Synthesis and magnetic behavior of the tetrahedral cage complex [(cyclen)₄V₄(CN)₆]⁶⁺

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Reaction of [(cyclen)V(CF₃SO₃)₂](CF₃SO₃) with 4 equiv. of Et₄N(CN) in DMF generates the seven-coordinate complex [(cyclen)V(CN)₃], while a reaction employing just 1.5 equiv. produces a tetrahedral cage complex, [(cyclen)₄V₄(CN)₆]⁶⁺, in which antiferromagnetic coupling leads to an $S = 0$ ground state.

The ability to substitute a variety of transition-metal ions into a given structure has afforded a wide adjustability in the magnetic properties of cyano-bridged solids.[1] Recently, a similar approach has been adopted in varying the magnetic properties of metal–cyanide coordination clusters.[2–4] Here, selected capping ligands can be used to control the cluster geometry, and of particular interest is the generation of new single-molecule magnets. Such species possess a ground state for which a high spin S and a large negative axial zero-field splitting D lead to magnetic blocking at low temperatures. Of the single-molecule magnets identified to date, most are oxo-bridged clusters containing V[III], Mn[III], Fe[III] or Ni[II] centers as a source of anisotropy.[5] While the latter three of these ions have been incorporated into exchange-coupled metal–cyanide clusters, and Mn[III] has even been used in producing some of the first cyano-bridged single-molecule magnets,[4] V[III] has been less explored for this purpose. We herein report the synthesis of several cyclen-capped (cyclen = 1,4,7,10-tetraazacyclododecane) V[III] complexes of potential utility as building units, and a tetrahedral cage complex featuring four antiferromagnetically-coupled V[III] centers.

Mononuclear cyclen complexes bearing triflate and cyanide ligands were sought as corner precursor units for assembling cyano-bridged clusters. Reaction of (cyclen)VCl₃·0.25DMF (**1**)† in neat triflic acid afforded [(cyclen)V(CF₃SO₃)₂](CF₃SO₃) (**2**)‡ in near quantitative yield. X-Ray analysis§ of a violet plate-shaped crystal of **2**, obtained by diffusing dichloromethane vapor into an acetonitrile solution of the compound, revealed a six-coordinate complex with two triflate anions bound in *cis* positions. Owing to constraints imposed by the cyclen ring, the coordination geometry at the V[III] center deviates significantly from an ideal octahedron, with N–V–N chelate angles in the range 77.4(2)–80.9(2)° and *trans*-N–V–N angles of 95.5(2)° and 147.1(2)°. Compound **2** is soluble in most polar organic solvents and decomposes in air. In DMF, it reacts with an excess of Et₄N(CN) to precipitate [(cyclen)V(CN)₃] (**3**)¶ as an air-sensitive solid that is insoluble in any common solvent.

Pink brick-shaped crystals of **3** were obtained by layering an acetonitrile solution of Et₄N(CN) onto a DMF solution of **2**. X-Ray analysis§ of one such crystal revealed the seven-coordinate tricyanide complex depicted in Fig. 1. To date, the only other seven-coordinate vanadium(III)–cyanide complex that has been characterized structurally is the pentagonal bipyramidal complex [V(CN)₇]⁴⁻.[6] In **3**, however, the four N atoms of the cyclen ligand are arranged in a square and the C atoms of the cyanide ligands are arranged in an opposing and essentially parallel triangle, resulting in a trigonal base–tetragonal base (or 4 : 3) coordination geometry.[7,8] To our knowledge, the only other complexes known to exhibit this rare seven-coordinate geometry all involve an η⁴-cyclobutadiene ligand.[8] The V–C distances of 2.154(4) and 2.166(6) Å are very close to the mean distance of
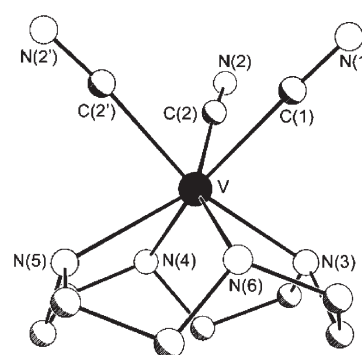

Fig. 1 Structure of the seven-coordinate complex [(cyclen)V(CN)₃] in **3**; H atoms are omitted for clarity. The molecule resides upon a crystallographic mirror plane, such that the cyclen ligand is disordered over two positions (only one of which is depicted). Selected mean interatomic distances (Å) and angles (°): V–N 2.23(6), V–C 2.162(7), C≡N 1.155(8); N–V–N 76(3), 121.0(8), C–V–C 82(2), V–C≡N 175(3).

2.15(1) Å in [V(CN)₇]⁴⁻.[6] Significantly, the C–V–C angles of 80.2(2) and 84.5(2)° in [(cyclen)V(CN)₃] are more acute than in six-coordinate corner building units such as [(tacn)Co(CN)₃] (tacn = 1,4,7-triazacyclononane),[3] suggesting its use in the formation of non-cubic clusters.

Indeed, an equimolar reaction between **2** and **3** in DMF produces a tetrahedral cluster unit, as isolated in [(cyclen)₄V₄(CN)₆] (CF₃SO₃)₆·0.75CH₂Cl₂ (**4**).‖ Alternatively, the cluster can be prepared *via* reaction of **2** with just 1.5 equiv. of Et₄N(CN) in DMF. Dark brown plate-shaped crystals of **4**·1.25CH₂Cl₂·CH₃NO₂ were obtained by diffusing dichloromethane vapor into a nitromethane solution of **4**. X-Ray analysis§ of one such crystal revealed the tetrahedral cage structure depicted in Fig. 2. Here, four cyclen-capped V[III] centers are arranged in a near perfect tetrahedron, with a cyanide ligand spanning each of its six edges. As necessitated by the C/N–V–C/N angles of 76.9(3)–80.1(3)°, the cyanide bridges are somewhat bent, with V–C/N–C/N angles falling in the range 165.7(1)–173.4(8)°. Note, however, that despite these outwardly-bowed edges, no guest molecule is present within the central cavity of the tetrahedron. Thus, the formation of [(cyclen)₄V₄(CN)₆]⁶⁺ appears to be guided strictly by the directionality of its building units. In contrast, formation of [M⊂Mo₄(CN)₆(CO)₁₂]⁵⁻ (M = Li, Na), the only other clusters known to exhibit this tetrahedral cage geometry, is driven by encapsulation of a central alkali metal cation.[9]

Variable-temperature magnetic susceptibility measurements were performed on **4** in order to examine the nature of magnetic exchange coupling within the cluster. As plotted in Fig. 3, the value of $\chi_M T$ at 300 K is 2.91 cm³ K mol⁻¹, significantly lower than the value of 4.00 cm³ K mol⁻¹ expected for four non-interacting V[III] ($S = 1$) centers with g = 2. With decreasing temperature, $\chi_M T$ drops steadily, reaching a value of 0.10 cm³ K mol⁻¹ at 5 K. This behavior is indicative of antiferromagnetic coupling between cyano-linked V[III] centers to give an $S = 0$ ground state. Assuming all four metal centers to be equivalent, the data were fit employing MAGFIT 3.1[10] and an exchange Hamiltonian of the form $\hat{H} = -2J(\hat{S}_{V(1)}\cdot\hat{S}_{V(2)} + \hat{S}_{V(1)}\cdot\hat{S}_{V(3)} + \hat{S}_{V(1)}\cdot\hat{S}_{V(3')} + \hat{S}_{V(2)}\cdot\hat{S}_{V(3)} + $
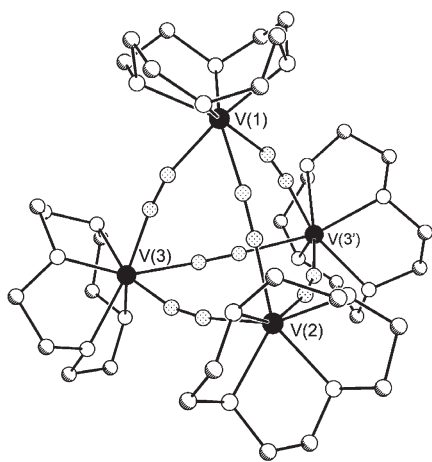
Fig. 2 Structure of the tetrahedral cage complex $[(\text{cyclen})_4\text{V}_4(\text{CN})_6]^{6+}$ in $4\cdot1.25\text{CH}_2\text{Cl}_2\cdot\text{CH}_3\text{NO}_2$. Black, shaded, and white spheres represent V, C and N atoms, respectively; H atoms are omitted for clarity. The C/N atoms of the bridging cyanide ligands (dotted spheres) could not be distinguished crystallographically. Each cyclen ligand is disordered over two positions, only one of which is depicted. Selected mean interatomic distances (Å) and angles (°): V···V 5.32(1), C/N–N/C 1.15(1), V(1)–N 2.20(2), V(2)–N 2.21(6), V(3)–N 2.21(6), V(1)–C/N 2.12(2), V(2)–C/N 2.134(5), V(3)–C/N 2.130(7); V–C/N–C/N 169(3), N–V(1)–N 77(3), 122.9(6), N–V(2)–N 77(5), 122(10), N–V(3)–N 77(3), 123(2), C/N–V(1)–C/N 78.3(8), C/N–V(2)–C/N 77.5(7), C/N–V(3)–C/N 78(2).

$\hat{S}_{\text{V}(2)}\cdot\hat{S}_{\text{V}(3')} + \hat{S}_{\text{V}(3)}\cdot\hat{S}_{\text{V}(3')}$). The best fit gave $J = -14.2$ cm^{-1} and $g = 1.93$, but necessitated inclusion of a substantial contribution from a paramagnetic impurity, despite the apparent purity of the compound. This discrepancy may be due to the fact that, by virtue of the cyanide ligand orientations, the vanadium centers within a given cluster cannot all be truly equivalent.** As a related complication, compound **4** likely contains a mixture of the four possible cyanide linkage isomers. Hence, the foregoing J value should be viewed as only approximate.
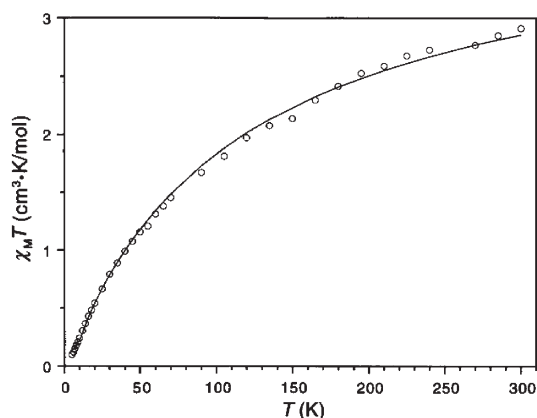
Fig. 3 Variable temperature magnetic data for compound **4** in an applied field of 1 T. The solid line represents a fit to the data, calculated with $J = -14.2$ cm^{-1}, $g = 1.93$, TIP = 668 × 10^{-6} cgsu mol^{-1}, and $P = 0.116$.

Further efforts will be directed toward studying the redox chemistry of $[(\text{cyclen})_4\text{V}_4(\text{CN})_6]^{6+}$, and employing $[(\text{cyclen})\text{V}(\text{CN})_3]$ in the synthesis of bimetallic clusters.

Acknowledgements

Notes and references

† **1**: A 10-ml DMF solution of VCl$_3$ (0.30 g, 1.9 mmol) and cyclen (0.33 g, 1.9 mmol) was heated at reflux under nitrogen for 1 h. The ensuing pink solid was collected by filtration and dried *in vacuo* to yield 0.58 g (89%) of product. $\mu_{\text{eff}} = 2.82\ \mu_{\text{B}}$ at 295 K. Anal. Calc. for C$_{8.75}$H$_{21.75}$Cl$_3$N$_{4.25}$O$_{0.25}$V: C, 30.21; H, 6.30; N, 17.11. Found: C, 30.44; H, 6.35; N 16.98%.

‡ **2**: Under a nitrogen atmosphere, solid **1** (3.10 g, 9.41 mmol) was added to 20 ml of anhydrous triflic acid, and the mixture was stirred for 1 h. The resulting violet solid was collected by filtration, washed with 50 ml of ether, and dried under nitrogen to yield 6.3 g (100%) of product. UV-vis (CH$_3$CN): λ_{max}/nm (ε_{M}/dm^3 mol^{-1} cm^{-1}) 305 (90), 425 (22), 664 (13). IR: ν(CH) 3215(m), ν(SO$_2$) 1237(s), ν(CF$_3$) 1225(s), δ(SO$_2$) 632(s) cm^{-1}. $\mu_{\text{eff}} = 2.72\ \mu_{\text{B}}$ at 295 K. Anal. Calc. for C$_{11}$H$_{20}$F$_9$N$_4$O$_9$S$_3$V: C, 19.71; H, 3.01; N, 8.36. Found: C, 19.65; H, 2.89; N 7.77%.

§ Crystal and refinement parameters for **2**: C$_{11}$H$_{20}$F$_9$N$_4$O$_9$S$_3$V: $M = 670.43$, orthorhombic, space group $Pna2(1)$, $a = 8.7126(9)$, $b = 22.149(2)$, $c = 12.2886(12)$ Å, $V = 2371.4(14)$ Å^3, $T = 139$ K, $Z = 4$, $D_c = 1.878$ g cm^{-3}, 9996 reflections collected, 3055 unique ($R_{\text{int}} = 0.0459$), no. parameters = 335, $R_1 = 0.0491$ [2907 data with $I > 4\sigma(I)$], $wR_2 = 0.1242$, GOF = 1.046, CCDC reference no. 247700. **3**: C$_{11}$H$_{20}$N$_7$V: $M = 301.28$, orthorhombic, space group $Pnma$, $a = 13.6325(10)$, $b = 12.2587(9)$, $c = 8.2450(6)$ Å, $V = 1377.88(17)$ Å^3, $T = 147$ K, $Z = 4$, $D_c = 1.452$ g cm^{-3}, 7521 reflections collected, 1478 unique ($R_{\text{int}} = 0.0316$), no. parameters = 85, $R_1 = 0.0668$ [1164 data with $I > 4\sigma(I)$], $wR_2 = 0.2052$, GOF = 1.067, CCDC reference no. 247701. $4\cdot1.25\text{CH}_2\text{Cl}_2\cdot\text{CH}_3\text{NO}_2$: C$_{47}H_{87}Cl_4F_{18}N_{23}O_{20}S_6V_4$: $M = 2174.32$, orthorhombic, space group $Pnma$, $a = 30.109(4)$, $b = 22.106(4)$, $c = 13.5995(18)$ Å, $V = 9052(2)$ Å^3, $T = 169$ K, $Z = 4$, $D_c = 1.595$ g cm^{-3}, 34320 reflections collected, 6363 unique ($R_{\text{int}} = 0.0844$), no. parameters = 531, $R_1 = 0.1155$ [4843 data with $I > 4\sigma(I)$], $wR_2 = 0.3290$, GOF = 1.128, CCDC reference no. 247702. See http://www.rsc.org/suppdata/dt/b4/b412804d/ for crystallographic data in CIF or other electronic format.

¶ **3**: Under a nitrogen atmosphere, solid Et$_4$N(CN) (0.44 g, 2.8 mmol) was added to a 10-ml DMF solution of **2** (0.47 g, 0.70 mmol), and the mixture was stirred for 1 h. The ensuing pink solid was collected by filtration and dried under nitrogen to yield 0.16 g (76%) of product. IR: ν(CH) 3225(m), ν(CN) 2102(w) cm^{-1}. $\mu_{\text{eff}} = 3.21\ \mu_{\text{B}}$ at 300 K and 3.12 μ_{B} at 5 K. Anal. Calc. for C$_{11}$H$_{20}$N$_7$V: C, 43.85; H, 6.69; N, 32.54. Found: C, 43.74; H, 6.39; N 32.39%.

‖ **4**: Under a nitrogen atmosphere, solid **2** (50 mg, 0.17 mmol) was added to a suspension of **3** (0.11 g, 0.16 mmol) in 3 ml of DMF, resulting in a dark brown solution within 10 min. Stirring for 12 h and subsequent addition of 10 ml of CH$_2$Cl$_2$ afforded 0.13 g (42%) of product as a brown solid. UV-vis (CH$_3$CN): λ_{max}/nm (ε_{M}/dm^3 mol^{-1} cm^{-1}) 338 (778), 477 (7050), 573 (2390). IR: ν(CH) 3214(m), ν(CN) 2156(w), ν(SO$_2$) 1236(s), ν(CF$_3$) 1223(s), δ(SO$_2$) 634(s) cm^{-1}. Anal. Calc. for C$_{44.75}$H$_{81.5}$Cl$_{1.5}$F$_{18}$N$_{22}$O$_{18}$S$_6$V$_4$: C, 26.78; H, 4.09; N, 15.35. Found: C, 27.13; H, 4.09; N 15.03%.

** Note that this discrepancy is probably not due to the presence of orbital angular momentum (as would arise if the V$^{\text{III}}$ centers were octahedrally-coordinated), since μ_{eff} for **3** shows little variation with temperature.

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