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A Pair of *Trans* and *Cis* Isomers of Platinum(II) Schiff Base Complex with N, S Chelate Containing Ferrocenyl Pendant Groups

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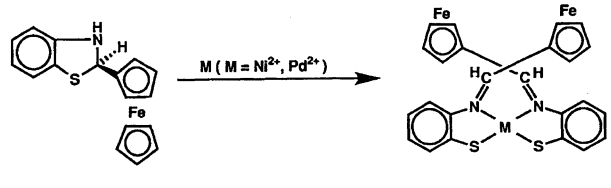
The reaction of bis(hexafluoroacetylacetonato)platinum(II) with 2-(ferrocenyl)benzothiazoline affords *trans* and *cis* isomers of platinum(II) Schiff base complex, *trans*-[Pt(fabt)$_2$] (**1**) and *cis*-[Pt(fabt)$_2$] (**2**) (fabt = 2-(ferrocenylmethyleneamino)benzenethiolato). The structures of **1** and **2** have been determined by the single crystal X-ray diffraction method. Crystal data for complex **1** are triclinic with space group $P\bar{1}$; $a = 15.283(15)$, $b = 13.180(8)$, $c = 9.847(12)$ Å; $\alpha = 72.91(6)$, $\beta = 98.02(9)$, $\gamma = 94.95(6)°$; $V = 1875.2(30)$ Å^3; $Z = 2$. Crystal data for complex **2** are orthorhombic with space group $P2_12_12_1$; $a = 20.593(7)$, $b = 12.300(5)$, $c = 11.754(4)$ Å; $V = 2977.0(18)$ Å^3; $Z = 4$. The complex **1** has a *trans*-planar N_2S_2 configuration and two fabt groups take an unique umbrella conformation. On the other hand, the complex **2** has a *cis*-planar N_2S_2 configuration and two fabt groups take a helical geometry with a stepped conformation. The space group $P2_12_12_1$, $Z = 4$ for **2** indicates that **2** is spontaneously resolved.

It is well-known that several metal ions induce rearrangement of the benzothiazoline derivatives to yield the corresponding Schiff base metal complexes with N, S or N, S, X (X = C, N) chelates.[1—4] To study the stereochemistry related to the N, S chelate Schiff base complexes, we have been investigating the reactions of several metal ions with 2-substituted benzothiazolines.[3,4] We recently reported on mononuclear helical complexes which were obtained by the reaction of palladium(II) or nickel(II) with 2-(ferrocenyl)benzothiazoline (Hfabt) (Scheme 1).[3] These complexes had a *cis*-planar N_2S_2 configuration; a molecular helicity was generated by a crossing of two pendant ferrocenyl groups. On the other hand, we failed to obtain the corresponding *trans* isomer, though the fabt ligand has a large steric hindrance.[3] Then we planned to investigate the reaction of kinetically inert platinum(II) with this Hfabt ligand, and we succeeded in obtaining the *trans* and *cis* isomeric pair of the platinum(II) complex. We report here the detailed account of the work. A preliminary report of part of this work has already appeared.[5]

Experimental

Materials. The compounds of bis(hexafluoroacetylacetonato)platinum(II), [Pt(hfacac)$_2$],[6] and 2-(ferrocenyl)benzothiazoline[7] were prepared by the literature methods. The toluene and acetonitrile were dried over molecular sieve 3A. Dichloromethane was dried over CaCl$_2$. Unless otherwise stated, commercial grade chemicals were used without further purification.



2-(ferrocenyl)benzothiazoline

cis-[M(fabt)$_2$]

Scheme 1.

Measurements. Electronic absorption spectra in dichloromethane solution and Nujol® mulls were recorded on a Hitachi U-3400 and a Shimadzu MPS-5000 spectrophotometer, respectively. Circular dichroism spectrum was recorded on a JASCO J-500A recording spectropolarimeter with a 1 cm light-path cell. IR spectra were obtained on a Perkin–Elmer 983G Infrared Spectrometer using Nujol® mulls between CsI plates. NMR spectra in CDCl$_3$ solution were recorded on a JEOL JNM EX-270 instrument using tetramethylsilane as an internal standard ($\delta = 0$). Cyclic voltammetry was performed in a three-electrode cell with a glassy carbon disk as working electrode, a platinum wire as counter electrode and a Ag–AgCl reference electrode, in dichloromethane containing 0.1 mol dm^{-3} tetrabutylammonium tetrafluoroborate.

Preparation of Primary Product. To a solution of 2-(ferrocenyl)benzothiazoline (0.110 g, 0.32 mmol) in toluene (20 ml) was added a 0.5 molar amount of [Pt(hfacac)$_2$] (0.100 g, 0.16 mmol) and the solution was heated under reflux for 3 h. The solvent was removed from the reaction mixture by using a rotary evaporator. A deep purple solid was obtained.

Separation by Using a Silica-Gel Plate. The primary product was dissolved in a minimum amount of dichloromethane and then purified on a silica-gel plate with dichloromethane as the eluent; this allowed clear separation of the three bands. Three colored bands, reddish purple, green, and red, were developed in this order from the top. A considerable amount (about 50%) of unidentified material in a dark red band did not move and remained on the original TLC plate.

***trans*-Bis[2-(ferrocenylmethyleneamino)benzenethiolato]platinum(II), *trans*-[Pt(fabt)$_2$] (1).** The reddish purple band was extracted with dichloromethane. The resulting fine red crystals were recrystallized from dichloromethane/pentane solution (yield 3.0%). IR 1576 $\mathrm{cm^{-1}}$ (C=N stretch). ^{1}H NMR (270 MHz, $\mathrm{CDCl_3}$) $\delta = 4.38$ (s, 10H), 4.38—4.55 (m, 8H), 6.60 (t, 2H), 6.97 (t, 2H), 7.11 (d, 2H), 7.54 (d, 2H), 8.72 (s, 2H); ^{13}C NMR (68 MHz, $\mathrm{CDCl_3}$) $\delta = 71.56$, 72.31, 73.50, 77.97, 120.32, 123.29, 128.01, 129.38, 144.49, 151.27, 166.34. CV ($v = 0.1$ V $\mathrm{s^{-1}}$) $E_{\mathrm{pa}} = 0.75$, 1.13 V, $E_{\mathrm{pc}} = 0.62$, 0.93 V. Found: C, 48.50; H, 3.38; N, 3.35%. Calcd for $\mathrm{C_{34}H_{28}Fe_2N_2Pt_1S_2}$: C, 48.88; H, 3.38; N, 3.35%.

Tris[2-(ferrocenyl-$\varkappa$C^2-methyleneamino-$\varkappa$N)benzenethiolato-$\varkappa$S]triplatinum(II), [Pt$_3$($\varkappa$C^2-fabt)$_3$]. The green band was extracted with dichloromethane. The resulting green crystals were recrystallized from dichloromethane/pentane solution (yield 1.4%). ^{1}H NMR (270 MHz, $\mathrm{CDCl_3}$) $\delta = 4.09$ (s, 5H), 4.11 (s, 5H), 4.21 (s, 5H), 4.35—4.50 (m, 9H), 7.10—7.90 (m, 12H), 8.63 (s, H), 8.67 (s, H), 8.74 (s, H). Found: C, 39.47; H, 2.71; N, 2.64%. Calcd for $\mathrm{C_{51}H_{39}Fe_3N_3Pt_3S_3}$: C, 39.70; H, 2.55; N, 2.72%.

***cis*-Bis[2-(ferrocenylmethyleneamino)benzenethiolato]platinum(II), *cis*-[Pt(fabt)$_2$] (2).** The red band was extracted with dichloromethane. The resulting deep red crystals were recrystallized from dichloromethane/pentane solution (yield 9.0%). IR 1592 $\mathrm{cm^{-1}}$ (C=N stretch). ^{1}H NMR (270 MHz, $\mathrm{CDCl_3}$) $\delta = 4.14$ (s, 10H), 4.29 (m, 2H), 4.40 (m, 2H), 4.44 (m, 2H), 5.72 (m, 2H), 6.7—6.8 (m, 4H), 7.01 (t, 2H), 7.45 (d, 2H), 7.99 (s, 2H); ^{13}C NMR (68 MHz, $\mathrm{CDCl_3}$) $\delta = 69.21$, 69.70, 69.90, 71.80, 72.34, 73.18, 73.75, 78.02, 78.46, 118.06, 121.83, 128.14, 129.26, 146.18, 152.89, 161.85. CV ($v = 0.1$ V $\mathrm{s^{-1}}$) $E_{\mathrm{pa}} = 0.77$, 1.04 V, $E_{\mathrm{pc}} = 0.59$, 0.85 V. Found: C, 48.67; H, 3.49; N, 3.39%. Calcd for $\mathrm{C_{34}H_{28}Fe_2N_2Pt_1S_2}$: C, 48.88; H, 3.38; N, 3.35%.

Crystal Structure Determination. The single crystals suitable for X-ray methods were obtained from 1,2-dichloroethane/pentane solution for **1**, from chloroform/methanol solution for **2**. All crystallographic measurements were made using a MAC science MXC3 diffractometer with Mo $K\alpha$ radiation (0.71073 Å) at room temperature. Empirical absorption corrections (ψ-scan) were applied (transmission factors were 0.77—0.99 for **1** and 0.76—0.99 for **2**). Lattice parameters were determined by application of the automatic diffractometer indexing routine to the positions of 22 reflections ($2\theta \leq 26^\circ$). Data were measured in the range $3^\circ \leq 2\theta \leq 50^\circ$ in the ω–2θ scan with three check reflections being measured every 100 data. Crystal data and relevant information for **1** and **2** are summarized in Table 1. The structures were solved by direct methods (SIR) and refined by full-matrix least squares on F. Refinement was anisotropic for all the non-hydrogen atoms.[8] The correct choice of the P-helix absolute configuration for **2** was confirmed by the η factor[9] value of 0.96(21).

Tables of the atom coordinates, the thermal parameters, the complete $F_{\mathrm{o}} - F_{\mathrm{c}}$ data, and all bond distances and angles are deposited as Document No. 71031 at the Office of the Editor of Bull. Chem. Soc. Jpn.

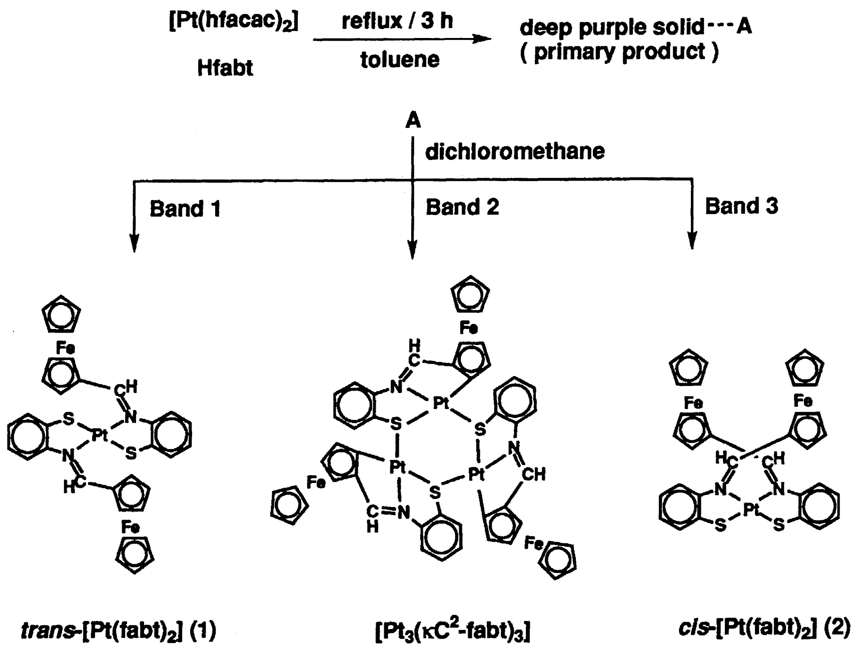
Results and Discussion

Preparation of 1 and 2. Treatment of 2-(ferrocenyl)-benzothiazoline with a 0.5 molar amount of [Pt(hfacac)$_2$] in hot toluene, followed by separation using a silica-gel plate, gave the mononuclear complexes **1**, **2**, and a trinuclear complex [Pt$_3$($\varkappa$C^2-fabt)$_3$] (yield 3.0, 9.0, 1.4%, respectively) (Scheme 2).[10] The neutral complexes **1** and **2**, which were obtained from the first and the third bands respectively, had the same chemical composition of [Pt(fabt)$_2$]. The com-

Table 1. Crystallographic Data

Complex	1	2
Formula	$\mathrm{C_{34}H_{28}Fe_2N_2Pt_1S_2 \cdot 1/2C_2H_4Cl_2}$	$\mathrm{C_{34}H_{28}Fe_2N_2Pt_1S_2}$
M	885.0	835.5
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$ (No. 2)	$P2_12_12_1$ (No. 19)
a/Å	15.283(15)	20.593(7)
b/Å	13.180(8)	12.300(5)
c/Å	9.847(12)	11.754(4)
α/°	72.91(6)	
β/°	98.02(9)	
γ/°	94.95(6)	
V/Å^3	1875.2(30)	2977.0(18)
Z	2	4
D_{c}	1.57	1.86
F(000)	866	1632
μ(Mo $K\alpha$)/mm^{-1}	4.80	5.86
$2\theta_{\mathrm{max}}$/°	50	50
Crystal dimensions/mm	$0.20 \times 0.10 \times 0.05$	$0.30 \times 0.20 \times 0.10$
No. of measured reflections	6052	3074
No. of unique reflections	4412	2643
No. of reflections used in refinement	3122 [$I > 2.5\sigma(I)$]	1836 [$I > 2.5\sigma(I)$]
No. of parameters	383	371
g. o. f.	3.11	2.41
$\Delta / \sigma_{\mathrm{max}}$	0.71	0.60
$\Delta\rho_{\mathrm{max}}$/eÅ^{-3}	1.42	1.60
R[a]	0.084	0.056
R_{W}[b]	0.110	0.071

a) $R = \Sigma||F_{\mathrm{o}}| - |F_{\mathrm{c}}||/\Sigma|F_{\mathrm{o}}|$. b) $R_{\mathrm{w}} = [\Sigma w(|F_{\mathrm{o}}| - |F_{\mathrm{c}}|)^2/\Sigma w(F_{\mathrm{o}})^2]^{1/2}$. Weighting scheme: $1/[\sigma^2(F_{\mathrm{o}}) + 0.02F_{\mathrm{o}}^2]$.



Scheme 2.

plexes **1** and **2** are *trans* and *cis* isomeric forms, as described below. The second green band was the trinuclear complex formulated in $[Pt_3(\kappa C^2\text{-fabt})_3]$, as explained in the preliminary report.[5]

Molecular Structure of Complex 1. The molecular structure of **1**, which has been determined by X-ray analysis, is shown in Fig. 1. The complex **1** is a square planar N_2S_2 Schiff base complex with nitrogen and sulfur atoms *trans* to each other. To our knowledge, this is the first example of a *trans* platinum(II) Schiff base complex in an N_2S_2 environment. The dihedral angle between the two five-membered N–Pt–S chelate planes is 13(8)°, which is regarded as noticeably distorted toward a tetrahedral arrangement. Moreover, the complex **1** has an unique umbrella conformation and the ϕ value between two phenyl moieties is 105(4)°.[11] This umbrella conformation is comparable to the corresponding one found for *trans*-bis(pyrazolethiolato)palladium(II), of which the ϕ value was 100°.[12] In addition, the complex **1** is a C_2 chiral, and the space group $P\bar{1}$ and $Z=2$ indicates that the crystals are racemic.

The molecular model examination indicates that, if the complex **1** had a stepped conformation,[1] the ferrocenyl groups would be too close to sulfur atom on the opposite side.[13] Thus, the complex **1** prefers an umbrella conformation in order to relax the C···S intramolecular repulsion, and this conformation allows free rotation of pendant ferrocenyl groups.

Molecular Structure of Complex 2. As shown in Fig. 2, the complex **2** is also a square planar Schiff base complex, but its coordination environment has a *cis* geometry with N_2S_2 donor atoms. Furthermore, in contrast to **1**, the complex **2** has a stepped conformation and its stepped angles θ between the phenyl moieties and the coordination plane are 156(3)° and 151(3)°. The dihedral angle between the two five-membered N–Pt–S chelate planes is 6(11)°. This complex **2** shows a molecular helicity with a crossing of two pendant ferrocenyl groups which is quite similar to $[Pd(fabt)_2]$ and $[Ni(fabt)_2]$.[3] Although many helical metal complexes had been reported in double helical mode containing several metal ions favoring the tetrahedral or the octahedral geometry,[14—22] this complex **2** is a rare example of a mononuclear monohelical complex.[3,4,23,24] In addition, in complex **2**, the space group $P2_12_12_1$ and $Z=4$ indicates that the crystals are spontaneously resolved. This resolution behavior was previously reported in a few helical compounds.[3,24—26] Based on the X-ray anomalous dispersion effect, the absolute configuration for **2** is determined to be the right-handed P-helix configuration.[27]

Comparison of 1 and 2. Some notable differences between **1** and **2** are observed in bond distances of the platinum atom and the coordinated sulfur atoms (see Table 2). The Pt–S bond distances of 2.32(2) and 2.33(2) Å for **1** are nor-

Table 2. Selected Bond Lengths (Å) and Angles (°)

	1	2
Bond lengths		
Pt–S1	2.32(2)	2.25(3)
Pt–S2	2.33(2)	2.27(3)
Pt–N1	2.01(6)	2.07(7)
Pt–N2	2.01(6)	2.04(9)
N1–C7	1.33(9)	1.28(10)
N2–C24	1.35(10)	1.27(13)
Bond angles		
S1–Pt–S2	167.6(8)	89.0(10)
S1–Pt–N1	81.5(16)	83.9(18)
S1–Pt–N2	96.7(17)	171.5(20)
S2–Pt–N1	97.4(16)	171.7(19)
S2–Pt–N2	83.3(17)	84.0(20)
N1–Pt–N2	174.3(21)	103.4(25)

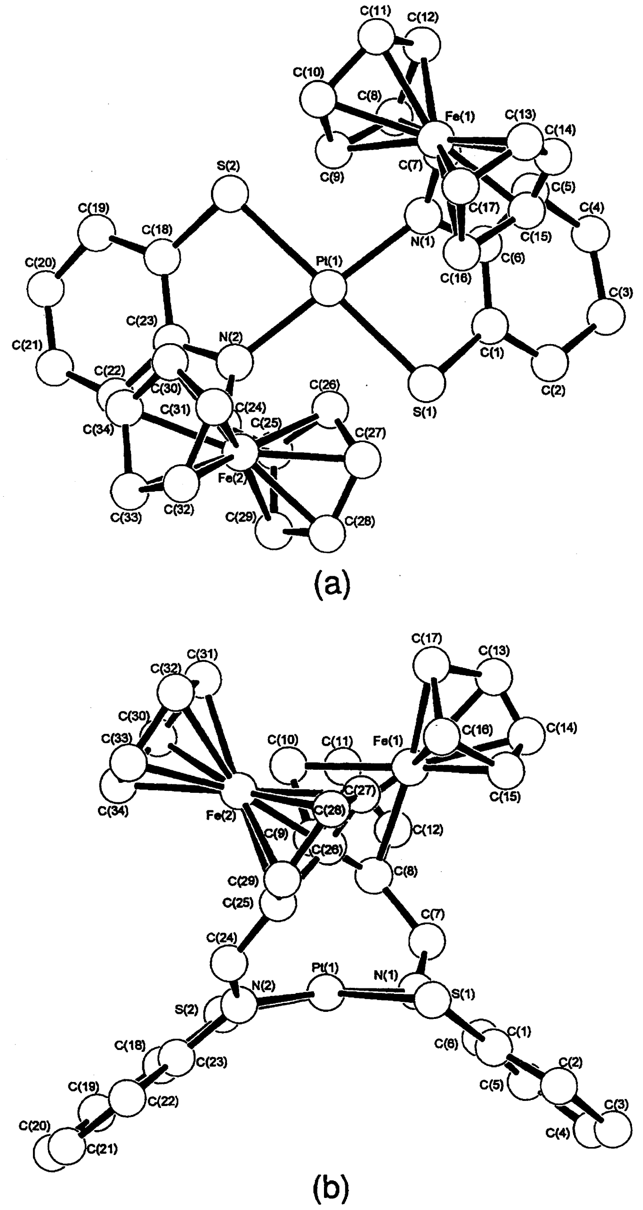


Fig. 1. The molecular structures of **1** (a) top view (b) side view.

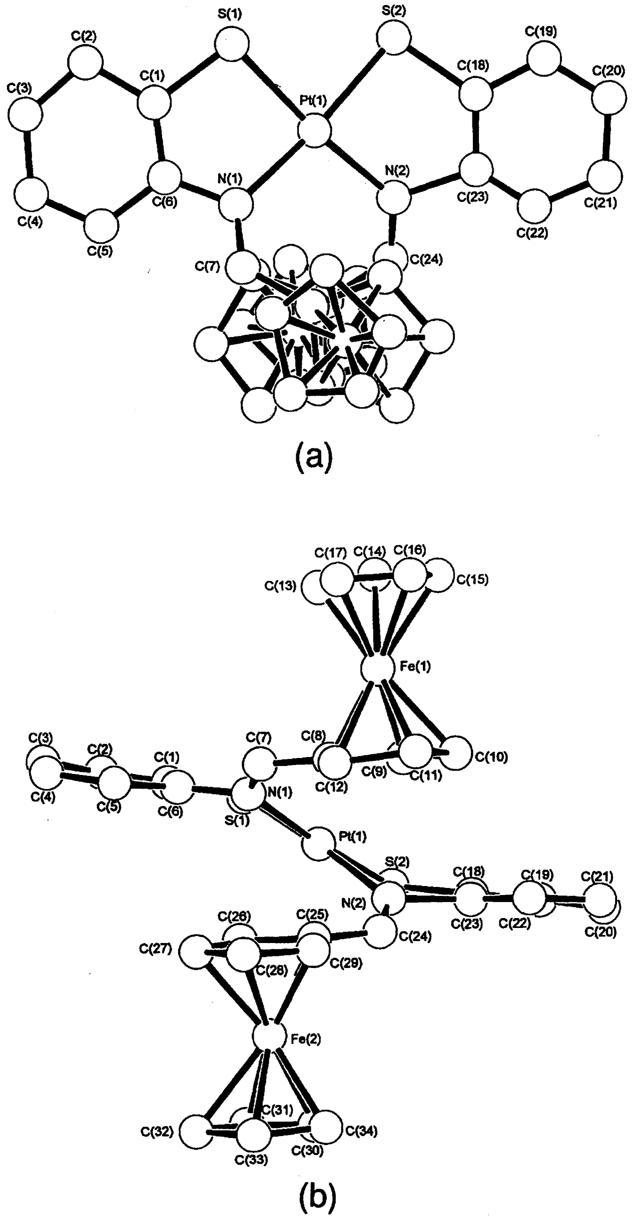


Fig. 2. The molecular structures of **2** (a) top view (b) side view.

mal values for Pt–thiolato S bond distances.[28] On the other hand, the Pt–S bond distances of 2.25(3) and 2.27(3) Å for **2** are shorter than those for **1**. The Pt–N bond distances of 2.07(7) and 2.04(9) Å for **2** are longer than those of 2.01(6) and 2.01(6) Å for **1**. Judging from the structures of these complexes, the results suggest the presence of some *trans* influence of the coordinated sulfur atoms.

The C=N bond distances of 1.33(9) and 1.35(10) Å for **1** are longer than those of 1.28(10) and 1.27(10) Å for **2**. Though these results do not clearly show the difference of the double bond character of the azomethine groups between **1** and **2**, the IR and NMR spectra for **1** and **2** (vide infra) also suggest that the double bond character of the azomethine groups in **1** is weaker than that in **2**. This result may be correlated to the reduction in planarity of ligand for **1**. Indeed, the torsion angles of C6–N1–C7–C8 and C23–N2–C24–C25 are 11(10)° and 7(11)° in **1**, which are slightly larger than those in **2** (4(13)° and 3(13)°, respectively).

Spectroscopic Characterization of the Complexes 1 and 2. NMR Spectrum. Proton NMR spectra of **1** and **2** in $CDCl_3$ solution are reported in the Experimental section. First, the appearance of only one azomethine signal for each compound as well as the presence of four sets for phenyl protons shows that both **1** and **2** complexes have C_2 symmetry. The C_2 axes in these complexes are perpendicular to the coordination plane for **1** and along the plane for **2**. Moreover, cyclopentadienyl protons were observed as a different pattern in **1** and in **2**. The spectrum of **1** gave three signals in the ferrocenyl region; the high-field sharp singlet ($\delta = 4.38$) was assigned to the unsubstituted cyclopentadienyl rings and two proton resonances ($\delta = 4.38$ and 4.55) were assigned to monosubstituted cyclopentadienyl α and β protons. This result indicates that the rotation of two ferrocenyl groups is not hindered in **1**. On the other hand, the spectrum of **2** gave five signals in the ferrocenyl region; the high-field sharp singlet ($\delta = 4.14$) was assigned to the unsubstituted cyclopentadienyl rings and four proton resonances ($\delta = 4.29$, 4.40, 4.44, and 5.72) were assigned to monosubstituted cyclopentadienyl α and β protons. Since monosubstituted cyclopentadienyl ligands normally provide just two proton resonances, the observation of the four signals suggests the existence of a certain rotational barrier involving the ferrocenyl groups in *cis* complex **2**. Moreover, by comparison with *trans* complex **1**, a significant downfield shift was clearly observed in one of α protons in *cis* complex **2** ($\delta = 5.72$). This deshielding indicates that the Pt···H–C interaction between α proton and platinum metal center has occured.[4] And this interaction can be considered the driving force affording the related *ortho*-metalated trinuclear complex, $[Pt_3(\varkappa C^2\text{-fabt})_3]$.[5] The signals of azomethine protons appear at $\delta = 8.72$ for **1** and $\delta = 7.99$ for **2**. These results indicate that the double bond character of azomethine groups of **1** is weaker than that of **2**. This view is supported by IR data, which the complex **1** and **2** revealed the ν(C=N) at 1576 and 1592 cm^{-1}, respectively.

In addition, large splitting of proton NMR signals was observed upon addition of one enantiomer of Pirkle's reagent[29] (*R*)-(−)-[9-(1-hydroxy-2,2,2-trifluoroethyl)anthracene] in a solution of **2** (Fig. 3). This is a clear demonstration that this system is chiral in solution state.

Absorption Spectrum. The electronic absorption spectra of **1** and **2** in dichloromethane solution are shown in Fig. 4. These complexes exhibit strong absorptions in the visible region, consistent with their intense colors, and their bands mask the d–d transitions. The electronic absorption spectrum of **1** showed four bands at 13.6 ($\varepsilon = 1300$), 19.3 (9100), 26.4 (sh, 13000), and 28.1×10^3 cm^{-1} (16400 dm^3 mol^{-1} cm^{-1}) and that of **2** showed four bands at 13.8 (sh, $\varepsilon = 340$), 16.9 (sh, 1700), 19.4 (6800), and 26.6×10^3 cm^{-1} (8330 dm^3 mol^{-1} cm^{-1}). It is known that the spectra of the complexes with ferrocenyl groups shows the band based on ferrocenyl groups around 20×10^3 cm^{-1}.[30] Moreover, in the complex $[Pt(mnt)_2]^{2-}$ (mnt = maleonitriledithiolato) having thiolato groups coordinating to platinum(II), Gray et al. had reported that the platinum(II) complex exhibited two absorption bands at 18.5×10^3 cm^{-1} ($\varepsilon = 1220$ dm^3 mol^{-1} cm^{-1}) and 21.1×10^3 cm^{-1} ($\varepsilon = 3470$ dm^3 mol^{-1} cm^{-1}) which were assigned to be metal-to-ligand charge transfer bands.[31] Thus we can estimate that the low-resolution bands in the 16×10^3—20×10^3 cm^{-1} region correspond to these bands.

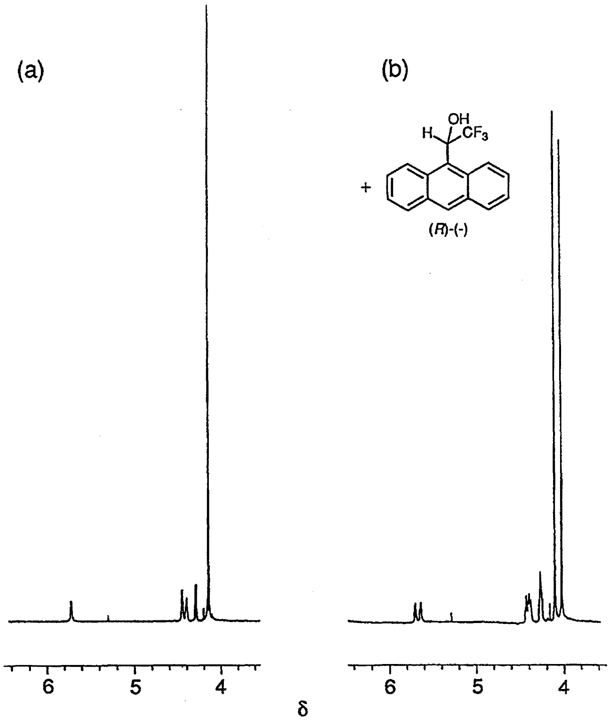


Fig. 3. (a) The ^{1}H NMR spectrum for cyclopentadienyl rings of **2**. (b) That of **2** in the presence of Pirkle's reagent.

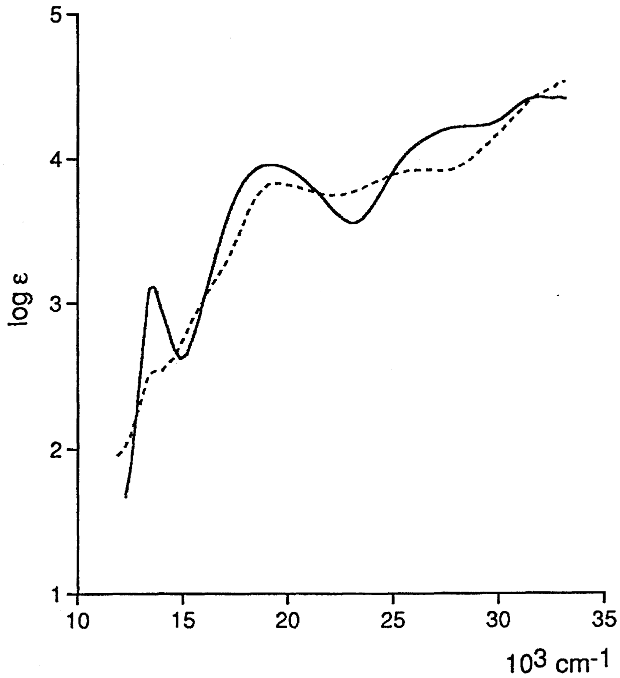


Fig. 4. The absorption spectra of **1** (solid line) and **2** (broken line).

The spectrum of *cis* complex **2**, which is similar to those of *cis*-$[Pd(fabt)_2]$ and *cis*-$[Ni(fabt)_2]$,[3] shows a different curve from that of *trans* complex **1**. In comparison with the spectra of **1** and **2**, a noticeable difference is observed in the intensity of the bands around 14.0×10^3 cm^{-1}. We could not assign these bands, but it is interesting that such a difference appears between *trans* and *cis* isomers.[32]

Conclusion

A pair of *trans* and *cis* isomers formulated in $[Pt(fabt)_2]$, which is the first example of Schiff base complexes bearing PtN_2S_2 configuration, was isolated and the molecular structures of both were determined by the X-ray diffraction method. The structure of *trans*-$[Pt(fabt)_2]$ has an N_2S_2 coordination geometry with a rare umbrella conformation, which allowed the substituted ferrocenyl groups to rotate freely.

The structure of *cis*-[Pt(fabt)$_2$] had an N_2S_2 coordination geometry with a stepped conformation, and the molecule showed molecular helicity by a crossing of substituted ferrocenyl groups. The absolute configuration determined by the X-ray diffraction method was P-helix.

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32) For cyclic voltammetry, each of **1** and **2** shows two oxidation potentials at 0.75 and 1.13 V for **1** and at 0.77 and 1.04 V for **2** (see Experimental section). Though we cannot explain the cause of such a large difference of oxidation potential values between **1** and **2** (1.13 and 1.04 V, respectively), we consider that this difference reflect to the observed difference in the absorption spectra of **1** and **2**.