

Synthesis and Linkage Isomerization of Thiolato-Bridged Ru^{II}Ag^IRu^{II} Trinuclear Complex with D-Penicillamate

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The reaction of [Ru(solvent)₂(bpy)₂]²⁺ (bpy = 2,2'-bipyridine) with D-H₂pen (D-penicillamine) in ethanol/water in the presence of Ag⁺ gave a thiolato-bridged Ru^{II}Ag^IRu^{II} trinuclear complex, [Ag{Ru(D-Hpen)(bpy)₂}₂]³⁺ ([1]³⁺), in which two octahedral [Ru^{II}(D-Hpen)(bpy)₂]⁺ units are linked by a linear Ag^I ion. Of three possible isomers (Δ_DΔ_D, Δ_DΛ_D, and Λ_DΛ_D), [1]³⁺ formed the Δ_DΔ_D and Λ_DΛ_D isomers that were separately isolated by fractional crystallization with the use of [Sb₂(R,R-tartrato)₂]²⁻. In [1]³⁺, each D-Hpen ligand chelates to a Ru^{II} center through thiolate and carboxylate groups, while an amine group of D-Hpen is protonated and does not participate in the coordination. On refluxing in ethanol/water, the Δ_DΔ_D isomer of [1]³⁺ was converted to Δ_DΔ_D-[2]³⁺, in which each D-Hpen ligand chelates to a Ru^{II} center through thiolate and amine groups with a non-coordinating carboxyl group. On the other hand, a similar thermal linkage isomerization was not noticed for the Λ_DΛ_D isomer of [1]³⁺ under the same conditions. The isolated Δ_DΔ_D-[1]³⁺, Λ_DΛ_D-[1]³⁺, and Δ_DΔ_D-[2]³⁺ were fully characterized by electronic absorption, CD, and NMR spectroscopies, along with single-crystal X-ray crystallography for Λ_DΛ_D-[1]³⁺ and Δ_DΔ_D-[2]³⁺.

Introduction

During the past decades, chiral ruthenium(II) complexes have attracted considerable interest in connection with their potential applications, such as enantioselective catalysis,

enantioselective quenching of luminescence, and DNA recognition.^{1–6} In particular, the use of bis(diimine)-type ruthenium(II) complexes having a Δ/Λ central chirality as an optically pure agent has been extensively studied^{3–6} because these complexes are, in general, fairly stable and readily resolved by column chromatography and/or fractional diastereomeric crystallization.^{5a–c,6a–c} For bis(diimine)-type

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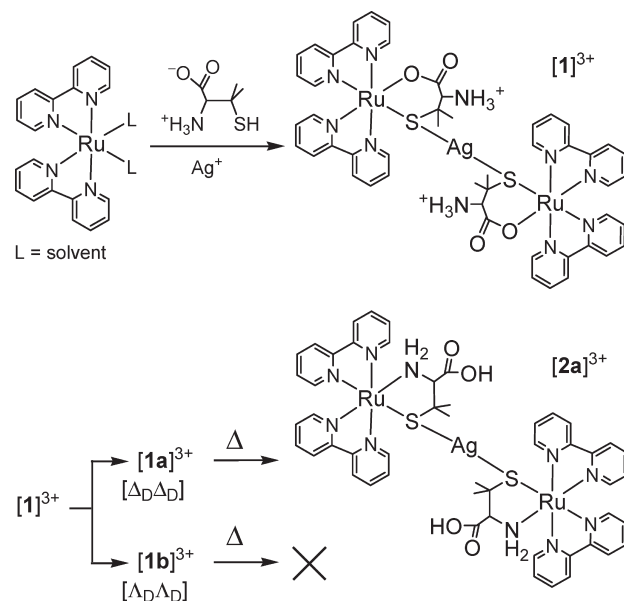
ruthenium(II) species, dinuclear ruthenium(II) complexes, which form meso ($\Delta\Delta$) and racemic ($\Delta\Delta/\Lambda\Lambda$) isomers, have also been prepared,⁶ and the characteristic properties based on the difference in the meso-racemic isomerism have been reported.^{6c-f} While most of diruthenium(II) complexes of this class are made up of two bis(diimine)ruthenium(II) units connected by bridging organic or inorganic ligand(s), we have recently synthesized a new class of a diruthenium(II) complex, $[\text{Ag}\{\text{Ru}(\text{aet})(\text{bpy})_2\}_2]^{3+}$ ($\text{Haet} = 2\text{-aminoethanethiol}$, $\text{bpy} = 2,2'\text{-bipyridine}$), in which two octahedral $[\text{Ru}(\text{aet})(\text{bpy})_2]^+$ units with an N,S-chelating aet ligand are linked by an Ag^{I} ion through thiolato groups.⁷ While the racemic isomer was isolated for $[\text{Ag}\{\text{Ru}(\text{aet})(\text{bpy})_2\}_2]^{3+}$, attempts to resolve this isomer into $\Delta\Delta$ and $\Lambda\Lambda$ forms were unsuccessful most likely because of the rapid exchange of Δ - and Λ - $[\text{Ru}(\text{aet})(\text{bpy})_2]^+$ units in solution, which was suggested by NMR spectroscopy.

To achieve the separation and isolation of optically active isomers of this class of complexes, we thought it worthwhile to introduce a chiral sulfur-containing amino acid, such as cysteine (H_2cys) and penicillamine (H_2pen), in the $\text{Ru}^{\text{II}}\text{-Ag}^{\text{I}}\text{Ru}^{\text{II}}$ trinuclear structure, because these amino acids have been shown to act as a bidentate-N,S chelating ligand toward a variety of metal ions, as in the case of aet.⁸⁻¹⁰ In this paper, we report on an S-bridged $\text{Ru}^{\text{II}}\text{-Ag}^{\text{I}}\text{Ru}^{\text{II}}$ trinuclear complex with D-Hpen, $[\text{Ag}\{\text{Ru}(\text{D-Hpen})(\text{bpy})_2\}_2]^{3+}$ ($[\mathbf{1}]^{3+}$), which was newly prepared from $[\text{RuCl}_2(\text{bpy})_2]$, D- H_2pen , and Ag^+ (Scheme 1). This complex was found to afford two optically active isomers, $\Delta_D\Delta_D\text{-}[\mathbf{1}]^{3+}$ ($[\mathbf{1a}]^{3+}$) and $\Lambda_D\Lambda_D\text{-}[\mathbf{1}]^{3+}$ ($[\mathbf{1b}]^{3+}$), which were purely isolated and characterized. A remarkable coordination mode of D-Hpen in $[\mathbf{1}]^{3+}$, along with its linkage isomerization by heating, is also reported.

Experimental Section

Preparation of $\Delta_D\Delta_D\text{-}[\text{Ag}\{\text{Ru}(\text{D-Hpen-O,S})(\text{bpy})_2\}_2](\text{ClO}_4)_3$ ($[\mathbf{1a}](\text{ClO}_4)_3$) and $\Lambda_D\Lambda_D\text{-}[\text{Ag}\{\text{Ru}(\text{D-Hpen-O,S})(\text{bpy})_2\}_2](\text{ClO}_4)_3$ ($[\mathbf{1b}](\text{ClO}_4)_3$). To a solution containing 1.00 g (1.92 mmol) of $[\text{RuCl}_2(\text{bpy})_2]\cdot 2\text{H}_2\text{O}$ ¹¹ in 120 cm^3 of 1:1 ethanol/water was added 1.20 g (5.79 mmol) of AgClO_4 . The mixture was refluxed at 120 °C for 80 min and then cooled to room temperature. The AgCl deposited was removed by filtration through Celite. To the red-orange filtrate was added 0.90 g (6.03 mmol) of D-penicillamine (D- H_2pen), which was stirred at room temperature for 1 day under a nitrogen atmosphere. The reaction solution was filtered through Celite to remove a solid of AgCl . To the brown filtrate was added 2 cm^3 of a 0.37 M aqueous solution of $\text{Na}_2[\text{Sb}_2(\text{R,R-tartrato})_2]$, followed by storing in the dark for 3 days. The resulting brown powder of $[\mathbf{1a}][\text{Sb}_2$

Scheme 1



(R,R-tartrato)₂]_{0.5}(ClO_4)₂ was collected by filtration (0.46 g, 0.24 mmol, 51% based on 1/2 $[\text{RuCl}_2(\text{bpy})_2]$). A portion of this product (0.40 g) was recrystallized from water by adding NaClO_4 to give a brown powder of $[\mathbf{1a}](\text{ClO}_4)_3$. Yield for $[\mathbf{1a}](\text{ClO}_4)_3\cdot 5.5\text{H}_2\text{O}$: 0.33 g, 95% based on $[\mathbf{1a}][\text{Sb}_2(\text{R,R-tartrato})_2]_{0.5}(\text{ClO}_4)_2$. Anal. Calcd for $[\mathbf{1a}][\text{Sb}_2(\text{R,R-tartrato})_2]_{0.5}(\text{ClO}_4)_2\cdot 9.5\text{H}_2\text{O}$: C, 34.70; H, 3.93; N, 7.49%. Found: C, 34.62; H, 3.73; N, 7.50%. Anal. Calcd for $[\mathbf{1a}](\text{ClO}_4)_3\cdot 5.5\text{H}_2\text{O}$: C, 36.88; H, 3.90; N, 8.60%. Found: C, 36.75; H, 3.77; N, 8.55%. ¹H NMR of $[\mathbf{1a}](\text{ClO}_4)_3\cdot 5.5\text{H}_2\text{O}$ (400 MHz, DMSO-d_6): δ , ppm 10.00 (1H, d, $J = 4.1$ Hz), 8.82–8.77 (3H, m), 8.73 (1H, d, $J = 8.1$ Hz), 8.33–8.23 (3H, m), 8.01 (1H, t, $J = 7.8$ Hz), 7.96 (1H, t, $J = 6.2$ Hz), 7.79 (1H, t, $J = 6.6$ Hz), 7.68 (3H, s), 7.58 (1H, t, $J = 7.6$ Hz), 7.50 (1H, d, $J = 5.6$ Hz), 7.36–7.30 (2H, m), 7.13 (1H, t, $J = 6.3$ Hz), 1.11 (3H, s), 0.90 (3H, s). ¹³C NMR of $[\mathbf{1a}](\text{ClO}_4)_3\cdot 5.5\text{H}_2\text{O}$ (125 MHz, DMSO-d_6): δ , ppm 171.34 (COO of D-pen); 158.36, 158.05, 157.90, 157.88, 153.22, 152.24, 150.40, 150.28, 136.82, 135.66, 134.61, 126.80, 126.24, 126.15, 126.09, 125.16, 123.78, 123.74, 123.59, 123.57 (CH of bpy); 64.99 (NC of D-pen); 41.90 (SC of D-pen); 35.16, 26.32 (CH₃ of D-pen). IR of $[\mathbf{1a}](\text{ClO}_4)_3\cdot 5.5\text{H}_2\text{O}$ (nujol mull, cm^{-1}): 1623 (COO⁻), 1601 ($\nu_{\text{C}=\text{C}}$, $\text{C}=\text{N}$), 1083 (ClO_4^-), 766 ($\delta_{\text{C}=\text{C}}$, $\text{C}=\text{N}$), 623 (ClO_4^-).

The remaining red-brown filtrate was allowed to stand in the dark, which gave a small amount of a brown powder containing $[\mathbf{1a}]^{3+}$. After the removal of this powder by filtration, a saturated aqueous solution of NaClO_4 was added to the solution, followed by storing in the dark for 3 days. The resulting brown powder of $[\mathbf{1b}](\text{ClO}_4)_3$ was collected by filtration and recrystallized from water by adding an aqueous solution of NaClO_4 . Yield for $[\mathbf{1b}](\text{ClO}_4)_3\cdot 6\text{H}_2\text{O}$: 0.40 g (51% based on 1/2 $[\text{RuCl}_2(\text{bpy})_2]$). Anal. Calcd for $[\mathbf{1b}](\text{ClO}_4)_3\cdot 6\text{H}_2\text{O}$: C, 36.67; H, 3.94; N, 8.55%. Found: C, 36.54; H, 3.75; N, 8.61%. ¹H NMR (DMSO-d_6): δ , ppm 10.20 (1H, d, $J = 5.2$ Hz), 9.07 (1H, d, $J = 5.4$ Hz), 8.78 (1H, d, $J = 8.0$ Hz), 8.75 (1H, d, $J = 8.0$ Hz), 8.68 (1H, d, $J = 8.3$ Hz), 8.34 (1H, d, $J = 8.3$ Hz), 8.28 (1H, t, $J = 7.4$ Hz), 8.12 (1H, t, $J = 7.9$ Hz), 8.02 (1H, d, $J = 7.2$ Hz), 8.01 (1H, d, $J = 6.9$ Hz), 7.86 (1H, t, $J = 6.4$ Hz), 7.63 (3H, s), 7.53 (1H, t, $J = 7.7$ Hz), 7.44–7.43 (2H, m), 7.38 (1H, t, $J = 6.3$ Hz), 7.09 (1H, t, $J = 6.3$ Hz), 3.18 (1H, s), 1.12 (3H, s), 0.86 (3H, s). ¹³C NMR (125 MHz, DMSO-d_6): δ , ppm 172.00 (COO of D-pen); 158.75, 158.23, 157.61, 157.35, 152.86, 151.70, 150.45, 150.41, 136.77, 136.51, 135.59, 134.62, 126.69, 126.43, 126.28, 126.10, 124.80, 123.96, 123.57, 123.27 (CH of bpy); 62.29 (NC of D-pen); 43.64 (SC of D-pen); 33.86, 32.14 (CH₃ of D-pen). IR (nujol mull,

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cm^{-1}): 1629 (COO^-), 1601 ($\nu_{\text{C}=\text{C}}$, $\text{C}=\text{N}$), 1094 (ClO_4^-), 769 ($\delta_{\text{C}=\text{C}}$, $\text{C}=\text{N}$), 624 (ClO_4^-).

Preparation of $\Delta_D\Delta_D$ -[Ag{Ru(D-Hpen-*N,S*)(bpy) $_2$] $_2$](ClO $_4$) $_3$ ([2a]**(ClO $_4$) $_3$).** A solution containing 0.40 g (0.22 mmol) of [**[1a]**][Sb $_2$ (*R,R*-tartrato) $_2$] $_{0.5}$ (ClO $_4$) $_2 \cdot 9.5\text{H}_2\text{O}$ in 40 cm 3 of 1:1 ethanol/water was refluxed for 30 h in the dark under a nitrogen atmosphere. After cooling to room temperature, a saturated aqueous solution of NaClO $_4$ (10 cm 3) was added to the brown reaction solution, which was then concentrated to dryness with a rotary evaporator. The residue was washed with water to give a dark-brown powder of [**[2a]**](ClO $_4$) $_3$. Yield for [**[2a]**](ClO $_4$) $_3 \cdot 3.5\text{H}_2\text{O}$: 0.34 g (92%). Anal. Calcd for [**[2]**](ClO $_4$) $_3 \cdot 3.5\text{H}_2\text{O}$: C, 37.71; H, 3.73; N, 8.80%. Found: C, 37.79; H, 3.85; N, 8.80%. ^1H NMR (500 MHz, DMSO- d_6): δ , ppm 9.94 (1H, d, $J = 5.4$ Hz), 9.56 (1H, s), 8.75 (1H, d, $J = 8.3$ Hz), 8.67 (1H, d, $J = 7.6$ Hz), 8.65 (1H, d, $J = 7.3$ Hz), 8.28 (1H, d, $J = 7.8$ Hz), 8.23 (1H, t, $J = 7.8$ Hz), 8.15 (1H, t, $J = 7.8$ Hz), 7.97–7.93 (2H, m), 7.81 (1H, t, $J = 6.3$ Hz), 7.72 (1H, d, $J = 5.1$ Hz), 7.54 (1H, t, $J = 7.4$ Hz), 7.35 (1H, t, $J = 6.7$ Hz), 7.20 (1H, d, $J = 5.1$ Hz), 7.10 (1H, t, $J = 6.5$ Hz), 4.68 (1H, d, $J = 9.8$ Hz), 3.99 (s, 1H), 1.38 (3H, s), 0.75 (3H, s). ^{13}C NMR of [**[2]**](ClO $_4$) $_3 \cdot 3.5\text{H}_2\text{O}$ (125 MHz, DMSO- d_6): δ , ppm 171.70 (COO of D-pen); 159.12, 158.35, 157.77, 157.20, 152.49, 152.11, 150.65, 150.41, 136.39, 136.25, 135.53, 134.87, 126.64, 126.33, 126.15, 126.07, 125.06, 123.90, 123.48, 122.98 (CH of bpy); 69.70 (NC of D-pen); 49.20 (SC of D-pen); 33.13, 33.03 (CH $_3$ of D-pen). IR of [**[2]**](ClO $_4$) $_3 \cdot 3.5\text{H}_2\text{O}$ (nujol mull, cm^{-1}): 1713 (COOH), 1602 ($\nu_{\text{C}=\text{C}}$, $\text{C}=\text{N}$), 1094 (ClO $_4^-$), 768 ($\delta_{\text{C}=\text{C}}$, $\text{C}=\text{N}$), 624 (ClO $_4^-$).

Caution! Perchlorate salts of metal complexes are potentially explosive and should be handled with great care.

Measurements. The electronic absorption spectra were recorded on a Ubest-55 spectrophotometer and the CD spectra on a Jasco J-600 spectropolarimeter at room temperature. The IR spectra were measured with a Jasco FT/IR-4100 infrared spectrophotometer by using nujol mull disks. 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 ^1H and ^{13}C NMR spectra were recorded on JEOL GSX-400 and JEOL ECA-500 spectrometers, respectively, at room temperature in DMSO.

X-ray Structure Determinations. Single crystals of [**[1b]**](PF $_6$) $_2 \cdot (\text{NO}_3) \cdot 6\text{H}_2\text{O}$ suitable for X-ray analysis were obtained by recrystallization of [**[1b]**](ClO $_4$) $_3$ from water by adding an aqueous solution containing NH $_4$ PF $_6$ and NaNO $_3$. Its X-ray diffraction measurements were performed on a Rigaku RAXIS RAPID imaging plate area detector with graphite-monochromated Mo K α 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 methods using SIR92 and refined by full-matrix least-squares techniques using SHELXL-97. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions except those of water molecules. A trinuclear complex cation, a nitrate anion, and two hexafluorophosphate anions were crystallographically independent. A nitrate and a hexafluorophosphate anions were disordered over two positions.

Single crystals of [**[2a] - H $^+$**](PF $_6$) $_{1.5}$ (NO $_3$) $_{0.5}$ suitable for X-ray analysis were obtained by recrystallization of [**[2a]**](ClO $_4$) $_3$ from water by adding an aqueous solution containing NH $_4$ PF $_6$ and NaNO $_3$. Its X-ray diffraction measurements were performed with graphite-monochromated Mo K α radiation on a Bruker AXS SMART-1000 CCD-area detector at 100 K. The intensity data were collected for Lorentz and polarization effects and an empirical absorption correction was applied. The structure was solved by direct methods using SHELXS-97 and refined by full-matrix least-squares techniques. Only Ru, Ag, and S atoms were refined anisotropically, while the other non-hydrogen atoms were refined isotropically because of its poor crystallinity. H atoms were included in calculated positions. Two complex

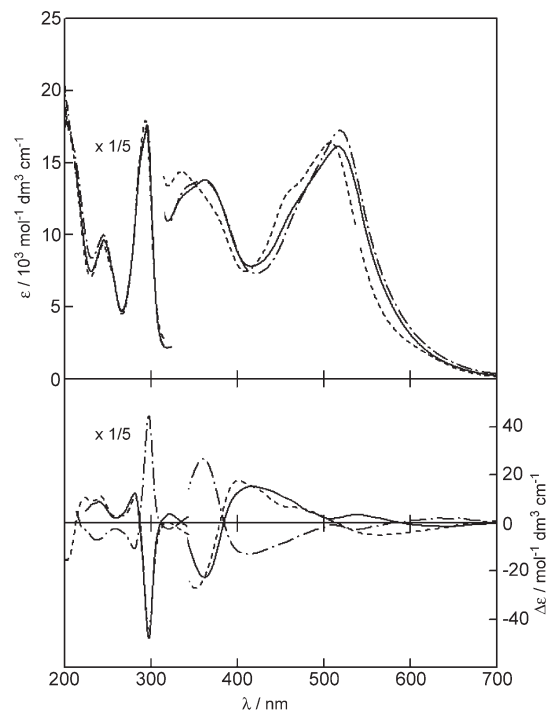


Figure 1. Electronic absorption and CD spectra of $\Delta_D\Delta_D$ -[Ag{Ru(D-Hpen-*O,S*)(bpy) $_2$] $_2$](ClO $_4$) $_3$ (**[1a]**(ClO $_4$) $_3$) (solid line), $\Delta_D\Delta_D$ -[Ag{Ru(D-Hpen-*O,S*)(bpy) $_2$] $_2$](ClO $_4$) $_3$ (**[1b]**(ClO $_4$) $_3$) (dot-dashed line), and [Ag{Ru(D-Hpen-*N,S*)(bpy) $_2$] $_2$](ClO $_4$) $_3$ (**[2a]**(ClO $_4$) $_3$) (dashed line) in CH $_3$ CN.

cations, one nitrate anion, and three hexafluorophosphate anions were crystallographically independent. A half nitrate anion, one and a half hexafluorophosphate anions, and several water molecules were disordered. All pyridine rings were fixed using AFIX 66 restraint, and DFIX restraints were used to model all bipyridine rings, four carboxyl groups, and two nitrate anions. The formula of this crystal was determined to be [Ag{Ru(D-pen)(bpy) $_2$ }{Ru(D-Hpen)(bpy) $_2$ }] $(\text{PF}_6)_{1.5}(\text{NO}_3)_{0.5}$ (**[2a - H $^+$]**)(PF $_6$) $_{1.5}$ (NO $_3$) $_{0.5}$), in which one of two carboxyl groups in the Ru $^{\text{II}}$ Ag $^{\text{I}}$ Ru $^{\text{II}}$ trinuclear structure is deprotonated, judging from the number of independent cations and anions in the unit cell. All calculations were performed using the CrystalStructure software package.¹²

Results and Discussion

Synthesis and Characterization. Treatment of a red-orange solution containing [Ru(bpy) $_2$ (solvent) $_2$] $^{2+}$ and Ag $^+$ which was in situ prepared from [RuCl $_2$ (bpy) $_2$] and AgClO $_4$ in ethanol/water, with excess D-H $_2$ pen at room temperature gave a brown-purple solution. The addition of an appropriate amount of Na $_2$ [Sb $_2$ (*R,R*-tartrato) $_2$] to the reaction solution led to the precipitation of a brown powder of [**[1a]**][Sb $_2$ (*R,R*-tartrato) $_2$] $_{0.5}$ (ClO $_4$) $_2$, which was then converted to [**[1a]**](ClO $_4$) $_3$ by adding AgClO $_4$ to its aqueous solution. From the remaining filtrate, a brown powder of [**[1b]**](ClO $_4$) $_3$ was obtained by adding NaClO $_4$, after the removal of a precipitate containing [**[1a]**] $^{3+}$.

X-ray fluorescence spectrometry suggested that both the compounds (**[1a]**(ClO $_4$) $_3$ and **[1b]**(ClO $_4$) $_3$) contain Ru and Ag in a 2:1 ratio, and their elemental analytical data were in agreement with the formula for a 2:1 adduct of [Ru(D-Hpen)(bpy) $_2$] $^+$ and Ag $^+$. As shown in Figure 1 and Table 1, the electronic absorption spectra of [**[1a]**](ClO $_4$) $_3$

Table 1. Electronic Absorption and CD Spectral Data of $\Delta_D\Delta_D$ -[Ag{Ru(D-Hpen-O,S)(bpy)₂}]₂(ClO₄)₃ (**1a**)(ClO₄)₃, $\Lambda_D\Lambda_D$ -[Ag{Ru(D-Hpen-O,S)(bpy)₂}]₂(ClO₄)₃ (**1b**)(ClO₄)₃, and $\Delta_D\Delta_D$ -[Ag{Ru(D-Hpen-N,S)(bpy)₂}]₂(ClO₄)₃ (**2a**)(ClO₄)₃ in CH₃CN

	abs max: $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/10^3 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$)	CD extrema: $\lambda_{\text{max}}/\text{nm}$ ($\Delta\epsilon/\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$)
$\Delta_D\Delta_D$ -[Ag{Ru(D-Hpen-O,S)(bpy) ₂ }] ₂ (ClO ₄) ₃ (1a)(ClO ₄) ₃	516 (16.1)	540 (+3.46)
	460 (11.4) ^{sh}	416 (+15.3)
	361 (13.8)	362 (-22.6)
	336 (12.7) ^{sh}	321 (+18.4)
	295 (86.5)	297 (-240)
	288 (76.3) ^{sh}	281 (+62.5)
	245 (48.2)	240 (+44.3)
$\Lambda_D\Lambda_D$ -[Ag{Ru(D-Hpen-O,S)(bpy) ₂ }] ₂ (ClO ₄) ₃ (1b)(ClO ₄) ₃	519 (17.3)	538 (-2.70)
	463 (11.2) ^{sh}	411 (-13.0)
	362 (13.8)	360 (+26.6)
	336 (13.0) ^{sh}	320 (-12.4)
	295 (88.2)	297 (+223)
	289 (79.7) ^{sh}	281 (-53.8)
	246 (49.9)	236 (-35.5)
$\Delta_D\Delta_D$ -[Ag{Ru(D-Hpen-N,S)(bpy) ₂ }] ₂ (ClO ₄) ₃ (2a)(ClO ₄) ₃	507 (16.4)	565 (-5.02)
	468 (13.4) ^{sh}	463 (6.62) ^{sh}
	360 (12.8) ^{sh}	401 (17.6)
	335 (14.4)	351 (-27.1)
	293 (89.7)	318 (1.75)
	245 (46.8)	297 (-228)
		282 (55.1)
		242 (55.4)
		224 (52.8)

and **1b**(ClO₄)₃ in acetonitrile are very similar to each other over the whole region, showing two intense bands at about 520 and 370 nm assignable as arising from metal-(Ru)-to-ligand(bpy) charge-transfer (MLCT) transitions, besides a more intense band at about 290 nm because of intraligand bpy $\pi-\pi^*$ transition.¹³ A similar absorption spectral feature has been observed for [Ag{Ru(aet)(bpy)₂}]₂³⁺, in which two octahedral [Ru(aet)(bpy)₂]²⁺ units having an N,S-chelating aet ligand are linked by an Ag^I ion through sulfur bridges,⁷ although the two MLCT bands for each of **1a**(ClO₄)₃ and **1b**(ClO₄)₃ are located at about 20 nm longer wavelength's side compared with those of [Ag{Ru(aet)(bpy)₂}]₂³⁺ (501 and 350 nm). From these results, it is assigned that **1a**³⁺ and **1b**³⁺ are isomers of an S-bridged Ru^{II}Ag^IRu^{II} trinuclear complex, [Ag{Ru(D-Hpen)(bpy)₂}]₂³⁺, the structure of which is analogous to that of [Ag{Ru(aet)(bpy)₂}]₂³⁺. Considering the chiral configurations (Δ_D and Λ_D) of each [Ru(D-Hpen)(bpy)₂]⁺ unit, three isomers ($\Delta_D\Delta_D$, $\Lambda_D\Lambda_D$, and $\Delta_D\Lambda_D$) are possible for [Ag{Ru(D-Hpen)(bpy)₂}]₂³⁺. Since the overall CD spectral patterns of **1a**(ClO₄)₃ and **1b**(ClO₄)₃ are enantiomeric to each other (Figure 1), it is considered that **1a**³⁺ and **1b**³⁺ are a pair of pseudo-enantiomers, $\Delta_D\Delta_D$ and $\Lambda_D\Lambda_D$. In the bpy $\pi-\pi^*$ transition region, **1a**(ClO₄)₃ gives a negative and a positive CD bands at 297 and 280 nm, respectively, while the corresponding CD bands for **1b**(ClO₄)₃ show opposite signs. Thus, **1a**³⁺ and **1b**³⁺ are assigned to the $\Delta_D\Delta_D$ and $\Lambda_D\Lambda_D$ isomers having C_2 symmetry,

respectively, based on the exciton theory.¹⁴ This assignment, together with the C_2 symmetrical S-bridged Ru^{II}Ag^IRu^{II} structure, was unambiguously confirmed by single-crystal X-ray analysis for **1b**(PF₆)₂(NO₃)₃·6H₂O (vide infra).

In the ¹H NMR spectrum in DMSO-*d*₆, each of **1a**(ClO₄)₃ and **1b**(ClO₄)₃ exhibits only 2 methyl proton signals due to 2 D-Hpen ligands in the complex, besides 16 aromatic proton signals due to 4 bpy ligands (Figure 2). Furthermore, 5 carbon signals due to D-Hpen ligands and 20 carbon signals due to bpy ligands are detected in the ¹³C NMR spectrum of each compound (Supporting Information, Figure S1).¹⁵ No NMR spectral change with time, as well as no absorption and CD spectral changes, was noticed at least for 1 day in the dark at room temperature. Thus, **1a**³⁺ and **1b**³⁺ are fairly stable in solution, retaining their S-bridged Ru^{II}Ag^IRu^{II} structures with C_2 symmetry. However, the ¹H NMR spectrum of a 1:1 mixture of **1a**(ClO₄)₃ and **1b**(ClO₄)₃ gave a new set of signals, besides the signals due to **1a**³⁺ and **1b**³⁺, just after the dissolution (Supporting Information, Figure S2).¹⁵ Since this ¹H NMR spectrum remained intact even after 1 day, it seems that a rapid intermolecular exchange of the [Ru(D-Hpen)(bpy)₂]⁺ units between **1a**³⁺ and **1b**³⁺ occurs in solution to generate the $\Delta_D\Lambda_D$ isomer of [Ag{Ru(D-Hpen)(bpy)₂}]₂³⁺, which is in equilibrium with the $\Delta_D\Delta_D$ and $\Lambda_D\Lambda_D$ isomers.⁷ Judging from the integration ratio of signals, the $\Delta_D\Delta_D$, $\Lambda_D\Lambda_D$, and $\Delta_D\Lambda_D$ isomers were evaluated to exist in a 1:1:0.7 ratio. The observation of a new split signal at about δ 10.1, located between two singlet signals (δ 10.00 and 10.20) for **1a**³⁺ and **1b**³⁺, is compatible with the C_1 symmetrical $\Delta_D\Lambda_D$ isomer, although other new signals are broadened and/or overlapped with signals for **1a**³⁺ and **1b**³⁺ (Supporting Information, Figure S2).^{15,16} Here, it should be noted that each ¹H NMR spectrum of **1a**(ClO₄)₃ and **1b**(ClO₄)₃ exhibits a broad singlet signal at δ 7.68 and 7.63, respectively (Figure 2). This signal is assignable to NH₃⁺ protons, based on the disappearance of this signal on adding triethylamine as a base, along with the 2D NMR spectroscopy that shows a coupling of this signal with a methine proton signal at δ 3.18 (Supporting Information, Figure S3).¹⁵ A similar NH₃⁺ proton signal has been observed for [{Ru^{II}(bpy)₂}(μ -Haet-S)₂]⁴⁺ (Haet = ⁺NH₃CH₂CH₂S⁻) having non-coordinating NH₃⁺ groups.^{6h} Thus, it is reasonable to assume that each D-Hpen ligand in **1a**³⁺ and **1b**³⁺ binds to a Ru^{II} center using a carboxylate group instead of an amine group that is protonated, besides a thiolate group. The observation of a C=O stretching band at about 1620 cm⁻¹ in each IR spectrum of **1a**(ClO₄)₃ (1623 cm⁻¹) and **1b**(ClO₄)₃ (1629 cm⁻¹) is compatible with the coordination of a carboxylate group (Supporting Information, Figure S4).¹⁵ This bidentate-O,S coordination was also established by X-ray analysis for **1b**³⁺ (vide infra).

Crystal Structure of **1b³⁺.** X-ray structural analysis of **1b**(PF₆)₂(NO₃)₃·6H₂O showed the presence of a discrete

(13) (a) Ceulemans, A.; Vanquickenborne, L. G. *J. Am. Chem. Soc.* **1981**, *103*, 2238–2241. (b) Juris, A.; Campagna, S.; Balzani, V.; Gremaud, G.; von Zelewsky, A. *Inorg. Chem.* **1988**, *27*, 3652–3655. (c) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85–277.

(14) (a) Bosnich, B. *Inorg. Chem.* **1968**, *7*, 178–180. (b) Bosnich, B. *Inorg. Chem.* **1968**, *7*, 2379–2386. (c) McCaffery, A. J.; Mason, S. F.; Norman, B. J. *J. Chem. Soc. A* **1969**, 1428–1441.

(15) See the Supporting Information.

(16) The ratio of $\Delta_D\Delta_D$: $\Lambda_D\Lambda_D$: $\Delta_D\Lambda_D$ in this mixture solution was roughly estimated to be ca. 1:1:0.5 based on the integration ratio of the signals at δ 10.00, 10.10, and 10.20.

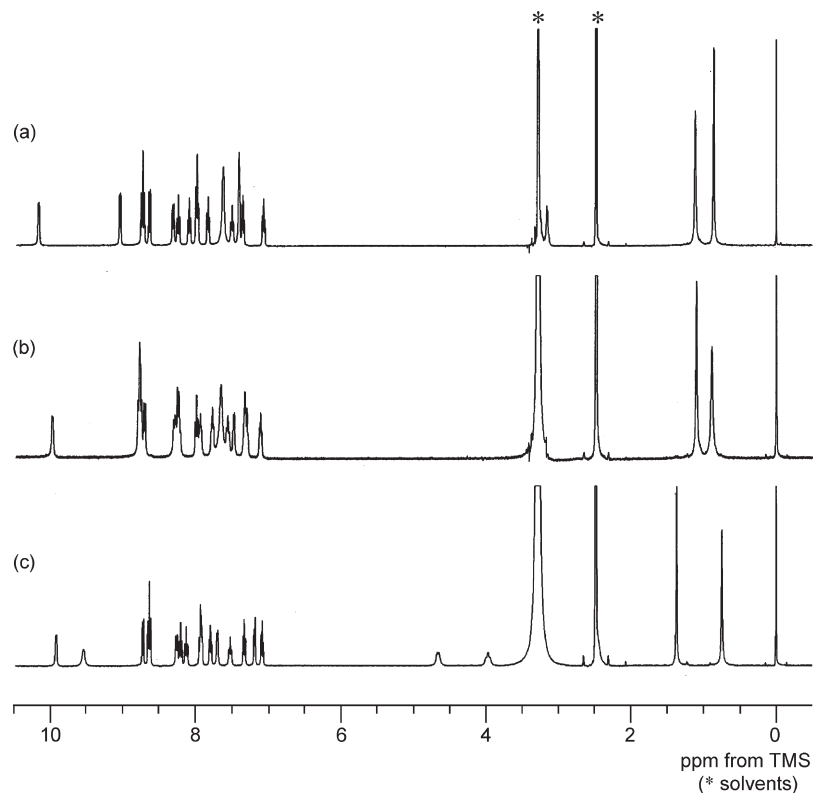


Figure 2. ^1H NMR spectra of the RuAgRu complexes in $\text{DMSO-}d_6$: (a) $\Lambda_D\Lambda_D$ - $[\text{Ag}\{\text{Ru}(\text{D-Hpen-O,S})(\text{bpy})_2\}_2](\text{ClO}_4)_3$ (**[1b]**(ClO_4) $_3$), (b) $\Delta_D\Delta_D$ - $[\text{Ag}\{\text{Ru}(\text{D-Hpen-O,S})(\text{bpy})_2\}_2](\text{ClO}_4)_3$ (**[1a]**(ClO_4) $_3$), and (c) $\Delta_D\Delta_D$ - $[\text{Ag}\{\text{Ru}(\text{D-Hpen-N,S})(\text{bpy})_2\}_2](\text{ClO}_4)_3$ (**[2a]**(ClO_4) $_3$).

complex cation and hexafluorophosphate and nitrate anions, besides water molecules of crystallization. The total number of anions implies that the entire complex is in a tricationic form. The crystallographic data of **[1b]**(PF_6) $_2(\text{NO}_3)\cdot 6\text{H}_2\text{O}$ are summarized in Table 2. A perspective drawing of the complex cation **[1b]** $^{3+}$ is shown in Figure 3, and its selected bond distances and angles are listed in Table 3.

The complex cation **[1b]** $^{3+}$ consists of two approximately octahedral $[\text{Ru}(\text{D-Hpen})(\text{bpy})_2]^+$ units that are linked by one linear Ag^{I} atom, forming an S-bridged $\text{Ru}^{\text{II}}\text{Ag}^{\text{I}}\text{Ru}^{\text{II}}$ trinuclear structure in $[\text{Ag}\{\text{Ru}(\text{D-Hpen})(\text{bpy})_2\}_2]^{3+}$. This trinuclear structure corresponds well with that of $[\text{Ag}\{\text{Ru}(\text{aet})(\text{bpy})_2\}_2]^{3+}$; the Ag–S (av. 2.3821(4) Å) and Ru–S (av. 2.3612(4) Å) bond distances in **[1b]** $^{3+}$ are similar to those in $[\text{Ag}\{\text{Ru}(\text{aet})(\text{bpy})_2\}_2]^{3+}$ (av. Ag–S = 2.373(2) Å and Ru–S = 2.376(2) Å). However, the S–Ag–S angle in **[1b]** $^{3+}$ (176.12(1) $^\circ$) is much closer to 180 $^\circ$ compared with that in $[\text{Ag}\{\text{Ru}(\text{aet})(\text{bpy})_2\}_2]^{3+}$ (164.30(4) $^\circ$). The most remarkable structural feature in **[1b]** $^{3+}$ is the coordination mode of D-Hpen that chelates to a Ru^{II} center using a carboxylate and a thiolate groups. While a number of mononuclear and polynuclear metal complexes with D-penicillamine have been reported to date,^{10,17} this is the second example of a structu-

rally characterized metal complex with bidentate-O,S D-penicillamine.^{10b} The Ru–O bond distances in **[1b]** $^{3+}$ (av. 2.113(7) Å) are within the range observed for ruthenium(II) complexes having carboxylate donors.¹⁸ In **[1b]** $^{3+}$, the two $[\text{Ru}(\text{D-Hpen})(\text{bpy})_2]^+$ units adopt the Λ configuration with the S configurational bridging S atoms. Each of six-membered O,S-chelate rings in **[1b]** $^{3+}$ has a chairlike conformation such that a non-coordinating NH_3^+ group points to an equatorial orientation. One of two NH_3^+ groups in the $\text{Ru}^{\text{II}}\text{Ag}^{\text{I}}\text{Ru}^{\text{II}}$ trinuclear cation is hydrogen-bonded to a coordinated COO^- group in the neighboring trinuclear cation ($\text{N}\cdots\text{O} = 2.850(1)$), constructing a 1D helix structure with a left-handedness (Supporting Information, Figure S5).¹⁵ The other NH_3^+ group forms a hydrogen bond with a PF_6^- counteranion ($\text{N}\cdots\text{F} = 2.834(1)$).

Linkage Isomerization. To investigate the thermal stability of the S-bridged $\text{Ru}^{\text{II}}\text{Ag}^{\text{I}}\text{Ru}^{\text{II}}$ structure with O,S-chelating D-Hpen ligands in solution, the ^1H NMR spectral change of **[1a]**(ClO_4) $_3$ ($\Delta_D\Delta_D$ -**[1]**(ClO_4) $_3$) was monitored at 85 $^\circ\text{C}$ in $\text{DMSO-}d_6$. As a result, the original proton signals due to **[1a]** $^{3+}$ decreased and almost disappeared after 6 h of heating, followed by the appearance and growth of a set of new signals (Supporting Information,

(17) (a) Freeman, H. C.; Stevens, G. N.; Taylor, I. F. *J. Chem. Soc., Chem. Commun.* **1974**, 366–367. (b) de Meester, P.; Hodgson, D. J. *J. Chem. Soc., Dalton Trans.* **1977**, 1604–1607. (c) Book, L.; Mak, T. C. W. *Inorg. Chim. Acta* **1984**, 92, 265–270. (d) Sheldrick, W. S.; Exner, R. *J. Organomet. Chem.* **1990**, 386, 375–387. (e) LeBlanc, D. J.; Britten, J. F.; Wang, Z.; Howard-Lock, H. E.; Lock, C. J. L. *Acta Crystallogr.* **1997**, C53, 1763–1765. (f) Honda, H.; Yoshimura, T.; Hirotsu, M.; Kawamoto, T.; Konno, T. *Inorg. Chem.* **2002**, 41, 2229–2237.

(18) (a) Goodwin, T. J.; Williams, P. A. *Inorg. Chim. Acta* **1984**, 88, 165–181. (b) Collin, J.-P.; Jouaiti, A.; Sauvage, J.-P.; Kaska, W. C.; McLoughlin, M. A.; Keder, N. L.; Harrison, W. T. A.; Stucky, G. D. *Inorg. Chem.* **1990**, 29, 2238–2241. (c) Tanase, T.; Yamada, Y.; Tanaka, K.; Miyazu, T.; Kato, M.; Lee, K.; Sugihara, Y.; Mori, W.; Ichimura, A.; Kinoshita, I.; Yamamoto, Y.; Haga, M.; Sasaki, Y.; Yano, S. *Inorg. Chem.* **1996**, 35, 6230–6239. (d) López-Hernández, A.; Müller, R.; Kopf, H.; Burzlaff, N. *Eur. J. Inorg. Chem.* **2002**, 671–677. (e) Bratsos, I.; Serli, B.; Zangrando, E.; Katsaros, N.; Alessio, E. *Inorg. Chem.* **2007**, 46, 975–992.

Table 2. Crystallographic Data of $\Lambda_D\Lambda_D$ -[Ag{Ru(D-Hpen-O,S)(bpy)₂}]₂(PF₆)₂(NO₃) (**[1b]**(PF₆)₂(NO₃))

[1b](PF ₆) ₂ (NO ₃)·6H ₂ O	
formula	C ₅₀ H ₆₄ AgF ₁₂ N ₁₁ O ₁₃ P ₂ Ru ₂ S ₂
fw	1691.19
crystal color, habit	red, needle
crystal system	orthorhombic
space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> (Å)	13.099(3)
<i>b</i> (Å)	20.340(3)
<i>c</i> (Å)	24.528(4)
<i>V</i> (Å ³)	6535(2)
<i>Z</i>	4
<i>T</i> (K)	200
radiation λ (Å)	0.71075
ρ_{calcd} (g cm ⁻³)	1.719
crystal size (mm)	0.30 × 0.10 × 0.10
μ (Mo <i>K</i> α) (cm ⁻¹)	9.67
Flack parameter	-0.015(14)
<i>R</i> ^a (<i>I</i> > 2 σ (<i>I</i>))	0.0349
<i>R</i> _w ^b (all data)	0.0456
<i>GOF</i> ^c (all data)	0.723
residual electron density (e/Å ³)	0.654/-0.366

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $R_w = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}$. ^c $GOF = [\sum [w(F_o^2 - F_c^2)^2] / (N_o - N_v)]^{1/2}$, where *N*_o: number of observations, *N*_v: number of variables. $w = 1/(\sigma^2(F_o^2) + (0.0126P)^2)$, $P = (F_o^2 + 2F_c^2)/3$.

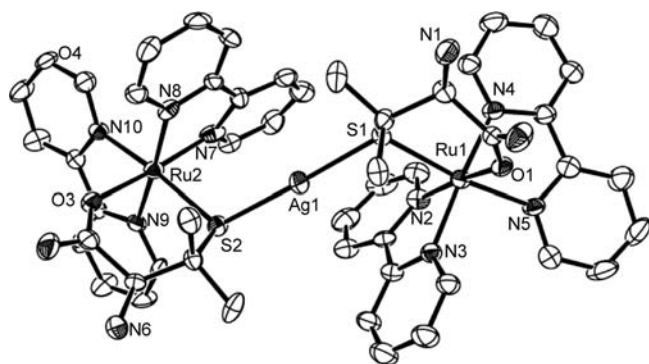
**Figure 3.** Perspective view of $\Lambda_D\Lambda_D$ -[Ag{Ru(D-Hpen-O,S)(bpy)₂}]₂³⁺ (**[1b]**³⁺) with the atomic labeling scheme. Ellipsoids represent 50% probability. Hydrogen atoms are omitted for clarity.

Figure S6).¹⁵ This spectral change suggests that **[1a]**³⁺ is converted to another bis(bipyridine)ruthenium(II) species (**[2a]**³⁺) by heating in solution. The ¹H NMR spectral feature observed after 6 h remained almost unchanged on further heating for 1 day, indicative of the thermal stability of **[2a]**³⁺ in solution.

Compound **[2a]**(ClO₄)₃ was successfully isolated in a high yield from a refluxed ethanol/water solution (1:1) of **[1a]**[Sb₂(*R,R*-tartrato)₂]_{0.5}(ClO₄)₂ by adding NaClO₄. The X-ray fluorescence spectrometry indicated the presence of Ru and Ag atoms in **[2a]**(ClO₄)₃, and its elemental analytical result was consistent with the formula for [Ag{Ru(D-Hpen)(bpy)₂}]₂³⁺. As shown in Figure 2c, **[2a]**(ClO₄)₃ gives 16 proton signals due to bpy ligands in the aromatic region and 2 methyl proton signals (δ 1.4 and 0.8) due to D-Hpen ligands in the ¹H NMR spectrum. Furthermore, its ¹³C NMR spectrum gives 5 carbon signals due to D-Hpen ligands and 20 carbon signals due to bpy ligands (Supporting Information, Figure S1).¹¹ These NMR spectral features resemble those of the starting **[1a]**³⁺, suggesting that **[2a]**³⁺ has a similar S-bridged

Table 3. Selected Bond Distances (Å) and Angles (deg) of $\Lambda_D\Lambda_D$ -[Ag{Ru(D-Hpen-O,S)(bpy)₂}]₂³⁺ (**[1b]**³⁺)

Distances			
Ag1–S1	2.3871(4)	Ag1–S2	2.3771(4)
Ru1–S1	2.3609(4)	Ru2–S2	2.3614(4)
Ru1–O1	2.1165(7)	Ru2–O3	2.1092(7)
Ru1–N2	2.0149(9)	Ru2–N7	2.0338(8)
Ru1–N3	2.0411(8)	Ru2–N8	2.0359(9)
Ru1–N4	2.0962(8)	Ru2–N9	2.0802(9)
Ru1–N5	2.0759(8)	Ru2–N10	2.0734(9)
Angles			
S1–Ag1–S2	176.12(1)	S2–Ru2–O3	92.22(2)
S1–Ru1–O1	91.85(2)	N7–Ru2–N8	79.07(3)
N2–Ru1–N3	79.25(3)	N9–Ru2–N10	78.91(4)
N4–Ru1–N5	78.03(3)	S2–Ru2–N10	171.96(2)
S1–Ru1–N5	171.74(2)	O3–Ru2–N7	171.97(3)
O1–Ru1–N2	171.65(3)	N8–Ru2–N9	173.60(3)
N3–Ru1–N4	173.99(3)	Ag1–S2–Ru2	117.36(1)
Ag1–S1–Ru1	115.40(2)		

Ru^{II}Ag^IRu^{II} structure with C₂ symmetry. However, the ¹H NMR spectrum of **[2a]**(ClO₄)₃ exhibits two broad signals at δ 4.7 and 4.0, with the lack of a broad signal due to NH₃⁺ protons observed for **[1a]**³⁺ (Figure 2). These two broad signals are characteristic of the presence of NH₂ groups bound to a metal center.^{7,19} Thus, it is assumed that each D-Hpen ligand in **[2a]**³⁺ chelates to a Ru^{II} ion through amine and thiolate groups, while carboxylate groups are not involved in the coordination. The observation of a C=O stretching band at 1717 cm⁻¹ in the IR spectrum of **[2a]**³⁺ is indicative of the presence of a protonated carboxyl group (Supporting Information, Figure S4),^{9e,9f,10a,10c} which is compatible with its non-coordination.

X-ray analysis for **[2a]**³⁺ was carried out with the use of a single crystal (**[2a** – H⁺](PF₆)_{1.5}(NO₃)_{0.5}) obtained by the recrystallization of **[2a]**(ClO₄)₃ from water by adding NH₄PF₆ and NaNO₃.^{15,20} Although a detailed structural discussion is precluded because of the poor crystal-quality, the S-bridged Ru^{II}Ag^IRu^{II} structure bearing N,S-chelating D-Hpen ligands was established (Figure 4). The chiral configuration about two [Ru(D-Hpen)(bpy)₂]⁺ units is Δ and the two bridging S atoms are fixed to the S configuration. Accordingly, it is seen that the bidentate-O,S coordination mode of D-Hpen in **[1a]**³⁺ is thermally converted to the bidentate-N,S mode (Chart 1), while the Δ_D chiral configuration of each [Ru(D-Hpen)(bpy)₂]⁺ unit is retained. The thermodynamic stability of five-membered chelate ring versus six-membered chelate ring, which has been established for coordination systems,²¹ accounts for this result.

The absorption spectral feature of **[2a]**³⁺ is very similar to that of **[1a]**³⁺ over the whole region, showing two absorption bands at 335 and 507 nm assignable to MLCT transitions (Figure 1). However, each absorption band

(19) (a) Brown, G. M.; Weaver, T. R.; Keene, F. R.; Meyer, T. J. *Inorg. Chem.* **1976**, *15*, 190–196. (b) Jandrasics, E.; Kolp, B.; Wolny, J. A.; von Zelewsky, A. *Inorg. Chim. Acta* **1998**, *272*, 153–161. (c) Kita, M.; Tamai, H.; Ueta, F.; Fuyuhito, A.; Yamanari, K.; Nakajima, K.; Kojima, M.; Murata, K.; Yamashita, S. *Inorg. Chim. Acta* **2001**, *314*, 139–146.

(20) Crystal data for **[2a** – H⁺](PF₆)_{1.5}(NO₃)_{0.5}·7.625H₂O: fw 3229.92, Orthorhombic, C222₁, a = 19.036(11) Å, b = 24.229(13) Å, c = 58.24(3) Å, V = 26863(26) Å³, Z = 4, D_{calcd} = 1.597 g cm⁻³, R (R_w) = 0.122 (0.308).

(21) (a) Hancock, R. D. *Chem. Rev.* **1989**, *89*, 1875–1914. (b) Hancock, R. D. *J. Chem. Educ.* **1992**, *69*, 615–621.

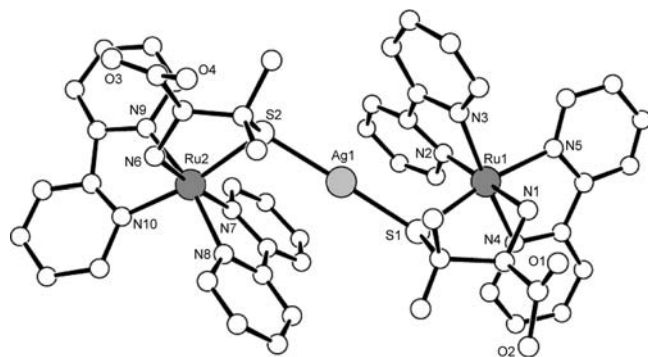
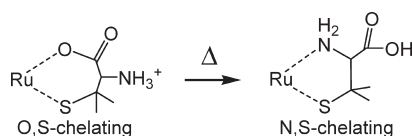


Figure 4. Perspective view of one of the two crystallographically independent complex cations, $\Delta_D\Delta_D$ -[Ag{Ru(D-pen-*N,S*)(bpy)₂}{Ru(D-Hpen-*N,S*)(bpy)₂}]²⁺ (**2a** - H⁺), with the atomic labeling scheme. Hydrogen atoms are omitted for clarity. The quality of the structure precluded the showing of anisotropic thermal parameters.

Chart 1



for [**2a**]³⁺ is slightly blue-shifted compared with that for [**1a**]³⁺, approaching the position of the corresponding band for [Ag{Ru(aet)(bpy)₂}]₂³⁺. This blue shift is rationalized by the lack of π donor character for an amine donor, which leads to a lower energy level of ruthenium $d\pi$ orbitals relative to that with a carboxylato donor. The CD spectrum of [**1b**]³⁺ is also similar to that of [**1a**]³⁺, indicative of the retention of the Δ_D chirality in the course of the thermal linkage isomerization (Figure 1).

Expecting that a similar linkage isomerization is caused by heating for [**1b**]³⁺ ($\Lambda_D\Lambda_D$ -[**1**]³⁺), its ¹H NMR spectral change was also monitored at 85 °C under the same conditions (Supporting Information, Figure S7).¹¹ However, the original proton signals due to [**1b**]³⁺ were still dominant after 6 h of heating, and a further heating resulted in the appearance of complicated, unidentified signals with the decrease of the original signals. This result implies that the $\Lambda_D\Lambda_D$ isomer of [Ag{Ru(D-Hpen)(bpy)₂}]₂³⁺ with N,S-chelating D-Hpen ligands is not thermally stable to be decomposed into several species by a prolonged heating, unlike the case for its $\Delta_D\Delta_D$ isomer. Molecular model examinations revealed that there exists a serious steric interaction between bpy and D-Hpen ligands in the Λ_D -[Ru(D-Hpen)(bpy)₂]⁺ unit when the D-Hpen ligand forms

a five-membered N,S-chelating ring (Supporting Information, Figure S8). On the other hand, such an unfavorable interaction does not exist in the corresponding Δ_D -[Ru(D-Hpen)(bpy)₂]⁺ unit, as well as in the Δ_D - and Λ_D -[Ru(D-Hpen)(bpy)₂]⁺ units with a six-membered O,S-chelating ring. Thus, it is considered that the steric factor existing in the Λ_D configurational [Ru(D-Hpen)(bpy)₂]⁺ unit prevents the formation of $\Lambda_D\Lambda_D$ -[Ag{Ru(D-Hpen)(bpy)₂}]₂³⁺ with N,S-chelating D-Hpen ligands.

Conclusion

In this study, the isolation of optically pure bis(bipyridine)-ruthenium(II) species, $\Delta_D\Delta_D$ -[**1**]³⁺ (**1a**)³⁺ and $\Lambda_D\Lambda_D$ -[**1**]³⁺ (**1b**)³⁺, were successfully achieved by the introduction of D-Hpen as a chelating ligand. Notably, each D-Hpen ligand in $\Delta_D\Delta_D$ -[**1**]³⁺ and $\Lambda_D\Lambda_D$ -[**1**]³⁺ does not adopt an expected N,S-chelating mode but an O,S-chelating mode. In neutral solution, D-H₂pen exists as a zwitter ionic form bearing NH₃⁺ and COO⁻ groups, which is most likely responsible for this result. It was found that $\Delta_D\Delta_D$ -[**1**]³⁺ is thermally converted to $\Delta_D\Delta_D$ -[**2**]³⁺ (**2a**)³⁺, in which each D-Hpen ligand has an N,S-chelating mode. This result clearly indicates that the O,S-chelating form with a six-membered ring is a kinetic product, while the N,S-chelating form with a five-membered ring is a thermodynamic product. Notably, such a thermal linkage isomerization was not noticed for $\Lambda_D\Lambda_D$ -[**1**]³⁺, which is explained by the steric demand. Thus, the stability of [1]³⁺ toward linkage isomerization is drastically affected by the Δ_D/Λ_D diastereoisomerism. Finally, the present results would provide insight not only into the design and creation of optically pure metal complexes with a bis(diimine)ruthenium(II) core, but also into the control of stability and reactivity of metal complexes by diastereoisomerism.

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Supporting Information Available: X-ray crystallographic files in CIF format for [**1b**](PF₆)₂(NO₃), parameters of X-ray analysis for [**2a** - H]²⁺, figures of IR and NMR spectra, the structure of [**1b**](PF₆)₂(NO₃), and a figure representing the steric repulsion. This material is available free of charge via the Internet at <http://pubs.acs.org>.