Angewandte
Chemie

Cluster Compounds

Synthesis and Characterization of the Nitrogen-Centered Trigonal Prismatic Clusters $[W_6NCl_{18}]^{n-}$ ($n = 1$–3)**

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The extraordinarily rich chemistry of octahedral transition metal halide and chalcohalide clusters has begun to see use in a variety of applications, ranging from catalysis to chemical sensing.[1] In facilitating the design of such cluster-based materials, new synthetic methods for adjusting the core electronic character by atom substitution and for exchanging the six outer terminal ligands are of considerable value.[2] However, the prospect of utilizing a wholly different type of cluster unit arose very recently with the discovery of the molecular species $[W_6CCl_{18}]^{n-}$ ($n = 0$–3).[3] Instead of an octahedron, these clusters feature a carbon-centered W_6 trigonal prism surrounded by twelve edge-bridging chloride anions and six radially extended terminal chloride ligands. Such units are also known to exist within the one-dimensional compounds $A_3Nb_6SBr_{17}$ (A = K, Rb, Cs, and Tl),[4] suggesting that this trigonal-prism structure type may be quite pervasive. Noting that the electronic character of the centered, edge-bridged octahedral clusters $[Zr_6ZCl_{18}]^{n-}$ is highly dependent upon the interstitial atom Z, we attempted to replace the carbon atom in $[W_6CCl_{18}]^{2-}$ with other atoms.[5] Herein, we report the introduction of an interstitial nitrogen atom, which permits ready access to more electron-rich trigonal prismatic clusters.

Synthesis of the molecular salt $Na[W_6NCl_{18}]$ (**1**) parallels the low-temperature solid-state process employed for producing the original carbon-centered cluster phase,[3b] although with NaN_3 used in place of CCl_4. Elemental bismuth is known to be highly effective as a reducing agent in the formation of clusters such as $[W_6Cl_{14}]^{2-}$ and $[W_6O_{12}Cl_{12}]^{2-}$,[6] and is thought to act here according to reaction (1). A stoichiometric

$$6\,WCl_6 + NaN_3 + 6\,Bi \rightarrow Na[W_6NCl_{18}] + 6\,BiCl_3 + N_2 \qquad (1)$$

mixture of the reactants was sealed in an evacuated pyrex ampule and heated at 500 °C for 3 days. Bismuth chloride was then removed by sublimation, which left a black solid containing hexagonal plate-shaped crystals of **1**. Reactions performed with less or more than one equivalent of NaN_3 resulted in lower yields of **1**.

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[**] This research was funded by DOE Grant No. DE-FG03–01ER15257.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

DOI: 10.1002/ange.200462585

X-ray crystallographic analysis[7] of **1** revealed the $[W_6NCl_{18}]^{1-}$ cluster (Figure 1), which has a structure fully analogous to that of the isoelectronic species $[W_6CCl_{18}]^{2-}$. The central $\{W_6N\}$ unit in the cluster is reminiscent of a fragment of WN, consisting of a nitrogen atom surrounded by a regular trigonal prism of tungsten atoms. The W–N bond length of 2.1682(4) Å in the cluster is very similar to the 2.188 Å bond length in WN,[8] but the latter possesses a trigonally compressed W_6 trigonal prism. Thus, the cluster exhibits a shorter $W\cdots W^{\Delta}$ distance of 2.6518(6) Å within the W_3 triangles and a longer $W\cdots W^{|}$ distance of 3.0705(7) Å along the remaining edges, while the corresponding bond lengths in WN are $W-W^{\Delta} = 2.893$ and $W-W^{|} = 2.826$ Å.[8] Note that these bond lengths are all somewhat longer than the W–W single bond distance of 2.607(4) Å observed in the face-capped octahedral cluster $[W_6Cl_{14}]^{2-}$.[9] The $\{W_6N\}$ unit in the cluster is surrounded by 18 chlorine atoms in a manner that preserves the D_{3h} symmetry, with one Cl atom bridging each triangular edge of the prism, two bridging each of the other edges, and one extending radially from each vertex. Interestingly, the structure of **1** is isotypic with that of W_6CCl_{18},[3a] featuring a hexagonal close packing of the clusters, but with Na^+ ions occupying the octahedral holes. Accordingly, compound **1** represents an expanded form of the NiAs structure.

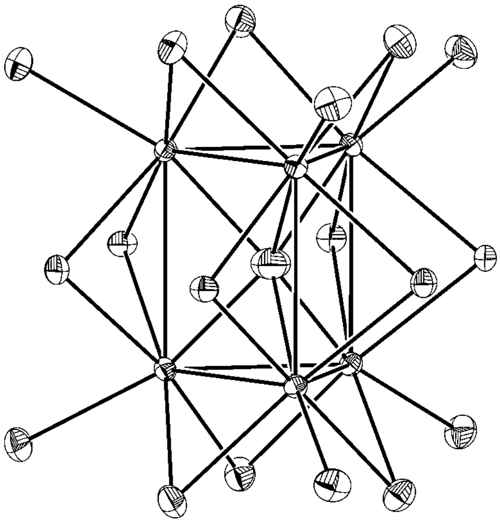

Figure 1. Structure of the nitrogen-centered trigonal prismatic cluster $[W_6NCl_{18}]^{1-}$ in **1**, with ellipsoids drawn at the 75% probability level. The lines connecting the W atoms are intended to emphasize the W_6 trigonal prism and do not necessarily represent full single bonds.[5b] Selected mean interatomic lengths [Å] and angles [°] for the $[W_6NCl_{18}]^{n-}$ ($n = 1$–3) clusters in **1**, **2′**, and **3′**, respectively (Δ = triangle edge, | = longer rectangle edge, b = bridging, t = terminal): $W\text{-}W^{\Delta}$ 2.6518, 2.67(1), 2.69(6); $W\text{-}W^{|}$ 3.0705, 3.07(1), 3.0(1); W-N 2.1682, 2.173(7), 2.16(2); $W\text{-}Cl^{b\Delta}$ 2.382(1), 2.397(5), 2.408(13); $W\text{-}Cl^{b|}$ 2.448(3), 2.453(15), 2.46(2); $W\text{-}Cl^{t}$ 2.409, 2.416(6), 2.440(8); $W\text{-}N\text{-}W^{\Delta}$ 75.39, 75(2), 77(2); $W\text{-}N\text{-}W^{|}$ 90.18, 89.8(7), 88(6); $W\text{-}Cl^{b\Delta}\text{-}W$ 67.62, 67.6(4), 69(2); $W\text{-}Cl^{b|}\text{-}W$ 77.63(12), 77.4(2), 75(3). For comparison, the corresponding mean bond lengths [Å] for the $[W_6CCl_{18}]^{2-}$ cluster in $(Bu_4N)_2[W_6CCl_{18}]$ are: $W\text{-}W^{\Delta}$ 2.667, $W\text{-}W^{|}$ 3.028, W-C 2.1595, $W\text{-}Cl^{b\Delta}$ 2.381(5), $W\text{-}Cl^{b|}$ 2.4585(5), $W\text{-}Cl^{t}$ 2.443.[3b]

Compound **1** is soluble in dilute HCl; however, the cluster undergoes a spontaneous one-electron reduction on work up, ultimately leading to formation of $(Bu_4N)_2[W_6NCl_{18}]$ (**2**). This behavior is consistent with the cyclic voltammogram of **2** in *N,N*-dimethylformamide (DMF), which displays a readily accessible $[W_6NCl_{18}]^{1-}/[W_6NCl_{18}]^{2-}$ couple at $E_{1/2} = 0.097$ V ($\Delta E_p = 63$ mV) versus the ferrocene/ferrocenium couple (Fc/Fc^+; Figure 2). Two further reduction events that correspond to a $[W_6NCl_{18}]^{2-}/[W_6NCl_{18}]^{3-}$ couple at $E_{1/2} = -0.527$ V ($\Delta E_p = 72$ mV) and a quasireversible $[W_6NCl_{18}]^{3-}/[W_6NCl_{18}]^{4-}$ couple at $E_{1/2} = -1.800$ V ($\Delta E_p = 152$ mV) are also apparent. Four additional peaks appear upon sweeping the potential past −1.8 V (as designated by circles in Figure 2). Presumably, these new smaller features are associated with the redox couples of cluster species wherein DMF has replaced one or more of the terminal chloride ligands, a process that should become more facile upon formation of $[W_6NCl_{18}]^{4-}$. In sum, the cyclic voltammetry results indicate that clusters with 24–27 $\{W_6N\}$-based valence electrons are chemically accessible. For comparison, the cyclic voltammogram of $(Bu_4N)_2[W_6CCl_{18}]$ in DMF shows four redox couples at $E_{1/2} = +0.974$, +0.407, −0.649, and −1.360 V versus Fc/Fc^+, indicating the accessibility of clusters having 22–26 $\{W_6C\}$-based valence electrons.[3b,10] Thus, the replacement of a carbon atom with a nitrogen atom in the cluster leads to significant stabilization of the species with higher electron counts, with the 24/25- and 25/26-electron couples shifting by +0.746 and +0.833 V, respectively.

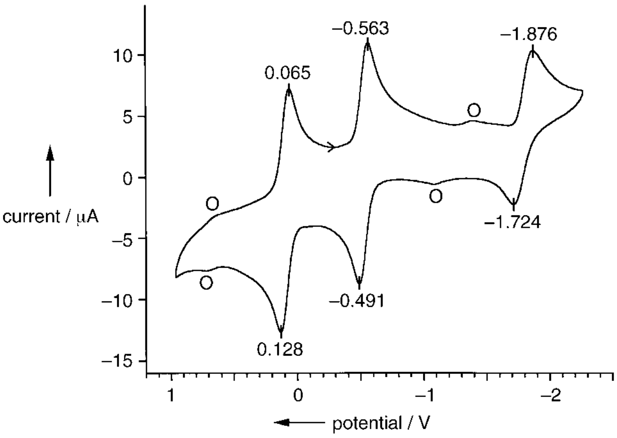

Figure 2. Cyclic voltammogram of **2** in DMF with potentials referenced to Fc/Fc^+. The measurements were performed on a platinum electrode at a scan rate of 100 mV s^{-1} with Bu_4NPF_6 (0.1 M) as the supporting electrolyte. Features marked with a circle appear only after the potential has been swept through the outermost couple on the right-hand side.

DFT calculations[11] were performed on $[W_6NCl_{18}]^-$ to assess how these changes in electron count affect the electronic structure of the cluster (Figure 3). The results are consistent with the rich electrochemistry of $[W_6NCl_{18}]^-$ and indicate closely spaced frontier orbitals, with a HOMO–LUMO gap of 0.70 eV. The a_2'' HOMO is tungsten based, with bonding character within the two W_3 triangles and antibond-

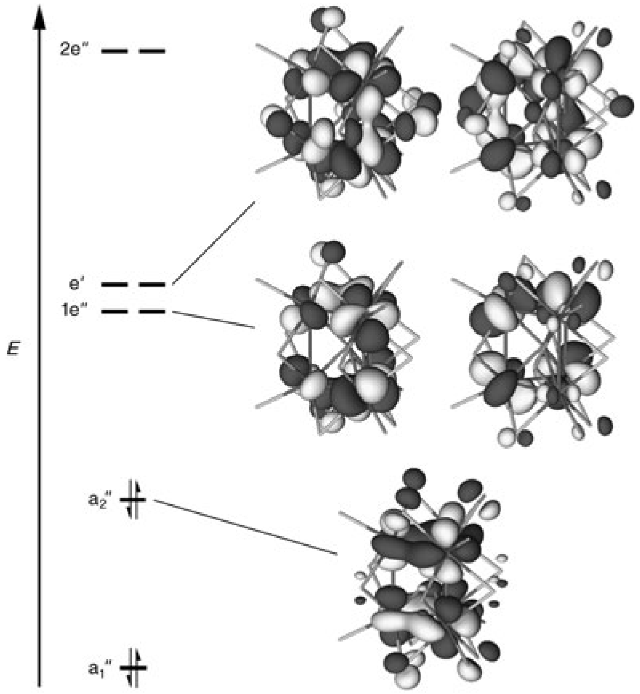

Figure 3. Frontier portion of the energy level diagram calculated for $[W_6NCl_{18}]^-$ along with depictions of selected molecular orbitals. Distortions observed in one- and two-electron-reduced clusters indicate that the added electrons populate the left-hand e′ orbital.

ing character between the triangles. The lowest unoccupied orbitals 1e″ and e′ are also mainly tungsten based and again feature a mixture of bonding and antibonding character. It is difficult to predict which one of these two pairs of orbitals would most readily accept an electron as they have an energy separation of just 0.099 eV; however, in either case a distortion away from the D_{3h} symmetry should occur upon reduction of the cluster by one electron. Depending upon the spin-pairing energy, further reduction by a second electron can then be expected either to amplify the distortion or give rise to a triplet ground state with reversion to the D_{3h} symmetry.

Crystallization of $(Bu_4N)[(Ph_3P)_2N][W_6NCl_{18}]$ (**2′**) afforded a structure[7] in which the 25-electron cluster $[W_6NCl_{18}]^{2-}$ exhibited no crystallographically imposed symmetry, thereby revealing the effects of the Jahn–Teller distortion. Most notably, two tungsten atoms are pinched together to give a shorter W···W$^{|}$ distance (3.0518(6) Å) relative to the structure of the 24-electron cluster. Furthermore, this shortened, right-hand edge of the trigonal prism is pulled slightly away from the opposing W_4 rectangle, thus resulting in longer W···W$^{\Delta}$ distances in the range 2.6585(6)–2.6835(6) Å (Figure 4b). The resultant structure has an approximate C_{2v} symmetry and is most consistent with population of the left-hand e′ orbital displayed in Figure 3. Although the magnitude of the distortion is somewhat less than that observed for the isoelectronic cluster $[W_6CCl_{18}]^{3-}$,[3b] it is comparable to that observed for octahedral Mo_6 and Re_6 clusters.[12]

Reduction of **2** with one equivalent of cobaltocene affords $(Bu_4N)_2(Cp_2Co)[W_6NCl_{18}]$ (**3**; Cp = cyclopentadienyl), which contains $[W_6NCl_{18}]^{3-}$, the first 26-electron cluster of its type. Subsequent crystallization as $(Bu_4N)_3[W_6NCl_{18}]\cdot MeCN$ (**3′**) gave a triclinic structure, in which the cluster geometry is again unconstrained by the symmetry of the crystal. The central $\{W_6N\}$ unit now exhibits a much more substantial form of the same distortion (Figure 4c). The two outermost tungsten atoms on the right-hand side are pinched together to give a short W···W$^{|}$ distance of 2.803(1) Å and are pulled away from the opposing $\{W_4\}$ rectangle to give elongated W···W$^{\Delta}$ distances in the range 2.730(1)–2.740(1) Å. Furthermore, a slight compression is evident in two edges of the opposing rectangle, thus resulting in shorter W···W$^{\Delta}$ distances of 2.592(1) and 2.606(1) Å. The overall nature of the distortion indicates pairing of the two added electrons in the left-hand e′ orbital in Figure 3, which is consistent with the observed diamagnetism of compound **3**. Interestingly, as the cluster is reduced and the average oxidation state of the tungsten centers changes from +3.33 to +3.17 to +3.00, the W···W$^{\Delta}$ and W···W$^{|}$ distances become more similar to (but certainly not identical to) the corresponding distances in WN (2.893 and 2.826 Å, respectively).[8]

Attempts to incorporate other transition metals and other interstitial atoms into trigonal prismatic clusters are currently underway. In particular, we are targeting fragments of solids, such as MoP and RuC, wherein the main group atoms are known to display a trigonal prismatic coordination geometry. Further efforts are directed toward exploring the ligand substitution chemistry of these clusters and developing solution-based methods for incorporating them within extended-framework materials.

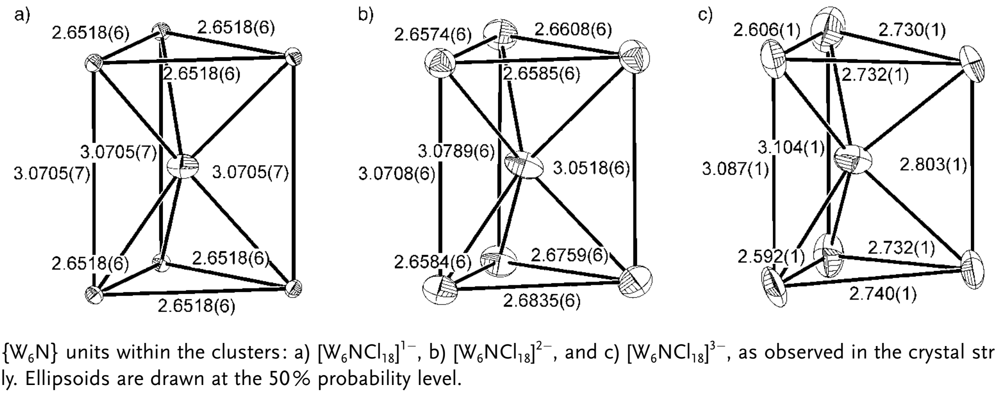

Figure 4. Central $\{W_6N\}$ units within the clusters: a) $[W_6NCl_{18}]^{1-}$, b) $[W_6NCl_{18}]^{2-}$, and c) $[W_6NCl_{18}]^{3-}$, as observed in the crystal structures of **1**, **2′**, and **3′**, respectively. Ellipsoids are drawn at the 50% probability level.

Experimental Section

Dark-blue WCl_6 (99.9+%, Aldrich) was purified prior to use by subliming away the usual impurity of red $[WOCl_4]$ at 140 °C under reduced pressure. The water used was distilled and deionized with a Milli-Q filtering system. Other reagents were used as received. UV/Vis absorption spectra were measured with a Hewlett–Packard 8453 spectrophotometer, and IR spectra were recorded on a Nicolet Avatar 360 FTIR spectrometer equipped with an attenuated total reflectance accessory. Mass-spectrometric measurements were performed in the negative-ion mode on a Micromass Quattro triple quadrapole mass spectrometer equipped with an electrospray ionization source or a Brüker Apex II 7 T actively shielded FTICR mass spectrometer equipped with an analytical electrospray ion source. Magnetic data were collected using a Quantum Design MPMSXL SQUID magnetometer and were corrected for diamagnetic contributions. Electrochemical measurements were conducted with a Bioanalytical Systems CV-50 potentiostat with platinum-disk working, platinum-wire auxiliary, and silver-wire reference electrodes. Samples were measured at a scan rate of $100\,mV\,s^{-1}$ in a supporting electrolyte of 0.1 M Bu_4NPF_6 in DMF. Ferrocene was added after each measurement as an internal reference.

1: A pyrex ampule (i.d. × o.d. × l = 21 × 25 × 260 mm) was loaded with WCl_6 (3.3 g, 8.4 mmol), NaN_3 (0.090 g, 1.4 mmol), and Bi powder (1.8 g, 8.4 mmol) in a nitrogen atmosphere and was then evacuated and sealed. The ampule was positioned in a tube furnace such that the end opposite to the reactants was located at the center of the furnace and elevated at an incline of approximately 30°. The furnace was heated up at a rate of $1\,°C\,min^{-1}$ to 500 °C and maintained at that temperature for 3 days. The ampule was cooled to room temperature and then repositioned with the product-containing end in the center of the furnace. The colorless $BiCl_3$ was sublimed away by heating at 360 °C for 16 h. The remaining black solid contained hexagonal plate-shaped crystals of **1** (2.1 g, 84%), which X-ray powder diffraction studies indicated to be the main crystalline product. Elemental analysis (%) calcd for $Cl_{18}NNaW_6$: C 0.00, H 0.00, N 0.77; found: C < 0.02, H < 0.02, N 0.56.

2: Compound **1** was pulverized and stirred in HCl (0.12 M, 50 mL) for 12 h to give a dark-purple solution. Addition of Bu_4NCl (0.50 g, 1.8 mmol) induced precipitation of an olive-green solid, which was collected by filtration, washed with water (3 × 20 mL), and dried in air. The solid was then stirred in acetonitrile (20 mL), which produced a dark-green solution that was collected by centrifugation and decantation. This process was repeated five times and then the supernatant solutions were combined and reduced to dryness under a stream of nitrogen gas. A solution of Bu_4NCl (0.25 g, 0.90 mmol) in water (30 mL) was added to the residue and the mixture was stirred for 5 min. The ensuing olive-green solid was collected by filtration, washed with water (3 × 20 mL), dried in air, and dissolved in acetonitrile (30 mL). Diffusion of diethyl ether vapor into the solution afforded black, octahedron-shaped crystals of **2**. The supernatant solution was decanted and the crystals were washed with diethyl ether (3 × 20 mL) and dried in air to yield 1.2 g (37%) of product. Absorption spectrum (MeCN): λ_{max} (ε_M) 300 (sh, 17000), 432 (sh, 3060), 607 (sh, 948), 700 (sh, 852), 846 nm (sh, 515); ESMS (MeCN): m/z calcd for $[W_6NCl_{18}]^{2-}$: 877.5687, found: 877.5734; $\mu_{eff} = 1.63\,\mu_B$ at 298 K; elemental analysis (%) calcd for $C_{32}H_{72}Cl_{18}N_3W_6$: C 17.16, H 3.24, N 1.88; found: C 17.31, H 3.42, N 1.84. Plate-shaped crystals of **2′** were obtained by slowly cooling a hot acetonitrile solution (4 mL) of **2** (50 mg, 22 μmol) and $[(Ph_3P)_2N]Cl$ (26 mg, 45 μmol).

3: A solution of cobaltocene (43 mg, 0.23 mmol) in acetonitrile (10 mL) was prepared in a nitrogen atmosphere. An aliquot (2 mL) of this solution was added to a solution of **2** (0.10 g, 0.046 mmol) in acetonitrile (3 mL). Addition of diethyl ether (20 mL) produced a green–brown precipitate, which was collected by centrifugation and decantation, washed with diethyl ether (3 × 10 mL), and dried under a stream of nitrogen gas to yield 88 mg (81%) of product as an olive-green powder. Absorption spectrum (MeCN): λ_{max} (ε_M) 262 (65600), 296 (sh, 15200), 565 (sh, 1810), 819 nm (sh, 497); ESMS: m/z: 877 ($[W_6NCl_{18}]^{2-}$); elemental analysis calcd for $C_{42}H_{82}Cl_{18}CoN_3W_6$: C 20.77, H 3.40, N 1.73; found: C 20.39, H 3.13, N 1.78. Brown needle-shaped crystals of **3′** were obtained by diffusing diethyl ether vapor into a solution of **3** (88 mg) in acetonitrile (4 mL).

Received: November 12, 2004

Keywords: cluster compounds · cyclic voltammetry · metal–metal bonding · nitrides · tungsten

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[7] Crystallographic analyses: **1** ($Cl_{18}NNaW_6$): $T = 160$ K, space group $P6_3/m$, $a = 8.8360(4)$, $c = 17.840(2)$ Å, $V = 1206.24(14)$ Å^3, $Z = 2$, $\rho_{calcd} = 4.896\,g\,cm^{-3}$, $R_1 = 0.0278$, $wR_2 = 0.0703$ for 5253 data (719 independent), 44 parameters, 0 restraints. **2′** ($C_{52}H_{66}Cl_{18}N_3P_2W_6$): $T = 162$ K, space group $P2_1/c$, $a = 21.782(2)$, $b = 14.0432(10)$, $c = 23.266(2)$ Å, $\beta = 100.5410(10)°$, $V = 6996.8(9)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.408\,g\,cm^{-3}$, $R_1 = 0.0420$, $wR_2 = 0.0613$ for 40136 data (14322 independent), 734 parameters, 0 restraints. **3′** ($C_{50}H_{111}Cl_{18}N_5W_6$): $T = 155$ K, space group $P2_1/c$, $a = 18.315(2)$, $b = 23.131(3)$, $c = 18.872(3)$ Å, $\beta = 96.780(2)°$, $V = 7939(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.111\,g\,cm^{-3}$, $R_1 = 0.0691$, $wR_2 = 0.1576$ for 34645 data (13044 independent), 689 parameters, 0 restraints. Data were collected on a Brüker APEX diffractometer using graphite monochromated $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å) radiation and were corrected for Lorentz, polarization, and absorption effects. Structures were solved by direct methods and refined against all data by using SHELXTL 5.0. The structure of **3′** exhibited disorder in the $(Bu_4N)^+$ ions, which was modeled by assigning appropriate peaks of electron density as partially occupied carbon atoms. Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-414409 (**1**). CCDC-250473 and -250472 (**2′** and **3′**) contain the supplementary crystallographic data for this paper. These data can be obtained

free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[10] Note that with just 22 {Nb_6S}-based valence electrons, the trigonal prismatic $Nb_6SBr_{18}{}^{4-}$ units in the one-dimensional compounds $A_3Nb_6SBr_{17}$ (A = K, Rb, Cs, and Tl) also have a lower electron count; see, Ref.[4]

[11] DFT calculations (HCTH407/LANL2DZ) utilized are HPCCG's NWChem, A Computational Chemistry Package for Parallel Computers, version 4.5; PNNL: Richland, WA, **2003**. See the Supporting Information for details.

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