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Ethylene or Carbonyl Platinum(II) Glycine Complexes

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The preparation and bond properties of platinum glycine complexes with ethylene or carbon monoxide and their i.r. spectra are reported. The platinum-olefin interaction is also discussed.

Introduction

Panunzi *et al.*[1] reported some monochloro-amino-acid olefin platinum(II) complexes of the formula [PtCl(ol)($NH_2CHRCOO$)], where ol = olefin and R = phenyl, and they proposed a monomeric structure in which the NH_2 of the amino acid is *trans* to the olefin. Later[2a] Kieft and Nakamoto also reported the complexes independently. The nitrogen bases are stronger than the oxygen bases and the amino group reacts preferentially with the more labile chlorine *trans* to the olefin in Zeise's type salts.

In this paper we have prepared the ethylene complex with glycine reported by the above mentioned authors as well as the carbonyl analog of the ethylene complex, *i.e.*, [PtCl(CO)(NH_2CH_2COO)] and have obtained the i.r. spectra of the deuterated species, [PtCl(C_2H_4)(ND_2CH_2COO)] and [PtCl(C_2D_4)(ND_2CH_2COO)], where the ethylene molecule was partially deuterated.

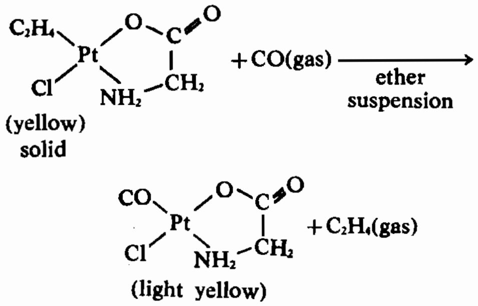
The low frequency i.r. spectra (600-200 cm^{-1}) of these complexes aided us to determine their structures. The carbonyl analog gives much simpler i.r. spectra and helps greatly in the assignment of the frequencies. The i.r. assignment for the undeuterated glycino ethylene complex was reported by Kieft and Nakamoto.[2a]

Experimental Section

Preparation of the compounds. 1. [PtCl(C_2H_4)(NH_2CH_2COO)]. This compound was prepared according to the procedures given by Panunzi *et al.*,[1] *i.e.*, reaction of Zeise's salt with the potassium salt of glycine. The precipitate was washed with water and dried. The yellow solid was crystallized from methanol and decomposed at 156°. The compound presented the carateristics of the salt prepared by Panunzi *et. al.*[1] and its spectrum was identical to that given by Kieft and Nakamoto.[2a]

2. [PtCl(C_2H_4)ND_2CH_2COO)]. The $-ND_2$ deuterated complex was obtained by storing the undeuterated complex in a dessicator in the presence of D_2O. However, ethylene also exchanges to form a little of [PtCl(C_2D_4)(ND_2CH_2COO)]. Complete $-ND_2$ deuteration was obtained by reacting Zeise's salt with the deuterated glycine salt, ND_2CH_2COOK obtained by recrystallizing the glycine salt in D_2O several times.

3. [PtCl(CO)NH_2CH_2COO)]. The carbonyl complex was prepared by reacting the ethylene analog with carbon monoxide:



The above reaction takes place in half an hour. The carbon monoxide passing through the suspension of [PtCl(C_2H_4)(NH_2CH_2COO)] dissolved the solid. By slow evaporation of the ether the carbonyl complex precipitated out. m.p. with decomp. 186°C. (Found: C, 10.64; H, 1.4; N, 4.45; Pt, 58.18. $C_3H_4ClNO_3Pt$ requires: C, 10.85; H, 1.2; N, 4.20; Pt, 58.6).

The i.r. spectra were observed with a Perkin-Elmer 621 double-beam infrared spectrophotometer in the 4000-200 cm^{-1} region. KBr, CsI disks and nujol or hexachlorobutadiene techniques were employed to record the spectra in the above region using KBr and CsI plates. Calibration of the frequency region was made with water vapor, carbon dioxide vapor and a polystyrene film. Positions of bands are occurate to within ±2 cm^{-1}.

Results and Discussion

The i.r. spectra of [PtCl(C_2H_4)(NH_2CH_2COO)], (A) [PtCl(C_2H_4)(ND_2CH_2COO)] ($-ND_2$–deuterated) (B) and the carbonyl analog, [PtCl(CO)(NH_2CH_2-

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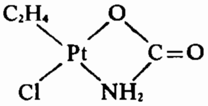
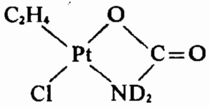
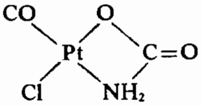
(1) A. Panunzi, R. Palumbo, C. Pedone, and G. Paiaro, *J. Organometal. Chem.*, *5*, (1966).

(2) (a) J. A. Kieft and K. Nakamoto, *J. Inorg. Nucl. Chem.*, *29*, 2561 (1967); *30*, 3103 (1968); (b) M. J. Grogan and K. Nakamoto, *J. Am. Chem. Soc.*, *88*, 5454 (1966); *90*, 918 (1968); (c) G. T. Behnke and K. Nakamoto, *Inorg. Chem.*, *7*, 2030 (1968).

Table I. I.R. Frequencies of Some Glycine Platinum(II) Complexes with ethylene or carbon monoxide (cm^{-1})

			Assignment	
3208 vs		3108 vs	ν_{as} N–H str.	
3117 vs		3078 s	ν_s N–H str.	
	3087 m		ν_{as}–C–H str.	C_2H_4
3001 m	3001 m		ν_s C–H str.	
2970 m	2975 w	2975 m	ν_{as} C–H str.	gly
2950 m	2950 w	2930	ν_s C–H str.	
2774		2641 m		
		2595 m	combination	
		2390 m		
	2410 s (1.34)		ν_{as} N–D str.	
	2365 sh			
	2300 s (1.35)		ν_s N–D str.	
		2134 vs	ν(CO)	
		2123 vs		
		2077 m		
1640 vs	1638 vs	1647 vs	νC=O str. (COO)	
1600		1596 vs	δNH_2 def.	
1567 ms				
1526 m	1526 m		νC⋯C str.	
1436 ms	1436 m		δCH_2 def.	
1421 s	1420 m	1421 ms	δs CH_2 def.	
1360 vs	1350 vs	1351 ms	νC=O str. (COO)	
1307 s	1307 s	1306 s	CH_2 twist.	
1257 m	1257 m	1286 sh	CH_2 rock.	
	1248 m			
1190 s	862 s (1.35)	1204 s	NH_2 and ND_2 twist.	
	1194 w			
1153 s	1165 w			
1032 m	1033 m	1027 m	νC–N str. and CH_2 wag.	
1017 s	1016 s			
1000 m	1000 m			
952 s	952 m	958 s	νC–C str. and CH_2 rock.	
917 s	862 s (1.35)	920 s	NH_2 and ND_2 wag.	
824 m	823 m		CH_2 rock.	
769 m	576 s (1.35)	780 s	NH_2 twist. and πC=O	
735 m	749 m	730 m	CH_2 twist.	
587 s	576 s	608 s	πC=O	
543 m	510 w	531 m	νPt–N str.	
499 s			NH_2 rock.	
478 m	480 s	478 s	νPt–C str.	
405 s	404 s	401 s	νPt–O str.	
382 m	383 s		νPt–C str.	
362 vs	362 vs	361 vs	νPt–Cl str.	
	354 sh	355 sh		
290 m	290 m	294 m	OCCN trs.	

vs, very strong; s, strong; m, medium; ms, medium strong; sh, shoulder; w, weak; str, stretching; as, assymetric; s, symmetric; def., deformation; twist., twisting; rock., rocking; wag., wagging; πC=O, out of plane bending; trs., torsion.

COO)] (C) are shown in Figure 1. In Table I are given the absorption maxima and their assignment is shown in the last column.

Previous work[2,3,4,5] on platinum ethylene complexes of Zeise's type aided us in reaching the assignments given in the last column of Table I. The substitution of ethylene by carbon monoxide in the complexes was also essential for our discussion on the metal-double bond interaction and the ethylene assignments. The spectra of the carbonyl analog are simpler in the finger print region and only the chelated glycine absorptions are observed. The carbonyl complex gives three strong and sharp absorptions at 2134, 2133 and 2077 cm^{-1} (see Figure 1). The carboxyl absorptions of the glycine molecule in the complexes are observed at 1647 and 1637 cm^{-1} for the carbonyl and ethylene complexes respectively (see Table I). The carboxyl absorption occurs at 1820 cm^{-1} in the free glycine molecule and is shifted on complexation. This assignment is the same as in the previous work.[2a] The deuteration of the $-NH_2$ groups of the ethylene complex is essential to separate the CH_2 absortpions from those involving the NH_2 groups. The strong band at 499 cm^{-1} is assigned to the NH_2 rocking frequency on the basis of the deuteration data. This band is sensitive to deuteration and it is completely removed on deuteration of the NH_2 groups ($-ND_2$) in the complex see

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(3) J. Pradilla-Sorzano and J. P. Frackler, Jr., *J. Mol. Spectroscopy*, *22*, (1967).

(4) H. P. Fritz and D. Sellmann, *J. Organometal. Chem.*, *6*, 558 (1966).

(5) P. C. Kong and T. Theophanides, *Can. Spectroscopy*, *14*, 104 (1969).

(6) A. A. Babuskin, L. A. Gribov, and A. D. Gel'man, *Russ. J. Inorg. Chem.*, *4*, 695 (1959).

Figure 1 and Table I. The removal of the 499 cm^{-1} band allows also the observation of the ν_{Pt-N} absorption of the $[Pt(C_2H_4)(ND_2CH_2COO)]$ at 510 cm^{-1} lowered on deuteration of the $-NH_2$ groups from 542 cm^{-1} for the $[Pt(C_2H_4)(NH_2CH_2COO)]$. The ν_{Pt-N} assignment is in agreement with that given by Kieft and Nakamoto[2a] in these complexes. However, the absorptions near 1190-1160 cm^{-1} are NH_2 absorptions, as well as the absorption at 917 cm^{-1} and 769 cm^{-1} (see Table I).

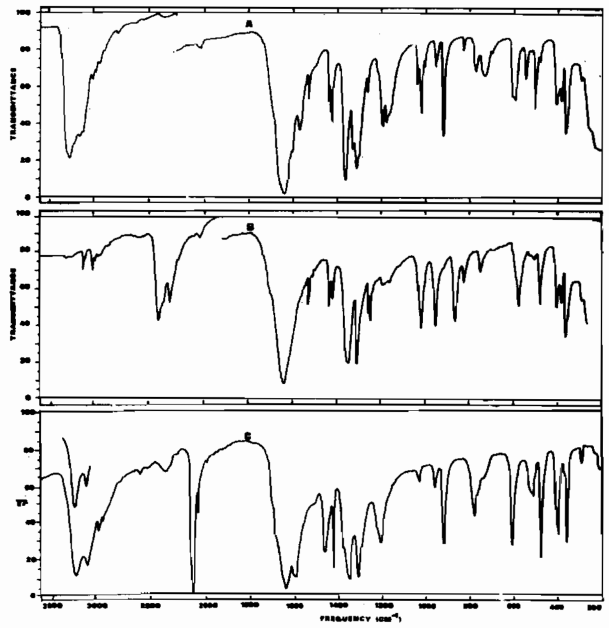
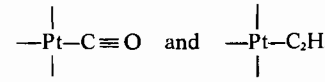


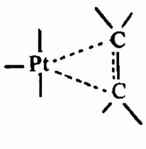
Figure 1. Infrared spectra of the complexes. A. $[PtCl(C_2H_4)(NH_2CH_2COO)]$ in KBr pellel. B. $[PtCl(C_2H_4)(ND_2CH_2COO)]$ in KBr pellet. C. $[PtCl(CO)(NH_2CH_2COO)]$ in CsI pellet. Samples of 3-4 mg per 200 mg of alkali halide were used.

The platinum-carbonyl and platinum-ethylene absorptions were carefully examined in the region 600-200 cm^{-1}:



$$-\overset{|}{\underset{|}{Pt}}-C\equiv O \quad \text{and} \quad -\overset{|}{\underset{|}{Pt}}-C_2H_4$$

In the carbonyl complex three bands are observed at 531, 511 and 478 cm^{-1}. These bands can be tentatively assigned to ν_{Pt-N}, ν_{Pt-C} and δ_{Pt-CO} respectively.[11] The highest and weakest band being assigned to the Pt–N vibration. The strong band at 401 cm^{-1} is assigned to ν_{Pt-O} frequency (see Table I), by comparison with the ethylene complex. In the ethylene complexes, absorptions due to the cyclic unity,

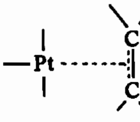


are observed at 481 cm^{-1}, 383 cm^{-1}, and at 480 cm^{-1}, 382 cm^{-1} for the $[PtCl(C_2H_4)(NH_2CH_2COO)]$ and $[PtCl(C_2H_4)(ND_2CH_2COO)]$ complexes respectively (see Table I and Figure 1). These two bands on deuteration of the ethylene in the complex (partial deuteration) are shifted to 436 and 366 cm^{-1} respectively. In a series of compounds of the formula $[X_2C_2H_4)Pt(NH_2CH_2CH_2NH_2)Pt(C_2H_4)X_2]$, with X=Cl and Br two bands were also observed approximately in the same region and are assigned to the Pt–C vibrations on the basis of deuteration data.[5] The two bands are shifted to 435-440 and 365 cm^{-1} respectively on deuteration of the ethylene molecule in the complex.

The unit PtC_2 gives three valence vibrations, two Pt–C in the region 370-600 cm^{-1} and one C–C vibration in the region 1000-16000 cm^{-1} depending on the interaction of the double bond with the metal. This cyclic structure was considered earlier by Babuskin *et al.*,[6] who presented spectral arguments in support of it. The Dewar-Chatt-Duncanson representation of the bonding in olefin complexes and its extension to acetylene complexes explained the general properties of these complexes with considerable success. However, spectroscopic data on the metal-olefin interaction is not conclusive.

X-ray data on the metal-olefin π-complexes[7,8] show the bond order of the C=C in the complexes to be reduced to 1½ from 2 on complexing of the free ethylene. The metal-olefin bond is approximately a symmetrycal π-type bond. The C=C distance is increased from 1.34 Å to 1.44 Å on complexing. This implies a certain amount of additional p caracter in the sp^2 hybrid of the two carbons, *i.e.*, sp^2–sp^3, which in turn implies a degree of covalency of the two carbon atoms with the metal.

The representation of the platinum-olefin interaction as follows:



with a weak overlap of the platinum orbitals and the π bond of the olefin could not justify a covalent Pt–C frequency in the region 400 cm^{-1}. This representation would mean the movement of a metal atom against a molecule. This type of vibration is similar to a lattice mode and should be observed at very low frequencies 100-50 cm^{-1}. The Dewar-Chatt-Duncanson model clearly implies covalent bonds between the metal and the two carbon atoms. The metal-olefin interaction could also be considered in terms of molecular orbitals as a three-center PtC_2 orbital resulting from the combination of atomic orbitals of the two carbon atoms and the metal atom.[12] If the platinum atom, however, is covalently bound to the two carbon atoms and obviously it is, the vibrations of the three

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(7) D. P. Mellor and J. A. Wunderlich, *Acta Cryst.*, *8*, 57 (1955).

(9) G. B. Bokii, and G. A. Kukina, *Zh. Strukt. Khim.*, *5*, 706 (1965).

(10) M. Black, R. H. B. Mais, and P. G. Owston, *Acta Cryst.*, *B 25*, 1753 (1969).

(11) R. G. Denning, and M. J. Ware, *Spectrochim. Acta*, *24A*, 1785 (1968).

(12) J. H. Nelson, K. S. Wheelock, L. C. Cusachs, and H. B. Jonassen, *Chem. Comm.*, 1019 (1969).

atoms in the triangular ring should be considered.[6] This conclusion is not in accord with the Pt–C_2H_4 assignment of Grogan and Nakamoto[2b] and Benkhe and Nakamoto,[2c] but it agrees with the results of other workers.[3,4]

The Pt–Cl bonds absorb in the region 350-360 cm^{-1} which is higher than the normal platinum-chlorine absorption region (335-345 cm^{-1}). This might be due to the very low *trans* effect of oxygen.

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