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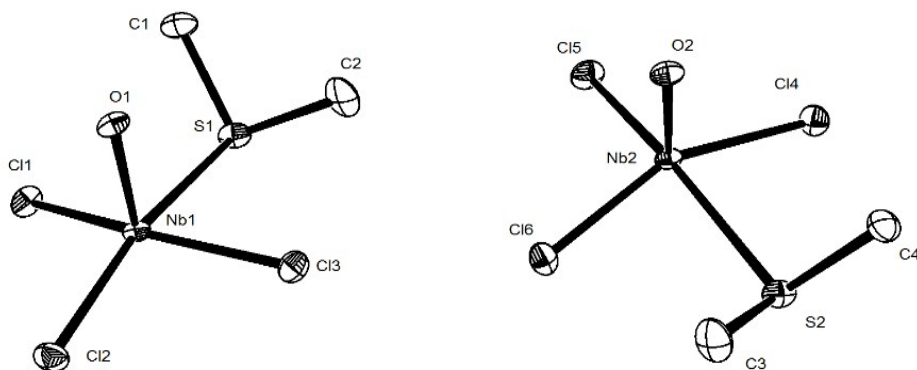
Niobium tetrachloride complexes with thio-, seleno- and telluro-ether coordination – synthesis and structures

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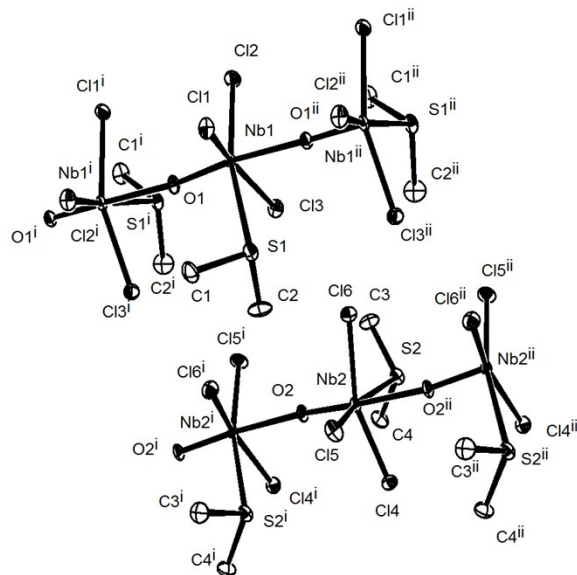
As noted in the main text, trace hydrolysis/air oxidation in the Nb(IV) systems can lead to Nb(V) products. Crystals of two examples containing NbOCl₃ were isolated in this work and their structures determined.

[NbOCl₃(Me₂S)]

The green crystals were formed during recrystallisation of brown [NbCl₄(Me₂S)₂] from CH₂Cl₂ by layered with n-hexane. The structure contains two slightly different molecules in the unit cell, both square pyramidal with an apical oxo-group which are linked into chains by asymmetric oxido-bridges, Nb1–O1 = 1.744(3), Nb1–O1ⁱⁱ = 2.224(3). (Figure S1). As observed for the Nb(IV) complexes, there is little difference in Nb–Cl_{transS} and Nb–Cl_{transCl}.



(a)



(b)

Figure S1 (a) The structure of $[\text{NbOCl}_3(\text{Me}_2\text{S})]$ showing the atom numbering scheme and with ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (\AA) and angles ($^\circ$): $\text{Nb1-O1} = 1.744(3)$, $\text{Nb1-O1}^{\text{ii}} = 2.224(3)$, $\text{Nb1-Cl1} = 2.336(1)$, $\text{Nb1-Cl2} = 2.310(1)$, $\text{Nb1-Cl3} = 2.360(2)$, $\text{Nb1-S1} = 2.692(2)$, $\text{Nb2-O2} = 1.746(3)$, $\text{Nb2-O2}^{\text{ii}} = 2.232(3)$, $\text{Nb2-Cl4} = 2.332(2)$, $\text{Nb2-Cl5} = 2.336(1)$, $\text{Nb2-Cl6} = 2.344(2)$, $\text{Nb2-S2} = 2.684(1)$; $\text{O1-Nb1-O1}^{\text{ii}} = 172.5(2)$, $\text{O1-Nb1-Cl1} = 97.6(1)$, $\text{O1-Nb1-Cl2} = 100.3(1)$, $\text{O1-Nb1-Cl3} = 96.3(1)$, $\text{O1-Nb1-S1} = 93.9(1)$, $\text{Nb1-O1-Nb1}^{\text{i}} = 171.9(2)$, $\text{O2-Nb2-O2}^{\text{ii}} = 173.16(7)$, $\text{O2-Nb2-Cl4} = 97.5(1)$, $\text{O2-Nb2-Cl5} = 99.7(1)$, $\text{O2-Nb2-Cl6} = 97.0(1)$, $\text{O2-Nb2-S2} = 93.3(1)$, $\text{Nb2-O2-Nb2}^{\text{ii}} = 168.9(2)$. Symmetry operation: $i = x, -y+1/2, z+1/2$, $ii = x, -y+1/2, z-1/2$, (b) the polymeric chain.

The Nb–Cl and Nb–S distances seem unexceptional, and the disparate Nb–O are similar to those found in solid NbOCl_3 ,^{S1} which is dimeric with each niobium in an edge-linked distorted octahedron of four chlorines and two *trans* oxides ($\text{Nb-O} = 2.203(3), 1.758(3) \text{ \AA}$), which weakly link the dimers into polymer chains.

$[\text{NbOCl}_3\{\text{MeS}(\text{CH}_2)_2\text{SMe}\}]$ This was obtained as the bulk product from one reaction, no doubt due to adventitious oxidation/hydrolysis.

NbCl_4 (73 mg, 0.3 mmol) was suspended in CH_2Cl_2 (15 mL) at room temperature. A solution of $\text{MeS}(\text{CH}_2)_2\text{SMe}$ (36.6 mg, 0.3 mmol) and CH_2Cl_2 (2 mL) was added and the mixture stirred overnight. After filtering the pale green solution was evaporated *in vacuo*, leaving a pale green powder. Yield: 39 mg, 36%. Required for $\text{C}_4\text{H}_{10}\text{Cl}_3\text{NbOS}_2$ (337.52): C, 14.23; H, 2.99. Found: C, 13.55; H 2.94. IR (Nujol, cm^{-1}): 939 (Nb=O), 325, 344, 363 (Nb-Cl). $^1\text{H NMR}$ (CDCl_3 , 295 K): $\delta = 2.19$ (br, [3H], CH_3), 2.48 (br, [3H], CH_3), 2.76 (br, [2H], CH_2), 3.16 (br, [2H], CH_2).

Pale green crystals were grown by allowing a CH_2Cl_2 solution of the complex to evaporate under a N_2 atmosphere.

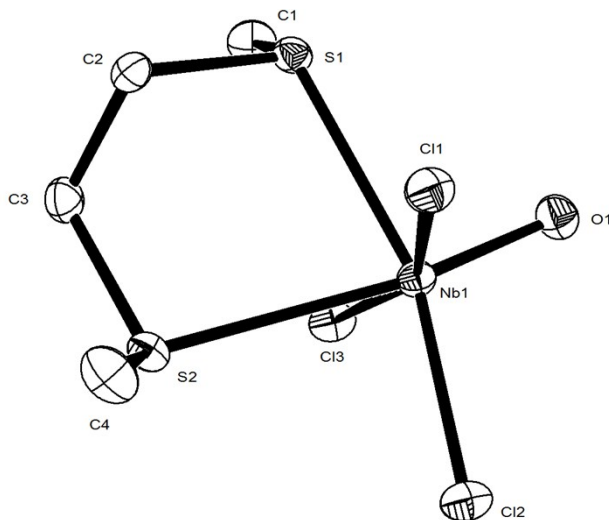


Figure S2. The structure of $[\text{NbOCl}_3\{\text{MeS}(\text{CH}_2)_2\text{SMe}\}]$ showing the atom numbering scheme and with ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (\AA) and angles ($^\circ$): $\text{Cl1-Nb1} = 2.375(1)$, $\text{Cl2-Nb1} = 2.339(1)$, $\text{Cl3-Nb1} = 2.369(1)$, $\text{O1-Nb1} = 1.718(4)$, $\text{S1-Nb1} = 2.664(1)$, $\text{S2-Nb1} = 2.856(1)$; $\text{Cl1-Nb1-Cl3} = 158.15(5)$, $\text{Cl2-Nb1-O1} = 105.17(15)$, $\text{S1-Nb1-S2} = 77.50(4)$, $\text{O(1)-Nb(1)-Cl(3)} = 97.22(14)$, $\text{Cl(2)-Nb(1)-Cl(3)} = 97.03(5)$, $\text{O(1)-Nb(1)-Cl(1)} = 98.34(14)$, $\text{Cl(2)-Nb(1)-Cl(1)} = 93.59(5)$, $\text{O(1)-Nb(1)-S(1)} = 93.95(14)$, $\text{Cl(3)-Nb(1)-S(1)} = 86.16(4)$, $\text{Cl(1)-Nb(1)-S(1)} = 77.56(4)$, $\text{Cl(2)-Nb(1)-S(2)} = 83.98(5)$, $\text{Cl(3)-Nb(1)-S(2)} = 76.86(5)$, $\text{Cl(1)-Nb(1)-S(2)} = 85.38(4)$.

References

S1. M. Ströbele and H.-J. Meyer, *Z. Anorg. Allg. Chem.*, 2002, **628**, 488.

On the structure of $[\text{Nb}_2\text{Cl}_4(\mu\text{-Se}_x)_2\{o\text{-C}_6\text{H}_4(\text{CH}_2)_2\text{Se}\}_4]$

As briefly described in the main text there is some ambiguity over the bridging unit. The molecule exhibits inversion symmetry at the centre of the $\text{Nb}_2\text{Cl}_2\text{Se}_{4+x}$ core – the discussions below are with reference to the asymmetric unit.

Initial refinements proceed as expected with the large electron density peak refined as a single Se atom, this has the expected geometry for such a species forming a μ^2 bridge (cf. Ta-Se in $[\text{Ta}_2\text{Cl}_4(\mu\text{-Se})_2\{o\text{-C}_6\text{H}_4(\text{CH}_2\text{SeMe})_2\}_2]$ ¹¹ 2.484(2), 2.489(2) \AA). However, significant electron density remains asymmetrically above (1.302 \AA) and below (0.982 \AA) this site and free refinement of the occupancies give the values below, and the geometry of the 2 new positions is consistent with an Se_2 unit²⁹ (2.73(1), 2.65(1) \AA). The difficulty of interpretation arises from the occupancy sum of 1.0 so that a mixture of single bridge and double bridge situations cannot exist without also involving a partially vacant bridge

site. The complex $[\text{Nb}_2\text{Cl}_4(\text{S}_2)\text{S}(\text{tht})_4]^{2+}$ is a sulphur bridged analogue of the minor component reported here.

Refined occupancies of the electron density peaks:

The difference peaks appear to represent real electron density (not Fourier truncation peaks).

Refined occupancies (EADP constraints) – 0.057, 0.89, 0.057

Refined occupancies (no ADP constraints) – 0.056, 0.89, 0.059

Selected Bond lengths:

Nb1–Se3 = 2.4579(8) Å

Nb1–Se3a = 2.731 Å (2.618, 2.642, 2.259 Å)

Nb1–Se3b = 2.715 Å

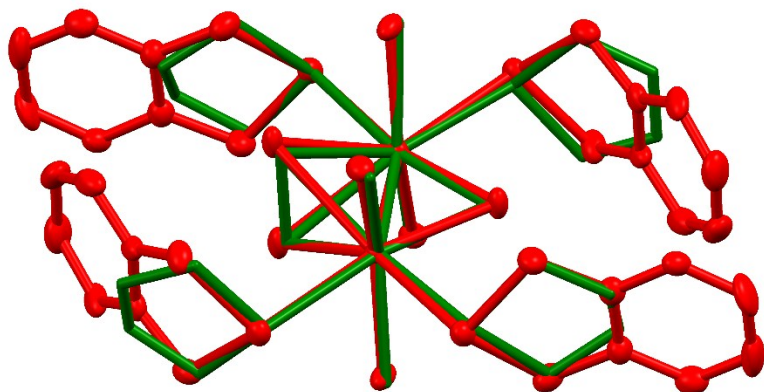
Se3a–Se3b = 2.283 Å (2.259 Å)

Nb1–Nb1ⁱ = 2.898 Å (2.972 Å)

Values in parentheses are from Reference 29 for comparison.

Refinement:

EADP Se3, Se3a & Se3b was required to retain realistic thermal parameters.



Overlay of CCDC CAMZUL (Nb-S)^{S2} and the current structure (Nb-Se) comparing the potentially similar bridging arrangements.

The minor species could also be interpreted as a single bridging Se with a butterfly shape (sometimes sitting above and sometimes below the plane of the major species). We thank a reviewer for this suggestion.

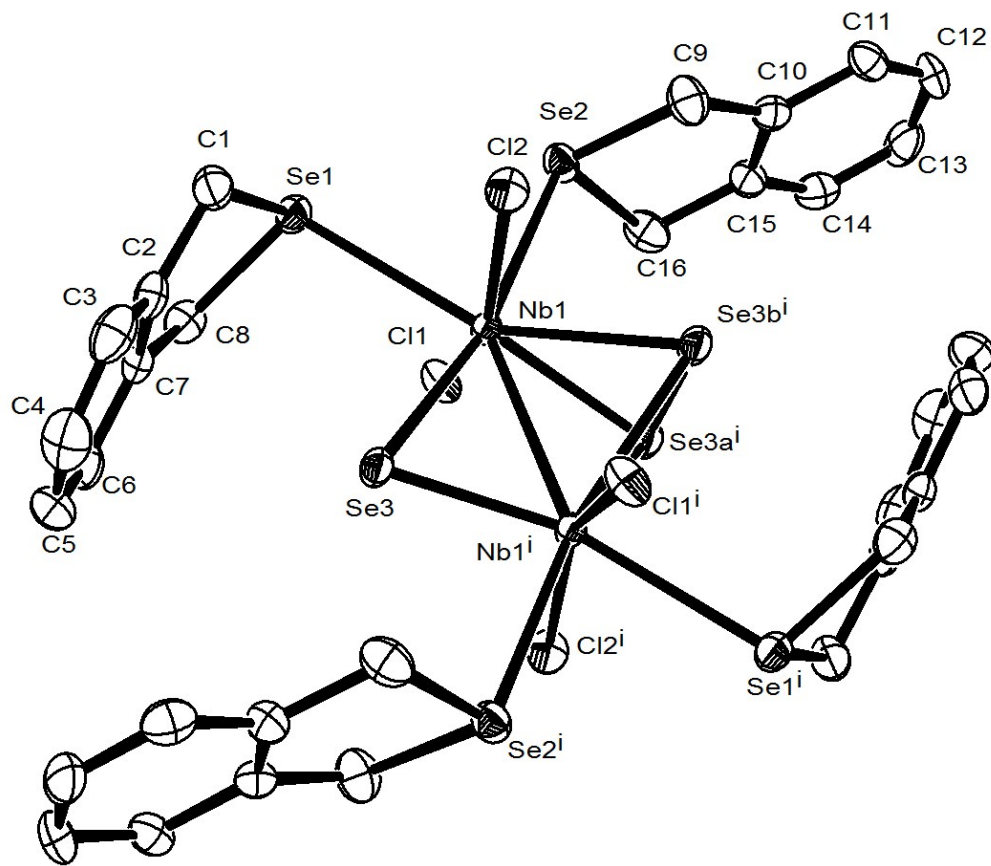


Figure S3. The structure of $[\text{Nb}_2\text{Cl}_4(\mu\text{-Se}_2)(\mu\text{-Se})\{o\text{-C}_6\text{H}_4(\text{CH}_2)_2\text{Se}\}_4]$ as refined showing the atom numbering scheme and with ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (\AA) and angles ($^\circ$): Nb–Cl1 = 2.384(1), Nb1–Cl2 = 2.372(2), Nb1–Nb1ⁱ = 2.8980(9), Nb1–Se1 = 2.8266(8), Nb1–Se2 = 2.8214(7), Nb1–Se3 = 2.4578(8), Nb1–Se3aⁱ = 2.73(1), Nb1–Se3bⁱ = 2.65(1); Cl1–Nb1–Cl2 = 152.68(6), Se1–Nb1–Se2 = 79.79(2). Symmetry operation: $i = 1-x, -y, -z$.

Table S1 X-ray crystallographic data

Compound	[NbOCl ₃ (SMe ₂)]	[NbOCl ₃ {MeS(CH ₂) ₂ SMe}]
Formula	C ₂ H ₆ Cl ₃ NbOS	C ₄ H ₁₀ Cl ₃ NbOS ₂
Formula weight	277.39	337.5
Crystal system	Monoclinic	Triclinic
Space group (no)	P2 ₁ /c (14)	P1 (1)
a/ Å	14.352(1)	6.7898(3)
b/ Å	14.9254(7)	6.9745(3)
c/ Å	7.9099(5)	7.2523(4)
α/ deg	90	108.917(4)
β/ deg	97.049(7)	99.404(4)
γ/ deg	90	113.677(4)
U/ Å ³	1681.6(2)	279.93(3)
Z	8	1
μ(Mo-Kα)/mm ⁻¹	2.548	2.112
F(000)	1072	166
Total no. reflections	13175	6650
Unique reflections	3295	2205
R _{int}	0.079	0.033
No. of parameters, restraints	149, 0	102, 3
R ₁ ^b [I _o > 2σ(I _o)]	0.041	0.025
R ₁ (all data)	0.074	0.027
wR ₂ ^b [I _o > 2σ(I _o)]	0.069	0.062
wR ₂ (all data)	0.080	0.063

Reference S2. M. G. B. Drew, D. A. Rice and D. M. Williams, *J. Chem. Soc., Dalton Trans.*, 1983, 2251.