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CIRCULAR DICHROISM AND ^{13}C-NMR SPECTRA OF SIX MEMBERED PLATINUM(II) CHELATES CONTAINING OPTICALLY ACTIVE DIAMINES

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The conformations of $[Pt(NH_3)_2(R,R\text{-dppn})]Cl_2$ and $[Pt(NH_3)_2(R,S\text{-dppn})]Cl_2$ (dppn=1,3-diphenyl-1,3-propanediamine) were decided to be chair forms on their ^{13}C-NMR spectra. The additive law did not hold among the absolute CD strength of six membered Pt(II) chelates containing (*S*)-1,3-butanediamine, (*S*,*S*)-2,4-pentanediamine and *R*,*R*-dppn. In evaluating their absolute CD strength, the vicinal effect of methyl and phenyl groups should be taken into consideration, especially the latter group showed abnormally large increment.

In previous papers we reported different antitumor activities among geometrical and optical isomers of the diamines, being used as ligands to form five or six membered chelate rings upon coordination with Pt(II) ion.[1-3] We presumed that there might be a some correlations between the structures of those Pt(II) complexes and their antitumor activities. In this paper we describe the structures of a series of Pt(II) complexes with diamines which form six membered chelate rings.

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 boat, or boat forms. Among them a chair conformation has been considered to be the most stable form and ^{1}H-NMR and ^{13}C-NMR spectral evidences supporting this view have been reported by Hall[4] and Yano, et al.[5]

Since few circular dichroism spectral studies of Pt(II) complexes containing optically active diamines forming six membered chelate rings upon coordination have been done, we synthesized Pt(II) complexes of (*S*)-1,3-butanediamine (=*S*-bn), (*S*,*S*)-2,4-pentanediamine (=*S*,*S*-ptn) and (*R*,*R*)-1,3-diphenyl-1,3-propanediamine (=*R*,*R*-dppn) and measured their CD spectra in H_2O. In order to clarify conformations of the Pt(II) complexes, ^{13}C-NMR spectra in D_2O were measured for $[Pt(NH_3)_2(R,R\text{-dppn})]Cl_2$ and $[Pt(NH_3)_2(R,S\text{-dppn})]Cl_2$ expecting that the bulky phenyl groups would restrict possible conformations for a six membered chelate ring.

Preparations of *S*-bn, *S*,*S*-ptn, *R*,*R*-dppn, and their Pt(II) complexes were made according to the method describe in literatures.[6-8] Elemental analyses of the Pt(II) complexes obtained are shown in Table I.

The values of $^3J_{Pt-C(1)}$, coupling constant between ^{195}Pt and phenyl C(1) which attaches on the carbon atoms of ethylenediamine moiety, depend upon the dihedral angle between Pt-N-C and N-C-C(1) in Pt(II) complexes containing stilbenediamine (=stien) and this relationship has been well established.[9,10] For examples, in $[Pt(en)((-)_D$-

Table I. Analytical data of the complexes

Complexes	C % Found	C % Calcd	H % Found	H % Calcd	N % Found	N % Calcd
$[Pt(en)(S\text{-bn})]Cl_2$	17.75	17.39	4.89	4.88	13.52	13.53
$[Pt(en)(S,S\text{-ptn})]Cl_2$	19.93	19.63	5.18	5.19	13.08	13.08
$[Pt(NH_3)_2(R,R\text{-dppn})]Cl_2$	34.42	34.22	4.79	4.60	10.13	10.65
$[Pt(NH_3)_2(R,S\text{-dppn})]Cl_2\cdot 1/2H_2O$	33.45	33.65	4.65	4.72	10.08	10.47
$[Pt(en)(R,R\text{-dppn})]Cl_2\cdot 3/2H_2O$	34.97	35.23	4.92	5.05	9.91	9.67

stien)]Cl_2 took phenyl groups diequatorial orientation and the value of $^3J_{Pt-C(1)}$ was reported to be 46.4 Hz, while their axial-equatorial orientation in [Pt(en)(meso-stien)]Cl_2 gave 24.4 Hz of $^3J_{Pt-C(1)}$ value.

Since the ligand dppn has two bulky phenyl groups, their conformational preference in the Pt(II) complexes would be expected. Therefore, ^{13}C-NMR spectra of $[Pt(NH_3)_2($*R*,*S*-dppn)]Cl_2 and $[Pt(NH_3)_2($*R*,*R*-dppn)]Cl_2 in D_2O were measured and the data obtained are presented in Table II. In the former complex, a chair conformation of the six membered chelate ring has two equatorially oriented phenyl groups, while a δ-skew boat form is accompanied by their axial-equatorial orientation. Between these conformations the chair one would be stable form. This prediction can be justified by the coupling constant found between ^{195}Pt and C(1) of the phenyl groups, $^3J_{Pt-C(1)}$, of 42.4 Hz. The value also corresponds to those of the Pt(II) complexes reported to take diequatorial orientation of methyl or phenyl groups in their five membered chelate rings.

On the other hand, chair and δ-skew boat conformations of $[Pt(NH_3)_2($*R*,*R*-dppn)]Cl_2 take axial-equatorial and diequatorial orientations, respectively, and the problem is which effect, a chair form of the chelate ring or diequatorial orientation of the bulky phenyl groups, would be preferencial in stabilizing the conformation. The values of $^3J_{Pt-C(1)}$ observed for the *R*,*R*-dppn complex was 25.6 Hz corresponding to those reported for axial-equatorial orientations found in [Pt(bipy)(meso-bn)]$^{2+}$ and [Pt(bipy)(C,C-Me_2-en)]$^{2+}$ (C,C-Me_2-en=1,1-dimethyl-1,2-ethanediamine), indicating rapid conformational puckering of the chelate ring. The puckering of the chelate ring in $[Pt(NH_3)_2($*R*,*R*-dppn)]Cl_2 seems to take place nearly to the same extend as those of meso-bn, C,C-Me_2-en Pt(II) complexes, although the former complex contains bulky phenyl groups. For the Pt(II) complexes containing *S*-bn and *R*,*R*-ptn, chair conformations have

Table II. Carbon-13 NMR chemical shifts[a] and coupling constants (^{195}Pt-^{13}C) in D_2O

Complexes	phenyl C(1)	phenyl C(2)	phenyl C(3)	phenyl C(4)	diamine ring CH	diamine ring CH_2
$[Pt(NH_3)_2(R,S\text{-dppn})]Cl_2$	141.43 (42.7)	126.59	129.70	129.12	59.77 (22.0)	42.07 (NO)[b]
$[Pt(NH_3)_2(R,R\text{-dppn})]Cl_2$	140.11 (25.6)	127.03	129.70	129.07	53.79 (22.0)	41.29 (22.0)

[a] Carbon-13 shifts in ppm from external Me_4Si. [b] NO indicates no platinum satellites observed.

been proposed by Yano, et al. based upon their $^{3}J_{Pt-C}$ coupling constants.

Fig. 1 shows typical CD spectra of the six membered chelates of diammine type of Pt(II) complexes containing optically active diamines together with their absorption spectra. The absorption bands of the *S*-bn and *S,S*-ptn Pt(II) complexes can be classified into bands II, III, IV and charge transfer according to Fujita's assignments.[11)]

Pt(II) complexes take square planar structures and when they contain optically active diamine ligands, there should appear CD bands due to the d-d* transitions. If their absolute CD strength is attributable to two factors, i.e. 1) conformational effect of chelate rings and 2) vicinal effect of asymmetric carbon atoms, CD strength of six membered chelates would be determined by the number of asymmetric carbon atoms. Because for six membered chelates the most stable form is a chair form, being deduced from ^{13}C-NMR spectra, which is optically inactive and the conformational effect can be excluded.

In Table III are presented the CD and AB spectral data and as can be seen the value of Δε at 35.6 kK for $[Pt(NH_3)_2(S\text{-bn})]Cl_2$ was -0.035 and that of $[Pt(NH_3)_2(S,S\text{-ptn})]Cl_2$ was -0.096 (at 35.1 kK). There does not exist additivity between the two values, although they have either one or two asymmetrical carbon atoms. Moreover, a large discrepancy from the law could be found in Δε value, -0.294 (at 34.5 kK), of $[Pt(NH_3)_2(R,R\text{-dppn})]Cl_2$ which was nearly three times as large as that of $[Pt(NH_3)_2(S,S\text{-ptn})]Cl_2$.

In ethylenediamine type complexes, the values of Δε at 35.7,

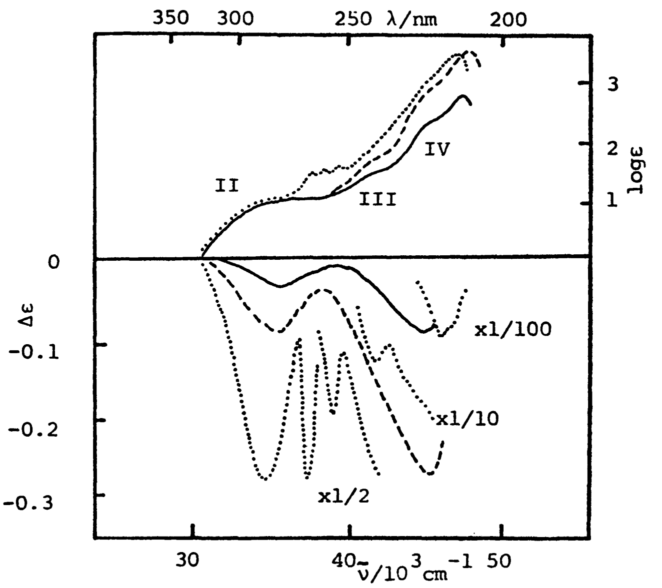

Fig. 1 Absorption and CD spectra of $[Pt(NH_3)_2(L)]Cl_2$ in H_2O, L=(*S*)-bn (——), (*S,S*)-ptn (---), and (*R,R*)-dppn (·······).

Table III. Absorption and CD spectral data in H_2O

Complexes	AB ν̃/max(logε)	CD ν̃/max(Δε)
$[Pt(NH_3)_2(S\text{-bn})]Cl_2$	35.7(1.22)	35.6(-0.035)
	41.7 sh	
	44.4(2.09)	45.0(-0.096)
	47.2(2.57)	
$[Pt(en)(S\text{-bn})]Cl_2$	35.7(1.30)	35.7(-0.017)
	41.7 sh	
	44.2(2.28)	44.6(-0.129)
	47.1(2.71)	
$[Pt(NH_3)_2(S,S\text{-ptn})]Cl_2$	35.1(1.21)	35.1(-0.096)
	41.7 sh	
	44.8(2.62)	44.8(-0.284)
	47.8(3.24)	
$[Pt(en)(S,S\text{-ptn})]Cl_2$	35.7(0.84)	34.1(-0.066)
	41.7 sh	
	44.8(1.80)	44.4(-0.618)
	47.6(2.32)	
$[Pt(NH_3)_2(R,R\text{-dppn})]Cl_2$	34.5 sh	34.5(-0.294)
	37.6 sh	37.6(-0.294)
	38.0(1.71)	
	38.9(1.80)	38.5(-0.398)
	40.0(1.66)	
	40.8 sh	
	41.7 sh	42.6(-1.533)
	47.6(3.17)	46.2(-11.820)
$[Pt(en)(R,R\text{-dppn})]Cl_2$	34.5 sh	34.5(-0.265)
	37.6 sh	37.5(-0.260)
	38.0(1.60)	
	38.9(1.70)	38.5(-0.302)
	40.0(1.70)	
	40.8 sh	
	41.7 sh	43.3(-2.085)
	47.6(3.16)	46.1(-10.354)

34.1, and 34.5 kK were −0.017, −0.066, and −0.265 for [Pt(en)(*S*-bn)]Cl_2, [Pt(en)(*S,S*-ptn)]Cl_2, and [Pt(en)(*R,R*-dppn)]Cl_2, respectively, and also there does not exist additivity among these values. Their absolute $\Delta\varepsilon$ values were smaller than those of the corresponding diammine type complexes and this might be attributable to the difference in the counter ligands of NH_3 and en.

From our data we found that the absolute CD strength of six membered Pt(II) chelates examined were influenced by 1) the vicinal effects of methyl or phenyl groups in addition to that of asymmetric carbon atoms, and furthermore 2) the counter ligands on Pt(II), i.e. NH_3 and en. More detailed discussion will be made in a following paper.

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