



Metal-metal multiple bond in low-valent diuranium porphyrazines and its correlation with metal oxidation state: A relativistic DFT study



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ABSTRACT

To explore the uranium-uranium bonding nature, a ligated diuranium complex that could be experimentally possible would show features with no bridging ligand constraints (i.e. discrete or unsupported ligand), rigid ligand skeleton and suitable U–ligand bond. In this respect, we have designed and examined a series of diuranium diporphyrazines ($U_2^m Pz_2$, $m = II, III$ and IV) using relativistic density functional theory. Optimizations on all possible electron-spin isomers find that the triplet, quintet and septet states are energetically lowest for $U_2^m Pz_2$ ($m = II, III$ and IV), respectively. They possess bond lengths of U–U at 2.37, 2.46 and 2.91 Å, bond orders of 3.48, 3.33 and 2.11, and stretching vibrational frequencies of 239, 172 and 108 cm^{-1} . Associated with the electronic-structure and QTAIM (quantum theory of atoms in molecules) analyses, a weak quadruple bond is suggested for the triplet state of $U_2^{II} Pz_2$, and the triple and double bonds for $U_2^{III} Pz_2$, and $U_2^{IV} Pz_2$, respectively. It shows that the uranium oxidation state approximately correlates with the number of multiple bonds.

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1. Introduction

Since the Re–Re quadruple bond was discovered [1–3], great attention has been paid to metal–metal bonding nature of a variety of complexes, its relationship with metal oxidation state, as well as its effects on structure, properties and applications [4–17]. The multiple bonds have been commonly found in the transition metal (TM) complexes [8]. In the last three decades, complexes featured with uranium–TM bond have been intensively investigated, where TM includes iron [5–7], ruthenium [5,9], cobalt [10–12], rhenium [13–15], nickel [17], palladium [17], platinum [17], and silver [16]. In contrast, uranium–uranium complex, particularly the experimental systems, remains rare [18]. Given the experimental difficulties in making complexes containing uranium–uranium bonds, theoretical computations based on accurate methodology would help improve our understanding of actinide–actinide bonding and provide some implication for future experimental synthesis.

The uranium dimeric species U_2 and U_2O_2 were firstly found in the gas phase by mass spectrometry [18]. Using complete active space wave function theory (WFT), Gagliardi and Roos elucidated the uranium–uranium interaction in the U_2 molecule as a quintuple

bond [19]. The same group also extended studies to other diactinides (like Ac_2 , Th_2 and Pa_2) [20], $PhUUPh$ [21], as well as diuranium chlorides and formates [22]. Kalstsoyannis and co-workers suggested triple bonds in model systems of $[U_2X_6]$ ($X = F, Cl, OH, NH_2$ and CH_3) and $[M_2X_8]^{2-}$ ($M = U, Np, Pu; X = Cl, Br$ and I) via density functional theory (DFT) studies [23,24]. The dimetalloendo-fullerene $U_2@C_n$ ($n = 60, 70$ and 84), the first one being detected in a Fourier transform ion cyclotron resonance mass spectrometry experiment [25], has been a subject of some DFT calculations [26,27]. It was concluded no natured U_2 bond in the fullerene systems, and the U_2 multiple bond present in $U_2@C_{60}$ is an artifact due to the constraints of small-size and rigid C_{60} cage.

A diuranium system with two discrete ancillary (unsupported) ligands is believed as a good candidate to explore metal–metal bonding nature. Organoactinides $An_2Cp_2^*$ ($Cp^* = C_5(CH_3)_5$, $An = Th-Pu$) [28] and $An_2(C_8H_8)_2$ ($An = Th, Pa, U$, and Np) [29], for instance, have been studied recently. Different from the $An-C$ bonds in above systems, our group have reported highly diverse bonding between two U^{III} ions ligated by a flexible Schiff-base polypyrrole [30]. Although our work has addressed bond-strength-suitable U–N interaction, the molecular system has the limitation of semi-open-ring (semi-unsupported) ligand structure.

In brief, to explore the uranium–uranium bond and unravel its nature, a ligated diuranium complex that could be experimentally possible would possess some features: (i) there are no geometrical

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constraints placed on the metal atoms by ligand. So discrete (unsupported) ancillary ligand is recommended, which does not structurally impose metal-metal interaction; (ii) the ligand is supposed to have a rigid skeleton and does not suffer great distortion due to U–ligand (U–L) bonds; and (iii) the U–L bonding strength is suitable [31,32]. It would be best if the U–L bond were not so strong as U–U one(s). To satisfy these conditions, we chose the porphyrazine (Pz) ligand, which is a tetrapyrrolic macrocycle and has a rigid conjugation structure. Notably, the N-type donors like oligomeric pyrroles are prospective candidates to complex uranium ions [33–49]. The U–N bond has been found to show some covalency, allowing for promising applications of this type of ligands in the separation science of uranium [50].

In this paper, we have studied a series of diuranium diporphyrazine complexes using relativistic DFT. Uranium oxidation state varies from II, III to IV. Short U–U distances (2.37–2.91 Å), large bond orders (more than 2), and high U–U stretch frequencies (239–108 cm⁻¹) suggest the presence of the U₂ multiple bond in these complexes, which were confirmed by analyses of electronic structures and quantum theory of atoms in molecules (QTAIM). The correlation between uranium oxidation state and multiple bond number has been built.

2. Computational details

We have investigated diuranium diporphyrazine complexes (U₂^mPz₂)ⁿ⁺. The oxidation state (m) changes from II, III to IV, corresponding molecular charges (n) of 0, 2 and 4, respectively. For convenience, the notation of U₂^mPz₂ was used throughout the work.

In a kind of stable structure, the U₂ line is perpendicular to the two Pz planes, named as the vertical model. Optimizations also result in other-model structure, for instance, where the U₂ line displays an angle with respect to the Pz planes. To address the uranium-uranium interaction, we applied the vertical model. On the other hand, two Pz ligands in this model can adopt two configurations along the vertical U–U bond, i.e. eclipsed (**e**) and staggered (**s**) as seen in Fig. 1. Table S1 of Supporting Information shows that these two isomers have quite close energy, because their two Pz ligands are located at relative long distance and have a slight interaction. In this work, unless otherwise noted, only the eclipsed isomers were discussed.

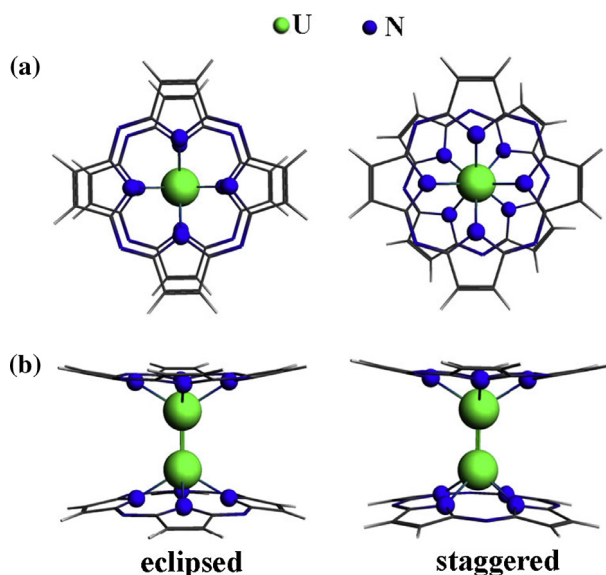


Fig. 1. Optimized structures of U₂^mPz₂ (m = II, III and IV): top view (a) and side view (b).

The various electron-spin states were taken into account for U₂^mPz₂ (m = II, III and IV). For example, the U₂^{II}Pz₂ complex has five spin states from singlet to nonet according to electron counting. And three spin-state isomers should be applicable for U₂^{IV}Pz₂. Unfortunately, we did not obtain its stable singlet-state structure, although many efforts were made.

Using the Priroda code (version 6), structures of diuranium complexes were fully optimized in the gas phase without symmetry constraints [51–55]. A scalar relativistic four-component all-electron (AE) approach [54,56] was used with spin-orbit projected out [57] and neglected from the full Dirac equation. We applied the GGA-PBE functional [58] and the all-electron correlation-consistent double- ζ polarized quality basis sets [52] (labeled as B-I). The basis sets were taken as U (34s33p24d18f6g)/(10s9p7d4f1g), N/C (10s7p3d)/(3s2p1d) and H(6s2p)/(2s1p). And thus, 970 orbital basis functions with 3242 auxiliary basis functions were used for the U^{II} complex, for instance. The gradients in the geometry optimizations were converged to 10⁻⁵ au, together with the criterion of 10⁻⁶ au for the SCF. These tight tolerances were used for calculations of most complexes, with the exception of the nonet state of U₂^{IV}Pz₂ that was only converged to 10⁻³ au for the geometry optimization. Analytical frequency calculations were performed. No imaginary frequencies were found, indicating these structures are minima on the potential energy surface. Total energy including zero-point vibrational energy (E₀), enthalpy (H) and free energy (G) were obtained simultaneously. Population-based (Mayer) [59] bond orders, charges (Mulliken) and electron-spin density were also calculated with both Priroda and ADF code.

Calculations of electronic properties were carried out using the ADF2014 code [60–62] on the basis of the Priroda optimized geometries. The default convergence criterion of 10⁻⁶ au was used, and an integration parameter of 6.0 was applied. The scalar relativistic ZORA approach of van Lanthe [63–66] and Slater-type ZORA-TZP basis sets (denoted as B-II) were used in these calculations. The core orbitals (1s–4f for U and 1s for C and N) were frozen, and 32 valence electrons (5s²5p⁶5d¹⁰6s²6p⁶5f³6d¹7s²) were considered for the U atom (small-core basis sets).

To provide deep insight into the uranium-uranium multiple bonds, we have carried out QTAIM [67,68] calculations. All spin-state complexes were calculated at the Priroda-optimized geometries with the Gaussian09 code [69]. Stuttgart relativistic large-core effective core potentials (RLC-ECPs) [70–72] was employed for uranium. The Stuttgart RLC basis sets was applied for uranium and 6-31G* for other atoms (labeled as B-III), together with the GGA-PBE functional [58]. QTAIM analysis were performed with the Multiwfn3.3.3 package [73]. Additionally, the ADF code was also used to calculate their BCP data for comparison.

3. Results and discussion

3.1. Relative energy

We optimized the complexes U₂^mPz₂ (m = II, III and IV) in various electronic states. Regarding the divalent diuranium complex, the triplet state was calculated to be the energetically lowest among all spin states as shown in Fig. 2. It is 13–30 kJ/mol more stable in total energy (ΔE), Table 1. The same trend was reproduced by the other thermodynamic energies ΔE_0 , ΔH and ΔG . Our calculations reveal that the quintet state is the ground state for both U₂^{III}Pz₂ and U₂^{IV}Pz₂. Additionally, hybrid functionals PBE0 and B3LYP were used to calculate energies of diuranium complex in various spin states. As seen in Table S2, the same energetic trends were obtained as those of GGA-PBE.

Notably, the quintet state of U₂^{III}Pz₂ was optimized to show two configurations, eclipsed (**e**) and staggered (**s**), in Table 1. They are

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