He(I) and He(II) Excited Photoelectron Spectra and Electronic Structure of ' Pseudo-octahedral ' Dichloro- and Dimethyl-bis(pentane-2,4-dionato)tin(IV)

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Vapour-phase He(I) and He(II) excited photoelectron spectra are reported for two prototype pseudo-octahedral ' tin complexes $SnR_2(pd)_2$ (R = Cl or Me; pd = pentane-2,4-dionate). The spectra indicate pronounced changes in the bonding depending on the stereochemical conformation of each complex. Notable variations in the band-intensity patterns are observed on going from He(I) to He(II) excitation. This provides information on the nature of the molecular subshells involved in the photoionization processes and on the inherent Sn 5*p* cross-section.

MANY tin complexes of general formula SnR_2L_2 (R = Me or halide, L = bidentate ligand) have been studied in order to throw some light on the relation between their molecular and electronic structure. The complexes generally possess a ' pseudo-octahedral ' geometry in the *cis* or *trans* arrangement depending on the ligands. Accurate Mössbauer studies are consistent with a model for the *trans*-SnR_2L_2 complexes in which the Sn 5*s* character is strongly concentrated in the Sn–R bonds, while the bonding in SnL_2 complexes is mainly Sn 5*p* in character.[1] In the *cis*-SnR_2 linkages the Sn 5*s* character is substantially less.[1]

In continuation of our studies dealing with the static and dynamic stereochemistry of some β-diketonato-complexes of Group 4 elements,[2] we report the He(I) and He(II) excited photoelectron (p.e.) spectra of two prototype tin complexes $SnMe_2(pd)_2$ and $SnCl_2(pd)_2$ (pd = pentane-2,4-dionate), having the pseudo-octahedral *trans* or *cis* configuration. This study was made, first, to check whether photoelectron spectroscopy can generally help in elucidating the stereochemistry of such complexes, and secondly to gain more direct insight into both the SnR_2 and SnL_2 bonding.

EXPERIMENTAL

Pentane-2,4-dione (Hpd), from commercial sources, was distilled twice before using in synthetic procedures. Both the complexes $SnCl_2(pd)_2$ and $SnMe_2(pd)_2$ were prepared according to literature methods [2b,3] and were purified by recrystallization followed by sublimation *in vacuo*. Their purity was checked by elemental analysis and n.m.r. spectroscopy.

He(I) and He(II) p.e. spectra were recorded on a commercial Perkin-Elmer PS 18 spectrometer modified by incorporating a hollow-cathode discharge lamp (Helectros Developments) giving a higher photon flux at the He(II) wavelength. The spectra, obtained at 87 and 130 °C respectively, were calibrated by reference to peaks of noble gases simultaneously admitted to the target chamber and to He $2s^{-1}$ self ionization. Band areas, used in intensity measurements, were evaluated with a Du Pont curve resolver. Due to overlapping, an inherent 10% error must be expected. The values obtained were further corrected to allow for the variation of the analyser transmission function with electron kinetic energy.

RESULTS

The He(I) p.e. spectrum of $SnMe_2(pd)_2$ shown in Figure 1 consists of six defined bands (labelled A—F) in the low-energy region (up to 11 eV).‡ The ionization-energy (i.e.) data and relative intensities are reported in Table 1. In the He(II) spectrum (Figure 1) only minor variations can be observed for the intensities of bands C and F whereas notable changes occur for those of bands D and E (Table 1).

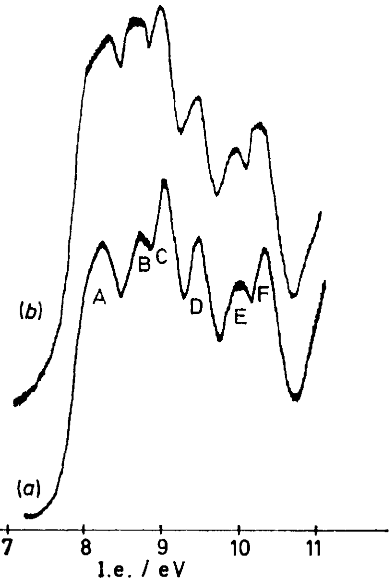

FIGURE 1 He(I) (*a*) and He(II) (*b*) p.e. spectra of $SnMe_2(pd)_2$ in the low-energy region

The general outline of the low-energy region (up to 12 eV) of the He(I) p.e. spectrum of $SnCl_2(pd)_2$ (Figure 2) does not show any resemblance to that of the dimethyl derivative: only four defined bands (labelled A—D), whose intensities are also not directly comparable (Table 2), are present. Band C shows additional features in the form of shoulders on its lower and higher intensity sides. The i.e. data are collected in Table 2. Profound changes in the relative band areas are observed in the He(II) spectrum (Figure 2). Namely, a marked decrease in intensity occurs

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‡ Throughout this paper: 1 eV ≈ 1.60×10^{-19} J.

for both bands B and C, whereas only a minor intensity reduction is observed for band D (Table 2). The higher-energy region (up to 17 eV) of the He(I) and He(II) spectra of both complexes consists of a series of diffuse overlapping structures that find counterparts in the spectra of the simple Hpd ligand and are due to ionization from the σ ligand manifold.[4] This region will not be considered further.

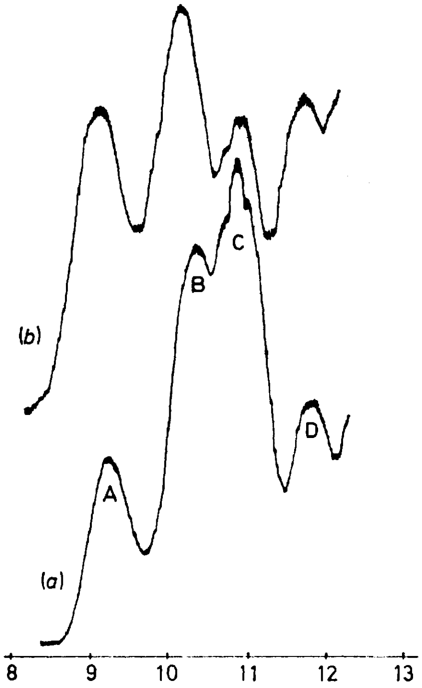

FIGURE 2 He(I) (*a*) and He(II) (*b*) p.e. spectra of $SnCl_2(pd)_2$ in the low-energy region

TABLE 1

Photoelectron data for $SnMe_2(pd)_2$

Band labelling	I.e./eV	Intensity		Assignment
		He(I)	He(II) *	
A	8.35	1.0	3.0	$b_{1u}(\pi_3)$
B	8.93	1.0		$b_{2g}(\pi_3)$
C	9.16	1.3		$b_{1g}(n_-)$
D	9.63	1.1	0.4	$b_{2u}(n_-)$
E	10.16	0.7	0.4	$b_{1u}[\sigma(Sn-C)]$
F	10.51	1.1	0.81	$a_g(n_+)$

* The intensities of bands D—F are normalized to the intensity of band A assumed as one third of the total intensity of the system A + B + C.

In the spectral region that follows (up to 20 eV) the He(II) spectra of both complexes reveal some new features not detectable in the corresponding He(I) spectra as a consequence of the well known decrease in intensity with decreasing p.e. kinetic energy, characteristic of the 127° sector analyser used in the Perkin-Elmer spectrometer. These are additional bands probably due to molecular orbitals (m.o.s) mostly based on 2*s* carbon and oxygen.

DISCUSSION

The Koopmans approximation will be used to relate the measured i.e.s to the m.o. eigenvalues. On the other hand, rescaling effects on ionization are not expected here because all the upper filled m.o.s are mainly ligand in character (the tin atoms have the formal s^0p^0 configuration). The related electronic structures can be usefully set-up in terms of a localized bond model using, as basis set, localized m.o.s appropriate to the molecular framework.[5] Therefore, the upper filled m.o.s localized on the pd^- anion (the effective ligand in the two complexes) must be considered in both cases, while the σ(Sn–C) bonds or the σ(Sn–Cl) together with

TABLE 2

Photoelectron data for $SnCl_2(pd)_2$. Related data for $Be(pd)_2$ and $SnCl_2$ are also given for comparison

(*a*) $SnCl_2(pd)_2$

Band labelling	I.e./eV	Intensity		Assignment
		He(I)	He(II)	
A	9.10	1.0	1.0	$a + b\ (\pi_3)$
B	10.20	2.9	1.5	$a + b\ (n_-) + a[\sigma(Sn-Cl)]$
	(10.57)			
C	10.74	4.2	0.9	Cl lone pairs
	(10.86)			
D	11.64	2.2	1.2	$a + b\ (n_-) + a[\sigma(Sn-Cl)]$

(*b*) $Be(pd)_2$ (refs. 4 and 11)

I.e./eV	Intensity *	Assignment
8.41	1.0, 1.0	(π_3)
9.67	1.3, 1.0	(n_-)
(10.86)	1.4, 1.0	(n_+)
11.13		

(*c*) $SnCl_2$ (ref. 17)

I.e./eV	Assignment
10.31	$b_1\ [\sigma(Sn-Cl)]$
11.31	Cl lone pairs
12.07	
12.72	$a_1\ [\sigma(Sn-Cl)]$

* The figures relate respectively to He(I) and He(II) excitation.

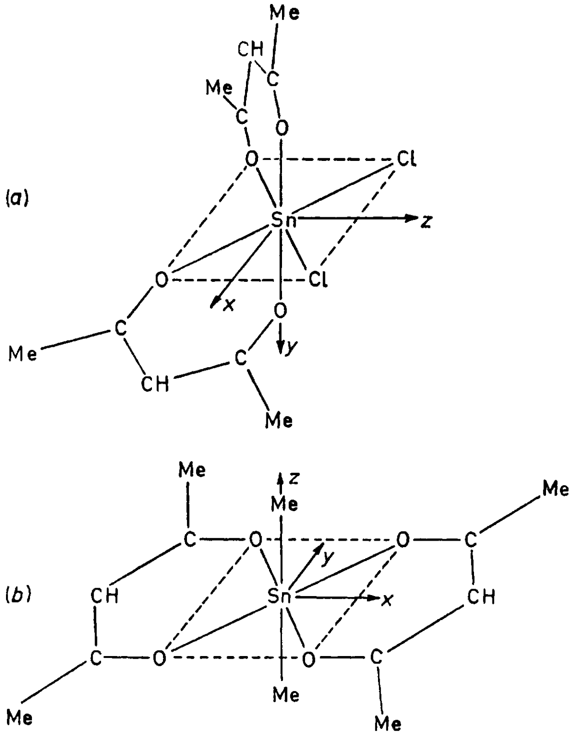

FIGURE 3 Geometrical arrangement of (*a*) $SnCl_2(pd)_2$ (C_2) and (*b*) $SnMe_2(pd)_2$ (D_{2h})

the chlorine lone pairs will also be taken into account in $SnMe_2(pd)_2$ and $SnCl_2(pd)_2$ respectively.

As far as the basis sets of the $>SnMe_2$ or $>SnCl_2$ fragments are concerned, the empty orbitals mainly localized on the tin atom must be considered. As to the pd^- basis set, p.e. data for various related systems indicate that the upper filled m.o.s, concerned mainly with metal–ligand bonding, are the in- and out-of-phase combinations of the oxygen lone pairs lying in the pd^- molecular plane and the uppermost out-of-plane π system. They will be labelled respectively n_+, n_-, and π_3 according to the notation of Evans *et al.*[4]

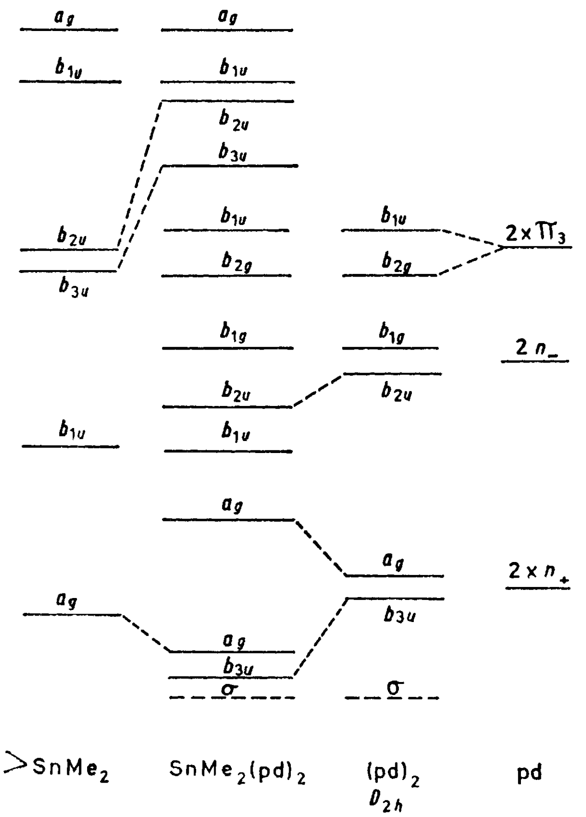

FIGURE 4 Qualitative m.o. scheme for $SnMe_2(pd)_2$ according to the localized-bond model. The m.o.s are filled up to b_{1u} (π_3)

The trans-' Pseudo-octahedral ' Complex $SnMe_2(pd)_2$.—The stereochemistry of $SnMe_2(pd)_2$ both in solution and in the solid state has been studied by various techniques including *X*-ray diffraction,[6] and n.m.r.,[7] i.r.–Raman,[8] and Mössbauer spectroscopy.[9] All the data indicate an octahedral arrangement about the tin atom with the two methyl groups lying in *trans* positions (Figure 3). The same geometry will be assumed in the vapour phase. The D_{2h} point group properly describes this structure. In this point group the basis set of the two pd^- ligands transforms as in Figure 4, while the two σ(Sn–C) (methyl) bonds form a basis for the b_{1u} and a_g representations. These latter two symmetry orbitals (s.o.s) clearly relate respectively to the t_2 and a_1 s.o.s of the simpler tetrahedral $SnMe_4$ molecule. Furthermore, the low-lying empty s.o.s mainly localized on the tin atom include the b_{2u} and b_{3u} non-bonding orbitals, practically pure tin $5p_x$ and $5p_y$ in character, and the b_{1u} and a_g orbitals, the obvious antibonding counterparts (mainly tin $5p_z$ and $5s$) of the above σ(Sn–C) bonding orbitals (Figure 4).

Assuming that the relative values of the diagonal Fock matrix elements over the basis orbitals reflect the i.e.s of the same orbitals as measured from the p.e. spectra of similar molecules, the relative ordering for the two sets of interacting basis orbitals can be set-up (Figure 4). In particular, for the $SnMe_2$ fragment, the p.e. data for the isoelectronic $ZnMe_2$ were considered.[10] For the basis set of the pd^- fragment, reference has been made to both the He(I)[4] and He(II)[11] spectra of $Be(pd)_2$. These data are consistent with a model where the i.e.s of the π_3, n_+, and n_- m.o.s are mainly determined by the potential field due to the metal atom, these orbitals being only slightly concerned in the metal–ligand bonding.

The interactions between the two sets of s.o.s will be determined by the off-diagonal Fock matrix elements which, in turn, depend on the corresponding group overlaps. In Table 3 are reported the most relevant ones. As to the $a_g(n_+)$–$a_g[\sigma(Sn–C)]$ and b_{1u}–$p_z[\sigma(Sn–C)]$ overlaps, it is noted that these refer to pure tin s or p_z atomic orbitals whilst in the $SnMe_2$ fragment they are expected to be mostly based on carbon $2p$.*

TABLE 3

The most relevant group-overlap integrals relative to some basis orbital of $SnMe_2(pd)_2$

Ligand orbital symmetrized combination	Metal orbital	G(M–L)
$a_g(n_+)$	s	$2^{\frac{1}{2}}S(s,p_\sigma)$
$b_{3u}(n_+)$	p_x	$S(p_\sigma,p_\sigma) + S(p_\pi,p_\pi)$
b_{1u} (π_3)	p_z	$2S'(p_\pi,p_\pi)$
$b_{2u}(n_-)$	p	$S(p_\sigma,p_\sigma) - S(p_\pi,p_\pi)$

Such considerations, on the whole, allow one to set-up the m.o. energy scheme pictured in Figure 4. Obviously, the final sequence of the filled m.o.s of $SnMe_2(pd)_2$ reflects both the above considerations and the He(I) and He(II) experimental findings discussed later. In particular, the first two bands (*A* and *B*) must be related to symmetrized combinations of the π_3 pd^- m.o.s split through non-bonded interligand interactions, even when interligand overlap integrals indicate relatively small interactions. The relative intensities of the bands, being invariant on passing from He(I) to He(II) excitations (Table 1), indicate the same composition for the corresponding orbitals. On the other hand, the only symmetry-allowed interaction between basis orbitals of $SnMe_2$ and the $b_{1u} + b_{2g}$ (π_3) s.o.s could involve the two b_{1u} orbitals (Figure 4). However, such an interaction, not favoured on overlap grounds, would introduce some Sn $5p$ contribution into the b_{1u} (π_3) s.o. Information obtained from the He(II) spectrum of $SnCl_4$ indicates that the He(II) Sn $5p$ cross-section is smaller

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* Reference to Bancroft *et al.*[10] suggests a *ca.* 70% C $2p$ contribution in those orbitals.

than the corresponding He(I) value.[12] Consequently, if the above interaction were to contribute to the splitting of the two bands in question the He(II) intensity of the p.e. band related to the b_{1u} (π_3) ionization would be smaller than that related to b_{2g} (π_3) ionization.

Interestingly, the i.e. baricentre of the two bands A and B (8.64 eV) practically coincides with the i.e. quoted for the π_3 ionizations in Be(pd)$_2$,[4] and this observation is also in accord with our proposed assignment.

The two bands (C and D) that follow are likely to belong respectively to ionizations from the b_{1g} and b_{2u} s.o.s mainly n_- (pd$^-$) in character (Figure 4). Their overall He(I) intensity when compared to the combined intensities of the A and B bands is $I_{C+D}/I_{A+B} = 1.21$, in good agreement with the value of 1.30 observed for the relative He(I) intensities of the n_- and π_3 ionizations in Be(pd)$_2$.[11]

A metal–ligand interaction must be invoked (Figure 4) for the mechanism determining the splitting of the two symmetrized combinations of the n_- m.o.s. In fact, the interaction between the combination having symmetry b_{2u} and the Sn $5p_y$ (b_{2u}), favoured to some extent on overlap grounds (Table 2), is further supported by the He(II) intensity of band D which is lower than the corresponding He(I) one. This indicates some Sn $5p$ contribution in the m.o. responsible for band D (see above).

The assignment of bands E and F, in the region up to 11.0 eV, poses some problems. In this region, in principle, both the symmetrized combinations of the n_+ pd$^-$ m.o.s ($a_g + b_{3u}$) and the two orbitals (a_g,b_{1u}) [σ(Sn–C) in character] could appear. The possibility that both bands E and F belong to $a_g(n_+)$ and $b_{3u}(n_+)$ ionizations can be ruled out for various reasons. In fact, these s.o.s may be involved, on overlap and symmetry grounds, in interactions with orbitals based on the SnMe$_2$ group. Such interactions would lead to a destabilized $a_g(n_+)$ s.o. but to a strong stabilization for the b_{3u} orbital. The observed i.e. separation between the E and F bands [Δi.e.(F$-$E) 0.35 eV] is too small to account for such an interaction. Furthermore, if bands E and F belong to both combinations of n_+(pd$^-$) m.o.s the ionizations related to the σ(Sn–C) m.o.s would be associated with a p.e. band beyond 12 eV; this is in contrast to the i.e. values quoted for the b_{1u} [σ(Sn–C)] orbital in ZnMe$_2$,[10] or for the corresponding s.o. (t_2 in T_d symmetry) in SnMe$_4$.[13] Therefore, we favour the assignment of band E to ionization of the b_{1u} [σ(Sn–C)] s.o., only slightly involved in any interaction with equatorial ligands; band F is due to ionization from the $a_g(n_+)$ s.o. destabilized through interaction with the a_+ [σ(Sn–C)] orbital (Figure 4).

This assignment is in good agreement with the trend to lower intensities, on passing from the He(I) to He(II) excitations, observed for bands E and F, and is clearly related, for band E, to the Sn $5p$ contribution in the corresponding orbital. For band F, the trend to lower intensity is less marked than that observed for bands E or D (Table 1), and probably results from a subtle balance between contributions to the total cross-section from the O $2p$, C $2p$, and Sn $5s$ atomic orbitals.

Finally, we consider the ill resolved band centred at 12.05 eV near the onset of the broad overlapping system due to the σ manifold. According to the proposed m.o. scheme (Figure 4) this band is likely to be due to the accidentally degenerate b_{3u} (n_+) and a_g [σ(Sn–C)] orbitals.

The cis-'*Pseudo-octahedral*' *Complex* SnCl$_2$(pd)$_2$.—The stereochemistry of this molecule in the solid state has been unequivocally assigned to the 'pseudo-octahedral' *cis* structure through Mössbauer[14] and *X*-ray diffraction analyses.[15] Furthermore, n.m.r. data[2b,7] indicate that this conformation is maintained also in solution. The same structure, belonging to the C_2 point group, will be assumed in the vapour phase (Figure 3).

The m.o. scheme relative to this molecule can be built-up using the basis orbitals reported in Table 4.

TABLE 4

Basis orbitals of SnCl$_2$(pd)$_2$ localized bond model. The orbitals are labelled according the C_2 point group. For the SnCl$_2$ basis set the corresponding labels relating to a hypothetical linear SnCl$_2$ fragment are also reported

SnCl$_2$			2 pd$^-$	
a	(Sn $5s$)	$\sigma_g{}^*$	$a + b$	($2 \times \pi_3$)
a	(Sn $5p_z$)	$\sigma_u{}^*$	$a + b$	($2 \times n_-$)
b	(Sn $5p_x$)	$\pi_g{}^*$	$a + b$	($2 \times n^+$)
b	(Sn $5p_y$)			
b	[σ(Sn–Cl)]	σ_u		
$a + b$	Cl	π_g		
$a + b$	lone pairs	π_u		
a	[σ(Sn–Cl)]	σ_g		
C_2		$D_{\infty h}$	C_2	

However, an inspection of this Table reveals that, because of the low molecular symmetry and of the consequent possible mixing between all the basis orbitals, such a scheme would be unhelpful. Therefore we are left with only two feasible assignment criteria: one, involving arguments based on comparison with simpler related molecules, and the other using the information about the composition of the m.o.s which give rise to the various p.e. bands obtained from a comparative analysis of the band intensities on passing from the He(I) to He(II) excitations. In fact, we should expect: (*i*) no changes in He(I)–He(II) cross-section for m.o.s based on mainly O $2p$;[11] (*ii*) a reduced He(II) cross-section for m.o.s having some σ(C–H) character; and (*iii*) a dramatic lowering of He(II) p.e. intensities of bands related to m.o.s based on Cl $3p$.[16] The expected intensity variations due to Sn $5p$ contributions have been discussed previously.

Accordingly, the first p.e. band (A) can be assigned to the unresolved ionizations of the $a + b$ (π_3) m.o.s based mainly on the pd$^-$ ligands: in the same spectral region, we find the corresponding m.o.s of Be(pd)$_2$ (Table 2). The He(I)–He(II) intensity pattern of this band, when compared to that of the bands that follow, strongly indicates a predominant oxygen contribution to the corresponding m.o. (Table 2). In the following region up to 12.0 eV the i.e. data of $SnCl_2$ suggest ionization of the filled basis orbitals belonging to the $SnCl_2$ fragment.[17] Moreover, the intensities of bands B—D decrease (relative to A) on passing from He(I) to He(II) excitation; this effect is most marked for band C (Table 2). Accordingly, we feel confident in assigning band C and its lower and higher energy shoulders to the slightly resolved ionizations from the $a + b$ (π_u) and $a + b$ (π_g) m.o.s. Again, reference to the i.r. data for $Be(pd)_2$ and $SnCl_2$ (Table 2) suggests that the two remaining bands B and D can be assigned to ionization from $a + b(n_+) + b[\sigma(Sn{-}Cl)]$ and $a + b(n_+) + a[\sigma(Sn{-}Cl)]$ m.o.s, respectively. It is to be noted that in $SnCl_2(pd)_2$ the i.e.s of the m.o.s belonging to the $SnCl_2$ basis set cover a narrower range than in the simpler $SnCl_2$. Such an effect can be connected with the wider Cl–Sn–Cl angle measured [15] in $SnCl_2(pd)_2$ with respect to the corresponding angle in $SnCl_2$.[18]

Conclusions.—Photoelectron spectra of the two 'pseudo-octahedral' tin complexes studied in the present work provide information about the extent to which the stereochemical conformation can influence bonding. In the *trans* complex $SnMe_2(pd)_2$ the m.o.s localized on the equatorial ligands are profoundly involved in interactions with the $5p_y$ and $5p_x$ orbitals belonging to the metal atom. Even if this observation supports the bonding model suggested by ^{119}Sn Mössbauer spectra of a series of related molecules,[1] the p.e. data do not allow one to say that the equatorial bonding involves *only* Sn 5*p* character; some Sn 5*s* electron density is, in fact, transferred to equatorial bonding *via* the $a_g[\sigma(Sn{-}C)]{-}a_g(n_+)$ interaction. Similarly, it can be argued that both the Sn 5*s* and 5*p* orbitals contribute to the Sn–Me linkages in agreement with the 50% 5*s* character deduced from the ^{119}Sn–H coupling constants in $SnMe_2(pd)_2$.[6,8]

Furthermore the transfer of electron density from the equatorial ligand to orbitals localized on the tin atom (Figure 3) results in a lowering of the apical bond strength because of the increased electrostatic repulsion. This model is in accord with the Sn–C(Me) distance measured [6] in $SnMe_2(pd)_2$ which is longer than the corresponding distance in $SnMe_2F_2$ where four fluorine atoms lie in the equatorial plane around the tin atom but the equatorial bonding is likely to be mostly ionic in character.[19]

For the *cis* complex $SnCl_2(pd)_2$, p.e. data do not indicate significant interaction between m.o.s localized on the pd^- ligand and those on the tin atom. The i.e.s of the π_3, n_-, and n_+ m.o.s are all equally shifted to higher energy ($\simeq$0.5 eV) with respect to the corresponding ones in $Be(pd)_2$. This means that these energies depend only on the potential field, due to the tin atom, experienced by the pd^- ligand. Moreover, the spread of the i.e.s of m.o.s mainly localized on the $SnCl_2$ fragment is smaller than in $SnCl_2$ (Table 2), suggesting reduced metal–ligand and/or ligand–ligand interactions.

The p.e. spectra of the two complexes studied indicate that their conformation profoundly affects the bonding pattern. Therefore, disregarding subtle effects connected with the presence of different unidentate ligands, p.e. spectroscopy gives indirect information on the stereochemistry adopted by these complexes in the vapour phase.

Finally, some further comments should be made about the change in band intensities on passing from He(I) to He(II) excitation. It transpires that the inherent tin 5*p* cross-section is substantially smaller than that for carbon or oxygen 2*p* subshells, at the shorter p.e. wavelength.

The changes in relative band intensities of structures associated with m.o.s having some tin 5*p* contribution provide an unequivocal criterion for assignment allowing, in turn, a better understanding of the bonding pattern.

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