The neutral complex, [GaF₃(L)] (L = 1-benzyl-4,7-dimethyl-1,4,7-triazacyclononane, BzMe₂-tacn), acts as a 'metalloligand' to Na⁺, K⁺ and [NH₄]⁺ cations in aqueous solution, forming supramolecular assemblies containing significant Na/K–F and H₃N⁺H–F coordination. K⁺[BF₄]⁻ and K⁺[PF₆]⁻ coordination is also evident to Na⁺ and K⁺, respectively.

Metal fluoride complexes often display quite different properties and reactivities compared to the corresponding chlorides and bromides, due to the small size and high electronegativity of the hard fluoride ligand. As part of our work investigating the potential of metal coordination complexes towards new classes of PET imaging agents we have reported the radio-fluorination of group 13 trichloride [GaCl₃(L)] and [GaCl₃(Me₃-tacn)] – a neutral 'metalloligand' towards alkali metal and ammonium cations in water†

In order to investigate this behaviour further, we used ESI MS to probe the speciation from 1 : 1 molar ratios of preferred [GaF₃(L)] with various alkali metal cations (via the salts LiBF₄, NaBF₄, KPF₆ and Cs₂CO₃) in 5 : 1 MeCN : H₂O. In each case peaks due to [GaF₃(L) + M⁺], with the correct isotopic distribution, were observed, as well as [[GaF₃(L)]₂ + M⁺] in some cases. Similarly, addition of NH₄PF₆ gave [GaF₃(L) + NH₄⁺] – see ESI† The high affinity of the alkali metal cations for water is well-known, and, with the exceptions of the ubiquitous crown ether and cryptand derivatives, and group 1 cation-π(arene) complexes which have attracted interest due to their relevance in biological systems (such as potassium-selective channels and sodium-dependent allosteric regulation of serine proteases), few coordination complexes of the group 1 cations formed in aqueous solution with neutral ligands are known.

We were able to prepare directly and isolate [[GaF₃(L)]₂Na₂(BF₄)₂] (1) and [[GaF₃(L)]₂K₂(OH)₂(PF₆)₂]·H₂O (2) by combining equimolar solutions of [GaF₃(L)] and NaBF₄ or KPF₆, respectively, in water and allowing the products to form as colourless crystals over several days. A few (poorly diffracting) crystals of the mixed Na⁺/NH₄⁺ compound [[GaF₃(L)]Na(NH₄)(PF₆)₂] (3) were also obtained from a 1 : 1 molar ratio of [GaF₃(L)] and NH₄PF₆ in water; the adventitious Na⁺ most likely originating from the glassware; further evidence, however, for the high affinity of the gallium fluoride complex for the group 1 cations.

† Electronic supplementary information (ESI) available: Full experimental details for the compounds reported, in situ ESI MS data from 1 : 1 molar ratios of [GaF₃(L)] with alkali metal salts and NH₄PF₆, plus all the crystallographic and spectroscopic data for all products. CCDC 1008581–1008583. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4cc05603e
Compound 1 crystallises in the monoclinic space group $P2_1/c$ with two GaF$_3$(L) moieties and two NaBF$_4$ units in the asymmetric unit. The structure shows (Fig. 1) two [GaF$_3$(L)] moieties bridged by two five-coordinate, distorted square based pyramidal ($t = 0.21$ (Na1), 0.23 (Na2)) sodium cations. Each sodium ion is coordinated through two $m^2$-bridging fluoride ligands from one [GaF$_3$(L)] unit ($k^3$), one fluoride from a ($k^4$) BF$_4^-$ ion, and a single $m^3$-bridging fluoride from each of two further distinct (symmetry-related) gallium moieties. This leads to an extended 1-D zig-zag chain structure. The $m^3$-F atoms form a Na$_2$F$_2$ rhombus at the core.

The Na–F bond distances involving the GaF$_3$ unit slightly longer for the $m^3$-F atoms (F3 and F6) than for the $m^2$-F atoms. The latter are little different from those observed in [GaF$_3$(Me$_3$-tacn)]·4H$_2$O$^2$, where the F atoms are involved in significant H-bonding with the H$_2$O solvate. The Na–F distances lie in the ranges 2.210(3)–2.426(3) Å (Na1) and 2.200(3)–2.421(3) Å (Na2). These mostly lie within the sum of the ionic radii for Na$^+$ and F$^-$ (1.16 and 1.19 Å respectively)$^{11}$ derived from crystalline NaF. Despite the hydrophilicity of the Na$^+$ cations, no water is retained in the crystal structure of 1.

IR spectroscopy and ESIMS mass spectrometry of compound 1 supported the formulation observed crystallographically, although in D$_2$O solution the $^1$H, $^{19}$F($^1$H), $^{23}$Na and $^{71}$Ga NMR resonances are not significantly different from those of the constituents in water. This indicates that 1 is extensively dissociated in water, typical of very labile alkali metal complexes.

Compound 2 crystallises in the triclinic space group $P\bar{1}$ with one half of a centrosymmetric tetranuclear entity (2) in the asymmetric unit. The structure also confirms coordination of the K$^+$ to [GaF$_3$(L)] through the fluorides (Fig. 2a). The structure is based upon eight-coordinate K$^+$, coordinated to two F atoms from one GaF$_3$(L) moiety (one of which is $m^2$, and the other $k^3$), one $m^3$-F from the second GaF$_3$(BzMe$_2$-tacn) unit, one terminal and two bridging OH$_2$ ligands. The coordination environment...
isolated sample of tetranuclear \((\text{Ga}_2\text{K}_2)\) species shows H-bonding interactions between the bridging OH ligands and two fluoride ligands of the gallium species (O1⋯F2 2.893(3), O1⋯F3 2.762(3) Å). In addition, further H-bonding is evident between the terminal OH ligands and a fluoride ligand from an adjacent ‘Ga\(_2\)K\(_2\)’ unit (O2⋯F1 2.740(4) Å), resulting in a 1D chain polymer motif (Fig. 2b). This results in a strongly H-bonded supramolecular assembly. The solvent water molecule also forms a Ga–F hydrogen bond (O3⋯F3 2.729(4) Å). The K–F distances lie in the range 2.578(3) to 2.928(3) Å, comparable with the sum of the hydrogen bond (O3⋯F3 2.729(4) Å) and F\(^-\) (1.19 Å).\(^{11}\) As expected, the Ga–N bond lengths are not significantly affected by the alkalimetal cation coordination in compounds 1 and 2.

Microanalytical, IR spectroscopic and ESI\(^+\) MS data from an isolated sample of 2 are consistent with the formula identified crystallographically. The IR spectra of 1 and 2 show significant broadening and splitting of the \(\nu(\text{BF}_4^-)\) and \(\nu(\text{PF}_6^-)\) stretching vibrations compared to the parent tetrahedral and octahedral anions, respectively, probably resulting from their coordination to the alkali metal ions.

Although the crystal data quality for compound 3 was much inferior compared to 1 and 2, analysis of the structure confirms the composition and reveals the key features of the coordination environment. The structure shows (Fig. 3) 3 is a chain polymer with two alternating types of six coordinate Na\(^+\) ions, both with \(\text{F}_6\) coordination; one type involving two \(\kappa^2\)-Ga\(_2\)F\(_3\)\((\text{L})\) units and two \(\kappa^3\)-[PF\(_6\)]\(^-\) anions, the second involving two \(\kappa^2\)-Ga\(_2\)F\(_3\)\((\text{L})\) units and two \(\kappa^3\)-[PF\(_6\)]\(^-\) anions. Interestingly, the \([\text{NH}_4]^+\) cations also form significant F⋯H–N hydrogen bonding interactions with adjacent F\(_k\) both from Ga\(_2\)F\(_3\)(L) and from [PF\(_6\)]\(^-\) anions. The presence of both Na\(^+\) and \([\text{NH}_4]^+\) ions in 3 is also supported by ESI\(^+\) mass spectrometry data on the isolated product.

We have shown that [GaF\(_3\)(L)] can function as a very effective F-donor ‘metalloligand’ towards alkali metal cations in water, leading to highly unusual and distinct structural types. The results suggest that rational development of new multimetallic frameworks and assemblies based upon metal fluoride coordination complexes as metalloligands towards other inorganic and organic cations should be possible.

This work was funded by EPSRC and GE Healthcare through a CASE studentship (G.S.). The authors thank Dr M. E. Light for help with the crystallographic analyses.

Notes and references
1. S. L. Benjamin, W. Levason and G. Reid, *Chem. Soc. Rev.*, 2013, 42, 1460; H. C. S. Clark and J. H. Holloway, in *Advanced Inorganic Fluorides*, ed. T. Nakajima, B. Žemva and A. Tressaud, Elsevier, Oxford, 2000, ch. 3; N. M. Doherty and N. W. Hoffman, *Chem. Rev.*, 1991, 91, 553; E. F. Murphy, R. Murugavel and H. W. Roesky, *Chem. Rev.*, 1997, 97, 3425.
2. R. Bhalla, C. Darby, W. Levason, S. K. Luthra, G. McRobbie, G. Reid, G. Sanderson and W. Zhang, *Chem. Sci.*, 2014, 5, 381.
3. F. N. Penkert, T. Weyhermüller and K. Wieghardt, *Chem. Commun.*, 1998, 557.
4. K. S. Pedersen, G. Lorusso, J. J. Morales, T. Weyhermüller, S. Piligkos, S. K. Singh, D. Larsen, M. Schau-Magnussen, G. Rajaraman, M. Evangelisti and J. Bendix, *Angew. Chem., Int. Ed.*, 2014, 53, 2394.
5. G. Kumar and R. Gupta, *Chem. Soc. Rev.*, 2013, 42, 9403.
6. M. Trámské and B. Žemva, *J. Fluorine Chem.*, 2006, 127, 1275 and references therein.
7. T. P. Hanusa, in *Comprehensive Coordination Chemistry II*, ed. J. A. McCleverty and T. J. Meyer, Elsevier, Oxford, 2004, ch. 1, vol. 3.
8. See for example: B. Werner, T. Kräuter and B. Neumüller, *Organometallics*, 1996, 15, 3746; G. B. Deacon, T. C. Feng, P. C. Junk, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1997, 1181.
9. R. I. Nakamura, J. A. Anderson and R. F. Gaber, *J. Biol. Chem.*, 1997, 272, 1011.
10. Q. D. Dang, E. R. Guinto and E. Di Cera, *Nat. Biotechnol.*, 1997, 15, 116.
11. R. D. Shannon, *Acta Crystallogr., Sect. A: Crystal., Phys., Differ., Theor. Gen. Crystallogr.*, 1976, 32, 751.