# Redox Chemistry of Niobium Chalcogenide Halides: a Mixed Valency $Nb^{III}/Nb^{IV}$ Tetramer. Preparation and Crystal Structure of a (μ-Diselenido-μ-selenido)-tetraniobium Complex, $Nb_4Br_{10}Se_3(NCMe)_4$

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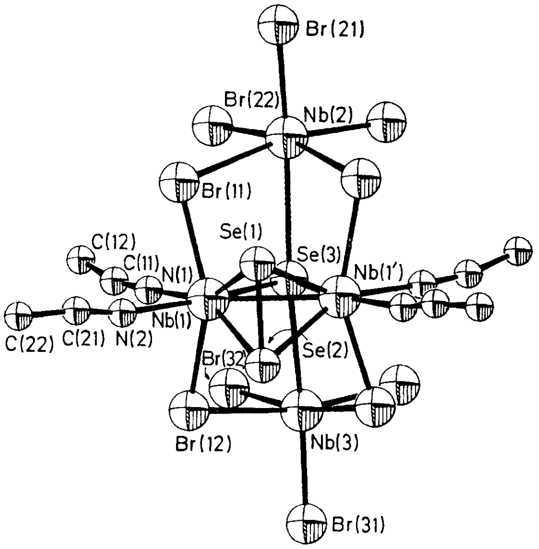
*Summary* The reaction of $NbBr_4(NCMe)_2$ with $Sb_2Se_3$ in MeCN solution yields a tetranuclear adduct $Nb_4Br_{10}Se_3(NCMe)_4$, in which two of the metal atoms have a valence state of four, the remaining two being tervalent; in the adduct the niobium(III) atoms are not involved in any metal–metal interaction and, since the compound is diamagnetic, they must have a doubly occupied $d_{z^2}$, ground state electronic configuration.

FEW reports exist of single crystal studies of halogeno-niobium-(III) or -(IV) adducts. Recently we reported the synthesis of the cyanomethane adducts of the niobium(IV) compounds $NbX_2S$ (X = Cl or Br) and the crystal structure of the chloro-compound, which exists as a sulphur-bridged dimer of formula $[\{NbCl_2S(NCMe)_2\}_2]$.[1] I.r. evidence suggests that the bromo-complex possesses the same type of structure. In an attempt to prepare the selenium analogue we allowed $NbBr_4(NCMe)_2$ to react with $Sb_2Se_3$ (3 : 1 molar ratio) in MeCN solution. We noted that even after stirring the mixture for some weeks at room temperature there appeared to be some unchanged $Sb_2Se_3$ left in the reaction mixture. Even heating the system for a prolonged period (50 °C for 7 days) did not produce any visible diminution in the quantity of $Sb_2Se_3$. Crystals of the niobium product from the reaction mixture were obtained, free from the antimony products, by the use of vacuum filtration and anaerobic recrystallisation techniques. Examination of these crystals by single crystal *X*-ray methods showed that they contained a tetranuclear niobium compound in which the metal exhibited valence states of plus three and plus four.

*Crystal data:* $Nb_4Br_{10}Se_3C_8H_{12}N_4$ $M$ = 1571·7, orthorhombic, space group *Pcmn* (No. 62), $a$ = 10·66(1), $b$ = 15·03(1), $c$ = 23·34(1) Å, $U$ = 3739·37 Å$^3$, $D_m$ = 2·82 g cm$^{-3}$, $D_c$ = 2·81 g cm$^{-3}$, $Z$ = 4. 1451 independent reflections above background with $2\theta < 45°$ and $I > 2\sigma(I)$ were collected on a diffractometer and refined to $R$ 0·104.† Heavy atoms were refined anisotropically, while the nitrogen and carbon atoms were refined isotropically.



FIGURE

The structure consists of four discrete tetranuclear adducts [formula $Nb_4Br_{10}Se_3(NCMe)_4$] in the unit cell and their structure is given in the Figure along with the atomic numbering scheme. The adduct has a crystallographically imposed mirror plane that passes through the three selenium atoms, Nb(2), Nb(3), Br(21), and Br(31). The molecule is best visualised as consisting of a central $(MeCN)_2Br_2Nb$-$\mu$-$(Se_2)$-$\mu$-Se-$NbBr_2(NCMe)_2$ fragment linked by bridging atoms to two $NbBr_3$ units. In the central fragment the two niobium atoms are bridged by a selenium atom [Nb–Se(3) 2·469(12)] and an $Se_2$ group [Nb–Se 2·585(13), 2·574(14) Å]. The arrangement about each metal atom of the mid-point of the $Se_2$ group, the bridging Se atom, the two Br atoms, and the two MeCN nitrogen atoms is approximately octahedral. The shared octahedral edge between the two metal atoms is defined by the mid-point of the $Se_2$ group and the Se atom. The niobium–niobium distance is 2·886(1) Å indicative of a niobium–niobium single bond [*cf.* $Nb_2Cl_4(Y_2)_2$ 2·871(4) Y = S,[2] 2·973(4) Y = Se,[2] and 2·837(1) Å in $Nb_2Br_4S_3(tht)_4$,[3] (tht = tetrahydrothiophen)]. Thus this central fragment contains two $Nb^{IV}$ atoms and so is the first reported species in which two $Nb^{IV}$ atoms are linked by a metal–metal bond together with $Se_2$ and Se bridging atoms. However, a related sulphur system is seen in $[Nb_2Br_4(S_2)S(tht)_4]$.[3] The most interesting aspects about the structure reported here are presented by the two $NbBr_3$ groups that are linked to the central fragment *via* long bridging bonds formed by the bromine atoms of $(MeCN)_2Br_2Nb^{IV}$-$\mu$-$(Se)_2$-$\mu$-Se–$Nb^{IV}Br_2(MeCN)_2$ [3·125(11) and 3·195(11) Å] and Se(3) [3·086(17) to Nb(2), 3·095(17) Å to Nb(3)]. Thus Se(3) is bound to all four niobium atoms within the cluster, being also 2·469(12) Å from Nb(1). Around Nb(2) and Nb(3) the bridging bromine atoms and Se(3) form a *fac* arrangement in the approximate octahedral geometry exhibited by these metal atoms. The remaining three positions in the co-ordination sphere of these atoms are filled by terminally bonded bromine atoms [Nb–Br range 2·504(25) to 2·545(17) Å]. As expected, the angles within the *fac* Nb-$Br_3$(terminal) groups [95·0(5) to 96·2(5)°] are larger than those within the Nb–$Br_2$Se unit [71·2(3) to 80·0(3)°]. Neither Nb(2) nor Nb(3) is within bonding distance of another metal atom, so this structure represents the first characterised niobium(III) halogeno-complex without metal–metal interaction.

Having accidently synthesised $Nb_4Br_{10}(Se_2)Se(NCMe)_4$, we attempted a direct synthesis under the conditions given in equation (1).

$$4NbBr_4(NCMe)_2 + Sb_2Se_3 \xrightarrow[50\ °C,\ 7\ d]{MeCN} Nb_4Br_{10}(Se_2)Se(NCMe)_4 + 2SbBr_3 \quad (1)$$

The product from the reaction was shown to be isomorphous with the sample whose structure had been determined, and its elemental analysis agreed with the proposed formulation. The sample was e.s.r.-inactive over the temperature range −195·8 to 20·0 °C and diamagnetic. These observations are in accord with the two niobium(III) atoms being in an approximately $C_{3v}$ environment and having a low lying and doubly occupied $d_{z^2}$ orbital, and the two niobium(IV) atoms exhibiting a metal–metal interaction.

The preparation reported here provides further insight into the redox chemistry of the niobium chalcogenide halides; while $Sb_2S_3$ reacts with $NbBr_4(NCMe)_2$ to yield the niobium(IV) compound $(MeCN)_2Br_2Nb$–$(S)_2$–$NbBr_2(NCMe)_2$, with no change in oxidation state of the sulphur atoms, $Sb_2Se_3$ and $NbBr_4(NCMe)_4$, in contrast, are involved in a redox process in which formally two $Se^{2-}$ ions form an $(Se_2)^{2-}$ ion with the concomitant release of two electrons that reduce two niobium(IV) atoms to niobium(III).

We thank the S.E.R.C. for their financial support (to A. J. B.) and Mr. A. Johans for help with the crystallography.

(*Received*, 18*th September* 1981; *Com.* 1108.)

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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