Cage Compounds

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Linking Rings through Diamines and Clusters: Exploring Synthetic Methods for Making Magnetic Quantum Gates**

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Those of us interested in polymetallic complexes still strive to control the structures formed, as this is vital if we are ever to exploit their properties. One of the more interesting approaches is to use "templates" to control either the size of clusters[1] or even their shape.[2] Beyond that challenge lies another: how do we assemble cage complexes into materials in a controlled manner? Further motivation to answer this latter question has arisen from theoretical studies,[3,4] which propose that $S = 1/2$ clusters could be used as quantum bits (qubits) in quantum information processing (QIP). Herein, we describe our initial experiments in which we link $S = 1/2$ wheels to each other. Linking two molecules with $S = 1/2$ will allow the study of conditioned dynamics of the magnetization of each molecule and thus let us examine the possibility of implementing quantum gates within molecular clusters.

Previously we reported the first heterometallic octanuclear rings, $[\{NH_2R_2\}\{Cr_7MF_8(O_2CCMe_3)_{16}\}]$ (R = alkyl side chains; M = Ni^{II}, Co^{II}, Fe^{II}, Mn^{II}, or Cd^{II}).[5] For QIP, single-qubit operations require an $S = 1/2$ ground state. Among the heterometallic $\{Cr_7M\}$ rings, this condition is met for M = Ni^{II}, which therefore represents an appealing candidate.[6] How-

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ever, the efficient implementation of a quantum computer requires the creation of a two-qubit quantum gate as pointed out by Loss and co-workers[3,4] and Troiani et al.[7] For such a purpose, it is necessary to have dimers of coupled $\{Cr_7Ni\}$ rings. As the ring is templated about protonated amine cations, a straightforward method is to use a diamine with a carbon chain of sufficient length so that a $\{Cr_7Ni\}$ ring can be attached at either end. In initial experiments we found that 1,8-diaminooctane (1,8-dao) and 1,9-diaminononane (1,9-dan) are suitable, while slightly more complex diamines such as 1,3-di(piperidine)propane (1,3-dpp) also produce a pair of linked clusters. Longer diamines are also suitable, such as 1,12-diaminododecane (1,12-dad), but the resulting crystal structures are significantly disordered. The linked clusters, $[\{1,8\text{-daoH}_2\}\{Cr_7NiF_8(O_2CCMe_3)_{16}\}_2]$ (**1**), $[\{1,9\text{-danH}_2\}\{Cr_7NiF_8(O_2CCMe_3)_{16}\}_2]$ (**2**), and $[\{1,3\text{-dppH}_2\}\{Cr_7NiF_8(O_2CCMe_3)_{16}\}_2]$ (**3**) were structurally characterized (Figure 1).[8] The Ni^{II} ions in these compounds may be replaced with other metal dications.

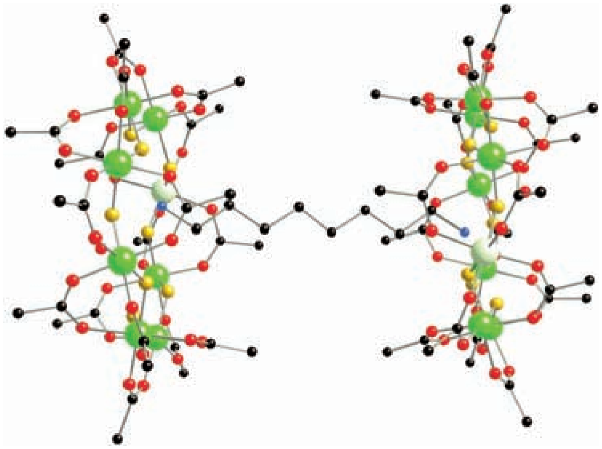

Figure 1. Crystal structure of **1** (hydrogen atoms and methyl groups of pivalate groups on rings have been omitted for clarity; Cr green, Ni light green, F yellow, O red, N blue, C black). Selected bond-length ranges: M–F 1.891–1.964, M–O 1.872–2.016 Å. Average estimated standard deviation (av esd): 0.012 Å.

The structure of the heterometallic octanuclear $\{Cr_7M\}$ rings is a regular octagon of metal ions with each side bridged by one fluoride and two carboxylate ions, as reported previously.[5]. Although it is not possible to distinguish between Ni^{II} and Cr^{III} sites in a single ring, elemental analysis confirmed the formulation given. The protonated amine head groups hydrogen bond to the fluoride ions within the ring.

We wished to include switchable links between the rings. To this end, we synthesized $[\{EtNH_2CH_2py\}\{Cr_7NiF_8(O_2CCMe_3)_{16}\}]$ (**4**; py = pyridine)[8] knowing that the ring will encapsulate the secondary ammonium group to leave the pyridine moiety free to bind to further metal sites. To illustrate the potential of such an approach, we treated **4** with the dinuclear metal complexes, $[Cu_2(O_2CCMe_3)_4(HO_2CCMe_3)_2]$ and $[M_2(H_2O)(O_2CCMe_3)_4(HO_2CCMe_3)_4]$ (M = Ni or Co). This gave the structures $[\{M_2(O_2CCMe_3)_4\}\{[EtNH_2CH_2py][Cr_7NiF_8(O_2CCMe_3)_{16}]\}_2]$ (**5**: M = Cu; **6**: M = Ni; **7**: M = Co),[8] as depicted in Figure 2.

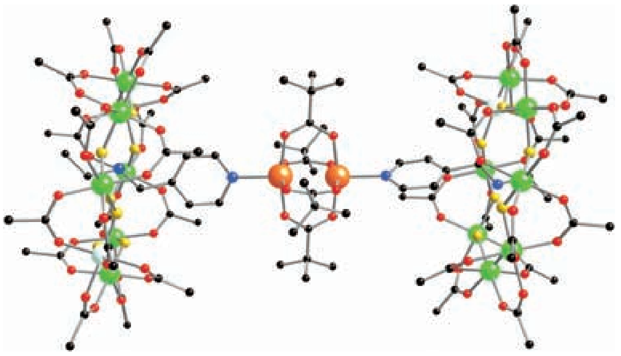

Figure 2. Crystal structure of **5** (see Figure 1 legend for color scheme; Cu orange). Selected bond-length ranges: M–F 1.909–1.967, M–O 1.914–1.997, Cu–O 1.953–1.960 Å. Av esd: 0.008 Å.

The pyridine group from **4** binds to the axial sites of the metal dimer. The M···M distance is fairly similar, at 2.63 Å in **5** and 2.61 Å in **6**. The Cu···Cu distance is similar to that reported for a previously reported copper dimer bridged by pivalate.[10] In related Ni dimers,[11] the Ni···Ni distance depends on the terminal ligands: approximately 2.60 Å for pyridine and longer (ca. 2.72 Å) for lutidines. Complex **4** therefore appears to be similar to pyridine in its donating properties. While these dimers are not switchable, we believe that we can prepare equivalent supramolecules in which M is a 4d or 5d metal and where we could vary the interaction between the $[Cr_7MF_8(O_2CCMe_3)_{16}]$ complexes by redox chemistry or photoexcitation of the multiply bonded dimer.[12]

Magnetic and specific heat studies of **1**–**3** and **5**–**7** were performed. The ac susceptibility was measured over the temperature range 2–100 K (Figure 3a). Each linked ring

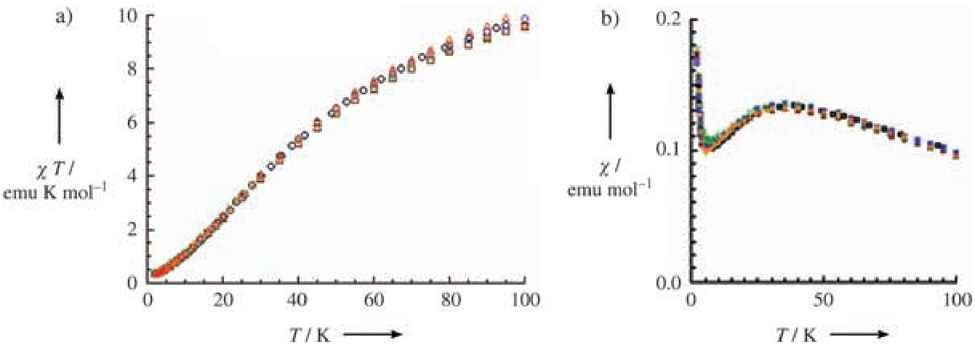

Figure 3. a) The χT product of $\{Cr_7Ni\}$ rings (black ○) and the molecular dimers **1** (brown □), **2** (blue ○), **3** (red △), **5** (green ×), and **6** (yellow +); for **5** and **6**, χ was normalized to half a mole) over the temperature range 2–100 K. Note that χT values saturate to the Curie value expected for an $S = 1/2$ system for all of the derivatives. b) Temperature dependence of the ac susceptibility χ (the susceptibility of dimer **7** is reported in the Supporting Information).

shows essentially the same χT versus T behavior for this temperature range, and after normalization to half a mole the $\chi T(T)$ curves overlap that of a single {Cr_7Ni} ring. The anomalies in the χ versus T plot (Figure 3b) are related to the pattern of the lowest lying states in a single {Cr_7Ni} ring[5,6] that comprises an $S=1/2$ ground state and an $S=3/2$ first excited multiplet. The field dependencies of the magnetization as collected at $T=0.4$ K for each linked ring almost overlap one another, and as only the ground state is significantly populated at this temperature no deviation from the Brillouin curve calculated for $S=1/2$ is observed (see Supporting Information).

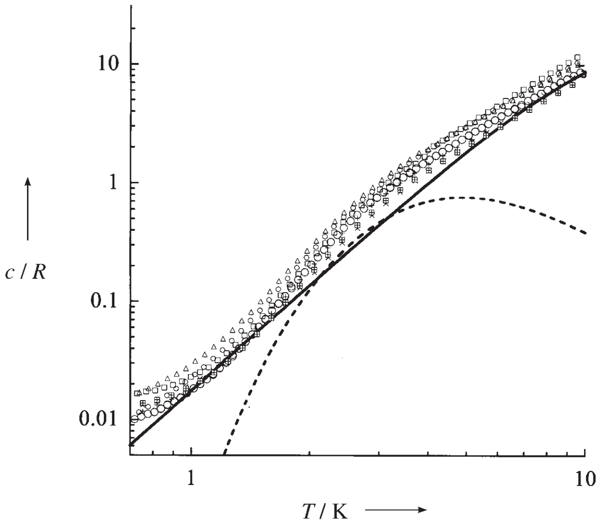

Figure 4. Specific heat c, normalized to the gas constant R, of {Cr_7Ni} rings (◯) and of the molecular dimers **1** (□), **2** (○), **3** (△), **5** (×), 6 (+), and **7** (square with cross); for **5**–**7**, c was normalized to half a mole for comparison with {Cr_7Ni} rings measured as a function of temperature at zero field. Continuous (——) and dotted (-----) lines represent the estimated lattice and magnetic contribution, respectively.

The temperature dependencies of the specific heat c, normalized to the gas constant R, were recorded over the temperature range 0.4–10 K. Figure 4 shows that after normalization to half a mole for the dimers the data overlap one another and with those of {Cr_7Ni}. The hump in the $c(T)$ curves at 3–5 K confirms the Schottky anomaly related to the main energy gap, approximately 9 cm^{-1}, between the ground state $S=1/2$ doublet and the $S=3/2$ quartet. As a magnetic field is applied, these multiplets are split and the Schottky anomaly evolves for all derivatives similarly to that observed for the {Cr_7Ni} ring (Figure 5). This behavior is well-accounted for by the spin Hamiltonian of a single wheel [Eq. (1)].

$$H=\sum_i J\,\boldsymbol{S}_i\cdot\boldsymbol{S}_{i+1}+\sum_i d_i\,[S_{z,i}^2-\mathrm{S}_i(\mathrm{S}_i+1)/3]+\sum_{i<j}\boldsymbol{S}_i\cdot\boldsymbol{D}_{ij}\cdot\boldsymbol{S}_j+\mu_B\sum_i g_i\,\boldsymbol{S}_i\cdot\boldsymbol{B}\qquad(1)$$

The first term corresponds to the dominant antiferromagnetic Heisenberg exchange between nearest-neighboring spins; the second and third anisotropic terms account for the coupling due to the crystal field and for the intracluster dipole–dipole interaction, respectively; the fourth term accounts for the Zeeman coupling to the external field. The microscopic parameters can be determined by fitting the magnetic-field-dependent specific heat data, and within the experimental accuracy for all derivatives the best set of parameters was $J_{Cr\text{-}Cr}=1.46$ meV, $J_{Cr\text{-}Ni}=1.69$ meV, $d_{Cr}=-0.03$ meV, $d_{Ni}=-0.35$ meV, $g_{Cr}=1.98$, and $g_{Ni}=2.2\pm0.2$. The addition of a coupling term between two wheels does not improve the quality of the fit for $T>0.4$ K.

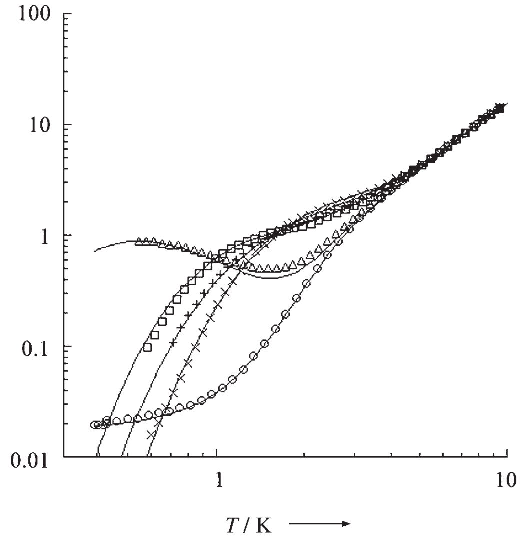

Figure 5. Specific heat c, normalized to the gas constant R, of **7** measured as a function of temperature at different magnetic fields: zero field (○); 1 T (△); 3 T (□); 5 T (×); 7 T (+). It is evident that the evolution of the Schottky anomaly is essentially due to the Zeeman effect on the lowest lying levels with $S=1/2$ and $S=3/2$ of the single {Cr_7Ni} wheels. Lines are fitting curves obtained by diagonalizing the spin Hamiltonian of single {Cr_7Ni} wheels, as described in the text.

These results show that for all these linked complexes, the pattern of the lowest lying states of a single wheel is very close to that of the isolated {Cr_7Ni} ring. We estimate an upper limit for a possible coupling interaction between two wheels to be less than about 0.1 cm^{-1}. To check this, we examined the magnetization of microcrystallites of **5** between 40 mK and 400 mK by using a micro-SQUID array and found no evidence for an interaction between the {Cr_7Ni} rings even at this temperature (see Supporting Information).

At one level, the lack of a sizeable magnetic coupling may seem disappointing, however this work demonstrates that [$Cr_7MF_8(O_2CCMe_3)_{16}$] complexes are relatively stable and that they can be attached to one another by different linkers. At another level, implementation of quantum computing will require one state where the single qubits in the gate do not communicate. These results show that the rings can be brought into close proximity without changing magnetic behavior due to through-space exchange. In the future we hope to switch on the interaction by using photo- or redox chemistry.

Experimental Section

All reagents were used as received from Aldrich. $[Cu_2(O_2CCMe_3)_4(HO_2CCMe_3)_2]$[13] and $[M_2(H_2O)(O_2CCMe_3)_4(HO_2CCMe_3)_4]$[14,15] were prepared according to published methods.

1: Me_3CCO_2H (20.0 g, 195 mmol), $H_2N(CH_2)_8NH_2$ (0.16 g, 1.11 mmol), and $CrF_3{\cdot}4H_2O$ (3.0 g, 16 mmol) were heated at 140 °C with stirring in a teflon flask for 0.5 h, then $2NiCO_3{\cdot}3Ni(OH)_2{\cdot}4H_2O$ (0.35 g, 0.6 mmol) was added. After 1 h the temperature of the reaction was increased to 160 °C for 8 h. The flask was cooled to room temperature, then acetone (35 mL) was added while stirring. The green microcrystalline product was collected by filtration, washed with a large quantity of acetone, dried in air, and then dissolved in hexane (100 mL). The solution was filtered, and the filtrate was evaporated to dryness. The product was recrystallized twice from toluene. Yield: 1.9 g (35 %; all yields based on Cr unless otherwise stated). Elemental analysis (%) calcd for $C_{168}H_{310}Cr_{14}F_{16}N_2Ni_2O_{64}$: Cr 16.06, Ni 2.59, C 44.53, H 6.90, N 0.62; found: Cr 16.62, Ni 2.51, C 45.48, H 7.06, N 0.50.

Compounds **2**–**4** were obtained by similar procedures to that for **1**, except that 1,8-diaminooctane was replaced with the amines listed below and the period of heating at 160 °C and the crystallization solvents were also varied.

2: 1,9-diaminononane**;** heated at 160 °C for 9 h; extracted and crystallized from 1:2 hexane/ethyl acetate. Yield: 1.5 g (28 %). Elemental analysis (%) calcd for $C_{169}H_{312}Cr_{14}F_{16}N_2Ni_2O_{64}$: Cr 16.01, Ni 2.58, C 44.65, H 6.92, N 0.62, F 6.69; found: Cr 15.81, Ni 2.64, C 44.37, H 6.96, N 0.54, F 6.68.

3: 1,3-bis(4-piperidinyl)propane monohydrate; heated at 160 °C for 11 h; extracted and crystallized from 5:1 pentane/acetone. Yield: 1.0 g (18 %). Elemental analysis (%) calcd for $C_{173}H_{316}Cr_{14}F_{16}N_2Ni_2O_{64}$: Cr 15.83, Ni 2.55, C 45.19, H 6.93, N 0.61; found: Cr 15.47, Ni 2.54, C 44.81, H 6.90, N 0.54.

4: Me_3CCO_2H (20.0 g, 196 mmol), 4-(ethylaminomethyl)pyridine (0.32 g, 2.4 mmol), $CrF_3{\cdot}4H_2O$ (3.0 g, 17 mmol), and $2NiCO_3{\cdot}3Ni(OH)_2{\cdot}4H_2O$ (0.3 g, 0.5 mmol) were heated while stirring at 140 °C for 2.0 h and then at 160 °C for 24 h. The teflon flask was cooled to room temperature, then acetone (35 mL) was added, and the mixture was stirred for 3 h. The precipitated product was collected by filtration and washed with acetone (3 × 15 mL). The solid was dissolved in pentane (40 mL), the solution was filtered, then the filtrate was diluted with acetone (60 mL). Evaporation of this solution at room temperature produced green crystals. Yield: 2.3 g (42 %). Elemental analysis (%) calcd for $C_{88}H_{157}Cr_7F_8N_2NiO_{32}$: Cr 15.62, Ni 2.52, C 45.37, H 6.79, N 1.20; found: Cr 15.58, Ni 2.65, C 45.33, H 6.84, N 1.18. Crystals suitable for X-ray studies were obtained by recrystallization from THF/MeCN.

5: $[Cu_2(O_2CCMe_3)_4(HO_2CCMe_3)_2]$[12] (0.077 g,0.105 mmol) was added to a solution of **4** (0.5 g, 0.2 mmol) in toluene (7 mL), and the mixture was stirred until the copper complex dissolved. Green microcrystalline product began to form during this time and was collected after 2 days, washed with toluene and acetone, and dried in air. Yield: 0.44 g (81.0 % based on Cu). Elemental analysis (%) calcd for $C_{196}H_{350}Cr_{14}F_{16}N_4Ni_2Cu_2O_{72}$: Cr 14.02, Ni 2.26, Cu 2.45, C 45.35, H 6.80, N 1.08; found: Cr 13.91, Ni 2.23, Cu 2.29, C 45.77, H 6.86, N 0.97. Crystals suitable for X-ray studies were obtained by slow evaporation of a solution of **5** in THF/toluene at room temperature.

6: $[Ni_2(H_2O)(O_2CCMe_3)_4(HO_2CCMe_3)_4]$[14] (0.1 g, 0.1 mmol) was added to a solution of **4** (0.5 g, 0.2 mmol) in Et_2O (7 mL) and briefly stirred. The solution was filtered and diluted with toluene (ca. 5 mL). Green crystals (including some that were suitable for X-ray studies) were formed by slow concentration of this solution at room temperature over 2 days. Crystals were washed with toluene and dried in air. Yield: 0.4 g (71 % based on Ni). Elemental analysis (%) calcd for $C_{196}H_{350}Cr_{14}F_{16}N_4Ni_4O_{72}$: Cr 14.05, Ni 4.53, C 45.43, H 6.81, N 1.08; found: Cr 13.77, Ni 4.45, C 45.55, H 6.90, N 1.03.

7: All manipulations were carried out under a N_2 atmosphere. $[Co_2(H_2O)(O_2CCMe_3)_4(HO_2CCMe_3)_4]$[14] (0.1 g, 0.1 mmol) was dissolved in Et_2O (5 mL), and the solution was added to a solution of **4** (0.5 g, 0.2 mmol) in toluene (10 mL). Green crystals (including some that were suitable for X-ray studies) were formed by slow concentration of this solution at room temperature over 2 days. Crystals were collected by filtration, washed with toluene, and dried under N_2. Yield: 0.31 g (57 % based on Co). Elemental analysis (%) calcd for $C_{196}H_{350}Co_2Cr_{14}F_{16}N_4Ni_2O_{72}$: Cr 14.05, Co 2.27, Ni 2.27, C 45.43, H 6.81, N 1.08; found: Cr 13.88, Co 2.29, Ni 2.21, C 45.09, H 6.71, N 0.99.

Magnetic and thermal measurements: The magnetic properties and the heat capacity of polycrystalline samples of **1**–**3** and **5**–**7** were investigated using a Quantum Design PPMS-7T system provided with an ac susceptometer and a microcalorimeter, respectively. Home-made Hall magnetometer and micro-SQUIDs were used for magnetization measurements below 1 K.

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[8] Crystal data for **1**: $C_{182}H_{328}Cr_{14}F_{16}N_2Ni_2O_{66}$; $M_r = 4749.88\,g\,mol^{-1}$: green plate, monoclinic, space group $P2_1/c$, $a = 25.247(3)$, $b = 16.668(2)$, $c = 31.313(4)$ Å, $\beta = 111.042(11)°$, $V = 12298(3)$ Å^3, $Z = 2$, $T = 100(2)$ K, $\rho = 1.283\,g\,cm^{-3}$, $F(000) = 4996$, $\mu(Mo_{K\alpha}) = 0.822\,mm^{-1}$. Crystal data for **2**: $C_{169}H_{314}Cr_{14}F_{16}N_2Ni_2O_{66}$; $M_r = 4579.64\,g\,mol^{-1}$, green prism, orthorhombic, space group $P2_12_12_1$, $a = 19.9276(10)$, $b = 25.4432(10)$, $c = 52.423(2)$ Å, $V = 26580(2)$ Å^3, $Z = 4$, $T = 100(2)$ K, $\rho = 1.144\,g\,cm^{-3}$, $F(000) = 9624$, $\mu(Mo_{K\alpha}) = 0.759\,mm^{-1}$. Crystal data for **3**: $C_{179}H_{316}Cr_{14}F_{16}N_2Ni_2O_{66}$; $M_r = 4570.72\,g\,mol^{-1}$: green prism, orthorhombic, space group $P\,2_12_12_1$, $a = 19.5184(13)$, $b = 25.5867(15)$, $c = 52.214(4)$ Å, $V = 26076(3)$ Å^3, $Z = 4$, $T = 100(2)$ K, $\rho = 1.164\,g\,cm^{-3}$, $F(000) = 9352$, $\mu(Mo_{K\alpha}) = 0.774\,mm^{-1}$. Crystal data for **4**: $C_{88}H_{157}Cr_7F_8N_2NiO_{32}$; $M_r = 2329.87\,g\,mol^{-1}$: green prism, orthorhombic, space group $P2_12_12_1$, $a = 23.8811(9)$, $b = 31.6801(13)$, $c = 18.1427(7)$ Å, $V = 13726.0(9)$ Å^3, $Z = 4$, $T = 100(2)$ K, $\rho = 1.127\,g\,cm^{-3}$, $F(000) = 4892$, $\mu(Mo_{K\alpha}) = 0.735\,mm^{-1}$. Crystal data for **5**: $C_{196}H_{350}Cr_{14}Cu_2F_{16}N_4Ni_2O_{72}$; $M_r = 5191.30\,g\,mol^{-1}$: green prism, monoclinic, space group $I2/a$, $a = 31.2663(15)$, $b = 17.4002(7)$, $c = 52.952(2)$ Å, $\beta = 101.873(4)°$, $V = 28182(2)$ Å^3, $Z = 4$, $T = 100(2)$ K, $\rho = 1.223\,g\,cm^{-3}$, $F(000) = 10896$, $\mu(Mo_{K\alpha}) = 0.870\,mm^{-1}$. Crystal data for **6**: $C_{196}H_{350}Cr_{14}F_{16}N_4Ni_4O_{72}$; $M_r = 5181.64\,g\,mol^{-1}$: green prism, orthorhombic, space group $Pna2_1$, $a = 31.1780(15)$, $b = 17.4191(11)$, $c = 51.967(3)$ Å, $V = 28223(3)$ Å^3, $Z = 4$, $T = 100(2)$ K, $\rho = 1.219\,g\,cm^{-3}$, $F(000) = 10888$, $\mu(Mo_{K\alpha}) = 0.852\,mm^{-1}$. Complex **7** is isostructural to **5** with cell parameters

$a = 30.8649(33)$, $b = 17.3439(19)$, $c = 52.5855(57)$ Å, $\beta = 101.734(9)°$; the structure was not refined. Data were collected on Bruker SMART CCD diffractometer (Mo$_{K\alpha}$, $\lambda = 0.71073$ Å). 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 produced with an Oxford Cryocooling device. Complete hemispheres of data were collected using ω scans (0.3°, 30 seconds/frame). Integrated intensities were obtained with SAINT+[9] and they were corrected for absorption using SADABS.[9] Structure solution and refinement were performed with the SHELX package.[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 794 parameters and 1491 restraints, $wR_2 = 0.4206$ (9618 unique reflections), $R_1 = 0.1572$ (6122 reflections with $I > 2\sigma(I)$); for **2**, using 1557 parameters and 8038 restraints, $wR_2 = 0.2888$ (16004 unique reflections), $R_1 = 0.1033$ (12655 reflections with $I > 2\sigma(I)$); for **3**, using 1757 parameters and 799 restraints, $wR_2 = 0.2317$ (20443 unique reflections), $R_1 = 0.0880$ (12520 reflections with $I > 2\sigma(I)$); for **4**, using 1594 parameters and 5111 restraints, $wR_2 = 0.2933$ (24202 unique reflections), $R_1 = 0.0957$ (18997 reflections with $I > 2\sigma(I)$); for **5**, using 1470 parameters and 2210 restraints, $wR_2 = 0.2814$ (14738 unique reflections), $R_1 = 0.0898$ (8692 reflections with $I > 2\sigma(I)$); for **6**, using 1292 parameters and 6095 restraints, $wR_2 = 0.2736$ (12046 unique reflections), $R_1 = 0.1040$ (8302 reflections with $I > 2\sigma(I)$). CCDC 278508–278513 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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