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VIBRATIONAL STUDIES OF PALLADIUM(II) ACETATE COMPOUNDS II. INFRARED SPECTRA OF THE DIETHYLAMINE ADDUCT OF PALLADIUM(II) ACETATE

KEY WORDS : Palladium(II) acetate; diethylamine; palladium acetate, diethylamine adduct; infrared spectra.

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ABSTRACT

Recorded and discussed are the infrared spectra of the diethylamine adduct of palladium(II) acetate. An empirical assignment of the spectra is proposed. The palladium-oxygen bonds in the adduct are not much different in strength from those in hexa-μ-acetato-*triangulo*-tripalladium(II)-water (2/1). The diethylamine molecules are present as such, as evidenced by the appearance of a rather strong band attributed to the N-H stretching vibrations.

INTRODUCTION

A number of various amine adducts of palladium(II) acetate were synthetized by Stephenson *et al.* [1]. These authors indicated that the ratio of palladium acetate to the amine is 1 : 2 so that the appropriate formula would be $Pd(OAc)_2 \cdot 2DEA$ where OAc stands for CH_3COO and DEA for $(C_2H_5)_2NH$. To the best of our knowledge, there have been no detailed structural studies on this compound and neither its spectra nor its crystal structure seem to have been studied except for our brief account [2].

The diethylamine adduct of palladium(II) acetate was prepared by us in the course of our extensive studies of palladium acetate and the products of its reactions, including those with amines [2-5]. Since high-quality infrared spectra were obtained, we decided to analyze them in some detail.

EXPERIMENTAL

The diethylamine adduct of palladium(II) acetate was prepared according to the procedure described by Stephenson *et al.* [1] and was recrystallized from petroleum ether, as suggested by these authors.

The infrared spectra were recorded, at room temperature and at the boiling temperature of liquid nitrogen (RT and LNT hereafter) on a Perkin-Elmer Model 580 infrared spectrophotometer.

Pellets in KBr were used to obtain the spectra, except for a few instances when mulls in Nujol or hexachlorobutadiene were employed (mainly in order to check that no interaction with the KBr matrix has taken place).

RESULTS AND DISCUSSION

The RT infrared spectra of $Pd(CH_3COO)_2 \cdot 2(C_2H_5NH)_2$ recorded from KBr pellets are given in Fig. 1 and the observed frequencies are listed in Table 1. This table contains also the results of a tentative assignment of the major infrared bands based on the assumption that the modes giving rise to the observed bands could be acceptably (at least to a first approximation) described as acetate, diethylamine and metal-to ligand vibrations.

Acetate vibrations

In the discussion which follows, the descriptions of the modes will be based on the results of a normal-coordinate analysis for the "free" acetate ion [7] and are only *approximate*. As a mere *label*, namely, we shall mention the coordinate with the major contribution to the normal mode. It should be borne in mind that for variously *bonded* acetates the form of the normal modes and the potential energy distribution may differ from those calculated for the "free" ion.

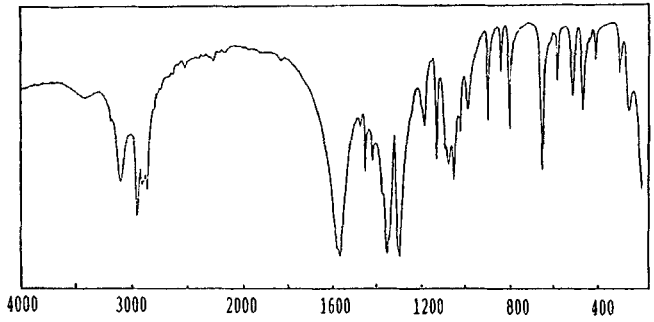

FIG. 1. Infrared spectrum of the diethylamine adduct of palladium(II)

Among the bands attributable to acetate vibrations, only those which *are not* due to methyl modes could be expected to be distinguishable from the bands which originate from the vibrations of the diethylamine molecules.

The location of the antisymmetric COO stretches presents no special problems. In the region around 1600 cm^{-1} where the appearance of the corresponding bands is expected, namely, the diethylamine molecules are not expected to absorb [6] although it is not impossible that the CNH in-plane bending *may* appear in this region. Since a band attributable to this latter mode was found around 1500 cm^{-1} and a shoulder which becomes visible at LNT around 1610 cm^{-1} may also originate from a vibration with CNH bending character, it was concluded that the closely spaced doublet observed at 1595/1585 cm^{-1} originates (mainly or entirely) from the antisymmetric stretchings of the carboxyl groups. It must be pointed out that these frequencies are only marginally higher than in the ionic acetates (e.g. $\approx$ 1578 cm^{-1} for sodium acetate) and slightly lower than in the case of the band encountered in the spectrum of hexa-μ-acetato-*triangulo*-tripalladium(II)–water (2/1) [5].

It should be noted that, although a *doublet* is observed in the presently investigated spectrum, the frequencies of its components have values which are not much different from the frequency of the centroid of the broad band found in the corresponding region of the infrared spectrum of $2[Pd_3(OAc)_6]\cdot H_2O$ [5]. The combined width of the feature in the present case is *less* than the width of the apparently symmetric band which was found in the

TABLE 1

Infrared frequencies and a tentative assignment of the major bands in the infrared spectrum of $Pd(OAc)_2 \cdot 2DEA$ (underlined are the frequencies of the bands which are undoubtedly due to acetate vibrations)

Frequency / cm^{-1}	I^*	Assignment**	Frequency / cm^{-1}	I^*	Assignment**
3115	m	NH stretch	1119	w	
			1104	m	CH_3 rock
2975	s	CH_3 *as* stretch			
2935	m	CH_3 *as* stretch	1080	ms	CH_3 rock
2905	m	CH_2 *as* stretch			
2890	m	CH_3 *s* stretch	1055	sh	
			1050	m	CC stretch
1610***	sh	CNH *ip* bend?	1041***	w	
1595	s	COO *as* stretch			
1586	vs	COO *as* stretch	1015	m	CH_3 rock
1500	m	CNH *ip* bend	927	m	CC stretch
1472	m	CH_3 *as* bend	869	mw	CN stretch
1465	vw	CH_3 *as* bend			
			832	m	CH_3 and/or
1441	m	CH_2 bend	805***	w	CH_2 rock
1428***	m	CH_3 bend	687	ms	OCO bend
1398	w	CH_3 *s* bend and	615	m	COO wag
1375	vs	COO *s* stretch			
			545	m	COO rock
1365	m	CH_3 *s* bend			
			500	m	CCN bend
1325	sh				
1319	vs	CH_2 wag	467	vw	CCN bend
1270	sh	CH_2 twist			
			441	w	Pd-ligand str.
1225	sh				
1213	m	CH_3 rock	335	m	Pd-ligand str.
1158	m	CN stretch	293	m	skeletal bend

* The abbreviations have the usual meaning : **s** - strong, **m** - medium, **w** - weak, **v** - very, **sh** -shoulder.

** Only the major contributions to a given mode are listed. The abbreviations ***as*** and ***s*** mean *antisymmetric* and *symmetric* respectively and ***ip*** and ***oop*** stand for *in-plane* and *out-of-plane* respectively.

*** LNT frequency.

infrared spectrum of hexa-μ-acetato-*triangulo*-tripalladium(II)–water (2/1) [5]. It would then seem that the quite symmetric appearance of the band observed in the latter case is a result of a fortuitous overlapping of a number of closely spaced bands.

As in the case of the just mentioned compound, the location of the band(s) attributable to the *symmetric* COO stretches in the spectrum of $Pd(OAc)_2 \cdot 2DEA$ is difficult. As seen in Fig. 1, namely, no significant change of intensity for any of the bands present at ≈ 1400 cm^{-1} is brought about when the temperature changes from RT to LNT. So, even the criterion of Heyns [8] (according to which the bands attributable to these vibrations should gain in intensity when the temperature is lowered) is not of much help here. Nevertheless, we are inclined to believe that one or more of the bands forming the complex feature centered around 1375 cm^{-1} should be attributed to the carboxyl symmetric stretches since, as explained below, the alternative assignment seems to be less probable.

Some doubts regarding the above assignment are aroused because of the *temperature conduct* of the band found around 1320 cm^{-1}. On lowering the temperature, namely, this band behaves in a vein similar to that reported by Kakihana *et al.* [9] for the band originating from the symmetric COO stretching in the spectra of sodium acetate or by Heyns [8] for the corresponding band in the spectrum of copper acetate dihydrate. At seen in Fig. 2, the splitting of the 1320 cm^{-1} band, barely visible at RT, becomes more pronounced as the temperature is lowered and a new band (with apparently increased intensity) develops around 1330 cm^{-1}. It would thus seem that the intensity of the complex feature around 1320 cm^{-1} might stem (at least partly) from the symmetric COO stretch. The above frequency (1330 cm^{-1}), however, appears to be *very low* for the symmetric COO stretch. Frequency values close to 1420 cm^{-1} (i.e. ≈ 100 cm^{-1} higher) were reported [7,9-12], namely, for sodium acetate and similar values were found in other cases.

The results of the analysis of the carboxyl stretches are, thus, inconclusive, especially if inferences regarding the structural role of the acetates in the presently studied compound are to be made. As is well known, namely, the shifts of the two COO stretches in the spectrum of a given compound with respect of the positions of the corresponding bands in the spectra of ionic acetates have been used to assess the structural role of the acetate (and other carboxylate) ligands [13]. Thus, for monodentate acetates the antisymmetric COO stretches

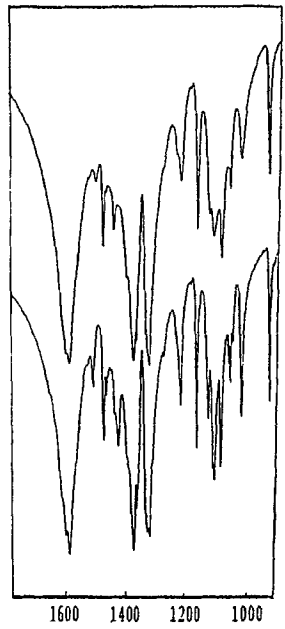

FIG. 2. The effect of temperature on the bands in the 1600-1400 cm^{-1} region of the infared spectrum of the diethylamine adduct of palladium(II) (**a** - RT spectrum; **b** - LNT spectrum)

are expected to have *higher* and the symmetric ones *lower* frequency than those in the ionic acetates (e.g. 1578 and 1414 cm^{-1} in the spectrum of sodium acetate [11]). If we take that the frequency of the symmetric COO stretch is close to 1375 cm^{-1} and that the frequency of the antisymmetric stretch is close to 1595 cm^{-1}, the separation between the two COO stretching frequencies would be somewhat larger than in the case of the ionic acetates but not as much so as to be considered a *proof* that the acetates *are* monodentate. In fact, the frequencies of the two COO stretching bands would not be significantly different from those in the spectrum of hexa-μ-acetato-*triangulo*-tripalladium(II)–water (1/2) [5]. If, on the other hand, the true frequency of the symmetric COO stretch is $\approx$ 1330 cm^{-1}, the separation would be closer to that expected for monodentate acetates but the relatively low frequency of the antisymmetric COO stretch would not be in line with the expectations for this type of acetate ligands. It should be pointed out that the validity of this and other similar criteria has been questioned quite long ago (e.g. in Ref. 14).

It should be stressed that if the COO symmetric stretches are located around 1320 cm^{-1} then the feature appearing there must be due to an overlap of the acetate COO symmetric stretchings and the CH_2 modes of the DEA ligands (see below).

Several bands which, according to some literature sources (e.g. [15]) might also be due to acetate vibrations, deserve attention. The bands in question are observed around 927, 869, 832 and 545 cm^{-1}.

In their work on the structural deductions from the infrared spectra of acetates, Stoilova *et al.* [15], namely, suggested that the existence of *monodentate* acetates is manifested by the presence of three bands in the 920-720 cm^{-1} region and of an additional band around 540 cm^{-1}. As seen, the four $Pd(OAc)_2 \cdot 2DEA$ bands mentioned above fall almost exactly in the regions quoted by Stoilova *et al.* [15]. It should be noted, however, that these authors have based their conclusions on the studies of *crystallohydrates* and some of the bands attributed to acetate modes (including the bands appearing in the presently discussed regions) are actually due to water librations.

In fact, the work in our laboratory [16,17] has shown that all strong bands in the 1000-700 cm^{-1} region of the spectrum of $Ni(OAc)_2 \cdot 4H_2O$ (one of the compounds studied in [15]) exhibit intensity changes and shift towards higher wavenumber values when the temperature is lowered. Furthermore they disappear on deuteration, leaving only a band around 945 cm^{-1} the intensity of which is only moderate. Such a behaviour is, of course, characteristic of bands due to water librations. Similar observations were made, in the case of nickel acetate tetrahydrate, by other authors as well [18,19], the situation being similar in the vibrational spectra of other hydrated acetates [18-20]. Bearing this in mind, of the enumerated above bands only the assignment of that observed around 927 cm^{-1} to an acetate CC stretching mode seems incontestable. On the other hand, the bands appearing in the 900-800 cm^{-1} region, are attributed to *diethylamine* modes with CN stretching, CH_3 rocking and CH_2 rocking character and will be discussed later.

As for the 560-540 cm^{-1} acetate band allegedly indicative of the existence of monodentate acetates, in the spectrum of $Pd(OAc)_2 \cdot 2DEA$ there is, as mentioned, a feasible candidate, located around 545 cm^{-1}. No DEA band is expected in this region [6] and none is found in our

spectrum of a DEA complex of Pd(0) [3]. The studies on the spectra of $Ni(CH_3COO)_2 \cdot 4H_2O$ and its deuterated analogues performed in our laboratory [16,17] seem to indicate that the 570 cm^{-1} band found there is insensitive to deuteration and should, consequently, be assigned to an *acetate* vibration. On the other hand, Baraldi and Fabbri [18] attributed to *water librations* the bands which appeared around 550 cm^{-1} in the spectra of tetrahydrates of the studied by them metal(II) acetates. As mentioned, our analysis of these spectra does not necessarily support such an assignment and there is no water in the structure of the presently studied compound. So, we prefer to assign (at least for the time being) the 545 cm^{-1} band to an acetate vibration, most probably with a COO rocking character. Such an assignment is supported by the appearance, in the spectrum of lithium acetate dihydrate [21], of a band found around 517 cm^{-1} and its assignment to the COO rocking vibration. The value given above, of course, is not significantly lower than that found in our case. It must be pointed out that the acetates in the structure of $LiCH_3COO \cdot 2H_2O$ are *not* of the monodentate type [22]. At this point we may add that a band of medium intensity is reported to exist in the spectrum of *anhydrous* lithium acetate [23] around 540 cm^{-1} but was left unassigned.

As far as the assignment of the 545 cm^{-1} band in our spectra is concerned, the only remaining possibility is to assign it to a metal-to-ligand mode but its frequency seems to be rather high for a mode which is either predominantly Pd-O stretching or predominantly Pd-N stretching in character.

The assignment of the most of the remaining acetate bands is not very difficult and the results are included in Table 1. Thus, the band around 1015 cm^{-1} is assigned to the acetate CH_3 rocking mode expected in this region. The OCO bending mode gives rise to the band at 687 cm^{-1} and the COO wagging one to the band around 615 cm^{-1}, both values being lower than those in the case of hexa-μ-acetato-*triangulo*-tripalladium(II)–water (1/2) (approximately 700 and 628 cm^{-1} respectively) [5].

Diethylamine bands

The majority of the diethylamine bands can be assigned (cf. Table 1) on the basis of the published work by Verma [6] which deals with the spectra of liquid and solid $(C_2H_5)_2NH$. We shall refrain from a detailed description of these bands and their assignment and shall only briefly enumerate some of the more important points.

Among the DEA bands, the first to mention is that observed at 3115 cm^{-1}. This band, namely, shows that the diethylamine *molecules* in a non-ionized form are present in the structure of the studied compound. The frequency of this band is lower than either in liquid or in solid DEA [6], an indication of a stronger hydrogen bonding present in $Pd(OAc)_2 \cdot 2DEA$ than in pure DEA. It is reasonable to assume that oxygens from the neighbouring structural units act as proton-acceptors.

The CNH in-plane bending probably gives rise to the weak band around 1500 cm^{-1} (which shifts slightly as the temperature is lowered), although it is also possible that the corresponding band is hidden under the very strong band which arises from the antisymmetric COO stretch of the acetate ligands. As mentioned, namely, a shoulder appears around 1620 cm^{-1} in the LNT spectra. The identification of the CNH out-of-plane bending band is problematical. One would, namely, expect this band to be found higher than 715 cm^{-1} (its value in solid DEA [6]) and, in addition to that, it should be temperature sensitive. In the RT spectrum there is indeed a shoulder, turning into a rather weak band, visible (around 800 cm^{-1}) at LNT but, as mentioned, its intensity is much lower than expected. The band found around 545 cm^{-1} also shifts towards higher frequencies, but its frequency is too low and, besides, it has already been assigned to an acetate mode (see above).

In gaseous and liquid DEA several bands were observed in the 1350-1320 cm^{-1} region and were interpreted [6] as due to the CH_2 wagging and CH_2 twisting modes. The existence of a complex feature in this region of the spectrum of $Pd(OAc)_2 \cdot 2DEA$ has already been discussed and it is certain that the above-mentioned modes give rise to bands appearing around 1320 cm^{-1}.

All bands in the 1250-1050 cm^{-1} region are interpreted as due to diethylamine vibrations (see Table 1).

The erroneous attribution by Stoilova *et al.* [15] to acetate vibrations of the bands which appear, between 900 and 800 cm^{-1} in the spectra of the studied by them acetates, has already been discussed. The conclusion that these assignments are inadequate is corroborated in the present study. In fact, *diethylamine* modes with CN stretching, and CH_3 and CH_2 rocking character are expected to appear in this region (four bands were observed in the spectra of *liquid* DEA whereas only three exist in the spectrum of *solid* diethylamine [6]). Bands in this region are observed also in the spectrum of the palladium(0) DEA complex studied by us [3] where they can only

be due to *diethylamine* vibrations. Therefore we attribute the bands appearing at 869 and 832 cm^{-1} in the spectrum of $Pd(OAc)_2 \cdot 2DEA$ to the CN stretching and CH_3 rocking modes of diethylamine. Since, in addition to that, a band is clearly visible around 805 cm^{-1} in our LNT spectra, suitable candidates seem to have been found for all DEA modes expected in the 900-800 cm^{-1} region.

The bands at 500 and 467 cm^{-1} are assigned to the CCN bending vibrations of the diethylamine molecules.

Metal-to-ligand modes

According to the results of the normal-coordinate analysis [7], all acetate vibrations have frequencies higher than 450 cm^{-1}. On the other hand, the bands of liquid diethylamine appearing below 492 cm^{-1} are reported [6] to be much weaker than the band at this latter frequency.

On the basis of these findings, it would seem that the bands located, in the spectrum of $Pd(OAc)_2 \cdot 2DEA$, below 400 cm^{-1} should be attributed to metal-to-ligand vibrations. The precise assignment of these bands is presently not possible and it is even hard to say whether they are predominantly Pd-O or Pd-N in character.

If we assume that these bands are due to *metal-to-acetate* vibrations, then from the fact that their frequencies are lower in the spectrum of the presently studied compound than in that of palladium acetate itself [5] it would follow that weaker metal-to-ligand interactions exist in the former than in the latter case.

The band at 440 cm^{-1} might also be due to a metal-to-ligand mode, probably mostly Pd-N in character. The problems with the assignment of the 545 cm^{-1} band were discussed above.

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