Spectroscopic and Structural Characterizations of Novel Water-Soluble Peroxo[polyaminocarboxylato bis(*N*-oxido)]niobate(V) Complexes

Daisy Bayot,[a] Bernard Tinant,[b] Benoît Mathieu,[b] Jean-Paul Declercq,[b] and Michel Devillers*[a]

Keywords: Niobium / Peroxo ligands / N,O ligands / NMR spectroscopy / IR spectroscopy

New water-soluble peroxo complexes of niobium(V) with polyaminocarboxylic acids (PAC) have been prepared and characterized by IR and NMR (^1H, ^{13}C, ^{15}N) spectroscopy, as well as by thermal analysis. The synthesis in presence of excess H_2O_2 leads to the oxidation of the nitrogen atoms of the PAC ligand into *N*-oxide groups. The compounds obtained correspond to the general formula $(A^I)_3[Nb(O_2)_2(LO_2)]\cdot xH_2O\cdot yH_2O_2$ [$A^I = NH_4^+$ or $CN_3H_6^+$ (gu) and L = edta, pdta] in which H_4LO_2 refers to the bis(*N*-oxide) derivative of the PAC ligand. The crystal structures of the guanidinium derivatives of the (edta)- and (pdta)Nb complexes have been determined, both showing an eight-coordinate Nb atom with two bidentate peroxo ligands and a quadridentate PAC bis(*N*-oxido) ligand, resulting in a distorted dodecahedral geometry. The structure of the guanidinium derivative of the edta bis(*N*-oxido) ligand is also described.

Introduction

Because multimetallic Nb-based oxides generate great interest as potential heterogeneous catalysts for several highly challenging industrial processes, like alkane oxidation or ammoxidation,[1−4] fundamental research on Nb coordination compounds that could be used as molecular precursors for the preparation of such catalysts, is definitely welcome. In particular, the aqueous chemistry of niobium is restricted to very few available precursors, some of them being poorly defined from the point of view of composition and molecular structure. Because peroxoniobium compounds are soluble in water, they are adequate candidates for that purpose. Several such complexes have already been described in the literature; they correspond either to homoleptic tetraperoxoniobates of general formula $(A^I)_3[Nb(O_2)_4]$ [$A^I = Na^+$, K^+, Rb^+, Cs^+, NH_4^+, and $CN_3H_6^+$ (guanidinium, gu^+)][5−7] or to heteroleptic carboxylato(peroxo) compounds such as $(A^I)_3[Nb(O_2)_3(L)]\cdot nH_2O$ ($A^I = K^+$ or NH_4^+ and L = tartrate, citrate, *o*-phenanthroline),[8−10] $(A^I)_3[Nb(O_2)_2(C_2O_4)_2]\cdot H_2O$ ($A^I = NH_4^+$ or $CN_3H_6^+$)[9,11] and $K[Nb(O_2)_2(L)_2]\cdot 3H_2O$ (L = 8-hydroxyquinolinate).[12] As far as the peroxo(polyaminocarboxylato) compounds are concerned, only a few studies have been reported and they are essentially restricted to the edta(peroxo) compound and its solution chemistry.[13,14] A bis(aqua)edta complex of Nb^{IV}, $[Nb(edta)(H_2O)_2]\cdot 2H_2O$, has also been described.[15]

Within the framework of the preparation of oxide materials, we have already reported on the use of carboxylato and carboxylato(peroxo)Nb complexes in the preparation of silica-dispersed Nb-Mo-O phases, by association with analogous Mo compounds.[9] The present work dedicates particular attention to new water-soluble peroxo(polyaminocarboxylato)Nb^V compounds corresponding to the general formula $(A^I)_3[Nb(O_2)_2(LO_2)]\cdot nH_2O\cdot nH_2O_2$ [$A^I = NH_4^+$ or guanidinium ($CN_3H_6^+$)]. Two different PAC ligands (L) have been selected: ethylenediaminetetraacetic acid (H_4edta) and propylenediaminetetraacetic acid (H_4pdta). There is so far only one report of *N*-oxide derivatives of polyaminocarboxylato complexes with some alkaline-earth and transition metal ions.[16] The present paper reports for the first time crystal structures of such compounds.

Results and Discussion

General Comments on the Synthetic Procedures

The peroxo(polyaminocarboxylato)Nb^V complexes were prepared by replacing peroxo groups by a PAC ligand of the tetraperoxoniobate anion $[Nb(O_2)_4]^{3-}$, formed in situ. The syntheses were adapted from the procedure used by Vuletic et al.[13] to obtain the ammonium edta(peroxo) complex. These syntheses were carried out in the presence of

---

[a] Unité de Chimie des Matériaux Inorganiques et Organiques
Place Louis Pasteur 1/3, 1348 Louvain-la-Neuve, Belgium
[b] Unité de Chimie Structurale et des Mécanismes Réactionnels,
Université Catholique de Louvain,
Place Louis Pasteur 1/3, 1348 Louvain-la-Neuve, Belgium
Fax: (internat.) + 32-10/472330
E-mail: devillers@chim.ucl.ac.be

Table 1. Infrared data (in cm^{-1}) for compounds **1**, **2a**, and **3** (s = strong, m = medium, w = weak)

Compound	ν(O−O)	$\nu_s[Nb(O_2)]$	$\nu_{as}[Nb(O_2)]$	$\nu_{as}(COO)$	$\nu_s(COO)$	ν(N−O)
1	870m 855m	646w	558m	1619s	1443s 1391s	904m
2a	872m 857m	642m	554m	1622s	1446s 1376s	905m
3	875m 860m	634w	544m	1674s 1609s	1401s 1373s	898m

excess hydrogen peroxide, which led to the direct formation of the *N*-oxide derivative of the PAC ligand. The PAC bis(*N*-oxido) ligands, H_4edtaO_2, and H_4pdtaO_2, were synthesized separately according to the procedure of Porter et al.[17] The peroxo(PAC)Nb^V complexes were also prepared starting from the pre-isolated reactants $(A^I)_3[Nb(O_2)_4]$ and $H_4LO_2{\cdot}nH_2O$ (with $A^I = NH_4^+$, gu^+ and L = edta, pdta) in aqueous media. Both synthetic pathways were shown to lead to the same compounds.

IR Spectroscopy

Table 1 lists the infrared bands assigned to the side-bonded peroxo ligands, the *N*-oxide groups and some representative vibrational modes of the coordinated PAC ligands for compounds **1**, **2a**, and **3**.

In addition to the bands arising from the PAC ligands, the IR spectra of the complexes systematically show two ν(O−O) bands of medium intensity in the range 855−875 cm^{-1}, assigned to a diperoxo species.[9,18] Other bands due to the presence of coordinated peroxo ligands also arise at ca. 550 and 650 cm^{-1} and correspond to $\nu_{as}[Nb(O_2)]$ and $\nu_s[Nb(O_2)]$, respectively. The asymmetric stretching frequency of the carboxylato groups bound to the niobium atom occurs in the spectra of the edta and pdta compounds as a broad band near 1600−1650 cm^{-1}. Coordination of the metal atom by these carboxylato groups is evidenced by the broadening of this $\nu_{as}(COO)$ band and by its significant shift in comparison with the free acid [$\nu_{as}(COO)$ at ca. 1700 cm^{-1}]. Finally, oxidation of the nitrogen atoms of the PAC ligand during the syntheses (excess H_2O_2 medium) is evidenced by the presence, in all IR spectra, of the ν(N−O) band at ca. 900 cm^{-1}. In the corresponding bis(*N*-oxide) derivative of the free ligand, $H_4edtaO_2{\cdot}1/2H_2O$ (**4a**) and $H_4pdtaO_2{\cdot}H_2O$ (**5**), this band appears at 890 and 909 cm^{-1}, respectively.

NMR Spectroscopy

Table 2 lists the ^{13}C and ^{15}N resonance lines occurring from compounds **1**, **3**, **4a**, **5**, and also from the commercial PAC ligands. The results obtained for the guanidinium edta compound **2a** are not reported because they are very similar to those obtained for the ammonium derivative.

Table 2. ^{13}C and ^{15}N NMR chemical shifts (δ, in ppm) for compounds **1**, **3**, **4a**, **5**, and commercial PAC ligands

Compound	^{13}C NMR[a]	^{15}N NMR[a]
1	57.4, 64.9, 70.8, 168.4, 169.9	121.2
3	19.3, 54.8, 66.6, 67.9, 168.8, 171.3	72.1, 128.1
4a/NaOD[b]	59.7, 67.5, 170.6	114.9
5/NaOD[b]	19.1, 64.9, 66.6, 171.4	123.6
H_4edta/NaOD[b]	50.9, 57.5, 176.9	38.5
H_4pdta/NaOD[b]	23.0, 53.2, 58.9, 179.3	53.1

[a] In D_2O. [b] H_4L and H_4LO_2 compounds are not soluble in D_2O at room temp. and were solubilized by adding an excess of NaOD.

Just like the IR spectra, the ^{15}N NMR spectra of the prepared complexes reveal the oxidation of the nitrogen atoms in the PAC ligand. The ^{15}N NMR spectrum of compound **1** displays one single line at δ = 121.2 ppm arising from the two identical nitrogen atoms in the ligand. This particularly high ^{15}N chemical shift confirms the formation of *N*-oxide groups by comparison with the values obtained for the species H_4edta and $H_4edtaO_2{\cdot}1/2H_2O$ (**4a**) (δ = 38.5 and 114.9 ppm, respectively). A similar effect of *N*-oxidation on ^{15}N chemical shifts was observed by Hadden et al. in alkaloid compounds.[19] In the ^{15}N NMR analysis of compound **3**, resonances occurring at δ = 72.1 and 128.1 ppm are assigned to the nitrogen atoms of the guanidinium counterions and the oxidized pdta ligand, respectively. In free H_4pdta and $H_4pdtaO_2{\cdot}H_2O$ (**5**), the related lines occur at δ = 53.1 and 123.6 ppm, respectively.

Information on the coordination mode of the bis(*N*-oxido) ligand is provided by ^{13}C NMR spectroscopy. The ^{13}C NMR spectrum of the anion $[Nb(O_2)_2(edtaO_2)]^{3-}$ shows three lines at δ = 57.4, 64.9, and 70.8 ppm, arising from the CH_2 groups of the edta ligand. These carbon atoms are clearly influenced by the complexation process. Whereas all four CH_2 moieties of the acetate groups occur as one single peak in the free ligand (δ = 50.9 ppm), they undergo a significant variation in chemical shift and are differentiated in the complex (δ = 57.4 and 64.9 ppm). Moreover, the CH_2 groups of the *N*-bound ethylene moiety are not differentiated (they appear as a single line as in H_4edta) but they are shifted from δ = 57.5 ppm in the free ligand to δ = 70.8 ppm in the complex. A similar value is observed for these carbon atoms in the free edta bis(*N*-oxido) ligand (**4a**;

δ = 67.5 ppm). This result confirms the presence of N−O groups in the complexed ligand. The signal corresponding to the quaternary carbon atoms of the carboxylato groups in the complex appears as two resonance signals rather than the single line found for the free ligand. The presence of two lines at δ = 168.4 and 169.9 ppm in the ^{13}C NMR spectrum implies that two carboxylato groups are coordinated to Nb and the other two remain free. The complete analysis of the ^{13}C NMR spectrum of compound **1** allows us to determine the coordination mode of the ligand to the niobium atom; the edta bis(*N*-oxide) is quadridentate, the four binding atoms being oxygen atoms of two of the carboxylate groups (each placed on a different N atom) and two *N*-oxide groups. A similar analysis based on the ^{13}C NMR spectrum obtained for compound **3** leads to the same conclusion about the coordination mode of the pdta bis(*N*-oxido) ligand.

X-ray Crystal Structures

The asymmetric part of the unit cell of **2b** consists of two $[Nb(O_2)_2(edtaO_2)]^{3-}$ anions, six guanidinium cations, six water molecules, and two hydrogen peroxide molecules. In **3**, only one half of the $[Nb(O_2)_2(pdtaO_2)]^{3-}$ entity is observed in the asymmetric part of the unit cell as a consequence of a crystallographic twofold axis passing through the Nb atom, the central carbon atom of the PAC ligand (C10) and the C and N atoms belonging to one guanidinium ion. In **4b**, only one half of the molecule is observed in the asymmetric part of the unit cell. Crystallographic data for **2b**, **3**, and **4b** are given in Table 4 and selected bond lengths for **2b** and **3** in Table 3.

Table 3. Selected bond lengths and maximum deviations from mean peroxo plane [Å] for both anionic moieties of **2b** and **3**

	2b		**3**
	Anion 1	Anion 2	
Distances			
Nb−O (carboxylate)	2.155(5)	2.147(5)	2.162(2)
	2.154(5)	2.140(5)	
Nb−O (*N*-oxide)	2.089(4)	2.087(5)	2.119(2)
	2.083(5)	2.074(4)	
Nb−O (peroxo)	1.966(5)	1.982(4)	1.973(2)
	1.968(5)	1.979(5)	1.988(2)
	1.977(5)	1.972(5)	
	1.992(5)	1.990(5)	
O−O (peroxo)	1.478(7)	1.485(7)	1.488(3)
	1.483(7)	1.475(7)	
N−O (*N*-oxide)	1.411(7)	1.414(7)	
	1.416(7)	1.407(7)	1.419(2)
Maximum deviation from mean plane through four O (peroxo)			
O (peroxo)	0.04	0.03	0.060
O (*N*-oxide)	2.72	2.75	2.75
	2.69	2.66	
O (carboxylate)	1.64	1.65	1.65
	1.78	1.78	
Nb	1.10	1.17	1.16

The crystal structures of complexes **2b** and **3** are similar in many ways. The bis(*N*-oxido) ligands, edtaO_2 and pdtaO_2, wrap around the Nb atom, essentially in the same manner. The quadridentate coordination mode of these ligands, deduced from the NMR analysis, is confirmed and, for each anion, coordination is completed by two bidentate peroxo groups. From this it is seen that the niobium atom exhibits an eightfold coordination as observed in all (peroxo)Nb compounds described so far in the literature.[5,6,9−12] Figures 1 and 2 show the molecular structure of the $[Nb(O_2)_2(edtaO_2)]^{3-}$ and $[Nb(O_2)_2(pdtaO_2)]^{3-}$ anions, respectively. The coordination polyhedron observed in both cases is identical to those reported for dioxalatodiperoxoNb^{V} compounds with different counterions.[9,11] The question of whether eightfold coordinated atoms display dodecahedral (DD) or square-antiprismatic (SAP) config-

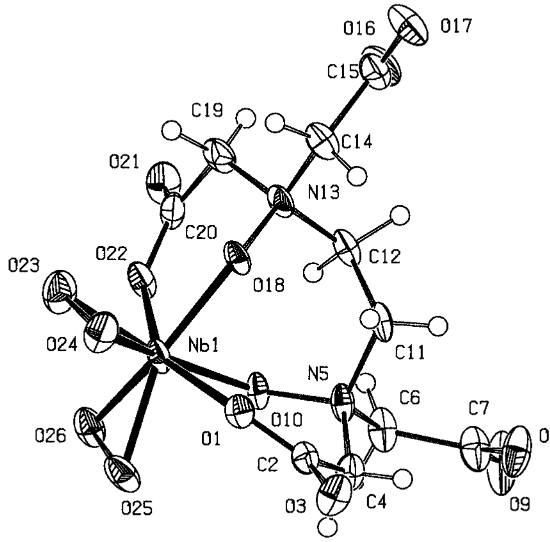

Figure 1. ORTEP plot of $[Nb(O_2)_2(edtaO_2)]^{3-}$ (50% probability)[24]

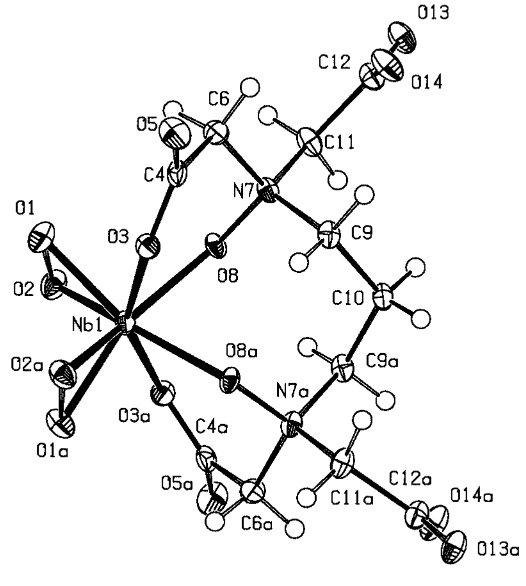

Figure 2. ORTEP plot of the molecular anion of $[Nb(O_2)_2(pdtaO_2)]^{3-}$ (50% probability)[24]

urations is not an obvious one to answer, and has been addressed from a theoretical point of view in the literature.[20] In relation to the fact that the energy balance between DD and SAP is very sensitive to small differences in electronic or steric effects, the obtention of intermediate configurations between them has also been discussed.[21] Theoretical considerations confirmed that "small-bite" ligands like O_2^{2-} definitely prefer the dodecahedral geometry,[20] as is observed in all peroxoniobate complexes described so far. In the present cases, the polyhedron may be described as a triangular dodecahedron that is rather distorted on one side. As indicated in Table 3, for the three anionic moieties encountered in these compounds, the four oxygen atoms of the peroxo groups are coplanar within experimental error. The maximum deviation from the best mean plane through these four O atoms is less than 0.06 Å. On the opposite side of the polyhedron, the four oxygen atoms of the PAC ligand are not coplanar. In all three anions described above, the oxygen atoms of the two carboxylate and the two *N*-oxide groups are observed with quite similar distances from the mean plane, of about 1.7 Å and 2.7 Å, respectively (see Table 3).

The mean Nb−O (*N*-oxide) bond length is 2.090(4) Å, a value which is larger than that observed in the related (hydroxyimino)niobium complex $(PPh_4)[Nb(hida)_2]$.[22] The other coordination distances are in the range of the values already reported.[6,9−11,22] The mean value for the Nb−O (carboxylato) distances is 2.152(5) Å and is slightly larger than the average of the sixteen values reported in the literature (2.095 Å). The Nb−O (peroxo) and (O−O) mean distances are 1.979(5) and 1.482(7) Å, respectively, and compare very well with the reported Nb−O distances (average over 36 values is 2.000 Å) and O−O distances (average over 14 values is 1.495 Å).[6,9−11,22] It is worth noting that, for both Nb complexes, the N−O (*N*-oxide) bond lengths range from 1.407(7) to 1.419(2) Å with a mean value of 1.413(5) Å. As expected, this value is slightly larger than the N−O distance observed in the free ligand [1.398(2) Å]. Moreover, as illustrated in Figure 3, which shows the molecular structure of the $[edtaO_2]^{4-}$ anion, there is a significant change of ligand conformation upon chelation. In the free anion, the N−O bands that are related by a symmetry center are in an "*anti*" orientation, pointing in opposite directions.

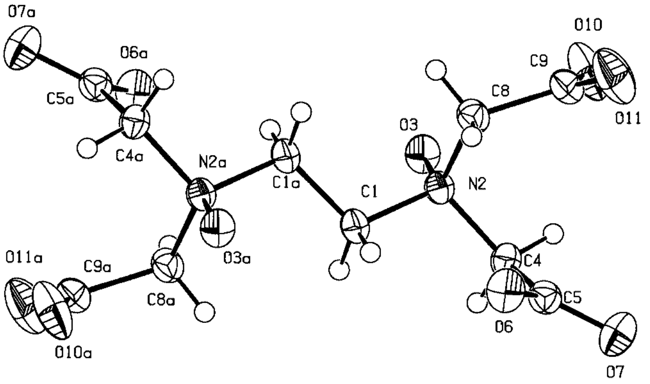

Figure 3. ORTEP plot of the molecular anion of $[edtaO_2]^{4-}$ (50% probability)[24]

For **2a**, the co-crystallized water and hydrogen peroxide molecules are involved in an intricate hydrogen bond network as illustrated in Figure 4. All the H-donors of the carboxylato groups and of the NH_2 groups of the guanidinium counterions participate in the network. There is no co-crystallized solvent molecule in crystals of **3** and **4b** but, in both structures, all carboxylate, peroxo, and amine groups are hydrogen-bonded.

Thermal Analyses

After dehydration, compound **1** undergoes a three-step degradation into Nb_2O_5 up to a final decomposition tem-

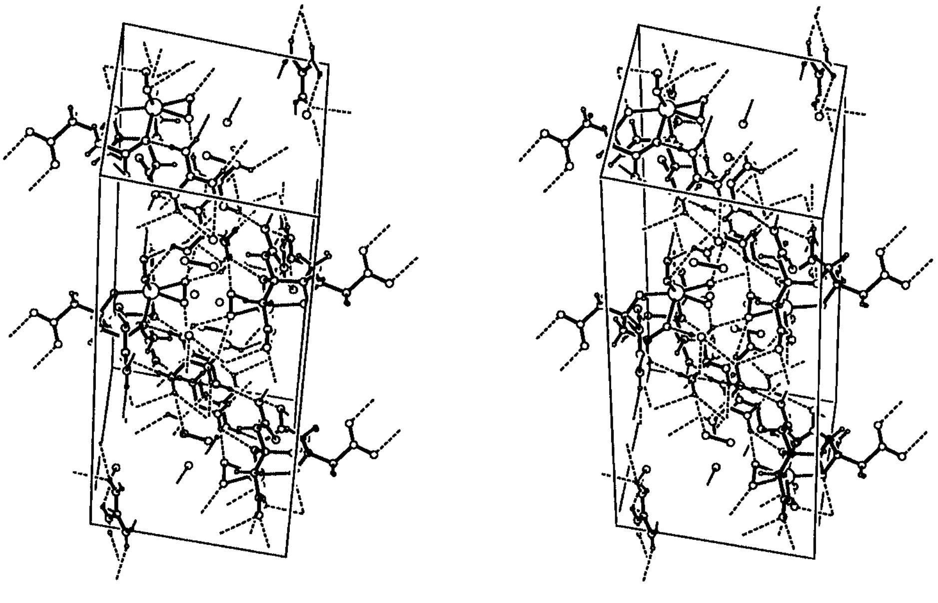

Figure 4. Stereoscopic view of the unit cell of **2b** showing the hydrogen bond network

perature of 620 °C. The thermal behavior of the guanidinium compounds **2a** and **3** is quite similar but their thermograms display an additional step, probably due to the counterion itself. The thermogravimetric analyses of the two edta(peroxo) compounds (**1** and **2a**) are illustrated in Figure 5.

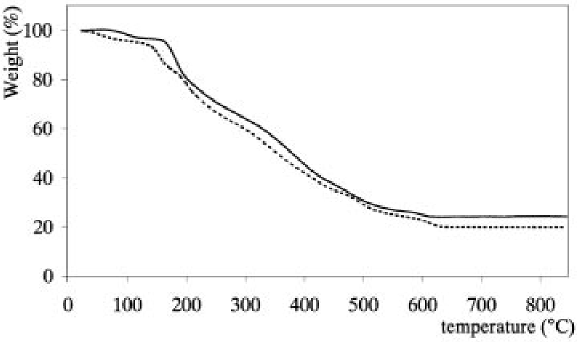

Figure 5. Thermogravimetric analyses of **1** (straight line) and **2a** (dashed line) in air (10 °C/min)

Conclusion

New niobium(V) complexes with *N*-oxide derivatives of polyaminocarboxylic acids have been prepared and characterized from the structural and spectroscopic point of view. Because these compounds exhibit a high solubility in water, they are ideal as precursors for Nb-based materials. The structures reported here are the first ones describing metal complexes with *N*-oxide derivatives of PAC ligands. The one-step synthesis of such compounds in the presence of hydrogen peroxide or their formation from the pre-isolated PAC (*N*-oxide)s opens new perspectives towards the obtention of PAC-type complexes with hard cations which, like Nb^{5+}, display a higher affinity towards oxygen than towards nitrogen.

Experimental Section

General: Ethylenediaminetetraacetic acid, H_4edta (Fluka), propylenediaminetetraacetic acid, H_4pdta (Fluka), and guanidinium carbonate, $(gu)_2CO_3$ (Aldrich), were commercial products and used as received. Niobic acid, $Nb_2O_5{\cdot}nH_2O$ was supplied by CBMM (Brazil). Hydrogen peroxide, H_2O_2 (35 wt-%, Acros), aqueous ammonia (25 wt-%), ethanol, and acetic acid 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 with an FTS-135 Bio-RAD spectrometer, using KBr pellets containing ca 1 wt-% of the powder. ^1H, ^{13}C, and ^{15}N NMR spectra were measured in D_2O at 500, 125, and 50 MHz, respectively, with a Bruker Avance 500 MHz spectrometer equipped with a broad-band inverse probe. ^{15}N NMR spectra were recorded using the HMBC pulse sequence with a mixing time of 100 ms. Chemical shifts are expressed in ppm and are referenced to TMS for ^1H and ^{13}C ($\delta = 0$ ppm) or nitromethane for ^{15}N ($\delta = 375$ ppm).

$(NH_4)_3[Nb(O_2)_2(edtaO_2)]{\cdot}H_2O{\cdot}H_2O_2$ (1): A slurry of niobic acid (1 g, 6.36 mmol) in distilled water (20 mL) was treated with a 35 wt-% solution of H_2O_2 (20 mL) and ammonia (6 mL of a 25 wt-% solution). The cloudy solution was stirred for a few hours. When the solid was totally dissolved, H_4edta (1.86 g, 6.36 mmol) was added gradually, reaching pH = 5−5.5. The pale yellow solution was then gently heated for 10 min (T = 60 °C) and the solvents evaporated to a final volume of 20 mL under reduced pressure. The addition of ethanol (100 mL) yielded a white solid that was filtered off, washed with ethanol, and air-dried. Yield: 2.09 g (56%). $C_{10}H_{28}N_5NbO_{17}$ (583.16): calcd. C 20.57, H 4.80, N 12.00; found C 20.51, H 4.78, N 11.97. ^1H NMR (500 MHz, D_2O): δ = 3.88 (d, J = 16.5 Hz, 2 H), 4.06 (d, J = 16.0 Hz, 2 H), 4.37 (d, J = 16.5 Hz, 2 H), 4.42 (d, J = 14.0 Hz, 2 H), 4.76 (d, J = 13.5 Hz, 2 H), 5.04 (d, J = 16.5 Hz, 2 H) ppm. ^{13}C (125 MHz, D_2O) and ^{15}N (50 MHz, D_2O) NMR: see Table 2.

$(gu)_3[Nb(O_2)_2(edtaO_2)]{\cdot}2H_2O$ (2a): This guanidinium compound was prepared according to the same procedure as used for the ammonium derivative **1** but replacing ammonia by guanidinium carbonate, $(gu)_2CO_3$ (1.72 g, 9.55 mmol). The complex was isolated as a crystalline light-yellow solid. Yield: 2.78 g (63%). $C_{13}H_{34}N_{11}NbO_{16}$ (693.16): calcd. C 22.50, H 4.90, N 22.21; found C 22.36, H 5.02, N 22.03. The slow concentration at 5 °C of an aqueous concentrated solution yielded after several days small crystals suitable for structure determination by single-crystal X-ray diffraction and similar to compound **2a**, but containing additional water and hydrogen peroxide molecules $\{(gu)_3[Nb(O_2)_2(edtaO_2)]{\cdot}3H_2O{\cdot}H_2O_2$, **2b**$\}$.

$(gu)_3[Nb(O_2)_2(pdtaO_2)]$ (3): A slurry of niobic acid (1 g, 6.36 mmol) in distilled water (50 mL) was treated with a 35 wt-% solution of H_2O_2 (50 mL) and $(gu)_2CO_3$ (1.72 g, 9.55 mmol). When the solid was totally dissolved, H_4pdta (1.95 g, 6.36 mmol) was added, reaching pH = 6. The pale yellow solution was then gently heated for 10 min (T = 60 °C) and the solvents evaporated to a final volume of 50 mL under reduced pressure. Addition of ethanol (100 mL) produced, after a few minutes, a pale yellow crystalline solid that was filtered off, washed with ethanol, and air-dried. Yield: 3.01 g (71%). $C_{14}H_{32}N_{11}NbO_{14}$ (671.18): calcd. C 25.03, H 4.77, N 22.94; found C 25.20, H 4.69, N 22.76. ^1H NMR (500 MHz, D_2O): δ = 2.2−2.3 (m, 2 H), 3.94 (d, J = 16.5 Hz, 2 H), 3.99 (d, J = 13.0 Hz, 2 H), 4.19 (d, J = 16.5 Hz, 2 H), 4.83 (d, J = 13.0 Hz, 2 H), 4.86 (d, J = 16.5 Hz, 2 H) ppm. ^{13}C (125 MHz, D_2O) and ^{15}N (50 MHz, D_2O) NMR: see Table 2. The slow concentration at room temperature of an aqueous concentrated solution yielded after several days small yellow crystals of compound **3**.

$H_4edtaO_2{\cdot}1/2\ H_2O$ (4a): H_4edta (2 g, 6.84 mmol) was dispersed in glacial acetic acid (100 mL) and 35 wt-% solution of H_2O_2 (50 mL). The suspension was stirred for 72 h at room temperature. The white solid was then filtered off, washed with water and ethanol and finally air-dried. Yield: 1.81 g (79%). $C_{10}H_{16}N_2O_{10}{\cdot}1/2H_2O$ (333.25): calcd. C 36.00, H 5.10, N 8.40; found C 36.19, H 4.91, N 8.27. ^1H NMR (500 MHz, D_2O): δ = 4.09 (d, J = 15.5 Hz, 4 H), 4.19 (s, 4 H), 4.37 (d, J = 15.5 Hz, 4 H), 4.70 (s, H_2O) ppm. ^{13}C (125 MHz, D_2O) and ^{15}N (50 MHz, D_2O) NMR: see Table 2. Crystallization of a guanidinium derivative of the edta bis(*N*-oxido) ligand was obtained after neutralizing the carboxylic groups by guanidinium carbonate; **4a** (1 g, 3 mmol) was dissolved in distilled water (10 mL) and the addition of $(gu)_2CO_3$ (2.16 g, 12 mmol) yielded a clear solution that was allowed to concentrate at room temperature. After several days, large crystals of $(gu)_4edtaO_2$ (**4b**) had formed. $C_{14}H_{36}N_{14}O_{10}$ (560.57): calcd. C 29.98, H 6.07, N 34.98; found C 30.40, H 6.22, N 35.40.

$H_4pdtaO_2{\cdot}H_2O$ (5): This compound was prepared according to the same procedure as used for the edta derivative but replacing H_4edta

Table 4. Crystallographic data and structure refinement parameters for **2b**, **3**, and **4b**

	2b	**3**	**4b**
Empirical formula	$C_{26}H_{76}N_{22}Nb_2O_{38}$	$C_{14}H_{32}N_{11}NbO_{14}$	$C_{14}H_{36}N_{14}O_{10}$
Formula mass	1490.9	671.2	560.6
Temperature [K]	100(2)	100(2)	293(2)
Crystal system, space group	triclinic, $P\bar{1}$	Monoclinic, $C2/c$	Monoclinic, $P2_1/c$
Unit cell dimensions			
a [Å]	11.233(4)	12.093(3)	10.670(4)
b [Å]	11.430(4)	19.206(5)	8.305(3)
c [Å]	23.220(8)	12.115(3)	14.454(5)
α [°]	101.01(3)	90	90
β [°]	102.07(3)	110.84(2)	91.84(2)
γ [°]	94.01(3)	90	90
V [Å^3]	2843(2)	2630(1)	1280(2)
Z	2	4	2
$D_{\text{calcd.}}$ [g·cm^{-3}]	1.75	1.71	1.45
Absorption coefficient [mm^{-1}]	0.526	0.545	0.122
$F(000)$	1532	1380	596
Crystal size [mm]	0.36 × 0.32 × 0.30	0.4 × 0.32 × 0.18	0.30 × 0.30 × 0.25
θ range for data collection [°]	3.5−23.2	3.5−27.5	2.8−26.4
Index range	$-12 \geq h \geq 8$ $-12 \geq k \geq 9$ $-24 \geq l \geq 25$	$-15 \geq h \geq 15$ $-24 \geq k \geq 24$ $-15 \geq l \geq 15$	$-13 \geq h \geq 13$ $-10 \geq k \geq 10$ $-18 \geq l \geq 18$
Reflections collected/unique	47090/7021	8094/2998	19424/2540
R_{int}	0.055	0.064	0.057
Data/restraints/parameters	7021/0/867	2998/0/185	2540/0/228
R_1, wR_2 [$I > 2\sigma(I)$]	0.068, 0.173 [6452]	0.038, 0.101 [2696]	0.054, 0.126 [2384]
R_1, wR_2 (all data)	0.072, 0.177	0.042, 0.102	0.055, 0.128
Goodness-of-fit on F^2	1.093	1.148	1.177
Larg. res. peak [e/Å^3]	2.67/−2.11	0.73/−0.62	0.51/−0.43

by H_4pdta (2 g, 6.53 mmol). Yield: 1.68 g (72%). $C_{11}H_{20}N_2O_{10}\cdot H_2O$ (356.25): calcd. C 37.05, H 5.61, N 7.86; found C 37.10, H 5.71, N 7.81. ^{1}H NMR (500 MHz, D_2O): δ = 2.41−2.51 (m, 2 H), 4.10 (t, J = 7.0 Hz, 4 H), 4.39 (d, J = 16.0 Hz, 4 H), 4.46 (d, J = 16.0 Hz, 4 H) ppm. ^{13}C (125 MHz, D_2O) and ^{15}N (50 MHz, D_2O) NMR: see Table 2.

X-ray Crystallography: The X-ray intensity data were measured at 100 K with an MAR345 image plate using Mo-K_α (λ = 0.71069 Å) radiation. Selected crystals of **2b** and **3** were mounted in inert oil and transferred to the cold gas stream for flash cooling. Data of **4b** were collected at room temperature. Crystal data and data collection parameters are summarized in Table 4. The unit cell parameters were refined using all the collected spots after the integration process. The three structures were solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXL-97.[23] All the non-hydrogen atoms were refined anisotropically. For **2b** and **3**, the hydrogen atoms were calculated with AFIX and included in the refinement with a common isotropic temperature factor. The H atoms of the carboxylic groups, the water and hydrogen peroxide molecules were not localized. For **4b**, the H atoms were localized by Fourier difference synthesis. In compound **2b**, the asymmetric part of the unit cell concsists of two complex units related to each other by a pseudo translation symmetry. There is only one half of the ligand molecule and two guanidinium cations in the asymmetric part of the unit cell of **4b**; the midpoint of the central C1−C1a bond corresponds to a crystallographic center of symmetry. The details of the refinement and the final R indices are presented in Table 4. In **2b** and **3**, the largest peak in the final Fourier difference synthesis is located near an Nb atom. CCDC-187664 (**2b**), -187665 (**3**), and -192609 (**4b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

The authors thank the Belgian National Fund for Scientific Research (FNRS) for the Research fellowship allotted to D. B. and financial support. They also thank the CBMM company (Brazil) for supplying the niobic acid.

---

[1] [1a] K. Ruth, R. Burch, R. Kieffer, *J. Catal.* **1998**, 16−26. [1b] K. Ruth, R. Burch, R. Kieffer, *J. Catal.* **1998**, 27−39.

[2] Y. Mimura, K. Ohyachi, I. Matsuura, *Stud. Surf. Sci. Catal.* **1999**, *21*, 69−74.

[3] M. Aouine, J. L. Dubois, J. M. M. Millet, *Chem. Commun.* **2001**, 1180−1181.

[4] S. A. Holmes, J. Al-Saeedi, V. V. Guliants, P. Boolchand, D. Georgiev, U. Hackler, E. Sobkow, *Catal. Today* **2001**, 403−409.

[5] L. C. Passoni, M. R. H. Siddiqui, A. Steiner, I. N. Kozhevnikov, *J. Mol. Catal. A* **2000**, *153*, 103−108.

[6] G. Mathern, R. Weiss, *Acta Crystallogr., Sect. B* **1971**, *27*, 1598−1609.

[7] R. N. Shchelokov, E. N. Traggeim, M. A. Michnik, *Russ. J. Inorg. Chem.* **1971**, *16*, 211−213.

[8] A. C. Dengel, W. P. Griffith, *Polyhedron* **1989**, *8*, 1371−1377.

[9] D. Bayot, B. Tinant, M. Devillers, *Catal. Today*, in press.

[10] G. Mathern, R. Weiss, *Acta Crystallogr., Sect. B* **1971**, *27*, 1582−1597.

[11] G. Mathern, R. Weiss, *Acta Crystallogr., Sect. B* **1971**, *27*, 1572−1581.

[12] V. de Oliveira, R. Aguilar da Silva San Gil, E. R. Lachter, *Polyhedron* **2001**, *20*, 2647–2649.

[13] N. Vuletic, E. Prcic, *Z. Anorg. Allg. Chem.* **1979**, *450*, 67–69.

[14] M. J. Kim, E. Matijevic, *J. Am. Ceram. Soc.* **1994**, *77*, 1950–1953.

[15] B-L. Ooi, Q. Xu, T. Shibahara, *Inorg. Chim. Acta* **1998**, *274*, 103–107.

[16] L. E. Freyer, Ph. D. Dissertation, University of Texas, **1975**.

[17] D. B. Porter, M. de Haro Rodriguez, P. P. Conesa, *Afinidad* **1976**, 489–495.

[18] R. N. Shchelokov, E. N. Traggeim, M. A. Michnik, M. Petrov, *Russ. J. Inorg. Chem.* **1972**, *17*, 1270–1272.

[19] C. E. Hadden, B. D. Kaluzny, R. H. Robins, G. E. Martin, *Magn. Reson. Chem.* **1999**, *37*, 325–327.

[20] J. K. Burdett, R. Hoffmann, R. C. Fay, *Inorg. Chem.* **1978**, *17*, 2553–2568.

[21] S. J. Lippard, B. J. Russ, *Inorg. Chem.* **1968**, *7*, 1686–1688.

[22] P. D. Smith, S. M. Harben, R. L. Beddoes, M. Helliwell, D. Collison, C. D. Garner, *J. Chem. Soc., Dalton Trans.* **1997**, 685–691.

[23] G. M. Sheldrick, *SHELX-97* and *SHELXL-97, Program for crystal structure refinement*, University of Göttingen, Germany, **1997**.

[24] A. L. Spek, *PLATON Molecular Geometry Program*, University of Utrecht, The Netherlands, **1998**.

Received June 25, 2002
[I02345]