Unwilling U–U bonding in U₂@C₈₀: cage-driven metal–metal bonds in di-uranium fullerenes†

Cina Foroutan-Nejad,ab Jan Vicha,abc Radek Marek,b Michael Patzschkeabd and Michal Strakaacd

Endohedral actinide fullerenes are rare and a little is known about their molecular properties. Here we characterize the U₂@C₈₀ system, which was recently detected experimentally by means of mass spectrometry (Akiyama et al., JACS, 2001, 123, 181). Theoretical calculations predict a stable endohedral system, U₂@C₈₀, derived from the C₈₀:7 IPR fullerene cage, with six unpaired electrons. Bonding analysis reveals a double ferromagnetic (one-electron-two-center) U–U bond at an r_{U-U} distance of 3.9 Å. This bonding is realized mainly via U(5f) orbitals. The U–U interaction inside the cage is estimated to be about −18 kcal mol⁻¹. U–U bonding is further studied along the U₂@Cₙ (n = 60, 70, 80, 84, 90) series and the U–U bonds are also identified in U₂@C₇₀ and U₂@C₈₄ systems at r_{U-U} ~ 4 Å. It is found that the character of U–U bonding depends on the U–U distance, which is dictated by the cage type. A concept of unwilling metal–metal bonding is suggested: uranium atoms are strongly bound to the cage and carry a positive charge. Pushing the U(5f) electron density into the U–U bonding region reduces electrostatic repulsion between enclosed atoms, thus forcing U–U bonds.

Actinide fullerenes have also attracted the attention of theoreticians. Mainly the An@C₂₈ compounds were studied. The An@C₂₆ and An@C₄₀ series and related compounds, such as U₄@C₆₆, Pu₄@C₄₄, and U₄@C₆₂, were investigated. To the best of our knowledge, the experimentally observed U₂@C₈₀ molecule has not been studied yet, and is the main concern of the present work.

The presence of two actinide atoms in a fullerene cage brings another interesting aspect that makes the endohedral actinide fullerenes attractive – the possibility of forming actinide–actinide bonds in the interior of a fullerene. Although numerous examples of metal–metal bonds for d-block elements have been documented in the transition-metal chemistry, actinide–actinide bonds are rare. The question of the existence of actinide–actinide bonding dates back to the early studies by Cotton et al. and was revived by Gagliardi and Roos in 2005 on a U₂ system, which is experimentally known, followed by sequels on actinide diatomics and studies of various compounds with actinide–actinide bonds.

Endohedral U–U bonding was suggested in 2007 by Wu and Lu who studied theoretically the U₂@C₆₀ system, observed previously in TOF-MS experiments. It was found, based on the MO framework, that the two U atoms confined in C₆₀ form six one-electron-two-center (1e-2c, or ferromagnetic) metal–metal bonds at a calculated minimum U–U distance, r_{U-U} = 2.72 Å. Infante et al. argued that the multiple U–U bonding in U₂@C₆₀ is, in fact, forced by the small interior of the cage. Hypothetical U₂@C₇₀ and U₂@C₈₄ fullerenes were calculated therein but the

1 Introduction

Endohedral fullerenes and particularly endohedral metallofullerenes (EMF) have been extensively studied as promising materials for practical applications. Despite the great developments in EMF science little is known of actinide endohedral fullerenes and their properties. Most of the experimentally reported actinide EMFs to date were only observed as signals in the time-of-flight mass spectra (TOF-MS), as for example U₄@C₇₂ (n = 14–36) and some of the U₄@C₇₄ (n = 25–30) systems. Akiyama et al. reported a series of An@C₃₂ (An = U, Np, Am) as well as An@C₈₄ (An = Th, Pa) fullerenes, and also U₂@C₇₀ that is of interest in this work. U₂@C₈₂ and Th₂@C₈₄ were prepared in larger amounts to be characterized by UV/vis/NIR spectroscopy. The experimental formation of U@C₂₈ was studied recently.

# References

† Electronic supplementary information (ESI) available: Table S1 with xyz coordinates of U₂@C₈₀ lowest minimum and Fig. S1 and S2 with IR and Raman spectra of U₂@C₈₀ lowest minimum. Fig. S3 with Laplacian of spin density for U₂@C₈₀ and Fig. S4–S8 with frontier molecular orbitals for U₂@C₈₀ (n = 60, 70, 80, 84, 90) compounds. See DOI: 10.1039/c5cp04280a

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* Institute of Organic Chemistry and Biochemistry, Academy of Sciences, Flemingovo nám. 2, CZ-16610, Prague, Czech Republic. E-mail: straka@uochb.cas.cz

† Correspondence to: Michael Patzschke, E-mail: Michael.Patzschke@uni-due.de

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U–U bonding in these systems was not investigated, possibly because of the calculated large U–U separation, r_{U-U} ~ 3.9 Å. Dai et al. predicted that in hypothetical U_2@C_{90}, the uranium atoms separate to r_{U-U} ~ 6.1 Å.\(^{46}\)

A recent study has predicted the UGd@C_{60} analogue of U_2@C_{60} fullerene to have a large encapsulation energy and a high-spin 11-et ground state with a twofold one-electron U–Gd bond.\(^{47}\) Studies of U_2@C_{64} revealed that the exochemical carbon atom has a strong influence on the U–U distance and ground-state spin multiplicity. Such defects can be used for tuning the electronic properties of EMFs.\(^{47,48}\)

Endohedral metal–metal bonding has been recently discussed in some experimentally known lanthanide and transition-metal fullerenes, for example, in Y_2@C_{79}N,\(^{49}\) Lu_2@C_{76},\(^{50-52}\) and anionic La_2@C_{90} fullerenes.\(^{53}\) For more examples and references, see ref. 53 by Popov et al., where the topic of endohedral metal–metal bonding is reviewed and studied in detail.

In this work we characterize fullerene U_2@C_{60} by means of theoretical calculations. A stable endohedral system with large encapsulation energy for U in the C_{80} cage is found. The energy and bonding analysis of U_2@C_{60} provides evidence for metal–metal bonding interactions between the trapped uranium atoms. To further reveal the general trends in the endohedral U–U bonding we investigate a series of U_2@C_n (n = 60, 70, 80, 84, 90) fullerenes and show newly the evidence for U–U bonding in hypothetical U_2@C_{70} and U_2@C_{84} cages as well as a correlation between the character of the U–U bonding and U–U distance inside a fullerene cage.

2 Methods

2.1 Molecular structure and properties

Following the previous experience,\(^{45}\) calculations were done with the BP86 density functional using the def-SVP basis sets for C and U atoms\(^{54,55}\) as implemented in the Turbomole 6.3.1 code. This basis set includes the effective core potential (SDD) for uranium atoms.\(^{55}\) The structure search was done using Turbomole 6.3.1 and Gaussian 09 programs.\(^{56,57}\) Natural population analysis (NPA) as implemented in the natural bond orbital\(^{58,59}\) analysis implemented in Gaussian 09 was used. Molecular Orbitals were plotted using the Multif dot\(^{60}\) and VMD software.\(^{61}\)

The search for the geometry of the U_2@C_{60} system was limited to the endohedral arrangement, U_2@C_{60}. This restriction is well justified by previous findings by Infante et al.\(^{45}\) that the endohedral bonding of U_2 is strongly preferred to the exohedral arrangement in fullerenes C_{60}, C_{70}, and C_{84}. In search for the lowest U_2@C_{60} minimum, local minima were searched by placing the U_2 unit (at r_{U-U} = 2.5 Å) in the center of the C_{60} cage along three different orientations (x, y, or z axis). All seven IPR C_{60} cages were checked by this procedure. The systems were minimized maintaining the septet electron state\(^{34,45}\) without symmetry constraints. The septet ground state was confirmed by calculating triplet, quintet, and nonet (all geometry optimized). The quality of the unrestricted Kohn–Sham wavefunction was confirmed by negligible spin-contamination, <0.1. The minima were checked by frequency analysis.

The empty C_{80} cage has topological I_8 symmetry which is a saddle point due to orbital degeneracy. The empty cage undergoes the Jahn–Teller distortion to a D_2 structure.\(^{62}\) For the encapsulation energy calculations we used the C_{80}:7 (I_8) geometry as a starting point and minimized it under D_2-symmetry constraints in the singlet ground state.

2.2 QTAIM analysis

The topological properties of critical points within the context of the Quantum Theory of Atoms in Molecules (QTAIM)\(^{63}\) have been employed many times for analyzing the bonding properties in various materials\(^{64}\) including fullerenes, see, e.g. ref. 53 and 65–67.

However, as some of us have shown recently,\(^{68}\) the presence or absence of line critical points (LCP) in a single geometry neither confirm nor invalidate the presence of a chemical bond. In this work, we rely on the profiles of the derivatives of the electron density and a unique quantitative measure of the covalency within the context of QTAIM, delocalization index, δ(A ↔ B) or DI.\(^{68}\)

Of the topological profiles, the Laplacian of the electron density, ∇^2 ρ(r), has been conventionally used to identify the electron density concentration (EDC) between atoms that are believed to be linked to covalency.\(^{63}\) Besides ∇^2 ρ(r), energy density, V(r), has been proposed to be an efficient tool for distinguishing covalent and polar covalent chemical bonds.\(^{69}\) Energy density at any point in space is defined as $V(r) = \nabla^2 \rho(r) + G(r)$, where $V(r)$ and $G(r)$ are potential and gradient kinetic energy densities. $V(r)$ is always negative at any point in space but $G(r)$ is always positive; a negative $H(r)$ value denotes the dominance of potential energy at a point, which has been interpreted in favour of covalency.

The DI defines the number of electrons that are shared between any pair of atoms,

$$\delta(A \leftrightarrow B) = -2\langle n_A n_B \rangle - \langle n_A \rangle \langle n_B \rangle,$$  \hspace{1cm} (1)

where $\langle n_A n_B \rangle$, $\langle n_A \rangle$, $\langle n_B \rangle$ are the localization index or in other word, the minimum electron populations of the atomic pair and single atoms, respectively.

The DI was suggested as a direct measure of electron exchange between atomic basins of two atoms A and B. Recent studies demonstrate that $\delta(A \leftrightarrow B)$ quantitatively reflects the magnitude of the exchange–correlation energy component for an atomic pair A–B.\(^{70,71}\) The magnitude of DI is close to unity for a typical single homonuclear (sigma) bond, e.g. a carbon–carbon bond in ethane.\(^{72}\) The magnitude of DI for a homonuclear bond reflects the bond order, e.g., it is close to 2, 3, and 4 for double, triple, and quadruple homonuclear bond, respectively. On the contrary, DI of a polar-covalent bond is smaller than the expected value based on the MO picture, which is consistent with chemical intuition for the formation of a polar covalent bond. Nevertheless, it is highly recommended to compare the DI of any system with an external reference to characterize the bond order of a system. Here, we chose U_2 as
our external reference for assessing the bond order between uranium atoms in the fullerene systems. Scalar-relativistic computations predicted that $U_2$ has a quintuple bond.\(^{33}\) Studying the $\delta(U \leftrightarrow U)$ of $U_2$ molecule, optimized at the same level of theory as $U_2@C_{80}$, demonstrates that the DI can recover the bond order of this system in a good agreement with previous studies; $\delta(U \leftrightarrow U) = 5.08$.

The wavefunction for the analysis of the electron density of the minimum structure was obtained by the BP86/SVP/SDD computational level (cf. above) by Gaussian 09.\(^{36}\) The electron density was analyzed within the context of the QTAIM\(^{44}\) by AIMAll suite of programs.\(^{73}\) For properly treating the uranium atoms in QTAIM analysis, auxiliary basis functions were added to the wavefunction of the molecule.\(^{73}\)

### 3 Results and discussion

#### 3.1 $U_2C_{80}$ is a stable endohedral $U_2@C_{80}$ system with a septet ground state. $U-U$ interactions inside the cage are attractive

Endohedral compounds of the $M_2@C_{80}$ formula, so far experimentally observed, are either $M_2^B@C_{78}$ systems, such as $T_1C_2@C_{70}$ or $M_2^C@C_{80}$ systems, such as $C_2^B@C_{80}$ fullerenes.\(^{47-49}\) Because the ionic radii of $U^{3+}$ and $Ce^{4+}$ are almost identical, 1.16 Å and 1.15 Å, while those of $Ti^{4+}$ and $U^{3+}$ are substantially different, 0.74 Å and 1.03 Å, ref. 77, it can be assumed that an $U^{3+}$@C$_{80}$ system would be formed rather than an $U^{3+}C_2@C_7$ system.

The lowest energy minimum structures for each of the seven possible IPR (isolated pentagon rule)\(^{38}\) $C_{80}$ cages with enclosed $U_2$, assuming the septet ground state,\(^{44-46}\) i.e., six unpaired electrons, are listed in Table 1. The lowest energy minimum derives from the $C_{80}$ cage whereas the optimized minima based on other IPR cages are ca. 10–40 kcal mol$^{-1}$ less stable. Indeed, the $U_2C_2@C_{78}$ isomer was calculated ca. 20 kcal mol$^{-1}$ higher in energy than the most stable $U_2@C_{80}$ isomer, Table 1.

#### Table 1 Calculated relative energies\(^{a}\), $\Delta E$, and $U-U$ distances\(^{b}\), $r_{U-U}$, for the IPR-based $U_2@C_{80}$ isomers and $U_2C_2@C_{78}$ system\(^{c}\)

<table>
<thead>
<tr>
<th>System</th>
<th>$\Delta E$ [kcal mol$^{-1}$]</th>
<th>$r_{U-U}$ [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$U_2@C_{80}$</td>
<td>0.0</td>
<td>5.917</td>
</tr>
<tr>
<td>$U_2@C_{80}$</td>
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<td>5.917</td>
</tr>
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<td>3.728</td>
</tr>
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<td>4.198</td>
</tr>
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<td>3.871</td>
</tr>
<tr>
<td>$U_2@C_{80}$</td>
<td>11.8</td>
<td>3.891</td>
</tr>
<tr>
<td>$U_2@C_{80}$</td>
<td>22.9</td>
<td>3.965</td>
</tr>
<tr>
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<td>3.894</td>
</tr>
<tr>
<td>$U_2@C_{80}$</td>
<td>13.4</td>
<td>3.872</td>
</tr>
<tr>
<td>$U_2C_2@C_{78}$</td>
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<td>2.526</td>
</tr>
<tr>
<td>$U_2C_2@C_{78}$</td>
<td>29.8</td>
<td>4.326</td>
</tr>
<tr>
<td>$U_2C_2@C_{78}$</td>
<td>42.1</td>
<td>4.325</td>
</tr>
</tbody>
</table>

\(^{a}\) Relative electronic energies wrt the ground state $U_2@C_{80}$ calculated at the BP86/SVP/SDD level. \(^{b}\) The closest $U-U$ separations are 2.35–2.50 Å. The $U-U$ distances in $U_2C_2@C_{78}$ are between 2.20 and 2.30 Å. \(^{c}\) Singlet $U_2@C_{80}$ could not be converged.

The optimized structure of $U_2C_{80}$ is shown in Fig. 1. The molecule has $C_2$ symmetry with the two uranium atoms located nearby a $D_{2h}$ axis of the $C_{80}$ cage. Analogous $^{3}Ce_2C_2@C_{80}$ has a $D_{2d}$ minimum structure with the cerium atoms and the two closest carbons located on a $D_{2d}$ axis.\(^{75}\) (It is a dynamical system, though.\(^{76}\)) Attempted optimization of $U_2C_{80}$ within $D_{2d}$ constraints did not converge to a stationary point. At the present level of theory a $C_{2h}$-symmetric stationary point (one imaginary frequency) could be found about 1 kcal mol$^{-1}$ above the $C_1$ minimum. With such a small difference, it cannot be excluded that the $C_{2h}$ stationary point becomes the lowest minimum if different computational levels are used.

The $U-U$ distance in the $U_2C_{80}$ minimum structure of 3.89 Å is rather long as compared to that predicted for $U_2@C_{80}$ ($\sim 2.72-2.74$ Å),\(^{44-46}\) or in bare $U_2$ and $U_2^+$ ($\sim 2.43$ and $\sim 2.30$ Å).\(^{33,35,45}\) It is also longer than twice the empirical single-bond radius of uranium ($2 \times 1.7$ Å $= 3.4$ Å),\(^{79}\) which suggests the $U-U$ bond order lower than one. However, see below.

The closest $U-C$ bond lengths in $U_2C_{80}$ are $2.40, 2.48$, and 2.51 Å, comparable to those found in the strongly bound $U_2C_2$, where the $r_{U-C}$ closest contacts are within 2.44–2.51 Å.\(^{25}\) In fact, the cage is significantly stretched along the $U-U$ axis in $U_2C_{80}$. The end-to-end distances between the carbon atoms connecting three hexagons on opposite sides of the cage (Fig. 1) vary from 8.16 to 8.33 Å in the empty $C_{80}$, and elongate to 8.68 Å along the $U-U$ axis and to 8.20 Å in the direction perpendicular to the $U-U$ axis in the $U_2C_{80}$ minimum structure.

The septet ground state of $U_2C_{80}$ with six unpaired electrons was confirmed by calculating the geometry-optimized nonet, quintet, and triplet, which lay 13, 18, and 23 kcal mol$^{-1}$ above the ground state septet, Table 1. Note that the previously studied di-uranium fullerenes, $U_2@C_{60}, U_2@C_{70}, U_2@C_{84}$, and $U_2@C_{90}$, were predicted to be septet in their ground state.\(^{44-46}\) These findings point to a general pattern in the electronic structure of $U_2@C_{2n}$ fullerenes. For the future experimental reference, the predicted structure, IR, and Raman spectra of the $U_2@C_{80}$ lowest minimum structure are given in Table S1 and Fig. S1 and S2 in the ESI.

The encapsulation energy, $\Delta E$, for the $U_2@g + C_{80}(g) = U_2C_{80}(g)$ reaction was calculated to be $-252.7$ kcal mol$^{-1}$ at the BP86/SVP/SDD level. The reaction enthalpy, approximated by the sum of the electronic and zero-point energy was predicted slightly lower, $\Delta H = -248.6$ kcal mol$^{-1}$. These results are consistent with the previous findings for $U_2@g_{60}, U_2@g_{70}$, and $U_2@g_{94}$ where the encapsulation energy was ranging from $-160$ to $-210$ kcal mol$^{-1}$.\(^{44,45}\) For a further comparison, we calculated encapsulation energies for the experimentally known analogous La$_2@g_{80}$ and Ce$_2@g_{80}$ complexes. The calculated $\Delta E$ for the $M_2@g + C_{80}(g) = M_2@g_{80}(g)$ reaction\(^{80,81}\) is predicted to amount to $-255$ and $-257$ kcal mol$^{-1}$ for $M = La, Ce$ at the BP86/SVP/SDD level.

Interaction between the enclosed uranium atoms in $U_2@g_{80}$ can be actually estimated from a hypothetical isodesmic reaction $2U@g = U_2@g + g_{80}$. Thanks to the symmetry of the system, the left side of the reaction corresponds to twice the
U–cage interaction and the right side has twice the U–cage plus the U–U interaction in it. The $\Delta E = -17.7 \text{ kcal mol}^{-1}$ is in favour of products and gives a thermodynamical evidence for endohedral U–U bonding interactions in U$_2$@C$_{80}$. This evidence is further supported by the bonding analysis given below.

Apparently, the encapsulation energy for U$_2$@C$_{80}$ of $-250 \text{ kcal mol}^{-1}$ is substantially larger than the U–U interaction estimated above, or than the dissociation energy of U$_2$, which was calculated to be $-70.1 \text{ kcal mol}^{-1}$ at the BP86/SVP/SDD level or $-33.6 \text{ kcal mol}^{-1}$ at the CASPT2 level at corresponding equilibrium distance ($r_{\text{U–U}} \sim 2.7 \text{ Å}$). The weaker U–U bonding will be strongly affected by the size/type of the cage keeping each uranium atom at a position dictated by the stronger U–C bonding, see Section 3.4.

### 3.2 MO analysis reveals endohedral U–U bonding orbitals in U$_2$@C$_{80}$

It is well known that in M$_2$@C$_{80}$7 systems, the C$_{80}$ cage formally accepts six electrons from the confined metal atoms. At the ionic limit, this leads to a C$_{80}^{6-}$ cage interacting with two positively charged M$^{3+}$ ions. However, the electrons are not fully localized on the cage but they are partly shared between the cage and the enclosed cluster. The bonding situation in 7U$_2$@C$_{80}$7 is akin to previously studied M$_2$@C$_{80}$ compounds. The level of electron transfer is seen on the calculated NPA charge on each uranium atom, $q_{\text{U}} = +0.82$ and on the natural electron configuration (U:7s$^2$5f$^{1.21}$5d$^{3.64}$6d$^{0.98}$) of enclosed atoms in comparison with the ground state configuration of neutral uranium atoms (U:7s$^2$5f$^{3.5}$6d$^1$). The six unpaired electrons in 7U$_2$@C$_{80}$7 are mainly in the U(5f) shell, and are, in fact, strongly localized between the encapsulated uranium atoms as seen from NPA analysis (details not shown) and the frontier orbitals in Fig. 2.

A closer look at the frontier singly-occupied molecular orbitals (SOMO) in Fig. 2 reveals a bonding situation between the enclosed uranium atoms. The SOMO and SOMO–1 orbitals have U–U antibonding character whereas the SOMO–2 through SOMO–5 have U–U bonding character. This situation can be interpreted as two (four bonding minus two antibonding) 1e–2c bonds, in other words a double ferromagnetic bond between the encapsulated uranium atoms. This bond is clearly U(5f)-based. The localization of the unpaired electrons between the uranium atoms is identified also by the calculated spin density in Fig. 3. The localization of the spin density on uranium atoms and its presence on some of the cage carbon atoms may allow for the future experimental identification of the U$_2$@C$_{80}$ system by ESR or paramagnetic $^{13}$C NMR spectroscopy.

### 3.3 QTAIM analysis gives evidence for a single U–U bond in U$_2$@C$_{80}$

The bonding between the encapsulated U–U atoms in U$_2$@C$_{80}$ is further studied by the QTAIM analysis (for details on QTAIM, see Methods section). In this work, rather than on the presence or absence of line critical points we rely on the profiles of the derivatives of the electron density and a unique quantitative measure of the covalency within the context of QTAIM, the delocalization index, $\delta(A \leftrightarrow B)$. Inspecting the Laplacian of the alpha-electron density reveals electron density concentration (EDC) between the uranium atoms, Fig. 4b, a.k.a. U–U bonding interaction. Interestingly, the EDC between the U atoms is not recognizable in the Laplacian of the total electron density, Fig. 4a, since the overall electron density masks the alpha-EDC between the uranium atoms, shown in Fig. 4b. An interesting picture emerges from the Laplacian of the spin density, Fig. 4c, which highlights the regions of spin-density concentration. A profile of f-orbitals and an EDC between two uranium atoms resulting from the f-orbital overlap is rather evident in Fig. 4c. For 3D representations of Fig. 4c, see Fig. S3 (ESI†).

In the contour map of energy density, $H(r)$, Fig. 4d, the C–C, U–C and U–U bonds fall in the negative energy density regions,
denoting a total stabilization arising from the covalent-type interactions, i.e. electron sharing among the cage carbon atoms, the carbon and the uranium atoms, and between the two uranium atoms.

The delocalization index, DI, for the U–U bond, $\delta(U \leftrightarrow U)$, was calculated to be 1.01 in $^{7}$U$_2$@C$_{80}$:7. Comparing this value with that for U$_2$ with a quintuple bond calculated at the same level of theory, $\delta(U \leftrightarrow U) = 5.08$, suggests that U–U bonding in the U$_2$@C$_{80}$:7 molecule corresponds to a single U–U bond. This is consistent with the MO picture of two 1e-2c U–U bonds in Fig. 2 above. Notably, calculated $\delta(M \leftrightarrow M)$ indices for Sc–Sc, Y–Y, Lu–Lu, or La–La interactions in similar dimetallofullerenes were found comparably lower than one, within 0.25–0.65, albeit obtained at different levels of theory. The largest value found was $\delta(Lu \leftrightarrow Lu)$ of 0.65 in Lu$_2$@C$_{82}$ at $r_{Lu-Lu} = 3.47$ Å. Details can be found in ref. 53.

The energetically higher multiplets of U$_2$@C$_{80}$:7 (Table 1) give similar DI as that for the septet, $\delta(U \leftrightarrow U) = 1.02$ for the triplet and $\delta(U \leftrightarrow U) = 1.37$ for the quintet state. Nonet could not be analyzed. The larger DI value for the quintet state is given by the fact that the corresponding electron moves from an U–U alpha antibonding to an U–U beta bonding orbital, while $r_{U-U} = 3.90$ Å remains similar to that for the septet ground state, where $r_{U-U} = 3.89$ Å, Table 1.

The magnitude of $\delta(U \leftrightarrow C)$ for single pair of atoms was found in the range of 0.12 to 0.36 for carbon atoms, which are within the distance of 2.98–2.39 Å from the uranium atoms. These values are within the range of the typical metal–carbon delocalization indices.

We have thus seen strong theoretical evidence for U–U bonding in the $^{7}$U$_2$@C$_{80}$:7 system, via the attractive U–U potential inside the cage, the presence of a double ferromagnetic bond, or the QTAIM delocalization index for U–U of 1.01.

Fig. 2 The six highest singly-occupied molecular orbitals (SOMOs) of the $^{7}$U$_2$@C$_{80}$:7 system.

Fig. 3 The calculated ground-state spin density for the U$_2$@C$_{80}$:7 system.
Notably, this U–U bonding is actually observed at relatively large $r_{U-U} = 3.89$ Å, which is beyond the sum of empirical single-bond radii of uranium of $2 \times 1.7 = 3.4$ Å. The endohedral metal–metal bonding at large M–M separations was recently noted for di-lanthanofullerene anions La$_2@C_{n}$, where $r_{La-La}$ as large as 3.7–5.2 Å gave $\delta$(La ↔ La) = ~0.3, ref. 53. Hence, we decided to investigate a series of previously studied di-uranium fullerenes to estimate how far can the U–U bonding reach and what are the cage-driving capabilities of fullerenes for U–U bonding.

3.4 The U–U bonding along the U$_2@C_{60}$ series reaches beyond U$_2@C_{80}$ and is determined by the cage type

In the following we shortly analyze the U–U bonding interactions and trends in the series of diuranium fullerenes, U$_2@C_n$ ($n = 60, 70, 80, 84, 90$). The selection of C$_{70}$–C$_{90}$ cages was motivated solely on the basis of previous studies to illustrate the metal–metal bonding vs. the size of the cage; lower-energy isomers may exist but were not searched for. Optimized structures of U$_2@C_n$ are shown in Fig. 5. Selected properties, calculated at the BP86/SVP/SDD level, are summarized in Table 2. We note that only U$_2@C_{60}$ and U$_2@C_{80}$ of the species in Table 2 have been observed experimentally so far. U$_2@C_{80}$ has the largest U–U encapsulation energy ($\sim 252.7$ kcal mol$^{-1}$) among the studied systems. Generally, the encapsulation energy of diuranium EMFs lies in the range of ~150 to ~250 kcal mol$^{-1}$, Table 2.

The U–U distance and the degree of U–U bonding, expressed by the $\delta$(U ↔ U) along the series in Table 2, in fact correlate with the (relative) size of the fullerene cage. No correlation with the encapsulation energies is observed. As noted for U$_2@C_{80}$, the encapsulation energy along the U$_2@C_n$ series is substantially larger (150–250 kcal mol$^{-1}$) than the energy of U–U binding in bare U$_2$ (70.1 kcal mol$^{-1}$ at the BP86/SVP/SDD level). The U–U interaction inside the cage is thus to a large extent dictated by the U–cage bonding. This argument is further supported by rather constant $r_{U-C}$ contact distances along the series, whereas $r_{U-U}$ is changing substantially, as seen in Table 2.

Following the U–U distance and $\delta$(U ↔ U) along the series, we confirm the argument of Infante et al. that multiple U–U bonding in U$_2@C_{60}$ is forced by the short U–U distance in the small cage interior. In a large enough cage, like C$_{90}$, the uranium atoms separate and practically do not interact with each other. This is confirmed by negligible $\delta$(U ↔ U) = 0.1 in U$_2@C_{90}$. The present results show newly the evidence for the

![Fig. 4 Contour maps of (a) Laplacian of electron density, (b) Laplacian of alpha-electron density, (c) Laplacian of spin density, and (d) energy density in the 7U$_2@C_{80}$ system; negative functions in all plots, implying electron concentration/sharing are presented by red lines.](image-url)
U–U bonding also in cages of intermediate size, U$_2$@C$_{70}$ through U$_2$@C$_{84}$, with $r_{U–U} \sim 3.9–4.0$ Å, as indicated by the QTAIM delocalization index, $\delta(U \leftrightarrow U) = 0.7–1.0$ in Table 2.

The QTAIM analysis shows some general features along the studied series, as is evident from Fig. 6. The EDC, corresponding to the U–U interaction, is absent in the Laplacian of electron densities of U$_2$@C$_{60}$ and U$_2$@C$_{70}$ (Fig. 6, panels 1a and 2a) but it appears for that of U$_2$@C$_{84}$ (Fig. 6, panel 3a). The EDC is also absent in the Laplacian of alpha-ED of U$_2$@C$_{60}$ (Fig. 6, panel 1b) but appears for the U$_2$@C$_{70}$ through U$_2$@C$_{84}$ (Fig. 4b and Fig. 6, panels 2b and 3b). This is due to the masking effect of the electron density of carbon atoms and also the masking of the alpha-ED by beta-ED in the total ED of smaller cages. In all compounds, the Laplacian of the spin density unveils the pattern of f-orbitals involved in accommodating the unpaired 5f-electrons (Fig. 6, panels 1c–4c). The energy-density profiles (Fig. 6, panels 1d–4d) delineate covalently bonded atoms. Notably, the level of U–U interaction can be easily identified qualitatively from the energy density profiles. The strongest effect is seen in U$_2$@C$_{60}$ and U$_2$@C$_{80}$, weaker in U$_2$@C$_{70}$ and U$_2$@C$_{84}$, and the profile of U$_2$@C$_{90}$ points to the absence of U–U interaction, see Fig. 6, panels 1d–4d, and Fig. 4d.

### Table 2

<table>
<thead>
<tr>
<th>System</th>
<th>$r_{U–U}$ [Å]</th>
<th>$r_{U–C}$ [Å]</th>
<th>$\Delta E$ [kcal mol$^{-1}$]</th>
<th>$q_U$</th>
<th>$\delta(U \leftrightarrow U)$ [au]</th>
<th>$\sum\delta(U \leftrightarrow C)$ [au]</th>
<th>NPA on U</th>
</tr>
</thead>
<tbody>
<tr>
<td>U$<em>2$@C$</em>{60}$</td>
<td>2.733</td>
<td>2.48–2.49</td>
<td>–200.7</td>
<td>0.07</td>
<td>2.1</td>
<td>4.5</td>
<td>7s$^{0.13}$, 5f$^{0.17}$, 6d$^{1.16}$</td>
</tr>
<tr>
<td>U$<em>2$@C$</em>{70}$</td>
<td>3.923</td>
<td>2.40–2.65</td>
<td>–189.1</td>
<td>0.41</td>
<td>0.7</td>
<td>4.9</td>
<td>7s$^{0.23}$, 5f$^{0.76}$, 6d$^{1.03}$</td>
</tr>
<tr>
<td>U$<em>2$@C$</em>{80}$</td>
<td>3.894</td>
<td>2.40–2.54</td>
<td>–252.7</td>
<td>0.82</td>
<td>1.0</td>
<td>4.1</td>
<td>7s$^{0.31}$5f$^{0.54}$, 6d$^{0.98}$</td>
</tr>
<tr>
<td>U$<em>2$@C$</em>{84}$</td>
<td>4.071</td>
<td>2.44–2.67</td>
<td>–152.2</td>
<td>0.78</td>
<td>0.7</td>
<td>4.4</td>
<td>7s$^{0.24}$, 5f$^{0.62}$, 6d$^{0.92}$</td>
</tr>
<tr>
<td>U$<em>2$@C$</em>{90}$</td>
<td>6.358</td>
<td>2.39–2.64</td>
<td>–183.0</td>
<td>0.74</td>
<td>0.1</td>
<td>4.9</td>
<td>7s$^{0.88}$, 5f$^{0.77}$, 6d$^{0.88}$</td>
</tr>
</tbody>
</table>

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**Fig. 5** Optimized structures of U$_2$@C$_{60}$, U$_2$@C$_{70}$, U$_2$@C$_{84}$, and U$_2$@C$_{90}$. The U–U and closest U–C interactions are shown by dotted lines with the corresponding interatomic distances.
The delocalization index serves as a seamless quantitative measure of the order of the U–U bond. With a small deviation for U2@C84 the $\delta(U \leftrightarrow U)$ decreases as the U–U distance increases in Table 2. In fact, an exponential correlation can be found with a correlation coefficient of $r^2 = 0.9802$ between $r_{U-U}$ inside a cage and $\delta(U \leftrightarrow U)$, see Fig. 7.

To complete the picture of bonding along the series, we analyzed also the frontier orbitals of the studied compounds, see Fig. S4–S8 in the ESI†. The trends in the MO framework along the series are less straightforward than the results of QTAIM analysis and are only discussed briefly. In accord with the work of Wu and Lu44 there are six 1e-2c U–U bonding orbitals (one $\sigma$-, three $\pi$-, and two $\delta$-orbitals) in U2@C60, see Fig. S4 (ESI†). This qualitatively correlates with $\delta(U \leftrightarrow U) = 2.1$. In U2@C70 most of the frontier orbitals are actually bonding but they do not overlap efficiently; only two $\sigma$-type orbitals show significant U–U overlap, Fig. S5 (ESI†), which explain lower $\delta(U \leftrightarrow U) = 0.7$ in U2@C70. In U2@C84, we recall the four U–U

![Fig. 6 Profiles of the Laplacian of (a) total electron density, (b) alpha-electron density, (c) spin density, and (d) the energy density for U2@C60 (1), U2@C70 (2), U2@C84 (3), and U2@C90 (4); red and blue lines depict negative and positive regions of each function, respectively.

![Fig. 7 The plot of $\delta(U \leftrightarrow U)$ versus U–U bond length in U2 (at DI ~ 5) and along the studied U2@Cn series.](image)
bonding and two U–U antibonding one-electron orbitals (Fig. 2 and Fig. S6, ESI†) and δ(U ↔ U) = 1.0. In U2@C84 there is one σ- and two π-type U–U bonding orbitals (Fig. S7, ESI†) but the latter are only weakly overlapping, which explains lower δ(U ↔ U) of 0.7. No U–U bonding orbitals are observed in U2@C90 (Fig. S8, ESI†). The definition of the bond order using MO analysis is thus not straightforward. The delocalization index appears as a more genuine and general parameter to be used in the present context.

Finally, the U–U bonding inside a fullerene cage can be regarded as an unwilling bonding. The uranium atoms strongly bind to the cage and acquire a positive charge.53 The calculated NPA charges in Table 2 on uranium atoms vary from 0.1 in U2@C60 and 0.4 in U2@C70 to ~0.8 in larger fullerenes. To compensate for the U–U charge repulsion, the electron density in U(5f) shells delocalizes between the uranium atoms thus making one-electron-two-center U–U bonds. In a small cage, like U2@C60, covalent multiple U–U bonding with DI(U ↔ U) = 2.1 is forced by the short U–U distance. In larger cages, C70 through C84, the U–U bonding of the order of single bond is still predicted, even at rU–U ~ 4 Å, with DI(U ↔ U) between 0.7 and 1.0. In U2@C90, strong U–cage interactions and the interior of the cage do not, in principle, prevent U–U bonding but the charge–charge repulsion forces the encapsulated atoms to separate at large distances.

4 Conclusions

In this work, we have theoretically characterized the U2@C60 compound, reported previously in the TOF-MS experiments. We show that it is an endohedral open-shell septet 7U2@C60 system with six unpaired electrons residing mainly in the U(5f) shell. It is derived from the C607 fullerene cage. The encapsulated uranium atoms are strongly bound to the cage by polarized covalent bonding, as evidenced by the large encapsulation energy of U2 in C60 and by bonding analysis. MO analysis reveals a double ferromagnetic 1e-2c U–U bond between uranium atoms in the 7U2@C607 minimum structure. The U–U bonding is further confirmed by the QTAIM delocalization index, δ(U ↔ U) = 1.01, corresponding to a single bond. This bonding is realized even at a relatively large U–U distance of ~3.9 Å and arises from U(5f)-U(5f)-based singly occupied MOs. The thermodynamical estimate of the U–U interactions inside 7U2@C607 was calculated to be attractive, -17.7 kcal mol⁻¹.

To obtain a more general picture of the endohedral U–U interactions, a series of di-uranium compounds, U2@Cn (n = 60, 70, 80, 84, 90), was analyzed. A U–U bonding of the order of a single bond was also identified in U2@C70 and U2@C84 with rU–U ~ 4 Å. The character of the U–U bonding and bond order correlates with the U–U distance dictated by the cage, and in this sense can be also tuned by the cage used. The U–U endohedral bonding can be termed as unwilling because it arises from the requirement of the system to decrease the charge–charge repulsion between the encapsulated atoms.

This concept can be extended to other endohedral actinide fullerenes. A preliminary study on the di-thorium fullerene points to the existence of endohedral Th–Th bonding in C80 and C70 cages. The results will be published elsewhere.

Note added in proof

A new report on experimental preparation of U2@C60 and other di-uranium fullerenes was published recently.86

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References


86 L. Echegoyen and D. Buck, in 227th ECS Meeting, Chicago, IL, 2015, abstract 817.