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Trimetallic Cubane-type Clusters: Transition metal Variation as a Probe of the Roots of Hypoelectronic Metallaheteroboranes

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ABSTRACT

In an effort to synthesize the chalcogen-rich metallaheteroborane clusters of group 5 metals, thermolysis of $[\text{Cp}^*\text{TaCl}_4]$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) with thioborate ligand $\text{Li}[\text{BH}_2\text{S}_3]$ was carried out that afforded trimetallic clusters $[(\text{Cp}^*\text{Ta})_3(\mu\text{-S})_3(\mu_3\text{-S})_3\text{B}(\text{R})]$, **1-3** (**1**: $\text{R} = \text{H}$, **2**: $\text{R} = \text{SH}$, and **3**: $\text{R} = \text{Cl}$). Clusters **1**, **2** and **3** are illustrious examples of cubane-type organotantalum sulfido clusters in which one of the vertices of the cubane is missing. In parallel to the formation of **1-3**, the reaction also yielded tetrametallic sulfido cluster $[(\text{Cp}^*\text{Ta})_4(\mu\text{-S})_6(\mu_3\text{-S})(\mu_4\text{-O})]$, **6**, having an adamantane core structure. Compound **6** is one of the rarest examples containing μ_4 -oxo unit with heavier early transition metal i.e. tantalum. In an effort to isolate selenium analogues of clusters **1-3**, we have isolated the trimetallic cluster $[(\text{Cp}^*\text{Ta})_3(\mu\text{-Se})_3(\mu_3\text{-Se})_3\text{B}(\text{H})]$, **4** from the thermolytic reaction of $[\text{Cp}^*\text{TaCl}_4]$ and $\text{Li}[\text{BH}_2\text{Se}_3]$. In contrast, the thermolysis of $[\text{Cp}^*\text{TaCl}_4]$ with $\text{Li}[\text{BH}_2\text{Te}_3]$ under the same reaction conditions yielded tantalum telluride complex $[(\text{Cp}^*\text{Ta})_2(\mu\text{-Te})_2]$, **5**. Compounds **1-4** are hypo-electronic clusters with an electron count of 50 cve (cve = cluster valence electrons). All these compounds have been characterized by the ^1H , $^{11}\text{B}\{^1\text{H}\}$, $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy, IR spectroscopy, mass spectrometry and single crystal X-ray crystallography. The density functional theory (DFT) calculations were also carried out to provide insight into the bonding and electronic structures of these molecules.

INTRODUCTION

Transition-metal-boron chemistry, comprehending a wide range of structural diversities with higher nuclearity metallaborane clusters to complexes with single boron, has sustained to gain continuous interest.^{1,2} In this regard, single boron-metal-chalcogen clusters are advancing in the rapidly growing metallaheteroboranes family, mostly due to their intriguing structure and

bonding. The chemistry of transition metal complexes with main group elements³ particularly with chalcogen ligands is of substantial importance due to their widespread use in the preparation of advanced materials^{4a-c} and industrial catalysis.^{4d,e} These complexes also play a significant role in the activity of metalloproteins in enzymatic catalytic cycle.⁵ The homo and heterometallic sulfido complexes with wide range of substrates are well documented in the literature.⁶⁻¹³ For example, $[(C_5H_4CH_3)_2V_2S_5]$,^{14a} $[(CpCr)_2S(S-t-Bu)_2]$,^{14b} $[Fe_2S_2(CO)_6]$,^{15a} $[Mn_2(CO)_7(\mu-S_2)]$,^{15b} $[Cp_2TiE_5]$ ($E = S$ or Se),¹⁶ and $[Cp^*_2Mo_2S_4]$ ¹⁷ have been involved in many organic synthesis, assembly of uncommon mixed-metal clusters and used as hydrogenation catalysts.

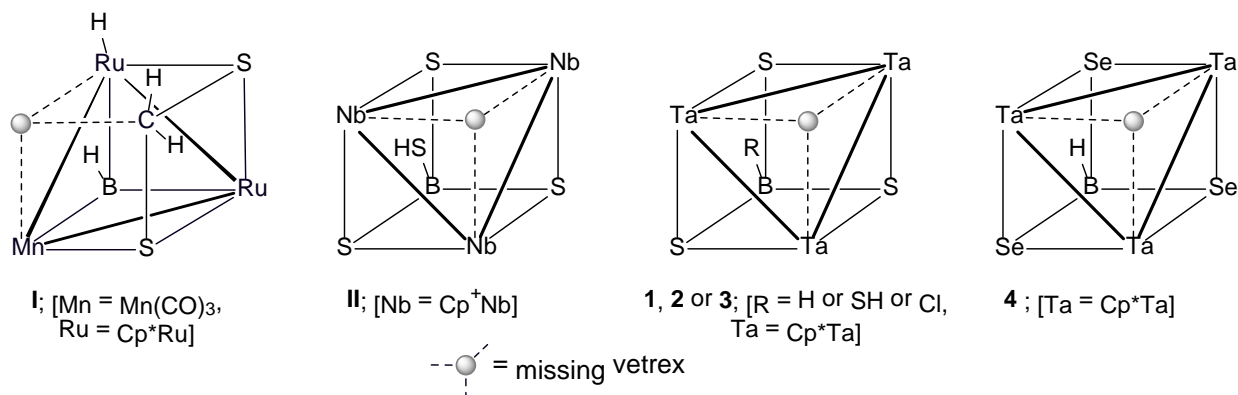


Chart 1. Metal and chalcogen-rich metallaheteroborane cubane-type clusters with one missing vertex (only the core geometry of **II** and **1-4** are shown for clarity).

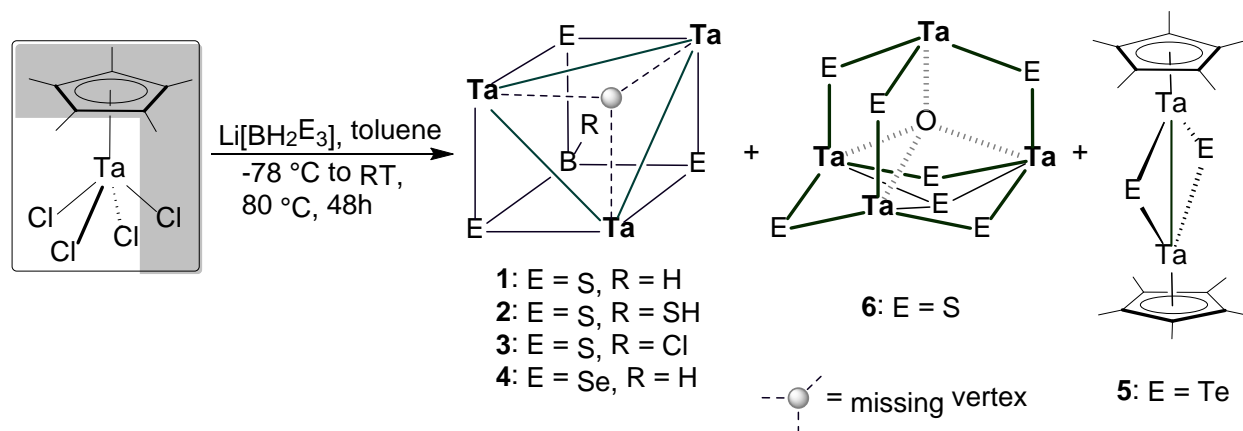
In contrast, thioborates are not regularly seen in the coordination sphere of transition metals, mostly due to the lack of synthetic routes. However, after the discovery of tetrathioborate containing complex, $[(Cp^+Nb)_3(\mu-S)_3(\mu_3-S)_3B(SH)]$ by Wachter, an investigation of related vanadium and tantalum systems became of interest.¹⁸ Although, the geometry of this tetrathioborate niobium complex was not fully defined, it may be considered as a cubane-type cluster having a M_3E_4 core. Cubane is a very well-known framework in the field of organometallic chemistry that has been used as model in various biological and industrial

process.¹⁹⁻²⁰ There are not many incomplete cubane-type clusters known, however, recently, our group reported a cubane-type cluster $[(\text{Cp}^*\text{Ru})_2\text{Mn}(\text{CO})_3\text{BH}_2(\text{CS}_2\text{H}_2)]$ which contains M_3E_4 core.²¹ Although in 1997, Tatsumi isolated and structurally characterized the trithioborate complex $[(\text{Cp}^*\text{Ta})_3(\mu\text{-S})_3(\mu_3\text{-S})_3\text{B}(\text{H})]$, **1** using two steps synthetic route, the chemistry was not explored with heavier chalcogen elements.²² Upon careful analysis of the single crystal X-ray structure of **1**, we assumed that the Ta_3 framework in **1** is stabilized by trithioborate (BHS_3^-) ligand. As a result, we introduced a simple and accessible synthetic route i.e. reaction of $[\text{Cp}^*\text{TaCl}_4]$ with trichalcogenoborate $\text{Li}[\text{BH}_2\text{E}_3]$,²³⁻²⁵ ($\text{E} = \text{S}$ or Se or Te). Herein, we report the isolation and structural elucidation of various chalcogen-stabilized metallaheteroboranes that show rare cubane-type clusters. In addition, theoretical calculations have established the stability and bonding of the new metallaheteroborane clusters.

RESULTS AND DISCUSSION

Reaction of $[\text{Cp}^*\text{TaCl}_4]$ with $\text{Li}[\text{BH}_2\text{E}_3]$ ($\text{E} = \text{S}$ or Se or Te). As shown in the Scheme 1, thermolysis of $[\text{Cp}^*\text{TaCl}_4]$ with four equivalents of $\text{Li}[\text{BH}_2\text{E}_3]$ ($\text{E} = \text{S}$ or Se) (prepared from the low temperature reaction of $[\text{LiBH}_4.\text{THF}]$ and chalcogen powders) resulted in the formation of $[(\text{Cp}^*\text{Ta})_3(\mu\text{-E})_3(\mu_3\text{-E})_3\text{B}(\text{R})]$, (**1**: $\text{E} = \text{S}$, $\text{R} = \text{H}$; **2**: $\text{E} = \text{S}$, $\text{R} = \text{SH}$; **3**: $\text{E} = \text{S}$, $\text{R} = \text{Cl}$ and **4**: $\text{E} = \text{Se}$, $\text{R} = \text{H}$). The $^{11}\text{B}\{^1\text{H}\}$ NMR spectra of **1-4** show single resonance appeared each at $\delta = 0.3$, 1.2, 5.6 and -11.2 ppm respectively. The $^{13}\text{C}\{^1\text{H}\}$ and ^1H NMR spectra suggest the presence of symmetry in **1-4** with respect to the Cp^* ligands. In addition, ^1H NMR chemical shifts at $\delta = 4.74$ and 4.71 ppm confirmed the presence of a terminal B-H proton for compounds **1** and **4** respectively. Furthermore, the presence of terminal B-H proton for **4** and S-H proton for **2** were confirmed by IR spectroscopy. The single crystal X-ray diffraction analyses were carried out to

endorse the spectroscopic assignments and to conclude the solid-state X-ray structures of compounds **1-4**.



Scheme 1. Synthesis of chalcogen-rich tantallaboranes (**1-4**) and inorganic adamantane type cluster (**6**) ($\mu\text{-S}$ in clusters **1**, **2** and **3**, and $\mu\text{-Se}$ in **4** are not shown for clarity; **Ta** = Cp^*Ta).

The solid-state X-ray structure analysis of **1-4** shows that these molecules consist of an equilateral Ta_3 triangular core and the edges of the Ta_3 -triangle are bridged by six monosulfide (for **1**, **2** and **3**) and monoselenide (for **4**) atoms. In case of **1**, **2** and **3**, three sulfide units are capped by $\{\text{B}(\text{H})\}$, $\{\text{B}(\text{SH})\}$ and $\{\text{B}(\text{Cl})\}$ fragments respectively. Three selenide units are bridged by $\{\text{B}(\text{H})\}$ fragment in **4**. The mean B-S and B-Se bond distances are comparable with the distance observed in BE_3R ($\text{E} = \text{S}$ or Se) tetrahedron. The existence of compounds **1-3** and **4** permits a structural and spectroscopic comparison with other cubane-type clusters containing different chalcogenoborate ligands (Table 1). It is interesting to note that the clusters in which the boron atom is coordinated to heavier chalcogen atoms i.e. selenium, the ^{11}B chemical shift appeared at upfield region compared to its sulfur analogue. Note that, Tatsumi reported compound **1** with low yield and the authors faced some difficulties in detecting the proton bound to boron in ^1H NMR spectrum. Having isolated **1** in good yield, we were able to reinvestigate the

spectroscopic characterizations. The ^1H chemical shift for the proton bound to boron appeared at $\delta = 4.74$ ppm. Further, the $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum revealed a peak at $\delta = 0.3$ ppm, which is very downfield shifted as compared to the ^{11}B chemical shift reported by Tatsumi ($\delta = -21.3$ ppm).

As shown in Figure 1, the geometries of **1-4** can be considered as cubane-type clusters with a missing vertex. According to Wade's rules, the stable electron count for a M_4E_4 type cubane is $(15 \times 4 + 5 \times 4) = 80$, in which there is no M-M or M-E bond present along the diagonals of the cube. The presence of M-M or M-E bonds alter the cluster electron counts, for example, each successive loss or gain of 2 electrons are supplemented by the formation or breaking of M-M/M-E bond respectively.^{1a} Earlier, Kennedy and his coworkers²⁶ proposed the cluster electron counts for the cubanes $[(\text{CpNi})_4\text{B}_4\text{H}_4]$ ²⁷ and $[(\text{Cp}^*\text{Ru})_3(\mu_3\text{-CO})\text{Co}(\text{CO})_2\text{B}_3\text{H}_3]$ ²⁸ as 68 and 60 with two and six metal-metal bonds respectively. Cubane cluster $[(\text{Cp}^*\text{Ru})_3(\mu_3\text{-CO})\text{Co}(\text{CO})_2\text{B}_3\text{H}_3]$ can also be described as tetracapped tetrahedron. Earlier, from our group we have reported a M_3E_4 type of

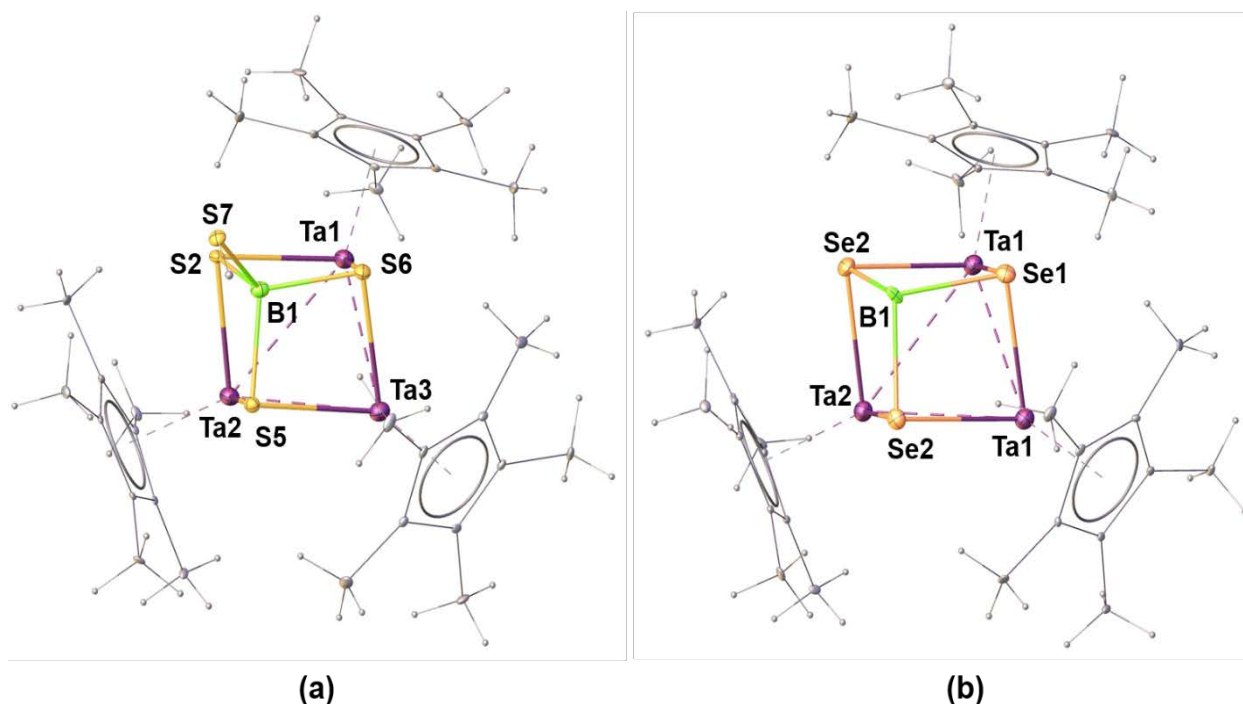
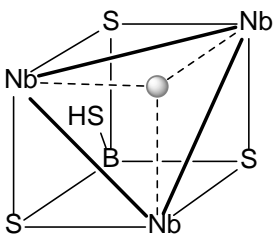
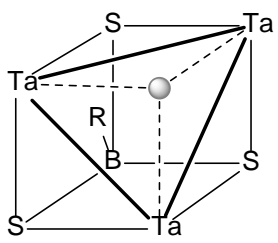
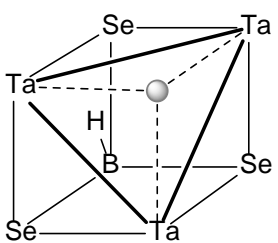



Figure 1. Molecular structures and labeling diagrams of **2** (a) and **4** (b). Selected bond lengths (Å) and angles (°): **2**: Ta1-Ta3 3.0974(6), Ta1-Ta2 3.1153(6), Ta2-Ta3 3.1054(7), B1-S6 1.899(16), B1-S7 1.854(15), Ta1-Ta3-Ta2 60.296(15), Ta3-Ta2-Ta1 59.725(15), S6-B1-S2 104.3(7), Ta2-S5-Ta3 75.57(8); **4**: Ta1-Ta2 3.213(2), Ta1-Ta2 3.2376(19), Ta1-Ta1 3.213(2), B1-Se1 2.02(5), B1-Se2 2.12(4), Ta1-Ta1-Ta2 60.25(2), Ta2-Se2-Ta1 74.76(8).

Table 1. Selected structural parameters and spectroscopic data of chalcogen-rich cubane-type clusters of group 5 metals.

Compounds	Av d_{M-M} [in Å]	Av d_{E-B} [in Å]	$^{11}\text{B}\{^1\text{H}\}$ NMR (in ppm)	Reference
 <p>[Nb = Cp⁺Nb] Cp⁺ = η⁵-C₅Me₄Et</p>	3.157	1.929	1.9	18
 <p>[Ta = Cp⁺Ta] R = H (1) or SH (2) or Cl (3)</p>	3.098 (R = H) 3.106 (R = SH) 3.094 (R = Cl)	2.02 (R = H) 1.926 (R = SH) 1.949 (R = Cl)	-21.3 (R = H) 1.2 (R = SH) 5.6 (R = Cl)	22 this work this work
 <p>[Ta = Cp⁺Ta] 4</p>	3.229	2.085	-11.2	this work

Av = Average, E = μ₃-chalcogen atom  = missing vertex

cubane cluster, $[(\text{Cp}^*\text{Ru})_2\text{Mn}(\text{CO})_3\text{BH}_2(\text{CS}_2\text{H}_2)]$ that can be derived from M_4E_4 by removing one metal vertex. As one transition metal vertex is missing and three M–M bonds are present, total valence electron count for this molecule should be $\{80 - 18 - (3 \times 2)\} = 56$, however the actual electron count is 54. Similarly, for molecule $[(\text{Cp}^+\text{Nb})_3\text{BHS}_7]$, reported by Wachter, consists of 50 cve. The metal sulfido and selenido clusters, $\text{Ta}_3\text{S}_3\text{B}$ or $\text{Ta}_3\text{Se}_3\text{B}$ (**1-4**), can very well be related with $[(\text{Cp}^+\text{Nb})_2\text{BHS}_7]$. Clusters **1-4** also consist 50 cve, which is 6 electrons short of the regular one (if we apply Kennedy's Scheme). Thus, these cubane-type clusters, having a missing vertex, can be defined as hypo-electronic clusters.

To get insight into the structure and bonding of **1-4**, computational analyses on the ground of DFT (Density Functional Theory)²⁹ at PBE0/Def2-SVP level were carried out. The frontier molecular orbitals of **1-4** showed that the HOMO of **1-4** made of d_z^2 orbitals of three Ta atoms and they are delocalized over three Ta atoms to form a Ta_3 triangular framework (Figures S26). The analyses further showed that the HOMO of **3** is further stabilized in contrast to others, which may be due to the presence of electronegative Cl atom attached to the boron. The energy gap between HOMO and LUMO of **1-4** indicate the stability of such hypo-electronic cubane-type clusters.

In an attempt to isolate the Te analogue of **1-4**, we explored the reactivity of $\text{Li}[\text{BH}_2\text{Te}_3]$ with $[\text{Cp}^*\text{TaCl}_4]$ in toluene at 80 °C that resulted in the formation of compound **5**. Although the reaction yielded some very low yielded compounds, they were too less in amount and highly unstable to be isolated. Compound **5** was isolated as yellow solid. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopic data displayed the presence of one Cp^* environment and the $^{11}\text{B}\{^1\text{H}\}$ NMR showed no peak that excludes the formation of any metallaborane cluster. Finally, the solid state X-ray diffraction analysis on a suitable crystal of **5** was performed to elucidate the structure of **5**.

As shown in Figure S4, the molecular structure of **5** can be described as two {Cp*Ta} units held together by two μ_2 -bridging telluride ligands. Both the two Ta and Te atoms are not in same plane. Although, there are known examples of Te bridged Ta complex (such as **IV**, Chart 2), they were mostly characterized by NMR, IR spectroscopy and to the best of our knowledge no solid-state X-ray structures are known till date.^{30,31}

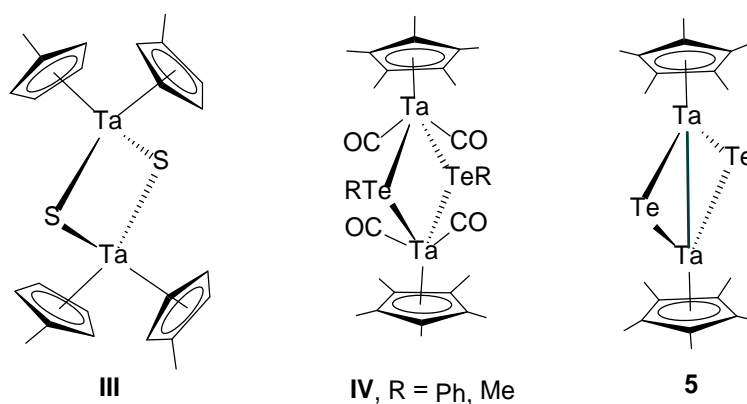


Chart 2. Binuclear Ta complexes containing bridging chalcogen atoms.

Having failed to isolate the Te analogue of **1**, we were curious to examine their apparent stabilities (**1**^{Te}, Te analogue of **1**). The calculated HOMO–LUMO gap for **1**^{Te} revealed that as one changes the chalcogen atom from S to Te, the apparent thermodynamic stability increases in the order **1**^{Te} < **4** < **1**. These results have also been verified with the calculated natural charges on boron (q_B) and chalcogen atoms (q_E) (Table S1). The positive charge on boron converted to negative and goes more negative when chalcogen atoms are changed from S to Te. Whereas, the charge on chalcogen increases in the order S < Se < Te. The chalcogen atom donates its electron density to the boron, which is the sign of an increase in natural valence population at boron center and a decrease at chalcogen atom. This study indirectly suggests that the synthesis of the Te analogue is synthetically challenging.

Tetrametallic μ_4 -oxo cluster, **6**:

As shown in the Scheme 1, along with the formation of **1-3**, thermolysis of [Cp*TaCl₄] with four equivalents of Li[BH₂S₃] also yielded compound **6** as brown solid. It was characterized by ¹H and ¹³C{¹H} NMR spectroscopy, mass spectrum and a single crystal X-ray crystallographic analysis. The ¹¹B{¹H} NMR shows no peak and the ¹H NMR spectrum shows the presence of two Cp* ligands, appeared at δ = 2.16 and 2.01 ppm in 3:1 ratio. This indicates two different metal environments, which was further confirmed by ¹³C{¹H} NMR spectrum. The mass spectrum of **6** displayed a molecular ion peak at m/z 1505.

An unambiguous explanation eluded us until an X-ray structure revealed the molecular formula of **6** as [(Cp*Ta)₄(μ -S)₆(μ_3 -S)(μ_4 -O)]. As shown in Figure 2, the solid-state X-ray structure of **6** represents adamantane like core. One of the most interesting features of **6** is the presence of six membered Ta₃-S₃ planar ring instead of a chair form. This may be due to the presence of μ_3 -S that brings three Ta atoms in one plane. Another noticeable feature of **6** is the presence of one μ_4 -oxo moiety inside the adamantane core.³² It is an example of inverse coordination complex, where non-metal oxygen is surrounded by four tantalum metals in a tetrahedral fashion.³³⁻⁴¹ Inverse coordination compounds have noteworthy applications, such as, hydrogen gas storage, precursors for novel materials for catalysis and radioactive protective agents.³⁴ The Ta-O bond length is slightly longer as compared to the M-O bond lengths observed in other adamantane-like inorganic compounds.^{38,41,42}

As shown in Table 2, a series of adamantane-like inorganic compounds of various transition metals, (such as, Cu,³⁴⁻³⁷ Mg,³⁸ Pb,³⁹ Cr⁴⁰ and Mn⁴¹) are known and several of them are utilized in industrial catalysis to biomedical activity. Apart from the wide range of applications,

their fascinating structural and bonding features make these complexes very important. Therefore, compound **6** could be a potential entry into the field of catalysis due to its structural similarity with other adamantane-like inorganic compounds. To the best of our knowledge, it is the first example

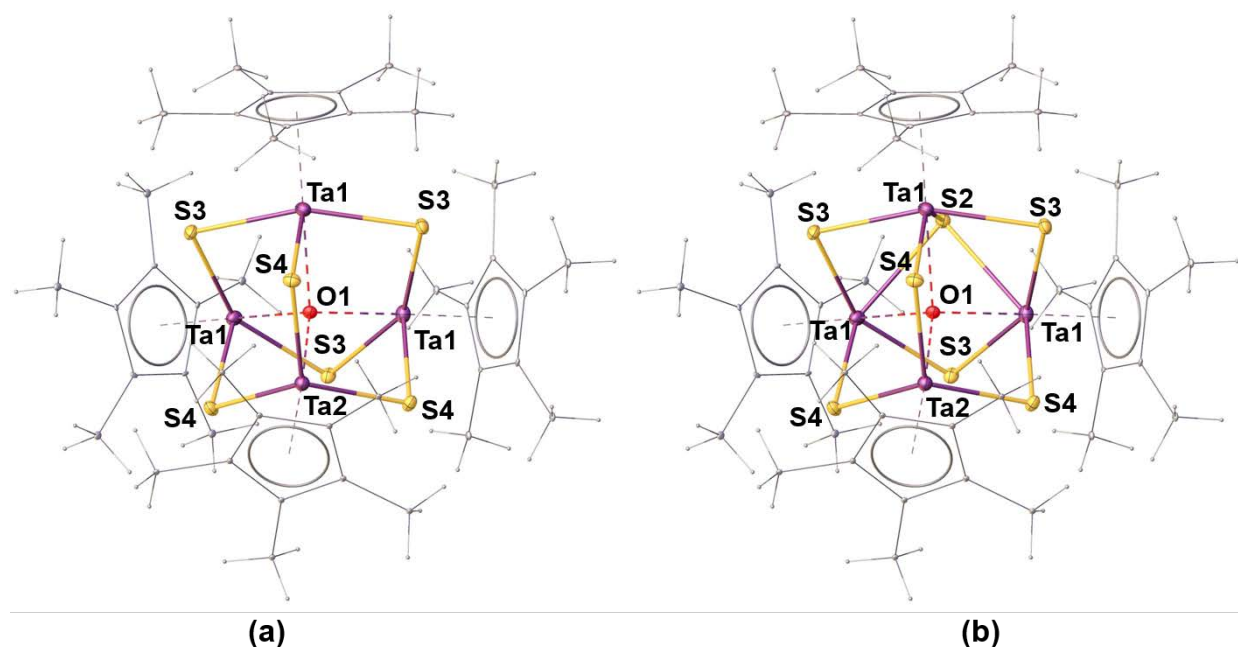
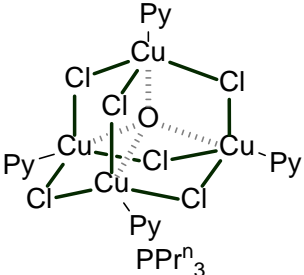
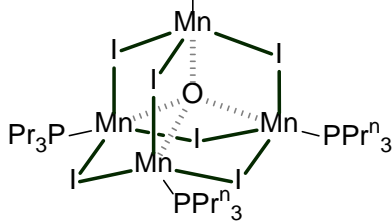
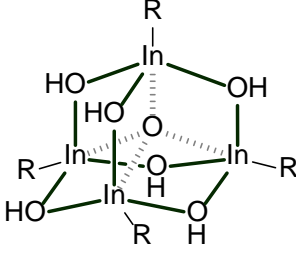


Figure 2. Molecular structure and labeling diagram of **6** without S2 (left side) and with S2 atom (right side). Selected bond lengths (Å) and angles (°): Ta1-O1 2.174(4), Ta2-O1 2.064(10), Ta2-S4 2.384(2), Ta1-S4 2.448(2); Ta1-O1-Ta2 115.0(2), Ta1-O1-Ta1 103.4(3), Ta1-S3-Ta1 89.68(8), Ta1-S4-Ta2 95.42(8).

of an oxo-centered adamantane-like inorganic compound comprising Ta and S. Although we have successfully isolated sulfur analogue of inorganic adamantane, all of our attempts to isolate the Se and Te analogue of **6** were failed. One of the reasons may be the higher atomic radius of Se and Te. The DFT investigation concur with our experimental observation. The frontier molecular orbital analysis clearly shows that the HOMO–LUMO gap reduces along the group 16 elements i.e. from S to Te, which gives an understanding for apparent instability of Se and Te

analogues (Table S2). Further, the calculated natural charge and natural valence population show that moving from S to Te, the electron density on oxygen as well as at chalcogen atoms was decreased and on tantalum the electron density was increased (Tables S2 and S3). In order to explain colors and corresponding HOMO- LUMO gaps of these complexes, the UV-Vis spectra were recorded in

Table 2. Structural parameters of selected μ_4 -oxo containing adamantane-like inorganic complexes.

Compounds	Av $d_{\mu_4\text{-O}}$ [in Å]	Av $\angle\text{M-O-M}$ [in °]	Av $d_{\text{M-M}}$ [in Å]	Reference
	1.90 (Cu-O)	109.5 (Cu-O-Cu)	3.10 (Cu-Cu)	30b
	2.063 (Mn-O)	109.5 (Mn-O-Mn)	3.369 (Mn-Mn)	40
 <p>R = C(SiMe₃)₃</p>	2.120 (In-O)	109.5 (In-O-In)	-	41

	1.969 (Mg-O)	109.7 (Mg-O-Mg)	3.220 (Mg-Mg)	37
<p style="text-align: center;">6</p>	2.146 (Ta-O)	109.2 (Ta-O-Ta)	3.493 (Ta-Ta)	This Work

Av = average, - = structural data not available

CH₂Cl₂. As shown in Figures S6-S8, compounds **1**, **2** and **4** show absorption bands at $\lambda = 428$, 423 and 500 nm respectively, which are consistent with their corresponding ΔE values.

CONCLUSION

In summary, we have established a facile synthetic route for the synthesis of chalcogen-rich trimetallic cubane-type clusters **1-4**. Our method overcomes the challenges, which was faced previously in isolating heavier chalcogen containing cubane-type cluster with tantalum. The theoretical study revealed the intriguing role of Ta₃ triangular framework for the stabilization of the chalcogenoborate ligand. Furthermore, we have isolated and structurally characterized the first adamantane-like inorganic cluster comprising of tantalum and sulfur. This compound shows inverse coordination due to the presence of μ_4 -oxo unit. Thus, the discovery of this cluster may open the gateway for the synthesis of other group 5 transition metals containing adamantane-like clusters.

EXPERIMENTAL SECTION

General Procedures and Instrumentation. All manipulations were conducted under an Ar/N₂ atmosphere by using standard Schlenk techniques or in a glove box. Solvents were distilled prior to use under an Ar atmosphere. [Cp*TaCl₄]⁴², [LiBH₄.THF], S powder, Se powder and Te powder were used as received (Aldrich). Li[BH₂E₃]²³⁻²⁵ (E = S, Se and Te) were synthesized according to the literature methods. Thin layer chromatography was carried out on 250- μ m diameter aluminum supported silica gel TLC plates (MERCK TLC Plates) to separate the reaction mixtures. NMR spectra were recorded on 500 MHz Bruker FT-NMR spectrometer. Residual solvent protons were used as reference (CDCl₃, δ = 7.26 ppm), while a sealed tube that contained, [Bu₄N(B₃H₈)] in [D₆] benzene (δ_B = -30.07 ppm) was used as an external reference for the ¹¹B NMR analysis. ESI mass spectra were recorded on Bruker MicroTOF-II mass spectrometer. Infrared spectra were recorded with a JASCO FT/IR-4100 spectrometer. Absorption spectra were recorded with Evolution 300 (Thermo Scientific) UV/Vis spectrophotometer at 298 K. Due to low yields and higher sensitivity of compounds **2**, **3**, **5** and **6**, the elemental analysis of them were not carried out. On the other hand, our several attempts to obtain the elemental analysis data of the compounds **1** and **4** gave unsatisfactory results. Thus, the combustion analysis of all the compounds, reported in this paper, are not provided.

Synthesis of 1-3 and 6: In a flame-dried Schlenk tube [Cp*TaCl₄] (0.200 g, 0.44 mmol) was suspended in 20 mL toluene and chilled to -78 °C. It was added to a freshly prepared solution of Li[BH₂S₃] in toluene. The reaction mixture was slowly warmed to room temperature over 1 h under stirring condition and then heated to 80 °C for 48 hrs. The volatile components were removed under vacuum and the residue was extracted into *n*-hexane and passed through Celite. After removal of the solvent, the residue was subjected to chromatographic work-up by using

TLC plates. Elution with *n*-hexane/CH₂Cl₂ (70:30 v/v) yielded green **1** (solid, 0.092g, 18%),⁴³ green **2** (solid, 0.084g, 16%), yellow **3** (solid, 0.026 g, 5%) and brown **6** (solid, 0.053g, 8%).

2: HRMS (ESI⁺): *m/z* calculated for C₃₀H₄₆BS₇Ta₃ + H⁺: 1185.0256, found: 1185.0236. ¹H NMR (500 MHz, CDCl₃, 22 °C): δ = 2.21 ppm (s, 45H; 3×Cp*); ¹¹B{¹H} NMR (160 MHz, CDCl₃, 22 °C): δ = 1.2 ppm; ¹³C{¹H} NMR (125 MHz, CDCl₃, 22 °C): δ = 117.5 (C₅Me₅), 13.0 ppm (C₅Me₅); IR (hexane, cm⁻¹): 2431.8 (S-H).

3: MS (ESI⁺): *m/z* calculated for C₃₀H₄₅BClS₆Ta₃ + H⁺: 1187.0145 found: 1187.0402. ¹H NMR (500 MHz, CDCl₃, 22 °C): δ = 2.13 ppm (s, 45H; 3×Cp*); ¹¹B{¹H} NMR (160 MHz, CDCl₃, 22 °C): δ = 5.6 ppm; ¹³C{¹H} NMR (125 MHz, CDCl₃, 22 °C): δ = 118.0 (C₅Me₅), 12.3 ppm (C₅Me₅).

6: MS (ESI⁺): *m/z* calculated for C₄₀H₆₀OS₇Ta₄ + H⁺: *m/z* 1505.0688, found: 1505.0736. ¹H NMR (500 MHz, CDCl₃, 22 °C): δ = 2.16 (s, 45H; 3×Cp*), 2.01 ppm (s, 15H; Cp*).

Synthesis of 4: In a flame-dried Schlenk tube [Cp*TaCl₄] (0.100 g, 0.40 mmol) was suspended in 20 mL toluene and chilled to -78 °C. Then the resultant solution was added to a freshly prepared solution of Li[BH₂Se₃] in toluene. The reaction mixture was slowly warmed to room temperature over 1 h under stirring condition and then heated to 80 °C for 48 hrs. The volatile components were removed under vacuum and the remaining residue was extracted into *n*-hexane and passed through Celite. After removal of the solvent, the residue was subjected to chromatographic work-up by using TLC plates. Elution with *n*-hexane/CH₂Cl₂ (70:30 v/v) afforded orange compound **4** (solid, 0.076 g, 12%).

4: HRMS (ESI⁺): *m/z* calculated for C₃₀H₄₆BSe₆Ta₃ + H⁺: 1440.7202, found: 1440.7198. ¹H NMR (500 MHz, CDCl₃, 22 °C): δ = 2.33 (s, 45H; 3×Cp*), 4.71 ppm (B-H₀); ¹¹B{¹H} NMR

(160 MHz, CDCl₃, 22 °C): δ = -11.2 ppm; ¹³C{¹H} NMR (125 MHz, CDCl₃, 22 °C): δ = 115.4 (C₅Me₅), 13.3 ppm (C₅Me₅); IR (hexane, cm⁻¹): 2458.8 (B-H_T).

Synthesis of 5: In a flame-dried Schlenk tube a suspension of [Cp*TaCl₄] (0.200 g, 0.80 mmol) in 20 mL toluene at -78 °C was charged with a freshly prepared solution of Li[BH₂Te₃]. The reaction mixture was slowly warmed to room temperature over 1 h under stirring condition and then heated to 80 °C for 48 hrs. The volatile components were removed under vacuum and the residue was extracted into *n*-hexane and passed through Celite. After removal of the solvent, the residue was subjected to chromatographic work-up by using TLC plates. Elution with *n*-hexane/CH₂Cl₂ (80:20 v/v) yellow **5** (solid, 0.024g, 6%).

5: ¹H NMR (500 MHz, CDCl₃, 22 °C): δ = 2.17 ppm (s, 30H; 2×Cp*); ¹³C{¹H} NMR (125 MHz, CDCl₃, 22 °C): δ = 110.0 (C₅Me₅), 11.7 ppm (C₅Me₅).

X-ray Structure Determination. The crystal data for **2**, **3**, **4** and **5** were collected and integrated using a Bruker axs kappa APEX-II CCD diffractometer with graphite-monochromated MoK α (λ = 0.71073 Å) radiation at 296 K. The crystal data for **6** was collected and integrated using a Bruker APEXII AXS diffractometer, equipped with a CCD detector, using MoK α radiation (λ = 0.71073 Å) at 150(2) K. The structures were solved by heavy atom methods using SHELXS-97 or SIR92 and refined using SHELXL-2014.⁴⁴

Table 3. Crystallographic Data and Structure Refinement Information for **2-6**.

	2	3	4	5	6
CCDC No.	1845949	1845950	1845951	1845952	1845953
Empirical formula	C ₃₁ H ₄₈ BCl ₂ S ₇ Ta ₃	C ₃₀ H ₄₅ BClS ₆ Ta ₃	C ₃₂ H ₅₀ BCl ₄ Se ₆ Ta ₃	C ₂₀ H ₃₀ Ta ₂ Te ₂	C ₄₀ H ₆₀ OS ₇ Ta ₄
Formula weight	1269.67	1187.13	1603.94	887.54	1505.10
Crystal system	monoclinic	triclinic	orthorhombic	triclinic	cubic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> -1	<i>Pnma</i>	<i>P</i> -1	<i>Pa</i> -3
<i>a</i> (Å)	12.7180(5)	11.8274(2)	16.7423(11)	9.7538(2)	20.847(2)
<i>b</i> (Å)	14.2356(4)	11.8523(3)	16.5272(13)	10.3073(3)	20.847
<i>c</i> (Å)	23.2024(11)	15.7067(3)	15.4896(12)	14.1709(4)	20.847
α (°)	90	74.1092(11)	90	86.6750(10)	90
β (°)	105.6697(15)	82.6421(7)	90	88.0540(10)	90
γ (°)	90	60.1030(8)	90	66.7390(10)	90
<i>V</i> (Å ³)	4044.6(3)	1835.75(7)	4286.0(6)	1306.57(6)	9060(3)
<i>Z</i>	4	2	4	2	8
ρ_{calc} (g/cm ³)	2.085	2.148	2.486	2.256	2.207
μ (mm ⁻¹)	8.611	9.353	13.008	10.557	9.983
<i>F</i> (000)	2416	1124	2952	800	5696
2 θ range (°)	3.334 to 49.998	2.696 to 50	3.582 to 40.226	2.878 54.318	to 5.862 to 54.89
Reflections collected	29216	27446	12484	22389	90464
Independent reflections	7116	6447	2115	5790	3461
Final R indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0487, w <i>R</i> ₂ = 0.1141	<i>R</i> ₁ = 0.0328, w <i>R</i> ₂ = 0.0714	<i>R</i> ₁ = 0.0604, w <i>R</i> ₂ = 0.1173	<i>R</i> ₁ = 0.0400, <i>R</i> ₁ = 0.0466, w <i>R</i> ₂ = 0.0919	w <i>R</i> ₂ = 0.0932
R indexes [all data]	<i>R</i> ₁ = 0.0822, w <i>R</i> ₂ = 0.1351	<i>R</i> ₁ = 0.0421, w <i>R</i> ₂ = 0.0759	<i>R</i> ₁ = 0.1038, w <i>R</i> ₂ = 0.1375	<i>R</i> ₁ = 0.1044, <i>R</i> ₁ = 0.0585, w <i>R</i> ₂ = 0.1192	w <i>R</i> ₂ = 0.1046

Computational Details. The quantum chemical calculations were carried out for **1-6** using DFT as implemented in the Gaussian09 package.²⁹ The calculations were performed with the Cp analogues, instead of Cp* in order to save computing time. Without any symmetry restrictions, all the geometry optimizations were carried out in gaseous state, (no solvent effect) using PBE0 functional⁴⁵ in combination with triple- ζ quality basis set Def2-SVP. The natural bond orbital (NBO) analysis⁴⁶ within the Gaussian09 package was carried out at PBE0/Def2-SVP level of theory. The ChemCraft package⁴⁷ was used for the visualizations.

ASSOCIATED CONTENT

Supporting Information. The supplementary spectroscopic data, DFT-computed results for **1-6** and other computational details. This material is available free of charge via the internet at <http://pubs.acs.org>.

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Notes

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Synthesis and structures of cubane-type organotantalum sulfido cluster with a missing vertex (A) and an adamantane-like inorganic sulfide cluster having an μ_4 -oxo moiety (B) are reported here (see picture).

