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The Obtention of Niobium Oxyalkoxides Derivatives by Direct Alkoxylation of the Oxychloride

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The niobium(V) oxyalkoxide derivatives $[NbO(OCH_2CF_3)_3 \cdot MeCN]_2$, $NbO(OCH_2CF_3)_2(OCH{=}CF_2)(CF_3CH_2OH)_{0.5}$, $[NbO(OEt)_3]_2$, $[NbOCl_2(OCH_3) \cdot CH_3OH]_2$ *and* $NbO(OCH_3)(OC_6H_4CHO)_2$ *have been obtained by direct alkoxylation of niobium oxychloride, and characterised. The molecular constitution of the solutions of* $[NbO(OEt)_3]_2$ *and* $[NbO(OCH_2CF_3)_3 \cdot MeCN]_2$ *in non-polar solvents was tentatively interpreted as a dynamic equilibrium between various μ-alkoxo and μ-oxo isomers, the latter being favoured by dilution. In polar media, dimeric units are retained for* $[NbO(OEt)_3]_2$, *while the trifluoroethoxide derivative is split into monomeric species.*

Introduction

During the past decade, the chemistry of transition metal alkoxides has received considerable attention [1]. By contrast, there is a paucity of data on the related oxyalkoxides, although these have various potential applications. For example, vanadiumoxytributoxide is known to catalyse the epoxidation of cycloalkenes [2], an oxyalkoxide of aluminium and iron(II) was found to act as a reversible molecular oxygen activator [3], and other polymetallic oxyalkoxides are efficient polymerisation catalysors [4].

While numerous adducts of the oxyhalides of the early transition metals, and especially of niobium and tantalum, have been described [1, 5], synthetic routes to well-characterized oxyalkoxide derivatives remain surprisingly scarce. Thus Leshchenko *et al.* [6] mention that the treatment of $NbOCl_3$ with methanol in benzene resulted only in a compound of composition $NbOCl_3 \cdot MeOH$, and an early attempt at a direct synthesis of oxyalkoxide compounds from $NbOBr(acac)_2$ failed as a result of the unexpected solvolysis of the oxo bond [7]. On the other hand, some transition metal oxyalkoxides such as $WO(OR)_4$ (R = Me, Et, n-Bu, n-Pr) [8] and $VO(OMe)_3$ [9] were successfully prepared when ammonia was bubbled through the alcohol metal oxyhalide solutions, and we recently reported the preparation of $NbOCl_2(OMe)2HMPA$ directly from $NbOCl_3$ [10]. We therefore undertook to reinvestigate the direct alkoxylation of niobium oxychloride. The various species $[NbO(OCH_2CF_3)_3 \cdot MeCN]_2$, $[NbO(OCH_2CH_3)_3]_2$, $[NbOCl_2(OCH_3) \cdot CH_3OH]_2$, $NbO(OCH_3)(OC_6H_4CHO)_2$ and $NbO(OCH_2CF_3)_2(OCH{=}CF_2)(CF_3CH_2OH)_{0.5}$ were obtained and characterised. The molecular constitution of the solutions in non-polar solutions of the first two compounds was tentatively interpreted as a dynamic equilibrium between various μ-alkoxo and μ-oxo dimeric units.

Experimental

All manipulations were carried out under dry nitrogen using Schlenk tube techniques. Solvents were dried and purified by standard methods. Niobium(V) oxychloride was prepared from the niobium pentaoxide and aluminium trichloride. 2,2,2-trifluoroethanol and 2,2,2-trichloroethanol were purified by distillation. Salicylaldehyde was distilled immediately before use.

NMR spectra were recorded on a C60-HL JEOL spectrometer equipped with a variable temperature attachment and a WH-90 Bruker spectrometer operating in the Fourier transform mode. Tetramethylsilane (^1H) and trifluorochloromethane (^{19}F) were used as internal references. Fluorine shifts are given positively to lower fields. IR spectra were recorded on a Perkin-Elmer 577 spectrometer on Nujol mulls. Molecular weight data were obtained from a Knauer vapor pressure osmometer. Elemental analyses and mass spectra (on a MS-30-AEI spectrometer at 70 eV) were carried out by the Service Central de Microanalyse of the CNRS.

Preparation of the Complexes

Oxotri(2,2,2-trifluoroethoxo)acetonitrile niobium(V), $NbO(OCH_2CF_3)_3MeCN$

2,2,2-trifluoroethanol (740 mg, 7.50 mmol) was added at room temperature to a solution of $NbOCl_3$

(520 mg, 2.41 mmol) in 20 ml acetonitrile. After 30 mn dry ammonia was bubbled through the solution for 1 h. Ammonium chloride was removed by filtration and the product was isolated by vacuum distillation (98 °C, 0.4 mm Hg) after evaporation of the solvents, yielding 807 mg (~75%) of a white solid (m.p. 35 °C) insoluble in aliphatic hydrocarbons, slightly soluble in toluene, soluble in dichloromethane, acetonitrile and other polar solvents. *Anal.* Calcd for ($C_8H_9F_9NNbO_4$): C, 21.47; H, 2.03; F, 38.25; N, 3.13. Found: C, 21.55; H, 2.08; F, 38.40; N, 3.02%. *IR*: 2305, 2298 (νC≡N); 1300, 1272, 1190, 1170 (νC–F); 1150–1020 (νCOR); 950 (νNb=O); 894, 840–650 (δC–F); 540 (νNb–OR); 360. *Mass spectrometry* (130 °C (m/e$^+$): [$NbOH(OCH_2CF_3)_3 \cdot 2CH_3CN$] (M) 3%; ($M-CH_2CF_2$) 8%; $M-2CH_2CF_2-CH_3CN$ 13%; $M-3CH_2CF_2$ 4%; $NbH_3(CH_2CF_3)$ 13%; NbO_2H_3F 20%; NbOF 100%.

$NbO(OCH_2CF_3)_2(OCH{=}CF_2)\cdot \frac{1}{2}CF_3CH_2OH$

The same procedure, but using toluene as a solvent, led to another crystalline product (m.p. 126 °C) isolated by vacuum distillation (105 °C,1 mm Hg) in 65% yield. *Anal.* : Calcd for ($C_7H_{6.5}F_{9.5}NbO_{4.5}$): C, 19.26; H, 1.51; F, 41.39. Found: C, 19.45; H, 1.67; F, 40.86%. *IR*: 3160 (νOH); 1655 (νC=C); 1300, 1280, 1165 (νC–F); 1089, 1020 (νCOR); 950, 935 (νNb=O); 830, 720 (δCF), 620, 600; 525 (νNb–OR); 360, 330. *Mass spectrometry* (130 °C): $M-HF-\frac{1}{2}H_2$ 2%; $M-\frac{1}{2}ROH-HF-CH_2CF_2$ 12%; $NbO_2H_3(OCHCF_2)$ 34%; $NbH_2(CH_2CF_3)$ 23%; NbO_2H_3F 27%; CF_2H_2 100%.

Oxotriethyoxoniobium(V), $NbO(OCH_2CH_3)_3$

The same procedure was applied to 1.66 g (7.7 mmol) of $NbOCl_3$ in 50 ml toluene and 1.5 ml (25.7 mmol) ethyl alcohol. The expected stoichiometric amount of ammonium chloride was filtered off, and the solvent was removed under vacuum. The crude product was purified by recrystallisation in a mixture of toluene and hexane (1/1); yielding 1.22 g (65%) of a very air-sensitive white solid (m.p. 191 °C) which is soluble in toluene, dichloromethane and acetonitrile. *Anal.*: Calcd for ($C_6H_{15}NbO_4$): C, 29.51; H, 6.19. Found: C, 29.43; H, 5.96%. *IR*: 1155, 1120, 1080, 1060 (νC–OR); 930, 910 (νNb=O); 860, 810, 740, 710; 580, 540, 470 (νNb–O–R). *Mass spectrometry* (150 °C): (D = $Nb_2O_2(OEt)_6$); $D-Me_2CO-\frac{1}{2}H_2$ 2%; $D-Me_2CO-\frac{1}{2}H_2-Et_2O$ 4%; $D-Me_2CO-Et_2O-CH_4$ 3%; $D-Me_2CO-2Et_2O-\frac{1}{2}H_2$ 8%; $D-Me_2CO-2Et_2O-CH_4$ 3%;$Nb_2(OEt)$ 4%; $NbO(OEt)_2$ 12%; $NbO(OC_2H_5)(OCH_2)$ 18%; $NbO_2H(OC_2H_5)$ 28%; NbO_2H_4 100%.

Oxodichloromethoxomethanolniobium(V), $NbOCl_2(OCH_3)\cdot CH_3OH$

Methanol (2 ml, 50 mmol) was added dropwise to a stirred suspension of $NbOCl_3$ (1.9 g, 8.8 mmol) in dry benzene (20 ml) at room temperature. The dissolution of niobium oxychloride was observed, and the clear solution was evaporated to dryness after stirring for 1 h. The crude product was washed with petroleum ether and recrystallized from toluene, yielding 0.71 g (63%) of white $NbOCl_2(OCH_3)\cdot CH_3OH$ (m.p. 180 °C). *Anal.*: Calcd for ($C_2H_7Cl_2NbO_3$): C, 9.88; H, 2.90; Cl, 29.22. Found: C, 10.04; H, 2.91; Cl, 29.62%. *IR*: 3310 (νOH); 1305, 1260, 1210 (r∥CH₃); 1170, 1080 (νC–OR); 962, 951, 932, 916; 770, 733, 720 (νNb–O–Nb); 560, 540, 520 (νNb–OR); 430, 408, 300 (νNb–Cl).

Oxomethoxodisalicylatoniobium(V), $NbO(OMe)(OC_6H_4CHO)_2$

Methanol (2 ml, 90 mmol) was added at room temperature to a stirred suspension of $NbOCl_3$ (1.09 g, 5.07 mmol) in 10 ml toluene. After 15 mn, 2 ml (17 mmol) salicylaldehyde were added to the clear solution, whose color immediately became yellow. After 20 mn, the solution was cooled to –45 °C and ammonia was slowly bubbled through the mixture for 1 h. The light yellow precipitate (0.80 g) was immediately filtered off, and washed with toluene and acetonitrile. The solvent was removed from the solution under vacuum, and a sticky orange solid was obtained. The crude product was recrystallized in a mixture of dichloromethane:toluene:pentane (2:2:1) at –20 °C, giving 968 mg (50%). The product is insoluble in CH_2Cl_2 and toluene, slightly soluble in CH_3CN, and more soluble in pyridine. *Anal.*: Calcd for $C_{15}H_{13}NbO_6$: C, 47.15; H, 3.45; Nb, 24.35. Found: C, 48.48; H, 3.58; Nb, 24.85%. *IR*: 1625 (νC=O); 1550 (νC=C); 1300, 1285; 1150, 1112, 1060, 1030 (ν(COR), 970; 930 (νNb=O), 890, 840; 750, 720, 610; 590 (νNb–OR). *NMR*: (CD_3CN): 4.58 ppm.

Results and Discussion

Synthesis and Characterisation

Leshchenko *et al.* [6] mentioned the obtention of a compound of composition $NbOCl_3\cdot MeOH$ by treating $NbOCl_3$ with methanol in benzene. In contrast to this, we found that the reaction between $NbOCl_3$ and methanol, when carried out at room temperature in benzene or toluene, led to the oxymethoxydichloride methanol adduct $NbOCl_2(OMe)\cdot MeOH$. No further substitution of chlorine was observed even in the presence of a large excess of the alcohol at room temperature. Addition of a slight excess of HMPA to a toluene solution of $NbOCl_2(OMe)\cdot MeOH$ led to $NbOCl_2(OMe)\cdot 2HMPA$, which was identified with a sample obtained through another route [10].

The 'ammonia method', which involved the bubbling of ammonia through the alcohol/metal halide solutions, has been widely used to obtain totally substituted transition metal alkoxides from the chlorides. It was also used successfully to prepare some oxyalkoxides, such as $WO(OR)_4$ [8] (R = Me, Et, n-Bu, nPr) and $VO(OMe)_3$ [9]. However, when applying this method to the preparation of niobium oxyalkoxides (eqn. 1):

$$NbOCl_3 + ROH_{excess} \xrightarrow[\text{To or } CH_3CN]{NH_3} NbO(OR)_3(S) + 3\,NH_4Cl \qquad (1)$$

$$(S) = MeCN$$

with various alkoxo groups (R = Me, Et, tBu, CH_2CF_3, CH_2CCl_3), we found it to be more limited. It nevertheless allowed us to obtain niobium oxytriethoxide using toluene as a solvent, but the corresponding 2,2,2-trifluoroethoxide $NbO(OCH_2CF_3)_3$ could not be freed from an additional molecule of acetonitrile when it was carried out in this solvent; the acetonitrile is bound strongly enough to prevent its loss during fractional vacuum distillation. When the reaction was performed in benzene or toluene we observed the elimination of hydrofluoric acid leading to the mixed oxyalkoxide adduct $NbO(OCH_2CF_3)_2(OCH{=}CF_2)(CF_3CH_2OH)_{0.5}$. This evolution towards an unsaturated alkoxide was also observed for MeCN solutions of $NbO(OCH_2CF_3)_3 \cdot MeCN$ after 1 week at room temperature, and was complete after 3 months (doublet on ^{19}F spectra at –50.5 ppm, J = 11.5 Hz). An oxo tantalum derivative having an enolate ligand has recently been obtained by allowing CO to react with an alkyl species [11].

But, although well defined niobium(V) oxyalkoxides such as $NbO(OEt)_3$, $NbO(OCH_2CF_3)_3 \cdot MeCN$ and $NbO(OMe)(OC_6H_4CHO)_2$ could be obtained by this method, the isolation of pure products was more often precluded by side reactions. The strong coordinative ability of ammonia towards transition metal oxychlorides [12] or their oxyalkoxides led for example to an exothermic reaction, and polymeric (neutral or ionic) [13] products (for R = Me), which could not be separated from ammonium chloride, or compounds containing a variable amount of ammonia (for R = tBu) were then obtained, even when the reaction was carried out at low temperature (–40 °C). The polymeric nature of these derivatives was confirmed by the presence of a broad absorption band in the 850 to 720 cm^{-1} (νNb–O–Nb) range in the infra-red. The formation of polynuclear oxomethoxo species, during a titration experiment on $NbOCl_3$ using sodium methylate, has already been mentioned by Gut [14]. We were able to limit the extent of formation of such polymeric compounds by adding the ammonia at –45 °C in the presence of an excess of a strong ligand; when salicylaldehyde was used, $NbO(OMe)(OC_6H_4CHO)_2$ formed and could be isolated in good yields when treated rapidly. Another side reaction, the solvolysis of the niobium oxo bond (evidenced by the disappearance of the νNb=O and νNb–O–Nb absorptions in the infra-red of the isolated metal derivatives), was observed with trichloroethanol, even at low temperature. Finally, it must be noticed that the various side reactions were generally unaffected by using triethylamine instead of ammonia as a base.

The new compounds were characterised by elemental analysis, infra-red and mass spectrometry, and, in solution, by molecular weight data and ^1H and ^{19}F NMR measurements. The obtention of oxyalkoxides was confirmed by the presence of the μ-oxo stretching absorption (770–720 cm^{-1}) for $NbOCl_2(OMe) \cdot MeOH$ or, for all other derivatives, by the presence of a νNb=O stretching frequency (strong band at 950–910 cm^{-1}, depending on the compound) in the IR of the solid state [7, 15]. The presence of a ligating acetonitrile molecule in the latter compound was confirmed by the increase of the νC≡N stretching frequency from 2254 in the free ligand to 2305 and 2298 cm^{-1}. The coordination of salicylaldehyde through its carbonyl group in $NbO(OMe)(OC_6H_4CHO)_2$ [16] is reflected by the lowering of the νC=O frequency by 35 cm^{-1}. The metal–alkoxo vibrations [17] were found between 600 and 525 cm^{-1}, their position depending on the nature of the alkoxo group and of the other ligands which surround the metal, while the metal–chlorine stretching frequencies were observed at 408 and 300 cm^{-1} for $NbOCl_2(OMe) \cdot MeOH$.

The volatility of the totally substituted oxyalkoxides allowed their characterisation by mass spectrometry. The parent peak corresponding to a dimeric structure in the gaseous phase was only observed for the ethoxo derivative $[NbO(OEt)_3]_2$. Indeed, the stability of the dimeric trifluoroethoxo derivative was lower, and the heaviest fragment found corresponds to $NbOH(OCH_2CF_3)_3 \cdot 2MeCN$, further confirming the strong coordinating ability of acetonitrile towards niobium oxytrifluoroethoxide [18].

Molecular Constitution in Solution

Structural information in solution was mainly gained by using NMR techniques and vapour pressure osmometry. Preceding studies have already established the high complexity of the molecular constitution of monomeric oxoniobium [10, 19] and oxotungsten [20] adducts in solution. In the case of the new oxyalkoxide derivatives, $NbOCl_2(OMe) \cdot MeOH$, $NbO(OEt)_3$ and $NbO(OCH_2CF_3)_3 \cdot MeCN$, the number of expected isomers is increased by the fact that they are dimeric (by osmometry, see below) in non polar solvents. On the other hand, as the synthesis of $NbO(OCH_3)_3$ failed, we were left with compounds having less convenient NMR probes, while ^{13}C NMR measurements were precluded by the

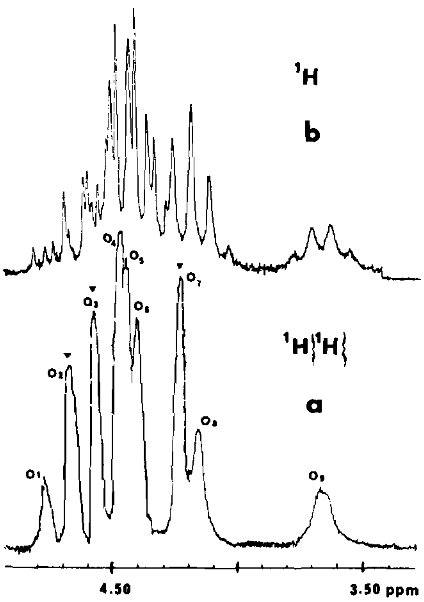


Fig. 1. Proton NMR spectra of $[NbO(OEt)_3]_2$ in CD_2Cl_2 (0.17 molar) at room temperature: a) undecoupled spectra; b) decoupled spectra ($\delta O_1 = 4.78$, $\delta O_2 = 4.67$, $\delta O_3 = 4.57$, $\delta O_4 = 4.46$; $\delta O_5 = 4.44$, $\delta O_6 = 4.40$, $\delta O_7 = 4.22$, $\delta O_8 = 4.17$, $\delta O_9 = 3.66$ ppm).

dilution of the solutions. Also note that the studies must be performed on fresh solutions, since the evolution to species having an enolate ligand occurs after *ca.* a week at room temperature in MeCN. Only a rough picture of the molecular constitution of the solutions could therefore be obtained.

As an instance of this, numerous isomers having μ-oxo (as identified by the IR solid state), μ-methoxo or μ-dichloro bridges are often compatible with the evidence available on $[NbOCl_2(OMe)\cdot MeOH]_2$ (M found 520, calcd. 486) solutions in non polar media. This may explain the complex NMR pattern observed at −57 °C in the methoxo region (six resonances ranging from 3.82 to 4.37 ppm) of its 0.04 molar solution in toluene. Since the relative ratios of all these signals vary when the temperature or the dilution is modified, this implies the presence of at least six distinct molecular species.

The proton NMR spectra of a 0.17 molar solution of $NbO(OEt)_3$ in CD_2Cl_2 at room temperature shows numerous signals (Fig. 1). The OCH_2 resonances region exhibits a complex pattern (from 4.84 to 4.03 ppm) resulting from the superposition of at least eight quadruplets, while another quadruplet is observed at distinctly higher field ($\delta O_9 = 3.66$ ppm, J = 7.2 Hz). No additional resonances were detected at lower temperature (to −50 °C), but the relative area of the most shielded quadruplet increased. The coalescence of all nine quadruplets at 60 °C indicates

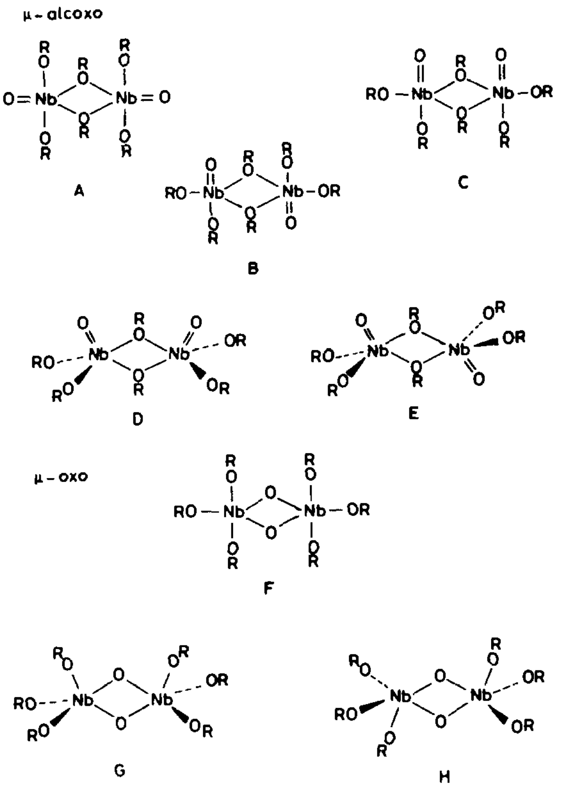


Fig. 2. Possible geometrical isomers of $[NbO(OEt)_3]_2$ and tentative assignments.

that the various species present are in dynamic equilibrium on the NMR time scale. Since the compound is dimeric (M found 525, calcd. 488 in C_6H_6) the metal is likely to be pentacoordinated in $[NbO(OEt)_3]_2$. Eight molecular species can then be expected, the μ-alkoxo isomers A to E and the μ-oxo derivatives F to H, if one assumes that the metal exhibits 'regular' trigonal bipyramidal or square pyramidal environments (Fig. 2). The simultaneous presence of all these species in solution would result in a maximum of 18 quadruplets. The analysis of the $^1H\{^1H\}$ NMR spectra (Fig. 1b) in various conditions of temperature and dilutions permitted the recognition of which signals keep constant area relationship and are therefore likely to belong to a same molecular species. The nine signals were thus found to belong to five independent sets (*i.e.* distinct species). Resonances O_2, O_3 and O_7 of Fig. 1 (16% of the protons) can reasonably be assigned to isomer B or C (but C is less probable for symmetry reasons), on the basis of the number and relative area (1:1:1) of the signals. Resonances O_4 and O_6 (2:1, 44%) may account for any species of Fig. 2 other than B or C. Although both trigonal bipyramidal and tetragonal pyramidal environments of the metal are plausible in the absence of special geometrical constraints

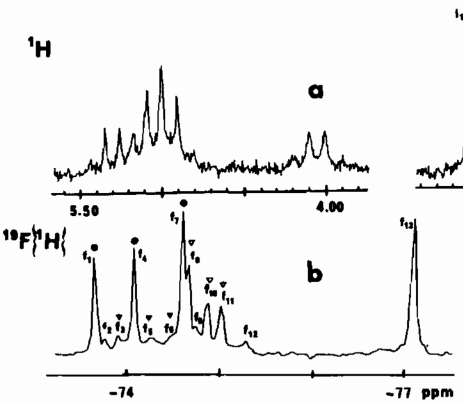


Fig. 3. NMR spectra of $[NbO(OCH_2CF_3)_3 \cdot MeCN]_2$ in $CDCl_3$ (0.02 molar solutions) at –40 °C: a) proton NMR spectra trifluoroethoxo region (δO_1 = 5.31, δO_2 = 5.00, δO_3 = 4.91 (J = 8 Hz) and δO_4 = 4.06 ppm (J = 9 Hz); and acetonitrile region (δl_1 = 2.59 ppm, δl_2 = 2.50 ppm, δl_3 = 2.35 δl_4 = 2.13 ppm); b) $^{19}F\{^1H\}$ spectra: (δf_1 = –73.64, δf_2 = –73.74 and δf_3 = –73.88, δf_4 = –74.06, δf_5 = 74.30, δf_6 = –74.55, δf_7 = –74.60, δf_8 = –74.66, δf_9 = –74.72, δf_{10} = –74.90, δf_{11} = –75.01, δf_{12} = –75.27, δf_{13} = –77.1 ppm).

[22] the former has more generally been found in solution [21] and has also been predicted to be more stable for d° compounds [20]; this would point to isomer A as the most probable species. A μ-oxo isomer (F, G or H) in which all the alkoxo groups would occupy terminal positions, and would exchange sites rapidly [23, 24], could account for the single quadruplet O_9 (28%).

The behaviour of $NbO(OEt)_3$ in polar solvents and/or in the presence of potential ligands was unexpected in so far as no coordination adduct was ever observed. For instance, the NMR spectra of its acetonitrile solutions exhibit the same general pattern, the most noticeable change being the increase (32% in 0.03 molar solutions) of the molecular species corresponding to quadruplet O_9 (δOCH_2 = 3.58 ppm, J = 7 Hz). Molecular weight data confirmed the preservation of dimeric units (M found 540 ± 50; M calcd. 488), but could not exclude the coordination of an additional solvent molecule; however, the IR data (MeCN solutions) give no evidence for coordinated MeCN. The addition of various amounts of stronger bases (pyridine) and especially of ligands such as $OP(NMe_2)_3$ or $OPMe_3$, which are known to split alkoxo bridges [24], to solutions of $[NbO(OEt)_3]_2$ in CD_2Cl_2, confirmed the preceding observations: no complexation of the niobium oxytriethoxide was detected in fresh solution. There was no change in the NMR of the added ligand, even at –80 °C, and the OCH_2 resonance region showed no new signal, but only the increase in area of quadruplet O_9 when the molar ratio L/Nb = R was increased and when the nature of the base was varied (the relative area of O_9 increased then in the order MeCN < Py < HMPA < $OPMe_3$). Only one metallic species was detected (quadruplet O_9) when the $OPMe_3$/Nb attained 5.83; its signal showed no further splitting down to –70 °C. The μ-oxo isomers F, G or H present the best agreement with the presently available experimental data.

The molecular constitution of the $NbO(OCH_2CF_3)_3 \cdot MeCN$ solution is even more complex, since it is accompanied by acid-base dissociation reactions. First, the behaviour of fresh solutions of $[NbO(OCH_2CF_3)_3 \cdot MeCN]_2$ (M found 910, calcd. 894) in non-polar solvents was investigated. The most useful information given by the proton spectra comes from the acetonitrile region. For example, at –40 °C, the ^1H spectra of a 0.02 molar solution of $[NbO(OCH_2CF_3)_3 \cdot MeCN]_2$ in $CDCl_3$ shows 4 ligand resonances (Fig. 3a). The addition of an excess of ligand established that l_4 (12% of the ligand resonance area), the relative area of which varies during the addition, corresponds to free acetonitrile, indicating that the adduct is partially dissociated. Peaks l_1, l_2 and l_3 must be attributed to 3 distinct molecular species. The OCH_2 region is very complicated and shows at least 4 quadruplets. The $^{19}F\{^1H\}$ spectra display 12 singlets f_1 to f_{12} from –73.4 to –75.27 ppm and one, f_{13}, at –77.1 ppm (Fig. 2b). The coalescence of all the signals above 50 °C shows that all species are in dynamic equilibrium.

According to the molecular weight data, the metal atom is hexacoordinated in $[NbO(OCH_2CF_3)_3 \cdot MeCN]_2$, and one can envisage 12 possible μ-alkoxo and 4 possible μ-oxo dimers in which the acetonitrile molecules would occupy equivalent sites. The presence of species having different acetonitrile environments is unlikely, as no signals having a 1:1 are ratio are found for MeCN.

The analysis of the $^{19}F\{^1H\}$ spectra registered in various conditions of dilution and temperature showed that some signals keep constant relative area in relation one to another, and thus are likely to belong to a same molecular species. Only 5 molecular species were identified; of these, 4 have 3 non-equivalent alkoxo groups in 1:1:1 ratio, the other one having apparently equivalent alkoxo groups. Finally it can be shown that peaks f_1, f_4, f_7 and l_2 (40% of all the metal derivatives) on one hand, and f_8, f_{10}, f_{11} and l_1 (19%) on the other, correspond to two molecular species. Resonances f_3, f_5, f_6 and f_2, f_9, f_{12} could correspond to $[NbO(OCH_2CF_3)_3]_2$ resulting from the dissociation reaction (12%). Inspection of the various possible isomers shows that only μ-alkoxo derivatives can account for species having 3 non-equivalent trifluoroethoxo groups, the most symmetrical being isomers I and J. It should be noted that the geometry of $[NbSCl_3 \cdot SPPh_3]_2$, as determined by X-rays [25], is similar to that of isomer J. The species for which all the OR

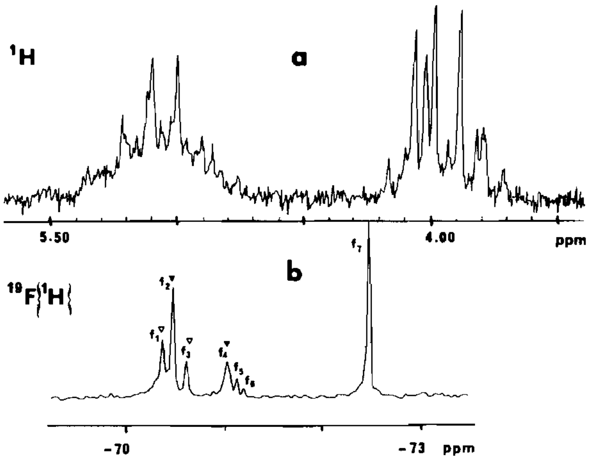
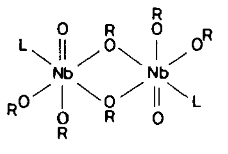
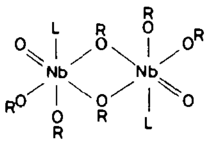


Fig. 4. NMR spectra of $NbO(OCH_2CF_3)_3 \cdot MeCN$ in CD_3CN solutions (0.02 molar) at −30 °C: a) ^1H spectra; b) $^{19}F\{^1H\}$ spectra: ($\delta f_1 = -70.38$, $\delta f_2 = -70.48$, $\delta f_3 = -70.62$, $\delta f_4 = -71.04$, $\delta f_5 = -71.14$, $\delta f_6 = -71.20$ and $\delta f_7 = -72.48$ ppm).





L = MeCN R = CH_2CF_3

I J

resonances remain equivalent even at −60 °C and are shifted to higher fields (δf_{13}, $\delta OCH_2 = 4.04$) may be a dimeric μ-oxo isomer, in which all the alkoxo groups would occupy terminal sites, or a monomeric $NbO(OCH_2CF_3)_3 \cdot MeCN$ species.

When dissolved in MeCN, $NbO(OCH_2CF_3)_3 \cdot MeCN$ became monomeric (found 440 ± 40, calcd. 447). Its ^1H or $^{19}F\{^1H\}$ spectra again show high complexity (Fig. 4), and dynamic behaviour. Four distinct molecular species, three of which have non-equivalent alkoxo groups in a 2:1 ratio: f_2, f_4 (38%), f_1, f_3 (26%), f_5, f_6 (5%), and another one which displays equivalent trifluoroethoxo groups (f_7 and $\delta OCH_2 = 3.91$ ppm, 31%) were observed. This last species was the only one detected in highly diluted medium (0.008 molar). One further difficulty stems from the fact that the molecular weight data may account for either $NbO(OCH_2CF_3)_3 \cdot MeCN$, in which the metal would be pentacoordinated (7 isomers derived from 'regular' trigonal bipyramidal and square pyramidal arrangements), or $NbO(OCH_2CF_3)_3 \cdot 2MeCN$, in which it would be hexacoordinated (3 octahedral isomers). A monoacetonitrile adduct is likely for the species displaying equivalent alkoxo groups, while mono or bisacetonitrile adducts may be responsible for the signals corresponding to the three other molecular species.

In conclusion, the molecular constitution of $[NbO(OEt)_3]_2$ and $[NbO(OCH_2CF_3)_3 \cdot MeCN]_2$ solutions in non-polar solvents can be rationalized by the presence in dynamic equilibrium of several μ-alkoxo and μ-oxo isomers, the latter being favoured by dilution. In polar media (MeCN for instance), dimeric units are retained for $[NbO(OEt)_3]_2$, while the trifluoroethoxide derivative is split into monomeric species.

Other routes to oxyalkoxides involving exchange reactions and elimination reactions starting from the metal alkoxides and alkoxychlorides are currently being investigated, in order to find a more general route to totally substituted oxyalkoxides.

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