Inorganica Chimica Acta, 40 (1980) 15–24
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

He-I and He-II Excited Photoelectron Spectra of Tetracoordinated Complexes of Transition Metal Ions with β-Diketonate Ligands

I. FRAGALÀ, L. L. COSTANZO, E. CILIBERTO, G. CONDORELLI
Istituto Dipartimentale di Chimica, Università di Catania, V. le A. Doria 6, Catania 95125, Italy

and C. D'ARRIGO
Osservatorio Astrofisico, Università di Catania, V. le A. Doria 6, Catania, 95125, Italy

Received August 4, 1979

Photoelectron spectra of d^n (n = 7, 8, 10) transition metals complexes with β-diketonate ligands are reported. In tetrahedral complexes of the zinc and cobalt elements, no evidence has been found of strong covalent metal–ligand interactions. In the case of square-planar complexes of d^8 transition metal ions, the bonding involves covalent interaction between external ligand orbitals and more internal d subshells. In the spectrum of the complex bis(acetylacetonate)nickel(II), structures have been detected around 11.5 eV which may relate to ionization of some of the 3d subshells. Similar features are not detectable in spectra of analogous palladium and platinum complexes; smaller relaxation energies in the ion states are, probably, responsible for this behaviour.

Introduction

Widespread interest has been attached, in recent years, to investigation on the electronic structure of transition element organometallic and classical coordination complexes by gas phase UV photoelectron (PE) spectroscopy [1]. Much effort has been directed toward organometallic complexes of a large part of the elements of the Periodic Table [1]. Less attention has been paid generally to classical coordination compounds the most reliable results being related to octahedral complexes of first row early transition elements in a formal +3 oxidation state [2]. Currently, bonding in tetracoordinated (both tetrahedral and square planar) complexes of transition metals in formal +2 oxidation states is far from being well established. Within classical crystal field theory it was customary to view metal d subshells in these complexes as being less tightly bound than molecular orbitals (MOs) belonging to ligand π or σ framework. Nonetheless, several experimental observations can hardly be fitted into a such simplified model. For instance when considering electronic spectroscopy data on tetracoordinated complexes, either the larger intensity associated, in some cases, with d–d electronic transition [3] or the electronic charge transfer bands occurring sometimes at a lower energy than d–d transition [4] may be indications that the crystal field model is not adequate.

Furthermore, UV–PE spectra of some tetra-coordinated coordination complexes of d^8, d^9 and d^{10} metals suggested that an MO model is better suited to describe bonding in these complexes and that MOs of predominant d character lie more internally than those having ligand nature [5, 6].

As part of an extensive programme involving PE measurements on a wide series of tetrahedral and square-planar complexes containing O_4, S_4, N_4 and O_2S_2 chromophores, we report here He-I and He-II excited PE spectra of complexes of d^n (n = 7, 8, 10) metals with pentane 2,4-dione (acac) and 2,2′-6,6′-tetramethylheptane 3,5-dione (dpm) anion ligands. The He-I PE spectra of $Ni(acac)_2$ has been already reported [6, 7].

Experimental

The complexes $M(acac)_2$ and $M(dpm)_2$ (M = Zn, Co, Ni, Pd, Pt) were prepared following literature methods [8]. They were purified by sublimation *in vacuo*. The air sensitive $Co(dpm)_2$ [9] has always been handled in an argon atmosphere.

Whilst the complexes $M(dpm)_2$ have been shown to be all monomers, the corresponding complexes $M(acac)_2$ are trimers in the solid state [8a]. There is however, clear evidence that the latter compounds are not associated in the vapour phase [8a].

Spectra were measured on a Perkin-Elmer PS18 spectrometer modified for He-II measurements by including a hollow cathode discharge lamp giving a high photon flux at He-II wavelength (Helectros Development). Calibration of the spectra were by

TABLE I. Pertinent IE and Intensity Data of $Zn(dpm)_2$ and of $Co(dpm)_2$.

	Band Label	IE (eV)	Intensities^a		Assignment
			He-I	He-II	
$Zn(dpm)_2$	A	8.15	0.8	1.0	$e(\pi_3)$
	B	8.95	1.0	1.0	$e(n_-)$
	C	10.00	–	–	$b_2(n_+)$
	D	10.30	–	–	$a_1(n_+)$
$Co(dpm)_2$	A	7.92	1.7	2.5	$e(\pi_3)$
	A'	8.24			^5E
	B	9.15	1.0	1.0	$e(n_-)$
	C	9.87	–	–	$b_2(n_+)$

^{a}Dupont curve resolver. Intensities are normalized with respect to band A.

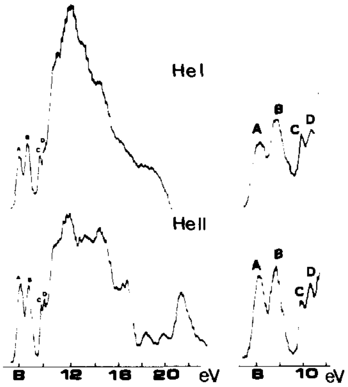

Fig. 1. He-I and He-II PE spectra of $Zn(dpm)_2$ and close-up of the low IE region.

reference to peaks due to admixed inert gases and to the He $1s^{-1}$ self-ionization. Relative band areas, when possible, were evaluated direct from raw spectra using a Dupont 310 curve resolver; in the case of strongly overlapped structures rough indications were gauged simply by peak heights. Intensities of bands, corrected to allow for variation of analyser transmission function with electron kinetic energy, are normalized relative to a band representing MOs with no metal d admixture.

Valence electron self-consistent field molecular orbital calculation (SCF-MO) on $Ni(acac)_2$ were performed within a CNDO scheme which proved suitable both for organometallic and classical coordination complexes [5, 10]. The D_{2h} symmetr has been adapted to the molecule lying in the x–y plane.

Results

The spectrum of the complex $Zn(dpm)_2$ consists, up to 10.5 eV, of four bands labelled A B C D in the figure (Fig. 1).

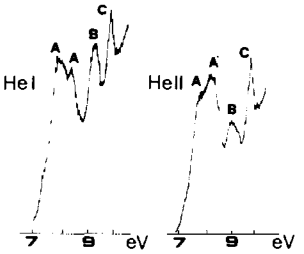

Fig. 2. He-I and He-II PE spectra of $Co(dpm)_2$. Low IE region.

In the case of the cobalt complex only the first three bands are evident (Fig. 2). In the He-II spectra the intensity of band A increases relative to B; this effect is definitely more pronounced in $Co(dpm)_2$ (Table I).

The evaluation of the intensities of the remaining bands is quite problematic, intensities being strongly influenced by the low energy tail of the following intense band. Nevertheless it seems evident that in the He-II spectrum of $Zn(dpm)_2$ band D becomes stronger.

The spectra of square-planar complexes are definitely more intricate. In the case of $Ni(acac)_2$ nine bands are present up to 12 eV (Fig. 3). The shoulder g' is also associated to the band g. Intensities of all these bands are rather uncertain in the He-I spectrum even using the peak height as criterion. In reality, intensities of bands beyond the band c are strongly influenced by the low energy tail of the intense structure beyond 12 eV. In the He-II spectrum intensities can be evaluated more reliably (Table III). So, information on the nature of MOs corresponding to various PE bands has been evaluated by considering deviations from the expected statistical intensities.

TABLE II. Theoretical CNDO Results on Ni(acac)$_2$.

Symmetry	Energy (eV)	Nickel			Acetylacetone					Dominant Character
		3d	4p	4s	Carbon		Oxygen		Hydrogen	
					2s	2p	2s	2p	1s	
$5b_{2u}$	8.57	–	–	–	–	26		57	11	n_-
$3b_{2g}$	8.71	4	–	–	–	37	–	59	–	$\pi_3 - d_{xz}$
$5b_{1g}$	9.17	7	–	–	–	34	–	45	10	$n_- - d_{xy}$
$2b_{1u}$	9.44	–	2	–	–	44	–	52	–	π_3
$6b_{3u}$	9.86	–	–	–	3	12	–	72	4	n_+
$8a_g$	9.96	12	–	–	2	12	–	61	4	$n_+ - d_{x^2-y^2}$
$5b_{3u}$	10.02	–	–	–	–	19	–	67	8	σ_+
$2b_{3g}$	11.81	40	–	–	–	23	–	35	–	$\pi_2 - d_{yz}$
$7a_g$	11.87	23	–	7	–	14	–	39	13	$\sigma_+ - d_{z^2}$
$4b_{1g}$	12.05	2	–	–	–	18	4	57	6	σ
$1a_u$	12.53	–	–	–	–	34	–	65	–	π_2
$4b_{2u}$	13.03	–	–	–	11	39	–	46	–	σ
$2b_{2g}$	13.30	89	–	–	–	6	–	–	–	d_{xz}
$6a_g$	13.42	70	–	–	–	9	–	5	5	$d_{z^2} - d_{x^2-y^2}$
$5a_g$	13.54	81	–	–	–	5	–	4	–	$d_{z^2} - d_{x^2-y^2}$

TABLE III. Pertinent IE and Intensity Data of Ni(acac)$_2$ and of Ni(dpm)$_2$.

Band Label	Ni(dpm)$_2$ IE (eV)	Ni(acac)$_2$			Assignment	Dominant contribution MO
		IE (eV)	Intensities[a]			
			He-I	He-II		
a	7.40	7.35	–	1.0 (1)	b_{2u}	n_-
b	7.85	7.84	–	0.7 (1)	b_{2g}	$\pi_3 - d_{xz}$
c	8.00	8.01	–	1.0 (1)	b_{1g}	$n_- - d_{xy}$
d	8.38	8.37	–	2.1 (2)	b_{1u}	π_3
e	8.65	8.76			b_{3u}	n_+
f	8.85	9.23	–	1.4 (2)	$a_g + b_{3u}$	$n_+ + \sigma_+$
f'	9.03					
g	9.80	10.04	–	2.8 (2)	$b_{3u} + b_{3g}$	$\sigma_+ + \pi_2$
g'	10.15	10.19				
h	–	10.94	–	–		
x	10.30	–			$a_u (\pi_2) + \sigma$	
i	–	11.32	–	–		
i'	–	11.65	–	–	b_{2g}	d_{xz}

[a] Intensities are normalized with respect to band *d*. Figures in parentheses are expected statistical values taken proportional to occupancy.

The PE spectra of complexes Pd(acac)$_2$ and Pt(acac)$_2$ (Fig. 3) are definitely more resolved; eleven bands are present up to 11 eV. In the figure these bands are correlated with corresponding bands in Ni(acac)$_2$. Because of the better resolution, intensities of various PE bands can be safely evaluated in both He-I and He-II spectra.

The PE spectra of the complexes Ni(dpm)$_2$ and Pd(dpm)$_2$ (Fig. 4) are analogous to those of parent acacetylacetonate complexes. Fewer bands are, however, detectable in the low IE region, some bands probably being obscured by the onset of the following intense strucure.

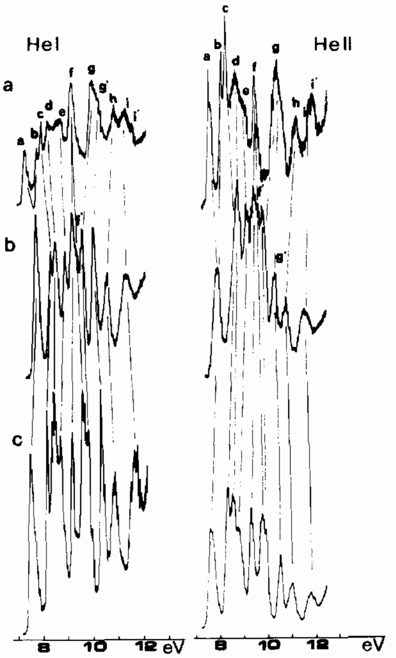

Fig. 3. Low IE region He-I and He-II spectra of (a) Ni(acac)$_2$, (b) Pd(acac)$_2$ and (c) Pt(acac)$_2$.

The higher IE region (up to 17 eV) of spectra of both acac and dpm complexes consists of very intense unresolved structures (see, for example, Fig. 1).

In both cases, remarkable intensity fall-off are associated with these structures in the He-II spectra. These bands, similar to those in spectra of the isolated acacH and dpmH molecules [2, 11, 12], represent ionization of σC–H and σC–C ligand bonding MOs with a greater contribution from carbon 2p orbitals than 2s.

Furthermore, the He-II spectra reveal, in the highest spectral region, some additional features not detectable in the He-I spectra. They consist of three broad bands respectively centered around 18.6, 20.0 and 21.6 eV in each spectrum; MOs of dominant O2s and C2s contributions are likely to be responsible of these bands. These σ MOs, as well as those previously discussed, are unlikely to be involved in the metal–ligand bonding. They will not be considered further.

Deductions on changes in intensity patterns on going from He-I to He-II spectra have been made on the assumption that, at He-II wavelength, the cross-section of metal 3d subshells slightly increases relative to those of O 2p orbitals. Reference to He-I and He-II PE spectra of complexes Cr(acac)$_3$ [13] and VO-(acac)$_2$ [14], both containing structures clearly related to metal 3d electrons, in fact, indicate rather similar cross-section profiles for first row transition metal 3d subshells and for O 2p orbitals.

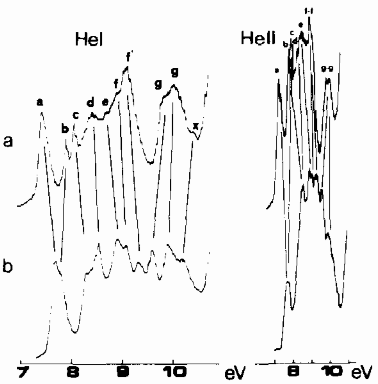

Fig. 4. Low IE region He-I and He-II spectra of (a) Ni(dpm)$_2$ and (b) Pd(dpm)$_2$.

Discussion

In the discussion below we first proceed to the assignment of spectra of tetrahedral molecules; in this case a rather simple molecular orbital model based on a localized orbital basis-set was suitable to describe bonding. When considering square-planar complexes, the spectral complexity precludes such a simple approach. Thus, SCF-MO calculations have been of guidance to interpret spectra, the reliability of theoretical results being always checked against experimental findings. Within the context of present discussion it is worth remembering that the valence electronic structure of the β-diketonate anions – the effective ligands in the complexes of interest – has been thoroughly described. The topmost electronic levels (up to 12 eV binding energy) consist of the in- and out-of-phase combination of oxygen lone-pairs lying in the molecular plane and of the two upper filled out-of-plane π orbitals. For these orbitals, the Evans notations [2] (respectively n_-, n_+, π_3 and π_2) will be maintained throughout this paper. Estimates of relative binding energies of these four MOs in the uncomplexed anion ligands can be gauged from PE spectra of Be(acac)$_2$ [2] or Be(dpm)$_2$ [15].

Currently in the latter complexes the ligand MOs are only sensitive to the electrostatic perturbation due to central metal atom, covalent interactions involving overlaps with metal valence subshells being of minor importance. In Fig. 5 we report the transformation properties of symmetry combinations of these basis orbitals in the point groups appropriate to various complexes under study. The magnitude of energy splittings between each couple of symmetry combinations has been taken proportional to corresponding interligand group overlaps.

Tetrahedral Complexes: Zn(dpm)$_2$ and Co(dpm)$_2$

X-ray diffraction studies indicated that these complexes are monomers and possess a tetrahedral

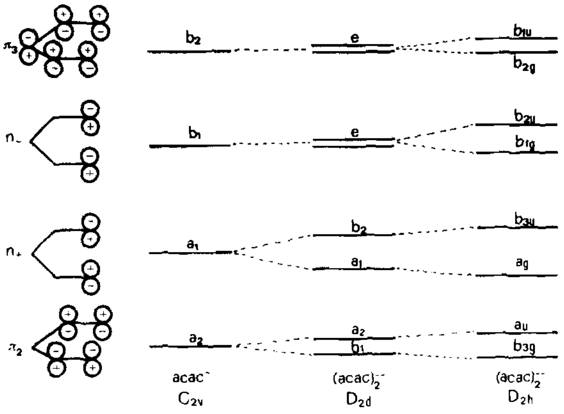

Fig. 5. Transformation properties of basis orbitals of the ligand acac$^-$ framework in various point groups.

crystal structure belonging to D_{2d} point group [16, 17]. The same symmetry has been adopted for the complexes in the vapour phase. In D_{2d} symmetry, the combinations of ligand basis orbitals transform as reported in Fig. 5. Through-space non-bonded interligand interactions with metal basis orbitals can explain details of PE spectra. In the case of the zinc complex, the metal basis set includes only the 4s and 4p orbitals; it is known that Zn 3d subshells are core-like and sensitive to ligand environment only via crystal field electrostatic perturbation [18]. Metal–ligand group overlaps suggest that significant interactions can only involve the Zn($4p_z$)–b_2(n_+) and Zn(4s)–a_1(n_+) couples, the latter interaction being of major importance. The proposed assignment of PE spectrum of Zn(dpm)$_2$ is given in Table I.

Bands A and B relate to ionization of practically unperturbed ligand levels e (π_3) and e (n_-). The energy separation between these bands as well as their variations in relative intensity on passing from the He-He-I to He-II excitation are, in fact, comparable with those of corresponding bands in the spectrum of the parent complex Be(dpm)$_2$. And the latter complex has been assumed *(vide supra)* as a model where metal–ligand 'covalent' interactions are of minor importance. Next bands C and D are taken to represent ionizations respectively from MOs b_2(n_+) and a_1(n_+) respectively admixtures with Zn 4p and 4s orbitals. That these two MOs have different composition is clearly indicated by the different variation of relative intensity on passing from He-I to He-II spectrum. In particular the higher intensity of band D under the He-II radiation (Fig. 1) may reflect a more pronounced increase of Zn 4s cross section than Zn 4p.

The spectra of Co(dpm)$_2$ (Fig. 2), are definitely more broadened and less resolved than those of the isomorphous complex Zn(dpm)$_2$. Such features are certainly connected with the multiplicity of ion states produced on ionization of open shell systems. The complex Co(dpm)$_2$ is an open shell d^7 complex having a $^4A_2$ ground state configuration [9]. Reference to PE spectrum of the complex Co(acac)$_3$ suggest that, also in Co(dpm)$_2$, the ionizations from cobalt 3d subshell should occur in the 8–10 eV region. Actually, even under a more symmetric field (T_d) ionization of d electrons from $^4A_2$ (e^4t^3) ground state gives rise to ^5E, ^3E (e^3t^3) and $^3T(e^4t^2)$ ion states [19]. In T_d symmetry, the crystal field energies of these states relative to that of ^5E are, to first order:

$$^3E(e^3t^3) = 8B + 4C \cong 2.6\ \text{eV}$$

$$^3T(e^4t^2) = 20B + 6C - \Delta \cong 4\ \text{eV}$$

where B, C (C = 4B) and Δ respectively are appropriate Racah parameters and crystal field splitting [3, 17]. Thus, first band (A, A'), which increases in relative intensity under He-II radiation, certainly relates to production of ^5E state but is likely to contain ionization of the nominally ligand e (π_3)MO as well. Actually, the feature A', more intense in the He-II spectrum, probably represents the ^5E state. Moreover, supposing the previous crystal field analysis to be correct, the PE bands associated with the remaining ^3E and $^3T_1$ ion states must be hidden by the very intense structure beyond 11 eV.

The rest of the features appearing in the low IE region can be assigned analogously to Zn(dpm)$_2$; so we associate bands B and C respectively to ionizations of MOs e (n_-) and b_2 (n_+). The PE band related to the MO a_1(a_+), apparent in the spectrum of Zn(dpm)$_2$, is, in this case, shifted to higher IE probably under the intense structure beyond 11 eV. Obviously, ionizations of ligand based MOs give rise to a multiplicity of ion state because of electrostatic coupling of hole states with unpaired 3d electrons. However, due to small values of corresponding exchange integrals, such effects are certainly of minor importance and can only lead to band broadening.

Square-Planar Complexes

The assignment of PE spectra of square-planar complexes is a less straightforward matter. Among PE bands present in the region up 12 eV (Fig. 3–4), there are no structures that may be obviously identified with ionizations of essentially metal nd electrons. For instance, any assignment by which some of the bands at the onset (7–8 eV) of various spectra are assigned to metal nd ionization should, in our opinion, be dismissed. In fact, in complexes of the latest elements of transition series the nd electrons should have a quite higher (11–12 eV) binding energy. This is clearly suggested i) by extrapolating reported IE values related to metal 3d subshells in complexes M(acac)$_3$ (M = Ti, V, Cr, Co) [2], ii) by

TABLE IV. Pertinent IE and Intensity Data of Pd(acac)$_2$ and of Pd(dpm)$_2$.

Band Label	Pd(dpm)$_2$ IE (eV)	Pd(acac)$_2$			Assignment	Dominant contribution to MO
		IE (eV)	Intensities[a]			
			He-I	He-II		
a	7.67	7.79	1.7(2)	0.7(2)	$b_{2u} + b_{2g}$	$n_-, \pi_3 - d_{xz}$
b	7.80					
c	8.28	8.38	0.8(1)	1.6(2)	b_{1g}	$n_- - d_{xy}$
d	8.50	8.59	1.5(1)		b_{1u}	π_3
e	8.90	8.99	1.0(1)	1.0(1)	b_{3u}	n_+
f	9.10	9.25	2.7(2)	1.2(2)	a_g	n_+
f'	9.30	9.40			b_{3u}	σ_+
g	9.55	9.65	1.6(1)	1.0(1)	a_g	σ_+
g'	9.90	10.12	1.5(1)	0.7(1)	b_{3g}	$\pi_2 - d_{yz}$
x	10.10	–				
h	–	10.65				
i	–	11.30				

[a] Intensities are normalized with respect to band *e*. Figures in parentheses are expected statistical values taken proportional to occupancy.

theoretical *ab initio* calculation on several metal d^8 complexes [20] and, finally, iii) by reported IE values (≅11 eV) for 3d ionization in (CuCl)$_3$ [21].

A possible explanation for the large number of bands in the low energy region of present spectra is that they represent ionizations of symmetry combinations of ligand orbitals split by covalent interactions with more internal metal nd subshells. Actually, when considering PE spectra of complexes of the same metal element, the IE of bands in question do not vary on changing from the acac to dpm ligand (Table III, IV). This means that IEs are not determined by factors electrostatic in origin (say, the inductive effect due to terminal t-butyl groups into the dpm ligand). Furthermore, the wider (than in nickel) number of bands in PE spectra of palladium and platinum complexes (Fig. 3) is evidence of the expected stronger covalent interaction in latter compounds. It turns out that simple qualitative models could not be appropriate to account for the metal–ligand bonding in these complexes; according to Jǿrgensen [22], we believe that relevant metal–ligand covalent interactions can be accounted for by MO schemes where interelectronic repulsion terms are not neglected.

Ni(acac)$_2$ and Ni(dpm)$_2$

In Table II we report results of CNDO calculation of Ni(acac)$_2$. The topmost filled MOs (up to 13 eV binding energy) all are mainly ligand in character. Some of them are essentially the symmetry combinations of n_-, π_3, n_+ and π_2 ligand basis orbitals already described. Among the others, the MO s $5b_{3u}$ and $7a_g$ are mainly O 2p based and posses some σ(C–O) character* (they are labelled σ_+ in Table II). The remaining MOs $4b_{1g}$ and $4b_{2u}$ are σ systems over the entire ligand skeleton again having high oxygen contribution.

Ionizations from these latter four MOs were not apparent in the low IE region of PE spectra of other β-diketonate complexes [2, 11, 12] but we believe that the shift toward lower energies in the present complexes is probably due to the higher (than in other cases) charge transferred from the central metal atom to the ligands.

The same origin probably has the inverted energy ordering (Table II) of MOs having n_- and π_3 dominant character ($n_- < \pi_3$) with respect to that observed in other β-diketonate complexes.

Next MOs (up to ~14.5 eV) have dominant metal 3d character. Actually, we expect higher relaxation energies to be associated with ionizations from these latter MOs than in the case of previous nominally ligand MOs. Anyhow differential (with respect to ligand MOs) relaxation energies can be as high as 3–4 eV [18]. Thus, PE bands representing the metal 3d MOs can appear, at most, in the 10–12 eV region.

With the above argument in mind, we turn to a detailed assignment of the PE spectrum of Ni(acac)$_2$ (Table III).

---

*They are analogous to the b_{3u} and ag (n_+) MOs but with the oxygen 2p orbitals pointing toward the adjacent carbon atoms.

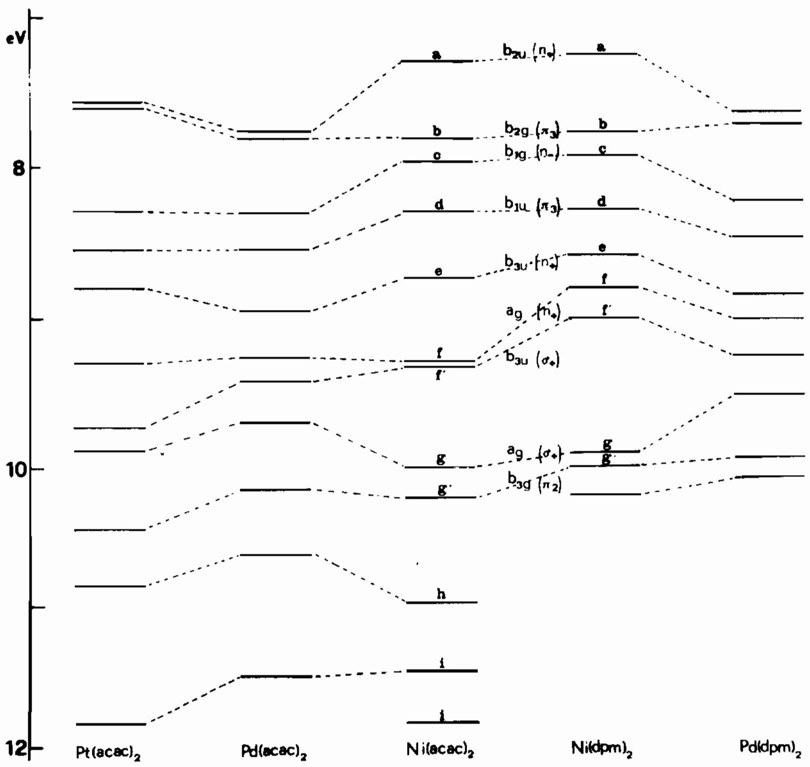

Fig. 6. Correlation between low energy bands in the studied square-planar complexes.

Band a, at the onset of the spectrum we take to represent the MO $b_{2u}(n_-)$ while the following bands b and c, respectively the MOs $b_{2g}(\pi_3)$ and $b_{1g}(n_-)$ both having nickel 3d contribution (Table II). It seems evident that the latter bands moderately increase in relative intensity on passing to the He-II spectrum (Fig. 3): a clear evidence of some metal 3d contribution into corresponding MOs. There is really no striking experimental evidence on the particular IE ordering $b_{2g} < b_{1g}$. However, in the He-II spectrum, the intensity ratio between bands c and b excedes the statistical (1:1) value (Table III). This observation agrees well with some higher nickel 3d contribution to the MO responsible for the band c while, in reality, the MO b_{1g} is expected more strongly admixed with nickel 3d orbitals both from CNDO calculation (Table II) and on simple ground of metal–ligand group overlap.

The next three bands d, e and f are best discussed collectively. According to CNDO calculation they represent respectively the MOs $b_{1u}(\pi_3)$, $b_{3u}(n_+)$ and $a_g(n_+)$ + $b_{3u}(\sigma_+)$. Although the energy spacing between the above PE bands (Table III) differs from theoretical anticipations, we believe that CNDO results provide the correct ordering. Again relative intensities in the He-II spectrum provide support to the assignment. It is evident, though qualitatively, that band e is less intense than band d while the quantitative intensity (Table III) of band f is less than statistical. This behaviour probably reflects the fairly small He-II cross-section of H 1s orbital whose contribution in symmetry combinations of n_+ and of σ_+ systems is clearly indicated by CNDO calculation. Nevertheless if CNDO results were completely sound, a more than statistical intensity should be associated with band f in the He-II spectrum because of the nickel 3d contribution to the MO $a_g(n+)$: probably present CNDO calculation overestimates metal-ligand interactions within above a_g manifold.

The overlapped bands g, g′ we associate to $b_{3g}(\pi_2)$ and $a_g(\sigma_+)$ MOs both having relevant nickel 3d contribution (Table II). The intensity of this system excedes, in fact, the statistical value in the He-II spectrum (Table III).

The assignment of the remaining bands below 12 eV appears rather puzzling. The CNDO calculation suggests the ionizations from the MOs $4b_{1g}$ $4b_{2u}$ (σ in character) and from the MO $1a_u$ as possible. Nonetheless, whatever the true assignment of all these three bands, one of them relates to the MO $1a_u(\pi_2)$ whose ionization must be expected in this spectral region. Furthermore, we feel reasonably confident in assigning the shoulder i′, barely discernible in the He-I spectrum but prominent at He-II wavelength, to the non bonding MO $2b_{2g}$ almost pure Ni $3d_{xz}$ in character. Really, CNDO calculation suggests that this MO is quite well separated from previous ligand orbitals; remarkable differential relaxation energies are, however, known to be associated with ion state produced upon removal of electrons from nearly pure metal d subshells [20].

The PE spectra of the complex Ni(dpm)$_2$ (Fig. 4) are obvious counterparts of those of parent Ni(acac)$_2$. The bands in the 10–12 eV region are, however, probably obscured by the very intense structure beyond 10 eV. Moreover, relative to Ni(acac)$_2$, changes of IEs are only limited to bands related to σ_+ and n_+ combinations (bands e, f, f′ and g in Table II). The observed low energy shifts certainly reflect the enhanced sensitivity of ligand MOs σ in nature to the presence of terminal ter-butyl groups into the dpm ligand.

Finally it must be noticed that the low intensity band (band x in Fig. 4), whose integrity was exhaustively checked, probably represents the ionization of some of the internal σ MOs ($4b_{2u}$, b_{1g}). They were definitely more internal in Ni(acac)$_2$ but shifts toward lower IEs are indeed expected in Ni(dpm)$_2$.

Pd(acac)$_2$

The correspondence between He-I PE spectra of Pd(acac)$_2$ and Ni(acac)$_2$ is fairly obvious (Figs. 3, 6). The analogy, however, could appear less evident in the He-II spectra. Nonetheless the He-II spectral patterns in palladium complexes become intelligible when considering that, by contrast to the nickel complexes, any metal d contributions probably result in lower He-II cross-section of corresponding MOs than those of ligand based MOs. The so called 'heavy metal effect' is an argument in favour of this conclusion [23]. Correlation with spectra of Ni(acac)$_2$ are outlined in Fig. 6.

The first three bands are taken to represent (Table IV) respectively the MOs $b_{2u}(n_-) + b_{2g}(\pi_3)$, $b_{1g}(n_-)$ and $b_{1u}(\pi_3)$ being the first two almost accidentally degenerate. The incipient splitting of the first band in the PE spectrum of Pd(dpm)$_2$ (Fig. 4) also points to the latter conclusion. Moreover, the lower intensities of bands a + b and c in the He-II spectrum are evidence of Pd 4d admixture respectively into the MOs $b_{2g}(\pi_3)$ and $b_{1g}(n_-)$. It is interesting to enquire after the notably different intensities of band systems a + b and c + d in the He-II spectrum despite the close correspondence existing between the related MOs (Table IV). It transpires that the lower intensity of the system a + b may be understood in terms of a major admixture of Pd $4d_{yz}$ atomic orbitals into the $b_{2g}(\pi_3)$ than of $4d_{xy}$ into the $b_{1g}(n_-)$. This is at variance to the case of Ni(acac)$_2$ where the opposite situation was observed.

The assignment of next four bands e, f, f′ and g implies further differences with respect to Ni(acac)$_2$: these are the removal of the accidental degeneracy of the MOs $a_g(n_+)$–$b_{3u}(\sigma_+)$ – bands f, f′ – and the consequent closer energy separation between symmetry combinations of n_+ and of σ_+ ligand orbitals (Fig. 6). Actually, closer lying n_+ and σ_+ combinations are indeed expected in Pd(acac)$_2$, the longer ligand–ligand distance certainly resulting in reduced non-bonded interligand interactions. Analogous, probably, is the origin of the lower IE shift (relative to Ni(acac)$_2$) of the band g ($a_g(\sigma_+)$MO). Nevertheless one could ask as to whether closer lying combinations of n_+ and of σ_+ orbitals only depend upon the mentioned effect or whether it may also depend upon better interaction with internal Pd 4d subshells which destabilize both the MOs $a_g(n_+$ and $\sigma_+)$. It turns out, however, that both the bands f and g do not consistently change their relative intensities in the He-II spectrum. And this means that latter interactions are, if existing, very small.

Assignment of the remaining bands below 12 eV follows analogously to Ni(acac)$_2$. We comment on only the reduced He-II intensity of band g′ providing evidence of important Pd $4d_{yz}$ admixture into the corresponding MO $b_{3g}(\pi_2)$ and the absence of any structure which may relate to the feature i′ apparent in spectra of Ni(acac)$_2$. The latter feature has been attributed to ionization of the $b_{2g}(d_{xz})$ metal orbital. Although more stable (than Ni 3d) palladium 4d subshells can be invoked, we believe that the absence of corresponding band in the spectrum of Pd(acac)$_2$ is the result of the expected smaller relaxation energies associated with removal of electrons from 4d subshells [24].

The assignment of PE spectra of Pd(dpm)$_2$ (Fig. 4) do not require further discussion; the relationship with spectra of Pd(acac)$_2$ follows as in corresponding series of nickel complexes.

Pt(acac)$_2$

The spectral patterns in both He-I and He-II PE spectra of Pt(acac)$_2$ are, as expected, much more similar to those of parent Pd complex than of Ni(acac)$_2$ (Fig. 3). The proposed assignment (Table V) implies a bonding model which evolves following the trend observed on descending from Ni(acac)$_2$ to Pd(acac)$_2$ (Fig. 6). Moreover, results are consistent with cross-section profiles of Pt 5d and O 2p orbitals leading to lower values of the former at He-II wavelength.

The most relevant metal 5d contributions reside (in order of increasing magnitude) into the MOs b_{2g} (π_3) and $b_{3g}(\pi_2)$. The relative intensity fall-off associated with corresponding bands a + b and g′ (Table V) indicates this conclusion. Further aspects worthy of consideration are the trend of IEs of bands representing ionizations from symmetry combinations of n_+ and of σ_+ ligand orbitals (bands e–f in Figs. 3, 6). We have already observed that the longer interligand distance, the closer are the IEs of each couple of above combinations. Actually in Pt(acac)$_2$

TABLE V. Pertinent IE and Intensity Data of $Pt(acac)_2$.

Band Label	$Pt(acac)_2$				
	IE (eV)	Intensities		Assignment[a]	Dominant contribution to MO
		He-I	He-II		
a + *b*	7.60	1.7(2)	1.1(2)	b_{2u}, b_{2g}	n_-, π_3–d_{xz}
c	8.28	0.8(1)		b_{1g}	n_-–d_{xy}
d	8.54		2.6(3)	b_{1u}	π_3
e	8.90	2.3(2)		b_{3u}	n_+
f	9.27	1.0(1)	1.0(1)	a_g	n_+
f'	9.70	2.3(2)	1.8(2)	b_{3u}	σ_+
g	9.85			a_g	σ_+
g'	10.43	1.2(1)	0.5(1)	b_{3g}	π_2–d_{yz}
h	10.90	–	–	–	–
i	11.71	–	–	–	–

[a] Intensities are normalized with respect to band *f*. Figures in parentheses are expected statistical values taken proportional to occupancy.

the interligand distance may be slightly increased with respect to $Pd(acac)_2$; and the near coincidence of bands f'–g is evidence of the expected trend toward an accidental degeneracy of σ_+ combinations. By way of contrast, a different trend is observed for IEs of bands e–f. Their energy separation (Fig. 6) is constant in $Ni(acac)_2$ and $Pt(acac)_2$ showing a minimum value in $Pd(acac)_2$. Although the n_+ symmetry combinations are expected to be less sensitive to variation of interligand distance because of the less favourable interligand group overlap, we believe that the anomalous stabilization of the MO $b_{3u}(n_+)$ in $Pd(acac)_2$ probably reflects some metal–ligand interactions involving palladium 5p empty orbitals.

Conclusions

The PE spectra of tetrahedral complexes $M(dpm)_2$ have been interpreted in terms of symmetry combinations of ligand basis orbitals perturbed to a minor extent by interacting with metal valence orbitals. In the case of $Co(dpm)_2$, evidence has been found of peculiar metal–ligand interactions involving only the MO $a_g(n_+)$ and metal 3d orbitals of appropriate symmetry. On the other hand the rather high value of the nephelauxetic parameter quoted for this particular cobalt complex also points to an 'ionic' bonding model.

The spectra of square-planar complexes have been interpreted also with the aid of quantum-mechanical calculation. However, the inferred bonding model finds, though *'a posteriori'*, experimental consistency on spectral patterns observed on traversing from the nickel to palladium and platinum complexes. Within this model all the filled metal d subshells lie internally beyond 11 eV binding energy. The metal–ligand bonding in square-planar complexes involves covalent interactions between d subshells and symmetry combinations of n_-, π_3 and π_2 ligand orbitals. In the nickel complexes σ interactions ($b_{2g}(n_-)$–d_{xy}) seem of particular importance. In the case of heavier metals, π interactions are predominant.

The remaining combinations of the ligand orbitals n_+ and σ_+ seem not particularly perturbed by internal metal d subshells. The IEs of the four related bands are, to first order, only sensible to variation of the ligand–ligand distance.

Finally it must be stressed the presence in the spectra of $Ni(acac)_2$ of a feature around 11.5 eV which may be related to ionization of the non-bonding $3d_{xz}$ metal orbital. This structure has no counterpart in spectra of the palladium and platinum complexes. In these latter cases smaller relaxation energies in the ion states are, probably, responsible for the absence.

References

1 C. Furlani and C. Cauletti, *Struct. Bonding (Berlin), 35,* 119 (1978).
2 S. Evans, A. Hamnett, A. F. Orchard and D. R. Lloyd, *Faraday Disc. Chem. Soc., 54,* 227 (1972).
3 A. B. P. Lever, 'Inorganic Electronic Spectroscopy', Elsevier, (1968).
4 A. L. Balch and R. H. Holm, *J. Am. Chem. Soc., 88,* 5201 (1966).
5 G. Condorelli, I. Fragalà, A. Centineo and E. Tondello, *Inorg. Chim. Acta, 7,* 725 (1973).

6 P. Fantucci, V. Valenti, F. Cariati and I. Fragalà, *Inorg. Nucl. Chem. Letters, 11,* 725 (1975).

7 H. G. Brittain, R. L. Disch, *J. Electron Spectrosc. Rel. Phen., 7,* 475 (1976).
C. Cauletti and C. Furlani, *J. Electron. Spectrosc. Rel. Phen., 6,* 465 (1975).

8 a) R. C. Mehrotra, R. Bohra and D. P. Gaur, 'Metal β-diketonates and allied derivatives', Academic Press (1978).
b) W. C. Fernelius and B. E. Bryant, *Inorg. Synth., 5,* 105 (1957).

9 F. A. Cotton and R.H. Soderberg, *Inorg. Chem., 3,* 1 (1964).

10 E. Tondello, *Inorg. Chim. Acta, 11,* L5 (1974).

11 I. Fragalà, G. Condorelli, E. Tondello and A. Cassol, *Inorg. Chem., 17,* 3175 (1978).

12 I. Fragalà, E. Ciliberto, P. Finocchiaro and A. Recca, *J. Chem. Soc. Dalton,* 240 (1979).

13 I. Fragalà, unpublished results.

14 I. Fragalà, to be published.

15 I. Fragalà, to be published.

16 F. A. Cotton and J. S. Wood, *Inorg. Chem., 3,* 245 (1964).

17 F. A. Cotton and R. H. Soderberg, *J. Am. Chem. Soc., 84,* 875 (1962).

18 G. M. Bancroft, D. K. Creber, M. A. Ratner, J. W. Moskowitz and S. Topiol, *Chem. Phys. Lett., 50,* 233 (1977).

19 P. A. Cox, *Struct. Bond (Berlin), 24,* 59 (1975).

20 M. F. Guest and I. H. Hillier, *Proc. S.R.C. Atlas Symposium No. 4, Oxford,* 205 (1974).

21 A. W. Potts and M. L. Lyus, *J. Electron Spectrosc. Rel. Phen., 13,* 305 (1978).

22 C. K. Jørgensen, *Chimia (Aarau), 27,* 203 (1973).

23 B. R. Higginson, D. R. Lloyd, P. Borroughs, D. M. Gibson and A. F. Orchard, *J. Chem. Soc. Faraday II, 69,* 1659 (1973).

24 R. G. Egdell and A. F. Orchard, *J. Chem. Soc. Faraday II, 74,* 485 (1978).