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THE ULTRAVIOLET AND VISIBLE SPECTRA OF π-ALLYLPALLADIUM COMPLEXES

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SUMMARY

The UV and visible spectra (50,000–14,300 cm^{-1}) of π-allylpalladium chloride have been recorded in a number of solvents. The spectra exhibit five bands, three relatively weak bands at about 29,500 cm^{-1}, 34,000 cm^{-1} and 40,500 cm^{-1} which are assigned to *d–d* transitions and two more intense bands at about 44,000 cm^{-1} and 46,500 cm^{-1} which are assigned to charge transfer transitions from the chloride p_π to the palladium d_{z^2} orbital and from the palladium d_{xz} to the allyl π^* orbitals respectively. The considerable dependence of the positions of the bands on the nature of the solvent used is discussed. It is suggested that in 4 *M* aqueous potassium chloride a dimer–monomer equilibrium exists in which the dimer is the predominant species.

INTRODUCTION

One of the important physical properties of a metal complex that can give an insight into the nature of the bonding is the UV and visible spectrum. A recent investigation of the UV and visible spectra of platinum–olefin complexes[1] enabled the relative energies of the platinum *d*-orbitals in these complexes to be evaluated. The present investigation of the spectra of π-allylpalladium complexes was undertaken in the hope that similar information might be obtained for these complexes. An earlier investigation of the spectra of π-allylpalladium complexes[2] was hampered by the failure of the authors to resolve the spectra into their component bands and by the absence of a complete treatment of the bonding in π-allylpalladium complexes. A complete treatment of the bonding has since been published[3].

EXPERIMENTAL

Preparation of the complexes

Di-μ-chlorodi(π-allyl)dipalladium(II). This compound was prepared by treating palladium(II) chloride with allyl chloride in 50% acetic acid[4]. (Found: C, 19.9; H, 2.7; Cl, 20.1. $C_6H_{10}Cl_2Pd_2$ calcd.: C, 19.7; H, 2.75; Cl, 19.4%.)

Dichloro(ethylenediamine)palladium(II). This compound was prepared by the standard method[5]. (Anal.: Found: C, 10.3; H, 3.2; Cl, 29.5; N, 11.7. $C_2H_8Cl_2N_2Pd$ calcd.: C, 10.1; H, 3.4; Cl, 29.9; N, 11.8%.) The spectrum (16,000–48,000 cm^{-1}) was

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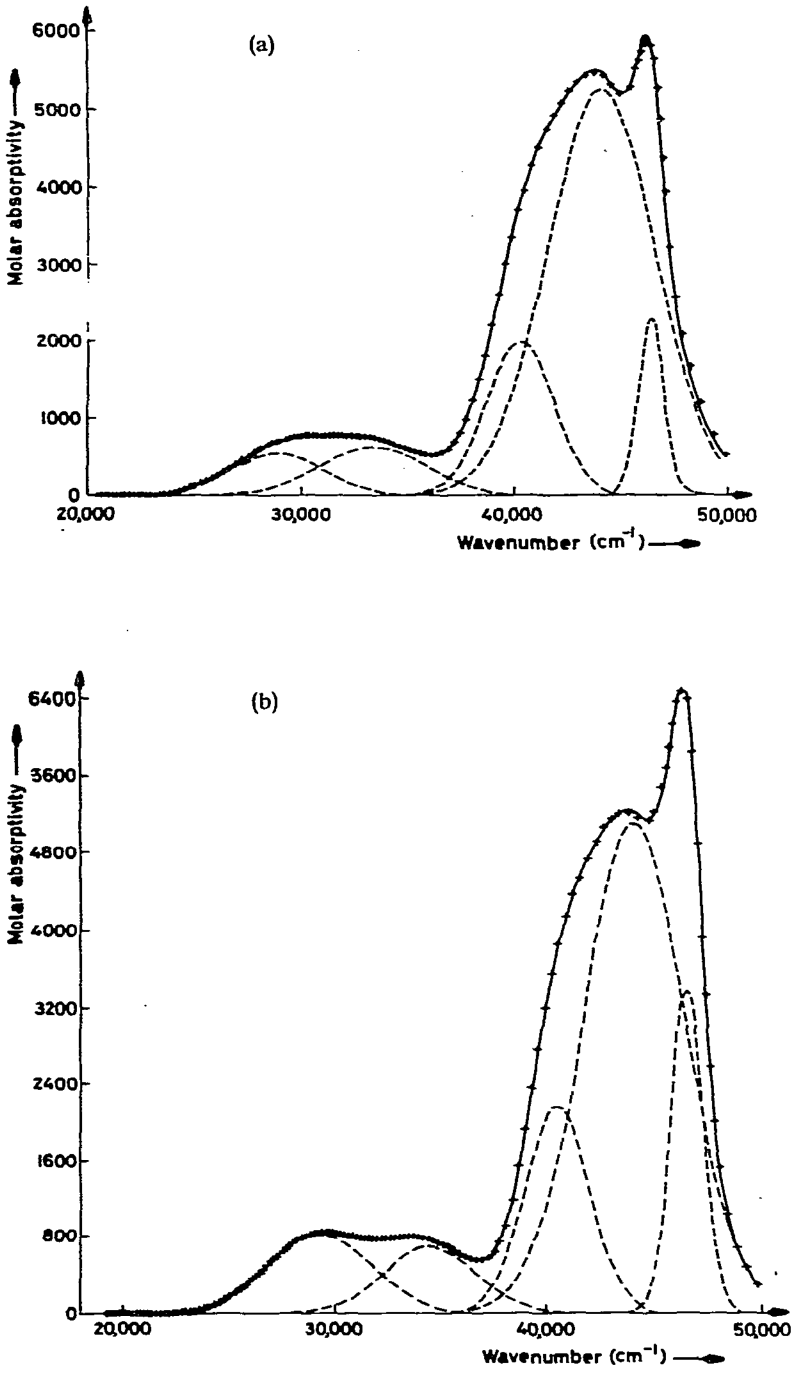


Fig. 1. The UV and visible spectra of π-allylpalladium chloride in (a) ethanol and (b) aqueous 4 *M* potassium chloride. The original spectra are represented by + + +. The component gaussian bands are represented by ----. The solid spectra are the sum of the component gaussian bands.

determined in 0.2 *M* potassium chloride to avoid aquation.

Spectra

The spectra were recorded using a Hitachi–Perkin–Elmer model 124 spectrophotometer and analysed into their component Gaussian bands using the iterative least squares procedure of Fraser and Suzuki[6] on a CDC 3600 computer. All the molar absorptivities quoted are referred to the molecular weight containing one atom of palladium.

RESULTS AND DISCUSSION

The UV and visible spectra of the π-allylpalladium complexes reported in the present work are rather more complex than those reported earlier[2,7]. Gaussian analyses of the spectra (Fig. 1) indicated that in ethanol and aqueous potassium chloride there are five bands, rather than three as originally reported. This arises from the failure of earlier workers to recognize that the broad band around 31,000 cm^{-1} is in fact composed of two separate bands and that there is a slight shoulder around 41,000 cm^{-1}. The bands observed in the spectra of π-allylpalladium complexes (Table 1) could arise from (a) transitions within the π-allyl ligand, (b) *d–d* transitions, (c) charge transfer from ligand to metal or (d) charge transfer from metal to ligand.

The possibility that the bands arise from transitions within the ligand [case (a)] is eliminated by the spectrum of the allyl radical[8] which exhibits no significant absorption below 43,000 cm^{-1} and only a weak absorption at 44,500 cm^{-1}. Not only would the intensity of this band prevent its being observed, but it would also be moved to higher energy on coordination.

The possibility that some of the bands arise from *d–d* transitions is supported by group theory which shows that three *d–d* transitions are allowed by symmetry. The symmetry around the palladium atom in π-allylpalladium chloride may be considered to be C_{2v}[3] since the X-ray structure at room temperature[9] indicates that the atoms C^1 C^3 Pd Cl^1 Cl^2 are virtually coplanar and C^2 lies 0.55 Å below this plane (Fig. 2).

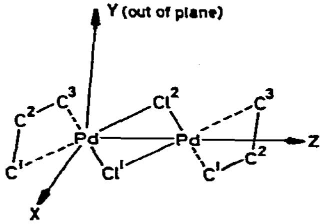


Fig. 2. The x, y and z axes used in this paper superimposed on the structure of π-allylpalladium chloride.

When the *d–d* transitions are being examined it is necessary to consider only the symmetry of the environment of the palladium atom and not the symmetry of the complex as a whole, because it has been found that there is no evidence for any electronic interaction between the palladium atoms in $[Pd_2Cl_6^{2-}]$[10], so that the regions of the spectra of $[PdCl_4^{2-}]$ and $[Pd_2Cl_6^{2-}]$ arising from *d–d* transitions are very similar [10,11]. Group theory indicates that of the four possible *d–d* transitions all but the $d_{xy} \rightarrow d_{z^2}$ transition are symmetry allowed in C_{2v} symmetry (the x, y and z axes referred to are shown in Fig. 2). Bands arising from *d–d* transitions have been observed

TABLE 1

THE UV AND VISIBLE SPECTRA OF π-ALLYLPALLADIUM CHLORIDE IN VARIOUS SOLVENTS[a]

Methyl cyanide		4 *M* aqueous KCl		Et_2O		EtOH		MeOH		DMF		$CHCl_3$		$EtOCOCH_3$	
λ (cm^{-1})[b]	ε	λ (cm^{-1})	ε	λ (cm^{-1})	ε	λ (cm^{-1})	ε	λ (cm^{-1})	ε	λ (cm^{-1})	ε	λ (cm^{-1})	ε	λ (cm^{-1})	ε
30,713	716	29,338	809	29,769	751	29,010	543	29,961	708	29,162	600	28,509	545	28,577	254
35,665	663	34,525	690	34,085	519	33,536	618	34,437	492	34,441	706	32,560	1,468	32,683	620
40,770	1,607	40,534	2,156	39,649	1,873	40,409	2,006	42,208	7,226			38,616	3,527		
44,477	5,771	44,169	5,073	42,741	6,573	44,235	5,222	44,818	4,639			40,519	10,239		
48,642	9,498	46,647	3,381	45,520	1,104	46,567	2,286	48,463	16,321						

[a] Bands obtained by analyzing the spectra into their component bands assuming Gaussian shape. The molar absorptivities (ε) given are per mole of palladium.

[b] λ=wavenumber.

TABLE 2

THE UV AND VISIBLE SPECTRA OF PALLADIUM(II) COMPLEXES IN AQUEOUS SOLUTION

$[PdCl_4^{2-}]$[a]		$[PdCl_2(l\text{-pn})]$[a]		$[PdCl_2(en)]$[b]	
λ (cm^{-1})	ε	λ (cm^{-1})	ε	λ (cm^{-1})	ε
16,500	6.5	22,500	19	21,277	61
21,000	145	26,200	235	27,030	118
23,700	53.7	28,700	182	29,998	193
30,500	501	~39,000	~500	35,994	3,264
35,700	10,000	>46,000		45,959	13,527
45,190	28,200				

[a] From ref. 5; *l*-pn = *l*-propylenediamine. [b] This work; en = ethylenediamine.

previously in the spectra of $[PdCl_4^{2-}]$, $[(l\text{-pn})PdCl_2]$ and $[(en)PdCl_2]$ (*l*-pn = *l*-propylenediamine and en = ethylenediamine). The bands observed in these spectra are shown in Table 2 and a number of assignments by previous workers are shown in Table 3 (it should be noted that the x, y and z axes in Table 3 have been altered from their conventional directions to correspond to the axes shown in Fig. 2 for π-allylpalladium chloride). Day *et al.*[10] have concluded that their final assignment, which is in agreement with a number of others (see Table 3), is now universally agreed upon as a consequence of its being supported by both polarized crystal spectroscopy and Faraday effect measurements. Since carbon-bonded ligands lie higher in the spectrochemical series than nitrogen-bonded ligands which in turn lie higher than chloride ions[16a] the bands arising from *d–d* transitions would be expected to shift to higher energy along the series of complexes $[PdCl_4^{2-}] < [(en)PdCl_2] < [(\pi\text{-allyl})PdCl_2]$. Thus the assignment of the bands at about 29,500 cm^{-1}, 34,000 cm^{-1} and 40,500 cm^{-1} in π-allylpalladium chloride to *d–d* transitions similar to those giving rise to the bands at 21,000 cm^{-1}, 23,700 cm^{-1} and 30,500 cm^{-1} in $[PdCl_4^{2-}]$ and at 27,030 cm^{-1}, 29,998 cm^{-1} and 35,994 cm^{-1} in $[(en)PdCl_2]$ is consistent with the position of the π-allyl ligand in the spectrochemical series. The molar absorptivities of these bands are rather higher than 200 which is the normal upper limit for *d–d* transitions[16b]. However bands with molar absorptivities of 500 to 5,000 have recently been assigned[17] to *d–d* transitions in complexes containing phosphine and arsine ligands, which like the π-allyl ligand are probably capable of accepting charge donated from the metal to empty non-bonding or anti-bonding orbitals on the ligand. The splitting of the *d*-orbitals in a symmetrical square planar D_{4h} environment and in a C_{2v} environment

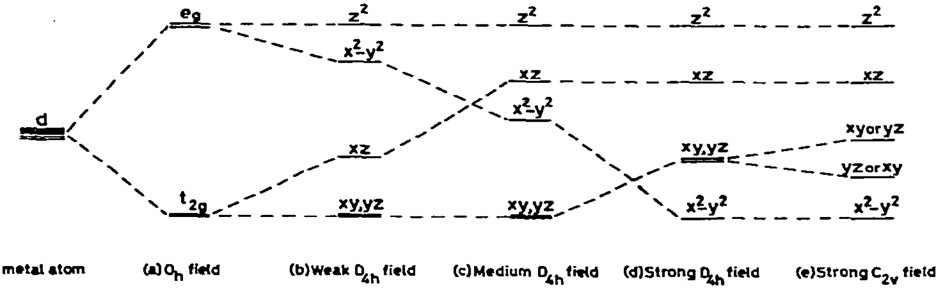


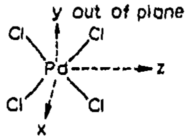
Fig. 3. The splitting of the energies of the *d*-orbitals in a symmetrical square planar D_{4h} environment and also a C_{2v} environment as in π-allylpalladium complexes; the axes used are those shown in Fig. 2.

TABLE 3

PREVIOUS ASSIGNMENTS OF THE SPECTRUM OF K_2PdCl_4[a]

Wavenumber of band (cm^{-1})	Gray *et al.*[b]	Day *et al.*[c]	Ito *et al.*[d]	Basch *et al.*[e] and Day *et al.*[f]	McGaffery *et al.*[g]
16,500	$d_{xz}\rightarrow d_{z^2}$	Singlet→triplet ($^1A_{1g}\rightarrow {}^3A_{2g}$)	$d_{xz}\rightarrow d_{z^2}$	Singlet→triplet ($^1A_{1g}\rightarrow {}^3B_{1g}$)	Not assigned
21,000	$d_{x^2-y^2}\rightarrow d_{z^2}$	$d_{xz}\rightarrow d_{z^2}$	$d_{yz}, d_{xy}\rightarrow d_{z^2}$	$d_{xz}\rightarrow d_{z^2}$	Not assigned
23,700	$d_{yz}, d_{xy}\rightarrow d_{z^2}$	$d_{yz}, d_{xy}\rightarrow d_{z^2}$ or $d_{x^2-y^2}\rightarrow d_{z^2}$	$d_{x^2-y^2}\rightarrow d_{z^2}$	$d_{yz}, d_{xy}\rightarrow d_{z^2}$	$d_{yz}, d_{xy}\rightarrow d_{z^2}$
30,500	*h*	$d_{x^2-y^2}\rightarrow d_{z^2}$ or $d_{yz}, d_{xy}\rightarrow d_{z^2}$	Spin forbidden charge transfer	$d_{x^2-y^2}\rightarrow d_{z^2}$	Not assigned
35,700	Cl(π non-bonding)$\rightarrow d_{z^2}$		Cl(p_π)$\rightarrow d_{z^2}$	Cl(p_π)$\rightarrow d_{z^2}$	Cl(p_π)$\rightarrow d_{z^2}$
45,190	Cl(π non-bonding)$\rightarrow d_{z^2}$		Cl(p_σ)$\rightarrow d_{z^2}$	Cl(p_σ)$\rightarrow d_{z^2}$	Cl(p_σ)$\rightarrow d_{z^2}$

[a] The x, y and z axes used are:



[b] Ref. 12. [c] Ref. 13. [d] Ref. 5. [e] Ref. 14. [f] Ref. 10. [g] Ref. 15. [h] This band was not considered by Gray and Ballhausen even though it was observed by Harris *et al.*[28] from whom Gray and Ballhausen took the spectrum. Gray and Ballhausen assigned the corresponding band in K_2PtCl_4, which occurs at 38,000 cm^{-1}, to a symmetry forbidden charge transfer transition.

is shown in Fig. 3. The final assignment of the spectrum of [$PdCl_4^{2-}$] by Day *et al.*[10] indicates that the order of the *d*-orbitals in this complex (using the axes of Table 3) is that shown in Fig. 3(d) as arising from the strong D_{4h} ligand field. Since carbon bonded ligands give rise to even stronger ligand fields than chloride ions[16a] the order of the energies of the *d*-orbitals in π-allylpalladium chloride will be that given in Fig. 3(e) in which the relative energies of the d_{xy} and d_{yz} orbitals are uncertain. Since the $d_{xy} \rightarrow d_{z^2}$ transition in π-allylpalladium complexes is not allowed by symmetry, the observed *d–d* transitions may be assigned as follows: 29,590 cm^{-1}, $d_{xz} \rightarrow d_{z^2}$; 34,000 cm^{-1}, $d_{yz} \rightarrow d_{z^2}$; 40,500 cm^{-1}, $d_{x^2-y^2} \rightarrow d_{z^2}$.

Ligand to metal charge transfer transitions [case (c)] can be divided into two groups: (1) transitions from chloride *p* orbitals to the metal and (2) transitions from the allyl orbitals to the metal. When considering transitions from the chloride ligands it is important to remember that these ligands are bridging ligands. A comparison of the spectra of [$PdCl_4^{2-}$] and [$Pd_2Cl_6^{2-}$] has shown that whereas in [$PdCl_4^{2-}$] there are only two charge transfer transitions from the chloride *p*-orbitals to the palladium d_{z^2} orbitals, there are four such transitions in [$Pd_2Cl_6^{2-}$], two from the bridging chloride ligands and two from the terminal chloride ligands[11]. The two transitions from the bridging chloride ligands, which are the only chloride ligands present in π-allylpalladium chloride, occur at 30,000 and 40,980 cm^{-1} respectively in [$Pd_2Cl_6^{2-}$] in methyl cyanide[11]. Group theory indicates that both these charge transfer transitions are allowed by symmetry in π-allylpalladium chloride. An approximate calculation suggests that the bridging chloride p_π to palladium d_{z^2} transition, which occurs at 30,000 cm^{-1} in [$Pd_2Cl_6^{2-}$], might be expected to be observed at about 43,000 cm^{-1} in [(π-allyl)PdCl]$_2$. It is assumed in this approximate calculation that the major effect of replacing two chloride ligands by other ligands is on the energy of the palladium *d*-orbitals and that the effect of this replacement on the energies of the chloride *p*-orbitals is small. Replacement of two chloride ligands in [$PdCl_4^{2-}$] by ethylenediamine shifts the *d–d* transitions about 6,000 cm^{-1} to higher energy and the chloride p_π to palladium *d* charge transfer transition 10,000 cm^{-1} to higher energy (see Table 2). Since replacement of the two terminal chloride ligands in [$Pd_2Cl_6^{2-}$] by π-allyl shifts the *d–d* transitions by about 8,000 cm^{-1} (comparing the results for [$Pd_2Cl_6^{2-}$][11] with the present results for [(π-allyl)PdCl]$_2$) the bridging chloride p_π to palladium *d* charge transfer transition might be expected to be shifted by about 13,000 cm^{-1} to higher energy in [(π-allyl)PdCl]$_2$ relative to [$Pd_2Cl_6^{2-}$]. Thus a chloride p_π to palladium *d* charge transfer transition might be expected at about 43,000 cm^{-1} in π-allylpalladium chloride. From Table 1 it can be seen that there are two bands of sufficient intensity to be assigned to charge transfer transitions at about this wavelength. Since on replacing chloride by bromide in [$Pd_2X_6^{2-}$] the halide to palladium charge transfer bands shift by about 4,000 cm^{-1} to lower energy[11], one might expect, using the principle of average environment[16a], that these charge transfer transitions would shift by about one third of this value (*i.e.* about 1330 cm^{-1}) on replacing chloride by bromide in [(π-allyl)PdX]$_2$. It has been found previously[7] that, when chloride was replaced by bromide in the π-allylic complex (4- methoxy-2-methylbutenyl)palladium halide, the band initially at 43,510 cm^{-1} in methanol was shifted 1320 cm^{-1} to lower energy whereas the band initially at 48,310 cm^{-1} was only shifted by 230 cm^{-1}. Thus the band at 44,235 cm^{-1} in [(π-allyl)PdCl]$_2$ in ethanol may be assigned to a chloride p_π to palladium d_{z^2} charge transfer transition. A comparison of the spectra of [$PdCl_4^{2-}$], [(en)$PdCl_2$] (Table 2) and [$Pd_2Cl_6^{2-}$][11] indicates that the chloride p_σ to palladium d_{z^2} charge transfer transition would be expected to occur at about 10,000 cm^{-1} or more above the chloride p_π transition, so that it would not be expected to be observed in the present region of investigation (up to 50,000 cm^{-1}).

Ligand to metal charge transfer transitions could also occur from the filled allyl π or allyl π(non-bonding) orbitals to palladium orbitals. An approximate calculation indicates that transitions to the palladium *d*-orbitals are unlikely because the energy of the palladium *d*-orbitals is less than the energy of the allyl π and π(non-bonding) orbitals. The other transitions would be expected to have the following approximate energies: allyl π to palladium 5*s*, 25,000 cm^{-1}; allyl π(non-bonding) to palladium 5*s*, 11,000 cm^{-1}; allyl π to palladium 5*p*, 66,500 cm^{-1}; allyl π(non-bonding) to palladium 5*p*, 52,000 cm^{-1}. These calculations were made using the following data. The net charge transferred from the chloride to palladium was assumed to be similar to that transferred from chloride to platinum in platinum–olefin complexes[1] and the net charge transferred from the allyl ligand to palladium, again by analogy with the platinum–olefin complexes, was assumed to be zero. This suggests that the charge on the palladium atom is slightly greater than +1 in agreement with an earlier independent estimate[3]. Thus the energies of the palladium orbitals in [(π-allyl)PdCl]$_2$ are as follows[18]: 4*d*, −84,000 cm^{-1}; 5*s*, −43,500 cm^{-1}; 5*p*, −2,500 cm^{-1}. The corresponding data for the allyl ligand are ionization potential, 68,000 cm^{-1} [19] and resonance energy, 24 kcal/mole[20], from whence the π–π(non-bonding) and π(non-bonding)–π^* separations may be calculated to be 14,400 cm^{-1}. All the above allyl to palladium charge transfer transitions are allowed by symmetry except the allyl π(non-bonding) to palladium 5*s* transition. Thus it might be expected that the allyl π to palladium 5*s* and allyl π(non-bonding) to palladium 5*p* transitions would be observed. However they would be expected to be of very low intensity because the intensity of a transition is proportional to the overlap integral[21] and the overlap integrals for these two pairs of orbitals are known to be very small[3]. Thus allyl to palladium charge transfer transitions are unlikely to account for any of the bands observed.

Metal to ligand charge transfer transitions [case (d)] can also be divided into two groups: (1) transitions from the metal *d*-orbitals to the allyl π^* orbital and (2) transitions from the metal *d* to chloride orbitals. The second possibility can be eliminated immediately since the energies of both the σ- and π-bonding chloride orbitals are lower than the energies of the metal *d*-orbitals so that no metal *d* to chloride charge transfer transitions are possible[13]. Group theory indicates that of the four possible metal *d* to allyl π^* transitions only three, from the $d_{x^2-y^2}$, d_{xy} and d_{xz} orbitals (see Fig. 2), are allowed. An approximate calculation using the data above indicates that a metal *d* to allyl π^* transition would be expected at about 45,000 cm^{-1}. The observation of an as yet unassigned band at about 46,570 cm^{-1} in π-allylpalladium chloride in ethanol with an extinction coefficient that suggests that it arises from a charge transfer transition is consistent with this. Further evidence that this band is due to a palladium *d* to allyl π^* transition is obtained from the observation that the position of this band in the π-allylic complex (4-methoxy-2-methylbutenyl)palladium halide in methanol is only shifted very slightly (230 cm^{-1}) to lower energy on replacing chloride by bromide[7]. Thus the band at about 46,570 cm^{-1} (in ethanol) in π-allylpalladium chloride may be assigned to a charge transfer transition from the highest occupied *d*-orbital (*i.e.* d_{xz}- see Fig. 3) to the allyl π^* orbital.

EFFECT OF SOLVENTS

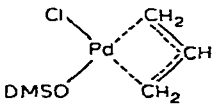
By studying the two lowest bands in the spectra of π-allylpalladium chloride in a series of solvents it is possible to arrange these solvents in an approximate spectrochemical series. From Table 1 this order is methyl cyanide > methanol > dimethylformamide > ethanol > ethyl acetate. The relative positions of methyl cyanide, methanol and ethyl acetate in this series are in agreement with earlier observations[22]. The band at about 40,500 cm^{-1} is unsuitable for studying the spectrochemical series because the position of this band in the various solvents is the least accurately known because it only appears as a weak shoulder on the side of the band which occurs at about 44,000 cm^{-1}.

The position of aqueous 4 *M* potassium chloride in the spectrochemical series is anomalous in that it fits in between methanol and dimethylformamide if the lowest band is considered and between methyl cyanide and methanol if the 34,000 cm^{-1} band is considered. Both positions are very high in the spectrochemical series for a solvent which introduces an atmosphere of chloride ions around the metal[16]. The explanation for the anomalous position of aqueous potassium chloride is that in this solvent the dimeric structure of π-allylpalladium chloride is at least partially destroyed giving monomeric [(π-allyl)PdCl$_2^-$] ions in solution[23]. A surprising feature of the spectrum of π-allylpalladium chloride is the great similarity of the positions and shapes of the bands in aqueous potassium chloride and the other solvents such as ethanol (Fig. 1). If the complex is monomeric in aqueous potassium chloride the chloride ligands would all be terminal ligands in contrast to the situation in ethanol where the complex is dimeric and the chloride ligands are all bridging ligands. As a result the chloride p_π to palladium d_{z^2} charge transfer band might have been expected, by comparison with [PdCl$_4^{2-}$] and [Pd$_2$Cl$_6^{2-}$], to have occurred at considerably higher energies in the monomeric complex. The fact that this charge transfer band, which has been assigned above to the band at 44,235 cm^{-1} in ethanol, is at virtually the same wavelength in aqueous 4 *M* potassium chloride (44,169 cm^{-1}) suggests that in the latter solvent a dimer–monomer equilibrium exists,

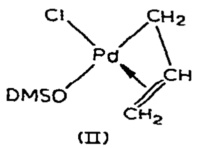
$$[(\pi\text{-allyl})\text{PdCl}]_2 + 2\ \text{KCl} \rightleftarrows 2\ \text{K}^+[(\pi\text{-allyl})\text{PdCl}_2^-]$$

and that it is only in the presence of a suitable large cation that this equilibrium is driven far to the right leading to the isolation of salts containing the [(π-allyl)PdCl$_2^-$] ion.

The spectrum of π-allylpalladium chloride in dimethylsulphoxide is very different to its spectrum in other solvents (Table 4). Furthermore the spectrum changes on standing. The weak band at 21,740 cm^{-1} gradually increases in intensity whilst the intensities of the other bands remain effectively unaltered. The considerable difference between the spectrum of π-allylpalladium chloride in dimethylsulphoxide as compared to other solvents is due to the fact that in dimethylsulphoxide the chloride bridge is split[24,25] with the formation of a monomeric complex (I) in which the



(I)



(II)

TABLE 4

THE UV AND VISIBLE SPECTRA OF π-ALLYLPALLADIUM CHLORIDE IN DIMETHYLSULPHOXIDE[a]

Immediately after dissolving		After 48 h	
λ (cm^{-1})[b]	ε	λ (cm^{-1})	ε
21,740	14.5	21,775	142
32,541	2,085	32,904	2,184
37,413	2,552	37,290	2,465
38,443	3,348	38,454	3,337

[a] Bands obtained by analysing the spectra into their component bands assuming Gaussian shape. The molar absorptivities (ε) given are per mole of palladium. [b] λ = wavenumber.

dimethylsulphoxide is bound to palladium via the sulphur atom[26,27]. In addition the NMR results suggest that the π-allyl complex (I) is in equilibrium with the σ-π-allyl complex (II)[24,25].

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