

## Class III Delocalization

## Class III Delocalization in a Cyanide-Bridged Trimetallic Mixed-Valence Complex\*\*

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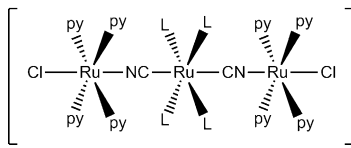
**Abstract:** The NIR and IR spectroscopic properties of the cyanide-bridged complex,  $trans-[Ru(dmap)_4(\mu-CN)Ru(py)_4Cl]_2^{3+}$  ( $py = \text{pyridine}$ ,  $dmap = 4\text{-dimethylaminopyridine}$ ) provide strong evidence that this trimetallic ion behaves as a Class III mixed-valence species, the first example reported of a cyanide-bridged system. This has been accomplished by tuning the energy of the fragments in the trimetallic complex to compensate for the intrinsic asymmetry of the cyanide bridge. Moreover, (TD)DFT calculations accurately predict the spectra of the  $trans-[Ru(dmap)_4(\mu-CN)Ru(py)_4Cl]_2^{3+}$  ion and confirms its delocalized nature.

Mixed-valence chemistry has been the focus of attention of inorganic chemists for more than 40 years, since the first example of a deliberate synthesis of a discrete binuclear system was reported by Creutz and Taube.<sup>[1]</sup> An early survey of the reported mixed-valence systems gave to rise to the Robin–Day classification, which consisted of three distinctive categories:<sup>[2]</sup> Class I, not interacting; Class II, interacting, but localized; and Class III, delocalized. A strong effort in the characterization of the inter-valence charge transfer (IVCT) of Class II systems was fueled by the two-state model proposed by Hush<sup>[3,4]</sup> and Sutin,<sup>[5,6]</sup> which provided an easy route to obtain valuable information about the parameters governing the electron transfer process. Later, the focus shifted to the exploration of systems close to delocalization, somewhere in the transition between Class II and Class III. Hence, a new Class, II/III, was proposed,<sup>[7]</sup> which comprises systems still localized, but solvent-averaged. The potential energy surface describing these systems possesses two minima of similar energy separated by a small barrier, so that both mixed-valence isomers coexist and interconvert into each other. This behavior has been demonstrated experimentally,<sup>[8,9]</sup> and the rate constant for electron transfer between the isomers has been measured.<sup>[10]</sup> In many of these nearly delocalized mixed-valence systems, the bridge plays an important role in the spectroscopy,<sup>[11–13]</sup> which requires a three-state model for an accurate interpretation.<sup>[14,15]</sup>

Another focus has been the characterization of higher nuclearity systems,<sup>[16]</sup> which also present challenging spectroscopy.<sup>[17–19]</sup>

We have recently reported<sup>[18]</sup> the spectroscopy of two trimetallic cyanide-bridged mixed-valence complexes of formula  $trans-[Ru(L)_4(\mu-CN)Ru(py)_4Cl]_2^{3+}$  ( $\mathbf{1}^{3+}$ , where  $L = \text{pyridine}$  and  $\mathbf{2}^{3+}$ , where  $L = 4\text{-methoxypyridine}$ ; Table 1). These systems exhibit two transitions in the near infrared

**Table 1:** Structures of the ruthenium complexes discussed in this work.



Salt	L
[1](PF <sub>6</sub> ) <sub>2</sub>	pyridine
[2](PF <sub>6</sub> ) <sub>2</sub>	4-methoxypyridine
[3](PF <sub>6</sub> ) <sub>2</sub>	4-dimethylaminopyridine

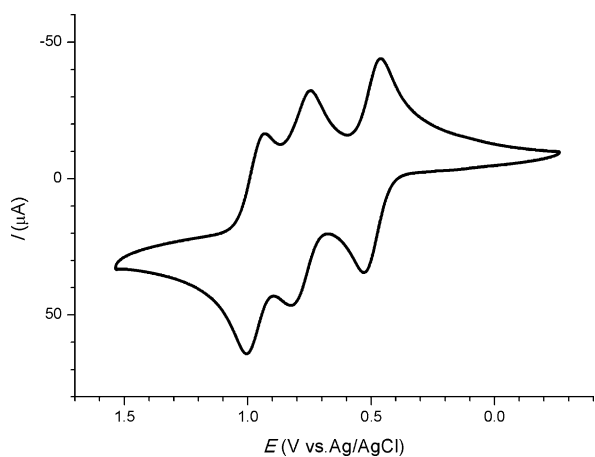
(NIR) that correspond to a charge transfer from the central ruthenium(II) unit to the neighboring terminal  $\{-Ru^{III}(py)_4Cl\}$  fragment (MMCT), and a charge transfer between the distant  $\{-Ru(py)_4Cl\}$  fragments (MMCT). The latter is the most intense, which suggests a strong interaction between the three metallic ions. These species demonstrate that diminishing the energy of the state located at the central  $Ru^{II}$  (the “bridge”) results in an increased intensity in both bands, as predicted by the three-state model.<sup>[15]</sup> Following this idea, one can conclude that, if the energy gap between the bridge and the other two states is small enough, and the coupling element between the vicinal states ( $H_{ab}$ ) is sufficiently large, a transition to Class III should be observed. In order to explore this scenario, we have prepared the trimetallic complex  $trans-[Ru^{II}(dmap)_4(\mu-CN)Ru^{II}(py)_4Cl]_2(PF_6)_2$  ( $\mathbf{3}(PF_6)_2$ ) where we have employed the extremely basic ligand 4-dimethylaminopyridine ( $dmap$ ), which considerably lowers the  $d\pi$  states energy centered on the ruthenium of the bridge.<sup>[20,21]</sup>

The complex  $\mathbf{3}(PF_6)_2$  (Table 1) was prepared following the reported methods for the other trimetallic complexes,<sup>[18]</sup> but using  $trans-[Ru^{II}(dmap)_4(CN)_2]$  as the starting material; its identity was established by NMR spectroscopy (for experimental details, see the Supporting Information). Electrochemical exploration of this complex in acetonitrile reveals three reversible one-electron oxidations (Figure 1). The assignment of the first oxidation process at 0.41 V is not straightforward. Based on Lever parameters,<sup>[20,22]</sup> the redox potentials for the oxidation of the terminal and central

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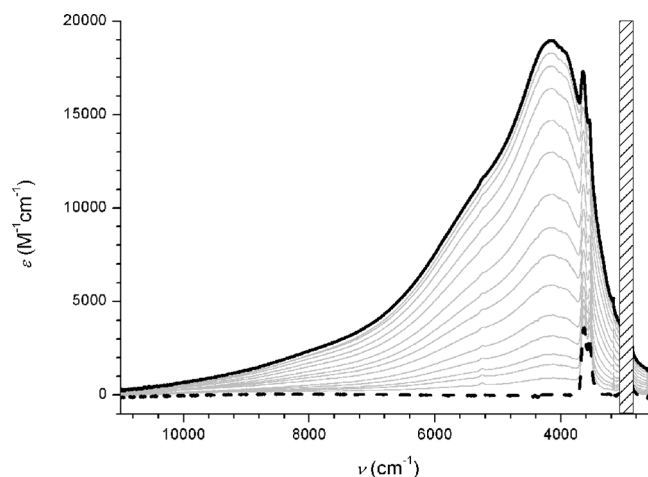


**Figure 1.** Cyclic voltammogram of  $[3](PF_6)_2$  in MeCN/0.1 M [TBA]PF<sub>6</sub> at a 200 mV s<sup>-1</sup> scan rate.

ruthenium moieties are expected to be around the same value. In the related trimetallic complexes  $1^{2+}$  and  $2^{2+}$  the first oxidation at 0.60 V is certainly centered at one terminal  $\{-Ru^{II}(py)_4Cl\}$  fragment,<sup>[18]</sup> whereas the oxidation of the central unit appears at a much higher potential. However, the redox potential for the oxidation of *trans*-[Ru<sup>II</sup>(dmap)<sub>4</sub>(CN)<sub>2</sub>] is 0.40 V lower than the one observed in *trans*-[Ru<sup>II</sup>(MeOpy)<sub>4</sub>(CN)<sub>2</sub>]<sup>[18]</sup> (Supporting Information, Table S1 and Figure S2), making the oxidation of the central moiety more favorable than in  $1^{2+}$  or  $2^{2+}$ . We propose that, in this case, this one-electron oxidation leads to a delocalized  $3^{3+}$  mixed-valence complex and hence cannot be assigned to the oxidation of a unique ruthenium center. The large separation of 0.28 V between the first two oxidations (at 0.41 V and 0.69 V), accounts for the high stability of  $3^{3+}$  towards disproportionation.

To confirm the nature of  $3^{3+}$ , we spectroelectrochemically recorded its electronic and vibrational spectra, employing an OTTLE cell.<sup>[23]</sup> The NIR spectrum of  $3^{3+}$  does not present the two-band pattern observed in the NIR of the trimetallic cations  $1^{3+}$  and  $2^{3+}$ .<sup>[18]</sup> Instead, it is dominated by a very strong and asymmetric band at 4150 cm<sup>-1</sup> ( $\epsilon_{\max} = 19500 \text{ M}^{-1} \text{ cm}^{-1}$ ; Figure 2). This narrow and intense absorption with a cutoff at lower energies resembles that of other Class III systems.<sup>[7,15,24–28]</sup> Moreover, this band is solvent insensitive, showing not only the same energy, but also the same shape in different solvents (Figure S3). This is also the expected behavior for a Class III compound,<sup>[7,15,24]</sup> as in a delocalized system the NIR band is no longer a charge transfer transition, but rather a charge resonance between delocalized states with similar electronic distributions. This behavior contrasts with that observed for  $1^{3+}$ , where the energy and the intensity of both transitions are solvent dependent (Figure S3).

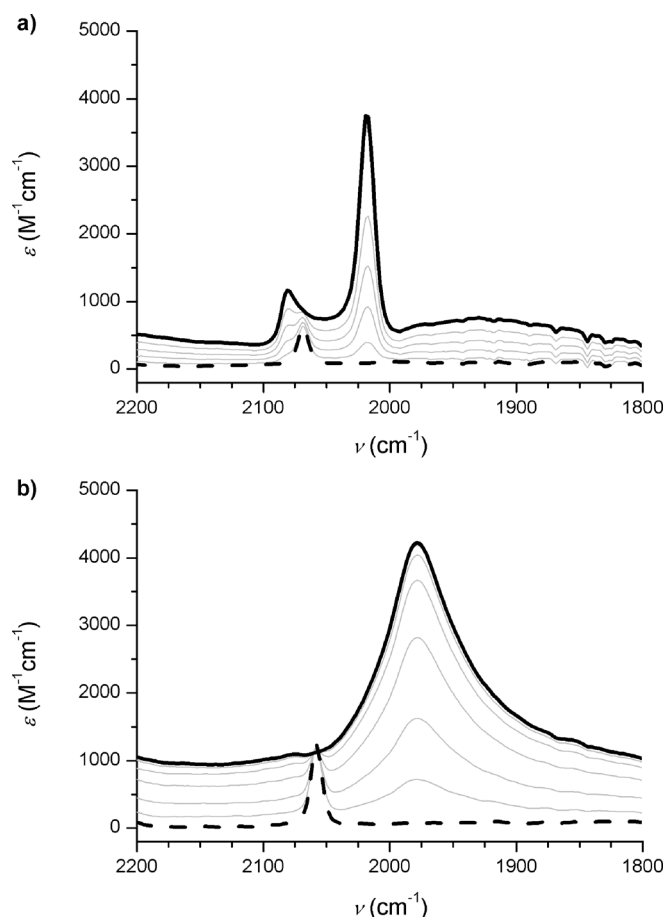
Localization/delocalization on the timescale of intramolecular vibrational motions can be probed by the presence/absence of IR activity in symmetric vibrations of the bridging ligands.<sup>[7]</sup> For the localized trimetallic complexes  $1^{3+}$  and  $2^{3+}$ , two cyanide stretching vibrations are observed, owing to the nonsymmetrical nature of the ground state configuration [Ru<sup>II</sup>-Ru<sup>II</sup>-Ru<sup>III</sup>].<sup>[18]</sup> The IR spectrum of  $3^{3+}$  shows a single



**Figure 2.** NIR spectroelectrochemistry (SEC) for the oxidation of  $3^{2+}$  (---) to  $3^{3+}$  (—) in MeCN/0.1 M [TBA]PF<sub>6</sub>.

cyanide stretching vibration instead, as expected for a completely delocalized Class III symmetrical ground state, where the symmetrical cyanide stretch mode is forbidden. Even when this behavior would also be compatible with a symmetrical Ru<sup>II</sup>-Ru<sup>III</sup>-Ru<sup>II</sup> configuration, we discard this possibility because the cyanide stretching vibration at 1980 cm<sup>-1</sup> is incompatible with a Ru<sup>III</sup> center. This band is more intense, wider, and strongly shifted to lower energies than in  $1^{3+}$  (Figure 3). Other cyanide-bridged mixed-valence systems with strong coupling display signals with similar characteristics,<sup>[18,29–34]</sup> although in the present case the cyanide stretching is particularly strong and wide (full width at half maximum (FWHM) = 65 cm<sup>-1</sup>). The shift to lower energies of the cyanide stretching, together with a more intense and wider band have been attributed to the presence of vibronic coupling between the IVCT and the asymmetric cyanide stretching mode.<sup>[31]</sup> A similar entanglement between the vibrational modes of the bridge and a IVCT has been observed for pyrazine bridged systems.<sup>[35,36]</sup>

To gain a better understanding of the electronic structure of  $3^{3+}$ , we performed a standard density functional calculation of this redox state. DFT calculations have shown a strong tendency to afford a delocalized ground state,<sup>[37–39]</sup> and hence they perform poorly when predicting the experimental spectroscopic properties of localized systems.<sup>[17]</sup> In spite of this limitation, the calculation yields the expected spectra of the delocalized configuration, which becomes a useful reference. For example, the calculations of the electronic structures of  $1^{3+}$  and  $2^{3+}$  yield a delocalized ground state. Instead of the two-band NIR pattern observed in these localized trimetallic complexes, the computations predict a single NIR band shifted to the red (Figure S4). In the case of  $3^{3+}$ , the (TD)DFT predicted spectrum is surprisingly accurate (Figure 4). The calculations result in a delocalized ground state with 34 % of the spin density on the terminal ruthenium atoms and 27 % on the central one (Figure 4). DFT results also afford a single IR active cyanide stretching vibration at 2005 cm<sup>-1</sup>, which corresponds to the asymmetric mode. This

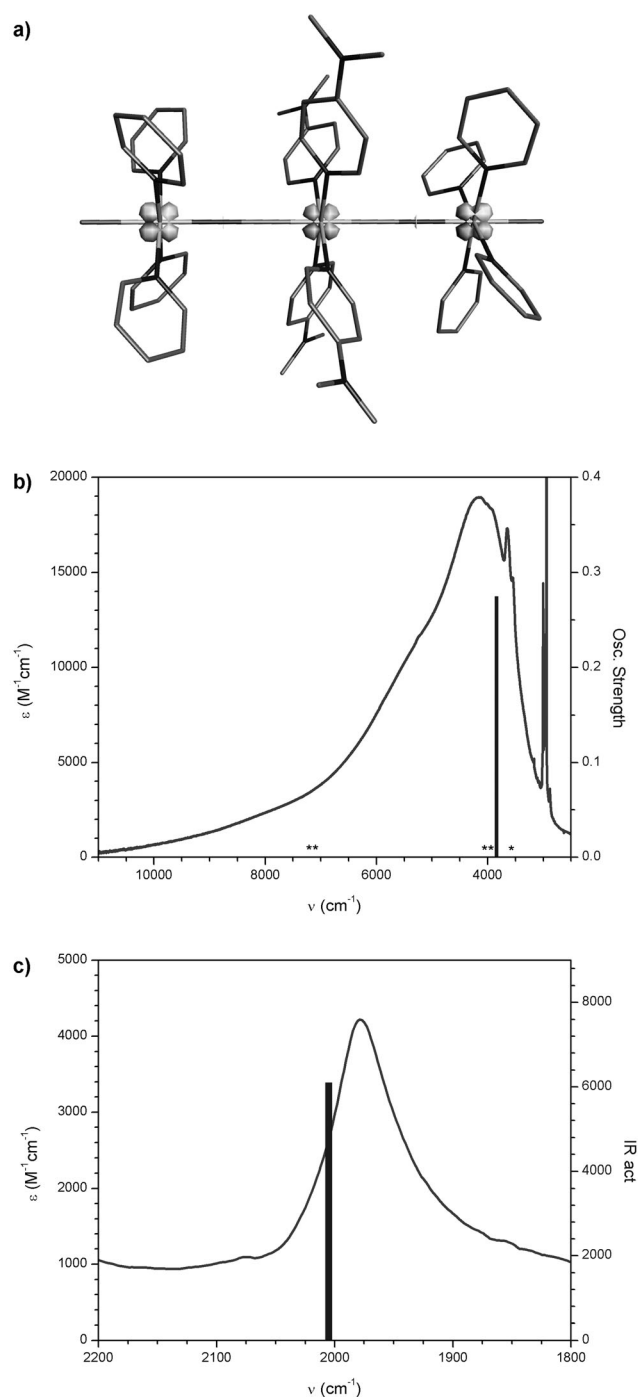


**Figure 3.** IR SEC for the oxidation of  $1^{2+}$  to  $1^{3+}$  (a), and  $3^{2+}$  to  $3^{3+}$  (b) in MeCN/0.1 M [TBA]PF<sub>6</sub>. Reduced form (-----), one-electron oxidized form (—).

vibration is lower in energy than what is usually observed and is in good agreement with experimental observations.

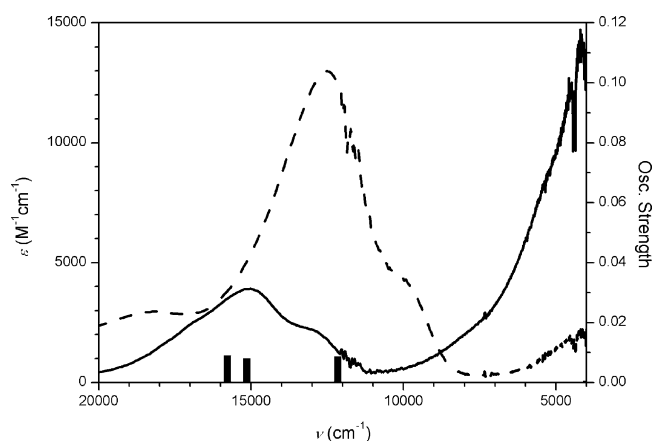
(TD)DFT also helps in the interpretation of the electronic spectrum. Two transitions are predicted in the visible region that are in agreement with the two bands observed experimentally (Figure 5). These bands correspond to transitions from orbitals centered on the electron-rich dmap ligands to acceptor orbitals delocalized over the metallic system, and are closely related to the dmap  $\rightarrow$  Ru<sup>III</sup> LMCT bands observed in *trans*-[Ru<sup>III</sup>(dmap)<sub>4</sub>(CN)<sub>2</sub>]<sup>+</sup> (Figure S6) and other Ru<sup>III</sup> complexes containing the dmap ligand,<sup>[20]</sup> including the fully oxidized trimetallic complex,  $3^{3+}$ , with a Ru<sup>III</sup>-Ru<sup>III</sup>-Ru<sup>III</sup> configuration (Figure 5). The main difference with the latter is that the band observed in the electronic spectrum of  $3^{3+}$  is shifted to the blue, and has approximately one third of its intensity. Both observations are compatible with an acceptor orbital that is delocalized over the trimetallic system instead of being concentrated on one Ru<sup>III</sup> unit. A similar band has been reported for a related trimetallic system, *trans*-[Ru(dmap)<sub>4</sub>{(μ-NC)Os(CN)<sub>5</sub>}<sub>2</sub>]<sup>4+</sup>, the crystal structure of which also suggests a delocalized ground state.<sup>[21]</sup>

(TD)DFT also provides an interpretation for the shoulder observed at ca. 7500  $\text{cm}^{-1}$ . A symmetry forbidden transition that involves a resonance between symmetric orbitals is



**Figure 4.** a) Computed spin density (0.02 a.u.). b,c) Comparison of the NIR (b) and IR (c) SEC of  $3^{3+}$  in MeCN/0.1 M [TBA]PF<sub>6</sub> and the energy of the transitions predicted by the DFT calculations. The \* denotes the energy of predicted transitions with an oscillator strength near or equal to zero.

predicted at 7153  $\text{cm}^{-1}$ . From an orbital point of view, it corresponds to the Ru(bridge)-to-Ru(terminal) transition observed in the localized trimers  $1^{3+}$  and  $2^{3+}$ . This transition is predicted to vanish for a Class III system in a three state model,<sup>[15]</sup> but even in the Class III regime some systems display related metal-to-bridge transitions.<sup>[11,13]</sup> In our example, the vibronic coupling with the asymmetric cyanide



**Figure 5.** The Vis/NIR SEC for  $3^{3+}$  (—) and  $3^{5+}$  (----) in MeCN/0.1 M [TBA]PF<sub>6</sub> plotted together with the calculated oscillator strength of each transition for  $3^{3+}$  (bars).

stretching vibration might provide a mechanism for an increase in intensity.

In summary, in this report we have shown strong evidence that  $3^{3+}$  behaves as a Class III mixed-valence species, the first example comprising a cyanide-bridged system. This has been accomplished by tuning the energy of the fragments in the trimetallic complex to compensate for the intrinsic asymmetry of the cyanide bridge. Given the well-established strategies to build supramolecular extended systems based on cyanide-bridged compounds, one can envision a rational way to tune the energy of the selected fragments that may lead to extended delocalized systems. The properties of these new materials could be of great utility in the design of molecular devices where fast electron transfer over long distances is required.

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