Six- and eight-coordinate thio- and seleno-ether complexes of NbF_5 and some comparisons with $NbCl_5$ and $NbBr_5$ adducts†

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Received 10th August 2009, Accepted 7th October 2009
First published as an Advance Article on the web 16th November 2009
DOI: 10.1039/b916336k

The reaction of $RS(CH_2)_2SR$ (R = Me, Et or ^iPr) with NbF_5 produces $[NbF_4\{RS(CH_2)_2SR\}_2][NbF_6]$ which contain distorted eight-coordinate (dodecahedral) cations and octahedral anions, whereas $RSe(CH_2)_2SeR$ (R = Me or Bu^n) form six-coordinate $[(NbF_5)_2(\mu\text{-}RSe(CH_2)_2SeR)]$. Et_2S and Me_2Se (L) also form six-coordinate $[NbF_5(L)]$, but Me_2S forms both $[NbF_5(Me_2S)]$ and an eight-coordinate cation in $[NbF_4(Me_2S)_4][NbF_6]$. $MeS(CH_2)_2SMe$ forms eight-coordinate cations in $[NbX_4\{MeS(CH_2)_2SMe\}_2]$-$[NbX_6]$ (X = Cl or Br), but other complexes of the heavier halides including $[NbX_5(L)]$ and $[(NbX_5)_2(\mu\text{-L–L})]$ (L–L = $RSe(CH_2)_2SeR$; $o\text{-}C_6H_4(CH_2SMe)_2$ and $o\text{-}C_6H_4(CH_2SeMe)_2$) contain six-coordinate niobium. The very unstable $[NbCl_5(Me_2Te)]$ was characterised spectroscopically, but all other attempts to form telluroether complexes resulted in decomposition, and NbI_5 was reduced even by thioethers. The complexes have been characterised by multinuclear NMR (^1H, ^{19}F, ^{93}Nb, ^{77}Se or ^{125}Te), IR and UV/visible spectroscopy, and X-ray crystal structures are reported for $[NbF_4\{RS(CH_2)_2SR\}_2][NbF_6]$ (R = Me, ^iPr), $[NbF_4(Me_2S)_4][NbF_6]$, $[NbCl_5(Me_2Se)]$, $[NbBr_5(Me_2S)]$, $[(NbCl_5)_2\{o\text{-}C_6H_4(CH_2SMe)_2\}]$ and $[(NbCl_5)_2\{MeSe(CH_2)_2SeMe\}]$. All the complexes are very moisture sensitive and the fluoride complexes decompose slowly with fluorination of the neutral ligand.

Introduction

Complexes of soft neutral thioether or selenoether ligands with hard oxophilic early transition metals in their highest oxidation states are relatively uncommon, and metal fluoride complexes are very rare.[1,2] We have reported dithioether and diselenoether adducts of MoO_2X_2 (X = Cl or Br),[3] WO_2X_2,[4] MCl_4 (M = Ti, Zr or Hf),[5,6] VOX_3 (X = F or Cl (thioethers only)),[7] and VCl_4,[7,8] all of which are extremely readily hydrolysed. Some of these complexes are single-source CVD precursors for metal dichalcogenide films.[6,8] In the case of niobium(V), the simplest six-coordinate adducts $[NbX_5(R_2S)]$ (X = F, Cl or Br; R = Me or Et) were prepared by Fairbrother and co-workers by direct reaction of NbX_5 with R_2S in the absence of a solvent and identified using a combination of vapour pressure measurements and microanalysis.[9,10] These, and the Me_2Se analogues, were also examined by Merbach and co-workers, and solution UV-visible and ^1H NMR spectra reported, although in many cases these were from complexes generated *in situ.*[11–13] Subsequently, detailed ^1H NMR studies revealed that ligand exchange proceeds by an associative mechanism, in contrast to ether analogues, which react by a dissociative mechanism.[14] There is very little information on dithioether complexes,[15] although a small number of thiacrown complexes $[(thiacrown)(NbCl_5)_x]$ have been described.[16] With the exception of $[(NbCl_5)_2([14]aneS_4)]$ ($[14]aneS_4$ = 1,4,8,11-tetrathiacyclotetradecane), none of these have been structurally characterised. Here we describe systematic studies of the reactions of NbF_5 with a range of chalcogenoether ligands and selected comparator data on $NbCl_5$ and $NbBr_5$ adducts, focusing particularly on structural and multinuclear NMR results. In a communication[17] we have described the structural characterisation of two sulfonium salts obtained as by-products from the reactions of NbF_5 with $o\text{-}C_6H_4(CH_2SMe)_2$ and $[9]aneS_3$ (1,4,7-trithiacyclononane).

Experimental

Infrared spectra were recorded as Nujol mulls between CsI plates using a Perkin-Elmer 983G or Spectrum 100 spectrometers over the range 4000–200 cm^{-1}. ^1H NMR spectra were recorded from $CDCl_3$ solutions using a Bruker AV300 spectrometer. $^{19}F\{^1H\}$, $^{77}Se\{^1H\}$, $^{125}Te\{^1H\}$ and ^{93}Nb NMR spectra were recorded using a Bruker DPX400 spectrometer and are referenced to external $CFCl_3$, neat Me_2Se, neat Me_2Te and $[Et_4N][NbCl_6]$ in MeCN respectively. UV/visible spectra were recorded from solid samples diluted with $BaSO_4$ using the diffuse reflectance attachment of a Perkin-Elmer Lambda 19 spectrometer. Microanalyses on new complexes were undertaken by Medac Ltd, except for some of the fluoride complexes which decomposed at room temperature in a few hours (see Discussion section), which precluded obtaining microanalytical data. Preparations were undertaken using standard Schlenk and glove-box techniques under a N_2 atmosphere. Solvents were dried by distillation from CaH_2 (CH_2Cl_2) or Na/benzophenone ketyl (hexane and diethyl ether). Anhydrous NbX_5 (X = F, Cl, Br or I) were obtained from Aldrich, Apollo or Strem and used as received. The ligands R_2S (R = Me or

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† Electronic supplementary information (ESI) available: Additional experimental and spectroscopic data for $[NbX_5L]$ complexes, and crystallographic data and ORTEPs for $[NbBr_5(Me_2S)]$ and $[NbCl_5(Me_2Se)]$. CCDC reference numbers 723266–723272. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b916336k

‡ Deceased 5th June 2009.

Et) and Me_2Se were obtained from Aldrich or Strem and stored over molecular sieves. Me_2Te, $RS(CH_2)_2SR$ (R = Me, Et or ^iPr), $RSe(CH_2)_2SeR$ (R = Me or ^nBu), $o\text{-}C_6H_4(CH_2EMe)_2$ (E = S or Se) and $MeTe(CH_2)_3TeMe$ were made by literature methods,[18–21] and stored over molecular sieves.

$[NbF_5(Me_2S)]$

Powdered NbF_5 (0.38 g, 2.0 mmol) was added to neat Me_2S (10 mL) with stirring, when the solid initially dissolved to give a yellow solution, and then over a period of *ca.* 30 min precipitated as a white powder. This was filtered off and dried *in vacuo*. Yield: 0.40 g, 80%. Required for $C_2H_6F_5NbS$ (250.0): C, 9.6; H, 2.4. Found: C, 9.3; H, 3.0%. ^1H NMR ($CDCl_3$, 295 K): δ 2.36 (s). UV/vis (d.r.)/cm^{-1}: 27800, 38000.

$[NbF_5(Et_2S)]$

Colourless oil made as described.[9] ^1H NMR ($CDCl_3$, 295 K): δ 1.40 (t) [3H], 2.95 (q) [2H]. UV/vis (d.r.)/cm^{-1}: 26000, 38400.

$[NbF_4(Me_2S)_4][NbF_6]$

NbF_5 (0.38 g, 2.0 mmol) was suspended in CH_2Cl_2 (10 mL) and Me_2S (0.36 g, 6.0 mmol) syringed in with stirring to give a colourless solution. This was refrigerated for 5 days (−18 °C), when colourless crystals separated. These were filtered off from the cold solution and dried in a stream of nitrogen. Yield: 0.35 g, 56%. The crystals lose Me_2S and crumble a little above room temperature or *in vacuo*, which prevented reproducible microanalyses being obtained. ^1H NMR ($CDCl_3$, 295 K): δ 2.28 (s); (220 K) δ 2.40. UV/vis (d.r.)/cm^{-1}: 27500.

$[NbF_5(Me_2Se)]$

NbF_5 (0.19 g, 1.0 mmol) was suspended in CH_2Cl_2 (10 mL) and Me_2Se (0.11 g, 1.0 mmol) syringed in with stirring to give a colourless solution. After 10 min the solvent was removed *in vacuo* to give a fawn solid, which was washed with hexane, filtered off and dried. Yield: 0.27 g, 90%. The solid darkens slowly in the dry-box, and solutions decompose in several hours, turning first brown and then green–black. Decomposition is slower in a freezer. ^1H NMR ($CDCl_3$, 295 K): δ 2.76 (s). UV/vis (d.r.)/cm^{-1}: 23000, 33800.

$[NbF_4\{MeS(CH_2)_2SMe\}_2][NbF_6]$

NbF_5 (0.37 g, 2.0 mmol) was suspended in anhydrous CH_2Cl_2 (20 mL) and a solution of $MeS(CH_2)_2SMe$ (0.245 g, 2.0 mmol) in CH_2Cl_2 (4 mL) added with stirring. A clear colourless solution formed rapidly, which was stirred for 30 min and then concentrated *in vacuo* to ~10 mL. Refrigeration for one week produced colourless crystals, which were filtered off and dried *in vacuo*. Yield: 0.45 g, 73%. Required for $C_8H_{20}F_{10}Nb_2S_4$ (620.3): C, 15.5; H, 3.3. Found: C, 15.0; H, 3.1%. ^1H NMR ($CDCl_3$, 295 K): δ 2.25 (s) [6H] Me, 3.03 (s) [4H] CH_2. UV/vis (d.r.)/cm^{-1}: 27700.

$[NbF_4\{EtS(CH_2)_2SEt\}_2][NbF_6]$

This was made similarly to $[NbF_4\{MeS(CH_2)_2SMe\}_2][NbF_6]$, as a white powder. Yield: 65%. Required for $C_{12}H_{28}F_{10}Nb_2S_4$ (676.4): C, 21.3; H, 4.2. Found: C, 21.2; H, 3.6%. ^1H NMR ($CDCl_3$, 295 K): δ 1.39 (br) [6H] Me, 2.91 (br) [4H] CH_2, 3.33 (s) [4H] CH_2. UV/vis (d.r.)/cm^{-1}: 27750.

$[NbF_4\{^iPrS(CH_2)_2S^iPr\}_2][NbF_6]$

NbF_5 (0.37 g, 2.0 mmol) was suspended in anhydrous CH_2Cl_2 (20 mL) and a solution of $^iPrS(CH_2)_2S^iPr$ (0.36 g, 2.0 mmol) in CH_2Cl_2 (4 mL) added with stirring. A clear colourless solution formed rapidly, which was stirred for 30 min and then concentrated *in vacuo* to ~5 mL. Refrigeration for 1 week produced large, clear crystals, which were filtered off and dried *in vacuo.* Yield: 0.45 g, 63%. Required for $C_{16}H_{36}F_{10}Nb_2S_4{\cdot}CH_2Cl_2$ (817.4): C, 25.0; H, 4.7. Found: C, 25.0; H, 4.9% ^1H NMR ($CDCl_3$, 295 K): δ 1.31 (d) $J = 6$ Hz, [12H] Me, 3.05 (s) [4H] CH_2, 3.52 (m) [2H] CH. UV/vis (d.r.)/cm^{-1}: 27700.

$[(NbF_5)_2\{MeSe(CH_2)_2SeMe\}]$

NbF_5 (0.37 g, 2.0 mmol) was suspended in anhydrous CH_2Cl_2 (20 mL) at 273 K, and a solution of $MeSe(CH_2)_2SeMe$ (0.22 g, 1.0 mmol) in CH_2Cl_2 (4 mL) added with stirring. After 5 min the colourless solution was concentrated *in vacuo* to *ca.* 5 mL, and the white solid produced filtered off and dried *in vacuo*. The solid slowly turns brown at ambient temperatures. ^1H NMR (CD_2Cl_2, 295 K): δ 2.54 (s) [6H] Me, 3.5 (s) [4H] CH_2. UV/vis (d.r.)/cm^{-1}: 28500, 33800.

$[(NbF_5)_2\{^nBuSe(CH_2)_2Se^nBu\}]$

NbF_5 (0.37 g, 2.0 mmol) was suspended in anhydrous CH_2Cl_2 (20 mL) at 273 K, and a solution of $^nBuSe(CH_2)_2Se^nBu$ (0.46 g, 1.0 mmol) in CH_2Cl_2 (4 mL) added with stirring. After 5 min the pale yellow solution was concentrated *in vacuo* to leave a clear yellow oil, which was washed with hexane (5 mL), the hexane removed by cannula, and the oil dried *in vacuo*. The oil turns dark in a few hours at room temperature. The solution stability is poor, solutions becoming red in about 30 min at room temperature although reaction is much slower at 243 K. ^1H NMR (CD_2Cl_2, 295 K): δ 1.0 (t) [6H] Me, 1.45 (m) [4H] CH_2, 1.9 (m) [4H] CH_2, 3.40 (m) [4H] CH_2, 3.50 (s) [4H] CH_2.

$[NbCl_4\{MeS(CH_2)_2SMe\}_2][NbCl_6]$

$NbCl_5$ (0.39 g, 1.5 mmol) was suspended in anhydrous CH_2Cl_2 (20 mL) and a solution of $MeS(CH_2)_2SMe$ (0.24 g, 2.0 mmol) in CH_2Cl_2 (8 mL) added with stirring. The $NbCl_5$ dissolved to give a deep yellow solution which rapidly precipitated a deep yellow powder. The mixture was stirred for 3 h, then concentrated *in vacuo* to ~10 mL, and the deep yellow powder filtered off and dried *in vacuo.* Yield: 0.52 g, 88%. Required for $C_8H_{20}Cl_{10}Nb_2S_4$ (784.8): C, 12.3; H, 2.6. Found: C, 12.6; H, 2.8%. ^1H NMR (CD_2Cl_2, 295 K): δ 2.46 (s) [6H] Me, 3.13 (s) [4H] CH_2. UV/vis (d.r.)/cm^{-1}: 21200 (sh), 25600, 34800.

$[NbBr_4\{MeS(CH_2)_2SMe\}_2][NbBr_6]$

This was made similarly to the chloride analogue above as a red–brown solid. Yield: 73%. Required for $C_8H_{20}Br_{10}Nb_2S_4$ (1229.4): C, 7.8; H, 1.6. Found: C, 7.7; H, 1.7%. ^1H NMR (CD_2Cl_2, 295 K): δ 2.34 (s) [6H] Me, 3.13 (s) [4H] CH_2. UV/vis (d.r.)/cm^{-1}: 19600 (sh), 23800, 26600, 34500.

$[(NbCl_5)_2\{o\text{-}C_6H_4(CH_2SMe)_2\}]$

$NbCl_5$ (0.49 g, 2.0 mmol) was suspended in anhydrous CH_2Cl_2 (20 mL) and a solution of $o\text{-}C_6H_4(CH_2SMe)_2$ (0.18 g, 1.0 mmol) in CH_2Cl_2 (8 mL) added with stirring. The $NbCl_5$ dissolved to give a deep orange–yellow solution which was stirred for 3 h, then concentrated *in vacuo* to ~ 10 mL, and the orange–yellow powder filtered off and dried *in vacuo*. Yield: 0.52 g, 70%. Required for $C_{10}H_{14}Cl_{10}Nb_2S_2$ (738.7): C, 16.3; H, 1.9. Found: C, 16.0; H, 2.3%. ^1H NMR ($CDCl_3$, 295 K): 2.46 (s) [6H] Me, 4.34 (s) [4H] CH_2, 7.34–7.43 (m) [4H] C_6H_4. UV/vis (d.r.)/cm^{-1}: 25600, 34100.

$[(NbBr_5)_2\{o\text{-}C_6H_4(CH_2SMe)_2\}]$

This was made similarly to the chloride analogue above using $NbBr_5$. Orange–red powder. Yield: 40%. Required for $C_{10}H_{14}Br_{10}Nb_2S_2$ (1183.2): C, 10.1; H, 1.1. Found: C, 9.4; H, 0.9%. ^1H NMR ($CDCl_3$, 295 K): δ 2.48 (s) [6H] Me, 4.36 (s) [4H] CH_2, 7.38–7.43 (m) [4H] C_6H_4. UV/vis (d.r.)/cm^{-1}: 22700 (sh), 25000, 32800.

$[(NbCl_5)_2\{o\text{-}C_6H_4(CH_2SeMe)_2\}]$

$NbCl_5$ (0.39 g, 1.5 mmol) was suspended in anhydrous CH_2Cl_2 (20 mL) and a solution of $o\text{-}C_6H_4(CH_2SeMe)_2$ (0.21 g, 0.72 mmol) in CH_2Cl_2 (8 mL) added with stirring. The $NbCl_5$ dissolved to give a deep orange solution which was stirred for 3 h, then concentrated *in vacuo* to ~10 mL, and the orange powder filtered off and dried *in vacuo*. Yield: 0.47 g, 78%. Required for $C_{10}H_{14}Cl_{10}Nb_2Se_2$ (832.5): C, 14.4; H, 1.7. Found: C, 13.7; H, 1.6%. ^1H NMR ($CDCl_3$, 295 K): δ 2.38 (s) [6H] Me, 4.36 (s) [4H] CH_2, 7.25–7.39 (m) [4H] C_6H_4. UV/vis (d.r.)/cm^{-1}: 24400, 32800.

$[(NbBr_5)_2\{o\text{-}C_6H_4(CH_2SeMe)_2\}]$

This was made similarly to the chloride analogue above using $NbBr_5$. Orange-red powder. Yield: 72%. Required for $C_{10}H_{14}Br_{10}Nb_2Se_2$ (1277.0): C, 9.4; H, 1.1. Found: C, 9.4; H, 1.0%. ^1H NMR ($CDCl_3$, 295 K): δ 2.43 (br, s) [6H] Me, 4.26 (br, s) [4H] CH_2, 7.28–7.42 (m) [4H] C_6H_4. UV/vis (d.r.)/cm^{-1}: 21750 (sh), 24800, 30030.

$[(NbCl_5)_2\{MeSe(CH_2)_2SeMe\}]$

$NbCl_5$ (0.39 g, 1.5 mmol) was suspended in anhydrous CH_2Cl_2 (20 mL) and a solution of $MeSe(CH_2)_2SeMe$ (0.16 g, 0.74 mmol) in CH_2Cl_2 (8 mL) added with stirring. The $NbCl_5$ dissolved to give a deep-orange solution which was stirred for 3 h, then concentrated *in vacuo* to ~10 mL, and the deep orange powder filtered off and dried *in vacuo*. Yield: 0.43 g, 76%. Required for $C_4H_{10}Cl_{10}Nb_2Se_2$ (756.4): C, 6.3; H, 1.3. Found: C, 6.1; H, 1.3%. ^1H NMR ($CDCl_3$, 295 K): δ 2.46 (s) [6H] Me, 3.3 (s) [4H] CH_2. UV/vis (d.r.)/cm^{-1}: 23500, 27700 (sh), 32800.

$[(NbBr_5)_2\{MeSe(CH_2)_2SeMe\}]$

This was made similarly to the chloride analogue above. Deep red–brown powder. Yield: 70%. Required for $C_4H_{10}Br_{10}Nb_2Se_2$ (1200.9): C, 4.0; H, 0.8. Found: C, 3.8; H, 0.9%. ^1H NMR (CD_2Cl_2, 223 K): δ 2.2 (s) [6H] Me, 3.3 (s) [4H] CH_2. UV/vis (d.r.)/cm^{-1}: 21750 (sh), 25250, 31250.

$[(NbCl_5)_2\{^nBuSe(CH_2)_2Se^nBu\}]$

This was made similarly to the diselenahexane complex as a red wax. Yield: 80%. ^1H NMR ($CDCl_3$, 295 K): δ 1.0 (t) [3H] Me, 1.45 (m) [2H] CH_2, 1.9 (m) [2H] CH_2, 3.2–3.5 (br) [4H] CH_2. UV/Vis (d.r.)/cm^{-1}: 23500, 28700 (sh), 33000.

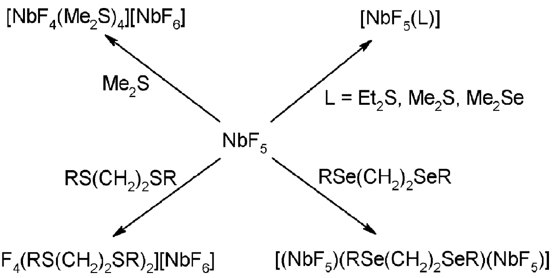
X-Ray crystallography

A summary of details of the crystallographic data collection and refinement are given in Table 1. Crystals of the fluoride complexes were obtained by refrigerating the synthesis solutions (see above), other crystals were grown by refrigerating the filtrates from the syntheses for several days at −18 °C. Data collection used a Nonius Kappa CCD diffractometer fitted with monochromated Mo-Kα X-radiation (λ = 0.71073 Å) and with the crystals held at 120 K in a nitrogen gas stream. Structure solution and refinement were straightforward,[22–24] with H atoms being placed in calculated positions using the default C–H distance. For $[(NbCl_5)_2\{o\text{-}C_6H_4(CH_2SMe)_2\}]$ the crystals examined were twins, but for the data reported the diffractometer software enabled satisfactory indexing of the major component.

Results and discussion

$[NbF_5(R_2E)]$ ($R_2E = Me_2S, Et_2S, Me_2Se$) and $[NbF_4(Me_2S)_4][NbF_6]$

Reactions are shown in Scheme 1.



Scheme 1 Reactions of NbF_5 with thio- and seleno-ethers.

The fluoride systems are extremely sensitive to moisture, and syntheses and measurements must be conducted under rigorously anhydrous conditions. Some of the complexes decompose in a few days even in sealed tubes in a freezer, turning green or brown as discussed below, and hence all measurements were made on freshly prepared complexes. The reaction of Et_2S with NbF_5 either in CH_2Cl_2 solution, or using neat Et_2S as solvent, followed by removal of volatiles *in vacuo*, left $[NbF_5(Et_2S)]$[9] as a colourless oil which solidified on cooling in an ice-bath. The IR spectrum (Table 2) shows three ν(NbF) modes as expected for a C_{4v} geometry. The solid-state UV/visible spectrum shows the transitions $\pi(R_2S) \rightarrow$ Nb at 26000 and 38400 cm^{-1}, which disagrees with the reported solution spectrum which quoted only a 38000 cm^{-1} band.[13] The $\pi(R_2S) \rightarrow$ Nb transitions are similar in energy to those in complexes of the heavier halides, whilst the $\pi(F) \rightarrow$ Nb CT bands which are expected in the far-UV region were not observed. In CH_2Cl_2 solution at 295 K, the ^{19}F NMR spectrum is a broad singlet (Table 2), indicating a dynamic system, probably reversible thioether ligand dissociation. On cooling the

Table 1 Crystal data and structure refinement details[a]

Compound	$[NbF_4(Me_2S)_4][NbF_6]$	$[NbF_4\{MeS(CH_2)_2SMe\}_2]$-$[NbF_6]$	$[NbF_4\{^iPrS(CH_2)_2S^iPr\}_2]$-$[NbF_6]$	$[(NbCl_5)_2\{o$-$C_6H_4(CH_2SMe)_2\}]$	$[(NbCl_5)_2\{MeSe$-$(CH_2)_2SeMe\}]$
Formula	$C_8H_{24}F_{10}Nb_2S_4$	$C_8H_{20}F_{10}Nb_2S_4$	$C_{16}H_{36}F_{10}Nb_2S_4$	$C_{10}H_{14}Cl_{10}Nb_2S_2$	$C_4H_{10}Cl_{10}Nb_2Se_2$
M	624.33	620.30	732.51	738.65	756.36
Crystal system	Tetragonal	Monoclinic	Triclinic	Orthorhombic	Monoclinic
Space group (no.)	$P4/ncc$ (130)	Cc (9)	$P\bar{1}$ (2)	$Pnc2$ (30)	$P2_1/n$ (14)
$a/Å$	12.283(5)	14.0661(10)	10.2850(10)	10.3087(5)	6.9033(15)
$b/Å$	12.283(5)	26.321(2)	11.6895(15)	22.4368(15)	13.020(4)
$c/Å$	13.860(4)	10.7327(10)	13.5404(15)	10.3102(5)	11.111(3)
$\alpha/°$	90	90	115.206(7)	90	90
$\beta/°$	90	101.252(5)	90.596(10)	90	98.812(15)
$\gamma/°$	90	90	110.136(10)	90	90
$U/Å^3$	2091.0(12)	3897.3(5)	1359.1(3)	2384.7(2)	986.9(5)
Z	4	8	2	4	2
μ(Mo-Kα)/mm^{-1}	1.571	1.685	1.223	2.252	6.184
$F(000)$	1232	2432	736	1432	708
Total number reflections	14628	23913	27957	15435	17501
R_{int}	0.150	0.037	0.058	0.060	0.103
Unique reflections	1196	8152	6180	4956	2267
No. of parameters, restraints	58, 0	442, 2	300, 0	218, 4	83, 0
R_1, wR_2 $[I > 2\sigma(I)]$[b]	0.069, 0.124	0.035, 0.081	0.047, 0.102	0.052, 0.113	0.060, 0.096
R_1, wR_2 (all data)	0.103, 0.135	0.039, 0.084	0.066, 0.113	0.058, 0.116	0.105, 0.112

[a] Common items: $T = 120$ K; λ(Mo-Kα) = 0.71073 Å; θ(max) = 27.5°. [b] $R_1 = \sum\|F_o| - |F_c\|/\sum|F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.

Table 2 Selected spectroscopic data for $[NbF_5(R_2E)]$, $[NbF_4(Me_2S)_4][NbF_6]$ and $[NbF_4\{R_2E(CH_2)_2ER_2\}_2][NbF_6]$

Compound	IR ν(Nb–F)/cm^{-1} (Nujol)	$\delta(^{93}Nb)$[a,b]	$\delta(^{19}F\{^1H\})$[a,c]
$[NbF_5(Et_2S)]$	662s, 641m, 600s	−1476 (7000) (295 K)	150.5 (br) (295 K) 146.0 [F], 134.4 [4F] (253 K)
$[NbF_5(Me_2Se)]$[d]	662s, 641m, 600s	−1509 (7000) (295 K)	143.2 (295 K) 144.2 (200 K)
$[NbF_5(Me_2S)]$	640sh, 614vs (br), 594s	−1440 (6000) (295 K)	141.6 (br) (295 K) 144.4 [F], 119.4 [4F] (253 K)
$[NbF_4(Me_2S)_4][NbF_6]$	678sh, 610s, 552m	−1460, −1553 (295 K) −1555 (7 lines, $J = 335$ Hz) (220 K)	136.3 (br) (295 K) 119.5 (s) [4F], 102.5 (s) [6F] 223 K; 119.5 (s) [4F] 102.5 (10 lines) [6F] (200 K)
$[NbF_4\{^iPrS(CH_2)_2S^iPr\}_2][NbF_6]$	655sh, 615s (br), 599s, 565sh	−1540 (295 K) −1551 (7 lines, $J = 335$ Hz) (220 K)	135.8, 105.2 (295 K) 132.8 (s) [4F], 103.8 (10 lines) [6F] (230 K)
$[NbF_4\{MeS(CH_2)_2SMe\}_2][NbF_6]$	640sh, 610vs, 599s, 570s	−1543 (295 K) −1552 (7 lines, $J = 335$ Hz) (243 K)	117.9 (sh), 111.5 (295 K) 114.6 (s) [4F], 104.5 (10 lines) [6F] (243 K)
$[NbF_4\{EtS(CH_2)_2SEt\}_2][NbF_6]$	645sh, 615s (br), 598s, 570sh	−1550 (295 K) −1554 (7 lines, $J = 335$ Hz) (243 K)	115.0, 104.0 (295 K) 112.5 (s) [4F], 103.8 (10 lines) [6F] (243 K)
$[(NbF_5)_2\{MeSe(CH_2)_2SeMe\}]$[f]	650sh, 620vbr, s	n.o.[e]	145.0 (br) (295 K) 144.0 (220 K)
$[(NbF_5)_2\{^nBuSe(CH_2)_2Se^nBu\}]$[g]	650sh, 610s (vbr)	n.o.	146.5 (br) (295 K) 144.0 137.0 (sh) (200 K)

[a] In anhydrous CH_2Cl_2. [b] Relative to $[NbCl_6]^-$ in MeCN δ 0, $W_{\frac{1}{2}}$ in Hz in parenthesis. [c] Relative to $CFCl_3$. [d] $\delta(^{77}Se) = +247.2$ (relative to neat external Me_2Se). [e] n.o = Not observed. [f] $\delta(^{77}Se) = +265$ at 295 K, ($MeSe(CH_2)_2SeMe$ exhibits $\delta(^{77}Se) = 121$). [g] $\delta(^{77}Se) = +330$ at 243 K, ($^nBuSe(CH_2)_2Se^nBu$ exhibits $\delta(^{77}Se) = 212$).

solution the resonance splits, and at low temperatures the spectrum contains a broad resonance at δ 146.0 [F] and a sharper feature at δ 134.4 [4F], consistent with the C_{4v} geometry expected; the behaviour is reversible with temperature. The ^{93}Nb spectrum§ is a broad feature at δ −1476, although neither Nb–F nor F–F couplings were resolved. The NbF_5/Me_2S system is more complicated. When excess Me_2S is distilled onto powdered NbF_5 at 77 K, and the mixture allowed to warm slowly, reaction occurs on melting to give a clear solution, which on further stirring deposits the white solid, $[NbF_5(Me_2S)]$. Mixing the reagents at ambient temperature results in a vigorous reaction, but gives the same product. The solid state spectroscopic properties are similar to the Et_2S analogue (Table 2). However, when NbF_5 reacts with excess Me_2S in rigorously anhydrous CH_2Cl_2 solution,

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§ ^{93}Nb, 100% abundance, $I = 9/2$, $\Xi = 24.44$ MHz, $Q = -0.2 \times 10^{-28}$ m^2, $D_c = 2740$ is one of the more sensitive nuclei and, despite the medium size quadrupole moment, is readily observed in many systems.[25]

Table 3 Bond lengths (Å) and angles (°) for $[NbF_4(Me_2S)_4][NbF_6]$

Nb1–F1	1.899(4)	Nb1–S1	2.724(2)
S1–C1	1.801(8)	S1–C2	1.800(7)
Nb2–F2	1.869(9)	Nb2–F4	1.901(8)
Nb2–F3	1.873(5)		
F1–Nb1–F1b	145.1(2)	S1–Nb1–S1b	67.67(8)
F1–Nb1–F1a	89.8(2)	S1–Nb1–S1a	143.48(8)
F1–Nb1–F1c	100.6(2)	S1–Nb1–S1c	125.19(8)
F1–Nb1–S1	71.27(13)	F1a–Nb1–S1	139.91(13)
F1–Nb1–S1c	74.51(12)	F1b–Nb1–S1	79.81(13)
C1–S1–C2	101.5(4)	Nb1–S1–C	103.6(3), 105.5(3)
F2–Nb2–F3	91.14(16)	F3–Nb2–F3d	89.977(7)
F3–Nb2–F4	88.86(16)		

Symmetry operations: a = 1/2 – *x*, 3/2 – *y*, *z*; b = *y* – 1/2, 1/2 + *x*, 1/2 – *z*; *c* = 1 – *y*, 1 – *x*, 1/2 – *z*; d = 1/2 – *y*, *x*, *z*.

a colourless solution forms, which on refrigeration for a few days, deposited colourless crystals. The crystals crumble and lose Me_2S on drying *in vacuo*, but although they are extremely moisture sensitive and difficult to handle, a satisfactory X-ray data set was collected that identified the compound as $[NbF_4(Me_2S)_4][NbF_6]$. The structure (Fig. 1, Table 3) reveals an octahedral anion and a dodecahedral cation. The dodecahedral (bisdisphenoid) cation shows interpenetrating flattened NbF_4 and elongated NbS_4 tetrahedra, the crystallographic symmetry requiring only one Nb–F (1.899(4) Å) and one Nb–S (2.724(2) Å) distance in the cation. The former is only slightly longer than the average Nb–F distance in the associated $[NbF_6]^-$ anion (1.869(9)–1.901(8) Å). Eight-coordination is well known in niobium(V) chemistry,[26] examples with sulfur-donor ligands including a range of dithiocarbamates, $[Nb(S_2CNR_2)_4]^+$ the disulfides $[NbCl_4(RSSR)_2]^+$, and there are Nb(IV) complexes, $[NbCl_4(dithioether)_2]$, although the present complexes are the first Nb(V) examples with dithioether or diselenoethers. In anhydrous CD_2Cl_2 solution at 295 K, the ^1H NMR spectrum shows a sharp singlet at δ 2.28 which remains sharp down to 190 K although the chemical shift drifts to higher frequency on cooling the solution, reaching δ 2.40 at 200 K. The $^{19}F\{^1H\}$ NMR spectrum at 295 K is a broad singlet at δ 136.3, but on cooling this splits and by 240 K resolves into a relatively sharp singlet at δ 119.5 and a broad feature at δ 102.5, the latter developing the characteristic ten-line pattern of $[NbF_6]^-$, with $^1J_{NbF}$ = 335 Hz, on further cooling.[27] The behaviour is reversible with temperature and clearly indicates a rapidly exchanging system at ambient temperatures. The ^{93}Nb NMR spectrum at 295 K shows a broad feature at δ −1460 ($W_{1/2}$ = 5000 Hz) and a sharper feature at δ −1556 ($W_{1/2}$ = 2500 Hz), which are assigned to the cation and anion respectively. On cooling, the higher frequency resonance broadens and disappears below ~240 K, but the anion resonance remains and the expected septet coupling to ^{19}F is resolved. Studies[28] of NbF_5 solutions in donor solvents including dmso, dmf and pyridine (L) showed the characteristic resonance of $[NbF_6]^-$, tentatively attributed to the formation of $[NbF_4L_4][NbF_6]$, but no resonances for the cations were observed, explained as due to fast relaxation (due to the lower symmetry) or exchange. Addition of a small excess of Me_2S to a solution of $[NbF_4(Me_2S)_4][NbF_6]$ in CH_2Cl_2 sharpens the cation resonance in the ^{93}Nb spectrum, but causes no change in the chemical shift, and the behaviour on cooling is essentially unchanged. On storing in sealed tubes (−18 °C) over several months the solid slowly becomes green, and ^{19}F and ^1H show new resonances, including ones assignable to $MeSCH_2F$,[29] F^- (and $[SiF_5]^-$ from attack on the glass) consistent with fluorination of the thioether and reduction of the niobium. Similar decomposition occurs in a few days in CH_2Cl_2 solution at room temperature.

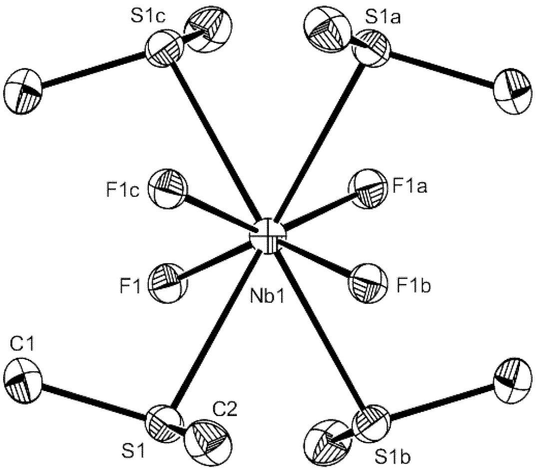


Fig. 1 Structure of the cation in $[NbF_4(Me_2S)_4][NbF_6]$ showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. The Nb1 is positioned on a 4a site of symmetry 222 (D_2). Symmetry operations: a = 1/2 – *x*, 3/2 – *y*, *z*; b = *y* – 1/2, 1/2 + *x*, 1/2 – *z*; *c* = 1 – *y*, 1 – *x*, 1/2 – *z*.

Colourless $[NbF_5(Me_2Se)]$ is formed from NbF_5 and Me_2Se in CH_2Cl_2 solution, and appears to be the only product even with excess selenoether. In contrast to the dialkyl sulfide complexes which can be stored in a glove-box for many weeks, the $[NbF_5(Me_2Se)]$ begins to darken within a few hours at room temperature, and more slowly in a freezer, turning brown and then green, indicative of a redox reaction. Examination of decomposed samples by ^{77}Se and ^{19}F NMR spectroscopy showed a number of new resonances (some unassigned), including ones attributable to $[NbF_6]^-$ and Me_2SeF_2 [δ(Se) = 789 (t) $^1J_{SeF}$ = 645 Hz; δ(F) = −69][29,30] again consistent with fluorination of the chalcogenoether. Spectroscopic data on the freshly prepared material (Table 2) are mostly similar to those of the dialkyl sulfide adducts, but although the broad singlet ^{19}F NMR resonance observed at room temperature sharpens on cooling the solution, even at 200 K only a singlet is observed, suggesting exchange processes remain significant, and indicating weaker binding of the Me_2Se compared to R_2S.

$[NbF_4\{RS(CH_2)_2SR\}_2][NbF_6]$ (R = Me, Et or ^{i}Pr)

In rigorously anhydrous CH_2Cl_2 solution, NbF_5 and the three 1,2-dithioethanes produce colourless solutions, which deposit colourless (R = Me or Et) or slightly yellow (R = ^{i}Pr) crystals on refrigeration. The crystals are extremely moisture sensitive and decompose instantly in air, and also deteriorate slowly in the glove-box, although they are more stable in a freezer. X-Ray crystal structures of two examples were obtained and both reveal distorted dodecahedral cations and octahedral anions. The $[NbF_4\{MeS(CH_2)_2SMe\}_2][NbF_6]$ (Table 4, Fig. 2) contains two chelating dithioethers in the DL configuration with chelate angles ∠S–Nb–S of 74.2 to 75.2° and Nb–S distances 2.697(2)–2.725(2) Å, similar to the Me_2S complex above. The NbF_4 unit

Table 4 Selected bond lengths (Å) and angles (°) for $[NbF_4\{MeS(CH_2)_2SMe\}_2][NbF_6]$

Nb1–F1	1.912(3)	Nb1–F3	1.911(3)
Nb1–F2	1.893(3)	Nb1–F4	1.889(3)
Nb1–S1	2.7176(13)	Nb1–S3	2.7205(14)
Nb1–S2	2.7105(14)	Nb1–S4	2.7039(14)
Nb2–F5	1.916(3)	Nb2–F7	1.901(3)
Nb2–F6	1.897(4)	Nb2–F8	1.875(4)
Nb2–S5	2.7138(15)	Nb2–S7	2.6970(15)
Nb2–S6	2.7252(16)	Nb2–S8	2.7212(14)
Nb3–F	1.843(5)–1.887(4)	Nb4–F	1.875(4)–1.893(4)
F1–Nb1–F3	144.63(13)	F5–Nb2–F7	145.08(13)
F2–Nb1–F4	144.54(13)	F6–Nb2–F8	144.54(17)
S1–Nb1–S2	74.74(4)	S5–Nb2–S6	75.21(5)
S3–Nb1–S4	75.07(4)	S7–Nb2–S8	74.21(4)

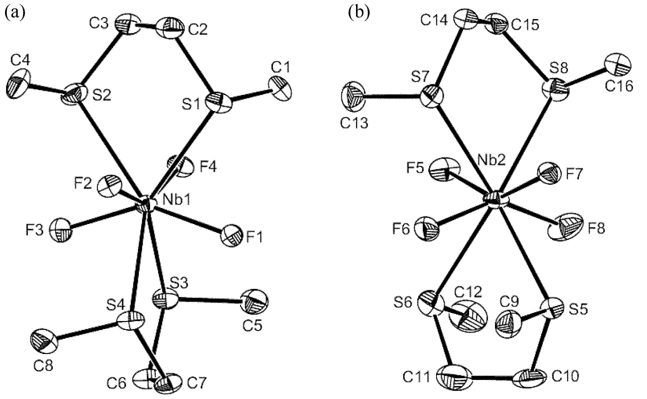


Fig. 2 Structure of the cations in $[NbF_4\{MeS(CH_2)_2SMe\}_2][NbF_6]$ showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. There are two crystallographically distinct cations with different conformations of the bidentate S ligand; (a) Nb1 centred cation, (b) Nb2 centred cation.

is a flattened tetrahedron with Nb–F 1.875(4)–1.916(3) Å. The two cations in the asymmetric unit are not the same as can be seen in Fig. 2(a) and 2(b). In Fig. 2(a) with the Nb1 centred cation the stereochemistry at S1–S4 is *SSSS*, whereas in Fig. 2(b) for the Nb2 cation the stereochemistry at S5–S8 is *SSRR*. In $[NbF_4\{^iPrS(CH_2)_2S^iPr\}_2][NbF_6]$ (Table 5, Fig. 3) the chelating dithioethers are both in the *meso* form, but the dimensions are otherwise very similar. In solution at 295 K the ^{19}F NMR spectra show two broad features (Table 2) which, on cooling the solutions, become a sharper singlet at higher frequency, and at lower frequency the characteristic ten-line pattern of $[NbF_6]^-$. In contrast to the spectrum of $[NbF_4(Me_2S)_4][NbF_6]$ discussed above, the ^{93}Nb spectra of the dithioether complexes show only the $[NbF_6]^-$ resonance. It seems likely that the added distortions produced by the chelating ligands generate a substantial electric field gradient which promotes fast quadrupolar relaxation of the niobium, and the resulting line-broadening accounts for the absence of the cation resonance. The NMR spectra of all the fluoride complexes suggest that exchange processes are occurring at ambient temperatures, but these slow on cooling. We have briefly described elsewhere[17] the synthesis and structure of $[\{NbF_4(o\text{-}C_6H_4(CH_2SMe)_2)\}_n][Nb_2F_{11}]_n$ which also contains an eight-coordinate Nb(V) cation but the dithioethers are bridging to form a polymeric chain.

Table 5 Selected bond lengths (Å) and angles (°) for $[NbF_4\{^iPrS(CH_2)_2S^iPr\}_2][NbF_6]$

Nb1–F1	1.904(2)	Nb1–F3	1.897(2)
Nb1–F2	1.905(2)	Nb1–F4	1.913(2)
Nb1–S1	2.7424(11)	Nb1–S3	2.7030(11)
Nb1–S2	2.7357(12)	Nb1–S4	2.7336(12)
Nb2–F	1.877(4)–1.888(3)	Nb3–F	1.881(3)–1.885(3)
F1–Nb1–F2	143.70(10)	S1–Nb1–S2	74.14(3)
F3–Nb1–F4	144.48(10)	S3–Nb1–S4	75.07(4)

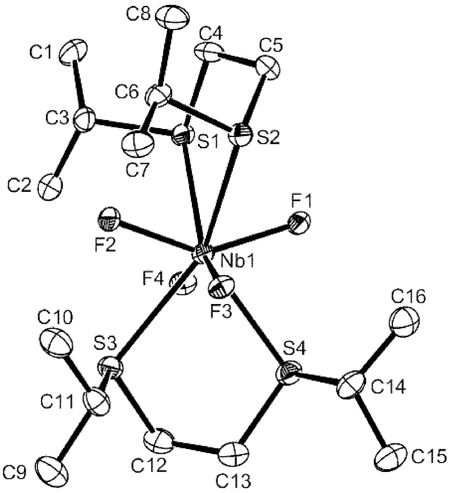


Fig. 3 Structure of the cation in $[NbF_4\{^iPrS(CH_2)_2S^iPr\}_2][NbF_6]$ showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.

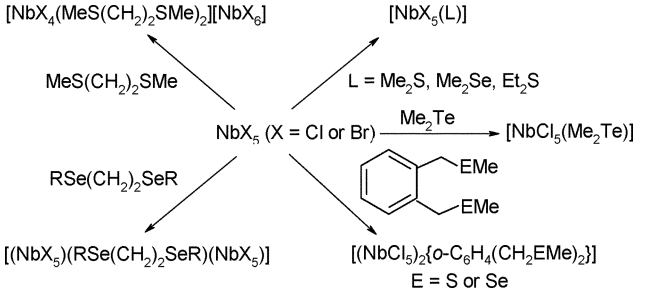
$[(NbF_5)_2\{RSe(CH_2)_2SeR\}]$ (R = Me or ^{n}Bu)

The reaction of NbF_5 with diselenoethers including $RSe(CH_2)_2SeR$ (R = Me or ^{n}Bu) in a 2 : 1 molar ratio in anhydrous CH_2Cl_2 solution at 295 K initially gives clear pale-yellow solutions, but these slowly darken. The reactions, conducted at 273 K, followed by rapid removal of the solvent, gave a yellow viscous oil for $^nBuSe(CH_2)_2Se^nBu$ and a fawn powder for $MeSe(CH_2)_2SeMe$ both of which darken slowly at ambient temperatures due to decomposition. They are formulated as $[(NbF_5)_2\{\mu\text{-}RSe(CH_2)_2SeR\}]$ on the basis of the spectroscopic data (their instability precludes accurate microanalytical measurements). Excess diselenoether (*e.g.* reaction in a 1 : 1 molar ratio) causes rapid reduction of the niobium with the formation of dark-red solutions. The low-temperature ^1H and ^{77}Se NMR spectra, which exhibit singlet δ(Me) and δ(Se) resonances, are consistent with the formulation of $[NbF_5\{\mu\text{-}MeSe(CH_2)_2SeMe\}NbF_5]$ for the former complex (analogous to the structurally characterised chloride complex reported below). The $^{19}F\{^1H\}$ spectrum at room temperature is a broad singlet which sharpens on cooling, but even at 200 K does not show clear splitting expected for the square pyramidal pentafluoride unit, suggesting exchange processes are still present. Notably no ^{93}Nb resonance was observed even at low temperatures (fast relaxation), although in the decomposed (red–brown) samples $[NbF_6]^-$ is clearly present. The reaction of NbF_5 with Me_2Te or $MeTe(CH_2)_3TeMe$ in anhydrous CH_2Cl_2, instantly gave insoluble brown–black tarry materials which were not pursued.

Selenoethers and especially telluroethers are softer ligands than thioethers,[2] and the inability of telluroethers to form stable complexes with a very hard Lewis acid like NbF_5 is therefore not unexpected. They are also much stronger reducing agents, and the dark coloured materials produced are no doubt the result of reduction of the niobium, accompanying oxidative fluorination of the ligands.

$[NbX_5(R_2E)]$ (X = Cl or Br, $R_2E = Me_2S, Et_2S, Me_2Se$; X = Cl, $R_2E = Me_2Te$)

Reactions are shown in Scheme 2.



Scheme 2 Reactions of NbX_5 (X = Cl or Br) with thio- and seleno-ethers.

These complexes were made to provide comparative NMR and X-ray data by direct combination of the constituents in anhydrous CH_2Cl_2 (see ESI†). All are very moisture-sensitive solids, ranging in colour from yellow $[NbCl_5(Me_2S)]$ through dark red $[NbBr_5(Me_2Se)]$, to purple $[NbCl_5(Me_2Te)]$, and are easily soluble in anhydrous CH_2Cl_2.[10–14] The purple $[NbCl_5(Me_2Te)]$ decomposes rapidly in solution and the solid becomes sticky in a few hours, turning dark green, clearly due to reduction of the niobium. All spectroscopic measurements were made on freshly prepared samples. Attempts to isolate $[NbBr_5(Me_2Te)]$ were unsuccessful, and reaction of NbI_5 with Me_2S gave a green–black paramagnetic product which was not studied further. Spectroscopic data and the crystal structures of $[NbBr_5(Me_2S)]$ and $[NbCl_5(Me_2Se)]$ are described in the ESI.†

$[(NbX_5)_2(L\text{–}L)]$ and $[NbX_4\{MeS(CH_2)_2SMe\}_2][NbX_6]$ (X = Cl or Br, L–L = $RSe(CH_2)_2SeR$ or $o\text{-}C_6H_4(CH_2EMe)_2$ (E = S or Se))

The reactions of NbX_5 (X = Cl or Br) with the dithio- and diselenoethers, $RSe(CH_2)_2SeR$ (R = Me or ^nBu), or $o\text{-}C_6H_4(CH_2EMe)_2$ (E = S or Se) gave complexes of composition $[(NbX_5)_2(L\text{–}L)]$, irrespective of the $NbX_5 : L\text{–}L$ ratio used. Uniquely within this series, $MeS(CH_2)_2SMe$ gave complexes with a 1 : 1 stoichiometry (see below). The reaction of $NbCl_5$ with the ditelluroether $MeTe(CH_2)_3TeMe$ in CH_2Cl_2 solution at 0 °C, initially gave a very dark solution, but this paled to dull khaki in less than one min, and deposited a khaki powder. The UV/visible spectrum of the latter has the lowest charge transfer band at ~27000 cm^{-1}, clearly indicating a lower niobium oxidation state. The $[(NbX_5)_2(L\text{–}L)]$ are ligand-bridged dimers, demonstrated by the structures of $[(NbCl_5)_2\{o\text{-}C_6H_4(CH_2SMe)_2\}]$ and $[(NbCl_5)_2\{MeSe(CH_2)_2SeMe\}]$ (Tables 6 and 7, Fig. 4 and 5). The selenium compound is centrosymmetric and the sulfur compound has a two-fold rotation axis which bisects the ligand backbone. The patterns of bond lengths and angles largely replicate those found in $[NbX_5(R_2E)]$, but the crystal structures serve to identify the molecular unit present. The complexes with alkane-backbones are very poorly soluble in chlorocarbon solvents which hindered solution measurements, but the xylyl-backboned ligands have better solubility and solution NMR data are given in Table 8. The chloro-complexes show broad ^{93}Nb NMR resonances at ambient temperatures, but for $[(NbBr_5)_2\{o\text{-}C_6H_4(CH_2EMe)_2\}]$ it was necessary to cool the solutions to ~273 K to observe the ^{93}Nb resonance, indicative of dissociation/exchange in solution at ambient temperatures. The $^{77}Se\{^1H\}$ NMR spectra of $[(NbX_5)_2\{o\text{-}C_6H_4(CH_2SeMe)_2\}]$ show large, high frequency shifts from the "free" ligand values (Table 8). ^{93}Nb NMR resonances were obtained for the poorly soluble $[(NbX_5)_2\{MeSe(CH_2)_2SeMe\}]$,

Table 6 Selected bond lengths (Å) and angles (°) for $[(NbCl_5)_2\{o\text{-}C_6H_4(CH_2SMe)_2\}]$

Nb1–Cl1	2.275(2)	Nb1–Cl2	2.320(2)
Nb1–Cl3	2.323(2)	Nb1–Cl4	2.3067(15)
Nb1–Cl5	2.303(2)	Nb1–S1	2.7043(19)
Cl1–Nb1–Cl2	98.11(9)	Cl2–Nb1–Cl3	89.16(9)
Cl1–Nb1–Cl3	96.97(8)	Cl2–Nb1–Cl5	89.55(10)
Cl1–Nb1–Cl4	96.76(8)	Cl4–Nb1–Cl3	88.68(7)
Cl1–Nb1–Cl5	97.77(8)	Cl4–Nb1–Cl5	88.80(7)
Cl2–Nb1–S1	79.18(7)	Cl4–Nb1–S1	85.98(6)
Cl3–Nb1–S1	78.06(7)	Cl5–Nb1–S1	87.25(7)

Table 7 Selected bond lengths (Å) and angles (°) for $[(NbCl_5)_2\{MeSe(CH_2)_2SeMe\}]$

Nb1–Cl1	2.280(2)	Nb1–Cl2	2.318(2)
Nb1–Cl3	2.319(2)	Nb1–Cl4	2.330(2)
Nb1–Cl5	2.334(2)	Nb1–Se1	2.8155(12)
Cl1–Nb1–Cl2	96.54(9)	Cl2–Nb1–Cl3	89.05(9)
Cl1–Nb1–Cl3	98.54(9)	Cl2–Nb1–Cl5	89.76(9)
Cl1–Nb1–Cl4	98.18(9)	Cl3–Nb1–Cl4	88.53(9)
Cl1–Nb1–Cl5	96.76(9)	Cl4–Nb1–Cl5	88.76(9)
Cl2–Nb1–Se1	80.76(7)	Cl4–Nb1–Se1	84.58(6)
Cl3–Nb1–Se1	85.42(6)	Cl5–Nb1–Se1	79.32(6)

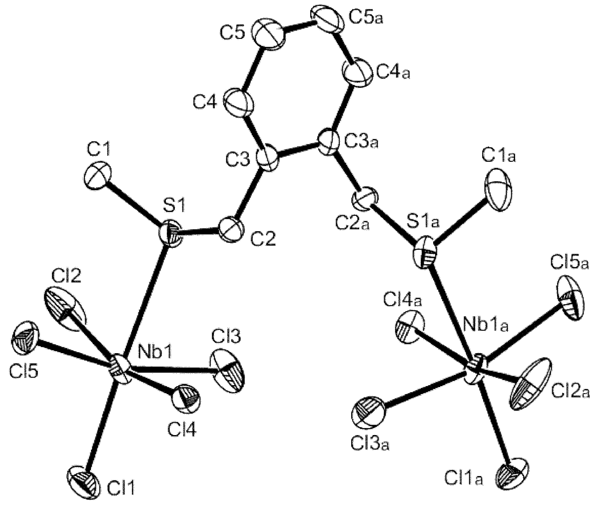


Fig. 4 Structure of $[(NbCl_5)_2\{o\text{-}C_6H_4(CH_2SMe)_2\}]$ showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. The molecule has two-fold symmetry. Symmetry operation: a = 2 – *x*, –*y*, *z*.

Table 8 Selected spectroscopic data for bidentate ligand complexes of NbX_5 (X = Cl or Br) at 295 K unless otherwise stated

Compound	$\delta(^{93}Nb)^{a,b}$	$\delta(^{77}Se)^{d}$	$\nu(Nb–X)/cm^{-1}$ (Nujol)
$[(NbCl_5)_2\{o\text{-}C_6H_4(CH_2SMe)_2\}]$	+80.5 (6000)		380sh, 365br, 346sh
$[(NbBr_5)_2\{o\text{-}C_6H_4(CH_2SMe)_2\}]$	+746 (12000) (273 K)^{h}		281s, 254s
$[(NbCl_5)_2\{o\text{-}C_6H_4(CH_2SeMe)_2\}]$	+96 (4000)	+247	361br, 346s
$[(NbBr_5)_2\{o\text{-}C_6H_4(CH_2SeMe)_2\}]$	+775 (5000) (243 K)^{h}	+228	280s, 250s
$[NbCl_4\{MeS(CH_2)_2SMe\}_2][NbCl_6]$	+3 (vs), +150 (vbr)	—	333vs, 310sh, 280sh^{i}
$[NbBr_4\{MeS(CH_2)_2SMe\}_2][NbBr_6]$	+722	—	257m, 248sh, 232vs^{j}
$[(NbCl_5)_2\{MeSe(CH_2)_2SeMe\}]$	+97 (poorly soluble)	n.o.	359br, 334s
$[(NbBr_5)_2\{MeSe(CH_2)_2SeMe\}]$	+750 (poorly soluble)	n.o.	294m, 233s
$[(NbCl_5)_2\{^{n}BuSe(CH_2)_2Se^{n}Bu\}]$	+95 (5000)	+284	367s, 335s

Footnotes as in Table 2. ^{h} No resonance at 295 K. ^{i} Raman: 360vs, 312vs cm^{-1}. ^{j} Raman: 250m (sh), 214vs cm^{-1}.

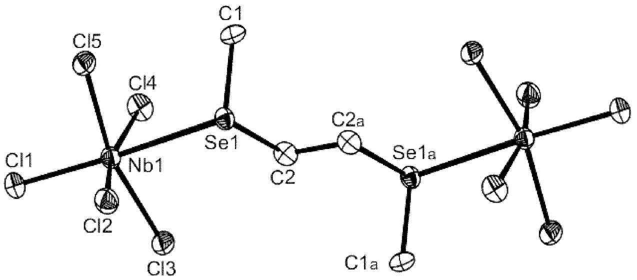


Fig. 5 Structure of the centrosymmetric $[(NbCl_5)_2\{MeSe(CH_2)_2SeMe\}]$ showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Symmetry operation: a = 1 − *x*, 1 − *y*, 1 − *z*.

but the solubility was too poor to observe ^{77}Se resonances. Solutions exposed briefly to air develop the ^{93}Nb NMR resonances of the corresponding $[NbX_6]^-$ anions,[25] consistent with ready hydrolysis.

In contrast, $MeS(CH_2)_2SMe$ gave 1 : 1 complexes with NbX_5 (irrespective of the ratio of reactants used) which are insoluble in chlorocarbons. The IR spectrum of the $NbCl_5$ adduct shows a very strong band at 333 cm^{-1} and the Raman spectrum has an intense band at 360 cm^{-1}, which correspond respectively to the t_{1u} and a_{1g} vibrations of $[NbCl_6]^-$, and there are corresponding vibrations in the bromide at 232 and 214 cm^{-1} due to $[NbBr_6]^-$.[31] This leads to the formulation $[NbX_4\{MeS(CH_2)_2SMe\}_2][NbX_6]$, analogous to the fluoride complexes (above), with other Nb–X vibrations (Table 8) being due to the (assumed) dodecahedral cation. The complexes are insoluble in CH_2Cl_2, but dissolve in a mixture of CH_2Cl_2–10% MeCN, from which solutions ^{93}Nb NMR spectra identify the $[NbX_6]^-$ anions (Table 8). The chloride-complex also exhibits a very broad resonance at δ +150 which is tentatively ascribed to the dodecahedral cation, but no corresponding resonance was found in the bromide complex, possibly due to greater dissociation, although line broadening by the quadrupolar nucleus in a more asymmetric field gradient is also likely. Attempts to obtain crystals of $[NbX_4\{MeS(CH_2)_2SMe\}_2][NbX_6]$ failed due to very poor solubility, but the constitution is not in doubt from the vibrational spectra and by analogy with the fluoride analogues. The failure of the other dithio- and diseleno-ethers to form compounds of this type may be due to slightly weaker donor power and increasing steric bulk, disfavouring the eight-coordinate cations.

Conclusions

This study has shown that the soft σ-donor thioether ligands readily form complexes with the hard Lewis acid NbF_5, and that the ligand steric demands influence significantly the coordination numbers obtained. Thus, eight-coordination is achieved by ligands with small steric demands, whereas bulkier thioethers form only six-coordinate complexes. Eight-coordination is also found with NbX_5 (X = Cl or Br) and $MeS(CH_2)_2SMe$, but other thioethers form only six-coordinate $[NbX_5(L)]$ or $[(NbX_5)_2(\mu\text{-}L–L)]$, and selenoether adducts with all three halides are six-coordinate. The complexes of NbX_5 (X = Cl or Br) appear stable indefinitely if protected from moisture, but the fluorides decompose readily even in the solid state *via* fluorination of the neutral ligand. The solution spectroscopic data suggest that the heavier halides form more stable complexes with thio- and especially seleno-ether ligands, but the isolation of the eight-coordinate fluoride complexes is remarkable, given the modest donor power of neutral soft sulfur ligands.

Acknowledgements

We thank EPSRC for support and the Royal Society of Chemistry for a Journals Grant (R. R.).

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