Quantum Chemistry Predicts Multiply Bonded Diuranium Compounds to Be Stable

ROOS, Björn O., GAGLIARDI, Laura

Abstract

Results from quantum chemical calculations that predict the existence of a series of diuranium molecules are reported. Two diuranium chlorides, $\text{U}_2\text{Cl}_6$ and $\text{U}_2\text{Cl}_8^{2-}$, and three different carboxylates, $\text{U}_2(\text{OCHO})_4$, $\text{U}_2(\text{OCHO})_6$, and $\text{U}_2(\text{OCHO})_4\text{Cl}_2$ have been studied. All species have been found to be stable with a multiply bonded U2 unit.

Reference


DOI: 10.1021/ic051665a
Quantum Chemistry Predicts Multiply Bonded Diuranium Compounds to Be Stable

Björn O. Roos and Laura Gagliardi

Department of Theoretical Chemistry, Chemical Center, P.O. Box 124, S-221 00 Lund, Sweden, and Department of Physical Chemistry, University of Geneva, 30, Quai Ernest Ansermet, CH-1211 Geneva 4, Switzerland

Received September 28, 2005

Results from quantum chemical calculations that predict the existence of a series of diuranium molecules are reported. Two diuranium chlorides, U₂Cl₆ and U₂Cl₈²⁻, and three different carboxylates, U₂(OCHO)₄, U₂(OCHO)₆, and U₂(OCHO)₄Cl₂ have been studied. All species have been found to be stable with a multiply bonded U₂ unit.

1. Introduction

Actinide chemistry poses a formidable challenge for chemists, both from an experimental and theoretical perspective. Actinide compounds are not easy to handle in the laboratory. Still, a good understanding of their chemistry is important in a number of areas. Quantum chemistry is now mature enough to model actinide properties and transformations with good accuracy. We have recently been able to describe how two uranium atoms bind to form the U₂ molecule, which has a quintuple bond and we have suggested that the U₂ unit could form the framework for a diuranium chemistry. We have also studied the U₂²⁺ system, which has a large number of low-lying electronic states. These states share a very small bond length of about 2.30 Å, compared to 2.43 Å in neutral U₂.

A few diuranium compounds have been found experimentally by matrix isolation, for example, H₂U–UH₂³ and OUUO. No real inorganic chemistry based on the U₂ unit has, however, yet been explored. This chemistry could occur in solution, analogous to the widely studied transition metal dimer chemistry.

The uranium atom has six valence electrons, and the U–U bond in U₂ is composed of three normal two-electron bonds, four electrons in different bonding orbitals, and two non-bonded electrons leading to a quintuple bond between the two uranium atoms. Multiple bonding is also found between transition metal atoms. The Cr, Mo, and W atoms have six valence electrons, and a hextuple bond is formed in the corresponding dimers, even if the sixth bond is weak. The similarity between these dimers and the uranium dimer suggests the possibility of an inorganic chemistry based on the latter. A number of compounds with the M₂ (M = Cr, Mo, W, Re, etc.) unit are known. Among them are the chlorides, for example, Re₂Cl₆ and Re₂Cl₈²⁻ and the carboxylates, for example, Mo₂(O₂CCH₃)₄. The simplest of them are the tetraformates, which in the absence of axial ligands have a very short metal–metal bond length.

Here, quantum chemical calculations have been used to show that corresponding diuranium compounds are also stable with a multiple U–U bond and short bond distances. We have studied two chlorides, U₂Cl₆ and U₂Cl₈²⁻, both with U(III) as the oxidation state of uranium, and three different carboxylates, U₂(OCHO)₄ (U(II) as the oxidation state of uranium), U₂(OCHO)₆, and U₂(OCHO)₄Cl₂ (U(III) as the oxidation state of uranium). All species have been found to be stable with a multiply bonded U₂ unit.

2. Methods

The quantum chemical calculations were performed using the software MOLCAS-6.2. The complete active space (CAS) SCF method was used to generate molecular orbitals and reference...
functions for subsequent multiconfigurational second-order perturbation calculations of the dynamic correlation energy (CASPT2). The method is based on a partitioning of the molecular orbital space into three subspaces: inactive, active, and external orbitals. The inactive orbitals are assumed to be doubly occupied. Remaining electrons occupy the active orbitals. The choice of these orbitals is crucial for the method. They should encompass all electronic structure features that can be expected to be important for the quantum chemical problem studied. For the molecules studied in the present work, the active orbitals are those that describe the U–U bond. Enough orbitals have been included such that the method can make the optimal choice between the 5f and 6d orbitals in forming the bonding and antibonding orbitals. The number of active electrons was eight for the U$^{4+}$ unit and six for U$^{6+}$. More details of the choice of active orbitals will be given when the different molecules are discussed. A basis set of the atomic natural orbital type was used. It has been developed especially for relativistic calculations with the DKH Hamiltonian. For uranium, a primitive set 26s23p17d13f5g was contracted to: 9s8p6d4f2g, while basis sets of TZP quality were used for H, C, O, and Cl.

For atoms as heavy as uranium, it is necessary to include relativistic effects. This was done using the second-order Douglas–Kroll–Hess (DKH) Hamiltonian. The scalar part of this Hamiltonian was used in the generation of the CASSCF/CASPT2 wave functions. Spin–orbit (SO) coupling was not included in the present study. It will have only a minor effect on the computed structures for singlet electronic states. It is known from a number of earlier studies, for example, on the uranium dimer, that SO effects vary only slowly in the region around the equilibrium geometry. SO effects will of course be important for calculating the binding energy when a system goes from a high-spin state to a bound singlet. We do not study this process here. It is described in detail in ref 15, which also gives references to papers describing the methods mentioned above. It has been applied to a number of heavy atom systems with good results both for ground-state properties and excited states. Examples may be found in refs 16–20.

Optimization of the geometries were performed at the CASPT2 level of theory using a numerical grid. For the formates, we optimized the structure of the ligands only for U$_2$(OCHO)$_4$ and the corresponding cation. The geometry was found to be the same in both cases (R(CO) = 1.268 Å (OCO = 120.0°). A fixed value (1.092 Å) was used for the CH bond distance. These geometrical parameters were kept fixed for the other U$_2$ formates. They are very close the values found experimentally and theoretically for Cr$_2$(OCHO)$_4$.

3. Results

3.1. Diuranium Chlorides. In a previous study of Re$_2$Cl$_6^{2-}$, it was shown that the ground-state configuration of Re$_2$Cl$_6^{2-}$ is $\alpha^2\pi^1\delta^2$ and that the effective bond order of the Re–Re bond is closer to three than to four due to the weakness of the $\delta$ bond.

Here we have considered the diuranium analogues (see Figures 1 and 2) of Re$_2$Cl$_6$ and Re$_2$Cl$_8^{2-}$. The formal charge of the uranium ion is +3 in both compounds. Thus, 6 of the 12 valence electrons are available, and a triple bond can in principle be formed. U$_2$Cl$_6$ can have either an eclipsed or a staggered conformation. Preliminary calculations have indicated that the staggered conformation is about 12 kcal/mol lower in energy than the eclipsed form. We will thus focus our analysis on the staggered structure.


(20) Roos, B. O. In Advances in Chemical Physics; Ab Initio Methods in Quantum Chemistry II; Lawley, K. P., Ed.; John Wiley and Sons Ltd.: Chichester, England, 1987; Chapter 69, p 399.


(29) Gagliardi, L.; La Manna, G.; Roos, B. O. Faraday Discuss. 2003, 124, 63.

We have used an active space formed by 6 electrons occupying 12 orbitals. These orbitals are linear combinations of U 7s, 7p, 6d, and 5f orbitals with Cl 3p orbitals. The U−U and U−Cl bond distances and the U−U−Cl angle have been optimized at the CASPT2 level of theory. The ground state of U₂Cl₆ is a singlet state with the electronic configuration (σ_u)²(π_u)²(δ_g)². The U−U bond distance is 2.43 Å, the U−Cl distance is 2.46 Å, and the U−U−Cl angle is 120.0° (see Figure 1 and Table 1). At the equilibrium bond distance, the lowest triplet lies within 2 kcal/mol from the singlet ground state. The two states are expected to interact via the spin−orbit coupling Hamiltonian. This will further lower the energy but will have a negligible effect on the geometry.

The dissociation of U₂Cl₆ to 2UCl₃ has been studied. UCl₃, unlike U₂Cl₆, is known experimentally and has been the object of previous computational studies. Single-point CASPT2 energy calculations have been performed on the experimental geometry, as reported in ref 24, namely a pyramidal structure with a U−Cl bond distance of 2.55 Å and a Cl−U−Cl angle of 95°. No further optimization of the structure of UCl₃ was carried out. The ground state is a quartet, 4Acer, with three unpaired electrons in the 5f U orbitals. U₂Cl₆ was found to be about 20 kcal/mol more stable than two UCl₃ moieties.

U₂Cl₆⁻ is the analogue of Re₂Cl₆⁻. We have considered both the staggered and the eclipsed conformation. Analogous to Re₂Cl₆⁻, the eclipsed conformation is lower in energy. We have thus optimized the structure for U₂Cl₆⁻ using an active space formed by 6 active electrons in 13 active orbitals, assuming D₃h symmetry. As in the U₂Cl₆ case, the molecular orbitals are linear combinations of U 7s, 7p, 6d, and 5f orbitals with Cl 3p orbitals. The ground state of U₂Cl₆⁻ is a singlet state with the electronic configuration (5fδ_u)²(5fπ_u)². The molecule presents a U−U triple bond. The U−U bond distance is 2.44 Å, the U−Cl bond distance is 2.59 Å, and the U−U−Cl angle is 111.2°. U₂Cl₆⁻ is different compared to Re₂Cl₆⁻ in terms of molecular bonding, in the sense that the bond in Re₂Cl₆⁻ is formally a quadruple bond, even though the δ_g bond is weak, because Re₃⁺ has four electrons available to form the metal−metal bond. Only a triple bond can form in U₂Cl₆⁻ because only three electrons are available on each U₃⁺ unit.

3.2. Diuranium Carboxylates. U₂(OCHO)₄ (Figure 3) is the analogue of Cr₂(OCHO)₄. In both cases, the formal charge of the metal atom is +2. Thus, 8 of the 12 valence electrons remain, and a quadruple bond can in principle be formed. The electronic configuration for the Cr−Cr bond in Cr₂(OCHO)₄ is (σ_u)²(π_u)²(δ_g)², a quadruple bond with a singlet ground state, but with a low-lying triplet state. The electronic configuration of U₂ is (σ_u)²(π_u)² plus six electrons distributed among the remaining 6d and 5f orbitals. It is therefore plausible that the electronic configuration of the U−U bond in U₂(OCHO)₄ will be the same as that in Cr₂(OCHO)₄, with the doubly occupied δ_g orbital directed such that the overlap with the ligand orbitals is minimized. Exchange stabilization will favor an open-shell triplet state with each of the two δ_g orbitals singly occupied, and it is also a possible candidate for the ground state.

After trial studies with different sets of uranium orbitals in the active space, it was clear that a quadruple bond was formed between the uranium atoms as in the corresponding dichromium compound. This bond can be described with 10 active orbitals (σ, σ*, π, π*, δ, δ*, δ, δ*, δ, δ*). In practice, 13 active orbitals were used in order to assure that no other bonding types would occur. They turned out have have very small occupation numbers. The active orbitals were formed from 5f and 6d atomic orbitals, with the dominant character indicated below. The same active orbitals have been used for all compounds discussed below. The main electronic configuration is (5fδ_u)²(6dπ_u)²(5fδ_u)². There is more 5f character in this bond than in the neutral U₂ molecule where the 7s and 6d orbitals dominate the wave function. As an example of the molecular orbitals appearing in the U−U bond of the various species discussed, we present in Figure 4 the bonding and antibonding molecular orbitals of U₂(OCHO)₄, together with the number of electrons occupying each of the orbitals. Two spin couplings are possible in the (5fδ_u) shell, either a closed-shell singlet state, 1A1g, with both electrons in the δ_g orbital pointing away from the oxygen ligands or a triplet state, 3A2g, with one electron in each of the two components. Both states give equal U−U bonding, but ligand repulsion is larger in the triplet state, which is balanced by a more favorable exchange interaction.

The closed-shell singlet state was first studied. Its geometry was optimized assuming all four ligands to be equivalent with D₄h symmetry. The C−H bond distance was fixed at 1.092 Å. All other geometrical parameters were optimized. Two energy minima were found, one with a very short U−U
distance of 2.33 Å (compare the result obtained for the U₂ molecule, 2.42 Å\(^1\)) and one with a longer distance and a weaker bond. Such a double minimum structure has also been found for the corresponding dichromium molecule,\(^{21}\) and it has been shown experimentally that the outer minimum is most stable in compounds with extra axial ligands where the Cr−Cr distance varies between 2.3 and 2.6 Å.\(^{25}\) Cotton et al. have synthesized a dichromium carboxylate with no extra ligands\(^8\) and a Cr−Cr distance of 1.966 Å. The outer minimum in U₂(OCHO)_4 has a U−U bond distance of 3.47 Å and a U−O distance of 2.39 Å. A single bond forms between the uranium atoms. The energy barrier between the inner and outer minimum is 16 kcal/mol, with the outer minimum 8 kcal/mol lower in energy. The triplet state was found 0.13 eV above the singlet state with almost the same geometry.

It might turn out to be very difficult to make U₂(OCHO)_4 even if it is a stable compound, the reason being that the U(II) oxidation state is not available. The dication U₂^2+ (OCHO)_4 has therefore also been studied. The same approach was used. No inner minimum (with a triple bond) was found, only the outer minimum with a U−U bond distance of 3.42 Å. A single σ bond is formed between the two uranium atoms with the remaining four electrons localized, two on each atom in 5f orbitals. The basic units for the dication is U(III), which is a stable oxidation state. It is therefore not impossible that a synthetic route can be found. A multiply bonded structure is regained if two axial chlorides ions are added to yield the molecule U₂(OCHO)_4Cl₂ (Figure 5). A triple bond is formed with the structure (π^4)δ^2 and a bond distance of 2.80 Å. The longer bond distance is explained by the weakness of the δ bond. The U−Cl distance is 2.51 Å, and the U−O distance 2.38 Å.

Another possibility to utilize the U(III) oxidation state is to form the hexaformate molecule U₂(OCHO)_6 (Figure 6).


how one can choose ligands that will enhance the binding to the positively charged metal dimer and further stabilize the inner minimum.

4. Conclusions

Quantum chemical calculations have shown that diuranium hexa- and octachloride and diuranium tetra- and hexaformate compounds are stable with a multiple diuranium bond. The diuranium molecule, previously predicted to have a quintuple bond, exists in the gas phase, together with a few diuranium molecules, for example, H₂UH₂ and OUO₂. It should be possible to synthesize the new series of compounds presented here using more standard methods of inorganic chemistry analogous to the corresponding transition metal compounds. A new, yet unexplored, branch of inorganic chemistry might then emerge.

Acknowledgment. This work has been supported by the Swedish Foundation for Strategic Research (SSF) and by Italian Ministero dell’Istruzione dell’Università e della Ricerca, MIUR. The authors are grateful to Professor Ingmar Grenthe for valuable discussions and information about the chemistry of uranium in different oxidation states.