



Short communication

Redox-induced linkage isomerization detected in $[\text{Ru}(\text{NH}_3)_5(\text{NVF})](\text{PF}_6)_2$ (NVF = *N*-vinylformamide)

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ABSTRACT

A new ruthenium (II) complex, of formula $[\text{Ru}(\text{NH}_3)_5(\text{NVF})](\text{PF}_6)_2$, **1** (with NVF = *N*-vinylformamide) was synthesized and characterized by chemical analyses, spectroscopic and electrochemical techniques. The presence of two coordination sites within NVF makes complex **1** capable of showing a redox-dependent linkage isomerization process, which was detected by cyclic voltammetry and spectroelectrochemical measurements. Upon oxidation of the metallic center from Ru (II) to Ru (III) of complex **1** in *N,N*-dimethylformamide, linkage isomerization takes place from a vinyl-coordinated Ru(II) to an amide-coordinated Ru(III). This is an additional example of a system that can be applied in molecular memory devices or engines of a molecular machine.

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The aim of this work was to synthesize a new ruthenium complex of formula $[\text{Ru}(\text{NH}_3)_5(\text{NVF})](\text{PF}_6)_2$, **1**, with NVF = *N*-vinylformamide acting as an ambidentate ligand. We propose that the presence of two coordination sites within NVF (the olefinic site and the amide function) would make this complex capable of displaying a redox-dependent linkage isomerization process in organic solvents. The structure of NVF is shown in Fig. 1.

N-vinylformamide was distilled by using an all-glass apparatus. *N,N*-dimethylformamide (DMF) was dried over molecular sieves and acetonitrile (CH_3CN) was freshly distilled over P_4O_{10} , for electrochemical measurements. Tetrakis(*n*-butyl)ammonium hexafluorophosphate (TBAH) was recrystallized three times from ethanol and dried at 150 °C for 72 hs. All other chemicals were analytical reagent grade and used without further purification. Chemical analyses were performed at INQUIMAE (University of Buenos Aires), with an estimated error of $\pm 0.5\%$. IR spectra were performed as KBr pellets on a FTIR Perkin-Elmer Spectrum RX-I spectrophotometer. UV–Vis spectra were recorded with a Varian Cary spectrophotometer in 1-cm quartz cells. Cyclic Voltammetry measurements were carried out in CH_3CN and DMF (0.1 TBAH) with a BAS Epsilon EC equipment. A standard three-electrode cell was used with vitrous C as working electrode, Pt wire as auxiliary electrode and Ag/AgCl (3 M KCl) as reference electrode. Spectroelectrochemical measurements in the UV/visible region were performed by using a Honeycomb Cell from PINE Research Instrumentation, while an OTTL cell was used for doing spectroelectrochemistry in the IR region [1]. Simulated data of cyclic voltamperograms were calculated through a Digisim 3.0 software provided by BAS.

Following synthetic methods reported by Meyer et al. [2], the complex of formula $[\text{Ru}(\text{NH}_3)_5(\text{NVF})](\text{PF}_6)_2$, **1**, was prepared by mixing 1 mL (14.4 mmol) of *N*-vinylformamide in 10 mL of acetone in a serum bottle, a solution that was deaerated in the dark under Ar for 35 min. Then, 90 mg (0.1 mmol) of $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})](\text{PF}_6)_2$, prepared as described by Sutton and Taube [3], were added and the mixture was stirred in the dark under Ar for 2 h. After completion, the solution was added to 100 mL of deaerated ether by using a previously purged syringe, and maintained at -15°C for 24 hs. The obtained white precipitate was filtered, washed with ether (3x10mL) and dried over P_4O_{10} under vacuum for 24 h. Yield: 48.6 mg (49%). Anal. % found (calculated) for $\text{C}_3\text{H}_{20}\text{N}_6\text{OP}_2\text{F}_{12}\text{Ru} \cdot (1/3)\text{CH}_3\text{C}(\text{O})\text{CH}_3$: C, 8.8 (8.5); H, 3.8 (3.9); N, 15.1 (14.8).

As shown in Fig. 2, the UV–Visible spectrum of complex **1** in CH_3CN shows three bands at $\lambda_{\text{max}} = 225, 243$ and 315 nm, with $\epsilon_{\text{max}} = 3700, 2500$ and $380 \text{ M}^{-1} \text{ cm}^{-1}$ respectively. The intense band at $\lambda_{\text{max}} = 225$ nm is an intraligand $\pi\text{-}\pi^*$ band of NVF, since it appears in the UV–visible spectrum of the free ligand. The medium-strong absorption band at $\lambda_{\text{max}} = 243$ nm, which is absent in the free ligand, can be assigned to a metal-to-ligand charge-transfer (MLCT) from a d_{π} orbital of Ru(II) to a π^* orbital of the coordinated alkane site of NVF. In effect, this value is similar to those displayed by previously described η^2 -bonding alkene species of ruthenium amines, such as $[\text{Ru}(\text{NH}_3)(\text{AM})]^{2+}$ ($\lambda_{\text{max}} = 231$ nm) with AM = acrylonitrile [4]. The band at $\lambda_{\text{max}} = 315$ nm is a typical ligand-field (LF) transition, as deduced from its low molar attenuation coefficient.

Fig. 3 shows the IR spectrum of complex **1** as a KBr pellet. The characteristic stretching mode $\nu_{\text{N-H}}$ and deformation mode $\delta_{(\text{NH}_3),\text{sym}}$ for aminoruthenium(II) complexes can be observed as strong bands at 3239 and 1315 cm^{-1} respectively. The strong band at 1645 cm^{-1} can be assigned to a $\nu_{\text{C=O}}$ stretching mode, while the intense band at

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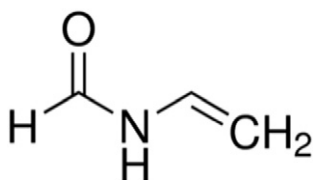


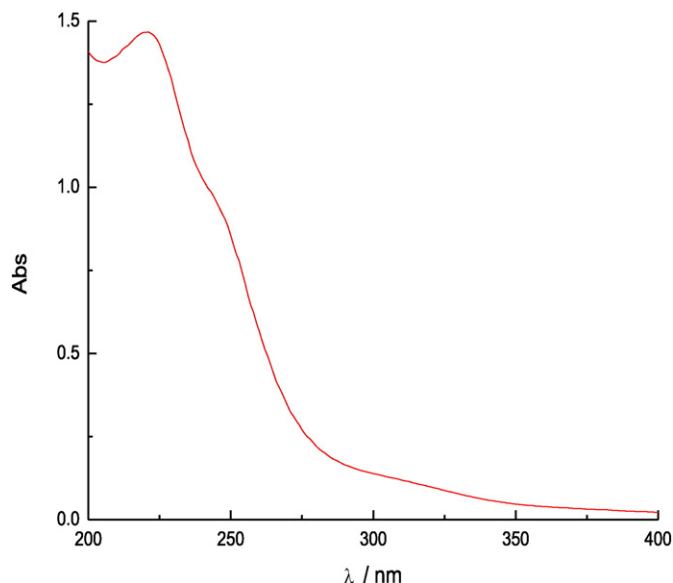
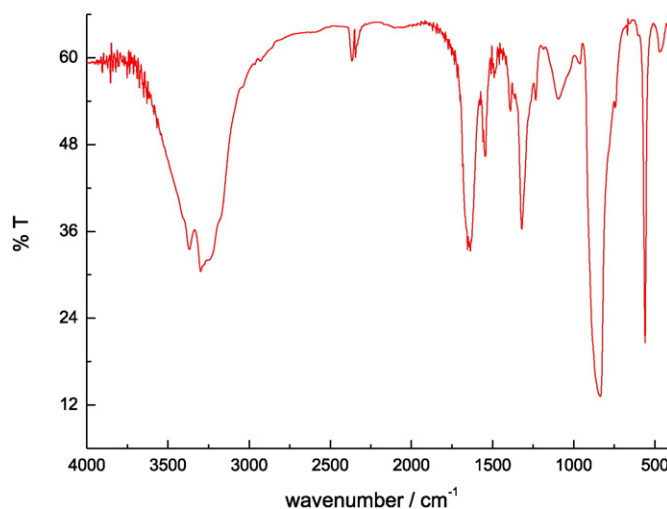
Fig. 1. Structure of NVF.

1550 cm^{-1} , absent in the free ligand, can be attributed to the $\nu_{\text{C}=\text{C}}$ stretching mode, displaced by $\Delta\nu = -113\text{ cm}^{-1}$ respect to the free ligand value, as expected for pentaammineruthenium(II)-alkene complexes [4].

The cyclic voltamperogram of **1** in DMF is shown in Fig. 4. At a scan rate of $\nu = 50\text{ mVs}^{-1}$, an irreversible oxidation wave was observed at $E_{1/2} = 0.95\text{ V}$ (vs. NHE), which can be attributed to a Ru(II)/Ru(III) couple of a η^2 -bonded complex, since olefin complexes of Ru(II) exhibit redox potentials around 1.4 V (in CH_3CN vs. NHE [4]). It is well known that redox potential values for ammineruthenium(II/III) couples increase when decreasing the donor number (DN) of the solvent (DN of $\text{CH}_3\text{CN} = 14.1$; DN of DMF = 26.6) [5]. The irreversible reduction wave at 0.1 V (vs. NHE) could be attributed to an amide-coordinated complex of Ru(III), since they show reduction potentials near 0.2 V (vs. NHE in water) [4]. Thus, a linkage isomerization process is disclosed, from a η^2 -alkene bonded complex of Ru(II) to an amide-bonded complex of Ru(III).

In CH_3CN , the oxidative and reductive waves appear - as expected - at higher values (1.31 and 0.31 V vs. NHE respectively). Besides, a solvolysis process occurs after the first cycle, as demonstrated by the reversible wave observed at $E_{1/2} = 0.92\text{ V}$ (vs. NHE) during the second scan of the cyclic voltammogram of complex **1** in CH_3CN , corresponding to the redox couple $[\text{Ru}(\text{NH}_3)_5(\text{CH}_3\text{CN})]^{3+/2+}$. In DMF, the behavior is different: due to the non-coordinating nature of the solvent, no reversible redox waves of the solvent-complex were detected.

Fig. 5 shows the simulated data calculated by proposing a “square scheme” mechanism (Scheme 1). By using a Digisim 3.0 software, a value of $K_{\text{eq}} = 1 \times 10^7$ was obtained for the equilibrium constant of the isomerization process: $\text{D} \leftrightarrow \text{A}$, while a value of $k_{\text{f isom}} = 1 \times 10^4\text{ s}^{-1}$ was obtained for the forward isomerization process: Ru(III)-olefin bonded \rightarrow Ru(III)-amine bonded complexes. $k_{\text{b isom}} (= 1 \times 10^{-3}\text{ s}^{-1})$

Fig. 2. UV-visible spectrum of **1** in CH_3CN ($C = 4 \times 10^{-4}\text{ M}$).Fig. 3. IR spectrum of **1** (as a KBr pellet).

was adjusted by default from: $K_{\text{eq}} = k_{\text{f isom}}/k_{\text{b isom}}$. Reciprocal values for K_{eq} , $k_{\text{f isom}}$ and $k_{\text{b isom}}$ were determined for the $\text{C} \leftrightarrow \text{B}$ process.

Another important issue that sustains the proposed mechanism is the scan-rate dependence of the two irreversible waves. When

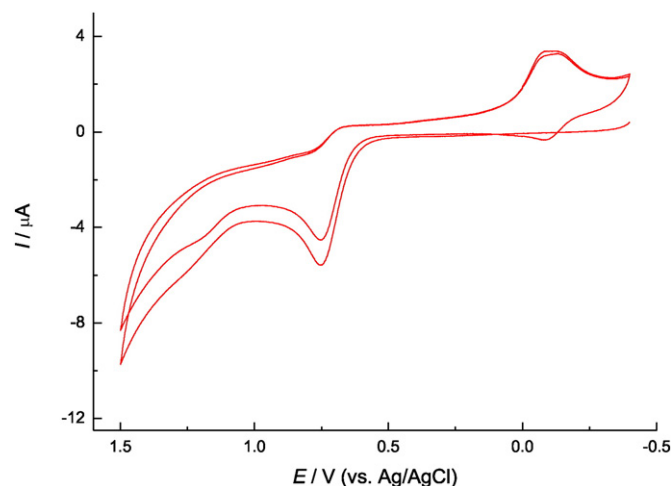
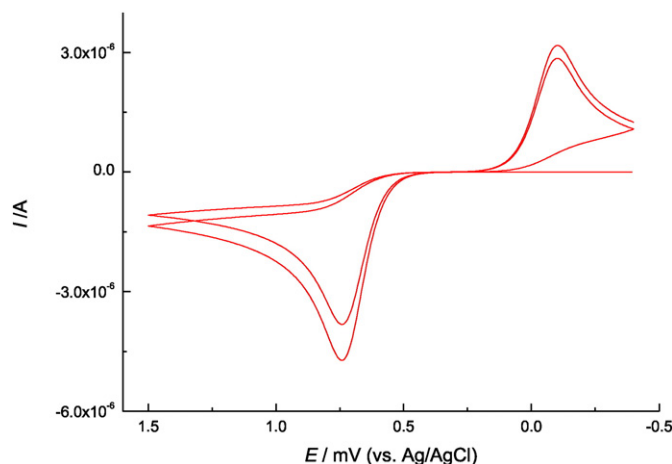
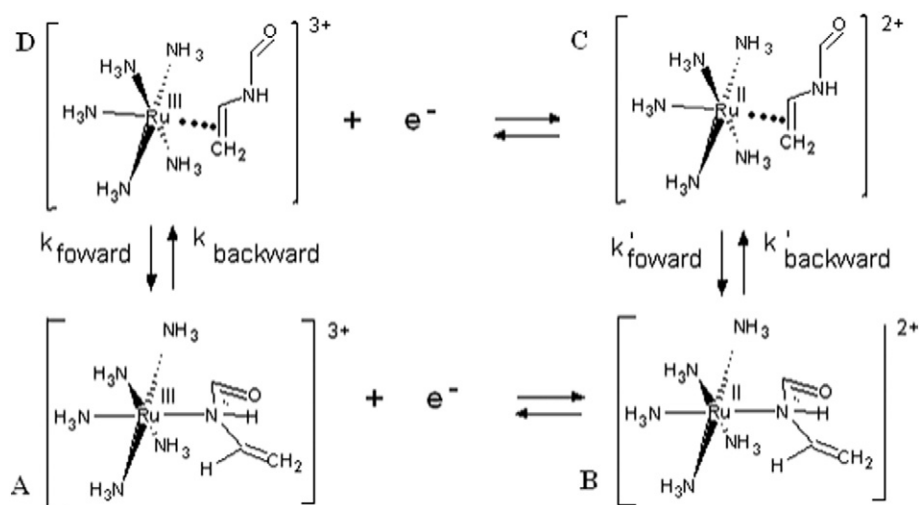
Fig. 4. Cyclic voltamperogram of **1** in DMF, 0.1 M TBHA , scan rate $\nu = 50\text{ mVs}^{-1}$.

Fig. 5. Simulated data.



Scheme 1. Mechanism of the redox-induced linkage isomerization process in $[\text{Ru}(\text{NH}_3)_5(\text{NVF})]^{2+}$

increasing the scan rate, the reversibility of these two redox-processes also increases. This behavior can be explained by considering that the rates of the two reactions (homogeneous and heterogeneous) involved in an EC mechanism depend differently with scan rate. If the scan rate increases, the rate of the redox process (heterogeneous reaction) competes with the isomerization process (homogeneous reaction) which has a rate governed intrinsically by its value of $k_{f \text{ isom}}$. When the redox process is faster than the isomerization step, a reduction (or oxidation) backward wave is detected.

A spectroelectrochemical experiment was carried out as shown in Fig. 6. After applying a potential of 1.3 V during 3 min, a new band appears on the spectra near 330 nm, which can be assigned to a LMCT (ligand-to-metal charge transfer transition) from amide to Ru(III), as expected when comparing to data of similar species, such as the amide-bonded acrylamide complex of pentaammineruthenium(III), which absorbs at $\lambda_{\text{max}} = 360 \text{ nm}$ [4].

In order to confirm that the formed product is indeed an amide-bonded Ru(III) complex, we have carried out an additional spectroelectrochemical experiment in the IR region. Fig. 7 shows the difference in absorbance $\Delta A = A_t - A_0$ (where A_t = absorbance

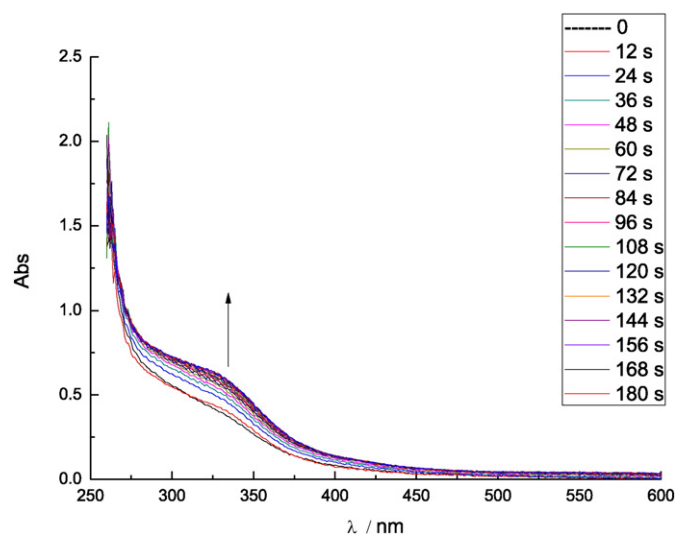


Fig. 6. UV/visible spectra obtained by electrolysis at 1.3 V of complex **1** in DMF, 0.1 M TBHA from 0 to 3 min.

at $t = 3 \text{ min}$ and A_0 = absorbance at $t = 0 \text{ min}$) measured after electrolyzing complex **1** at 1.3 V. These differences compensate the absorptions due to solvent and the supporting electrolyte in both solutions. A negative ΔA was measured at $\nu = 1526 \text{ cm}^{-1}$, while a positive ΔA was measured at $\nu = 1605 \text{ cm}^{-1}$. This shift can be attributed to the change in the stretching frequency $\nu(\text{C}=\text{C})$ that occurs when going from an alkene-bonded Ru(II) pentaammine complex to an amide-bonded Ru(III) pentaammine species. The obtained difference between these values, $\Delta \nu = +79 \text{ cm}^{-1}$, is consistent with that expected for the proposed isomerization process, as discussed before in the IR section.

All these changes (both in UV/visible and FTIR) are reversible and the results put into evidence that the operating mechanism is that depicted in Scheme 1.

Complex **1** is another example of a system that can be applicable to devices such as liquid crystals or engines of a molecular machine [6]. It can also be used as a building block of a device that presents “molecular hysteresis”, such as previously described in pentaammineruthenium complexes of dimethylsulfoxide [7], in organometallic species [8], in pyrazine-bridged ruthenium amines [9] and in a dinuclear ruthenium polypyridyl complex [10].

In conclusion, upon oxidation of the metallic center from Ru (II) to Ru (III) of complex **1** in *N,N*-dimethylformamide, linkage isomerization takes place from a vinyl-coordinated Ru(II) to an amide-coordinated

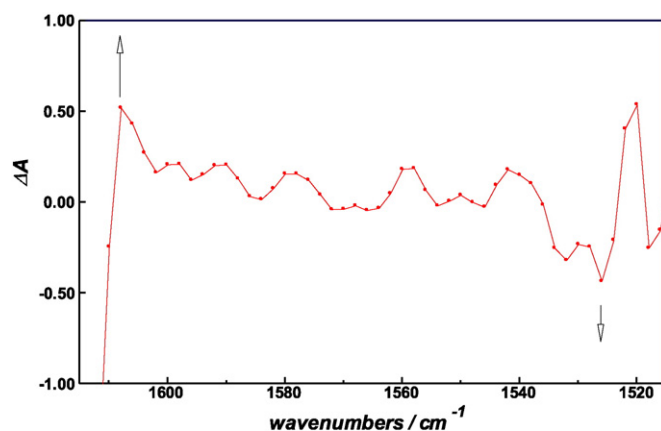


Fig. 7. Difference FTIR spectra obtained by electrolysis at 1.3 V of complex **1** in DMF, 0.1 M TBHA after 3 min.

Ru(III). This redox-induced phenomenon can be applied in the design of nanoscopic memory devices or molecular machines.

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