H, 3.8; N, 3.8. ^{1}H NMR (Me$_2$CO-d_6): identical with that of its enantiomorph.

[*SP*-4-2-(*S*,*S*)]-Bis[1-amino-2-(methylphenylarsino)ethane]platinum(II) Hexafluorophosphate, (−)-*cis*-Pt((*S*)-1)$_2$](PF$_6$)$_2$. Potassium tetrachloroplatinate(II) (0.53 g) was dissolved in water (4 mL), and acetonitrile (15 mL) was added: the mixture was briefly heated at 60 °C and then a solution of (*R*)-**1** in acetonitrile (5 mL) was added. The colorless solution was filtered and the filtrate taken to dryness. The residue was redissolved in water and an excess of NH$_4$PF$_6$ was added: the product separated as a white precipitate that was recrystallized from dichloromethane–diethyl ether as colorless crystals: mp 258–260 °C (0.94 g, 89%); $[\alpha]_D$ −209° (*c* 0.95, Me$_2$CO). Anal. Calcd for C$_{18}$H$_{28}$As$_2$F$_{12}$N$_2$P$_2$Pt: C, 23.8; H, 3.1; N, 3.1. Found: C, 23.7; H, 3.1; N, 3.2. ^{1}H NMR (Me$_2$CO-d_6): δ 1.76 (s, 3, $^3J_{PtH}$ = 24 Hz, AsMe), 2.55 (m, 2, AsCH$_2$), 3.16 (m, 2, NCH$_2$), 5.74 (m, 2, NH$_2$), 7.5–7.9 (m, 5, aromatics). ^{13}C NMR (Me$_2$SO-d_6): δ 6.13 ($^2J_{PtC}$ = 61 Hz, AsMe), 30.48 ($^2J_{PtC}$ = 34 Hz, AsCH$_2$), 44.12 (NCH$_2$), 129.38, 131.43, 131.66 (aromatics). Λ_M = 221 Ω^{-1} cm^2 mol^{-1} (Me$_2$CO).

The following compounds were prepared similarly in high yield. **[*SP*-4-2-(*R*,*R*)]-Bis[1-amino-2-(methylphenylarsino)ethane]platinum(II) hexafluorophosphate, (+)-*cis*-[Pt((*R*)-1)$_2$](PF$_6$)$_2$:** colorless crystals; mp 250–252 °C dec; $[\alpha]_D$ +206° (*c* 0.93, Me$_2$CO); Λ_M = 216 Ω^{-1} cm^2 mol^{-1} (Me$_2$CO). Anal. Calcd for C$_{18}$H$_{28}$As$_2$F$_{12}$N$_2$P$_2$Pt: C, 23.8; H, 3.1; N, 3.1. Found: C, 24.1; H, 3.1; N, 2.9. ^{1}H NMR (Me$_2$CO-d_6): identical with that of its enantiomorph. **(±)-[*SP*-4-2]-Bis[1-amino-2-(methylphenylarsino)ethane]platinum(II) hexafluorophosphate, (±)-*cis*-[Pt((*R*,*S*)-1)$_2$](PF$_6$)$_2$:** colorless needles from an acetone solution of an equimolar mixture of the enantiomers; mp 205–208 °C; 50% yield; Λ_M = 217 Ω^{-1} cm^2 mol^{-1} (Me$_2$CO). Anal. Calcd for C$_{18}$H$_{28}$As$_2$F$_{12}$N$_2$P$_2$Pt: C, 23.8; H, 3.1; N, 3.1. Found: 23.7; H, 3.1; N, 3.1. ^{1}H NMR (Me$_2$CO-d_6): identical with that of either pure enantiomer. **[*SP*-4-2-(*S*,*S*)]-Bis[1-amino-2-(methylphenylphosphino)ethane]platinum(II) hexafluorohosphate, (−)-*cis*-[Pt((*S*)-2)$_2$](PF$_6$)$_2$:** colorless crystals; mp 280° dec; $[\alpha]_D$ −224° (*c* 0.50, Me$_2$CO); Λ_M = 208 Ω^{-1} cm^2 mol^{-1} (Me$_2$CO). ^{1}H NMR (Me$_2$CO-d_6): δ 1.65 (d, 3, $^2J_{PH}$ = 11.7 Hz, $^3J_{PtH}$ = 39.6 Hz, PMe), 2.50 (m, 2, PCH$_2$), 3.29 (m, 2, NCH$_2$), 5.68 (m, 2, NH$_2$), 7.6–8.0 (m, 5, aromatics). ^{31}P NMR (Me$_2$CO-d_6): δ 21.8 (s, $^1J_{PtP}$ = 3221 Hz). **{*SP*-4-2-(*R*,*R*)]-Bis[1-amino-2-(methylphenylphosphino)ethane]platinum(II) hexafluorophosphate, (+)-*cis*-[Pt((*R*)-2)$_2$](PF$_6$)$_2$:** colorless crystals; mp 280° dec; $[\alpha]_D$ +227° (*c* 0.50, Me$_2$CO); Λ_M = 210 Ω^{-1} cm^2 mol^{-1} (Me$_2$CO). ^{1}H and ^{31}P NMR (Me$_2$CO-d_6): identical with that of its enantiomorph. **(±)-[*SP*-4-2]-Bis[1-amino-2-(methylphenylphosphino)ethane]platinum(II) hexafluorophosphate, (±)-*cis*-[Pt((*R*,*S*)-2)$_2$](PF$_6$)$_2$:** colorless crystals from acetone–propan-2-ol mixture; mp 252–254 °C. Anal. Calcd for C$_{18}$H$_{28}$F$_{12}$N$_2$P$_4$Pt: C, 26.4; H, 3.4; N, 3.4. Found: C, 26.7; H, 3.6; N, 3.5. Λ_M = 209 Ω^{-1} cm^2 mol^{-1} (Me$_2$CO). ^{1}H and ^{31}P NMR (Me$_2$CO-d_6): identical with that of enantiomers.

Condensation Reactions. [*SP*-4-4-(*R*,*R*)][1,9-bis(methylphenylarsino)-4,6,6-trimethyl-3,7-diazanon-3-ene]platinum(II) Hexafluorophosphate (8a/8b). A small quantity of (*S*)-**1** was added to a solution of (+)-[Pt((*R*)-**1**)$_2$](PF$_6$)$_2$ (0.1 g) in acetone (50 mL), and the reaction mixture was allowed to stand for 16 h at 25 °C. The volume of the solution was then reduced, and the product was precipitated by the addition of diethyl ether. Recrystallization of this material from an acetone–diethyl ether mixture gave the pure mixture of epimers **8a**/**8b** as colorless needles: mp 158–159 °C (0.08 g, 74%); $[\alpha]_D$ +107.1° (*c* 0.24, Me$_2$CO). Anal. Calcd for C$_{24}$H$_{36}$As$_2$F$_{12}$N$_2$P$_2$Pt: C, 29.2; H, 3.7; N, 2.8. Found: C, 29.3; H, 3.9; N, 2.9. ^{13}C NMR (Me$_2$SO-d_6): δ 4.98, 5.19, 5.64, 6.69 (AsMe), 20.79, 21.40, 25.32, 25.70, 25.75, 25.96 (C*C*H$_3$), 26.92, 27.07, 29.11, 29.06 (AsCH$_2$), 46.54, 47.36 (*C*H$_2$C(Me)=), 54.84, 55.48 (*C*Me$_2$), 55.13, 56.06, 56.50, 56.68 (NHCH$_2$, =NCH$_2$), 128.24–131.93 (m, aromatics), 182.96, 183.37 (C=N). IR (Nujol): 1644 cm^{-1} (br s, $\nu_{C=N}$). Λ_M = 214 Ω^{-1} cm^2 mol^{-1} (Me$_2$CO).

(±)-8a/8b. This substance was isolated in 30% yield by fractional crystallization of the product obtained from use of (±)-[Pt((*R*,*S*)-**1**)$_2$](PF$_6$)$_2$ as starting material: colorless crystals from acetone–diethyl ether; mp 258–260 °C dec. Anal. Calcd for C$_{24}$H$_{36}$As$_2$F$_{12}$N$_2$P$_2$Pt: C, 29.2; H, 3.7; N, 2.8. Found: C, 29.3; H, 3.9; N, 2.7. ^{13}C NMR (Me$_2$SO-d_6): identical with that of optically active material. Λ_M = 211Ω^{-1} cm^2 mol^{-1} (Me$_2$CO).

(±)-8c/8d: colorless crystals; mp 260 °C dec. Anal. Calcd for C$_{24}$H$_{36}$As$_2$F$_{12}$N$_2$P$_2$Pt: C, 29.2; H, 3.7; N, 2.8. Found: C, 29.3; H, 3.8; N, 2.8. ^{13}C NMR (Me$_2$SO-d_6): δ 6.31, 6.72, 6.92, 7.88 (AsMe), 20.82, 21.32, 25.11, 25.37, 25.72, 25.87 (C*C*H$_3$), 26.13, 26.28, 28.88, 29.08 (AsCH$_2$), 46.43, 47.52 (*C*H$_2$CH(Me)=), 54.78, 55.39 (*C*Me$_2$), 55.10, 55.92, 56.33, 56.68 (NHCH$_2$, =NCH$_2$), 127.45–131.69 (m, aromatics), 183.11, 183.43 (C=N). IR (Nujol): 1640 cm^{-1} (br s, $\nu_{C=N}$). Λ_M = 214 Ω^{-1} cm^2 mol^{-1} (Me$_2$CO).

Registry No. (±)-**1**, 90971-53-2; (*S*)-**1**, 91049-53-5; (*R*)-**1**, 91049-58-0; (±)-**2**, 90971-54-3; (*S*)-**2**, 91049-54-6; (*R*)-**2**, 91049-55-7; (*R*)-**3**, 80145-77-3; (*R*,*S*)-**4**, 90971-56-5; (*R*,*R*)-**4**, 91049-57-9; (*R*,*R*)-**5**, 90971-58-7; (*R*,*S*)-**5**, 91049-60-4; **8a**(PF$_6$)$_2$, 90971-68-9; **8b**(PF$_6$)$_2$, 91049-76-2; **8c**(PF$_6$)$_2$, 91049-78-4; **8d**(PF$_6$)$_2$, 91049-80-8; (−)-*cis*-[Pd((*S*)-**1**)$_2$](PF$_6$)$_2$, 90971-60-1; (+)-*cis*-[Pd((*R*)-**1**)$_2$](PF$_6$)$_2$, 91049-62-6; (±)-*cis*-[Pd((*R*,*S*)-**1**)$_2$](PF$_6$)$_2$, 91049-64-8; (−)-*cis*-[Pd((*S*)-**2**)$_2$](PF$_6$)$_2$, 90971-62-3; (+)-*cis*-[Pd((*R*)-**2**)$_2$](PF$_6$)$_2$, 91049-66-0; (−)-*cis*-[Pt((*S*)-**1**)$_2$](PF$_6$)$_2$, 90971-64-5; (+)-*cis*-[Pt((*R*)-**1**)$_2$](PF$_6$)$_2$, 91049-68-2; (±)-*cis*-[Pt((*R*,*S*)-**1**)$_2$](PF$_6$)$_2$, 91049-70-6; (−)-*cis*-[Pt((*S*)-**2**)$_2$](PF$_6$)$_2$, 90971-66-7; (+)-*cis*-[Pt((*R*)-**2**)$_2$](PF$_6$)$_2$, 91049-72-8; (±)-*cis*-[Pt((*R*,*S*)-**2**)$_2$](PF$_6$)$_2$, 91049-74-0; ClCH$_2$CH$_2$NH$_2$, 689-98-5; MeI, 74-88-4; methylphenylarsine, 53979-86-5; (±)-1-amino-2-(phenylphosphino)ethane, 90971-69-0; lithium tetrachloropalladate(II), 15525-45-8; potassium tetrachloroplatinate(II), 10025-99-7; acetone, 67-64-1.

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Synthesis and Characterization of New Mononuclear and Dinuclear Complexes of Palladium(II) with Glycyl Chloride

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Received May 3, 1983

The complexes *cis*- and *trans*-PdCl$_2$(NH$_2$CH$_2$COCl)$_2$ and *trans*-Pd$_2$Cl$_4$(NH$_2$CH$_2$COCl)$_2$ are obtained in the reaction of Pd(GlyO)$_2$ with SOCl$_2$. Products have been characterized by elemental analysis and infrared and proton nuclear magnetic resonance spectroscopy. *cis*- and *trans*-PdCl$_2$(NH$_2$CH$_2$COOH)$_2$ have been prepared, similarly characterized, and studied by potentiometry.

Introduction

The importance of coordination compounds of transition-metal ions in the vital biological processes and their potential applications as antitumor agents have been stressed elsewhere.[1,2] The first complexes of Pd(II) with α-amino acids as ligands were described by Sharrat et al.[3] Shestanova[4]

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Table I

compd	% C		% H		% N		% Cl	
	found	calcd	found	calcd	found	calcd	found	calcd
cis-$PdCl_2(NH_2CH_2COOH)_2$	15.9	15.1	3.1	3.1	8.6	8.5	21.4	21.6
trans-$PdCl_2(NH_2CH_2COOH)_2$	15.7	15.1	3.0	3.1	8.6	8.5	21.5	21.6
cis-$PdCl_2(NH_2CH_2COCl)_2$	14.0	13.4	2.5	2.2	7.7	7.6	38.7	38.9
trans-$PdCl_2(NH_2CH_2COCl)_2$	13.1	13.4	2.6	2.2	7.5	7.6	38.6	38.9
trans-$Pd_2Cl_4(NH_2CH_2COCl)_2$	8.5	8.8	1.7	1.5	5.0	5.1	39.9	39.5

Table II

compd	structure	point group	active zone	tension	
				Pd-Cl	Pd-N
cis-$PdCl_2$-$(NH_2CH_2COOH)_2$	square plane	C_{2v}	infrared	A_1; B_2	A_1; B_2
			Raman	A_1; B_2	A_1; B_2
trans-$PdCl_2$-$(NH_2CH_2COOH)_2$	square plane	D_{2h}	infrared	B_{3u}	B_{2u}
			Raman	A_g	A_g

Table III. Principal Frequencies (cm^{-1}) in the IR Spectra of *cis*- and *trans*-$PdCl_2(NH_2CH_2COOH)_2$

compd	NH_2	CH_2	COOH	C-N, (R-C-NH_2)	Pd-Cl	Pd-N
cis-$PdCl_2$-$(NH_2CH_2COOH)_2$	3280	2940	1720			
	3237	2860	1700			
	3125	1425	1250	1065	380	480
	3100	1415	1220	1055	340	440
	1610		945			
	1570					
trans-$PdCl_2$-$(NH_2CH_2COOH)_2$	3280	2940	1705			
	3218	2870	1248	1058	348	475
	3100	1430	940			
	1565					

obtained the α and β forms of *cis*-$Pd(GlyO)_2$ and the dimer[5] $K_2Pd_2(GlyO)_6 \cdot H_2O$.

The first complexes with α-amino acid chloride as ligand were described by Beck et al.[6] $PtCl_4(NH_2CHRCOCl)_2$ was obtained by chlorination of the α-amino acid complexes by PCl_5. Recently the complexes of glycyl chloride with Cu(II) and Co(II) have been obtained in our laboratories.[7]

Although the synthesis of Pd(II) complexes of the general type $M_2X_4L_2$ (X = halogen; L = PMe_3, PEt_3, PPh_3, SMe_2, etc.) has been reported,[8-11] there are very few compounds in the literature[12] with metal–halogen bridges and with L = α-amino acid or its derivatives.

The first reaction of complexes of the type $M(NH_2CHRCOO)_2$, where both chelate rings are opened, was described by Volshtein and Volodina[13] for cis and trans isomers. Other authors[14-16] have obtained similar results, but the reactions of palladium(II) glycinate, however, have not been reported. We present here the synthesis and characterization of the following compounds: *cis*-$PdCl_2(NH_2CH_2COOH)_2$ (**1**-*cis*), *trans*-$PdCl_2(NH_2CH_2COOH)_2$ (**1**-*trans*), *cis*-$PdCl_2(NH_2CH_2COCl)_2$ (**2**-*cis*), *trans*-$PdCl_2(NH_2CH_2COCl)_2$ (**2**-*trans*), *trans*-$Pd_2Cl_4(NH_2CH_2COCl)_2$ (**3**-*trans*).

Experimental Section

1-*cis* and 1-*trans*. *cis*- or *trans*-$Pd(GlyO)_2$ is dissolved in water (trans) or in ethanol/water (2:1) (cis). The solution is then mixed with HCl (1 N) in a equimolar ratio and is maintained at ca. 80 °C for 30 min. After removal of solvent, an ethanol/THF mixture (1:1) is added. The solution is again reduced in volume by 8–10 mL, resulting in a yellow-orange crystalline solid after 2 or 3 days at room temperature. Analytical data for these complexes are summarized in Table I.

2-*cis* and 2-*trans*. The corresponding $Pd(GlyO)_2$ isomer is reacted with $SOCl_2$ or SO_2Cl_2. Although the reaction proceeds satisfactorily with both chlorating agents, $SOCl_2$ gives larger yields and reacts more easily than SO_2Cl_2.

cis- or *trans*-$Pd(GlyO)_2$ (3.0 g) is dissolved in 200 mL of dioxane, and 5 mL of $SOCl_2$ is slowly added. The solution changes color from pale yellow to brown-red. The mixture is refluxed for 12 h, and after filtration a brown-red solid is obtained. This is washed several times with ether and then dried under vacuum.

3-*trans*. The solution resulting during the synthesis of **2**-*trans* is reduced in volume, extracted with ether, refluxed for 30 min, and maintained for 2 days at 5 °C, giving a red precipitate. Chemical analysis of these complexes are summarized in Table I.

Materials and Apparatus

Potentiometric curves were obtained with an automatic Radiometer TTT-60 titrigraph, a 62 pH-meter 62, an ABU-12 autoburet, and an REA-160 recorder. All the measurements were performed at 21 °C. Infrared spectra of the solid complexes were recorded by using KBr pellets in the 4000–600-cm^{-1} range and Nujol mulls with polyethylene disks in the 600–200-cm^{-1} range on a Perkin-Elmer 577 spectrometer.

The proton nuclear magnetic resonance spectra have been recorded on a 60-MHz Perkin-Elmer R-12 continuous-wave spectrometer.

Results and Discussion

1-*cis* and 1-*trans*. The two complexes are very soluble in water. In other solvents the solubility decreases as follows: $CH_3CH_2OH > CH_3COCH_3 > CH_3CH_2OCH_2CH_3$. Generally the cis isomer shows lower solubility than the trans isomer.

Potentiometric Curves. Each compound is dissolved in ca. 50 mL of water and then titrated with a NaOH (0.107 N) solution. The initial pH of the solution was 3.75 (cis) and 3.70 (trans). The titration curves showed a steep rise between pH 4.5 and 8.5, the equivalence point recorded at pH 6.82 (cis) or 6.62 (*trans*) corresponding to the addition of 2 mequiv of NaOH/mmol of complex. This result confirms the presence of two free carboxylic acid groups in each complex. The equivalent and molecular weights obtained in this experiment are in good agreement with the theoretical values.

Infrared Spectra. The principal features of the IR spectra of the cis and trans isomers of **1** are included in Table II. As expected from symmetry considerations, the cis isomer exhibits more IR bands than does the trans isomer.

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Table IV. Principal Frequencies (cm^{-1}) in the IR Spectra of *cis*- and *trans*-$PdCl_2(NH_2CH_2COCl)_2$

compd	NH_2	CH_2	COCl	C-N	Pd-Cl	Pd-N
cis-$PdCl_2$-$(NH_2CH_2COCl)_2$	3210	2960	1755	1050	350	500
	3140	2910	1725	1070	335	470
	3165	1435	860			
	1590	1430				
	1485	910				
	1570	900				
trans-$PdCl_2$-$(NH_2CH_2COCl)_2$	3220	2970	1750	1040	330	490
	3170	2920	1720			
	1595	1440	855			
	1485	900				

The absorption bands corresponding to the amine function appear at the characteristic positions[17,18] for coordinated amines. The absorptions assigned to the C–H bonds in the methylene group are seen at the characteristic positions for methylene between an electronegative N (amine) atom and a carbonyl group of the carboxylic acid.[19]

The band corresponding to the C=O stretching mode of the carboxylic acid group is recorded between 1720 and 1700 cm^{-1}. In this range, the cis isomer shows two ν(C=O) bands, while the trans isomer exhibits only one. On the other hand the band corresponding to the stretching of the C=O group and the deformation on the plane corresponding to C—O—H is recorded between 1250 and 1220 cm^{-1}. Both bands include some interaction between both vibration modes. One other characteristic band is that of the out-of-plane deformation of the π O–H bond at ca. 940 cm^{-1}.

In the low-frequency region, the cis isomer shows two bands corresponding to ν(M–N) and ν(M–Cl) at 480 and 440 cm^{-1} and at 310 and 340 cm^{-1}, respectively, while the trans isomer exhibits only one band for each of these modes at 475 and 348 cm^{-1}. These correspond to the group-theoretical prediction given in Table. III.

^{1}H NMR Spectroscopy. Each complex, **1**-*cis* or **1**-*trans*, shows only two singlets due to the methylene and amine groups. According to the literature,[20] the methylene signal appears at δ 3.53 (cis) and δ 3.30 (trans). The proton of the amine group is also identified as a singlet at δ3.30 (cis) and δ 3.55 (trans).

2-*cis* and 2-*trans*. The formation of the glycyl chloride complex is consistent with Scheme I. The intermediate $PdCl_2(NH_2CH_2COOH)_2$ is identical with that obtained from $Pd(GlyO)_2$ and HCl.

Scheme I

$$SOCl_2 + H_2O \rightarrow SO_2 + 2HCl$$

$$Pd(NH_2CH_2COO)_2 + 2HCl \xrightarrow[60\ ^\circ C,\ 5\ min]{dioxane}$$

$$PdCl_2(NH_2CH_2COOH)_2 \xrightarrow[dioxane\ 12\text{-}h\ reflux]{+2SOCl_2}$$

$$2SO_2 + 2HCl + PdCl_2(NH_2CH_2COCl)_2$$

The **2**-*cis* and **2**-*trans* complexes are very soluble in dimethyl sulfoxide and insoluble in acetone, ether, and dioxane. The solubility in alcohol could not be determined because these compounds react with these solvents.

Infrared Spectra. Characteristic absorptions of **2** are shown in Table IV. A band at 1485 cm^{-1} is seen for both complexes **2** that was not seen for **1**. This band is characteristic of the N–H bonds in coordinated amine groups and is influenced by neighboring chloride ions, i.e. characteristic of the chloride–glycine function. The position of this band shifts to 1200 cm^{-1} (cis) and 1120 cm^{-1} (trans) upon deuteration, these shifts coinciding with those expected for pure deformation modes δ(N–D) of perdeuterated amine groups δ-ND_2.

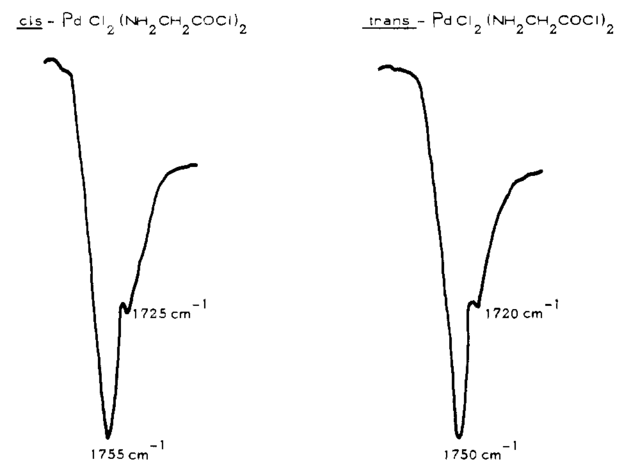

Figure 1. ν(C=O) of the acid chloride function in *cis*- and *trans*-$PdCl_2(NH_2CH_2COCl)_2$.

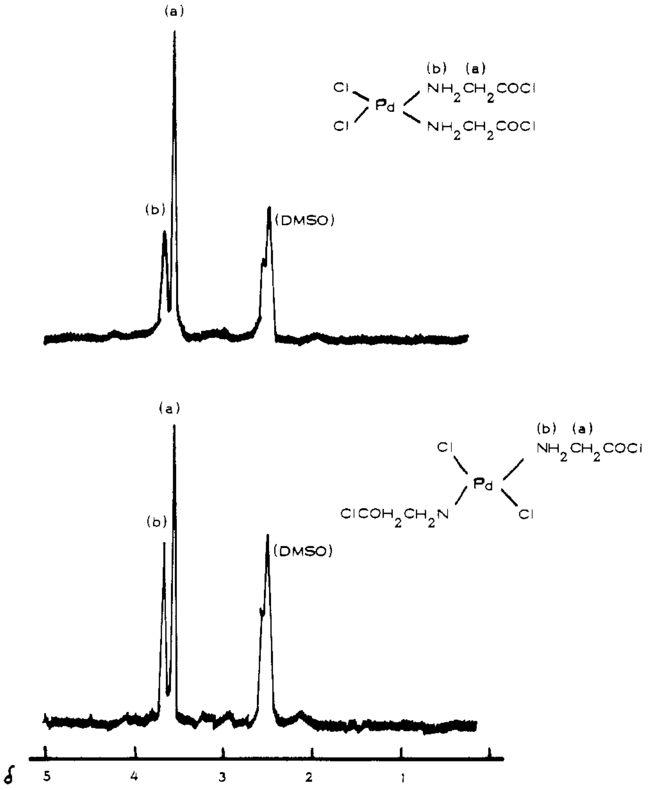

Figure 2. ^{1}H NMR spectra of *cis*- and *trans*-$PdCl_2(NH_2CH_2COCl)_2$ in Me_2SO.

The ν(C=O) absorption of the acid chloride is shown in Figure 1; this appears as a sharp band together with a shoulder at 1755, 1725 cm^{-1} (cis) or 1750, 1720 cm^{-1} (trans), as a result of Fermi resonance between the ν(C=O) stretching mode and an overtone of the lower energy band at 860 cm^{-1} (cis) or 855 cm^{-1} (trans).

^{1}H NMR Spectra. Spectra of **2**-*cis* and **2**-*trans* (50 mg in 1 mL of perdeuterated Me_2SO) are shown in Figure 2. The signal of the methylene group is recorded as a singlet at δ 3.60 (cis) and δ 3.55 (trans). However, this signal shifts to δ 3.53 (cis) and δ 3.30 (trans) in the case of **1**-*cis* and **1**-trans complexes. This shift can be due to the difference in the electron

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Table V. Principal Frequencies between 4000 and 600 cm^{-1} in the IR Spectrum of *trans*-$Pd_2Cl_4(NH_2CH_2COCl)_2$

N-H	COCl	C-H	C-N
3160	1750	2965	1030
3120	1720	2890	
1595	880	1440	
		910	

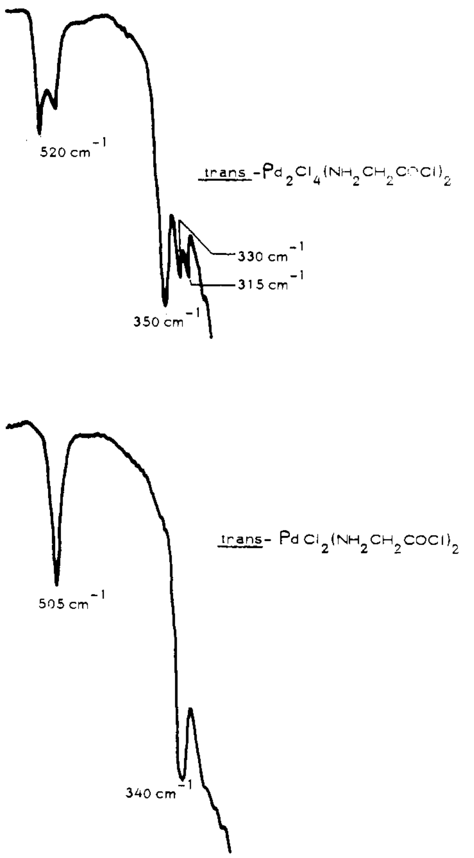

Figure 3. Far-infrared spectra of *trans*-$PdCl_2(NH_2CH_2COCl)_2$ and *trans*-$Pd_2Cl_4(NH_2CH_2COCl)_2$.

density at the methylene group proton. In complexes with the ligand NH_2CH_2COCl, less shielding is expected due to the presence of the highly electronegative chlorine atom. The resonance of the proton of the amine group is identified as a broad singlet at δ 3.70 (cis) and δ 3.68 (trans).

3-*trans*. This complex is soluble in dioxane and dimethyl sulfoxide and insoluble in acetone and ether.

Infrared Spectrum. The IR spectrum is given in Table V. This is analogous to those of **2**. An analysis of the IR spectrum in the 600–200-cm^{-1} range of the spectrum is assisted by comparison with that of **2**-*trans*; see Figure 3.

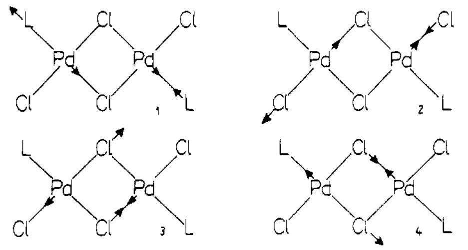

Figure 4. IR-active symmetry modes for *trans*-Pd_2Cl_4-$(NH_2CH_2COCl)_2$: (1) M–L tension, (2) M–Cl_t tension, (3) M–Cl_b tension for the trans position with respect to Cl, and (4) M–Cl_b tension for the trans position with respect to L (L = NH_2CH_2COCl).

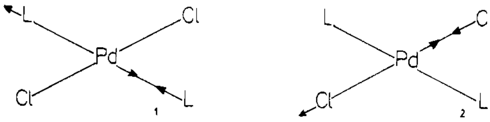

Figure 5. IR-active symmetry modes for *trans*-$PdCl_2$-$(NH_2CH_2COCl)_2$: (1) M–L (B_{2u}) tension and (2) M–Cl (B_{3u}) tension (L = NH_2CH_2COCl).

3-*trans* shows four bands while **2**-*trans* shows only two bands. According to the literature,[8,9,21,22] it is concluded that the frequencies of the briding metal–chlorine stretching modes are lower than those of terminal metal–chlorine units. In **3**-*trans* with chloro bridges, the symmetry point group of the bridging unit is C_{2h}, while in *2-trans* it is D_{2h}. Only the B_u symmetry modes are active in $M_2Cl_4L_2$, and they are described in Figure 4. As these modes belong to the same symmetry, there is coupling between them, and all modes are mixed character.[8] For **3**-trans, we propose that the band at ca. 520 cm^{-1} corresponds to ν(M–N) and that the stretching vibration M–Cl(terminal) is at ca. 350 cm^{-1}. The band appearing at ca. 330 cm^{-1} is related to ν(M–Cl(bridged)) in the trans position with respect to terminal chlorine, and the band at ca. 315 cm^{-1} is ascribed to ν(M–Cl(bridged)) in the trans position with respect to the amino group, since this bond is more sensitive to the nature of the trans ligand.[8]

As in the previous case, only the B_{2u} and B_{3u} symmetry modes are infrared active in MCl_2L_2, and their description is included in Figure 5. The B_{2u} mode corresponds to the stretching vibration of the M–N bond being recorded at 505 cm^{-1} and the B_{3u} mode to the stretching vibration of M–Cl at 340 cm^{-1} (see Figure 3).

^{1}H NMR Spectrum. After 50 mg of **3**-*trans* was dissolved in 0.5 mL of Me_2SO-d_6, the spectrum was recorded. The methylene proton signal turns up as a singlet at δ 4.25, and the amine proton is identified as a broad singlet at δ 3.65.

Acknowledgment. The authors wish to thank Prof. Dr. W. Beck of the Institut für Anorganische Chemie, University of Munich, for advice and suggestions.

Registry No. **1**-*cis*, 90865-45-5; **1**-*trans*, 79351-56-7; **2**-*cis*, 90790-92-4; **2**-*trans*, 90865-46-6; **3**-*trans*, 90790-93-5; *cis*-$Pd(GlyO)_2$, 14281-81-3; *trans*-$Pd(GlyO)_2$, 23678-00-4; $GlyO^-$, 23297-34-9.

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