

Giant Metal–Cyanide Coordination Clusters: Tetracapped Edge-Bridged Cubic $\text{Cr}_{12}\text{Ni}_{12}(\text{CN})_{48}$ and Double Face-Centered Cubic $\text{Cr}_{14}\text{Ni}_{13}(\text{CN})_{48}$ Species

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Received February 19, 2002

The crystal structures of two new metal–cyanide clusters with record high nuclearities are reported. A direct assembly reaction involving $[(\text{Me}_3\text{tacn})\text{Cr}(\text{CN})_3]$ ($\text{Me}_3\text{tacn} = N,N,N'$ -trimethyl-1,4,7-triazacyclononane), Ni_2 , and KCN in aqueous solution affords $[(\text{Me}_3\text{tacn})_{12}\text{Cr}_{12}\text{Ni}_{12}(\text{CN})_{48}]^{12+}$. The structure of this 24-metal cluster features a cube of eight Cr^{III} centers linked along the edges by 12 trans-coordinated $[\text{Ni}(\text{CN})_4]^{2-}$ units, and capped on four faces by $[(\text{Me}_3\text{tacn})\text{Cr}]^{3+}$ moieties. Its metal–cyanide cage encloses a 900 Å³ cavity that is accessible through the two noncapped cube faces. A still larger cluster, $[(\text{Me}_3\text{tacn})_{14}\text{Cr}_{14}\text{Ni}_{13}(\text{CN})_{48}]^{20+}$, was obtained from a related reaction excluding the addition of KCN. This 27-metal species possesses a highly anisotropic geometry in which two face-centered cubic units are fused through a common Ni^{II} vertex.

The possibility of generating single-molecule magnets¹ with higher blocking temperatures has prompted a widespread interest in high-nuclearity metal–cyanide clusters.^{2–4} In general, the approach adopted for synthesizing such species has paralleled preparations of magnetic Prussian blue analogues,⁵ but with the use of multidentate capping ligands that prevent growth of an extended solid. Thus, for example,

employing N,N,N' -trimethyl-1,4,7-triazacyclononane (Me_3tacn) as a tridentate capping ligand permits assembly of the face-centered cubic cluster $[(\text{Me}_3\text{tacn})_8\text{Cr}_8\text{Ni}_6(\text{CN})_{24}]^{12+}$.^{3b} The advantage of metal–cyanide cluster systems is similar to that established for Prussian blue type solids:⁵ once a new structure type is identified, its properties can be adjusted via substitution of a range of different metal ions. Indeed, analogues of the aforementioned face-centered cubic cluster have now been synthesized in which Cr^{III} is replaced with Co^{III} or Mo^{III} and Ni^{II} is replaced with Cu^{II} , Pd^{II} , or Pt^{II} .^{3c,6} We hope to utilize such substitutions in still larger cluster geometries to produce high-spin molecules exhibiting magnetic bistability.¹ Herein, we disclose the structures of $[(\text{Me}_3\text{tacn})_{12}\text{Cr}_{12}\text{Ni}_{12}(\text{CN})_{48}]^{12+}$ and $[(\text{Me}_3\text{tacn})_{14}\text{Cr}_{14}\text{Ni}_{13}(\text{CN})_{48}]^{20+}$, the highest nuclearity metal–cyanide clusters yet reported.

Previous work had shown that cyanide-rich $[(\text{Me}_3\text{tacn})_8\text{Cr}_8\text{Ni}_5(\text{CN})_{24}]^{10+}$ reacts with $[\text{Ni}(\text{CN})_4]^{2-}$ to generate a C_3 -symmetric $[(\text{Me}_3\text{tacn})_{10}\text{Cr}_{10}\text{Ni}_9(\text{CN})_{42}]^{6+}$ cluster.^{3c} In an effort to obtain this species in greater yield, direct assembly reactions involving a 10:9:12 molar ratio of $[(\text{Me}_3\text{tacn})\text{Cr}(\text{CN})_3]$, Ni_2 , and KCN were attempted. In concentrated

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aqueous solution these reactions were in fact observed to precipitate significant quantities of the 19-metal cluster, albeit with a small amount of some unidentified impurity.

In more dilute solution, however, closely related reactions were found to generate an even higher nuclearity cluster. A solution of $[(\text{Me}_3\text{tacn})\text{Cr}(\text{CN})_3]^{3b}$ (50 mg, 0.17 mmol) and NiI_2 (47 mg, 0.15 mmol) in 15 mL of water was heated at 65 °C for 2 h. Solid KCN (9.2 mg, 0.14 mmol) was added to the brown solution over a span of 5 min, inducing formation of a pale orange precipitate. Upon addition of 1 mL of water, the mixture was allowed to cool to room temperature, and the precipitate was removed by filtration. Diffusion of THF vapor into the orange filtrate over the course of 2 weeks afforded orange triangular prism-shaped crystals suitable for X-ray analysis.⁷ The crystals were collected by filtration, washed with successive aliquots of THF (2×2 mL) and ether (2×2 mL), and dried in air to afford 19 mg (22%) of $[(\text{Me}_3\text{tacn})_{12}\text{Cr}_{12}\text{Ni}_{12}(\text{CN})_{48}]\text{I}_{12} \cdot \text{KCN} \cdot 2\text{THF} \cdot 32\text{H}_2\text{O}$ (**1**).⁸

Figure 1 depicts the structure of the unexpected 24-metal cluster, $[(\text{Me}_3\text{tacn})_{12}\text{Cr}_{12}\text{Ni}_{12}(\text{CN})_{48}]^{12+}$, in which 12 $[(\text{Me}_3\text{tacn})_{12}\text{Cr}]^{3+}$ moieties are joined via 12 $[\text{Ni}(\text{CN})_4]^{2-}$ units. Eight of the chromium atoms reside at the vertexes of an approximate cube and are connected through trans ligands of the $[\text{Ni}(\text{CN})_4]^{2-}$ units, one of which is located along each cube edge. Four faces of the cube are capped by $[(\text{Me}_3\text{tacn})_{12}\text{Cr}]^{3+}$ moieties, leading to a slight compression along a 4-fold rotation axis (as reflected in the $\text{Cr} \cdots \text{Cr}$ edge distances of 9.456(9) and 9.827(6) Å). Consequently, the four $[\text{Ni}(\text{CN})_4]^{2-}$ units around the waist of the cluster deviate from the usual square planar geometry, each flexing outward toward an associated iodide anion (not shown) to give a Ni–I separation of 2.70(1) Å. Note that, as previously observed in related assembly reactions,^{3bc} formation of the cluster involves isomerization of the cyanide ligands to the thermodynamically favored $\text{Cr}^{\text{III}}-\text{NC}-\text{Ni}^{\text{II}}$ bridging arrangement. Accordingly, the nickel(II) centers assume a diamagnetic electron configuration.

The metal–cyanide cage of the $\text{Cr}_{12}\text{Ni}_{12}$ cluster encloses a sizable cavity with a volume of 900 Å³.⁹ The largest openings in the cage are situated above the two noncapped faces of the Cr_8 cube and possess a *minimum* diameter

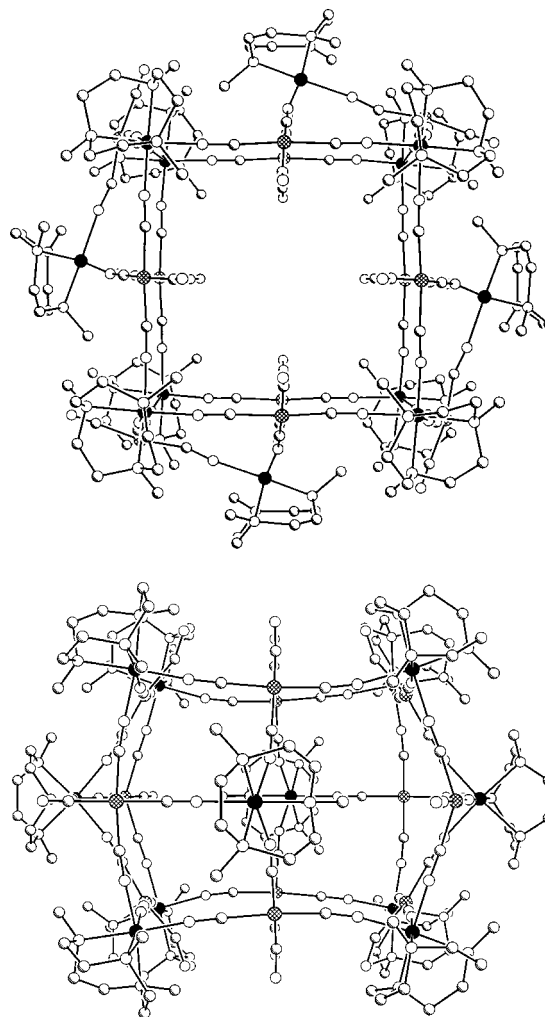


Figure 1. Structure of the tetracapped edge-bridged cubic cluster $[(\text{Me}_3\text{tacn})_{12}\text{Cr}_{12}\text{Ni}_{12}(\text{CN})_{48}]^{12+}$ in $\mathbf{1} \cdot 2\text{THF} \cdot 10\text{H}_2\text{O}$, as viewed parallel (upper) and perpendicular (lower) to its 4-fold rotation axis. Black, crosshatched, shaded, and white spheres represent Cr, Ni, C, and N atoms, respectively; H atoms are omitted for clarity. The cluster conforms to its maximal point group symmetry of C_{4h} in the crystal. Selected mean interatomic distances (Å) and angles (deg): $\text{Cr}-\text{N}_{\text{tacn}}$ 2.06(6), $\text{Cr}-\text{N}_{\text{CN}}$ 2.02(7), $\text{Ni}-\text{C}$ 1.83(3), $\text{C}-\text{N}_{\text{CN}}$ 1.152(3), $\text{Cr} \cdots \text{Ni}$ 4.98(4), $\text{N}_{\text{tacn}}-\text{Cr}-\text{N}_{\text{tacn}}$ 85(2), $\text{N}_{\text{tacn}}-\text{Cr}-\text{N}_{\text{CN}}$ 92(3), $\text{N}_{\text{CN}}-\text{Cr}-\text{N}_{\text{CN}}$ 91(2), $\text{Cr}-\text{N}_{\text{CN}}-\text{C}$ 171(4), $\text{Ni}-\text{C}-\text{N}$, 168(11), $\text{C}-\text{Ni}-\text{C}$ 89(4).

defined by the $\text{N} \cdots \text{N} = 7.01(6)$ Å separation between opposing terminal cyanide ligands. In the crystal structure, the cluster cavity contains a central $[\text{K}(\text{THF})_4(\text{H}_2\text{O})_2]^+$ complex and at least two additional water molecules. Solution IR spectra, together with the results from mass spectrometry,⁸ indicate that the cluster remains intact in aqueous solution. Methods for probing its host–guest chemistry are currently under consideration.

A still larger 27-metal cluster was encountered in a related reaction that excluded the addition of KCN. A solution of $[(\text{Me}_3\text{tacn})\text{Cr}(\text{CN})_3]$ (66 mg, 0.22 mmol) and NiI_2 (50 mg, 0.16 mmol) in 12 mL of water was heated at 75 °C for 2 days and cooled to room temperature. Evaporation of the

(7) Crystal and structure refinement parameters: $\mathbf{1} \cdot 2\text{THF} \cdot 10\text{H}_2\text{O}$, $\text{C}_{173}\text{H}_{368}\text{Cr}_{12}\text{I}_{12}\text{KN}_{85}\text{Ni}_{12}\text{O}_{46}$, $T = 154$ K, $I4/m$, $Z = 2$, $a = 24.249(2)$ Å, $c = 31.304(3)$ Å, $V = 18408(2)$ Å³, $d_{\text{calc}} = 1.311$ g/cm³, $R_1 = 0.1132$, $wR_2 = 0.2802$; **2**, $\text{C}_{174}\text{H}_{434}\text{Cr}_{14}\text{I}_{20}\text{N}_{90}\text{Ni}_{13}\text{O}_{70}$, $T = 160$ K, $Pbca$, $Z = 4$, $a = 23.2283(9)$ Å, $b = 34.683(2)$ Å, $c = 46.900(2)$ Å, $V = 37784(3)$ Å³, $d_{\text{calc}} = 1.571$ g/cm³, $R_1 = 0.1703$, $wR_2 = 0.4228$. Data were collected on a Siemens SMART diffractometer using graphite-monochromated $\text{Mo K}\alpha$ ($\lambda = 0.71073$ Å) radiation and were corrected for Lorentz, polarization, and absorption effects. The structures were refined against all data using SHELXTL 5.0. Owing to an extreme degree of disorder among the iodide anions and solvate water molecules, both structures suffer from poor resolution. Consequently, the interatomic distances and angles resulting from the refinements should be viewed with some skepticism. In the structure of **1**, the largest regions of solvate water were treated using SQUEEZE.

(8) Characterization of **1**: IR (solid, ATR) ν_{CN} 2144, 2138 cm⁻¹; $\mu_{\text{eff}} = 13.26 \mu_{\text{B}}$ at 295 K; ES⁺-MS ($\text{H}_2\text{O}/\text{MeOH}$) m/z 1412 ($\{[(\text{Me}_3\text{tacn})_{12}\text{Cr}_{12}\text{Ni}_{12}(\text{CN})_{48}]\text{I}_8\}^{4+}$), 1104 ($\{[(\text{Me}_3\text{tacn})_{12}\text{Cr}_{12}\text{Ni}_{12}(\text{CN})_{48}]\text{I}_7\}^{5+}$). Anal. Calcd for $\text{C}_{165}\text{H}_{332}\text{Cr}_{12}\text{I}_{12}\text{N}_{85}\text{Ni}_{12}\text{O}_{34}$: C, 28.55; H, 4.82; N, 17.15. Found: C, 28.78; H, 5.20; N, 17.50. The solvent content of this compound was confirmed by thermogravimetric analysis.

(9) This volume is based on the van der Waals radii of the cluster atoms and was calculated using a procedure described previously: Shores, M. P.; Beauvais, L. G.; Long, J. R. *J. Am. Chem. Soc.* **1999**, *121*, 775.

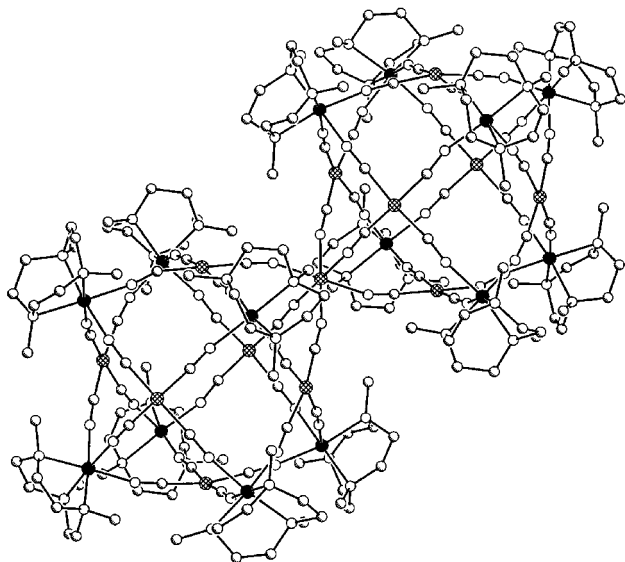


Figure 2. Structure of the double face-centered cubic cluster $[(\text{Me}_3\text{tacn})_{14}\text{Cr}_{14}\text{Ni}_{13}(\text{CN})_{48}]^{20+}$ in **2**. Black, crosshatched, shaded, and white spheres represent Cr, Ni, C, and N atoms, respectively; H atoms are omitted for clarity. The molecule resides on a crystallographic inversion center and, ignoring Me_3tacn conformations, has a maximal point group symmetry of D_{3d} .

solution to near dryness gave a solid containing dark red hexagonal plate-shaped crystals of $[(\text{Me}_3\text{tacn})_{14}\text{Cr}_{14}\text{Ni}_{13}(\text{CN})_{48}]\text{I}_{20} \cdot \sim 70\text{H}_2\text{O}$ (**2**)¹⁰ suitable for X-ray analysis.⁷ Efforts to isolate this compound in pure form are ongoing.

As shown in Figure 2, the crystal structure of **2** features a $[(\text{Me}_3\text{tacn})_{14}\text{Cr}_{14}\text{Ni}_{13}(\text{CN})_{48}]^{20+}$ cluster, in which two face-

centered cubic units (of the type exemplified by $[(\text{Me}_3\text{tacn})_8\text{Cr}_8\text{Ni}_6(\text{CN})_{24}]^{12+}$)^{3b} are fused through a common vertex. The central metal consists of a presumably high spin Ni^{2+} ion that is octahedrally coordinated by the nitrogen atoms of six cyanide ligands. With an end-to-end span of $\text{Cr}\cdots\text{Cr} = 23.81(2)$ Å, the cluster exhibits a more anisotropic shape than most other known high-nuclearity metal–cyanide clusters. It therefore presents an attractive target geometry for generating molecules with a large overall magnetic anisotropy.

Future work will endeavor to incorporate a range of paramagnetic metal centers into the new metal–cyanide cluster geometries established herewith.

Acknowledgment. This research was supported by NSF Grant No. CHE-0072691, the Camille and Henry Dreyfus Foundation, and the Alfred P. Sloan Foundation. We thank the NSF for providing J.J.S. with a predoctoral fellowship, Elf-Atochem for partial support of M.P.S., and Dr. C. Crawford and Unilever for a donation of Me_3tacn .

Supporting Information Available: Tables of crystallographic information for the structures of **1**·2THF·10H₂O and **2**. An X-ray crystallographic file (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(10) Characterization of **2**: IR (solid, ATR) ν_{CN} 2150 (br) cm^{-1} ; ES⁺-MS ($\text{H}_2\text{O}/\text{MeOH}$) m/z 1408 ($\{[(\text{Me}_3\text{tacn})_{14}\text{Cr}_{14}\text{Ni}_{13}(\text{CN})_{48}]\text{I}_{15}\}^{5+}$), 1152 ($\{[(\text{Me}_3\text{tacn})_{14}\text{Cr}_{14}\text{Ni}_{13}(\text{CN})_{48}]\text{I}_{14}\}^{6+}$), 970 ($\{[(\text{Me}_3\text{tacn})_{14}\text{Cr}_{14}\text{Ni}_{13}(\text{CN})_{48}]\text{I}_{13}\}^{7+}$), 832 ($\{[(\text{Me}_3\text{tacn})_{14}\text{Cr}_{14}\text{Ni}_{13}(\text{CN})_{48}]\text{I}_{12}\}^{8+}$).