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Synthesis and Characterization of a Novel Tantalum Chalcogen-Rich Molecular Cluster with Square Planar Metal Core

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Black single crystals of $Ta_4Se_9I_8$ are obtained in a high yield by heating Ta, Se, and I_2 at 300 °C in 1:2.2:1.0 molar ratio. In the structure, the tantalum atoms form a square, with four Se_2 ligands bridging the Ta–Ta edges and one capping the square. Each Ta atom has two terminal iodine atoms. The compound is diamagnetic and has only two electrons for metal–metal bonding.

Discrete chalcogenide clusters of tantalum are extremely rare. Ta^V derivatives with no M−M bonding and clusters with mixed oxo−chalcogenide and chalcogenide−halide bridges aside,[1] the only clusters falling into this category are $Ta_2(\mu_2\text{-}S)_2{}^{4+}$ in $[Ta_2S_2Cl_4(PR_3)_4]$, closely related $Ta_4S_4{}^{8+}$ with a zigzag Ta_4 chain in $[Ta_4S_4Cl_8(PMe_3)_6]$, a linear Ta_4 unit in $Ta_4(Se_2)_8Br_2$, and tetrahedral $Ta_4(\mu_3\text{-}Se)_4{}^{5+}$ in $GaTa_4Se_8$.[2−5] The much better developed chemistry of Nb chalcogenide clusters cannot always serve as a guide for the preparation of their Ta analogues. Despite well-known similarities in the chemistry of both elements, the methods employed for the preparation of various Nb clusters often give completely different products when applied to tantalum-containing systems. For example, while heating stoichiometrical mixtures of elements gives rather stable binuclear Nb^{IV} clusters, $[Nb_2(\mu\text{-}Q_2)_2X_{8/2}]$ and $[Nb_2(\mu\text{-}Q_2)(\mu\text{-}X)_2X_{4/2}X_2]$ (Q = S, Se; X = Cl, Br, I), their tantalum analogues are nonexistent.[6] The trinuclear clusters M_3QI_7 (Q = Se, Te) can be prepared for both Nb and Ta, but the Ta clusters have much less thermal stability.[7] We have embarked upon a systematic study of the compounds which can form in high-temperature reactions in ternary systems Ta−Q−X (Q = S, Se, Te; X = Cl, Br, I). In this paper, we describe a unique tetranuclear Ta cluster, $Ta_4Se_9I_8$, for which no Nb analogue exists, and which contains a planar Ta_4 core bridged by one μ_4-Se atom, and by four μ_2-Se_2 units.

Single crystals of $Ta_4Se_9I_8$ (**1**) are easily obtained by heating Ta, Se, and I_2 at 300 °C in 1:2.2:1.0 molar ratio, in the form of black well-shaped needles.[8] The crystals are air-stable, insoluble in common organic solvents, and diamagnetic. Raising the temperature to 400 °C significantly decreases the yield. As in the case of $[Ta(Se_2)_2]_2(TaBr_6)$ in the Ta−Se−Br system,[13a] under conditions and with stoichiometries leading to Nb^{IV} binuclear clusters $[Nb_2(\mu\text{-}Se_2)_2X_{8/2}]$ (X = Br, I),[6a,b] Ta forms totally different products,

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(1) Sokolov, M. N.; Fedin, V. P. *Coord. Chem. Rev.* **2004**, *248*, 925−944.

(2) Babaian-Kibala, E.; Cotton, F. A. *Inorg. Chim. Acta* **1991**, *182*, 77−82.

(3) Babaian-Kibala, E.; Cotton, F. A.; Kibala, P. A. *Inorg. Chem.* **1990**, *29*, 4002−4005.

(4) Grenouilleau, P.; Meerschaut, A.; Guemas, L.; Rouxel, J. *J. Solid State Chem.* **1987**, *66*, 293−303.

(5) Yaich, H. B.; Jegaden, J. C.; Potel, M.; Sergent, M.; Rastogi, A. K.; Tournier, R. *J. Less-Common Met.* **1984**, *102*, 9−22.

(6) (a) Schäfer, H.; Beckmann, W. *Z. Anorg. Allg. Chem.* **1966**, *347*, 225. (b) Rijnsdorp, J.; De Lange, G. J.; Wiegers, G. A. *J. Solid State Chem.* **1979**, *30*, 365−373. (c) Franzen, H. F.; Hönle, W.; v. Schnering, H.-G. *Z. Anorg. Allg. Chem.* **1983**, *497*, 13−26.

(7) Smith, M. D.; Miller, G. J. *J. Am. Chem. Soc.* **1996**, *118*, 12238−12239.

(8) Ta powder (0.60 g, 3.3 mmol), Se powder (0.59 g, 7.47 mmol), and I_2 (0.84 g, 3.3 mmol) were sealed in an evacuated glass ampule and heated at 200 °C (1 day) and at 300 °C (3 days) in a furnace with a small natural temperature gradient. The shiny black crystals of the compound form in the hotter end of the ampule. Yield of **1**: 87%. Satisfactory analyses for Ta, Se, I (EDAX). Raman (cm^{-1}): 384 vw, 301 sh, 293 sh, 283 w, 278 w, 250 m, 224 m, 202 sh, 192 vs, 167 m, 154 m, 142 m, 135 sh, 102 s, 88 s, 85 s, 66 m, 60 s, 50 m. Magnetic susceptibility was measured at 300 K: $\chi_M = -635 \times 10^{-6}$ $cm^3\ mol^{-1}$. The X-ray powder diffraction pattern of the bulk of the crystals corresponds to the calculated from the single crystal X-ray data.

(9) Tremel, W. *J. Chem. Soc., Chem. Commun.* **1992**, 126−128.

(10) The diffraction data were collected on a Bruker X8APEX CCD diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å) using ϕ-scans of narrow (0.5°) frames. The structure was solved by direct methods and refined by full-matrix least-squares method against $|F|^2$ in anisotropic approximation using SHELXTL programs set.[11] Crystal size $0.035 \times 0.025 \times 0.104$ mm^3, orthorhombic, space group $Pna2_1$, $a = 14.3251(4)$ Å, $b = 14.8440(5)$ Å, $c = 13.0603(4)$ Å, $T = 293(2)$ K, $Z = 4$, $V = 2777.17(15)$ $Å^3$, $\rho_{calcd} = 5.859$ $g{\cdot}cm^{-3}$, $2\theta_{max} = 55°$, $\mu = 36.387$ mm^{-1}, 23515 reflections collected within $-17 \le h \le 18$, $-19 \le k \le 19$, $-16 \le l \le 15$, 6221 unique ($R_{int} = 0.0300$), 5880 $F_o \ge 4\sigma(F)$, 190 parameters, R1 = 0.0168, wR2 = 0.0377, residual electron density peaks of 0.968 and −0.821 $e{\cdot}Å^{-3}$. Absorption corrections were applied empirically using SADABS program ($T_{min}/T_{max} = 0.500$).[12] Further details 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-414138.

(11) *SHELXTL*, version 6.22; Bruker AXS Inc.: Madison, WI, 2003.

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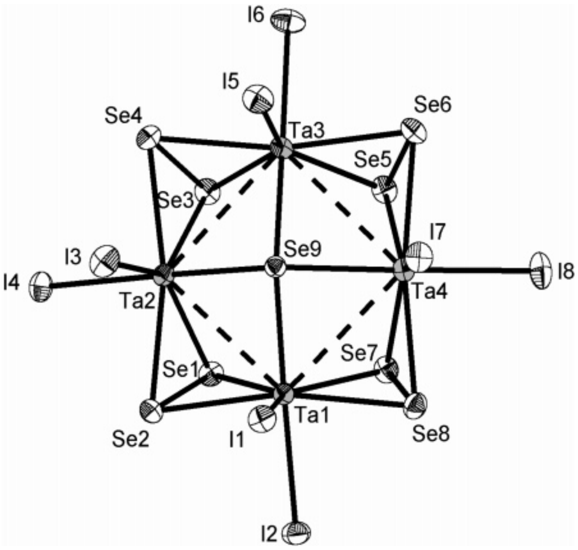

Figure 1. Molecule **1** in crystal (ellipsoids at 50% probability level). Average bond distances [Å]: Ta−Ta, 3.3231(4)−3.3924(5), av 3.358[29]; Ta−Se_{eq}, 2.6333(9)−2.6647(9), av 2.647[11]; Ta−Se_{ax}, 2.6003(8)−2.6425(8), av 2.624[15]; Ta−(μ_3-Se), 2.5705(8)−2.5978(8), av 2.584[11]; Ta−I, 2.7282(6)−2.8076(5), av 2.746[26], Se−Se, 2.3367(11)−2.3581(10), av 2.345[10].

and in higher formal oxidation state (+4.5 and +5 in the case of the bromide, +4.5 in the case of iodide, **1**). This is understandable since Ta forms lower oxidation states less readily then Nb. Other reaction stoichiometries produce one-dimensional chain cluster $[Ta(Se_2)_2]_2I$ (Se in excess) or triangular Ta_3SeI_7 (Ta and I_2 in excess).[7,13b]

Structure of **1** is shown in Figure 1.[10] The tantalum atoms form a square, deviation from the plane being within ±0.006 Å. Four Se_2 ligands are asymmetrically coordinated to the Ta−Ta edges in a η^2,η^2,μ_2-manner. Four of selenium atoms of the Se_2 ligands lie almost in the Ta_4 plane (±0.14 Å, equatorial, Se_{eq}), and another four deviate from the Ta_4 plane by about 1.86 Å oppositely to the μ_4-Se atom (axial, Se_{ax}). Each Ta atom has two terminal iodine atoms. The coordination polyhedron around Ta can be described as pentagonal bipyramidal with μ_4-Se and one of the I atoms trans to it in the axial position (I_{trans}), and the two groups Se_2 and another I atom (I_{cis}) in the equatorial position. The rather large distances between metal atoms (3.3231(4)−3.3924(5) Å) are in agreement with average Ta oxidation state of +4.5 in this highly electron-deficient cluster. In $[Ta(Se_2)_2]_2(TaBr_6)$ and $[Ta(Se_2)_2]_2I$, the distances between Ta atoms in the same average oxidation state are 3.18−3.23 and 3.20 Å, respectively.[13] The Se−Se distances correspond to single bonds as expected for the Se_2^{2-} formalism. We have analyzed molecular packing and intermolecular contacts in the crystal of **1** using the TOPOS program set and found that one of the terminal iodine atoms, I(1), forms four $I_{cis}\cdots Se_{ax}$ contacts of 3.4838(9)−3.5816(9) Å (the sum of van der Waals radii 3.86 Å).[14] The $Se_{eq}-Se_{ax}\cdots I_{cis}$ angle is 167.7°. The molecules are joined via those contacts forming chains running along the *a*-direction (Figure 2). The molecular packing is rather distorted due to these specific interactions and is topologically related to the hexagonal close packing. Each molecule is surrounded by eight nearest (the distances between the molecular centroids are 7.74−9.98 Å) and four farther molecules (11.63, 13.06 Å). The shortest distance of 7.74 Å corresponds to two molecules in the chain (Figure 2).

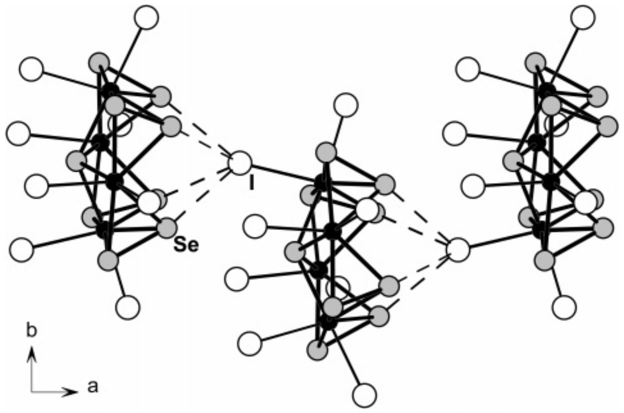

Figure 2. Chain of molecules in the crystal packing of **1** (view along *c*-axis). The short $Se\cdots I_{cis}$ contacts of 3.4838(9)−3.5816(9) Å are shown as dashed lines.

The structure is interesting from several points of view. It belongs to a still very rare type of square planar clusters. The most recent addition to this family was $K_4[Ti_4(\mu_4\text{-}O)(\mu\text{-}I)_8I_4]$ with short Ti−Ti bonds.[15] For the group 5 elements, such clusters were observed in $[Nb_4(\mu_4\text{-}S)_2(\mu\text{-}SPh)_8(SPh)_4]^{4-}$ and $[Nb_4(\mu_4\text{-}S)_2(\mu\text{-}SPh)_8(PMe_2R)_4]$, which, being the Nb^{III} derivatives, have the required eight electrons for the four single M−M bonds in the cluster. Accordingly, the Nb−Nb distances are short (2.81−2.83 Å, typical Nb−Nb single bond length value in the sulfido-bridged clusters[1]). However, this cluster type topologically is rather close to $[Ta_4(\mu_4\text{-}Se)(\mu\text{-}Se_2)_4I_8]$ if one takes into account equivalence of two bridging SPh and one Se_2^{2-}, and of four terminal iodines and one μ_4-S.[16] It also shows a very strong structural similarity to the recently prepared Ln(III)−Se clusters $[Ln_4(\mu_4\text{-}Se)(\mu\text{-}Se_2)_4(THF)_6I_2]$ (Ln = Tm, Ho, Er, Yb).[17] And in a broader sense, both **1** and the Ln clusters can be regarded as higher homologues of $M_3(\mu_3\text{-}Q)(\mu,\eta^2\text{-}Q_2)_3$ (M = Ti, V, Mo, W, Re; Q = O, S, Se, Te) clusters with three metal atoms and three bridging dichalcogen ligands instead of four.[18] In both cluster types, the μ_2-Q_2 ligands are tilted to M_n (n = 3, 4) plane, permitting the distinction to be made between axial and equatorial chalcogen atoms. The M−Se_{eq} bond distances are

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(12) Sheldrick, G. M. *SADABS. Program for absorption Correction with the SMART system*; University of Göttingen: Göttingen, Germany, 1996.

(13) (a) Sokolov, M.; Imoto, H.; Saito, T.; Fedorov, V. *Polyhedron* **1998**, *17*, 3735−3738. (b) Gressier, P.; Guemas, L.; Meerchaut, A. *Acta Crystallogr., Sect. B* **1982**, *38*, 2877−2879.

(14) (a) Blatov, V. A.; Shevchenko, A. P.; Serezhkin, V. N. *J. Appl. Crystallogr.* **2000**, *33*, 1193. http://topos.ssu.samara.ru. (b) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441−448.

(15) Jongen, L.; Mudring, A.-V.; Möller, A.; Meyer, G. *Angew. Chem., Int. Ed.* **2004**, *43*, 3183−3185.

(16) Seela, J. L.; Huffmann, J. C.; Christou, G. *J. Chem. Soc., Chem. Commun.* **1987**, 1258−1259. Babaian-Kibala, E.; Cotton, F. A.; Kibala, P. A. *Polyhedron* **1990**, *9*, 1689−1694.

(17) Kornienko, A.; Melman, J. H.; Hall, G.; Emge, T. J.; Brennan, J. C. *Inorg. Chem.* **2002**, *41*, 121−126.

(18) Sokolov, M. N.; Fedin, V. P.; Sykes, A. G. *Compr. Coord. Chem. II*; Elsevier: New York, 2003; Vol. 4, pp 761−824.

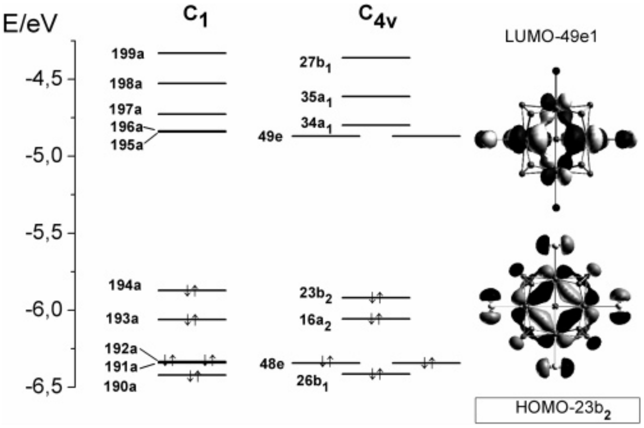

Figure 3. DFT energy level diagrams for two $[Ta_4Se_9I_8]^0$ models and schematic figures of HOMO and LUMO for C_{4v}-$Ta_4Se_9I_8$. Indicated are the numbers and symmetry types of calculated MO.

sufficiently longer than M−Se_{ax} (by 0.02−0.08 Å), though this difference is less pronounced in the square clusters probably due to the general elongation of metal−chalcogen bonds. Each M atom both in M_4Q_9 and in M_3Q_7 cores coordinates two terminal atoms. Moreover, just like **1**, the crystal structures of M_3Q_7 clusters contain a negatively charged atom or ion nearly equidistant from three Q_{ax} atoms, with short nonbonding contacts between them. The contacts are much shorter then the sum of van der Waals radii. Thus, the bridging Se_2^{2-} group in $[Ta_4(\mu_4\text{-}Se)(\mu,\eta^2\text{-}Se_2)_4I_8]$ has similar electrophilic character as Q_2^{2-} in the M_3Q_7 clusters.

We have performed quantum chemical calculations for **1** using the density functional theory (DFT) approach.[19] The calculated atomic arrangement in $Ta_4Se_9I_8$ molecules was found to be almost identical in both C_{4v} (idealized) and C_1 (real) symmetry (within of 0.01 A), as well as the energy level diagrams (Figure 3) and the binding energies (−88.87 and −88.89 eV, respectively). We will use only C_{4v}-$Ta_4Se_9I_8$ in the discussion. The calculated HOMO−LUMO energy gap is 1.05 eV. The HOMO is a nondegenerate $23b_2$-orbital (Figure 3), consisting of bonding 5d AO of 4Ta (∼48%), antibonding 5p AO of $4I_{cis}$ (∼25%), and antibonding 4p and 4p AO of $4Se_{eq}$ (slightly less of 10%); other contributions do not exceed 5%. The calculated ground state of $Ta_4Se_9I_8$ molecule is spin-paired (diamagnetic) which correlates well with the experimental data. Only two electrons are thus available for metal−metal bonding, which gives the bond order between each pair of Ta atoms as 0.25, in accordance with the observed elongated Ta−Ta. The bonding μ_4-Se−Ta_4 corresponds to MO 39e (−9.954 eV; not shown in Figure 3). The LUMO is antibonding double degenerate MO 49e consisting of 5d AO of 4Ta (∼68%), 5p AO of $2I_{trans}$ (13%), 5p AO of $2I_{cis}$ (8%), and small contributions of Se AO. The atomic net charges were calculated using the Hirshfeld analysis:[25] Ta 0.15; Se_{ax} 0.03; Se_{eq} 0.05; μ_4-Se −0.06; I_{trans} −0.09; I_{cis} −0.12. Thus, the observed $I_{cis}\cdots Se_{ax}$ interaction may be favored electrostatically. The minor charge values may indicate the preferentially covalent character of the interactions in $Ta_4Se_9I_8$. Calculations of the Mo_3S_7 clusters similarly attribute a small positive charge to the S atoms of bridging S_2 group and a negative charge, to μ_3-S and terminal ligands.[26]

To conclude, in $Ta_4Se_9I_8$ we have not only the first square planar Ta cluster with interesting electronic structure, with Ta in noninteger formal oxidation state, not only a rare member of emerging M_4Q_9 family of clusters, but also a higher homologue of triangular M_3Q_7 clusters, whose versatile chemistry was used in construction of higher nuclearity clusters. The deep structural and electronic analogy between both types of clusters, stressed in this work, permits us to envision similar rich synthetic possibilities for $Ta_4Se_9I_8$.[18]

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) Density functional theory (DFT) calculations were carried out using the ADF2002 code.[20] The local-exchange VWN correlation potential was used for the local density (LDA) approximation,[21] with Becke's nonlocal corrections to the exchange energy,[22] and Perdew's nonlocal corrections to the correlation energy were added.[23] The relativistic corrections for all atoms were accounted by the scalar ZORA (zeroth-order relativistic approximation) method.[24] A frozen-core approximation was used to treat the core electrons of Ta (1s5p), Se (1s3p), and I(1s4p). The triple-ζ STO basic set was used for the valence atomic orbitals. The electronic structure calculations and full optimizations were carried out for different models $(Ta_4Se_9I_8)^0$ of C_{4v} and C_1 symmetry. The calculations of the electronic binding energy have been performed for the formal reaction $4Ta + 9Se + 8I \rightarrow (Ta_4Se_9I_8)^0$.

(20) (a) *Amsterdam Density Functional (ADF) program*, release 2002.02; Vrije Universteit: Amsterdam, The Netherlands, 2002. (b) Te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Fonseca Guerra, C.; Van-Gisbergen, S. J. A.; Snijders, J. G.; Ziegler, T. *J. Comput. Chem.* **2001**, *22*, 931.

(21) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200−1211.

(22) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098−3100.

(23) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822−8824.

(24) Van Lenthe, E.; Ehlers, A.; Baerends, E. J. *J. Chem. Phys.* **1999**, *110*, 8943−8953.

(25) Hirshfeld, F. L. *Theor. Chim. Acta* **1977**, *44*, 129−138.

(26) Mayor-Lopez, M. J.; Weber, J.; Hegetschweiler, K.; Meyenberger, M. D.; Jobo, F.; Leoni, S.; Nesper, R.; Reiss, G.; Frank, W.; Kolesov, B.; Fedin, V.; Fedorov, V. *Inorg. Chem.* **1998**, *37*, 2633−2644.