

Substitution of bridging S₂ ligands in the [Nb₂(μ-S₂)₂]⁴⁺ core: a simple route to [Nb₂(Se₂)₂]⁴⁺, [Nb₂(S)(Te₂)]⁴⁺ and [Nb₂(S)₂]⁴⁺

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Reactions of [Nb₂(μ-S₂)₂(dte)₄] **1** (dte = diethyldithiocarbamate, S₂CNEt₂) with chalcogen-transfer reagents PEt₃Y (Y = Se or Te) were investigated. With PEt₃Se, fully substituted [Nb₂(μ-Se₂)₂(dte)₄] **2** forms if a catalytic amount of free PEt₃ is present. However PEt₃Te gives [Nb₂(S)(Te₂)(dte)₄] **3** which has a new core with two different chalcogens acting as bridges. The structures of both **2** and **3** were determined by X-ray analysis [**2**: Nb–Nb 2.974(2), Se–Se 2.303(2). **3**: Nb–Nb 2.920(4), Te–Te 2.648(3) Å]. Electrochemistry of **2** and **3** was studied and a reversible one-electron oxidation was found for **2**, giving a blue ESR-active (19-plet, *g* = 2.0489, *A* = 52.5 G) species [Nb₂(μ-Se₂)₂(dte)₄]⁺ at 638 mV vs. NHE. By contrast in the reaction of [Nb₂(μ-S₂)₂(acac)₄] **4** (Hacac = acetylacetonate) with PEt₃Te only the sulfur abstraction product [Nb₂(μ-S)₂(acac)₄] **5** formed, which could be more directly prepared from **4** and PEt₃. Crystal structures of **4** and **5** were determined.

Introduction

During the last few years we have devoted a part of our synthetic efforts to niobium clusters with bridging chalcogen atoms in the cluster core, in particular those with a Nb₂(μ-S₂)₂ core, including the preparation and structural characterization of the first niobium aqua-complex [Nb₂(μ-S₂)₂(H₂O)₈]⁴⁺.^{1–3} The key stage in this chemistry is the transformation of easily accessible but very inert polymeric NbS₂Cl₂^{5,6} into soluble salts [Nb₂S₄(NCS)₈]^{4–} by reaction with molten KNCS at 180 °C.^{1,4} The NCS ligand can be then either directly substituted by various 1,1'-dithioacid ligands like [–]S₂CNEt₂ (dte) yielding in that particular case the air-stable molecular complex [Nb₂(μ-S)₂(dte)₄] **1**¹ or it can be destroyed by heating with concentrated HCl to give the aqua-complex, a convenient material for preparation of other Nb₂(μ-S₂)₂ complexes.^{2,3} When NbSe₂Cl₂ reacts with KNCS under similar conditions, chalcogen scrambling gives the whole spectrum of possible species Nb₂S_xSe_{4–x}.^{7,8} The same reaction proceeds cleanly between the solids in a vibration mill to give K₄[Nb₂Se₄(NCS)₈], from which [Nb₂Se₄{S₂P(OR)₂}]₄ and [Nb₂Se₄(S₂COR)₄] (R = Et or Prⁱ) complexes were prepared.^{9a} A disadvantage of this approach is the necessity to use rather exotic for most laboratories, though constructively simple, equipment.⁹ We report here chalcogen substitution reactions in the Nb₂(μ-S₂)₂ core with PEt₃Y (Y = Se or Te) as chalcogen-transfer reagents as a new synthetic approach to Nb/Se and Nb/Te clusters.

Experimental

Starting materials

The compounds [Nb₂(μ-S₂)₂(dte)₄] **1**, [Nb₂(μ-S₂)₂(acac)₄] **4** and PEt₃Te were prepared by procedures described in the literature.^{1,3,10} PEt₃Se was prepared by treating PEt₃ (20% w/w toluene solution) with amorphous selenium powder in toluene at room temperature. All solvents were purified by standard methods and degassed before use. Standard Schlenk techniques were used throughout the preparation and isolation of selenium

and tellurium derivatives, though **2**, once prepared, is stable enough to be manipulated in air.

Preparations

[Nb₂(μ-Se₂)₂(dte)₄] 2. To a solution of complex **1** (0.20 g, 0.22 mmol) in 10 ml CH₂Cl₂ was added solid PEt₃Se (0.38 g, 1.3 mmol) followed by 0.15 ml of a toluene solution of PEt₃ (20% w/w). The solution immediately turned golden-brown. After 1 h stirring at room temperature, the solution was evaporated to dryness, the solid washed with diethyl ether and dissolved in a small amount of CHCl₃. Ethanol was then carefully layered on the top of the solution to produce dark brown crystals after standing overnight (**2**·2CHCl₃). They easily lose solvent chloroform in air (within minutes) to give solvent-free **2**. The elemental analysis refers to the unsolvated product (Found: C, 21.8; N, 5.0; H, 3.8; S, 23.0. Calc. for C₁₀H₂₀N₂Nb₂S₄Se₂: C, 21.9; N, 5.1; H, 3.7; S, 23.4%). Yield 0.15 g (65%). UV/VIS (CHCl₃, 300–1400 nm): 355 (sh), 412 and 615 (sh) nm. CV (THF, 0.1 M Bu₄NClO₄, vs. NHE, mV): –510 (reduction, irreversible), –78 (reduction, irreversible), 638 (quasireversible) and 1188 (oxidation, irreversible). IR (KBr, 4000–250 cm^{–1}): 270s, 365w, 400w, 575w, 780w, 815w, 875w, 915w, 1005m, 1080s, 1090 (sh), 1100 (sh), 1150s, 1195w, 1215s, 1305m, 1360s, 1380s, 1435s, 1460s, 1495s and 1540m. FAB-MS: *m/z* 1095 (3.9, [M – H]⁺), 1063 (25.5, [M – SH]⁺), 1015 (28.6, [M – SeH]⁺) and 867 (11.0%, [M – SeH – dte]⁺). ¹H NMR (CDCl₃): δ 3.77 (2 H, center of broad multiplet), 1.32, 1.24 and 1.21 (m, 3 H).

[Nb₂(μ-S)(μ-Te₂)(dte)₄] 3. To a solution of complex **1** (0.16 g, 0.18 mmol) in 10 ml CHCl₃ solid PEt₃Te (0.19 g, 0.8 mmol) was added. The solution turned dark-brown immediately upon the PEt₃Te addition and some Te precipitated. After 3 h stirring at room temperature, the solution was evaporated to dryness, the solid was washed with ether (2 × 10 ml) and extracted with 5 ml CH₂Cl₂. The golden-brown solution was filtered and on the top of the filtrate diethyl ether (10 ml) was carefully layered to produce dark brown crystals after standing overnight

Table 1 Summary of crystallographic data for complexes 1–5

	1	2·2CHCl ₃	3·CHCl ₃	4	5·CH ₂ Cl ₂
Empirical formula	C ₂₀ H ₄₀ N ₄ Nb ₂ S ₁₂	C ₂₀ H ₄₀ N ₄ Nb ₂ S ₈ Se ₄ ·2CHCl ₃	C ₂₀ H ₄₀ N ₄ Nb ₂ S ₉ Te ₂ ·CHCl ₃	C ₂₀ H ₂₈ Nb ₂ O ₈ S ₄	C ₂₀ H ₂₈ Nb ₂ O ₈ S ₂ ·2CH ₂ Cl ₂
<i>M</i>	907.10	1333.45	1185.49	710.49	816.23
<i>T</i> /K	296	296	173	293	173
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	<i>C2/c</i>	<i>P2₁/n</i>	<i>P$\bar{1}$</i>	<i>C2/c</i>	<i>P$\bar{1}$</i>
<i>a</i> /Å	24.010(3)	10.899(5)	13.030(3)	23.923(3)	9.00(1)
<i>b</i> /Å	6.957(4)	12.42(1)	14.391(5)	7.868(3)	11.15(3)
<i>c</i> /Å	21.172(2)	17.406(5)	12.053(4)	17.819(3)	8.868(6)
<i>a</i> ^o			97.61(3)		101.5(1)
<i>β</i> ^o	94.460(9)	104.25(3)	110.81(2)	121.036(8)	95.69(10)
<i>γ</i> ^o			78.40(3)		73.3(2)
<i>U</i> /Å ³	3526(1)	2282(2)	2064(1)	2873(1)	834(2)
<i>Z</i>	4	2	2	4	1
<i>D</i> _c /g cm ⁻³	1.710	1.940	1.907	1.642	1.625
<i>μ</i> /cm ⁻¹	13.81	44.31	26.10	11.27	11.70
Diffractometer	Rigaku AFC5R	Rigaku AFC5R	Rigaku AFC7R	Rigaku AFC5R	Rigaku AFC7R
2 θ _{max} ^o	55.0	60.0	55.1	55.0	44.9
No. reflections (total)	4479	7261	9893	3634	967
unique	4372	6934	9476	3547	798
observed [<i>I</i> > 2σ(<i>I</i>)]	2550	2981	3191	1917	784
No. variables	172	208	245	210	77
Structure solution	DIRDIF 92 PATTY ¹¹	SIR 92 ¹²	SIR 92	DIRDIF 92 PATTY	SIR 92
<i>R</i>	0.042	0.079	0.091	0.040	0.074
<i>R</i> '	0.027	0.049	0.055	0.024	0.078

(3·CHCl₃). They easily lose the solvent to give unsolvated **3**. The elemental analysis refers to the unsolvated product (Found: C, 22.8; N, 5.3; H, 3.8; S, 23.0. Calc. for C₂₀H₄₀N₄Nb₂S₉Te₂: C, 22.5; N, 5.3; H, 3.8; S, 23.4%). Yield 0.11 g (58%). UV/VIS (CHCl₃, 300–1400 nm): 369 and 785 nm. CV (THF, 0.1 M Bu₄NClO₄, vs. NHE, mV): 674 (oxidation, irreversible), 1100 (oxidation, irreversible), 900 (reduction, irreversible), 440 (reduction, irreversible) and –110 (reduction, irreversible).

[Nb₂(μ-S)₂(dte)₄]PF₆ **1a** and [Nb₂(μ-Se)₂(dte)₄]PF₆ **2a**. A mixture of complex **2** (0.1 g, 0.09 mmol) and [FeCp₂]PF₆ (0.03 g, 0.09 mmol) was stirred in methylene chloride for 1 h. On the top of the resulting blue solution a double volume of hexane was layered. After standing for 2 d at –20 °C, 72 mg of crystalline **2a** were isolated as long needles. Yield 64% (Found: C, 21.0; H, 3.5; N, 4.3. Calc. for C₂₀H₄₀F₆N₄Nb₂PS₈Se₄: C, 19.4; H, 3.3; N, 4.5%). IR (KBr, 4000–250 cm⁻¹): 378m, 565s, 778w, 840vs, (PF₆), 900w, 1000w, 1075m, 1090w, 1150m, 1205s, 1272s, 1300w, 1355s, 1375m, 1439s, 1456s, 1517s, 2867w, 2922m and 2955m. UV/VIS in CH₂Cl₂ (λ/nm; ε/M⁻¹ cm⁻¹): 675 (sh) (5200), 598 (8150) and 397 (5300). ESR (CH₂Cl₂, 293 K): *g* = 2.0489, *A* = 52.5 G.

Complex **1a** was prepared and isolated (as a blue-violet powder) similarly except that three times the stoichiometric amount of oxidant was used owing to the less favourable oxidation potential of **1** compared to **2** (Found: C, 22.5; H, 3.7; N, 4.9. Calc. for C₂₀H₄₀F₆N₄Nb₂PS₁₂: C, 22.8; H, 3.8; N, 4.9%). IR (KBr, 4000–250 cm⁻¹): 285m, 375m, 560s, 780w, 840vs, 915w, 1000m, 1075m, 1090m, 1145m, 1205m, 1275s, 1300m, 1355s, 1380m, 1450s, 1460m, 1505 (sh) and 1515s. UV/VIS in CH₂Cl₂ (λ/nm): 592, 518 (sh) and 364; ε values were not quantified due to instability of the solutions. The ESR spectrum is reported elsewhere.¹

[Nb₂(μ-S)₂(acac)₄] **5**. To a red solution of [Nb₂(μ-S)₂(acac)₄] **4** (0.18 g, 0.25 mmol) in 10 ml CH₂Cl₂ solid PEt₃Te (0.38 g, 1.56 mmol) was added, causing immediate darkening and precipitation of elemental Te. The mixture was left stirring overnight, then filtered and the filtrate reduced to 2 ml. After keeping for 1 h at –20 °C, 0.12 g of dark green crystalline **5** was collected. Yield 75% (Found: C, 37.8; H, 5.0; S, 8.9. Calc. for C₁₀H₁₄NbO₄S: C, 37.2; H, 4.4; N, 9.9%).

Crystallography

A summary of the crystal data, data collection and structure solution details is given in Table 1. Crystals of complexes **1** and **4** were mounted in air on a glass fiber, those of 2·2CHCl₃ in a capillary together with a drop of mother-liquor and sealed in air. Crystals of 3·CHCl₃ and 5·2CH₂Cl₂ were picked up from the mother-liquor, immersed in glue under N₂, fixed on a glass fiber and immediately cooled to 173 K. Unit cell dimensions were determined and refined from 25 reflections in the 2θ ranges (°) 24.34–32.46 for **1**, 23.54–35.09 for 2·2CHCl₃, 29.71–29.97 for 3·CHCl₃ and 21.21–27.51 for **4**. For 5·2CH₂Cl₂, 14 reflections in the range 7.61–15.87° were used to determine the cell. Intensity data were collected with the ω–2θ scan mode using graphite-monochromated Mo-Kα radiation (λ 0.71069 Å). In the case of **2** a 10.4% decrease in the intensity of standards over the course of data collection was observed and the intensity data were linearly corrected.

The structures were solved by the Patterson method (**1** and **4**) or by the direct method (2·2CHCl₃, 3·CHCl₃ and 5·2CH₂Cl₂) and expanded using Fourier techniques. The reflections were empirically corrected for absorption by the program DIFABS¹³ after all non-hydrogen atoms were isotropically refined. Finally the structures were refined by the full-matrix least-squares method. In **1**, 2·2CHCl₃, and **4**, all non-hydrogen atoms were anisotropically refined. In 3·CHCl₃, only heavy atoms (Nb, S, Te and Cl) were anisotropically treated, other non-hydrogen atoms being refined isotropically. Hydrogen atoms were located in the calculated positions in **1**, 2·2CHCl₃, 3·3CHCl₃, while they were isotropically refined in **4**.

The data collection of complex 5·2CH₂Cl₂ had to be discontinued due to trouble with the diffractometer. Since the crystals became amorphous quickly by losing solvent molecules the measurement of reflection intensities could not be continued. Therefore, the structure was determined based on a partial set of reflections. All non-hydrogen atoms were isotropically refined and hydrogen atoms were not included in the calculation. We report the structure to show the non-quantitative geometry of complex **5**.

The structure of [Nb₂S₄(Et₂NCS₂)₄] **1'** reported previously¹⁴ appeared to be disordered. We employed a different solvent system to grow single crystals of **1** (CH₃CN–CH₂Cl₂ instead of CH₂Cl₂–hexane). The cell constants of **1'** [*a* = 21.181(8),

$b = 6.958(1)$, $c = 16.623(6)$ Å, $\beta = 133.95^\circ$, $V = 1764(2)$ Å³, space group $C2/m$, $Z = 2$] are different from those of **1** but are convertible into them by the following transformation: $a' = a + 2c$, $b' = -b$, $c' = a$. The cell volume of the converted cell is $V' = 3528$ Å³ and the resulting lattice is also C -centered. No disorder was found in **1**. It is possible that **1** and **1'** are genuine polymorphs (ordered and disordered) or **1'** may be the same as **1** but only its subcell was determined.

For the acac complex **4** cell parameters have been reported (space group $C2$) but the structure could not be refined.³ We have finally solved the structure in the $C2/c$ space group.

CCDC reference number 186/1238.

See <http://www.rsc.org/suppdata/dt/1999/85/> for crystallographic files in .cif format.

Results and discussion

Chalcogen substitution reactions

In the early 90s we suggested PPh_3Se and KNcSe as effective chalcogen-transfer reagents for introduction of Se into the $[\text{Mo}_3(\mu\text{-S})(\mu\text{-S}_2)_3]^{4+}$ cluster core to give a $[\text{Mo}_3(\mu\text{-S})(\mu\text{-SSe})_3]^{4+}$ core with novel SSe ligands.¹⁵ Ibers and co-workers found that Se in polyselenido complexes can be substituted by using PEt_3Te instead of the non-existent PPh_3Te . This works for polyselenido complexes of Ni, Pt,¹⁶ Zn, Cd and Hg.¹⁷ We found, however, that **1** does not react with pure PEt_3Se , whereas adding small amounts of free PEt_3 to the mixture immediately brings about a colour change and gives **2** as the sole product. No mixed S/Se species were observed in this case. The necessity of adding free PEt_3 suggests that the reaction proceeds *via* initial abstraction of S from S_2 by phosphine giving a $\text{Nb}(\mu\text{-S})(\mu\text{-S}_2)\text{Nb}$ unit. The bridging monosulfide ligand thus produced is nucleophilic enough to abstract Se from PEt_3Se thus forming a SSe unit and regenerating free phosphine. The reaction proceeds further with repeating cycles of sulfur abstraction/selenium insertion up to the final product, **2**. The P=S bond is energetically preferable over P=Se, and phosphines attack S–S bonds much faster (orders of magnitude!) than Se–Se bonds.¹⁸ The same observations are valid for PMe_2PhSe , which also gives **2**. In the case of PEt_3Te there is always some free phosphine present in the solution as a result of partial dissociation into PEt_3 and Te, thus enabling the substitution to proceed without an extra PEt_3 source.¹⁰

Complex **3** is a rare example (and the first for Nb) of a cluster having both Te and S in the cluster core. As for its formation in place of the expected $\text{Nb}_2(\text{Te}_2)_2$ derivative, two comments may be relevant. First, chalcogen substitution reactions with PEt_3Te often proceed beyond simple substitution and may involve dramatic changes in structure.¹⁶ Secondly, the $\text{Nb}_2(\text{Te}_2)_2$ core is known in $[\text{Nb}_2(\text{Te}_2)_2][\text{Te}_2\text{I}_6]_2$, prepared by high temperature reaction from the elements and thus thermodynamically stable.¹⁹ With **4**, where dtc ligands are replaced by acac, the reaction with PEt_3Te takes another course leading to sulfur abstraction only with the formation of the bis(monosulfido) bridged **5**. As acac is more electronegative than dtc, the nucleophilicity of bridging sulfur in **5** is probably not high enough to form an intermediate with a S–Te bridge. The use of PEt_3 instead of PEt_3Te in the reaction with **4** gives the same complex **5** in a more straightforward manner. Sulfur abstraction by PPh_3 was used before to prepare $[\text{Nb}_2(\mu\text{-S})_2\text{Cl}_4(\text{tht})_4]$ from $[\text{Nb}_2(\mu\text{-S})(\mu\text{-S}_2)\text{Cl}_4(\text{tht})_4]$ (tht = tetrahydrothiophene), where the reaction time was 3 months at 50°C .²⁰ Another approach to $\text{Nb}_2\text{S}_2^{4+}$ involves methathesis of NbCl_4L_2 with Sb_2S_3 or $(\text{Me}_3\text{Si})_2\text{S}$ ($\text{L} = \text{MeCN}$ or THF).^{21,22}

Molecular complexes with the $[\text{Nb}_2(\mu\text{-Se}_2)_2]^{4+}$ core were first prepared by treating NbSeCl_3 (structure unknown) with thioesters. The products thus prepared were $[\text{Nb}_2\text{Se}_4\text{Cl}_4(\text{tht})_4]$ and $[\text{Nb}_2\text{Se}_4\text{Cl}_4(\text{Me}_2\text{S})_4]$.^{23,24} The compounds NbSe_2X_2 ($\text{X} = \text{Cl}$, Br or I) which contain $[\text{Nb}_2(\mu\text{-Se}_2)_2]^{4+}$ units linked by halide

bridges into an infinite layer structure are far too inert within the ordinary range of reaction temperatures and solvents; NbSe_2I_2 reacts with Te and I_2 (effectively TeI_2) at 500°C to give $[\text{Nb}_2(\mu\text{-Se}_2)_2][\text{Te}_2\text{I}_6]_2$ with $\text{Te}_2\text{I}_6^{2-}$ acting as a tetradentate ligand.²⁵ Taking the greater accessibility and stability of Nb_2S_4 derivatives into account, chalcogen substitution of Se for S suggests itself as a viable synthetic alternative for preparation of their Nb_2Se_4 analogs.

Oxidation of $[\text{Nb}_2(\mu\text{-Y})_2(\text{dtc})_4]$

Chemical oxidation of $[\text{Nb}_2(\mu\text{-S}_2)_2(\text{dtc})_4]$ **1** by Fc^+ has been reported.¹ The one-electron oxidation product, cation-radical $\mathbf{1}^+$, was characterized in solution by ESR spectroscopy. We found that **2** is also oxidized by Fc^+ to give ESR active species $\mathbf{2}^+$. The ESR spectra of both $\mathbf{1}^+$ and $\mathbf{2}^+$ give a similar 19-plet pattern due to the hyperfine interaction of the single unpaired d electron with the two ⁹³Nb nuclei. The A and g parameters are similar for $\mathbf{1}^+$ and $\mathbf{2}^+$ (A : $\mathbf{1}^+$, 54.0; $\mathbf{2}^+$, 52.5 G; g : $\mathbf{1}^+$, 2.0113; $\mathbf{2}^+$, 2.0489). They differ from those expected for a simple d^1 system which probably reflects a contribution of the p orbitals of the bridging dichalcogen units and/or of the dtc ligands.¹ The solutions of $\mathbf{1}^+$ are not stable and decompose at room temperature within 2–3 d into unidentified products; $\mathbf{2}^+$ is more stable in solutions. Solid samples of $[\mathbf{1}]\text{PF}_6$ and $[\mathbf{2}]\text{PF}_6$ have also been prepared. Similarly, the BF_4 and BPh_4 salts were also isolated. Our efforts to obtain good quality single crystals have failed so far.

Cyclic voltammetry studies

Cyclic voltammetry was performed for complexes **1**, **2** and **3** in THF in the presence of 0.1 M Bu_4NClO_4 . Complexes **1** and **2** show similar quasireversible waves at 770 (**1**) and 638 mV (**2**) vs. NHE which can be attributed to a one electron oxidation identical with that effected by Fc^+ . For both cases $I_c = I_a$ but ΔE for **1** was 294 mV, for **2** 207 mV. This can be explained by changes in geometry of the complexes after oxidation, primarily because one would expect elongation of the Nb–Nb bond as one d electron is removed and the formal bond order is thus reduced to 0.5. The second oxidation is irreversible and takes place at rather high positive potentials, about 1600 mV for **1** and 1188 mV for **2**. No reversible reduction behaviour was found for **1** and **2** (and for **3** and **4** as well). It is interesting that the disulfide bridged cluster **1** is oxidized at about 130 mV more positive potential than is **2**.

Crystal structures

The complexes **1**, **2**, **4** and **5** all have an inversion center at the midpoint of the bonded Nb atoms; **3** has no crystallographic symmetry but has a pseudomirror plane perpendicular to the Nb–Nb bond.

Nb₂S₄ clusters. Views of $[\text{Nb}_2\text{S}_4(\text{dtc})_4]$ **1** and $[\text{Nb}_2\text{S}_4(\text{acac})_4]$ **4** are shown in Figs. 1 and 2, respectively. Bond distances are given in Tables 2 and 3. The parameters of the Nb_2S_4 core vary only slightly with the change of other “external” ligands at Nb.^{1–3,5,6,14} In agreement with this, a typical S–S distance of 2.033(2) Å was found in **1**, instead of the previously reported value 2.282(5) Å for **1'**.¹⁴ The Nb–Nb distances in all known $\text{Nb}_2\text{S}_4^{4+}$ clusters fall within the 2.86–2.91 Å range which is longer than 2.81–2.86 Å for isoelectronic $\text{Mo}_2\text{S}_4^{6+}$ clusters and might reflect a weaker Nb–Nb bonding, but it does not necessarily mean greater stability of the Mo_2S_4 species. Indeed we found that the latter are prone to transform internally under conditions where their niobium counterparts are stable.^{2,26} It is also interesting to compare the geometries of the acac complex **4** and of $[\text{Nb}_2\text{S}_4(\text{tfa})_4]$ [tfa represents O,O' co-ordinating $\text{CF}_3\text{C}(\text{O})\text{CHC}(\text{O})\text{CH}_3$ ligand].³ In the latter the Nb_2S_4 core is “compressed” as compared with **4** [Nb–Nb 2.879(1) vs.

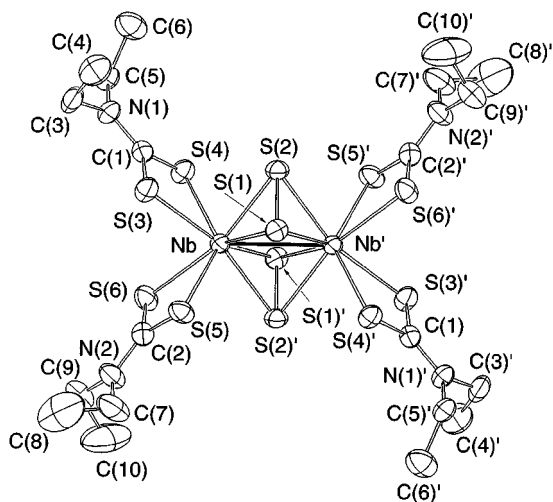


Fig. 1 View of the structure of $[\text{Nb}_2\text{S}_4(\text{Et}_2\text{NCS}_2)_4]$ 1.

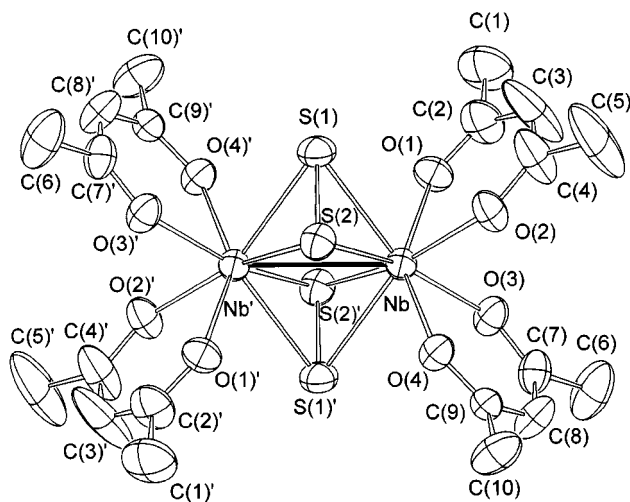


Fig. 2 View of the structure of $[\text{Nb}_2\text{S}_4(\text{acac})_4]$ 4.

Table 2 Selected bond lengths (Å) in complex 1

Nb–Nb	2.8928(9)	Nb–S(1)	2.520(1)
Nb–S(2)	2.492(1)	Nb–S(3)	2.598(2)
Nb–S(4)	2.586(1)	Nb–S(5)	2.569(2)
Nb–S(6)	2.619(2)	S(1)–S(2)	2.033(2)
S(3)–C(1)	1.727(5)	S(4)–C(1)	1.708(5)
S(5)–C(2)	1.705(6)	S(6)–C(2)	1.723(6)
N(1)–C(1)	1.325(5)	N(1)–C(3)	1.472(7)
N(1)–C(5)	1.471(6)	N(2)–C(2)	1.324(6)
N(2)–C(7)	1.468(8)	N(2)–C(9)	1.463(7)
C(3)–C(4)	1.492(8)	C(5)–C(6)	1.508(7)
C(7)–C(8)	1.477(9)	C(9)–C(10)	1.500(8)

Table 3 Selected bond lengths (Å) in complex 4

Nb–Nb	2.9039(9)	Nb–S(1)	2.535(1)
Nb–S(1)	2.534(1)	Nb–S(2)	2.498(1)
Nb–S(2)	2.508(2)	Nb–O(1)	2.147(4)
Nb–O(2)	2.127(4)	Nb–O(3)	2.131(3)
Nb–O(4)	2.143(3)	S(1)–S(2)	2.019(2)
O(1)–C(2)	1.245(6)	O(2)–C(4)	1.250(7)
O(3)–C(7)	1.252(6)	O(4)–C(9)	1.245(5)
C(1)–C(2)	1.506(10)	C(2)–C(3)	1.394(9)
C(3)–C(4)	1.39(1)	C(4)–C(5)	1.51(1)
C(6)–C(7)	1.508(9)	C(7)–C(8)	1.398(9)
C(8)–C(9)	1.400(7)	C(9)–C(10)	1.487(9)

2.9039(9) in 4; S–S 2.008(4) vs. 2.019(2) and Nb–S (average) 2.504 vs. 2.519 Å]. This may be simply due to the higher electronegativity of the fluorinated ligand, which reduces the

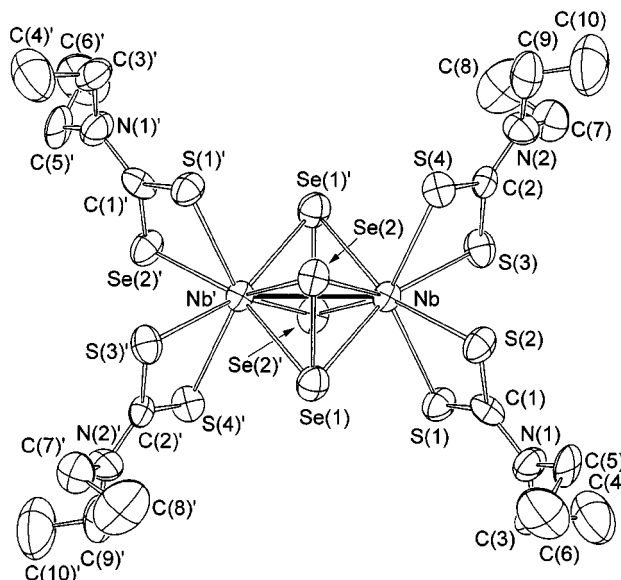


Fig. 3 View of the structure of $[\text{Nb}_2\text{Se}_4(\text{Et}_2\text{NCS}_2)_4]$ 2.

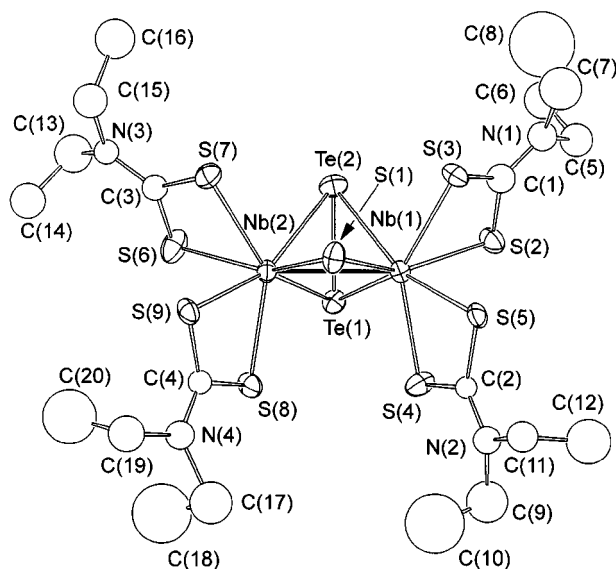


Fig. 4 View of the structure of $[\text{Nb}_2(\text{S})(\text{Te}_2)(\text{Et}_2\text{NCS}_2)_4]$ 3.

Table 4 Selected bond lengths (Å) in complex 2

Nb–Nb	2.974(2)	Nb–Se(1)	2.639(2)
Nb–Se(1)	2.625(2)	Nb–Se(2)	2.644(2)
Nb–Se(2)	2.649(2)	Nb–S(1)	2.585(3)
Nb–S(2)	2.607(4)	Nb–S(3)	2.609(4)
Nb–S(4)	2.593(4)	Se(1)–Se(2)	2.303(2)
Cl(1)–C(11)	1.67(1)	Cl(2)–C(11)	1.65(1)
Cl(3)–C(11)	1.76(2)	S(1)–C(1)	1.73(1)
S(2)–C(1)	1.68(1)	S(3)–C(2)	1.68(1)
S(4)–C(2)	1.73(1)	N(1)–C(1)	1.40(1)
N(1)–C(3)	1.45(2)	N(1)–C(5)	1.45(1)
N(2)–C(2)	1.34(1)	N(2)–C(7)	1.46(2)
N(2)–C(9)	1.43(2)	C(3)–C(4)	1.47(2)
C(5)–C(6)	1.45(2)	C(7)–C(8)	1.48(2)
C(9)–C(10)	1.42(2)		

electron density (and effective radius) at Nb and thus enhances the donation from $\text{S}_2 \pi^*$ to niobium d_π orbitals.

Nb_2Se_4 core. The Nb–Nb bonds are further elongated when Se is substituted for S (Fig. 3, Table 4). The Nb–Nb distance found in 2, 2.974(2) Å, is close to those observed in $[\text{Nb}_2\text{Se}_4][\text{Te}_2\text{I}_6]_2$ [2.926(2) Å],²⁵ $[\text{Nb}_2\text{Se}_4\text{Cl}_4(\text{Me}_2\text{S})_4]$ [2.962(3) Å], $[\text{Nb}_2\text{Se}_4\text{Cl}_4(\text{tht})_4]$ [2.972(5) Å]^{20,23} and in polymeric NbSe_2Cl_2 [2.973(4) Å].²⁷ The Se–Se distance [2.303(2) Å] is longer than in

Table 5 Selected bond lengths (Å) in complex **3**

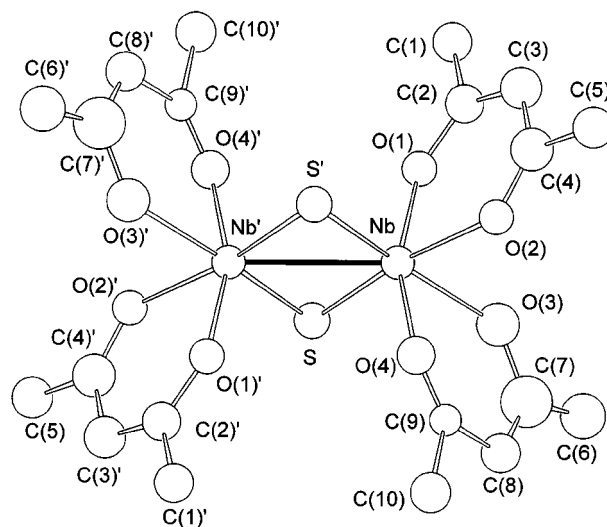
Te(1)–Te(2)	2.648(3)	Te(1)–Nb(1)	2.844(3)
Te(1)–Nb(2)	2.854(3)	Te(2)–Nb(1)	2.848(3)
Te(2)–Nb(2)	2.842(3)	Nb(1)–Nb(2)	2.920(4)
Nb(1)–S(1)	2.376(7)	Nb(1)–S(2)	2.625(8)
Nb(1)–S(3)	2.581(8)	Nb(1)–S(4)	2.499(7)
Nb(1)–S(5)	2.618(7)	Nb(2)–S(1)	2.387(8)
Nb(2)–S(6)	2.581(8)	Nb(2)–S(7)	2.581(7)
Nb(2)–S(8)	2.511(7)	Nb(2)–S(9)	2.593(8)
Cl(1)–C(21)	1.33(6)	Cl(2)–C(21)	1.78(6)
Cl(3)–C(21)	2.01(5)	S(2)–C(1)	1.69(3)
S(3)–C(1)	1.73(3)	S(4)–C(2)	1.75(2)
S(5)–C(2)	1.70(2)	S(6)–C(3)	1.71(2)
S(7)–C(3)	1.74(3)	S(8)–C(4)	1.72(2)
S(9)–C(4)	1.67(2)	N(1)–C(1)	1.32(3)
N(1)–C(5)	1.51(3)	N(1)–C(7)	1.62(4)
N(2)–C(2)	1.33(3)	N(2)–C(9)	1.58(4)
N(2)–C(11)	1.43(3)	N(3)–C(3)	1.33(3)
N(3)–C(13)	1.50(4)	N(3)–C(15)	1.55(3)
N(4)–C(4)	1.33(3)	N(4)–C(17)	1.64(4)
N(4)–C(19)	1.65(4)	C(5)–C(6)	1.52(4)
C(7)–C(8)	1.24(8)	C(9)–C(10)	1.40(7)
C(11)–C(12)	1.50(5)	C(13)–C(14)	1.51(4)
C(15)–C(16)	1.55(4)	C(17)–C(18)	1.24(8)
C(19)–C(20)	1.45(6)		

both Me₂S [2.288(3) Å] and tht [2.260(5) Å] complexes,^{20,23} but somewhat shorter than in the complex with Te₂I₆²⁻ ligands [2.310–2.311(2) Å].²⁵ The average Nb–S (dtc) distances are almost identical for **1** and **2**, being 2.593 Å in the former and 2.598 Å in the latter compound.

Nb₂STe₂ core. Cluster **3** has a unique Nb₂(S)(Te₂)⁴⁺ core (Fig. 4, Table 5). The Te₂ ligand is co-ordinated unsymmetrically with one Te atom in the Nb₂S plane and the other out of the plane. The Nb–Te distances are however almost identical [Nb–Te(1) 2.844(3)–2.854(3), Nb–Te(2) 2.842(3)–2.848(3) Å]. In [Nb₂(μ-S)(μ-S₂)X₄(tht)₃] (X = Cl or Br) the S₂ ligand adopts a more symmetrical co-ordination with the two Nb atoms, bridging S atom and the midpoint of the S₂ unit being almost coplanar.²⁸ The Te–Te distance, 2.648(3) Å, is close to that observed in [Nb₂(Te₂)₂][Te₂I₆]₂ [2.682(1) Å], the only Nb₂(Te₂)₂⁴⁺ cluster so far known. The Nb–Nb distance in the latter is however much longer than in **3** [3.083(2) vs. 2.920(4) Å].¹⁹ As calculations show that the potential minimum for Nb–Nb interaction is rather flat between 2.9 and 3.1 Å,¹⁹ the continuous elongation of the Nb–Nb distance on going from Nb₂S₄ via Nb₂Se₄ to Nb₂Te₄ is caused by the necessity to accommodate two larger dichalcogenido groups, keeping the van der Waals repulsion between them minimal. The steric requirements of one S and one Te₂ group are more modest compared to those of two Te₂ ligands, thus allowing two Nb atoms to be almost as close as they are in Nb₂S₄ clusters.

Et₂NCS₂ ligands. In the complexes **1**, **2** and **3** the dtc ligands have their usual geometry where a nitrogen atom, two sulfur atoms, and 3 carbon atoms are coplanar. The two terminal CH₃ groups may be either *cis* or *trans* with regard to this plane. In the case of **1** each Nb has one of each sort (Fig. 1) and in the case of **2** they are all *trans* (Fig. 3). Again, **3** has one of each kind similarly to **1** (Fig. 4). It is unlikely that the energy differences between *cis* and *trans* forms are large and the configuration in the crystal is dictated mainly by the packing forces.

Co-ordination around Nb. In terms of a formalism in which the niobium co-ordination in bis(dichalcogenido) bridged dimers **1**, **2** and **4** is described as pseudooctahedral by taking the midpoints of the Y₂ units to be the positions of imaginary monodentate ligands, each of these octahedra possesses chirality at the Nb. Using Λ and Δ designations, the observed

**Fig. 5** View of the structure of [Nb₂S₂(acac)₄] **5**.**Table 6** Selected bond lengths (Å) in complex **5**

Nb–Nb	2.880(5)	Nb–S	2.393(7)
Nb–S	2.37(1)	Nb–O(1)	1.99(1)
Nb–O(2)	2.15(1)	Nb–O(3)	2.29(3)
Nb–O(4)	1.98(2)	Cl(1)–C(11)	1.75(3)
Cl(2)–C(11)	1.75(4)	O(1)–C(2)	1.35(3)
O(2)–C(4)	1.30(3)	O(3)–C(7)	1.39(5)
O(4)–C(9)	1.22(5)	C(1)–C(2)	1.57(3)
C(2)–C(3)	1.42(2)	C(3)–C(4)	1.47(3)
C(4)–C(5)	1.57(3)	C(6)–C(7)	1.41(5)
C(7)–C(8)	1.45(3)	C(8)–C(9)	1.56(5)
C(9)–C(10)	1.64(3)		

configurations in the centrosymmetrical molecules of **1**, **2** and **4** are represented as ΛΔ, *i.e.* they all are *meso* isomers. Other such d¹–d¹ dimers existing as *meso* forms are [V₂S₄(Et₂NCS₂)₄], [Mo₂S₄(Et₂NCS₂)₄][BF₄]₂ and [W₂S₄(Et₂NCS₂)₄][I₃].^{29,30} An equilibrium between *meso* ΛΔ and a racemic mixture of chiral ΛΛ + ΔΔ isomers may exist in solution. Indeed, the ¹H NMR spectrum of the acac complex **4** at room temperature (in CDCl₃) shows two well separated sharp singlets (at δ 5.55 and 5.52) for the proton attached to the central C atom of the acac ligand. This pattern arises from coexistence of the two isomers. In the case of [V₂S₄(S₂CN^tBu₂)₄] it is the racemic mixture that crystallizes from solutions.³¹ In **5** (Fig. 5, Table 6) the geometry around Nb is octahedral (2S + 4O') and it also exists in the *meso* form in the crystal. Complex **3** has two independent Nb atoms. The co-ordination of Nb(1) may be described as distorted pentagonal bipyramidal with basal S(1), S(2), S(3), S(4) and Te(1) and apical S(5) and Te(2) atoms or as distorted monocapped octahedral with Te(2) capping the face formed by Te(1), S(3) and S(2). The co-ordination around Nb(2) is too distorted to be approximated as a simple polyhedron.

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