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Bis(bipyridine)ruthenium(II) Complexes with an Aliphatic Sulfinato Donor: Synthesis, Characterization, and Properties

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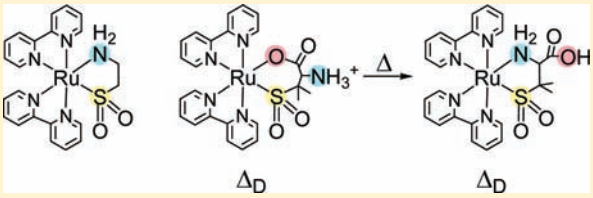
Supporting Information

ABSTRACT:



Treatment of a thiolato-bridged $Ru^{II}Ag^{I}Ru^{II}$ trinuclear complex, $[Ag\{Ru(aet)(bpy)_2\}_2]^{3+}$ (aet = 2-aminoethanthiolate; bpy = 2,2′-bipyridine), with NaI in aqueous ethanol under an aerobic condition afforded a mononuclear ruthenium(II) complex having an S-bonded sulfinato group, $[\mathbf{1}]^+$ ($[Ru(aesi\text{-}N,S)(bpy)_2]^+$ (aesi = 2-aminoethanesulfinate)). Similar treatment of optically active isomers of an analogous $Ru^{II}Ag^{I}Ru^{II}$ trinuclear complex, $Δ_DΔ_D$- and $Λ_DΛ_D$-$[Ag\{Ru(D\text{-}Hpen\text{-}O,S)(bpy)_2\}_2]^{3+}$ (D-pen = D-penicillaminate), with NaI also produced mononuclear ruthenium(II) isomers with an S-bonded sulfinato group, $Δ_D$- and $Λ_D$-$[\mathbf{2}]^+$ ($[Ru(D\text{-}Hpsi\text{-}O,S)(bpy)_2]^+$ (D-psi = D-penicillaminesulfinate)), respectively, retaining the bidentate-*O*,*S* coordination mode of a D-Hpen ligand and the absolute configuration (Δ or Λ) about a Ru^{II} center. On refluxing in water, the $Δ_D$ isomer of $[\mathbf{2}]^+$ underwent a linkage isomerization to form $Δ_D$-$[\mathbf{3}]^+$ ($[Ru(D\text{-}Hpsi\text{-}N,S)(bpy)_2]^+$), in which a D-Hpsi ligand coordinates to a Ru^{II} center in a bidentate-*N*,*S* mode. Complexes $[\mathbf{1}]^+$, $Δ_D$- and $Λ_D$-$[\mathbf{2}]^+$, and $Δ_D$-$[\mathbf{3}]^+$ were fully characterized by electronic absorption, CD, NMR, and IR spectroscopies, together with single-crystal X-ray crystallography. The electrochemical properties of these complexes, which are highly dependent on the coordination mode of sulfinate ligands, are also described.

INTRODUCTION

Metal−thiolate chemistry has been a considerably active area of research for a long time not only in the field of fundamental coordination chemistry, because of the versatile properties of thiolato metal complexes,[1] but also in the field of bioinorganic and biological chemistry in connection with the active sites of metallo-enzymes that involve metal−thiolate bonds.[2] One of the most significant properties of thiolato groups coordinated to a metal center is their relatively high nucleophilicity, which leads to derivatives modified at sulfur atoms.[2c,3−5] To date, a large number of metal complexes containing sulfenato, sulfinato, or disulfide group(s) have been prepared by the chemical and/or electrochemical oxidations of a variety of thiolato metal complexes.[2c,3c,4,5] However, this is not the case for ruthenium(II) complexes; the reactivity of a thiolato group bound to a Ru^{II} center has been investigated to a much less extent.[5] This is mainly because of the difficulty in the isolation of ruthenium(II) complexes with thiolato donor(s) that tends to stabilize a higher oxidation state of a metal center.[5b]

Recently, we reported the synthesis of a thiolato-bridged Ru^{II}-$Ag^{I}Ru^{II}$ trinuclear complex composed of two $[Ru(aet)(bpy)_2]^+$ mononuclear units, $[Ag\{Ru(aet)(bpy)_2\}_2]^{3+}$ (aet = 2-aminoethanthiolate; bpy = 2,2′-bipyridine), which is the first example of N,S-chelation of an aliphatic aminothiolate ligand to a bis(diimine)-type ruthenium(II) core.[6] The subsequent study indicated that D-Hpen can be introduced in this trinuclear structure in place of aet, leading to the isolation of optically pure bis(bipyridine)ruthenium-(II) species, $Δ_DΔ_D$- and $Λ_DΛ_D$-$[Ag\{Ru(D\text{-}Hpen)(bpy)_2\}_2]^{3+}$ (D-pen = D-penicillaminate).[7] Remarkably, the removal of a linking Ag^I ion in $[Ag\{Ru(aet)(bpy)_2\}_2]^{3+}$ by treatment with HCl was accompanied by the autoxidation of coordinated thiolate to coordinated disulfide, producing a disulfide-bridged $Ru^{II}Ru^{II}$ complex, $[Ru_2(cysta)(bpy)_4]^{4+}$ (cysta = cystamine).[6] This result implies that the thiolato group in $[Ru^{II}(aet)(bpy)_2]^+$ is highly reactive toward oxidation. Thus, we started to investigate the oxidation reactions of $[Ag\{Ru(aet)(bpy)_2\}_2]^{3+}$ and $[Ag\{Ru(D\text{-}Hpen)(bpy)_2\}_2]^{3+}$, which lead to the formation of mononuclear ruthenium(II) complexes with a sulfenato or sulfinato donor group.

In this paper, we report that the air oxidations of $[Ag\{Ru(aet)(bpy)_2\}_2]^{3+}$ and $[Ag\{Ru(D\text{-}Hpen)(bpy)_2\}_2]^{3+}$ give mononuclear ruthenium(II) complexes with a sulfinato donor, $[Ru(aesi)(bpy)_2]^+$ and $[Ru(D\text{-}Hpsi)(bpy)_2]^+$ (aesi = 2-aminoethanesulfinate, D-psi = D-penicillaminesulfinate), assisted by the removal of a linking Ag^I ion by treatment with I^- (Scheme 1). Spectroscopic and structural characterizations of these sulfinato ruthenium(II) complexes, together with

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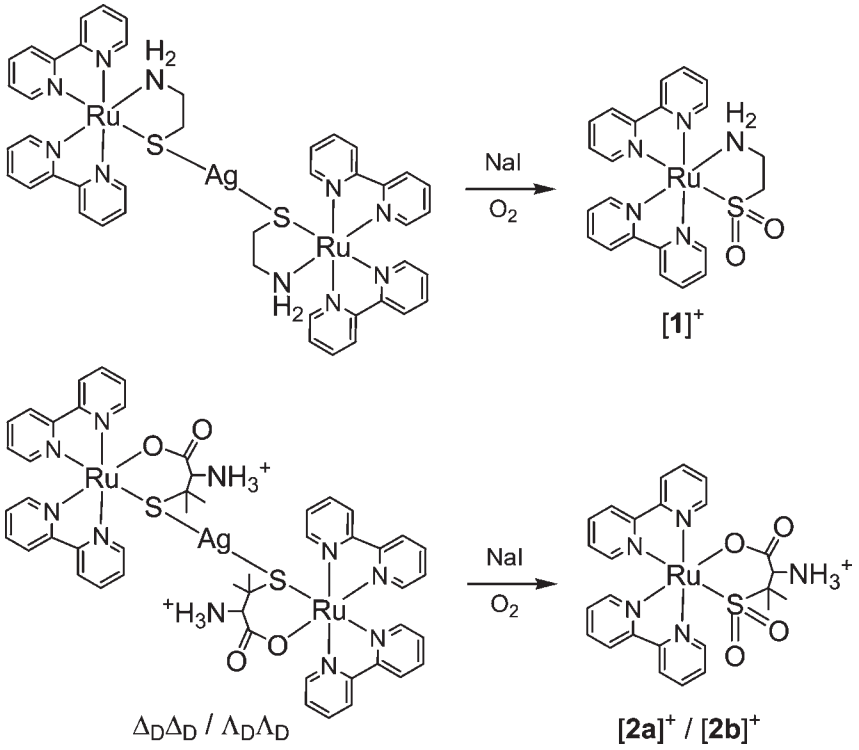
Scheme 1



their thermal and electrochemical stabilities in solution, are also reported. It should be noted that there are only three precedents of bis(diimine)-type ruthenium(II) complexes with a sulfinato donor,[5b,8] and furthermore, those with an aliphatic sulfinato donor have not been reported to date.

EXPERIMENTAL SECTION

Preparation of [Ru(aesi-*N*,*S*)(bpy)$_2$]PF$_6$ ([1]PF$_6$). *Method A.* To a dark brown solution containing 0.100 g (0.064 mmol) of [Ag{Ru(aet)(bpy)$_2$}$_2$](PF$_6$)$_3$·2H$_2$O[6] in 50 mL of 1:1 ethanol/water was added 0.050 g (0.33 mmol) of NaI. The mixture was stirred at room temperature for 12 h under air bubbling, during which time the solution color turned to dark orange. The deposited AgI was removed by filtration through Celite, and the filtrate was concentrated to about 10 mL with a rotary evaporator. The concentrated solution was chromatographed on an SP-Sephadex C-25 column (Na$^+$ form, ϕ 2.5 cm ×10 cm). After the column had been washed with water, an orange band was eluted with a 0.05 M aqueous solution of NaCl. The orange eluate was concentrated to dryness with a rotary evaporator, and then 100 mL of ethanol was added to it. After removal of deposited NaCl by filtration, the filtrate was concentrated to about 5 mL with a rotary evaporator, followed by the addition of a 1 M aqueous solution of NH$_4$PF$_6$ (0.3 mL). The mixture was stored at room temperature for 4 days, and the resulting red-orange crystals were collected by filtration, washed with cold water, and then dried in air. Yield: 0.041 g (45%). Anal. Calcd for [**1**]PF$_6$·2H$_2$O: C, 37.61; H, 3.73; N, 9.97%. Found: C, 37.74; H, 3.68; N, 10.07%. ^{1}H NMR (400 MHz, DMSO-d_6): δ, ppm 10.48 (1H, d, J = 5.7 Hz), 9.09 (1H, d, J = 5.4 Hz), 8.69−8.65 (3H, m), 8.55 (1H, d, J = 8.1 Hz), 8.21−8.16 (2H, m), 8.03 (1H, t, J = 7.8 Hz), 7.89 (1H, t, J = 7.8 Hz), 7.82 (1H, t, J = 6.6 Hz), 7.77 (1H, t, J = 6.6 Hz), 7.61 (1H, d, J = 4.6 Hz), 7.54 (1H, d, J = 4.9 Hz), 7.43 (1H, t, J = 6.5 Hz), 7.28 (1H, t, J = 6.6 Hz), 4.69 (1H, br t, J = 6.3 Hz), 4.05 (1H, br t, J = 6.5 Hz), 2.79−2.74 (1H, m), 2.61−2.54 (3H, m). ^{13}C NMR (125 MHz, DMSO-d_6): δ, ppm 157.52, 157.33, 155.75, 154.00, 151.32, 150.51, 150.11, 137.40, 136.54, 136.33, 135.45, 126.25, 126.18, 126.01, 125.77, 123.41, 123.03, 122.82, 122.79, 122.77 (*C*H of bpy); 63.51 (*C*H$_2$N), 40.12 (*C*H$_2$S). IR (KBr, cm^{-1}): 1604 ($\nu_{C=C,\ C=N}$), 1110 ($\nu_{asym\ S=O}$), 1010 ($\nu_{sym\ S=O}$), 838 (PF$_6^-$), 767 ($\delta_{C=C,\ C=N}$), 557 (PF$_6^-$). ESI-MS: m/z = 522 for [M-PF$_6$]$^+$.

Method B. To a solution containing 0.10 g (0.19 mmol) of [RuCl$_2$(bpy)$_2$]·2H$_2$O in 80 mL of 1:1 ethanol/water was added 0.015 g (0.20 mmol) of Haet and 0.008 g (0.2 mmol) of NaOH. The mixture was refluxed for 1 h under a nitrogen atmosphere, followed by being allowed to stand at room temperature in air overnight, which gave a dark brown solution. This solution was concentrated to dryness with a rotary evaporator, and then the residue was dissolved in a small amount of water, which was chromatographed on an SP-Sephadex C-25 column (Na$^+$ form, ϕ 2.5 cm ×15 cm). After the column had been washed with water, an orange band was eluted with a 0.05 M aqueous solution of NaCl. The orange eluate was concentrated to dryness with a rotary evaporator, and 50 mL of ethanol was added to it. After removal of deposited NaCl by filtration, the filtrate was concentrated to about 5 mL with a rotary evaporator, followed by the addition of a 1 M aqueous solution of NH$_4$PF$_6$ (0.3 mL). The mixture was stored at room temperature for 3 days, and the resulting red-orange crystals of [**1**]PF$_6$·2H$_2$O were collected by filtration, washed with cold water, and then dried in air. Yield: 0.058 g (43%).

Preparation of Δ_D-[Ru(D-Hpsi-*O*,*S*)(bpy)$_2$]PF$_6$ ([2a]PF$_6$). To a dark brown solution containing 0.300 g (0.18 mmol) of $\Delta_D\Delta_D$-[Ag{Ru(D-Hpen-*O*,*S*)(bpy)$_2$}$_2$](ClO$_4$)$_3$·5.5H$_2$O[7] in 100 mL of 1:1 ethanol/water was added 0.137 g (0.91 mmol) of NaI. The mixture was stirred at room temperature for 2 days under air bubbling, during which time the solution turned to dark orange. The deposited AgI was removed by filtration through Celite, and the filtrate was concentrated to about 10 mL with a rotary evaporator. The concentrated solution was

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chromatographed on an SP-Sephadex C-25 column (Na^+ form, ϕ 4.0 cm ×12 cm). After the column had been washed with water, an orange band was eluted with a 0.05 M aqueous solution of NaCl. The orange eluate was concentrated to dryness with a rotary evaporator, and then 50 mL of ethanol was added to it. After removal of deposited NaCl by filtration, the filtrate was concentrated to about 30 mL with a rotary evaporator, followed by the addition of a 1 M aqueous solution of NH_4PF_6 (0.4 mL) and 2 mL of water. The mixture was allowed to stand at room temperature in the dark for 2 weeks, and the resulting red-orange crystals were collected by filtration, washed with cold water, and then dried in air. Yield: 0.145 g (46%). Anal. Calcd for [**2a**]$PF_6 \cdot 6.5H_2O$: C, 35.09; H, 4.59; N, 8.18%. Found: C, 34.72; H, 4.27; N, 8.47%. ^{1}H NMR (400 MHz, DMSO-d_6): δ, ppm 10.48 (1H, d, J = 4.6 Hz), 8.74−8.71 (3H, m), 8.61 (1H, d, J = 5.1 Hz), 8.56 (1H, d, J = 8.3 Hz), 8.21 (1H, t, J = 8.0 Hz), 8.17 (1H, t, J = 7.9 Hz), 8.09 (1H, t, J = 7.8 Hz), 7.89 (1H, t, J = 7.8 Hz), 7.82 (1H, d, J = 5.9 Hz), 7.77−7.74 (2H, m), 7.54 (3H, br s), 7.41 (1H, t, J = 7.0 Hz), 7.37 (1H, d, J = 4.4 Hz), 7.28 (1H, t, J = 6.7 Hz), 3.61 (1H, s), 0.90 (3H, s), 0.87 (3H, s). ^{13}C NMR (125 MHz, DMSO-d_6): δ, ppm 172.22 (*C*OO of D-psi); 159.28, 158.80, 157.99, 156.41, 155.42, 152.76, 149.65, 149.49, 137.87, 136.84, 136.58, 135.17, 126.15, 126.13, 125.64, 125.40, 123.37, 123.30, 123.13, 122.90 (*C*H of bpy); 60.31 (*C*N of D-psi); 57.52 (*C*S of D-psi); 18.93, 15.25 (CH_3 of D-psi). IR (KBr, cm^{-1}): 1637 (COO^-), 1604 ($\nu_{C=C,\ C=N}$), 1116 ($\nu_{asym\ S=O}$), 1010 ($\nu_{sym\ S=O}$), 847 (PF_6^-), 768 ($\delta_{C=C,\ C=N}$), 558 (PF_6^-). ESI-MS: m/z = 594 for $[M\text{-}PF_6]^+$.

Preparation of Λ_D-[Ru(D-Hpsi-*O,S*)(bpy)$_2$]PF_6 ([2b]PF_6). This complex was prepared by the same procedure as that employed for [**2a**]PF_6, using $\Lambda_D\Lambda_D$-[Ag{Ru(D-Hpen-*O,S*)(bpy)$_2$}$_2$]$(ClO_4)_3 \cdot 6H_2O$[7] instead of $\Delta_D\Delta_D$-[Ag{Ru(D-Hpen-*O,S*)(bpy)$_2$}$_2$]$(ClO_4)_3 \cdot 5.5H_2O$. Yield: 0.126 g (42%). Anal. Calcd for [**2b**]$PF_6 \cdot 4.5H_2O$: C, 36.63; H, 4.30; N, 8.54%. Found: C, 36.84; H, 4.33; N, 8.40%. ^{1}H NMR (400 MHz, DMSO-d_6): δ, ppm 10.89 (1H, d, J = 5.6 Hz), 8.90 (1H, d, J = 5.6 Hz), 8.67 (3H, d, J = 8.1 Hz), 8.52 (1H, d, J = 8.1 Hz), 8.20 (1H, t, J = 7.4 Hz), 8.18 (1H, t, J = 6.8 Hz), 8.08 (1H, t, J = 7.8 Hz), 7.89−7.78 (4H, m), 7.66 (3H, s), 7.44 (1H, t, J = 6.6 Hz), 7.39 (1H, d, J = 4.9 Hz), 7.26 (1H, t, J = 6.6 Hz), 3.47 (1H, s), 0.92 (3H, s), 0.84 (3H, s). ^{13}C NMR (125 MHz, DMSO-d_6): δ, ppm 172.67 (COO of D-psi); 159.69, 158.79, 158.10, 156.11, 154.96, 152.62, 150.52, 149.54, 137.93, 136.92, 136.76, 135.34, 126.27, 126.09, 125.60, 125.54, 123.45, 123.25, 123.01, 122.78 (*C*H of bpy); 61.08 (*C*N of D-psi); 57.12 (*C*S of D-psi); 18.56, 16.94 (CH_3 of D-psi). IR (KBr, cm^{-1}): 1632 (COO^-), 1604 ($\nu_{C=C,\ C=N}$), 1119 ($\nu_{asym\ S=O}$), 1011 ($\nu_{sym\ S=O}$), 846 (PF_6^-), 763 ($\delta_{C=C,\ C=N}$), 557 (PF_6^-). ESI-MS: m/z = 594 for $[M\text{-}PF_6]^+$.

Preparation of Δ_D-[Ru(D-Hpsi-*N,S*)(bpy)$_2$]PF_6 ([3a]PF_6). A red-orange solution containing 0.150 g (0.18 mmol) of [**2a**]$PF_6 \cdot 6.5H_2O$ in 200 mL of water was refluxed for 5 h under a nitrogen atmosphere in the dark. After cooling to room temperature, the solution was concentrated to dryness with a rotary evaporator. The residue was dissolved in 5 mL of ethanol, and then diethyl ether was slowly diffused into the solution. The mixture was allowed to stand at room temperature in the dark for 1 week, and the resulting orange powder was collected by filtration, washed with cold water, and then dried in air. Yield 0.118 g (85%). Anal. Calcd for [**3a**]$PF_6 \cdot 0.5C_2H_5OH \cdot 2H_2O$: C, 39.15; H, 4.17; N, 8.78%. Found: C, 39.25; H, 4.24; N, 8.68%. ^{1}H NMR (400 MHz, DMSO-d_6): δ, ppm 10.56 (1H, d, J = 5.6 Hz), 9.63 (1H, d, J = 5.4 Hz), 8.70 (1H, d, J = 7.8 Hz), 8.69 (1H, d, J = 8.3 Hz), 8.62 (1H, d, J = 7.6 Hz), 8.53 (1H, d, J = 8.1 Hz), 8.18 (1H, t, J = 6.2 Hz), 8.17 (1H, t, J = 6.6 Hz), 8.04 (1H, t, J = 7.9 Hz), 7.89 (1H, t, J = 7.8 Hz), 7.84 (1H, t, J = 6.3 Hz), 7.74 (1H, t, J = 5.6 Hz), 7.73 (1H, t, J = 4.8 Hz), 7.45 (1H, d, J = 5.9 Hz), 7.44 (1H, d, J = 6.3 Hz), 7.27 (1H, t, J = 6.1 Hz), 4.72 (1H, dd, J = 12.4, 3.4 Hz), 4.29 (1H, t, J = 12.4 Hz), 2.78 (1H, dd, J = 12.4, 3.4 Hz), 1.03 (3H, s), 0.79 (3H, s). ^{13}C NMR (125 MHz, DMSO-d_6): δ, ppm 172.19 (COO of D-psi); 158.61, 158.35, 158.21, 156.60, 154.43, 153.23, 150.89, 150.08, 137.63, 137.02, 136.86, 135.71, 126.31, 125.89, 125.77, 125.76, 123.57, 123.16, 123.10, 122.90 (*C*H of bpy); 65.73 (*C*N of D-psi); 62.57 (*C*S of D-psi); 19.28, 17.51 (CH_3 of D-psi). IR (KBr, cm^{-1}): 1719 (COOH), 1604 ($\nu_{C=C,\ C=N}$), 1117 ($\nu_{asym\ S=O}$), 1013 ($\nu_{sym\ S=O}$), 845 (PF_6^-), 768 ($\delta_{C=C,\ C=N}$), 559 (PF_6^-). ESI-MS: m/z = 594 for $[M-PF_6]^+$.

Measurements. The electronic absorption spectra were recorded on a Jasco V-660 spectrophotometer and the CD spectra were recorded on a Jasco J-600 spectropolarimeter at room temperature. The IR spectra were measured with a Jasco FT/IR-4100 infrared spectrophotometer by using KBr pellets. The elemental analyses (C, H, N) were performed by the Analysis Center of Osaka University. The X-ray fluorescence analyses were made on a Horiba MESA-500 spectrometer. The ^{1}H and ^{13}C NMR spectra were recorded on JEOL GSX-400 and JEOL ECA-500 spectrometers, respectively, at room temperature in DMSO-d_6 or D_2O. Cyclic voltammetric studies were performed by a BAS CV-600A apparatus using a glassy-carbon working electrode (3 mm ϕ), a Ag/0.01 mol dm^{-3} $AgNO_3$ reference electrode, and a Pt-wire auxiliary electrode. ESI mass spectra were recorded in a positive-ion mode on ABsciex QSTAR Elite controlled by Analyst QS 2.0 software package.

X-ray Structure Determinations. All X-ray diffraction experiments were performed on a Rigaku R-AXIS VII or Rigaku RAXIS RAPID imaging plate diffractometer with a graphite-monochromated Mo Kα radiation at 200 K. The intensity data were collected by the ω scan mode and were empirically corrected for absorption. The structure was solved by direct method using SHELXS-97 and refined by full-matrix least-squares techniques using SHELXL-97.[9] Crystallographic data are summarized in Supporting Information, Table S1.[10]

Single crystals for $[\mathbf{1}]^+$ ($[\mathbf{1}](PF_6)_{0.5}(CF_3SO_3)_{0.5} \cdot CH_3CN \cdot 0.5625H_2O$) suitable for X-ray analysis were obtained by slow diffusion of diethyl ether into an acetonitrile solution of an orange powder, which was produced by the addition of sodium trifluoromethanesulfonate to a 1:1 acetonitrile/water solution of [**1**]PF_6 and collected by filtration.[11] Two complex-cations, two hexafluorophosphate anions with site occupancy factors of 0.75 and 0.25, one trifluorosulfate anion, two acetonitrile molecules, and water molecules were crystallographically independent. All non-hydrogen atoms were refined anisotropically, while the other atoms were refined isotropically. H atoms were included in calculated positions except those of water molecules. The O8 and O9−O11 atoms of four water molecules were refined with site occupancy factors of 0.125 and 0.333, respectively.

Single crystals for $[\mathbf{3a}]^+$ ($[\mathbf{3a}](PF_6)_{0.5}(NO_3)_{0.5} \cdot 0.5C_2H_5OH \cdot H_2O$) suitable for X-ray analysis were obtained by slow diffusion of diethyl ether into an ethanol solution containing [**3a**]PF_6, NH_4PF_6, and $NaNO_3$.[11] One complex-cation, a half nitrate anion, a half hexafluorophosphate anion, a half ethanol molecule, and water molecules were crystallographically independent. All non-hydrogen atoms except for the solvent molecules were refined anisotropically, while the other atoms were refined isotropically. H atoms were included in calculated positions except those of water molecules. Water oxygen atoms (O8 and O9) were refined with site occupancy factors of 0.5.

RESULTS AND DISCUSSION

Synthesis and Characterization of $[\mathbf{1}]^+$. Treatment of $[Ag\{Ru(aet)(bpy)_2\}_2](PF_6)_3$ with excess NaI in ethanol/water (1:1) under air bubbling afforded a dark orange solution, accompanied by the deposition of AgI. From this solution, a red-orange complex ([**1**]PF_6) was isolated as the PF_6^- salt after the purification by means of a cation-exchange column chromatography (SP-Sephadex C-25). X-ray fluorescent spectrometry indicated that [**1**]PF_6 contains only Ru as a metal component, and its elemental analytical data were in agreement with the formula for a mononuclear ruthenium(II) species. In the IR

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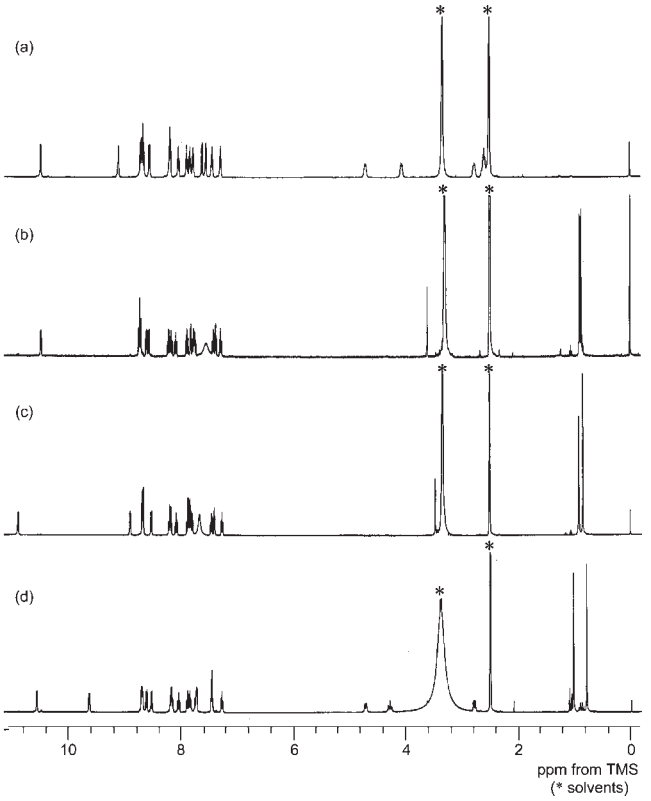

Figure 1. ^{1}H NMR spectra of (a) [Ru(aesi-*N*,*S*)(bpy)$_2$]PF$_6$ ([**1**]PF$_6$), (b) Δ_D-[Ru(D-Hpsi-*O*,*S*)(bpy)$_2$]PF$_6$ ([**2a**]PF$_6$), (c) Λ_D-[Ru(D-Hpsi-*O*,*S*)(bpy)$_2$]PF$_6$ ([**2b**]PF$_6$), and (d) Δ_D-[Ru(D-Hpsi-*N*,*S*)(bpy)$_2$]PF$_6$ ([**3a**]PF$_6$) in DMSO-d_6.

spectrum (Supporting Information, Figure S1),[10] [**1**]PF$_6$ exhibits two strong bands at 1110 cm^{-1} and 1010 cm^{-1} assignable to $\nu_{asym\ S=O}$ and $\nu_{sym\ S=O}$ that are characteristically observed for metal complexes with a sulfinato-S donor.[4a−4e,5a−5e] Based on these results, [**1**]$^+$ is assigned to a mononuclear ruthenium(II) complex, [Ru(aesi-*N*,*S*)(bpy)$_2$]$^+$ (aesi = 2-aminoethanesulfinate), having two N,N-chelating bpy and one N,S-chelating aesi ligands.[12] Compatible with this assignment, the ^{1}H NMR spectrum of [**1**]$^+$ in DMSO-d_6 shows two multiplet methylene signals at δ 2.77 ppm and 2.57 ppm and two broad amine proton signals at δ 4.69 ppm and 4.05 ppm due to one aesi ligand, besides aromatic proton signals due to two bpy ligands in the region of δ 10.48−7.28 ppm (Figure 1). In addition, two methylene carbon signals are observed at δ 40.12 ppm for CH_2S and δ 63.51 ppm for CH_2N due to one aesi ligand in its ^{13}C NMR spectrum, besides aromatic carbon signals due to two bpy ligands in the region of δ 122−158 ppm (Supporting Information, Figure S2).[10]

The structure of [**1**]$^+$ was determined by single-crystal X-ray analysis.[11] A perspective drawing of the complex cation [**1**]$^+$ is shown in Figure 2, and their selected bond distances and angles are listed in Supporting Information, Table S2.[10] The complex cation [**1**]$^+$ has an expected mononuclear structure in [Ru(aesi)(bpy)$_2$]$^+$, in which a Ru^{II} atom is surrounded by one aesi and two bpy ligands in an approximately octahedral geometry. The aesi ligand coordinates to a Ru^{II} center through amine-N and sulfinato-S atoms to form a five-membered chelate ring with an *ob* (δ for Δ and λ for Λ) conformation. While a number of bis(bipyridine)ruthenium(II) complexes have been crystallographically

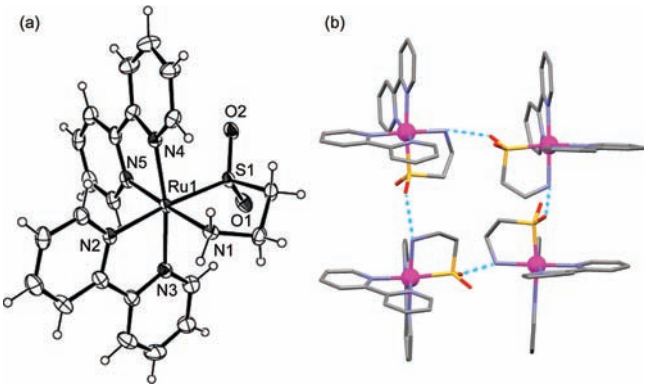

Figure 2. (a) Perspective view of [Ru(aesi-*N*,*S*)(bpy)$_2$]$^+$ ([**1**]$^+$) with the atomic labeling scheme. Ellipsoids represent 30% probability. (b) Tetramer structure of [**1**]$^+$. Hydrogen atoms are omitted for clarity.

characterized, this is the third example of this class of compounds that contain a sulfinato donor.[5b,8] The S−O bond distances (av. 1.481(4) Å) of the sulfinato group in [**1**]$^+$ are typical for those found in S-bonded sulfinato complexes, such as [Ni(*N*-{2-[(2-sulfinyl-2-methylpropyl)amino]ethyl}-1-methylimidazole-2-carboxamido)] (av. 1.473(3) Å) and [Co(aesi)(en)$_2$]$^{2+}$ (av. 1.466(4) Å).[4a,4d] The Ru−S bond distances in [**1**]$^+$ (av. 2.246(1) Å) are slightly shorter than those in the parental [Ag{Ru(aet)(bpy)$_2$}$_2$]$^{3+}$ (av. 2.376(2) Å).[6] This is most likely due to the poorer π-donating ability of a sulfinato S donor compared with that of a thiolato S donor, thus leading to a weaker dπ-pπ antibonding interaction in [**1**]$^+$.[5a] On the other hand, the Ru−N$_{amine}$ and Ru−N$_{imine}$ distances in [**1**]$^+$ (av. 2.144(4) Å and 2.083(4) Å) are similar to those in [Ag{Ru(aet)(bpy)$_2$}$_2$]$^{3+}$ (av. Ru−N$_{amine}$ = 2.139(3) Å, Ru−N$_{imine}$ = 2.056(4) Å).[6] Note that the aesi amine group of each complex cation is hydrogen-bonded to the sulfinato group of an adjacent cation (av. N···O = 2.930(5) Å) so as to form a cyclic tetrameric aggregate (Figure 2b).

The electronic absorption spectrum of [**1**]PF$_6$ in acetonitrile is characterized by an intense band at 453 nm, which is assignable as arising from a metal(Ru)-to-ligand(bpy) charge-transfer (MLCT) transition, and a more intense band at 290 nm due to an intraligand $\pi-\pi^*$ transition of bpy (Figure 3 and Table 1).[13] The energy of MLCT for [**1**]$^+$ is higher than that for [Ag{Ru(aet)(bpy)$_2$}$_2$]$^{3+}$ (λ_{max} = 501 nm),[6] indicative of the stabilization of dπ orbitals by the conversion of a μ_2-thiolato to an S-bonded sulfinato donor. Here, it should be noted that the conversion reaction rarely proceeded either when an aqueous ethanol solution of [Ag{Ru(aet)(bpy)$_2$}$_2$]$^{3+}$ was treated with NaI under a nitrogen atmosphere or when air was bubbled through this solution without adding NaI. In addition, no spectral change of the solution was observed upon the addition of NaI under a nitrogen atmosphere. Thus, it is most likely that the formation of [**1**]$^+$ is achieved by the attack of an O_2 molecule to the μ_2-thiolato groups in [Ag{Ru(aet)(bpy)$_2$}$_2$]$^{3+}$, collaborated with the attack of an I$^-$ ion to the linking Ag$^+$ ion, which weakens the Ag−S bonds, although other reaction mechanisms cannot be ruled out. Complex [**1**]$^+$ was also formed by the direct reaction of [RuCl$_2$(bpy)$_2$] with aet in an aqueous ethanol under a nitrogen atmosphere, followed by the exposure to air. This result implies that the thiolato group of aet bound to a [Ru(bpy)$_2$]$^{2+}$ core is highly reactive toward air oxidation.

Synthesis and Characterization of [2a]$^+$ and [2b]$^+$. Similar treatment of $\Delta_D\Delta_D$- or $\Lambda_D\Lambda_D$-[Ag{Ru(D-Hpen-*O*,*S*)(bpy)$_2$}$_2$]$^{3+}$

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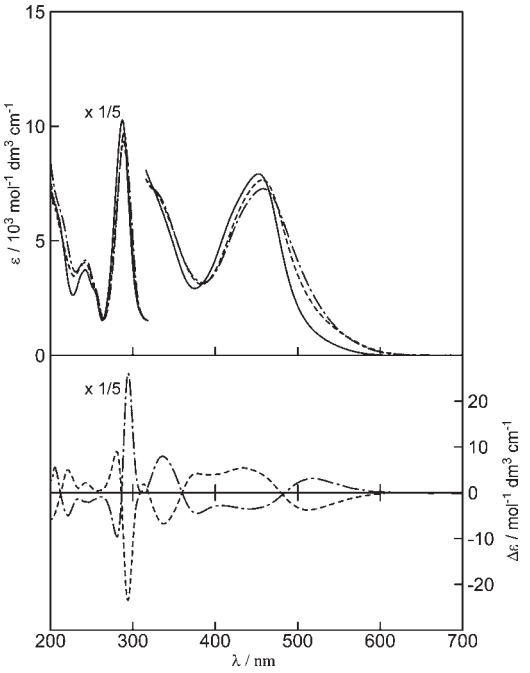

Figure 3. Electronic absorption and CD spectra of [Ru(aesi-*N*,*S*)-(bpy)$_2$]PF$_6$ ([**1**]PF$_6$) (solid line), Δ_D-[Ru(D-Hpsi-*O*,*S*)(bpy)$_2$]PF$_6$ ([**2a**]PF$_6$) (dashed line), and Λ_D-[Ru(D-Hpsi-*O*,*S*)(bpy)$_2$]PF$_6$ ([**2b**]PF$_6$) (dot-dashed line) in CH_3CN.

with excess NaI also produced a dark orange solution, from which a red-orange complex ([**2a**]PF$_6$ or [**2b**]PF$_6$) was isolated as the PF_6^- salt after the purification by means of a cation-exchange column chromatography. The absence of Ag atom in [**2a**]PF$_6$ and [**2b**]PF$_6$ was confirmed by X-ray fluorescence spectroscopy, and the elemental analytical data of these compounds were consistent with the formula for a mononuclear ruthenium(II) complex with a D-Hpsi ligand, [Ru(D-Hpsi)(bpy)$_2$]PF$_6$.

As shown in Figure 3, the electronic absorption spectra of [**2a**]PF$_6$ and [**2b**]PF$_6$ in acetonitrile are essentially the same as each other. These spectra are very similar to the spectrum of [**1**]$^+$ over the whole region, showing an intense MLCT band at about 458 nm and a more intense $\pi-\pi^*$ transition band at 290 nm. On the other hand, the CD spectra of [**2a**]$^+$ and [**2b**]$^+$ are substantially enantiomeric to each other, which correspond well with those of the $\Delta_D\Delta_D$ and $\Lambda_D\Lambda_D$ isomers of [Ag{Ru(D-Hpen-*O*,*S*)(bpy)$_2$}$_2$]$^{3+}$, respectively.[7] Thus, [**2a**]$^+$ and [**2b**]$^+$ are assigned to the Δ_D and Λ_D isomers of [Ru(D-Hpsi)(bpy)$_2$]$^+$ having a sulfinato-S donor,[12] that is, the μ_2-thiolato group in each of $\Delta_D\Delta_D$- and $\Lambda_D\Lambda_D$-[Ag{Ru(D-Hpen-*O*,*S*)(bpy)$_2$}$_2$]$^{3+}$ is converted to an S-bonded sulfinato group with retention of the chiral configuration (Δ, Λ) about a Ru^{II} center. The presence of an S-bonded sulfinato group in [**2a**]PF$_6$ and [**2b**]PF$_6$ is supported by their IR spectra (Supporting Information, Figure S1),[10] each of which exhibits strong $\nu_{asym\ S=O}$ and $\nu_{sym\ S=O}$ bands (1116 and 1010 cm^{-1} for [**2a**]$^+$ and 1119 and 1011 cm^{-1} for [**2b**]$^+$). In addition to these strong bands, the IR spectrum of each [**2a**]PF$_6$ and [**2b**]PF$_6$ shows a strong $\nu_{C=O}$ band at about 1640 cm^{-1}, indicative of the presence of a deprotonated carboxyl group.[7,14] In the ^{1}H NMR spectrum in DMSO-d_6, a broad signal assignable to NH_3^+ protons was noticed at δ 7.54 ppm for [**2a**]PF$_6$ and δ 7.66 ppm for [**2b**]PF$_6$,[15] besides two methyl and one methine proton signals due to a D-Hpsi ligand and aromatic proton signals

Table 1. Electronic Absorption and CD Spectral Data of Complexes in Acetonitrile[a]

abs max: λ_{max}/nm (ε/10^3 mol^{-1} dm^3 cm^{-1})	CD extrema: λ_{max}/nm ($\Delta\varepsilon$/mol^{-1} dm^3 cm^{-1})
[Ru(aesi-*N*,*S*)(bpy)$_2$]PF$_6$ ([**1**]PF$_6$)	
453 (7.92)	
287 (51.4)	
242 (18.7)	
Δ_D-[Ru(D-Hpsi-*O*,*S*)(bpy)$_2$]PF$_6$ ([**2a**]PF$_6$)	
457 (7.67)	512 (−3.76)
322 (7.32)^{sh}	433 (+5.46)
288 (46.7)	378 (+4.18)
242 (20.3)	337 (−6.80)
	294 (−117)
	280 (+44.9)
	243 (+10.9)
	221 (+24.9)
Λ_D-[Ru(D-Hpsi-*O*,*S*)(bpy)$_2$]PF$_6$ ([**2b**]PF$_6$)	
458 (7.27)	518 (+3.12)
325 (7.29)^{sh}	440 (−3.54)
289 (48.5)	378 (−4.50)
243(20.8)	336 (+7.95)
	294 (+130)
	281 (−48.1)
	247 (−10.3)
	221 (−25.1)
Δ_D-[Ru(D-Hpsi-*N*,*S*)(bpy)$_2$]PF$_6$ ([**3a**]PF$_6$)	
450 (8.33)	484 (−2.92)
289 (51.1)	408 (+4.57)
242 (20.4)	362 (+2.53)^{sh}
	326 (−8.39)
	294 (−121)
	280 (+56.8)
	238 (+16.5)
	222 (+28.4)

[a] sh denotes shoulder.

due to two bpy ligands (Figure 1). These spectral features imply that a Hpsi ligand in each of [**2a**]PF$_6$ and [**2b**]PF$_6$ coordinates to a Ru^{II} center through carboxylate-O and sulfinate-S donors, while an amine group is protonated and is not involved in the coordination. This coordination mode of a Hpsi ligand is the same as that of a Hpen ligand in the parental $\Delta_D\Delta_D$- and $\Lambda_D\Lambda_D$-[Ag{Ru(D-Hpen-*O*,*S*)(bpy)$_2$}$_2$]$^{3+}$,[7] indicating the retention not only of the chiral configuration but also the coordination environment about a Ru^{II} center in the course of the oxidation reaction. From single-crystal X-ray crystallography, it was confirmed that [**2a**]$^+$ and [**2b**]$^+$ have the mononuclear structures in Δ_D- and Λ_D-[Ru(D-Hpsi-*O*,*S*)(bpy)$_2$]$^+$ with an O,S-chelating D-Hpsi ligand, respectively (Supporting Information, Figures S3 and S4), although their data were of poor quality.[10,11]

Linkage Isomerization of [2]$^+$. In a previous paper, we reported that an O,S-chelating mode of D-Hpen in $\Delta_D\Delta_D$-[Ag-{Ru(D-Hpen-*O*,*S*)(bpy)$_2$}$_2$]$^{3+}$ is thermally converted to an N,S-chelating mode with the retention of the chiral configuration of each [Ru(D-Hpen)(bpy)$_2$]$^+$ unit, although a similar linkage

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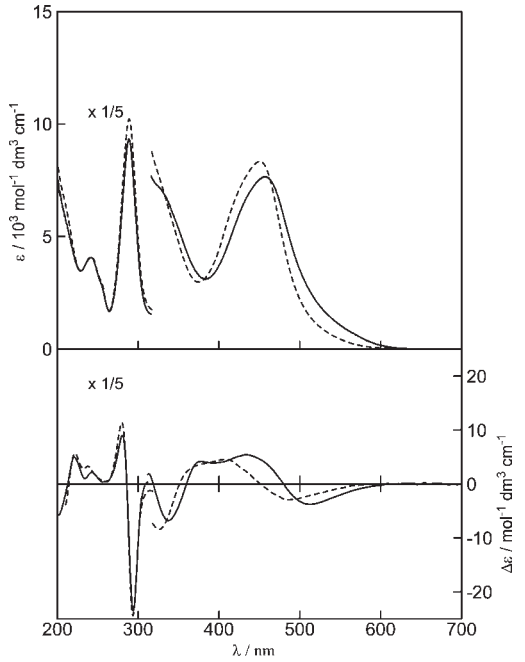


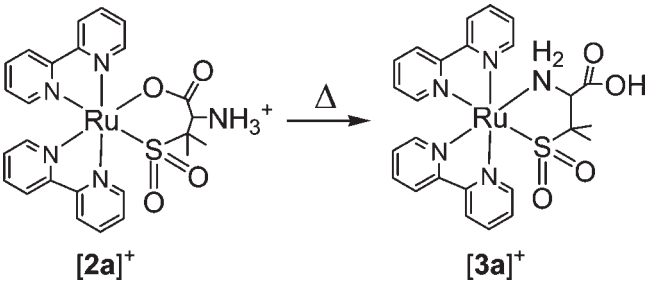
Figure 4. Electronic absorption and CD spectra of Δ_D-[Ru(D-Hpsi-*O*,*S*)$(bpy)_2$]PF_6 ([**2a**]PF_6) (solid line) and Δ_D-[Ru(D-Hpsi-*N*,*S*)-$(bpy)_2$]PF_6 ([**3a**]PF_6) (dashed line) in CH_3CN.

isomerization was not noticed for $\Lambda_D\Lambda_D$-[Ag{Ru(D-Hpen-*O*,*S*)$(bpy)_2$}$_2$]$^{3+}$ under the same conditions.[7] To investigate whether a thermal linkage isomerization occurs for [**2a**]$^+$ and [**2b**]$^+$ (Δ_D- and Λ_D-[**2**]$^+$), the ^{1}H NMR spectral change with time was monitored at 100 °C in D_2O.

In the case of [**2a**]$^+$, the original proton signals decreased with time and almost disappeared after 6 h of heating with the concomitant appearance and growth of a set of new signals for [**3a**]$^+$ (Supporting Information, Figure S5).[10] The spectral feature observed after 6 h remained almost unchanged on further heating for 6 h. Compound [**3a**]$^+$ was isolated as the PF_6^- salt from a refluxed aqueous solution of [**2a**]PF_6. The elemental analytical data of this compound are in good agreement with the formula for [Ru(D-Hpsi)$(bpy)_2$]$^+$, and its electronic absorption and CD spectral features resemble those of [**2a**]$^+$ over the whole region (Figure 4), although a MLCT transition band for [**3a**]$^+$ (λ_{max} 450 nm) is slightly blue-shifted relative to that for [**2a**]$^+$. Furthermore, the ^{1}H NMR spectral feature of this compound is also similar to that of [**2a**]$^+$, giving expected proton signals corresponding to one Hpsi and two bpy ligands (Figure 1). However, two broad signals assignable to NH_2 protons are observed at δ 4.72 ppm and 4.29 ppm for [**3a**]$^+$, with the lack of a broad signal due to NH_3^+ protons observed for [**2a**]$^+$. Judging from these results, [**3a**]$^+$ is assigned to a linkage isomer of [**2a**]$^+$ having the Δ_D configuration, in which a D-Hpsi ligand coordinates to a Ru^{II} center through amine-N and sulfinate-S donors, whereas the carboxyl group is protonated and not participated in the coordination (Scheme 2). Consistent with this assignment, the IR spectrum of [**3a**]$^+$ shows a $\nu_{C=O}$ band due to a protonated carboxyl group at 1719 cm^{-1}, besides $\nu_{asym\ S=O}$ and $\nu_{sym\ S=O}$ bands due to an S-bonded sulfinato group at 1117 and 1013 cm^{-1} (Supporting Information, Figure S1).[10]

This assignment for [**3a**]$^+$ was unambiguously confirmed by single-crystal X-ray analysis. As shown in Figure 5, [**3a**]$^+$ has an octahedral structure in [Ru(D-Hpsi)$(bpy)_2$]$^+$, in which a Ru^{II}

Scheme 2



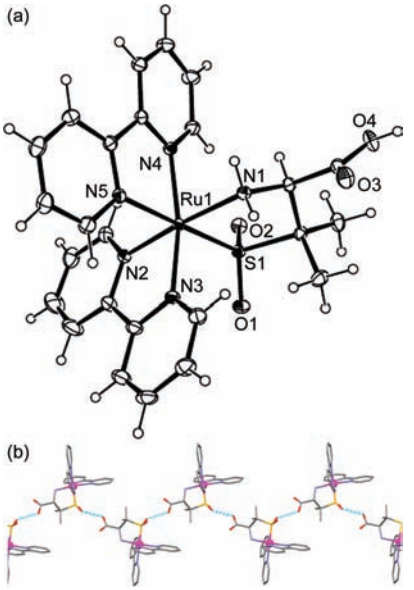


Figure 5. (a) Perspective view of Δ_D-[Ru(D-Hpsi-*N*,*S*)$(bpy)_2$]$^+$ ([**3a**]$^+$) with the atomic labeling scheme. Ellipsoids represent 30% probability. (b) 1D chain structure of [**3a**]$^+$. Hydrogen atoms are omitted for clarity.

center is coordinated by a D-Hpsi ligand through amine and sulfinato groups to form a five-membered chelate ring with a δ conformation. The noncoordinated carboxyl of the D-Hpsi ligand in [**3a**]$^+$ is protonated and forms a hydrogen-bond with the sulfinato group of an adjacent cation (O···O = 2.699(3) Å) to construct a one-dimensional (1D) chain structure (Figure 5b).[16] The absolute configuration about a Ru^{II} center is Δ, indicative of the retention of the chirality during the linkage isomerization. The bond distances around a Ru^{II} center in [**3a**]$^+$ (av. Ru−S = 2.2423(8) Å, Ru−N_{amine} = 2.156(2) Å, Ru−N_{imine} = 2.082(2) Å), as well as the sulfinato S−O distances (av. 1.491(2) Å), are comparable well with the corresponding distances in [**1**]$^+$ (Supporting Information, Table S5).[10]

In the ^{1}H NMR spectrum of [**2b**]$^+$ in D_2O, the original proton signals were dominantly observed even after the solution was heated at 100 °C for 6 h, unlike the case for [**2a**]$^+$ (Supporting Information, Figure S6).[10] A further heating of the solution resulted in the growth of complicated, unidentified signals with the decrease of the original signals, indicating that the Λ_D isomer of [Ru(D-Hpsi-*N*,*S*)$(bpy)_2$]$^+$ having a N,S-chelating D-Hpsi ligand is not thermally stable and decomposed into several species upon prolonged heating. This is in parallel with the thermal instability of the $\Lambda_D\Lambda_D$ isomer of [Ag{Ru(D-Hpen-*N*,*S*)$(bpy)_2$}$_2$]$^{3+}$,[7] which has been ascribed to the presence of a

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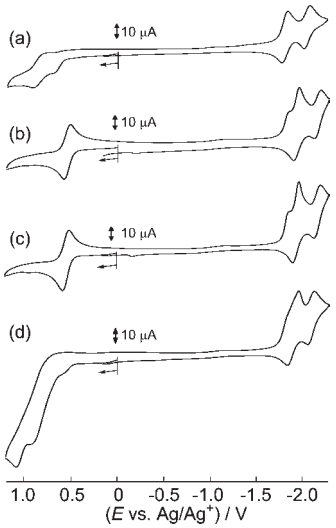

Figure 6. Cyclic voltammograms of (a) $[Ru(aesi\text{-}N,S)(bpy)_2]PF_6$ ($[\mathbf{1}]PF_6$), (b) Δ_D-$[Ru(D\text{-}Hpsi\text{-}O,S)(bpy)_2]PF_6$ ($[\mathbf{2a}]PF_6$), (c) Λ_D-$[Ru(D\text{-}Hpsi\text{-}O,S)(bpy)_2]PF_6$ ($[\mathbf{2b}]PF_6$), and (d) Δ_D-$[Ru(D\text{-}Hpsi\text{-}N,S)(bpy)_2]PF_6$ ($[\mathbf{3a}]PF_6$) in CH_3CN/0.1 M $[Bu_4N]PF_6$ at 25 °C. The concentration of each complex is 1.0 mM, and the scan rate is 100 mV s^{-1}.

steric interaction between bpy and D-Hpen ligands in the Λ_D-$[Ru(D\text{-}Hpen\text{-}N,S)(bpy)_2]^+$ unit having a five-membered N,S-chelate ring. It is assumed that a similar steric interaction exists between bpy and D-Hpsi ligands in Λ_D-$[Ru(D\text{-}Hpsi\text{-}N,S)(bpy)_2]^+$, which is most likely responsible for this result. Here, it should be noted that the S-coordination of a sulfinato group to a Ru^{II} center is retained during the thermal conversion from $[\mathbf{2a}]^+$ to $[\mathbf{3a}]^+$, despite the possibility of the O-coordination of a sulfinato group.[2c,4k,17]

Electrochemical Properties. Electrochemical properties of $[\mathbf{1}]^+$, $[\mathbf{2a}]^+$, $[\mathbf{2b}]^+$, and $[\mathbf{3a}]^+$ were examined by cyclic voltammetry at a grassy-carbon electrode in acetonitrile solutions containing 0.1 M $[Bu_4N]PF_6$ as the supporting electrolyte. As shown in Figure 6, the cyclic voltammogram (CV) of each complex commonly displays bpy-centered redox couples in the negative potential region between −1.7 and −2.3 V (vs Ag/Ag^+).[18] In the positive potential region, the CVs of $[\mathbf{2a}]^+$ and $[\mathbf{2b}]^+$ with an O,S-chelating D-Hpsi ligand are each dominated by a single redox couple at $E_{1/2}$ = +0.54 V (vs Ag/Ag^+), which is attributed to the Ru^{II}/Ru^{III} process. The peak currents are proportional to the square root of the scan rates, and the ratio of anodic and cathodic peak currents is nearly unity. At a scan rate of 100 mV s^{-1}, the observed peak separation ($E_{pc} - E_{pa}$) is 70 mV for the redox couple of each isomer. These results establish that the redox process observed for $[\mathbf{2a}]^+$ and $[\mathbf{2b}]^+$ is reversible, indicating the retention of the coordination environment about a metal center in the course of the Ru^{II}/Ru^{III} redox reaction. A similar reversible redox couple has been observed for a related bis(bipyridine)ruthenium(II) complex with 1,2-benzinedisulfinate.[5b] However, the $E_{1/2}$ value for this complex (+1.41 V vs NHE) is much more positive than that for $[\mathbf{2a}]^+$ and $[\mathbf{2b}]^+$ (+1.05 V vs NHE), which is explained by the greater π-electron-accepting ability of the S,S-chelating 1,2-benzinedisulfinate compared with the O,S-chelating D-penicillaminesulfinate, thus leading to the higher stability of a Ru^{II} oxidation state.

On the other hand, the CV of $[\mathbf{3a}]^+$, which contains an N,S-chelating D-penicillaminesulfinate, shows consecutive irreversible oxidation waves in the positive potential region (E_{pa} = +0.90 V and +1.08 V vs Ag/Ag^+). This is also the case for $[\mathbf{1}]^+$ with an N,S-chelating 2-aminoethanesulfinate, giving irreversible oxidation waves at E_{pa} = +0.69 V and +0.92 V (vs Ag/Ag^+). The oxidation waves of this type have been found in bis(bipyridine)ruthenium(II) complexes with a primary amine donor group, and this process has been assigned to a Ru^{II}-to-Ru^{III} oxidation that is followed by the rapid deprotonation from a primary amine group and the additional one-electron oxidation to produce an imine donor group.[18c,19]

CONCLUDING REMARKS

In this study, we showed that the removal of a linking Ag^I ion in $[Ag\{Ru(aet)(bpy)_2\}_2]^{3+}$, which consists of two $[Ru(aet)(bpy)_2]^+$ units, by treatment with NaI in the presence of air affords $[Ru(aesi\text{-}N,S)(bpy)_2]^+$ ($[\mathbf{1}]^+$). This result clearly indicates that a thiolato group in $[Ru(aet)(bpy)_2]^+$ is highly reactive toward dioxygen to be converted into a sulfinato group with the retention of the S-coordination to a Ru^{II} center. Recently, we reported that treatment of $[Ag\{Ru(aet)(bpy)_2\}_2]^{3+}$ with HCl produces a disulfide-bridged $Ru^{II}Ru^{II}$ complex, $[Ru_2(cysta)(bpy)_4]^{4+}$, because of the autoxidation of coordinated thiolate to coordinated disulfide.[6] Thus, the thiolate-to-sulfinate versus thiolate-to-disulfide conversions for $[Ru(aet)(bpy)_2]^+$ can be controlled by the solution pH that affects a redox potential of thiolate group. The analogous $[Ru(D\text{-}Hpsi\text{-}O,S)(bpy)_2]^+$ ($[\mathbf{2}]^+$) was obtained in optically active forms by similar treatment of $[Ag\{Ru(D\text{-}Hpen\text{-}O,S)(bpy)_2\}_2]^{3+}$ that consists of two $[Ru(D\text{-}Hpen\text{-}O,S)(bpy)_2]^+$ units. In this case, the use of the $\Delta_D\Delta_D$ and $\Lambda_D\Lambda_D$ isomers of $[Ag\{Ru(D\text{-}Hpen\text{-}O,S)(bpy)_2\}_2]^{3+}$ led to the formation of the Δ_D and Λ_D isomers of $[\mathbf{2}]^+$, respectively, demonstrating the retention of the chiral configuration about a Ru^{II} center, as well as the O,S-chelating mode of D-Hpen, in the course of the trinuclear-to-mononuclear conversion. Importantly, the Δ_D isomer of $[\mathbf{2}]^+$ was found to experience the thermal linkage isomerization to give Δ_D-$[Ru(D\text{-}Hpsi\text{-}N,S)(bpy)_2]^+$ (Δ_D-$[\mathbf{3}]^+$) in solution. In this reaction, the formation of other linkage isomers, such as $[Ru(D\text{-}Hpsi\text{-}N,O)(bpy)_2]^+$, was not noticed, indicating that the N,S-chelating mode of Hpsi to a $[Ru(bpy)_2]^{2+}$ core is most thermodynamically stable. On the other hand, a similar linkage isomerization was not observed for the Λ_D isomer of $[\mathbf{2}]^+$ under the same conditions. Thus, the thermal stability of the O,S-chelating versus N,S-chelating modes of Hpsi is highly dependent on the diastereoisomerism (Δ_D vs Λ_D), as has been found in the $[Ag\{Ru(D\text{-}Hpen)(bpy)_2\}_2]^{3+}$ trinuclear system.[7] It may be worth to note that the diastereoisomerism affects not only the thermal stability but also the intermolecular hydrogen-bonding interactions in the solid state. That is, $[\mathbf{2a}]^+$ and $[\mathbf{2b}]^+$ form $NH_3\cdots O_2S$ and $NH_3\cdots O_2C$ hydrogen bonds to construct an infinite-chain and a discrete-tetramer supramolecular structure, respectively. Finally, $[\mathbf{2a}]^+$ and $[\mathbf{2b}]^+$ were shown to be electrochemically stable, as evidenced by the observation of a reversible Ru^{II}/Ru^{III} redox couple in the positive potential region. This is not the case for the thermodynamically stable $[\mathbf{3a}]^+$ owing to the presence of a coordinated amine group that is converted to an imine group by the electrochemical oxidation.

ASSOCIATED CONTENT

Supporting Information. X-ray crystallographic files in CIF format for all complexes, crystallographic data, selected bond distances and angles, and Figures of IR, NMR, and ESI-MS spectra.

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(11) The electronic absorption, ^{1}H NMR, and IR spectra of each crystalline sample used for X-ray analysis were essentially identical with those of the corresponding bulk sample of the PF_6^- salt.

(12) The electrospray mass spectrum of $[\mathbf{1}]^+$ in methanol gave a main signal at m/z = 522, the calculated mass and the isotopic distribution of which match well with those for $[Ru(aesi)(bpy)_2]^+$ (Supporting Information, Figure S7), while the spectrum of each of $[\mathbf{2a}]^+$, $[\mathbf{2b}]^+$, and $[\mathbf{3a}]^+$ gave a main signal at m/z = 594, the calculated mass and the isotopic distribution of which match well with those for $[Ru(D\text{-}Hpsi)(bpy)_2]^+$ (Supporting Information, Figures S8-S10).[10]

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