

INFRARED SPECTRA OF A ZERO-VALENT PALLADIUM COMPLEX WITH ETHYLENEDIAMINE

Lidija Šoptrajanova, Maja Popova and Bojan Šoptrajanov

Institut za hemija, PMF, Univerzitet "Kiril i Metodij"
P.O. Box 162, 91001 Skopje, Macedonia

From the reaction system in which acetic acid solutions of palladium(II) acetate and ethylenediammonium acetate were present, a product was obtained in the infrared spectra of which there were no acetate bands. With some reservations, this unexpected result was interpreted as an indication that a palladium(0) complex was obtained.

1. INTRODUCTION

In the course of our studies of various palladium compounds [1-5], two unexpected outcomes of our attempted preparations took place.

The first was encountered during the study of complexes with complex cations and complex anions. When tetraamminpalladium(II) chloride and potassium tetracyanopalladate(II) were mixed in an equimolar ratio, a product separated in the infrared spectrum of which the expected NH_3 and CN^- bands were found. As it turned out later, the compound was *not* the expected double complex but rather *cis*-diamminedicyanopalladium, as unequivocally shown when the crystal structure of this product was solved by X-ray diffraction [5].

The second surprising result is reported in the present paper.

2. EXPERIMENTAL

2.1. Preparations

The trimeric palladium(II) acetate was synthesized according to the method described by Stephenson *et al.* [6]. Ethylenediammonium acetate was prepared by dissolving appropriate amounts of ethylenediamine in glacial acetic acid. The product obtained from the reaction mixture was a colorless crystalline compound.

Solutions of palladium(II) acetate and of ethylenediammonium acetate in glacial acetic acid were prepared. The solute concentration in the case of the palladium acetate solution was $3 \cdot 10^{-3}$ mol/dm³ whereas the ethylenediammonium acetate concentration in its solution was $1.5 \cdot 10^{-2}$ mol/dm³.

In an attempt to prepare an ethylenediamonium tetraacetatopalladate complex, portions of the palladium acetate and ethylenediamonium acetate solutions were mixed in a stoichiometric ratio and kept in a vacuum desiccator with CaCl_2 as a drying agent. On standing, a small quantity of yellow-orange, needle-like crystals separated. The quantity was insufficient to try to analyze them but adequate to run infrared spectra of crystals hand-picked under a microscope.

2.2. Instrumental conditions

The infrared spectra were recorded (from KBr pellets) on a Perkin-Elmer 580 Infrared Spectrophotometer both at room temperature (RT) and at the boiling temperature of liquid nitrogen (usually abbreviated LNT). A VLT-2 (RIIC-London) cell was used for the low-temperature measurements.

3. RESULTS AND DISCUSSION

The LNT spectra of the two starting compounds, palladium(II) acetate and ethylenediamonium acetate are given in Fig. 1 whereas the RT and LNT spectra of the obtained product are reproduced in Fig. 2.

As seen, the spectrum of the product consists of a number of very sharp bands, showing that a well-defined and nicely crystallized compound has been obtained.

The presence of the two sharp and intense bands around 3285 and 3215 cm^{-1} was an indication that NH_2 groups from the coordinated ethylenediamine were present in the

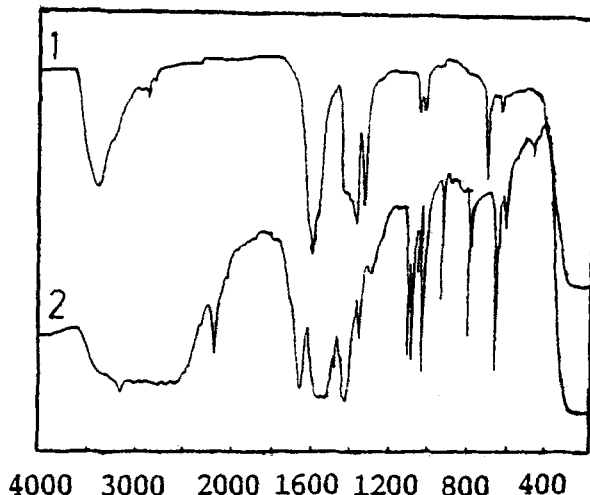


Fig. 1. LNT spectra of palladium(II) acetate (1) and ethylenediamonium acetate (2)

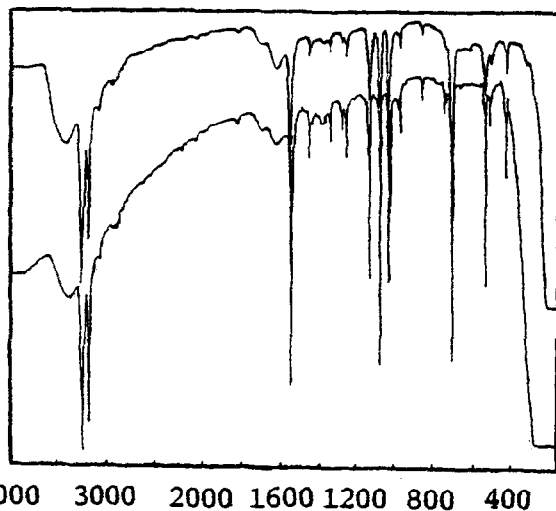


Fig. 2. RT and LNT spectra of the reaction product

structure of the obtained product. The shoulder at 3245 cm^{-1} is also due to ethylenediamine vibrations, whereas (the broad band at higher frequencies is undoubtedly due to adsorbed water).

In fact, all bands expected for coordinated ethylenediamine [7] could be located at frequencies quite close to those of the bands in the spectrum of $[\text{Pd}(\text{en})_2]\text{Cl}_2$. The assignment of the ethylenediamine bands is, thus, straightforward. For our present purposes, the exact assignment is not relevant.

To our utter surprise, however, in the spectra of the product the acetate bands were absent. This is particularly obvious in the region around 1600 cm^{-1} where broad and very intense bands due to the anti-symmetric COO^- stretching modes are expected to appear (the weak bands above 1600 cm^{-1} can not be due to the expected carboxylate stretches and apparently result from the bending modes of adsorbed water). No other band assignable to acetate vibrations could be found either.

Since the acetate anions were the only ones present in the initial reaction system, it was difficult to reconcile two apparently contradictory facts: well-defined crystals which certainly contained palladium and gave a spectrum in which ethylenediamine bands are present, on the one hand, and the absence of bands attributable to the anions, on the other.

The obvious conclusion was that the product was a complex of zero-valent palladium with ethylenediamine.

Complexes of $\text{Pd}(0)$ are known [8] but, to the best of our knowledge, always with a soft Lewis base in Pearson's [9,10] classification, whereas the amines are hard bases. In fact, according to the so-called HSAB principle of Pearson, compounds of soft acids and hard bases are expected to be unstable.

This did not seem to be a serious problem since palladium(II) acetate, itself being a compound of a soft acid and a hard base, is not very unstable. It is true that from acetic acid solutions colloidal palladium separates on standing (a disproportionation reaction apparently taking place) but the crystals (once obtained) could be kept unchanged for a long period.

The above-mentioned spontaneous separation of elemental palladium from acetic acid solutions of palladium(II) acetate, on the other hand, indicates that a mechanism is available for the reduction of palladium to a zero-valent oxidation state.

Our self-confidence was strengthened when, using the same experimental procedure, we successfully prepared another analogous compound, this time with diethylamine [11]. Again, no acetate bands were present in the infrared spectra of the product.

Apparently, a convenient route has been inadvertently found for the preparation of complexes of zero-valent palladium with amines.

A dose of caution was introduced in our reasoning when the procedure was repeated, but using silica-gel as a desiccant. This time the reaction product gave an infrared spectrum clearly different from that of the initially prepared crystals. Acetate bands were present in this spectrum.

This made us suspect that, after all, what we obtained was not a complex of zero-valent palladium, but a chloride complex of palladium(II), the chloride ions being provided by calcium chloride particles floating in the vacuum desiccator. This seems rather unlikely

but we are presently investigating such an alternative since, if it turns out to be true, it is worth knowing that it is not always safe to use calcium chloride as a drying agent.

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