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Preliminary communication

He(I) AND He(II) EXCITED PHOTOELECTRON SPECTRA OF DICYCLOPENTADIENYLDICARBONYLTITANIUM(II)

IGNAZIO FRAGALÀ, ENRICO CILIBERTO and JOSEPH L. THOMAS

Dipartimento di Chimica, Università di Catania, V. le A. Doria 6 (95125) Catania (Italy) and Department of Chemistry, California University, Fullerton California 92634 (U.S.A.)

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Summary

The first data on the electronic structure of Group IVA element carbonyl complexes are reported. Details of He(I) and He(II) excited photoelectron spectra of dicyclopentadienyldicarbonyltitanium(II) provide information about the metal—ligand bonding.

There has been much interest in the photoelectron (PE) spectra of carbonyl complexes of *d* transition metals [1], but the corresponding spectra of carbonyl complexes of *d* Group IVA elements have not been studied. Only the dicarbonyl derivatives of dicyclopentadienyl-titanium(II), -zirconium(II) and -hafnium(II) are known [2].

We report here the results of a preliminary study of the PE spectra of $Cp_2Ti(CO)_2$ ($Cp = (\eta^5\text{-}C_5H_5)$), carried out with several objectives in mind: (i) to gain information on the bonding in Group IVA element carbonyl complex, (ii) to study the electronic properties of a Group IVA element in the unusually low 2+ formal oxidation state, and finally, (iii) to determine directly the photoionization cross-section of *d* subshells in Group IVA metals.

He(I) and He(II) spectra of $Cp_2Ti(CO)_2$ are presented in Fig. 1, and pertinent ionization energy (*IE*) and relative intensity data are listed in Table 1. The analysis of the PE bands (Table 1) can be attempted, at least in terms of assignment of the bands to ionizations of groups of molecular subshells, on the simple bases of (i) comparison with PE spectra of similar complexes, and (ii) variations of relative intensities on switching from He(I) to He(II) photoionizing radiation. The complex $Cp_2Ti(CO)_2$ is a diamagnetic d^2 species [3], and so the lowest *IE* band (band *a* in the figure) in its spectrum is expected to be associated with a molecular orbital (MO) which is mainly 3*d* based. The trend toward higher relative intensity (with respect to band b which relates to MOs essentially Cp based) of band a on switching from He(I) to He(II) radiation, agrees with the well known higher metal 3*d* photoionization cross-section at the He(II) wave-

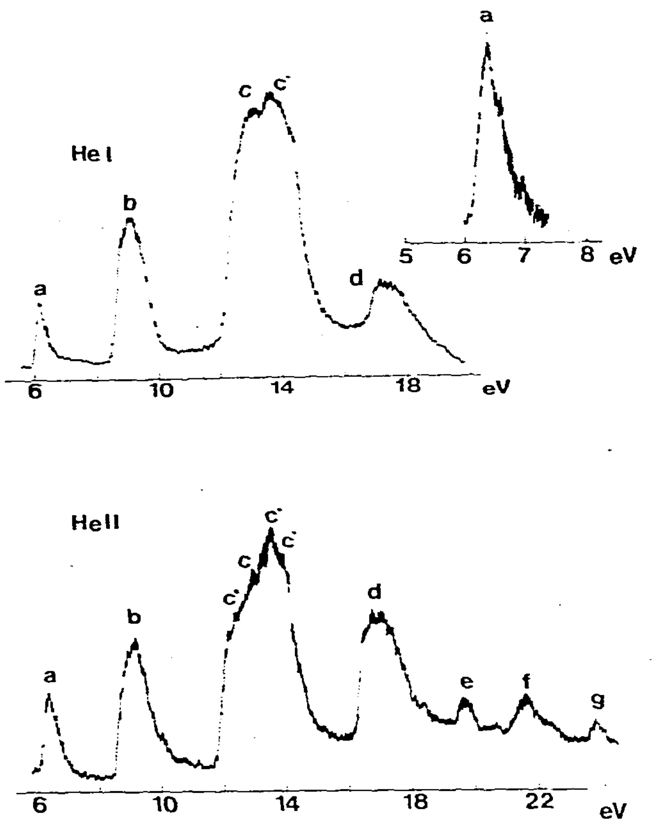

Fig. 1. The He(I) and He(II) PE spectra of $Cp_2Ti(CO)_2$. Close-up of first band a.

TABLE 1

PHOTOELECTRON SPECTRAL DATA OF $Cp_2Ti(CO)_2$

Band label	*IE* (eV)	Intensities		Assignment
		He(I)	He(II)	
a	6.35 (6.63) (6.88)	0.2	0.5	Ti 3*d*
b	9.15	1.0	1.0	Cp π
c^{o}	12.67^{a}	7.1	3.8	Cp a_1 π
c	13.19			Cp σ(C—H)
c^{o}	13.61^{a}			Cp σ(C—C)
c'	14.01			CO 5σ, 1π
d	16.87 17.30	1.3	2.0	Cp σ(C 2*p*)
e	19.63	—	—	Cp σ(C 2*s*)
f	21.77	—	—	CO 4σ
g	23.91	—	—	—

^{a}Detected in the He(II) spectrum.

length [4]. However, there is doubt about whether the MO in question possesses non-bonding or bonding character. The choice between the two alternatives depends upon assessment of the effects of involvement in the metal—ligand bonding of (i) simple $3d$-σ interaction with filled ligand MOs (probably the carbonyl 5σ MO) which leaves the lowest laying metal $3d$ subshell unperturbed, or (ii) $3d$-π back bonding resulting in stabilization of the relevant metal orbital. The vibrational progression associated with band a (Fig. 1) can give crucial assistance in discriminating between the two possibilities, and the interval observed in the PE spectrum of $Cp_2Ti(CO)_2$ (2300 ± 150 cm^{-1}) agrees well with the frequency of the CO stretching modes (ν_1 1975, ν_2 1897 cm^{-1}) in the IR spectrum of the same complex [2]. However, the higher wavenumber measured in the PE spectrum suggests that in the $3d^1$ ion state produced by removal of one electron from the $3d^2$ ground configuration, the C—O distance is shorter than that in the un-ionized complex. This in turn, is a clear indication of a smaller $3d$-π back donation in the $3d^1$ hole state due to the increased positive charge on the metal. Such mechanism leads to a reduced charge density in antibonding MOs, and thus to a shorter bond length.

The band b can be attributed with confidence to ionization of MOs based on cyclopentadienyl rings. An analogous band has been found in the PE spectrum of the parent complex Cp_2TiCl_2 [5]. The poor resolution of the structure of the band in question, compared with that in Cp_2TiCl_2, (where three components are evident) is indicative of a minor involvement of Cp orbitals in the metal—ligand bonding. The bands which follow in the higher *IE* region can be confidently assigned by reference to PE spectra of complexes in which the same ligands are present. In particular the assignments proposed in Table 1 are based on the PE spectra of Cp_2TiCl_2 [5] and of $Cr(CO)_6$ [6].

The two main points which emerge from PE data and which, in turn, provide a very accurate description of the metal—ligand bonding in $Cp_2Ti(CO)_2$ are thus as follows. First, there is evidence for significant metal—ligand back bonding donation involving Ti $3d$ orbitals and empty carbonyl π orbitals. Secondly, there is no evidence of important overlap between the metal and Cp orbitals; the titanium atom can be assumed to cause a small electrostatic perturbation of the cyclopentadienyl ligands.

Acknowledgements

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