Acta Chim. Slov. **1999**, *46*(2), pp. 229-238

NOVEL SYNTHESES OF SOME BINARY FLUORIDES: THE ROLE OF ANHYDROUS HYDROGEN FLUORIDE *

Zoran Mazej, Karel Lutar and Boris Žemva
Jožef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia

(Received 3.4.1999)

Abstract

The novel syntheses of MnF_3, CoF_3, BiF_3, Pd_2F_6, PdF_4, LaF_3 and SmF_3, using the approach in liquid anhydrous hydrogen fluoride as a solvent at room temperature are described. Some advantages, like mild reaction conditions and purity of the reaction products, are discussed in comparison to the methods described so far for the syntheses of these binary fluorides.

Introduction

Anhydrous hydrogen fluoride (aHF) has a very important and versatile role in the syntheses of binary fluorides. It can be used as fluorinating agent, solvent, catalyst, protecting atmosphere, etc. Only a few of the binary fluorides can be prepared just by dissolving corresponding element in liquid aHF, in majority of cases elevated temperature and use of gaseous aHF are necessary. A lot of fluorination reactions of different starting compounds (e.g. oxides, halides, carbonates, etc.) with either pure aHF or its concentrated water solutions are described in the literature. Most of them proceed at higher temperatures.

Anhydrous HF has a very long usable redox potential range of about 4.5 V. This

---

*Dedicated to the memory of Prof. Dr. Jože Šiftar unique property makes it an excellent solvent for oxidative or reductive syntheses of binary fluorides at room and even lower temperatures. E.g., in liquid aHF elemental fluorine oxidizes AgF to AgF_2 [1], I_2 to IF_5 or IF_7 [2] and with KrF_2 tetrafluorides of terbium and praseodymium can be obtained from Tb_4O_7 and Pr_6O_{11} [3]. The reduction of hexafluorides of Mo, Re, Os and Ir in aHF by hydrogen or silicon leads to the corresponding pentafluorides or tetrafluorides [4,5]. Another approach for the preparation of binary fluorides in liquid aHF is their precipitation from corresponding anions with strong fluoride ion acceptors [6]. In this way some previously unknown compounds were prepared, e.g. AgF_3 [7], NiF_4 and NiF_3 [8] beside some already known compounds, like pentafluorides of Nb, Mo, W, and Os [9], and PdF_4 [10]. With the addition of fluoro bases to the aHF solutions of ternary compounds binary fluorides from corresponding cationic part are precipitated, e.g. PdF_2 from $Pd(SbF_6)_2$ solution [11]. The oxidation of MF_6^- anions (M = Pt, Ru) by solvated cationic Ni^{IV} and Ag^{III} species in aHF gives corresponding hexafluorides [12]. Solvolysis of some ternary compounds in aHF is also a route to binary fluorides, e.g. dissolutions of $XeF_2\mathbf{A}CrF_4$ or Na_2PrF_6 in aHF yield CrF_4 [13] and PrF_4 [14] respectively. Thermal decomposition of complex compounds which are stable in liquid aHF only at lower temperatures leads to very pure binary fluorides, e.g. MnF_4 [15]. Metathetic reactions could also be useful for the preparation of binary fluorides, e.g. mixing of solutions of K_2NiF_6 and $Ni(AsF_6)_2$ yields black precipitate of NiF_3 [8].

Catalytic influence of aHF in many syntheses is well known, e.g. at photochemical preparation of XeF_2 and XeF_4 [16]. Anhydrous HF is sometimes used to prevent the hydrolysis, e.g. in the preparation of pure anhydrous binary fluorides *via* removal of hydrated water at high temperatures from corresponding hydrated fluorides in the flow of gaseous aHF.

In this paper a few novel syntheses of already known compounds in aHF as a solvent are described.

Experimental part

1. Apparatus and reagents. A nickel vacuum line with a mechanical pump, a mercury diffusion pump, and soda lime scrubbers were used for the manipulation of volatile fluorides. The part of the vacuum line used for the transfer of aHF, AsF_5, and KrF_2 was made entirely from Teflon or FEP (tetrafluoroethylene-hexafluoropropylene copolymer) in order to diminish the corrosion and to avoid the formation of hydrogen. This part of the line was equipped with a Monel Helicoid pressure gauge (0-1500 Torr, ∀ 0.3%, Bristol Babcock. Inc.) connected to the line *via* Teflon valve. The manipulation of the nonvolatile materials was done in a drybox (MBraun). The residual water in the atmosphere within the drybox never exceeded 1 ppm. PFA (tetrafluoroethylene-perfluoroalkylvinylether copolymer) reaction vessels (16 mm i.d. x 19 mm o.d., V . 40 ml) equipped with Teflon valves and Teflon coated stirring bars were used for all experiments. Prior to their use the reaction vessels were passivated with elemental fluorine.

Anhydrous hydrogen fluoride (aHF) (Praxair, 99.9%) was treated with K_2NiF_6 for several days prior to use. Fluorine was used as supplied (Solvay, 99.98%). KrF_2 was prepared by the irradiation of a liquified mixture of fluorine and krypton with near-UV light at 77 K [17]. AsF_5 was prepared from As_2O_3 and fluorine as described for the syntheses of PF_5 [18]. K_2MnF_6 was prepared from a mixture of 9.00 mmol KF (0.523 g) (Merck, 99.9%) and 4.50 mmol MnF_2 (0.418 g) (Riedel - De Haën) which was loaded in a PFA reaction vessel in a drybox. After evacuation of the reaction vessel on a vacuum line, aHF (6 ml) and KrF_2 2.800 g (23 mmol) were condensed onto a mixture at 77 K. After warming to the room temperature the reaction was completed and clear orange solution was obtained. After the removal of aHF and gaseous decomposition products Kr and F_2, a yellow solid K_2MnF_6 was obtained (calcd. 1.112 g; found 1.109 g), what was confirmed by X-ray powder diffraction pattern. $Mn(AsF_6)_2$ was prepared from MnF_2 and AsF_5 as described previously [19]. CoF_2 was prepared from cobalt powder (Aldrich, 99.9%) and aHF in a flow reaction at 523 K [20]. Pd powder (Aldrich, 99.9%), and Bi powder (Alfa Johnson Matthey, 99.999%) were used as supplied. La_2O_3 (Koch Light Laboratories Ltd., 99.9 % (REO)) and Sm_2O_3 (Ventron, Alfa Products, 99.9 % (REO)) were heated prior to use at 1373 K for two hours in air to remove absorbed H_2O and CO_2 [21]. Chemical analysis of lanthanoid oxides on metals after the heating gave: La_2O_3: La, calcd: 85.27%, found: 85.4%; Sm_2O_3: Sm, calcd: 86.23%, found: 86.1%. Both oxides were characterized also by X-ray powder diffraction patterns.

2. Instrumentation. X-ray powder diffraction patterns were obtained by the Debye-Scherrer method using CuKα radiation on Seifert apparatus. Raman spectra were recorded on Renishaw Raman Imaging Microscope System 1000, with He-Ne laser with wavelength 632.8 nm.

3. Chemical analysis. After complete decomposition of the sample in alkaline melt total fluoride ion content was determined with an ion-selective electrode using ORION 960 Autochemistry System Analyser. Metals were determined by complexometric titrations.

4. Preparation of binary fluorides. Synthesis of MnF_3. For this experiment the reaction vessel was combined from two PFA tubes in a T-shape manner. In the dry-box 4.18 mmol (1.034 g) of K_2MnF_6 was loaded in one arm and 4.18 mmol (1.810 g) of $Mn(AsF_6)_2$ in the other arm. Then aHF was condensed onto both compounds at 77 K. After warming to room temperature colourless solution of $Mn(AsF_6)_2$ and red solution of K_2MnF_6 were obtained, both without any undissolved material. Then the solution of $Mn(AsF_6)_2$ was slowly poured onto the solution of K_2MnF_6 during simultaneous stirring. Red precipitate formed instantly and at the end of the reaction the solution was colourless. The precipitate was purified by decanting of the solution with $KAsF_6$ and back distilling of aHF. This procedure was repeated several times. During this separation always some losses of MnF_3 were observed due to incomplete sedimentation of MnF_3. Therefore, the weight of the obtained product did not correspond to calculated one. The purity of obtained MnF_3 was checked by X-ray powder diffraction pattern (the strongest lines of MnF_3 were only observed) and by chemical analysis (Table 2). The product in another arm was $KAsF_6$, as shown by X-ray powder diffraction pattern.

Syntheses of CoF_3, BiF_3, Pd_2F_6, PdF_4, LaF_3 and SmF_3. Particular starting materials were loaded in PFA reaction vessels in a drybox. Then aHF was condensed onto the solid at 77 K and reaction mixture was warmed to room temperature. The detailes of reaction conditions are given in Table 1. For the preparation of CoF_3, BiF_3 and Pd_2F_6 fluorine was slowly added at the room temperature to the final pressure in reaction vessel as given in Table 1. The excess of fluorine was cca 1.5 to 4. After reactions were completed, aHF and F_2 were removed and products of typical colours (light brown CoF_3, black Pd_2F_6 , grey-white BiF_3) were obtained. In the case of La_2O_3 or Sm_2O_3 reactions were carried out without the addition of elemental fluorine. After reactions were completed white LaF_3 and SmF_3 were isolated. For the preparation of PdF_4 krypton difluoride was added to the mixture of palladium and aHF immediately at 77 K. Already at 253 K yellow solution occurred and close to room temperature red solid started to precipitate. After one day

Table 1: Reaction conditions for the syntheses of CoF_3, BiF_3, Pd_2F_6, PdF_4, LaF_3 and SmF_3

Starting compound	Mass		aHF (ml)	P_{F2} (torr)	KrF_2 (g)	Time of reaction (days)	Final product
	(g)	(mmol)					
CoF_2	0.253	2.61	6	2000	-	4	CoF_3
Bi	1.040	4.98	10	6000	-	1	BiF_3
Pd	0.242	2.27	6	6500	-	7	Pd_2F_6
Pd	0.042	0.39	4	-	1.4	1	PdF_4
La_2O_3	0.206	0.63	7	-	-	4	LaF_3
Sm_2O_3	0.216	0.62	7	-	-	4	SmF_3

Table 2: Mass balances and chemical analyses of obtained binary fluorides

Compound	Mass balance		Chemical analyses			
	Calculated	Obtained	Calculated		Obtained	
	(g)	(g)	%M	%F	%M	%F
MnF_3	-	-	49.1	50.9	47.1	50.9
CoF_3	0.303	0.306	50.8	49.2	50.4	48.7
BiF_3	1.325	1.324	78.6	21.4	78.3	20.4
Pd_2F_6	0.371	0.401	65.1	34.9	63.9	34.6
PdF_4^*	0.071	0.083	-	-	-	-
LaF_3	0.247	0.247	70.9	29.1	70.6	29.0
SmF_3	0.257	0.257	72.5	27.5	72.2	27.5

* Not enough sample for chemical analysis.

aHF and gaseous decomposition products Kr and F_2 were removed. A brick-red solid PdF_4 was obtained.

Mass balances and chemical analyses of MnF_3, CoF_3, BiF_3, Pd_2F_6, PdF_4, LaF_3 and SmF_3 are collected in Table 2. All products with the exception of PdF_4 were confirmed by X-ray powder diffraction patterns. PdF_4 was poorly crystallised and, therefore, it was not possible to obtain X-ray powder diffraction pattern. The Raman spectra of PdF_4 and Pd_2F_6 were recorded.

Results and discussion

Three binary fluorides of manganese are known, MnF_2, MnF_3 and MnF_4. Preparations of MnF_3 may involve contaminations with MnF_2 or MnF_4, depending on the synthetic route. MnF_3 is usually prepared by flow fluorination of MnX_2 (X = F, Cl, I) at higher temperatures [22]. Other preparations include reactions between $Mn(IO_3)_2$ and BrF_3, where it is necessary to remove BrF_3 at high temperature (773 K) [22], and reactions of MnO or Mn_3O_4 with fluorine [22]. The metathetic reaction between Mn(II) and Mn(IV) ternary fluorides is based on the method used for synthesis of NiF_3 [8], and proceeds according to the equation:

$$Mn(AsF_6)_2 + K_2MnF_6 \xrightarrow[\text{R.T.}]{\text{aHF}} ?\ 2MnF_3 + 2KAsF_6$$

This reaction offers MnF_3 without MnF_2 and MnF_4 as impurities. However, possible impurity here is $KAsF_6$. Therefore thorough washing of MnF_3 precipitate with aHF, in which $KAsF_6$ is rather well soluble, is necessary. $(XeF_5)_2MnF_6$ is even better starting compound as K_2MnF_6, because XeF_5AsF_6 is much more soluble in aHF than $KAsF_6$. Chemical analysis of MnF_3 in Table 2 shows that some $KAsF_6$ can still be present in the sample, although X-ray powder diffraction pattern showed only the strong lines of MnF_3.

Reactions between CoF_2, Bi and Pd in aHF with excess of elemental fluorine proceed smoothly and the course of reactions was followed by changing of the colours of the solids where possible (starting compounds and products are not soluble in aHF), and by consumption of fluorine followed by the drop of its pressure. The mass balances and chemical analyses showed that obtained products are CoF_3, BiF_3 and Pd_2F_6 (Table 2). X-ray powder diffraction photographs showed only the lines attributed to these compounds.

The literature methods for the syntheses of above mentioned binary fluorides in all cases quote more severe conditions, e.g. temperatures above 473 K. Fluorination in liquid aHF is especially appropriate for the synthesis of BiF_3. With direct reaction of elements without the presence of aHF, BiF_5 is formed [23]. BiF_3 is usually prepared from Bi_2O_3 or BiOCl in aqueous HF [24, 25]. In this case water is a by-product and must be removed. Another problem can be the formation of bismuth oxide-fluorides [25]. The suggested methods for the preparation of Pd_2F_6 are reactions between $PdCl_2$ or $PdBr_2$ with BrF_3 and subsequent decomposition of PdF_3/BrF_3 adducts [26], or fluorination of palladium metal [27]. In the first case there is a problem of removing last traces of BrF_3. For the second reaction high temperature is needed and there is also a possibility that some PdF_4 will form.

Synthesis of PdF_4 requires fluorination of Pd_2F_6. For this reaction it is important that the starting compound is nearly amorphous [28], otherwise fluorination process is slow. The contamination with the starting compound may be avoided only by fluorination over a period of several days. More efficient preparation is the precipitation of PdF_4 with Lewis acids from PdF_6^{2-} salts [10]. In this case, similarly to the case of MnF_3, it is necessary to remove by-product. The course of the reaction between palladium and KrF_2 in aHF is similar to the one in the system MnF_2/KrF_2/aHF [15]. The reaction started to proceed already at lower temperatures (~253 K) with the formation of yellow-coloured solution, indicating that the adduct between PdF_4 and KrF_2 exists (PdF_6^{2-} ions are yellow). With further reaction the yellow soft-lumped material is formed. This intermediate adduct is thermally unstable, and close to room temperature, without the excess of KrF_2 decomposes to PdF_4, krypton and fluorine. At the end of reaction homogeneous brick-red PdF_4 and colourless solution are obtained. It was not possible to obtain X-ray powder diffraction pattern of isolated reaction product. In the Raman spectrum beside all characteristic bands of PdF_4 [29], the strongest band of Pd_2F_6 (565 cm^{-1}) was always present. This is in accordance with Bartlett [29] noticing that it is very difficult to prepare PdF_4 without Pd_2F_6 as an impurity. In the described method the reason for the partial formation of Pd_2F_6 can be the presence of insoluble soft-lumps, specifically lighter material then aHF, which covered some Pd_2F_6 and hindered further reaction. With the purpose of obtaining completely soluble intermediate products the reaction between Pd and KrF_2 in aHF was carried out with the addition of AsF_5. First completely clear green-blue solution of $Pd(AsF_6)_2$ was obtained [30], already below ambient temperature. The colour of this solution quickly turned to yellow which for a short period contained no solid residues. Obviously KrF_2 was able to oxidize cationic Pd^{2+} to PdF_6^{2-}. From this solution then brick-red solid started to precipitate owing to thermal decomposition of KrF_2/PdF_4 adduct. The formed PdF_4 is strong enough fluoro acid that it does not react with AsF_5 in aHF. The X-ray powder diffraction pattern of the isolated PdF_4 showed only the lines attributable to PdF_4. The Raman spectrum of the red solid material in aHF solution was without the strongest band for the Pd_2F_6, while the isolated PdF_4 showed this band again. Therefore, one can take into account also the possibility that PdF_4 decomposes in the laser beam.

There are previous reports about reactions between Ln_2O_3 and gaseous aHF, however, only at elevated temperatures (873-1073 K) [31, 32]. Our results show that reactions between some Ln_2O_3 (Ln = La, Sm) and liquid aHF can proceed at room temperature without the addition of fluorine, and that pure LaF_3 or SmF_3 form. Reactions of less basic representatives in the lanthanoid series are very slow and, therefore, the described approach is inconvenient in these cases.

Conclusions

The described syntheses of some binary fluorides (MnF_3, CoF_3, BiF_3, Pd_2F_6, PdF_4, LaF_3 and SmF_3) in aHF as a solvent at room temperature offer novel, milder approach for the formation of these compounds. All reactions were carried out in reaction vessels made of PFA, which is very resistant and inert material and therefore there is no danger of final product contamination by by-products formed between reagents and reaction vessel material. This possibility should be taken into account when metal reaction vessels and very high temperatures are involved. The advantages of reactions in solution are easier control of fluorination and homogeneous products with uniform particle sizes. Metathetic reactions in liquid aHF offer an access to intermediate oxidation states of binary fluorides which are sometimes difficult to prepare in high purity. Reactions between metals and KrF_2 in liquid aHF can give binary fluorides of very high purity with metals in the highest oxidation states. The choice of starting material in this approach is sometimes also important, e.g. in the case of the synthesis of Pd_2F_6, the reaction of palladium and fluorine in aHF proceeds rather quickly in comparison with PdO, whereas there is no reaction with PdF_2.

Therefore, the described approach deserves more frequent use in the preparation of various binary fluorides, not only for ones described here. However, this approach can be used only in laboratories properly equipped for the work with aHF.

Acknowledgements

The authors are grateful to Robert Moravec for help in preparative work, Borka Sedej for chemical analyses, and Ministry of Science and Technology of the Republic of Slovenia for financial support.

References

[1] A.W. Jache, G.H. Cady, *J. Chem. Physics* **1953**, *56*, 1106-1109.

[2] T.A. O'Donnell,*Superacids and Acidic Melts as Inorganic Chemical Reaction Media*, VCH Publishers, Inc., New York, 1993, p. 212.

[3] J.M. Kiselev, V.B. Sokolov, *Zh. Neorg. Khim*. **1984**, *29*, 857-859.

[4] R.T. Paine, L.B. Asprey, *Inorg. Chem.* **1975**, *14*, 1111-1113.

[5] R.T. Paine, L.B. Asprey, *Inorg. Chem.* **1974**, *13*, 1529-1531.

[6] B. Žemva, K. Lutar, A. Jesih, W.J. Casteel Jr., N. Bartlett, *J. Chem. Soc. Chem. Commun*. **1989**, 346-347.

[7] B. Žemva, K. Lutar, A. Jesih, W.J. Casteel Jr., A.P. Wilkinson, D.E. Cox, R.B. Von Dreele, H. Borrmann, N. Bartlett, *J. Am. Chem. Soc*. **1991**, *113*, 4192-4198.

[8] B. Žemva, K. Lutar, L. Chac∴n, M. Fele-Beuermann, J. Allman, C. Shen, N. Bartlett, *J. Am. Chem. Soc*. **1995**, *117*, 10025-10034.

[9] T.A. O'Donnell, T.E. Peel, *J. Inorg. Nucl. Chem. Supplement* **1976**, 61-62.

[10] G.M. Lucier, C. Shen, S.H. Elder, N. Bartlett, *Inorg. Chem*. **1998**, *37*, 3829-3824.

[11] G. Lucier, S.H. Elder, L. Chac∴n, N. Bartlett, *Eur. J. Solid State Inorg. Chem*. **1996**, *33*, 809-820.

[12] G. Lucier, C. Shen, W.J. Casteel, Jr., L. Chac∴n, N. Bartlett, *J. Fluorine Chem.* **1995**, *72*, 157-163.

[13] K. Lutar, I. Leban, T. Ogrin, B. Žemva, *Eur. J. Solid State Inorg. Chem*. **1992**, *29*, 713-727.

[14] J. Sorlano, M. Givon, J. Shamir, *Inorg. Nucl. Chem. Letters* **1966**, *2*, 13-14.

[15] K. Lutar, A. Jesih, B. Žemva, *Polyhedron* **1988**, *7*, 1217-1219.

[16] K. Lutar, A. Šmalc, J. Slivnik, *Vestn. Slov. Kem. Drus*. **1979**, *26*, 435-450.

[17] A. Šmalc, K. Lutar, B. Žemva, *Inorg. Synth.* **1992**, *29*, 11-15.

[18] A. Jesih, B. Žemva, *Vestn. Slov. Kem. Drus.* **1986**, *33*, 25-28.

[19] B. Frlec, D. Gantar, *J. Fluorine Chem*. **1982**, *19*, 485-500.

[20] G. Brauer, *Handbuch der Pr≡parativen Anorganischen Chemie*, Vol.1, Ferdinand Enke Verlag, Stuttgart, 1975, p. 275.

[21] B.G. Mηller, *Lanthanide Fluorides*, in *Synthesis of Lanthanide and Actinide Compounds*, Eds. G. Meyer, L.R. Morrs, Kluwer Academic Publishers, Dordrecht, 1991.

[22] R. Colton, J.H. Canterford, *Halides of the First Row Transition Metals*, Wiley-Interscience, 1969, p. 214.

[23] J.D. Smith, *The Chemistry of Arsenic, Antimony and Bismuth*, Pergamon Press, Oxford, 1975, p. 648.

[24] J.D. Smith, *The Chemistry of Arsenic, Antimony and Bismuth*, Pergamon Press, Oxford, 1975, p. 588.

[25] G. Brauer, *Handbuch der Pr≡parativen Anorganischen Chemie*, Vol.1, Ferdinand Enke Verlag, Stuttgart, 1975, p. 218.

[26] N. Bartlett, P.R. Rao, J. Chem. Soc., **1964**, 393-394.

[27] G. Brauer, *Handbuch der Pr≡parativen Anorganischen Chemie*, Vol.1, Ferdinand Enke Verlag, Stuttgart, 1975, p. 280.

[28] P.R. Rao, A. Tressaud, N. Bartlett, *J. Inorg. Nucl. Chem. Supplement* **1976**, 23-25.

[29] N. Bartlett, B. Žemva, L. Graham, *J. Fluorine Chem*. **1976**, *7*, 301-319.

[30] Z. Mazej, H. Borrmann, K. Lutar, B. Žemva, J. Darriet, J. Grannec, A. Tressaud, Palladium chemistry in anhydrous hydrogen fluoride acidified with arsenic pentafluoride, 12th European Symposium on Fluorine Chemistry, Berlin, 1998, Abstracts, p. B20.

[31] L.R. Bacanova, *Uspehi Himii* **1971**, *40*, 945-979.

[32] B.G. Mηller, *Lanthanide Fluorides*, in *Synthesis of Lanthanide and Actinide Compounds*, Eds. G. Meyer, L.R. Morss, Kluwer Academic Publishers, Dordrecht, 1991.

Povzetek

Opisane so nove sinteze MnF_3, CoF_3, BiF_3, Pd_2F_6, PdF_4, LaF_3 in SmF_3 z uporabo brezvodnega vodikovega fluorida kot topila pri sobni temperaturi. Diskutirane so nekatere prednosti, npr. blagih reakcijskih pogojev in čistote reakcijskih produktov v primerjavi z doslej opisanimi metodami za sintezo teh binarnih fluoridov.