

On a Pt(II)-Poly(4-vinylpyridine) Complex

INTRODUCTION

The possibility of converting a homogeneous catalyst for organic reactions into a heterogeneous one is a powerful tool in the hands of the chemists for the operation and optimization of industrial processes.

As part of our studies on this subject, it seemed interesting to take into consideration the reactivity of platinum compounds with polymers containing functional groups. In this preliminary note, we report some results on the reactivity of P-4VP with Pt(II) compounds. It is known that Pt(II) halides react quite easily with electron-donating groups (Lewis bases); quadratic planar complexes are formed, which can display cis-trans isomerism. P-4VP can be considered, in a first approximation, as a particular case of a diamine chelating agent which forms cis complexes; however, its polymeric structure can allow also the formation of crosslinked structures.

In this work, we describe the synthesis and some physicochemical properties of a Pt(II) complex.

EXPERIMENTAL

Materials

Poly(4-vinylpyridine) was prepared by modifying previous methods reported in the literature¹ and described recently by us.²

Synthesis of Pt(II)-P-4VP Complex

A solution of $K[PtC_2H_4Cl_3]$ (0.329 g = 0.887 mmole) in 10 ml MeOH was added slowly, with vigorous stirring, at room temperature to a solution of P-4VP (0.181 g = 1.77 mmole) in 120 ml MeOH. The complex precipitates immediately as a yellow powder. It was filtered after about 3 hr, and washed with H_2O , MeOH, and finally diethyl ether. The product was dried for 3 hr under vacuum (0.5 mm Hg). Yield 0.386 g (91%).

ANAL. Calcd. for $PtC_{14}H_{14}N_2Cl_2$: C, 35.30%; H, 2.96%; N, 5.88%; Cl, 14.88%. Found: C, 36.31%; H, 3.29%; N, 5.64%; Cl, 13.87%.

Spectra

The IR spectra were recorded with a Perkin-Elmer spectrophotometer, Model 225. Samples of the complex were prepared by placing a dispersion of the powder in Nujol between two CsI windows. P-4VP films were cast on a KBr plate by evaporation of solutions in $CHCl_3$ and CH_2Cl_2 .

RESULTS AND DISCUSSION

The IR spectra of complexes of Pt(II) with amines and pyridine have been extensively investigated.^{3,4,5} In particular, Clark studied the complexes with α, α' -dipyridyl and *o*-phenanthroline and did not find evidence for the stretching of the Me-N bond down to 200 cm^{-1} ; however, later he demonstrated that the stretching for the Me-pyridine bond can be situated in the spectral region between 287 and less than 200 cm^{-1} .^{6,7,8}

Additional spectral data are available for *cis*- and *trans*-Pt(II)(NH_3)₂Cl₂.⁹ *cis*-Pt(II)-(NH₃)₂Cl₂, for example, has a low stretching absorption for the Me-N bond at 510 cm^{-1} , two strong bands at 330 and 323 cm^{-1} for the stretching of the Me-Cl bond, and a relatively weak absorption at 250 cm^{-1} for the bending of the Me-N bond.⁹

The spectrum of our product shows, in addition to vibrational bands belonging to P-4VP, only one relatively weak band in the spectral region of the Me ligand absorption,

which can be assigned to the Me-halogen bond. The most significant modifications, in comparison with the spectrum of the polymer, are found for the stretching of the carbon-carbon and carbon-nitrogen double bonds.¹⁰ The very strong and sharp absorption at 1595 cm^{-1} is much broader and shifted to 1615 cm^{-1} in the spectrum of our product; the maxima at 1554 and 1491 cm^{-1} are shifted to 1552 (broad) and 1492 cm^{-1} , and a new shoulder appears at 1510 . On the other hand, the maxima at 1450 and 1414 cm^{-1} (eventually shifted to 1459) can both be covered by the Nujol absorption. For P-4VP, the two maxima at 1219 and 1067 cm^{-1} were assigned to the bending in the plane of the unsaturated C-H bonds.¹¹⁻¹³ The corresponding absorptions for our product appear as broader bands at 1217 and 1064 cm^{-1} ; the band at 990 cm^{-1} (breathing mode of the aromatic ring¹¹) is not present in the spectrum of our product. New bands appear at 342 and 228 cm^{-1} : the first may correspond to the symmetric stretching of the Me-halogen bond, the second, to a breathing mode of the Me-N bond. It does not seem possible to assign an absorption to the stretching of the Me-N bond, but this was the case also for other complexes.^{7,8}

CONCLUSIONS

From an analysis of the IR spectra of P-4VP and of our reaction product, and from the data in the literature for complexes between transition metal halides and donating systems, it seems reasonable to conclude that a coordination complex is obtained by the reaction of P-4VP with $\text{K}[\text{Pt}(\text{II})\text{C}_2\text{H}_4\text{Cl}_3]$.

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