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Synthesis, structures, and properties of the niobium and tantalum telluride cubane clusters $[M_4(\mu_4\text{-O})(\mu_3\text{-Te})_4(CN)_{12}]^{6-}$ (M = Nb or Ta)

V. P. Fedin,[a]* ***I. V. Kalinina,***[a] ***A. V. Virovets,***[a] ***and D. Fenske***[b]

[a]*Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences,*
3 prosp. Akad. Lavrent'eva, 630090 Novosibirsk, Russian Federation.
Fax: +7 (383 2) 34 4489. E-mail: cluster@che.nsk.su
[b]*Institute of Inorganic Chemistry, Karlsruhe University,*
30.45 Engesser Strasse Geb., 76128 Karlsruhe, Germany.
*Fax: +49 (072 1) 66 1921. E-mail: dieter.fenske@chemie.uni-karlsruhe.de**

The new cubane cluster complex $K_6[Ta_4(\mu_4\text{-O})(\mu_3\text{-Te})_4(CN)_{12}]\cdot KOH\cdot 4H_2O$ was prepared from a mixture of $TaTe_4$ and KCN by the high-temperature synthesis followed by crystallization from aqueous solutions. The compound was characterized by cyclic voltammetry, X-ray diffraction analysis, and IR, Raman, and electronic spectroscopy. A comparative study of the clusters $[M_4(\mu_4\text{-O})(\mu_3\text{-Te})(CN)_{12}]^{6-}$ (M = Nb or Ta) containing the μ_4-O ligands was carried out. These clusters are the first molecular chalcogenide cubane complexes of Group V metals.

Key words: niobium, tantalum, cluster complexes, telluride complexes, synthesis, X-ray diffraction analysis, cyclic voltammetry.

The formation of small metal chalcogenide clusters is an important characteristic feature of compounds containing simultaneously polyvalent transition metal atoms and chalcogenide ligands. Homo- and heterometallic chalcogenide cubane clusters are known for a large number of transition metals. These complexes are among the basic structures in the cluster chemistry.[1—9] Generally, the number of electrons beared by the metal atoms in the cubane complexes $[M_4(\mu_3\text{-Q})_4L_n]$ (Q = S, Se, or Te; L is a neutral or anionic ligand) with four μ bridging chalcogenide ligands is sufficient for the formation of the M—M bond in the M_4 tetrahedron. The chemistry of telluride complexes, unlike that of thio and seleno cubane complexes of transition metals, is poorly studied.

The present investigation was undertaken as part of our continuing studies on the synthesis of chalcogenide cluster complexes of the early transition metals. Previously,[10,11] the complete series of the molybdenum and tungsten cubane cluster complexes $[M_4Q_4(CN)_{12}]^{n-}$ (M = Mo or W; Q = S, Se, or Te; n = 5 or 6) has been

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* Institüt für Anorganischen Chemie, Universität Karlsruhe, 30.45 Engesserstraße Geb., 76128 Karlsruhe, Deutschland. Fax: +49 (072 1) 66 1921. E-mail: dieter.fenske@chemie.uni-karlsruhe.de

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synthesized. Only one compound containing the cubane fragment, *viz.*, $Nb_4Se_4I_4$, is known for Group V elements.[12] The latter was prepared by heating the elements and contains the Nb_4Se_4 cubane fragments and the I_4 tetrahedra alternating in the crystal lattice according to the NaCl motif. Recently,[13] we have described the first molecular chalcogenide-bridged niobium cubane complex $[Nb_4(\mu_4\text{-}O)(\mu_3\text{-}Te)_4(CN)_{12}]^{6-}$. A distinguishing feature of the latter is the presence of the μ_4-O ligand in the cubane cluster. In the present study, we synthesized and characterized the analogous tantalum compound and carried out a comparative study of the $[M_4OTe_4(CN)_{12}]^{6-}$ clusters (M = Nb or Ta).

Results and Discussion

The chemistry of transition-metal telluride complexes was less well studied than the chemistry of the corresponding sulfide and even selenide complexes. The synthesis of telluride complexes presents difficulties associated with the fact that many traditional reagents, which are widely used in the solution chemistry of sulfide and selenide complexes (including cluster complexes), cannot be extended to the chemistry of telluride compounds.[7] Thus, H_2Te is unstable, while the mononuclear tetratellurometallates $[MTe_4]^{n-}$ remain unknown.

We have developed[10,11] a new procedure for the synthesis of the telluride-bridged molybdenum and tungsten cubane complexes $[M_4(\mu_3\text{-}Te)_4(CN)_{12}]^{5-/6-}$ from tellurides and tellurohalides of these metals. We used this method also for the preparation of niobium and tantalum cubane complexes from tellurides of these metals (MTe_4).

Heating of MTe_4 with KCN in an evacuated sealed tube at 440—460 °C (M = Nb) or 340—360 °C (M = Ta) afforded a product, which was treated with water in air. In the case of niobium, an intensely colored greenish-brown solution was obtained. Heating of tantalum telluride gave rise to a red-violet solution containing primarily potassium polytelluride, which rapidly decomposed in air to form elemental tellurium, while the solution became bright-red. Single crystals of the $K_6[Nb_4OTe_4(CN)_{12}] \cdot K_2CO_3 \cdot KOH \cdot 8H_2O$ complex (**1**) were obtained by slow evaporation of an aqueous solution in air.[13] Single crystals of the $K_6[Ta_4OTe_4(CN)_{12}] \cdot KOH \cdot 4H_2O$ complex (**2**) were prepared by crystallization using diffusion of methanol into an aqueous solution. Complexes **1** and **2** were obtained in 29 and 7% yields, respectively. The syntheses are well reproducible. The above-mentioned temperature conditions of the syntheses proved to be optimum. Thus only polytelluride was obtained at higher temperature, whereas the metal tellurides did not react with KCN at lower temperature.

According to the X-ray diffraction data, the niobium and tantalum complexes contain the μ_4-O ligands. It can be assumed that the μ_4-O bridges in complexes **1** and **2** were formed a) from H_2O molecules at the stage of treatment of the product obtained in the high-temperature synthesis; b) from H_2O or O_2 molecules adsorbed on walls of the tube and/or on the initial compounds. To test these assumptions, we performed a series of runs in which complexes **1** and **2** were synthesized after removal of adsorbed H_2O and O_2. The tubes with the reagents were heated under high vacuum at 150 °C for 3 h after which either the tubes were immediately sealed or a stoichiometric amount of $H_2{}^{18}O$ was added, the tubes were sealed, and then the experiment was performed as described above. Complexes **1** and **2** were obtained in none of the runs. The addition of $H_2{}^{18}O$ to the product of the high-temperature synthesis did not afford $[M_4(\mu_4\text{-}{}^{18}O)(\mu_3\text{-}Te)_4(CN)_{12}]^{6-}$. Based on these data, it is reasonably safe to suggest that O_2 molecules adsorbed on walls of the tube and/or on the initial compounds served as a source of oxygen involved in complexes **1** and **2**. It should be noted that niobium and tantalum are typical oxophilic elements. Interestingly, the compounds of compositions $Nb_4OTe_9I_4$,[14] $[V_4O(edt)_2Cl_8]^{2-}$ (edt is ethane-1,2-dithiolate)[15] and $[Nb_4(\mu_4\text{-}O)(\mu\text{-}Cl)_4]^{2-}$ (Refs. 16 and 17) also contain the μ_4-O ligands and were prepared either in evacuated sealed tubes or in anhydrous solvents under an atmosphere of inert gas.

The structure of the anionic complex $[Ta_4OTe_4(CN)_{12}]^{6-}$ is shown in Fig. 1. The $[Nb_4OTe_4(CN)_{12}]^{6-}$ complex has an analogous structure.[13] The selected bond lengths in the anionic complexes are given in Table 1. The known cubane clusters $[M_4Q_4(CN)_{12}]^{n-}$ (M = Mo, W, or Re; Q = S, Se, or Te) have virtually the same structure.[1—11,18] In all these molecules, the metal and chalcogen atoms form a distorted cube and each metal atom is additionally coordi-

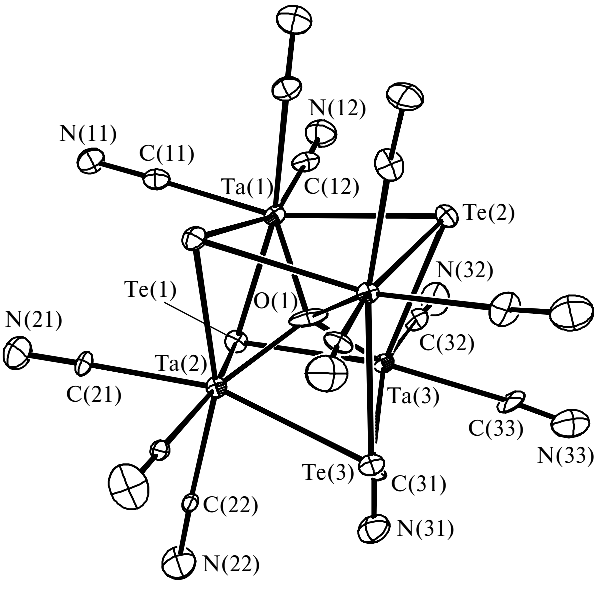

Fig. 1. Cluster anion **2** (the atomic displacement ellipsoids with the 50% probability). The notations are given only for the crystallographically independent atoms.

Table 1. Selected bond lengths (d/Å) in cluster complexes **1** and **2**

Cluster anion	d(M—M)	d(M—Te)	d(M—O)
$[Nb_4OTe_4(CN)_{12}]^{6-}$	3.189(2)—3.211(2) 3.202*	2.842(1)—2.859(1) 2.850*	1.94(1)—1.99(1) 1.96*
$[Ta_4OTe_4(CN)_{12}]^{6-}$	3.191(1)—3.258(1) 3.215*	2.834(1)—2.891(2) 2.861*	1.90(2)—2.00(2) 1.96*

* Average value.

nated by three C atoms of the terminal CN ligands. The Nb_4 and Ta_4 tetrahedra are distorted with the lowering of the ideal symmetry T_d to the crystallographic symmetry C_s. The distinguishing feature of complexes **1** and **2** is the fact that they, unlike the Mo, W, and Re clusters, contain the μ_4-O atom in the center of the tetrahedron. The Nb—O and Ta—O distances are in the ranges of 1.94(1)—1.99(1) and 1.90(2)—2.00(2) Å, respectively. The average M—M distances in complex **2** (3.215 Å) are somewhat longer than those in the niobium analog (3.202 Å). The same regularity is observed for the M—μ_3-Te distances (2.850 and 2.861 Å for M = Nb and Ta, respectively). In both complexes, the M—M distances are substantially longer than those in the corresponding metals and compounds containing the single M—M bond.[19]

The crystal structure of complex **2** is shown in Fig. 2. The K cations have the coordination numbers of 5—6 and are surrounded by the O atoms of the H_2O molecules, the Te atoms, and the N atoms of the CN ligands. The H_2O molecules of solvation and the N atoms of the CN groups are linked by weak hydrogen bonds. The N...O distances are 2.95 Å.

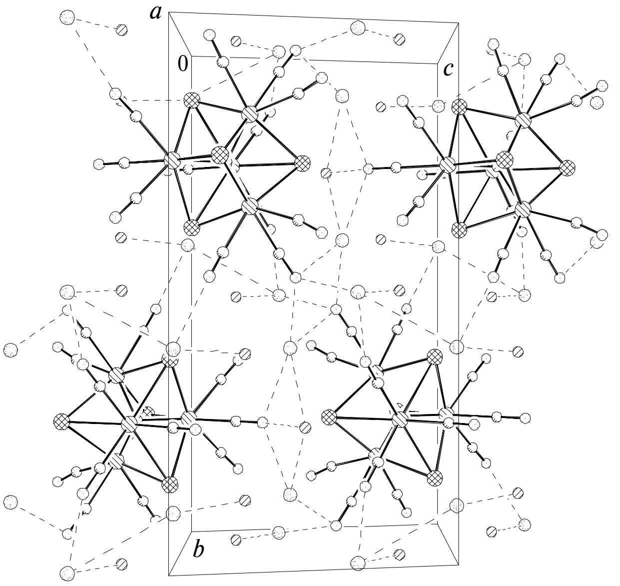

Fig. 2. The crystal packing of complex **2**. The bonds involving the K^+ cations and the hydrogen bonds are indicated by dotted lines. *1*, K^+ cations; *2*, the O atoms of the water molecules and OH^- anions.

Compounds **1** and **2** containing the cluster anions $[M_4OTe_4(CN)_{12}]^{6-}$ are diamagnetic. In the structure of **2**, the charge of the K^+ cations is compensated by the charge of the OH^- anions. Crystallization was carried out in air from solutions at pH ~10, which accounts for the presence of the OH^- anions in the structure. Unfortunately, the quality of the crystals did not allow us to reveal the positions of the H atoms from the X-ray diffraction data. However, analysis of the positions of the K and O atoms and the K—O distances made it possible to locate the K—OH pairs in the structure. In the crystal structure of **2**, there is the ordered K(4)...O(1OH) pair located on a mirror plane (the K—O distance is 2.70(3) Å), which is in agreement with the published data[20] for KOH.

The vibrational spectra of complexes **1** and **2** are similar. The cyano groups are readily identified in the IR spectra based on the ν(CN) stretching vibrations (2095 cm^{-1} for **1**; 2106 and 2101 cm^{-1} for **2**) and also based on the mixed ν(MC)/δ(MCN) vibrations at 410 and 399 cm^{-1} for **1** and **2**, respectively. The stretching vibrations of the M—O fragment are characterized by high intensities in the IR spectra (510 cm^{-1} for **1** and 522 cm^{-1} for **2**) and by low intensities in the Raman spectra.

The electronic absorption spectra of complexes **1** and **2** were measured in water. By analogy with the mononuclear octacyano transition metal complexes, the very intense band in the UV spectra ($\varepsilon \approx 10^4$ $M^{-1} \cdot cm^{-1}$) of **1** and **2** was assigned to CN→M charge-transfer bands. The visible region of the spectra has two bands at 450 and 564 nm and at 426 and 541 nm for complexes **1** and **2**, respectively. The absorption bands of the tantalum complex are shifted to the UV region. An analogous tendency is observed on going from the molybdenum telluride cubane complexes to the corresponding tungsten complexes.[11]

An important characteristic feature of the molybdenum and tungsten chalcogenide cubane complexes $[M_4Q_4(CN)_{12}]^{n-}$, which we have studied previously, is the redox conversions of the complexes with n = 6, 7, or 8. The electrochemical behavior of complexes **1** and **2** was studied by cyclic voltammetry in aqueous solutions. Complex **1** underwent quasi-reversible one-electron oxidation at 309 mV, which corresponds to the formation of $[Nb_4OTe_4(CN)_{12}]^{5-}$ in solution.

$$[Nb_4OTe_4(CN)_{12}]^{5-} + e \rightleftarrows [Nb_4OTe_4(CN)_{12}]^{6-}.$$

When the potential was increased to 900 mV, the niobium cluster underwent further irreversible oxidation accompanied by its decomposition. One-electron oxidation of complex **2** was not observed and only irreversible oxidation occurred at E = 642 mV.

Quantum-chemical calculations for the cluster anions $[M_4OTe_4(CN)_{12}]^{6-}$ (M = Nb or Ta) were carried out by the extended Hückel method using the CACAO program. The results of calculations for complexes **1** and **2** are qualitatively identical. The energy diagram of the molecular levels in $[M_4OTe_4(CN)_{12}]^{6-}$ is shown in Fig. 3. First, noteworthy are a substantial difference in the energies of HOMO (21e) and the lower-lying block of the occupied MOs and a large difference (~1.6 eV) in the energies of HOMOs (21e) and LUMOs ($18a_1$). The highest occupied molecular orbitals (21e) are doubly degenerate, contain four electrons, are weak M—M bonding in character, and have no contribution of the oxygen orbitals. The formally nondegenerate $18a_1$ LUMOs are simultaneously weak M—O antibonding and M—M nonbonding. The doubly degenerate unoccupied 22e MOs are energetically similar to $18a_1$ LUMOs. The doubly degenerate HOMOs (21e) have no contribution of the oxygen orbitals and belong to M—M weakly bonding MOs; LUMOs are occupied and contain four electrons, which agrees well with the diamagnetism of the compounds. The contribution of the atomic orbitals of Te, C, and N to the frontier orbitals is insignificant. According to the results of quantum-chemical calculations, the orders of the M—Te and M—O bonds are close to unity.

The results of quantum-chemical calculations agree well with the simple ionic model of the $[M_4OTe_4(CN)_{12}]^{6-}$ clusters. Within the framework of this model, the metal atoms are in the formal oxidation state +4 and the M_4 cluster has four electrons. This conclusion is consistent with the X-ray diffraction data for the $[M_4OTe_4(CN)_{12}]^{6-}$ complexes, where the M—M bonds are substantially longer than the usual single M—M bonds.

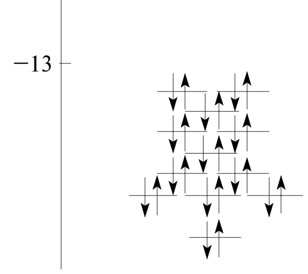

Fig. 3. Energy diagram of the molecular levels in the $[M_4(\mu_4\text{-}O)(\mu_3\text{-}Te)(CN)_{12}]^{6-}$ complexes.

Therefore, the molecular niobium and tantalum chalcogenide clusters $[M_4OTe_4(CN)_{12}]^{6-}$ belong to a new structural type of cubane cluster complexes of transition metals. Four metal atoms in the niobium and tantalum complexes, unlike those in the molybdenum, tungsten, and rhenium chalcogenide complexes, form covalent bonds with the μ_4-O atom located inside the M_4Q_4 cube.

Experimental

The reagents of analytical grade were used. Compound **1** was prepared according to a procedure described previously.[13] Tantalum tetratelluride was prepared by heating a mixture of the elements with a 15% excess (with respect to the stoichiometric amount) of Te in a quartz tube at 740 °C.[21] Elemental analysis was performed at the Laboratory of Microanalysis of the Novosibirsk Institute of Organic Chemistry of the Siberian Branch of the Russian Academy of Sciences. The IR spectra were recorded on a Bruker IFS-85 Fourier spectrometer in KBr pellets. The Raman spectra were measured on a Triplemate SPEX spectrometer equipped with a CCD detector and a microscope for recording inverse scattering; the He—Ne laser excitation wavelength was 632.8 nm. The electronic absorption spectra in the region of 200—900 nm were recorded on a Shimadzu UV-1202 spectrophotometer. The magnetic susceptibility was measured at 25 °C using the Faraday method. The representability of the single crystals was proved by comparing the theoretically calculated diffraction patterns with those obtained experimentally (Philips APD 1700 diffractometer, Cu Kα radiation, 2θ = 5—60°). The cyclic voltammetric measurements were carried out on a CV-50W instrument at 25 °C in an aqueous solution of K_2SO_4 (0.1 mol L^{-1}) with a scan rate of 100 mV s^{-1}. The solutions of the complexes (the concentrations were 10^{-3} mol L^{-1}) were degasses by passing a stream of N_2. The reference electrode (Ag/AgCl) was calibrated against the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ pair. All potentials are given relative to the standard hydrogen electrode.

Heptapotassium dodecacyanotetra-μ_3-telluro-μ_4-oxotetratantalate(Ta-Ta) hydroxide tetrahydrate, $K_7[Ta_4OTe)_4(CN)_{12}](OH)\cdot 4H_2O$ (2). A mixture of $TaTe_4$ (3.00 g) and KCN (3.00 g) was placed in a tube. The tube was evacuated for 3 min to the residual pressure of 10^{-1} Torr and sealed. Then the reaction mixture was heated in an evacuated sealed tube at 350 °C for 48 h. The reaction product was heated with water (30 mL) at 65—70 °C for 2 h. The resulting colored solution was filtered. Dark crystals of complex **2** were prepared by diffusion of MeOH into the filtrate. The compound was washed with MeOH (30 mL) and dried in air. The yield was 0.17 g (7%). Found (%): C, 7.46; H, 0.45; N, 8.43. $C_{12}H_9K_7N_{12}O_6Ta_4Te_4$. Calculated (%): C, 7.49; H, 0.47; N, 8.73. IR, ν/cm^{-1}: 3240 (s, broad), 2106, 2101 (s), 1633 (m, broad), 536 (s), 399 (s). The electronic absorption spectrum in water, λ/nm (ε/cm^{-1} mol^{-1}): 426 (3740) and 541 (1715). The magnetic susceptibility is $-680\cdot 10^{-6}$ cm^3 mol^{-1}.

X-ray diffraction study of complex 2. The crystallographic characteristics and details of X-ray diffraction study are given in Table 2. The X-ray data for a dark needle-like single crystal of **2** (0.02×0.3×0.92 mm) were collected according to a conventional technique on an automated four-circle STOE STADI4 diffractometer (Mo-Kα, λ = 0.7107 Å, graphite monochroma-

Table 2. Principal crystallographic characteristics and details of X-ray diffraction study for cluster **2**

Parameter	Value
Molecular formula	$C_{12}H_9K_7N_{12}O_6Ta_4Te_4$
Molecular weight	1925.21
System	Monoclinic
Space group	$P2_1/m$
Z	2
a/Å	9.9409(11)
b/Å	18.837(2)
c/Å	10.1249(15)
β/deg	101.917(14)
V/Å^3	1855.1(4)
d_{calc}/g cm^{-3}	3.447
T/K	209
$2\theta_{\max}$/deg	50
Number of measured /independent reflections	3563/3363
Number of observed reflections ($F_{hkl} \geq 4\sigma(F)$)	2808
R_{int}	0.0590
λ/Å	0.71073
μ/mm^{-1}	15.672
R_1 for observed reflections	0.0429
wR_2 for all reflections	0.1196
GOF for all reflections	1.159

tor) at 209 K. The intensities of reflections were measured using the standard $\theta/2\theta$ scanning technique to $2\theta_{\max} = 50°$ in the region of indices $-14 \leq h \leq 14$, $0 \leq k \leq 26$, $0 \leq l \leq 19$ for **1** and $-11 \leq h \leq 11$, $0 \leq k \leq 22$, $0 \leq l \leq 12$ for **2**. The absorption corrections were applied using the azimuth scanning curves. The structure was solved by the direct method and refined anisotropically by the full-matrix least-squares method using the SHELX-97 program package.[22] The X-ray diffraction data set, the information on details of X-ray study, and the complete tables of the atomic coordinates, bond lengths, and bond angles can be obtained from the authors. The tables of the atomic coordinates, bond lengths, and bond angles were deposited with the Cambridge Structural Database.

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