

S-6, 6'-Dimethyl-2, 2'-diaminobiphenyl

리간드의 디클로로백금(II) 착물

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Dichloro Platinum(II) Complex of S-6, 6'-Dimethyl-2, 2'-diaminobiphenyl

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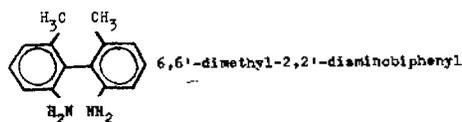
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요 약. *l*-Tartaric acid 를 이용하여 두자리 아민리간드인 6, 6'-dimethyl-2, 2'-diaminobiphenyl (dmdabp)를 분할하여 S광학이성질체인 *s*-dmdabp를 얻었다. S-dmdabp로부터 평면사각형 착물 [Pt(S-dmdabp)Cl₂]를 합성하였으며, 이 착물에서 S-dmdabp 리간드가 δ -conformation으로 배위되어 있음을 확인하였다.

ABSTRACT. The S-enantiomer of the 6, 6'-dimethyl-2, 2'-diaminobiphenyl (dmdabp) has been obtained by resolving dmdabp with *l*-tartaric acid. The square planar dichloro platinum(II) complex has been prepared with the optically active S-dmdabp, which is found to take the conformation in the [Pt(S-dmdabp)Cl₂] complex.

The ligand, 6, 6'-dimethyl-2, 2'-diaminobiphenyl (dmdabp), belongs to the skewed biaryl group. When this ligand is coordinated to a metal ion in square planar geometry, the only contribution to the optical activity of the complex is the conformation of the chelate ring which the ligand forms upon coordination.



Investigations involving dmdabp have so far been limited to octahedral complexes of cobalt (III)^{1,2}. In the present investigation the 6, 6'-dimethyl-2, 2'-diaminobiphenyl ligand has been resolved with the *l*-tartaric acid to obtain the

S-enantiomer and the dichloro platinum(II) complex of S-dmdabp in square planar geometry has been prepared to study the stereospecificity exhibited by this ligand.

EXPERIMENTAL

6, 6'-Dimethyl-2, 2'-diaminobiphenyl. This was prepared by the method known in the literature³. mp 135~136°C (*lit.*³, 136°C)

Resolution of 6, 6'-Dimethyl-2, 2'-diaminobiphenyl. The S-enantiomer of dmdabp was obtained by resolving the optically inactive dmdabp using *l*-tartaric acid after the procedure given by Meisenheimer and Horing⁴ with modifications. 8.2g of dmdabp was dissolved in 50ml of not absolute ethanol. 6.0g of

l-tartaric acid was dissolved in 35ml of hot aqueous ethanol. The two solutions were combined and stirred. When the solution cooled, white crystals formed. The product was filtered, washed with cold ethanol and dried overnight in vacuum. The *S*-dmdabp-*l*-tartrate was recrystallized twice from boiling absolute ethanol. The *S*-dmdabp-*l*-tartrate was dissolved in hot dilute HCl. Ammonia gas was bubbled through the solution. White crystals of *S*-dmdabp precipitated. The final product was collected by filtration, washed with cold ethanol and air dried. $[\alpha]_D = -109^\circ$ (C=0.7, dioxane) $[M]_D = -31.0$ K_2PtCl_4 This was purchased from Alfa Products, Danvers, Ma., U.S.A. and used without further purification.

$[Pt(S\text{-dmdabp})Cl_2]$ 0.40g of K_2PtCl_4 and 0.21g of *S*-dmdabp were suspended in 80ml of water. The mixture was stirred and heated gently until the temperature reached $70^\circ C$. Slowly a yellow-beige solid formed. The mixture was cooled and the yellow-beige solid was collected on a sintered glass funnel, washed successively with ice-cold water and aqueous ethanol, and air dried. The solid product was triturated with ether. The product was filtered, washed with ice-cold water and aqueous ethanol, and air dried.

Anal. Calcd. for $PtC_{14}H_{16}N_2Cl_2 \cdot 1.5H_2O$: C, 33.26; H, 3.79; N, 5.54; Cl, 14.04; Pt, 38.62. Found: C, 33.41; H, 3.81; N, 5.50; Cl, 14.31; Pt, 38.29.

Physical Measurements. The electronic absorption spectra were obtained using a Unicam SP 800A Spectrophotometer. Circular dichroism spectra were measured using a Jasco ORD/CD-5 Spectrophotometer. Elemental analyses were performed by Micro-Tech Laboratories, Skokie, Illinois, U.S.A.

RESULTS AND DISCUSSION

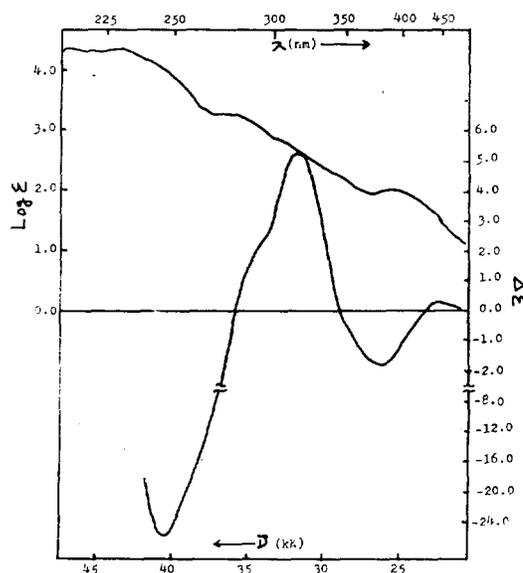


Fig. 1. Absorption and circular dichroism spectra of $Pt(S\text{-dmdabp})Cl_2$.

Fig. 1 shows the electronic absorption spectrum of $[Pt(S\text{-dmdabp})Cl_2]$. The ligand dmdabp contains two aromatic rings which should affect the intensity of the absorption spectrum of the $[Pt(S\text{-dmdabp})Cl_2]$ complex. Thus, all of the bands in the spectral range 210~450nm are more intense than the corresponding bands for the platinum(II) complexes of optically active propylenediamine and *trans*-1,2-diaminocyclohexane⁶. Comparison of the extinction coefficients of $[Pt(S\text{-dmdabp})Cl_2]$ with those of $[Pt(R\text{-pn})Cl_2]$ in the d-d range 300~450nm shows clearly that these ordinarily weak transitions are picking up considerable intensity from the nearby charge transfer bands.

Douglas, *et al.*² observed the same sort of masking of d-d transitions by the aromatic ligands in their study of $[Co(en)_2(dabp)]^{3+}$, $[Co(en)_2(R\text{-dmdabp})]^{3+}$, and $[Co(trien)(dabp)]^{3+}$, where trien and dabp are, respectively, triethylenetetraamine and 2,2'-diaminobiphenyl. Similar activity was noted with complexes coordinated with the ligands, 2,2'-bipyridyl

and 1, 10-orthophenanthroline⁶. The complexes, $[\text{Fe}(\text{bipy})_3]^{2+}$ and $[\text{Fe}(\text{phen})_3]^{2+}$, exhibit much higher absorption intensities in the visible region than is typical for d^6 complexes.

In the free ligand there is steric hindrance from the methyl groups at the 6 position. An activation energy for racemization of 17 kcal/mol or more at room temperature has been estimated for the dmdabp enantiomers.⁷ This high activation energy assures the configurational stability of this compound. Once the ligand is coordinated the barrier to racemization is even greater. From a molecular model of the free ligand it can be seen that S-dmdabp can coordinate only in the δ -conformation and only in the λ conformation in the case of R-dmdabp. This fact has been substantiated by Douglas, *et al.*² in their work on the stereospecific formation of R-dmdabp in the complex $\Delta(\lambda)-[\text{Co}(\text{en})_2(\text{R-dmdabp})]^{3+}$ as well as an X-ray crystallographic determination of R-dmdabp in the backbone of salicyladiminato tetradentate.⁸

The CD spectrum of $[\text{Pt}(\text{S-dmdabp})\text{Cl}_2]$ is shown in Fig. 1. In the long wavelength region there is a positive CD band centered at about 450nm and a much stronger negative CD band at about 380 nm. This negative CD band is not symmetrical which suggests that more than one component is present. Saito, *et al.*⁵ suggest that the E component should be found at a shorter wavelength than the A_2 component in the dichloro platinum(II) complexes of optically active diamines. For the complex $[\text{Pt}(\text{S-dmdabp})\text{Cl}_2]$ the weak positive CD band at 450nm is thus assigned to the A_2 component and the strong negative CD band at near 380 nm to the E component.

The circular dichroism spectrum of the free ligand S-dmdabp is shown in Fig. 2. Two peaks of opposite sign are observed in the 250~340

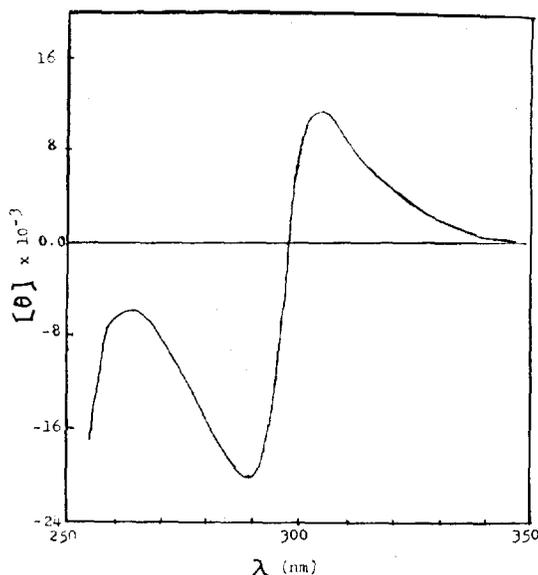


Fig. 2. Circular Dichroism spectrum of S-6,6'-dimethyl-2,2'-diaminobiphenyl.

nm region with the positive band at the lower energy. The CD spectrum of $[\text{Pt}(\text{S-dmdabp})\text{Cl}_2]$ has a strong positive CD band at 315 nm and a negative shoulder at near 250nm. The intensity and position of the band in the complex indicate that they derive much of their character from ligand transitions coupled with charge transfer. Since the pattern of the splitting in the ligand CD spectrum is indicative of the ligand conformation, the same would hold true for the spectrum of the complex.

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REFERENCES

1. T. Tanimura, H. Ito, J. Fugita, K. Saito, H. Hirai and K. Yamasaki, *J. Coord. Chem.*, **3**,

- 161 (1973).
2. W. T. Jordan, C. Y. Lin and B. E. Douglas, *ibid.*, **3**, 103 (1973).
3. R. B. Carlin and G. E. Foltz, *J. Amer. Chem. Soc.*, **78**, 1997 (1956).
4. J. Meisenheimer and M. Horring, *Chem. Ber.*, **60**, 1425 (1927).
5. H. Ito, J. Fugita and K. Saito, *Bull. Chem. Soc. Japan*, **40**, 2584 (1967).
6. J. Hidaka and B. E. Douglas, *Inorg. Chem.*, **3**, 1180 (1964) and references are therein.
7. F. H. Westheimer n "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., Ch. 12, 1956.
8. L. H. Piskolet, R. P. Taylor and W. Horrocks, *J. Amer. Chem. Soc.*, **91**, 5457 (1969).