Influencing the nuclearity and constitution of heterometallic rings *via* templates†

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Heterometallic wheels can be templated about tertiary amines and imidazoles, leading to new octa-, nona- and deca-nuclear rings.

The idea that a polymetallic structure can be controlled by use of a templating ion or molecule is extremely attractive as it offers the possibility that those of us interested in making multimetallic compounds can escape from serendipity[1] and begin to indulge in designed synthesis. Key contributions to this concept have been made by Saalfrank who has shown that hexa- or octa-nuclear rings can be selected based on the ionic radius of the alkali metal ion template chosen,[2] and by Raymond, who has shown that the nuclearity and shape of gallium clusters can be directed by appropriate templates.[3] However for this to be a widely used method it would be useful if the templates chosen could generate one from many possible structures, rather than the binary differentiation currently possible. We have shown, in a system of heterometallic $\{Cr_nNi\}$ rings (n = 7 or 8), that we can choose between octa- and nona-nuclear wheels by using appropriate secondary ammonium ions as templates.[4,5] Here we show that other templates lead to other rings, differing in size and metal composition. The new templates also influence the bridging ligands involved in the rings, which presents the possibility of doing ligand substitution chemistry on the ring backbone in the future.

The reaction is straightforward. Chromium(III) fluoride tetrahydrate is added to a mixture of a secondary or tertiary amine or imidazole and in a large excess of carboxylic acid (here we report reactions with pivalic acid) then a source of the second metal is added (typically the carbonate or chloride salt), and the mixture is heated to 140 °C or 160 °C. The products are precipitated by addition of acetone or MeCN and can be crystallized from a range of solvents such as hexane, ethyl acetate, toluene or mixtures of solvents. A typical synthesis is detailed in the footnote‡ and details of all syntheses are given as supplementary information.

Previously we have chosen secondary amines with linear alkyl chains, *e.g.* NH^nPr_2 – which give $\{Cr_7Ni\}$ rings[4] – and branched alkyl chains, *e.g.* $NH(cy\text{-}C_6H_{11})_2$ – which give $\{Cr_8Ni\}$ rings.[5] If we use a tertiary amine, $NEt(cy\text{-}C_6H_{11})_2$, $[HNEt(cy\text{-}C_6H_{11})_2][Cr_9NiF_{12}(O_2CCMe_3)_{18}]$ **1** can be crystallized in *ca.* 20% yield.‡ X-ray studies§ show formation of a decanuclear ring (Fig. 1). Eight of the edges of the decagon are bridged by two pivalates and one fluoride while two are bridged by two fluorides and a single carboxylate. Therefore, unlike the octanuclear rings, the metal ions do not lie on the vertices of a regular polygon.

There are two distinct metal coordination environments: six M ions are bound to two F- and four O-atoms, while four are bound to three F- and three O-atoms. Structural studies do not clearly differentiate a unique Ni site (as is true of all structures reported here), but we believe the Ni ions are disordered between the four M-sites with the 3F and 3O coordination spheres. The protonated tertiary amine lies at the centre of the heterometallic wheel, and forms a single H-bond to an F-atom in one of the two edges bridged by two fluorides and a single carboxylate. The tertiary ammonium template therefore changes the nuclearity and modifies the bridging in the ligand backbone.

Using $NMe(cy\text{-}C_6H_{11})_2$ two decametallic wheels can be separated and crystallised,§ differing in the number of Ni centres in the ring. The first is $[HNMe(cy\text{-}C_6H_{11})_2][Cr_9NiF_{12}(O_2CCMe_3)_{18}]$ **2**, while the second complex is $[HNMe(cy\text{-}C_6H_{11})_2]_2[Cr_8Ni_2F_{12}(O_2CCMe_3)_{18}]$ **3**; in **2** the protonated amine is localized in the wheel, while in **3** a second protonated amine is found in wide channels between the anions. **2** and **3** have very different solubilities and polarities that allow them to be separated

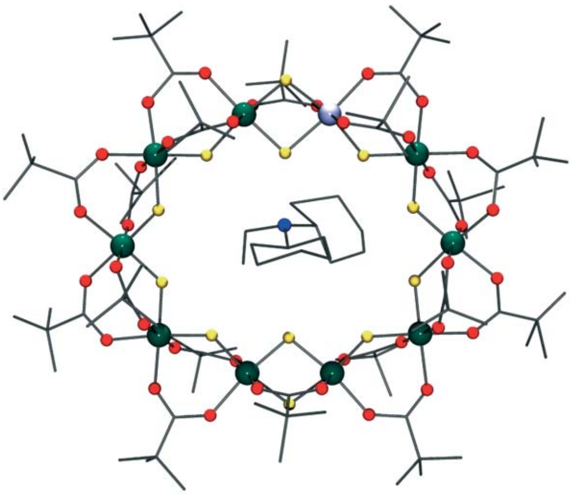

Fig. 1 Structure of **1** in the crystal. The Ni site is disordered. Colours: Cr, dark green; Ni, light grey; O, red; N, blue; F, yellow; C, grey lines.

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† Electronic supplementary information (ESI) available: details of syntheses. See http://dx.doi.org/10.1039/b504912a

by fractional crystallization and/or chromatography. The anionic structure appears identical in both cases to that of **1** (Fig. 1).

If $NH^tBu^{is}Pr$ is used, and the second metal is Cd^{2+}, a nonametallic wheel $[H_2N^tBu^{is}Pr][Cr_8CdF_9(O_2CCMe_3)_{18}]$ **4** was isolated (Fig. 2); while we have reported a nonanuclear $\{Cr_8Ni\}$ wheel previously,[5] this is the first occasion where we have a full crystal structure determination for this ratio of metals. The Cd position here also appears to be ordered, and the Cd is found attached to the F-bridges that H-bond to the protonated amine. If Ni^{2+} is the second metal we find an equivalent nonametallic wheel $[H_2{}^tBuN^{is}Pr][Cr_8NiF_9(O_2CCMe_3)_{18}]$ **5** as the major product, but we also crystallise, in low yield, a decametallic ring $[H_2N^tBu^{is}Pr][Cr_9NiF_{10}(O_2CCMe_3)_{20}]$ **6** (Fig. 3)§. In these structures all M···M edges are bridged by one fluoride and two pivalates. For the slightly smaller nickel ion it appears that the decametallic ring is a possible product as well as the nonametallic wheel found exclusively for cadmium. This suggests the balance between wheel structures can be very fine for specific templates.

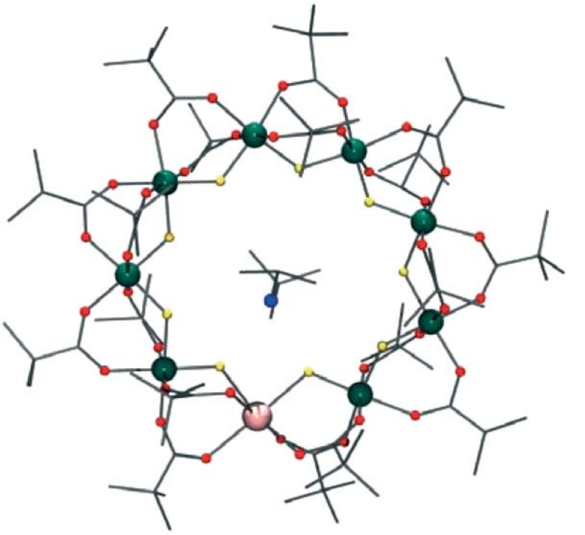

Fig. 2 Structure of **4** in the crystal. Colours as Fig. 1, plus Cd, pink.

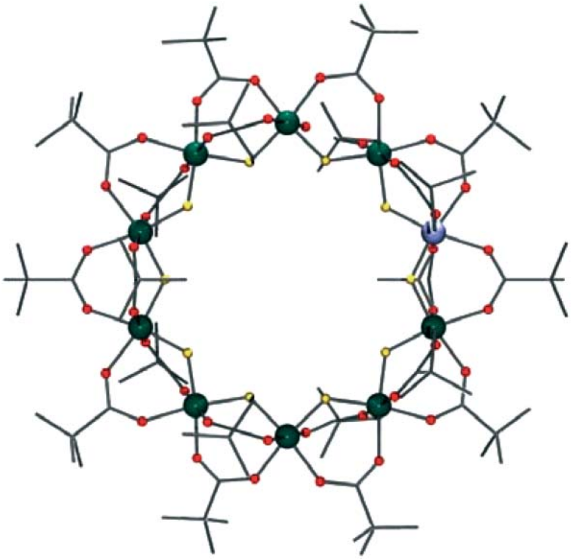

Fig. 3 Structure of **6** in the crystal. Colours as Fig. 1. The amine template is impossible to refine due to severe disorder.

We could study still further saturated amine templates, but we felt it worth looking at templates involving N-atoms in an unsaturated environment. With imidazole (imid) we can make a further octa- and nona-nuclear wheels, with the difference that in both cases two imidazolium templates are closely bound to dianionic rings; with saturated amines we normally see mono-anionic rings. $[Himid]_2[Cr_6Ni_2F_8(O_2CCMe_3)_{16}]$ **7**, an octanuclear compound, and $[Himid]_2[Cr_8NiF_{11}(O_2CCMe_3)_{17}]$ **8** (Fig. 4),§ a nonanuclear ring, are products of one synthesis. They have different solubilities in hexane which allows them to be separated by extraction and crystallization. While **7** is a regular metal octagon, with each edge bridged in an equivalent manner, in **8** eight of the edges of the metal ring are bridged by two pivalates and a fluoride, while one is bridged by a single fluoride and a carboxylate. Each of the two M ions in this edge has a single terminal fluoride attached to it, and these fluorides form H-bonds to the templating imidazolium; the N···F distance for these bonds (2.66 Å) is shorter than the N···F distances for the H-bonds in other heterometallic wheels. The second N-atom of the imidazolium is also involved in a H-bond, this time to a bridging fluoride and the N···F distance is more typical (2.84 Å). There is also a significant π–π stacking interaction between the imidazolium rings, *e.g.* the centroid of one ring lies 3.35 Å above one of the N-atoms of the second.

N-methylimidazole (Meimid) and *N*-^{n}butylimidazole (Buimid) give decanuclear rings $[HRimid]_2[Cr_8Ni_2F_{12}(O_2CCMe_3)_{18}]$ (R = Me **9**, R = ^{n}Bu **10**), again with two imidazoliums found inside the wheel (Fig. 5).§ The interactions are similar to those in **7** and **8**, but with a slightly greater distance between the imidazolium rings (3.58 Å in **9** and 3.54 Å in **10** for centroid – alkylated N-atom). These results show that the products of these reactions are not restricted to saturated amine templates, but that potentially heterocycles can be used. Perhaps more intriguingly, it suggests that different classes of N-containing templates stabilise rings of different overall charge, allowing introduction of more than one

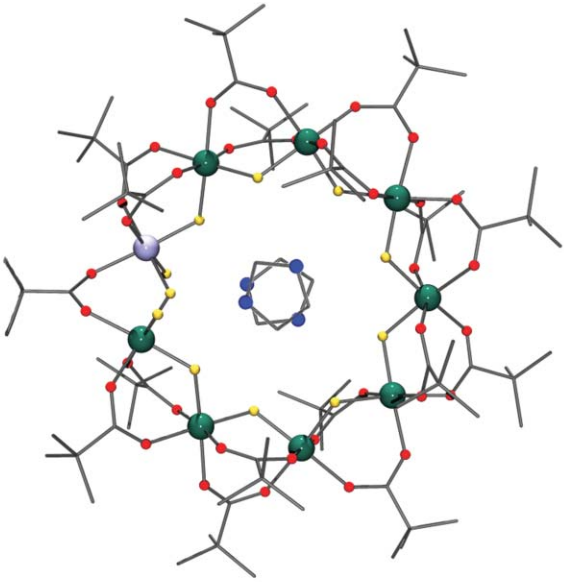

Fig. 4 Structure of **8** in the crystal. Colours as Fig. 1.

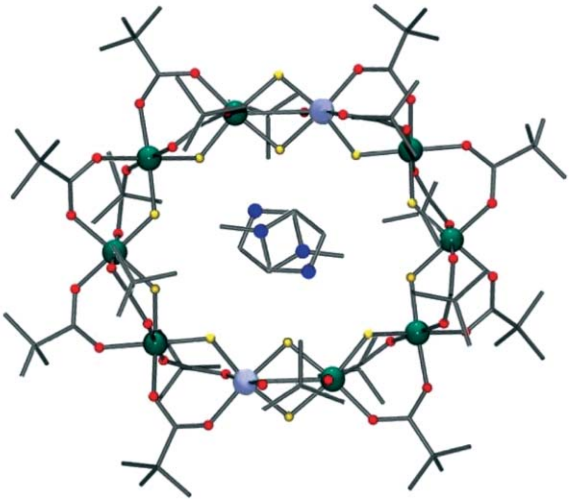

Fig. 5 Structure of **9** in the crystal. Colours as Fig. 1.

heterometal or leading to different arrangements of ligands around the ring backbone. Conceptually perhaps the most intriguing idea is to use a bifunctional template containing an imidazole group on one end and an amine on the other; this should allow us to link different rings in a controlled manner.

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Notes and references

‡ Elemental analysis (C, H, N and both metals) confirms the identity of all the compounds discussed here. Supplementary data includes synthetic details for **1**–**10**. The synthesis of **1** is given as a representative example: $CrF_3{\cdot}4H_2O$ (5.0 g, 28 mmol), *N*-ethyldicyclohexylamine, $(cy\text{-}C_6H_{11})_2NEt$ (2.47 g, 11.8 mmol), $2NiCO_3{\cdot}3Ni(OH)_2{\cdot}4H_2O$ (0.5 g, 0.9 mmol) and Me_3CCO_2H (15.0 g, 147 mmol) were heated while stirring at 140 °C for 8.0 h. The flask was cooled to room temperature and acetone (50 ml) was added and stirred for 15 min. The microcrystalline product was filtered, washed with a large quantity of acetone, dried in air, and then dissolved in hot hexane (100 ml), filtered and the filtrate evaporated to dryness. The product was crystallized from a THF/toluene mixture by slow cooling of the solution and partial evaporation of the solvents. The crystals rapidly desolvate giving a green powder. Yield 1.45 g (17%, calculated from $CrF_3{\cdot}4H_2O$). Elemental analysis (%): calcd for $C_{104}H_{190}Cr_8F_{12}N_1NiO_{36}$: Cr 16.80, Ni 2.11, C 44.85, H 6.88, N 0.50, F 8.19; found: Cr 17.08, Ni 2.10, C 44.77, H 7.17, N 0.47, F 8.32. Electrospray mass spectroscopy (ES-MS) (sample dissolved in THF, run in MeOH) *m*/*z*: − 2574 $[M - NHEt(cy\text{-}C_6H_{11})_2]^-$; + 2807 $[M + Na]^+$.

§ Crystal data for $C_{108}H_{198}Cr_9F_{12}NNiO_{37}$, **1**: monoclinic, *C*2, $a = 31.133(2)$, $b = 17.213(1)$, $c = 32.873(2)$ Å, $\beta = 112.945(1)°$, $V = 16222.6(17)$ Å^3, $M = 2857.6$, $R1 = 0.103$. Crystal data for $C_{104}H_{199}Cr_9F_{12}NNiO_{40}$, **2**: monoclinic, $P2_1/n$, $a = 19.9340(12)$, $b = 16.0192(11)$, $c = 26.2060(17)$ Å, $\beta = 90.054(5)°$, $V = 8368.3(9)$ Å^3, $M = 2858.4$, $R1 = 0.144$. Crystal data for $C_{116}H_{214}Cr_8F_{12}N_2Ni_2O_{36}$, **3**: monoclinic, $I2/a$, $a = 26.003(3)$, $b = 19.882(2)$, $c = 31.266(3)$ Å, $\beta = 102.99(1)°$, $V = 15751(3)$ Å^3, $M = 2974.31$, $R1 = 0.068$. Crystal data for $C_{97}H_{182}CdCr_8F_9NO_{37}$, **4**: monoclinic, $P2_1/n$, $a = 19.3987(8)$, $b = 22.2606(8)$, $c = 31.3094(14)$ Å, $\beta = 91.663(4)°$, $V = 13514.5(10)$ Å^3, $M = 2653.8$, $R1 = 0.123$. Crystal data for $C_{107}H_{197}Cr_9F_{10}NNiO_{40}$, **6**: orthorhombic, *Cmca*, $a = 32.686(3)$, $b = 20.8976(19)$, $c = 22.154(2)$ Å, $V = 15132(2)$ Å^3, $M = 2854.4$, $R1 = 0.149$. Crystal data for $C_{91}H_{167}Cr_8F_{11}N_4NiO_{37}$, **7**: trigonal, *P*-3*c*1, $a = 36.0766(12)$, $c = 19.0328(7)$, $V = 21442.7(13)$ Å^3, $M = 2591.0$, $R1 = 0.126$. Crystal data for $C_{89}H_{159}Cr_6F_8N_4Ni_2O_{32}$, **8**: monoclinic, $P2_1/c$, $a = 24.9758(6)$, $b = 16.6444(5)$, $c = 31.0706(9)$ Å, $\beta = 111.149(2)°$, $V = 12.046.3(6)$ Å^3, $M = 2421.7$, $R1 = 0.0620$. Crystal data for $C_{100}H_{183}Cr_8F_{12}N_4Ni_2O_{39}$, **9**: monoclinic, $P2_1/n$, $a = 20.328(2)$, $b = 17.410(2)$, $c = 23.585(2)$ Å, $\beta = 114.734(9)°$, $V = 7581.2(14)$ Å^3, $M = 2798.9$, $R1 = 0.150$. Crystal data for $C_{104}H_{186.5}Cr_8F_{12}N_4Ni_2O_{36.75}$, **10**: monoclinic, $P2_1/n$, $a = 12.5916(19)$, $b = 21.808(3)$, $c = 27.727(4)$ Å, $\beta = 93.890(3)°$, $V = 7596.2(2)$ Å^3, $M = 2832$, $R1 = 0.1248$. CCDC 231872 and 268355–268362. See http://dx.doi.org/10.1039/b504912a for crystallographic data in CIF or other electronic format.

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