Inorganic Chemistry
COMMUNICATION
pubs.acs.org/IC

A Homometallic Tricapped Cubane Cluster: $[(Cp^*Mo)_4B_4H_4(\mu_4\text{-}BH)_3]$ $(Cp^* = \eta^5\text{-}C_5Me_5)$

Arunabha Thakur, Satyanarayan Sahoo, and Sundargopal Ghosh*

Department of Chemistry, Indian Institute of Technology Madras, Chennai 600 036, India

S *Supporting Information*

ABSTRACT: The reaction of $[Cp^*MoCl_4]$ with an excess of $LiBH_4$, followed by thermolysis with tellurium powder in toluene, afforded a tricapped cubane cluster, $[(Cp^*Mo)_4B_4H_4(\mu_4\text{-}BH)_3]$ (**1**), which represents an unprecedented metal-rich metallaborane cluster with a cubane core containing 58 cluster valence electrons (cve) and three metal−metal bonds.

In the past several years, a number of compounds containing cubic or distorted-cubic M_8 or M_4E_4 (M = transition metal; E = main-group elements) geometries have been encountered, in which some or all of the faces are capped by main-group element fragments.[1−5] Cubane clusters containing an M_4E_4 core are known to have different types of structures, especially with respect to the M−M bonding of the cubane core.[6] We recently described a simple method for the preparation of sulfur- and selenium-containing cubane clusters, $[(Cp^*Mo)_2(\mu_3\text{-}E)_2B_2H(\mu\text{-}H)\{Fe(CO)_2\}_2Fe(CO)_3]$ (**I**, E = S; **II**, E = Se),[7] from the thermolysis of $[(Cp^*Mo)_2B_4E_2]$ (E = S, Se) in the presence of $Fe_2(CO)_9$ at elevated temperature. In a similar fashion, the reaction of a yellow solution of *arachno*-$[(Cp^*RuCO)_2B_2H_6]$ with an excess of $Fe_2(CO)_9$ resulted in the formation of a heterometallic cubane cluster, $[(Cp^*Ru)_2(\mu_3\text{-}CO)_2B_2H(\mu\text{-}H)\{Fe(CO)_2\}_2Fe(CO)_3]$ (**III**), similar to the structures of **I** and **II**.[7]

Cubane is a quite popular shape, especially for combinations of heterometal and main-group elements.[8] Structurally characterized metallaheteroboranes containing group 16 elements, in particular tellurium, are very rare. Therefore, our efforts to incorporate main-group elements, in particular, heavier elements into transition metal cubane clusters have recently been focused on the Te atom. Thus, the reactions of different chalcogen sources containing Te atoms, e.g., tellurium powder, Ph_2Te_2, etc., were performed with an intermediate, generated from the reaction of $[Cp^*MoCl_4]$ with $LiBH_4$ at low temperature.[9] Although the objective of incorporating a Te atom into a molybdaborane cluster was not achieved, an interesting cubane cluster has been generated. We report herein the synthesis and structural characterization of a novel metal-rich molybdaborane cluster, $[(Cp^*Mo)_4B_4H_4(\mu_4\text{-}BH)_3]$ (**1**), with a Mo_4B_4 distorted-cubane core.

The geometry of **1** can be viewed as a cubane made of four Mo and four B atoms, and out of the six square faces of the cubane, three of them are capped by BH units to build the $[(Cp^*Mo)_4B_7H_7]$ core (Figure 1).[10] The capping on the other three sites is hindered by the metal−metal bonds. The X-ray diffraction study of a single crystal of **1** shows that the Mo_4B_4 core is highly distorted. Three Mo−Mo bond distances (Mo1−Mo3, Mo2−Mo4, and Mo2−Mo3) are much shorter [2.6508(9)−2.8475(10) Å] than the other three [3.1869(9)−3.2038(10) Å]. The longer Mo−Mo distances correspond to the absence of intermolybdenum bonds. Among the three Mo−Mo bonds in **1**, two of them are significantly shorter (0.2 Å) than the corresponding bond distances in other single- and double-cubane clusters.[11] Alternatively, the observed geometry of **1** can be viewed as a tetracapped tetrahedron in which four Mo atoms define a pseudo-tetrahedron. The triangular faces of this pseudo-tetrahedron are capped by B1, B3, B4, and B6 atoms and three of the six resulting square faces, Mo1−B1−Mo2−B3, Mo1−B3−Mo4−B6, and Mo4−B4−Mo3−B6, being capped by B2, B7, and B5 atoms, respectively. All of the Mo−B and B−B distances are in the normal range like other molybdaborane clusters.[12] This localization of the Mo−Mo bonds renders the top four-membered ring of Mo_2B_2 and the bottom one twisted with respect to each other by ca. 21°. In this way, the Mo3−B6−Mo1 bond angle of the cube is distorted (69.71°). Interestingly, the top and bottom four-membered rings of Mo_2B_2 are nearly planar (dihedral angle 0.24°).

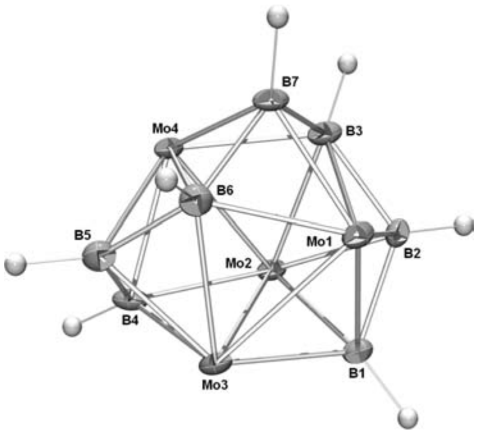
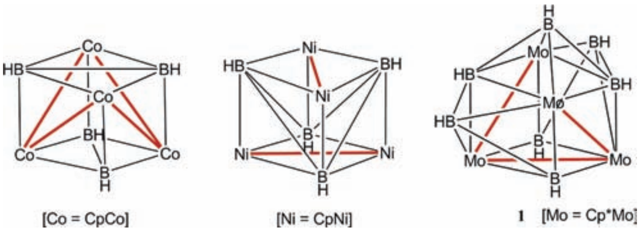


Figure 1. Molecular structure of **1**. Thermal ellipsoids are shown at the 40% probability level. Cp* are omitted for clarity. Selected bond lengths (Å) and angles (deg): Mo1−Mo3 2.6599(10), Mo2−Mo4 2.6508(9), Mo2−Mo3 2.8475(10), Mo1−B1 2.220(9), Mo1−B2 2.136(11), Mo1−B3 2.309(10), Mo2−B2 2.1589(9); Mo3−B6−Mo1 69.71(11).

The spectroscopic data of **1** are fully consistent with the solid-state structure. The IR spectrum of **1** features strong bands at 2490 and 2471 cm^{-1} due to terminal B−H stretches. The molecular ion peak in the fast atom bombardment mass spectrometry (FAB MS) spectrum corresponds to $[(Cp^*Mo)_4B_4H_4(\mu_4\text{-}BH)_3]$

Received: June 4, 2011
Published: August 11, 2011

Chart 1. Homometallic Cubane-Type Metallaborane Clusters



1

Table 1. Selected Structural Parameters of Homo- and Heterometallic Cubane-Type Clusters

clusters	cve	sep	avg *d* (M−M)	no. of M−M bonds	ref
$[(Cp)_4Ni_4B_4H_4]$	68	10	2.35	2	16
$[(Cp)_4Co_4B_4H_4]$	64	8	2.47	4	17
1	58	5	2.71	3	this work
I	60	6		6	7
II	60	6	2.92	6	7
III	60	6	2.72	6	7
IV	60	6	2.74	6	21

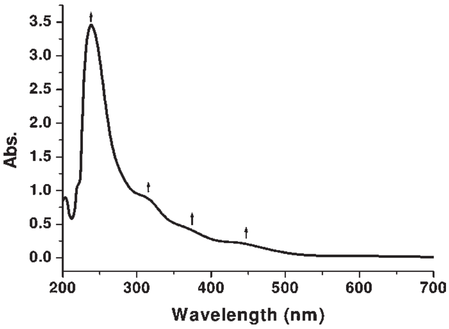


Figure 2. UV−vis spectra of compound **1** in CH_2Cl_2 (10^{-3} M).

Table 2. UV−Vis Spectra of 1 and Analogous Cubane Clusters

compound	λ_{max}, nm (log ε)	ref
$[(CpNi)_4B_4H_4]$	543 (4.54), 423 (4.43), 335 (4.69), 284 (4.72)	16
$[(CpNi)_4B_5H_5]$	548 (2.84), 365 (3.99), 302 (4.35), 257 (4.45)	16
1	440 (2.58), 367 (2.95), 315 (2.67), 239 (3.54)	this work
$[(Cp^*Cr(\mu\text{-}O)]_4$	596	28
$[(MeCp)_4Mo_4S_4]$	520	6

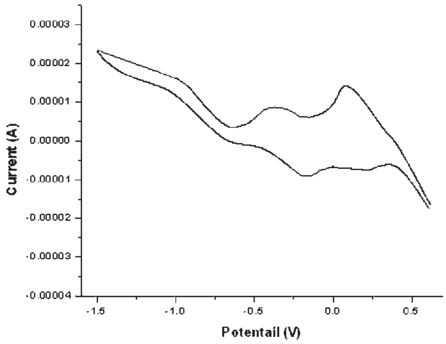


Figure 3. Cyclic voltammetry of compound **1** in CH_2Cl_2/CH_3CN (8.5:1.5, v/v).

showing the isotopic distribution for four Mo and seven B atoms. Consistent with the X-ray results, the ^{11}B NMR spectrum of **1** rationalizes the presence of seven B atoms in the ratio of 2:2:3. The $^{11}B\{^1H\}$ NMR spectrum of **1** features one downfield resonance at δ 131.5, accounting for two five-coordinated B atoms, and the chemical shift at δ 94.4 has been assigned to four-coordinated B atoms situated on the opposite face of the cubane. The ^{1}H NMR spectrum of **1** shows two different singlets for the Cp* fragments each appearing at δ 2.14 and 1.58 in the ratio of 1:1. The presence of these peaks was further confirmed by ^{13}C NMR spectra.

Homometallic cubane clusters containing chalcogen elements are well documented in the literature;[13−15] however, up until now, only two homometallic cubane clusters containing boron as a main-group element are known in the literature[16,17] (Chart 1). Note that metal-rich molybdaboranes are very rare; all the structurally characterized molybdaboranes reported previously contain one or two metal atoms.[18]

Although the qualitative shape of cluster **1** is similar to those of the other cubane-type clusters, listed in Table 1, the M−M bond distances reveal changes in the cluster electronic structure accompanying the addition and loss of electrons.[19] Kennedy[20] described $[(CpNi)_4B_4H_4]$[16] and $[(CpCo)_4B_4H_4]$[17] as 68- and 64-electron clusters with two and four metal−metal bonds. Further, he suggested that the putative $[(CpFe)_4B_4H_4]$ cluster with 60 electrons should exhibit a cubane structure with six Fe−Fe bonds and a fully bonded metal tetrahedron. Interestingly, metallaboranes **I**−**III** and $[(Cp^*Ru)_3(\mu_3\text{-}CO)Co(CO)_2B_3H_3]$ (**IV**),[21] which connect these clusters, have 60 cluster valence electrons (cve 6) and six M−M bonds. A shortening of the M−M bonds and high distortion of the Mo_4 core from regular T_d symmetry are observed with deviation from the expected cluster valence electron number (60 cve).[22] Compound **1** has five skeleton electron pairs (sep), two electrons fewer for the structure based on a tetrahedron, whereas other heterometallic cubane-type clusters, **I**−**IV**, contain six sep's, indicating that structures are based on the tetrahedron geometry.

Usually, the lower number of valence electrons and the higher metal orbital energies of the group 6 Cp*M fragments lead to the observation of electronic unsaturation in the cluster-bonding network.[23,24] The low-electron-count Cp*Mo fragment induces the borane fragments to compensate by adopting a highly capped structure.

The electronic spectrum of compound **1** in the visible region (measured in a CH_2Cl_2 solution) is shown in Figure 2. In essence, there is a single absorption band at 239 nm (ε = 3500), with indications of several weaker bands at lower energy. The pattern of this spectrum is very similar to the homometallic metallaborane cubane cluster, $[(CpNi)_4B_4H_4]$. As shown in Table 2, the higher intensity band at 239 nm has been blue-shifted by 45 nm on going from $[(CpNi)_4B_4H_4]$ to compound **1**. This may be due to the presence of the $\{\eta\text{-}C_5(CH_3)_5\}$ ligand, which generally produces a stronger ligand field than the $\{\eta\text{-}C_5H_5\}$ ligand.[25] The high-energy band at 239 nm may be attributed to the ligand (B atoms in the cubane core) to metal charge-transfer (LMCT) transition, whereas the lower energy bands at 367 and 315 nm may be assigned to the LMCT (capped B) transition.

In order to evaluate the redox properties, cyclic voltammetry experiments of cluster **1** were carried out as shown in Figure 3.[26] Cluster **1** underwent one quasi-reversible redox along with one reversible redox process, which is a manifestation of the delocalized nature of the metal electrons in the species. For a scan from -1.6 to 0.6 V at 50 mV s^{-1}, the $\mathbf{1}^0/\mathbf{1}^+$ couple is found at $E_{1/2}$ = 0.16 V (E_a = 0.097 V and E_c = 0.213 V) and the difference in the half-wave potentials for $\mathbf{1}^0/\mathbf{1}^+$ and $\mathbf{1}^+/\mathbf{1}^{2+}$ is 0.55 V.

In conclusion, cluster **1** is the first example of a novel class of homometallic cuboidal metallaborane clusters having group 13 atoms (three BH units) as capping units. The electronic structure and alternative interpretation of the electron counts of cluster **1** will be described in the full paper. Furthermore, the systematic reactivity studies along with the full mechanistic details of this new chemistry and that of the new metal-rich molybdaborane with capped cubane geometry will be forthcoming.

■ ASSOCIATED CONTENT

Supporting Information. Supplementary crystallographic data and X-ray crystallographic file for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: sghosh@iitm.ac.in.

■ ACKNOWLEDGMENT

Generous support of the Department of Science and Technology, DST (Grant SR/S1/IC-19/2006), New Delhi, India, is gratefully acknowledged. We also thank Mass lab, SAIF, CDRI, Lucknow, India, for FAB MS analysis. A.T. thanks the Council of Scientific and Industrial Research (CSIR) India for senior research fellowships.

■ REFERENCES

(1) (a) Lower, L. D.; Dahl, L. F. *J. Am. Chem. Soc.* **1976**, *98*, 5046. (b) Fenske, D.; Basoglu, R.; Hachgenei, J.; Rogel, F. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 160.

(2) Fenske, D.; Krautscheid, H.; Müller, M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 321.

(3) (a) Fenske, D.; Ohmer, J.; Hachgenei, J.; Merzweiler, K. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1277. (b) Fenske, D.; Hachgenei, J.; Rogel, F. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 982.

(4) (a) Pohl, S.; Opitz, U. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 863. (b) Pohl, S.; Barklage, W.; Saak, W.; Opitz, U. *J. Chem. Soc., Chem. Commun.* **1993**, 1251.

(5) (a) Junghans, C.; Saak, W.; Pohl, S. *J. Chem. Soc., Chem. Commun.* **1994**, 2327. (b) Pohl, S.; Saak, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 907.

(6) Williams, P. D.; Curtis, M. D. *Inorg. Chem.* **1986**, *25*, 4562.

(7) Geetharani, K.; Bose, S. K.; Sahoo, S.; Ghosh, S. *Angew. Chem.* **2011**, *123*, 3994.

(8) Hernndez-Molina, R.; Sykes, A. G. *Coord. Chem. Rev.* **1999**, *187*, 291.

(9) Synthesis of **1**: To [Cp*MoCl$_4$] was added at -40 °C (0.5 g, 1.34 mmol) in 20 mL of toluene a 6-fold excess of LiBH$_4$·THF (4.03 mL, 8.05 mmol). The mixture was stirred at room temperature for 1 h. After removal of toluene, the residue was extracted with hexane. The extract was filtered through a frit using Celite. The yellowish-green hexane extract was dried under vacuum and taken in 25 mL of toluene. The resulting solution was heated at 100 °C with a 6-fold excess of tellurium powder (1.03 g, 8.05 mmol) for 30 h. The solvent was evaporated in vacuo, and the residue was extracted with hexane. The residue was subjected to chromatographic workup using silica gel thin-layer chromatography (TLC) plates. Elution with hexane/CH_2Cl_2 (95:5, v/v) yielded orange [(η^5-$C_5Me_5Mo)_2B_5H_9$] (0.18 g, 25%) and [(η^5-$C_5Me_5Mo)_2B_4H_4Te_2$] (0.12 g, 15%) and green [(η^5-$C_5Me_5Mo)_4B_4H_4$-(μ_4-BH)$_3$] (**1**; 0.04 g, 8%). MS (FAB) P$^+$(max): *m*/*z* (%) 1007 (isotopic pattern for four Mo and seven B atoms). ^{11}B NMR (400 MHz, benzene-*d*$_6$, 22 °C): δ 131.5 (br, 2B), 94.5 (br, 2B), 58.8 (br, 3B). ^{1}H NMR (400 MHz, benzene-*d*$_6$, 22 °C): δ 9.92 [partially collapsed quartet (pcq), 2BH$_t$], 8.93 (pcq, 2BH$_t$), 6.12 (pcq, 3BH$_t$), 2.14 (s, 15H, Cp*), 1.58 (s, 15H, Cp*). ^{13}C NMR (400 MHz, benzene-*d*$_6$, 22 °C): δ 105.8 (s, η^5-C_5Me$_5$), 103.4 (s, η^5-C_5Me$_5$), 14.0 (s, η^5-C$_5$*Me*$_5$), 12.6 (s, η^5-C$_5$*Me*$_5$). IR (hexane, cm^{-1}): 2490w, 2471m (B-H$_t$).

(10) Suitable crystals of **1** were obtained from a hexane/CH_2Cl_2 (9:1) mixture at -10 °C. The crystal data were collected and integrated using a Bruker AXS Kappa Apex2 CCD diffractometer system equipped with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) radiation at 150 K. The structures were solved by heavy-atom methods using *SHELXS-97*[27] and refined using *SHELXL-97* (Sheldrick, G. M., University of Göttingen, Göttingen, Germany). Crystal data for **1**: formula, $C_{40}H_{67}B_7Mo_4$; fw, 1007.37 g mol^{-1}; crystal system, space group triclinic, $P\bar{1}$. Unit cell dimensions, a = 11.2490(7) Å, b = 11.9772(8) Å, c = 18.7277(12) Å, α = 77.172(3)°, β = 86.647(3)°, γ = 87.738(3)°; Z = 2. Final R indices [$I > 2\sigma(I)$]. R1 = 0.0624, wR2 = 0.1791. Density (calcd) = 1.363 Mg m^{-3}. Reflections collected 26 189, independent reflections 8424 [R_{int} = 0.0524], GOF on F^2 = 1.111.

(11) (a) Feliz, M.; Guillamón, E.; Llusar, R.; Vicent, C.; Stiriba, S. E.; Pérez-Pireto, J.; Barberis, M. *Chem.—Eur. J.* **2006**, *12*, 1486. (b) Curtis, M. D.; Riaz, U.; Curnow, O. J.; Kampf, J. W.; Rheingold, A. L.; Haggerty, B. S. *Organometallics* **1995**, *14*, 5337.

(12) Weller, A. S.; Shang, M.; Fehlner, T. P. *J. Am. Chem. Soc.* **1998**, *120*, 8283.

(13) Trinh, T.; Teo, B. K.; Ferguson, J. A.; Meyer, T. J.; Dahl, L. F. *J. Am. Chem. Soc.* **1977**, *99*, 408.

(14) (a) Houser, E. J.; Amarasekera, J.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1991**, *113*, 7440. (b) Houser, E. J.; Rauchfuss, T. B.; Wilson, S. R. *Inorg. Chem.* **1993**, *32*, 4069.

(15) Inomata, S.; Tobita, H.; Ogino, H. *J. Am. Chem. Soc.* **1990**, *112*, 6145.

(16) Bowser, J. R.; Bonny, A.; Pipal, J. R.; Grimes, R. N. *J. Am. Chem. Soc.* **1979**, *101*, 6229.

(17) Pipal, J. R.; Grimes, R. N. *Inorg. Chem.* **1979**, *18*, 257.

(18) (a) Aldridge, S.; Shang, M.; Fehlner, T. P. *J. Am. Chem. Soc.* **1997**, *119*, 2339. (b) Sahoo, S.; Dhayal, R. S.; Varghese, B.; Ghosh, S. *Organometallics* **2009**, *28*, 1586. (c) Green, M. L. H.; Leach, J. B.; Kelland, M. A. *J. Organomet. Chem.* **2005**, *690*, 4203.

(19) Fehlner, T. P.; Halet, J.-F.; Saillard, J.-Y. Molecular Clusters. *A Bridge to Solid-State Chemistry*; Cambridge University Press: Cambridge, U.K., 2007.

(20) Kennedy, J. D. *Prog. Inorg. Chem.* **1984**, *34*, 211.

(21) Lei, X.; Shang, M.; Fehlner, T. P. *Organometallics* **2000**, *19*, 4429.

(22) Burdett, J. K.; Miller, G. J. *J. Am. Chem. Soc.* **1987**, *109*, 4081.

(23) Bandy, J. A.; Davies, C. E.; Green, J. C.; Green, M. L. H.; Prout, K.; Rodgers, D. P. S. *J. Chem. Soc., Chem. Commun.* **1983**, 1395.

(24) Aldridge, S.; Shang, M.; Fehlner, T. P. *J. Am. Chem. Soc.* **1997**, *119*, 11120.

(25) Maitlis, P. M. *Acc. Chem. Res.* **1978**, *11*, 301.

(26) The cyclic voltammetry of cluster **1** was carried out in CH_2Cl_2/CH_3CN (8.5:1.5, v/v) using a platinum working electrode, a platinum wire counter electrode, a Ag/Ag$^+$ reference electrode, and a 0.1 M Bu$_4$NPF$_6$ supporting electrolyte. Under these conditions, the ferrocene/ferrocenium ion couple appeared at 0.45 V.

(27) Sheldrick, G. M. *SHELXS-97* and *SHELXL-97*; University of Göttingen, Göttingen, Germany, 1997.

(28) Bottomley, F.; Chen, J.; MacIntosh, S. M. *Organometallics* **1991**, *10*, 906.