Hexacyanoosmate(III) chemistry: preparation and magnetic properties of a pentanuclear cluster and a Prussian blue analogue with Ni(II)†

Matthew G. Hilfiger,[a] Michael Shatruk,[b] Andrey Prosvirin[a] and Kim R. Dunbar*[a]

Received (in Berkeley, CA, USA) 5th August 2008, Accepted 26th September 2008
First published as an Advance Article on the web 15th October 2008
DOI: 10.1039/b813413h

The hexacyanoosmate(III) anion was used to prepare a pentanuclear cyanide bridged molecular cluster with ligand-protected Ni(II) ions as well as the corresponding Prussian blue phase from a reaction with aqueous Ni(II) ions.

Paramagnetic cyanide compounds are of considerable current interest due to their remarkable properties which include high temperature magnetic ordering,[1,2] single molecule magnetism (SMM),[3–6] single chain magnetism,[7,8] photomagnetism,[9,10] and spin crossover.[11,12] An overarching goal of the field, particularly in the case of SMMs, is to achieve a thorough understanding of the role of single ion and global anisotropy in dictating the magnetic properties.

The prototype for SMM research, *viz*., $[Mn_{12}O_{12}(O_2CMe)_{16}(H_2O)_4]\cdot 2CH_3COOH\cdot 4H_2O$,[13,14] exhibits strong negative axial anisotropy ($-D_z$) owing to the presence of high spin Mn(III) ions which are subject to Jahn–Teller distortions that effectively quench first order spin–orbit coupling effects. A different type of SMM is possible for ions with strong unquenched orbital angular momenta for which the spin value, *S*, is no longer a good quantum number for describing the magnetic behavior; instead one must resort to a model based on the total angular momentum *J*.[15–19] In this vein, heavier transition metals are an excellent source of highly anisotropic magnetic molecules due to their tendency to exhibit strong spin–orbit coupling. Examples of clusters incorporating cyanometallates of 4d and 5d metal ions include those with the cyanometallates $[Mo^V(CN)_8]^{3-}$,[20,21] $[W^V(CN)_8]^{3-}$,[22,23] $[Re^{II}(triphos)CN_3]^-$,[4,24] $[Ru^{III}(acac)_2(CN)_2]^-$,[25] and $[Re^{IV}(CN)_7]^{3-}$.[26] SMM behavior has been reported for compounds based on the Re^{II},[4] Re^{IV},[26] and W^V [27] precursors.

Given the success with Group 6 and 7 transition elements, we have extended our exploration of cyanometallate anion chemistry to the Group 8 analog $[Os^{III}(CN)_6]^{3-}$. Although it has been known in the literature for some time,[28–30] this anion was only recently structurally characterized as the tetraphenylarsonium salt, $[Ph_4As]_3[Os^{III}(CN)_6]$,[28] and the magnetic properties determined. Herein we report the synthesis and magnetic properties of a trigonal bipyramidal (TBP) cluster and a Prussian blue phase of Os^{III} in combination with Ni^{II} ions, the first cyanide-bridged materials based on the hexacyanoosmate(III) anion.

The salt $[PPN]_3[Os(CN)_6]$ (PPN = bis(triphenylphosphine)iminium) was reacted with $[Ni(H_2O)_6](BF_4)_2$ and tmphen (tmphen = 3,4,7,8-tetramethyl-1,10-phenanthroline) in CH_3CN to form the pentanuclear complex $\{[Ni(tmphen)_2]_3[Os(CN)_6]_2\}\cdot 6CH_3CN$ (**1**)‡ in the manner previously reported by our group for other TBP clusters.[31] After one week, the product was collected as red-brown crystals suitable for X-ray diffraction experiments. The crystal structure determination§ revealed that the cluster consists of two axial $[Os(CN)_6]^{3-}$ units connected *via* bridging cyanide ligands to three equatorial $[Ni(tmphen)_2]^{2+}$ groups to yield a trigonal bipyramidal geometry (Fig. 1).

The reaction of $[PPN]_3[Os(CN)_6]$ with $[Ni(H_2O)_6](BF_4)_2$ in a water : methanol solution (9 : 1 v/v) led to the instantaneous formation of a red-brown solid formulated as $Ni_3[Os(CN)_6]_2\cdot 4H_2O$ (**2**) based on elemental data and thermal gravimetric analysis. The powder diffraction pattern (Fig. S1†) was indexed in a face centered cubic unit cell with a = 10.435(3) Å, consistent with the edge being Os–CN–Ni–NC–Os as estimated from the metrical parameters of **1** (~10.61 Å).

Infrared spectral measurements performed on compounds **1** and **2** revealed $\nu_{C\equiv N}$ stretches of 2148, 2129, 2099 cm^{-1} and 2141, 2102 cm^{-1}, respectively. The higher energy stretches located at 2148 and 2141 cm^{-1} correspond to a bridging cyanide mode[31] whereas the features at ~2100 cm^{-1} are assigned to terminal cyanide groups on the basis of the IR spectrum of $[PPN]_3[Os(CN)_6]$ for which $\nu_{C\equiv N}$ occurs at 2098 cm^{-1}.

The magnetic properties of **1** and **2** were investigated by magnetic susceptibility measurements in the temperature range of 2–300 K and field dependent magnetization measurements in an applied field of 0–70 kOe. For **1**, these measurements were carried out on crushed polycrystalline material, whereas for **2** the measurements were performed on the microcrystalline precipitate from the reaction solution.

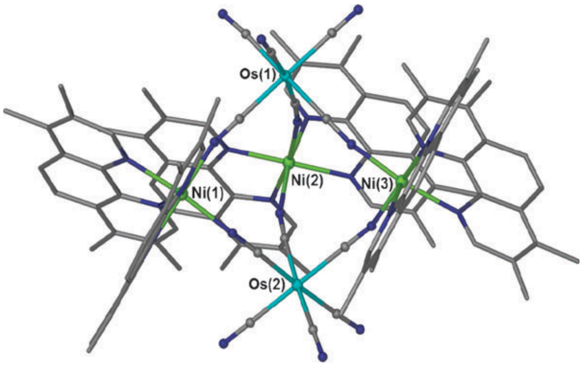

Fig. 1 Equatorial view of the molecular structure of **1**. Hydrogen atoms have been removed for the sake of clarity.

---

[a] *Dept. of Chemistry Texas A&M University, College Station TX, USA. E-mail: dunbar@mail.chem.tamu.edu; Fax: 1-979-845-7177; Tel: 1-979-845-5235*
[b] *Dept. of Chemistry and Biochemistry Florida State University, Tallahassee, FL, USA. E-mail: shatruk@chem.fsu.edu*

† Electronic supplementary information (ESI) available: CIF file of **1** and magnetic data of **1** and **2**. CCDC 685552. See DOI: 10.1039/b813413h

For compound **1**, a χT value of 4.73 emu K mol^{-1} was observed at 300 K which is higher than the expected value for three $S = 1$ and two $S = 1/2$ spin centers in the absence of magnetic interactions (3.64 emu K mol^{-1}) due to an orbital contribution from the Ni(II) ions. The expected value was calculated using the experimental room temperature value of the $[PPN]_3[Os(CN)]_6$ starting material (0.32 emu K mol^{-1}). The plot of χT *vs.* T shows a slight increase as the temperature is lowered and reaches a maximum of 5.29 emu K mol^{-1} at 21.6 K. Such behavior is indicative of weak ferromagnetic coupling between the Ni(II) and Os(III) centers.

The magnetic properties of **1** were modeled taking into account the effects of intracluster superexchange and zero field splitting:

$$\begin{aligned} \boldsymbol{H} = & -2J_{\text{Ni–Os}}(\boldsymbol{S}_{\mathbf{Os1}} + \boldsymbol{S}_{\mathbf{Os2}})(\boldsymbol{S}_{\mathbf{Ni1}} + \boldsymbol{S}_{\mathbf{Ni2}} + \boldsymbol{S}_{\mathbf{Ni3}}) \\ & - 3D[S^{z}{}_{\text{Ni}}{}^{2} - S_{\text{Ni}}(S_{\text{Ni}} + 1)/3] \\ & + \beta H[g_{\text{avg}}(\boldsymbol{S}_{\mathbf{Os1}} + \boldsymbol{S}_{\mathbf{Os2}} + \boldsymbol{S}_{\mathbf{Ni1}} + \boldsymbol{S}_{\mathbf{Ni2}} + \boldsymbol{S}_{\mathbf{Ni3}})] \end{aligned}$$

Application of this Hamiltonian using Magpack[32] resulted in the best fit parameters of $g_{\text{avg}} = 2.09$, $J_{\text{Ni–Os}} = 2.3$ cm^{-1}, and $D_{\text{Ni}} = 19.5$ cm^{-1}, confirming the ferromagnetic coupling between Ni$^{\text{II}}$ and Os$^{\text{III}}$ ions. Clearly the D parameter is unrealistically large for the Ni$^{\text{II}}$ ion, but it must be emphasized that the model cannot account for the spin–orbit coupling effects of the Os$^{\text{III}}$ centers or anisotropic superexchange. Contributions from these factors would account for an overestimation of the D value. The strong magnetic anisotropy of the cluster is clearly evident from the variable temperature reduced magnetization curves (Fig. 2, inset).

It is important to point out at this stage that a theoretical study was recently undertaken by Mironov[33] (who was not aware of our experimental results) in which the behavior of hypothetical $M_3^{\text{II}}Os_2^{\text{III}}$ trigonal bipyramidal clusters (M = 3d metal ion) was modeled in an effort to identify possible candidates for SMM behavior. In the case of the Ni_3Os_2 analog, the results indicated that the molecule would be unlikely to be a SMM due to the presence of low lying excited states that facilitate relaxation of the magnetization. Indeed, AC magnetic susceptibility data for **1** did not exhibit an out-of-phase signal down to 1.8 K. Moreover, the field dependent magnetization curve of **1** at 1.8 K does not saturate (Fig. S2†), which is in accord with the presence of low lying excited states as predicted from theory.

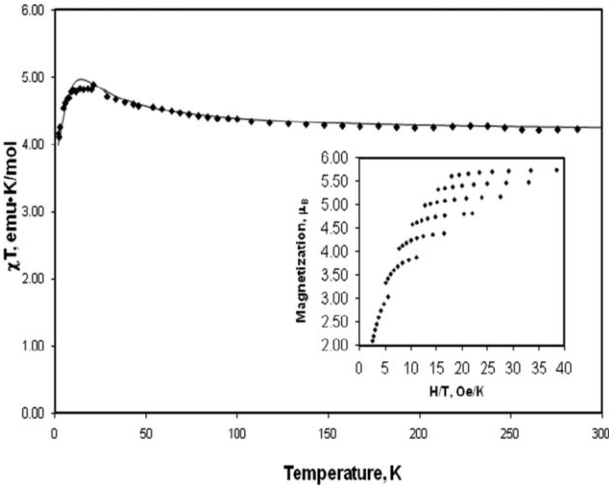

Fig. 2 Temperature dependence of χT for **1**. Solid line represents the simulation using MAGPACK with best fit parameters, $g_{\text{avg}} = 2.09$, $J_{\text{Ni–Os}} = 2.3$ cm^{-1}, $D_{\text{Ni}} = 19.5$ cm^{-1}. Inset: reduced magnetization plot, measured fields: 1–7 Tesla.

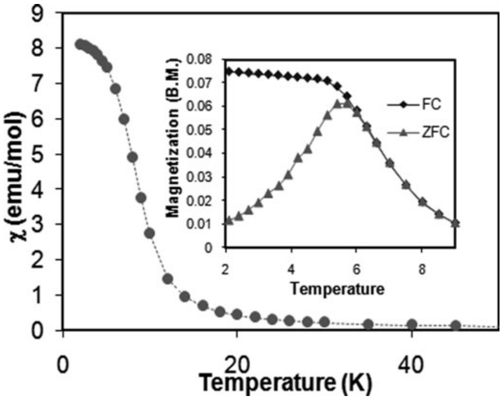

Fig. 3 A plot of χ *vs.* T for $Ni_3[Os(CN)_6]_2$ Prussian blue analogue exhibiting ferromagnetic ordering at 6.2 K. Inset: zero field cooled *vs.* field cooled magnetization measured in an applied field of 10 Oe.

Compound **2** exhibits a χT value of 3.65 emu K mol^{-1} at 300 K. This is slightly larger than the value predicted for non-interacting spins (3.54 emu K mol^{-1}) and the fact that the value is not even higher due to an orbital contribution from Ni(II) is attributed to a small amount of entrapped diamagnetic impurities such as the PPN$^+$ cation. This is a common problem for rapidly precipitating Prussian blue phases. The χ *vs.* T curve shows a rapid increase at lower temperatures and reaches saturation below 5 K (Fig. 3). The temperature dependence of $1/\chi$ was fitted to a Curie–Weiss law in the 100–300 K range to give a θ value of 14.5 K (Fig. S3†). This behavior suggests that Ni(II) and Os(III) ions are coupled ferromagnetically in **2**, and that the material undergoes long-range ferromagnetic ordering at very low temperatures. An examination of the field dependent magnetization at 2 K revealed hysteretic behavior with a coercivity $H_C = 500$ Oe (Fig. S4†), while zero field cooled *vs.* field cooled magnetization measurements clearly revealed a bifurcation of the two temperature dependent curves around 6.2 K (Fig. 3, inset). The collective magnetic data indicate that **2** is a soft ferromagnet with a T_c of 6.2 K. The magnetic exchange constant ($J_{\text{Ni–Os}}$) for **2** was estimated from the Langevin–Weiss–Neél equation[34] to be ~1.1 cm^{-1}.

This new study provides us with a convenient opportunity to compare properties of a TBP cluster incorporating a 5d cyanometallate with homologous 3d derivatives. Earlier work reported in the literature included the preparation of the $Ni_3^{\text{II}}Fe_2^{\text{III}}$ TBP clusters with various capping ligands[35–37] and the PB derivative $K_{0.4}Ni_{1.3}[Fe(CN)_6]\cdot 6.3H_2O$.[38] The Ni_3Fe_2 TBP's exhibit ferromagnetic coupling with $J = 3.3$ and 5.4 cm^{-1},[35,36] which are slightly larger than that found in the present case for compound **1**. The PB analogue exhibits ferromagnetic ordering at a higher blocking temperature, ($T_c = 25$ K) as compared to **2**. Further theoretical work is being undertaken to help elucidate these differences in magnetic properties.

These results indicate that $[Os(CN)_6]^{3-}$ is a useful building block for the preparation of magnetic clusters and extended magnetic solids. In light of on-going theoretical efforts in the field of molecular magnetism, and especially single molecule magnetism, it is imperative that one couples theory and experimental observations in order to gain insight into the parameters that affect the behavior, especially for highly anisotropic systems for which simple isotropic models are unsatisfactory. Extensions of this $[Os(CN)_6]^{3-}$ chemistry and related $[Ru(CN)_6]^{3-}$ studies are in progress and will be reported in due course.

We would like to acknowledge Carolina Avendaño and Dr Nattamai Bhuvanesh for providing assistance and for useful discussions. This research was supported, in part, by the National Science Foundation (PI grant CHE-0610019) and the Department of Energy (grant DE-FG03-02ER45999). Funding of the CCD diffractometer by the NSF (CHE-9807975) is gratefully acknowledged.

Notes and references

‡ Synthesis of $\{[Ni(C_{16}H_{16}N_2)_2]_3[Os(CN)_6]_2\}$ (**1**): a 4 mmol acetonitrile solution of $[PPN]_3[Os(CN)_6]$ (yellow solution) and $[Ni(H_2O)_6][BF_4]_2$ with tmphen was prepared. The solutions were combined and left to stand for 1 week after which time red-brown crystals suitable for X-ray diffraction had formed. Synthesis of (**2**): $Ni_3[Os(CN)_6]_2{\cdot}4.04H_2O$ was prepared by mixing a solution of 0.1 mmol of $[Ni(H_2O)_6][BF_4]_2$ in H_2O and reacted with a 9 : 1 H_2O–MeOH solution of 0.1 mmol $[PPN]_3[Os(CN)_6]$. A microcrystalline red-orange solid formed instantaneously. Elemental analysis calculated: C 15.20, H 0.91, N 17.74, O 7.26, Ni 18.35, Os 40.53. Found: C 15.01, H 0.90, N 17.20, O 7.15, Ni 17.30%.

§ Crystal data for **1**. $C_{120}H_{114}N_{30}Os_2Ni_3$ = 2524.39, monoclinic, $P2_1/c$ (No.14), a = 19.40(1) Å, b = 25.61(2) Å, c = 24.96(2) Å, β = 98.15(1)°, V = 12 280(15) Å^3, Z = 4, ρ_c = 1.340 g cm^{-3}, μ = 2.570 mm^{-1}, T = 110 K, Mo Kα (λ = 0.71073 Å) radiation, 19 015 reflections (10 721 unique, R_{int} = 0.1331) with 2θ = °, 502 variables, R = 0.0892, $R_w(F_o^2)$ = 0.1566 [4972 data, $I > 2\theta(I)$], GOF = 1.149. CCDC 685552. Powder X-ray diffraction was performed on a Bruker-AXS GADDS diffractometer using microdiffraction techniques as previously described.[39]

1 S. Ferlay, T. Mallah, R. Ouahes, P. Veillet and M. Verdaguer, *Nature*, 1995, **378**, 701–703.
2 W. R. Entley and G. S. Girolami, *Science*, 1995, **268**, 397–400.
3 D. Li, R. Clerac, S. Parkin, G. Wang, G. T. Yee and S. M. Holmes, *Inorg. Chem.*, 2006, **45**, 5251–5253.
4 E. J. Schelter, F. Karadas, C. Avendano, A. V. Prosvirin, W. Wernsdorfer and K. R. Dunbar, *J. Am. Chem. Soc.*, 2007, **129**, 8139–8149.
5 J. N. Rebilly and T. Mallah, *Struct. Bonding*, 2006, **122**, 103–131.
6 C. P. Berlinguette, D. Vaughn, C. Canada-Vilalta, J. R. Galan-Mascaros and K. R. Dunbar, *Angew. Chem., Int. Ed.*, 2003, **42**, 1523–1526.
7 M. Ferbinteanu, H. Miyasaka, W. Wernsdorfer, K. Nakata, K. Sugiura, M. Yamashita, C. Coulon and R. Clerac, *J. Am. Chem. Soc.*, 2005, **127**, 3090–3099.
8 N. E. Chakov, W. Wernsdorfer, K. A. Abboud and G. Christou, *Inorg. Chem.*, 2004, **43**, 5919–5930.
9 C. Mathoniere, R. Podgajny, P. Guionneau, C. Labrugere and B. Sieklucka, *Chem. Mater.*, 2005, **17**, 442–449.
10 O. Sato, T. Iyoda, A. Fujishima and K. Hashimoto, *Science*, 1996, **272**, 704–705.
11 M. Shatruk, A. Dragulescu-Andrasi, K. E. Chambers, S. A. Stoian, E. L. Bominaar, C. Achim and K. R. Dunbar, *J. Am. Chem. Soc.*, 2007, **129**, 6104–6116.
12 M. Nihei, M. Ui, M. Yokota, L. Han, A. Maeda, H. Kishida, H. Okamoto and H. Oshio, *Angew. Chem., Int. Ed.*, 2005, **44**, 6484–6487.
13 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**, 1804–1816.
14 S. M. J. Aubin, Z. Sun, I. A. Guzei, A. L. Rheingold, G. Christou and D. N. Hendrickson, *Chem. Commun.*, 1997, 2239–2240.
15 A. V. Palii, S. M. Ostrovsky, S. I. Klokishner, B. S. Tsukerblat, E. J. Schelter, A. V. Prosvirin and K. R. Dunbar, *Inorg. Chim. Acta*, 2007, **360**, 3915–3924.
16 V. S. Mironov, L. F. Chibotaru and A. Ceulemans, *J. Am. Chem. Soc.*, 2003, **125**, 9750–9760.
17 S. M. Ostrovsky, S. I. Klokishner, A. V. Palii and K. R. Dunbar, *J. Mol. Struct.*, 2007, **838**, 138–143.
18 B. S. Tsukerblat, A. V. Palii, S. M. Ostrovsky, S. V. Kunitsky, S. I. Klokishner and K. R. Dunbar, *J. Chem. Theory Comput.*, 2005, **1**, 668–673.
19 A. V. Palii, S. M. Ostrovsky, S. I. Klokishner, B. S. Tsukerblat, C. P. Berlinguette, K. R. Dunbar and J. R. Galan-Mascaros, *J. Am. Chem. Soc.*, 2004, **126**, 16860–16867.
20 D. E. Freedman, M. V. Bennett and J. R. Long, *Dalton Trans.*, 2006, 2829–2834.
21 F. Bonadio, M. Gross, H. Stoeckli-Evans and S. Decurtins, *Inorg. Chem.*, 2002, **41**, 5891–5896.
22 Z. J. Zhong, H. Seino, Y. Mizobe, M. Hidai, A. Fujishima, S. i. Ohkoshi and K. Hashimoto, *J. Am. Chem. Soc.*, 2000, **122**, 2952–2953.
23 R. Podgajny, C. Desplanches, B. Sieklucka, R. Sessoli, V. Villar, C. Paulsen, W. Wernsdorfer, Y. Dromzee and M. Verdaguer, *Inorg. Chem.*, 2002, **41**, 1323–1327.
24 E. J. Schelter, A. V. Prosvirin, W. M. Reiff and K. R. Dunbar, *Angew. Chem., Int. Ed.*, 2004, **43**, 4912–4915, S4912/4911.
25 W. F. Yeung, P. H. Lau, T. C. Lau, H. Y. Wei, H. L. Sun, S. Gao, Z. D. Chen and W. T. Wong, *Inorg. Chem.*, 2005, **44**, 6579–6590.
26 D. E. Freedman, D. M. Jenkins, A. T. Iavarone and J. R. Long, *J. Am. Chem. Soc.*, 2008, **130**, 2884–2885.
27 Y. Song, P. Zhang, X. M. Ren, X. F. Shen, Y. Z. Li and X. Z. You, *J. Am. Chem. Soc.*, 2005, **127**, 3708–3709.
28 P. Albores, L. D. Slep, L. M. Baraldo, R. Baggio, M. T. Garland and E. Rentschler, *Inorg. Chem.*, 2006, **45**, 2361–2363.
29 J. J. Alexander and H. B. Gray, *J. Am. Chem. Soc.*, 1968, **90**, 4260–4271.
30 L. A. Gentil, A. Navaza, J. A. Olabe and G. E. Rigotti, *Inorg. Chim. Acta*, 1991, **179**, 89–96.
31 M. Shatruk, K. E. Chambers, A. V. Prosvirin and K. R. Dunbar, *Inorg. Chem.*, 2007, **46**, 5155–5165.
32 J. J. Borras-Almenar, J. M. Clemente-Juan, E. Coronado and B. S. Tsukerblat, *J. Comput. Chem.*, 2001, **22**, 985–991.
33 V. S. Mironov, *Dokl. Phys. Chem.*, 2007, **415**, 199–204.
34 L. Neel, *Ann. Phys. (Paris, Fr.)*, 1948, **3**, 137–198.
35 C. P. Berlinguette, J. R. Galan-Mascaros and K. R. Dunbar, *Inorg. Chem.*, 2003, **42**, 3416–3422.
36 B. M. Bartlett, T. D. Harris, M. W. DeGroot and J. R. Long, *Z. Anorg. Allg. Chem.*, 2007, **633**, 2380–2385.
37 K. Van Langenberg, S. R. Batten, K. J. Berry, D. C. R. Hockless, B. Moubaraki and K. S. Murray, *Inorg. Chem.*, 1997, **36**, 5006–5015.
38 O. Sato, *J. Solid State Electrochem.*, 2007, **11**, 773–779.
39 N. S. P. Bhuvanesh and J. H. Reibenspies, *J. Appl. Crystallogr.*, 2003, **36**, 1480–1481.