

# Sol–gel synthesis of $K_3InF_6$ and structural characterization of $K_2InC_{10}O_{10}H_6F_9$ , $K_3InC_{12}O_{14}H_4F_{18}$ and $K_3InC_{12}O_{12}F_{18}$

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## Abstract

$K_3InF_6$  is synthesized by a sol–gel route starting from indium and potassium acetates dissolved in isopropanol in the stoichiometry 1:3, with trifluoroacetic acid as fluorinating agent. The crystal structures of the organic precursors were solved by X-ray diffraction methods on single crystals. Three organic compounds were isolated and identified:  $K_2InC_{10}O_{10}H_6F_9$ ,  $K_3InC_{12}O_{14}H_4F_{18}$  and  $K_3InC_{12}O_{12}F_{18}$ . The first one, deficient in potassium in comparison with the initial stoichiometry, is unstable. In its crystal structure, acetate as well as trifluoroacetate anions are coordinated to the indium atom. The two other precursors are obtained, respectively, by quick and slow evaporation of the solution. They correspond to the final organic compounds, which give  $K_3InF_6$  by decomposition at high temperature. The crystal structure of  $K_3InC_{12}O_{14}H_4F_{18}$  is characterized by complex anions  $[In(CF_3COO)_4(OH_x)_2]^{(5-2x)-}$  and isolated  $[CF_3COOH_{2-x}]^{(x-1)-}$  molecules with  $x = 2$  or 1, surrounded by  $K^+$  cations. The crystal structure of  $K_3InC_{12}O_{12}F_{18}$  is only constituted by complex anions  $[In(CF_3COO)_6]^{3-}$  and  $K^+$  cations. For all these compounds, potassium cations ensure only the electroneutrality of the structure. IR spectra of  $K_2InC_{10}O_{10}H_6F_9$  and  $K_3InC_{12}O_{12}F_{18}$  were also performed at room temperature on pulverized crystals.

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**Keywords:** Fluoride; Sol–gel;  $K_3InF_6$ ;  $K_2InC_{10}O_{10}H_6F_9$ ;  $K_3InC_{12}O_{14}H_4F_{18}$ ;  $K_3InC_{12}O_{12}F_{18}$ ; Crystal structure; Trifluoroacetate

## 1. Introduction

In a previous paper we have already described the synthesis of an oxyfluoride:  $K_{0.31}Gd_{0.69}F_{1.84}O_{0.27}$  [1], by a sol–gel process derived from that described by Fujihara et al. [2–4]. Our goal is the realization of thin films deposited on different beforehand engraved substrates in order to obtain afterwards new materials with specific features for particular optical applications. The present work is devoted to the synthesis of  $K_3InF_6$  using this sol–gel route and particularly to the crystal structures of the intermediate organic phases. The aim of this work is to understand the mechanism of the formation of the organic precursors in order to optimize

in the future the synthesis of different fluorides by the sol–gel method.

## 2. Synthesis of $K_3InF_6$ by a sol–gel route

Indium (Aldrich 99.99%) and potassium (Aldrich 99+%) acetates, in the stoichiometric proportion 1:3, are dissolved in isopropanol, in a Teflon reactor, under an argon atmosphere. The fluorinating agent added in excess in the solution is trifluoroacetic acid (Aldrich 99%). Then this solution is stirred for 3 h at room temperature, but it cannot be used immediately to obtain pure  $K_3InF_6$ . It is kept in a closed container and a 20 days maturation step is necessary. During this time, a compound, formulated  $K_2InC_{10}O_{10}H_6F_9$ , crystallizes

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temporarily and dissolves spontaneously 3 or 4 days later. One crystal was collected in order to solve its structure.

A part of the solution was also rapidly evaporated at room temperature within 4 days and at the final stage of the evaporation some little crystals appear among the powder. One crystal formulated  $\text{K}_3\text{InC}_{12}\text{O}_{14}\text{H}_4\text{F}_{18}$ , was collected and its structure was solved.

Another part of the solution was slowly evaporated during 34 days, at room temperature and a lot of hexagonal crystals appeared. The crystal structure of one of them, formulated  $\text{K}_3\text{InC}_{12}\text{O}_{12}\text{F}_{18}$ , was solved too.

After 20 days of maturation, the solution preserved in a hermetically sealed bottle, is transparent and a weak quantity is deposited on a silica sheet by spin coating. The silica sheet was preliminary depolished in a mix solution of sulfuric and hydrofluoric acids, in order to ameliorate the adhesion of the coating on the sheet. The silica sheet is then heated in a tubular furnace between 200 and 500 °C for 40 min, under a dehydrated argon stream in order to minimize alteration of the synthesized fluoride:  $\text{K}_3\text{InF}_6$ .

Fig. 1a shows the evolution of the X-ray powder patterns of thin films as a function of the temperature. At 200 °C, the presence of some extra diffraction lines in comparison with the X-ray diffraction pattern of  $\text{K}_3\text{InF}_6$  given in the ICDD-database, indicates clearly that the departure of the organic groups is not completed. From 300 °C, these extra diffraction lines disappear and all observed lines correspond unambiguously to those reported for the X-ray powder pattern of  $\text{K}_3\text{InF}_6$  (cubic  $Fd\bar{3}$ ,  $a = 17.71 \text{ \AA}$ ). This observation is in agreement with the DTA–TGA experiment (Fig. 1b),

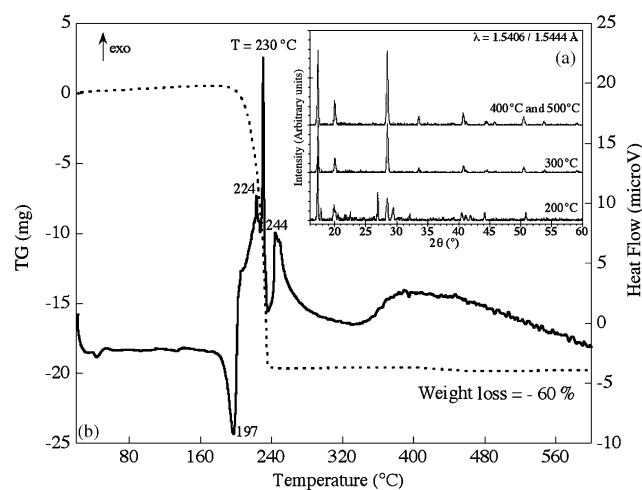


Fig. 1. (a) Evolution of the X-ray diffraction patterns recorded at room temperature of thin films deposited by spin coating of the solution on silica sheets versus treatment temperature. (b) Thermogravimetric (dotted curve) and differential thermal (full curve) analyses of the powdered precursor of  $\text{K}_3\text{InF}_6$  obtained by evaporation of the solution at room temperature.

which indicates a departure of the organic groups between 190 and 250 °C. The profile of the X-ray pattern of the sample heated at 500 °C and its cell parameter were then refined using the Fullprof suite programs [5] and the refined cell parameter reaches the value:  $a = 17.672(2) \text{ \AA}$ .

### 3. Experimental section

#### 3.1. Strategy of crystal structure determination

Crystals are mounted with Paratone-N oil (Hampton Research) coating and immediately placed in a nitrogen cold stream in order to avoid the damage of the crystal by air and also to reduce the thermal motion of atoms. X-ray intensity data are collected at 100 K on a Bruker-Nonius X8-APEX2 CCD area-detector diffractometer using Mo- $K_\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Data reductions are accomplished using SAINT V7.03 [6]. The substantial redundancy in data allows to apply a semi-empirical absorption correction (SADABS V2.10) [6], on the basis of multiple measurements of equivalent reflections. The structures are solved by direct methods, developed by successive difference Fourier syntheses and refined by full-matrix least squares on all  $F^2$  data using SHELXTL V6.12 [7]. The conditions of the data collections are summarized in Table 1.

#### 3.2. Infrared spectra

Infrared spectra are recorded on a BIORAD spectrometer at room temperature. The powder obtained from pulverized single crystals, is mixed with dry KBr and pressed as a pellet. Data collections are performed under a dry argon stream in order to eliminate the carbon dioxide.

#### 3.3. Powder diffraction measurements

X-ray powder patterns are recorded at room temperature on a vertical Philips PW1050/25 goniometer mounted in the Bragg Brentano configuration (Cu- $K_\alpha$  radiation, Ni filtered).

### 4. Description of the crystal structure of $\text{K}_2\text{InC}_{10}\text{O}_{10}\text{H}_6\text{F}_9$

The crystal structure of  $\text{K}_2\text{InC}_{10}\text{O}_{10}\text{H}_6\text{F}_9$  is built up from an isolated indium complex anion formulated  $[\text{In}(\text{CH}_3\text{COO})_2(\text{CF}_3\text{COO})_3]^{2-}$  and from two non-coordinating  $\text{K}^+$  cations, which ensure the electroneutrality. In the complex anion  $[\text{In}(\text{CH}_3\text{COO})_2(\text{CF}_3\text{COO})_3]^{2-}$ , indium is seven-coordinated to oxygen atoms (Fig. 2).

Table 1

Crystal data, data collections and refinement characteristics for  $K_2InC_{10}O_{10}H_6F_9$ ,  $K_3InC_{12}O_{14}H_4F_{18}$  and  $K_3InC_{12}O_{12}F_{18}$ 

Formula	$K_2InC_{10}O_{10}H_6F_9$	$K_3InC_{12}O_{14}H_4F_{18}$	$K_3InC_{12}O_{12}F_{18}$
Formula weight	650.17 g mol <sup>-1</sup>	942.24 g mol <sup>-1</sup>	910.24 g mol <sup>-1</sup>
Temperature	100(2) K	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system, space group	Monoclinic, $P2_1/c$ (no. 14)	Triclinic, $P-1$ (no. 2)	Trigonal $P-3$ (no. 147)
Unit cell dimensions	$a = 9.4208(4)$ Å $b = 16.6553(8)$ Å $c = 14.4737(6)$ Å $\alpha = 90^\circ$ $\beta = 121.471(2)^\circ$ $\gamma = 90^\circ$	$a = 7.6428(4)$ Å $b = 7.8702(4)$ Å $c = 12.4449(5)$ Å $\alpha = 71.932(2)^\circ$ $\beta = 76.816(2)^\circ$ $\gamma = 82.170(2)^\circ$	$a = 10.0241(2)$ Å $b = 10.0241(2)$ Å $c = 7.3990(4)$ Å $\alpha = 90^\circ$ $\beta = 90^\circ$ $\gamma = 120^\circ$
Volume	1936.96(15) Å <sup>3</sup>	691.16(6) Å <sup>3</sup>	643.83(4) Å <sup>3</sup>
Z, calculated density	4; 2.230 g cm <sup>-3</sup>	1; 2.264 g cm <sup>-3</sup>	1; 2.348 g cm <sup>-3</sup>
Absorption coefficient	1.784 mm <sup>-1</sup>	1.490 mm <sup>-1</sup>	1.590 mm <sup>-1</sup>
$F(000)$	1256	452	436
Crystal size	0.14 × 0.08 × 0.04 mm	0.10 × 0.08 × 0.02 mm	0.28 × 0.20 × 0.10 mm
$\theta$ range for data collection	2.45–38.65°	1.76–30.51°	2.35–30.04°
Limiting indices	$-16 \leq h \leq 16$ $-29 \leq k \leq 29$ $-25 \leq l \leq 24$	$-10 \leq h \leq 10$ $-11 \leq k \leq 10$ $-17 \leq l \leq 17$	$-14 \leq h \leq 14$ $-12 \leq k \leq 13$ $-10 \leq l \leq 10$
Reflections collected/unique:	95444/10955 [ $R_{int} = 0.0328$ ]	11399/4197 [ $R_{int} = 0.0342$ ]	15080/1269 [ $R_{int} = 0.0419$ ]
Completeness to $\theta$	38.65 99.4%	30.51 99.5%	30.04 100%
Absorption correction		Semi-empirical from equivalents	
Max. and min. transmission	0.9321 and 0.7883	0.9708 and 0.8653	0.8572 and 0.6645
Refinement method		Full-matrix least-squares on $F^2$	
Data/restraints/parameters	10955/0/291	4197/0/223	1269/0/72
Goodness-of-fit on $F^2$	1.027	1.045	1.151
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0374$ $wR_2 = 0.0962$	$R_1 = 0.0361$ $wR_2 = 0.0837$	$R_1 = 0.0165$ $wR_2 = 0.0445$
$R$ indices (all data)	$R_1 = 0.0472$ $wR_2 = 0.0996$	$R_1 = 0.0473$ $wR_2 = 0.0882$	$R_1 = 0.0169$ $wR_2 = 0.0448$
Electron density in Fourier difference map (max height and min height)	3.06 <sup>a</sup> and $-1.53$ e Å <sup>-3</sup>	1.10 and $-1.04$ e Å <sup>-3</sup>	0.58 and $-0.59$ e Å <sup>-3</sup>

<sup>a</sup>At 0.58 Å from indium.

Four of them belong to two independent  $[CH_3COO]^-$  acetate anions, while the three other oxygen atoms belong to three independent  $[CF_3COO]^-$  trifluoroacetate anions. Table 2 gathers the refined atomic positions and isotropic displacement values for  $K_2InC_{10}O_{10}H_6F_9$ .

The chelating character of the two acetate anions is in agreement with the infrared spectrum recorded at room temperature on pulverized crystals (Fig. 3), which shows a difference in wavenumber between  $\nu_{asym}$  and  $\nu_{sym}$  of the carboxyl group of the acetate in the range 80–100 cm<sup>-1</sup> [8]. The distances between oxygen atoms of an acetate anion and the indium atom are 2.226 and 2.382 Å for the first anion and 2.214 and 2.325 Å for the second (Table 3). The trifluoroacetate anions are monodentate ligands with In–O distances varying between 2.136 and 2.163 Å (Table 3). Fig. 4 shows the projection of the structure along the [100] direction.

## 5. Description of the crystal structure of $K_3InC_{12}O_{14}H_4F_{18}$

Table 4 gathers the refined atomic positions and isotropic displacement values for  $K_3InC_{12}O_{14}H_4F_{18}$ . As hydrogen atoms cannot be localized easily by X-ray diffraction in  $K_3InC_{12}O_{14}H_4F_{18}$ , two solutions can be proposed for the formulation of the precursor:  $K_3[In(CF_3COO)_4(H_2O)_2][CF_3COO]_2$  (a) and  $K_3[In(CF_3COO)_4(OH)_2][CF_3COOH]_2$  (b).

The choice of the first formulation (a) is based on a careful examination of the final difference Fourier map, which shows two electron density peaks ( $\sim 1$  e Å<sup>-3</sup>) that may correspond to two hydrogen atoms close to the O(7) atom connected to In. The H–O distances ( $\sim 0.8$  and  $0.7$  Å) and the H–O–H angle ( $\sim 108.5^\circ$ ) are in agreement with those observed for a water molecule. Moreover, the In–O(7) bond length is rather long (2.190(2) Å), in agreement with those encountered

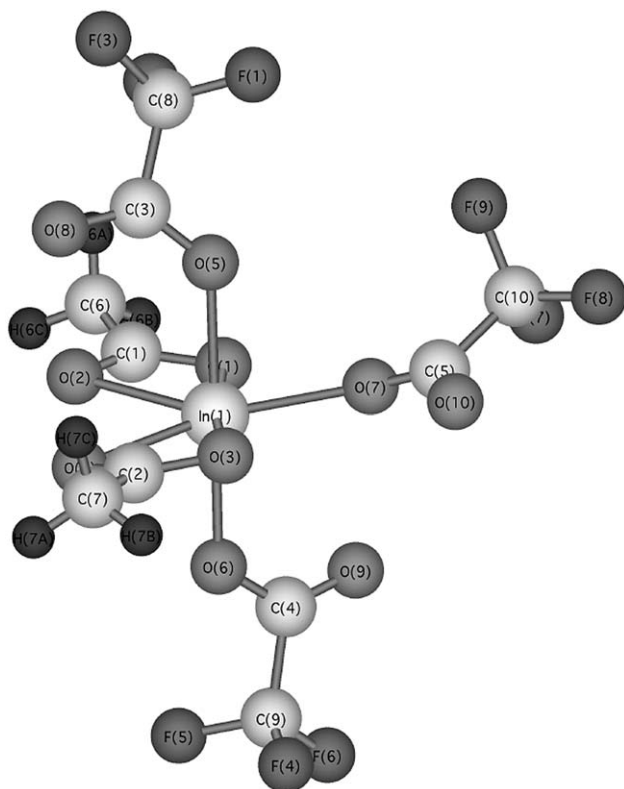


Fig. 2. Molecular structure of the complex anion  $[\text{In}(\text{CH}_3\text{COO})_2(\text{CF}_3\text{COO})_3]^{2-}$  in  $\text{K}_2\text{InC}_{10}\text{O}_{10}\text{H}_6\text{F}_9$ .

in aqua and aqua-chloride complexes of indium [9] and in  $\text{In}_2(\text{HPO}_3)_3(\text{H}_2\text{O})$  [10], while  $\text{In}-\text{OH}^-$  bond lengths are really shorter than the  $\text{In}-\text{OH}_2$  ones : 2.056(5) Å in  $\text{In}(\text{OH})(\text{CF}_3\text{COO})_2(\text{CH}_3\text{CN})$  [11] and 2.084(7) in  $\text{NH}_4\text{In}(\text{OH})\text{PO}_4$  [12]. The major argument in favour of the second formulation (b) is the carbon–oxygen distances in the isolated  $[\text{CF}_3\text{COO}]^-$  or  $[\text{CF}_3\text{COOH}]$  groups. Indeed, the values of the distances  $\text{C}(5)-\text{O}(5)$  and  $\text{C}(5)-\text{O}(6)$  must be identical in a  $[\text{CF}_3\text{COO}]^-$  trifluoroacetate anion [13] in respect with the delocalization of the charge on both oxygen atoms. In  $\text{K}_3\text{InC}_{12}\text{O}_{14}\text{H}_4\text{F}_{18}$ , the  $\text{C}(5)-\text{O}(5)$  and  $\text{C}(5)-\text{O}(6)$  bond lengths are different with a  $\text{C}(5)-\text{O}(5)$  distance (1.225(4) Å) shorter than  $\text{C}(5)-\text{O}(6)$  (1.276(3) Å). Therefore, we can consider that  $\text{O}(6)$  is not only bonded to  $\text{C}(5)$  but also to a hydrogen atom. So, in order to respect the electroneutrality of the crystal structure, in this case the indium atom must be connected to two hydroxide anions. In fact, the two formulations are probably encountered in different domains of the crystal structure, X-ray diffraction allowing only to determine an average structure. Nevertheless, domains with the first formulation  $\text{K}_3[\text{In}(\text{CF}_3\text{COO})_4(\text{H}_2\text{O})_2][\text{CF}_3\text{COO}]_2$  (a) seem to be predominant, because the  $\text{In}-\text{O}(7)$  bond length appears to be the strongest argument (Table 5).

Table 2

Atomic coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for the crystal structure of  $\text{K}_2\text{InC}_{10}\text{O}_{10}\text{H}_6\text{F}_9$  (e.s.d. in parentheses)

Atom	x	y	z	$U_{\text{eq}}$
In	2486(1)	3215(1)	4207(1)	17(1)
O(1)	2747(2)	3059(1)	5817(1)	22(1)
O(2)	4654(2)	3813(1)	5831(1)	28(1)
O(3)	2075(2)	3222(1)	2555(1)	23(1)
O(4)	3816(2)	4118(1)	3681(1)	21(1)
O(5)	4193(2)	2237(1)	4672(1)	25(1)
O(6)	798(2)	4207(1)	3819(1)	21(1)
O(7)	712(2)	2263(1)	3854(1)	23(1)
O(8)	6600(2)	2716(1)	4899(1)	23(1)
O(9)	-1158(2)	3650(1)	4080(2)	40(1)
O(10)	-431(2)	1747(1)	2165(1)	27(1)
C(1)	4097(2)	3459(1)	6342(2)	21(1)
C(2)	3119(2)	3788(1)	2764(2)	20(1)
C(3)	5723(2)	2219(1)	4991(2)	19(1)
C(4)	-569(2)	4184(1)	3807(2)	21(1)
C(5)	24(2)	1732(1)	3124(1)	17(1)
C(6)	5000(3)	3456(2)	7556(2)	31(1)
C(7)	3496(4)	4028(2)	1915(2)	32(1)
C(8)	6549(3)	1438(1)	5617(2)	26(1)
C(9)	-1562(2)	4970(1)	3381(2)	21(1)
C(10)	-234(3)	942(1)	3579(2)	24(1)
F(1)	5638(3)	804(1)	5186(2)	69(1)
F(2)	6809(4)	1509(2)	6619(2)	72(1)
F(3)	8029(2)	1309(1)	5764(2)	52(1)
F(4)	-2169(3)	5084(1)	2354(1)	52(1)
F(5)	-546(2)	5589(1)	3926(2)	42(1)
F(6)	-2767(2)	5005(1)	3598(2)	45(1)
F(7)	-818(2)	1075(1)	4237(1)	35(1)
F(8)	-1314(3)	452(1)	2795(1)	42(1)
F(9)	1194(3)	549(1)	4159(2)	46(1)
K(1)	9955(1)	2507(1)	5618(1)	18(1)
K(2)	7065(1)	4327(1)	5468(1)	22(1)

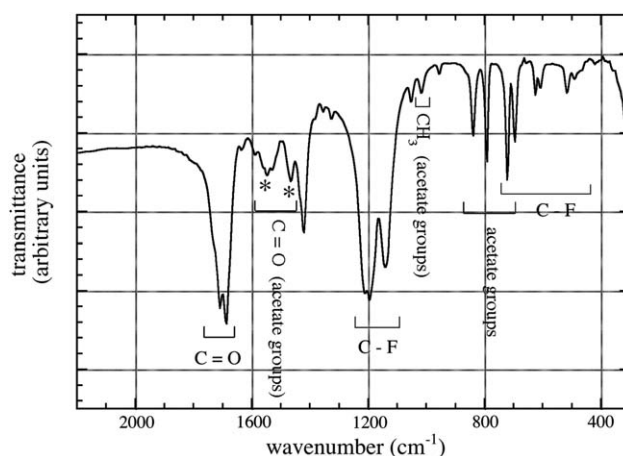


Fig. 3. Infrared spectrum of powdered  $\text{K}_2\text{InC}_{10}\text{O}_{10}\text{H}_6\text{F}_9$  obtained by pulverization of single crystals.

In comparison with the previous crystal structure of  $\text{K}_2\text{InC}_{10}\text{O}_{10}\text{H}_6\text{F}_9$ , the indium atom exhibits here a six-coordinated environment, with four trifluoroacetate

Table 3

Interatomic distances (Å) and bond angles (°) around indium and in the acetate and trifluoroacetate anions (e.s.d. in parentheses) for  $K_2InC_{10}O_{10}H_6F_9$

In	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)	O(7)
O(1)	<b>2.226(2)</b>						
O(2)	56.44(5)	<b>2.382(2)</b>					
O(3)	172.84(6)	129.81(5)	<b>2.214(2)</b>				
O(4)	129.39(5)	73.88(5)	57.53(5)	<b>2.325(1)</b>			
O(5)	85.84(6)	83.75(6)	91.31(6)	98.68(6)	<b>2.136(2)</b>		
O(6)	91.49(6)	94.20(6)	91.42(6)	82.48(5)	177.24(6)	<b>2.154(2)</b>	
O(7)	79.10(6)	134.28(6)	94.04(6)	151.48(5)	82.92(6)	92.27(6)	<b>2.163(1)</b>

*Two independent chelating acetate anions connected to the indium atom:*

C(1)	O(1)	O(2)	C(6)	C(2)	O(3)	O(4)	C(7)
O(1)	<b>1.277(2)</b>			O(3)	<b>1.280(2)</b>		
O(2)	119.2(2)	<b>1.254(2)</b>		O(4)	118.9(2)	<b>1.259(2)</b>	
C(6)	118.4(2)	122.4(2)	<b>1.500(3)</b>	C(7)	119.0(2)	122.1(2)	<b>1.500(3)</b>

*Three independent trifluoroacetate anions connected to the indium atom:*

C(8)	F(1)	F(2)	F(3)	→	C(3)	O(5)	O(8)	C(8)
F(1)	<b>1.296(3)</b>				O(5)	<b>1.264(2)</b>		
F(2)	107.0(3)	<b>1.344(3)</b>			O(8)	130.6(2)	<b>1.224(2)</b>	
F(3)	108.9(2)	105.0(2)	<b>1.313(3)</b>		C(8)	111.3(2)	118.1(2)	<b>1.544(3)</b>

C(9)	F(4)	F(5)	F(6)	→	C(4)	O(6)	O(9)	C(9)
F(4)	<b>1.298(3)</b>				O(6)	<b>1.280(2)</b>		
F(5)	108.2(2)	<b>1.347(3)</b>			O(9)	130.1(2)	<b>1.218(3)</b>	
F(6)	110.2(2)	105.2(2)	<b>1.327(3)</b>		C(9)	112.1(2)	117.8(2)	<b>1.539(3)</b>

C(10)	F(7)	F(8)	F(9)	→	C(5)	O(7)	O(10)	C(10)
F(7)	<b>1.344(3)</b>				O(7)	<b>1.267(2)</b>		
F(8)	106.9(2)	<b>1.335(2)</b>			O(10)	131.0(2)	<b>1.221(2)</b>	
F(9)	106.7(2)	107.9(2)	<b>1.328(3)</b>		C(10)	111.4(2)	117.6(2)	<b>1.546(3)</b>

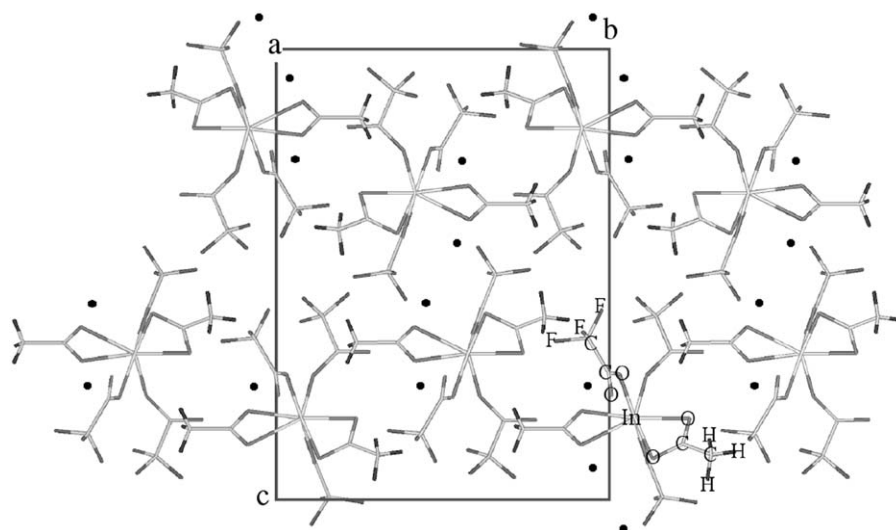


Fig. 4. Projection of the crystal structure of  $K_2InC_{10}O_{10}H_6F_9$  along the [100] direction. The isolated circles represent the potassium cations.

Table 4

Atomic coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for the crystal structure of  $\text{K}_3\text{InC}_{12}\text{O}_{14}\text{H}_4\text{F}_{18}$  (e.s.d. in parentheses)

Atom	x	y	z	$U_{\text{eq}}$
In	0	0	5000	8(1)
K(1)	4386(2)	1872(1)	2529(1)	14(1)
K(2) <sup>a</sup>	2078(3)	-4213(3)	4060(2)	44(1)
F(1)	1393(2)	4080(3)	6734(2)	22(1)
F(2)	3104(3)	1739(3)	7389(2)	27(1)
F(3)	4254(2)	4045(2)	6091(2)	20(1)
F(4)	9348(4)	2348(3)	767(2)	41(1)
F(5)	1541(3)	3290(5)	1096(2)	76(1)
F(6)	8978(5)	4761(3)	1195(2)	74(1)
F(7)	1057(3)	-1551(3)	1365(2)	35(1)
F(8)	3463(4)	-796(3)	1666(2)	37(1)
F(9)	3034(3)	-213(3)	-67(2)	31(1)
O(1)	989(3)	1871(3)	5612(2)	12(1)
O(2)	3970(3)	1834(3)	4850(2)	13(1)
O(3)	491(3)	1740(3)	3273(2)	12(1)
O(4)	7632(3)	1798(3)	3057(2)	16(1)
O(5)	3722(3)	-4436(3)	1869(2)	23(1)
O(6)	4438(3)	-3439(3)	-61(2)	20(1)
O(7)	2641(3)	-1278(3)	4451(2)	12(1)
C(1)	2628(4)	2182(3)	5513(2)	10(1)
C(2)	2845(4)	3055(4)	6430(2)	13(1)
C(3)	9204(4)	2141(4)	2711(2)	12(1)
C(4)	9785(4)	3169(4)	1429(2)	18(1)
C(5)	3742(4)	-3285(4)	942(2)	16(1)
C(6)	2814(4)	-1427(4)	962(3)	19(1)

<sup>a</sup>This site is a half occupied by potassium.

anions and two water molecules (*a*) or hydroxide anions (*b*) (Fig. 5A). This feature leads to an indium complex anion formulated  $[\text{In}(\text{CF}_3\text{COO})_4(\text{H}_2\text{O})_2]^-$  (*a*) or  $[\text{In}(\text{CF}_3\text{COO})_4(\text{OH})_2]^{3-}$  (*b*). Three  $\text{K}^+$  cations ensure the electroneutrality of the structure. As in  $\text{K}_2\text{InC}_{10}\text{O}_{10}\text{H}_6\text{F}_9$ , the trifluoroacetate anions are monodentate ligands with an In–O distance of 2.141(2) Å. The water molecules (*a*) or hydroxide anions (*b*) are in trans positions with an In–O distance of 2.190(2) Å. This crystal structure exhibits a particular feature with the presence of two isolated  $[\text{CF}_3\text{COO}]^-$  trifluoroacetate anions (*a*) or  $[\text{CF}_3\text{COOH}]$  trifluoroacetic acid molecules (*b*) per cell (Fig. 6).

## 6. Description of the crystal structure of $\text{K}_3\text{InC}_{12}\text{O}_{12}\text{F}_{18}$

The crystal structure of  $\text{K}_3\text{InC}_{12}\text{O}_{12}\text{F}_{18}$  is built up from isolated indium complex anions formulated  $[\text{In}(\text{CF}_3\text{COO})_6]^{3-}$  (Fig. 5B) and from three non-coordinating  $\text{K}^+$  cations, which ensure the electroneutrality. This crystal structure derives from that of  $\text{K}_3\text{InC}_{12}\text{O}_{14}\text{H}_4\text{F}_{18}$ . This latter compound loses two water molecules and the isolated trifluoroacetate anions (or those issued from the isolated trifluoroacetic acid molecules) are now connected to the indium atom. In  $\text{K}_3\text{InC}_{12}\text{O}_{12}\text{F}_{18}$ , the indium atom is then in a rather regular six-coordinated octahedral environment of

Table 5

Interatomic distances (Å) and bond angles (°) around indium and in the trifluoroacetate anions (e.s.d. in parentheses) for  $\text{K}_3\text{InC}_{12}\text{O}_{14}\text{H}_4\text{F}_{18}$

In	$2 \times \text{O}(1)$	$2 \times \text{O}(3)$	$2 \times \text{O}(7)$					
$2 \times \text{O}(1)$	<b>2.141(2)</b>							
$2 \times \text{O}(3)$	91.07(7)	<b>2.141(2)</b>						
$2 \times \text{O}(7)$	96.00(7)	83.80(7)	<b>2.190(2)</b>					
<i>Two independent trifluoroacetate anions connected to the indium atom:</i>								
C(2)	F(1)	F(2)	F(3)	→	C(1)	O(1)	O(2)	C(2)
F(1)	<b>1.334(3)</b>				O(1)	<b>1.280(3)</b>		
F(2)	107.2(2)	<b>1.349(3)</b>			O(2)	129.4(2)	<b>1.219(3)</b>	
F(3)	107.8(2)	107.2(2)	<b>1.328(3)</b>		C(2)	111.8(2)	118.7(2)	<b>1.552(4)</b>
C(4)	F(4)	F(5)	F(6)	→	C(3)	O(3)	O(4)	C(4)
F(4)	<b>1.312(4)</b>				O(3)	<b>1.284(3)</b>		
F(5)	105.2(3)	<b>1.318(4)</b>			O(4)	128.6(2)	<b>1.217(3)</b>	
F(6)	106.8(3)	109.4(3)	<b>1.297(4)</b>		C(4)	113.9(2)	117.5(2)	<b>1.540(4)</b>
<i>Isolated trifluoroacetate anion (a) or isolated trifluoroacetic acid molecule (b):</i>								
C(6)	F(7)	F(8)	F(9)	→	C(5)	O(5)	O(6)	C(6)
F(7)	<b>1.328(4)</b>				O(5)	<b>1.225(4)</b>		
F(8)	107.4(3)	<b>1.340(4)</b>			O(6)	127.5(3)	<b>1.276(3)</b>	
F(9)	107.8(3)	107.5(3)	<b>1.329(3)</b>		C(6)	117.5(3)	115.0(2)	<b>1.541(4)</b>

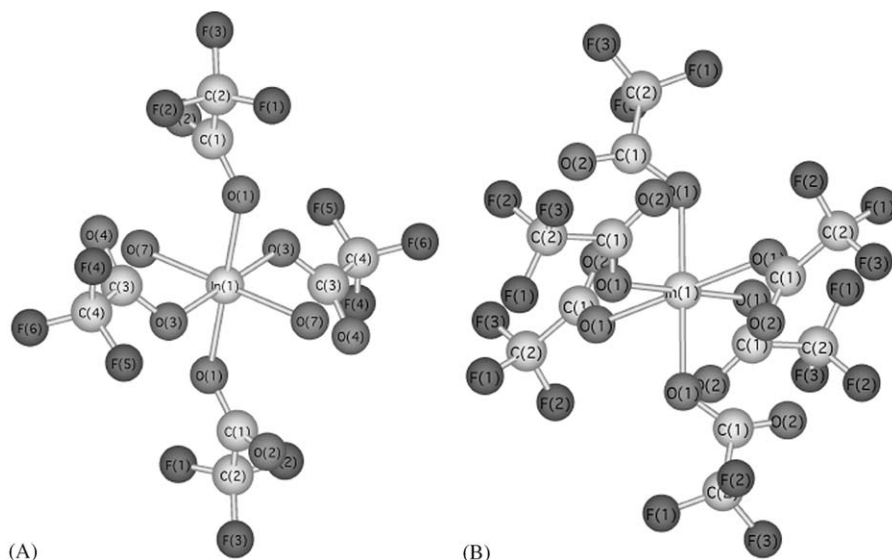


Fig. 5. (A) Molecular structure of the complex anion  $[\text{In}(\text{CF}_3\text{COO})_4(\text{H}_2\text{O})_2]^-$  (a) or  $[\text{In}(\text{CF}_3\text{COO})_4(\text{OH})_2]^{3-}$  (b) in  $\text{K}_3\text{InC}_{12}\text{O}_{14}\text{H}_4\text{F}_{18}$ . (B) Molecular structure of the complex anion  $[\text{In}(\text{CF}_3\text{COO})_6]^{3-}$  in  $\text{K}_3\text{InC}_{12}\text{O}_{12}\text{F}_{18}$ .

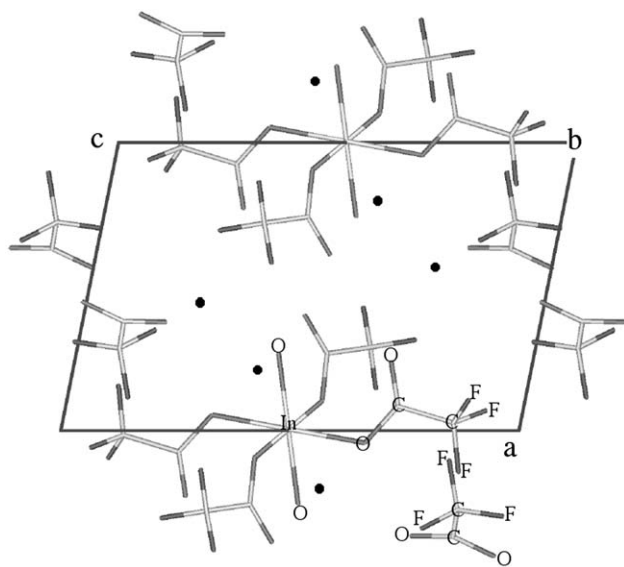


Fig. 6. Projection of the crystal structure of  $\text{K}_3\text{InC}_{12}\text{O}_{14}\text{H}_4\text{F}_{18}$  along the  $[010]$  direction. The isolated circles represent the potassium cations.

monodentate trifluoroacetate anions, with six In–O distances of 2.153(1) Å and O–In–O angles of 180, 81.26(3) and 98.74(3)°. Table 6 gathers the refined atomic positions and isotropic displacement values for  $\text{K}_3\text{InC}_{12}\text{O}_{12}\text{F}_{18}$  and Table 7 gives the distances and angles in the trifluoroacetate anion. Fig. 7 shows the projection of the crystal structure along the  $[001]$  direction.

The infrared spectrum recorded at room temperature on pulverized crystals of  $\text{K}_3\text{InC}_{12}\text{O}_{12}\text{F}_{18}$  is shown in Fig. 8. This one differs from that of  $\text{K}_2\text{InC}_{10}\text{O}_{10}\text{H}_6\text{F}_9$  by the absence of the peaks between 950 and 1100  $\text{cm}^{-1}$  corresponding to the  $[\text{CH}_3]$  groups and by the peak

Table 6

Atomic coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{Å}^2 \times 10^3$ ) for the crystal structure of  $\text{K}_3\text{InC}_{12}\text{O}_{12}\text{F}_{18}$  (e.s.d. in parentheses)

Atom	x	y	z	$U_{\text{eq}}$
In	0	0	0	8(1)
O(1)	1392(1)	1770(1)	1918(1)	13(1)
O(2)	2616(1)	3827(1)	80(1)	21(1)
C(1)	2390(1)	3142(1)	1510(2)	13(1)
C(2)	3489(1)	4013(1)	3098(2)	17(1)
F(1)	2799(1)	3588(1)	4706(1)	31(1)
F(2)	4661(1)	3722(1)	3126(1)	22(1)
F(3)	4105(1)	5532(1)	2949(1)	32(1)
K(1)	0	0	5000	17(1)
K(2)	6667	3333	793(1)	18(1)

profiles between 1450 and 1650  $\text{cm}^{-1}$  corresponding to the carboxyl group of the trifluoroacetate. This spectrum is close to that of  $\text{CF}_3\text{COOH}$  listed in the NIST database [14]. It is then in agreement with the crystal structure of  $\text{K}_3\text{InC}_{12}\text{O}_{12}\text{F}_{18}$ , which exhibits only six trifluoroacetate anions connected to one indium atom.

## 7. Discussion and conclusion

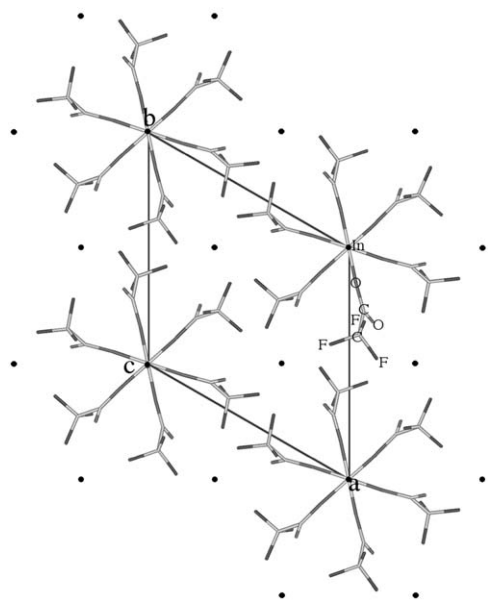
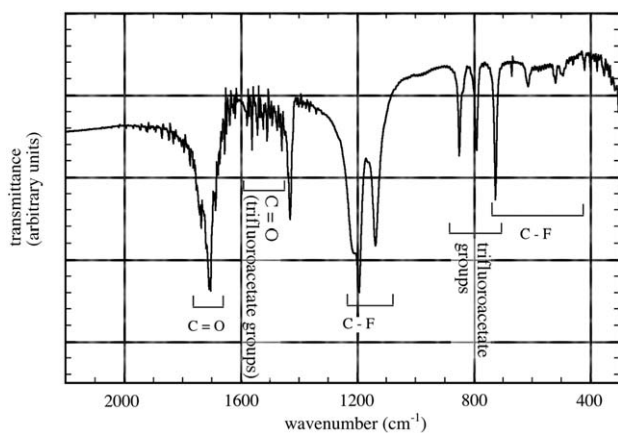
The synthesis of the organic precursors of  $\text{K}_3\text{InF}_6$  is performed according to a complex process. At the beginning, the indium and potassium acetates, in the stoichiometric proportion 1:3, are dissolved in an isopropanol solution with an excess of trifluoroacetic acid.

This complex process, which leads to trifluoroacetate compounds, can be explained by the acid strength

Table 7

Interatomic distances (Å) and bond angles (°) in the trifluoroacetate anion (e.s.d. in parentheses) for  $K_3InC_{12}O_{12}F_{18}$ 

C(2)	F(1)	F(2)	F(3)	→	C(1)	O(1)	O(2)	C(2)
F(1)	<b>1.334(2)</b>				O(1)	<b>1.268(1)</b>		
F(2)	106.6(1)	<b>1.345(1)</b>			O(2)	129.9(1)	<b>1.219(1)</b>	
F(3)	108.0(1)	107.1(1)	<b>1.331(2)</b>		C(2)	112.6(1)	117.5(1)	<b>1.547(2)</b>

Fig. 7. Projection of the crystal structure of  $K_3InC_{12}O_{12}F_{18}$  along the  $[001]$  direction. The isolated circles represent the potassium cations.Fig. 8. Infrared spectrum of powdered  $K_3InC_{12}O_{12}F_{18}$  obtained by pulverization of single crystals.

difference between trifluoroacetic and acetic acids due to the higher electronegativity of fluorine in comparison with that of hydrogen. The  $pK_a$  values in water for trifluoroacetic ( $CF_3COOH/CF_3COO^-$ ) and acetic

( $CH_3COOH/CH_3COO^-$ ) acids are, respectively: 0.3 and 4.8 [15]. If the  $pK_a$  values are probably different in isopropanol, the relative acid strengths between the two acids should not change. Thus,  $CF_3COO^-$  and  $CH_3COOH$  species are all the more privileged in the solution because trifluoroacetic acid is in excess and this feature leads finally to privilege trifluoroacetate complexes. The exchange between acetate and trifluoroacetate ions occurs slowly and can allow the crystallization of unstable intermediate compounds such as  $K_2InC_{10}O_{10}H_6F_9$ , in which the indium complex anion  $[In(CH_3COO)_2(CF_3COO)_3]^{2-}$  exhibits chelating acetate and monodentate trifluoroacetate anions. It is noticeable that the stoichiometry of this compound is not in agreement with that of the initial solution (1In:3K). Few days after their apparition in the solution, the crystals of  $K_2InC_{10}O_{10}H_6F_9$ , unstable, dissolve spontaneously, probably by bond breaking between indium and acetate anions and their substitution by trifluoroacetate anions. The evaporation on a sand-bath at  $100^\circ C$  of the solution at this stage of the maturation process gives a powder with at least a second intermediate compound rich in potassium. The X-ray diffraction pattern of this powder shows the diffraction lines of  $K_2InC_{10}O_{10}H_6F_9$  with some extra lines of an unknown compound. Indeed, this one is not recorded in the ICDD-database.

At the end of the maturation process, the solution is thoroughly limpid and the crystals obtained for the precursor of  $K_3InF_6$  depend on the evaporation mode:

By rapid evaporation of the solution  $K_3InC_{12}O_{14}H_4F_{18}$ , in which chelating acetate anions are replaced by water molecules (a) or hydroxide anions (b) and trifluoroacetate anions, is obtained. The potassium rate corresponds now to the attempted value i.e., 3 potassium for 1 indium. This compound exhibits a particular feature with the presence of isolated trifluoroacetate anions (a) or trifluoroacetic acid molecules (b) in the crystal structure. The presence of water (a) or hydroxide (b) anions is attributed to the water always present in small quantities in isopropanol and trifluoroacetic acid.

By slow evaporation of the solution, another kind of compound, formulated  $K_3InC_{12}O_{12}F_{18}$ , crystallizes in the trigonal system, space group  $P-3$ . In this latter, the indium atom is completely coordinated to six trifluor-



oacetate anions. It is probable that  $\text{K}_3\text{InC}_{12}\text{O}_{12}\text{F}_{18}$  corresponds to the most achieved and stable precursor of  $\text{K}_3\text{InF}_6$ . In comparison with  $\text{K}_3\text{InC}_{12}\text{O}_{14}\text{H}_4\text{F}_{18}$ , water (*a*) or hydroxide (*b*) anions in the coordinating sphere of indium are replaced by trifluoroacetate anions and the crystal structure does not exhibit any more isolated trifluoroacetate anions (*a*) nor trifluoroacetic acid molecules (*b*).

By heating above 200 °C, these precursors are degraded according to the results of DTA–TGA experiments. The compounds during their degradation lose probably water and organic groups such as  $\text{COF}_2$ , CO ... [16]. Among these ones, some organic fluorinated products act as fluorinating agents and a fluorine environment substitutes the oxygen environment of the indium atom in the precursors to form finally  $\text{K}_3\text{InF}_6$ .

Nevertheless, if the adopted sol–gel process is the same for all the synthesized fluorides or oxyfluorides, it appears that the precursors exhibit different kinds of crystal structures as a function of the elements. IR experiments have shown that the precursor of the synthesis of  $\text{K}_{0.31}\text{Gd}_{0.69}\text{F}_{1.83}\text{O}_{0.27}$  [1] for example, contains bridging acetate anions.

Our investigations, as well as works conducted by previous authors [2–4] show that this sol–gel process is well adapted to synthesize a large range of fluorinated and oxyfluorinated compounds [1–4]. Some compounds doped with trivalent rare earths, particularly europium, are synthesized and luminescence properties on thin films deposited on glass substrates are investigated. The results of these works will be published in further papers.

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