Ultraviolet Photoelectron Spectra of Square Planar Complexes of Nickel Triad Metals, I

He(I) and He(II) Spectra of \([M\{C_6H_5(CH_2NMMe_2)_2o,o}\}X]\), \(M = \text{Ni, Pt}; X = \text{Cl, Br, I}; M = \text{Pd}; X = 

Jaap N. Louwen, David M. Grove, Henk J. C. Ubbels, Derk J. Stufkens, and Ad Oskam*

Laboratorium voor Anorganische Chemie, J. H. van’t Hoff Instituut, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

Z. Naturforsch. 38b, 1657–1664 (1983); received June 20, 1983

UV–PE Spectra, Square Planar Complexes, Nickel Triad Metals

UV photoelectron spectra of the title compounds are reported. Assignments based on He(I)/He(II) intensity differences, shift effects, and comparison with related molecules allow an assignment of the upper valence bands. Electronic differences between nickel and both platinum and palladium are reflected in the spectra, especially with respect to bands due to ionization of electrons from the metal.

Strong evidence is found for \(\pi\) interaction of the ligand phenyl system with metal orbitals.

Introduction

In past years, metal complexes containing the terdentate, formally anionic ligand \(\text{trans N,N',C-2,6-bis[(dimethylamino)methyl}]+)phenyl, from now on to be named L, have been studied extensively [1–15] (Fig. 1). The complexes with nickel triad metals are especially interesting because of their unusual chemistry.

![Fig. 1. General formula of the compounds](image)

\(X = \text{Cl, Br, I}\) complexes platinum can be oxidized to a formal 4+ state [15] and also, very remarkably, the analogous Ni(II) compounds can be oxidized to paramagnetic compounds \([\text{Li}X'X]\) (X and X' being halogen atoms) [3].

Furthermore, the complexes \([\text{LMX}]\) \((M = \text{Pt, Pd}; X = \text{Cl, Br, I})\) have been successfully used as starting compounds for novel dinuclear species [12].

In view of this versatile chemical behaviour and a recent report of a related system that shows catalytic activity [16], a study of the electronic structure of these complexes is of obvious interest.

As yet, molecular orbital calculations with theoretically sound schemes is almost impossible for compounds of this size, so we have to rely upon indirect evidence from physical measurements. At present, UPS is probably the most direct method to study valence electrons. With this in mind we have undertaken the present study.

Experimental

All compounds were synthesized according to previously published procedures [2, 3].

The spectra were recorded on a Perkin-Elmer PS 18 photoelectron spectrometer modified to include a Helectros He(I)/He(II) hollow cathode light source.

Vacuum sublimation of the compounds was carried out to check the absence of decomposition in the gas phase prior to running the spectra.

All spectra were internally calibrated with respect to He, Ar and Xe.

---

* Reprint requests to Prof. Dr. Ad Oskam.
0340–5087/83/1200–1657/$ 01.00/0

---

Dieses Werk wurde im Jahr 2013 vom Verlag Zeitschrift für Naturforschung in Zusammenarbeit mit der Max-Planck-Gesellschaft zur Förderung der Wissenschaften e.V. digitalisiert und unter folgender Lizenz veröffentlicht:
Creative Commons Namensnennung-Keine Bearbeitung 3.0 Deutschland Lizenz.

Zum 01.01.2015 ist eine Anpassung der Lizenzbedingungen (Entfall der Creative Commons Lizenzbedingung „Keine Bearbeitung“) beabsichtigt, um eine Nachnutzung auch im Rahmen zukünftiger wissenschaftlicher Nutzungsf orm zu ermöglichen.

This work has been digitalized and published in 2013 by Verlag Zeitschrift für Naturforschung in cooperation with the Max Planck Society for the Advancement of Science under a Creative Commons Attribution-NoDerivs 3.0 Germany License.

On 01.01.2015 it is planned to change the License Conditions (the removal of the Creative Commons License condition "no derivative works"). This is to allow reuse in the area of future scientific usage.
Results and Discussion

In dealing with the ionizations the validity of Koopmans theorem [17] will be implicitly assumed, so each ionization will be identified with a molecular orbital. In the chemical way of thinking molecular orbitals are either highly localized or consist of simple combinations of localized orbitals. In photoelectron spectroscopy this model view has the advantage of enabling us to use empirical assignment criteria like He(I)/He(II) intensity differences and shift effects upon substitution.

He(I) and He(II) intensity differences follow from the different ionization cross sections for different orbitals. These can, in cases of localized orbitals, be approximated by the cross sections of the dominant atomic orbitals, which are well tabulated for elements up to Cl [18]. Also for Br and I cross sections for the free atom orbitals are known [19].

Transition metal d-orbitals are commonly found to possess a moderate He(I) and a high He(II) cross section. This has been of indispensable use in assigning a wide range of photoelectron spectra of transition metal complexes [20].

To discuss the basic electronic structure of the compounds it is convenient to break the (essentially planar) molecule [LMX] down into three parts. One is an M 2+ ion. The eight valence electrons are divided over four d-orbitals, the d_{x^2-y^2} being empty and suited for donation from the four coordinating atoms.

The second part is the X- ion. In UPS only ionization from the three valence p-orbitals will give rise to ionization bands. Two of these p-orbitals will be perpendicular to the M-X bond, and be found at about the same energy, while the third will be colinear with the bond, and will mix with metal orbitals to provide M-X bonding.

By far the most complex is the third part, L-. From the spectra of its constituent groups (benzene and tri alkyl amines) ionizations from five valence orbitals are to be expected. Firstly, we have the two well known upper \pi MO's on the phenyl moiety (a_2 and b_1 in C_{2v} symmetry). In the UP spectrum of [LInMe_2] the two bands arising from these orbitals have both been assigned within a broad band at 8.53 eV (see Table I).

Secondly, we have a high lying phenyl \sigma orbital to carry the negative charge and to form a metal-carbon bond in the complexes.

Finally, there are two N lone pair type orbitals. Because of the influence of the empty d_{x^2-y^2} orbital we will have to consider the symmetric and antisymmetric combinations of these (see Fig. 2).

![Fig. 2. Symmetric and antisymmetric combinations of two lone pairs in trans position around a metal.](image)

Table I. Ionization Energies* of [LMX] and [LInMe_2] in eV. Values between brackets are approximate values, taken as the maximum of an overlapping band.

<table>
<thead>
<tr>
<th>MX/Level</th>
<th>( \pi_{b_1} )</th>
<th>( \sigma^- )</th>
<th>d_{x^2}</th>
<th>X_{nombonding}</th>
<th>d_{yz}, d_{xy}</th>
<th>( \pi_{a_2} )</th>
<th>( \sigma^+ )</th>
<th>( \pi_{b_2}^+ )</th>
<th>( \pi_N )</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiCl</td>
<td>7.16</td>
<td>7.70</td>
<td>(8.72)</td>
<td>9.44</td>
<td>(8.72)</td>
<td>9.93</td>
<td>10.47</td>
<td>10.06</td>
<td>(11.18)</td>
</tr>
<tr>
<td>NiBr</td>
<td>7.22</td>
<td>7.75</td>
<td>(8.66)</td>
<td>8.66</td>
<td>(8.66)</td>
<td>8.66</td>
<td>(10.27)</td>
<td>(10.27)</td>
<td>(11.22)</td>
</tr>
<tr>
<td>NiI</td>
<td>7.07</td>
<td>7.54</td>
<td>(8.75)</td>
<td>8.07/8.29</td>
<td>(8.75)</td>
<td>9.10</td>
<td>(10.00)</td>
<td>(10.00)</td>
<td>(11.12)</td>
</tr>
<tr>
<td>PtBr</td>
<td>7.65</td>
<td>7.79</td>
<td>8.15</td>
<td>8.75</td>
<td>(8.75)</td>
<td>9.34</td>
<td>(10.12)</td>
<td>(10.12)/(11.08)</td>
<td>(11.30)</td>
</tr>
<tr>
<td>PtCl</td>
<td>7.16</td>
<td>7.78</td>
<td>8.05</td>
<td>9.01</td>
<td>(8.90)</td>
<td>9.66</td>
<td>10.14</td>
<td>10.42</td>
<td>(11.30)</td>
</tr>
<tr>
<td>PtBr</td>
<td>7.29</td>
<td>7.87</td>
<td>8.05</td>
<td>8.78</td>
<td>(9.02)</td>
<td>9.48</td>
<td>10.19</td>
<td>10.53</td>
<td>/ 11.34</td>
</tr>
<tr>
<td>PtI</td>
<td>7.12</td>
<td>7.57</td>
<td>8.06</td>
<td>8.21/8.54</td>
<td>(8.96)</td>
<td>9.33</td>
<td>10.05</td>
<td>10.58</td>
<td>/ 11.13</td>
</tr>
<tr>
<td>InMe_2[21]</td>
<td>(8.58)</td>
<td>8.03</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* Values are correct within 0.02 eV.
and \( \sim 10.5 \text{ eV} \) on going from the Br to the Cl complex.

In the He(I) spectra of both [LNiCl] and [LNiBr] the band at lowest Ionization Energy (IE) exhibits some fine structure (see Fig. 5). The fine splitting of 910 cm\(^{-1}\) (from the symmetric ring breathing mode vibration) suggested a phenyl localized orbital as source of this ionization. On the other hand this band exhibits a relatively large intensity in the He(II) spectra, which normally signifies ionization from a metal d-type orbital.

To reconcile these two arguments, and in the light of the rather low Ionization Energy (IE) for this band, this ionization has finally been assigned to a \( \pi \) antibonding combination of the phenyl \( b_1 \) orbital and the Ni \( d_{xz} \) orbital (Fig. 6). This type of level interaction between the \( b_1 \) orbital of benzene and filled levels on non-metallic substituents is quite common [19] and apparently also holds true for metallic groups as well.

The second band (at 7.70 eV in the spectrum of the chloride and 7.75 eV in the spectrum of the bromide compound) has, in contrast to the one at lowest energy, a poor He(II) intensity. Because of this and since other possibilities can be excluded (\textit{vide infra}) it is assigned to the phenyl-metal bonding orbital, probably with some metal-halogen mixed in in an antibonding fashion (antisymmetric orbital, compare Fig. 2). This band also exhibits fine structure (Fig. 5), in keeping with its phenyl
localized character. In this case the splitting is \( \sim 1720 \text{ cm}^{-1} \), indicating that the vibration involved is a skeletal vibration mode of the \( \text{L}^- \) part.

The halogen type ionizations can be recognized on the basis of two criteria; a) their very low He(II) intensity \([18, 19]\) and b) the shift upon substitution of Cl for Br.

It will be noted that the composite band between 8 and 9 eV in the He(I) spectrum of the Br compound has an intense and sharp maximum at 8.66 eV. In He(II) the sharpness of this maximum has been removed and its position has shifted somewhat. In the He(I) spectrum of the Cl complex the sharp maximum is absent, but the composite band has gained a shoulder at 9.44 eV, with very low He(II) intensity. Thus the bands due to ejection of non bonding halogen electrons can be assigned at 9.44 and 8.66 eV in the spectra of the Cl and Br compounds respectively.

A similar reasoning allows us to assign the bands at 10.77 eV (Br) (composite) and 10.47 eV (Cl) to ionizations from the symmetric \( \sigma \) orbital (mainly \( \text{M}^-\text{X} \)).

The fact that the composite band at 8–9 eV remains rather intense in He(II), despite the depletion of the halogen bands, suggests that this region also contains three bands due to photoelectrons from Ni 3d orbitals. The remaining d-orbital is partly taken up into the Ni-phenyl \( \pi \) antibonding orbital which gives rise to the first band in the spectrum. Its counterpart, the band due to the bonding \( \pi \) orbital, is assigned to the bands at 10.06 eV ([LNiCl]) and 10.27 (composite, [LNiBr]) respectively on the basis of relatively high cross section in He(II) and IE.

The ionization band due to the \( \pi_{\text{eq}} \) orbital of the phenyl part will lie within the 8–9 eV band in the Br complex while in the Cl analogue it is tentatively assigned to the shoulder on the corresponding band at 9.03 eV. A value of about 9 eV compares well with the value found in [LNiMe\(_2\)], when the electron withdrawing capacity of the halogen substituent is taken into account.

The band at \( \sim 11 \) eV in both spectra will contain ionizations due to the nitrogen lone pair orbitals, possibly together with some high lying orbitals of the phenyl part.

There are two significant differences between the spectrum of [LNiI] (Fig. 7) and those of the Cl and Br complexes. First, in contrast to the two spectra already discussed, the lowest IE band now has a very poor He(II) intensity. Second, there are now two extra bands between the two lowest IE bands and the broad one at 8–9 eV.

Fig. 7. The He(I) and He(II) spectra of [LNiI].

The last feature is the simplest to explain. The band due to the two non bonding halogen orbitals, already shifted to lower IE upon replacing Cl by Br has now been destabilized to the extent that two bands (with spin-orbit coupling due to the near-degeneracy of the two levels) become separately visible. Their low He(II) intensity, indicating a large degree of halogen localization \([19]\), supports this assignment.

However, the first feature, a band of low He(II) intensity, is explainable using the fact that in transition metal iodine complexes a strong interaction often exists between I non bonding \( p \)-orbitals and metal d-orbitals of the same symmetry \([22,23]\). One must make the assumption that the orbital of the \([\text{MX}]^+ \) part which interacts with the \( \pi_{\text{eq}} \) orbital on the \( \text{L}^- \) part now has sufficient iodine character to strongly decrease the overall He(II) cross section of the corresponding ionization band.

There is a third important feature worth noting and that is the significantly lower IE for the second band. This indicates that, with decreasing orbital
energy of the halogen orbitals on going from Cl or Br to I, the mixing with the M–C orbital becomes stronger and the antisymmetric σ orbital is now destabilized since the extra halogen character is combined in an antibonding fashion.

All other bands in the spectrum are assigned as in [LNiBr].

The spectra of the palladium and platinum compounds

A comparison of the spectra of [LPdBr] (Fig. 8) and the platinum compounds (Figs 9, 10, 11) shows many similarities especially in the lower IE region, while the spectra of the Ni compounds are clearly different. It is therefore natural to discuss the spectra of the Pd and Pt compounds together.

The most significant difference between the spectra of [LPdBr] and [LPtBr] is the IE of the first (lowest IE) band which is significantly stabilized upon substitution of Pt by Pd. Furthermore, although the He(II) cross section in the Pt compound seems to indicate significant d-participation, in [LPdBr] this first band has very little relative intensity in He(II). This, in keeping with the assignment for the Ni complexes, suggests that this band is due to a \( \pi \) antibonding orbital. Due to relativistic effects the d-orbitals of Pt will interact more strongly with their environment than those of Pd [24] and therefore the IE of the first band is lower for Pt than Pd. These effects may also explain the difference in He(II) intensity as resulting from larger d involvement in the \( \pi \) antibonding orbital of the platinum compound.

The second band in the spectra of [LPdBr], [LPtCl] and [LPtBr] exhibits a very low He(II) intensity and only a very small shift upon halogen substitution. Thus it is assigned to the σ antisymmetric orbital, mainly M–C in character.
The third band is a new feature, not evident in the spectra of the Ni compounds, with a \( \text{He(I)}/\text{He(II)} \) intensity difference that shows it to be due to a rather pure metal \( d_z^2 \) orbital. This band is assigned as due to the metal \( d_z^2 \) orbital, destabilized as a result of antibonding \( \sigma \) interactions with the bonding orbitals between the metal and the coordinating atoms (analogous to the destabilization due to electrostatic repulsion in classical crystal field theory). An extra argument for this assignment is the fact that Slater \( X_a \) MO calculations on \([\text{PH}_3)_2\text{M(C=CH)}_2]\) and \([\text{PH}_3)_2\text{MCl}_2\) (\( M = \text{Pd, Pt} \)) have indicated a high lying orbital consisting mainly of the metal \( d_z^2 \) orbital. Indeed, the spectra of the \( \text{PET}_3 \) compounds exhibit a band due to the ionization of a \( d \)-electron at low IE \([25]\).

The low IE of the \( d_z^2 \) is interesting, since it affords the metal with a high lying orbital with density in the free coordination sites existing above and below the square planar coordination plane. This may well be an essential feature in the ability, of certain related Pt compounds, to form a donative metal-metal bond perpendicular to the phenyl-metal plane \([8-11]\).

Again, as in the spectra of the Ni complexes, there is in the region 8–9 eV a band composed of ionizations from the halogen non bonding electrons, the remaining metal \( d \)-orbitals and the phenyl \( \pi_{s_u} \) orbital. It may be noted that the maximum of the band due to non bonding halogen electrons (to be recognized by a scrutiny of the \( \text{He(I)}/\text{He(II)} \) intensity difference) is shifted to somewhat higher IE in the spectrum of the Pd-complex.

The M–X orbital (formally \( \sigma \) symmetric) appears to be in a different position from that in the spectra of the Ni complexes. It can be seen that the small band at higher IE side of the composite band at 8–9 eV shifts significantly upon halogen substitution, so marking it as due to the M–X bonding orbital. From Table I it is seen that the separation between the bands due to bonding and non bonding halogen electrons increases in the order \( \text{Pd < Pt < Ni} \), and this implies increasing covalent character of the M–X bond.

The \( \pi \) binding combination of the phenyl \( \pi_{b_u} \) and metal \( d_{xz} \) orbitals again gives rise to a band at about 10 eV as is confirmed by \( \text{He(I)}/\text{He(II)} \) intensity differences. Next to this band (or collapsing with it) is the band due to the antisymmetric combination of \( N \) lone pairs. The symmetric combination gives a band within the complex b and at higher IE.

Finally it should be noted that there appears to be no obvious spin-orbit coupling in the Pt \( d \)-bands (although absolute certainty in this matter is not possible, due to strong overlapping of bands). However, such an effect is not expected, since there are no degeneracies among Pt \( d \)-levels.

The spectrum of \([\text{LPtI}]\) shows differences in appearance from the spectra of the Cl and Br compounds which are similar to those encountered within the spectra of the nickel series. In \([\text{LPtI}]\), like in \([\text{LNiI}]\), the relative \( \text{He(II)} \) intensity of the first band is low although the band is not so much depleted as it appeared in the nickel case. Similarly, the second band has again been destabilized somewhat as a result of different \( \sigma \) interaction between the \( \sigma_{M-C} \) and \( \sigma_{M-X} \) orbitals.

![Fig. 11. The He(I) and He(II) spectra of \([\text{LPtI}]\).](image-url)

On the basis of \( \text{He(I)}/\text{He(II)} \) cross section differences bands at 8.21 eV and 8.54 eV are assigned to the 3/2 and 1/2 levels of non-bonding iodine electrons (with spin-orbit coupling). The band at 8.06 eV is assigned to the \( d_z^2 \) orbital.

The spin-orbit coupling parameter of .33 eV compares well with the value found in the Ni compound (.22 eV). These values are rather low presumably as the consequence of the low symmetry (small second order spin-orbit coupling).
The overall maximum for the d-bands can be located at 8.96 eV with a tentative assignment of 8.78 eV as the location of the $\pi_d^2$ band on the basis of He(I)/He(II) intensity comparisons.

At 11.13 eV is a sharp band which, because of its large He(II) intensity and its location, is assigned to the symmetric $n_N$ orbital, with some $d_{z^2}$ character mixed in. This confirms the approximate assignment in the other spectra where this band seems to have been obscured.

**Comparison of the electronic structures**

From a comparison of the above data some important features can be noted.

Firstly, with the Pd and Pt compounds the presence of a high lying $d_{z^2}$ orbital has been shown. This orbital is significant as the frontier orbital for interaction of the transition metal in a donative sense to metal centres which can behave as Lewis acids. However, the presence of a high lying metal $d_{z^2}$ orbital is by no means unique to the compounds studied, but seems a general feature in square planar complexes of Pd and Pt [25]. Indeed, cases are known in which one Pt atom (in a formally 2+ state) coordinates to another Pt atom via the $d_{z^2}$ orbital [26]. Furthermore, other transition metals such as square planar Ir and Rh can also form bonds, perpendicular to their coordination plane, with post-transition metals [27-31].

Although this suggests that square planar complexes of the platinum metals (Pt, Pd, Ir, Rh) all have a frontier orbital suitable for a donative metal-metal interaction the isolation of such dinuclear species is strongly dependent upon the co-ligands. In fact, in all cases reported so far of bonding between one of the above transition metals in a 2+ state and a post transition metal a bridging ligand is present between the two metals.

Secondly, it has been shown that the compounds (especially the Ni and Pt ones) show a very low first IE due to the presence of a $\pi$ type orbital delocalized over a large part of the molecule with M-C antibonding character. Since the bonding counterpart of this orbital is also occupied this does not imply multiple bonding between C and M. However, the presence of a high lying delocalized $\pi$ orbital on the compounds might be of relevance to their chemistry.

Thirdly, a significant difference is found between the electronic structure of the Ni compounds on the one hand and the Pd and Pt on the other. In view of the electronic structures of the free atoms (Ni $s^2d^9$, Pd $d^{10}$, Pt $s^1d^9$ [32]) it is possible that the valence s orbital on the metal is playing an important role in causing these differences. This hypothesis gains some support from the fact that the most significant differences between the spectra of the Ni and those of the other compounds are the location of $\sigma$ levels ($\sigma_{M-X}$, $\sigma_{M-C}$ and $\pi_N$ type levels) and of the $d_{z^2}$ level (which is also of $\sigma$ symmetry). However, at present not enough comparative UP data on square planar complexes of Ni, Pd and Pt is present to warrant a thorough discussion. More research into this subject is required for a full picture.

**Conclusions**

The UP spectra of the title compounds can be assigned with the use of empirical criteria. Some important features of these complexes have been indicated.

The first, a strong level interaction between $\pi$ levels on the phenyl part and metal d-orbitals of the proper symmetry, significantly lowers the first IE of the compounds.

Also, the presence is indicated of a high lying frontier orbital, which rationalizes the existence of donative metal-metal bonds in related compounds.

Mr R. Hengelmolen and Drs R. R. Andéa are acknowledged for stimulating discussions.

    b) J. Terheijdien, G. van Koten, and K. Vrieze, manuscript in preparation (see also [3]).
[21] The structure of [LInMe2] in the gas phase is not known, but it does contain a C-In o bond between the L~ and the InMe2+ parts. Thus, values found for phenyl localized orbitals may serve as indica-
    tion for values in the other compounds. The upper valence region of the UP spectra consists of one
    broad band at 8.58 eV with two shoulders that decrease somewhat in intensity upon going from
    He(I) to He(II), and are accordingly assigned to M-C o type ionizations.