Investigation of the Dithiolene Ligand Conformation in Analogous U(IV)/U(V) Complexes: X-ray Diffraction and Density Functional Theory Analysis of the U···(C═C) Interaction

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Elucidation of the crystal structure of the dianionic complex [Na(18-crown-6)(thf)$_2$]$_2$[U(COT)(dddt)$_2$] (COT = η^8-C_8H_8, dddt = 5,6-dihydro-1,4-dithiin-2,3-dithiolate), complementing that of [Na(18-crown-6)(thf)][U(COT)(dddt)$_2$], allowed the first structural comparison of analogous uranium(IV) and -(V) compounds with anionic sulfur ligands. The distinct conformations of the dithiolene ligands, *exo*−*exo* and *exo*−*endo* in the uranium (IV) and -(V) complexes, respectively, are the observable manifestation of the differences in the metal−ligand bonding according to the oxidation state of the metal. The relationship between electronic structure, bonding, and conformational changes in these dianionic uranium(IV) and anionic uranium(V) species and the hypothetical neutral uranium(VI) counterpart has been investigated in the framework of relativistic density functional theory. The calculations reveal the occurrence in the uranium(V) anionic species of a significant intramolecular interaction involving the 5f metal orbitals and the C═C double bond of the *endo* dithiolene ligand, which stabilizes its peculiar *exo*−*endo* conformation. Such an interaction does not exist in the uranium(IV) complex.

Introduction

In the past few years we have investigated the chemistry of dithiolene compounds of the f-elements. We isolated a series of homoleptic dithiolene complexes of cerium(III), neodymium(III), and uranium(IV), which exhibit either mononuclear, infinite chain, or honeycomb network crystal structures.[1,2] We have been interested in organouranium compounds too, with the neutral mono(cyclooctatetraenyl) uranium(IV) complexes of general formula [{U(COT)(dithiolene)}$_2$], their Lewis base adducts [U(COT)(dithiolene)(L)$_2$] (COT = η-C_8H_8; L = Lewis base),[3] and the dianionic complex [Na(18-crown-6)(thf)$_2$]$_2$[U(COT)(dddt)$_2$] (**1**) (dddt = 5,6-dihydro-1,4-dithiin-2,3-dithiolate), precursor of the unique example of a uranium(V) complex with metal−sulfur bonds, the monoanionic derivative [Na(18-crown-6)(thf)][U(COT)(dddt)$_2$] (**2**).[4] Very recently, our investigations focused on the family of bis(pentamethylcyclopentadienyl) complexes, a model in organo-f-element chemistry.[5] The synthesis of [K(15-crown-5)$_2$][Ln(Cp*)$_2$(dddt)] (Ln = Ce, Nd; Cp* = η-C_5Me_5) and [Na(18-crown-6)(thf)$_2$][U(Cp*)$_2$(dddt)] allowed the first structural comparison of analogous lanthanide(III) and actinide(III) compounds with anionic sulfur ligands. The theoretical calculations using density functional methodology including relativistic scalar corrections brought to light the major metal−ligand orbital interactions leading to lanthanide/actinide differentiation. Structural comparison and theoretical calculations of the two uranium [U(Cp*)$_2$(dddt)]$^{-,0}$ complexes show that ligand-to-metal donation is enhanced when passing from the U(III) to the U(IV) species.[6] Moreover, the molecular orbital analysis highlighted the important role played by the 5f uranium orbitals in the metal−ligand bonding. Although the latter complexes exhibit a folded MS_2C_2 metallacycle, theoretical calculations indicate that a direct interaction between the dithiolene C═C double bond and the metal ion seems unlikely mainly because of steric constraints due to the Cp* ligands.

In light of these new results we decided to reinvestigate the other oxido-reduction uranium compound couple, namely, the uranium(IV) and uranium(V) complexes [U(COT)(dddt)$_2$]$^{-2,-1}$. This decision was strengthened by the elucidation of the crystal structure of the dianionic U(IV) compound, which reveals that the conformation of the dddt ligand is quite different from that previously found in the monoanionic U(V) counterpart. As previously done,[6] we make use of relativistic density functional theory (DFT) to study the electronic structure of these complexes

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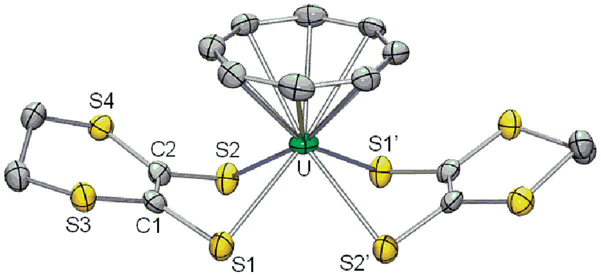

Figure 1. View of the crystal structure of the dianion [U(COT)(dddt)$_2$]$^{2-}$ in **1**·2thf. Hydrogen atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. Symmetry code: ′ = 1−*x*, *y*, 1.5−*z*.

in order to explain their geometric features and properties. In this paper we shall also consider the hypothetical [U(COT)(dddt)$_2$], the neutral uranium(VI) congener of these two uranium(IV) and -(V) complexes.

Results and Discussion

Crystal Structures of the Complexes. A view of the dianion in [Na(18-crown-6)(thf)$_2$]$_2$[U(COT)(dddt)$_2$]·2thf (**1**·2thf) is shown in Figure 1. The crystal structure of the uranium(V) compound **2** has already been described in a preliminary report;[4] however here we will discuss the U···C(C═C) bond distances, a feature that has not been developed in the previous communication; its main geometrical features will be recalled too, for comparison with its uranium(IV) counterpart. The dianion [U(COT)(dddt)$_2$]$^{2-}$ in **1** has a crystallographic binary axis containing the uranium atom and the centroid of the COT moiety, while the cations [Na(18-crown-6)(thf)$_2$]$^+$ are located either on a symmetry center (Na(1)) or on a binary axis (Na(2)), the latter being highly disordered.

The uranium atom is five-coordinate in a distorted square pyramidal arrangement if the cyclooctatetraene is considered as a monodentate ligand. The U atom is 1.5245(12) Å above the basal plane formed by the four S atoms (rms deviation 0.059 Å), the latter being parallel to the planar COT ring. In agreement with the variation of the radii of the uranium(IV) and uranium(V) ions,[7] the U−S bond lengths in **1** [mean value 2.7782(6) Å] are larger by ca. 0.09 Å than in **2** [mean value 2.693(5) Å] (Table 1). These distances are similar to those observed in other uranium(IV) dithiolene complexes.[2,3] The characteristic features of the dddt^{2-} ligand, i.e., the C−S [average 1.77(2) Å] and C═C [1.360(8) Å] bond lengths, are consistent with those found in [Mo(Cp)$_2$(dddt)] [1.76(1) and 1.33(1) Å],[8] [Ti(Cp)$_2$(dddt)] [1.739(4) and 1.366(8) Å][9] (Cp = η-C$_5$H$_5$), and the other uranium(IV) dithiolene complexes [U(COT)(dddt)(OPPh$_3$)$_2$] [1.78(2) and 1.35(2) Å] or [U(COT)(dddt){OP(NMe$_2$)$_3$}$_2$] [1.765(8) and 1.343(10) Å].[3] The US$_2$C$_2$ ring in **1** is strongly folded along the S−S axis, with a dihedral angle θ of 64.75(11)° between the US$_2$ and S$_2$C$_2$ planes (Figure 2), more important than those encountered in the bis-Cp* compound [U(Cp*)$_2$(dddt)][6] owing to lower steric interactions. However, the carbon atoms of the C═C double bond remain at a distance from the uranium atom larger than 3 Å.

Table 1. Selected Bond Lengths (Å) and Angles (deg) in the Anions of 1 and 2

	[U(COT)(dddt)$_2$]$^{2-}$ **1**	[U(COT)(dddt)$_2$]$^{-}$ **2**
U−S(1)	2.7775(16)	2.694(2)
U−S(2)	2.7788(16)	2.687(2)
U−S(5)		2.700(2)
U−S(6)		2.690(2)
⟨U−S⟩	2.7782(6)	2.693(5)
⟨U−C(COT)⟩	2.752(3)	2.724(17)
U···centroid	2.047	2.033(3)
U−C(1)	3.236(6)	3.119(7)
U−C(2)	3.218(5)	3.108(7)
U−C(5)		2.947(7)
U−C(6)		2.960(7)
U−C(1)═C(2)	3.155(6)	3.027(9)
U−C(5)═C(6)		2.867(9)
S(1)−C(1)	1.761(6)	1.751(7)
S(2)−C(2)	1.760(6)	1.744(7)
S(3)−C(1)	1.772(6)	1.756(7)
S(4)−C(2)	1.768(6)	1.776(6)
S(5)−C(5)		1.750(7)
S(6)−C(6)		1.761(7)
S(7)−C(5)		1.757(7)
S(8)−C(6)		1.757(7)
C(1)−C(2)	1.360(8)	1.357(9)
C(5)−C(6)		1.363(9)
S(1)−U−S(2)	72.87(5)	75.15(6)
S(5)−U−S(6)		74.78(6)
S(1)−U−S(2′)[a]	72.13(5)	
S(1)−U−S(5)		77.75(6)
S(2)−U−S(6)		79.53(6)
θA	64.75(11)	65.7(2)
θB		76.2(2)

[a] Symmetry code: ′ = 1−*x*, *y*, 1.5−*z*.

The most remarkable feature in the crystal structure of **1** is the dramatic structural change induced by the variation of the metal oxidation state. In **1**, the dithiolene ligands adopt an *exo*−*exo* conformation, which contrasts with the marked *exo*−*endo* conformation in the uranium(V) species **2**. Previous studies on dithiolene compounds of the d transition metals have shown that θ increases upon lowering the electron density on the metal, reflecting the strength of the interaction of an empty metal orbital with the HOMO of the dithiolene ligand.[9,10] The mono(cyclooctatetraenyl) complexes are the perfect candidates to validate this proposition with an f transition metal since, in contrast to the bis(pentamethylcyclopentadienyl) family, there is no steric limitation to the folding angle of the US$_2$C$_2$ metallacycle. Indeed, in compound **2** the θ value of 76.2(2)° in the *endo* conformation, adopted by the dddt ligand, brings the C5 and C6 atoms in close contact with the uranium atom. The U−C5 and U−C6 bond lengths of 2.947(7) and 2.960(7) Å are similar to the average U−C distances observed in the strongly folded uranium dithiolene complexes.[3] One could imagine that, in these compounds, the θ value would echo a direct interaction between the dithiolene C═C double bond and the metal ion.

The crystal packing shows the presence of a weak intermolecular S···S interaction between atom S4 and its image through the symmetry center, giving chains of alternating upside-down molecules along the *c* axis. The corresponding distance [3.601(3) Å], which is in the range of previously reported nonbonding S···S distances,[11] is shorter than those observed in [W(Cp)$_2$-

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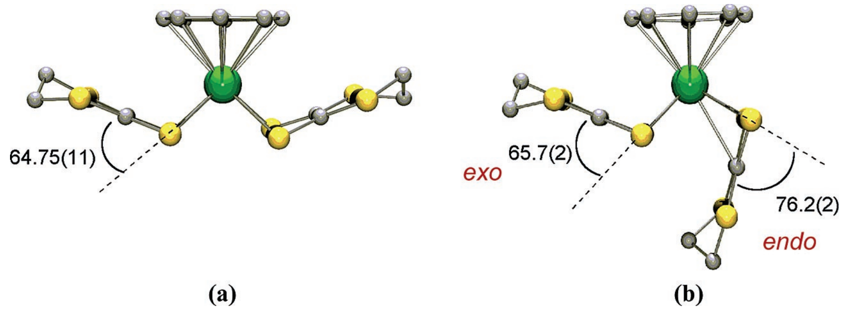

Figure 2. Side view of the (a) U(IV) and (b) U(V) anions. The folding angles (deg) are indicated.

(dddt)][tcnq] (3.730 Å) or [tcnqf$_4$][W(η-$C_5H_4Bu^t$)$_2$(C_3S_5)] (3.793 and 3.811 Å) (tcnq = tetracyanoquinodimethane; tcnqf4 = 7,7,8,8-tetracyano-1,2,4,5-tetrafluoroquinodimethane).[12] The location of the solvated cations [Na(18-crown-6)(thf)$_2$]$^+$ prevents a face-to-face arrangement, which could have led to intermolecular magnetic interactions.

Density Functional Theory Calculations. As mentioned before, the computational method we chose to apply is relativistic DFT in the framework of the zero order regular approximation (ZORA). The computational details and references are given in the Experimental Section. Several studies have shown that the DFT/ZORA method reproduces the experimental geometries and properties of f-element compounds with a satisfying accuracy.[13] Indeed, although an accurate description of the electronic structure of open-shell organoactinide compounds needs high-level post-Hartree−Fock multiconfigurational computations, it has been shown that single-reference DFT methods give generally a reasonable account of their ground-state structure and properties. This subject is well documented.[13j,m,n]

With the exception of the hypothetical neutral form, not yet characterized, the [(U(COT)(dddt)$_2$]^x dianionic ($x = -2$) and anionic ($x = -1$) species exhibit an open-shell structure. The formal oxidation state of the uranium atom is respectively equal to +4 (5f^2 configuration), +5 (5f^1), and +6 (5f^0) in the dianionic, anionic, and neutral complexes. For all complexes, we considered the highest spin state as the ground state, i.e., a triplet state for the dianion and a doublet one for the anion; such states can be correctly described by a single Kohn−Sham determinantal wave function. However, the 5f metal orbitals generally exhibit degeneracy or near-degeneracy in a molecule, which often makes it difficult to achieve convergence in the SCF processes.[13a] To accelerate these processes, the "smearing" recipe allowing the 5f electrons to spread over a wide range of 5f orbitals has been applied, leading thus to no integral MO occupancies. This recipe has already been successfully applied to organoactinide compounds.[6,13b,k,m] The geometries of all the species under consideration were fully optimized. At the convergence geometry, the highest MOs, which are very close energetically to one another, were obtained respecting an Aufbau electronic structure.

Molecular Geometry Optimizations. The molecular geometry optimizations of the open-shell species have been performed in two steps: first making use of spin-restricted calculations, then, starting from the obtained spin-restricted geometry, a more rigorous spin-unrestricted calculation has been carried out; in the latter case, α and β electrons are described by MOs that might be different. We have found that the computed geometries at the spin-unrestricted level are very close to the restricted ones. Energetically, the highest spin state is always more stable than the fictitious spin-restricted one.

Several conformations of the [U(COT)(dddt)$_2$]^x species can be considered because of the apparent US_2C_2 metallacycle flexibility.[3] We have been able to determine different structures, among the most stable ones, which we have labeled A, B, C, D, and E for the dianionic U(IV) species, F, G, H, and I for the anionic U(V) one, and J and K for the hypothetical neutral U(VI) form.

Starting from the standard symmetrical idealized structure of Figure 3, the geometry optimizations led us to different forms depending on the electronic charge borne by the complex. This indicates that the molecular conformations of the species under consideration are driven by electronic factors.

First, considering the dianionic complex, the optimization without any symmetry constraint gives form A. When enforcing the C_s symmetry, the optimization leads to form B. Geometry C results from the optimization without symmetry constraints of the experimental X-ray structure, labeled D. The different F, G, H, and I conformations of the anionic species [U(COT)(dddt)$_2$]$^-$ have been obtained in the same way; structure G results from the optimization of the symmetric standard geometry without any constraint, whereas for the F form, the C_s symmetry has been imposed. Form H derives from the optimization of the experimental geometry (I). Finally, the dianionic E structure has been obtained from the reoptimization of the G geometry of the anion after reduction. The J and K structures relative to the hypothetical neutral species [U(COT)(dddt)$_2$], with a uranium ion formally +6, result respectively from the optimizations of the oxidized anionic geometry G and from the initial standard geometry (Figure 3).

Figures 4 and 5 show the different optimized structures with the indication of their relative stability as well as the main bond lengths. As expected, the different conformations of a given species are close in energy.

It appears that the optimization of the initial symmetric standard geometry (Figure 3) for the anion leads to dissymmetric structures (forms F or G), in agreement with experiment, whereas a symmetric structure is kept for the dianion (forms A

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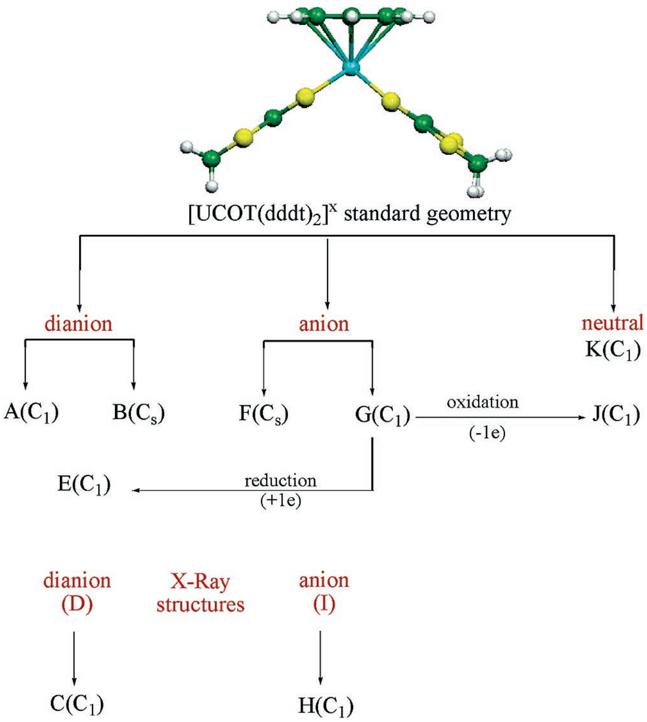

Figure 3. Different geometries resulting from the optimization of a standard symmetric structure.

and B). The observed folding of the US$_2$C$_2$ metallacycle in these complexes is thus well reproduced by our ab initio computations. For the dianionic species (Figure 4), the most stable structure is form C, which has C_1 symmetry, but is very close to the C_2 one experimentally observed in the solid state. For the anionic species (Figure 4), the most stable form, H, is also the experimentally observed one. For the neutral species (Figure 5), with no experimental data available, form K is predicted to be the most stable. The total bonding energy (TBE), which is the energy difference between the molecule and its constituting atoms, of the three most stable species C, H, and K are respectively equal to −239.614, −240.865, and −237.804 eV. The low energetic gap of 1.25 eV between the U(IV) and U(V) complexes is in agreement with their facile electrochemical interconversion. On the contrary, this gap is relatively high (3.1 eV) between the U(V) and U(VI) species.

In Figure 4, the computed geometric parameters for the different conformations under study and the corresponding experimental data are compared (see also Table 1 in the Supporting Information). In our discussion, we will consider the most stable structures, i.e., form C for the dianion, form H for the anion, and form K for the neutral complex, unless otherwise specified: U−COT is the distance between the metal and the centroid of the C$_8$H$_8$ ring, the U−C(COT) values are the shortest and the longest of the eight uranium−COT carbon atom bond lengths, U−S and S−C are the average distances for each of the two dddt ligands as indicated in Figure 6, U···(C═C) is the distance between the metal and the middle of the C═C bond, and θ is the folding angle of the US$_2$C$_2$ metallacycle.

The computed geometries are found to be close to the experimental crystal structures; however, the U−COT and U−C(COT) computed distances are, in a general manner, slightly overestimated compared to experiment. The metal-to-ligand distances diminish with the increase of the metal ion formal charge; this variation parallels that of the radii of the metal ions.[7]

As mentioned above, a striking structural difference appears when we compare the dianionic and anionic complexes, the latter one undergoing a spectacular distortion of one of the two US$_2$C$_2$ metallacycles upon oxidation (Figure 2). Such structural modification is not expected in regard to the redox properties of the organo-uranium complexes, which are supposed to concern mainly electrons localized on the central metal atom. In general, the actinide complexes known for their catalytic properties undergo oxidation and reduction processes, with a minor modification of their molecular geometry. Besides the *endo* distortion of one UC$_2$S$_2$ metallacycle in the anion relative to the dianion, it is worth comparing the structural data, in particular those concerning the U···(C═C) distance and the dihedral angle θ relative to the *endo* and *exo* US$_2$C$_2$ metallacycles.

For the anionic species, the value of the *endo* angle θ is large in all conformations. This value, which averages 74.2° for the F and G conformations, is very close to that obtained for the most stable H form (72.7°) and that observed in the crystal structure (76.2°). The U···(C═C) distances, 2.812, 2.911, and 2.930 Å in the F, G, and H forms, indicate that the double bond corresponding to the *endo* dithiolene is very close to the metal center. Indeed, the average value of 2.884 Å for the U···(C═C) computed distances is comparable to the U−C(Cp*) "long organometallic distances" observed in tris(pentamethylcyclopentadienyl) U(IV) complexes (2.780−2.920 Å).[14] On the contrary, a direct U···(C═C) η^2 bonding interaction is less probable in the dianionic complex; not only is the value of the folding angle θ lower, but the U···(C═C) distance is longer than in the anionic case, e.g., 3.130 Å in form C versus 2.930 Å in form H.

Furthermore, the comparative crystallographic study of a series of neutral mono(cyclooctatetraenyl) dithiolene uranium complexes of general formula [U(COT)(dithiolene)L$_n$] (L = Lewis base) brought to light particularly short U···(C═C) distances, from 2.879(5) to 2.969(11) Å.[3] In these uranium(IV) complexes, the US$_2$C$_2$ metallacycle can adopt an *endo* conformation with θ values varying from 65.9° to about 80.6°. However, U···(C═C) distances larger than 3.0 Å can also be observed in some sterically crowded complexes bearing chelate or polydentate groups. In the latter species, the co-ligand overcrowds the neighborhood of the double bond and consequently hinders its interaction with the metal center in the complex.

Thus, an η^2-*endo* interaction between the *endo* dithiolene ligand and the uranium(V) atom can be expected in the anionic complex, owing to the short U···(C═C) distance and large θ angle observed for that species. Moreover, the C═C double bond length in *endo* position is slightly longer than that in *exo* position, being respectively equal to 1.363 and 1.357 Å, as indicated in Figure 4. As we shall see later, this structural feature is also in favor of the supposed interaction. Such an intramolecular interaction in actinide complexes has been reported in other theoretical and experimental studies. Marks et al. highlighted metal−diene interaction in the case of thorium and uranium(IV) [An(Cp*)$_2$(diene)] complexes.[15] Recently, other experimental and theoretical studies emphasized this intramo-

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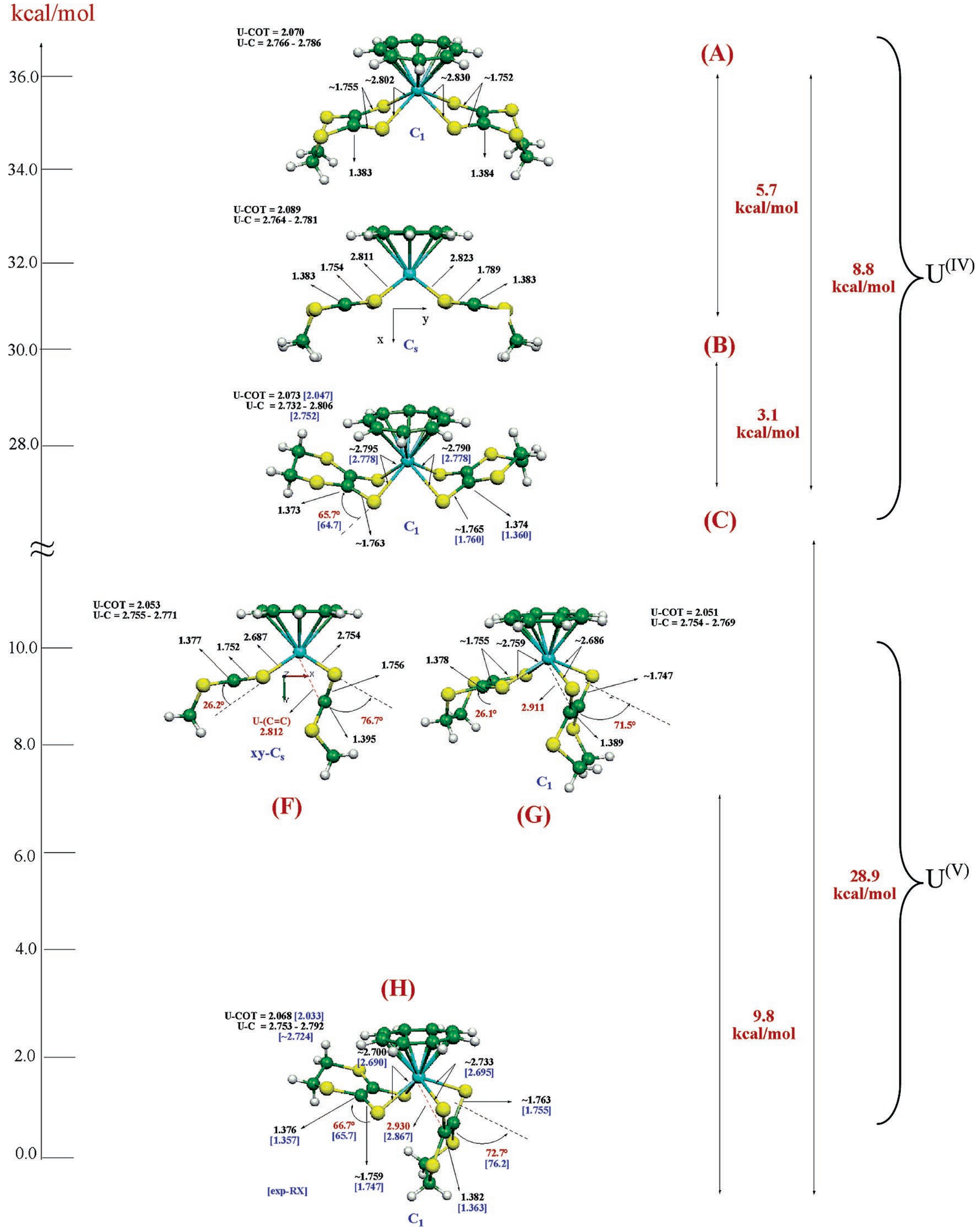

Figure 4. Geometries and relative energies of different computed conformations of the U(IV) dianionic and U(V) anionic complexes $[U(COT)(dddt)_2]^{-2}$ and $[U(COT)(dddt)_2]^{-}$ (distances in Å, COT is the centroid of the C_8H_8 ring).

lecular interaction, which appears to be one of the most interesting features of actinide complexes. In their crystallographic structural analysis of some sterically unsaturated systems,[14] Evans et al. have reported that the common occurrence of agostic interactions in 5f-element complexes is indicative of their tendency to increase their electrostatic stabilization by interacting with any nearby available electron density. Kiplinger et al. have also reported this intramolecular phenomenon in high-valent organoactinide compounds.[16]

On a theoretical level, Bursten et al.[17] have reinforced this hypothesis; through X_α electronic structure calculations they highlighted the actinide ions' propensity to interact with neighboring unsaturated bonds or to activate inert C−H bonds. Indeed, this type of agostic interaction is favored by the presence of 5f diffuse metal-based orbitals and the sizable coordination spheres of actinide ions, sterically and electronically unsaturated.[17c,d]

Two forms, J and K, have been computed for the neutral species. The latter form exhibits an *exo*-type US_2C_2 metallacycle

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(16) (a) Kiplinger, J. L.; Morris, D. E.; Scott, B. L.; Burns, C. J. *Chem. Commun.* **2002**, 30. (b) Kiplinger, J. L.; John, K. D.; Morris, D. E.; Scott, B. L.; Burns, C. J. *Organometallics* **2002**, *21*, 4306.

(17) (a) Bursten, B. E.; Strittmatter, R. J. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1069. (b) Strittmatter, Richard J.; Bursten, B. E. *J. Am. Chem. Soc.* **1991**, *113*, 552. (c) King, R. B. *Inorg. Chem.* **1992**, *31*, 1978. (d) Kaltsoyannis, N.; Scott, P. *The f Elements*; Oxford Chemistry Publications, 1999.

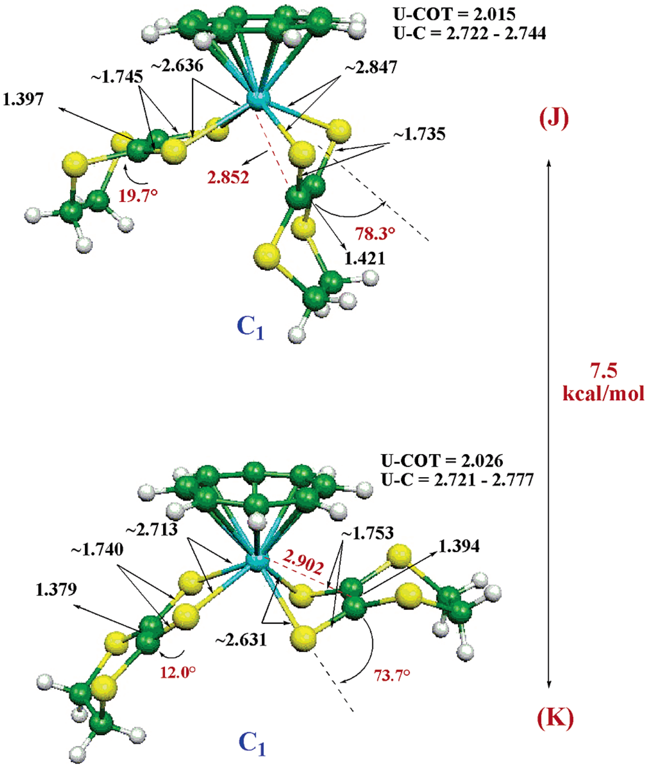

Figure 5. Geometries and relative energies of different computed conformations of the hypothetical U(VI) neutral complex [U(COT)(dddt)] (distances in Å, COT is the centroid of the C_8H_8 ring).

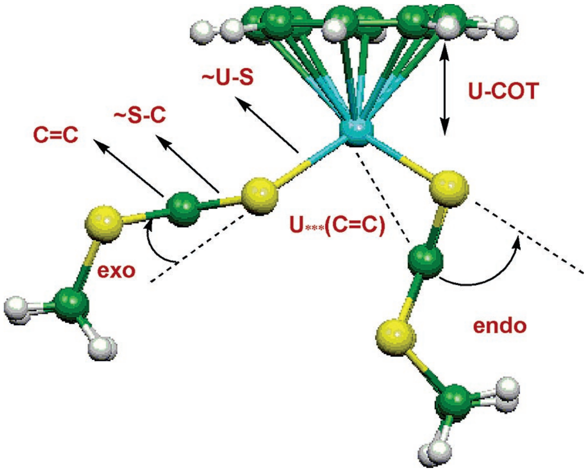

Figure 6. Definition of the geometrical parameters.

and a quasi-planar one, the corresponding θ folding angle being only 12.0° (Figure 5). The results bring to light the contraction of the shortest U···(C═C) distance, from 2.930 to 2.902 Å when passing from the anionic H form to the neutral K one. All the other distances U−(COT), U−C(COT), and U−S are shorter in the neutral species K according to the ionic radii $r^{+5} > r^{+6}$ variation for the same coordination sphere.[7] On the contrary, the C═C bond length increases from 1.382 in the *endo* position in anion H to 1.394 Å in the *exo* dithiolene of the neutral K complex. Moreover, the related θ dihedral angle increases from 72.7° to 73.7°. These structural variations seem to indicate a stronger interaction between the uranium atom and the C═C double bond of the folded metallacycle in the neutral form.

Comparing the most stable conformations of $[U(COT)(dddt)_2]^x$, we note that the average length of the $C(sp^2)-S$ bond diminishes slightly from 1.764 to 1.761 and 1.747 Å going from the dianionic to the anionic and neutral complexes. On the contrary, the length of the C═C bond of the more folded metallacycle increases notably in the same direction (1.374, 1.382, and 1.394 Å). Thus, the oxidation of the dianionic species affects not only its conformation but also the bond lengths of the dithiolene ligand in *endo* position, indicating a partial contribution of the dithiolene ligand in the oxidation process, as observed[18] in transition metal complexes such as $Cp_2Mo(dithiolene)^{0,+}$ or $Cp^*Mo(dithiolene)_2^{-,0}$.

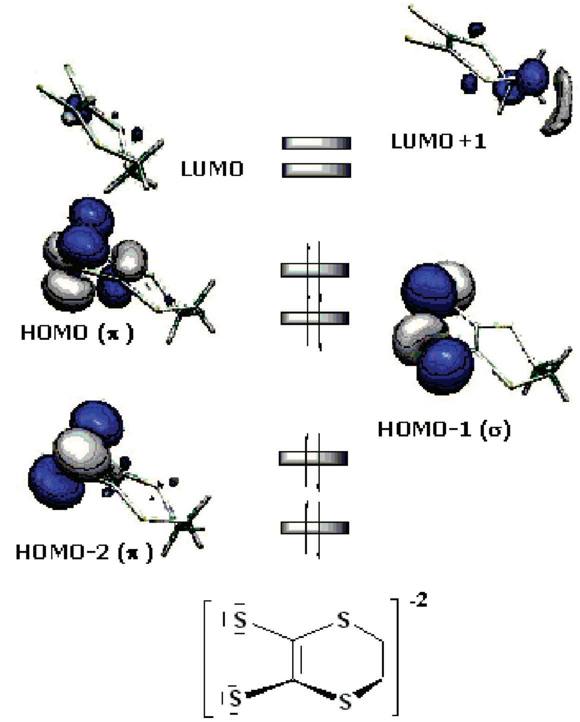

Figure 7. Frontier MOs of the dithiolene free ligand.

Electronic Structure Analysis. The electronic structure of the species under investigation will be considered in order to rationalize the observed peculiar geometries of the dianionic and anionic complexes. The frontier MOs of the dithiolene ligand will first be described, then those of the complexes. In the last part of this paper, we shall consider the results of Mulliken and Mayer population analyses and the interaction of the $U(COT)^y$ and $dddt_2^{-4}$ constituting fragments of the complexes will be considered.

Dithiolene dddt^{-2} Ligand. The dddt^{-2} dithiolene group is a dianionic ligand whose −2 formal charge is borne by the terminal sulfur atoms as shown in Figure 7. As can be seen from its σ and π frontier MOs, the dithiolene ligand is attractive for its potential to serve not only as a σ-donor but also as a π-donor. This explains its properties and capacity to stabilize high oxidation states of the uranium atom.

The presence of the "big" sulfur electron pairs in the direction of the metal plays a major role in the flexible character of the dithiolene ligand. These electron pairs may interact strongly with metal-based orbitals, in particular with the 5f ones, whatever the dithiolene conformation.

U(IV) Complex. The MO compositions of the different forms of the dianionic $[U(COT)(dddt)_2]^{-2}$ species are very similar. Figure 8 shows the MO diagram obtained at the spin-unrestricted level for structure C in its triplet state.

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[18] (a) Domercq, B.; Coulon, C.; P. Feneyrou, P.; Dentan, V.; Robien, P.; Fourmigué, M. *Adv. Funct. Mater.* **2002**, *12*, 359. (b) Domercq, B.; Coulon, C.; Fourmigué, M. *Inorg. Chem.* **2001**, *40*, 371.

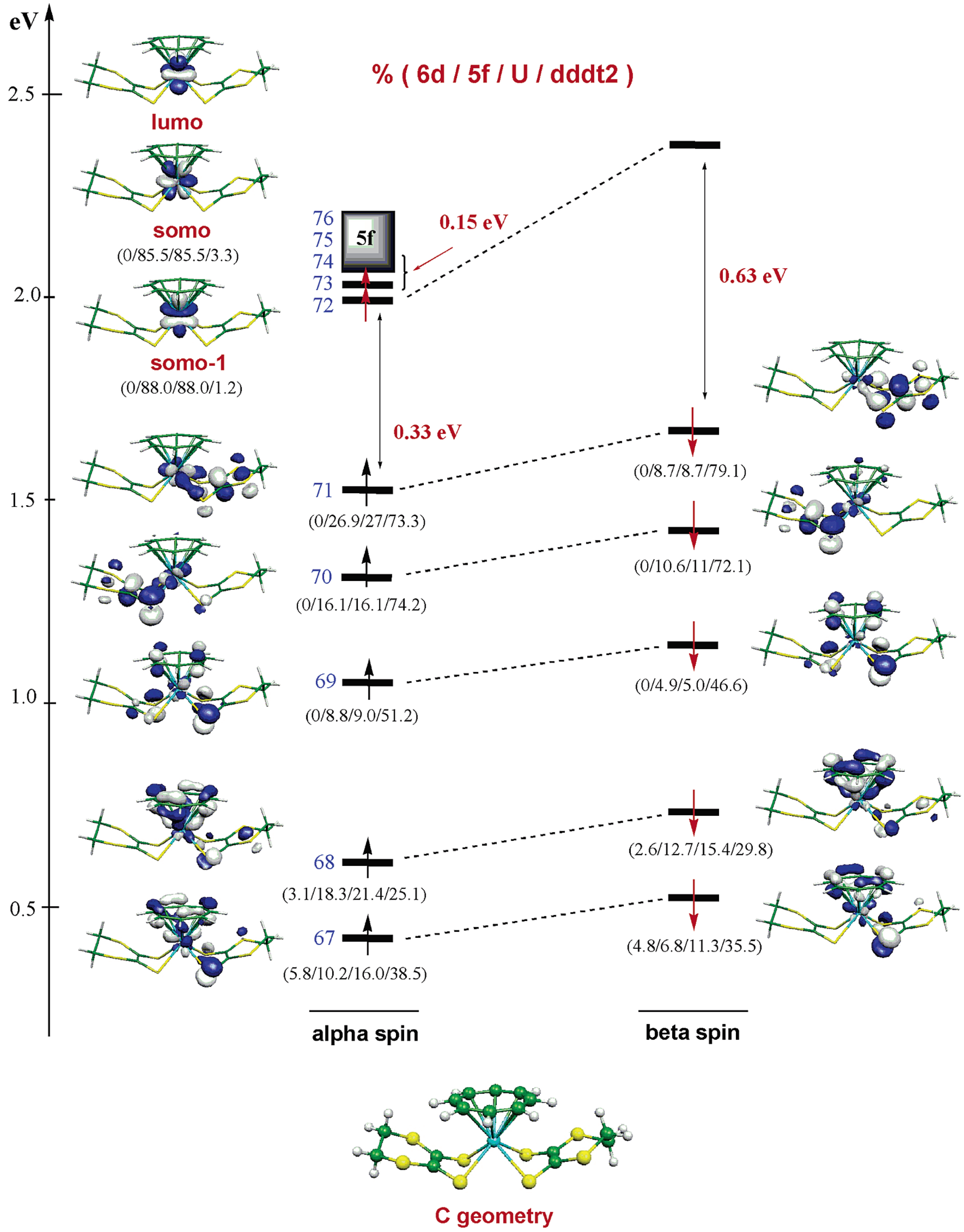

Figure 8. MO diagram of the dianionic $[U^{(IV)}(COT)(dddt)_2]^{2-}$ complex in the triplet state.

This diagram shows that the SOMO (MO 73) and SOMO−1 levels are essentially metallic, with a strong 5f orbital character as indicated by the percentage orbital composition %(d/f/U/ligand). On this diagram, the α and β distinct MOs, immediately below the SOMO−1, are slightly different in energy and composition. The delocalization of these latter MOs on the metal and the different COT and dddt ligands reflects the covalent character of the metal−ligand interactions in the complex. The important interactions between the uranium 5f orbitals and the electron pairs of the adjacent sulfur atoms in the frontier MOs 70 and 71 and with the COT π and π^* orbitals in the MOs of lower energy are particularly noticeable.

U(V) Complex. The MO diagram of the anionic $[U(COT)(dddt)_2]^-$ complex in its doublet state for geometry H is given in Figure 9a. The MO composition is given by the (6d/5f/U/dddt$_2$) percentages.

The expected 5f character of the SOMO is evidenced. The α and β MOs, immediately lower than the SOMO, exhibit a high covalent character. The metallic character and the weight of the 5f orbitals in the frontier MOs (71 and 70) are important and higher for the α than for the β MOs. Compared to the dianionic form C, the weights of the dddt$_2$ ligands in the latter MOs are less important. The MO compositions indicate that the 6d contribution to MOs 68 up to 71, except MO 68, is almost zero. This result indicates that U^{5+}−dddt

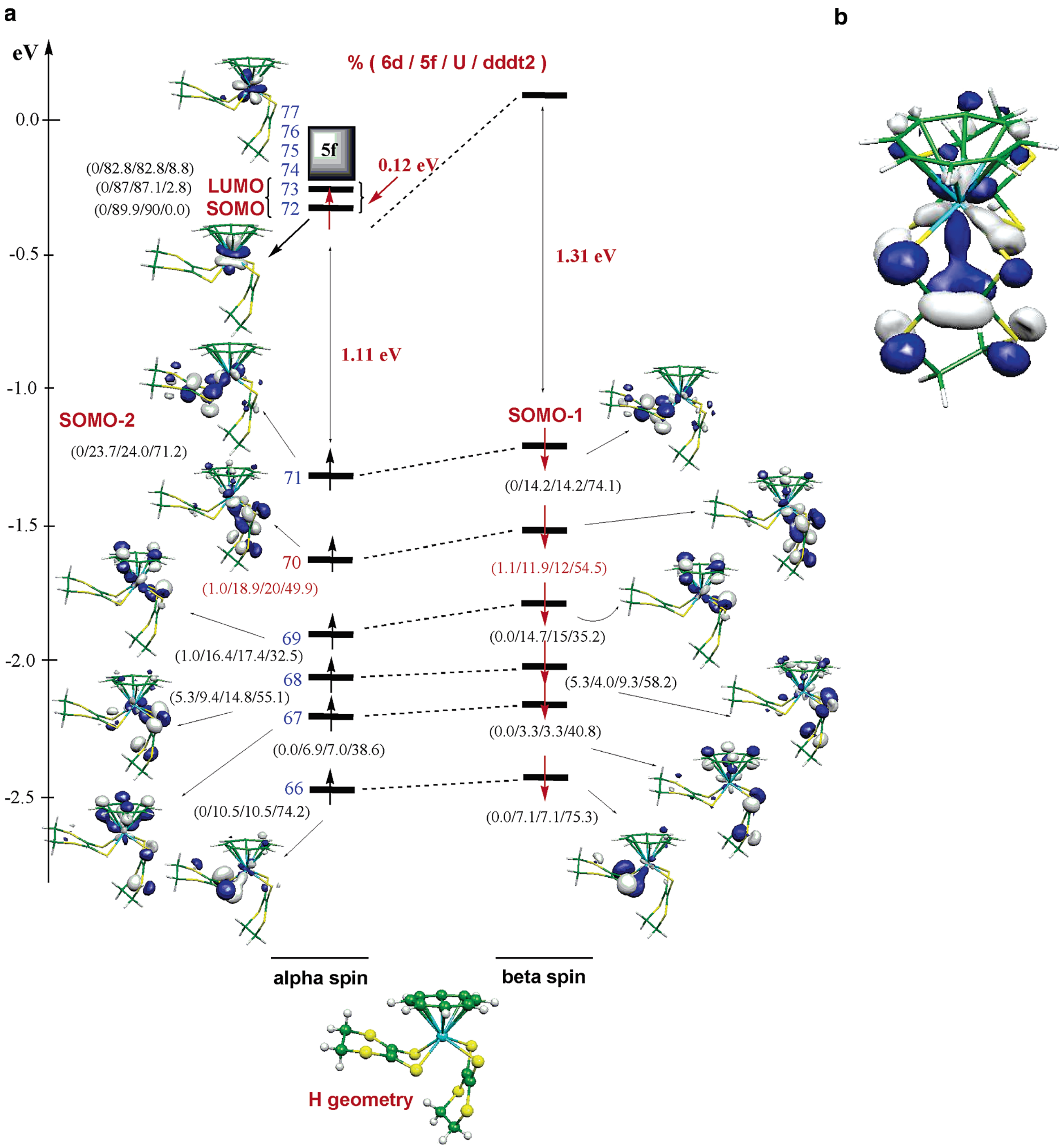

Figure 9. (a) MO diagram of the anionic $[U^{(V)}(COT)(dddt)_2]^-$ complex in its doublet state. (b) α MO 70 of the anionic $[U^{(V)}(COT)(dddt)_2]^-$ complex in its doublet state.

π-coordination is dominated by interactions between the 5f(U) orbitals and the 3p(S) electrons pairs; consequently the geometry of the complex is mainly driven by the 5f orbitals. This result is not surprising since it is known that these orbitals often play a crucial role in the metal−ligand bond stabilization at higher oxidation states.[13b,m] The splitting of the 5f block orbitals (MOs 72 and up) is also indicative of such an interaction.

The strong *endo* US_2C_2 distortion upon oxidation of the dianion makes the C=C bond closer to the metal center. It is worth noting that the α and β MOs 70 (Figure 9b) exhibit a significant bonding interaction between the uranium(V) ion, the *endo* dddt including the C_2 bridge, and the COT ligand to a lesser extent; this element is indicative of a U···(C=C) interaction.

In case of such an interaction, both electron donation from the π(C=C) MO of the *endo* dithiolene ligand to the metal and back-donation to the π*(C=C) MO should occur; both transfers should lead to a lengthening of the C=C distance. Indeed, the structural parameters for structure H indicate that the C=C distance in the *endo* dddt ligand (1.389 Å) is longer than in the *exo* C=C form (1.376 Å). Other electronic evidence for this interaction will be developed later.

U(VI) Complex. The hypothetical neutral species $[U(COT)(dddt)_2]$ bears formally a uranium(VI) metal ion with the $6d^0$-$5f^0$ configuration. This complex is a closed-shell system: its

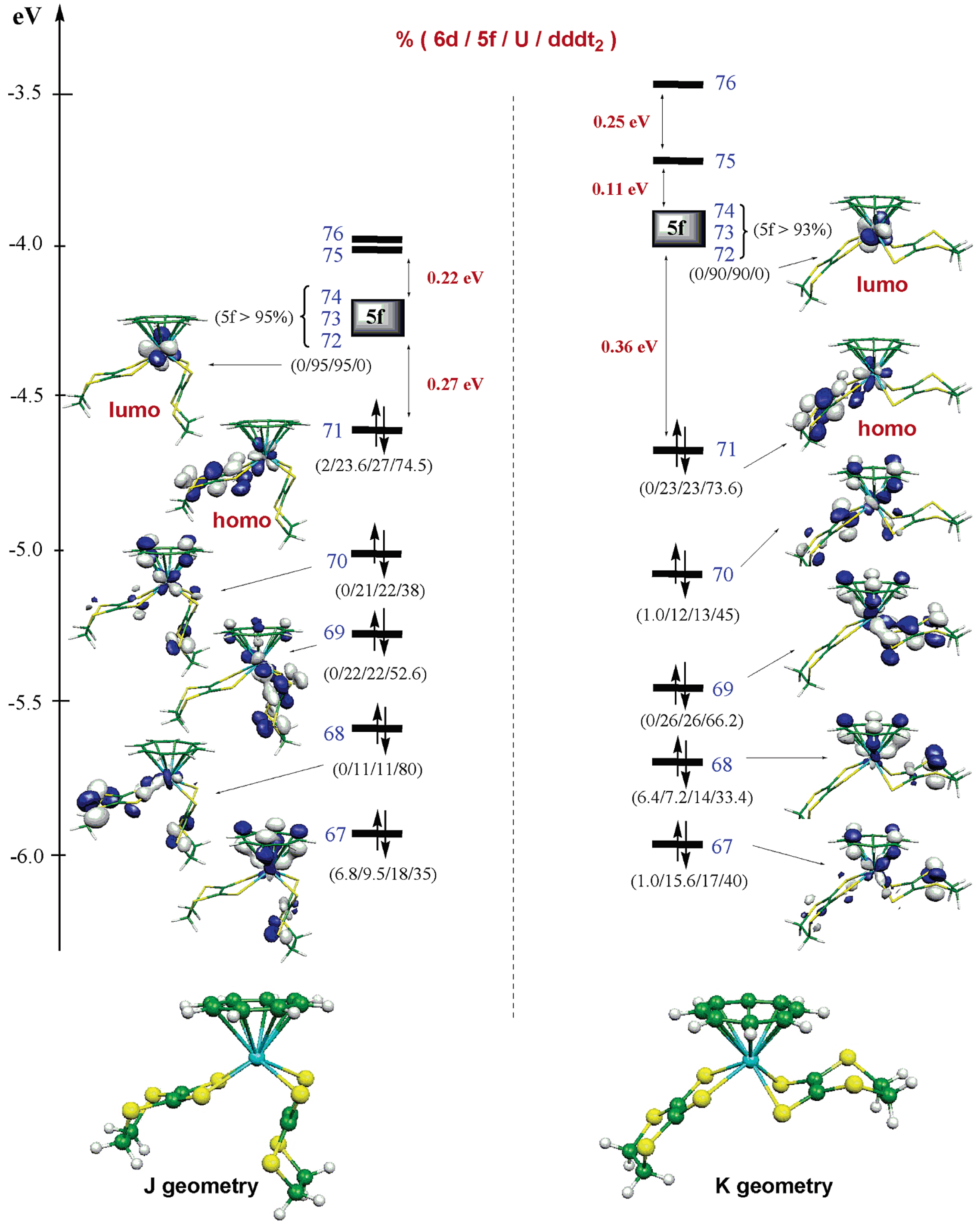

Figure 10. Comparative MO diagrams of the J and K forms of $[U^{(VI)}(COT)(dddt)_2]$.

fundamental state is a singlet. In regard to the good quality of DFT-optimized geometries, we expect that the most stable computed conformation, i.e., form K, is very close to that of the real structure if it exists.

The MOs of the two hypothetical J and K species are compared in Figure 10. We emphasize that form J derives from the geometry optimization of the oxidized anionic species (form G), whereas K is obtained directly by optimization of the standard structure of Figure 3, form K being more stable than form J by 7.5 kcal/mol.

The electronic structure of these two forms resembles those of the dianionic and anionic species. The MO diagram shows that the HOMO is mainly delocalized on the central metal and the less distorted dithiolene ligand. The block of 5f metallic vacant orbitals is located above the HOMO of the neutral species. For the two J and K geometries, MO 69 exhibits an interaction implying the C═C π MO of the distorted dithiolene ligand. As indicated above, the corresponding U···(C═C) distance is shorter in the neutral than in the dianionic and anionic species. In form K, the orbital compositions $\%(6d/5f/U/dddt_2)$ show the important contribution of the metal 5f orbitals to the bonding MO 69. The splitting of the 5f block (MOs 72 and up) is also indicative of the strong interaction of these orbitals with the ligand orbitals in form K.

Electronic Population Analysis. The Mulliken population analysis will first be considered, then that of Mayer.[19] The latter

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[19] Mayer, I. *Chem. Phys. Lett.* **1983**, *97* (3), 270−274.

Table 2. Mulliken Population Analysis

U(COT)(dddt)$_2$ Spin state		Metallic spin density	Net charge			Metallic orbital population					Atom-atom overlap population			
			Metal	Ligand										
			U	~S	COT	spin	6s+7s	6p+7p	6d	5f	U–S	C=C	U–(C=C)	U–(COT)
U(IV) Dianion Triplet	A					α	1.11	3.16	1.04	2.60	0.087	0.208	–0.025	0.029
						β	1.09	3.14	0.90	0.52	0.071	0.220	–0.016	–0.001
		2.26	**+0.44**	**–0.21**	**–0.52**	α+β	**2.20**	**6.30**	**1.94**	**3.12**	**0.158**	**0.428**	**–0.041**	**0.028**
		RESTR	*+0.35*	*–0.20*	*–0.51*		*2.20*	*6.32*	*1.96*	*3.16*	*0.165*	*0.427*	*–0.025*	*0.030*
	B					α	1.11	3.16	1.05	2.60	0.089	0.210	–0.024	0.025
						β	1.08	3.14	0.90	0.52	0.072	0.218	–0.016	–0.003
		2.28	**+0.44**	**–0.21**	**–0.53**	α+β	**2.19**	**6.30**	**1.95**	**3.12**	**0.161**	**0.428**	**–0.040**	**0.022**
		RESTR	*+0.36*	*–0.20*	*–0.55*		*2.19*	*6.26*	*2.16*	*3.10*	*0.176*	*0.401*	*–0.039*	*0.026*
	C					α	1.11	3.13	0.96	2.68	0.072	0.214	–0.025	0.030
						β	1.08	3.11	0.84	0.56	0.055	0.215	–0.014	–0.004
		2.29	**+0.53**	**–0.25**	**–0.52**	α+β	**2.19**	**6.24**	**1.80**	**3.24**	**0.127**	**0.429**	**–0.039**	**0.026**
											endo / exo	***endo / exo***	***endo / exo***	
	E					α	1.11	3.15	1.04	2.64	0.063 / 0.097	0.211 / 0.214	–0.022/–0.014	0.031
						β	1.09	3.12	0.89	0.54	0.045 / 0.078	0.219 / 0.221	–0.020/–0.030	–0.0021
		2.30	**+0.40**	**–0.22**	**–0.49**	α+β	**2.20**	**6.27**	**1.93**	**3.18**	**0.108 / 0.175**	**0.430 / 0.435**	**–0.042/–0.044**	**0.029**
		RESTR	*+0.39*	*–0.23*	*–0.53*		*2.21*	*6.28*	*1.95*	*3.17*	*0.111 / 0.178*	*0.435 / 0.428*	*–0.048/–0.039*	*0.031*
											endo / exo	***endo / exo***	***endo / exo***	
U(V) Anion Doublet	F					α	1.10	3.13	1.13	2.18	0.061 / 0.100	0.166 / 0.205	0.027 /–0.024	0.018
						β	1.09	3.12	1.02	0.91	0.051 / 0.084	0.170 / 0.213	–0.013 /–0.018	0.009
		1.40	**+0.27**	**–0.11**	**–0.21**	α+β	**2.19**	**6.25**	**2.15**	**3.09**	**0.112 / 0.184**	**0.336 / 0.418**	**0.014 /–0.042**	**0.027**
		RESTR	*+0.29*	*–0.10*	*–0.20*		*2.18*	*6.26*	*2.16*	*3.10*	*0.111 / 0.185*	*0.335 / 0.423*	*0.011 /–0.038*	*0.024*
	G					α	1.11	3.14	1.12	2.19	0.060 / 0.101	0.168 / 0.206	0.016 /–0.022	0.028
						β	1.09	3.12	1.02	0.91	0.051 / 0.085	0.171 / 0.214	–0.003 /–0.017	0.011
		1.41	**+0.30**	**–0.10**	**–0.20**	α+β	**2.20**	**6.26**	**2.14**	**3.10**	**0.111 / 0.186**	**0.339 / 0.420**	**0.013 /–0.039**	**0.039**
		RESTR	*+0.27*	*–0.11*	*–0.18*		*2.19*	*6.27*	*2.16*	*3.08*	*0.114 / 0.182*	*0.338 / 0.421*	*0.012 /–0.033*	*0.034*
	H					α	1.10	3.13	1.09	2.22	0.056 / 0.081	0.176 / 0.194	0.014 /–0.010	0.032
						β	1.09	3.11	1.00	0.95	0.047 / 0.076	0.183 / 0.201	–0.005 /–0.023	0.001
		1.39	**+0.31**	**–0.12**	**–0.21**	α+β	**2.19**	**6.24**	**2.09**	**3.17**	**0.103 / 0.157**	**0.359 / 0.395**	**0.009 /–0.033**	**0.033**
		RESTR	*+0.28*	*–0.09*	*–0.16*		*2.22*	*6.25*	*2.14*	*3.11*	*0.142 / 0.181*	*0.318 / 0.354*	*0.010 /–0.029*	*0.037*
											endo / exo	***endo / exo***	***endo / exo***	
U(VI) Neutral Singlet	*J*	*RESTR*	*+0.24*	*–0.05*	*+0.14*		*2.24*	*6.38*	*2.05*	*3.09*	*0.146 / 0.163*	*0.283 / 0.420*	*0.017 / –0.026*	*0.056*
											exo / planar	***exo / planar***	***exo / planar***	
	K	*RESTR*	*+0.10*	*+0.01*	*+0.17*		*2.22*	*6.32*	*2.28*	*3.08*	*0.144 / 0.185*	*0.319 / 0.417*	*0.007 / –0.013*	*0.043*

provides bond orders, resembling classical bond multiplicities, which have been shown to be useful tools in inorganic chemistry.[20]

Mulliken Analysis. The results are reported in Table 2 for both the spin-restricted (RESTR label) and spin-unrestricted calculations. The spin density, the uranium net charge, the sulfur average net charge, and the global net charge of the COT group are given in the first four columns of this table.

The population of the uranium metallic orbitals s(6s+7s), p(6p+7p), 6d, and 5f are given as well as the U−S, C=C, U⋯(C=C), and U−(COT) bond overlap populations for the α and β spin molecular orbitals. The sum of the α and β populations is compared to the spin-restricted global population. The global populations from spin-restricted and -unrestricted calculations are very close in our case. The average U−S value is that of the four bonds. In the case of the dianion, the C=C population is the average value between the two dddt ligands. For the other species, except form K, this population is given for the two *endo* and *exo* ligands. The U⋯(C=C) population is the sum of the overlap populations of the two U⋯C(C=C) populations. In the column relative to the U⋯(C=C) interaction, the values for the dianionic complex are an average for the two dddt ligands. The U−(COT) population is the average value of the overlap population between the uranium atom and a carbon atom of the COT ligand.

For all computed species, the net charge borne by the metal is very small compared to the formal oxidation states +4, +5, and +6 of the uranium ion in the dianionic, anionic, and neutral complexes, respectively. This is the result of the important ligands → metal charge transfers, in our case the donations $(COT)^{-2} \rightarrow U$ and $(dddt_2)^{-4} \rightarrow U$. The metallic positive charge decreases when the complex passes from the dianionic U(+4) form to the anionic U(+5) and neutral U(+6) ones. Concomitantly, the negative charges of the sulfur and the COT group are reduced. This signifies that a stronger electronic donation by the ligands occurs when the metallic charge increases.

The computed metallic spin density (first column in Table 2) is the difference between the total α and β electronic populations of the metal. The computed values of 2.29 for the dianion and 1.39 for the anion deviate respectively from 2 and 1, which are the actual numbers of unpaired electrons in the complexes. This means that a small negative spin density is spread over the ligands.

As expected for the actinide-to-ligand bonding, the overlap population values, in particular those relative to the U−S coordination, are generally important. This result, as well as the orbital analysis made previously, confirms the importance

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[20] Bridgeman, A. J.; Cavigliasso, G.; Ireland L. R.; Rothery J. *J. Chem. Soc., Dalton Trans.* **2001**, 2095.

Table 3. Mayer Population Analysis

			orbital-orbital overlap population					
			sulfur		C═C	bond order		
structure	ion	AO	3s	3p	2p	U−S	U−C(C═C)	C═C
dianion (C)	U(IV)	6d	0.030	0.054	−0.003	0.70/0.72	0.05/0.08	1.43/1.47
		5f	0.016	0.123	0.004			
			endo/exo	*endo/exo*	*endo/exo*	*endo/exo*	*endo/exo*	*endo/exo*
dianion (E)	U(IV)	6d	0.027/0.025	0.058/0.052	−0.002/−0.009	0.72/0.79	0.06/0.03	1.47/1.44
		5f	0.013/0.010	0.130/0.144	0.003/−0.001			
anion (G)	U(V)	6d	0.019/0.010	0.068/0.064	0.006/−0.004	0.90/0.95	0.17/0.01	1.27/1.33
		5f	0.010/0.012	0.117/0.128	0.017/−0.007			
anion (H)	U(V)	6d	0.020/0.017	0.084/0.073	0.015/0.002	1.03/1.05	0.19/0.02	1.31/1.35
		5f	0.004/0.012	0.132/0.138	0.018/0.001			
neutral (J)	U(VI)	6d	0.024/0.010	0.075/0.063	0.009/−0.014	1.01/1.02	0.17/0.01	1.22/1.32
		5f	0.010/0.011	0.137/0.128	0.019/−0.004			
			exo/planar	*exo/planar*	*exo/planar*	*exo/planar*	*exo/planar*	*exo/planar*
neutral (K)	U(VI)	6d	0.026/0.019	0.081/0.078	0.007/−0.005	1.09/1.00	0.17/0.01	1.31/1.39
		5f	0.015/0.017	0.161/0.129	0.016/−0.021			

of covalence between the uranium atom and the COT and dithiolene ligands. However, in the case of the U−(COT) coordination, the computed overlap population is only equal to 0.026 for the dianion (form C) and 0.033 for the anion (form H) or 0.043 for the neutral species (form K).

In the anion, the overlap population relative to the *endo* U···(C═C) interaction is weak but has a positive value, which brings to light the bonding character of the interaction. This bonding interaction is due to the α electrons. On the contrary, such an interaction should be antibonding in the dianion, as indicated by the negative value of the overlap population. This result is obtained even in form E, which adopts *endo* and *exo* dddt conformations similar to those of the anionic forms (note that this dianionic E form has been obtained by optimization of the geometry of the dissymmetric G structure of the reduced anion). In parallel, the overlap population of the *endo* C═C double bond is significantly weaker than that in *exo* position, i.e., 0.359 versus 0.395 in form H of the anionic species. This effect, which is a result of the U···(C═C) interaction, is amplified when passing from the anionic to the neutral complex. In contrast, the *endo* and *exo* C═C bonds in form E exhibit nearly the same population, i.e., 0.430 versus 0.435.

Mayer Analysis. The results for the dianionic C and E forms, the G and H anions, and the hypothetical neutral J and K structures are reported in Table 3. The contribution of the 6d and 5f uranium orbitals to the *endo* and *exo* U···(C═C) interaction is also given, as well as the metal−sulfur orbital−orbital population for the two *endo* and *exo* dithiolene ligands. The Mayer bond order is reported for the U−S, U−C(C═C), and C═C bonds.

The orbital−orbital populations appear to be more important between the 5f orbitals and the sulfur 3p electrons pairs; for instance, considering the *endo* dithiolene ligand in the anionic H complex, the respective values are 0.132 and 0.084 for the 5f and 6d orbitals. This difference is even higher in the anionic form C, 0.123 versus 0.054. This is not surprising since it was seen on the MO diagrams (Figures 8−10) that the dithiolene ligands interact mainly with the metal atom by the sulfur lone pairs. Moreover, as discussed in detail in the previous section, the weight of the 5f orbitals and their interaction with the adjacent sulfur lone pairs in the frontier MOs are more important than those of the 6d ones for all species. The orbital−orbital overlap populations listed in Table 3, which give us an overall view of these interactions, confirm these findings. Regarding the U···(C═C) interaction, for the same anionic form H, the 5f(U)−(C═C) population is equal to 0.018, whereas the 6d(U)−(C═C) amounts to 0.015. This difference between these 5f and 6d contributions is more important in the neutral complex, i.e., 0.016 versus 0.007. Moreover it is worth noting that this overlap population is negative or almost equal to zero for the *exo* dddt ligand. Calculated bond orders for the U−S, U−C(dddt), and C═C bonds agree with the Mulliken overlap populations (Table 2). The U−C(C═C) bond order relative to the *endo* dddt ligand of 0.19 for the anionic complex is equal to 0.17 in the neutral species, indicating a similar U···(C═C) interaction in both complexes. The value of this bond order is significant, as for the U−C(COT) bond we found that this bond order is roughly equal to 0.30. The values obtained for the Mayer bond order constitute additional evidence for the U···(C═C) bond in the folded dithiolene ligand. On the contrary, this bond order is very low in the dianionic form E, indicating that the bonding interaction is not effective in this species. Furthermore, as observed through the Mulliken analysis, the C═C bond order relative to the *endo* dithiolene ligand is weaker than that of the *exo* one, owing to the electronic density loss through the π-(C═C) → 5f(U) partial charge transfer.

Molecular Fragment Analysis. The interaction between the two molecular [U(COT)]$^{+y}$ and (dddt$_2$)$^{-4}$ fragments constituting the [U(COT)(dddt)]^{x} species will be considered so as to support these conclusions.. The electronic structure of these fragments has been computed in order to investigate the different electron transfers that occur. The results of the calculations, performed at the spin-restricted level, for structures C of the dianionic complex, G and H of the anionic species, and J and K of the neutral one are given in Table 4.

In this table, the electronic occupation of the frontier MOs of the fragments, before and after the interaction, are given for each complex. The frontier MO occupations of the metallic molecular fragments U(COT)$^{+y}$ and dddt$_2$$^{-4}$ change significantly after interaction. Indeed, the dddt$_2$$^{-4}$ → U(COT)$^{+y}$ donation is reflected by the partial loss of the electronic density of the levels initially occupied in the dithiolene dddt$_2$$^{-4}$ entity, which are predominantly of S(3p) π character. Comparing forms C, H, and K, respectively, the most stable for the dianion, the anion, and the neutral species, we see that the HOMO, HOMO−1, and HOMO−2 of dddt$_2$$^{-4}$, for instance, transfer a total amount of 1.38, 1.68, and 2.41 electrons to the U(COT)$^{+y}$ fragment. As expected, this electron transfer is more marked for the dddt$_2$$^{-4}$ moieties of the neutral form. Moreover, it is worth noting that the dddt$_2$$^{-4}$ to U(COT)$^{+3,+4}$ donation populates MOs that are essentially of 5f metallic character.

In the case of the anionic complex, the presence of an evenly weak U(COT)$^{+3}$ → dddt$_2$$^{-4}$ back-donation is evidenced by the occupation of the initially vacant dithiolene LUMO and

Table 4. Electronic Populations of the Frontier MOs of the $U(COT)^{+2,+3,+4}$ and $dddt_2^{-4}$ Fragments before and after Interaction

	molecular fragments										
	$[U^{IV}(COT)]^{+2}$	$[U^{V}(COT)]^{+3}$		$[U^{VI}(COT)]^{+4}$		$(dddt_2)^{-4}$ after					
MO	C bef/aft	G bef/aft	H bef/aft	J bef/aft	K bef/aft	before	C	G	H	J	K
75	0/0.30	0/0.41	0/0.26	0/0.01	0/0.23	0	0.02	0.13	0.07	0.03	0.05
74	0/0.12	0/0.21	0/0.66	0/0.00	0/0.39	0	0.02	0.01	0.12	0.02	0.03
73	0/0.11	0/0.18	0/0.41	0/0.04	0/0.30	0	0.49	0.24	0.06	0.09	0.23
72	0/0.36	0/0.34	0/0.24	0/0.61	0/0.22	0	0.05	0.13	0.36	0.26	0.22
71	2/0.97	1/0.63	1/0.57	0/0.54	0/0.10	2	1.18	1.42	1.15	1.47	1.03
70	2/1.88	2/1.89	2/1.75	2/1.99	2/1.87	2	1.74	1.36	1.56	1.52	1.62
69	2/1.88	2/1.97	2/1.92	2/1.99	2/1.70	2	1.70	1.50	1.61	1.76	0.94
68	2/1.98	2/1.77	2/1.95	2/1.97	2/1.99	2	1.78	1.62	1.71	1.64	1.57
67	2/1.98	2/1.69	2/1.98	2/1.96	2/1.99	2	1.77	1.70	1.72	1.80	1.64
66	2/1.99	2/1.99	2/1.98	2/1.95	2/1.97	2	1.81	1.73	1.69	1.50	1.82
65	2/2.00	2/1.99	2/1.95	2/1.94	2/1.98	2	1.88	1.86	1.73	1.52	1.83
64	2/1.99	2/1.97	2/1.98	2/1.99	2/1.98	2	1.84	1.82	1.83	1.47	1.73
63	2/1.99	2/1.99	2/1.99	2/1.96	2/1.96	2	1.96	1.94	1.88	1.86	1.81

LUMO+1. In particular, the electronic occupation of the SOMO of the $U(COT)^{+3}$ fragment decreases from 1 to 0.63 for the G form and from 1 to 0.57 for the H one after interaction with $dddt_2^{-4}$. In structure H, for example, the electronic transfer from $U(COT)^{+3}$ to the LUMO and LUMO+1 levels of the dithiolene ligands gains 0.36 and 0.06 electron, respectively.

Considering the MO interaction diagram of the two fragments $U(COT)^{+3}$ and $dddt_2^{-4}$ in form H (Figure 11) as obtained by our spin-restricted calculations, we can see that the $U(COT)^{+3}$ frontier MOs exhibit major 5f character, thus confirming the driving role of these metal orbitals. At the right side of Figure 11, the dithiolene fragment MO (FMO) exhibits the π character of the lone pairs of the sulfur atoms pointing toward the central metal. In this diagram the MO compositions indicated by %($dddt_2^{-4}$/$UCOT^{+3}$) show the important mixing between the FMOs, except for the SOMO, which is, as indicated before, essentially a 5f metal orbital.

In accordance with the previous discussion of Table 4, the interactions between fragments appear mainly between the sulfur lone pairs and the metallic 6d and 5f orbitals within the $dddt_2^{-4} \rightarrow UCOT^{+3}$ donation. At the same time, the $UCOT^{+3} \rightarrow dddt_2^{-4}$ back-donation occurs from the partially occupied levels of the $UCOT^{+3}$ toward the vacant dithiolene ones.

Conclusions

The dithiolene complexes of general formula $[U(COT)(dddt)_2]^x$ ($x = -2$, -1, and 0) are good examples of stabilization of high uranium oxidation states thanks to metal-based orbitals. Furthermore these complexes present some peculiar structural properties. Indeed, although in the dianionic U(IV) species the two dddt ligands are symmetrically bonded to the metal, this is not the case in the anionic U(V) one, since one U-dithiolene metallacycle is strongly distorted, so that two distinct *endo* and *exo* conformations of the dddt ligands appear in the anionic complex. Relativistic DFT/ZORA calculations of the different conformations of the dddt ligands led to optimized geometries in good agreement with the available crystallographic data. The theoretical results reproduce correctly the spectacular folding of the *endo* US_2C_2 metallacycle when the dianionic species undergoes an oxidation. The calculations bring to light a significant U···(C═C) interaction between the metal center and the C═C bond of the *endo* dithiolene ligand in the anionic complex, which does not exist in the dianionic species. The Mulliken and Mayer population analysis as well as the frontier MOs of the different computed species confirm this U···(C═C) interaction. This interaction explains the shortening of the U···(C═C) distance, the lengthening of the C═C double bond, and the increase of the θ folding angle in the *endo* ligand relative to the *exo* one. We note that this interaction should occur also in the hypothetical neutral uranium(VI) complex.

Furthermore, the electronic structure analysis shows the importance of the uranium 5f orbitals, which play a driving role in the bonding between the metal and the dithiolene ligands. These metal orbitals interact strongly with the orbitals of the dithiolene C═C bond and the "big" electron pairs borne by the adjacent sulfur atoms. As shown by the MO diagram and the overlap populations, these interactions with the dithiolene orbitals are stronger with the metal 5f orbitals than the 6d ones. The resulting charge transfers lead to a partial relocalization of the dithiolene π(C═C) density toward the partially filled 5f orbitals. In parallel, a metal → ligand back-donation occurs in the dianion and anionic complexes from the partially occupied uranium 5f orbitals toward the vacant π^*(C═C) antibonding MO of the dithiolene ligand, which becomes partly occupied after interaction. We are currently exploring the generality of this property on new classes of actinide complexes.

Experimental Section

The synthesis and characterization of $[Na(18\text{-crown-}6)]_2[U(COT)(dddt)_2]$ and $[Na(18\text{-crown-}6)][U(COT)(dddt)_2]$, including the X-ray crystal structure of $[Na(18\text{-crown-}6)(thf)][U(COT)(dddt)_2]$, have been previously described.[4]

Crystallographic Data Collection and Structure Determination. The data for compound **1**·2thf were collected at 100(2) K on a Nonius Kappa-CCD area detector diffractometer[21] using graphite-monochromated Mo Kα radiation (0.71073 Å). The crystal was introduced into a Lindemann glass capillary with a protecting Paratone oil (Exxon Chemical Ltd.) coating. The unit cell parameters were determined from the reflections collected on 10 frames and were then refined on all data. The data were processed with HKL2000.[22] The structure was solved by Patterson map interpretation with SHELXS-97 and subsequent Fourier-difference synthesis and refined by full-matrix least-squares on F^2 with SHELXL-97.[23] Absorption effects were empirically corrected with the program DELABS from PLATON.[24] Two carbon atoms of the thf molecule bound to Na(1) have been found to be disordered over two positions, which were refined with occupancy parameters constrained to sum to unity. The crown ether bound to Na(2) is disordered over two positions related to one another by the binary axis containing Na-

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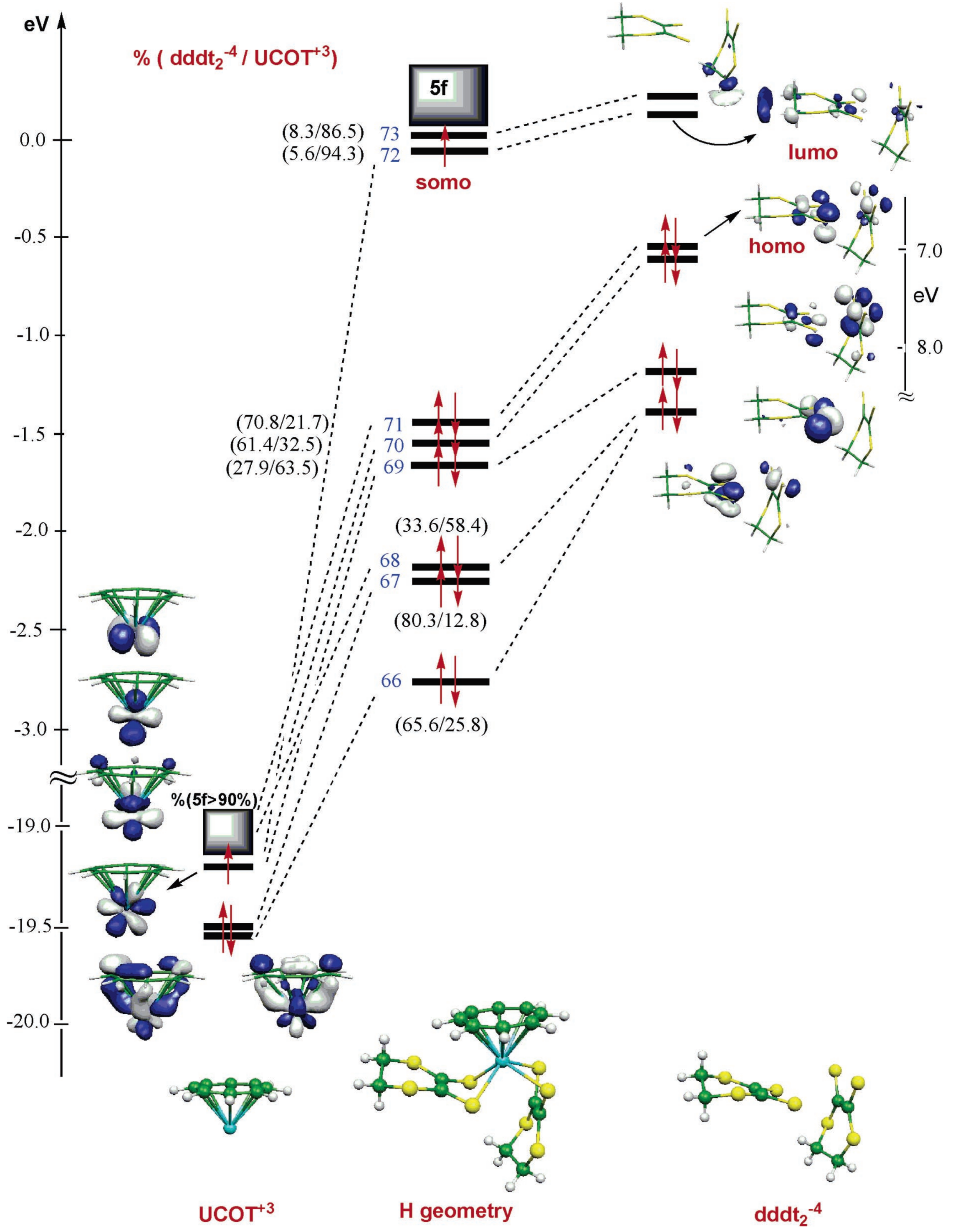

Figure 11. MO diagram of $[U^{(V)}(COT)(dddt)_2]^-$ and its two $U(COT)^{+3}$ and $(dddt_2)^{-4}$ fragments.

(2), which have been refined as one complete molecule with an occupancy factor of 0.5. All non-hydrogen atoms were refined with anisotropic displacement parameters. Some restraints on bond lengths and/or displacement parameters have been applied in the disordered parts. The hydrogen atoms were introduced at calculated positions and were treated as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent atom. An intermolecular H···H contact of 2.10 Å between hydrogen atoms pertaining to the disordered and solvent thf molecules is likely due to the rather low resolution of both molecules. The molecular plots were drawn with SHELXTL[25] and ORTEP-3/POV-Ray.[26]

Crystal data and refinement details: $[Na(18\text{-crown-6})(thf)_2]_2[U(COT)(dddt)_2]\cdot2thf$, **1**·2thf, $C_{64}H_{112}Na_2O_{18}S_8U$, $M = 1710.03$, monoclinic, space group $C2/c$, $a = 17.3620(10)$ Å, $b = 17.2660$-

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(10) Å, $c = 25.3040(15)$ Å, $\beta = 91.720(4)°$, $V = 7582.0(8)$ Å^3, $Z = 4$, $D_c = 1.498$ g cm^{-3}, $\mu = 2.436$ mm^{-1}, $F(000) = 3528$. Refinement of 518 parameters on 6701 independent reflections out of 13 130 measured reflections ($R_{int} = 0.050$) led to R1 = 0.047 [5340 reflections with $I > 2\sigma(I)$], wR2 = 0.116 (all data), and $S = 0.971$.

Computational Details. The calculations were performed using density functional theory (DFT).[27] Relativistic corrections were introduced via the zero order regular approximation (ZORA).[28] Spin−orbit effects were not taken into account. The DFT/ZORA calculations were performed using the Amsterdam Density Functional (ADF) program package.[29] Triple-ζ Slater-type valence orbitals (STO) augmented by one set of polarization functions were used for all atoms. For all elements, the basis sets were taken from the ADF ZORA/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 and 1s/2s/2p core electrons were frozen respectively for carbon C[1s] and sulfur S[2p]. The U[5d] valence space of the heavy element includes the 5f/6s/6p/6d/7s/7p shells (14 valence electrons). The Vosko−Wilk−Nusair functional[30a] for the local density approximation (LDA) and the nonlocal corrections respectively for exchange and correlation of Becke[30b] and Perdew[30c] have been used. Molecular orbital plots were generated using the using the MOLEKEL 4.3 program.[31]

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Supporting Information Available: Crystallographic data for **1**·2thf in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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