

INFRARED SPECTRA OF THE HYDRATE OF TETRAAMMINEPALLADIUM(II)
ACETATE

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In the infrared spectrum of the title compound a number of deuteration-sensitive bands is observed at the high-frequency side of the antisymmetric CDO stretching band. It is proposed that they are due mainly to anharmonic interactions between the fundamental NH_3 bending vibrations falling in the same region and second-order transitions involving the NH_3 rocking mode.

Although tetraammine complexes of various palladium(II) salts are well-known /1/, the corresponding acetate has not apparently been prepared until recently /2/. As a part of our work on various palladium compounds /2-4/, we now report the results of the investigation of the infrared spectra (recorded at room and liquid-nitrogen temperature, on a Perkin-Elmer 580 instrument) of the hydrate of tetraamminepalladium(II) acetate. Colorless crystals of this complex were obtained by action of gaseous NH_3 or concentrated aqueous solution of ammonia on solid palladium(II) acetate.

RESULTS AND DISCUSSION

The RT and LNT spectra of tetraamminepalladium acetate monohydrate are shown in Fig. 1. The comparison of the two spectra

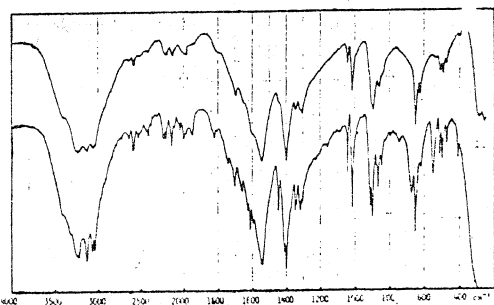


Fig. 1. RT and LNT spectra of tetraamminepalladium acetate monohydrate

reveals the existence, in the LNT spectra, of bands whose frequencies (680 and 550 cm^{-1}) are higher and which are much more intense than in the RT spectra - a behaviour typical for water librational bands (other temperature-sensitive bands, easily related to ammonia vibrations, are also present, but their intensity changes are not nearly as dramatic as those of the two above-mentioned bands). The infrared spectra thus indicated the formation of a hydrate, the results of the elemental analysis being in a

fair agreement with the assumption that a monhydrate is in fact obtained. It should be mentioned that the LNT band around 750 cm^{-1} could also be due to water libration. All these bands disappear on deuteration (Fig. 2), in line with the proposed assignment.

It is difficult to locate the stretching and bending water

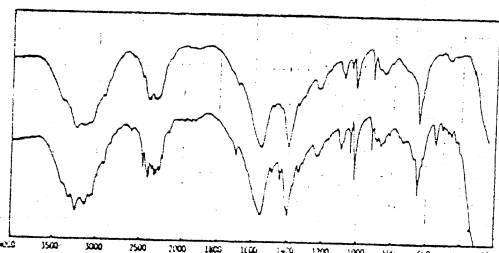


Fig. 2. RT and LNT spectra of partially deuterated tetraamminepalladium acetate monohydrate

bands since they are expected in regions where other intense bands (some also deuteration-sensitive) are present. It should be noted however that on deuteration quite a large number of bands disappear from the high-frequency side of the intense band which is centered around 1550 cm^{-1} and is due to the asymmetric COO stretching. The whole picture is similar to that observed in practically all other, hydrated or anhydrous, am-

mine complexes of palladium studied by us /2-4/ so that a common origin could be suspected (this, of course, does not rule out the possibility that some of the bands could originate from HOH bendings). In agreement, then, with the explanation proposed earlier /4/, the multiple bands (all or some) in the NH_3 bending region should be explained as due to anharmonic interactions of the fundamental ammonia modes with second-order transitions (true overtones and/or combinations of various unit-cell modes) involving the NH_3 rockings. Such a conclusion is supported by the absence of structure in the NH_3 bending region in cases (such as in hexaamminenickel tetracyanopalladate(II) /2/) where the rocking NH_3 frequency is low and thus unable to give overtones with frequencies in the range appropriate for interactions with the ammonia bending fundamentals.

Since water molecules are also present in the studied here case and the appearance of multiple bands has been observed in the HOH bending region as well /5/, it is quite possible that the water modes also participate in interactions with second-order transitions. The precondition for such interactions to take place is, of course, the anharmonicity of the corresponding vibrations which, in turns, implies an asymmetric environment of the ammonia and/or water molecules.

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