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A DV-Xα Theoretical Investigation of the Electronic Structure of some Tris(cyclopentadienyl) Complexes of U(IV)

A. VITTADINI, M. CASARIN*, D. AJÒ

Istituto di Chimica e Tecnologia dei Radiolementi del CNR, Padua, Italy

R. BERTONCELLO

Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Università di Padova, Padua, Italy

E. CILIBERTO, A. GULINO and I. FRAGALÀ

Istituto Dipartimentale di Chimica e Chimica Industriale, Catania, Italy

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The recent growth of organoactinide chemistry [1] has spurred the need for suitable, updated models of the metal–ligand bonding in this large class of molecules, thus offering several intriguing challenges to electronic structural chemists. Among them, the nature and the magnitude of the metal–ligand covalency is probably the most puzzling aspect. Recently we have shown [2] that discrete variational (DV)-Xα calculations, even at non-relativistic level, provide an accurate description of the electronic structure of molecules containing heavy metal atoms like actinides.

In this study we report preliminary results of an extensive investigation on the electronic structure of $(\eta^5\text{-}C_5H_5)_3UX$ (X = F, Cl, Br) complexes (hereafter **I**, **II** and **III** respectively) studied through a combination of He(I)/He(II) UV photoelectron (PE) spectroscopy and non-relativistic DV-Xα first principle molecular orbital calculations.

The PE spectra of **II** have already been reported [3]. In the present study, however, we have accumulated high resolution PE spectra (see Fig. 1) using an IBM PC XT computer directly interfaced to the spectrometer equipped with an Helectros He(I)/He(II) source.

Deconvolutions were carried out by optimizing a series of asymmetrical Gaussian curves to the experimental spectral profiles, after subtraction of background.

Atomic coordinates for title compounds were taken from structural data [4] and were idealized to C_{3v} symmetry. The molecular electron density was approximated with an s-wave expansion in calculating the potential, and the SCF equations were converged by a self-consistent charge (SCC) procedure which has been found to give very good outcomes for molecules containing 5f metals [2, 5]. Numerical atomic orbitals (through 7p on U, 2p on F and C, 3d on Cl, 4d on Br) from an atomic Hartree–Fock–Slater calculation were used as basis functions. A frozen core approximation has been used because of the complexity of the investigated molecular systems. Transition state ionization energies (*TSIE*) have been evaluated [6] only for the outer most occupied molecular orbitals (MOs) of the chlorine derivative. All the molecular calculations were carried out by running the DV-Xα code on a VAX-11/750 minicomputer.

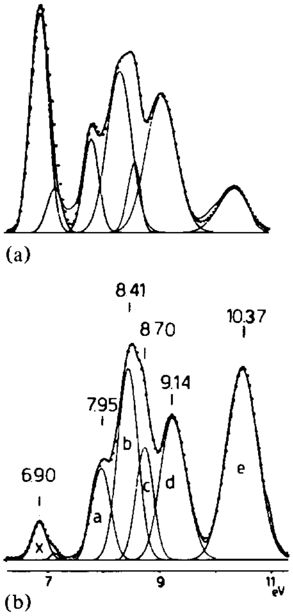

Fig. 1. (a) He(II) and (b) He(I) deconvoluted excited PE spectra of $(\eta^5\text{-}C_5H_5)_3UCl$. Ionization energies refer to the maxima of asymmetric Gaussians.

The ground state charge density data of the eleven outermost MOs of **I**, **II** and **III** (see Tables I, II, III) indicate that in **I** the corresponding eigenvalues are grouped in three well defined energy ranges (see Table I). Each group includes MOs which, in terms of a qualitative localized bonding model, reproduce: (i) almost pure uranium 5f filled AOs; (ii) the combinations of upper-filled π MOs of cyclopentadienyl rings (transforming like $a_1 + a_2 + e + e$ in the C_{3v} symmetry) and finally (iii) the F 2p lone pairs (e in symmetry). By contrast, the cyclopentadienyl and the halogen based MOs are significantly admixed in **II** and in **III** (see Tables II, III).

TSIE values evaluated for upper lying MOs of **II** are compared in Table II with experimental *IE* values. The agreement between the two sets of values is remarkable and, moreover, the He(I) relative inten-

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*Author to whom correspondence should be addressed.

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TABLE I. Orbitals, Eigenvalues and Atomic Orbital Character for Ground State Cp_3UF

MO	Energy (eV)	Character (%)					
		U				F	3Cp
		s	p	d	f		
$6a_2$	−3.97	0	0	0	69	0	31
17e	−4.10	0	0	0	77	6	17
$14a_1$	−4.33	0	1	4	82	9	4
$13a_1$	−4.70	0	0	1	95	0	4
16e (HOMO)	−4.71	0	0	1	94	1	4
$5a_2$	−5.93	0	0	0	27	0	73
15e	−6.21	0	2	1	13	1	83
$12a_1$	−6.21	0	6	0	6	13	74
14e	−6.87	0	1	5	3	4	86
13e	−8.01	0	2	4	3	83	8
$11a_1$	−8.11	1	6	7	7	62	17

TABLE III. Orbitals, Eigenvalues and Atomic Orbital Character for Ground State Cp_3UBr

MO	Energy (eV)	Character (%)					
		U				Br	3Cp
		s	p	d	f		
$6a_2$	−3.96	0	0	0	70	0	30
17e	−4.26	0	0	1	74	8	17
$14a_1$	−4.60	1	0	0	92	6	1
$13a_1$	−4.65	0	0	1	94	1	4
16e (HOMO)	−4.75	0	0	1	94	3	2
$5a_2$	−5.96	0	0	0	25	1	74
15e	−6.05	0	0	0	22	42	36
$12a_1$	−6.13	1	6	0	3	48	42
14e	−6.31	0	2	3	3	39	53
$11a_1$	−6.99	0	0	9	5	36	50
13e	−7.00	0	0	9	0	6	84

TABLE II. Orbitals, Eigenvalues and Atomic Orbital Character for Ground State Cp_3UCl

MO	Energy (eV)	*TSIE*	*IE*	Character (%)					
				U				Cl	3Cp
				s	p	d	f		
$6a_2$	−3.82			0	0	0	67	0	33
17e	−4.12			0	0	1	75	7	17
$14a_1$	−4.43			1	0	1	89	8	1
$13a_1$	−4.54			0	0	1	94	0	5
16e (HOMO)	−4.61	7.07	6.90	0	0	1	94	2	3
$5a_2$	−5.76	7.90	7.95	0	0	0	28	0	72
15e	−6.07	8.24	8.41	0	2	1	17	2	78
$12a_1$	−6.10	8.29	8.70	0	7	0	3	30	60
14e	−6.53	8.73	9.14	0	2	3	5	38	52
13e	−7.06	10.10	10.37	0	0	9	1	49	41
$11a_1$	−7.26	9.98		1	2	8	6	50	33

sity of bands up to 11 eV exactly reproduces the values expected on occupancy ground. Finally, it is noteworthy that the general variations of relative intensities on passing from the He(I) to the He(II) excited PE spectra (see Fig. 1) reproduce very well the character of the corresponding MOs.

These considerations lead us to conclude that, despite the non-relativistic and spin-restricted nature of the present calculations, they can provide a good starting point both to assign PE spectra and describe an adequate bonding model of actinide organometallics. On the other hand, the detailed analysis of the low lying eigenvectors (Tables I–III) seems to indicate a poor contribution from U 6d AOs. This is a well known consequence of the non-relativistic approach [7], which underestimates the role played by the 6d AOs (relative to 5f AOs) in the description of metal ligand interactions in actinide complexes. Therefore, a more rigorous approach certainly needs a fully relativistic treatment.

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