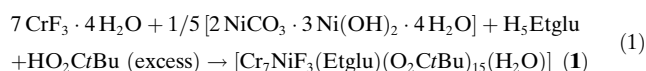


Heterometallic Rings Made From Chromium Stick Together Easily**

Grigore A. Timco,* Eric J. L. McInnes, Robin G. Pritchard, Floriana Tuna, and Richard E. P. Winpenny*

The idea that coordination complexes could be used in quantum information processing (QIP) was introduced by Leuenberger and Loss,^[1] and later developed by them^[2] and others.^[3] Our contribution has been to look at the $S = 1/2$ ground state $\{\text{Cr}_7\text{Ni}\}$ anti-ferromagnetically coupled rings,^[4,5] including measuring spin coherence times.^[6] For QIP to work there is a need to link such rings into more sophisticated structures; we have previously reported such a chemical link via an amine-template,^[7] but in that link there was no exchange interaction between the two $\{\text{Cr}_7\text{Ni}\}$ rings in the structure. Therefore we have looked for new methods to link such rings.

Previously^[4] we have used simple secondary amines as a template about which to grow $\{\text{Cr}_7\text{Ni}\}$ rings. These rings are octagonal, with each edge of the octagon bridged by a fluoride and two carboxylate ligands. If we use *N*-ethyl-D-glucamine (H_3Etglu , $\text{C}_8\text{H}_{14}\text{NO}_5\text{H}_5$) as a secondary amine, the polyol becomes deprotonated and the polyalkoxide replaces the fluoride bridging ligands. The reaction is:



The yield of the reaction is approximately 30%, and the structure^[8] of **1** (Figure 1) shows the formation of an octagon of metals, but with the glucamine penta-deprotonated and bound to the metal sites through all available O-donors. It is noteworthy that this ligand can be multiply-deprotonated in an organic acid, presumably because of coordination to the metal centers. There are five bridging alkoxide groups within the ring, with only three bridging fluorides. Seven of the eight edges of the octagon have two bridging pivalate ligands attached, however the eighth edge has only a single bridging pivalate and a bridging fluoride. The compound is purple, whereas all $[\text{H}_2\text{NR}_2][\text{Cr}_7\text{M}'\text{F}_8(\text{O}_2\text{CR}')_{16}]$ rings are dark green; the change in color is due to replacing fluoride with alkoxide within the coordination sphere of the majority of Cr^{III} ions; $[\{\text{Cr}(\text{OH})(\text{O}_2\text{CtBu})_2\}_8]$ is also purple.^[12]

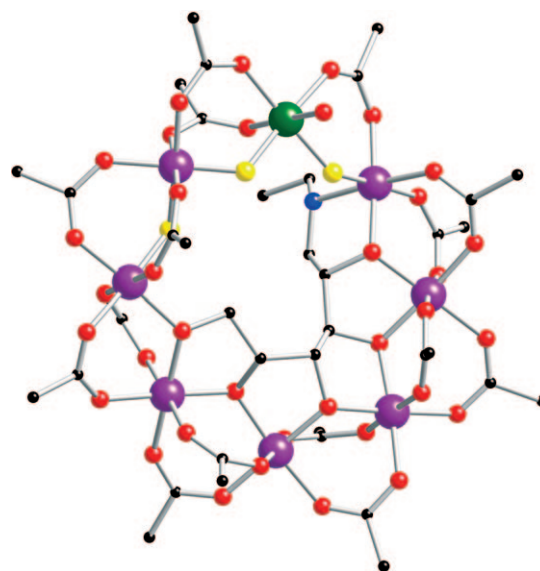


Figure 1. The structure of **1**·Et₂O in the crystal. F yellow, O red, N blue, Cr purple, Ni green, C black. Methyl groups of pivalates and ethyl groups of ether excluded for clarity.

A further new feature is the presence of a terminal ligand which could either be a fluoride or a water molecule. If this ligand is water, then one metal site is divalent, and the formula is as written. Elemental analysis confirms the stoichiometry and X-ray refinement strongly supports the site to which the terminal ligand is attached being assigned as a nickel center, therefore we assume the terminal ligand is water and reaction chemistry supports this assumption; we can exchange the water with neutral pyridine-based ligands, hence it is likely to be a neutral group.

The template is chiral, and the chirality is retained in the structure of **1**. While use of polyols in cluster synthesis is common, for example, work on metallomacrocycles from Saalfrank^[13] and on more compact clusters by Brechin^[14] and others,^[15] glucamine does not appear to have been used previously. Use of sugars as polyol ligands was explored by Klüfers.^[16] We could, perhaps, regard these new structures as “sugared donuts” of chromium.

The presence of a terminal ligand in **1** presents a new opportunity for linking rings. Initially we reacted **1** with 4-phenylpyridine (phpy), both to demonstrate that the terminal ligand was neutral and available for substitution. This produces $[\text{Cr}_7\text{NiF}_3(\text{Etglu})(\text{O}_2\text{CtBu})_{15}(\text{phpy})]$ (**2**) in quantitative yield from **1**. The structure^[8] is identical with **1**, other than displacement of water by 4-phenylpyridine (Figure S1), and again X-ray refinement supports the proposition that the terminal ligand is bound to the nickel site of the ring.

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The reaction also works with 4,4'-bipyridyl (bipy) and *trans*-1,2-dipyridylethene (dipyet) giving $[[\text{Cr}_7\text{NiF}_3(\text{Etglu})(\text{O}_2\text{CtBu})_{15}]_2(\text{bipy})]$ (**3**) and $[[\text{Cr}_7\text{NiF}_3(\text{Etglu})(\text{O}_2\text{CtBu})_{15}]_2(\text{dipyet})]$ (**4**), shown in Figure 2 and Figure S2, respectively.

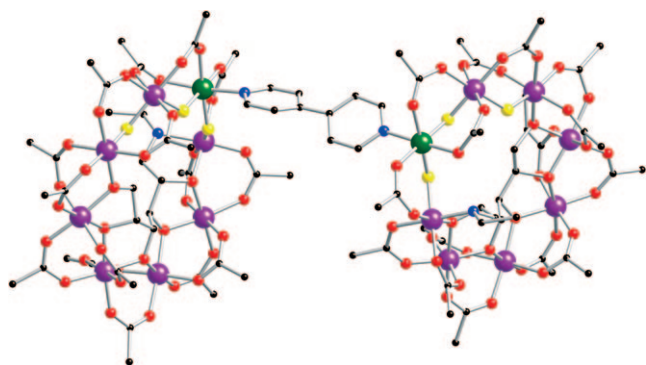


Figure 2. The structure of **3** in the crystal. Colors as in Figure 1.

Again the yield is high and core of the individual rings unchanged from **1**. The work was extended further by using 5,10,15,20-tetra(4-pyridyl)porphyrin (H_2TPP) as a linker. This organic group is rather insoluble, however on addition of a solution containing **1** H_2TPP was found to dissolve and crystals could be grown in 45 % yield after 7 days. A further crop of crystalline material was obtained later to give a total yield of 68 %. The structure^[8] (Figure 3) shows formation of $[[\text{Cr}_7\text{NiF}_3(\text{Etglu})(\text{O}_2\text{CtBu})_{15}]_4(\text{H}_2\text{TPP})]$ (**5**), where each pyridyl group of the porphyrin is bound to a Ni^{II} site of a heterometallic ring. The chirality of all four rings is retained so we get a single enantiomer.

Magnetic characterization of **3–5** show anti-ferromagnetic exchange within the rings with no evidence for inter-ring interactions in **3–5** (Figure S3); however susceptibility measurements can be insensitive to small exchange interactions in

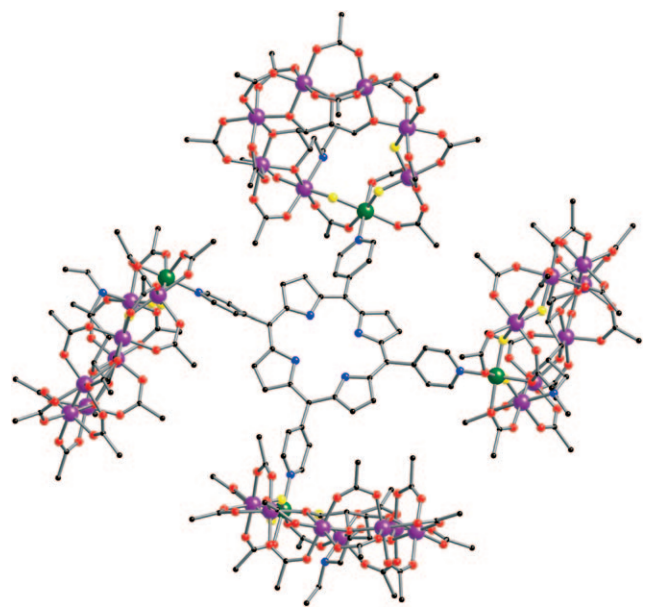


Figure 3. The structure of **5** in the crystal. Colors as in Figure 1.

complex molecules. EPR spectroscopy is much more sensitive and multi-frequency studies at Q-band (Figure 4) and X-band (Figure S4) show there is an interaction between the individual rings in the linked complexes.

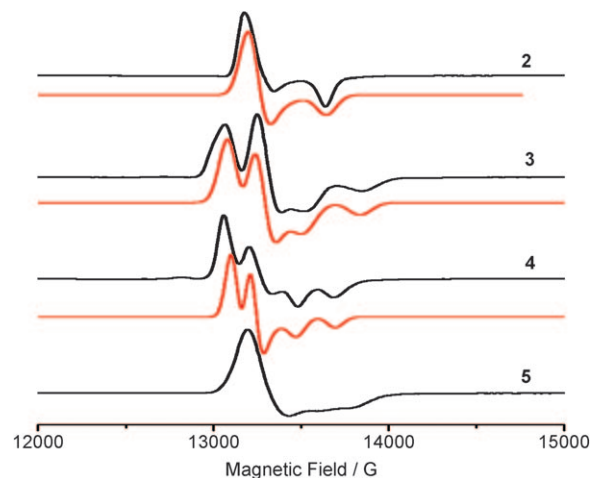


Figure 4. EPR spectra of powdered samples of **2–5** measured at Q-band and 5 K: experimental (black) and simulated (red) with parameters as described in the text.

The single $[\text{Cr}_7\text{Ni}]$ ring **2** shows low temperature spectra consistent with an $S = 1/2$ ground state with axially symmetric g -values of $g_z = 1.78$ and $g_{x,y} = 1.84$ in **2**. The ground state g -anisotropy is better resolved than that found in previous studies of $[\text{NH}_2\text{R}_2][\text{Cr}_7\text{NiF}_8(\text{O}_2\text{CtBu})_{16}]$ rings;^[4] this is partly due to a slightly larger g -anisotropy in **2** but mainly due to a reduction in line-width.

The linked dimers of rings **3** and **4** both show EPR spectra where only an $S = 1$ state is observed below 10 K (Figure 4). Hence, the rings are communicating generating a spin triplet and singlet well-separated from other excited states. In both cases the product of the spectral intensity (double integral) with temperature (proportional to χT) increases as temperature falls from 10 to 4 K, suggesting the $S = 1$ state is the ground state and the rings are coupled ferromagnetically through the diimine linker. Fitting the Bleaney–Bowers equation to these data, assuming only the triplet and singlet states are populated, gives a triplet–singlet gap of ca. 2 cm^{-1} with an error bar of $\pm 2 \text{ cm}^{-1}$ which arises from the double integrals. Therefore while the best fit gives a ferromagnetic exchange we cannot exclude an anti-ferromagnetic exchange (which would be predicted by a spin polarization model^[17]). Very weak interactions have been reported in Ni^{II} coordination polymers linked by bipy and dipyet.^[18]

We have simulated the 5 K Q-band spectra using the Hamiltonian where D is the axial zero-field splitting param-

$$H = \mu_B \mathbf{B} \mathbf{g} \hat{\mathbf{S}} + D[\hat{S}_z^2 - S(S+1)/3] \quad (2)$$

eter of a spin triplet (it is not necessary to introduce rhombic $\mathbf{g}$ or $\mathbf{D}$). For both **3** and **4** the g -values deviate slightly from those of the isolated ring **2**. Fitting gives $g_z = 1.77$, $g_{x,y} = 1.84$,

$D = +0.013 \text{ cm}^{-1}$ in **3** and $g_z = 1.79$, $g_{x,y} = 1.84$, $D = +0.009 \text{ cm}^{-1}$ in **4**.^[19] The calculated spectra are sensitive to the sign of D and the positive sign implies that it is dominated by exchange rather than dipolar interactions. The larger D for **3** versus **4** implies stronger exchange in the former where the bridging π -system is shorter; the conclusion is that we can tune the interaction between rings by choice of linker, very important for any potential use in QIP.

For **5** the spectra are much less well-resolved (Figure 4), but are clearly different from **3**, which shows that the four rings in **5** are communicating with one another, and the spectrum results from population of the resultant $S = 2$, three $S = 1$ and two $S = 0$ states. Further studies using pulsed EPR techniques are planned to quantify the interaction here. As H_2TPP is known to have a long-lived triplet excited state we also intend to examine the photophysics of **5**. Other versions of the sugared donuts can also be made with different combinations of metals and with other carboxylates.

Experimental Section

Detailed synthetic procedures are given in the Supporting Information.

1: Yield 3.2 g (30 %, based on Cr). Elemental analysis calcd (%) for $\text{C}_{83}\text{H}_{151}\text{Cr}_7\text{F}_3\text{N}_2\text{NiO}_{36}$: Cr 16.40, Ni 2.65, C 44.93, H 6.86, N 0.63; found: Cr 16.40, Ni 2.54, C 44.42, H 7.11, N 0.55. ES-MS (sample dissolved in Et_2O , run in MeOH): $+2200 [M]^+(100\%)$; $+2223 [M+\text{Na}]^+$.

2: Yield 0.56 g (70 % based on **1**). Elemental analysis (%): calcd for $\text{C}_{94}\text{H}_{158}\text{Cr}_7\text{F}_3\text{N}_2\text{NiO}_{35}$: Cr 15.45, Ni 2.49, C 47.92, H 6.76, N 1.19; found: Cr 15.43, Ni 2.46, C 47.67, H 6.94, N 2.46.

3: Yield 0.73 g (71 % based on bipy). Elemental analysis (%): calcd for $\text{C}_{176}\text{H}_{306}\text{Cr}_{14}\text{F}_6\text{N}_4\text{Ni}_2\text{O}_{70}$: Cr 15.97, Ni 2.58, C 46.38, H 6.77, N 1.23; found: Cr 15.06, Ni 2.48, C 45.76, H 6.69, N 1.17.

4: Yield 91 % (based on dipyt). Elemental analysis (%): calcd for $\text{C}_{178}\text{H}_{308}\text{Cr}_{14}\text{F}_6\text{N}_4\text{Ni}_2\text{O}_{70}$: Cr 15.88, Ni 2.56, C 46.64, H 6.77, N 1.22; found: Cr 15.48, Ni 2.60, C 46.11, H 6.87, N 1.14.

5: Yield (total) 68 % (based on H_2TPP). Elemental analysis (%): calcd for $\text{C}_{372}\text{H}_{622}\text{Cr}_{28}\text{F}_{12}\text{N}_{12}\text{Ni}_4\text{O}_{140}$: Cr 15.45, Ni 2.49, C 47.42, H 6.65, N 1.78; found: Cr 14.80, Ni 2.45, C 47.08, H 6.67, N 1.74.

Magnetic susceptibility measurements were performed on polycrystalline samples in the temperature range 2.0 to 298 K in applied fields of 0.1 and 1 T 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 subtracted from the raw data. X- and Q-band EPR spectra were recorded on Bruker EMX and Elexsys spectrometers.

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- [8] Crystal data for **1** ($\text{C}_{93}\text{H}_{174}\text{Cr}_7\text{F}_3\text{N}_2\text{NiO}_{37.5}$; $M_r = 2385.6 \text{ g mol}^{-1}$): purple needles, orthorhombic, space group $P2_12_12_1$, $a = 16.4250(5)$, $b = 24.9950(5)$, $c = 31.7760(11) \text{ \AA}$, $V = 13045.4(7) \text{ \AA}^3$, $Z = 4$, $T = 100(2) \text{ K}$, $\rho = 1.214 \text{ g cm}^{-3}$, $F(000) = 5047$, $\mu(\text{MoK}\alpha) = 0.773 \text{ mm}^{-1}$. Crystal data for **2** ($\text{C}_{100}\text{H}_{174}\text{Cr}_7\text{F}_3\text{N}_2\text{NiO}_{39}$; $M_r = 2508.1 \text{ g mol}^{-1}$): purple block, orthorhombic, space group $P2_12_12_1$, $a = 17.0600(2)$, $b = 26.3540(3)$, $c = 30.4220(4) \text{ \AA}$, $V = 13677.7(3) \text{ \AA}^3$, $Z = 4$, $T = 150(2) \text{ K}$, $\rho = 1.218 \text{ g cm}^{-3}$, $F(000) = 5292$, $\mu(\text{MoK}\alpha) = 0.724 \text{ mm}^{-1}$. Crystal data for **3**: ($\text{C}_{179}\text{H}_{314}\text{Cr}_{14}\text{F}_6\text{N}_4\text{Ni}_2\text{O}_{72}$; $M_r = 4633.8 \text{ g mol}^{-1}$): purple needles, monoclinic, space group $C2$, $a = 54.7570(6)$, $b = 16.9650(2)$, $c = 35.8310(5) \text{ \AA}$, $\beta = 125.6330(10)^\circ$, $V = 27053.1(6) \text{ \AA}^3$, $Z = 4$, $T = 150(2) \text{ K}$, $\rho = 1.138 \text{ g cm}^{-3}$, $F(000) = 9752$, $\mu(\text{MoK}\alpha) = 0.725 \text{ mm}^{-1}$. Crystal data for **4**: ($\text{C}_{178}\text{H}_{308}\text{Cr}_{14}\text{F}_6\text{N}_4\text{Ni}_2\text{O}_{70}$; $M_r = 4583.7 \text{ g mol}^{-1}$): purple rods, orthorhombic, space group $P2_12_12_1$, $a = 23.4760(4)$, $b = 32.8770(7)$, $c = 17.6110(3) \text{ \AA}$, $V = 13592.5(4) \text{ \AA}^3$, $Z = 2$, $T = 150(2) \text{ K}$, $\rho = 1.12 \text{ g cm}^{-3}$, $F(000) = 4820$, $\mu(\text{MoK}\alpha) = 0.738 \text{ mm}^{-1}$. Crystal data for **5**: ($\text{C}_{381}\text{H}_{642}\text{Cr}_{28}\text{F}_{12}\text{N}_{12}\text{Ni}_4\text{O}_{145}$; $M_r = 9629.9 \text{ g mol}^{-1}$): purple plates, monoclinic, space group $P2_1$, $a = 30.6109(3)$, $b = 30.4267(3)$, $c = 34.6144(5) \text{ \AA}$, $\beta = 115.9480(10)^\circ$, $V = 28989.4(6) \text{ \AA}^3$, $Z = 2$, $T = 150(2) \text{ K}$, $\rho = 1.103 \text{ g cm}^{-3}$, $F(000) = 10128$, $\mu(\text{MoK}\alpha) = 0.696 \text{ mm}^{-1}$. Data were collected on a Bruker Nonius Kappa CCD diffractometer ($\text{MoK}\alpha$, $\lambda = 0.71073 \text{ \AA}$). In all cases the selected crystals were mounted on the tip of a glass pin using Paratone-N oil and placed in the cold flow (150 K) produced with an Oxford Cryosystems cryostream. Data was collected using ϕ and ω scans chosen to give a complete asymmetric unit. Integrated intensities were obtained with HKL Denzo and Scalepack^[9] and were corrected for absorption using Sortav.^[10] Structure solution and refinement was performed with the Shelx package.^[11] 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 1308 parameters and 882 restraints, $wR_2 = 0.1699$ (6509 unique reflections), $R_1 = 0.0625$ (4914 reflections with $I > 2\sigma(I)$); for **2**: 1335 parameters and 1896 restraints, $wR_2 = 0.2054$ (9089 unique reflections), $R_1 = 0.0808$ (6293 reflections with $I > 2\sigma(I)$); for **3**: 2517 parameters and 6025 restraints, $wR_2 = 0.2363$ (15040 unique reflections), $R_1 = 0.0871$ (7984 reflections with $I > 2\sigma(I)$); for **4**: 1206 parameters and 1845 restraints, $wR_2 = 0.2317$ (16499 unique reflections), $R_1 = 0.0844$ (10707 reflections with $I > 2\sigma(I)$); for **5**: 5224 parameters and 21175 restraints, $wR_2 = 0.2559$ (27414 unique reflections), $R_1 = 0.0939$ (13166 reflections with $I > 2\sigma(I)$). CCDC-696012 (**1**), -696014 (**2**), -696015 (**3**), -696016 (**4**), and -696017 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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