

TRIMETHYLTRIAZACYCLONONANECHROMIUM(III) COMPLEXES AND A CHROMIUM(III)-NICKEL(II)-CYANIDE CLUSTER WITH A FACE-CENTERED CUBIC GEOMETRY

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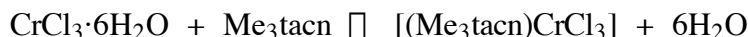
The recent discovery that certain metal-oxo clusters can sustain a remanent magnetization has prompted interest in the synthesis of new “single-molecule magnets” as potential media for high-density information storage.¹ Unfortunately, the broad structural variability inherent to metal-oxo cluster systems severely hampers the design of species with higher magnetic moment reversal barriers. Alternative cluster systems that might permit better control over magnetic properties such as the spin and anisotropy associated with the ground state are therefore sought.

Toward this end, we and others have begun to explore transition metal-cyanide cluster chemistry.²⁻⁶ The preference of cyanide for adopting a linear bridging geometry allows a more directed approach to synthesis, as well as a means of predicting the nature of the pairwise magnetic exchange interactions.⁷ Indeed, recognition of these factors has enabled the design of Prussian blue type solids exhibiting bulk magnetic ordering above room temperature.⁸ By using appropriate capping ligands on the metal complex precursors, analogous reactions can direct the formation of molecular metal-cyanide clusters instead of extended solids. Such synthetic control has been demonstrated with the assembly of a cubic $[(\text{tacn})_8\text{Co}_8(\text{CN})_{12}]^{12+}$ ($\text{tacn} = 1,4,7\text{-triazacyclo-nonane}$) cluster from $[(\text{tacn})\text{Co}(\text{CN})_3]$ and $[(\text{tacn})\text{Co}(\text{H}_2\text{O})_3]^{3+}$.^{2,9} More recently, we have shown how the use of a capping ligand on just one of the reactant species can lead to even larger metal-cyanide clusters.^{3,4} For example, the reaction of $[(\text{Me}_3\text{tacn})\text{Cr}(\text{CN})_3]$ ($\text{Me}_3\text{tacn} = N,N',N''\text{-trimethyl-1,4,7-triazacyclononane}$) with $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ generates a fourteen-metal $[(\text{Me}_3\text{tacn})_8\text{Cr}_8\text{-Ni}_6(\text{CN})_{24}]^{12+}$ cluster bearing the unique face-centered cubic geometry depicted in Figure 1.³

Herein, we report the detailed syntheses of $[(\text{Me}_3\text{tacn})_8\text{Cr}_8\text{Ni}_6(\text{CN})_{24}]\text{Br}_{12}\cdot 25\text{H}_2\text{O}$ and a sequence of mononuclear chromium(III) precursors, $[(\text{Me}_3\text{tacn})\text{CrX}_3]$ ($\text{X} = \text{Cl}, \text{CF}_3\text{SO}_3, \text{CN}$). The preparation of the trichloride complex is adapted from previous reports,^{10,11} while the preparations for the other precursors represent modifications of those described for the analogous (tacn) -containing complexes.¹²

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**A. *N,N',N''*-TRIMETHYL-1,4,7-TRIAZACYCLONONANETRICHORO-
CHROMIUM(III)**



Procedure

A 10 mL, round-bottomed flask is charged with a Teflon-coated magnetic stirring bar, dimethylsulfoxide (3 mL, commercial, dried over 3 Å sieves), and solid $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (3.76 g, 14.1 mmol, Fisher). A small portion of methanol is used to wash all of the $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ into the flask. The resulting green solution is stirred and heated to 120 °C for one hour to drive off the water and methanol, forming a deep purple solution. Approximately thirty granules of Zn (30 mesh, Fisher) are added to the solution, and, with the solution maintained at a temperature of 70 °C, Me_3tacn (2.41 g, 14.0 mmol, Unilever[†]) is added dropwise over a five minute period. The resulting dark green mixture must be stirred vigorously to prevent solidification. Small aliquots of methanol can be added to wash in all the Me_3tacn as well as to break up the mixture. The mixture is heated at 120 °C for two hours, cooled to room temperature, then transferred to a 250 mL beaker and mixed with water (100 mL, distilled and deionized) and cooled at 5 °C in a refrigerator for four hours. The mixture is filtered, washed with water (50 mL) and diethyl ether (2 × 20 mL), and dried in air to afford $[(\text{Me}_3\text{tacn})\text{CrCl}_3]$ (2.65 g, 8.04 mmol) as a green solid.[‡] Yield 57%.

Anal. Calcd. for $\text{C}_9\text{H}_{21}\text{Cl}_3\text{CrN}_3$: C, 32.79; H, 6.42; N, 12.75. Found: C, 32.69; H, 6.48; N, 12.67.

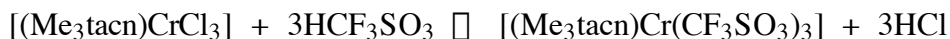
Properties

The compound $[(\text{Me}_3\text{tacn})\text{CrCl}_3]$ is a green solid that is air and moisture stable at room temperature. It is soluble in dimethylformamide and dimethylsulfoxide, and insoluble in water and most other common solvents. Its UV-visible absorption spectrum (DMF) shows maxima at 468 ($\epsilon = 132 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$) and 634 nm (111).

[†] We gratefully acknowledge Dr. C. Crawford and Unilever for a donation of crude Me_3tacn , which was purified by vacuum distillation (36 °C, ca. 80 mTorr) prior to use. For a preparation of Me_3tacn , see reference 11. This compound can also be purchased from Aldrich Chemical Co., Milwaukee, WI 53233.

[‡] In the event that only a small amount of green precipitate is obtained, the product can be extracted from the purple filtrate by reducing it to dryness using a rotary evaporator, heating the residue *in vacuo* at 120 °C for four hours, and washing the resulting solid twice with 50 mL of water.

B. *N,N',N''*-TRIMETHYL-1,4,7-TRIAZACYCLONONANETRIS(TRIFLUOROMETHANESULFONATO)CHROMIUM(III)



Procedure

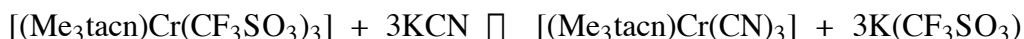
A 150 mL Schlenck flask is charged with a Teflon-coated magnetic stirring bar and $[(\text{Me}_3\text{tacn})\text{CrCl}_3]$ (**A**, 2.60 g, 7.89 mmol). Under a flow of dinitrogen and while stirring, trifluoromethanesulfonic acid (15 mL, 170 mmol, Acros, 99%) is slowly added, producing a thick purple solution and gaseous hydrochloric acid. The flask is fitted with an oil bubbler, and dinitrogen is passed over the solution while it is stirred and heated for six hours at 50 °C. The flask is cooled to room temperature, and diethyl ether (100 mL) is added to precipitate a purple solid. The solid is filtered on a fine sintered-glass funnel, washed with diethyl ether (4 \times 25 mL) and dried in air briefly to afford $[(\text{Me}_3\text{tacn})\text{Cr}(\text{CF}_3\text{SO}_3)_3]$ (5.28 g, 7.88 mmol) as a violet solid. Yield 99%.

Anal. Calcd. for $\text{C}_{12}\text{H}_{21}\text{CrF}_9\text{N}_3\text{O}_9\text{S}_3$, 21.50; H, 3.16; N, 6.27; S, 14.34. Found: C, 21.22; H, 3.10; N, 6.20; S, 14.16.

Properties

The compound $[(\text{Me}_3\text{tacn})\text{Cr}(\text{CF}_3\text{SO}_3)_3]$ is a violet solid when anhydrous. After prolonged exposure to air, its color deepens to dark purple as it picks up water. It is soluble in dimethylformamide and dimethylsulfoxide, and insoluble in water and methanol. Its IR spectrum shows $\nu(\text{SO})$ as a broad, intense band at 1203 cm^{-1} . Its UV-visible absorption spectrum (DMF) shows maxima at 417 ($\epsilon = 35 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) and 566 nm (162).

C. *N,N',N''*-TRIMETHYL-1,4,7-TRIAZACYCLONONANETRICYANO-CHROMIUM(III)



Procedure

A 150 mL Schlenck flask fitted with a gas bubbler is charged with a Teflon-coated magnetic stirring

bar, dimethylsulfoxide (40 mL, commercial, dried over 3 Å sieves), [(Me₃tacn)Cr(CF₃SO₃)₃] (**B**, 5.25 g, 7.83 mmol), and KCN (10.25 g, 157 mmol, Mallinckrodt, ground with mortar and pestle). The purple mixture is stirred and heated under a dinitrogen atmosphere at 110 °C for 24 hours, whereupon a color change to orange-brown is observed. The mixture is cooled to room temperature and transferred to a 250 mL beaker containing 150 mL dichloromethane to complete precipitation of the raw product. The mixture is filtered and washed with dichloromethane (2 × 15 mL) to obtain a yellow solid and a brown filtrate. The filtrate is discarded. To separate the product from unreacted KCN, a yellow solution is extracted from the solid with hot (ca. 50 °C) dimethylformamide (6 × 50 mL). The solvent is removed using a rotoevaporator, and the resulting yellow solid is washed with diethyl ether (50 mL). The product is redissolved in water (40 mL), concentrated with heat to 25 mL, and cooled in a refrigerator at 5 °C to precipitate a first crop of [(Me₃tacn)Cr(CN)₃] (1.29 g, 4.28 mmol) as yellow crystals. The precipitate is washed with acetone (5 mL) and diethyl ether (5 mL), and dried in air. Concentration of the mother liquor to 8 mL and cooling as above yields a second crop of yellow solid (0.328 g, 1.09 mmol), which is washed similarly. Further concentration of the mother liquor to 1 mL yields a third crop (0.136 g, 0.452 mmol) upon cooling. Total yield 74% (1.76 g, 5.83 mmol).

Anal. Calcd. for C₁₂H₂₁CrN₆: C, 47.83; H, 7.02; N, 27.89. Found: C, 47.79; H, 7.30; N, 27.79.

Properties

The compound [(Me₃tacn)Cr(CN)₃] is a yellow microcrystalline solid which is air and moisture stable at room temperature. It is soluble in polar solvents such as water, methanol, acetonitrile, dimethylformamide and dimethylsulfoxide. It is insoluble in common organic solvents such as ether, dichloromethane, and acetone. Its IR spectrum shows $\nu(\text{CN})$ as a sharp but very weak band at 2132 cm⁻¹. Its UV-visible absorption spectrum (H₂O) shows maxima at 339 (ϵ = 52 L·mol⁻¹·cm⁻¹) and 425 nm (43). At 295 K, the compound exhibits an effective magnetic moment of $\mu_{\text{eff}} = 3.85 \mu_{\text{B}}$. Single crystals suitable for X-ray analysis can be grown by slow evaporation of an aqueous solution of the complex. It crystallizes as the monohydrate in orthorhombic space group *P*2₁2₁2₁ with unit cell dimensions $a = 8.3292(2)$ Å, $b = 13.6144(4)$ Å, $c = 13.6916(4)$ Å, $V = 1552.59(7)$ Å³, and $Z = 4$.

**D. OCTAKIS(*N,N',N''*-TRIMETHYL-1,4,7-TRIAZACYCLONONANE-
CHROMIUM(III))HEXAKIS(TETRACYANONICKELATE(II)) BROMIDE
HYDRATE**



Procedure

A 50 mL, round-bottomed flask is charged with a Teflon-coated stirring bar, $[(\text{Me}_3\text{tacn})\text{Cr}(\text{CN})_3]$ (C, 150 mg, 0.50 mmol), and water (15 mL). To the stirring mixture is added solid $\text{NiBr}_2 \cdot 6\text{H}_2\text{O}$ (130 mg, 0.38 mmol, Aldrich). Within five minutes, an orange solution forms. The solution is stirred and heated at reflux for ten hours, concentrated to 2 mL, then cooled to room temperature and allowed to stand for twelve hours. A first crop of orange crystals precipitates from the solution. The crystals are filtered, washed with ethanol (5 mL), acetone (5 mL) and diethyl ether (5 mL) and dried in air to afford $[(\text{Me}_3\text{tacn})_8\text{Cr}_8\text{Ni}_6(\text{CN})_{24}]\text{Br}_{12} \cdot 25\text{H}_2\text{O}$ (98 mg, 24 μmol) as an orange microcrystalline powder. The mother liquor is further concentrated with heat to 0.5 mL to yield a second crop of crystals, which are washed as described above to give more orange powder (86 mg, 21 μmol). Total yield 67% (180 mg, 44 μmol).

Anal. Calcd. for $\text{C}_{96}\text{H}_{218}\text{Br}_{12}\text{Cr}_8\text{N}_{48}\text{Ni}_6\text{O}_{25}$: C, 27.64; H, 5.27; N, 16.11. Found: C, 27.89; H, 5.54; N, 15.90. The water content of this compound varies somewhat with humidity, and was confirmed by thermogravimetric analysis.

Properties

The compound $[(\text{Me}_3\text{tacn})_8\text{Cr}_8\text{Ni}_6(\text{CN})_{24}]\text{Br}_{12} \cdot 25\text{H}_2\text{O}$ is an orange microcrystalline solid which is air and moisture stable at room temperature. It is soluble in water and methanol, and insoluble in common organic solvents such as ether, acetonitrile, and acetone. Its IR spectrum shows $\nu(\text{CN})$ as a strong band at 2148 cm^{-1} with shoulders at 2175 and 2111 cm^{-1} . Its UV-visible absorption spectrum (H_2O) shows a maximum at 463 nm ($\epsilon = 52\text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$). At 280 K , the compound exhibits an effective magnetic moment of $\mu_{\text{eff}} = 11.3\ \mu_{\text{B}}$. Single crystals suitable for X-ray analysis can be grown by slow evaporation of an aqueous solution of the compound. It crystallizes with approximately 20 additional solvate water molecules in trigonal space group $R\bar{3}$ with unit cell dimensions $a = 19.4604(3)\text{ \AA}$, $c = 41.7172(1)\text{ \AA}$, $V = 13682.0(3)\text{ \AA}^3$, and $Z = 3$.

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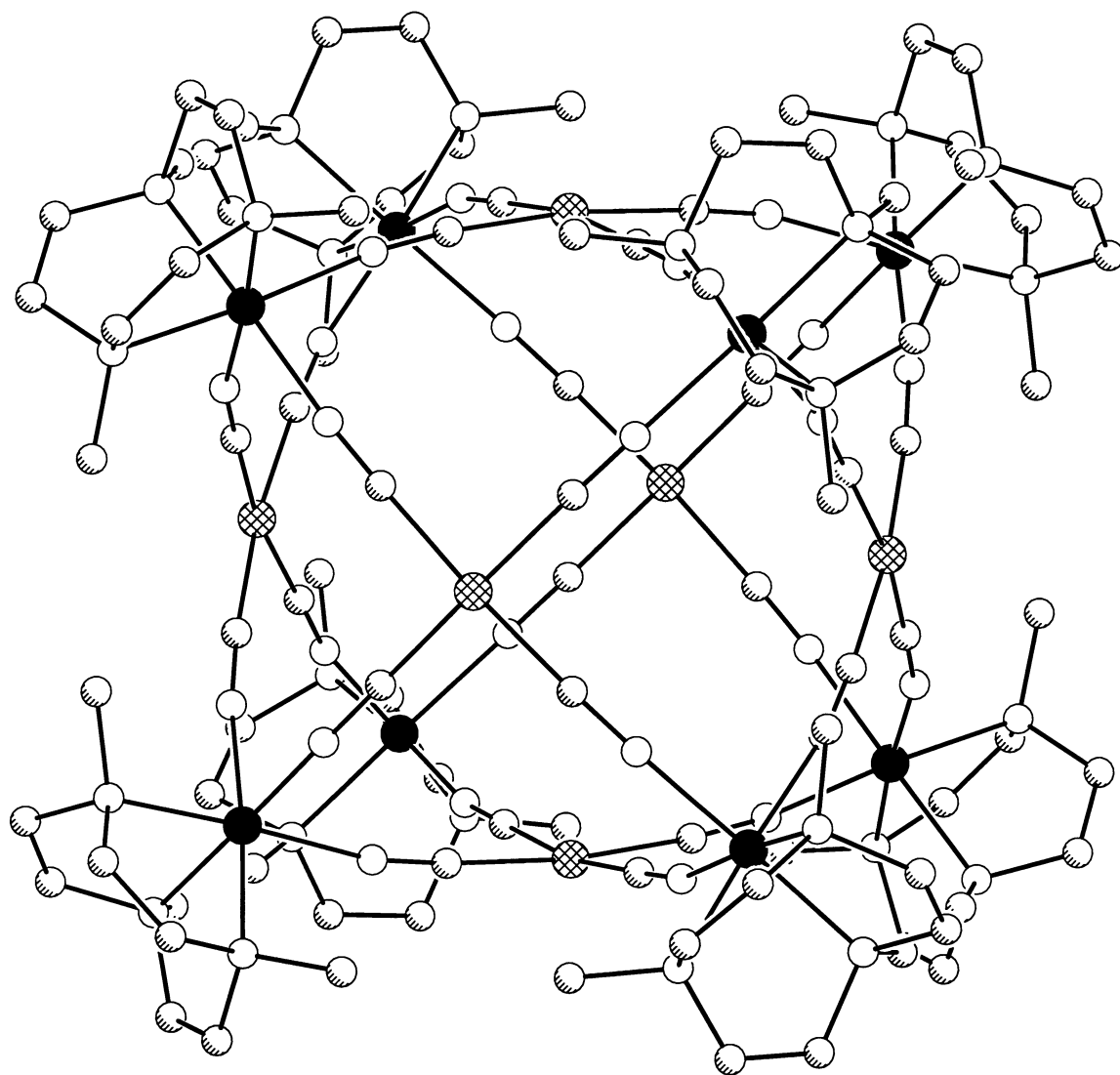


Figure 1. Structure of the face-centered cubic cluster $[(\text{Me}_3\text{tacn})_8\text{Cr}_8\text{Ni}_6(\text{CN})_{24}]^{12+}$. Black, crosshatched, shaded, and white spheres represent Cr, Ni, C, and N atoms, respectively; H atoms are omitted for clarity.