Electronic Structure and Bonding in 2,2-Diphenyl-1,3-dithiacyclopentanes of IV A Group Elements Studied by UV Photoelectron Spectroscopy

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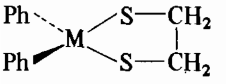
Received July 21, 1982

As part of an extended programme of studies by UV photoelectron spectroscopy (UPS) of the bonding properties of IV A group elements, particularly with oxygen- and sulphur-containing ligands [1, 2], we devoted our attention to a class of molecules in which the metal–sulphur bond is involved in ring:



2,2-diphenyl-metal-1,3-dithiacyclopentane
(M = Si, Sn, Pb)

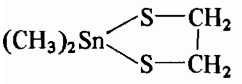
UPS measurements are of great help in elucidating the nature and the extent of the possible interactions between various valence orbitals: in this case we expected evidence of intermixing of the 3p orbitals of the two sulphur atoms, both with each other and with the phenyl orbitals of appropriate symmetry. Furthermore, we were interested in observing the ionization energies of the σ_{M-C} and σ_{M-S} bonding orbitals, to be compared with the analogous data previously obtained for other IV A group compounds.

Experimental

The compounds were prepared following literature methods [3–5]. The UP spectra were recorded on a Perkin-Elmer PS 18 spectrometer modified with a HeI/HeII lamp (Helectron Development) at temperatures of 73 °C, 100 °C, 127 °C (respectively M = Si, Sn, Pb). Calibration was done by Ar, CH_3I and self-ionizing He.

Results and Discussion

The HeI and HeII spectra are shown in Fig. 1 and the I.E.s are reported in Table I. Figure 2 shows the spectra of



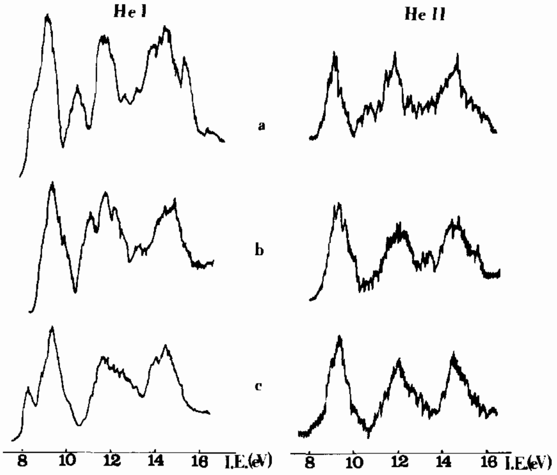
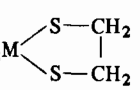


Fig. 1. Gas-phase UP spectra of Ph_2M



(a: M = Si; b: M = Sn; c: M = Pb).

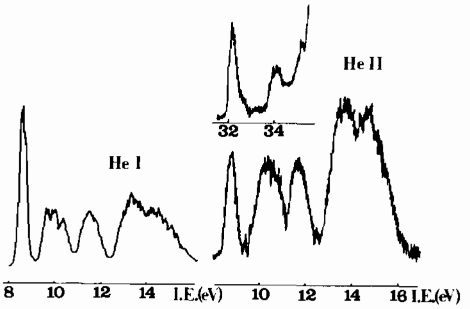
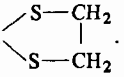


Fig. 2. Gas-phase UP spectra of $(CH_3)_2Sn$



already studied by other authors, with HeI radiation [6, 7] which we measured as a useful term of comparison. The HeII spectrum of the latter compound, displaying a profound decrease in intensity of the first band with respect to the others, confirms the assignment [6, 7] of the sulphur 3p orbitals to antisymmetric and symmetric combinations (consistent with the variation of the cross-section of these orbitals on switching from HeI to HeII ionizing radiation). It is more difficult to discriminate between the two alternative assignments proposed for the following bands ($\sigma^{+}_{Sn-S} < \pi(C-Sn-C) < \sigma^{-}_{Sn-S}$ in order of increasing I.E. for ref. 6, $\sigma^{+}_{Sn-S} < \sigma^{-}_{Sn-S} < \pi(C-Sn-C)$ for ref. 7). In the case of our phenyl-derivatives the spectral region around 9 eV is complicated by the presence of the ionizations from the π phenyl orbitals (e_{1g} in benzene, I.E. 9.25 eV); in fact in the spectra of all of the three compounds may be observed a broad band in this region, whose intensity does not diminish on passing from HeI to HeII since the dominating ionizations are those of the π orbitals

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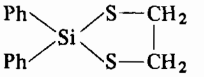
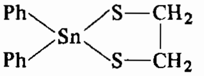
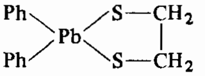
TABLE I. Ionization Energy Values (eV) for some IV A Group 2,2-Diphenyl-1,3-dithiacyclopentanes.

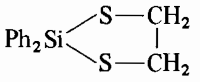
Compound	$\pi^a + n_+ + n_-$ ⌬	$2 \times \sigma$ $\mathrm{M}{<}\genfrac{}{}{0pt}{}{S}{C}$	$\pi^b + \sigma$ ⌬ $\mathrm{M}{<}\genfrac{}{}{0pt}{}{S}{C}$	$^2D_{5/2}$
	(8.5) 9.07	10.47	11.70	
	9.34	(9.94)	11.11 11.8 12.29	
	(8.94) 9.44	(10.16)	11.6	28.06

$^a e_{1g}$ in benzene. $^b e_{2g}$ in benzene.

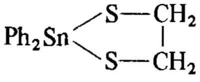
of the phenyl rings (two for each ring). There is also the contribution of the n_+ and n_- combinations of the sulphur lone pairs. This band, though quite broad, does not show separate components, suggesting that the interactions between the orbitals ionized in this energy region are quite weak.

Of the σ bonding orbitals between the central metal and the ligands, which are likely to be strongly intermixed due to the low symmetry of the molecules, the highest are probably associated with the band at 10.47 eV in the silicon derivative (shoulders at 9.94 and 10.16 eV for tin, respectively lead derivative).

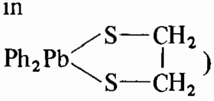
The highest I.E. of this band for the silicon compound is consistent with the lower metallic character of Si with respect to Sn and Pb, producing a more covalent bonding in the former compound. The band centered at 11.70 eV in



(to which correspond three bands at 11.11, 11.85, 12.29 eV in



and a broad envelope with main maximum at 11.6 eV in



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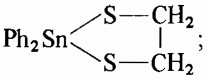
accounts for σ ionizations of the phenyl rings (e_{2g} in benzene, I.E. 11.53 eV) plus at least one of the lowest two σ metal-ligand orbitals. The following spectral region corresponds to several ionizations giving rise to broad envelopes of overlapping bands.

An interesting feature of the spectrum of the lead derivative is the presence of a band accounting for the ionization of the 5d orbitals of Pb: this band appears in the HeI spectrum at an apparent I.E. of 8.47 eV but it originates actually from the HeII radiation, with a real I.E. = 28.06 eV.

This represents the $^2D_{5/2}$ spin-orbit component, and its I.E. is higher than the one observed in Pb(II) halides (27.34 eV in $PbCl_2$, 27.02 eV in $PbBr_2$, 26.48 eV in PbI_2) [8]; the $^2D_{3/2}$ component is masked under the broad envelope around 11 eV in the HeI spectrum, since the spin-orbit splitting for the 5d levels of lead is *ca.* 2.5 eV.

It would be useful to compare the I.E. of these orbitals with that one of the 4d levels of Sn in



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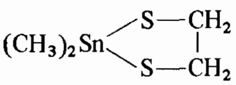
for some compounds these ionizations are observed as satellite peaks in the HeII spectrum, originating from the HeIIβ radiation (48.37 eV). Unfortunately this is not the case for our diphenyl derivatives, probably because these bands fall at higher I.E.s and are therefore masked by the much more intense HeI peaks.

We could on the contrary observe such ionizations in the HeII spectrum of



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they fall at the apparent I.E.s of 26.52 ($^2D_{5/2}$) and 27.63 eV ($^2D_{3/2}$), corresponding to the true values of 34.08 and 35.07 eV. These I.E.s are slightly lower than in $SnCl_4$ (34.91 and 36.05 eV [9]) and higher than in Me_2SnCl_2 (32.59 and 33.61 eV [9]), suggesting that the bidentate ligand acts as an electronegative group.

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