

Chalcogen stabilized cubane-type cluster: Synthesis and structure of $[(\text{Cp}^*\text{Ta})_3(\mu\text{-Se})_3(\mu_3\text{-Se})_3\text{B}(\text{OBuCl})]$

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In an effort to isolate the heavier chalcogen-rich metallaheteroborane analogue of $[(\text{Cp}^*\text{Ta})_3(\mu\text{-S})_3(\mu_3\text{-S})_3\text{BH}]$, thermolysis of $[\text{Cp}^*\text{TaCl}_4]$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) and $\text{Li}[\text{BH}_2\text{Se}_3]$ was carried out that afforded cubane-type cluster $[(\text{Cp}^*\text{Ta})_3(\mu\text{-Se})_3(\mu_3\text{-Se})_3\text{B}(\text{OBuCl})]$, **1**. Compound **1** is an example of cubane-type organotantalum selenido cluster, in which one of the vertices of the cubane is missing. Compound **1** is a hypo-electronic cluster with an electron count of 50 cve (cve = cluster valence electrons). In parallel to the formation of **1**, trimetallic selenide cluster $[(\text{Cp}^*\text{Ta})_3(\mu\text{-Se})_6]$, **2** has also been isolated and structurally characterized. All these compounds were characterized by the multi-nuclear NMR spectroscopy, mass spectrometry and single crystal X-ray crystallography. The density functional theory (DFT) calculations were also performed to provide insight into the bonding and electronic structures of these novel clusters.

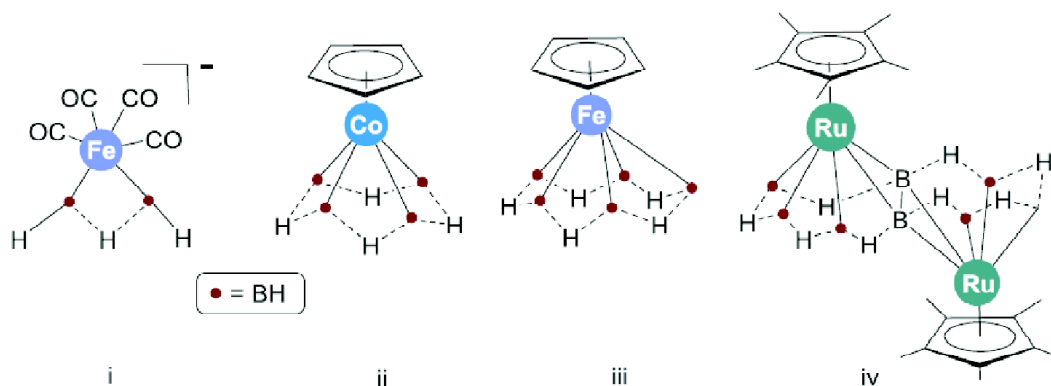
Keywords: Cubane, selenium, tantalum, boron, chalcogenide ligand.

Introduction

Boron in union with hydrogen shows abundant catenation chemistry similar to that of carbon¹. The major enthralling aspect of metallaborane chemistry is that their analogues often mimic classic organometallic complexes². In most of the cases, the geometric structures can be generated by replacing carbon with boron combined with B-H-B bridging hydrogen atoms and/or net charge to match the valence electron count³. There are various examples of such type i.e. $[(\eta^2\text{-C}_2\text{H}_4)\text{Fe}(\text{CO})_4]$ vs $[\text{B}_2\text{H}_5\{\text{Fe}(\text{CO})_4\}]^-$; $[(\eta^4\text{-C}_4\text{H}_4)\text{CoCp}]$ vs $[(\text{B}_4\text{H}_8)\text{CoCp}]^5$; $[(\eta^5\text{-C}_5\text{H}_5)\text{FeCp}]$ vs $[(\text{B}_5\text{H}_{10})\text{FeCp}]^6$; and

$[(\text{Cp}^*\text{Ru})\text{C}_8\text{H}_6(\text{RuCp}^*)]$ vs $[(\text{Cp}^*\text{Ru})\text{B}_8\text{H}_{14}(\text{RuCp}^*)]^7$ (Scheme 1).

In that connection, we have reported various metallaboranes⁸ and metallaheteroboranes⁹. In recent, diruthenium pentalene analogue, $[(\text{Cp}^*\text{Ru})\{(\text{Cp}^*\text{Ru})_2\text{B}_6\text{H}_{14}\}(\text{RuCp}^*)]$ and a metal indenyl complex $[(\text{Cp}^*\text{Ru})_2\text{B}_2\text{H}_6\text{C}_6\text{H}_3(\text{CH}_3)]$ have also been isolated, in which the $\{(\text{Cp}^*\text{Ru})_2\text{B}_6\text{H}_{14}\}$ fragment in the former may be considered as a true metal-boron analogue of $\eta^5\text{-}\eta^5\text{-pentalene}$ ligand (C_8H_6) and $\{(\text{Cp}^*\text{Ru})\text{B}_2\text{H}_6\text{C}_6\text{H}_3(\text{CH}_3)\}$ fragment in later is an analogue of $\eta^5\text{-indenyl}$ ligand¹⁰. Subsequently, we structurally characterized chalcogen sta-



Scheme 1. Examples of metallaboranes containing borane fragments analogous to π -ligands: (i) $[(\text{CO})_4\text{Fe}(\text{B}_2\text{H}_5)]^-$, (ii) $[(\text{CpCo})\text{B}_4\text{H}_8]$, (iii) $[(\text{CpFe})\text{B}_5\text{H}_{10}]$ and (iv) $[(\text{Cp}^*\text{Ru})_2\text{B}_8\text{H}_{14}]$.

bilized dimetallaheteroboranes, $[(\text{CpV}(\mu\text{-EPh}))_2\{\mu\text{-}\eta^2\text{-}\eta^2\text{-BH}_3\text{E}\}]$, (E = S or Se) which are iso-structural and iso-electronic with vanadium diborane complex, $[(\text{CpV})_2(\text{B}_2\text{H}_6)_2]$ ¹¹. The chemistry of metallaborane particularly, metalla-heteroborane complexes is of extensive importance due to their application in the hydrogenation of olefins and activation of H₂¹². Therefore, we have explored the reaction of $[\text{Cp}^*\text{TaCl}_4]$ with chalcogenoborate ligand, $\text{Li}[\text{BH}_2\text{Se}_3]$ under thermolytic condition. Herein, we report the synthesis and characterization of selenium stabilized tantallaheteroborane as well as tantalum selenide clusters. Density functional theory (DFT) studies were performed to understand the bonding in these clusters.

Experimental

General procedures and instrumentation

The reactions are exploited entirely in argon atmosphere by using standard Schlenk techniques or in a glove box. All the solvents were distilled prior to use under an argon atmosphere. $[\text{Cp}^*\text{TaCl}_4]$ ¹³, $[\text{LiBH}_4\cdot\text{thf}]$ and Se powder were used as received (Aldrich). $\text{Li}[\text{BH}_2\text{Se}_3]$ ^{14,15} was synthesized according to the literature method. The reaction mixtures was separated using thin layer chromatography and it was carried out on 250- μm diameter aluminium supported silica gel TLC plates. NMR spectra were recorded on 500 MHz Bruker FT-NMR spectrometer. Residual solvent protons (CDCl_3 , $\delta = 7.26$ ppm) were used as reference while a sealed tube contained $[\text{Bu}_4\text{N}(\text{B}_3\text{H}_8)]$ ¹⁶ in *d*₆-benzene ($\delta_{\text{B}} = 30.07$ ppm) was used as an external reference for the $^{11}\text{B}\{^1\text{H}\}$ NMR analysis. ESI mass spectrum was recorded on Bruker MicroTOF-II mass spectrometer.

Synthesis of 1 and 2: In a flame dried Schlenk tube, $[\text{Cp}^*\text{TaCl}_4]$ (0.2 g, 0.44 mmol) was suspended in 20 mL toluene and chilled to -78°C . To it a freshly prepared solution of $\text{Li}[\text{BH}_2\text{Se}_3]$ was added in toluene medium. The reaction mixture was slowly warmed to room temperature over 1 h under stirring condition and then heated at 90°C for 60 h. The volatile components were removed under vacuum and the residue was extracted into *n*-hexane and passed through Celite. After the removal of the solvent, the residue as subjected to chromatographic work-up by using TLC plates. Elution with *n*-hexane/ CH_2Cl_2 (70:30 v/v) yielded orange **1** (0.034 g, 5%) and green **2** (0.046 g, 7%).

1: MS (ESI⁺): *m/z* Calcd. for $\text{C}_{34}\text{H}_{53}\text{Ta}_3\text{Se}_6\text{BOCl} + \text{Na}^+$:

1568.7, Found: 1568.9. ^1H NMR (500 MHz, CDCl_3 , 22°C): $\delta = 3.50$ (t, $^3J_{\text{HH}} = 6.9\text{Hz}$, 2H, OCH_2CH_2), 3.28 (t, $^3J_{\text{HH}} = 6.1\text{Hz}$, 2H, ClCH_2), 2.32 (s, 45H, $3\times\text{Cp}^*$), 2.03 (tt, 2H, ClCH_2CH_2), 1.73 ppm (tt, $^3J_{\text{HH}} = 6.9\text{Hz}$, 2H, OCH_2); $^{11}\text{B}\{^1\text{H}\}$ NMR (160 MHz, CDCl_3 , 22°C): $\delta = -5.6$ ppm.

2: MS (ESI⁺): *m/z* Calcd. for $\text{C}_{30}\text{H}_{45}\text{Se}_6\text{Ta}_3 + \text{Na}^+$: 1450.6, Found: 1450.4. ^1H NMR (500 MHz, CDCl_3 , 22°C): $\delta = 2.33$ (s, 30H, $2\times\text{Cp}^*$), 2.26 ppm (s, 15H, $1\times\text{Cp}^*$).

X-Ray structure determination: The crystal data for **1** and **2** were collected and integrated using a Bruker axis kappa APEX-II CCD diffractometer with graphite-monochromated MoK_α ($\lambda = 0.71073 \text{ \AA}$) radiation at 296 K. The structures were solved by heavy atom methods using SHELXS-97 or SIR92 and refined using SHELXL-2014¹⁷⁻¹⁹.

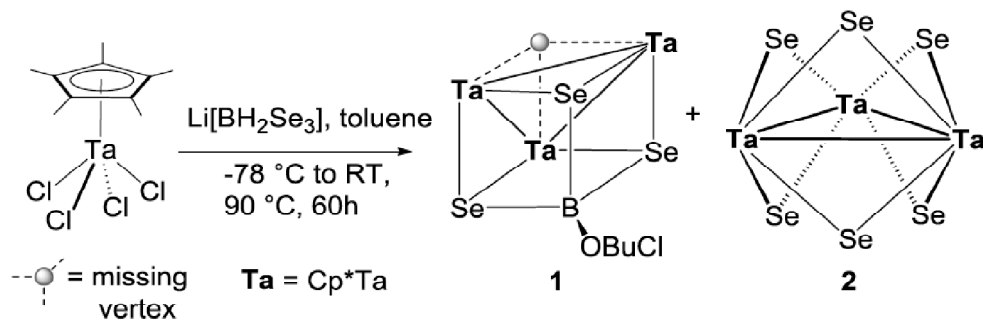
Crystal data for **1**: CCDC 1852570, $\text{C}_{35}\text{H}_{35}\text{BCl}_3\text{OSe}_6\text{Ta}_3$, $M_r = 1625.56$, monoclinic, space group C2, $a = 17.0363(7) \text{ \AA}$, $b = 14.1966(6) \text{ \AA}$, $c = 19.8869(9) \text{ \AA}$, $\beta = 108.1220(10)^\circ$, $V = 4571.2(3) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calcd}} = 2.362 \text{ g cm}^{-3}$, $\mu = 12.143 \text{ mm}^{-1}$, $F(000) = 3008$, $R_1 = 0.0425$, $wR_2 = 0.0973$, 5634 independent reflections [$\theta \leq 24.9^\circ$] and 522 parameters.

Crystal data for **2**: CCDC 1852569, $\text{C}_{30}\text{H}_{45}\text{Se}_6\text{Ta}_3$, $M_r = 1422.27$, trigonal, space group R-3, $a = 20.4432(7) \text{ \AA}$, $c = 15.2282(5) \text{ \AA}$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$, $V = 5511.6(4) \text{ \AA}^3$, $Z = 6$, $\rho_{\text{calcd}} = 2.571 \text{ g cm}^{-3}$, $\mu = 14.874 \text{ mm}^{-1}$, $F(000) = 3888$, $R_1 = 0.0878$, $wR_2 = 0.2383$, 3698 independent reflections [$\theta \leq 24.2^\circ$] and 228 parameters.

Computational details: The quantum chemical calculations were carried out for **1** and **2** using DFT as implemented in the Gaussian09 package²⁰. The calculations were carried out with the Cp analogues, instead of Cp* in order to save computing time. Without any symmetry restrictions, all the geometry optimizations were performed in the gaseous state, (no solvent effect) using PBE0 functional²¹ in combination with triple- ζ quality basis set Def2-TZVP. The natural bond orbital (NBO) analysis^{22,23} within the Gaussian09 package was carried out at PBE0/Def2-TZVP level of theory. The ChemCraft package²⁴ was used for the visualizations.

Results and discussion

The room temperature reaction of $[(\text{SCPh}_3)(\text{Cp}^*\text{Ta})\text{Cl}(\text{S})]$ with $\text{Na}[\text{BH}_4]$ was explored by Tatsumi and a cubane-type cluster $[(\text{Cp}^*\text{Ta})_3(\mu\text{-S})_3(\mu_3\text{-S})_3\text{BH}]$ was isolated²⁵. Therefore, in an order to isolate the heavier analogue of this cubane-type cluster, $[\text{Cp}^*\text{TaCl}_4]$ was treated with heavier chalcogenoborate ligand.



Scheme 2. Reactivity of chalcogenated borohydride, $\text{Li}[\text{BH}_2\text{Se}_3]$ with $[\text{Cp}^*\text{TaCl}_4]$.

generated borohydride i.e. $[\text{LiBH}_2\text{Se}_3]$, at elevated temperature for prolonged hours, which led to the formation of cubane type cluster $[(\text{Cp}^*\text{Ta})_3(\mu\text{-Se})_3(\mu_3\text{-Se})_3\text{B}(\text{OBuCl})]$, **1** and trimetallic selenide cluster $[(\text{Cp}^*\text{Ta})_3(\mu\text{-Se})_6]$, **2**. These new compounds have been characterized by multi-nuclear NMR, IR spectroscopy, mass spectrometry and X-ray diffraction analyses. The $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **1** reveals a single peak at $\delta = -5.5$ ppm which suggests that boron in **1** is attached to electronegative atom. The ^1H NMR spectrum of **1** reveals a peak at $\delta = 2.32$ ppm corresponding to Cp^* protons. Beside the chemical shifts for Cp^* ligands, ^1H NMR spectrum also showed signals in the alkyl regions ($\delta = 1.73\text{--}3.50$ ppm) that match well with the chemical shift of a substituted butyl group. The structural elucidation of **1** was not possible as the spectral data were not conclusive. Therefore, single crystal X-ray diffraction analysis was performed on a suitable crystal of compound **1**. As shown in Fig. 1(a),

the solid state structure of **1** can be considered as cubane-type cluster. The core consists of an equilateral Ta_3 triangular core and the tetrahedral boron (B1) atom is attached with three $\mu_3\text{-Se}$ atoms and an OBuCl moiety. The average Ta-Ta bond distance (3.2354 Å) lies within the Ta-Ta single bond distance²⁶. The B-O bond distance in **1** (1.38(2) Å) is comparable as observed in the carborane cluster, $[\text{PPh}_4][2\text{-Cl}(\text{CH}_2)_4\text{-O-closo-1-CB}_{11}\text{H}_{11}]$ (1.409(3) Å)²⁷.

Note that, the addition of $[\text{LiBH}_2\text{Se}_3]$ to a toluene solution of $[\text{Cp}^*\text{TaCl}_4]$ resulted cubane-type cluster with alkoxy-substituted borate moiety. Probably, this OBuCl unit was generated by the cleavage of tetrahydrofuran ring via ether-cleavage reaction in presence of selenium. This process is faster than the functionalised boron insertion. Similar instance was observed in the case of 2-substituted icosahedral carborane where formation of OBuCl unit occurred in two steps. First the $\text{Me}_2\text{S}\cdot\text{BCl}_3$ adduct underwent $\text{Me}_2\text{S}/\text{thf}$ ligand

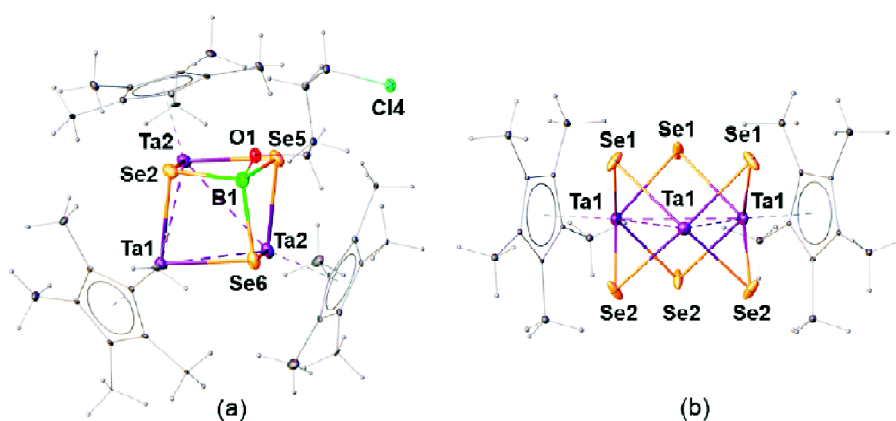


Fig. 1. (a) Molecular structure and labeling diagram of **1**. ($\mu_2\text{-Se}$ atoms are omitted for clarity). Selected bond lengths (Å) and angles ($^\circ$): Se2-B1 1.95(7), Se5-B1 2.19(5), Se6-B1 2.18(7), Se2-Ta1 2.650(4), Se2-Ta2 2.654(4), B1-O1 1.38(2), Ta1-Ta2 3.2291(18), Ta1-Ta3 3.2368(18), Ta2-Ta3 3.2402(5); Se2-B1-Se5 102(2), Se6-B1-Se5 95(2), Se2-B1-Se6 102.9(19), O1-B1-Se6 123(5); (b) Molecular structure and labeling diagram of **2**. Cp^* ring of one of the Ta1 atoms is omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): Se1-Ta1 2.545(4), Se1-Ta1 2.545(4), Ta1-Se1-Ta1 78.82(14), Se2-Ta1-Se1 140.39(13), Ta1-Se2-Ta1 78.80(15), Se1-Ta1-Se2 80.7(3), Se1-Ta1-Se1 86.6(4).

exchange followed by subsequent ether-cleavage reaction of the thf ligand²⁷.

Compound **1** can be considered as an incomplete cubane-type cluster having Ta₃Se₃B cage which is evident from the the solid state X-ray structure. In order to compare the cve (cluster valence electron) of **1** with the similar incomplete cubane-type clusters, we have counted the cve of **1**. The cve of these cubane-type clusters can be counted by considering conventional localized 2-center-2-electron bonding²⁸. For example, the cluster valence electron count predicted for a M₄E₄ type cubane is 80 (for a three-connected polyhedron i.e. cubane, cve = 15n+5n = 15*4+5*4), in the absences of M-M, M-E or E-E bond along the diagonals of the cube. Each successive two-electron loss is generally accompanied by the formation of one M-M, M-E, or E-E bond²⁹. An M₃E₄ "regular" cubane-like cluster is generally stable for a count of 6830 and for **1**, a count of 56 should be observed since there are three M-M bonds along the diagonals of the "cube". However, the cluster valence electron count for compound **1** is 50 and it is six electrons shorter than expected. Similarly, other clusters having M₃E₃B cage (for example, [(Cp*Ta)₃(μ-S)₃(μ₃-S)₃BH]²⁵ and [(Cp+Nb)₃BHS₇]³¹; Cp* = η⁵-C₅Me₄Et) also possess the same cve i.e. 50. Thus, cluster **1**, can be defined as hypo-electronic cluster.

To get insight into the structure and bonding of **1**, computational analyses on the ground of DFT (Density Functional Theory)²¹ at PBE0/Def2-TZVP level were executed. The frontier molecular orbitals of **1** showed that the HOMO of **1** made of d₂₂ orbitals of three Ta atoms and they are delocalized over three Ta atoms to form a Ta₃ triangular framework (Fig. 2). The energy gap between HOMO and LUMO of **1** indicates the thermal stability of such hypo-electronic cubane-type cluster. These results have also been verified with the calculated natural charges on boron (qB) and chalcogen atoms (qE).

Along with compound **1**, compound **2** has been isolated in moderate yield and characterized by ¹H NMR spectroscopy and single crystal X-ray diffraction analyses. The ¹¹B{¹H} NMR showed no resonances and the ¹H NMR showed chemical shifts at δ = 2.33 and 2.26 ppm in 2:1 ratio, attributed to inequivalent Cp* protons. The mass spectrum of compound **2** in ESI(+) mode shows molecular ion peak at m/z 1450.4 ([M+Na]⁺). However, the spectroscopic and mass spectrometric data were not adequate to predict the identity of **2**.

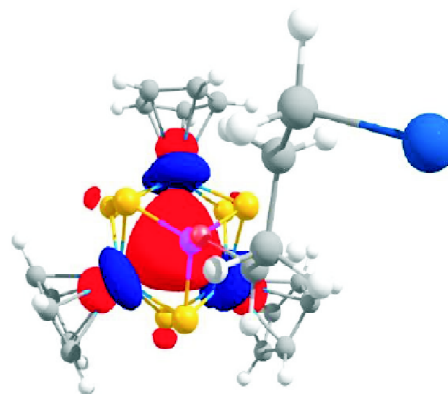


Fig. 2. HOMO of compound **1** (three d₂₂ orbitals of Ta atoms are delocalized).

Therefore, an X-ray diffraction study on a suitable crystal of **2** was carried out which revealed the molecular structure as [(Cp*Ta)₃(μ-Se)₆]. The solid-state X-ray structure of **2**, shown in Fig. 1(b), clearly shows that in the cluster, three tantalum atoms are at the vertices of a triangle, with six equivalent symmetrically bridging selenide ligands. The Ta-Ta bond distances (ca. 3.232 Å) are identical and lies within the single bond distances that makes the Ta₃ triangle a regular one. Each Ta atoms in **2**, is surrounded by four bridging selenium atoms at basal position and a Cp* ligand at the apical position and displays a distorted square pyramidal geometry. The distortion of this geometry from the ideal can be well understood from the values of each basal axial angles (∠Se2-Ta1-Se1 = 140.39(13)°), with the three metals displaced out of the mean plane of their basal selenium atoms toward the Cp* ligand.

The geometry of cluster **2** can be compared with the related trinuclear complex [Co₃(μ-SEt)₃(PEt₃)₃][BPh₄]³² and can be described in an alternative manner, where six selenium atoms can be viewed as occupying the vertices of a trigonal prism, with the three tantalum atoms outside the rectangular faces. Looking at the Se...Se contacts, those parallel to the pseudo-three-fold axis of the prism are short enough to suggest that some inter ligand selenium-selenium interactions could be operational (Se1-Se2 3.297 Å; van der Waals radius of selenium is 1.90 Å). The possibility of such interaction suggest their role in the stabilization of the trigonal-prismatic geometry instead of the octahedral one³³. Compound **2** possesses the cve count of 54 which is four electron more than the trinuclear complex [Co₃(μ-SEt)₃(PEt₃)₃][BPh₄]³² and

satisfies the 18 electron count around each metal centre. Similar to **1**, the HOMO-1 of **2** shows that d_{z^2} orbitals of three Ta atoms are delocalized over three Ta atoms to form the Ta_3 triangular framework (Fig. 3). The energy gap of 2.45 eV between HOMO and LUMO of **2** points to the stability of such cluster.

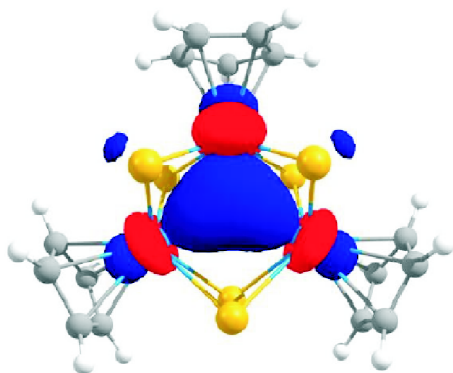


Fig. 3. HOMO-1 of compound **2** (three d_{z^2} orbitals of Ta atoms are delocalized).

Conclusions

The synthesis of incomplete cubane-type cluster containing heavier chalcogen atom i.e. selenium, provides a viable synthetic route for the heavier chalcogen incorporated metalla-heteroborane clusters, and shows promise as a general synthetic strategy. The boron atom in cluster **1** contains an $OBuCl$ unit which is unique in nature and gives extra stability to this hypoelectronic cluster. On the other hand, the tantalum-selenide cluster, **2** possesses interligand selenium-selenium interactions which play a role in the stabilization of the trigonal-prismatic geometry. Thus, the discovery of this type of cluster may open the entry for the synthesis of other chalcogen-rich clusters containing group 5 transition metals.

Acknowledgements

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