \text{Co}, \text{Ni}$) confirmed the presence of SO_2 [13]. The colours of compounds containing SbF_3 and SO_2 are within slight variation of intensities the same as of respective AsF_3 compounds.

6. Preparation of single crystals of $\text{M}(\text{AsF}_6)_2 \cdot 2\text{AsF}_3$ ($\text{M} = \text{Co}, \text{Fe}$). Several attempts were made to prepare single crystals of $\text{M}(\text{AsF}_6)_2 \cdot 2\text{AsF}_3$ ($\text{M} = \text{Fe}, \text{Co}, \text{Ni}$) compounds using supersaturated solutions in AsF_3 , unfortunately without success. Solutions of these compounds in aHF were also not suitable for growing crystals as they are quickly solvolysed losing AsF_3 . Single crystals of $\text{Co}(\text{AsF}_6)_2 \cdot 2\text{AsF}_3$ were finally obtained from reaction between CoF_3 (0.96 g, 8.3 mmol), AsF_5 (7.68 g, 452 mmol), and aHF (0.35 g, 18 mmol) in a special stainless autoclave with a Teflon liner ($V = 9.2$ ml). The autoclave was heated for 18 days to 393 K, a temperature above the critical temperature of AsF_5 [14]. A homogeneous batch of pink crystals was obtained. Colourless single crystals of $\text{Fe}(\text{AsF}_6)_2 \cdot 2\text{AsF}_3$ were also prepared in a solvothermal reaction. FeF_2 (0.46 g, 4.90 mmol), AsF_5 (3.80 g, 224 mmol) and AsF_3 (2.11 g, 160 mmol) were heated in a stainless steel autoclave with a Teflon liner ($V = 6.0$ ml) at 383 K for five days. After isolation of the solid product some powder material was found, but majority was in the shape of well developed crystals.

7. Structural investigations. Crystals of $\text{Co}(\text{AsF}_6)_2 \cdot 2\text{AsF}_3$ and $\text{Fe}(\text{AsF}_6)_2 \cdot 2\text{AsF}_3$ are very sensitive even to traces of moisture. Therefore, they were selected in a drybox using a surgical microscope ($f = 300$ mm, Opton) and mounted into 0.3 mm quartz glass capillaries which were temporarily closed by Kel-F grease and later flame-sealed outside the drybox. Single crystal data for both compounds were collected on a diffractometer with an area detector (Stoe IPDS). Details of the diffraction experiments are given in Table 3. For crystallographic calculations the program systems SHELXTL-Plus [15] and SHELXL-97 [16] were used.

Table 3. Crystal Data and Structure Refinement for $\text{Fe}(\text{AsF}_6)_2 \cdot 2\text{AsF}_3$ and $\text{Co}(\text{AsF}_6)_2 \cdot 2\text{AsF}_3$.

empirical formula	$\text{Fe}(\text{AsF}_6)_2 \cdot 2\text{AsF}_3$	$\text{Co}(\text{AsF}_6)_2 \cdot 2\text{AsF}_3$
formula weight	697.53	700.61
crystal system	monoclinic	
space group	$\text{P}2_1/n$ (no. 14)	
a , pm	733.8(4)	725.9(4)
b , pm	1303.0(8)	1292.9(7)
c , pm	735.4(5)	727.6(5)
β , deg.	91.43(7)	91.64(5)
V , pm ³	$702.9(7) \cdot 10^6$	$682.6(7) \cdot 10^6$
Z	2	
T , K	292 ± 2	288 ± 2
$d_{\text{calc.}}$, g/cm ³	3.296	3.409
λ , pm	71.073	
μ , mm ⁻¹	10.612	11.081
2θ -range, deg.	6 – 51	8 – 55
reflections measured	3936	3671
independent refl., R_{int}	1183, 0.0326	1410, 0.0351
refinement method	full matrix least-squares on F^2	
extinction coeff.	-	0.002(2)
no. parameters	109	110
R indices (all data)	$R1 = 0.0364$, $wR2 = 0.0654$	$R1 = 0.0432$, $wR2 = 0.1023$
Goof	1.091	1.076

8. Description of the $\text{M}(\text{AsF}_6)_2 \cdot 2\text{AsF}_3$ ($\text{M} = \text{Co}, \text{Fe}$) structures. The compounds $\text{Co}(\text{AsF}_6)_2 \cdot 2\text{AsF}_3$ and $\text{Fe}(\text{AsF}_6)_2 \cdot 2\text{AsF}_3$ turned out to be isostructural. They crystallize in the monoclinic space group $\text{P}2_1/n$ (no. 14) with two formula units in the unit cell. Crystallographic data are given in Table 3, positional and isotropic displacement parameters for both compounds are given in Table 4, while interatomic distances and selected angles are compared in Table 5. Complete listings including anisotropic displacement parameters are available in supplementary material.

Table 4. Final Positional and Equivalent Displacement Parameters for $\text{Fe}(\text{AsF}_6)_2 \cdot 2\text{AsF}_3$ and $\text{Co}(\text{AsF}_6)_2 \cdot 2\text{AsF}_3$.

Atom	x	y	z	$U_{\text{eq}}(\text{pm}^2)^{\text{a}}$
Fe1	0	0	0	200(2)
Co1	0	0	0	219(2)
As1	0	0	0.5	267(2)
	0	0	0.5	271(2)
F1	0.0507(5)	0.0276(2)	0.2707(3)	449(7)
	0.0543(5)	0.0268(3)	0.2696(4)	411(8)
F2	0.0679(7)	0.1179(3)	0.5601(4)	826(14)
	0.0698(7)	0.1190(4)	0.5614(5)	648(12)
F3	0.2129(6)	-0.0432(4)	0.5373(4)	832(14)
	0.2157(5)	-0.0437(4)	0.5400(5)	649(13)
As2	0.5	0	0	251(2)
	0.5	0	0	257(2)
F4	0.2699(4)	0.0311(2)	-0.0505(4)	440(7)
	0.2677(4)	0.0319(3)	-0.0510(4)	404(8)
F5	0.4412(5)	-0.0498(3)	0.2033(4)	604(10)
	0.4408(4)	-0.0497(4)	0.2062(5)	560(11)
F6	0.5291(5)	0.1153(3)	0.0967(5)	643(10)
	0.5314(5)	0.1168(3)	0.0974(6)	592(10)
As3	-0.01517(9)	0.28179(4)	0.06135(8)	423(2)
	-0.01707(8)	0.28127(5)	0.05960(9)	406(2)
F7	-0.0475(5)	0.1568(2)	-0.0368(4)	450(7)
	-0.0518(5)	0.1548(3)	-0.0390(4)	423(7)
F8	-0.1522(6)	0.2544(2)	0.2368(5)	589(9)
	-0.1516(6)	0.2538(3)	0.2391(6)	549(10)
F9	0.1792(6)	0.2449(3)	0.1716(6)	666(10)
	0.1813(6)	0.2443(4)	0.1672(7)	615(11)

^a) U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table 5. Selected Interatomic Distances (pm) and Angles (deg.) for $\text{Fe}(\text{AsF}_6)_2 \cdot 2\text{AsF}_3$ and for $\text{Co}(\text{AsF}_6)_2 \cdot 2\text{AsF}_3$.

	$M = \text{Fe}$	$M = \text{Co}$
$M - \text{F1}$	204.8(3) 2x	202.0(3) 2x
– F4	206.4(3) 2x	203.1(3) 2x
– F7	208.9(3) 2x	205.4(4) 2x
As1 – F2	167.1(4) 2x	167.7(4) 2x
– F3	167.7(4) 2x	168.2(4) 2x
– F1	177.2(3) 2x	176.7(3) 2x
As2 – F6	167.4(3) 2x	168.1(4) 2x
– F5	169.5(3) 2x	169.8(3) 2x
– F4	176.7(3) 2x	176.5(3) 2x
As3 – F9	169.3(4)	168.8(4)
– F8	169.3(4)	169.1(4)
– F7	179.5(3)	180.1(3)
F1 – M – F4	89.4(1) 2x	89.0(1) 2x
F1 – M – F4'	90.6(1) 2x	91.0(1) 2x
F1 – M – F7	88.8(1) 2x	89.8(1) 2x
F4 – M – F7	86.7(1) 2x	87.1(1) 2x
As1 – F1 – M	148.4(2)	147.7(2)
As2 – F4 – M	146.4(2)	145.8(2)
As3 – F7 – M	144.6(2)	143.8(2)

As requested from the number of formula units the transition metal has to be located on a center of symmetry. The basic structural unit is depicted in Figure 1. Atoms As1 and As2 also occupy centers of symmetry resulting in an arrangement with rather high symmetry. Both AsF_6 octahedra about these arsenic atoms are bridging transition metal atoms through *trans* fluorine ligands. An immediate consequence of this particular arrangement is the formation of a layer composed from a square network. The interatomic distances between the transition metal center and its fluorine ligands within the layer are not significantly different within the error limits, but clearly all Fe-F distances are slightly longer than respective Co-F distances. The same holds for the

apical fluorine ligands which are provided by AsF_3 molecules. As indicated by their very similar functionality both crystallographically distinct AsF_6 octahedra in the structure exhibit no significant differences. Distances to non-bridging F atoms among AsF_6 octahedra are well within the typical range observed in isolated AsF_6 octahedra. Distances to bridging fluorines are considerably longer by about 10 pm, but with no difference for the Fe compound as compared to its Co relative. In all AsF_6 moieties no angle deviates by more than 0.6° from the ideal value of 90° while slightly larger deviations are observed for the metal octahedra. Most pronounced deviations are associated with the ligands donated by the solvent. While distances of non-bridging fluorine atoms in AsF_3 compare well with those in AsF_6 octahedra the bridging distances are longer by about 3 pm. The lone-pairs of the As(III) ions are directed towards the rather open ring centers in neighbouring layers. Finally this arrangement results in a ABAB... type stacking sequence (Figure 2 and Figure 3).

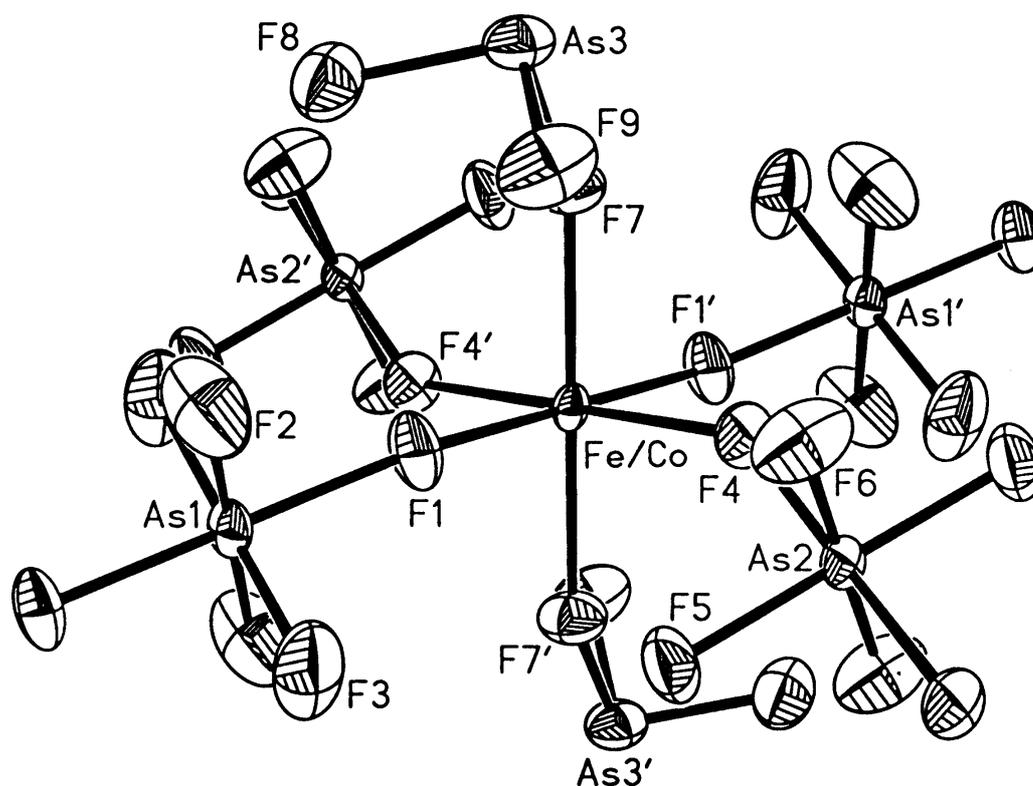


Figure 1. The environment of transition metal atoms in the $\text{M}(\text{AsF}_6)_2 \cdot 2\text{AsF}_3$ structure with the labelling scheme. The ellipsoids are drawn at the 40% probability level.

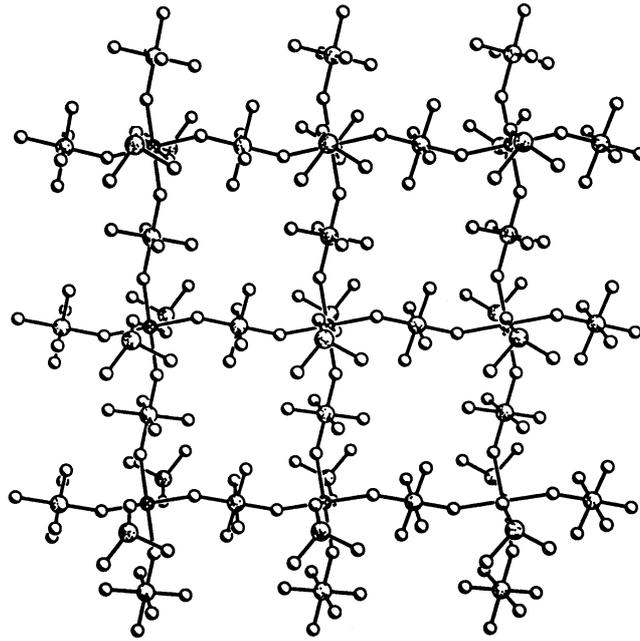


Figure 2. Part of the layer in the $M(\text{AsF}_6)_2 \cdot 2\text{AsF}_3$ structure showing the characteristic rings.

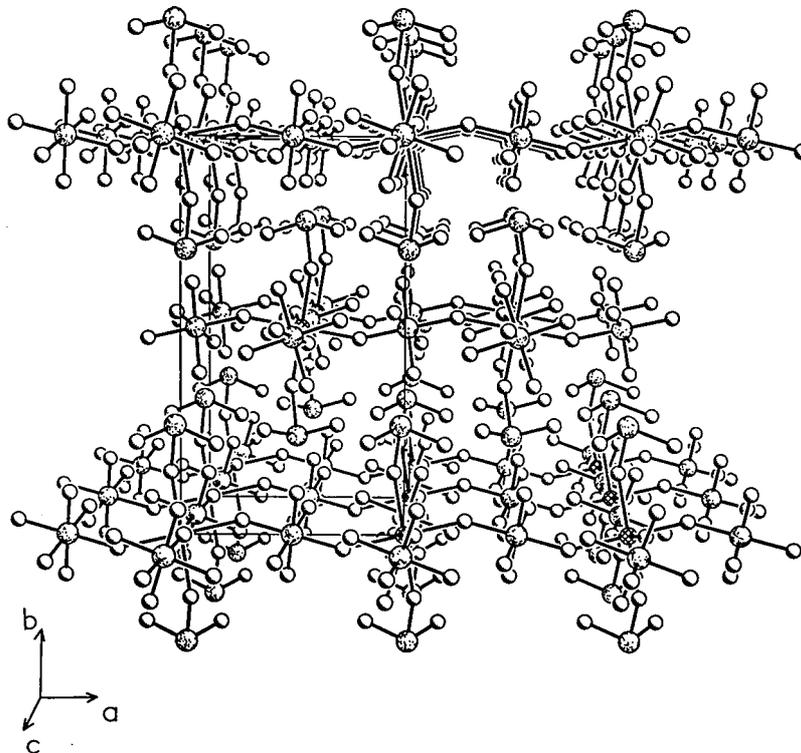
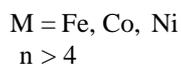


Figure 3. Part of the $M(\text{AsF}_6)_2 \cdot 2\text{AsF}_3$ type structure showing the stacking sequence of the layers and the unit cell.

Results and Discussion

1. Synthesis and some chemistry. Reactions between Cr, Mn, Fe, Co, Ni, Cu metals and AsF₅ in AsF₃ as a solvent gave solutions of solvated M²⁺ cations and AsF₆⁻ anions from which metal(II) hexafluoroarsenates were isolated at room temperature. In the case of Cr, Mn and Cu already known compounds CrFAsF₆, Mn(AsF₆)₂ and CuFAsF₆ were obtained [1,2,17]. In the case of Fe, Co and Ni two molecules of solvent as additional ligands were coordinated to the M(AsF₆)₂. These reactions proceed according to the equation:



The oxidation of some metals of the first row of transition elements with AsF₅ in other solvents, e.g. aHF [17] and SO₂ [18,19] has already been described. Lanthanoid metals can also be oxidised with AsF₅ in SO₂ [20], however the dissolution of some lanthanoid metals in aHF proceeds already in neat aHF leading to cations in low oxidation states (Eu²⁺, Yb²⁺, Sm²⁺) [17]. Preliminary experiments of oxidation of some lanthanoid metals with AsF₅ in AsF₃ have been carried out for comparison in the course of this work. The results show that compounds of the type Ln(AsF₆)₃·xAsF₃ (x = 2 and/or 3) may be obtained [21]. Novel approach in our work is to use AsF₃ as a solvent, a compound which is produced during these reactions. This method provides access to very clean products and can be especially useful in cases where possible higher oxidation states of the metals than (+2) have to be avoided.

The reactions of Mn, Fe, Co, Ni and Cu with AsF₅ in SO₂ gave in all cases compounds of the type M(AsF₆)₂·2SO₂ (Cr was not investigated). All compounds show considerable dissociation pressure at ambient temperature and already at 323 K hexafluoroarsenates without coordinated solvent were obtained [18]. However, M(AsF₆)₂·2SO₂ type compounds have been isolated at lower temperatures [13,19], and in the case of Co also Co(AsF₆)₂·4SO₂ was obtained [22]. With the exception of the latter compound [23], structures of these compounds are not known. Comparison of the results with those obtained in AsF₃ as a solvent shows that AsF₃ is a slightly weaker ligand than SO₂. In the case of Mn and Cu compounds without coordinated AsF₃ were isolated at room temperature, while for Fe, Co and Ni compounds with analogous composition (M(AsF₆)₂·2X, X = solvent molecule) exist in both solvents. Particular compositions and related structures are clearly driven by quite subtle effects, Cr(II) and

Cu(II) being particularly interesting due to pronounced Jahn-Teller effect usually observed with these ions. However, only the structure of CuFAsF_6 has been solved recently [24]. In the case of Fe only FeFAsF_6 and $\text{Fe}_2\text{F(AsF}_6)_3$ were described in the literature [2], but the structures are not known. $\text{Mn(AsF}_6)_2$ has a quite unique structure [12] which is clearly different from the yet unknown structure of the isostructural pair $\text{Co(AsF}_6)_2$ and $\text{Ni(AsF}_6)_2$ as indicated by X-ray powder diffraction patterns.

$\text{Co(AsF}_6)_2 \cdot 2\text{AsF}_3$ crystals were obtained by the reaction between CoF_3 and supercritical AsF_5 containing some aHF as catalyst. Possible route for AsF_3 formation is reduction of AsF_5 , which permanently diffused through a Teflon liner, on the metal walls of the protective vessel. Further it is known that in the presence of AsF_5 in aHF as a solvent Co(III) is reduced to Co(II) and elemental fluorine is obtained [25]. It was shown that $\text{Co(AsF}_6)_2 \cdot 2\text{AsF}_3$ may also be prepared by reaction of $\text{Co(AsF}_6)_2$ and AsF_3 . This implies that analogous reaction with isostructural $\text{Ni(AsF}_6)_2$ should also proceed. It was also found that $\text{M(AsF}_6)_2 \cdot 2\text{AsF}_3$ ($\text{M} = \text{Fe, Co, Ni}$) compounds solvolyze in aHF losing AsF_3 molecules. This is the reason why work in aHF with these systems always leads to compounds without coordinated AsF_3 , although it is always present as reaction product.

Further, we have been interested whether it is possible to exchange AsF_3 in $\text{M(AsF}_6)_2 \cdot 2\text{AsF}_3$ ($\text{M} = \text{Fe, Co, Ni}$) by some stronger ligands, e.g. by SbF_3 or SO_2 . The results show that it is possible to replace AsF_3 in $\text{M(AsF}_6)_2 \cdot 2\text{AsF}_3$ compounds with SbF_3 even in AsF_3 . So far only reactions with $\text{M} = \text{Co or Ni}$ have been carried out and new compounds $\text{Co(AsF}_6)_2 \cdot 2\text{SbF}_3$ and $\text{Ni(AsF}_6)_2 \cdot 2\text{SbF}_3$ were synthesized using this approach. It was also shown that AsF_3 is replaced by SO_2 in reactions of $\text{M(AsF}_6)_2 \cdot 2\text{AsF}_3$ ($\text{M} = \text{Co, Ni}$) in liquid SO_2 . The analogous, already known, compounds $\text{Co(AsF}_6)_2 \cdot 2\text{SO}_2$ and $\text{Ni(AsF}_6)_2 \cdot 2\text{SO}_2$ [13,19] were obtained. This confirms previous observations that SO_2 is coordinated more strongly than AsF_3 . Even more, in reactions where AsF_3 is formed as by-product, but which were carried out in SO_2 as a solvent, only adducts with SO_2 are isolated [20]. The dissolution of $\text{Fe(AsF}_6)_2 \cdot 2\text{AsF}_3$ in liquid SO_2 is quite vigorous even at temperatures below 273 K and only decomposition products without coordinating solvent have been identified.

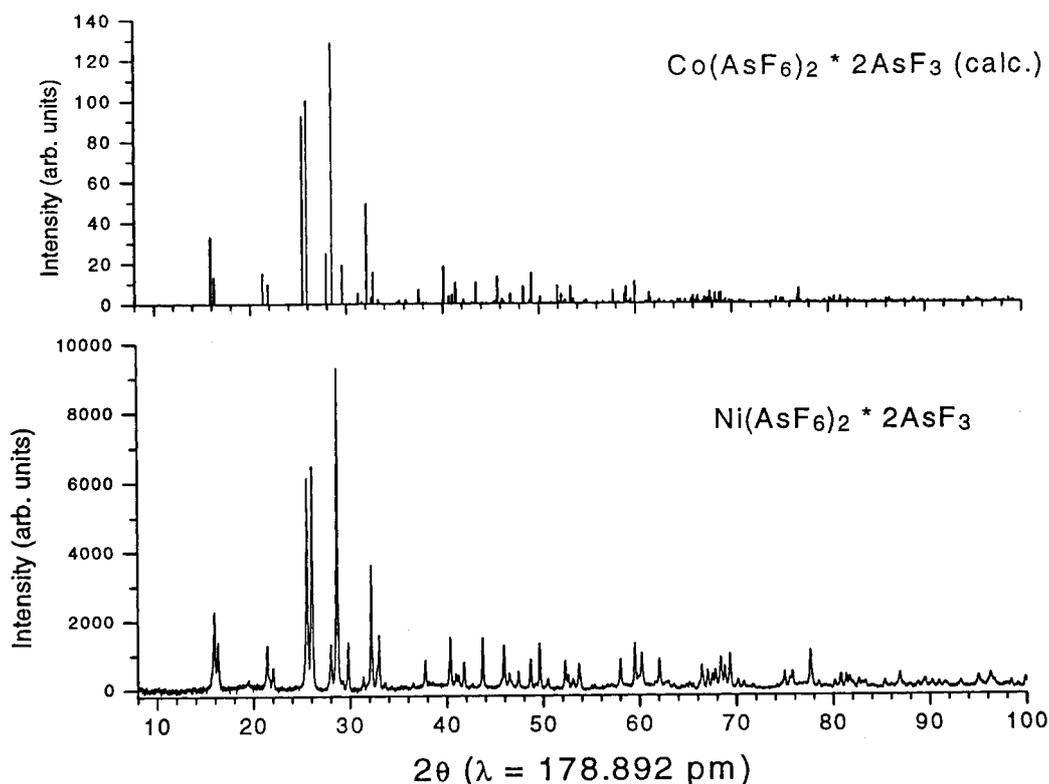


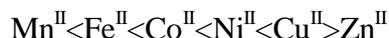
Figure 4. Powder pattern of Ni(AsF₆)₂·2AsF₃ obtained with an image plate based Guinier camera applying Co-K_{α1} radiation in comparison to the diagram of the Co analogue calculated from the refined single crystal structure.

2. Structure. X-ray powder diffraction diagrams of M(AsF₆)₂·2AsF₃ for the three isolated phases indicate that they are most likely isostructural with the size of the unit cell becoming smaller going from iron to cobalt and finally to the nickel compound. While the Fe and Co complexes are clearly isostructural as proved by respective single crystal structure determinations, due to special circumstances a slight uncertainty remains for the Ni analogue. As depicted in Figure 4 the observed powder pattern of the Ni compound very closely resembles the one calculated from the refined structural model of the Co analogue. Despite the narrow line width in connection with high resolution an unambiguous indexing is prevented by accidental overlapping of prominent lines. Most likely a- and c-axis of the unit cell are almost identical for the Ni compound. In connection with the monoclinic angle rather close to 90° this makes twinning most likely for this compound. Twinning was frequently observed even with the Fe and Co

compounds, thus hampering the structure solution for quite some time.

The characteristic rings within the infinite layers are well known with fluorides of octahedrally coordinated transition metals in particular with tetrafluorides. However, in the present structure all bridging fluorine ligands are replaced by AsF_6^- ions while the non-bridging apical positions are occupied by AsF_3 molecules. The rather special situation with the transition metal as well as the centers of the AsF_6^- ions on centers of symmetry directly relates the distance between neighbouring layers to the b-axis of the unit cell. On the other hand this parameter resembles quite directly the bonding of the AsF_3 which is clearly weaker for the Fe compound than in the Co compound. Well in accordance with this interpretation is the observation that the Fe complex loses AsF_3 quite readily. However, the Fe system is more complicated as $\text{Fe}(\text{AsF}_6)_2$ is not stable in dry unsolvated form. Unsolvated Fe^{2+} is probably a sufficiently powerful fluoride ion acceptor to take F^- from AsF_6^- in $\text{Fe}(\text{AsF}_6)_2$, which thus loses AsF_5 and finally FeFAsF_6 is formed.

The stabilities of corresponding complexes of divalent ions of the first transition series irrespective of the particular ligands involved, usually vary in the Irving-Williams [26] order which is the reverse of the order for the cation radii:



In the case of manganese only $\text{Mn}(\text{AsF}_6)_2$ is obtained while in the case of iron, cobalt and nickel the stability of these complexes is increasing in the same direction. In the case of copper the compound $\text{Cu}(\text{AsF}_6)_2$ is not formed even in solvated form in aHF acidified by AsF_5 .

The structure of $\text{Co}(\text{AsF}_6)_2 \cdot 2\text{AsF}_3$ is closely related to the structure of $\text{H}_3\text{OC}(\text{AsF}_6)_3$ [25] in the way that the AsF_3 ligands are replaced by bridging AsF_6^- ions. Of course, the now connected layers are stacked directly above one another and not shifted as in the $\text{M}(\text{AsF}_6)_2 \cdot 2\text{AsF}_3$ type compounds. On the other hand the open centers of the rings are forming channels in which the oxonium ions are located. Well in accordance with the above arguments this three-dimensional network shows typical features of an MX_3 type structure as indicated by the composition.

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Supplementary material. Further details on the crystal structures may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, upon quoting the numbers CSD-410833 (Fe-compound), CSD-410834 (Co-compound), names of the authors and journal citation.

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Povzetek

Oksidacija prehodnih elementov prve vrste z AsF_5 v AsF_3 kot topilu pri sobni temperaturi: sinteza in struktura $\text{M}(\text{AsF}_6)_2 \cdot 2\text{AsF}_3$, $\text{M} = \text{Fe, Co, Ni}$

Raziskali smo novo sintezno metodo – reakcije med nekaterimi kovinami (Cr, Mn, Fe, Co, Ni in Cu) in AsF_5 v AsF_3 kot topilu. Ugotovili smo, da AsF_5 oksidira kovine do oksidacijskega stanja (+2). V primeru Cr, Mn in Cu smo dobili enake spojine kot v superkislem sistemu $\text{MF}_2\text{-AsF}_5\text{-aHF}$ (aHF = brezvodni vodikov fluorid): CrFAsF_6 , $\text{Mn}(\text{AsF}_6)_2$ in CuFAsF_6 . V primeru Fe, Co in Ni pa smo sintetizirali nov tip heksafluoroarzenatov: $\text{M}(\text{AsF}_6)_2 \cdot 2\text{AsF}_3$. Te spojine so izostrukturane in kristalizirajo v monoklinski prostorski skupini $\text{P2}_1/\text{n}$ (št. 14) z $Z=2$. Dimenzije osnovne celice spojine $\text{Fe}(\text{AsF}_6)_2 \cdot 2\text{AsF}_3$ pri 292 K so: $a = 733,8(4)$ pm, $b = 1303,0(8)$ pm, $c = 735,4(5)$ pm, $\beta = 91,43(7)^\circ$, za spojino $\text{Co}(\text{AsF}_6)_2 \cdot 2\text{AsF}_3$ pri 288 K pa: $a = 725,9(4)$ pm, $b = 1292,9(7)$ pm, $c = 727,6(5)$ pm, $\beta = 91,64(5)^\circ$. Strukturo sestavljajo plasti dosežene s transkoordinacijo enot AsF_6 v osnovni ravnini oktaedra okoli prehodne kovine. Oba aksialna položaja v tem oktaedru sta zasedena z molekulama AsF_3 . Glavna značilnost posamezne plasti so obroči, sestavljeni iz oktaedrov AsF_6 in MF_6 , ki si delijo skupna oglišča. Molekule AsF_3 sosednjih plasti so lokalizirane nad in pod središčem posameznega obroča, zato je razvrstitev plasti v ABAB...skladu.