Six- and eight-coordinate thio- and seleno-ether complexes of NbF$_5$ and some comparisons with NbCl$_5$ and NbBr$_5$ adducts

Marek Jura, William Levason, Raju Ratnani, Gillian Reid, and Michael Webster

$[\text{NbX}_5(R_2E)]$ (X = Cl or Br; R$_2E$ = Me$_2$S, Et$_2$S, Me$_2$Se; X = Cl R$_2E$ = Me$_2$Te): (see Scheme 1). These complexes were made by direct combination of the constituents in anhydrous CH$_2$Cl$_2$ for comparison purposes. All are very moisture-sensitive solids, ranging in colour from yellow $[\text{NbCl}_5(\text{Me}_2\text{S})]$ through dark red $[\text{NbBr}_5(\text{Me}_2\text{Se})]$, to purple $[\text{NbCl}_5(\text{Me}_2\text{Te})]$, and are easily soluble in anhydrous CH$_2$Cl$_2$. The purple $[\text{NbCl}_5(\text{Me}_2\text{Te})]$ decomposes rapidly in solution and the solid becomes sticky in a few hours, turning dark green, clearly due to reduction of the niobium, and all spectroscopic measurements were made on freshly prepared samples.

The $^1$H NMR data on the isolated complexes are in agreement with published values.$^{11,12,14}$ The complexes exhibit two or three strong metal-halogen stretching modes in the IR spectra (Table SUP 1) (theory $C_{av} = 2a_1 + e$). The diffuse reflectance spectra for these d$^0$ metal systems show the expected $\pi(X) \rightarrow$ Nb and $\pi($chalcogen$) \rightarrow$ Nb charge transfer transitions, which are in generally good agreement with the more limited set of solution data of Valloton and Merbach.$^{13}$ Multinuclear NMR spectroscopic data are given in Table SUP 1. The halide present is the dominant factor determining the observed chemical shifts (relative to $[\text{NbCl}_6]^{-}$ in MeCN at $\delta = 0$) with $[\text{NbCl}_5(L)]$ $\delta \sim +80$ and $[\text{NbBr}_5(L)]$ $\delta \sim +750$, with changing S for Se or changing the R group having only small effects. The resonances sharpen on gentle cooling and then broaden at low temperatures, probably due to a combination of some dissociation at ambient temperatures and the effect of temperature upon the niobium quadrupolar relaxation rate. Addition of excess R$_2E$ to the solutions has no effect on $\delta(^{93}\text{Nb})$, in agreement with the conclusions of Merbach from $^1$H NMR data, that seven-coordinate species do not form.$^{11,14}$ Attempts to
obtain $[\text{NbCl}_4(\text{Me}_2\text{S})_2]^{+}$ from reaction in CH$_2$Cl$_2$ solution of NbCl$_5$ with two mol. equivs. Me$_2$S and FeCl$_3$ (as chloride abstractor), failed, the $^{93}\text{Nb}$ NMR spectrum showing only $[\text{NbCl}_3(\text{Me}_2\text{S})]$, and using the stronger abstractor SbCl$_5$ results in decomposition. The $^{77}\text{Se}\{^1\text{H}\}$ NMR spectra show large high frequency shifts from free Me$_2$Se which fall $X = F > Cl > Br$ (Table SUP 1).

Crystal structures on two examples were obtained (Tables SUP 2 and SUP 3, Figs. SUP 1 and SUP 2). The $[\text{NbBr}_5(\text{Me}_2\text{S})]$ shows a distorted octahedral geometry with the angles Br–Nb–Br involving the apical bromine $\sim 97^\circ$, those in the equatorial plane near 90$^\circ$, and S–Nb–Br $< 90^\circ$. The apical Nb–Br$_{\text{trans-S}}$ distance is significantly shorter (2.4203(7) Å) than those in the equatorial plane (2.4762(8)–2.5113(8) Å), whilst the Nb–S is long at 2.7076(14) Å. This pattern of bond lengths and angles is replicated in $[\text{NbCl}_5(\text{Me}_2\text{Se})]$.

**Table SUP 1** Selected spectroscopic data for $[\text{NbX}_5(\text{R}_2\text{E})]$ ($X = \text{Cl, Br}; R = \text{Me, Et}; E = \text{S, Se}$)

<table>
<thead>
<tr>
<th>Compound</th>
<th>IR. $\nu$(Nb–X)/cm$^{-1}$ (Nujol)</th>
<th>$\delta(^{93}\text{Nb})^\text{[a,b]}$</th>
<th>$\delta(^{77}\text{Se} / ^{125}\text{Te})^\text{[a,c]}$</th>
<th>UV/vis d. r./cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{NbCl}_5(\text{Me}_2\text{S})]$</td>
<td>382(s), 343(m)</td>
<td>+84 (1300)</td>
<td></td>
<td>26200, 34150</td>
</tr>
<tr>
<td>$[\text{NbBr}_5(\text{Me}_2\text{S})]$</td>
<td>332(sh), 307(vs), 257(s)</td>
<td>+761 (900)</td>
<td>+752 (253 K)</td>
<td>24200, 28000 (sh), 32250</td>
</tr>
<tr>
<td>$[\text{NbCl}_5(\text{Et}_2\text{S})]$</td>
<td>362(vs), 340(sh)</td>
<td>+88 (1500)</td>
<td></td>
<td>24500, 34000</td>
</tr>
<tr>
<td>$[\text{NbBr}_5(\text{Et}_2\text{S})]$</td>
<td>331(sh), 300(vs), 260(s)</td>
<td>+757 (1500)</td>
<td></td>
<td>24400, 28000 (sh), 33700</td>
</tr>
<tr>
<td>$[\text{NbCl}_5(\text{Me}_2\text{Se})]$</td>
<td>373(s), 340(sh)</td>
<td>+103 (1300)</td>
<td>140</td>
<td>22700, 25600, 32600</td>
</tr>
<tr>
<td>$[\text{NbBr}_5(\text{Me}_2\text{Se})]$</td>
<td>332(sh), 310(s)</td>
<td>+764 (1200)</td>
<td>+750 (253 K)</td>
<td>22270, 26800, 32400</td>
</tr>
<tr>
<td>$[\text{NbCl}_5(\text{Me}_2\text{Te})]$</td>
<td>370(s), 345(sh)</td>
<td>+135 (2500)</td>
<td>+153 (2200) (273 K)</td>
<td>200</td>
</tr>
</tbody>
</table>

[a] In anhydrous CH$_2$Cl$_2$ at 295 K unless otherwise indicated. [b] Relative to $[\text{NbCl}_6]^-$ in MeCN, $\delta = 0$, $W_{1/2}$ in parenthesis in Hz. [c] Relative to neat external Me$_2$Se or Me$_2$Te.
### Table SUP 2  Selected bond lengths (Å) and angles (°) for [NbBr$_5$(Me$_2$S)]

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb1–Br1</td>
<td>2.4203(7)</td>
<td>Nb1–Br2</td>
<td>2.5113(8)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nb1–Br3</td>
<td>2.4762(8)</td>
<td>Nb1–Br4</td>
<td>2.4775(7)</td>
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<td></td>
</tr>
<tr>
<td>Nb1–Br5</td>
<td>2.4830(8)</td>
<td>Nb1–S1</td>
<td>2.7076(14)</td>
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<tr>
<td>Br1–Nb1–Br2</td>
<td>97.44(3)</td>
<td>Br2–Nb1–Br3</td>
<td>87.76(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Br1–Nb1–Br3</td>
<td>97.33(3)</td>
<td>Br2–Nb1–Br5</td>
<td>86.42(3)</td>
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<tr>
<td>Br1–Nb1–Br4</td>
<td>96.74(3)</td>
<td>Br3–Nb1–Br4</td>
<td>92.02(3)</td>
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<td></td>
</tr>
<tr>
<td>Br1–Nb1–Br5</td>
<td>96.99(3)</td>
<td>Br4–Nb1–Br5</td>
<td>90.28(3)</td>
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<td></td>
</tr>
<tr>
<td>Br2–Nb1–S1</td>
<td>88.13(4)</td>
<td>Br4–Nb1–S1</td>
<td>77.86(3)</td>
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<tr>
<td>Br3–Nb1–S1</td>
<td>78.41(4)</td>
<td>Br5–Nb1–S1</td>
<td>87.72(4)</td>
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### Table SUP 3  Selected bond lengths (Å) and angles (°) for [NbCl$_5$(Me$_2$Se)]

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
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<th>Length (Å)</th>
<th>Bond</th>
<th>Length (Å)</th>
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<tr>
<td>Nb1–Cl1</td>
<td>2.2947(16)</td>
<td>Nb1–Cl2</td>
<td>2.3293(16)</td>
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<tr>
<td>Nb1–Cl3</td>
<td>2.3178(11)</td>
<td>Nb1–Cl4</td>
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<tr>
<td>Nb1–Se1</td>
<td>2.8163(9)</td>
<td>Se1–C1</td>
<td>1.946(5)</td>
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<tr>
<td>Cl1–Nb1–Cl2</td>
<td>96.91(6)</td>
<td>Cl2–Nb1–Cl3</td>
<td>88.11(4)</td>
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<tr>
<td>Cl1–Nb1–Cl3</td>
<td>97.38(3)</td>
<td>Cl3–Nb1–Cl4</td>
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<td></td>
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<tr>
<td>Cl1–Nb1–Cl4</td>
<td>95.87(6)</td>
<td>Cl2–Nb1–Se1</td>
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<tr>
<td>Cl3–Nb1–Se1</td>
<td>82.63(3)</td>
<td>Cl4–Nb1–Se1</td>
<td>83.31(4)</td>
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### Fig. SUP 1  Structure of [NbBr$_5$(Me$_2$S)] 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 molecules in the asymmetric unit, the second of which involving Nb2 shows disorder at S2 (and the bonded C atoms)
**Fig. SUP 2** Structure of [NbCl$_5$(Me$_2$Se)] showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. The molecule has mirror plane symmetry. Symmetry operation: $a = 2 - x$, $y$, $z$.

**X-ray Crystallography (SUP):** Summary details of the crystallographic data collection and refinement of [NbCl$_5$(Me$_2$Se)] and [NbBr$_5$(Me$_2$S)] are given in Table SUP 4.
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 except as detailed below, with H atoms being placed in calculated positions using the default C–H distance. For [NbBr₅(Me₂S)] with two molecules in the asymmetric unit, the Nb2 centred molecule showed disorder in the S atom position (S2), and this was modelled as two components (S2A/S2B) where ‘A’ was the major component (sof 0.60). The C atoms bonded to the S (C3, C4) overlapped and could not be separated into their A and B components however for the purposes of adding H atoms in calculated positions they were treated as A and B using EXYZ and EADP commands on C3A/B and C4A/B.
Table SUP 4  Crystal data and structure refinement details for [NbCl₅(Me₂Se)] and [NbBr₅(Me₂S)]

<table>
<thead>
<tr>
<th>Compound</th>
<th>[NbCl₅(Me₂Se)]</th>
<th>[NbBr₅(Me₂S)]</th>
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<tr>
<td>Formula</td>
<td>C₂H₆Cl₅NbSe</td>
<td>C₂H₆Br₅NbS</td>
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<td>M</td>
<td>379.19</td>
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<tr>
<td>Crystal system</td>
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<tr>
<td>Space group (no.)</td>
<td>Cmc₂₁(36)</td>
<td>P₂₁/c (14)</td>
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<tr>
<td>a /Å</td>
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<td>7.2922(5)</td>
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<tr>
<td>b /Å</td>
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<td>c /Å</td>
<td>10.796(3)</td>
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<td>α /°</td>
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<tr>
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<td>Z</td>
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<tr>
<td>μ(Mo-Kα)/mm⁻¹</td>
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<tr>
<td>F(000)</td>
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<td>Total number reflections</td>
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<tr>
<td>Unique reflections</td>
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<td>5097</td>
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<tr>
<td>No. of parameters, restraints</td>
<td>50, 1</td>
<td>175, 2</td>
</tr>
<tr>
<td>R₁, wR₂ [I &gt; 2σ(I)] b</td>
<td>0.025, 0.058</td>
<td>0.034, 0.066</td>
</tr>
<tr>
<td>R₁, wR₂ (all data)</td>
<td>0.027, 0.060</td>
<td>0.049, 0.073</td>
</tr>
</tbody>
</table>

a  Common items: temperature = 120 K; wavelength (Mo-Kα) = 0.71073 Å; θ(max) = 27.5°.
b  \( R₁ = \Sigma | |F_o| - |F_c| \| / \Sigma |F_o| \); \( wR₂ = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma wF_o^4]^{1/2} \)