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The synthesis and structural characterization of the $[Nb(Se)_3S^tBu]^{2-}$, $[Nb(O)(Se_2)SeH]^{2-}$, $[(Nb(O)(Se_2)_2)_2Se_4]^{4-}$ and $\{[Nb(Se)_3]_2O\}^{4-}$ anions. New elementary selenoniobates

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Abstract—The reaction of $NbCl_5$, NaS^tBu, Se and Et_4NCl in CH_3CN in a 1 : 6 : 1 : 1.6 molar ratio affords crystalline $(Et_4N)_2[Nb(Se)_3(S^tBu)]$, **1**. The same salt is obtained in about 25% yield by the oxidation of $[Nb(S)(S^tBu)_4]^-$ with 1 equiv. of Se. Oxidation of **1**, or its Ph_4P^+ analog with 1.5 equiv. of Se in the presence of water, results in the formation of the $[Nb(O)(Se_2)_2SeH)]^{2-}$ anion, **2**, that can be isolated as Ph_4P^+ or Et_4N^+ salts. The Se–H vibration in the Et_4N^+ salt of **2** is found at 2526 cm^{-1} and the proton in the anion is easily exchanged with D_3COD. The $(Et_4N)_4[(Nb(O)(Se_2)_2)_2Se_4]$ dimer, **3** was obtained by the oxidation of $(Et_4N)_2[Nb(O)(Se_2)_2SeH)]$ with 2 equiv. of elemental selenium. The reaction of $(Et_4N)_2[Nb(Se)_3(S^tBu)]$ with water in CH_3CN, led to isolation of the oxo-bridged dimer, $(Et_4N)_4[(Se)_3Nb\text{-}O\text{-}Nb(Se)_3]$, **4**. The crystal structures of **1**–**4** have been determined. Single crystal X-ray diffraction data for **1**–**4** were collected on a Nicolet P3/F diffractometer using Mo-Kα radiation and the structures solved using a combination of heavy atom Patterson techniques, direct methods and Fourier techniques. The number of parameters refined and the final R factors obtained for each structure at the conclusion of refinement are: (**1**) 280, 0.0463; (**2**), 518, 0.0941; (**3**), 318, 0.0886 and (**4**), 205, 0.0625 respectively. The anion in **1** exhibits tetrahedral geometry while the structure of the anion in **2** shows the Nb^{5+} ion in a pentagonal pyramidal geometry with the two η^2-Se_2^{2-} and the η^1-SeH^- ligands in the equatorial plane and the oxo ligand in the apical position. The Nb atom is located 0.70 Å above the plane defined by the five equatorial Se atoms. In **2**, the Nb═O, Nb—SeH and Nb—Se_2 bonds are found at 1.671(11), 2.608(4) and 2.60(1) Å, respectively. The structure of the anion in **3** shows 2 $[Nb(O)(Se_2)_2]$ units, bridged by a tetraselenido ligand to give a dimer with pentagonal pyramidal $[Nb(O)(Se_2)_2Se]$ subunits and the oxo ligands in an *anti* conformation. In **4** the μ-oxo ligand of the anion is located on a crystallographic centre of symmetry and the Nb—O bond, in the linear Nb—O—Nb unit is 1.916(1) Å. The two $Nb(Se)_3$ units are oriented in a staggered fashion to give an idealised D_{3d} symmetry. © 1997 Elsevier Science Ltd

Keywords: niobium; selenides; polyselenides; chalcogenides.

Few soluble transition metal complexes with selenido ligands were known prior to 1987 [1]. Among these were included the anions $[MSe_4]^{2-}$ (M = Mo, W) and $[Fe_2Se_{12}]^{2-}$ [2], an exact analog of $[Fe_2S_{12}]^{2-}$ [3]. Since then, a wide variety of other complexes have been synthesized [4]. Solid state compounds, obtained in molten polyselenides [5,6] include: $K_3CuNb_2Se_{12}$ [7]. KCu_2NbSe_4 [8b] and $K_6Nb_4Se_{22}$ [9].

The Nb/Se compounds obtained have shown structural similarities with their sulfido counterparts [10], although in some instances there exist differences. Such is the case for $W_2Se_9^{2-}$, which does not have a sulfur counterpart [11]. The structural differences usually manifest themselves in the type of polychalcogenide ligands present and the way they coordinate to metal centers. Some of the differences between sulfides and selenides, as ligands for niobium, may be attributed to differences in their relative redox properties and also size factor which in the Nb/S complexes affect stoichiometry, structure and coordination number. The chemistry of the soluble selenido complexes has been reviewed [12]. Various synthetic procedures have been employed for the gen-

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eration of selenido ligands in solution. They include the use of the organo-silicon selenide reagents [1], reduction of elemental selenium by CaH_2 or metallic sodium in DMF at 70°C [2] and the use of $SbSe_3$ [13].

In this paper we report on the synthesis, structure determinations and properties of the new soluble, 'mixed-chalcogenido' Nb/Se/E complexes (E = S, O), $(Et_4N)_2[Nb(Se)_3SBu^t]$, **1**, $(Ph_4P)_2[Nb(O)(Se_2)_2SeH]$, **2**, $(Et_4N)_4[Nb(O)(Se_2)_2Se_2]_2$, **3**, and $(Et_4N)_4[(Se)_3Nb\text{-}O\text{-}Nb(Se)_3]$, **4**.

The synthetic approach followed in this work exploits the oxidation of thiolate ligands by elemental selenium in the synthesis of the $[Nb(Se)_3SBu^t]^{2-}$ dianion **1**, from $[(S)Nb(SBu^t)_4]^-$ [14]. The synthesis and structure of **1** have been communicated previously [14]. Subsequent reactions of **1** with elemental selenium and hydrolysis lead to the new Nb/Se/O complexes reported herein.

EXPERIMENTAL

General procedures

$NbCl_5$ was purchased from Strem Chemical company and used without further purification. The salts Ph_4PBr and $Et_4NCl \cdot xH_2O$ were obtained from Strem and Aldrich chemical companies respectively and were purified as follows. Ph_4PBr was dissolved in water and extracted with diethylether to remove any traces of triphenylphosphine. The salt was extracted with, and recrystallized from 1,2-dichloroethane. To remove/reduce the amount of water in $Et_4NCl \cdot xH_2O$ the salt was dissolved in a small amount of CH_3CN over 3 Å sieves and allowed to sit for at least 72 h. After filtering, the filtrate was pumped to dryness. The solid was then washed with ether and finally dried *in vacuo* overnight. Elemental sulfur and selenium were purchased from Aldrich chemical company and used without further purification.

The NaS^tBu salt was prepared from the reaction of sodium ribbon and the neat thiol in diethylether. The salt was washed with diethyl ether and dried at 60°C under vacuum for at least 12 h.

All solvents were dried and distilled before use [15]. Acetonitrile (CH_3CN) was dried twice over 3 Å molecular sieves at a loading of about 10% *w*/*v* [15]. It was refluxed and subsequently distilled over activated B_2O_3 and was stored over 3 Å molecular sieves. Anhydrous N,N-dimethylformamide (DMF) was purchased from Aldrich, stored over 3 Å molecular sieves and used without further purification. When ordinary DMF was used it was dried by stirring over CaH_2 for over a week then distilled under reduced pressure at a temperature lower than 40°C and stored over 3 Å molecular sieves. In all cases DMF was degassed by the freeze/pump/thaw technique. This step helps in removing the decomposition product dimethyl amine which is a common impurity [16].

Diethylether was distilled from sodium/benzophenone ketyl radical mixture after 12 h stirring under reflux. The deuterated NMR solvents purchased from Cambridge isotopes, were dried over molecular sieves.

All solid reactants were stored and weighed out in a dry glove box under an argon atmosphere. The reactions were carried out under dinitrogen on a standard Shlenk line and solvents were introduced using cannula and rubber septa.

Physical methods

Middle energy region infrared spectra were obtained on a Nicolet 5-DXB FT-IR spectrometer at a resolution of 4 cm^{-1} in KBr discs. Far-IR spectra were obtained in CsI discs on a Nicolet 740 FT-IR spectrometer and proton NMR spectra were obtained on a Bruker 300-MHz pulse FT-NMR spectrometer. CHN analyses were performed at the analytical services laboratory of the University of Michigan chemistry department.

Preparation of compounds

Tetraethylammonium sulfido tetrakis tert-*butylthiolato niobate*(*V*), $(Et_4N)[Nb(S)(S^tBu)_4]$. To a mixture of $NbCl_5$ (1.0 g, 3.70 mmole), NaS^tBu (2.5 g, 22.3 mmole) and Et_4NCl (0.6 g, 3.62 mmole) in a reaction vessel attached to the shlenk line was added 50 cm^3 of MeCN. The resulting reddish mixture was stirred for 1 h and then filtered to give a red filtrate which was concentrated to about 20 cm^3 *in vacuo*. Some microcrystalline product was apparent at this point. Careful addition of ether to this solution (as to not disturb the interface) and cooling to −4°C afforded more crystals upon standing. The crystalline product was isolated by decanting the supernatant via cannula and washing the red–orange product with two portions of ether then drying *in vacuo*. The yield of the previously characterized [10a] $(Et_4N)[Nb(S)(S^tBu)_4]$ was 1.6 g, 72%. FT-IR: Nb═S 490 and Nb—S, 428, 408 cm^{-1}. ^1H NMR: singlets at 1.56 and 1.38 ppm in a ratio of 9:1 due to thiolate ligand protons from two different species (*vide infra*). The cation shows a quartet at 3.2 and triplet at 1.2 ppm. This complex was used in the syntheses that follow.

Bis(*tetraethylammonium*)*tris*(*selenido*)tert*butylthiolatoniobate*(*V*)$(Et_4N)_2[Nb(Se)_3(S^tBu)]$, (**1**). (*A*) *From* $NbCl_5$. To a mixture of $NbCl_5$ (1.0 g, 3.70 mmole), NaS^tBu (2.5 g, 22.3 mmole) elemental selenium (0.30 g, 4.81 mmole) and Et_4NCl (1 g, 6.0 mmole) in a reaction vessel attached to the Shlenk line was added 100 cm^3 of MeCN. The resulting dark reddish mixture was stirred for at least 6 h, preferably overnight, then filtered to give a dark red filtrate which was concentrated to about 40 cm^3 *in vacuo*. Diffusion of diethyl ether (at room temperature) into this solution resulted in the formation of dark red/black crystals which were isolated by sedimentation and washed twice with ether then dried under vacuum to give a yield of 0.75 g, 93% (based on Se). FT-IR: ν (Nb=Se) 478 cm^{-1}, 460 cm^{-1} and νNb—S 418 cm^{-1}. Assignment of the Nb—S stretch was based on the IR data available for V that contains only Nb—S bonds. ^{1}H NMR: $[Nb(S)_3S^tBu]^{2-}$ at 1.48 ppm due to the ^{t}Bu thiolate protons. The cation shows up as a quartet at 3.2 and triplet at 1.2 ppm. Analysis calculated for $NbSe_3SN_2C_{20}H_{49}$: C, 35.35; H, 7.27; N, 4.12. Found: C, 35.35; H, 7.58; N, 4.18. UV-vis (nm, in CH_3CN solution) 400; 298. The $[Nb(Se)_3(S^tBu)]^{2-}$ anion also can be obtained with the $(Ph_4P)^+$ cation by a similar synthetic procedure, as a dark red microcrystalline salt in 44% yield (based on Se). FT-IR: Nb=Se 470 (shoulder), 460, 447 and Nb—S 420 cm^{-1}.

(*B*) *From* $(Et_4N)[Nb(S)(S^tBu)_4]$. To a mixture of $(Et_4N)[Nb(S)(S^tBu)_4]$ (1.0 g, 1.6 mmole) and elemental selenium (0.13 g, 1.63 mmole) in a reaction vessel attached to the shlenk line was added 100 cm^3 of MeCN. The dark red mixture was stirred for at least 2 h and filtered through a fine porosity fritted funnel. The dark red filtrate was reduced in volume to about 40 cm^3, layered with diethyl ether and allowed to stand. Dark red crystals of **1** formed at room temperature in about 25% yield and were isolated and characterised as described previously.

Bis(*tetraethylammonium*)*hydroselenido bis*(*diselenido*) *oxo niobate*(*V*), $(Et_4N)_2[Nb(O)(Se_2)_2(SeH)]$, (**2**). *Method* (*A*). *From* $(Et_4N)_2[Nb(Se)_3(S^tBu)]$ (**1**). To a mixture of **1** (1.0 g, 1.472 mmole) and elemental selenium (0.17 g, 2.153 mmole) in a reaction vessel attached to the shlenk line was added *via* cannula 80 mL of DMF. After stirring for 30 min, about 0.03 mL of water were added to the red mixture by syringe and the stirring continued for at least 12 h. At this time a small amount of diethyl ether (10–20 cm^3) was added to the mixture to precipitate reaction byproducts, and the mixture was filtered. The reddish-brown filtrate was layered with ether and allowed to stand at room temperature. Dark red crystals and some powder formed over a period of 3 days, were isolated, and dried. The yield of (**2**) was 0.9 g, 51% (based on Nb). FT-IR: ν(Nb=O), 913 cm^{-1} (vs), ν(Se—Se)/(Nb—Se) 325, 318 cm^{-1} (vs) ν(Se—H) 2526 cm^{-1}. ^{1}H NMR: δ(Se—H) = 0.358 ppm and this was easily exchanged with D_3COD, cation peaks, $\delta = 3.15$ ppm (quartet) and 1.2 ppm (triplet). Anal. calcd for $NbSe_5ON_2C_{16}H_{40}$: C, 25.11; H, 5.4; N, 3.69 found: C, 27.67; H, 5.83; N, 3.93. These crystals were not good enough for crystallography, so the anion was isolated with tetraphenyl phosphonium as a countercation following the same procedure as before. The crystals obtained exhibited the following features: FT-IR: ν(Nb=O), 910 cm^{-1} (vs), ν(Se—Se)/(Nb—SeH), 322 cm^{-1}, 312 cm^{-1} (sh), ν(Se—H) 2516 cm^{-1} ν(C=O), DMF, 1662 cm^{-1} (w). Anal. calcd for $(Ph_4P)_2[Nb(O)(Se_2)_2(SeH)]\cdot 0.5$ DMF, $NbSe_5P_2O_3N_{0.5}C_{49.5}H_{44.5}$: C, 48.76; H, 3.69; N, 0.58 found: C, 49.62; H, 3.69; N, 0.4.

Tetrakis(*tetraethylammonium*) (μ-Se_4)-(*bis*(*diselenido*) *bis oxoniobate*)(*V*), $(Et_4N)_4[Nb(O)(Se_2)_2Se_2]_2$. (**3**). An amount of **2**, $(Et_4N)_2[Nb(O)(Se_2)_2SeH]$, (0.6 g, 0.784 mmol) and elemental selenium, (0.13 g, 1.646 mmol) were placed in a reaction vessel which was attached to the Shlenk line. 100 cm^3 of MeCN were added by cannula to give a dark reddish brown mixture. The mixture was stirred for at least 12 h (overnight) filtered and the filtrate layered with ether to give 0.6 g of the crude product as a dark reddish powder. Recrystallization form DMF gave a dark red microcrystalline product (0.45 g, 69% Nb basis), some of which was recrystallized from MeCN to give X-ray quality crystals. FT-IR: ν(Nb=O), 903 cm^{-1}; ν(Se—Se)/(Nb—Se), 324 (vs), 299 (ms), 275 (w) cm^{-1}. Anal. calcd for $(Et_4N)_4[Nb(O)(Se_2)_2Se_2]_2$, $Nb_2Se_8O_2N_4C_{32}H_{80}$: C, 22.79; H, 4.78; N, 3.32, Found: C, 22.81 H, 4.54; N, 3.32.

Tetrakis(*tetraethylammonium*) (μ-*oxo*)-*tris*(*selenido*) *diniobate*(*V*), $(Et_4N)_4[(Se)_3Nb\text{-}O\text{-}Nb(Se)_3]$, (**4**). An amount of **1** (1.0 g, 1.472 mmole) was placed in a Shlenk reaction vessel and 70 mL of MeCN was added to give a red solution. A small amount of water (about 0.02 cm^3) was introduced by syringe into a Shlenk tube that contained 20 cm^3 of MeCN and this solution gradually added (over 30 min) *via* cannula to the solution of **1**. Stirring was continued through the addition of the water solution and was carried on for a further 4–5 h. The reaction mixture became cloudy and lighter in color as time went on and was finally filtered. To the filtrate a layer of ether was added. Upon standing, a flocculant powder appeared within a few hours which became oily and finally started to crystallize. A mixture of red and orange–red crystals were obtained initially (both forms of the compound gave virtually identical elemental analysis) (0.9 g, 51.1% yield). Recrystallization from MeCN gave X-ray quality FT-IR: ν(Nb=Se), 450, and ν(Nb—O—Nb) 716 cm^{-1}. Anal. calcd for $Nb_2Se_6ON_4C_{32}H_{80}$: C, 32.12; H, 6.74; N, 4.68. Found C, 30.50; H, 6.15; N, 4.18.

X-ray diffraction measurements

Crystal data, reflection collection information and structure refinement parameters for the compounds **1**–**4** are compiled in Table 1. Diffraction data were collected at ambient temperature on a Nicolet P3/F four-circle computer driven diffractometer using graphite monochromatized ($2\theta_{max} = 12.50°$) Mo-Kα radiation ($\lambda = 0.71073$ Å). Intensity data were collected by using a θ–2θ step scan technique and for all data sets the condition of the crystal was monitored by measuring 3 standard reflections [every 97 (2, 4) or 197 (1, 3) reflections]. Accurate parameters for all crystals were obtained from the least-squares refinement on the 2θ, φ, χ, and $\bar{\omega}$ values of 20 machine centered reflections. The raw data were reduced to net intensities and appropriate corrections applied

Table 1. Summary of crystal data, intensity collection and structure refinement parameters for **1**, **2**, **3**, **4**

Formula	$NbSe_3SN_2C_{20}H_{49}$	$C_{48}H_{41}OP_2Se_5Nb$	$C_{32}H_{80}O_2N_4Se_{12}Nb_2$	$C_{32}H_{80}ON_4Se_6Nb_2$
Mol. Wt	679.56	1183.44	1686.36	1196.60
a (Å)	17.476(4)	16.235(3)	9.359(3)	10.865(7)
b (Å)	10.155(2)	16.204(3)	10.482(4)	11.576(7)
c (Å)	18.399(4)	18.323(4)	29.486(6)	11.803(5)
α (°)	90	90	92.79(2)	111.8(4)
β (°)	115.05(2)	100.95(3)	96.49(2)	102.4(5)
γ (°)	90	90	103.89(3)	110.9(5)
V (Å^3)	2958.5(11)	4733(2)	2781.5	1180(3)
Z	4	4	2	1
Space group	$P2_1/c$ (No. 14)	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
Radiation	Mo-Kα (λ = 0.71073 Å)	Mo-Kα	Mo-Kα	Mo-Kα
Data collected (octants)	4–45 ($+h$, $+k$, $\pm l$)	3–35 ($+h$, $+k$, $\pm l$)	4–45 ($\pm h$, $\pm k$, $\pm l$)	4–45 ($\pm h$, $\pm k$, $\pm l$)
Unique data	3883	6119	7200	2967
Refined reflections	2298	6117	3401	2581
No. of variables	280	518	318	205
Data/parameter ratio	8.2	11.8	10.7	12.2
R^a (%)	4.63	9.41	8.8	6.25
Rw (%)	4.63	22.41^b	8.86	6.80

$^a R_1 = \Sigma(|F_o - F_c|)/\Sigma|F_o|$.

$^b wR_2 = [\Sigma(w|F_o - F_c|)^2/\Sigma w(F_o)^2]^{1/2}$.

according to previously described protocols [17]. The computer programs were those of the SHELXTL structure determination packages 88 and 94 (Nicolet XRD Corp., Fremont, CA).

(A). $(Et_4N)_2[Nb(Se)_3(S^tBu)]$ (**1**). Crystals suitable for X-ray measurements were grown by the slow diffusion of diethylether into a solution of **1** in CH_3CN. A suitable dark red crystal was lodged in a glass capillary and was held in place by Apiezone grease. A total of 3883 unique reflections were collected in 1/4 of the reciprocal lattice sphere to $2\theta_{max} = 45°$.

(B). $(Ph_4P)_2[Nb(O)(Se_2)_2SeH]$ (**2**). Crystals marginally suitable for X-ray measurements were grown by the slow diffusion of diethylether into a solution of **2** in DMF. A red crystal was mounted in a glass capillary as outlined in (A) and a total of 6119 unique reflections collected on 1/4 of the reciprocal lattice sphere to $2\theta_{max} = 35°$.

(C). $(Et_4N)_4[(Nb(O)(Se_2)_2)_2Se_4]$ (**3**). Red crystals of **3** were grown by the slow diffusion of diethylether into a solution of **3** in MeCN. A crystal was mounted in a glass capillary as outlined in (a) and a total of 7200 unique reflections were collected in the whole sphere of the reciprocal lattice to $2\theta_{max} = 45°$.

(D). $(Et_4N)_4[(Se)_3Nb—O—Nb(Se)_3]$ (**4**). Crystals suitable for X-ray measurements were grown by the slow diffusion of diethylether into a solution of **4** in MeCN. A crystal was mounted in a glass capillary as outlined in (A) and a total of 2967 unique reflections collected on the whole sphere of the reciprocal lattice to $2\theta_{max} = 45°$.

Solution and refinement of structures

The solutions of the structures **1**, **3** and **4** were carried out by a combination of heavy atom Patterson techniques and direct methods routine SOLV of the SHELXTL 88 package of crystallographic programs. The solution of **2** used the SHELXTL 94 package of crystallographic programs. The structures were refined by the block-cascade least-squares method. All Nb, Se, S, P, O, N and C of the anions were refined anisotropically and the hydrogen atoms of the organic counterions were included in the refinement at their calculated positions (d C—H = 0.95 Å).

Crystallographic results

Selected interatomic distances and angles are given in Table 2. The labeling schemes for the various anions (**1**–**4**) are shown in Fig. 1. Positional and thermal parameters for all atoms including the H atoms for **2**–**4** have been deposited as supplementary material (6 tables). The crystallographic data for **1** have been deposited as indicated in Ref. [14].

RESULTS AND DISCUSSION

Description of the structures

$(Et_4N)_2[Nb(Se)_3(S^tBu)]$, (**1**). We have previously reported the structure of **1** and its sulfido analog [14]. The anion (Fig. 1) has the metal center tetrahedrally

Table 2. Selected interatomic distances (Å) and angles (°) in the $[Nb(Se)_3S^tBu]^{2-}$ (**1**); $[Nb(O)(Se_2)_2SeH]^{2-}$ (**2**); $[Nb(O)(Se_2)_2]_2Se_4]^{4-}$ (**3**) and $[(Se_3Nb)_2O]^{4-}$ (**4**) anions

	(**1**)	(**2**)	(**3**)	(**4**)
Nb—S(1)	2.422(3)			
Nb(x)[a]—Se(1),(11)	2.360(2)	2.584(3)	2.611(4), 2.629(4)	2.364(2)
Nb(x)—Se(2),(12)	2.326(2)	2.632(3)	2.557(4), 2.561(4)	2.375(2)
Nb(x)—Se(3),(10)	2.313(3)	2.572(4)	2.551(4), 2.611(4)	2.331(2)
Nb(x)—Se(4),(9)		2.623(3)	2.630(5), 2.380(4)	
Nb(x)—Se(5),(8)		2.608(4)	2.645(3), 2.630(3)	
Nb(x)—Se(6)		2.625(13)		
Nb(1, 2)-O(1, 2)		1.671(11)	1.682(21), 1.689(19)	1.914(1)
Se(1)—Se(2)		2.342(4)	2.325(4)	
Se(3)—Se(4)		2.308(5)	2.320(6)	
Se(5)—Se(6)		2.52(2)	2.357(4)	
Se(6)—Se(7)			2.366(6)	
Se(7)—Se(8)			2.356(4)	
Se(9)—Se(10)			2.321(4)	
Se(11)—Se(12)			2.328(4)	
S(1)—C(1)—C(2)	109.5(10)			
Nb—S(1)—C(1)	115.8(4)			
Se(1)—Nb(1)—Se(2)	109.6(1)	53.35(9)	53.5(1)	109.7(1)
Se(1)—Nb(1)—Se(3)	112.6(1)		84.7(1)	107.4(1)
Se(2)—Nb(1)—Se(3)	111.9(1)	150.9(2)	128.4(2)	109.4(1)
Se(3)—Nb(1)—Se(4)		52.74(12)	53.2(1)	
Se(3)—Nb(1)—Se(5)		81.9(2)		
Se(1)—Nb(1)—S(1)	113.2(1)			
Se(2)—Nb(1)—S(1)	112.3(1)			
Se(3)—Nb(1)—S(1)	96.9(1)			
Se(1)—Nb(1)—O(1)		107.3(4)	100.9(6)	110.3(1)
Se(2)—Nb(1)—O(1)		103.3(3)	108.1(5)	110.4(?)
Nb(1)—O(1)—Nb(1A)				180.0(1)

[a] For the anions, **1, 2** and **3**, x in Nb(x) is 1 and the Se atoms are numbered from 1 to 5 inclusive. For anion **3**, x can be either 1 or 2. When $x = 1$, the Se atoms are numbered as in the previous case and the corresponding interatomic distances are found in the first sub column of column 3 and when $x = 2$, the Se atoms are numbered from 8 to 12 and the corresponding distances are found in the second sub column.

coordinated by **3** selenido and 1 *tert*-butythiolato ligands. The mean Nb=Se bond length in **1** at 2.333(3) is shorter than the Nb=Se bonds in K_3NbSe_4 [8], which fall in the range 2.387(1)–2.403(1) Å and in $K_2CuNbSe_4$ [7] (2.413(1) Å). In these solid state synthesis materials, the selenium ligands are either found bridging 2 Nb^{5+} metal centres or interacting with the metal counter cations in the lattice. The chalcogenide–cation interactions that appear to be ubiquitous with the structurally characterized $[NbE_4]^{3-}$ anions (E = S, Se), may be necessary to dissipate the excessive negative charge in these highly charged anions [18]. In **1**, the excess charge anticipated in the $[NbSe_4]^{3-}$ anion is partially neutralized by the S-bound $^tBu^+$ cation. This may explain the exceptional stability of **1** relative to the triselenothio- or the tetraselenometallate trianions.

$(PPh_4)_2[Nb(O)(Se_2)_2(SeH)]$, (**2**). The anion (Fig. 1) possess the same distorted pentagonal pyramidal geometry exhibited by its sulfur analogue which we have already reported [14]. The metal is located 0.70 Å in the direction of the terminal oxo ligand above the plane formed by the five equatorial selenium based ligands (two chelating diselenides and a hydroselenido ligand). A disorder was found in the base of the pentagonal bipyramid where a minor component (20%) of the anion was located, rotated relative to the major component (80%) and situated at the same site (Fig. 2). The Nb=O at 1.671(11) Å is shorter than that in the sulfido analogue at 1.729(9) Å [20] or that reported in the molecule $Nb(O)(S_2CNEt_2)_3$ [19] at 1.74(1) Å. The Se—Se distances in **2** at 2.342(4) and 2.308(5) Å are unexceptional [12] and will not be discussed any further.

The Nb^V—Se distances with the η^2-Se_2^{2-} ligands range from 2.572(4) to 2.632(3) Å. The possibility that the proton in **2** is located on an η^2-Se_2^{2-} can be ruled out by (a) the symmetric mode of chelation of the Se_2^{2-} ligands to the metal center and (b) the comparatively longer Nb—Se(5)H bond length (compared to Nb=Se bonds in **1**) that suggests a selenolate rather than a selenido bond (Fig. 1, Table 2). The Nb=O bond length at 1.671(11) Å is slightly shorter than that reported for other similar molecules [20].

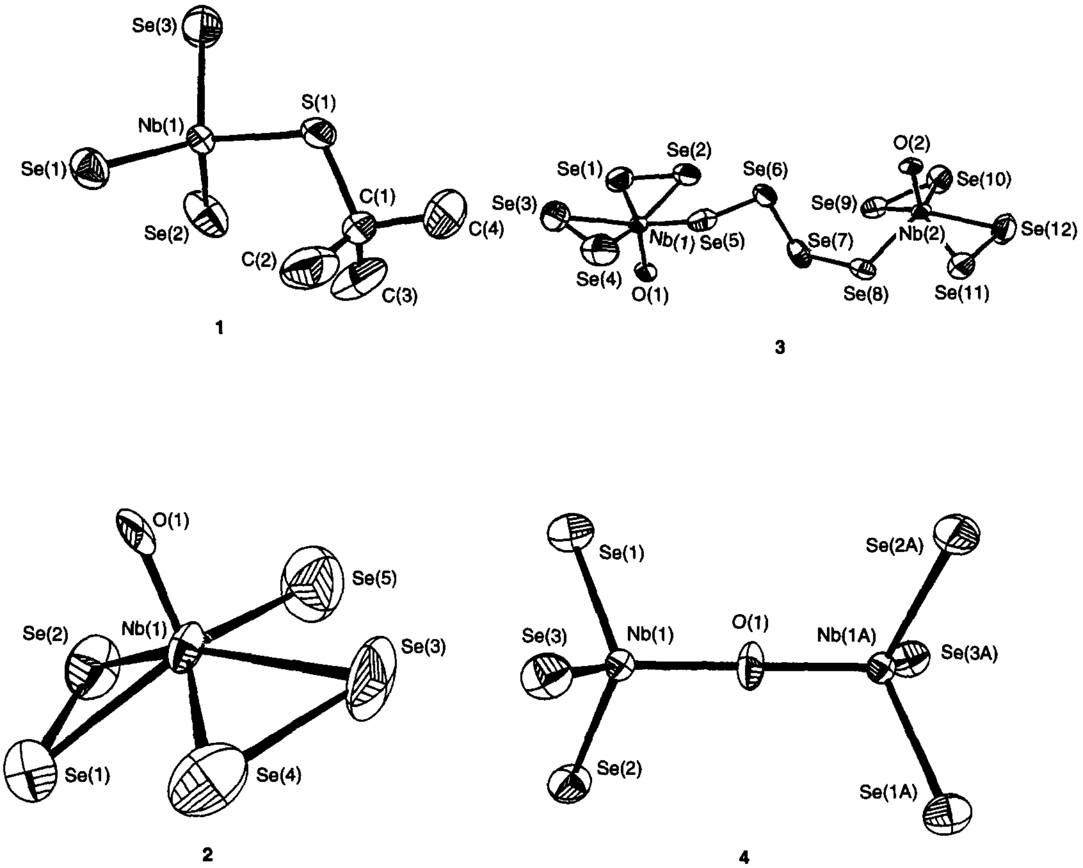

Fig. 1. Structure and labelling of the anions in (Et$_4$N)$_2$[Nb(Se)$_3$SBu^t], **1**, (Ph$_4$P$_2$)$_2$[Nb(O)(Se$_2$)$_2$SeH], **2**, (Et$_4$N)$_4$[Nb(O)(Se$_2$)$_2$Se$_2$]$_2$, **3**, and (Et$_4$N)$_4$[(Se)$_3$Nb—O—Nb(Se)$_3$], **4**. Thermal ellipsoids as drawn by ORTEP represent the 40% probability surfaces.

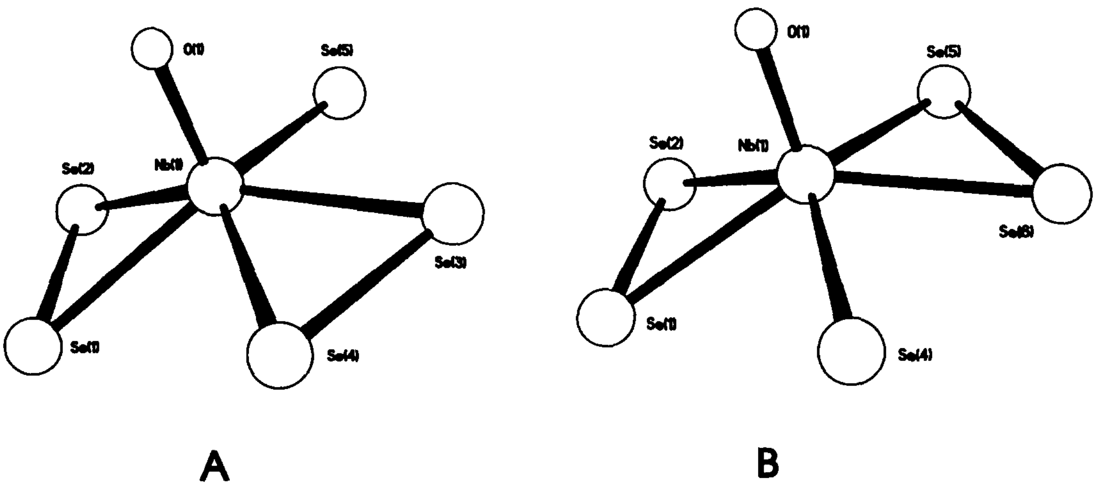

Fig. 2. The two anions that occupy the same site in the crystal lattice of **2**. *A* the major component (80%), *B* the minor component (20%).

The $[Nb(O)(Se_2)_2]^-$ unit in **2** is structurally similar to the $[V(O)(S_2)_2]^-$ unit in the pentagonal bipyramidal $[V(O)(S_2)_2(bipy)]^-$ anion [21] and also similar to the $[Mo(O)(S_2)_2(S)]^-$, $[Ta(S)(S_2)_2(S)]^{2-}$, $[Nb(Se)(Se_2)_2(Se)]^{2-}$ and $[W(S)(S_2)_2(S)]$ subunits in the known $\{[Mo(O)(S_2)_2]_2(S)\}^{-2}$ [22], $\{[Ta(S)(S_2)_2]_2S\}^{4-}$ [9], $[Nb_4Se_{22}]^{6-}$ [9] and $\{[W(S_2)_2(S)]_2S\}^{2-}$ [23] anions and also oxo-peroxo molybdate units in complexes such as: $[Mo_2O_3(O_2)_4(H_2O)_2]^{2-}$ [24a], $[Mo_3O_7(O_2)_4]^{4-} \cdot 2H_2O$ [24b], $[Mo_4O_{12}(O_2)_2]^{4-}$ [24c], $[Mo_5O_{10}(O_2)_8]^{6-} \cdot 5H_2O$ [24d], $[Mo_7O_{22}(O_2)_2]^- \cdot 8H_2O$ [24e], and $[Mo_{10}O_{22}(O_2)_{12}]^{8-} \cdot 16H_2O$ [24f].

The Nb—SeH bond at 2.608(4) Å is much longer than the Nb=Se bonds (Table 2) but similar to the Nb—Se_4 bonds in **3** as expected for the selenolate type of coordination for both of these ligands. The apparent stability of the SeH ligand in **2** again may have its origin in the need of a hypothetical $[Nb(O)(Se_2)_2(Se)]^{3-}$ anion to dissipate negative charge by accepting a positively charged species (a proton!) on one of its ligand. Among examples of thiometallate anions that contain the SH^- anion as a terminal ligand are included the $(S_3WSH)^-$ [25] and $[W_2S_{11}H]^-$ [26] anions.

$(Et_4N)_4[(Nb(O)(Se_2)_2)Se_4]$ (**3**). The anion in the molecule (Fig. 1) could be described as an oxidation product of **2** by the Se_4^0 fragment in a reaction that the SeH^- ligands in two molecules of **2** are oxidatively replaced by a bridging Se_4^{2-} anion. The oxo ligands in **3** are found in the *anti* conformation. Each of the two Nb^V atoms show a similar distorted pentagonal pyramidal geometry, as found in **2**, and no indications of intramolecular axial interactions toward a pentagonal bipyramidal geometry. The Se—Se distances in the η^2-Se_2^{2-} ligands lie in a close range of 2.320(6)–2.328(4) Å, and are unexceptional [12]. The mean value of the 'end' Se(5)—Se(6) and Se(7)—Se(8) bonds in the μ_2-Se_4^{2-} ligand (Fig. 1) is 2.357(4) Å, while the 'middle' Se(6)—Se(7) bond is longer, but not significantly different at 2.366(6) Å. A similar trend is seen in the *trans* salt $[Ba\text{-}2,2,2\text{-crypt}][Se_4] \cdot en$ [27], where the internal Se—Se separation at 2.344(5) Å is longer than the terminal one at 2.325(5) Å. This effect is more pronounced in $[PPN]_2[Se_4] \cdot 4MeCN$ [28] where the internal distance is 2.397(4) Å and the terminal is 2.312(2) Å. The Se—Se bond distances in α-selenium [29] lie in the range 2.31–2.37 Å and in β-selenium [30] the range is 2.21–3.04 Å. The Nb=O distances are comparable to that in **2** and will not be discussed any further. Another example of a bridging E_x^{2-} chalcogenido ligand between structurally similar $O{=}M(E_2)_2$ subunits exists in the $[O{=}Mo(S_2)_2](\mu\text{-}S_7)(\mu\text{-}NH_2NH_2)[O{=}Mo(S_2)_2]$ complex [31]. In the latter the $[O{=}Mo^{VI}(S_2)_2]^0$ units are bridged by a μ_2-S_7^{2-} ligand and by a μ_2-hydrazine molecule and the Mo^{VI} atoms have a pentagonal bipyramidal geometry.

$(Et_4N)_4[(Se)_3Nb{-}O{-}Nb(Se)_3]$ (**4**). The anion in this molecule (Fig. 1) is isostructural to the previously reported [14] $[(S)_3Nb{-}O{-}Nb(S)_3]^{4-}$ anion with the oxo ligand located at a crystallographic centre of symmetry and possessing a rigorously linear Nb—O—Nb bridge. In the refinement process an apparent disorder in the Se(3) site was successfully modelled by 50:50, Se:S partial occupancy.

The terminal selenido ligands are in a staggered conformation giving the anion an idealized D_3d symmetry. The mean Nb=Se bond length at 2.357(2) falls in the expected range and is longer than that in **1**. The formation of **4**, with an oxo bridge between two $Nb(Se)_3^-$ units, rather than $[NbO(Se)_3]^{3-}$ with a terminal Nb=O group may again be a consequence of the need to avoid the accumulation of excessive negative charge [18] around the $[Nb(Se)_3L]^{3-}$ units.

Spectroscopic properties

The infrared spectra of the complexes are useful not only for identification, diagnostic reasons but also for a qualitative analysis of Nb—Se bonding. A comparison of the vibrational frequencies associated with the Nb=Se chromophores in **1**, with the Nb=S vibrations observed in the analogous sulfido complex [14] shows both sets of vibrations occuring at essentially the same frequencies. The expected lowering in frequency for the Nb=Se bonds is not observed and the data suggest a larger force constant for the Nb=Se bond and a higher affinity of the Nb atom for selenido than for sulfido ligands. A comparison between Nb=S and Nb=O frequencies however, shows changes that qualitatively are predictable on the basis of the mass frequency relationship which may indicate similar force constants for the Nb=S and Nb=O bonds. The far infrared spectra of the complexes are only useful for 'fingerprinting' purposes. The frequent overlap between Nb—Se and Se—Se vibrational frequencies makes definite assignments difficult in the absence of isotopic substitutions.

Synthetic aspects and bonding

All of the complexes, **1–4**, can be described as derivatives of either the $[Nb(Se)_3]^-$ or the 'Se-rich' $[(Se)Nb(Se_2)_2]^-$ units. A scheme that outlines possible pathways toward the syntheses of the complexes (Fig. 3) is based on well known sulfur addition or hydrolysis reactions [14,20] and many of the intermediates have been chemically or structurally characterized in Nb/S chemistry. Thus the synthesis and structural characterization of the $[(S)_3Nb(SH)]^{2-}$ [14] and $[(S)_3Nb(OCH_3)]^{2-}$ [20] dianions, analogous to the proposed $[(Se)_3Nb(SeH)]^{2-}$ and $[(Se)_3Nb(OH)]^{2-}$ complexes (Fig. 3 B, C) have been reported. Similarly, partial chemical characterization of the reaction products between $(R_3Si)_2S$ and either $[(O)Nb(S_2)_2SH]^{2-}$ or $[(S)_3Nb{-}O{-}Nb(S)_3]^{4-}$ suggests the existence of the $[(S)Nb(S_2)_2SH]^{2-}$ and $[(S)_3Nb{-}S{-}Nb(S)_3]^{4-}$ anions (the latter eventually gives the known [32] $[Nb_6S_{17}]^{4-}$ anion) which would be analogous to the proposed selenium intermediates (Fig. 3 A, D). The

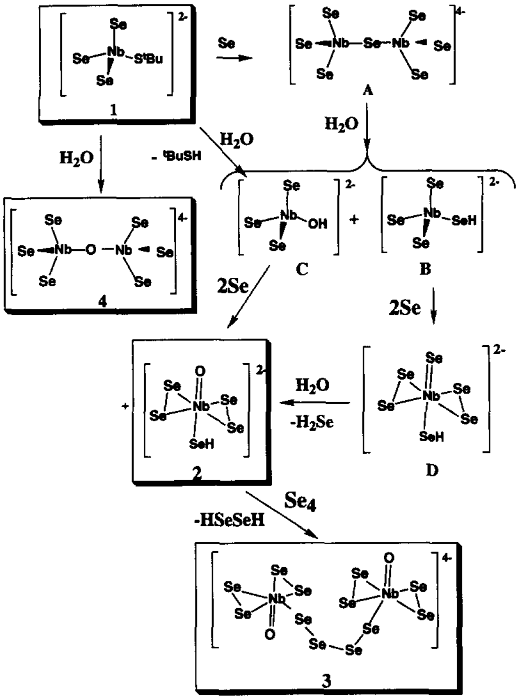

Fig. 3. A proposed pathway for the synthesis of $(Et_4N)_2[Nb(Se)_3SBu^t]$, **1**, $(Ph_4P)_2[Nb(O)(Se_2)_2SeH]$, **2**, $(Et_4N)_4[Nb(O)Se_2)_2Se_2]_2$, **3**, and $(Et_4N)_4[(Se)_3Nb—O—Nb(Se)_3]$, **4**. The anions within the rectangle enclosures have been structurally characterized, those labelled **A–D** are analogous to characterized counterparts with sulfido ligands.

$[(Se)_3Nb(S^tBu)]^{2-}$ is readily obtained from either $NbCl_5{}^{2-}$ or the $[Nb(S)(S^tBu)_4]^-$ complex [20]. In these reactions the Se^{2-} anions are generated as elemental selenium is reduced by the $^tBuS^-$ ligands. The reaction of $(Et_4N)[Nb(S)(S^tBu)_4]$ with only one equivalent of Se was expected to give the product, $(Et_4N)_2[Nb(S)(Se)(S^tBu)_2]$ (eq. 1):

$$(Et_4N)[Nb(S)(S^tBu)_4] + Se \rightarrow \text{‘}(Et_4N)_2[Nb(S)(Se)(S^tBu)_2]\text{’} + {}^tBuSS^tBu \quad (1)$$

The isolation of $[(Se)_3Nb(S^tBu)]^{2-}$, **1**, however, suggests that its exceptional thermodynamic stability drives its formation, following ligand redistribution reactions among various $[(Se,S)_xNb(^tBuS)_{4-x}]$ thioanions ($x = 1, 2$).

The behavior is similar to that observed in our attempts [33] to oxidise $(Ph_4P)[Nb(O)(S^tBu)_4]$ with elemental sulfur to generate the Nb–oxo–thio chromophore in a complex such as $(Ph_4P)_2[Nb(S)(O)(S^tBu)_2]$. In this reaction $(Ph_4P)_2[Nb(S)_3(S^tBu)]$, $(Ph_4P)[Nb(S)_2(S^tBu)_2]$ and unidentified Nb=O containing compounds were isolated [20].

In the synthesis of **1**, **2** or **3** any attempts to use more equivalents of selenium, as would be stoichiometrically required, led to the isolation of either completely different products, usually difficult to purify oils, or difficult to separate mixtures of **1**, **2**, **3** or **4**. In the oxidation of **1** to **2** in the presence of water, the use of more than 1.5 equiv. of selenium led to the isolation of some **3**. The oxidation of **2** to **3** with the generation of diselenide [Fig. 3, eq. (2)] is believed to be similar to the oxidation of the corresponding sulfido complex that generates disulfide.

$$2(Et_4N)_2[Nb(O)(Se_2)_2(SeH)] + 1/2Se_8 \rightarrow (Et_4N)_4[(Nb(O)(Se_2)_2)_2Se_4] + HSe\text{–}SeH \quad (2)$$

The reaction of **1** with water to give **4**, very likely involves an initial attack of the water molecule on the metal in an S_N2 fashion. Once the water molecule coordinates it becomes acidic enough to protonate the $^tBuS^-$ ligand to give the thiol and the transient anion ‘$[Nb(Se)_3(OH)^{2-}$’ (Fig. 3C). The latter reacts either with **1** with the release of more ^tBuSH (Fig. 3), or with ‘$[Nb(Se)_3(SeH)]^{2-}$’ (Fig. 3B) with the release of H_2Se to generate the dimer **4**.

A comparison between the $[(S_2)_2M(O)]^0$ *structural unit,* (M = Mo, W) *and* $[(Se_2)_2Nb(O)]^{-1}$

The $(\eta^2\text{-}Se_2)_2Nb(O)$ unit in **2** structurally resembles the $(\eta^2\text{-}S_2)_2M(O)$ unit [22,23] (M = Mo, W). The $[O{=}Mo^{VI}(S_2)_2]$ unit electronically is related by internal electron transfer to the $[O{=}Mo^{IV}(S_4)]$ unit and under certain circumstances, the two may exist in equilibrium. This type of equilibrium is a consequence of the close energy matching between the Mo 4*d* orbitals and the sulfur 3*p* orbitals and accounts for the apparent similar energies between the pentagonal bipyramidal $[E{=}Mo^{VI}(S_2)_2(L\text{–}L)]^n$ complexes and the square pyramidal $[E{=}Mo^{IV}(S_4)(L\text{–}L)]^n$ complexes (L = a bidentate chelating ligand, E = S, Se, Fig. 4). The pentagonal bipyramidal, $[E{=}Mo^{VI}(S_2)_2(L)]^n$ complexes, are quite common and a number of monomeric, pentagonal bipyramidal complexes of the type $[O{=}Mo(S_2)_2(L)]$ have been reported. The complex with L = 2,2-bipyridyl [34] is obtained from MoO_4^{2-} and aqueous S_x^{2-} in the presence of 2,2-bipyridyl. The corresponding W complex also is known and has been structurally characterized [35]. A similar complex with L = monothiooxalate $(C_2O_3S)^{2-}$, has been isolated [36] serendipitously by the reaction of $Cs_2[Mo_2O_4(C_2O_4)_2(H_2O)_2]\cdot 2H_2O$ with $Cs_2(S_2C_2O_2)$. The square pyramidal complexes with the $O{=}Mo^{IV}(S_4)$ unit are not as common and with the exception of $[E{=}Mo(S_4)_2]^{2-}$ [37] and $[(Cp)Mo(S_4)_2]^-$ [38] the only other square pyramidal complex of this

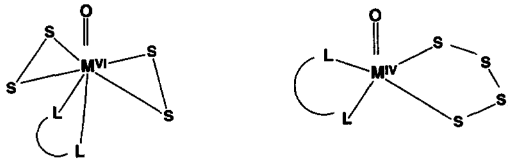

Fig. 4. The ($[O{=}Mo^{VI}(S_2)_2(\eta^2\text{-}L]$ and ($[O{=}Mo^{IV}(S_4)(\eta^2\text{-}L]$ internal-redox isomers.

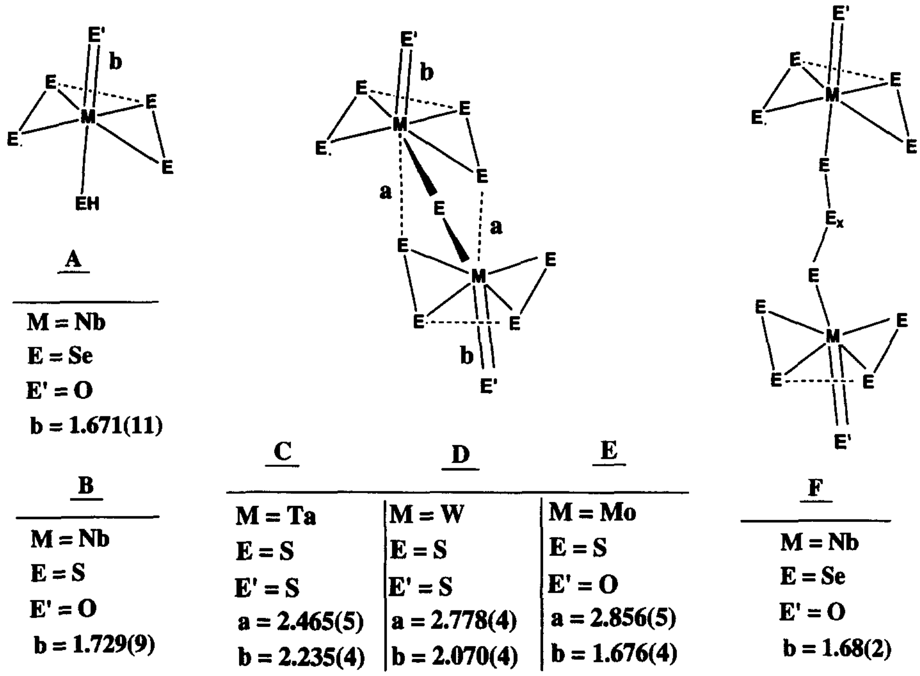

Fig. 5. Correlation of the axial M=E bond length (b) with *trans* intramolecular interactions (a) evident in the structurally characterized anions **A** (this work), **B** [14], **C** [9], **D** [23], **E** [22], and **F** (this work).

structural type is the structurally characterized $[O{=}Mo^{IV}(S_4)(MNT)]^{2-}$ obtained by a substitution reaction between the $\{[O{=}Mo^{VI}(S_2)_2]_2Cl\}^-$ complex [22] and Na_2MNT [39]. In this latter reaction substitution of the Cl^- ligand by the MNT^{2-} ligand is accompanied by internal electron transfer and the concomitant oxidative coupling of the two S_2^{2-} ligands.

To our knowledge, examples of internal electron transfer that converts the $[(\eta^2\text{-}Se_2)_2Nb^V(O)]^-$ unit to the $[O{=}Nb^{III}(Se_4)]^-$ are not known. This difference between the Mo/S and the Nb/Se systems could be attributed to unfavorable energy matching between the appropriate Nb *d* and Se *p* orbitals. In such a case π bonding interactions, between the Nb d_{xz} and d_{yz} orbitals and the out of plane *p* orbitals of the equatorially located Se donors will be as pronounced.

In the $[(\eta^2\text{-}Se_2)_2Nb^V(O)]^-$ unit, the minimal involvement of the Nb d_{xz} and d_{yz} orbitals in π bonding in the equatorial $Nb(Se_2)_2$ plane, allows for their greater interaction with the axial oxo-ligand *p* orbitals to give a stronger Nb≡O triple bond. This bond in **2** and **3** is rather short (1.671(11) 1.68(2) and (1.69(2) Å, respectively). By comparison, the Nb=O bond in the $[(\eta^2\text{-}S_2)_2Nb^V(O)]^-$ unit [14], is 1.729(9) Å. The Nb=O stretching frequencies in **2** and **3** at 913 and 903 cm^{-1} are similar to the one in the $[(\eta^2\text{-}S_2)_2Nb^V(O)]^-$ at 908 cm^{-1}. It is quite likely that kinematic effects associated with the heavier $[(\eta^2\text{-}Se_2)_2Nb^V]$ unit lower the frequency of the Nb=O stretch in **2** and **3**.

The strength of the axial M=E bonding may determine the extent to which pentagonal pyramidal $[(L)(\eta^2\text{-}E_2)_2M(E')]$ units undergo axial bonding interactions *trans* to the M=E group. The longer (and presumably weaker) M=E bonds facilitate stronger *trans* interactions that impart stability to the pentagonal bipyramidal $[(L')(L)(\eta^2\text{-}E_2)_2M(E')]$ structure. Examples of structural characteristics emerging from these bonding effects can be found in the structures of **2**, **3** the $[Mo_2S_9(O)_2]^{2-}$, $[Mo_4S_{18}O_4]^{2-}$ and $[Mo_2S_8Cl(O)_2]^-$ anions [22], the $[W_2S_{11}]^{2-}$ and the $[W_2S_{11}H]^-$ anions [23], the $[TaS_{11}]^{4-}$ anion [9] and the $[Nb_4Se_{22}]^{6-}$ anion [9] (Fig. 5). The effects of axial bonding in these complexes also are manifested in their reactivity characteristics. Weak axial interactions account for the ready dissociation of the $[Mo_2S_8Cl(O)_2]^-$ anion to the $[O{=}Mo^{VI}(S_2)_2]$ and $[O{=}Mo^{VI}(S_2)_2(Cl)]^-$ fragments [22,40] that make this complex ideally suited as a reagent for the synthesis of seven-coordinate pentagonal bipyramidal [16] $([O{=}Mo^{VI}(S_2)_2(\eta^2\text{-}L]$ complexes or square pyramidal [39] $([O{=}Mo^{IV}(S_4)(\eta^2\text{-}L]$ complexes in reactions with bidentate chelating ligands (L).

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