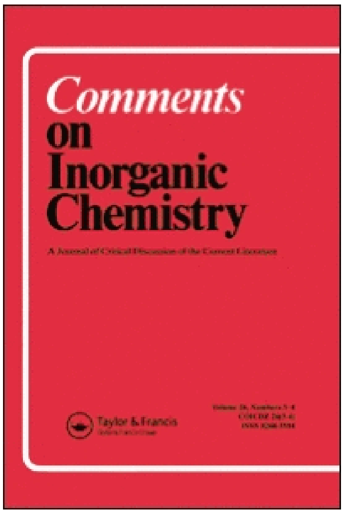

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Gas Phase UV Photoelectron Spectroscopy as a Tool for the Investigation of Electronic Structures of Coordination Compounds

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Gas Phase UV Photoelectron Spectroscopy as a Tool for the Investigation of Electronic Structures of Coordination Compounds

1. INTRODUCTION

1.1. Fundamental Processes of Photoemission

Photoelectron spectroscopy is nothing but the application of the photoelectron effect to the study of the photoionization processes occurring in matter interacting with electromagnetic radiation. More precisely, photoelectronic spectroscopy deals with the measurement of the kinetic energy of the electrons emitted by matter owing to this interaction. When the matter is in the gas phase, and the light is of short wavelength, i.e., in the far ultraviolet, the entities involved in the photoionization are free molecules and the photoelectrons are ejected from the occupied molecular orbitals. The kinetic energy (KE) of a photoelectron ejected from the jth MO is given by the difference between the energy of the monochromatic radiation and the ionization energy corresponding to the removal of an electron from the j^{th} MO:

$$\mathrm{KE} = h\nu - \mathrm{IE}_j \tag{1.1}$$

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provided we disregard, as a first approximation, additional possibilities of vibrational or rotational excitation on ionization. Gas-phase UV photoelectron spectroscopy (UPS) is the study of the energies, abundances and angular distributions of photoelectrons. Knowledge of the ionization energies for the various molecular orbitals in a molecule is of fundamental importance in the study of molecular electronic structure. In fact, following an approximation known as Koopmans' theorem,[1] each ionization energy IE_j is equal in magnitude to the calculated SCF MO eigenvalue ϵ_j

$$\mathrm{IE}_j = -\epsilon_j \tag{1.2}$$

This approximation is not always valid, first of all because of the neglect of electronic correlation and relativistic effects, and second, because of neglect in Eq. (1.1) of a factor accounting for the relaxation energy, that is, the energy involved in the reorganization processes of the remaining orbitals following the ejection of an electron from the j^{th} orbital. This relaxation energy may vary quite a lot depending on the type of orbital involved in the photoionization. In particular, the reorganization energy is usually larger for d-metal orbitals than for ligand-based orbitals, sometimes causing an inversion in the MO sequence in the molecular ion with respect to the neutral molecule. Nevertheless, the assumption of Koopmans' approximation is often very useful, at least at a first level of approximation, especially when comparing orbitals of similar character in a series of homologous compounds.

1.2. Main Features of a Photoelectron Spectrum

The most commonly used ionizing radiation in a gas-phase UP spectrometer are the resonance lines He I (21.22 eV) and He II (40.81 eV). A photoelectron spectrum appears as a sequence of bands representing a plot of the number of electrons detected at each energy (KE or IE) versus that energy. Each band in the spectrum corresponds, to a first approximation, to ionization from a molecular orbital of binding energy less than the energy of the ionizing radiation. However, sometimes there are more bands in the spectrum than MO in the molecule. In fact, additional bands are sometimes found that correspond to the ionization of one electron with simultaneous excitation of a second electron to an unoccupied orbital. Furthermore, orbitals that are degenerate in the molecule may not be so in the positive ion, due to mechanisms such as spin-orbit coupling or the Jahn–Teller effect. In this case, ionization from a degenerate occupied MO can give rise to as many bands in the spectrum as there are orbital components. Finally, in open-shell molecules the ionization of the open shell itself, or of subsequent closed shells, may give rise to a multiplicity of ion states. In this case Koopmans' theorem does not apply.

1.3. Intensities of UPS Bands

An extensive discussion of the factors determining intensity ratios and their variation with photon energy in the photoelectron spectra would exceed the limits of an introductory note. We will mention here a few empirical rules and observed trends that are helpful in the assignment of UP spectra, particularly of d-metal compounds.

(i) The partial photoionization cross section to a particular ionic state, and consequently the intensity of the corresponding photoelectron band, is proportional to the number of equivalent electrons available for ionization (in the case of closed-shell molecules) or to the statistical weight of the ionic state produced (in the case of atoms and open-shell molecules). Furthermore, it depends on the character of the orbitals, i.e., their size, number of nodes and localization in the molecule.

(ii) The photoionization cross section of metal *n*d orbitals increases as the quantum number *n* increases.

(iii) The intensity of bands related to the ionization of orbitals of main metal d-character usually increases with respect to ligand-based MO bands on passing from He I to He II ionizing radiation. The increase is pronounced especially when the donating ligand atoms belong to the third or following periods, corresponding to a decrease of the relative photoionization cross section of 3p, 4p, etc. orbitals.

1.4. Content and Purposes of This Comment

From the above introductory remarks it should be readily apparent how powerful a tool UPS is in the investigation of the electronic structure, i.e., the energy and composition of the molecular orbitals and the bonding situation in free molecules. This technique has been widely and effectively used in studies of coordination compounds, where it complements the information yielded by electronic absorption spectroscopy. The results obtained were usually of remarkable interest and gave a fundamental contribution to the knowledge of coordination chemistry, although application in the gas phase introduces the obvious limitation to volatile compounds, excluding, for instance, ionic species.

In this Comment we want to provide a view on significant results in this field, which sometimes confirmed and completed concepts already known and studied, and sometimes opened new horizons to the coordination chemist. We will confine ourselves to just a few examples of UPS studies on d-metal compounds, assumed as representative, referring to literature reviews 2–4 for a more complete treatment of this subject.

2. UPS AS AN AID TO THE COORDINATION CHEMIST

2.1. Are the d-Metal Orbitals Always Higher in Energy Than the Ligand-Based Orbitals?

The relative ordering d-metal/ligand orbitals is an intriguing and fascinating problem in coordination chemistry, since the application of UV photoelectronic spectroscopy to the study of volatile complexes in the early 1970s introduced what was effectively named by C. K. Jørgensen "the third revolution in ligand field theory"[5]: at variance with the widely accepted concept that d-metal orbitals are less stable than ligand-based orbitals, in view of their antibonding or nonbonding nature, sometimes they have higher ionization energy than orbitals mainly localized on ligand atoms or groups. It must at the outset be pointed out, however, that sometimes the sequence of energy levels in a molecule may be different from the one in the molecular ion, due to the already mentioned breakdown of Koopmans' theorem in some molecules, especially of d-metal complexes.

From a comprehensive analysis of the UPS studies on d-metal compounds so far performed a few general observations may be drawn:

(i) d-ionization bands appear before any other ionization (i.e., at lower IE) in complexes of early transition metals having few d electrons, for instance, Ti(III) (d^1), V(III) (d^2), Cr(III) (d^3). d^{10} metal orbitals are always deeper than ligand orbitals. In intermediate cases, the IE sequence very much depends on the nature of the ligands, i.e., on the energy and composition of their valence orbitals.

(ii) Highly electronegative ligands push the d-ionizations to quite low IE values, usually lower than those of their own orbitals.

(iii) When the donor atoms bear a strong negative charge, d-bands definitely fall below the ligand ionization.

(iv) MO with main contributions from the ligands may ionize at very early IE because of destabilizing interactions with other orbitals (for instance, in case of conjugation of highly delocalized π systems).

We will next discuss some cases exemplifying the above points. A series of chelated compounds extensively studied by UPS is the one with β-diketone ligands and metals with a wide variety of d-electron configurations.[6-17] A brief description of the electronic structure of the most representative ligand of the series, acetylacetone, will be helpful for the following discussion. The highest occupied MO(π_3) is one of the five MO (two of which are empty) constituted by the conjugated π-system and is the only π-orbital able to interact appreciably with d-orbitals (π_2 and π_1 being too inner). It is followed by the symmetric (n_+) and antisymmetric (n_-) combinations of the oxygen lone pairs. In the tris-chelates ML_3[6-10,15,16] where L may be acetylacetone, trifluoroacetylacetone, hexafluoroacetylacetone, γ-derivative of acetylacetone, with a pseudooctahedral array of the oxygen atoms around the metal, these orbitals give rise to the symmetry-adapted combinations displayed in Figure 1. The same figure shows the interaction between these combinations and the d-metal orbitals; it is clearly apparent that the nature of the highest occupied MO, which is the most easily ionized one in the framework of Koopmans' approximation, very much depends on the relative ordering d-metal/ligand orbitals. As a matter of fact, the photoelectron spectra give unambiguous evidence of early d-ionizations in d^1 Ti(III), d^2 V(III), d^3 Cr(III) compounds (see band Y in Figure 2), while being less easily interpretable in derivatives of heavier metals, such as Mn(III),

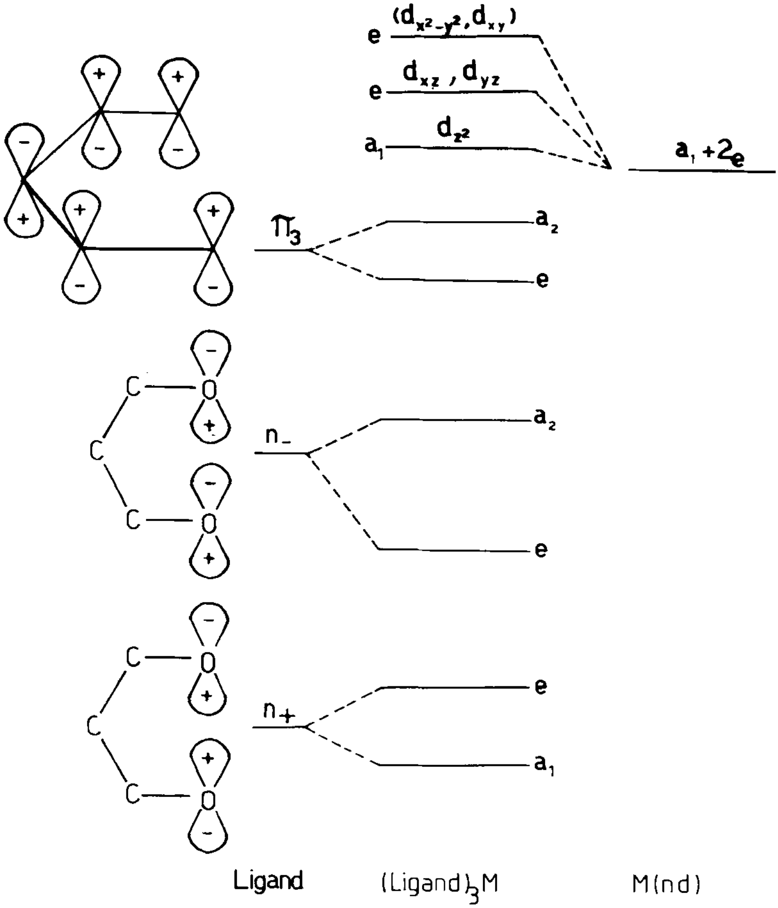

FIGURE 1 Symmetry-adapted combination of ligand orbitals and interaction with d-metal orbitals in tris-β-diketonato complexes (from Ref. 10).

Fe(III) and Co(III). For the last case clearcut evidence was obtained by Van Dam and Oskam[15] by the observation of band-intensity variations on switching from He I to He II ionizing radiation. The enhancement of the first band of the spectrum (see Figure 3) indicated that the most easily ionized orbital is of d-nature, followed by the π_3 orbital.

Table I reports the IE and the proposed assignment for a series of tris-β-diketonato complexes. It is interesting to note that the

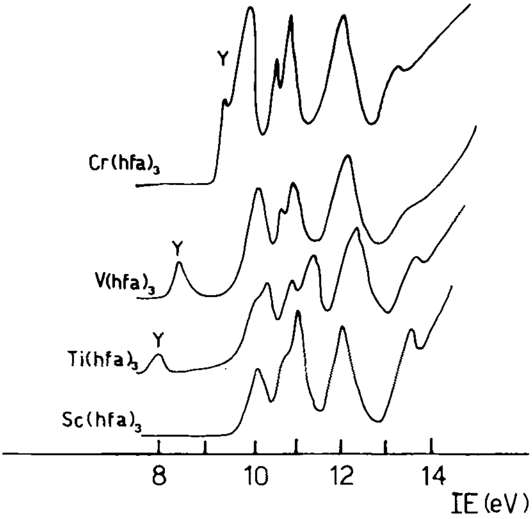

FIGURE 2 HeI UP spectra of Sc(hfa)$_3$, Ti(hfa)$_3$, v(hfa)$_3$, and Cr(hfa)$_3$. hfa = hexafluoroacetylacetone (from Ref. 10).

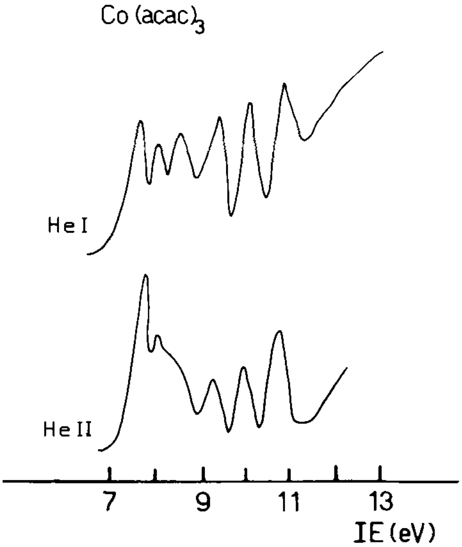

FIGURE 3 He I and He II UP spectra of Co(acac)$_3$. acac = acetylacetone (from ref. 15).

TABLE I

Ionization energies (eV) and proposed assignments for some tris-β-diketonato complexes[a]

Complex	Formal Metal Electronic Configuration	d^n	$a_2 + e(\pi_3)$	$a_2(n_-)$	$e(n_-)$	$a_1 + e(n_+)$
$Sc(hfa)_3$	d^0		10.13	10.82	11.12	12.05
$Ti(hfa)_3$	d^1	7.94	10.24	10.87	11.28	12.24
$V(hfa)_3$	d^2	8.68	10.10	10.96	11.39	12.20
$Cr(hfa)_3$	d^3	9.57	10.18	11.10	11.61	12.44
$Cr(tfa)_3$	d^3	8.58	9.12	10.01	10.54	11.40
$Cr(acac)_3$	d^3	7.46	8.06	8.96	9.48	10.26
$Ru(hfa)_3$	d^5	8.85, 9.07	10.30	11.06	11.65	12.50
$Co(hfa)_3$	d^6	$9.73(e), 10.13(a_1)$	$10.13(a_2), 10.73(e)$	11.15	11.75	12.56
$Co(acac)_3$	d^6	$7.52(e), 8.03(a_1)$	$8.03(a_2), 8.49(e)$	8.99	9.54	10.36

[a] Data from Ref. 10. hfa = hexofluoroacetylacetone, tfa = trifluoroacetylacetone, acac = acetylacetone.

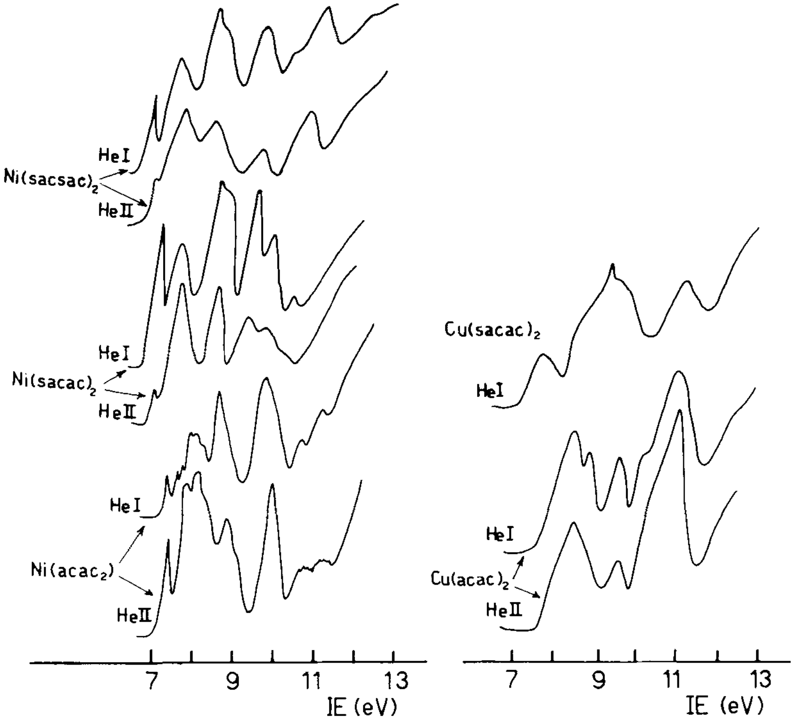

FIGURE 4 UP spectra of Ni(acac)$_2$, Ni(sacac)$_2$, Ni(sacsac)$_2$, Cu(acac)$_2$ and Cu(sacac)$_2$. acac = acetylacetone, sacac = monothioacetylacetone, sacsac = dithioacetylacetone (from Reference 13).

splitting $a_2(n_-)$ − e(n_-) increases progressively on crossing the transition series; this is due to an increase in importance of the interaction between $e(n_-)$ and the metal d orbitals which are progressively stabilized along the series and therefore more closely approach the energy of the ligand orbitals. A similar approach can be used to discuss the electronic structure of bis-β-diketonates and their mono and dithio analogues.[11–14] In this case the comparative use of the He I and He II ionizing radiations permitted the assignment of the photoelectron spectra. Figure 4 shows the spectra of NiL$_2$ (L = acetylacetone, monothioacetylacetone and dithioacetylacetone) and of CuL$_2$ (L = acetylacetone and monothioacetylacetone). It clearly appears that in the d^8 Ni(II) complexes, which are planar in the gas phase, the most easily ionized orbital is mainly localized on the ligands (it is the b_{3g} component of the

π_3 orbital), though with a contribution of the d_{yz} nickel orbital, while the d-levels are more stable, being associated with the second, third and fourth UPS bands, which increase in intensities on going from He I to He II. The d-orbitals are even more stable in d^9 Cu(II) derivatives, also planar in vapor-phase, apart from the single d_{xy} electron, whose ionization contributes to the first UPS band. The remaining eight d-electrons are associated with the fourth band, around 10.5 eV, which also contains a contribution from the ionization of the n_+ orbital. The π_3 and n_- orbitals are related to the first three bands. The situation is more uncertain in the d^7 Co(II) complexes, where the intensity variations suggest a strong mixing of metal-d and ligand orbitals. In any event, the IE of d-orbitals are comparable to π_3, the actual sign of the inequality being uncertain and the difference certainly small. n_- and n_+ in these complexes lie at deeper levels.

Difluorodithiophosphates are examples of metal complexes with highly electronegative ligands, due to the strong inductive effect of fluorine, which lowers the orbital energies of the $S_2PF_2^-$ ligand moieties. As a consequence, in all the complexes of metals with partly filled d-shell studied by UPS[18] d-ionizations fall at lower IE with respect to ionizations of ligand-based orbitals, as shown in Table II. The only case in which the d-orbitals are deeper than the ligand orbitals is in the d^{10} Zn(II) derivative, as is usual for a metal with such an electronic configuration. In the UP spectrum of this compound d-bands are masked by the broad band envelope beyond 16 eV. An interesting case in which the d-metal ionizations fall beyond the ligand ones due to the high negative charge on the donor atom is that of some bis(trimethylsilyl)amides $M[N(SiMe_3)_2]_3$.[19] The UP spectra of the d^0 Sc(III), d^1 Ti(III), d^3 Cr(III) and d^5 Fe(III) complexes are very similar, as shown in Figure 5, not offering any evidence of d-ionizations before ligand bands (the first two being attributed to ionizations of nitrogen lone pairs). The behavior is in contrast with that of the dialkylamido-complexes,[20] where the single d-electron on $V(NMe_2)_4$ gives rise to the first band of the spectrum shown in Figure 6 together with the one of d^0 $Ti(NMe_2)_4$. The authors explain this discrepancy by the fact that in the alkylamides the d-levels are destabilized by a

$\ddot{N}-M\ \pi$

TABLE II

Ionization energies (eV) and proposed assignments for some difluorodithiophosphato complexes[a]

Complexes	Formal Metal Electron Configuration	d^n	Ligands	$\sigma_{M\ S}$	$\sigma_{P\cdot S}$
$Cr(S_2PF_2)_3$	d^3	9.41	10.02 10.93	11.98 13.04	13.34 15.10
$Mn(S_2PF_2)_2$	d^5	9.38	10.08 10.60	11.30 11.50 12.44	13.00 15.14
$Co(S_2PF_2)_2$	d^7	(9.18) 9.62 9.98		(12.3) (13.2)	(14.00) 15.02
$Ni(S_2PF_2)_2$	d^8	8.62 8.76 (8.94)	10.45 10.58	11.44 12.84 (13.04)	13.47 14.76
$Zn(S_2PF_2)_2$	d^{10}		10.12 10.34	11.70 13.14	13.74 15.15

[a] Data and assignments from Ref. 18. Shoulders in parenthesis.

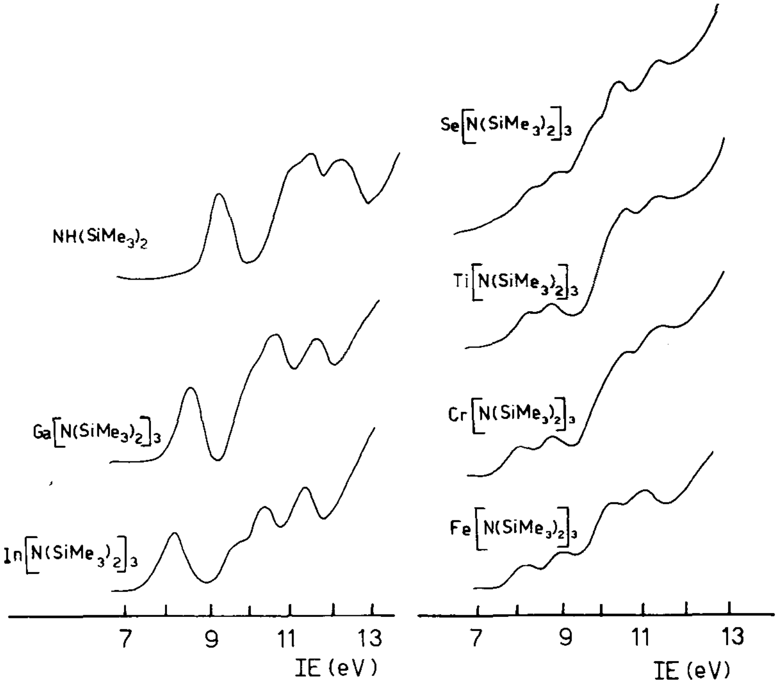

FIGURE 5 He I UP spectra of $NH(SiMe_3)_2$ and $M[N(SiMe_3)_2]_3$. M = Ga, In, Sc, Ti, Cr, Fe (from Reference 19).

interaction, which is suppressed in the dialkylamides due to a competing $\overset{\curvearrowright}{N}{-}Si$ (p → d) π bonding.

An example of stabilization of the d-metal orbitals by interaction with ligand π-orbitals is provided by the mesotetraphenylporphin complexes,[21] where the possibility of extensive conjugation between the ligand π-system and the d-orbitals pushes the latter orbitals to quite low energy, certainly lower than that of highly negative nitrogen donor atoms.

2.2. Trends in Ionization Energies

Regular variations in IE of corresponding UPS bands in a series of related compounds can be very meaningful also because deviations from Koopmans' theorem are likely to be constant for corresponding orbitals in a series of homologous molecules. The observed trends in IE may therefore be confidently assumed parallel

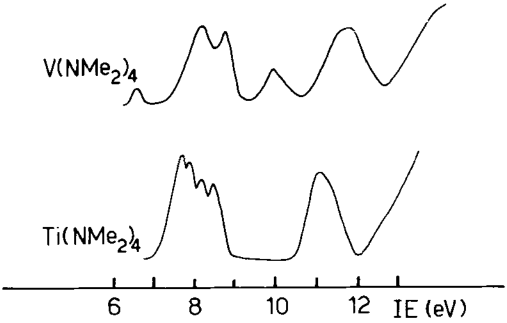

FIGURE 6 He I UP spectra of Ti(NMe$_2$)$_4$ and V(NMe$_2$)$_4$ (from Ref. 20).

to those in orbital energies. In coordination compounds it is of interest to follow the behavior of typical MO along series, for instance, of d-metal orbitals on crossing the periodic table, or of ligand level on varying the metal or substituents, etc.

Sandwich compounds (cyclopentadienyl, arenes and their derivatives) are very suitable for this kind of discussion, due to the large variety of coordinating metals and of ligand molecules, and to the large number of UPS studies on this class of complexes (see References 1–3 and references therein). In the isoelectronic series (η-

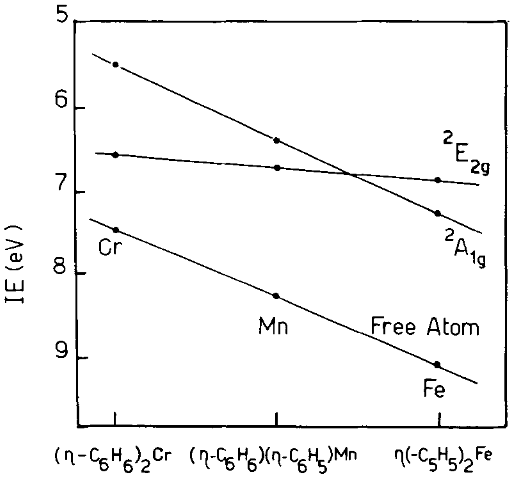

FIGURE 7 Trends in ionization energies of a_{1g} and e_{2g} molecular orbitals of the sandwich complexes (η-C$_6$H$_6$)$_2$Cr, (η-C$_6$H$_6$)(η-C$_5$H$_5$)Mn and (η-C$_5$H$_5$)$_2$Fe and of d-orbitals of Cr, Mn nd Fe free atoms. (Data from Refs. 22, 23 and 28.)

$C_6H_6)_2Cr$, $(\eta\text{-}C_6H_6)(\eta\text{-}C_3H_5)Mn$, and $(\eta\text{-}C_5H_5)_2Fe$,[22–28] whose d^6 electronic configuration of the metals gives rise to the $^2A_{1g}$ and $^2E_{2g}$ ionic states, the trend in IE of the former state parallels that of the d-ionization for the free atoms (see Figure 7) indicating a high degree of metal character in the a_{1g} MO. For the $^2E_{2g}$ ionic state the increase in IE on going from the chromium to the iron compound is less drastic, consistent with a mixed metal–ligand nature of the corresponding e_{2g} MO, with significant contribution from the ring orbitals.

The low-energy region of the He I and He II photoelectron spectra of $(\eta\text{-}C_5H_5)_2Fe$ is shown in Figure 8. The first two bands, around 7 eV, arise from ionization of the already mentioned e_{2g} and a_{1g} metal-based MO (in order of increasing IE), the third and fourth bands, around 9 eV, from the e_{1u} and e_{1g} MO, mainly localized on the cyclopentadienyl rings. On passing from the ferrocene to the ruthenocene[25,28] and to the 1, 1′-dimethylosmocene[25] (where, however, the situation is complicated by the presence of spin-orbit components in the d-region) the $a_{1g}(d) - e_{2g}(d)$ IE difference decreases, probably due to the stabilization of the e_{2g} orbital following the increased covalency on going down the group. Also the e_{1g} MO is stabilized on passing from Fe to Ru to Os, this trend being attributed to a progressively increasing d-π mixing, in addition again to a greater covalency.

One can observe regular variations of IE upon substitution on the rings. For instance, the presence of two methyl groups in a metallocene uniformly decreases the d-ionization energies, while affecting the ligand ionization slightly more. The effect is roughly additive, i.e., the shift to lower IE in decamethylmetallocenes is approximately five times that of 1,1′-dimethylmetallocenes (see Table III).

The comparison between trends in IE in some mixed-ring sandwich compounds of 3d and 4d transition metals, $(\eta\text{-}C_5H_5)M(\eta\text{-}C_7H_7)$ (M = Ti, V, Cr;[29] M = Zr, Nb, Mo[30]) is interesting. The trends observed for the orbitals of π-symmetry, consisting mainly of the e_2 orbitals of the C_7H_7 ring and the $d_{x^2-y^2}$ and d_{xy} orbitals of the metal, are similar in the 3d and 4d transition metal series, while a remarkable difference is found for the a_1' orbital, of mainly d_{z^2} character. For the 3d metal compounds the IE of this orbital decreases markedly on going from M = V to M = Cr, whereas

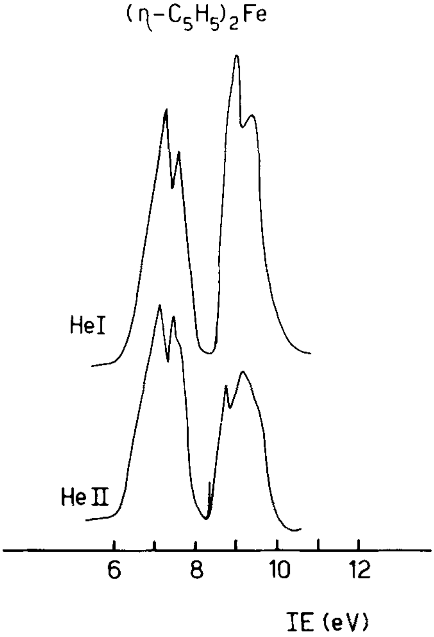

FIGURE 8 He I and He II UP spectra of (η-C_5H_5)$_2$Fe (from Ref. 28).

only a slight decrease is observed for the corresponding 4d metal (M = Nb, Mo) complexes, precisely 0.83 versus 0.12 eV. The authors of Ref. 30 attribute this phenomenon to the smaller pairing energy of the electrons in 4d transition metals than in the 3d series. Differences in ionization of third- and second-row transition metal

TABLE III

Average shifts (in eV) to lower IE upon methyl substitution in metallocenes[a]

Orbital	$M(C_5H_4Me)_2$	$M(C_5Me_5)_2$
$a_{1}g$	0.19	0.95
e_{2g}	0.18	0.88
e^*_{1g}	0.22	0.77
e_{1u}	0.26	1.25
e_{1g}	0.24	1.11

[a] Shifts relative to the unsubstituted analogues. Data from Ref. 28.

complexes versus first-row ones were also observed in some "half-sandwich" complexes of formula (η-C_5R_5)M$(CO)_2$ (M = Co, Rh, Ir; R = Me;[31] M = Co, Rh; R = H, Me[32]) nd (η-C_5H_5)M(PMe_3)X (M = Co, Rh; X = CO, CS).[33] These differences parallel those found in the chemical behavior of the cobalt and iridium complexes and seem to indicate a stronger interaction of the 4d orbitals with the π-orbitals of the cyclopentadienyl ring, with respect to the 3d ones. On the contrary they should be less involved in π-back donation to the empty π^* levels of the other ligand molecules (CO, CS, PMe_3). Lichtenberger *et al.*,[32] however, suggest that the large differences observed in the UP spectra of these compounds could be ascribed to excited-state effects in the positive ions, associated with electron relaxation.

Figure 9 gives a picture of the trend in d ionization energies across the first transition period in the already discussed tris-hexafluoroacetylacetonato complexes.[8-10] One notices a progressive stabilization of the d-levels on passing from the titanium to the cobalt derivative.

The trend in d ionization energies across a subgroup is often irregular, due to the operation of different and sometimes opposite effects. For instance, in the series of M $(dtc)_2$ (M = Ni(II), Pd(II), Pt(II); dtc = diethyldithiocarbamate)[34] the d ionization energies

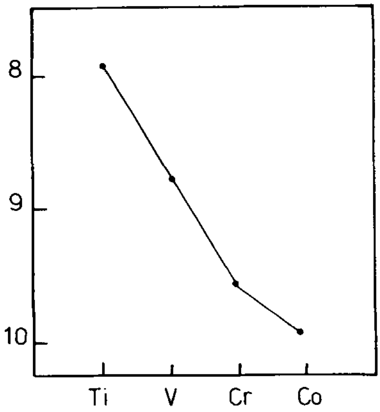

FIGURE 9 Trends in ionization energy of d metal orbitals in tris-hexafluoroacetylacetonato complexes of transition metals (Data from Ref. 10.)

decrease on passing from Ni(II) to Pd(II) derivative and rise again in the Pt(II) complex. The authors ascribe this phenomenon to the fact that in $Pd(dtc)_2$ the large d-energy stabilization (greater metallic character) overrides the destabilization following the larger antibonding interaction with the ligand orbitals (greater covalency), while the latter effect is prevailing in $Pd(dtc)_2$. When considering such trends, however, one has to take into account possible differences in relaxation energies which could affect differently the d ionization energies of the various metal complexes.

2.3. Role of the Pseudovalence Metal Orbitals in Bonding

The role of d-subshells of metals with d^{10} electronic configurations (for instance, zinc, cadmium, mercury, iridium, thallium) are usually regarded as being essentially core-like, but some participation of these orbitals in the covalent bonding cannot be completely ruled out. Different hypotheses on possible mechanisms for such a participation have been put forward. One author[35] postulated that in compounds with unsaturated ligands a significant donation of d-electron density into empty antibonding π-orbitals ($d(\pi) \rightarrow \pi^*$ back-bonding) occurs, others[36,37] invoked a $nd_{z^2}/(n-1)s$ hybridization at the metal atom to explain the preference for linear 2-coordination shown by many $(nd)^{10}$ cations.

The development of the UPS technique, with the use of He II radiation, has greatly enhanced its diagnositc power in this field. In fact, the d^{10} subshells, ionizing at around 20 eV and beyond, are either inaccessible to He I radiation or give rise to very weak signals, while being associated with intense and easily recognizable peaks in He II spectra. These levels are subjected in a coordination compounds to two main effects, the spin-orbit effect leading to a splitting in two sublevels ($^2D_{5/2}$ and $^2D_{3/2}$), and the ligand–field effect, leading to a further splitting in up to five sublevels. From the analysis of the multiplet structure associated with the latter effect one can deduce whether the d-orbitals participate in the covalent bond and, if so, to which extent.

Only high-resolution photoelectron spectra of zinc and cadmium dialkyls[38,39] give evidence of both ligand–field and spin-orbit splitting (see Figure 10). The authors, however, attribute this splitting to an electrostatic ligand perturbation, rather than to bonding, also

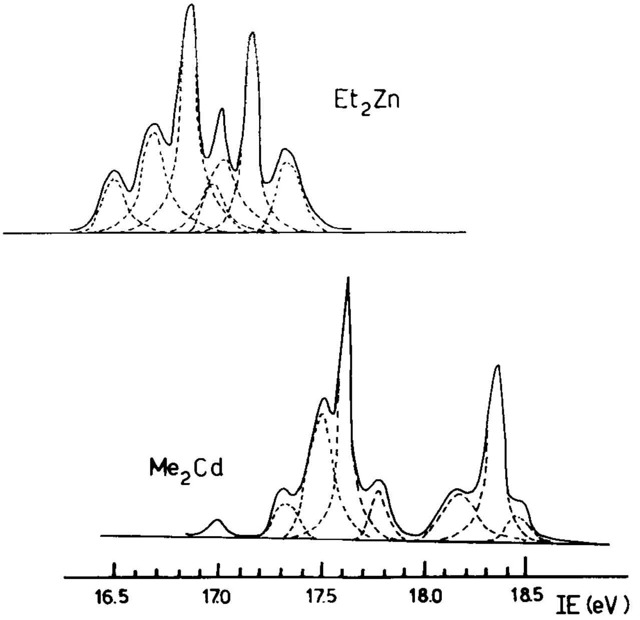

FIGURE 10 He II UP spectra (d-region) of Me_2Cd and Et_2Zn (from Ref. 39).

on the grounds of a comparison between the experimental IE and crystal-field calculations. They suggest for the d-levels the ordering of orbital energy $\sigma\,(d_{z^2}) > \pi(d_{xz}, d_{yz}) > \delta(d_{x^2-y^2}, d_{zy})$, which is just that expected for a purely electrostatic perturbation. Interestingly, the same ordering is suggested by the *ab initio* calculation on Me_2Cd by Bancroft *et al.*[40] which also indicated little or no involvement of the 4d electrons in the bonding. In contrast, all the authors who studied the dialkyl derivatives of mercury, R_2Hg,[39,41–43] agree that in these compounds Hg 5d orbitals are involved, though slightly, in bonding. In particular, Coatsworth *et al.*[43] obtained high-resolution He I and He II spectra (see Figure 11) and proposed the orbital energy ordering $\pi > \delta > \sigma$, implying that the Hg $5d_{z^2}$ orbital participates in the bonding. This participation is confirmed by the slight decrease in intensity of the band associated with the Hg-C σ_g-bonding level on passing from He I to He II, at variance with the analogous band in zinc and cadmium derivatives, where the M-C σ_g levels are largely C2p in character.[39]

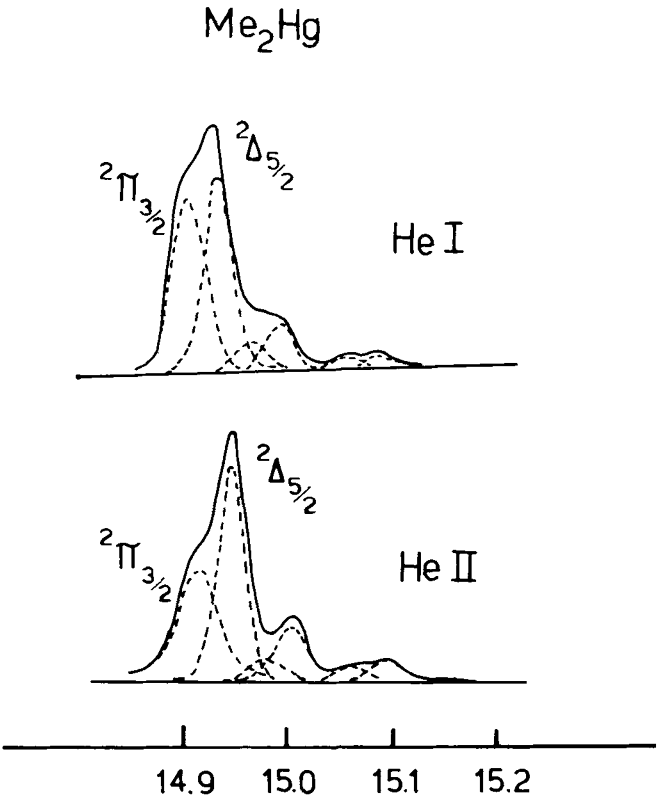

FIGURE 11 He I and He II UP spectra (part of $5d_{5/2}$ region) of Me_2Hg (from Reference 43).

In the spectra of MeHgCN and $Hg(CN)_2$ [42] the multiplet structure (see Figure 12) is interpreted as $^2\Delta_{5/2} < {}^2\Sigma_{1/2} < {}^2\Pi_{3/2} < {}^2\Delta_{3/2} < {}^2\Pi_{1/2}$, corresponding to the d-orbital sequence $\delta > \sigma > \pi$. The stabilization of the $d(\pi)$ level is a consequence of back-donation of electron density from the d_π metal orbitals to the antibonding π-orbitals of cyanide.

Evidence for d_π–p_π interaction was also studied by UPS in a series of alkynyl-mercury derivatives:[44,45]

$$R{-}C{\equiv}C{-}Hg{-}C{\equiv}C{-}R \qquad [I]$$

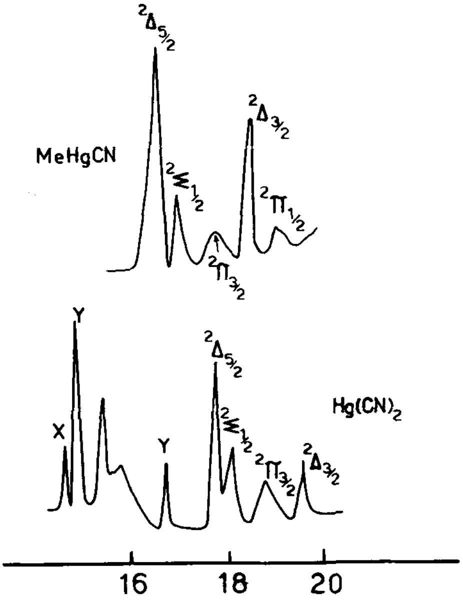

FIGURE 12 He I UP spectra (d-region) of MeHgCN and $Hg(CN)_2$. Bands *X* and *Y* are due to cyanogen and atomic mercury impurities, respectively (from Reference 42).

$R'-Hg-C\equiv C-R$ [II]

$R'-Hg-C\equiv C-Hg-R'$ [III]

The analysis of the spectra, a selection of which is reported in Figure 13, indicated that a significant interaction between the mercury 5d orbitals and the π-orbitals of the acetylenic moieties (revealed by the presence of d(π) ionizations at higher IE with respect to d(δ) and d(σ)) occurs in all the diethyne derivatives of the series [I], while being negligible, if any, in series [II] and [III]. Such a different behavior was not observed between MeHgCN and $Hg(CN)_2$,[42] suggesting a specific role for the two π-systems of the ethyne units in promoting the d_π–p_π interaction. The extent of such an interaction is probably very small since the ^{13}C NMR specroscopy, normally very sensitive to this type of interaction, failed to detect it in this case.

It is of interest at this point to briefly mention a study of a Au(I) compound, $AuMe(PMe_3)^{46}$ in which the involvement of metal 5 d(σ) electrons in bonding appeared to be only slightly larger than in Me_2Hg, although the 5d orbitals are definitely valence orbitals (with IE between 10 and 11.5 eV). There are not many examples of UPS studies on indium and thallium complexes. A common feature is that in no case were ligand-field components observed

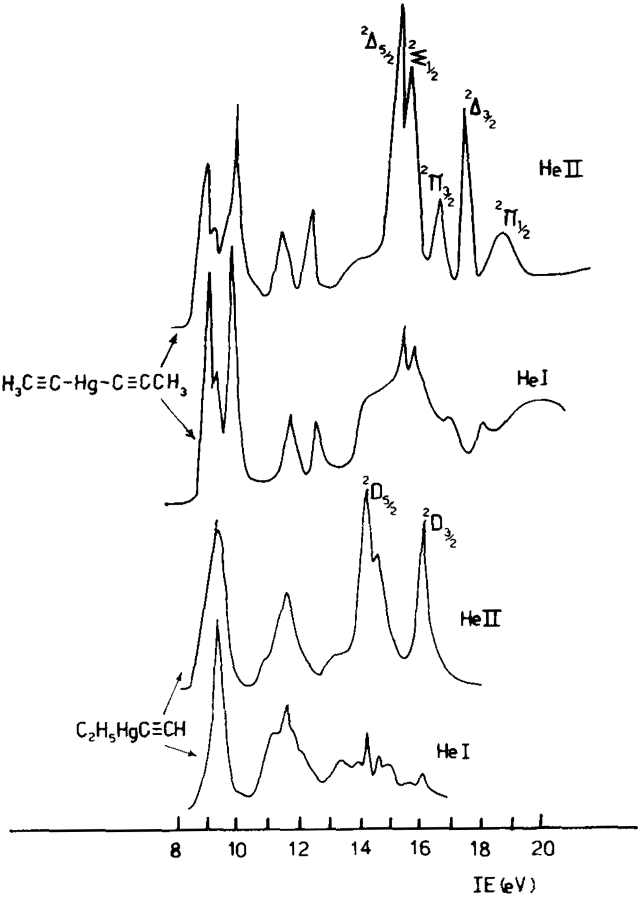

FIGURE 13 He I and He II UP spectra of $C_2H_5HgC\equiv CH$ and $CH_3C\equiv C-Hg-C\equiv CCH_3$ (from Refs. 44 and 45).

in the d-region of the spectra. This is at variance with the He II results on Tl(I) halides[47–50] where fine structure was observed. Egdell *et al.*, who investigated indium(I) and thallium(I) cyclopentadienyls,[51] attributed this phenomenon, apparently in contrast with the higher position in the spectrochemical series of the ligand C_5H_5 with the respect to halide ligands, to the fact that in Tl(I) and In(I) compounds the ligand-field structure is purely electrostatic in origin and that the internal electrostatic field experienced by the metal d-shell is weaker in the MC_5H_5 species than in the halides. Another interesting aspect of this research is the observation that the average metal d-ionization energies in InC_5H_5 and TlC_5H_5 are lower than in the atomic species[52] and in the halides[47–50] (see Table IV). Straightforward application of a charge-potential model for the d-chemical shift:

$$\Delta E = \frac{q}{r} + \sum_i \frac{\delta q_i}{R_i} \tag{2.1}$$

where ΔE is the change in IE produced by a charge q in an outer valence shell of radius r, and R_i is the distance from the atom of interest to the ith other atom carrying charge δq_i, would lead to the counterintuitive conclusion that the metal atoms bear a negative partial charge in MC_5H_5 species. It is likely, however, that extra-atomic relaxation phenomena, i.e., polarization of the ligand electron density by the localized d-hole on the metal, stabilize the d^{-1} ionic states of the MC_5H_5 molecules.

Analogous results were obtained for the d-ionizations in some Tl(I) β-diketonates, investigated together with the corresponding

TABLE IV

Average Metal d-ionization energies (eV) in Tl(I) and In(I) halides and in the neutral metal atoms[a]

Tl	21.38	In	25.58
TlCl	22.07	InCl	25.79
TlBr	21.30	InBr	25.59
TlI	21.61	InI	25.50
TlC_5H_5	20.30	InC_5H_5	24.03

[a]Data from Refs 47–52.

dialkyl derivatives.[53,54] An interesting feature of the photoelectron spectra of these compounds (see Figure 14) is the presence of a well-resolved band (the third one around 9 eV), accounting, in the Tl(I) compounds, for the ionization of the two 6s electrons of thallium, behaving practically as a lone pair, and for the two $\sigma_{\text{Tl-C}}$ bonding orbitals in the dialkyl-derivatives. It is significant that the shape of this band completely changes on passing from the Tl(I) to the dialkyl-thallium complexes; it is in fact sharp in the former complexes, consistent with the essentially nonbonding nature of the 6s orbital, while being more intense, broader and partially resolved in two components in the latter ones. Analogous ionizations were found at IE between 9 and 10 eV in the Tl(I) halides[47-50,55-61] and in TlC_5H_5.[51,62].

Other Tl(I) and dialkylthallium chelates investigated by UPS are some complexes with sulfur-containing ligands: dimethyldithiocarbamates, diethyldithiophosphinates, dimethyldithiophosphates.[63] Again the observed d-bands do not show any appreciable ligand-field effect, confirming that the 5d orbitals of thallium are not significantly involved in covalent bonding in the complexes.

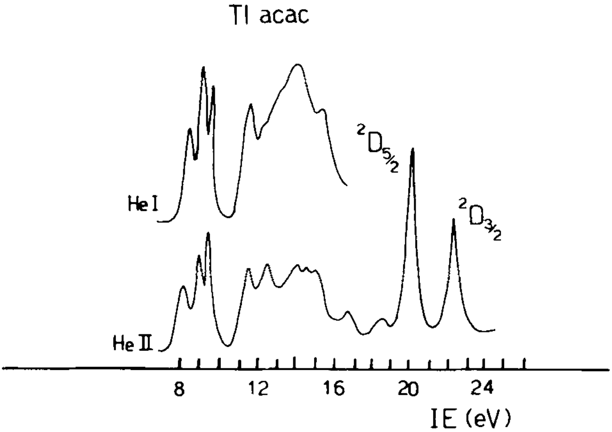

FIGURE 14 He I and He II UP spectra of Tl(acac). acac = acetylacetone.

2.4. Developments and Perspectives

In the last decade the development of synthetic methods for polynuclear complexes has offered the opportunity of investigating the mechanism and the nature of metal–metal interactions.[64] Interest in these researches derives also from the possibility of using polynuclear species as models for the study of catalytic processes, i.e., establishing correlations between metal clusters and metal surfaces with chemisorbed molecules.[65] Such a challenge could not leave the photoelectron spectroscopists indifferent, and in fact many UPS studies have already been performed in this field. It would be too lengthy here to give even only a partial view of these investigations; we will just point out some of the main problems in which this technique may be of help. In compounds with metal–metal multiple bonds[66] UPS, in comparison with the results of theoretical calculations, may give an evaluation of the correctness of approximate descriptions of metal–metal bonds, for instance, describing triple and quadruple bonds as $\sigma^2\pi^4$ and $\sigma^2\pi^4\delta^2$, respectively, without any admixture of ligand orbitals. The actual situation is usually different, and mixing of orbitals of metal and ligand character takes place, as already revealed by several UPS studies. Just to mention some of these, we recall the paper on $(RCO_2)_2M{\equiv}M(O_2CR)_2$ (M = Cr, Mo; R = H, Me, Et, CMe_3, CF_3),[67–71] $L_3Mo{\equiv}MoL_3$ (L = OCH_2CMe_3, NMe_2),[72] MM′ $(mhp)_4$ (MM′ = Cr_2, CrMo, Mo_2, MoW, W_2; mhp = 2-oxo-6-methylpyridine ion).[73]

The nature of the metal–metal interaction in ligand-bridged binuclear compounds has also been extensively discussed,[74–76] the most intriguing aspect being to ascertain, case by case, whether the interaction occurs directly, or through some ligand orbitals. Again, photoelectron spectroscopy has proved very useful in clarifying this problem, in conjunction with quantum-mechanical calculations. The studies performed so far pointed out that the bonding situation in these compounds very much depends on the relative ordering of the d-metal and of ligand orbitals and also that the empty ligand orbitals play an important role. Complexes of different metal with bridging carbonyls have been studied: $(\eta\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)_2$,[77] $(\eta\text{-}C_5H_5)_2Ni_2(\mu\text{-}CO)_2$,[78] $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(\mu\text{-}CO)$.[79] Analogous investigation was performed on (η-$C_5H_5)_2Mn_2(CO)_4(\mu$-$CH_2)$.[80] Compounds with bridging sulfur atoms of formula $Fe_2(CO)_6LL'$ (L = L' = S, (i-propyl)S; L,L' = t-butyl-NS) were studied by Van Dam *et al.*[81] and, only for L = L' = S, by Anderson *et al.*[82] and DeKock *et al.*[83] Sulfur-bridged complexes were also investigated by Chesky and Hall: $SH_{n-1}Co_{3-n}Fe_n(CO)_9$ (n = 1–3), $SH_2Ru_3(CO)_9$,[84] and $SCo_3(CO)_9$, $SH_{n-1}Fe_nCo_{3-n}(CO)_9$ (n = 1–3), $S_2Fe_3(CO)_9$, $SH_2M_3(CO)_9$ (M = Fe, Ru, Os).[85] Much attention was devoted to bridging alkyne and alkene complexes: $Co_2(CO)_6(\mu$-$C_2R_2)$,[86,87] (η-$C_5H_5)_2Ni_2(\mu$-$C_2R_2)$,[88] $Ru_4(CO)_{12}(\mu$-RCR'$)$,[89] $Fe_3(CO)_9(\mu_3$-η^2-$EtC_2Et)$,[90] $Fe_2(CO)_6(\mu$-$C_4H_4)$ (C_4H_4 = butatriene).[91] Compounds with both bridging alkyne and hydrogen were studied: $M_3(CO)_9(\mu$-H$)(\mu_3$-$C_2R)$ (M = Ru, Os; R = Me, CMe_3).[92] The effect of bridging hydrogens on metal–metal bonds was also investigated by Green *et al.*: $H_3Re_3(CO)_{12}$, $H_4Re_4(CO)_{12}$, $H_2Os_3(CO)_{10}$, $H_4Os_4(CO)_{12}$[93] and by DeKock *et al.*: $Fe_3(\mu$-$H)_3(CO)_9(\mu$-$CCH_3)$.[94]

Further developments and more refined tools could be offered by photoelectron spectroscopy to the coordination chemist if the use of ionization by the synchrotron radiation, already succesfully and profitably applied to studies of small or relatively simple molecules[95] would be extended to investigations on coordination compounds. In this case a better knowledge of the involvement of d-metal orbitals in bonding would be achieved, deriving from observations of angular distribution of photoelectrons and changes in spectral intensity, i.e., photoionization cross sections of the various MO, upon continuous variation of the photon energy.

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