

Structural and Spectroscopic Evidence of Strong Electronic Delocalization through a Cyanido Bridge in a Mixed-Valence Os–Ru Complex

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We report the properties of a trinuclear cyanido-bridged complex, *trans*-[(dmap)₄Ru^{II}{(μ-NC)Os^{III}(CN)₅}₂]⁴⁻ [**1**⁴⁻; dmap = 4-(dimethylamino)pyridine], whose structure and elec-

tronic and vibrational spectra present strong evidence of partial redox states for the three metal ions, an unprecedented feature for cyanido-bridged systems.

Over the last 40 years, considerable attention has been given to mixed-valence complexes, systems where an element presents more than one oxidation state, with transition metal compounds of group 8 as the more outstanding examples.^[1] One of the areas of interest in this field is to identify systems in the frontier between the so-called localized systems or Class II,^[2] according to the classification proposed by Robin and Day,^[3] and the delocalized systems or Class III. To identify systems as Class III or Class II/III (localized, but solvent-averaged)^[4] several experimental criteria have been proposed^[4,5] including (1) the shape, intensity and solvent dependence of the intervalence transition, (2) direct evidence of localization from crystal structure, spectroscopic markers, the appearance of symmetrical bridging-ligand vibrations and the appearance of non-averaged spectator vibrations. Due to all the effort devoted to this area, several examples of Class III mixed-valence complexes have been identified,^[6] and a few of them show identical coordination spheres for both centers in their crystal structures.^[7] Non-symmetrical mixed-valence complexes have also been explored. The absence of symmetry could be due to the presence of a different ligand set for each metal atom, the presence of a non-symmetrical bridge or different elements with different redox states. In this case, a delocalized Class III system would not be symmetrical, and some of the previous experimental criteria can not be applied as they rely on the symmetry of the delocalized system.

Cyanido-bridged dinuclear dimers are one of the most intensively studied families of mixed-valence complexes.^[8] The exploration of the properties of these dimers, which are non-symmetrical due to the intrinsic asymmetric nature of the bridge, points to a strong coupling, measured through

Hush's H_{ab} parameter. However, all the reported systems up to date belong to Class II, probably due to the very different energies of the frontier orbitals of the metal atoms caused by the non-symmetric bridge.

Herein, we report the properties of a trinuclear cyanido-bridged complex, *trans*-[(dmap)₄Ru^{II}{(μ-NC)Os^{III}(CN)₅}₂]⁴⁻ [**1**⁴⁻; dmap = 4-(dimethylamino)pyridine], whose structural, electronic and vibrational spectroscopic data present unambiguous evidence of partial redox states for the three metal ions, an unprecedented feature for cyanido-bridged systems. Additionally, the one-electron oxidized Ru^{III} species, *trans*-[(dmap)₄Ru^{III}{(μ-NC)Os^{III}(CN)₅}₂]³⁻ (**1**³⁻), has also been isolated as well as the related complexes *trans*-[(dmap)₄Ru^{II}{(μ-NC)Fe^{III}(CN)₅}₂]⁴⁻ (**2**⁴⁻), and *trans*-[(dmap)₄Ru^{III}{(μ-NC)Co^{III}(CN)₅}₂]³⁻ (**3**³⁻), which help in the interpretation of the novel properties of the Os system (see Supporting Information).

The reaction between [Ru^{II}(dmap)₆]Cl₂^[9] and an excess of tetraphenylphosphonium (tpp⁺) hexacyanoosmate(III) in refluxing ethanol results in a brown-grey solid, which, according to single-crystal X-ray diffraction data and elemental analysis, is formulated as the tpp⁺ salt of **1**⁴⁻. The crystal structure of **1**⁴⁻ (Figure 1) displays a linear and totally eclipsed configuration of the three coordination spheres, where the three metal centres are connected by two cyanido bridges as observed in other related trinuclear complexes previously reported.^[10]

Remarkably, the Ru–N(dmap) mean bond length (2.089 Å) is between the value observed for this Ru–N bond length in the Ru^{II} cyanide trinuclear complex *trans*-[(dmap)₄Ru^{II}{(μ-NC)Fe^{III}(CN)₅}₂]⁴⁻ (**2**⁴⁻; 2.104 Å; see also the compounds reported in ref.^[10]) and the value observed for the Ru–N bond length in the Ru^{III}-containing trinuclear compound [(dmap)₄Ru^{III}{NCCo^{III}(CN)₅}₂]³⁻ (**3**³⁻; 2.077 Å; see Supporting Information, Figure S1). Additionally, the C–N_{bridge} bond is slightly longer [1.170(9) Å in **1**⁴⁻ vs. 1.15(1) Å in **2**⁴⁻], whereas the Os–C_{bridge} distance is shorter than that observed in the terminal cyanido ligands [1.992(9)

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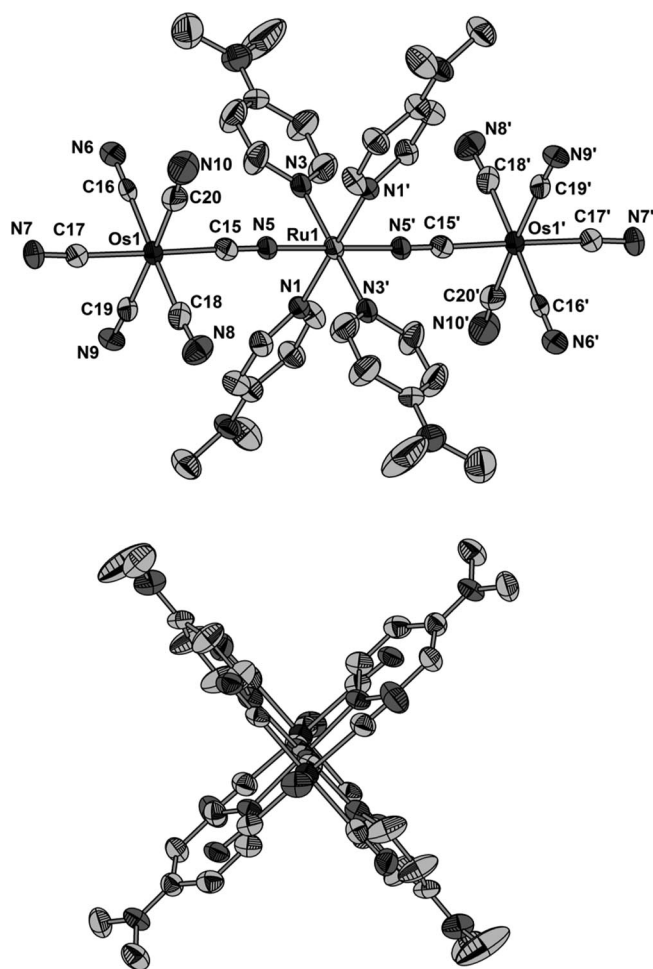


Figure 1. Top: ORTEP representation of complex 1^{4+} (30% ellipsoid probability). Bottom: Perspective view along the intermetallic axis.

vs. 2.043 Å for the mean *cis* Os–C bond length]. The Ru–N_{nitrile} bond is also shorter than the distance observed for the same bond in the related trinuclear compounds [1.959(7) vs. 2.016(6) in 2^{4+} and 2.019(3) in 3^{3+}]. This comparative metric data strongly support the existence of an enhanced π bonding in this complex between two $d\pi$ orbitals of the three metal ions and the π^* orbitals of the cyanido bridges. This results in shorter and stronger Ru–N_{nitrile} and Os–C_{bridge} bonds and a weaker C–N_{bridge} bond, which is confirmed by the presence of an additional wide and very strong cyanide stretch (not observed in complex 2^{4+}), at noticeably lower energies for a C–N vibration mode (1961 cm^{-1}), in the IR spectrum of solid [1][PPh₄]₄ (see Supporting Information, Figure S2). This enhanced interaction effectively delocalizes the charge of the formally Ru^{II} over the Os^{III} moieties resulting in a partial III/II character for the three ions.

The electrochemistry of 1^{4+} in different solvents shows three well-resolved reversible waves (see Supporting Information, Figure S3). The $E_{1/2}$ values of two of them show the characteristic solvent dependence previously observed for other cyanido complexes,^[11] and we assign them as the

redox processes centered at the OsCN₆ moieties. It is generally accepted that this solvent effect is based on the specific donor–acceptor interaction between the exposed cyanido ligands with the solvent molecules, that makes the cyanide ion a better π acceptor towards the metal ion. This results in a stabilization of the Os^{II} state, and a linear correlation of the $E_{1/2}$ value with the Gutman acceptor number of the solvent is observed (see Supporting Information, Figure S4).

The third redox process corresponds to the Ru fragment, and its $E_{1/2}$ value is much less sensitive to the solvent identity. Due to this different behavior, the choice of solvent tunes the difference between the $E_{1/2}$ values of the Ru and Os fragments, being more than 800 mV in dimethylacetamide (dma), but less than 300 mV in methanol. The proximity on the redox potentials of the Ru and Os centers has a strong impact on the interaction between the terminal Os fragments. In dma, the separation between the $E_{1/2}$ values of the Os centers is ca. 200 mV, but in methanol it is 580 mV. The latter value is significant and points to a stronger interaction between the three metal atoms in this solvent.

More pieces of evidence of this phenomenon arise from the electronic spectroscopy data (Figure 2 and Table 1). In the absence of strong interaction between the metal atoms, this trinuclear compound should behave spectroscopically like the superposition of two low-spin $d\pi^6(\text{Ru}^{\text{II}})\text{--}d\pi^5(\text{Os}^{\text{III}})$ donor–acceptor systems. To a first approximation, only one metal-to-metal charge transfer (MM'CT) transition is expected, but the spin-orbit coupling (SOC) and the crystal field can split both the ground state, $d\pi^6(\text{Ru}^{\text{II}})\text{--}d\pi^5(\text{Os}^{\text{III}})$, and the excited state, $d\pi^5(\text{Ru}^{\text{III}})\text{--}d\pi^6(\text{Os}^{\text{II}})$, in three levels, resulting in three MM'CT and two intra-configurational (IC) $d\pi \rightarrow d\pi$ transitions. However, resolution of these bands depends on the magnitude of the SOC. Usually, the IC bands are observed for Os^{III} systems ($\xi \approx 3000 \text{ cm}^{-1}$), but not for Ru^{III} ($\xi \approx 800 \text{ cm}^{-1}$) ones. Whereas three MM'CT bands are observed for Os^{II}–M^{III} systems, the resolution of the latter in an Ru^{II}→M^{III} system requires a particularly narrow bandwidth affording normally a unique band.^[13]

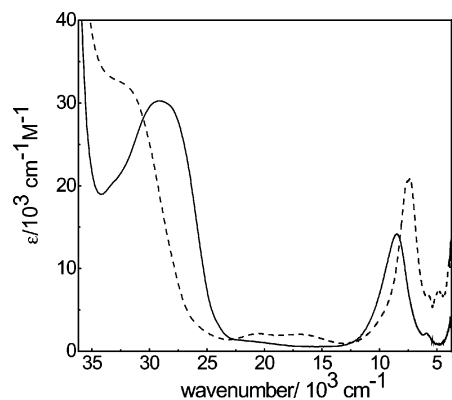


Figure 2. Electronic spectra of 1^{4+} in [D₃]acetonitrile (–) and [D₄]–methanol (---).

Table 1. Electronic spectroscopic data of $\mathbf{1}^{4-}$ and $\mathbf{1}^{3-}$.

	MLCT [cm^{-1}]	LMCT [cm^{-1}]	MM'CT + IC [cm^{-1}]
$\mathbf{1}^{4-}$	acetonitrile	29100 (30200)	–
	methanol	32500 (32500)	8500 (14200) 5900 (2170) 7600 (20500) 7300 (20800) 5600 (6700) 4900 (7300) 3700 (14000)
$\mathbf{1}^{3-}$	acetonitrile	23700 (10500)	14500 (17200)
	methanol	27600 (11000)	14600 (18300)

The spectrum of $\mathbf{1}^{4-}$ in acetonitrile closely resembles that observed for the Fe^{III} analogue,^[10] with a metal-to-ligand charge transfer (MLCT) transition, $\text{Ru}^{\text{II}} \rightarrow \pi^*(\text{dmap})$, at 29100 cm^{-1} ($\epsilon = 30200 \text{ M}^{-1} \text{ cm}^{-1}$) and an MM'CT transition at 8500 cm^{-1} ($\epsilon = 14200 \text{ M}^{-1} \text{ cm}^{-1}$) (Figure 2). The main difference relies on the intensity of the MM'CT band, which suggests a stronger interaction between the metal ions through the cyanido bridge as expected for the replacement of a first-row transition metal ion for a third-row one. The energy of this band in other solvents correlates with the difference between the redox potential of the Os and Ru moieties (see Supporting Information, Figure S5) confirming its MM'CT character. At lower energies, a less intense and rather narrow band at 5800 cm^{-1} ($\epsilon = 1800 \text{ M}^{-1} \text{ cm}^{-1}$) is clearly visible. This band is also present in other solvents, like dimethylacetamide, and in the spectra of $\mathbf{1}^{3-}$ at exactly the same energy, and we assign it as an IC transition (see Supporting Information, Figure S6). The increased intensity compared to the IC bands observed for $[\text{Os}(\text{CN})_6]^{3-}$ ^[14] is caused by some mixing with an MM'CT state promoted through the bridge, as previously observed.^[15] The other expected IC transition is probably less intense and is buried in the tail of the MM'CT band. The observed pattern of the spectrum of $\mathbf{1}^{4-}$ in these solvents indicates that it behaves as a localized mixed-valence compound with markers for Ru^{II} (the MLCT band) and for Os^{III} (the IC band). This is probably related to the very different frontier orbital energies of the fragments in this solvent, as measured by their redox potentials.

A completely different picture is found in methanol (Figure 2). In the visible region, the MLCT band is considerably shifted to higher energies (32500 cm^{-1}), and new bands appear at 20500 cm^{-1} ($\epsilon = 2100 \text{ M}^{-1} \text{ cm}^{-1}$) and 16900 cm^{-1} ($\epsilon = 2050 \text{ M}^{-1} \text{ cm}^{-1}$). These bands resemble the ones observed for $\mathbf{1}^{3-}$ (see Supporting Information, Figure S7) and for other Ru^{III} compounds containing the dmap ligand,^[9] which have been assigned as ligand-to-metal charge transfer (LMCT) transitions $\pi(\text{dmap}) \rightarrow \text{Ru}^{\text{III}}$. In the NIR region, several transitions are apparent, a sharp and strong band at 7300 cm^{-1} ($20800 \text{ M}^{-1} \text{ cm}^{-1}$) and a set of strong bands at low energy at 5600 , 4900 and 3700 cm^{-1} . The presence of multiple bands in the NIR indicates a split of the excited state. This split could be due to the SOC action on the $\text{Os}^{\text{II}}\text{--}\text{Ru}^{\text{III}}\text{--}\text{Os}^{\text{III}}/\text{Os}^{\text{III}}\text{--}\text{Ru}^{\text{III}}\text{--}\text{Os}^{\text{II}}$ excited state, which would result in several close-spaced MM'CT transitions.

The patterns of these spectra may seem contradictory. The presence of an $\text{Ru}^{\text{II}} \rightarrow \pi^*(\text{dmap})$ MLCT suggests an $\text{Os}^{\text{III}}\text{--}\text{Ru}^{\text{II}}\text{--}\text{Os}^{\text{III}}$ configuration for the ground state. On the other hand, the observation of an LMCT band, involving the ruthenium and the dmap ligand, and the split of the MM'CT transition, point to a ground state with $\text{Ru}^{\text{III}}\text{--}\text{Os}^{\text{II}}$ character. All these pieces of evidence suggest that the nature of the ground state of $\mathbf{1}^{4-}$ in methanol is better described as a combination of the three possible configurations $\text{Os}^{\text{III}}\text{--}\text{Ru}^{\text{II}}\text{--}\text{Os}^{\text{III}}$, $\text{Os}^{\text{II}}\text{--}\text{Ru}^{\text{III}}\text{--}\text{Os}^{\text{III}}$ and $\text{Os}^{\text{III}}\text{--}\text{Ru}^{\text{III}}\text{--}\text{Os}^{\text{II}}$, with fractional redox states between II and III for the Ru and Os metal centers, similar to what is observed in the crystal structure. This composition is the result of the enhanced mixing between osmium and ruthenium sites, promoted by the cyanido bridge due to a better match between the energies of the frontier orbitals of both metal fragments in this solvent. It is interesting to note that the bands assigned as LMCT have a lower intensity than the ones observed in other Ru^{III} complexes, which is in line with the partial Ru^{III} character proposed for the ground state.

Recent calculations have shown that π bonding in bridging cyanido ligands is not the dominant feature,^[16] but the results presented here indicate otherwise for this system. Given the actual interest in developing extended structures based in cyanido-bridged building blocks, these results should encourage chemists in taking advantage of these properties.

Experimental Section

$[(\text{CN})_5\text{Os}^{\text{III}}(\mu\text{-CN})\text{Ru}^{\text{II}}(\text{dmap})_4(\mu\text{-NC})\text{Os}^{\text{III}}(\text{CN})_5](\text{PPh}_4)_4 \cdot 10\text{H}_2\text{O}$ [$\mathbf{1} \cdot (\text{PPh}_4)_4 \cdot 10\text{H}_2\text{O}$]: $[\text{Ru}^{\text{II}}(\text{dmap})_6]\text{Cl}_2 \cdot 9\text{H}_2\text{O}$ (100 mg, 0.094 mmol) was dissolved in ethanol (5 mL). The resulting yellow solution was added to a solution (2.5 mL) of $[\text{Os}^{\text{III}}(\text{CN})_6](\text{tpp})_3 \cdot 2\text{H}_2\text{O}$ (525 mg, 0.37 mmol) in ethanol. The mixture was heated under reflux with stirring for 1 h. The grey-brown solid obtained was collected by filtration, washed with ethanol and vacuum-dried. Yield: 149 mg (55%). $\text{C}_{136}\text{H}_{120}\text{N}_{20}\text{Os}_2\text{P}_4\text{Ru} \cdot 10\text{H}_2\text{O}$ (2817); calcd. C 57.9, H 5.0, N 9.9; found C 57.6, H 4.9, N 10.2.

$[(\text{CN})_5\text{Os}^{\text{III}}(\mu\text{-CN})\text{Ru}^{\text{III}}(\text{dmap})_4(\mu\text{-NC})\text{Os}^{\text{III}}(\text{CN})_5](\text{PPh}_4)_3 \cdot 10\text{H}_2\text{O}$ [$\mathbf{1} \cdot (\text{PPh}_4)_3 \cdot 10\text{H}_2\text{O}$]: $[(\text{CN})_5\text{Os}^{\text{III}}(\mu\text{-CN})\text{Ru}^{\text{II}}(\text{dmap})_4(\mu\text{-NC})\text{Os}^{\text{III}}(\text{CN})_5](\text{PPh}_4)_4 \cdot 10\text{H}_2\text{O}$ [$\mathbf{1} \cdot (\text{PPh}_4)_4 \cdot 10\text{H}_2\text{O}$] (100 mg, 0.04 mmol) was dissolved in methanol (50 mL). $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ (25 mg, 0.05 mmol) was added, which afforded a blue solution. Water (10 mL) was added, and the resulting solution was concentrated under reduced pressure, until only a few mL of water remained. The blue solid obtained was filtered off, washed with cold water and vacuum-dried. Yield: 50 mg (50%). $\text{C}_{112}\text{H}_{100}\text{N}_{20}\text{Os}_2\text{P}_3\text{Ru} \cdot 10\text{H}_2\text{O}$ (2481); calcd. C 54.2, H 4.8, N 11.3; found C 53.2, H 4.6, N 11.6.

Synthesis of Auxiliary Complexes

$[(\text{DMAP})_4\text{Ru}^{\text{II}}\{\mu\text{-NC}\text{M}^{\text{III}}(\text{CN})_5\}_2](\text{PPh}_4)_4 \cdot 7\text{H}_2\text{O}$ (M = Fe, Co): In a typical preparation, $[\text{Ru}(\text{DMAP})_6]\text{Cl}_2 \cdot 9\text{H}_2\text{O}$ (0.2 mmol) was dissolved in absolute ethanol (10 mL). To this solution, $(\text{PPh}_4)_3\text{[M}(\text{CN})_6]$ (1.6 mmol), dissolved in absolute ethanol (5 mL), was added. A yellow solid immediately appeared. This suspension was refluxed, while protected from sunlight, with vigorous stirring. After 10 min, the suspended solid was completely dissolved, and, after additional 30 min, a new yellow precipitate had developed. This

latter suspension was further heated for 15 min and then left to cool to room temp. The product was filtered, washed with cold absolute ethanol (3×10 mL) and vacuum-dried. M = Fe (**2**): Yield: 80%. $C_{136}H_{120}N_{20}P_4Fe_2Ru \cdot 7H_2O$: calcd. C 65.4, H 5.4, N 11.2; found C 65.6, H 5.1, N 10.9. M = Co: Yield: 52%. $C_{136}H_{120}N_{20}P_4Co_2Ru \cdot 7H_2O$: calcd. C 65.3, H 5.4, N 11.2; found C 65.2, H 4.8, N 11.3.

[(DMAP)₄Ru^{III}{(μ-NC)Co^{III}(CN)₅}]₂(PPh₄)₃·5H₂O: To [(DMAP)₄Ru^{III}{(μ-NC)Co^{III}(CN)₅}]₂(PPh₄)₄·7H₂O (0.04 mmol), dissolved in methanol (50 mL), solid (NH₄)₂Ce^{IV}(NO₃)₆ (0.045 mmol) was added. The solution turned immediately deep blue. Water (10 mL) was added, and the resulting solution was concentrated under reduced pressure until only a few mL remained. The blue solid obtained was filtered off, washed with cold water and vacuum-dried. To remove some insoluble cerium salts, the solid was dissolved in methanol and filtered. To this clear solution some water was added, and the final solution was slowly concentrated at room temp. Blue crystals of the desired product appeared after a few days. They were filtered, washed with water and vacuum-dried. Yield: 91%. $C_{112}H_{100}N_{20}P_3Co_2Ru \cdot 5H_2O$ (**3**): calcd. C 63.2, H 5.2, N 13.2; found C 63.3, H 5.0, N 12.4.

CCDC-622554 (for **2**), -754739 (for **1**), and -754740 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Materials; physical measurements; tables of crystal data and structure refinement (Table S1), selected bond lengths and angles (Table S2) of **1** and **3**; ellipsoid representation of the molecular structure of complex **3**³⁻ (Figure S1); infrared spectra of complex **1** and **2** (Figure S2); cyclic voltammetry of complexes **1** and **2** (Figure S3); correlation of $E_{1/2}$ with the Gutman acceptor number of the solvent for complex **1** (Figure S4); correlation of the wave-number of the MM'CT band with the difference between the redox potential of the Os and Ru moieties (Figure S5); electronic spectrum of complex **1**⁴⁺ in DMA (Figure S6), of complex **1**³⁻ in different organic solvents (Figure S7), of complexes **3**³⁻ and **2**⁴⁺ in methanol (Figure S8).

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