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## Electron affinities of biscyclopentadienyl and phospholyl uranium(IV) borohydride complexes: Experimental and DFT studies

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## ARTICLE INFO

## Article history:

Received 12 January 2010

Accepted after revision 10 May 2010

Available online 29 June 2010

## Keywords:

Electron affinity

Uranium complexes

DFT

COSMO

Half-wave potentials

## ABSTRACT

Electron affinities (EAs) of a series of biscyclopentadienyl and phospholyl uranium(IV) complexes  $L_2U(BH_4)_2$  [ $L_2 = Cp_2, (tmp)_2, (tBuCp)_2, (Cp^*)(tmp)$  and  $Cp^*_2$ ] related to the U(III)/U(IV) redox system were calculated using relativistic Density Functional Theory (DFT) based methods coupled with the Conductor-like Screening Model for Real Solvents (COSMO-RS) approach. Electrochemical measurements of half-wave potentials in solution (tetrahydrofuran THF) were carried out for all these compounds under the same rigorous conditions. A good correlation ( $r^2 = 0.99$ ) is obtained between the calculated EA values, at the ZORA/BP86/TZ2P level, and the half-wave reduction potentials measured by electrochemistry. The investigations bring to light the importance of spin-orbit coupling and solvent effect and the use of a large basis set in order to achieve such a good agreement between theory and experiment. The study confirms the instability of the  $Cp_2U(BH_4)_2$  complex during the reduction process. The influence of the substituted aromatic ligand  $L_2$ , namely their electron donating ability, on EA was studied. The role of involved orbitals (singled occupied molecular orbital –SOMO– of anionic species or lowest unoccupied molecular orbital –LUMO– of neutral species) in the redox process was revealed.

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### 1. Introduction

The energy difference between an uncharged species and its negative ion, referred to as its electron affinity (EA), is an important property of atoms and molecules which was discussed in detail by Schaefer's group [1]. Organic molecules and ligands with high EA are interesting for the design of systems exhibiting flexible reduced states. In this context, actinide complexes with the cyclopentadienyl Cp or  $Cp^*$  ligands ( $Cp = C_5H_5$ ;  $Cp^* = C_5Me_5$ ) deserve a special

attention. For about 30 years the organometallic chemistry of actinides (uranium in particular) has witnessed a spectacular development, with the synthesis of new molecular compounds exhibiting interesting structural, physical and chemical properties [2–6]. Cyclopentadienyl complexes play a major role in catalytic reactions, as well as in multi-electron reductants chemistry combining the traditional U(III)/U(IV) couple and formal ligand based reductions involving the  $Cp^-/Cp$  system [7].

Very few experimental or theoretical studies of the EA of actinide compounds have been published up to now. Among them, a study of Kiplinger and co-workers [8] concerns the fluoroketimide complexes  $(Cp^*)_2U(-N=CMeR)_2$  ( $R = 4-F-C_6H_4$  or  $C_6F_5$ ), while a relatively few

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voltammetry experiments exist for tris- and biscyclopentadienyl compounds in relation with the U(IV)/U(III), U(V)/U(IV) and U(VI)/U(V) redox systems [9–16].

Recently, our group, using relativistic DFT calculations, showed that the EAs of the tris- and biscyclopentadienyl uranium complexes  $Cp_3UX$  ( $X = Cl, BH_4, SPh, S^iPr$  and  $O^iPr$ ) and  $Cp_2^*UX_2$  [ $X_2 = (BH_4)_2, (NEt_2)_2, Cl, Me_2$  and  $(OEt)_2$ ] correlate very nicely with the electron donating capacity of the ligand  $X$  following the order:  $Cl < BH_4 < SPh < S^iPr < O^iPr$  for the first series [17] and  $(BH_4)_2 < (NEt_2)_2 < Cl < Me_2 < (OEt)_2$  for the second one [18]. These studies showed that the quantum method selected, namely the ZORA/DFT technique coupled with the COSMO approach for taking into account solvent effects, is very reliable to study the redox process of organo-uranium complexes. Therefore, we found interesting to estimate the electron affinity of several biscyclopentadienyl uranium(IV) bisborohydride complexes, related to the U(IV)/U(III) redox system, using current relativistic ZORA/DFT techniques (see computational details). Our aim is to investigate the influence of the aromatic L ligand on the electron affinity of the following series of uranium complexes  $L_2U(BH_4)_2$  [ $L_2 = Cp_2$  [19],  $(tmp)_2$  [20,21],  $(tBuCp)_2$  [22],  $(Cp^*)(tmp)$  [23] and  $Cp_2^*$  [23] where  $tmp =$  tetramethylphospholyl ( $C_4Me_4P$ ) and  $tBuCp = t-BuC_5H_4$ ] for which half-reduction potentials are available. Comparison of compounds with aromatic ligands which are isosteric but have distinct electron donating capacities like  $Cp^*$  and  $tmp$  [23], highlighted the importance of the electronic effects of the ligands to explain and predict the structure and the stability of uranium complexes.

The main goals of the work are: (i) to correlate the calculated EA values and the measured half-wave potentials; (ii) to study the role of involved orbitals (singly occupied molecular orbital –SOMO– of anionic U(III) species or lowest unoccupied molecular orbital –LUMO– of neutral U(IV) species) in the redox process; (iii) to investigate the influence of the nature of the L ligand.

## 2. Computational details

The calculations were performed using Density Functional Theory (DFT) [24]. Relativistic corrections were introduced via the Zero Order Regular Approximation (ZORA) [25]. Solvents effects have been taken into account using the Conductor-like Screening Model (COSMO) [26]. The ZORA/DFT calculations were performed using the Amsterdam Density Functional (ADF2008.01) program package [27c]. The Vosko-Wilk-Nusair functional (VWN) [28] for the local density approximation (LDA) and the gradient corrections for exchange and correlation of Becke and Perdew [29], respectively, i.e. the BP86 functional, have been used.

Triple- $\zeta$  Slater-type valence orbitals (STO) augmented by one set of polarization functions (TZP) were used for all atoms. For all elements, the basis sets were taken from the ZORA/DFT/TZP database. The frozen-core approximation where the core density is obtained from four-component Dirac-Slater calculations has been applied for all atoms. 1s core electrons were frozen respectively for boron B.1s and carbon C.1s. For phosphorus P.2p, the 1s/2s/2p cores were

frozen. The U.5d valence space of the heavy element includes the 5f/6s/6p/6d/7s/7p shells (14 valence electrons). Several studies have shown that the ZORA/DFT approach reproduces the experimental geometries and ground states properties of f-block element compounds with a satisfying accuracy [30–34].

The theoretical determination of electron affinities has been so far a difficult task [1]. EA computations generally involve odd-electron systems where spin contamination and SCF convergence problems add to the difficulty of producing reliable results.

Since available experimental molecular EAs are largely adiabatic, the most direct theoretical method comes from the calculation of the difference of the energies of both the neutral and anionic forms of the complexes at their respective optimized geometries, i.e. the “ $\Delta E$  method”.

In terms of the energies  $E$  at optimized geometries, the theoretical definition of EA is:

$$EA = \Delta E = E(\text{neutral}) - E(\text{anion}).$$

The ADF program that we use produces Total Bonding Energies (TBE) rather than total energies, so that EA is computed in our case as the TBE(neutral) – TBE(anion) difference.

## 3. Results and discussion

### 3.1. Molecular geometry optimizations

We have considered the highest spin states of all species, i.e. a triplet state ( $5f^2$ ) for the U(IV) neutral complexes and a quartet state ( $5f^3$ ) for the anionic U(III) ones. All compounds have been taken in the  $C_1$  symmetry.

First, the complete geometry optimizations of the neutral complexes  $Cp_2U(BH_4)_2$ ,  $(tBuCp)_2U(BH_4)_2$ ,  $(tmp)_2U(BH_4)_2$ ,  $(Cp^*)(tmp)U(BH_4)_2$  and  $Cp_2^*U(BH_4)_2$  and their anionic forms were carried out in the gas phase, at the spin unrestricted level of the theory.

Geometries were then further reoptimized in the tetrahydrofuran (THF) solvent using the COSMO approach. The non-default Delley type of cavity was used, the solvent being considered with its dielectric constant of 7.58 and a radius of 3.18 Å. Then, in a third step, we carried out single-point calculations in order to estimate spin-orbit corrections, using the previously optimized geometries, for both the gas phase and solution.

As will be seen later in the text, we also carried out calculations using the more extended ZORA TZ2P basis set which contains two sets of polarization functions (Supporting Information (SI) for more details). Molecular geometry and molecular orbital plots were generated, respectively, by using the MOLEKEL 4.3 [35] and the ADFVIEW [27c] programs.

In Table 1, we give the most relevant computed geometric parameters, i.e. metal–ligand distances and bond angles for the two U(IV) and U(III) species in the gas phase, as well as in solution (for more details, see the SI where one can find all the optimized structures and coordinates).

First of all, the analysis of Table 1 shows a good agreement between the computed geometrical parameters and the available crystallographic data, namely for

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