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MIXED-VALENCE PROPERTIES OF RUTHENIUM–POLYPYRIDINE DIMERS BRIDGED BY IMIDAZOLATE AND TRIAZOLATE LIGANDS

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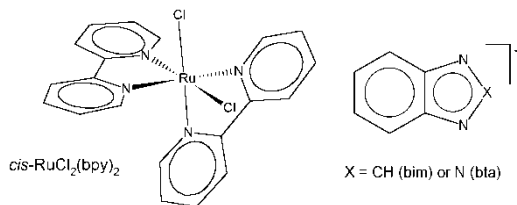
The dinuclear complex *cis,cis*-[(bpy)₂ClRu(μ -bim)RuCl(bpy)₂]ⁿ⁺ (bpy = 2,2'-bipyridine; bim = benzimidazole; *n* = 1, 2, or 3) was synthesized, isolated as a hexafluorophosphate salt, and investigated in organic solutions by cyclic voltammetry and UV/visible/NIR spectroelectrochemistry. The mixed-valent species (*n* = 2) displays significant metal–metal electronic coupling in the ground state but exhibits localized Ru(III) and Ru(II) oxidation states, as deduced from its intervalence charge transfer (IVCT) band and redox parameters. On the basis of the resonance energy (H_{AB}) estimated in the context of Hush's semiclassical theory, the extent of intermetallic communication was found to be larger than that recently reported for the bta-bridged analog (bta = benzotriazole). Some differences between the IVCT features of these systems have been rationalized in terms of the degree of σ,π -basic character of the bridging ligands, according to an electron superexchange mechanism of the "hole-transfer" type. The stabilization of the mixed-valent complexes is attributed mainly to cooperative metal-to-ligand/ligand-to-metal charge-transfer effects. The combined π -acceptor and σ,π -donor abilities of the ancillary (bpy) and bridging (bim or bta) ligands, respectively, are also responsible for the high stability of the fully oxidized (Ru^{III}–L–Ru^{III}) and fully reduced (Ru^{II}–L–Ru^{II}) isovalent species.

Keywords: Imidazole; Triazole; Ruthenium–polypyridine; Mixed-valence; Electron transfer; Intervalence charge transfer

INTRODUCTION

The mixed-valence chemistry [1] of polynuclear transition metal complexes has been a subject of much investigation since the late 1960s [2,3]. Among the various interesting aspects of such systems is the possibility that optically-induced intervalence transfer (IT) or metal-to-metal charge transfer (MMCT) transitions can be exploited to assess rate constants and activation barriers for thermal intramolecular electron transfer (ET) between separated redox sites [4–6]. In addition, the extent of metal–metal electronic interactions between donor–acceptor complexes can be varied or modulated by a series of replacements or relatively simple chemical modifications either on the

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SCHEME 1.

intervening (bridging) ligand or on the nonbridging (ancillary) ligands surrounding the metal ions [7–11].

The most important role in mediating electronic communication in bridged mixed-valence systems is, naturally, played by the bridging ligand, whose chemical nature can determine the magnitude and mechanism of the donor–acceptor electronic coupling [7]; for instance, pyridine, pyrazine, and pyrimidine derivatives [12–14] are usually electron-poor ligands and mediate metal–metal interactions through low-lying unoccupied π^* orbitals (LUMOs) by invoking electron-transfer mechanisms. By contrast, electron-rich bridging ligands, such as imidazolate [15–17] and triazolate [18–20] derivatives mediate intermetallic interactions via hole-transfer mechanisms, taking advantage of relatively high-lying occupied π molecular orbitals (HOMOs). Dinuclear mixed-valence complexes of the latter type with ionizable ligands as bridges are of interest because their proton-coupled electron transfer [21] properties can be fine-tuned by control of pH [8]. Indeed, we have recently reported a rather interesting case of proton-induced electron-coupling switching and related phenomena based on a benzotriazolate-bridged system [22].

Some of our recent contributions involve benzotriazolate-bridged systems exhibiting stereochemical mobility [18,22–24]. In particular, we have observed [23] contrasting mixed-valence behavior in symmetrical ruthenium–edta binuclear complexes containing benzotriazolate and benzimidazolate (Scheme 1) bridging ligands in aqueous solutions. Because of the structural similarities of such ligands, the unexpected differences were tentatively interpreted in terms of a fluxional coordination model regarding the benzotriazolate species. In the present work we extended the study of these bridges to dimers of 2,2'-bipyridine ruthenium complexes, in which structural/fluxional effects on the bridging ligand are not observed owing to a sterically more hindered environment. The IT properties and redox behavior of the mixed-valent species in organic media were explored by electrochemical and spectroelectrochemical methods.

EXPERIMENTAL

Abbreviations

$\mathbf{1}^{n+} = cis-[RuCl(bpy)_2(bimH)]^{n+}$; $\mathbf{2}^{n+} = cis-[RuCl(bpy)_2(btaH)]^{n+}$; $\mathbf{11}^{n+} = cis,cis-[(bpy)_2ClRu(bim)RuCl(bpy)_2]^{n+}$; $\mathbf{22}^{n+} = cis,cis-[(bpy)_2ClRu(bta)RuCl(bpy)_2]^{n+}$; bimH = benzimidazole; bim = benzimidazolate; btaH = 1H-benzotriazole; bta = benzotriazolate; bpy = 2,2'-bipyridine; tea = tetraethylammonium.

Starting Materials

BimH was purchased from Aldrich and recrystallized by evaporation of saturated solutions in a 3 : 1 (v/v) ethanol : water mixture. Chemical and spectral characterizations of the neutral ligand and the corresponding lithium salt of its anionic form are available elsewhere [24,25]. *cis*-RuCl₂(bpy)₂ · 2H₂O was synthesized as described by Sullivan *et al.* [26]. (tea)ClO₄ was prepared according to a standard procedure [27], recrystallized twice from hot water, and vacuum dried at 100°C overnight. [Caution: Perchlorate salts are potentially explosive and must be treated as hazardous materials. Only small quantities should be prepared and handled with appropriate care.] All other chemicals and organic solvents employed in the syntheses were analytical reagent grade and used as supplied.

Syntheses

Synthesis of **11**⁺

The method was similar to that used recently for **22**⁺ [28]: *cis*-RuCl₂(bpy)₂ · 2H₂O (520 mg; 1.0 mmol) and bimH (53.1 mg; 0.45 mmol) were suspended in 30 cm³ of a 2 : 1 (v/v) ethanol : water mixture. After heating at reflux for 30 min, LiOH · H₂O (21.0 mg; 0.50 mmol) was added to the reaction mixture and the reflux, under Ar, continued for *ca.* 5 h. Following cooling to ambient temperature, the solution was filtered and vacuum dried in a rotary evaporator. The solid was dissolved in *ca.* 5 cm³ of water and added dropwise to about the same volume of a stirred concentrated (1 M) aqueous solution of NH₄PF₆, yielding a dark precipitate. The product was collected on a glass frit by suction filtration, washed with a few portions of cold water and dried in vacuum in the presence of a desiccant. Further purification was performed by column chromatography, using neutral alumina (activity I; 70–300 mesh; particle size: 60–200 μm) as the filling material and acetonitrile [or, alternatively, a 10 : 1 (v/v) acetonitrile : ethanol mixture] as the eluant. The collected product sample was precipitated from acetonitrile with anhydrous ethyl ether and air-dried. Yield: ~70%. Anal. Calcd. for C₄₇H₄₁N₁₀O₂F₆Cl₂PRu₂(%): C, 47.2; H, 3.5; N, 11.7 (MW = 1195.9 g mol⁻¹). Found: C, 47.0; H, 3.7; N, 11.6.

Synthesis of **1**²⁺ and **11**³⁺

The mixed-valent (**11**²⁺) and the fully oxidized (**11**³⁺) species were generated *in situ* by controlled-potential electrolysis of **11**⁺ during the electrochemical and spectroelectrochemical measurements.

Synthesis of **1**ⁿ⁺

The mononuclear, protonated complex was synthesized and isolated as a PF₆ salt in the divalent state (*n* = +1), and characterized in organic solutions by electrochemistry and spectroelectrochemistry in all of its accessible oxidation states (i.e., *n* = +2, +1, -1), as reported elsewhere [29].

Physical Measurements

UV/visible and NIR electronic spectra were recorded, respectively, on a Hewlett-Packard 8453 diode-array spectrophotometer and on a Guided-Wave 260 fiber-optic instrument. Cyclic voltammetric measurements were conducted using a PAR 283

potentiostat and a conventional three-electrode system comprising a Pt working electrode, a Luggin capillary with an Ag/Ag⁺ (1.0×10^{-2} M AgNO₃) reference electrode ($E^\circ = +0.503$ V versus SHE) and a Pt wire as the auxiliary electrode. The sample solutions were thoroughly degassed with Ar prior to running each experiment. Working electrodes were polished with alumina paste. Voltammograms were recorded at sweep rates of 10–1000 mV s⁻¹. The potentials given in this article are referred against standard hydrogen electrode – SHE. (tea)ClO₄ was used as supporting electrolyte ($I = 0.10$ M) for both electrochemistry and spectroelectrochemistry.

UV/visible spectroelectrochemical measurements were carried out using a PAR 366 bi-potentiostat in parallel with the diode-array spectrophotometer. A three-electrode system was specially designed for a rectangular OTTLE quartz cell of 0.25-mm internal optical length. A transparent Au minigrad was used as working electrode, in the presence of a small Ag/Ag⁺ reference electrode and a Pt auxiliary electrode. NIR spectroelectrochemistry by reflectance was performed using a fiber-optic probe for *in situ* measurements in a quartz, flat-bottom electrochemical cell. The fiber-optic probe was placed perpendicularly to the mirror surface of the Pt electrode, providing a constant optical length.

Elemental analyses were acquired by the Microanalytical Laboratory of the University of São Paulo. Molecular mechanics (MM+) and semiempirical quantum chemical (ZINDO) calculations were performed as described in detail elsewhere [18,30–32].

RESULTS AND DISCUSSION

Electrochemistry

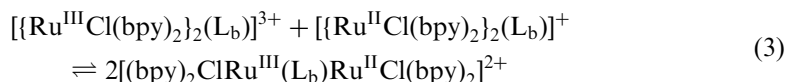
The cyclic voltammograms of **11**⁺ in acetonitrile display: (a) two pairs of reversible waves with $E_{1/2}^{(1)} = 1.21$ V and $E_{1/2}^{(2)} = 0.95$ V (both exhibiting $i_a/i_c = 1$, $\Delta E_p \sim 65$ – 70 mV at 100 mV s⁻¹, and $i_p \propto \nu^{1/2}$), associated to the redox couples centered on the metal ion [Eqs. (1) and (2)]; (b) two poorly resolved wave couples in the very negative region of potentials with $E_c^{(1)} = -1.30$ V and $E_c^{(2)} = -1.46$ V (with nearly twice the current intensity relative to those in the positive region), related to the typical two, closely spaced, ligand-centered reductions of the bpy ligands on each ruthenium moiety [29,33].



As expected, the redox potential for the couple **11**³⁺/**11**²⁺ is rather more positive (i.e., 440 mV) than that for the precursors **1**²⁺/**1**⁺ ($E_{1/2} = 0.77$ V) [29]. The reason for this is twofold: the extra positive charge on the fully oxidized dimer if compared to its monomer, and the extra stabilization of the mixed-valence state (**11**²⁺) attributed to electronic coupling and charge transfer effects (*v. infra*). It is interesting to observe, however, that $E_{1/2}^{(2)}$ for **11**²⁺/**11**⁺ is still 180 mV more positive than $E_{1/2}$ for **1**²⁺/**1**⁺, even though both have the same total charge (2+). This is because charge donation from bim into dπ orbitals — which stabilizes the oxidized (Ru^{III}) species — is reinforced in the mixed-valent dimer by the presence of π-back-donation from the Ru(II) center and

hence, the donor(π -L_b)/acceptor($d\pi$) effect localized on the Ru(III) moiety becomes more pronounced compared to the monomer species.

The separation between $E_{1/2}^{(1)}$ and $E_{1/2}^{(2)}$ (i.e., $\Delta E_{1/2}$) can be used to estimate K_c , the comproportionation constant associated with the stability of the mixed-valent species ($\mathbf{11}^{2+}$) with respect to its reduced ($\mathbf{11}^+$) and oxidized ($\mathbf{11}^{3+}$) counterparts [Eq. (3)].



By using classical thermodynamic expressions [1,34] K_c was found to be 2.5×10^4 , which means considerable stabilization of the mixed-valent state over $\mathbf{11}^+$ and $\mathbf{11}^{3+}$ (whose concentration relative to $\mathbf{11}^{2+}$ is assumed to be negligible in the equilibrium).

Spectroelectrochemistry

The UV/visible electronic spectra of $\mathbf{11}^{n+}$ ($n = 1, 2$, or 3) are collected and assigned in Table I. In agreement with the results of cyclic voltammetry, the electrode reactions were all chemically and electrochemically reversible in the spectroelectrochemistry as indicated by the complete spectral recovery upon either reduction or oxidation processes.

The visible absorption spectra of the dimers are dominated by charge-transfer transitions involving the Ru(II/III) ions and the peripheral bpy ligands, analogously to the monomeric species studied previously [29]. Absorptions associated with the bridging ligand might also occur in the same region but with lower intensities, and detection may be precluded by the intense bands involving bpy. The shifts observed from monomers to dimers as well as those accompanying oxidation/reduction can be understood in terms of π -acid/base and synergistic $M \leftrightarrow L$ π -backbonding and/or $M \leftrightarrow L \leftrightarrow M$ charge-transfer effects [28].

Mixed-valence Properties

The mixed-valent species $\mathbf{11}^{2+}$ was produced *in situ* by electrochemical oxidation of $\mathbf{11}^+$ at $E_{\text{app}} = 1.1$ V, and its NIR spectrum is shown in Fig. 1. Both reduced ($\mathbf{11}^+$) and oxidized ($\mathbf{11}^{3+}$) isoivalent complexes are transparent in the NIR region.

TABLE I UV/visible spectral data for some 2,2'-bipyridine complexes of ruthenium

Complex	MLCT λ/nm ($\epsilon/10^3 \text{ M}^{-1} \text{ cm}^{-1}$)	LMCT λ/nm ($\epsilon/10^3 \text{ M}^{-1} \text{ cm}^{-1}$)	Intraligand ($\pi \rightarrow \pi^*$) λ/nm ($\epsilon/10^4 \text{ M}^{-1} \text{ cm}^{-1}$)
cis-Ru ^{II} Cl ₂ (bpy) ₂ ^a	380 (8.8); 553 (9.1)	–	243 (2.1); 297 (5.0)
cis-[Ru ^{III} Cl ₂ (bpy) ₂] ³⁺ ^a	–	380 (5.6)	298 (2.5); 310 (2.2)
cis-[Ru ^{II} Cl(bpy) ₂ (bimH)] ⁺ ; ($\mathbf{11}^+$) ^b	353 (7.6); 512 (7.3)	–	240 (2.6); 294 (4.4)
cis-[Ru ^{III} Cl(bpy) ₂ (bimH)] ²⁺ ; ($\mathbf{11}^{2+}$) ^b	–	414; 495 (sh)	248 (2.5); 297 (2.4)
cis,cis-[(bpy) ₂ ClRu ^{II} (bim)- Ru ^{II} Cl(bpy) ₂] ⁺ ; ($\mathbf{11}^+$)	344 (9.0); 464/505 (7.3)	–	287 (5.2)
cis,cis-[(bpy) ₂ ClRu ^{II} (bim)- Ru ^{III} Cl(bpy) ₂] ²⁺ ; ($\mathbf{11}^{2+}$)	390 (sh); 450 (4.7)	650 (2.0)	287 (4.2)
cis,cis-[(bpy) ₂ ClRu ^{III} (bim)- Ru ^{III} Cl(bpy) ₂] ³⁺ ; ($\mathbf{11}^{3+}$)	–	720 (4.8)	247 (3.4); 302 (3.1)

^aRef. [35]. ^bRef. [29].

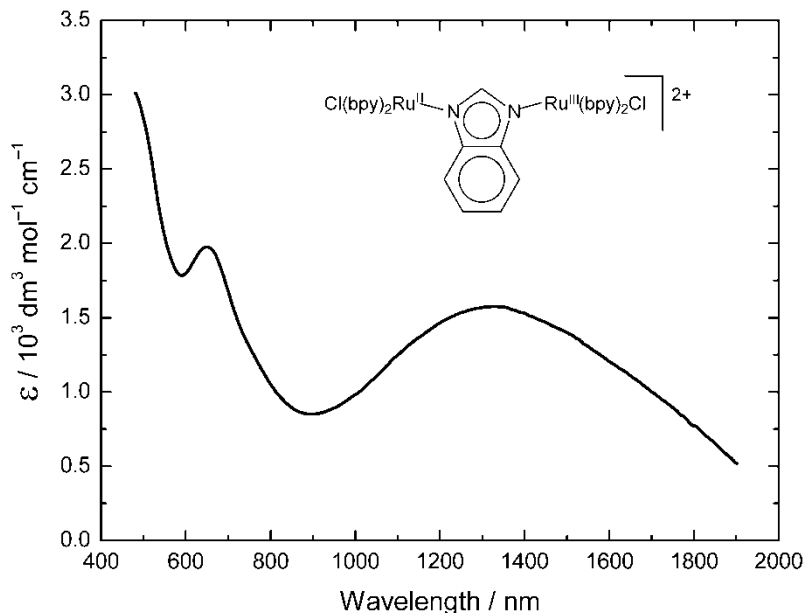
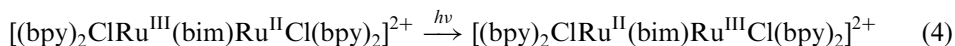


FIGURE 1 Electronic spectrum of $\mathbf{11}^{2+}$ in CH_3CN ($I=0.10\text{ M}$ (tea) ClO_4).

In addition to the metal-to-ligand charge transfer (MLCT) and ligand-to-metal charge transfer (LMCT) transitions involving the bpy ligands on the reduced and oxidized moieties, respectively, the NIR spectrum of $\mathbf{11}^{2+}$ (Fig. 1) displays a broad and intense band ($\lambda_{\text{max}}=1330\text{ nm}$; $\bar{\nu}_{\text{max}}=7.5 \times 10^3\text{ cm}^{-1}$; $\epsilon=1.6 \times 10^3\text{ M}^{-1}\text{ cm}^{-1}$; $\Delta\bar{\nu}_{1/2}=6.0 \times 10^3\text{ cm}^{-1}$), which is associated with the IT transition illustrated in Eq. (4).



The IT bandwidth ($\Delta\bar{\nu}_{1/2}$) observed for $\mathbf{11}^{2+}$ is larger than that predicted ($4.2 \times 10^3\text{ cm}^{-1}$) on the basis of the Hush model [36], reinforcing the charge-localized nature of this system (class-II type in Robin and Day's categorization [37]). Since this criterion for a weakly interacting two-state system is satisfied, Eqs. (5) and (6) can be used to estimate α^2 and H_{AB} , the electronic delocalization and coupling parameters for the ground state, respectively. In these formulas, the quantities $\bar{\nu}_{\text{max}}=E_{\text{op}}$ and $\Delta\bar{\nu}_{1/2}$ are given in cm^{-1} , ϵ_{max} is the molar extinction coefficient in $\text{M}^{-1}\text{ cm}^{-1}$, and d is the donor-acceptor distance in \AA .

$$\alpha^2 = 4.2 \times 10^{-4} \left(\frac{\epsilon_{\text{max}} \cdot \Delta\bar{\nu}_{1/2}}{\bar{\nu}_{\text{max}} \cdot d^2} \right) \quad (5)$$

$$H_{\text{AB}} = \alpha \cdot \bar{\nu}_{\text{max}} \quad (6)$$

By assuming an electron transfer distance (d) of 5.9 \AA , which is actually the calculated metal-metal separation in the dimer (Fig. 2), α^2 and H_{AB} were determined to be 1.5×10^{-2} and $9.2 \times 10^2\text{ cm}^{-1}$ respectively. Although this system evidently exhibits

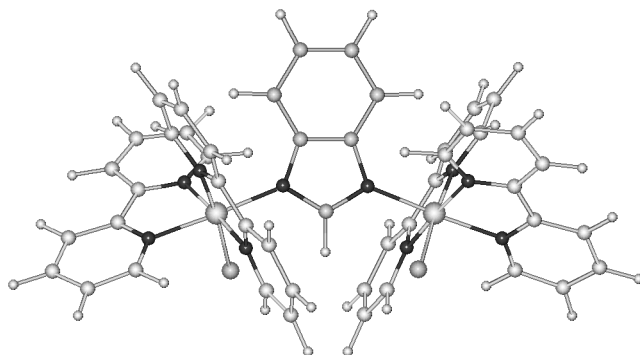


FIGURE 2 Calculated molecular structure of 11^+ ($d_{\text{Ru-Ru}} = 5.92 \text{ \AA}$).

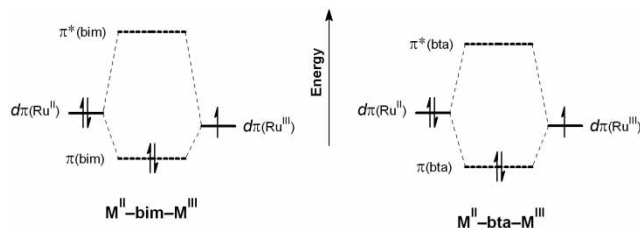
localized Ru(III) and Ru(II) oxidation states with slight delocalization, the magnitude of the electronic interaction is remarkable for this type of complex (e.g., $[(\text{bpy})_2\text{ClRu}^{\text{III}}(\text{pz})\text{Ru}^{\text{II}}\text{Cl}(\text{bpy})_2]^{3+}$ presents $H_{\text{AB}} = 390 \text{ cm}^{-1}$ and $K_c \sim 10^2$) [12,38,39].

The fact that 11^{2+} displays a larger electronic coupling than 22^{2+} ($\alpha^2 = 9.9 \times 10^{-3}$ and $H_{\text{AB}} = 6.8 \times 10^2 \text{ cm}^{-1}$) [28] is consistent with the expected trend for dimers of bpy-ruthenium moieties containing σ, π -basic bridging ligands, in which promotion of electronic communication is dictated by the ability of the intervening ligand to provide efficient $d\pi(\text{M}^{\text{II}}) - \pi(\text{L}_b) - d\pi(\text{M}^{\text{III}})$ orbital conjugation.

As pointed out in the Introduction, the electronic character of the bridging ligand is important in determining the degree of electron delocalization in the ground state and defining the type of mechanism involved in the electron exchange [7]. Given that polypyridine ligands are known as good π -acidic/acceptors and as such interact with d_{π}^5/d_{π}^6 metal ions stabilizing/lowering their redox orbital levels, then, in mixed-valent dimers of the type $[(\text{bpy})_2\text{ClRu}(\text{L}_b)\text{RuCl}(\text{bpy})_2]^{n+}$ containing cationic or neutral π -acceptor L_b (e.g., pyrazine) the most likely orbital pathway for Ru(II)–Ru(III) interactions is via mixing of $d\pi(\text{Ru}^{\text{II}})$ and $d\pi(\text{Ru}^{\text{III}})$ with unoccupied $\pi^*(\text{L}_b)$ orbitals, characterizing the so-called electron-transfer mechanism. On the other hand, if the dimer contains a neutral or anionic σ, π -donor L_b (e.g., azole/azolate-derivatives), the major pathway for the intermetallic electronic interaction is via mixing of the $d\pi$ levels of the terminal donor (reduced) and acceptor (oxidized) metal ions and the occupied π orbitals of L_b , leading to a hole-transfer mechanism.

Therefore, since the same type of mechanism (hole-transfer) should prevail in both 11^{2+} and 22^{2+} , the former is expected to present greater electronic coupling. This conclusion is based on the fact that bim is a stronger base than bta and, hence, would promote a better energy match between the metallic $d\pi$ orbitals and the high-lying π occupied orbitals of the donor bridging ligand (Scheme 2).

A relevant comparison here involves the symmetrical mixed-valent complexes $[(\text{edta})\text{Ru}(\text{L}_b)\text{Ru}(\text{edta})]^{4-}$ ($\text{edta} = \text{ethylenediaminetetraacetate}$; $\text{L}_b = \text{bim}$ or bta) [23,24]. In those examples, the bta species displays larger electronic delocalization. In the current cases with Ru–bpy, in contrast, a more pronounced electronic coupling is exhibited by the bim species. This is because, besides the coupling through a hole-transfer mechanism of electron exchange, a dynamic coordination involving bta takes place in $[(\text{edta})\text{Ru}(\text{bta})\text{Ru}(\text{edta})]^{4-}$, whose structural arrangement enables a symmetrical approximation of the ruthenium–edta moieties toward each other via a fluxional

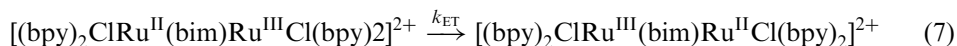


Scheme 2 Qualitative D-L_b-A orbital diagram for $\mathbf{11}^{2+}$ and $\mathbf{22}^{2+}$.

binding mode of the type $M-\eta^2-(N1,N2)bta(N2,N3)-\eta^2-M$ [23,24]. The results presented herein for the bpy-ruthenium dimers are consistent with the absence of such effects, leading to the expected trend (in terms of coupling) as for the replacement of L_b (bim/bta) within the context of the hole-transfer superexchange mechanism.

Electron Transfer

On the basis of the magnitude of H_{AB} for $\mathbf{11}^{2+}$, one can conclude that electronic coupling between the donor (Ru^{II}) and acceptor (Ru^{III}) redox sites is sufficient for the related thermal intramolecular electron transfer (ET) reaction of Eq. (7) to be totally adiabatic in the sense used in the semiclassical ET kinetic theory of Marcus [42,43].



The expression for the ET rate (k_{ET}) in a symmetric system with no net free energy change (ΔG°) is given by Eq. (8) [44], where, κ is the adiabaticity factor (unity for the adiabatic case), λ is the free energy term corresponding to the reorganization energy (can be approximated as E_{op} or \bar{v}_{max} , the IT energy), and ν_n is the nuclear frequency factor (usually assumed to be $5 \times 10^{12} \text{ s}^{-1}$ in the working conditions of this study [12]). By making such typical assumptions, k_{ET} for the mixed-valent dimer $\mathbf{11}^{2+}$, at 298 K, was estimated using Eq. (8) to yield $2.8 \times 10^{10} \text{ s}^{-1}$. As might be expected from its lower energy barrier ($\Delta G^* = \lambda/4 - H_{AB} + H_{AB}^2/\lambda$) as a result of a larger H_{AB} , $\mathbf{11}^{2+}$ displays a slightly faster ET rate than the bta-bridged $\mathbf{22}^{2+}$ analog ($k_{ET} = 2.5 \times 10^{10} \text{ s}^{-1}$) [28].

$$k_{ET} = \kappa \cdot \nu_n \exp \left[- \left(\frac{\lambda/4 - H_{AB} + H_{AB}^2/\lambda}{RT} \right) \right] \quad (8)$$

CONCLUSIONS

In the mixed-valence ion *cis,cis*-[(bpy)₂ClRu(bim)RuCl(bpy)₂]²⁺, there is experimental evidence for discrete Ru(III) and Ru(II) valences and slight delocalization. Even so, the key parameter for electronic coupling, H_{AB} , is quite large for this type of complex.

The difference in IT properties between $\mathbf{11}^{2+}$ and $\mathbf{22}^{2+}$ can be explained in terms of a hole-transfer superexchange mechanism, in which the higher occupied (HOMO)

π levels of the bim bridge promote more efficient overlap between the metal orbitals via a $d\pi - \pi_{L_b} - d\pi$ conjugation type. These examples emphasize the fact that donor-acceptor electronic interactions in bridged oligomers can be tuned by subtle chemical modifications, as in the case of replacement of the intermediate N(2) atom in bta with the CH group in bim, whose electron-donor character is more pronounced (electron richer) and therefore favors electronic delocalization across the bridging ligand by mixing the $d\pi$ and π orbitals. It is noteworthy that both bim and bta provide almost identical donor-acceptor distances, emphasizing that this is not always the most relevant parameter in estimating through-bond-mediated electronic coupling.

An important issue for comparing electrochemical and spectral properties of mixed-valence systems can be illustrated here. Although this system exhibits a large redox potential separation between the $\text{Ru}^{\text{III}}(\text{bim})\text{Ru}^{\text{III}}/\text{Ru}^{\text{III}}(\text{bim})\text{Ru}^{\text{II}}$ and $\text{Ru}^{\text{III}}(\text{bim})\text{Ru}^{\text{II}}/\text{Ru}^{\text{II}}(\text{bim})\text{Ru}^{\text{II}}$ couples – which translates in stabilization of the mixed-valent species – only 0.014 eV (113 cm^{-1}) contributes to the comproportionation energy (ΔG_c) of 0.260 eV for $\mathbf{11}^{2+}$, as determined electrochemically from $\Delta E_{1/2}$; i.e., only a small fraction (*ca.* 5%) of it originates in the intermetallic electronic coupling. Most of the comproportionation driving force should be attributed to synergistic/cooperative charge-transfer interactions of the type $\text{Ru}^{\text{II}}(d\pi) \rightarrow L_b(\pi^*)$ (MLCT) and $L_b(\pi) \rightarrow \text{Ru}^{\text{III}}(d\pi)$ (LMCT), which yield a vectorial net effect ($\text{Ru}^{\text{II}} \rightarrow L_b \rightarrow \text{Ru}^{\text{III}}$) in the mixed-valent state.

Unlike bim/bta-bridged ruthenium-edta dimers, no evidence of dynamic/structural factors, such as fluxionality, influencing the metal-metal coupling were observed. Instead, in the current examples, the main factor involved in the promotion of the electronic communication is the electronic character of the intervening ligand in providing efficient $d\pi(\text{M}^{\text{II}}) - \pi(L_b) - d\pi(\text{M}^{\text{III}})$ orbital conjugation. These results reinforce previous conclusions [18,22–25,45] on the interesting properties of bim and bta as very efficient conductor (electron-rich) bridging linkers.

The comparisons made herein between the mixed-valence features of bim- and bta-bridged bpy- and edta-ruthenium dimers reinforce the idea that the extent of metal-metal and cooperative electronic/charge-transfer interactions between ligand-bridged donor-acceptor complexes can be modulated by a series of relatively simple molecular changes either on the intervening bridging ligand or on the nonbridging (ancillary) ligands surrounding the metal ions.

Acknowledgments

Support from CNPq and FAPESP is gratefully acknowledged.

Notes

(i) The measurements were performed at room temperature. (ii) As a general precaution, the reaction mixtures and sample solutions containing bis(2,2'-bipyridine)ruthenium(II) derivatives were protected from light during the syntheses and measurements.

Analysis of their charge-transfer energies shows that E_{MLCT} is systematically higher than E_{LMCT} .

The basicity of bim and bta can also be inferred from their $\text{p}K_{\text{a}}$ values (with respect to the $\text{LH} \rightleftharpoons \text{L}^- + \text{H}^+$ dissociation): 12.78 ± 0.04 (bim; ref. [40]); 8.38 ± 0.03 (bta; ref. [41]). In addition, molecular orbital (ZINDO) calculations on these ligands showed that the highest π and the lowest π^* orbital energy levels for bim are 0.43 and 0.56 eV higher than those of bta. The partial charges localized at the coordinating nitrogen atoms are, as expected, lower for bta: $\delta q \sim 0.15/\text{N}$.

Molecular modeling and quantum (semiempirical level) calculations indicated a high degree of steric hindrance involving the neighbor, hydrophobic polypyridine and also the electrostatic repulsion between the chloride ligands from each $\{\text{RuCl}(\text{bpy})_2\}$ moiety, preventing an "extra" coupling based on a metal-metal distance shortening from the fluxionality of the bridging ligand. In this case, intermetallic communication most likely propagates across benzotriazolate by a "usual" orbital conjugation involving the two extreme binding sites on the bridge [i.e., $(\text{M})\text{d}_\pi\text{-p}_\pi(\text{N1})\text{bta}(\text{N3})\text{p}_\pi\text{-d}_\pi(\text{M})$], analogous to that observed in linear, symmetrical two-site bridging ligands such as pyrazine.

Delocalization/resonance term calculated from the spectroscopic, IVCT parameters as $\Delta G_d = (H_{AB})^2/\lambda$, where the reorganization energy, λ , is taken as $E_{\text{op}} = \bar{\nu}_{\text{max}}$; see Ref. [12].

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