Synthesis and Structure of $Mo_3Te_{10}I_{10}$ containing TeI_3^- Ligands coordinated to a Triangular Cluster Fragment $[Mo_3(\mu_3\text{-}Te)(\mu_2\text{-}Te_2)_3]^{4+}$

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High-temperature reaction of molybdenum, tellurium and iodine produces $Mo_3Te_{10}I_{10}$, which contains triangular cluster fragment $[Mo_3(\mu_3\text{-}Te)(\mu_2\text{-}Te_2)_3]^{4+}$ and three TeI_3^- ligands.

The coordination chemistry of inorganic telluride ligands with their larger size, diffuse orbitals and increased metallic character is quite undeveloped in comparison with inorganic sulfide (and also selenide) coordination chemistry.[1–4] This is true both for molecular and solid-state compounds. Halide sulfides and halide selenides of the transition metals, which simultaneously contain metal–chalcogen and metal–halogen bonds, often form isotypic series, in which the different halogen and chalcogen atoms can replace each other without changing the structure type.[5–7] An excellent example for this are compounds with the formula $M_3Y_7X_4$ (M = Mo, W; Y = S, Se; X = Cl, Br, I). All these triangular cluster compounds which have a single μ_3-chalcogenido and three μ-dichalcogenido bridging ligands have been prepared either by direct combination of the elements or by reactions of the lower molybdenum/tungsten halides with the chalcogens.[7–11] These chain-like solid-state compounds were found to be excellent starting materials for the preparation of molecular clusters by extrusion. The corresponding tellurium compounds (both molecular or solid-state) are unknown.[4]

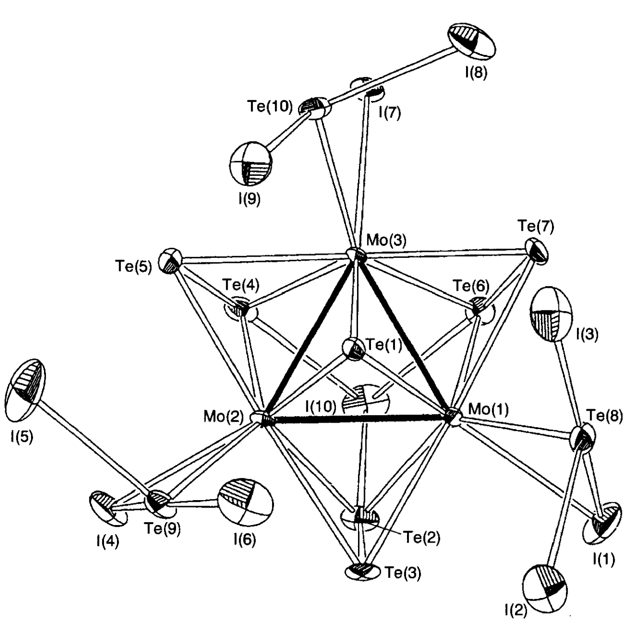

Fig. 1 ORTEP drawing of $[Mo_3Te_7(TeI_3)_3]I$ **1** showing the atom labelling scheme. All atoms are represented by the thermal ellipsoids at the 50% probability. Selected interatomic distances (Å): Mo(1)–Mo(2) 2.851(3), Mo(1)–Mo(3) 2.851(3), Mo(2)–Mo(3) 2.860(3), I(1)–Te(8) 3.048(2), I(1)–Mo(1) 2.869(2), I(2)–Te(8) 2.739(3), I(3)–Te(8) 2.828(3), I(4)–Te(9) 3.080(2), I(4)–Mo(2) 2.882(2), I(5)–Te(9) 2.748(3), I(6)–Te(9) 2.794(2), I(7)–Te(10) 3.047(2), I(7)–Mo(3) 2.876(2), I(8)–Te(10) 2.748(2), I(9)–Te(10) 2.811(2), I(10)–Te(2) 3.259(2), I(10)–Te(4) 3.346, I(10)–Te(6) 3.316(2), Te(1)–Mo(1) 2.661(2), Te(1)–Mo(2) 2.659(2), Te(1)–Mo(3) 2.663(2), Te(2)–Te(3) 2.710(2), Te(2)–Mo(1) 2.755(2), Te(2)–Mo(2) 2.737(2), Te(3)–Mo(1) 2.769(2), Te(3)–Mo(2) 2.839(2), Te(4)–Te(5) 2.705(2), Te(4)–Mo(2) 2.770(2), Te(4)–Mo(3) 2.727(3), Te(5)–Mo(2) 2.773(2), Te(5)–Mo(3) 2.844(2), Te(6)–Te(7) 2.699(2), Te(6)–Mo(1) 2.738(2), Te(6)–Mo(3) 2.760(2), Te(7)–Mo(1) 2.837(2), Te(7)–Mo(3) 2.778(2), Te(8)–Mo(1) 2.789(2), Te(9)–Mo(2) 2.791(2), Te(10)–Mo(3) 2.787(2).

Our recent efforts have been therefore focusing on the development of a high-temperature technique to synthesize solid-state molybdenum/tungsten telluride halides and to prepare molecular telluride clusters by extrusion. Some pioneering work has been done for investigation of M/Te/X systems and the results demonstrate that the compounds built from tellurium polycations and halide metalate anions dominate in these ternary systems.[4,12,13] Halide tellurides are in minority and examples for molybdenum and tungsten are (*i*) $Mo_4Te_7X_8$ (X = Cl, Br) with $Mo_2(Te_2)_3(TeX)$ chains,[4] (*ii*) $W_2O_2Te_4Br_5$ with $(WOTe_4Br)_n$ chains,[4] and (*iii*) octahedral cluster compounds $[Mo_6X_7Te]X_{6/2}$ (X = Cl, Br, I)[14] and $[Mo_6Te_{8-n}X_n]$ (*n* = 1–3).[15]

Reported in this communication is the preparation and crystal structure of a new tellurium-rich triangular cluster compound $Mo_3Te_{10}I_{10}$ **1** formally containing TeI_3^- ligands coordinated to molybdenum atoms of the cluster fragment $Mo_3Te_7^{4+}$. Compound **1** can be obtained in moderate yield by reaction of molybdenum, tellurium and iodine (3 : 10 : 10) together with other (mostly still unidentified) reaction products.[†] Compound **1** is diamagnetic and air-stable. Although $Mo_3Te_{10}I_{10}$ exists as a discrete ion pairs $[Mo_3Te_{10}I_9]^+I^-$ (see below), it does not dissolve in organic solvents such as THF, MeCN or DMF. High-yield synthesis of the triangular cluster $[Mo_3Te_7(CN)_6]^{2-}$ by reaction of the title compound with KCN proves the existence of the Mo_3Te_7 cluster fragment in **1**.[16]

The structure of **1** has been determined by single-crystal X-ray diffraction.[‡] The structure is shown in Fig. 1.

The three Mo atoms almost define an equilateral triangle with an apical Te(1) atom [Mo-μ_3-Te(1) = 2.66 Å]. The Te_2 ligands have asymmetrical coordination with respect to the Mo_3 plane (equatorial Te(3), Te(5), Te(7) atoms and axial Te(2), Te(4), Te(6) atoms). The average Te_{eq}–Te_{ax} distances in the Te_2 ligands are normal at 2.71 Å. The three μ_2–Te_2 ligands are strongly tilted toward the Mo_3 plane and three axial tellurium atoms form a cavity. The short contacts $3Te_{ax}\cdots I(10)$ (3.26–3.35 Å) result in the formation of the ion pairs $[Mo_3Te_7(TeI_3)_3]^+I^-$. Such an arrangement of the metal and chalcogen atoms and also $3Y_{ax}\cdots Z$ (Z-atom with lone electron pair) short contacts are typical of the $M_3Y_7^{4+}$ (M = Mo, W; Y = S, Se) fragments.[17,18]

The three molybdenum atoms of compound **1** are bound to terminal TeI_3^- ligands in an unusual fashion. In the TeI_3^- ligands, the adjacent Te and I atoms, are bound to Mo atoms (*trans* position in respect to the apical Te(1) atom for I and *cis* position for Te), while the other terminal I atoms are left alone. Owing to this mode of coordination the angles TeMoI (65.3°) in compound **1** are smaller by 10–15° compared with the angles LMoL of the known $Mo_3Y_7L_6$ (Y = S, Se) compounds.[18,19] Tellurium atoms of the ligands TeI_3^- have trigonal bipyramidal geometry as predicted from VSEPR model consideration. The distortion of the polyhedron around the Te atom is caused by coordination to Mo and by the stereochemically active equatorial lone pair directed from the Te atom toward a vertex of the trigonal bipyramidal polyhedron. This mode of coordination for the TeI_3^- ligands has a pronounced effect on the $Mo_3Te_7^{4+}$ fragment so it has two substantially different types of Mo–Te_{eq} bond lengths (2.77 and 2.84 Å). The Te–I distances (3.05 Å) of the triangular MoTeI are rather long in comparison with Te–I bond lengths of 2.74–2.83 Å for the terminal I atoms of the ligands TeI_3^-, but still shorter than Te–I bond lengths of 3.061 and 3.215 Å in the central four-membered Te_2I_2 ring of compound $Te_2I_6^{2-}$.[20]

As compared to the chemistry of the Te^{IV} halides, knowledge of the corresponding halides with oxidation number +2 is less well developed.[20] Recently, the first example of the complex $Nb_2Te_8I_{12}$ with halotellurate(II) ligands $Te_2I_6^{2-}$ has been described.[21] To the best of our knowledge the structure of discrete T-shaped TeI_3^- is unknown and compound **1** is the first structurally characterized compound with TeI_3^- ligands.

The bonding in diamagnetic **1** can be rationalized in a straightforward manner. Counting iodine and tellurium as I^- and Te^{2-}, the Te_2 groups as Te_2^{2-}, and TeI_3 ligands as TeI_3^- leads to the formulation $[(Mo^{4+})_3(Te^{2-})(Te_2^{2-})_3(TeI_3^-)_3]^+I^-$, where six electrons are shared by three Mo atoms. In fact, the Mo–Mo bond distances in **1** (2.85–2.86 Å) are in good agreement with formal Mo–Mo single bond distances of the other $Mo_3Y_7^{4+}$ (Y = S, Se) triangular thio (2.71–2.76 Å)[17,18] and seleno (2.75–2.79 Å)[19] cluster compounds.

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Footnotes

† A mixture of Mo (1.00 g; 10.4 mmol), Te (4.43 g; 34.7 mmol) and I_2 (4.41 g; 17.4 mmol) was heated (395 °C; 48 h) in a sealed tube. The dark well-formed crystals of **1** were selected manually from the reaction mixture; Yield: 1.77 g (18%). Satisfactory elemental analyses were obtained. The magnetic susceptibility was measured at room temp.: $\chi = -0.37 \times 10^{-6}$ $cm^3\ g^{-1}$ (MSB-AUTO, Sherwood Scientific Ltd.).

‡ *Crystal data* for $Mo_3Te_{10}I_{10}$: triclinic, space group $P\bar{1}$, a = 10.792(2), b = 17.152(3), c = 10.717(2) Å, α = 103.54(1), β = 113.09(1), γ = 83.68(1)°, V = 1773.7(5) $Å^3$, D_c = 5.30 g cm^{-3}, μ(Mo-Kα) = 178 cm^{-1}, Z = 2, λ = 0.71073 Å, dark-red prismatic crystal, dimensions 0.20 × 0.20 × 0.20 mm^3, data collection at room temp. on a Rigaku AFC 7R diffractometer, empirical absorption correction based on azimuthal scans of several reflections, 10315 unique reflections of which 6513 are observed [with $I \geq 5\sigma(I)$; structure solved by direct methods and refined by full-matrix least squares procedures with R = 0.061 and R_w = 0.055.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Fachinformationszentrum Karlsrühe. See Information for Authors, Issue No. 1.

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