Bull. Chem. Soc. Jpn., 54, 713—718 (1981)

Nuclear Magnetic Resonance and Circular Dichroism Spectra of 2-(Aminomethyl)cyclohexylamine Platinum(II) Complexes

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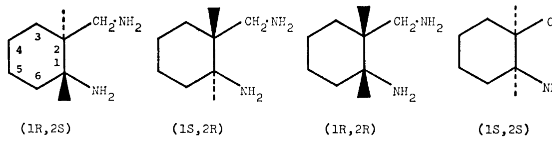
(Received June 30, 1980)

Six-membered platinum(II) complexes of 2-(aminomethyl)cyclohexylamine (=amcha), whose four isomers are (1*R*,2*R*)-, (1*S*,2*S*)-, (1*R*,2*S*)-, and (1*S*,2*R*)-amcha, were synthesized. The conformations of [Pt(en)(1*S*,2*R*-amcha)]Cl_2, [Pt$(NH_3)_2$(1*S*,2*R*-amcha)]Cl_2, [Pt(en)(1*R*,2*R*-amcha)]Cl_2, and [Pt$(NH_3)_2$(1*R*,2*R*-amcha)]Cl_2 were determined by ^{1}H-NMR, ^{13}C-NMR, and CD spectra. It is proposed that [Pt(en)(1*S*,2*R*-amcha)]Cl_2 and [Pt$(NH_3)_2$(1*S*,2*R*-amcha)]Cl_2 take a fixed chair form with a dihedral angle (Pt–N–C(1)–C(6)) of 180°, while [Pt(en)(1*R*,2*R*-amcha)]Cl_2 and [Pt$(NH_3)_2$(1*R*,2*R*-amcha)]Cl_2 are interconverting between two chair forms.

2-(Aminomethyl)cyclohexylamine (=amcha) has four isomers, which are represented as 1*R*,2*S* (*trans-l*), 1*S*,2*R* (*trans-d*), 1*R*,2*R* (*cis-l*) and 1*S*,2*S* (*cis-d*) isomers (Fig. 1). Various platinum(II) complexes containing these amcha isomers were synthesized and their antitumor activities were tested against leukemia P388.[1] Some differences were found among their activities. Therefore, it would be meaningful to study the conformations of six-membered platinum(II) complexes of amcha isomers.

In general, a six-membered chelate ring is more flexible than a five-membered one and the possible conformations of the former are chair, skew, or boat forms. The chair conformation has been considered to be the most stable form, and ^{1}H-NMR and ^{13}C-NMR spectral data supporting this view have been reported by Hall[2] and Yano *et al.*[3] But few CD spectral studies of platinum(II) complexes containing optically active diamine forming six-membered chelate have been done. In order to determine the conformations of amcha we prepared the following types of complexes for the first time: [Pt(en)(amcha)]Cl_2 and [Pt$(NH_3)_2$(amcha)]Cl_2 (amcha=(1*S*,2*R*)- and (1*R*,2*R*)-2-(aminomethyl)cyclohexylamine). In the present paper, we will discuss the conformations of these platinum(II) complexes from NMR and CD spectral data.



(1R,2S) (1S,2R) (1R,2R) (1S,2S)

Fig. 1. Absolute configurations of 2-(aminomethyl)-cyclohexylamine.

Experimental

Ligands. *1) Synthesis of* cis- *and* trans-*2-(Aminomethyl)-cyclohexylamine*: They were prepared from the corresponding *cis*- and *trans*-1,2-cyclohexanedicarboxylic acid according to the method reported by Armarego *et al.*[4]

2) Resolution of trans-*2-(Aminomethyl)cyclohexylamine*: A hot filtered solution of (2*R*,3*R*)-di-*O*-benzoyltartaric acid monohydrate (46.7 g) in ethanol (307 cm^3) was added to a solution of freshly distilled *trans-dl*-amcha (15.9 g) in water (307 cm^3). After the solution was kept standing overnight at 0 °C, fibrous crystals and a few plate crystals were deposited. When the solution was kept standing for several hours at room temperature, only the plate crystals were dissolved again. The fibrous crystals were collected by filtration and were recrystallized from an aqueous ethanol (1:1 V/V) solution, giving 6.9 g of (1*R*,2*S*)-amcha (2*R*,3*R*)-di-*O*-benzoyltartrate with $[\alpha]_D=-106°$ (1% H_2O:EtOH=1:1 V/V). Found: C, 59.50; H, 6.30; N, 5.55%. Calcd for $C_{25}H_{30}N_2O_8 \cdot H_2O$: C, 59.50; H, 6.41; N, 5.55%.

The filtrate of (1*R*,2*S*)-amcha (2*R*,3*R*)-di-*O*-benzoyltartrate was evaporated to dryness and the residue was recrystallized from an aqueous ethanol (1:1 V/V) solution. The plate crystals of (1*S*,2*R*)-amcha (2*R*,3*R*)-di-*O*-benzoyltartrate obtained showed $[\alpha]_D=-75°$ (1% H_2O: EtOH=1:1 V/V).

The free amine from the (2*R*,3*R*)-di-*O*-benzoyltartrate was regenerated by the method of Bosnich.[5] The free (1*R*,2*S*)-amcha (1.5 g) and (1*S*,2*R*)-amcha (2.5 g) gave specific rotations of $[\alpha]_D=-39°$ and $+40°$ (1% EtOH), respectively.

3) Resolution of cis-*2-(Aminomethyl)cyclohexylamine*: A hot solution of (2*R*,3*R*)-di-*O*-benzoyltartaric acid monohydrate (44 g) in ethanol (395 cm^3) was added to a solution of freshly distilled *cis-dl*-amcha (15 g) in water (80 cm^3). When the resultant solution was kept standing overnight at 0 °C, prism crystals were deposited. They were collected by filtration, washed with ethanol, and dried in air, yielding 26 g of (1*R*,2*R*)-amcha (2*R*,3*R*)-di-*O*-benzoyltartrate with a specific rotation of $[\alpha]_D=-87°$ (1% H_2O: EtOH=1:1 V/V). According to the method of Bosnich,[5] 3.6 g of free (1*R*,2*R*)-amcha were obtained with a specific rotation of $[\alpha]_D=-15°$ (1% EtOH).

The filtrate was allowed to stand overnight at 0 °C to precipitate fibrous crystals. Alkalization and extraction[5] with ether gave 0.2 g of free (1*S*,2*S*)-amcha with a specific rotation of $[\alpha]_D=+14°$ (1% EtOH).

Among the four resolved optical isomers, (1*S*,2*R*)- and (1*R*,2*R*)-amcha were used as the ligands in this work because of their better specific rotations.

Preparation of 2-(Aminomethyl)cyclohexylamine Platinum(II) Complexes. [Pt(en)(1*S*,2*R*-amcha)]Cl_2, [Pt$(NH_3)_2$(1*S*,2*R*-amcha)]Cl_2, [Pt(en)(1*R*,2*R*-amcha)]Cl_2, and [Pt$(NH_3)_2$(1*R*,2*R*-amcha)]Cl_2 were synthesized according to the method reported by Appleton and Hall,[6] and their analytical data are tabulated in Table 1.

Measurements. ^{1}H-NMR spectra were recorded at 100 MHz (JEOL JNM-MH-100). DSS was used as an internal reference.

FT ^{13}C-NMR spectra were obtained at 25 MHz with broad-band proton decoupling on a JEOL JNM-FX-100 spectrometer employing the solvent deuterium signal as an internal lock. A total of 1000—21200 FID's (8192 points) was averaged to provide the desired signal to noise ratio in the 2.5-kHz frequency spectra. Pulse angles of 45° were employed with no pulse delay. The ambient temperature was room temperature. TMS sealed in a capillary was used as an external reference. All NMR spectra were measured in D_2O solutions.

Table 1. Analytical data of the amcha Pt(II) complexes

Complexes	C%		H%		N%	
	Found	Calcd	Found	Calcd	Found	Calcd
[Pt(en)(1*S*,2*R*-amcha)]Cl_2	23.71	23.79	5.18	5.33	12.61	12.33
[Pt$(NH_3)_2$(1*S*,2*R*-amcha)]$Cl_2 \cdot 1/2H_2O$	19.21	19.22	5.07	5.31	12.06	12.81
[Pt(en)(1*R*,2*R*-amcha)]Cl_2	23.55	23.79	5.32	5.33	12.49	12.33
[Pt$(NH_3)_2$(1*R*,2*R*-amcha)]$Cl_2 \cdot 3/2H_2O$	18.70	18.46	5.27	5.55	11.65	12.31

Absorption spectra were obtained in H_2O with a Shimadzu UV 200 Recording Spectrometer.

CD spectra were measured in H_2O with a JASCO J-40 Spectropolarimeter. All measurements were performed at room temperature.

Results and Discussion

^{1}H-NHR Spectra. As shown in Fig. 2, two multiplet peaks around 1.20 and 1.78 ppm can be assigned to the axial and equatorial methylene protons in the cyclohexane ring of (1*S*,2*R*)-amcha. From the integrated intensities, a peak of the methine proton (>CH–C) in the cyclohexane ring seems to be overlapping with these equatorial methylene protons. Two multiplet peaks around 2.48 and 2.88 ppm are attributable to the resonance of aminomethyl protons ($-CH_2-N$) and the methine proton (>CH–N). For (1*S*,2*R*)-amcha, two chair forms with diequatorial or diaxial orientation of amino and aminomethyl groups can be expected. But the behavior of the methylene protons in the cyclohexane ring indicates a fixed chair form with preferential diequatorial orientation.

The multiplet peak around 1.50 ppm (Fig. 2(b)) can be assigned to eight methylene protons and a methine proton (>CH–C) in the cyclohexane ring of (1*R*,2*R*)-amcha. Two multiplet peaks around 2.56 and 3.08 ppm can be assigned to aminomethyl protons ($-CH_2-N$) and a methine proton (>CH–N) by the integrated intensities. For (1*R*,2*R*)-amcha, two chair forms with axial and equatorial orientations of the amino and aminomethyl groups are possible, but the multiplet peak of the methylene protons in the cyclohexane ring indicates an averaging of axial and equatorial protons by rapid interconversion between two chair forms on the NMR time scale.

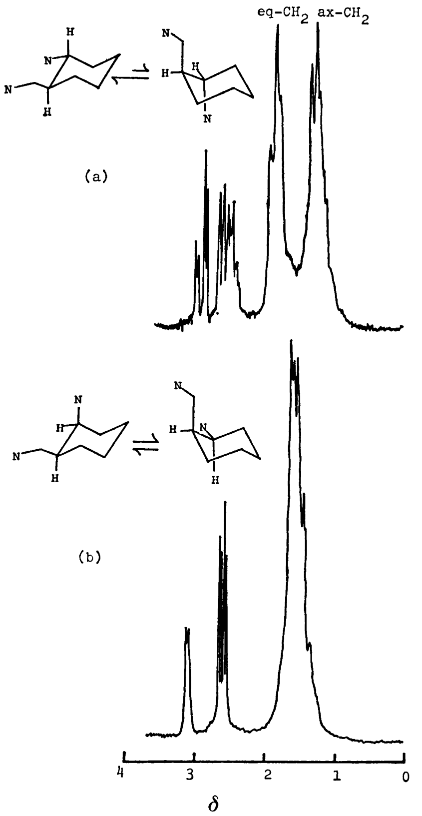


Fig. 2. ^{1}H-NMR spectra of (a) (1*S*,2*R*)-amcha and (b) (1*R*,2*R*)-amcha.

Figure 3 shows ^{1}H-NMR spectra of [Pt(en)(amcha)]-Cl_2 and [Pt$(NH_3)_2$(amcha)]Cl_2 (amcha=(1*S*,2*R*)- and (1*R*,2*R*)-amcha) in D_2O. In the spectrum of [Pt-(en)(1*S*,2*R*-amcha)]Cl_2, multiplets due to axial and equatorial methylene protons in the cyclohexane ring were observed at 1.26 and 1.70 ppm, respectively. This behavior of the methylene protons suggests that the cyclohexane ring takes a fixed chair form preferentially. In the spectrum of [Pt(en)(1*R*,2*R*-amcha)]Cl_2, a multiplet due to methylene protons in the cyclohexane ring was observed at 1.30 ppm, suggesting the averaging of axial and equatorial protons by rapid interconversion between two chair forms. ^{1}H-NMR spectra of [Pt$(NH_3)_2$(1*S*,2*R*-amcha)]Cl_2 and [Pt$(NH_3)_2$(1*R*,2*R*-amcha)]Cl_2 are almost similar to those of [Pt(en)(1*S*,2*R*-amcha)]Cl_2 and [Pt(en)(1*R*,2*R*-amcha)]Cl_2, respectively, except for peaks of ethylenediamine.

Recent studies[2,7] suggest that the dihedral angle dependence of the vicinal coupling constant $^3J_{Pt-H}$ in Pt–N–C–H fragments would parallel the Karplus equation for the $^3J_{H-H}$ in H–C–C–H fragments. The $^3J_{Pt-H}$ value has offered very important information for determining the conformation of 1,2-diamine and 1,3-diamine platinum(II) complexes. [Pt(en)(1*S*,2*R*-amcha)]Cl_2 and [Pt(en)(1*R*,2*R*-amcha)]Cl_2 gave a single sharp peak, together with satellite peaks due to the coupling with ^{195}Pt ($I=1/2$, 34% abundance) at 2.73 ppm. The single sharp peak and the satellite peaks are overlapping with the aminomethyl protons ($-CH_2-$N) and the methine proton (>CH–N), but by comparing [Pt(en)(1*S*,2*R*-amcha)]Cl_2 and [Pt(en)(1*R*,2*R*-amcha)]Cl_2 with [Pt$(NH_3)_2$(1*S*,2*R*-amcha)]Cl_2 and [Pt-$(NH_3)_2$(1*R*,2*R*-amcha)]Cl_2, the single sharp peak can be assigned to methylene protons of ethylenediamine. The observed $^3J_{Pt-H}$ values of [Pt(en)(1*S*,2*R*-amcha)]-Cl_2 and [Pt(en)(1*R*,2*R*-amcha)]Cl_2 were 41.0 Hz. This $^3J_{Pt-H}$ value is in good harmony with $^3J_{Pt-H}$ values previously reported for [Pt$(en)_2$]Cl_2 (41.0 Hz) and

TABLE 2. ^{13}C-NMR CHEMICAL SHIFTS[a] AND COUPLING CONSTANTS[b]

Complexes	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	N-CH$_2$
[Pt(en)(1*S*,2*R*-amcha)]Cl$_2$	57.75 (23.8)	41.40 (17.7)	29.73	25.02	24.24	33.53 (43.3)	48.97 (28.7)
[Pt(NH$_3$)$_2$(1*S*,2*R*-amcha)Cl$_2$	57.94 (22.6)	41.44 (18.9)	29.92	25.17	24.41	33.65 (43.9)	49.22 (26.9)
[Pt(en)(1*R*,2*R*-amcha)]Cl$_2$	53.53 (26.3)	37.13 (21.4)	27.51	22.88	21.03	28.75 (20.2)	44.03 (28.1)
[Pt(NH$_3$)$_2$(1*R*,2*R*-amcha)]Cl$_2$	53.63 (25.0)	37.23 (22.0)	27.48	22.90	21.37	28.97 (22.0)	44.42 (27.5)

a) ^{13}C shifts in ppm from external TMS. b) The values in parentheses are the coupling constants (^{195}Pt–^{13}C).

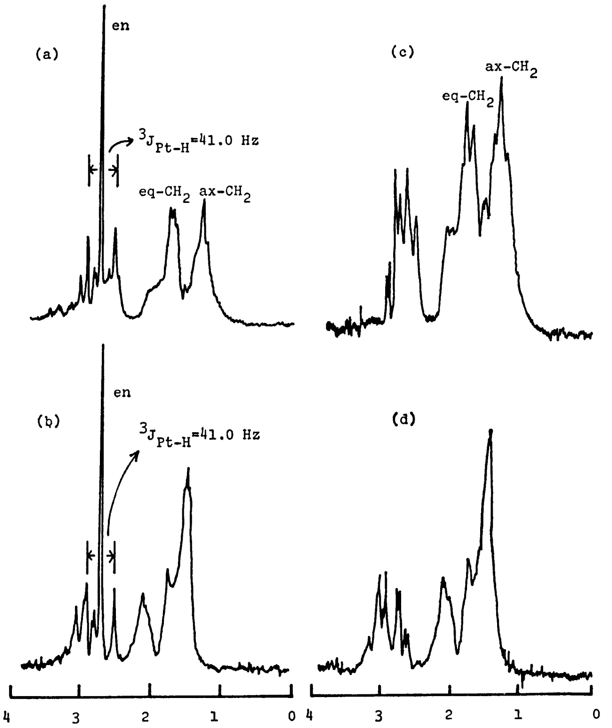


Fig. 3. ^{1}H-NMR spectra of (a) [Pt(en)(1*S*,2*R*-amcha)]-Cl$_2$, (b) [Pt(en)(1*R*,2*R*-amcha)]Cl$_2$, (c) [Pt(NH$_3$)$_2$-(1*S*,2*R*-amcha)]Cl$_2$, and (d) [Pt(NH$_3$)$_2$(1*R*,2*R*-amcha)]Cl$_2$.

[Pt(en)(NH$_3$)$_2$]Cl$_2$ (41.5 Hz),[2] indicating that the chelate ring of ethylenediamine shows a rapid conformational interconversion.

Unfortunately, other satellite peaks could not be assigned, and information on six-membered chelate ring could not be obtained from the $^3J_{Pt-H}$ value.

^{13}C-NMR Spectra. Figure 4 shows ^{13}C-NMR spectra of [Pt(en)(1*S*,2*R*-amcha)]Cl$_2$ and [Pt(en)(1*R*,2*R*-amcha)]Cl$_2$ in D$_2$O. In both complexes, assignments of C(1), C(2), C(6), aminomethyl carbons, and methylene carbons of ethylenediamine were facilitated on the basis of the spectrum with off-resonance proton decoupling. Three peaks on the upfield side are attributable to the resonance of C(3), C(4), and C(5) carbons, but assignments of these three peaks may be difficult because of complicated steric factors.

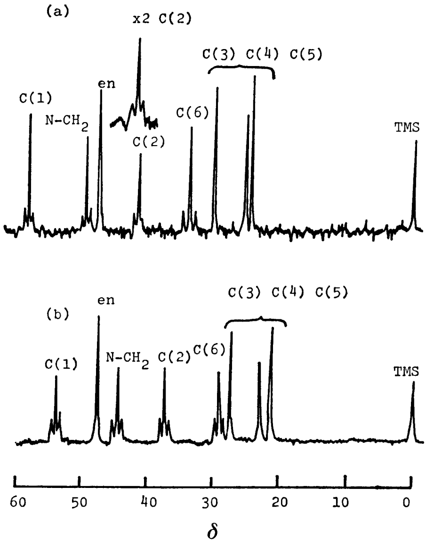


Fig. 4. ^{13}C-NMR spectra of (a) [Pt(en)(1*S*,2*R*-amcha)]-Cl$_2$ and (b) [Pt(en)(1*R*,2*R*-amcha)]Cl$_2$.

Table 2 shows chemical shifts and coupling constants (^{195}Pt–^{13}C) of these platinum(II) complexes. By comparing the coupling constants of these complexes, a significant difference in $^3J_{Pt-C(6)}$ values was detected. [Pt(en)(1*S*,2*R*-amcha)]Cl$_2$ and [Pt(NH$_3$)$_2$(1*S*,2*R*-amcha)]Cl$_2$ gave 43.3 and 43.9 Hz, respectively, while [Pt(en)(1*R*,2*R*-amcha)]Cl$_2$ and [Pt(NH$_3$)$_2$(1*R*,2*R*-amcha)]Cl$_2$ gave 20.2 and 22.0 Hz. Recently, Bagger[8] and Erickson *et al.*[9] have demonstrated that in five-membered platinum(II) complexes the coupling constant $^3J_{Pt-N-C-C}$ shows a Karplus-type angle dependence on the dihedral angle between the planes Pt–N–C and N–C–C. It turns out that the significant difference in $^3J_{Pt-C}$ found would be explained if the relationship $^3J_{Pt-N-C-C}=a\cos^2\phi$ is also valid in six-membered platinum(II) complexes, ϕ being the dihedral angle between the planes Pt–N–C and N–C–C, and *a* being a constant. The molecular models suggest that [Pt(en)(1*S*,2*R*-amcha)]Cl$_2$ and [Pt(NH$_3$)$_2$ (1*S*,2*R*-amcha)]Cl$_2$ may take either a chair form or a δ-skew form. Whichever form these platinum(II) complexes take, the dihedral angle of Pt–N–C(1)–C(6) is about 180° (Fig. 5). The $^3J_{Pt-C(6)}$ values for [Pt(en)(1*S*,2*R*-amcha)]Cl$_2$ and [Pt(NH$_3$)$_2$(1*S*,2*R*-amcha)]Cl$_2$ were 43.3 and 43.9 Hz, respectively. A

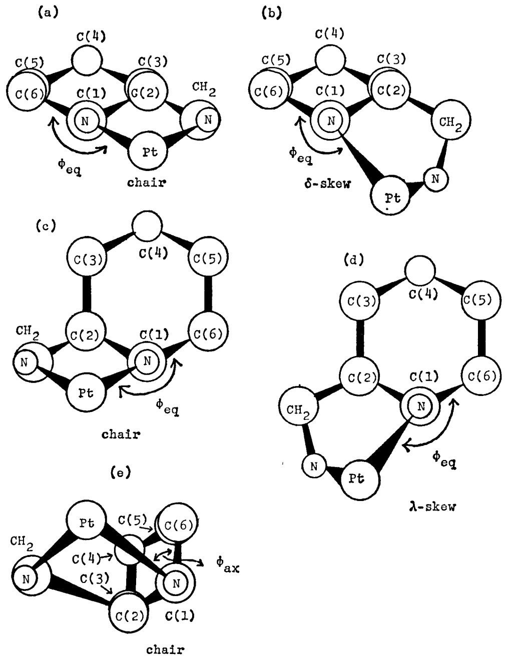


Fig. 5. The chelate ring viewed down an N–C bond. (a) and (b) for [PtX(1*S*,2*R*-amcha)]Cl_2; (c), (d), and (e) for [PtX(1*R*,2*R*-amcha)]Cl_2 (X=en, $(NH_3)_2$).

similar value has been reported for (*R*,*S*)-1,3-diphenyl-1,3-propanediamine platinum(II) complexes in which both phenyl groups are equatorial.[10] The *a* values in the equation $^3J_{\text{Pt-N-C-C}}=a\cos^2\phi$ seem to be 43—44 Hz. [Pt(en)(1*R*,2*R*-amcha)]Cl_2 and [Pt$(NH_3)_2$(1*R*,2*R*-amcha)]Cl_2 may take two chair forms or a λ-skew form, but may not take a δ-skew form because of the steric hindrance. As shown in Fig. 5, an angle of 180° may be expected for one chair form or the λ-skew form and about 60° for the other chair form. The ^{1}H-NMR data show that the cyclohexane ring of (1*R*,2*R*)-amcha platinum(II) complexes is interconverting between two chair forms, and hence that the chelate ring will interconvert. When two chair forms interconvert with each other rapidly on a NMR time scale, the averaged coupling constant due to a rapid ring interconversion would be $^3J_{\text{Pt-C(6)}}=1/2$ ($a\cos^2 180°+a\cos^2 60°$) (a=43—44 Hz), that is $^3J_{\text{Pt-C(6)}}=$ 27.0—27.5 Hz. If the population of a λ-skew intermediate which appears in interconverting between two chair forms cannot be neglected, the $^3J_{\text{Pt-C(6)}}$ value is expected to be larger than 27.0—27.5 Hz. According to the conformational analysis of the planar ML_2(tn) type complex (L=a monodentate ligand, tn=1,3-propanediamine), the interconversion occurred *via* a skew intermediate,[3,11] but the population of the intermediate conformer was small at room temperature.[3,11] Experimental values of $^3J_{\text{Pt-C(6)}}$ for [Pt(en)(1*R*,2*R*-amcha)]Cl_2 and [Pt$(NH_3)_2$(1*R*,2*R*-amcha)]Cl_2 were 20.2 and 22.0 Hz, respectively. Thus the λ-skew may be neglected because the experimental values are smaller than the values calculated from the 1:1 abundance ratio of the two chair forms. Assuming the equatorial and axial C–C(6) chair form exactly take the angles of 180° and 60°, respectively, the population of the former conformer may be smaller than the latter.

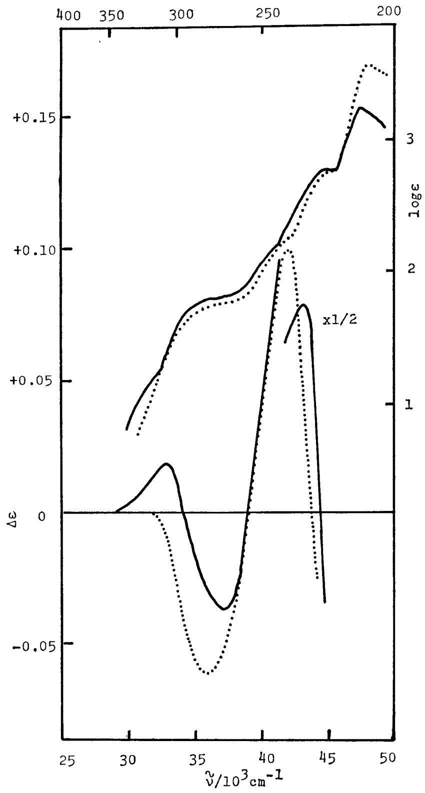


Fig. 6. Absorption and CD spectra of ——: [Pt(en)-(1*S*,2*R*-amcha)]Cl_2 and ······: [Pt$(NH_3)_2$(1*S*,2*R*-amcha)]Cl_2.

Absorption and CD Spectra. In aqueous solution, [Pt(en)(1*S*,2*R*-amcha)]Cl_2 exhibited five absorption bands in the ultraviolet region, as shown in Fig. 6. The band at 37000 cm^{-1}, on the basis of D_{4h} symmetry, can be assigned to $^1A_{1g}$-^3E_g (band II), and those at 41700 (shoulder), 44400, and 47000 cm^{-1} to $^1A_{1g}$-$^1A_{2g}$ (band III), $^1A_{1g}$-^1E_g (band IV), and charge transfer transitions, respectively. The shoulder at 31300 cm^{-1} may be assigned to the $^1A_{1g}$-$^3A_{2g}$ (band I) transition.[12] Similarly, [Pt$(NH_3)_2$(1*S*,2*R*-amcha)]Cl_2 exhibited four bands. The band at 35700 cm^{-1} can be assigned to band II and the bands at 41700 (shoulder), 44400, and 48100 cm^{-1} to band III, band IV, and charge transfer transitions, respectively. As shown in Fig. 7, [Pt(en)(1*R*,2*R*-amcha)]Cl_2 and [Pt$(NH_3)_2$(1*R*,2*R*-amcha)]Cl_2 exhibited four absorption bands. The bands at 35700, 41700 (shoulder), 44400, and 48100 cm^{-1} may be assigned to band II, band III, band IV, and charge transfer transitions, respectively.[12]

Figure 6 also shows the CD spectra of [Pt(en)(1*S*,2*R*-amcha)]Cl_2 and [Pt$(NH_3)_2$(1*S*,2*R*-amcha)]Cl_2 in water. [Pt(en)(1*S*,2*R*-amcha)]Cl_2 exhibited three CD bands at 32700, 37000, and 42600 cm^{-1} with signs of positive, negative, and positive, respectively. These CD bands correspond to bands I, II ,and III in the absorption spectrum. [Pt$(NH_3)_2$(1*S*,2*R*-amcha)]Cl_2 exhibited two CD bands, corresponding to bands II and III in the absorption spectrum. Although the peak of band IV in both complexes could not be detected in the CD spectra, its sign can be estimated to be negative, as shown in Fig. 6. The CD spectral data of the platinum(II) complexes are presented in Table 3. The absolute CD strength ($=|\Delta\varepsilon|$) of [Pt(en)(1*S*,2*R*-amcha)]Cl_2 and [Pt$(NH_3)_2$(1*S*,2*R*-amcha)]Cl_2 is lower than that of the five-membered platinum(II) complexes containing (*R*)-1,2-propanediamine and (*R*,*R*)-1,2-cyclohexanediamine.[12] The optical activity due to the chelate ring of amcha may be expected to arise from (i) the conformational effect of the chelate ring and (ii) the vicinal effect of the asymmetric carbon. However, only the vicinal effect of the asymmetric carbon seems to contribute to the $|\Delta\varepsilon|$ values of [Pt(en)(1*S*,2*R*-amcha)]Cl_2 and [Pt$(NH_3)_2$(1*S*,2*R*-amcha)]Cl_2. Namely, the observed low $|\Delta\varepsilon|$ values of these complexes can be explained by considering as preferential the chair form which does not make any conformational contribution to the CD spectra. The chair and the λ-skew form could not be distinguished by ^{13}C-NMR analyses, but the CD spectral data indicate a fixed chair form with a dihedral angle of 180° (Fig. 8). As shown in Fig. 7, the CD spectra of [Pt(en)(1*R*,2*R*-amcha)]Cl_2 and

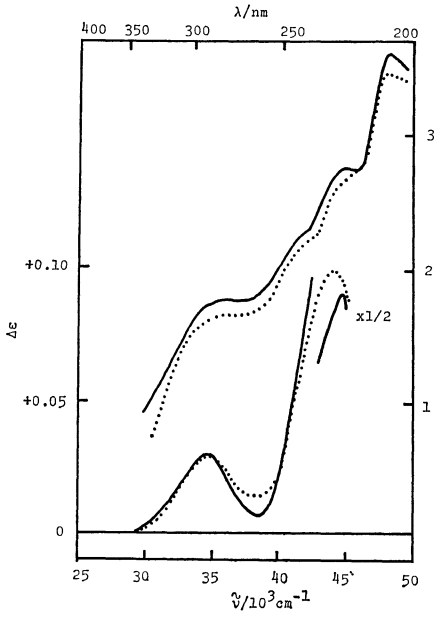


Fig. 7. Absorption and CD spectra of ——: [Pt(en)(1*R*,2*R*-amcha)]Cl_2 and ······: [Pt$(NH_3)_2$(1*R*,2*R*-amcha)]Cl_2.

Table 3. Absorption and CD spectral data

Complexes	Absorption $\tilde{\nu}/10^3$ cm^{-1} (log ε)	CD $\tilde{\nu}/10^3$ cm^{-1} (Δε)
[Pt(en)(1*S*,2*R*-amcha)]Cl_2	31.3(1.15)	32.7(+0.019)
	37.0(1.82)	37.0(−0.036)
	41.7 sh	42.6(+0.160)
	44.4(2.78)	
	47.0(3.23)	
[Pt$(NH_3)_2$(1*S*,2*R*-amcha)]Cl_2	35.7(1.75)	35.7(−0.061)
	41.7 sh	41.7(+0.099)
	44.4(2.74)	
	48.1(3.57)	
[Pt(en)(1*R*,2*R*-amcha)]Cl_2	35.7(1.77)	34.5(+0.060)
	41.7 sh	
	44.4(2.75)	44.4(+0.358)
	48.1(3.63)	
[Pt$(NH_3)_2$(1*R*,2*R*-amcha)]Cl_2	35.7(1.66)	34.5(+0.060)
	41.7 sh	
	44.4(2.66)	43.7(+0.203)
	48.1(3.47)	

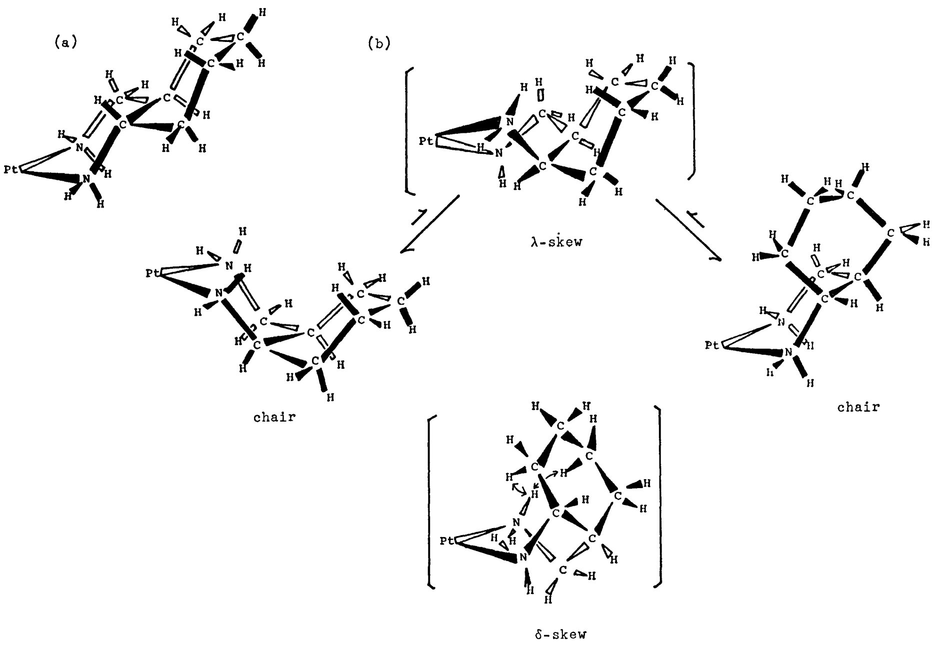


Fig. 8. Proposed conformations of (a) [PtX(1*S*,2*R*-amcha)]Cl_2 and (b) [PtX(1*R*,2*R*-amcha)]Cl_2 (X=en, $(NH_3)_2$).

$[Pt(NH_3)_2(1R,2R\text{-amcha})]Cl_2$ showed positive bands at 34500 and *ca.* 44000 cm^{-1}, corresponding to bands II and IV in their absorption spectra. As shown in Table 3, the $|\Delta\varepsilon|$ values of $[Pt(en)(1R,2R\text{-amcha})]Cl_2$ and $[Pt(NH_3)_2(1R,2R\text{-amcha})]Cl_2$ indicate that these complexes take a chair form, which has no conformational effect. Although two chair forms may be interconverting with each other *via* a λ-skew intermediate, the population of the λ-skew form can be neglected, according to the ^{13}C-NMR and CD spectral data. It is concluded that $[Pt(en)(1R,2R\text{-amcha})]Cl_2$ and $[Pt(NH_3)_2(1R,2R\text{-amcha})]Cl_2$ are apparently interconverting between two chair forms (Fig. 8).

The authors are sincerely grateful to Dr. John C. Bailar, Jr., University of Illiois, for his helpful advice and suggestions in reviewing this paper. This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan.

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