Interaction of Some Lewis Acids with the Oxide-Bridge of (μ -Oxo)di(μ -acetato)diruthenium (III, III) Complexes and Its Electrochemical Consequence

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Interaction of some Lewis acids to the oxide bridge of $[\text{Ru}_2(\mu\text{-O})(\mu\text{-CH}_3\text{COO})_2(2,2'\text{-bipyridine})_2(\text{L})_2]^{2+}$ ($\text{L} = 1\text{-methylimidazole (1), pyridine (2)}$) and its electrochemical consequence were examined. The complexes themselves show reversible $\text{Ru}_2(\text{III}, \text{III}) / \text{III}, \text{IV}$ and $\text{Ru}_2(\text{II}, \text{III}) / \text{III}, \text{III}$ processes and an irreversible $\text{Ru}_2(\text{II}, \text{II}) / \text{II}, \text{III}$ process in acetonitrile (0.1 M $n\text{-Bu}_4\text{NPF}_6$) at 0.78 (0.95) ($E_{1/2}$), -0.55 (-0.39) ($E_{1/2}$) and -1.16 (-1.09) V (Epa) vs. Ag/AgCl , respectively, for **1** (data in parentheses are for **2**). On addition of BF_3 and Al^{3+} , all the redox potentials shift to the positive direction. Addition of Li^+ and Na^+ causes the shift of only the most negative $E_{1/2}$ to overlap with the middle one to show an apparent one-step two-electron process $\text{Ru}_2(\text{II}, \text{II}) / \text{III}, \text{III}$ at -0.55 V. BF_3 and Al^{3+} interact with the oxide bridge of the complexes at the oxidation states $\text{Ru}_2(\text{III}, \text{III})$, (II, III) and (II, II) while the alkali metal ions do only at the $\text{Ru}_2(\text{II}, \text{II})$ state.

Key Words: Diruthenium μ -Oxo Complexes, Lewis Acid Interaction, Cyclic Voltammetry

1 Introduction

In our recent paper, we have demonstrated that the protonation at the oxide bridge of the oxo-bridged diruthenium(III, III) complexes, $[\text{Ru}_2(\mu\text{-O})(\mu\text{-CH}_3\text{COO})_2(\text{bpy})_2(\text{L})_2]^{2+}$ ($\text{L} = 1\text{-methylimidazole (Meim) (1), pyridine (py) (2)}$) (Scheme 1), causes significant positive shift of the reduction potentials of the $\text{Ru}_2(\text{II}, \text{III}) / (\text{III}, \text{III})$ and $\text{Ru}_2(\text{II}, \text{II}) / (\text{II}, \text{III})$ processes in acetonitrile.^{1,2)} The protonation was attained by adding a strong proton donor, *p*-toluenesulfonic acid (Hpts), to the solution. Extent of the shifts in the case of **1** amounts to 0.82 (from -0.55 to $+0.27$ V vs. Ag/AgCl) and 0.89 V (from -1.16 to -0.27 V), respectively.^{1,2)} Formation of the hydroxo bridge at the $\text{Ru}_2(\text{III}, \text{III})$ state on addition of the acid can be monitored by UV-vis and NMR spectra also.¹⁻³⁾ It was subsequently of great interest to us to find whether other Lewis acids behave similarly as protons to cause a

significant shift of the redox potentials. To our knowledge, no report showing unambiguously that metal-centered redox reactions are coupled with Lewis acid adduct formation at a ligand Lewis base center of metal complexes (oxide bridge in the present case), has appeared previously. In this communication, we wish to present our preliminary results on the interaction of some Lewis acids such as BF_3 , Al^{3+} , Li^+ and Na^+ with **1** or **2** in acetonitrile.

2 Experimental

Hexafluorophosphate salts of the diruthenium(III) complexes, **1** and **2**, were prepared as described in the literatures.^{1,4-6)} UV-visible spectra were recorded on a Hitachi U3410 and a JASCO Ubest-30 spectrophotometer. IR spectra were recorded on a Hitachi 270-30 infrared spectrophotometer. The ^1H NMR spectra were obtained by a JEOL JNM-EX 270 FT-NMR spectrometer. All peaks were referenced to the methyl signals of TMS at $\delta = 0$. Cyclic voltammetry was performed with a Hokuto Denko HA-501G potentiostat with an HB-105 function generator and a BAS CV-50W voltammetric analyzer with the scan rate of 50 mV/sec. The working and the counter electrodes were a glassy-carbon disk (3 mm in diameter) and a platinum wire, respectively. The reference electrode was Ag/AgCl against which the half-wave potential of Fc^+ / Fc ($E_{1/2}(\text{Fc}^{+/0})$) ($\text{Fc} = \text{ferrocene}$) was 0.43 V.

Scheme 1 Structures of $[\text{Ru}_2(\mu\text{-O})(\mu\text{-CH}_3\text{COO})_2(\text{bpy})_2(\text{L})_2]^{2+}$.

3 Results and Discussion

3.1 Interaction with BF₃

BF₃ was added to the acetonitrile solution of **2** quantitatively as a form of Et₂O·BF₃ by using the syringe technique. Figure 1 shows the UV-vis spectral change on successive addition of BF₃. The spectrum changed on increasing amount of BF₃ with isosbestic points accompanying with a new peak appearing at 520 nm (the μ -hydroxo complex shows the peak at *ca.* 525 nm). The change was almost completed with *ca.* 3 eq of BF₃ at the complex concentration of 1.0 mM. The final spectrum was similar to that of the hydroxo-bridged Ru₂(III, III) complex. The spectral change must be ascribed to the attachment of BF₃ to the oxide bridge. The BF₃ adduct formation is more favorable than the protonation, since *ca.* 10 eq of Hpts were required for the complete formation of the μ -hydroxo complex at the similar complex concentration.²⁾ The adduct formation was completed with 1 eq of BF₃ when the solvent was CH₂Cl₂. The ¹H NMR spectrum of **2** in the presence of BF₃ in CD₃CN showed somewhat broader ligand signals at wider frequency range as observed in the case of the addition of Hpts. For example, the 6, 6'-proton signals of bpy shifted from *ca.* 6 to *ca.* -2 ppm. Change in the ¹H NMR spectrum is also taken as an evidence for the adduct formation with BF₃.

Figure 2 shows the cyclic voltammogram of **2** in acetonitrile with 0.1 M *n*-Bu₄NPF₆ in the presence of BF₃. With 0.5 eq of BF₃, two reduction waves of Ru₂(II, II / II, III) and Ru₂(II, III / III, III) shifted to positive potentials. On further addition of BF₃, further shifts of the waves were observed with some deterioration of their reversibility. The new waves

Fig. 1 Change in the visible absorption spectra of **2** on addition of BF₃ in acetonitrile.

observed at one equivalent or more BF₃ should be assigned to the BF₃ adduct. The extent of the shift (1.1 V) of the Ru₂(II, II / II, III) potential was even larger than that for the protonation (0.99 V).²⁾ The initial shift which was completed with only 0.5 eq of BF₃ may be explained by partial contributions of the protons produced by the interaction of contaminated H₂O with BF₃.

deprotonation (2)

In the presence of one equivalent of BF₃, the Ru₂(III, III / III, IV) wave was irreversible probably because of the slow dissociation of BF₃ from the oxide bridge after the oxidation to Ru₂(III, IV). When excess of (C₂H₅)₂O was added, the oxidation wave showed improved reversibility as (C₂H₅)₂O could assist the dissociation of BF₃.

Attempts to isolate the BF₃ adduct of **2** gave a reddish violet solid, but its unequivocal characterization has not been successful so far. A BF₃ adduct of a mononuclear rhenium(V) complex, [Re(O)(OBF₃)(Meim)₄]⁺, was X-ray structurally characterized recently.^{7,8)}

3.2 Interaction with Al³⁺

Al(ClO₄)₃·(H₂O)₉ was used as a source of Al³⁺. On addition of Al³⁺ to **1** in acetonitrile, the UV-vis absorption spectrum showed a similar change as in the case of BF₃ addition. The new peak appeared at

Fig. 2 Cyclic voltammograms of **2** in acetonitrile (0.1 M *n*-Bu₄NPF₆). (a) Without any additive, (b) 0.5 eq of BF₃ added, (c) 1.0 eq of BF₃ added, (d) excess of Et₂O was added after the addition of 2 eq of BF₃.

ca. 500 nm. One equivalent of Al^{3+} was sufficient to complete the change. The ^1H NMR spectrum also showed the similar trend as that observed for the addition of BF_3 . It was concluded that Al^{3+} also interacts with the oxide bridge at the $\text{Ru}_2(\text{III}, \text{III})$ state.

Cyclic voltammogram of **1** in acetonitrile (0.1 M $n\text{-Bu}_4\text{NPF}_6$) changed significantly on addition of Al^{3+} (Fig. 3). With 1 eq of Al^{3+} , all the redox potentials shifted to the positive direction which must be due to the formation of the Al^{3+} adduct. Poor reversibility of the $\text{Ru}_2(\text{III}, \text{III}) / \text{III}, \text{IV}$ process would indicate the slow dissociation of Al^{3+} from the $\mu\text{-OAl}(\text{H}_2\text{O})_n$ bridge after the oxidation to the $\text{Ru}_2(\text{III}, \text{IV})$ state. As in the case of BF_3 , the shift with 0.5 eq of Al^{3+} would be at least partly due to protons produced by Al^{3+} .

$[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ ($\text{p}K_a = 5.1$)¹⁰ is certainly a much stronger acid as compared with $[\text{Ru}_2(\mu\text{-OH})(\mu\text{-CH}_3\text{COO})_2(\text{bpy})_2(\text{Meim})_2]^{(n+1)+}$ ($n=0, 1$) (the $\text{p}K_a$ values were estimated to be 14 and > 25 for $n=1$ and 0, respectively).¹¹

3. 3 Interaction with Li^+ and Na^+

Figure 4 shows the CV change on addition of LiClO_4 to the acetonitrile solution of **1** with 1.0 M ($n\text{-Bu}_4\text{N})\text{ClO}_4$. In the presence of 10 eq of LiClO_4 , the original reduction wave of the $\text{Ru}_2(\text{II}, \text{II}) / \text{II}, \text{III}$ process completely coalesced with the wave of the $\text{Ru}_2(\text{II}, \text{III}) / \text{III}, \text{III}$ process. The $2e^-$ nature of the reduction wave was confirmed by the coulometric

Fig. 3 Cyclic voltammograms of **1** in acetonitrile (0.1 M $n\text{-Bu}_4\text{NPF}_6$). (a) Without any additive, (b) 0.5 eq of Al^{3+} added, (c) 1.0 eq of Al^{3+} added.

measurement. The observation is reminiscent the electrochemical behavior recorded when a weak proton donor imidazole was added to the acetonitrile solution of **1**. It was concluded that Li^+ attaches the oxide bridge only at the $\text{Ru}_2(\text{II}, \text{II})$ state. The redox potential for the $\text{Ru}_2(\text{II}, \text{II}) / \text{II}, \text{III}$ process coupled with the Li^+ adduct formation must be > -0.55 V in order to observe the apparent one-step two electron transfer reaction.

Poor reversibility of the two-electron step may indicate the slower dissociation rate of Li^+ from the $\mu\text{-OLi}$ on reoxidation to $\text{Ru}_2(\text{II}, \text{III})$. Because of the adduct formation of the $\mu\text{-oxo}$ bridge with Li^+ at the lowest oxidation state $\text{Ru}_2(\text{II}, \text{II})$, the CV's of **1** in acetonitrile with two supporting electrolytes 0.1 M ($n\text{-Bu}_4\text{N})\text{ClO}_4$ and 0.1 M LiClO_4 were different at the negative potential region. A similar CV to that with 0.1 M LiClO_4 was observed when 0.1 M NaClO_4 was used as a supporting electrolyte, indicating that Na^+ also acts as a Lewis acid during the reduction of **1**.

4 Conclusion

Although proton-coupled electron-transfer reactions have been the subject of extensive study, to our

Fig. 4 Cyclic voltammograms of **1** in acetonitrile (0.1 M $n\text{-Bu}_4\text{NPF}_6$). (a) Without any additive, (b) 5 eq of Li^+ added, (c) 10 eq of Li^+ added.

knowledge no explicit example of electron transfer reactions coupled with an adduct formation with a Lewis acid other than proton has been reported. This study provides some examples of such reactions in aprotic solvent acetonitrile. The oxo-bridged diruthenium complexes **1** and **2** show three one-electron redox processes, $\text{Ru}_2(\text{II}, \text{II} / \text{II}, \text{III})$, $\text{Ru}_2(\text{II}, \text{III} / \text{III}, \text{III})$, and $\text{Ru}_2(\text{III}, \text{III} / \text{III}, \text{IV})$. BF_3 and Al^{3+} interact with the oxide bridge at the oxidation states $\text{Ru}_2(\text{III}, \text{III})$, (II, III) and (II, II) so that all the potentials shift to positive direction. Alkali metal ions, Li^+ and Na^+ interact with the oxide bridge only at the $\text{Ru}_2(\text{II}, \text{II})$ state. Thus only the $\text{Ru}_2(\text{II}, \text{II} / \text{II}, \text{III})$ wave shifts to positive potentials to coalesce with the $\text{Ru}_2(\text{II}, \text{III} / \text{III}, \text{III})$ wave to show one-step two-electron transfer reaction.

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