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Stereospecific Coordination of 2, 2'-Diaminobiphenyl in the Square Planar Platinum(II) Comdlexes

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2,2'-Diaminobiphenyl platinum (II) complexes of optically active *trans*-1,2-diaminocyclohexane and 1.2-diaminopropane, [Pt(S,S-chxn)(dabp)]Cl$_2$, [Pt(R,R-chxn)(dabp)]Cl$_2$, [Pt(S-pn)(dabp)]Cl$_2$, and [Pt(R-pn)(dabp)]Cl$_2$, where S,S-chxn and R,R-chxn are, respectively, S and R isomers of *trans*-1,2-diaminocyclohexane, and S-pn and R-pn are, respectively, S and R isomers of 1.2-diaminopropane, and dabp the 2,2'-diaminobiphenyl, have bene prepared. The dabp ligand has been found to take the δ conformation in the S,S-chxn and S-pn platinum (II) complexes, while it takes the λ conformation in the R,R-chxn and R-pn platinum (II) complexes.

The 2,2'-diaminobiphenyl (dabp) belongs to the skewed biaryl group. When dabp coordinates to a metal ion, there is an equal probability that the freely rotating dabp molecule can assume either the λ or the δ conformation. The only contribution of this ligand to the optical activity is then the conformation of the chelate ring formed upon coordination.

Investigations involving the dabp ligand have so far been limited to the octahedral cobalt(III) complexes.[1,2] Recently, square planar Pt(II) complexes containing dabp and R,R-*trans*-1,2-diaminocyclohexane (R,R-chxn) have been prepared and the X-ray crystallographic study has shown that the dabp ligand takes the λ conformation in the [Pt (R, R-chxn)-dabp)] Cl$_2\cdot$3H$_2$O complex.[3] In this work a series of dabp platinum (II) complexes involving optically active isomers of 1,2-diaminopropane(pn) and *trans*-1,2-diaminocyclohexane has been prepared so that the dabp ligand can take the δ conformation. It is shown that the dabp ligand can take λ or δ conformation depending on the conformation of the pn and chxn ligands in the square planar configuration.

Experimental

2,2-Diaminobiphenyl. The preparation of this ligand has been accomplished by the method known in the literature.[4]

Resolution of 1,2-Diaminopropane. This was resolved according to the method of Dwyer, *et al*[6] using *d*-tartaric acid. It was then conerted to the dihydrochloride according to the procedure of Bailar, *et al.*[7] Resolution of *trans*-1,2-Diaminocyclohexane. The method of Asperger and Liu[8] was followed to resolve this compound. $[\alpha]_D = -19.6$.

[*Pt(S-pn)Cl$_2$*] *and* [*Pt(R-pn)Cl$_2$*]. These were prepared according to the method used for [Pt(en) Cl$_2$] using optically active 1,2-diaminopropane in place of ethylenedialine.[9] Calcd. for Pt (C$_3$H$_{10}$N$_2$)Cl$_2$: C, 10.60; H, 2.96; N. 8.24. Found; C, 10.51; H, 2.93; N, 8.27 for [Pt (S-pn)(dabp)] Cl$_2$. C, 10.45; H, 2.94; N, 8.29 for Pt (R-pn) (dabp) Cl$_2$.

[*Pt (S,S-chxn) Cl$_2$*] *and* [*Pt (R,R-chxn) Cl$_2$*]. These were prepared by the same method used for [Pt (en) Cl$_2$] using optically active *trans*-1,2-diaminocyclohxane.[9] Calcd. for Pt (C$_6$H$_{14}$N$_2$) Cl$_2$; C, 18.96; H, 3.71; N, 7.37. Found: C, 18.92; H, 3.73; N, 7.29 for Pt (S,S-chxn) Cl$_2$ C, 18.88; H, 3.68; N, 7.25 for Pt (R,R-chxn) Cl$_2$

[*Pt(S-pn)(dabp)*]*Cl$_2$ and* [*Pt(R-pn)dabp)*]*Cl$_2$.* 0.58g of [Pt (S-pn) Cl$_2$] and 0.31g of 2,2'-diaminobiphenyl were suspended in 300 m*l* of water in a 500-m*l* three neck round bottom flask equipped with a mechanical stirrer, thermometer, and condenser. The mixture was stirred and heated at a temperature of 60-70°C for 7 hrs. Gradually the suspension dissolved and the solution changed from yellow to colourless. The solution was cooled and filtered, and then concentrated on a rotary evaporator until crystallization occurred. The

product was placed in an ice bath and was collected on a sintered glass funnel ,and washed with ice-cold water, ethanol and ether. The product was recrystallized from warm water to which one of $3M$ HCl was added. Yield: 0.30g. The [Pt-(R-pn) (dabp)]Cl$_2$ was prepared by the same way described above. Calcd. for Pt(C$_3$H$_{10}$N$_2$)(C$_{12}$H$_{12}$N$_2$)Cl$_2$·H$_2$O; C, 33.22; H, 4.46; N, 10.33. Found; C, 34.00; H, 4.61; N, 10.40 for [Pt(S-pn) (dabp)]Cl$_2$·H$_2$O C, 34.10; H, 4,36; N, 9.89 for [Pt (R-pn)(dabp)]Cl$_2$·H$_2$O. [Pt(S,S⁻chxn)(dabp)]Cl$_2$·3H$_2$O. This was prepared by the same procedure used for [Pt(S-pn) (dabp)]Cl$_2$ using, respectively, S,S-*trans*-1,2-diaminocyclohexane and R,R-*trans*-1,2,-diaminocyclohexane in place of S-pn. Yield; 0.38g (60 %) for S,S-chxn cpomlex and 0.43g (53 %) for R, R-chxn xomplex. Calcd. for Pt (C$_6$H$_{14}$N$_2$)-(C$_{12}$H$_{12}$N$_2$) Cl$_2$·3H$_2$O; C, 34.94; H, 5.22; N, 9.06. Found: C, 34.99; H,5.26; N, 9.10 for [Pt(S,S-chxn) (dabp)]Cl$_2$·3H$_2$O. C, 35.10; H, 5.20; N, 9.09 for [Pt(R,R-chxn)(dabp)]Cl$_2$·3H$_2$O.

Instruments Used. The electronic absorption spectra were obtained using a Shimadzu UV-240 Spectrophotometer. Circular dichroism spectra were measured using a Jasco ORD/CD-5 Spectrophotometer. Elemental analyses were performed by Micro-Tech Laboratoies, Skokie, Illinois, U.S.A.

Results and Discussion

A square planar platinum (II) environment has been utilized in this work to investigate the stereoselectivity of the skewed biaryl, 2,2'-diaminobiphenyl. Dissymmetric square planar complexes containing two chiral ligands provide a simple model for stereoselective reactions. The dabp ligand was specifically selected for these reactions because of its ability to rotate freely about the C-C bond joining the two phenyl rings.

CD curves of [Pt(S, S-chxn)(dabp)]Cl$_2$ and [Pt (R,R-chxn) (dabp)]Cl$_2$ are shown in Figure 1 along with the electronic absorption spectra. The absolute configuration of the [Pt(R,R-chxn)(dabp)]Cl$_2$ complex has been unambiguously determined through X-ray crystallographic study.[3] A perspective view of this molecule is shown in Figure 2 and Figure 3 clearly shows the λ conformation of the dabp ligand in the complex. From the known absolute configuration of the R,R-chxn ligand a λ conformation should be expected when this ligand coordinates to platinum (II) ion, which is shown in Figure 2. The major contribution to the rotational strength comes from the λ conformation of the two chelate
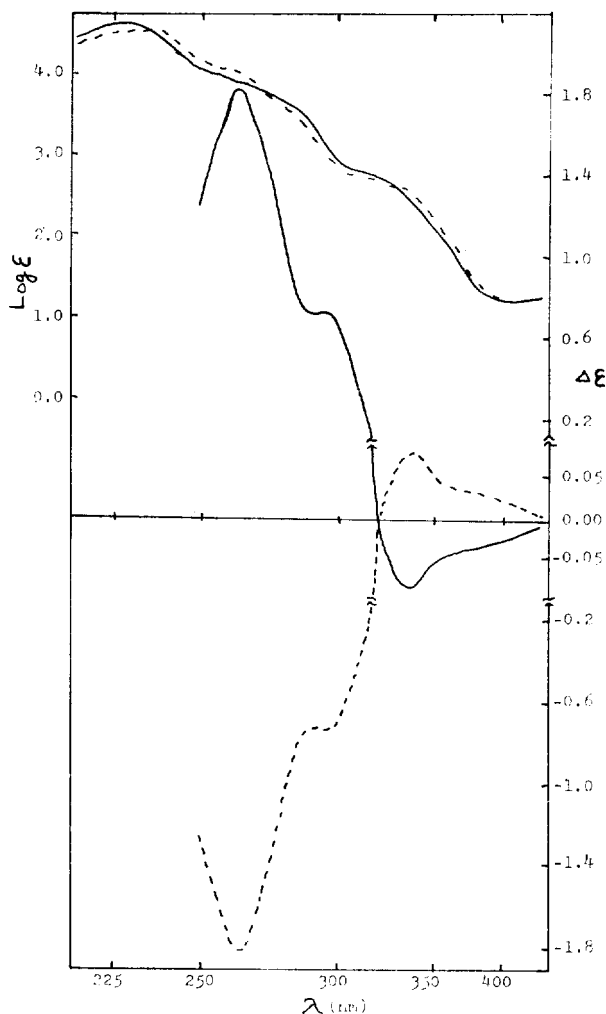

Figure 1, Electronic absorption and CD spectra of [Pt(R,R-chxn) (dabp)] Cl$_2$·3H$_2$O (——) and [Pt(S,S-chxn) (dabp)]Cl$_2$·3H$_2$O (······).
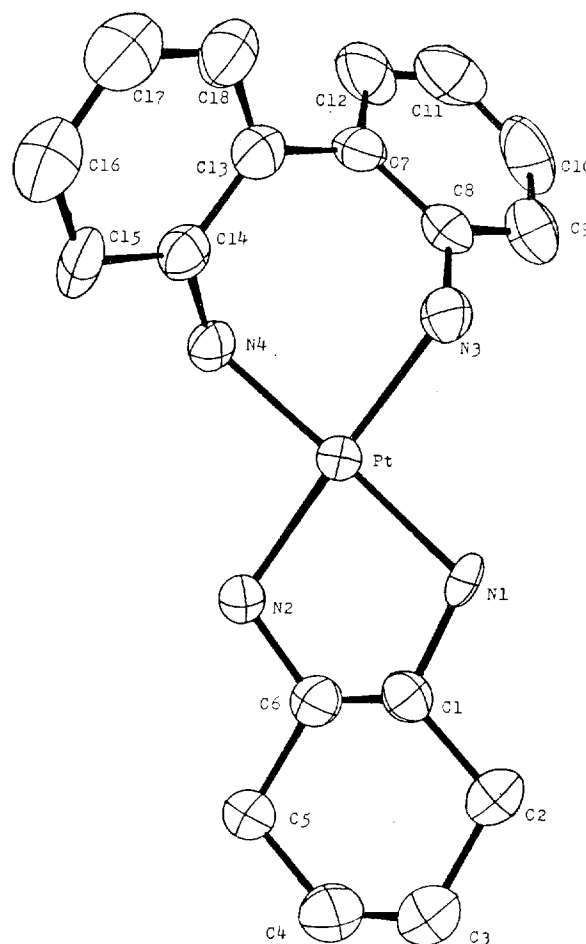

Figure 2. Perspective view of a molecule of [Pt(R,R-chxn). (dabp)]Cl$_2$. Hydrogen and chlorine atoms are omitted for clarity.
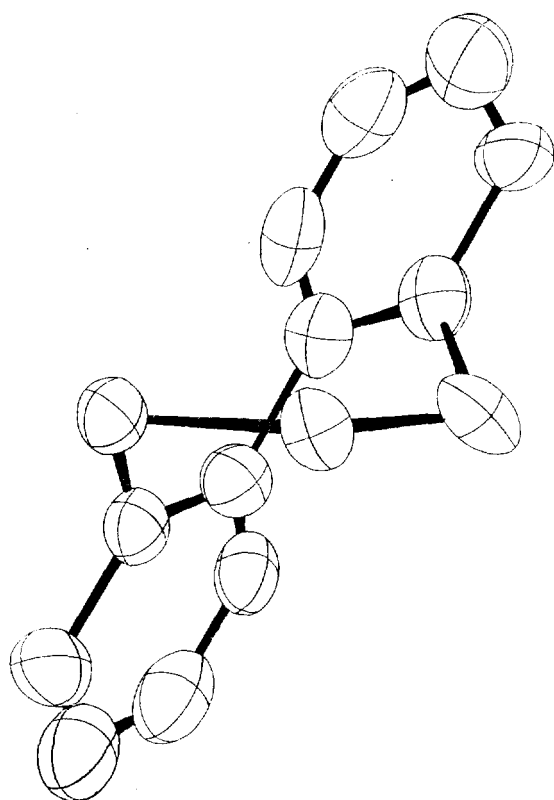
Figure 3. View through 2.2'-diaminobiphenyl.

rings as opposed to the vicinal effect of the asymmetric carbon atom.

Comparison of the CD curves of the $[Pt(S,S-chxn)(dabp)]^{2+}$ complex and the $[Pt(R,R-chxn)(dabp)]^{2+}$ complex in Figure 1 indicates that their absolute configurations are mirror images each other, which means that both the, SS-chxn and the dabp ligands take the δ chelate ring conformation upon complex formation. The absolute configuration of S,S-chxn tells that it will take a δ conformation upon complex formation. From the CD curve of $[Pt(S,S-chxn)(dabp)]^{2+}$ it is reasonable to say that the dabp ligand takes a δ conformation in the complex.

The CD curves of $[Pt(R-pn)$ (dabp)$]Cl_2$ and $[Pt(S-pn)-$ (dabp)$]Cl_2$ (Figure. 4) suggest that the absolute configurations of these complexes are mirror imges aech other. The similanty in the pattern and position of the negative and positive CD bands observed in the $[Pt (R,R-chxn)(dabp)]Cl_2$ and $[Pt(R-pn)(dabp)]Cl_2$ (Figures 1 and 4) indicates that the dabp ligand has the sane λ conformation in both complexes. Likewise, the CD spectra of $[Pt(S,S-chxn)$ (dabp)$]Cl_2$ and $[Pt(S-pn)(dabp)]Cl_2$ show a similarity in the pattern and position of the negative and positive CD bands. Since the S-pn should take a δ conformation upon coordination to platinum(II) ion, a δ conformation is assigned to the dabp chelate ring in both complexes.

The dabp ligand has shown a remarkable stereoselectivity upon coordination. considering the fact that statistically there is an equal probability that the freely rotating dabp molecules can assume either the δ or the λ conformation
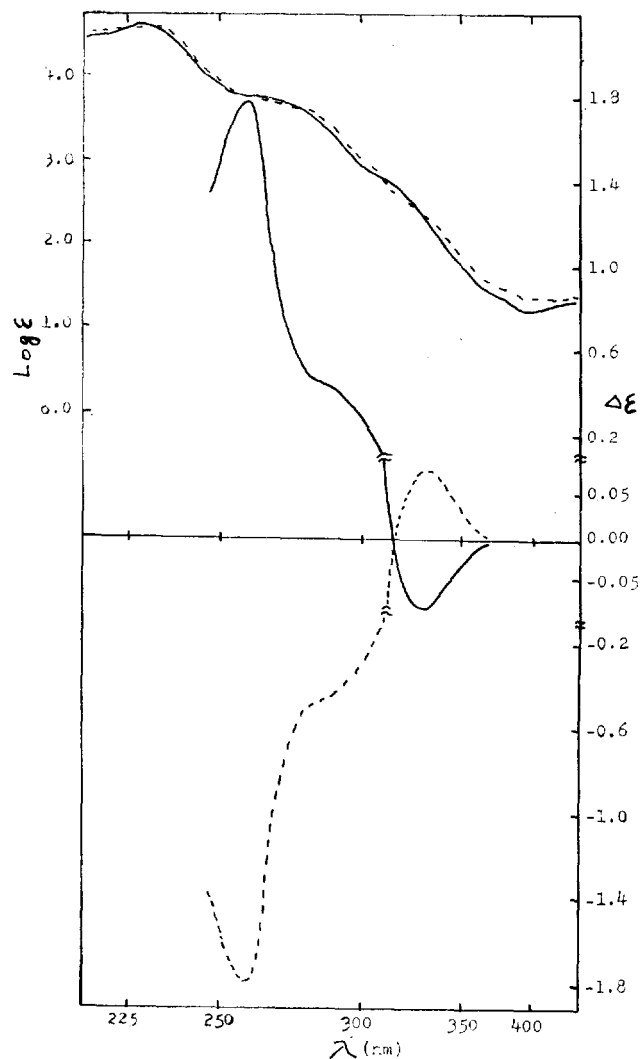

Figure 4. Electronic absorption and CD spectra of $[Pt (R-pn)-$ (dabp)$]Cl_2 \cdot H_2O$ (———) and $[Pt (S-pn) dabp)] Cl_2 \cdot H_2O$ (······).

upon complex formation. Such behaviour can be understood from a study using molecular models of chxn. pn, and dabp ligands. In the R,R-chxn and R-pn complexes, in which these ligands take the λ conformation, the hydrogens on opposing nitrogens are staggered when the dabp takes the λ conformation. When the model containing dabp with δ conformation is made with those same two ligands in the λ conformation, on the other hand, the hydrogens are almost totally eclipsed. The complete stereoselectivity observed is due to such nonbonded interaction between the hydrogens bonded to the nitrogen atoms. A similar argument can be applied to the S,S-chxn and S-pn copmlexes: in the S,S-chxn and S-pn complexes, where they take the δ conformation, the hydrogens on opposing nitrogens are staggered when the dabp ligand takes the δ conformation. If the dabp ligand takes the λ conformation, those hydrogens are almost totally eclipsed.

These observations are substantiated by Douglas, *et al*[1] who observed stereoselectivity in the reaction of dabp with $[Co(en)_2Cl_2]^+$ and with cis-α-[Co (trien)Cl_2]^+$, where en and trien are, respectively, ethylenediamine and triethylenetetraamine. Tanimura, *et al*[2] also report that the complexes

[Co(R-pn)₂ (dabp)]³⁺, [Co(R, R–chxn)₂ (dabp)]³⁺, *cis–α–*[Co (2S, 9S–dimetrien) (dabp)]³⁺, and *cis–α–*[Co(3S,8S–dimetrien)]³⁺ gave one isomer each. The 2S,9S–dimetrien and 3S,8S–dimetrien are 2S,9S–dimethyltriethylenetetraamine and 3S,8S–dimethyltriethylenetetraamine.

In those bis(diamine)(dabp) Co complexes there are two possible diastereoisomers, $\Delta(\lambda\lambda\lambda)$ and $\Lambda(\lambda\lambda\lambda)$, though the $\Delta(\lambda\lambda\lambda)$ isomer is known to be more stable. The display of stereoselectivity in those cobalt(III) complexes has been attributed to the interactions between the hydrogens of dabp and the hydrogens of the tetradentate ligands or the hydrogens of the *cis–bis*(diamine). In those octahdral complexes. however, other influences from adjacent ligands and chelate rings give complications in determining stereoselectivity. The platinum (II) complexes designed in the present investigation have eliminated those influences in determining stereospecificity. Therefore the conformation of the dabp ligand in the square planar platinum complexes can be displayed with much greater certainty than in octahedral complexes.

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Reduction of Selected Carbonyl Compounds with 8-Oxyquinoline Dihydroboronite. Selective Reduction of Aldehydes in the Presence of Ketones

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8-Oxyquinoline dihydroboronite is prepared by mixing equimolar amounts of 8-hydroxyquinoline and borane–dimethyl sulfide complex in tetrahydrofuran at room temperature and its structure is determined by spectroscopic methods. The reagent is shown to be an extremely mild reducing agent and reduces aldehydes, cyclohexanones, and acid chlorides to some extent. The reagent in the presence of 0.1 equiv of boron trifluoride etherate in tetrahydrofuran at room temperature reduces selectively aldehydes in the presence of ketones, while the reagent in the presence of 1 equiv of boron trifluoride etherate rapidly reduces simple aldehydes and ketones but does not reduce carboxylic acids, esters, and amides.

Introduction

While amine-borane complexes have been extensively investigated as hydride reducing agents for a long time,[1] they failed to gain widespread use in synthetic organic chemistry, though they are remarkably stable and soluble in a variety of protic and aprotic solvents.[2] This is due in part to previous studies obtained with tertiary amine-borane and pyridine-borane complexes. These studies showed that tertiary amine-borane complexes in the absence of Lewis acid catalyst react with aldehyes and ketones very sluggishly even at elevated temperature, transferring only one of the three available hydrides. However, it has been recently reported that primary amine-borane complexes are somewhat different from tertiary amine-borane complexes as carbonyl reducing agents and can be utilized effectively for selective reductions.[3] Furthermore, amine-borane complexes derived from optically active amines,[4] sodium salts of optically active amino acids,[5] and methyl esters optically active amino acids have been utilized in asymmetric reduction of ketones. In contrast with many studies of amine-borane complexes, there are relatively few reports on amine-borane complexes with certain organic difunctional groups.[7]

As part of our research program directed toward the development of new hydride reducing agents,[8] we have recently communicated that aldehydes are selectively reduced to the corresponding alcohols in the presence of ketones with 8-oxyquinoline dihydroboronite in the presence of a catalytic amount of boron trifluoride etherate.[9] This paper describes a detail of reducing properties of a new hydride reducing agent,