FTIR Spectroelectrochemical Investigation of the *trans*-[Ru(NO)(dimethylglyoximate)$_2$Cl] Complex: Vibrational Characterization of the NO$^{/0}$ and Ru$^{III/II}$ Redox Couples

Izilda A. Bagatin[a]; Henrique E. Toma[a]

[a] Institute de Química - Universities de São Paulo, São Paulo, SP, Brazil

PLEASE SCROLL DOWN FOR ARTICLE

FTIR SPECTROELECTROCHEMICAL INVESTIGATION OF THE

trans-[Ru(NO)(DIMETHYLGLYOXIMATE)$_2$Cl] COMPLEX:

VIBRATIONAL CHARACTERIZATION OF THE NO$^{+/0}$ AND Ru$^{III/II}$ REDOX

COUPLES

Key words: FTIR spectroelectrochemistry, ruthenium-nitrosyl complexes, ruthenium-dioximate complexes.

Izilda A. Bagatin and Henrique E. Toma*

Instituto de Química - Universidade de São Paulo, Caixa Postal 26077
CEP 05599-970, São Paulo, SP, Brazil.

ABSTRACT

This paper deals with the spectroelectrochemical characterization of the Ru$^{III/II}$ and NO$^{+/0}$ oxidation states of the *trans*-[Ru(NO)(dmgH)$_2$Cl] complex (dmgH = dimethylglyoximate ion). The cyclic voltammograms of the complex in acetonitrile solution exhibited a reversible wave at -0.09 V *versus* SHE, and two less intense waves at 1.19 and 1.41 V. Visible-UV spectra were recorded at -0.4 and 1.5 V, however, the absorption bands collapsed into a single tail, providing little information on the redox states involved. In contrast, in the FTIR measurements at -0.4 V, the ν(NO) peak shifted from 1878 to 1855 cm^{-1}, without changing the vibrational peaks of the dmgH ligand, indicating an electrochemical process involving the NO$^{+/0}$ redox couple. At 1.5 V, the changes in the vibrational peaks of the NO and dmgH ligands indicated a redox process associated with the Ru$^{III/II}$ redox couple. The existence of an open and a cyclic hydrogen

bridged configuration was proposed, in order to explain the occurrence of two electrochemical waves at positive potentials.

INTRODUCTION

The chemistry of nitrosyl complexes has been a subject of great interest, particularly after the recognition of the key role of NO in biological systems.[1-2] In general, the behavior of the nitrosyl complexes is modulated by the non-innocent character of the NO ligand, which can vary from NO^+ to NO^o and NO^-, depending on the nature of the metal ion. Typical π-electron donors, such as ruthenium(II) and low-spin iron(II) complexes, usually prefer NO^+, because of its strong π-electron acceptor character, yielding very stable complexes. As a consequence, the redox potentials for $Ru^{III/II}$-nitrosyl complexes can exceed 2 V, and the E^o of reduction of the NO^+ ligand will vary according to the nature of the complex.[3,4]

The present work focuses on the spectroelectrochemical characterization of the $Ru^{III/II}$ and $NO^{+/o}$ oxidation states of the trans-[Ru(NO)(dmgH)$_2$Cl] complex, in acetonitrile solution. The use of visible-uv spectroelectrochemical techniques was attempted, but with little success, because of the poor definition of the electronic spectra obtained at several applied potentials. For this reason, a parallel FTIR spectroelectrochemical investigation was carried out for this system.

EXPERIMENTAL

[Ru(NO)(dmgH)$_2$Cl] was prepared according to the procedure previously reported in the literature.[5-7]

Cyclic voltammetry was carried out using a Princeton Applied Research Corp. model 173 potentiostat and a model 175 universal programmer. A platinum working electrode was employed for the measurements, and the reference electrode was Ag/Ag^+ (0.01 mol dm^{-3}) in 0.1 mol dm^{-3} tetraethylammonium perchlorate. The auxiliary electrode was a platinum wire. All potentials were referred to SHE by adding 0.503 V.

Visible-UV spectroelectrochemical measurements were carried out by using a Hewlet-Packard 8452-A diode-array spectrophotometer in parallel with the potentiostat. A three electrode system was designed for a rectangular quartz cell of 0.025 cm optical

pathlength. A gold minigrid was used as a transparent working electrode, in the presence of a small Ag/Ag^+ reference electrode and a Pt auxiliary electrode. Spectroelectrochemical measurements in the infrared region were carried out by using a Midac FTIR spectrometer in parallel with the potentiostat. The electrochemical cell consisted of a home made rectangular Kel-F cuvette with a 5 mm horizontal hole sealed with two IRTRAN windows, providing an internal 0.010 cm optical pathlength. The electrodes were the same ones employed in visible-ultraviolet spectroelectrochemistry.

RESULTS AND DISCUSSION

The trans-[Ru(NO)(dmgH)$_2$Cl] complex exhibits two dioximate ligands in a planar macrocyclic arrangement, and two axial NO^+ and Cl^- ligands in a linear configuration. The macrocyclic structure is kept by intramolecular hydrogen bonding, displaying,[5] however, two oxime (N-O) distances: 1.319 and 1.371 Å. The proton lies closer to the oxygen atom of the long N-O bond.

Typical cyclic voltammograms for the nitrosyl complexes can be seen in Fig.1. By starting at 0.5 V and scanning the potential in the negative direction, a reversible wave can be detected at $E_{1/2}$ = -0.09 V versus SHE, preceded by a weak shoulder at 0.10 V, ascribed to an adsorption process. The voltammetric response was consistent with a reversible, monoelectronic electron transfer process. By scanning the potential in the positive direction, two nearly reversible waves can be observed at 1.19 and 1.41 V, exhibiting a sum of intensities equivalent to the single wave observed at -0.09 V.

The electronic spectrum of the trans-[Ru(NO)(dmgH)$_2$Cl] complex (Fig. 2) consists of a relatively weak absorption band at 430 nm (ε = 1100 mol dm^{-3} cm^{-1}) ascribed to the Ru^{II}→NO$^+$, d_π→p$_\pi$* charge-transfer transition, and a more intense band at 345 nm (ε = 5300), ascribed to the Ru^{II}→dmgH, d_π→p$_\pi$* charge-transfer transition.[5-7] A strong absorption can also be observed around 250 nm. This band has been tentatively assigned to a π→π* transition in the conjugated ligand.[5] By applying negative potentials, e.g. -0.4 V, the low energy electronic bands become less discernible, while the high energy band is shifted to 280 nm (Fig. 2.a). At positive potentials, e.g. 1.40 V, the absorption bands collapse into a single tail, as one can see in Fig. 2.b. Therefore, the assignment of the redox states based on visible-ultraviolet spectroelectrochemistry becomes very risky, if not impossible.
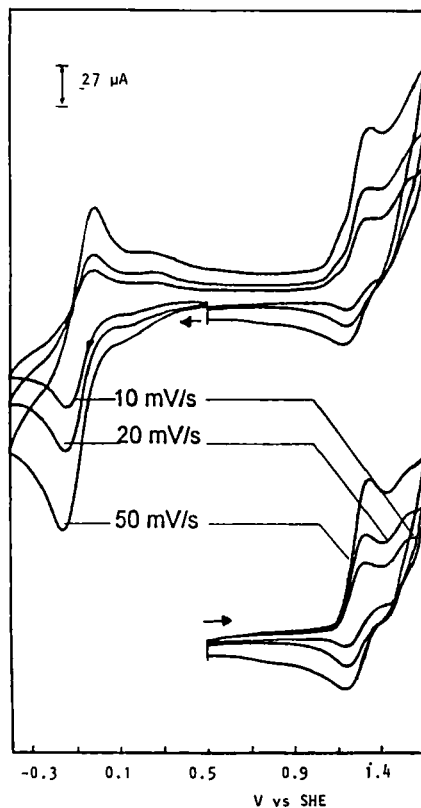
Fig. 1: Cyclic voltammograms of the *trans*-[Ru(NO)(dmgH)$_2$Cl] complex (5 mmol dm^{-3}) in acetonitrile solution, 0.10 mol dm^{-3} tetraethylammonium perchlorate, at several scan rates.

The spectroelectrochemical changes can be monitored by means of the FTIR technique, using IRTRAN windows. Fortunately, the strong absorption bands of the acetonitrile solvent do not mask the spectral regions of interest, i.e., 2100-1700 cm^{-1} and 1350-1150 cm^{-1}, associated with the ν(N≡O) and the ν(CC + NO) stretching frequencies of the axial and equatorial ligands, respectively. Typical FTIR spectroelectrochemical changes in these two regions, at negative (-0.4 V) and positive (1.40 V) applied potentials, can be seen in Fig. 3.

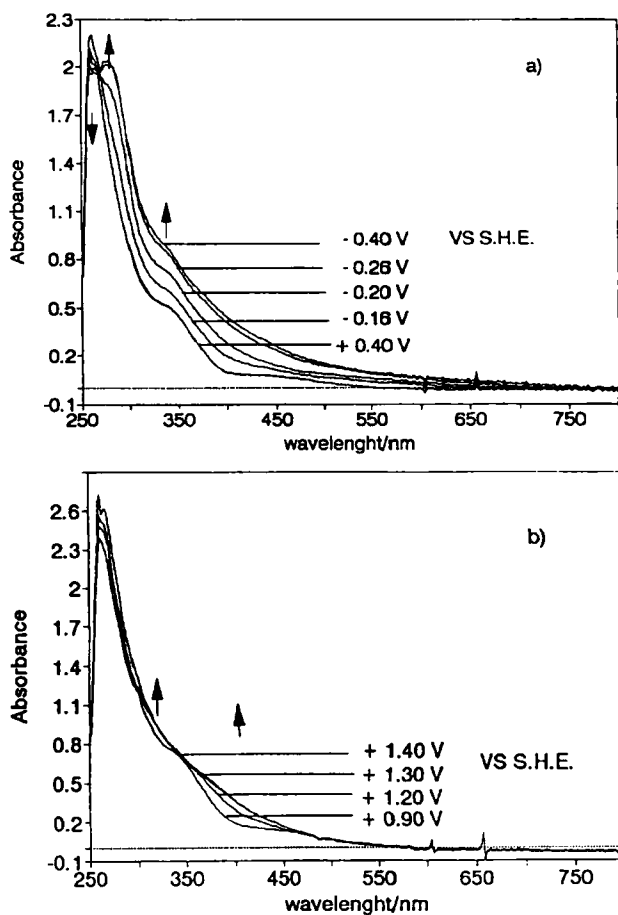Fig. 2: Visible-UV spectroelectrochemistry of the *trans*-[Ru(NO)(dmgH)$_2$Cl] complex (5 mmol dm^{-3}) in acetonitrile solution, 0.10 mol dm^{-3} tetraethylammonium perchlorate: a) reduction process at negative potentials, b) oxidation process at E > 1.2 V.
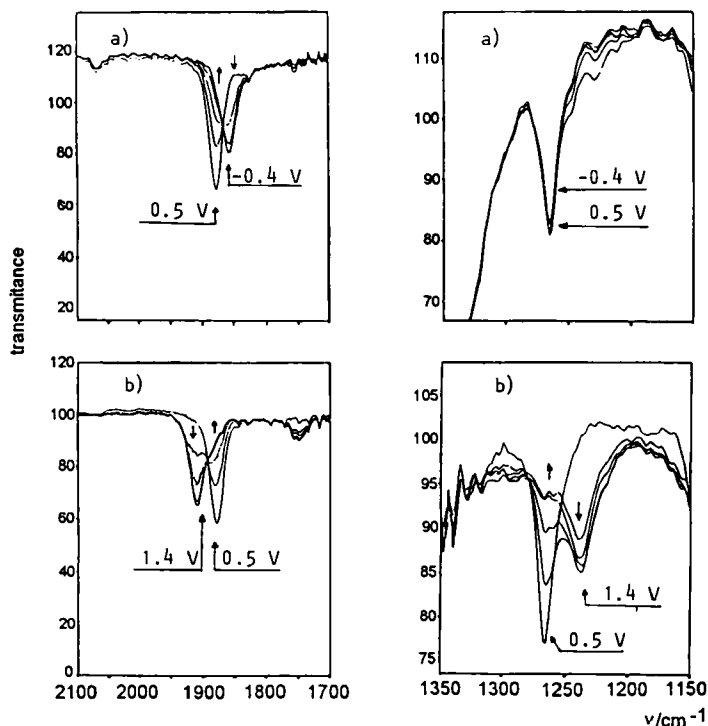
Fig. 3.   Successive FTIR spectroelectrochemical measurements for the *trans*-
[Ru(NO)(dmgH)$_2$Cl] complex (5 mmol dm^{-3})   in acetonitrile solution, at a)
-0.4 V and b) + 1.4 V, in the presence of 0.10 mol dm^{-3} lithium perchlorate.

At -0.4 V, the $v(N\equiv O)$ vibrational peak at 1878 cm^{-1}, in the starting complex,
shifts to 1855 cm^{-1}, exhibiting an isosbestic point characteristic of a well behaved
process (Fig. 3.a). The $v(CC + NO)$ vibrational peak at 1264 cm^{-1} remains practically
unchanged, indicating that the redox process is localized at the axial   N$\equiv$O   ligand.
Therefore, the reversible electrochemical wave at -0.09 V can unequivocally be assigned
to the formal NO$^{+/o}$ redox couple.

At 1.4 V, the $v(N\equiv O)$ vibrational peak shifts from 1878 cm^{-1} to 1906 cm^{-1},
while $v(CC + NO)$ shifts from 1264 to 1236 cm^{-1} (Fig. 3.b), with no isosbestic point. The

simultaneous changes in the vibrational spectra of the axial and equatorial ligands observed at positive potentials can only be explained by the oxidation of the ruthenium(II) ion.

It should be noticed that the binding of NO^* to π-backbonding metals, always leads to a decrease of $v(NO)$, e.g., from 2200 cm^{-1} (for the free NO^* ion) to less than 1900 cm^{-1}, due to the population of the π^* antibonding orbitals. The electrochemical reduction of the NO^* ligand also leads to a decrease of $v(NO)$, for similar reasons. In contrast, the oxidation of the Ru^{II} ion can have a dramatic effect in the vibrational frequencies of the axial and equatorial ligands, since the π-backbonding properties practically disappear in the Ru^{III} state. As a consequence, $v(NO)$ is shifted to higher frequencies, reflecting an increase in the NO^* character of the ligand.

The lack of isosbestic points in the region of 1350 to 1150 cm^{-1} (Fig. 3.b) indicates that the oxidation of the Ru^{II} complex involves more than a single species. This observation is consistent with the detection of two electrochemical waves at 1.19 and 1.41 V in the cyclic voltammograms of Fig. 1. Since there are two non-equivalent N-O (oxime) bonds in the complex, one of the oxygen atoms should be weakly bound to the hydrogen, and in solution, an equilibrium between the cyclic and open structures can take place. Such a hypothesis is corroborated by the fact that the trans-[Ru(NO)(dmgH)$_2$Cl] complex can add a second proton,[6] yielding two vicinal N-OH groups. Presumably, if the short distance N-O bonding is available for protonation, it can also exist in an open structure in equilibrium with the cyclic hydrogen bridged species. These two forms would be responsible for the the electrochemical waves observed at 1.19 (open structure) and 1.41 V (hydrogen bridged structure) in the cyclic voltammograms. This type of equilibrium, involving a short N-O and a long N-OH group, can be compared with a nitroso-oxime equilibrium previously reported in the literature.[8]

REFERENCES

1.   Traylor, T. G., Sharma, V. S., Biochemistry, 1992; 31: 2847.

2.   Clarke, M. J., Gaul, J. B., Struc. Bond., 1993; 81: 147.

3.   Callahan, R. W., Meyer, T. J., Inorg. Chem., 1977; 16: 574.

4.   Pipes, D. W., Meyer, T. J., Inorg. Chem., 1984; 23: 2466.

5.   Muller, J. G., Takaeuchi, K. J., Inorg. Chem., 1990; 29: 2185.

6.   Sczepura, L. F., Muller, J. G., Bessel, C. A., See, R. F., Janik, T. S., Churchill, M. R., Takeuchi, K. J., Inorg. Chem., 1992; 31: 859.

7.   Bagatin, I. A., Toma, H. E., Trans. Metal Chem., 1996; in press.

8.   Toma, H. E., Santos, P. S., Inorg. Chem., 1987; 26: 3218.