Soc., **101**, 129 (1979)

(12) U. Mazucato, *Pure Appl. Chem.*, **54**, 1705 (1982).

(13) (a) D Schulte-Frohlinde, H. Blume, and H. Güsten, *J. Phys. Chem.*, **66**, 2486 (1962); (b) D. V. Bent and D. Schulte-Frohlinde, *J. Phys. Chem.*, **78**, 446 (1974); (c) D. V. Bent and D. Schulte-Frohlinde, *J. Phys. Chem.*, **78**, 451 (1974); (d) H. Görner and D. Schulte-Frohlinde, *J. Phys. Chem.*, **82**, 2653 (1978).

(14) E. J. Shin, B. S. An, and S. C. Shim, to be published.

(15) N. Nakashima and K. Yoshihara, *J. Chem. Phys.*, **77**, 6040 (1982).

(16) P-H. Bong, K.H. Chae, S.C. Shim, N. Nakashima, and K. Yoshihara, *J. Photochem.* in press.

(17) S. P. McGlynn, R. Ajumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State," Prentice-Hall, Englewood Cliffs, N. J., p. 251-256, 1969

Platinum(II) Complexes of 6,6'-Dimethyl-2,2' diaminobiphenyl

Moo-Jin Jun

Department of Chemistry, Yonsei University, Seoul 121, Korea (Received March 28, 1985)

Carbonato and diammine platinum(II) complexes of resolved 6,6'-dimehtyl-2,2'-diaminobiphenyl have been prepared. The absolute configuration of the square planar platinum(II) complexes is determined on the basis of stereospecificity of the 6,6'-dimethyl-2,2'-diaminobiphenyl ligand, circular dichroism spectra of the complexes, and nonempirical circular dichroism method.

6,6'-Dimethyl-2,2'diaminobiphenyl (dmdabp) belongs to the skewed biaryl group. The two phenyl rings of R- or S-dmdabp have been found to be puckered by more than 70 degrees in angle[1] and thus provide a good source of dissymmetry owing to such nonplanarity of the chelate rings when coordinated to a metal ion. Investigations involving dmdabp have been with cobalt (III) complexes[2,3] and more recently with dichloro and 2,3-diaminobutane platinum(II) complexes.[5] The present work has been undertaken to prepare carbonato and diammine platinum(II) complexes of resolved dmdabp and to determine the absolute configuration of those complexes based on the nonempirical CD method.

The nonempirical determination of absolute configuration has been applied to the metal complexes of particular ligands containing two non-coplanar chromophores.[6-9] This method has been successful in predicting the absoulte configuration of metal complexes of 1,10'-phenanthroline,[10,11] 2,2'-bipyridine[11], acetylacetonate,[12] and catecholate.[13] The sterically hindered dmdabp has the electric dipole π-π^* transitions in the near ultraviolet region and should provide an ideal background material for the application of nonempirical CD determination of absolute configuration.

Experimental

Preparation and resolution of 6,6'-dimethyl-2,2'diaminobiphenyl. This has been reported elsewhere.[1,2]

[Pt-(R-dmdabp)Cl₂] and [Pt-(S-dmdabp)Cl₂]. The preparation of these complexes is similar to that used for [Pt(en)Cl₂][4].

[Pt(R-dmdabp)CO₃]. 0.48g of [Pt-(R-dmdabp)Cl₂] and 0.14 g K_2CO_3 were supended in 300 ml of water in 500-ml three-neck round bottom flask equipped with a mechanical stirrer, thermometer and water cooled condenser. The mixture was stirred and heated at a temperature of 65-75°C for 7 hours.

The Gradually the suspension dissolved. The solution was cooled and filtered. The filtrate was concentrated on a rotary evaporator until crystallization The mixture was placed in an ice bath. The white crystals were collected on a sintered glass funnel, washed with ethanol and ether. The product was recrystallized once from warm water to which a few drops of 1M HCl were added. *Anal.* Calcd for Pt(C₁₄H₁₆N₂)CO₃ : C, 38.54; H, 3.43; N, 6.00 Found : C, 38.57; H, 3.40; N, 5.95.

[Pt(NH₃)₂Cl₂]. This was preapred by the method of Johnson.[14]

[Pt(R-dadabp) (NH₃)₂]Cl₂. 1.12 g of Pt(NH₃)₂Cl₂ and 0.80 g of R-dmdabp were suspended in 300 ml of water ina 500-ml three-neck round bottom flask equipped with a mechanical stirrer, thermometer, and water cooled condenser. The mixture was stirred and heated at a temperature of 60-70°C for 8 hurs. Gradually the suspension dissolved and the solution changed from yellow to almost colorless. The solution was cooled and filtered to remove any unreacted materials. The filtrate was concentrated on a rotary evaporator until crystallization. The mixture was placed in an ice bath. The product was collected on a sintered glass funnel, washed with ethanol and ether, air dried. It was recrystallized from warm water (Yield 0.84 g (46%). *Anal.* Calcd for [Pt((C₁₄H₁₆N₂))]Cl₂·H₂O : C, 32.20; H, 4.60; N, 10.72; Cl, 13.60 Found : C, 31.18; H, 4.63; N, 10.68; Cl, 13.66

[Pt(S-dmdabp) (NH₃)₂]Cl₂. This was prepared in the same way as that used for [Pt(S-dmdabp) (NH₃)₂]Cl₂ using S-dmdabp in place of R-dmdabp. (Yield 0.47 g (48%)). The infrared spectra of the two compounds were identical. Physical measurements. The electronic absorption spectra were obtained using a Cary 17 UV-Visible Spectrophotometer. The infrared spectra were recorded using Shimadzu IR-435 Spectrophotometer. The circular dichroism spectra were measured using a Jasco-20 CD Spectrophotometer.

Results and Discussion

The CD spectrum of [Pt(R-dmdabp)CO₃] (Figure 1) shows a postive CD band centered at about 325 nm, a negative CD band at near 290 nm, and a much stronger positive CD band at 245 nm. The major contribution to the rotational strength must come from the conformation of R-dmdabp. In the free ligand there is steric hindrance from the methyl groups at the sixth position of dmdabp. An activation energy for racemization of 17 kcal/mole or more at room temperature has been estimated for the dmdabp enantiomers.[16] This high activation energy assures the configurational stabilaity of this compound. Once the ligand is coordinated, the barrier to racemization is even much greater. From a molecular model of the free ligand it is seen that R-dmdabp can coordinate only in the λ conformation and only in the δ conformation in the case of S-dmdabp. This fact has been substantiated by Douglas *et al²* in their work on the stereospecific formation of R-dmdabp in the complex Δ(λ)-[Co-(en)₂ (R-dmdabp)]³⁺ as well as an X-ray crystallographic determination of R-dmdabp in the backbone of salicyladiminato tetradentate'. Since the carbonato ligand is almost planar, practically all the contribution to the rotational strength observed in [Pt(R-dmdabp)-CO₃] is due to the λ conformation of dmdabp.

The CD spectra of [Pt(R-dmdabp) (NH₃)₂]Cl₂ and [Pt(S-dmdabp) (NH₃)₂]Cl₂ are shown in Figure 2. The CD of these two complexes are mirror images, but are quite different from the CD spectrum of [Pt(R-dmdabp)CO₃]. A change in CD bands was also observed in the case of [Pt(R-Pn)Cl₂] and [Pt(R-Pn)(en)]Cl₂. In the R-Pn complexes the band that was assigned to the $^1A_1 \rightarrow {}^3E$ transition was blue-shifted to 35.7 kK in the en complex. An inspection of CD of [Pt(R-dmdabp)(NH₃)₂]Cl₂ reveals a negative band at 320 nm, a weak positive
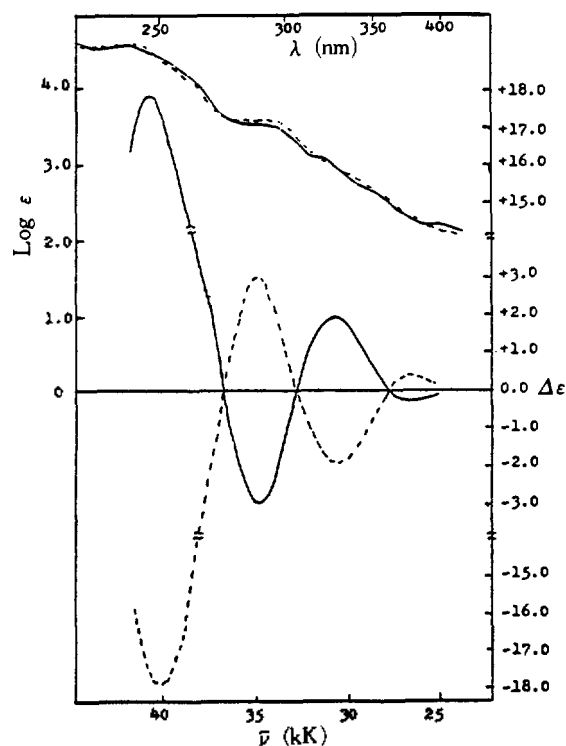
band at 301 nm, and an intense negative band at 281 nm.

Mason and coworkers[6,10-13] have developed a nonempirical approach[17,18] based on ligand transitions and have applied it to octahedral complexes containing conjugated ligands which are tyified by 2,2'-bipyridyl(bipy) and 1,10-phenthroline(phen). Briefly, the π-π* transitions of the free ligands, dipy and phen, are polarized in the molecular plane and are directed either along the short axis(x) or the long axis(y) of the ligands, Upon comlex formation these transitions remain largely unmodified.[19] Complexes containing only one of these ligands such as [Co(en)₂phen]³⁺ show comparatively weak circular dichroism in the regions of the π-π* ligand transitions[19]. When two or more conjugated ligands are present, the circular dichroism shown by the short-axis-polarized ligand transitions remains weak, but that associated with the long-axis-polarized transitions is very strong. The short-axis-polarized ligand transitions couple to give only electric transition dipole moments in the zere order and therefore cannot give rise to excition optical activity. The long-axis-polarized transitions, however, couple to give parallel electric and magnetic transition dipole moments in the zero order, and the rotational strengths produced by this mechanism are very large. It is this circular dichroism associated with the long-axis-polarized transitions of the complexed ligands which allows for the nonempirical determination of the absoulte configurations.

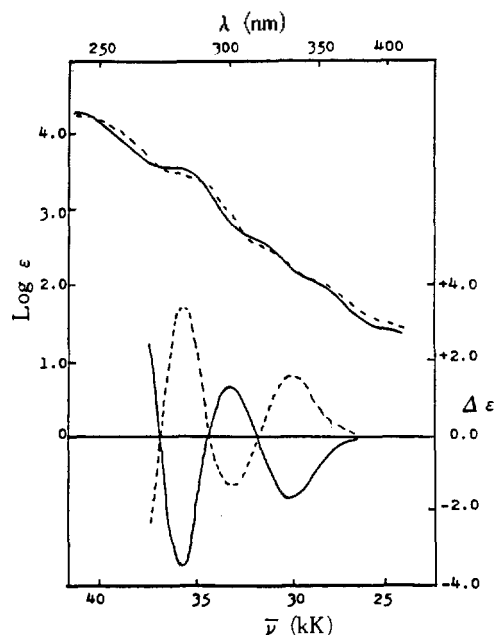The crucial issue in the application of the nonempirical

Figure 2. Electronic absorption and circular dichroism spectra of [Pt(R-dmdabp)(NH₃)₂]Cl₂ (————) and [Pt(S-dmdabp)(NH₃)₂]Cl₂ (----).

Figure 1. Electronic absorption and circular dichroism spectra of [Pt(R-dmdabp)CO₃] (————) and [Pt(S-dmdabp)CO₃] (----).

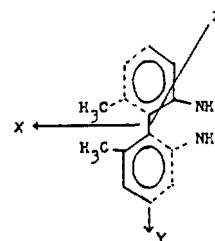**Figure 3.** Coordinate axes for λ-6,6'-dimethyl-2,2'-diaminobiphenyl.

method lies in the assignment of the components of the ligand absorption bands for which the circular dichroism has been measured.[17-18] For the tris complexes, electrostatic interactions between the three ligands remove the threefold degeneracy associated with electronic excitation energy on one of the ligands. As a result, there are two excited states, an A_2 state and a two fold degenerate E state, within the D_3 symmetry of the complex. For the bis complexes, the corresponding states are A and B for the C_2 symmetry of the molecule. The relative energy order obtained by using the dipole-dipole approximation for the intermolecular potential places the B component at higher energy for the bis complexes and the A_2 component at higher energy for the tris complexes.

Grinter and Mason[20] have analyzed the absorption and CD spectra of 1,1′-bianthryls, a skewed biaryl group, and successfully assigned the absolute configuration on this nonempirical method. The closely related dmdabp can be treated in a similar manner.

Figure 3 shows the λ configuration and the coordinate axes of dmdabp. The x and y axes are in the plane of the paper. The z axis is perpendicular to the plane of the paper. The dotted portion is below the plane, and the dihedral angle is less than 90°. The electronic states of the biphenyl system are either symmetric A or ant symmetric B with respect to rotation by π about the z axis. The long-axis-polarized transitions of A and B symmetry will have rotational strength, while in the short-axis-polarized transitions only the one with B symmetry will have rotational strength. When the diaminobiphenyl moiety takes the λ conformation, the long-axis tansition with A symmetry will have one component on each of the molecular halves, directed along the z-axis. The other components will be antiparallel and produce a counter-clockwise displacement of charge, with a magnetic moment along z. Thus, the A-transition should be seen as a negative CD band. For the transitions with B symmetry the parallel components will be along the x-axis, whereas the antiparallel components will produce a clockwise displacement of charge along the x axis. A positive CD band will result from the B-transition. Grinter and Mason calculated the A band to be at a higher energy than the B band in the bianthryls.

The long-axis-polarized band occurs at 291 nm for dmdabp[21], and the [Pt(R-dmdabp)CO_3] complex shows a shoulder in the absorption spectrum in the region of the long-axis-polarized band. The CD spectrum in this region reveals a negative band at near 290 nm and a positive band centered at about 325 nm. According to Grinter and Mason's calculation on the closely related bianthryls a positive B-band followed by a negative higher energy A-band in the region of the long-axis-polarized absorption band indicates a λ conformation. The R-dmdabp should take the λ conformation from the study of stereospecificity of the ligand[20] and the X-ray crystallographic study of R-dmdabp in the backbone of salicyladiminato tetradentate.[1] The CD spectrum of [Pt(R-dmdabp)(NH_3)]Cl_2 shows a negative high energy band at 281 nm followed by a positive band at 301 nm. The splitting pattern corresponds to the λ-ligand conformation. The CD peaks of [Pt(R-dmdabp) (NH_3)$_2$]Cl_2 are shifted, when compared with those corresponding CD peaks of [Pt(R-

dmdabp)CO_3], toward the higher energy side by more than 9 to 20 nm. Such shift has been expected and corresponds to the difference in the spectrochemical series between carbonato and ethylenediamine ligands. Figure 2 also shows the mirror image CD spectrum for [Pt(S-dmdabp) (NH_3)$_2$]Cl_2. The low energy B-band is negative and the higher energy A band is positive as expected for the d conformation.

In this work an example of the nonempirical determination of absolute configuration has been demonstrated. The nonempirical approach to absolute configuration determination is a powerful technique because it eliminates the doubt about the contribution from the vicinal effect, the conformational effect and the configurational effect, although it is limited to complexes containing special types of ligands.

References

(1) L. H. Pignolet, R. P. Taylor, and W. D. Horrocks, *J. Am. Chem. Soc.* **91**, 5457 (1969).

(2) W. T. Jordan, C. Y. Lin, and B. E. Douglas, *J. Coord. Chem.*, **3**, 103 (1973).

(3) T. Tanimura, H. Ito, J. Fujita, K. Saito, H. Hirai, and K. Yanasaki, *ibid*, **3**, 161 (1973).

(4) G. Johnson, *Inorg. Syn.*, **8**, 242 (1966)

(5) M. J. Jun and C. F. Liu, *Bulletin Kor. Chem. Soc* Submitted for Publication (1984).

(6) S. F. Mason, *Inorg. Chim. Acta Revs.*, **2**, 89 (1968)

(7) B. Bosnich, *Accounts Chem. Res.*, **2**, 266 (1969); *J. Am. chem. Soc* **90**, 627 (1968).

(8) W. Moffit and A. Moscowitz, *J. Chem. Phys.*, **30**, 648 (1959)

(9) E. Chandross and J. Ferguson, *J. Chem. Phys.*, **45**, 397, 3554 (1966).

(10) A. J. McCaffery and S. F. Mason, *Proc. Chem. Soc.*, 211 (1963).

(11) A. J. McCaffery, S. F. Mason, and B. J. Norman, *ibid.*, 259 (1964).

(12) E. Larsen, S. F. Mason, and G. H. Searle, *Acta Chem. Scand.*, **20**, 191 (1966).

(13) J. Mason and S. F. Mason, *Tetrahedron*, **23**, 1919 (1967).

(14) G. L. Johnson, *Inorg. Syn.*, **8**, 242 (1966)

(15) (a) F. Dickey, W. Fickett, and H. Lucas, *J. Am. Chem. Soc.*, **74**, 950 (1952), (b) B. Bosnich and W. Kneen, *Inorg. Chem.*, **9**, 2191 (1970).

(16) F. H. Westheimer, "Steric Effects in Organic Chemistry", M. Newman, ed, John Wiley and Sons. New York, 1956, Chap. 12.

(17) C. J. Hawkins, "Absolute Configuration of Metal Complexes, Wiley-Interscience, New York, 1971.

(18) F. Ciardelli and P. Salvadori, "Fundamental Aspects and Recent Developments in ORD and CD, Heyden & Sons Ltd. New York, 1973.

(19) J. Hidaka and B. E. Douglas, *Inorg. Chem.*, **3**, 1180 (1954).

(20) R. Grinter and S. Mason, *Trnas. Faraday Soc.*, **60**, 274 (1964)

(21) P. Newman, P. Rutkin, and K. Mislow, *J. Am. Chem. Soc.* **80**, 465 (1958).