VIBRATIONAL STUDIES OF PALLADIUM(II) ACETATE COMPOUNDS I. INFRARED SPECTRA OF HEXA-μ-ACETATO-*triangulo*-TRIPAL-LADIUM—WATER (2/1)

KEY WORDS : Palladium(II) acetate; hexa-μ-acetato-*trian-gulo*-tripalladium(II)—water (2/1); hexa-μ-acetato-*trian-gulo*-tripalladium(II) hemihydrate; infrared spectra.

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ABSTRACT

The infrared spectra of palladium(II) acetate crystals obtained from a benzene-acetic acid solution show that hexa-μ-acetato-*trian-gulo*-tripalladium(II)—water (2/1) i.e. the hemihydrate of hexa-μ-acetato-*triangulo*-tripalladium(II) was obtained. An empirical assignment of the observed bands is proposed.

INTRODUCTION

The acetate salt of palladium(II) and a number of amine adducts were originally synthetized by Stephenson *et al.* [1]. These authors indicated that palladium acetate is *trimeric* in benzene solution at 37 °C.

The trimeric nature of palladium acetate was later confirmed by Skapski and Smart [2] in the preliminary account of their X-ray work on the crystals isolated

from the benzene-glacial acetic acid solution. It was shown that the compound synthetized according to the procedure described by Stephenson *et al.* [1] crystallizes in the monoclinic space group *P2₁/n*. The unit cell contains two crystallographically non-equivalent (albeit rather similar) trimeric [Pd₃(CH₃COO)₆] molecules and a single water molecule so that the studied compound can be formulated as a hemihydrate of the trimeric palladium acetate. The systematic name of this form of palladium acetate would be, as mentioned, hexa-*μ*-acetato-*triangulo*-tripalladium(II) hemihydrate or, even better, hexa-*μ*-acetato-*triangulo*-tripalladium(II)—water (2/1) [3]. Both names will be used hereafter. The actual structure would thus be best reflected by the formula 2[Pd₃(OAc)₆]·H₂O, where **OAc** denotes an acetate group. The three palladium atoms within each trimer make, according to Skapski and Smart [2], an approximately equilateral triangle and are bonded to each other by six bridging acetates. Four oxygens are located around each palladium atom so that the usual square-planar coordination is reached. The role played by the water molecules was not elucidated.

Later on, Cotton and Han [4] undertook a more detailed crystallographic study of crystals prepared according to the method of Stephenson *et al.* [1] but found that the crystals contained *benzene* and **not** *water*. The space group of these crystals was reported to be *C2/c* and the above-mentioned triangles formed by palladium atoms were found to be isosceles rather than equilateral.

Still later, Cotton and Han reported [5] the existence of a third form of trimeric palladium acetate. It was obtained, this time, from dichloromethane solutions. The formula of the product was reported to be Pd₃(OAc)₆·½CH₂Cl₂. The existence of still another form of palladium acetate, again obtained from dichloromethane, was reported by Barton [6]. The content of dichloromethane was said to be twice as large as that in the form reported by Cotton and Han [5]. In addition to that, Barton confirmed the existence of the hemihydrate.

In all studied cases, the guest molecules (those of benzene, water or dichloromethane) apparently play only a space-filling role. It is thus plausible that other similar species could also be formed and the existence of two forms, containing varying ammounts of dichloromethane becomes understandable.

To the best of our knowledge, only the frequencies of a few infrared bands were given by Stephenson *et al.* [1] and by Brandon and Claridge [7]. The complete spectrum

of palladium acetate was *briefly* discussed, some time ago, by us [8]. Since the vibrational spectra of palladium acetate does not seem to have not been studied in detail, we decided to undertake a systematic study of the vibrational spectra of the known forms of palladium acetate and of some of its amine adducts the existence of which was reported by Stephenson *et al.* [1].

In the present communication we report the results of our study of the hemihydrate of hexa-μ-acetato-*triangulo*-tripalladium(II), whereas the spectra of some other forms and of the amine adducts will be analyzed in the subsequent papers of this series.

EXPERIMENTAL

The crystals of the title compound was prepared following closely the procedure described by Stephenson *et al.* [1] and were recrystallized from benzene-acetic acid mixture, again as described in Ref. 1. The water content in the acetic acid was not checked. As discussed later, the spectra of the obtained product demonstrated the presence of water bands, so that obviously the hemihydrate of hexa-μ-acetato-*triangulo*-tripalladium(II) has been obtained.

The infrared spectra of the studied compound were recorded, on a Perkin-Elmer 580 spectrophotometer, at room temperature (RT) and at the boiling temperature of liquid nitrogen (LNT hereafter). Except for a few instances when mulls in Nujol or hexachlorobutadiene (HCB) were employed, KBr disks were used throughout.

RESULTS AND DISCUSSION

The RT and LNT infrared spectra of $2[Pd_3(OAc)_6] \cdot H_2O$ recorded from KBr pellets are given in Fig. 1. The observed frequencies are listed in Table 1, together with the tentative assignment the basis of which will be discussed below.

Acetate vibrations

Taking into account the existence of *twelve* crystallographically non-equivalent acetate ligands, the infrared
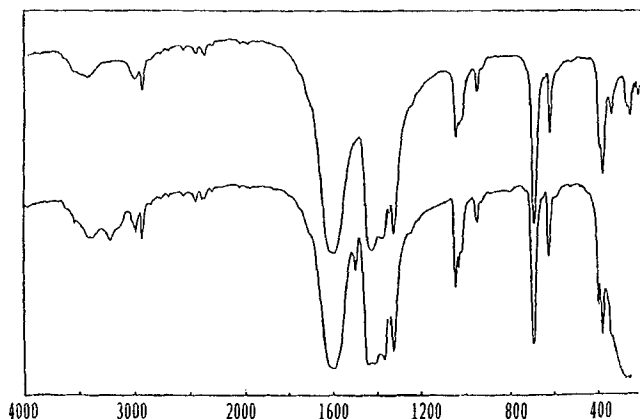
FIG. 1. RT and LNT spectra of hexa-μ-acetato-*triangulo*-
tripalladium(II)-water(2/1)

spectra are surprisingly simple. Thus, in the region
around 1600 cm^{-1} where the appearance of the antisymmet-
ric COO stretches is expected, only a single, quite sym-
metric, band is observed which even at LNT shows practi-
cally no splitting. The same is true for the bands ap-
pearing around 700 cm^{-1} and around 630 cm^{-1}.

The conclusion which immediately follows is that, des-
pite their non-equivalence, all acetato ligands are
structurally quite similar. Unfortunately, such a con-
clusion could not be tested by a direct analysis of the
reported [2] X-ray data, since only some average values
were given by Skapski and Smart and it does not seem
that the details of the structure of this form of palla-
dium acetate were presented later on, either by Skapski
and Smart [2] themselves or by other authors [6].
Furthermore, the width of the band is considerable so
that it is likely that what we see is not really a band
but an envelope encompassing a number of separate bands
with frequencies which are not identical.

Using the results of a normal-coordinate analysis for
the "free" acetate ion [8] as a guide, most of the
acetate bands can be assigned without difficulty. In the
discussion which follows we shall attribute the observed
bands (single or split) to the vibrations of an *indivi-
dual* acetate, bearing in mind that, in fact, *twelve*

TABLE 1

Infrared frequencies and a tentative assignment of the major
bands in the spectrum of *triangulo*-hexa-μ-acetatopalladium(II)

Frequency cm^{-1}	I*	Assignment**	Frequency cm^{-1}	I*	Assignment**
3655	vw	H2O *as* stretch	1048	m	CH3 rock
3570	vw	H2O *s* stretch	1032	m	CH3 rock
			950	w	CC stretch
2990	w	CH3 *as* stretch			
2935	w	CH3 *s* stretch	700	s	OCO bend
			628	m	COO wag
1605	vs	COO *as* stretch	590***	vw	H2O libration
1430	vs	CH3 *as* bend	395	m	PdO stretch
1400***	vs	COO *s* stretch ?	378	s	PdO stretch
			340	w	PdO stretch
1370	s	COO *s* stretch			
1350	w	CH3 *s* bend	270	sh	OPdO bend
1330	m	CH3 *s* bend	255	w	OPdO 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 abbre-
viations *as* and *s* mean *antisymmetric* and *symmetric* respectively.

*** LNT frequency.

modes of each kind must be taken into account. Such an
approach seems justified since, as mentioned above, the
majority of the acetate bands either show no splitting
at all or appear as closely spaced doublets or multi-
plets. In order to simplify the description, only the
coordinate with the major contribution to the normal
mode will be used as a label.

The only notable exception to the ease with which the
acetate bands can be assigned is the proper identifica-
tion of the bands originating from the symmetric COO

stretching vibration. These bands, namely, are expected
in the same region where the methyl antisymmetric ben-
dings appear and it is difficult to distinguish the
former from the latter. With the experimental data which
we had in hands, the only possibility for tentatively
locating the band(s) due to the symmetric COO stretch
was to use as a criterion the temperature dependence of
the intensities of the bands in the 1400 cm^{-1} region.
Heyns has, namely, shown [10] that the intensity of the
band originating from the symmetric COO stretch increa-
ses on lowering the temperature.

In the region around 1400 cm^{-1}, there are apparently
only two bands whose intensity increases on passing from
RT to LNT. The enhancement is more evident for the band
at ≈ 1370 cm^{-1} but it seems that an intensity increase
is present also for the band found at almost exactly
1400 cm^{-1}. It would thus seem that the former band
should certainly be assigned to the symmetric COO
stretch whereas the assignment of the latter one is open
to discussion. In any case, the frequencies of the
discussed modes of the acetato ligands in hexa-μ-
acetato-*triangulo*-tripalladium(II)—water (2/1) are *low-
er* than in the case of the *ionic* acetates, a value of
1414 cm^{-1} being reported [11] for sodium acetate.

This finding is somewhat surprising. It is usually be-
lieved, namely, that for *bridging* acetates (or, in gene-
ral, carboxylates) the frequency separation between the
two COO stretches (the antisymmetric and the symmetric
one) should be comparable to that found in ionic ace-
tates, but the frequency of both stretches should be
higher than in ionic acetates [12]. It must be noted,
however, that the validity of the above-mentioned crite-
rion (as well as that of the similar criteria for the
monodentate and chelate carboxylates) has already been
questioned [13].

If the assignment of the bands which are due to the
symmetric COO stretch is accepted, then the bands *above*
1400 cm^{-1} would be assigned to the antisymmetric CH$_3$
bendings. There is little doubt that to *methyl* vibra-
tions belongs also the weak band at 1350 cm^{-1} (attribu-
ted to the symmetric CH$_3$ bending) as well as the complex
of overlapped bands centered around 1040 cm^{-1} (the com-
ponents of the complex originate from two different
rocking vibrations of the methyl groups).

In addition to the modes which are predominantly COO
stretches and were discussed above, three additional COO
bands (due to the OCO bending, and to the wagging and

rocking COO vibrations respectively) are expected for each acetate ion. The bands around 700 and 628 cm^{-1} can be assigned to the former two modes, whereas there is no clear candidate for the rocking COO vibration. In our spectra, namely, there is no strong band in the region between 600 and 400 cm^{-1} assignable to such a vibration. Such a finding, on the other hand, is in agreement with the work of Stoilova *et al.* [14] who proposed, as a spectroscopic criterion for the existence of *bridging* acetates, the *absence* of a strong band around 540 cm^{-1}.

Metal-to-ligand modes

According to [9], all acetate vibrations have frequencies higher than 450 cm^{-1}. Several rather strong bands (accompanied by some weaker ones) are, however, observed below 400 cm^{-1} in the spectra of hexa-μ-acetato-*triangulo*-tripalladium(II)—water (2/1). The appearance of these bands (which certainly originate from vibrations with a Pd-O character) is a clear indication of the existence of metal-to-ligand bonding.

The exact assignment of these bands is presently not possible but it seems reasonable to assume that those with the *highest* frequencies should be due to modes which have more pronounced Pd-O stretching character, whereas those below 300 cm^{-1} may be a result of modes which can be approximately described as O-Pd-O bending vibrations.

It should be noted that the frequencies of the bands assigned to Pd-O stretches are appreciably *lower* than, for example, the frequencies of the similarly assigned bands in the spectrum of palladium acetylacetonate [15,16]. In this latter compound, namely, the frequency of the Pd-O stretch is 464 cm^{-1}. Thus, it seems certain that the Pd-O bonds are considerably weaker in hexa-μ-acetato-*triangulo*-tripalladium(II)—water (2/1) than in palladium acetylacetonate.

Water modes

For a compound with an acetate-to-water ratio of 12 to 1, it is to be expected that the intensity of the bands originating from water vibrations should be *quite low* and perhaps *negligible*.

In fact, only after making the concentration of the sample in the KBr pellet *very high*, two bands origina-
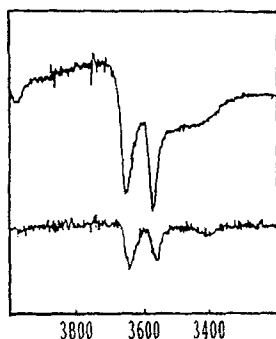
FIG. 2. Water stretching bands in the infrared spectra of
hexa-μ-acetato-*triangulo*-tripalladium(II)-water(2/1)
(a - in KBr; b - in hexachlorobutadiene)

ting from the stretching vibrations of the structural
water molecules are clearly seen at 3655 and 3570 cm^{-1}.
This finding is confirmed by recording the spectra of a
hexachlorobutadiene mull (see Fig. 2). The frequencies
of these two bands are very high, indicating practically
no hydrogen bonding. Thus, our spectra are in line with
the finding of Cotton and Han [5,6] that the guest mole-
cules have practically no structure-building role.

As for the rest of the expected water bands, it is
likely that the shoulder which is barely visible (below
600 cm^{-1}) at RT and becomes slightly more intense at LNT
originates from a water librational mode. The H-O-H
bending band is even more difficult to locate since it
is expected in the region dominated by the very strong
band which is due to the antisymmetric COO stretching
vibration. The important point, however, is that water
bands *have been* observed so that the identity of the
sample can be considered as proven.

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