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Another Example of a Rare Reaction of Coordinated Nitro Ligand to Give Monooxygen Ligand. From trans-[Ru(NO_2)$_2$(py)$_4$] to trans-[Ru(ONO)(O)(py)$_4$]$^+$

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trans-[Ru(NO_2)$_2$(py)$_4$] is oxidized chemically to give trans-[Ru(ONO)(O)(py)$_4$]$^+$, via the formation of a precursor species, trans-[Ru(NO_2)(H_2O)(py)$_4$]$^+$. The process was confirmed by electrochemical investigations.

We have reported a novel oxidation reaction where the complexes with monooxygen ligand are formed selectively by different reaction mechanisms: from trans-[Ru^{II}Cl(NO_2)(py)$_4$] (**1**) to trans-[Ru^{IV}Cl(O)(py)$_4$]$^+$ (**2**) and from trans-[Ru^{II}(NO_2)(H_2O)(py)$_4$]$^+$ (**3**) to trans-[Ru^{IV}(ONO)(O)(py)$_4$]$^+$ (**4**).1,2) Our continuing research has revealed that the same nitrito oxo complex of Ru(IV) **4** is also obtainable even by the oxidation of trans-[Ru^{II}(NO_2)$_2$(py)$_4$] (**5**), but through a different process from those mentioned above. The present paper reports on the oxidation process of **5** , which gives **4** , as a further example of a study of the rare reaction of a coordinated nitro ligand. The result gives clear evidence that the conversion process of (XRu^{II}NO_2) moiety (X=Cl, NO_2) depends on the disintegration mode of the transient dimeric intermediate species, ({X(py)$_4$RuNO(O)N(O)ORu(py)$_4$X}$^{2+}$),3) which is involved in the present reaction.

When **5** reacts with NaClO, used as an oxidant, **4** is formed as a final product (as identified by analysis and IR spectra). Under rather mild conditions, we also found that **5** gave a brown material which is believed to be **3** , based on the observation of IR spectra (though **3** was analytically impure),1) at a stage before **4** was formed. This result suggests that at least the following two reaction steps are operating in the chemical oxidation of **5** : the first step gives **3**, and it undergoes a further conversion into **4**.

The conversion process was proved by both cyclic voltammetry and coulometry, which were carried out at various temperatures. Cyclic voltammograms of the complex (in MeCN, Fig. 1A) displayed a chemically irreversible oxidation wave at 0.52 V ($[Ru(NO_2)_2(py)_4]^{+/o}$), whose Nernstein and diffusion controlled nature could be confirmed. On multiple scanning, small cathodic peaks, due to $[RuNO(NO_2)(py)_4]^{2+/+/o}$, were observed at -0.14 and -1.00 V. The controlled potential electrolysis of the solution beyond 0.52 V (n=1 by coulometry) showed that the shapes of two waves of $[Ru^{II}(NO^+)(NO_2)(py)_4]^{2+}$ developed as the electrolysis progressed. Appearance of the nitrosyl species proves that the conversion does occur through the dimeric intermediate process proposed for the oxidation of **1** to give **2** (see Eqs. 1-4).[1] Another new wave (whose Epa is consistent with that of $[Ru(NO_2)(H_2O)(py)_4]^{2+/+}$) appeared at 0.81 V during the period; it then developed (Fig. 1B). The cyclic voltammetry was carried out at -40 °C. The one-electron oxidation wave, observed for $[Ru(NO_2)_2(py)_4]^{+/o}$ at 0.52 V, was still irreversible even at this low temperature, and gave two new small reduction peak at 0.35 and -0.05 V, in addition to the waves of $[Ru(NO)(NO_2)(py)_4]^{2+/+/o}$. Both peaks can best be explained as due to isomerized species of Ru(III), $[Ru(ONO)(NO_2)(py)_4]^{+/o}$ and $[Ru(ONO)_2(py)_4]^{+/o}$, which are essential species for the formation of the dimeric intermediate consisting of nitro and nitrito com-

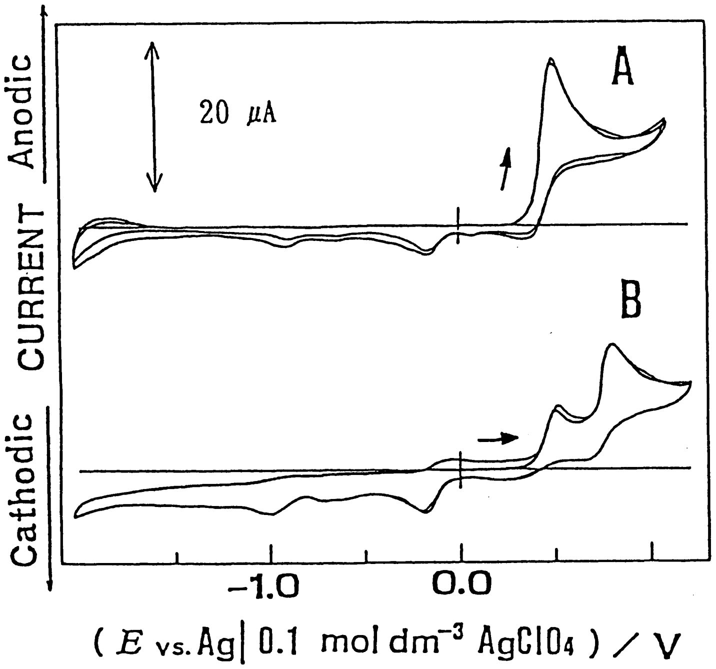


Fig. 1. Cyclic voltammograms of trans-$[Ru(NO_2)_2(py)_4]$ (0.08 mmol dm^{-3} in CH_3CN at 25 °C stationary Pt electrode), Et_4NClO_4 (0.1 mol dm^{-3}): (A) before electrolysis; (B) after electrolysis (n=0.65) at 0.52 V (100 mV s^{-1}).

plexes of Ru(III).[3] When a coulometry was performed under the same conditions, a further new coupled wave appeared at 0.06 V ($E_{1/2}$). If the coupled wave observed at 0.06 V is attributable to $[Ru(NO_2)(ONO_2)(py)_4]^{+/o}$, the results can be explained in this way: the reaction proceeds by the dimeric intermediate process,[1] and also a 1-electron oxidation of **5** gives **3** (see Eqs. 5-9) which can be changed to **4** by a further 2-electron oxidation.[2] No evidence for the generation of any oxo complex of Ru(IV) could be observed by the cyclic voltammetry during the stage of 1-electron oxidation. In combination with the proceeding work on the oxidation of **1** to give **2** (Eqs. 1-4),[1]

$$2(ClRu^{II}NO_2)\ \mathbf{1} \longrightarrow 2(ClRu^{III}NO_2)^+ + 2e^- \qquad (1)$$

$$2(ClRu^{III}NO_2)^+ \rightleftharpoons (ClRu^{III}NO_2)^+ + (ClRu^{III}ONO)^+ \qquad (2)$$

$$\longrightarrow \{ClRuNO(O)N(O)ORuCl\}^{2+} \longrightarrow \qquad (3)$$

$$(ClRu^{II}NO^+)^{2+} + 1/2(ClRu^{IV}O^{2-})^+\ \mathbf{2} + 1/2(ClRu^{II}OH) + NO_2^- \qquad (4)$$

the following scheme (Eqs. 5-9) is proposed for the present conversion reaction:[4]

$$2(-Ru^{II}NO_2)\ \mathbf{5} \longrightarrow 2(-Ru^{III}NO_2)^+ + 2e^- \qquad (5)$$

$$2(-Ru^{III}NO_2)^+ \rightleftharpoons (-Ru^{III}NO_2)^+ + (-Ru^{III}ONO)^+ \qquad (6)$$

$$\longrightarrow \{-RuNO(O)N(O)ORu-\}^{4+} \longrightarrow \qquad (7)$$

$$\longrightarrow (-Ru^{III}NO)^{2+} + (O_2NORu^{II}-) \qquad (8)$$

$$\longrightarrow (-Ru^{II}NO^+)^{2+} + (H_2ORu^{II}-)^+\ \mathbf{3} + NO_3^- \qquad (9)^{2,5)}$$

(Both py and one of the NO_2 ligands were omitted for clarity)

The H_2O ligand in Eq. 9 is presently assumed to come from an impurity water of the CH_3CN solvent.[6] Essentially the same results are obtainable when trans-$[Ru^{II}(NO_2)(NH_3)(py)_4]^+$ (Epa=0.57 V) undergoes electrochemical oxidations: it gives trans-$[Ru^{II}(NH_3)(H_2O)(py)_4]^{2+}$ (Epa=0.82 V), by 1-electron oxidation (by coulometry), as a precursor of trans-$[Ru^{IV}(NH_3)(O)(py)_4]^+$, along with trans-$[Ru^{II}(NO^+)(NH_3)(py)_4]^{3+}$ ($E_{1/2}$=0.08 V, Epc= -0.76 V). The scheme (Eqs. 5-9) illustrates that two more electron oxidations are required to give **4**.[2]

Evidently, the difference between the process in Eqs. 5-9 and that in Eqs. 1-4 stems from the different disintegration modes of the two intermediate species, $\{XRuNO(O)N(O)ORuX\}^{2+}$ (X=Cl, NO_2 (NH_3)). When NO_2 (or NH_3) exists at the terminal position of the intermediate species (Eq. 7) as a co-ligand, it affects the disintegration mode to give a final product with a lower oxidation state, while Cl ligand allows a transient "$(Cl\text{-}Ru\text{-}O)^+$" moiety with a higher oxidation state to be generated.[7] Although the study on the co-ligand effect needs to be continued, it is clear that the conversion process of ($XRu^{II}NO_2$) moiety depends on the disintegration mode of the transient dimeric intermediate ($\{X\text{-}(py)_4RuNO\text{-}(O)N(O)ORu(py)_4\text{-}X\}^{2+}$), for which a remakable influence due to X ligand is observed. It is also worth noting that either **5** or $[Ru^{II}(NO_2)(NH_3)(py)_4]^+$ gives aqua complexes of Ru(II)(**3** and $[Ru^{II}(NH_3)(H_2O)(py)_4]^+$), whose oxidation potentials are observed at more positive regions (0.82 V and 0.81 V, respectively) then those of their mother nitro complexes of Ru(II) (0.52 V for **5** and 0.57 V for $[Ru^{II}(NH_3)(NO_2)(py)_4]^+$).$^{8)}$

In conclusion, the present work clarified that, in addition to the first and the second mechanistic pathways (Eqs. 1-4 and 10-11, respectively), a third mechanistic pathway (Eqs. 5-9) exists in the formation process of ($X\text{-}Ru^{II}\text{-}NO_2$) moiety.

References

1) H. Nagao, H. Nishimura, Y. Kitanaka, F. S. Howell, M. Mukaida, and H. Kakihana, Inorg. Chem., 29, 1693 (1990).

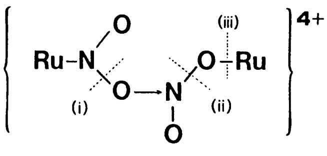
2) H. Nishimura, H. Nagao, F. S. Howell, M. Mukaida, and H. Kakihana, Chem. Lett., 1988, 491; 1990, 133. It has been explained that trans-$[Ru(NO_2)(H_2O)(py)_4]^+$, generated from trans-$[Ru(NO)(OH)(py)_4]^{2+}$ under basic conditions, is oxidized into trans-$[Ru(ONO)(O)(py)_4]^+$ by two-electron oxidation:

$$(H_2ORu^{II}NO_2)^+ \longrightarrow (HORu^{III}ONO)^+ + e^- + H^+ \qquad (10)$$

$$\longrightarrow (O{=}Ru^{IV}ONO)^+ + e^- + H^+ \qquad (11)$$

3) The intermediate process was proposed by Meyer et al. in the study of oxidation of cis-$[RuCl(NO_2)(bpy)_2]$ which gave cis-$[RuCl(ONO_2)(bpy)_2]$: F. R. Keene, D. J. Salmon, J. L. Walsh, H. D. Abruna, and T. J. Meyer, Inog. Chem., 19, 1986 (1980).

4) When the dimeric intermediate (proposed in a previous work (Ref. 1) disintegrates at (i) and (ii), the conversion reaction proceeds by Eqs. 1-4, while Eqs. 5-9 are possible to assume if the bonds break at (i) and (iii).



5) The generated nitrosyl species, $[Ru(NO)(NO_2)(py)_4]^{2+}$, is often decomposed to give the known $[Ru(NO)(OH)(py)_4]^{2+}$ (Epc=-0.69 V) during the electrolysis.

6) The water content of the solvent, as determined by Karl Fisher titration, was about 10^{-3} mol dm^{-3}(Ref. 1).

7) $(ClRu^{II}O^{o})^+$, $(ClRu^{III}OH^-)^+$, and $(ClRu^{IV}O^{2-})^+$ are isoelectronic.

8) More simply, the potentials of **3** and $[Ru(NH_3)(H_2O)(py)_4]^+$ are located at a more positive region than those applied for the oxidative electrolyses of their mother nitro complex of Ru(II), while no such precursor species is generated in the oxidation of **1** to give **2**.

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