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Reduction of the Amido-Bonded (2-Picolinamido)pentaammineruthenium(III) Followed by Formation of *cis*-(2-Picolinamide)tetraammineruthenium(II)

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Recently, Creutz et al.[1] reported an isomerization reaction from an amido- to a pyridyl-bonded pentaammineruthenium(II) complex upon reduction of Ru^{III}(NH$_3$)$_5$(NHC(O)-4-py) (NHC(O)-4-py = deprotonated isonicotinamide) or Ru^{III}(NH$_3$)$_5$(NHC(O)-3-py) (NHC(O)-3-py = deprotonated nicotinamide) through aromatic η^2-bonded intermediates.[1,2] Later, Katz et al.[3] described an isomerization reaction from amide to olefinic η^2-bonded (acrylamide)pentaammineruthenium(II) complex upon reduction of the amido-bonded Ru^{III}(NH$_3$)$_5$(am) (am = acrylamido). Nitriles are able to undergo hydrolysis to amides[1,2,4−16] when coordinated to pentaammineruthenium(III) 10^6 times faster than to pentaammineruthenium(II),[4] and thus, the amido-bonded pentaammineruthenium(III) complex can be made from oxidation of the corresponding pentaammineruthenium(II)−nitrile complex followed by the hydrolysis of the nitrile. We have been working in our laboratory with nitriles, cyanopyridines, cyanopyridinium, and 1-R-cyanopyridinium complexes of ruthenium ammines.[9−17] During our investigations we found out that the reduction of Ru^{III}(NH$_3$)$_5$(NHC(O)-2-py) (**III**) (NH$_2$C(O)-2-py = picolinamide (**VI**))—formed by hydrolysis of the nitrile bonded 2-cyanopyridine after the Ru(II) oxidation to Ru(III) in Ru^{II}(NH$_3$)$_5$(2-NCpy) (**I**) (2-NCpy = 2-cyanopyridine)—to the corresponding Ru(II) complex is followed by a chelation reaction to *cis*-Ru^{II}(NH$_3$)$_4$(NH$_2$C(O)-2-py) (**V**) along with an aquation reaction to form Ru^{II}(NH$_3$)$_5$(OH$_2$) and free picolinamide (**VI**), which we report here. The reactions here described are depicted in Scheme 1.

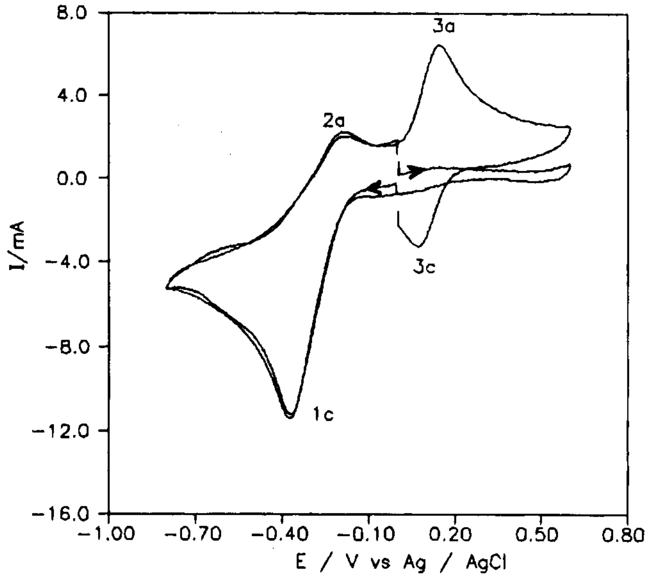
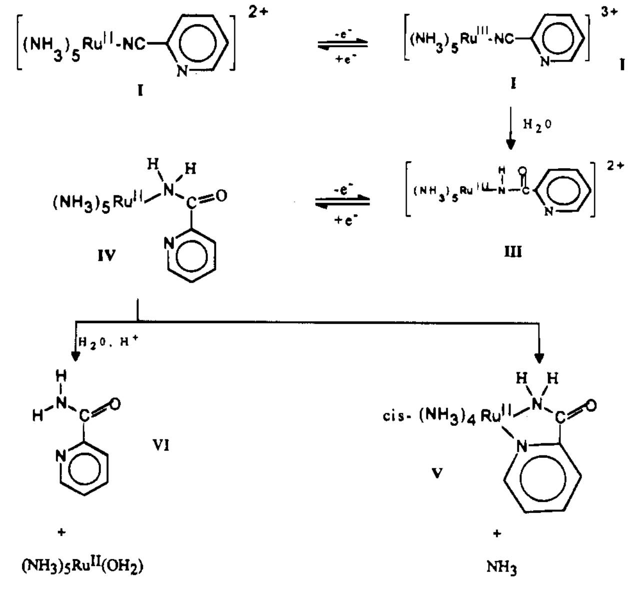


Figure 1. Cyclic voltammogram of [Ru^{III}(NHC(O)-2-py)], scanned after the electrolysis of 1 × 10^{-3} M [Ru^{II}(2-NCpy)] in 1 M HAc/Ac$^-$ at pH = 4.65.

Scheme 1



Ru^{II}(NH$_3$)$_5$(2-NCpy) (**I**) was synthesized and characterized as described.[18] The UV−vis spectrum of its aqueous solution shows a metal-to-ligand charge-transfer (MLCT) band at 408 nm (log ϵ = 3.97) and intraligand (IL) bands at 256 nm (log ϵ = 4.18) and 222 nm (log ϵ = 3.94), in good agreement with

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(1) Chou, M. H.; Brunschwig, B. S.; Creutz, C.; Sutin, N.; Yeh, A.; Chang, R. C.; Lin, C.-T. *Inorg. Chem.* **1992**, *31*, 5347.

(2) Chou, M. H.; Szalda, D. J.; Creutz, C.; Sutin, N. *Inorg. Chem.* **1994**, *33*, 1674.

(3) Katz, N. E.; Fagalde, F. *Inorg. Chem.* **1993**, *32*, 5391.

(4) Zanella, A. W.; Ford, P. C. *Inorg. Chem.* **1975**, *14*, 42.

(5) Diamond, S. E. Ph.D. Thesis, Stanford University, Stanford, CA, 1975.

(6) Diamond, S. E.; Taube, H. *J. Chem. Soc. Chem. Comm.* **1974**, *15*, 622.

(7) Diamond, S. E.; Grant, B.; Tom, G. M.; Taube, H. *Tetrahedron Lett.* **1974**, *46*, 4025.

(8) Hung, H. Y.; Chen, W. J.; Yang, C. C.; Yeh, A. *Inorg. Chem.* **1991**, *30*, 1862.

(9) Rocha, Z. N. Master Dissertation, Instituto de Química de Araraquara da UNESP, Araraquara, SP, Brazil, 1987.

(10) Naal, Z.; Tfouni, E.; Rocha, Z. N.; Benedetti, A. V. *Anais do VI SIBEE (VI Brazilian Symposium on Electrochemistry and Electroanalytical Chemistry);* Organizing Committee: São Paulo, SP, Brazil, 1988; p 3.

(11) Tfouni, E.; Rocha, Z. N.; Benedetti, A. V.; Naal, Z. Presented at the VIII Latin-American Meeting on Electrochemistry and Corrosion, Córdoba, Argentina, Oct. 10−Nov 4 1988.

(12) Naal, Z.; Benedetti, A. V.; Tfouni, E. *Anais VII SIBEE (VII Brazilian Symposium on Electrochemistry and Electroanalytical Chemistry)*; Organizing Committee: Ribeirão Preto, SP, Brazil, 1990; Vol. I, p, 66.

(13) Naal, Z.; Benedetti, A. V.; Tfouni, E. Presented at the IX Congreso Iberoamericano de Electroquímica, La Laguna, Tenerife, Spain, July 16−22, 1990.

(14) Naal, Z. Master Dissertation. Instituto de Química de Araraquara da UNESP. Araraquara, SP, Brazil, 1991.

(15) Naal, Z.; Benedetti, A. V.; Tfouni, E.; Chiericato, G.; Jr. *Anais VIII SIBEE (VIII Brazilian Symposium on Electrochemistry and Electroanalytical Chemistry);* Organizing Committee: Campinas, SP, Brazil, 1992; p 286.

(16) Naal, Z.; Tfouni, E.; Benedetti, A. V. *Polyhedron* **1994**, *13*, 133.

(17) Rocha, Z. N.; Tfouni, E. *Polyhedron* **1992**, *11*, 2375.

0020-1669/94/1333-4619$04.50/0

reported values.[18] The cyclic voltammogram of 1×10^{-3} M **I** in 1 M HAc/Ac$^-$, at pH = 4.65 (deaerated aqueous solution), shows a reversible one-electron pair of peaks with E_f = 340 mV vs Ag/AgCl,[19] corresponding to the Ru(III)/(II) process, as expected for a pentaammineruthenium complex with an unsaturated ligand.[20]

Controlled-potential electrolysis of 1×10^{-3} M aqueous solution of **I** (1 M HAc/Ac$^-$; pH = 4.65) at +0.450 V vs Ag/AgCl showed a consumption of 0.99 faraday mol^{-1}. The UV−vis spectra, recorded during electrolysis, showed decrease of the MLCT band at 408 nm and of the IL bands at 256 and 222 nm, and the appearance of bands at 390, 354, 330, and 260 nm with isosbestic points at 300 and 360 nm. As for other nitriles,[1,2,4−16] oxidation of Ru(II) is followed by hydrolysis of the coordinated nitrile to the corresponding amide. The spectrum in the 300−400 nm range of the final product is similar to those of other amide-bonded pentaammineruthenium(III) complexes.[4,8,16] Thus, is reasonable to conclude that oxidation of **I** to [Ru^{III}(NH$_3$)$_5$(2-NCpy)] (**II**) is followed by hydrolysis to [Ru^{III}(NHC(O)-2-py)] (**III**) (NHC(O)-2-py = deprotonated picolinamide). The estimated rate constant for the hydrolysis of **II** was $1.38 \times 10^{-3} \pm 0.014 \times 10^{-3}$ s^{-1}, close to $4.23 \times 10^{-3} \pm 3.6 \times 10^{-5}$ s^{-1} obtained for the 4-cyanopyridine (4-NCpy) analog, as determined by the same techniques,[21] and also close to the spectrophotometrically determined rate constant of 2.85×10^{-3} s^{-1} for the same [Ru^{III}(NH$_3$)$_5$(4-NCpy)], obtained from chemical oxidation of the Ru(II) analog.[8] In addition, the rate of hydrolysis of **II** is 100 times smaller than for 4-rcp complexes,[16] and 10^5−10^6 times smaller than analogous complexes with acetonitrile or benzonitrile.[4] As a matter of fact, examination of the literature shows that the rate of hydrolysis of the coordinated nitrile is dependent on the nature of the nitrile and the pH of the medium.[1,2,4−9,14,16]

The cyclic voltammogram of **III**, scanned right after the electrolysis of **I** and in the same solution, in the −0.800 to +0.600 V range (Figure 1) shows interesting features. When the potential sweep begins at 0.0 V and goes toward positive potentials no peak is seen. Reversing the scan at +0.600 V, now toward negative potentials, only one cathodic peak (1c) is seen at −0.372 V vs Ag/AgCl. Reversing once more the sweep, now at −0.800 V, toward positive potentials results in the appearance of two anodic peaks, at −0.192 (2a) and +0.142 V (3a) vs Ag/AgCl. These latter peak shows a corresponding cathodic peak at +0.072 V (3c) vs Ag/AgCl, with a E_f (arithmetic average) of +0.110 V vs Ag/AgCl (or +0.337 V vs SHE). Aging of the solution leads to the progressive disappearance of peak 1c and to the appearance of a pair of peaks at −0.280 and −0.216 V vs Ag/AgCl. Aged solutions do not show the pair of peaks 3a and 3c. These results indicate that the pair of peaks (3a and 3c) with E_f of +0.337 vs SHE is dependent on the reduction of **III**. The pair of peaks at −0.280 and −0.216 V vs Ag/AgCl can be assigned to the [Ru$^{III/II}$(NH$_3$)$_5$(OH$_2$)] couple,[20] and it indicates that a slow dissociation of the coordinated amide in the Ru(III) complex is taking place.

Controlled-potential electrolysis of **III** (1 M HAc/Ac$^-$; pH = 4.65) at −0.500 V, with simultaneous UV−vis spectrophotometrical monitoring, showed that upon reduction of **III**, the absorption bands of **III** are bleached, and absorption bands at 524, 398, 264, and 234 nm develop. Chemical reduction of **III** with Zn(Hg) leads to the same spectral changes. The appearance of two bands in the visible range of the spectra is highly suggestive of a *cis*-tetraammine complex.[22−25] Recent results from our laboratory[26] indicate that the reaction of [Ru^{II}(NH$_3$)$_5$(OH$_2$)] with bidentate 2-substituted pyridines and pyrazines leads to the formation of *cis*-[Ru^{II}(NH$_3$)$_4$(L)] (L = 2-substituted pyridine or 2-substituted pyrazine, with a coordinating substituent) in one step,[26] as occurs for [Ru^{II}(NH$_3$)$_5$(OH$_2$)] with 2-pyridinecarboxaldehyde.[22,23] In those cases,[22,23,26] initial coordination through the pyridine nitrogen is rapidly followed by chelation with the displacement of one cis coordinated ammonia. Specifically, reaction of **VI** with [Ru^{II}(NH$_3$)$_5$(OH$_2$)][26] or *cis*-[Ru^{II}(NH$_3$)$_4$(OH$_2$)$_2$][22,23] leads to the formation of *cis*-[Ru^{II}(NH$_3$)$_4$(NH$_2$C(O)-2-py)] (**V**). The UV−vis spectrum of **V** shows two MLCT absorption bands at 544 nm ($\epsilon = 4.15 \times 10^3$ M^{-1} cm^{-1}) and 397 nm ($\epsilon = 4.35 \times 10^3$ M^{-1} cm^{-1}) along with bands at 262 nm ($\epsilon = 12.13 \times 10^3$ M^{-1} cm^{-1}) and 222 nm ($\epsilon = 10.51 \times 10^3$ M^{-1} cm^{-1}) in 1.2 M HCl,[23] or at 524 and 393 nm (recorded in the reaction solution at pH ~ 3.0 (F$_3$CCOOH)).[26] Thus, the spectral changes observed upon the chemical or electrochemical reduction of **III** are indicative of the formation of *cis*-[Ru^{II}(NH$_3$)$_4$(NH$_2$C(O)-2-py)] (**V**).

The formal reduction potential (arithmetic average of cathodic and anodic peaks potentials) of **V**, measured from the isolated complex is 0.349 V vs SHE.[23] The cyclic voltammogram[26] of the reaction solution of **V** (in 0.1 M F$_3$CCOOH/F$_3$CCOO$^-$, at pH 3.0) shows peaks at +0.380 and +0.310 V vs SHE, with an average of +0.345 V. These data give further support to the assignment of the peaks 3a and 3c (E_f = 0.337 V vs SHE), in the cyclic voltammogram of **III**, to *cis*-[Ru^{II}(NH$_3$)$_4$(NH$_2$C(O)-2-py)] (**V**).

Reduction of amido-bonded pentaammineruthenium(III) complexes to the ruthenium(II) species is followed by linkage isomerization of the amide and/or amide aquation,[1−3,5−7,9,14,16] and thus, it is reasonable to expect similar reactions after reduction of **III** to [Ru^{II}(NH$_2$C(O)-2-py)] (**IV**). So, the present results clearly indicate that reduction of **III** to **IV** is followed by amide aquation and chelation with displacement of one cis coordinated ammonia (see Scheme 1).

The observed chelation can be compared to what happens with the 4-NCpy complex.[1,2] In this case a linkage isomerization occurs through a series of stepwise η^2-bonded Ru(II)−isonicotinamide complexes. This, in principle, should also occur for the 2-substituted isomer. However, rather than net linkage isomerization, forming the pyridyl-bonded (picolinamide)-pentaammineruthenium(II) complex, a chelated complex with a five-membered ring is formed. The chelate is formed in ~70% according to the spectra. The other 30% corresponds to aquation. The main source of aquation is from the reduction of **III**. The observed direct aquation of **III** is a slow process and thus is only a minor contributor to the total aquation.

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Supplementary Material Available: Figure 2, showing spectral changes during electrolysis of [Ru^{III}(NHC(O)-2-py)] (1 page). Ordering information is given on any current masthead page.

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(18) Clarke, R. E.; Ford, P. C. *Inorg. Chem.* **1970**, *9*, 495.

(19) The Ag/AgCl reference electrode used throughout this work has a value of −0.017 V vs SCE.

(20) Lim, H. S.; Barclay, D. J.; Anson, F. C. *Inorg. Chem.* **1972**, *11*, 1460.

(21) Rocha, Z. N.; Chiericato, G., Jr.; Tfouni, E. Unpublished results.

(22) Alvarez, V. E.; Allen, R. J.; Matsubara, T.; Ford, P. C. *J. Am. Chem. Soc.* **1974**, *96*, 7686.

(23) Alvarez, V. E. PhD. Thesis, University of California, Santa Barbara, CA, 1974.

(24) Pavanin, L. A.; Rocha, Z. N.; Giesbrecht, E.; Tfouni, E. *Inorg. Chem.* **1991**, *30*, 2185.

(25) Pavanin, L. A. PhD. Thesis, University of São Paulo, São Paulo, SP, Brazil, 1988.

(26) Paula, A. S. A.T. Master Dissertation, University of São Paulo, Ribeirão Preto, SP, Brazil, 1991.