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Synthesis and Alkali Metal Ion-Binding Properties of a Chromium(III) Triacetylide Complex

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The prospect of discovering new single-molecule magnets[1] with higher blocking temperatures has prompted much recent interest in the synthesis of high-spin clusters. Metal-cyanide coordination clusters are particularly attractive in this arena, because the linear bridging geometry favored by cyanide permits some predictability as to product geometry and magnetic ground state. Here, much of our own effort has focused on the incorporation of corner units such as $[(Me_3tacn)Cr(CN)_3]$ ($Me_3tacn = N,N',N''$-trimethyl-1,4,7-triazacyclononane) into high-nuclearity clusters.[2] To increase the strength of the magnetic exchange coupling in these species, we now propose to replace cyanide with the isoelectronic acetylenediide ligand, $C{\equiv}C^{2-}$, for which the symmetric nature and higher charge are expected to enhance the overlap between ligand and metal orbitals. Toward that end, we herein report the synthesis of the triacetylide precursor complex $[(Me_3tacn)Cr(CCH)_3]$, along with the structures and magnetic properties of its alkali metal ion complexes.

Initially, a trimethylsilyl-protected derivative of the complex was prepared. Under a dinitrogen atmosphere, $Me_3SiCCLi$ was generated by addition of ^nBuLi (27 mL, 67 mmol, 2.5 M hexane solution) to a solution of Me_3SiCCH (9.5 mL, 68 mmol) in 30 mL of THF chilled at −78 °C. Upon warming the mixture to room temperature and stirring for 1 h, solid $[(Me_3tacn)Cr(CF_3SO_3)_3]$[3] (3.5 g, 5.2 mmol) was added, prompting formation of a pale orange precipitate. After the mixture was stirred for an additional 2 h, the solvent was removed in vacuo, and the resulting orange solid was washed with hexanes (2 × 30 mL) and recrystallized from a minimal volume of hot methanol (ca. 150 mL). The orange microcrystals were collected by filtration, washed with ether (30 mL), and dried in air to afford 2.3 g (86%) of $[(Me_3tacn)Cr(CCSiMe_3)_3]$ (**1**).[4]

Conversion of **1** to the triacetylide complex was achieved through a fluoride ion-mediated reaction. Under a dinitrogen atmosphere, a suspension of **1** (1.4 g, 2.7 mmol) and slightly wet Bu_4NF (0.52 g, ∼2.0 mmol) in 15 mL of THF was heated at reflux. Over the course of 2 h, **1** dissolved, and a new orange precipitate appeared. After allowing the reaction mixture to cool to 40 °C, the THF was filtered off via cannula, and the orange powder was washed with ether (2 × 15 mL) and dried in air to afford 0.73 g (90%) of $[(Me_3tacn)Cr(CCH)_3]$ (**2**).[5]

Orange triangular prism-shaped crystals suitable for X-ray analysis[6] were obtained by diffusing ether into a concentrated solution of **2** in THF. As shown in Figure 1, the complex approximates an octahedral geometry with slightly splayed C−Cr−C angles of 94.14(9)° and the usual pinched N−Cr−N angles of 81.10(9)°. The Cr−C separation of 2.057(3) Å is nearly the same as the mean Cr−C distance of 2.073(8) Å observed in $[(Me_3tacn)Cr(CN)_3]$.[2a] Consistent with the expected triple bond, the C−C distance of 1.201(4) Å is comparable to that in acetylene (1.2033(2) Å),[7] and the Cr−C−C angle of 175.5(2)° closely approaches linearity. To our knowledge, this represents the first structural characterization of a chromium acetylide complex of any type. Indeed, while many transition metal complexes with more than two acetylide ligands are known,[8] only the tetrahedral anions $[M(CCH)_4]^{2-}$ (M = Zn, Cd) have been structurally characterized.[9,10]

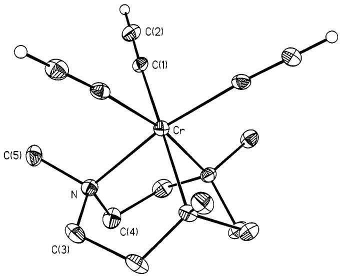

Figure 1. Structure of the triacetylide complex $[(Me_3tacn)Cr(CCH)_3]$ (**2**); for clarity, only the acetylide H atoms are shown. The complex resides on a three-fold rotation axis of the crystal. Selected interatomic distances (Å) and angles (deg): Cr−C(1) 2.057(3), Cr−N 2.166(2), C(1)−C(2) 1.201(4), C(1)−Cr−C(1′) 94.14(9), C(1)−Cr−N 90.1(1), N−Cr−N 81.10(9), Cr−C(1)−C(2) 175.5(2).

The electronic absorption spectrum of a solution of **2** in acetonitrile features bands centered at 368 and 454 nm. The corresponding transitions in the absorption spectrum of $[(Me_3tacn)Cr(CN)_3]$ occur at 339 and 425 nm,[2a] indicating that acetylide is only a slightly weaker field ligand than cyanide.[11]

Attempts to utilize **2** in forging $Cr{-}C{\equiv}C{-}M$ bridges via established coupling methods[12] are ongoing. Initiating these experiments, we discovered that the effectiveness of CuI as a catalyst appears to be thwarted by coordination of the Cu^+ ion through side-on interactions with two of the acetylide ligands. The relation to the multitude of "tweezer" complexes,[13] in which a metal ion is bound between the $C{\equiv}C$ units of a *cis*-$M(CCR)_2$ moiety, prompted us to investigate the alkali metal ion-binding properties of **2** as a possible means of achieving magnetic exchange coupling.

A 2:1 complex of K^+ is readily isolated from solutions that are limited in **2**. Diffusion of ether into a solution of **2** (20 mg, 0.066 mmol) and $K(CF_3SO_3)$ (12 mg, 0.066 mmol) in 2 mL of DMF produced 15 mg (57%) of orange rod-shaped crystals of $\{[(Me_3tacn)Cr(CCH)_3]_2K\}(CF_3SO_3)$ (**3**).[14] X-ray analysis[6] of one of these crystals revealed the sandwich complex depicted at the top of Figure 2. Displaying minimal C−Cr···Cr−C torsion angles of 19.3°, 20.8°, and 26.5°, the two $[(Me_3tacn)Cr(CCH)_3]$ entities are more nearly eclipsed than staggered with respect to each other. The K^+ ion is coordinated by the six $C{\equiv}C$ units in a slightly skewed side-on fashion, such that it is closer to the C atoms bound to Cr (K−C = 3.003(5)−3.099(5) Å) than to the C atoms bound to H (K−C = 3.133(5)−3.366(5) Å).

With larger alkali metal cations, triangular 3:1 complexes are obtained. Orange needlelike crystals of $\{[(Me_3tacn)Cr(CCH)_3]_3Cs\}Br$ (**4**)[15] were isolated in 51% yield by a procedure analogous to

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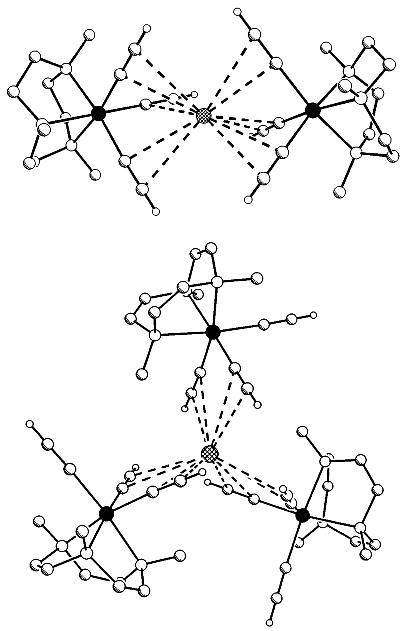

Figure 2. Structures of the alkali metal ion complexes $\{[(Me_3tacn)Cr(CCH)_3]_2K\}^+$ (upper) and $\{[(Me_3tacn)Cr(CCH)_3]_3Cs\}^+$ (lower) in **3** and **4**. Crosshatched, black, shaded, large white, and small white spheres represent K or Cs, Cr, C, N, and H atoms, respectively; for clarity, only the acetylide H atoms are shown. The Cs^+ complex exhibits crystallographically imposed C_{3h} symmetry. Selected mean interatomic distances (Å) and angles (deg) from **3**/**4** (A = K/Cs): Cr−C 2.044(6)/2.04(2), C≡C 1.198(8)/1.18(3), A−C 3.05(3), 3.27(8)/3.38(1), A···Cr 3.67(7)/4.373, Cr···Cr 7.318/7.877, C−Cr−C 92(1)/94(3), Cr−C≡C 177(2)/177(1), Cr···A···Cr 169.9/120.

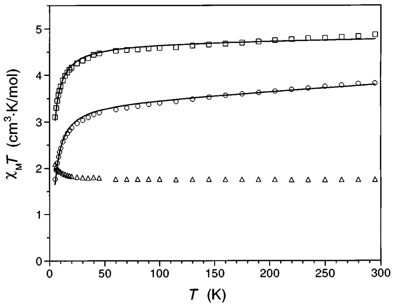

Figure 3. Magnetic behavior of compounds **2** (△), **3** (○), and **4** (□) in applied fields of 10 000, 100, and 100 G, respectively. All samples were restrained in eicosane to prevent torquing. Solid lines represent calculated fits to the data.

that employed for crystallizing **3**. The crystal structure[6] of **4** features the complex shown at the bottom of Figure 2, in which three $[(Me_3tacn)Cr(CCH)_3]$ molecules bind a central Cs^+ ion, each through only two of its acetylide ligands. Note that this triangular geometry permits close approach of the alkali metal ions to the π clouds of the C≡C units while avoiding the necessarily shorter A···Cr separations of the 2:1 complex in **3**. Unlike in the 2:1 complex, the η^2 interactions between the Cs^+ and the six surrounding acetylides are not skewed, displaying nearly equal Cs−C distances of 3.375(5) and 3.394(5) Å. An analogous reaction employing RbBr produced the isostructural compound $\{[(Me_3tacn)Cr(CCH)_3]_3Rb\}Br$.

Weak antiferromagnetic interactions between the Cr^{III} centers are observed in both types of alkali metal ion complexes (see Figure 3). Consistent with an isolated $S = {}^3/_2$ ion for which $g = 1.93$, **2** displays a $\chi_M T$ of 1.75 cm^3 K/mol that is essentially invariant with temperature.[16] In contrast, the values of $\chi_M T$ drop steadily for both compounds **3** and **4** as the temperature decreases. Assuming that antiferromagnetic interactions associated with alkali metal ion-mediated pathways are solely responsible for the drop, the data for **3** were fit using an exchange Hamiltonian of the form $\hat{H} = -2J\hat{S}_{Cr(1)}\cdot\hat{S}_{Cr(2)}$, to give $J = -0.8$ cm^{-1} and $g = 1.90$. Similarly, the data for **4** were fit using an exchange Hamiltonian of the form $\hat{H} = -2J(\hat{S}_{Cr(1)}\cdot\hat{S}_{Cr(2)} + \hat{S}_{Cr(2)}\cdot\hat{S}_{Cr(3)} + \hat{S}_{Cr(3)}\cdot\hat{S}_{Cr(1)})$, to give $J = -0.3$ cm^{-1} and $g = 1.83$. This weaker coupling may result from the fewer Cr−C−A−C−Cr pathways per Cr_2 pair in the triangular complex. Regardless, for both complexes the coupling is so weak that population is not restricted to the respective $S = 0$ and $S = {}^1/_2$ ground states even at the lowest measured temperature of 5 K.

Future work will endeavor to probe the strength of the magnetic exchange coupling in high-spin clusters generated using triacetylide complex **2**.

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Supporting Information Available: Tables for the structures of **2**, **3**, and **4** (PDF). 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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(4) Characterization of **1**: Absorption spectrum (MeCN), λ_{max} (ϵ_M) 281 (1180), 298 (1980), 312 (2400), 325 (2980), 340 (2670) 448 (46) nm. IR: ν_{CC} 2003 (m), ν_{CSi} 850 (s), 830 (s) cm^{-1}. Anal. Calcd for $C_{24}H_{48}CrN_3Si_3$: C, 55.98; H, 9.40; N, 8.17. Found: C, 55.62; H, 9.54; N, 8.03.

(5) Characterization of **2**: Absorption spectrum (MeCN), λ_{max} (ϵ_M) 305 (3000), 368 (163), 454 (40) nm. IR: ν_{CH} 3249 (m), ν_{CC} 1930 (w) cm^{-1}. μ_{eff} = 3.74 μ_B at 295 K. ES$^+$-MS (MeOH/H_2O): *m*/*z* 321 ([**2** + Na]$^+$). Anal. Calcd for $C_{15}H_{12}CrN_3 \cdot 0.5H_2O$: C, 58.65; H, 8.20; N, 13.68. Found: C, 58.61; H, 7.99; N, 13.74. This compound is air stable and is not shock sensitive.

(6) Crystal and structure refinement parameters: **2**, $C_{15}H_{24}CrN_3$, $T = 160$ K, R3, $Z = 3$, $a = 13.7219(11)$, $c = 7.1949(8)$ Å, $V = 1173.2(2)$ Å^3, $R_1 = 0.0238$, w$R_2 = 0.0601$. **3**: $C_{31}H_{48}Cr_2F_3KN_6O_3S$, $T = 160$ K, $P2_1/c$, $Z = 4$, $a = 12.2852(8)$, $b = 20.4722(13)$, $c = 14.9007(9)$ Å, $\beta = 90.54°$, $V = 3747.4(4)$ Å^3, $R_1 = 0.0519$, w$R_2 = 0.1253$. **4**: $C_{45}H_{72}BrCr_3CsN_9$, $T = 120$ K, $P6_3/m$, $Z = 2$, $a = 16.1420(9)$, $c = 11.8364(9)$ Å, $V = 2670.9(3)$ Å^3, $R_1 = 0.0571$, w$R_2 = 0.1650$. Data were collected on a Siemens SMART diffractometer using graphite monochromated Mo Kα (λ = 0.71073 Å) radiation. Structures were solved by direct methods and refined against all data using SHELXTL 5.0.

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(14) Characterization of **3**: IR, ν_{CH} 3276, 3230 (w), ν_{CC} 1931 (w) cm^{-1}. μ_{eff} = 5.53 μ_B at 295 K. ES$^+$-MS (MeCN/DMF): *m*/*z* 635 ([**3** − CF_3SO_3]$^+$). Anal. Calcd for $C_{31}H_{24}Cr_2F_3KN_6O_3S$: C, 47.43; H, 6.16; N, 10.71. Found: C, 47.59; H, 6.29; N, 10.79.

(15) Characterization of **4**: IR, ν_{CH} 3278 (w), 3201 (m), ν_{CC} 1927 (w) cm^{-1}. μ_{eff} = 6.24 μ_B at 295 K. ES$^+$-MS (MeCN/DMF): *m*/*z* 1027 ([**4** − Br]$^+$). Anal. Calcd for $C_{45}H_{72}BrCr_3CsN_9$: C, 48.78; H, 6.55; N, 11.38. Found: C, 48.49; H, 6.32; N, 11.03.

(16) The very slight rise in $\chi_M T$ apparent below 20 K is attributed to weak ferromagnetic interactions between neighboring complexes.

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