Studies of Niobium Selenido-halides: Crystal Structure of $[Nb_2Cl_4(Se_2)_2(SMe_2)_4]$ †

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The reactions of $[NbCl_3Se]$ with the sulphur-donor ligands dimethyl sulphide (dms), tetrahydrothiophen (tht), and 1,2-bis(phenylthio)ethane(bpte), and the reaction of $[NbBr_3Se]$ with tht under moisture- and oxygen-free conditions are described. The reactions gave insoluble products with analyses close to those expected for 1 : 2 (dms, tht) or 1 : 1 (bpte) adducts. Recrystallisation of the product from the reaction of $[NbCl_3Se]$ with dms, nominally ' $NbCl_3Se{\cdot}2dms$ ', yielded the niobium(IV) compound $[(dms)_2Cl_2Nb(Se_2)_2NbCl_2(dms)_2]$ whose structure has been determined. Crystals are monoclinic, space group $P2_1/n$ with $a = 8.366(10)$, $b = 13.121(14)$, $c = 11.204(14)$ Å, $\beta = 99.53(10)°$, and $Z = 2$. 1 855 Reflections above background were collected on a diffractometer; the structure was solved by direct methods and has been refined to $R = 0.068$. The structure contains centrosymmetric dimers in which each niobium atom is bonded to two chlorine atoms [Nb–Cl 2.527(5), 2.510(5) Å], four selenium atoms in two bridging Se_2^{2-} groups [Nb–Se 2.638(2), 2.630(2), 2.640(2), 2.625(3) Å], and two sulphur atoms from the dms group [Nb–S 2.739(4), 2.739(4) Å].

A large number of niobium–selenium–halogen phases have been discovered but only recently have a few been characterised. From the reaction of niobium, niobium(IV) halides, and selenium in quartz ampoules, compounds with compositions $NbXSe_3$, Nb_3XSe_{12}, $Nb_2X_2Se_2$, and $Nb_3X_7Se_5$ (X = Cl or Br) were isolated as well as a range of other phases that were not characterised.[1] The structure of the compound $Nb_3Cl_7Se_5$ has been determined [2] and consists of $Cl_2Nb(Se_2)_2NbCl_2$ chlorine-bridged chains containing Nb^{IV} with pendant $NbCl_3Se$ groups in which Nb^{V} and a terminal Nb=Se bond are present.[2] The niobium(IV) compound $[(MeCN)_2Cl_2Nb(\mu\text{-}S)_2NbCl_2(MeCN)_2]$ was prepared from $NbCl_4{\cdot}2NCMe$ and Sb_2S_3[3] but attempts to prepare the selenium analogue led to the isolation of a mixed niobium(III)–niobium(IV) compound of formula $Nb_4Br_{10}Se_3(NCMe)_4$ in which two niobium(IV) atoms are bridged by an Se_2^{2-} group and an Se atom; the remaining two niobium atoms being niobium(III).[4] Thus it appears that niobium(IV) is reduced by Se^{II} which is itself oxidised to Se_2^{2-}.

Recently, structural studies have been carried out on the compounds $[NbBr_3Se]$, $[NbBr_3Te]$, and $[NbI_3Te]$ which were prepared by allowing the elements to react at >1 000 K in sealed ampoules.[5] All the species have the same basic structural unit and consist of chains of niobium(IV) atoms having alternately short and long niobium–niobium distances. The shorter Nb–Nb distances are bridged by two halogen atoms and a Y_2^{2-} group (Y = Se or Te). Thus these simple ternary compounds, formulated as $[NbX_3Y]$, contain only niobium(IV). In this latter study all the starting materials were in the zero oxidation state.

We have recently reported the low-temperature preparation of compounds of formulation $[NbX_3Se]$ (X = Br or Cl) from the treatment of niobium(V) halides with Sb_2Se_3 at low temperature, a route more likely to lead to the formation of niobium(V) species than the high-temperature route discussed above. Unfortunately we have been unable to obtain single crystals for *X*-ray study.[6] Accordingly, to characterise these compounds they were allowed to react with a range of simple sulphur-donor molecules [dms = dimethyl sulphide, tht = tetrahydrothiophen, or bpte = 1,2-bis(phenylthio)ethane]. We now report the results of this study and the crystal structure determination of $[Nb_2Cl_4(Se_2)_2(dms)_4]$, a compound obtained from $[NbCl_3Se]$.

Experimental

All the compounds that were isolated were extremely air and moisture sensitive and so all preparations, filtrations, *etc.* were carried out using an all-glass vacuum line. Samples for spectroscopic investigation were prepared in a dry-box which was fitted with a drying train in which nitrogen was dried, deoxygenated, and recirculated through the box. To ensure that there were no complications from moisture or oxygen on the surface of glassware all reaction ampoules *etc.* were evacuated for >3 h while being maintained at *ca.* 100 °C. Following such treatment the apparatus was allowed to cool and if chemicals were to be added it was filled with dry nitrogen. The pentahalides were prepared by halogenation of niobium metal at high temperature in a stream of dried halogen gas. Antimony triselenide was prepared by reaction of the elements at high temperature in a sealed evacuated silica tube.

Preparation of $[NbX_3Se]$ (X = Br *or* Cl).—The niobium pentahalide (*ca.* 5 g) was placed in a previously weighed reaction ampoule under a stream of dried nitrogen. The ampoule was quickly evacuated and left to pump for 0.5 h, refilled with nitrogen, and reweighed. Sufficient antimony triselenide was then weighed so that the pentahalide was slightly in excess of that required for a 3 : 1 molar ratio of pentahalide : triselenide. The selenide was pumped at 200 °C overnight. After being allowed to cool it was added to the pentahalide. Dry deoxygenated carbon disulphide (40 cm³) was distilled into the reaction ampoule which was cooled to liquid-nitrogen temperature. Following the addition of the solvent the ampoule was sealed and allowed to reach room temperature. It was stirred using the magnetic follower contained in the ampoule for 3 d (25 °C for the chloride and 50 °C for the bromide). The ampoule was quickly opened under a vigorous stream of dry nitrogen and the contents filtered on the vacuum line. The desired products were insoluble in CS_2 while the other product (antimony trihalide) was soluble in the solvent. The precipitated product was washed with fresh solvent until all traces of occluded antimony trihalide were removed. Finally the pro-

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† Bis[dichlorobis(dimethyl sulphide)-μ-diselenido-niobium(IV)].

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duct was pumped for 24 h to ensure all traces of solvent were removed (Found: Cl, 37.8; Nb, 33.6. Cl_3NbSe requires Cl, 38.2; Nb, 33.4%. Found: Br, 58.6; Nb, 23.1. Br_3NbSe requires Br, 58.2; Nb, 22.6%).

Preparation of the Adducts.—The reactions were carried out in sealed ampoules containing a magnetic follower. In a typical reaction the selenido-halide, $[NbX_3Se]$ (*ca.* 2 g), was weighed under dry nitrogen into the ampoule which was then rapidly evacuated. For the liquid ligands tht and dms, the dry deoxygenated ligand (40 cm^3) was distilled into the ampoule. The ampoules were cooled to liquid-nitrogen temperature and sealed under vacuum.

Reactions with Tetrahydrothiophen.—The reactions with the chloride initially gave a red solution but on stirring for 8 weeks a green precipitate was also obtained. The green material was isolated by vacuum-line filtration and on removal of the excess of ligand under reduced pressure a red gelatinous material was isolated [Found (green solid): Cl, 19.8; Nb, 20.0 (Nb : Cl = 1 : 2.6). Found (red product): Cl, 24.0; Nb, 20.4 (Nb : Cl = 1 : 3.1). $C_8H_{16}Cl_3NbS_2Se$ requires Cl, 23.4; Nb, 20.4%].

A similar reaction with the bromide $[NbBr_3Se]$ gave an orange precipitate and a red solution, after stirring at room temperature for 5 weeks. The solid was isolated by vacuum-line filtration and the excess of ligand removed under reduced pressure to give a red oil from which no solid could be isolated [Found (orange solid): Br, 39.8; Nb, 15.7 (Nb : Br = 1 : 2.9). $C_8H_{16}Br_3NbS_2Se$ requires Br, 40.8; Nb, 15.8%].

Reaction of $[NbCl_3Se]$ *with Neat Dimethyl Sulphide.*—On stirring the reaction mixture at room temperature for 4 weeks a red solid and a red solution formed. The solid was obtained and separated by vacuum-line filtration but only an intractable oil was obtained from the solution [Found (red solid): Cl, 19.9; Nb, 17.6 (Nb : Cl = 1 : 3.0). $C_4H_{12}Cl_3NbS_2Se$ requires Cl, 20.3; Nb, 17.7%].

Reaction with 1,2-*Bis*(*phenylthio*)*ethane.*—The reaction of $[NbCl_3Se]$ with this ligand was carried out in an evacuated ampoule as described above with the reactants in a 1 : 1 molar ratio. Dry deoxygenated CS_2 was used as solvent. The reaction mixture was stirred and kept at 50 °C for 4 weeks, the only product being a brown insoluble powder that was isolated by filtration [Found: Cl, 19.9; Nb, 17.6 (Nb : Cl = 1 : 3.0). $C_{14}H_{14}Cl_3NbS_2Se$ requires Cl, 20.3; Nb, 17.7%].

Crystal Data and the Solution of the Structure.—Red crystals in the form of thin plates were isolated from a solution obtained by extracting with CS_2 the insoluble product from the reaction of $[NbCl_3Se]$ and dms. The crystal selected for study had dimensions 0.50 × 0.35 × 0.10 mm. The crystal was monoclinic, $a = 8.366(10)$, $b = 13.121(14)$, $c = 11.204(14)$ Å, $\beta = 99.53(10)^\circ$, $U = 1\,212.95$ Å^3, $D_m = 2.35(5)$, $Z = 2$, $D_c = 2.45$ g cm^{-3}, $F(000) = 844$, $\mu = 86.3$ cm^{-1}, $\lambda(\text{Mo-}K_\alpha) = 0.7107$ Å. The space group was established as $P2_1/n$ by the absences $0k0$, $k = 2n + 1$ and $h0l$, $h + l = 2n + 1$. The crystal was set up to rotate about the b axis on a Stoe Stadi 2 diffractometer, 2 147 independent reflections with $2\theta < 50^\circ$ were measured by variable ω scan and corrected for absorption using SHELX 76.[7] Maximum and minimum transmission factors were 0.438 and 0.074. 1 855 Reflections with $I > 3\sigma(I)$ were used in the subsequent refinement. The structure was solved by direct methods. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in tetrahedral positions at 0.95 Å from the carbon atoms and refined isotropically. The weighting scheme, chosen to give average values of F_o over ranges of F_o and $\sin\theta/\lambda$ was $w = 1/[\sigma^2(F) + 0.003F^2]$. The structure was refined by full-matrix least squares using SHELX 76 [7] at the University of Manchester Regional Computing Centre. The final R value was 0.068 ($R' = 0.072$). Atomic co-ordinates are given in Table 1 and the major bond distances and angles in Table 2.

Table 1. Atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses

Atom	x	y	z
Nb	5 168(2)	764(1)	5 987(1)
Se(1)	4 227(3)	1 199(1)	3 678(1)
Se(2)	2 418(2)	302(1)	4 592(2)
Cl(1)	7 156(6)	2 162(3)	5 722(4)
Cl(2)	3 410(6)	410(3)	7 550(4)
S(1)	7 090(6)	999(3)	8 199(4)
S(2)	3 721(6)	2 617(3)	6 172(4)
C(11)	7 022(33)	−66(16)	9 220(19)
C(12)	9 266(25)	957(17)	8 103(20)
C(21)	1 598(24)	2 547(14)	6 113(21)
C(22)	4 314(25)	3 041(18)	7 710(20)

Results and Discussion

The reactions of $[NbCl_3Se]$ with dms and bpte and that of $[NbBr_3Se]$ with tht all gave insoluble products with analyses close to those expected for 1 : 2 (dms, tht) or 1 : 1 (bpte) adducts. However, from the reaction of $[NbCl_3Se]$ with tht it proved possible to isolate both soluble and insoluble products that had different metal : chlorine ratios. This reaction appeared to mimic the reactions of $[NbX_3S]$ (X = Br or Cl) with tht where a number of products were isolated including $[NbX_3S(tht)_2]$ (X = Br), tht adducts of NbX_5, and the niobium(IV) compounds $[Nb_2X_4S_3(tht)_4]$.[8] In the formation of the latter compound, S^{2-} was oxidised to S_2^{2-} and niobium(V) reduced to niobium(IV).

With these sulphide compounds it is possible to detect from their i.r. spectra the presence of terminal Nb=S bonds and S_2^{2-} groups and so monitor the redox processes. The i.r. data on the related selenium species are not so well documented. It has been claimed that the Nb=Se terminal stretching mode occurs at 371 and 334 cm^{-1} in $[NbCl_3Se]$ and $[NbBr_3Se]$ respectively,[9] while stretching modes for Se_2^{2-} have been assigned to bands at 352 and 343 cm^{-1} in $[NbCl_2Se_2]$ and $[NbBr_2Se_2]$ respectively.[10] This region overlaps with that associated with the niobium-halogen and niobium-sulphur (ligand) modes.

This overlap makes it impossible to assign the type of Nb–Se bonding on the evidence of the i.r. spectra. However, there were marked differences between the spectra of the soluble and insoluble products from the reaction of $[NbCl_3Se]$ with tht. The former had a strong absorption at 377 cm^{-1} that was completely absent in the spectrum of the latter. In an attempt to clarify the situation attempts were made to obtain crystals for *X*-ray investigation. All attempts to obtain crystals from the $[NbCl_3Se]$–tht compounds failed; however, recrystallisation of the product from the reaction of $[NbBr_3Se]$ with tht gave a variety of products among which was a small amount of crystalline material that was shown by *X*-ray methods to be elemental selenium. Thus evidence was obtained for the occurrence of redox processes in which niobium was reduced from niobium(V) to some unknown oxidation state while the selenium was oxidised. These results suggest that the products initially obtained were formed for kinetic reasons and that recrystallisation led to the thermodynamically favoured products. Having failed to isolate crystalline niobium-containing material from the reactions with tht, our attention

Table 2. Bond distances (Å) and angles (°) *

(*a*) Metal co-ordination sphere

Nb–Se(1)	2.638(2)
Nb–Se(2)	2.630(2)
Nb–Se(A)	2.372(2)
Nb–Cl(1)	2.527(5)
Nb–Cl(2)	2.510(5)
Nb–S(1)	2.739(4)
Nb–S(2)	2.739(4)
Nb–Nb′	2.962(3)
Nb–Se(1′)	2.640(2)
Nb–Se(2′)	2.625(3)
Nb–Se(A′)	2.370(2)
Se(1)–Nb–Se(2)	51.51(7)
Se(A)–Nb–Cl(1)	104.42(13)
Se(A)–Nb–Cl(2)	103.67(12)
Cl(1)–Nb–Cl(2)	133.61(17)
Se(A)–Nb–S(1)	172.60(12)
Cl(1)–Nb–S(1)	74.03(15)
Cl(2)–Nb–S(1)	73.40(15)
Se(A)–Nb–S(2)	103.67(13)
Cl(1)–Nb–S(2)	70.91(16)
Cl(2)–Nb–S(2)	78.09(15)
S(1)–Nb–S(2)	91.87(13)
Se(A′)–Nb–Cl(1)	103.54(13)
Se(A′)–Nb–Cl(2)	105.34(12)
Se(A′)–Nb–S(1)	84.69(11)
Se(A′)–Nb–S(2)	174.15(12)
Se(A′)–Nb–Se(A)	102.69(8)
Nb–Se(1)–Nb′	68.29(8)
Nb–Se(2)–Nb′	68.63(6)
Nb–Se(A)–Nb′	77.31(7)

(*b*) Other dimensions

Se(1)–Se(2)	2.289(3)
S(1)–C(11)	1.812(19)
S(1)–C(12)	1.843(22)
S(2)–C(21)	1.769(21)
S(2)–C(22)	1.800(20)
Nb–S(1)–C(11)	114.1(7)
Nb–S(1)–C(12)	112.5(7)
C(11)–S(1)–C(12)	98.6(11)
Nb–S(2)–C(21)	113.9(6)
Nb–S(2)–C(22)	106.9(7)
C(21)–S(2)–C(22)	99.7(10)

* Primed atoms refer to the symmetry element 1 − *x*, − *y*, 1 − *z*.

was transferred to the product from the reaction of $[NbCl_3Se]$ and dms which on recrystallisation from CS_2 gave red crystals suitable for *X*-ray study, together with a green powder. The crystals were shown to contain $[(dms)_2Cl_2Nb(Se_2)_2NbCl_2(dms)_2]$ (see below). The green powder was in such a small yield that it could not be isolated and identified.

Structure of $[(dms)_2Cl_2Nb(Se_2)_2NbCl_2(dms)_2]$ (1).—The structure (1) consists of discrete centrosymmetric $[(dms)_2Cl_2Nb(Se_2)_2NbCl_2(dms)_2]$ molecules containing niobium(IV), as shown in the Figure where the atom numbering scheme is also given. The niobium atom is bonded to two chlorine atoms [Nb–Cl(1) 2.527(5), Nb–Cl(2) 2.510(5) Å], four selenium atoms, of two Se_2^{2-} groups [Nb–Se 2.638(2), 2.630(2), 2.640(2), and 2.625(3) Å] and two sulphur atoms from the dms molecules [Nb–S(1) 2.739(4), Nb–S(2) 2.739(4) Å].

The crystal structure of the parent chalcogenide halide $[Nb_2Cl_4(Se_2)_2]$ (2) has been recently determined [1] and shown to consist of $[Nb_2(Se_2)_2]^{4+}$ units linked into chains by halogen bridges. Not surprisingly the major differences in dimensions between (1) and (2) concern the niobium–chlorine distances, those in (1) being shorter (terminal bonds) than those in (2) (bridging bonds) by *ca.* 0.08 Å [2.527(5), 2.510(5) *vs.* 2.586(7), 2.612(7), 2.587(12), 2.608(10) Å respectively]. The niobium–selenium distances in both structures are equivalent but the Se–Se distances are slightly different, being 2.289(3) Å in (1) compared with 2.272(5) Å in (2). The cause of this difference can be attributed to an increase in electron density on the niobium atoms in (1), relative to (2), caused by donation from the dms molecules that thus reduces donation from the filled π^* orbitals on the Se_2 groups to the empty d_π orbitals on niobium.

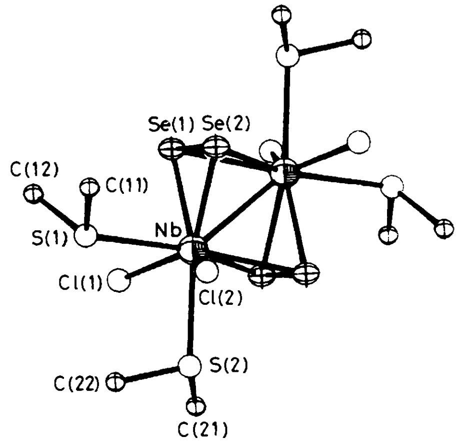

Figure. Structure of $[(dms)_2Cl_2Nb(Se_2)_2NbCl_2(dms)_2]$

A least-squares plane calculation for (1) showed that Nb, S(1), S(2), and the midpoint of the Se_2 group [designated Se(A)] are coplanar within experimental error, the maximum deviation for a contributing atom being 0.02 Å. The Se_2 groups are perpendicular to this plane. The midpoints of the Se_2 groups, the two chlorine atoms, and the two ligand sulphur atoms provide an octahedral environment for the metal atom. The niobium–niobium distance [2.962(3) Å] in (1) is comparable to that observed in (2) [2.973(4) Å] but both values are greater than those observed in $[NbCl_2S_2]$ [2.871(4) Å],[1,11] $[\{NbCl_2S(NCMe)_2\}_2]\cdot MeCN$ [2.862(2)—2.872(3) Å],[3] and in $[Nb_2Cl_4(S_2)S(tht)_4]$ [2.844(2) Å] [8] thus reflecting the influence of changing the bridging group from sulphur to selenium on the niobium–niobium distance.

In spite of the length of the niobium–niobium distance it is believed there is a metal–metal interaction as the chlorine atoms are bent well away from the Nb–Nb′ bond, the Nb–Nb–Cl angles being 113.6(1) and 112.7(1) [*cf.* 110.5(2), 110.9(2)° in (2)]. In addition, the Nb–Se(A)–Nb′ angles are much smaller than the Se(A)–Nb–Se(A′) angles [77.3(1) and 102.7(1)° respectively]. The niobium–sulphur (ligand) distances are comparable to those found in $[Nb_2Cl_4(S_2)S(tht)_4]$ and the ligand dimensions are unremarkable.

Conclusions

From the above study it is concluded that the reaction of niobium(V) chloride or bromide with Sb_2Se_3 at room temperature leads to the formation of the niobium(V) compounds of formulation $[NbX_3Se]$. This suggestion is supported by an *X*-ray structural study carried out on the $[NbCl_5Se]^{2-}$ anion which was obtained from a sample of $[NbCl_3Se]$ (see Experimental section).[12] However, it would appear that the niobium(V) form of $[NbX_3Se]$ is a kinetically trapped product as it has been shown that in solutions containing sulphur ligands redox processes take place in which niobium is reduced; selenium is oxidised so that a niobium(IV) selenido halide or elemental selenium is formed. In the formation of (1) or selenium from [NbX_3Se] some low-oxidation-state forms of niobium must also have been produced but so far we have been unable to isolate them. However, the reaction of $NbBr_4 \cdot 2NCMe$ and Sb_2Se_3 led to the isolation of a species of composition $Nb_4Br_{10}Se_3 \cdot 4NCMe$ in which two $NbBr_3$ fragments bridged a $Nb^{IV}(\mu\text{-}Se_2)(\mu\text{-}Se)Nb^{IV}$ moiety.[4] It would be interesting to ascertain if the high-temperature form of [$NbBr_3Se$] [which has been shown to be a niobium(IV) compound][5] would also react with dms to give [$(dms)_2Br_2Nb(Se_2)_2NbBr_2(dms)_2$] and a niobium halide adduct.

Acknowledgements

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