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Separation and Optical Resolution of a Pair of atrop Diastereomers of the Octahedral Rhodium(III) Complex with a Nine-Membered *S,S*-Chelate Ring

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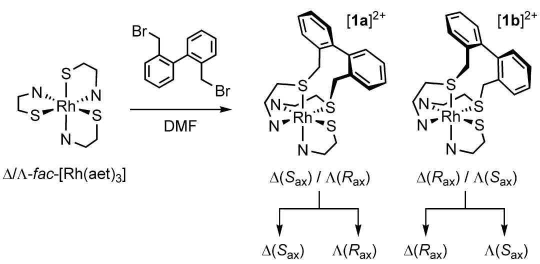
Treatment of *fac*-[Rh(aet)$_3$] (aet = 2-aminoethanethiolate) with 2,2′-bis(bromomethyl)-1,1′-biphenyl gave a mononuclear rhodium(III) complex with a nine-membered *S,S*-chelate ring, *fac*-[Rh(aet)(L)]$^{2+}$ ([**1**]$^{2+}$, L = 2,2′-bis(2-aminoethylthiomethyl)-1,1′-biphenyl). Complex [**1**]$^{2+}$ afforded a pair of atrop diastereomers, $\Delta SS(S_{ax})/\Lambda RR(R_{ax})$-[**1**]$^{2+}$ ([**1a**]$^{2+}$) and $\Delta SS(R_{ax})/\Lambda RR(S_{ax})$-[**1**]$^{2+}$ ([**1b**]$^{2+}$), which involves the axial chirality (R_{ax}/S_{ax}) about a biphenyl moiety of L, besides the central chirality (Δ/Λ) about a Rh^{III} ion bound by two asymmetric (*R*/*S*) thioether donors. The atrop diastereomers ([**1a**]$^{2+}$ and [**1b**]$^{2+}$) were successfully separated, isolated, and optically resolved, and the circular dichroism (CD) contribution from the axial chirality was evaluated by CD spectral analyses.

Over the past decades, transition-metal complexes with axially chiral (atrop isomeric) biaryl ligands, represented by 2,2′-bis(diphenylphosphino)-1,1′-binaphtyl (binap), have received intense attention not only because of their significance in fundamental stereochemistry but also because of their application as asymmetric catalysts in organic synthesis.[1−3] In general, axially chiral biaryl compounds are divided into two classes in terms of the rotation energy barrier around a chiral axis; one is typified by 2,2′,6,6′-substituted biphenyls and 2,2′-substituted binaphthyls with a large rotation barrier, and the other is typified by 2,2′-substituted biphenyls without enough of a rotation barrier. The former class of chiral compounds can be optically resolved into the R_{ax} and S_{ax} atrop forms because of their conformational stability and therefore has been utilized as optically active ligands in asymmetric catalysis.[1,2] On the other hand, the latter class of compounds is commonly unresolvable and exits as a racemate in solution with rapid interconversion between R_{ax} and S_{ax} forms.[3] Furthermore, it has been shown that the R_{ax} and S_{ax} forms of these compounds are easily interconverted in solution even when they coordinate to a metal center in a chelating mode, and the mechanism of interconversion has been explained by an on-metal inversion through a planar transition state or a one-arm off prior to rotation.[3,4] To this end, the optical resolution of a pair of atrop isomers for metal complexes containing an axially chiral 2,2′-substituted biphenyl moiety has rarely been achieved, and the circular dichroism (CD) contribution from the axial chirality remains unknown. Thus, the creation of resolvable 2,2′-substituted biphenyl coordination systems that resist the rotation around a chiral biphenyl axis is still a challenging subject. In this Communication, we report on the synthesis and structural characterization of an octahedral rhodium(III) complex with a 2,2′-substituted biphenyl moiety, *fac*-[Rh(aet)(L)]$^{2+}$ ([**1**]$^{2+}$, L = 2,2′-bis(2-aminoethylthiomethyl)-1,1′-biphenyl). This complex was obtained as a pair of atrop diastereomers, $\Delta SS(S_{ax})/\Lambda RR(R_{ax})$-[**1**]$^{2+}$ ([**1a**]$^{2+}$) and $\Delta SS(R_{ax})/\Lambda RR(S_{ax})$)-[**1**]$^{2+}$ ([**1b**]$^{2+}$), which are discriminated by a combination of the axial chirality (R_{ax}/S_{ax}) due to a biphenyl moiety in tetradentate-N,S,S,N ligand L and the central chirality (Δ/Λ) due to a skew pair of three *N*,*S*-chelate rings around a Rh^{III} ion bound by two asymmetric (*R*/*S*) thioether donors (Scheme 1). Remarkably, these atrop diastereomers were very

Scheme 1



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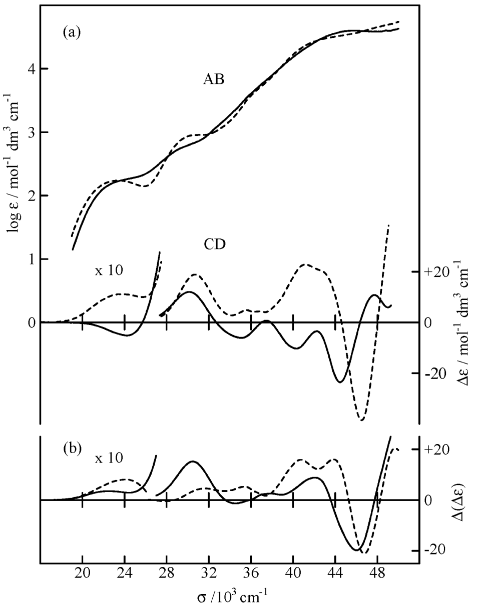

Figure 1. (a) Absorption and CD spectra of $(+)^{CD}_{330}$-Λ*RR*(R_{ax})-[Rh(aet)(L)]$^{2+}$ (Λ*RR*(R_{ax})-[**1a**]$^{2+}$) (—) and $(+)^{CD}_{330}$-Λ*RR*(S_{ax})-[Rh(aet)(L)]$^{2+}$ (Λ*RR*(S_{ax})-[**1b**]$^{2+}$) (- - -) in H_2O. (b) Calculated CD curves for $^1/_2$[Δϵ(Λ*RR*(R_{ax})-[**1a**]$^{2+}$) + Δϵ(Λ*RR*(S_{ax})-[**1b**]$^{2+}$)] (—) and $^1/_2$[Δϵ(Λ*RR*(S_{ax})-[**1b**]$^{2+}$) -Δϵ(Λ*RR*(R_{ax})-[**1a**]$^{2+}$)] (- - -)].

stable, and their separation and optical resolution were achieved by column chromatography. As far as we know, this is the first example of direct separation and optical resolution of a pair of atrop diastereomers of metal complexes involving axial chirality.[5]

The reaction of a yellow suspension of *fac*-[Rh(aet)$_3$][6a] in *N*,*N*-dimethylformamide (DMF) with 1 mol equiv of 2,2′-bis(bromomethyl)-1,1′-biphenyl gave a clear orange solution. After the extraction of DMF with diethyl ether, the remaining product was chromatographed on a cation-exchange SP-Sephadex C-25 column, eluting with a 0.15 M aqueous solution of NaCl. Only two orange bands, [**1a**]$^{2+}$ and [**1b**]$^{2+}$, were eluted in this order, and an orange compound was isolated from each eluate as the chloride salt. Elemental analyses of [**1a**]Cl$_2$ and [**1b**]Cl$_2$ were in good agreement with the formula for a 1:1 adduct of [Rh(aet)$_3$] and [$(C_6H_4CH_2)_2$]$^{2+}$, and their molar conductivities in water (241 Ω^{-1} cm^2 mol^{-1} for [**1a**]Cl$_2$ and 230 Ω^{-1} cm^2 mol^{-1} for [**1b**]Cl$_2$) were compatible with a 1:2 electrolyte. The electronic absorption spectra of [**1a**]$^{2+}$ and [**1b**]$^{2+}$ are similar to each other, showing two d−d bands at ca. 23 × 10^3 cm^{-1} and 30 × 10^3 cm^{-1} and a broad charge-transfer (CT) band at ca. 44 × 10^3 cm^{-1} (Figure 1a). This absorption spectral feature is reminiscent of that of the previously reported *fac*-[Rh(aet)(baete)]$^{2+}$ [baete = 1,2-bis(2-aminoethylthio)ethane] with bidentate-N,S aet and tetradentate-N,S,S,N baete ligands, which was prepared by the reaction of *fac*-[Rh(aet)$_3$] with 1,2-dibromoethane.[7] Thus, [**1a**]$^{2+}$ and [**1b**]$^{2+}$ are each assignable to an analogous mononuclear complex, *fac*-[Rh(aet)(L)]$^{2+}$, in which two of the three thiolato groups in *fac*-[Rh(aet)$_3$] are intramolecularly linked by a [$(C_6H_4CH_2)_2$]$^{2+}$ spacer, in place of a $(CH_2CH_2)^{2+}$ spacer in *fac*-[Rh(aet)(baete)]$^{2+}$. Consistent with this assignment, each of [**1a**]$^{2+}$ and [**1b**]$^{2+}$ shows two clusters of signals centered at *m*/*z* 255 and 510 in the electrospray ionization (ESI) mass spectrum, the calculated molecular masses and the isotropic distributions of which match well with those of [Rh(aet)(L)]$^{2+}$ and {[Rh(aet)(L)] − H}$^+$ ions, respectively.[8] Note that the absorption spectral curve of [**1a**]$^{2+}$ is not superimposed on that of [**1b**]$^{2+}$, suggesting that [**1a**]$^{2+}$ and [**1b**]$^{2+}$ are diastereomeric with each other.

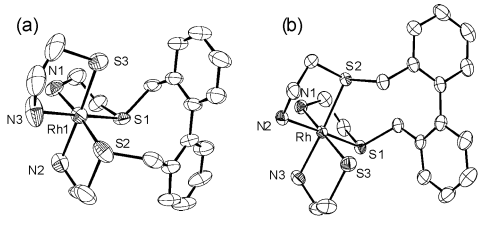

Figure 2. Perspective views of [**1a**]$^{2+}$ (a) and [**1b**]$^{2+}$ (b) with the atomic labeling scheme. The Λ*RR* enantiomer is selected for each complex. H atoms are omitted for clarity.

The crystal structure of [**1a**]Cl$_2$ was determined by single-crystal X-ray crystallography. As shown in Figure 2a, [**1a**]$^{2+}$ is a dicationic mononuclear rhodium(III) complex with an octahedral *fac* geometry, *fac*-[Rh(aet)(L)]$^{2+}$, in which two thiolato S atoms of the parental *fac*-[Rh(aet)$_3$] are intramolecularly linked by a [$(C_6H_4CH_2)_2$]$^{2+}$ group through C−S bonds to form a nine-membered *S*,*S*-chelate ring. To our knowledge, this is the first example of a structurally characterized mononuclear complex having a nine-membered *S*,*S*-chelate ring.[9] As indicated by the space group *P*2/*a*, crystal [**1a**]$^{2+}$ contains the Δ and Λ isomers in a 1:1 ratio. Two thioether S atoms in [**1a**]$^{2+}$ adopt the *S* configuration for the Δ isomer and the *R* configuration for the Λ isomer.[10] A remarkable feature of this structure is the presence of axial chirality (R_{ax}/S_{ax}) about the biphenyl moiety of L, which is S_{ax} for the Δ isomer and R_{ax} for the Λ isomer with an averaged dihedral angle of 74.7(6)° between the two benzene rings.[11] Thus, crystal [**1a**]$^{2+}$ is a racemic compound consisting of a pair of enantiomers, Δ*SS*(S_{ax}) and Λ*RR*(R_{ax}). The Rh−S$_{thioether}$ bond distances [ave 2.326(5) Å] are ca. 0.04 Å longer than the corresponding Rh−S$_{thioether}$ distances in [Rh(aet)(baete)]$^{2+}$ [ave 2.2858(8) Å], while the Rh−S$_{thiolato}$

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(5) Enantiopure R_{ax} and S_{ax} atrop isomers have been indirectly isolated for a bis(diphenylphosphino)biphenylplatinum(II) complex assisted by the introduction of a rigid, enantiopure 2,2′-substituted binaphtyl coligand. (a) Becker, J. J.; White, P. S.; Gagné, M. R. *J. Am. Chem. Soc.* **2001**, *123*, 9478. (b) Mikami, K.; Kakuno, H.; Aikawa, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 7257.

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(8) See the Supporting Information.

(9) We found only one paper that presents a metal complex with a nine-membered *S*,*S*-chelate ring, but the structure of this complex has not been determined by X-ray analysis. (a) Gahan, L. R.; O'Connor, M. J. *Aust. J. Chem.* **1978**, *31*, 511.

(10) While a total of eight configurations (Δ*RR*, Δ*RS*, Δ*SR*, Δ*SS*, Λ*RR*, Λ*RS*, Λ*SR*, and Λ*SS*) are possible, only the Δ*SS* and Λ*RR* configurations were formed for [Rh(aet)(L)]$^{2+}$ because of steric demand. The same stereochemical behavior has been recognized for *fac*-[Rh(aet)(baete)]$^{2+}$.[7]

(11) The asymmetric unit of [**1a**]Cl$_2$ contains three and a half independent, yet nearly identical complex cations.

distances [ave 2.316(8) Å] are very close to the corresponding Rh−S$_{\rm thiolato}$ distance in *fac*-[Rh(aet)(baete)]$^{2+}$ [2.3347(7) Å].[7] The longer Rh−S$_{\rm thioether}$ bonds in [**1a**]$^{2+}$ can be ascribed to the large nine-membered *S*,*S*-chelate ring, which also results in the larger S−Rh−S bite angle [ave 99.68(19)°] compared with that in *fac*-[Rh(aet)(baete)]$^{2+}$ [87.69(3)°].

X-ray structural analysis was also carried out for [**1b**]Cl$_2$, which established the dicationic octahedral structure bearing a bidentate-N,S aet ligand and a tetradentate-N,S,S,N L ligand (Figure 2b). The overall structure in [**1b**]$^{2+}$ is similar to that in [**1a**]$^{2+}$; the averaged Rh−S [2.3207(6) Å] and Rh−N [2.1180(18) Å] bond distances are comparable with those in [**1a**]$^{2+}$ [Rh−S = 2.319(8) Å and Rh−N = 2.12(2) Å]. However, the bite angle of the nine-membered *S*,*S*-chelate ring in [**1b**]$^{2+}$ [96.43(2)°] is closer to the ideal 90° relative to that in [**1a**]$^{2+}$. This is indicative of a less strained octahedral structure in [**1b**]$^{2+}$, which is compatible with the formation ratio [**1a**]$^{2+}$:[**1b**]$^{2+}$ = 1:2. Crystal [**1b**]Cl$_2$ also contains the Δ and Λ isomers in a 1:1 ratio. Like in [**1a**]$^{2+}$, two thioether donors in [**1b**]$^{2+}$ have the *S* configuration for the Δ isomer and the *R* configuration for the Λ isomer. On the other hand, the axial chirality about the biphenyl moiety in [**1b**]$^{2+}$ is opposite to that in [**1a**]$^{2+}$, having $R_{\rm ax}$/$S_{\rm ax}$ configurations for the Δ*SS*/Λ*RR* isomers with a dihedral angle of 72.07(8)°. Thus, [**1b**]$^{2+}$ is a racemic compound consisting of a pair of enantiomers, Δ*SS*($R_{\rm ax}$) and Λ*RR*($S_{\rm ax}$), which is diastereomeric with a pair of Δ*SS*($S_{\rm ax}$) and Λ*RR*($R_{\rm ax}$) isomers in [**1a**]$^{2+}$.

The ^{13}C{^{1}H} NMR spectrum of [**1a**]$^{2+}$ in D$_2$O shows 12 sharp signals for 12 aromatic C atoms in the region of δ 130−145 and 8 sharp signals for 8 methylene C atoms in the region of δ 32−54.[8] A similar NMR spectral feature is observed for [**1b**]$^{2+}$, although each signal is slightly shifted from the corresponding signal of [**1a**]$^{2+}$. This implies that the C_1symmetrical structures in [**1a**]$^{2+}$ and [**1b**]$^{2+}$ are retained in solution. Each of [**1a**]$^{2+}$ and [**1b**]$^{2+}$ was optically resolved into the $(+)^{\rm CD}_{330}$ and $(-)^{\rm CD}_{330}$ isomers, which show CD spectra enantiomeric to each other, by SP-Sephadex C-25 column chromatography using an aqueous solution of Na$_2$[Sb$_2$(*R*,*R*-tartrato)$_2$] as the eluent. To determine the absolute configuration of each optically active isomer for [**1a**]$^{2+}$ and [**1b**]$^{2+}$, the Δ isomer of *fac*-[Rh(aet)$_3$],[6b,c] instead of its racemate, was reacted with 2,2′-bis(bromomethyl)-1,1′-biphenyl. From SP-Sephadex C-25 column chromatography, the product was found to contain two optically active isomers, the absorption and CD spectra of which were identical with those of $(-)^{\rm CD}_{330}$-[**1a**]$^{2+}$ and $(-)^{\rm CD}_{330}$-[**1b**]$^{2+}$. Thus, the following assignment was done: $(+)^{\rm CD}_{330}$-[**1a**]$^{2+}$ and $(-)^{\rm CD}_{330}$-[**1a**]$^{2+}$ correspond to the Λ*RR*($R_{\rm ax}$) and Δ*SS*($S_{\rm ax}$) isomers, while $(+)^{\rm CD}_{330}$-[**1b**]$^{2+}$ and $(-)^{\rm CD}_{330}$-[**1b**]$^{2+}$ correspond to the Λ*RR*($S_{\rm ax}$) and Δ*SS*($R_{\rm ax}$) isomers, respectively. The CD spectra of a pair of atrop diastereomers, $(+)^{\rm CD}_{330}$-Λ*RR*($R_{\rm ax}$)-[**1a**]$^{2+}$ and $(+)^{\rm CD}_{330}$-Λ*RR*($S_{\rm ax}$)-[**1b**]$^{2+}$, which are discriminated by the opposite axial chirality about the biphenyl moiety, are illustrated in Figure 1a. The CD curves of these isomers differ significantly from each other over the whole region, except the common positive CD band at ca. 30 × 10^3 cm^{-1}, suggestive of an appreciable CD contribution from the axial chirality. Assuming that the CD contributions from the central and axial chiralities are additive,[12] the CD curves calculated from the equations

$$\frac{1}{2}[\Delta\varepsilon\{\Lambda RR(R_{\rm ax})-[\mathbf{1a}]^{2+}\} + \Delta\varepsilon\{\Lambda RR(S_{\rm ax})-[\mathbf{1b}]^{2+}\}] \quad (1)$$

and

$$\frac{1}{2}[\Delta\varepsilon\{\Lambda RR(S_{\rm ax})-[\mathbf{1b}]^{2+}\} - \Delta\varepsilon\{\Lambda RR(R_{\rm ax})-[\mathbf{1a}]^{2+}\}] \quad (2)$$

would represent the CD contribution from the Λ configurational Rh$^{\rm III}$ center having two *R* configurational S donors (Λ*RR*) and the CD contribution from the $S_{\rm ax}$ configurational biphenyl moiety, respectively. From the calculated CD curves illustrated in Figure 1b, it is clear that the axial chirality contributes to the CD not only in the CT and π−π* transition regions (ca. 36 × 10^3−50 × 10^3 cm^{-1}) but also in the d−d transition region (ca. 20 × 10^3−32 × 10^3 cm^{-1}) and that its contribution is comparable with that from the central chirality about the Rh$^{\rm III}$ center with two asymmetric S donors.[7] Here it should be noted that no significant CD spectral changes, as well as the absorption and NMR spectral changes, were recognized for these isomers at least for 1 month at room temperature. This result indicates that the atrop diastereomers of [**1**]$^{2+}$ are remarkably stable and show no interconversion between the $R_{\rm ax}$ and $S_{\rm ax}$ forms.[13]

In summary, we showed that the two thiolato groups in *fac*-[Rh(aet)$_3$] are intramolecularly linked by a [(C$_6$H$_4$-CH$_2$)$_2$]$^{2+}$ group to afford the mononuclear *fac*-[Rh(aet)(L)]$^{2+}$ ([**1**]$^{2+}$) bearing a rare nine-membered *S*,*S*-chelate ring. Notably, [**1**]$^{2+}$ was found to form a pair of atrop diastereomers, Δ*SS*($S_{\rm ax}$)/Λ*RR*($R_{\rm ax}$)-[**1**]$^{2+}$ ([**1a**]$^{2+}$) and Δ*SS*($R_{\rm ax}$)/Λ*RR*($S_{\rm ax}$)-[**1**]$^{2+}$ ([**1b**]$^{2+}$). Thanks to the great stability of this complex in solution, these isomers were directly separated and optically resolved by column chromatography, which enables us to evaluate the CD contribution from the axial chirality for the first time. The involvement of a biphenyl moiety in the sterically crowded nine-membered chelate ring, along with the inert Rh$^{\rm III}$−S bonds supported by the tetradentate-N,S,S,N chelating mode, is key to the prevention of skew interconversion between the $R_{\rm ax}$ and $S_{\rm ax}$ atrop forms. With this in mind, further studies will be concentrated on creating other coordination systems that form stable, resolvable atrop isomers without the use of any chiral coligands.

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Supporting Information Available: Crystallographic data in CIF format and detailed experimental and spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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[13] The atrop diastereomers of [1]$^{2+}$ are stable even at higher temperature (90 °C), which was shown by the variable-temperature ^{1}H NMR study.