Niobium-93 Nuclear Magnetic Resonance Studies of the Solvolysis of $NbCl_5$ by Alcohols

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Niobium-93 and ^1H NMR spectroscopy have been used to identify the substitution products $NbCl_{5-x}(OMe)_x$ formed by the stepwise substitution of $NbCl_5$ by MeOH in non-co-ordinating solvents. This reveals evidence for all of the possible substitution products, $NbCl_{5-x}(OMe)_x$, whilst phase equilibria favour the formation of $[NbCl_4(OMe)]_2$ and $[NbCl_2(OMe)_3]_2$ dimer species over $[NbCl_3(OMe)_2]_2$ in mixed MeOH–aromatic solvents. In co-ordinating solvents such as acetonitrile ^{93}Nb NMR spectroscopy distinguishes between the unco-ordinated dimeric $[NbCl_{5-x}(OMe)_x]_2$ species and the monomeric adduct species $NbCl_{5-x}(OMe)_x{\cdot}MeCN$. Monitoring of $NbCl_5$ solvolysis in ROH (R = Me, Et or Pr^i) by ^{93}Nb NMR spectroscopy thus identifies all $NbCl_{5-x}(OR)_x$ species present and reveals that the solution composition is both concentration and temperature dependent.

Sol–gel processing of metal alkoxides offers a convenient route to single-component and mixed metal oxide ceramics from pure starting materials.[1] This route is also extremely useful in casting thin ceramic films.[2] In work aimed at producing sol–gel derived electrochromic thin films[3] of Nb_2O_5 we became interested in the reactions of $NbCl_5$ with alcohols to chloroalkoxides which are precursors to Nb-containing oxides and ceramics in the sol–gel process. A precise knowledge of these precursors is necessary for full elaboration of the sol–gel processing mechanism, in order to permit rational modification of the final ceramic. In a recent review[4] the reaction of $NbCl_5$ with ROH is said to give $NbCl_{5-x}(OR)_x$, where $x = 2$ or 3 [equation (1)]. However, other

$$NbCl_5 + xROH \longrightarrow NbCl_{5-x}(OR)_x + xHCl \quad (1)$$

workers have claimed that only one species, $NbCl_2(OR)_3$, is present when excess of ROH is added to $NbCl_5$.[5–7]

We felt that a detailed ^{93}Nb NMR investigation of this system would resolve this problem, in a similar manner to the study of $[NbCl_{6-x}Br_x]^-$ species.[8,9] Although ^{93}Nb is quadrupolar ($I = \frac{9}{2}$, $Q/10^{-28}\ m^2 = -0.2$)[9] the broadness of the lines is compensated for by a wide niobium(V) chemical shift range (δ −1500 to +500) and good sensitivity (^{93}Nb is in 100% abundance).

Experimental

All reactions were done under N_2 and in dry glassware. The ^{93}Nb NMR spectra were run on a Bruker MSL 500 spectrometer, and ^1H NMR on a AM300 or WP80 spectrometer. Fourier-transform infrared (FTIR) spectra were obtained on a Perkin-Elmer 1710 spectrometer, and Raman spectra on a Spex Ramalog. Mass spectroscopy was performed on a INCOS GCMS spectrometer.

For *in situ* generation of $NbCl_{5-x}(OR)_x$ species in aromatic solvents, $NbCl_5$ (99%+, Aldrich), was suspended in benzene or toluene (Aldrich reagent grade dried over Na and 4A molecular sieves) and controlled equivalents of methanol (spectroscopic grade, Aldrich) added. For *in situ* generation of $NbCl_{5-x}(OR)_x$ species in alcohols, weighed amounts of $NbCl_5$ (99%+, Aldrich) were dissolved in the required alcohol (spectroscopic grade, Aldrich) to give the specified molarity. For *in situ* generation of $[NbCl_{6-x}(OR)_x]^-$ species, weighed amounts of $CsNbCl_6$ (standard preparation[10]) were dissolved in methanol (spectroscopic grade, Aldrich) to give the specified molarity.

To confirm our assignments of *in situ* generated species we isolated and characterized $NbCl_4(OMe)$, $NbCl_2(OMe)_3$ and $Nb(OMe)_5$ prior to redissolution in deuteriated toluene (sodium dried, Aldrich) and anhydrous acetonitrile (Aldrich) for ^{93}Nb and ^1H NMR spectroscopy.

$Nb(OMe)_5$.—Authentic $Nb(OMe)_5$ was prepared by the method of Bradley *et al.*[11] and characterized by FTIR[7] and Raman,[12] mass,[13] and ^1H NMR spectroscopy.[14–17]

$NbCl_2(OMe)_3$.—Niobium(V)chloride (8.1 g) was suspended in toluene (50 cm^3), MeOH (6.06 cm^3, 0.15 mol) was added and stirred for 1 d, after which excess of MeOH and toluene were evaporated until a saturated solution formed. After the addition of light petroleum (b.p. 40–60 °C, 3 cm^3) the solution was allowed to crystallize at −10 °C. The crystals were filtered off and washed with cold toluene. FTIR[7] (cm^{-1}): 1150w, 1075s [ν(CO)]; 570w [ν(Nb–O)]. Mass spectrum:[13] *m/z* 221, $[NbCl(OMe)_3]^+$. ^1H NMR ($[^2H_8]$toluene) at low temperatures gave a complex set of lines, similar to those reported with CD_2Cl_2 as solvent.[18]

$NbCl_4(OMe)$.—Methanol (1.22 cm^3) was added to a suspension of $NbCl_5$ (8.1 g) in dry toluene (50 cm^3) and stirred for 24 h. The $NbCl_4(OMe)$ precipitate was filtered off and recrystallized from benzene. FTIR (cm^{-1}): 1600ms, 1100w, 1060s, 1020 (sh) [ν(CO)]; 595 [ν(Nb–O)]; lit.,[7] 1055 [ν(CO)] and 595 cm^{-1} [ν(Nb–O)]. Mass spectrum: *m/z* 264/266, $[NbCl_4(OMe)]^+$; 213, $[NbCl_3Me]^+$; 210, $[NbCl_3C]^+$; and 198, $[NbCl_3]^+$.

The compounds $Nb(OEt)_5$ (Aldrich 99%) and $Nb(OPr^i)_5$ were prepared by the method of Bradley and Holloway.[17]

Results and Discussion

Synthesis of $NbCl_{5-x}(OMe)_x$ *in Aromatic Solvents.*—To determine the identity of all probable species present in the alcohol solutions, controlled equivalents of MeOH were added to a 0.1 mol dm^{-3} suspension of $NbCl_5$ in benzene. The ^{93}Nb NMR spectrum of Nb_2Cl_{10} in benzene consists of a single peak at $\delta \approx 2.6$, somewhat broader than the $NbCl_6^-$ reference peak run under the same conditions. This reflects the lower pseudo-octahedral symmetry about Nb in the dimer Nb_2Cl_{10} compared to $NbCl_6^-$. On incremental addition of MeOH much HCl gas and heat is liberated. The solutions change colour from red through orange to pale yellow, and the ^{93}Nb NMR spectra reveal the successive growth and decay of four different peaks during the course of the experiment (Table 1).

Upon addition of 1 equivalent of MeOH the $NbCl_5$ species is replaced by a single peak at δ −495, whilst in the ^1H NMR spectra only a single peak at δ 3.80 and no free methanol peak (δ 3.5) is observed, implying that all the MeOH has co-ordinated with the $NbCl_5$ to form $NbCl_4(OMe)$. Thus the value of the ^{93}Nb chemical shift for 1 : 1 MeOH : $NbCl_5$ is consistent with the methoxy species $NbCl_4(OMe)$ rather than the simple solvent adduct $NbCl_5{\cdot}MeOH$ which would be expected to have a peak near δ +60. Dissolving $NbCl_5$ in diethyl ether produces the solvent adduct $NbCl_5{\cdot}OEt_2$[4] which gives a single ^{93}Nb NMR peak at δ +60. We can also rule out the possibility of Nb=O species being formed since the spectra dramatically altered on addition of wet benzene to a suspension of $NbCl_5$ in benzene to give a sharp signal at δ −535, due to $NbOCl_3$.[9] On standing small amounts of the $NbCl_4(OMe)$ species precipitated. The assignment of the ^{93}Nb peak to $NbCl_4(OMe)$ was confirmed by dissolving an authentic sample in deuteriated toluene (see Experimental section). It gave a single ^{93}Nb NMR peak at δ −495.

Kepert and Nyholm[19] have shown that in non-co-ordinating solvents such as carbon tetrachloride $NbCl_5$ exists as the dimer Nb_2Cl_{10}. Likewise Riess and Hubert-Pfalzgraf[15,16,20] have shown that $Nb(OMe)_5$ is dimeric in toluene. It seems highly probable then that in toluene $NbCl_4(OMe)$ would exist as the dimer $[NbCl_4(OMe)]_2$ and low-temperature ^1H NMR spectroscopy of $NbCl_4(OMe)$ in deuteriated toluene confirms this: two peaks are seen in a 1 : 1 ratio (Table 2) due to the axial and equatorial methoxy groups of the dimer. The absence of ^1H bridging MeO resonances is surprising since bridging/terminal exchange should have been frozen out at this low temperature. We can only conclude that the thermodynamically most stable isomers are those with bridging Cl^- ligands.

Table 1 Assignment of ^{93}Nb NMR signals* to $NbCl_{5-x}(OMe)_x$ species

Solvent	$x = 0$	1	2	3	4	5
Benzene	2.6	−497		−810	−1010	−1160
Toluene	2.0	−495		−810		−1150
Acetonitrile	−0.5	−495/−560		−850		−1160
Methanol		−480		−820	−1015	−1155
Ethanol		−470		−830	−1020	−1180
Isopropanol		−470		−830	−1025	−1135

* All signals ±5 ppm.

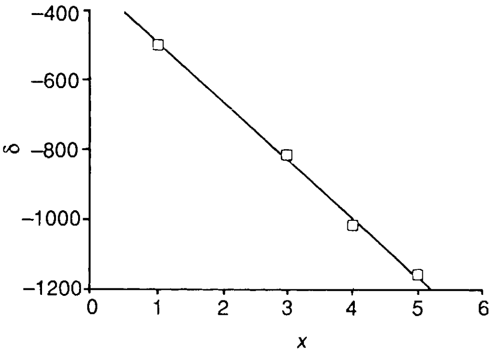

Fig. 1 Plot of the degree of substitution (x) *vs.* observed ^{93}Nb NMR peak position for the species $NbCl_{5-x}(OMe)_x$, dissolved in aromatic solvent

Schönherr and Kolditz[7] isolated $NbCl_2(OMe)_3$ on the addition of 5 equivalents of MeOH to a suspension of $NbCl_5$ and observed that further addition of MeOH did not give $NbCl(OMe)_4$. Upon reaction of a 5 : 1 MeOH : Nb mixture in benzene a single ^{93}Nb NMR peak is observed at δ −810 due to $NbCl_2(OMe)_3$. The corresponding ^1H NMR spectrum shows a peak due to unreacted MeOH at δ 3.5 in addition to a second peak at δ 4.10 assigned to $NbCl_2(OMe)_3$. The ratio of the peak areas is 2 : 3 confirming that two molecules of MeOH have failed to react. After some time, the $NbCl_2(OMe)_3$ species separated out from the benzene solvent as a dense lower layer. To confirm the assignment, authentic $NbCl_2(OMe)_3$ dissolved in deuteriated toluene exhibits a single peak at δ −810 in the ^{93}Nb NMR spectrum. In the ^1H NMR spectrum at low temperatures a complex pattern is observed, very similar to that observed by Riess and co-workers[18] for the dimer $[NbCl_2(OMe)_3]_2$ in CD_2Cl_2. These authors attributed the peaks to a mixture of isomers and redistribution products.

Complete substitution to yield $Nb(OMe)_5$ was enforced by bubbling NH_3 through the solution.[11] In practice if only 5 equivalents of MeOH are added to 1 equivalent of $NbCl_5$, rather than an excess, then in the ^{93}Nb NMR spectra a small peak at δ −1010 is observed and assigned to the $NbCl(OMe)_4$ species as well as the main peak at δ −1160 attributable to $Nb(OMe)_5$, and confirmed by spectra of an authentic $Nb(OMe)_5$ sample (see Tables 1 and 2).

The preceding data provide good evidence for the assignment of x = 1, 3, 4 or 5 species (Table 1). However, it will be noted that a peak due to $NbCl_3(OMe)_2$ is not observed. When MeOH : Nb = 2 : 1 only peaks assigned to $NbCl_4(OMe)$ and $NbCl_2(OMe)_3$ are observed. We propose that, in non-co-ordinating solvents such as benzene and toluene, $NbCl_3(OMe)_2$ rapidly disproportionates to give $NbCl_4(OMe)$ and $NbCl_2(OMe)_3$ [equation (2)].

$$2NbCl_3(OMe)_2 \longrightarrow NbCl_4(OMe) + NbCl_2(OMe)_3 \quad (2)$$

The main driving forces for this reaction are the lower solubility of $NbCl_4(OMe)$ and the stability of $NbCl_2(OMe)_3$. Furthermore, at >2 equivalents MeOH, there is always some

Table 2 Proton NMR signals observed for $NbCl_{5-x}(OMe)_x$ species at given temperatures*

		T/K									
Deuteriated solvent	Species	200		220			233		255		310
Toluene	$NbCl_4(OMe)$	3.62 (1)	3.12 (1)				3.78 (1)	3.15 (1)			3.75 (br)
Toluene	$NbCl_4(OMe){\cdot}MeCN$						3.90 (1)	2.35 (1)	3.98 (1)	2.38 (1)	
Toluene	$Nb(OMe)_5$			4.28 (2)	4.24 (2)	4.03 (1)			4.26 (4)	4.02 (1)	4.25
Acetonitrile	$Nb(OMe)_5$			4.25 (2)	4.15 (2)	3.95 (1)					3.95

* Figures in parentheses are the relative signal areas.

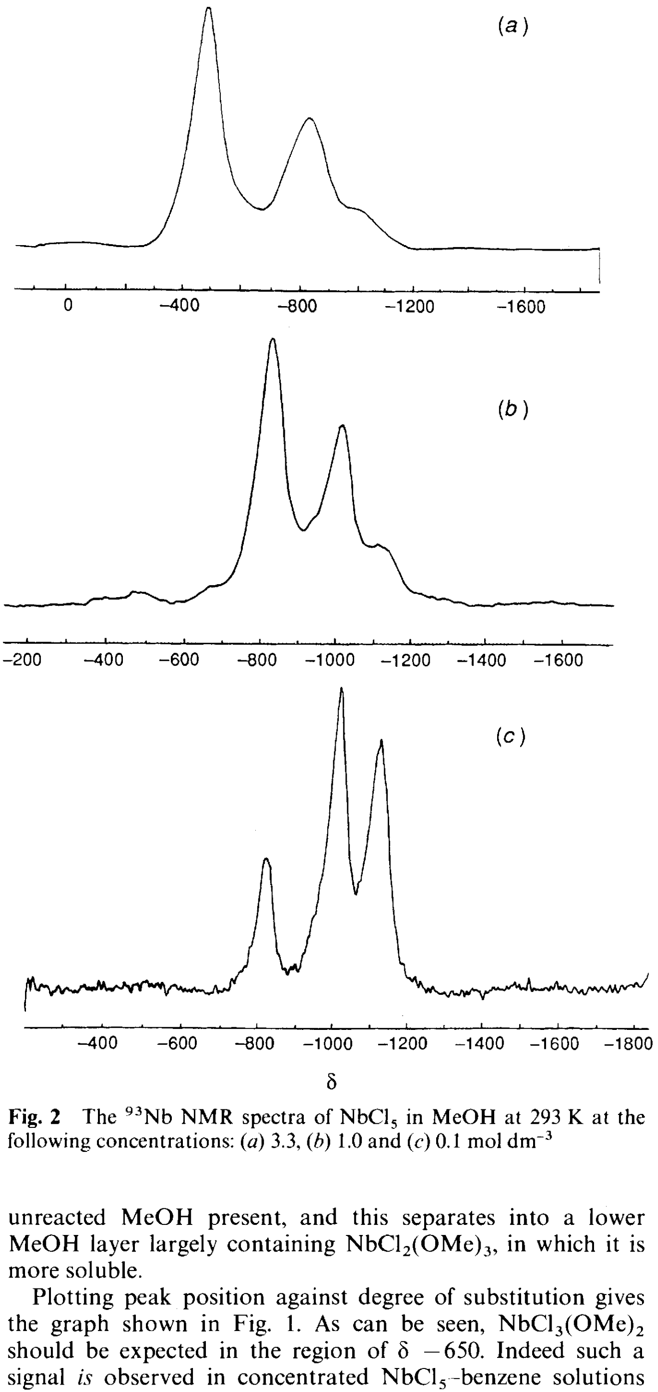

Fig. 2 The ^{93}Nb NMR spectra of $NbCl_5$ in MeOH at 293 K at the following concentrations: (*a*) 3.3, (*b*) 1.0 and (*c*) 0.1 mol dm^{-3}

unreacted MeOH present, and this separates into a lower MeOH layer largely containing $NbCl_2(OMe)_3$, in which it is more soluble.

Plotting peak position against degree of substitution gives the graph shown in Fig. 1. As can be seen, $NbCl_3(OMe)_2$ should be expected in the region of δ −650. Indeed such a signal *is* observed in concentrated $NbCl_5$–benzene solutions (>0.5 mol dm^{-3}) when 2 equivalents of MeOH are added. The integrated area of this peak is only 5% of the total integrated peak areas, the other major peaks being due to $NbCl_4(OMe)$ and $NbCl_2(OMe)_3$.

Attempted Synthesis of $NbCl_3(OMe)_2$ *from* $NbCl_5$–$Nb(OMe)_5$ *Mixtures*.—The ^{93}Nb NMR spectra of redissolved $NbCl_4(OMe)$, $NbCl_2(OMe)_3$ and $Nb(OMe)_5$ (isolated and characterized samples) confirmed the assignments given in Table 1, but did not explain why $NbCl_3(OMe)_2$ was not seen. A different approach was tried in an attempt to prepare this species, namely the addition of controlled amounts of $Nb(OMe)_5$ to the $NbCl_5$ solution.

A 0.082 mol dm^{-3} solution of $NbCl_5$ and a 0.099 mol dm^{-3} solution of $Nb(OMe)_5$ in toluene were made and mixed in the ratios Cl:OMe 4:1, 3:2 and 2:3. Gut *et al.*[21] claimed this produced $NbCl_4(OMe)$, $NbCl_3(OMe)_2$ and $NbCl_2(OMe)_3$ respectively. As expected, the 4:1 Cl:OMe solution gives a single peak for $NbCl_4(OMe)$, and the 2:3 solution gives a single peak for $NbCl_2(OMe)_3$. However, the 3:2 solution did not give a single peak at δ −650 but instead two peaks at the positions for $NbCl_4(OMe)$ and $NbCl_2(OMe)_3$. Despite the apparent differences in peak height and broadness, integration of these two peaks gives a ratio of 45:55 $NbCl_4(OMe)$:$NbCl_2(OMe)_3$, consistent with the equal amounts expected if disproportionation occurs according to equation (2).

As $NbCl_3(OMe)_2$ at these concentrations and temperature appears to be unstable a low-temperature study was undertaken. The $NbCl_5$ solution was frozen in the NMR tube by placing it in liquid N_2. The $Nb(OMe)_5$ solution was then poured on top and likewise frozen (Cl:OMe 1:1). The frozen sample was then placed in the NMR spectrometer and held at 223 K. As the layers thawed, spectra were taken every 100 s to try and observe any formation of $NbCl_3(OMe)_2$. Initially at 223 K only $NbCl_5$ was seen, but after 100 s some $NbCl_4(OMe)$ appeared. Over the 19 spectra taken the peak due to $NbCl_5$ decreased in size whilst the $NbCl_4(OMe)$ peak increased. At this point the temperature was raised to 253 K. In the time it took to do so some $NbCl_2(OMe)_3$ had been formed. After 29 more spectra had been taken, only peaks due to $NbCl_4(OMe)$ and $NbCl_2(OMe)_3$ were observed and at no time was a peak seen at δ −650. On elevating the temperature to 293 K the two peaks were found to be in the ratio 20:80 $NbCl_4(OMe)$:$NbCl_2(OMe)_3$. For a 1:1 mixture that had disproportionated the ratio should be 25:75. For better resolution of the $NbCl_3(OMe)_2$ peak, the spectral width was limited to the area in which it might occur and so we were unable to monitor the $Nb(OMe)_5$ resonance.

Acetonitrile Adducts $NbCl_{5-x}(OMe)_x$·MeCN.—The ^{93}Nb NMR peak positions of $NbCl_4(OMe)$, $NbCl_2(OMe)_3$ and $Nb(OMe)_5$ when dissolved in acetonitrile are given in Table 1. Whereas in toluene a single peak is observed at δ −495 due to the dimer of $NbCl_4(OMe)$, in acetonitrile two peaks are observed at δ −495 and −560. The latter is shifted downfield from the dimer by the appropriate amount for a monomeric Nb·MeCN species.[9] This acetonitrile adduct $NbCl_4(OMe)$·MeCN was isolated by removal of excess of solvent to give an orange solid. The IR spectrum showed shifted acetonitrile stretches at 2325 [$\delta(CH_3)$ + ν(C–C)] and 2296 cm^{-1} [ν(C≡N)] for co-ordinated MeCN.[18,22] and a shifted ν(CO) at 1075 cm^{-1}. The $NbCl_4(OMe)$·MeCN was then added to deuteriated toluene; two new peaks were seen to arise in the low-temperature ^1H NMR spectrum in a 1:1 ratio (Table 2), and a new peak was observed at δ −550 in the ^{93}Nb spectrum. The ^1H peaks can be assigned to Nb(OMe) (δ 3.90) and Nb·MeCN (δ 2.35)[23] groups.

When solid $NbCl_2(OMe)_3$ (prepared from $NbCl_5$–MeOH–toluene) is dissolved in acetonitrile it gives a single peak at δ −850 in the ^{93}Nb NMR spectrum, shifted downfield from the dimeric species in toluene, implying the formation of an acetonitrile adduct species. Removal of the acetonitrile solvent gives a yellow solid whose FTIR spectrum consists of shifted acetonitrile stretches at 2313 [$\delta(CH_3)$ + ν(C–C)] and 2285 cm^{-1} [ν(C≡N)] as well as peaks at 1090 [ν(CO)] and 560 cm^{-1} [ν(Nb–O)], for the proposed monomer adduct $NbCl_2(OMe)_3$·MeCN. When the adduct is redissolved in deuteriated toluene it gives rise to a complex pattern of peaks in the low-temperature ^1H NMR spectrum. This pattern is less complex than that observed for the dimer but apart from a peak at δ 2.35 (Nb·MeCN) it has proved impossible to assign the peaks and hence confirm the adduct formation.

Finally $Nb(OMe)_5$ displays a main ^{93}Nb resonance at δ −1160 for the dimer and a small side-peak at δ −1185 due to oligomeric species.

$NbCl_5$ *dissolved in Pure Alcohols*.—When $NbCl_5$ is dissolved in MeOH the ^{93}Nb NMR spectrum at 293 K consists of a set of lines, the number and intensity of which is heavily dependent on the concentration of the $NbCl_5$ (see Fig. 2). The lines may now be readily assigned to the $NbCl_{5-x}(OMe)_x$ species and sharpen on warming to 343 K. On cooling back to 293 K the original spectrum was reproduced except for the 3.3 mol dm^{-3} $NbCl_5$ solution. Initially this consisted of a single broad peak from δ -400 to -900, which on heating and subsequent cooling converted into the spectrum shown. A possible explanation for this is that the high viscosity of the solution at 293 K limits diffusion of MeOH to the $NbCl_5$ so that less-substituted species [including $NbCl_3(OMe)_2$] are observed. On warming, the viscosity decreases allowing for unhindered diffusion and $NbCl_3(OMe)_2$ disproportionates *via* equation (2). A similar set of lines are observed when $CsNbCl_6$ is dissolved in MeOH.

When 0.5 mol dm^{-3} $NbCl_5$ is dissolved in the higher alcohols ROH (R = Et or Pr^i) it is apparent that as the steric bulk of R increases the degree of substitution decreases. Table 1 includes a summary of the assignments for the $NbCl_{5-x}(OR)_x$ species formed.

In summary, this work shows that ^{93}Nb NMR spectroscopy can be used to identify the $NbCl_{5-x}(OMe)_x$ series of molecules and distinguish between the dimeric and monomeric species. It also confirms Kolditz and Schönherr's report[7] that only $NbCl_2(OMe)_3$ is formed in non-polar solvents on adding excess of MeOH to $NbCl_5$ and indicates that $NbCl_3(OMe)_2$ appears to be unstable, disproportionating to $NbCl_4(OMe)$ and $NbCl_2(OMe)_3$. In neat ROH a mixture of chloroalkoxides is observed whose composition is strongly dependent on the total niobium concentration.

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