

## 글리신 및 스티렌의 백금(II) 착물

田 玗 鏞 · 피 터 후\*

경북대학교 공과대학 응용화학과

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## Platinum (II) Complexes Containing Glycine and Styrene

Moo Jin Jun and Peter P. Fu\*

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

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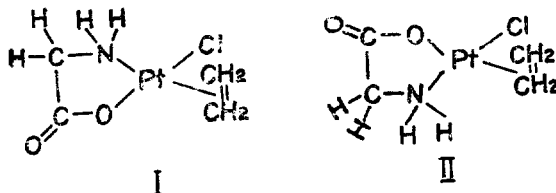
요 약. Glycine (또는 glycino 음이온)과 styrene 을 리간드로 하는 백금(II) 착물이 합성되었다. 적외선 분광법에 의하면 *N*-트랜스 이성체에서는 킬레이트를 이루는 glycino 음이온의 질소원자가 styrene 에 대하여 트랜스 위치에 있음이 확인되었다.

**ABSTRACT.** Several Pt(II) complexes containing glycine (or glycino anion) and styrene have been prepared, and their structures have been confirmed by infrared spectroscopy. The results confirm the structure of chloro(glycino)(styrene)platinum(II) in which the nitrogen atom of the chelated glycino anion is coordinated to the platinum in the *trans* position to styrene (*N-trans* isomer).

### INTRODUCTION

Since both olefin and glycine form a wide variety of Pt(II) complexes, it is possible to prepare the Pt(II) complexes containing both olefin and glycine. The first complex of this type has been prepared by Kieft and Nakamoto<sup>1</sup> by reacting Zeise's salt with glycine, and has the formula of PtCl(C<sub>2</sub>H<sub>4</sub>)(gly) (gly=glycino anion, NH<sub>2</sub>CH<sub>2</sub>COO<sup>-</sup>). They proposed structure I in which the nitrogen atom of the chelated glycino anion is coordinated to the platinum

\*Department of Chemistry, Illinois Institute of Technology Chicago, Illinois, U. S. A



atom in the position *trans* to ethylene (*N-trans* isomer). They explained that structure I was preferred to structure II (*O-trans* isomer) because ethylene is one of the strongest *trans*-directing groups, and that the Pt atom prefers to form a bond with the nitrogen rather than the oxygen atom of the glycino anion. Recently, Nakamoto

*et al.*<sup>2</sup>. prepared Pt(II)-ethylenec complexes of both structures I and II with optically active alanine and proline. We have attempted to prepare the styrene analogs of I and II. In this paper we report the synthesis and spectra of four novel Pt(II) complexes containing glycine and styrene. The distinction of the geometrical isomers (*cis* and *trans* and N and O-*trans* isomers) has been made based on their infrared spectra.

### EXPERIMENTAL

**Preparation of Compounds.** (1) *cis*-PtCl<sub>2</sub>-(C<sub>6</sub>H<sub>5</sub>CH=CH<sub>2</sub>)(GlyH): *cis*-PtCl<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)(glyH)·H<sub>2</sub>O<sup>2,3</sup> (5.0×10<sup>-3</sup> mole) was dissolved in 30 ml of acetone, and about 0.01 mole of styrene was added. The solution was heated for two hours on a steam bath and the temperature was maintained at about 40°C. The solution was evaporated using nitrogen gas, and washed several times with ether to remove excess styrene. The residue was then dissolved in a minimum amount of absolute ethanol, and about 20 ml of ether was added to the solution. Yellow needle crystals were slowly precipitated over a 24 to 48 hour period in each preparation. The product was filtered off, washed with ether, and dried under vacuum over P<sub>2</sub>O<sub>5</sub>.

*Anal.* Calcd for C<sub>10</sub>H<sub>12</sub>Cl<sub>2</sub>NO<sub>2</sub>Pt: C, 26.98; H, 2.94; N, 3.15. Found: C, 27.12; H, 3.02; N, 3.14.

(2) PtCl(C<sub>6</sub>H<sub>5</sub>CH=CH<sub>2</sub>)(gly) (O-*trans* isomer): This complex was prepared by dissolving *cis*-PtCl<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>CH=CH<sub>2</sub>)(glyH) in a minimum amount of warm water (about 50°C). The solution was warmed on a steam bath for half an hour. After cooling it in an ice bath, the product was filtered off, washed with ethanol and ether, and then dried over P<sub>2</sub>O<sub>5</sub>.

*Anal.* Calcd. for C<sub>10</sub>H<sub>12</sub>ClNO<sub>2</sub>Pt: C, 29.38; H, 2.96; N, 3.43. Found: C, 30.31, H, 3.09;

N, 3.38.

(3) PtCl(C<sub>6</sub>H<sub>5</sub>CH=CH<sub>2</sub>)(gly): (N-*trans* isomer). K[PtCl<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>CH=CH<sub>2</sub>)]<sup>4</sup> (0.01 mole) and glycine (0.01 mole) and glycine (0.01 mole) were dissolved in 40 ml of water and KHCO<sub>3</sub> was added to the solution by portions to keep the pH value between 6~7. The solution was heated on a steam bath for 5 minutes. The solution was cooled to room temperature and evaporated under moving air until pale yellow crystals precipitated. The product was filtered. Our effort to purify this product by washing with a small amount of cold water, ethanol and ether proved fruitless. Therefore no analysis was performed. The question, why only in the case of N-*trans* isomer the purification is so difficult, is open. This compound was used as the starting material to prepare the following complex.

(4) *Trans*-PtCl<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>CH=CH<sub>2</sub>)(glyH): This complex was prepared by dissolving PtCl(C<sub>6</sub>H<sub>5</sub>CH=CH<sub>2</sub>)(gly) (N-*trans* isomer) in a minimum amount of concentrated HCl and then by evaporating it to complete dryness in a desiccator over P<sub>2</sub>O<sub>5</sub>. The product was washed with absolute ethanol and ether.

*Anal.* Calcd. for C<sub>10</sub>H<sub>13</sub>Cl<sub>2</sub>NO<sub>2</sub>Pt: C, 26.98; H, 2.94; N, 3.15. Found: C, 26.80; H, 3.05; N, 3.26.

**Spectral Measurement.** A Beckman IR-12 infrared spectrophotometer was employed to obtain the infrared spectra in the 4000~300 cm<sup>-1</sup> region. The spectra were obtained using the KBr-disk method. The UV spectra were obtained using a Cary Model 14 spectrophotometer in the 6500~2100 Å region. All spectral measurements were made at room temperature.

**Symbols Used.** The following symbols were utilized in describing the modes of vibration:  $\nu$ , stretching;  $\delta$ , bending;  $\rho_r$ , rocking;  $\rho_w$ , wagging;  $\rho_t$ , twisting;  $\pi$ , out-of-plane bending; *s*, symmetric; *as*, asymmetric; *def*, deforma-

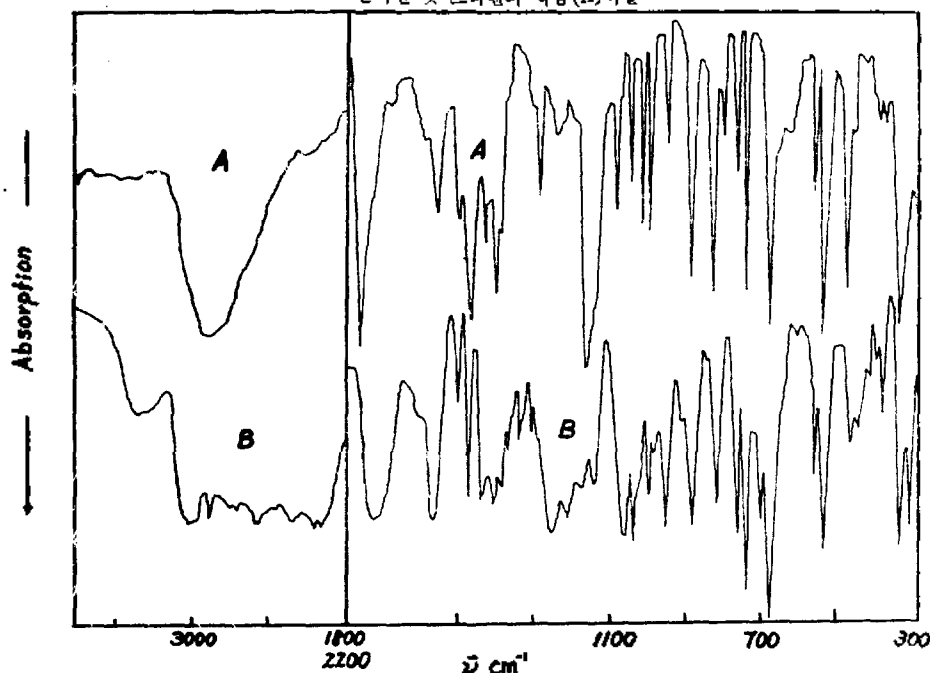


Fig. 1. Infrared spectra of A, *trans*-dichloro(styrene)(glycine)-platinum(II) and B, *cis*-dichloro(styrene)(glycine)-platinum(II).

tion. Intensities of absorption bands are symbolized: *v*, very; *b*, broad; *s*, strong; *m*, medium; *w*, weak; *sh*, shoulder.

## RESULTS

**Preparation.** Four novel Pt(II) complexes containing glycine and styrene have been prepared. *cis*-PtCl<sub>2</sub>(str)(glyH) (str=styrene and glyH=glycine) has been prepared from *cis*-PtCl<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)(glyH) by substituting ethylene by styrene and obtained as yellow crystals. The *N-trans* isomer of PtCl(str)(gly) was prepared essentially by the method of Kieft and Nakamoto<sup>1</sup> except that K[PtCl<sub>3</sub>(str)] was used as the starting material. No analysis was performed due to the instability of the complex. The structure, we feel, is confirmed through an analysis of its infrared spectrum, and a comparison of this spectrum with that expected for PtCl<sub>2</sub>(glyH)<sub>2</sub><sup>5</sup> and K[PtCl<sub>3</sub>(str)]<sup>4</sup> as well as the fact that it can be used as the starting material

to prepare *trans*-PtCl<sub>2</sub>(str)(glyH), which has a good analytical result. *O-trans* isomer of PtCl(str)(gly) and *trans*-PtCl<sub>2</sub>(str)(glyH) were derived from *cis*-PtCl<sub>2</sub>(str)(glyH) and *N-trans* isomer of PtCl(str)(gly), respectively, through hydrolysis.

**Infrared Spectra.** (1) *Trans*-PtCl<sub>2</sub>(str)(glyH): The spectrum is shown in Fig. 1. The band assignments given Table 1 were obtained by comparing the observed frequencies with those<sup>4-8</sup> of dichlorodi(glycine) platinum(II) and potassiumtrichloro(styrene) platinum(II). Two strong bands at 3210 and 3140 cm<sup>-1</sup> are due to N—H stretching vibrations. The other two strong bands at 3000 and 2960 cm<sup>-1</sup> are assigned to C—H stretching vibrations. The stretching vibration of the carboxyl group is at 1769 cm<sup>-1</sup> which is 60 cm<sup>-1</sup> higher than that of the diglycine complex, PtCl<sub>2</sub>(glyH)<sub>2</sub>. The C=C stretching vibration of coordinated styrene is at 1513 cm<sup>-1</sup>, 5 cm<sup>-1</sup> lower than that of the tri-

Table 1. Comparison of the observed frequencies of *trans*- and *cis*-PtCl<sub>2</sub>(glyH)<sub>2</sub>, *trans*- and *cis*-PtCl<sub>2</sub>(str)(glyH), and K(PtCl<sub>3</sub>(str))

PtCl <sub>2</sub> (glyH) <sub>2</sub>		PtCl <sub>2</sub> (str)(glyH)		K(PtCl <sub>3</sub> (str))	Band Assignment
<i>Trans</i>	<i>Cis</i>	<i>Trans</i>	<i>Cis</i>		
3290( <i>s</i> )	3280( <i>s</i> ) 3272( <i>sh</i> )	3210( <i>s</i> ) 3140( <i>s</i> )	3220( <i>s</i> ) 3125( <i>s</i> )		} ν (N—H)
3240( <i>s</i> )	3240( <i>s</i> )				
2950( <i>w</i> )	2940( <i>w</i> )	3000( <i>s</i> ) 2960( <i>s</i> )	2980( <i>s</i> ) 2890( <i>s</i> )	2980( <i>s</i> ) 2870( <i>s</i> )	} ν (C—H)
1708( <i>s</i> )	1730( <i>s</i> )	1769( <i>s</i> )	1720( <i>s</i> )		
1580( <i>s</i> )	1590( <i>s</i> ) 1573( <i>sh</i> )	1599( <i>w</i> ) 1565( <i>m</i> )	1580( <i>s</i> )	1597( <i>w</i> ) 1583( <i>w</i> )	} δ (CH <sub>2</sub> ) or ν(C=C)φ
		1513( <i>m</i> )	1518( <i>m</i> )	1518( <i>w</i> )	
		1485( <i>s</i> ) 1447( <i>m</i> )	1488( <i>s</i> ) 1445( <i>s</i> )	1488( <i>s</i> ) 1455( <i>s</i> ) 1448( <i>s</i> )	} ν (C=C), φ
1442( <i>m</i> )	1420( <i>s</i> )	1425( <i>s</i> )	1428( <i>s</i> )		
1415( <i>m</i> )	1400( <i>s</i> )	1400( <i>m</i> )	1405( <i>w</i> ) 1385( <i>w</i> ) 1375( <i>w</i> )		} δ(NH <sub>2</sub> ) or δ(CH <sub>2</sub> ) δ(OH) or ν (C—O)
1360( <i>w</i> )		1316( <i>w</i> )		1316( <i>w</i> )	
1345( <i>w</i> )	1345( <i>s</i> )	1300( <i>m</i> )	1255( <i>s</i> )		} ρ <sub>w</sub> or δ <sub>r</sub> (CH) <sub>2</sub> or δ(C—H)
1262( <i>s</i> )	1255( <i>s</i> )	1255( <i>w</i> )	1215( <i>s</i> )	1260( <i>w</i> )	
1207( <i>m</i> )	1180( <i>s</i> )	1170( <i>s</i> ) 1157( <i>m</i> ) 1102( <i>sh</i> ) 1055( <i>m</i> )	1185( <i>s</i> ) 1155( <i>s</i> ) 1080( <i>s</i> ) 1050( <i>m</i> )	1190( <i>m</i> ) 1081( <i>m</i> ) 1055( <i>m</i> ) 1028( <i>m</i> )	} δ(C—H), φ o ρ <sub>w</sub> (NH) <sub>2</sub> or ρ <sub>w</sub> (CH) <sub>2</sub>
		1005( <i>m</i> )	1013( <i>m</i> )	1005( <i>m</i> )	
		962( <i>m</i> )	970( <i>s</i> )	960( <i>m</i> )	ρ <sub>w</sub> (—C—H) ρ <sub>w</sub> (CH) <sub>2</sub>
926( <i>m</i> )	920( <i>w</i> )	900( <i>s</i> ) 843( <i>s</i> ) 823( <i>w</i> )	898( <i>s</i> ) 837( <i>s</i> )	847( <i>w</i> ) 828( <i>m</i> )	} ρ <sub>r</sub> (NH) <sub>2</sub> or ρ <sub>r</sub> (CH) <sub>2</sub>
		783( <i>m</i> ) 758( <i>s</i> )	780( <i>s</i> ) 755( <i>s</i> )	780( <i>s</i> ) 752( <i>s</i> )	
			720( <i>m</i> )		π(OH)
		692( <i>s</i> )	695( <i>s</i> )	692( <i>s</i> )	π(C—H), φ
555( <i>w</i> )	552( <i>w, b</i> )	566( <i>m</i> ) 544( <i>s</i> ) 486( <i>s</i> )	568( <i>m</i> ) 550( <i>s</i> ) 480( <i>m</i> )	568( <i>s</i> ) 550( <i>s</i> ) 492( <i>m</i> )	} δ(C—C—C), φ or ν(Pt—N)
		401( <i>w</i> )	395( <i>m</i> )		
344( <i>s</i> )	356( <i>s</i> ) 339( <i>s</i> )	333( <i>s</i> )	343( <i>s</i> ) 315( <i>s</i> )	340( <i>s</i> ) 313( <i>s</i> )	ν(Pt—str) ν(Pt—Cl)

chlorostyrene complex. This band is of medium intensity, whereas the corresponding band in the ethylene complex is very weak, because the C=C bond of styrene is not symmetric as that of ethylene. The bands at 1565 and 1485 cm<sup>-1</sup> are due to the phenyl C=C stretching vibrations of styrene. Many bands dueto styrene appear in the region from 1300

to 1000 cm<sup>-1</sup>. Only tentative assignments are given for this region. The band at 1005 cm<sup>-1</sup> is attributed to the —C—H out-of-plane bending mode of coordinated styrene. It has exactly the same value as that of the trichlorostyrene complex. The C—H out-of-plane bending vibrations of the phenyl group give three bands at 793, 750, and 692 cm<sup>-1</sup>, which are slightly

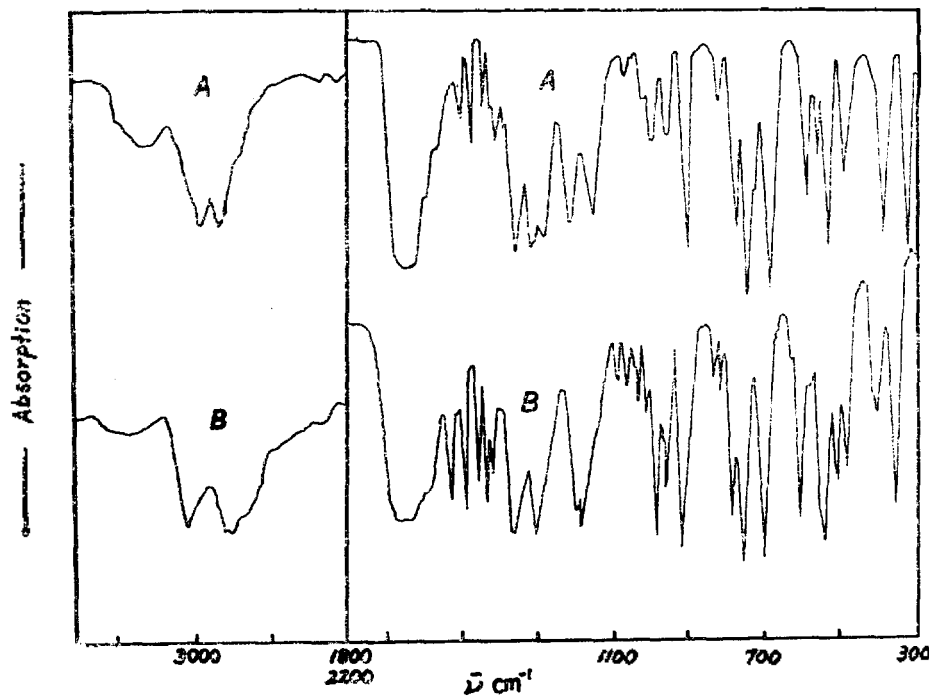


Fig. 2. Infrared spectra of O-*trans* isomer (A) and N-*trans* isomer (B) of chloro(strene)(glycino) platinum(II).

higher than those of the trichlorostyrene complex. Three sharp bands at 566, 544, and 486  $\text{cm}^{-1}$  are assigned to the C—C—C bendings of styrene. Usually, the Pt—N stretching band appears at about 550  $\text{cm}^{-1}$ . In this complex it is hidden by the three bands mentioned above. The Pt—str stretching is at 401  $\text{cm}^{-1}$ , which is 9  $\text{cm}^{-1}$  higher than that of the trichlorostyrene complex. The strong band at 333  $\text{cm}^{-1}$  is assigned to the Pt—Cl stretching. This frequency is about 10  $\text{cm}^{-1}$  lower than that of diglycine complex.

(2) *Cis*-PtCl<sub>2</sub>(str)(glyH): The spectrum is also shown in Fig 1. Table 1 also lists the frequencies and band assignments obtained by comparing the observed frequencies with those of dichlorodiglycineplatinum (II).<sup>5-8</sup> The *cis* form shows more bands than the *trans* form due to the difference in symmetries of these two types of compounds. The N—H and C—H stretching frequencies are similar to those of the

*trans* form. The carbonyl stretching vibration is at 1720  $\text{cm}^{-1}$ , which is lower than that of *trans* form. The C=C stretching band of coordinated styrene is at 1518  $\text{cm}^{-1}$ . This frequency is the same as that of the trichlorostyrene complex, but is 5  $\text{cm}^{-1}$  higher than that of the *trans* form. The region from 1423 to 1050  $\text{cm}^{-1}$  shows many bands which are difficult to assign. Only tentative assignments are given in Table 1. The band at 1013  $\text{cm}^{-1}$  is attributed to the —C—H out-of-plane bending of the coordinated styrene. Three strong bands at 780, 755, and 695  $\text{cm}^{-1}$  are assigned to C—H out-of-plane bendings of the phenyl group. The Pt—N stretching is hidden by the sharp bands due to C—C—C bendings of the phenyl group. The Pt—str stretching is at 395  $\text{cm}^{-1}$ , 6  $\text{cm}^{-1}$  lower than that of the *trans* form. Two strong bands at 343 and 315  $\text{cm}^{-1}$  are due to Pt—Cl stretchings. This result confirms the *cis* structure since the *trans* form shows only one Pt—Cl stretching.

Table 2 Comparison of the observed frequencies of K[PtCl<sub>2</sub>(gly)], N- and O-*trans* isomers of PtCl(str)(gly), and K[PtCl<sub>3</sub>(str)]

K[PtCl <sub>2</sub> (gly)]	PtCl(str)(gly)		K[PtCl <sub>3</sub> (str)]	Band assignment
	N- <i>Trans</i> isomer	O- <i>Trans</i> isomer		
3260( <i>s</i> ) 3220( <i>s</i> )	3230( <i>s</i> )	3220( <i>s</i> ) 3100( <i>s</i> )		} $\nu(\text{N-H})$
	3000( <i>s</i> ) 2930( <i>s</i> )	2990( <i>m</i> )	2980( <i>s</i> ) 2870( <i>s</i> )	
1645( <i>s</i> )	1650( <i>s</i> )	1660( <i>s</i> )		$\nu(\text{C=O})$
1575( <i>s</i> )	1585( <i>m</i> )	1605( <i>s</i> ) 1585( <i>s</i> )	1597( <i>w</i> ) 1583( <i>w</i> )	} $\delta(\text{CH}_2)$ or $\nu(\text{C=C})$
	1525( <i>m</i> )	1515( <i>m</i> )	1518( <i>m</i> )	
	1488( <i>m</i> ) 1446( <i>m</i> )	1488( <i>s</i> ) 1450( <i>w</i> )	1488( <i>s</i> ) 1455( <i>s</i> ) 1448( <i>s</i> )	} $\nu(\text{C=C})$
1412( <i>m</i> )	1418( <i>m</i> ) 1408( <i>m</i> )	1422( <i>w</i> )		
1355( <i>s</i> )	1362( <i>s</i> )	1368( <i>s</i> )		$\nu(\text{C-O})$
1310( <i>s</i> )	1300( <i>s</i> )	1320( <i>s</i> )		$\nu(\text{C-N})$
1303( <i>sh</i> )		1297( <i>s</i> ) 1230( <i>s</i> )	1260( <i>w</i> )	$\delta(\text{C-H})$ $\delta(\text{OH})$ or $\rho_r(\text{CH}_2)$
1160( <i>s</i> ) 1025( <i>w</i> )	1193( <i>s</i> ) 1180( <i>s</i> ) 1080( <i>w</i> ) 1060( <i>w</i> ) 1024( <i>w</i> )	1172( <i>s</i> ) 1085( <i>w</i> ) 1055( <i>w</i> )	1190( <i>m</i> ) 1081( <i>m</i> ) 1055( <i>m</i> ) 1028( <i>m</i> ) 1013( <i>m</i> )	} $\rho_w(\text{CH}_2)$ or $\delta(\text{C-H})$ , or $\rho_w(\text{NH}_2)$
	982( <i>s</i> ) 953( <i>m</i> )	1010( <i>m</i> ) 965( <i>m</i> )	1005( <i>m</i> ) 960( <i>m</i> )	
	908( <i>s</i> ) 842( <i>w</i> )	912( <i>s</i> ) 833( <i>w</i> )	847( <i>w</i> ) 828( <i>m</i> )	} $\rho_r(\text{CH}_2)$
	778( <i>s</i> ) 750( <i>s</i> ) 692( <i>s</i> )	775( <i>s</i> ) 755( <i>s</i> ) 692( <i>s</i> )	780( <i>s</i> ) 752( <i>s</i> ) 692( <i>s</i> )	
585( <i>s</i> )	595( <i>s</i> )	605( <i>s</i> )		$\pi(\text{C=O})$
550( <i>w</i> )	528( <i>s</i> ) 502( <i>m</i> ) 476( <i>m</i> )	573( <i>m</i> ) 548( <i>s</i> ) 500( <i>s</i> )	568( <i>s</i> ) 550( <i>s</i> ) 492( <i>m</i> )	} $\delta(\text{C-C-C})$ , $\phi$ and $\nu(\text{Pt-N})$
510( <i>s</i> )	501( <i>s</i> ) 399( <i>m</i> )	502( <i>s</i> ) 400( <i>s</i> )	500( <i>s</i> ) 392( <i>m</i> )	
388( <i>s</i> )	396( <i>sh</i> )	395( <i>sh</i> )		$\nu(\text{Pt-O})$
320( <i>s</i> )	346( <i>s</i> )	335( <i>s</i> )	340( <i>s</i> ) 313( <i>s</i> )	} $\nu(\text{Pt-Cl})$
	300( <i>w</i> )	300( <i>w</i> )		

(3) PtCl(str)(gly) (*N-trans* isomer): The spectrum is shown in Fig 2. Table 2. lists the frequencies. The band assignments were made by comparing the observed frequencies with those of K[PtCl<sub>2</sub>(gly)] and K[PtCl<sub>3</sub>(str)].<sup>4-8</sup> The strong band at 1650 cm<sup>-1</sup> is due to the car-

boxyl stretching. The low frequency of this band indicates that glycine is in a chelate form.<sup>1</sup> A medium intensity peak at 1525 cm<sup>-1</sup> is assigned to the C=C stretching of coordinated styrene. A strong C-N stretching band is found at 1300 cm<sup>-1</sup>. This frequency is 10 cm<sup>-1</sup> lower

than that of  $K[PtCl_2(gly)]$ . Three strong peaks at 778, 750, and  $692\text{ cm}^{-1}$  are attributed to the  $-C-H$  out-of-plane bendings of the phenyl group. They have almost the same values as those of the trichlorostyrene complex. The  $C=O$  out-of-plane bending is assigned at  $595\text{ cm}^{-1}$  which is  $10\text{ cm}^{-1}$  higher than that of the dichloroglycine complex. The Pt-N stretching is again hidden by the broad bands due to the C-C-C bending vibrations of the phenyl group at 528, 502, and  $476\text{ cm}^{-1}$ . The ring deformation band characteristic of the chelated glycine at  $501\text{ cm}^{-1}$  is also overlapped by these broad bands. The Pt-str and Pt-O stretching vibrations overlap on each other at ca.  $400\text{ cm}^{-1}$ . As a result, one broad band is observed in this region. The strong band at  $346\text{ cm}^{-1}$  is attributed to the Pt-Cl stretching.

(4)  $PtCl(str)(gly)$  (O-*trans* isomer): The spectrum is shown in Fig 2. Table 2 gives the frequencies and the band assignments. The strong carboxyl stretching band is at  $1660\text{ cm}^{-1}$ , which is  $10\text{ cm}^{-1}$  higher than that of the N-*trans* isomer. A medium intensity peak at  $1515\text{ cm}^{-1}$  is due to the C=C stretching of the coordinated styrene. This band is  $10\text{ cm}^{-1}$  lower than that of the N-*trans* isomer. The band at  $1320\text{ cm}^{-1}$  is assigned to the C-N stretching of glycine. Three strong bands at 775, 755, and  $695\text{ cm}^{-1}$  are attributed to the  $-C-H$  out-of-

plane bendings of the phenyl group. The carbonyl out-of-plane bending is at  $605\text{ cm}^{-1}$ , which is  $10\text{ cm}^{-1}$  higher than that of the N-*trans* isomer. The Pt-N stretching band is again hidden by the broad C-C-C bending bands of phenyl group at 573, 548, and  $500\text{ cm}^{-1}$ . These values are quite different from those of the N-*trans* isomer, but similar to those of the trichlorostyrene complex. The ring deformation band of the chelated glycine is at  $502\text{ cm}^{-1}$ , which is also overlapped by these broad bands. The Pt-str stretching is at  $400\text{ cm}^{-1}$ , exactly the same position as that of the N-*trans* isomer. A shoulder at  $395\text{ cm}^{-1}$  is attributed to the Pt-O stretching. The strong peak at  $335\text{ cm}^{-1}$  is definitely due to the Pt-Cl stretching.

### DISCUSSION

Nakamoto and his coworkers<sup>6-8</sup> investigated the infrared spectra of a number of platinum-olefin complexes in the range from 4000 to  $300\text{ cm}^{-1}$ . From the normal coordinate analysis, they concluded that the Pt-C<sub>2</sub>H<sub>4</sub> stretching force constant is 2.23 mdyne/A including repulsive terms between nonbonded atoms. A semiempirical Self-Consistent Charge and Configuration (SCCC) molecular orbital calculation has been carried out on Zeise's salt by Moore.<sup>9</sup> Earlier Grinberg and Volshtein<sup>10</sup> have shown that glycine in particular coordinates to Pt(II) both

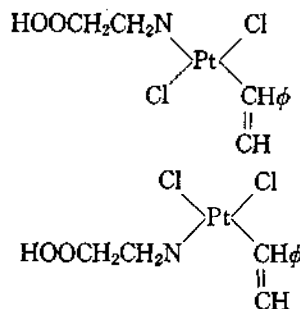
Table 3. Observed frequencies of Pt(II) complexes containing glycine and styrene ( $\text{cm}^{-1}$ ).

PtCl <sub>2</sub> (glyH) <sub>2</sub>		PtCl <sub>2</sub> (str)(glyH)		K(PtCl <sub>3</sub> (str))	Band assignment
<i>Trans</i>	<i>Cis</i>	<i>Trans</i>	<i>Cis</i>		
1708( <i>s</i> )	1730( <i>s</i> )	1769( <i>s</i> )	1720( <i>s</i> )		$\nu(\text{COOH})$
		1513( <i>m</i> )	1518( <i>m</i> )	1518( <i>w</i> )	$\nu(\text{C}=\text{C})$
555( <i>w</i> )	552( <i>w</i> )	(hidden) <sup>a</sup>	(hidden) <sup>a</sup>		$\nu(\text{Pt}-\text{N})$
		401( <i>m</i> )	395( <i>s</i> )	392	$\nu(\text{Pt}-\text{str})$
344( <i>s</i> )	356( <i>s</i> )	333( <i>s</i> )	343( <i>s</i> )	340( <i>s</i> )	$\nu(\text{Pt}-\text{Cl})$
	339( <i>s</i> )		315( <i>s</i> )	313	

<sup>a</sup> Hidden by styrene absorption.

as uni- and bi-dentate ligands. In unidentate glycine complexes, the ligand to metal bond occurs through the nitrogen atom while in bi-tentate complexes bonding occurs through the nitrogen and oxygen atoms of the carbonyl group. Other ir studies of metal-glycine complexes have dealt with bidentate complexes.<sup>11-14</sup> The empirical band assignments for the ir spectra of several uni- and bi-dentate complexes of glycine with platinum(II) have been made by Varshauskii *et al.*<sup>15</sup>

***trans*-PtCl<sub>2</sub>(str)(glyH) and *cis*-PtCl<sub>2</sub>(str)(glyH).** The infrared spectra of these two isomers can be interpreted on the basis of the band assignments previously obtained for PtCl<sub>2</sub>(glyH)<sub>2</sub> and K[PtCl<sub>3</sub>(str)]. Table 3. compares the observed frequencies of five key bands for these isomers and related complexes. It is noted that the carbonyl stretching frequency of the unidentate, unionized glycine is higher in *trans* (1769 cm<sup>-1</sup>) than in the *cis* isomer (1720 cm<sup>-1</sup>). The Pt-str stretching band was clearly observed near 400 cm<sup>-1</sup> in both complexes. It's frequency is higher in the *trans* (401 cm<sup>-1</sup>) than in the *cis* isomer (395 cm<sup>-1</sup>). The styrene molecule is *trans* to nitrogen in the *trans* isomer while it is *trans* to chlorine in the *cis* isomer. Since the *trans*-effect of chlorine is stronger than that of nitrogen,



it is expected that the Pt-str bond of the *cis* isomer is weaker than that of the *trans* isomer. Thus, our observation is in good agreement with the theory of *trans*-effect. The Pt-Cl stretching bands appear strongly in the 350~310 cm<sup>-1</sup> region. The *trans* isomer gives one band at 333 cm<sup>-1</sup>. The Pt-N stretching band which is usually very weak at about 550 cm<sup>-1</sup> was not located because it is hidden by the phenyl C—C—C bending modes.

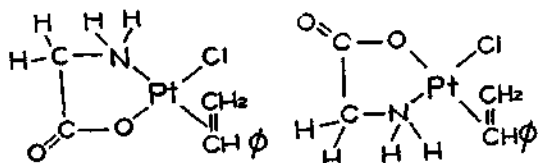
**The N- and O-*trans* Isomers of Pt-Cl(str)(gly).** In general, the spectra of both isomers are similar in the whole frequency region. They can be distinguished, however, by comparing the detailed feature of the spectra. For example, the N-*trans* isomer exhibits eight bands while O-*trans* isomer shows only five bands in the 1200~950 cm<sup>-1</sup> region. Table 4 lists the observed frequencies of six key bands for both isomers

Table 4. Observed frequencies of Pt(II) complexes containing glycine anion and styrene.

K [PtCl <sub>2</sub> (gly)]	PtCl(str)(gly)		K [PtCl <sub>3</sub> (str)]	Band assignment
	N- <i>Trans</i> isomer	O- <i>trans</i> isomer		
1645( <i>s</i> )	1650( <i>s</i> )	1660( <i>s</i> )	1518( <i>m</i> )	$\nu$ (C=O)
550( <i>w</i> )	1525( <i>m</i> )	1515( <i>m</i> )		$\nu$ (C=C)
	(hidden) <sup>a</sup>	(hidden) <sup>a</sup>	392( <i>m</i> )	$\nu$ (Pt-H)
388( <i>s</i> )	399( <i>m</i> ) <sup>b</sup>	400( <i>s</i> ) <sup>c</sup>		$\nu$ (Pt-str)
	320( <i>s</i> )	396( <i>sh</i> )	395( <i>sh</i> )	$\nu$ (Pt-O)
	346( <i>s</i> )	335( <i>s</i> )	340( <i>s</i> )	$\nu$ (Pt-Cl)
			313( <i>s</i> )	

<sup>a</sup>Hidden by styrene absorption, <sup>b</sup>Styrene absorbs at 405 cm<sup>-1</sup> (shoulder), <sup>c</sup>Styrene absorbs at 425 cm<sup>-1</sup>





and related complexes. As is seen in Fig. 2, the spectra near  $400\text{cm}^{-1}$  are complicated by the overlap of several bands; the *N-trans* isomer shows three peaks at  $405(\text{sh})$ ,  $399$  and  $396(\text{sh})\text{cm}^{-1}$  whereas the *O-trans* isomer gives two strong peaks at  $400$  and  $395(\text{sh})\text{cm}^{-1}$ . In this region, one expects three vibrations: styrene vibration ( $435\text{cm}^{-1}$  in free styrene), Pt-str stretching and Pt-O (glycine) stretching. We have listed our tentative assignments in Table 2. No attempts have been made to correlate these frequencies with the structure. The Pt-Cl stretching frequency is definitely higher in the *N-trans* isomer ( $346\text{cm}^{-1}$ ) than in the *O-trans* isomer ( $335\text{cm}^{-1}$ ). The chlorine atom is *trans* to oxygen in the *N-trans* isomer whereas it is *trans* to nitrogen in the *O-trans* isomer. Since the *trans*-effect of the  $\text{NH}_2$  group is stronger than that of the oxygen of the  $-\text{COO}^-$  group, the Pt-Cl bond of the *O-trans* isomer is expected to be weaker than that of the *N-trans* isomer. Thus, our infrared observation is again consistent with the theory of the *trans*-effect. All chelated glycino complexes show Pt-O stretching, C=O out-of-plane bendings, ring deformation, and carboxyl stretching bands characteristic of the chelated glycine. Thus, both isomers show the coordinated carboxyl stretching band at about  $1655\text{cm}^{-1}$  and the out of plane C=O bending band at about  $595\text{cm}^{-1}$ . Therefore, they definitely contain chelated glycine. Furthermore, a strong ring deformation band at around  $500\text{cm}^{-1}$  also indicates the presence of a chelated glycine ring.

**Ultraviolet-Visible Spectra.** Similar to Zeise's salt, all the Pt(II)-olefin complexes studied

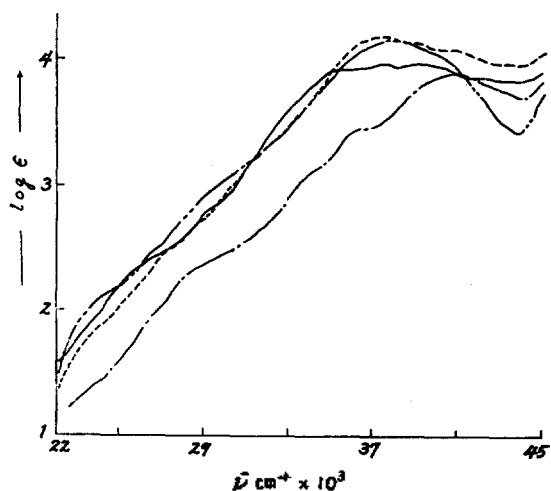


Fig. 3. UV spectra of *trans*-dichloro(styrene) (glycine) platinum (II).

(—), *cis*-dichloro (styrene) (glycine) platinum(II)  
 (- · - ·), *O-trans* isomer and *N-trans* isomer  
 (·····) of chloro(styrene) (glycino) platinum(II).

here exhibit three strong bands ( $\log \epsilon = 4.2 - 2.85$ ) in the region  $45000 \sim 31000\text{cm}^{-1}$  and two medium intensity bands ( $\log \epsilon$  below 2.5) in the region  $31000 \sim 17000\text{cm}^{-1}$  (Fig. 3). Denning *et al.*<sup>16</sup> assigned the former to the charge-transfer transitions from metal *d*-orbitals to olefin orbitals, and the latter to the *d-d* transitions characteristic of square-planar Pt(II) complexes.<sup>17,18</sup> The positions of these absorption maxima can not be determined accurately since the bands are broad and partially overlap on each other. It is noted, however, that the *trans* isomer absorbs more strongly than the *cis* isomer in  $\text{PtCl}_2(\text{str})(\text{glyH})$  in the former region. As expected, the spectra of the *N* and *O-trans* isomers are almost identical in the whole region of spectra.<sup>2</sup>

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