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

The N,N-diethylcarbamates NbE(O_2CNEt)_3, E = O, S, have been prepared in high yields by treating NbOCl_3 or NbSCl_3(CH_2CN)_2 with CO_2/NHEt_2 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(O_2CNEt)_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(O_2CNEt)_3 compounds have been reproduced by DFT calculations, showing substantial similarity despite the different nature of the chalcogen atom.

Introduction

Based on the Ahrland, Chatt and Davies classification of metal ions into two groups according to their preference for various ligands,[3] 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.[5] Such acids and bases were called hard to distinguish 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.[5]

In apparent contrast with the previous statement, Merbach and coworkers reported that the stability of MX_3(ER_3) (M = Nb, Ta; X = Cl, Br; E = O, S) increases 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 MX_3 (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 TaF_3 provided scarcely-stable compounds, which partially dissociated in non-coordinating solvents.

MOX_3 derivatives (M = Nb, Ta) are known for all the halides even if the literature reports are rather sparse,[6] whilst the sulfido-fluorides MSF_3 have not been described so far. On the other hand, ME(E,E) (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-2-pyridinolato-N-oxide)_3,[7] NbO(O,O-8-hydroxyquinolinolato)_3,[8] NbO(S,S-CNEt)_3,[9] and ME(S,CNEt)_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(O_2CNEt)_3 (E = O, S) compounds by reaction of the readily available chloride precursors, NbECl_5.[13, 14] with CO_2/NHEt_2 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(O_2CNEt)_3, 1, was prepared by the reaction of NbOCl_3 with CO_2/NHEt_2 in toluene, according to Scheme 1. After 24 h stirring at room temperature, the mixture was removed of [NH_2Et_2]Cl by filtration, then 1 was obtained in good yield as colourless precipitate upon concentration of the solution and addition of heptane.

\[
\text{NbCl}_3 + (\text{Me}_3\text{Si})_2\text{O} \rightarrow \text{NbOCl}_3 + \text{Me}_3\text{SiCl}
\]

\[
\text{CO}_2 + \text{NHEt}_2 + \text{[NH}_2\text{Et}_2]\text{Cl} \rightarrow \text{NbO(O}_2\text{CNEt)}_3
\]

Scheme 1. Synthesis of NbO(O_2CNEt)_3.

Compound 1 is stable in air for short periods of time and releases CO_2 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).
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,OO-tropolonato)\(^{[6]}\) and in other similar complexes.\(^{[7, 8]}\)

Thus, each Nb atom is bonded to one oxo, two chelating and two bridging carbamates. 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) [1.714(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 carbamato 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 carbamato ligands is similar to that available in the literature.\(^{[9]}\)

The salient IR feature found for complex 1 (solid state) regards the absorption due to the carbamato 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.\(^{[10]}\)

The \(^{1}H\) NMR spectrum of 1 shows the resonances typical of transition metal-bonded diethylcarbamates.\(^{[11]}\) Particularly informative is the \(^{13}C\) 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>
<thead>
<tr>
<th>Table 1. Selected bond distances (Å) and angles (°) for 1.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond Distance</td>
</tr>
<tr>
<td>---------------</td>
</tr>
<tr>
<td>Nb(1)-O(1)</td>
</tr>
<tr>
<td>Nb(1)-O(5)</td>
</tr>
<tr>
<td>Nb(1)-O(6)</td>
</tr>
<tr>
<td>Nb(1)-O(9)</td>
</tr>
<tr>
<td>Nb(2)-O(10)</td>
</tr>
<tr>
<td>Nb(2)-O(13)</td>
</tr>
<tr>
<td>Nb(2)-O(11)</td>
</tr>
<tr>
<td>C(1)-O(11)</td>
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<tr>
<td>O(6)-C(16)</td>
</tr>
<tr>
<td>O(7)-C(11)</td>
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<tr>
<td>C(11)-N(3)</td>
</tr>
<tr>
<td>O(10)-C(16)</td>
</tr>
<tr>
<td>O(11)-C(21)</td>
</tr>
<tr>
<td>C(21)-N(5)</td>
</tr>
<tr>
<td>O(14)-C(26)</td>
</tr>
</tbody>
</table>

In view of the reactivity usually exhibited by N,N-dialkylcarbamates with protic species,\(^{[12]}\) we treated the previously reported NbO(O,OCNEt\(_2\))\(_3\) with controlled amounts of water. Hydrolysis of two carbamato moieties according to Scheme 2 would provide an alternative synthetic route to compound 1.

Scheme 2. Synthesis of NbO(O,OCNEt\(_2\))\(_3\), 1, via hydrolysis of NbO(O,OCNEt\(_2\)).

A fast reaction occurred with evolution of two equivalents of carbon dioxide, thus a compound of composition (C, H, N and Nb analysis) NbO(O,OCNEt\(_2\))\(_3\). 2, was obtained after work up (see Experimental). IR and NMR spectra resemble those of the tantalum cage TaO(O,OCNEt\(_2\))\(_2\)Cl\(_3\).\(^{[13]}\) 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 NbO(O,OCNEt\(_2\))\(_3\), 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 NbO(O,OCNEt\(_2\))\(_3\), 3. Displacement ellipsoids are at the 50% probability level.

The crystals of NbO(O,OCNEt\(_2\))\(_3\), are isomorphous with regard to TaO(O,OCNEt\(_2\))\(_2\)Cl\(_3\)\(^{[14]}\). The Nb-centre is eight-coordinate, surrounded by eight oxygen atoms of two mono- and three bi-dentate carbamato ligands in a slightly distorted square-antiprismic geometry. The two mono-dentate carbamato 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 isosctructural TaO(O,OCNEt\(_2\))\(_2\)Cl\(_3\).\(^{[15]}\) Conversely, the previously reported X-ray structure of the related complex NbO(O,NMe\(_2\))\(_2\)\(^{[16]}\) displays the two monodentate carbamates in mutual cis position [O–Nb–O 90.5(7)°] and the NbO\(_3\) moiety which does not correspond to any idealized MX\(_4\) 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 TaO(O,OCNEt\(_2\))\(_2\) and NbO(O,NMe\(_2\))\(_2\).
The sulfido derivative NbSCl₂, in the form of the bis(acetonitrile) adduct NbSCl₂(MeCN)₂, [4] 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 sulfocarbammato NbS₂O₂CNEt₂Cl₂, 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 NbS₂(O₂CNEt₂)₃, 5.](image)

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 NbS₂S₂O₂CNEt₂Cl₂ 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, with the corresponding value for NbS₂S₂O₂CNEt₂Cl₂ is 497 cm⁻¹ [10].

![Figure 3. View of the calculated structure of NbS₂(O₂CNEt₂)₃, 5.](image)

The figure has been placed at the end of the manuscript.

Table 3. Selection of DFT-calculated distances (Å) and angles (°) for NbS₂(O₂CNEt₂)₃, 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 |

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 bond 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), Nb₂E₃(O₂CNEt₂)₉ (E = O, S), are easily obtained by treatment of the NbECl₃ precursors with CO₂/NHEt₂ in toluene.

The structure of Nb₂O₂O₂CNEt₂₉ 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 Nb₂E₃(O₂CNEt₂)₉ (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.

![Scheme 4. Preparation of Nb₂E₃(O₂CNEt₂)₉, 1.](image)

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. 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 (10⁻³ mmHg) and then filled with nitrogen. Commercial NbCl₅ (Strem, 99+%) was stored under argon atmosphere as received. NbOCl₃ [21] and Nb₂O₃(O₂CNEt₂)₉ [18] were prepared according to literature methods. (Me₂S)₂O and (Me₂S)₂S (Sigma-Aldrich) were used as received without further purification. CH₂Cl₂ and CH₂CN were distilled before use under nitrogen atmosphere from P₂O₅, 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 10⁻⁵ 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)₉, 1. A solution of NbCl₅ (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 Nb₂O₂O₂CNEt₂₉ 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 C₃S₂H₉N₅NbO₅: C, 39.39; H, 6.61; N, 9.19;
Reaction of NbO$_2$(O$_2$CNEt)$_3$, with H$_2$O. A solution of NbO$_2$(O$_2$CNEt)$_3$ (0.25 g, 0.38 mmol) in toluene (5 ml) was treated with 1.96 g (6.25 mmol) of NbSCl$_2$ according to a slight modification of the published procedure. A fast reaction was observed with evolution of gas (CO$_2$ was evolved up to CO/Nb molar ratio = 2.6). After 2 h stirring at room temperature, the volume of the solution was reduced to 5 ml and the residue was treated with heptane. A solid was recovered by filtration, dried in vacuo at room temperature and identified as NbSCl$_2$.

Preparation of NbSCl$_2$(CH$_3$CN)$_3$. A solution of NbCl$_3$ (2.3 g, 10.5 mmol) in MeCN (20 ml) was cooled at ca. −30 °C and added of (Me$_3$Si)$_2$S (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 3 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 NbSCl$_2$(CH$_3$CN)$_3$ (analytical and IR data).

Preparation of NbSO$_2$(O$_2$CNEt)$_3$. A solution of NH$_4$Et$_2$ (4.01 ml, 38.8 mmol) in toluene (100 ml) was treated with CO$_2$. When the absorption of gas ceased, the solution was cooled at ca. −10 °C and treated with 1.96 g (6.25 mmol) of NbSCl$_2$(CH$_3$CN)$_3$. 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 (NH$_4$)NEt$_2$(O$_2$CNEt)$_3$ was recovered as pale-brown microcrystalline solid by filtration in vacuo.

X-ray Crystallographic Study. Crystal data and collection details for Nb$_2$O$_3$(O$_2$CNEt)$_3$·1, and Nb$_2$O$_3$(O$_2$CNEt)$_3$·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). Structures were solved by direct methods and refined by full-matrix least-squares based on all data using F2. 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 NEt$_2$ group in Nb$_2$O$_3$(O$_2$CNEt)$_3$·1, and one Et group in Nb$_2$O$_3$(O$_2$CNEt)$_3$·3, are disordered over two positions. Disordered atomic positions were split and refined anisotropically using one occupancy parameter per disordered group. Similar U restraint (s.u. 0.01) were applied to the C atoms in Nb$_2$O$_3$(O$_2$CNEt)$_3$, and to the disordered Et-group of Nb$_2$O$_3$(O$_2$CNEt)$_3$·3. The geometries of the two images of the disordered NEt$_2$ group in Nb$_2$O$_3$(O$_2$CNEt)$_3$ were restrained to be similar (SAME line in SHELXL, s.u. 0.01). The C–C distances in the disordered Et-group of Nb$_2$O$_3$(O$_2$CNEt)$_3$·3, were restrained to 1.53 Å (s.u. 0.01).

Table 4. Crystal data and details of the structure refinement for Nb$_2$O$_3$(O$_2$CNEt)$_3$·1 and Nb$_2$O$_3$(O$_2$CNEt)$_3$·3.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Nb$_2$O$_3$(O$_2$CNEt)$_3$·1</th>
<th>Nb$_2$O$_3$(O$_2$CNEt)$_3$·3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>Ca$_5$H$_9$N$_2$O$_5$</td>
<td>Ca$_5$H$_9$N$_2$MoO$_5$</td>
</tr>
<tr>
<td>F$_w$</td>
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<td>914.66</td>
</tr>
<tr>
<td>T</td>
<td>100(2)</td>
<td>100(2)</td>
</tr>
<tr>
<td>δ</td>
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</tr>
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<td>a, Å</td>
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<td>b, Å</td>
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<td>c, Å</td>
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<tr>
<td>Cell Volume, Å$^3$</td>
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<tr>
<td>D$_d$, g cm$^{-3}$</td>
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<td>μ, μm$^{-1}$</td>
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<td>1.10 - 26.00</td>
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<td>8248 [R$_{int}$ = 0.1307]</td>
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<tr>
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</tr>
<tr>
<td>wR$_2$ (all data)</td>
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<td>0.1418</td>
</tr>
<tr>
<td>Largest diff. peak / hole, e Å$^3$</td>
<td>0.466 / -0.466</td>
<td>0.974 / -0.892</td>
</tr>
</tbody>
</table>

Computational studies. The computational geometry optimisation of 1 and 5 was carried out without symmetry constraints, using the hybrid DFT ED2 functional [29] in combination with the LACVP basis set [30]. 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 pseudopot.

Dispersive correction was added through the Grimme’s approach [31] and COSMO implicit solvation model for dichloromethane was added. 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. DFT ED2 calculations were carried out using Spartan 08 [31], while Dmol$^3$ 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

The authors thank the Ministero dell’Istruzione, dell’Università e della Ricerca (PRIN 2009 project: ‘New strategies for the control of
reactions: interactions of molecular fragments with metallic sites in unconventional species”) for financial support.

References and note

[14] V. C. Gibson, A. Shaw, D. N. Williams, *Polyhedron* 1989, 8, 549-550. Compound 4 was prepared according to a modification of the published procedure, see Experimental.
[22] Compound 5 is stable in air for short periods of time but gas is released upon treatment with water. A precipitate formed upon such gas was allowed to pass through a water solution of BaO (test for CO₂) or HgCl₂ (test for HS).
FIGURES

Figure 1. View of the molecular structure of Nb₂(O)₆(O₂CNEt)₆, 1. Displacement ellipsoids are at the 50% probability level.

Figure 2. View of the molecular structure of Nb(O₂CNEt)₅, 3. Displacement ellipsoids are at the 50% probability level.

Figure 3. View of the calculated structure of Nb₂S₆(O₂CNEt)₆, 5.
Oxo and sulfido carbamates

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

\[ \text{NbE(O}_2\text{CNEt}_2)_3, \ E = O, \ S, \text{ have been prepared from NbECl}_3 \text{ and fully characterized. The structures of both products have been optimized by DFT calculations.} \]
Oxo- and Sulfido $N,N$-Diethylcarbamates of Niobium(V): Synthesis, Characterization and DFT Study

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

SUPPORTING INFORMATION
Figure S1: View of the calculated structure of Nb$_2$O$_2$(O$_2$CNEt$_2$)$_6$, 1.
<table>
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<tr>
<th>Bond/Angle</th>
<th>Value 1</th>
<th>Value 2</th>
<th>Value 3</th>
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