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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 NbCl₅ 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 [NbCl₄(OMe)]₂ and [NbCl₂(OMe)₃]₂ dimer species over [NbCl₃(OMe)₂]₂ in mixed MeOH-aromatic solvents. In co-ordinating solvents such as acetonitrile ⁹³Nb 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·MeCN. Monitoring of NbCl₅ solvolysis in ROH (R = Me, Et or Prⁱ) by ⁹³Nb 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 Nb₂O₅ we became interested in the reactions of NbCl₅ with alcohols to chloroalkoxides which are precursors to Nb-containing oxides and ceramics in the solgel 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 review⁴ the reaction of NbCl₅ with ROH is said to give NbCl_{5-x}(OR)_x, where x = 2 or 3 [equation (1)]. However, other

$$NbCl_5 + xROH \longrightarrow NbCl_{5-x}(OR)_x + xHCl$$
 (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 ⁹³Nb 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 ⁹³Nb is quadrupolar ($I = \frac{9}{2}, Q/10^{-28} \text{ m}^2 = -0.2$)⁹ the broadness of the lines is compensated for by a wide niobium(v) chemical shift range ($\delta - 1500$ to + 500) and good sensitivity (⁹³Nb is in 100% abundance).

Experimental

All reactions were done under N_2 and in dry glassware. The ⁹³Nb 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, NbCl₅ (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 NbCl₅ (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 CsNbCl₆ (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 NbCl₄(OMe), NbCl₂(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 FTIR⁷ and Raman,¹² mass,¹³ and ¹H NMR spectroscopy.^{14–17}

NbCl₂(OMe)₃.—Niobium(v)chloride (8.1 g) was suspended in toluene (50 cm³), MeOH (6.06 cm³, 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 cm³) 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 [v(CO)]; 570w [v(Nb–O)]. Mass spectrum: ¹³ m/z 221, [Nb-Cl(OMe)₃]⁺. ¹H NMR ([²H₈]toluene) at low temperatures gave a complex set of lines, similar to those reported with CD₂Cl₂ as solvent.¹⁸

NbCl₄(OMe).—Methanol (1.22 cm³) was added to a suspension of NbCl₅ (8.1 g) in dry toluene (50 cm³) and stirred for 24 h. The NbCl₄(OMe) precipitate was filtered off and recrystallized from benzene. FTIR (cm⁻¹): 1600ms, 1100w, 1060s, 1020 (sh) [v(CO)]; 595 [v(Nb–O)]; lit.,⁷ 1055 [v(CO)] and 595 cm⁻¹ [v(Nb–O)]. Mass spectrum: m/z 264/266, [NbCl₄(OMe)]⁺; 213, [NbCl₃Me]⁺; 210, [NbCl₃C]⁺; and 198, [NbCl₃]⁺.

The compounds Nb(OEt)₅ (Aldrich 99%) and Nb(OPrⁱ)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 NbCl₅ in benzene. The ⁹³Nb NMR spectrum of Nb₂Cl₁₀ in benzene consists of a single peak at $\delta \approx 2.6$, somewhat broader than the NbCl₆⁻ reference peak run under the same conditions. This reflects the lower pseudo-octahedral symmetry about Nb in the dimer Nb₂Cl₁₀ compared to NbCl₆⁻. 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 ⁹³Nb 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 NbCl₅ 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 NbCl₅ to form $NbCl_4(OMe)$. Thus the value of the ⁹³Nb chemical shift for 1:1 MeOH: NbCl₅ is consistent with the methoxy species NbCl₄(OMe) rather than the simple solvent adduct NbCl₅·MeOH which would be expected to have a peak near δ +60. Dissolving NbCl₅ in diethyl ether produces the solvent adduct NbCl₅·OEt₂⁴ which gives a single ⁹³Nb 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 NbCl₅ in benzene to give a sharp signal at δ -535, due to NbOCl₃.⁹ On standing small amounts of the NbCl4(OMe) species precipitated. The assignment of the ⁹³Nb peak to NbCl₄(OMe) was confirmed by dissolving an authentic sample in deuteriated toluene (see Experimental section). It gave a single ⁹³Nb NMR peak at $\delta - 495.$

Kepert and Nyholm¹⁹ have shown that in non-co-ordinating

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	<u>+</u> 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

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solvents such as carbon tetrachloride NbCl₅ exists as the dimer Nb₂Cl₁₀. 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 NbCl₄(OMe) would exist as the dimer [NbCl₄(OMe)]₂ and low-temperature ¹H NMR spectroscopy of NbCl₄(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.

Schönherr and Kolditz⁷ isolated NbCl₂(OMe)₃ on the addition of 5 equivalents of MeOH to a suspension of NbCl₅ 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 ⁹³Nb NMR peak is observed at $\delta - 810$ due to NbCl₂(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 NbCl₂(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 NbCl₂(OMe)₃ species separated out from the benzene solvent as a dense lower layer. To confirm the assignment, authentic NbCl₂(OMe)₃ dissolved in deuteriated toluene exhibits a single peak at $\delta - 810$ in the ⁹³Nb NMR spectrum. In the ¹H NMR spectrum at low temperatures a complex pattern is observed, very similar to that observed by Riess and co-workers¹⁸ for the dimer [NbCl₂(OMe)₃]₂ in CD₂Cl₂. These authors attributed the peaks to a mixture of isomers and redistribution products.

Complete substitution to yield Nb(OMe)₅ was enforced by bubbling NH₃ through the solution.¹¹ In practice if only 5 equivalents of MeOH are added to 1 equivalent of NbCl₅, rather than an excess, then in the ⁹³Nb NMR spectra a small peak at $\delta - 1010$ is observed and assigned to the NbCl(OMe)₄ species as well as the main peak at $\delta - 1160$ 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 NbCl₃(OMe)₂ is not observed. When MeOH:Nb = 2:1 only peaks assigned to NbCl₄(OMe) and NbCl₂(OMe)₃ are observed. We propose that, in non-coordinating solvents such as benzene and toluene, NbCl₃(OMe)₂ rapidly disproportionates to give NbCl₄(OMe) and NbCl₂-(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 NbCl₄(OMe) and the stability of NbCl₂(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 *
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Deuteriated solvent	Species	T/K									
		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	NbCl4(OMe)•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 ⁹³Nb NMR spectra of NbCl₅ 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, NbCl₃(OMe)₂ should be expected in the region of δ –650. Indeed such a signal *is* observed in concentrated NbCl₅-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 NbCl₄(OMe) and NbCl₂(OMe)₃.

Attempted Synthesis of NbCl₃(OMe)₂ from NbCl₅-Nb(OMe)₅ Mixtures.—The ⁹³Nb NMR spectra of redissolved NbCl₄(OMe), NbCl₂(OMe)₃ and Nb(OMe)₅ (isolated and characterized samples) confirmed the assignments given in Table 1, but did not explain why NbCl₃(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 NbCl₅ solution.

A 0.082 mol dm⁻³ solution of NbCl₅ 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 NbCl₄(OMe), NbCl₃(OMe)₂ and NbCl₂(OMe)₃ respectively. As expected, the 4:1 Cl:OMe solution gives a single peak for NbCl₄(OMe), and the 2:3 solution gives a

single peak for NbCl₂(OMe)₃. However, the 3:2 solution did not give a single peak at δ -650 but instead two peaks at the positions for NbCl₄(OMe) and NbCl₂(OMe)₃. Despite the apparent differences in peak height and broadness, integration of these two peaks gives a ratio of 45:55 NbCl₄(OMe):NbCl₂(OMe)₃, consistent with the equal amounts expected if disproportionation occurs according to equation (2).

As NbCl₃(OMe)₂ at these concentrations and temperature appears to be unstable a low-temperature study was undertaken. The NbCl₅ 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 NbCl₃(OMe)₂. Initially at 223 K only NbCl₅ was seen, but after 100 s some NbCl₄(OMe) appeared. Over the 19 spectra taken the peak due to NbCl₅ decreased in size whilst the NbCl₄(OMe) peak increased. At this point the temperature was raised to 253 K. In the time it took to do so some NbCl₂(OMe)₃ had been formed. After 29 more spectra had been taken, only peaks due to NbCl₄(OMe) and NbCl₂(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 NbCl₄(OMe):Nb- $Cl_2(OMe)_3$. For a 1:1 mixture that had disproportionated the ratio should be 25:75. For better resolution of the NbCl₃(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 ⁹³Nb NMR peak positions of NbCl₄(OMe), NbCl₂(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 NbCl₄(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 NbCl₄(OMe)· MeCN was isolated by removal of excess of solvent to give an orange solid. The IR spectrum showed shifted acetonitrile stretches at 2325 [δ (CH₃) + v(C-C)] and 2296 cm⁻¹ [v(C=N)] for co-ordinated MeCN.^{18,22} and a shifted v(CO) at 1075 cm⁻¹. The NbCl₄(OMe)·MeCN was then added to deuteriated toluene; two new peaks were seen to arise in the lowtemperature ¹H NMR spectrum in a 1:1 ratio (Table 2), and a new peak was observed at $\delta - 550$ in the ⁹³Nb spectrum. The ¹H peaks can be assigned to Nb(OMe) (δ 3.90) and Nb·MeCN (δ 2.35)²³ groups.

When solid NbCl₂(OMe)₃ (prepared from NbCl₅-MeOHtoluene) is dissolved in acetonitrile it gives a single peak at δ -850 in the ⁹³Nb 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 [δ (CH₃) + v(C-C)] and 2285 cm⁻¹ [v(C=N)] as well as peaks at 1090 [v(CO)] and 560 cm⁻¹ [v(Nb-O)], for the proposed monomer adduct NbCl₂(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 ⁹³Nb resonance at δ – 1160 for the dimer and a small side-peak at δ – 1185 due to oligomeric species.

NbCl₅ dissolved in Pure Alcohols.—When NbCl₅ is dissolved in MeOH the ⁹³Nb 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 NbCl₅ (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 NbCl₅ 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 NbCl₅ so that lesssubstituted species [including NbCl₃(OMe)₂] are observed. On warming, the viscosity decreases allowing for unhindered diffusion and NbCl₃(OMe)₂ disproportionates *via* equation (2). A similar set of lines are observed when CsNbCl₆ is dissolved in MeOH.

When 0.5 mol dm⁻³ NbCl₅ is dissolved in the higher alcohols ROH (R = Et or Prⁱ) 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 report⁷ that only NbCl₂(OMe)₃ is formed in non-polar solvents on adding excess of MeOH to NbCl₅ and indicates that NbCl₃(OMe)₂ appears to be unstable, disproportionating to NbCl₄(OMe) and NbCl₂(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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References

- 1 L. L. Hench and J. K. West, Chem. Rev., 1990, 90, 33.
- 2 M. Sayer and K. Sreenivas, *Science*, 1990, **247**, 1056; M. Nabavi, S. Doeuff, C. Sandez and J. Livage, *Mater. Sci. Eng.*, 1989, **3**, 203.
- 3 G. R. Lee and J. A. Crayston, J. Mater. Chem., 1991, 1, 381.
- 4 L. G. Hubert-Pfalzgraf, M. Postel and J. G. Riess, *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, Pergamon, Oxford, 1987, vol. 3, pp. 585–698.
- 5 C. Sanchez, J. Livage, M. Henry and F. Babonneau, J. Non-Cryst. Solids, 1988, 100, 65.
- 6 C. Alquier, M. T. Vandenborne and M. Henry, J. Non-Cryst. Solids, 1986, 79, 383.
- 7 M. Schönherr and L. Kolditz, Z. Chem., 1970, 10, 72.
- 8 R. K. Harris and B. E. Mann, *NMR and the Periodic Table*, Academic Press, London, 1978, p. 208.
- 9 R. G. Kidd and H. G. Spinney, Inorg. Chem., 1973, 12, 1967.
- 10 D. Brown, *Inorganic Synthesis*, vol. 9, ed. S. Y. Tyree, jun., McGraw-Hill, New York, 1967, pp. 88–91.
- 11 D. C. Bradley, W. Wardlaw and A. Whitley, J. Chem. Soc., 1955, 726.
- 12 G. Rob Lee, J. A. Crayston and T. J. Dines, unpublished work
- 13 H. Preiss, Z. Anorg. Allg. Chem., 1961, 311, 121.
- 14 L. G. Hubert-Pfalzgraf and J. G. Riess, Inorg. Chem., 1975, 14, 2854.
- 15 J. G. Riess and L. G. Pfalzgraf, Bull. Soc. Chim. Fr., 1968, 2401.
- 16 L. G. Pfalzgraf and J. G. Riess, Bull. Soc. Chim. Fr., 1968, 4348.
- 17 D. C. Bradley and C. E. Holloway, J. Chem. Soc. A, 1968, 219.
- 18 L. G. Hubert-Pfalzgraf, A. A. Pinkerton and J. G. Riess, Inorg. Chem., 1978, 17, 663.
- 19 D. L. Kepert and R. S. Nyholm, J. Chem. Soc., 1965, 2871.
- 20 J. G. Riess and L. G. Hubert-Pfalzgraf, J. Chim. Phys., 1973, 70, 646.
- 21 R. Gut, H. Buser and E. Schmid, Helv. Chim. Acta, 1965, 48, 878.
- 22 C. Chavant, J. C. Daran, Y. Jeannin, G. Constant and R. Morancho, Acta Crystallogr., Sect. B, 1975, 31, 1828.
- 23 A. Merbach and J. C. Bunzli, Helv. Chim. Acta, 1971, 54, 2543.

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