Al, Ga and In heterometallic wheels and their by-products†

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Cyclic octanuclear complexes, each containing seven group 13 metals and one d-block metal are reported and preliminary physical characterisation of the compounds discussed.

The heterometallic wheel complexes of general formula $[R_2NH_2][M_7M'F_8(O_2C^tBu)_{16}]$ are known where M = V(III), Cr(III) and Fe(III); M′ = Ni(II), Co(II), Mn(II), Fe(II), Zn(II), Cd(II), Mg(II); and R = Me, Et, ^{n}Pr.[1] Interest in antiferromagnetically coupled cyclic complexes has grown since they were identified as a possible qubit in a quantum computer.[2] In this area, and in related fields such as studies of single molecule magnets[3] and single chain magnets,[4] it is very important that we can understand and control the magnetic anisotropy of the cluster, and specifically how it relates to the anisotropy of the single ions of which it is composed. One way to do so is to synthesize isostructural analogues containing predominantly diamagnetic metals, leaving single paramagnetic metal centres which could then be studied in isolation. Use of group 13 elements as the trivalent ions in heterometallic wheels seemed ideal. The second aim, but not less in importance, was driven by purely synthetic interest to check how far we can extend the reaction which leads to isolation and characterization of the $[R_2NH_2][Cr_7M'F_8(O_2C^tBu)_{16}]$ wheels.[5]

The idea seemed even more attractive as polymetallic carboxylate complexes of these metals are comparatively rare, and also as group 13 wheels may be useful, *e.g.* as precursors for new materials. The first group 13 oxo-centered carboxylate was $[Ga_3O(PhCO_2)_6(4\text{-Mepy})_3]GaCl_4$.[6] Since then, a few high nuclearity Ga(III)[7] and In(III) complexes[8] have been reported in the literature. Many more Al(III) complexes are known, including trinuclear basic carboxylates of Al(III).[9] Of especial relevance to this work are Saalfrank's report on Ga cyclic complexes[10] and In wheels and their mixed-metal analogues with Mn.[11] The Christou group has also very recently reported $\{Ga_{10}\}$ and $\{Ga_{18}\}$ rings.[12]

The synthesis of $[R_2NH_2][M_7M'F_8(O_2C^tBu)_{16}]$ rings involves a four component reaction where a mixture of metal(III) fluoride, secondary amine (R_2NH) and a source of the divalent M′(II) are reacted in a large excess of pivalic acid at 160 °C.[1,5] If $MF_3{\cdot}3H_2O$, where M(III) = Al, Ga and In, $(C_3H_7)_2NH$, are used with nickel or cobalt salts, $[(C_3H_7)_2NH_2][Ga_7M'F_8(O_2C^tBu)_{16}]$ (M′ = Co, **1**; Ni, **2**) $[(C_3H_7)_2NH_2][In_7M'F_8(O_2C^tBu)_{16}]$ (M′ = Ni, **3**; Co, **4**) and $[(C_3H_7)_2NH_2][Al_7NiF_8(O_2C^tBu)_{16}]$ **5** can be obtained. The procedures are very similar‡, involving precipitation of a crude product by addition of MeCN, washing of this crude product with further MeCN, then recrystallisation from a non-polar solvent. Yields vary depending on the group 13 element: 70–90% for **1** and **2**, 40–60% for **3** and **4** and 7–10% for **5**. The colour of the new complexes are a characteristic pink for an octahedral Co(II) ion in **1** and **4** and light green for an octahedral Ni(II) centre in **2**, **3** and **5**.

The crystal structure§ of **1** consists of seven Ga(III) ions and a Co(II) centre arranged at the vertices of a regular octagon (Fig. 1). Each pair of ions is bridged by a fluoride and two pivalate groups in the common 2.11-bridging mode (Harris notation[13]). X-Ray crystallography does not allow us to distinguish between the Ga(III) and the Co(II) centres and all the metal positions were refined with 7/8 Ga and 1/8 Co(II) occupancies, however mass spectroscopy is unequivocal that this is the only metal ratio found in these rings. In Fig. 1, one metal site has been labelled as Co(II) for aesthetic purposes only. The same problem arises with the crystal structure of complexes **2–5** and was treated the same way. Other disorder problems are also found in these structures, especially for **5**. A dipropylammonium cation is found in the cavity, hydrogen bonding to the nearest fluoride bridges at N···F distances between 3.06 and 2.94 Å. The connectivity in structures **2–5** are the same as that of **1**, and isostructural with their Cr, V and Fe analogues.[1]

The high yields of the {Ga$_7$M′ wheels} **1** and **2**, and their stability, is consistent with the absence of by-products from these reactions, and with the proposition that Ga(III) is the most

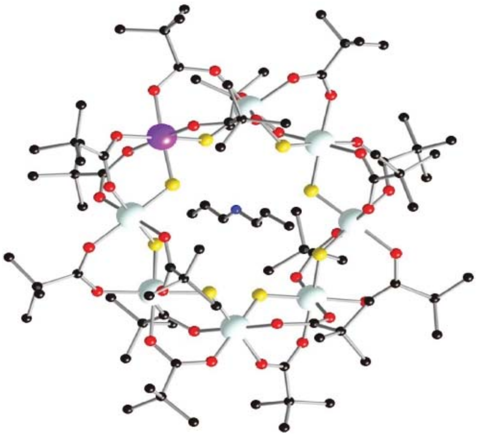

Fig. 1 The structure of **1** in the crystal. **2–4** are isostructural. Colours: Ga, white; Co, purple; O, red; F, yellow; N, blue; C, black. H, not shown.

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appropriate size for forming an octanuclear ring, with Al(III) too small and In(III) slightly too large. From the MeCN wash of the crude product of the reactions which give **3–5** several other heterometallic species could be isolated. From the In–Ni reaction two types of light green crystals grew in the fridge after a few days. These were identified by X-Ray crystallography as [In$_2$Ni(OH)(O$_2$C^{t}Bu)$_7$(HO$_2$C^{t}Bu)] **6** and the solid state mixture of [In$_2$Ni$_2$(OH)$_2$(O$_2$C^{t}Bu$_3$)$_8$(HO$_2$C^{t}Bu)$_2$]· [In$_2$Ni$_2$(OH)$_2$(O$_2$C^{t}Bu)$_8$(MeCN)$_2$] **7·8**. From the In–Co reaction we have isolated [In$_2$Co$_2$(OH)$_2$(O$_2$C^{t}Bu)$_8$(MeCN)$_2$] **9**, which is isostructural to **8**. From the MeCN wash in the reaction that gives **5**, the homometallic cage [(C$_3$H$_7$)$_2$NH$_2$]$_4$[Al$_4$F$_{14}$(O$_2$C^{t}Bu)$_2$] **10** was isolated.

These by-products were obtained in very low yields and were hard to isolate in pure form from reactions intended to make heterometallic wheels. We can make **6** and **7** in a pure form from direct reaction of indium acetate, pivalic acid and nickel carbonate by varying the ratio of In : Ni. **8** can be made by recrystallising **7** from MeCN. **9** can be made using cobalt acetate instead of nickel carbonate and a In : Co ratio of 1 : 1. Synthetic details are also included in the ESI.†

In **6**, a pyramidal OH$^-$ bridges the Ni(II) and the two In(III) centres (Fig. 2). The two In(III) ions are heptacoordinated, with a pentagonal bipyramid geometry. The coordination sphere consists of the central μ_3-OH and oxygen donors from four distinct pivalate groups. One pivalate adopts the 2.11-mode between the two In(III) ions while a second bridges in a 2.11-mode between In(II) and Ni(II). The third pivalate adopts the 2.21-mode, chelating to In(III) while also bridging through one of its oxygen atoms to the Ni(II) centre. Finally there is a chelating pivalate. The Ni(II) has a distorted octahedral coordination, bound to the μ_3-OH, O-donors from four pivalate bridges, and a terminal pivalic acid. This trinuclear complex is structurally very different from the known basic carboxylates of the transition metals, which usually possess a flat μ_3-O and six 2.11-carboxylates. In **6**, the μ_3-OH atom is pyramidal, with In–O–In angle of 127° and In–O–Ni angles of 100 and 102°.

The asymmetric unit of **7** and **8** contains two half molecules that differ only in the terminal ligands on the Ni(II) ions: MeCN and pivalic acid, respectively. The structure contains a In$_2$Ni$_2$O$_2$ core similar to the known 'butterfly' cores found in many tetranuclear transition metal complexes (Fig. 3). The main difference is the location of the divalent and trivalent ions; in transition metal 'butterfly' complexes that contain M(II), these M(II) ions are in the tips, never in the central M$_2$O$_2$ unit. In **7**, **8** and **10** the In(III) metals are at the wing-tips while the divalent metals are at the centre. The In(III) ions display distorted octahedral coordination, completed by a chelating pivalate group and three 2.11-pivalates. Each Ni(II) is also hexa-coordinated, bound to the two μ_3-oxides, three 2.11-pivalates and a terminal ligand (MeCN or a monodentate pivalic acid respectively).

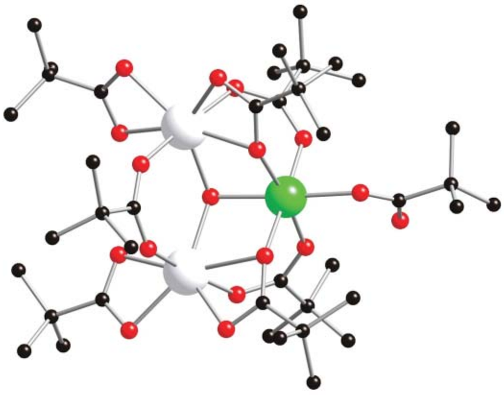

Fig. 2 The structure of **6** in the crystal. Colours as Fig. 1 plus In, white and Ni, light green.

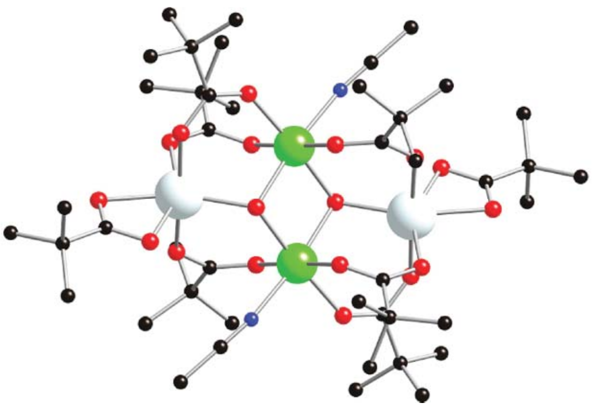

Fig. 3 The structure of **8** in the crystal. Colours as Fig. 2.

The crystal structure of **10** consists of four Al(III) ions arranged at the corners of a rectangle (Fig. 4). Along the long sides the two Al(III) are bridged by a μ_2-fluoride, and along the short sides, they are bridged by two μ_2-fluorides and one 2.11-pivalate. Each Al(III) ion has a distorted octahedral coordination with two terminal fluorides. Four dipropylammonium groups are present per formula unit to balance charge, and ten ^{t}BuCO$_2$H molecules per unit are found in the lattice.

The solid-state structure of the wheel complexes is retained in solution, as shown by mass spectrometry and by the ^{1}H NMR of **1** in CDCl$_3$. The spectrum shows seven resonances in the −10 to 15 ppm region in 1 : 1 : 1 : 2 : 1 : 1 : 1 ratio, as expected for eight types of pivalates in the cluster (four equatorial and four axial pivalate groups, two of which accidentally overlap in the spectrum). Additionally, in the −15 to −80 ppm region, six peaks are observed that are assigned to resonances of the dipropylammonium cation, which is sitting in the cavity: two peaks for each diastereotopic CH$_2$, one for the Me groups and one for the NH$_2$ protons. The proton NMR resonances observed for **1** are sharper and better defined than those of the {Cr$_7$Co} complex,[14] as expected due to the presence of only one paramagnetic centre in

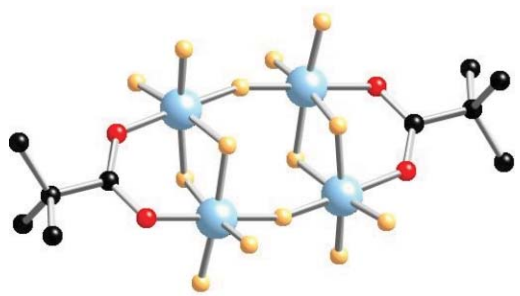

Fig. 4 The structure of the anion of **10** in the crystal. Colours as Fig. 1 plus Al, blue.

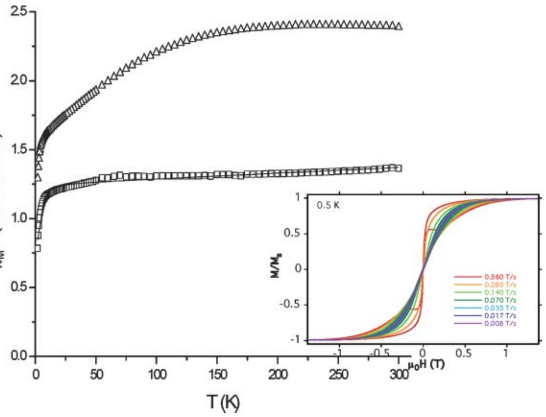

Fig. 5 Dc magnetic susceptibility of complexes **1** (△) and **2** (□). The solid line is the best fit of the experimental data.

the cluster, but they are still broadened not only due to the Co(II) but due to the seven quadrupolar Ga(III) nuclei.

Preliminary dc magnetic susceptibility measurements on crushed crystalline samples of **1** and **2** were performed. As expected, both display behaviour typical of a Co(II) and Ni(II) monomer respectively, with very little or no intermolecular interactions. The data of complex **2** were fitted using a hamiltonian that includes axial and rhombic zero-field splitting: $\hat{\boldsymbol{H}} = \boldsymbol{g\beta B\hat{S}} + D[\boldsymbol{S}_z^2 - \boldsymbol{S}(\boldsymbol{S}+1)] + E[\boldsymbol{S}_x^2 - \boldsymbol{S}_y^2]$ and the best fit is shown as a solid line in Fig. 5. The fitting parameters were $g = 2.23$ and $D = |7.6|\ \mathrm{cm}^{-1}$. This compares with the D_{Ni} inferred from inelastic neutron scattering of {Cr$_7$Ni} of 4.8 cm^{-1}.[15]

For **1** we must allow for the very strong spin–orbit coupling of a Co(II) centre; the drop observed in the $\chi_M T$ *vs.* T plot is due to depopulation of the $J = 5/2$ state and the preferential population of the $J = 1/2$. Deriving zero-field splitting parameters would therefore be meaningless. A crystal of **1** was studied using a micro-SQUID array. Despite the absence of an energy barrier for spin reversal, the system shows hysteresis due to a phonon bottleneck (inset Fig. 5), a phenomenon that has been previously seen and studied in detail in a {V$_{15}$} complex,[16] as well as the {Cr$_7$Ni} complex[16] of the same structure as **1**.

In conclusion, we have synthesised a family of heteronuclear cyclic complexes of the group 13 elements Al(III), Ga(III) and In(III). Several by-products of the synthesis of the cyclic complexes have been identified, and in some cases synthesized *de novo*. The ease of synthesis and stability of the rings varies, suggesting this structure is most stable for Ga(III) rather than the larger or smaller In(III) or Al(III).

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Notes and references

‡ Elemental analysis (C, H, N, F and both metals) confirms the identity of all the compounds discussed here. Electrospray mass spectroscopy confirms that only the specific nuclearities given are found in **1–5**. The ESI† includes synthetic details for **1–10**.

§ *Crystal data*: $C_{86}H_{160}CoF_8Ga_7NO_{32}$, **1**, triclinic, $P\bar{1}$, $a = 16.4095(12)$, $b = 16.4309(12)$, $c = 26.131(2)$ Å, $\alpha = 73.942(5)$, $\beta = 73.998(5)$, $\gamma = 75.933(1)°$, $V = 6401.38(90)$ Å^3, $R1 = 0.0763$. $C_{93}H_{168}F_8Ga_7NNiO_{32}$, **2**: monoclinic, $P2_1/c$, $a = 25.041(2)$, $b = 16.621(3)$, $c = 31.514(4)$ Å, $\beta = 102.172(9)°$, $V = 12821(3)$ Å^3, $R1 = 0.0493$. $C_{86}H_{160}CoF_8In_7NO_{32}$, **3**: monoclinic, $P2_1/c$, $a = 25.907(4)$, $b = 16.463(3)$, $c = 31.224(5)$ Å, $\beta = 110.983(15)°$, $V = 12435(4)$ Å^3, $R1 = 0.1241$. **4** is isomorphous with **3**. $C_{86}H_{160}Al_7CoF_8NO_{32}$, **5**: monoclinic, $C2/c$, $a = 26.016(5)$, $b = 20.219(4)$, $c = 25.986(5)$ Å, $\beta = 111.00(3)°$, $V = 12717(4)$ Å^3, $R1 = 0.1184$. $C_{57}H_{107}In_2NNiO_{23}$, **6**: monoclinic, $P2_1/c$, $a = 15.0221(7)$, $b = 12.3977(6)$, $c = 39.2275(15)$ Å, $\beta = 94.561(3)°$, $V = 7282.6(6)$ Å^3, $R1 = 0.0932$. $C_{64.5}H_{120}In_2NNi_2O_{27}$, **7**: orthorhombic, $Aba2$, $a = 26.3713(15)$, $b = 23.9207(16)$, $c = 29.0728(16)$ Å, $V = 18339.7(19)$ Å^3, $R1 = 0.0916$. $C_{44}H_{80}In_2N_2Ni_2O_{18}$, **8**: triclinic, $P\bar{1}$, $a = 13.6807(5)$, $b = 14.6160(7)$, $c = 16.7701(6)$ Å, $\alpha = 95.458(4)$, $\beta = 102.446(3)$, $\gamma = 116.862(3)°$, $V = 2849.0(2)$ Å^3, $R1 = 0.0246$. $C_{44}H_{80}Co_2In_2N_2O_{18}$, **9**: triclinic, $P\bar{1}$, $a = 13.7366(4)$, $b = 14.6428(4)$, $c = 16.7555(7)$ Å, $\alpha = 95.802(8)$, $\beta = 102.151(3)$, $\gamma = 116.952(2)°$, $V = 2861.24(17)$ Å^3, $R1 = 0.0266$. $C_{84}H_{182}Al_4F_{14}N_4O_{24}$, **10**: triclinic, $P\bar{1}$, $a = 12.2414(18)$, $b = 15.4122(13)$, $c = 16.570(3)$ Å, $\alpha = 87.559(13)$, $\beta = 69.407(13)$, $\gamma = 77.147(9)°$, $V = 2851.9(7)$ Å^3, $R1 = 0.0958$. CCDC 622129–622137. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b613877b

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