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Evidence for SO₂, C₂H₄Cl₂ and CH₂Cl₂ soluble salts of bismuth homopolyatomic cations and $[Bi_4OF_2Cl_6(C_6Me_6)_4][Al(OC(CF_3)_3)_4]_2 \cdot C_6Me_6,$ containing the novel $[Bi_4OF_2Cl_6]^{2+}$ cation

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Abstract

Evidence is presented that the SO₂, C₂H₄Cl₂ and CH₂Cl₂ soluble salts of composition $[Bi_x]$ [Al(OC(CF₃)₃)₄]₃ (1), *x* close to 4.33, and $[Bi_5(C_6Me_6)_4]$ [Al(OC(CF₃)₃)₄]₃ (2), have been prepared in moderate yields by the metathesis reaction of $[Bi_5]$ [AsF₆]₃ and Li[Al-(OC(CF₃)₃)₄]₁ (2), have been prepared in moderate yields by the metathesis reaction of $[Bi_5]$ [AsF₆]₃ and Li[Al-(OC(CF₃)₃)₄]₁ in SO₂, and in CH₂Cl₂ in the presence of C₆Me₆, respectively. The compositions of 1 and 2 are supported by elemental analysis, IR, NMR and EI-MS. The UV–Vis spectra of 1 and 2 in SO₂ and C₂H₄Cl₂ were consistent with the presence of the bismuth cations $[Bi_5]^{3+}$, $[Bi_8]^{2+}$, $[Bi]^+$ and possibly $[Bi_9]^{5+}$. The 1:2 salt $[Bi_4OF_2Cl_6(C_6Me_6)_4]$ [Al(OC(CF₃)₃)₄]₂ · C₆Me₆ (3 · C₆Me₆) was isolated from a solution of **2**, and characterized by preliminary X-ray crystal structure, NMR and IR. Complex **3** contains a discrete oxygen-centered fluorine and chlorine-bridged bismuth cluster $[Bi_4OF_2Cl_6]^{2+}$ with each bismuth weakly coordinated to hexamethylbenzene.

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1. Introduction

Bismuth homopolyatomic cations have been studied extensively during the last 30 years. A number of salts containing $[Bi]^+$ [1], $[Bi_2]^{4+}$ [2], $[Bi_5]^+$ [3], $[Bi_5]^{3+}$ [4], $[Bi_6]^{2+}$ [3], $[Bi_8]^{2+}$ [1a,4a,5] and $[Bi_9]^{5+}$ [1a,1b,1c,5a,6] cations have been synthesized either by molten and solid state routes or in SO₂ or in superacid systems [1–6]. The resulting salts are insoluble, $[Bi_5]$ [AsF₆]₃ having very low solubility in SO₂, thus, restricting the further exploration of their chemistry. The subvalent bismuth cations including $[Bi_5]^{3+}$ and $[Bi]^+$ have been observed in In– BiCl₃–GaCl₃–benzene and Bi–GaCl₃–benzene solutions [7], from which $[Bi_5]$ [GaCl₄]₃ was isolated.

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During the last three decades we have discovered a rich chemistry of the polyatomic cations of main group elements [8]. A wide range of salts containing novel cations, e.g., sulfur and selenium halide cations $[M_2I_4]^{2+}$ M = S, Se [9], $[M_3X_3]^+ X = Cl$, Br, I [10], $[S_7X]^+$ [11], $[Se_6I_2]^{2+}$ [12], and heterocyclic compounds $[(CNSSS)_2]^{2+}$ [13], $[(CNSSS)_2]^{2+\cdots}$ [14], $[CF_3CNSSS]^{+\cdot}$ [15] and $[F_3CCSSSCCF_3]^+$ [16] that possess novel electronic and magnetic properties have been obtained from reactions of homopolyatomic cations of group 16 and 17 in the solvent SO₂. One aim of this work was the preparation of soluble salts of bismuth homopolyatomic cations as precursors to new bismuth containing compounds.

In order to prepare soluble salts of bismuth polyatomic cations, we investigated the reaction of $[Bi_5][AsF_6]_3$ and $Li[Al(OC(CF_3)_3)_4]$ in the solvents (a) SO₂, (b) CH₂Cl₂ in the presence of the molecular donor ligand C₆Me₆. We

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Fig. 1. The crystal structure of the $\{[Bi_4OF_2Cl_6](C_6Me_6)_4\}^{2+}$ cation.

found that the [Bi₅][AsF₆]₃ salt has sufficient solubility in SO₂ for the [17] metathesis reaction, replacing the [AsF₆]⁻ anion (0.110 nm³ [18]) by the larger [Al(OC(CF₃)₃)₄]⁻ anion (0.758 nm³ [19]). The estimated lattice energy of the [Bi₅][Al(OC(CF₃)₃)₄]₃ of 1571 kJ/mol is about 900 kJ/mol lower than that of the [Bi₅][AsF₆]₃ 2467 kJ/mol¹ and is therefore comparable in energy to those of the SO₂ soluble salts containing homopolyatomic cations of group 16, e.g., U_{POT} ([S₄][AsF₆]₂) = 1557 kJ/mol, U_{POT} -([Se₄][AsF₆]₂) = 1544 kJ/mol, [Te₄][AsF₆]₂, 1518 kJ/mol.¹

2. Results and discussion

2.1. Reaction of $[Bi_5][AsF_6]_3$ and $Li[Al(OC(CF_3)_3)_4]$ in SO_2

The reaction of SO₂ soluble Li[Al(OC(CF₃)₃)₄] and NO[SbF₆] [17] gave the insoluble Li[SbF₆] (s) and NO[Al(OC(CF₃)₃)₄]. In contrast the corresponding reaction of Li[Al(OC(CF₃)₃)₄] and excess of the weakly soluble [Bi₅][AsF₆]₃ afforded insoluble Li[AsF₆] and the reaction product [Bi_x][Al(OC(CF₃)₃)₄]₃ (1), x close to 4.33 according to the elemental analysis (Eq. (1)), contaminated with 10% of starting material Li[Al-(OC(CF₃)₃)₄], determined by quantitative ⁷Li NMR

$$3\text{Li}[\text{Al}(\text{OC}(\text{CF}_3)_3)_4] + [\text{Bi}_5][\text{As}\text{F}_6]_3$$

$$\xrightarrow{\text{SO}_2, \text{r.t.}} [\text{Bi}_x][\text{Al}(\text{OC}(\text{CF}_3)_3)_4]_3 + 3\text{Li}[\text{As}\text{F}_6](s) \qquad (1)$$

The bismuth containing product is very soluble in SO₂ and contains $[Al(OC(CF_3)_3)_4]^-$ anion $[^{19}F, ^{27}Al$ NMR] showing that the anion has remained a spectator anion. The UV-Vis spectrum contained the band maxima (Table 1, column 2, actual spectra see S.I.) at 405, 450, 523 nm (Table 1) and 347 nm (shoulder) close to those of $[Bi_5]^{3+}$, $[Bi_8]^{2+}$ and probably $[Bi_9]^{5+}$ cations (Table 1) (a full interpretation of the UV spectra of $[Bi_5]^{3+}$, $[Bi_8]^{2+}$, $[Bi_9]^{5+}$ is given in [20]). The digital Gaussian deconvolution of the UV-Vis spectrum vielded the relative intensities of the bands allowing to calculate the molar absorptivities 5.1×10^3 (409 nm), 4.6×10^3 (453 nm), 3.1×10^3 (517 nm), 1×10^2 (804 nm), which are in agreement with the literature data for the $[Bi_5]^{3+}$ or $[Bi_8]^{2+}$ [24,7b,26]. Resolved bands arising from the presence of [Bi]⁺ cation were not detected, however, a better fit of the calculated curve was obtained by postulating a weak band of $[Bi]^+$ 677 nm superimposed upon the more intense $[Bi_5]^{3+}$ (or $[Bi_8]^{2+}$) absorptions

$$3[Bi_{5}]^{3+} \stackrel{SO_{2},r.t.}{\rightleftharpoons} [Bi_{8}]^{2+} + 7[Bi]^{+} 2[Bi_{5}]^{3+} \rightleftharpoons [Bi_{9}]^{5+} + [Bi]^{+}$$
(2)

Thus, the SO₂ solution of the reaction product contained a mixture $[Bi_5]^{3+}$, $[Bi_8]^{2+}$, $[Bi_9]^{5+}$ and the $[Bi]^+$. The given cations could be generated by Eqs. (2) from the $[Bi_5]^{3+}$. We note that $[Sb_8][GaCl_4]$ was isolated from solutions of SbCl₃ in the Ga–GaCl₃–benzene system [21], whereas previously $[Bi_5]^{3+}$ and $[Bi]^+$ have been observed in Bi–GaCl₃–benzene solutions [7] and a products suggested to be $[M_5][GaCl_4]_3$ (M = Sb, Bi) were isolated from the MCl₃–Ga–GaCl₃ molten salt systems [4c].

The major IR absorption bands of the reaction products are due to the nonafluorobutoxide ligands. The bands at 832, 864 cm⁻¹, which are not observed in the spectrum of Li[Al(OC(CF₃)₃)₄] have been assigned [22] to the Al–O vibrations of **1**. Energies of these bands are close to those of Li[Al(OC(CF₃)₃)₄] (S.I., Section 2) with differences ca. 10 cm⁻¹. Thus, the local geometry around the Al atom in **1** is distorted and lower symmetry than tetrahedral, much like that in the Li[Al-(OC(CF₃)₃)₄], as the bismuth cation could have strong Bi–F and Bi–O contacts reminiscent of those of [Li]⁺ in Li[Al(OC(CF₃)₃)₄]² [23].

2.2. Reaction of $[Bi_5][AsF_6]_3$ with $Li[Al(OC(CF_3)_3)_4]$ and C_6Me_6 in CH_2Cl_2

The metathesis reaction of $[Bi_5][AsF_6]_3$ and $Li[Al(OC-(CF_3)_3)_4]$ in the presence of C_6Me_6 in CH_2Cl_2 yields dark brown, $Li[Al(OC(CF_3)_3)_4]$ free, highly soluble regularly

¹ Lattice energies have been calculated using the volume-based equation given in [18]. Volume of $[Bi_5]^{3+}$ 0.143 nm³ was obtained by subtracting the three volumes of $[AlCl_4]^-$ anion 0.156 nm³ from the molecular volume of the $[Bi_5]$ [AlCl_4]₃ 0.611 nm³ [4b]. Volume of the $[AsF_6]$ was taken from [18], lattice energies of $[M_4]$ [AsF₆]₂ M = S, Se, Te were taken from [18].

² [Li]⁺ in the Li[Al(OC(CF₃)₂Ph)₄] [23a] and Li[Al(OC(CF₃)₃)₄] [23b] is coordinated to the 2 oxygen and 4 fluorine atoms of the ligand, lowering the local symmetry around aluminium atom from T_d to C_{2v} .

UV–Vis bands (nm) for on cationic bismuth ch	und in this study for J usters	product of interaction c	of [Bi5][AsF6]3 and Li[A		$_{2}(A)$, and for compound	l 4 in DCE – dichloı	roethane compared w	ith the literature data
A in SO_2	4 in DCE	$[Bi_5]^{3+}$ in H ₂ SO ₄ [4d]	[Bi ₅] ³⁺ in NaCl–AlCl ₃ [24]	[Bi] ⁺ in NaCl-AlCl ₃ [24.25]	[Bi] ⁺ in GaCl ₃ –NaCl [7b]	[Bi ₈] ²⁺ in Bi-GaCl ₃ (175 °C) [7b]	[Bi ₈] ²⁺ in AlCl ₃ -NaCl (250 °C) [26]	[Bi9] ⁵⁺ in MeBzImCl/AlCl3 melt [20]
$347 [0.71] (9.4 \times 10^3)$	$348 (8.7 \times 10^3)$	$362 (2.39 \times 10^3)$	345 ^b	- -			$350 (1.2 \times 10^3)$	1
409 [0.38] (5.1×10^3)	$407 (6.7 \times 10^3)$	425 (1.5×10^3)	$390 \ (6.5 \times 10^3)$			387 [1.00]		
$452 \ [0.34] \ (4.6 \times 10^3)$	$447 (4.8 \times 10^{2})$ $468^{a} (4 \times 10^{3})$	460^{b}	$455 (3 \times 10^3)$			440 [0.76]	450 (0.62 \times 10 ³)	450 (s) ^e
$517 [0.23] (3.1 \times 10^3)$	$522(3 \times 10^3)$	$525 \ (0.29 \times 10^3)$	$540(1.5 \times 10^3)$			530 [0.36]	$530(0.4 \times 10^3)$	
	591 ^a [0.24] 651 ^a [0.10]			585 (3.2×10^2) 657 (1.2×10^2)	587 (7×10^2)			
677^{a} [0.09] 804^{c} [0.07] (1 × 10 ²)	$770 (8 \times 10^2)$	720 (1.1 × 10^2)	770 (3.0×10^2)	$694 (1.0 \times 10^{2})$ 730 (0.9 × 10 ²)	675 (3×10^2) 691 (3×10^2)			750 (w)
d r	875° (4 × 10 ²)	$821(1.8 \times 10^2)$	$875(5.0 \times 10^2)$	900 (ca. 5)	920 (ca. 10)			830 (w)
Absorption maxima ar ^a Band maxima is no	e given in nm with n t resolved and obtain	nolar absorptivities in ned only by Gaussian	brackets and relative in deconvolution.	ntensities in square b	rackets.			

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Table 1

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Relative intensities and molar absorptivities are not given

Instrumental cut off at 820 nm.

^c Very broad signal.

^b Observed in the reflectance spectrum.

shaped crystals, which did not diffract X-rays. The reaction product is interpreted as a salt containing the $[Bi_5]^{3+}$ cation, e.g., $[Bi_5(C_6Me_6)_4][Al(OC(CF_3)_3)_4]_3$ (2) based on the elemental analysis (Eq. (3))

$$3\text{Li}[\text{Al}(\text{OC}(\text{CF}_3)_3)_4] + [\text{Bi}_5][\text{As}\text{F}_6]_3 + 4\text{C}_6\text{Me}_6$$

$$\xrightarrow{\text{CH}_2\text{Cl}_2}_{+5\ \text{\circ}\text{C}} \rightarrow [\text{Bi}_5(\text{C}_6\text{Me}_6)_4][\text{Al}(\text{OC}(\text{CF}_3)_3)_4]_3 + 3\text{Li}[\text{As}\text{F}_6]_2$$
(3)

The UV–Vis spectrum (Table 1, spectrum is shown in the S.I. Figs. 8 and 9) of **2** in $C_2H_4Cl_2$ was consistent with $[Bi_5]^{3+}$, $[Bi_8]^{2+}$, $[Bi_9]^{5+}$ cations in solution as well as $[Bi]^+$. Reported band maxima of $[Bi_5]^{3+}$ and $[Bi_8]^{2+}$ and that at 450 nm for the $[Bi_9]^{5+}$ are close to each other, hence these cations might be in equilibrium with **2** (Eq. (2)) in $C_2H_4Cl_2$. The molar absorptivities of $[Bi_5]^{3+}$ in **2** are in the same range but higher, as those of $[Bi_5]^{3+}$ in NaCl–AlCl₃ melts, strongly supporting our assignment of the bands to $[Bi_5]^{3+}$ and the presence of $[Bi]^+$, $[Bi_8]^{2+}$ and probably $[Bi_9]^{5+}$.

The IR absorption bands of C_6Me_6 in **2** are slightly shifted from those of C_6Me_6 (Tables 2 and 3), implying weak interaction between the bismuth cation and C_6Me_6 . In addition, the IR spectrum contains only one Al–O band 832 cm⁻¹ in the range 800–900 cm⁻¹ [22] consistent with T_d site symmetry around the aluminium atom and very weak cation–anion interaction in **2**.

2.3. Evidence for $[Bi_4OF_2Cl_6(C_6Me_6)_4]$ - $[Al(OC(CF_3)_3)_4]_2 \cdot C_6Me_6$

Crystals of **2** { $[Bi_5(C_6Me_6)_4]$ [Al(OC(CF₃)₃)₄]₃} were deposited from the reaction mixture during a period of 1–6 days. For the next 10 days, crystals of **2** were contaminated with yellow crystals assigned to **3** and [C₆Me₆H][Al(OC(CF₃)₃)₄]³ and after an additional 5 days only yellow and orange crystals of **3**, [C₆Me₆H][Al-(OC(CF₃)₃)₄] and colourless crystals⁴ were obtained.

We propose that the homopolyatomic cations generated in the metathesis reaction in CH_2Cl_2 are very chem-

³ Yellow crystals **4** refined in C1, a = 9.825, b = 20.046, c = 21.148, $\alpha \approx \beta \approx \gamma \approx 90^\circ$, Z = 2 to the *R* factor close to 25% and was consistent with the presence of $[Al(OC(CF_3)_3)_4]^-$ and $\{C_6Me_6\}$ or $([C_6Me_6H]^+)$ moieties. Problem of disordering $-C(CF_3)_3$ groups in the anion precluded further refinement. It could be Li[Al(OC(CF_3)_3)_4] \cdot C_6Me_6 or $[C_6Me_6H][Al(OC(CF_3)_3)_4]$. A ⁷Li resonance was not observed at r.t. and low temperature for the solution of yellow reaction product, hence $[C_6Me_6H][Al(OC(CF_3)_3)_4]$ formulation seems to be more feasible, additional IR evidence of $[C_6Me_6H]^+$ is described in Section 4.

⁴ Colourless crystals that deposits from solution in a period of 1 month at -24 °C refined in C1, a = 14.330(2), b = 18.114(3), c = 22.492(4), $\alpha = 84.252(2)$, $\beta = 72.851(2)$, $\gamma = 82.616(2)$, Z = 4 to the *R* factor close to 20%. The proposed structure obtained at this point of refinement consistent of $[Al(OC(CF_3)_3)_4]^-$ and $[Al_7O_4F_{14}]^-$ and/or $[Al_7O_3F_{15}]$ moieties. Problem of disordering $-C(CF_3)_3$ groups in the anion precluded further refinement.

Table 2 Raman of **2**, bands of $[Al(OC(CF_3)_3)_4]^-$ anion (assignment see [17,22b,22c]) are omitted for clarity

Observed band	Literature data	Assignment
108 (sh)	103 (sh)	$v_6(E'')[Bi_5]^{3+}$
119 (s)	119	lattice mode, also observed
		previously for anion and C ₆ Me ₆
138 (sh)	142 (sh)	$v_1(A'_1)[Bi_5]^{3+}$
336 (w)	343(w)	CH ₃ motion
380(w)	378 (w)	CH ₃ motion perpendicular to the
		plane of benzene skeleton
450 (m)	450 (m)	deformation mode of benzene
		skeleton
554 (s)	553 (s)	breathing, benzene skeleton
1294 (vs)	1295 (m)	v(C–CH ₃)
1373 (w)	1364 (m)	δCH_3 symmetry
1396 (m)	1385 (m)	δCH_3 degenerate
1418 (w)	1438 ^a	δCH_3 degenerate
1495 (m)	1462 ^a	δCH_3 degenerate
1581 (b, w)	1583 (w)	v(C=C)
2875 (sh)	2939 (vs)	v(C–H)
2924 (b, vs)	2985 (vs)	v(C–H)

Assignment for $[Bi_5]^{2+}$ [4d,7b], C₆Me₆ [46].

^a Observed at low temperature in crystalline hexamethylbenzene [46a].

Table 3 Observed IR bands of C_6Me_6 in 2, $3 \cdot C_6Me_6$, 4 and assignment [47]

2	3	4	C_6Me_6	Assignment
		682		
793	780		796	out of plane ring bending mode
		889		
1018	1022		998	in plane CH ₃ rocking
1062	1069	1061	1057	out of plane CH ₃ rocking
1074		1071		
	1102			
		1596		$\left[\mathrm{C_{6}Me_{6}H} ight]^{+\mathrm{a}}$

^a Band at 1590 cm^{-1} is one of the characteristic benzoid C=C skeletal stretching modes of the carbocation [48].

ically active and abstract oxygen and fluorine from the nonafluorobutoxide ligand of the $[Al(OC(CF_3)_3)_4]^-$ anion and chlorine from the CH_2Cl_2 (see S.I. for a detailed discussion). Abstraction of oxygen and fluorine from the $[Al(OC(CF_3)_3)_4]^-$ was observed previously by degradation of phosphorus iodine cations⁵ [27]. Bismuth alkoxides $Bi(OR_f)_3 R_f = (C_6H_2(CF_3)_3)$ [28,29] decomposed with C-F activation. C-Cl activation by electrophilic metal centers followed by the chlorine transfer to the metal have been observed for a wide range of metals

[30] (e.g., for CHCl₃ by the rhodium complex $LRh(CO)_2$ L = tris(3,5-dimethyl,4-chloropyrazolyl)borate [30a]).

The salt $3 \cdot C_6 Me_6$ (Fig. 1) is the first example of a 1:2 salt of the bulky polyfluoroalkoxyaluminate anion, the first example of a discrete oxygen-centered tetrahedral arrangement of group 15, and a rare example of a Bi(III) fluoride complex [31,32]. Four-coordinate oxygen centers have been reported in bismuth alkoxide clusters having complex oligometric structures (i.e., $Bi_4(\mu_4-O)$ - $(\mu$ -OR)₆{ μ_3 -OBi(μ -OR)₃}₂(C₆H₅CH₃)) [33] as well as for main group [34,35], d-block [36,37] and f-block [38,39] metal complexes. The structure of $3 \cdot C_6 Me_6$ was obtained from crystals of poor quality, albeit many unsuccessful attempts made to improve their quality. However, the connectivity in $[Bi_4OF_2Cl_6]^{2+}$ has been established and the data clearly show the presence of C_6Me_6 and the $[Al(OC(CF_3)_3)_4]^-$ anion. The quality of the X-ray structure does not allow unambiguous assignment of the bridging light atoms as oxygen or fluorine within the Bi₄X₂Cl₄Y core and the atom type assignment has been made based on chemical arguments bond valence theory, ESR and NMR data. The sum of four Bi-O(1) contacts is 2.17 v.u. and consistent with a valence of 2 for oxygen, while four Bi-(F1) contacts would give 1.64 v.u.⁶ [40] for fluorine, strongly supporting the assignment of the central atom as oxygen. In addition, a Bi₄F₅ would result in a mixed oxidation state for bismuth and 1 unpaired electron for the dication. However, an ESR signal was not detected for the solid sample, as well as a solution of $3 \cdot C_6 Me_6$. The same method was applied to assign F2 and F3. The sum of two Bi-F(2), Bi-F(3) contacts is 0.71 and 0.67 v.u., while two Bi-O(2) and Bi-O(3) contacts would give 0.97 and 0.95 v.u., hence bridging atoms are most likely fluorine. In addition, the fluorine NMR spectrum of the freshly prepared SO2 solution of $\textbf{3} \cdot C_6 Me_6$ at $-70~^\circ\text{C}$ shows major ¹⁹F and ²⁷Al NMR resonances of the $[Al(OC(CF_3)_3)_4]^-$ anion and a minor singlet resonance at -220.5 ppm in the ¹⁹F NMR attributed to the fluorine atoms in the $[Bi_4OF_2Cl_6]^{2+}$ cation.

The dication contains four bismuth atoms at the apex of an oxygen centered distorted tetrahedron, linked across the edges by bridging halogen atoms (Figs. 2 and 3). The Bi1–F–Bi2 and Bi(1,2)–Cl–Bi(3,4) angles in 3 are close to 90° within 2° and the Bi3–Cl–Bi4 angles are 83.0(4)° and 85.0(4)°. Also, the estimated Bi4–Bi3 distance is 3.602(1) Å, shorter than the Bi1–Bi2 and Bi3–Bi4 contacts 3.93(±0.04) Å. Each bismuth atom is capped by a weakly bound η^6 C₆Me₆ ring⁷ [41,42]

⁵ The proposed [27a,27b] decomposition mechanism of the salt of $[P_2I_3]^+$ involved the formation of a tight ion pair $[P_2I_3]^+[Al(OC(CF_3)_3)_4]^-$ followed by liberation of $[P_2I_3][OC(CF_3)_3]$ and the very strong Lewis acid $Al(OC(CF_3)_3)_3$ which abstract fluorine from the $[OC(CF_3)_3]$ and react with the $[Al(OC(CF_3)_3)_4]^-$ forming dimeric anion $[(OC(CF_3)_3)_3Al(\mu-F)Al(OC(CF_3)_3)_3]^-$. The phosphorus iodine cation abstract oxygen from the $[OC(CF_3)_3]$ forming P_2O_3 , P_4 , C_4F_8 . The final products of decomposition were $[P_2I_3][(OC-(CF_3)_3)_3Al(\mu-F)Al(OC(CF_3)_3)_3]$, phosphorus oxide, phosphorus alkoxide, P_4 and fluorocarbon species.

⁶ Values used: Bi(+3)–F(-1) $R_{o} = 1.99$, B = 0.37, Bi(+3)–O(-2) $R_{o} = 2.094$, B = 0.37, Bi(+3)–Cl(-1) $R_{o} = 2.48$, B = 0.37.

 $^{^7}$ The separation distances between Bi(1) and C(301)–C(306) aromatic ring 2.69 Å, Bi(2) and C(101)–C(106) aromatic ring 2.67 Å, Bi(3) and C(401)–C(406) aromatic ring 2.75 Å, Bi(4) and C(201)–C(206) aromatic ring 2.61 Å.



Fig. 2. Environment of the Bi(1) atom in 3, neighbouring bismuth atom and C_6Me_6 molecules are omitted for clarity.



Fig. 3. Environment of the Bi(3) atom in 3, neighbouring bismuth atom and C_6Me_6 molecules are omitted for clarity.

approximately perpendicular to the corresponding Bi–O bond as illustrated in Fig. 1. The bismuth halogen dication core may be formally regarded as constructed from one $[BiF_2]^+$ moiety, three $[BiCl_2]^+$ units, and $[O]^{2-}$ which donates electron density to the four bismuth atoms with the sum of the Bi–O valency units calculated at 2.14(2) v.u.⁶ [40].

In VESPR terms [43], the first coordination around Bi1 and Bi2 can be described as $AX_2X'_2YE$ (X = Cl, X' = F, Y = O, E = lone pair) and that of Bi3 and Bi4 as AX_4YE illustrated for Bi1 and Bi3 in Figs. 2 and 3, respectively, which include bond distances and valence units. The corresponding figures for Bi2 and Bi4 are included in the Supplemental materials. All the F–Bi–F, F–Bi–Cl, Cl–Bi–Cl, O–Bi–F and O–Bi–Cl angles in **3** are in the range 72.3–76.4°. The sum of the valence units around Bi3 is 2.78 v.u. (Bi1 is 1.98 v.u., Bi2 2.05 v.u., Bi4 2.66 v.u.), the remaining Bi valence units are derived from the donation of electrons from the C₆Me₆ ring to the positively charged bismuth in to the second coordination sphere of bismuth. We have estimated the lattice energy $U_{POT}([Bi_4OF_2-Cl_6(C_6Me_6)_4][Al(OC(CF_3)_3)_4]_2)$ as 912 kJ/mol⁸ [44]. This is significantly larger than that of 1:1 salt with the same anion, $U_{POT}(Li[Al(OC(CF_3)_3)_4])$ 361 kJ/mol [19], but smaller than the 1:2 salts $U_{POT}(Ca[NO_3]_2)$ 2209 kJ/mol and $U_{POT}(MgI_2)$ 1944 kJ/mol [18 (Table 2)]. Therefore, the higher solubility of $\mathbf{3} \cdot C_6Me_6$ in SO₂ compared with the poor solubility of Ca(NO_3)_2 and MgI_2 may arise from the smaller lattice energy of 1:2 salts with the large anion.

The X-ray microanalysis confirms that $3 \cdot C_6 Me_6$ contains Bi and Cl, as well as Al, F, C and O (S.I.). The EI-MS shows $[C_6Me_6^+]$ and as well as fluorocarbon cations derived from $[Al(OC(CF_3)_3)_4]^-$ on decomposition of $3 \cdot C_6Me_6$. The IR spectrum of $3 \cdot C_6Me_6$ contains very strong absorption bands of the perfluorinated ligand of the anion. One Al-O band of the $[Al(OC(CF_3)_3)_4]^-$ anion was detected at 833 cm⁻¹ consistent with an almost tetrahedral symmetry at the aluminium center. The observed absorption bands of the C_6Me_6 in $3 \cdot C_6Me_6$ (Table 3) are shifted slightly higher in energy, relative to the band for free C_6Me_6 [47], due to coordination to the $[Bi_4OF_2Cl_6]^{2+}$ cation. For comparison, the Ln(III) complexes [LnCl₂(C₆Me₆)][AlCl₄]₃ Ln = Nd, Sm, Gd, Yb exhibit the out of plane mode at 770–780 cm⁻¹ and v(CH₃) vibrations at 1010– 1030 cm^{-1} [45], close to those of 3.

3. Conclusions

Evidence is presented that we have prepared the SO₂, CH₂Cl₂ and C₂H₄Cl₂ soluble salts [Bi_x][Al(OC(CF₃)₃)₄] (1) and [Bi₅(C₆Me₆)₄][Al(OC(CF₃)₃)₄]₃ (2), in a moderate yields by the metathesis reaction between [Bi₅][AsF₆]₃ and Li[Al(OC(CF₃)₃)₄] in SO₂ solution and in a solution of CH₂Cl₂ that contained C₆Me₆. This implies that the metathesis reaction in the presence of appropriate donor ligand (arene) in SO₂ and CH₂Cl₂ may generate several of the related salts containing bismuth polyatomic cations. The UV–Vis of solutions of 1 in SO₂ and 2 in C₂H₄Cl₂ were consistent with the presence of [Bi₅]³⁺, [Bi₈]²⁺, [Bi₉]⁵⁺ and [Bi]⁺.

The bismuth homopolyatomic cations were shown to be chemically reactive and the novel 1:2 salt $[Bi_4O-F_2Cl_6(C_6Me_6)_4][Al(OC(CF_3)_3)_4]_2 \cdot C_6Me_6$ containing the bismuth cluster cation $[Bi_4OF_2Cl_6]^{2+}$ was isolated from a solution of **2** in CH₂Cl₂. Formation of $[Bi_4OF_2Cl_6]^{2+}$ may be regarded as a self assembly of bismuth halide and oxohalide moieties, however, it is difficult to assess

⁸ The volume of the C₆Me₆ ($V_m = 0.252 \text{ nm}^3$) [44] was subtracted from the volume of $\mathbf{3} \cdot C_6 \text{Me}_6$ ($V_m = 3.402 \text{ nm}^3$), obtained from crystallographic data in order to provide the volume of $\mathbf{3}$ ($V_m = 3.150 \text{ nm}^3$). The obtained volume was used for calculation of $U_{\text{POT}}(\mathbf{3})$ using Eq. (3) [18] and parameters $\alpha = 133.5$, $\beta = 60.9$.

the features that governed the $[Bi_4OF_2Cl_6]$ stoichiometry by decomposition of the bismuth homopolyatomic cations under the prevailing experimental conditions. We propose that the process involved fluorine and oxygen transfer from the nonafluorobutoxide ligand and chlorine transfer from the CH₂Cl₂ and conclude that the bulky anion facilitates the formation of a discrete oxygen-centered fluorine- and chlorine-bridged bismuth cluster in a complex with hexamethylbenzene.

4. Experimental

4.1. General remarks

All operations were performed using standard Schlenk line techniques under a purified nitrogen atmosphere. Solid reagents and crystals were manipulated in a Vacuum Atmospheres Dri-Lab equipped with a Dri-Train (HE-493) and 1 kg of 3 Å molecular sieves contained in an internal circulating drying unit. Reactions in SO_2 were carried out in a jointless, single apparatus fitted with Teflon in glass Rotoflo valves (HP 6K) and consisting of two thick walled bulbs (V = 50 ml) linked by a glass tube incorporating a sintered fine-porosity glass frit. The compounds $[Bi_5][AsF_6]_3 \cdot SO_2$ and Li[Al- $(OC(CF_3)_3)_4$ were prepared by the literature methods [23a,4d] and the identity of $[Bi_5][AsF_6]_3 \cdot SO_2$ was supported by IR. The IR spectrum of $Li[Al(OC(CF_3)_3)_4]$ included in the S.I. has not been previously reported. Sulfur dioxide was dried over P₂O₅ and distilled prior to use. CH₂Cl₂ and CDCl₃ were dried over CaH₂ and degassed. NMR spectra were recorded using Varian 400 NMR spectrometer. Proton and ¹³C chemical shifts are reported in δ units downfield from Me₄Si with the solvent as the reference signal. CClF₃ was used as a reference for ¹⁹F spectra and aqueous solutions of AlCl₃ and Li[ClO₄] were used as a references in ²⁷Al and ⁷Li NMR spectra, respectively. NMR samples were prepared in 10 and 5 mm thick walled NMR tubes fitted with J. Young valves. Mass spectra were recorded using a KRATOS ms 50 TC mass spectrometer equipped with the EI source, 30 ev. by the direct inlet method from samples sealed in dried glass m.p.t. tubes. FT-IR spectra (resolution 1 cm^{-1} , 128 scans) were recorded using a Thermo Nicolet spectrometer (Nexus 470 FT-IR). FT-Raman spectra were obtained from neat samples, sealed under nitrogen atmosphere in glass capillaries, using Bruker RFS 100 FT-Raman spectrometer incorporating a Nd:YAG laser (emission wavelength: 1.06 µm; maximum output laser power: 80 mW), 1000 scans, resolution 4 cm^{-1} . We attempted to record FT-Raman spectra of all species; however, the coloured samples 1 and 3 showed fluorescence, compound 2 gave a Raman spectrum with a low signal-to-noise ratio. The UV-Vis spectrum of 1 in SO₂ was measured using HP-8452A

Crystallo	graphic da	ata of the	X-ray	diffraction	studies	of 3	$\mathbf{S} \cdot \mathbf{C}$	$C_6 Me_6$
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	$3 \cdot C_6 Me_6$
Formula	C92H90Al2Bi4Cl6F75O8
Molecular formula	$[Bi_4OF_2Cl_6(C_6Me_6)_4]$
	$[Al(OC(CF_3)_3)_4]_2 \cdot C_6Me$
$M_{ m r}$	3848.22
Temperature (K)	198(1)
Radiation used (λ [Å])	Μο Κα (0.71073)
Crystal description	orange, needle
Crystal size (mm)	$0.1 \times 0.1 \times 0.5$
Crystal system	orthorhombic
Space group	$P2_{1}2_{1}2_{1}$
a (Å)	15.8671(10)
b (Å)	25.8211(18)
<i>c</i> (Å)	33.209(2)
α (°)	90
β (°)	90
γ (°)	90
$V(\text{\AA}^3)$	13605.8(16)
Z	4
<i>F</i> (000)	7360
$\rho_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.879
$\mu (mm^{-1})$	5.437
Total reflections	94818
Unique reflections	30455
R _{int}	0.1001
Scan range Θ (°)	1.2-27.50
Completeness to Θ_{\max} (%)	99.2
Index ranges	$-20 \leqslant h \leqslant 20; -32 \leqslant k \leqslant 33;$
	$-42 \leqslant l \leqslant 39$
Data/restrains/parameters	30455/125/712
$R_1, wR_2 [I \ge 2\sigma(I)]$	0.0858, 0.2289
R_1 , wR_2 (all data)	0.2036, 0.2622
Goodness-of-fit on F^2	1.009
Maximum/minimum	3.016 and -1.425
electron density (e A ³)	0.000
Mınımum/maxımum	0.860
transmission ratio	

 $wR_2 = \left(\sum \left[w(F_o^2 - F_c^2)^2 \right] / \sum [F_o^4] \right)^{1/2}, R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, \text{ weight} = 1 / [\sigma^2(F_o^2) + (0.0745 * P)^2]; \text{ where } P = \left(\max(F_o^2, 0) + 2 * F_c^2 \right) / 3.$

diode array spectrophotometer, at room temperature, 300-820 nm range, 14 mg of solid containing 90% 1 and 10% Li[Al(OC(CF₃)₃)₄] in (6 g, 4.11 ml) of SO₂ 0.1 cm cell. The compound 2 were measured using a Cary 5E UV-Vis-NIR spectrometer, at room temperature, in 0.2 cm cells. Two spectra, one containing data collected from 3000 to 400 nm and one from 800 to 300 nm were measured using 23.5 mg of sample 2 and 3.8636 g of $C_2H_4Cl_2$. Melting points were measured in sealed capillary tubes under nitrogen and are not corrected. X-ray microanalysis was performed with a JEOL JSM-6400 SEM, equipped with an Edax Genesis X-ray micro analyser. Operating conditions: vacuum close to 10^{-6} Torr, accelerating voltage 15 kV, probe current 1.5 nA, spectra collection time 60 s. Samples were coated with carbon, using an Edwards vacuum evaporator. Elemental analysis was carried out by Galbraith Laboratories, Inc.

4.2. Preparation of salts 1

A dried two bulbed (50 ml) vessel equipped with Teflon in glass with Rotoflo valves (HP 6K), was charged with the Li[Al(OC(CF₃)₃)₄] (0.8 g, 0.8 mmol) and $[Bi_5][AsF_6]_3 \cdot SO_2$ (2.7 g, 1.6 mmol). SO₂ (15 ml) was condensed onto the mixture of reagents at -196 °C. The resulting mixture was rigorously stirred at r.t. for 5 days. A dark brown solution was filtered from 2.6 g of yellow insoluble solid and SO₂ was removed under dynamic vacuum to give a brown solid. Yield: 0.9 g, 70% based on the Eq. (1). The relative amount of Li[A $l(OC(CF_3)_3)_4$ in the reaction product was established as 10% by measuring the intensity of the ⁷Li NMR resonance relative to that in the spectrum of a solution of $Li[Al(OC(CF_3)_3)_4]$ in SO₂ at a known concentration. 1 could be a mixture of individual compounds. Result of elemental analysis could be interpreted based on the model 90% of [Bi₅(SO₂)₃][Al(OC(CF₃)₃)₄]₃ and 10% of $Li[Al(OC(CF_3)_3)_4]$ or alternatively $[Bi_{4,33}][Al(OC (CF_3)_3)_4]_3$ and 10% of Li[Al(OC(CF_3)_3)_4]: Calc. C, 14.49; Bi, 22.73; F, 51.65. Found: C, 14.24; Bi, 21.41; F, 51.73%. EI-MS (30 eV, heating r.t. -170 °C): m/z(%) = 706 (1) [An⁺-C₃F₁₁O], 691 (1) [An⁺-C(CF₃)₃-3F], 504 (30) $[An^+-C(CF_3)_3-3CF_3-2F]$, 489 (10) $[An^+-L-C_3F_{10}O], 371 (2) [An^+-2L-CF_3-3F], 302 (4)$ $[An^+-2L-2CF_3-3F], 287 (12) [An^+-2C(CF_3)_3-3CF_3-2F],$ 64 (25) $[SO_2^+]$, An = $[Al(OC(CF_3)_3)_4]$, L = OC(CF_3)_3, non-volatile solid residue left, calculated theoretical isotopes distribution matched that experimentally observed for all peaks. ²⁷Al NMR (104.2 MHz, SO₂, r.t.), δ_{A1} (ppm) = 32.5 (s, [Al(OC-(CF_3)_3)_4]^-). ¹⁹F NMR $(376.3 \text{ MHz}, \text{ SO}_2, \text{ r.t.}), \delta_{\text{F}} \text{ (ppm)} = -72.4; -74.1 \text{ decom-}$ position products of $[Al(OC(CF_3)_3)_4]^-$, -74.9 (s, [Al-(OC(CF₃)₃)₄]⁻); IR (KBr, cm⁻¹, Nujol): 1377 (s), 1364 (m), 1355 (s), 1299 (s), 1273 (s), 1247 (s), 1215 (s), 1173 (s), 1120 (m), 972 (vs), 892 (w), 864 (w), 841 (m), 832 (m), 798 (m), 781 (w), 770 (w), 760 (w), 755 (w), 744 (w), 726 (vs), 620 (w), 580 (m), 571 (m), 561 (m), 550 (w), 537 (s), 480 (m), 450 (m), 397 (w).

Note: The metathesis reaction between the poorly SO₂ soluble $[Bi_5][AsF_6]_3$ and 2,3 equivalents of highly soluble Li[Al(OC(CF₃)₃)₄] in SO₂ followed by removal of the insoluble products afforded a mixture of $[Bi_x][Al-(OC(CF_3)_3)_4]$ and Li[Al(OC(CF₃)₃)₄] (IR, ⁷Li NMR, EI-MS), with the Li[Al(OC(CF₃)₃)₄] as the major product.

4.3. Preparation of $[Bi_5(C_6Me_6)_4][Al(OC(CF_3)_3)_4]_3$ (2)

A mixture of Li[Al(OC(CF₃)₃)₄] (1.87 g, 1.9 mmol), [Bi₅][AsF₆]₃ (3.1 g, 1.9 mmol) and C₆Me₆ (0.6 g, 3.8 mmol) in a 100 ml Schlenk flask was stirred in CH₂Cl₂ (40 ml) for 4 h. The dark brown solution was filtered and concentrated to approximately 4 ml and held at -24 °C for 2 days. The dark brown (almost black) crystals that formed were separated by filtration. The next crop of the crystalline dark brown solid was obtained from the supernatant solution by crystallization at -24 °C for 2 days. Yield of [Bi₅(C₆Me₆)₄][Al(OC- $(CF_3)_3)_4]_3$ (1.64 g, 55% based the Li[Al(OC(CF_3)_3)_4]). C₉₆H₇₂F₁₀₈O₁₂Al₃Bi₅: Calc. C, 25.07; H, 1.56; F, 44.66; Al, 1.76; Bi, 22.74. Found: C, 24.84; H, 2.01; F, 43.80; Al, 1.26; Bi, 23.91%. 184-186 °C decomposition. EI-MS (30 eV, heating r.t. -170 °C): m/z (%) = 197 (5) $[L^+ - 2F]$, 167 (17) $[L^+ - CF_3]$, 162 (100) $[C_6Me_6^+]$, 147 (12) $[L^+ - CF_4]$, 97 (15) $[L^+ - C_2F_3O]$, L =OC(CF₃)₃. A non-volatile solid residue remained. ²⁷Al NMR (104.2 MHz, SO₂, r.t.); δ_{A1} (ppm) = 31.6. ¹⁹F NMR (376.3 MHz, SO₂, r.t.), δ_F (ppm) = -75.9 (s); ¹³C NMR (100.6 MHz, SO₂, r.t.), $\delta_{\rm C}$ (ppm) = 16.5 (C_6Me_6) , 121.7 (q, $C(CF_3)_3$, J = 291 Hz), 134.3 (C_6Me_6) ; ¹H NMR (400 MHz, SO₂, r.t.), δ_H (ppm) = 5.2 (s), 4.7 (s), 3.3 (s), 3.1(s), 2.8 (s), 2.6 (s, C₆Me₆ in complex, major signal, relative intensity 85%), 2.5 (s), 2.1 (s), 2.0 (s). The 5.2–2.7 and 2.1–2.0 ppm minor resonances are assigned to the products of oxidation of C₆Me₆, see Supplemental materials, relative intensity is measured relative to all resonances in spectrum; IR of 2 (KBr, cm⁻¹, Nujol): 1301 (vs), 1276 (vs), 1241 (vs), 1216 (vs), 1165 (s), 1135 (m), 1074 (w, C₆Me₆, Table 5), 1062 (w, C₆Me₆), 1018 (vw, C₆Me₆), 973 (vs), 832 (m, Al-O), 793 (w, C₆Me₆), 755 (w), 728 (vs), 571 (w), 561 (m), 537 (m), 447 (m).

Note: keeping the supernatant solution longer than 5 days at -24 °C lead to formation of yellow crystals **3**, **4** and a grey powder Bi (X-ray elemental micro-analysis).

4.4. Isolation of $[Bi_4OF_2Cl_6(C_6Me_6)_4]$ - $[Al(OC(CF_3)_3)_4]_2 \cdot C_6Me_6 \ \mathbf{3} \cdot C_6Me_6$: and $[C_6Me_6H][Al(OC(CF_3)_3)_4] \ (\mathbf{4})$

A mixture of Li[Al(OC(CF₃)₃)₄] (1.5 g, 1.5 mmol), $[Bi_5][AsF_6]_3$ (0.86 g, 0.5 mmol) and C_6Me_6 (0.4 g, 2.5 mmol) in CH₂Cl₂ (40 ml) was stirred for 4 h in a 100 ml Schlenk flask. The dark brown solution was filtered and concentrated to approximately 10 ml and left at -24 °C for 2 weeks. Yellow crystals, a red-brown solid and a grey powder (Bi, X-ray elemental microanalysis) deposited. The solution was filtered and concentrated to 2-3 ml and held at -24 °C for 3 weeks. Orange crystals (yellow as a powder) formed and were separated manually (0.45 g) from the reaction products. The resulting crystals were a mixture of $3 \cdot C_6 Me_6$, 4 $(yellow)^3$ and colourless crystals,⁴ the presence of the $[C_6Me_6H]^+$ cation was confirmed by IR. Result of elemental analysis was interpreted based on the model 75% of 3 · C₆Me₆ and 25% of 4: Calc. C, 28.93; H, 2.17; F, 42.88. Found: C, 30.31; H, 2.16; F, 42.89%.

Compound $[Bi_4OF_2Cl_6(C_6Me_6)_4][Al(OC(CF_3)_3)_4]_2$. $C_6Me_6 \mathbf{3} \cdot C_6Me_6$: EI-MS (30 eV, heating r.t. -170 °C): m/z (%) = 679 (4) [An⁺-C(CF₃)₃-CF₃], 477 (20) [An⁺-L-C(CF₃)₃-2F], 461 (10) [An⁺-2L-2F], 447 (2), [An⁺- $2C(CF_3)_3-C_2F_4$], 443 (10) [An⁺-L-C(CF_3)_3-CF_3], 162 (100) $[C_6Me_6^+]$, non-volatile black solid residue remained; ¹⁹F NMR (376.3 MHz, CDCl₃, r.t.), δ_F (ppm) = -74.1 (s), -75.3 (s); ¹H NMR (400 MHz, $CDCl_3$, r.t.), δ_H (ppm) = 3.8 (s), 2.3 (s). The compound was very poorly soluble in CDCl₃, initially dissolved in SO₂ followed by the deposition of a solid over 10-30 min. NMR spectra were measured for the freshly prepared clear SO₂ solution at low temperature. ¹⁹F NMR $(376.3 \text{ MHz}, \text{SO}_2, -70 \text{ °C}), \delta_F \text{(ppm)} = -73.9 \text{ (s)}, -75.0 \text{ cm}$ (s), -75.5 (s), -195.1 (s, Al–F), -220.6 (s, Bi–F); ¹H NMR (400 MHz, SO₂, -70 °C), δ_{H} (ppm) = 7.4 ($\Delta \omega_{1/2}$ 91 Hz), 4.9 ($\Delta \omega_{1/2}$ 13 Hz, 2H, C₆Me₅H₂OC(CF₃)₃), 4.56 (s, $\Delta \omega_{1/2}$ 1.3 Hz, 2H, (C₆Me₆)₂CH₂), 3.20 ($\Delta \omega_{1/2}$ 3 Hz, weak), 3.13 ($\Delta \omega_{1/2}$ 3 Hz, 3H, C₆Me₅- $CH_2OC(CF_3)_3$, 3.05 ($\Delta \omega_{1/2}$ 3 Hz, 3H, ($C_6Me_6)_2CH_2$), 2.95 ($\Delta \omega_{1/2}$ 3 Hz, 6H, C₆*Me*₅CH₂OC(CF₃)₃), 2.86 $(\Delta \omega_{1/2} \ 3 \ \text{Hz}, \ 6\text{H}, \ (\text{C}_6 M e_6)_2 \text{CH}_2), \ 2.64 \ (\Delta \omega_{1/2} \ 3 \ \text{Hz}, \ 6\text{H}, \ 6\text{H})$ $C_6Me_5CH_2OC(CF_3)_3$), 2.58 ($\Delta\omega_{1/2}$ 3 Hz, 6H, (C_6Me_6)₂-CH₂), 2.40 ($\Delta \omega_{1/2}$ 9 Hz), 1.85 ($\Delta \omega_{1/2}$ 3 Hz, weak), 1.76 $(\Delta \omega_{1/2} \text{ 3 Hz C}_6 \text{Me}_6 \text{ or } [\text{C}_6 \text{Me}_6 \text{H}]^+), 0.47-0.35 \text{ (aliphatic$ protons). ²⁷Al NMR (104.2 MHz, CH₂Cl₂, r.t.); δ_{A1} (ppm) = 31.6 (s). IR (KBr, cm⁻¹, Nujol): 1593 (w), 1300 (vs), 1277 (vs), 1251 (vs), 1240 (vs), 1218 (vs), 1165 (s), 1102 (w, C₆Me₆), 1069 (w, C₆Me₆), 1022 (w, C₆Me₆), 973 (vs), 831 (m), 780 (sh, C₆Me₆), 728 (w), 623 (w, Al-F*), 610 (w, Al-F*), 569 (w), 560 (m), 537 (m), 447 (m), * impurity of aluminium fluoride complexes resulted by degradation of $[Al(OC(CF_3)_3)_4]^-$.

Compound $[C_6Me_6H][Al(OC(CF_3)_3)_4]$ (4): EI-MS (30 eV, heating r.t. -170 °C): m/z (%) = 850 (5) $[An^+-C_2F_4O], 675 (8) [An^+-L-3F], 536 (1) [An^+-L 2CF_{3}-3F$], 478 (10) [An⁺-2L-F], 477 (20) [An⁺-L- $C(CF_3)_3-2F]$, 461 (10) [An⁺-2L-2F], 447 (2), $[An^+-2C(CF_3)_3-C_2F_4], 445 (10) [An^+-L-C(CF_3)_3-C_2F_4]$ CF_3], 443 (10) [An⁺-L-C(CF_3)_3-CF_3], 441 (10) $[An^+-2L-3F]$, 162 (100) $[C_6Me_6^+]$; NMR spectra of 4 are similar to that of 3 since the yellow crystals are a mixture of both compounds. IR (KBr, cm^{-1} , Nujol): 3300 (br), 1596 (m, $[C_6Me_6H]^+$), 1301 (vs), 1276 (vs), 1251 (vs), 1240 (vs), 1217 (vs), 1165 (s), 1071 (w, $[C_6Me_6H]^+$), 1061 (w, $[C_6Me_6H]^+$), 973 (vs), 889 (w, $[C_6Me_6H]^+$), 831 (m), 756 (w), 728 (w), 682 (w, $[C_6Me_6H]^+$), 571 (w), 560 (w), 537 (w), 447 (m). Absorption band at 1590 cm^{-1} is one of the characteristic benzoid C=C skeletal stretching modes of the carbocations [48].

4.5. Crystal growth and X-ray crystallography

Crystals of $3 \cdot C_6Me_6$ were grown from a saturated supernatant solution in CH₂Cl₂ at -24 °C. Single crys-

tals were coated with Paratone-N oil, mounted using a glass fibre and frozen in the cold nitrogen stream of the goniometer. A hemisphere of data was collected on a Bruker AXS P4/SMART 1000 diffractometer using ω and θ scans with a scan width of 0.3° and 30 s exposure times. The detector distance was 5 cm. The data were reduced (SAINT) [49] and corrected for absorption (SADABS) [50]. The structure was solved by direct methods and refined by full-matrix least squares on F^2 (SHEL-XTL) [51] (Table 4). The compound was a racemic mixture. Anisotropic refinement was employed for all Bi, Cl and Al atoms and F2–F3, O1–O9 and C1–C8. All other atoms were refined isotropically. Hydrogen atoms were included in calculated positions and refined using a riding model. Hexamethylbenzene molecules were restraint to equal distances within the ring and between the methyl groups. CF₃ groups were refined as regular tetrahedra with fixed bond distances of 1.32 Å. The isotropic thermal parameter for C72 was fixed. Refinement was non-convergent and anisotropic refinement lead to many non-positive definites.

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Appendix A. Supplementary data

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Center as Supplementary Publication No. CCDC 250743. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.ukor http:// www.ccdc.cam.ac.uk). X-ray microanalysis of reaction products, NMR Reactions in situ and NMR investigation of oxidation of C₆Me₆, IR spectrum of Li[Al(OC(CF₃)₃)₄] 350–4000 cm⁻¹, UV–Vis spectra 300–800 and 400– 1100 cm⁻¹, structure $3 \cdot C_6Me_6$, details of discussion. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2005.06.032.

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