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Influence of an Axial Ligand in the Oxidation of the Nitrosyl Complex of Ruthenium(II), *trans*-$[RuX(NO)(py)_4]^{2+}$ (X=Cl, OH), to Give Oxo Complex of Ruthenium(IV)

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Oxidation of *trans*-$[Ru(OH)(NO)(py)_4]^{2+}$ gives *trans*-$[Ru(ONO)(O)(py)_4]^+$, while that of *trans*-$[RuCl(NO)(py)_4]^{2+}$ yields *trans*-$[RuCl(O)(py)_4]^+$. The two complexes differ in the origin of the oxo ligand. Their formation proceses were proved to be influenced by the ligand trans to the nitrosyl.

We have reported the reaction in which *trans*-$[RuCl(NO)(py)_4]^{2+}$ was oxidized by NaClO to give the oxo complex of Ru^{IV}, *trans*-$[RuCl(O)(py)_4]^+$.[1)] The reaction is initiated by the formation of the nitro complex of Ru^{II}, *trans*-$[RuCl(NO_2)(py)_4]$, *via* the known nitrosyl-nitro conversion reaction.[2)] The nitro complex of Ru^{II} is subsequently oxidized to the reactive nitro complex of Ru^{III} which gives a dimeric intermediate consisting of both reactive nitro (Ru^{III}-NO_2^-) and its isomerized nitrito (Ru^{III}-ONO^-) moieties.[3)] This results in the formation of the hydroxo complex of Ru^{III}, *trans*-$[RuCl(OH)(py)_4]^+$, along with the oxo complex of Ru^{IV}, *trans*-$[RuCl(O)(py)_4]^+$, as final products.[1)] The same oxidation procedure applied to *trans*-$[Ru(OH)(NO)(py)_4]^{2+}$ has been shown in the present study to lead to the formation of *trans*-$[Ru(ONO)(O)(py)_4]^+$. Although the resulting nitrito and chloro complexes have identical oxo ligands, the origin of the oxo ligand in each complex is clearly different. We report here the synthesis of *trans*-$[Ru(ONO)(O)(py)_4]^+$, as the first example of the reaction where the source of the product oxygen is influenced by the ligand trans to the nitrosyl.

Addition of an excess of NaClO solution (available chlorine 10%, 3 cm^3) to an aqueous solution of *trans*-[Ru(OH)(NO)(py)$_4$](ClO$_4$)$_2$ (100 mg in 10 cm^3) gave immediately a red solution, due to the formation of *trans*-[Ru(OH)(NO$_2$)(py)$_4$].4) The red solution changed to pale green solution when it was kept for 24 h in a refrigerator. A pale green product can be obtained as a ClO$_4$ salt. Yield, 60-70%. The product was identified as *trans*-[Ru(ONO)(O)(py)$_4$]ClO$_4$ by the following experiments. Satisfactory elemental analyses were obtained.5) The effective magnetic moment of 2.92 B.M. is almost the same as that of *trans*-[RuCl(O)(py)$_4$]$^+$.1) The IR absorption bands observed at 1484 and 990 cm^{-1}, which shifted respectively to 1464 and 965 cm^{-1} by ^{15}N substitution, support the characterization as the nitrito complex of Ru^{IV} rather as a nitro or nitrato complexes.6) A nitro ligand isomerizes rapidly to a nitrito form when the (Ru-NO$_2^-$) moiety undergoes an oxidation in its metal site.3) An IR absorption band assignable to Ru=O stretching vibration appeared around 795 cm^{-1} region. The existence of the oxo ligand was also evidenced by the oxygen transfer reaction with PPh$_3$.7)

Cyclic and normal pulse voltammetries with Pt disk electrode (ϕ = 1.99 mm) revealed, in conformity with the results observed for *trans*-[RuCl(O)(py)$_4$]$^+$, that the complex in MeCN underwent a nearly one-electron reduction at -0.99 V (*vs.* Ag|AgClO$_4$ 0.1 mol dm^{-3} (MeCN)). The reduction species having the oxo ligand appears to decompose with a fairly fast rate.8) X-Ray structure determination of *trans*-[Ru(ONO)(O)(py)$_4$]$^+$ was unsuccessful, since the single crystals decomposed during the intensity data collection. The trans form of [Ru(ONO)(O)(py)$_4$]$^+$ was deduced from the result that *trans*-[Ru(OH)(NO)(py)$_4$]$^{2+}$, used as a starting material of the present reaction, was regenerated when [Ru(ONO)(O)(py)$_4$]$^+$ was refluxed with a mixed solution of water and ethanol (1:1).

As has been reported,1) *trans*-[RuCl(NO)(py)$_4$]$^{2+}$ in aqueous solution can be oxidized to give *trans*-[RuCl(O)(py)$_4$]$^+$ (Eqs. 1-3, py ligands are omitted for simplicity):

$$\dashrightarrow (\mathrm{Cl\text{-}Ru^{II}\text{-}NO^{+}}) \xrightarrow{(\mathrm{OH^{-}})} (\mathrm{Cl\text{-}Ru^{II}\text{-}NO_2^{-}}) \longrightarrow (\mathrm{Cl\text{-}Ru^{III}\text{-}NO_2^{-}}) + e^{-} \qquad (1)$$

$$(\mathrm{Cl\text{-}Ru^{III}\text{-}NO_2^{-}}) \rightleftharpoons (\mathrm{Cl\text{-}Ru^{III}\text{-}ONO^{-}}) \qquad (2)$$

$$(\mathrm{Cl\text{-}Ru^{III}\text{-}NO_2^{-}}) + (\mathrm{Cl\text{-}Ru^{III}\text{-}ONO^{-}}) \longrightarrow \{\mathrm{Cl\text{-}Ru\text{-}N(O)ON(O)O\text{-}Ru\text{-}Cl}\}^{2+}$$

$$\longrightarrow \boxed{(\mathrm{Cl\text{-}Ru^{II}\text{-}NO^{+}})} + (\mathrm{Cl\text{-}Ru^{IV}{=}O^{2-}}) + \mathrm{NO_2^{-}} \qquad (3)^{9)}$$

A rupturing of the Ru-N(nitrosyl) bond, via the process in which the reactive nitro and its isomerized nitrito moieties combine (Eq. 3), is necessary for oxo complex formation.$^{1,3)}$ In contrast, *trans*-$[Ru(OH)(NO)(py)_4]^{2+}$ gave *trans*-$[Ru(ONO)(O)(py)_4]^+$ under the same conditions with retention of the nitrosyl nitrogen, as was indicated by a ^{15}N labelling experiment. The present reaction can be represented by the following Eqs. 4-6:

$$(HO\text{-}Ru^{II}\text{-}NO^+) \xrightarrow{(OH^-)} (HO\text{-}Ru^{II}\text{-}NO_2^-) \longrightarrow (HO\text{-}Ru^{III}\text{-}NO_2^-) \;+\; e^- \qquad (4)$$

$$(HO\text{-}Ru^{III}\text{-}NO_2^-) \longrightarrow (HO\text{-}Ru^{III}\text{-}ONO^-) \qquad (5)$$

$$(HO\text{-}Ru^{III}\text{-}ONO^-) \longrightarrow (O^{2-}{=}Ru^{IV}\text{-}ONO^-) \;+\; e^- \;+\; H^+ \qquad (6)$$

A remarkable difference between the former scheme (Eqs. 1-3) and the latter one (Eqs. 4-6) is that, in the latter, no reaction to give the intermediate consisting of $(Ru^{III}\text{-}NO_2^-)$ and $(Ru^{III}\text{-}ONO^-)$ moieties can be seen. The source of the oxo ligand in the present complex can reasonably be assumed to be due to the oxidation of the hydroxo ligand (Eq. 6) which existed originally in *trans*-$[Ru(OH)(NO)(py)_4]^{2+}$.$^{10)}$

In conclusion, a new oxidation process which depends on the ligand trans to the nitrosyl has been observed; the presence of Cl ligand in *trans*-$[RuX(NO)(py)_4]^{2+}$ facilitates the oxygen transfer reaction (Eq. 3) *via* the process proposed by Meyer et al.,$^{3)}$ resulting in the formation of the oxo ligand at the nitrosyl position,$^{1)}$ while the presence of OH group, in place of Cl, acts so as to interrupt it. The complex having nitrito ligand is therefore built up without oxygen transfer reaction which should give *trans*-$[Ru(OH)(O)(py)_4]^+$ or *trans*-$[Ru(O)_2(py)_4]$ if it occurred.

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References

1) Y. Yukawa, K. Aoyagi, K. Shirai, M. Kurihara, K. Shimizu, M. Mukaida, T. Takeuchi, and H. Kakihana, Chem. Lett., 1985, 283; K. Aoyagi, Y. Yukawa, K. Shimizu, M. Mukaida, T. Takeuchi, and H. Kakihana, Bull. Chem. Soc. Jpn., 59, 1493 (1986); H. Nagao, F. S. Howell, M. Mukaida, and H. Kakihana, J. Chem.

Soc., Chem. Commun., 1987, 1618.

2) J. H. Swinehart and P. A. Rock, Inorg. Chem., 5, 573 (1966).

3) F. R. Keene, D. J. Salmon, J. L. Walsh, H. D. Abruna, and T. J. Meyer, Inorg. Chem., 19, 1896 (1980).

4) F. Bottomley and M. Mukaida, J. Chem. Soc., Dalton Trans., 1982, 1933.

5) Found: C, 38.23; H, 3.10; N, 11.03%. Calcd for $[Ru(ONO)(O)(py)_4]PF_6$: C, 38.43; H,3.20; N, 11.21%. Found: C, 41.13; H, 3.50; N, 12.06%. Calcd for $[Ru(ONO)(O)(py)_4]ClO_4$: C, 41.15; H, 3.45; N, 12.09%.

6) K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds," 3rd ed, John Wiley and Sons, New York (1978), pp. 220-226; H. Nagao, F. S. Howell, M. Mukaida, and H. Kakihana, Inorg. Chem., 25 ,4312 (1986).

7) When the complex in MeCN was mixed with PPh_3, the mixed green solution immediately faded away. The brown material which deposited by adding an ether to the solution was filtrated. Ph_3PO (ν(P=O), 1180 cm^{-1}) could be obtained from the mother liquid by adding a small amount of water.[1)]

8) Electrochemical study of *trans*-$[RuCl(O)(py)_4]^+$ in MeCN solution indicates that the following reaction occurs (H. Nagao, to be published):

$$[RuCl(O)(py)_4]^+ + 2e^- + 2H^+ \longrightarrow [RuCl(H_2O)(py)_4]^+$$

$$[RuCl(O)(py)_4]^+ + [RuCl(H_2O)(py)_4]^+ \longrightarrow 2[RuCl(OH)(py)_4]^+$$

Although the result observed for *trans*-$[Ru(ONO)(O)(py)_4]^+$ in MeCN was not well understood, a similar reaction is expected to occur.

9) The following reaction is also expected to occer:

$$\{Cl\text{-}Ru\text{-}N(O)ON(O)O\text{-}Ru\text{-}Cl\}^{2+} \xrightarrow{(H_2O)} (Cl\text{-}Ru^{II}\text{-}NO^+) + (Cl\text{-}Ru^{II}\text{-}OH_2) + NO_3^-$$

trans-$[RuCl(H_2O)(py)_4]^+$ is then oxidized to give *trans*-$[RuCl(O)(py)_4]^+$ under the conditions.

10) The reaction which gives *trans*-$[RuCl(O)(py)_4]^+$ by the oxidation of either *trans*-$[RuCl(OH)(py)_4]^+$ or *trans*-$[RuCl(H_2O)(py)_4]^+$ has been clarified; H. Nagao, K. Aoyagi, Y. Yukawa, F. S. Howell, M. Mukaida, and H. Kakihana, Bull. Chem. Soc. Jpn., 60, 3247 (1987).

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