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# Conversion of 2-Aminoethanethiolate (aet) to 2-Benzoylaminoethanethiolate (L) in a *S*-Bridged Diruthenium(II) Complex Composed of Two *cis*-[Ru(bpy)$_2$] Units. Crystal Structures of ΔΔ/ΛΛ-[{Ru(bpy)$_2$}$_2$-($\mu$-Haet)$_2$]$^{4+}$ and ΔΔ/ΛΛ-[{Ru(bpy)$_2$}$_2$($\mu$-L)$_2$]$^{2+}$

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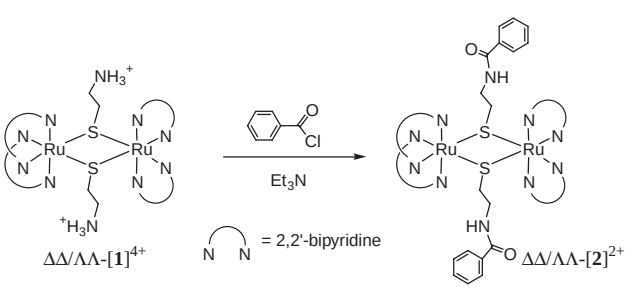
A diruthenium(II) complex, ΔΔ/ΛΛ-[{Ru(bpy)$_2$}$_2$($\mu$-L)$_2$]$^{2+}$ (ΔΔ/ΛΛ-[**2**]$^{2+}$), in which two *cis*-[Ru(bpy)$_2$]$^{2+}$ units are bridged by two S atoms from two 2-benzoylaminoethanethiolate (L) ligands, was synthesized by the reaction of ΔΔ/ΛΛ-[{Ru(bpy)$_2$}$_2$($\mu$-Haet)$_2$]$^{4+}$ (aet = 2-aminoethanethiolate; ΔΔ/ΛΛ-[**1**]$^{4+}$) with benzoyl chloride in the presence of a base. The molecular structure and electrochemical properties of ΔΔ/ΛΛ-[**2**]$^{2+}$ were discussed in comparison with those of ΔΔ/ΛΛ-[**1**]$^{4+}$.

During the past three decades, a number of diruthenium(II) complexes composed of two *cis*-[Ru(bpy)$_2$]$^{2+}$ units have been synthesized with the aim of investigating the spectroscopic and electrochemical characteristics based on the electronic communication between two metal centers.[1–3] In many cases, conjugated bridging ligands with two or more donor atoms, such as pyrazine and 4,4′-bipyridine, have been employed to bridge two *cis*-[Ru(bpy)$_2$]$^{2+}$ units.[2] On the other hand, reports on the use of bridging ligands with a single donor atom have been limited in number,[3] presumably because of the presence of an intramolecular non-bonding interaction between bpy and bridging ligands, which causes difficulty in the isolation of this kind of dinuclear species. Recently, we have shown that 2-aminoethanethiolate (aet = $^-$SCH$_2$CH$_2$NH$_2$) can be used to create isolable *meso* (ΔΛ) and *racemic* (ΔΔ/ΛΛ) isomers of [{Ru$^{II}$(bpy)$_2$}$_2$($\mu$-Haet)$_2$]$^{4+}$ ([**1**]$^{4+}$), in which two *cis*-[Ru(bpy)$_2$]$^{2+}$ units are bridged by two thiolato S atoms from two protonated Haet ($^-$SCH$_2$CH$_2$NH$_3^+$) ligands.[4] Notably, the electrochemical behavior of [**1**]$^{4+}$ was found to be significantly altered by the deprotonation of terminal NH$_3^+$ groups of Haet ligands despite the presence of an aliphatic C$_2$H$_4$ group between the N atom and the Ru$_2$S$_2$ core. Thus, we carried out chemical modification of the terminal free NH$_2$ groups in this *S*-bridged diruthenium(II) structure in order to clarify the effect of pendant groups attached to the bridging S atoms on the electrochemical property. In this paper, we report on the synthesis, crystal structure, and properties of a *S*-bridged diruthenium(II) complex with 2-benzoylaminoethanethiolate (L = $^-$SCH$_2$CH$_2$NH(CO)C$_6$H$_5$), ΔΔ/ΛΛ-[{Ru$^{II}$(bpy)$_2$}$_2$($\mu$-L)$_2$]$^{2+}$ (ΔΔ/ΛΛ-[**2**]$^{2+}$), which was successfully derived from ΔΔ/ΛΛ-[{Ru$^{II}$(bpy)$_2$}$_2$($\mu$-Haet)$_2$]$^{4+}$ (ΔΔ/ΛΛ-[**1**]$^{4+}$) by reaction with benzoyl chloride in the presence of a base (Scheme 1), along with the crystal structure of ΔΔ/ΛΛ-[**1**]$^{4+}$.

Treatment of a red-purple solution containing ΔΔ/ΛΛ-[**1**](ClO$_4$)$_4$ and excess Et$_3$N in dry ethanol with 3 molar equiv of benzoyl chloride at 50 °C produced a red-purple solution, from which a dark brown powder (ΔΔ/ΛΛ-[**2**](PF$_6$)$_2$) was isolated in a high yield after the addition of aqueous NH$_4$PF$_6$. The electronic absorption spectral features of ΔΔ/ΛΛ-[**2**]$^{2+}$ in CH$_3$CN are very similar to those of ΔΔ/ΛΛ-[**1**]$^{4+}$ over the whole region,[4] showing two intense bands at 518 and 375 nm assignable to metal(Ru)-to-ligand(bpy) charge-transfer (MLCT) bands, as well as a more intense band at 290 nm due to an intraligand bpy $\pi$–$\pi^*$ transition, although the two bands are located at the longer wavelength side relative to the corresponding bands (501 and 359 nm) for ΔΔ/ΛΛ-[**1**]$^{4+}$.[5] In the $^{13}$C NMR spectrum in DMSO-$d_6$, ΔΔ/ΛΛ-[**2**]$^{2+}$ gives aromatic carbon signals at $\delta$ 126.71, 127.86, 130.85, and 133.78 due to phenyl rings and a signal at $\delta$ 164.67 due to a carbonyl carbon atom, in addition to the signals found in the $^{13}$C NMR spectrum of ΔΔ/ΛΛ-[**1**]$^{4+}$.[5] Furthermore, in the $^1$H NMR spectrum of ΔΔ/ΛΛ-[**2**]$^{2+}$, a broad signal was observed at $\delta$ 7.5[5] that is characteristic of an amide NH proton.[6] From these results, along with the elemental analysis, it is assigned that ΔΔ/ΛΛ-[**2**]$^{2+}$ is a *S*-bridged diruthenium(II) complex, ΔΔ/ΛΛ-[{Ru(bpy)$_2$}$_2$($\mu$-L)$_2$]$^{2+}$, in which NH$_3^+$ groups in ΔΔ/ΛΛ-[**1**]$^{4+}$ are replaced by NHCOPh groups. The *S*-bridged structure in ΔΔ/ΛΛ-[**2**](PF$_6$)$_2$, along with the structure in ΔΔ/ΛΛ-[**1**](PF$_6$)$_4$, was established by X-ray crystallography.

ORTEP drawings of the complex cations ΔΔ/ΛΛ-[**1**]$^{4+}$ and ΔΔ/ΛΛ-[**2**]$^{2+}$ are shown in Fig. 1. Consistent with the assignment made in a previous paper,[4] the complex cation ΔΔ/ΛΛ-[**1**]$^{4+}$ consists of two octahedral *cis*-[Ru(bpy)$_2$]$^{2+}$ units that are linked by two S atoms from two protonated Haet ligands, forming a *S*-bridged diruthenium(II) structure in [{Ru(bpy)$_2$}$_2$($\mu$-Haet)$_2$]$^{4+}$ with a Ru$_2$S$_2$ diamond core (Fig. 1a). The two *cis*-[Ru(bpy)$_2$]$^{2+}$ units in ΔΔ/ΛΛ-[**1**]$^{4+}$ have the same chiral configuration (Δ or Λ) to afford a *racemic* compound. The bond distances around the Ru atoms (av. Ru–S = 2.405(2) Å and Ru–N = 2.069(4) Å) in ΔΔ/ΛΛ-[**1**]$^{4+}$ are similar to those found in the *meso* (ΔΛ) isomer of [**1**]$^{4+}$ (av.




Scheme 1.

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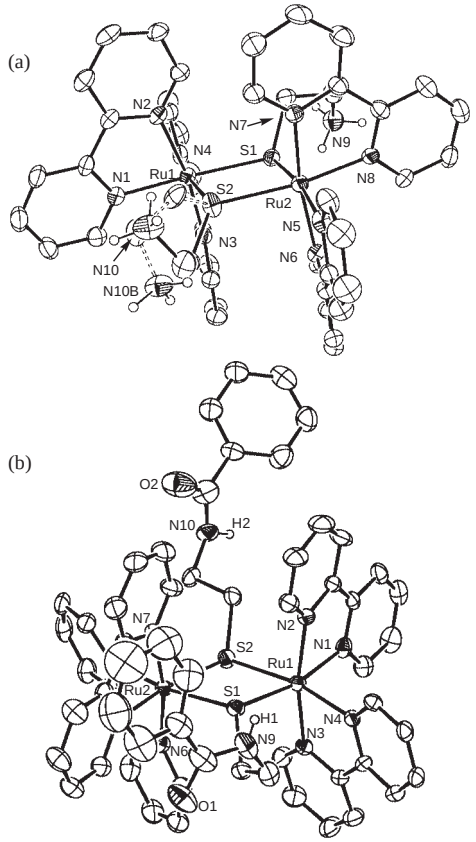


Fig. 1. Perspective views of $\Delta\Delta/\Lambda\Lambda$-[**1**]$^{4+}$ (a) and $\Delta\Delta/\Lambda\Lambda$-[**2**]$^{2+}$ (b). The $\Delta\Delta$ isomer is selected for each complex. Aromatic and methylene H atoms are omitted for clarity.

Ru–S = 2.417(1) Å and Ru–N = 2.066(5) Å), which has been structurally characterized.[4] However, the *trans* N–Ru–N and the *cis* S–Ru–S angles in $\Delta\Delta/\Lambda\Lambda$-[**1**]$^{4+}$ (av. N–Ru–N = 169.6(2)° and S–Ru–S = 80.74(6)°) are closer to the idealized octahedral angles than those in $\Delta\Lambda$-[**1**]$^{4+}$ (av. N–Ru–N = 168.1(2)° and S–Ru–S = 77.79(5)°). In addition, the Ru–S–Ru bridging angles in $\Delta\Delta/\Lambda\Lambda$-[**1**]$^{4+}$ (99.26(6)°) are smaller than those in $\Delta\Lambda$-[**1**]$^{4+}$ (102.22(5)°), leading to a Ru···Ru distance (3.665(3) Å) shorter than that in $\Delta\Lambda$-[**1**]$^{4+}$ (av. 3.763(2) Å). These observations can be ascribed to the steric congestion between bpy ligands belonging to the different *cis*-[Ru(bpy)$_2$]$^{2+}$ units, which is less critical in the *racemic* isomer. It is noticed that $\Delta\Delta/\Lambda\Lambda$-[**1**]$^{4+}$ adopts a mixture of *syn* and *anti* configurations with respect to the two Haet pendant arms (Fig. 1a). This is distinct from the selective formation of a sterically favorable *anti* configuration in $\Delta\Lambda$-[**1**]$^{4+}$,[4] which is also ascribed to the difference in the steric congestion between $\Delta\Delta/\Lambda\Lambda$-[**1**]$^{4+}$ and $\Delta\Lambda$-[**1**]$^{4+}$. Note that $\Delta\Delta/\Lambda\Lambda$-[**1**]$^{4+}$ has been shown to give a single set of $^1$H and $^{13}$C NMR signals in DMSO-$d_6$,[4] suggestive of the selective formation of an *anti* configuration in solution, rather than the *syn–anti* interconversion that is fast on the NMR time scale.

As shown in Fig. 1b, the complex cation $\Delta\Delta/\Lambda\Lambda$-[**2**]$^{2+}$ also has a *S*-bridged diruthenium(II) structure ([{Ru(bpy)$_2$}$_2$-($\mu$-L)$_2$]$^{2+}$), in which two *cis*-[Ru(bpy)$_2$]$^{2+}$ units are linked by two S atoms to form a Ru$_2$S$_2$ diamond core (av. Ru–S = 2.394(2) Å, Ru–S–Ru = 100.09(7)°, and S–Ru–S = 79.81(6)°). The overall structure in $\Delta\Delta/\Lambda\Lambda$-[**2**]$^{2+}$ is essentially the same as that in $\Delta\Delta/\Lambda\Lambda$-[**1**]$^{4+}$, except that $C_2H_4NH_3^+$ pendant arms in $\Delta\Delta/\Lambda\Lambda$-[**1**]$^{4+}$ are replaced by $C_2H_4NH$-COPh arms. The bond distances and angles around the Ru and S atoms in $\Delta\Delta/\Lambda\Lambda$-[**2**]$^{2+}$ are comparable with those in $\Delta\Delta/\Lambda\Lambda$-[**1**]$^{4+}$. Furthermore, $\Delta\Delta/\Lambda\Lambda$-[**2**]$^{2+}$ exists as a *racemic* compound with $\Delta\Delta$ and $\Lambda\Lambda$ configurations, as does $\Delta\Delta/\Lambda\Lambda$-[**1**]$^{4+}$. Thus, the reaction of $\Delta\Delta/\Lambda\Lambda$-[**1**]$^{4+}$ with benzoyl chloride in the presence of a base proceeds with retention of the *S*-bridged diruthenium(II) structure. It is worth noting that $\Delta\Delta/\Lambda\Lambda$-[**2**]$^{2+}$ adopts only an *anti* configuration, unlike the case for $\Delta\Delta/\Lambda\Lambda$-[**1**]$^{4+}$. This may be related to the existence of an intermolecular C=O···HN hydrogen-bonding interaction between amide groups in $\Delta\Delta/\Lambda\Lambda$-[**2**]$^{2+}$ (N10···O1′ = 2.816(7) Å), forming a one-dimensional chain structure.[5]

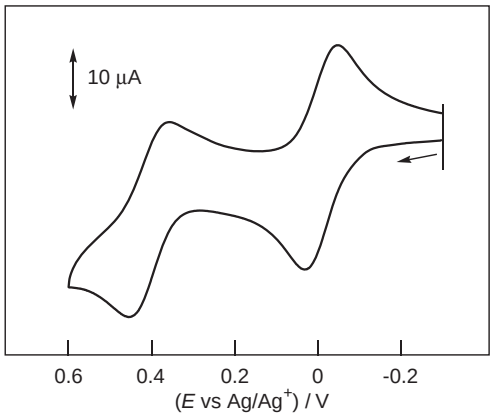


Fig. 2. A cyclic voltammogram of $\Delta\Delta/\Lambda\Lambda$-[**2**]$^{2+}$ in $CH_3CN$ (scan rate of 0.1 V s$^{-1}$ and complex concentration of 1.0 mmol dm$^{-3}$).

In the cyclic voltammogram (CV) in $CH_3CN$, $\Delta\Delta/\Lambda\Lambda$-[**2**]$^{2+}$ displays two reversible one-electron redox couples at −0.01 and +0.41 V (vs Ag/Ag$^+$) (Fig. 2), which are attributed to the stepwise oxidation of two Ru$^{II}$ centers,[3,4] as well as bpy-centered redox couples in the region of −1.7–−2.4 V.[5] From the separation between the two redox couples, a comproportionation constant ($K_c$) was evaluated to be $6 \times 10^6$, suggesting that the Ru$^{III}$Ru$^{II}$ mixed-valence species is relatively stable.[2,7] Consistent with this, in the potential step spectroelectrochemistry of $\Delta\Delta/\Lambda\Lambda$-[**2**]$^{2+}$ in $CH_3CN$, a broad intervalence charge-transfer (IVCT) band was observed at ca. 1060 nm on increasing the potential from −0.3 to +0.2 V, which disappeared on further increasing the potential to +0.6 V.[5] It has been shown that the CV of $\Delta\Delta/\Lambda\Lambda$-[**1**]$^{4+}$ also gives two reversible redox couples in the positive potential region.[4] However, they appear at +0.17 and +0.55 V, which are ca. 0.15 V more positive than the two redox couples for $\Delta\Delta/\Lambda\Lambda$-[**2**]$^{2+}$. Since the deprotonated form of $\Delta\Delta/\Lambda\Lambda$-[**1**]$^{4+}$ ($\Delta\Delta/\Lambda\Lambda$-[{Ru(bpy)$_2$}$_2$($\mu$-aet)$_2$]$^{2+}$) has been found to exhibit two redox processes at similar potentials (+0.05 and +0.40 V) to those for $\Delta\Delta/\Lambda\Lambda$-[**2**]$^{2+}$,[4] it is assumed that the overall charge of complex cations significantly affects the redox potentials because of the electrostatic effect. It should be noted that the redox processes at +0.05 and +0.40 V for $\Delta\Delta/\Lambda\Lambda$-[{Ru(bpy)$_2$}$_2$($\mu$-aet)$_2$]$^{2+}$ are almost irreversible,[4] while those for

$\Delta\Delta/\Lambda\Lambda$-$[\mathbf{2}]^{2+}$ are reversible. The irreversibility of $\Delta\Delta/\Lambda\Lambda$-$[\{Ru(bpy)_2\}_2(\mu\text{-aet})_2]^{2+}$ seems to be due to the coordination of the terminal $NH_2$ groups toward Ru centers to give mononuclear species, while the NHCOPh groups in $\Delta\Delta/\Lambda\Lambda$-$[\mathbf{2}]^{2+}$ remain uncoordinated in the course of the redox reactions.

## Experimental

**Preparation of $\Delta\Delta/\Lambda\Lambda$-[1]$(PF_6)_4$.** To a solution containing 0.02 g of $\Delta\Delta/\Lambda\Lambda$-$[\mathbf{1}](ClO_4)_4\cdot 5H_2O$[4] in 10 $cm^3$ of 1:1 ethanol/water was added a 1 mol $dm^{-3}$ aqueous solution of $NH_4PF_6$ (1 $cm^3$), followed by standing at room temperature for 1 day. The resulting dark brown powder was collected by filtration, washed with cold water, and then dried in air. Yield: 0.02 g. Anal. Calcd for $[\mathbf{1}](PF_6)_4\cdot 2H_2O$: C, 33.09; H, 3.16; N, 8.77%. Found: C, 33.15; H, 3.11; N, 8.73%. A single crystal used for X-ray analysis ($\Delta\Delta/\Lambda\Lambda$-$[\mathbf{1}](PF_6)_4\cdot 2CH_3CN\cdot H_2O$) was obtained by slow diffusion of diethyl ether into an acetonitrile solution of this powder.

**Preparation of $\Delta\Delta/\Lambda\Lambda$-[2]$(PF_6)_2$.** To a cold solution (0 °C) containing 0.10 g (0.07 mmol) of $\Delta\Delta/\Lambda\Lambda$-$[\mathbf{1}](ClO_4)_4\cdot 5H_2O$ and 0.15 g (1.50 mmol) of triethylamine in 100 $cm^3$ of dry ethanol was slowly added 0.03 g (0.21 mmol) of benzoyl chloride in 15 $cm^3$ of ethanol. The mixture was stirred at 0 °C for 1 h, and then stirred at 50 °C for 3 h under a nitrogen atmosphere. The resulting red-purple solution was concentrated to ca. 15 $cm^3$ with a rotary evaporator. To this solution was added 2 $cm^3$ of a 1 mol $dm^{-3}$ aqueous solution of $NH_4PF_6$, which was allowed to stand at room temperature for 2 days. The resulting dark brown powder was collected by filtration, washed with cold water, and then dried in air. Yield: 0.10 g (90%). Anal. Calcd for $[\mathbf{2}](PF_6)_2\cdot 3H_2O$: C, 45.49; H, 3.82; N, 9.15%. Found: C, 45.22; H, 3.60; N, 9.17%. A single crystal used for X-ray analysis ($\Delta\Delta/\Lambda\Lambda$-$[\mathbf{2}](PF_6)_2\cdot CH_3CN$) was obtained by slow diffusion of diethyl ether into an acetonitrile solution of this powder.

**Measurements.** The electronic absorption spectra were recorded with a JASCO Ubest-55 spectrophotometer. The NMR spectra were recorded with a JEOL JNM-A500 NMR spectrometer at room temperature in DMSO-$d_6$ using tetramethylsilane (TMS) as an internal standard. Electrochemical experiments were performed by a CV-600A apparatus (BAS) at 25 °C in 0.1 mol $dm^{-3}$ $[Bu_4N]PF_6/CH_3CN$ with a glassy-carbon working electrode, a $Ag/AgNO_3$ (0.01 mol $dm^{-3}$) reference electrode, and a Pt-wire auxiliary electrode. Spectroelectrochemical measurements were performed under the same conditions, except for the use of a thin-layer quartz cell (0.5 mm light-path length) with a Pt-mesh (100 mesh) as a working electrode.

**X-ray Structural Determinations.** Single-crystal X-ray diffraction experiments for $\Delta\Delta/\Lambda\Lambda$-$[\mathbf{1}](PF_6)_4\cdot 2CH_3CN\cdot H_2O$ and $\Delta\Delta/\Lambda\Lambda$-$[\mathbf{2}](PF_6)_2\cdot CH_3CN$ were performed on a Rigaku RAXIS RAPID imaging plate diffractometer with graphite-monochromated Mo K$\alpha$ radiation at 200 K. Unit-cell parameters were determined by a least-squares refinement. The intensity data were collected by the $\omega$ scan mode up to $2\theta_{max} = 55.0°$. Empirical absorption corrections were applied. The structures were solved by direct methods and Patterson methods, respectively, and expanded using Fourier techniques. Non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods. Hydrogen atoms of NHCO groups in $\Delta\Delta/\Lambda\Lambda$-$[\mathbf{2}](PF_6)_2\cdot CH_3CN$ were found from difference Fourier maps, while other hydrogen atoms except those of solvated molecules were placed at calculated positions but were not refined. For $\Delta\Delta/\Lambda\Lambda$-$[\mathbf{1}](PF_6)_4\cdot 2CH_3CN\cdot H_2O$, two sets of disordered atoms of Haet ligands (C43, C44, N10 and C43B, C44B, N10B) were refined with site occupancy factors of 0.6 and 0.4, respectively. All calculations were performed using the CrystalStructure software package.[8] Crystal data for $\Delta\Delta/\Lambda\Lambda$-$[\mathbf{1}](PF_6)_4\cdot 2CH_3CN\cdot H_2O$: fw = 1661.17, triclinic, $P\bar{1}$, $a$ = 12.49(1) Å, $b$ = 13.454(9) Å, $c$ = 19.17(2) Å, $\alpha$ = 96.33(3)°, $\beta$ = 98.47(3)°, $\gamma$ = 92.28(2)°, $V$ = 3162(4) Å$^3$, $Z$ = 2, $D_{calcd}$ = 1.745 g $cm^{-3}$, $R$ ($R_w$) = 0.043 (0.085). Crystal data for $\Delta\Delta/\Lambda\Lambda$-$[\mathbf{2}](PF_6)_2\cdot CH_3CN$: fw = 1518.35, monoclinic, $P2_1/c$, $a$ = 11.512(7) Å, $b$ = 24.73(2) Å, $c$ = 22.56(2) Å, $\beta$ = 97.23(5)°, $V$ = 6371(7) Å$^3$, $Z$ = 4, $D_{calcd}$ = 1.583 g $cm^{-3}$, $R$ ($R_w$) = 0.045 (0.077). Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition numbers CCDC-285596 and -285597. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

## Supporting Information

Figures S1–S6 in PDF format. This material is available free of charge on the web at: http://www.csj.jp/journals/bcsj/.

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