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SCF-Xα SCATTERED-WAVE MO STUDY OF THOROCENE AND URANOCENE

NOTKER RÖSCH and ANDREW STREITWIESER, Jr. *
Lehrstuhl für Theoretische Chemie, Technische Universität, D 8000 München (Germany)
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Summary

SCF-Xα scattered wave calculations are presented for di-π-cyclooctatetraenethorium (thorocene) and -uranium (uranocene). Relativistic effects are not included; nevertheless, agreement with experimental photoelectron spectra is remarkably good. The calculations show that $5f_{\pm 2}$ orbitals of the central metal contribute to ring—metal bonding, as proposed at the time of the first preparations of these compounds, but that 6*d* orbitals are also at least equally important in such bonding.

1. Introduction

Uranocene (di-π-cyclooctatetraeneuranium) was first prepared to examine the possibility of an interaction between ligand π-orbitals and metal *f*-orbitals of a type analogous to that found in the di-π-cyclopentadienyl compounds of the *d* transition metals [1]. Extensive chemical and physical studies and extensions to preparations of other actinide compounds indicate that these systems involve substantial ring—metal covalent bonding, but provide little evidence of the role of *f* orbitals in such bonding [2].

Interaction of metal $f_{\pm 2}$ orbitals with e_2 ligand π-MO's leads to the level ordering $e_{2g} > e_{2u}$ [3]. The first photoelectron spectra of uranocene and thorocene were interpreted on this basis [4,5], but a later study by Clark and Green [6], in which He-I and He-II were compared, led instead to the MO assignment $e_{2u} > e_{2g}$. This ordering would indicate a substantial contribution of the metal 6*d* orbitals to the metal—ring bonding. In the only previous MO study of these compounds, employing the extended Hückel method, the possible role of *d* orbitals was not considered [7]. In the present paper we report the results of our Xα scattered-wave (SW) treatment of uranocene and thorocene.

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* Permanent address: Department of Chemistry, University of California, Berkeley, California 94720 (U.S.A.)

Although these results do not take into account relativistic effects, which must be important with such heavy metals, they can still give important information about the ring—metal bonding in these compounds. They also serve as a useful basis for comparison with experimental results and for evaluating the chemical role of relativistic effects with subsequent calculations in which these effects are included.

2. Details of the calculations

The SCF-Xα-SW method has been successfully used to study the electronic structure of a wide variety of systems, among them typical organometallic compounds, such as ferrocene [8] and Zeise's anion [9]. The SCF-Xα-SW method is an all-electron method which employs Slater's local Xα approximation to the exchange potential [10], the muffin-tin approximation of the electronic potential and the scattered-wave formalism [11] to solve the one-electron Schrödinger equation. It has been described in detail elsewhere [12].

The structure of both compounds was assumed to be of D_{8h} symmetry, as determined by X-ray crystallography [13], with the hydrogens in the plane of the carbon ring system. The same geometry was used for both thorocene and uranocene with a metal—carbon bond length of 2.67 Å, in between that in the uranium (2.647 Å) and that in the thorium compound (2.701 Å). We hoped in this manner to be able to compare the electronic structure independently of geometry changes; the structural differences are in any event small. A "standard" cyclooctatetraene (COT) ring with C—C bond lengths of 1.40 Å and C—H bond lengths of 1.09 Å was employed. The resulting ring—ring distance is 3.89 Å.

The radii for the muffin-tin spheres surrounding the various atoms are determined by symmetry and the requirement of touching spheres. In order to increase the realism of the description of the carbon π-systems we chose the overlapping sphere parametrisation to enlarge the ring spheres by a factor of $\sqrt[3]{2} \simeq 1.26$ [14]. The resulting radii thus determined are (in Å): $r_{\text{metal}} = 1.788$, $r_C = 0.882$, $r_H = 0.491$, and $r_{\text{outer}} = 3.999$.

The atomic exchange parameters α for the exchange potential were taken from the tabulation by Schwarz [12,15]: $\alpha_{\text{metal}} = 0.692$, $\alpha_C = 0.753$, $\alpha_H = 0.777$. The α values for the interatomic and the extramolecular regions were set equal, and taken as the weighted average over the atomic values ($\alpha = 0.762$). The core charges $C1s^2$ and at the metal up to $5p^6$ were kept fixed as determined from atomic SCF-Xα calculations. The remaining 102 electrons for thorocene (and 104 for uranocene) were fully taken into account during the iterations to self-consistency. The spin-polarization of uranocene was neglected at the present level of sophistication. To compute the ionization potentials, Slater's "transition-state" procedure was used [10]. To evaluate the ring—ring interaction in the absence of metal, the corresponding Xα-SW calculation was made for the same geometry of two COT's (a "dimer") without the core charge of the metal sphere. To compensate for the 4 negative charges of the two COT dianions, a uniform surface charge of +4 was included on the outer sphere (Watson's technique [11]). The plus and minus combinations of ring σ orbitals showed little splitting in the "dimer", generally 0.001 to 0.005 Ry. The π levels showed greater splitting, 0.04 to 0.05 Ry and also showed significant population in the "metal" sphere.

The order of the π levels, a_{1g}, a_{2u}, e_{1u}, e_{1g}, e_{2g}, e_{2u}, is exactly as expected on simply ring—ring overlap considerations.

3. Results and discussion

The resulting orbital energies for thorocene and uranocence are summarized in Fig. 1 and compared to the "dimer" energies. Only the relatively high occupied and the lowest unoccupied orbitals are shown. A substantial degree of similarity between the electronic structure of thorocene and uranocene may be deduced, except, of course, for the two electrons in the HOMO e_{3u} orbital of uranocene which are highly localized in the U sphere. The level ordering is similar to that found for ferrocene [8]. In particular, the highest occupied MO s involving ligand are π-type MO s but the lowest π-MO s have energies comparable to the highest σ-type MO s. A comparison of the experimental ionization potentials as determined by photoelectron spectroscopy (PES) [4—6] with our calculated values (see Table 1) shows excellent agreement, and lends confidence in the Xα-SW approach. The calculated level ordering among the highest occupied MO s, $e_{2u} > e_{2g}$, agrees with the recent PES interpretation of Clark and Green [6].

These levels are depressed when compared with the corresponding "dimer" levels, indicating their bonding character. The role of f orbitals in the bonding e_{2u} level is also demonstrated by the ordering of the metal f orbitals, $e_{2u} > e_{1u}$

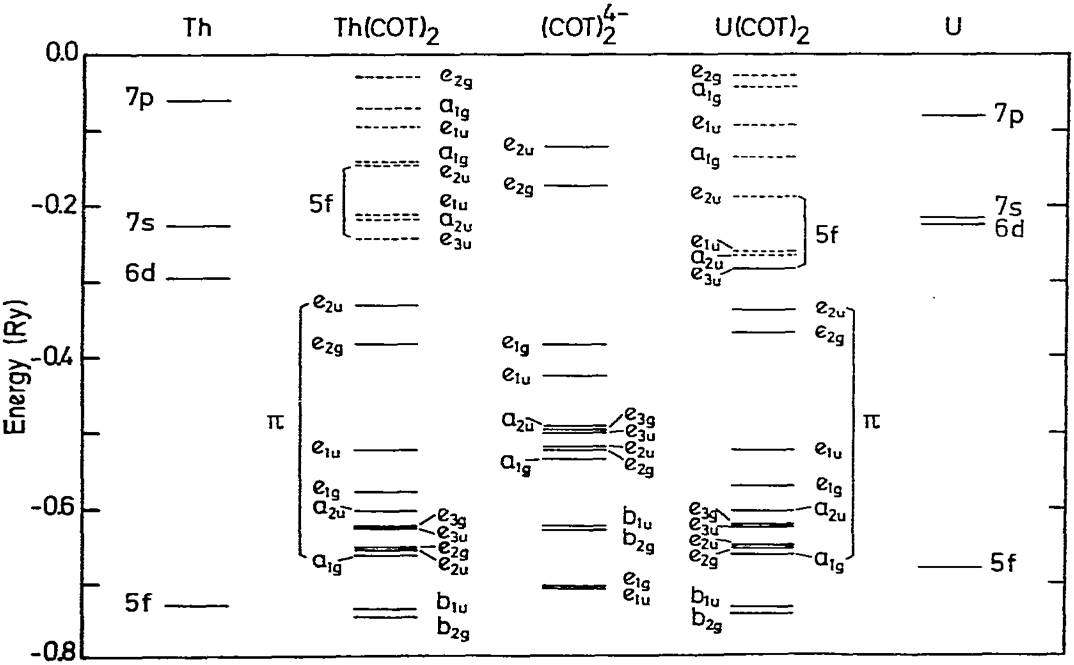

Fig. 1. Comparison of SCF-Xα scattered-wave ground state orbital energies for thorocene and uranocene. Solid lines represent occupied MO s, dashed lines empty ones. The SCF-Xα orbital energies for the various free atoms and the cyclooctatetraene dimer $(COT)_2^{4-}$ are also shown.

TABLE 1

COMPARISON OF $X\alpha$ SCATTERED-WAVE TRANSITION STATE ORBITAL ENERGIES WITH THE PHOTOELECTRON SPECTRUM OF THOROCENE AND URANOCENE

Irred. repr.	Thorocene		Uranocene	
	Trans. state	Exp. [a]	Trans. state	Exp. [a]
$e_{3u}(f)$			6.30	6.20
$e_{2u}(\pi)$	6.57 [b]	6.79	6.83	6.90
$e_{2g}(\pi)$	7.21	7.91	7.00	7.85
$e_{1u}(\pi)$	9.10	9.90	9.11	9.95
$e_{1g}(\pi)$	9.87	10.14	9.74	10.28
$a_{2u}(\pi)$	10.19	10.65	10.20	10.56
e_{3g}	10.49	11.48	10.44	11.50
e_{3u}	10.49		10.46	
e_{2g}	10.90		10.84	
e_{2u}	10.90		10.85	
$a_{1g}(\pi)$	10.99	12.32	10.99	12.37

[a] Ref. 6. [b] All energies in eV.

$\simeq a_{2u} > e_{3u}$. In an axial field the f orbitals are expected to split as $a_{2u} > e_{1u} > e_{2u} > e_{3u}$. The elevation of the antibonding e_{2u} level above this sequence indicates the substantial contribution of f orbitals to the bonding e_{2u} level which is depressed by a comparable amount. The metal involvement in the bonding $e_{2u}(\pi)$ orbital is also indicated by the contour plot of this function in Fig. 2a. Contours of significant value encompass both ligand and metal. The $f_{\pm 2}$ orbitals project towards the carbon atoms to overlap with practically undistorted carbon π orbital.

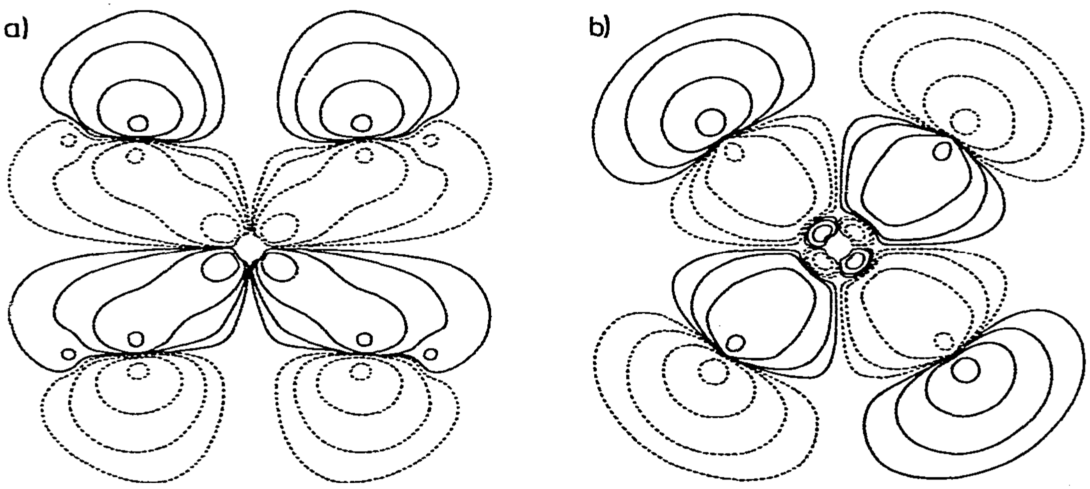

Fig. 2. Contour plots for two ring—metal bonding molecular orbital wave functions of thorocene shown in a plane containing the metal atom and two carbon and hydrogen atoms in both rings. Different signs of the orbitals are indicated by solid and dashed lines. The contour values decrease in absolute value by a factor of $\sqrt{10}$ for every line with the maximum value being 0.12. The interior nodes at the thorium atom are not shown for clarity of presentation. (a) e_{2u} π-orbital at —4.50 eV, (b) e_{1g} π-orbital at —7.86 eV.

Thus, f orbitals contribute to ring—metal bond exactly as suggested originally in the first preparation of uranocene [1]. Nevertheless, the level ordering $e_{2u} > e_{2g}$ in both uranocene and in thorocene points to a significant bonding role also of $6d$ orbitals in the e_{2g} interaction. The e_{2u}—e_{2g} splitting (0.71 eV in the ground state of thorocene, 0.44 eV for uranocene) is comparable to that of the ligand interaction without involvement of metal orbitals which is 0.73 eV in the cyclooctatetraene "dimer". This comparison emphasizes that the contribution of $5f_{\pm 2}$ and $6d_{\pm 2}$ orbitals in these MO s must be comparable; that is, the ligand contributions are about equal in both the $e_{2u}(\pi)$ and $e_{2g}(\pi)$ MO s. Accordingly, we expect ring substituents to have comparable effects on both MO s and the e_{2u}—e_{2g} splitting should be approximately independent of substituents. This corollary is consistent with the only PE spectrum of a substituted case currently available, that of bis(trimethylsilylcyclooctatetraene)uranium in which the splitting of the first two π-orbital peaks, 0.95 eV, is unchanged from uranocene itself [16].

Nevertheless, the lesser e_{2u}—e_{2g} splitting for uranocene compared to thorocene indicates greater f-orbital covalency for the uranium compound. The extent of such covalency is further suggested by the high metal sphere population in the e_{2u} MO. The population is 0.46 for the metal sphere, 0.34 for the carbon spheres and 0.18 for the intersphere region; that is, metal and ligand contribute roughly equally to this MO. The corresponding e_{2u} MO in thorocene shows a smaller metal contribution: 0.33 metal, 0.43 carbons and 0.22 intersphere.

These ring—metal bonding contributions by $f_{\pm 2}$ and $d_{\pm 2}$ orbitals are unique to these COT organometallic compounds. The $5f$ orbitals are, of course, unique to actinides but even the $d_{\pm 2}$ role differs from that in transition metal metallocenes. In such compounds, these d orbitals (in-plane d_{xy} and d_{x^2-y}) participate but little and then only in a back-bonding mode in which occupied d orbitals of a central metal cation interact with vacant e_2 MO s of the cyclopentadienyl rings. In the COT actinide compounds, both sets of orbitals provide a pathway for charge transfer from the COT dianion ligands to the central M^{4+} ion, or, equivalently, from the neutral central metal to neutral COT ligands.

Furthermore, the $d_{\pm 1}$ (d_{xz}, d_{yz}) — e_g interaction so important in ring—metal bonding of transition metal metallocenes is also significant in the present COT actinide compounds. This conclusion stems from the reversal of the level ordering $e_{1g} > e_{1u}$ in the "dimer" to $e_{1u} > e_{1g}$ in both uranocene and thorocene (Fig. 1). The importance of this bonding interaction is also shown by the contour plot of the e_{1g} MO in Fig. 2b. Not only do wave function contours of significant value encompass both metal and ligand but the carbon π type orbitals are distinctly bent towards the metal. This orbital bending provides an explanation for the observed inward bending of methyl groups in bis(1,3,5,7-tetramethylcyclooctatetraene)uranium [17].

We conclude that significant ring—metal bonding results not just from the high-lying e_2 π-MO s of two COT rings but also from the subjacent e_1 π-MO s, and that metal $5f$ and $6d$ orbitals contribute significantly to such bonding.

Finally, it is necessary to emphasize again that these results are limited by the neglect of relativistic effects in the heavy atoms. We intend to extend this work by specific evaluation of relativistic effects; however, we expect that the $6p$ orbitals in Fig. 1 will decrease in energy and become more core-like, and that the relative energies of $6d$ and $5f$ orbitals may change somewhat, but that these effects will not qualitatively change the major conclusions above. We also plan to use the present results to determine the parameters required for more extensive Hückel-type MO treatments, which can then be applied to less-symmetrical compounds.

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