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

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Reaction of [(cyclen)VCl₃][CF₃SO₃] with 4 equiv. of Et₃N(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)V₄(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. A similar approach has been adopted in varying the magnetic properties of metal-cyanide coordination clusters. 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(VII), Mn(II), Fe(II) or Ni(II) centers as a source of anisotropy. While the latter three of these ions have been incorporated into exchange-coupled metal–cyanine clusters, and Mn(III) has even been used in producing some of the first cyano-bridged single-molecule magnets, V(VII) has been less explored for this purpose. We herein report the synthesis of several cyclen-capped (cyclen = 1,4,7,10-tetraazaacyclodecane) V(VII) complexes of potential utility as building units, and a tetrahedral cage complex featuring four antiferromagnetically-coupled V(III) centers.

Mononuclear cyclen complexes bearing triffid and cyanide ligands were sought as corner precursor units for assembling cyano-bridged clusters. Reaction of (cyclen)VCl₃·0.25DMF (1) in neat triffic acid afforded [(cyclen)VC₃SO₃][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 triffid anions bound in cis positions. Owing to constraints imposed by the cyclen ring, the coordination geometry at the V(VII) center deviates significantly from an ideal octahedron, with N–V–N chelate angles in the range 77.4(2)–80.9(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 Et₃N(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 Et₃N(CN) onto a DMF solution of 2. X-Ray analysis of one such crystal revealed the seven-coordinated 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)₆]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. To our knowledge, the only other complexes known to exhibit this rare seven-coordinate geometry all involve an 11-cyclobutadiene ligand. The V–C distances of 2.154(4) and 2.166(6) Å are very close to the mean distance of

![Figure 1](https://www.rsc.org/dalton/)

**Structure of the seven-coordinate complex [(cyclen)V(CN)₃]⁻**

- 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)]⁻ (tacn = 1,4,7,10-tetraazacyclodecane), 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)V₄(CN)₆]⁻ (CF₃SO₃)₂·0.75CH₃Cl (4). Alternatively, the cluster can be prepared via reaction of 2 with just 1.5 equiv. of Et₃N(CN) in DMF. Dark brown plate-shaped crystals of 4·1.25CH₃Cl·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)V₄(CN)₆]⁶⁺ appears to be guided strictly by the directionality of its building units. In contrast, formation of [M(C₆H₄CN)₃(CO)₆]²⁻ (M = Li, Na), the only other clusters known to exhibit this tetrahedral cage geometry, is driven by encapsulation of a central alkali metal cation.

Variable-temperature magnetic susceptibility measurements were performed on 4 in order to examine the nature of magnetic exchange within the cluster. As plotted in Fig. 3, the value of χ(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(VII) (S = 1) centers with g = 2. With decreasing temperature, χ(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-bridged V(III) centers to give an S = 0 ground state. Assuming all four metal centers to be equivalent, the data were fit employing MAGFIT 3.1⁰ and an exchange Hamiltonian of the form H = −2J (Sᵥ₁Sᵥ₂ + Sᵥ₂Sᵥ₃ + Sᵥ₃Sᵥ₄ + Sᵥ₄Sᵥ₁) + 2K (Sᵥ₁Sᵥ₃ + Sᵥ₂Sᵥ₄) + 2L (Sᵥ₁Sᵥ₄ − Sᵥ₂Sᵥ₃) + 2M (Sᵥ₁Sᵥ₃ − Sᵥ₂Sᵥ₄),

where J, K, L and M were determined to be −0.67(2) cm⁻¹, 0.16(4) cm⁻¹, −0.34(1) cm⁻¹ and 0.24(2) cm⁻¹, respectively.
yield 0.58 g (89%) of product. \( \mu_{\text{eff}} = 2.82 \mu_{B} \) at 295 K. Anal. Calc. for \( \text{C}_{12}\text{H}_{24}\text{Cl}_{2}\text{N}_{6}\text{O}_{2}\text{S}_{2}\text{V}_{C} \): C 30.21; H 6.30; N 17.11. Found: C 30.44; H 6.35; N 16.38%.

2. Under a nitrogen atmosphere, solid (1.30 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 for 6 h. The yield was 6.3 g (100%) of product. UV-vis (CHCl\(_3\)): \( \lambda_{\text{max}}(\text{nm}) \): 259 (6060), 218 (2350) cm\(^{-1}\). IR: v(C\(_\infty\)CH\(_\infty\)) 1396, 1403 cm\(^{-1}\) (solid).

3. Crystal and refinement parameters for \( \text{C}_{12}\text{H}_{24}\text{Cl}_{2}\text{N}_{6}\text{O}_{2}\text{S}_{2}\text{V}_{C} \): \( M = 670.43 \), orthorhombic, space group \( Pmna \), \( a = 8.3928(9) \), \( b = 22.2886(12) \), \( c = 2715.41(14) \), \( A = 193.12 \), \( Z = 4 \), \( D_{\text{calc}} = 1.878 \) g cm\(^{-3}\). 1999 reflections collected, 3976 unique (\( R_{\text{int}} = 0.0312 \)), \( R = 0.0312 \), \( R_{w} = 0.0496 \) [2907 data with \( I > 4 \sigma(I) \)], \( wR_{F} = 0.3290 \), GOF = 1.128, CCDC reference no. 247700.

4. Variable temperature magnetic data for compound \( \text{C}_{12}\text{H}_{24}\text{Cl}_{2}\text{N}_{6}\text{O}_{2}\text{S}_{2}\text{V}_{C} \): \( M = 670.43 \), orthorhombic, space group \( Pmna \), \( a = 8.3928(9) \), \( b = 22.2886(12) \), \( c = 2715.41(14) \), \( A = 193.12 \), \( Z = 4 \), \( D_{\text{calc}} = 1.878 \) g cm\(^{-3}\). 1999 reflections collected, 3976 unique (\( R_{\text{int}} = 0.0312 \)), \( R = 0.0312 \), \( R_{w} = 0.0496 \) [2907 data with \( I > 4 \sigma(I) \)], \( wR_{F} = 0.3290 \), GOF = 1.128, CCDC reference no. 247702. See http://www.rsc.org/suppdata/bf/b4/b412804d for crystallographic data in CIF or other electronic format.

5. Under a nitrogen atmosphere, solid \( \text{Et}_{2}\text{N(CN)} \): \( 0.44 \) g, 2.56 mmol was added to a 10-ml DMF solution of \( \text{VCl}_{3} \). The mixture was stirred for a few hours. The ensuing pink solid was collected by filtration and dried under nitrogen to yield 6.3 g (100%) of product. UV-vis (CHCl\(_3\)): \( \lambda_{\text{max}}(\text{nm}) \): 259 (6060), 218 (2350) cm\(^{-1}\). IR: v(C\(_\infty\)CH\(_\infty\)) 1396, 1403 cm\(^{-1}\) (solid).

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Notes and references

† 1: A 10-ml DMF solution of \( \text{VCl}_{3} \) (0.30 g, 1.9 mmol) and cyclo-\( 1\) (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 \( \text{vacuo} \) to...


