



Niobium persulfide complexes: synthesis and structural characterization of $[\text{Et}_4\text{N}][\text{NbO}(\text{S}_2)_2(\text{bpy})]\cdot\text{DMF}$, $[\text{PPN}][\text{NbO}(\text{CS}_3)(\text{S}_2)(\text{bpy})]$ and $[\text{Et}_4\text{N}][\text{NbO}(\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2)(\text{S}_2)(\text{bpy})]\cdot\text{DMF}$ complexes

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Abstract

The novel monomeric niobium persulfide complex, $[\text{Et}_4\text{N}][\text{NbO}(\text{S}_2)_2(\text{bpy})]\cdot\text{DMF}$ (**I**) was synthesized by the reaction of $\text{NbO}(\text{SPh})_4^-$ with elemental sulfur in the presence of 2,2'-dipyridyl in DMF. The reaction of **I** with carbon disulfide (CS_2) and dimethylacetylene dicarboxylate (DMA) affords $[\text{PPN}][\text{NbO}(\text{CS}_3)(\text{S}_2)(\text{bpy})]$ (**II**) and $[\text{Et}_4\text{N}][\text{NbO}(\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2)(\text{S}_2)(\text{bpy})]\cdot\text{DMF}$ (**III**) complexes, respectively. In this reaction, insertion reactions of the electrophile occurred at only one site of two equivalent disulfide ligands. In each complex, the Nb atom is seven coordinated and the anion has a distorted pentagonal bipyramidal geometry. © 2001 Published by Elsevier Science Ltd.

Keywords: Niobium; Sulfide ligand; Dithiolene ligand; Trithiocarbonate ligand

1. Introduction

Over the last few decades, the early transition metal sulfide chemistry has held a continued interest in the sense that the complexes can serve as models for industrial catalysts and biological systems [1–6] and exhibit structural varieties and characteristic reactivities [7–11]. Although the Group VI sulfide chemistry, especially for molybdenum, is well developed and the systematic synthesis of binary and ternary Mo/S and Mo/S/O complexes [12,13] are established, the Group V species have remained a relatively unexplored area because of the unavailability of starting materials.

An attempt to derive thionobates has been made by several groups. Soluble tetrathionobate, $\text{Li}_3[\text{NbS}_4]\cdot 2\text{TMEDA}$, was first reported by the Holm group [14,15] and a series of thionobates, $[\text{Nb}(\text{S})_2(\text{tBuS})_2]^-$, $[\text{Nb}(\text{S})_3(\text{tBuS})]^{2-}$, $[\text{Nb}(\text{S})_3(\text{SH})]^{2-}$, and $[\text{NbO}(\text{S}_2)_2(\text{SH})]^{2-}$ complexes [16,17] were synthesized from the

$[\text{NbS}(\text{tBuS})_4]^-$ by Coucouvanis' group. Recently, we have reported on the synthesis of the $[\text{NbO}(\text{SPh})_4]^-$ complex [18] and a couple of persulfide niobium complexes, $[\text{NbO}(\text{S}_2)_2(\text{SPh})]^{2-}$ and $[\text{NbS}(\text{S}_2)_2(\text{SPh})]^{2-}$, using $[\text{NbO}(\text{SPh})_4]^-$ as a precursor [19]. Despite the progressive work on thionobates and oxo-thionobate derivatives, the reactivity of the sulfide ligand in niobium complexes toward small organic molecules has not yet been reported to our knowledge.

In this work, we have reported on the synthesis and structural characterization of new monomeric niobium persulfide complexes, $[\text{Et}_4\text{N}][\text{NbO}(\text{S}_2)_2(\text{bpy})]\cdot\text{DMF}$ (**I**), $[\text{PPN}][\text{NbO}(\text{CS}_3)(\text{S}_2)(\text{bpy})]$ (**II**) and $[\text{Et}_4\text{N}][\text{NbO}(\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2)(\text{S}_2)(\text{bpy})]\cdot\text{DMF}$ (**III**).

2. Experimental

All manipulations were performed using standard Schlenk line techniques under N_2 atmosphere. *N,N*-dimethylformamide (DMF) was stored over CaH_2 for a week and distilled under reduced pressure before use.

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Tetrahydrofuran (THF) and diethyl ether were distilled after being refluxed with sodium/benzophenone. Acetonitrile was distilled after being refluxed over CaH_2 before use. The $[\text{Et}_4\text{N}][\text{NbO}(\text{SPh})_4]$ complex was synthesized according to the literature method [8].

2.1. $[\text{Et}_4\text{N}][\text{NbO}(\text{S}_2)_2(\text{bpy})]\cdot\text{DMF}$ (I)

A 250 ml Schlenk flask was charged with 2 g $[\text{Et}_4\text{N}][\text{NbO}(\text{SPh})_4]$ (2.96 mmol), 0.38 g elemental sulfur (11.85 mmol), 0.47 g of 2,2'-dipyridyl(bpy) (3.2 mmol) and a stirring bar. To this mixture, 50 ml DMF was added via cannula with stirring at ambient temperature. The color of the solution changed from dark red to bright red. After further stirring for 6 h, the solution was filtered through a fine-porosity fritted funnel and to the red filtrate, 100 ml diethyl ether was added and then the solution was made to stand at ambient temperature. Dark red crystals were isolated and dried under vacuum. Finally, 0.8 g (51.3% yield) of the dark red crystals were obtained. FTIR (KBr disk, cm^{-1}): $\nu(\text{Nb}=\text{O})$ 893, $\nu(\text{S}-\text{S})$ 528, $\nu(\text{C}=\text{S}$ in CS_3 ligand) 1017. Anal. Found: C, 57.78; H, 3.94; N, 4.12. Calc. for $\text{NbS}_5\text{N}_3\text{OP}_2\text{C}_{47}\text{H}_{38}$: C, 57.84; H, 3.89; N, 4.30%. ^1H NMR ($\text{DMSO}-d_6$): $\delta = 7.18-7.22$, $7.70-7.79$, $8.30-8.43$, $8.65-8.68$, 9.71 (m, CH in cation and ligand). ^{13}C NMR ($\text{DMSO}-d_6$): $\delta = 253$ (CS_3^{2-} ligand).

2.2. $[\text{Et}_4\text{N}][\text{NbO}(\text{CS}_3)(\text{S}_2)(\text{bpy})]$ (IIA)

A 100 ml Schlenk flask was charged with 1 g $[\text{Et}_4\text{N}][\text{NbO}(\text{S}_2)_2(\text{bpy})]$ (1.91 mmol) and a stirring bar. To this mixture, 50 ml DMF was added via cannula and then 1 ml of CS_2 was injected using a syringe. The reaction mixture was stirred at ambient temperature. The color of the solution changed from dark red to bright red. The reaction mixture was stirred for a further 6 h. The solution was filtered through a fine-porosity fritted funnel and to the red filtrate, 100 ml diethyl ether was added and then the solution was made to stand at ambient temperature. The red microcrystalline product was isolated and dried under vacuum. Finally, 0.6 g (63% yield) of the red microcrystalline product was obtained. FTIR (KBr disk, cm^{-1}): $\nu(\text{Nb}=\text{O})$ 878, $\nu(\text{S}-\text{S})$ 517, $\nu(\text{C}=\text{S}$ in CS_3^{2-}) 980. Anal. Found: C, 41.02; H, 5.21; N, 7.98. Calc. for $\text{NbS}_4\text{N}_3\text{OC}_{19}\text{H}_{28}$: C, 40.24; H, 4.94; N, 7.41%. ^1H NMR ($\text{DMSO}-d_6$): $\delta = 1.18$ (t, 12H, CH_3 in cation), 3.18 (q, 8H, CH_2 in cation), $7.18-7.22$, $7.70-7.79$, $8.30-8.43$, $8.65-8.68$, 9.71 (m, 8H, CH in ligand). ^{13}C NMR ($\text{DMSO}-d_6$): $\delta = 252$ (CS_3^{2-} ligand).

2.3. $[\text{PPN}][\text{NbO}(\text{CS}_3)(\text{S}_2)(\text{bpy})]$ (II)

A 100 ml Schlenk flask was charged with 1 g $[\text{Et}_4\text{N}][\text{NbO}(\text{CS}_3)(\text{S}_2)(\text{bpy})]$ (1.76 mmol), 1.01 g

bis(triphenylphosphoranylidene)ammonium chloride (PPNCl) (1.76 mmol) and a stirring bar. To this mixture, 50 ml CH_3CN was added via cannula and the reaction mixture was refluxed for 3 h. An orange powder was isolated after filtration through a fine-porosity funnel, washed with several portions of diethyl ether and dried under vacuum. Red crystals were obtained in DMF/diethylether (83% yield). FTIR (KBr disk, cm^{-1}): $\nu(\text{Nb}=\text{O})$ 893, $\nu(\text{S}-\text{S})$ 528, $\nu(\text{C}=\text{S}$ in CS_3 ligand) 1017. Anal. Found: C, 57.78; H, 3.94; N, 4.12. Calc. for $\text{NbS}_5\text{N}_3\text{OP}_2\text{C}_{47}\text{H}_{38}$: C, 57.84; H, 3.89; N, 4.30%. ^1H NMR ($\text{DMSO}-d_6$): $\delta = 7.18-7.22$, $7.70-7.79$, $8.30-8.43$, $8.65-8.68$, 9.71 (m, CH in cation and ligand). ^{13}C NMR ($\text{DMSO}-d_6$): $\delta = 253$ (CS_3^{2-} ligand).

2.4. $[\text{Et}_4\text{N}][\text{NbO}(\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2)(\text{S}_2)(\text{bpy})]\cdot\text{DMF}$ (III)

A 100 ml Schlenk flask was charged with 1 g $[\text{Et}_4\text{N}][\text{NbO}(\text{S}_2)_2(\text{bpy})]$ (1.91 mmol) and a stirring bar. To this mixture, 50 ml CH_3CN was added via cannula and 0.5 ml dimethylactylenedicarboxylate (DMA) (3.30 mmol) was injected using a syringe. The reaction mixture was stirred at ambient temperature. The color of solution turned from dark red to bright red, and the reaction mixture was stirred for 6 h. The solution was filtered through a fine-porosity fritted funnel and to the red filtrate, 100 ml THF was added, and then the solution was made to stand at ambient temperature. A red microcrystalline product was isolated and dried under vacuum. Finally, 0.8 g (64.5% yield) of the red crystals were obtained. FTIR (KBr disk, cm^{-1}): $\nu(\text{Nb}=\text{O})$ 893, $\nu(\text{S}-\text{S})$ 528, $\nu(\text{C}=\text{O}$ in DMA ligand) 1680. Anal. Found: C, 43.56; H, 5.46; N, 7.89. Calc. for $\text{NbS}_4\text{N}_4\text{O}_6\text{C}_{27}\text{H}_{41}$: C, 43.89; H, 5.55; N, 7.58%. ^1H NMR ($\text{DMSO}-d_6$): $\delta = 1.15$ (t, 12H, CH_3 in cation), 3.32 (q, 8H, CH_2 in cation), $7.38-7.41$, $7.85-7.98$, $8.33-8.46$, $8.67-8.70$, $9.55-9.57$ (m, 8H, CH in bpy ligand), 3.58 , 3.44 (s, 6H, CH_3 in $\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2^{2-}$ ligand), 2.73 , 2.88 (s, 6H, CH_3 in DMF).

2.5. X-ray crystallography

All the crystals were mounted into a glass capillary under N_2 atmosphere and then sealed. A summary of X-ray diffraction data is presented in Table 1. Diffraction data were collected at ambient temperature on a Bruker P4 four-circle diffractometer using Mo $\text{K}\alpha$ radiation. Intensity data were collected by using a $\theta-2\theta$ step scan technique and for all data sets, the condition of the crystal was monitored by measuring two standard reflections. The solutions of structures I, II, and III were carried out by a combination of heavy-atom Patterson techniques, direct methods, and Fourier techniques. The refinement of the structures by full-matrix least-squares methods was based on 3236 unique reflections ($2\theta = 45$, $I > 2\sigma$) for I, 5657 unique reflections

($2\theta = 45$, $I > 2\alpha$) for **II**, and 2309 unique reflections ($2\theta = 45$, $I > 2\alpha$) for **III**. Anisotropic temperature factors were used for all non-hydrogen atoms in **I**, **II**, and **III**. At the current stage of refinement on 289 parameters for **I**, 570 parameters for **II**, and 384 for **III** with all atoms present in the asymmetric units, $R = 0.0378$, $R_w = 0.0955$ for **I**, $R = 0.0511$, $R_w = 0.1258$ for **II**, and $R = 0.0873$, $R_w = 0.2264$ for **III**.

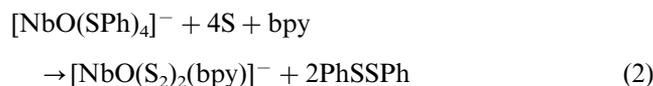
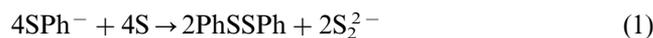
2.6. Other physical measurements

^1H NMR spectra (300 MHz) were obtained with a Varian Gemini 300 spectrometer. Infrared spectra were measured with a Nicolet Magna-IR 760 spectrometer. CHN analyses were obtained with a Thermoquest EA-1110 CHNS analyzer.

3. Results and discussion

3.1. Syntheses

The reaction of $[\text{Et}_4\text{N}][\text{NbO}(\text{SPh})_4]$ with 4 equiv. elemental sulfur in the presence of 2,2'-dipyridyl(bpy) yielded a deep red solution. After being stirred for 12 h at ambient temperature under N_2 atmosphere, the reaction mixture was filtered and black-red crystals of $[\text{Et}_4\text{N}][\text{NbO}(\text{S}_2)_2(\text{bpy})]$ (**I**) were obtained by slow diffusion of diethylether into the filtrate solution. The Ph_4P^+ salts of $[\text{NbO}(\text{S}_2)_2(\text{bpy})]^-$ were also obtained in 67% yield from $[\text{Ph}_4\text{P}][\text{NbO}(\text{SPh})_4]$. The reaction scheme is presented in Eqs. (1) and (2).



In the synthesis of $[\text{NbO}(\text{S}_2)_2(\text{bpy})]^-$, elemental sulfur oxidized the four coordinated thiophenolate ligands with a concomitant generation of the two disulfide (S_2^{2-}) ligands. Christou's group had reported on the synthesis of the isostructural $[\text{VO}(\text{S}_2)_2(\text{bpy})]^-$ anion [20], which was obtained from the $\text{VOCl}_4^-/2.5\text{S}/2.5\text{Li}_2\text{S}/\text{bpy}$ reaction mixture. In their experiment, Li_2S and elemental sulfur were used as potential sources of S_2^{2-} . The introduction of 2,2'-dipyridyl was attempted to avoid the generation of polymeric niobium sulfides. Our previous efforts [19] to prepare monomeric oxo-niobium sulfides by the reaction of $[\text{NbO}(\text{SPh})_4]^-$ with elemental sulfur (1:1–1:4 in molar ratio) have only given the $[\text{NbO}(\text{S}_2)_2(\text{SPh})]^{2-}$ complex and unidentified insoluble polymeric oxo-niobium sulfides.

The reaction of $[\text{Et}_4\text{N}][\text{NbO}(\text{S}_2)_2(\text{bpy})]$ with small organic electrophiles, such as CS_2 and DMA, proceeded readily at ambient temperature to yield the complexes **II** and **III**. The reaction chemistry of sulfide ligands in other transition metal complexes toward electrophiles such as CS_2 and DMA has been studied extensively [21–27]. In this study, the insertion reaction of the electrophile occurred at only one of two equivalent disulfide ligands. Attempts to prepare $[\text{NbO}(\text{CS}_3)_2(\text{bpy})]^-$ or $[\text{NbO}(\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2)_2(\text{bpy})]^-$ complexes using a large excess of CS_2 and DMA under refluxing condition gave only the complexes **II** and **III**,

Table 1
Crystal data for $[\text{Et}_4\text{N}][\text{NbO}(\text{S}_2)_2(\text{bpy})]\cdot\text{DMF}$ (**I**), $[\text{PPN}][\text{NbO}(\text{CS}_3)(\text{S}_2)]$ (**II**) and $[\text{Et}_4\text{N}][\text{NbO}(\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2)(\text{S}_2)(\text{bpy})]\cdot\text{DMF}$ (**III**)

	I	II	III
Empirical formula	$\text{NbS}_4\text{N}_4\text{O}_2\text{C}_{21}\text{H}_{35}$	$\text{NbS}_5\text{P}_2\text{N}_3\text{OC}_{47}\text{H}_{38}$	$\text{NbS}_4\text{N}_4\text{O}_6\text{C}_{27}\text{H}_{41}$
Formula weight	596.36	975.95	738.79
Temperature, T (°C)	20	20	20
Wavelength, λ (Å)	0.71073	0.71073	0.71073
Crystal system	orthorhombic	triclinic	monoclinic
Space group	$Pbca$ (No. 61)	$P\bar{1}$ (No. 2)	$P2_1$ (No. 4)
Unit cell dimensions			
a (Å)	16.278(1)	9.102(2)	9.949(4)
b (Å)	16.253(1)	15.767(4)	14.641(5)
c (Å)	19.281(2)	17.364(3)	11.693(3)
α (°)		115.02(1)	
β (°)		90.59(1)	93.90(2)
γ (°)		94.48(2)	
V (Å ³)	5101.1(7)	2248.6(8)	1699.3(10)
Z	8	2	2
ρ_{calc} (g cm ⁻³)	1.550	1.441	1.444
Absorption coefficient, μ (cm ⁻¹)	8.18	6.11	6.43
R^a	0.0378	0.0511	0.0873
R_w^b	0.0955	0.1258	0.2264

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$.

^b $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(|F_o|^2)]^{1/2}$, where $w = 1/\alpha^2(|F_o|)$.

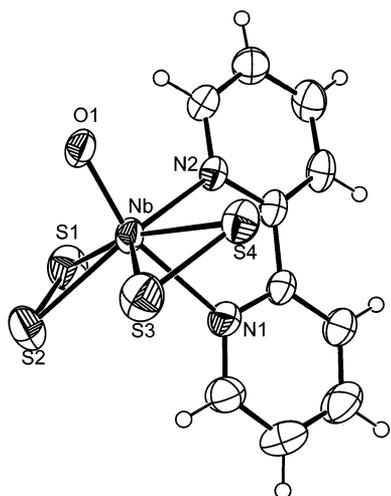


Fig. 1. Structure and labeling of the anion in the $[\text{Et}_4\text{N}][\text{NbO}(\text{S}_2)_2(\text{bpy})]\cdot\text{DMF}$ complex. Thermal ellipsoids as drawn by ORTEP represent the 40% probability surfaces.

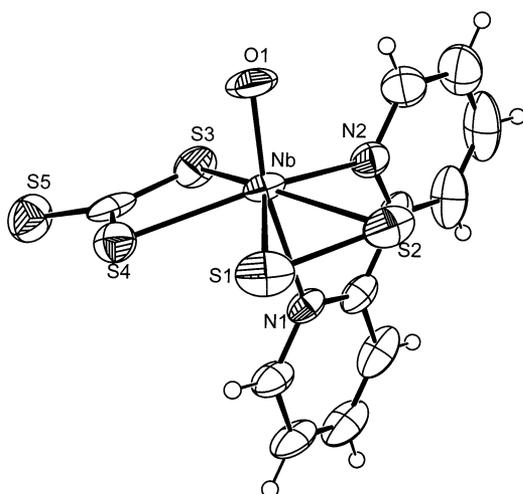


Fig. 2. Structure and labeling of the anion in the $[\text{PPN}][\text{NbO}(\text{CS}_3)(\text{S}_2)(\text{bpy})]$ complex. Thermal ellipsoids as drawn by ORTEP represent the 40% probability surfaces.

respectively. This result is probably due to the steric effect between neighboring ligands. In the $[\text{NbO}(\text{S}_2)(\text{L})(\text{bpy})]^-$ ($\text{L} = \text{CS}_3^{2-}$ and $\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2^{2-}$) complex, an additional attack of electrophile into the unreacted S_2^{2-} ligand induces steric interaction between L and the bpy ligand. Therefore, the formation of an $[\text{NbO}(\text{L})_2(\text{bpy})]^-$ complex is thermodynamically unfavorable. However, it is thought that the $[\text{NbO}(\text{L})_2]^-$ complex can be generated in the absence of the bpy ligand. In fact, from the organic cation substitution reaction of $[\text{Et}_4\text{N}][\text{NbO}(\text{S}_2)(\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2)(\text{bpy})]$ and PPNCl , $[\text{Et}_4\text{N}][\text{NbO}(\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2)_2]$ could be isolated as a minor product (less than 10% yield) as evidenced by IR and NMR analyses.

3.2. Crystal structures

The structures of **I**, **II**, and **III** have been determined and the ORTEP diagrams of the anions are shown in Figs. 1–3. The selected bond lengths and angles of anions in complexes **I**, **II**, and **III** are presented in Table 2. In each complex, the Nb atom is seven coordinated and the anion has a distorted pentagonal bipyramidal geometry.

3.2.1. $[\text{Et}_4\text{N}][\text{NbO}(\text{S}_2)_2(\text{bpy})]\cdot\text{DMF}$ (**I**)

In complex **I**, the terminal oxygen atom and one of the nitrogen atoms, N(1), of the bpy ligand are located in the axial positions ($\text{O}-\text{Nb}-\text{N}(1) = 158.18(14)^\circ$). The four sulfur atoms and the other nitrogen atom, N(2), are located in the equatorial positions, which are approximately planar. The $\text{Nb}=\text{O}$ distance (1.727 Å) is slightly longer than that of the complex $[\text{NbO}(\text{SPh})_4]^-$ (1.710 Å). This increase in bond length is probably due to the difference in ligand basicity. As the basicity of the bpy ligand is stronger than that of the thiophenolate ligand, the $\text{Nb}=\text{O}$ bond is weakened by the stronger interaction between the niobium and bpy ligand. Also, as expected, there is a significant *trans* effect of the terminal oxygen atom on $\text{Nb}-\text{N}(1)$ (2.407(4) Å), which is noticeably longer than equatorial $\text{Nb}-\text{N}(2)$ (2.208(4) Å). The S–S distances in complex **I** ranged between 2.070(2) and 2.072(2) Å as expected for a $\eta^2\text{-S}_2^{2-}$ ligand, and other bond lengths and angles are comparable to those reported for other similar molecules [20,28].

3.2.2. $[\text{PPN}][\text{NbO}(\text{CS}_3)(\text{S}_2)(\text{bpy})]$ (**II**)

In complex **II**, the $\text{Nb}=\text{O}$ bond distance (1.717 Å) is shorter than that of complex **I**. Also, there are rather longer $\text{Nb}-\text{N}$ (2.430(5) and 2.300(5) Å) bonds in complex **II** than those of complex **I**, which is due to the steric interaction between the trithiocarbonate and bpy

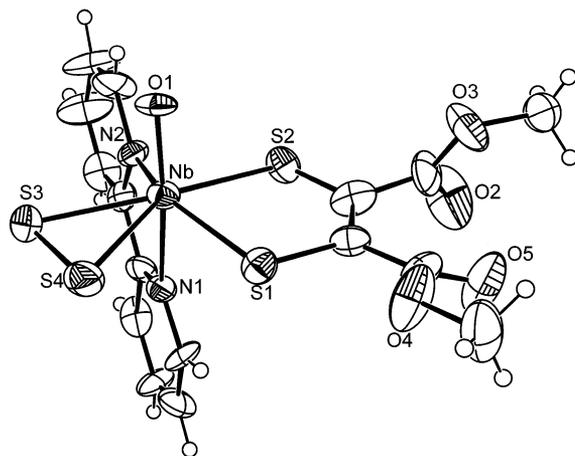


Fig. 3. Structure and labeling of the anion in the $[\text{Et}_4\text{N}][\text{NbO}(\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2)(\text{S}_2)(\text{bpy})]\cdot\text{DMF}$ complex. Thermal ellipsoids as drawn by ORTEP represent the 40% probability surfaces.

Table 2
Selected bond lengths (Å) and angles (°) for anionic complexes **I**, **II** and **III**

	I	II	III
<i>Bond distances</i> ^a			
Nb=O _t ^b	1.727(3)	1.717(4)	1.738(14)
Nb–S in S ₂ ²⁻	2.471	2.464	2.468
Range	2.437(1), 2.504(1)	2.446(2), 2.481(2)	2.489(7), 2.447(7)
S–S in S ₂ ²⁻	2.070(2), 2.072(2)	2.067(3)	2.041(10)
Nb–S ^c		2.516(2), 2.576(2)	2.501(6), 2.580(6)
Nb–N (axial)	2.407(4)	2.430(5)	2.46(2)
Nb–N (equatorial)	2.280(4)	2.300(5)	2.447(7)
<i>Bond angles</i> ^a			
S–Nb–O _t	101.17	100.15	100.15
Range	97.55(11), 104.82(11)	93.9(2), 105.2(2)	92.7(6), 105.5(6)
S–M–S in S ₂ ²⁻	49.61(6), 49.47(5)	49.61(7)	48.8(3)
N–Nb–O _t (axial)	158.18(14)	161.9(2)	158.9(8)
N–Nb–O _t (equatorial)	89.6(1)	94.2(2)	91.0(7)

^a Mean values of crystallographically independent, chemically equivalent structural parameters when more than two values are available. The number in parentheses represents the individual standard deviation.

^b O_t = terminal oxo ligand at apical position.

^c In CS₃²⁻ for **II** and in S₂C₂(CO₂Me)₂²⁻ for **III**.

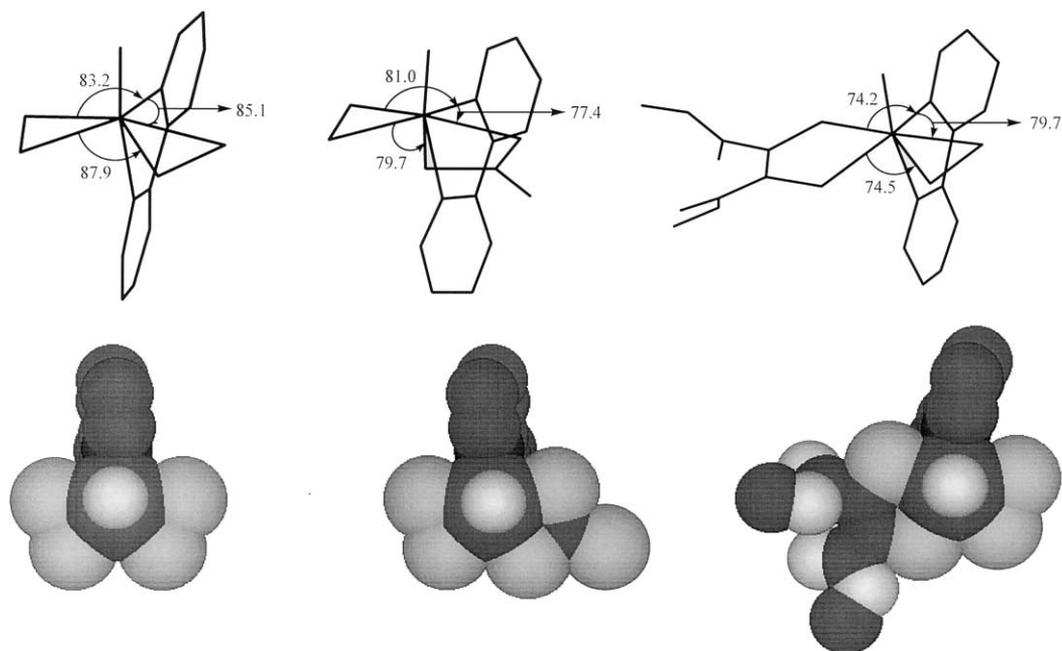


Fig. 4. Selected bond angles and space filling models for complexes **I**, **II** and **III**.

ligand. The S–Nb–S bond angle in the trithiocarbonate ligand is 67.65°, which is significantly wider than that of the disulfide ligand (49.61°). The S–Nb–S bond angle between the disulfide and trithiocarbonate ligand is 155.83°, and this narrower bond angle than that of complex **I** (159.81°, between disulfide ligands) has an effect on the steric interaction with the bpy ligand. The geometry of the CS₃²⁻ ligand attached to the Nb atom is nearly planar and the C–S bond distances are 1.646(8), 1.673(7), and 1.752(7) Å. The comparison of

these values with those of the localized and delocalized forms in the structure K₂CS₄·CH₃OH [29] shows that the CS₃²⁻ ligand can be assigned the localized charge formation.

3.2.3. [Et₄N][NbO(S₂C₂(CO₂Me)₂)(S₂)(bpy)]·DMF (**III**)

A rather longer Nb=O distance (1.738 Å) is found in complex **III** compared to those of complexes **I** and **II**. The Nb–S bond distances in the disulfide ligand are 2.489(7) and 2.447(7) Å, which are comparable to those

of complexes **I** and **II**. While the Nb–S distances in the dithiolene ligand are observed in the range from 2.501(6) to 2.580(6) Å, rather longer Nb–N bond distances (2.46(2) and 2.447(6) Å) than those in complexes **I** and **II** are found and the *trans* effect of the terminal oxygen atom on the axial nitrogen Nb–N(1) is negligible.

In Fig. 4, selected bond angles and space filling models for complexes **I**, **II**, and **III** are represented. Bond angles reflect the interactions between L (S_2^{2-} , CS_3^{2-} , and $S_2C_2(CO_2Me)_2^{2-}$) and the bpy ligand.

3.3. Spectroscopic data

The infrared spectra of **I**, **II**, and **III** exhibited the characteristic stretching vibrational peak from a terminal Nb=O bond at 884, 878, and 893 cm^{-1} , respectively. These values are significantly lower than those found in $[NbO(SPh)_4]^-$ (918 cm^{-1}) and $[NbO(S_2)_2(SPh)]^{2-}$ (905 cm^{-1}). This can be explained by the *trans* effect of an axial nitrogen atom in the bpy ligand and the basicities of the ligands. The S–S bond stretching vibrations were observed at 517 (for **I** and **II**) and 528 (for **III**) cm^{-1} and these values are similar to those for $[NbO(S_2)_2(SPh)]^{2-}$ (524 cm^{-1}) or isostructural complexes $[VO(S_2)_2(bpy)]^-$ (535 cm^{-1}) [18], $[MoO(S_2)_2(bpy)]$ (540 cm^{-1}) [26] as expected. The 1H NMR spectrum in $DMSO-d_6$ displayed the characteristic Et_4N^+ cation and bpy ligand resonances with an integral ratio of 1:1. In complex **II**, the presence of a strong absorption in the infrared at 1017 cm^{-1} is attributed to the C=S asymmetric stretching vibration of the CS_3^{2-} ligand. Also, the characteristic resonance of a coordinated CS_3^{2-} ligand at 253 ppm appeared in ^{13}C NMR spectra. The intense absorption peak at 1680 cm^{-1} in the IR spectra of complex **III** is attributed to C=O vibrations of the ester group in the $S_2C_2(CO_2Me)_2^{2-}$ ligand. The 1:1 integral ratio between Et_4N^+ and the $S_2C_2(CO_2Me)_2^{2-}$ ligand in 1H NMR spectra are in agreement with solid state structures.

4. Supplementary data

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 150462 for compound **I**, CCDC No. 150463 for compound **II** and CCDC No. 150464 for compound **III**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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