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Crystal and Molecular Structure of the Tetra-tetrahydrothiophene Adduct of $Nb_2Br_4S_3$: a Species containing a Single Metal–Metal Bond and a Nb–μ–S–μ–(S_2)–Nb Bridge

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The reaction of the sulphur halides MX_3S (M = Nb or Ta X = Cl or Br) with an excess of tetrahydrothiophene (tht) yields non-stoicheiometric products and it is believed complex redox reactions take place [1]. From the reaction of $TaBr_3S$ with tht (1:2 molar ratio in CS_2) $TaBr_3S{\cdot}2tht$ molecules were obtained and established as octahedral monomers by X-ray crystallographic studies [2]. A similar reaction with $NbBr_3S$ follows a more complex route two products being formed one red and the other green. Although both products are readily obtained and can be recrystallised from CS_2 it is difficult to separate them by chemical methods. However a crystal of the green material was isolated and a single crystal study executed which showed it to be $Nb_2Br_4S_3{\cdot}4tht$.

The compound $Br_4C_{16}H_{32}Nb_2S_7$ (Mol. Wt. = 954.13) crystallizes as green parallelopipeds in the triclinic system, space group $P\bar{1}$ with a = 11.826(17), b = 12.021(15), c = 10.813(15) Å, α = 101.4(1), β = 96.2(2), γ = 98.8(2)°, U = 1473.30 Å^3, D_m = 2.20(5) g cm^{-3}, D_c = 2.15 g cm^{-3}, Z = 2. The intensities of 1866 reflections ($2\theta < 40°$) were measured on a diffractometer using zirconium filtered Mo-K_α radiation and the stationary crystal-stationary counter technique. Of these reflections 1522 were used in the final refinement which led to a conventional R factor of 0.061.

The asymmetric unit contains a discrete $Nb_2Br_4S_3{\cdot}4tht$ molecule (Fig. 1) which has approximate C_{2v} symmetry with the two fold axis running through the midpoint of the S_2 moiety and the bridging sulphur atom. As well as being bonded to two bromine atoms [mean Nb–Br = 2.609(6) Å] and two sulphur atoms of tetrahydrothiophene molecules [mean Nb–S = 2.721(12) Å], the metal atoms are bridged by a sulphur atom [mean Nb–S = 2.333(11) Å] and a S_2 group [mean Nb–S = 2.487(12) Å]. The arrangement about each metal atom of the midpoint of the S_2 group and the three sulphur and two bromine atoms to which it is bonded is approximately octahedral.

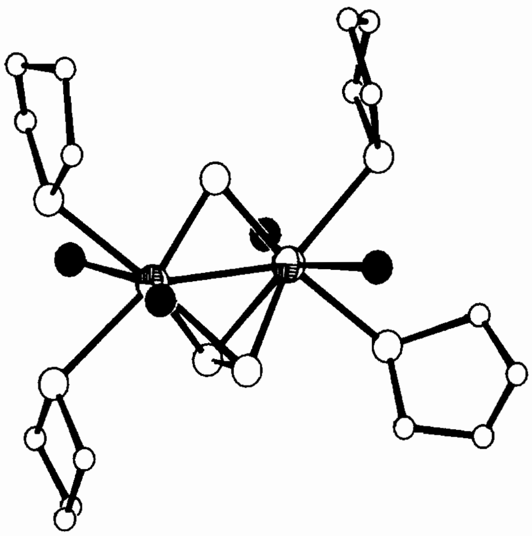

Fig. 1. Hashed circles Niobium; closed circles bromine; open circles large sulphur, small carbon.

The niobium atoms are pushed out of the plane of the four bromine atoms [0.17, 0.16 Å] away from the bridging sulphur atom and towards the S_2 group.

There is a small fold in the Nb_2S_3 bridge. The angle between the planes formed by the two niobium atoms with the bridging sulphur atom and the midpoint of the S_2 moiety is 4.9°.

There is evidence for the existence in the molecule of a single metal–metal bond, thus the four bromine atoms are pushed away from the bridge (Br–Nb–Br = 148.2° and 145.9°) and the niobium–niobium distance is 2.8371(7) Å. The metal–metal distance we believe indicates the presence of a single–single metal bond for while it is shorter than those found in $NbCl_2S_2$ (2.90 Å) [3] and in $NbCl_4$ [3.029(2) Å] [4], these two exist as chain structures with alternate short-long niobium distances. Furthermore the distance reported here is considerably longer than the niobium–niobium double bond distances found in the discrete $Nb_2Cl_9^{3-}$ (2.70 Å) [5] and $Nb_2Br_6{\cdot}3tht$ [2.728(5) Å] [6] species.

The sulphur–sulphur distance [2.014(15) Å] is shorter than that observed for ionic S_2^{2-} in Na_2S_2 (α form 2.20, β form 2.15 Å [7]) but is comparable with sulphur–sulphur distances for a number of bridging S_2 groups [$NbCl_2S_2$, 2.03 Å [3]; $\{(S_2)_2\text{-}Mo\text{–}(\mu S_2)_2\text{–}Mo(S_2)_2\}^{2-}$, 2.035(6) to 2.063(6) Å [8]; $Mo_2Cl_4Cl_{4/2}\text{–}(\mu S_2)_2$, 1.98 Å [9]; $Mo_3Cl_4(\mu\text{-}S_2)_3$, 20.3 Å [9]].

The crystal structure reported here illustrates an added complexity to the chemistry of the sulphido–halides of the transition metals not found for the related oxohalides namely the ability of sulphur bound to a metal to undergo oxidation with consequent reduction of the metal. Thus from $NbBr_3S$ which contains Nb(V) and S^{2-}, a species containing Nb(IV) and a S_2^{2-} unit has been isolated [10].

The isolation of the Nb(IV)–μ(S)–μ(S_2)–Nb(IV) bridge is interesting as it relates to recent studies on NbS_3 and $NbSe_3$. These two trichalcogenides exist as trigonal prismatic chain structures in which the chalcogenide atoms form approximate isosceles triangles with two long and one short side (NbS_3 short S–S 2.05 Å, long S–S from 3.32 to 3.78 Å [11], $NbSe_3$ short Se–Se 2.374, 2.485 Å [12]) suggesting the structures should formally be considered as Nb(IV)(Y^{2-})(Y_2^{2-}) (Y = S or Se). This idea is supported by studies of the electronic structure of $NbSe_3$ [13] and the discovery of Nb(IV)–μ(S)–μ(S_2)–Nb(IV) in the molecule reported here where the S_3 triangle has sides of 2.014(14), 3.740(14) and 3.802(14) Å.

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