(13.5 mg, 0.0420 mmol) in $CHCl_3$ (0.15 mL) was added by syringe. After 4 hours, additional O-acylated azlactone (13.5 mg, 0.0420 mmol) in $CHCl_3$ (0.15 mL) was added. After 24 hours (total), the carbamate was isolated by flash chromatography (25% EtOAc/hexanes) (7.3 mg; HPLC analysis: 79% *ee*). For *ee* analysis, the unreacted amine was acylated (NEt_3, Ac_2O, CH_2Cl_2, RT) and then purified by flash chromatography (EtOAc) to furnish the amide (11.4 mg; GC analysis: 42% *ee*). These *ee* values correspond to a selectivity factor *s* of 13 at 35% conversion.

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[13] A study of stereoselectivity as a function of catalyst *ee* is consistent with the presence of one catalyst molecule in the stereochemistry-determining step of the process.

High-Nuclearity Chromium–Nickel–Cyanide Clusters: An Open $Cr_8Ni_5(CN)_{24}$ Cage and a C_3-Symmetric $Cr_{10}Ni_9(CN)_{42}$ Cluster Incorporating Three Forms of Cyanonickelate**

Jennifer J. Sokol, Matthew P. Shores, and Jeffrey R. Long*

High-nuclearity metal–cyanide clusters may ultimately provide a vehicle for the design of new single-molecule magnet molecules possessing an energy barrier for magnetic moment reversal.[1] This contention is partly supported by recent work in which an understanding of the factors influencing superexchange interactions across a bridging cyanide ligand has led to the synthesis of Prussian blue type solids[2] with magnetic ordering temperatures as high as 373 K.[3] Typically, such solids are obtained from aqueous assembly reactions between octahedral $[M(H_2O)_6]^{x+}$ and $[M'(CN)_6]^{y-}$ complexes. The synthesis of molecular clusters with similarly adjustable magnetic properties is expected to require inhibition of some reactive sites on the precursor complexes through substitution of inert blocking ligands. For example, the use of 1,4,7-triazacyclononane (tacn) as a face-capping tridentate ligand on each metal complex can direct the formation of $[(tacn)_8M_4M'_4(CN)_{12}]^{z+}$ clusters with core structures consisting of a single cubic unit excised from the Prussian blue type framework.[4, 5]

However, to produce the exceptionally large spin states desired—along with magnetic anisotropy—for increasing the spin reversal barrier in single-molecule magnets, it is necessary to develop methods for constructing larger cluster geometries in which more metal centers can be magnetically coupled.[6] A simple strategy for achieving higher nuclearities involves the use of a blocking ligand on just one of the reaction components, thereby permitting cluster growth to propagate further before a closed structure forms. Accordingly, the reaction between $[Ni(H_2O)_6]^{2+}$ and $[(Me_3tacn)Cr(CN)_3]$ (Me_3tacn = *N,N′,N″*-trimethyl-1,4,7-triazacyclononane) in aqueous solution generates $[(Me_3tacn)_8Cr_8Ni_6(CN)_{24}]^{12+}$, a 14-metal cluster featuring a cube of eight Cr^{3+} ions with each square face spanned by a $[Ni(CN)_4]^{2-}$ unit.[7] In further pursuing reactions of this type, we have discovered two new cluster geometries, including a 19-metal species that represents the largest metal–cyanide cluster reported to date.

Reaction of NiI_2 with $[(Me_3tacn)Cr(CN)_3]$ in aqueous solution does not lead to the face-centered cubic $[(Me_3tacn)_8Cr_8Ni_6(CN)_{24}]^{12+}$ cluster obtained with chloride, bromide, nitrate, or perchlorate as counteranions.[7] Instead, crystallographic analysis[8] of a red-brown crystal isolated from the reaction mixture revealed a product of composition **1**,

$[(Me_3tacn)_8Cr_8Ni_5(CN)_{24}]I_{10} \cdot 27\,H_2O$ **1**

featuring the open-cage cluster depicted in Figure 1. The core structure of this $[(Me_3tacn)_8Cr_8Ni_5(CN)_{24}]^{10+}$ cluster most notably differs from the complete face-centered cubic geometry by having a Ni^{2+} ion missing from one of the cube faces.

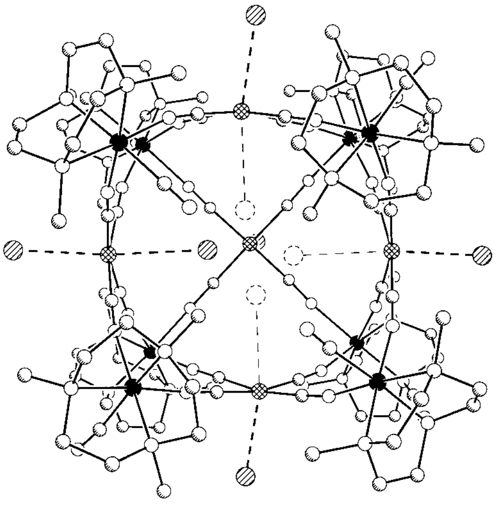

Figure 1. Structure of the $[(Me_3tacn)_8Cr_8Ni_5(CN)_{24}]^{10+}$ cluster and associated I^- anions, as observed in **1**. Black, cross-hatched, shaded, white, and hatched spheres represent Cr, Ni, C, N and I atoms, respectively; H atoms are omitted for clarity. The cluster has maximal point group symmetry C_{2v}. Selected mean interatomic distances [Å] and angles [°]: Cr-N_{CN} 2.05(6), Cr-C 2.04(5), Ni-C 1.86(2), C-N_{CN} 1.14(3), Ni···I_{outer} 2.91(3), Ni···I_{inner} 3.09(3); N_{CN}-Cr-N_{CN} 87(2), N_{CN}-Cr-C 93(3), Cr-N-C_{CN} 170(4), Cr-C-N 172(4), C-Ni-C 89(1), Ni-C-N 177(1).

As with $[(Me_3tacn)_8Cr_8Ni_6(CN)_{24}]^{12+}$,[7] the thermal energy delivered in the course of forming the cluster is apparently sufficient to reorient the cyanide ligands from the Cr^{III}-C-N connectivity of the reactant complex to the more stable Cr^{III}-N-C-Ni^{II} bridging arrangement. This, rather than the reverse bridging cyanide orientation, was clearly favored in the crystal

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structure refinement, and is consistent with the Ni-C-N angles (175.8(9) – 179.5(9)°) being closer to linearity than the Cr-N-C angles (161(2) – 176.0(8)°), as well as with the short Ni–C distances (1.84(1) – 1.893(9) Å). Note, however, that the absence of a nickel atom from one face of the cluster leaves four terminal cyanide ligands retaining the Cr^{III}-C-N connectivity, two of which are directed away from the center of the open cube face. Thus, while the opening appears sizable, the methyl groups on the nitrogen atoms coordinated *trans* to these two cyanide ligands somewhat inhibit access to the cluster interior, constricting the entryway to a minimum width of approximately 0.6 Å (based on van der Waals radii). In contrast to the empty $[(Me_3tacn)_8Cr_8Ni_6(CN)_{24}]^{12+}$ cluster reported previously,[7] a single iodide anion resides within the metal–cyanide cage of the $[(Me_3tacn)_8Cr_8Ni_5(CN)_{24}]^{10+}$ cluster. As depicted in Figure 1, the encapsulated ion is disordered over four positions in the crystal structure, each approaching an axial ligand site on a nickel center with a mean Ni$\cdots$I distance of 3.09(3) Å; interestingly, no disposition toward the fifth nickel center is evident in the residual electron density. Stronger axial interactions are formed between all five nickel centers and iodide ions located outside the cluster at a mean Ni$\cdots$I separation of 2.91(3) Å. Attempts to extract the central iodide ion by metathesis reactions are underway, with the intention of probing the potential host–guest chemistry of this voluminous open-cage cluster.

The square-planar $[Ni(CN)_4]^{2-}$ complex has long been known to react with excess cyanide ions in aqueous solution to generate $[Ni(CN)_5]^{3-}$.[9] Although the latter species favors a square-pyramidal coordination geometry,[10] a slightly distorted trigonal-bipyramidal structure lies close in energy, as highlighted by the presence of both forms in the crystal structure of $[Cr(en)_3][Ni(CN)_5] \cdot 1.5\,H_2O$ (en = ethylenediamine).[11] In a surprising parallel, $[Ni(CN)_4]^{2-}$ reacts with the cyanide-rich $[(Me_3tacn)_8Cr_8Ni_5(CN)_{24}]^{10+}$ cluster in aqueous solution to yield **2**, a compound that incorporates square-

$[(Me_3tacn)_{10}Cr_{10}Ni_9(CN)_{42}][Ni(CN)_4]_3 \cdot 55\,H_2O$ **2**

pyramidal and trigonal-bipyramidal $[Ni(CN)_5]^{3-}$ and square-planar $[Ni(CN)_4]^{2-}$ units in a single cluster. The structure[8] of this C_3-symmetric $[(Me_3tacn)_{10}Cr_{10}Ni_9(CN)_{42}]^{6+}$ cluster bears no obvious relationship to its Cr_8Ni_5 predecessor, and consists of a barrel-shaped cage enclosing a bound central $[(Me_3tacn)Cr(NC-)_3]$ moiety (Figure 2). The surrounding cage framework is made up of three tiers, each with six metal centers. The top and bottom tiers exhibit pseudo-hexagonal $Cr_3Ni_3(CN)_6$ rings, which are joined through cyanide bridges to the three linear $CrNi(CN)_2$ units of the middle tier. Once again, a Cr^{III}-N-C-Ni^{II} connectivity is adopted by all bridging cyanide ligands. The square-planar nickel centers in the middle tier are each capped by a square-planar $[Ni(CN)_4]^{2-}$ counteranion (not shown in Figure 2) through a weak Ni$\cdots$Ni bonding contact of 3.12 Å. This type of interaction also occurs in the structure of **3**, and is attributed to admixing of empty p_z orbitals with the filled d_{z^2} orbitals in the Ni$^{II}\cdots$Ni^{II} pairs.[7]

$[(Me_3tacn)_8Cr_8Ni_6(CN)_{24}][Ni(CN)_4]_6 \cdot 47\,H_2O$ **3**

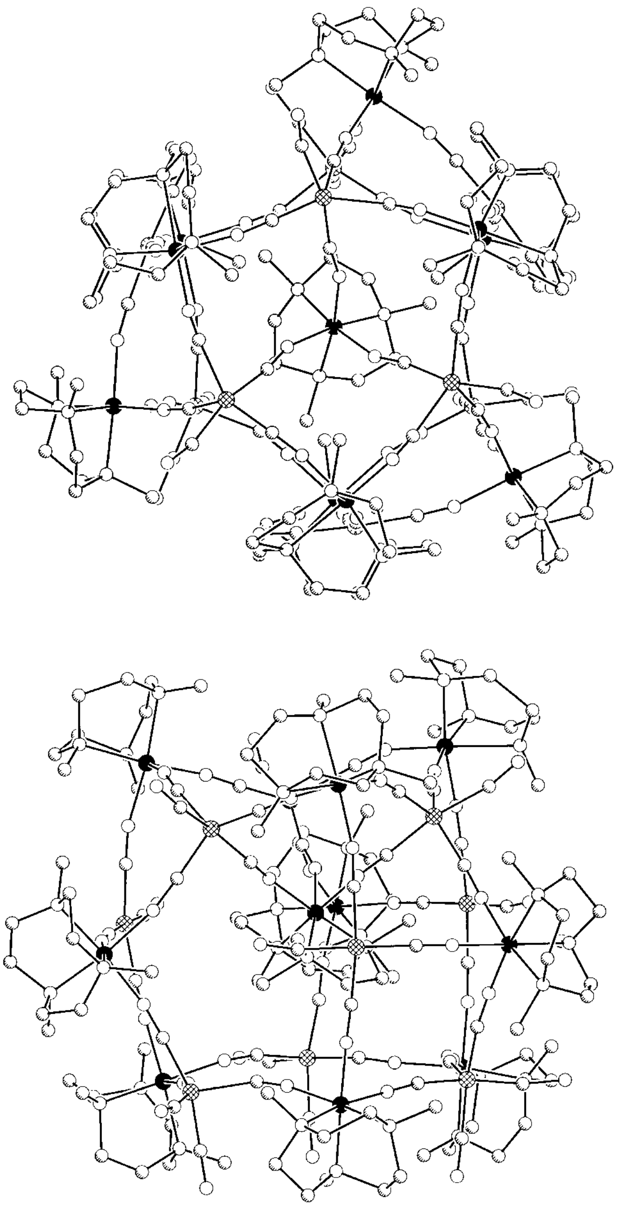

Figure 2. Structure of the $[(Me_3tacn)_{10}Cr_{10}Ni_9(CN)_{42}]^{6+}$ cluster in **2**, viewed parallel (top) and perpendicular (bottom) to the crystallographic 6_3 screw axis. Black, cross-hatched, shaded, and white spheres represent Cr, Ni, C, and N atoms, respectively; H atoms are omitted for clarity. The nickel centers adopting square-planar (Ni(1)), square-pyramidal (Ni(2)), and trigonal-bipyramidal (Ni(3)) coordination geometries are located in the middle, lower, and upper tiers of the cluster, respectively. Selected mean interatomic distances [Å] and angles [°]: Cr-N$_{CN}$ 2.01(5), Ni(1)-C 1.84(3), C-N$_{CN}$ 1.16(3); N$_{CN}$-Cr-N$_{CN}$ 90(1), Cr-N-C$_{CN}$ 169(4), C-Ni(1)-C 90(3), Ni-C-N 173(5). Additional distances and angles are listed in the legend of Figure 3.

Compound **2** gradually dissolves in DMSO to give an orange solution exhibiting an IR spectrum consistent with the presence of intact $[(Me_3tacn)_{10}Cr_{10}Ni_9(CN)_{42}]^{6+}$ clusters and dissociated $[Ni(CN)_4]^{2-}$ counterions.

The two distinct $[Ni(CN)_5]^{3-}$ units in the structure of **2** are displayed in Figure 3. Analysis of a subset of angles between the normals to adjacent faces of the coordination polyhedra provides a means of distinguishing square-pyramidal and trigonal-bipyramidal coordination geometries.[12] The perti-

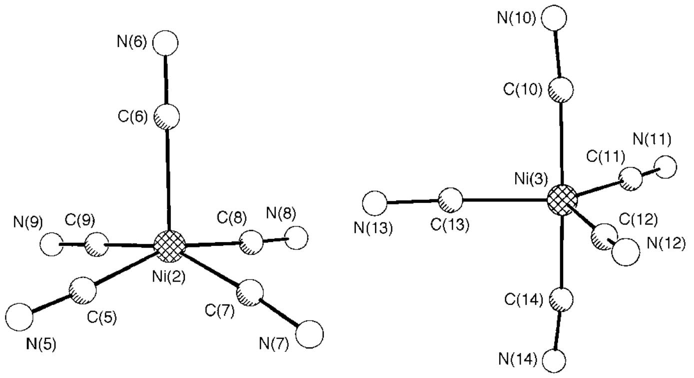

Figure 3. Structures of the two distinct nickel pentacyanide units in the $[(Me_3tacn)_{10}Cr_{10}Ni_9(CN)_{42}]^{6+}$ cluster. Selected interatomic distances [Å] and angles [°]: Ni(2)-C(6) 2.03(2), mean Ni(2)-C_{basal} 1.84(4), mean Ni(3)-C_{ax} 1.84(4), Ni(3)-C(11) 1.82(2), Ni(3)-C(12) 1.98(4), Ni(3)-C(13) 1.83(3); mean C(6)-Ni(2)-C_{basal} 100(8), mean C_{basal}-Ni(2)-C_{basal} 88(3), C(10)-Ni(3)-C(14) 175(2), mean C_{ax}-Ni(3)-C_{eq} 90(4), C(11)-Ni(3)-C(12) 121(1), C(12)-Ni(3)-C(13) 108(1), C(11)-Ni(3)-C(13) 130(1).

nent torsion angles characteristic of the coordination geometry are given in Equations (1)–(6). For comparison, the

Ni(2):

$$e_1 = 180^\circ - [\text{C(5)-C(6)-C(7)-C(8)}] = 68.0^\circ \tag{1}$$

$$e_2 = 180^\circ - [\text{C(5)-C(9)-C(6)-C(8)}] = 80.4^\circ \tag{2}$$

$$e_3 = 180^\circ - [\text{C(8)-C(9)-C(7)-C(5)}] = 4.4^\circ \tag{3}$$

Ni(3):

$$e_1 = 180^\circ - [\text{C(14)-C(11)-C(13)-C(10)}] = 41.4^\circ \tag{4}$$

$$e_2 = 180^\circ - [\text{C(14)-C(12)-C(11)-C(10)}] = 55.6^\circ \tag{5}$$

$$e_3 = 180^\circ - [\text{C(10)-C(12)-C(13)-C(14)}] = 64.6^\circ \tag{6}$$

corresponding angles are $e_1 = e_2 = 75.7^\circ$ and $e_3 = 0.0^\circ$ for an ideal square pyramid, and $e_1 = e_2 = e_3 = 53.1^\circ$ for an ideal trigonal bipyramid. Thus, primarily by virtue of having four surrounding carbon atoms that are approximately coplanar, the coordination geometry of Ni(2) is best described as square-pyramidal, while that of Ni(3), which has no such common plane, is closer to trigonal-bipyramidal. To our knowledge, this represents only the second incidence of nickel pentacyanide in a trigonal-bipyramidal geometry. And indeed, the bond distances and angles for both geometries are remarkably consistent with those observed in $[Cr(en)_3][Ni(CN)_5] \cdot 1.5\,H_2O$.[11] The similarity extends even to the nature of the distortion in the coordination of Ni(3) away from D_{3h} symmetry, which mainly involves a lengthening of one equatorial Ni–C bond (Ni(3)–C(12) 1.98(4) Å) and a widening of the opposite C-Ni-C angle (C(11)-Ni(3)-C(13) 130(1)°). Compound **2** therefore lends support to the claim that this particular distortion from an ideal trigonal bipyramid is not simply a consequence of packing forces, but represents a local energy minimum for the free $[Ni(CN)_5]^{3-}$ ion.[11] Regardless, the deviation from square-pyramidal geometry is most likely due to stabilization of the trigonal-bipyramidal form through external forces imposed by the surrounding Cr^{3+} ions or hydrogen bonds[11, 13] in the two respective instances.

As reflected in the magnetic properties of compounds **1** and **2** (Figure 4), ligation by the strong-field carbon end of cyanide results in exclusively diamagnetic nickel(II) centers, eliminating the possibility of exchange coupling directly between cyanide-bridged metal sites. For both compounds, the measured values of $\chi^M T$ at temperatures above 30 K closely approximate the predicted spin-only values of 15 and 18.75 $cm^3\,K\,mol^{-1}$, corresponding to eight and ten isolated $S = 3/2$ Cr^{3+} ions per formula unit. In each case, a steady rise in $\chi^M T$ below 30 K suggests the onset of weak ferromagnetic coupling between paramagnetic chromium centers. The minimum intercluster Cr···Cr separations of 8.98 and 9.27 Å in the crystal structures of **1** and **2**, respectively, are significantly longer than the minimum intracluster Cr···Cr separations of 6.64 and 6.92 Å, implying that the coupling more likely originates from superexchange within the clusters. In contrast, a weak antiferromagnetic coupling has been postulated to occur between chromium(III) centers in the face-centered cubic $[(Me_3tacn)_8Cr_8Ni_6(CN)_{24}]^{12+}$ cluster.[7] Although well-established for $[Ni(CN)_4]^{2-}$ and square-pyramidal $[Ni(CN)_5]^{3-}$,[9] the low-spin character of the trigonal-bipyramidal form of the latter complex appears not to have been documented previously.

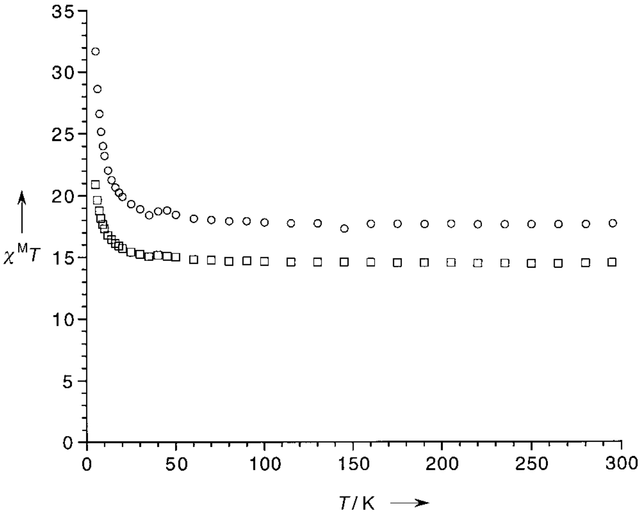

Figure 4. Magnetic behavior of **1** (□) and **2** (○) in an applied field of 1 kG. The data collected at 10 kG for each sample are essentially superimposable. $\chi^M T$ in $cm^3\,K\,mol^{-1}$.

Two high-nuclearity chromium–nickel–cyanide clusters with unprecedented geometries have been prepared. The synthesis of related species utilizing paramagnetic cobalt(II) centers in place of nickel(II) is now being explored as a possible means of generating new single-molecule magnets.

Experimental Section

Absorption spectra were measured with a Hewlett-Packard 8453 spectrophotometer. The IR spectra were recorded on a Nicolet Avatar 360 FTIR spectrometer equipped with an attenuated total reflectance accessory. Mass spectrometric measurements were performed in the positive-ion mode on a Bruker Apex II 7 T actively shielded FTICR mass spectrometer equipped with an analytical electrospray ion source instrument. The water content of each compound was verified by thermogravimetric analysis using a TA instrument TGA 2950. Magnetic data were collected using a Quantum Design MPMS2 SQUID magnetometer, and were corrected for diamagnetic contributions.

1: Solid NiI_2 (54 mg, 0.17 mmol) was added to a solution of $[(Me_3tacn)Cr(CN)_3]$[7] (72 mg, 0.24 mmol) in 20 mL of water. The deep red-brown mixture was stirred and heated at reflux for 8 h, and the solution volume was reduced to 4 mL with further heating. Upon cooling to room temperature, a small amount of yellow solid was separated from the reaction mixture by filtration. The filtrate was allowed to stand for 2 d, leading to formation of large red-brown rhombic plate-shaped crystals, which were collected by filtration, washed with Et_2O (4 × 2 mL), and dried in air to yield 85 mg (64 %) of product. Absorption spectrum (H_2O): λ_{max} (ε_M): 365 (13340), 500 nm (6295, sh); IR: $\tilde{\nu} = 2143$, 2171 (sh) cm^{-1} (ν_{CN}); ES^+ MS: m/z: 1197.331 ($[\mathbf{1} - 3I - 27H_2O]^{3+}$), 886.272 ($[\mathbf{1} - 4I - 27H_2O]^{4+}$), 667.636 ($[\mathbf{1} - 5I - 27H_2O]^{5+}$), 535.046 ($[\mathbf{1} - 6I - 27H_2O]^{6+}$); elemental analysis calcd for $C_{96}H_{222}Cr_8I_{10}N_{48}Ni_5O_{27}$: C 25.86, H 5.02, N 15.08; found: C 26.14, H 4.96, N 14.75.

2: A solution (20 mL) of compound **1** was prepared by treating $[(Me_3tacn)Cr(CN)_3]$[7] (130 mg, 0.44 mmol) with NiI_2 (100 mg, 0.32 mmol) as described above. Instead of allowing this solution to stand for 2 d, a solution of $Na_2[Ni(CN)_4]$ (410 mg, 2.0 mmol) in 12 mL of water was added, producing a fine yellow precipitate. The mixture was centrifuged, and the supernatant solution was decanted and allowed to stand for 3 d. The resulting orange hexagonal plate-shaped crystals were collected by filtration, washed with THF (2 × 1 mL), and dried in air to yield 42 mg (18 %) of product. IR: $\tilde{\nu} = 2123$, 2145, 2160 cm^{-1} (ν_{CN}); elemental analysis calcd for $C_{144}H_{320}Cr_{10}N_{84}Ni_{12}O_{55}$: C 32.43, H 6.05, N 22.07; found: C 32.48, H 5.77, N 21.94.

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[8] Crystallographic analyses: **1** ($C_{96}H_{214}Cr_8I_{10}N_{48}Ni_5O_{23}$): $T = 138$ K, triclinic, space group $P\bar{1}$, $a = 16.3879(3)$, $b = 17.6461(3)$, $c = 18.1958(2)$ Å, $\alpha = 65.885(1)$, $\beta = 64.679(1)$, $\gamma = 74.817(1)°$, $V = 4317.0(1)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.688\ g\,cm^{-3}$, $R_1 = 0.0729$, $wR_2 = 0.2154$ for 21589 data (13758 independent), 914 parameters, and 40 restraints. **2** ($C_{144}H_{288}Cr_{10}N_{84}Ni_{12}O_{39}$): $T = 143$ K, hexagonal, space group $P6_3$, $a = 22.084(2)$, $c = 31.999(4)$ Å, $V = 13516(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.240\ g\,cm^{-3}$, $R_1 = 0.1173$, $wR_2 = 0.2793$ for 51793 data (10313 independent), 576 parameters, and 173 restraints. Single crystals were obtained directly from the reaction products; a slightly low water content was observed in each crystal structure. Data were collected on a Siemens SMART diffractometer using graphite monochromated $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å) radiation, and were corrected for Lorentz, polarization, and absorption effects. Structures were solved by direct methods and refined against all data using SHELXTL 5.0. In the structure of **1**, the cluster is disordered over a crystallographic inversion center, superimposing the open face with the opposite closed face of the cage. Also in this structure, 7 iodide anions and 13 solvate water molecules are disordered over multiple sites and were refined accordingly. The crystal of **2** was found to be a racemic twin, and eight of the solvate water molecules were modeled as disordered over multiple positions in the structure. The final agreement factors for both structures are high due to the extensive disorder present in the crystals and the accompanying poor data quality. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-146872 (**1**) and CCDC-146873 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Chelate Formation around a Hexarhenium Cluster Core by the Diphosphane Ligand $Ph_2P(CH_2)_6PPh_2$[**]

Zhong-Ning Chen, Takashi Yoshimura, Masaaki Abe, Yoichi Sasaki,[*] Shoji Ishizaka, Haeng-Boo Kim, and Noboru Kitamura

The octahedral hexametal cluster core $M_6(\mu_3\text{-}E)_8$ (E = chalcogenide or halide ions) is one of the most common structural units in metal cluster complexes.[1–7] Each metal ion possesses an axial (terminal) coordination site, and a pair of the axial ligands at two adjacent M sites are oriented perpendicular to each other. Thus, the unit can be regarded as a giant octahedral center. Mimicking mononuclear octahe-

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