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Nitro-Nitrito Isomerization Induced by Oxidation-Reduction of Central Metal Site: $[Ru^{II}(NO_2)(H_2O)(py)_4]^+ \rightleftarrows [Ru^{IV}(ONO)(O)(py)_4]^+$

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Nitro-Nitrito isomerization occurs reversibly when a formal oxidation state of the central metal atom is changed; a nitro complex of Ru(II) gives a nitrito complex of Ru(IV), which is capable of being returned to the original complex by a moderate reduction.

Although linkage isomerizations of nitro-nitrito ligands are considered to be heat-sensitive,[1,2] a rare example which is induced by a change of the formal oxidation state in the central metal atom has been reported.[3] We found that such isomerization occurs reversibly between aquanitrotetrakis(pyridine)ruthenium(II) ion (**1**) and nitritooxotetrakis(pyridine)ruthenium(IV) ion (**2**), both isolated as ClO_4 salts. This appears to be the first reported example where isomeric pairs were synthesized with different formal oxidation states of their metal ions. A nitrito complex of ruthenium prepared so far, without a change of the oxidation state, was the mixture of nitro complex.[4]

The nitrito complex of Ru(IV) **2** is obtained when the nitro complex of Ru(II) **1** is oxidized by NaClO under aqueous basic conditions.[5] Both nitrito and nitro complexes were characterized by satisfactory elemental analyses, IR spectra, magnetic properties, and cyclic voltammetric parameters. For trans-$[Ru(NO_2)(H_2O)(py)_4]ClO_4$ **1**: Found: C, 41.0; N, 11.9; H, 3.6%. Calcd: C, 40.7; N, 11.9; H, 3.9%. ν_{as} (1310 cm^{-1}), ν_s (1290 cm^{-1}), diamagnetic, E_{pa}=0.79 V vs. Ag|$AgClO_4$ (0.1 mol dm^{-3} in CH_3CN) (1e oxidation wave). For trans-$[Ru(ONO)(O)(py)_4]ClO_4$ **2**: Found: C, 41.1; N. 12.1; H, 3.5%. Calcd: C, 41.2; N, 12.1; H, 3.5%. $\nu_{N=O}$ (1485 cm^{-1})

and ν_{N-O} (983 cm^{-1}); (1460 and 977 cm^{-1} respectively in ^{15}N labelling experiment), $\nu_{Ru=O}$ (798 cm^{-1}), 2.92 B.M., E_{pc}=-1.0 V (2e reduction wave).

The occurrence of linkage isomerization of 1 could also be deduced from cyclic voltammetry: On the first scan at 25 °C, a one-electron oxidation wave due to the formation of $[Ru(NO_2)(H_2O)(py)_4]^{2+}$ appears at 0.79 V (E_{pa}, wave 1 in Fig. 1a). The wave is irreversible as evidenced by the absence of a corresponding cathodic wave in the cyclic voltammograms. Lowering the temperature to -40 °C increases the cathodic wave current (wave i in Fig. 1b), however, though the irreversibility is still observed. Such behavior is characteristic of an oxidation followed by a chemical reaction (EC), the rate of which is decreased by lowering the temperature. In fact, a similar cyclic voltammogram could be observed in a one-electron oxidation of trans-$[RuCl(NO_2)(py)_4]$, analogous to 1, in which the linkage isomerization into trans-$[Ru(ONO)Cl(py)_4]^+$ was confirmed to occur.[6)]

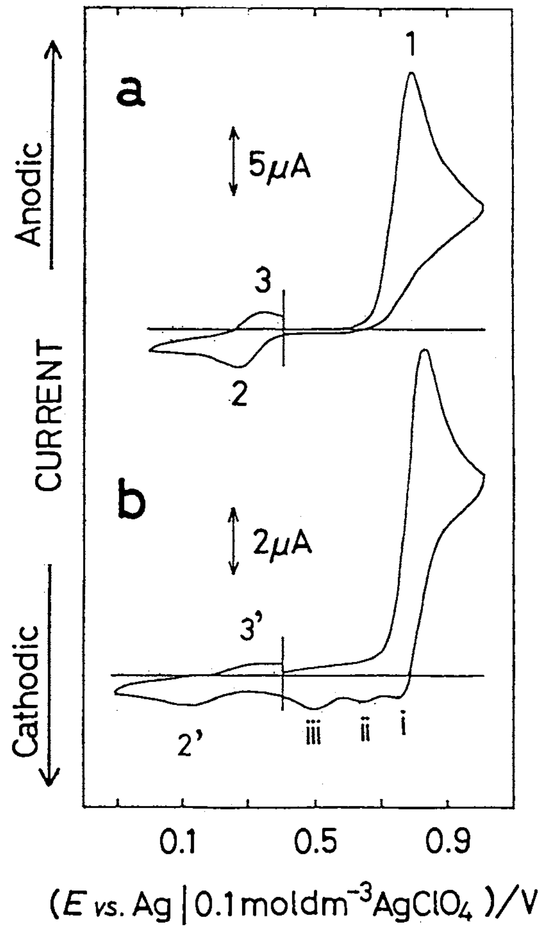

Fig. 1. Cyclic voltammograms of trans-$[Ru(NO_2)(H_2O)(py)_4]ClO_4$ 1 (1×10^{-3} mol dm^{-3}) in CH_3CN. 200 mV s^{-1}, Et_4NClO_4 (1×10^{-3} mol dm^{-3}), stationary Pt electrode. a, at 25 °C: 1, $[Ru(NO_2)(H_2O)(py)_4]^{1+/2+}$; 2 and 3, $[Ru(ONO)(OH)(py)_4]^{0/1+}$. b, at -40 °C: i, $[Ru(NO_2)(H_2O)(py)_4]^{1+/2+}$; ii and iii, either $[Ru(NO_2)(OH)(py)_4]^{0/1+}$ or $[Ru(ONO)(H_2O)(py)_4]^{1+/2+}$; 2' and 3', the same to 2 and 3 at 25 °C.

Thus the generated nitro species, $[Ru(NO_2)(H_2O)(py)_4]^{2+}$, will isomerize rapidly to give a nitrito species which undergoes a reduction at 0.27 V (E_{pc}, wave 2 in Fig. 1a).
The isomerized nitrito species was tentatively identified, based on a low temperature experiment, as being $[Ru(ONO)(OH)(py)_4]^+$ rather than $[Ru(ONO)(H_2O)(py)_4]^{2+}$, since an aqua ligand in Ru(III) complex releases

its proton rapidly to give a hydroxo complex of Ru(III).[7)]

Two more waves appeared at 0.65 and 0.45 V (both E_{pc}, Fig. 1b) on the reductive scan, but these waves not observed in the experiment at 25 °C. The splitting observed is only explainable by assuming that either $[Ru(NO_2)(OH)(py)_4]^+$ or $[Ru(ONO)(H_2O)(py)_4]^{2+}$ species exist for a short life time at the surface of an electrode, along with $[Ru(ONO)(OH)(py)_4]^+$ which is reduced at 0.1 V (E_{pc}, wave 2' in Fig. 1b).

A reverse reaction, from nitrito **2** into nitro **1**, can be observed when **2** reacts with methanol as a reductant. A freshly prepared methanol solution of **2** exhibits an intense absorption band at 264 nm. The solution changes within an hour from pale green to yellow, while standing at room temperature; a characteristic absorption band appears at 342 nm, while the band at 264 nm disappears. The UV spectra observed at this stage is the same to that of **1** used as the authentic sample. When the experiment was attempted in a preparative scale, **1** could be isolated as PF_6^- salt from the yellow solution by reducing the solution volume.

The reduction process of nitrito **2** was studied by cyclic voltammetry, with the intention of obtaining evidence for the isomerization (from **2** to **1**): A single two-electron reduction occurs irreversibly first at ($Ru^{IV}=O^{2-}$) unit in **2**, and the resultant species causes a complicated voltammogram for this reduction process. Thus unexplainable results remained, without any proof for the isomerization.

Nitro-Nitrito isomerization can be observed by cyclic voltammetry, as refered earlier, for chloronitrotetrakis(pyridine)ruthenium(II) **3**, which is analogous to **1**, when **3** undergoes a one-electron oxidation to give <u>trans</u>-$[RuCl(NO_2)(py)_4]^+$.[6)] The isomeric pair, chloronitritotetrakis(pyridine)ruthenium(III) ion **4**, was difficult to isolate because **4** is reactive and it undergoes a rapid dimerization to give a transient intermediate consisting of $[RuCl(NO_2)(py)_4]^+$ and **4**, $\{Cl(py)_4RuNO(O)\text{-}N(O)ORu(py)_4Cl\}^{2+}$,[3)] which gives both <u>trans</u>-$[RuCl(O)(py)_4]^+$ and <u>trans</u>-$[RuCl(NO)(py)_4]^{2+}$ as final products.[6)]

In conclusion, a one-electron oxidation of **1** gives at 25 °C predominantly $[Ru(ONO)(OH)(py)_4]^+$; further one-electron oxidation results in the formation of **2**, which can be isolated as the isomeric pair of **1**.

References

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