Journal of Fluorine Chemistry 110 (2001) 157–163

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# Novel synthetic route to fluorofullerenes: reaction with binary and complex lead fluorides

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Received 13 February 2001; accepted 24 March 2001

## Abstract

We have recently developed methods of preparation of fluorofullerenes with specific fluorine content. Our previous successful synthesis of $C_{60}F_{36}$ and $C_{60}F_{18}$ with the use of transition metal fluorides inspired us to probe other high oxidation metal fluorides. In this work we report on the use of the binary lead fluorides ($PbF_2$, $PbF_4$, $Pb_2F_6$) and their complexes with alkali metal and alkaline earth metal fluorides ($M_2PbF_6$, $M_3PbF_7$ and $M'PbF_6$) as fluorinating reagents for fullerenes. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Fullerene; Fluorofullerene; Fluorination; Lead fluorides; Preparation

## 1. Introduction

For the first time, the preparation of fluorofullerene mixtures ($C_{60}F_n$, $n = 6$–48) in the reaction of fullerene extracts with fluorine gas was reported in 1991 by Selig et al. [1]. Later detailed studies of the direct fluorination of [60]fullerene under different conditions were performed, and formation of fluorinated products was observed [2–5]. Gakh et al. [6] made the first approach in the selective preparation of fluorofullerenes: a sample with high content of $C_{60}F_{48}$ (68%) was synthesized by two-stage fluorination of $C_{60}$ in a sodium fluoride matrix at 280°C. On the basis of $^{19}F$ NMR spectra of this sample the authors proposed a possible structure of $C_{60}F_{48}$ ($D_3$ symmetry). Synthesis of $C_{60}F_{48}$ (purity >95%) with 75–80% yield in the reaction of fullerene with fluorine gas at 350°C was reported in 1997 [7]. Fluorination at lower temperatures (290–300°C) led to the formation of $C_{60}F_{46}$ as the main product. Notably, attempts to prepare specific fluorofullerenes with low fluorine content ($C_{60}F_n$, $n < 46$) by direct fluorination failed.

Application of transition metal fluorides allowed the synthesis and characterization of some new fluorinated fullerenes [8–11]. Reaction of [60]fullerene with manganese(III) fluoride results in the samples of $C_{60}F_{36}$ [12]. The sample $C_{60}F_{18}$ forms as the main product of fluorination with the use of potassium hexafluoroplatinate ($K_2PtF_6$) [13]. Pure $C_{60}F_{18}$ was isolated with the use of HPLC on the crude material and its X-ray single crystal structure was reported [14]. However, difficulties in isolation and low yields of the reaction limit the availability of $C_{60}F_{18}$. Other inorganic fluorides ($CoF_3$, $TbF_4$) give rise to $C_{60}F_n$, $n = 36$–48 [15]. In all syntheses reported till now the product composition depends on the properties of fluorinating reagents: more reactive fluorides afford products with higher fluorine content [16].

Aiming at the alternative synthetic routes to fluorofullerenes, we have undertaken a systematic study of the reactions of [60]fullerene with binary and complex lead fluorides. Variation in the reagent activity was achieved by changing the fluorine content in the binary fluorides or by using complexes with different alkali and alkaline earth metals.

## 2. Results and discussion

### 2.1. Fluorination with binary lead fluorides

It is well known that lead tetrafluoride decomposes at high temperature to fluorine gas and a compound with the empirical formula $PbF_3$ [17]. Charpin et al. obtained a single crystal structure of this fluoride and determined its composition $PbF_4 \cdot PbF_2$ [18]. In our work, three binary lead fluorides ($PbF_4$, $Pb_2F_6$, $PbF_2$) were prepared and their reactions with [60]fullerene were studied.

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PII: S0022-1139(01)00424-9

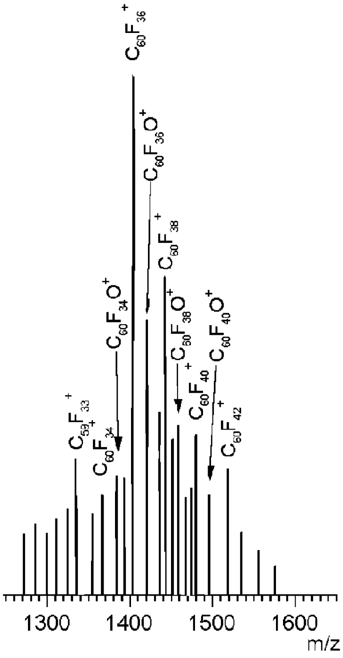

Fig. 1. EI mass spectrum of the product prepared with the use of $PbF_4$.

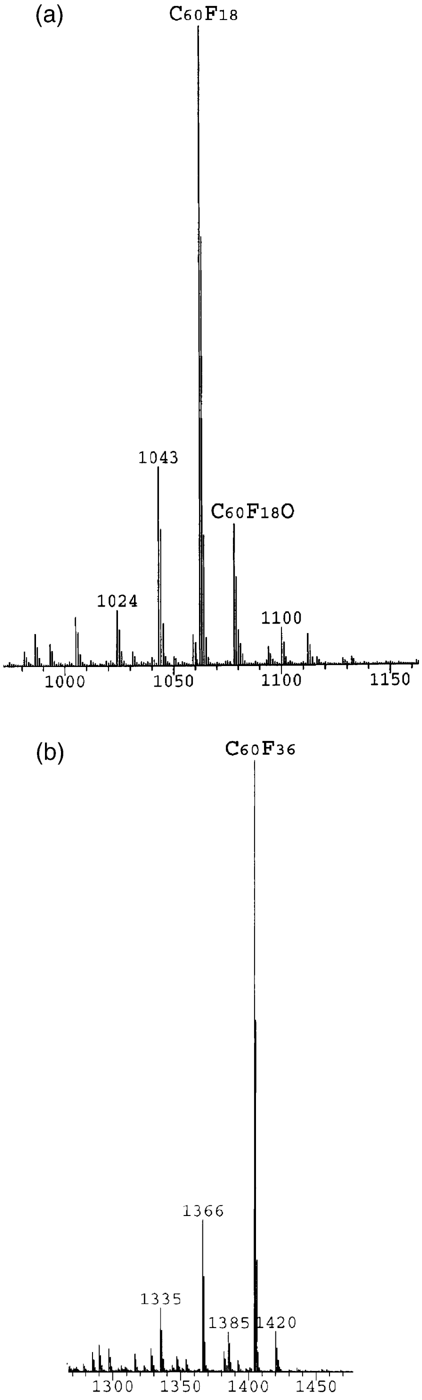

Fig. 2. EI mass spectra of the $C_{60}F_{18}$ (a) and $C_{60}F_{36}$ (b) samples prepared with $Pb_2F_6$.

Lead difluoride does not fluorinate $C_{60}$. Only the peak of initial $C_{60}^+$ was detected in the EI mass spectrum of the sublimed material (not shown).

Lead(IV) fluoride reacts with $C_{60}$ at 290°C and produces a mixture of fluorofullerenes. The EI mass spectrum (MI 1201) of the sample contains species of fluorinated fullerenes $C_{60}F_n$ ($n = 34$–42) and similar oxofluorofullerenes (see Fig. 1). Formation of the latter could be explained by the partial degradation of lead tetrafluoride to $PbO_2$ on exposure of the reaction mixture in air [19]. Hence, we deliberately introduced lead dioxide into the reaction mixtures and observed a significant increase in the relative content of the oxygenated species in the products ($C_{60}F_{36}O$, $C_{60}F_{34}O$, $C_{60}F_{18}O$).

The fluorinating activity of the reagent $PbF_4 + Pb_2F_6$ (2:1, as found by analysis) was found to be lower than that observed in the case of $PbF_4$, giving $C_{60}F_{36}$ as a main product and traces of $C_{60}F_{38}$, $C_{60}F_{34}$ and various oxofluorofullerenes. No species with higher fluorine content than $C_{60}F_{38}$ were detected in the mass spectrum of the product.

A mixture of $C_{60}F_{36}$ and $C_{60}F_{18}$ forms in the reaction of $C_{60}$ with $PbF_2{\cdot}PbF_4$ at 450°C. We managed to separate this mixture by fractional vacuum sublimation of the crude product. Fluorofullerene, $C_{60}F_{36}$, as the most volatile component was removed at 290°C ($6 \times 10^{-3}$ mmHg), whereas $C_{60}F_{18}$ was sublimed at 350°C. EI mass spectra of the isolated fluorofullerenes are shown in Fig. 2. The sample of $C_{60}F_{36}$ contained admixtures of $C_{60}F_{34}$ (1366 amu) and $C_{60}F_{36}O$ (1420 amu). The ions $C_{60}F_{35}^+$ (1385 amu) and $C_{59}F_{33}^+$ (1335 amu) are formed due to fragmentation of the $C_{60}F_{36}$ molecule. Fragmentation of $C_{60}F_{18}$ occurs via loss of $n$(F) atoms yielding $C_{60}F_{18-n}^+$ (Fig. 2b). Peaks at 1078, 1100, 1112 amu correspond to the presence of $C_{60}F_{18}O$, $C_{60}F_{20}$ and $C_{60}F_{17}CF_3$ in the sample of $C_{60}F_{18}$. All three were isolated and their structures are described elsewhere [9–11].

We found that yields and the composition of the crude products in the reaction between $C_{60}$ and $Pb_2F_6$ depend on the ratio of the reagents. Increase in the fullerene content in the reaction mixture led to the decrease in the $C_{60}F_{18}/C_{60}F_{36}$

Table 1
Influence of the $C_{60}/Pb_2F_6$ ratio on the crude product composition

| Mole ratio of $C_{60}/Pb_2F_6$ | $C_{60}F_{36}$ (%) | $C_{60}F_{18}$ (%) |
|---|---|---|
| 1:26 | 70 | 8 |
| 1:18 | 50 | 15 |
| 1:9 | 40 | 12 |

ratio, while the total yield of the fluorinated products drops (see experimental data in Table 1). This observation can be explained by the formation of lead(II, IV) fluoride with lower fluorine content ($PbF_x$, $x < 3$), which enables formation of $C_{60}F_{18}$ at the final stage of fluorination. The observed sequence of the fluorination stages in the reactions with binary lead fluorides is schematically presented in Fig. 3.

### 2.2. *Fluorination with the use of complex lead fluorides*

Alkali and alkaline earth ions stabilize high oxidation states of transition metals in their complex fluorides [20]. This stabilization effect results in the increase in thermal stability and in the decrease in the reactivity of complexes in comparison with similar binary fluorides [21]. According to the theoretical predictions and experimental observations, compounds $M_3PbF_7$ are less active than $M_2PbF_6$, and reactivity of both types of complex fluorides decreases with the size of ion in going from lithium to cesium [22].

#### 2.2.1. *Reactions with complex lead fluorides $MPbF_6$*

We studied reactions of [60]fullerene with complex lead fluorides $MgPbF_6$, $CaPbF_6$, $SrPbF_6$ and $BaPbF_6$. All fluorinating reagents react with $C_{60}$ at 250–320°C and produce $C_{60}F_{36}$ with very high yield (90–96%). Purity of one of the prepared samples was found to be particularly high: neither oxofluorides nor other admixtures were detected by mass spectrometry and HPLC. The IR and EI mass spectra of the $C_{60}F_{36}$ sample are shown in Fig. 4.

The IR spectrum (Fig. 4b) contains partly resolved main bands at 1163 and 1175 $cm^{-1}$, which characterize two main bands of the isomers of $C_{60}F_{36}$. The observed IR spectrum is identical to the one reported by us previously for the crude sample of $C_{60}F_{36}$ obtained with the use of $MnF_3$ which contained 1:3 ratio of the *T* and $C_3$ isomers [12].

Notably, variation in temperature of fluorination and ratio of reagents in the reaction mixture did not affect yield and composition of the product.

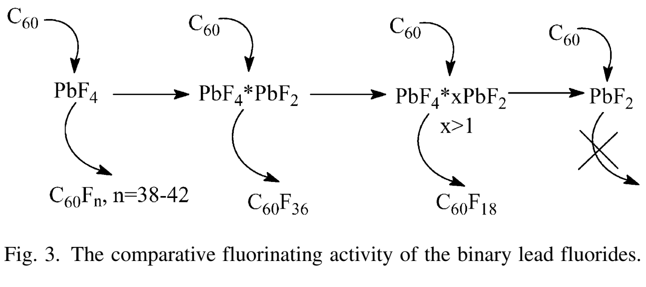

Fig. 3. The comparative fluorinating activity of the binary lead fluorides.

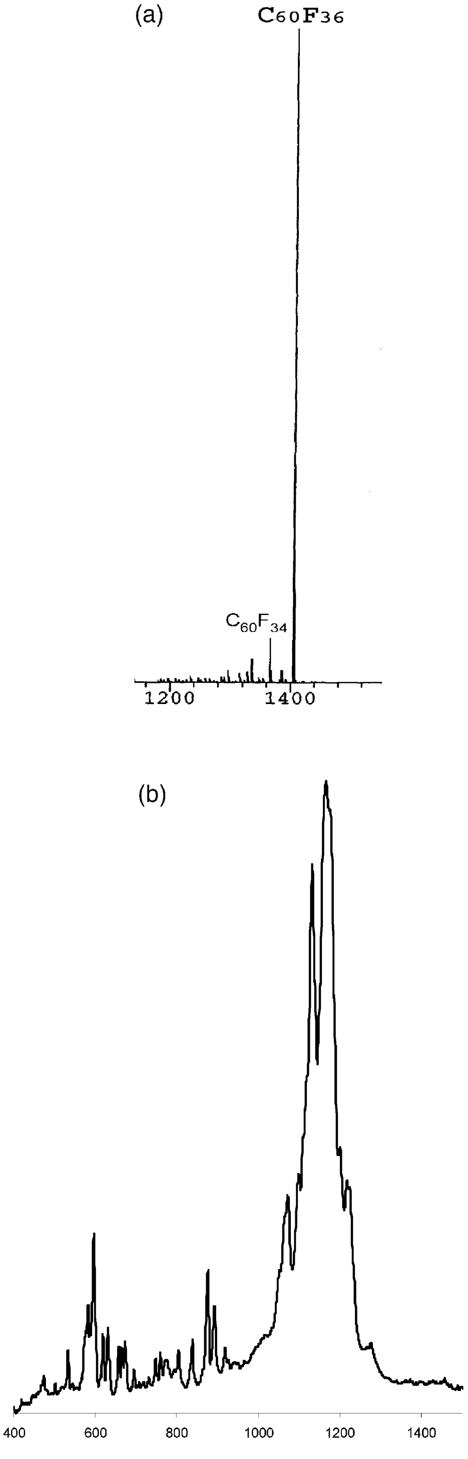

Fig. 4. EI mass spectra (a) and IR (b) spectra of the synthesized $C_{60}F_{36}$.

#### 2.2.2. *Fluorination with the use of lead complex fluorides with alkali metals*

Fluorinating activity of the complex lead fluorides with alkali metals $M_2PbF_6$ and $M_3PbF_7$ (M = Li, Na, K, Rb, Cs) was studied in the reactions with [60]fullerene. Reactions of $C_{60}$ with lithium, sodium, potassium and rubidium complex fluorides afforded mainly $C_{60}F_{36}$ with $C_{60}F_{18}$ as a minor product. The sample $C_{60}F_{36}$ was separated from the crude

Table 2
Intensities of the main species in the EI mass spectra of the $C_{60}F_{36}$ samples

| Reagent | $C_{60}F_{36}$ (%) | $C_{60}F_{34}$ (%) | $C_{60}F_{36}O$ (%) | $C_{60}F_{34}O$ (%) |
|---|---|---|---|---|
| $Li_2PbF_6$ | 100 | 25 | 4 | 3 |
| $K_2PbF_6$ | 100 | 13 | 2 | 2 |
| $Na_3PbF_7$ | 100 | 14 | 2 | 0 |
| $K_3PbF_7$ | 100 | 16 | 2 | 0 |

material by vacuum sublimation with yields 60–90%, the purity of thus isolated samples evaluated by means of EI mass spectra analysis is given in Table 2. The presence of oxygenated fluorofullerenes (for some reagents up to 3–4%) can be probably explained by the partial hydrolysis of fluorofullerenes in the reaction vessel, though detailed investigation of the origin of these species has not been performed in the present work.

Noteworthy is the fact that content of $C_{60}F_{18}$ estimated from the HPLC traces of the crude samples increases going from lithium to rubidium for both $M_2PbF_6$ and $M_3PbF_7$ complexes used for fluorination. The latter reagent, however, yielded higher relative content of $C_{60}F_{18}$ than the former, when comparing the same alkali metal complex (see Table 3). The sample $C_{60}F_{18}$ does not form in the reaction with $Li_2PbF_6$, the highest yield (15%) (but still insignificant for large-scale preparations) was observed in the case of $Rb_3PbF_7$. We may conclude that the stability of the fluorinating agents significantly affects yield of $C_{60}F_{18}$: the more stable the complex lead fluoride the higher the yield of $C_{60}F_{18}$ is achieved. We found that variation in the ratio of the reagents in the reacting mixtures does not affect the product yields and compositions.

In contrast, in reactions with cesium complexes compositions of the crude products were found to depend significantly on the reagents' ratio (Table 4). We suppose that by analogy with binary lead fluorides, initial samples of $Cs_2PbF_6$ and $Cs_3PbF_7$ get partially reduced during the reaction with fullerene forming complexes $Cs_2PbF_x$ $(4 < x < 6)$ and $Cs_3PbF_y$ $(5 < y < 7)$, respectively. The latter are believed to be responsible for the $C_{60}F_{18}$ formation.

We observed a considerable increase in the relative content of $C_{60}F_{18}$ in the crude products of reactions with $Cs_2PbF_6$ ($T_r = 480°C$) and $Cs_3PbF_7$ ($T_r = 490°C$) reaching the yields 35 and 65%, respectively, which is sufficient for its large-scale preparation. EI mass spectra of the $C_{60}F_{18}$ and $C_{60}F_{36}$ samples obtained as a result of fractional sublimation of the crude are shown in Fig. 5.

Table 3
Effect of the reagent activity on the product composition

| Reagent | $T_r$ (°C)[a] | $C_{60}F_{36}$ (2%) | $C_{60}F_{18}$ (2%) |
|---|---|---|---|
| $Li_2PbF_6$ | 380 | 34 | 0 |
| $Na_2PbF_6$ | 420 | 90 | 6 |
| $K_2PbF_6$ | 430 | 87 | 6 |
| $Rb_2PbF_6$ | 460 | 70 | 10 |
| $Li_3PbF_7$ | 400 | 90 | 3 |
| $Na_3PbF_7$ | 450 | 88 | 8 |
| $K_3PbF_7$ | 460 | 85 | 9 |
| $Rb_3PbF_7$ | 490 | 85 | 15 |

[a] The temperature $T_r$ was estimated by the appearance of the product in the cold zone of the reactor.

Table 4
Influence of the reagent ratio on the crude product composition

| $Cs_2PbF_6$ | | $Cs_3PbF_7$ | |
|---|---|---|---|
| Mole reagents ratio of $C_{60}/Cs_2PbF_6$ | Yield of $C_{60}F_{18}$ (%) | Mole reagents ratio of $C_{60}/Cs_3PbF_7$ | Yield of $C_{60}F_{18}$ (%) |
| 1:30 | 12 | 1:24 | 40 |
| 1:18 | 30 | 1:19 | 38 |
| 1:13 | 35 | 1:12 | 65 |

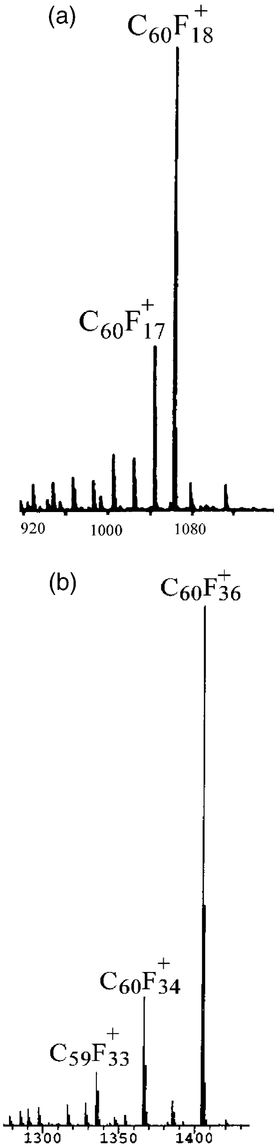

Fig. 5. EI mass spectra of $C_{60}F_{18}$ (a) and $C_{60}F_{36}$ (b) synthesized using $Cs_2PbF_6$.

## 3. Conclusions

In this study, the first thorough systematic investigation of the reaction between $C_{60}$ and lead fluorides has been performed. Our intention was to find out what are the main factors that determine specific routes of the fluorination process of fullerene and result in the distribution of products with varying fluorine content. For this purpose, the whole series of binary and complex lead fluorides were prepared and characterized.

The first conclusion that can be drawn from our experiments is indeed striking: in spite of the use of over a dozen fluorinating reagents based on lead(II, IV) fluorides, only two dominant products are formed: $C_{60}F_{36}$ and $C_{60}F_{18}$.

Controlling fluorinating ability of the reagents by changing relative content of the active Pb(IV) fluoride in case of binary fluorides or by varying the stability of the complexes by changing the metal ion radii, we did not find conditions under which fluorinated fullerenes with very low fluorine content $n(\mathrm{F}) < 18$ would preferably be formed.

Both $C_{60}F_{36}$ and $C_{60}F_{18}$ can be synthesized in these reactions with remarkable yields and purity and on a larger preparative scale than reported previously with the use of other fluorinating agents (sometimes quite expensive). Thus, we found new perspective synthetic routes for the preparation of $C_{60}F_{18}$ (purity ~85%) in the reactions with $Cs_2PbF_6$ and $Cs_3PbF_7$ and $C_{60}F_{36}$ (purity >95%) and in the reactions with alkaline earth metal complexes $MPbF_6$ (M = Mg, Ca, Sr, Ba).

We conjectured that a two-stage reduction of $Pb_2F_6$ via $PbF_x$ ($2 < x < 3$) to $PbF_2$ could be the cause of the two consecutive stages in the fluorination process, that is, formation of the two dominant products ($C_{60}F_{36}$ and $C_{60}F_{18}$). Similarly, in fluorination with complex cesium lead fluorides the two-stage process can be explained by the formation of the intermediate complex which is responsible for the generation of $C_{60}F_{18}$ at the final reaction stage.

## 4. Experimental

### 4.1. General experimental procedures

#### 4.1.1. XRD diffraction

DRON-3 diffractometer (Cu Kα-radiation, $\lambda = 1.5418$ Å) was applied for X-ray powder diffraction (XRD) analysis of fluorinating agents. All experiments were carried out at room temperature with $\alpha$-$Al_2O_3$ as a standard. While recording X-ray data, we protected our samples from degradation in air with a perfluoroalkane matrix. We indexed the unit cell parameters from XRD data using Treor and Pirum programs (Table 5).

#### 4.1.2. IR spectroscopy

IR spectra (KBr disk) were recorded on the VECTOR22, Bruker spectrometer.

#### 4.1.3. EI mass spectrometry (70 eV)

It was performed with the use of two instruments: double focusing VG Autospec (UK), DCI probe; and magnetic sector MI-1201 (USSR) with the incorporated Ni effusion cell.

#### 4.1.4. HPLC

This was carried out on the Cosmosil Buckyprep column (toluene eluent, 10 mm × 25 cm). At flow rate 4.7 ml min$^{-1}$ retention times of $C_{60}F_{36}$, $C_{60}$, and $C_{60}F_{18}$ are 2.8, 7.8, and 38.0 min, respectively.

Table 5
XRD data for synthesized fluorides

| Fluoride | Lattice | Unit cell parameters (Å) | | | | | |
|---|---|---|---|---|---|---|---|
| | | Our data | | | Literature data[a] | | |
| | | *a* | *b* | *c* | *a* | *b* | *c* |
| $PbF_2$ | Orthorhombic | 6.42(2) | 3.92(1) | 7.66(3) | 6.44 | 3.90 | 7.65 |
| $Pb_2F_6$ | Tetragonal | 5.22(1) | 5.22(1) | 4.52(3) | 5.201 | 5.201 | 4.523 |
| $PbF_4$ | Tetragonal | 4.25(2) | 4.25(2) | 8.03(3) | 4.25 | 4.25 | 8.03 |
| $MgPbF_6$ | Hexagonal | 5.24(2) | 5.24(2) | 13.98(1) | 5.25 | 5.25 | 13.96 |
| $CaPbF_6$ | Cubic | 8.49(3) | 8.49(3) | 8.49(3) | 8.476 | 8.476 | 8.476 |
| $SrPbF_6$ | Tetragonal | 5.20(1) | 5.20(1) | 8.89(3) | 5.21 | 5.21 | 8.96 |
| $BaPbF_6$ | Hexahonal R | 7.43(1) | 7.43(1) | 7.53(2) | 7.451 | 7.451 | 7.533 |
| $Li_2PbF_6$ | Tetragonal | 6.30(3) | 6.30(3) | 8.36(3) | – | – | – |
| $Na_2PbF_6$ | Tetragonal | 5.09(3) | 5.09(3) | 10.29(1) | – | – | – |
| $K_2PbF_6$ | Tetragonal | 6.33(2) | 6.33(2) | 8.94(3) | – | – | – |
| $Rb_2PbF_6$ | Tetragonal | 7.27(2) | 7.27(2) | 9.09(3) | – | – | – |
| $Rb_2PbF_6$ | Tetragonal | 6.46(4) | 6.46(4) | 4.55(1) | – | – | – |
| $Cs_2PbF_6$ | Tetragonal | 6.40(2) | 6.40(2) | 4.56(1) | – | – | – |
| $Na_3PbF_7$ | Tetragonal | 5.38(1) | 5.38(1) | 10.65(2) | – | – | – |
| $K_3PbF_7$ | Tetragonal | 5.31(2) | 5.31(2) | 11.32(1) | – | – | – |
| $Cs_3PbF_7$ | Tetragonal | 6.52(2) | 6.52(2) | 4.58(3) | – | – | – |

[a] Available XRD databases do not contain any information about the structures of the lead complexes with the alkali metals.

Table 6
Experimental conditions in the syntheses of the lead fluorides

| Fluoride | Reagents | Fluorination conditions[a] | |
|---|---|---|---|
| | | $T$ (°C) | Time (h) |
| $PbF_4$ | $PbCl_2$ | 300 | 4 |
| $PbF_2 \cdot PbF_4$ | $PbO_2$ | 520 | 3 |
| $Li_2PbF_6$ | $2LiCl + PbO_2$ | 520 | 3 |
| $Na_2PbF_6$ | $2NaCl + PbO_2$ | 460 | 3 |
| $K_2PbF_6$ | $2KCl + PbO_2$ | 460 | 3 |
| $Rb_2PbF_6$ | $2RbCl + PbO_2$ | 520 | 4 |
| $Cs_2PbF_6$ | $2CsCl + PbCl_2$ | 460 | 3 |
| $Li_3PbF_7$ | $3LiCl + PbCl_2$ | 460 | 3 |
| $Na_3PbF_7$ | $3NaCl + PbCl_2$ | 460 | 3 |
| $K_3PbF_7$ | $3KCl + PbCl_2$ | 460 | 3 |
| $Rb_3PbF_7$ | $3RbCl + PbCl_2$ | 460 | 3 |
| $Cs_3PbF_7$ | $3CsCl + PbCl_2$ | 520 | 5 |
| $MgPbF_6$ | $MgCl_2 + PbO_2$ | 520 | 4 |
| $CaPbF_6$ | $CaCl_2 + PbO_2$ | 520 | 4 |
| $SrPbF_6$ | $SrCl_2 + PbO_2$ | 520 | 4 |
| $BaPbF_6$ | $BaCl_2 + PbO_2$ | 520 | 4 |

[a] All syntheses were performed with the use of mixture $F_2$ (10 vol.%) and $N_2$ under the pressure $10^5$ Pa.

Table 7
Chemical analysis data

| Fluoride | Fluorine content (%) | |
|---|---|---|
| | Experimental | Stoichiometric |
| $PbF_2$ | 16.0 | 15.5 |
| $Pb_2F_6$ | 21.1 | 21.5 |
| $PbF_4$ | 25.9 | 26.8 |
| $MgPbF_6$ | 33.2 | 33.0 |
| $CaPbF_6$ | 30.6 | 31.6 |
| $SrPbF_6$ | 25.3 | 27.9 |
| $BaPbF_6$ | 24.1 | 24.9 |
| $Li_2PbF_6$ | 31.9 | 34.1 |
| $Na_2PbF_6$ | 31.6 | 31.1 |
| $K_2PbF_6$ | 28.8 | 28.6 |
| $Rb_2PbF_6$ | 21.0 | 23.2 |
| $Cs_2PbF_6$ | 18.8 | 19.5 |
| $Li_3PbF_7$ | 37.3 | 36.8 |
| $Na_3PbF_7$ | 30.0 | 32.5 |
| $K_3PbF_7$ | 26.8 | 29.1 |
| $Rb_3PbF_7$ | 22.6 | 22.4 |
| $Cs_3PbF_7$ | 17.8 | 18.1 |

### *4.1.5. Preparation of fluorinating reagents*

Lead(II) fluoride was prepared by dissolving lead carbonate in hydrofluoric acid (see details in [23]). Synthesis of other binary and complex lead fluorides ($PbF_4$, $PbF_{3.7}$,[1] $Pb_2F_6$, $PbF_2$) was carried out in a nickel reactor using a mixture of fluorine gas (10%) and nitrogen. As starting materials for the preparation of binary fluorides $PbF_4$, and $PbF_4 \times PbF_2$ either lead(II) chloride or $PbO_2$ were applied. Stoichiometric mixtures of PbO or $PbO_2$ with halides of alkali and alkali earth metals were subject to direct fluorination in the synthetic procedure of the complex fluorides (details are given in Table 6). The fluorinating agents prepared were immediately packed into the sealed glass tubes and then characterized by chemical analysis (CA) and XRD. The data on the composition obtained from CA are given in Table 7, indexed unit cell parameters see in Table 5.

### *4.1.6. Fluorination of [60]fullerene*

An intimately ground mixture of the fullerene ($C_{60}$, 99.9%, Term, USA) and a fluorinating agent was placed into the nickel boat that was embedded into the glass tube and evacuated ($5 \times 10^{-3}$ mmHg). All these procedures were done in air in 1–2 min, as a result we did not observe substantial degradation of the fluorinating reagents except for lead tetrafluoride where partial (<5%) hydrolysis to $PbO_2$ occurred. We then heated the nickel container with the reaction mixture and due to the high volatility of the products of fluorination the latter were collected in the cold end of the tube. As a result further purification from unreacted starting materials was not necessary except for the cases when the reaction was carried out at high temperatures ($T > 500$) and small amounts of unreacted $C_{60}$ were sublimed along with the fluorofullerenes. In such cases, we used fractional sublimation in order to get rid of impurities. We obtained a range of colored polycrystalline products: from light yellow to dark brown, and these were subjected to the IR spectroscopy and EI mass spectrometry. A few milligrams of the products were dissolved in toluene and analyzed by HPLC, which provided us with information on the relative distribution of the components in the mixture.

## Acknowledgements

We are indebted to Drs. R. Taylor and A. Abdul Sada of Sussex University, UK, for cooperation in the HPLC analysis and mass spectrometry. The invaluable assistance of Drs. V.M. Danilenko and S.E. Semenov of Moscow Chemical Liceum, Russia, is greatly appreciated. This work was partially supported by the INTAS Project 97-30027, RFBR Project 99-15-33391a and Scientific Program Fullerenes and Atomic Clusters (Project Sfera).

## References

[1] H. Selig, C. Lifshitz, T. Peres, J.E. Fischer, A.R. McGhie, W.J. Romanow, J.P. McCauley Jr., A.B. Smith III, J. Am. Chem. Soc. 113 (1991) 5475–5476.

[2] J.H. Holloway, E.G. Hope, R. Taylor, G.J. Langley, A.G. Avent, T.J. Dennis, J.P. Hare, H.W. Kroto, R.M. Walton, J. Chem. Soc., Chem. Commun. (1991) 966–969.

[3] S.K. Chowdhury, S.D. Cameron, D.M. Cox, K. Kniaz, R.A. Strongin, M.A. Cichy, J.E. Fischer, A.B. Smith III, Org. Mass Spec. 28 (1993) 860–866.

[4] K. Kniaz, J.E. Fischer, H. Selig, G.M.B. Vaughan, W.J. Romanow, D.M. Cox, S.K. Chowdhury, J.P. McCauley Jr., R.A. Strongin, A.B. Smith III, J. Am. Chem. Soc. 115 (1993) 6060–6064.

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[1] $PbF_{3.7}$ is the mixture of $2PbF_4 + Pb_2F_6$.

[5] T. Nakajima, Y. Matsuo, S. Kasamatsu, K. Nakanishi, Carbon 6 (1994) 1117–1190.
[6] A.A. Gakh, A.A. Tuinman, J.L. Adcock, R.A. Sachleben, R.N. Compton, J. Am. Chem. Soc. 116 (1994) 819–820.
[7] O.V. Boltalina, L.N. Sidorov, V.F. Bagryantsev, V.A. Seredenko, A.S. Zapol'skii, J.M. Street, R. Taylor, J. Chem. Soc., Perkin Trans. 2 (1996) 2275–2278.
[8] G. Avent, O.V. Boltalina, A.Y. Lukonin, J.M. Street, R. Taylor, J. Chem. Soc., Perkin Trans. 2 (2000) 1–3.
[9] O.V. Boltalina, J.H. Holloway, J.M. Street, R. Taylor, J. Chem. Soc., Perkin Trans. 2 (1998) 1845–1850.
[10] O.V. Boltalina, A.Y. Lukonin, A.G. Avent, J.M. Street, R. Taylor, J. Chem. Soc., Perkin Trans. 2 (2000) 683–686.
[11] O.V. Boltalina, J.M. Street, R. Taylor, Chem. Commun. (1998) 1827–1828.
[12] O.V. Boltalina, J.M. Street, R. Taylor, J. Chem. Soc., Perkin Trans. 2 (1998) 649–653.
[13] O.V. Boltalina, V.Y. Markov, R. Taylor, M.P. Waugh, Chem. Commun. (1996) 2549–2550.
[14] I.S. Neretin, K.A. Lyssenko, M.Y. Antipin, Y.L. Slovokhotov, O.V. Boltalina, P.A. Troshin, A.Y. Lukonin, L.N. Sidorov, R. Taylor, Angew. Chem. Int. Edn. 39 (2000) 3273.
[15] O.V. Boltalina, A.Y. Lukonin, V.K. Pavlovich, L.N. Sidorov, R. Taylor, A.K. Abdul-Sada, Fullerene Sci. Technol. 6 (1998) 469.
[16] O.V. Boltalina, A.Yu. Lukonin, A.A. Gorjunkov, V.K. Pavlovich, A.N. Rykov, L.N. Sidorov, in: K. Kadish, R. Ruoff (Eds.), Recent Advances in Chemistry and Physics of Fullerenes and Related Materials, Vol. 4, Pennigton, New Jersey, 1997, p. 257.
[17] R. Brauner, J. Chem. Soc. 65 (1894) 393.
[18] P. Charpin, H. Marquete, N.G. Nguen, P. Plurien, C.R. Seances Acad. 275 (1972) 1503.
[19] H. Wartenberg, Z. Anorg. Chem. 244 (1940) 337.
[20] I.G. Ryss, Khimia ftora I ego neorganicheskikh soedinenii, Goskhimizdat, Moskva, 1956 (in Russian).
[21] R.L. Davidovich, Atlas derivatogramm kompleksnykh ftoridov metallov II–V grupp, Nauka, Moskva, 1976 (in Russian).
[22] J. Clark, J. Am. Chem. Soc. 41 (1919) 480.
[23] G. Brauer (Ed.), Rukovodstvo po neorganicheskomu Sintezu, Mir, Moskva, 1986 (in Russian).