

Linkage isomerism in a face-centered cubic $\text{Cu}_6\text{Cr}_8(\text{CN})_{24}$ cluster with an $S = 15$ ground state†

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Access to the new complex $[\text{TpCr}(\text{CN})_3]^-$ enables isolation of two metastable linkage isomers of a face-centered cubic cluster, $[\text{Tp}_8(\text{H}_2\text{O})_6\text{Cu}_6\text{Cr}_8(\text{CN})_{24}]^{4+}$, both exhibiting an $S = 15$ ground state.

Over the past fifteen years, certain transition metal clusters have been found to exhibit magnetic bistability, owing to the presence of a high-spin ground state (S) with negative uniaxial magnetic anisotropy (D).¹ Although much of the work in this area has focused on oxo-bridged clusters,^{1,2} the use of cyanide as a bridging ligand has also attracted considerable attention.³ Here, controlled assembly can sometimes be achieved through a bottom-up approach, in which ligand-capped cyanometalates are employed as building units. For example, the complex $[(\text{Me}_3\text{tacn})\text{Cr}(\text{CN})_3]$ ($\text{Me}_3\text{tacn} = N,N',N''$ -trimethyl-1,4,7-triazacyclononane) was shown to react with $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ in boiling water to generate the face-centered cubic cluster $[(\text{Me}_3\text{tacn})_8\text{Cr}_8\text{Ni}_6(\text{CN})_{24}]^{12+}$.⁴ During formation of the cluster, a thermally-induced cyanide linkage isomerism occurs, wherein the bridging cyanide ligands reorient such that the carbon ends bind the Ni^{II} centers instead of the Cr^{III} centers. The stronger ligand field then induces a change in the coordination geometry of the Ni^{II} centers from octahedral to square planar, thereby rendering them diamagnetic. By performing the reaction in methanol at -40°C , a metastable precursor species could be isolated that retained high-spin Ni^{II} and exhibited magnetic properties suggestive of an $S = 18$ ground state.⁴ Unfortunately, the high charge of this species, tentatively formulated as $[(\text{Me}_3\text{tacn})_8(\text{H}_2\text{O})_{12}\text{Ni}_6\text{Cr}_8(\text{CN})_{24}]^{12+}$, prohibited its crystallization at low temperature.

Recent work has exposed a means of reducing the charge of such clusters through use of the compact, monoanionic ligand hydrotris(pyrazol-1-yl)borate (Tp^-). The complex $[\text{TpFe}(\text{CN})_3]^-$, which had previously been employed in the synthesis of several cyano-bridged clusters,^{5,6} was found to react with $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ to yield the face-centered cubic cluster $[\text{Tp}_8(\text{H}_2\text{O})_6\text{Cu}_6\text{Fe}_8(\text{CN})_{24}]^{4+}$.⁷ This species possesses an $S = 7$ ground state, arising from ferromagnetic exchange coupling between the low-spin Fe^{III} centers ($S = 1/2$) and the square pyramidal Cu^{II} centers ($S = 1/2$). While it does not display signs of linkage isomerism, the cluster does, by virtue of its lower charge, provide a high-spin building unit with improved solubility and terminal water ligands that can potentially be substituted. Herein, we report the synthesis

of an analogous face-centered cubic cluster, $[\text{Tp}_8(\text{H}_2\text{O})_6\text{Cu}_6\text{Cr}_8(\text{CN})_{24}]^{4+}$, which displays a higher spin ground state of $S = 15$ and, unexpectedly, undergoes a partial cyanide linkage isomerism.

The complex $[\text{TpCr}(\text{CN})_3]^-$ could not be obtained cleanly using procedures analogous to any of those employed in preparing $[\text{TpFe}(\text{CN})_3]^-$,^{5,8} but rather required utilization of pure $[\text{TpCrCl}_3]^-$ as a precursor. Treatment of $(\text{Bu}_4\text{N})[\text{TpCrCl}_3]$ with excess NaCN in hot DMF for 3 days afforded $(\text{Bu}_4\text{N})[\text{TpCr}(\text{CN})_3]$ (**1**). Diffusion of Et_2O vapor into a wet acetonitrile solution of **1** gave yellow block-shaped crystals of $1 \cdot 3\text{H}_2\text{O}$ suitable for X-ray analysis.† The resulting crystal structure features the expected octahedral coordination geometry for Cr^{III} , with a mean Cr–C distance of 2.072(4) Å and a mean C–Cr–C angle of 90.1(1)°. A magnetic susceptibility measurement gave $\mu_{\text{eff}} = 3.64 \mu_{\text{B}}$ at 300 K, confirming an $S = 3/2$ spin state. We note that this is only the second complex of the type $[\text{TpM}(\text{CN})_3]^-$. Although two closely related species, $[\text{Tp}^*\text{M}(\text{CN})_3]^-$ ($\text{Tp}^* =$ hydrotris(3,5-dimethylpyrazol-1-yl)borate; $\text{M} = \text{V}, \text{Fe}$), have also been reported,⁹ these have not yet been shown to generate face-centered cubic clusters.

Reaction of **1** with $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ in a mixture of acetonitrile and methanol, followed by crystallization *via* THF vapor diffusion at room temperature, produces orange cube-shaped crystals of $[\text{Tp}_8(\text{H}_2\text{O})_6\text{Cu}_6\text{Cr}_8(\text{CN})_{24}](\text{ClO}_4)_4 \cdot 7\text{H}_2\text{O} \cdot 13\text{THF}$ (**2**).‡ The structure of the $[\text{Tp}_8(\text{H}_2\text{O})_6\text{Cu}_6\text{Cr}_8(\text{CN})_{24}]^{4+}$ clusters in **2** features a cubic arrangement of eight Tp^- -capped Cr^{III} ions connected *via* cyanide bridges to six Cu^{II} ions, one situated slightly above the center of each cube face (see Fig. 1). Each Cu^{II} experiences square pyramidal coordination, with four cyanide ligands constituting the basal plane and a water molecule bound in the apical position. Most notably, two *trans* cyanide ligands have reoriented, such that they bind the Cu^{II} through carbon instead of nitrogen. Consequently, four Cr^{III} centers arranged in a tetrahedron have switched from bearing carbon-bound cyanide ligands to having nitrogen-bound cyanide ligands, thereby lowering the idealized cluster symmetry from O_h to T_d . This linkage isomerism follows a thermodynamic rationale, as the softer carbon end of cyanide prefers the softer Cu^{II} center over the harder Cr^{III} center. Although a number of instances of such cyanide linkage isomerism have been reported, particularly for Prussian blue-type solids,¹⁰ to our knowledge, this represents the first example of a molecule that undergoes a partial isomerism.

Evidence for cyanide ligand reorientation in **2** stems from both structural and spectroscopic analyses. The asymmetric unit in the crystal structure of **2** consists of two $\text{M}–\text{CN}–\text{M}'$ linkages, which model the data significantly better as one $\text{Cr}–\text{CN}–\text{Cu}$ linkage and one $\text{Cr}–\text{NC}–\text{Cu}$ linkage. For example, refining the structure with both cyanide linkages as $\text{Cr}–\text{CN}–\text{Cu}$ leads to residual factors of

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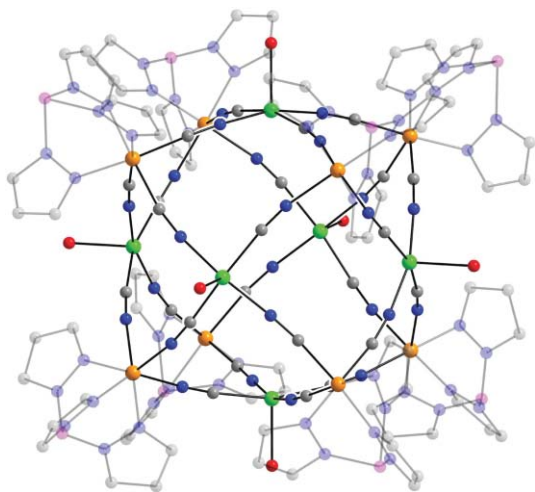


Fig. 1 Structure of the half-isomerized face-centered cubic cluster $[\text{Tp}_8(\text{H}_2\text{O})_6\text{Cu}_6\text{Cr}_8(\text{CN})_{24}]^{4+}$, as observed in **2**. Orange, green, purple, gray, blue, and red spheres represent Cr, Cu, B, C, N, and O atoms, respectively; H atoms are omitted for clarity. The Tp^- ligands are drawn transparently for better visualization of the core structure. The molecule resides on a T symmetry site within the crystal. Selected mean interatomic distances (\AA) and angles ($^\circ$): Cr–C 2.02(2), Cr–N_{CN} 1.99(1), Cu–N 2.07(2), Cu–C 1.98(1), Cr⋯Cr 7.04, *cis*-Cu⋯Cu 6.70, *trans*-Cu⋯Cu 9.47; Cr–C=N 169, Cr–N=C 170, Cu–C=N 172, Cu–N=C 171.

$R_1 = 6.66\%$ and $wR_2 = 23.08\%$, and thermal parameters for C and N of 0.031 \AA^2 and 0.046 \AA^2 , respectively. However, reorientation of one cyanide ligand results in $R_1 = 6.46\%$ and $wR_2 = 22.48\%$, and gives C and N thermal parameters of 0.038 \AA^2 and 0.043 \AA^2 . Moreover, the difference between the mean Cu–C and Cu–N distances of 1.99(1) and 2.07(2) \AA , respectively, is consistent with this assignment. Further support for the presence of a half-isomerized cluster arises from the IR spectrum of **2**, which displays two distinct ν_{CN} stretches at 2123 and 2167 cm^{-1} . These are assigned to the Cr–NC–Cu and Cr–CN–Cu linkages, respectively.

In an effort to forestall the linkage isomerism and isolate the kinetically-favored isomer of the cluster, the reaction of **1** with $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ was carried out at 0°C . Diffusion of THF vapor into the ensuing chilled solution afforded green cube-shaped crystals of $[\text{Tp}_8(\text{H}_2\text{O})_6\text{Cu}_6\text{Cr}_8(\text{CN})_{24}](\text{ClO}_4)_4 \cdot 15\text{H}_2\text{O} \cdot 13\text{THF}$ (**3**). X-Ray analysis confirmed the presence of the usual face-centered cubic cluster geometry; however, a complete structural refinement could not be performed owing to the combined effects of crystal desolvation and four-fold twinning.[§] Consistent with an O_h -symmetry cluster isomer featuring only Cr–CN–Cu linkages, the IR spectrum of **3** displays a single ν_{CN} stretch at 2183 cm^{-1} .

Over time, samples of **3** gradually change color from green to orange and eventually to red. The IR spectra associated with these color changes, as induced by heating a solid sample at 80°C , are shown in Fig. 2. After 1 h, the original peak has shifted slightly and a new peak has appeared at lower energy to yield a spectrum matching that of half-isomerized compound **2**. Further isomerization is significantly slower, with complete loss of the original peak only occurring after 30 h of heating. The resulting red solid is insoluble in water and common organic solvents, and low-temperature magnetic susceptibility measurements indicate the absence of magnetic exchange coupling. We hypothesize that further isomerization of cyanide ligands destabilizes the square

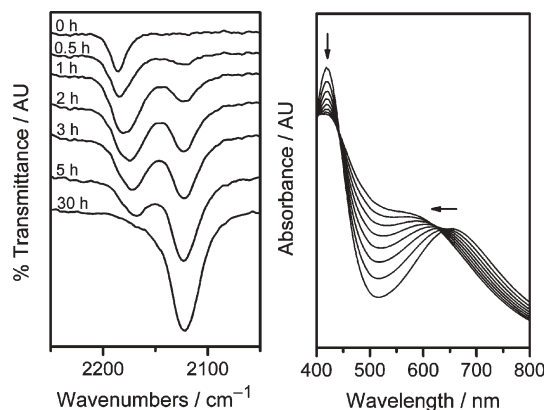


Fig. 2 Left: Time-resolved IR spectra for a pulverized sample of **3** heated at 80°C . Right: UV-visible spectra collected at 10-min intervals for a room-temperature solution of **3** in a 2 : 1 mixture of acetonitrile and ethanol. Arrows indicate the direction of peak shifts with time.

pyramidal coordination of the Cu^{II} centers, leading to disintegration of the cluster. Indeed, we could find no reliable crystal structures containing Cu^{II} centers with four carbon-bound cyanide ligands.

In an attempt to elucidate the kinetics of the linkage isomerism, time-resolved UV-vis absorption spectra were collected for a solution of **3** (see Fig. 2). Here, the color changes are similar, but the isomerization occurs much more rapidly at room temperature. Over the course of an hour, the solution color changes from green to orange, as the peak at 420 nm decreases in intensity and the peak at 657 nm shifts to higher energy. Upon further standing for up to 24 h, the solution gradually turns red and a red precipitate forms. The observed spectral changes do not occur as a linear function of time. Moreover, the initial spectra lack clean isosbestic points, suggesting that the isomerization does not proceed through a simple two-step process, with each step involving the simultaneous reorientation of twelve cyanide ligands. Instead, it likely proceeds through a complex series of intermediates, with the half-isomerized product isolated in **2** representing a local minimum along the reaction coordinate.

Variable-temperature magnetic susceptibility measurements were performed on **2** and **3** to probe the magnetic coupling within the isomeric clusters (see Fig. 3). At 285 K, **3** exhibits $\chi_{\text{M}}T = 19.13 \text{ cm}^3 \text{ K mol}^{-1}$, which is slightly higher than the value of $17.25 \text{ cm}^3 \text{ K mol}^{-1}$ expected for eight Cr^{III} centers ($S = 3/2$) and six Cu^{II} centers ($S = 1/2$) assuming $g = 2.00$ and no exchange coupling. As the temperature decreases, $\chi_{\text{M}}T$ rises, attaining a maximum of $108.5 \text{ cm}^3 \text{ K mol}^{-1}$ at 16 K. This behavior indicates the presence of ferromagnetic exchange coupling, as expected for cyanide bridges between octahedral Cr^{III} (t_{2g}^3) and square pyramidal Cu^{II} (b_{1g}) centers.¹¹ The maximum for $\chi_{\text{M}}T$ is close to the $120 \text{ cm}^3 \text{ K mol}^{-1}$ expected for an $S = 15$ ground state with $g = 2.00$. The downturn in the data below 18 K is attributed to Zeeman splitting of the M_S levels in the presence of an applied magnetic field, as evidenced by the calculated behavior for an $S = 15$ state in a 5000 Oe field (solid line in Fig. 3). The magnetic data for **2** follow a similar trend, reaching a maximum of $107.8 \text{ cm}^3 \text{ K mol}^{-1}$ at 18 K. Notably, the two data sets do not superimpose, with the $\chi_{\text{M}}T$ data for **2** rising more rapidly as the temperature decreases. This indicates that the ferromagnetic coupling is somewhat stronger in

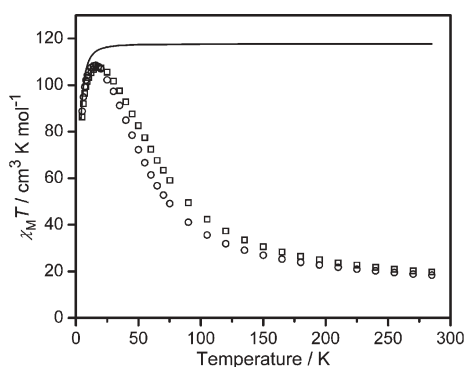


Fig. 3 Temperature dependence of $\chi_M T$ for **2** (squares) and **3** (circles), as measured in an applied field of 5000 Oe. The solid line indicates the values calculated for population of only an $S = 15$ state with $g = 2.00$ and inclusion of the Zeeman splitting.

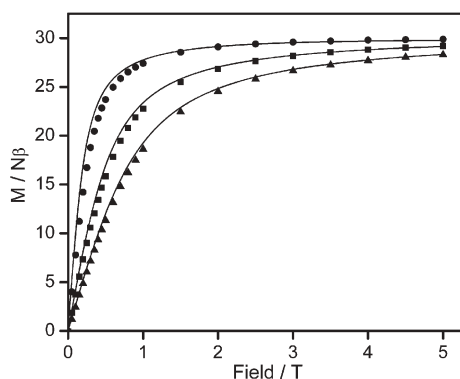


Fig. 4 Magnetization data for **3** collected at 2 (circles), 5 (squares) and 8 K (triangles). The solid lines represent the simulated Brillouin function for an $S = 15$ molecule with $g = 1.99$.

the half-isomerized cluster of **2** than in the unisomerized cluster of **3**. Unfortunately, the large number of spins associated with the cluster precludes a quantitative determination of the magnitude of the coupling.

Low-temperature magnetization data collected for **2** and **3** confirm the high-spin ground states (see Fig. 4 and ESI†). In each case, the observed data at 2, 5 and 8 K closely agree with the calculated Brillouin functions, indicating the presence of a well-isolated $S = 15$ ground state with negligible zero-field splitting. To our knowledge, this is the second highest ground state spin yet observed in a metal–cyanide cluster, behind the $S = 39/2$ ground states of the centered, face-capped octahedral clusters $(\text{ROH})_{24}\text{Mn}_9\text{M}_6(\text{CN})_{48}$ ($M = \text{Mo}, \text{W}$; $R = \text{Me}, \text{Et}$).¹² Consistent with the apparent lack of magnetic anisotropy, no out-of-phase signal was observed for either sample in ac magnetic susceptibility measurements performed at temperatures as low as 1.8 K with switching frequencies of up to 1500 Hz.

The foregoing results demonstrate the utility of the new $S = 3/2$ complex $[\text{TpCr}(\text{CN})_3]^-$ in generating face-centered cubic clusters with high-spin ground states. These clusters are soluble in a variety of common solvents, and future efforts will focus on their use as building units *via* substitution of the outer water ligands. Additional experiments will be directed toward substituting heterometals at either the corner or face-centering metal sites as a means of enhancing anisotropy and generating single-molecule magnets.

Notes and references

† *X-Ray crystal analysis*: For **1**: $3\text{H}_2\text{O}$ ($\text{C}_{28}\text{H}_{52}\text{BCrN}_{10}\text{O}_3$, $M = 639.61$) at $T = 150$ K: space group $P\bar{1}$, $a = 11.193(2)$, $b = 11.258(2)$, $c = 16.323(3)$ Å, $\alpha = 76.275(3)$, $\beta = 87.493(3)$, $\gamma = 60.506(3)^\circ$, $V = 1732.8(6)$ Å³, $Z = 2$, $\mu = 0.372$ mm⁻¹, 6336 unique reflections, 9825 total reflections, $R_{\text{int}} = 0.0187$, $R_1 = 0.0622$, $wR_2 = 0.1821$. For **2** ($\text{C}_{148}\text{H}_{210}\text{B}_8\text{Cl}_4\text{Cr}_8\text{Cu}_6\text{N}_{75}\text{O}_{42}$, $M = 4695.40$) at $T = 160$ K: space group $F\bar{4}3c$, $a = 34.994(1)$, $V = 42853(15)$ Å³, $Z = 8$, $\mu = 1.103$ mm⁻¹, 3678 unique reflections, 56 940 total reflections, $R_{\text{int}} = 0.0731$, $R_1 = 0.0646$, $wR_2 = 0.2248$. CCDC 624588 and 624589. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b615141h

§ *X-Ray crystal analysis* for **3** at $T = 156$ K: space group $P4/m$, $a = 25.183(3)$, $c = 32.984(3)$ Å, $V = 20917(6)$ Å³, $Z = 4$.

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