

Crystal Structure and Electronic and Magnetic Properties of Hexacyanoosmate(III)

Pablo Albores,[†] Leonardo D. Slep,^{*†} Luis M. Baraldo,[†] Ricardo Baggio,[‡] María Teresa Garland,[§] and Eva Rentschler^{||}

Departamento de Química Inorgánica, Analítica y Química Física, INQUIMAE, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Pabellón 2, Ciudad Universitaria, C1428EHA Buenos Aires, Argentina, Comisión Nacional de Energía Atómica (CNEA), Av. Gral Paz 1499, 1650 San Martín, Pcia. de Buenos Aires, Argentina, Departamento de Física, Facultad de Ciencias Físicas y Matemáticas, y CIMAT, Universidad de Chile, Avenida Blanco Encalada 2008, Casilla 487-3, Santiago, Chile, and Institute of Inorganic and Analytical Chemistry, Johannes Gutenberg—University of Mainz, Duesbergweg 10–14, D-55128 Mainz, Germany

Received September 29, 2005

The $[\text{Os}^{\text{III}}(\text{CN})_6]^{3-}$ anion is prepared by chemical oxidation in aqueous solution and isolated as yellow prisms of $[\text{Ph}_4\text{P}]_3[\text{Os}^{\text{III}}(\text{CN})_6] \cdot 6\text{H}_2\text{O}$ (**1**). This species crystallizes in the triclinic space group $P\bar{1}$ with cell parameters $a = 13.7609(11)$ Å, $b = 16.2275(13)$ Å, $c = 17.0895(14)$ Å, $\alpha = 91.4040(10)^\circ$, $\beta = 109.3600(10)^\circ$, $\gamma = 102.3970(10)^\circ$, $V = 3497.4(5)$ Å³, and $Z = 2$. The slightly distorted octahedral moiety displays Os–C and C–N bond lengths that average 2.058 and 1.146 Å, respectively. Spin–orbit-coupling splitting of the ground-state term dominates the NIR region of the electronic spectrum and the magnetic behavior of **1**. The experimental information points to higher spin delocalization over the coordinated cyanides than in $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$.

The past decade witnessed an unexpected revival of the hexacyanometalate chemistry, driven by a great deal of publications reporting the use of these molecules as building blocks to prepare discrete and extended systems with potential applications as molecular wires and memory storage devices.¹ The most widespread $[\text{M}(\text{CN})_6]^{n-}$ moiety is by far the hexacyanoferrate system because of its availability, its inertness against loss of cyanide molecules, and the accessibility of two oxidation states with low-spin d^6 or d^5 electronic configurations, well suited for electron-transfer studies. The unpaired electron in the commercially available

$[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$ makes it also an attractive fragment to integrate magnetic materials.²

The exploration of multinuclear fragments involving the hexacyanometalates of the other two members of group VIII (Ru and Os) appears as a logical followup, provided their similar chemical behavior and the fact that the increase in orbital extension when going down in the group may enhance the electronic communication or the exchange interactions with other metallic fragments. All three d^6 species have been thoroughly characterized, but it was only recently,³ even when it has been known for decades,⁴ that $[\text{Ru}^{\text{III}}(\text{CN})_6]^{3-}$ could be isolated as its $[\text{Ph}_4\text{As}]^+$ salt, which provided the first opportunity to study its crystal structure and magnetic properties.

The last M^{III} member of the family is still partially characterized. It has been obtained by oxidation of $[\text{Os}^{\text{II}}(\text{CN})_6]^{4-}$ under air in organic media^{5,6} or by using Ce^{IV} ⁷ to explore its spectroscopic [UV–vis and magnetic circular dichroism (MCD) spectroscopies] and kinetic properties. So far, a structural characterization of this species has not been reported.

The addition of $[\text{Ph}_4\text{P}]\text{Cl}$ to an aqueous solution of $[\text{Os}^{\text{III}}(\text{CN})_6]^{3-}$ obtained by oxidation with a stoichiometric amount of Ce^{IV} induces the precipitation of a yellow powder of the Os^{III} species.⁸ The compound showed no signs of decomposition in solution or in the solid state. Single crystals suitable for X-ray structural analysis were obtained by slow evaporation of a concentrated aqueous solution. The X-ray structure determination⁹ of $[\text{Ph}_4\text{P}]_3[\text{Os}^{\text{III}}(\text{CN})_6] \cdot 6\text{H}_2\text{O}$ (**1**)

* To whom correspondence should be addressed. E-mail: slep@qi.fcen.uba.ar.

[†] Universidad de Buenos Aires.

[‡] Comisión Nacional de Energía Atómica.

[§] Universidad de Chile.

^{||} Johannes Gutenberg—University of Mainz.

(1) (a) Mallah, T.; Thiébaud, S.; Verdaguer, M.; Veillet, P. *Science* **1993**, 1554. (b) Bignozzi, C. A.; Argazzi, R.; Bortolini, O.; Scandola, F.; Harriman, A. *New J. Chem.* **1996**, 20, 731. (c) Entley, W. R.; Girolami, G. S. *Science* **1995**, 268, 397. (d) Dunbar, K. R.; Heintz, R. A. *Prog. Inorg. Chem.* **1997**, 283. (e) Launay, J. P.; Coudret, C. *Wires based on metal complexes*; Wiley-VCH: Weinheim, Germany, 2001; Vol. 5.

(2) Berlinguette, C. P.; Dunbar, K. R. *Chem. Commun.* **2005**, 2451.

(3) Bendix, J.; Steenberg, P.; Sotofte, I. *Inorg. Chem.* **2003**, 42, 4510.

(4) DeFord, D. D.; Davidson, A. W. *J. Am. Chem. Soc.* **1951**, 73, 1469.

(5) Kang, H. W.; Moran, G.; Krausz, E. *Inorg. Chim. Acta* **1996**, 249, 231.

(6) Alexander, J. J.; Gray, H. B. *J. Am. Chem. Soc.* **1968**, 90, 4260.

(7) Forlano, P.; Baraldo, L. M.; Olabe, J. A.; Dellavedova, C. O. *Inorg. Chim. Acta* **1994**, 223, 37.

COMMUNICATION

reveals the presence of the $[\text{Os}(\text{CN})_6]^{3-}$ anionic unit (crystallographically materialized in two independent moieties standing on two different symmetry centers), three $[\text{Ph}_4\text{P}]^+$ cations providing for charge balance, and six hydration water molecules.

The Os^{III} center is located in a slightly distorted octahedral environment, very similar to those observed in the other hexacyanometalates of the group. The Os–C bond lengths range between 2.044 and 2.070 Å, with an average value of 2.058 Å. This value follows the increasing trend observed in the group (1.945 and 2.050 Å for Fe^{III} and Ru^{III} , respectively) and is slightly larger than the average 2.042 Å observed in $\text{Na}_4[\text{Os}^{\text{II}}(\text{CN})_6] \cdot 10\text{H}_2\text{O}$.¹¹ The average C–N bond length in **1** is 1.146 Å, a number that compares well with those observed in the Os^{II} species (1.140 Å) and the other $[\text{M}^{\text{III}}(\text{CN})_6]^{3-}$ of the group (1.146 and 1.150 Å for Fe^{III} and Ru^{III} , respectively).^{3,12}

Solutions of **1** can be reversibly reduced to the Os^{II} state. Cyclic voltammetry experiments show one-electron-revers-

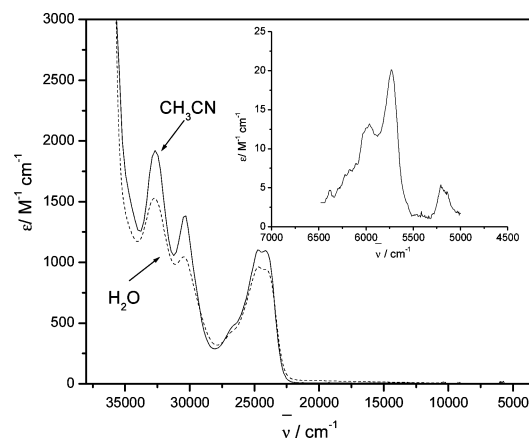


Figure 1. UV–vis–NIR spectra of $[\text{PPh}_4]_3[\text{Os}^{\text{III}}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$ in water and acetonitrile.

ible waves with ΔE_p between 80 and 100 mV depending on the solvent. The redox potentials for the $\text{Os}^{\text{III/II}}$ couple are solvent-dependent, being 437, –96, and –593 mV (vs AgCl/Ag^0) in water, methanol, and acetonitrile, respectively. These values correlate linearly with the acidity of the solvent measured by Gutmann’s acceptor number (AN),¹³ with a slope of 28 mV/AN, and reflect the specific cyanide–solvent interactions in the M^{II} state.¹⁴ As a comparison, a similar study performed over ferri/ferrocyanide yields a slope of 33 mV/AN.¹⁵ The shift in E° , and consequently in the energy of the lowest unoccupied molecular orbital, barely influences the charge-transfer features observed in the UV–vis spectrum of the Os^{III} species (Figure 1), indicating considerable mixing of the filled π_{CN} orbitals with the t_{2g} set of metal orbitals. Strong overlap with the charge-transfer transitions prevents the observation of the spin-allowed d–d transitions, a complication that has already been assessed in the literature.⁶ The use of MCD did not contribute substantially to palliate this difficulty.⁵ Nevertheless, valuable information can still be recovered from the NIR region of the spectrum. The intra- $^2T_{2g}$ term spin–orbit interaction splits the ground-state term into states that span the irreducible representations $E'_{1g(1/2)} + G'_{g(3/2)}$ of the double group O_h .¹⁶ The magnitude of the splitting is, to first order, close to $3/2\xi$ ($\xi \approx 3000 \text{ cm}^{-1}$),¹⁷ giving rise to intraconfigurational (IC) electronic transitions that show up in the NIR region. We found two groups of bands close to 5850 and 5200 cm^{-1} that are solvent-independent. These two transitions originate from further splitting of the excited $G'_{g(3/2)}$ term upon distortion from the ideal O_h symmetry. An extra-sharp feature at 4110 cm^{-1}

- (8) A total of 100 mg (0.200 mmol) of $\text{K}_4\text{Os}(\text{CN})_6$ was dissolved in 5 mL of water and treated with a stoichiometric amount of $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ (110 mg, 0.200 mmol). Almost immediately a small amount of a greenish-brown powder precipitated from the reaction mixture. This impurity was removed by filtration, leaving a deep-yellow solution. The addition of a slight excess of $[\text{Ph}_4\text{P}]\text{Cl}$ (250 mg, 0.67 mmol) precipitated the product. The solid was collected by filtration, washed with small portions of chilled water, and dried under vacuum. Yield: 208 mg (74%) of yellow needles. Anal. Calcd for $[\text{PPh}_4]_3[\text{Os}^{\text{III}}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$ ($\text{C}_{78}\text{H}_{64}\text{P}_3\text{N}_6\text{O}_2\text{Os}$): C, 66.9; H, 4.6; N, 6.0. Found: C, 66.6; H, 5.3; N, 5.9. IR (KBr pellet): 2130 (w), 2100 (vs), 2080 cm^{-1} (vs) ($\nu_{\text{C-N}}$).
- (9) Crystal data for $[\text{PPh}_4]_3[\text{Os}^{\text{III}}(\text{CN})_6] \cdot 6\text{H}_2\text{O}$ (**1**) at 298(2) K: $\text{C}_{78}\text{H}_{64}\text{P}_3\text{N}_6\text{O}_6\text{Os}$, MW = 1472.53, yellow prism, $0.42 \times 0.40 \times 0.12 \text{ mm}$, $P1$, $a = 13.7609(11) \text{ \AA}$, $b = 16.2275(13) \text{ \AA}$, $c = 17.0895 \text{ \AA}$, $\alpha = 91.4040(10)^\circ$, $\beta = 109.3600(10)^\circ$, $\gamma = 102.3970(10)^\circ$, $V = 3479.4(5) \text{ \AA}^3$, $Z = 2$, $d_{\text{calcd}} = 1.398 \text{ g cm}^{-3}$, Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$), $\mu = 1.819 \text{ mm}^{-1}$, final $R/R_w = 0.046/0.097$, goodness of fit on $F^2 = 0.969$ for 899 parameters and 10 106 unique reflections with $I > 2\sigma(I)$. The final Fourier difference synthesis showed minimum and maximum peaks of -0.649 and 1.479 e \AA^{-3} . Data were collected on a Bruker AXS SMART APEX CCD diffractometer with SMART^{10a} as the driving software; data integration was performed with SAINT^{10b} and a multiscan absorption correction applied using SADABS.^{10c} The structure was solved by direct methods and difference Fourier and refined by least squares on F^2 with anisotropic displacement parameters for non-H atoms. H atoms attached to C were idealized (C sp²–H: 0.93 Å) and allowed to ride. Those corresponding to water molecules were found in the difference density maps and refined with restraints, both in distances (O–H: 0.85 Å) as in their isotropic temperature factors [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{equiv}}(\text{O})$]. All calculations to solve the structures, refine the models proposed, and obtain derived results were carried out with the computer programs SHELXS97 and SHELXL97^{10d} and SHELXTL/PC.^{10e} Full use of the CCDC package was also made for searching in the CSD database.^{10f} Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 284552. Copies of the data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax (44) 1223 336-033; e-mail deposit@ccdc.cam.ac.uk).
- (10) (a) SMART, version 5.624; Bruker AXS Inc.: Madison, WI, 2001. (b) SAINT, version 6.02a; Bruker AXS Inc.: Madison, WI, 2000. (c) Sheldrick, G. M. SADABS; Multiscan Absorption Correction Program; University of Göttingen: Göttingen, Germany, 2001. (d) Sheldrick, G. M. SHELXS-97 and SHELXL-97; Programs for Structure Resolution and for Structure Refinement; University of Göttingen: Göttingen, Germany, 1997. (e) Sheldrick, G. M. SHELXTL-PC, version 5.0; Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1994. (f) Allen, F. H. *Acta Crystallogr.* **2002**, *B58*, 380.
- (11) Gentil, L. A.; Navaza, A.; Olabe, J. A.; Rigotti, G. E. *Inorg. Chim. Acta* **1991**, *179*, 89.
- (12) Dean, P. A. W.; Fisher, K.; Craig, D.; Jennings, M.; Ohene-Fianko, O.; Scudder, M.; Willett, G.; Dance, I. *Dalton Trans.* **2003**, 1520.

- (13) Gutmann, V. *Electrochim. Acta* **1976**, *21*, 661.
- (14) (a) Estrin, D. A.; Baraldo, L. M.; Slep, L. D.; Barja, B. C.; Olabe, J. A.; Paglieri, L.; Corongiu, G. *Inorg. Chem.* **1996**, *35*, 3897. (b) Timpson, C. J.; Bignozzi, C. A.; Sullivan, B. P.; Kober, E. M.; Meyer, T. J. *J. Phys. Chem.* **1996**, *100*, 2915. (c) Baraldo, L. M.; Forlano, P.; Parise, A. R.; Slep, L. D.; Olabe, J. A. *Coord. Chem. Rev.* **2001**, *219*, 881. (d) Slep, L. D.; Baraldo, L. M.; Olabe, J. A. *Inorg. Chem.* **1996**, *35*, 6327. (e) Slep, L. D.; Olabe, J. A. *J. Am. Chem. Soc.* **2001**, *123*, 7186.
- (15) Parise, A. R. Ph.D. Thesis, University of Buenos Aires, Buenos Aires, Argentina, 2000.
- (16) Balasubramanian, K. *Relativistic Effects in Chemistry*; John Wiley & Sons: New York, 1997.
- (17) Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier Science Publishing Co.: New York, 1984.

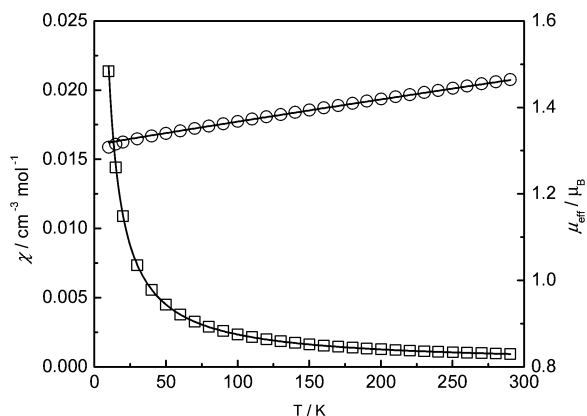


Figure 2. Temperature dependence of the magnetic susceptibility (\square) and moment (\circ) of **1**.

previously⁵ attributed to IC spin-orbit coupling (SOC) is presently discarded because it is also present in $[\text{Ph}_4\text{P}]_3[\text{Fe}^{\text{III}}(\text{CN})_6]$ at exactly the same energy. It has to be therefore vibrational in origin.

The variable-temperature susceptibility response of **1** is displayed in Figure 2. It is customary to model low-spin d^5 species with close-to-degenerate electronic ground states by means of a simplified Hamiltonian that operates over the ${}^2T_{2g}$ microstates, which are assumed to be well separated from the other excited configurations.¹⁸ In our case, however, the larger value for the SOC constant in Os^{III} induces small but nonnegligible mixing of the ${}^2T_{2g}$ state with electronically excited states. Omission of this fact when dealing with the susceptibility data still produces apparently good fittings but leads to either too large values for the SOC constant or an $E'_{1g(1/2)} - G'_{g(3/2)}$ energy gap that is not consistent with the NIR spectroscopy. For this reason, we chose to perform a full ligand-field (LF) computation including all of the microstates derived from a d^5 configuration, employing the standard LF Hamiltonian for an octahedral species parametrized in terms of Dq and Racah's parameters with the inclusion of the SOC terms and a tetragonal distortion contribution described as $H_{\text{so}} = \kappa \sum_i \xi_i l_i s_i$ and $H_{\text{tet}} = \Delta_{\text{tet}}(2 - L_z^2)/3$, respectively.

The magnetic and electronic data can be well reproduced with $Dq = 3850 \pm 50 \text{ cm}^{-1}$, $\zeta = 3100 \pm 40 \text{ cm}^{-1}$, $\kappa = 0.655 \pm 0.005$, and $\Delta_{\text{tet}} = -950 \pm 60 \text{ cm}^{-1}$. As for the Racah parameters, it must be noted that the contribution of the interelectronic repulsion to the ${}^2T_{2g}$ term is only indirect through its mixing to suitable excited states. According to our estimations, the contributions of the lowest-lying 4E_g and ${}^4A_{2g}$ to the ${}^2T_{2g}$ microstates are at most 5%. For this reason, ground-state properties and IC-SOC energies are, in this case,

poor probes to get accurate values for Racah's B and C . We achieved equally good fitting quality with C/B ratios close to the values found in gaseous ions ($B = 340 \text{ cm}^{-1}$, $C = 1360 \text{ cm}^{-1}$, and $C/B = 4.0$),^{17,18a,b} but also for ratios as large as 9.3 ($B = 263 \text{ cm}^{-1}$ and $C = 2450 \text{ cm}^{-1}$), with essentially no impact on the other parameters. Though deviations from the expected $C/B = 4-4.2$ might be indicative of covalency,¹⁷ we felt that such large values, even when they are close to those reported in the literature,⁶ are probably unrealistic and continued our analysis by constraining the C/B ratio to 4.0.

This set of parameters positions the IC transitions at 5720 and 5120 cm^{-1} , in excellent agreement with the NIR determinations. The LF parameters follow the trend expected for the group. The negative value of Δ_{tet} indicates a slight tetragonal elongation along the z axis.

X-band electron paramagnetic resonance (EPR) determinations of frozen solutions of **1** in water show a single broad resonance at $g = 1.82$. Evaluation of the Zeeman splitting of the ground Kramers doublet obtained from the LF calculation yields an effective axial \mathbf{g} matrix with principal values $g_{\perp} = 1.79$ and $g_{\parallel} = 1.21$. While the calculated g_{\perp} agrees with the measured one, we were not able to observe any signal at higher field probably because of severe broadening. Covalency of the Os-CN bonds, anticipated theoretically in ref 3, is reflected in the small value of the orbital reduction factor. However, there are no indications of hyperfine splittings in the X-band spectrum that could reflect spin delocalization on the cyanides.

We have recently shown that $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$ can be successfully employed to synthesize in a controlled way building blocks for extended materials.¹⁹ Replacement of the Fe moiety by the Os one will surely open an interesting new family of cyano-bridged oligomers with stronger electronic and magnetic coupling between metal centers, owing to the greater radial extension of the d orbitals and the higher degree of electron density delocalization over the bridging cyanides, in comparison with the lighter members of the group. We are currently exploring this possibility.

Acknowledgment. The authors thank the Universidad de Buenos Aires, Consejo Nacional de Investigaciones Científicas y Técnicas (Conicet), and Fundación Antorchas for economic funding. We thank Dr. E. Bill for the EPR and SQUID determinations. We are also thankful to Johnson Matthey for a generous loan of K_2OsO_4 . L.M.B., R.B., and L.D.S. are members of the scientific staff of Conicet.

Supporting Information Available: Crystallographic data in CIF format, IR and EPR spectra of **1**, and details on the LF analysis and magnetic susceptibility calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC0516818

(18) (a) Griffith, J. S. *The Theory of Transition-Metal Ions*, 1st ed.; Cambridge University Press: New York, 1961. (b) Ballhausen, C. J. *Introduction to Ligand Field Theory*, 1st ed.; Cambridge University Press: New York, 1962. (c) Figgis, B. N. *J. Chem. Soc., Dalton. Trans.* **1975**, 598.

(19) Alborés, P.; Slep, L. D.; Weyhermüller, T.; Baraldo, L. M. *Inorg. Chem.* **2004**, *43*, 6762.