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Oxo- and Sulfido *N,N*-Diethylcarbamates of Niobium(V): Synthesis, Characterization and DFT Study

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The *N,N*-diethylcarbamates NbE(O₂CNEt₂)₃, E = O, S, have been prepared in high yields by treating NbOCl₃ or NbSCl₃(CH₃CN)₂ with CO₂/NH₂Et₂ in toluene at *ca.* -10°C. The products have been characterized by spectroscopic techniques, elemental analysis and by X-ray diffractometry in the case of NbO(O₂CNEt₂)₃. The molecular structure of the latter consists of a niobium centre coordinated to the oxo moiety and six O-atoms belonging to bridging and bidentate carbamates, in a slightly distorted pentagonal

bipyramidal arrangement. The structures of both NbE(O₂CNEt₂)₃ compounds have been reproduced by DFT calculations, showing substantial similarity despite the different nature of the chalcogen atom.

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Introduction

Based on the Ahrlund, Chatt and Davies classification of metal ions into two groups according to their preference for various ligands,^[1] in 1963 R. G. Pearson generalized the correlation and noted that small and not very polarizable type (a) metal ions preferred the coordination of Lewis bases that were also small and less polarizable.^[2] Such acids and bases were called hard to distinguish them from large and polarizable species which were called soft. An empirical relationship could be qualitatively expressed by the statement: *hard acids prefer to bind hard bases and soft acids prefer soft bases.*^[2]

In apparent contrast with the previous statement, Merbach and coworkers reported that the stability of MX₅(ER₂) (M = Nb, Ta; X = Cl, Br; E = O, S) increased on passing from X = Br to X = Cl, and on increasing the atomic weight of the chalcogen.^[3]

Recently, Levason and coworkers prepared thio and selenoether coordination compounds of MX₅ (M = Nb, Ta; X = F, Cl, Br),^[4] and observed that, in the case of tantalum,^[4c] the chloro and bromo derivatives were stable under controlled atmosphere. Conversely TaF₅ provided scarcely-stable compounds, which partially dissociated in non-coordinating solvents.

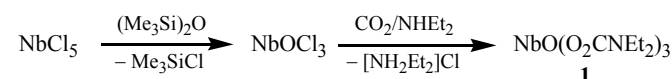
MOX₃ derivatives (M = Nb, Ta) are known for all the halides even if the literature reports are rather sparse,^[5] whilst the sulfido-fluorides MSF₃ have not been described so far. On the other hand, ME(*E,E*)₃ (*E,E* = anionic bidentate ligand) compounds have been

reported for all the possible combinations of hard/soft metal-ligated atoms. Examples are: NbO(*O,O*-tropolonato)₃,^[6] NbO(*O,O*-pyridinolato-*N*-oxide)₃,^[7] NbO(*O,O*-8-hydroxyquinolinato)₃,^[8] NbO(S₂CNEt₂)₃,^[9] and ME(S₂CNEt₂)₃^[10] (M = Nb, Ta; E = O, S). This series does not include dialkylcarbamato species. Therefore, in view of our recent interest in the chemistry of niobium and tantalum pentahalides^[11] and related penta-*N,N*-dialkylcarbamates,^[12] we decided to investigate the possibility of obtaining oxido- and sulfido-dialkylcarbamato Nb(V) derivatives.

In this paper, we report the synthesis of stable NbE(O₂CNEt₂)₃ (E = O, S) compounds by reaction of the readily available chloride precursors NbECl₃^[13, 14] with CO₂/NH₂Et₂ in hydrocarbon medium.^[15] DFT calculations have been performed in order to allow a structural comparison between the two new systems.

Results and Discussion.

The oxocarbamate NbO(O₂CNEt₂)₃, **1**, was prepared by the reaction of NbOCl₃ with CO₂/NH₂Et₂ in toluene, according to Scheme 1. After 24 h stirring at room temperature, the mixture was removed of [NH₂Et₂]Cl by filtration, then **1** was obtained in good yield as colourless precipitate upon concentration of the solution and addition of heptane.



Scheme 1. Synthesis of NbO(O₂CNEt₂)₃.

Compound **1** is stable in air for short periods of time and releases CO₂ upon treatment with diluted acids. It has been fully characterized by means of IR and NMR spectroscopy and elemental analysis. Moreover, the molecular structure has been ascertained by X ray diffraction (Figure 1 and Table 1).

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Figure 1. View of the molecular structure of NbO(O₂CNEt₂)₃, **1**. Displacement ellipsoids are at the 50% probability level.

Table 1. Selected bond distances (Å) and angles (°) for **1**.

| | | | |
|-----------------|-------------|------------------|-------------|
| Nb(1)–O(1) | 1.704(4) | Nb(1)–O(7) | 2.029(4) |
| Nb(1)–O(5) | 2.131(4) | Nb(1)–O(3) | 2.142(4) |
| Nb(1)–O(6) | 2.149(4) | Nb(1)–O(4) | 2.169(4) |
| Nb(1)–O(9) | 2.224(4) | Nb(2)–O(2) | 1.716(4) |
| Nb(2)–O(10) | 2.024(4) | Nb(2)–O(14) | 2.127(4) |
| Nb(2)–O(13) | 2.145(4) | Nb(2)–O(12) | 2.154(4) |
| Nb(2)–O(11) | 2.178(4) | Nb(2)–O(8) | 2.226(5) |
| O(3)–C(1) | 1.288(7) | O(4)–C(1) | 1.281(7) |
| C(1)–N(1) | 1.339(8) | O(5)–C(6) | 1.299(7) |
| O(6)–C(6) | 1.297(7) | C(6)–N(2) | 1.322(8) |
| O(7)–C(11) | 1.311(7) | O(8)–C(11) | 1.258(7) |
| C(11)–N(3) | 1.318(9) | O(9)–C(16) | 1.277(7) |
| O(10)–C(16) | 1.304(7) | C(16)–N(4) | 1.327(8) |
| O(11)–C(21) | 1.305(7) | O(12)–C(21) | 1.295(7) |
| C(21)–N(5) | 1.323(8) | O(13)–C(26) | 1.296(7) |
| O(14)–C(26) | 1.296(7) | C(26)–N(6) | 1.320(8) |
| O(1)–Nb(1)–O(9) | 173.69(18) | O(2)–Nb(2)–O(8) | 175.15(18) |
| O(7)–Nb(1)–O(9) | 88.54(16) | O(10)–Nb(2)–O(8) | 87.25(16) |
| O(1)–Nb(1)–O(7) | 96.98 (19) | O(1)–Nb(1)–O(5) | 97.37 (19) |
| O(1)–Nb(1)–O(3) | 94.54 (18) | O(1)–Nb(1)–O(6) | 97.00 (18) |
| O(1)–Nb(1)–O(4) | 98.04 (18) | O(1)–Nb(1)–O(9) | 173.69 (18) |
| O(3)–Nb(1)–O(4) | 61.03 (15) | O(3)–Nb(1)–O(6) | 137.39 (16) |
| O(3)–Nb(1)–O(9) | 79.25 (15) | O(5)–Nb(1)–O(3) | 76.28 (16) |
| O(7)–Nb(1)–O(3) | 139.07 (17) | O(7)–Nb(1)–O(6) | 79.73 (16) |
| O(7)–Nb(1)–O(5) | 140.06 (16) | O(7)–Nb(1)–O(9) | 88.54 (16) |
| O(7)–Nb(1)–O(4) | 78.49 (16) | | |

Compound **1** displays a dinuclear structure containing four chelating and two bridging carbamates as well as two terminal oxo-ligands. Each Nb-centre is seven coordinate, being bonded to seven oxygen atoms that form a distorted pentagonal bipyramid. A similar geometry has been found in the mononuclear complex NbO(O,*O*-tropolonato)₃^[6] and in other similar complexes.^[7, 8] Thus, each Nb atom is bonded to one oxo, two chelating and two bridging carbamate ligands. The two chelating and one of the two bridging carbamates are located in the equatorial plane of the pentagonal bipyramid, whereas the terminal oxo-ligand and the second bridging carbamate occupy the two axial positions. As expected, the Nb(1)–O(1) [1.704(4) Å] and Nb(2)–O(2) [1.716(4) Å] distances, which possess a double bond character, are considerably shorter than all other Nb–O interactions [2.024(4)–2.226(5) Å] involving the carbamate ligands. The longest Nb–O distances are those trans to the oxo-ligand [Nb(1)–O(9) 2.224(4) Å; Nb(2)–O(8) 2.226(5) Å], in view of the *trans* influence of the latter. The two Nb-atoms and the two bridging carbamate ligands form a non-planar 1,5-dimetalla-octa-cycle, with the two oxo-ligands in equatorial positions and the chelating carbamates in axial ones. The metric within the carbamate ligands is similar to that available in the literature.^[15]

The salient IR feature found for complex **1** (solid state) regards the absorption due to the carbamate moieties, falling in the range 1600–1400 cm⁻¹, in accordance with the bidentate coordination mode. Moreover, a strong absorption is present at 840 cm⁻¹, which has been assigned to the Nb=O stretching vibration.^[16]

The ¹H NMR spectrum of **1** shows the resonances typical of transition metal-bonded diethylcarbamates.^[15] Particularly informative is the ¹³C NMR spectrum which shows two resonances at 162.0 and 168.1 ppm, assigned to the two non equivalent types of carbamates (i.e. bridging and terminal).

The optimized structure of **1** (obtained by two distinct DFT methods) is dinuclear and in a rather good agreement (see Table 2) with the experimental determination. A view of the calculated structure is reported in Figure S1 given as Supporting Information.

Table 2. Selection of observed (X-ray) and calculated (DFT EDF2) distances (Å) and angles (°) for Nb₂(O)₂(O₂CNEt₂)₆, **1**

| | Observed | Calculated |
|------------------|------------|------------|
| Nb(1)–O(1) | 1.704(4) | 1.729 |
| Nb(2)–O(2) | 1.716(4) | 1.730 |
| Nb(1)–O(3) | 2.142(4) | 2.158 |
| Nb(1)–O(4) | 2.169(4) | 2.166 |
| Nb(1)–O(7) | 2.029(4) | 2.047 |
| Nb(1)–O(9) | 2.224(4) | 2.296 |
| Nb(2)–O(8) | 2.226(5) | 2.293 |
| Nb(2)–O(10) | 2.024(4) | 2.047 |
| Nb(2)–O(13) | 2.145(4) | 2.193 |
| Nb(2)–O(14) | 2.127(4) | 2.163 |
| O(7)–C(11) | 1.311(7) | 1.305 |
| O(8)–C(11) | 1.258(7) | 1.251 |
| O(11)–C(21) | 1.305(7) | 1.285 |
| O(12)–C(21) | 1.295(7) | 1.288 |
| O(1)–Nb(1)–O(7) | 96.98 (19) | 96.4 |
| O(1)–Nb(1)–O(9) | 173.69(18) | 174.6 |
| O(1)–Nb(1)–O(3) | 94.54 (18) | 96.6 |
| O(1)–Nb(1)–O(4) | 98.04 (18) | 97.3 |
| O(2)–Nb(2)–O(8) | 175.15(18) | 173.9 |
| O(10)–Nb(2)–O(8) | 87.25(16) | 88.9 |

In view of the reactivity usually exhibited by *N,N*-dialkylcarbamates with protic species,^[15] we treated the previously reported Nb(O₂CNEt₂)₅ with controlled amounts of water. Hydrolysis of two carbamate moieties according to Scheme 2 would provide an alternative synthetic route to compound **1**.



Scheme 2. Synthesis of NbO(O₂CNEt₂)₃, **1**, via hydrolysis of Nb(O₂CNEt₂)₅.

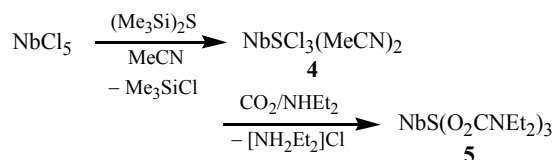
A fast reaction occurred with evolution of two equivalents of carbon dioxide, thus a compound of composition (C, H, N and Nb analysis) Nb₂O₃(O₂CNEt₂)₄, **2**, was obtained after work up (see Experimental). IR and NMR spectra resemble those of the tantalum cage Ta₈O₁₂(O₂CNEt₂)₁₆.^[17] Unfortunately, we were not able to grow crystals of **2** suitable for a X-ray analysis, therefore the exact nature of such hydrolysis product could not be ascertained.

During one of these attempts we got colourless crystals of the starting material Nb(O₂CNEt₂)₅, **3**. The ORTEP representations of the molecular structure of **3** is shown in Figure 2, whereas relevant bond lengths and angles are reported in Table S1 given as Supplementary Material.

Figure 2. View of the molecular structure of Nb(O₂CNEt₂)₅, **3**. Displacement ellipsoids are at the 50% probability level.

The crystals of Nb(O₂CNEt₂)₅ are isomorphous with regard to Ta(O₂CNEt₂)₅.^[18] The Nb-centre is eight-coordinate, surrounded by eight oxygen atoms of two mono- and three bi-dentate carbamate ligands in a slightly distorted square-antiprismatic geometry. The two mono-dentate carbamate ligands are in a relative trans arrangement with the O(9)–Nb(1)–O(7) angle [151.71(5)°] almost identical to the one found in the isostructural Ta(O₂CNEt₂)₅ [151.7(2)°]. Conversely, the previously reported X-ray structure of the related complex Nb(O₂CNMe₂)₅^[19] displays the two monodentate carbamates in mutual *cis* position [O–Nb–O 90.5(7)°] and the NbO₈ moiety which does not correspond to any idealized MX₈ polyhedron. In **3**, the Nb–O distances for the two monodentate ligands [Nb(1)–O(9) 1.9695(12) Å; Nb(1)–O(7) 1.9752(12) Å] are considerably shorter than the ones involving bidentate carbamates [2.1034(12)–2.1546(12) Å], as previously found in both Ta(O₂CNEt₂)₅ and Nb(O₂CNMe₂)₅.

The sulfido derivative NbSCl₃, in the form of the bis(acetonitrile) adduct NbSCl₃(MeCN)₂, **4**,^[14] slowly reacts with CO₂/NHET₂ in toluene at room temperature affording a pale-brown suspension after 24 h stirring at room temperature, see Scheme 3. After separation from the ammonium salt, the sulfidocarbamate NbS(O₂CNEt₂)₃, **5**, was isolated in good yield. Compound **5**, once isolated in the solid state, results quite insoluble in the common organic solvents, is stable in air for short period of times and, likewise **1**, readily releases carbon dioxide by treatment with diluted acids.



Scheme 3. Synthesis of NbS(O₂CNEt₂)₃, **5**.

The spectroscopic features of **5** are rather similar to those of **1**: absorptions due to bidentate carbamates are observed in the 1600–1450 cm⁻¹ region in the IR spectrum, while the ¹³C-NMR spectrum shows two well defined resonances at 161.9 and 168.0 ppm. The medium-strong IR absorption at 502 cm⁻¹ has been assigned to the Nb=S stretching vibration, coherently with literature reports (the corresponding value for NbS(S₂CNEt₂)₃ is 497 cm⁻¹^[10]).

The spectroscopic data suggest for compound **5** a structure similar to that of compound **1**. We did several attempts to grow X-ray quality crystals of **5**, but the limited solubility in common organic solvents frustrated our attempts.

Due to the good agreement between the observed and the calculated data reported in Table 2, we carried out a DFT study in order to gain an optimized structure for the sulfido derivative **5**.

Both the DFT methods employed gave comparable results, hence a view of the calculated structure is reported in Figure 3, while Table 3 lists a selection of calculated bond distances and angles. According to the computational outcomes, **5** bears a dinuclear structure rather similar to that of **1**, with two bridging-carbamates, four terminal bidentate carbamates and two Nb=S units.

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Figure 3. View of the calculated structure of Nb₂S₂(O₂CNEt₂)₆, **5**.

Table 3. Selection of DFT-calculated distances (Å) and angles (°) for Nb₂S₂(O₂CNEt₂)₆, **5**.

| | | | |
|-----------------|-------|------------------|-------|
| Nb(1)–S(1) | 2.183 | Nb(2)–S(2) | 2.183 |
| Nb(1)–O(5) | 2.036 | Nb(2)–O(6) | 2.263 |
| Nb(1)–O(7) | 2.266 | Nb(2)–O(8) | 2.037 |
| Nb(1)–O(1) | 2.164 | Nb(2)–O(11) | 2.167 |
| Nb(1)–O(2) | 2.186 | Nb(2)–O(12) | 2.161 |
| Nb(1)–O(3) | 2.168 | Nb(2)–O(9) | 2.187 |
| Nb(1)–O(4) | 2.163 | Nb(2)–O(10) | 2.263 |
| S(1)–Nb(1)–O(1) | 96.1 | S(2)–Nb(2)–O(9) | 99.6 |
| S(1)–Nb(1)–O(2) | 99.6 | S(2)–Nb(2)–O(10) | 96.3 |
| S(1)–Nb(1)–O(7) | 173.3 | S(2)–Nb(2)–O(11) | 97.8 |
| S(1)–Nb(1)–O(5) | 98.4 | S(2)–Nb(2)–O(12) | 95.9 |
| S(1)–Nb(1)–O(3) | 95.9 | S(2)–Nb(2)–O(8) | 98.7 |
| S(1)–Nb(1)–O(4) | 97.6 | O(10)–Nb(2)–O(8) | 173.4 |

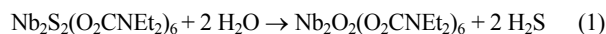
Once corrected for the difference between the covalent radius of sulfur and oxygen (0.35 Å),^[20] the Nb–S distance (2.183 Å) in **5** is similar to the Nb–O separation observed in **1** (average value 1.710 Å, X-ray). This result suggests a comparable Nb–E (E = O, S) bond order in **1** and **5**, respectively. The coordination sphere at niobium, and the bond distances between niobium and the oxygen atoms of the carbamates are similar to those observed in **1**.

Conclusions

Stable dinuclear oxo- and sulfido carbamates of niobium(V), Nb₂(E)₂(O₂CNEt₂)₆ (E = O, S), are easily obtained by treatment of the NbECl₃ precursors with CO₂/NHET₂ in toluene.

The structure of Nb₂O₂(O₂CNEt₂)₆ shows the presence of bridging and terminal bidentate carbamates and terminal Nb-oxygen double bonds. Based on DFT calculations, a similar structure has been found for the sulfido derivative.

The isolation of the latter confirms the previous observations that “hard” O-ligands may coexist with a “soft” S-ligand in high valent Nb(Ta) species. In fact both Nb₂E₂(O₂CNEt₂)₆ (E = O, S) resist thermal treatment; however, the calculated enthalpy variation for the reaction reported in equation (1) is –58.6 kJ mol⁻¹ (in the gas phase) and –46.0 kJ mol⁻¹ when solvation is added.



In consideration of the higher strength of the O–H bond in H₂O (464.4 kJ mol⁻¹)^[21] with respect to the S–H bond in H₂S (338.9 kJ mol⁻¹),^[21] the computer outcomes indicates that the niobium(V) cation has some larger affinity for the hard oxygen dianion rather than for the soft sulfido species.^[22] More in detail, the difference between the Nb=O and the Nb=S bond energies based on equation (1) corresponds to 192.4 kJ mol⁻¹. This value resembles the difference between the P=O and P=S bond dissociation energies measured respectively in POCl₃ and PSCl₃ (167.4 kJ mol⁻¹).^[21]

Experimental Section

General Considerations.

All manipulations of compounds were performed under atmosphere of pre-purified nitrogen using standard Schlenk techniques. The reaction vessels were oven dried at 150 °C prior to use, evacuated (10⁻² mmHg) and then filled with nitrogen. Commercial NbCl₅ (Strem, 99+%) was stored under argon atmosphere as received. NbOCl₃^[13a] and Nb(O₂CNEt₂)₅^[18] were prepared according to literature methods. (Me₃Si)₂O and (Me₃Si)₂S (Sigma-Aldrich) were used as received without further purification. CH₂Cl₂ and CH₃CN were distilled before use under nitrogen atmosphere from P₄O₁₀, while toluene, toluene-d₈ and heptane were distilled from sodium metal. A water-saturated toluene solution was prepared by stirring a biphasic toluene-water system for 15 h at 25 °C. The concentration of water in toluene was assumed to be 2.4 10⁻² M.^[23] Infrared spectra were recorded at 298 K on FT IR-Perkin Elmer Spectrum One Spectrometer, equipped with UATR sampling accessory, or on FT IR-Perkin Elmer Spectrum 100 Spectrometer, equipped with Csl beam splitter. NMR measurements were recorded on Varian Gemini 200BB instrument at 298 K, unless otherwise specified. The chemical shifts for ¹H and ¹³C were referenced to the non-deuterated aliquot of the solvent. Niobium was analyzed as Nb₂O₅ obtained by high temperature treatment of the solid sample with HNO₃ solution, followed by calcination in a platinum crucible.

Preparation of NbO(O₂CNEt₂)₃, **1.** A solution of NHET₂ (1.90 ml, 18.4 mmol) in toluene (50 ml) was treated with CO₂. When the absorption of gas ceased, the solution was cooled at ca. –10 °C and treated with 0.570 g (2.63 mmol) of NbOCl₃. The solution immediately turned orange and evolution of gas was noticed. While warming to room temperature, the colour of the solution turned from orange to colourless. After 24 h stirring at room temperature, the reaction mixture was filtered and the colourless solid (NH₂Et₂Cl, 0.82 g, 95% yield) was washed with toluene (2 x 10 ml). The volume of the collected colourless solution was reduced to ca. 10 ml and the residue was treated with heptane (30 ml). The colourless microcrystalline solid product was recovered by filtration and dried *in vacuo* at room temperature. Yield 0.87 g, 72%. Anal. Calcd. for C₁₅H₃₀N₃NbO₇: C, 39.39; H, 6.61; N, 9.19;

Nb, 20.32; CO₂, 28.88. Found: C, 38.68; H, 6.41; N, 8.95; Nb, 20.01; CO₂, 28.43. IR (solid state, cm⁻¹): 2974w, 2935w, 2876w, 1620m, 1576s, 1558s, 1484, 1433vs, 1380m, 1321s, 1301s, 1209m, 1100w-m, 1074m, 1022w, 977w-m, 929vs, 840s, 782s. ¹H NMR (toluene-d₈) δ 0.86 (m, 18 H, CH₃); 3.03 (m, 12 H, CH₂) ppm. ¹³C{¹H} NMR (toluene-d₈) δ 12.1, 13.1 (CH₃), 39.5, 41.7 (CH₂), 162.0, 168.1 (CO) ppm.

Crystals suitable for a X-ray analysis were grown from toluene/hexane mixture at ca. -30 °C.

Reaction of Nb(O₂CNEt₂)₅, **3, with H₂O.** A solution of Nb(O₂CNEt₂)₅ (0.25 g, 0.38 mmol) in toluene (5 ml) was treated with a saturated solution of H₂O in toluene (16 ml, corresponding to 0.38 mmol of H₂O). A fast reaction was observed with evolution of gas (CO₂ was evolved up to CO₂/Nb molar ratio = 2,6). After 24 h stirring at room temperature, the volume of the solution was reduced to 5 ml and the residue was treated with heptane. A solid of composition Nb₂O₃(O₂CNEt₂)₄, **2**, was recovered by filtration and dried in vacuo (yield 0.88 g). Anal. Calcd. for C₂₀H₄₀N₄Nb₂O₁₁: C, 34.40; H, 5.77; N, 8.02; Nb, 26.61; CO₂, 25.12. Found: C, 33.81; H, 5.21; N, 8.65; Nb, 25.79; CO₂, 24.82. IR (solid state, cm⁻¹): 2973m, 2933m, 1651w, 1538vs, 1508s, 1460s, 1433m, 1380m, 1330s, 1209m, 1100w-m, 1076m, 979w, 840s, 782s. ¹H NMR (toluene-d₈) δ 1.30-1.05 (broad m, 3 H, CH₃), 3.30-3.40 (broad m, 2 H, CH₂) ppm. ¹³C{¹H} NMR (toluene-d₈) δ 13.1 (broad, CH₃), 42.5 (broad, CH₂), 161.5, 155.3 (CO) ppm.

Preparation of NbSCl₃(CH₃CN)₂, **4.** Compound **4** was prepared according to a slight modification of the published procedure.^[14] A suspension of NbCl₅ (2.83 g, 10.5 mmol) in MeCN (20 ml) was cooled at ca. -30 °C and added of (Me₃Si)₂S (2.37 ml, 10.5 mmol). At the end of the addition (1 h), the green solution was allowed to warm to room temperature, and the stirring was maintained for additional 36 h. The colour of the solution turned pale green. The volume of the solution was reduced to 5 ml, heptane was added and the suspension was stirred at room temperature overnight. The solid was recovered by filtration, dried in vacuo at room temperature and identified as NbSCl₃(CH₃CN)₂ (analytical and IR data).

Preparation of NbS(O₂CNEt₂)₃, **5.** A solution of NH₄Et₂ (4.01 ml, 38.8 mmol) in toluene (100 ml) was treated with CO₂. When the absorption of gas ceased, the solution was cooled at ca. -10 °C and treated with 1.96 g (6.25 mmol) of NbSCl₃(CH₃CN)₂. While warming to room temperature, the colour of the solution turned from green to brown. After 24 h stirring at room temperature, the reaction mixture was filtered and the colourless solid (NH₂Et₂Cl, 1.94 g, 94% yield) was washed with toluene (2 x 10 ml). The volume of the collected colourless solution was reduced to ca. 10 ml and the residue was treated with heptane (30 ml). The product was recovered as pale-brown microcrystalline solid by filtration and dried *in vacuo* at room temperature. Yield 2.24 g (76% yield). Anal. Calcd. for C₁₅H₃₀N₃NbO₆S: C, 38.06; H, 6.39; N, 8.88; Nb, 19.63; CO₂, 27.90. Found: C, 37.69; H, 6.22; N, 8.78; Nb, 19.20; CO₂, 27.52. IR (solid state, cm⁻¹): 2975w, 2935w, 2875w, 1613m, 1575vs, 1558vs, 1485vs, 1456s, sh, 1432vs, 1378m, 1321s, 1302vs, 1207m, 1092m, 1075m, 980w-m, 931m-s, 888w, 839m-s, 781s. IR (Nujol mull, cm⁻¹): 1615vs, 1579vs, 1487vs, 1460vs, 1378vs, 1323vs, 1306vs, 1209m-s, 1164w-m, 1094m, 1076m, 981m, 932m-s, 890w-m, 840m-s, 792m-s, 722m, 648s, 616m, 502m. ¹H NMR (toluene-d₈) δ 1.27 (m, 18 H, CH₃), 3.24 (m, 12 H, CH₂) ppm. ¹³C{¹H} NMR (toluene-d₈) δ 11.4, 13.7 (CH₃), 39.5, 42.8 (CH₂), 161.9, 168.0 (CO) ppm.

X-ray Crystallographic Study. Crystal data and collection details for Nb₂(O)₂(O₂CNEt₂)₆, **1**, and Nb(O₂CNEt₂)₅, **3**, are listed in Table 4. Crystals of **3** suitable for X-ray analysis were collected by slow cooling to ca. -30 °C of a saturated heptane solution. The diffraction experiments were carried out on a Bruker APEX II diffractometer

equipped with a CCD detector and using Mo-Kα radiation. Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS).²⁴ Structures were solved by direct methods and refined by full-matrix least-squares based on all data using *F*².²⁵ All non-hydrogen atoms were refined with anisotropic displacement parameters. H-atoms were placed in calculated positions and treated isotropically using a riding model. One NEt₂ group in Nb(O₂CNEt₂)₅ and one Et group in Nb₂(O)₂(O₂CNEt₂)₆ are disordered over two positions. Disordered atomic positions were split and refined anisotropically using one occupancy parameter per disordered group. Similar *U* restraints (*s.u.* 0.01) were applied to the C atoms in Nb(O₂CNEt₂)₅ and to the disordered Et-group of Nb₂(O)₂(O₂CNEt₂)₆. The geometries of the two images of the disordered NEt₂ group in Nb(O₂CNEt₂)₅ were restrained to be similar (SAME line in SHELXL, *s.u.* 0.01). The C–C distances in the disordered Et-group of Nb₂(O)₂(O₂CNEt₂)₆ were restrained to 1.53 Å (*s.u.* 0.01).

Table 4. Crystal data and details of the structure refinement for Nb(O₂CNEt₂)₅ and Nb₂(O)₂(O₂CNEt₂)₆.

| Complex | Nb(O ₂ CNEt ₂) ₅ | Nb ₂ (O) ₂ (O ₂ CNEt ₂) ₆ |
|----------------------------------------------------|------------------------------------------------------------------|-----------------------------------------------------------------------------------|
| Formula | C ₂₅ H ₅₀ N ₅ NbO ₁₀ | C ₃₀ H ₆₀ N ₆ Mo ₂ O ₁₄ |
| <i>F</i> _w | 673.61 | 914.66 |
| <i>T</i> , K | 100(2) | 100(2) |
| <i>λ</i> , Å | 0.71073 | 0.71073 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | <i>P</i> 2 ₁ / <i>n</i> | <i>P</i> 2 ₁ / <i>c</i> |
| <i>a</i> , Å | 13.3651(17) | 19.331(3) |
| <i>b</i> , Å | 17.254(2) | 11.4620(17) |
| <i>c</i> , Å | 14.6917(19) | 19.838(3) |
| <i>β</i> , ° | 101.835(2) | 107.410(2) |
| Cell Volume, Å ³ | 3315.8(7) | 4194.3(11) |
| <i>Z</i> | 4 | 4 |
| <i>D</i> _c , g cm ⁻³ | 1.349 | 1.448 |
| <i>μ</i> , mm ⁻¹ | 0.419 | 0.612 |
| <i>F</i> (000) | 1424 | 1904 |
| Crystal size, mm | 0.23×0.21×0.15 | 0.16×0.15×0.13 |
| <i>θ</i> limits, ° | 1.84–27.00 | 1.10–26.00 |
| Reflections collected | 27099 | 38956 |
| Independent reflections | 7229 [<i>R</i> _{int} = 0.0271] | 8248 [<i>R</i> _{int} = 0.1307] |
| Data / restraints / parameters | 7229 / 118 / 416 | 8248 / 32 / 488 |
| Goodness on fit on <i>F</i> ² | 1.031 | 1.039 |
| <i>R</i> ₁ (<i>I</i> > 2σ(<i>I</i>)) | 0.0278 | 0.0539 |
| <i>wR</i> ₂ (all data) | 0.0701 | 0.1418 |
| Largest diff. peak / hole, e Å ⁻³ | 0.466 / -0.466 | 0.974 / -0.892 |

Computational studies. The computational geometry optimisation of **1** and **5** was carried out without symmetry constraints, using the hybrid DFT EDF2 functional^[26] in combination with the LACVP** basis set.^[27] Geometry optimisations were also performed using the pure GGA functional PBE^[28] in combination with an atom-centred doubly-numerical polarized basis set and DFT semi-core pseudopotentials.^[29] Dispersion correction was added through the Grimme's approach^[30] and COSMO implicit solvation model for dichloromethane was added.^[31] The "restricted" formalism was applied in all the cases and the stationary points were characterized by IR simulations (harmonic approximation), from which zero-point vibrational energies were obtained.^[32] DFT EDF2 calculations were carried out using Spartan 08,^[33] while Dmol³ was used for PBE/COSMO calculations.^[34]

CCDC 922103 and CCDC 922104 contains the supplementary crystallographic data for **1** and **3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

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reactions: interactions of molecular fragments with metallic sites in unconventional species') for financial support.

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FIGURES

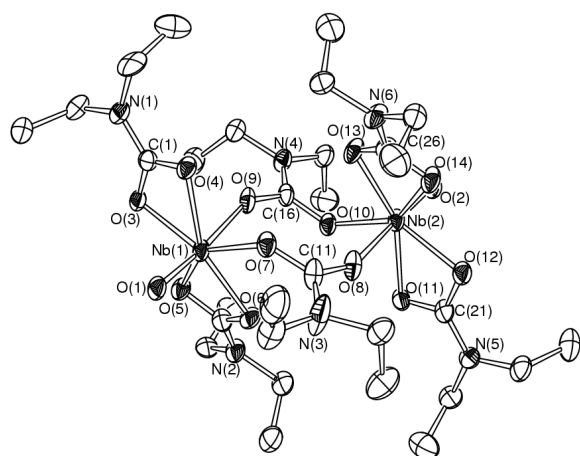


Figure 1. View of the molecular structure of $\text{Nb}_2(\text{O})_2(\text{O}_2\text{CNEt}_2)_6$, **1**. Displacement ellipsoids are at the 50% probability level.

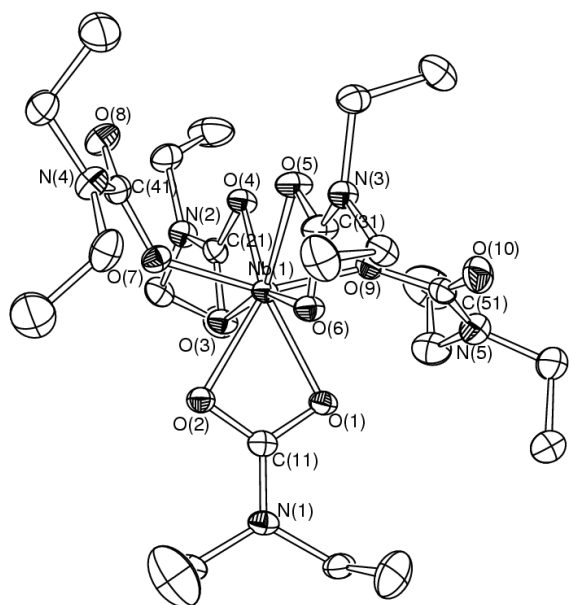


Figure 2. View of the molecular structure of $\text{Nb}(\text{O}_2\text{CNEt}_2)_5$, **3**. Displacement ellipsoids are at the 50% probability level.

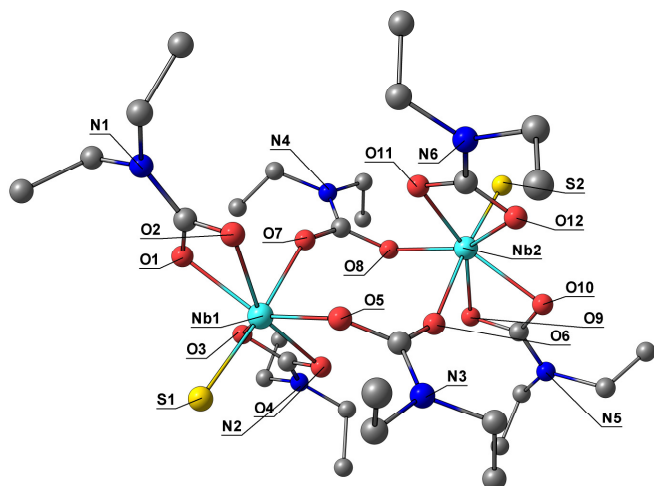
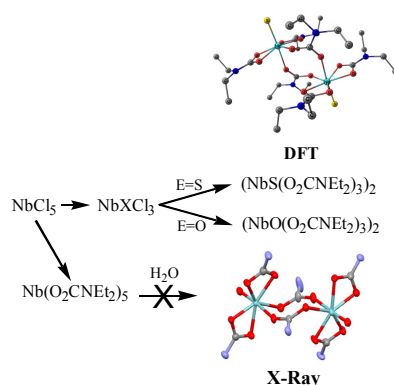


Figure 3. View of the calculated structure of $\text{Nb}_2\text{S}_2(\text{O}_2\text{CNEt}_2)_6$, **5**.

Entry for the Table of Contents

$\text{NbE}(\text{O}_2\text{CNEt}_2)_3$, $\text{E} = \text{O}, \text{S}$, have been prepared from NbECl_3 and fully characterized. The structures of both products have been optimized by DFT calculations.



**Marco Bortoluzzi, Franco Ghini,
Mohammad Hayatifar, Fabio Marchetti,
Guido Pampaloni,* Stefano Zacchini**

Oxo- and Sulfido *N,N*-Diethylcarbamates of Niobium(V): Synthesis, Characterization and DFT Study

Keywords: Niobium / *N,N*-dialkylcarbamates / Oxo ligand / Sulfido ligand / X-ray structure / DFT calculations

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Characterization and DFT Study**

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Zacchini

SUPPORTING INFORMATION

Figure S1: View of the calculated structure of $\text{Nb}_2\text{O}_2(\text{O}_2\text{CNET}_2)_6$, **1**.

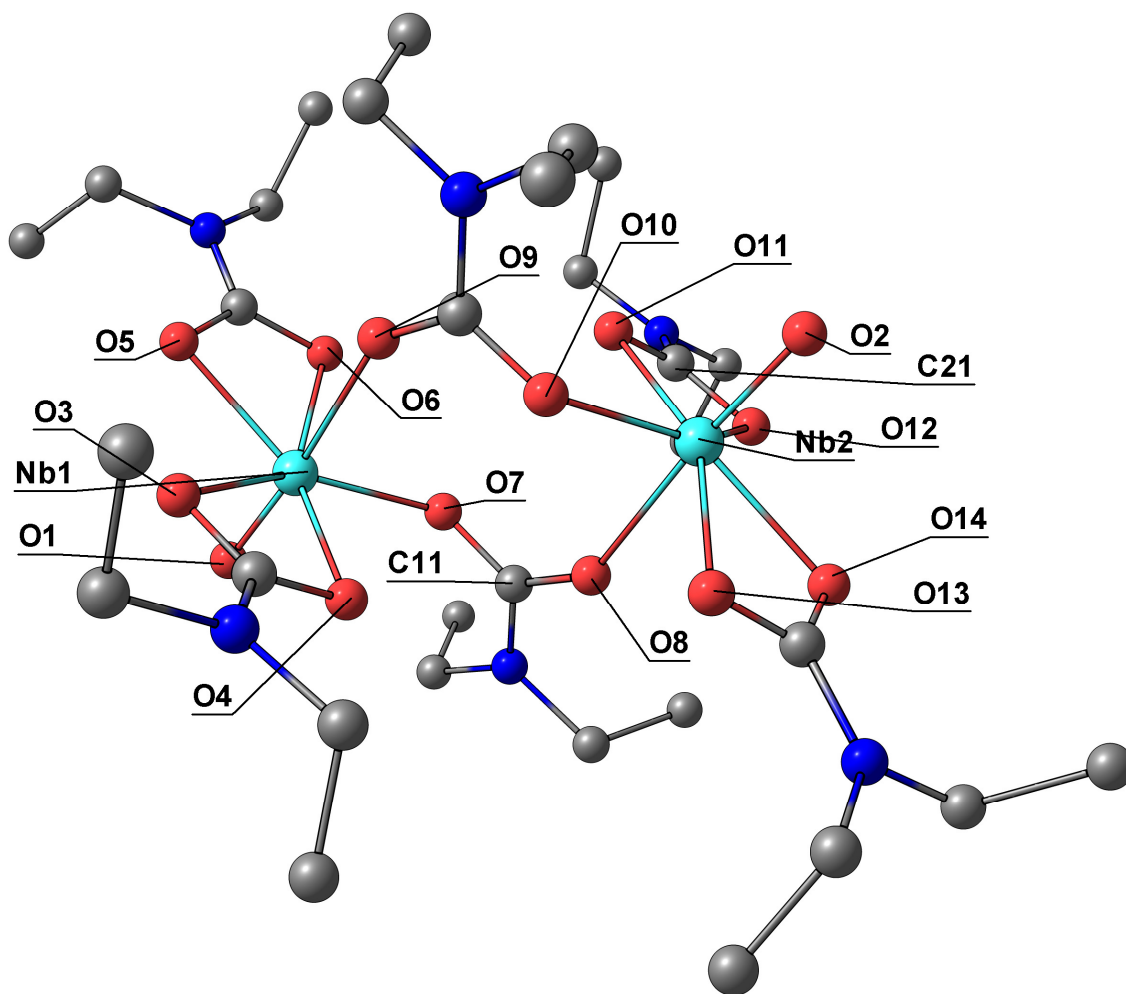


Table S1. Selected bond distances (Å) and angles (°) for Nb(O₂CNEt₂)₅, **3**.

| | | | |
|-----------------|------------|-----------------|------------|
| Nb(1)–O(9) | 1.9695(12) | Nb(1)–O(7) | 1.9752(12) |
| Nb(1)–O(6) | 2.1034(12) | Nb(1)–O(3) | 2.1065(11) |
| Nb(1)–O(1) | 2.1377(11) | Nb(1)–O(4) | 2.1484(11) |
| Nb(1)–O(2) | 2.1521(12) | Nb(1)–O(5) | 2.1546(12) |
| O(1)–C(11) | 1.294(2) | O(2)–C(11) | 1.286(2) |
| O(3)–C(21) | 1.306(2) | O(4)–C(21) | 1.282(2) |
| O(5)–C(31) | 1.287(2) | O(6)–C(31) | 1.297(2) |
| O(7)–C(41) | 1.338(2) | O(8)–C(41) | 1.218(2) |
| O(9)–C(51) | 1.345(2) | O(10)–C(51) | 1.213(2) |
| <hr/> | | | |
| O(9)–Nb(1)–O(7) | 151.71 (5) | O(9)–Nb(1)–O(6) | 93.07 (5) |
| O(7)–Nb(1)–O(6) | 92.64 (5) | O(9)–Nb(1)–O(3) | 93.11 (5) |
| O(7)–Nb(1)–O(3) | 91.96 (5) | O(6)–Nb(1)–O(3) | 157.82 (4) |
| O(9)–Nb(1)–O(1) | 74.97 (5) | O(7)–Nb(1)–O(1) | 133.32 (5) |
| O(6)–Nb(1)–O(1) | 78.87 (4) | O(3)–Nb(1)–O(1) | 82.22 (4) |
| O(9)–Nb(1)–O(4) | 76.96 (5) | O(7)–Nb(1)–O(4) | 81.08 (5) |
| O(6)–Nb(1)–O(4) | 140.54 (4) | O(3)–Nb(1)–O(4) | 61.64 (4) |
| O(1)–Nb(1)–O(4) | 132.29 (4) | O(9)–Nb(1)–O(2) | 135.33 (5) |
| O(7)–Nb(1)–O(2) | 72.95 (5) | O(6)–Nb(1)–O(2) | 81.14 (4) |
| O(3)–Nb(1)–O(2) | 79.51 (4) | O(1)–Nb(1)–O(2) | 60.42 (4) |
| O(4)–Nb(1)–O(2) | 132.11 (4) | O(9)–Nb(1)–O(5) | 79.57 (5) |
| O(7)–Nb(1)–O(5) | 78.95 (5) | O(6)–Nb(1)–O(5) | 61.42 (4) |
| O(3)–Nb(1)–O(5) | 140.73 (4) | O(1)–Nb(1)–O(5) | 131.05 (5) |
| O(4)–Nb(1)–O(5) | 79.16 (4) | O(2)–Nb(1)–O(5) | 131.58 (5) |
