Heterometallic Complexes

Templating Open- and Closed-Chain Structures around Metal Complexes of Macrocycles**

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The ability to control the structures of polymetallic complexes is a key concern if we are ever to exploit their properties. A lot of beautiful science has emerged with this challenge, as shown by the grid structures created by Lehn[1] and Thompson,[2] or the panel structures created by Fujita.[3] A particularly attractive idea is to template the structure about an otherwise innocent ion to modify the structure without changing electronic properties. The work of Saalfrank et al. in which different sized metallocryptands were templated is particularly relevant here,[4] as is the work of Raymond and coworkers in which the geometry of the molecule is varied from a dimetallic helix to a tetrahedron depending on the presence of a tetrahedral counterion.[5] Our work has concerned new methods to influence structure, and, in the case of cyclic chromium fluoride cages, we have shown that the size of metal rings can be influenced by the choice of secondary ammonium cations.[6,7] Here we use metal complexes of macrocycles as templates to show that further unusual structures can be formed.

Previously we reported the first heterometallic rings of the type $[NH_2R_2][Cr_7MF_8(O_2CCMe_3)_{16}]$ (R = alkyl sidechain; M = Ni^{2+}, Co^{2+}, Fe^{2+}, Mn^{2+}, or Cd^{2+}).[6] The facile synthesis of these compounds led us to look more widely at a reaction matrix that contains chromium fluoride, pivalate ion, a second metal ion, and templates that contain NH groups. When the second metal is nickel and the template is a simple azacrown ether, either 1,4,7-triazacyclonane (tacn) or 1,4,7,10-tetraazacyclododecane (cyclen), the macrocycle binds the nickel ion and the resultant complex then acts as the template.

Initially, chromium fluoride, nickel carbonate, and tacn were treated in pivalic acid to give $[Ni(tacn)_2][Cr_8Ni_2F_{10}(O_2CCMe_3)_{20}]$ (**1**),[8] in which the dicationic mononuclear nickel complex was found within a dianionic ring (Figure 1).

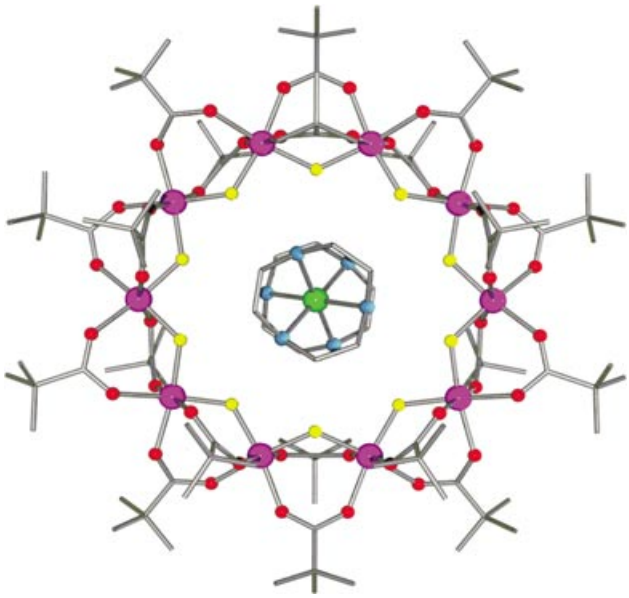

Figure 1. The crystal structure of **1**: the M_{10} wheel contains two disordered Ni atoms (see text for details). Hydrogen atoms have been omitted for clarity. Selected bond-length ranges: M–F 1.930–1.949, M–O 1.874–2.111, Ni–N 2.115–2.135 Å (average estimated standard deviation: 0.009 Å). Colors: Cr, purple; Ni, green; F, yellow; O, red; N, blue; C, grey lines.

A better route to **1** involved the prior preparation of $[Ni(tacn)_2](O_2CCMe_3)_2$ and addition of this complex to the reaction mixture (CrF_3, $NiCO_3$, and pivalic acid). The metal sites within the dianion are disordered: two Ni^{2+} ions are present according to microanalytical measurement and charge-balance considerations. The structure of the mononuclear dication is very similar to that of $[Ni(tacn)_2]^{2+}$ crystallized with simpler anions,[10] however, disorder in the structure renders a meaningful comparison of bond lengths difficult. Each of the M···M edges of the ten-metal ring, which is almost planar, is bridged by one fluoride and two pivalate ions in a similar manner to $[Cr_7NiF_8(O_2CCMe_3)_{16}]^-$. Each of the NH groups of the two tacn ligands are involved in hydrogen bonds; these bonds are longer than the hydrogen bonds found when simpler amines are used (N···F contacts range from 2.98 to 3.30 Å rather than 2.7–2.9 Å).[6]

With the Cr–F–pivalate system, octa-,[6] nona-,[7] and decanuclear metal rings could be synthesized by variation of the template. If 1,4,7,10-tetrazacyclododecane (cyclen or [12]-ane-N_4) is used as a template in this chemistry, $[\{Ni(cyclen)\}_2Cr_{12}NiF_{20}(O_2CCMe_3)_{22}]$ (**2**, see Figure 2)[8] results. The fifteen metal sites define an "S", in which a Ni^{2+} ion is located at the center of the "S" and two Ni^{2+}–[12]-ane-N_4 complexes lie at the termini. The cyclen macrocycles bind in the usual

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[**] This work was supported by the EPSRC(UK), the EC-TMR Network "QuEMolNa" (MRTN-CT-2003–504880), the University of Manchester, and the Italian MIUR (for FIRB and PRIN funding).

  DOI: 10.1002/ange.200461006

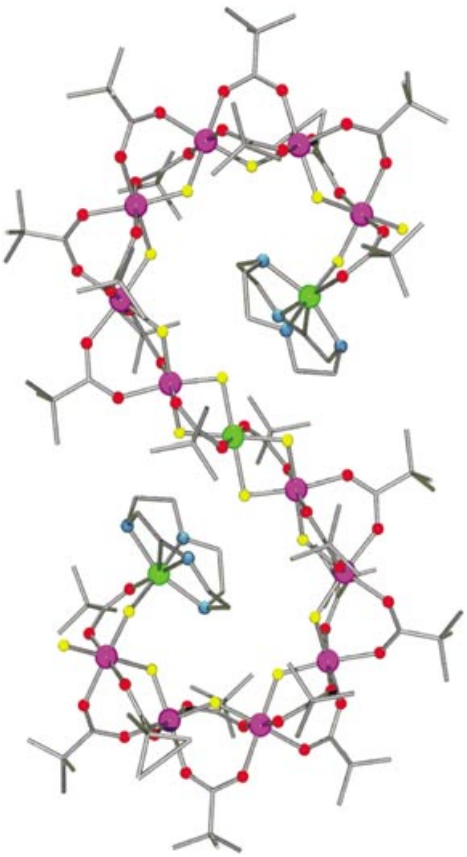

Figure 2. The crystal structure of **2**. Hydrogen atoms have been omitted for clarity. Bond-length ranges: Cr–O 1.824–2.003, Cr–F 1.893–1.966, Ni–O 1.995–2.073, Ni–F 2.015–2.093, Ni–N 2.063–2.116 (average estimated standard deviation: 0.005 Å). Colors: Cr, purple; Ni, green; F, yellow; O, red; N, blue; C, gray lines.

manner to leave *cis* vacancies on the coordinated Ni^{2+} ions, and it is the two atoms that occupy these *cis* sites which link the $[Ni([12]\text{-ane-}N_4)]^{2+}$ fragments to the termini of the metal chain. An analogous molecule with 2,2-dimethylbutyrate as the carboxylate moiety was also prepared.

The twelve Cr^{3+} ions form two hexametallic chains, which are very similar to the anionic Cr_6 horseshoes we have previously reported.[11] However, in the previous structures, the horseshoes were linked by hydrogen bonds to secondary ammonium cations, whereas here fluoride ions directly bridge to a nickel site to create the "S" shape. The Cr···Cr vectors in the structure are all bridged by two pivalate ions and one fluoride ion, whereas the two Cr···Ni contacts at the center of the "S" are each bridged by two fluoride ions and one pivalate ion. The terminal $[Ni(cyclen)]^{2+}$ units are each attached by one μ-F bridge and the oxygen atom of a pivalate ion, which chelates the final Cr^{3+} ion of the chain and also bridges to the Ni site. The metal core is almost planar with a mean deviation from planarity of 0.25 Å. There is a single N–H··F hydrogen bond (N··F contact of 2.94 Å) between the cyclen unit and the bridging fluoride ion.

Preliminary magnetic studies of **1** and **2** were performed. A χT value of 16.2 emu K mol^{-1} was obtained for **1** at room temperature which is slightly smaller than the uncorrelated value for three $S=1$ ($g_{Ni}\approx 2.2$) and eight $S=3/2$ ($g_{Cr}\approx 2.0$) centers (18.6 emu K mol^{-1}) and suggests that an antiferromagnetic interaction is present as often found in fluoro-bridged Cr^{3+} rings.[13] Whereas χT decreases, the χ value reaches a plateau around 30 K and undergoes a steep increase below 10 K (Figure 3). The χT value levels off at low

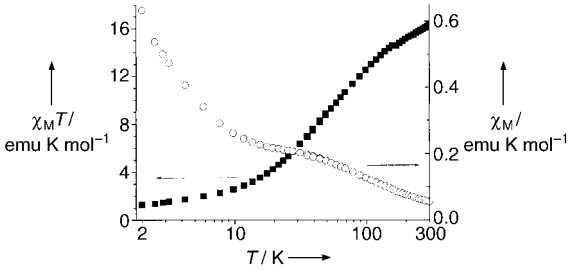

Figure 3. Temperature dependence of the magnetic susceptibility, χ (○), and its product, χT (■), for **1**.

temperature and the lowest measured value, 1.27 emu K mol^{-1}, is compatible with an uncoupled spin for Ni^{2+} (1.21 emu K mol^{-1} for $g=2.2$). This behavior can be rationalized if we assume that the antiferromagnetic-coupled ring has a $S=0$ ground state, and its contribution is superimposed on the paramagnetic ground state of the isolated $[Ni(tacn)_2]^{2+}$ cation. The ring is expected to have a diamagnetic ground state only if the two Ni^{2+} ions occupy an even and an odd site of the ring. In a random distribution, the ions have a significant probability (4/9 versus 5/9) to occupy sites of the same parity to give an uncompensated $S=1$ ground state, which is not observed. Impurities, such as rings with Cr:Ni stoichiometries of 9:1 or 7:3, would also influence the value of χT at low temperature, but the presence of such impurities is not compatible with the observed behavior. The most likely explanation for the $S=0$ ground state of the ring is that the Ni^{2+} ions, even if they are disordered, are always located next to each other within the rings as observed in $[(VO)_2Cr_6]$[11] and $[(VO)_2Cr_7]$ ring systems.[7]

To our knowledge, **2** is the longest open-chain structure prepared (except for infinite 1D chains)—the longest finite acyclic chain previously reported contained seven metal ions.[14] The magnetic behavior of **2** was measured from 1.8 to 300 K (Figure 4). The χT value at room temperature of 23.0 emu K mol^{-1}, which is smaller than the uncorrelated value (27.3 emu K mol^{-1}), is consistent with moderate antiferromagnetic exchange between the metal centers within the chain. The curve for χ versus T (Figure 4) is qualitatively similar to that of **1**, with a plateau at ≈ 30 K and a rapid increase at lower temperature. At low temperature, the curve tends to a constant value of ≈ 1 emu K mol^{-1}, which is consistent with a ground state of $S=1$.

The odd-member open-chain structure of **2** should stabilize a ferrimagnetic structure with a resultant spin of $S=1$. To confirm this, the magnetic data were fitted by employing a classical Monte Carlo simulation together with the MINUIT[15] minimization routine. A full quantum mechanical treatment was hampered by the large number of spins in the cluster. However, a quantum correction was used on spin values, and a combination of Metropolis[16] and

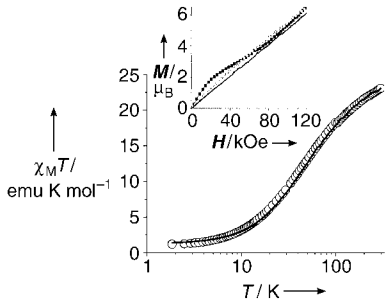

Figure 4. Temperature dependence of the product χT for **2** (1 kOe = 0.1 T). The solid line represents the fitting performed with a classical Monte Carlo simulation. Inset: magnetization (***M***) versus applied field (***H***) curves recorded at three different temperatures: 2 K ■, 5 K ○, 10 K ——.

overrelaxed algorithms[17] were applied to reduce the correlation time. The Hamiltonian ($\mathscr{H}$) that was used for the calculation is shown in Equation (1), in which $S_i = [S_i(S_i+1)]^{1/2}$ ($i = Ni^{2+}, Cr^{3+}$) is the scaled classical spin and J is the exchange interaction:

$$\mathscr{H} = -J_{Ni-Cr}(S_{Ni} \cdot S_{Cr}) - J_{Cr-Cr}(S_{Cr} \cdot S_{Cr}) \quad (1)$$

Values of $S_{Ni} = 1$, $g_{Ni} = 2.2$, $S_{Cr} = 3/2$, and $g_{Cr} = 2.0$ were used. The best-fit values obtained were $J_{Ni-Cr} = -20.8$ and $J_{Cr-Cr} = -20.3\ cm^{-1}$, with an agreement factor of $R = 1.03 \times 10^{-3}$. Despite there being two distinct Cr···Ni interactions, no significant improvement in the fitting was observed upon including two Cr···Ni exchanges. The classical Monte Carlo simulation did not provide information about the energy spectrum of the spin levels. However, the curves of magnetization (***M***) versus field strength (***H***) recorded at different temperatures (Figure 4, inset) show some features typical of level crossings, which are induced by the field, that stabilize states with larger spins.[13,18] The magnetization at 2 K, relative to that at 5 K, rapidly reaches $2\mu_B$ and then begins to level off. Above 80 kOe, the slope of the curve slightly increases, as expected for a level crossing occurring in this field range. As the energy spacing is not expected to follow a regular trend like the Landeé rule,[18] fitting of the data was not attempted. Nevertheless, the data from ***M*** versus ***H*** confirm that the ground spin state has $S = 1$, and this state is well separated, by 5–10 cm^{-1}, from the first excited state as expected for the ferrimagnetic structure of this unusual open-chain cluster.

Experimental Section

All reagents were used as received from Aldrich, except cyclen, which was obtained from Strem Chemicals. 1,4,7-triazacyclononane[19] and $[Ni_2(\mu\text{-}OH_2)(O_2CCMe_3)_4(HO_2CCMe_3)_4]$[20] were prepared according to reported methods. Complexes **1** and **2** were prepared in teflon flasks supplied by Fisher.

$[Ni(tacn)_2][(O_2CCMe_3)_2]\cdot 2Me_3CCO_2H\cdot H_2O$ (complex **A**): $[Ni_2(\mu\text{-}OH_2)(O_2CCMe_3)_4(HO_2CCMe_3)_4]$ (0.70 g, 0.74 mmol) in toluene (5 mL) was added to a solution of tacn (0.35 g, 2.7 mmol) in toluene (5 mL), and the resultant blue solution was stirred for 5 min. Pink crystals of **A** began to form during this time. The solution was allowed to stand at room temperature for one day, then the crystals were collected by filtration, washed with toluene, and dried in air (0.44 g, 40 %). Elemental analysis: calcd for $C_{32}H_{70}N_6NiO_9$: Ni 7.91, C 51.82, H 9.51, N 11.33; found: Ni 7.81, C 51.96, H 9.73, N 11.33 %.

1: Complex **A** (0.25 g, 0.34 mmol), Me_3CCO_2H (10.0 g, 98 mmol), $CrF_3\cdot 4H_2O$ (0.8 g, 4.4 mmol), and basic nickel carbonate $[2NiCO_3\cdot 3\text{-}Ni(OH)_2\cdot 4H_2O]$ (0.07 g, 0.12 mmol) were heated with stirring at 140 °C for 0.5 h, then the temperature was increased to 160 °C and the mixture was heated for 5 h. The mixture was cooled to room temperature, acetone (30 mL) was added and the contents were stirred for 15 min. The product was filtered, washed with a large quantity of acetone, and dried in air. The solid (0.5 g)was then added to a solution of Me_3CCO_2H (0.5 g) in THF (50 mL) and the solution was heated at reflux for 15–20 min with stirring. The green mixture was filtered hot, and the filtrate was diluted at room temperature with CH_3CN (1–2 mL) until it became cloudy and then reheated to obtain a clear solution. Slow cooling and then partial evaporation of the solvent at ambient temperature produced light green crystals. After 1 week, the crystals were collected by filtration, washed with THF/CH_3CN (10:1), and dried in air (0.18 g, 17.5 %). Elemental analysis calcd (%) for $C_{112}H_{210}Cr_8F_{10}N_6Ni_3O_{40}$: Cr 13.58, Ni 5.75, C 43.92, H 6.91, N 2.74, F 6.20; found: Cr 13.61, Ni 5.74, C 43.84, H 7.00, N 2.60, F 6.20.

2: Basic nickel carbonate (1.0 g, 1.7 mmol) was dissolved in pivalic acid (15 g, 147 mmol) at 100 °C, and the solution was stirred for 15 min to produce a lime-green solution. The temperature was then raised to 120 °C and cyclen (0.7 g, 4.0 mmol) was added to produce a blue solution, which indicates the production of Ni(cyclen)$(piv)_2$. The temperature was then maintained at 140 °C for 10 min before $CrF_3.4H_2O$ (5.0 g, 28 mmol) was added. The temperature was increased to 160 °C for 5 h and the mixture was then left to cool overnight. The product was collected by filtration, washed with acetone, dried, and then recrystallized from hot THF/MeCN (4.2 g, 53 %). Elemental analysis calcd (%) for $C_{136}H_{256}Cr_{12}F_{18}N_8Ni_3O_{48}$: Cr 15.94, Ni 4.50, C 41.74, H 6.59, N 2.86, F 8.74; found: Cr 15.89, Ni 4.51, C 41.39, H 6.74, N 2.74, F 8.64.

The byproducts of the syntheses of **1** and **2** have very high solubility in acetone and have not yet been fully characterized. The magnetic properties of polycrystalline samples of **1** and **2** were investigated by using a Cryogenic M600 SQUID magnetometer and a VSM magnetometer based on the Oxford Instruments MAGLAB platform.

Received: June 18, 2004
Revised: July 19, 2004

Keywords: chromium · heterometallic complexes · nickel · supramolecular chemistry · template synthesis

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[8] Crystal data for **1**·H_2O: $C_{112}H_{206}Cr_8F_{10}N_6Ni_3O_{40.5}$; $M_r = 3066.96\ g\,mol^{-1}$: green prisms, orthorhombic, space group *C mca*, $a = 33.586(4)$, $b = 21.249(3)$, $c = 22.741(3)$ Å, $V = 16230(4)$ Å^3, $Z = 4$, $T = 150(2)$ K, $\rho = 1.255\ g\,cm^{-3}$, $F(000) = 6440$, $\mu(MoK_\alpha) = 0.930\ mm^{-1}$. Crystal data for **2**·5.5 THF·1.5 MeCN: $C_{161}H_{298.5}Cr_{12}F_{18}N_{9.5}Ni_3O_{53.5}$; $M_r = 4365.7\ g\,mol^{-1}$, green blocks, triclinic, space group $P\bar{1}$, $a = 15.978(3)$, $b = 16.249(2)$, $c = 23.260(4)$ Å, $\alpha = 79.721(13)$, $\beta = 72.172(15)$, $\chi = 84.778(13)°$, $V = 5652.6(16)$ Å^3, $Z = 1$ (the molecule lies on an inversion center), $T = 100(2)$ K, $\rho = 1.281\ g\,cm^{-3}$, $F(000) = 2293$, $\mu(MoK_\alpha) = 0.877\ mm^{-1}$. Data were collected on Bruker SMART CCD diffractometer (Mo–K_α, $\lambda = 0.6892$ Å for **1** and 0.71073 for **2** 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 produced by an Oxford Cryocooling device. Complete hemispheres of data were collected using ω-scans (0.3°, 30 seconds/frame). Integrated intensities were obtained with SAINT+ and were corrected for absorption by using SADABS; structure solution and refinement were performed with the SHELX-package (reference [9]). 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 **1**: using 431 parameters and 430 restraints, $wR_2 = 0.3106$ (8450 unique reflections), $R_1 = 0.1079$ (6865 reflections with $I > 2\sigma(I)$); for **2:** using 1297 parameters and 611 restraints, $wR_2 = 0.3248$ (19910 unique reflections), $R_1 = 0.1105$ (12282 reflections with $I > 3\sigma(I)$). CCDC 242096 and CCDC 231875 contains 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 CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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