

# Quantum Chemistry Predicts Multiply Bonded Diuranium Compounds to Be Stable

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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  $\text{U}_2$  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  $\text{U}_2$  molecule, which has a quintuple bond<sup>1</sup> and we have suggested that the  $\text{U}_2$  unit could form the framework for a diuranium chemistry. We have also studied the  $\text{U}_2^{2+}$  system,<sup>2</sup> 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  $\text{U}_2$ .

A few diuranium compounds have been found experimentally by matrix isolation, for example,  $\text{H}_2\text{U}-\text{UH}_2$ <sup>3</sup> and  $\text{OUUO}$ .<sup>4</sup> No real inorganic chemistry based on the  $\text{U}_2$  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  $\text{U}-\text{U}$  bond in  $\text{U}_2$  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 sextuple 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  $\text{M}_2$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}, \text{Re}, \text{etc.}$ ) unit are known. Among them are the chlorides, for example,  $\text{Re}_2\text{Cl}_6$  and  $\text{Re}_2\text{Cl}_8^{2-}$ ,<sup>5</sup> and the carboxylates, for example,  $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ .<sup>6,7</sup> The simplest of them are the tetraformates, which in the absence of axial ligands have a very short metal–metal bond length.<sup>8</sup>

Here, quantum chemical calculations have been used to show that corresponding diuranium compounds are also stable with a multiple  $\text{U}-\text{U}$  bond and short bond distances. We have studied two chlorides,  $\text{U}_2\text{Cl}_6$  and  $\text{U}_2\text{Cl}_8^{2-}$ , both with  $\text{U}(\text{III})$  as the oxidation state of uranium, and three different carboxylates,  $\text{U}_2(\text{OCHO})_4$  ( $\text{U}(\text{II})$  as the oxidation state of uranium),  $\text{U}_2(\text{OCHO})_6$ , and  $\text{U}_2(\text{OCHO})_4\text{Cl}_2$  ( $\text{U}(\text{III})$  as the oxidation state of uranium). All species have been found to be stable with a multiply bonded  $\text{U}_2$  unit.

## 2. Methods

The quantum chemical calculations were performed using the software MOLCAS-6.2.<sup>9</sup> The complete active space (CAS) SCF method<sup>10</sup> was used to generate molecular orbitals and reference

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functions for subsequent multiconfigurational second-order perturbation calculations of the dynamic correlation energy (CASPT2).<sup>11</sup> 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  $U_2^{4+}$  unit and six for  $U_2^{6+}$ . 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.<sup>12–13</sup> For uranium, a primitive set 26s23p17d13f5g was contracted to: 9s8p6d4f2g,<sup>14</sup> 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 effects 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<sup>16–20</sup>.

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 ( $R(CO) = 1.268 \text{ \AA}$  ( $\angle OCO = 126.0^\circ$ ). A fixed value (1.092  $\text{\AA}$ ) was used for the CH bond distance. These geometrical parameters were kept fixed for the other  $U_2$  formates. They are

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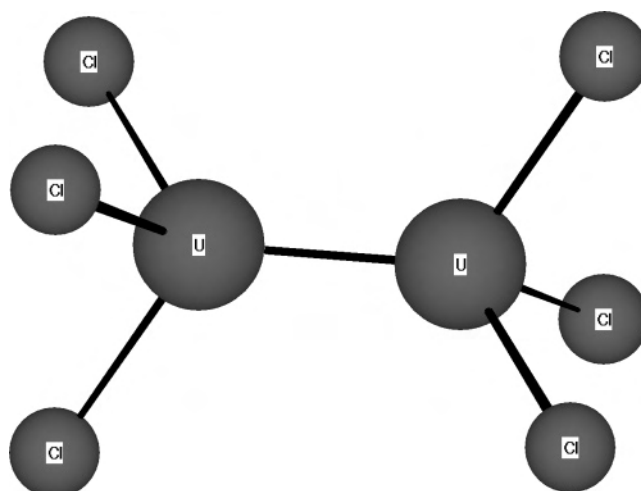


Figure 1. Structure of  $U_2Cl_6$ .

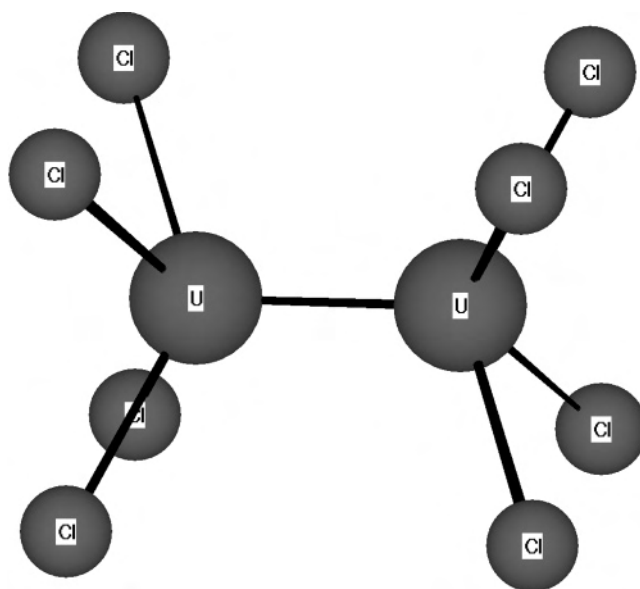


Figure 2. Structure of  $U_2Cl_8^{2-}$ .

very close the values found experimentally and theoretically for  $Cr_2(OCHO)_4$ .<sup>21</sup>

### 3. Results

**3.1. Diuranium Chlorides.** In a previous study of  $Re_2Cl_8^{2-}$ ,<sup>22</sup> it was shown that the ground-state configuration of  $Re_2Cl_8^{2-}$  is  $\sigma^2\pi^4\delta^2$  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  $Re_2Cl_6$  and  $Re_2Cl_8^{2-}$ . 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.  $U_2Cl_6$  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.

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**Table 1.** Most Significant Structural Parameters in the Various Species<sup>a</sup>

	U <sub>2</sub> Cl <sub>6</sub>	U <sub>2</sub> Cl <sub>8</sub> <sup>2-</sup>	U <sub>2</sub> (OCHO) <sub>4</sub>	U <sub>2</sub> (OCHO) <sub>6</sub>	U <sub>2</sub> (OCHO) <sub>4</sub> Cl <sub>2</sub>
U–U	2.43	2.44	2.33	2.40	2.80
U–Cl(O)	2.46	2.59	2.44	2.46	2.38(UO), 2.51(UCl)
U–U–Cl	120.0	111.2			
U–U–O			89.2	88.4	83.4

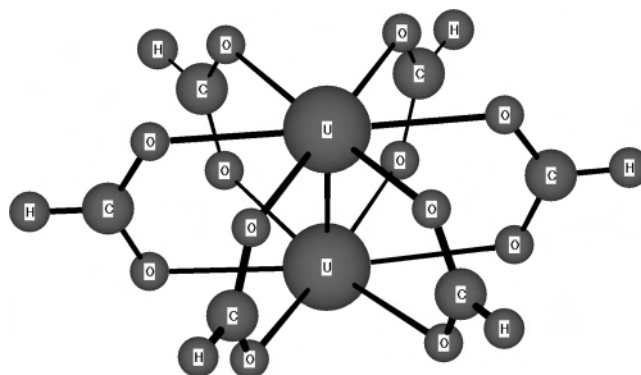
<sup>a</sup> Distance in Å and angles in deg (only parameters for the inner minimum are presented for the formates). See Figures 1–6 for a description of the structures.

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 U<sub>2</sub>Cl<sub>6</sub> is a singlet state with the electronic configuration  $(\sigma_g)^2(\pi_u)^4$ .<sup>4</sup> 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 U<sub>2</sub>Cl<sub>6</sub> to 2UCl<sub>3</sub> has been studied. UCl<sub>3</sub>, unlike U<sub>2</sub>Cl<sub>6</sub>, is known experimentally<sup>23</sup> and has been the object of previous computational studies.<sup>24</sup> 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 UCl<sub>3</sub> was carried out. The ground state is a quartet, <sup>4</sup>A'', with three unpaired electrons in the 5f U orbitals. U<sub>2</sub>Cl<sub>6</sub> was found to be about 20 kcal/mol more stable than two UCl<sub>3</sub> moieties.

U<sub>2</sub>Cl<sub>8</sub><sup>2-</sup> is the analogue of Re<sub>2</sub>Cl<sub>8</sub><sup>2-</sup>. We have considered both the staggered and the eclipsed conformation. Analogous to Re<sub>2</sub>Cl<sub>8</sub><sup>2-</sup>, the eclipsed conformation is lower in energy. We have thus optimized the structure for U<sub>2</sub>Cl<sub>8</sub><sup>2-</sup> using an active space formed by 6 active electrons in 13 active orbitals, assuming D<sub>4h</sub> symmetry. As in the U<sub>2</sub>Cl<sub>6</sub> case, the molecular orbitals are linear combinations of U 7s, 7p, 6d, and 5f orbitals with Cl 3p orbitals. The ground state of U<sub>2</sub>Cl<sub>8</sub><sup>2-</sup> is a singlet state with the electronic configuration  $(5f\sigma_g)^2(5f\pi_u)^4$ .<sup>4</sup> 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°. U<sub>2</sub>Cl<sub>8</sub><sup>2-</sup> is different compared to Re<sub>2</sub>Cl<sub>8</sub><sup>2-</sup> in terms of molecular bonding, in the sense that the bond in Re<sub>2</sub>Cl<sub>8</sub><sup>2-</sup> is formally a quadruple bond, even though the  $\delta_g$  bond is weak, because Re<sup>3+</sup> has four electrons available to form the metal–metal bond. Only a triple bond can form in U<sub>2</sub>Cl<sub>8</sub><sup>2-</sup> because only three electrons are available on each U<sup>3+</sup> unit.

**3.2. Diuranium Carboxylates.** U<sub>2</sub>(OCHO)<sub>4</sub> (Figure 3) is the analogue of Cr<sub>2</sub>(OCHO)<sub>4</sub>. In both cases, the formal charge

**Figure 3.** Structure of U<sub>2</sub>(OCHO)<sub>4</sub>.

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 Cr<sub>2</sub>(OCHO)<sub>4</sub> is  $(\sigma_g)^2(\pi_u)^4(\delta_g)^2$ , a quadruple bond with a singlet ground state,<sup>21</sup> but with a low-lying triplet state. The electronic configuration of U<sub>2</sub> is  $(\sigma_g)^2(\pi_u)^4$  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 U<sub>2</sub>(OCHO)<sub>4</sub> will be the same as that in Cr<sub>2</sub>(OCHO)<sub>4</sub>, with the doubly occupied  $\delta_g$  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  $\delta_g$  orbitals singly occupied, and it is also a possible candidate for the ground state.

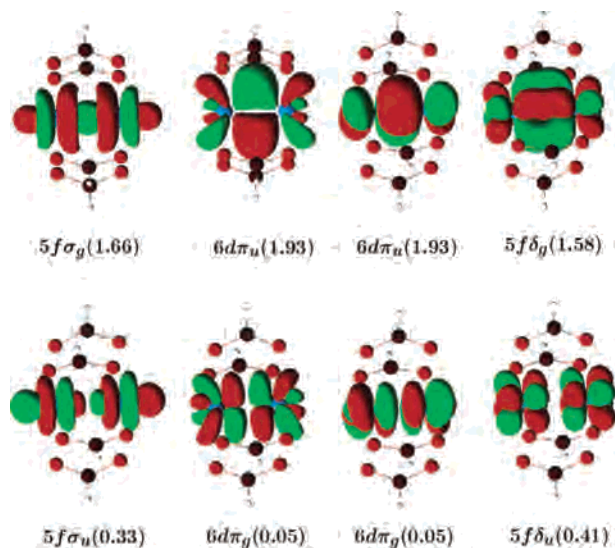
After trial studies with different sets of uranium orbitals in the active space, it was clear that a quadruple bond was formed between the uranium atoms as in the corresponding dichromium compound. This bond can be described with 10 active orbitals ( $\sigma$ ,  $\sigma^*$ ,  $\pi$ ,  $\pi^*$ ,  $\delta$ , and  $\delta^*$ ). In practice, 13 active orbitals were used in order to assure that no other bonding types would occur. They turned out to 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  $(5f\sigma_g)^2(6d\pi_u)^4(5f\delta_g)^2$ . There is more 5f character in this bond than in the neutral U<sub>2</sub> 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 U<sub>2</sub>(OCHO)<sub>4</sub>, together with the number of electrons occupying each of the orbitals. Two spin couplings are possible in the  $(5f\delta_g)$  shell, either a closed-shell singlet state, <sup>1</sup>A<sub>1g</sub>, with both electrons in the  $\delta$  orbital pointing away from the oxygen ligands or a triplet state, <sup>3</sup>A<sub>2g</sub>, 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 D<sub>4h</sub> 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

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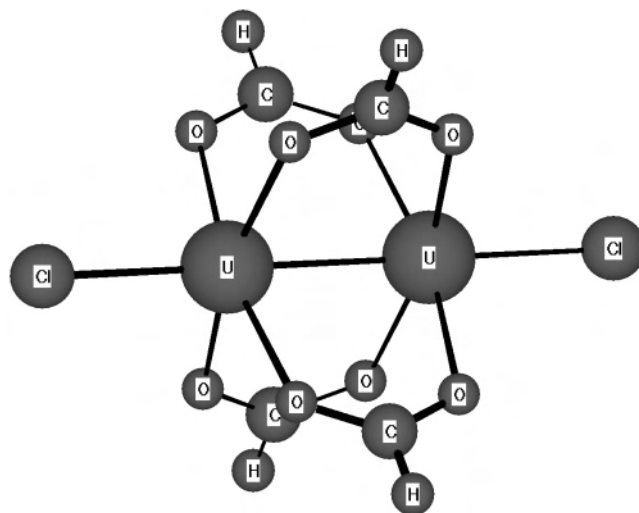


**Figure 4.** Eight molecular orbitals contributing to the quadruple bond in the diuranium tetraformate compound. The number of electrons occupying each orbital is also given. Orbital labels for linear symmetry are used.

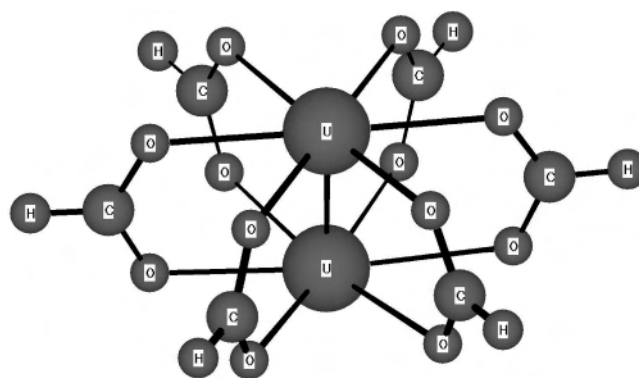
distance of 2.33 Å (compare the result obtained for the  $U_2$  molecule, 2.42 Å<sup>1</sup>) and one with a longer distance and a weaker bond. Such a double minimum structure has also been found for the corresponding dichromium molecule,<sup>21</sup> and it has been shown experimentally that the outer minimum is most stable in compounds with extra axial ligands where the Cr–Cr distance varies between 2.3 and 2.6 Å.<sup>25</sup> Cotton et al. have synthesized a dichromium carboxylate with no extra ligands<sup>8</sup> and a Cr–Cr distance of 1.966 Å. The outer minimum in  $U_2(OCHO)_4$  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  $U_2(OCHO)_4$  even if it is a stable compound, the reason being that the U(II) oxidation state is not available. The dication  $U_2(OCHO)_4^{2+}$  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  $\sigma$  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  $U_2(OCHO)_4Cl_2$  (Figure 5). A triple bond is formed with the structure  $(\pi_u)^4(\delta_g)^2$  and a bond distance of 2.80 Å. The longer bond distance is explained by the weakness of the  $\delta$  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  $U_2(OCHO)_6$  (Figure 6).



**Figure 5.** Structure of  $U_2(OCHO)_4Cl_2$ .



**Figure 6.** Structure of  $U_2(OCHO)_6$ .

This molecule has also been found to be stable with an inner and an outer minimum, separated by a barrier of 13 kcal/mol. The outer minimum is 31 kcal/mol more stable. The electronic structure is similar to that of  $U_2(OCHO)_4$  with a triple bond in the inner minimum and a single bond in the outer. The U–U bond distance in the outer minimum is considerably shorter than in the tetraformate, 3.11 Å instead of 3.42 Å, indicating a stronger U–U single bond in the hexaformate. In 1984, Cotton et al. synthesized a series of  $U_2$  alkoxides.<sup>26</sup> These had U–U distances varying between 3.6 and 3.8 Å. No evidence for a direct U–U bond was found. The uranium atoms were connected via an almost linear U–O–U bridge. The oxidation state was U(IV), so one would not expect to find a U–U bond. The single bond distances found here are shorter, and the wave functions show clear evidence of the formation of a direct chemical bond between the two U atoms. The results for all the species studied shows that the U(III)–U(III) triple bond is about 2.4 Å, while the weak U–U triple bond in  $U_2(OCHO)_4Cl_4$  is about 2.8 Å.

The present study has, for simplicity, been performed using the simplest carboxylate ion, formate. More-complex ions can of course be used in the experiment. It is well-known from studies of the corresponding transition metal compounds

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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,  $H_2UUH_2$  and  $O UUO$ . 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.

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