Strong magnetic exchange coupling in the cyano-bridged coordination clusters $[(PY5Me_2)_4V_4M(CN)_6]^{5+}$ (M = Cr, Mo)†

Danna E. Freedman, David M. Jenkins‡ and Jeffrey R. Long*

Reaction of $[(PY5Me_2)V(MeCN)]^{2+}$ with $[M(CN)_6]^{3-}$ (M = Cr, Mo) affords the star-like clusters $[(PY5Me_2)_4V_4M(CN)_6]^{5+}$, exhibiting $S = 9/2$ ground states that are exceptionally well-isolated in energy.

Molecular clusters possessing a high-spin ground state S with a negative axial anisotropy D can sometimes display slow magnetic relaxation at very low temperatures.[1] In order to raise the blocking temperatures for such single-molecule magnets, it is important not just to increase the anisotropy barrier ($U = S^2|D|$ for S even), but also to ensure that the magnetic ground state is well-separated in energy from excited spin states. Since this energy separation is directly proportional to the strength of the magnetic exchange coupling within a cluster, it is of value to develop synthetic routes to high-spin species in which the pairwise exchange constants J between metal centers are large in magnitude. While the use of cyanide as a bridging ligand has led to a wide range of high-spin clusters and even single-molecule magnets, most exhibit rather weak exchange coupling, with $|J|$ values below 10 cm^{-1}.[1c,2,3] One well-recognized means of achieving strong magnetic superexchange through a cyanide bridge is *via* use of early, low-valent transition metals, for which the diffuse d orbitals can give rise to a large overlap with the π and π^* orbitals of cyanide.[4] Indeed, the combination of V^{II} (t_{2g}^3) and Cr^{III} (t_{2g}^3) metal centers in Prussian blue analogues has led to bulk magnetic ordering temperatures well above room temperature.[5] Herein, we demonstrate that such an approach can also be used to generate high-spin clusters with large $|J|$ values. Moreover, we show that the replacement of Cr^{III} with Mo^{III} can lead to even stronger magnetic exchange coupling, as expected for the more diffuse wavefunctions of the 4d electrons.[6]

A long-established method for synthesizing discrete star-like clusters is through the reaction of a transition metal complex bearing a pentadentate capping ligand with a cyanometalate complex.[2a,e,f,m] The ligand 2,6-bis(1,1-bis(2-pyridyl)ethyl)pyridine[7,8] (PY5Me$_2$) was selected as a capping moiety likely to ensure magnetic isolation of the clusters and enforce an octahedral coordination geometry at the encapsulated metal center. Reaction of four equivalents of [(PY5Me$_2$)-V(MeCN)](CF$_3$SO$_3$)$_2$ with (Bu$_4$N)$_3$[Cr(CN)$_6$] in acetonitrile

Department of Chemistry, University of California, Berkeley, CA 94720-1460, USA. E-mail: jrlong@berkeley.edu
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‡ *Current address*: Department of Chemistry, University of Tennessee, Knoxville, TN 37996, USA.

afforded $[(PY5Me_2)_4V_4Cr(CN)_6](CF_3SO_3)_5$ (**1**), while an analogous reaction employing [(PY5Me$_2$)V(MeCN)](PF$_6$)$_2$ and Li$_3$[Mo(CN)$_6$]·6DMF[9] gave [(PY5Me$_2$)$_4$V$_4$Mo(CN)$_6$](PF$_6$)$_5$ (**2**).§ In each case, well-formed crystals could be obtained only by employing PF$_6^-$ as the counteranion.

X-Ray analysis of a single crystal of [(PY5Me$_2$)$_4$V$_4$Cr(CN)$_6$]-(PF$_6$)$_5$ (**1′**) revealed a structure consisting of a central [Cr(CN)$_6$]$^{3-}$ complex with peripheral [(PY5Me$_2$)V]$^{2+}$ units attached to all but two *cis* cyanide ligands (see Fig. 1). The [(PY5Me$_2$)$_4$V$_4$Cr(CN)$_6$]$^{5+}$ cluster resides at the intersection of two crystallographic mirror planes, giving rise to rigorous C_{2v} point group symmetry for the molecule. The coordination geometry around the Cr^{III} center is close to an ideal octahedron, with C–Cr–C bond angles in the range 88(2)–90(3)°, and linear Cr–C≡N angles in the range 174.0(4)–180.0(3)°. In contrast, to accommodate the steric bulk of the [(PY5Me$_2$)V]$^{2+}$ units, the V–N≡C angles are significantly bent (161.6(7)° and 172.2(7)°) in a manner that pushes the V^{II} centers away from one another and leads to a saddle point at the Cr^{III} center. To our knowledge, this is the first cyano-bridged cluster incorporating vanadium(II). Compound **2** is isostructural to **1**, featuring a [(PY5Me$_2$)$_4$V$_4$Mo(CN)$_6$]$^{5+}$ cluster with a completely analogous geometry. The main difference between the two structures arises in the increased metal–carbon distances associated with the slightly larger Mo^{III} center: Cr–C = 2.04(1)–2.066(8) Å *versus* Mo–C = 2.07(1)–2.19(1) Å. This represents just the second cluster
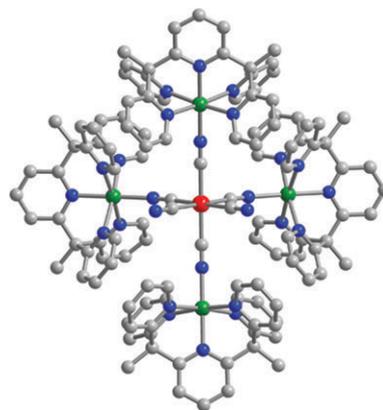
Fig. 1 Structure of the star-like clusters $[(PY5Me_2)_4V_4M(CN)_6]^{5+}$ (M = Cr, Mo), as observed for M = Mo in **2**. Red, green, gray, and blue spheres represent M, V, C, and N atoms, respectively; H atoms are omitted for clarity. Selected mean interatomic distances (Å) and angles (°) for M = Cr and Mo, respectively: M–C 2.053(9), 2.15(2); V–N$_{CN}$ 2.058(8), 2.01(1); V–N$_{py}$ 2.131(6), 2.119(8); M···V 5.168(2), 5.219(2); M–C≡N 175.6(8), 175(4); V–N≡C 161.6(7), 161(1) and 172.2(7), 173(1); C–M–C 90.0(3), 90.0(1) and 178.3(5), 178(6).

incorporating an octahedral Mo^{III} center, the only prior example being $[Mo_2(CN)_{11}]^{5-}$.[9]

To probe the nature of the magnetic exchange coupling within the V_4Cr cluster, variable-temperature magnetic susceptibility data were collected for **1** under an applied field of 5 T (see Fig. 2). At room temperature, the product $\chi_M T$ is 7.12 cm^3 K mol^{-1}, well below the spin-only value of 9.375 cm^3 K mol^{-1} expected for five $S = 3/2$ metal centers in the absence of magnetic coupling. This, together with the steady rise in $\chi_M T$ with decreasing temperature, is indicative of strong antiferromagnetic exchange coupling, as expected between Cr^{III} and V^{II}.[4] Accordingly, the data above 50 K were fit using MAGFIT 3.1[10] and an exchange Hamiltonian of the form $\hat{H} = -2J\hat{S}_{Cr}(\hat{S}_{V(1)} + \hat{S}_{(2)} + \hat{S}_{(3)} + \hat{S}_{V(4)})$ to give $J = -49$ cm^{-1} and $g = 1.89$. Note that a g value significantly below 2.00 is commonly observed for octahedral V^{II} complexes.[11] At low temperatures, the $\chi_M T$ data turn downward, mainly due to Zeeman splitting of the M_S levels in the presence of the applied magnetic field. Indeed, the behavior below 50 K closely follows that expected when taking the Zeeman splitting into account for a well-isolated $S = 9/2$ ground state (as shown by the red line in Fig. 2).

The magnetic susceptibility data for **2** are analogous to those observed for **1**, but indicate even stronger antiferromagnetic coupling within the V_4Mo cluster (see Fig. 3). Here, a fit to the data above 50 K gave $J = -61$ cm^{-1} and $g = 1.86$, corresponding to an $S = 9/2$ ground state that is even further isolated in energy. Thus, the replacement of Cr^{III} with Mo^{III} affords a 24% increase in the magnetic coupling strength, consistent with the presence of more diffuse spin-containing orbitals on the central metal ion. Note that similar increases in coupling strength have been demonstrated upon moving down a column in the transition series,[2d,12] although never for exchange constants of such large magnitude.

The V_4Cr and V_4Mo clusters exhibit by far the strongest magnetic exchange coupling yet observed for a cyano-bridged cluster with a non-zero spin ground state. To the best of our knowledge, the previous record was held by the star-like cluster $[(tren)_6Cu_6Cr(CN)_6]^{9+}$ (tren = tris(2-aminoethyl)amine), which displays an exchange constant of $J = 22.5$ cm^{-1} and an $S = 9/2$ ground state.[2e] Indeed, the magnitude of the J values

Fig. 3 Variable-temperature magnetic data for **2** collected in an applied field of 5 T. The black line corresponds to a fit to the high-temperature data resulting in $J = -61$ cm^{-1} and $g = 1.86$. The red line corresponds to the behavior calculated for a pure $S = 9/2$ state with $g = 1.95$ and in the absence of zero-field splitting.

observed here are eclipsed only by $[(tren)_2Cu_2(\mu-CN)]^{3+}$ ($J = -88$ cm^{-1})[13] and $[Mo_2(CN)_{11}]^{5-}$ ($J = -113$ cm^{-1}),[9] each possessing an $S = 0$ ground state. Significantly, this strong magnetic exchange results in $S = 9/2$ ground states that are exceptionally well-isolated, with the lowest-lying excited levels corresponding to $S = 7/2$ states that are 147 and 183 cm^{-1} higher in energy (see Fig. 4).

While possessing well-isolated high-spin ground states, the V_4Cr and V_4Mo clusters do not exhibit substantial anisotropy barriers. Fits to the magnetization data collected for **1** and **2** yielded axial zero-field splitting parameters of $D = -0.29$ and -0.27 cm^{-1}, respectively (see ESI†), while AC susceptibility experiments revealed no evidence for a relaxation barrier at temperatures down to 1.8 K. Future efforts will focus on the synthesis of related clusters incorporating metal centers such as Cr^{II} and Mo^{II}, for which both strong coupling and a large orbital-based magnetic anisotropy can be anticipated.

Fig. 2 Variable-temperature magnetic susceptibility data for **1** collected in an applied field of 5 T. The black line corresponds to a fit to the high-temperature data resulting in $J = -49$ cm^{-1} and $g = 1.89$. The red line corresponds to the behavior calculated for a pure $S = 9/2$ state with $g = 1.90$ in the absence of zero-field splitting.
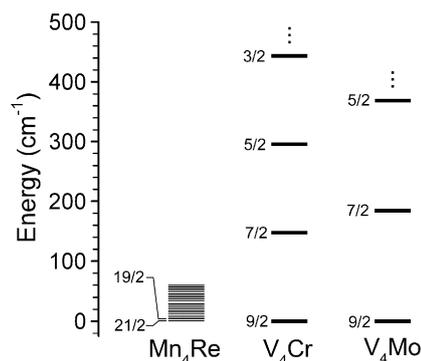
Fig. 4 Spin ladder showing the lowest spin energy levels for the clusters in **1** and **2**, as calculated from the fit of the magnetic susceptibility data. The results for a previously reported cluster, $[(PY5Me_2)_4Mn_4Re(CN)_7]^{5+}$, exhibiting weak ferromagnetic exchange coupling ($J = 2.3$ cm^{-1}), are shown at the left for comparison.[2m] Note that all of the energy levels for the spin manifold of the Mn_4Re cluster are depicted.

Notes and references

§ The compound $[V(MeCN)_6](CF_3SO_3)_2$ has been reported previously,[14] but a somewhat modified synthesis was utilized, as detailed below. The pentadentate ligand PY5Me$_2$ was synthesized in a manner analogous to that reported for PY5H$_2$;[15] an alternative preparation has also been reported.[7] The compounds $(Bu_4N)_3[Cr(CN)_6]$[16] and $Li_3[Mo(CN)_6]\cdot6DMF$[9] were synthesized as previously reported. Diethyl ether and acetonitrile were passed over alumina and degassed by three freeze–pump–thaw cycles prior to use. THF was dried over sodium–benzophenone, and distilled under nitrogen. All other reagents were purchased from commercial vendors and used without further purification. Single crystal X-ray diffraction measurements were collected on a Bruker APEX diffractometer. Structures were solved by Patterson maps with the aid of successive difference Fourier maps, and were refined against all data using the SHELXTL 5.0 software package.

Synthesis of $[V(MeCN)_6](CF_3SO_3)_2$. A 100 mL Schlenk flask was charged with vanadium powder (5.2 g, 0.10 mol) and cooled to 0 °C in an ice bath. Degassed water (10 mL, 0.55 mol) was added via canula, and the reaction mixture was stirred. Under a backflow of N$_2$, trifluoromethanesulfonic acid (10 mL, 0.11 mol) was added dropwise. The reaction mixture was heated at reflux overnight. The liquids were then removed by distillation under N$_2$ into an acid trap filled with KOH, leaving a green-gray solid. The solid was washed with 50 mL of ether and the resulting solution was separated by filtration. The remaining solid was then extracted into acetonitrile (6 × 75 mL) by rigorously stirring the mixture for 12 h. The green acetonitrile solution was concentrated under reduced pressure to a volume of 75 mL. Diffusion of ether vapor into this solution yielded 9.2 g (28%) of green crystalline product. UV-vis (MeCN) λ_{max}, nm (ε): 446(50), 615(55). IR (cm^{-1}): 3371, 3000, 2939, 2319, 2287, 1656, 1420, 1373, 1262, 1225, 1145, 1028, 753. Anal. Calcd for $C_{14}H_{18}F_6N_6O_6S_2V$: C, 28.24; H, 3.05; N, 14.12. Found: C, 28.56; H, 2.95; N, 13.90.

Synthesis of $[(PY5Me_2)V(MeCN)]I_2\cdot MeCN$. Solid PY5Me$_2$ (1.47 g, 3.31 mmol) was added to a solution of $[V(MeCN)_6](CF_3SO_3)_2$ in 60 mL of acetonitrile, and the mixture was stirred for two days. A solution of $(Bu_4N)I$ (2.69 g, 7.27 mmol) in 10 mL of acetonitrile was added, and the mixture was stirred for another two days. The resulting red powder was collected on a medium sintered-glass frit, washed with THF (40 mL) and ether (40 mL), and dried under nitrogen to yield 2.47 g (95%) of product. UV-vis (MeCN) λ_{max}, nm (ε): 405(3600), 485(5700). IR (cm^{-1}): 2254, 1594, 1474, 1462, 1450, 1436, 1404, 1305, 1273, 1147, 1065, 1021, 863, 790, 766, 754. ESI-TOF MS m/z: $[M]^{2+}$ 267.6. Anal. Calcd for $C_{33}H_{31}I_2N_7V$: C, 47.73; H, 3.76; N, 11.63. Found: C, 47.63; H, 3.66; N, 11.73.

Synthesis of $[(PY5Me_2)V(MeCN)](PF_6)_2$. A solution of TlPF$_6$ (0.987 g, 2.82 mmol) in 3 mL of acetonitrile was added to a stirring solution of $[(PY5Me_2)V(MeCN)]I_2\cdot MeCN$ (1.12 g, 1.35 mmol) in 14 mL of acetonitrile. After stirring for 12 h, a yellow precipitate (TlI) was removed by filtering through Celite. Diffusion of diethyl ether vapor into the filtrate yielded 1.09 g (94%) of red crystalline product. UV-vis (MeCN) λ_{max}, nm (ε): 408(3600), 485(5800). IR (cm^{-1}): 2252, 1595, 1467, 1454, 1438, 1062, 881, 829, 792, 756. ESI-TOF MS m/z: $[M]^{2+}$ 267.5. Anal. Calcd for $C_{31}H_{28}N_6F_{12}P_2V$: C, 45.11; H, 3.42; N, 10.18. Found: C, 44.92; H, 3.22; N, 10.07.

Synthesis of $[(PY5Me_2)_4V_4Cr(CN)_6](CF_3SO_3)_5$ (1). A yellow solution of $(Bu_4N)_3[Cr(CN)_6]$ (14 mg, 0.015 mmol) in 3 mL of acetonitrile was added to a red-purple solution of $[(PY5Me_2)V(MeCN)](CF_3SO_3)_2$ (50 mg, 0.060 mmol) in 3 mL of acetonitrile, affording a deep purple solution. Diffusion of diethyl ether vapor into the solution yielded 22 g (50%) of product as purple parallelpiped-shaped crystals. IR (cm^{-1}): ν_{CN} 2088. Anal. Calcd for $C_{127}H_{100}CrF_{15}N_{26}O_{15}S_5V_4$: C, 52.04; H, 3.44; N, 12.42. Found: C, 51.72; H, 3.74; N, 12.17.

Synthesis of $[(PY5Me_2)_4V_4Mo(CN)_6](PF_6)_5$ (2). A colorless solution of $Li_3[Mo(CN)_6]$ (6 mg, 0.02 mmol) in 3 mL of acetonitrile was added to a red-purple solution of $[(PY5Me_2)V(MeCN)](PF_6)_2$ (50 mg, 0.06 mmol) in 3 mL of acetonitrile. The mixture was heated at reflux for two days to give a purple solution. Diffusion of diethyl ether and dichloromethane vapors into this solution afforded 17 mg (26%) of product as purple block-shaped crystals suitable for X-ray analysis. IR (cm^{-1}): ν_{CN} 2100. Anal. Calcd for $C_{128}H_{134}Cl_8F_{30}MoN_{26}OP_5V_4$ (2·4CH$_2$Cl$_2$·Et$_2$O): C, 45.70; H, 3.48; N, 10.65. Found: C, 45.79; H, 3.29; N, 10.22.

1 (a) R. Sessoli, H. L. Tsai, A. R. Schake, S. Wang, J. B. Vincent, K. Folting, D. Gatteschi, G. Christou and D. N. Hendrickson, J. Am. Chem. Soc., 1993, 115, 1804; (b) R. Sessoli, D. Gatteschi, A. Caneschi and M. A. Novak, Nature, 1993, 365, 141; (c) J. R. Long, in Chemistry of Nanostructured Materials, ed. P. Yang, World Scientific, Hong Kong, 2003, p. 291; (d) D. Gatteschi, R. Sessoli and J. Villain, Molecular Nanomagnets, Oxford University Press, New York, 2006, and references therein; (e) C. J. Milios, A. Vinslava, W. Wernsdorfer, S. Moggach, S. Parsons, S. P. Perlepes, G. Christou and E. K. Brechin, J. Am. Chem. Soc., 2007, 129, 2754.

2 (a) A. Scuiller, T. Mallah, M. Verdaguer, A. Nivorozkhin, J. L. Tholence and P. Veillet, New J. Chem., 1996, 20, 1; (b) K. Van Langenberg, S. R. Batten, K. J. Berry, D. C. R. Hockless, B. Moubaraki and K. S. Murray, Inorg. Chem., 1997, 36, 5006; (c) Z. J. Zhong, H. Seino, Y. Mizobe, M. Hidai, A. Fujishima, S. Ohkoshi and K. Hashimoto, J. Am. Chem. Soc., 2000, 122, 2952; (d) J. J. Sokol, A. G. Hee and J. R. Long, J. Am. Chem. Soc., 2002, 124, 7656; (e) V. Marvaud, C. Decroix, A. Scuiller, C. Guyard-Duhayon, J. Vaissermann, F. Gonnet and M. Verdaguer, Chem.–Eur. J., 2003, 9, 1677; (f) V. Marvaud, C. Decroix, A. Scuiller, C. Tuyèras, C. Guyard-Duhayon, J. Vaissermann, J. Marrot, F. Gonnet and M. Verdaguer, Chem.–Eur. J., 2003, 9, 1692; (g) C. P. Berlinguette, D. Vaughn, C. Cañada-Vilalta, J. R. Galán-Mascarós and K. R. Dunbar, Angew. Chem., Int. Ed., 2003, 42, 1523; (h) L. M. C. Beltran and J. R. Long, Acc. Chem. Res., 2005, 38, 325; (i) D. F. Li, S. Parkin, G. B. Wang, G. T. Yee, A. V. Prosvirin and S. M. Holmes, Inorg. Chem., 2005, 44, 4903; (j) C.-F. Wang, J.-L. Zuo, B. M. Bartlett, Y. Song, J. R. Long and X.-Y. You, J. Am. Chem. Soc., 2006, 128, 7162; (k) T. Glaser, M. Heidemeier, T. Weyhermüller, R.-D. Hoffmann, H. Rupp and P. Müller, Angew. Chem., Int. Ed., 2006, 45, 6033; (l) J. H. Yoon, J. H. Lim, H. C. Kim and C. S. Hong, Inorg. Chem., 2006, 45, 9613; (m) D. E. Freedman, D. M. Jenkins, A. T. Iavarone and J. R. Long, J. Am. Chem. Soc., 2008, 130, 2884.

3 Here we employ exchange Hamiltonians of the form $\hat{H} = -2J\hat{S}_i\cdot\hat{S}_j$.

4 (a) W. R. Entley, C. R. Trentway and G. S. Girolami, Mol. Cryst. Liq. Cryst., 1995, 273, 153; (b) H. Weihe and H. U. Güdel, Comments Inorg. Chem., 2000, 22, 75.

5 (a) S. Ferlay, T. Mallah, R. Ouhes, P. Veillet and M. Verdaguer, Nature, 1995, 378, 701; (b) Ø. Hatlevik, W. E. Buschmann, J. Zhang, J. L. Manson and J. S. Miller, Adv. Mater., 1999, 11, 914; (c) S. M. Holmes and G. S. Girolami, J. Am. Chem. Soc., 1999, 121, 5593.

6 This expectation has been explicitly confirmed using electronic structure calculations: E. Ruiz, A. Rodríguez-Fortea, S. Alvarez and M. Verdaguer, Chem.–Eur. J., 2005, 11, 2135.

7 A. J. Canty, N. J. Minchin, B. W. Skelton and A. H. White, J. Chem. Soc., Dalton Trans., 1986, 2205.

8 For a lead reference on the extensive chemistry of complexes of the closely related ligand PY5, see: R. J. M. Klein Gebbink, R. T. Jonas, C. R. Goldsmith and T. D. P. Stack, Inorg. Chem., 2002, 41, 4633.

9 L. G. Beauvais and J. R. Long, J. Am. Chem. Soc., 2002, 124, 2110.

10 E. A. Schmitt, PhD thesis, University of Illinois at Urbana-Champaign, 1995.

11 (a) F. A. Cotton, S. A. Duraj, L. E. Manzer and W. J. Roth, J. Am. Chem. Soc., 1985, 107, 3850; (b) P. B. Hitchcock, D. L. Hughes, J. Leigh, J. R. Sanders, J. de Souza, C. J. McGarry and L. F. Larkworthy, J. Chem. Soc., Dalton Trans., 1994, 3683.

12 (a) M. P. Shores, J. J. Sokol and J. R. Long, J. Am. Chem. Soc., 2002, 124, 2279; (b) D. Visinescu, C. Desplanches, I. Imaz, V. Bahers, R. Pradhan, F. A. Villamena, P. Guionneau and J.-P. Sutter, J. Am. Chem. Soc., 2006, 128, 10202.

13 D. S. Bieksza and D. N. Hendrickson, Inorg. Chem., 1977, 16, 924.

14 P. Ghosh, H. Taube, T. Hasegawa and R. Kuroda, Inorg. Chem., 1995, 34, 5761.

15 G. Dyker and O. Muth, Eur. J. Org. Chem., 2004, 4319.

16 H. L. Schlafer, H. Wagener, F. Wasgestian, G. Herzog and A. Ludi, Ber. Bunsen-Ges. Phys. Chem., 1971, 75, 878.