

## Preparation of Optically Active N-alkyl-substituted (S)-1,2-propanediamines and CD Studies of their Palladium(II) Complexes

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Some new N-alkyl-substituted derivatives of (S)-1,2-propanediamines were synthesized; they are N<sup>1</sup>, N<sup>1</sup>-dimethyl-, N<sup>1</sup>, N<sup>1</sup>-diethyl-, N<sup>2</sup>, N<sup>2</sup>-dimethyl- and N<sup>1</sup>-methyl-N<sup>1</sup>-ethyl-(S)-1,2-propanediamine. The chelates of these diamines with general formulae, [PdCl<sub>2</sub>(AA')] and [Pd(AA')<sub>2</sub>]<sup>2+</sup>, were prepared and their CD spectra were measured. It was found that for [PdCl<sub>2</sub>(AA')], the replacement of two hydrogens on N<sup>1</sup>- or N<sup>2</sup>-atom of S-pn by alkyl groups causes a marked change in the CD; [PdCl<sub>2</sub>(N<sup>1</sup>-Me<sub>2</sub>(S)-pn)], [PdCl<sub>2</sub>(N<sub>2</sub>-Me<sub>2</sub>(S)-pn)] and [PdCl<sub>2</sub>(N<sup>1</sup>-Me, Et-(S)-pn)] exhibit (-,+) sign pattern in the d-d region, which is the reversed sign pattern of [PdCl<sub>2</sub>(S-pn)]. In contrast to the case of [PdCl<sub>2</sub>(AA')], the CD spectra of [Pd(AA')<sub>2</sub>]<sup>2+</sup> complexes resemble that of [Pd(S-pn)<sub>2</sub>]<sup>2+</sup>.

### Introduction

In a previous paper [1] we reported that [PdCl<sub>2</sub>((R)tmpn)] exhibits a plus-minus pattern (from the lower energy side) in the d-d circular dichroism (CD), the pattern of which resembles the inverted pattern of [PdCl<sub>2</sub>(R-pn)] (for the abbreviation of the ligands see Table I); the replacement of all amino hydrogens of R-pn by methyl groups causes the inversion of the CD sign pattern. Since the (R)-tmpn chelate ring should take λ conformation like the R-pn chelate ring from the examination of a stereomodel, the inversion of the CD sign pattern of [PdCl<sub>2</sub>((R)-tmpn)] should be ascribed to the influence of the dimethyl groups linked to the nitrogen atoms. It was also found that the CD spectra of [Pd(R-pn)((R)-tmpn)]<sup>2+</sup> and [Pd(en)((R)-tmpn)]<sup>2+</sup> are similar to that of [Pd(R-pn)<sub>2</sub>]<sup>2+</sup> [1]. The CD of these ternary complexes was interpreted in terms of an intramolecular interligand steric interaction [1].

In order to investigate more extensively the influence of the N-alkyl groups of diamine chelates on the CD, we prepared various [PdCl<sub>2</sub>(AA')] and

TABLE I. List of Ligands.

Ligand	Abbreviation
(CH <sub>3</sub> ) <sub>2</sub> NCH(CH <sub>3</sub> )CH <sub>2</sub> N(CH <sub>3</sub> ) <sub>2</sub>	(R)-tmpn
(CH <sub>3</sub> ) <sub>2</sub> NCH(CH <sub>2</sub> ) <sub>4</sub> CHN(CH <sub>3</sub> ) <sub>2</sub>	(R)-tmchxn
H <sub>2</sub> NCH(CH <sub>3</sub> )CH <sub>2</sub> N(CH <sub>3</sub> ) <sub>2</sub>	N <sup>1</sup> -Me <sub>2</sub> (S)-pn
H <sub>2</sub> NCH(CH <sub>3</sub> )CH <sub>2</sub> N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	N <sup>1</sup> -Et <sub>2</sub> (S)-pn
H <sub>2</sub> NCH(CH <sub>3</sub> )CH <sub>2</sub> N(CH <sub>3</sub> )(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	N <sup>1</sup> -Me, Et-(S)-pn
(CH <sub>3</sub> ) <sub>2</sub> NCH(CH <sub>3</sub> )CH <sub>2</sub> NH <sub>2</sub>	N <sup>2</sup> -Me <sub>2</sub> (S)-pn

[Pd(AA')<sub>2</sub>]<sup>2+</sup> complexes and measured their CD spectra. In this report we will discuss their CD in comparison with those obtained previously for (R)-tmpn complexes.

### Experimental

#### Syntheses

##### (R)-tmchxn

This was obtained from (R)-cyclohexane diamine by a method similar to that for tmen [2].

##### N<sup>1</sup>-Me<sub>2</sub>(S)-pn, N<sup>1</sup>-Et<sub>2</sub>(S)-pn and N<sup>1</sup>-Me, Et-(S)-pn

To a suspension of N-phthaloyl-L-alanine [3- (0.11 mol) in 100 ml of benzene was added an excess of SOCl<sub>2</sub> (0.23 mol) and the mixture was refluxed for 1 hr. Benzene and excess SOCl<sub>2</sub> were evaporated under reduced pressure and the residue was dissolved in 100 ml of benzene. To this solution, a benzene solution of dimethylamine, diethylamine or methyl-ethylamine (0.23 mol) was added dropwise with vigorous stirring at -10 °C. The hydrochloride of the amine formed was filtered off and washed several times with benzene. The filtrate and washings were evaporated under reduced pressure and the resultant

TABLE II. Elemental Analyses<sup>a</sup> of Complexes.

Complex	C (%)	H (%)	N (%)
[PdCl <sub>2</sub> ((R)-tmchxn)]	34.56(34.55)	6.45(6.38)	7.89(8.06)
[PdCl <sub>2</sub> (N <sup>1</sup> -Me <sub>2</sub> (S)-pn)] · 1/2H <sub>2</sub> O	20.67(20.81)	5.26(5.24)	9.63(9.70)
[PdCl <sub>2</sub> (N <sup>1</sup> -Et <sub>2</sub> (S)-pn)]	27.20(27.34)	5.84(5.90)	9.16(9.11)
[PdCl <sub>2</sub> (N <sup>1</sup> -Me, Et(S)-pn)]	24.45(24.54)	5.46(5.49)	9.51(9.54)
[PdCl <sub>2</sub> (N <sup>2</sup> -Me <sub>2</sub> (S)-pn)]	21.20(21.48)	5.12(5.05)	9.84(10.02)
[Pd(N <sup>1</sup> -Me <sub>2</sub> (S)-pn) <sub>2</sub> ]Cl <sub>2</sub> · H <sub>2</sub> O	30.05(30.25)	7.56(7.57)	14.01(13.49)
[Pd(N <sup>1</sup> -Et <sub>2</sub> (S)-pn) <sub>2</sub> ]Cl <sub>2</sub> · H <sub>2</sub> O	36.80(36.89)	8.18(8.40)	11.94(12.29)
[Pd(N <sup>2</sup> -Me <sub>2</sub> (S)-pn) <sub>2</sub> ]Cl <sub>2</sub> · 1/2H <sub>2</sub> O	30.74(30.74)	7.30(7.48)	14.27(14.34)

<sup>a</sup>Calculated values in parentheses.

oil was dissolved in 100 ml of ethanol. Hydrazine monoacetate (0.11 mol) was added to this solution and the mixture was stirred overnight. A white precipitate formed was filtered off and washed several times with ethanol. The filtrate and washings were evaporated to dryness and the oily residue (amide acetate) was used in the following reactions without further purification. The crude amide acetate was reduced with LiAlH<sub>4</sub> (0.2 mol) in THF. The subsequent procedures were the same as those in the literature [4]. The fraction boiling at 110–130°, 120–140° and 115–135 °C was collected as N<sup>1</sup>-Me<sub>2</sub>(S)-pn, N<sup>1</sup>-Et<sub>2</sub>(S)-pn and N<sup>1</sup>-Me,Et(S)-pn, the yields being 2.4, 3.5 and 1.7 g respectively.

#### N<sup>2</sup>-Me<sub>2</sub>(S)-pn

N,N-Dimethyl-L-alanine prepared according to the method described in the literature [5] was converted to methyl ester by the usual method [6]. The ester (14 g) was added to 200 ml of methanol saturated with ammonia and the solution was allowed to stand at room temperature for 7 days. The excess reagent and solvent were evaporated under reduced pressure and the oily residue was used in the following reactions without further purification. The residue (3 g) was reduced with LiAlH<sub>4</sub> (1.7 g) in THF. The subsequent procedures were the same as those in the literature [4]. The fraction boiling at 110–130 °C was collected as product; yield 1.2 g.

#### [PdCl<sub>2</sub>(AA')] complexes (AA': N<sup>1</sup>-Me<sub>2</sub>(S)-pn, N<sup>1</sup>-Et<sub>2</sub>(S)-pn, N<sup>1</sup>-Me, Et(S)-pn, N<sup>2</sup>-Me<sub>2</sub>(S)-pn or (R)-tmchxn)

To an aqueous solution (10 ml) of K<sub>2</sub>[PdCl<sub>4</sub>] (1 mmol) was added an equimolar amount of the corresponding diamine and the mixture was heated on a water bath until the solution turned yellow. The yellow solution was allowed to stand overnight in a refrigerator. Yellow crystals were obtained.

#### [Pd(AA')<sub>2</sub>]<sup>2+</sup> (AA': N<sup>1</sup>-Me<sub>2</sub>(S)-pn, N<sup>1</sup>-Et<sub>2</sub>(S)-pn or N<sup>2</sup>-Me<sub>2</sub>(S)-pn)

To an aqueous solution (10 ml) of K<sub>2</sub>[PdCl<sub>4</sub>] (1 mmol) was added the corresponding diamine (2 mmol) and the mixture was heated on a water bath until a colorless solution was obtained. The solution was evaporated to dryness and the residue was dissolved in 20 ml of ethanol. The ethanol solution was allowed to stand at room temperature for two days. White crystals were collected and recrystallized from ethanol (95%) (Table II).

#### Spectral Measurements

The CD spectra were measured at room temperature with a JASCO J-20 recording spectropolarimeter. The absorption spectra were obtained at room temperature with a Hitachi EPS-3T recording spectrophotometer. The PMR spectra were measured in D<sub>2</sub>O with a Hitachi Model R-24 NMR spectrometer using sodium 3-(trimethylsilyl)-1-propanesulfonate (NaTMS) as the internal standard.

#### Results and Discussion

In a previous paper [1] we reported that the (R)-tmpn chelate ring should adopt λ conformation in [PdCl<sub>2</sub>((R)-tmpn)] from the examination of a stereomodel. This is supported by the fact that the CD spectrum of [PdCl<sub>2</sub>((R)-tmpn)] is quite similar to that of [PdCl<sub>2</sub>((R)-tmchxn)] in which the (R)-tmchxn chelate ring is fixed at the λ conformation (Fig. 1).

The examination of a stereo model showed that the equatorial C-methyl conformer (δ conformer) is energetically favored for Pd(II) chelates of N<sup>1</sup>-Me<sub>2</sub>(S)-pn, N<sup>1</sup>-Et<sub>2</sub>(S)-pn and N<sup>1</sup>-Me,Et(S)-pn as well as S-pn. Erickson *et al.* [7] measured the C<sup>13</sup> NMR of [Pt(N<sup>1</sup>-Me<sub>2</sub>-pn)(bpy)]<sup>2+</sup> and concluded that the equatorial C-methyl conformer is predominant in an aqueous solution. This implies that for the optically

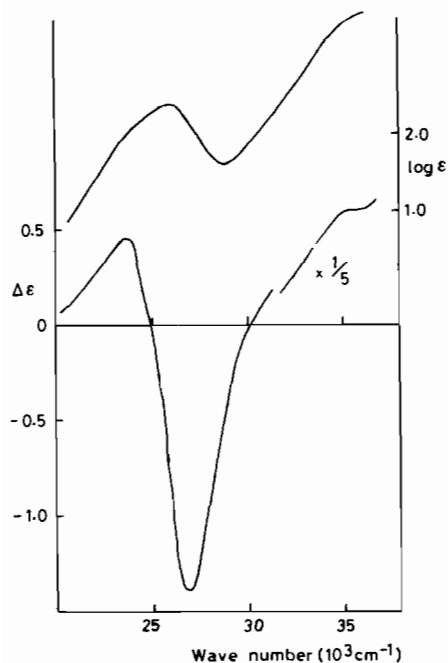


Fig. 1. Absorption and CD spectra of  $[\text{PdCl}_2((\text{R})\text{-tmchxn})]$  in 0.2 *N* KCl aqueous solution.

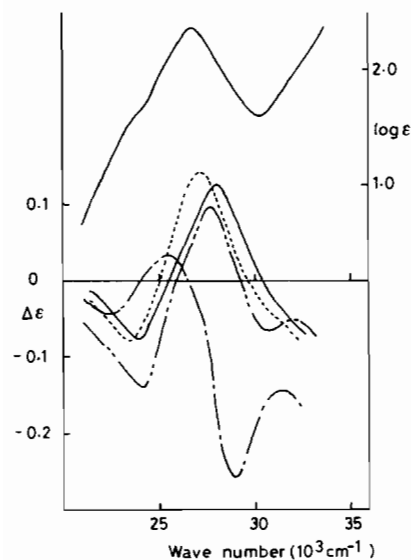


Fig. 2. Absorption spectrum of  $[\text{PdCl}_2(\text{N}^1\text{-Me}_2(\text{S})\text{-pn})]$  (—) and CD spectra of  $[\text{PdCl}_2(\text{N}^1\text{-Me}_2(\text{S})\text{-pn})]$  (---),  $[\text{PdCl}_2(\text{N}^1\text{-Et}_2(\text{S})\text{-pn})]$  (-·-),  $[\text{PdCl}_2(\text{N}^1\text{-Me,Et}(\text{S})\text{-pn})]$  (···) and  $[\text{PdCl}_2(\text{N}^2\text{-Me}_2(\text{S})\text{-pn})]$  (- - - -) in 0.2 *N* KCl aqueous solution.

active  $\text{N}^1\text{-Me}_2(\text{S})\text{-pn}$  chelate ring, the  $\delta$  conformation is preferred.

The CD spectra of  $[\text{PdCl}_2(\text{AA}')]_2$  are shown in Fig. 2. For  $[\text{PdCl}_2(\text{N}^1\text{-Me}_2(\text{S})\text{-pn})]$ , inversion of the CD sign pattern occurs compared to  $[\text{PdCl}_2(\text{S-pn})]$  which exhibits a (+, -) sign pattern from the lower energy side. Thus the CD spectra of  $[\text{PdCl}_2(\text{N}^1\text{-$

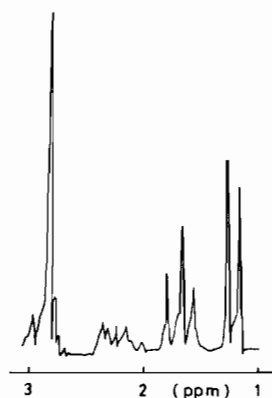


Fig. 3. PMR spectrum of  $[\text{Pd}(\text{OD}_2)_2(\text{N}^1\text{-Me,Et}(\text{S})\text{-pn})^{2+}]$  in  $\text{D}_2\text{O}$ .

$\text{Me}_2(\text{S})\text{-pn}]$  and  $[\text{PdCl}_2((\text{S})\text{-tmpn})]$  [8] indicate that the replacement of four amino hydrogens ( $\text{N}^1\text{-}$  and  $\text{N}^2\text{-}$ hydrogens) or two  $\text{N}^1\text{-}$ hydrogens of  $\text{S-pn}$  by methyl groups causes the inversion of the CD sign pattern, though these  $\text{N}$ -substituted  $\text{S-pn}$  chelate rings adopt the  $\delta$  conformation as does the  $\text{S-pn}$  chelate ring.

Erickson *et al.* [7] also reported that in  $[\text{Pt}(\text{N}^2\text{-Me}_2\text{-pn})(\text{bpy})]^{2+}$ , the axial and equatorial  $\text{C}$ -methyl conformers are in nearly equal distribution in an aqueous solution. This implies that for an optically active  $\text{N}^2\text{-Me}_2(\text{S})\text{-pn}$  complex,  $\delta$  and  $\lambda$  conformers are nearly equally distributed. Although direct evidence is lacking, we presume that the  $\delta$  conformation is preferred for the  $\text{N}^2\text{-Me}_2(\text{S})\text{-pn}$  chelate ring by comparing the CD spectrum of  $[\text{PdCl}_2(\text{N}^2\text{-Me}_2(\text{S})\text{-pn})]$  with those of  $[\text{PdCl}_2(\text{N}^1\text{-Me}_2(\text{S})\text{-pn})]$  and  $[\text{PdCl}_2((\text{S})\text{-tmpn})]$ .  $[\text{PdCl}_2(\text{N}^2\text{-Me}_2(\text{S})\text{-pn})]$  shows inverted CD sign pattern of  $[\text{PdCl}_2(\text{S-pn})]$  but a similar CD to that of  $[\text{PdCl}_2(\text{N}^1\text{-Me}_2(\text{S})\text{-pn})]$  (Fig. 2). Since for  $[\text{PdCl}_2((\text{S})\text{-tmpn})]$  and  $[\text{PdCl}_2(\text{N}^1\text{-Me}_2(\text{S})\text{-pn})]$ , the replacement of four amino hydrogens ( $\text{N}^1\text{-}$  and  $\text{N}^2\text{-}$ hydrogens) or  $\text{N}^1\text{-}$ hydrogens of  $\text{S-pn}$  by methyl groups causes the inversion of the CD sign pattern without generating the change of ring conformation as was mentioned above, it seems reasonable to suppose that the origin of the inversion of the CD sign pattern for  $[\text{PdCl}_2(\text{N}^2\text{-Me}_2(\text{S})\text{-pn})]$  is the same as that for  $[\text{PdCl}_2(\text{N}^1\text{-Me}_2(\text{S})\text{-pn})]$  and  $[\text{PdCl}_2((\text{S})\text{-tmpn})]$ . Therefore, the  $\delta$  conformation may be preferable for the  $\text{N}^2\text{-Me}_2(\text{S})\text{-pn}$  chelate ring.

$[\text{PdCl}_2(\text{N}^1\text{-Et}_2(\text{S})\text{-pn})]$  shows a CD different from those of the other complexes studied here (Fig. 2). The sign of the main component of this complex is the same as that of  $[\text{PdCl}_2(\text{S-pn})]$ , where the main component means the largest Cotton effect. This suggests that the ethyl groups on the  $\text{N}^1\text{-}$ nitrogen atom have no appreciable effect on the CD.

When  $\text{N}^1\text{-Me,Et}(\text{S})\text{-pn}$  coordinates to a metal ion, the tertiary amine-nitrogen becomes asymmetric. Figure 3 shows the pmr spectrum of  $[\text{Pd}(\text{OD}_2)_2(\text{N}^1\text{-$

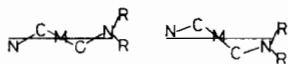


Fig. 4. Dissymmetric displacement of the donor nitrogen atoms in twisting sense with respect to the square plane and dissymmetric arrangement of the alkyl groups on the nitrogen atoms.

$\text{Me}_2\text{Et}(\text{S})\text{-pn}]^{2+}$  in  $\text{D}_2\text{O}$ .  $[\text{PdCl}_2(\text{N}^1\text{-Me}_2\text{Et}(\text{S})\text{-pn})]$  could not be characterized by pmr because of the insolubility in  $\text{D}_2\text{O}$ , and was converted to a very soluble diaqua complex by the addition of  $\text{AgClO}_4$ . The addition of conc. hydrochloric acid regenerated the starting material. The diaqua complex exhibits only one N-methyl signal at 2.82 ppm and only one triplet at 1.66 ppm assigned to the methyl protons of ethyl group. This indicates that this complex is not a racemic mixture but has an R or S nitrogen center. As far as we know, this complex is the first example having an asymmetric tertiary amine-nitrogen center. The CD spectrum of  $[\text{PdCl}_2(\text{N}^1\text{-Me}_2\text{Et}(\text{S})\text{-pn})]$  is similar to those of  $[\text{PdCl}_2(\text{N}^1\text{-Me}_2(\text{S})\text{-pn})]$  and  $[\text{PdCl}_2(\text{N}^2\text{-Me}_2(\text{S})\text{-pn})]$ . From this CD spectrum, however, we could not elucidate the effect of the asymmetric tertiary amine-nitrogen center.

According to the so called perturbation model [9, 10] for the optical activity of transition metal complexes, the CD of the d-d bands arises from dissymmetric interaction between the electrons and nuclei of the dissymmetrically oriented ligand and the d electrons on the metal ion. Bosnich and Harrowfield [11, 12] suggested that an isolated conformationally dissymmetric complex has two principal sources of dissymmetric perturbation which are of comparable magnitude and which can be opposing in sign for the generated CD. The first is the obvious puckering of the chelate ring and the second, less obvious but probably in many cases just as important, is the chiral displacements of the donor atoms. For N-alkyl-substituted (S)-pn chelates studied here, there are two additional sources of dissymmetric perturbation which require consideration, that is, the methyl group ( $\text{CHCH}_3$ ) on the diamine chelate ring and alkyl groups on the nitrogen atoms (Fig. 4). However, it is probable that the methyl group ( $\text{CHCH}_3$ ) on the diamine chelate ring has only a minor contribution [12-15]. Since the (S)-tmpn,  $\text{N}^1\text{-Me}_2(\text{S})\text{-pn}$  and  $\text{N}^2\text{-Me}_2(\text{S})\text{-pn}$  chelate rings should adopt  $\delta$  conformation, we suspect that the inversion of the CD sign pattern for these complexes is principally governed by the change of dissymmetric displacement of the donor nitrogen atoms and the effect of dissymmetric arrangement of the methyl groups on the nitrogen atoms. Crystallographic data are necessary to discuss these problems more fully. Therefore, X-ray analyses of  $[\text{PdCl}_2(\text{N}^1\text{-Me}_2(\text{S})\text{-pn})]$  and  $[\text{PdCl}_2(\text{N}^1\text{-Et}_2(\text{S})\text{-pn})]$  are in progress.

For  $[\text{Pd}(\text{AA}')_2]^{2+}$ , two possible geometrical isomers can be considered with respect to the two

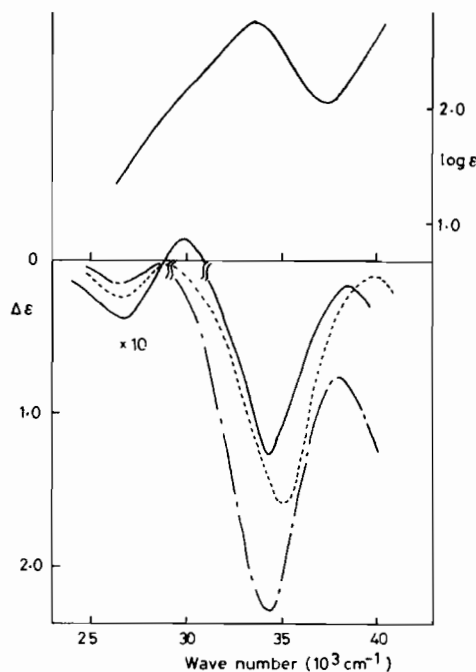


Fig. 5. Absorption spectrum of  $[\text{Pd}(\text{N}^1\text{-Me}_2(\text{S})\text{-pn})_2]^{2+}$  (—) and CD spectra of  $[\text{Pd}(\text{N}^1\text{-Me}_2(\text{S})\text{-pn})_2]^{2+}$  (—);  $[\text{Pd}(\text{N}^1\text{-Et}_2(\text{S})\text{-pn})_2]^{2+}$  (---) and  $[\text{Pd}(\text{N}^2\text{-Me}_2(\text{S})\text{-pn})_2]^{2+}$  (-----) in water.

tertiary amine-nitrogens. However, the *cis* isomer is considered to be less stable owing to the interligand steric hindrance between alkyl groups on the nitrogen atoms, and hence  $[\text{Pd}(\text{AA}')_2]^{2+}$  presumably exists as the *trans* isomer.

The CD spectra of  $[\text{Pd}(\text{AA}')_2]^{2+}$  studied here are given in Figure 5. The CD spectra of  $[\text{Pd}(\text{N}^1\text{-Me}_2(\text{S})\text{-pn})_2]^{2+}$  and  $[\text{Pd}(\text{N}^2\text{-Me}_2(\text{S})\text{-pn})_2]^{2+}$  are quite similar to that of  $[\text{Pd}(\text{S-pn})_2]^{2+}$ . This is in contrast with the fact that the CD spectra of  $[\text{PdCl}_2(\text{N}^1\text{-Me}_2(\text{S})\text{-pn})]$  and  $[\text{PdCl}_2(\text{N}^2\text{-Me}_2(\text{S})\text{-pn})]$  are quite different from that of  $[\text{PdCl}_2(\text{S-pn})]$ . A similar phenomenon has also been found in the CD spectra of  $[\text{PdCl}_2((\text{S})\text{-tmpn})]$ ,  $[\text{Pd}(\text{S-pn})(\text{S})\text{-tmpn}]^{2+}$  and  $[\text{Pd}(\text{en})(\text{S})\text{-tmpn}]^{2+}$ ;  $[\text{PdCl}_2((\text{S})\text{-tmpn})]$  showed inverted CD sign pattern of  $[\text{PdCl}_2(\text{S-pn})]$ , while  $[\text{Pd}(\text{S-pn})(\text{S})\text{-tmpn}]^{2+}$  and  $[\text{Pd}(\text{en})(\text{S})\text{-tmpn}]^{2+}$  showed a CD similar to that of  $[\text{Pd}(\text{S-pn})_2]^{2+}$  [1]. For  $[\text{Pd}(\text{S-pn})(\text{S})\text{-tmpn}]^{2+}$  and  $[\text{Pd}(\text{en})(\text{S})\text{-tmpn}]^{2+}$ , we suggest that there exists an intramolecular interligand steric interaction between diamine chelate rings and such steric interaction may be the main origin of the CD features of these complexes. For  $[\text{Pd}(\text{AA}')_2]^{2+}$  studied here, it is also suspected that there exists an intramolecular interligand steric interaction between diamine chelate rings. Since, whatever the steric interaction, there is no reason to alter the ring conformation, it seems plausible to suppose that the CD features of these complexes are attributable to different dissymmetric displacement of the donor

nitrogen atoms and different dissymmetric arrangement of the methyl groups on the nitrogen atoms arising from an intramolecular interligand steric interaction between diamine chelate rings compared to the case of  $[\text{PdCl}_2(\text{AA}')]_2$ .

Thus the CD spectral features of  $[\text{PdCl}_2(\text{AA}')]_2$  and  $[\text{Pd}(\text{AA}')_2]^{2+}$  may be interpreted in terms of dissymmetric displacement of the donor nitrogen atoms and dissymmetric arrangement of the alkyl groups on the nitrogen atoms. This will be supported by the CD spectral behavior of  $[\text{Cu}(\text{AA}')_2]^{2+}$  in various solvents [16].

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#### References

- 1 M. Suzuki and Y. Nishida, *J. Inorg. Nucl. Chem.*, **39**, 1459 (1977).
- 2 R. W. Moshier and L. Splater, *J. Org. Chem.*, **21**, 1050 (1956).
- 3 G. H. L. Nefkens, G. I. Tesser and R. J. F. Nivard, *Rec. Trav. Chim.*, **79**, 688 (1960).
- 4 M. Saburi, Y. Tsujito and S. Yoshikawa, *Inorg. Chem.*, **9**, 1467 (1970).
- 5 R. E. Brown and H. H. Stroud, *J. Chem. Soc.*, 1342 (1950).
- 6 M. Brenner and W. Huber, *Helv. Chim. Acta*, **36**, 1109 (1953).
- 7 L. E. Erickson, J. E. Sarneski and C. N. Reilly, *Inorg. Chem.*, **14**, 3007 (1975).
- 8 For simplicity, hereafter we will use S-pn and (S)-tmpn instead of R-pn and (R)-tmpn respectively. The CD spectra of the S-pn and (S)-tmpn complexes are enantiomorphous to those of the R-pn and (R)-tmpn complexes, respectively.
- 9 F. S. Richardson, *J. Chem. Phys.*, **54**, 2453 (1971).
- 10 S. F. Mason, *J. Chem. Soc. A*, 667 (1971).
- 11 B. Bosnich and J. MacB. Harrowfield, *Inorg. Chem.*, **14**, 828 (1975) and references therein.
- 12 B. Bosnich and J. MacB. Harrowfield, *J. Am. Chem. Soc.*, **94**, 3425 (1972).
- 13 C. J. Hawkins, *Chem. Commun.*, 777 (1969).
- 14 C. J. Hawkins, "Absolute Configuration of Metal Complexes", Wiley-Interscience, New York, N.Y. (1971), Chapter 5.
- 15 S. Yano, M. Saburi, S. Yoshokawa and J. Fujita, *Bull. Chem. Soc. Jpn.*, **49**, 101 (1976).
- 16 M. Suzuki and Y. Nishida, to be published.