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 rings\(^1\) has led us to examine carefully the reaction of hydrated chromium tri fluoride 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\(_2\)(O\(_2\)CR)]\(_2\) ring,\(^5\) creating a solution containing a mixture of Cr\(_3\) chains. Given the great interest in H-bonded structures\(^3\) 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 reported\(^4\) that hexametallic horseshoes can be made from:

\[
12 \text{CrF}_3 \cdot 4\text{H}_2\text{O} + 20 \text{ HO}_2\text{C} \cdot \text{Bu} + 6 \text{HNR}_2 \rightarrow \left[ (\text{R}_2\text{NH}_2)_3\{\text{Cr}_3\text{F}_8\text{(O}_2\text{C} \cdot \text{Bu})_{10}\} \right]_2
\]

R = Et or \(\text{Pr}_2\text{NH}_2\), and yields > 70%. We have therefore examined what happens if we change the secondary amine added to this reaction. If dimethylpropylamine is used we can make \(\left[(\text{Pr}_2\text{NH}_2)_3\{\text{Cr}_3\text{F}_8\text{(O}_2\text{C} \cdot \text{Bu})_{12}\} \right]_2\ 3\) in 20% yield. This compound contains heptanuclear Cr\(^{II}\) chains linked by H-bonding into a dimeric superstructure (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\(_3\) \(\cdot\) 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 \(\text{Pr}_2\text{NH}_2\) cation is found at the centre of each horseshoe, and four \(\text{Pr}_2\text{NH}_2\) groups are involved in H-bonds with the terminal fluorides, leading to the dimer.

If \(\text{di-n-octylamine}\) is used in this reaction we can crystallise two products. A dimeric \(\{\text{Cr}_9\}\) horseshoe structure similar to \(\text{I}\) 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: \((\text{C}_6\text{H}_5\text{NH}_3\cdot\text{Cr}_3\text{F}_8\text{(O}_2\text{C} \cdot \text{Bu})_6}\) \(\text{HO}_2\text{C} \cdot \text{Bu})_2\) \(\text{I}\) (Fig. 2). The structure of the anion consists of a bent array of three chromium centres, with both Cr\(_3\) \(\cdot\) Cr edges bridged by a \(\mu\)-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 trinetallic units while two bridge between terminal fluorides linking the trinetallic chains into a polymer.

The horseshoes within compounds 1–4 all belong to the general formula, \(\{\text{Cr}_x\text{F}_y\text{+}_x\cdot\text{I}_{2-x}\text{=}\_3\}^{3+}\); 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 hexametallic horseshoes, but they are linked into a tetrahorseshoe

\[
[(\text{Pr}_2\text{NH}_2)_3\{\text{Cr}_3\text{F}_8\text{(O}_2\text{C} \cdot \text{Bu})_{12}\} \right]_2
\]

\[
[(\text{Pr}_2\text{NH}_2)_3\{\text{Cr}_3\text{F}_8\text{(O}_2\text{C} \cdot \text{Bu})_{12}\} \right]_2
\]
assembly $\{[\text{Me}_2\text{NH}_2][\text{Cr}_6\text{F}_{11}(\text{O}_2\text{C}^{\text{tBu}})_{10}]\}_4$ 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$_2$NH$_2$ 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 $\{\text{Ln(hfac)}_3,\text{diglyme}\}$ ($\text{Ln} = \text{La, Ce, Pr}$; hfac = 1,1,1,5,5,5-hexafluoroacetylacetonate). This gives $\{[\text{Et}_2\text{NH}_2][\text{Cr}_6\text{F}_{11}(\text{O}_2\text{C}^{\text{tBu}})_{10} \text{hfac})_2]\}_6$ 6 in yields of 55–65%, depending on the Ln used. 6 can 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:

$$[\text{Et}_2\text{NH}_2][\text{Cr}_6\text{F}_{11}(\text{O}_2\text{C}^{\text{tBu}})_{10}]_2 + 8 \text{RCOCH}_2\text{COR}' \rightarrow 2$$
$$[\text{Et}_2\text{NH}_2][\text{Cr}_6\text{F}_{11}(\text{O}_2\text{C}^{\text{tBu}})_{10}(\text{RCOCHCOR'})_2] + 4$$
$$[\text{Et}_2\text{NH}_2][\text{RCOCHCOR'}'] + 8 \text{HF}$$

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. $\{[\text{Et}_2\text{NH}_2][\text{Cr}_6\text{F}_{11}(\text{H}_2\text{O})_{10}]_4[\text{Cr}_6\text{F}_{11}(\text{O}_2\text{C}^{\text{tBu}})_{10}]_4\}_7$ 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$_6$ 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
are seven coordinate—bound to one O- and six F-donors, and
six three-coordinate—with two of these sites having a six
flouride donor-set, and the other having five F and one McCN
ligand attached to it. Cages of alkali metals are well-known 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 μ₂- and two μ₃-fluorides. These
sites are five-coordinate. Unlike in the other structures involving
horseshoe there is no ammonium cation at the centre of the
horseshoe. The fluorides show four different bridging modes:
μ₂-bridging for the fluorides within the horseshoe, μ₃ or μ₄ for
the terminal fluorides of the horseshoe and μ₅ 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 supra-
molecule. To prove the solution stability of the array, the mass
spectroscopy of

\[
\text{molecule.}
\]

to prove the solution stability of the array, the mass
spectrometric experiments on 7 in THF/CH₂CN (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. Two species can be identified that are related to the parent cluster. Both species are doubly charged and the observed pattern corresponds to: (i)
\[
C_{203}H_{390}N_{13}Cr_{25}F_{48}Na_{14}O_{89}, \text{ i.e. the molecular species} - H_2O, - 2F: \text{actual (3408.7) observed (3408.5)};
\]
and (ii)
\[
C_{203}H_{388}N_{13}Cr_{25}F_{50}Na_{14}O_{87} \text{ (i.e. the molecular species} - H_2O, - 2OH: \text{actual (3410.8) observed (3410.5). There is a} \Delta = 0.3 \text{ 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 [Mn₄₀Na₄] loop,\(^9\) or a [Ni₄Na]\(^{2+}\) cage.\(^{10}\) Much more rare are examples where a polymetallic alkaline metal cage links the 3d-metal cages; the only example we have found is a [Na₄] octahedron linking four Ni heterocubanes.\(^{11}\) However the most unusual aspect of 7 is that the [Cr₉₁] horseshoe acts as

a polynucleating fluoride donor and that the resulting supra-
molecular 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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