

Chemistry and supramolecular chemistry of chromium horseshoes†‡§

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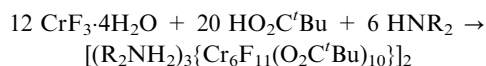
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Synthetic and structural studies of Cr horseshoes are reported which show that these compounds demonstrate a rich supramolecular chemistry through H-bonding interactions, and can act as ligands for metal clusters.

Our interest in the formation of heterometallic rings¹ has led us to examine carefully the reaction of hydrated chromium trifluoride with carboxylic acids in the presence of amines. Our thought was that H-bonding of protonated amines to terminal fluoride groups prevented formation of a homometallic [CrF(O₂CR)₂]₈ ring,² creating a solution containing a mixture of Cr_x chains. Given the great interest in H-bonded structures³ we were curious whether we could involve such chains in supramolecular arrays. We were also interested to see if individual chains, which have six terminal fluoride ligands, could also act as polydentate fluoride donor ligands towards hard metals.

Previously we have reported⁴ that hexametallc horseshoes can be made from:



R = Et **1** or ⁿPr **2**, and yields >70%. We have therefore examined what happens if we change the secondary amine added to this reaction. If diisopropylamine is used we can make

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‡ Elemental analysis (C, H, N, F and all metals) confirm the identity of all the compounds discussed here.

§ Crystal data: C₁₅₇H₃₁₆Cr₁₄F₂₄N₆O₄₉, **3**: monoclinic, *P* 2₁/*n*, *a* = 27.106(2), *b* = 32.551(3), *c* = 27.3129(19) Å, β = 93.509(6)°, *V* = 24 054(3) Å³, *M* = 4256.2, *D*_c = 1.175 g cm⁻³, *Z* = 4 (reported for a dimer of horseshoes), *R*₁ = 0.0986 for 10 288 reflections; C₇₈H₁₆₂Cr₃F₈N₃O₁₂, **4**: triclinic, *P*1̄, *a* = 16.835(5), *b* = 17.057(5), *c* = 18.219(5) Å, α = 71.765(5), β = 85.874(5), γ = 72.304(5)°, *V* = 4732(2) Å³, *M* = 1642.1, *D*_c = 1.152 g cm⁻³, *Z* = 2, *R*₁ = 0.0892 for 6440 reflections; C₂₂₄H₄₆₆Cr₂₄F₄₄N₁₂O₉₀, **5**: triclinic, *P*1̄, *a* = 16.709(3), *b* = 23.500(5), *c* = 25.771(5) Å, α = 78.41(3), β = 76.04(3), γ = 71.68(3)°, *V* = 9236(3) Å³, *M* = 6852.1, *D*_c = 1.232 g cm⁻³, *Z* = 1, (reported for a tetramer of horseshoes), *R*₁ = 0.0943 for 12 547 reflections; C₆₄H₁₀₆Cr₆F₁₉NO₂₄, **6**: monoclinic, *P* 2₁/*c*, *a* = 28.7650(5), *b* = 15.4800(3), *c* = 22.2360(8) Å, β = 91.7810(8)°, *V* = 9896.5(4) Å³, *M* = 1946.5, *D*_c = 1.306 g cm⁻³, *Z* = 4, *R*₁ = 0.0818 for 4795 reflections; C₂₁₅H_{402.5}Cr₂₅F₅₀N_{6.5}Na₁₄O₈₇, **7**: monoclinic, *P* 2₁/*n*, *a* = 23.4569(11), *b* = 20.8495(10), *c* = 41.501(2) Å, β = 104.1300(10)°, *V* = 19 682.6(17) Å³, *M* = 7042.8, *D*_c = 1.188 g cm⁻³, *Z* = 2, *R*₁ = 0.1022 for 11 616 reflections. CCDC 668927–668931.

[(ⁿPr₂NH₂)₃{Cr₇F₁₂(O₂C^tBu)₁₂}]₂ **3** in 20% yield. This compound contains heptanuclear Cr^{III} chains linked by H-bonding into a dimeric suprastructure (Fig. 1). The chains are bent into “horseshoes”, and can be regarded as fragments of the complete rings, missing a metal site to complete an octanuclear wheel. The Cr···Cr edges in the structure are all bridged by a single fluoride and two pivalate groups. The Cr groups at the end of the horseshoes have three terminal fluoride groups attached to them. An ⁿPr₂NH₂ cation is found at the centre of each horseshoe, and four ⁿPr₂NH₂ groups are involved in H-bonds with the terminal fluorides, leading to the dimer.

If di-*n*-octylamine is used in this reaction we can crystallise two products. A dimeric {Cr₆} horseshoe structure similar to **1** can be made in 33% yield; the long alkyl chains of the diammonium salt leads to a poor quality X-ray structure, but the metal connectivity is clear. In lower yield (7%) we isolate a polymer of chains: {[(C₈H₁₅)₂NH₂]₃Cr₃F₈(O₂C^tBu)₄(HO₂C^tBu)₂]_{*n*} **4** (Fig. 2). The structure of the anion consists of a bent array of three chromium centres, with both Cr···Cr edges bridged by a μ-F and two bridging pivalates. The two terminal Cr sites each have three terminal fluorides attached to them. The ammonium cations have two distinct roles; one H-bonds to the bridging fluorides within the trimetallic units while two bridge between terminal fluorides linking the trinuclear chains into a polymer.

The horseshoes within compounds **1–4** all belong to the general formula, [Cr_{*x*}F_{*x*+5}L_{2*x*-2}]_{*n*}³⁻; while we have isolated *x* = 3, 6 and 7 our supposition is that the solution contains an equilibrium mixture of chains, and that separation and crystallisation leads us to isolating specific horseshoes. The equilibrium is presumably dynamic, with exchange of metal ions between different chains. Isolation of **4**, rather than *x* = 4 or 5, is therefore due to ideal crystallisation conditions.

If dimethylamine is used the product contains the hexametallc horseshoes, but they are linked into a tetrahorseshoe

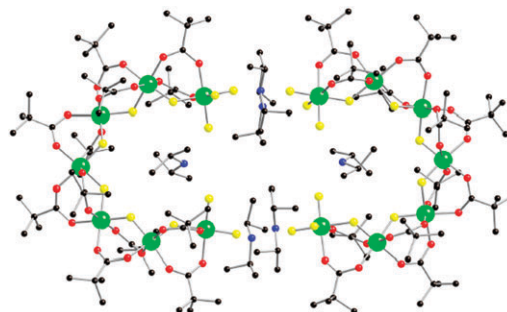


Fig. 1 The structure of **3** in the crystal. Colours: Cr, green; O, red; F, yellow; N, blue; C, black. H, not shown.

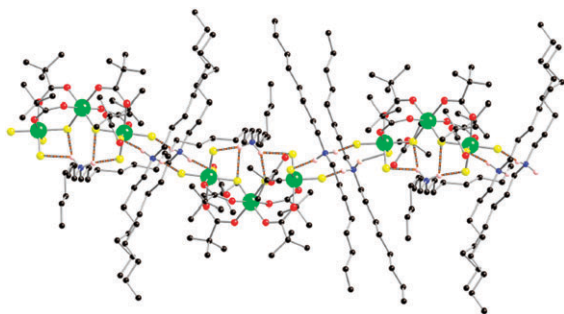


Fig. 2 The structure of **4** in the crystal. Colours as Fig. 1.

assembly $\{[\text{Me}_2\text{NH}_2][\text{Cr}_6\text{F}_{11}(\text{O}_2\text{C}^t\text{Bu})_{10}]\}_4$ **5** (Fig. 3). The horseshoes themselves are very similar to those in **1** and **2**, with a single dimethylammonium cation at the centre of each horseshoe. However in **5** the H-bonding involving the terminal fluoride groups is much more extensive, leading to a tetramer. The eight Me_2NH_2 cations involved in linking horseshoes lie on the vertices of a distorted square antiprism. The formation of the tetramer is presumably favoured by the short chain diamine; with a longer alkyl chain it would be impossible to accommodate the central assembly of ten amines. Variation in alkyl chain therefore allows us to isolate different chain lengths, and to vary the supramolecular assembly of the horseshoes.

We were also interested to see if we could use the terminal fluorides as ligands for other metals, *i.e.* establish that the horseshoes could be used as “cluster ligands”. Given the highly fluorophilic nature of the lanthanides and their large ionic radii we thought they might be ideal subjects for binding. Therefore we reacted **1** with $\{\text{Ln}(\text{hfac})_3\text{-diglyme}\}$ ($\text{Ln} = \text{La}, \text{Ce}, \text{Pr}$; $\text{hfac} = 1,1,1,5,5,5\text{-hexafluoroacetylacetonate}$). This gives $\{[\text{Et}_2\text{NH}_2][\text{Cr}_6\text{F}_7(\text{O}_2\text{C}^t\text{Bu})_{10}(\text{hfac})_2]\}_2$ **6** in yields of 55–65%, depending on the Ln used. **6** can be made more directly, and in a yield of 91%, by reaction of **1** with Hhfac . Other β -diketonates can also be included in analogous compounds by the reaction:

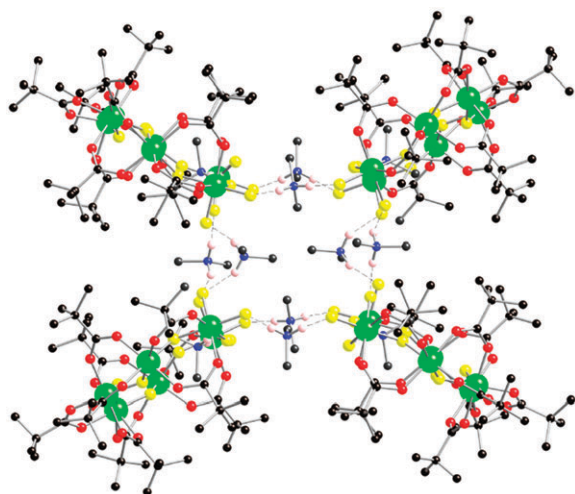
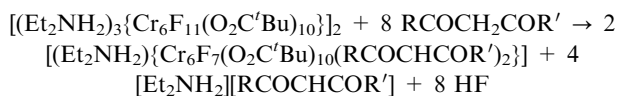


Fig. 3 The structure of **5** in the crystal. Colours as Fig. 1.

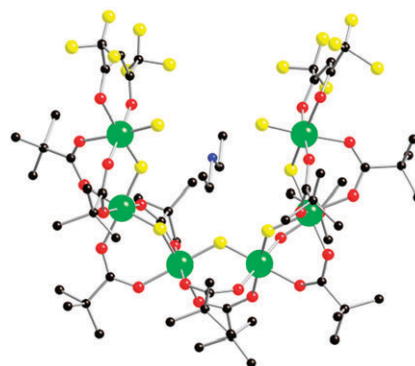


Fig. 4 The structure of **6** in the crystal. Colours as Fig. 1.

The structure of **6** (Fig. 4) shows that at each terminal Cr centre two of the three terminal fluorides have been displaced by hfac ligands. This reduces the possibility of H-bonding, and makes the horseshoe into a monoanion. Therefore the ammonium cation found at the centre of the horseshoe is sufficient to balance charge, and the result is that no H-bonding between horseshoes is found, and a mono-horseshoe compound results.

This result encouraged us to look at other substitution reactions at the terminal fluorides. Therefore **1** was reacted with a series of sodium salts of pseudo-halides. Reaction with both NaN_3 and NaOCN produced crystals of a totally unexpected compound which is consistent with our original idea that the horseshoe could act as a ligand. $\{[\text{NH}_2\text{Et}_2]\{\text{CrNa}_{14}\text{F}_6(\text{H}_2\text{O})_{10}\}\{\text{Cr}_6\text{F}_{11}(\text{O}_2\text{C}^t\text{Bu})_{10}\}_4\}$ **7** can be crystallised in 88% yield. The structure (Fig. 5) shows the formation of a heterometallic $\{\text{CrNa}_{14}\}$ cage surrounded by four $\{\text{Cr}_6\}$ horseshoes; the Cr from the heterometallic cage lies on an inversion centre. Twelve of the fourteen Na centres lie on the vertices of a distorted icosahedron, and are bound to a central CrF_6^{3-} octahedron (Fig. 6). These Na sites are also bound to terminal fluorides from the four $\{\text{Cr}_6\}$ horseshoes. The coordination geometries about each Na is irregular; three of these Na sites

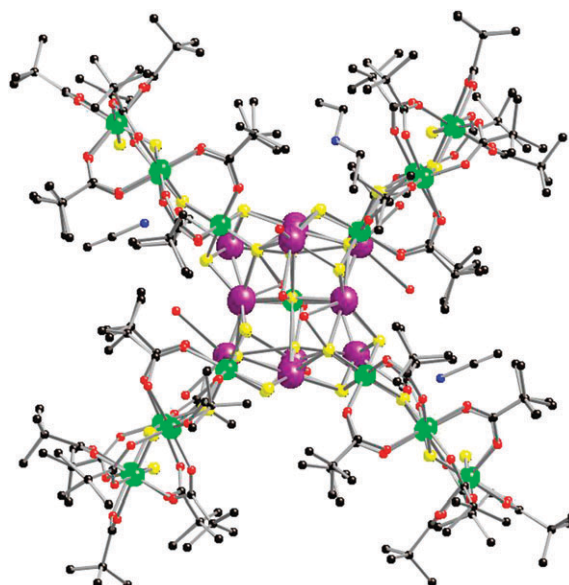


Fig. 5 The structure of **7** in the crystal. Colours as Fig. 1; Na purple.

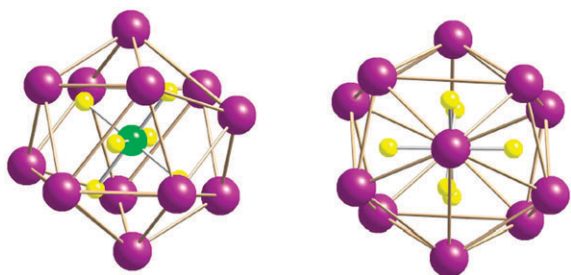


Fig. 6 Two views of the central Na icosahedron in **7** showing the central CrF_6 unit. Colours as Fig. 5.

are seven coordinate—bound to one O- and six F-donors, and three six-coordinate—with two of these sites having a six fluoride donor-set, and the other having five F and one MeCN ligand attached to it. Cages of alkali metals are well-known⁵ but we are unaware of a previous report of a sodium icosahedron.

The other two Na sites are disordered and are attached to the central icosahedron through one μ_4 - and two μ_3 -fluorides. These sites are five-coordinate. Unlike in the other structures involving horseshoes there is no ammonium cation at the centre of the horseshoes. The fluorides show four different bridging modes: μ_2 -bridging for the fluorides within the horseshoe, μ_3 or μ_4 for the terminal fluorides of the horseshoe and μ_5 for the fluorides of the central octahedron. Perhaps the most extraordinary aspect of this structure is that this is crystallised in very high yield after the compound is passed down a chromatographic silica column. **7** seems to carry the Na ions with the Cr horseshoes in a fairly robust supramolecule.

Compound **7** was isolated in high yield after purification by column chromatography on a silica gel. This suggests **7** carries the Na ions with the Cr horseshoes in a fairly robust supramolecule. To prove the solution stability of the array, the mass spectroscopy of **7** was studied. Although electrospray measurements did not allow the observation of the intact cluster, cryospray^{6,7} mass spectrometric experiments on **7** in THF/CH₃CN (70 : 30) at -40°C showed the supramolecular assembly is present as a dication (Fig. 5). The parent cluster ion can be found in two overlapping envelopes centered at a m/z of ca. 3410.2.⁸ Two species can be identified that are related to the parent cluster. Both species are doubly charged and the observed pattern corresponds to: (i) $\text{C}_{204}\text{H}_{390}\text{N}_1\text{Cr}_{25}\text{F}_{48}\text{Na}_{14}\text{O}_{89}$, *i.e.* the molecular species – H_2O , – 2F: actual (3408.7) observed (3408.5); and (ii) $\text{C}_{204}\text{H}_{388}\text{N}_1\text{Cr}_{25}\text{F}_{50}\text{Na}_{14}\text{O}_{87}$ (*i.e.* the molecular species – H_2O , – 2OH: actual (3410.8) observed (3410.5). There is a $\Delta = 0.3$ between the observed and calculated spectra. CS-MS in water or methanol does not show the molecular ion, which suggests that **7** is only stable in non-polar solvents (Fig. 7).

There are many cases reported where individual Na centres link polymetallic 3d-metal complexes; recent examples include a $[\text{Mn}_{10}\text{Na}]_4$ loop,⁹ or a $[\text{Ni}_8\text{Na}]_2$ cage.¹⁰ Much more rare are examples where a polymetallic alkali metal cage links the 3d-metal cages; the only example we have found is a $\{\text{Na}_6\}$ octahedron linking four Ni heterocubanes.¹¹ However the most unusual aspect of **7** is that the $\{\text{Cr}_6\}$ horseshoe acts as

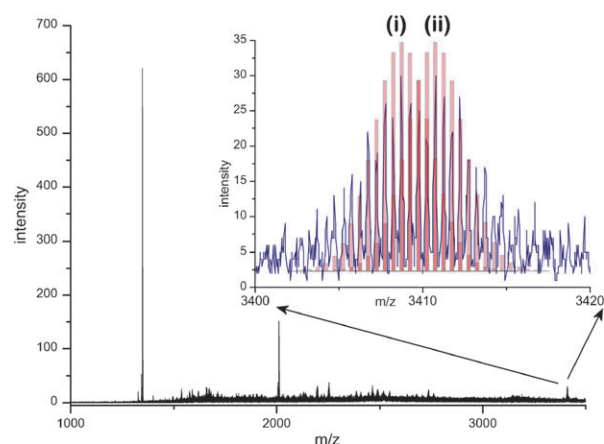


Fig. 7 CS-MS of **7** at -40°C in THF/CH₃CN (70 : 30) between 1000 and 3500 m/z . The insert shows the molecular ion between 3400–3420 m/z . Two species can be clearly identified as being related to the parent cluster (blue spectrum); isotropic distributions calculated for species discussed in the text are shown by the faded red columns.

a polynucleating fluoride donor and that the resulting supramolecular assembly has significant solution stability. CS-MS is the only tool currently available that could demonstrate this structural integrity. Previous polydentate fluoride donors for sodium include a macrocyclic ligand designed by Takemura *et al.*¹² In the future we will examine whether this behaviour is restricted to alkali metal ions, or whether clusters of d-block metals can be assembled using this cluster-ligand.

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