Synthesis and Crystal Structure of Tris(diethyldithiocarbamato-*S,S′*)(disulfido-*S,S′*)niobium(V)†

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The reaction of $[Nb^{V}O(S_2CNEt_2)_3]$ with boron sulfide was investigated under a variety of conditions. The major product in all cases was yellow $[Nb^{V}S(S_2CNEt_2)_3]$ **1**. In dichloromethane at room temperature, orange $[Nb^{V}(S_2)(S_2CNEt_2)_3]$ **2** and orange-brown $[Nb^{IV}_2(\mu\text{-}S_2)_2(S_2CNEt_2)_4]$ **3** were also formed. At higher temperatures the same products were formed but a higher proportion of **1** was observed. Crystals of **2**$\cdot 0.5CH_2Cl_2$ were monoclinic, space group $C2/c$ with $a = 16.360(2)$, $b = 10.959(1)$, $c = 30.637(3)$ Å, $\beta = 92.34(1)°$ and $Z = 8$. The structure was refined to final $R = 0.034$ for 2310 reflections with $I \geqslant 2.5\sigma(I)$. The eight-co-ordinate complex exhibits an *mmmm* dodecahedral structure analogous to that of its tantalum counterpart.

The contemporary focus of niobium–sulfur chemistry is on molecular thioniobates,[1,2] co-ordinatively unsaturated thio and polysulfido complexes,[2–4] and synthetic and mechanistic aspects of C–S bond cleavage or formation.[3–6] Earlier work in this field concentrated on structural aspects of the high-co-ordination-number complexes formed with small-bite-angle dialkyldithiocarbamate ligands. A number of seven- and eight-co-ordinate complexes, including $[Nb(S_2CNEt_2)_4]$,[7] $[Nb(S_2CNEt_2)_nX_{5-n}]$ (n = 2–4)[8,9] and $[NbS(S_2CNEt_2)_3]$ **1**,[8–11] have been reported. The best synthesis of **1** involves the sulfidation of $[NbO(S_2CNEt_2)_3]$ by $(Me_3Si)_2S$.[11] Analogous dithiocarbamate complexes are known for tantalum.[7–10,12] The eight-co-ordinate, dodecahedral complex $[Ta(S_2)(S_2CNEt_2)_3]$ has also been isolated and structurally characterised.[10,13] Interestingly, its niobium counterpart, $[Nb(S_2)(S_2CNEt_2)_3]$ **2**, has not yet been reported.

Unlike the reported sulfidation of $[NbO(S_2CNEt_2)_3]$ by $(Me_3Si)_2S$, the reactions of $[VO(S_2CNEt_2)_3]$ and $[MoO(S_2CNEt_2)_3]^+$ with boron sulfide result in reduction and the formation of $[V_2(\mu\text{-}S_2)_2(S_2CNEt_2)_4]$[14] and $[Mo_2(\mu\text{-}S_2)_2(S_2CNEt_2)_4]^{2+}$,[15] respectively. We were interested to learn whether the reaction of $[NbO(S_2CNEt_2)_3]$ and boron sulfide would produce **1** or provide access to $[Nb_2(\mu\text{-}S_2)_2(S_2CNEt_2)_4]$ **3**.[16] In fact, both complexes form along with small amounts of **2**. This paper describes the synthesis, physical and spectroscopic properties, and crystal structure of **2**, the hitherto 'missing member' in the otherwise parallel series of dithiocarbamate compounds of niobium and tantalum.

Experimental

Materials and Methods.—Unless otherwise stated, all reactions were performed under an atmosphere of dinitrogen using dried deoxygenated solvents and standard Schlenk-line techniques. The method of Do *et al.*[17] was employed in the synthesis of $[NbO(S_2CNEt_2)_3]$ and boron sulfide was obtained from Alfa Chemicals. Infrared spectra were obtained on a JASCO A-302 spectrophotometer as KBr discs, NMR spectra on a Bruker AM-300 Fourier-transform spectrometer; chemical shifts were referenced against internal $CHCl_3$ (δ 7.24). Electron impact (70 eV, *ca.* 1.12×10^{-17} J) mass spectra were obtained on a VG-TRIO-1 spectrometer with an ion-source temperature of 200 °C. Column chromatography was performed on a 50 × 2 cm column of Merck Artikel 7734 Kieselgel 60, thin-layer chromatography on Merck Artikel 5735 DC-Plastikfolien Kieselgel F_{254}. Microanalyses were performed by Atlantic Microlabs, Norcross, GA, USA.

Syntheses.—Dichloromethane (60 cm^3) was added to a mixture of $[NbO(S_2CNEt_2)_3]$ (1.95 g, 3.52 mmol) and B_2S_3 (0.28 g, 2.40 mmol). The reaction mixture was stirred for 3 d then filtered and reduced to dryness *in vacuo*. The residue was dissolved in the minimum of dichloromethane and eluted on a silica gel column using dichloromethane as eluent. The principal yellow band (containing complex **1**), a brown fore-run to this band (containing **1** and **3**) and a second orange band (containing **2**) were collected, reduced in volume and the residues recrystallised from dichloromethane–pentane.

Complex **1**: yield 1.48 g (74%) (Found: C, 31.75; H, 5.35; N, 7.45; S, 39.50. $C_{15}H_{30}N_3NbS_7$ requires C, 31.60; H, 5.30; N, 7.40; S, 39.40%). IR (KBr): ν(CN) 1510, ν(NbS) 495 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.28 (t, 18 H, J 7.0, 6Me) and 3.80 (q, 12 H, J 7.0 Hz, $6CH_2$). Mass spectrum (highest peak in multiplet): m/z 569 ($[M]^+$, 20), 537 ($[M - S]^+$, 5), 505 ($[M - 2S]^+$, 10), 453 ($[M - SCNEt_2]^+$, 30), 421 ($[M - S_2CNEt_2]^+$, 26), 405 (4), 389 (15) and 116 (100%).

Complex **2**: yield 0.40 g (18%) [Found: C, 29.10; H, 4.80; N, 6.55; S, 39.75. $C_{15.5}H_{31}ClN_3NbS_8$ (*viz.* **2**$\cdot 0.5CH_2Cl_2$) requires C, 28.90; H, 4.80; N, 6.55; S, 39.85%]. IR (KBr): ν(CN) 1510s, ν(S–S) 530m cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.23 (t, 12 H, J 7.0, 4Me), 1.30 (t, 6 H, J 7.0, 2Me), 3.75 (q, 8 H, J 7.0, $4CH_2$) and 3.83 (q, 4 H, J 7.0 Hz, $2CH_2$). Mass spectrum (highest peak in multiplet): m/z 568 ($[M - SH]^+$, 28), 536 ($[M - 2S - H]^+$, 10), 504 ($[M - 3S - H]^+$, 12), 452 ($[M - H - S_2CNEt_2]^+$, 35), 420 ($[M - H - S_3CNEt_2]^+$, 35), 404 (8), 388 (15) and 116 (100%).

Complex **3**: Yield 0.05 g (3%). Mass spectrum (highest peak in multiplet): m/z 906 ($[M]^+$, 18), 842 ($[M - 2S]^+$, 8), 758 ($[M - S_2CNEt_2]^+$, 10), 726 ($[M - S_3CNEt_2]^+$, 8), 694 ($[M - 2S - S_2CNEt_2]^+$, 4), 569 (20), 505 (12), 453 (30), 421 (25) and 116 (100%).

Crystallography.—Intensity data for an orange-brown crystal of complex **2**$\cdot 0.5CH_2Cl_2$ (0.11 × 0.18 × 0.18 mm) were

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

measured at room temperature on an Enraf-Nonius CAD4*F* diffractometer fitted with graphite-monochromatized Mo-Kα radiation, $\lambda = 0.7107$ Å. The ω–2θ scan technique was employed to measure 4803 data (θ_{max} 45.0°); of these 3594 were unique and 2310 absorption-corrected data satisfied the criterion $I \geqslant 2.5\sigma(I)$ and were used in the subsequent analysis.

Crystal data. $C_{15.5}H_{31}ClN_3NbS_8$, $M = 644.3$, monoclinic, space group *C*2/*c*, $a = 16.360(2)$, $b = 10.959(1)$, $c = 30.637(3)$ Å, $\beta = 92.34(1)°$, $U = 5488.3$ Å^3, $Z = 8$, $D_c = 1.560$ g cm^{-3}, $F(000) = 2648$, $\mu = 10.71$ cm^{-1}, maximum and minimum transmission factors 0.913 and 0.762.

The structure was solved by conventional heavy-atom methods and refined by a full-matrix least-squares procedure based on *F*.[18] Non-hydrogen atoms were refined with anisotropic thermal parameters and H atoms were included in the model at their calculated positions (C–H 0.97 Å) and assigned a common isotropic thermal parameter. In addition to a complex molecule there is a dichloromethane molecule of crystallisation in the lattice, situated on a two-fold axis, such that the complex : solvent ratio is 2 : 1. A weighting scheme of the form $w = k/[\sigma^2(F) + gF^2]$ was introduced and at convergence $R = 0.034$, $k = 4.62$, $g = 0.0001$ and $R' = 0.033$. The analysis of variance showed no special features and the maximum peak in the final difference map was 0.82 e Å^{-3}. Scattering factors for neutral Nb (corrected for f' and f'') were from ref. 19 and for the remaining atoms those incorporated in SHELX 76.[18] Refinement was performed on a SUN4/280 workstation.

Fractional atomic coordinates are listed in Table 1 and the numbering scheme employed is shown in Fig. 1 which was drawn with the ORTEP program[20] with 15% probability ellipsoids. Selected bond distances and angles are presented in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Addition of boron sulfide to colourless dichloromethane solutions of $[NbO(S_2CNEt_2)_3]$ resulted in the immediate formation of a yellow coloration, which intensified with time to produce orange or brown reaction mixtures. The course of the reaction was monitored by thin-layer chromatography, which revealed the formation of three products. The major yellow band due to complex **1** (R_f 0.85) was observed immediately below a minor orange-brown band containing **3**; following both these bands, at R_f 0.60, an orange band containing **2** was observed. The various products were isolated by column chromatography, but whereas the principal products of the reaction, **1** and **2**, were obtained in high purity, only impure orange-brown **3** could be isolated. The major product under all the reaction conditions examined was **1**, which was formed in yields as high as 90%. Only small amounts of **2** and **3** were produced in the reactions, but the yield of **3** increased slightly at higher temperatures and when an excess of boron sulfide was employed. Indeed, reaction of **2** with an excess of boron sulfide led to the production of **3** according to TLC studies of the reaction at temperatures greater than *ca.* 50 °C. Orange **2** was obtained in low variable yields (*ca.* 5–18%); the actual yield depends critically on the history of the boron sulfide used in the reaction, fresh samples being more effective in general than aged ones.

Compounds **1** and **2** are diamagnetic, air-stable crystalline compounds soluble in chlorinated hydrocarbons but insoluble in alcohols and hydrocarbons. Complex **3** is formulated as the niobium(IV) complex $[Nb_2(\mu\text{-}S_2)_2(S_2CNR_2)_4]$[16] but its complete characterisation was prevented by its low yield, limited purity and apparent air-sensitivity. While infrared spectra confirmed the presence of dithiocarbamate ligands they were otherwise uninformative. Mass spectral evidence for the presence of $[Nb_2(\mu\text{-}S_2)_2(S_2CNR_2)_4]$ ($[M]^+$ at *m*/*z* 906) was obtained; whether it constitutes the bulk of the sample or is only formed in the mass spectrometer is uncertain. The high-mass peaks observed for **3** were not present in the spectra of **1** or **2**.

Table 1 Fractional atomic coordinates for the non-hydrogen atoms of complex **2**·$0.5CH_2Cl_2$

Atom	*x*	*y*	*z*
Nb	−0.132 09(3)	0.496 27(5)	0.381 12(2)
S(1)	−0.284 3(1)	0.472 9(2)	0.360 5(1)
S(2)	−0.216 9(1)	0.406 2(2)	0.444 1(1)
S(3)	0.020 6(1)	0.515 7(2)	0.365 2(1)
S(4)	−0.036 2(1)	0.425 7(2)	0.445 6(1)
S(5)	−0.134 3(1)	0.461 3(2)	0.298 1(1)
S(6)	−0.116 3(1)	0.270 0(2)	0.361 4(1)
S(7)	−0.144 2(1)	0.705 6(2)	0.351 0(1)
S(8)	−0.136 7(1)	0.689 9(2)	0.416 5(1)
N(1)	−0.373 1(3)	0.354 3(5)	0.419 2(2)
N(2)	0.121 8(3)	0.417 0(5)	0.426 9(2)
N(3)	−0.139 2(4)	0.223 9(5)	0.276 4(2)
C(1)	−0.301 9(3)	0.404 9(5)	0.409 6(2)
C(2)	−0.383 1(4)	0.292 7(6)	0.461 8(3)
C(3)	−0.418 1(5)	0.372 9(7)	0.494 9(3)
C(4)	−0.442 5(4)	0.354 0(7)	0.387 3(3)
C(5)	−0.495 7(4)	0.466 1(7)	0.390 0(3)
C(6)	0.046 4(3)	0.449 9(5)	0.414 2(2)
C(7)	0.138 2(3)	0.353 5(6)	0.468 7(2)
C(8)	0.138 2(4)	0.215 4(7)	0.462 9(3)
C(9)	0.191 9(3)	0.434 1(6)	0.399 3(3)
C(10)	0.247 5(5)	0.536 1(8)	0.415 7(3)
C(11)	−0.130 5(3)	0.305 7(6)	0.307 1(2)
C(12)	−0.133 4(6)	0.092 0(7)	0.286 9(3)
C(13)	−0.211 9(8)	0.039 5(11)	0.294 1(4)
C(14)	−0.158 1(5)	0.255 8(8)	0.229 9(3)
C(15)	−0.089 2(5)	0.238 4(9)	0.201 4(3)
C(100)	0	−0.301 9(12)	0.25(−)
Cl(1)	0.085 1(3)	−0.218 2(5)	0.265 6(2)

Table 2 Selected bond distances (Å) and angles (°) for complex **2**·$0.5CH_2Cl_2$

Nb–S(1)	2.556(2)	S(2)–C(1)	1.711(6)
Nb–S(2)	2.614(2)	S(3)–C(6)	1.705(7)
Nb–S(3)	2.574(1)	S(4)–C(6)	1.711(6)
Nb–S(4)	2.591(2)	S(5)–C(11)	1.728(6)
Nb–S(5)	2.571(2)	S(6)–C(11)	1.714(7)
Nb–S(6)	2.569(2)	S(7)–S(8)	2.015(3)
Nb–S(7)	2.478(2)	C(1)–N(1)	1.333(7)
Nb–S(8)	2.386(2)	C(6)–N(2)	1.327(7)
S(1)–C(1)	1.714(7)	C(11)–N(3)	1.304(8)
S(1)–Nb–S(2)	66.6(1)	S(4)–Nb–S(7)	126.7(1)
S(1)–Nb–S(3)	154.8(1)	S(4)–Nb–S(8)	87.0(1)
S(1)–Nb–S(4)	135.4(1)	S(5)–Nb–S(6)	67.7(1)
S(1)–Nb–S(5)	76.5(1)	S(5)–Nb–S(7)	76.8(1)
S(1)–Nb–S(6)	87.2(1)	S(5)–Nb–S(8)	125.7(1)
S(1)–Nb–S(7)	86.5(1)	S(6)–Nb–S(7)	144.4(1)
S(1)–Nb–S(8)	98.8(1)	S(6)–Nb–S(8)	166.3(1)
S(2)–Nb–S(3)	136.0(1)	S(7)–Nb–S(8)	48.9(1)
S(2)–Nb–S(4)	69.4(1)	C(1)–S(1)–Nb	91.4(2)
S(2)–Nb–S(5)	133.4(1)	C(1)–S(2)–Nb	89.5(2)
S(2)–Nb–S(6)	82.6(1)	C(6)–S(3)–Nb	90.3(2)
S(2)–Nb–S(7)	126.0(1)	C(6)–S(4)–Nb	89.6(2)
S(2)–Nb–S(8)	88.4(1)	C(11)–S(5)–Nb	89.4(2)
S(3)–Nb–S(4)	66.9(1)	C(11)–S(6)–Nb	89.8(2)
S(3)–Nb–S(5)	78.4(1)	S(8)–S(7)–Nb	63.2(1)
S(3)–Nb–S(6)	85.8(1)	S(7)–S(8)–Nb	67.9(1)
S(3)–Nb–S(7)	85.2(1)	S(2)–C(1)–S(1)	112.1(3)
S(3)–Nb–S(8)	93.5(1)	S(4)–C(6)–S(3)	112.8(3)
S(4)–Nb–S(5)	133.9(1)	S(6)–C(11)–S(5)	112.5(4)
S(4)–Nb–S(6)	80.1(1)		

The infrared spectrum of complex **1** exhibited strong ν(CN) and ν(Nb=S) bands at 1510 and 495 cm^{-1}, respectively, consistent with previous reports.[10,11] At room temperature, the ^{1}H NMR spectrum exhibited simple triplet (δ 1.28) and quartet (δ 3.80) resonances, indicative of fluxionality on the NMR time-scale. The spectrum of [NbO(S_2CNEt_2)$_3$] consisted of broad and overlapping triplet (δ *ca.* 1.30) and quartet (δ *ca.* 3.8) resonances, consistent with partial site exchange at room temperature. Interestingly, [WS(S_2CNR_2)$_3$]$^+$ complexes are also fluxional[21] but this is not the case with analogous [MoO(S_2CNR_2)$_3$]$^+$.[22] The mass spectrum of **1** showed a well defined parent ion at *m/z* 569 (20%) with the expected isotope pattern, as well as peaks at *m/z* 537, 505, 453, 421 and 389, corresponding to the loss of S, 2S, $SCNEt_2$, S_2CNEt_2 and S + S_2CNEt_2, respectively, from [*M*]$^+$. The most abundant Nb-containing ion (*m/z* 453, 30%) and the dominant ion (*m/z* 116, 100%) point to an abstraction of S from a dithiocarbamate ligand during fragmentation.

The infrared spectrum of complex **2** was virtually identical to that of **1** except that the ν(NbS) band at 495 cm^{-1} was replaced by a medium-intensity ν(S–S) band at 530 cm^{-1}. The ^{1}H NMR spectrum consisted of pairs of triplet (2:4 intensity ratio) and quartet (2:4 ratio) resonances consistent with rapid two-site exchange on the NMR time-scale. A parent ion was not observed in the mass spectrum; a cluster of peaks with *m/z* 568 corresponds to the effective loss of SH$^-$ upon ionisation. The fragmention pattern from the resultant ion was the same as that observed for [**1**]$^+$ except the ions produced were one mass unit lighter than those observed for **1**.

The molecular structure of complex **2**, along with the atomic labelling scheme, is shown in Fig. 1. The Nb atom is eight-co-ordinate with an *mmmm* dodecahedral environment. The four edges of the dodecahedron are occupied by a side-on bonded disulfide ligand and three *S,S'*-bidentate dithiocarbamate ligands. Atoms S(2), S(4), S(5) and S(7) occupy the A sites in the dodecahedron and S(1), S(3), S(6) and S(8) the B sites. For all four ligands, the Nb–S$_A$ distance is longer than the associated Nb–S$_B$ distance, consistent with the greater steric interactions of the atoms in the A sites; Nb–S$_A$: Nb–S$_B$ = 1.01 : 1 for $S_2CNEt_2{}^-$, 1.04 : 1 for $S_2{}^{2-}$. The dodecahedral geometry is favoured by the small bites of the dithiocarbamate [1.11, average S–Nb–S$_{av}$ 67.1°] and disulfide ligands [0.86, S(7)–Nb–S(8) 48.9(1)°]. Following the treatment of [Ta(S_2)(S_2CNEt_2)$_3$] provided by Drew *et al.*,[10] the φ_A and φ_B values determined using S(2) and S(4) as the reference girth for the trapezoid are 34.5 and 79.1°, respectively, *cf.* 34.5 and 78.2° for [Ta(S_2)(S_2CNEt_2)$_3$]. The atoms S(1)–S(4) are planar [maximum deviation 0.028(2) Å for S(2)] and the Nb atom lies 0.2012(6) Å out of this plane towards S(8). This results from a bending of atoms S(1) and S(3) away from S(7), probably due to steric interactions. Atoms S(5)–S(8) are strictly planar and the Nb is 0.0622(6) Å out of this plane towards S(1) and S(2). The dihedral angle between the S_4 trapezoids of the structure defined above is 89.6°. The Nb–S(7)–S(8) plane subtends dihedral angles of 97.3, 92.7 and 176.9° with the NbS_2 planes of ligands I, II and III, respectively.

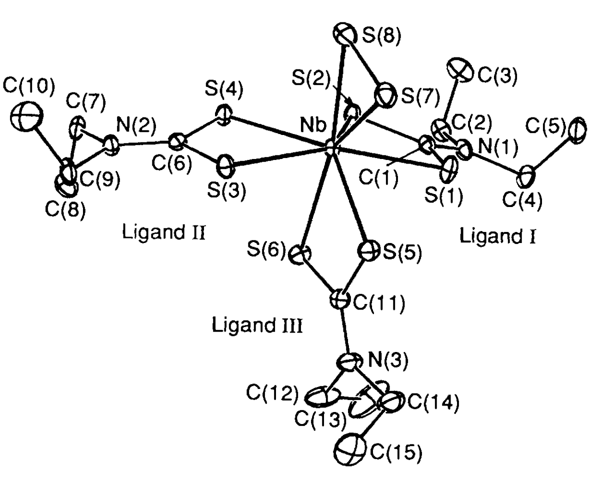

Fig. 1 Molecular structure and crystallographic numbering scheme for complex **2**

The disulfide ligand is asymmetrically co-ordinated to the Nb atom [Nb–S(7) 2.478(2), Nb–S(8) 2.386(2) Å] and exhibits a S(7)–S(8) distance [2.015(3) Å] characteristic of the side-on co-ordination mode of this ligand.[23,24] The Nb–S distances associated with the dithiocarbamate ligands fall in the range 2.556–2.614 Å (average 2.579 Å). Each such ligand is planar [maximum deviation 0.076(9) Å for C(14)] and only a slight twisting around each of the C–N bonds is observed; dihedral angles between the S_2C and NC_2 planes are 3.3, 4.9 and 4.3°, respectively, for ligands I, II and III. The Nb atom is not coplanar with the S_2CNC_2 portions of the dithiocarbamate ligands, being 0.3186(6) and 0.3263(6) Å towards atom S(6) from the planes of ligands I and II, respectively, and 0.3461(6) Å toward ligand I from the plane of ligand III. The average C–N distance is 1.32 Å, consistent with a considerable double-bond character. The metrical parameters of the dithiocarbamate ligands are typical.[24] The structure of **2** is analogous to that reported for [Ta(S_2)(S_2CNEt_2)$_3$], right down to the conformations adopted by the ethyl substituents. Dichloromethane is incorporated into the lattice but there are no unusually close intermolecular contacts between the constituent molecules.

Acknowledgements

We gratefully acknowledge the financial assistance of the Australian Research Council.

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Received 24*th December* 1993; *Paper* 3/07577J