

1999-08-28

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### Recommended Citation

Shengpei Chen, Shigang Sun. In situ FTIRS Studies of the Electrochemically Induced Coupling of Osmium Nitrido Species in Acetonitrile[J]. *Journal of Electrochemistry*, 1999 , 5(3): Article 8.

DOI: 10.61558/2993-074X.3184

Available at: <https://jelectrochem.xmu.edu.cn/journal/vol5/iss3/8>

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## In situ FTIRS Studies of the Electrochemically Induced Coupling of Osmium Nitrido Species in Acetonitrile

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The search for inorganic systems that can cleave N-N triple bond under mild conditions is an important subject. It is well known that the metal nitrido (M-N) complexes are possible intermediates in nitrogen fixation<sup>[1]</sup> and in the reduction of nitrite to ammonia<sup>[2,3]</sup>. Recently, these complexes have received considerable attention<sup>[4-9]</sup> for their intriguing photochemical and electrochemical properties. Among different high valence metal nitrido complexes, some osmium(VI) nitrido species are stable enough to be isolated<sup>[4-10]</sup>, demonstrating that the study on this class of complexes becomes feasible. Meyer and co-workers<sup>[4]</sup> have reported the electrochemical interconversion between  $[\text{Os}^{\text{VI}}(\text{N})(\text{terpy})\text{Cl}_2]^+$  and  $[\text{Os}^{\text{II}}(\text{NH}_3)(\text{terpy})\text{Cl}_2]$  (terpy = 2,2':6',2''-terpyridine). Recently, Che et al. have reported the isolation of an osmium(VI) nitrido complex  $[\text{Os}^{\text{VI}}(\text{N})(\text{NH}_3)_4\text{Cl}]^{2+}$  through oxidation of  $[\text{Os}^{\text{III}}(\text{NH}_3)_5\text{Cl}]^{2+}$ <sup>[8]</sup>. Photolysis of an acetonitrile solution of  $[\text{Os}^{\text{VI}}(\text{N})(\text{NH}_3)_4](\text{CF}_3\text{SO}_3)_3$  in the presence of an organic electron donor resulted in the formation of the dinitrogen-bridged osmium (II, III) dimer  $\{[\text{Os}(\text{NH}_3)_4(\text{CH}_3\text{CN})_2(\text{N}_2)]\}^{5+}$ <sup>[7,8]</sup>. It has been found that the one-electron reduced  $\text{Os}^{\text{V}}\text{-N}$  reacts with the starting  $\text{Os}^{\text{VI}}\text{-N}$  to yield the  $\mu$ -dinitrogen  $\text{Os}^{\text{II}}\text{-N-N-Os}^{\text{III}}$  complex with a second order rate constant of  $(3.75 \pm 0.30) \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  in acetonitrile at room temperature<sup>[8]</sup>. Recently, Taube and co-workers<sup>[11]</sup> reported that the electrochemical reduction of  $[\text{Os}^{\text{VI}}(\text{N})(\text{NH}_3)_4]^{3+}$  in acetonitrile resulted also in similar N-N coupling reaction.

To our knowledge there is no report, up to now, concerning the in situ FTIR spectroscopic studies of direct coupling of nitrogen atoms of metal nitrido compounds. In the present study, the potential cycling was used to induce the formation of a  $\mu$ -dinitrogen complex through electrochem-

Received 31 March 1999; Supported by the Hong Kong Polytechnic University Foundation

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ical reduction of  $[\text{Os}^{\text{VI}}(\text{N})(\text{NH}_3)_4](\text{CF}_3\text{SO}_3)_3$  in acetonitrile (donor). The intermediates and products of the reaction on Pt electrode was investigated by means of in situ FTIRS and UV/Vis spectroscopy.

## 1 Experimental

The UV/Vis spectra were obtained on a Shimadzu UV-240 spectrophotometer. Electrochemical measurements were performed by using a BAS model 130w potentiostat system. A conventional electrochemical cell of three-electrodes was used. The working electrode used was either a plane platinum electrode (Pt) or a glassy carbon electrode (GC). The exposed apparent area was approximately  $0.502 \text{ cm}^2$  for the Pt electrode and  $0.283 \text{ cm}^2$  for the GC electrode. A platinized platinum electrode was used as the auxiliary electrode. A Ag/AgNO<sub>3</sub> (0.1 mol/L in acetonitrile) electrode served as the reference electrode, and all potentials reported in this paper were referred to this Ag/AgNO<sub>3</sub> electrode scale. The potential sweep rate was at 100 mV/s for all experiments. The experiments were carried out at room temperature.

Before measurements, Pt or GC electrode was polished sequentially with 1.0, 0.3 and 0.05  $\mu\text{m}$  -alumina (Linde)/water slurries on a microcloth until a shiny, mirror-like finish was obtained. The electrode was then sonicated for 2 min in Millipore water supplied from a Mili-Q Lab system. Finally, the electrode was washed with acetone and acetonitrile respectively.

The experiments of in situ FTIR spectroscopy were carried out on a Nicolet 750 FTIR apparatus equipped with a Spectra-tech reflection accessories. The spectrum was defined as

$$R/R = [R(E_S) - R(E_R)] / R(E_R) \quad (1)$$

where  $R(E_S)$  and  $R(E_R)$  represent the single beam spectra of IR reflection at  $E_S$  and  $E_R$ , respectively. The  $R/R$  represents the resulting spectrum, in which the negative-going bands indicate that more IR energy is absorbed at  $E_S$  than at  $E_R$  due to the formation of intermediate or product species, while the positive-going bands denote a greater IR absorption at  $E_R$  than that at  $E_S$  corresponding to the consumption of reactant or other species.

## 2 Results and Discussion

### 2.1 Cyclic voltammetric (CV) properties of electrochemically induced coupling of osmium nitrido compounds at a GC electrode

Fig. 1 shows the typical cyclic voltammograms of GC electrode in a solution containing about 2 mM  $[\text{Os}^{\text{VI}}(\text{N})(\text{NH}_3)_4](\text{CF}_3\text{SO}_3)_3$  in acetonitrile with 0.1 mol tetrabutylammonium hexafluorophosphate (TBAH) as supporting electrolyte. The measurement started at 0.4 V, and the electrode potential was cycled between 0.4 and -1.0 V. It can be observed from Fig. 1 that, at the first cycle, the reduction current is started to appear near -0.45 V in the negatively going potential sweep (N GPS), and is increasing along with the decrease of potential. One reduction current peak near -0.62 V (peak I) is observed, which can be assigned to the reduction of Os(VI) to Os(V)<sup>[11]</sup>. Upon the reverse of potential scan, i. e. in the positively going potential sweep (P G

PS), one oxidation current peak (peak II) at around 0.15 V is appeared. Worthy of mention is that there is a great difference consisting not only in the current measured in the potential range between 0.4 and -0.4 V for the first and the second cycle, but also in the appearance of a new reduction current peak (peak III) at about 0.05 V in the N GPS. Following the increase of the number of potential cycling, the current of peak I is decreased quickly, while the current of both peak II and peak III is increased progressively. The potential separation between peak II and III is about 100 mV, that is close to the theoretical value expected for a quasi-reversible redox process. We attribute the behavior to the formation of a dinitrogen-bridged species, because the  $E_{1/2}$  is identical to that reported in the literature<sup>[11]</sup>.

Suggesting that the coupling is much more efficient when Os(VI) is reduced, the first product of the reduction is presumably Os(V). The above results illustrated that the reduction process associated to peak I is irreversible, because the oxidation wave of the Os(VI)/Os(V) couple cannot be observed. It appears also that the chemical reaction following the reduction of  $[\text{Os}^{\text{VI}}(\text{N})(\text{NH}_3)_4]^{3+}$  is a very fast reaction, since the amplitude of the reduction peak at -0.62 V diminished quickly, due to the N-N coupling of two osmium nitrido species, i. e., the electrochemically generated  $\text{Os}^{\text{V}}\text{N}$  species reacts with the starting  $\text{Os}^{\text{VI}}\text{N}$  to give  $\mu$ -dinitrogen Osmium species, which lead to the decrease of the  $[\text{Os}^{\text{VI}}(\text{N})(\text{NH}_3)_4]^{3+}$ . Most importantly,  $\mu$ -dinitrogen mixed-valence osmium species deposited on the GC electrode surface block the active sites of the GC surface and inhibit the further reduction of  $[\text{Os}^{\text{VI}}(\text{N})(\text{NH}_3)_4]^{3+}$  species. There is a distinctive change in the GC electrode surface before and after the potential cycling, for that a surface complex of dark blue-green color was observed on the GC electrode after potential cycling between 0.4 and -1.0 V for a long time (about 0.5 hr). Moreover, with a change in color of the solution from yellow to green was also observed.

The resulting UV-visible spectrum shows an absorption maximum at ca 720 nm. The UV-visible spectrum resembles those of  $\mu$ -dinitrogen osmium (III, II) complexes<sup>[5, 13, 14]</sup>, i. e., with the 720 nm band assignable to d-d transition within molecular orbitals delocalized over both metal centers. Thus, it is likely confirmed that the N-N coupling has occurred and a  $\mu$ -dinitrogen mixed-valence osmium species has formed. Similar cyclic voltammetric results were obtained on a

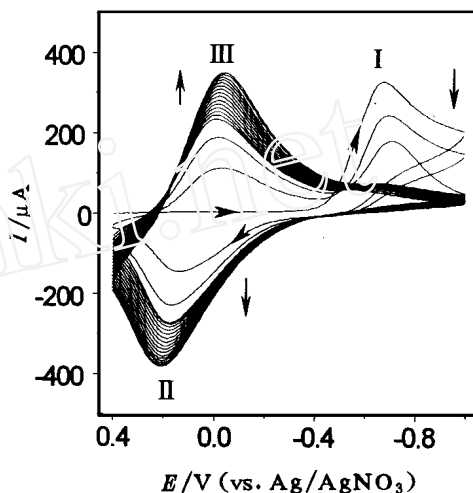


Fig. 1 Cyclic voltammograms of ca. 2m mol  $\text{L}^{-1}$   $[\text{Os}^{\text{VI}}(\text{N})(\text{NH}_3)_4](\text{CF}_3\text{SO}_3)_3$  in  $\text{CH}_3\text{CN}$  with 0.1 mol  $\text{L}^{-1}$  TBAH as supporting electrolyte. Working electrode: glassy carbon (GC). Scan rate: 100  $\text{mVs}^{-1}$

Pt electrode. Though the current density on a Pt is much higher than that on a GC electrode, there is no new current peaks appearing in the potential range. The above results demonstrated that the electrochemically induced coupling of osmium nitrido species on Pt and GC electrodes may undergo the same reaction mechanism.

## 2.2 Studies of the role of $\mu$ -dinitrogen mixed valence complexes on Pt surface using in situ FTIR spectroscopy

In order to investigate further the electrochemically induced coupling of osmium nitrido species in acetonitrile on Pt electrode, the surface of Pt electrode was cleaned by potential cycling between 1.0 and -1.0 V in acetonitrile solution until a stable voltammogram was recorded. The electrode was then taken out from the cell, and transferred to the IR cell. Repetitive potential scanning between 0.4 and -1.0 V was then carried out in acetonitrile solution containing about 2 mM  $[\text{Os}^{\text{VI}}(\text{N})(\text{NH}_3)_4](\text{CF}_3\text{SO}_3)_3$  until another stable voltammogram was recorded. It is interesting to note that a dark blue-green complex was also produced on the surface of Pt electrode. The in situ FTIR spectra between 1 800 and 2 200  $\text{cm}^{-1}$  shown in Fig. 2a were obtained on the Pt electrode in solution containing 2 mmol/L  $[\text{Os}^{\text{VI}}(\text{N})(\text{NH}_3)_4](\text{CF}_3\text{SO}_3)_3$ , with  $E_R$  at 0.4 V and  $E_S$  varying from 0.0 to -1.0 V. When  $E_S < 0.2$  V, we can observe a positive-going band around 2 019  $\text{cm}^{-1}$  (Fig. 2a), which can be assigned to vibration of (N-N) mode of the  $\mu$ -dinitrogen moiety in this dark blue-green complex. The IR features are similar to those of  $\mu$ -dinitrogen mixed-valence osmium species [III, II] complex. Richardson and co-workers have report-

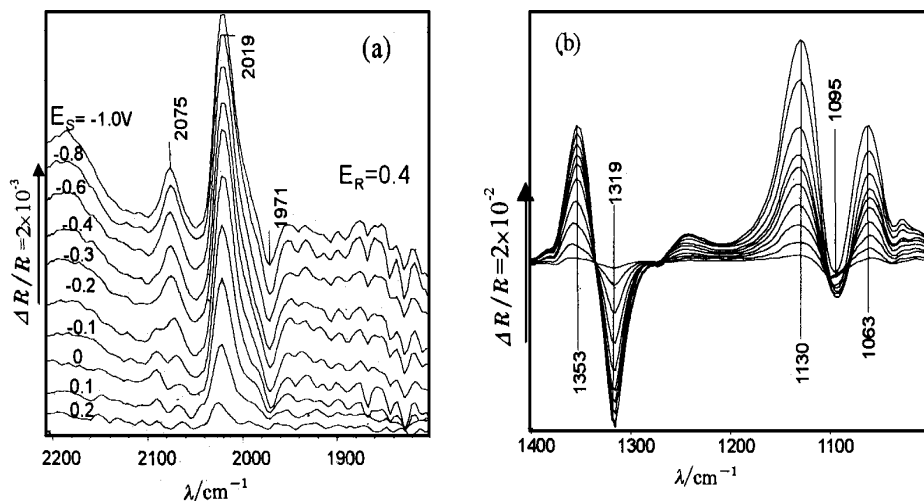


Fig. 2 MSFTIR spectra for ca. 2 mmol L<sup>-1</sup>  $[\text{Os}^{\text{VI}}(\text{N})(\text{NH}_3)_4](\text{CF}_3\text{SO}_3)_3$  in  $\text{CH}_3\text{CN}$  with 0.1 mol L<sup>-1</sup> TBAH. Working electrode: platinum (Pt).  $E_R$  at 0.4 V, and  $E_S$  is indicated for each spectrum. The wavenumber range is between 2 200 and 1 800  $\text{cm}^{-1}$  (a), and between 1 000 and 1 400  $\text{cm}^{-1}$  (b)

ed<sup>[12]</sup> that the particular peculiar stability of the osmium [ III, II ] state is reflected also in the frequency of N-N stretching vibrational mode, which was registered as lower than that of the (II, II) stage (1990 and 2 010 cm<sup>-1</sup>, respectively; both in aqueous solution). The intensity of this band increased with the decrease of E<sub>s</sub> in this potential range. When E<sub>s</sub> = 0.0 V, a new negative-going band at about 1 971 cm<sup>-1</sup> began to appear, indicating the production of μ-dinitrogen osmium [ II, II ] complex. The intensity of the band around 2 019 cm<sup>-1</sup> decreased while that of the band at about 1970 cm<sup>-1</sup> increased. Moreover, another new positive-going band near 2 075 cm<sup>-1</sup> starts to appear when the potential E<sub>s</sub> was below - 0.2 V, which may indicate the presence of osmium [ III, III ] state unit. On further decrease of the E<sub>s</sub> values, the intensity of IR bands corresponding to osmium [ III, II ] and [ III, III ] species decreased while that of [ II, II ] species increased.<sup>[11,12,13,15.]</sup>

The above results indicates that there are probably three types of μ-dinitrogen mixed-valence osmium species [OsNNOs] unit such as [ III, III ], [ III, II ] and [ II, II ], co-existed at the Pt surface under these conditions.

Fig. 2 (b) shows the spectra in the wavenumber range between 1 000 and 1 400 cm<sup>-1</sup>. Five strong bands appeared at around 1 063, 1 094, 1 130, 1 317 and 1 352 cm<sup>-1</sup>, which could be assigned respectively to the stretching vibration of Os-N groups, the stretching vibration of CF<sub>3</sub> groups, the stretching vibration of S=O groups and the stretching vibration of NH<sub>3</sub> groups<sup>[4,9,12]</sup>. It can be seen that the intensity of the positive-going band at 1 063 cm<sup>-1</sup> (Os<sup>VI</sup>N) is increasing with the decrease of E<sub>s</sub> in this potential range, while that the negative-going band at 1 094 cm<sup>-1</sup> (Os<sup>V</sup>N) decreases at first and then reaches a constant value, which may indicate the facts that the Os<sup>VI</sup>N is consumed continuously and the intermediate Os<sup>V</sup>N is maintained at a stationary concentration during the process.

### 3 Conclusions

In this communication, the electrochemical cyclic voltammetry, UV/Vis and in situ FTIR spectroscopy were used to study the electrochemically induced coupling of osmium nitrido species on GC and Pt electrode in a solution containing about 2 mmol L<sup>-1</sup> [Os<sup>VI</sup>(N)(NH<sub>3</sub>)<sub>4</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> in acetonitrile. The results demonstrated that the N-N coupling can occur between [Os<sup>VI</sup>(N)(NH<sub>3</sub>)<sub>4</sub>]<sup>3+</sup> and [Os<sup>V</sup>(N)(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> species generated at the electrode. It is interesting to note that the surface of Pt electrode have produced a dark blue-green complex. As Os<sup>V</sup>N is a highly reactive species, trace quantity of protons in the solution would compete effectively with the Os<sup>VI</sup>N

N and suppress the dimerization reaction. This can probably explain the formation of small amount of μ-dinitrogen species. It has revealed for the first time, by using in situ FTIR spectroscopy, that the IR absorption of the (N-N) mode of the μ-dinitrogen osmium [ III, II ] and [ II, II ] complex yields positive-going band at around 2 019 cm<sup>-1</sup> and negative-going band near 1 971 cm<sup>-1</sup>, respectively. The results provided new insights in understanding the mechanism of

the coupling reaction  $[\text{Os}^{\text{V}} \text{N}] + [\text{Os}^{\text{VI}} \text{N}] \rightleftharpoons [\text{Os}^{\text{II}} \text{N} \text{N} \text{Os}^{\text{III}}]$ .

**Key words** In situ FTIR spectroscopy, N-N coupling, Osmium nitrido complex, Glassy carbon, Pt electrode

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# 乙腈溶液中钷氮化合物电化学诱导桥氮偶联过程的原位 FTIR 反射光谱研究

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**摘要** 采用原位红外反射光谱 (in-situ FTIRS) 结合紫外可见光谱 (UV/Vis) 和电化学循环伏安技术 (CV), 研究了  $[\text{Os}^{\text{VI}}(\text{N})(\text{NH}_3)_4](\text{CF}_3\text{SO}_3)_3$  的电化学诱导桥氮偶联过程. 首次在 Pt 电极上检测到桥氮混合价钷物种  $[\text{Os}^{\text{N}}-\text{N}-\text{Os}]$  及其随电位的变化过程. 在约  $2\text{ mol/L } [\text{Os}^{\text{VI}}(\text{N})(\text{NH}_3)_4](\text{CF}_3\text{SO}_3)_3 + 0.1\text{ mol/L TBAH}$  的乙腈溶液中, 选取  $0.4 \sim -1.0\text{ V}$  电位区间  $100\text{ mV/s}$  扫描速度, 对 Pt 或 GC 电极进行电化学循环伏安处理, 处理后的电极表面均可积累一层深绿色的沉积物, 表明电化学诱导 N-N 偶联效应已在电极上发生, 并形成了混合价桥氮络合物. 同时, 在上述过程中所生成的混合价钷氮物种, 有可能较强地吸附在电极表面, 且形成一定厚度的表面层, 从而减缓了体系中  $\text{Os}^{\text{VI}}-\text{N}$  物种在电极上的继续还原. 同时可以看到, 随着 CV 的不断进行, 溶液颜色将逐渐地由黄变绿. 经过长时间 (约  $0.5\text{ h}$ ) 循环伏安连续扫描后的实验溶液和电极表面深兰绿色沉积物的水溶液的 UV 检测结果, 均可观察到位于  $720\text{ nm}$  附近的紫外可见光谱吸收峰, 可指认为络合中心 Os 离子的 d-d 跃迁过程. 在  $1800 \sim 2200\text{ cm}^{-1}$  区间的原位红外反射光谱图上 (图 2a), 给出三个较强的 IR 吸收峰, 分别位于  $2075\text{ cm}^{-1}$  和  $2020\text{ cm}^{-1}$  的正向峰以及位于  $1971\text{ cm}^{-1}$  的负向峰, 可指认为钷氮偶联的混合价物种  $[\text{Os}^{\text{N}}-\text{N}-\text{Os}]$ , 价态分别为 +6, +5 和 +4 价. 随着电位负移, 其吸收强度逐渐增大, 当电位低于  $-0.8\text{ V}$  以后, 谱峰趋于稳定. 另外, 在  $1000 \sim 1400\text{ cm}^{-1}$  区间的原位红外反射光谱图中, 观察到 5 个很强的红外吸收谱峰, 分别位于  $1063, 1094, 1130, 1317$  和  $1352\text{ cm}^{-1}$ . 其中  $1063\text{ cm}^{-1}$  可指认为  $\text{Os}^{\text{VI}}-\text{N}$ , 正向峰表示物种随着电位负移而消耗;  $1094\text{ cm}^{-1}$  为  $\text{Os}^{\text{V}}-\text{N}$ , 负向峰意味着物种生成;  $1130\text{ cm}^{-1}$  为 S=O 和 C-F 的叠加;  $1317\text{ cm}^{-1}$  为  $\text{NH}_3$  中的 N-H;  $1352\text{ cm}^{-1}$  为 C-F 的另一特征吸收谱峰. 随着电位负移, 谱峰强度逐渐增大. 其中可指认为  $\text{Os}^{\text{VI}}-\text{N}$  ( $1063\text{ cm}^{-1}$ ) 的谱峰强度, 随着电位负移一直在增大, 说明随着电位负移,  $\text{Os}^{\text{VI}}-\text{N}$  不断被消耗; 而指认为  $\text{Os}^{\text{V}}-\text{N}$  ( $1094\text{ cm}^{-1}$ ) 的谱峰强度, 随着电位负移起初略有增大, 后来却几乎不变, 说明体系中所生成中间体 ( $\text{Os}^{\text{V}}-\text{N}$ ) 的浓度在一定的范围内保持稳定. 综上所述表明: 在电化学诱导偶联过程中, 可能经历多种中间物种的过程. 这为进一步深入研究  $[\text{Os}^{\text{VI}}(\text{N})(\text{NH}_3)_4](\text{CF}_3\text{SO}_3)_3$  在乙腈溶液中的电化学诱导偶联过程, 探讨其中间体的稳定性和反应机理提供了有益的实验数据.

**关键词** 原位 FTIR 反射光谱, 桥氮偶联, 钷氮络合物, 玻碳, 铂电极