Meso and Racemic Isomers of a New S-Bridged Diruthenium(II) Complex with Pendant Aminoalkyl Groups

Noriyuki Matsuura, Asako Igashira-Kamiyama, Tatsuya Kawamoto, and Takumi Konno*
*Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043*

A diruthenium(II) complex, $[\{Ru(bpy)_2\}_2(\mu\text{-Haet})_2]^{4+}$ ($[\mathbf{1}]^{4+}$, Haet = $^{-}SCH_2CH_2NH_3^{+}$), which consists of two *cis*-$[Ru(bpy)_2]^{2+}$ units bridged by two thiolato groups, was newly prepared and separated into meso and racemic isomers. The spectroscopic and electrochemical properties of $[\mathbf{1}]^{4+}$, together with the crystal structure of its meso isomer, are reported.

Diruthenium(II) complexes consisting of two *cis*-[Ru-$(bpy)_2]^{2+}$ units (bpy = 2,2′-bipyridine) have attracted considerable attention, because of their intriguing photophysical and electrochemical properties based on $Ru^{II/III}$ redox centers.[1–3] To date, a variety of conjugated multidentate ligands, such as 2,2′-bipyrimidine and 3,6-bis(2-pyridyl)tetrazine, which can mediate metal–metal interaction, have been employed to connect two *cis*-$[Ru(bpy)_2]^{2+}$ units.[2] On the other hand, the use of monodentate bridging ligands is relatively rare, and only a few diruthenium complexes bearing a Ru_2X_2 diamond core, such as $[\{Ru^{II}(bpy)_2\}_2(\mu\text{-CH}_3O)_2]^{2+}$ and $[\{Ru^{II}(bpy)_2\}_2(\mu\text{-}C_6H_5S)_2]^{2+}$, have been reported.[3] Considering the chirality (Δ and Λ) around two ruthenium centers, meso ($\Delta\Lambda$) and racemic ($\Delta\Delta/\Lambda\Lambda$) isomers are possible for diruthenium(II) complexes composed of two *cis*-$[Ru(bpy)_2]^{2+}$ units. However, the separation of meso and racemic isomers has not been performed for diruthenium(II) complexes with a Ru_2X_2 core, and thus the influence of the meso–racemic isomerism on their chemical properties remains unknown. Here we report on the first isolation of meso and racemic isomers of a new S-bridged diruthenium(II) complex, $[\{Ru^{II}(bpy)_2\}_2(\mu\text{-Haet})_2]^{4+}$ ($[\mathbf{1}]^{4+}$, aet = 2-amino-ethanethiolate), which exhibits unique electrochemical behavior that is highly affected by the meso–racemic isomerism. The influence due to the deprotonation of free NH_3^{+} groups in $[\mathbf{1}]^{4+}$ is also reported.

Treatment of a red-orange solution of $[Ru(bpy)_2$-$(\text{solvent})_2]^{2+}$, which was freshly prepared from $[RuCl_2(bpy)_2]$ and 2 equiv. of $AgClO_4$ in ethanol/water (1:1), with 1 equiv. of Haet·HCl under reflux gave a dark brown solution, from which almost black crystals ($[\mathbf{1}](ClO_4)_4$) were isolated by adding aqueous $NaClO_4$ (70% yield).[4] The elemental analytical data of $[\mathbf{1}](ClO_4)_4$ were in agreement with the formula of $[\{Ru(bpy)_2\}_2$-$(\text{Haet})_2](ClO_4)_4$, and its ^1H NMR spectrum in DMSO-d_6 showed signals corresponding to bpy and aet ligands. The presence of two sets of eight bpy signals (δ 7.2–10.6) in the ^1H NMR spectrum suggested that $[\mathbf{1}](ClO_4)_4$ is not a single species. Indeed, $[\mathbf{1}](ClO_4)_4$ was separated into the less soluble $[\mathbf{1a}](ClO_4)_4$ and the more soluble $[\mathbf{1b}](ClO_4)_4$,[5] each of which gives a single set of ^1H NMR signals,[6] by fractional crystallization from an aqueous solution.

The crystal structure of $[\mathbf{1a}](ClO_4)_4$ was established by X-ray analysis.[7] As shown in Figure 1, the complex cation $[\mathbf{1a}]^{4+}$ consists of two *cis*-$[Ru^{II}(bpy)_2]^{2+}$ units that are connected by two S atoms from two Haet ligands, forming a S-bridged diruthenium(II) structure in $[\{Ru^{II}(bpy)_2\}_2(\mu\text{-Haet})_2]^{4+}$ with a Ru_2S_2 core (av. Ru–S = 2.417(1) Å, Ru–S–Ru = 102.22(5)°, S–Ru–S = 77.79(5)°). Each Ru^{II} atom is situated in a highly distorted octahedral $(N)_4(S)_2$ environment (av. trans N–Ru–N = 168.1(2)°, trans N–Ru–S = 169.8(2)°), so as to avoid the non-bonding interaction between bpy ligands belonging to the different Ru^{II} units. The terminal N atom of each bridging ligand exists as a protonated NH_3^{+} form. In $[\mathbf{1a}]^{4+}$, the two Ru^{II} chiral centers have Δ and Λ configurations to form the meso ($\Delta\Lambda$) isomer. Of two possible geometrical configurations, syn and anti, which arise from the arrangement of two Haet arms, $[\mathbf{1a}]^{4+}$ adopts the sterically favorable anti configuration.[8]
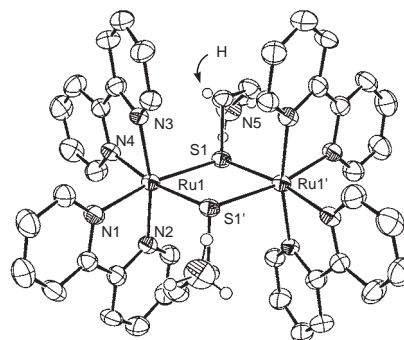
Figure 1. A perspective view of one of the two independent complex cations $[\mathbf{1a}]^{4+}$.

The electronic absorption spectrum of $[\mathbf{1b}]^{4+}$ in CH_3CN is very similar to that of $[\mathbf{1a}]^{4+}$,[5] showing intense absorption bands at ca. 500 and ca. 360 nm assignable to metal(Ru)-to-ligand(bpy) charge-transfer (MLCT) bands, besides a more intense band at ca. 290 nm due to intraligand bpy π–π^* transition.[3] Complex $[\mathbf{1b}]^{4+}$ was optically resolved into a pair of enantiomers by an SP-Sephadex C-25 column chromatography eluting with aqueous $Na_2[Sb_2(R,R\text{-tartrato})_2]$,[9] while $[\mathbf{1a}]^{4+}$ was not resolved. From these results, it is confidently assigned that $[\mathbf{1b}]^{4+}$ is the racemic isomer of $[\{Ru^{II}(bpy)_2\}_2(\mu\text{-Haet})_2]^{4+}$.

As illustrated in Figure 2a, the cyclic voltammogram (CV) of $[\mathbf{1b}]^{4+}$ in CH_3CN shows two reversible one-electron redox couples at +0.17 and +0.55 V (vs Ag/Ag$^+$), which are attributed to the stepwise oxidation of two Ru^{II} centers.[3] From the separation between the two redox couples, a comproportionation constant (K_c) was evaluated to be 3×10^6, suggesting that the $Ru^{III}Ru^{II}$ mixed-valence species is relatively stable.[2,10] Consistent with this, in the potential step spectroelectrochemistry of $[\mathbf{1b}]^{4+}$ in CH_3CN, an intervalence charge-transfer (IVCT) band was observed at ca. 1050 nm on increasing the potential from -0.3 to $+0.4$ V, which disappeared on further increasing the potential to $+0.8$ V. One may assume that the electrochemical
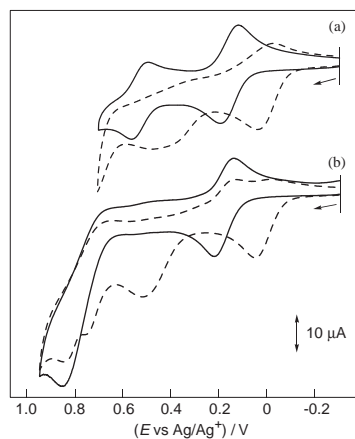
Figure 2. Cyclic voltammograms of (a) $[\mathbf{1b}]^{4+}$ and (b) $[\mathbf{1a}]^{4+}$ in the absence of Et_3N (——) and in the presence of 6 equiv. Et_3N (- - -). At $25\,°C$ in $0.1\,mol\,dm^{-3}$ Bu_4NClO_4/CH_3CN at a glassy-carbon working electrode and a Pt wire counter electrode with scan rate of $0.1\,V\,s^{-1}$ and complex concentrations of $1.0\,mmol\,dm^{-3}$.

behavior of the meso $[\mathbf{1a}]^{4+}$ is essentially the same as that of the racemic $[\mathbf{1b}]^{4+}$. However, for $[\mathbf{1a}]^{4+}$ only a quasi-reversible oxidation wave ($I_{pc}/I_{pa} = 0.89$) was observed at $+0.18\,V$, followed by an irreversible oxidation wave at $+0.88\,V$ (Figure 2b).[11,12] This is indicative of the lower stability of the higher oxidation states for $[\mathbf{1a}]^{4+}$ relative to those for $[\mathbf{1b}]^{4+}$. Model examinations revealed that in the racemic $[\mathbf{1b}]^{4+}$ there exists no serious steric repulsion between bpy ligands, in contrast to the case for the meso $[\mathbf{1a}]^{4+}$, which would be related to the electrochemical difference between $[\mathbf{1a}]^{4+}$ and $[\mathbf{1b}]^{4+}$.

When excess Et_3N was added to a CH_3CN solution of $[\mathbf{1a}]^{4+}$ or $[\mathbf{1b}]^{4+}$, the MLCT band red-shifted from ca. 500 to ca. 520 nm. In parallel with this spectral change, a broad ^1H NMR signal at $\delta \approx 7.0$ for $[\mathbf{1a}]^{4+}$ or $[\mathbf{1b}]^{4+}$, which is assignable to the NH_3^+ proton of Haet, was not observed in this region on adding excess Et_3N, although the signals due to bpy ligands remained almost unchanged.[6] These absorption and NMR spectra were reverted back to the original spectra by the neutralization of the solution. Thus, the reversible protonation–deprotonation of the terminal amine groups occurs for $[\mathbf{1}]^{4+}$ with retention of its S-bridged dinuclear structure. The CV of the deprotonated form of $[\mathbf{1b}]^{4+}$ shows two almost irreversible oxidation waves at significantly lower potentials of $+0.05$ and $+0.40\,V$ (Figure 2a). This implies that the Ru^{II} centers of the deprotonated form ($[\{Ru^{II}(bpy)_2\}_2(\mu\text{-aet})_2]^{2+}$) are oxidized more easily than those of the parental $[\mathbf{1b}]^{4+}$ to be converted into the unstable $Ru^{III}Ru^{II}$ and $Ru^{III}Ru^{III}$ species.[11] It should be noted that the neutralization of this solution recovered the original CV.

In summary, in this study two cis-$[Ru(bpy)_2]$ units were linked by two Haet ligands to form a new S-bridged diruthenium(II) structure in $[\mathbf{1}]^{4+}$, such that a $C_2H_5NH_3^+$ group is attached to each bridging S atom as a pendant arm. Complex $[\mathbf{1}]^{4+}$ afforded both the meso and racemic isomers that were successfully separated and optically resolved. This is the first example of the separation and isolation of the meso and racemic isomers for this class of diruthenium(II) complexes, which enable one to recognize a marked difference in the electrochemical behavior between these isomers for the first time.[13] In addition, it

was found that $[\mathbf{1}]^{4+}$ shows notable spectroscopic and electrochemical changes by deprotonation of the NH_3^+ groups, despite the presence of an "aliphatic" ethyl group between each terminal N atom and the Ru_2S_2 core.

References and Notes

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4   The formation of $[\mathbf{1}]^{4+}$ was not recognized when Haet was used instead of $Haet\cdot HCl$.

5   Anal. Calcd for $[\mathbf{1a}](ClO_4)_4\cdot5H_2O$: C, 35.97; H, 3.84; N, 9.53%. Found: C, 35.80; H, 3.69; N, 9.55%. UV–vis spectrum in CH_3CN $[\sigma_{max}, 10^3\,cm^{-1}$ $(\log\varepsilon, mol^{-1}\,dm^3\,cm^{-1})]$: 20.0 (4.15), 27.1 (4.14), 33.4 (4.8)^{sh}, 34.8 (4.86), 41.3 (4.65). Anal. Calcd for $[\mathbf{1b}]$-$(ClO_4)_4\cdot5H_2O$: C, 35.97; H, 3.84; N, 9.53%. Found: C, 36.01; H, 3.71; N, 9.76%. UV–vis spectrum in CH_3CN $[\sigma_{max}, 10^3\,cm^{-1}$ $(\log\varepsilon, mol^{-1}\,dm^3\,cm^{-1})]$: 19.8 (4.14), 27.6 (4.15), 33.4 (4.8)^{sh}, 34.6 (4.86), 41.3 (4.68).

6   See Supporting Information.

7   Crystal data for $[\mathbf{1a}](ClO_4)_4\cdot3CH_3CN$: fw 1502.13, monoclinic, $P2_1/n$, $a = 19.153(6)$ Å, $b = 12.397(4)$ Å, $c = 25.539(4)$ Å, $\beta = 90.74(2)°$, $V = 6063(3)$ Å^3, $Z = 4$, $D_{calcd} = 1.646\,g\,cm^{-3}$, $R (R_w) = 0.063$ (0.163) for 13788 reflections with $I > 2.0\sigma(I)$. The NH_3^+ hydrogen atoms of Haet ligands were found from difference maps and refined isotropically.

8   This S-bridged diruthenium(II) structure in $[\mathbf{1a}]^{4+}$ corresponds with that of $[\{Ru(bpy)_2\}_2(\mu\text{-}SC_6H_5)_2]^{2+}$,[3a] which is the only one example of a diruthenium(II) complex with a Ru_2S_2 core so far reported.

9   The CD spectrum for one of the enantiomers ($\Lambda\Lambda$ isomer): $[\sigma_{max}, 10^3\,cm^{-1}$ $(\Delta\varepsilon, mol^{-1}\,dm^3\,cm^{-1})]$: 18.8 ($-5.09$), 22.4 ($+12.8$), 26.9 ($-13.1$), 30.4 ($+20.5$), 32.5 ($-73.8$), 33.5 ($+112$), 35.2 ($-64.6$), 39.5 ($+28.3$), 42.0 ($-14.5$), 43.6 ($-15.3$).

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11   Almost irreversible oxidation waves were also observed for the deprotonated form of $[\mathbf{1a}]^{4+}$ at lower potentials ($+0.06$ and $+0.53$ V). Complex $[\mathbf{1a}]^{4+}$ and the deprotonated forms of $[\mathbf{1a}]^{4+}$ and $[\mathbf{1b}]^{4+}$ showed IVCT bands at ca. 1030 nm, ca. 960 nm, and ca. 950 nm on increasing the potential to $+0.4$, $+0.2$, and $+0.2$ V, respectively. This implies that the first oxidation for each compound occurs at a Ru^{II} center to produce a $Ru^{III}Ru^{II}$ mixed-valence species.

12   Complexes $[\mathbf{1a}]^{4+}$ and $[\mathbf{1b}]^{4+}$ displayed essentially the same bpy-centered redox couples in the region of $-1.6\,V$–-2.4 V. See Supporting Information.

13   The CV for $[\mathbf{1a}]^{4+}$ and $[\mathbf{1b}]^{4+}$ are reminiscent of those reported for $[\{Ru(bpy)_2\}_2(\mu\text{-}C_6H_5S)_2]^{2+}$ and $[\{Ru(bpy)_2\}_2(\mu\text{-}CH_3O)_2]^{2+}$, respectively,[3a,3b] indicating that the CV difference is based on the difference in the meso–racemic isomerism, rather than the difference in the bridging ligands.