$Nb_4OTe_9I_4$: a One-dimensional Chain Compound containing Tetranuclear Oxygen-centred Niobium Clusters

Wolfgang Tremel*

Anorganisch-Chemisches Institut der Universität, Wilhelm-Klemm-Str. 8, D-4400 Münster, Germany

The new one-dimensional chain compound $Nb_4OTe_9I_4$ is prepared; its structural key feature is a distorted tetrahedral oxygen-centred cluster of niobium atoms with terminal iodine atoms and ditelluride-bridged edges; the individual clusters are linked to a one-dimensional chain by isolated Te atoms.

Clusters of metal atoms are of special interest in materials chemistry and the impinging fields of chemistry and physics. Generally, the electron concentration in group 6 (*i.e.* molybdenum) compounds is large enough to support metal–metal cluster bonding, but many clusters of the electron-poor transition metals in groups 3 and 4 (*e.g.* $Zr_6Cl_{15}N$ and Sc_7ZCl_{12}; Z = B, C, N, Mn, Fe, Co, Nb) are stabilized by interstitial atoms.[1] Group 5 element clusters are borderline cases. Only three discrete species containing heteroatoms, $Nb_6I_{11}H$,[2] $[M_6S_{17}]^{4-}$ (M = Nb, Ta)[3] and $[V_4O(edt)_2Cl_8]^{2-}$ (edt = ethane-1,2-dithiolate),[4] and one extended system Ta_4SiTe_4[5] are known. In this paper we describe a novel niobium cluster compound, $Nb_4OTe_9I_4$ **1** the structure of which contains infinite one-dimensional stacks of tetranuclear oxygen-centred metal clusters linked by tellurium atoms.

Initially, $Nb_4OTe_9I_4$ was obtained serendipitously as a side product from reactions (niobium : tellurium : iodine = 3 : 9 : 4, T = 620 °C) aimed at obtaining niobium telluride iodides analogous to the quasi one-dimensional materials $(NbSe_4)_nI$ (n = 2,3,10/3),[6] the source of oxygen presumably being water contamination of the ampoule. This assumption is supported by the fact that the yield of **1** is increased when drying steps are omitted from the experiments. In two related cases[4,7,8] it was reported to be almost impossible to obtain oxide-free product even under rigorous anoxygenic/anhydrous conditions. After the composition of **2** was known, a more rational synthetic procedure was developed. Following the synthesis of $[V_4O(edt)_2Cl_8]^{2-}$ by reaction of $VOCl_4^{2-}$, VCl_3 and edt (1 : 3 : 2)[4] a similar approach provided a synthetic access to **1** in slightly improved yields.†

The structure‡ (Fig. 1) of **1** consists of infinite one-dimensional $Nb_4OTe_9I_4$ chains running parallel to the crystallographic *b* direction. The chains are held together by van der Waals contacts only.

The shortest interchain contacts are 3.512(2) Å (Te···I), the shortest intrachain contacts (Te···Te) are 3.603(2) Å. Therefore, **1** can be considered a truly one-dimensional compound. The individual chains consist of $Nb_4OTe_9I_4$ monomer clusters containing crystallographically imposed C_2 symmetry. They are linked by common Te atoms which are located on the twofold axis. The monomer unit contains a flattened tetrahedral metal core, which is centred by the oxygen atom. The Nb–O distances are 2.001(8) and 2.050(10) Å. The four short edges ($\bar{d}_{Nb-Nb}$: 3.055 Å) of the tetrahedral core are bridged by Te_2 groups ($\bar{d}_{Te-Te}$: 2.709 Å), the two longer edges ($\bar{d}_{Nb-Nb}$: 3.764 Å) are bridged by isolated Te atoms, which are surrounded tetrahedrally by four metal atoms and which provide the link to the neighbouring clusters (Fig. 2). Each metal atom is coordinated by one I, one O and five Te in a pentagonal bipyramidal fashion, where the equatorial plane is made up of five Te atoms; the axial positions are occupied by the terminal iodine and the interstitial oxygen atoms.

The mean I–Nb–O angle is 167.6°, the mean Nb–I distances is 2.829 Å. The maximum distance of an atom from the equatorial plane is 0.084 Å. The importance of metal-interstitial bonding is documented by the fact that all metal atoms are shifted from the equatorial plane towards the centre of the cluster, *i.e.* the central oxygen atom. The importance of metal–metal bonding for the cluster stability is indicated by the short metal–metal distances ($\bar{d}_{Nb-Nb}$: 3.055 Å for the short edges).

In contrast, the Ti–Ti distances in the molecular compound $[Ti_4O(S_2)_4C_6]$,[8] where topologically similar cluster units occur, are 3.123 Å. The titanium atoms must be formally regarded here as Ti^{4+}. Interestingly, the Te_2 bridging groups show a distinct asymmetry in the Nb–Te distances. One Nb–Te distance is consistently ≈0.1 Å shorter ($\bar{d}_{Nb-Te}$: 2.781 *vs.* 2.897 Å) than the second one. The Nb–Te distances involving the isolated Te atom bridging the clusters are with 3.009(3) Å significantly longer than the remaining ones.

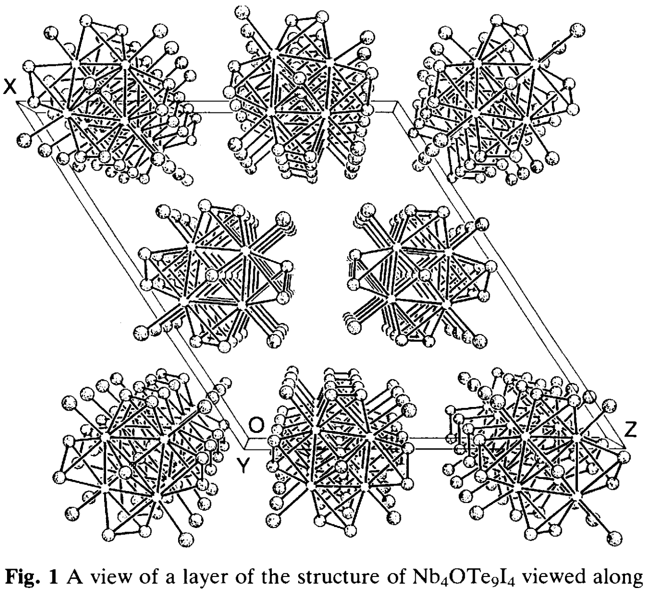

Fig. 1 A view of a layer of the structure of $Nb_4OTe_9I_4$ viewed along [010] (small dotted circles: Nb atoms, medium dotted circles: Te atoms, large dotted circles: I atoms, crossed circles: O atoms)

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* *New address*: Institut für Anorganische Chemie und Analytische Chemie, Universität Mainz, Becherweg 24, W-6500 Mainz.

† Experimental: $NbOI_3$, I_2, Nb, and Te (1 : 1 : 3 : 4) were heated at 620 °C for 14 days. Black crystals (yield ≈10%) separated in the natural temperature gradient of the furnace and could be selected manually from the remaining (still unidentified) products.

‡ *Crystal data* for $Nb_4OTe_9I_4$: monoclinic, space group $C2/m$, a = 21.966(9), b = 6.195(2), c = 19.926(9) Å, β = 122.43(3)°, V = 2288.72 Å^3, D_c = 5.030 g cm^{-3}, μ(Mo-Kα) = 14.56 mm^{-1}, Z = 4, λ = 0.71073 Å, crystal platelet shape, dimensions 0.1 × 0.02 × 0.12 mm^3, R = 0.056, R_w = 0.054, for 2012 reflections with $I > 2\sigma(I)$, empirical absorption correction, data collected at room temperature (298 K) on a Siemens R3 four-circle diffractometer; structure solved and refined using the SHELXTL PLUS program system. Further details on the crystal structure investigation are available on request from the Fachinformation-szentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2, Germany, by quoting the depository number CSD-55926, 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.

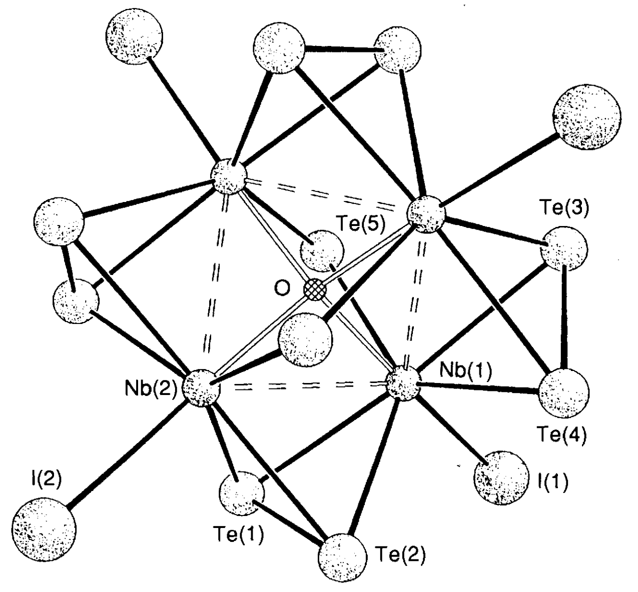

Fig. 2 A view of a $Nb_4OTe_{10}I_4$ fragment of a single $Nb_4OTe_9I_4$ chain

The formation of many zirconium and lanthanide clusters requires the encapsulation of a heteroatom, Z. It serves (*i*) as an electron donor to stabilize metal–metal bonds and (*ii*) stabilizes the cluster by the formation of strong M–Z bonds. **2** is one rare example of a group 5 metal cluster compound containing an interstitial atom and the first group 5 metal cluster species centred on oxygen. A few examples of the electron poorer transition metal clusters, discrete and extended, containing interstitial oxygen have been reported, among them $[Cp_4Ti_4OSe_7]$,[9] $[(MeCp)_4Ti_4OS_8]$[10] and $[Ti_4O(S_2)_4Cl_6]$.[8]

Molecular orbital calculations at the extended Hückel level show that metal–interstitial bonding is important for the cluster stability. Calculations on a discrete $[Nb_4OTe_{10}I_4]^{2-}$ model cluster and the corresponding cluster without the oxygen atom show that the uncentred species is stabilized substantially upon insertion of the interstial by formation of strong Nb–O bonds. Metal-interstitial bonding causes a sharp decrease in metal–metal bonding. Band structure calculations on a one-dimensional $Nb_4OTe_9I_4$ chain show that the metal bands are very narrow (bandwidth W ≈0.3 eV). Therefore, insulating behaviour is expected for the extended system.

Further studies of the properties and the chemical reactivity (*e.g.* to solubilize the monomeric clusters) of **1** are currently in progress.

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