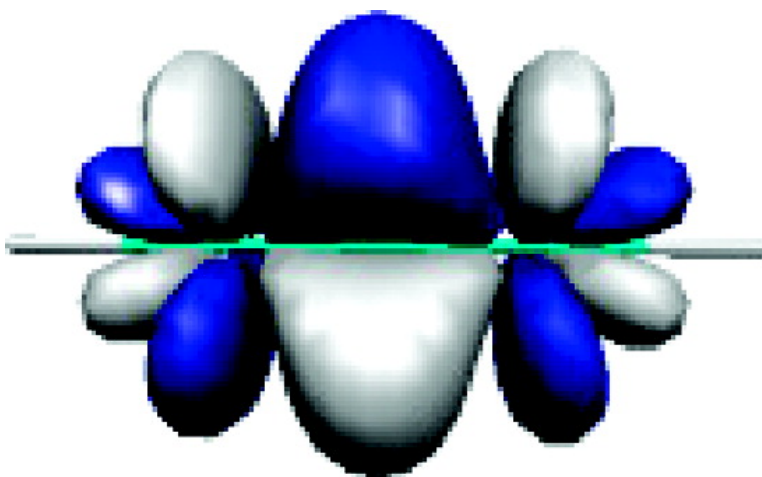


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## Linear HThThH: A Candidate for a Th–Th Triple Bond

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Despite numerous examples of metal–metal bonding in main-group and transition-metal chemistry, only a few experimental systems with an actinide–actinide bond have been reported to date. The observed species are limited to gaseous  $U_2^{1-2}$  and matrix-isolated uranium hydrides.<sup>3</sup> State-of-the-art calculations<sup>4</sup> of  $U_2$  revealed a unique bonding pattern with a quintuple U–U bond ( $R = 243$  pm) and a multiradical character. The charged, metastable  $U_2^{2+}$  had a calculated triple bond with  $R = 230$  pm.<sup>5</sup> Uranium hydrides  $U(\mu-H)_2U$  and  $H_2UUH_2$  were claimed in an argon matrix.<sup>3</sup> The DFT calculated U–U distances of 218 pm for the former and 227 pm for the latter suggest multiple U–U bonds. The analogous Th species were not directly observed in matrix-isolation experiments by Souter et al.<sup>6</sup> who also mentioned that the linear HThThH was calculated at a singlet state minimum, only 0.001 eV above the calculated global quintet minimum  $Th(\mu-H)_2Th$ . The experimentally known and/or computationally studied  $M_2H_2$  hydrides appear to be open-shell  $M(\mu-H)_2M$  systems.<sup>3,7,8</sup>

The linear singlet HThThH is a potential candidate for the so far unknown Th–Th triple bond and thus deserves more attention. In this work we report quasirelativistic density functional (B3LYP) calculations of  $Th_2H_2$  in order to stimulate the further experimental hunt of a Th–Th bond. Structures, energies, and vibrational modes of possible  $Th_2H_2$  species in various spin states up to quintet are calculated and discussed. The bonding in linear HThThH is analyzed.

The calculations were carried out with the Gaussian 98 program<sup>9</sup> using the B3LYP functional.<sup>10</sup> A Stuttgart relativistic 30-valence-electron (30-VE) pseudopotential with a corresponding valence basis set (12s11p10d8f/8s7p6d4f) was employed for Th and a TZVP basis set was used for hydrogen.<sup>11,12</sup> Natural localized molecular orbital (NLMO) and population (NPA) analyses described in detail in ref 13 employed the NBO-3.1 routines built in the Gaussian 98 program. The wave function symmetry was not maintained in the open-shell calculations of linear isomer to ensure convergence to the lowest state of a given multiplet. The present DFT method was further tested against CCSD(T).<sup>14</sup>

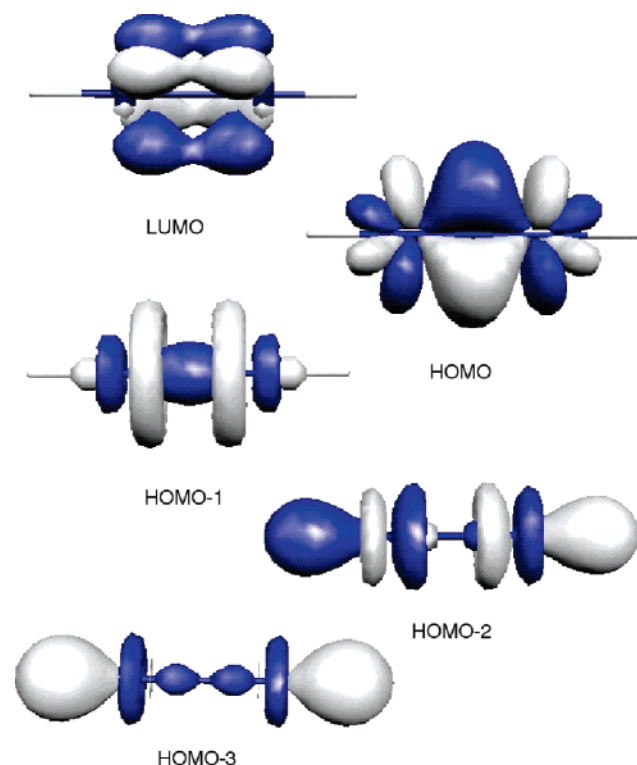
Table 1 summarizes structures and relative energies,  $\Delta E$ , of the various  $Th_2H_2$  minima. Only linear  $D_{\infty h}$ , rhombic  $D_{2h}$ , and butterfly-shaped  $C_{2v}$  minima were found. All minima in Table 1 have short Th–Th distances, far below twice the Th covalent radius of 165 pm and close to twice the Th triple-bond covalent radius of 136 pm.<sup>15</sup> The present linear HThThH structure was actually used to develop these triple bond radii.<sup>15</sup> Interestingly, a Th–Th distance in linear  $^1\Sigma_g$  HThThH of 271.1 pm is almost unaffected by exciting the electrons to the triplet or quintet state. This can be understood by inspecting the HOMO and LUMO orbitals of HThThH in Figure 1: Both are bonding. For the same reason, the Th–Th bonds in calculated linear triplet and quintet HThThH are also triple bonds (cf. below).

The calculated harmonic vibrational frequencies listed in Table 2 show strong absorption at about  $1370\text{ cm}^{-1}$  for linear HThThH (with slightly higher values for its excited states) corresponding to

**Table 1.** Bond Lengths (pm) and Relative Energies<sup>a</sup> (kJ/mol) for  $Th_2H_2$  Isomers<sup>b</sup> Calculated at the B3LYP Level

structure	state	Th–Th	Th–H	H–H	$\Delta E$
linear, $D_{\infty h}$	$^1\Sigma_g$	271.1	211.8		5.7(1.5)
	triplet	271.1	211.8		59.3(54.2)
	quintet	271.8	211.4		100.8(95.8)
rhombic, $D_{2h}$	$^1A_g$	278.1	216.2	331.0	25.4(24.4)
	$^3A_u$	286.7	219.2	331.5	0.0(0.0)
butterfly, $C_{2v}$	$^3A_2$	274.6	218.5	324.0	17.1(16.0)
	$^5A_2$	289.6	215.8	219.0	7.1(8.8)

<sup>a</sup> Zero-point energy corrected values in parentheses. <sup>b</sup> Missing  $D_{2h}$  quintet,  $C_{2v}$  singlet as well as any cis, trans and peroxide-like minima not found.



**Figure 1.** Valence molecular orbitals in  $^1\Sigma_g$  HThThH.

the asymmetric  $\sigma_u$  stretching mode. The experimental Th–H stretching frequencies<sup>6</sup> for  $ThH_n$  ( $n = 1-4$ ) ranged from  $1485$  to  $1435\text{ cm}^{-1}$ . It is not excluded that the present  $\sigma_u$  were among the observed “broad bands”<sup>6</sup> between  $1368$  and  $1427\text{ cm}^{-1}$ . The frequencies for the rhombic and butterfly-like isomers have rather small intensities (Table 2); only the vibration mode at  $849\text{ cm}^{-1}$  for triplet rhombic system may be observed.

The thermodynamic stability of the  $Th_2H_2$  can be estimated. Souter et al mentioned that the calculated energy of dimerization of ThH is highly exothermic (no numbers reported).<sup>6</sup> Our calculated exothermic dimerization energy  $2ThH \rightarrow ^1\Sigma_g$  HThThH is about  $300\text{ kJ/mol}$ . The dimer is unstable with respect to  $ThH_4$  (reaction

**Table 2.** Harmonic Frequencies ( $\text{cm}^{-1}$ ) and Their Intensities ( $\text{km mol}^{-1}$ )<sup>a</sup> Calculated at the B3LYP Level

structure	state	
linear, $D_{\infty h}$	$^1\Sigma_g$	1367(1479), 209(143)
	triplet	1387(1526), 223(129)
	quintet	1399(1520), 163(155)
rhombic, $D_{2h}$	$^1A_g$	1075(27), 544(17), 537(2)
	$^3A_u$	1104(92), 846(1149)
butterfly, $C_{2v}$	$^3A_2$	1167(18), 1130(110), 911(287), 306(3)
	$^5A_2$	1176(74), 1162(48), 1028(207), 475(43)

<sup>a</sup> Only frequencies with nonzero IR intensities listed.

**Table 3.** NLMO Analysis of Linear HThThH

bond	NLMO character
$1^*\sigma(\text{Th}_1-\text{Th}_2)$	50%Th <sub>1</sub> (86% s, 10% d, 4% f) + 50%Th <sub>2</sub> (86% s, 10% d, 4% f)
$2^*\pi(\text{Th}_1-\text{Th}_2)$	50%Th <sub>1</sub> (0% s, 78% d, 22% f) + 50%Th <sub>2</sub> (0% s, 78% d, 22% f)
$2^*\sigma(\text{Th}_1-\text{H}_3)$	13%Th <sub>1</sub> (35% s, 50% d, 14% f) + 2%Th <sub>2</sub> (2% s, 52% d, 46% f) + 84%H <sub>3</sub> (100% s)

$^1\Sigma_g$  HThThH +  $3\text{H}_2 \rightarrow 2\text{ThH}_4$ ) by about 230 kJ/mol. All three isomers and their lower excited states seem to lie energetically very close, so it is hard to judge relative energy ordering of the systems in Table 1, as various effects (spin-orbit coupling, matrix effects) might be of the same order of magnitude.

Noticeably, DFT calculations of an analogous  $\text{Ti}_2\text{H}_2$  system show a substantially larger energy separation between linear and H-bridged isomers, favoring the H-bridged structures over the linear one by about 40–60 kJ/mol.<sup>8</sup> Other d-element analogues of  $\text{Th}_2\text{H}_2$  seem to prefer H-bridged open-shell structures to the linear ones.<sup>3,7</sup>  $\text{Th}_2\text{H}_2$  seems to be a special case with a stabilized linear HThThH structure, an analogue of acetylene, HCCH. A certain analogy between ThO and CO molecules has been suggested before.<sup>16</sup> They are both  $^1\Sigma_g$  in their ground state. Notice that TiO is a  $^3\Delta$  in its ground state.<sup>17</sup>

The shape of the molecular orbitals in Figure 1 and the NLMO analysis in Table 3 confirm a triple Th–Th bond in linear  $^1\Sigma_g$  HThThH. The molecular orbitals correspond to  $\sigma(\text{Th}-\text{H})$  bonds ( $\sigma_g$  HOMO-3 and  $\sigma_u$  HOMO-2), one  $\sigma(\text{Th}-\text{Th})$  bond ( $\sigma_g$  HOMO-1), and a double  $\pi(\text{Th}-\text{Th})$  bond ( $\pi_u$  HOMO). The NLMO analysis of linear HThThH in Table 3 is consistent with the orbital picture: two  $\sigma(\text{Th}-\text{H})$  bonds, one  $\sigma(\text{Th}-\text{Th})$  bond, and two  $\pi(\text{Th}-\text{Th})$  bonds. Similar bonding patterns with Th–Th bonds are observed in the orbital pictures and NLMO analysis of the other systems from Table 1 (analysis not reported).

The NPA analysis of linear ground-state singlet HThThH shows populations  $7s^{0.95} 6d^{1.8} 5f^{0.54}$  on Th and a large negative charge of  $-0.7$  on each of the hydrogens. In this sense linear HThThH is unlike acetylene in which a positive charge is expected on the hydrogens. The hypothetical  $\text{Th}_2^{2+}$  has at the DFT level a  $^1\Sigma_g$  ground-state minimum with a very short Th–Th distance of 256.8 pm, a clear triple bond. The triplet and quintet  $\text{Th}_2^{2+}$  minima, with Th–Th distances of 273.9 and 277.8 pm, were found 19.4 and 58.8 kJ/mol above the singlet.

Both the orbital picture and the NLMO/NPA analyses suggest substantial f-character of Th–Th bonding. Is the f orbital participation in bonding the reason for seemingly stabilized linear geometry? To investigate this we removed the f functions from the Th basis set and studied a “d-only” Th species. Reoptimizing the linear singlet and rhombic triplet  $\text{Th}_2\text{H}_2$  results in elongation of the

Th–Th distances by about 25 pm. The energy difference between the two isomers increases from about 6 kJ/mol (Table 1) to about 74 kJ/mol, mainly due to energetic destabilization of the linear system. Thus, at least at the scalar relativistic DFT level, the f orbitals seem to stabilize the linear HThThH isomer with respect to the rhombic one. This is not unexpected as the spatial bonding preferences of gerade d orbitals are different from those of ungerade f orbitals.<sup>18</sup> Concluding, the present calculations show that linear HThThH is a minimum with a singlet ground state and triple Th–Th bond. Calculated frequencies suggest that it may already have been seen in matrix.<sup>6</sup> The relative stability of the linear HThThH system with respect to the H-bridged isomers is caused by participation of f orbitals in bonding. Analogous LThThL systems may exist.<sup>19</sup>

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**Supporting Information Available:** Complete ref 9. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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