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Nuclear Magnetic Resonance Study of Metal Complexes. 2. Conformations of 1,2-Diamine Chelate Rings with *C*-Phenyl Group(s) in Cobalt(III) and Platinum(II) Complexes

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The proton magnetic resonance spectra of $[Co(CN)_4(R\text{-phenen})]^-$ (*R*-phenen = (*R*)-phenylethylenediamine), $[Pt(NH_3)_2(pn\text{-}d_1)]^{2+}$ (pn-d_1, = 2-deuterio-1,2-diaminopropane), $[Pt\ (S\text{-pn-}d_2)_2]^{2+}$ (*S*-pn-d_2 = (2*S*)-1,1-dideuterio-1,2-diaminopropane), $[Pt(S,S\text{-bn})_2]^{2+}$ (*S*,*S*-bn = (2*S*,3*S*)-2,3-butanediamine), and $[Pt\ (en)((-)_D\text{-stien})]^{2+}$ ($(-)_D$-stien = stilbenediamine) have been measured. The ^{13}C NMR spectra of these Pt(II) complexes and $[Pt(en)(R\text{-phenen})]^{2+}$ have been obtained. Values of $J_{H-C-C-H}$ indicate a strong preference for the equatorial orientation of $C-C_6H_5$ in (*R*)-phenylethylenediamine of Co(III) complexes. For Pt(II) complexes, values of $J_{Pt-N-C-H}$ and $J_{Pt-N-C-C}$ suggest that 1,2-diaminopropane (propylenediamine) and (*R*)-phenylethylenediamine chelate rings have unsymmetrical gauche conformations and (2*S*,3*S*)-2,3-butanediamine and $(-)_D$-stilbenediamine chelate rings take symmetrical gauche conformations, while *meso*-stilbenediamine chelate changes its conformation rapidly from λ to δ and vice versa rapidly on the NMR time scale. For the diamine chelates with *C*-phenyl group(s) a Karplus-like dihedral angle dependence for the $J_{Pt-N-C-C^*}$, where C* is a phenyl carbon atom which attaches on the membered-carbon atom, was observed. These $^3J_{Pt-C^*}$ values were very similar to those for the $J_{Pt-N-C-CH_3}$ in the diamine chelates with *C*-methyl group(s).

Introduction

Methyl groups substituted to diamines or tetraamines are capable of affecting the configurations of metal complexes. Little information has, however, been obtained for other substituted groups. In our recent research,[1] abnormal circular dichroism (CD) curves were observed for *trans*-$[CoCl_2(R\text{-phenen})_2]^+$ and *trans*-$[CoCl_2((-)_D\text{-stien})_2]^+$, where *R*-phenen and $(-)_D$-stein are (*R*)-phenylethylenediamine and $(-)_D$-stilbenediamine, respectively. It is accepted that the puckered dissymmetric conformation of ligand in the *trans*-$[CoCl_2(\text{optically active 1,2-diamine})_2]^+$ ions contributes predominantly to the CD curve.

It is very interesting to clarify the stereochemical behavior of a phenyl group substituted to 1,2-diamines such as phenen and stien.

Our earlier NMR study of Co(III), Pd(II), and Pt(II) complexes of (*R*)-propylenediamine (*R*-pn) established the ligand conformation in aqueous solution on the basis of the J_{H-H} value of the ligand H–C–C–H fragments.[2]

Since the methylene and methine parts of the *R*-phenen chelate ring have an ABC spin system which is formally equivalent to those of the propylenediamine chelate ring, the conformational analysis method which has been useful in analyzing the propylenediamine chelate ring would be applicable to this diamine.

On the other hand, $(-)_D$-stein has two chemically equivalent methine protons, and the $J_{H-C-C-H}$ value could not be observed. Therefore, it is impossible to employ the conformational analysis based on the J_{H-H} value to this ligand. Some recent research[3,4] suggests that the dihedral angle dependence of the J_{Pt-H} value for Pt-N-C-H fragments in Pt(II) complexes of amino acid or 1,3-diamine seems to parallel that of the J_{H-H} for H-C-C-H fragments. We suppose it will be possible to achieve the conformational analysis of the stien chelate ring by employing the $J_{Pt-N-C-H}$ value.

It is well-known that amino acidato chelate rings are nearly planar compared with 1,2-diamine chelate rings and the angle at the metal for the 1,3-diamine chelate ring is larger than

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that for 1,2-diamine.[5] Therefore, it is expected that these chelates differ from one another in the dihedral angle for Pt–N–C–H fragments in Pt(II) complexes. Consequently, it is not appropriate to use the $J_{\text{Pt-N-C-H}}$ value reported for amino acids and 1,3-diamines for conformational analysis of the 1,2-diamine chelate ring.

To obtain the standard $J_{\text{Pt-N-C-H}}$ value, we prepared two deuterated propylenediamines; one is (2*S*)-1,1-dideuterio-1,2-diaminopropane (pn-d_2) and the other is 2-deuterio-1,2-diaminopropane (pn-d_1). Recently Erickson et al.[6] have demonstrated that in 13 different 1,2-diamine complexes of platinum(II) the coupling constant $J_{\text{Pt-N-C-C}}$ shows a Karplus-type angle dependence on the dihedral angle between the planes Pt–N–C and N–C–C. Thus, conformational information for platinum chelates can be obtained from ^{13}C ($I = {}^{1}/_{2}$, 1% abundance) spectra as is suggested by a ^{13}C study of platinum chelates of meso and racemic 2,3-butanediamines.[7]

In this study, we prepared Pt(II) complexes of these diamines, along with Co(III) and Pt(II) complexes of (*R*)-phenylethylenediamine, (2*S*,3*S*)-2,3-butanediamine (*S*,*S*-bn), $(-)_D$-stilbenediamine ($(-)_D$-stien), and *meso*-stilbenediamine (*ms*-stien), and measured their ^{1}H and ^{13}C NMR spectra. We discuss the conformational behavior of 1,2-diamine chelates on the basis of $J_{\text{H-C-C-H}}$, $J_{\text{Pt-N-C-H}}$, and $J_{\text{Pt-N-C-C}}$ values.

Experimental Section

Preparations. α-Deuterio-(*R*,*S*)-alanine.[8] (*S*)-Alanine (15.0 g) was dissolved in 45 mL of warm D_2O. To the solution was added 75 mL of D_2O solution containing 1.0 g of $CuSO_4$ and 1.5 g of freshly distilled salicylaldehyde with stirring. The pH of the solution was adjusted to 10.0 by adding 20% NaOD in D_2O, and then the resultant solution was warmed to 80 °C for 15 h. The ORD spectrum of the solution revealed that the optical activity had completely disappeared. A small amount of concentrated HCl was added to acidify the solution, and then H_2S gas was bubbled through the solution for 10 min. Activated charcoal was added and then filtered off. The filtrate was evaporated almost to dryness. The residue was dissolved in a small amount of water, and the pH of the solution was adjusted to 10.0 by adding dilute NaOH solution. White crystals were precipitated out by adding a large excess of ethanol. The product was separated by filtration and was dried under vacuum. The yield of pure α-deuterio-(*R*,*S*)-alanine was about 9.0 g.

2-Deuterio-1,2-diaminopropane (pn-d_1). α-Deuterioalaninamide (9.0 g) obtained from α-deuterioalanine by a usual method[9] was added to a suspension of lithium aluminum hydride (7.2 g) in 150 mL of anhydrous tetrahydrofuran, and the mixture was heated under reflux for 24 h. After cooling, 15 g of H_2O was added dropwise to the reaction mixture which was then filtered. The residue was extracted with 100 mL of tetrahydrofuran under reflux and filtered. To the combined filtrate and washings was added concentrated HCl (22.5 g). Tetrahydrofuran was removed under reduced pressure, and a large excess of NaOH pellets was added to the oily residue. The separated diamine layer was extracted with ether, and the ether was removed by distilling at atmospheric pressure. The product was purified by distillation. The isotopic purity of this diamine was examined by a measurement of its ^{1}H NMR spectrum, which revealed that the doublet of the methyl group in nondeuterated 1,2-diaminopropane had converted to a singlet.

(2*S*)-1,1-Dideuterio-1,2-diaminopropane (*S*-pn-d_2). This diamine was prepared by a method similar to that described for the pn-d_1, using lithium aluminum deuteride, (*S*)-alaninamide deuterated at the NH protons, and D_2O in the place of lithium aluminium hydride, α-deuterio-(*R*,*S*)-alaninamide, and H_2O, respectively. The ^{1}H NMR spectrum of this diamine showed that the multiplet corresponding to the methylene protons had disappeared.

(2*S*,3*S*)-2,3-Butanediamine (*S*,*S*-bn),[10] (*R*)-phenyethylenediamine (*R*-phenen),[1] $(-)_D$-stilbenediamine ($(-)_D$-stien), and *meso*-stilbenediamine (*ms*-stien)[11] were prepared by known methods.

K[Co(CN)$_4$(*R*-phenen)]·2H$_2$O. $K_3[CoCl(CN)_5]$ (3.6 g) was dissolved in 20 mL of H_2O, and a solution of 1.4 g of *R*-phenen in 20 mL of ethanol was added. The solution was warmed on a water bath at 80 °C for 5 h. The reaction mixture was cooled, filtered, and evaporated to almost dryness under reduced pressure. The residue was treated with 30 mL of methanol and filtered. This treatment with methanol was repeated three times. The combined methanolic solution was evaporated and then the yellow powder was obtained. The powder was dried under vacuum. Anal. Calcd for $CoC_{12}H_{16}N_6O_2K$: C, 38.50; H, 4.31; N, 22.45. Found: C, 38.74; H, 3.80; N, 23.10.

[Pt(*S*-pn-d_2)$_2$]Cl$_2$. To 0.83 g of K_2PtCl_4 in 30 mL of water was added 0.3 g of *S*-pn-d_2 (the molar ratio of Pt to diamine is 1:2), and the solution was heated on a water bath at 80 °C for 1 h. Then, 0.83 g of K_2PtCl_4 was added to the solution. The purple precipitates which formed were filtered off and washed successively with water, ethanol, and ether. To the purple compound (Magnus-type salt) suspended in 30 mL of water was added 0.3 g of *S*-pn-d_2, and the mixture was heated under reflux for 7 h. During this time, the mixture turned to a slightly yellow solution. This was filtered to remove any insoluble material, and the filtrate was evaporated to dryness on a water bath. The crude product thus obtained was recrystallized from a minimum amount of hot water. These white crystals were filtered and washed with ethanol and ether. The compound was dried under vacuum. Anal. Calcd for $PtC_6H_{16}D_4N_4Cl_2$: C, 17.23; H and D, 5.78; N, 13.40. Found: C, 17.60; H, 5.50; N, 13.62.

[Pt(*S*-pn)$_2$]Cl$_2$. This complex was prepared in our previous work.[2]

[Pt(*S*,*S*-bn)$_2$]Cl$_2$·2H$_2$O. This compound was prepared by a method similar to that described for the [Pt(*S*-pn-d_2)$_2$]Cl$_2$, using *S*,*S*-bn in place of *S*-pn-d_2. Anal. Calcd for $PtC_8H_{28}N_4O_2Cl_2$: C, 20.09; H, 5.90; N, 11.71. Found: C, 20.01; H, 5.52; N, 11.93.

[Pt(NH$_3$)$_2$(pn-d_1)]Cl$_2$. [PtCl$_2$(pn-d_1)] was prepared by a modification of the method for preparation of [PtCl$_2$(en)]. K_2PtCl_4 (2.1 g) was dissolved in 10 mL of water, and the solution was cooled in an ice bath. pn-d_1 (1.1 g) in 30 mL of water was added in small portions over a period of approximately 4 h. Insoluble yellow crystals of [PtCl$_2$(pn-d_1)] separated slowly and were removed on a filter every 15–20 min to prevent contamination of possible by-products [Pt(pn-d_1)$_2$]Cl$_2$ and [Pt(pn-d_1)$_2$][PtCl$_4$]. These crystals were purified by recrystallization of the crude material from hot water acidified with hydrochloric acid. The product was washed with water and ethanol and air-dried. The yellow crystalline [PtCl$_2$(pn-d_1)], thus obtained, was then suspended in 40 mL of concentrated aqueous ammonia. The solution was heated on the water bath at 75 °C until the yellow crystals dissolved. The solution was evaporated to dryness and white crystals were obtained. The crude product was collected and recrystallized from a minimum amount of hot water. The product was washed with ethanol and ether and dried under vaccum. Anal. Calcd for $PtN_4C_3H_{15}DCl_2$: C, 9.73; H and D, 4.09; N, 15.14. Found: C, 9.45; H, 4.38; N, 15.25.

[Pt(en)($(-)_D$-stien)]Cl$_2$. To a suspension of [PtCl$_2$(en)] (0.8 g) obtained by the known method in 10 mL of water was added $(-)_D$-stien (0.53 g), and the mixture was refluxed for 3 h and then filtered. White crystals were obtained by evaporating the filtrate almost to dryness and by adding ethanol. They were filtered off, washed with ethanol and ether, and dried in vacuo. Anal. Calcd for $PtN_4C_{16}H_{24}Cl_2$: C, 35.96; H, 3.77; N, 10.49. Found: C, 36.24; H, 4.53; N, 10.41.

[Pt(en)(*ms*-stien)]Cl$_2$. This compound was prepared by a method similar to that described for the [Pt(en)($(-)_D$-stien)]Cl$_2$, using *ms*-stien in place of $(-)_D$-stien. Anal. Calcd for $PtN_4C_{16}H_{24}Cl_2$: C, 35.96; H, 3.77; N, 10.49. Found: C, 35.91; H, 3.91; N, 10.58.

[Pt(en)(*R*-phenen)]Cl$_2$. This compound was prepared by a method similar to that for [Pt(en)($(-)_D$-stien)]Cl$_2$, using *R*-phenen in place of $(-)_D$-stien. Anal. Calcd for $PtC_{10}H_{20}N_4Cl_2$: C, 25.98; H, 4.36; N, 12.12. Found: C, 25.91; H, 4.62; N, 12.09.

NMR Spectra. FT carbon-13 spectra were obtained at 25.15 MHz with broad-band proton decoupling on a JEOL PS-99.5 spectrometer employing the solvent deuterium signal as an internal lock. A total of 1500–2000 FID's (16 800 points) were averaged to provide the desired signal-to-noise ratio in the 5-kHz frequency spectra. A pulse angle of 45° was employed with no pulse delay. The ambient temperature was 39 °C. Me$_4$Si sealed in a capillary was used as an external reference. Proton NMR spectra were recorded at 100 MHz (JEOL PS-100). DSS was used as an internal reference. The ambient temperature was 39 °C. All NMR spectra were measured in D_2O solution.

Results and Discussions

Proton and carbon-13 NMR spectra of the complexes are summarized in Table I. Typical features of ^{1}H and ^{13}C spectra of these complexes are illustrated by the spectra of $[Pt(S\text{-pn-}d_1)_2]^{2+}$, $[Co(CN)_4(R\text{-phenen})]^-$, [Pt(en)(*R*-phe-

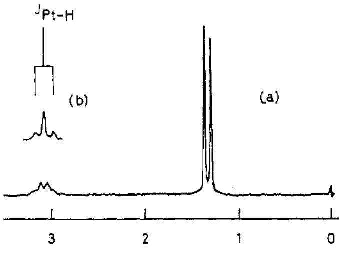


Figure 1. ^{1}H NMR spectra of $[Pt(S\text{-pn-}d_2)_2]^{2+}$: (a) in D_2O; (b) double-resonance spectrum irradiated on the methyl signal.

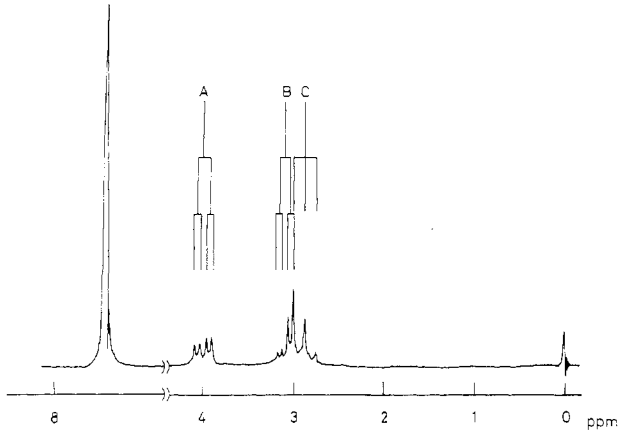


Figure 2. ^{1}H NMR spectrum of $[Co(CN)_4(R\text{-phenen})]^-$ in D_2O. The HOD resonance is not reported.

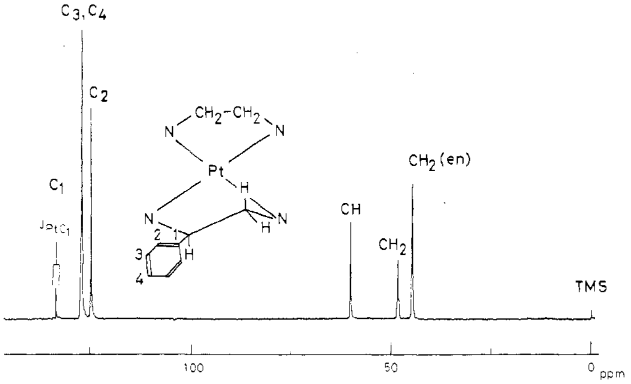


Figure 3. ^{13}C NMR spectrum of $[Pt(en)(R\text{-phenen})]^{2+}$ in D_2O.

nen)]$^{2+}$, $[Pt(en)((-)_D\text{-stien})]^{2+}$, and $[Pt(en)(ms\text{-stien})]^{2+}$ (Figures 1–5).

Where any doubt about assignments for the ^{13}C NMR spectra could exist, gated 1 proton-decoupled ^{13}C spectra were obtained to characterize the spectra. The assignment of the downfield peaks associated with carbons 1, 2, 3, and 4 of the phenyl ring is facilitated by comparison with data for aniline.[12] Differentiation between the C(3) and the C(4) resonances could not be observed except for the *ms*-stien resonance. The C(1) of phenyl group and C-CH$_3$ carbons show similar coupling constants to the platinum nucleus.

The assignment of ^{1}H NMR spectra are explained in the following parts of this report.

Deuterated Propylenediamines. When the amino protons are deuterated, *S*-pn-d_2, $ND_2CH(CH_3)CD_2ND_2$, gives an AX$_3$ pattern. The doublet (J = 6.0 Hz) and the quartet (J = 6.0 Hz) are, therefore, assigned to the methyl and the methine signals, respectively. No observation of the methylene signal indicates complete deuteration of methylene protons in our preparation. The broadening of the lower field quartet is due to the proton–deuterium (I = 1) spin–spin coupling between the methine proton and the methylene deuteriums.

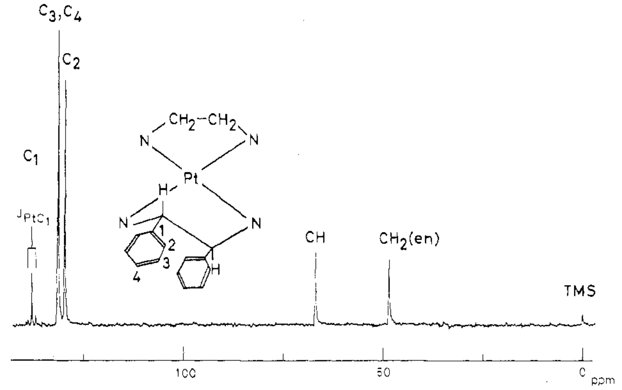


Figure 4. ^{13}C NMR spectrum of $[Pt(en)((-)_D\text{-stien})]^{2+}$ in D_2O.

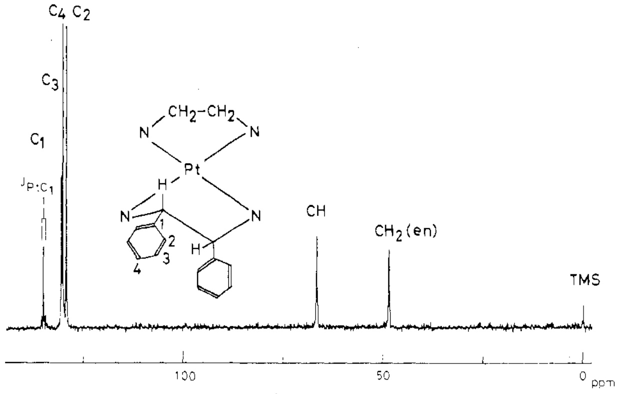


Figure 5. ^{13}C NMR spectrum of $[Pt(en)(ms\text{-stien})]^{2+}$ in D_2O.

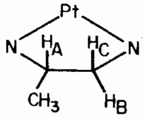
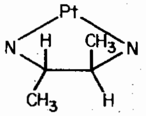
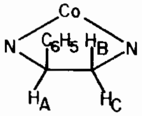
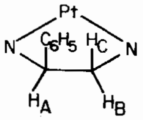
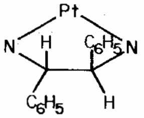
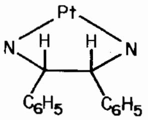
In the ^{1}H NMR spectrum of pn-d_1, one sharp methyl singlet and a broad methylene signal were observed. This suggests that the methine proton is deuterated completely in the course of preparation.

Propylenediamine Complexes. The cis and trans methyl isomers are possible for the $[Pt(S\text{-pn-}d_2)_2]^{2+}$. The chemical environment for protons should be different between these two geometrical isomers. However, it is expected that such a difference would be too small to be detected by the present ^{1}H NMR spectrometer.[2,3]

The 100-MHz ^{1}H NMR spectrum of the $[Pt(S\text{-pn-}d_2)_2]^{2+}$ in D_2O (Figure 1) gives one sharp methyl doublet (1.30 ppm) and one broad methine multiplet (3.05 ppm) as expected. Since the methine signal is too complicated to observe the ^{195}Pt–H coupling constant, the nuclear magnetic double-resonance technique was used. Upon irradiation of the sample at 1.30 ppm (the region of the methyl signal), the multiplet became a less complicated signal (see Figure 1(b)) consisting of a 1:4:1 signal, which was considered as one singlet (3.05 ppm) accompanied with ^{195}Pt ($I = {}^1/_2$) satellites (^{195}Pt = 33.8% of naturally occurring platinum), $J_{Pt-N-C-H}$ = 20.0 Hz (Table I).

In the spectrum of the $[Pt(NH_3)_2(pn\text{-}d_1)]^{2+}$ in D_2O, one sharp methyl singlet (1.30 ppm) and a methylene multiplet (2.4–3.5 ppm) were observed. This methylene multiplet can be regarded as an AB pattern which consists of four signals with ^{195}Pt satellites. The coupling constant value between the methylene protons is 12.8 Hz which agrees with the previously reported geminal H–H coupling constant value for the $[Pt(R\text{-pn})_2]^{2+}$.[2] It has been also shown that the upfield two signals and the downfield two signals correspond to the axial and the equatorial methylene protons, respectively. Therefore, the J_{Pt-H} value of the upfield doublet (10.0 Hz) corresponds to the $J_{Pt-N-C-H_{ax}}$ coupling constant. On the other hand, the J_{Pt-H} value (64.0 Hz) observed around the downfield doublet as ^{195}Pt satellites is the ^{195}Pt–N–C–H$_{eq}$ coupling constant. Thus, the

Table I. Carbon and Proton NMR Chemical Shifts[a,b] and Coupling Constants ($^{195}Pt-^{13}C$ and $^{195}Pt-H$)

		^{13}C resonances							H resonances				
		phenyl				diamine ring		methyl	phenyl	diamine ring			methyl
complex	diamine structure	C(1)	C(2)	C(3)	C(4)	CH	CH_2	CH_3	C_6H_5	CH	CH_2 (H_B, H_C)		CH_3
$[Pt(S\text{-pn})_2]^{2+}$						56.33 (n.o.)[c]	53.10 (11.8)[d]	17.44 (36.6)		3.05 (A)[e]	2.8 (B)[e]	2.6 (C)[e]	1.3
$[Pt(S\text{-pn-}d_2)_2]^{2+}$										3.05 (20.0)			1.3
$[Pt(NH_3)_2(\text{pn-}d_1)]^{2+}$											2.8 (64.0)	2.6 (10.0)	1.3
$[Pt(S,S\text{-bn})_2]^{2+}$						59.92 (n.o.)		18.65 (48.8)		2.65 (10.0)			1.4
$[Co(CN)_4(R\text{-phenen})]^-$									7.5	4.0 (A')[f]	3.1 (B')[f]	2.9 (C')[f]	
$[Pt(en)(R\text{-phenen})]^{2+}$		132.70 (39.1)	126.65	126.65	124.36	59.69 (n.o.)	48.04 (14.6)						
$[Pt(en)((-)_D\text{-stien})]^{2+}$		137.04 (46.4)	130.51	130.51	128.99	66.72 (n.o.)			D[g]	E[g] (10.0)		F[g] (38.8)	
$[Pt(en)(ms\text{-stien})]^{2+}$		134.50 (24.4)	130.60	129.72	128.82	66.47 (11.0)			7.3	4.5 (40.0)		2.8 (38.8)	

[a] Carbon-13 shifts in ppm from external Me_4Si. [b] Hydrogen-1 shifts in ppm from DSS (see Experimental Section). [c] n.o. indicates platinum satellites not observed. These observations are explained via a multipath coupling mechanism as is suggested by Erickson et al.[6] [d] Coupling constants (Pt–C and Pt–H) are found in parentheses; in Hz. [e] $J_{A-B} = 10.0$ Hz, $J_{B-C} = 12.3$ Hz, and $J_{A-C} = 4.3$ Hz.[2] [f] $J_{A'-B'} = J_{B'-C'} = 12.5$ Hz and $J_{A'-C'} = 5.0$ Hz, obtained from 100-MHz spectra. [g] The internal reference (DSS) was not contained, because some insoluble precipitates occurred. A relative chemical shift between $D(C_6H_5)$ of $(-)_D$-stien and E(CH) of $(-)_D$-stien is 2.9 ppm. A relative chemical shift between $E(CH_2)$ and $F(CH_2)$ of en is 1.7 ppm.

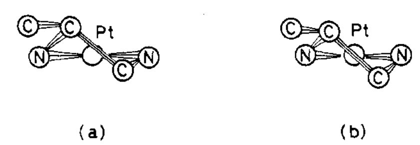


Figure 6. Unsymmetrical (a) and symmetrical (b) conformations of propylenediamine chelate.

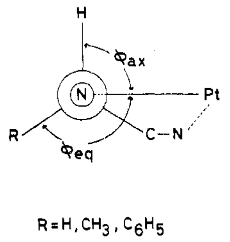


Figure 7. The chelate ring viewed down an N–C bond.

J_{Pt-H} values of 20.0 and 10.0 Hz observed for $[Pt(S\text{-pn-}d_2)_2]^{2+}$ and for $[Pt(NH_3)_2(pn\text{-}d_1)]^{2+}$, respectively, correspond to the coupling constant between the platinum and the axially oriented proton in the propylenediamine chelate ring.

In general, the magnitude of the vicinal coupling constant depends upon an electronic property or a dihedral angle. It has been reported that $[Pt(NH_3)_2(R\text{-pn})]^{2+}$ and $[Pt(R\text{-pn})_2]^{2+}$ showed quite similar electronic absorption results.[13] Therefore, $[Pt(NH_3)_2(pn\text{-}d_1)]^{2+}$ and $[Pt(S\text{-pn-}d_2)]^{2+}$ will have similar electronic properties. Consequently, it can be suggested that the difference in $^3J_{Pt-H}$ value (10.0 Hz) between the $J_{Pt-H_{ax}}$(methine) and the $J_{Pt-H_{ax}}$(methylene) may be corresponding to geometrical factors. There are two possible conformations for the propylenediamine chelate ring (with the equatorial methyl group), which are symmetrical and unsymmetrical with regard to the N–Pt–N plane (Figure 6). Gollogly and Hawkins[14] calculated a conformational energy of metal complexes containing diamine chelate rings. They suggested that the energies of symmetrical and unsymmetrical conformations of propylenediamine are very similar. Some X-ray structural data on propylenediamine chelate rings in metal complexes indicated that the propylenediamine chelate ring always takes an unsymmetrical conformation in the crystalline state.[15] The Newman projections of the chelate ring along the C–N bond and the central C–C bond are shown in Figure 7. The dihedral angle between the planes Pt–N–C and N–C–H (ϕ_{ax}) is in the vicinity of 70° and ϕ_{eq} is in the vicinity of 170° for the unsymmetrical conformation. The values for the methine proton and for the axial methylene proton are about 60° and about 80°, respectively. The dihedral angle between the platinum and the axial proton of a chelate ring of the methine part is equal to that for the methylene part in the symmetrical conformation.

If the dihedral angle dependence of the vicinal coupling constant J_{Pt-H} in Pt–N–C–H fragments would parallel the Karplus equation for the J_{H-H} in H–C–C–H fragments, $J_{Pt-N-C-H}$ should be a maximum for ϕ (dihedral angle) near 0 or 180° and should approach a minimum for ϕ near 90°. Consequently, if the Pt–N–C–H dihedral angle for the methine proton is smaller than that for the axial methylene proton, the J_{Pt-H} value for the methine proton could be smaller than that for the axial methylene proton. This prediction agrees with the experimental result. Therefore, the difference in the J_{Pt-H} values indicates that the propylenediamine chelate in Pt(II) complex has an unsymmetrical conformation in aqueous solution.

The $J_{Pt-N-C-H_{ax}}$ for the propylenediamine chelate ring is estimated at 15.0 Hz which is the average $J_{Pt-N-C-H_{ax}}$ value of $[Pt(S\text{-pn-}d_2)_2]^{2+}$ (20.0 Hz) and $[Pt(NH_3)_2(pn\text{-}d_1)]^{2+}$ (10.0 Hz), and the coupling constant to an equatorial proton which has been observed for $[Pt(NH_3)_2(pn\text{-}d_1)]^{2+}$ is 64.0 Hz. It has been reported that the observed J_{Pt-H} values (38.8-40.0 Hz) for *ms*-bn and 1,1-dimethyl-1,2-ethanediamine in the Pt(II) complexes would be an average of $J_{Pt-N-C-H_{eq}}$ and $J_{Pt-N-C-H_{ax}}$.[6] The average $J_{Pt-N-C-H}$ value for axial and equatorial orientations should be calculated as follows: $^1/_2(J_{Pt-N-C-H_{eq}}$ (64.0 Hz) + $J_{Pt-N-C-H_{ax}}$ (15.0 Hz)) = 39.5 Hz. This calculated value agrees well with the observed values (38.8–40.0 Hz). This result suggests that the $J_{Pt-N-C-H}$ value for the axial proton is about 15.0 Hz and that for the equatorial proton is about 64.0 Hz. This conclusion could be used to determine the preferred conformation of the five-membered diamine chelate ring in the Pt(II) complexes.

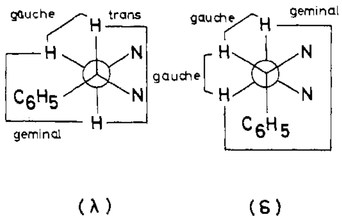


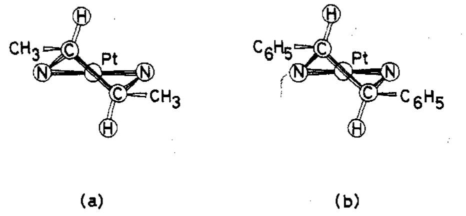
Figure 8. Schematic diagrams of the spin–spin coupling for λ- and δ-gauche conformers of *R*-phenen.

The coupling $J_{Pt-N-C-CH_3}$ of 36.6 Hz in $[Pt(S\text{-pn})_2]^{2+}$ corresponds to the reported value (38 Hz) for pn in $[Pt(bpy)(pn)]^{2+}$ (Table I). These data suggest that the $^3J_{Pt-C}$ value for the equatorial substitutent on the unsymmetrical puckered 1,2-diamine ring is about 36 Hz.

(*R*)-Phenylethylenediamine Complexes. The ^1H NMR spectrum of $[Co(CN)_4(R\text{-phenen})]^+$ in D_2O is shown in Figure 2. One multiplet, which consists of one triplet and one quartet, and one quartet were observed at about 3.0 and 4.0 ppm, respectively. The integrated intensity ratio of two signals is 1 s. This indicates that the signals at the higher region of the multiplet correspond to methylene protons and those at the lower region of the quartet correspond to the methine proton. Since the broad singlet at 7.55 ppm is 5 times as large as the methine quartet, this singlet is assigned to the phenyl signal. Whenever amino group hydrogens are deuterated, methylene and methine protons of *R*-phenen should give an ABC pattern spectrum.

We denote tentatively the lower methine quartet, the higher methylene quartet, and the methylene triplet as A, B, and C, respectively. Their integrated intensities are equal to each other. Consequently, it is clear that B and C are due to protons of the methylene group and A is due to that of the methine group (Figure 2). We could obtain three kinds of H–H coupling constants (Table I).

Two conformers can exist when *R*-phenen coordinates to a metal ion: λ-gauche and δ-gauche forms with the phenyl group equatorial and axial with respect to the chelate ring, respectively (Figure 8). The λ-gauche form can provide three kinds of coupling: a geminal, a trans, and a gauche. On the other hand, the δ-gauche form gives two different kinds of coupling: one geminal and two gauche. Vicinal coupling constants, which are dependent on the dihedral angle between two vicinal C–H bonds,[16] and geminal coupling constants for methane derivatives[17] have been calculated theoretically. These values and the corresponding data for $[Co(CN)_4(R\text{-pn})]^+$ are given in Table I. The coupling constant J_{B-C} (12.5 Hz) is undoubtedly responsible for the geminal coupling, because B and C are the signals of methylene protons. J_{A-C} and J_{A-B} are, therefore, of vicinal couplings. Of these, J_{A-C} (5.0 Hz) is in good agreement with the theoretical and experimental values of the gauche coupling constants. J_{A-B} is 12.5 Hz and agrees well with the reported trans coupling constants. These results indicate that the (*R*)-phenylethylenediamine chelate ring has a λ-gauche form like the



(a) (b)

Figure 9. Chelate conformation of *S*,*S*-bn (a) and *S*,*S*-stien (b). The absolute configuration of the (−)$_D$-stien was assigned to the (*S*,*S*) configuration in our circular dichroism study.[1]

(*R*)-propylenediamine chelate ring.

Figure 3 shows the ^{13}C NMR spectrum of the [Pt(en)(*R*-phenen)]$^{2+}$. Assignment was made considering the factors described earlier. The coupling $J_{\text{Pt-N-C-C}_1}$ of 39.1 Hz is reasonable for an equatorial substitutent on the puckered five-membered ring; 36.6 and 48.8 Hz were observed in the *S*-pn and *S*,*S*-bn chelates. $J_{\text{Pt-N-C}}$ (CH$_2$ of *R*-phenen) (14.6 Hz) resembles the geminal coupling constants for *S*-pn (11.8 Hz). This resemblance supports the conclusion that the two diamine chelates take similar conformations.

(2*S*,3*S*)-2,3-Butanediamine Complex. In the ^{1}H NMR spectrum of the [Pt(*S*,*S*-bn)$_2$]$^{2+}$ in D$_2$O solution one methyl doublet and one broad methine multiplet were observed at 1.40 and 2.65 ppm, respectively. The methine signal of the methyl-decoupled spectrum gave a sharp singlet (2.65 ppm) with ^{195}Pt satellites ($J_{\text{Pt-N-C-H}}$ = 10.0 Hz). This $J_{\text{Pt-N-C-H}}$ value is very similar to that for the axial protons of Pt(II) complexes with deuterated propylenediamines. Therefore, the $J_{\text{Pt-N-C-H}}$ value of the *S*,*S*-bn complex is attributed to that for an axial methine proton. This assignment leads to the conclusion that the *S*,*S*-bn chelate ring has a fixed δ-gauche form with two equatorially situated methyl groups. Since only one methyl signal has been observed in the ^{1}H NMR spectrum, the *S*,*S*-bn chelate should have a symmetrical δ-gauche conformation as shown in Figure 9(a).

The $J_{\text{Pt-N-C-CH}_3}$ value (48.8 Hz) for [Pt(*S*,*S*-bn)$_2$]$^{2+}$ agrees with the reported values of *S*,*S*-bn in the Pt(II) complexes.[6,7] This result also suggests that the $^3J_{\text{Pt-C}}$ value for the equatorial substituent on the symmetrically puckered 1,2-diamine ring is about 50 Hz, in agreement with data for [Pt(bpy)(diamine)]$^{2+}$ complexes.[6]

(−)$_D$-Stilbenediamine Complex. One methylene singlet with ^{195}Pt satellites (38.8 Hz) of ethylenediamine, a methine singlet with ^{195}Pt satellites (10.0 Hz), and a broad phenyl signal of the stilbenediamine have been observed in the ^{1}H NMR spectrum of the [Pt(en)((−)$_D$-stien)]$^{2+}$. The last two signals correspond to the protons of (−)$_D$-stien. The $J_{\text{Pt-H}}$ value for ethylenediamine indicates rapid conformational exchange of this chelate ring. The $J_{\text{Pt-H}}$ value for the methine proton of the (−)$_D$-stien is very similar to that for the axially oriented protons of propylenediamine and (2*S*,3*S*)-2,3-butanediamine complexes. Therefore, this datum indicates that the (−)$_D$-stein chelate ring has a gauche form with two equatorial phenyl groups in D$_2$O solution. The observation of only one methine signal in the ^{1}H NMR spectrum suggests that two methine protons and two phenyl groups are chemically equivalent. These results indicate the symmetrical conformation of the (−)$_D$-stien chelate ring as shown in Figure 9(b).

Figure 4 shows the ^{13}C NMR spectrum of [Pt(en)((−)$_D$-stien)]$^{2+}$. Assignment was made considering the factors described earlier. The coupling constant $J_{\text{Pt-N-C-C}_1}$(phenyl) of 46.3 Hz agrees with that for the equatorially orientated methyl carbons of the *S*,*S*-bn complexes (Table I). This agreement indicates that two diamine chelates have a similar conformation.

***meso*-Stilbenediamine Complex.** The ^{1}H NMR spectrum of [Pt(en)(*ms*-stien)]$^{2+}$ gives two sharp singlets due to the methine part of *ms*-stien and the methylene part of en. Both signals have "satellites" due to coupling with ^{195}Pt. Since the $J_{\text{Pt-H}}$ value for ethylenediamine (38.8 Hz) indicates rapid conformational interconversion of this chelate ring, that for *ms*-stien (40.0 Hz) corresponds to rapid conformational exchange of this chelate ring on the NMR time scale.

The C(1) resonance of the phenyl ring in the proton-decoupled ^{13}C NMR spectrum has well-resolved satellite peaks due to coupling with ^{195}Pt (Figure 5). This $^3J_{\text{Pt-C}}$ value (24.0 Hz) resembles that for the *ms*-bn (27.3 Hz) and 1,1-dimethyl-1,2-ethanediamine (24.3 Hz) chelates. It has been concluded[8] that the conformational inversion of both chelate rings is rapid on the NMR time scale. Consequently, this result suggests the rapid conformational inversion of the *ms*-stien chelate ring in this complex. It is interesting that the energy barrier of conformational interconversion between λ- and δ-gauche forms may be small even when bulky phenyl groups are attached to the chelate.

The observed $^3J_{\text{Pt-C}}$ values for this complex will be an average of $^3J_{\text{Pt-C}_{\text{eq}}}$ and $^3J_{\text{Pt-C}_{\text{ax}}}$. Since the $^3J_{\text{Pt-C}_{\text{eq}}}$ value was obtained for the (−)$_D$-stien chelate in [Pr(en)((−)$_D$-stien)]$^{2+}$, $^3J_{\text{Pt-C}_{\text{ax}}}$ should be calculated as follows: $^1/_2(^3J_{\text{Pt-C}_{\text{eq}}}$ (46.0 Hz) + $^3J_{\text{Pt-C}_{\text{ax}}}$ (? Hz)) ≈ $^3J_{\text{Pt-C}_{\text{av}}}$ (24.0 Hz). This calculated $^3J_{\text{Pt-C}_{\text{ax}}}$ value (∼0) agrees well with reported values (∼0), which are derived from the diamines with *C*-methyl groups in the Pt(II) complexes.[6,7]

Coupling of Platinum to the Membered Carbon Atoms. Coupling between ^{195}Pt and the carbon nuclei forming the five-membered ring is much smaller than coupling to C–CH$_3$ or C–C$_6$H$_5$ carbons (Table I). This coupling (denoted $^{2,3}J_{\text{Pt-C}}$) may be the sum of coupling via two-bond and three-bond paths. In δ-bond networks ^2J and ^3J are expected to possess opposite signs.[18] Therefore, coupling of platinum-195 to the ring ^{13}C nuclei proceeds by two oppositely signed paths diminishing the observed value of this interaction ($^{2,3}J_{\text{Pt-C}}$) by cancelation effects. Thus, the observations of quite small coupling constant values of $^{2,3}J_{\text{Pt-C}}$ for the present Pt(II) complexes are explained via a multipath coupling mechanism as suggested by Erickson et al.[6]

Conclusions. The $^3J_{\text{Pt-C}}$ values of unsymmetrical diamine chelates (39.1 Hz for *R*-phenen and 36.6 Hz for *S*-pn) are smaller than those for symmetrical diamine chelates (46.0 Hz for (−)$_D$-stien and 48.8 Hz for *S*,*S*-bn). If $^3J_{\text{Pt-C}}$ follows a Karplus-type angular dependence, $^3J_{\text{Pt-C}}$ should be a maximum for ϕ (dihedral angle between the planes Pt–N–C and N–C–C) near 0 or 180° and should approach a minimum for ϕ near 90° as is suggested by Bagger.[7]

As expected from the X-ray structural analysis of the pn complexes,[15] if *S*-pn and *R*-phenen chelate rings take on similar unsymmetrical conformations, the dihedral angle between the planes Pt–N–C and N–C–C$_{\text{eq}}$ is in the vicinity of 170°. For the symmetrical conformation, the dihedral angle is about 180°. Consequently, the $^3J_{\text{Pt-C}}$ values for the unsymmetrical diamines must be smaller than those for the symmetrical diamines. This prediction agrees with the experimental results. Therefore, it is possible that the observed differences in $^3J_{\text{Pt-C}}$ and $^3J_{\text{Pt-H}}$ (which were mentioned in our earlier arguments for *S*-pn-d_2 and pn-d_1 chelate rings) may reflect differences in the degree of puckering of the ring at the conformational energy minimum rather than significant differences in relative amounts of the λ and δ conformers. Our results seem quite reasonable considering the conformational analysis of the five-membered diamine chelate rings by Gollogly and Hawkins[14] and the X-ray structural analysis of the pn complexes.[15]

It is interesting that the $^3J_{\text{Pt-C}}$ values for the aromatic carbon nuclei of the phenyl ring are similar to those of the aliphatic carbon nuclei of the methyl group. Thus such coupling can be used to indicate the conformational preference of phenyl groups as well as methyl groups on diamine chelates. For the complexes reported here, conformational influences of phenyl groups and methyl groups are quite smaller.

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Registry No. α-Deuterio-(R,S)-alanine, 31024-91-6; pn-d_1, 67031-29-2; S-pn-d_2, 67031-30-5; K[Co(CN)$_4$(R-phenen)], 67031-32-7; [Pt(S-pn-d_2)$_2$]Cl$_2$, 67031-33-8; [Pt(S-pn)$_2$]Cl$_2$, 17830-46-5; [Pt(S,S-bn)$_2$]Cl$_2$, 67031-34-9; [Pt(NH$_3$)$_2$(pn-d_1)]Cl$_2$, 67031-35-0; [Pt(en)((−)$_D$-stien)]Cl$_2$, 67144-40-5; [Pt(en)(ms-stien)]Cl$_2$, 67031-36-1; [Pt(en)(R-phenen)]Cl$_2$, 67031-37-2.

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Electronic and Resonance Raman Spectra of One-Dimensional Mixed-Valence Platinum–Ethylamine Complexes at Ca. 80 K

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The resonance Raman spectra of the mixed-valence complexes [Pt(etn)$_4$][Pt(etn)$_4$X$_2$]X$_4$·4H$_2$O, where X = Cl or Br, and [Pt(etn)$_4$][Pt(etn)$_4$X$_2$]X$_4$, where X = Br or I and etn = ethylamine, have been recorded at ca. 80 K. The spectra are characterized by the appearance of intense progressions $v_1\nu_1$ and $\nu_n + v_1\nu_1$, where ν_1 is the symmetric X–Pt^{IV}–X stretching mode. The $v_1\nu_1$ progression reaches at most to $v_1 = 16$, while the subsidiary progressions are rather shorter and less intense; these data permit various spectroscopic constants to be calculated. The nature of the observed progressions is discussed in terms of distortions of the structures of the complexes in the excited state, the principal geometric change being an increase in the platinum(IV)–halogen bond length. The relation between the maxima of the excitation profiles of the ν_1 band and those of the resonant mixed-valence bands is also outlined.

Introduction

A vast amount of research has been and is being carried out on a wide range of materials which have anisotropic physical properties, such as organic and inorganic one-dimensional materials.[1] Of the many techniques which have been applied to the study of such compounds, resonance Raman (RR) spectroscopy has, so far, played only a small but nevertheless useful part.[2] In this paper we intend to show how RR spectroscopy can be used as an indicator of geometrical changes in such a system, caused by a transition from the ground to an excited electronic state. The compounds which we have investigated are mixed-valence compounds of platinum which contain four-coordinate platinum(II) and six-coordinate platinum(IV) units arranged alternately in chains (Figure 1A). The platinum(IV) complex contains two trans halogen atoms oriented along the chain axis, and the remaining coordination sites are occupied by ethylamine molecules. The platinum(II) complex contains four coordinated ethylamine molecules, and the occupied d$_{z^2}$ orbital of the platinum atom is also directed along the chain axis. The relative positions of the highest filled and lowest unfilled orbitals are depicted in Figure 2. From the diagram it can be seen that the lowest axially polarized mixed-valence transition involves the transfer of an electron from the filled 5d$_{z^2}$ orbital of the Pt(II) complex to the empty 5d$_{z^2}$ orbital of the Pt(IV) complex. Day has reported[3] the 4 K single-crystal electronic absorption spectrum of Wolffram's red salt (WR), [Pt(etn)$_4$][Pt(etn)$_4$Cl$_2$]Cl$_4$·4H$_2$O (etn = ethylamine), which apparently has axially polarized mixed-valence transitions in the 17 500–21 000-cm^{-1} region. The room temperature RR spectrum of this complex consists[4] of a progression in the ν(Cl–Pt^{IV}–Cl) axial breathing mode (ν_1) which reaches 9ν_1. A rather similar behavior has been observed[5] for Reihlen's green (RG), which is the bromo analogue of WR. Recent technical advances have enabled us now to record RR spectra of complexes at ca. 80 K with an oscillating laser beam to avoid the deleterious effects of thermal heating of the sample. Spectra so obtained on WR and RG are much more detailed and spectacular than those obtained at room temperature, and they open the way to presenting a discussion of the observed progressions in terms of distortions of the structure of the complexes in the excited state. Related results are also presented on the anhydrous form of Reihlen's green, (ARG) and on the anhydrous iodide recently reported by Textor and Stieger[6] (TSI), viz., [Pt(etn)$_4$][Pt(etn)$_4$X$_2$]X$_4$, X = Br or I.

Experimental Section

Preparation of Complexes. WR was prepared by an improvement to the method of Reihlen and Flohr.[7] A solution containing 1 g of

0020-1669/78/1317-2526$01.00/0