

Two new Fluoro complexes: Tetramethylammonium trifluoroplumbate (TMATriFP) and Tripropylammonium tetrafluoroantimonate(TriPATFA)

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Abstract

Two new complexes synthesized by tetralkylammonium fluoride salts. Tetramethylammonium trifluoroplumbate and tripropylammonium tetrafluoroantimonate have been prepared from $N(CH_3)_4F$ and PbF_2 or $N(C_3H_7)_3$, HF and SbF_3 using either CH_3CN , or excess PbF_2 or SbF_3 as a solvents. The structure of the PbF_3^- and SbF_4^- anion was studied by ^{19}F NMR spectroscopy, IR, UV/Visible spectroscopy.

Introduction

The number of Antimony (III) and Lead (II) fluoro complexes are still scarce, and very few studies on their reactivity have been reported. Particularly the fluorides have been subject of an intense scientific discussion since the first synthesis of such a compound [1, 2]. This is because of the important prerequisites for a fluorinating agents to be useful which are their mildness, versatility, selectivity and operational simplicity. The subject of this investigation is obtaining of inorganic fluorides and complexes [3]. Lead and Antimony fluoro complexes have more attraction because these compounds could be prepared by reaction of fluorinating agents such as CsF , NaF , HF with a complexes.

For this purpose we used a new and strong fluorinating agent that is tetramethylammonium fluoride produced at 1990 in anhydrous form [4].

Many fluoro compounds of main group elements were produced using this reagent, namely: PF_4^- [5], SeF_5^- , TeF_5^- , [6] IF_8^- [7], and in few amounts row of transition metals fluoro complexes like $(CH_3)_4NMoO_3F$ [8], $(CH_3)_4NCrO_3F$ [9], MoF_7^- , WF_7^- , $ReOF_6^-$ [10], MoO_3F^- [11].

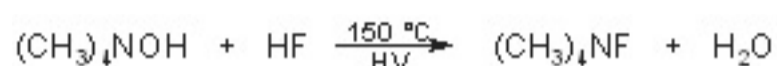
There were two primary incentives for selection of $(CH_3)_4N^+$ and $(C_3H_7)_3NH$ with HF as the

counter ion. Firstly, quaternary ions such as tetramethylammonium and tripropylammonium are often used as phase transfer catalysts. Secondly, quaternary ions such as tetramethylammonium and tripropylammonium are used as crystal growing agents. In this article a direct, simple one-step method has been used to obtaining these compounds.

Another reason that encouraged researchers for synthesizing this range of fluorinated compounds is the fewer and rare amounts of the spectroscopic data of this compounds, especially ^{19}F -NMR data. Some of data were reported in [12-15].

Results and discussion

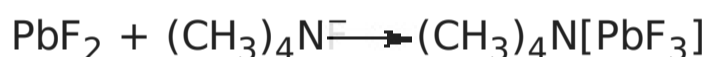
Tetramethylammonium fluoride is an ionic compound and many efforts have been made for preparation of its anhydrous form. It produces by reaction of tetramethylammonium hydroxide with hydrofluoric acid as follow:



Reagent grade PbF_3 was used. Anhydrous tetramethylammonium fluoride $(\text{CH}_3)_4\text{NF}$ was prepared by the method reported by Christie. [20]

Tetramethylammonium trifluoroplumbate (III) $(\text{CH}_3)_4\text{N}[\text{PbF}_3]$, TMATriFPb

$(\text{CH}_3)_4\text{N}[\text{PbF}_3]$ was prepared by the reaction of $(\text{CH}_3)_4\text{NF}$ and PbF_3 in a 1:1 ratio in MeCN solvent as follows:



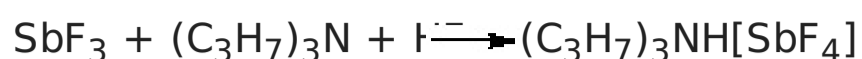
The reactant solution color was bright green, and the product color was light green, The typical absorption lines in IR spectra at $469(\text{s})\text{ cm}^{-1}$ have been attributed to Pb-F. Absorption lines at $1472(\text{ms})$, $3095(\text{sh})$, $499(\text{w, br})\text{ cm}^{-1}$, have been attributed to $^{15}\text{N}-\text{C}$, $^{13}\text{C}-\text{H}$ and $^{19}\text{N}-\text{C}$ of $(\text{CH}_3)_4\text{N}^+$ counter ion respectively (Table 1).

There are two absorption lines in the compound electronic spectra. Electronic spectra of TMATriFPb shows two shifts for Lead $232\text{ nm } \epsilon = 280\text{ mol}^{-1}\text{lit. cm}^{-1}$ and $259\text{ nm } \epsilon = 145\text{ mol}^{-1}\text{lit. cm}^{-1}$ and that belongs to E and A_1 shifts (Table 3). These shifts are expected in mono substituted Plumbate ions, because of Lead position making of strong crystalline field complexes.

The expected signals were found in the ^1H -NMR and ^{13}C -NMR.

Tripropylammonium tetrafluoroantimonate (III) $(\text{C}_3\text{H}_7)_3\text{NH}[\text{SbF}_4]$, TriPATF

The inner mobility of fluorine ions and electrophysical characteristics of complex fluorides NaSbF_4 , KSbF_4 , RbSbF_4 , CsSbF_4 and SbF_3 are studied by means of ^{19}F NMR method and impedance spectroscopy. Types of ion motions in the fluorine subsystem of these compounds in the range of temperatures 180 - 510K are determined. Discrete mononuclear units have been characterized in the form of the matrix-isolated SbF_3 molecule and of the anion SbF_4^- , identified for the first time, in association with appropriately bulky cations in the solid phase and in organic solvents solution; the vibrational spectra of the SbF_4^- anion imply C_2 symmetry. $(\text{C}_3\text{H}_7)_3\text{NH}[\text{SbF}_4]$ was prepared by the reaction of $(\text{C}_3\text{H}_7)_3\text{N}$ and SbF_3 and HF in a 1:1:1 ratio in MeCN solvent as follows:



The method for the reaction of $(\text{C}_3\text{H}_7)_3\text{N}$ with SbF_3 and HF is as for to $(\text{CH}_3)_4\text{NF}$ and its analytical and spectroscopic data are: The reactant solution color was pale white, and the product color was white, IR spectrum at 520 (W, br) cm^{-1} have been attributed to Sb-F and absorptions at 1443 (m), 3065 (sh), 1100 (w) cm^{-1} , have been attributed to ν_{15} N-C, ν_{CH_2} C-H and ν_{CN} of $(\text{C}_3\text{H}_7)_3\text{N}^+$ counter ion respectively (Table 2). There are one absorption bands in this compound electronic spectrum Electronic spectrum of TriPATFA shows one transitions for Antimony at 271nm ($\epsilon = 244 \text{ mol}^{-1}\text{lit.cm}^{-1}$) that belongs to $\Gamma_1 \rightarrow A_1$ shift (Table 4). The expected signals were found in the ^{19}F -NMR, ^1H -NMR and ^{13}C -NMR.

Experimental

Material and instruments

Acetonitrile (Fluka, P.A.) was distilled and dried by phosphorus pentoxide before using, thereby reducing its water content to <4 ppm. Tetramethylammonium fluoride or Tripropylammonium and fluoric acid were bought from Merck. PbF_2 and SbF_3 (Merck, p.a.) were used without further purification. Solvents were purified by standard methods. Infrared spectra were recorded as KBr disks on a Shimadzu model 420 spectrophotometer. The UV/Visible measurements were made on an Uvicon model 922 spectrometer. ^1H and ^{13}C -NMR were recorded on a Bruker AVANCE DRX 500 spectrometer at 500 and 125 MHz, respectively. All the chemical shifts are quoted in ppm using the high-frequency positive convention; ^1H and ^{13}C -nmr spectra were referenced to external SiMe_4 . Antimony and Lead were estimated iodometrically. The percent compositions of elements were obtained from the Microanalytical Laboratories, Department of Chemistry, OIRC, Tehran.

Synthesis of Tetramethylammonium trifluoroplumbate (II), $[(\text{CH}_3)_4\text{N}][\text{PbF}_3]$

Tetramethylammonium trifluoroplumbate (II), $[(\text{CH}_3)_4\text{N}][\text{PbF}_3]$ was prepared by dissolving PbF_2 (07.1 mg, 2.9 mmol) in MeCN and adding this solution to a solution of tetramethylammonium fluoride (0.29 g, 3.1 mmol) in MeCN under stirring at room temperature until a white precipitate was formed. After 2 hours stirring, the mixture was filtered, washed with ether and dried at room temperature. The tetraethylammonium salts are some what hygroscopic, and it was better to be stored under a layer of hexane, whereas all of the salts are photosensitive and moisture-sensitive, both in solution and solids. Mp: 196°C . $\text{C}_4\text{H}_{12}\text{F}_3\text{NPb}$: Calcd. %C, 14.19; %H, 3.54; %N, 4.13. Found: %C, 15.30; %H, 3.56; %N, 4.15. UV/Visible, IR, ^1H -NMR and ^{13}C -NMR were all consistent with the TMA TriFPb structure.

Synthesis of Tripropylammonium tetrafluoroantimonate (III), $(\text{C}_3\text{H}_7)_3\text{NH}[\text{SbF}_4]$

Tripropylammonium tetrafluoroantimonate (III), $[(\text{C}_3\text{H}_7)_3\text{NH}][\text{SbF}_4]$ was prepared as follow: SbF_3 (8.9 mg, 5 mmol) was dissolved in MeCN in a beaker and tripropylamine (1.36 ml, 10 mmol) was added dropwise under stirring over a period of 0.5 h and the stirring was continued for 0.5 h at 0°C . To the resultant clear white solution, hydrofluoric acid 40% (0.2 ml, 5 mmol) was added under stirring at 0°C . The precipitated white solid was isolated by filtration, washed with hexane and dried under vacuum for 2 h at room temperature. Mp: 275°C . $\text{C}_9\text{H}_{22}\text{F}_4\text{NSb}$: Calc. %C, 31.60; %H, 6.43; %N, 4.09. Found: %C, 33.15; %H, 6.45; %N, 4.11. UV/Visible, IR, ^1H -NMR and ^{13}C -NMR were all consistent with the TriPATFA structure.

Conclusion

Two tetramethylammonium fluoride and tripropylammonium fluoride salts of SbF_3 were synthesized simply. $(\text{CH}_3)_4\text{N}[\text{PbF}_3]$ was prepared by the reaction of $(\text{CH}_3)_4\text{NF}$ and PbF_2 in a 1:1 ratio in MeCN solvent and $(\text{C}_3\text{H}_7)_3\text{NH}[\text{SbF}_4]$ was prepared by the reaction of $(\text{C}_3\text{H}_7)_3\text{N}$, HF and SbF_3 in a 1:1:1 ratio in MeCN solvent. Electronic and vibrational spectra of these two new Fluoro-complexes were studied. These compounds were characterized by IR, UV/Visible, and ^{13}C -NMR and ^1H -NMR techniques. Production of these compounds shows the ability of tetramethylammonium fluoride and tripropylammonium With fluoric acid in fluoride addition to main group elements compounds.

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Table1. The frequencies (cm^{-1}) and assignment of cation and anion of $(\text{CH}_3)_4\text{N}[\text{PbF}_3]$

$\nu(\text{cm}^{-1})$	Assignment	Intensity	$\nu(\text{cm}^{-1})$	Assignment	Intensity
$(\text{CH}_3)_4\text{N}^+$			1472	$\nu_{15}, \text{CH}_3, \text{asym. def}$	(ms)
3415	$\nu_{\text{CH}_3} + \nu_{19}$	(m, br)	1396	$\nu_{16}, \text{CH}_3, \text{sym. str}$	(s)
3260	$\nu_{\text{CH}_3} + \nu_8$	(w, br)	1298	$\nu_{\text{rock}}, \text{CH}_3, \text{rocking}$	(m)
3095	$\nu_{\text{CH}_3}, \text{asym. str}$	(sh)	990	$\nu_{18}, \text{NC}_4, \text{asym. str}$	(ms)
2980	$\nu_{13}, \nu_{\text{CH}_3}, \text{asym. str}$	(w, br)	499	$\nu_{19}, \text{NC}_4, \text{def.}$	(w, br)
2975	$\nu_{14}, \text{asym. str}$	(w, br)	428	$\nu_{19}, \text{NC}_4, \text{def.}$	(w, br)
2780	$\nu_{14}, \nu_{\text{CH}_3}, \text{asym. str}$	(w, br)	$[\text{PbF}_3]^-$		
2655	$\nu_7 + \nu_{16}$	(w)			
2458	$\nu_3 + \nu_8 + \nu_{16}$	(w)	469	Pb-F (E)	(s)
1850	$\nu_8 + \nu_{15}$	(w, br)	421	Pb-F (A_1)	(ms)

Table 2. The frequencies (cm^{-1}) and assignment of cation and anion of $(\text{C}_3\text{H}_7)_3\text{NH}[\text{SbF}_4]$

$\nu(\text{cm}^{-1})$	Assignment	Intensity	$\nu(\text{cm}^{-1})$	Assignment	Intensity
$(\text{C}_3\text{H}_7)_3\text{NH}^+$			1443	$\nu_{15}, \nu_{\text{CH}_3}, \text{asy, def}$	(m)
3430	$\nu_{\text{NH}} + \delta_{\text{CN}}$	(ms)	1421	ν_{CH_2}	(m)
3225	$\nu_{\text{CH}_3} + \delta_{\text{CN}}$	(sh)	1370	$\nu_{22} + \nu_{23}$	(w, br)
3300	$\nu_{14}, \nu_{\text{CH}_3}, \text{asy}$	(w)	1210	$\nu_{\text{rock}}, \nu_{\text{CH}_3}$	(w)
3065	$\nu_{\text{CH}_3}, \text{sym}$	(sh)	1100	$\nu_{\text{CN}}, \text{str}$	(w)
2915	$\delta_{\text{CH}_3}, \text{Com. Over}$	(w, br)	733	$\delta_{\text{NH}}, \text{oop}$	(sh)
2610	$\delta_{\text{CH}_3} + \Gamma_{\text{CH}_3}$	(w, br)	$[\text{SbF}_4]^-$		
1460	$\nu_{\text{NH}}, \text{str}$	(w, br)	520	Sb-F (B_1)	(w, br)
1410	$\nu_3 + \nu_8 + \nu_{16}$	(w, br)	476	Sb-F (A_1)	(w, br)
			446	Sb-F (A_1)	(s)

Table 3. Transitions specifications of $\text{TMA}(\text{TriFPb})$

λ_1 ($\epsilon, M^{-1}cm^{-1}$)	λ_2 ($\epsilon, M^{-1}cm^{-1}$)
232(280)	259(145)
$E \rightarrow E$	$E \rightarrow A_1$

Table 4. *Transitions specifications of TriPATFA*

λ ($\epsilon, M^{-1}cm^{-1}$)
271(244)
$B_1 \rightarrow A_1$