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

Pablo Albores,† Leonardo D. Slep,*† Luis M. Baraldo,† Ricardo Baggio,† Maria 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, CI428EHA 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, Duessbergweg 10–14, D-55128 Mainz, Germany

The [OsIII(CN)6]3– anion is prepared by chemical oxidation in aqueous solution and isolated as yellow prisms of [Ph4P][OsIII(CN)6]·6H2O (1). This species crystallizes in the triclinic space group P1 with cell parameters a = 13.7609(11) Å, b = 16.2275(13) Å, c = 17.0895(14) Å, α = 91.4040(10)°, β = 109.3600(10)°, γ = 102.3970(10)°; 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 [FeIII(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 complexes as building blocks to prepare discrete and extended systems with potential applications as molecular wires and memory storage devices.1 The most widespread [M(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 d6 or d5 electronic configurations, well suited for electron-transfer studies. The unpaired electron in the commercially available [FeIII(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 d6 species have been thoroughly characterized, but it was only recently,3 even when it has been known for decades,4 that [RuIII(CN)6]3– could be isolated as its [Ph4As]+ salt, which provided the first opportunity to study its crystal structure and magnetic properties.

The last MIII member of the family is still partially characterized. It has been obtained by oxidation of [OsIII(CN)6]4− under air in organic media5,6 or by using CeIV7 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 [Ph4P]Cl to an aqueous solution of [OsIII(CN)6]3– obtained by oxidation with a stoichiometric amount of CeIV induces the precipitation of a yellow powder of the OsIII 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 [Ph4P]3[OsIII(CN)6]·6H2O (1)

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* 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.

Cyclic voltammetry experiments show one-electron-reversible waves with $\Delta E_p$ between 80 and 100 mV depending on the solvent. The redox potentials for the Os$^{III/II}$ couple are solvent-dependent, being 437, $-96$, and $-593$ mV (vs AgCl/Ag$^+$) 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. As a comparison, a similar study performed over ferri/ferrocyanide yields a slope of 33 mV/AN.$^{15}$ The shift in $E^\circ$, 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 $\pi_{Os}$ orbitals with the $1\pi_g$ 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 palliating this difficulty.$^5$ Nevertheless, valuable information can still be recovered from the NIR region of the spectrum. The infrared $T_{2g}$ term spin–orbit interaction splits the ground-state term into states that span the irreducible representations $E_g(3/2)$ and $G_g(1/2)$ of the double group $O_h^{2}$.$^{16}$ The magnitude of the splitting is, to first order, close to $2\zeta_2^2$ ($\zeta \approx 3000$ 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-strong feature at 4110 cm$^{-1}$ reveals the presence of the [Os(CN)$_6^{3-}$] anionic unit (crystallographically materialized in two independent moieties standing on two different symmetry centers), three [Ph$_3$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).$^{3,12}$

This impurity was removed by filtration, leaving a deep-yellow solution. The addition of a slight excess of [Ph$_4$ P]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.


Figure 2. Temperature dependence of the magnetic susceptibility (C) and moment (O) of 1.

previously\(^6\) attributed to IC spin–orbit coupling (SOC) is presently discarded because it is also present in [Ph₃P]₃[Fe\(^{III}\)(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 \(^2\)T\(_{2g}\) microstates, which are assumed to be well separated from the other excited configurations.\(^8\) In our case, however, the larger value for the SOC constant in Os\(^{III}\) induces small but nonnegligible mixing of the \(^2\)T\(_{2g}\) 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 \(E'_{\text{g}(1/2)} - G_{\text{g}(3/2)}\) 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 \(H_{\text{so}} = s\Sigma_{i\neq j} |\mathbf{S}_i| |\mathbf{S}_j|\) and \(H_{\text{tet}} = \Delta_{\text{so}} (2 - L^2)/3\), respectively.

The magnetic and electronic data can be well reproduced with \(Dq = 3850 \pm 50 \text{ cm}^{-1}\), \(\xi = 3100 \pm 40 \text{ cm}^{-1}\), \(\kappa = 0.655 \pm 0.005\), 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 \(^2\)T\(_{2g}\) term is only indirect through its mixing to suitable excited states. According to our estimations, the contributions of the lowest-lying \(^4\)E\(_g\) and \(^4\)A\(_{2g}\) to the \(^2\)T\(_{2g}\) 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 \(C/B = 4.0\)\(^7\)\(^\text{a,b}\) 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,\(^7\) 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 \(\Delta_{\text{so}}\) 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 \(g\) matrix with principal values \(g_\perp = 1.79\) and \(g_\parallel = 1.21\). While the calculated \(g_\parallel\) 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 [Fe\(^{III}\)(CN)₆]⁻ can be successfully employed to synthesize in a controlled way building blocks for extended materials.\(^9\) 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.

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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.

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