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The Metal–Oxygen Bond in Some 1-(Pyridine N-oxide)-3-ethylene-2,4-dichloroplatinum(II) Complexes

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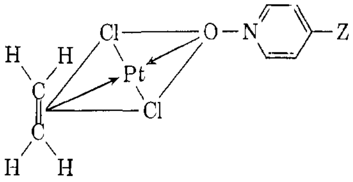
The infrared spectra of six 1-(4-substituted pyridine N-oxide)-3-ethylene-2,4-dichloroplatinum(II) complexes were determined in the CsBr region. The spectrum of each of these complexes shows a band at about 323 cm.$^{-1}$, which is thought to be the Pt–O stretching frequency. The insensitivity of this band to substitution in the 4-position of pyridine N-oxide corroborates the earlier postulate that the Pt–O bond is essentially a σ-bond with little if any back-bonding contribution from the metal.

Introduction

Previous work in this laboratory[1] has demonstrated the effect on the N^{+}—O^{-} and C=C stretching frequencies caused by substituents, Z, of the pyridine N-oxide ligand in 1-(4-Z-pyridine N-oxide)-3-ethylene-2,4-dichloroplatinum(II) complexes (I).



I, Z = CH_3O, CH_3, H, Cl, CO_2CH_3, and NO_2

The purpose of this investigation was to determine the effect of Z on the Pt←O bond by an analysis of the Pt←O stretching frequencies in the complexes, I. Because recent work[2] has shown that metal–oxygen stretching frequencies in divalent metal–pyridine N-oxide complexes occur in the 350–320 cm.$^{-1}$ region, particular attention was focused on this region.

Experimental

Compounds.—The preparation and properties of the olefin complexes[1,3] and of uncomplexed 4-pyridine N-oxides[4] have already been reported. An improved method for the preparation of Zeise's salt, $K[C_2H_4PtCl_3]$, has been published,[5] but only after our preparation by an earlier method[3] had been used.

Spectra.—All spectra were recorded on a Perkin-Elmer Model 421 grating spectrophotometer with CsBr optics. All compounds were examined as Nujol mulls. As typical of the results, the spectra of 4-methylpyridine N-oxide and its complex with platinum are shown in Fig. 1.

Results and Discussion

Table I lists the observed frequencies for the various pyridine N-oxides. The data for pyridine[2] are included for comparative purposes. Table II lists the observed frequencies for the same pyridine N-oxides complexed to the platinum and *trans* to ethylene. Also included in this table are data for Zeise's salt, $K[C_2H_4PtCl_3]$, to the best of our knowledge previously unreported in this region, and the published[6,7] data for K_2PtCl_4.

Comparison of Tables I and II shows that most of the absorption maxima listed for the pyridine N-oxide complexes are also present either in the corresponding uncomplexed N-oxide or in Zeise's salt. The maxima common to all the pyridine N-oxide complexes are in the 325–322 cm.$^{-1}$ range. This absorption might conceivably be related to the 320 cm.$^{-1}$ absorption in K_2PtCl_4. However, Zeise's salt does not absorb at this frequency, and because the complexes all have approximate C_{2v} symmetry, it would be expected that they would more nearly resemble Zeise's salt, also of C_{2v} symmetry, than $PtCl_4^{2-}$ of D_{4h} symmetry. It thus appears quite reasonable to assign the 325–322 cm.$^{-1}$ frequencies to the M←O stretching frequency, and this assignment is well within the 350–300 cm.$^{-1}$ range previously reported[2] as characteristic of this group.

The insensitivity of $\nu_{M\leftarrow O}$ to changes in Z is in marked contrast to the results of our previous study,[1] which showed that $\nu_{C=C}$ and $\nu_{N^{+}—O^{-}}$ of complexes I were both very sensitive to the nature of Z. The X-ray structures of Zeise's salt[8] and the corresponding bromo complex[9] show that the Pt–X bond *trans* to ethylene is longer than that expected from the sum of the atomic radii of Pt and X. X-Ray studies of styrene–palladous chloride dimer, $(C_8H_8PdCl_2)_2$,[10] also show that the M–X bridging bonds opposite the olefin are longer (2.41 Å.) than the bridging ones opposite the Cl (2.32 Å.); the terminal M–X bonds are the shortest (2.27 Å.). However, the crystal structure of *trans*-$[Pt(C_2H_4)NH(CH_3)_2Cl_2]$[11] and infrared studies[12,13] of complexed amines show that the Pt–N bond is normal in spite of the *trans*-ethylene.[11] It has been suggested[11]

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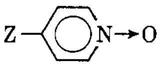
TABLE I

INFRARED BANDS (CM.$^{-1}$) OF  IN THE CsBr REGION[a]

(Ring Skeletal Vibrations)

Z							
CH_3O	CH_3	H	Cl	CO_2CH_3	CN	NO_2	Pyridine[2]
				647 s		655 m	652 (sh) vw
534 s		550 s			553 s		605 m
	524 s	516 m	523 vs	521 m		516 m	
	482 s		484 vs				
467 m	467 m	466 s			463 s		
460 m							
405 m							405 s
		371 vw	371 vw	371 vw	371 vw	371 vw	374 vw
	335 s		334 m				
	316 m						318 w

[a] vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder.

TABLE II

INFRARED BANDS (CM.$^{-1}$) OF 1-(4-Z-PYRIDINE N-OXIDE)-3-ETHYLENE-2,4-DICHLOROPLATINUM(II) COMPLEXES, STRUCTURE I, IN THE CsBr REGION[a]

Z						Zeise's salt	K_2PtCl_4[6,7]
CH_3O	CH_3	H	Cl	CO_2CH_3	NO_2		
				647 s	652 m		
569 m	569 m	575 vs	572 m	568 m	563 w		
551 mw					541 w		
500 vs	503 s	510 m	507 s	514 m	516 m	490 s	
					508 (sh) w		
450 m	464 s		478 vs		462 m		
	433 m	448 m	428 s	443 m	449 s		
				428 s			
416 s	417 m	411 vw	402 m	412 (sh) m		397 s	
339 vs	339 vs	341 s	345 vs	338 vs	342 vs	340 s	
329 w	329 (sh) w	329 (sh) w	333 s	333 (sh) s	328 (sh) w	331 w	328 (sh)
323 (sh) mw	323 (sh) mw	323 (sh) m	325 (sh) m	322 (sh) m	323 (sh) m		
							320
314 (sh)	318 w						

[a] vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder.

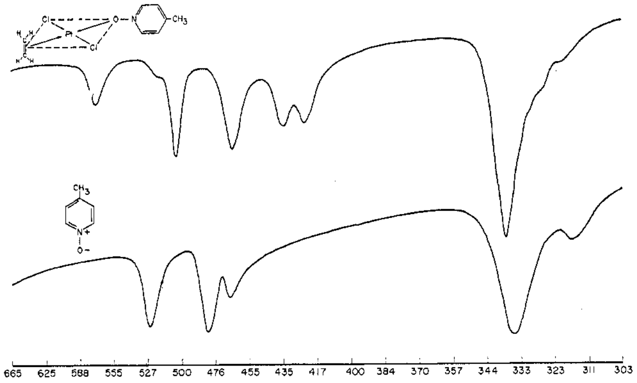


Fig. 1.—Typical N-oxide ligand and complex spectra (cm.$^{-1}$).

that this difference in the effect of *trans*-ethylene on the M–X and M–N bonds arises because the ethylene has little effect on the *trans* σ-bond, but does influence the *trans* π-bond since the ethylene competes with a π-bonding *trans* ligand for the dpπ metal orbitals. Hence the M–N bond is unaffected since N cannot partake in back-bonding, but the M–X bond is weakened by the *trans* olefin which does compete with X for the M dpπ electrons. The insensitivity of the M←O bond in our complexes is consistent with our previous proposal[1] that there is little or no back-bonding to the N-oxide in complexes of structure I and that the Pt–O bond is essentially a σ-bond.

Finally, the band at 330 ± 3 cm.$^{-1}$, since it is common to all the complexes in Table II, might reasonably be assigned[7] to a Pt–Cl stretching mode.[14]

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(14) One of the referees has pointed out that the band at 342 ± 3 cm.$^{-1}$ may be the antisymmetric Pt–Cl stretching mode, which would then make the 330 cm.$^{-1}$ band the symmetric stretch. The weak intensity of the 330 cm.$^{-1}$ band, he points out, is consistent with a small deviation from linearity in the Cl–Pt–Cl group.