

Supplementary information

for

[GaF₃(BzMe₂-tacn)] – a neutral ‘metalloligand’ towards alkali metal and ammonium cations in water

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Experimental Procedures

The [GaF₃(BzMe₂-tacn)] and [GaF₃(Me₃-tacn)] were prepared as hydrates by the reported method.¹ Alkali metal and ammonium salts were used as supplied. Freshly distilled water and chromatography grade MeCN (undistilled) were used in all reactions. ESI mass spectrometry was recorded using a Waters (Manchester, UK) ZMD mass spectrometer equipped with a single quadrupole analyser. Samples were introduced to the mass spectrometer via flow injection using a Waters 600 pump (flow rate 0.1 mL / min MeCN) and Waters 2700 autosampler. ¹H, ¹⁹F{¹H} and ⁷¹Ga NMR spectra were recorded in D₂O solutions at 293 K using a Bruker DPX-400 or AV-400 spectrometer and are referenced to the residual solvent protons (¹H), CCl₃F (¹⁹F) and [Ga(H₂O)₆]³⁺ in HNO₃/D₂O (pH = 1). *In situ* ESI⁺ MS data were obtained using a VG Biotech Platform with [MF₃(BzMe₂-tacn)] or [MF₃(Me₃-tacn)] and the appropriate alkali metal salt or ammonium salt dissolved in water in a 1:1 molar ratio. Microanalyses were undertaken by Stephen Boyer at London Metropolitan University.

[{GaF₃(BzMe₂-tacn)}₂Na₂(BF₄)₂] (1)

[GaF₃(BzMe₂-tacn)]·H₂O (0.010 g, 0.026 mmol) dissolved in 0.5 mL MeCN was added to NaBF₄ (0.003 g, 0.026 mmol) in 0.1 mL H₂O. The solutions were mixed and the reaction solution was left to

evaporate slowly at room temperature, resulting in the formation of large colourless crystals suitable for single crystal X-ray diffraction. Yield: 0.012 g, 92%. Required for $C_{30}H_{50}B_2F_{14}Ga_2N_6Na_2 \cdot 3H_2O$: C: 33.5, H: 5.8, N: 7.8. Found; C: 33.7, H: 4.8, N: 7.7%. IR (Nujol): 3656, 3435 v br (ν O-H), 1640 br (δ OH₂), 1500 w (C-H aromatic), 1073 vs br, 1024 sh (ν BF₄⁻), 536 m (δ BF₄⁻), 520 m, 514 sh (Ga-F) cm⁻¹. ESI⁺ MS (MeCN/H₂O): m/z 396.1 (100%) [GaF₃(BzMe₂-tacn) + Na]⁺, 771.2 (30%) [{GaF₃(BzMe₂-tacn)}₂ + Na]⁺. ¹H and ⁷¹Ga NMR: spectra unchanged from [GaF₃(BzMe₂-tacn)].¹ ¹⁹F{¹H} NMR: δ = -150.58, -150.63 (BF₄⁻), -172.41 (br, [GaF₃(BzMe₂-tacn)]). ²³Na NMR: δ = 0.0 (Na⁺ in water).

[{GaF₃(BzMe₂-tacn)}₂K₂(OH)₄(PF₆)₂·H₂O (2)

Method as above using [GaF₃(BzMe₂-tacn)]·H₂O (0.010 g, 0.026 mmol) and KPF₆ (0.005 g, 0.026 mmol). Colourless crystals. Yield: 0.014 g, 97%. Required for $C_{30}H_{60}F_{18}Ga_2K_2O_5N_6P_2$: C, 29.9; H, 5.0; N, 7.0. Found: C, 30.0; H, 4.9; N, 7.1%. IR (Nujol): 3656, 3435 v br (ν O-H), 1631 br (δ OH₂), 1500 w (C-H aromatic), 845 vs br (ν PF₆⁻), 558 s (δ PF₆⁻), 527 m br (Ga-F) cm⁻¹. ESI⁺ MS (MeCN/H₂O): m/z 412.1 (100%) [GaF₃(BzMe₂-tacn) + K]⁺, 771.2 (20%) [{GaF₃(BzMe₂-tacn)}₂ + K]⁺.

[{GaF₃(BzMe₂-tacn)}₂Na(NH₄)(PF₆)₂] (3)

Method as above using [GaF₃(BzMe₂-tacn)]·H₂O (0.010 g, 0.026 mmol) and NH₄PF₆ (0.002 g, 0.026 mmol). White solid, including a few very small, weakly diffracting needle-like crystals. Yield 0.011 g. ESI⁺ MS (MeCN/H₂O): m/z 391.1 (100%) [GaF₃(BzMe₂-tacn) + NH₄]⁺, 396.1 (18%) [GaF₃(BzMe₂-tacn) + Na]⁺.

Crystals of **1**, **2** and **3** were obtained by slow evaporation of aqueous solutions of [GaF₃(BzMe₂-tacn)] containing 1 mol. equiv. of NaBF₄, KPF₆ or NH₄PF₆ in a glass vial. Details of the crystallographic data collection and refinement are in Table S1. Diffractometer: *Rigaku AFC12* goniometer equipped with an enhanced sensitivity (HG) *Saturn724+* detector mounted at the window of an *FR-E+ SuperBright* molybdenum rotating anode generator ($\lambda_1 = 0.71073$ Å) with VHF *Varimax* optics (70 or 100 μm focus). Cell determination, data collection, data reduction, cell refinement and absorption correction: CrystalClear-SM Expert 2.0 r7.² Structure solution and refinement were carried out using WinGX and software packages within.³ H atoms attached to C atoms were placed in geometrically assigned positions, with C—H distances of 0.95 Å (CH), 0.98 Å (CH₃) or 0.99 Å (CH₂) and refined using a riding model, with $U_{iso}(H) = 1.2U_{eq}(C)$ (CH, CH₂) or $1.5U_{eq}(C)$ (CH₃). For compound **2** the difference map contains peaks that approximately correspond to possible hydrogen positions, however, it was not possible to refine these into a mutually consistent arrangement. The hydrogen atoms for both the

coordinated and isolated water molecules have therefore been omitted from the refined model but are included in the formula and derived parameters. The crystals of $[\{\text{GaF}_3(\text{BzMe}_2\text{-tacn})\}_2\text{Na}(\text{NH}_4)(\text{PF}_6)_2]$ (**3**) were very small and poorly diffracting, leading to very weak diffraction data and no significant reflections beyond 40° (even with increased exposure times). This weak, low resolution data has affected the final quality of the refinement and associated statistics; however, the structure is clearly defined (although detailed comparisons of bond lengths are not justified). The H atoms associated with the NH_4^+ cation were not convincingly located in the difference map, and given the data quality, these were excluded from the refinement, although the $\text{N4}\cdots\text{F}(1)$ 2.728, $\text{N}(4)\cdots\text{F}(2)$ 2.769 Å distances are well within the normal H-bonding range. Thus, while the structure determination for this compound serves to confirm the connectivities, close analysis and comparison of geometric parameters must be treated with caution.

CCDC reference numbers 1008581, 1008581 and 1008583 contain crystallographic data in CIF format.

Table S1 Crystallographic data for the compounds reported in this paper (L = BzMe₂tacn).^a

| Compound | [{GaF₃(L)}₂Na₂(BF₄)₂] (1) | [{GaF₃(L)}₂K₂(OH)₂(PF₆)₂·H₂O] (2) | [{GaF₃(L)}Na(NH₄)(PF₆)₂] (3) |
|--------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|
| Formula | C ₃₀ H ₅₀ B ₂ F ₁₄ Ga ₂ N ₆ Na ₂ | C ₃₀ H ₆₂ F ₁₈ Ga ₂ K ₂ N ₆ O ₆ P ₂ | C ₁₅ H ₂₉ F ₁₅ GaN ₄ NaP ₂ |
| <i>M</i> /g mol ⁻¹ | 967.80 | 1224.43 | 705.07 |
| Crystal system | monoclinic | triclinic | monoclinic |
| Space group (No.) | <i>P</i> 2 ₁ / <i>c</i> (14) | <i>P</i> -1 (2) | <i>C</i> 2/ <i>c</i> (15) |
| <i>a</i> /Å | 10.967(2) | 9.5708(10) | 31.23(2) |
| <i>b</i> /Å | 15.793(3) | 10.2233(10) | 10.037(5) |
| <i>c</i> /Å | 22.313(3) | 13.1728(10) | 18.142(12) |
| <i>α</i> /° | 90 | 95.498(7) | 90 |
| <i>β</i> /° | 90.057(6) | 91.765(7) | 116.85(2) |
| <i>γ</i> /° | 90 | 112.970(8) | 90 |
| <i>U</i> /Å ³ | 3864.8(11) | 1177.96(19) | 5073(6) |
| <i>Z</i> | 4 | 1 | 8 |
| <i>μ</i> (Mo-Kα) /mm ⁻¹ | 1.517 | 1.506 | 1.353 |
| <i>F</i> (000) | 1968 | 624 | 2832 |
| Total reflections | 16094 | 8591 | 19561 |
| Unique reflections | 8511 | 4590 | 4978 |
| <i>R</i> _{int} | 0.049 | 0.053 | 0.232 |
| <i>R</i> ₁ ^b [<i>I</i> _o > 2σ(<i>I</i> _o)] | 0.052 | 0.055 | 0.119 |
| <i>R</i> ₁ (all data) | 0.085 | 0.085 | 0.248 |
| <i>wR</i> ₂ ^b [<i>I</i> _o > 2σ(<i>I</i> _o)] | 0.090 | 0.108 | 0.274 |
| <i>wR</i> ₂ (all data) | 0.098 | 0.122 | 0.360 |

^a Common items: temperature = 100 K; wavelength (Mo-K_α) = 0.71073 Å;

^b $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}$

***In situ* ESI⁺ MS Experiments – [GaF₃(L)] (L = Me₃-tacn or BzMe₂-tacn)**

The complexes [GaF₃(RMe₂-tacn)] (R = Me, Bz) were treated with an equimolar quantity of an appropriate metal / ammonium salt in aqueous MeCN (5:1 MeCN:H₂O). The mixture was shaken and the solution further diluted in MeCN(aq) to provide a sample of suitable concentration for mass spectrometry. Weakly/non-coordinating anions were used.

Samples were studied by positive ion electrospray (ESI⁺) mass spectrometry (neat MeCN mobile phase).

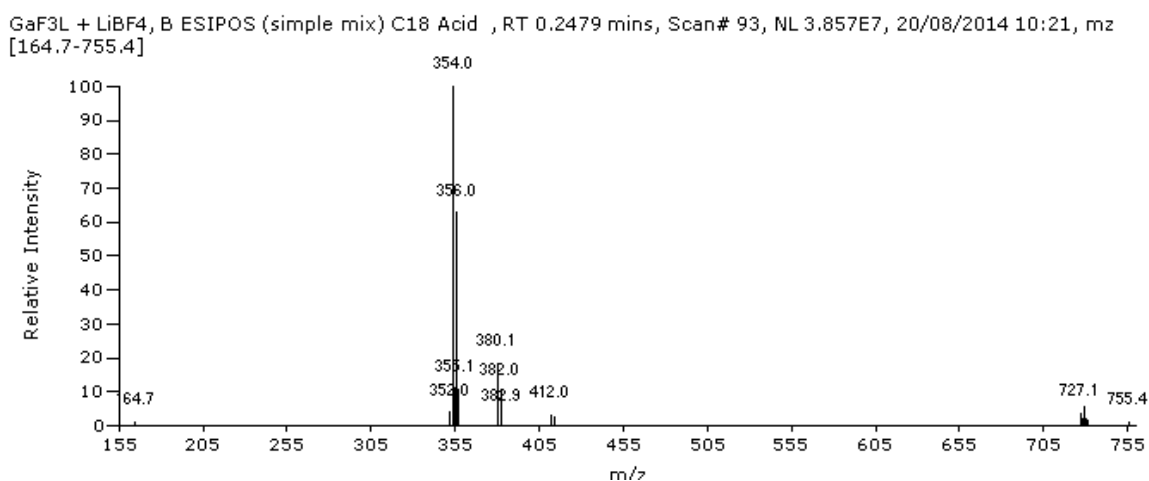


Figure S1a: ESI⁺ Mass spectrum from the reaction of [GaF₃(BzMe₂-tacn)] with LiBF₄ in aqueous MeCN. Found; m/z = 354 (100%) [GaF₂(BzMe₂-tacn)]⁺, 381 (18%) [GaF₃(BzMe₂-tacn) + Li]⁺.

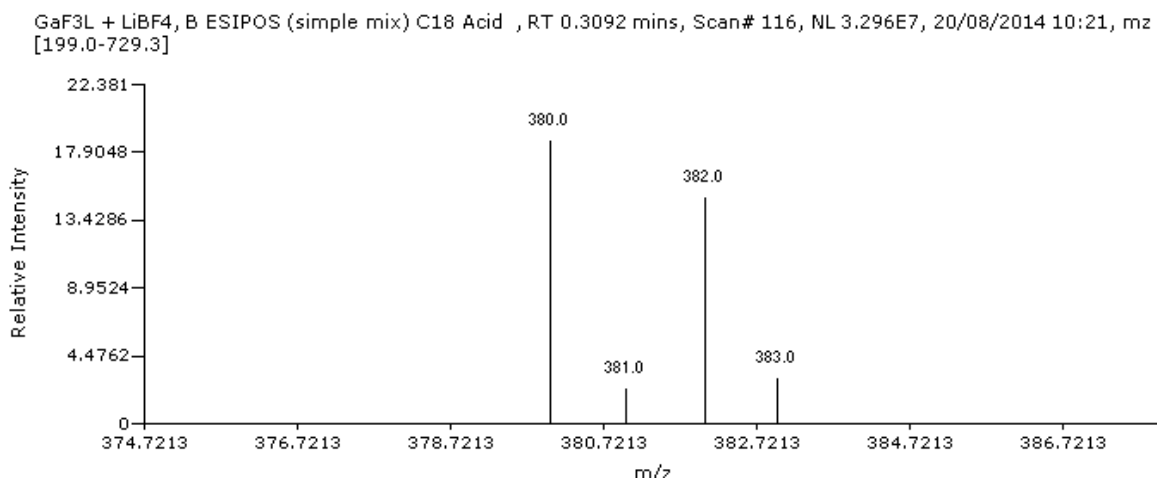


Figure S1b: Expansion of the isotope pattern from the peak at m/z = 380.0, attributed to [GaF₃(BzMe₂-tacn) + Li]⁺.

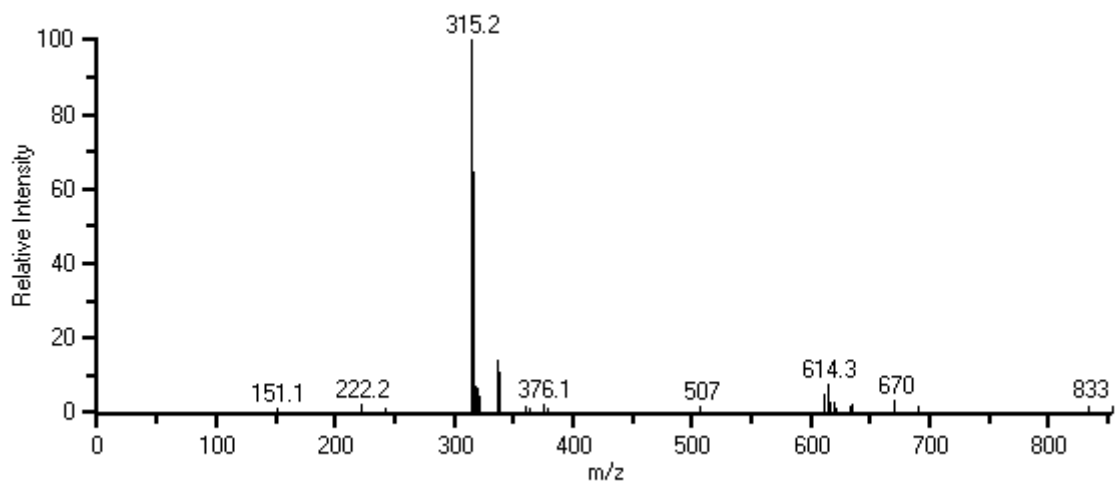


Figure S2a: ESI⁺ mass spectrum of [GaF₃(Me₃-tacn)] + NH₄PF₆; found $m/z = 315.2$ (100%) [GaF₃(Me₃-tacn) + NH₄]⁺; 614.3 (15%) [{GaF₃(Me₃-tacn)}₂ + NH₄]⁺

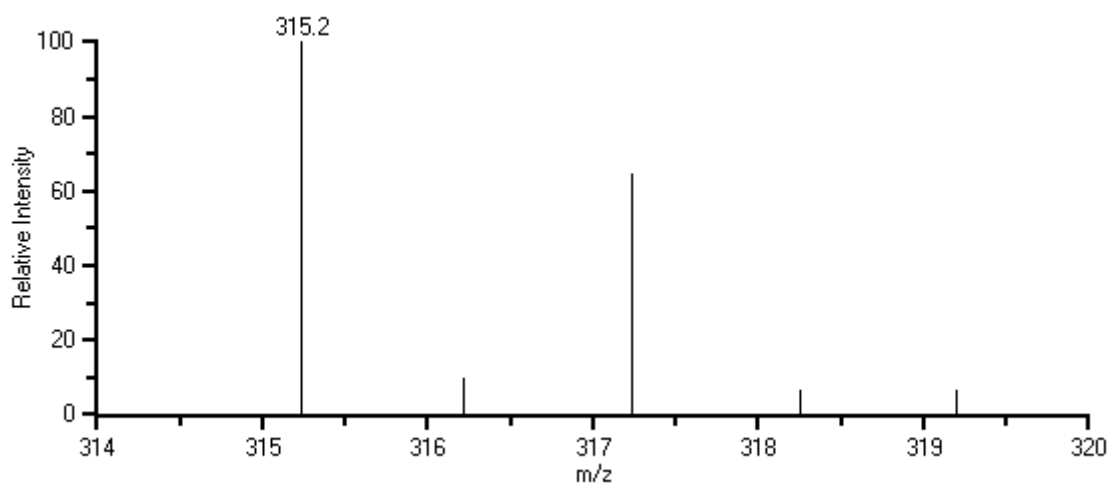


Figure S2b: Expansion of the isotope pattern from the peak at $m/z = 315.2$, attributed to [GaF₃(Me₃-tacn) + NH₄]⁺.

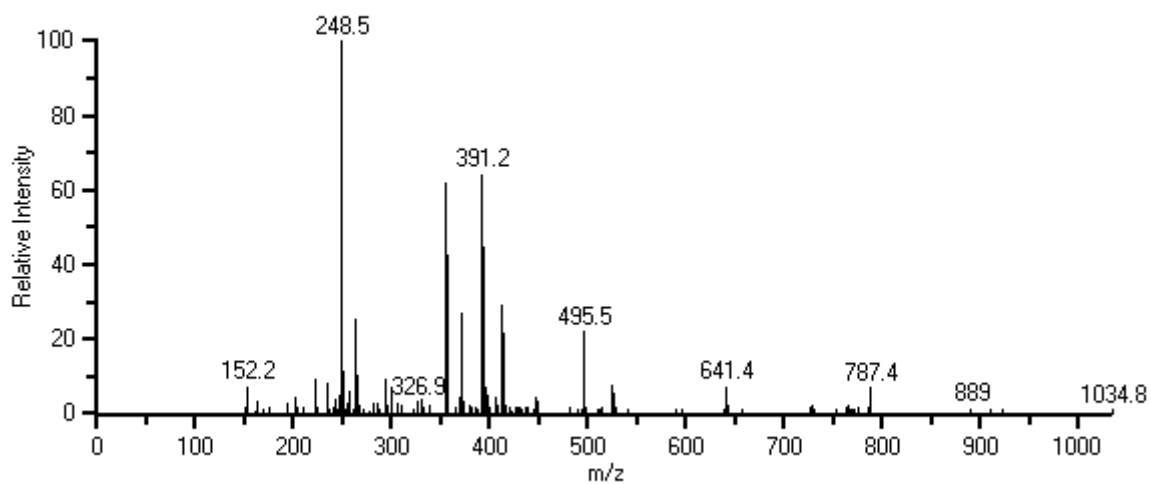


Figure S3a: ESI⁺ mass spectrum of [GaF₃(BzMe₂-tacn)] + NH₄PF₆; found $m/z = 412.1$ (28%) [GaF₃(L) + K]⁺; 391.2 (64%), [GaF₃(BzMe₂-tacn) + NH₄]⁺; 354 (62%) [GaF₂(BzMe₂-tacn)]⁺

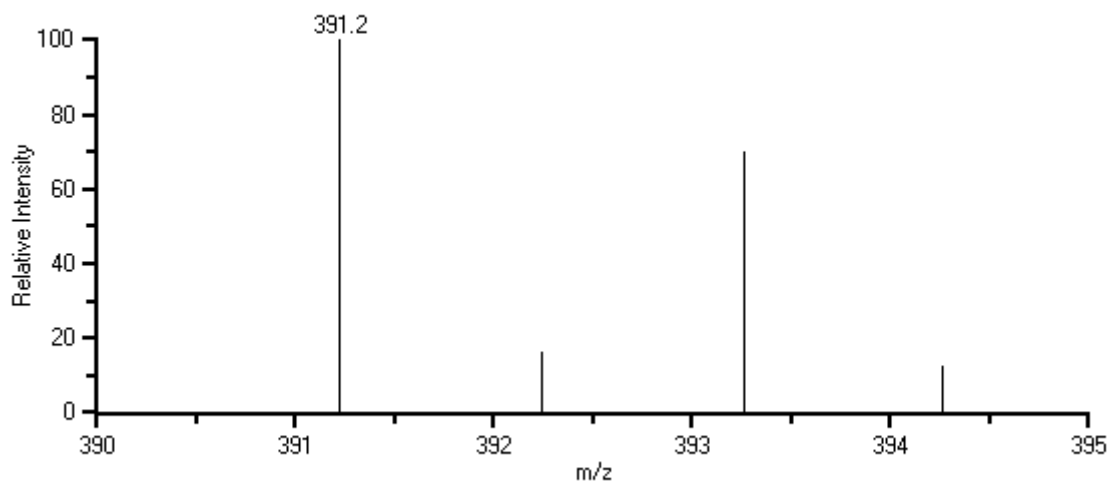


Figure S3b: Expansion of the isotope pattern from the peak at $m/z = 391.2$, attributed to [GaF₃(BzMe₂-tacn) + NH₄]⁺.

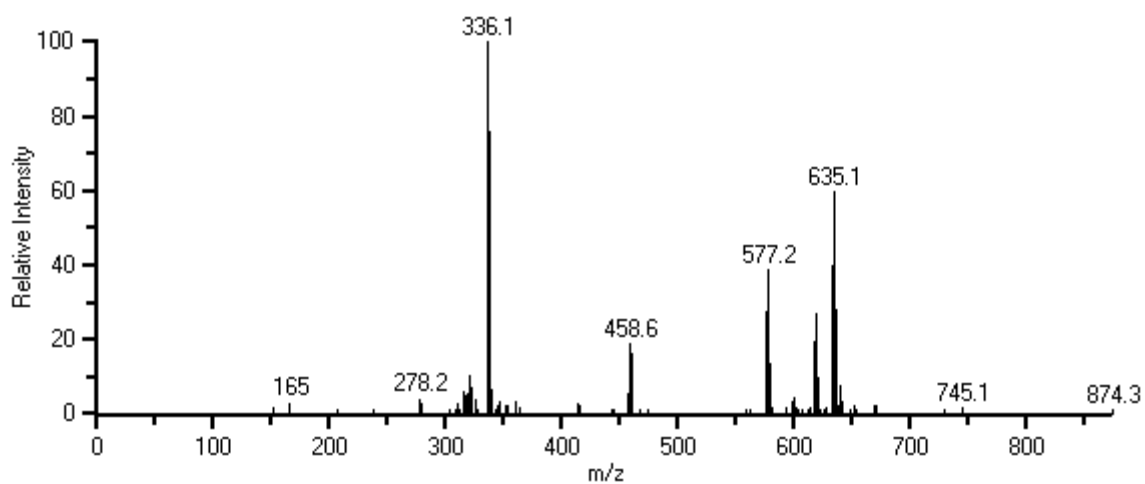


Figure S4a: ESI⁺ mass spectrum of [GaF₃(Me₃-tacn)] + KPF₆; found *m/z* 336.1 (100%) [GaF₃(Me₃-tacn) + K]⁺; 619.2 (25%) [{GaF₃(Me₃-tacn)}₂ + Na]⁺; 635.1 (60%) [{GaF₃(Me₃-tacn)}₂ + K]⁺

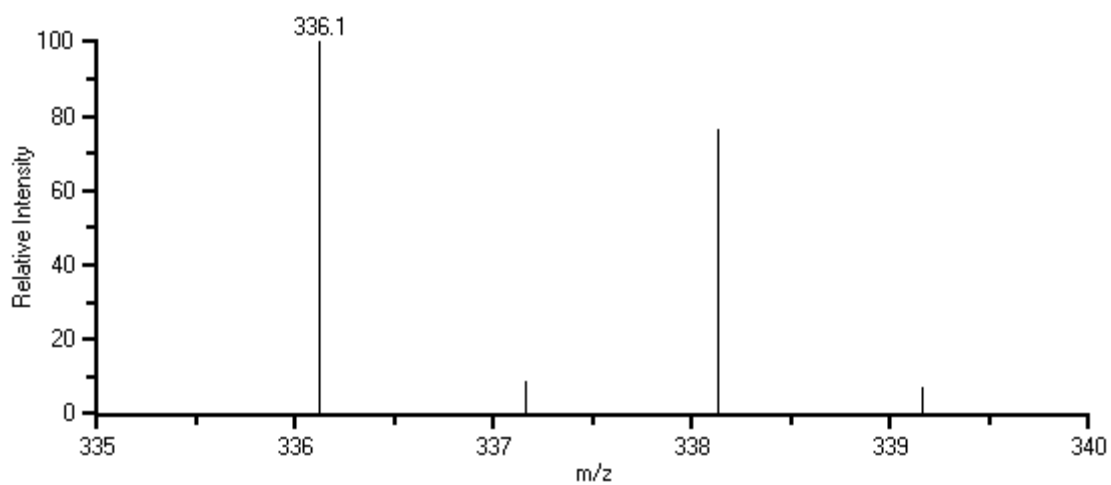


Figure S4b: Expansion of the isotope pattern from the peak at *m/z* = 336.1 attributed to [GaF₃(Me₃-tacn) + K]⁺.

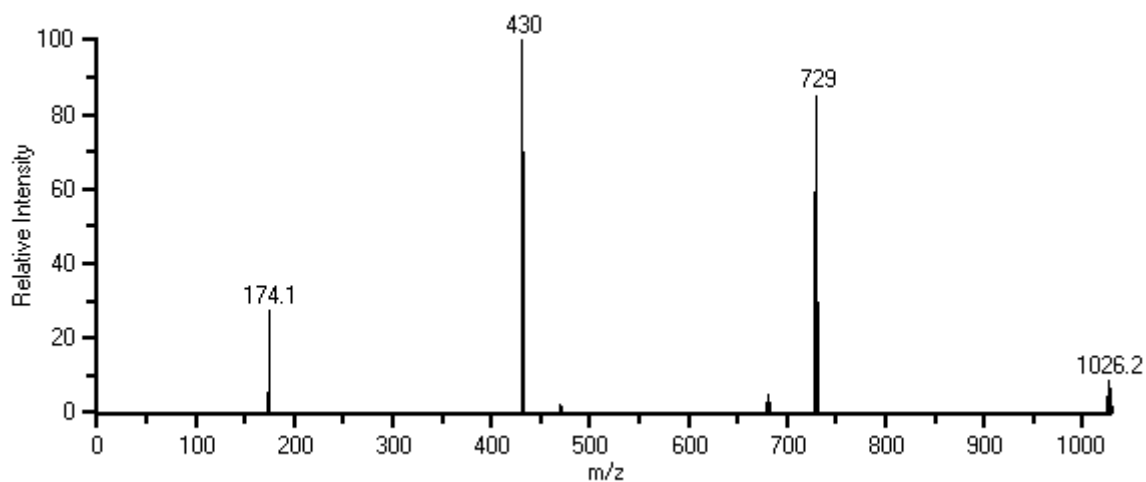


Figure S5a: ESI⁺ mass spectrum for [GaF₃(Me₃-tacn)] + Cs₂CO₃. Found $m/z = 430$ (100%) [GaF₃(Me₃-tacn) + Cs]⁺; $m/z = 729$ (85%) [{GaF₃(Me₃-tacn)]₂ + Cs]⁺, 1026.2 (13%) [{GaF₃(Me₃-tacn)]₃ + Cs]⁺.

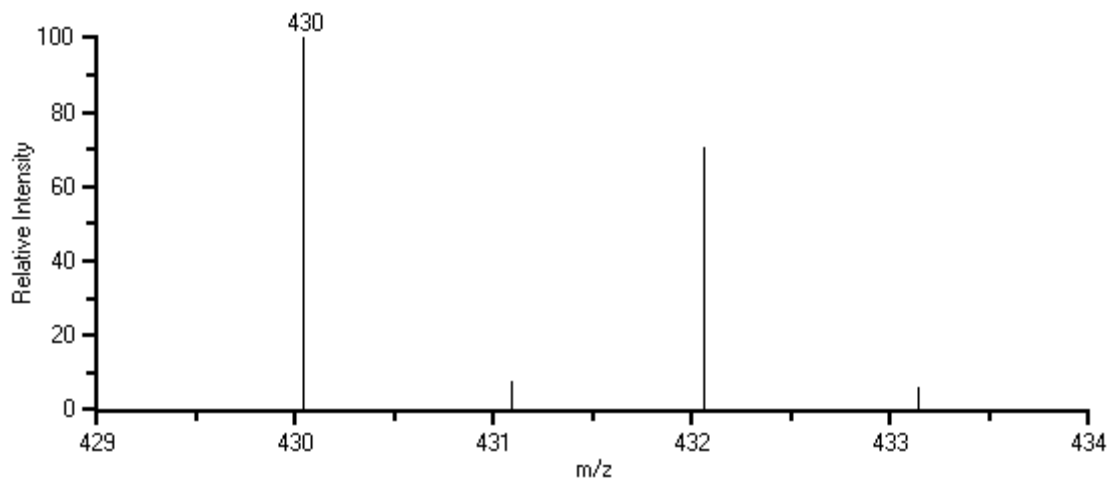


Figure S5b: Expansion of the isotope pattern from the peak at $m/z = 430$ attributed to [GaF₃(Me₃-tacn) + Cs]⁺.

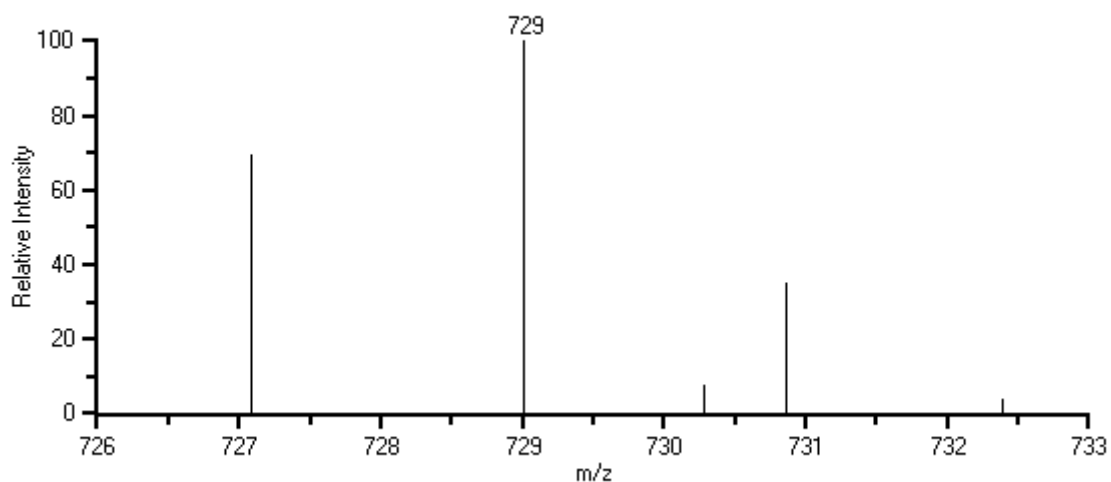


Figure S5c: Expansion of the isotope pattern from the peak at $m/z = 729$ attributed to $[\{\text{GaF}_3(\text{Me}_3\text{-tacn})\}_2 + \text{Cs}]^+$.

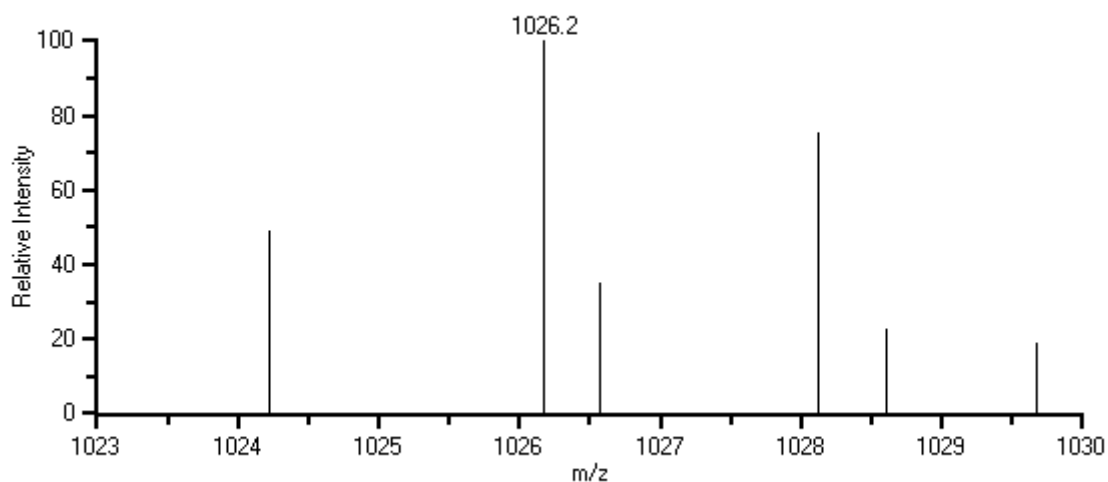


Figure S5d: Expansion of the isotope pattern from the peak at $m/z = 1026.2$ attributed to $[\{\text{GaF}_3(\text{Me}_3\text{-tacn})\}_3 + \text{Cs}]^+$.

References

1. R. Bhalla, C. Darby, W. Levason, S. K. Luthra, G. McRobbie, G. Reid, G. Sanderson and W. Zhang, *Chem. Sci.*, 2014, **5**, 381.
2. CrystalClear-SM Expert 2.0 r13, Rigaku Corporation, Tokyo, Japan, 2011.
3. L. J. Farrugia, *J. Appl. Cryst.*, 2012, **45**, 849.