

Synthesis and Characterization of Two New Fluoroplumbate(II) Complexes: Tetrabutylammonium Fluorodihaloplumbate, (But)₄N[PbX₂F] (X = Cl, I)

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Tetrabutylammonium Fluorodichloroplumbate(II), N(C₄H₉)₄[PbCl₂F], TBAFDiCP and Tetrabutylammonium Fluorodiodoplumbate(II), [(C₄H₉)₄N][PbI₂F], TBAFDiIP are the first examples of fluoroplumbate salts that have been prepared from the reaction of (C₄H₉)₄NF with PbCl₂ and PbI₂ respectively using either CH₃CN solvent. These new compound characterized by elemental analysis, IR, UV/Visible, ¹H NMR, and ¹⁹F NMR techniques.

Key Words : Tetrabutylammonium fluoride, Lead complexes, Fluoride addition, Fluorocomplexes, Synthesis

Introduction

The unique properties of fluorine impart an unusual reactivity to the metal-fluorine bond which can be exploited in preparative inorganic chemistry or in catalysis.^{1,2} In addition, the development of main metal mediated M-F bond formation processes is still a virtually unexplored field. In recent years there has been a great deal of interest in the metal fluorocompounds. Particularly the fluorides have been subject of an intense scientific discussion since the first synthesis of such a compound. The important prerequisites for a fluorinating agent are mildness, versatility, selectivity and operational simplicity.³⁻⁶ One of the most famous fluorinating agent is tetramethylammonium fluoride. The main reaction for its synthesis is the reaction of Tetramethylammonium hydroxide with hydrofluoric acid. By using this reagent many fluorocompounds of main group elements produced such as: (CH₃)₄N[PF₄],⁷ (CH₃)₄N[SeF₅], (CH₃)₄N[TeF₅],⁸ (CH₃)₄N[IF₈],⁹ and in fewer amount some of transition metal fluorocomplexes synthesized like (CH₃)₄N[MoO₃F],¹⁰ (CH₃)₄N[CrO₃F],¹¹ (CH₃)₄N[MoF₇], (CH₃)₄N[WF₇], (CH₃)₄N[ReOF₆]¹² and (CH₃)₄N[WO₃F].¹³ There were two primary incentives for selection of (R)₄N⁺ as the counter ion. Firstly, quaternary ions such as Tetrabutylammonium which are often used as phase transfer catalysts. Secondly, quaternary ions such as Tetrabutylammonium are used as crystal growing agents. The numbers of lead(II) fluorocompounds are still scarce, and very few studies on their reactivity have been reported. In this paper, a direct, simple and one-step method has been used to synthesize two new lead fluorocompounds.

Results and Discussion

Fluorides have been subject of many scientific discussions

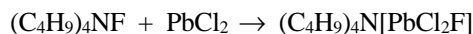
firstly because of the synthetic possibility^{3,4} and secondly, because of rare amounts of the spectroscopic data especially ¹⁹F-NMR chemical shifts of these compounds.¹⁴⁻¹⁷

We now report the synthesis of the tetrabutylammonium fluorodihaloplumbate TBAFDiXP that are analog of the other halocompounds such as fluorochromate compounds. The method used for the synthesis does not involve direct use of HF or reaction of MHF₂ (M = NH₄, K, Rb or Cs) with lead compounds and is based on the concept of strong action of tetrabutylammonium fluoride (C₄H₉)₄NF and its power to fluoride addition to many compounds.

The advantages of the new method are:

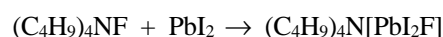
a) there is no side product, b) the reaction is quite fast, c) mild conditions and d) the accompanied color change that providing visual means for ascertaining the progress of the reaction.

(C₄H₉)₄N[PbCl₂F] was prepared by the reaction of (C₄H₉)₄NF and PbCl₂ in a 1:1 ratio in MeCN solvent as follows:



In the vibrational spectrum of this compound the known bands of cation were seen that confirmed with literature data (Table 1). Electronic spectrum of compound shows two absorptions at 225 nm ($\epsilon = 741 \text{ mol.}^{-1}\text{lit.cm}^{-1}$) and 275 nm ($\epsilon = 241 \text{ mol.}^{-1}\text{lit.cm}^{-1}$) that belongs to A'→A' and A'→A' transition.

(C₄H₉)₄N[PbI₂F] was prepared by the reaction of (C₄H₉)₄NF and PbI₂ in a 1:1.1 ratio in MeCN solvent as follows:



In the vibrational spectrum of this compound the known bands of tetrabutylammonium cation and fluoroanion were seen that confirmed with literature data (Table 2).

Table 1. The frequencies (cm^{-1}) and assignment of cation and anion of $(\text{C}_4\text{H}_9)_4\text{N}[\text{PbCl}_2\text{F}]$

Intensity	$\nu(\text{cm}^{-1})$	Assignment	$\nu(\text{cm}^{-1})$	Assignment	Intensity
	$(\text{C}_4\text{H}_9)_4\text{N}^+$		1435	$\nu_{15}, \text{CH}_2, \text{asym.def}$	(w)
3445	$\nu_{\text{CH}_2} + \nu_{19}$	(w, br)	1395	$\nu_{16}, \text{CH}_2, \text{sym.str}$	(w)
3305	$\nu_{\text{CH}_2} + \nu_8$	(w, br)	1170	$\nu_{\text{rock}}, \text{CH}_2, \text{rocking } \nu_{14}$	(w)
3220	$\nu_{\text{CH}_2}, \text{asym.str}$	(sh)	876	$\nu_{18}, \text{NC}_4, \text{asym.str}$	(w, br)
3015	$\nu_{13}, \nu_{\text{CH}_2}, \text{asym.str}$	(w, br)	468	$\nu_{19}, \text{NC}_4, \text{def.}$	(ms)
2950	$\nu_{14}, \text{CH}_2, \text{asym.str}$	(s)	446	$\nu_{19}, \text{NC}_4, \text{def.}$	(ms)
2850	$\nu_{14}, \text{CH}_2, \text{asym.str}$	(s)	[PbCl_2F] ⁻		
2770	$\nu_7 + \nu_{16}$	(w)	433	Pb-F (A)	(w, br)
2390	$\nu_3 + \nu_8 + \nu_{16}$	(w)	303	Pb-Cl (E)	(w)
1995	$\nu_8 + \nu_{15}$	(w, br)			

Table 2. The frequencies (cm^{-1}) and assignment of cation and anion of $(\text{C}_4\text{H}_9)_4\text{N}[\text{PbI}_2\text{F}]$

$\nu(\text{cm}^{-1})$	Assignment	Intensity	$\nu(\text{cm}^{-1})$	Assignment	Intensity
	$(\text{C}_4\text{H}_9)_4\text{N}^+$		1463	$\nu_{15}, \text{CH}_2, \text{asym.def}$	(s)
3435	$\nu_{\text{CH}_2} + \nu_{19}$	(w, br)	1376	$\nu_{16}, \text{CH}_2, \text{sym.str}$	(m)
3350	$\nu_{\text{CH}_2} + \nu_8$	(w)	1146	$\nu_{\text{rock}}, \text{CH}_2, \text{rocking } \nu_{14}$	(m)
3110	$\nu_{\text{CH}_2}, \text{asym.str}$	(sh)	873	$\nu_{18}, \text{NC}_4, \text{asym.str}$	(w)
3080	$\nu_{13}, \nu_{\text{CH}_2}, \text{asym.str}$	(w)	525	$\nu_{19}, \text{NC}_4, \text{def.}$	(w)
2950	$\nu_{14}, \nu_{\text{CH}_2}, \text{asym.str}$	(s)	403	$\nu_{19}, \text{NC}_4, \text{def.}$	(ms)
2840	$\nu_{14}, \nu_{\text{CH}_2}, \text{asym.str}$	(s)	[PbI_2F] ⁻		
2590	$\nu_7 + \nu_{16}$	(w)	483	Pb-F (A)	(w, br)
2420	$\nu_3 + \nu_8 + \nu_{16}$	(w)			
1860	$\nu_8 + \nu_{15}$	(w, br)			

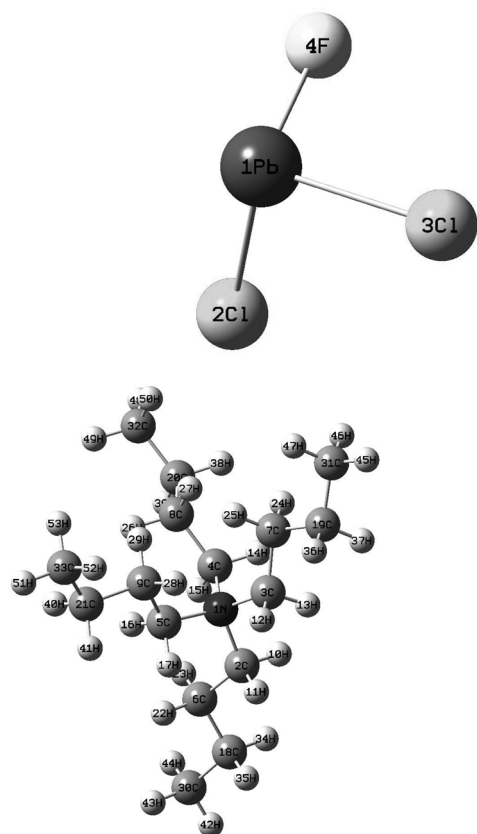

Figure 1. The calculated structure for $(\text{C}_4\text{H}_9)_4\text{N}[\text{PbCl}_2\text{F}]$.

Table 3. A number of the theoretical frequencies (cm^{-1}) of cation and anion of $(\text{C}_4\text{H}_9)_4\text{N}[\text{PbCl}_2\text{F}]$

$\nu(\text{cm}^{-1})$	Assignment	$\nu(\text{cm}^{-1})$	Assignment
	$(\text{C}_4\text{H}_9)_4\text{N}^+$		
1449	$\nu_{15}, \text{CH}_2, \text{asym.def}$	1449	$\nu_{15}, \text{CH}_2, \text{asym.def}$
3014	$\nu_{13}, \nu_{\text{CH}_2}, \text{asym.str}$	1392	$\nu_{16}, \text{CH}_2, \text{sym.str}$
2953	$\nu_{14}, \text{CH}_2, \text{asym.str}$	1176	$\nu_{\text{rock}}, \text{CH}_2, \text{rocking } \nu_{14}$
2770	$\nu_7 + \nu_{16}$	870	$\nu_{18}, \text{NC}_4, \text{asym.str}$
2390	$\nu_3 + \nu_8 + \nu_{16}$	[PbCl_2F] ⁻	
1995	$\nu_8 + \nu_{15}$	433	Pb-F

For more clear characterization the theoretical calculation of vibration modes have been done by the method and basis set: B₃LYP/LANL2DZ. The calculations shown that the structures of these two fluorodihaloplumbate salts, are not formed dimer, trimer, or more multi nuclear structures in solid states. The calculated data and structure of one of these fluorodihaloplumbate salts are shown in Figure 1 and Table 3.

Electronic spectrum of compound shows four absorptions at 245 nm ($\epsilon = 1330 \text{ mol}^{-1}\text{lit.cm}^{-1}$), 320 nm ($\epsilon = 124 \text{ mol}^{-1}\text{lit.cm}^{-1}$), 336 nm ($\epsilon = 230 \text{ mol}^{-1}\text{lit.cm}^{-1}$) and 369 nm ($\epsilon = 226 \text{ mol}^{-1}\text{lit.cm}^{-1}$), the first two absorptions belong to A'→A', A'→A' and two another seconds belong to A''→A' transitions. Tables 4 and 5 show the electronic transitions data of these two fluorodihaloplumbate compounds respectively. In the ¹⁹F NMR of these compounds a signal is seen in the -60 ppm that confirmed the bonding between fluoride and lead.

Table 4. Transitions specifications of TBAFDiCP

λ_2 ($\epsilon, M^{-1}cm^{-1}$)	λ_1 ($\epsilon, M^{-1}cm^{-1}$)
275(241)	225(741)
A'→A'	A'→A'

Table 5. Transitions specifications of TBAFDiIP

λ_4 ($\epsilon, M^{-1}cm^{-1}$)	λ_3 ($\epsilon, M^{-1}cm^{-1}$)	λ_2 ($\epsilon, M^{-1}cm^{-1}$)	λ_1 ($\epsilon, M^{-1}cm^{-1}$)
245(1330)	320(124)	336(230)	369(226)
A'→A'	A'→A'	A''→A'	A''→A'

Experimental

Material and instruments. Acetonitrile (Fluka, P.A.) was distilled several times from phosphorus pentoxide before using, thereby reducing its water content to <4 ppm. Tetrabutylammonium fluoride was bought from Merck. PbX₂ (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 ¹⁹F-NMR were recorded on a Bruker AVANCE DRX 500 spectrometer. All the chemical shifts are quoted in ppm using the high-frequency positive convention; ¹H NMR and ¹⁹F-NMR spectra were referenced to external SiMe₄ and CFCl₃ respectively. The percent compositions of elements were obtained from the Microanalytical Laboratories, Department of Chemistry, OIRC, Tehran.

Synthesis of Tetrabutylammonium Fluorodichloroplumbate (TBAFDiCP), (C₄H₉)₄N[PbCl₂F]. To a solution of tetrabutylammonium fluoride (0.50 g, 1.9 mmol) was added a solution of lead dichloride, PbCl₂ (0.51 g, 1.83 mmol) in MeCN under stirring. A yellowish white precipitate was formed. After 24 hours stirring, the mixture was filtered, washed with ether and dried at room temperature. The tetrabutylammonium salts are somewhat hygroscopic, and it was better to be stored under a layer of hexane. Mp: 245 °C. Calcd. C₁₆H₃₆Cl₂FNPb: C. 35.60; H. 6.67; N. 2.59; % found C. 36.49; H. 6.78; N. 2.61; A 0.001 mole solution conductivity is 129 Ω⁻¹cm² mol⁻¹. UV/Visible, IR, ¹H-NMR and ¹³C-NMR were all consistent with the TBAFDiCP structure. In ¹⁹F-NMR of this compound a broad peak was seen near -61 ppm.

Tetrabutylammonium fluorodichloroplumbate is soluble in ethanol and dimethyl sulphoxide (DMSO) and not soluble in dichloromethane, ether and toluene.

Synthesis of Tetrabutylammonium Fluorodiiodoplumbate (TBAFDiIP), (C₄H₉)₄N[PbI₂F]. Tetrabutylammonium fluorodiiodoplumbate (II), [(C₄H₉)₄N][PbI₂F] was prepared by dissolving PbI₂ (0.51 g, 1.83 mmol) in MeCN and addition of this solution to a solution of tetrabutylammonium fluoride (0.50 g, 1.9 mmol) in MeCN under stirring at room temperature until yellow precipitate was formed. After

24 hours stirring, the mixture was filtered, washed with ether and dried at room temperature. Mp: 180 °C. for C₁₆H₃₆FNPbI₂: C. 26.58; H. 4.98; N. 1.93; % found C. 27.38; H. 5.00; N. 1.95; A 0.001 mole solution conductivity is 118 Ω⁻¹cm²mol⁻¹. UV/Visible, IR, ¹H-NMR and ¹³C-NMR were all consistent with the TBAFDiIP structure. Tetrabutylammonium fluorodiiodoplumbate is soluble in diethylether, metanol (DMSO), acetone and not soluble in chloroform and toluene.

Conclusion

Two new fluorocompounds of PbX₂ was synthesized simply. (C₄H₉)₄N[PbCl₂F] was prepared by the reaction of (C₄H₉)₄NF and PbCl₂ and (C₄H₉)₄N[PbI₂F] was prepared by the reaction of (C₄H₉)₄NF and PbI₂ in a 1:1 ratio in MeCN solvent. Electronic and vibrational spectra of these new Fluoro-complexes were studied. These compounds were characterized by elemental analysis, IR, UV/Visible, and ¹³C-NMR, ¹H-NMR and ¹⁹F-NMR techniques. Production of this compound shows the ability of tetrabutylammonium fluoride in fluoride addition to main group elements compounds.

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