The Reactions of Tetrahydrothiophene (tht) with Tribromosulphidoniobium(v) and Trichlorosulphidoniobium(v) and the Crystal Structures of Three of the Products $Nb_2Cl_4S_3$·4tht, $Nb_2Br_4S_3$·4tht, and $NbBr_3S$·2tht *

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The niobium(IV) compounds $[(tht)_2X_2Nb(\mu\text{-}S)(\mu\text{-}S_2)NbX_2(tht)_2]$ [X = Cl (1) or Br (2)] are formed through a complex redox–disproportionation reaction when NbX_3S is treated with tetrahydrothiophene (tht). The reduction occurs *via* the oxidation of two formal S^{2-} ions to S_2^{2-}. It is thought that initially NbX_3S·2tht (3) is formed in the reaction. The reaction has been characterised by crystal-structure determinations of compounds (1), (2), and (3; X = Br): (1), monoclinic, space group $P2_1/c$, a = 12.483(15), b = 11.818(17), c = 19.798(17) Å, β = 97.3(1)°, and Z = 4; (2), triclinic, space group $P\bar{1}$, a = 11.826(11), b = 12.021(11), c = 10.813(13) Å, α = 101.4(1), β = 96.2(2), γ = 98.8(2)°, and Z = 2; (3), monoclinic, space group $P2_1/m$, a = 8.018(12), b = 8.802(15), c = 11.887(12) Å, β = 103.9(1)°, and Z = 2. 1 968 Independent diffractometer data for (1) have been refined to R 0.068, 1 522 and 571 to 0.061 and 0.064 for (2) and (3) respectively. The structures of compounds (1) and (2) are similar in that they contain two niobium atoms bridged by a sulphur atom and a disulphide group. The Nb–Nb distances of 2.844(2) and 2.830(5) Å respectively are indicative of a single metal–metal interaction. The metal co-ordination spheres are completed by two halogen atoms and two sulphur atoms of the tht ligands. In compound (3) the metal atom is six-co-ordinate, being bonded to a terminal sulphur, three bromine atoms, and two tht ligands through sulphur atoms. The multiple Nb=S bond is *trans* to a tht ligand. Both compounds (1) and (3) are disordered.

The niobium(v) compounds NbX_3S (X = Cl or Br) have been isolated by the careful reaction of the appropriate pentahalide and antimony(III) sulphide (3 : 1 molar ratio) in carbon disulphide.[1] The reaction conditions must be carefully monitored for it has been noted in the $NbCl_5 + Sb_2S_3$ reaction that if the product is not isolated within 24 h it darkens and a species is formed with a Nb : Cl ratio lower than 1 : 3.[2] Nevertheless pure samples of $NbCl_3S$ can be made as shown by the formation of the triphenylphosphine sulphide adduct $NbCl_3S(SPPh_3)$. Crystallographic studies of this adduct have revealed it to exist as a five-co-ordinate monomer and a chlorine-bridged dimer.[3]

It is against this background that the reaction of NbX_3S (X = Cl or Br) with the unidentate sulphur-donor tetrahydrothiophene (tht) is reported.

Results and Discussion

The Reactions of NbX_3S (X = Cl *or* Br) *with tht.*—The reactions of NbX_3S (X = Cl or Br) with tetrahydrothiophene (tht) in either a 1 : 2 or a 1 : 5 molar ratio or in neat tht gave compounds whose niobium to halogen ratio lay within the range 1 : 2.6—2.9. The value of the ratio varied with reaction time and temperature as did the colour of the insoluble product. We will describe some of the reactions carried out with $NbBr_3S$–tht mixtures. Reactions between $NbCl_3S$ and tht followed a similar pattern as did those between NbX_3S (X = Cl or Br) and dimethyl sulphide.

The reaction of $NbBr_3S$–tht mixtures (either 1 : 2 or 1 : 5 stoicheiometry) at 25 °C gave after 1 week greenish brown materials having Nb : Br ratios of 1 : 2.9. Repeating the reactions and either increasing the reaction time to 3 weeks or the temperature to 70 °C led to light brown materials with Nb : Br ratios of 1 : 2.6. When heated to 70 °C in neat tht for periods greater than 24 h, $NbBr_3S$ gave lime green insoluble powders with a Nb : Br ratio of 1 : 2.8. All the reactions gave pale green filtrates that on pumping gave dark green oils.

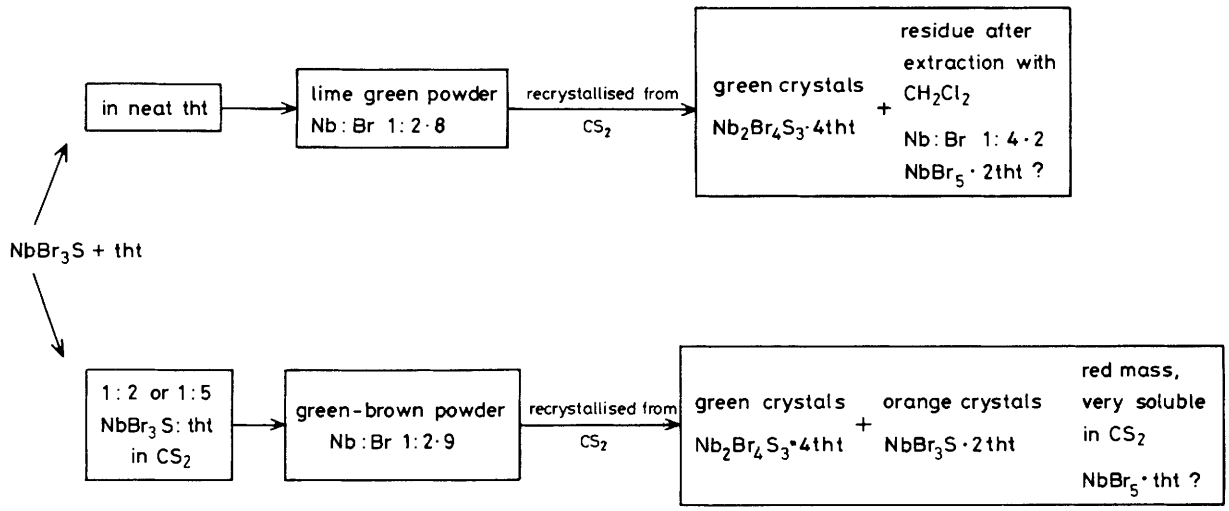
From the detailed description given in the Experimental section it can be seen that great care was taken in carrying out the reactions and in the preparation of the starting materials so it was believed that the apparent non-stoicheiometric nature of the products was caused by the occurrence of complex reactions leading to mixed products, rather than faulty techniques. This was supported by the i.r. spectra of the products which, although they varied with Nb : X ratio, contained no bands assignable to oxoniobium modes.

Attempts were made to obtain crystals from the products of the various reactions from CS_2 solutions. As with the preparations the complete picture can be understood by considering the $NbBr_3S$ + tht system (see Scheme). Recrystallisation of the green-brown products with Nb : Br ratios of 1 : 2.9 (from 1 : 2 and 1 : 5 stoicheiometric reactions between $NbBr_3S$ and tht) gave three products. The first species deposited was in the form of green crystals that single-crystal *X*-ray work revealed contained $Nb_2Br_4S_3$·4tht (2) (see next section). Secondly, orange crystals were deposited and these were shown by *X*-ray studies to contain $NbBr_3S$·2tht (3) (see next section). Finally a very soluble material was deposited as a red crystalline mass together with traces of the orange material. Unfortunately we were unable to isolate the red material free from traces of the orange product so its exact nature remains unknown, although it may be $NbBr_5$·tht.[4]

Recrystallisation (from CS_2 solution) of the lime green product obtained by the reaction of $NbBr_3S$ and neat tht (which had a Nb : Br ratio of 1 : 2.8) gave only one soluble product which was deposited as green crystals identical to those reported above and which contained $Nb_2Br_4S_3$·4tht. The insoluble residue that did not dissolve in CS_2 was extracted

* μ-Disulphido-μ-sulphido-bis[dichlorobis(tetrahydrothiophene-*S*)-niobium] and -bis[dibromobis(tetrahydrothiophene-*S*)niobium], and tribromosulphidobis(tetrahydrothiophene-*S*)niobium.

Supplementary data available (No. SUP 23679, 40 pp.): thermal parameters, ligand geometries, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.



Scheme. The reaction of $NbBr_3S$ with tht

with CH_2Cl_2. Further small quantities of the green crystals were extracted leaving a brown material whose i.r. spectrum contained no bands attributable to ν(Nb=S) and only weak ones that could be associated with ν(Nb–S–Nb). The Nb : Br ratio of this product was 1 : 4.2. Attempts to extract further quantities of the green product led to a halogen-exchange reaction with the CH_2Cl_2 used as solvent. Thus the exact nature of this insoluble residue is unknown but we believe it to contain $NbBr_5$·2tht.[5] Naturally a range of other solvents in place of CH_2Cl_2 were investigated but none proved useful.

Thus from the reaction of $NbBr_3S$ with tht, $NbBr_3S$·2tht (3), $Nb_2Br_4S_3$·4tht (2), and probably $NbBr_5$·tht (from 1 : 2 and 1 : 5 reactions) and $NbBr_5$·2tht (from the reaction of $NbBr_3S$ and neat tht) can be obtained. The reaction of $NbBr_5$ with tht has been reported to yield a red soluble 1 : 1 complex (in C_6H_6 solution [4]) as well as a dark orange insoluble 1 : 2 species (in neat tht [5]) and we found these reactions to be repeatable. The i.r. spectrum of the very soluble red material obtained from the 1 : 2 or 1 : 5 stoicheiometric reactions is not inconsistent with it being a mixture of $NbBr_5$·tht and $NbBr_3S$·2tht, while that of the insoluble residue from the reaction in neat tht resembles the spectrum of $NbBr_5$·2tht containing a trace of $Nb_2Br_4S_3$·4tht.

The reaction route to the products is suggested to be as in equations (i) and (ii). The second reaction involves sulphur

$$NbBr_3S + 2\ tht \longrightarrow NbBr_3S{\cdot}2tht \quad (i)$$

$$3NbBr_3S{\cdot}2tht \longrightarrow Nb_2Br_4S_3{\cdot}4tht + NbBr_5{\cdot}ntht \quad (ii)$$

abstraction from $NbBr_3S$ and an alternative sulphur-abstraction step could involve tht [equation (iii)]. Sulphur abstraction

$$2NbBr_3S{\cdot}2tht + tht \longrightarrow Nb_2Br_4S_3{\cdot}4tht + Br(CH_2)_4Br \quad (iii)$$

from tht has been observed in reactions with tungsten(VI) chloride.[6] Accordingly the filtrates from the reactions of $NbBr_3S$ with neat tht were examined by g.l.c. and no evidence was obtained for 1,4-dibromobutane or any other species that could have been formed by sulphur abstraction from tht. Thus it is believed that the formation of $Nb_2Br_4S_3$·4tht proceeds by sulphur abstraction from $NbBr_3S$ even though unequivocal evidence for the formation of $NbBr_5$ was not obtained.

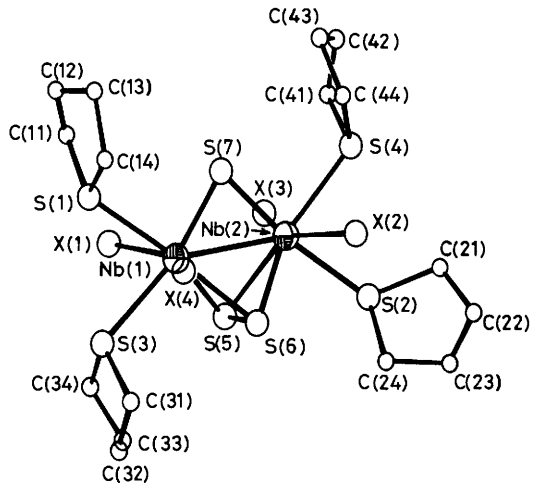


Figure 1. The $Nb_2X_4S_3$·4tht molecule (together with atomic numbering scheme). The diagram is for compound (2; X = Br) but (1) differs only in the carbon-atom position

The Crystal Structures of $Nb_2Cl_4S_3$·4tht (1), $Nb_2Br_4S_3$·4tht (2), *and* $NbBr_3S$·2tht (3).—The structures of compounds (1) and (2) are very similar in that both contain the species depicted in Figure 1 together with the atomic numbering scheme, namely $[(tht)_2X_2Nb(\mu\text{-}S)(\mu\text{-}S_2)NbX_2(tht)_2]$ (X = Cl or Br). The two niobium atoms are linked by a bridging sulphur atom and a bridging S_2 group. In compound (1) the bridge is disordered with the A positions of the S_2 and S bridges having 0.66 occupancy while the B positions had 0.34. The disorder was only observed in the chloro-compound and was restricted to the bridging atoms. This is not surprising as the positions of the remaining atoms were not dependent on those of the bridging groups. For the purpose of discussion we will only consider configuration A. Dimensions associated with B are reasonable although with much higher standard deviations (see Table 5).

The four halogen atoms are coplanar with the niobium atoms slightly out of the planes towards the S_2 group [Nb(1) 0.06 and Nb(2) 0.04 Å in (1); Nb(1) 0.17 and Nb(2) 0.16 Å in (2)]. The two niobium atoms, the four ligand sulphur atoms, the bridging sulphur atom, and the midpoint of the S_2 bridge

are also coplanar to within 0.06 (1) and 0.12 Å (2). The two planes in each structure are approximately perpendicular [89.8 (1) and 89.1° (2)] (see Table 7).

The most interesting aspect of the structures of compounds (1) and (2) is the Nb–μ-S–Nb–μ-(S_2) ring. The Nb · · · Nb distances [2.844(2) and 2.830(5) Å] indicate that a niobium–niobium interaction must take place either directly or through the mediation of the bridging atoms. These distances suggest the presence of a single metal–metal interaction; from the niobium(v) compounds NbX_3S (X = Cl or Br), niobium(IV) species have been obtained. The niobium distances are shorter than the single bonds found in $NbCl_2S_2$ [2.871(4) Å],[7] $NbCl_4$ [3.029(2) Å],[8] and in NbS_3 [3.037(3) Å] [9] but the latter compounds all contain strings of niobium atoms in which there are alternate short and long Nb–Nb distances. A more direct comparison is provided by the niobium(IV) compound $[\{NbCl_2S(NCMe)_2\}_2]$ which has a range of Nb · · · Nb distances [2.862(2)—2.872(3) Å].[10] The observed distances are much longer than the double bonds found in the discrete niobium(III) species $[(tht)Br_2Nb(\mu\text{-}Br)_2(\mu\text{-}tht)NbBr_2(tht)]$ [2.728(5) Å].[11] Various angles within the $(tht)_2X_2Nb(\mu\text{-}S)(\mu\text{-}S_2)NbX_2(tht)_2$ fragment indicate a metal–metal interaction; thus the Nb–Nb–X angles range from 103.1(1) to 109.3(2)° showing that the halogen atoms are bent away from the Nb · · · Nb interaction while the Nb–S(7)–Nb angles are small [76.9(2) and 74.7(2)°] and comparable to the Nb–S–Nb angles in $[\{NbCl_2S(NCMe)_2\}_2]$ [75.2(1) and 75.6(2)°].[10]

The difference in Nb · · · Nb distance between compounds (1) and (2) is probably significant. Unfortunately the disorder problem associated with the bridging sulphur atoms and S_2 groups makes direct comparison of the Nb–S distances shown by (1) and (2) difficult. The Nb–S bond lengths to the S_2 group are shorter in compound (2) than in (1A) [complex (1) configuration A] and conversely the Nb–S distances to the bridging sulphur atom S(7) are longer in (2) than in (1A). The most likely reason for the differences is intramolecular interactions involving the halogen atoms. The X–Nb–X angles are all within the range 143.9(1)—148.2(1)° and as the Nb–X (X = Cl or Br) bond lengths are not too different from those observed in NbX_6^{n-} where the X–Nb–X angles are 90°, the halogen–halogen interaction cannot be important. There are several Cl to S_2 distances *ca.* 3.15 Å in compound (1A) while the shortest Br distances in (2) are *ca.* 3.27 Å. The distances to S(7) are in the range 3.60—3.63 for Cl (1A) and 3.68—3.75 Å for Br (2). Comparison of these four ranges of distances suggests that the major intramolecular interaction will be between the bromine atoms and the S_2 group in compound (2). To alleviate this strain, the four bromine atoms are bent back away from the S_2 group [as stated earlier, Nb(1) and Nb(2) are some 0.17 and 0.16 Å above the plane of the four bromine atoms] and the S_2 to Nb bonds could be envisaged as being compressed in the bromide leading to a commensurate lengthening of niobium to S(7) distances.

In both structures the three sulphur atoms form isosceles triangles [3.78(1), 3.76(1), and 2.01(1) Å in (1A) and 3.74(1), 3.80(1), and 2.01(1) Å in (2)]. Similar isosceles triangles have been found in a number of cases; for example in NbS_3 [3.781(5), 3.828(5), and 2.021(15) Å],[9] while in $[Cl_4W(\mu\text{-}Se)(\mu\text{-}Se_2)WCl_4]^{2-}$ an isosceles triangle of selenium atoms was observed.[12] The sulphur–sulphur distances [2.013(11) and 2.014(14) Å] are slightly shorter than in ionic S_2^{2-}.[13] This may indicate a bond order slightly greater than one, facilitated by weak $\pi^*(S_2)$–π(Nb) interaction from the two orthogonal filled π^* orbitals to the two metal atoms.

The Nb–S(ligand) bond lengths in both structures fall within the same range [2.711(4)—2.744(4) Å] with no significant differences between the bond lengths *trans* to the sulphur atom and those *trans* to the S_2 group.

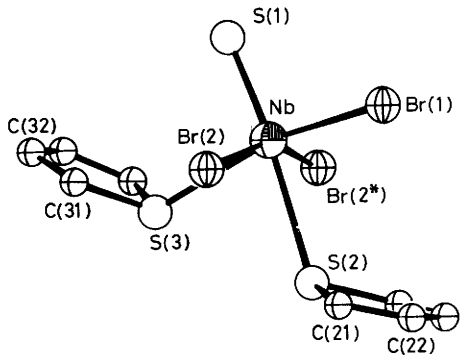


Figure 2. The $NbBr_3S{\cdot}2tht$ adduct present in compound (3)

The orange crystals obtained from the reaction of $NbBr_3S$ and tht in a 1 : 2 or 1 : 5 stoicheiometry were shown by *X*-ray crystallography to contain discrete $NbBr_3S(tht)_2$ molecules (3) (Figure 2) with the niobium(v) atom being six-co-ordinate. There is a crystallographic mirror plane through atoms Nb, Br(1), S(1), S(2), and S(3). As discussed in the Experimental section, there was disorder between Br(1) and terminal S(1) and two configurations (A and B) were refined with occupancies 0.73 (A) and 0.27 (B). It is interesting that $TaBr_3S(tht)_2$[14] also had mirror-plane disorder between S and Br but in a different space group, *Pnma*.

In the present structure two effects should be noted. First all the atoms in each of the tht rings should be disordered reflecting that sometimes the tht molecule is *trans* to Nb=S and sometimes *cis*. We were unable to detect such disorder but this is not surprising as the difference between the two types of Nb–S(tht) distances is likely to be only *ca.* 0.2 Å. The effect of the Nb=S multiple bond is apparent in the Nb–S(ligand) distance. The Nb–S(3) distance [2.835(17) Å] which is 73% *trans* to Nb=S is considerably longer than Nb–S(2) [2.691(15) Å] which is 73% *cis* to Nb=S. Beside the lengthening of the *trans* bond the Nb=S moiety would be expected to cause an increase above 90° in the angles it forms with the groups *cis* to it and this occurs in compound (3) [97.1(1) to 105.1(2)°]. All these angles of course involve disorder. One angle that remains unchanged between the two configurations is Br(2)–Nb–Br(2*) [154.2(4)°] which indicates that the Nb=S fragments do cause an effect on the angle it makes with *cis* groups. The Nb=S bond length [2.09(8) Å] is directly comparable to those observed in the triphenylphosphine sulphide adduct of $NbCl_3S$ [2.114(4) and 2.129(4) Å], while the Nb–Br distances are typical for six-co-ordinate niobium(v) (2.492—2.508 Å) in $[PPh_4][NbBr_6]$.[15]

Conclusions

The reaction of NbX_3S and tht is complex. Initially $NbX_3S(tht)_2$ is formed and for X = Br the crystal structure (3) was determined. For X = Cl a powdered form of $NbCl_3S(tht)_2$ was obtained on recrystallisation of the products from the $NbCl_3S$ + tht reactions in solution (either CS_2 or neat tht). Complex redox processes occur with these $NbX_3S(tht)_2$ niobium(v) compounds. Thus it is envisaged that the $Nb_2X_4S_3$ moiety is formed as depicted in reaction (ii) and that two formally S^{2-} ions form S_2^{2-} releasing two electrons that reduce the two niobium centres from niobium(v) to niobium(IV). Similar studies with TaX_3S and tht do not appear to lead to tantalum(IV) compounds, reflecting the increased stability to reduction of tantalum(v) compared to niobium(v).

Table 1. Crystal data and refinement details

	$Nb_2Cl_4S_3$·4tht (1)	$Nb_2Br_4S_3$·4tht (2)	$NbBr_3S$·2tht (3)
Formula	$C_{16}H_{32}Cl_4Nb_2S_7$	$C_{16}H_{32}Br_4Nb_2S_7$	$C_8H_{16}Br_3NbS_3$
M	776.3	954.1	540.9
Crystal system	Monoclinic	Triclinic	Monoclinic
a/Å	12.483(15)	11.826(11)	8.018(12)
b/Å	11.818(17)	12.021(11)	8.802(15)
c/Å	19.798(17)	10.813(13)	11.887(12)
α/°	(90)	101.4(1)	(90)
β/°	97.3(1)	96.2(2)	103.9(1)
γ/°	(90)	98.8(2)	(90)
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/m$
Systematic absences	$h0l$, $l = 2n + 1$ $0k0$, $k = 2n + 1$	—	$0k0$, $k = 2n + 1$
U/Å^3	2 896.9	1 473.3	814.2
Z	4	2	2
D_m/g cm^{-3}	1.80(5)	2.20(5)	2.1(2) [a]
D_c/g cm^{-3}	1.78	2.15	2.21
μ/cm^{-1}	20.5	73.9	92.3
λ(Mo-K_α)/Å	0.7017	0.7017	0.7017
F(000)	1 560	924	516
Crystal size (mm)	0.1 × 0.25 × 0.5	0.5 × 0.35 × 0.75	0.44 × 0.2 × 0.60
Rotation axis	a	c^*	c^*
Independent reflections measured	2 262	1 866	837
Reflections used in refinement	1 968	1 522	571
R	0.068	0.061	0.064
R'	0.065	0.064	0.068

[a] Crystal dissolved quickly.

Table 2. Atomic co-ordinates (× 10^4) for compound (1) with estimated standard deviations in parentheses. Atoms marked A, B refer to molecules with occupancy factors 0.66, 0.34 respectively

Atom	x	y	z	Atom	x	y	z
Nb(1)	3 195(1)	4 702(1)	8 142(1)	C(11)	2 566(14)	7 414(15)	9 058(10)
Nb(2)	1 864(1)	4 080(1)	6 925(1)	C(12)	2 722(18)	8 603(16)	8 865(11)
Cl(1)	2 095(4)	4 684(4)	9 063(2)	C(13)	3 242(21)	8 606(17)	8 270(11)
Cl(2)	2 968(3)	4 149(3)	5 999(2)	C(14)	4 134(15)	7 763(14)	8 325(9)
Cl(3)	53(3)	3 741(3)	7 201(2)	C(21)	2 320(16)	1 403(15)	5 912(10)
Cl(4)	4 976(3)	5 161(4)	7 846(2)	C(22)	2 079(20)	206(18)	6 073(14)
S(1)	3 757(4)	6 633(4)	8 864(2)	C(23)	1 670(26)	181(18)	6 683(14)
S(2)	1 199(4)	2 222(4)	6 175(2)	C(24)	771(16)	1 069(16)	6 688(11)
S(3)	4 582(4)	3 732(4)	9 166(2)	C(31)	5 510(15)	2 773(16)	8 819(10)
S(4)	575(4)	5 127(3)	5 908(2)	C(32)	5 151(30)	1 622(24)	8 976(16)
S(5A)	2 244(7)	2 791(6)	7 956(3)	C(33)	4 523(27)	1 555(21)	9 459(16)
S(6A)	3 508(7)	2 988(9)	7 429(5)	C(34)	3 960(16)	2 640(16)	9 603(9)
S(7A)	2 163(8)	5 843(6)	7 381(4)	C(41)	−387(15)	6 063(15)	6 220(10)
S(5B)	2 834(11)	6 062(11)	7 096(7)	C(42)	−184(24)	7 174(19)	5 949(14)
S(6B)	1 560(11)	5 866(13)	7 634(7)	C(43)	726(19)	7 330(18)	5 618(12)
S(7B)	2 928(16)	3 008(13)	7 652(9)	C(44)	1 316(16)	6 256(14)	5 510(9)

Table 3. Atomic co-ordinates (× 10^4) for compound (2) with estimated standard deviations in parentheses

Atom	x	y	z	Atom	x	y	z
Nb(1)	7 568(3)	3 934(3)	2 732(3)	C(13)	7 343(39)	4 471(39)	−1 766(44)
Nb(2)	7 739(3)	1 724(3)	3 192(3)	C(14)	8 054(37)	4 787(40)	−465(39)
Br(1)	5 402(3)	4 170(3)	2 695(4)	C(21)	9 666(30)	1 398(31)	6 084(33)
Br(2)	9 844(3)	1 488(3)	2 847(4)	C(22)	9 357(41)	1 991(40)	7 377(43)
Br(3)	5 704(3)	691(4)	3 483(4)	C(23)	8 360(38)	1 194(39)	7 594(42)
Br(4)	9 607(3)	4 662(4)	2 211(4)	C(24)	7 470(33)	862(34)	6 418(35)
S(1)	7 037(8)	4 856(8)	688(8)	C(31)	7 102(33)	7 061(33)	3 489(36)
S(2)	8 321(9)	662(8)	5 122(10)	C(32)	6 348(40)	7 434(42)	4 436(41)
S(3)	7 978(8)	6 135(8)	4 135(9)	C(33)	6 922(33)	7 412(31)	5 703(34)
S(4)	7 542(10)	−454(9)	1 793(10)	C(34)	7 363(30)	6 324(29)	5 603(32)
S(5)	7 137(9)	3 283(8)	4 711(9)	C(41)	6 153(39)	−1 011(41)	816(43)
S(6)	8 831(9)	3 579(8)	4 548(9)	C(42)	6 412(52)	−1 279(54)	−542(55)
S(7)	7 210(9)	2 180(8)	1 239(9)	C(43)	7 504(53)	−1 342(56)	−651(61)
C(11)	5 863(32)	3 872(32)	−444(33)	C(44)	8 376(38)	−557(37)	437(39)
C(12)	6 406(41)	3 535(41)	−1 663(45)				

Table 4. Atomic co-ordinates ($\times 10^4$) for compound (3) with estimated standard deviations in parentheses. Atoms marked A, B refer to molecules with occupancy factors 0.73, 0.27 respectively

Atom	*x*	*y*	*z*
Nb	2 236(8)	2 500(0)	2 751(5)
Br(1A)	2 305(18)	2 500(0)	712(10)
S(1A)	2 418(86)	2 500(0)	1 029(69)
Br(1B)	5 145(40)	2 500(0)	3 877(22)
S(1B)	4 908(38)	2 500(0)	3 439(22)
Br(2)	1 609(7)	5 284(5)	2 883(4)
S(2)	1 303(17)	2 500(0)	4 779(13)
S(3)	−1 401(21)	2 500(0)	2 019(13)
C(21)	2 355(48)	3 967(44)	5 709(33)
C(22)	3 528(62)	3 272(49)	6 707(42)
C(31)	−2 297(64)	3 929(58)	994(42)
C(32)	−3 093(53)	3 318(43)	−94(33)

Table 5. Molecular dimensions of compounds (1) and (2); distances in Å, angles in degrees

	(1)	(2)		(1)	(2)
(*a*) Bridging unit			(*b*) Metal–halogen		
Nb(1)–Nb(2)	2.844(2)	2.830(5)	Nb(1)–X(1)	2.419(4)	2.617(5)
Nb(1)–S(5A)	2.556(7)	2.496(10)	Nb(1)–X(4)	2.432(4)	2.596(5)
Nb(1)–S(6A)	2.528(10)	2.482(10)	Nb(2)–X(2)	2.429(4)	2.607(5)
Nb(1)–S(7A)	2.292(6)	2.336(10)	Nb(2)–X(3)	2.427(4)	2.614(5)
Nb(2)–S(5A)	2.543(7)	2.481(10)			
Nb(2)–S(6A)	2.520(10)	2.490(10)	Nb(2)–Nb(1)–X(1)	108.08(11)	107.69(16)
Nb(2)–S(7A)	2.282(6)	2.329(10)	Nb(2)–Nb(1)–X(4)	107.83(11)	103.10(10)
Nb(1)–S(5B)	2.615(14)		Nb(1)–Nb(2)–X(2)	107.72(11)	104.10(16)
Nb(1)–S(6B)	2.557(14)		Nb(1)–Nb(2)–X(3)	108.17(11)	109.30(19)
Nb(1)–S(7B)	2.231(16)				
Nb(2)–S(5B)	2.639(13)		(*c*) Metal–ligand		
Nb(2)–S(6B)	2.588(15)		Nb(1)–S(1)	2.736(4)	2.719(10)
Nb(2)–S(7B)	2.225(15)		Nb(1)–S(3)	2.744(4)	2.719(10)
S(5A)–S(6A)	2.013(11)	2.014(14)	Nb(2)–S(2)	2.720(4)	2.733(10)
S(5B)–S(6B)	2.037(22)		Nb(2)–S(4)	2.711(4)	2.715(11)
Nb(1)–S(5A)–Nb(2)	67.80(18)	69.31(30)	Nb(2)–Nb(1)–S(1)	137.87(11)	137.25(23)
Nb(1)–S(6A)–Nb(2)	68.59(25)	69.40(27)	Nb(2)–Nb(1)–S(3)	139.78(11)	136.50(27)
Nb(1)–S(7A)–Nb(2)	76.89(21)	74.68(31)	Nb(1)–Nb(2)–S(2)	140.87(11)	141.19(23)
Nb(1)–S(5B)–Nb(2)	65.54(34)		Nb(1)–Nb(2)–S(4)	137.62(10)	137.37(30)
Nb(1)–S(6B)–Nb(2)	67.13(36)				
Nb(1)–S(7B)–Nb(2)	79.30(5)				

Experimental

All manipulations involved in the preparation and isolation of the niobium compounds were carried out using an all-glass vacuum line. To ensure complete absence of any oxo-compounds, antimony(III) sulphide was precipitated by passing H_2S through a solution formed by dissolving antimony(III) oxide in hydrochloric acid and the pentahalides were made by halogenation of niobium sheet.

Solvents and ligands were first dried with P_2O_5 and then distilled onto a further quantity of dehydrating agent on the vacuum line. After 24 h they were distilled onto further quantities of fresh dehydrating agent where they remained under vacuum until needed.

The compounds NbX_3S were prepared in the following manner. The niobium pentahalide was accurately weighed (*ca.* 10.0 g) into a reaction ampoule containing a magnetic follower. This manipulation was carried out under rigorously dried nitrogen. Sufficient antimony(III) sulphide was weighed out to give a slight excess of pentahalide above a 3 : 1 stoicheiometry. While being maintained at 200 °C this sulphide was pumped on a vacuum line for 16 h, then cooled and quickly transferred (under dried N_2) onto the pentahalide, followed by rapid evacuation of the reaction ampoule. At liquid-nitrogen temperature, carbon disulphide (40—50 cm^3) was distilled into the ampoule which was then sealed under vacuum. The reaction mixture was allowed to warm to room temperature and was then stirred for 24 h. Following this period the ampoule was opened under dry nitrogen and quickly transferred to the vacuum line where the insoluble product was isolated by filtration. The product was pumped free of solvent and any SbX_3, followed by washing with aliquots of fresh solvent (CS_2). Analyses for niobium (gravimetrically as Nb_2O_5) and halogen (titrimetrically) were carried out, and niobium ratios of 1 : 3 with percentage figures in close agreement with the formulation NbX_3S (X = Cl or Br) were obtained. The i.r. spectra of the compounds showed no modes attributable to the presence of oxoniobium species.

The reactions with the sulphur donors were carried out in sealed ampoules containing magnetic followers. A quantity of the sulphido-halide (*ca.* 2.5 g) was weighed into the reaction vessel and the requisite volume of dry and degassed ligand distilled in at liquid-nitrogen temperature (30 cm^3 for a reaction with a neat ligand). If a stoicheiometric reaction was carried out, carbon disulphide (*ca.* 30.0 cm^3) was also added. Following the addition of the materials the ampoules were sealed under vacuum and the reactants stirred. The nature of the products is discussed in the Results and Discussion section. The insoluble products were isolated by vacuum-line filtration and washed with carbon disulphide. The filtrates were all pale green in colour and on removal of the solvent or excess of ligand, green oils were obtained.

Crystal Structure Determinations.—Suitable crystals of compounds (2) and (3) were obtained by recrystallisation from CS_2 of the products from the reaction of $NbBr_3S$ and tht (1 : 5 molar ratio). A similar procedure using the product from a $NbCl_3S$ + tht reaction gave crystals of (1). Crystal data for all three compounds are given in Table 1. Data for (2) and (3) were collected using a General Electric XRD5 apparatus. The general techniques employed are given in ref. 16. In this case 10-s counts of peak heights were measured. Data for compound (1) were collected on a Stoe STADI2 diffractometer using variable-width, *w*, scans. Background

Table 6. Dimensions of compound (3); distances in Å, angles in degrees

Nb–Br(1A)	2.438(12)	Nb–S(1A)	2.09(8)
Nb–Br(1B)	2.393(29)	Nb–S(1B)	2.101(29)
Nb–Br(2)	2.514(4)	Nb–S(2)	2.691(15)
		Nb–S(3)	2.835(17)
S(1A)–Nb–Br(1B)	105.1(19)	S(1B)–Nb–S(2)	97.4(8)
Br(1A)–Nb–S(1B)	97.0(8)	Br(2)–Nb–S(2)	80.84(16)
Br(1A)–Nb–Br(2)	96.61(19)	Br(1A)–Nb–S(3)	87.88(49)
S(1A)–Nb–Br(2)	97.11(39)	S(1A)–Nb–S(3)	90.5(18)
Br(1B)–Nb–Br(2)	98.49(23)	Br(1B)–Nb–S(3)	164.4(8)
S(1B)–Nb–Br(2)	100.15(22)	S(1B)–Nb–S(3)	175.1(8)
Br(1A)–Nb–S(2)	165.6(5)	Br(2)–Nb–S(3)	79.20(18)
S(1)–Nb–S(2)	168.2(18)	S(2)–Nb–S(3)	77.72(44)
Br(1B)–Nb–S(2)	86.7(8)	Br(2)–Nb–Br(2*)	154.2(4)

The asterisk refers to the symmetry element $x, \frac{1}{2} - y, z$.

counts were 20 s and the scan rate of 0.0333° s^{-1} was applied to a width of (1.5 + sinμ/tanθ).

An absorption correction was applied in the case of compounds (2) and (3) but not (1). In (1) and (3) the co-ordinates of the niobium atoms were found from a Patterson function. The remaining non-hydrogen atoms were located by Fourier methods. In (1) the three sulphur atoms between the niobium atoms were disordered. There were two alternative orientations of the S,S_2 bridge such that the sulphur atom of one orientation was at the midpoint of the S_2 bond of the other orientation. The disorder was incorporated into the refinement by assigning site-occupancy factors of x and $1 - x$ to the two sets of sulphur atoms; x refined to 0.66(1). For (2) the positions of the Nb and Br atoms were obtained by direct methods using SHELX 76. Fourier methods were used to locate the remaining non-hydrogen atoms. Compound (3) was found to be disordered between the terminal sulphur and one of the bromine atoms. Two positions for each atom were given and the Nb–S and Nb–Br bond lengths constrained to be equivalent. Site-occupancy factors of x and $1 - x$ were given to these atoms and x refined to 0.73(1). In the final cycles of refinement the bond constraints were freed. Although this disorder must affect the positions of the tht ligands, we were not able to distinguish two peaks for any atom.

In all three structures the hydrogen atoms were placed in tetrahedral positions. Those bonded to the same atom were given a common thermal parameter. All three structures were refined using full-matrix least squares. All non-hydrogen atoms, except for the carbon atoms in compound (2) were refined anisotropically.

The weighting scheme was chosen to give equivalent values of $w\Delta^2$ over ranges of $(\sin\theta)/\lambda$: for (1), $w = 1/[\sigma^2(I) + 0.003F^2]$ where $\sigma(F)$ was taken from counting statistics; for (2) and (3), $\sqrt{w} = 1$ for $F < F^*$ and $w = F^*/F$ for $F > F^*$ with $F^* = 29.9$ in (2) and 22.0 in (3). Scattering factors were taken from ref. 17. Calculations were made using SHELX 76 [18] at the University of Manchester Computer Centre. Atomic co-ordinates are given in Tables 2, 3, and 4 for compounds (1), (2), and (3) respectively; bond lengths and angles in Table 5 for (1) and (2) and in Table 6 for (3), and least-squares planes in Table 7.

Table 7. Least-squares planes for compounds (1) and (2) with distances (Å) of atoms from planes in square brackets. Atoms not contributing to the planes are marked with an asterisk

S(0) is the midpoint of S(5)–S(6)

Plane 1: compound (1) Cl(1), Cl(2), Cl(3), Cl(4)

[Cl(1) −0.02, Cl(2) −0.02, Cl(3) 0.02, Cl(4) 0.02, Nb(1) * −0.06, Nb(2) * −0.04, S(7A) * 1.74]

compound (2) Br(1), Br(2), Br(3), Br(4)

[Br(1) 0.02, Br(2) 0.02, Br(3) −0.02, Br(4) −0.02, Nb(1) * −0.17, Nb(2) * −0.16, S(7) * 1.68]

Plane 2: compound (1) Nb(1), Nb(2), S(1), S(2), S(3), S(4), S(7A)

[Nb(1) −0.01, Nb(2) 0.01, S(1) −0.04, S(2) −0.02, S(3) 0.06, S(4) 0.04, S(7A) −0.00, S(0A) * −0.04]

compound (2)

[Nb(1) −0.02, Nb(2) −0.03, S(1) −0.00, S(2) 0.03 S(3), 0.11, S(4) 0.08, S(7A) −0.05, S(0) * −0.12]

Angle (°) between planes 1 and 2: for (1), 89.8; for (2), 89.1

Acknowledgements

We thank the S.E.R.C. for support and Mr. A. W. Johans for his assistance with the crystallographic investigations.

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Received 9th February 1983; *Paper* 3/207