# Niobium(IV) Sulphidohalides: Preparation of $Nb_2X_4S_3$ and $Nb_2X_4S_3{\cdot}nL$ [X = Br or Cl; $n$ = 4, L = NCMe, $SMe_2$, or Tetrahydrothiophene (tht); $n$ = 2, L = $PhSCH_2CH_2SPh$]. Crystal and Molecular Structure of $Nb_2Cl_4S_2{\cdot}4tht$ *

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The niobium(IV) compounds $Nb_2Cl_4S_3$ (X = Br or Cl) were formed by the reaction of $NbX_5$ and $Sb_2S_3$ (2:1 molar ratio) in $CS_2$ at 50 °C. These species contain the $[\mathrm{Nb{-}S{-}Nb{-}S_2}]^{4+}$ moiety. A range of adducts $Nb_2X_4S_3{\cdot}nL$ [$n$ = 4, L = NCMe, $SMe_2$, or tetrahydrothiophene (tht); $n$ = 2, L = $PhSCH_2CH_2SPh$] were prepared and $Nb_2Cl_4S_2{\cdot}4tht$ was obtained from $Nb_2Cl_4S_3{\cdot}4tht$ by the abstraction of a sulphur atom with $PPh_3$. A crystal of $Nb_2Cl_4S_2{\cdot}4tht$ was found to be monoclinic, space group $P2_1/n$, with $a$ = 19.958(11), $b$ = 12.616(8), $c$ = 11.530(10) Å, β = 97.0(1)°, and $Z$ = 4. 2 741 Independent reflections above background were measured on a diffractometer and the structure refined to $R$ 0.053. The structure is dimeric with two niobium atoms [Nb–Nb 2.868(2) Å] being linked by bridging sulphur atoms. Each metal atom is six-co-ordinate being bound to two chlorine atoms and two ligand sulphur atoms as well as the bridging atoms.

The synthesis and structure of metal–metal bonded species involving niobium and tantalum is a topic of current interest, a number of niobium(III) and tantalum(III) species having been synthesised and structurally studied.[1–3] Recently the serendipitous isolation of two niobium(IV) compounds having the formula $Nb_2X_4S_3{\cdot}4tht$ (X = Br or Cl, tht = tetrahydrothiophene) was reported.[4] It was decided in view of current interest in metal–metal bonded species and the small number of dimeric niobium–niobium bonded species known, to investigate systematically the preparation of these compounds.

The background to the study is as follows. The niobium chalogenide halides of formulation $NbX_3S$ (X = Br or Cl) can be obtained by the carefully controlled reaction of niobium(V) chloride or bromide with antimony(III) sulphide (the reactants being in a 3:1 molar ratio) in carbon disulphide solution.[5] The chloride, $NbCl_3S$, is lemon-yellow but if this material is left in the reaction medium for more than 24 h a darker material is obtained that has a niobium to chloride ratio of less than 1:3. Further interesting reactions occur when the species $NbX_3S$ (X = Br or Cl) are treated with tetrahydrothiophene. Initially $NbX_3S{\cdot}2tht$ is formed but in $CS_2$ solution complex disproportionation reactions take place leading to the formation of the niobium(IV) species $Nb_2X_4S_3{\cdot}4tht$ [see equation (1)].[4] In

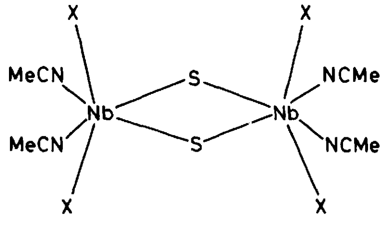
$$3NbX_3S{\cdot}2tht \xrightarrow{CS_2} Nb_2X_4S_3{\cdot}4tht + NbX_5{\cdot}n\,tht \quad (1)$$
$$(n = 1 \text{ or } 2)$$

these niobium(IV) species the two metal atoms are bridged by a sulphur atom and a $S_2$ group with the niobium–niobium distance being of such a length [2.830(5) Å for X = Br and 2.844(2) Å for X = Cl] that an interaction of some form between the two metal atoms must be present.

The mild conditions that led to the formation of a niobium(IV) compound suggest that the change in colour observed when $NbCl_3S$ is allowed to stand in its preparative medium may be evidence for the spontaneous formation of some niobium(IV) compounds. Furthermore as the niobium to sulphur ratio in $Nb_2X_4S_3$ is 2:3 it was thought worthwhile to treat $NbX_5$ with $Sb_2S_3$ in a 2:1 molar ratio (thus having a Nb:S ratio of 2:3) in an attempt to obtain directly pure $Nb_2X_4S_3$ [equation (2)].

$$2NbX_5 + Sb_2S_3 \longrightarrow Nb_2X_4S_3 + 2SbX_3 \quad (2)$$

A second type of niobium(IV) sulphidohalide is formed when $NbX_4{\cdot}2NCMe$ is allowed to react with $Sb_2S_3$.[6] The compounds formed have been shown to be dimeric in which two sulphur atoms bridge the two metal centres (see below). An alternative



route to these types of compounds would be to take the compounds containing the $\mathrm{Nb{-}S_2{-}Nb{-}S}$ core and to carry out reactions designed to remove a sulphur atom from the $S_2$ group.

Accordingly reported herein are the results of studies in which $NbX_5$ and $Sb_2S_3$ have been allowed to react in a 2:1 molar ratio together with the attempts to remove a sulphur atom from a $S_2$ group in $Nb_2X_4S_3$.

## Results and Discussion

Typical analyses of the products of the reaction of $NbX_5$ (X = Br or Cl) and $Sb_2S_3$ in a 2:1 molar ratio are in accord with the products being $Nb_2X_4S_3$. Unfortunately all attempts to obtain reproducible sulphur analyses either by the authors, or by commercial laboratories were unsuccessful. Similarly, experiments designed to grow single crystals by sublimation were unsuccessful. Accordingly in order to characterise the products the compounds were treated with tetrahydrothiophene (tht) in an endeavour to prepare the well characterised 1:4 adducts, $Nb_2X_4S_3{\cdot}4tht$. In addition a number of other co-ordination products [of MeCN, 1,2-bis(phenylthio)ethane (bpte), and

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* Di-μ-sulphido-bis[dichlorobis(tetrahydrothiophene-*S*)niobium(IV)].

*Supplementary data available* (No. SUP 56107, 7 pp.): thermal parameters, H-atom co-ordinates, remaining bond distances and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

dimethyl sulphide (dms)] were prepared to ensure that the formation of $Nb_2X_4S_3$ is not a function of the presence of tht and to investigate the absorption bands in the i.r. spectrum that are characteristic of $Nb_2X_4S_3$. The analyses of the tht, MeCN, and dms adducts are in accord with the formulation $Nb_2X_4S_3 \cdot 4L$ (L = ligand), while those of (bpte) are in agreement with those required for 1:2 compounds (Table 1). Furthermore *X*-ray powder diffraction patterns of the tht adducts were identical to those of $Nb_2X_4S_3 \cdot 4tht$ (X = Br or Cl), whose single-crystal *X*-ray structures have been determined.[4]

**Table 1.** Analyses of the adducts (calculated values in parentheses)

| Adduct | Colour | % Nb | % Halogen |
|---|---|---|---|
| $Nb_2Cl_4S_3 \cdot 4dms$ | Bright green | 27.9 (27.6) | 20.9 (21.1) |
| $Nb_2Br_4S_3 \cdot 4dms$ | Bright green | 21.9 (21.9) | 37.5 (37.6) |
| $Nb_2Cl_4S_3 \cdot 4tht$ | Green | 23.8 (23.9) | 18.9 (18.3) |
| $Nb_2Br_4S_3 \cdot 4tht$ | Green | 19.2 (19.5) | 18.9 (18.3) |
| $Nb_2Cl_4S_3 \cdot 4NCMe$ | Dull yellow | 31.4 (31.6) | 24.0 (24.1) |
| $Nb_2Br_4S_3 \cdot 4NCMe$ | Dull yellow | 24.5 (24.3) | 42.3 (41.7) |
| $Nb_2Cl_4S_3 \cdot 2bpte$ | Dark brown | 20.1 (20.3) | 15.7 (15.5) |
| $Nb_2Br_4S_3 \cdot 2bpte$ | Brown | 16.8 (17.0) | 29.5 (29.2) |

Finally, each of the reactions leading to the formation of complexes led to the isolation of single products. Thus it is concluded that the niobium(IV) compounds are formed directly at low temperatures *via* the oxidation of two $S^{2-}$ groups to $(S_2)^{2-}$ and the concomitant reduction of two niobium(V) atoms to niobium(IV). Recently the compounds $NbBr_3Se$, $NbBr_3Te$, and $NbI_3Te$ (prepared from the elements at approximately 1 000 °C) were shown to be dimeric niobium(IV) compounds containing $Se_2^{2-}$ or $Te_2^{2-}$ groups.[7]

The i.r. and Raman spectra of the adducts are given in Table 2 together with the i.r. spectra of $Nb_2X_4S_3$ (X = Br or Cl) and the Raman spectrum of $Nb_2Br_4S_3$; the chloride decomposed in the laser beam. The modes associated with the co-ordinated ligands are as seen in other well documented complexes of the various ligands and show the changes from the spectra of the free ligands that have been associated with adduct formation. The spectrum of bpte has not been assigned but the ligand spectra exhibited by $Nb_2X_4S_3 \cdot 2bpte$ are identical to that of $TaCl_3S \cdot bpte$ in which the ligand adopts a *gauche,gauche,trans* configuration.[8] Assignments of the modes associated with the Nb–S–Nb–$S_2$ cores are given in Table 2. The highest energy absorptions (591—564 cm$^{-1}$) are vibrations involving the

**Table 2.** Vibrational spectra of the complexes (600—200 cm$^{-1}$)

| | ν(S–S) | | ν(Nb–S–Nb) | | ν(Nb–Cl) or ν(Nb–S) | | ν(Nb–Br) | | Other peaks | |
|---|---|---|---|---|---|---|---|---|---|---|
| | I.r. | Raman | I.r. | Raman | I.r. | Raman | I.r. | Raman | I.r. | Raman |
| $Nb_2Cl_4S_3$[a] | | | 462m | | 380m,br | | | | | |
| | | | | | 343s,br | | | | | |
| | | | | | 315s | | | | | |
| | | | | | 280s,br | | | | | |
| $Nb_2Br_4S_3$ | 589w | 591s | 461m | 462vs | 381w | 383w | 260m,br | 258m,br | | |
| | | | | | 355m (sh) | 350vs | 205s | 200s,br | | |
| | | | | | 340s,br | 335m | | | | |
| | | | | | 315m | 316m | | | | |
| $Nb_2Cl_4S_3 \cdot 4dms$ | 583w | 585m | 450s | 451s | 349vs | 348s | | | 280 (sh) | |
| | 565w | 564m | | | 335 (sh) | 338m | | | | |
| | | | | | 305m | 312m | | | | |
| | | | | | 290s | 291vs | | | | |
| $Nb_2Br_4S_3 \cdot 4dms$ | 581m | 581m | 450s | 451vs | 355 (sh) | 348m,br | 250m,br | 245m,br | | |
| | 565m | 566m | | | 340s | 340w | 205vs,br | | | |
| | | | | | 305m | 305w | | | | |
| $Nb_2Cl_4S_3 \cdot 4tht$ | 589m | 591m | 450s | 451s | 345vs,br | 347s | | | 517m[b] | |
| | | 582w | | | 307s | 309s | | | 470w[b] | |
| | | | | | 288vs | 290m | | | | |
| $Nb_2Br_4S_3 \cdot 4tht$ | 584w | 585m | 449s | 449s | 350s | 347vs | 250m,br | 245m | 515m[b] | 515w[b] |
| | 569w | 571s | | | 331s | 329s | 215s | 220m,br | 469w[b] | 478m[b] |
| | | | | | 303s | 304m | 205m | | | |
| $Nb_2Cl_4S_3 \cdot 2bpte$[a] | 582w | | 455s | | 350s | | | | 466s[b] | |
| | | | | | 345s | | | | | |
| | | | | | 329s | | | | | |
| | | | | | 310s | | | | | |
| | | | | | 302s | | | | | |
| | | | | | 280m | | | | | |
| $Nb_2Br_4S_3 \cdot 2bpte$[a] | 580m | | 455s | | 332m,br | | 245s | | 463m[b] | |
| | | | | | 305m | | 215s,br | | | |
| $Nb_2Cl_4S_3 \cdot 4NCMe$ | 580w | 581s | 449s | 450s | 345m,br | 359s | | | 400m[c] | 410m[c] |
| | | | | | 321m | 325m | | | | 390w[b] |
| | | | | | 281s | | | | | |
| $Nb_2Br_4S_3 \cdot 4NCMe$ | 589w | 590s | 449s | 451s | | 360s | 250br | *a* | 400m[c] | 410m[c] |
| | | | | | 342m | 345w | 210s,br | | | |
| | | | | | 320m | 319w | | | | |
| | | | | | | 289m | | | | |
| $Nb_2Cl_4S_2 \cdot 4tht$[a] | | | 463m (sh) | | 345vs,br | | | | 518m[b] | |
| | | | 460vs | | 330m (sh) | | | | | |
| | | | | | 302s | | | | | |

[a] No Raman data. [b] Probably internal ligand mode. [c] ν(Nb–N).

stretching of the $S_2$ group; similar assigments having been made for the spectra of $Nb_2X_4S_4$ (X = Br or Cl).[9–11] It is more difficult to assign modes to the Nb–S–Nb group. In the compounds $Nb_2X_4S_2$·4MeCN, containing Nb–S–Nb–S rings,[6] bands in the range 476—468 cm$^{-1}$ and 330—320 cm$^{-1}$ were attributed to the Nb–S–Nb modes. Examination of the spectra recorded in Table 2 indicate that for the $Nb_2Br_4S_3$ adducts the comparable bands occur in the regions 462—449 cm$^{-1}$ and 355—332 cm$^{-1}$. The assignment of the lower energy band for the chloride adducts is difficult as one of the Nb–Cl modes occurs in the same region. The structures of the chalcogenide halides $Nb_2X_4S_3$ are likely to consist of Nb–S–Nb–$S_2$ fragments that are linked through halogen bridges giving rise to polymeric structures as seen in $Nb_2X_4S_4$.[12,13]

All the adducts were diamagnetic which besides confirming the presence of some form of magnetic interaction between the metal atoms allowed the measurement of their n.m.r. spectra. The MeCN adducts lacked solubility in suitable solvents but for the remaining complexes the $^1H$ spectra showed a shift to higher p.p.m. (relative to the free ligand in the same solvent as the complex) of the ligand resonances as expected on co-ordination. From the *X*-ray structure of the tht adducts it is known that there are two positions for the ligands, one in which the tht molecule is *trans* to a bridging S atom while in the other tht is *trans* to an $S_2$ group.[4] The n.m.r. measurements showed no evidence for two ligand sites. The limited n.m.r. facilities available restricted measurements on these air-sensitive compounds to 60 MHz and room temperature and so it proved impossible to decide if the failure to detect two sets of resonances for each ligand was caused by magnetic equivalence of the co-ordination sites or rapid exchange processes.

The second aspect of the present study concerned the reaction of niobium(IV) compounds, containing a Nb–$S_2$–Nb–S core, with phosphorus ligands in an attempt to remove one of the atoms from the $S_2$ group and so isolate another form of niobium(IV) compound in which two metal centres are linked by two bridging sulphur atoms. The compound chosen for the study was $Nb_2Cl_4S_3$·4tht. The reasons for the choice were first that the compound, unlike the parent chalcogenide halide, has a detectable S–S vibration in its i.r. spectrum. Secondly it is a well characterised species having been the subject of a single-crystal *X*-ray study.[4] Thus the reaction of $Nb_2Cl_4S_3$·4tht with triphenylphosphine was carried out. The i.r. spectrum of the insoluble brown niobium-containing product did not show any of the bands associated with a S–S group or triphenylphosphine. The analytical data were in accord with the product being $Nb_2Cl_4S_2$·4tht. The i.r. spectrum of the soluble product was consistent with it being a mixture of triphenylphosphine and triphenylphosphine sulphide; a strong band occured at 638 cm$^{-1}$ in accord with the presence of the P=S bond of triphenylphosphine sulphide.

**Table 3.** Selected bond lengths (Å) and angles (°) for $Nb_2Cl_4S_2$·4tht

| | | | |
|---|---|---|---|
| Nb(1)–Nb(2) | 2.868(2) | Nb(2)–Cl(1) | 2.374(3) |
| Nb(1)–Cl(3) | 2.374(3) | Nb(2)–Cl(2) | 2.369(3) |
| Nb(1)–Cl(4) | 2.372(3) | Nb(2)–S(1) | 2.355(3) |
| Nb(1)–S(1) | 2.350(3) | Nb(2)–S(2) | 2.353(3) |
| Nb(1)–S(2) | 2.350(3) | Nb(2)–S(3) | 2.777(3) |
| Nb(1)–S(5) | 2.769(3) | Nb(2)–S(4) | 2.768(3) |
| Nb(1)–S(6) | 2.768(3) | | |
| | | | |
| Nb(2)–Nb(1)–Cl(3) | 104.19(8) | Cl(3)–Nb(1)–S(2) | 98.44(11) |
| Nb(2)–Nb(1)–Cl(4) | 103.85(8) | Cl(4)–Nb(1)–S(2) | 97.74(11) |
| Cl(3)–Nb(1)–Cl(4) | 151.94(11) | S(1)–Nb(1)–S(2) | 105.01(10) |
| Nb(2)–Nb(1)–S(1) | 52.53(7) | Nb(2)–Nb(1)–S(5) | 139.01(7) |
| Cl(3)–Nb(1)–S(1) | 98.26(11) | Cl(3)–Nb(1)–S(5) | 80.41(10) |
| Cl(4)–Nb(1)–S(1) | 99.49(11) | Cl(4)–Nb(1)–S(5) | 79.17(10) |
| Nb(2)–Nb(1)–S(2) | 52.48(7) | | |
| | | | |
| S(1)–Nb(1)–S(5) | 86.50(9) | Cl(4)–Nb(1)–S(6) | 78.61(10) |
| S(2)–Nb(1)–S(5) | 168.46(10) | S(1)–Nb(1)–S(6) | 165.96(10) |
| Nb(2)–Nb(1)–S(6) | 141.51(7) | S(2)–Nb(1)–S(6) | 89.02(10) |
| Cl(3)–Nb(1)–S(6) | 78.91(10) | S(5)–Nb(1)–S(6) | 79.48(9) |
| | | | |
| Nb(1)–Nb(2)–Cl(1) | 103.52(8) | Cl(1)–Nb(2)–S(3) | 80.08(10) |
| Nb(1)–Nb(2)–Cl(2) | 103.76(8) | Cl(2)–Nb(2)–S(3) | 77.92(11) |
| Cl(1)–Nb(2)–Cl(2) | 152.68(11) | S(1)–Nb(2)–S(3) | 88.40(10) |
| Nb(1)–Nb(2)–S(1) | 52.37(7) | S(2)–Nb(2)–S(3) | 166.79(10) |
| Cl(1)–Nb(2)–S(1) | 97.89(11) | Nb(1)–Nb(2)–S(4) | 139.38(7) |
| Cl(2)–Nb(2)–S(1) | 97.49(11) | Cl(1)–Nb(2)–S(4) | 79.73(10) |
| Nb(1)–Nb(2)–S(2) | 52.38(7) | Cl(2)–Nb(2)–S(4) | 80.62(11) |
| Cl(1)–Nb(2)–S(2) | 98.99(11) | S(1)–Nb(2)–S(4) | 168.25(10) |
| Cl(2)–Nb(2)–S(2) | 98.75(11) | S(2)–Nb(2)–S(4) | 87.01(10) |
| S(1)–Nb(2)–S(2) | 104.75(10) | S(3)–Nb(2)–S(4) | 79.86(9) |
| Nb(1)–Nb(2)–S(3) | 140.76(7) | | |
| | | | |
| Nb(1)–S(1)–Nb(2) | 75.10(9) | Nb(1)–S(2)–Nb(2) | 75.14(9) |

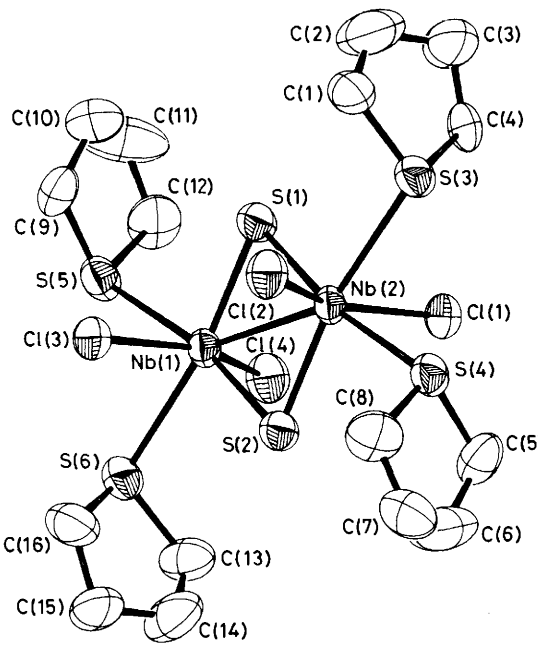

**Figure.** Structure of $Nb_2Cl_4S_2$·4tht

To prove that the desired reaction had actually taken place a crystal of the niobium-containing product was studied by single-crystal *X*-ray methods. The unit cell contains four discrete units of $Nb_2Cl_4S_2$·4tht confirming that the desired reaction product had been obtained, an atom having been removed from an $S_2$ group. Significant bond lengths and angles are given in Table 3 and the molecule is depicted in the Figure which also contains the atomic numbering scheme. There is no symmetry within the dimeric unit and the two metal atoms are linked by two bridging sulphur atoms [Nb–S 2.350(3)—2.355(3) Å] thus forming a Nb–S–Nb–S ring whose geometry is similar to that in $Nb_2Cl_4S_2$·4NCMe.[6] The angles within this ring [at S(1) 75.10(9), S(2) 75.14(9), Nb(1) 105.01(10), and Nb(2) 104.75(10)°] suggest the presence of a niobium–niobium interaction and this is supported by the distance of separation [2.868(2) Å] which is within the range observed in $Nb_2X_4S_2$·4NCMe (X = Br or Cl) [2.862(2)—2.872(3) Å]. The distance is slightly longer than that in the parent compound

$Nb_2Cl_4S_3$·4tht [2.844(2) Å],[4] where the two metal atoms are linked by *via* a sulphur atom and an $S_2$ group. In the type of species under discussion it is normal for the other bonds formed to the metal centre to bend away from the metal–metal vector and this is observed in the present structure [Cl–Nb–Nb angles range from 103.52(8) to 104.19(8)°]. The angles involving the chlorine atoms are slightly larger than those found in $Nb_2Cl_4S_2$·4NCMe [100.34(17)—101.64(18)°] while the angles involving the ligand atoms are comparable in both systems. The lengths of the niobium–chlorine bonds [2.369(3)—2.374(3) Å] are intermediate between those in $Nb_2Cl_4S_3$·4tht[4] and $Nb_2Cl_4S_2$·4NCMe.[6]

## Conclusions

It has been shown that the reaction of $NbX_5$ (X = Br or Cl) with $Sb_2S_3$ (2:1 molar ratio) in carbon disulphide media leads to the formation of the niobium(IV) compounds $Nb_2X_4S_3$ (X = Br or Cl) in quantitative yield. The reduction of niobium(V) to niobium(IV) occurs with concomitant oxidation of two (in a formal sense) $S^{2-}$ ions to yield a $S_2^{2-}$ group. Thus it would appear that in these simple ternary systems two niobium(V) centres are reduced when bridged by three sulphur atoms. A similar bridging situation is seen in $NbS_3$ which contains niobium(IV).[14] By contrast there is a three-atom oxygen bridge between two niobium(V) atoms in the porphyrin complex tri-μ-oxobis[5,10,15,20-tetraphenylporphyrinatoniobium(V)].[15,16] Attempts to prepare analogous selenido-niobium(IV) species by the reaction of $NbX_5$ with $Sb_2Se_3$ in a 2:1 molar ratio led to a complex mixture of products among which was elemental selenium. These observations are obviously related to trends in the stabilities of oxidation states on descending Group 6B. Further investigation of trends in oxidation state stability were carried out by treating $TaX_5$ with $Sb_2S_3$ in a 2:1 molar ratio. The products obtained were $TaX_3S$ together with unreacted $Sb_2S_3$. These results reflect the greater resistance of tantalum(V) to reduction compared to niobium(V). Finally the stability of dimeric sulphur-bridged niobium(IV) dimers is illustrated by the formation of $Nb_2Cl_4S_2$·4tht from $Nb_2Cl_4S_3$·4tht by reaction with $PPh_3$. This retention of the dimeric nature is in contrast to the situation with niobium(IV) chloride, which although exhibiting metal–metal bonding in the binary compound, becomes monomeric on complex formation.

## Experimental

All preparations were carried out using in all-glass vacuum line. Nujol or hexachlorobutadiene mulls of the various compounds were made in a dry-box fitted with a recycling system in which nitrogen was pumped over molecular sieves and a heated de-oxygenating catalyst.

*Preparation of* $Nb_2X_2S_3$ (X = Br *or* Cl).—(*a*) *In carbon disulphide*. The pentahalide $NbX_5$ (5 g) was quickly tipped under a stream of dry nitrogen into an ampoule (previously weighed) which contained a magnetic follower. The ampoule was rapidly evacuated and then filled with dry nitrogen and re-weighed. A quantity of antimony(III) sulphide required to give a slight excess of pentahalide above the desired 2:1 stoicheiometry was taken and heated to 150 °C overnight while being pumped. The sulphide was allowed to cool and quickly poured onto the pentahalide in the ampoule. The ampoule was cooled to liquid nitrogen temperature, dry carbon disulphide (40 cm³) was distilled onto the sulphide and the ampoule sealed. The mixture was stirred and kept at 50 °C for 10 d. The ampoule was opened under dry nitrogen and the product isolated by vacuum line filtration. The insoluble sulphidohalide product was washed with fresh quantities of dry carbon disulphide to remove the antimony(III) halide also produced in the reaction. The chloride, $Nb_2Cl_4S_3$, was also prepared in dichloromethane but in an attempted reaction to prepare the analogous bromide a halogen exchange reaction took place.

(*b*) *A sealed tube reaction*. The chloride $Nb_2Cl_4S_3$ was prepared by heating (110 °C) niobium(V) chloride (5 g) and antimony(III) sulphide (2:1 molar ratio) in a sealed evacuated sublimation tube for 2 d. The antimony(III) chloride was sublimed out of the reaction mixture by shaking all the reaction products to one end of the sealed tube and maintaining this end of the tube at 110 °C while the other end was at room temperature. Attempts to prepare the bromide by reactions in sealed tubes lead to incomplete reaction.

Typical analyses (Found: Nb, 43.2; Cl, 33.8. $Nb_2Cl_4S_3$ requires Nb, 43.8; Cl, 33.5%. Found: Nb, 30.6; Br, 53.5. $Nb_2Br_4S_3$ requires Nb, 30.9; Br, 53.2%).

*Preparation of Co-ordination Compounds*.—Reactions were carried out in sealed ampoules identical to those used for the preparation of the chalcogenide halides. The reactions of $Nb_2X_4S_3$ (X = Br or Cl) (2 g) with the liquid ligands (dms, tht, and methyl cyanide) were carried out in a large excess of neat ligand (30 cm³) while the reactions with the solid ligand bpte were carried out in a 1:1 molar stoicheiometry with carbon disulphide (40 cm³) as solvent. The ligands showed different reactivity towards the chalogenide halides, thus while with dms the reactions were complete on stirring the reactants for 24 h at room temperature, it was necessary to heat the reactants to 50 °C for a period of 7 d to faciliate complete reaction with tht and MeCN. The reactions with bpte took 4 weeks at 50 °C to go to completion. All the products were insoluble in the reaction media. Very small amounts of materials were obtained on evaporation of the filtrates. The colour and i.r. spectra of the trace soluble products were identical to those of the related insoluble products.

**Table 4.** Atomic co-ordinates (× $10^3$) with estimated standard deviations in parentheses for $Nb_2Cl_4S_2$·4tht

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Nb(1) | 1 918(0) | 1 166(1) | 4 254(1) |
| Nb(2) | 3 105(0) | 590(1) | 5 780(1) |
| Cl(1) | 3 981(1) | 727(2) | 4 569(3) |
| Cl(2) | 2 690(1) | 182(3) | 7 567(3) |
| Cl(3) | 1 029(1) | 1 011(2) | 5 439(3) |
| Cl(4) | 2 333(1) | 1 585(3) | 2 467(3) |
| S(1) | 2 383(1) | −535(2) | 4 571(3) |
| S(2) | 2 631(1) | 2 290(2) | 5 472(3) |
| S(3) | 3 866(1) | −1 179(3) | 6 530(3) |
| S(4) | 4 101(1) | 1 536(3) | 7 317(3) |
| S(5) | 947(1) | 218(2) | 2 668(3) |
| S(6) | 1 134(1) | 2 907(2) | 3 521(3) |
| C(1) | 3 329(7) | −2 298(10) | 6 773(12) |
| C(2) | 3 383(9) | −3 079(12) | 5 842(16) |
| C(3) | 4 003(8) | −2 968(11) | 5 334(16) |
| C(4) | 4 207(7) | −1 814(10) | 5 305(14) |
| C(5) | 4 414(5) | 2 724(10) | 6 625(13) |
| C(6) | 4 138(9) | 3 679(13) | 7 143(22) |
| C(7) | 3 976(13) | 3 431(14) | 8 263(16) |
| C(8) | 3 719(7) | 2 300(11) | 8 422(12) |
| C(9) | 568(6) | −926(11) | 3 324(12) |
| C(10) | 856(10) | −1 890(12) | 2 843(19) |
| C(11) | 1 072(8) | −1 688(13) | 1 711(17) |
| C(12) | 1 359(8) | −613(11) | 1 698(12) |
| C(13) | 1 653(7) | 4 054(9) | 3 238(13) |
| C(14) | 1 550(9) | 4 866(13) | 4 110(18) |
| C(15) | 898(8) | 4 711(12) | 4 588(17) |
| C(16) | 789(6) | 3 577(10) | 4 724(14) |

*Reaction of* $Nb_2Cl_4S_3$·4tht *with Triphenylphosphine*.—Triphenylphosphine and $Nb_2Cl_4S_3$·4tht (3:1 molar ratio) were placed with toluene (50 $cm^3$) in an ampoule indentical to those used for the preparation of the chalogenide halides. The mixture was kept at 50 °C and stirred for three months during which period the colour of the insoluble material changed from green to brown. The insoluble material was isolated by filtration and crystals of $Nb_2Cl_4S_2$·4tht suitable for single-crystal *X*-ray investigation obtained by recrystallisation from $CH_2Cl_2$ using the double-ampoule technique. The i.r. spectrum of the solid obtained by evaporation of the solvent contained a band at 638 $cm^{-1}$, the position of the P=S stretch in $SPPh_3$.

*Crystal Structure Determination of* $Nb_2Cl_4S_2$·4tht.—*Crystal data*. $C_{16}H_{32}Cl_4Nb_2S_6$, $M = 744.2$, monoclinic, $a = 19.958(11)$, $b = 12.616(8)$, $c = 11.530(10)$ Å, $\beta = 97.0(1)°$, $U = 2\,881.6$ Å$^3$, $Z = 4$, $F(000) = 1\,496$, $D_c = 2.03$ g $cm^{-3}$, $\lambda = 0.7107$ Å, $\mu(Mo\text{-}K_\alpha) = 15.6$ $cm^{-1}$, space group $P2_1/n$ from systematic absences $0k0$, $k = 2n + 1$, $h0l$, $h + l = 2n + 1$.

Intensity data were collected on a Stoe STADI2 diffractometer using variable width ω scans. Background counts were 20 s and a scan rate of 0.0333° $s^{-1}$ was applied to a width of (1.5 + sin μ/tan θ). 5 054 Independent reflections were measured with $2\theta < 50°$. 2 741 Data with $I > 3\sigma(I)$ were used in subsequent calculations.

The positions of the Nb atoms were obtained from a Patterson function and the remaining non-hydrogen atoms from Fourier maps. The hydrogen atoms were placed in tetrahedral positions and those in the same ligand given a common (refined) thermal parameter. Non-hydrogen atoms were given anisotropic thermal parameters and the structure was refined by full-matrix least squares. The final *R* value was 0.053 (*R'* 0.057).

Calculations were done at the University of Manchester Regional Computing Centre using SHELX 76[17] with scattering factors taken from ref. 18. Atomic co-ordinates are given in Table 4.

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