

2, 2-비스(메틸아미노메틸)-1, 3-dioxolane의 백금(II) 착물*

田 環 鎭

경북대학교 공과대학 응용화학과

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Platinum(II) Complexes of 2, 2-bis(Methylaminomethyl)-1, 3-dioxolane*

Moo-Jin Jun

Department of Applied Chemistry, College of Engineering,
Kyungpook National University, Taegu, Korea

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요 약. 새로운 두자리 아민리간드 2, 2-bis(메틸아미노메틸)-1, 3-dioxolane(mexo)가 합성되었고 이 리간드로부터 디클로로 및 *trans*-R-cyclohexanediamine(R-chxn) 백금(II) 착물이 합성되었다. 착물은 평면 사각형의 구조이며 원소분석, 핵자기공명, 흡수분광법 및 원편광이색성분광분석을 이용하여 리간드와 착물의 구조를 설명하였다.

ABSTRACT. The synthesis of a bidentate secondary amine ligand, 2, 2-bis(methylaminomethyl)-2, 3-dioxolane(methylaminomethyl)-1, 3-dioxolane(mexo) and the preparation of dichloro and *trans*-R-cyclohexanediamine platinum(II) complexes of this ligand are reported. The structures of the ligand and complexes prepared have been elucidated via elemental analyses, nmr, electronic absorption, and CD spectra.

INTRODUCTION

The stereochemistry of platinum(II) and platinum(IV) amine complexes has been attractive subjects for study because of their high stability and favorable solubility properties. Secondary amines form stable chelates with Pt(II). The Pt(II) complexes of diethylenetriamine have been thoroughly studied with respect to complex

formation¹ and base substitution.^{2,3} Of interest are chelates of N-methylethylenediamine⁴⁻⁶ and N,N'-dimethylenediamine^{7,8} in which the coordinated secondary nitrogen exist as an asymmetric center due to the non-planar ring conformation.

In this paper we report the synthesis of a secondary amine ligand, 2, 2-bis(methylaminomethyl)-1, 3-dioxolane(mexo) and the preparation of dichloro and *trans*-R-cyclohexanediamine platinum(II) complexes of this ligand. As a bidentate the mexo ligand has been expected to

*Part of the work done at Department of Chemistry, University of Illinois at Chicago Circle, Chicago, Illinois, U. S. A.

show a six-membered non-planar chelate ring conformation. The ligand and complexes have been prepared in the following series of experiments.

EXPERIMENTAL

Reagents. 1,3-dichloropropane, ethylenglycol, cyclohexanediamine, 40% aqueous methylamine solution and *p*-toluenesulfonic acid were purchased from Aldrich Chemical Co., and K_2PtCl_4 from Ventron Corp.

Instrumental Measurements. Proton nmr spectra were recorded on a Varian T-60 spectrometer for 60 MHz spectra and on a Bruker HFX-90 90 MHz spectrometer using DSS as an internal standard in D_2O solvent. The electronic absorption spectra were measured on a Unicam SP 800A UV Spectrophotometer. CD spectra were obtained on a Jasco ORD/CD-5 Spectrophotometer.

Analyses. Elemental analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Michigan.

Preparation of 2,2-bis(Chloromethyl)-1,3-Dioxolane. 1,3-Dichloro 2-propanone (75.0 g) was dissolved in 300 ml benzene and ethylene glycol (42.2 g) was added while stirring, followed by 1.50 g of *p*-toluenesulfonic acid. The mixture was refluxed azeotropically for 18 hrs. at 84 °C. The benzene was removed on a rotary evaporator. The resulting oil was fractionally vacuum distilled and the 64 °C/2 mmHg fraction was collected: Yield 60.9 g.

Anal. Calcd. for $C_5H_8O_2Cl_2$: C, 35.12; H, 4.72; Cl, 41.46.

Found: C, 35.19; H, 4.78; Cl, 41.50.

Preparation of 2,2-bis(Methylaminomethyl)-1,3-Dioxolane Dihydrochloride(mexo·2HCl). Eleven sealed glass tubes containing a total of 20.35 g of 2,2-bis(chloromethyl)-1,3-

dioxolane and 165.0 g of 40% aqueous methylamine solution were heated at 141~145 °C for 13 hrs. The combined reaction mixtures were extracted with 15 portions of 50 ml anhydrous ether. The aqueous layer was evaporated on steam to give a yellow oil containing a white solid. The oil was triturated with 50 ml ethyl alcohol and the white solid filtered and washed with alcohol, ether, and air dried. A second crop was obtained by adding acetone to the filtrate, Yield 9.05 g.

Anal: Calcd. for $C_7H_{18}N_2O_2Cl_2$: C, 36.38; H, 6.98; N, 12.12; Cl, 30.68.

Found: C, 36.07; H, 7.87; N, 11.92; Cl, 30.25.

Preparation of $[Pt(mexo)Cl_2]$. To a solution containing 1.80 g of K_2PtCl_4 dissolved in 50 ml water was added 1.00 g of *mexo*·2HCl while stirring. The initial pH was 4.0. The mixture was heated and stirred at 85 °C. The solution was cooled and the platinum black filtered. The pH was slowly adjusted to pH 5.5 using 1.0 M NaOH. Platinum black was formed and filtered. The pH was slowly adjusted to pH 5.5 using 1.0 M NaOH. Platinum black was formed and filtered whenever the pH became greater than 6.0. The addition of NaOH was repeated until there was no drop in the pH. A total of 1.053 g platinum black was collected. The reaction mixture was evaporated on a steam bath, and a small amount of a light brown residue was filtered. The filtrate was evaporated to dryness to leave a yellow residue which was suspended in a small amount of H_2O , and filtered, washed with alcohol, ether, and air dried. A second crop can be isolated from the yellow filtrate. The first crop yield was 0.890 g. 48.4% theoretical.

Anal. Calcd. for $PtC_7H_{16}N_2O_2Cl_2$: C, 19.73; H, 3.78; N, 6.57; Pt, 45.77; Cl, 16.64.

Found: C, 19.56; H, 3.87; N, 6.68;
Pt, 46.03; Cl, 16.74.

Resolution of *trans*-Cyclohexanediamine.

This was resolved according to the method of Asperger and Liu.⁹

Preparation of [Pt(mexo)(R-chxn)]Cl₂. A suspension of 0.53g of [Pt(mexo)Cl₂] in 50 ml water was stirred and heated to 70 °C and a 15 ml aqueous solution of 0.156 g of *trans*-R-cyclohexanediamine(R-chxn) was added. The pH was initially 4.0. A total of 2.0 ml of 0.083 M LiOH was added dropwise keeping the pH less than 5.5, while the temperature was kept at 70~80 °C. The clear solution was evaporated on a steam bath and the product was isolated from alcohol and ether. Yield was 0.321 g, 79 % theoretical.

Anal. Calcd. for PtC₁₃H₃₀N₄O₂Cl₂: C, 28.89; H, 5.60; N, 10.37; Cl, 13.12; Pt, 36.10.
Found: C, 28.48, H, 5.53; N, 10.60; Cl, 12.95; Pt, 36.06.

RESULTS AND DISCUSSION

In the pmr spectrum of 2,2-*bis*(chloromethyl)-1,3-dioxolane (Fig. 1a) the 220 Hz resonance is assigned to the methylene protons(b) since this resonance would appear at a higher field

than the ethylene protons(d) (at 244 Hz). A comparison of the pmr spectrum of 2,2-*bis*(chloromethyl)-1,3-dioxolane (Fig. 1a) and that of 2,2-*bis*(methylaminomethyl)-1,3-dioxolane. (mexo)(Fig. 1b) would result in assigning the 170 Hz singlet to the N-methyl protons(c), the 208 Hz resonance to the methylene protons(b) outside the dioxolane ring and the 253 Hz singlet to the dioxolane ring protons. In the pmr spectrum (Fig. 2) of [Pt(mexo)(R-chxn)]Cl₂ the

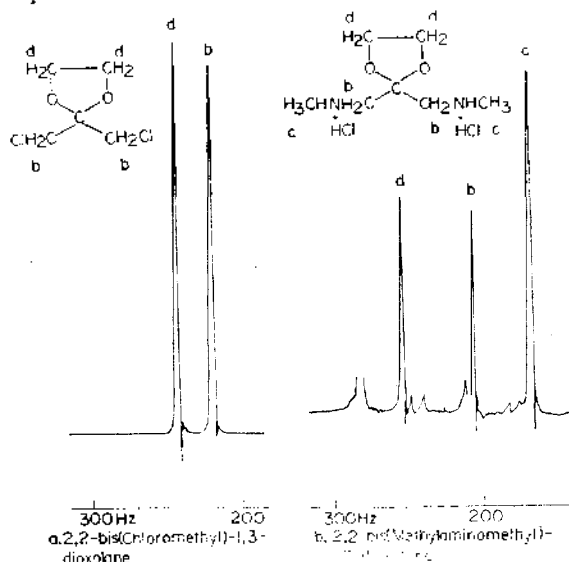


Fig. 1. The 60 MHz nmr spectra of: a, 2,2-*bis*(chloromethyl)-1,3-dioxolane and b, 2,2-*bis*(methylaminomethyl)-1,3-dioxolane. b, d and c indicate protons in the compounds shown in the Figure.



Fig. 2. The 90 MHz nmr spectra of [Pt(mexo)(R-chxn)]Cl₂. b, d and c indicate protons in mexo ligand as shown in Fig. 1.

broad high field bands are due to cyclohexane-diamine(chxn), the doublet centered at near 280 Hz to the N-methyl protons, and the peak at 304 Hz and its neighbors to the methylene and ethylene protons.

The $[\text{Pt}(\text{mexo})\text{Cl}_2]$ complex has been prepared from the reaction of K_2PtCl_4 with mexo ligand, and the $[\text{Pt}(\text{mexo})(\text{R-chxn})]\text{Cl}_2$ from the reaction of $[\text{Pt}(\text{mexo})\text{Cl}_2]$ with R-chxn.

It has been generally accepted using X-ray diffraction that the configuration of Pt(II) complexes is square-planar.¹⁰ The arrangement of chloride ions about Pt(II) in K_2PtCl_4 is square-planar.¹¹ The crystal structures of Pt(II) complexes with two nitrogen and two chloride donors and the structures of Pt(II) complexes with four nitrogen donors are also known to be square-planar. Anderson, *et al.* determined the crystal structure of *trans*- $[\text{Pt}(\text{NH}_3)_2(\text{NH}(\text{CH}_3)_2)_2]\text{Cl}_2$ and found it to be square-planar.¹²

The electronic structures of d^8 complexes have

Table 1. Absorption spectrum of K_2PtCl_4 .¹⁵

Absorption Band	ν_{max}^*	ϵ_{max}	Excited state assignment
1	17.1 sh*	2.7	$^3A_{2g}$
2	21.1	12.9	3E_g
3	25.3	52.1	$^1A_{2g}$
4	30.9	62.5	1E_g
5	38.5 sh	456	CT (forbidden)
6	44.4	6300	CT
7	46.3	8080	

* $\nu_{\text{max}} \times 10^{-3} \text{cm}^{-1}$; sh, shoulder.

Table 2. Absorption Spectra of $[\text{Pt}(\text{mexo})\text{Cl}_2]$ and $[\text{Pt}(\text{mexo})(\text{R-chxn})]\text{Cl}_2$.

Complex	Band2(3E_g)		Band3($^1A_{2g}$)		Band4(1E_g)	
	ν_{max}^*	ϵ_{max}	ν_{max}	ϵ_{max}	ν_{max}	ϵ_{max}
$[\text{Pt}(\text{mexo})\text{Cl}_2]$	28.7	37.9	33.2sh*	88	37.0	160
$[\text{Pt}(\text{mexo})(\text{R-chxn})]^{2+}$	35.8	31.3	41	142	44.1	378

* $\nu_{\text{max}} \times 10^{-3} \text{cm}^{-1}$; sh, shoulder.

been studied extensively, and PtCl_4^{2-} is the most thoroughly studied⁸ complex ion.¹³⁻¹⁶ Table 1 shows the absorption spectrum of K_2PtCl_4 .¹⁵ All of the absorption spectra for the complexes studied in this work (Table 2 and Fig. 3) show d-d bands that can be assigned according to Ito, *et al.*¹⁵ In general these absorption spectra retain the features of the PtCl_4^{2-} spectrum, but as more nitrogen donor atoms are added, the spectrum is shifted toward higher energy and band 3 disappears. Ito reported similar results for R-pn complexes of Pt(II) and Pd(II).¹⁵ Fig. 3 shows that as one diamine chelate ligand is substituted onto PtCl_4^{2-} , there is shift of approximately $7000 \sim 8000 \text{cm}^{-1}$ for each band toward higher energy, and band 3 nearly disappears under band 4. As expected, the shift toward higher energy occurs as two more nitrogen donor atoms are coordinated to Pt(II) in $[\text{Pt}(\text{mexo})(\text{R-chxn})]^{2+}$ ion. Bands 2 and 4 are both shifted by about $7000 \sim 8000 \text{cm}^{-1}$, and band 3 disappears except for a slight asymmetry on the low energy side of band 4.

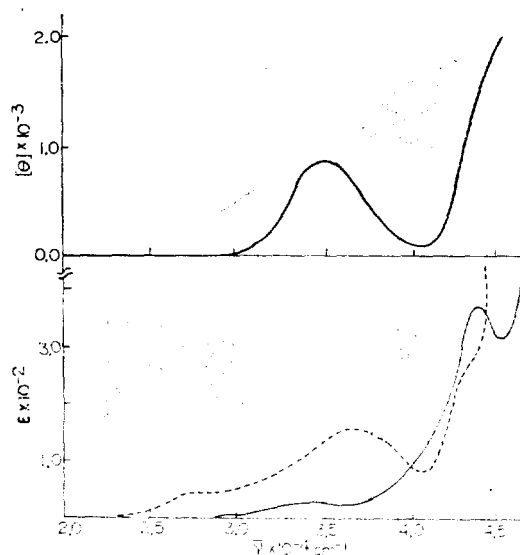


Fig. 3. Electronic absorption spectra² of $[\text{Pt}(\text{mexo})\text{Cl}_2]$ (—), and CD and electronic absorption spectra of $[\text{Pt}(\text{mexo})(\text{R-chxn})]^{2+}$ (.....).

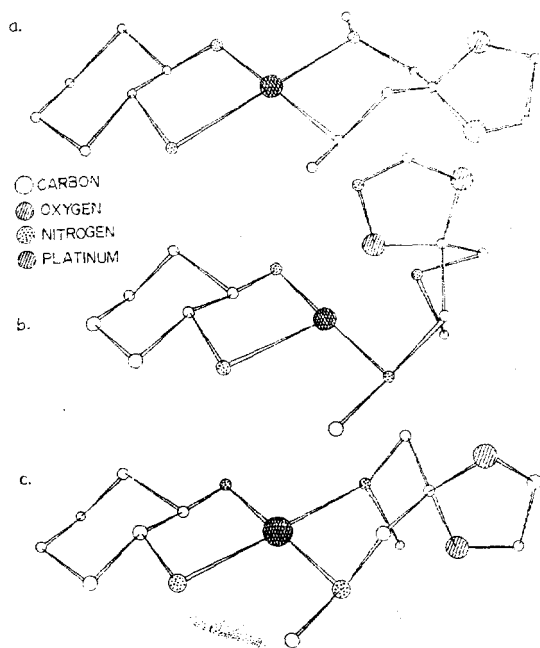


Fig. 4. Sketch of $[\text{Pt}(\text{mexo})(\text{R-chxn})]^{2+}$ showing the mexo chelate ring in: a, the skew-boat conformation, b, the boat conformation and c, the chair conformation.

The CD spectrum of the $[\text{Pt}(\text{mexo})(\text{R-chxn})]^{2+}$ ion (Fig. 3) shows positive rotation in the region of bands 2 and 4. Band 3 is not observed except for a slight shoulder. Fig. 4a is a sketch of $[\text{Pt}(\text{mexo})(\text{R-chxn})]^{2+}$ with the six-membered mexo chelate ring in the skew-boat conformation, where both N-methyl groups are equatorial. Fig. 4b and Fig. 4c show the same complex with the chelate ring, respectively, in boat conformation and in chair conformation, in each of which one N-methyl group is axial. Although the skew-boat form seems to be favored (because of both N-methyl groups in equatorial positions) and the chair form seems to be less favored (because of the nonbonded interaction between one axial N-methyl group and the dioxolane ring), it is not, at this stage, possible to tell exactly which conformation the

mexo chelate ring would take. It is known that, in solution, the six-membered chelate ring of Pt(II) complexes undergo rapid conformational interconversion compared to the nmr time scale.¹⁷ The mexo chelate ring is then probably best explained in terms of an equilibrium mixture among those possible conformations. In all cases the five-membered R-chxn chelate ring must take a λ^{18} conformation since the absolute configuration of chxn is known and both of the amino groups of chxn should be equatorial. Contributions to the CD rotational strength of square-planar Pt(II) complexes arise from either the effect of an asymmetric donor atom, the conformation of the chelate ring, the effect of an asymmetric center on the ring, or a combination of all three. In the $[\text{Pt}(\text{mexo})(\text{R-chxn})]^{2+}$ ion the effect of an asymmetric donor atom can not be considered because the RR and SS N* configurations should be formed in equal amounts unless there is some source of dissymmetry present. The CD curve observed in this study is therefore from the conformation of the chxn chelate ring and the asymmetric centers on the chxn ring.

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