Synthesis and structure of a tetranuclear niobium telluride cuboidal cluster with a central μ_4-O ligand

Vladimir P. Fedin,*[a] Irina V. Kalinina,[a] Alexander V. Virovets,[a] Nina V. Podberezskaya,[a] Ivan S. Neretin[b] and Yuri L. Slovokhotov[b]

[a] *Institute of Inorganic Chemistry, Russian Academy of Sciences, pr. Lavrentjeva 3, Novosibirsk 630090, Russia. E-mail: fedin@che.nsk.su*

[b] *Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow 117813, Russia.*

Received (in Basel, Switzerland) 29th July 1998, Accepted 21st September 1998

High-temperature reaction of $NbTe_4$ with KCN at 450 °C and further crystallization from aqueous solution produces an oxygen-centered tetranuclear niobium cubane-type complex, isolated here as $K_6[Nb_4OTe_4(CN)_{12}]\cdot K_2CO_3\cdot KOH\cdot 8H_2O$, and characterized by X-ray crystallography.

Many small clusters of the electron poor transition metals in groups 3 and 4 are stabilized by an interstitial atom, Z,[1] which serves as an electron donor to stabilize metal–metal bonds and/or stabilizes the cluster by the formation of strong M–Z bonds. A few examples of group 5 transition metal cluster complexes, discrete and extended, containing interstitial atoms have been reported, among them $Nb_4OTe_9I_4$,[2] $Nb_6I_{11}H$,[3] $[M_6S_{17}]^{4-}$ (M = Nb, Ta),[4] $[V_4O(edt)_2Cl_8]^{2-}$ (edt = ethane-1,2-dithiolate),[5] $[Nb_4(\mu_4\text{-}O)(\mu\text{-}Cl)_4\{\mu\text{-}(PhC)_4\}_2Cl_4]^{2-}$,[6] Ta_4SiTe_4[7] and $[Nb_6SBr_{17}]^{3-}$.[8]

The metal atoms in the cuboidal cluster complexes $[M_4(\mu_3\text{-}Q)_4L_n]$ (Q = S, Se, Te; L denotes ligating atoms with either neutral or anionic ligands) with four μ_3-Q bridging chalcogenide ligands generally have enough electrons to support metal–metal bond formation. These cluster complexes are known for a wide variety of transition metals, and they appear to be one of the most important common basic structures of small-sized transition metal cluster complexes.[9] So far only one example of a cubane-type niobium compound $Nb_4Se_4I_4$ has been reported.[10] There are as yet no examples of cuboidal clusters M_4ZQ_4 stabilized by an interstitial atom Z.

In the course of our study on the syntheses and reactivities of solid-state molybdenum and tungsten chalcogenides, we recently obtained new cyanocomplexes with cubane-type W_4S_4, W_4Se_4, W_4Te_4 and Mo_4Te_4 cluster cores.[11] Here we report the synthesis and characterization of the first oxygen-centered cubane-type complex $[Nb_4(\mu_4\text{-}O)(\mu_3\text{-}Te)_4(CN)_{12}]^{6-}$. Tetrameric metal complexes which have a $M_4(\mu_4\text{-}O)(\mu\text{-}L)_6$ core are not uncommmon.[2,12] These complexes are known for a wide variety of metals with six μ-bridging ligands, but they are not known for tetranuclear clusters with four μ_3-bridging ligands (cuboidal complexes).

Dark brown crystals of $K_6[Nb_4(\mu_4\text{-}O)(\mu_3\text{-}Te)_4(CN)_{12}]\cdot KOH\cdot K_2CO_3\cdot 8H_2O$ (**1**)† were obtained in moderate yield by high-temperature reaction of $NbTe_4$ with KCN at 450 °C in a sealed ampoule and further crystallization within 5–7 days from aqueous solution. The source of oxygen was presumed to be water/oxygen contamination of the ampoule/reagents. In related studies it has already been reported that it was almost impossible to obtain an oxide-free product even under rigorous oxygen-free/anhydrous conditions.[2,6,12*d*] Furthermore, hydrolysis and oxidative degradation of KCN may explain the existence of CO_3^{2-} anions in the structure of **1**.

Owing to the presence of H_2O and CO_3^{2-} intense bands were observed in the IR spectra of **1** in KBr or Nujol. The cyanocomplex can be easily identified since it exhibits ν(CN) at 2095 cm^{-1} and also a ν(NbC)/δ(NbCN) band at 410 cm^{-1}.[11*b*,13] Another band in the low-energy region at 510 cm^{-1} belongs to the asymmetrical vibration of the Nb_4O core.[12*c*]

The crystal structure of the compound $K_6[Nb_4(\mu_4\text{-}O)(\mu_3\text{-}Te)_4(CN)_{12}]\cdot KOH\cdot K_2CO_3\cdot 8H_2O$ (**1**) contains two independent cluster anions $[Nb_4Te_4(\mu_4\text{-}O)(CN)_{12}]^{6-}$ with similar geometries (one of which is shown in Fig. 1), carbonate anion, some K^+ cations and solvent water.‡ One K^+ and one O form a pair (K···O of 2.7 Å) which is disordered over two positions with site occupancies 0.643(8) and 0.357(8). The overall content of K^+ in the unit cell is 36 (9 per formula unit). The pH of the solution during crystallization was greater than 7 and therefore the carbonate anion must not be protonated (CO_3^{2-}, not HCO_3^-). This means that we have 7 K^+ per cluster anion and oxygen atoms which may be H_2O or OH^-. Quantum chemical calculations on the diamagnetic compound **1** gave a total cluster anion charge of −6 (see below). In accordance with this, we assume that one of the independent oxygen atoms corresponds to OH^- and the remainder to H_2O. It is possible that OH^- corresponds to the oxygen in the disordered pair $K^+\cdots O$, since their observed interatomic distance is close to that which is found for $K^+\cdots OH^-$ in KOH (2.57–2.83 Å[14]).

The cluster anion (Fig. 1) has a structure which is similar to the well-known $[M_4Q_4(CN)_{12}]^{n-}$ cubane-type clusters (M = Mo, W, Re, Q = S, Se, Te[11,13,15]). As usual, the metal and chalcogen atoms form a distorted cube surrounded by 12 terminal CN ligands. The main difference is the presence of a μ_4-oxygen atom in the center of the Nb_4 tetrahedron with Nb–μ_4-O distances at 1.941(7)–1.98(1) Å. The Nb–Nb distances (3.189(2)–3.211(2) Å) are longer than in those compounds which formally possess a Nb–Nb single bond.[16]

Quantum chemistry calculations for the cluster anion $[Nb_4OTe_4(CN)_{12}]^{6-}$ were performed with the extended Hückel method using the CACAO program.[17] Frontier orbital energies for **1** reveal a substantial gap (0.54 eV) between the 21e MO and the top of the lower-lying non-bonding block as well as a large (1.62 eV) 21e (HOMO)–$18a_1$ (LUMO) separation (Fig. 2). The

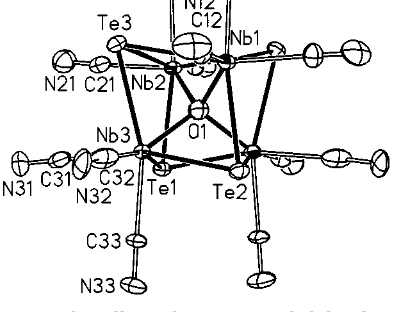

Fig. 1 Anion in **1** (a.d.p. ellipsoids at 50% probability level). All Nb–Nb bonds are omitted for clarity. Some geometrical parameters (Å): Nb–Nb, 3.189(2)–3.211(2), av. 3.202[7]; Nb–μ_4-O, 1.941(7)–1.98(1), av. 1.96[2]; Nb–μ_3-Te, 2.832(2)–2.859(1), av. 2.849[7]; Nb–C, 2.20(2)–2.29(1), av. 2.25[3], C–N, 1.11(2)–1.19(2), av. 1.15[3].

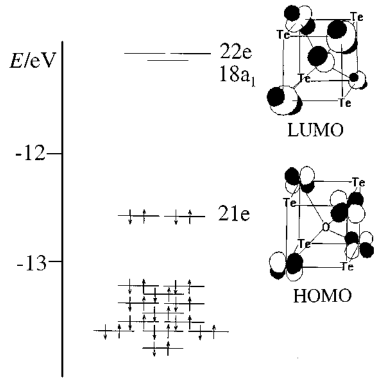

Fig. 2 Extended Hückel MO results for **1**. The corresponding LUMO and HOMO are depicted on the right of the scheme. Only the cluster core Nb_4Te_4O is shown for clarity.

formally non-degenerate $18a_1$ LUMO has both weak Nb–O antibonding and Nb–Nb nonbonding character. The doubly degenerate empty 22e MO, which is very close to $18a_1$ in energy, has a similar bonding pattern. Similarly the degenerate 21e HOMO with a zero contribution of oxygen orbitals is slightly Nb–Nb bonding. The contribution of Te, C and N atomic orbitals in the frontier MOs is negligibly low. According to a bond overlap population analysis Nb–Te bond orders are approximately 1 and Nb–O bond orders are slightly less then 1, generally supporting the model of the centered cubane-like framework tightened with single bonds.

EHMO calculations are in agreement with simple qualitative concepts. Counting oxygen and cyanide as O^{2-} and CN^- and the bridging Te groups as Te^{2-} leads to the formulation $[(Nb^{4+})_4(O^{2-})(Te^{2-})_4(CN^-)_4]^{6-}$, where four electrons are shared by four Nb atoms in the tetrahedral Nb_4 fragment.

Preliminary characterization of the redox behaviour of **1** was performed by cyclic voltammetry (scanning interval: −600 to 1000 mV *vs.* NHE in 0.1 M Na_2SO_4). The oxidation potential occurring at 309 mV has quasi-reversible behaviour. Further oxidation occurring at 900 mV is irreversible.

The authors are grateful to Dr. Davide Proserpio (University of Milano) for the CACAO program package and Dr. M. N. Sokolov for CV experiments. This work was supported by the Russian Foundation for Basic Research (research grants 96-03-33018 and 96-03-32684) and an EU INTAS collaboration (research grant 96-1256).

Notes and references

† *Preparation of* $K_6[Nb_4OTe_4(CN)_{12}]\cdot K_2CO_3\cdot KOH\cdot 8H_2O$ (**1**). $NbTe_4$ was synthesized directly from the elements.[18] A mixture of $NbTe_4$ (2.00 g; 3.31 mmol) and KCN (2.00 g; 30.7 mmol) was heated (450 °C; 48 h) in a sealed Pyrex tube. The product of the reaction was added to 30 ml of water and the mixture was refluxed for 2 h. After filtration, the green-brown solution was allowed to stand at 20 °C for 5–7 days. During this time, the volume was decreased to 3 ml. Dark brown crystals, together with some colourless powder, were isolated by filtration, washed by 60% methanol in order to remove the colourless powder, and dried in air. Yield 0.42 g of $K_6[Nb_4OTe_4(CN)_{12}]\cdot K_2CO_3\cdot KOH\cdot 8H_2O$ (29%). Satisfactory elemental analyses (C, H, N, K, Nb and Te) were obtained. The UV–VIS absorption spectrum of **1** in H_2O gave peak positions [λ/nm (ε/M^{-1} cm^{-1}) per Nb_4] at 450 (1300) and 564 (640). The magnetic susceptibility was measured at 300 K: $\chi_M = -590 \times 10^{-6}$ cm^3 mol^{-1}.

‡ *Crystallography:* a dark brown crystal of $K_6[Nb_4(\mu_3\text{-}Te)_4(\mu_4\text{-}O)(CN)_{12}]\cdot KOH\cdot K_2CO_3\cdot 8H_2O$ (**1**) (0.56 × 0.32 × 0.14 mm) was prepared as described above. X-Ray structural analysis was carried out at room temperature on an Enraf-Nonius CAD4 four-circle diffractometer (MoKα, $\lambda = 0.7107$ Å, graphite monochromator, standard techniques). *Crystal data*: $C_{13}H_{17}K_9N_{12}Nb_4O_{13}Te_4$, $M = 1783.33$, monoclinic, space group $P2_1/m$, $a = 12.4688(9)$, $b = 22.658(4)$, $c = 16.318(2)$ Å, $\beta = 91.584(9)°$, $U = 4608(1)$ Å^3, $Z = 4$, $D_c = 2.570$ g cm^{-3}. A total of 8724 reflections were collected up to $2\theta_{max} = 50°$, of which 8316 were unique ($R_{int} = 0.0144$). Absorption corrections ($\mu = 4.325$ mm^{-1}) were applied by integration from the crystal shape, transmission factors ranging from 0.5629 to 0.2942. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 with an anisotropic approximation using SHELX-97.[19] Hydrogen atoms were not located. One of the potassium cations and one oxygen atom appeared to be disordered. Their occupancy factors were refined together with other parameters. Final R values: $R1 = 0.0490$, $wR2 = 0.1151$ for 5272 $F_o \geqslant 4\sigma(F)$, $R1 = 0.0823$, $wR2 = 0.1347$, GOF = 1.022 for all unique data. CCDC 182/1068. See http://www.rsc.org/suppdata/cc/1998/2579/, for crystallographic files in .cif format.

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Communication 8/05956J