Electronic Supporting Information

Triaza-Macrocyclic Complexes of Aluminium, Gallium and Indium Halides: Fast ^{18}F and ^{19}F Incorporation *via* Halide Exchange under Mild Conditions in Aqueous Solution

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Preparations

[$AlBr_3$(Me_3-tacn)]: $AlBr_3$ (0.133 g, 0.50 mmol) was added to a solution of Me_3-tacn (0.086 g, 0.50 mmol) in CH_2Cl_2 (5 mL) at room temperature with stirring which leads a formation of precipitate. After 30 mins. the solvent was removed by filtration. The white precipitate was washed with small amount of CH_2Cl_2 solvent and dried *in vacuo*. Yield: 0.16 g, 74%. Required for $C_9H_{21}A1Br_3N_3$: C, 24.7; H, 4.8; N, 9.6. Found: C, 24.6; H, 5.3; N, 8.9. ^{1}H NMR (CD_2Cl_2, 297 K): δ 3.43 (m, [6H], CH_2), 2.98 (m, [9H], CH_3), 2.73 (m, [6H], CH_2). IR (Nujol, ν/cm^{-1}): 324 (Al–Br).

[$AlBr_3$($BzMe_2$-tacn)]: Method as for [$AlBr_3$(Me_3-tacn)] but using $AlBr_3$ (0.133 g, 0.50 mmol) and $BzMe_2$-tacn (0.13 g, 0.50 mmol). White solid. Yield: 0.19 g, 74%. ^{1}H NMR (CD_2Cl_2, 298 K): δ 7.31 (m, [5H], ArH), 4.75 (m, [2H], Ar-CH_2), 3.72 (m, [2H], tacn-CH_2), 3.46 (m, [4H], tacn-CH_2), 3.04 (m, [6H], CH_3), 2.70 (m, [4H], tacn-CH_2), 2.33 (m, [2H], tacn-CH_2). IR (Nujol, ν/cm^{-1}): 343, 325 sh (Al–Br).

[$GaBr_3$(Me_3-tacn)]: Method as for [$GaCl_3$(Me_3-tacn)] but using Me_3-tacn (0.086 g, 0.50 mmol) and $GaBr_3$ (0.150 g, 0.50 mmol). White solid. Yield: 0.106 g, 45%. Required for $C_9H_{21}Br_3GaN_3$: C, 22.5; H, 4.4; N, 8.7. Found C, 22.4; H, 4.6; N, 8.6%. ^{1}H NMR (CD_2Cl_2, 298 K): δ 3.3 (br m, [6H], CH_2), 2.9 (br s, [9H], Me), 2.7 (br m, [6H], CH_2).

[$InBr_3$(Me_3-tacn)]: Method as for [$GaCl_3$(Me_3-tacn)], but using Me_3-tacn (0.087 g, 0.50 mmol) and $InBr_3$ (0.177 g, 0.50 mmol). White solid. Yield: 0.162 g, 61%. Required for $C_9H_{21}Br_3InN_3$: C, 20.5; H, 4.0; N, 8.0. Found C, 19.8; H, 4.0; N, 7.4%. ^{1}H NMR (CD_2Cl_2, 298 K): δ 3.18 (br m, [6H], CH_2), 2.78 (br s, [9H], Me), 2.67 (br m, [6H], CH_2).

$[NMe_4]_3[Al_2F_9]$: $AlF_3 \cdot 3H_2O$ (0.250 g, 1.8 mmol) was suspended in 10 mL freshly distilled water. A solution of $[NMe_4]F$ (0.167 g, 1.8 mmol) in 3 mL water was added and the resulting mixture refluxed for 15 hours. The solution was cooled to room temperature and the white solid was isolated by filtration and dried under high vacuum for six hours. Yield 0.220 g, 70%. IR (Nujol, ν/ cm^{-1}): 674 (br), 358 (s) (Al–F). ^{1}H NMR (CD_3CN, 298 K): δ 3.07 (s [12H] CH_3) ppm. ^{19}F NMR (CD_3CN, 298 K): δ –150.0 (m F^-), –194.1 (m, $[AlF_4]^-$) ppm. ^{27}Al NMR (CD_3CN, 298 K): 48.8 (quintet, $[AlF_4]^-$) ppm. Washing with MeCN, followed by slow evaporation of the filtrate yielded colourless crystals suitable for X-ray diffraction.

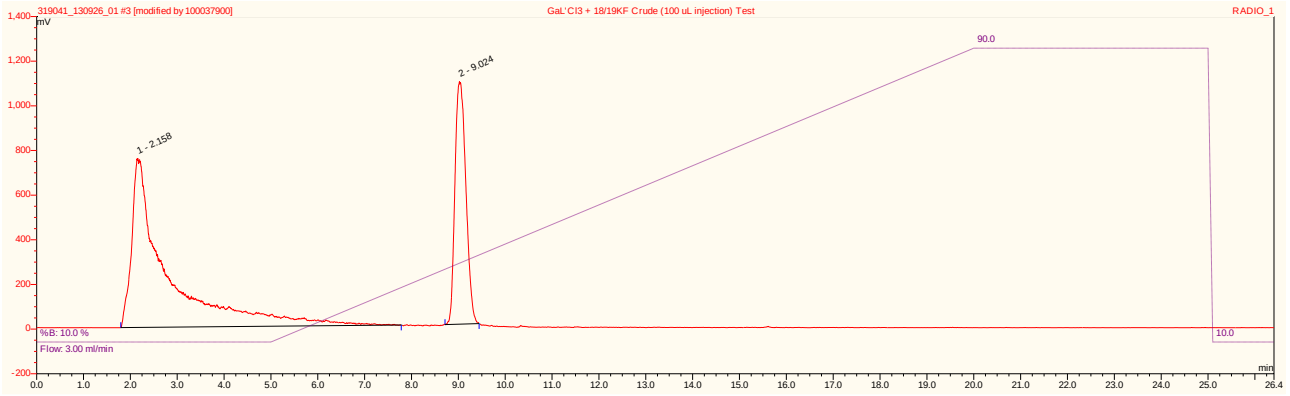

Figure S1: Preparative HPLC radio trace of the crude reaction mixture for the labelling of [$GaCl_3$($BzMe_2$-tacn)] with $^{18}F/K^{19}F$. Peak 1: R_t 2.1 mins. ($^{18}F^-$). Peak 2: Rt 9.0 mins. ([$Ga^{18}F^{19}F_2$($BzMe_2$-tacn)]).

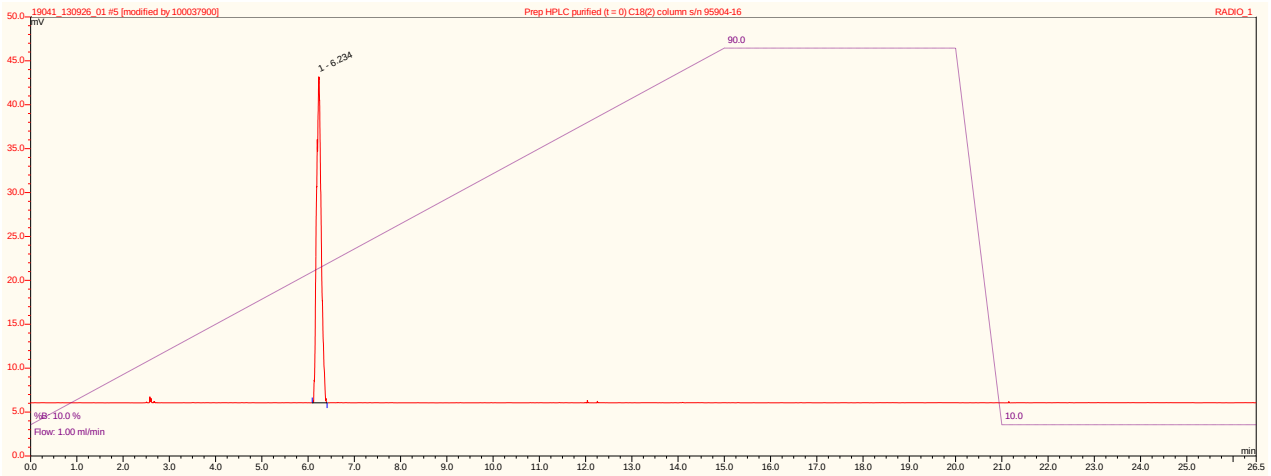

Figure S2: Analytical HPLC radio trace of [$Ga^{18}F^{19}F_2$($BzMe_2$-tacn)] formulated in PBS:EtOH (90:10) at t = 0. Peak: Rt 6.2 mins. RCP = 99.6%.

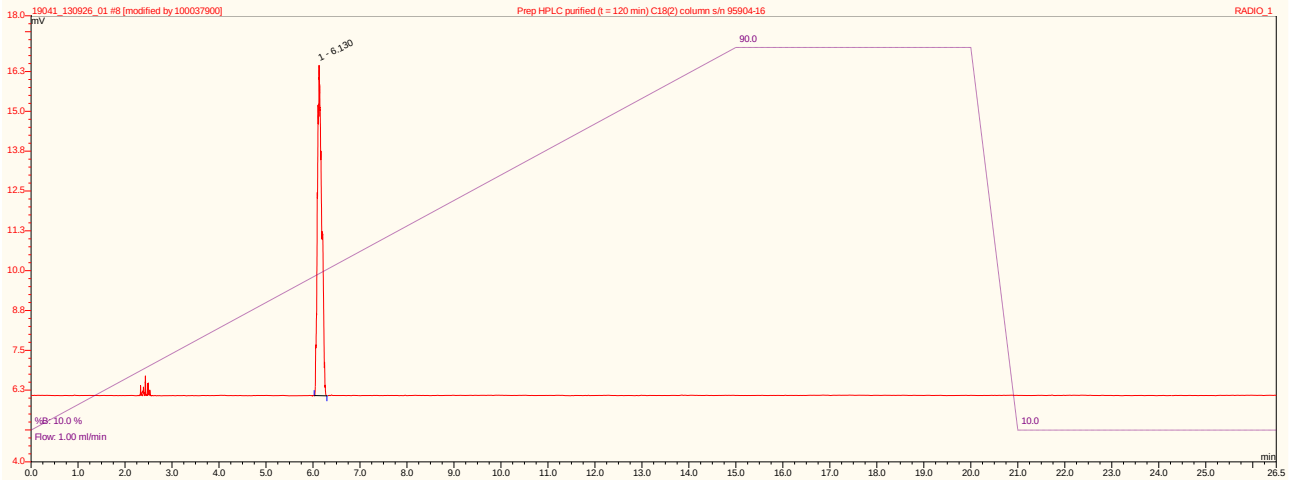

Figure S3: Analytical HPLC radio trace of [$Ga^{18}F^{19}F_2$($BzMe_2$-tacn)] formulated in PBS:EtOH (90:10) at t = 120 min. Peak: Rt 6.1 mins. RCP = 98.8%.

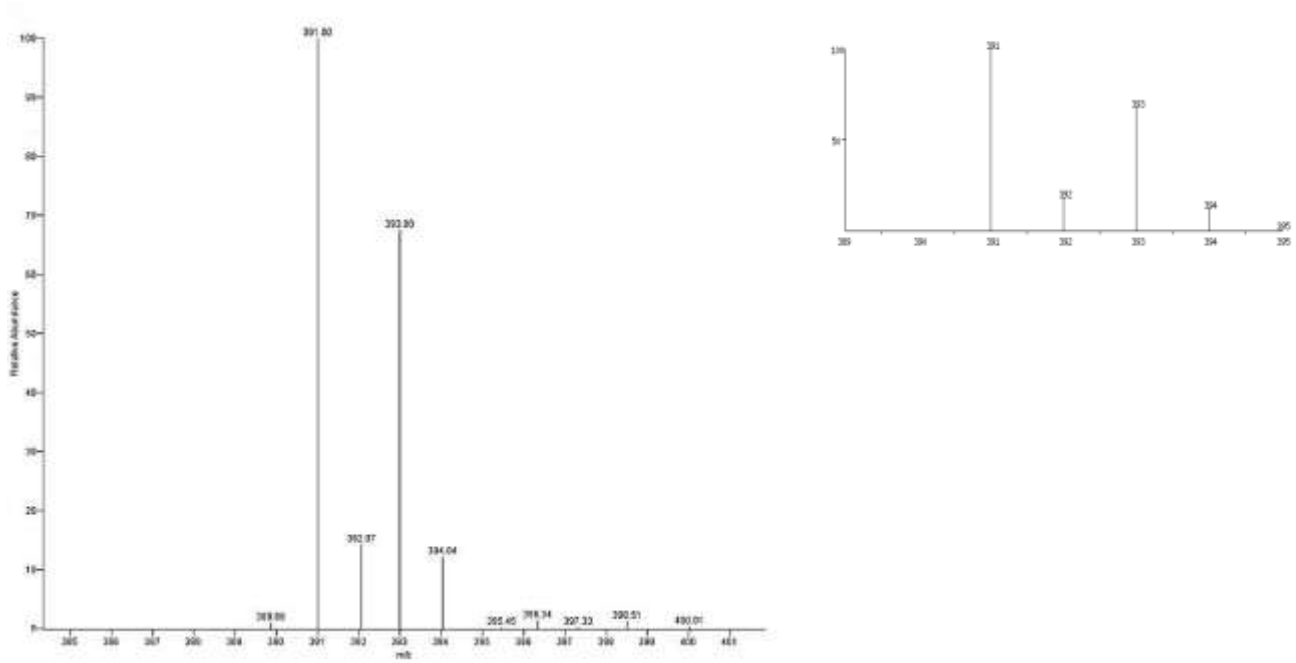

Figure S4: ESI$^+$ mass spectrum of $[GaF_3(BzMe_2\text{-tacn})]+NH_4]^+$ taken from radiolabelling reaction (left) and the predicted isotope pattern for $[GaF_3(BzMe_2\text{-tacn})]+NH_4]^+$ (right).

Table S1 Crystal data and structure refinement details[a]

Compound	$[AlF_3(Me_3\text{-tacn})]\cdot 4H_2O$	$[GaF_3(Me_3\text{-tacn})]\cdot 4H_2O$	$[InF_3(Me_3\text{-tacn})]\cdot 4H_2O$	$[InF_3(BzMe_2\text{-tacn})]\cdot 1.2H_2O$	$[AlCl_3(Me_3\text{-tacn})]$	$[GaCl_3(Me_3\text{-tacn})]$
Formula	$C_9H_{29}AlF_3N_3O_4$	$C_9H_{29}F_3GaN_3O_4$	$C_9H_{29}F_3InN_3O_4$	$C_{15}H_{27}F_3InN_3O_{1.20}$	$C_9H_{21}AlCl_3N_3$	$C_9H_{21}Cl_3GaN_3$
M	327.33	370.07	415.17	440.42	304.62	347.36
crystal syst	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	Pbca (no. 61)	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)
A [Å]	8.8131(15)	13.420(4)	6.8679(10)	6.7721(10)	12.128(5)	12.173(3)
B [Å]	13.356(2)	8.871(2)	20.187(4)	13.666(3)	7.185(2)	7.2253(10)
C [Å]	26.551(5)	13.542(3)	12.014(2)	18.998(3)	15.695(6)	15.696(6)
α [deg]	90	90	90	90	90	90
β [deg]	90	97.816(15)	99.482(10)	96.106(10)	90.07(5)	90.239(6)
Γ [deg]	90	90	90	90	90	90
U [Å^3]	3125.3(10)	1597.3(7)	1642.8(5)	1748.2(5)	1367.7(8)	1380.5(6)
Z	8	4	4	4	4	4
μ(Mo Kα) [mm^{-1}]	0.178	1.769	1.484	1.389	0.713	2.552
total reflns	8255	12911	19404	23249	8994	6378
unique reflns	3570	3645	3750	4005	3059	3150
R_{int}	0.051	0.049	0.028	0.028	0.053	0.022
No. of params, restraints	209, 8	216, 85	209, 0	226, 0	149, 0	148, 0
R_1[b] [$I_o > 2\sigma(I_o)$]	0.079	0.058	0.0219	0.022	0.058	0.021
R_1 [all data]	0.124	0.076	0.0254	0.025	0.078	0.024
wR_2[b] [$I_o > 2\sigma(I_o)$]	0.168	0.124	0.044	0.046	0.107	0.052
wR_2 [all data]	0.196	0.133	0.046	0.048	0.119	0.053

[a] Common items: temperature = 120 K; wavelength (Mo–Kα) = 0.71073 Å; θ(max) = 27.5°; [b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$.

Table S1 continued

Compound	$[InBr_3(Me_3\text{-tacn})]\cdot CH_2Cl_2$	$[InCl_3(BzMe_2\text{-tacn})]$	$[\{(Me_3\text{-tacn})Ga\}_2(\mu\text{-}OH)_3]Br_3 \cdot 3CH_2Cl_2$	$[NMe_4]_3[Al_2F_9]$
Formula	$C_{10}H_{23}Br_3Cl_2InN_3$	$C_{15}H_{25}Cl_3InN_3$	$C_{21}H_{51}Br_3Cl_6Ga_2N_6O_3$	$C_{12}H_{36}Al_2F_9N_3$
M	610.76	468.55	1027.55	447.40
crystal syst	Monoclinic	Monoclinic	Hexagonal	Hexagonal
Space group	C2/c (no. 15)	$P2_1/c$ (no. 14)	$P6_3/m$ (no. 176)	$P6_3/m$ (no. 176)
a [Å]	16.276(3)	7.2893(15)	12.979(2)	7.997(5)
b [Å]	16.175(3)	15.026(4)	12.979(2)	7.997(5)
c [Å]	14.815(2)	18.528(4)	13.565(4	18.178(7)
α [deg]	90	90	90	90
β [deg]	105.595(2)	100.924(15)	90	90
γ [deg]	90	90	120	120
U [Å^3]	3756.9(11)	1992.5(8)	1978.9(7)	1006.8(10)
Z	8	4	2	2
μ(Mo Kα) [mm^{-1}]	7.916	1.588	4.826	0.227
total no. reflns	21458	19924	15378	4622
unique reflns	4306	4522	1356	799
R_{int}	0.078	0.057	0.074	0.064
no. of params, restraints	176, 0	201, 0	72, 0	49, 0
$R_1{}^b$ [$I_o > 2\sigma(I_o)$]	0.045	0.053	0.044	0.043
R_1 [all data]	0.071	0.0758	0.054	0.063
$wR_2{}^b$ [$I_o > 2\sigma(I_o)$]	0.080	0.096	0.091	0.098
wR_2 [all data]	0.088	0.107	0.097	0.107

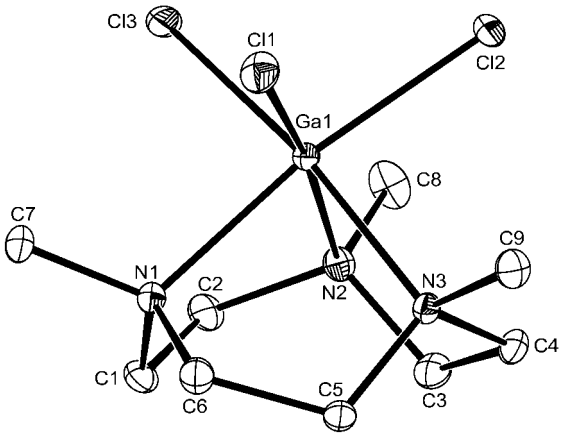

Figure S5 Structure of [$GaCl_3$(Me_3-tacn)] showing the atom labelling scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ga1–N3 = 2.1644(13), Ga1–N1 = 2.1755(13), Ga1–N2 = 2.1960(14), Ga1–Cl2 = 2.3087(5), Ga1–Cl1 = 2.3177(9), Ga1–Cl3 = 2.3217(5), N3–Ga1–N1 = 81.90(5), N3–Ga1–N2 = 80.80(5), N1–Ga1–N2 = 80.83(5), Cl2–Ga1–Cl1 = 94.38(2), Cl2–Ga1–Cl3 = 93.98(2), Cl1–Ga1–Cl3 = 94.49(2).

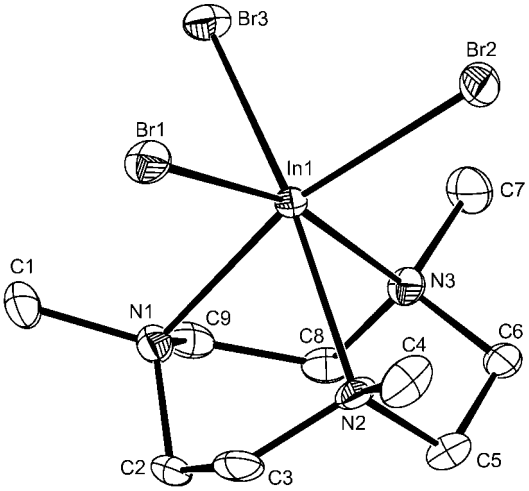

Figure S6 Structure of [$InBr_3$(Me_3-tacn)] showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): In1–N3 = 2.344(4), In1–N1 = 2.345(5), In1–N2 = 2.347(4), In1–Br2 = 2.5987(8), In1–Br3 = 2.6006(8), In1–Br1 = 2.6046(8), N3–In1–N1 = 76.4(2), N3–In1–N2 = 76.8(2), N1–In1–N2 = 76.2(2), Br2–In1–Br3 = 96.66(3), Br2–In1–Br1 = 95.06(2), Br3–In1–Br1 = 96.15(3).

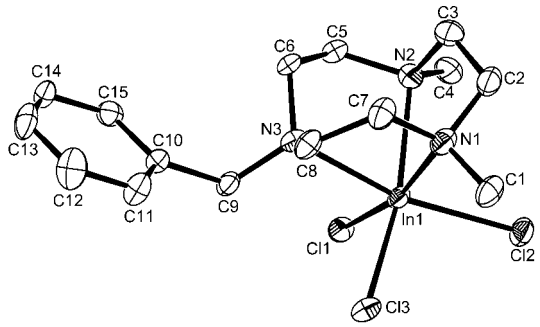

Figure S7 Structure of $[InCl_3(BzMe_2\text{-tacn})]$ with atom numbering scheme. Ellipsoids are shown at the 50% probability level and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): In1–N1 = 2.312(4), In1–N2 = 2.342(4), In1–N3 = 2.371(4), In1–Cl1 = 2.4443(13), In1–Cl2 = 2.4518(14), In1–Cl3 = 2.4581(14), N1–In1–N2 = 77.1(2), N1–In1–N3 = 77.4(2), N2–In1–N3 = 76.3(2), Cl1–In1–Cl2 = 95.32(5), Cl1–In1–Cl3 = 96.26(5), Cl2–In1–Cl3 = 98.31(5).

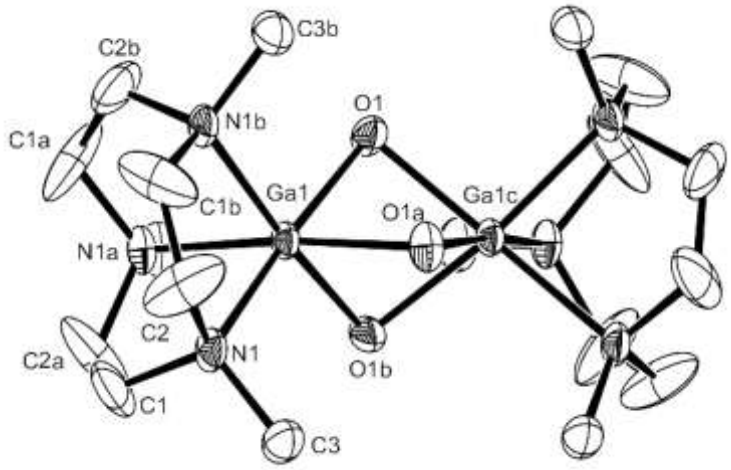

Figure S8 View of the structure of the cation in $[\{(Me_3\text{-tacn})Ga\}(\mu\text{-}OH)_3]Br_3\cdot 3CH_2Cl_2$. Ellipsoids are drawn at the 40% probability level and H atoms are omitted for clarity. Symmetry operations: a = 1–y, x–y, z ; b = 1–x+y, 1–x, z ; c = x, y, 1/2–z. The cation has C_{3h} (–6) symmetry. Selected bond lengths (Å) and angles (°): Ga1–O1 = 1.955(4), Ga1–N1 = 2.078(4), Ga1···Ga1c = 2.668(2), O1–Ga1–O1a = 78.6(2), N1–Ga1–N1a = 84.7(2), Ga1–O1–Ga1a = 86.0(2).

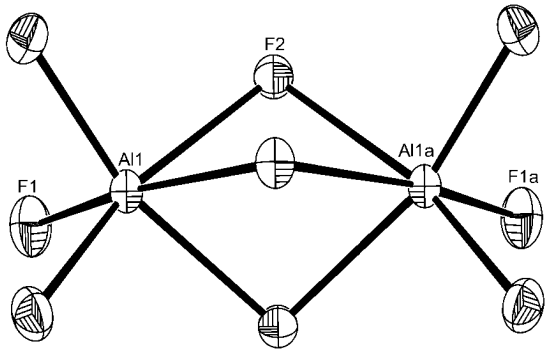

Figure 9 View of the anion in $[NMe_4]_3[Al_2F_9]$ with atoms numbering scheme. Atoms are shown at the 50% probability level. The anion has D_{3h} (-6m2) crystallographic symmetry. Symmetry operation: a = x, y, 3/2 – z. Selected bond lengths (Å) and angles (°): Al1–F1 = 1.7389(14), Al1–F2 = 1.9136(14), F1–Al1–F1a = 96.94(6), F1–Al1–F2 = 91.89(6), F1–Al1–F2a = 165.19(6), F2–Al1–F2a = 75.63(7), Al1–F2–Al1 = 89.86(8).

Crystal structure determination of $[Me_4N]_3[Al_2F_9]$: The crystal system is hexagonal with the likely Laue group 6/m. Possible space groups from the absences are $P6_3/m$ (no. 176) and $P6_3$ (no.173). Structure solution in space group $P6_3/m$ reveals a discrete $[Al_2F_9]^-$ anion (D_{3h} point group), with two overlapping $[Me_4N]^+$ cations (like two face-sharing tetrahedra – the common face positioned on a mirror planes), which refined well to a final R1 = 0.043. Structure solution was also attempted in space group $P6_3$ to establish whether this might remove the overlapping cations. However, while the individual moieties were evident in the difference map, the pseudo mirror plane was very clear in the anion and two of the Me4N cations, and the third cation (N2) did not show the overlapping problem. Refinement was less satisfactory and the final R1 = 0.052. The Flack parameter was 1.1 with a very large esd. Attempts to get the absolute structure (BASF/TWIN) failed (the L.S. blew-up). Hence, while chemically the same structure was evident in both space groups, the solution in $P6_3/m$ (176) was preferred.