cubic crystals of $C_{60}F_{48}\cdot 2C_6H_3Me_3$ of X-ray quality were grown from the mesitylene solution. A crystal with dimensions $0.3\times 0.3\times 0.2$ mm was investigated on an image-plate diffractometer (IPDS, Stoe) at 180 K (graphite monochromatized $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $2\theta(\max) = 53.5°$). A primitive cubic unit-cell parameter was refined with 1267 reflections to $a = 23.229(3)$ Å, $V = 12534(3)$ Å^3, $Z = 8$. The intensities of 99277 measured reflections were corrected for Lorentz and polarization factors and averaged, yielding 4526 unique reflections. Absorption correction was not applied ($\mu = 2.16$ cm^{-1}). Space group $Pa\bar{3}$ was established on the basis of systematic absences. The structure was solved by direct methods (SHELXS-97) resulting in a raw model with a $C_{60}F_{48}$ molecule on a three-fold axis. However, a high R_1 value (20%) and splitting of some atoms were indicative of disorder. It was found that the duplicate positions of some atoms correspond to an overlap of the R and S configurations of two hemispheres. The different R/S ratios for hemisphere I (83/17) and hemisphere II (56/44) can be interpreted as overlap of $C_{60}F_{48}$ molecules with a noncrystallographic D_3 (R,R' and S,S') and S_6 (R,S' and S,R') point symmetry. In the mixture of two isomers in the single crystals, the estimated content of D_3 is in the range of 39–73%. The final refinement on F^2 with 4331 reflections and 474 parameters was carried out anisotropically for all non-hydrogen atoms (except for the 17% component on hemisphere I and H atoms of mesitylene in calculated positions), and converged to $wR_2 = 0.1589$ and $R_1 = 0.0508$(SHELXL-97).[13] As a result of a different degree of disorder, the positions of C and F atoms belonging to the main component on hemisphere I were determined with better precision (standard deviations 0.003–0.004 Å for C–C and C–F bonds), than for hemisphere II (standard deviations 0.003–0.007 Å) The more reliable values for C–C and C–F bond lengths on hemisphere I were used for comparison with the results of theoretical calculations (Table 1).

The geometry optimization was performed by using density functional theory (DFT) calculations with the PRIRODA program, which employs an economic calculating approach with insignificant loss of accuracy.[14] The PBE exchange-correlation functional[15] and a Gaussian-type basis set of TZ2P quality[14] was used. The validity of our approximations was tested on $C_{60}F_{18}$ and some other fluorocarbons, revealing good accuracy with only slight bond length overestimations (0.01 Å on average).

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$Bi_4Te_4^{4+}$—A Cube-Shaped, Polycationic Main Group Element Cluster**

Johannes Beck,* Michael Dolg, and Stefan Schlüter

Electron-rich main group elements are able to form polycationic clusters. Such ligand-free clusters are known for the halogens chlorine to iodine, for all chalcogens, for bismuth, for cadmium, and for mercury.[1] There are several methods for their synthesis, all of which involve electrophilic and acidic media such as H_2SO_4, HSO_3F, anhydrous HF, molten salts such as Na[$AlCl_4$], or liquid SO_2. The respective elements are oxidized and converted to the polycationic clusters by suitable oxidants such as AsF_5, SbF_5, WCl_6, or $MoOCl_4$, or by an element halide in the presence of a strong halide-ion acceptor such as $AlCl_3$ or $ZrCl_4$. The number of known structure types increases with the atomic mass of the elements. Only three homonuclear cations of sulfur are known and have been structurally characterized, S_4^{2+},[2] S_8^{2+},[3] and S_{19}^{2+}.[4] In contrast, for tellurium more than a dozen ring- or chain-shaped species have been described. The situation is similar for the elements belonging to Group 15. Sb_5^{3+}[5] is poorly characterized; for bismuth, however, a family of cluster ions exists, such as Bi_5^{3+},[6] Bi_8^{2+},[7] Bi_9^{5+},[8] which were isolated as the corresponding chloroaluminates, hexachlorozirconates, and -hafnates, and Bi_5^{+} and Bi_6^{2+}, which were discovered in the structure of the subbromide $Bi_{34}Ir_3Br_{37}$.[9]

Like no other element tellurium is able to form hetereonuclear polycations besides homonuclear molecules. A number of mixed clusters are known containing the lighter chalcogens sulfur and selenium, for example $Te_4Se_3^{2+}$[10] and $Te_3S_3^{2+}$.[11] So far no other mixed polycations apart from Te/Se

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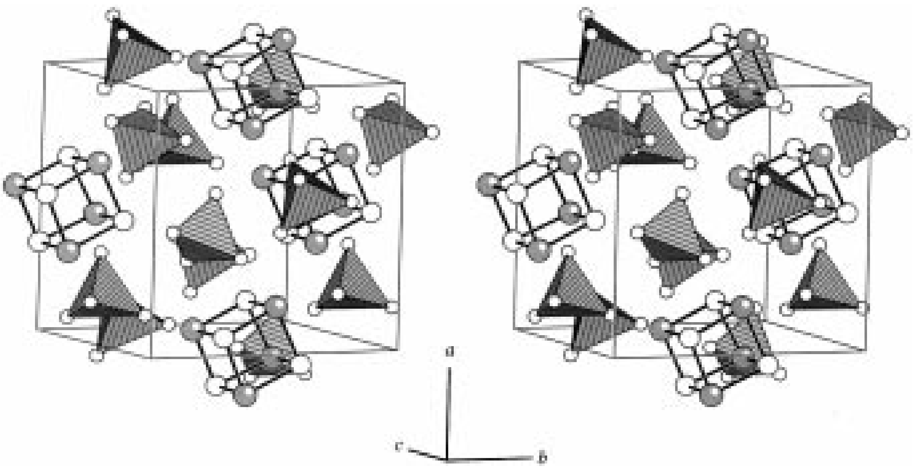


Figure 1. The unit cell of $Bi_4Te_4[AlCl_4]_4$ (**1**) (stereoview). $[AlCl_4]^-$ ions are depicted as tetrahedra.

and Te/S element combinations have been reported. Since Bi- and Te-containing polycations can be obtained from $Na[AlCl_4]/AlCl_3$ melts we have tried to synthesize mixed polycationic Bi/Te clusters.

Black crystals of $Bi_4Te_4[AlCl_4]_4$ (**1**) were formed from elemental Te and Bi, as well as $TeCl_4$ and $BiCl_3$ in a $Na[AlCl_4]/AlCl_3$ melt. The crystal structure analysis shows that **1** is built of $Bi_4Te_4^{4+}$ and tetrachloroaluminate ions (Figure 1). The cations exhibit crystallographic S_4 symmetry, and have the shape of a slightly distorted cube whose corners are occupied alternately by Bi and Te atoms (Figure 2). The two slightly different Bi–Te bond lengths of 294.9(1) and 301.7(1) pm are shorter than the Bi–Bi bonds in homonuclear polybismuth cations (307–328 pm), but they are in agreement with the Te–Te bonds in tellurium polycations. For instance, in the structurally related ion Te_8^{4+},[12] Te–Te bonds are present with lengths between 274 and 301 pm. The angles in the cation of **1** are between 87.70(2) and 92.25(1)° and underline the only slightly distorted cubic shape of the ion. The tetrachloroaluminate ions have a moderately distorted tetrahedral structure in which the Al–Cl bond lengths range between 210.4(4) and 216.0(3) and the Cl-Al-Cl angles between 103.5(1) and 114.3(2)°.

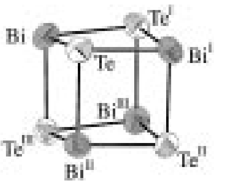
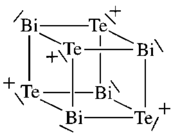


Figure 2. The $Bi_4Te_4^{4+}$ ion in the structure of **1**. The displacement ellipsoids represent a probability of 90%. The uppercase roman numerals denote the following symmetry operations: I = $-x, -y+1, z$; II = $y-½, -x+½, -z+½$; III = $-y+½, x+½, -z+½$.

Strong cation–anion interactions are a typical feature of structures with naked charged clusters. Such interactions are present in the structure of **1**. The Bi and Te atoms of the cation are coordinated by five and six Cl atoms of the neighboring $[AlCl_4]^-$ ions, respectively, within an arbitrary cutoff of 400 pm. The Bi–Cl distances start at 305 pm and are thus significantly shorter than the Te–Cl distances which start at 367 pm. This is consistent with the higher electronegativity and therefore reduced positive charge on the Te atoms.

A straightforward Lewis valence formula can be set up for the $Bi_4Te_4^{4+}$ ion (Scheme 1). Each edge of the cube represents a covalent bond, and in addition each atom carries a nonbonding lone pair of electrons. The Zintl–Klemm concept can be used to explain the formal charges. Each atom exhibits three bonds, which is consistent with neutrality for Bi as a Group 15 element. With three bonds Te as an element of Group 16 behaves as a pseudoelement of Group 15 with a positive charge. Thus $Bi_4Te_4^{4+}$ belongs to the electron-precise clusters.



Scheme 1. Lewis valence formula for the $Bi_4Te_4^{4+}$ ion.

A striking feature of the cubic shape of $Bi_4Te_4^{4+}$ is the structural difference compared to the homonuclear Bi polycations Bi_5^{+} (square pyramidal), Bi_5^{3+} (trigonal bipyramidal), Bi_6^{2+} (octahedral), Bi_8^{2+} (square antiprismatic), and Bi_9^{5+} (tricapped trigonal prismatic). The pronounced tendency for deltahedral structures, all of which can be interpreted with the help of the Wades rules, is not continued with $Bi_4Te_4^{4+}$ since here the polyhedron exhibits only quadrangular faces.

To obtain an explanation we have carried out quantum-chemical ab initio calculations based on second-order Møller–Plesset perturbation theory (MP2), gradient-corrected density functional theory (DFT), relativistic, energy-consistent ab initio pseudo potentials (PP), and core polarization potentials (CPP) with the programs TURBOMOLE[13] and MOLPRO.[14] The optimization of the molecular structure led to the higher T_d symmetry for $Bi_4Te_4^{4+}$. The PP/CPP/MP2 calculations resulted in Bi–Te bond lengths of 297.8 pm and in angles Bi-Te-Bi of 86.13° and Te-Bi-Te of 93.71°. The corresponding PP/DFT calculations under exclusion of the core polarization yielded bond lengths of 304.1 pm, and angles of 87.8° for Bi-Te-Bi and 92.2° for Te-Bi-Te, respectively. The distortion of the cation resulting in the lower S_4 symmetry is caused by the cation–anion interactions in the structure of **1**. The molecular orbital schemes based on the 32 s and p valence orbitals for $Bi_4Te_4^{4+}$ and Bi_8^{2+} are shown in Figure 3.

$Bi_4Te_4^{4+}$ has $4 \times 5+4 \times 6-4=40$ valence electrons, whereas Bi_8^{2+} has only $8 \times 5-2=38$. A square-antiprismatic cluster with 38 valence electrons like Bi_8^{2+} has a stable closed-shell ground state with a large HOMO–LUMO gap. The addition of two electrons would result in a hypothetical uncharged Bi_8 cluster with D_{4d} symmetry, which would be isoelectronic to $Bi_4Te_4^{4+}$ with an occupation of the nearly degenerate LUMOs with b and e symmetry. This would lead to a Jahn–Teller distortion of first or second order. In contrast, a neutral Bi_8 cluster with 40 valence electrons and a cube-shaped structure with O_h symmetry would have a closed-shell ground state with a large HOMO–LUMO gap. Removing two electrons from the triply degenerate HOMO would again lead to a Jahn–Teller distortion. Thus, in a cube-shaped 38-electron cluster and in a square-antiprismatic 40-electron cluster the HOMO–LUMO gap and the stability would be diminished.

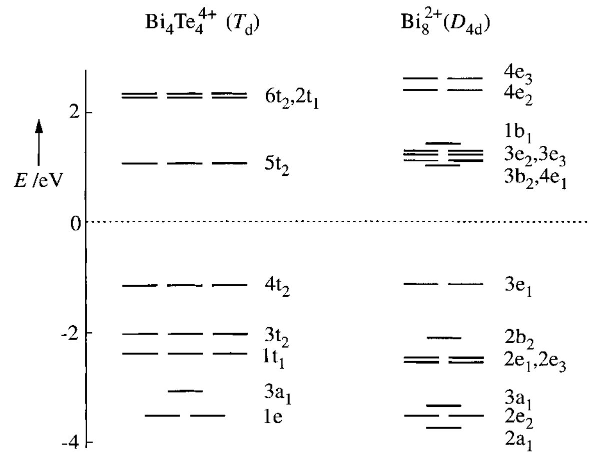


Figure 3. MO schemes for the clusters $Bi_4Te_4^{4+}$ (T_d symmetry) and Bi_8^{2+} (D_{4d} symmetry). All MOs below the Fermi energy (dashed line) are fully occupied, all others are empty. a and b denote nondegenerate, e and t doubly and triply degenerate orbitals, respectively. The lowest energy MOs are each derived from the eight s^2 orbitals; depicted are only those MOs which are derived from the p-valence orbitals. The zero level of the energy scale was defined as the Fermi energy in the middle of the HOMO–LUMO gap, since only in this case the relative orbital energies (E) of the two differently charged clusters become comparable.

This general principle of the structure-determining effect of the number of valence electrons is supported by the recently discovered Zintl anion Sn_8^{6-}, which has 38 valence electrons, a square-antiprismatic structure and is isoelectronic to Bi_8^{2+}.[15] The partial charges in $Bi_4Te_4^{4+}$ can be calculated by different methods. A Mulliken population analysis of the Kohn–Sham wave function yields partial charges of +0.74 for Bi and +0.26 for Te. An alternative analysis according to Roby and Davidson yields similar values of +0.68 for Bi and +0.32 for Te. The analysis of orbital localization according to Foster and Boys shows that both Bi and Te carry a lone pair of electrons. The single bond between both kinds of atoms is slightly polarized towards Te in a ratio 3:2. The formal oxidation numbers are therefore +0.6 for Bi and +0.4 for Te. The observed alternating arrangement of the atoms on the corners of the cube in $Bi_4Te_4^{4+}$ permits a maximal number of interactions between atoms of different electronegativity and leads to an increased, stabilizing ionic contribution in the covalent Bi–Te bonds. The hypothetical P_8, a product of dimerization of P_4 molecules, also represents a 40 valence electron cluster. For several years the structure of P_8 was the subject of theoretical work with sometimes contradictory results. The cubic structure and the cuneane-analogous structure, however, were always calculated to be the most stable modifications.[16] These results find an impressive confirmation with the structure of the presented cube-shaped 40 valence electron cluster.

Experimental Section

$BiCl_3$, $TeCl_4$, and $AlCl_3$ were purified by sublimation; elemental Bi and Te were used as purchased, NaCl was dried in vacuo at 140°C. A glass ampoule was filled with Bi (100.4 mg, 0.48 mmol), Te (91.8 mg, 0.72 mmol), $BiCl_3$ (75.6 mg, 0.24 mmol), $AlCl_3$ (246 mg, 1.98 mmol), and NaCl (10.5 mg, 0.18 mmol). The ampoule was evacuated, sealed, and placed in a horizontal tube furnace for six days at 130°C, and then cooled to room temperature with $20\,K\,h^{-1}$. An in principle difficulty of reactions in chloroaluminate melts is the crystallization of the melt below about 80°C, which causes the inclusion of the crystals in a hard solid mass. To overcome this problem, the ampoule was opened under argon and the content of the ampoule was heated to a maximum of 150°C using an electrically heated sand bath in an argon-filled glove box. At this temperature, the solidified $Na[AlCl_4]/AlCl_3$ mixture became liquid again, and the crystals could be separated mechanically. Crystals of **1** are black and commonly occur grown together with rectangular and hexagonal faces. Compound **1** was obtained in a yield of about 10%. The composition was determined by energy-dispersive X-ray fluorescence. Crystals of **1** are sensitive towards hydrolysis in moist air. For the crystal structure analysis, crystals were sealed under Ar in glass capillaries.

Crystal structure analysis of **1**: Crystal dimensions $0.18 \times 0.14 \times 0.15\,mm^3$, crystal system tetragonal, space group $I\bar{4}$ (no. 82), four-circle diffractometer Nonius KappaCCD, $Mo_{K\alpha}$ radiation ($\lambda = 71.073$ pm), room temperature 293(2) K, lattice constants $a = 1227.26(6)$ pm, $c = 1145.35(7)$ pm, unit cell volume $1725.1(2) \times 10^6\,pm^3$, calculated density $\rho = 3.892\,g\,cm^{-3}$, measurement range $6.64° < 2\Theta < 54.94°$, intensities of 46386 reflections measured, 1981 independent reflections, $R_{int} = 0.091$, structure solution by direct methods (SHELXS-97[17]), refinement with anisotropic displacement factors for all atoms, 64 parameters, absorption coefficient $250\,cm^{-1}$, numerical absorption correction (HABITUS[18]), $R(|F|) = 0.027$, $R(F^2) = 0.067$ (SHELXL-97[19]), Flack parameter $x = 0.025(5)$, max./min. residual electron density $1.60\,e \times 10^{-6}/-2.00\,e \times 10^{-6}\,pm^{-3}$. Further details on the crystal structure investigation 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-411714.

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Hybrid Molecular Materials Based on Covalently Linked Inorganic Polyoxometalates and Organic Conjugated Systems**

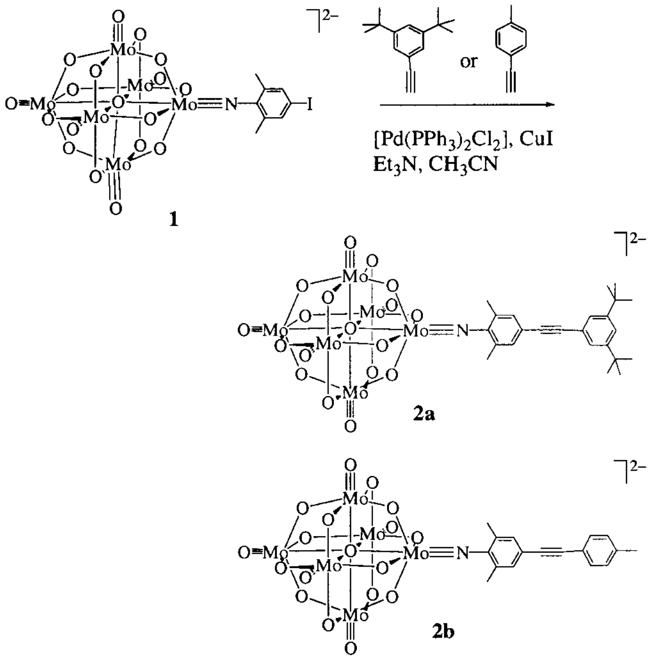
Bubin Xu, Yongge Wei, Charles L. Barnes, and Zhonghua Peng*

Polyoxometalate (POM) chemistry has advanced dramatically during the past two decades, and numerous new structural types with fascinating topological beauty and important electronic, optical, and catalytic properties have been developed.[1–4] Parallel to the rapid progress made on these inorganic metal–oxygen cluster anions, studies on organic and polymeric conjugated materials have also exploded and flourished.[5–8] The fact that the Nobel Prize in chemistry for 2000 went to three preeminent scientists working on conjugated polymers is the ultimate testimony to the important developments in organic conjugated systems.[9]

Although they are vastly different in molecular structures, POMs and organic conjugated molecules/polymers are both electrically active materials with similar electrical and optical properties such as photochromism, electrochromism, and conductivity. The underlying mechanisms of these properties are, however, different for the two types of materials, with dπ electrons responsible for the inorganic clusters, and delocalized π electrons responsible for the organic counterpart. While both areas have been enjoying considerable success, there has been little success in bringing these two types of materials together through covalent bonds.[10, 11] Not only will such hybrid materials combine the advantages of organic materials, such as ease in processing and structural fine tuning, with those of inorganic clusters, but the close interaction of organic delocalized π electrons with the cluster d electrons may bring exciting synergistic effects. Such materials with their unique structures are extremely interesting not only to synthetic chemists and materials scientists, but also to theoretical and experimental physicists.

Herein, we report the synthesis of such hybrid materials through Pd-catalyzed coupling reactions and demonstrate, for the first time, that iodo-functionalized hexamolybdates can undergo Pd-catalyzed coupling reactions with ethynylarenes. These reactions open an exciting research arena where a variety of hybrid materials containing covalently bonded POM clusters and organic conjugated segments can be prepared in a controllable and rational way.

Scheme 1 shows the structures and synthesis of the hybrid materials. Compound $[Bu_4N]_2$-**1** was synthesized by using an approach developed in our laboratory.[12] The coupling of $[Bu_4N]_2$-**1** with 1-ethynyl-3,5-di(*tert*-butyl)benzene or 1-ethynyl-4-methylbenzene was carried out in acetonitrile at room temperature under the protection of nitrogen.[13] The reaction is unusually fast and is completed in a few minutes as monitored by thin-layer chromatography. The cluster not only survived under the reaction conditions, it apparently activates the coupling reaction. The enhanced reactivity of the iodo function in **1** is presumably due to the electron-withdrawing nature of the Mo–N triple bond. Prolonged reaction time is found to be detrimental, as the coupling product slowly decomposes to its parent $\{Mo_6O_{19}\}$ cluster under the reaction conditions. Nevertheless, pure products $[Bu_4N]_2$-**2a** and $[Bu_4N]_2$-**2b** can be synthesized in excellent yields.



Scheme 1. Pd-catalyzed coupling of the iodo-funtionalized hexamolybdate anion **1** with alkynes.

Both $[Bu_4N]_2$-**2a** and $[Bu_4N]_2$-**2b** exhibit excellent solubility in common organic solvents such as dichloromthane, chloroform, acetone, acetonitrile, THF, and DMF. They also show remarkable stability against O_2 and moisture. No obvious

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