THE ELECTRONIC STRUCTURE OF η⁵-PENTAMETHYLCYCLOPENTADIENYL COMPLEXES OF GROUP IV ELEMENTS FROM He(I) AND He(II) PHOTOELECTRON SPECTROSCOPY

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Summary

The bonding between the pentamethylcyclopentadienyl ligand and the Group IV elements germanium and tin has been studied by photoelectron spectroscopy. Despite the bent structures, the complexes exhibit photoelectron spectral patterns similar to those expected for a higher symmetry (D_{5d}). There is no unambiguous evidence for the involvement of metal p subshells in the metal–ring bonding. The high ionization energies associated with ns^2 ($n = 4,5$) electrons are indicative of a pronounced "inertness" of the metal lone pair and, therefore, of almost ionic metal–ligand bonding character.

Introduction

In the application of vapour phase photoelectron (PE) spectroscopy to investigation of the electronic structures of organometallic compounds of Group IV elements Ge^{II} complexes have been little studied, even though they are of special importance in gaining insight into the effect of the so called ns^2 "inert lone-pair" in the metal–ligand bonding.

In this paper we consider the He(I) and He(II) PE spectra of bent sandwich bis(η^5-pentamethylcyclopentadienyl) complexes of Ge^{II} and Sn^{II} subsequently denoted by Ge(Cp')$_2$ and Sn(Cp')$_2$). The η^5-pentamethylcyclopentadienyl germanium chloride, Ge(Cp')Cl, was also included in this study as a simpler model compound.

Further stimulus to this study was provided by reports on the electronic structure of pentamethylcyclopentadienides of d [1a,b] and $5f$ [1c] transition metals. The special nature of the permethylated cyclopentadienyl ligand makes it desirable to extend such studies to complexes of Main Group elements.

The He(I) PE spectrum of $Sn(Cp')_2$ has been described by Cowley [2].

Experimental

The compounds were prepared by literature methods [3]. They were purified by sublimation in vacuo and gave satisfactory mass spectrometric analyses. The PE spectra were recorded on a PS 18 Perkin–Elmer spectrometer modified by the inclusion of a hollow cathode discharge source to give a high output of He(II) photons (Helectros Development Corp.). The spectra were accumulated in the "multiple scan mode" with the aid of a MOSTEK computer directly interfaced to the spectrometer. The energy scale of consecutive scans was locked to the reference values of the Ar $^2P_{3/2}$ and of He $1s^{-1}$ self ionization.

Deconvolution of the spectra was carried out by fitting the experimental profiles to a series of asymmetrical Gaussian curves after subtraction of the background. The areas of bands thus evaluated are estimated to be accurate within 5%. The integrity of fine structure features associated with low IE bands was exhaustively checked by repetitive scans with an instrumental resolution of 20 meV (measured on Ar lines). Relevant spectral data are listed in Table 1.

Results and discussion

We consider first the PE spectrum of $Ge(Cp')Cl$ (Fig. 1). It shows three bands (labelled **a**, **b** and **c**) in the region below 11 eV. The intensity of band **c** relative to all the other bands falls greatly on going to the He(II) spectrum. A further band, with a

TABLE 1

RELEVANT SPECTRAL DATA FOR GROUP IV METAL PENTAMETHYLCYCLOPEN-TADIENIDES

Compound	Band label	IE (eV) [a]	Intensities [b]		Half-width (eV) [c]	Assignment [d]
			He(I)	He(II)		
$Ge(Cp')Cl$	**a**	8.03	1.0	1.0	0.80 [e]	e_1 (ring-π)
	a'	8.43	1.0	0.8		
	b	9.07	0.7	0.9	0.46	a_1 (Ge $4s^2$)
	c	10.47	1.7	0.2	0.58 [f]	e_1 (Cl $3p$)
$Ge(Cp')_2$	**a**	6.60	1.0	1.0	0.48	e_{1u} (ring-π)
	a'	6.88	0.7	0.6		
	b	7.91	0.7	0.5	0.49	e_{1g} (ring-π)
	b'	8.19	0.8	0.6		
	c	8.46	0.5	0.7	0.42	a_1 (Ge $4s^2$)
$Sn(Cp')_2$	**a**	6.55	1.0	1.0	0.52	e_{1g} (ring-π)
	a'	6.78	1.0	0.9		
	b	7.50	0.9	0.7	0.52	e_{1u} (ring-π)
	b'	7.73	0.9	0.6		
	c	8.39	0.7	0.9	0.48	a_1 (Sn $5s^2$)

[a] Values refer to peaks of deconvoluted bands. [b] Corrected for the analyser transmission function. [c] Values referred to convoluted components. [d] The notation refers to the C_{5v} point group for $Ge(Cp')Cl$ and to D_{5d} for $M(Cp')_2$ (M = Ge, Sn). [e] The corresponding value measured in $Tl(\eta^5\text{-}C_5H_5)$ is 0.70 eV (see ref. 5). [f] The corresponding value measured in $Sn(CH_3)_3Cl$ is 0.58 eV (see ref. 15).

peak at 11.52 eV, as well as some more diffuse structures appear in the higher *IE* region. The latter features, common to all the spectra presently studied, find analogous counterparts in the PE spectra of other pentamethylcyclopentadienyl [1c,2] complexes, and can unambiguously related to inner π and σ molecular orbitals (MO's) of minor relevance for the metal–ligand bonding.

Electron diffraction data [4] have indicated a bent structure for the Ge(Cp')Cl molecule, with Ge–Cl and Ge–Cp' (ring centroid) distances of ~ 2.2 and ~ 2.1 Å, respectively. The (Cp')–Ge–Cl bond angle is 110°. Despite the lower symmetry, the spectrum of Ge(Cp')Cl shows analogies to the spectra of the highly symmetric (C_{5v}) half-sandwich complexes In(C_5H_5) and Tl(C_5H_5) [5], isoelectronic with the Ge(Cp') fragment, as well as with those of many linear monochlorides [6]. Therefore, simple comparisons with relevant PE data for these reference compounds suggest that the bands **a**, **b** and **c** in Fig. 1 are due to ionizations from (i) the e_1 (π) ring MO (in C_{5v} symmetry), (ii) the Ge $4s^2$ lone pair, and (iii) the Cl $3p$ lone pairs. The assignment of band **c** to accidentally degenerate Cl $3p$ lone pairs (e_1 in C_{5v}) is straightforward because the decrease in the band intensity for the He(II) radiation (Tab. 1) is as expected for Cl $3p$ based MO's.

Thus, whatever the relative energy ordering, the bands **a** and **b** are left for the ionizations of the remaining $e_1(\pi)$ and Ge$(4s^2)$ orbitals. Simple relative intensity arguments suggest that the $e_1(\pi)$ MO is the lowest in energy, and is thus the

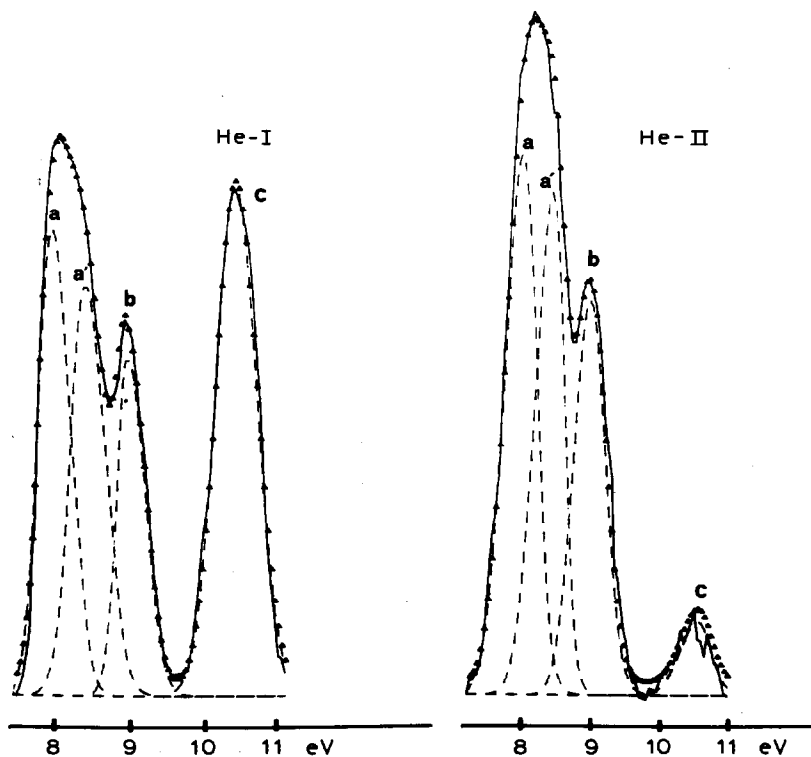Fig. 1. He(I) and He(II) photoelectron spectra of Ge(Cp')Cl. The solid line refers to the experimental data; the dashed line shows the Gaussian components; the triangles refer to the convoluted Gaussian components.

HOMO. In contrast, ground-state ab initio calculations recently reported by Haaland et al. [7] indicate the reverse ordering for the two MO's in question. They also indicate that the e_1 (π) MO does not remain accidentally degenerate in the lower C_{2v} symmetry, the energy separation between the two resulting components (a' and a'' in C_s symmetry) being 0.5 eV. However, it is significant that the same authors also report a remarkable lowering of the binding energy of the Ge $4s^2$ lone pair in the case of the ground-state of $GeCl_2$ [7]; in this case, again, the HOMO possesses almost pure Ge $4s^2$ character. This contrasts with PE data as well as with results of accurate transition state IE's derived from Hartree-Fock-Slater calculations by Jonkers et al. [8] who suggest that the IE associated with the removal of one electron from the Ge $4s^2$ lone pair ($2a_1$ in ref. 8) is considerably higher than the energies associated with ionizations from MO's representing Cl $3p$ lone pairs and Ge–Cl bonds. Hence it may be that ab initio calculations do not satisfactorily reproduce the sequence of energies of ion states formed by ionization of both $GeCl_2$ and Ge(Cp')Cl.

In this context we note that the trend in variation of relative intensities on passing from the He(I) to the He(II) spectrum of Ge(Cp')Cl supports the MO sequence which we propose on a purely experimental basis. The increased relative intensity of band **b** in the He(II) spectrum (Table 1) agrees well with a Ge $4s^2$ character of the corresponding MO (vide infra). Finally we note that there is no unambiguous experimental evidence for electronic effects due to the lower (than C_{5v}) symmetry. Both bands **a** and **c** (which have been assumed to represent ionizations from degenerate MO's) have half-widths (Table 1) comparable to or even narrower than those of corresponding bands observed in the spectra of various closely related compounds of higher symmetry (Table 1). Thus the structure in the higher IE side of band **a** may arise from Jahn-Teller effects in the ^2E ion state, as found in the case of the highly symmetric $Tl(C_5H_5)$ or $In(C_5H_5)$.

Turning now to $Sn(Cp')_2$ and $Ge(Cp')_2$, we note that structural data point to bent sandwich structures of C_{2v} symmetry having small bending angles [3,4,9]. These low symmetry structures, however, are not reflected in intricate spectral patterns. The spectra of $Ge(Cp')_2$ and $Sn(Cp')_2$, in fact, show a strong doublet (labelled **a**, **b** in Figs. 2, 3) at 6.5–8 eV, followed by a less intense band (labelled **c**) around 8.4 eV. Both the **a** and **b** bands are structured in two components. This pattern presents intriguing analogies with PE spectra of highly symmetrical sandwich complexes of ns^0 metals such as $Mg(Cp)_2$ [10] and $Mg(Cp')_2$ [1a], and of half-sandwich complexes of ns^2 metals such as $Tl(Cp)$ [5] and $In(cp)$ [5]. Therefore, analogy arguments and simple consideration of relative intensities (Table 1) indicate that bands **a** and **b** can be taken to represent the ionizations of MO's e_{1g} and e_{1u}, respectively (assuming an idealized structure of D_{5d} symmetry), which are the symmetry combinations of e_1'' (D_{5h}) MO's belonging to Cp' rings. The remaining band **c** is left for the ^2A ion state associated with ionization of the metal ns^2 lone pair (Table 1). The energy separation between the barycenters of envelopes **a** and **b** parallels the decrease in the inter-ring distance [11] on going from the Sn to the Ge complex. It, therefore, transpires that the e_{1g}–e_{1u} energy splitting is influenced, in addition to other factors, by inter-ring non-bonded interactions. Analogous general conclusions were reached by Cowley through an elegant X_α study of $Sn(Cp')_2$ [2]. The calculations, however, point to a specific metal($6p$)–ligand(π) interaction, due to the lower symmetry, which lift the accidental degeneracy of the e_{1g} and of e_{1u} MO's. The X_α

data unambiguously indicate that this effect is of a major relevance for the e_{1g} MO, thus giving the well split $11a_1$ and $6b_1$ MO's (in C_{2v} symmetry). Experimental intensity data, however, might lead to other conclusions. Inspection of Table 1 clearly indicates that while the relative intensities of the two components (a and a') of band **a** remain almost unchanged upon switching to He(II) radiation for both $Sn(Cp')_2$ and $Ge(Cp')_2$, those of the two components of band **b** vary in the He(II) spectra. In particular the component b' is somewhat smaller in both cases. This might be indication of metal np admixture into the corresponding MO, since it has been shown unequivocally that the He(II) cross-sections of metal p subshells decrease in the order $C \gg Ge > Si > Sn$ [12], so that any metal np admixture must result in a smaller relative intensity of the band associated with that particular MO. Nevertheless, as in the case of the previously discussed $Ge(Cp')Cl$, we note that even though the He(II) vs. He(I) intensity variations might be indicative of a preferential metal–ligand interaction, thus explaining the origin of the splitting of the low IE bands, there is some experimental indication of other possible explanations. The observed bands **a** and **b** show an incipient splitting in two components with comparable ~ 0.25 eV intervals (Table 1). Moreover the total half-widths of bands **a** and **b** are comparable (Table 1) to each other and do not show a significant metal dependence, and all these effects are completely comparable to those for the corresponding bands in spectra of highly symmetrical $Mg(Cp)_2$, $Tl(C_5H_5)$ and
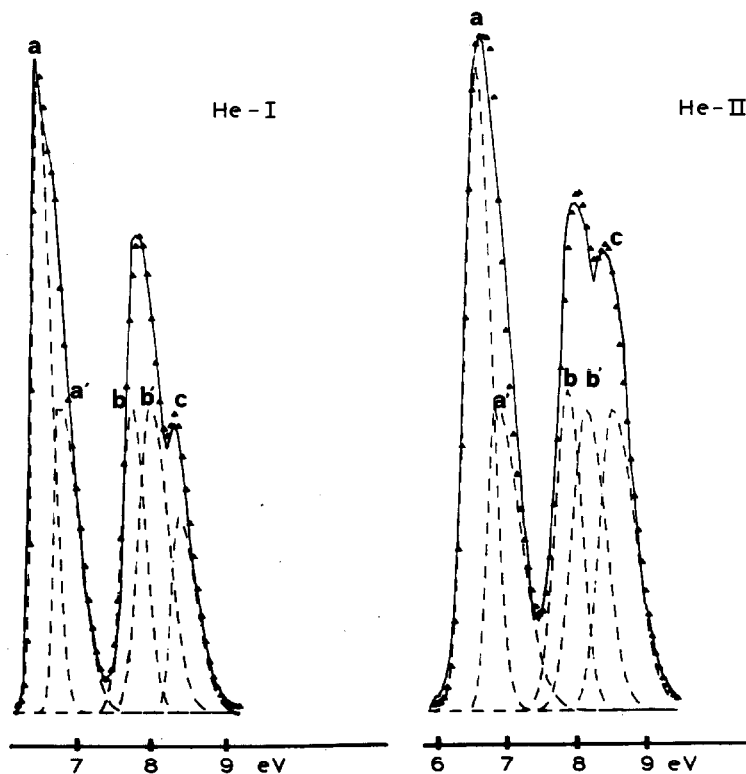

Fig. 2. He(I) and He(II) photoelectron spectra of $Ge(Cp')Cl_2$. The solid line refers to the experimental data; the dashed line shows the Gaussian components; the triangles refer to the convoluted Gaussian components.

In(C_5H_5). These observations may indicate that a higher symmetry (than C_{2v}) is actually experienced by the metal atom [13] and that the features of multiplet splitting are not particularly metal-dependent but simply correlated with a process which is almost entirely ligand-centered. In particular, they could be related to a vibronic excitation of ring ligand modes in the ^2E ion states.

It is noteworthy that the present energy ordering of uppermost filled MO's proposed for Ge(Cp′)$_2$: $e_{1g} > e_{1u} > a_{1g}$ (D_{5d} labelling) contrasts with that provided by ab initio calculations on Ge(Cp)$_2$ which indicate that a_{1g} (the Ge $5s^2$ lone pair) is the HOMO. We note, however, that these data indicate that the *IE* of the a_{1g} MO, both in the Koopman approximation and using the ΔSCF approach, strongly depends upon the chosen geometry. In particular, within a 10% variation of inter-ring distance, the final ordering becomes identical to that which we proposed. Therefore we believe that extrapolation of theoretical results for Ge(Cp)$_2$ to Ge(Cp′)$_2$ is not appropriate.

Finally we comment on band c. Table 2 lists metal ns^2 lone pair *IE*'s for a series of Ge^{II} and Sn^{II} complexes. As in the cases of dimethyl and diamide complexes [14], the *IE* for Ge(Cp′)$_2$ lies very close to that of the analogous tin complex. Interestingly the *IE* values are the highest in the two series. Ignoring relaxation effect in the ion states, there are two factors that may relevant in determining the *IE* of *ns* subshells. First, of course, the lower the partial charge on the metal atom the lower is
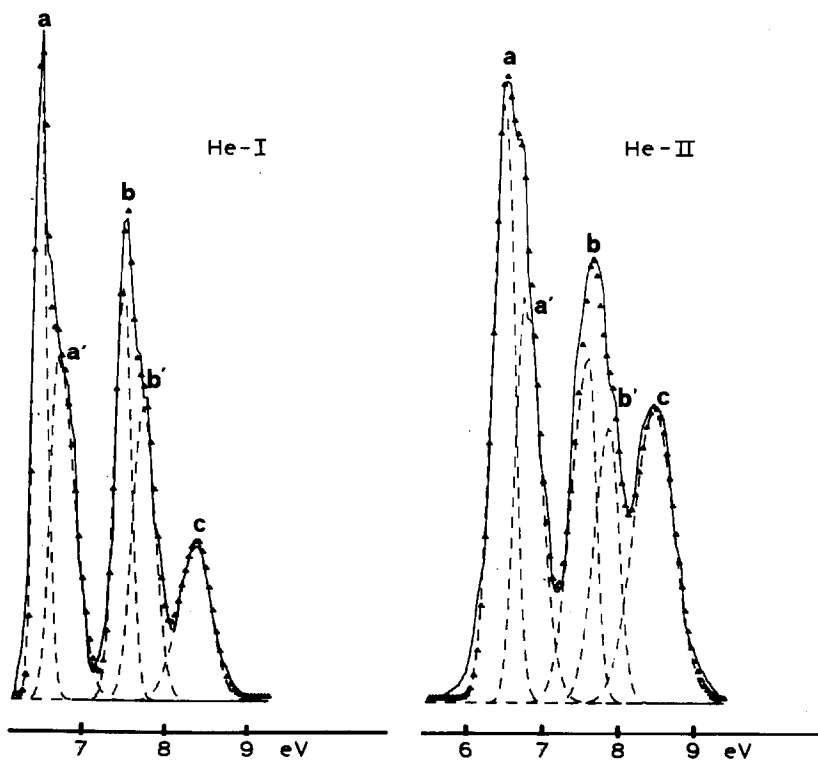

Fig. 3. He(I) and He(II) photoelectron spectra of Sn(Cp′)$_2$. The solid line refers to the experimental data; the dashed line shows the Gaussian components.

TABLE 2

IONIZATION ENERGIES (eV) OF ns ($n = 4,5$) SUBSHELLS IN SOME ML_2 COMPLEXES OF GROUP IV ELEMENTS

Compound [a]	IE (eV)	Compound [a]	IE (eV)	Ref.
Ge	7.5	Sn	7.0	14
GeR_2	7.75	SnR_2	7.42	14
$Ge(NR'_2)_2$	7.71	$Sn(NR'_2)_2$	7.75	14
$Ge(NR'R'')_2$	7.24	$Sn(NR'R'')_2$	7.26	14
$GeCl_2$	16.7	$SnCl_2$	15.9	8,16
		$Sn(C_5H_5)_2$	16.4	17
$Ge(Cp')Cl$	9.07	–		this work
$Ge(Cp')_2$	8.46	$Sn(Cp')_2$	8.39	this work

[a] $R = (CH(SiMe_3)_2$, $R' = (N(SiMe_3)_2$, $R'' = N(CMe_3)(SiMe_3)$.

the IE. Secondly, the energy may be influenced by covalent mixing with suitable ligand MO's. Simple overlap considerations indicate that such interactions would be the strongest for the interaction involving the totally symmetric combination of the a_1 (D_{5h}) cyclopentadienyl orbitals. However, since the energy of the corresponding MO has been located above 12 eV [1c,5,10], the afore mentioned interaction, if relevant, would result in a shift of the metal lone pair towards low IE. Therefore, the very high values found in both present Ge^{II} and Sn^{II} complexes point to a minor involvement of metal lone pair in covalent interactions. They are likely to be associated with a higher positive charge on the metal atoms and, hence, to an almost ionic nature of the metal–ligand bonding. The trend of increasing $4s^2$ IE on passing from $Ge(Cp')_2$ to $Ge(Cp')Cl$ (Table 2) is consistent with this.

Conclusion

This study, which complements reports on the electronic structure of permethylated cyclopentadienyl d and $5f$ transition metal complexes provides a description of the bonding between the Cp' ligand and of the Main Group IV elements. In spite of the bent sandwich structures these complexes exhibit PE spectral patterns comparable to those of more symmetrical metallocenes. There is evidence, though it is not conclusive, for an admixture of metal p orbitals with those MO's which are combinations of the locally out-of-plane ring C_{2p} orbitals. Fine structures associated with ionizations of these ligand-based MO's may be assigned to specific metal–ligand interactions but may also arise from vibronic excitation of ligand modes in the ^2E ion states.

The very high values, relative to those in other series, of IE's associated with ns^2 ($n = 4$, 5) electrons are indicative of a higher positive charge borne by the central metal atoms, and so of a highly ionic metal–ligand bond. The bent sandwich structure exhibited by the present complexes can thus be explained in terms of repulsive effects due to truly inert metal ns^2 lone pairs.

Finally, we notice that the present study has provided evidence (in the case of Ge complexes) for some discrepancies between PE experimental MO orderings and the results of ab initio calculations for some much simpler related complexes. This could be due either to inadequate extrapolative procedures or to a specific failure of the ab

initio method with the particular Ge complexes. X_α studies of the Ge complexes examined in the present work are currently in progress in this laboratory.

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