# A Relationship between the Circular Dichroism and the Configuration of Asymmetric Nitrogen in *trans*(*N*,Ethylene)-chloro-L-aminocarboxylato-$\eta^2$-ethyleneplatinum(II)

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The circular dichroism (CD) peaks of *trans*(*N*, ethylene)[PtCl(L-am)($C_2H_4$)] (L-am, L-amino carboxylate) in acetonitrile (AN) at 33000 and 37000 cm$^{-1}$ are characteristic of those complexes with asymmetric nitrogen. The CD sign depends on the substituents on the asymmetric nitrogen, and the additivity law holds for methyl and benzyl derivatives of L-prolinato, L-hydroxyprolinato, and L-valinato complexes. The quadrant rule is applicable to the contribution of the substituents on the nitrogen. On the preparation of the benzyl-L-valinato complex from Zeise's salt in a weakly acid medium the nitrogen exhibits a marked stereoselectivity to give *R* configuration.

Optical rotatory dispersion (ORD) and circular dichroism (CD) of asymmetric nitrogen on *N*-alkyl-L-amino carboxylate ligand have been mostly studied with cobalt(III) complexes. The absolute configuration of asymmetric nitrogen of $(+)_{589}$-[Co(sar)(en)$_2$]$^{2+}$ (sar, sarcosinate; en, ethylenediamine) was determined by X-ray diffraction to be *R*.[1] This complex gives a plus CD peak in 20000 to 25000 cm$^{-1}$ region (first d-d transition band region), which was assigned to the asymmetric nitrogen.[2,3] Crystal structure[4] and CD spectra of copper(II) complexes containing asymmetric nitrogen[5,6] were studied but their relationship has not been discussed.

We have extended CD studies of square planar platinum(II) complexes containing amino carboxylates and $\eta^2$-olefins,[7] and synthesized various complexes of the type *trans*(*N*, ethylene)[PtCl(L-am)($C_2H_4$)], where L-am stands for amino carboxylates having asymmetric nitrogens. This paper deals with the syntheses and the relationship between CD spectra and absolute configurations of the coordinated asymmetric nitrogens.

## Experimental

*Materials. Ligands*: L-Allohydroxyproline (2*S*, 4*S*) (L-ahyp) was prepared from L-hydroxyproline (L-hyp) by the known method.[8,9] *N*-Methyl- and *N*-benzyl derivatives of L-proline (L-pro), L-hydroxyproline, L-valine (L-val), L-phenylalanine (L-phe), and L-alanine (L-ala) were synthesized by known methods.[10,11] Guaranteed grade L-proline, L-hydroxyproline, L-valine, L-phenylalanine, and L-alanine were used without further purification. (The abbreviations in parentheses indicate their deprotonated forms.)

*Complexes.* *trans*(*N*,Ethylene)-isomers of various [PtCl(L-am)($C_2H_4$)] and *cis*(*N*,ethylene)[PtCl(L-pro)($C_2H_4$)] were prepared by the reported methods.[7,12] New *trans*(*N*,ethylene) complexes containing L-hyp, L-ahyp, *N*-me-L-hyp, and *N*-bz-L-val were identified by elemental analysis of carbon, hydrogen, and nitrogen, and ultraviolet (UV) absorption spectra.

*Measurements.* The UV absorption and CD spectra were recorded in acetonitrile (AN) at room temperature with a Hitachi 323 and a JASCO J-40 Spectrophotometer, respectively.

## Results and Discussion

*CD Pattern.* The UV absorption pattern of all the *trans*(*N*, ethylene) complexes is similar to one another and exemplified in Fig. 1A by *trans*(*N*, ethylene)-[PtCl(L-pro)($C_2H_4$)]. The CD spectra of *trans*(*N*, ethylene) complexes containing L-pro, L-hyp, and L-

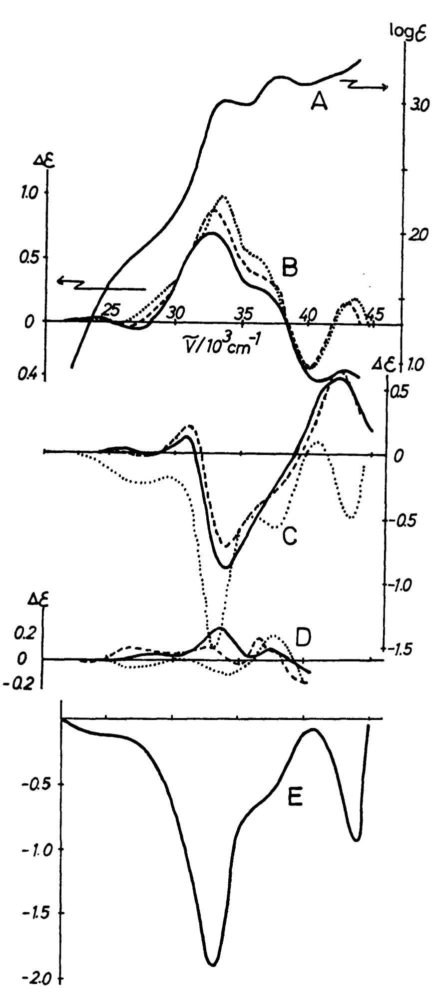

Fig. 1. Ultraviolet absorption and circular dichroism (CD) spectra of *trans*(*N*,ethylene)[PtCl(L-am)($C_2H_4$)] in acetonitrile at room temperature. (L-am=L-amino carboxylate).
A: UV absorption of L-prolinato complex.
B: CD of — L-pro, --- L-hyp, and- -- L-ahyp complex.
C: CD of — *N*-me-L-pro, --- *N*-me-L-hyp, and --- *N*-bz-L-pro complex.
D: CD of — L-ala, --- L-phe, and --- L-val complex.
E: CD of *N*-bz-L-val complex.

ahyp have large plus components with $\Delta\varepsilon$ 0.7 to 1.0 in the 33000 $cm^{-1}$ region. (Fig. 1B). In the same region, similar complexes containing substituted L-prolinate, *i.e* *N*-me-L-pro, *N*-me-L-hyp, and *N*-bz-L-pro, have large minus CD peaks with $\Delta\varepsilon$'s $-1$ to $-2$. (Fig. 1C). All these complexes have a fixed configuration of the coordinated asymmetric nitrogen. On the other hand, complexes without asymmetric nitrogen, *i.e.* L-ala, L-val, and L-phe complexes fail to show large CD peaks in this region. (Fig. 1D). Hence the characteristics of CD peaks in 33000 $cm^{-1}$ region must depend on the configuration around coordinated asymmetric nitrogen.

These complexes have other absorption peaks in the regions *ca.* 25000, 37000, and 45000 $cm^{-1}$, and CD peaks are observable in these regions. However, the CD peaks corresponding to the first and the last absorption peak are irregular, and do not seem to be directly related to the coordinated asymmetric nitrogen. The CD peaks in the 37000 $cm^{-1}$ region of the complexes with asymmetric nitrogens are large, and have the same sign as those in the 33000 $cm^{-1}$ region. Hence we consider that these peaks are also related to the asymmetric nitrogen (*vide infra*).

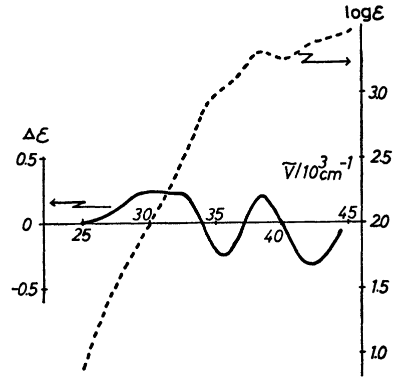

Fig. 2. UV absorption and CD spectra of *cis*(*N*,ethylene)-[PtCl(L-pro)($C_2H_4$)] in acetonitrile.

The *cis*(*N*, ethylene) complex gives an absorption peak at *ca.* 38000 $cm^{-1}$ and three shoulders at 28000, 35000, and 42000 $cm^{-1}$. CD peaks are observed in these regions corresponding to the absorption peak and shoulders. (Fig. 2). The absorption pattern is similar to that of the trans isomer. The CD peaks, however, are not very large and the signs are not equal to those of the *trans*(*N*, ethylene) complexes. Hence no further discussion will be made with the *cis* complex.

*Stereoselectivity.* The nitrogen of *N*-benzyl-L-valinate can coordinate to a metal ion in either *R* or *S* configuration, and its complex *trans*(*N*, ethylene)[PtCl-(*N*-bz-L-val)($C_2H_4$)] can exist as a pair of diastereoisomers, *S*(N)*S*(C) and *R*(N)*S*(C). Its CD spectrum is very similar both in location and intensity to that of the *N*-bz-L-pro complex, which can be only in *R*(*N*)*S*(C) configuration. It appears as if the *R*(N)*S*(C) diastereoisomer was obtained almost exclusively, when *N*-benzyl-L-valinate underwent substitution reaction with Zeise's salt in a very wealky acid aqueous solution of pH 5—6.[7] Saburi and Yoshikawa found that *N*-methyl-L-alaninate coordinates to cobalt(III) in a basic solution stereospecifically in *R* form, to give [Co(*R*(N)-*N*-me-L-ala)$(NH_3)_4]^{2+}$.[13]

The common preference of *R* configuration around coordinated nitrogen in these complexes may be understood by a molecular model study; *S*-configuration around coordinated nitrogen gives *N*-substituents in *cis* position to the substituents on the asymmetric α-carbon in *S* configuration, to result in large steric hindrance between the substitutents on *S*-nitrogen and *S*-carbon. Thus the *R*(N)*S*(C) configuration should be prefered regardless of the other moieties of the complex.

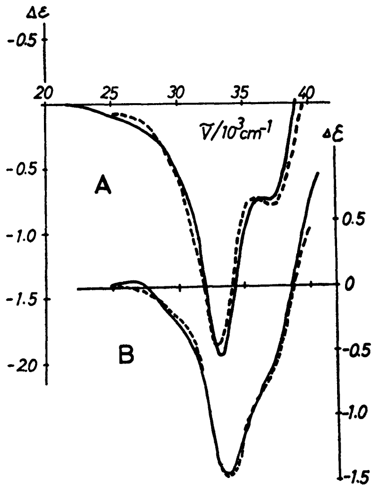

Fig. 3. Difference in CD between two complexes of the type *trans*(*N*,ethylene)[PtCl(L-am)($C_2H_4$)] in AN.
A: $\delta\Delta\varepsilon$, — between *N*-bz-L-pro and L-pro, and --- between *N*-bz-L-val and L-val.
B: $\delta\Delta\varepsilon$, — between *N*-me-L-pro and L-pro, and --- between *N*-me-L-hyp and L-hyp.

*Additivity of CD.* Figure 1B and 1C indicate that the curves in 33000 and 37000 $cm^{-1}$ regions show CD' of reverse signs. In Fig. 3A the differences of CD's between the *N*-benzyl-L-prolinato and L-prolinato, and between *N*-benzyl-L-valinato and L-valinato complexes are plotted against the wave number. Both $\delta\Delta\varepsilon$ curves are very similar to each other. In Fig. 3B similar plots of $\delta\Delta\varepsilon$'s between *N*-methyl-L-hydroxyprolinato and L-hydroxyprolinato, and between *N*-methyl-L-prolinato and L-prolinato complexes are shown. Again both curves are similar to each other. These curves should reflect the contribution of *N*-benzyl and *N*-methyl group upon the asymmetric nitrogen, the $\delta\Delta\varepsilon$ being $-1.9$ and $-1.5$, respectively. Hence additivity law should hold between the contribution of *N*-substituent and the L-prolinato moiety. The contribution of the former should be independent of the amino carboxylate framework.

*Application of Quadrant Rule.* Scott and Wrixon found an empirical rule between the absolute configuration of asymmetrically coordinated prochiral $\eta^2$-olefins and the CD sign of their platinum(II) complexes in 25000 $cm^{-1}$ region, and interpreted the results on the basis of quadrant rule.[14] We have applied this rule to the interpretation of the CD spectra coming from asymmetric nitrogen. A projection of *trans*(*N*, ethylene)-

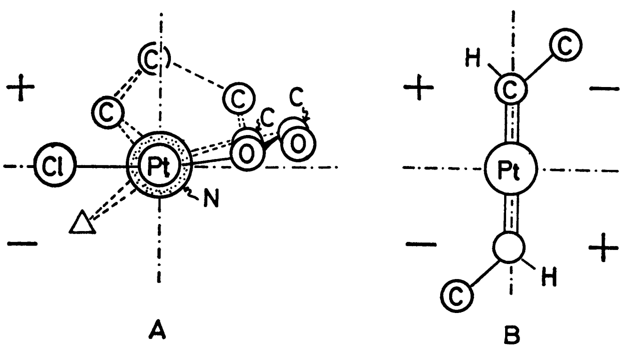

Fig. 4. Projection of the square planar complexes.
A: *N*-substituted-L-am moiety, the Pt–N bond is perpendicular to the paper and N is beneath Pt.
B: *trans*-2-butene moiety, the C–C axis is across the square plane of the Pt(II) complex behind the paper, and Pt-olefin bond is perpendicular to the paper.

[PtCl(*N*-alkyl-L-pro)($C_2H_4$)] is shown in Fig. 4A. The square plane of the complex is represented by the horizontal line, and the Pt–N bond is perpendicular to the paper plane. The asymmetric nitrogen is beneath the platinum(II) and shown by a large dotted circle. When the quadrant rule is to be applied on the basis of this projection, the contribution of the minus quadrant at below left side behind the paper should depend on the size of the moiety, shown by a triangle on Fig. 4A. The larger the size of this substituent (benzyl, methyl, or hydrogen), the greater the contribution of the minus component. The substitution of benzyl or methyl for the hydrogen on the asymmetric nitrogen gives a large minus contribution. The apparently reverse CD sign in these regions in Fig. 1B and 1C and the additivity law are thus accounted for.

The UV absorption of all the present complexes shows peaks with log $\varepsilon$ *ca.* 3 from 31000 to 45000 $\text{cm}^{-1}$ region. Denning, Hartley, and Venanzi assigned the absorption bands of Zeise's salt in these regions to that d-$\pi^*$ (ethylene) transition.[15] We have observed CD peaks at *ca.* 35000 and 39500 $\text{cm}^{-1}$ with $\Delta\varepsilon$'s $-1.3$ and $+3.3$, respectively, for the tetraphenylphosphonium salt of $[\text{PtCl}_3(^2S,^3S\text{-}trans\text{-}2\text{-butene})]^-$ in AN.[16] The absorption peak at 35000 $\text{cm}^{-1}$ must correspond to the same transition to which the main CD of Fig. 3 owes.[17] In Fig. 4B a similar projection of this Zeise-type complex is shown, the C–C moiety being placed across the square plane of platinum(II) behind the paper surface. Application of the quadrant rule discloses that the contribution of the same minus regions behind the paper predominates for the Zeise- type complex, as it does to the present complexes with asymmetric nitrogens. It is thus suggested that the d-$\pi^*$(ethylene) transition is perturbed by the asymmetric nitrogen trans to the ethylene, so that a remarkable CD appears in this region.

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