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THE ELECTRONIC STRUCTURE AND PHOTOELECTRON SPECTRA OF DICHLORODI-π-CYCLOPENTADIENYL-TITANIUM(IV),-ZIRCONIUM(IV) AND -HAFNIUM(IV)

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Summary

The He^I photoelectron spectra of $(\pi\text{-}C_5H_5)_2MCl_2$, where M = Ti, Zr and Hf, are reported and discussed. The spectra are very similar to each other, and are essentially due to ionization of electrons mainly localized on the cyclopentadienyl rings. An MO calculation, using appropriate CNDO approximations, agrees fairly satisfactorily with the experimental results.

Introduction

The dichlorides of titanocene, zirconocene and hafnocene, $(\pi\text{-}C_5H_5)_2MCl_2$ where M = Ti, Zr or Hf, have been widely studied, mainly in connection with the reactions yielding the disubstituted σ-alkyl and σ-aryl derivatives, much used in homogeneous catalysis [1].

Crystal studies on these metallocene dichlorides have established that the molecular structures show a distorted tetrahedral arrangement of the π-cyclopentadienyl and chloride ligands with idealized C_2 and C_{2v} symmetries [2]. Proton magnetic resonance measurements showed that all cyclopentadienyl protons are chemically equivalent, the signal consisting of one sharp peak with a relative area of ten units [3]. There is thus no evidence for restricted rotation around the metal—ring axes as far as solutions at room temperature are concerned.

The average metal—chloride bond distances are long compared with those found in other tetrahedral complexes which do not contain cyclopentadienyl ligands, and so π-bonded rings may be considered to weaken the metal—halide bonds. Moreover, IR data suggest a considerable ionic character in the ring—metal bonds [4]. Very few attempts have been made to discuss the bonding situation in terms of molecular orbital considerations. To throw light on these matters, the photoelectron spectra of these metallocene derivatives have been recorded and are discussed below.

Experimental and computational details

Commercial samples were purified by sublimation under reduced pressure.

Photoelectron spectra, with the He^I resonance line at 21.21 eV, were recorded on a Perkin—Elmer PS 18 spectrometer using a heated inlet probe. The spectra were obtained at various temperatures and were reproducible with a deviation of 0.05 eV in the peaks positions. The reported ionization energy data refer to spectra obtained at 166, 133 and 121° for the titanium, zirconium and hafnium compounds, respectively. At these temperatures the maximum count rate was several thousand counts s^{-1}. Calibration of spectra was carried out by introducing Xe and Ar mixtures into the ionization chamber, therefore the energy scale in the Figs. is not absolute. Calculations on the electronic structures of such compounds were restricted to the titanium complex. Bond distances and angles were taken from the X-ray determination and neutron diffraction structure of dichloro-1,1'-trimethylenedi-π-cyclopentadienyltitanium [2]. All the atoms of the cyclopentadienyl moiety were assumed to be in the same plane so that the molecule consists of the $TiCl_2$ fragment sandwiched between two non parallel rings.

All valence electron SCF-MO calculations have been carried out by the CNDO method which has given satisfactory results for the electronic structures of some transition metal complexes [5]. This method uses one-centre quantities evaluated from atomic spectroscopic data, assuming that each valence orbital is angular independent. Thus, average energies of the electronic configurations of the atom for three adjacent oxidation states were fitted with the U_i core integrals and with the two-electron γ integrals. More exactly, a single Slater exponent ξ for a *s*-like function was assigned to each valence orbital in order to reproduce all the two-electron integrals.

All the one- and two-centre coulomb integrals were shown to be of the pure theoretical *s*-type. Other computational details are described in ref. 5.

Results and discussion

The method of calculation used has been found useful in investigating the electronic and photoelectronic spectra of transition metal compounds, even though CNDO eigenvalues are expected to be lower than $-I$ energies, using Koopman's approximation. The molecular orbital levels for Cp_2TiCl_2 are listed in Table 1 and characterized by C_s point group symmetry. There are 11 upper filled MO's essentially located on the cyclopentadienyl rings and then a set of MO's located on the chlorine atoms, with the exception of $15a'$. The other low lying MO's up to $11\ a'$ are mainly located in the rings. The PE bands are thus expected to arise from electron ionization of the rings along with a contribution from the chlorine atoms in the region near the calculated 14 eV value; these latter ionization energies are very similar to the averaged ionization energy of the 3*p* shell of the neutral chlorine.

(continued on p 315)

TABLE 1

MOLECULAR ORBITAL SCHEME FOR Cp_2TiCl_2[a]

Symmetry	Eigenvalues (eV)	Composition
...	...	....
$23a'$	0.29	$0.75\ z^2$, $0.04\ x^2-y^2$
$16a''$	0.28	$0.70\ xy$
$22a'$	−0.08	$0.82\ zy$
$15a''$	−0.10	$0.78\ zx$
$21a'$	−0.31	$0.04\ z^2$, $0.80\ x^2-y^2$
$20a'$	−9.38	Cp rings[b]
$14a''$	−10.19	
$13a''$	−10.90	
$19a'$	−11.64	Cp rings
$18a'$	−11.79	
$12a''$	−11.95	
$17a'$	−12.11	
$11a''$	−12.36	
$16a'$	−12.60	
$10a''$	−12.61	
$9a''$	−12.77	
$8a''$	−12.98	Cl (σ, π)
$15a'$	−13.04	Cp rings
$14a'$	−13.53	Cl (σ, π)
$13a'$	−13.56	Cl (σ, π)
$7a''$	−13.62	Cl (π)
$6a''$	−13.68	
$12a'$	−14.69	
$11a'$	−17.93	Cp rings
$10a'$	−20.59	
$9a'$	−21.16	
..	...	....

[a] MO's are filled up to 20 a'. [b] These MO's are characterized by chlorine orbitals up to 0.20 in composition.

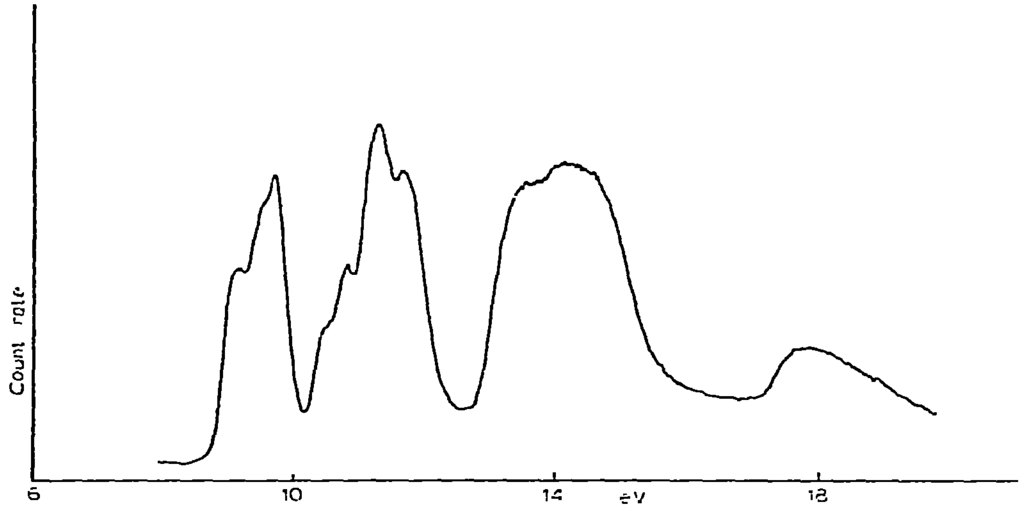

Fig. 1. PE spectrum of $(Cp)_2TiCl_2$.

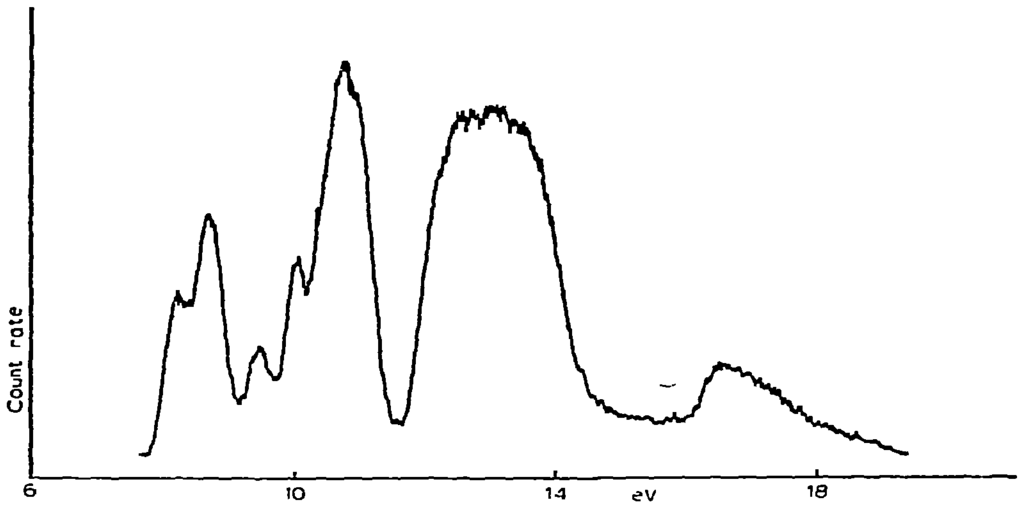

Fig. 2. PE spectrum of (Cp)$_2$ZrCl$_2$.

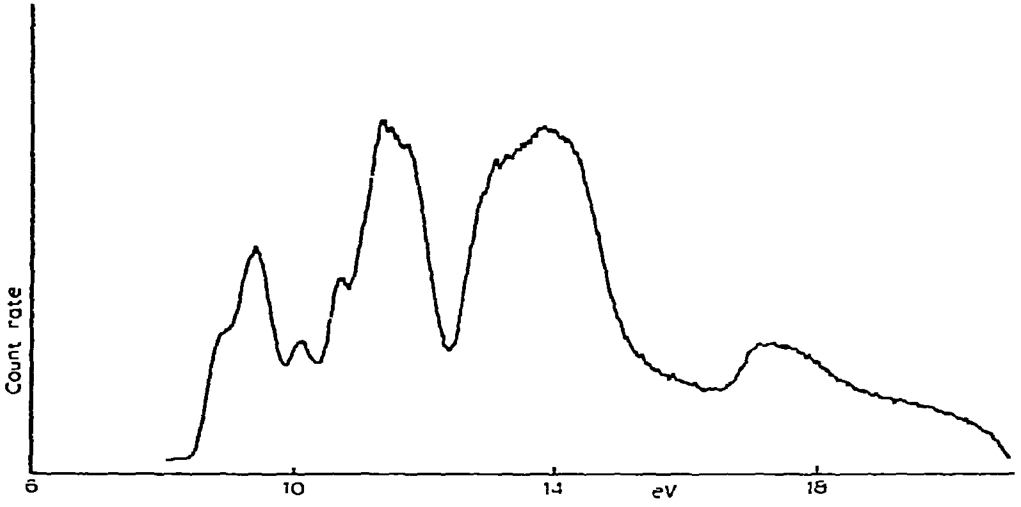

Fig. 3. PE spectrum of (Cp)$_2$HfCl$_2$.

TABLE 2

IONIZATION ENERGY DATA (eV)^a

(Cp)$_2$TiCl$_2$	(Cp)$_2$ZrCl$_2$	(Cp)$_2$HfCl$_2$
8.46	8.60	(8.87)
(8.87)		
9.07	9.08	9.30
(9.95)	9.84	10.00
10.24	10.45	10.60
10.65	11.12	11.32
11.12	11.33	11.60
13.1	13.1	13.2
13.8	13.8	13.7
17.1	17.1	17.8

^{a} Values in parentheses indicate shoulders.

TABLE 3

CALCULATED TRANSITION ENERGIES (eV)

Excited state	Calculated energies	Observed bands[a]
$20a' \rightarrow 21a'$	3.03	
$20a' \rightarrow 15a''$	3.19	3.2
$14a'' \rightarrow 21a'$	3.78	
$20a' \rightarrow 16a''$	3.79	
$20a' \rightarrow 23a'$	3.88	3.9
$20a' \rightarrow 22a'$	3.95	
$14a'' \rightarrow 22a'$	3.97	
$14a'' \rightarrow 23a'$	4.38	
$13a'' \rightarrow 21a'$	4.67	
$14a'' \rightarrow 16a''$	4.71	4.7
$13a'' \rightarrow 22a'$	4.71	
$14a'' \rightarrow 15a''$	4.75	
$13a'' \rightarrow 23a'$	5.16	
$13a'' \rightarrow 15a''$	5.17	
$13a'' \rightarrow 16a''$	5.70	

[a] From ref. 7.

The PE spectra of the examined compounds are reported in Figs. 1, 2 and 3 and summarized in Table 2. Previous photoelectron investigations of some di-π-cyclopentadienyl-metal complexes showed that the PE spectra mainly originate from the bands due to the metal electrons which appear in the low energy region [6]. Since our spectra are closely related to these, the 12-18 eV band system has thus to be assigned to the cyclopentadienyl rings. The calculated and qualitatively expected ionizations characteristic of the chlorine certainly occur in this region, but are hardly detectable in the large envelope of the bands.

The molecular orbital description of $(Cp)_2TiCl_2$ has also been used to investigate the electronic spectrum. The calculated one-electron transition energies are reported in Table 3 together with the experimental band maxima [7]. The agreement is quite good, and thus suggests that the transitions involving electron transfer from the rings to the empty titanium *d* orbitals occur at lower energy than those arising from the chlorine ligands.

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