Notes

Redox-Induced Linkage Isomerizations of Acrylamide Complexes of Pentaammineruthenium(II) and -(III)

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Introduction

Linkage isomerization processes in $[Ru(NH_3)_5(L)]^{2+/3+}$ complexes, where L is an ambidentate ligand, are already known for L = glycine,[1] hypoxanthine,[2] dimethylsulphoxide,[3] urea,[4] benzotriazole,[5] acetone,[6] nicotinamide,[7] and isonicotinamide[7] and for complexes of tetraammineruthenium(II) and -(III) with glycinamide and derivatives.[8] There are no reports, however, concerning ambidentate ligands that involve an olefinic coordination site. Unsaturated hydrocarbons can act as π-acceptors and so are capable of bonding strongly to Ru(II) in an η^2-mode.[9,10] For L = acrylonitrile,[11] and L = 4-vinylpyridine,[12] no evidence was found for olefin bonding to Ru(II): the preferred coordination sites were the nitrile group and the pyridyl nitrogen, respectively. An η^2-arene intermediate was reported in the case of L = nicotinamide or isonicotinamide.[7] In this work, we wish to report the first example of isomerization reactions that occur when changing the oxidation state of Ru in complexes of pentaammineruthenium(II/III) with a ligand capable of a *stable* η^2-bonding (olefin site): acrylamide, of structural formula $H_2C{=}CH{-}C(O){-}NH_2$, abbreviated as AM. The use of this ligand as a building block in a system that could exhibit "molecular hysteresis", similar to that described recently for a dinuclear complex of ruthenium,[13] is discussed. An organometallic example of this phenomenon has also been recently reported.[14]

Experimental Section

Materials. CH_3CN for electrochemical measurements was distilled over P_4O_{10}. Water was triply distilled by using an all-glass apparatus. Tetrakis(*n*-butyl)ammonium hexafluorophosphate (TBAH) was recrystallized three times from ethanol. All other chemicals were analytical reagent grade and used without further purification.

Synthesis. The complex $[Ru(NH_3)_5(AM)](PF_6)_2$ was prepared by following synthetic methods developed by Meyer *et al.*[15] First, 213 mg (3 mmol) of acrylamide (Aldrich) was dissolved in 5 mL of acetone, and the solution was deareated with Ar for 20 min in a serum bottle. Then, 50 mg (0.1 mmol) of $[Ru(NH_3)_5(H_2O)](PF_6)_2$, prepared as described by Sutton and Taube,[16] was added, and the mixture was stirred under Ar for 3 h. A 50-mL aliquot of deareated ether was then added with a syringe, and the precipitate was cooled at 4° C, filtered in a Schlenk tube under Ar, washed with ether (2 × 10 mL), and dried in a vacuum dessicator over KOH. Yield: 41 mg (75 %). Anal. Calcd for $C_3H_{20}N_6OP_2F_{12}Ru$: C, 6.58; H, 3.68; N, 15.35. Found: C, 7.56; H, 3.82; N, 15.89. The C content was rather high, probably because of the reactivity of η^2-bonded complexes of ruthenium.[6] A poor C analysis was reported for the related complex $[Os(NH_3)_5(styrene)](PF_6)_2$.[12] However, the purity of the compound was assessed by satisfactory H and N analyses and by IR, UV-vis, and CV results, as described below.

Table I. Electronic Spectral Data for Olefin-Bonded Complexes of Pentaammineruthenium(II), $[Ru(NH_3)_5(L)]^{2+}$, in Aqueous Solutions

L	λ_{max}, nm (log ϵ)	ref
ethylene	385 (2.5), 270 sh, 217 (3.3)	9
acrylamide	385 (2.6), 290 sh, 233 (3.5)	this work
isobutene	390 (1.7), 315 sh, 237 (3.2)	9

Instrumentation and Techniques. IR spectra were recorded as KBr pellets on a Perkin-Elmer 983G spectrophotometer. UV-vis data were obtained by using a Shimadzu UV-160A spectrophotometer. Cyclic voltammograms were obtained with a L.Y.P. Model M5 potentiostat/galvanostat, a L.Y.P. signal generator and a Hewlett-Packard X-Y recorder. For the electrochemical experiments, an H-type conventional cell with glassy C as working electrode, Pt as auxiliary electrode, and Ag/AgCl as reference electrode was used. The supporting electrolyte was 0.1 M TBAH in CH_3CN, and pure Ar was bubbled before measurements. Chemical analyses were carried out at UMYMFOR, Universidad de Buenos Aires, Argentina.

Results and Discussion

The previously unreported complex $[Ru(NH_3)_5(AM)](PF_6)_2$ can be characterized by IR and UV-vis spectroscopies. Free acrylamide shows a band at 1612 cm^{-1} in the IR spectrum, which can be assigned to a carbon-carbon double bond stretching vibration, $\nu_{C=C}$.[17] This band is shifted to 1499 cm^{-1} in the IR spectrum (as a KBr pellet) of $[Ru(NH_3)_5(AM)](PF_6)_2$, as shown in Figure 1. The significant decrease in $\nu_{C=C}$, $\Delta\nu_{C=C} = -113$ cm^{-1}, is due to $d_\pi(Ru) \rightarrow \pi^*(AM)$ back-bonding and is typical of pentaammineruthenium(II)-alkene complexes.[9] The observed value of $\Delta\nu_{C=C}$ lies between that found for ethylene ($\Delta\nu_{C=C} = -82$ cm^{-1}) and isobutene ($\Delta\nu_{C=C} = -134$ cm^{-1}) complexes of pentaammineruthenium(II).[9] The characteristic wagging and twisting vibrations of AM at 990 and 962 cm^{-1} are not present in Figure 1, also indicating π-coordination to the olefinic function.[11] Finally, new and strong bands at 3292 and 1299 cm^{-1} (see Figure 1) can be assigned to ν_{N-H} and $\delta_{(NH_3),sym}$ respectively, and are distinctive[18,19] of ammineruthenium(II) complexes. The proposed structure for the studied species is therefore that of an η^2-bonded AM complex:

Although the UV-vis spectrum is not very informative on the π-acceptor abilities of unsaturated hydrocarbons,[10] it can be quite useful for distinguishing between linkage isomers. Thus, for an amide-bound acrylamide complex of Ru(II), one would expect

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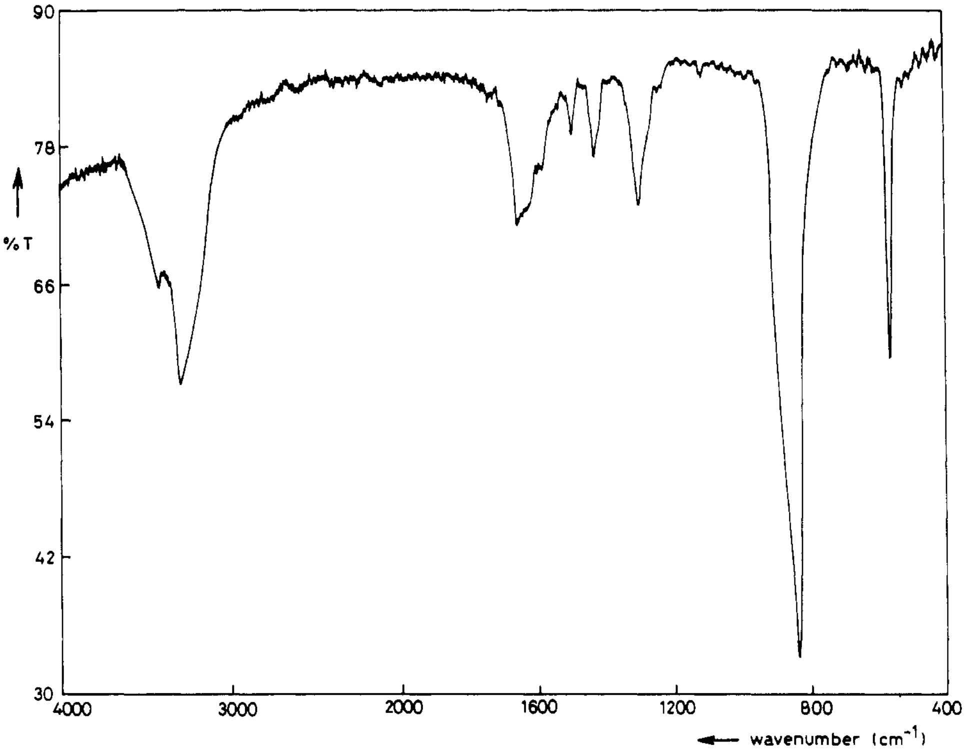

Figure 1. IR spectrum (as a KBr pellet) of $[Ru(NH_3)_5(acrylamide)](PF_6)_2$.

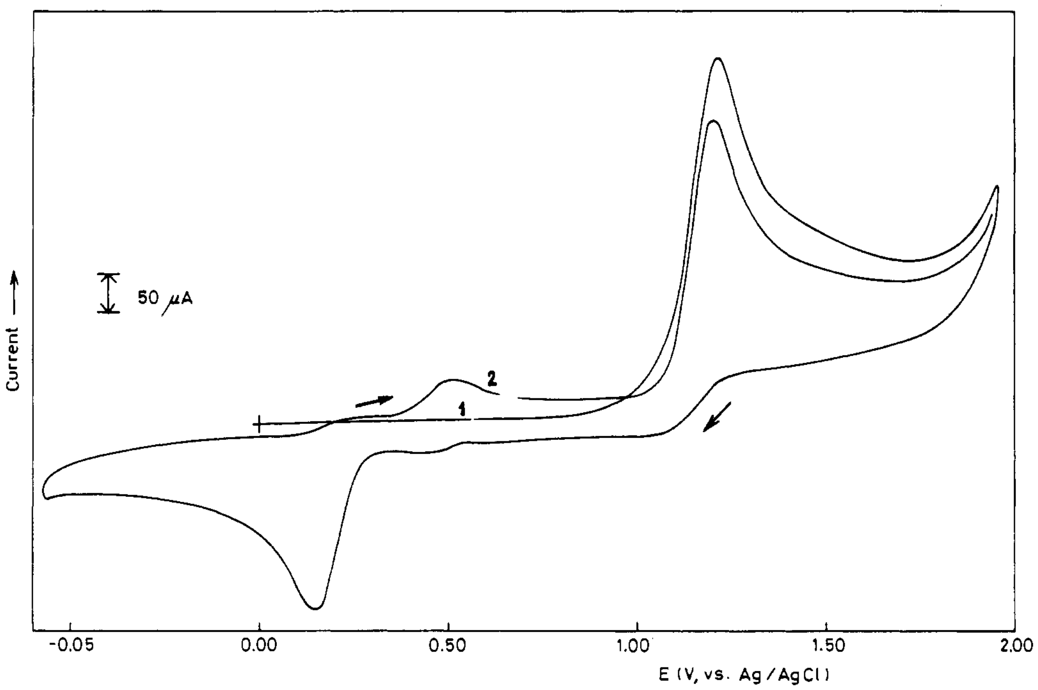

Figure 2. Cyclic voltammograms of $[(NH_3)_5Ru^{II}(acrylamide)]^{2+}$ in CH_3CN containing 0.1 M TBAH (v = 200 mV s^{-1}; t = 22 °C): (1) first scan; (2) second scan.

a spectrum similar to that of $Ru(NH_3)_6^{2+}$; *i.e.*, weak bands at *ca.* 390 and 310 nm and a medium-strong band near 275 nm in water.[20] For an alkene-bonded species, instead, in addition to weak ligand-field (LF) transitions that appear at *ca.* 400 and 300 nm, an intense ($\log \epsilon \cong 3.3$) metal-to-ligand charge-transfer (MLCT) d_π(metal) $\rightarrow$ π^*(ligand) transition is expected in the UV region, between 210 and 250 nm.[9] As shown in Table I, the $[Ru(NH_3)_5(AM)]^{2+}$ ion has weak bands at 385 and 290 nm and a strong one at 233 nm in aqueous (acidic or neutral) solution (whereas in CH_3CN, the corresponding absorptions appear at 405, 290, and 231 nm, respectively). Moreover, the values are found between those for the ethylene and isobutene complexes of pentaammineruthenium(II), in agreement with the IR results. Thus, the UV-vis data are also consistent with η^2-bonding.

When Ru(II) is oxidized to Ru(III) by adding excess $S_2O_8^{2-}$ in neutral aqueous solution, a new band at λ_{max} = 363 nm ($\log \epsilon = 3.5$) develops completely after *ca.* 5 h. (The oxidation process is slow probably because of the closeness of the redox potentials of both couples). Since η^2-olefin complexes of Ru(III) are known to be substitutionally labile,[21] one would expect the final product to be the solvento complex: $[Ru(NH_3)_5(H_2O)]^{3+}$. However, the spectrum does not correspond to this species, but rather to a

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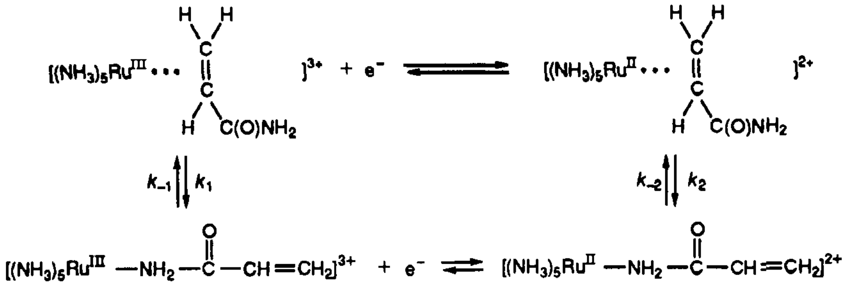
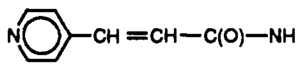
Scheme I



(deprotonated)amide-bonded acrylamide complex of Ru(III): $[(NH_3)_5Ru^{III}—NH—C(O)—CH═CH_2]^{2+}$. Indeed, amide pentaammineruthenium(III) complexes present strong bands in the 300–400-nm region, assigned to ligand-to-metal charge-transfer (LMCT) transitions. Besides, the absorption peaks are shifted to lower energies and increase in intensity upon deprotonation of the amido group.[4,8,22,23] Thus, when a few drops of concentrated H_2SO_4 are added to the oxidized solution, the absorption maximum is shifted to 345 nm (and its intensity decreases by a factor of *ca.* 2), which can be assigned to the (protonated)amide complex: $[(NH_3)_5Ru^{III}—NH_2—C(O)—CH═CH_2]^{3+}$. The linkage isomerization that occurs when the oxidation state of Ru is changed is confirmed by the cyclic voltammetry results.

As shown in Figure 2, the voltammogram of $[Ru(NH_3)_5(AM)]^{2+}$ (both in H_2O and CH_3CN) indicates irreversible behavior, typical of a "square reaction scheme" that involves the mechanism shown in Scheme I. The irreversible oxidation wave observed at 1.42 V (in CH_3CN, vs NHE, v = 200 mV s^{-1}) can be attributed to the oxidation of the η^2-bonded complex $[Ru(NH_3)_5(AM)]^{2+}$, since olefin complexes of Ru(II) exhibit redox potentials *ca.* 1 V (vs NHE) in aqueous solution.[9,10] In CH_3CN, the values of $E_{1/2}$ for ruthenium ammines are higher than those in water,[24] and besides, one would expect the carboxamide moiety to increase the π-accepting ability of the olefin group and thus to stabilize the +2 oxidation state. For the analogous fumaric acid complex, the value of $E_{1/2}$ is 1.40 V (vs NHE, in CH_3CN).[9] An irreversible reduction wave is observed for the studied complex at +0.34 V (vs NHE, in CH_3CN; see Figure 2). Amide complexes of Ru(III) normally have redox potentials near 0.2 V (vs NHE, in water).[23] Thus, a rapid isomerization of the η^2-bonded complex of Ru(III) to the amide-bonded species is occurring, together with a solvolysis process, as demonstrated by the reversible wave appearing during the second scan (see Figure 2), corresponding to the $[(Ru(NH_3)_5(CH_3CN)]^{2+/3+}$ couple ($E_{1/2}$ = 0.68 V, vs NHE, in CH_3CN; ΔE = 70 mV).[25] This behavior is similar to that already observed in (acetone)pentaammineruthenium(III) and -(II) complexes,[6] and in *N*-methylpyrazinium complexes of ethylenediaminetetraacetateruthenium(III) and -(II).[26] From Nicholson and Schain's treatment[27] for electrochemical charge transfer followed by an irreversible chemical reaction, we calculate rate constants for isomerizations (k_1, k_{-2}) of *ca.* 8 s^{-1} at 22 °C. These values are higher than those expected for solvation,[4] so that the mechanism seems to be intramolecular, with a parallel solvation reaction pathway.

Recently,[13] S- to O-isomerization that occurs in the $[(NH_3)_5Ru(dimethyl\ sulfoxide)]^{2+}$ complex on electron transfer was used in the design of a compound with "molecular hysteresis", with a redox couple bracketed within the potentials of the sulfoxide couples. We propose that a dinuclear complex with the ligand 4-pyridineacrylamide



(or an analogous structure) bridging two pentaammineruthenium moieties could present a similar behavior.

To conclude, the observed linkage isomerization that occurs on electron transfer for acrylamide complexes of $Ru(NH_3)_5^{2+/3+}$ can be accounted for by the great affinity of Ru(II) ammines to strong π-acceptors, such as alkenes, and that of Ru(III) ammines to strong π-donors, such as amides. This fact points to possible applications of related ligands for obtaining compounds that may exhibit "molecular hysteresis".

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