ELSEVIER

Coordination Chemistry Reviews
158 (1997) 69–101

COORDINATION CHEMISTRY REVIEWS

Organometal fluorides of aluminium, gallium, indium and thallium

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Received 5 September 1995; accepted 23 October 1995

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Abstract

Diorganometal fluorides can be synthesized by reaction of the corresponding metallanes with synthons like $BF_3 \cdot (OEt)_2$ and Me_3SnF. A second general synthesis strategy is the fluoridation of diorganometal halides with alkali metal fluorides or silver fluoride. Organometal difluorides of Al, Ga and In are either unknown or can be obtained in special cases only. Arylthallium difluorides are the result of the reaction of arylthallium bis(trifluoroacetates) and alkali or ammonium fluorides. Various types of salts with anions like

PII S0010-8545(96)01256-8

$[R_3MF]^-$, $[R_2MF_2]^-$, $[RMF_3]^-$ and $[R_3MFMR_3]^-$ have been synthesized by the treatment of the corresponding educts R_3M, R_2MX, RMX_2 with salt-like fluorides. The IR and NMR spectroscopical data and the structural investigation show the mainly ionic character of the metal fluorine bond.

Keywords: Organometal fluoride; Organoaluminium fluorides; Organofluoro gallates; Organogallium fluorides; Organoindium fluorides; Organothallium fluorides

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1. Introduction

Organometal fluorides of the Group 13 metals differ in some important features from the other organometal halides of this group. One significant difference concerns the synthesis of the compounds [1–3]. The two commonly used methods for the preparation of such species: (1) the commutation reaction of organometallanes and metal halides and (2) the treatment of metal halides with lithium alkyls or Grignard reagents do not lead to the desired products. This is mainly due to the low reactivity of the metal(III) fluorides.

The second important difference lies in the highly ionic character of the metal(III) fluorine bond. This, for example, has consequences for the observed structures of the organometal fluorides because of the tendency of the fluorine atoms to form linear M–F–M bridges.

This review lists the various synthesis routes for the organometal fluorides, but also gives a comparison of their structures and chemical properties.

2. Synthesis and reactions of organoaluminium fluorides

2.1. *Synthesis and characterization of diorganoaluminium fluorides*

Diorganoaluminium fluorides can be synthesized by several well-established routes [4–6] (Eqs. (1)–(4)). The routes have been used for the preparation of several dialkyl derivatives R_2MF with R = Me [4], Et [4,5], ^{n}Pr [4], ^{i}Pr [4,6], ^{n}Bu [7], ^{i}Bu [4], ^{t}Bu [6] and ^{n}Hex [7].

$$R_2AlCl + NaF \rightarrow R_2AlF + NaCl \quad [4] \qquad (1)$$

$$2R_2AlCl + MF_2 \rightarrow 2R_2AlF + MCl_2 \quad [5] \qquad (2)$$

M = Ca, Sr, Ba

$$3R_3Al \cdot (OEt)_2 + BF_3 \cdot (OEt)_2 \rightarrow 3R_2AlF + BR_3 + 4Et_2O \quad [6] \qquad (3)$$

$$R_3Al + BF_3 \cdot (OEt)_2 \rightarrow R_2AlF + RBF_2 + Et_2O \quad [6,7] \qquad (4)$$

Strong fluorination agents like XeF_2 [8] and laser photosensitized SF_6 [9] can react also with organoalanes (Eqs. (5)–(7)) to form the corresponding diorganoaluminium fluorides.

$$Et_3Al \xrightarrow{XeF_2} Et_2AlF \tag{5}$$

$$(^iBu)_2AlH \xrightarrow{XeF_2} (^iBu)_2AlF \tag{6}$$

$$Me_3Al \xrightarrow{SF_6} Me_2AlF \tag{7}$$

Diorganoaluminium fluorides are colourless air-sensitive compounds. The derivatives with small alkyl groups are pyrophoric [4]. The compounds R_2AlF are tetrameric in solution and the solid state for $R = Me$ [10], Et [10], ^iPr [6], ^tBu [6] and trimeric for $R = {}^nPr$ [11], ^iBu [11]. IR and RE measurements suggest planar molecules with D_{4h} symmetry for $[Me_2AlF]_4$ and $[Et_2AlF]_4$ [10] (Table 1). However, a gas phase electron diffraction showed, at least for the dimethyl derivative, a puckered ring geometry with C_s symmetry [28] (Fig. 1). The trimeric molecules $[(^nPr)_2AlF]_3$ and $[(^iBu)_2AlF]_3$ have a planar geometry with D_{3h} symmetry [11].

The observed Al–F distance in $[Me_2AlF]_4$ of 181.0(3) pm is expected for a μ_2-bridging F atom and is significantly longer than a terminal Al–F bond in gaseous monomeric AlF_3 (163(1) pm) [30]. The angle Al–F–Al of 146(3)° is indicating a highly ionic character of the Al–F bond, which agrees well with the high-field ^{19}F NMR signals of -144.9 ppm [9] ($[Me_2AlF]_4$) and -160 ppm [31] ($[Et_2AlF]_4$) (see Table 2).

2.2. *Synthesis and characterization of organoaluminium difluorides*

The knowledge of the synthetic methods leading to RMF_2 and the properties of these compounds is sparse. The reported syntheses are limited to just a few patents, with only one exception. This concerns the reaction of $EtAlCl_2$ with NaF in chlorobenzene at 150°C to give $EtAlF_2$ [35] (Eq. (8)).

$$EtAlCl_2 \xrightarrow[-NaCl]{NaF;\,\Delta} EtAlF_2 \tag{8}$$

Treatment of the sesquihalides $R_3Al_2X_3$ with CaF_2, SrF_2 and BaF_2 at 180°C in the absence of a solvent leads to a 1 : 1 mixture of R_2AlF and $RAlF_2$ [36] (Eq. (9)).

$$R_3Al_2X_3 \xrightarrow[-MCl_2]{MX_2,\,\Delta} R_2AlF + RAlF_2 \tag{9}$$

$M = Ca, Sr, Ba$; $R = alkyl$

The reaction of BF_3 and R_3Al ($R = alkyl$) gives the corresponding alkylaluminium difluorides $RAlF_2$ [7] (Eq. (10)).

$$3R_3Al + 2BF_3 \rightarrow 3RAlF_2 + 2R_3B \tag{10}$$

Table 1
Vibrational spectroscopic data and symmetries of organometal fluorides

Compound	ν_{MF} (cm^{-1})		Localsymmetry	Reference
	IR	RE		
Me_2AlF	638, 614		D_{4h}^{a}, C_s^{b}	[10]
Et_2AlF	872	875	D_{4h}^{a}	[10]
$(^nPr)_2AlF$	620	620	D_{3h}^{a}	[11]
$(^iBu)_2AlF$	650	615	D_{3h}^{a}	[11]
Me_2GaF	511, 498, 439	518, 501, 555	$D_{3h}^{a,d}$	[12]
	490		$D_{4h}^{a,e}$	[13]
Et_2GaF	490, 429	484, 430	D_{3h}^{a}	[12]
$(^iPr)_2GaF$	488, 398	517	D_{3h}^{a}	[14]
$(PhCH_2)_2GaF$	496	493	C_i^{a}	[14]
Mes_2GaF	473, 450	440	D_2^{c}	[14,15]
$K[(PhCH_2)_2GaF_2]$	513, 485		–^{f}	[16]
$Cs[(PhCH_2)_2GaF_2]$	519, 483		–^{f}	[16]
$K[MesGaF_3]$	533, 510		–^{f}	[17]
$Cs[MesGaF_3]$	563, 521		–^{f}	[17]
$K[Me_3GaF]$	380		D_{3h}^{a}	[18]
$K[Et_3GaF]$	361		D_{3h}^{a}	[18]
$[NMe_4][(Me_3Ga)_2F]$	379		D_{3h}^{a}	[18]
$[NMe_4][(Et_3Ga)_2F]$	429		D_{3h}^{a}	[18]
$[Mes_6Ga_6F_4O_4]$	407, 426		C_3	[15]
$[Mes_2Ga(F)NH_2^tBu]$	460		C_i	[19]
$(^iPr)_2InF$	386		–^{f}	[20]
$(PhCH_2)_2InF$	347		C_i^{a}	[21]
Mes_2InF	385		C_1^{d}	[19,21]
$[\{(^iPr)_2InF\}_5\{CsF \cdot 2MeCN\}]$	359		–^{f}	[22]
$(C_6F_5)_2TlF$	318		–^{f}	[23,24]
$PhTlF_2$	525, 499.5		C_{2v}^{g}	[25,26]
$[NMe_4][(Me_3Tl)_2F]$	250		D_{3h}^{a}	[27]

[a] Proposed. [b] Gas phase electron diffraction. [c] Dimeric. [d] Trimeric. [e] Tetrameric. [f] Polymeric. [g] Theoretical considerations.

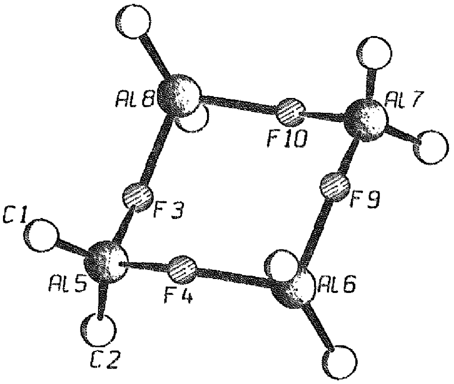

Fig. 1. Computer-generated plot of $[Me_2AlF]_4$ (SCHAKAL [29]) according to gas phase electron diffraction.

Table 2
^{19}F NMR data of organometal fluorides[a]

Compound	δ (ppm)	Reference
Me_2AlF	−144.9	[9]
Et_2AlF	−160.0	[31]
$Na[(Et_3Al)_2F]$[b]	−160.6	[32,33]
$[Cp^*(Me)ZrF_3AlMe_2]_2$	−108.1, −69.5, −32.5	[34]
$(^iPr)_2GaF$	−186.4	[14]
$(PhCH_2)_2GaF$	−169.7	[14]
Mes_2GaF	−152.7	[14]
$K[MesGaF_3]$	−174.0	[17]
$Cs[MesGaF_3]$	−170.0	[17]
$K[(PhCH_2)_2GaF_2]$	−177.6	[16]
$Cs[(PhCH_2)_2GaF_2]$	−171.1	[16]
$[Mes_2Ga(F)NH_2(^tBu)]$	−170.3	[19]
$[Mes_6Ga_6F_4O_4]$	−104.0, −90.7	[15]
$(^iPr)_2InF$	−201.5	[20]
$(PhCH_2)_2InF$	−186.0	[21]
Mes_2InF	−173.0	[21]
$[\{(^iPr)_2InF\}_5\{CsF \cdot 2MeCN\}]$	−183.3	[22]
$[(MesInF_2)_{10}MgF_2]$	−160.4, −150.0, −151.5, −134.6	[22]

[a] Standard: $CFCl_3$. [b] Mixture $Na[(Et_3Al)_2F]/Et_3Al$.

A variety of organoaluminium difluorides can be obtained by reacting R_3Al with HF [37] (Eq. (11)).

$$R_3Al + 2HF \rightarrow RAlF_2 + 2RH \tag{11}$$

$$R = Me, Et, {}^nPr, {}^iPr, {}^iBu, C_6H_{11}, Ph, CH_2Ph$$

Ziegler and Köster reported in 1957 the synthesis of $EtAlF_2$ by a commutation reaction of $AlEt_3$ and freshly prepared AlF_3 (Eqs. (12) and (13)) [4].

$$AlEt_3 + BF_3 \rightarrow AlF_3 + BEt_3 \tag{12}$$

$$AlEt_3 + 2AlF_3 \rightarrow 3EtAlF_2 \tag{13}$$

However, there is almost no data on the characterization of the above mentioned compounds available.

The mixed fluorine–chlorine compound EtAlClF can be obtained by the reaction of Et_2AlCl with XeF_2 [8].

The reaction of $[Me_2AlO]^-$ with C_6F_6 in the gas phase gives the methyltrifluoroalanate $[MeAlF_3]^-$ in 20% yield [38]. Theoretical studies of $MeAlF_2$ suggest the molecular symmetry C_s [39].

2.3. Reactions and derivatives of organoaluminium fluorides

Fluorotriorgano alanates can be obtained by reaction of triorganoalanes with alkali fluorides (Eq. (14)) [40,41].

$$R_3Al+MF \rightarrow M[R_3AlF] \qquad (14)$$

$M=Na$; $R=Me, Et, {}^nPr, {}^nBu, {}^iBu$

$M=K$; $R=Me, Et, {}^nPr, {}^nBu, {}^iBu, {}^nHex, {}^nOct$

An electrochemical variant is the electrolysis of organoalanes in the presence of fluoride ions [42].

The diorganodifluoro alanate $Na[Me_2AlF_2]$ is the product of the reaction of Me_2AlF with NaF in boiling xylene (Eq. (15)) [4].

$$R_2AlF+NaF \rightarrow Na[R_2AlF_2] \qquad (15)$$

The already mentioned reaction of $[Me_2AlO]^-$ with C_6F_6 in the gas phase leads, besides other products, to $[Me_2AlF_2]^-$ in 20% yield [38].

The fluoride ion can be introduced as a nucleophile either having a terminal function as shown above, or as a bridging ligand in an M–F–M framework. The reaction of fluoride ions with two equivalents of a triorganoalane gives the dialanofluorides $[R_3MFMR'_3]^-$ (Eq. (16)) [40].

$$R_3M+R'_3M+MF \rightarrow M[R_3MFMR'_3] \qquad (16)$$

$M=Na$; $R=R'=Me, Et, {}^nPr, {}^nBu, {}^iBu$

$R=Me, R'=Et$

$M=K$; $R=R'=Me, Et, {}^nPr, {}^nBu, {}^iBu, {}^nOct, {}^iOct$

$R=Me, R'=Et$

$R=Me, R'={}^iBu$

$R=Et, R'={}^iBu$

$M=Rb$; $R=R'=Et$

Despite the fact that the first synthesis of a organofluoro alanate was carried out about 35 years ago, little spectroscopic data and structural parameters have been reported to date. The IR spectra of salts of the types $[R_3AlF]^-$ and $[R_3AlFAlR'_3]^-$ were recorded in the region of 4000 to 400 cm^{-1} [43,44]. However, in both cases the interesting vibrational modes, Al–F stretch and Al–F–Al stretch respectively, are below 400 cm^{-1}. This is caused in $M[R_3AlF]$ by additional M–F interactions, which weakens the Al–F bond. In $M[R_3AlFAlR'_3]$ the Al–F–Al bands should be observed below 400 cm^{-1} because of the μ_2-bridging mode of the fluorine atom.

The facile exchange between $Na[(Et_3Al)_2F]$ and $AlEt_3$ has been investigated at variable temperature by ^{19}F and ^{27}Al NMR studies. The dissociation enthalpy of the ion $[Et_3AlFAlEt_3]^-$ was determined to be 85.4 kJ mol^{-1} [32,33].

Dialanofluorides $K[Et_3AlFAlEt_3]$ [45,46] (Fig. 2) and $K[Me_3AlFAlMe_3] \cdot C_6H_6$ [47] (Fig. 3) were characterized by X-ray structure determinations. Both compounds show linear Al–F–Al backbones, which once more points to an ionic character of the Al–F bonds. The Al–F distances are in the same range as observed for $[Me_2AlF]_4$ [28], 182.0(3) pm in $[Et_3AlFAlEt_3]^-$ and 178.2(2) pm in $[Me_3AlFAlMe_3]^-$ (see Table 3). The potassium ions are not involved in the coordination sphere of the fluoride ligands; however, there are contacts between the K^+ ion and the aromatic π system of the benzene rings (K···C: 330 to 395 pm) in $K[Me_3AlFAlMe_3] \cdot C_6H_6$.

Another way of obtaining compounds with organoaluminium fluoride subunits is the reaction of reactive organometallic aluminium compounds with molecular fluoride donating agents. The reaction of Cp^*ZrF_3 ($Cp^* = Me_5C_5$) with Me_3Al gives the Zr–Al–F complex $[Cp^*(Me)ZrF_3AlMe_2]_2$ (Eq. (17)) [34,49].

$$2[Cp^*ZrF_3] + 2AlMe_3 \rightarrow [Cp^*(Me)ZrF_3AlMe_2]_2 \qquad (17)$$

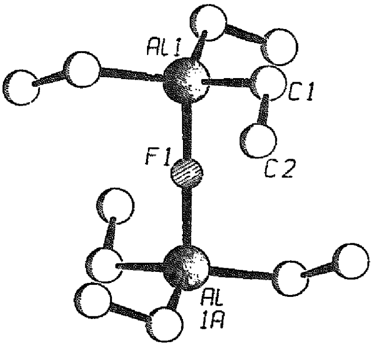

Fig. 2. Graphic representation (SCHAKAL [29]) of the anion in $K[Et_3AlFAlEt_3]$.

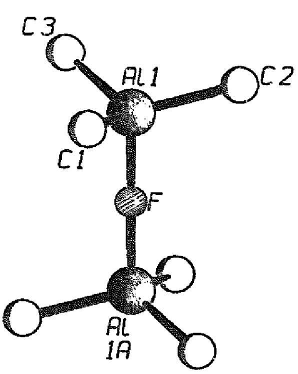

Fig. 3. Graphic representation (SCHAKAL [29]) of the anion in $K[Me_3AlFAlMe_3] \cdot C_6H_6$.

Table 3
M–F distances (pm) in organometal fluorides

Compound	Terminal	μ_2-Bridge[a]	μ_3-Bridge[a]	Reference
$[Me_2AlF]_4^b$		181.0(3)		[28]
$K[(Me_3Al)_2F]\cdot C_6H_6$		178.2(2)		[47]
$K[(Et_3Al)_2F]$		182.0(3)		[45,46]
$[Cp^*(Me)ZrF_3AlMe_2]_2$		177.6(4), 178.6(4)		[34]
$[\{(Cp^*AlF)_2SiPh_2\}_2]$		184.3(1), 184.8(1)		[48]
$[Mes_2GaF]_2\cdot THF$		194.7(2)		[15]
$Cs[MesGaF_3]$	178.4(7), 180.7(4)			[17]
$Cs[(PhCH_2)_2GaF_2]$	184^c			[16]
$[Mes_2Ga(F)NH_2^tBu]\cdot 2.5THF$	183.8(3)			[19]
$[Mes_6Ga_6F_4O_4]\cdot THF$			214^c, $252.1(3)^d$	[15]
$[Mes_2InF]_3$		212^c		[19]
$[(^iPr_2InF)_5(CsF\cdot 2MeCN)]$			223^c, $259^{c,d}$	[22]
$[(MesInF_2)_{10}MgF_2]\cdot 5Toluol$		210^c	223^c	[22]

[a] Bridge connecting the metals Al, Ga, In, Zr, Mg. [b] Gas phase electron diffraction. [c] Average value. [d] Pseudo-μ_3-bridge.

One methyl group is transferred to each Zr atom and all fluorine atoms have a μ_2-bridging function (Fig. 4). The molecule has almost perfect C_{2v} symmetry with Al–F distances of approximately 178 pm [50,51]. NMR experiments at variable temperature show that only the cis product is represented in solution and in the solid state. Therefore, the ^{19}F NMR spectra exhibits only three signals (intensity 4 : 1 : 1) at −108.2, −69.5 and −32.5 ppm respectively.

The treatment of the Al(I) compound $[(Cp^*Al)_4]$ with two equivalents Ph_2SiF_2 leads to a formal insertion of Ph_2Si units and F atoms into the Al–Al bonds of the

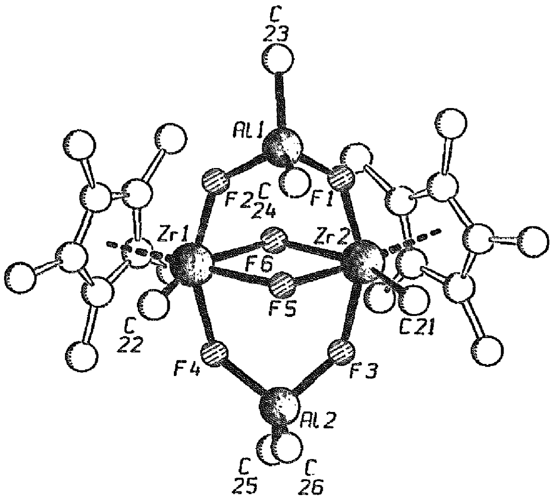

Fig. 4. Plot of one of the crystallographically independent molecules $[Cp^*(Me)ZrF_3AlMe_2]_2$ (SCHAKAL [29]).

educt (Eq. (18)) [48].

$$[(Cp^*Al)_4] + 2Ph_2SiF_2 \rightarrow [\{(Cp^*AlF)_2SiPh_2\}_2] \qquad (18)$$

The molecule of the point group S_4 formally still has the tetrahedral arrangement of the Al atoms of the educt $[(Cp^*Al)_4]$. All four F atoms are μ_2-bridging ligands with the expected large Al–F–Al angle of 149.0(1)° (Fig. 5).

The Lewis acidity of the diorganoaluminium fluorides can be used in various reactions. An obvious reaction is the formation of donor– acceptor complexes by combining R_2AlF with amines or ethers to give e.g. $[Et_2AlF(NMe_3)]$ [52] or $[(^tBu)_2AlF(dioxane)]$ [6].

3,3-Bis(chloromethyl)oxetane (BCMO) undergoes a slow ring-opening reaction with Et_2AlF to form polymeric BCMO [53]. This low reactivity can be attributed to the great strength of the Al–F bond [53] and the resulting low Lewis acidity [6]. In general, Al–F compounds are expected to be weaker Lewis acids owing to stabilization of the sp^2 hybridized Al atom through Al–F π interactions. Ring-opening and installation of a fluorine function in one step is possible when anhydrothymidine is treated with Et_2AlF [54]. The real importance of organoaluminium fluorides lies in their employment as co-catalyst in Zieger–Natta-type reactions [5,36,55–57]. Owing to the lower Lewis acidity of fluorides in comparison with the other halides, the organoaluminium fluorides could not displace the conventional co-catalysts. Diazomethane polymerizes in the presence of Et_2AlF [58].

3. Synthesis and reactions of organogallium fluorides

3.1. Synthesis and characterization of diorganogallium fluorides

Although both $BF_3 \cdot (OEt)_2$ and Me_3SnF are important agents for the preparation of organogallium fluorine derivatives, the first synthesis of such compounds was

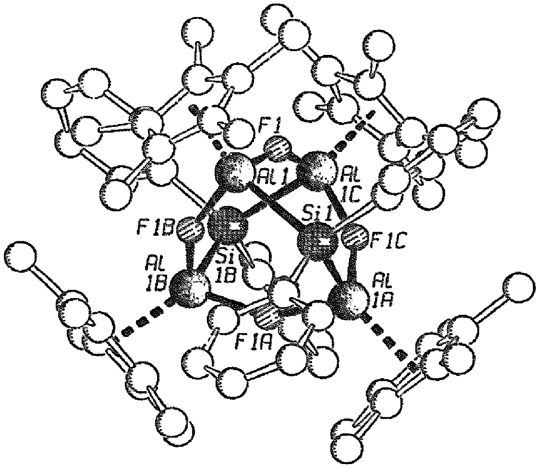

Fig. 5. Schematic drawing of the molecule $[\{(Cp^*AlF)_2SiPh_2\}_2]$ (SCHAKAL [29]).

carried out in the system Et_2GaCl/KF at high temperature without solvent (Eq. (19)) [59].

$$Et_2AlCl + KF \xrightarrow{\Delta} Et_2AlF + KCl \quad (19)$$

Under these conditions the halide exchange process is feasible only in those cases where the organometallic educt is thermally stable [60].

The reactions with $BF_3 \cdot (OEt)_2$ and Me_3SnF can be carried out at mild conditions in Et_2O (Eqs. (20) and (21)) [61,12,14].

$$R_3Ga + Me_3SnF \rightarrow R_2GaF + Me_3SnR \quad [61] \quad (20)$$

R = Me, Et

$$3R_3Ga + BF_3 \cdot (OEt)_2 \rightarrow 3R_2GaF + R_3B + Et_2O \quad [12,14] \quad (21)$$

R = Me. Et, ^{i}Pr, CH_2Ph, Mes

Mes = 2,4,6-trimethylphenyl

The slow decomposition of $[Me_2GaOP(NMe)F_2]_2$ also leads to Me_2GaF [62].

A variation of the halide exchange reaction (Eq. (19)) is more suitable for the synthesis of the thermally sensitive gallium and indium compounds (Eq. (22)) [14].

$$(^iPr)_2GaBr + KF \xrightarrow{MeCN;\ -20^\circ C} (^iPr)_2GaF + KBr \quad (22)$$

All diorganogallium fluorides are colourless, very hygroscopic and air-sensitive liquids or solids. Molecular weight determinations give the degrees of aggregation in solution shown in Fig. 6.

The proposed solid state structures and symmetries of all derivatives except the mesityl compound are based on IR and RE data (see Table 1). The region of 500 to 400 cm^{-1} is characteristic for the ring-stretching vibrations [12,14,13]. Although the analysis of the vibrational spectra of solid $(^iPr)_2GaF$ suggest a trimer, it should

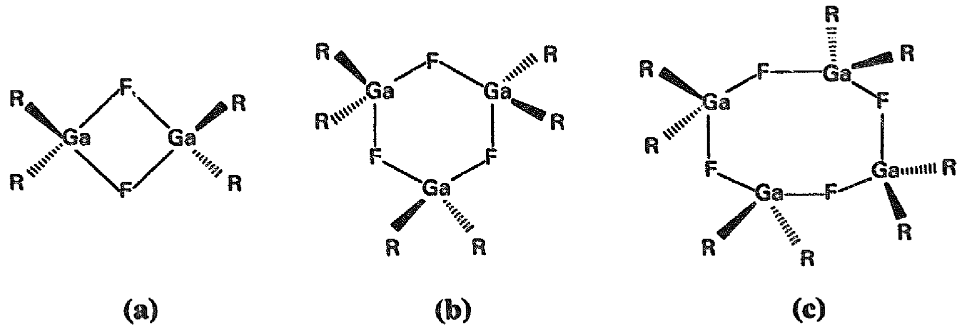

Fig. 6. Degree of aggregation for diorganogallium fluorides in solution: (a) R = CH_2Ph [17], Mes [17]; (b) R = Me [63], Et [63], ^{i}Pr [17]; (c) R = Me [64].

be mentioned that the EI mass spectra show fragments of hexamers and heptamers [14]. This implies the possible existence of a polymeric structure for $(^{i}Pr)_2GaF$. Once again, the ^{19}F NMR spectra are a useful probe to prove the ionic character of the metal fluorine bond (see Table 2). Values found for the ^{i}Pr, the CH_2Ph and the Mes derivatives are −186.4 ppm, −169.7 ppm and −152.7 ppm respectively.

The confirmation of the spectroscopically derived structures turned out to be difficult, owing to the needle-shaped crystals which were unsuitable for an X-ray structure determination. An exception is the mesityl derivative which can be recrystallized from THF as $[Mes_2GaF]_2 \cdot THF$ (Fig. 7) [15]. The molecule possesses D_2 symmetry with a planar Ga_2F_2 rhombic distorted four-membered ring. All four equivalent Ga–F are 194.7(2) pm long. Equivalent Ga–F bonds also have been observed in solid state compounds containing μ_2-bridging F atoms [63]. The angles in the Ga_2F_2 ring are 101.1(2)° for Ga1–F1–Ga1a and 78.9(1)° for F1–Ga1–F1a.

3.2. Synthesis and characterization of organofluoro gallates

The synthesis of compounds of the general formula $RGaF_2$ has proved to be difficult. The common fluorinating agents applicable for the synthesis of many other diorganogallium fluorides, Me_3SnF and $BF_3 \cdot (OEt)_2$, are not practicable for the preparation of the difluoro derivatives. The intermediates R_2GaF are not reactive enough to undergo further alkyl(aryl)–fluorine exchange. The treatment of R_2GaF with those synthons, leads to the isolation of the starting materials.

The only known derivatives are the organotrifluorogallates $M[MesGaF_3]$ (M = K, Cs) [17], obtained by halide exchange in acetonitrile (Eq. (23)). It should be noted

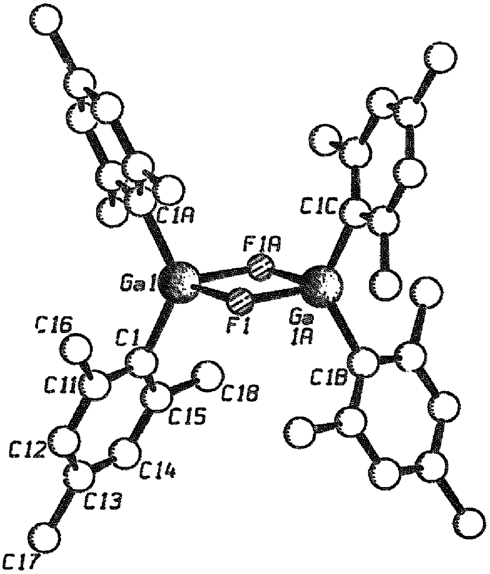

Fig. 7. Structure of the molecule $[Mes_2GaF]_2$ in $[Mes_2GaF]_2 \cdot THF$ (SCHAKAL [29]).

that only the very reactive and air-sensitive $MesGaBr_2$ could be employed in this reaction.

$$\mathrm{MesGaBr_2} \xrightarrow[-\mathrm{MBr}]{\mathrm{MF},\ -15^{\circ}\mathrm{C},\ \mathrm{MeCN}} \mathrm{M[MesGaF_3]} \tag{23}$$

M = K, Cs

It should be mentioned at this point that the analogous reaction of $MesInBr_2$ with KF does not yield the difluoro derivative but the organotribromoindate $K[MesInBr_3]$ [17], which shows the basic structural principles of $Cs[MesGaF_3]$.

The structure of $Cs[MesGaF_3]$ consists of layers of gallate units parallel to (100) (Fig. 8). The layers are separated by the bulky mesityl groups (Fig. 9), whereas the interionic contacts are formed in the centre of the layer. Every caesium ion possesses the coordination number (CN) eight (see Fig. 10). The coordination sphere is divided into two different sides, a tripod-like arrangement of three F atoms and an arrangement of five F atoms which lay approximately in one plane. The Cs–F distances are in the range of 322.9(5) to 291.0(7) pm, compared with 300.5 pm of crystalline CsF [66]. The mesityl ligand is disordered. Two positions of the aryl ring could be refined. The Ga–F bond lengths of 187.4(7) and 180.7(4) pm are the shortest measured in organogallium fluoride chemistry to date.

The bulk of the mesityl substituents are responsible for an acceptable solubility of $K[MesGaF_3]$ and $Cs[MesGaF_3]$ in solvents like acetonitrile. The observed high-field ^{19}F NMR signals of -174.0 and -170.0 ppm indicate the ionic character of the Ga–F bonds. The short Ga–F bond lengths correspond to the position of the Ga–F valence vibrations of 553 (ν_{as} GaF_3) and 510 cm^{-1} (ν_s GaF_3) ($K[MesGaF_3]$) or 563 (ν_{as} GaF_3) and 512 cm^{-1} (ν_s GaF_3) ($Cs[MesGaF_3]$).

Triorganofluorogallates can be synthesized easily by the reaction of the corre-

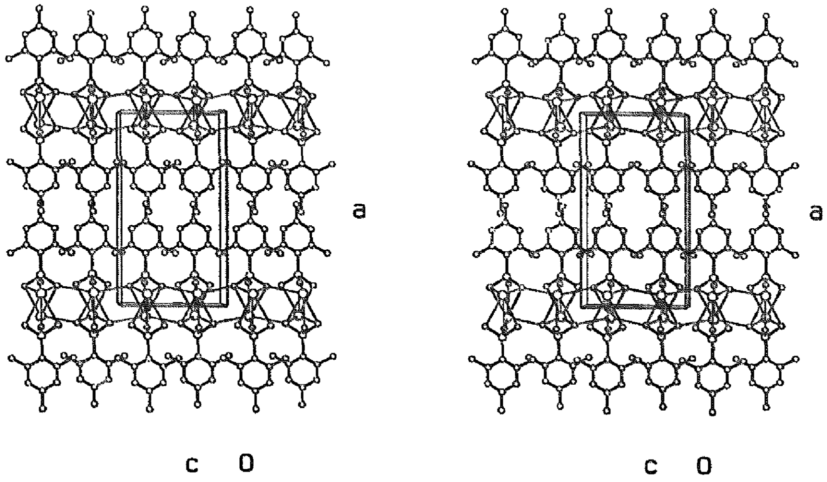

Fig. 8. Stereoscopic view of the unit cell of $Cs[MesGaF_3]$ parallel to (100) (ORTEP [65]).

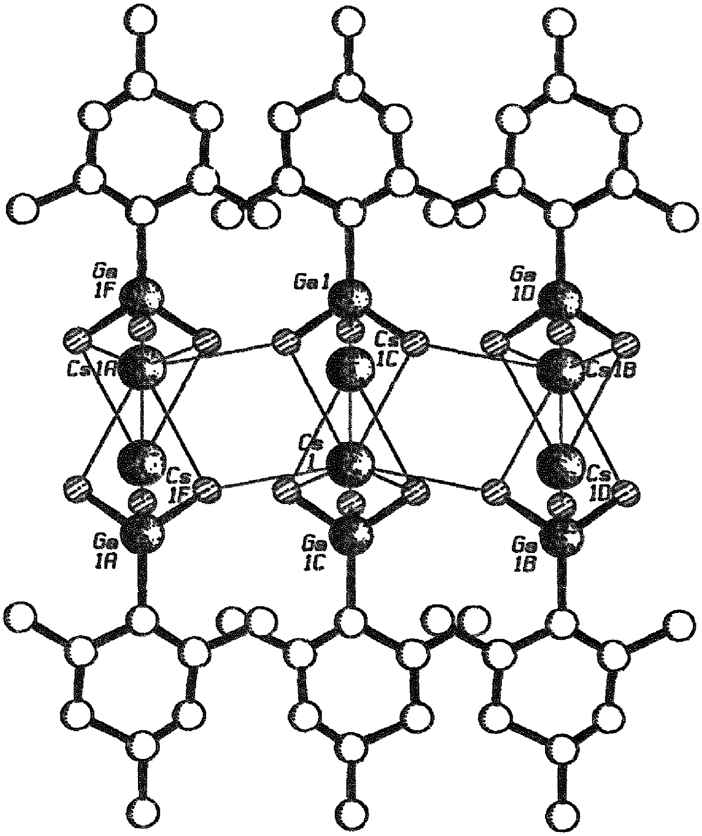

Fig. 9. Plot of one layer of Cs[MesGaF$_3$] (SCHAKAL [29]).

sponding fluorides and gallanes without solvent (Eq. (24)) [64,67,68,18].

$$R_3Ga + MF \rightarrow M[R_3GaF] \qquad (24)$$

M = K; R = Me [18], Et [64,67,18]

M = NMe$_4$; R = Et [67]

M = Me$_3$NCH$_2$Ph; R = Et [67,68]

M = Et$_3$NCH$_2$Ph; R = Et [68]

Polymeric chains with local D_{3h} symmetry are proposed for the potassium salts K[R$_3$GaF] (R = Me, Et) [18] by the interpretation of the IR spectra (Fig. 11). The asymmetric stretching vibrations are observed at 380 (K[Me$_3$GaF]) and 361 cm^{-1} (K[Et$_3$GaF]).

Quite similar reaction conditions form salts like [NMe$_4$][R$_3$GaFGaR$_3$] (Eq. (25))

[67,68,18].

$$2R_3Ga + [NMe_4]F \rightarrow [NMe_4][R_3GaFGaR_3] \qquad (25)$$

R = Me [18]

R = Et [67,68,18]

The interpretation of the vibrational spectra gives rise to D_{3h} symmetry for the anions $[R_3GaFGaR_3]^-$ (Fig. 11) (R = Me, $\nu_{as}(Ga_2F) = 379$ cm^{-1}; R = Et, $\nu_{as}(Ga_2F) = 429$ cm^{-1}).

While the reaction of $(^iPr)_2GaBr$ with KF gives the diorganogallium fluoride $(^iPr)_2GaF$ [14], $(PhCH_2)_2GaF$ is not the product of the halide exchange of $(PhCH_2)_2GaCl$ with KF or CsF respectively. In both cases the diorganodifluoro gallate $M[(PhCH_2)_2GaF_2]$ can be isolated (Eq. (26)) [16].

$$(PhCH_2)_2GaCl \xrightarrow[-MCl]{MF;\ MeCN} M[(PhCH_2)_2GaF_2] \qquad (26)$$

M = K, Cs

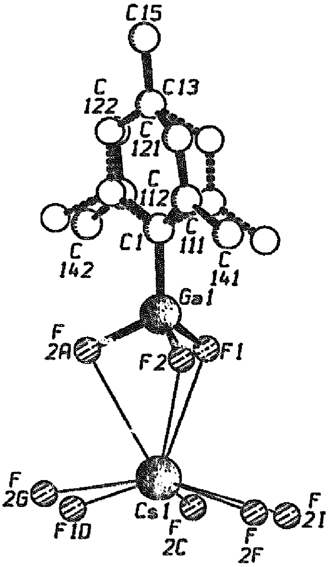

Fig. 10. Coordination sphere of a Cs$^+$ ion with disorder behaviour of the Mes group (SCHAKAL [29]).

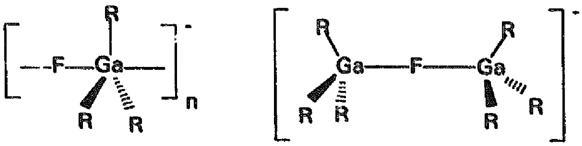

Fig. 11. Possible structures of the anions in $K[R_3GaF]$ and $[NMe_4][R_3GaFGaR_3]$.

The moisture-sensitive gallates show the typical high-field ^{19}F NMR resonances of -177.6 ($M=K$) and -171.1 ppm ($M=Cs$) in acetonitrile. This points to solvated gallate units of the type $[M(MeCN)_n][(PhCH_2)_2GaF_2]$. The CN four for the gallium centre dominates the organogallium–fluorine chemistry, causing a distorted tetrahedral coordination sphere for the Ga atom. This leads to two bands for the asymmetric and the symmetric stretching vibrations respectively. Indeed, two absorptions are found for $K[(PhCH_2)GaF_2]$ (513, 485 cm^{-1}) and for $Cs[(PhCH_2)_2GaF_2]$ (519, 483 cm^{-1}).

The structural data of $Cs[(PhCH_2)_2GaF_2]$ confirm this interpretation. The solid state structure consists of ladder-type polymeric chains. The ladder is build up by small and large Cs–F four-membered rings. The range of the Cs–F bond lengths covers a region from 293(1) to 357(1) pm. The gallium centres have the CN four, while the Cs^+ ions show a CN of five concerning the F^- ions. This topological way of describing the structures is only one interpretation. The polymer can also be described as a string of Cs_2F_2 and $Cs_2F_4Ga_2$ rings by omitting the long Cs–F contacts (Fig. 12). The Ga–F distances are somewhat longer (183(1)–186(1) pm) than the comparable values in $Cs[MesGaF_3]$, owing to the higher number of electronegative fluorine ligands in $Cs[MesGaF_3]$. The coordination sphere of the Cs^+ ions is completed by the coordination of two phenyl rings from two different gallate units ($Cs–C_{mean}$: 370 pm) (Fig. 13). This causes the polymeric chain to be shielded by an 'organic hose', which separates the different chains with interionic contacts in the centre of the string (Fig. 14).

3.3. Reactions and derivatives of organogallium fluorides

Diorganogallium fluorides react with proton active agents like primary amines or water. The adduct $[Mes_2GaF\{NH_2(^tBu)\}]$ is the result of the reaction of $(^tBu)NH_2$ and Mes_2GaF (Eq. (27)) [19], while the reaction of H_2O with Mes_2GaF yields the

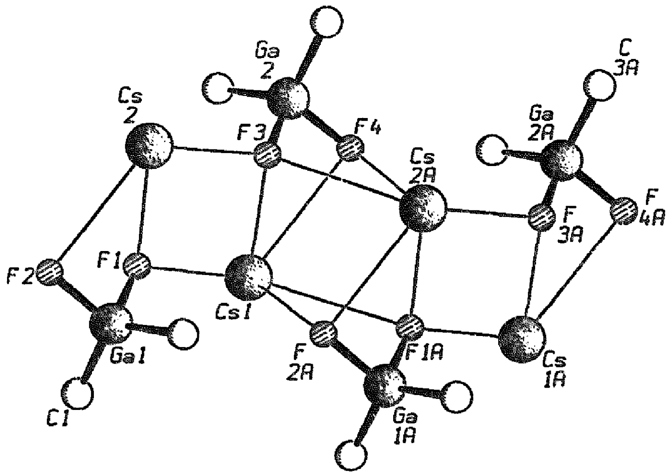

Fig. 12. Basic skeleton of the F–Cs–Ga chain in $Cs[(PhCH_2)_2GaF_2]$.

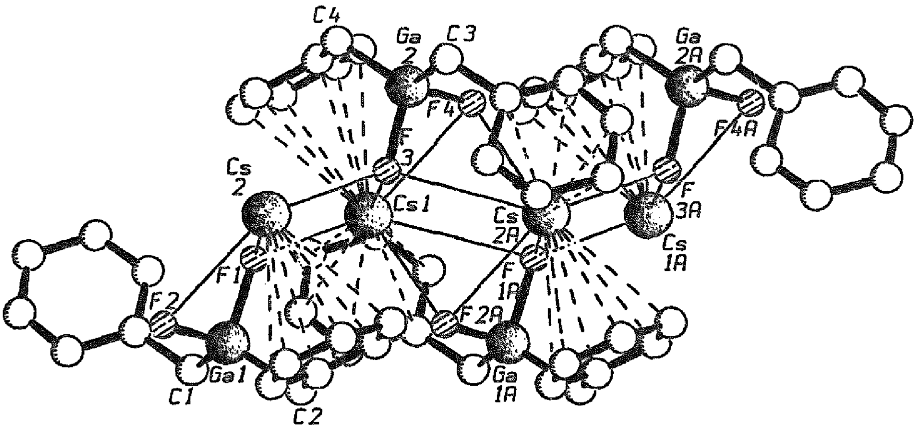

Fig. 13. Section of the infinite chain of $Cs[(PhCH_2)_2GaF_2]$ with Cs-aryl-coordination (SCHAKAL [29]).

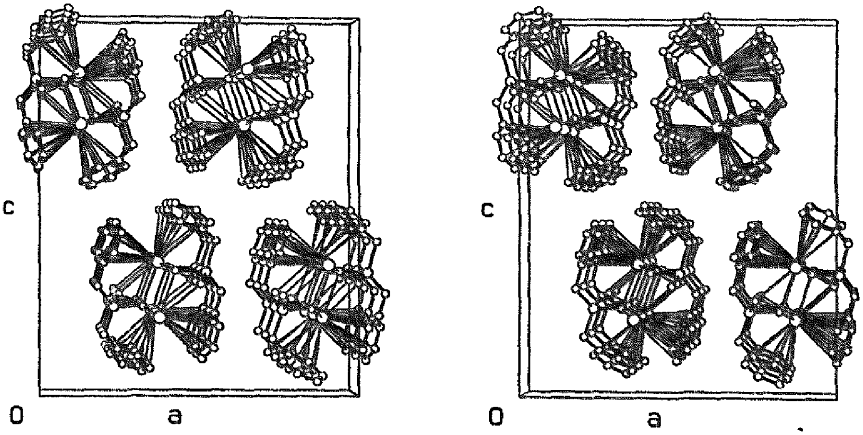

Fig. 14. Stereoscopic view of the unit cell of $Cs[(PhCH_2)_2GaF_2]$ along the *b* axis (ORTEP [65]).

hexanuclear organogallium fluoride oxide $[Mes_6Ga_6F_4O_4]$ (Eq. (28)) [15]. An elimination of mesitylene was also observed when $[Mes_2GaF\{NH_2({}^tBu)\}]$ was heated in boiling toluene. The product of this reaction is an oligonuclear complex of unknown composition [60].

$$Mes_2GaF + ({}^tBu)NH_2 \rightarrow [Mes_2GaFNH_2({}^tBu)] \qquad (27)$$

$$6Mes_2GaF + 4H_2O \rightarrow [Mes_6Ga_6F_4O_4] + 2HF + 6MesH \qquad (28)$$

The formation of the fluoride oxide is on the one hand due to the higher acidity of water compared with the amine. On the other hand, the Ga–F bond is strong enough to resist a further attack by water. The compound can also be obtained by a careful hydrolysis of $Cs[MesGaF_3]$ [60].

$[Mes_2GaF\{NH_2({}^tBu)\}]$ crystallizes from THF as $[Mes_2GaF\{NH_2({}^tBu)\}]\cdot$

2.5 THF and forms dimers $\{[Mes_2GaF\{NH_2(^tBu)\}]\cdot THF\}_2$ in the solid state, held together by hydrogen bridges (Fig. 15). The distance N···F(a) of 288.9(5) pm indicates a N–H···F bridge, while the long distance O1···N of 323.1(6) pm suggests only a weak N–H···O interaction. The adduct possesses a remarkably short Ga–N bond length of 204.9(4) pm, considering that it is a donor–acceptor complex [69,70]. The most likely reason is due to the electronic pulling effect of the terminal fluorine ligand.

$[Mes_6Ga_6F_4O_4]$, which crystallizes from THF as $[Mes_6Ga_6F_4O_4]\cdot THF$, can be described as a distorted Ga_6 octahedron, in which the faces are capped by eight electronegative ligands. The molecule has C_3 symmetry with the atoms O1 and F2 on the threefold axis. All electronegative ligands have a μ_3-bridging function, except for F1 and the symmetry-equivalent atoms, which have a pseudo-μ_3-bridging function, recognizable by two short Ga–F distances of 197.3(3) and 222.3(2) pm and a weak Ga···F interaction of 252.1(3) pm (Fig. 16).

Recently, two complexes $[Mes_6Ga_6(OH)_4O_4]$ [71] and $[(^tBu)_6Al_6(OH)_4O_4]$ [72] have been reported, which basically have the geometry of $[Mes_6Ga_6F_4O_4]$. The sites of the F^- ions are occupied with the isoelectronic OH^- ions. Which position in the complex is occupied by an O^{2-} anion, and which by an anion with one negative charge, can be determined from different metal ligand distances, or by an estimation of the valence according the method of Donnay and Allmann [73,74]. The molecular weight determination and the ^{19}F NMR spectra suggest that the hexanuclear complex $[Mes_6Ga_6F_4O_4]$ is stable in THF solution. The two signals at −90.7 (3 F) and −104.0 ppm (1 F) are also consistent with the bridging function of all F atoms. The terminal F atom in $[Mes_2GaF\{NH_2(^tBu)\}]$ gives rise to only one signal at

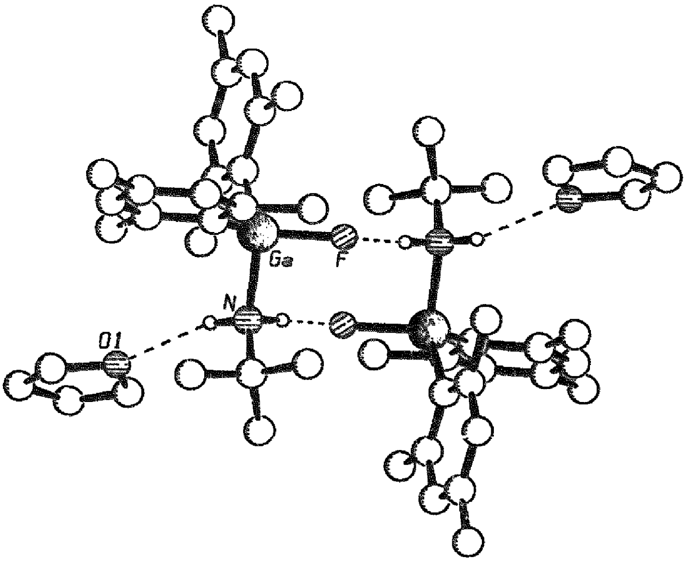

Fig. 15. Centrosymmetric dimer of $[Mes_2Ga(F)NH_2(^tBu)]$ in $[Mes_2Ga(F)NH_2(^tBu)]\cdot 2.5THF\}\}$ (SCHAKAL [29]).

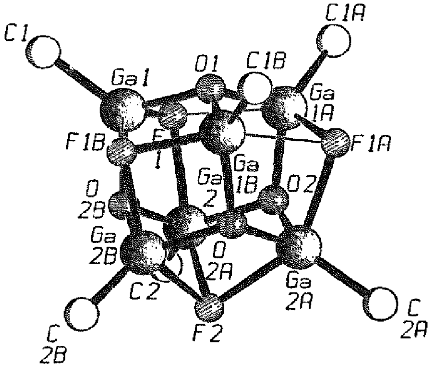

Fig. 16. Schematic drawing of the Ga–O–F skeleton in $[Mes_6Ga_6F_4O_4] \cdot THF$. The mesityl substituents are represented by the *ipso*-C atoms (SCHAKAL [29]).

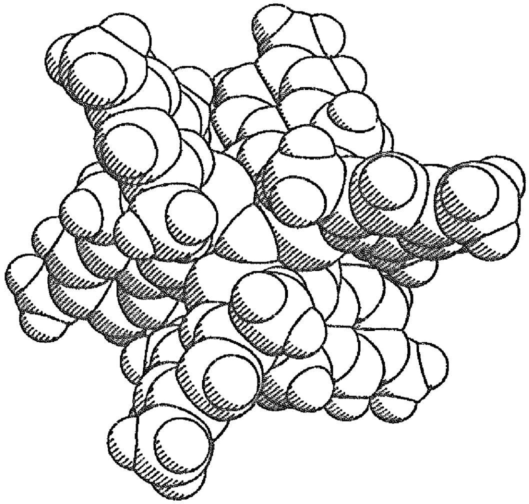

Fig. 17. Space-filling model of $[Mes_6Ga_6F_4O_4]$ in $[Mes_6Ga_6F_4O_4] \cdot THF$ (SHELXTL-PLUS [75]). View along the threefold axis.

−170.3 ppm. The acceptable solubility of $[Mes_6Ga_6F_4O_4]$ in toluene is due to the protecting effect of the mesityl groups, which can be demonstrated by a space filling model (Fig. 17).

4. Synthesis and reactions of organoindium fluorides

4.1. Synthesis and characterization of diorganoindium fluorides

$BF_3 \cdot (OEt)_2$ and triorganotin fluorides are not only useful synthons in organogallium chemistry, they can also be employed in the preparation of the indium analogues. Diorganoindium fluorides can be isolated from the treatment of triorganoindanes with $BF_3 \cdot (OEt)_2$ (Eq. (29)) [76,21]

$$3R_3In + BF_3 \cdot (OEt)_2 \rightarrow 3R_2InF + BR_3 + Et_2O \qquad (29)$$

R = Me [76], CH_2Ph [21], Mes [21]

The reaction is free of detectable by-products, except for the Mes derivative. In this case a small amount of the boroxin $[MesBO]_3$ is always found. This could be the result of an ether cleavage caused by $MesBF_2$ [77,78]; however, a reaction with traces of water cannot be excluded. Surprisingly, the formation of a boroxin can only be observed in the presence of a Mes ligand.

The reaction of Et_3In with Et_3SnF yields the diorganoindium fluoride Et_2InF (Eq. (30)) [79].

$$Et_3In + Et_3SnF \rightarrow Et_2InF + SnEt_4 \qquad (30)$$

The treatment of $(^iPr)_3In$ with $BF_3 \cdot (OEt)_2$ does not lead to the desired product $(^iPr)_2InF$ but to the salt $[(^iPr)_2In][BF_4]$ (see Section 4.2. On the contrary, stirring of $(^iPr)_2InCl$ in MeCN at −15°C in the presence of KF gives the product (Eq. (31)) [20].

$$^iPr_2InCl \xrightarrow[-KCl]{KF;\ MeCN;\ -15^\circ C} {^iPr_2InF} \qquad (31)$$

The use of crown ethers is not helpful in optimizing the yield of $(^iPr)_2InF$ because of the formation of the salt $[K(15\text{-crown-}5)_2][(^iPr)_2InCl_2]$ (Eq. (32)) [20].

$$2(^iPr)_2InCl \xrightarrow{KF;\ 15\text{-crown-}5;\ MeCN} [K(15\text{-crown-}5)_2][(^iPr)_2InCl_2] + (^iPr)_2InF \qquad (32)$$

Diorganoindium fluorides are colourless, air-sensitive, very hygroscopic solids. According to their solubility [20], cryoscopic data and NQR spectra [80–82] the Me and Et derivatives are polymeric, while $(PhCH_2)_2InF$ and Mes_2InF are dimers in solution (Fig. 18). The ⁱPr derivative shows an average degree of aggregation of 3.9, but there is evidence for the presence of different molecule sizes in solution. This is supported by the low solubility even in donor solvents like MeCN.

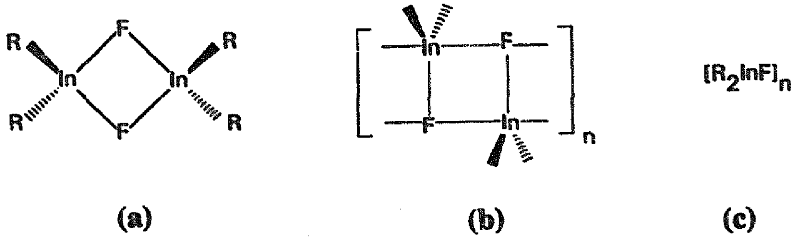

Fig. 18. Degree of aggregation for diorganoindium fluorides in solution: (a) R = CH_2Ph [21], Mes [21]; (b) R = ⁱPr [20]; (c) R = Me [76], Et [79].

The structures of $[({}^{i}Pr)_2InCl]_n$ [20] and $[\{({}^{i}Pr)_2InF\}_5\{CsF \cdot 2\ MeCN\}]$ [22] show a polymeric ladder-type arrangement of the indane units also assumed for $({}^{i}Pr)_2InF$. The graduation of the ^{19}F NMR signals is identical to the corresponding Ga compounds (($({}^{i}Pr)_2InF$: −201.5; $(PhCH_2)_2InF$: −186.0; Mes_2InF: −173.0 ppm) but shifted to higher field. This is in accordance with the higher ionic character of the In–F bonds in comparison with the Ga–F bonds. An extreme example is $({}^{i}Pr)_2InF$, because of the μ_3-bridging function of the fluorine ligands. This leads to an easy release and transfer of F^- ions [16]. Solutions of $({}^{i}Pr)_2InF$, $(PhCH_2)_2InF$ and Mes_2InF in MeCN show low-field shifted ^{19}F NMR resonances (($({}^{i}Pr)_2InF$: −186.4; $(PhCH_2)_2InF$: −163.8; Mes_2InF: −173.0 ppm) caused by the solvate complexes $[R_2InF(MeCN)_n]$. This is surprising because aluminium and gallium compounds exhibit high field shifts by reducing the function of the fluorine atoms from a bridging mode to a terminal one. There are two explanations for this effect. On the one hand, the Al and Ga centres are harder Lewis acids than the corresponding In centres, and a connection to two or more metal centres reduces the partial negative charge on the fluorine atom which causes a down-field shift of the NMR signal. On the other hand, there is a strong tendency of the higher homologues In and Tl to form linear cations R_2M^+ [21,83] which are valence-isoelectronic to the linear mercury species R_2Hg. Thus, in In compounds the bridging halogen atom possesses a higher ionic character than a terminal halogen function (see Table 2).

Broad strong absorbances in the region of 350 to 390 cm^{-1} are characteristic for solid diorganoindium fluorides (see Table 1). Despite the fact that Mes_2InF is a dimer in solution, the X-ray structure analysis determines a trimeric molecule [19] (Fig. 19). The six-membered ring is strongly distorted to a boat form (Fig. 20) caused by small inner ring angles F–In–F of 85.6° (average) and large angles In–F–In of 139.2° (average). A mean In–F bond length of 212 pm is typical for μ_2-bridged F atoms [33,63]. The sterical demand of the Mes groups force a face-to-face arrangement of the aryl substituents with an average distance of 360 pm.

If $({}^{i}Pr)_2InCl$ is treated with CsF, only impure $({}^{i}Pr)_2InF$ is isolated. Even after recrystallization from acetonitrile, traces of excessive CsF are detectable. Apparently, more fluoride ions are transferred to the indium centres because of the higher fluoridation potential of CsF compared with KF. Therefore, the reaction of $({}^{i}Pr)_2InCl$ with an excess of CsF in boiling MeCN yields, after hot filtration, the unusual compound $[\{({}^{i}Pr)_2InF\}_5\{CsF \cdot 2\ MeCN\}]$ (Eq. (33)) [22].

$$5\,{}^{i}Pr_2InCl \xrightarrow[-CsCl]{CsF;\ MeCN;\ \Delta} [({}^{i}Pr_2InF)_5(CsF \cdot 2MeCN)] \qquad (33)$$

The compound loses the weakly coordinated acetonitrile molecules completely in a low stream of inert gas. The ^{19}F NMR signal of −183.3 pm is almost identical with that of $({}^{i}Pr)_2InF$. This points to a complete solvation of the indane and indate units with a rapid F^- exchange. The cryoscopic weight determinations in benzene suggest the existence of $[\{({}^{i}Pr)_2InF\}_5CsF]$ units; the determined average molecular weight is 1671 g mol^{-1}. The In–F bonds give only one broad IR band at 359 cm^{-1}.

The structure of the compound was elucidated by X-ray structure analysis. From

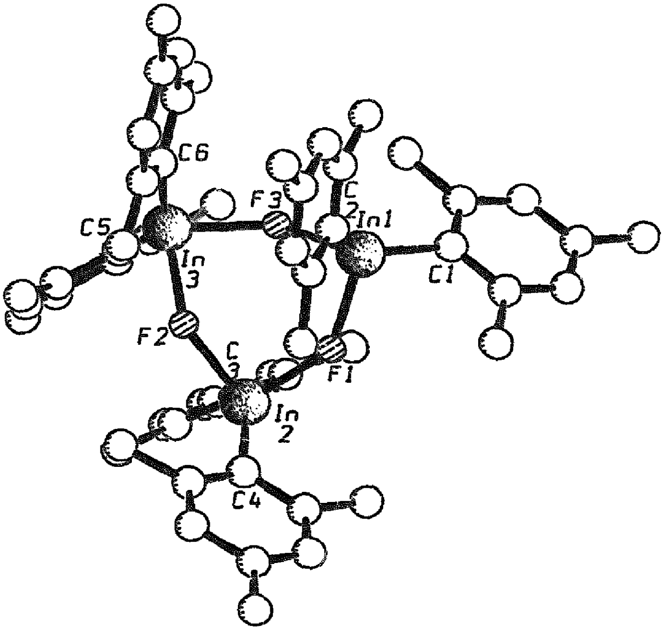

Fig. 19. SCHAKAL [29] plot of the trimer [Mes$_2$InF]$_3$.

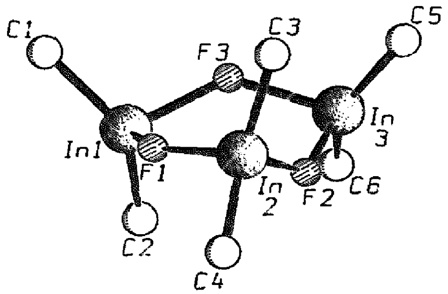

Fig. 20. Distorted boat-form of the In$_3$F$_3$ framework in [Mes$_2$InF]$_3$. The mesityl substituents are reduced to their *ipso*-C atoms (SCHAKAL [29]).

a topological point of view [{(^{i}Pr)$_2$InF}$_5${CsF·2 MeCN}] consists of a polymeric ladder-type chain with an alternate arrangement of {(^{i}Pr)$_2$InF}$_5$ and CsF units (Fig. 21). The 'rungs' of the ladder are always shorter (212.1(5)–215.6(5) pm) than the sides (223.1(5)–260.7(5) pm). The coordination geometry of the In atoms is a distorted trigonal bipyramid, while the coordination sphere of the Cs$^+$ ions is built up by three fluorine contacts (287.2(5)–311.0(6) pm) and three molecules of acetonitrile. One molecule has a terminal (317(1) pm), two molecules have a μ_2-bridging function (320.9(9), 334(1) pm) forming a centrosymmetric four-membered Cs$_2$N$_2$ ring (Fig. 22). Although the Cs–N interactions are weak, the MeCN

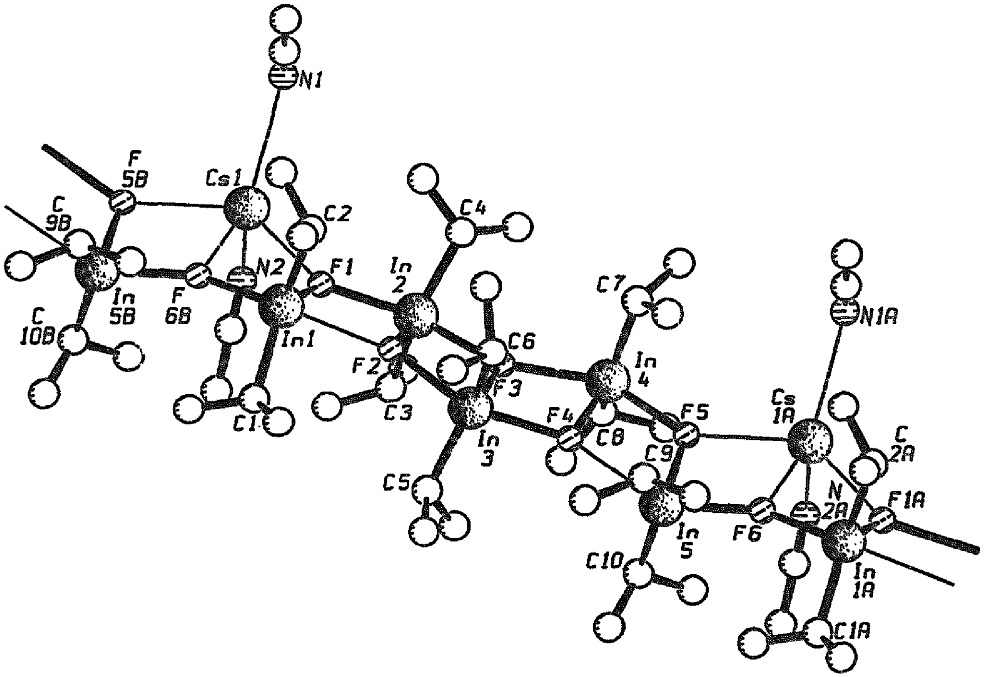

Fig. 21. Part of the polymeric chain of $[\{(^iPr)_2InF\}_5\{CsF\cdot 2MeCN\}]$ (SCHAKAL [29]).

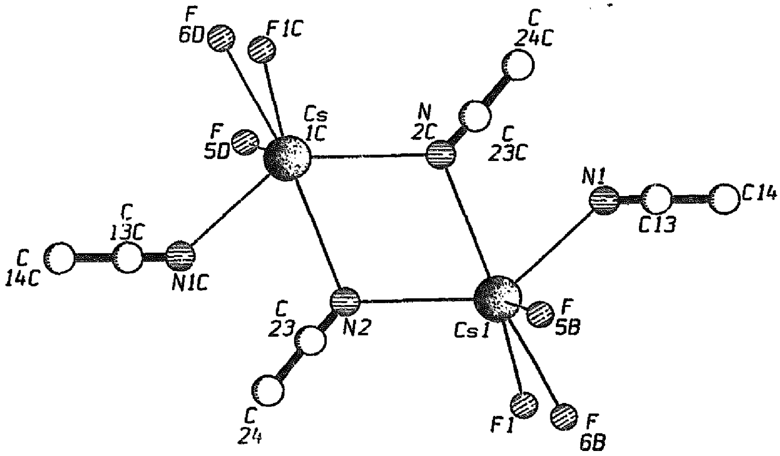

Fig. 22. Centrosymmetric dimer formed by Cs^+ ions and acetonitrile molecules in $[\{(^iPr)_2InF\}_5\{CsF\cdot 2MeCN\}]$. The complete coordination sphere of the caesium cations is shown (SCHAKAL [29]).

molecules are important to stabilize the resulting polymeric double chain which is aligned along the *b* axis (Fig. 23).

From a chemical point of view, the structure consists of indane $[\{(^iPr)_2InF\}_3]$ and indate $(Cs[\{(^iPr)_2InF\}_2F])$ subunits.

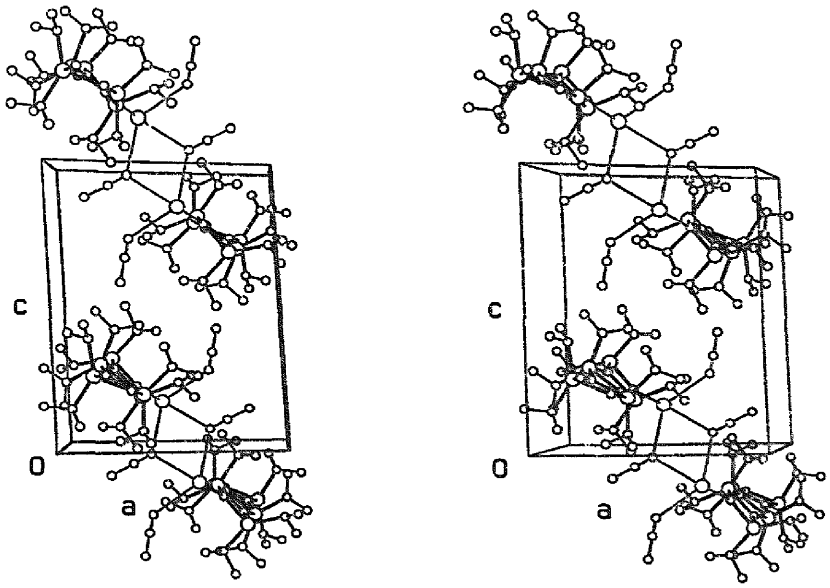

Fig. 23. Stereoscopic view of the unit cell of $[\{(^iPr)_2InF\}_5\{CsF \cdot 2MeCN\}]$ along the *b* axis.

4.2. Synthesis and characterization of organoindium difluorides

The only known derivative of this class of compound is the complex $[(MesInF_2)_{10}MgF_2]$. The substance can be isolated as a by-product during the synthesis of Mes_2InF, if the educt Mes_3In still contains traces of magnesium salts from the Grignard reaction of $InCl_3$ with MesMgBr (Eq. (34)) [22].

$$20Mes_2InF + MgF_2 \xrightarrow{\text{toluene, 80°C}} [(MesInF_2)_{10}MgF_2] + 10Mes_3In \qquad (34)$$

The complex crystallizes from toluene as $[(MesInF_2)_{10}MgF_2] \cdot 5$ toluene. The complex framework is build up by two half-spheres of $(MesInF_2)_5$ which enclose a linear MgF_2 unit (Fig. 24). Four μ_3-bridging fluorine atoms, belonging to the equatorial plane of the MgF_6 octahedron, hold the spheres together. The MgF_6 octahedron is distorted because of a weak In–F interaction of 252.2(3) pm (In4···F11), and the existence of four μ_3-bridging and two terminal F ligands. All μ_2 F atoms show a large In–F–In angle of about 135°. The In centres possess a distorted square pyramidal coordination sphere, in which the Mes ligands are protecting the In–Mg–F core (Fig. 25).

The ^{19}F NMR spectra of $[(MesInF_2)_{10}MgF_2]$ show four signals for four geometrically different F positions (−150.0, 8 F; −151.5, 8 F; −134.6, 4 F; −160.4 ppm, 1 F), indicating that the cage is stable in solution. There is a topological relationship between $[(MesInF_2)_{10}MgF_2]$ and oxometallate complex ions like $[W_6O_{19}]^{2-}$ [84] and $[V^{IV}_{16}V^{V}_{18}O_{82}]^{10-}$ [85–87].

Attempts to synthesize the salt $K[MesInF_3]$ failed. The reaction of $MesInBr_2$ with

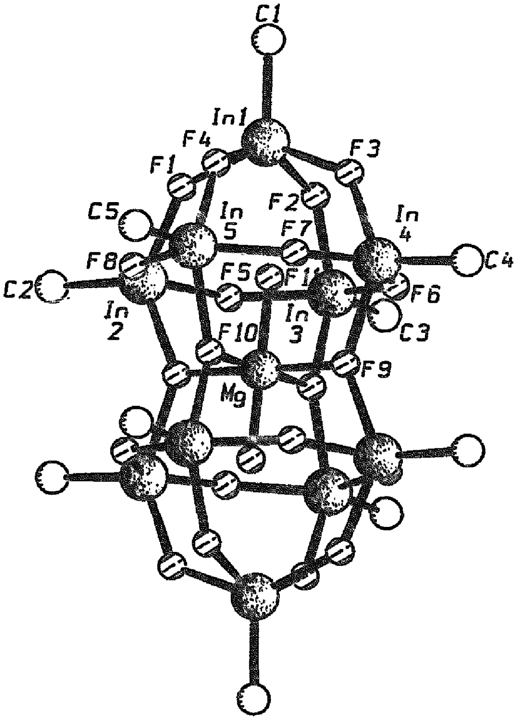

Fig. 24. Plot of the molecule $[(MesInF_2)_{10}MgF_2]$ in $[(MesInF_2)_{10}MgF_2]\cdot 5$toluene. The mesityl substituents are represented by the *ipso*-C atoms (SCHAKAL [29]).

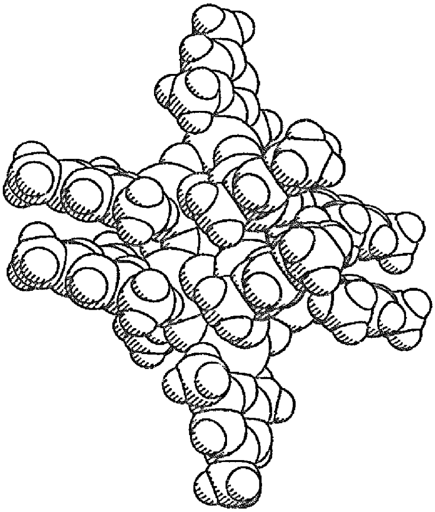

Fig. 25. Space-filling model of $[(MesInF_2)_{10}MgF_2]$.

KF and crown ether leads to the compound $[K(15\text{-crown-}5)_2][Mes_2InBr_2]$ formed by a ligand distribution [17]. In the absence of crown ether, an insoluble fluorine-containing material besides the indate $K[MesInBr_3]$ can be isolated (Eq. (35)) [17].

$$MesInBr_2 \xrightarrow{KF;\ MeCN;\ -15^{\circ}C} K[MesInBr_3] + ...? \qquad (35)$$

The structure of $K[MesInBr_3]$ possesses the same characteristics as $Cs[MesGaF_3]$, although the coordination sphere of the K^+ ion is different (Fig. 26). The potassium ions are surrounded by seven bromine atoms. Two bromine atoms of two indate units bond in a chelating fashion, while three bromine atoms belong to three different indate units (average distance K–Br: 342.5(5) pm). $K[MesInBr_3]$ forms layers parallel to (100), having the interionic contacts in the centre of the layers and the hydrophobic protection of the Mes groups on the surface of the layers (Fig. 27). The layers are stacked along the *c* axis (Fig. 28).

4.3. *Reactions and derivatives of organoindium fluorides*

The synthesis of $[Me_3NCH_2Ph][Me_3InF]$ by reacting $InMe_3$ with $[Me_3NCH_2Ph]F$ is mentioned in the patent literature, but no further characterization is reported [88].

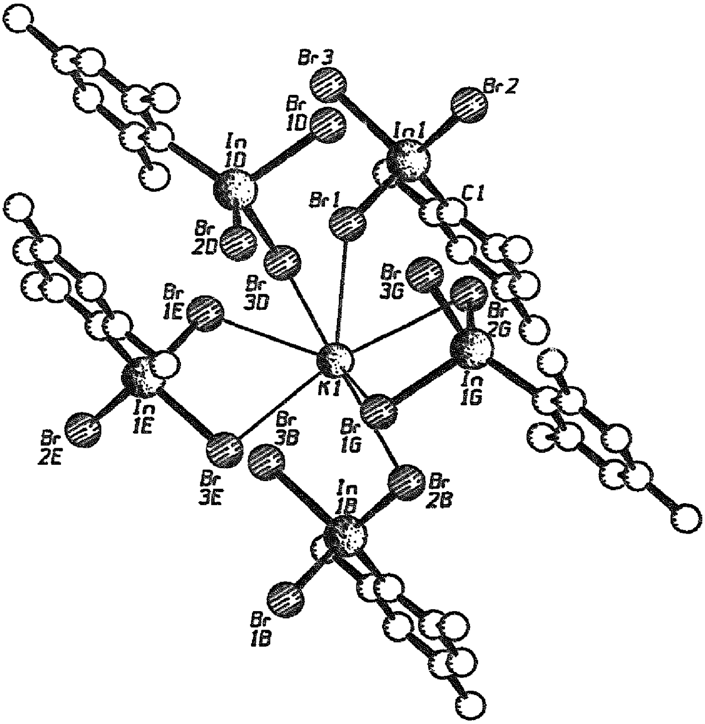

Fig. 26. Coordination sphere of the K^+ ion in $K[MesInBr_3]$ (SCHAKAL [29]).

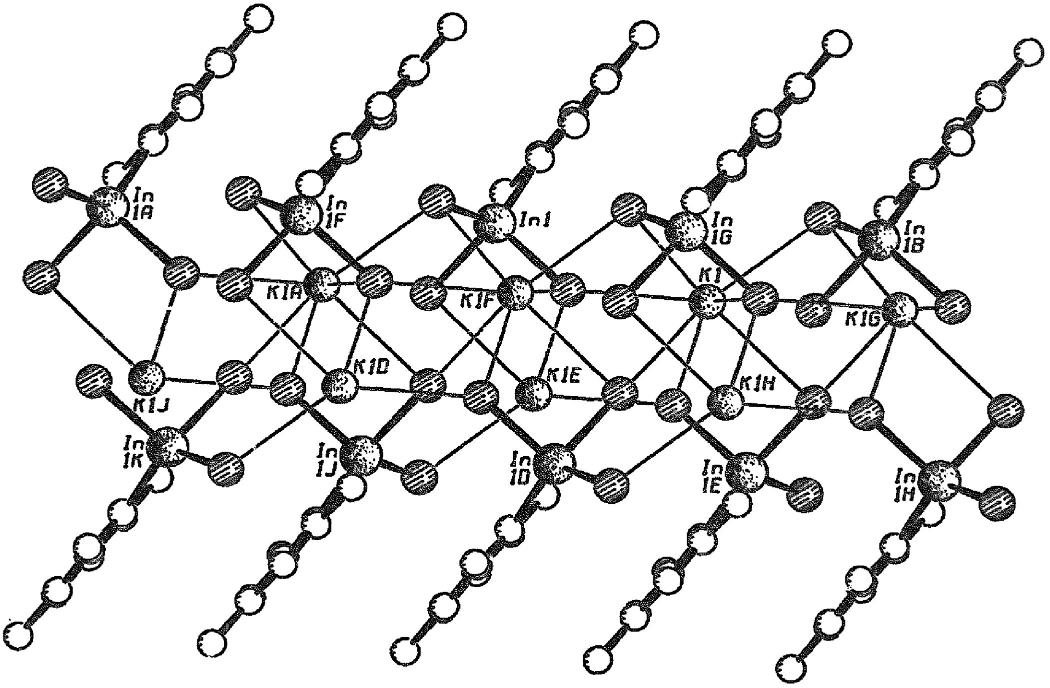

Fig. 27. Part of one layer in K[MesInBr$_3$] (SCHAKAL [29]).

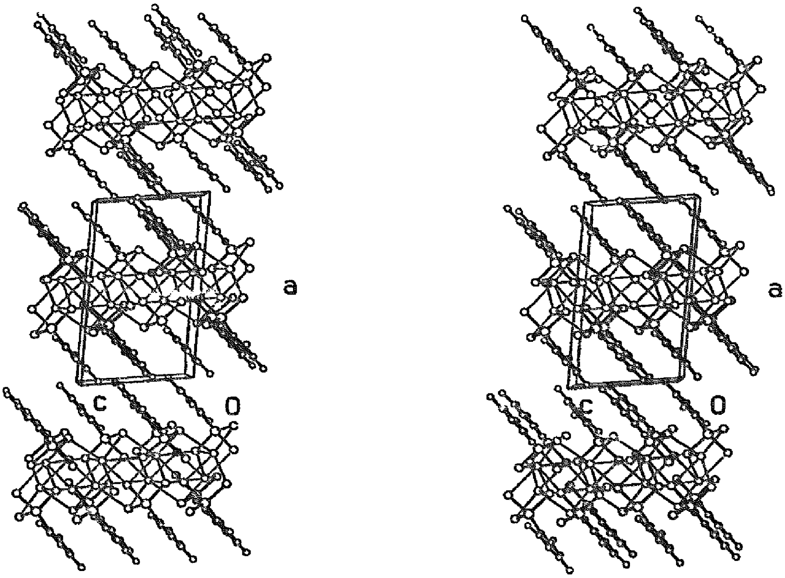

Fig. 28. Stereoscopic view of the unit cell of K[MesInBr$_3$]. The layers are stacked along the *b*-axis.

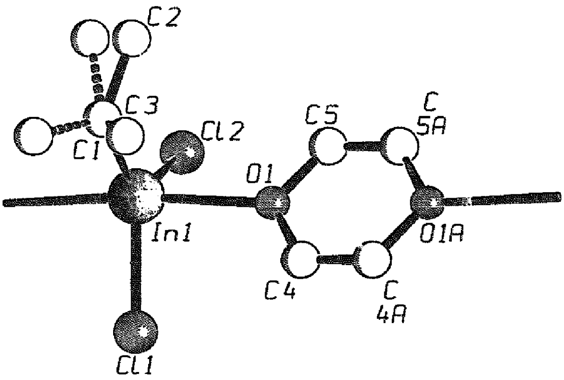

Fig. 29. Segment of the chain of $[(^{i}Pr)InCl_2(dioxane)]_n$ with disorder behaviour of the ^{i}Pr group (SCHAKAL [29]).

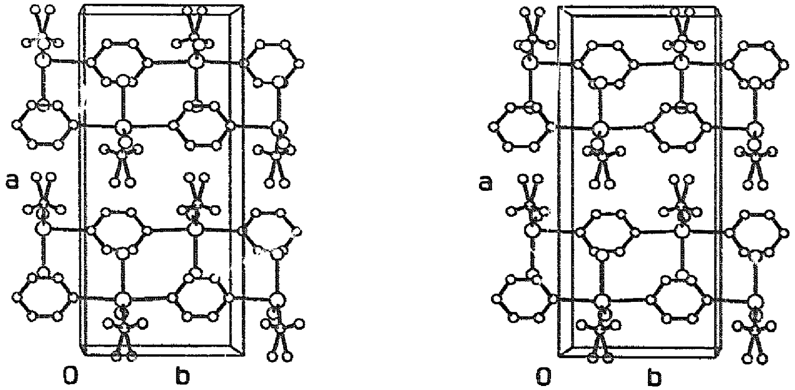

Fig. 30. Stereoscopic view of the unit cell of $[(^{i}Pr)InCl_2(dioxane)]_n$.

The tendency of $(^{i}Pr)_2InF$ to transfer F^- ions could be demonstrated by the treatment of $(^{i}Pr)_2InF$ with $SnCl_2(dioxane)$ [19]. The halide exchange gives an insoluble Sn–F compound and the coordination polymer $[(^{i}Pr)InCl_2(dioxane)]_n$ (Eq. (36)).

$$^{i}Pr_2InF + [SnCl_2(dioxane)] \rightarrow [^{i}PrInCl_2(dioxane)] + \ldots ? \qquad (36)$$

The product consists of polymeric chains with an alternating arrangement of donor solvent molecules and indane units, reported also for $[Me_3In\{S(CH_2)_4S\}]_n$ [89] (Fig. 29). The polymeric strings are directed along the *b* axis (Fig. 30). The ^{i}Pr group is disordered and occupies two positions.

The ability of diorganoindium(thallium) compounds to form stable linear R_2M^+ cations has already been mentioned [3,21,83]. $(PhCH_2)_2InF$ and Mes_2InF can donate F^- ions to a Lewis-acid-like $BF_3 \cdot (OEt)_2$ (Eq. (37)) [83] at 80°C in toluene.

$$R_2InF + BF_3 \cdot (OEt)_2 \xrightarrow{80°C;\ toluene} [R_2In][BF_4] + Et_2O \tag{37}$$

$$R = CH_2Ph,\ Mes$$

$({}^iPr)_3In$ reacts with $BF_3 \cdot (OEt)_2$ directly to $[({}^iPr)_2In][BF_4]$ at room temperature [21] (Eq. (38)). An analogous compound can be obtained by the reaction of $(PhCH_2)_3In$ or Mes_3In with $BF_3 \cdot (OEt)_2$ at 80°C.

$$3R_3In + 4BF_3 \cdot (OEt)_2 \rightarrow 3[R_2In][BF_4] + BR_3 + 4Et_2O \tag{38}$$

$$R = {}^iPr,\ CH_2Ph,\ Mes$$

All mentioned compounds are very moisture sensitive colourless salts. The solubility in donor solvents like MeCN is based on the formation of $[R_2In(NCMe)_n]^+$ ions. Only $[Mes_2In][BF_4]$ is slightly soluble in toluene. The prediction of the C–In–C angle in R_2In-fragments is possible for R = Me because of the quantity of structural data [90]. For a linear arrangement of the sequence $[R–In–R]^+$ the difference between the asymmetric and the symmetric stretching frequency is a maximum. The large $\Delta\nu$ in $[({}^iPr)_2In][BF_4]$ (ν_{as} 519, ν_s 474 cm^{-1}) points to a linear, or almost linear, C–In–C–axis [21]. The IR spectra of the benzyl and mesityl derivative show only one In–C band. Structural data of the solvent-free $[Mes_2In][BF_4]$ do not allow to determine, whether the Mes_2In^+ ion is linear or not because of a disorder of the ligands (Fig. 31) [83].

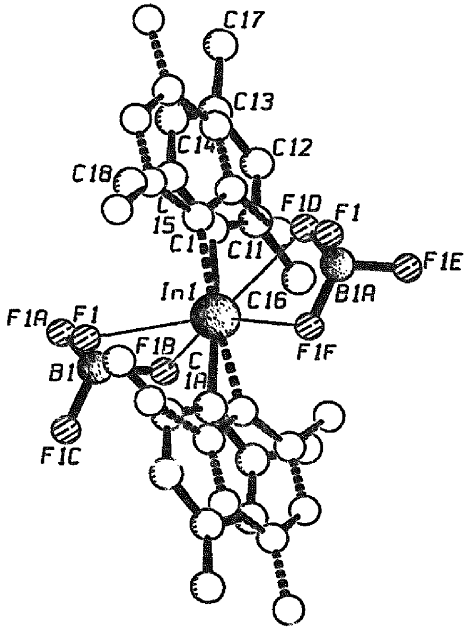

Fig. 31. Coordination of the In centre in $[Mes_2In][BF_4]$ with disorder behaviour of the $[Mes_2In]^+$ fragment (SCHAKAL [29]).

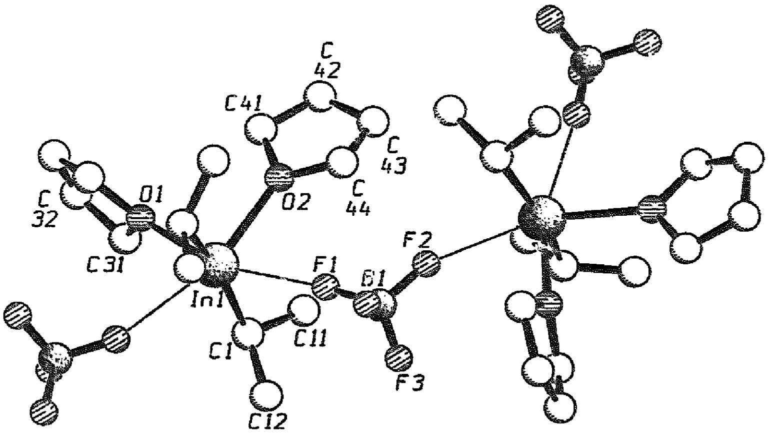

Fig. 32. Chain formed by $[(^{i}Pr)_2In(THF)_2]^+$ and $[BF_4]^-$ ions (SCHAKAL [29]).

However, a linear sequence can be assumed considering the linear geometry of the ion Mes_2Tl^+ in $[Mes_2Tl][MesTlCl_3]$ [99]. The coordination sphere of the In centre contains the two Mes ligands and four weakly bound fluorine atoms (In···F 271.3(7) pm) from two different BF_4^- ions. Every following R_2In^+ fragment is perpendicular to the fragment before, and all units are arranged perpendicular to the direction of the strings formed by the ions (*c* axis).

An infinite chain is also the principle for the structure of the solvate $[(^{i}Pr)_2In(THF)_2][BF_4]$ (Fig. 32) [21]. The metal centre possesses a CN of six. Two ^{i}Pr groups (trans configuration, C–In–C 160.3(4)°), two THF molecules in a cis configuration and two long In···F interactions (259.1(6) and 264.6(4) pm) complete a strongly distorted octahedron. The connection of the $[(^{i}Pr)_2In(THF)_2]^+$ ions with BF_4^- ions ensues along the *a* axis forming an infinite chain in a zig-zag fashion.

5. Synthesis and reactions of organothallium fluorides

5.1. *Synthesis and characterization of diorganothallium fluorides*

Surprisingly, diorganothallium fluorides were synthesized about 30 years before the first corresponding aluminium compound was published [4,91]. The reason is probably based on the fact that the thallium derivatives are usually stable towards air, water and alcohols.

Therefore, the synthesis can be carried out without working under an inert gas atmosphere. Halide exchange in combination with the formation of silver salts is the principle of the synthesis (Eq. (39)) [91–93,23,24].

$$R_2TlBr + AgF \rightarrow Me_2TlF + AgBr \qquad (39)$$

$R = Me$ [91], Et [91], ^{n}Bu [92], ^{i}Am (Am = amyl) [92,93], ^{i}Bu [93], ^{n}Hex [93],
Ph [91], C_6F_5 [23,24]

The reactions can be carried out in water, which first gives water-containing products. The water can be easily removed by drying the products in the presence of P_4O_{10} [91].

The formation of Me_2TlF in low yield could be observed in the reaction of Me_3Tl with F_3CI [94]. Et_2TlF is obtained in good yield by treating Et_3Tl with F_2HCNO_2 [95].

The diorganothallium fluorides are colourless, thermally stable and not very air-sensitive compounds. None of the derivatives has been structurally characterized. However, the presence of the ^{205}Tl isotope gives the possibility for ^{205}Tl NMR measurements as a helpful analytical probe ($\delta(Me_2TlF)$: -3420 (DMSO), -3500 ppm (H_2O); standard $TlNO_3$).

The IR data of $(C_6F_5)_2TlF$ support the existence of four-membered Tl_2F_2 rings connected to a coordination polymer in the solid state (ν_{TlF}: 318 cm^{-1}) [23,24].

The cryoscopic molecular weight determinations of $^nHex_2TlF$, $^iAm_2TlF$ and $^iBu_2TlF$ at various concentrations [93] are interesting. The *n*-hexyl and the isoamyl derivative contain species ranging from $n=2$ to $n=7.6$. The degree of aggregation is nearly independent of the concentration in the case of the isobutyl derivative.

5.2. *Synthesis and characterization of organothallium difluorides*

The organothallium difluorides are limited to the aryl-substituted derivatives to date. The hydroxide $PhTl(OH)_2$ can be used to form the desired fluorides (Eq. (40)) [96].

$$PhTl(OH)_2 \xrightarrow[-H_2O]{HF} PhTlF_2 \qquad (40)$$

The most commonly used synthesis method is the reaction of organothallium trifluoroacetates with various fluorides [97,98] (Eq. (41)).

$$RTl[OC(O)CF_3]_2 \xrightarrow[-M[OC(O)CF_3]]{MF} RTlF_2 \qquad (41)$$

$R=Ph$, $4\text{-}Cl\text{-}C_6H_4$, $2,4\text{-}Me_2C_6H_3$, $2,5\text{-}Me_2C_6H_3$, $2,6\text{-}Me_2C_6H_3$,

Mes, $4\text{-}MeOC_6H_4$ [97], $4\text{-}Me_2NC_6H_4$ [98]

The reaction medium may be water or alcohols. According to IR spectra and a normal coordinate analysis, the absorptions of $PhTlF_2$ at 525 and 499.5 cm^{-1} can be assigned to the asymmetrical TlF_2 and the symmetrical TlF_2 vibrations respectively [96,25]. Theoretical considerations suggest a molecule with C_{2v} symmetry, a Tl–F distance of 187.8 pm and an F–Tl–F angle of 116° [26].

5.3. *Reactions of organothallium fluorides*

There is only one salt known which contains an anion of the type $[R_3TlFTlR_3]^-$. The synthesis takes place according to Eq. (32) in toluene [27].

$$2Me_3Tl+[NMe_4]F \rightarrow [NMe_4][Me_3TlFTlMe_3] \qquad (42)$$

The IR spectra give rise to an anion with D_{3h} symmetry with an asymmetric stretching vibration ν_{as}(Tl–F–Tl) of 250 cm^{-1}.

Acknowledgements

Generous financial support by the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

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