

The Preparation and Structure of $[\text{Te}_4\text{Nb}_3\text{O}(\text{Te}_2)_2\text{I}_6]\text{I}$ containing a Te_4^{2+} Polycation Coordinated to a Transition Metal Cluster

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High temperature reaction of niobium, NbOI_3 , tellurium and iodine produces $[\text{Te}_4\text{Nb}_3\text{O}(\text{Te}_2)_2\text{I}_6]\text{I}$ **1**, which contains one square planar Te_4 ring and two Te_2 groups coordinated to a trinuclear metal cluster.

Polycations of the main group elements such as S_8^{2+} ,¹ Te_4^{2+2} or Bi_9^{5+3} have been known for almost 30 years. They are usually made and stabilized by the use of highly acidic or

superacidic media, solutions and melts. These compounds are fairly well studied spectroscopically, and their bonding has been investigated theoretically by calculations at various levels of sophistication.^{2,4} Similarly, their anionic analogues, the so-called Zintl-anions, have been prepared and investigated during the previous two decades especially by Corbett and coworkers.⁵ Recently, metallated polyanionic main group

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clusters such as $[\text{Sn}_9\text{Cr}(\text{CO})_3]^{4-}$,^{6a} $[\text{Sn}_9\text{Cr}(\text{CO})_3]^{4-}$,^{6b} $[\text{As}_7\text{Mo}(\text{CO})_3]^{3-}$ ^{6c} and $[\text{Sb}_7\text{Mo}(\text{CO})_3]^{3-}$ ^{6d} have been made. Metallated polycations of the main group elements on the other hand are almost unknown. Some pioneering work has been done in this field. Initial studies showed that reaction of Se_4^{2+} with the metal carbonyls $\text{Mo}(\text{CO})_6$ or $\text{W}(\text{CO})_6$ in liquid SO_2 lead to $[\text{M}_2(\text{CO})_{10}\text{Se}_4]^{2+}$ ($\text{M} = \text{Mo}, \text{W}$) where two $\text{M}(\text{CO})_5\text{Se}_2^+$ groups are linked by weak Se-Se bonds of length 3.15 Å.⁷ $[(\text{CO})_4\text{M}(\eta^3\text{-Te}_3)]^{2+}$ ($\text{M} = \text{Mo}, \text{W}$),⁸ which formally contain a triangular Te_3^{2+} cation, have been obtained through reaction of Te_4^{2+} with $\text{M}(\text{CO})_6$ in $\text{SO}_2\text{-AsF}_3$. These compounds can be considered as cationic counterparts of the so-called 'Zintl metal carbonylates'.⁹

Reported in this communication are the synthesis and crystal structure of a new cluster compound $[\text{Te}_4\text{Nb}_3\text{O}(\text{Te}_2)_2\text{I}_6]^{+}$ **1** formally containing a Te_4^{2+} polycation coordinated to a transition metal cluster. Initially, **1** was obtained serendipitously in low yields from high temperature reactions aimed at the synthesis of niobium iodine tetratellurides (niobium : tellurium : iodine *ca.* 3 : 11 : 4, $T = 680^\circ\text{C}$).[‡] Black needle-like crystals were separated by hand and investigated by single crystal X-ray diffraction.[‡] After the composition of **1** was known, a more rational synthetic procedure has been worked out. Complex **1** can be obtained in moderate yields by reaction of niobium, NbOI_3 , tellurium and iodine (2 : 1 : 8 : 4) together with other (mostly still unidentified) reaction products.¹⁰ The structure of **1** consists of the cationic cluster $[\text{Te}_4\text{Nb}_3\text{O}(\text{Te}_2)_2]^{+}$ **2** and a well separated I^- counterion, the shortest cation(anion)-anion contacts being 3.321(2) and 3.723(2) Å, respectively. A graphic drawing of the cation **2** is shown in Fig. 1. Complex **2** possesses idealized C_s symmetry, where the plane bisecting the molecule is defined by the atoms Nb(3), I(5), I(6) and the distance of O to the plane is 0.065 Å.

The metal core portion of **2** contains three niobium atoms arranged in the form of an isosceles triangle, the metal-metal distances within the triangle being 3.013(2), 3.048(2) and 3.861(2) Å. This metal core is capped by one oxygen atom [$d_{\text{Nb-O}}$: 1.945(8), 1.955(8) and 2.133(2) Å]. Each metal atom possesses two terminal iodine neighbours. Each of the two short sides of the Nb_3 triangle is bridged by one Te_2 group, while a square planar Te_4 group ($\bar{d}_{\text{Te-Te}}$: 2.797 Å) is bonded in a $\mu, \eta^2 : \eta^2$ -fashion to the longer side. Thus, disregarding metal-metal bonds, each Nb atom has a distorted pentagonal bipyramidal coordination with O and one of the I atoms in the axial positions. The Nb-Te distances are in the range 2.784(2) to 2.963(2) Å (compared with 2.90 Å as the sum of the

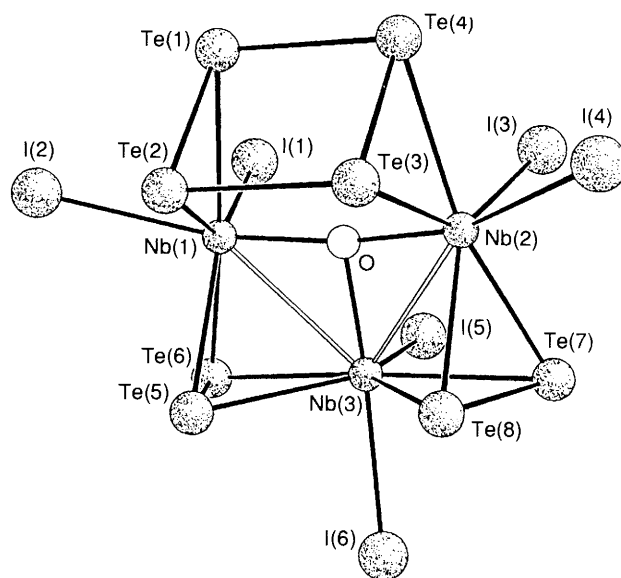


Fig. 1 Ball-and-stick representation of the $[\text{Te}_4\text{Nb}_3\text{O}(\text{Te}_2)_2\text{I}_6]^{+}$ cation **2**

metallic radii).¹¹ The Te-Te distances of 2.691(2)–2.963(2) Å are typical for single bonds [Te-Te distances in Te_4^{2-} anions of $(\text{hmtn})_2\text{Te}_{13}$ ¹² are 2.72–2.96 Å; Te-Te distances in elemental Te¹³ are 2.84 Å]. Te-Te distances of the Te_2 groups [$d_{\text{Te-Te}}$: 2.691(2) and 2.692(2) Å] are identical within experimental error and approximately 0.1 Å shorter than those of the Te_4 ring, which are similar but not identical [$d_{\text{Te-Te}}$: 2.778(2), 2.801(2), 2.820(2) and 2.788(2) Å]. However, they are substantially longer than the corresponding ones in the free Te_4^{2+} species ($\bar{d}_{\text{Te-Te}}$: 2.684 Å, mean value from six different compounds^{2,10,14}), where the formal bond order is 1.25, and in the recently reported $[(\text{CO})_4\text{MTe}_3]^{2+}$ ($\text{M} = \text{Mo}, \text{W}$) containing a three membered tellurium ring coordinated in a π -fashion to the metal carbonyl fragment ($d_{\text{Te-Te}}$: 2.72 Å).⁸ This bond lengthening could result from back donation of metal d electrons into the empty π^* orbital of the Te_4 ring. Back donation is not possible in the naked Te_4^{2+} cation.

The bonding in the title compound can be rationalized in a straightforward manner. Counting oxygen and iodine as O^{2-} and I^- , the Te_2 groups as Te_2^{2-} and the Te_4 ring as Te_4^{2+} leads to the formulation $[(\text{Te}_4^{2+})(\text{Nb}^{3+})(\text{Nb}^{4+})_2(\text{O}^{2-})_2(\text{Te}_2^{2-})_2(\text{I}^-)_6]^{+}$, where four electrons are shared by three Nb atoms ($1 \times \text{Nb}^{3+}$, $2 \times \text{Nb}^{4+}$). This picture is consistent with the presence of two localized Nb-Nb single bonds, and it is in accordance with the observed C_s symmetry of the cation. In fact, the Nb-Nb bond distances of 3.013(2) and 3.048(2) Å in **2** are in good agreement with formal Nb-Nb single bond distances in other compounds such as NbCl_4 ($d_{\text{Nb-Nb}}$: 3.06 Å)¹⁵ or $\text{Nb}_2\text{Te}_2\text{I}_6$ ($d_{\text{Nb-Nb}}$: 2.932 Å).¹⁶ Still, there is an alternative way to look at the structure of **2**. The Te_4Nb_2 core portion of **2** [Te(1)–Te(4), Nb(1), Nb(2)] has a distorted prismane type structure where one of the axial bonds is broken. Using the isolobal relationships¹⁷ $d^2\text{-ML}_7 \rightarrow \text{CH}_2 \rightarrow \text{Te}$ and $d^1\text{-ML}_7 \rightarrow \text{CH}_2^+ \rightarrow \text{Te}^+ 2$ can be viewed as a trigonal prismatic Te_6^{6+} species¹⁸ where one edge bond is broken and the corresponding edge is bridged by an additional Te atom to give the isolobal analogue of a Te_7^{4+} cation instead. The formal electron count for this polycation species is $22 + 2 \times 4 + 6 = 36$ in agreement with electron counting rules.

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‡ Although the reagents and apparatus were degassed in a normal way before the reaction, oxygen was incorporated into the structure. Its source is presumed to be traces of water trapped inside the ampoules. This conclusion is supported by the fact that the yield of **1** was increased when the quartz ampoules were not dried before the experiments.

§ Crystal data for $[\text{Te}_4\text{Nb}_3\text{O}(\text{Te}_2)_2\text{I}_6]^{+}$: monoclinic, space group $P2_1/n$, $a = 8.952(2)$, $b = 15.803(3)$, $c = 19.418(5)$ Å, $\beta = 101.26^\circ$, $V = 2694.01$ Å³, $D_c = 5.434$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 17.24$ mm⁻¹, $Z = 4$, $\lambda = 0.71073$ Å, needle-shape crystals, dimensions $0.015 \times 0.035 \times 0.08$ mm³, $2\theta_{\text{max}} = 60^\circ$, data collected at room temperature (298 K) on a Siemens R3 four-circle diffractometer; structure solved and refined using the SHELXTL PLUS program system, empirical absorption correction, 7156 unique reflections of which 6127 are 'observed' [with $I \geq 2\sigma(I)$], $R = 0.047$, $R_w = 0.053$ ($R = 0.057$, $R_w = 0.058$ for all data). Further details on the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2, Germany, by quoting the depository number CSD-55928, the names of the authors and the Journal citation.

Atomic coordinates, bond lengths and angles, and thermal parameters have also been deposited at the University of Bonn. See Notice to Authors, Issue No. 1.

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