

He I and He II Photoelectron Spectra of *trans*-[MCl₂L₂] (M = Pd, L = PEt₃ or AsEt₃; M = Pt, L = NMe₃, PMe₃, PEt₃, or AsEt₃) and *trans*-[PtH(Cl)(PEt₃)₂], and Hartree-Fock-Slater Calculations on Model Compounds†

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U.v. photoelectron spectra of *trans*-[MCl₂L₂] (M = Pd, L = PEt₃ or AsEt₃; M = Pt, L = NMe₃, PMe₃, PEt₃, or AsEt₃) are reported, as well as Hartree-Fock-Slater calculations on the model compounds *trans*-[MCl₂(EH₃)₂] (M = Pd, E = N or P; M = Pt, E = N). The results from these calculations and empirical assignment criteria such as He I/He II intensity differences and shift effects upon substitution have enabled a full assignment of the upper valence ionizations. Evidence is found for a through-space interaction of phosphorus and arsenic orbitals with orbitals localized on the chloride ligands. The energy levels for ionizations in corresponding complexes of Pd and Pt are rather similar, with the exception of ionizations from orbitals due to π interaction of chloride orbitals with *d* orbitals of appropriate symmetry. It appears that these interactions are much stronger with Pt than with Pd.

Square-planar complexes of Pd^{II} and Pt^{II} play a central role in the chemistry of Pd and Pt,¹ and exhibit a versatile chemistry as a consequence of several features. First, they are co-ordinatively unsaturated with only 16 electrons in their valence shell. Hence, the possibility of attack by nucleophilic agents exists. Secondly, the presence of an unshielded and filled *d*_{z² orbital is of great importance in redox reactions at the metal site and the formation of donative metal-metal bonds (see refs. cited in ref. 2). Thirdly, reductive elimination of ligands is possible.}

The combination of these features indicates the possibility of catalytic behaviour for these complexes.³⁻⁵ Recently, there has been great interest in *cis*-diamminedichloroplatinum(II) and its derivatives as it has been found to be effective against some tumours. The *trans* compounds, however, exhibit no anti-tumour activity whatsoever. This is explained by the existing model for the effectiveness of the *cis* compounds in which structural effects are as important as electronic effects.^{6,7}

The *trans*-dichloride compounds of Pd^{II} and Pt^{II}, which are the subject of this study, are among the simplest representatives of the square-planar complexes of these metals. A combined ultraviolet photoelectron spectroscopy (u.p.s.) and Hartree-Fock-Slater (h.f.s.) molecular-orbital (m.o.) study of these compounds is of interest since it may yield insight in the electronic structure that may be relevant to a larger range of square-planar complexes of Pd and Pt. Furthermore, the data may also be helpful in understanding the u.p. spectra of more complicated square-planar complexes of Pd and Pt, which are currently under study in our laboratory.^{2,8}

Some time ago, a very short He I photoelectron study on square-planar complexes of Pt^{II} including bis(phosphine) dichloride compounds was published, in which the assignments made were in many cases only tentative and in which little detailed information was given.⁹ Recently, a short communication was also published on the He I and He II photoelectron spectra of [PdCl₂(PEt₃)₂] and [PdBr₂(PEt₃)₂] in which again no detailed assignments were given.¹⁰ We feel that the importance of these types of complexes warrants a full and detailed study of their electronic structure.

The compound [PtH(Cl)(PEt₃)₂], which was the first (1957)

reported¹¹ platinum hydride, is also included in the present series to study the effect of an asymmetric perturbation on the dichloride compounds. Platinum hydrides are becoming increasingly important due to the simple nature of the hydride ligand (enabling theoretical considerations and ¹H n.m.r. spectroscopy) and the facility of alkene and alkyne insertion reactions.¹²

Experimental

All compounds were synthesized according to literature methods.¹³⁻¹⁵ The compounds were sublimed prior to running the spectra, and their purity and identity were checked by elemental analysis.

The spectra were recorded on a Perkin-Elmer PS18 photoelectron spectrometer equipped with a hollow-cathode light source (Helectros Developments) at temperatures ranging from 120 to 180 °C. All spectra were calibrated with respect to He, Ar, and Xe as internal references.

Calculations and Geometry.—The h.f.s. calculations were carried out using the method of Baerends and Ros.¹⁶ This method differs from the Hartree-Fock method in using Slater's local-exchange approximation. The resulting equations are then solved in a linear combination of atomic orbitals (l.c.a.o.) formulation and the matrix elements are calculated by a numerical integration scheme. The exchange scaling factor was taken as $\alpha = 0.7$. A double- ζ basis was used except for the phosphorus *d* orbitals which were represented with a single- ζ basis and metal *d* orbitals for which a triple- ζ basis was employed. In the calculation for the platinum complex the perturbation method of Snijders *et al.*¹⁷ was used to analyze relativistic corrections to be applied to the numerical results.

Geometrical parameters were taken as follows. All bond lengths involving the metal were chosen to be the same for Pd and Pt because of the similar radii of the two metals.³ For the amine model complexes the angle H-N-H and the distance R(N-H) were taken as those of the free amine (107.3° and 100.8 pm, respectively¹⁸), while R(M-N) was chosen as 210 pm on the basis of X-ray data.^{19,20} For the phosphine complexes R(P-H) was taken as the value for the free ligand;²⁰ H-P-H was chosen as 105°, the value for co-ordinated PR₃,²¹ rather than the value for free phosphine (93°).²² On the basis of X-ray

† Non-S.I. unit employed: eV = 1.60 × 10⁻¹⁹ J.

crystallographic data, $R(\text{M}-\text{P})$ was chosen as 230 pm²³ and $R(\text{M}-\text{Cl})$ as 210 pm.¹⁹

The calculations were performed in C_{2v} symmetry. Ligands were orientated in such a fashion that mirror planes pass through both the Cl-M-Cl and E-M-E axes, perpendicular to the plane of the molecule.

Results and Discussion

Throughout the discussion for each ionization a canonical m.o. is supposed to exist that corresponds to the electron to be ejected. Since in h.f.s. theory the eigenvalues of the canonical m.o.s are not equal to the Koopmans ionization energies (see ref. 24), the ionization energies should be compared with those of transition states (removal of half an electron) calculated in the Slater $X\alpha$ scheme by using Slater's transition-state method.²⁵ However, (expensive) transition-state calculations very often result in an almost equal shift for all orbitals. Thus, to economize on computation time, we have compared the relative ordering of h.f.s. orbital energies and ionization energies.

Although the h.f.s. calculations have been carried out in C_{2v} symmetry (see Experimental section), a centre of inversion will sometimes be assumed in the discussion. This, however, only involves the trivial operation of rotating one of the ER_3 groups (E = N, P, or As; R = Me or Et) around its three-fold symmetry axis by 180° (bringing the molecule to C_{2h} symmetry with Cl-M-Cl as principal axis) which does not affect the argument at all.

For the sake of brevity, all compounds are assumed to be in *trans* configuration.

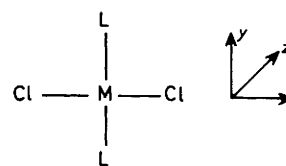
Breakdown into Fragments.—It is helpful to consider the molecules (Figure 1) as consisting of several fragments, and the molecular orbitals as built up from fragment orbitals. At the centre of the molecule is an M atom (Pd or Pt), surrounded by two ER_3 molecules in *trans* positions. Since valence *s* and especially *p* orbitals play a minor role in the bonding of Pd and Pt,* only valence *d* orbitals on the metal will be taken into account.

In Figure 2 the interactions between the metal *d* orbitals and fragment orbitals on the ER_3 fragments are qualitatively displayed. The energy of the two n_E levels is obviously fully arbitrary, as it will be dependent on the actual atom E. These two lone pairs transform as gerade and ungerade in local linear symmetry of the $\text{M}(\text{ER}_3)_2$ fragments {as is also the case in C_{2h} symmetry for the molecule $[\text{MCl}_2(\text{ER}_3)_2]$, see above}. The gerade combination will interact with the d_{z^2} and $d_{x^2-y^2}$ orbitals, resulting in a low-energy $\sigma_{\text{M-E}}^g$ orbital providing M-E bonding, and, both due to M-E antibonding, a weakly destabilized d_{z^2} and a strongly destabilized $d_{x^2-y^2}$ orbital. The ungerade combination of E lone pairs, unable to interact with *d* orbitals, will remain as a non-bonding level.

The molecules ER_3 also possess relatively high energy $\sigma_{\text{E-R}}$ orbitals (*e* in local C_{3v} symmetry) and the gerade combinations of these orbitals on the two ER_3 ligands will have some interaction with d_{xy} and d_{yz} , effectively destabilizing these metal orbitals.

Within the molecule $[\text{MX}(\text{Y})(\text{ER}_3)_2]$ the fragment $\text{M}(\text{ER}_3)_2$ will formally be considered to have a charge of 2+ with the $d_{x^2-y^2}$ orbital formally unoccupied. Co-ordinated to this fragment are either two chloride ions or a chloride and a hydride

* The role of transition-metal valence *s* orbitals is not negligible. However, since in square-planar complexes the metal d_{z^2} and *s* orbitals are always both in the point group of highest symmetry (since the *z* axis is not interchangeable with any other), the occurrence of metal *s* orbitals in the upper valence m.o.s will always be in a metal hybrid orbital which has predominantly d_{z^2} character.



M = Pd; L = PEt_3 or AsEt_3

M = Pt; L = NMe_3 , PMe_3 , PEt_3 , or AsEt_3

Figure 1. Structure of the molecules with the axis system used in the Discussion. The structure of the chloride hydride compound is similar to that of the dichlorides with one chloride ligand replaced by a hydride

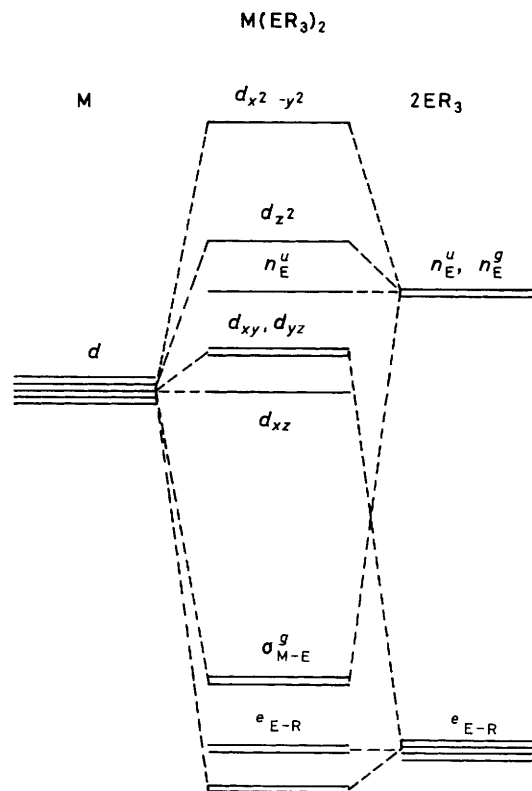


Figure 2. Interaction diagram for fragment orbitals on the metal and ER_3 groups

ion. The hydride ion has one doubly occupied 1*s* orbital, and the chloride ion has three doubly occupied 3*p* orbitals.

In Figure 3 is given the qualitative interaction diagram for the fragment orbitals of the dichloride compounds. The six Cl 3*p* orbitals on the two Cl^- ions will give six symmetry-adapted combinations, three gerade and three ungerade. The gerade combination of *p* orbitals along the Cl-M-Cl axis will interact with the empty $d_{x^2-y^2}$ orbital to yield a $\sigma_{\text{M-Cl}}^g$ orbital and a high-energy antibonding orbital (not indicated in Figure 3). Furthermore, it will also interact somewhat with the d_{z^2} orbital, destabilizing it. The ungerade combination of chloride *p* orbitals along the Cl-M-Cl axis will be somewhat stabilized by interaction with the empty metal p_x orbital.

The other four orbitals are from the non-bonding Cl 3*p* orbitals (perpendicular to the M-Cl axes). Two combinations are within the plane of the molecule ($p_{\text{Cl}}^{\text{in}}$) and two are perpendicular to it ($p_{\text{Cl}}^{\text{out}}$). The gerade representative of both

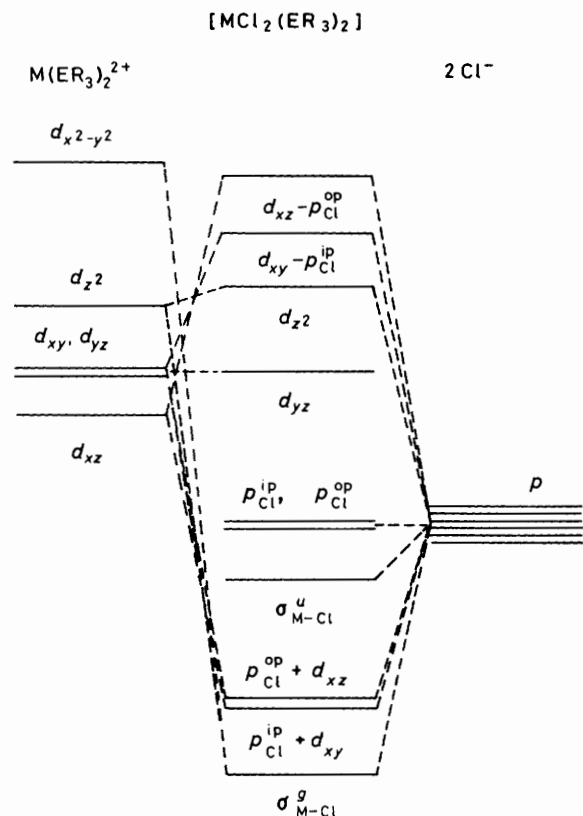


Figure 3. Interaction diagram for the M(ER₃)₂²⁺ and Cl⁻ fragment orbitals (only occupied combinations have been included)

classes can interact with the orbitals of appropriate symmetry (d_{xz} and d_{xy}), as will be discussed in a later section. The metal d_{yz} orbital has, because of its symmetry, no interaction with chloride orbitals.

Of special help in the assignment of the spectra will be the He I/He II intensity differences, caused by the difference in cross-section between He I and He II photons and the orbitals from which an electron is ejected. From calculated data on atomic cross-sections²⁶ and much u.p. data for organometallic compounds,²⁷ the following empirical rules for the present compounds can be derived. Since the He II cross-section for metal d orbitals is larger than the He I cross-section, a significant enhancement of the ionizations from these orbitals should be expected upon going from He I to He II. Halogen-type ionization bands will be depleted in He II spectra. Furthermore, bands due to ionizations from localized H $1s$ orbitals will also have a very low He II cross-section. For C and N orbitals the He I and He II cross-sections are approximately the same, thus these orbitals will lose intensity in He II with respect to the metal d bands, but will gain intensity with respect to halogen-type bands. Ionization bands from C-H and C-C σ orbitals normally exhibit a poorer He II than He I cross-section.

The Spectrum of [PtCl₂(NMe₃)₂].—The most striking feature in the spectra of [PtCl₂(NMe₃)₂] [Figure 4, ionization energies (i.e.s) in Table 1] is the dramatic intensity enhancement of the four lowest i.e. bands (1–4), with respect to the other bands on going from He I to He II irradiation. As stated above, this means that these bands belong to ionizations from the four doubly occupied metal d orbitals. At higher i.e. (9.5–11.5 eV) five bands (5–9) are observed with a very poor He II cross-section, indicating localized chloride character. Further scrutiny

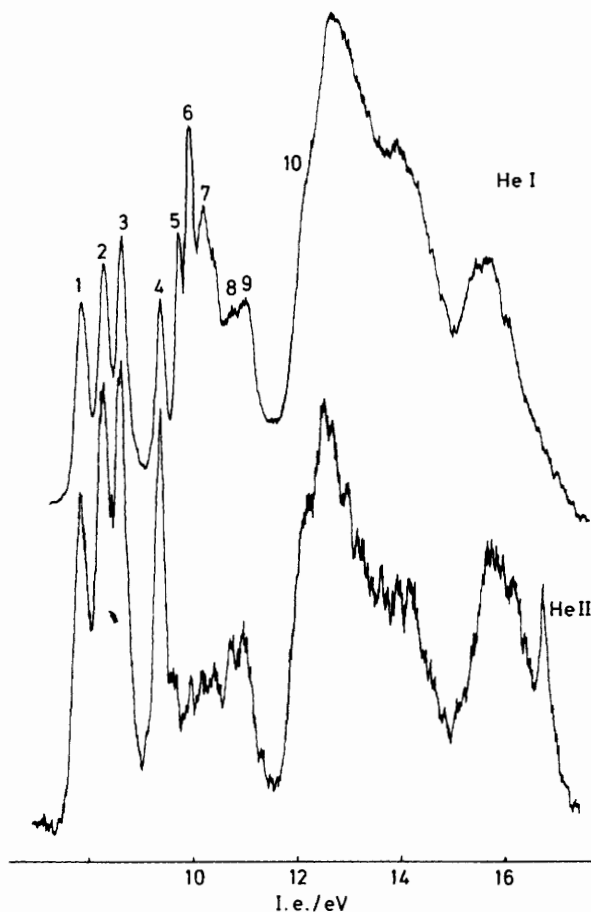


Figure 4. The He I and He II spectra of [PtCl₂(NMe₃)₂]

Table 1. Ionization energies (eV) for [MCl₂(ER₃)₂]*

| M = ER ₃ = | Pt NMe ₃ | Pt PMe ₃ | Pt PEt ₃ | Pd PEt ₃ | Pd AsEt ₃ | Pt AsEt ₃ |
|--------------------------|------------------------|------------------------|------------------------|------------------------|-------------------------|-------------------------|
| Assignment | | | | | | |
| $d_{xz}-p_{Cl}^{op}$ | 7.86 | 7.80 | 7.69 | 8.10 | 8.07 | 7.65 |
| $d_{xy}-p_{Cl}^{ip}$ | 8.31 | 8.38 | 8.18 | 8.47 | 8.51 | (8.42) |
| d_z^2 | 8.65 | 8.75 | 8.49 | 8.47 | 8.51 | 8.42 |
| d_{yz} | 9.44 | 9.68 | 9.40 | 9.35 | 9.30 | 9.31 |
| $p_{Cl}^{op}-n_E^u$ | 9.79 | 8.57 | 8.34 | 8.10 | 8.07 | (8.42) |
| p_{Cl}^{ip} | 10.05 | 10.05 | 9.81 | 9.61 | (9.79) | (9.95) |
| σ_{M-Cl}^u | 10.33 | 10.38 | 10.06 | 9.83 | (9.79) | (9.95) |
| $n_{Cl}^{op} + d_{xz}$ | 10.47 | 11.13 | | | | |
| $n_{Cl}^{ip} + d_{xy}$ | 10.94 | 11.13 | | | | |
| $n_E^u + p_{Cl}^{op}$ | 12.35 | 10.38 | 10.06 | 9.83 | (9.79) | (9.95) |

* Values in parentheses are for the maxima of enveloping bands.

of the band intensities indicates that although the He I and He II cross-sections of bands within the first and second set are of the same order of magnitude minor differences between bands within one set exist. Thus it is clear that the He II intensity of band 1 (at 7.86 eV) is somewhat less than that of the other bands in the lowest i.e. set. At the same time the He II intensity of the two highest i.e. bands (8 and 9) in the second set is somewhat larger than that of the other bands within this set. These variations in cross-section indicate mixing between localized metal and chloride orbitals. This mixing occurs between orbitals which are of π symmetry with respect to the M-Cl axes in the Cl-M-Cl fragment (although they may be of σ symmetry in the molecule). Examples of this have been found before, (see e.g., ref. 8).

Table 2. H.f.s. results for *trans*-[PtCl₂(NH₃)₂]: upper valence orbitals

| Orbital | Energy/eV | | Character/% | | Classification | Experimental i.e. ^a /eV |
|-----------------|-----------|-------|-------------------|---|---|---------------------------------------|
| | REL | NREL | Cl | Pt | | |
| 5b ₂ | 4.51 | 4.73 | 69 p _z | 30 d _{zz} | d _{zz} -p _{Cl} ^{pp} | 7.86 |
| 3a ₂ | 5.10 | 5.08 | 73 p _y | 24 d _{xy} | d _{xy} -p _{Cl} ^{pp} | 8.31 |
| 7a ₁ | 5.39 | 5.40 | | 72 d _{x²-y²} , 15 s | d _{x²-y²} | 8.65 |
| 6a ₁ | 5.99 | 5.99 | 96 p _z | | p _{Cl} ^{pp} | 9.79 |
| 5b ₁ | 6.10 | 6.04 | 94 p _y | | p _{Cl} ^{pp} | 10.05 |
| 4b ₁ | 6.55 | 6.64 | | 96 d _{yz} | d _{yz} | 9.44 |
| 4b ₂ | 6.67 | 6.55 | 93 p _x | | σ _{M-Cl} ^u | 10.33 |
| 3b ₂ | 7.71 | 7.82 | 29 p _z | 70 d _{zz} | p _{Cl} ^{pp} + d _{zz} | 10.94 |
| 2a ₂ | 8.06 | 7.93 | 25 p _y | 70 d _{yz} | p _{Cl} ^{pp} + d _{xy} | 11.14 |
| 5a ₁ | 9.29 | 8.97 | 49 p _x | 22 d _{x²-y²} , 14 d _{z²} | σ _{M-Cl} ^u | |
| 3b ₁ | 9.57 | 9.32 | b | | n _N ^u | 12.35 |
| 4a ₁ | 11.90 | 11.44 | c | 24 d _{x²-y²} | σ _{M-N} ^u | |

^a For the corresponding NMe₃ compound. ^b 94% n_N from NH₃. ^c 65% n_N from NH₃.

Table 3. H.f.s. results for *trans*-[PdCl₂(NH₃)₂]: upper valence orbitals

| Orbital | Energy/eV | Character/% | | Classification |
|-----------------|-----------|-------------------|---|---|
| | | Cl | Pd | |
| 5b ₂ | 4.69 | 58 p _z | 40 d _{zz} | d _{zz} -p _{Cl} ^{pp} |
| 3a ₂ | 4.98 | 60 p _y | 36 d _{xy} | d _{xy} -p _{Cl} ^{pp} |
| 7a ₁ | 5.39 | | 77 d _{x²-y²} , 11 s | d _{x²-y²} |
| 6a ₁ | 5.99 | 96 p _z | | p _{Cl} ^{pp} |
| 5b ₁ | 6.01 | 91 p _y | | p _{Cl} ^{pp} |
| 4b ₁ | 6.17 | | 94 d _{yz} | d _{yz} |
| 4b ₂ | 6.59 | 92 p _x | | σ _{M-Cl} ^u |
| 3b ₂ | 7.23 | 39 p _z | 60 d _{zz} | p _{Cl} ^{pp} + d _{zz} |
| 2a ₂ | 7.29 | 36 p _y | 60 d _{xy} | p _{Cl} ^{pp} + d _{xy} |
| 5a ₁ | 8.82 | 49 p _x | 12 d _{x²-y²} , 14 d _{x²-y²} | σ _{M-Cl} ^u |
| 3b ₁ | 9.16 | a | | n _N ^u |
| 4a ₁ | 10.95 | b | 25 d _{x²-y²} | σ _{M-N} ^u |

^a 92% n_N from NH₃. ^b 66% n_N from NH₃.

Thus, band 1 is assigned to a platinum *d* orbital with antibonding interaction with an orbital combination on the two chloride fragments of the appropriate symmetry (gerade), while the two highest i.e. bands of chloride type (8 and 9) are due to two gerade chloride non-bonding orbitals mixed with a *d* orbital in a bonding fashion. As the difference in i.e. for bands 8 and 9 is small, that between the bands due to the orbitals that are the counterpart of the bonding combinations will also be small. Thus, bearing in mind that band 1 was assigned to one of the antibonding combinations, 2 is assigned to the other one.

The third metal-localized ionization (band 3) is assigned to the d_{z²} orbital, incorporating some σ-antibonding interactions with the ligands, while band 4 is assigned to the d_{yz} orbital, which can interact only with ligand orbitals on NMe₃ that have π symmetry with respect to the plane of the molecule. However, since between Pt and N only a donative interaction exists, the Pt-N distance is too large to allow a π interaction as strong as with the chloride ligands.

The chloride ionization bands of lowest i.e. (5 and 6) are very sharp, indicating ionizations from orbitals of almost purely non-bonding character. Thus, the bands are assigned to the ungerade combinations of chloride non-bonding *p* orbitals which are unable to mix with platinum *d* orbitals. The broader band 7 is assigned to the σ_{M-Cl}^u orbital.

H.f.s. calculations on the model compound [PtCl₂(NH₃)₂] (Table 2) correctly predict two low i.e. ionizations due to antibonding combinations of platinum *d* and chloride non-bonding orbitals. The character, however, is calculated to be mainly Cl, in contrast to the spectral results that indicate largely

metal *d* character. Since the interaction strongly depends upon the relative location of two levels close in energy, the fact that 3*d* orbitals on Cl were not included in the basis set might cause this discrepancy. As the localized metal and chloride levels are very close in energy (*cf.* the energy difference for the d_{yz} and p_{Cl}^{pp} ionizations), the character can easily be reversed by a somewhat unbalanced basis set.

The occurrence of a high-lying d_{x²-y²}-type orbital (with a significant amount of platinum *s* character) is predicted well, and confirms an earlier assignment in another series of square-planar complexes of the nickel triad.⁸

In agreement with the spectral assignments an almost pure d_{yz} orbital is calculated at higher orbital energy. The relative ordering of this almost pure metal orbital and three almost pure chloride orbitals (two non-bonding *p* orbitals and the σ_{Cl}^{pp} orbital) is reversed, as could be expected from the above. The relative ordering among the three chloride-type orbitals is predicted well. The two orbitals which consist of bonding combinations of *d* and p_{Cl} orbitals, the counterparts of the highest two orbitals, are obviously calculated with the relative participations of metal and chloride orbitals reversed in importance.

The calculations also indicate that, with the repulsive effect of three extra Me groups per N atom taken into account, the n_N^u ionization should occur at relatively low i.e. Accordingly, the shoulder at 12.35 eV (band 10) is assigned to this ionization.

At higher i.e. strong overlapping of bands (mostly due to σ orbitals on the NMe₃) makes further assignments impossible.

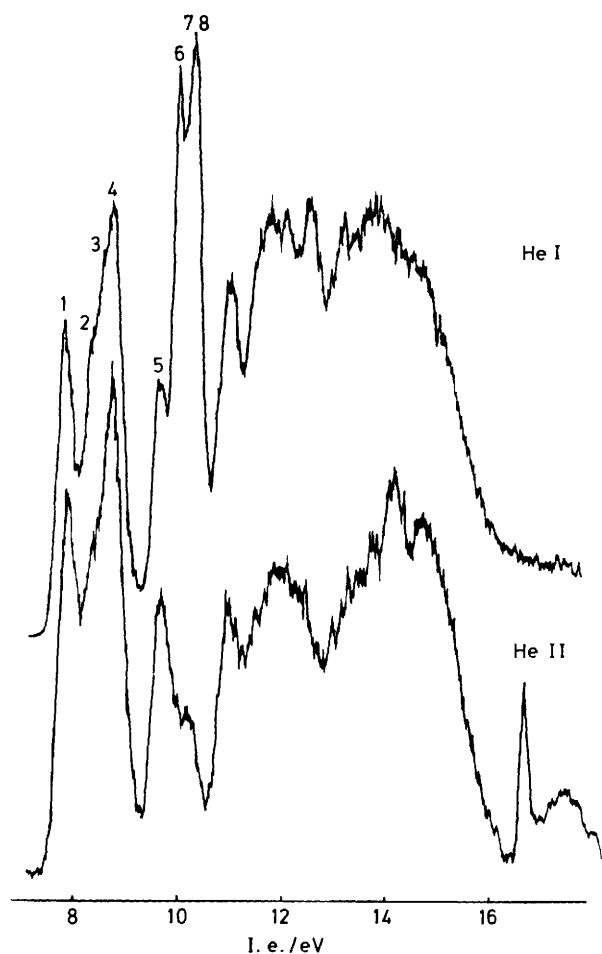
In Table 2 the non-relativistic (NREL) orbital energies are listed along with the relativistically (REL) corrected ones. The differences appear to be rather small. As this has also been found in relativistic h.f.s. calculations on other square-planar complexes of the type [PtX₂L₂],² it may be concluded that relativistic effects²⁸ play only a minor role in these types of complexes (as opposed to the important role they play in complexes containing, for instance, a metal of the zinc triad²⁹). It also appears from a calculation on the analogous palladium complex (see Table 3) that differences between corresponding orbitals in the complexes of Pd and Pt are generally small, the largest being found between the energies of some orbitals that are mainly metal *d* in character and in σ gerade M-N and M-Cl orbitals. The orbital characters for the two metals are comparable.

The Spectra of [PtCl₂(PMe₃)₂] and [PtCl₂(PEt₃)₂].—The spectrum of the PMe₃ compound is displayed in Figures 5 and 6 (expanded first part), and that of the PEt₃ compound in Figure 7, i.e. values are in Table 1. Calculations on the model compound [PdCl₂(PH₃)₂] (Table 4) indicate that the strongest

Table 4. H.f.s. results for *trans*-[PdCl₂(PH₃)₂]: upper valence orbitals

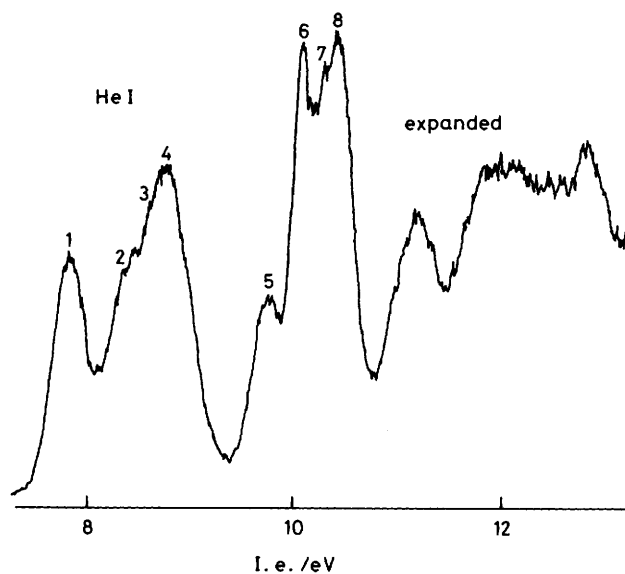
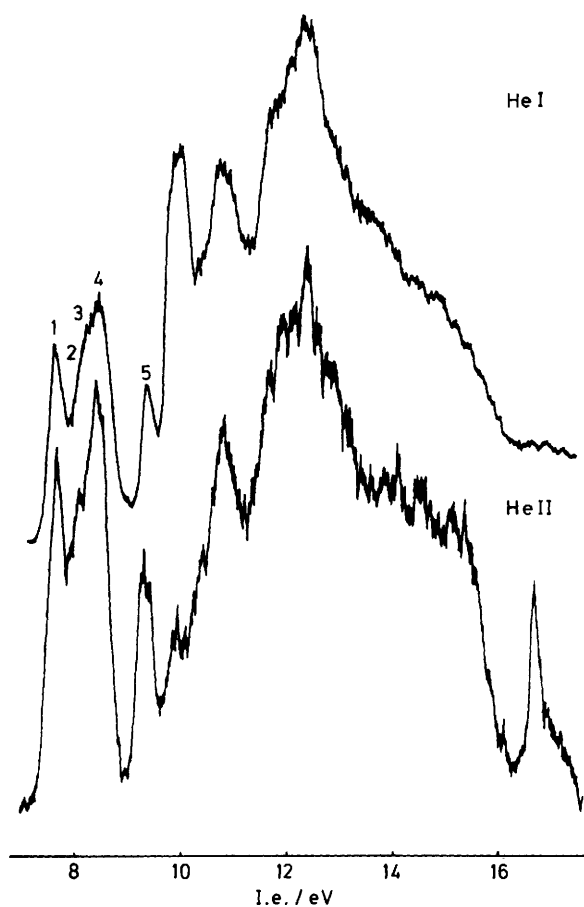
| Orbital | Orbital energy/ eV | Character/% | | Classification | Experi- mental i.e./ eV |
|-----------------|-----------------------|--------------------------------|--------------------------------------|--|-------------------------------|
| | | Cl | Pd | | |
| 5b ₂ | 5.04 | 62 p _z | 33 d _{xz} | d _{xz} -p _{Cl} ^{pp} | 8.10 |
| 3a ₂ | 5.38 | 73 p _y | 24 d _{xy} | d _{xy} -p _{Cl} ^{pp} | 8.47 |
| 7a ₁ | 5.72 | | 72 d _{z²} , 15 s | d _{z²} | 8.47 |
| 5b ₁ | 5.80 | 79 p _y ^a | | n _{Cl} ^{pp} -n _P ^{pp} | 8.10 |
| 6a ₁ | 6.06 | 92 p _z | | n _{Cl} ^{pp} | 9.61 |
| 4b ₂ | 6.70 | 84 p _x | | σ _{M-Cl} ^{pp} | 9.83 |
| 4b ₁ | 6.88 | | 84 d _{yz} | d _{yz} | 9.35 |
| 3b ₂ | 7.31 | 35 p _z | 61 d _{xz} | n _{Cl} ^{pp} + d _{xy} | |
| 2a ₂ | 7.57 | 20 p _y ^b | 63 d _{xy} | n _{Cl} ^{pp} + d _{xy} | |
| 3b ₁ | 7.58 | 17 p _y ^b | | n _P ^{pp} + p _{Cl} ^{pp} | |

^a 18% n_p from PH₃, ^b 75% n_p from PH₃.

**Figure 5.** The He I and He II spectra of [PtCl₂(PMe₃)₂]

effect upon substituting P for N is the destabilization of the n_P^{pp} level and because of this and a greater diffusivity of the phosphine orbitals significant interaction occurs between the n_P^{pp} and ungerade p_{Cl}^{pp} level. In view of the negligible participation of the platinum p orbitals in bonding, this must be considered a through-space interaction.

The calculation on [PdCl₂(NH₃)₂] (Table 3) yielded almost the same character and energy for the n_N^{pp} orbital as for [PtCl₂(NH₃)₂] (Table 4). Thus with these complexes replacing the metal has little effect on the ligand lone-pair levels.

**Figure 6.** The He I spectra of [PtCl₂(PMe₃)₂] (expanded first part)**Figure 7.** The He I and He II spectra of [PtCl₂(PEt₃)₂]

Furthermore, there is a large energy shift for the n_P^{pp} level on substituting P for N with palladium. One may therefore conclude that the corresponding level with platinum will also be shifted on substitution.

At 7.80 and 9.68 eV two bands (1 and 5) can be found in the spectrum of $[\text{PtCl}_2(\text{PMe}_3)_2]$ corresponding to the bands (1 and 4) at 7.86 and 9.44 eV in the spectrum of the NMe_3 compound; accordingly they are assigned to the $d_{xz}-p_{\text{Cl}}^{\text{op}}$ and d_{yz} orbitals, as these orbitals have little or no n_{E} character. Instead of the separate bands 2 and 3 in the NMe_3 case, only one broad band at 8.75 eV is now observed. Scrutiny of the band intensities in the He I spectra indicates that this composite band is due to three overlapping bands (see Figure 6). Two of these must be the equivalents of bands 2 and 3 in the spectrum of $[\text{PtCl}_2(\text{NMe}_3)_2]$. The maximum at 8.75 eV (band 4) is assigned to the d_{z^2} -type orbital. Since either band 2 or 3 is a new feature compared to the spectrum of the NMe_3 compound, the bands are assigned to the $d_{xy}-p_{\text{Cl}}^{\text{op}}$ orbital and to the $n_{\text{P}}^{\text{p}}-p_{\text{Cl}}^{\text{op}}$ combination, in agreement with the calculations.

Due to strong overlapping of bands 2–4 a deconvolution into three separate band shapes is unfortunately not possible. Thus in the absence of any detailed information about the He I/He II intensity ratio of band 3, it is not possible to assess whether or not the character calculated for the corresponding orbital in $[\text{PdCl}_2(\text{PH}_3)_2]$ (about 80% Cl) is realistic. However, since a band of this character was absent in the spectrum of the NMe_3 compound and, moreover, since the energy separation from the pure chloride levels (6,7/8) is large (both in an absolute sense and compared to the splittings in the spectrum of the NMe_3 compound) it is clear that the orbital giving rise to this ionization must have significant n_{P} character.

At 10.05 and 10.38 eV two bands are observed which are nearly depleted in He II. Band 6 is assigned to the $p_{\text{Cl}}^{\text{op}}$ orbital located at the same energy as in the spectrum of the NMe_3 compound. The band at 10.38 eV is due to two coincident bands (7 and 8, as can be seen from Figure 6). One of them is due to the $\sigma_{\text{M-Cl}}^{\text{op}}$ orbital, while the other is due to the $n_{\text{P}}^{\text{p}} + p_{\text{Cl}}^{\text{op}}$ orbital. Finally, the band at 11.13 eV is tentatively assigned to the bonding combinations between the gerade p_{Cl} orbitals and metal d orbitals of the appropriate symmetry. Further assignments are not possible, due to strongly overlapping bands.

It may be noted that the above assignments for $[\text{PtCl}_2(\text{PMe}_3)_2]$ are in many points at variance with previous assignments for this compound and related ones by Behan *et al.*⁹ This is not surprising since their conclusions were reached not only without the benefit of He II spectra but also without comparison with the u.p. spectra of analogous compounds $[\text{PtCl}_2(\text{ER}_3)_2]$ (E = N or As). Furthermore, their energy levels were estimated from optical spectroscopy and extended-Huckel calculations.

The spectrum of $[\text{PtCl}_2(\text{PEt}_3)_2]$ is, of course, in many respects similar to that of the PMe_3 compound, the most significant difference at first sight being the extra bands due to ionizations from the σ orbitals on the six added methyl groups. Further, due to the greater repulsive effect of an Et *vs.* a Me group, all i.e. values of bands due to the phosphine or metal are shifted to lower values (see Table 1). The i.e. for the $p_{\text{Cl}}^{\text{op}}$ level has not changed significantly, but the $\sigma_{\text{M-Cl}}^{\text{op}}$ level, which is dependent upon the actual charge of the metal, seems to have been destabilized somewhat. The two orbitals due to interaction between localized n_{P} and p_{Cl} orbitals are obviously also destabilized. For further details see Table 1.

The Spectrum of $[\text{PdCl}_2(\text{PEt}_3)_2]$.—The spectrum of $[\text{PdCl}_2(\text{PEt}_3)_2]$ is given in Figure 8; i.e. values are collected in Table 1. In the lowest-i.e. part of the He I and He II spectra of $[\text{PdCl}_2(\text{PEt}_3)_2]$ two partly overlapping envelopes (1 + 2 and 3 + 4) can be observed which are of equal intensity in the He I spectrum. (The actual presence of four bands can be proved by comparing the He I intensity of those two low-i.e. bands with that for the complex band 5–7.) In the He II spectrum the intensity of the envelope at 8.47 eV (bands 3 and 4) is strongly

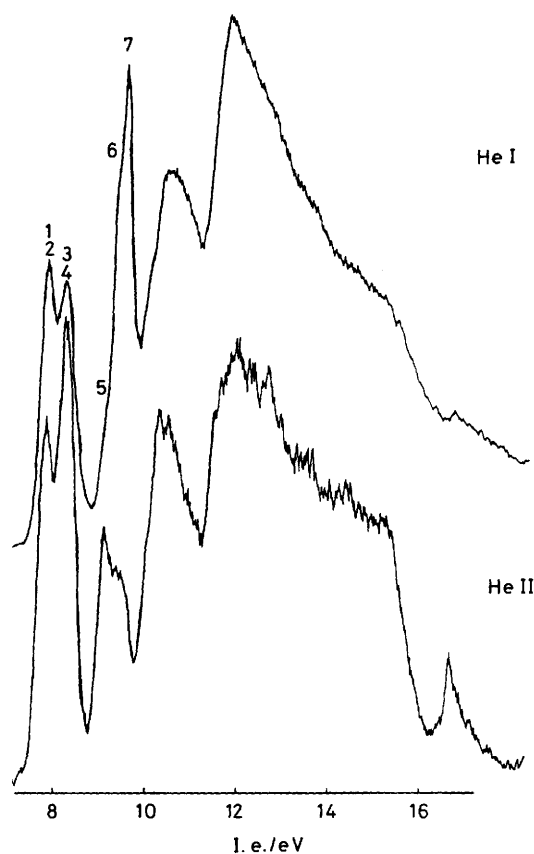


Figure 8. The He I and He II spectra of $[\text{PdCl}_2(\text{PEt}_3)_2]$

enhanced with respect to the other at 8.10 eV (1 and 2). Since very large differences between the electronic structures of corresponding compounds of Pd and Pt are not expected (and not found upon comparing results from the h.f.s. calculations on $[\text{PdCl}_2(\text{NH}_3)_2]$ and $[\text{PtCl}_2(\text{NH}_3)_2]$), four individual bands should be present in this part of the spectrum. These will be due to two orbitals of π antibonding character between Pd and Cl (one of mainly d_{z^2} character) and the orbital that is a combination of phosphorus and chloride non-bonding orbitals. In view of the relative enhancement of the envelope 3 + 4 upon going from He I to He II, the d_{z^2} orbital is assigned to one of the bands 3 and 4. For the other bands this leaves two alternative assignments. Either 1 and 2 are due to the two π -antibonding orbitals and the $p_{\text{Cl}}-n_{\text{P}}$ orbital ionization is within the envelope 3 + 4, or the latter band is within the composite envelope 1 + 2 and one of the π -antibonding ionizations is within 3 + 4. In view of the large splitting between the two $d-p_{\text{Cl}}$ levels in the platinum case, it is not expected that the two ionizations due to these orbitals would occur at almost the same energy in this compound. Hence, the second assignment is preferred.

Band 5 at 9.35 eV (in He I only visible as a low-energy shoulder on the composite band at 9.83 eV) must be assigned to the d_{yz} orbital on the basis of its large He II intensity. The remainder of this composite band (with another shoulder at 9.61 eV) consists of bands due to the $\sigma_{\text{M-Cl}}^{\text{op}}$, $p_{\text{Cl}}^{\text{op}} + n_{\text{P}}^{\text{p}}$, and $p_{\text{Cl}}^{\text{op}}$ orbitals. The shoulder (6) at 9.61 eV is assigned to the lowest pure chloride level, i.e. the $p_{\text{Cl}}^{\text{op}}$ ionization. The other two ionizations cannot be separated due to strong overlapping of bands.

It may be noted, upon comparing i.e.s for corresponding bands in the spectra of the compounds of Pd and Pt (see above), that the i.e.s for the d_{z^2} and d_{yz} orbital ionizations are rather

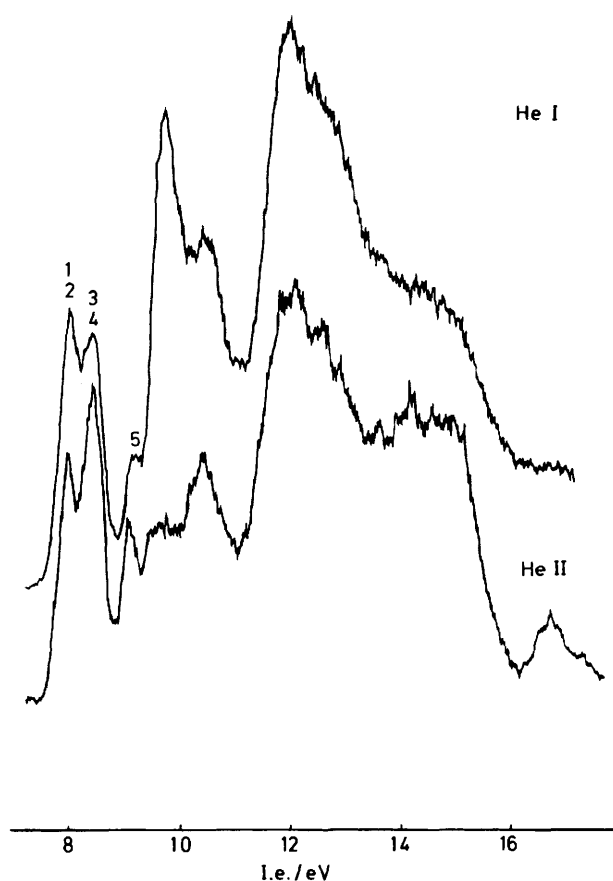


Figure 9. The He I and He II spectra of $[\text{PdCl}_2(\text{AsEt}_3)_2]$

similar. For the $d-p_{\text{Cl}}$ ionizations, however, the i.e.s are significantly higher with Pd than with Pt. Since the i.e. of these levels is lowered with respect to the localized metal levels by interaction it can be inferred that with Pd the measure of interaction is significantly less than with Pt. The low He II cross-section also indicates rather less metal d participation in the corresponding orbitals than with Pt. Similar conclusions could be drawn for a previous series of square-planar complexes of the nickel triad.² I.e. values for chloride-localized ionizations are all somewhat decreased upon substituting Pd for Pt.

The agreement with the calculations (Table 4) is fair; again the character of the two highest orbitals is shown to be predominantly chloride as with $[\text{PdCl}_2(\text{NH}_3)_2]$. However, in this case this result might reflect the actual situation more accurately since no definite data on the cross-sections of the individual bands can be obtained from the spectra (due to strong overlapping of bands) and no assessment of the amount of chloride character in the corresponding orbitals can be made.

The assignments given in this section are quite different from those in ref. 10. However, due to the very limited series of compounds studied, such features as the merging of the first four bands into two appear to have been overlooked in the earlier study.

The Spectra of $[\text{PdCl}_2(\text{AsEt}_3)_2]$ and $[\text{PtCl}_2(\text{AsEt}_3)_2]$.—The low-i.e. parts of the spectra of $[\text{PdCl}_2(\text{AsEt}_3)_2]$ (Figure 9) and $[\text{PtCl}_2(\text{AsEt}_3)_2]$ (Figure 10) appear to be much like those in the spectra of the corresponding PEt_3 complexes, with i.e. values for corresponding ionization bands being only somewhat smaller than found for the PEt_3 complexes (see Table 1). Assignments are therefore similar to those previously made in the PEt_3 cases.

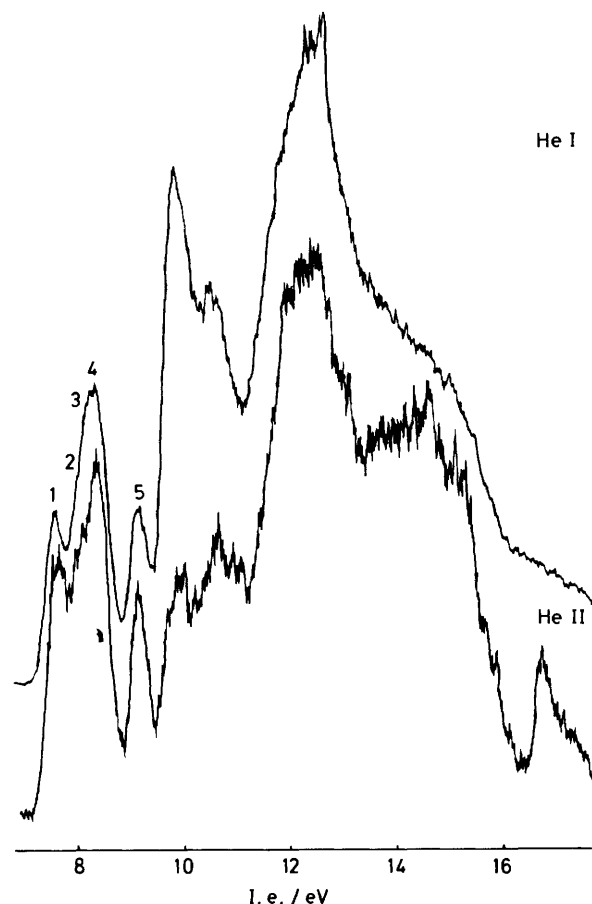


Figure 10. The He I and He II spectra of $[\text{PtCl}_2(\text{AsEt}_3)_2]$

With these compounds detailed assignments pertaining to the chloride-type ionizations are not possible due to strong overlapping with $\sigma_{\text{As-C}}$ orbitals which exhibit ionizations at much lower i.e. than the $\sigma_{\text{P-C}}$ orbitals. However, the values also appear to be rather similar to the corresponding values for the phosphine complexes.

The Spectrum of $[\text{PtH}(\text{Cl})(\text{PEt}_3)_2]$.—The structure of the closely related $[\text{PtH}(\text{Cl})(\text{PPh}_2\text{Et}_2)]$ has been determined by X-ray crystallography.³⁰ As regards the Cl–Pt–P angles and coplanarity there are only minor deviations from the ideal situation. The Pt–Cl distance is significantly longer (242 p.p.m.) than in the corresponding dichloride compounds and was ascribed to the *trans* effect of the hydride ligand.³⁰ Hence, it may be concluded that differences in electronic structure between $[\text{PtCl}_2(\text{PEt}_3)_2]$ and $[\text{PtH}(\text{Cl})(\text{PEt}_3)_2]$ are caused by the replacement of a chloride by a hydride ion rather than by geometrical differences.

In Figure 11 the He I and He II spectra of $[\text{PtH}(\text{Cl})(\text{PEt}_3)_2]$ are shown (i.e. values in Table 5). At lowest i.e. two bands are observed with large He II intensity. That at 7.81 eV is due to two coincident bands (1 and 2), while that (3) at 8.24 eV is a single one. Two of the three bands correspond to the two lowest-i.e. bands in the spectrum of $[\text{PtCl}_2(\text{AsEt}_3)_2]$, i.e. antibonding combinations between p_{Cl} and platinum d orbitals of appropriate symmetry. Since in this case only one chloride ion is present, the p_{Cl} orbitals taking part in this interaction are now simply the two p orbitals perpendicular to the M–Cl bond, instead of the gerade combinations of chloride p orbitals in the previous cases.

Lifting of the symmetry will also have its bearing upon the d_{z^2} -type orbital. In the dichloride compounds this orbital was

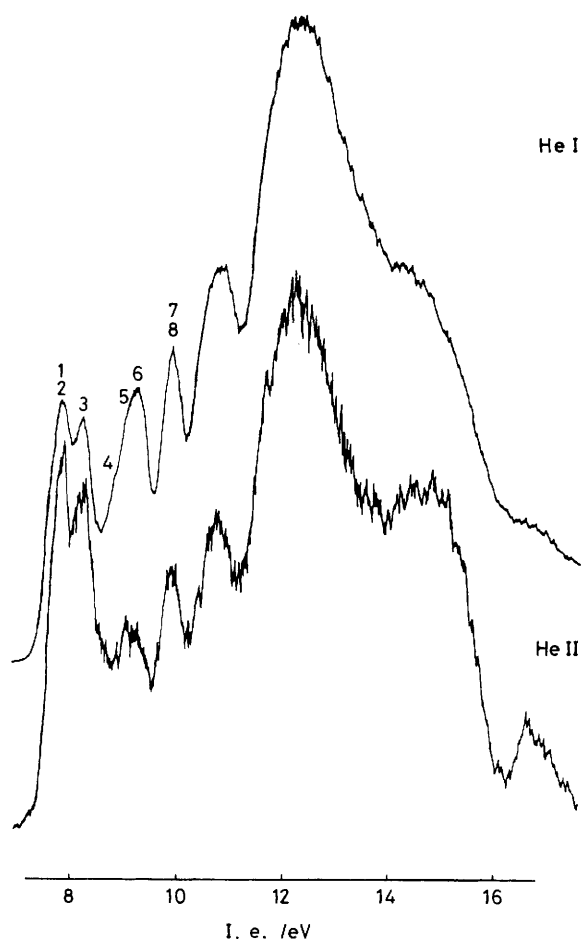


Figure 11. The He I and He II spectra of $[\text{PtH}(\text{Cl})(\text{PEt}_3)_2]$

unable to interact with the higher σ orbitals (which were of ungerade symmetry). In the present compound, with its lower symmetry, such an interaction is no longer forbidden, and it will lead to a decrease in the i.e. of the d_{z^2} -type orbital in addition to the decrease already caused by the lower charge on Pt relative to the dichloride compound. Thus, in view of the large He II cross-section of band 1, the latter is assigned to the d_{z^2} orbital ionization, while bands 2 and 3 (nearly coincident) are assigned to the $d_{xy}-p_{\text{Cl}}^{\text{p}}$ and $d_{xy}-p_{\text{Cl}}^{\text{d}}$ orbital ionizations.

At higher i.e. in the He I spectrum a composite band with an overall maximum of 9.38 eV is observed with a pronounced sloping low-i.e. side due to the presence of two shoulders (4 and 5). On the basis of the i.e. value of the d_{yz} band in the spectrum of $[\text{PtCl}_2(\text{PEt}_3)_2]$ and consideration of the lower charge on Pt in the present compound, it may be assumed that the d_{yz} ionization band will be within this composite band. The remainder of this composite band in He II with its maximum (4) at 8.88 eV must for a large part be due to this d_{yz} band.

The band due to the n_{P}^{p} orbital is also within this envelope. Since interaction with p_{Cl} orbitals will now be much less, the i.e. value will be increased with respect to that of the dichloride compound. The third individual band within the composite one is assigned to a high-lying σ level (corresponding to the $\sigma_{\text{M-Cl}}^{\text{p}}$ level in the dichloride compound) that is here a combination of localized Pt-H and Pt-Cl orbitals. Since the He II cross-sections of both Cl 3p and H 1s orbitals are very small, this band will be nearly depleted in He II. Tentatively band 5 is assigned to the n_{P}^{p} and 6 to the $\sigma_{\text{M-Cl}}^{\text{p}}$ ionizations.

The bands 7 and 8 at 10.01 eV are assigned to the bonding combinations between p_{Cl} and d orbitals of appropriate

Table 5. Ionization energies (eV) for $[\text{PtH}(\text{Cl})(\text{PEt}_3)_2]^*$

| d_{z^2} | $d_{xz}-p_{\text{Cl}}^{\text{p}}$ | $d_{xy}-p_{\text{Cl}}^{\text{d}}$ | d_{yz} | n_{P}^{p} | $\sigma_{\text{H-Pt-Cl}}^{\text{p}}$ | $p_{\text{Cl}}^{\text{p}} + d_{xz}$ | $p_{\text{Cl}}^{\text{d}} + d_{xy}$ |
|-----------|-----------------------------------|-----------------------------------|----------|---------------------------|--------------------------------------|-------------------------------------|-------------------------------------|
| 7.81 | 7.81 | 8.24 | 8.88 | 9.19 | 9.38 | 10.01 | 10.01 |

* n_{H}^{p} and $\sigma_{\text{H-Pt-Cl}}^{\text{p}}$ correspond to n_{P}^{p} and $\sigma_{\text{M-Cl}}^{\text{p}}$ in the dichloride compound.

symmetry. Apparently, in view of the rather large He II intensity, the amount of platinum d character of the corresponding orbitals, giving rise to bands 7 and 8, is not insignificant. Their coincidence is in agreement with the same behaviour exhibited by their counterparts (2 and 3).

At higher i.e. strong overlapping of bands makes further assignments impossible.

Conclusions

The u.p. spectra of a series of dichloride complexes of Pd^{II} and Pt^{II} and of $[\text{PtH}(\text{Cl})(\text{PEt}_3)_2]$ can be assigned with the help of He I/He II intensity differences, shift effects, and h.f.s. calculations. In the case of the bis(phosphine) complexes the earlier assignments appear to be incorrect. Some important features of the electronic structures of the compounds are: a high-lying d_{z^2} orbital, somewhat hybridized with the metal s orbital, that is of great importance for the chemistry of these complexes; strong π interaction between non-bonding orbitals on the metal and the chloride ligands; and through-space interactions between ionic and neutral ligands.

Although the agreement between the h.f.s. calculations and the experimental results is not perfect, the calculations still provide an insight into the electronic structure. They also indicate, in the case of Pt, that relativistic effects are much less important than with some other third-row metals.

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