Can stable molecular compounds of Th(V) and Pa(VI) exist?

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Gibson and coworkers have recently shown that the PaO_2^{2+} ion, which formally contains Pa(VI), can be prepared in the gas phase.[1] As far as we are aware, this was the first report of the preparation of a "hypervalent" Pa compound. However, the energy necessary to produce this species is large, as the ionization energy of the "actinyl" ion PaO_2^+ that contains Pa(V) was calculated to be 16.6 eV. One would normally imagine that such high-energy species cannot exist as stable compounds. Yet the ionization energy of UO_2^+ is estimated [2] to be 15.2 eV, not much less than 16.6 eV, and the uranyl ion, UO_2^{2+}, which formally contains U(VI), is of course stable in both the solid state and in aqueous solution (at low pH). Since the ionization energy of ThO_2 is "only" 8.7 eV,[3] it is therefore worthwhile asking the question posed in the title: can stable molecular compounds of Th(V) exist? And are there any compounds of Pa(VI) that might be thermodynamically stable? We have used DFT to try to answer these questions, convinced that its application to actinide thermochemistry is relatively reliable.[4]

Possible Th (V) and Pa (VI) Compounds

In general, high-oxidation state species are most stable as oxides, fluorides and oxide-fluorides. We therefore considered the gas-phase thermodynamic stability of compounds such as ThO_2F, $ThOF_3$ and ThF_5, all of which appear to contain Th(V), together with PaO_2F_2 and PaF_6 (Pa(VI)), relative to analogous compounds of Th(IV) and Pa(V), respectively. In other words, we calculated ΔE for the following reactions:

$ThO_{2\ (g)} + 0.5F_{2\ (g)} \rightarrow ThO_2F_{\ (g)}$ R1

$ThOF_{2\ (g)} + 0.5F_2 \rightarrow ThOF_{3\ (g)}$ R2

$ThF_{4\ (g)} + 0.5F_{2\ (g)} \rightarrow ThF_{5\ (g)}$ R3

$PaO_2F_{\ (g)} + 0.5F_{2\ (g)} \rightarrow PaO_2F_{2\ (g)}$ R4

$PaOF_{3\ (g)} + 0.5F_2 \rightarrow PaOF_{4\ (g)}$ R5

$PaF_{5\ (g)} + 0.5F_{2\ (g)} \rightarrow PaF_{6\ (g)}$ R6

Using standard DFT (B3LYP, small-core pseudopotentials for the actinides and TZP bases for O and F, we calculate the following reaction energy changes (kJ/mol, purely electronic energies, no zero-point or other thermal effects):

R1, -308: R2, -273; R3, +55; R4, -229; R5, -152; R6, +61.

Although it is clear that DFT reaction energies for actinide compounds cannot be expected to be accurate to within a few kJ/mol, we feel confident that reactions R1 and R2 are clearly exothermic. In other words, ThO_2F, $ThOF_3$ and PaO_2F_2 appear to be potentially stable molecular compounds of Th(V) or Pa(VI), since they are clearly thermodynamically stable compared to their Th(IV) precursors. However, the fluorides ThF_5 and PaF_6 are not stable, especially as entropic factors mean that ΔG for these reactions is less favourable than ΔE.

As a method check, we also studied reaction R1 at the more reliable CCSD(T) level of theory, using larger basis sets (TZ+2df on F and O, TZ+2gh on Th), at the geometries obtained with DFT. We obtain ΔE = -279(-282) kJ/mol for R1 at the CCSD(CCSD(T)) levels of theory, adopting the B3LYP geometries. These values are so close to the DFT result that the latter is confirmed. Henceforth, we rely on DFT energies.

The Nature of these New Compounds

What can we say about the nature of these new compounds? Do they "really" contain Th(V) or Pa(VI)? Although the stoichiometry appears to say "yes", other aspects incite caution. For example, the Th-O distance in $ThOF_3$ is 2.215 Å, whereas in $ThOF_2$ it is only 1.882 Å. The unpaired electron in $ThOF_3$ is almost completely localized (98%) on the O atom, which is hardly compatible with the presence of Th (V) and a double bond between Th and O. In ThO_2F and PaO_2F_2, the unpaired electron is more evenly spread, but is still extensively delocalized: 18% on Th and 39% on each O in ThO_2F, 26% on Pa and 32% on each O in PaO_2F_2.

Now the addition of F_2 to OSF_4, which contains S(VI), is weakly exothermic at B3LYP:

$OSOF_4 + 0.5F_2 \rightarrow OSF_5$

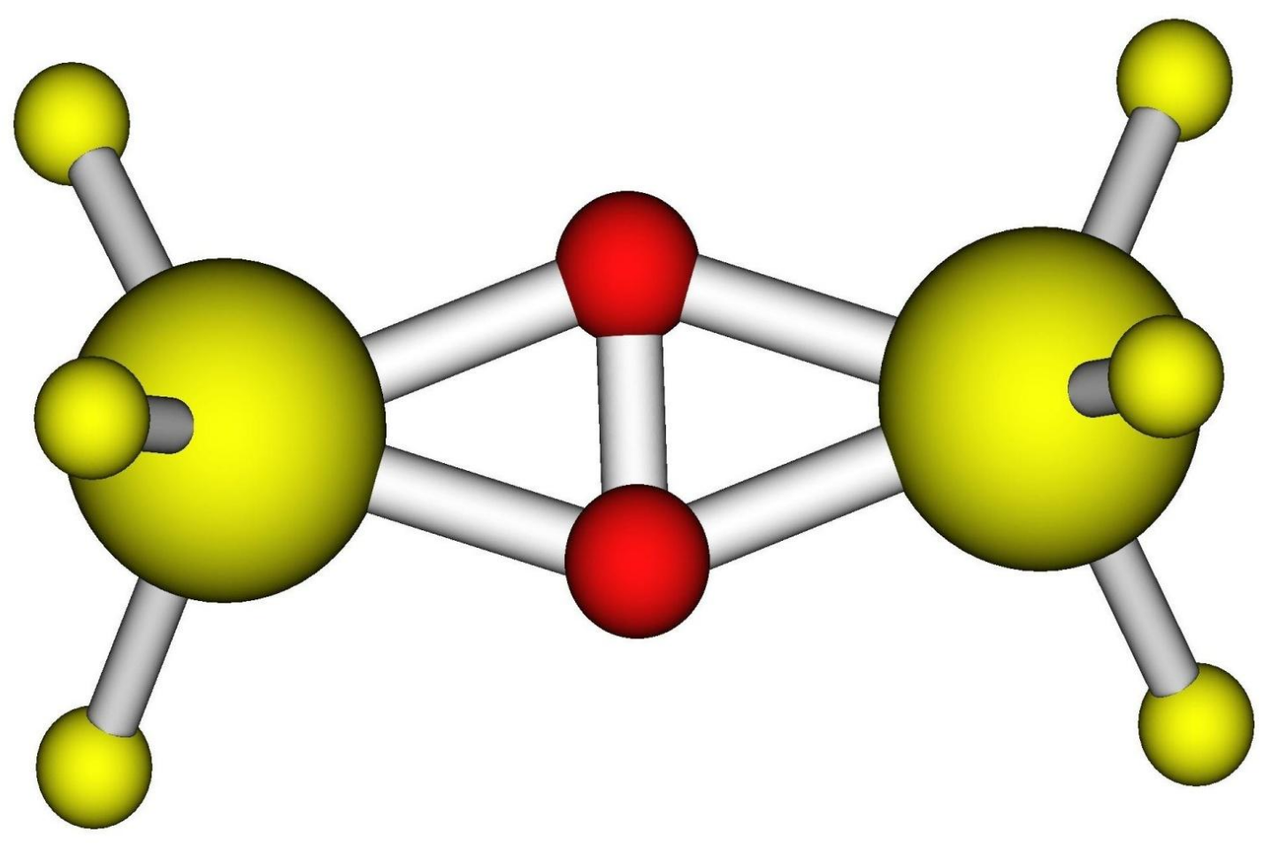
but the product, OSF_5, does not contain S(VII): it is an O-centred radical that dimerizes to produce the peroxide, F_5SOOSF_5.

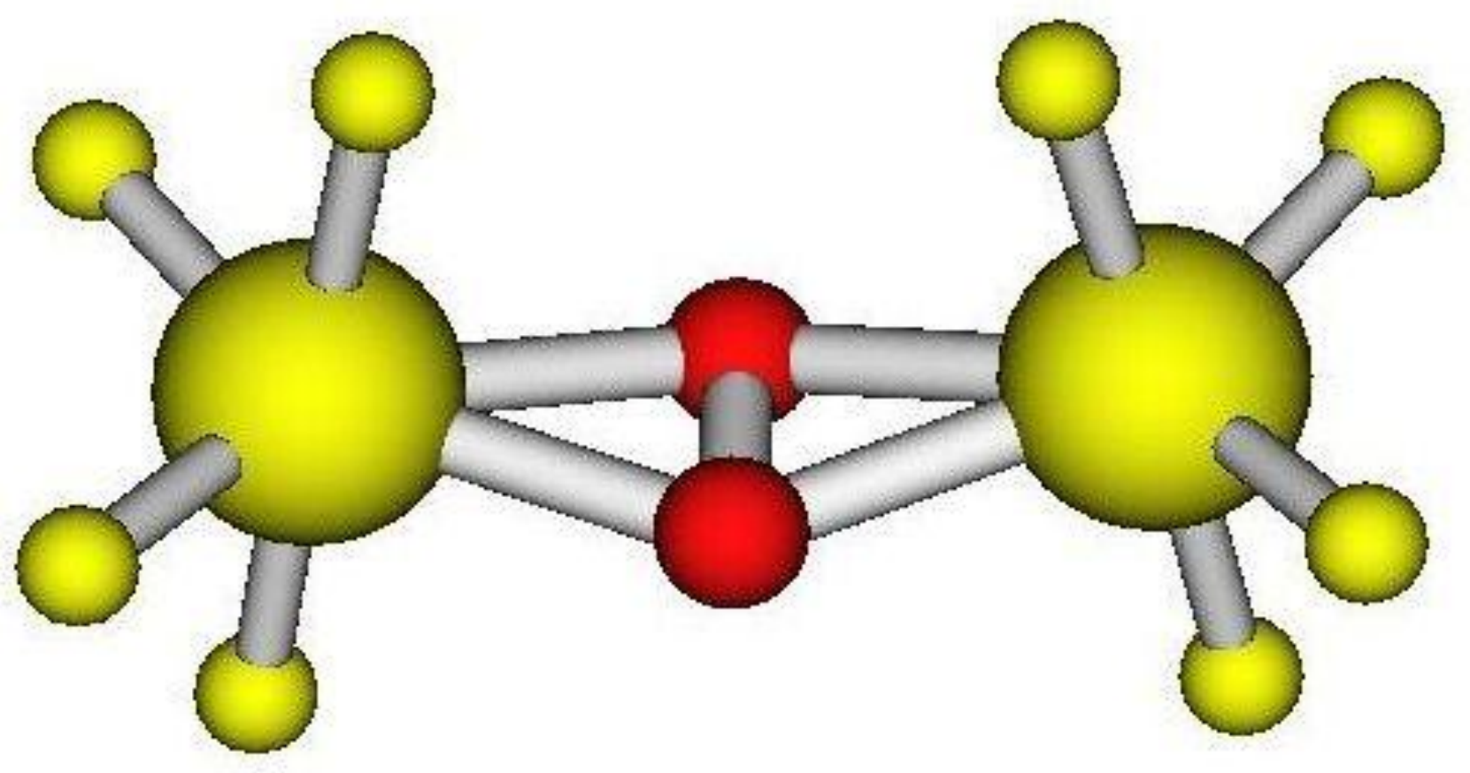
Both $ThOF_3$ and $PaOF_4$, which are O-centred radicals analogous to OSF_5, will dimerize spontaneously, but the products are not peroxides (see right-hand column).

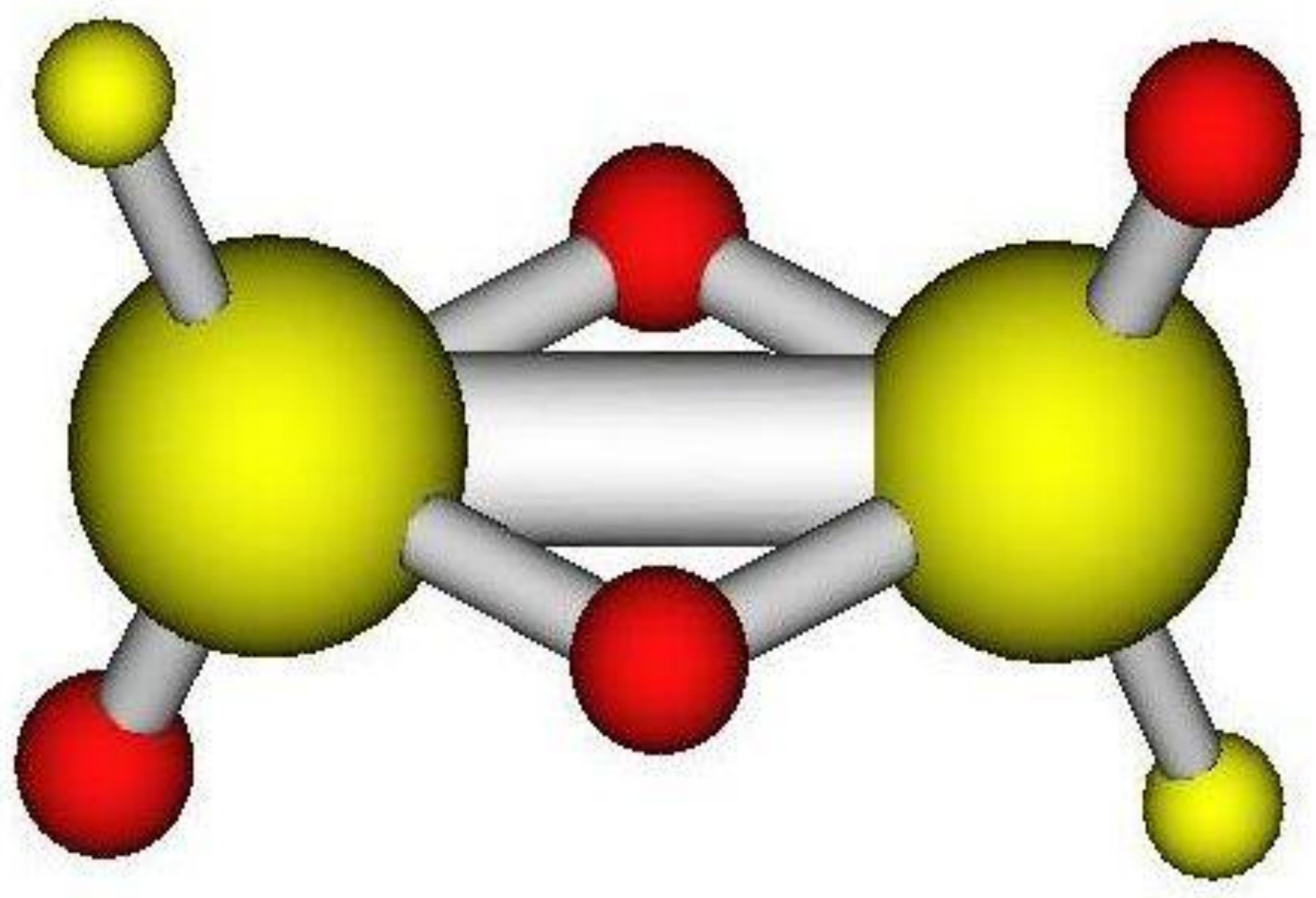
Since these oxy-fluorides are highly polar and have low coordination numbers, their polymerization is highly favourable. We investigate the start of this process with DFT.

347 kJ are liberated by the formation of one mole of the dimer of $ThOF_3$, or 320 kJ for $PaOF_4$. These singlet species are not peroxides, but contain four-membered An_2O_2 rings.

Do they contain Th(V) or Pa(VI)? Although the stoichiometry $(ThOF_3)_2$ might be thought to imply Th(V), in fact the O-O distance in the four-membered ring is only 1.50 Å, showing the presence of an O_2^{2-} unit: Th is thus present in the oxidation state IV. In $(PaOF_4)_2$, there is also a peroxide unit, so Pa is present as Pa(V).


The dimer of $ThOF_3$ (C_{2v} symmetry)


The dimer of $PaOF_4$ (also C_{2v} symmetry)



The formation of the dimer of ThO_2F liberates 312 kJ. It also contains a four-membered ring, but the O-O bridging distance is now 2.6 Å, sufficiently large to exclude the existence of a peroxide unit. Does this therefore imply that $(ThO_2F)_2$ contains Th(V)? No, because this species is a triplet; the two unpaired electrons are localised on the terminal oxygen atoms.

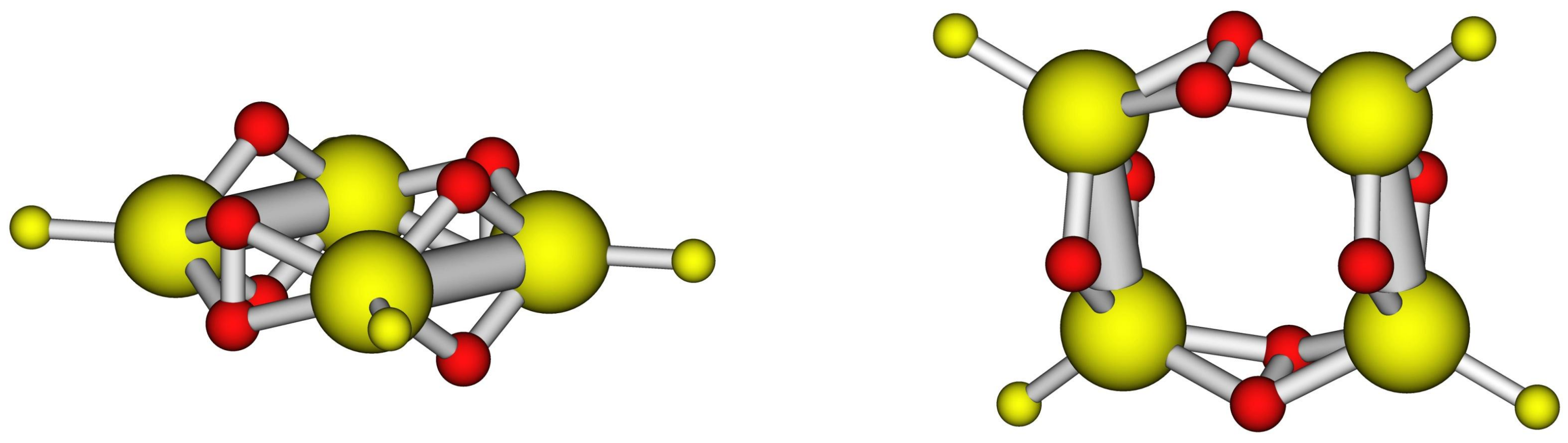
There are several plausible structures for the tetramer of ThO_2F. The most stable that we have found is a singlet, based on a pseudo-square of Th atoms bridged by pairs of oxygens (D_{2h} symmetry). Two views are shown below. Note the alternation of peroxide groups and four-membered rings in which the oxygens are not bound.

This tetramer is particularly stable: the reaction below liberates 1344 kJ, ie 336 kJ per mole of monomeric ThO_2F: the tetramer of ThO_2F is thus slightly <u>more</u> stable relative to (tetrameric) ThO_2 and F_2 than is the monomer.

$(ThO_2)_{4(g)} + 2F_{2\ (g)} \rightarrow (ThO_2F)_{4\ (g)}$ R1'

It thus seems possible that ThO_2F can exist as a thermodynamically stable solid compound, though we have not yet established that.

The instability of molecular ThF_5 (see endothermic reaction R3) is consistent with the higher IE of ThF_4 (13.2 eV) than for ThO_2 (8.7 eV).



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