Cage Compounds

Horseshoes, Rings, and Distorted Rings: Studies of Cyclic Chromium-Fluoride Cages**

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We recently reported the first heterometallic rings, $[NH_2R_2][Cr_7MF_8(O_2CCMe_3)_{16}]$ (R = a range of alkyl side chains; M = Ni^{II}, Co^{II}, Fe^{II}, Mn^{II}, or Cd^{II}),[1] based on the neutral homometallic ring, $[Cr_8F_8(O_2CCMe_3)_{16}]$ **1**.[2] These cyclic structures are interesting because they are antiferromagnetically coupled rings, but have a resulting ground state spin. This should allow studies of the dynamics in antiferromagnetic rings, which are often used as models for 1D antiferromagnets.[3] It has also been suggested that such compounds should show macroscopic quantum coherence.[4]

The heterometallic complexes are isolable based on the simple principle that replacement of a single Cr^{III} ion in **1** by a dication generates a ring that is a monoanion.[1] Therefore, in the presence of a suitable counterion—provided by a secondary ammonium ion—it is possible to separate the charged heterometallic species from **1**. The synthesis left several questions unanswered: first, what would happen if the reaction was performed under the usual reaction conditions, but in the absence of the second metal? Second, what might result if the second metal could not occupy the octahedral metal coordination sites found in **1** and in the heterometallic rings? Herein we consider both these questions: the answer is of much wider interest because the resulting structures suggest new methods for controlling the shape of cyclic cage complexes, and perhaps future routes to designed polycyclic metal cages.

Complex **1** is formed from reaction of hydrated chromium trifluoride with pivalic acid in the presence of dimethylformamide (DMF), followed by crystallization from a range of solvents.[2] To produce the heterometallic rings,[1] a source of a second metal is required and also the addition of a secondary amine, to act as the cation for the ion pair produced. If only the secondary amine is added, dark green crystals can still be grown; however, the X-ray structural analysis[5] of these crystals reveals the formation of a new structural type (Figure 1).

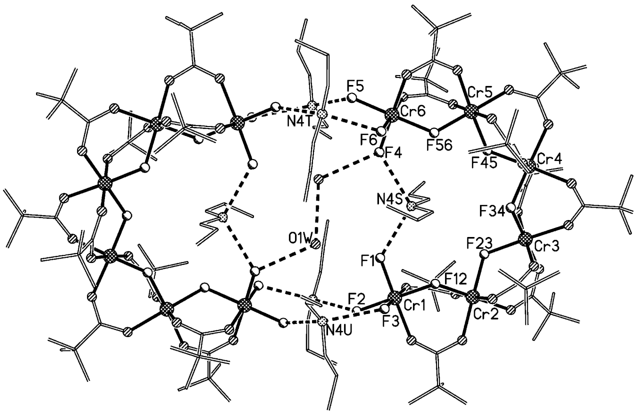

Figure 1. The structure of **2** in the crystal. The hydrogen atoms not involved in hydrogen bonding have been omitted for clarity. Hydrogen bonds are shown as dotted lines. Selected bond-length ranges [Å]: Cr-F(terminal) 1.855–1.883, Cr-F(bridging) 1.899–1.963, Cr(terminal)-O 1.991–2.001, Cr(internal)-O 1.931–1.970; average estimated standard deviation (esd) 0.006 Å. Selected bond angle ranges [°]: *cis* at Cr 86.1–93.3, *trans* at Cr 177.2–179.5; average esd 0.2°.

The general formula for these new cages is $[(R_2NH_2)_3\{Cr_6F_{11}(O_2CCMe_3)_{10}\}sol]_2$ (sol = solvent molecule): here we restrict discussion to R = *n*Pr, sol = H_2O **2** (Figure 1); derivatives have been made with other secondary ammonium ions. The $[Cr_6F_{11}(O_2CCMe_3)_{10}]^{3-}$ horseshoes can be described as derived from **1** by removal of two of the Cr sites. The Cr sites within the horseshoe are bridged by μ_2-F atoms and 1,3-bridging carboxylates in an analogous manner to that found in **1**. The two Cr sites at the tips of the horseshoe have three terminal fluoride ligands, and these terminal fluorides are involved in the hydrogen bonding that links the horseshoes. Two fluoride ions on each chromium hydrogen bond to H atoms of $[R_2NH_2]^+$ ions, which lie between the tips of the horseshoes. These eight F···H–N bonds therefore create a dodecanuclear pseudo-macrocycle. The third fluoride ion on each terminal Cr site is involved in an additional hydrogen-bonding interaction. These four fluoride ions accept hydrogen bonds from two further $[R_2NH_2]^+$ ions that are encapsulated within the pseudo-macrocycle.

Two water molecules are encapsulated within the pseudo-macrocycle (Figure 1). The water molecule hydrogen bonds to two fluoride ligands, with one fluoride ion derived from each of the pair of fluoride ions within the supramolecule. This interaction therefore provides an additional bridge between the two horseshoes. The result is a supramolecule

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consisting of two hexametallic trianions, six ammonium ions, and two water molecules.

The bond lengths to chromium in **2** show two clear trends. First, the Cr−F bonds to the terminal fluoride ligands are significantly shorter (about 1.87 Å) than the Cr−F bonds involving the bridging fluoride ligands (about 1.91 Å). Second, bond lengths to the bridging carboxylate oxygen atoms depend on the position of Cr center. For the terminal chromium sites, the bond lengths are close to 1.99(1) Å, while for the inner chromium atoms the Cr−O bonds average 1.95(1) Å. It is noticeable that the hydrogen bonding only involves the terminal F ligands, and not those that bridge between Cr centers. The N···F distances range between 2.64 Å and 2.73 Å.

If a second metal ion that does not favor a regular octahedral geometry is added, further new structural types are formed. If the second metal ion is vanadyl, one site is blocked by the oxide, thus fewer sites are available for bridging. The resulting cage **3**,[5] from the reaction of chromium trifluoride, pivalic acid, and diethylamine in the presence of vanadyl acetate, is shown in Figure 2. Complex **3** has the formula $[Et_2NH_2][Cr_6(VO)_2F_8(O_2CCMe_3)_{15}]$ and contains an octanuclear core, bridged by eight fluorides as in **1**. The two vanadyl units are next to one another, and bridged by one pivalate in addition to a μ-fluoride ion, whereas all the Cr···Cr and Cr···V vectors are bridged by two pivalates and a fluoride ion. The ring is a monoanion, and encapsulates a secondary ammonium ion as in the $\{Cr_7M\}$ rings. It is noticeable that the V−F bond *trans* to the oxo group is very long (av 2.20 Å) compared to the V−F bonds *cis* to the oxo (av 1.98 Å). The coordination geometry about the V atom is therefore an extremely distorted octahedron, while the Cr^{III} ions have comparatively regular geometries. The relationship between **3** and the "horseshoes" in **2** appears clear: the horseshoe has been completed by the addition of two VO^{2+} ions. The $\{Cr_6(VO)_2\}$ anion can be isolated with other secondary ammonium counterions.

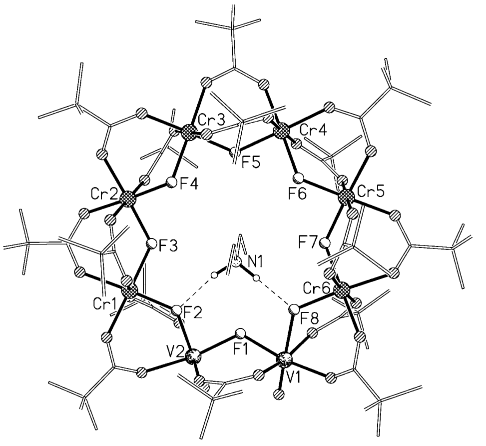

Figure 2. The structure of **3** in the crystal. The hydrogen atoms not involved in hydrogen bonding have been omitted for clarity. Bond-length ranges [Å]: Cr-O(O_2CCMe_3) 1.932–1.980, Cr-F 1.886–1.945 V-O 1.569–1.578, V-O(O_2CCMe_3) 2.006–2.036, V-F 1.979–2.210; average esd 0.006.

If we use basic copper carbonate in the same reaction, the resulting cage is less easily rationalized:[5] $[Me_2NH_2]_2[Cr_{10}Cu_2F_{14}(O_2CCMe_3)_{22}]$ (**4**) contains a distorted dodecanuclear ring in which five Cr^{III} centers lie between the two Cu^{II} centers (Figure 3). The copper(II) centers are five-coordinate, bridged to one Cr^{III} through one fluoride ligand and two pivalates, and to a second Cr^{III} through only one fluoride ion and one pivalate. A terminal fluoride ion (F7) is found on the neighboring chromium. The Cr···Cr vectors are all bridged in an analogous manner to **1**–**3**.

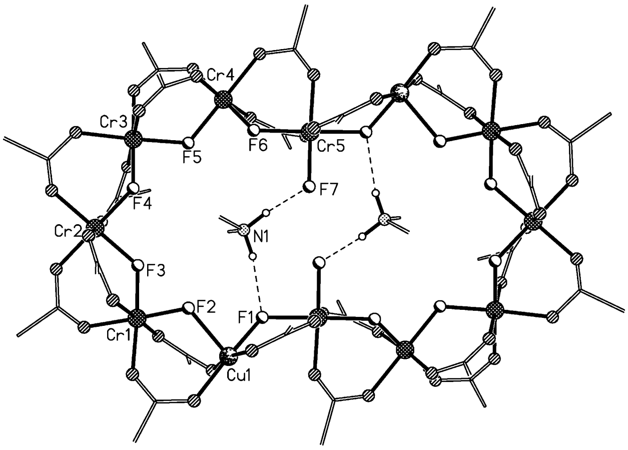

Figure 3. The structure of **4** in the crystal. The hydrogen atoms not involved in hydrogen bonding have been omitted for clarity. Bond-length ranges [Å]: Cr-O(O_2CCMe_3) 1.853–2.013, Cr-F 1.853–1.931, Cu-O(O_2CCMe_3) 1.916–1.957, Cu-F 1.878–2.104; average esd 0.013.

The presence of two dicationic metal ions in the ring makes the ring a dianion. Therefore two secondary ammonium ions are found at the center of the structure. They form hydrogen bonds to the terminal fluoride ions (N···F 2.65 Å), and to the fluoride ion that bridges the Cu^{II} and Cr^{III} centers (N···F 3.03 Å). It is possible that this need to form hydrogen bonds leads to a pronounced distortion of the dodecanuclear ring. In previous dodecanuclear rings, the structure is regular, for example, in $\{Ni_{12}\}$[7] and $\{Co_{12}\}$ rings[8] the molecule has S_6 crystallographic symmetry, while in a recently reported $\{Fe_{12}\}$ ring[9] the array of metal centers has approximate sixfold symmetry. Complex **4** is the first example of a cyclic 3d-metal complex in which there are regions of negative and positive curvature: Müller et al. have stressed that growth of nanoscale polyoxomolybdates (and other nanoscale molecules) may depend on such symmetry breaking.[10] The distortion also suggests that if the two terminal fluoride bridges could be displaced by a single extended bridge it might be possible to convert **4** into a bicyclic system. This would be a first for coordination chemistry.

The next rational extension was to try a metal ion with a preference for tetrahedral geometry, which led us to try Zn^{II}. However, this ion can adopt an octahedral geometry when required and the reaction produced $[NH_2Et_2][Cr_7ZnF_8(O_2CCMe_3)_{16}]$ (**5**; Figure 4), which is the analogue of the heterometallic derivatives of **1**, found with other metal dications.[1] The structure consists of an octametallic ring, with

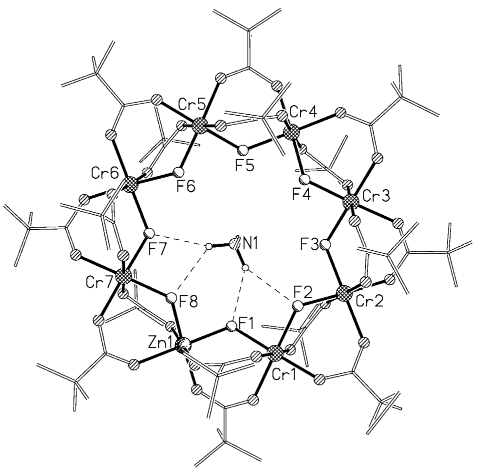

Figure 4. The structure of **5** in the crystal. The hydrogen atoms not involved in hydrogen bonding have been omitted for clarity. Bond length ranges [Å]: Cr-O(O_2CCMe_3) 1.937–1.989, Cr-F 1.915–1.966, Zn-O(O_2CCMe_3) 1.946–1.977, Zn-F 1.940–1.957; average esd 0.0026.

each edge bridged by two fluoride ions and a carboxylate ligand. Unlike in the other heterometallic rings,[1] the Zn^{II} ion may be ordered, with one of the eight octahedral metal sites refining well as a Zn site. The unique site is bound to two fluoride ions that both hydrogen bond to the central ammonium ion: it is noticeable in **3** that the fluoride ions involved in hydrogen bonding are bound to vanadyl centers.

Magnetic studies of the complexes show antiferromagnetic exchange between the paramagnetic metal centers. For **2** the room temperature value of $\chi_m T$ per horseshoe, is around 9.4 emu K mol^{-1}, lower than predicted for six noninteracting $S=3/2$ centers (S = spin angular momentum; calcd for $g=1.99$, 11.1 emu K mol^{-1}; g is the g factor). Complex **2** is diamagnetic at low temperature. For **3** the antiferromagnetic exchange again leads to a diamagnetic ground state; the magnetic behavior has been fitted by using a single exchange parameter, which gives $g=2.007$ and $J=-14.9$ cm^{-1}. The fit is excellent, but clearly the Cr···Cr exchange should be different to the (VO)···(VO) exchange; previously we have found[1,2] that the Cr···Cr exchange is around -12 cm^{-1}. This suggests the (VO)···(VO) exchange is a little larger to obtain an average exchange of -14.9 cm^{-1}. For **5** the magnetic data can be modeled with $g=1.98$, $J=-11.8$ cm^{-1}. However at low temperature the model diverges from the measured values, possibly because intermolecular exchange between the $S=3/2$ spin ground states becomes important.

The magnetic behavior of **4** also suggests a very low spin, probably diamagnetic, ground state. Analysis of the magnetism is complicated because a cyclic $\{Cr_{10}Cu_2\}$ array is too large to be solved by matrix diagonalization. By using an imaginary $\{Cr_8Cu_2\}$ ring as a model allows approximate exchange parameters to be derived; a similar procedure has been used for $\{Fe_{10}\}$ rings previously.[11] By this procedure we derive the Cr···Cr exchange as antiferromagnetic, with a magnitude of -6.8 cm^{-1}. One of the Cr···Cu exchange paths involves the Cu $d_{x^2-y^2}$ orbital in the exchange path, and this exchange is also considered to be -6.8 cm^{-1}. The second Cr···Cu exchange involves the Cu d_{z^2} orbital, and this is modeled as $+2$ cm^{-1}; the model is not very sensitive to this final parameter, except at very low temperature.

The key result here relates to structural chemistry. Saalfrank et al. have previously shown that use of alkali-metal ions can control the size of metallocrowns.[12] Here we have demonstrated that hydrogen-bonding templates can be used to influence complex topology in cyclic structures. Specifically exciting is the observation of the "templating" of the $\{Cr_{10}Cu_2\}$ cage by incorporation of two ammonium ions. This suggests that use of designed di- and polyamine templates might lead to still greater structural complexity—in a designed manner.

Experimental Section

2: $CrF_3{\cdot}4H_2O$ (3.0 g, 17 mmol), nPr$_2$NH (1.7 g, 16 mmol), and pivalic acid (9.0 g, 88 mmol) were stirred together at 115 °C for 2.0 h. The mixture was cooled to about 80 °C and MeCN (100 mL) added. The solution was heated to reflux for 5 min, and the resulting microcrystalline precipitate was collected by filtration and washed with MeCN prior to recrystallization from acetone. Yield 0.90 g (19 %). Elemental analysis calcd (%) for $C_{136}H_{280}Cr_{12}F_{22}N_6O_{42}$: Cr 16.80, C 43.99, H 7.60, N 2.26, F 11.25; found: Cr 16.48, C 43.73, H 7.52, N 2.22, F 11.10.

3: $CrF_3{\cdot}4H_2O$ (5.0 g, 28 mmol), Et_2NH (0.85 g, 12 mmol), and pivalic acid (14.0 g, 140 mmol) were stirred together at 140 C for 1.5 h in a Teflon flask. $[VO(O_2CCMe_3)_2]_n$[13] (1.5 g) was added and the temperature of reaction increased to 160 °C for 2 h. A green crystalline product was formed. The flask was cooled to room temperature and acetone/acetonitrile (50 mL; 1:1) was added with stirring. The product was filtered, washed with a large quantity of acetone/acetonitrile (1:1), dried in air, and recrystallized from hexane. Yield 3.7 g (37 %). Elemental analysis calcd (%) for $C_{79}H_{147}Cr_6F_8N_1O_{32}V_2$: Cr 14.25, V 4.65, C 43.35, H 6.77, N 0.64, F 6.94; found: Cr 13.66, V 5.06, C 42.46, H 6.72, N 0.63. F 6.65. ES-MS (THF): m/z: -2113 $[Cr_6(VO_2F_8(O_2CCMe_3)_{15}]^-$; $+2188$ M^+; $+2211$ $[M+Na]^+$.

4: $CrF_3{\cdot}4H_2O$ (3.0 g, 17 mmol), dimethylamine (3.0 mL, 2.0 M solution in THF, 6.0 mmol), and pivalic acid (14.0 g, 140 mmol) were stirred together at 140 °C for 2.0 h in a Teflon flask. Basic copper carbonate (1.0 g, 4.5 mmol) was added and the solution heated for a further 3 h. The flask was cooled to room temperature and acetone (30 mL) was added with stirring. A green crystalline product was formed. The product was filtered, washed with a large quantity of acetone, dried in air and recrystallized from ethyl acetate/acetone (1:1). Yield 3.2 g (60 %). Elemental analysis calcd (%) for $C_{114}H_{214}Cr_{10}Cu_2F_{14}N_2O_{44}$: Cr 16.10, Cu 3.93, C 42.80, H 6.68, N 0.87, F 8.23; found: Cr 14.93, Cu 3.76, C 43.47, H 7.04, N 0.68. F 7.23.

5: $CrF_3{\cdot}4H_2O$ (3.0 g, 17 mmol), Et_2NH (0.85 g, 12 mmol), and pivalic acid (14.0 g, 140 mmol) were stirred together at 140 °C for 1.5 h in a Teflon flask. $[Zn(O_2CCMe_3)_2]_n$ (1.0 g) was added and the temperature of reaction increased to 160 °C for 2.5 h. The flask was cooled to room temperature and acetone (50 mL) was added and the solution was stirred for 15 min. A green crystalline product was formed. The product was collected by filtration, washed with a large quantity of acetone and dried in air, then recrystallized from ethyl acetate. Yield: 2.1 g (39 %). Elemental analysis calcd (%) for $C_{84}H_{156}Cr_7F_8N_1O_{32}Zn$: Cr 16.01, Zn 2.88, C 44.38, H 6.92, N 0.62, F 6.69; found: Cr 15.74, Zn 2.99, C 44.41, H 6.99, N 0.60, F 6.57. ES-MS (THF): m/z: -2199 $[Cr_7ZnF_8(O_2CCMe_3)_{16}]^-$; $+2296$ $[M+Na]^+$.

Measurements: Magnetic susceptibility measurements were performed on polycrystalline samples in the temperature range 2.0 to 298 K in an applied field of 1 T by using a Quantum Design MPMS SQUID magnetometer. Corrections for diamagnetic contributions were applied by using Pascal's Constants. The sample holder diamagnetism was measured and substracted from the raw data.

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[5] Crystal data for **2**. $1.5\,Me_2CO$: $C_{140.5}H_{289}Cr_{12}F_{22}N_6O_{43.5}$; $M_r = 3800.8\,g\,mol^{-1}$): dark green block, monoclinic, space group $P2_1/c$, $a = 19.807(4)$, $b = 25.715(5)$, $c = 21.874(5)$ Å, $\beta = 111.747(3)°$, $V = 10348(4)$ Å^3, $Z = 2$ (the supramolecule lies on an inversion center), $T = 150.0(2)$ K, $\rho = 1.220\,g\,cm^{-3}$, $F(000) = 4016$, $\mu(Mo_{K\alpha}) = 0.685\,mm^{-1}$. Crystal data for **3**: ($C_{79}H_{147}Cr_6F_8NO_{32}V_2$; $M_r = 2189.02\,g\,mol^{-1}$): green plate, orthorhombic, space group $Aba2$, $a = 30.173(2)$, $b = 35.201(2)$, $c = 23.449(1)$ Å, $V = 24906(2)$ Å^3, Z = 8, $T = 120.0(2)$ K, $\rho = 1.167\,g\,cm^{-3}$, $F(000) = 9168$, $\mu(Mo_{K\alpha}) = 0.718\,mm^{-1}$. Crystal data for **4**: ($C_{114}H_{214}Cr_{10}Cu_2F_{14}N_2O_{44}$; $M_r = 3230.08\,g\,mol^{-1}$): dark green plate, tetragonal, space group $I4cd$, $a = 30.950(1)$, $c = 37.950(2)$ Å, $V = 36351(3)$ Å^3, Z = 8, $T = 120.0(2)$ K, $\rho = 1.180\,g\,cm^{-3}$, $F(000) = 13504$, $\mu(MoK_\alpha) = 0.875\,mm^{-1}$. Crystal data for **5**: ($C_{86}H_{160}Cr_7F_8NO_{33}Zn$; $M_r = 2317.68\,g\,mol^{-1}$): dark green plate, monoclinic, space group $P2_1/c$, $a = 25.000(1)$, $b = 16.6383(9)$, $c = 30.884(2)$ Å, $\beta = 110.037(1)°$, $V = 12069(1)$ Å^3, $Z = 4$, $T = 120.0(2)$ K, $\rho = 1.275\,g\,cm^{-3}$, $F(000) = 4868$, $\mu(Mo_{K\alpha}) = 0.879\,mm^{-1}$. Data were collected on Bruker SMART CCD diffractometer ($Mo_{K\alpha}$, $\lambda = 0.71069$ Å). In all cases the selected crystals were mounted on the tip of a glass pin by using Paratone-N oil and placed in the cold flow (120 K) produced with an Oxford Cryocooling device. Complete hemispheres of data were collected by using ω scans (0.3°, 30 seconds/frame). Integrated intensities were obtained with SAINT+[6] and they were corrected for absorption using SADABS.[6] Structure solution and refinement was performed with the SHELX-package.[6] The structures were solved by direct methods and completed by iterative cycles of ΔF syntheses and full-matrix least-squares refinement against F^2 to give: for **2**: by using 927 parameters and 147 restraints, $wR_2 = 0.2316$ (13519 unique reflections), $R_1 = 0.0713$ (9155 reflections with $I > 2\sigma(I)$); for **3:** using 1152 parameters, $wR_2 = 0.077$ (14988 unique reflections), $R_1 = 0.046$ (11779 reflections with $I > 3\sigma(I)$); for **4:** 673 parameters, $wR_2 = 0.114$ (10560 unique reflections), $R_1 = 0.095$ (5352 reflections with $I > 3\sigma(I)$); for **5:** 1219 parameters, $wR_2 = 0.077$ (27372 unique reflections), $R_1 = 0.057$ (18955 reflections with $I > 3\sigma(I)$). CCDC-216507 (**2**) and CCDC-216509 to CCDC-216511 (**3**–**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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