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Spectroscopic and structural characterizations of water-soluble peroxo complexes of niobium(V) with N-containing heterocyclic ligands

D. Bayot [a], M. Degand [a], B. Tinant [b], M. Devillers [a,*]

[a] Université Catholique de Louvain, Unité de Chimie des Matériaux Inorganiques et Organiques, Place Louis Pasteur 1/3, B-1348 Louvain-la-Neuve, Belgium
[b] Université Catholique de Louvain, Unité de Chimie Structurale et des Mécanismes Réactionnels, Place Louis Pasteur 1/3, B-1348 Louvain-la-Neuve, Belgium

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Abstract

New water-soluble heteroleptic peroxo complexes of niobium^{V} have been prepared with N-containing heterocyclic ligands. The compounds correspond to the general formula $(gu)_x[Nb(O_2)_3(L)]\cdot nH_2O$ (gu = guanidinium). Three different ligands (L) have been used: picolinic acid (Hpic), picolinic acid N-oxide (HpicO) and pyrazine 2,5-dicarboxylic acid (2,5-H_2pzdc). The Nb^{V} complexes have been characterized on the basis of elemental and thermal analysis as well as by IR and ESI-mass spectrometry. The crystal structure of the peroxo complex with the picolinato N-oxide ligand, $(gu)_2[Nb(O_2)_3(picO)]$ (**II**) has been determined, showing an eightfold-coordinated Nb atom surrounded by three peroxide groups and a picO ligand bound in a bidentate mode via the carboxylato and the N-oxide groups. The coordination polyhedron around the metal is a triangular dodecahedron.

Keywords: Peroxo complexes ; N-containing heterocyclic ligands; Niobium; Crystal structure

1. Introduction

In the last decade, peroxo species of transition metals (i.e., Mo, W, V, Nb) have attracted considerable attention because of their extended coordination chemistry as well as their role in several challenging domains. Peroxo species of d^0 transition metals, e.g., V^{V}, Ti^{IV}, Mo^{VI}, W^{VI} and Nb^{V}, are potential oxygen donors to organic substrates in the liquid phase [1–5]. They can act as stoichiometric oxidants or as catalysts in the presence of oxidizing agents, like H_2O_2 or *t*BuOOH, used to regenerate in situ the starting peroxo metal species. Such peroxo complexes can oxidize some electrophilic species and a large variety of nucleophilic substrates, such as phosphines, sulphides, alcohols, olefins, enolates, imines, amides, etc. [3]. A further interest in peroxo complexes results from the important role they play in biological systems. Peroxo vanadium^{V} complexes have been found to have anti-tumour and insulin mimetic activities, while others have been studied as functional models for the vanadium haloperoxidase enzymes [6,7]. Finally, because such peroxo-type coordination compounds are most of the time soluble in water, they are also of great interest as precursors for the preparation of oxide materials and more particularly, multimetallic oxides involving highly polarizing d^0 transition metals, like Ti^{IV}, Zr^{IV}, Nb^{V} or Ta^{V}, for which the availability of water-soluble compounds is very limited [8–13]. This ''peroxo way'' has recently been shown to be a valuable approach for the synthesis of mixed oxides containing niobium and/or tantalum from well defined and pre-isolated complexes [14,15].

The present work describes new water-soluble Nb^{V} peroxo compounds with N-containing heterocyclic ligands corresponding to the general formula $(A^{I})_x[Nb(O_2)_3(L)]\cdot nH_2O$ with A^{I} = guanidinium (gu, $CN_3H_6^+$). Three different ligands (L) have been used: picolinic acid (Hpic), picolinic acid N-oxide (HpicO) and pyrazine 2,5-dicarboxylic acid (2,5-H_2pzdc).

* Corresponding author. Tel.: +32 10 472831; fax: +32 10 472330.
E-mail address: devillers@chim.ucl.ac.be (M. Devillers).

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2. Experimental

2.1. General procedures

All the manipulations were carried out in aqueous solution. The heteroleptic peroxo Nb^V complexes were prepared by substituting peroxo groups by the heterocyclic ligand in the tetraperoxoniobate anion $[Nb(O_2)_4]^{3-}$. The homoleptic guanidinium tetraperoxoniobate complex, $(gu)_3[Nb(O_2)_4]$, was synthesized following a reported procedure [14].

Picolinic acid, Hpic (99%, Acros), picolinic acid N-oxide, HpicO (97%, Acros) and pyrazine 2,5-dicarboxylic acid, 2,5-H_2pzdc were commercial products used as received. Hydrogen peroxide, H_2O_2 (35 wt%, Acros) and ethanol were used without purification. Elemental analyses (C, H, N) were carried out at the University College of London. IR spectra in the 4000–400 cm^{-1} range were recorded on a FTS-135 Bio-RAD spectrometer, using KBr pellets containing ca. 1 wt% of the powder. Thermogravimetric analyses (TGA) were performed in air at the heating rate of 10°/min using a Mettler Toledo TGA/SDTA851^e analyser. The nano-electrospray ionization mass spectrometry (NESI-MS) measurements were obtained on a Finnigan MAT LCQ instrument (San Jose, CA). The samples were introduced by injection of the complex (0.001 mol L^{-1}) dissolved in CH_3OH/H_2O (1:1 vol.).

2.2. Preparation of the complexes

2.2.1. Preparation of $(gu)_2[Nb(O_2)_3(pic)]$ (*I*)

$(gu)_3[Nb(O_2)_4]$ (0.502 g, 1.25 mmol) was dissolved in 5 ml of distilled water and 5 ml of a 35 wt% H_2O_2 solution. The resulting clear solution was first cooled down with an ice bath before adding Hpic (0.154 g, 1.25 mmol) progressively and then, slowly warmed up to 60 °C for a few minutes. The addition of 25 ml of ethanol and storage at 5 °C for two days yielded a white precipitate which is eliminated as a hydrolysis product. The subsequent storage of the filtrate at 5 °C during 3 days provided small white needles which were filtered-off, washed with ethanol and air-dried. Yield 0.19 g, 31%. *Anal.* Calc. for $C_8H_{16}NbN_7O_8$: C, 22.27; H, 3.71; N, 22.74. Found: C, 22.03; H, 3.75; N, 22.46%.

2.2.2. Preparation of $(gu)_2[Nb(O_2)_3(picO)]$ (*II*)

$(gu)_3[Nb(O_2)_4]$ (0.502 g, 1.25 mmol) was dissolved in 5 ml of distilled water and 5 ml of a 35 wt% H_2O_2 solution. HpicO (0.183 g, 1.25 mmol) was then added and the resulting clear solution was warmed up to 60 °C for a few minutes. Upon cooling with an ice bath, small transparent monocrystals appeared, which were filtered-off and air-dried. Yield 0.42 g, 66%. *Anal.* Calc. for $C_8H_{16}NbN_7O_9$: C, 21.47; H, 3.57; N, 21.92. Found: C, 21.68; H, 3.54; N, 21.61%. Some of these crystals (**II**) were kept in solution waiting for X-ray analysis.

2.2.3. Preparation of $(gu)_3[Nb(O_2)_3(2,5\text{-}pzdc)]\cdot H_2O$ (*III*)

$(gu)_3[Nb(O_2)_4]$ (0.2 g, 0.498 mmol) was dissolved in 5 ml of distilled water and 5 ml of a 35 wt% H_2O_2 solution. The resulting clear solution was first cooled down with an ice bath before adding 2,5-H_2pzdc (0.084 g, 0.498 mmol) progressively and then, slowly warmed up to 60 °C for a few minutes. The cooling down of the solution at room temperature followed by the addition of 150 ml of ethanol yielded a white precipitate. The suspension was stored at 5 °C during 2 days and the solid was then filtered-off, washed with ethanol and air-dried. Yield 0.12 g, 44%. *Anal.* Calc. for $C_9H_{22}NbN_{11}O_{11}$: C, 19.53; H, 3.98; N, 27.85. Found: C, 19.86; H, 4.00; N, 28.68%.

2.3. Single crystal X-ray diffraction

The X-ray intensity data were collected at 100 K with a MAR345 image plate using Mo Kα ($\lambda = 0.71069$ Å) radiation. The crystal was mounted in inert oil and transferred to the cold gas stream for flash cooling. The data were not corrected for absorption, but the data collection mode partially takes the absorption phenomena into account (180 images, $\Delta\Phi = 3°$, 33929 reflections measured for 6265 independent reflections). The crystal data and the data collection parameters are summarized in Table 1. The unit cell parameters were refined using all the collected spots after the integration process.

Table 1
Crystallographic data and structure refinement for crystals **II**, $(gu)_2[Nb(O_2)_3(picO)]$

	II
Empirical formula	$C_{16}H_{32}N_{14}Nb_2O_{18}$
Formula weight	894.4
Temperature (K)	100(2)
Crystal system	monoclinic
Space group	$P2_1$
Unit cell dimensions	
a (Å)	10.761(5)
b (Å)	8.518(4)
c (Å)	16.856(7)
α (°)	90
β (°)	92.95(2)
γ (°)	90
V (Å^3), Z	1543(1), 2
D_{calc} (g cm^{-3})	1.92
Absorption coefficient (mm^{-1})	0.85
F(000)	884
Crystal size (mm)	$0.28 \times 0.22 \times 0.20$
θ Range for data col (°)	2.7 to 26.4
Index range	$-13 \leqslant h \leqslant 13$; $-10 \leqslant k \leqslant 10$; $-21 \leqslant l \leqslant 21$
Reflections collected/unique	33929/6265
Reflections observed [$I > 2\sigma(I)$]	6237
R_{int}	0.052
Completeness %	98.6
Data/restraints/parameters	6265/13/452
R_1, wR_2 [$I > 2\sigma(I)$]	0.042, 0.121 [6237]
Goodness-of-fit on F^2	1.244
Largest residual peak (e Å^{-3})	1.40, −1.83

The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXL97 [16]. All the non-hydrogen atoms were refined anisotropically. A restraint was applied to atom O4 to avoid that the temperature factor become non-positive defined; we have no explanation for this abnormal temperature factors only of this particular atom. The hydrogen atoms were calculated with AFIX and included in the refinement with a common isotropic temperature factor. The details of the refinement and the final R indices are presented in Table 1. The largest peak in the final Fourier difference synthesis is located near a Nb atom.

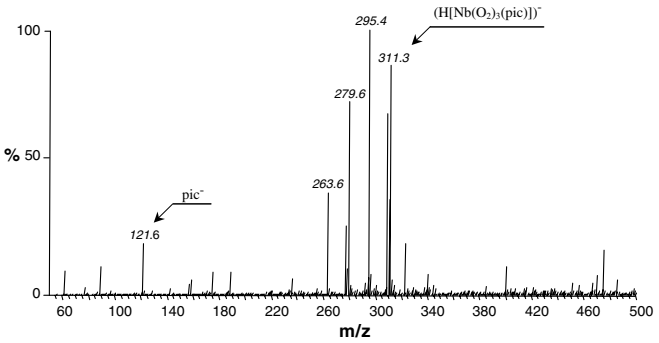

Fig. 1. Negative ion mass spectrum of compound **I** in CH_3OH/H_2O.

3. Results and discussion

3.1. Infrared spectroscopy

Table 2 lists, for compounds **I**–**III**, the infrared bands which can clearly be assigned to the typical vibration modes of the coordinated side-bonded peroxo ligands, the O–O stretching, ν(O–O) and the antisymmetric metal-peroxo stretching, ν_{as}[Nb(O_2)] arising near 550 cm^{-1}. Some representative vibrational modes of the coordinated heterocyclic ligands and bands arising from the N-oxide group in compound **II** are also listed.

The IR spectra of compounds **I** and **II** display three ν(O–O) bands of high intensity in the range 820–870 cm^{-1}. This spectral shape can be assigned to triperoxo species [17]. The spectrum of compound **III** only shows one such band centred at 830 cm^{-1} but which is quite broad. Next to this, the stretching frequencies of the carboxylato groups complexed to niobium appear, in complexes **I**–**III**, as two strong broad bands in the range 1650–1670 cm^{-1} and near 1430 cm^{-1} for the antisymmetric and symmetric modes, respectively. Finally, the IR spectrum of compound **II** displays a ν(N–O) band at 1196 cm^{-1}. According to the literature, coordination of a N-oxide group with a transition metal leads to a shifting of the ν(N–O) band of 30–40 cm^{-1} towards lower wavenumbers [18–20]. This band appears on the IR spectrum of the free ligand HpicO at 1253 cm^{-1}.

3.2. Mass spectrometry

The mass spectrum of compound **I**, illustrated in Fig. 1, displays a signal at m/z 311.3 corresponding to the parent ion associated with a proton, $(H[Nb(O_2)_3(pic)])^-$ (m/z calculated 311.9). It also shows monoanionic fragments corresponding to the successive losses of three oxygen atoms at m/z values 295.4, 279.6 and 263.6 but without charge variation (m/z calculated 295.9, 279.9 and 263.9). These oxygen atoms most probably occur from each one of the three peroxo groups present around the niobium atom. A signal observed at m/z 121.6 was attributed to the deprotonated ligand (m/z calculated 122.0). In the case of complex **II**, we observed on the mass spectrum two signals of weak intensity, at m/z 386.6 and 327.6, corresponding to the parent anion combined to one guanidinium cation, $(gu[Nb(O_2)_3(picO)])^-$ (m/z calculated 387.0), or to one proton, $(H[Nb(O_2)_3(picO)])^-$ (m/z calculated 328.0), respectively. We also observed a peak at m/z 137.9 corresponding to the free deprotonated ligand, $picO^-$ (m/z calculated 138.0). Other signals of moderate to strong intensity are present on the spectrum but cannot be interpreted on the basis of simple fragmentation schemes of the starting complex. Finally, the mass spectrum of complex **III** displays signals at m/z 474.7, 415.5 and 356.7 corresponding to the parent ion associated with two guanidinium, $((gu)_2[Nb(O_2)_3(2,5\text{-pzdc})])^-$ (m/z calculated 474.9), one guanidinium and one proton, $(Hgu[Nb(O_2)_3(2,5\text{-pzdc})])^-$ (m/z calculated 415.9) and two protons, $(H_2[Nb(O_2)_3(2,5\text{-pzdc})])^-$ (m/z calculated 356.9).

Table 2
Infrared data (in cm^{-1}) for compounds **I**–**III**

	ν(O–O)	ν_{as}(Nb[O_2])	ν_{as}(COO)	ν_s(COO)	ν(N–O)
I	867 858 817	649	1663 br	1446 br	
II	864 833 819	610	1675 br	1437 br	1196
III	830 br	600	1655 br	1383 br	

br, broad band.

3.3. Thermal analyses

The thermal behaviour of compounds **I** and **II** is quite similar. The N-oxide group present in the ligand of complex **II** has only little influence on the thermal degradation of the complex. Compounds **I** and **II** undergo decomposition in four main steps up to a final degradation temperature into Nb_2O_5 of 600 and 620 °C, respectively. In the case of compound **III**, after dehydration between 50 and 100 °C (% H_2O: Found 3.91, Calc. 3.25), the thermal degradation into Nb_2O_5 occurs in several steps up to a final temperature of 600 °C. The thermogravimetric analyses of **I** and **II** are illustrated in Fig. 2.

3.4. Single-crystal X-ray structure analysis

The asymmetric part of the unit cell of **II** consists of two $[Nb(O_2)_3(picO)]^{2-}$ anions and four guanidinium cations. In

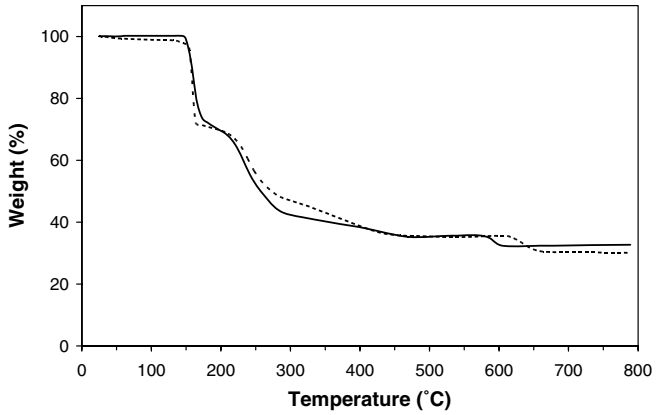

Fig. 2. Thermogravimetric analyses of compounds **I** (straight line) and **II** (dashed line) in air (10°/min).

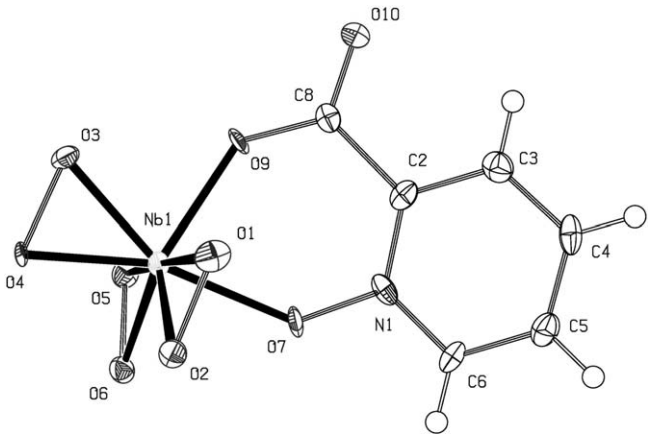

Fig. 3. ORTEP plot of the molecular anion of $[Nb(O_2)_3(pic)]^{2-}$ (50% probability) [30].

this cell, the carboxylato groups, the peroxo ligands and the NH_2 groups from the guanidinium counter-ions are involved in a hydrogen bond network. Crystallographic data for **II** are given in Table 1 and selected bond lengths in Table 3.

Fig. 3 shows the structure of the molecular anion of compound **II**, $[Nb(O_2)_3(picO)]^{2-}$. In that complex, the niobium atom is surrounded by eight oxygen atoms belonging to three η^2-peroxo groups, one carboxylato, and the N-oxide group from a deprotonated picolinato N-oxide ligand. The NO group is bound to the metal via a η^1 coordination mode.

The coordination polyhedron around the metal atom can be described as a triangular dodecahedron as already observed in all Nb or Ta peroxo compounds described so far in the literature [14,21–28]. Two trapezoidal planes are defined by the *O1*, *O2*, *O5*, *O6* and *O3*, *O4*, *O7*, *O9* atoms, respectively and can be considered as perpendicular to each other because the angle between both planes reaches 90(1)° for each anionic entity. As indicated in Table 3, the maximum deviation from the best mean plane through each group of four O atoms is less than 0.07 Å.

The coordination Nb–O distances are in the range of the values already reported for peroxo complexes of niobium^V [14,21,25,26] and no significant difference is observed between both anionic moieties present in the asymmetric part of the unit cell. The mean value for the Nb–O(carboxylato) and Nb–O(N-oxide) distances reach 2.136 and 2.147 Å, respectively. The Nb–O(peroxo) and (O–O) mean distances are of 2.002 and 1.502 Å, respectively. It is worth noting that, for both Nb complexes, the N–O(N-oxide) bond lengths are of 1.344(7) and 1.320(9) Å. This N–O distance value was determined in the free ligand and reaches 1.341(2) Å [29].

Table 3
Selected bond lengths and maximum deviations from mean peroxo plane (Å) for both anionic moieties of **II**, $(gu)_2[Nb(O_2)_3(picO)]$

	Anion 1	Anion 2
Distances		
Carboxylate		
Nb–O9	2.106(5)	2.166(4)
N-oxide		
Nb–O7	2.167(4)	2.127(4)
Peroxo		
Nb–O1	2.024(5)	2.023(5)
Nb–O2	2.011(5)	2.029(5)
Nb–O3	2.009(4)	2.014(4)
Nb–O4	1.967(4)	1.999(5)
Nb–O5	2.001(5)	2.002(5)
Nb–O6	2.011(5)	1.937(5)
O1–O2	1.518(7)	1.520(7)
O3–O4	1.491(6)	1.513(6)
O5–O6	1.520(6)	1.452(7)
N1–O7	1.344(7)	1.320(9)
Maximum deviation from mean plane through four O (peroxo)		
Plane 1		
O1	0.04	0.02
O2	−0.06	−0.03
O5	−0.04	0.03
O6	0.06	−0.02
Plane 2		
O3	−0.06	−0.07
O4	0.05	0.05
O7	−0.02	0.04
O9	0.04	−0.02

4. Conclusions

New water-soluble heteroleptic peroxo complexes of niobium^V with N-containing heterocyclic ligands have been prepared and characterized by thermal analyses, IR spectroscopy and mass spectrometry. The crystal structure of one of them has been resolved.

5. Supplementary material

Crystallographic data for the structures in this paper have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 279905 for **II**. Copies of the data

can be obtained, free of charge, on application to The Director, CCDC, Union Road 12, Cambridge CB2 1EZ, UK (fax: +44 1223/336 033 or e-mail: deposit@ccdc.cam.ac.uk).

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