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Early Metal Di- and Tricyanometalates: Useful Building Blocks for Constructing Magnetic Clusters

Dongfeng Li,[†] Sean Parkin,[†] Guangbin Wang,[‡] Gordon T. Yee,[‡] and Stephen M. Holmes*[,†]

Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506-0055, and Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061

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Treatment of *mer*-$\mathrm{VCl_3(THF)_3}$ with KTp* [Tp* $=$ hydridotris(3,5-dimethylpyrazol-1-yl)borate], followed by $\mathrm{[NEt_4]CN}$ in acetonitrile, affords $\mathrm{[NEt_4][(Tp^*)V^{III}(CN)_3]\cdot H_2O}$ ($\mathbf{1}\cdot\mathrm{H_2O}$); aerobic oxidation affords $\mathrm{[NEt_4][(Tp^*)V^{IV}(O)(CN)_2]}$ (**2**). Subsequent treatment of **2** with $\mathrm{Mn^{II}(OTf)_2}$ (OTf $=$ trifluoromethanesulfonate) and 2,2′-bipyridine affords $\mathrm{\{[(Tp^*)V(O)(CN)_2]_2[Mn^{II}(bipy)_2]_2[OTf]_2\}\cdot 2MeCN}$ (**3**). Magnetic measurements indicate that **1**–**3** exhibit $S = 1$, $^1/_2$, and 4 spin ground states, respectively.

The use of cyanometalate complexes as building blocks for the engineering of well-defined magnetic networks and clusters has seen extensive activity over the past decade.[1−3] To date, the most common structural building blocks for constructing cyanometalate clusters are complexes of [*fac*-$\mathrm{LM}^n(\mathrm{CN})_m$] stoichiometry, where L is a tripodal ligand such as 1,4,7-triazacyclononane, 1,4,7-trimethyltriazacyclononane, 1,3,5-triaminocyclohexane, or 1,1,1-tris(diphenylphosphanylmethyl)ethane.[2]

However, despite the ubiquitous nature of poly(pyrazolyl)borate complexes in inorganic literature, only tris(pyrazolyl)borate (Tp) and tris(3,5-dimethylpyrazolyl)borate (Tp*) tricyanoferrate(III) salts have been employed to construct cyanometalate magnetic clusters and extended arrays.[3] Tricyanometalate building blocks such as $\mathrm{[LFe^{III}(CN)_3]^-}$ (L $=$ Tp, Tp*) exhibit significant orbital contributions to their magnetic moments and are useful for the construction of anisotropic clusters and networks that exhibit frequency-dependent magnetic relaxation behavior that is characteristic of so-called single-molecule magnets[3c,d,4a−g] and single-chain magnets.[4h−j]

As part of a continuing effort to prepare such materials, we have developed a series of cyanometalate complexes (building blocks) that self-assemble with their structures intact, into well-defined clusters and networks. In the present Communication, we describe the synthesis, spectroscopic, and magnetic characterization of two early metal di- and tricyanometalates and an $S = 4$ cluster.

Treatment of *mer*-$\mathrm{VCl_3(THF)_3}$ with KTp*, followed by tetraethylammonium cyanide in acetonitrile (MeCN), affords yellow crystals of $\mathrm{[NEt_4][(Tp^*)V^{III}(CN)_3]\cdot H_2O}$ ($\mathbf{1}\cdot\mathrm{H_2O}$) stoichiometry. Anhydrous crystals (**1**) are obtained via recrys-

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* To whom correspondence should be addressed. E-mail: smholm2@uky.edu.

[†] University of Kentucky.

[‡] Virginia Polytechnic Institute and State University.

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tallization of **1**·H_2O from anhydrous MeCN/Et_2O mixtures. An additional green complex, $[NEt_4][(Tp^*)V^{IV}(O)(CN)_2]$ (**2**), is obtained upon air exposure of **1** or **1**·H_2O in MeCN.[5a]

The infrared spectrum of **1** contains intense ν_{BH} and ν_{CN} stretching absorptions that are shifted to higher energies relative to tetraethylammonium cyanide.[5b] For **1**, the frequencies of the ν_{BH} and ν_{CN} stretching absorptions are found at 2557 and 2073 cm^{-1}, while hydrated samples (**1**·H_2O) exhibit strong ν_{BH} (2557 cm^{-1}), ν_{CN} (2075 cm^{-1}), ν_{OH} (3484 cm^{-1}), and δ_{HOH} (1637 cm^{-1}) absorptions.[6a] For **1**, the ν_{CN} absorptions are lower in energy than those found for $[(cyclen)V^{III}(CN)_3]$[5h] (2102 cm^{-1}; cyclen = 1,4,7,10-tetraazacyclododecane) and the axial cyanides in $K_4[V^{III}(CN)_7]\cdot 2H_2O$[5c−f] [2100 (ax) and 2070 (eq) cm^{-1}]. We propose that efficient π back-bonding is present in **1** and **1**·H_2O.[1,6a]

The infrared spectrum of **2** contains intense ν_{BH} (2552 cm^{-1}) and ν_{CN} (2132 and 2125 cm^{-1}) absorptions that are found at higher energies relative to **1** and **1**·H_2O; an additional ν_{VO} stretch (962 cm^{-1}) is also found, signaling the presence of a vanadyl group.[6a] The ν_{CN} absorptions of **2** are close in energy to the equatorial cyanide stretches present in $K_3[V(O)(CN)_5]$ [ν_{CN} = 2126(s) (eq) and 2040(m) (ax) cm^{-1}; ν_{VO} = 929 cm^{-1}], suggesting that the cyanides are cis rather than trans to the vanadyl group.[5c,d,k,6a] The ν_{CN} and ν_{VO} stretches appear at higher energies relative to $K_3[V(O)(CN)_5]$, suggesting that inefficient charge delocalization and π back-bonding occurs in **2**.

Compound **1** crystallizes in the trigonal *P*3$_2$ space group.[5a,7] The pseudo-C_{3v}-symmetric anions exhibit V−C distances that range from 2.065(3) to 2.104(4) Å, while the V−N bond distances range from 2.093(3) to 2.129(3) Å, respectively. The V−C bond lengths are shorter than those observed for $[(cyclen)V^{III}(CN)_3]$ [2.154(4) and 2.166(6) Å], while the average C−N distance [1.165(4) Å] is slightly longer than those in $[V(CN)_7]^{4-}$ [1.15(1) Å] and $[(cyclen)V^{III}(CN)_3]$ [1.155(8) Å].[5g,h]

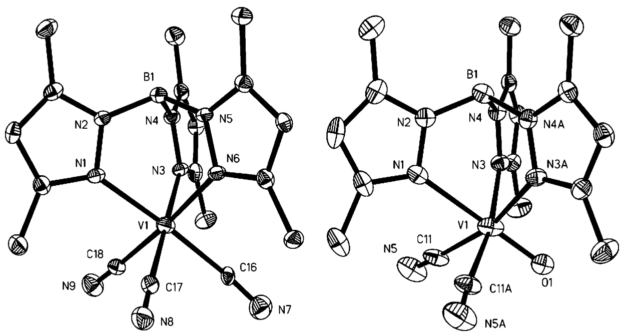

Figure 1. X-ray structures of **1**·H_2O (left) and **2** (right). Thermal ellipsoids are at the 50% level, and all hydrogen atoms and cations are eliminated for clarity. Selected bond distances (Å) and angles (deg): **1**·H_2O, V1−C16 2.189(2), V1−C17 2.174(2), V1−C18 2.191(2), C16−V1−C17 95.33(7), C16−V1−C18 92.29(7), N1−V1−N3 84.66(6); **2**, V1−O1 1.700(3), V1−C11 2.141(4), V1−N3 2.130(3), C11−V1−C11A 94.9(2), C11−V1−O1 95.2(2), C11−V1−N3 88.1(1).

Hydrated crystals of **1** (**1**·H_2O) are in the triclinic *P*1 space group (Figure 1). The $[(Tp^*)V^{III}(CN)_3]^-$ anions are linked into one-dimensional zigzag chains that propagate along the crystallographic *a* direction, by means of hydrogen bonds between two cyanide nitrogens (N8 and N9) and lattice water. The hydrogen-bonded cyanides exhibit V−C bond distances, 2.133(3) Å (V1−C17) and 2.129(3) Å (V1−C18), that are longer than those in **1**, while the shortest bond [2.073(3) Å; V1−C16] is found for the terminal cyanide; an average cyanide C−N distance of 1.158(4) Å is also found.[5a]

Under an inert atmosphere, **1** is unstable with respect to decomposition and disproportionation. Fresh crystals of **1** (or **1**·H_2O) are initially soluble in MeCN, affording a yellow solution. However, when these crystals are dried under vacuum for several hours, they become nearly insoluble and exhibit significantly reduced (ca. 90%) ν_{CN} absorption intensities, relative to fresh samples. Moreover, **1**·H_2O disproportionates under an argon atmosphere, forming **2** and $[NEt_4]_2[(Tp^*)V^{II}(CN)_3]$, as judged via infrared and crystallographic studies; no seven-coordinate tetracyanovanadate(III) complexes [e.g., $[(Tp^*)V^{III}(CN)_4]^{2-}$] have been isolated in the presence of excess cyanide.[5a,c−j,l]

Furthermore, attempts to prepare cyanide-bridged clusters from **1** in MeCN or dimethylformamide (DMF) have consistently met with failure. Treatment of **1** with a series of divalent trifluoromethanesulfonates (OTf^-) or $M(OTf)_2$/2,2′-bipyridine mixtures (M^{II} = Mn, Co, Ni) consistently afforded intractable amorphous precipitates. We propose that solvolysis of **1**, followed by rapid $[NEt_4]CN$ extrusion, quickly precipitates the divalent centers presented.

Compound **2** crystallizes in the orthorhombic (*Cmc*2$_1$) space group (Figure 1).[5a,7] For **2**, the V−CN bond distances [2.141(4) Å] are shorter than, and comparable to, the axial [2.31(1) Å] and equatorial [2.14(1) Å] V−C distances in $K_3[V(O)(CN)_5]$; similar V−O bond lengths [1.700(3) Å] are also found.[5k] Surprisingly, the V−C distances in **2** are only slightly longer than those in **1** and **1**·H_2O.

Treatment of **2** with $Mn^{II}(OTf)_2$ and 2 equiv of 2,2′-biyridine in MeCN affords $\{[(Tp^*)V^{IV}(O)(CN)_2]_2[Mn^{II}$-

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(7) Crystal and structure refinement parameters. **1**: $C_{26}H_{42}BN_{10}V$, *P*3$_2$, $Z = 3$, $a = 9.8608(2)$ Å, $b = 9.8608(2)$ Å, $c = 26.3896(6)$ Å, $V = 2222.22(8)$ Å^3, R1 = 0.0480, wR2 = 0.0989. **1**·H_2O: $C_{26}H_{44}BN_{10}OV$, *P*1, $Z = 1$, $a = 9.7770(2)$ Å, $b = 9.8950(2)$ Å, $c = 10.0920(2)$ Å, $\alpha = 113.4260(7)°$, $\beta = 118.5931(8)°$, $\gamma = 92.6420(9)°$, $V = 1503.98(3)$ Å^3, R1 = 0.0342, wR2 = 0.0742. **2**: $C_{25}H_{42}BN_9OV$, *Cmc*2$_1$, $Z = 4$, $a = 11.8166(3)$ Å, $b = 15.6797(5)$ Å, $c = 15.5843(6)$ Å, $V = 2887.5(2)$ Å^3, R1 = 0.0539, wR2 = 0.1117. **2**·2H_2O: $C_{25}H_{46}BN_9O_3V$, $P\bar{1}$, $Z = 2$, $a = 9.7526(1)$ Å, $b = 9.9164(1)$ Å, $c = 18.1829(2)$ Å, $\alpha = 84.3780(4)°$, $\beta = 79.4659(7)°$, $\gamma = 61.6161(7)°$, $V = 152088(3)$ Å^3, R1 = 0.0859, wR2 = 0.2303. **3**: $C_{80}H_{82}B_2F_6Mn_2N_{26}O_8S_2V_2$, $P\bar{1}$, $Z = 2$, $a = 11.1754(2)$ Å, $b = 14.2552(3)$ Å, $c = 14.7102(3)$ Å, $V = 2307.39(8)$ Å^3, R1 = 0.0535, wR2 = 0.1263. All data were collected on a Nonius-Kappa CCD diffractometer at 90.0(2) K using Mo Kα ($\lambda = 0.710\,73$ Å) radiation. Structures were solved by direct methods and refined against all data using *SHELXL-97*.

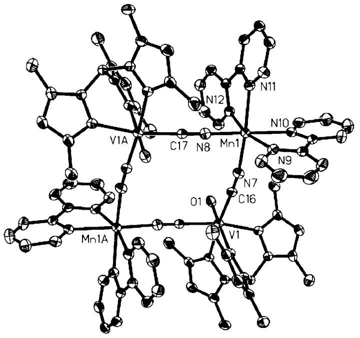

Figure 2. X-ray structure of **3**. Thermal ellipsoids are at the 50% level, and all hydrogen atoms and anions are eliminated for clarity. Selected bond distances (Å) and angles (deg): V1−C16 2.135(3), V1−C17A 2.138(3), V1−O1 1.663(2), Mn1−N7 2.155(3), Mn1−N8 2.180(3), C17A−V1−C16 90.18(11), Mn1−N7−C16 170.3(3), Mn1−N8−C17 173.8(3), O1−V1−C16 92.6(1).

(bipy)$_2$]$_2$[OTf]$_2$}·2MeCN (**3**), as a tetranuclear cluster. The infrared spectrum of **3** exhibits intense ν_{BH} (2556 cm^{-1}), ν_{CN} (2157 and 2149 cm^{-1}), and ν_{VO} (968 cm^{-1}) stretches that are shifted to higher energies relative to **2**, suggesting the formation of Mn^{II}−NC−V^{IV}O linkages.[6a]

Compound **3** crystallizes in the $P\bar{1}$ space group.[5a,7] The vanadyl and Mn^{II} centers reside in alternate corners of the rectangular cluster and are linked via cyanides (Figure 2).[3c] The vanadyl groups are related by an inversion center, in an anti orientation relative to the V$_2$Mn$_2$(CN)$_4$ plane. A single methyl group per Tp* ligand projects perpendicular to and above [ca. 3.06(3) Å] this plane, located opposite to the oxo group; the closest intercluster contacts [ca. 3.716(3) Å] are between the Tp* (methyl group) and bipy ligands. The Mn−N bond distances [2.155(3) and 2.180(3) Å] are smaller than those in the structurally related {[(Tp*)Fe^{III}(CN)$_3$]$_2$[Mn^{II}(DMF)$_4$]$_2$[OTf]$_2$}·2DMF cluster, suggesting that less electron density is localized onto the cyanide nitrogens by the vanadyl centers.[3d,6a]

Magnetic studies indicate that **1**·H$_2$O and **2** are paramagnetic complexes. Room-temperature magnetic studies using crushed single crystals indicate that the effective magnetic moment values (μ_{eff}) of **1**·H$_2$O and **2** are 2.49 and 1.78 μ_B. Assuming that deviations from spin-only behavior are due to spin−orbit coupling, the spin ground states are $S = 1$ and $^1/_2$, with calculated g values of 1.76 and 2.06, for **1**·H$_2$O and **2**, respectively.[6b]

Variable-temperature magnetic studies suggest that **3** exhibits an $S = 4$ spin ground state. For **3**, the room-temperature χT value of 9.49 emu K mol^{-1} is close to that expected (9.50 emu K mol^{-1}) for a tetranuclear cluster containing magnetically isolated, isotropic Mn^{II} and vanadyl spin centers (Figure 3). The χT product gradually decreases between 300 and 55 K and increases monotonically below 55 K, reaching a maximum value of 10.63 emu K mol^{-1} at 7.52 K, in close agreement with that expected (11.03 emu K mol^{-1}; $g = 2.1$ assumed) for an antiferromagnetically coupled cluster.[6b]

Fitting of the magnetic data between 50 and 300 K using the Curie−Weiss equation suggests that the transition-metal centers are antiferromagnetically coupled. The calculated Curie and Weiss constants of 9.62 cm^3 K mol^{-1} and −11.96 K indicate that antiferromagnetic exchange occurs between the Mn^{II} and V^{IV}O centers. Additionally, nonlinear least-squares fitting of the data via the Kambe method affords g(cluster), intracluster coupling constants (V1···Mn1, J_1; V1···V1A and Mn1···Mn1A, J_2), and intercluster coupling constants (zJ', where $z = 2$) of 2.07, −7.85, −0.010, and 3.4 × 10^{-4} cm^{-1}, respectively (Figure 3).[6b,c]

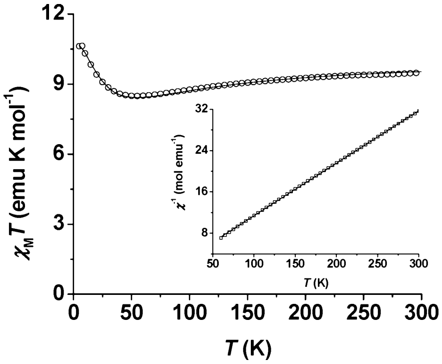

Figure 3. Temperature dependence of $\chi_M T$ for **3** in an applied dc field of 1 kG. The line represents a least-squares fitting of the $\chi_M T$ data. Inset: Temperature dependence of the reciprocal susceptibility (χ^{-1}) at 1 kG.

Additional magnetic measurements verify that **3** contains isotropic spin centers and that the clusters are magnetically isolated. For **3**, the field dependence of the magnetization is rapidly saturated, affording a maximum value of 43.23 kG cm^3 mol^{-1} at 1.8 K and 7 kG; the experimental value is close to the 44.68 kG cm^3 mol^{-1} value expected for an antiferromagnetically coupled cluster. The hysteresis loop is closed and exhibits no discernible coercive field, while ac susceptibility measurements show no frequency-dependent behavior, confirming that **3** contains isotropic Mn^{II} ($S = {}^5/_2$) and V^{IV}O ($S = {}^1/_2$) spin centers.[5a,6b]

In summary, we have described the preparation of two early metal cyanovanadates and the first cyanide-bridged heterobimetallic cluster containing vanadium centers. To our knowledge, **1** is also the first well-defined six-coordinate mononuclear cyanovanadate(III) complex. The steric demand of the Tp* ligand apparently directs the self-assembly of building blocks toward the exclusive formation of rectangular clusters. Future efforts will investigate how the steric demand of the poly(pyrazolyl)borate ligands impacts the molecular shape and magnetic properties of the cyanometalate clusters.

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Supporting Information Available: X-ray crystallographic data (for **1**−**3** in CIF format) and synthetic details and additional magnetic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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