Stabilization of Octahedral Thorium Clusters by Interstitial Hydrogen

Thomas P. Braun* and Arndt Simon

Abstract: The synthesis, structure, and characterization of the cluster compounds $Th_6H_xBr_{15}$ ($x = 5$ and 7) are reported. The compounds can be prepared by a reversible hydrogenation/dehydrogenation process; their structures have been determined by X-ray and neutron diffraction methods. Both compounds form a body-centered cubic structure of octahedral cluster units with five or seven hydrogen atoms in eight disordered positions above the faces of the octahedron. The chemical bonding in these diamagnetic compounds has been analyzed: the simple counting rules for octahedral cluster compounds are fulfilled, and MO and band structure calculations confirm the hydridic nature of the bonding.

Keywords
chemical bonding · hydrides · interstitial atoms · magnetic properties · thorium clusters

Introduction

Several thorium cluster compounds have been synthesized over the last few years.[1, 2] Like the discrete clusters of the rare earth and Group IV metals, they are all stabilized by interstitial atoms. The incorporation of the interstitial atoms formally adds to the total electron count of the clusters, often leading to the "magic" numbers for optimal stabilization of the respective cluster type. However, this descriptive counting scheme does not deal with the nature of the chemical bond in such compounds. As various calculations on the bonding in clusters occupied by interstitials demonstrate, the metal–metal bonds are weakened as a consequence of the incorporation of the interstitial atoms.[3–11] Instead, the bonding interactions between the interstitial and the metal atoms stabilize the clusters as topological moieties.

The compound $Th_6H_7Br_{15}$[2] offers the first example of a cluster in which the number of interstitial atoms exceeds the number of metal atoms. The arrangement of the heavy elements corresponds to the structure of Nb_6F_{15}.[12] Th_6Br_{12} clusters with an octahedral Th_6 core and twelve bromine atoms, one over each edge, are connected by linear bridges of additional bromine atoms above all six vertices of the octahedron. Two of the resulting primitive nets interpenetrate to build a body-centered cubic cell. The hydrogen atoms in these clusters are disordered on eight positions slightly above the centers of the triangular faces of the Th_6 core (Fig. 1).

According to the counting rule mentioned above, the total electron count for $Th_6H_7Br_{15}$ is sixteen, corresponding to the "magic" number for M_6X_{12} type clusters. Since the electron count can vary even for empty clusters (as in, e.g., $Ta_6Cl_{12}^{n+}$: for $n = 2$ the count is 16 electrons, and for $n = 4$ it is 14[13]), it has been speculated that it should be possible to alter the hydrogen content.[2]

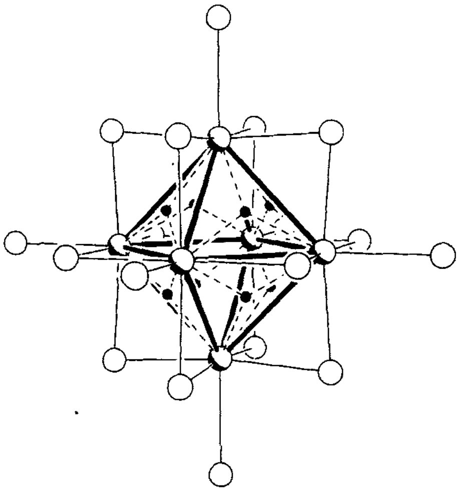

Fig. 1. The structure of the $Th_6H_xBr_{15}$ clusters.

Further investigation showed that $Th_6H_7Br_{15}$ can be dehydrogenated. In the following we report on the preparation and characterization of phases $Th_6H_xBr_{15}$ and present a general scheme of the chemical bonding.

Results and Discussion

Synthesis: Samples of $Th_6H_7Br_{15}$ prepared according to ref. [2] inevitably contain traces of $ThBr_{3.5}H_y$.[14] In the first step of that reaction sequence, a mixture of ThH_2 and $ThBr_4$ is homogenized at 1200 K for several hours. Any traces of $ThBr_{3.5}H_y$ formed during this prereaction apparently cannot be transformed into $Th_6H_7Br_{15}$ in the subsequent hydrogenation reaction. However, if a thoroughly ground mixture of the two reagents is slowly heated under an atmosphere of hydrogen, the formation of the impurity can be suppressed. Due to the significant vapor pressure of $ThBr_4$ (≈5 mbar at 875 K[15]) it is necessary to run the reaction in sealed tantalum ampoules. At

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875 K hydrogen diffuses quickly through the container wall, while the thorium-to-bromine ratio can be kept constant.

The dehydrogenation of $Th_6H_7Br_{15}$—prepared by either method—is possible under similar conditions but under reduced pressure, and yields the new phase $Th_6H_5Br_{15}$ as a fine black powder. There is no indication of the formation of any phase with intermediate hydrogen content. It is also not possible to incorporate more than seven hydrogen atoms per formula unit under the given conditions. An attempt to reduce the hydrogen content below the limit of five resulted in the decomposition of the sample.

Characterization: From mass spectrometry experiments it was evident that a significant amount of hydrogen is released from a sample of $Th_6H_7Br_{15}$ at temperatures above 750 K under reduced pressure. However, the X-ray powder diffractogram of this supposedly dehydrogenated phase and that of the fully hydrogenated one appear to be the same. Both show the simple pattern of a body-centered cubic arrangement and no significant changes in the relative intensities of the individual peaks. Even the strongest peaks of the pattern of $ThBr_{3.5}H_y$ are missing in both diffractograms; this indicates that only traces of this impurity might be present in the investigated samples. The lattice constants ($Th_6H_7Br_{15}$: 1141.05(6) pm, $Th_6H_5Br_{15}$: 1140.85(9) pm) have been calculated by averaging over a number of diagrams. The difference between the two phases is within a factor of only 1.5 of the standard deviation. Thus it is hardly possible to differentiate between them on the basis of X-ray crystallographic experiments alone.

On the other hand, the determination of the magnetic properties clearly indicates that the two phases are indeed different. Since both substances are diamagnetic above 100 K, it can be concluded that both compounds contain an even number of electrons.[16] Consequently the number of hydrogen atoms per cluster unit must be odd for the fully hydrogenated as well as for the dehydrogenated phase. Detailed analysis of the low-temperature susceptibility data yields two significantly different values for the corrected diamagnetic susceptibilities χ_0 ($Th_6H_7Br_{15}$: -260×10^{-6} emu mol^{-1}, $Th_6H_5Br_{15}$: -1350×10^{-6} emu mol^{-1}).

The sum of the diamagnetic increments for the hypothetical empty cluster "Th_6Br_{15}" (calculated from the ionic values for Th^{4+} and Br^- according to ref. [18]) is -678×10^{-6} emu mol^{-1}. This leads to a surprising distinction between the two phases: for the fully hydrogenated phase $Th_6H_7Br_{15}$ the difference between the measured and the calculated values yields a temperature-independent paramagnetic contribution of about 420×10^{-6} emu mol^{-1}, which is a typical value for octahedral cluster compounds;[19] however, for the dehydrogenated phase $Th_6H_5Br_{15}$ the observed diamagnetic contribution is larger than the calculated one by a factor of two. Apparently there is an additional diamagnetic shielding component that can overcompensate for the weaker temperature-independent paramagnetism of these clusters.

Solid-state NMR studies clearly confirmed the difference between the fully hydrogenated and the dehydrogenated phase. These studies also showed that the disorder of the hydrogen atoms is dynamic even at very low temperatures. A rather complex temperature dependence of the dynamics of the hydrogen atoms has been determined and assigned to different modes of motion.[20]

The hydrogen content of various samples has been determined analytically by means of combustion analysis.[21] As in the previous study of $Th_6H_7Br_{15}$, the hydrogen content as determined is somewhat lower than the actual value. However, the difference in the hydrogen content of $Th_6H_7Br_{15}$ and $Th_6H_5Br_{15}$ was found to be about two (see Table 1).

Table 1. Results of the analytical determination of the hydrogen content of $Th_6H_yBr_{15}$.

Sample	Amount [mg]	H_2O [mg]	y
$Th_6H_7Br_{15}$ [a]	238.4	4.529	5.48
	177.0	3.481	5.67
$Th_6H_7Br_{15}$ [b]	65.3	1.313	5.80
	70.7	1.516	6.18
$Th_6H_5Br_{15}$ [b]	105.7	1.298	3.54
	87.9	1.143	3.75

[a] Ref. [2]. [b] This work.

The composition of $Th_6D_7Br_{15}$ has already been unambiguously established by a neutron diffraction experiment.[1,2] In order to confirm the assumed composition of the dehydrogenated compound we performed an additional neutron diffraction study. Although the accuracy of this room-temperature structure determination is not as good as in the case of $Th_6D_7Br_{15}$, the refined composition of $Th_6D_{5.0(2)}Br_{15}$ clearly confirms the conclusions drawn from the determination of the magnetic susceptibility and of the quantitative analysis of the hydrogen content.

Chemical bonding: For an appropriate description of the chemical bonding in these ternary cluster compounds it is very helpful to recall the bonding in the corresponding binary cluster compounds. These have been investigated since the early 1950's and by various different theoretical methods.[22–30] A pictorial summary of all these calculations for both M_6X_8- and M_6X_{12}-type clusters has been given by Andersen.[31,32] According to his "d^4 model" there are four d orbitals per metal center available for metal–metal bonding (one d orbital being utilized in the bonds to the inner ligands). Complementary to the orientation of the inner ligand sphere these orbitals either form twelve two-center two-electron bonds above all edges (for M_6X_8-type clusters) or eight three-center two-electron bonds above all faces of the octahedron in the case of M_6X_{12}-type clusters. This leads to the well-known "magic" numbers of twenty-four and sixteen electrons in metal–metal bonds for the closed shell configurations of M_6X_8- and M_6X_{12}-type clusters, respectively. As Kettle has shown, these two types are isoelectronic forty-electron systems if the inner ligand sphere is included.[26] For M_6X_8-type clusters there are twenty-four metal-centered plus sixteen ligand-centered electrons, whilst for M_6X_{12}-type clusters the optimal electron count comprises sixteen metal-centered plus twenty-four ligand-centered electrons.

It has been shown that the class of interstitially stabilized clusters can be treated in an analogous way if the valence electrons of the interstitial(s) are formally added to fill the available cluster orbitals.[3–11,33] If this procedure is followed, it is found that $Th_6H_7Br_{15}$ completely corresponds to binary cluster compounds such as Nb_6Cl_{14}, with sixteen electrons available for metal–metal bonding.[19] The implied electron transfer from the hydrogen atoms to the cluster core does not reflect the actual polarity of the metal hydrogen bonds. In this model the hydrogen atoms have been described as "covalent sensors" for electron density "adorning" the three-center metal–metal bonds.

Alternatively the cluster $Th_6H_7Br_{15}$ can be regarded as a superposition of both a M_6X_{12} and a $M_6X'_8$ (or rather $M_6X'_7\square$) type cluster. Following Kettle's description, all forty valence electrons of this hypothetical $M_6X'_8X_{12}$ cluster would be localized on the ligands (sixteen electrons on the eight X' atoms plus twenty-four electrons on the twelve X atoms). Since $Th_6H_7Br_{15}$ as the corresponding forty-electron system leaves one triangular position empty, the analogous counting scheme yields twenty-four electrons for the bromine atoms, fourteen electrons for the hydrogen atoms plus two additional electrons for one two-electron three-center metal–metal bond.

To achieve a deeper understanding of the chemical bonding in these ternary cluster compounds we performed Extended Hückel-type molecular orbital and band structure calculations.[34, 35] While the MO calculations have been extended over the whole series $Th_6H_xBr_{15}$ ($x = 0-8$), the band structures have only been calculated for the compounds $Th_6H_7Br_{15}$ and $Th_6H_5Br_{15}$. There are three different isomers, that is, three different static pictures of vacancies in the X_8 subunit of $Th_6H_5Br_{15}$ with symmetry classes C_{3v} ($\times 1$) and C_s ($\times 2$). They are very similar in energy and most likely all three isomers are present in the solid state in a dynamic equilibrium. Thus all three have been included in the investigation.

The energy diagrams of all MO calculations can be interpreted as interaction diagrams of two fragments. The eight cluster orbitals of the hypothetical empty Th_6Br_{12} octahedron interact with the molecular orbitals of the appropriate hydrogen polyhedron. This interaction requires that the respective wavefunctions have significant overlap and that they are of the same symmetry. The eight metal-centered orbitals span the symmetry classes a_{1g}, t_{1u}, t_{2g}, and a_{2u} in the octahedral point group O_h. Given the symmetry classes of the hydrogen-based orbitals in the point groups of the appropriate polyhedra and the correlation of the symmetry classes of the octahedral point group, one can easily construct the interaction diagrams for all possible species. The results are summarized in the generalized interaction diagram given in Figure 2.

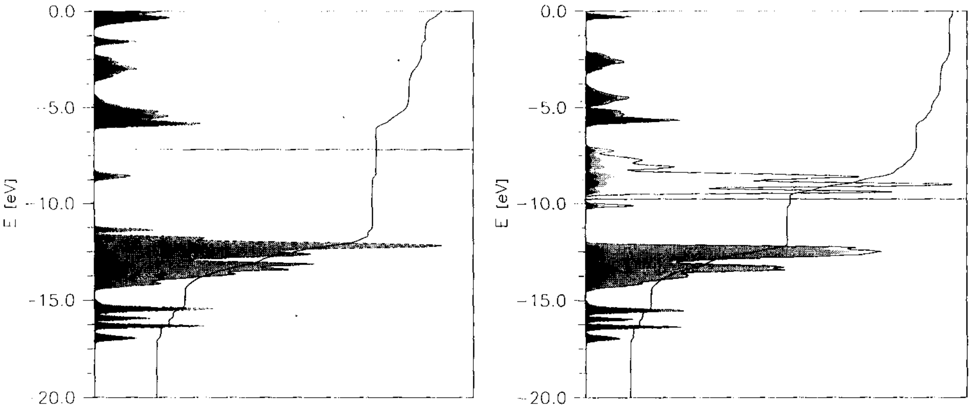

Fig. 3. Left: Density of states (DOS) for $Th_6H_7Br_{15}$; right: DOS including Th 5f states. Atomic projections are shown as shaded areas. The grey scale lightens in the order H 1s (black), Th 7s +6d, Br 4s +4p, Th 5f (white).

While the antibonding Th 6d* states and the essentially bromine-centered block remain almost unchanged, the mixing of hydrogen 1s states into some of the bonding cluster orbitals stabilizes these states significantly. Their energy is lowered below that of the bromine-centered orbitals, confirming the hydridic nature of the metal–hydrogen bonds. As anticipated by the description of these clusters as a superimposed "M_6 X'_8X_{12}" cluster, there is only one directly metal–metal bonding orbital for $Th_6H_7Br_{15}$. As expected, this orbital is located above that trigonal face of the octahedron that is not capped by a hydrogen atom.

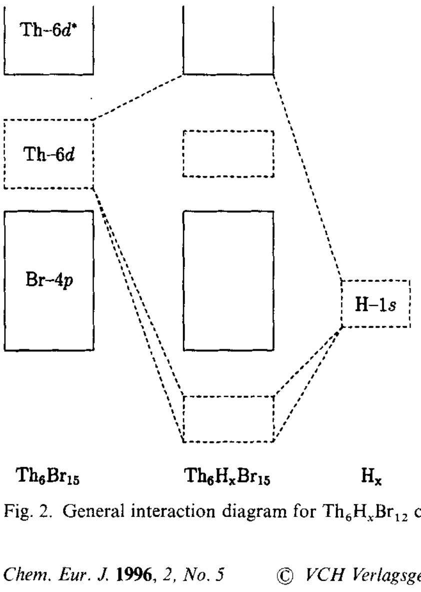

Fig. 2. General interaction diagram for $Th_6H_xBr_{12}$ cluster units.

For the three isomers of $Th_6H_5Br_{15}$ there are two such metal–metal bonding orbitals. While they are degenerate in the high symmetry form, they split in two sets of symmetry a' and a'' for the other two isomers. In any case there are four electrons delocalized over more than just one octahedral face. Due to the dynamic disorder in the cubic structures for both compounds, this localization of metal–metal bonds is not observed as a distortion of the regular octahedron.

The density of states for $Th_6H_7Br_{15}$ as a result of the band structure calculation is shown in Figure 3. The respective diagrams for the three isomers of $Th_6H_5Br_{15}$—not given here—are very similar and follow the same general outline (see below). As the sharp peaks indicate, the dispersion is very weak in these systems. This justifies the use of the molecular orbital calculations, since the individual clusters are not only structurally but also electronically isolated.

The pattern of the generalized energy diagram can be easily recognized. For $Th_6H_7Br_{15}$ there is one metal–metal bonding band just below the Fermi level. This band is well separated from the block of bands that are predominantly centered at the bromine atoms. The four very sharp peaks below arising from seven hydrogen-centered bands are again clearly separated. The main difference in the density of states plots of $Th_6H_5Br_{15}$ is found around the Fermi level. Firstly, there is one unoccupied but metal–metal bonding orbital above the Fermi level. This is equivalent to a lack of two electrons compared with the compound with the "magic" number of 16 electrons. Secondly, for the two low-symmetry forms the splitting of the two metal–metal bonding bands can clearly be seen.

We started to study reduced thorium halides in order to find out whether 5f electrons could be participating in metal–metal bonding in contrast to the energetically low-lying 4f electrons of the reduced lanthanide halides. The inclusion of Th 5f states in the band structure calculations yields two significant changes. As expected, the density of states just above the Fermi level is greatly enlarged; this leads to a reduced band gap. It seems that the 5f orbitals contribute significantly to the metal–metal bonding states for both $Th_6H_7Br_{15}$ and $Th_6H_5Br_{15}$. However, it must be stressed that this finding needs to be confirmed by calculations on a more sophisticated level.

Experimental Procedure

The thorium hydride bromides decompose within minutes if exposed to air or moisture. Hence all relevant operations have to be carried out under inert conditions. All reactions and characterizations were performed under dry argon in specially dried glassware.

Preparation: In a typical reaction $ThBr_4$ (1 g, 1.80 mmol, prepared by reaction of thorium (99.5%, Goodfellow) with a stoichiometric amount of bromine (p.a., Merck), purified by subsequent sublimation) was mixed with ThH_2 (253 mg, 1.08 mmol, made by direct reaction of thorium with hydrogen) and sealed in tantalum ampoules of 1 cm diameter and 5 cm length under an atmosphere of approximately 500 mbar of argon. These containers were transferred into a quartz glass tube and heated under an atmosphere of 1 bar of hydrogen to 875 K within a few hours and kept under these conditions for three days. The resulting $Th_6H_7Br_{15}$ can be dehydrogenated under similar conditions (sealed tantalum ampoules, quartz glass tube, 875 K, 3 d) by applying reduced pressure (5×10^{-5} mbar) to yield $Th_6H_5Br_{15}$.

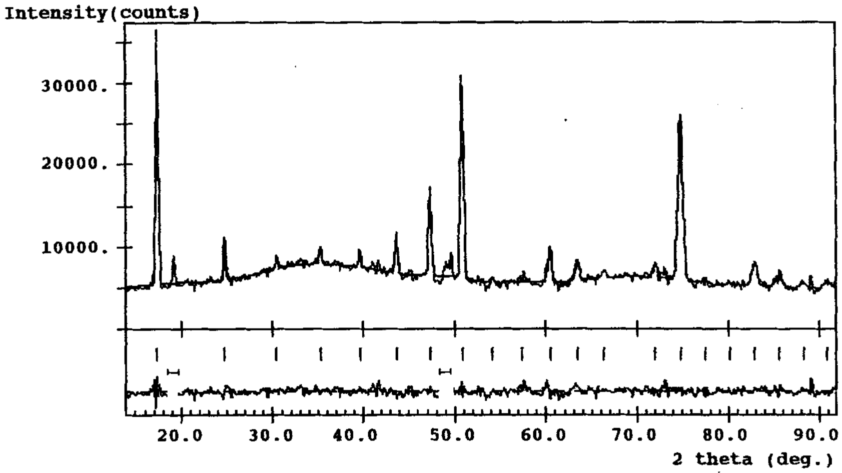

Fig. 4. Simulated and measured neutron powder diffractogram of $Th_6D_5Br_{15}$ including the difference function and the calculated positions of the Bragg reflections.

Decomposition experiment: $Th_6D_5Br_{15}$ (1.3 g, 0.5 mmol) was sealed into a tantalum ampoule and transferred into a quartz glass apparatus of a measured volume of 460 mL equipped with a Bourdon manometer (0–1000 mbar). This apparatus was evacuated to 5×10^{-5} mbar and sealed. The temperature was then slowly raised to 875 K and maintained overnight. The temperature was raised further in steps of 50 K and kept constant for 20 min each time, until the pressure began to increase at 1025 K. The evolution of hydrogen was very slow, and the system was kept under unchanged conditions for three days. After that period the final pressure was about 60 mbar, indicating that most of the hydrogen had been released from the sample (theoretical value: 61.8 mbar). The product was identified by its powder diffractogram as a mixture of Th, $ThBr_4$, $ThBr_{3.5}H_y$, and other unidentified products, while the lines of the cubic lattice of $Th_6H_xBr_{15}$ were missing. We propose that the slow reaction proceeds via the formation of ThH_2, which is known to decompose by a kinetically controlled mechanism at temperatures below 1075 K [36].

X-ray diffractometry: All samples were characterized by the modified Guinier technique, ref. [37], with silicon (a = 543.102 pm [38]) as internal standard. The films were exposed (Cu $K\alpha_1$ radiation) and then read into an optical microdensitometer [39,40]. After correction for absorption and geometrical errors (program SCANPI [41]), the lattice constants could be refined by least-squares methods by means of the program PIRUM [42].

Neutron diffractometry: Structure determination of $Th_6D_5Br_{15}$ was performed at the Hahn-Meitner Institut Berlin on the two-axis powder diffractometer E3 (research proposal CHE-01-267). Owing to limited beam time it was only possible to collect the data at room temperature. A wavelength of approximately 2.4 Å was selected with a Ge(311) monochromator. The exact wavelength, calibrated against a recorded diffractogram of iron and also against the known lattice constant of the sample, was 2.453 Å. Diffraction data were recorded with a ^3He multidetector in a total of four measurements in the range from 13.0 to 93.1° in 2θ within 19000 s for each run. The data were corrected for detector intensities and calibrated for total intensity before being merged into one data file. Because of its radioactivity, the thorium sample was enclosed in a special anhydrous quartz glass ampoule. The resulting background was subtracted manually. The background data were iteratively smoothed at the end of the refinement.

The structure was refined with the program DBW9006 [43] with a total of 11 parameters (4 profile parameters, zero point correction plus 5 structural parameters) after exclusion of two small regions (18.5–20.0 and 48.5–50.0° in 2θ) that showed contaminating peaks (see Fig. 4). The refinement converged to values of $R_{wp} = 0.059$ and $R_{Bragg} = 0.064$ with a Gaussian profile function with the profile parameters $u = 1.101(16)$, $v = -0.485(12)$, and $w = 0.141(2)$, and an asymmetry parameter of 0.32(36). All standard deviations were multiplied by a factor of 1.836 to account for local correlations [44]. The following structural parameters were obtained for $Th_6D_5Br_{15}$: space group $Im\bar{3}m$ (no. 229), $Z = 2$, $a = 1140.85$ pm, x parameters: Th (12e) 0.2428(20), Br1 (24h) 0.2578(13), Br2 (6b), D (16f) 0.0823(20). The isotropic displacements were refined with one common value for the thorium and the bromine atoms, while the displacement of the deuterium atoms was set to five times that value. ($B_{Th} = 1.65(61)$, $B_D = 8.26(61)$.)

Thermal decomposition was investigated by means of a mass spectrometer (Balzers, QMG511). About 50 mg of the sample was transferred into the spectrometer and heated to 1000 K over three hours.

Quantitative analysis of the hydrogen content was achieved by combustion analysis. The samples were heated in the presence of V_2O_5 as catalyst in an oxygen flow, and the emerging water was titrated by means of the Karl Fischer method [21]. The results are summarized in Table 1.

Magnetic susceptibilities of powder samples with masses of 10–50 mg were determined with a SQUID magnetometer (Quantum Design). The samples were contained in carefully dried SUPRASIL ampoules that were long enough to extend over the coils of the magnetometer. Thus no explicit correction was necessary. For fixed temperatures the susceptibilities were recorded in external fields ranging from 0.5 to 5 T. Honda-Owen plots were performed to correct for ferromagnetic impurities [45,46]. Finally, a χ_{mol} versus $1/T$ plot as described in ref. [47] and extrapolation to infinite temperature allowed an estimate of the contribution of spurious paramagnetic impurities.

Band structure calculations: Band structures and molecular orbital diagrams were calculated within the EH approximation with the program EHMACC [48]. The experimental values (X-ray and neutron diffraction) of the positional coordinates of $Th_6H_7Br_{15}$ [2] were used. The disorder of the hydrogen atoms was not treated explicitly, that is, seven (for $Th_6H_7Br_{15}$) and five (for $Th_6H_5Br_{15}$) of the partially occupied positions were used, respectively.

The band structures were calculated at 55 k points within the unreducible wedge of the Brillouin zone of the body-centered cubic cell. To analyze the dispersion the bands were also calculated along the high symmetry lines. MO calculations were performed for the cluster units $[Th_6H_xBr_{18}]^{3-}$ for $x = 0$–8. Similar MO calculations on the series of hydrogen-stabilized thorium clusters have been reported in a previous publication [1]. Because of inappropriate basis functions (especially concerning the radial distribution of the Th 6d functions) those calculations yielded a reversed order of the metal-based molecular orbitals. Here we used parameters that had been adjusted to spectroscopic measurements on actinocenes by Pyykkö et al. [49]. The following parameters were used for the Slater-type orbitals of the atoms (H_{ii} [eV], ζ_1, c_1, ζ_2, c_2): H 1s: −13.00, 1.3; Br 4s: −27.01, 2.588; Br 4p: −12.44, 2.131; Th 7s: −5.31, 1.834; Th 6p: −27.75, 3.55; Th 6d: −10.048, 2.462, 0.76, 1.167, 0.408; Th 5f: −9.291, 4.48, 0.7677, 1.84, 0.4269.

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