VIBRATIONAL SPECTRA OF SOLID BIS(ACETONITRILE-d_3) PLATINUM(II) DICHLORIDE*

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The IR absorption (4000—200 cm^{-1}) and Raman spectra (800—100 cm^{-1}, He-Ne laser) of solid [$(MeCN)_2PtCl_2$]-d_0 and -d_6 complexes, prepared under the same conditions, were measured. With d_6-species, a single IR band at 2331 cm^{-1} for the fundamental CN stretching frequency was found instead of a multiplet typical for d_0-species. Such multiplet has been usually taken as an indirect evidence of a *cis*-configuration of the ligands around the Pt atom. The vibrational spectra of the d_6-species do not corroborate proposals of either *cis*- or *trans*-configuration.

Organonitrile coordination complexes with transition elements, especially Pd(II), proved to be efficient homogeneous catalysts[1]. Moreover, an antitumor activity of some *cis*-dichloro Pt(II) complexes has been discovered[2]. For these reasons, electronic and geometrical structures of the complexes are of interest to chemists[3]. To our knowledge, no crystallographic study of [$(MeCN)_2$.$PtCl_2$] has been made. This basic structural information has been therefore deduced indirectly from chemical reactions of this compound[4] and "corroborated" by an interpretation of its vibrational spectra[5,6].

[$(H_3CCN)_2PtCl_2$] is assumed to have a planar structure, both acetonitrile ligands being linked to the central Pt atom by the lone electron pairs located essentially on the N atoms (end-on coordination), and their mutual configuration is *cis*. Under this assumption the complex belongs to the C_{2v} point group of symmetry, neglecting the orientation of the methyl groups. It implies that two stretching vibrations of both CN groups, coupled together in-phase (i—p) and out-of-phase (o—o—p), are infrared active. In other words, appearance of more than one IR absorption band around 2300 cm^{-1} seems to be an evidence of such molecular geometry: "The IR spectrum (solid state) agrees with *cis*-stereochemistry since there is a sharp band at 2320 cm^{-1} with shoulders at 2341 and 2405 cm^{-1}" (ref.[5]).

However, uncoordinated acetonitrile itself has a complicated IR spectrum in the 2400—2000 cm^{-1} region and several absorption maxima exist in the spectrum of liquid[7]. Analogous situation is encountered in the IR spectra of other free organonitriles[8]. Under these circumstances, it is difficult to interpret the IR multiplets in the spectra of the complexes as an evidence of a *cis*-configuration of organonitrile ligands. The problem can be attacked by isotopic substitutions in the organonitrile molecule which influence mutual positions of the interacting vibrational levels and thus the intensities and separation of branches of the multiplets.

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The aim of this work was to prepare both non- and perdeuterated complexes $[(MeCN)_2PtCl_2]$ under the same conditions and to compare their IR spectra in the 2400–2000 cm^{-1} region.

EXPERIMENTAL

The perdeuterated as well as nondeuterated bis(acetonitrile) platinum(II) dichlorides were prepared under the same conditions according to the published method[9]. Absence of SO_2 ligands in the starting K_2PtCl_4 was checked by its IR spectrum in the 1500–600 cm^{-1} region. Acetonitrile-d_3 was a commercial NMR solvent (Thompson Packard Inc., New Jersey; 99·0% D) and its IR spectrum was identical with that of the standard[7].

The IR absorption spectra (4000–400 cm^{-1}) of solid samples of the complexes in KCl discs, Nujol or perchloro-1,3-butadiene suspensions were measured on a double beam prism instrument Zeiss (Jena), model UR-20. The wave number scale of the instrument was calibrated with a polystyrene film, the reproducibility being ±2 cm^{-1}. The IR spectrum of the CsBr pellet in the 500–200 cm^1 region was recorded on a grating instrument Perkin–Elmer, model 580.

The Raman spectra of solid stationary samples of $[(D_3CCN)_2PtCl_2]$ were measured on two JEOL instruments equipped with either Ar^+ ion or He–Ne laser. In the former case, the measurements were unsuccessful due to decomposition of the compound in the laser beam. Using He–Ne laser, a reasonable spectrum was obtained only within the 800–100 cm^{-1} range where the signal-to-noise ratio was acceptable.

RESULTS AND DISCUSSION

The original interpretation[10,11] of the vibrational spectra of free acetonitrile-d_0 and -d_3 is firmly established[12]. The relevant data are summarized in Table I together with those[6,13] for solid $[(H_3CCN)_2PtCl_2]$. Our IR data for solid $[(D_3CCN)_2PtCl_2]$ are in the last column and partly in Fig. 1. Positions of the absorption maxima were practically insensitive to the technique of measurements (suspensions *vs* pressed discs). The overall pattern of the spectrum is very simple likewise for the nondeuterated compound.

Assuming a planar arrangement of the skeleton atoms in $[(MeCN)_2PtCl_2]$, mutual configuration of the acetonitrile ligands can be either *cis* or *trans* and, neglecting the positions of hydrogen atoms, the overall symmetry of the complex is either C_{2v} or D_{2h}. In both cases the normal vibrations of the identical ligands should be strongly coupled together as the in-phase and out-of-phase combinations. For instance, there should be two such stretching vibrations for the —C≡N— bonds and two for the Cl–Pt–Cl grouping. For C_{2v} symmetry of the *cis*-configuration these four stretching fundamentals should be all infrared-active, for the centrosymmetric *trans*-configuration (D_{2h}) the i–p fundamental transitions are forbidden in the infrared by the selection rules. In other words, *trans*-configuration would be characterized by two single IR bands near 2300 and 350 cm^{-1} for $\nu(C\equiv N)$ and $\nu(Pt–Cl)$, respectively, *cis*-configuration by two doublets in the mentioned regions.

Two IR multiplets are observed for the nondeuterated acetonitrile complex[5,6] but not for the perdeuterated species prepared by us under the same conditions. For $[(D_3CCN)_2PtCl_2]$ we observed only one IR doublet at 349 and 362 cm^{-1} speaking tentatively in favour of *cis*-configuration, and a single band at 2331 cm^{-1} for $\nu(C{\equiv}N)$ which could be in accordance with *trans*-configuration of the ligands. It is clear from Fig. 1 that the 2331 cm^{-1} band for $\nu(C{\equiv}N)$ of the perdeuterated species is well separated from the others and its asymmetry, if any, is very slight. Such an isolated IR band (at 2267 cm^{-1} in Ar matrix[14]) has also been recorded for the free $D_3C{-}CN$ monomer. Thus, the question of IR doublets in the $\nu(C{\equiv}N)$ region must be settled first for the free acetonitrile molecules -d_0 and -d_3.

The free molecule of $H_3C{-}CN$ in the electronic ground state has a linear $C{-}C{\equiv}N$ skeleton and owing to three hydrogen atoms outside this axis it belongs to C_{3v}

TABLE I

The Vibrational Frequencies[a] (cm^{-1}) of Acetonitrile-d_0 and -d_3, Free or Coordinated in $[(MeCN)_2PtCl_2]$

S	Fundamentals[a] (assignment)	d_0		d_3	
		free[b]	coord.[c]	free[b]	coord.[d]
	ν_1 (stretching Me)	2 954	2 923 2 910	2 126	2 107 s
a_1	ν_2 (stretching CN)	2 267	2 309 sh 2 305	2 278	2 331 s
	ν_3 (sym. deformation Me)	1 385	1 363	1 110	1 096 w
	ν_4 (stretching C—C)	920	975	831	872 w
	ν_5 (stretching Me)	3 009	2 971	2 257	2 232 s
e	ν_6 (deformation Me)	1 448	1 415	1 046	1 019 m
	ν_7 (rocking Me)	1 041	1 030	847	840 s
	ν_8 (deformation CCN)	362	?	331	? 349 m
	stretching $PtCl_2$	—	360, 345	—	362 s
?	deformation $PtCl_2$		175	—	170 s[e]
	stretching Pt—N	—	120	—	126 m[e]

[a] Combinations from 2400—2000 cm^{-1} (assignment):
Free $-d_0$ (liq.)[10]: 2074 ($2\nu_7$), 2204 ($2\nu_4 + \nu_8$), $\underline{2253}$(ν_2), 2293($\nu_3 + \nu_4$) Coord. $-d_0$ (s)[6,13]: 2305 (i-p ν_2) $\underline{2309}$ (o-o-p ν_2), 2333($\nu_3 + \nu_4$), 2390 (?) Free $-d_3$ (liq.)[11]: 2059 ($2\nu_6$), $\underline{2116}$(ν_1), 2212 ($2\nu_3$), 2263(ν_2 and ν_5) Coord. $-d_3$ (s): 2100 ($2\nu_6$), 2207 ($2\nu_3$)

[b] selected value of frequency[12]; [c] from refs[6] and [13]; [d] this work; [e] from Raman.

point group of symmetry, containing doubly degenerate symmetry species *e*. Under these circumstances, only eight fundamental frequencies ($4a_1 + 4e$) can be observed for the twelve normal vibrations of the molecule and the same holds for $D_3C—CN$. The other observed bands, mostly weak ones, should be assigned to overtone or combination frequencies. The only exception is a strong IR doublet with 2253 and 2293 cm^{-1} maxima observed[7] for liquid d_0-species (Table I). The higher wavenumber branch at 2293 cm^{-1} of the doublet has been assigned[10] to the $(\nu_3+\nu_4)$ combination frequency borrowing its intensity from the $\nu(C{\equiv}N)$ fundamental at 2254 cm^{-1} due to a Fermi resonance between the corresponding levels of the same a_1 symmetry. As to the experimental frequencies[7] the values 2253 and 2293 cm^{-1} represent perturbed positions of the ν_2 and $(\nu_3+\nu_4)$ levels "repelling" each other: the ν_2 frequency is lowered and $(\nu_3+\nu_4)$ is increased with respect to an ideal case without the vibrational interaction. Even relatively small changes in the positions of unperturbed ν_2 and $(\nu_3+\nu_4)$ levels will result in much pronounced changes in intensities of the doublet maxima. This is clearly seen after changing the state of acetonitrile-d_0, *e.g.*, from liquid to gas[10] or to solid phase[14] as well as after dissolving acetonitrile-d_0 in a series of solvents with different polarities[15,16].

When hydrogen atoms in the acetonitrile molecule are substituted by deuterium, the mutual positions of the ν_2 and $(\nu_3+\nu_4)$ levels are strongly influenced and thus the overall pattern of the IR spectrum in the 2400–2000 cm^{-1} region is markedly changed[7]. The $(\nu_3+\nu_4)$ combination level is shifted from 2293 to about 1950 cm^{-1} and the Fermi resonance with ν_2 practically vanishes. There exist other possible candidates for interactions with ν_2, *e.g.*, the $2\nu_3$ level (a_1) at about 2200 cm^{-1}; however, the numerical value of the interaction constant is presumably small. The net result is that for free $D_3C—CN$ only one strong IR band is observed in the 2400–2000 cm^{-1} region[7] at 2263 cm^{-1}. This band is assigned to the $C{\equiv}N$ stretching fundamental frequency $\nu_2(a_1)$ practically coinciding with the CD_3 stretching fundamental frequency $\nu_5(e)$. Within the harmonic approximation these two symmetry species *e* and a_1 do not interact and are clearly resolved in the Raman spectrum of the liquid[7].

There is one interesting feature in the experimental vibrational spectra of free acetonitrile-d_0 and -d_3 molecules. The IR value of the $\nu(C{\equiv}N)$ frequency in d_0-species is lower than that for d_3-species in all cases of gas (2266→2279 cm^{-1}), liquid (2253→2263 cm^{-1}), and solid in Ar matrix (2258→2267 cm^{-1}). These unusual upward shifts of the $\nu(C{\equiv}N)$ frequency after deuteration are easily explained by disappearance of the Fermi resonance which was "pushing down" the $\nu(C{\equiv}N)$ in free d_0-species.

In $[(MeCN)_2PtCl_2)$ -d_0 and -d_6 complexes both compounds are composed of fifteen-atomic molecules vibrating with 39 internal degrees of freedom each. Despite this, the total number of IR absorption bands assignable to these fundamental frequencies of the complexes is smaller. After coordination of the acetonitrile molecule to Pt(II), the degeneracy is removed, however, the splitting of the vibrational levels can be only slight. Instead of distinct multiplets, only their (eventually asymmetric) envelopes are observed for the polycrystalline samples in pressed discs or in suspensions under low resolution. This can explain a small number of bands observed for both complexes d_0 and d_6.

The asymmetric IR bands in Fig. 1, centered at 2232 and 2107 cm^{-1}, are assigned to the fundamental stretching frequencies of the CD_3 groups in the ligands, an isolated IR band at 2331 cm^{-1} to one of the two stretching frequencies of both coupled —C≡N— bonds. Its position is shifted by some 70 cm^{-1} to higher wavenumbers compared to liquid C_3D—CN (2267 cm^{-1}). An accidental near-coincidence of the ν(C≡N) and $\nu(CD_3)$ frequencies in free d_3-species is removed by coordination. The ν(CN) frequency of the coordinated species is free of original interactions but it is impossible to decide if it is characteristic for *trans*-configuration of the acetonitrile-d_3 ligands. A single Raman band at 356 cm^{-1} supports such a proposal, the IR doublet (362, 349 cm^{-1}) is contradictory evidence. There is a possibility that one branch of the IR doublet represents the missing[13] fundamental frequency of the C—C≡N deformation vibration, the other branch being the ν(Pt–Cl) stretching frequency (Table I).

We do not oppose the chemical evidence[4] which indirectly indicated *cis*-configuration of the ligands in $[(MeCN)_2PtCl_2]$. We only state that the vibrational spectra of this complex do not corroborate the proposed *cis*-planar structure. In this particular case we only believe that vibrational spectra cannot substitute a regular crystallographic study of the acetonitrile–Pt(II) complex.

As to the position of the ν(CN) band near 2330 cm^{-1} for d_6-species we can state that it is close to those observed[17] for the addition compound $H_3{}^{10}B$—NC—CH_3 (2345 cm^{-1}) and its deuterio-analogues. It means that a coordinative bond between the CN group and Pt atom is very similar to a classical one-directional electron donation from —CN to B atom. In other words, the coordinative bond —CN—Pt

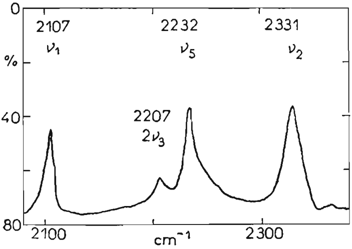

FIG. 1

The IR Absorption Spectrum of Solid $[(D_3CCN)_2PtCl_2]$ in the Region of CD_3 and CN Stretching Fundamental Frequencies (Nujol suspension) is relatively weak (the Pt-ligand stretching frequency is about 120 cm^{-1}, *cf.*[13] and Table I) compared to cases of other ligands of Pt(II) like C_2H_4 (about 400 cm^{-1}, *cf.*[18]), CO (about 500 cm^{-1}, *cf.*[19]), *etc.*

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