The Solid-State Lanthanoid-Assisted Hydrolysis of the Solvolytically “Inert” $[AsF_6]^-$ Ion

Maja Ponikvar,*[a] Borka Sedej,[a] and Joel F. Liebman[b]

Keywords: Arsenic / Hydrolysis / $LnF_n(AsF_6)_{3-n}$ compounds / Rare-earth elements / Solid-state reactions

Results of elemental chemical analyses of the coordination compounds of the type $LnF_n(AsF_6)_{3-n}$ (Ln = Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) indicated unexpectedly low stability of the generally highly hydrolytically stable $[AsF_6]^-$ ion. Experiments conducted on model compounds of the type $NdF_n(AsF_6)_{3-n}$ have shown that hydrolysis proceeded instantaneously during the reaction of the solid compound with water. The ligand substitution catalysis of the compounds is explained in terms of the distortion of the $[AsF_6]^-$ octahedra earlier shown by vibrational spectroscopy. The study contrasts formally related reactions on the solid–solvent interface as opposed to those in homogeneous solution. A new look at some long studied and well-known inorganic species is offered.

Introduction

The rare earth(III) fluoroarsenates(V) [$LnF_n(AsF_6)_{3-n}$ compounds] were isolated in the system LnF_3/AsF_5/aHF at room temperature and characterized by: (1) X-ray powder diffraction analysis; (2) spectroscopic methods (Infrared and Raman spectroscopy); (3) monitoring mass balances throughout the experiments; and (4) chemical analyses.[1] The results of elemental chemical analyses indicated the presumed composition of the obtained compounds.[1] Crystal structure data are still lacking for these compounds.

As reported in the literature, the $[AsF_6]^-$ ion is highly stable towards hydrolysis[2,3] and can be determined gravimetrically.[4,5] Klapötke confirmed the stability towards aqueous hydrolysis also for coordinated $[AsF_6]^-$ ions.[6] As part of their study, Clark and Jones[7] suggested that the $[AsF_6]^-$ ion partially hydrolyses through hard acid−hard base interactions. Ghorab and Winfield[8] studied ^{18}F exchange processes of this and other hexafluoropnictates in acetonitrile.

The results of chemical analyses of the $[AsF_6]^-$ ion in $LnF_n(AsF_6)_{3-n}$ compounds synthesized and characterized in our laboratories were low, irreproducible and in disagreement with the calculated amounts of the metal Ln^{III}, total fluoride $(F^-)_t$ and arsenic(V) (results of the determinations of $[AsF_6]^-$ were not reported or interpreted because of lack of the material for supporting experiments).

The aim of the current paper is to demonstrate the instantaneous process of hydrolysis of the generally highly hydrolytically stable $[AsF_6]^-$ ion in $NdF_n(AsF_6)_{3-n}$ compounds during suspension of these solid compounds in water and to offer a plausible interpretation of the obtained results.

Results and Discussion

The results of the determination of the $[AsF_6]^-$ ion in $LnF_n(AsF_6)_{3-n}$ compounds[1] were lower than theoretically calculated values and did not agree with the amount of determined Ln^{III} and $(F^-)_t$ ions [the following abbreviations are used within this paper: $(F^-)_t$ = total fluoride, $(F^-)_P$ = total fluoride in the precipitate, $(F^-)_F$ = free fluoride in the filtrate, $(F^-)_f$ = free fluoride in solution]. Moreover, repetition with several weights of the sample after suspension in water showed that the results were irreproducible. The amount of free fluoride $(F^-)_f$ [9] after suspending these solid compounds in water was also determined. The results of these analyses are presented in Table 1.

Judging by the results presented in Table 1, the differences between two independent parallel determinations of $[AsF_6]^-$ ions seem to increase with increasing fluoroacidity[1,10,11] of the rare-earth trifluorides along the series. The determined amounts of $(F^-)_f$ were abnormally high since binary compounds of the type LnF_3 do not release fluoride ions, as determined in aqueous suspension of the sample directly with a fluoride-ion-selective electrode. The amount of $(F^-)_f$ ions determined in these (binary) compounds was not higher than 0.1−0.2 % of the expected amount, that is, in the range of experimental error of the analytical procedure for fluoride ions.[12]

---

[a] Jožef Stefan Institute,
Jamova 39, SI-1000 Ljubljana, Slovenia
Fax: (internat.) +386-1-423-21-25
E-mail: maja.ponikvar@ijs.si
[b] Department of Chemistry and Biochemistry, University of Maryland, Baltimore County, Baltimore, MD 21250, USA
Fax: (internat.) +1-410-455-2608
E-mail: jliebman@umbc.edu

DOI: 10.1002/ejic.200300632

Table 1. Results of $[AsF_6]^-$ and $(F^-)_f$ analyses for in the coordination compounds of the type $LnF_n(AsF_6)_{3-n}$

Compound	$[AsF_6]^-$ [%] Calcd.	Found[a] 1	2	$(F^-)_f$ [%] Found
$YF(AsF_6)_2$	77.78	67.9	68.3	5.1
$La(AsF_6)_3$	80.32	67.9	/	1.9
$CeF(AsF_6)_2$	70.37	68.6	68.6	0.5
$PrF(AsF_6)_2$	70.26	62.4	/	0.9
$PrF(AsF_6)_2$	70.26	68.1	68.0	0.5
$NdF(AsF_6)_2$	69.83	66.0	66.0	1.4
$SmF(AsF_6)_2$	69.05	63.3	63.1	1.0
$EuF(AsF_6)_2$	68.85	63.9	63.2	0.7
$GdF(AsF_6)_2$	68.19	58.6	59.2	/
$TbF(AsF_6)_2$	67.68	57.1	/	4.4
$DyF(AsF_6)_2$	67.55	55.3	56.6	6.7
$HoF(AsF_6)_2$	67.26	52.7	59.9	5.8
$ErF(AsF_6)_2$	66.98	59.2	60.2	4.8
ErF_2AsF_6	47.93	47.1	43.7	4.0
$TmF(AsF_6)_2$	66.78	62.2	65.1	2.5
$Tm_2F_3(AsF_6)_3$	58.94	53.5	49.8	5.5
$Yb_2F_3(AsF_6)_3$	58.44	51.5	50.9	4.5
$Lu_2F_3(AsF_6)_3$	58.21	52.8	51.2	3.9

[a] Amount of $[AsF_6]^-$ determined in two separate weights of the sample.

To explain the obtained results, ligand substitution catalysis through solution-phase hard acid−hard base interactions[7,8] was studied. Experiments conducted by using solid $KAsF_6$, solid lanthanide trifluorides or standard solutions of trivalent lanthanide salts revealed that addition of Ln^{III} or LnF_3 to acidic (HCl) aqueous solutions of $KAsF_6$ [with or without addition of solid NaF that represented a source of $(F^-)_f$] did not catalyze the fluoride exchange process in $[AsF_6]^-$ ions. The amounts of the $[AsF_6]^-$ ion determined (ranging from 82.2−82.6 %) in such samples agreed well with theoretically calculated amounts (82.85 %). The possibility of solution-phase catalysis was thus rejected.

The stability of the $[AsF_6]^-$ ion in coordination compounds of the type $LnF_n(AsF_6)_{3-n}$ in aqueous media was further studied in the neodymium model compounds $NdF(AsF_6)_2$ and $Nd(AsF_6)_3$ synthesized for this purpose in our laboratories. Elemental chemical analyses were conducted for both compounds. The results obtained are presented in Table 2.

The results revealed high precision of the obtained results for the determination of Nd^{III} and $(F^-)_t$ ions and high purity of the synthesized compounds, although the stoichiometry was not exact. However, for the purpose of our experiment, the stoichiometry of $NdF(AsF_6)_2$ and $Nd(AsF_6)_3$ was not important. The amount of $[AsF_6]^-$ ion was also determined (see Table 3). The results of these determinations were too low and irreproducible. It was obvious that during the process of suspending the solid compounds in water, the $[AsF_6]^-$ ion decomposed into the fluorohydroxyarsenic(v) species.

Table 3. Results of parallel determinations of $[AsF_6]^-$ in $NdF(AsF_6)_2$ and $Nd(AsF_6)_3$ including the results of determination of the amount of total fluoride in the precipitate $(F^-)_P$ and free fluoride in filtrate $(F^-)_F$

Compound	$[AsF_6]^-$ [%] Calcd.	Found	$(F^-)_P$ [%] Calcd.	Found	$(F^-)_F$ [%] Found
$NdF(AsF_6)_2$	69.83	61.2	19.93	19.6	9.3
		63.2		19.5	8.6
$Nd(AsF_6)_3$	79.71	66.3	19.93	19.5	9.5
		60.5		19.6	11.6
		62.2		19.6	10.6

As reported along with $[AsF_6]^-$, $[AsF_5OH]^-$ can also be determined gravimetrically by precipitation with tetraphenylarsonium chloride (TPAC).[5] Therefore, we investigated whether the precipitate formed was pure or whether $[AsF_5OH]^-$ coprecipitated with $[AsF_6]^-$. In this way, the amount of total fluoride ions in the precipitates $(F^-)_P$ and the amount of fluoride in the filtrates $(F^-)_F$ collected during the filtration of the precipitates were determined. The results are presented in Table 3.

These results indicated that the precipitates formed during the reaction of TPAC with $[AsF_6]^-$ ions in strongly acidic (HCl) media were pure and did not include any TPA-AsF_5OH. In Table 4, the sums of the amounts of fluoride present in the precipitates (calculated from the amount of determined $[AsF_6]$) and the filtrates in individual samples arecompared with the amount of $(F^-)_t$ determined.

As seen from the results, the differences between the sum of $(F^-)_P$ and $(F^-)_F$ and $(F^-)_t$ ranged from 0.8−2.2 %. Considering that precipitation is performed in hot (ca. 70−80 °C), strongly acidic (HCl) solution from which fluoride is lost in the form of relatively volatile HF, these differences are negligible. This indicates that during the initial stage of reaction of the sample with water, the strongly distorted AsF_6 unit partially decomposes. As a result, the fluorohydroxyarsenic(v) species are formed, which decom-

Table 2. The results of elemental chemical analysis of $NdF(AsF_6)_2$ and $Nd(AsF_6)_3$ compounds synthesized in our laboratories

Compound	Nd^{III} [%] Calcd.	Found	RSD[a] [%]	$(F^-)_t$ [%] Calcd.	Found	RSD [%]	As^V [%] Calcd.	Found	RSD [%]
$NdF(AsF_6)_2$	26.66	25.60	0.23	45.65	47.60	0.00	27.69	26.70	1.72
$Nd(AsF_6)_3$	20.29	20.60	0.28	48.10	50.30	0.11	31.61	27.30	1.48

[a] RSD = Relative Standard Deviation.

Table 4. Sum of fluoride determined in the precipitate and in the filtrate compared to the amount of determined total fluoride

Compound	(F^-) in AsF_6^- [a] [%]	$(F^-)_F$ [%]	Sum [%]	Difference [%][b]
$NdF(AsF_6)_2$	36.9	9.3	46.2	−1.4
	38.1	8.6	46.7	−0.9
$Nd(AsF_6)_3$	40.0	9.5	49.5	−0.8
	36.5	11.6	48.1	−2.2
	37.8	10.6	48.4	−1.9

[a] The theoretical amount (%) of fluoride in $[AsF_6]^-$ is 60.34 %. [b] The amount of $(F^-)_t$ determined in $NdF(AsF_6)_2$ was 47.6 % and in $Nd(AsF_6)_3$ 50.3 % (see Table 1).

pose to a hydrated arsenic(V) species and fluoride and are subsequently determined in the filtrate according to the [Equation (1)].

$$[AsF_6]^- + 2\,nH_2O \rightarrow [AsF_{6\text{-}n}(OH)_n]^- + nF^- + nH_3O^+ \qquad (1)$$

The amount of fluoride in the filtrates was determined in two ways: (1) after total decomposition with alkali hydroxide fusion; and (2) directly without prior decomposition. It is interesting to note that the amount of $(F^-)_F$ determined by the two ways was in agreement. This indicated that all the fluoride ions in the filtrate were present as free fluoride ions that can be determined by a fluoride-ion-selective electrode. Therefore, in a separate experiment with $Nd(AsF_6)_3$, we determined the amount of $(F^-)_f$ ions as a function of the pre-treatment conditions of an aliquot of the aqueous filtered suspension of the sample. Subsequently, the amount of $(F^-)_f$ was determined. The results are listed in Table 5.

Table 5. The amount of $(F^-)_f$ determined in $Nd(AsF_6)_3$ as a function of pre-treatment conditions of the sample

Pre-treatment conditions	$(F_f)^-$ [%]
Aqueous filtered suspension	1.6
An aliquot was heated to boiling	1.6
Conc. HCl (0.2 mL) was added to an aliquot	1.8
Conc. HCl (0.2 mL) was added to an aliquot and heated to boiling	9.2

The results indicated that the amount of $(F^-)_f$ determined in the filtered suspension of the sample increased in acidic (HCl) solution at higher temperatures. This observation is in agreement with previously conducted experiments. The covalently bonded fluorides in $LnF_n(AsF_6)_{3\text{-}n}$ compounds are therefore released into the solution under conditions of gravimetric determination of $[AsF_6]^-$.

Plausible Interpretation

In the vibrational spectra of rare earth(III) fluoroarsenates(V) more bands were observed than would be expected for a regular $[AsF_6]^-$ anion with O_h symmetry. Additionally, the strongest Raman (697−711 cm^{-1}) and the strongest infrared bands (765−768 cm^{-1}) are shifted to higher frequencies than that of the strongest band of the octahedral $[AsF_6]^-$ ion in $CsAsF_6$ [13] in which Raman-active symmetrical stretching, $v_1(A_{1g})$ appears at 685 cm^{-1} and infrared-degenerate stretching $v_3(F_{1u})$ at 699 cm^{-1}.[1]

The composition of rare earth(III) fluoroarsenates(V) and the fluorine acceptor abilities of AsF_5 suggests formation of a fluorine bridge between the Ln and As atoms (in agreement with the expected shifts in electron density according to “Gutmann’s second rule” [14]). Consequently, the distorted octahedral $[AsF_6]^-$ ions of maximally C_{4v} symmetry are anticipated. The observed number of bands in vibrational spectra of rare earth(III) fluoroarsenates(V) support that assumption and indicate a covalent contribution to the bonding between LnF_3 and AsF_5 through fluorine bridges.[1]

Molecules undergo whatever distortion necessary to maximize the stability of the entire species (cations + anions). However, that the anion is distorted makes it easier for a positive, protic hydrogen to pull off a fluorine atom from the $[AsF_6]^-$ ion (presumably, at least one F has a longer Ln−F bond and so is enroute to dissociation) when suspending these solid compounds in water. Additionally, the arsenic atom has been made more vulnerable to attack by solvent H_2O or added $[OH]^-$ or other nucleophiles such as $[CO_3]^{2-}$, because the irregular octahedron provides more space around the As center, either because of stretched bonds or opened angles or both. Our suggested mechanism of the solid state F^-/OH^- exchange is schematically shown in Figure 1.

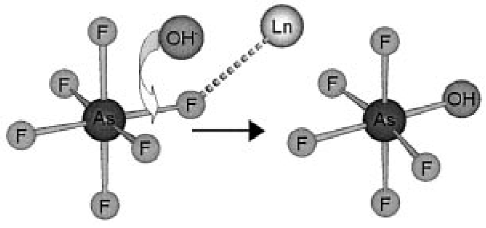

Figure 1. Schematic presentation of our suggested mechanism of the solid state F^-/OH^- exchange (Ln = Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu)

This reasoning that the distortion is stabilized by the rare-earth element is reminiscent of the generally accepted explanation for enzyme activity in terms of the enzyme stabilizing the transition state of the reaction.[15,16,17] The rare-earth ion stabilizes a distorted $[AsF_6]^-$ ion and so the energy of activation of hydrolysis is reduced relative to the free, undistorted anion. The Ln^{3+} cation may bind the F^- anion so strongly that the $[AsF_6]^-$ hydrolysis is not catalyzed; instead a complex was formed and the reaction is merely accelerated. This too, has counterparts in terms of some modes of enzyme inhibition.

In contrast to the observed process of hydrolysis of rare earth(III) fluoroarsenates(V) after suspension of the solid compounds in water, we noted no acceleration of the hydrolysis of the $[AsF_6]^-$ ion in a homogeneous aqueous solution to which a rare-earth trifluoride or a dissolved rare-earth ion had been added. This observation is explained by coordinative saturation of Ln^{III} (completely and strongly complexed or solvated) by either a F^- anion or a water molecule; the anion is thus protected from hydrolysis. The difference is analogous to inner- and outer-sphere electron transfer and the ease of redox reactions. We close by noting that solvation of the $[AsF_6]^-$ ion by neutral water as opposed to complexation with some cation will also kinetically stabilize this anion. Disappointingly, literature spectroscopic and structural data needed to further corroborate our understanding are lacking.

Experimental Section

General: All reagents were of analytical grade and all solutions were prepared using double-distilled water.

Sample Preparation: Coordination compounds of the general type $LnF_n(AsF_6)_{3-n}$ are sensitive to traces of moisture.[1] Therefore, test samples for determination of the total amount of each element, the $[AsF_6]^-$ ion, and free fluoride $(F^-)_f$ were prepared by weighing in a dry box, with a precision of ± 0.05 mg into air- and moisture-tight Teflon containers. The containers were cooled in liquid nitrogen in order to moderate subsequent reaction with water (20 mL) during suspension in a closed Erlenmeyer flask.

Analyses: Accurate and precise results of chemical analyses with an absolute error of less than 0.2−0.3 % for the determination of the Ln^{III} cation and the $[AsF_6]^-$ anion were obtained by the use of classical analytical methods;[18] a modified analytical technique with a fluoride-ion-selective electrode that enabled us to achieve an absolute error of analysis of less than 0.3 %[12] was applied to the determination of the fluoride anion. The amount of the $[AsF_6]^-$ anion was determined gravimetrically by precipitation with TPAC.[19] The amounts of $(F^-)_t$ and total fluoride in the precipitate $(F^-)_P$ were determined after total decomposition of the sample with alkali carbonate fusion using solid $KNaCO_3$. The amounts of $(F^-)_f$ and free fluoride $(F^-)_F$ in the filtrate after precipitation of the $[AsF_6]^-$ ions were estimated in aqueous suspension and acidic solution of the sample, respectively.[3,12] The analyses were performed by direct potentiometry with a fluoride-ion-selective electrode.[12] The amounts of rare earths(III) were determined by complexometric titrations with EDTA.[20,21,22] Solid $KAsF_6$ (Ozark Mahoning), solid LnF_3 (all from Alfa; the experiment with TmF_3 has not been conducted), standard solutions of Ln^{III} [C = 1000 mg/L, all from Merck, the Y^{III}, La^{III}, Ce^{III} and Tb^{III} standard solutions are declared as nitrates(V) in 2−3 % HNO_3 and the Ce^{III}, Pr^{III}, Nd^{III}, Sm^{III}, Eu^{III}, Gd^{III}, Dy^{III}, Ho^{III}, Er^{III}, Yb^{III} and Lu^{III} standard solutions are declared as the trivalent oxides in 2−3 % HNO_3], solid NaF (Merck), and $NdF(AsF_6)_2$ and $Nd(AsF_6)_3$ synthesized in our laboratories were used during the study of the stability of $[AsF_6]^-$ species.

Acknowledgments

J. F. L. thanks the American Chemical Society for funding for his European travel through its education division, international activities programs. We are grateful to Dr. David Berne (O.B.M.), Dr. Anna Berne, Prof. Boris Žemva, Prof. James S. Vincent and Prof. Ralph M. Pollack for their helpful comments related to this study and to Dr. Zoran Mazej for the preparation of the model compounds. We gratefully acknowledge the financial support of the Ministry of Education, Science and Sport of the Republic of Slovenia.

---

[1] M. Fele-Beuermann, K. Lutar, Z. Mazej, S. Milićev, B. Žemva, *J. Fluor. Chem.* **1998**, *89*, 83−89.
[2] M. Ponikvar, B. Pihlar, B. Žemva, *J. Fluor. Chem.* **2003**, *122*, 215−217.
[3] M. Ponikvar, B. Žemva, J. F. Liebman, *J. Fluor. Chem.* **2003**, *123*, 217−220.
[4] W. Lange, E. Müller, *Ber. Dtsch. Chem. Ges.* **1930**, *63*, 1058−1070.
[5] H. M. Dess, R. W. Parry, G. L. Vidale, *J. Am. Chem. Soc.* **1956**, *78*, 5730−5734.
[6] T. Klapötke, *Spectrosc. Lett.* **1989**, *22*, 183−190.
[7] H. R. Clark, M. M. Jones, *J. Am. Chem. Soc.* **1970**, *92*, 816−822.
[8] M. F. Ghorab, J. M. Winfield, *J. Fluor. Chem.* **1990**, *49*, 367−383.
[9] B. Sedej, *Talanta* **1976**, *23*, 335−336.
[10] M. Fele-Beuermann, S. Milićev, K. Lutar, B. Žemva, *Eur. J. Solid State, Inorg. Chem.* **1994**, *31*, 545−556.
[11] K. Lutar, H. Bormann, Z. Mazej, M. Tramšek, P. Benkič, B. Žemva, *J. Fluor. Chem.* **2000**, *101*, 155−160.
[12] M. Ponikvar, B. Sedej, B. Pihlar, B. Žemva, *Anal. Chim. Acta* **2000**, *418*, 113−118.
[13] G. M. Begun, A. C. Rutenberg, *Inorg. Chem.* **1967**, *6*, 2212−2216.
[14] V. Gutmann, *The Donor-acceptor approach to molecular interactions*, Plenum Press, New York, **1978**, p. 12−14.
[15] L. Pauling, *Am. Sci.* **1948**, *36*, 58.
[16] R. Wolfenden, *Acc. Chem. Res.* **1972**, *5*, 10−19.
[17] G. E. Lienhard, *Science* **1973**, *180*, 149−154.
[18] C. M. Beck II, *Anal. Chem.* **1991**, *63*, 993A−1003A.
[19] A. I. Vogel, *Vogel's textbook of quantitative inorganic analysis: Including elementary instrumental analysis*, Longman, London, 4th ed., **1978**, p. 482−483.
[20] J. S. Fritz, R. T. Oliver, D. J. Pietrzyk, *Anal. Chem.* **1958**, *30*, 111−114.
[21] G. Schwarzenbach, H. Flascka, *Complexometric titrations*, Methuen, London, **1969**, p. 194−197.
[22] D. D. Perrin, *Masking and demasking of chemical reactions*, Wiley-Interscience, New York, **1970**, p. 56−57.

Received September 5, 2003
Early View Article