

Hydroxyethylmethacrylate as a source of ethyleneglycolate ligands. Synthesis and characterization of $\text{Nb}_4(\mu, \eta^1, \eta^2\text{-OC}_2\text{H}_4\text{O})_2(\mu_3, \eta^1, \eta^2\text{-OC}_2\text{H}_4\text{O})_2(\mu\text{-OC}_2\text{H}_4\text{O})(\text{OPr}^i)_{10}$

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The reaction between niobium isopropoxide and 2-hydroxyethylmethacrylate (HEMA) at room temperature (1:1 stoichiometry) afforded $[\text{Nb}_4(\mu, \eta^1, \eta^2\text{-OC}_2\text{H}_4\text{O})_2(\mu_3, \eta^1, \eta^2\text{-OC}_2\text{H}_4\text{O})_2(\mu\text{-OC}_2\text{H}_4\text{O})(\text{OPr}^i)_{10}]$ as characterized by X-ray diffraction.

Hybrid organic–inorganic materials have stimulated increasing research due to the diversity of their applications.¹ One approach to such materials is based on the modification of metal alkoxides either in processing conditions (*in situ*) or prior to processing with reactants and/or ligands allowing differential hydrolysis and/or polymerization *via* unsaturated moieties.² Derivatives with vinyl or methacrylate groups are the most commonly used for access to hybrid materials of class I or class II, where organic and inorganic components are respectively weakly or covalently bonded, over a broad range of compositions and morphologies.³ 2-Hydroxyethylmethacrylate (HEMA) was selected as an organic monomer with silicon⁴ and zirconium alkoxides⁵ for access to non-shrinking sol–gel composites. However, the differences in the reactivity patterns between silicon and zirconium meant that the silicon alkoxide $\text{Si}(\text{OR})_4$ ($\text{R} = \text{OC}_2\text{H}_4\text{OC}(\text{O})\text{CH}=\text{CH}_2$) could be isolated while more complex reactions affording gels were observed in the case of zirconium n-propoxide and n-butoxide. We have previously shown that titanium mediated the C–O bond cleavage of HEMA giving an unusual titanium pentanuclear diolate cluster,⁶ $\text{Ti}_5(\text{OC}_2\text{H}_4\text{O})_5(\mu\text{-OPr}^i)(\text{OPr}^i)_9$. We wish to report here our investigations into HEMA and niobium isopropoxide.

The reaction between niobium isopropoxide and 2-hydroxyethylmethacrylate (HEMA) was carried out in toluene at room temperature (1:1 stoichiometry). ¹H NMR and FT-IR monitoring indicated evolution of the unsaturated ligand subsequent to the substitution reactions. The absorption band at 1640 cm^{-1} due to the $\nu\text{C}=\text{C}$ vibration progressively disappeared. In the ¹H NMR spectra, one can notice the decrease of the multiplets attributed to the CH and CH₂ groups. After work-up, a crystalline compound **1** no longer having unsaturated functionalities, as evidenced by the absence of $\nu\text{C}=\text{C}$ absorption bands around 1636 cm^{-1} in the FT-IR spectrum, was isolated. Compound **1** was obtained in high and reproducible yields.† Its elemental analysis accounts for a composition corresponding roughly to two isopropoxides to one ethyleneglycolate ligand. The essential features of the ¹H NMR spectra at room temperature are two septuplets at 4.85 and 4.81 ppm (integration 2:8) corresponding to the CH groups of the OPrⁱ ligands together with numerous peaks between 4.7 and 4.00 ppm. Low temperature spectra indicated splitting of the peak at 4.81 ppm and thus non-equivalence of the corresponding isopropoxide ligands.

The molecular structure of **1** corresponds to $[\text{Nb}_4(\mu, \eta^1, \eta^2\text{-OC}_2\text{H}_4\text{O})_2(\mu_3, \eta^1, \eta^2\text{-OC}_2\text{H}_4\text{O})_2(\mu\text{-OC}_2\text{H}_4\text{O})(\text{OPr}^i)_{10}]$ as established by X-ray diffraction (Fig. 1).‡ The structure is based on a centrosymmetrical tetranuclear open-shell framework, the angles being $139.2(1)^\circ$ and $138.1(1)^\circ$ for $\text{Nb}(1)\cdots\text{Nb}(2)\cdots\text{Nb}(3)$ and $\text{Nb}(2)\cdots\text{Nb}(3)\cdots\text{Nb}(4)$ respectively. The metallic

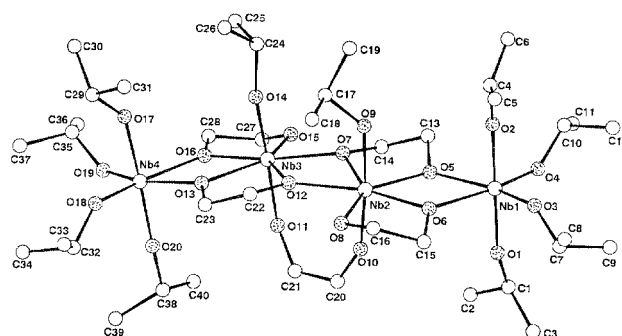


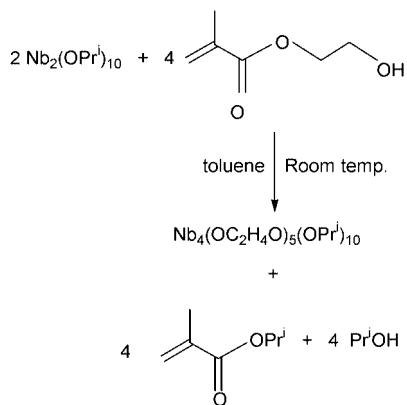
Fig. 1 Molecular structure of $[\text{Nb}_4(\mu, \eta^1, \eta^2\text{-OC}_2\text{H}_4\text{O})_2(\mu_3, \eta^1, \eta^2\text{-OC}_2\text{H}_4\text{O})_2(\mu\text{-OC}_2\text{H}_4\text{O})(\text{OPr}^i)_{10}]$ showing the atom numbering scheme. Selected bond distances (Å): $\text{Nb}\cdots\text{Nb}$ 3.54 (av.), $\text{Nb}\text{-OPr}^i$ 1.84(1)–1.91(1), $\text{Nb}(4)\text{-O}(16)$ 2.11(1), $\text{Nb}(3)\text{-O}(16)$ 2.11(1), $\text{Nb}(4)\text{-O}(13)$ 2.09(1), $\text{Nb}(3)\text{-O}(13)$ 2.12(1), $\text{Nb}(3)\text{-O}(12)$ 2.11(1), $\text{Nb}(3)\text{-O}(15)$ 1.92(1), $\text{Nb}(2)\text{-O}(12)$ 2.11(1), $\text{Nb}(2)\text{-O}(7)$ 2.196(9), $\text{Nb}(3)\text{-O}(7)$ 2.09(1), $\text{Nb}(3)\text{-O}(11)$ $\text{Nb}(2)\text{-O}(10)$ 1.89(1).

centers are of two types, Nb(1) and Nb(4) are six-coordinate while Nb(2) and Nb(3) are seven-coordinate. They are connected by ethyleneglycolate ligands derived from 2-hydroxyethylmethacrylate. The ethyleneglycolate ligands all assemble the metal cluster but display different types of coordination mode namely bridging and bridging-chelating. The bridging-chelating ones are of two types assembling either two or three metals. The Nb–OR bond lengths vary from 1.84(1) to 2.196(9) Å with the ranking $\text{Nb}\text{-OPr}^i < \text{Nb}\text{-}\eta^2\text{-OC}_2\text{H}_4\text{O} < \text{Nb}\text{-}\mu\text{-OC}_2\text{H}_4\text{O} \approx \text{Nb}\text{-}\mu_3\text{-OC}_2\text{H}_4\text{O}$. The isopropoxide ligands are all in terminal positions, the longest bond distance being *trans* to μ_3, η^2 -ethyleneglycolate ligands. The Nb–O–C angles of the alkoxide ligands vary from $135.1(10)$ to $166.3(13)^\circ$, the smallest values are observed for the equatorial bonds. The bridging diolate possesses quite large Nb–O–C angles [$152.2(14)^\circ$ av.] as compared to the bridging-chelating ones which are more acute [$114.2(8)$ – $127.7(10)^\circ$]. The central, heptacoordinated metals have a slightly distorted bipyramidal pentagonal environment [$\text{O}(11)\text{-Nb}(3)\text{-O}(14)$ $174.7(4)^\circ$, $\text{O}(9)\text{-Nb}(2)\text{-O}(10)$ $170.4(4)^\circ$]. The stereochemistry of the hexacoordinated metals is more severely distorted [$\text{O}(4)\text{-Nb}(1)\text{-O}(3)$ $106.7(5)^\circ$, $\text{O}(5)\text{-Nb}(1)\text{-O}(6)$ $65.9(4)^\circ$]. Indeed the small bite angles of the ethyleneglycolate ligands (74.45° av.) as well as the acute intrabridge angles (65.6° av.) are more in agreement with the steric demands of the equatorial ligands in a pentagonal bipyramidal environment than with an octahedral geometry. The Nb \cdots Nb distances are quite long (av. 3.54 Å) as compared to other polynuclear niobium alkoxide derivatives which display more compact structures [e.g. 3.177(1)–2.268(1) Å for tri- or tetranuclear pinacولات].⁷ The formation of the tetranuclear framework can formally be seen as the assembly of two dinuclear units $[\text{Nb}_2(\text{OPr}^i)_5(\text{OC}_2\text{H}_4\text{O})_2(\text{OC}_2\text{H}_4\text{OH})]$ and $[\text{Nb}_2(\text{OPr}^i)_6(\text{OC}_2\text{H}_4\text{O})_2]$, in which the metals are six-coordinate. The assembly proceeds by

deprotonation of the residual hydroxyl functionality, elimination of one molecule of isopropanol and transformation of the μ, η^2 -diolates into μ_3, η^2 -ligands leading to seven-coordinate metals (Fig. 1). The structure of **1** is related to that of $[\text{Ti}_4(\mu, \eta^2\text{-OCH}_2\text{CH}=\text{CHCH}_2\text{O})_4(\text{OPr}^i)_8]$, obtained by reacting $\text{Ti}(\text{OPr}^i)_4$ and 2-butene-1,4-diol,⁸ although the coordination numbers of the metals are lower, being 5 and 6.

A number of tetranuclear niobium(v) species have been reported. They are generally oxo-species and the structures are based on close-packed octahedra. Typical examples are $[\text{Nb}_4(\mu\text{-O})_4(\mu, \eta^2\text{-R}'\text{CO}_2)_4(\text{OR})_8]$ ($\text{R} = \text{Pr}^i$, $\text{R}' = \text{methacrylate}$,⁹ acetate),¹⁰ $[(\mu\text{-BHMP})\text{Nb}_2(\mu\text{-O})(\text{OEt})_2]_2$ ($\text{BHMPH}_3 = \text{bis}(\text{hydroxymethyl})\text{propionic acid}$)¹¹ and $[\text{Nb}_4(\mu\text{-O})_2(\mu_3\text{-O})_2(\mu, \eta^2\text{-OCMe}_2\text{-CMe}_2\text{O})_2(\text{OPr}^i)_8]$.⁷ Hexacoordination was retained despite the presence of polydentate ligands. Compound **1** corresponds to an open-shell polyhedron. The only other example of a tetranuclear open-shell framework for pentavalent heavy Group 5 metals seems to be the $[\text{M}_2(\mu\text{-O})\text{Cl}_2]_2^{2-}$ ($\text{M} = \text{Nb, Ta}$) anions.¹² Assembly into a tetrameric unit is achieved *via* two bridging chloro ligands but all the metals are six-coordinate. Hepta-coordination has been observed for pentavalent niobium and is quite common for low valent species.^{12,13} However, structurally characterized niobium alkoxide derivatives displaying hepta-coordination have, to the best of our knowledge, not been reported.

The ¹H NMR data of **1** are consistent with the retention of the solid state structure in solution. The formation of compound **1** can be summarized by Scheme 1.



Scheme 1

The reaction between niobium isopropoxide and HEMA proceeds by transesterification generating stable five-membered chelates. If this system is used for access to hybrid materials *via* polymerization of the organic and inorganic network, the formation of materials of class II will most probably be limited to the early stages of the condensation. It is noteworthy that the use of HEMA as a source of diolate ligands affords species with unusual coordination numbers and without oxo-ligands, by contrast to a system using pinacol in which the assembly between the metals proceeds with generation of oxo-ligands.⁷ As anticipated and despite the fact that all isopropoxide ligands are in terminal positions and thus quite accessible, **1** is less susceptible to hydrolysis than niobium isopropoxide. Its poor solubility in isopropanol however requires the use of solvents different from the parent alcohol such as THF or toluene. Clear sols were obtained for hydrolysis ratios in the range 1–5 (0.02 M in THF).

Notes and references

† All manipulations were routinely performed under a nitrogen atmosphere using Schlenk tubes and vacuum line techniques with dried and distilled solvents. $\text{Nb}(\text{OPr}^i)_5$ was prepared as reported in the literature.¹⁴ HEMA was stored over molecular sieves. ¹H NMR spectra were recorded on solutions on a Bruker AC-200 spectrometer. Infrared spectra were recorded with a Perkin Elmer Paragon spectrometer as Nujol mulls between KBr plates. Analytical data were obtained from the Centre de Microanalyses du CNRS.

Synthesis of $\text{Nb}_4(\text{O}^i\text{Pr})_{10}(\text{OC}_2\text{H}_4\text{O})_5$ **1**. 0.48 ml (3.81 mmol) of 2-

hydroxyethylmethacrylate in 10 ml of toluene were added to 1.48 g (1.9 mmol) of $[\text{Nb}(\text{O}^i\text{Pr})_5]_2$ in 15 ml of toluene. Evaporation of the solvent after 24 h gave a pasty compound which was dissolved in hexane-toluene (1:1). 1.05 g (87%) of crystals soluble in usual organic solvents except alcohols were obtained by crystallization at room temperature. Anal. found: C, 38.51; H, 7.43. Calc. for $\text{C}_{40}\text{H}_{90}\text{O}_{20}\text{Nb}_4$, C, 38.04; H, 7.3%. IR cm^{-1} : 1324m, 1271m, 1254m, 1156s, 1133s, 1082s, 1003s, 983s, 925m, 906m, 848m $\nu\text{C-O}$, $\nu\text{C-C}$; 632m; 594s, 534s, 486s, 461s, 442s $\nu(\text{Nb-OR})$. ¹H NMR (CDCl_3 , ppm): 4.85, 4.81 (2:8) (sept, $J = 6$ Hz, 10H, CH); 4.7–4.00 (overlapping of peaks, CH_2 , 20H); 1.2 (d, $J = 6$ Hz, Me); 1.05 (d, $J = 6$ Hz, Me).

‡ Crystal data for **1**: $\text{C}_{40}\text{H}_{90}\text{O}_{20}\text{Nb}_4$, $M = 1262.77$, triclinic, space group $P\bar{1}$, $a = 17.938(5)$, $b = 17.960(5)$, $c = 9.335(5)$ Å, $U = 2807(4)$ Å³, $Z = 2$, $\mu(\text{Mo-K}\alpha) = 8.23$ cm^{-1} . Intensity data were collected at -112 °C on an Enraf Nonius CAD4 diffractometer. The intensities of the reflections were quite low and only a small range of θ could be used. No better crystals could be grown. Empirical absorption correction (DIFABS) was applied. Computations were performed by using the PC version of CRYSTALS.¹⁵ The structure was solved by direct methods (SHELXS 86)¹⁶ and successive Fourier maps. Only niobium and oxygen atoms were anisotropically refined because of the low number of reflections. Hydrogen atoms were theoretically located, they were refined isotropically. Least squares refinement (2703 reflections $I > 2\sigma(I)$) reached convergence with $R = 0.069$ and $R_w = 0.080$, 276 parameters. In the last stages of the refinement, each reflection was assigned a weight $w = w'[1 - (|F_o| - |F_c|)/6\sigma(F_o)]^2$ with $w' = 1/\text{SrArTr}(x)$ with 3 coefficients 7.67, -0.295 and 4.22 for a Chebyshev series, for which x is $F_o/F_c(\text{max})$.¹⁷ CCDC reference number 186/1542. See <http://www.rsc.org/suppdata/dt/1999/2407/> for crystallographic files in .cif format.

- H. Schmidt, *J. Sol-Gel Sci. Technol.*, 1994, **1**, 217.
- U. Schubert, N. Husing and A. Lorenz, *Chem. Mater.*, 1995, **7**, 2010; U. Schubert, E. Arpac, W. Glaubitt, A. Helmerich and C. Chau, *Chem. Mater.*, 1992, **4**, 291; C. Sanchez, F. Ribot and B. Lebeau, *J. Mater. Chem.*, 1999, **9**, 35; U. Schubert, *J. Chem. Soc., Dalton Trans.*, 1996, 3343; C. Sanchez and F. Ribot, *New J. Chem.*, 1994, **18**, 1007; L. G. Hubert-Pfalzgraf, *Coord. Chem. Rev.*, 1998, **178–180**, 967.
- C. Sanchez, M. In, P. Toledano and P. Griesmar, *Better Ceramics through Chemistry VI, Mater. Res. Soc. Proceedings*, 1992, **271**, 669; C. Sanchez and M. In, *J. Non-Cryst. Solids*, 1992, **147**, 1; K. Y. Blohowick, D. R. Treadwell, B. L. Mueller, M. L. None, S. Jouppi, P. Kansal, K. W. Chew, C. L. S. Scotto, F. Babonneau, J. Kampf and R. M. Laine, *Chem. Mater.*, 1994, **6**, 2177.
- B. M. Novak and C. Davies, *Macromolecules*, 1991, **24**, 5481; M. W. Ellsworth and B. M. Novak, *Chem. Mater.*, 1993, **5**, 839.
- R. Di Maggio, L. Fambri and A. Guerriero, *Chem. Mater.*, 1998, **19**, 1777.
- N. Pajot, R. Papiernik, L. G. Hubert-Pfalzgraf, J. Vaissermann and S. Parraud, *J. Chem. Soc., Chem. Commun.*, 1995, 1817.
- L. G. Hubert-Pfalzgraf, V. Abada and J. Vaissermann, *Polyhedron*, 1999, **18**, 845.
- N. Pajot, PhD Thesis, University of Nice, 1996; N. Pajot-Miele, R. Papiernik, L. G. Hubert-Pfalzgraf and J. Vaissermann, to be published.
- (a) L. G. Hubert-Pfalzgraf, V. Abada, J. Vaissermann and J. Rozière, *Polyhedron*, 1997, **16**, 581; (b) W. A. Nugent and R. L. Harlow, *J. Am. Chem. Soc.*, 1994, **116**, 6142; (c) D. A. Brown, W. Errington and M. G. H. Wallbridge, *J. Chem. Soc., Dalton Trans.*, 1993, 1067.
- N. Stenou, C. Bonhomme, C. Sanchez, J. Vaissermann and L. G. Hubert-Pfalzgraf, *Inorg. Chem.*, 1998, **37**, 901.
- J. Boyle, T. M. Alam, D. Dimos, G. J. Moore, C. D. Buchheit, H. N. Al-Shareef, E. R. Mechenbier, R. R. Bear, J. W. Ziller, *Chem. Mater.*, 1997, **9**, 3187.
- L. G. Hubert-Pfalzgraf, M. Postel and J. G. Riess, *Comprehensive Coordination Chemistry*, 1987, Pergamon Press, London, ch. 34; L. G. Hubert-Pfalzgraf, *Encyclopedia of Inorganic Chemistry*, ed. B. King, Wiley, New York, 1994.
- D. R. Taylor, J. C. Calabrese and E. M. Larsen, *Inorg. Chem.*, 1977, **16**, 721; E. Hey, F. Weller and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 1984, **514**, 25.
- D. C. Bradley, R. C. Mehrotra and D. P. Gaur, *Metal Alkoxides*, Academic Press, London, 1978.
- D. J. Watkin, J. R. Carruthers and P. W. Betteridge, *Crystals User, Chemical Crystallography Laboratory*, Oxford, UK, 1988.
- G. M. Sheldrick, SHELXS 86, Program for Crystal Structure Solution, University of Göttingen, Germany, 1986.
- L. J. Pearce and D. J. Watkin, Cameron, Chemical Crystallography Laboratory, Oxford, UK, 1992.