Supporting Information for
Linkage Isomerism in a Face-Centered Cubic $Cu_6Cr_8(CN)_{24}$ Cluster with an $S = 15$ Ground State

T. David Harris and Jeffrey R. Long*

Department of Chemistry, University of California

Berkeley, CA 94270-1460 USA

Contents Page

Experimental Section

General Considerations. The compounds KTp[1] and $CrCl_3(THF)_3$[2] were prepared following literature procedures. The compounds NaCN and $Cu(ClO_4)_2 \cdot 6H_2O$ were purchased from Aldrich and used as received.

Caution! Although we have experienced no problems while working with them, perchlorate salts are potentially explosive and should be handled with care and only in small quantities.

$(Bu_4N)[TpCrCl_3] \cdot 2H_2O$. This compound was prepared via a modified literature procedure.[3] Under a dinitrogen atmosphere, a colorless solution of KTp (1.8 g, 7.1 mmol) in 20 mL of acetonitrile was added dropwise via cannula to a stirred purple solution of $CrCl_3(THF)_3$ (2.7 g, 7.1 mmol) in 30 mL of acetonitrile, resulting in a green slurry. After the slurry had stirred for 20 min, Bu_4NCl (2.0 g, 7.2 mmol) was added, and the stirring was continued for 2 h. The reaction mixture was then filtered in air through Celite. The green filtrate was reduced to dryness *in vacuo*, and then sonicated under 20 mL of water to solidify the oily residue. The green solid was washed with successive aliquots of water (2 × 10 mL) and Et_2O (3 × 10 mL), and dried *in vacuo* for 6 h to yield 3.0 g (65%) of product. Anal. Calcd for $C_{28}H_{50}BCrN_{10}O_2$: C, 46.22; H, 7.70; N, 15.10. Found: C, 45.85; H, 7.68; N, 15.64.

$(Bu_4N)[TpCr(CN)_3]$ (1). Under a dinitrogen atmosphere, a green solution of (Bu_4N)-$[TpCrCl_3] \cdot 2H_2O$ (0.507 g, 0.781 mmol) in 8 mL of DMF was added to solid NaCN (0.298 g, 6.08 mmol) to give a green mixture. The mixture was stirred and heated at 150 °C for 3 days. During this period, the color of the reaction mixture changed from green to orange to yellow. The reaction mixture was reduced in volume to ca. 1 mL by heating at 70 °C under reduced pressure. In air, 40 mL of Et_2O was added to the slurry to give a yellow precipitate. The solid was collected via filtration, and 5 mL of water was added to the yellow filtrate. With stirring, Bu_4NCl (0.241 g, 0.867 mmol) was added to the mixture, resulting in the precipitation of additional yellow solid. The solid was collected by filtration, washed with successive aliquots

1 S. Trofimenko, *Inorg. Synth.*, 1970, **12**, 99.
2 J. Shamir, *Inorg. Chim. Acta*, 1989, **156**, 163.
3 R. Rojas, M. Valderrama and G. Wu, *Inorg. Chem. Commun.*, 2004, **7**, 1295.

of water (2 × 5 mL) and Et_2O (3 × 15 mL), and dried *in vacuo* at 50 °C for 12 h to yield 0.307 g (67%) of product. Absorption spectrum (CH_3CN): λ_{max}/nm 420 (ε/L mol^{-1} cm^{-1} 73). IR (ATR): ν_{max}/cm^{-1} 2114 (CN) and 2512 (BH). ES-MS$^-$ (CH_3CN): *m*/*z* 343 ([TpCr(CN)$_3$]$^-$). μ_{eff} = 3.64 μ_B at 300 K. Anal. Calcd for $C_{28}H_{46}BCrN_{10}$: C, 57.45; H, 7.87; N, 23.94. Found: C, 57.31; H, 7.91; N, 23.86.

[Tp$_8$(H$_2$O)$_6$Cu$_6$Cr$_8$(CN)$_{24}$](ClO$_4$)$_4$·7H$_2$O·13THF (2). Solid Cu(ClO$_4$)$_2$·6H$_2$O (84 mg, 0.23 mmol) was added to a stirred yellow solution of **1** (94 mg, 0.16 mmol) in 6 mL of a 2:1 (v/v) mixture of acetonitrile and ethanol, resulting in the immediate formation of a green solution. After stirring for 5 min, the solution was filtered. Diffusion of THF vapor into the filtrate at room temperature afforded 67 mg (71%) of product as orange block-shaped crystals. IR (ATR): ν_{max}/cm^{-1} 2123 and 2167 (CN) and 2528 (BH). Anal. Calcd for $C_{148}H_{210}B_8Cl_4Cr_8Cu_6N_{72}O_{42}$: C, 37.86; H, 4.51; N, 21.48. Found: C, 37.88; H, 4.49; N, 21.65.

[Tp$_8$(H$_2$O)$_6$Cu$_6$Cr$_8$(CN)$_{24}$](ClO$_4$)$_4$·15H$_2$O·13THF (3): Solid Cu(ClO$_4$)$_2$·6H$_2$O (82 mg, 0.22 mmol) was added to a stirred yellow solution of **1** (100 mg, 0.17 mmol) in 6 mL of a 2:1 (v/v) mixture of acetonitrile and ethanol chilled in an ice bath, resulting in the immediate formation of a green solution. After stirring for 5 min, the solution was filtered. Diffusion of THF vapor into the filtrate at 0 °C afforded 87 mg (84%) of **3** as green cube-shaped crystals. IR (ATR): ν_{max}/cm^{-1} 2183 (CN) and 2521 (BH). Anal. Calcd for $C_{148}H_{236}B_8Cl_4Cr_8Cu_6N_{72}O_{50}$: C, 36.73; H, 4.71; N, 20.84. Found: C, 36.59; H, 4.55; N, 20.89.

Magnetic Measurements. Magnetic data were collected using a Quantum Design MPMS-XL SQUID magnetometer. DC susceptibility data were collected at temperatures ranging from 5 to 300 K at fields of 500, 1000, and 5000 Oe. Magnetization data were collected at 2, 5 and 8 K, with applied fields ranging from 0 to 5 T. All data were corrected for diamagnetic contributions employing both a background subtraction and Pascal's constants. Samples were restrained with petroleum jelly to prevent torquing of the crystallites.

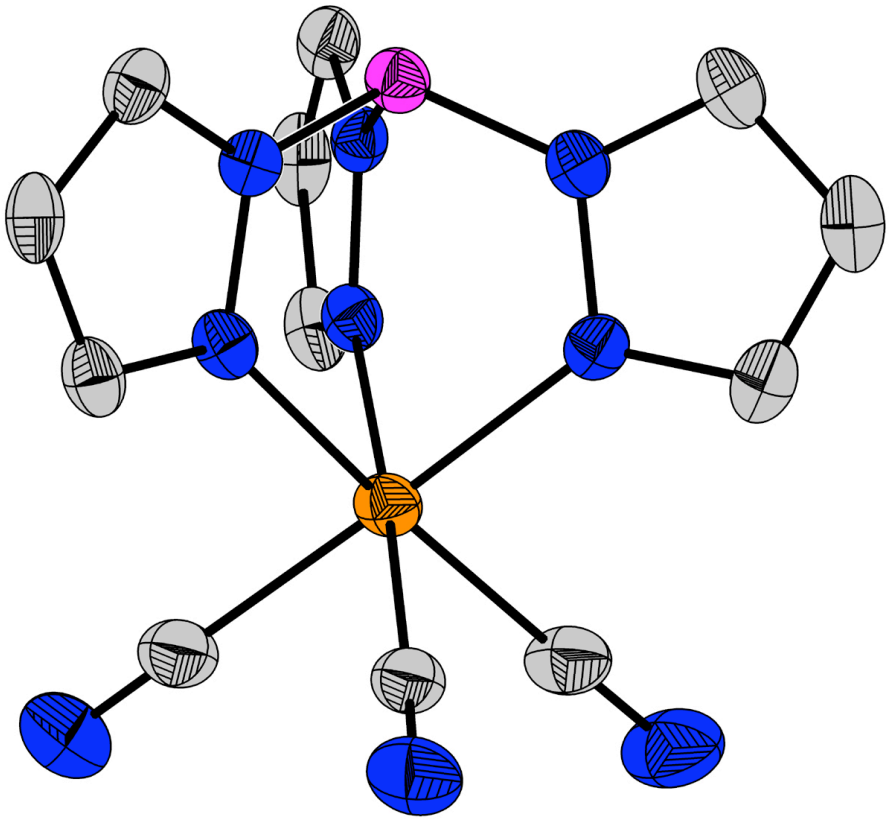

Fig. S1 Structure of $[TpCr(CN)_3]^-$, as observed in **1**·$3H_2O$. Orange, pink, gray, and blue ellipsoids represent Cr, B, C, and N atoms, respectively; H atoms are omitted for clarity. Selected mean interatomic distances (Å) and angles (deg): Cr–C 2.072(4), Cr–N 2.056(3), C≡N 1.154(5), N–Cr–N 86.4(1), C–Cr–C 90.1(1), Cr–C≡N 177.0(4).

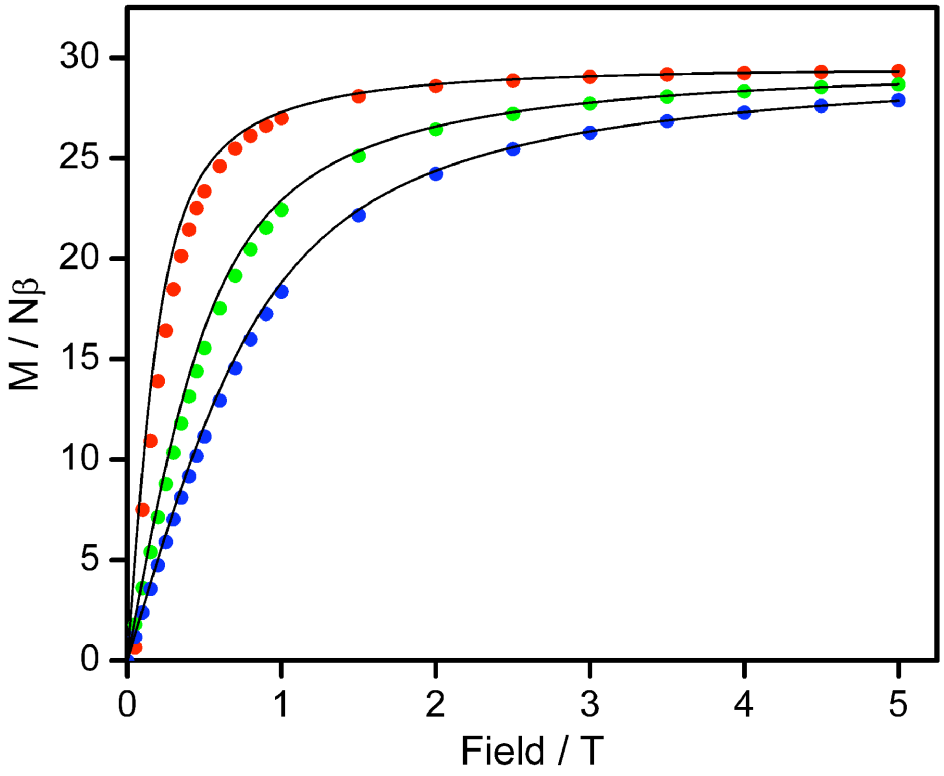

Fig. S2 Magnetization data for **2** collected at 2 (red), 5 (green), and 8 (blue) K. The solid lines represent the Brillouin function for an $S = 15$ molecule with $g = 1.96$.