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$[GaF_3(BzMe_2\text{-tacn})]$ – a neutral 'metalloligand' towards alkali metal and ammonium cations in water†

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The neutral complex, $[GaF_3(L)]$ (L = 1-benzyl-4,7-dimethyl-1,4,7-triazacyclononane, $BzMe_2$-tacn), acts as a 'metalloligand' to Na^+, K^+ and $[NH_4]^+$ cations in aqueous solution, forming supramolecular assemblies containing significant Na/K–F and $H_3N^+H\cdots F$ coordination. κ^1-$[BF_4]^-$ and κ^2-$[PF_6]^-$ 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.[1] 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 complexes based upon the triaza-macrocyclic ligand scaffold,[2] showing that ^{18}F incorporation into $[GaCl_3(L)]$ (L = 1-benzyl-4,7-dimethyl-1,4,7-triazacyclononane, $BzMe_2$-tacn) occurs readily in aqueous MeCN at room temperature *via* halide exchange. The formation of the $[Ga^{18/19}F_3(L)]$ is driven by the high Ga–F bond energy, and the trifluoride complex is extremely stable both in water and in phosphate buffered saline. Crystallographic studies showed that $[MF_3(L)]$ and $[MF_3(Me_3\text{-tacn})]$ are heavily hydrated and form extended supramolecular networks through strong $F\cdots H$–OH hydrogen bonding. Earlier work by Wieghardt and co-workers had reported that first observation of the S_6-symmetric methanol hexamer, crystallised within the hydrophobic cavity present in the complex $[GaF_3(L')]$ (L′ = 1,4,7-tris(2-amino-3,5-di-*tert*-butylbenzyl)-1,4,7-triazacyclononane).[3] Further, we found from ESI^+ mass spectrometry studies on the HPLC purified radio-product $[Ga^{18/19}F_3(L)]$ that $[GaF_3(L) + NH_4]^+$ was the major ionic species observed, and proposed[2] that association of $[NH_4]^+$ (from the NH_4OAc(aq) HPLC mobile phase) with the highly electronegative region created by the three facial fluorides of $[GaF_3(L)]$. A very recent report of $[Gd^{III}{}_3M^{III}{}_2]$ based molecular magnets derived from $Gd(NO_3)_3\cdot 5H_2O$ with $[M^{III}F_3(Me_3\text{-tacn})]\cdot xH_2O$ (M = Cr, Fe, Ga)[4] further fuelled our interest in exploiting the wider scope of the $[GaF_3(L)]$ complex to act as a robust 'metalloligand' towards other cations, building novel complexes with (functional) supramolecular architectures, adding a new type of building block for this type of application.[5] Binary p-block fluorides such as XeF_2 and AsF_3 can coordinate to Ln^{3+} and alkaline earth dications in extreme solvents, *i.e.* anhydrous HF or liquid AsF_3.[6]

In order to investigate this behaviour further, we used ESI^+ MS to probe the speciation from 1 : 1 molar ratios of preformed $[GaF_3(L)]$ with various alkali metal cations (*via* the salts $LiBF_4$, $NaBF_4$, KPF_6 and Cs_2CO_3) in 5 : 1 MeCN : H_2O. In each case peaks due to $[GaF_3(L) + M]^+$, with the correct isotopic distribution, were observed, as well as $[\{GaF_3(L)\}_2 + M]^+$ in some cases. Similarly, addition of NH_4PF_6 gave $[GaF_3(L) + NH_4]^+$ – see ESI.† The high affinity of the alkali metal cations for water is well-known,[7] and, with the exceptions of the ubiquitous crown ether and cryptand derivatives, and group 1 cation–π(arene) complexes[8] which have attracted interest due to their relevance in biological systems (such as potassium-selective channels[9] and sodium-dependent allosteric regulation of serine proteases[10]), few coordination complexes of the group 1 cations formed in aqueous solution with neutral ligands are known.[7]

We were able to prepare directly and isolate $[\{GaF_3(L)\}_2Na_2(BF_4)_2]$ (**1**) and $[\{GaF_3(L)\}_2K_2(OH_2)_4(PF_6)_2]\cdot H_2O$ (**2**) by combining equimolar solutions of $[GaF_3(L)]$ and $NaBF_4$ or KPF_6, respectively, in water and allowing the products to form as colourless crystals over several days. A few (poorly diffracting) crystals of the mixed Na^+/NH_4^+ compound $[\{GaF_3(L)\}Na(NH_4)(PF_6)_2]$ (**3**) were also obtained from a 1 : 1 molar ratio of $[GaF_3(L)]$ and NH_4PF_6 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.

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† Electronic supplementary information (ESI) available: Full experimental details for the compounds reported, *in situ* ESI^+ MS data from 1 : 1 molar ratios of $[GaF_3(L)]$ with alkali metal salts and NH_4PF_6, 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

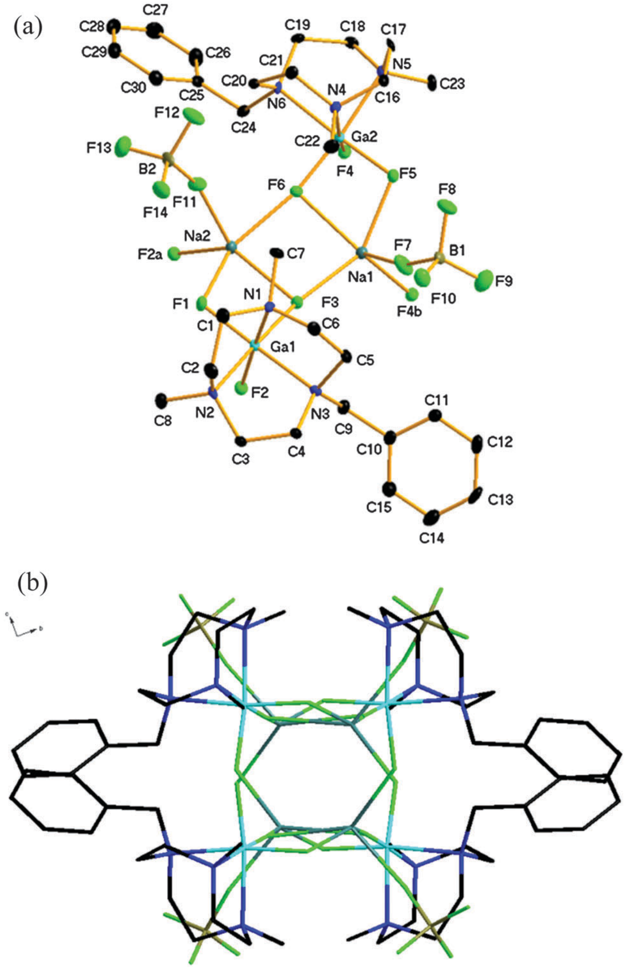

Fig. 1 (a) View of the asymmetric unit for compound **1**, including the symmetry related atoms (F2a and F4b) that complete the coordination environment at Na1 and Na2 with associated numbering scheme. H atoms are omitted for clarity. Selected bond lengths (Å): Ga1–F1 1.842(2), Ga1–F2 1.848(2), Ga1–F3 1.902(2), Ga2–F5 1.834(2), Ga2–F4 1.849(2), Ga2–F6 1.896(2), Na1–F4b 2.210(3), Na1–F5 2.241(3), Na1–F7 2.254(3), Na1–F3 2.377(2), Na1–F6 2.426(3), Na2–F2a 2.200(3), Na2–F1 2.229(2), Na2–F11 2.264(3), Na2–F6 2.355(3), Na2–F3 2.421(3), F7–B1 1.399(5), F8–B1 1.378(5), F9–B1 1.385(5), F10–B1 1.403(5), F11–B2 1.412(5), F12–B2 1.394(5), F13–B2 1.381(6), F14–B2 1.386(5). Symmetry codes: *a* = 2 − *x*, 1 − *y*, −*z*; *b* = 1 − *x*, 1 − *y*, −*z*. (b) View down the *a*-axis of **1**. Colour key: turquoise = Ga, teal = Na, pink = P, green = F, blue = N, black = C.

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 ($\tau = 0.21$ (Na1), 0.23 (Na2)) sodium cations. Each sodium ion is coordinated through two μ^2-bridging fluoride ligands from one $[GaF_3(L)]$ unit (κ^2), one fluoride from a (κ^1) BF_4^- ion, and a single μ^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 μ^3-F atoms form a Na_2F_2 rhombus at the core.

The Na–F bond distances involving the GaF_3 unit slightly longer for the μ^3-F atoms (F3 and F6) than for the μ^2-F atoms. The latter are little different from those observed in $[GaF_3(Me_3\text{-tacn})]\cdot 4H_2O$,[2] where the F atoms are involved in significant H-bonding with the H_2O 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 ESI^+ mass spectrometry of compound **1** supported the formulation observed crystallographically, although in D_2O solution the ^1H, $^{19}F\{^1H\}$, ^{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 μ^2, and the other μ^3), one μ^3-F from the second $GaF_3(BzMe_2\text{-tacn})$ unit, one terminal and two bridging OH_2 ligands. The coordination environment

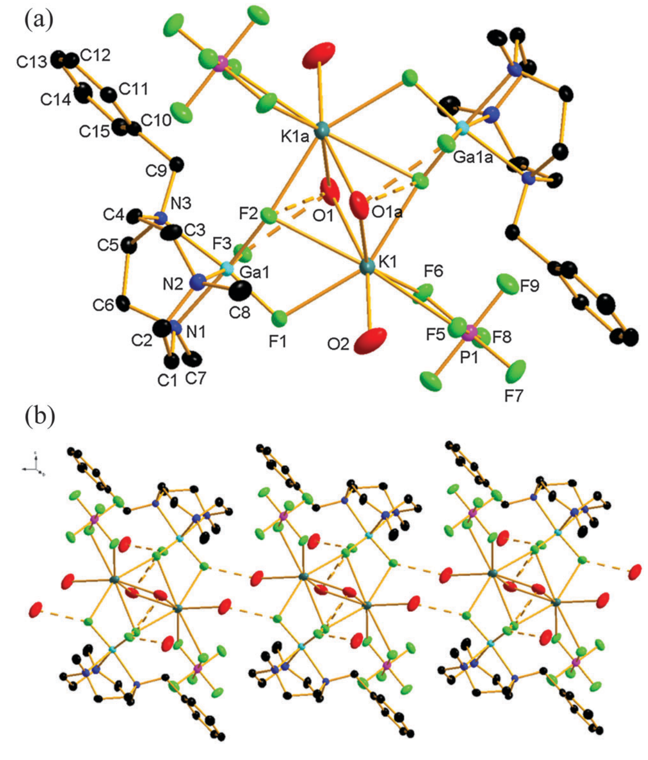

Fig. 2 (a) View of the structure of the centrosymmetric 'Ga_2K_2' species present in compound **2** with associated numbering scheme. Dashed bonds indicate H-bonding contacts. H atoms associated with the macrocycle are omitted for clarity (H atoms on the water were not located in the difference map – see Experimental). Selected bond lengths (Å): Ga1–F2 1.838(2), Ga1–F1 1.872(3), Ga1–F3 1.872(3), K1a–F2 2.578(3), K1–F1 2.649(3), K1–F5 2.866(3), K1–O2 2.887(4), K1–F2 2.882(3), K1–O1 2.914(4), K1–F6 2.928(3), K1–O1a 2.959(4), P1–F7 1.588(3), P1–F4 1.590(3), P1–F6 1.597(3), P1–F9 1.600(3), P1–F8 1.600(3), P1–F5 1.609(3). Symmetry operation: *a* = 2 − *x*, 1 − *y*, −*z*. (b) View of the extended structure formed by compound **2** (excluding the H_2O solvent molecules). Colour key: turquoise = Ga, teal = K, pink = P, green = F, blue = N, black = C.

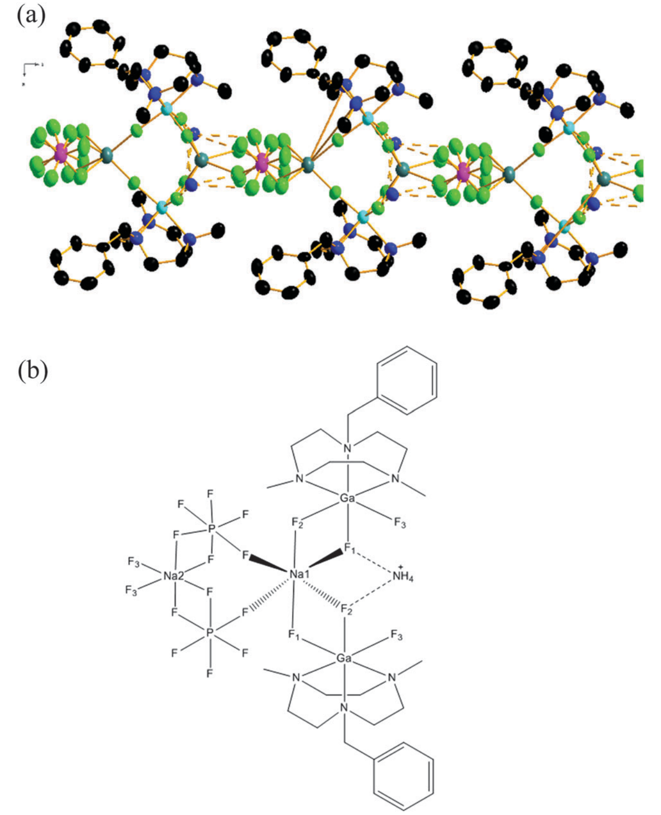

Fig. 3 (a) View of the structure of a portion of the polymeric structure formed by **3**. Ellipsoids are drawn at 50% probability level. H-atoms on the BzMe$_2$-tacn ligand are omitted for clarity; those of the NH$_4^+$ cation were not located (see ESI†). Colour key: turquoise = Ga, teal = Na, pink = P, green = F, blue = N, black = C. (b) Line drawing illustrating the coordination environment at Na$^+$ and the F···HNH$_3^+$ hydrogen bonding interactions in **3**.

at each K$^+$ ion is completed by a κ^2-coordinated PF$_6^-$ ion. This tetranuclear (Ga$_2$K$_2$) species shows H-bonding interactions between the bridging OH$_2$ ligands and two fluorides ligand 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$_2$ 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···H–OH 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 ionic radii of K$^+$ (1.65 Å for eight coordination) and F$^-$ (1.19 Å).[11]

As expected, the Ga–N bond lengths are not significantly affected by the alkali metal 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 ν(BF$_4^-$) and ν(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 F$_6$ coordination; one type involving two κ^2-GaF$_3$(L) units and two κ^1-[PF$_6$]$^-$ anions, the second involving two κ^1-GaF$_3$(L) units and two κ^2-[PF$_6$]$^-$ anions. Interestingly, the [NH$_4$]$^+$ cations also form significant F···H–N hydrogen bonding interactions with adjacent Fs both from GaF$_3$(L) and from [PF$_6$]$^-$ anions. The presence of both Na$^+$ and [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.

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