Inorg. Chem. **2007**, *46*, 6834–6836

Inorganic Chemistry
Communication

Thiolato-Bridged $Ru^{II}Ag^{I}Ru^{II}$ Trinuclear Complex Composed of Bis(bipyridine)ruthenium(II) Units with Chelating 2-Aminoethanethiolate: Conversion to a Disulfide-Bridged $Ru^{II}Ru^{II}$ Dinuclear Complex

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Received March 26, 2007

The reaction of $[Ru(solvent)_2(bpy)_2]^{2+}$ (bpy = 2,2′-bipyridine) with Haet (2-aminoethanethiol) in ethanol/water in the presence of Ag^+ gave a thiolato-bridged $Ru^{II}Ag^{I}Ru^{II}$ trinuclear complex, $[Ag\{Ru(aet)(bpy)_2\}_2]^{3+}$, in which two $[Ru^{II}(aet)(bpy)_2]^+$ units are linked by an Ag^I atom. When this complex was treated with HCl in acetonitrile/water, a disulfide-bridged $Ru^{II}Ru^{II}$ dinuclear complex, $[Ru_2(cysta)(bpy)_4]^{4+}$ (cysta = cystamine), was produced as a result of the removal of an Ag^I atom and the autoxidation of thiolato groups. It was found that the dinuclear structure in $[Ru_2(cysta)(bpy)_4]^{4+}$ is reverted back to $[Ag\{Ru(aet)(bpy)_2\}_2]^{3+}$ by treatment with Ag^+ assisted by Zn reduction.

Over the past decades, a number of octahedral bis(bipyridine)ruthenium(II) complexes have been prepared to investigate fundamental spectroscopic, electrochemical, and photochemical properties of Ru^{II} species with diimine-type ligands.[1] In many cases, the remaining two coordination sites of bis(bipyridine)ruthenium(II) complexes are occupied by N and/or O donors, while those with an S donor are less common. In particular, examples of bis(bipyridine)ruthenium(II) complexes containing a thiolate ligand are limited in number,[2] presumably because of the strong electron-donating ability of a thiolato donor that tends to stabilize a higher oxidation state of a Ru center. 2-Aminoethanethiolate (aet = $^-SCH_2CH_2NH_2$) is the simplest aliphatic aminothiolate ligand that is expected to chelate to a Ru center via N and S donors.[3] However, no bis(diimine)-type ruthenium(II) complexes with a chelating aet ligand have appeared to date. Our previous attempts to prepare $[Ru(aet)(bpy)_2]^+$ from $[Ru(solvent)_2(bpy)_2]^{2+}$ and Haet resulted in the formation of a Ru^{II}_2 complex, $[\{Ru(bpy)_2\}_2(\mu\text{-Haet-}S)_2]^{4+}$, in which two $[Ru(bpy)_2]^{2+}$ moieties are bridged by two S atoms from two $^-SCH_2CH_2NH_3^+$ ligands.[4] In our continuing efforts to investigate the binding behavior of aet toward a Ru center, we found that a thiolato-bridged $Ru^{II}Ag^{I}Ru^{II}$ trinuclear complex composed of two $[Ru(aet)(bpy)_2]^+$ units is produced by the reaction of $[Ru(solvent)_2(bpy)_2]^{2+}$ with Haet in the presence of Ag^+ (Scheme 1). This complex is the first example of N,S-chelation of an aliphatic aminothiolate ligand to a bis(diimine)-type ruthenium(II) core, although several bis(diimine)-type ruthenium(II) complexes with an aromatic iminothiolate ligand with an N,S-donor set have been presented.[2,5,6] Notably, this thiolato-bridged $Ru^{II}Ag^{I}Ru^{II}$ complex was found to be converted into a rare single-disulfide-bridged $Ru^{II}Ru^{II}$ dinuclear complex.[7] In this Communication, we report on the syntheses and properties of these Ru^{II} complexes, along with their structural characterization.

Treatment of a red-orange solution containing $[Ru(solvent)_2(bpy)_2]^{2+}$ and Ag^+ in a 1:1 ratio, which was in situ

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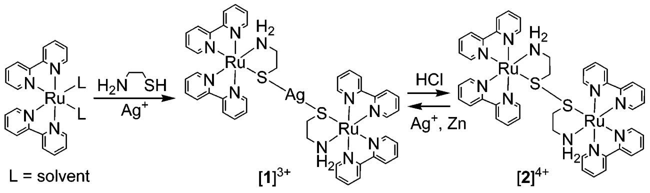
Scheme 1



prepared from [RuCl$_2$(bpy)$_2$][8] and 3 equiv of AgClO$_4$ in ethanol/water (1:1), with excess Haet under reflux gave a red-brown solution, from which a dark-red-brown powder (**1**) was isolated by the addition of aqueous NH$_4$PF$_6$.[9] The electronic absorption spectrum of **1** in acetonitrile is characterized by an intense (metal-to-ligand charge-transfer) MLCT band at 501 nm with a shoulder at the shorter wavelength side, besides a more intense band at 293 nm assignable to a bpy $\pi-\pi^*$ transition (Figure 1).[5,10] X-ray fluorescence spectrometry suggested that **1** contains Ru and Ag atoms in a 2:1 ratio, and its elemental analytical data were in agreement with the formula for a 2:1 adduct of [Ru(aet)(bpy)$_2$]$^+$ and Ag$^+$. The crystal structure of **1**, which is composed of a complex cation and three PF$_6^-$ anions, was established by single-crystal X-ray analysis.[9] As shown in Figure 2, the complex cation of **1** consists of two approximately octahedral [Ru(aet)(bpy)$_2$]$^+$ units with an N,S-chelating aet ligand and an Ag^I atom. The two thiolato S atoms from two [Ru(aet)(bpy)$_2$]$^+$ units coordinate to the Ag^I atom in a roughly linear geometry [S−Ag−S = 164.30(4)°] to form an S-bridged Ru^{II}Ag^{I}Ru^{II} trinuclear structure in [Ag{Ru(aet)(bpy)$_2$}$_2$]$^{3+}$. The Ru−S bond distances in **1** [av 2.376(2) Å] are slightly shorter than those in [Ru$_2$(μ-Haet)$_2$(bpy)$_4$]$^{4+}$ with a Ru$_2$S$_2$ diamond core [av 2.417(1) Å for the meso isomer and 2.405(2) Å for the racemic isomer].[4] The Ag−S bond distances [av Ag−S = 2.373(2) Å] are ca. 0.03 Å shorter than those found in the related linear-type Co^{III}Ag^{I}Co^{III} trinuclear complexes, [Ag{Co(aet)(en)$_2$}$_2$]$^{5+}$ [av 2.400(1) Å] and $\Lambda_L\Lambda_L$-[Ag{Co(L-cysteinato-*N*,*S*)(en)$_2$}$_2$]$^{3+}$ [av 2.393(1) Å],[11] indicating the stronger binding nature of the thiolato group in each [Ru(aet)(bpy)$_2$]$^+$ unit toward an Ag^I center. Considering the chiral configurations of the two [Ru(aet)(bpy)$_2$]$^+$ units (Δ and Λ) and the two bridging S atoms (*R* and *S*), 10 isomers are possible for [Ag{Ru(aet)(bpy)$_2$}$_2$]$^{3+}$. Crystal **1** consists of the $\Delta R-\Delta R$ and $\Lambda S-\Lambda S$ isomers, which combine to form a racemic compound. The same stereochemical behavior has been found in [Ag{Co(aet)(en)$_2$}$_2$]$^{5+}$.

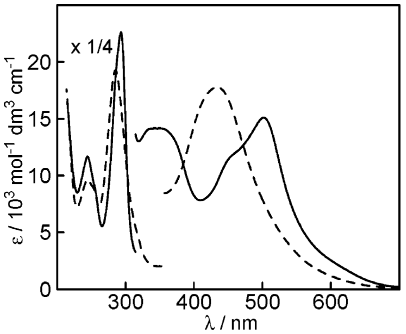


Figure 1. Electronic absorption spectra of **1** (—) and **2** (- - -) in acetonitrile.

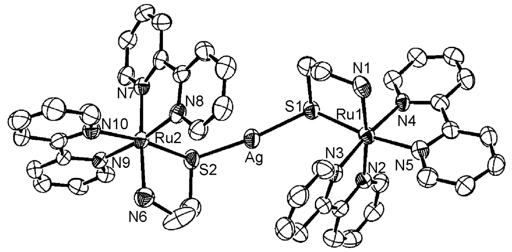


Figure 2. Perspective view of the complex cation of **1** with the atomic labeling scheme. H atoms are omitted for clarity.

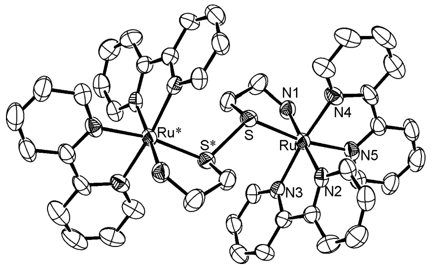


Figure 3. Perspective view of the complex cation of **2** with the atomic labeling scheme. H atoms are omitted for clarity.

Attempts to remove Ag^I from **1** by treatment with excess NaCl were unsuccessful. On the other hand, treatment of **1** with 1 M HCl in acetonitrile/water (1:1) resulted in the precipitation of AgCl and the isolation of a brown powder (**2**).[9] The absorption spectral feature of **2** is distinct from that of **1** in the visible region, showing an intense MLCT at 434 nm (Figure 1). The absence of an Ag atom in **2** was confirmed by X-ray fluorescence spectrometry, and its elemental analytical result was in good agreement with a formula for [Ru(aet)(bpy)$_2$](PF$_6$)$_2$, rather than that for [Ru(aet)(bpy)$_2$](PF$_6$). X-ray analysis revealed that the complex cation of **2** does not have an expected mononuclear structure but a dinuclear structure bearing a cystamine (cysta) ligand that bridges two Ru centers through a bis(bidentate-N,S) binding mode (Figure 3).[9] A crystallographic inversion center is located at the midpoint of a S−S bond, and thus half the complex cation is crystallographically independent. The presence of four PF$_6^-$ anions per one complex cation in the unit cell implies that the entire complex cation of **2** is tetravalent. Thus, the complex cation of **2** is formulated as [Ru$_2$(cysta)(bpy)$_4$]$^{4+}$, having two Ru centers with a formal charge of 2+. The S−S bond distance in **2** is 2.163(3) Å, which is comparable with the S−S distance in the related dinuclear structure in [M$_2$(aet)$_4$(cysta)]$^{2+}$ [2.158(3) Å for M = Ir^{III} and 2.147(1) Å for M = Rh^{III}].[11] It is interesting to note that the Ru−S distance in **2** with a neutral cysta ligand [2.291(2) Å] is appreciably shorter than those in **1** with anionic aet ligands [av 2.376(2) Å], while the Ru−N$_{aet}$ [av 2.139(3) Å in **1** and 2.133(5) Å in **2**] and Ru−N$_{bpy}$ distances [av 2.056(4) Å in **1** and 2.068(6) Å in **2**] are similar. This

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implies that a Ru^{II} center coordinated by two bpy ligands prefers a disulfide S donor to a thiolato S donor. In **2**, the two octahedral Ru^{II} units have Δ and Λ configurations with *R* and *S* configurational disulfide S atoms to form a meso compound. The selective formation of the $\Delta R{-}\Lambda S$ meso isomer has also been found in $[M_2(aet)_4(cysta)]^{2+}$.

The ^1H NMR spectrum of **1** in acetonitrile-d_3 at room temperature exhibits a single set of sharp signals corresponding to a $[Ru(aet)(bpy)_2]^+$ unit.[9,13] This is also the case for its ^{13}C NMR spectrum, which gives two methylene C signals (δ 29.88 and 49.15) for two aet ligands and 19 aromatic C signals (δ 123.90−159.39) for four bpy ligands in the complex.[9] When the temperature is lowered, broadening of the ^1H NMR spectral signals was recognized for **1**.[9] The NMR spectral behavior suggests the existence of two or more isomers of $[Ag\{Ru(aet)(bpy)_2\}_2]^{3+}$ in solution,[14] which are rapidly interconverted not to be discriminated by NMR spectroscopy, rather than the existence of a single racemic isomer found in the crystal. On the other hand, the ^1H NMR spectrum of **2** in acetonitrile-d_3 at room temperature shows considerably broad signals over the whole region.[15,16] However, lowering the temperature leads to a sharpening of the signals. A closer inspection of the variable-temperature ^1H NMR spectra suggested that in solution **2** exists as a mixture of asymmetrical and symmetrical isomers of $[Ru_2(cysta)(bpy)_4]^{4+}$,[9,14] which are interconverted with each other on the NMR time scale. The ^{13}C NMR spectrum of **2** in acetonitrile-d_3 at −30 °C is consistent with the existence of the two isomers in solution, giving six methylene C signals (δ 40.77−44.33) in addition to aromatic C signals (δ 124.66−158.80).[9] The cyclic voltamogram of **2** in acetonitrile under N_2 displays two reductions at −0.40 and −0.53 V and an oxidation at −0.31 V (vs Ag/Ag^+), besides two bpy-centered redox couples at −1.90 and −2.19 V (Figure 4).[9] It is most likely that the two reductions are due to the $[Ru^{II}_2(cysta)(bpy)_4]^{4+}/2[Ru^{II}(aet)(bpy)_2]^+$ conversion for the two isomers, which is coupled with the oxidation at −0.31 V. Spectroelectrochemical experiments for **2** were carried out using an optically transparent thin-layer electrode (OTTLE) cell under N_2. When the potential is decreased from 0 to −0.70 V, the absorption spectrum of **2** gradually changes with the isosbestic points at 482, 387, and 332 nm (Figure 4). The absorption spectrum recorded at −0.70 V shows a visible band at 538 nm with a shoulder at the shorter wavelength side. This spectral feature resembles that of **1**, which is compatible with the generation of $[Ru^{II}(aet)(bpy)_2]^+$ by the electrochemical reduction of **2**. Here, it should be noted that **2** was not reverted back to **1** by treatment only with Ag^+ in acetonitrile/water (1:1). However, the addition of Zn powder, which acts as a reducing agent, to a mixture of **2** and Ag^+ led to the isolation of **1**.[9]

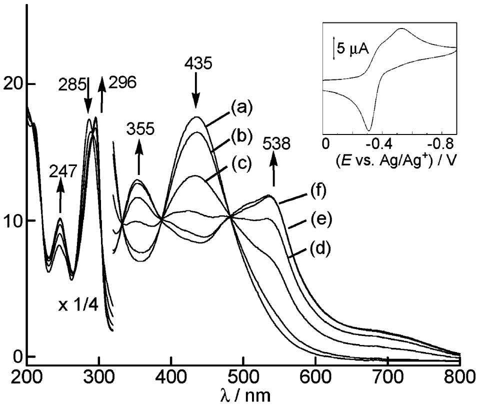

Figure 4. Sequential absorption spectra obtained during an OTTLE spectropotentiostatic experiment on **2** (0.5 mM) in $CH_3CN/[Bu_4N]PF_6$ (0.1 M) at (a) 0, (b) −300, (c) −350, (d) −375, (e) −400, and (f) −700 mV (vs Ag/Ag^+).

In summary, we showed that the thiolato-bridged $Ru^{II}Ag^{I}Ru^{II}$ complex composed of two $[Ru(aet)(bpy)_2]^+$ units, $[Ag\{Ru(aet)(bpy)_2\}_2]^{3+}$ ($[\mathbf{1}]^{3+}$), is successfully prepared from the reaction of $[Ru(solvent)_2(bpy)_2]^{2+}$ with Haet in the presence of Ag^+. Interestingly, the removal of the linking Ag^I atom in $[\mathbf{1}]^{3+}$ by treatment with HCl is accompanied by the autoxidation of coordinated thiolate to coordinated disulfide, producing the disulfide-bridged $Ru^{II}Ru^{II}$ complex, $[Ru_2(cysta)(bpy)_4]^{4+}$ ($[\mathbf{2}]^{4+}$). This result implies that the mononuclear $[Ru^{II}(aet)(bpy)_2]^+$ is difficult to isolate under aerobic conditions, which is understood by the fairly negative reduction potentials of **2**. The strong σ- and π-donating character of an aliphatic thiolato group, together with the lack of π-accepting character of an amine group, is responsible for this result. The reverse conversion of $[\mathbf{2}]^{4+}$ into $[\mathbf{1}]^{3+}$ was also achieved by treatment with Ag^+ assisted by Zn reduction. Thus, the present result showed the unique interconversion between the $[Ru^{II}(RS^-)]$ and $[Ru^{II}(RSSR)Ru^{II}]$ species with retention of the octahedral [Ru(bidentate-*N,S*)$(bpy)_2$] unit.

Acknowledgment. This work was partially supported by Grants-in-Aid for Scientific Research on Priority Areas (18033030) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

Supporting Information Available: Crystallographic data in CIF format and experimental procedures, crystallographic data, and several spectra in PDF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) (a) The electrospray mass spectrometry (ES-MS) spectrum of **1** in acetonitrile showed a cluster of signals centered at $m/z = 363.0$ corresponding to $[Ag\{Ru(aet)(bpy)_2\}_2]^{3+}$, besides those at $m/z = 521.9$, 490.0, 337.7, and 320.1 corresponding to $[Ru(NH_2CH_2CH_2SO_2)(bpy)_2]^+$, $[Ru(aet)(bpy)_2]^+$, $[Ag\{Ru(aet)(bpy)_2\}\{Ru(aet)(CH_3CN)_2(bpy)\}]^{3+}$, and $[\{Ru(aet)(bpy)_2\}Ag(CH_3CN)]^{2+}$, respectively. See the Supporting Information.

(14) The electronic spectrum of each of **1** and **2** in acetonitrile is essentially the same as that in the solid state, which suggests the retention of the thiolato-bridged $Ru^{II}Ag^{I}Ru^{II}$ and the disulfide-bridged $Ru^{II}Ru^{II}$ structures in solution. See the Supporting Information.

(15) The magnetic measurement at room temperature indicated that the solid sample of **2** is diamagnetic, consistent with the low-spin d^6 electronic configuration of Ru^{II} centers. The diamagnetic nature of **2** in the solid state and in acetonitrile is also supported by the EPR spectra that are essentially silent.

(16) The ES-MS spectrum of **2** in acetonitrile gave a main signal at $m/z = 635.0$, the calculated molecular mass and the isotopic distribution of which match well with those for a mixture of $\{[Ru^{III}(aet)(bpy)_2](PF_6)\}^+$ and $\{[Ru^{II}_2(cysta)(bpy)_4](PF_6)_2\}^{2+}$. See the Supporting Information.