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Structural and Stereodynamic Studies on Molecular Early Transition Metal Derivatives. I. Niobium Oxochloride-Dimethyl Sulfoxide Adducts

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The structure of compound $NbOCl_3 \cdot 2OSMe_2$ was investigated mainly through ^1H low-temperature nmr in acetonitrile solution. The data were interpreted to mean that the solution consists of a mixture of monomeric, partially dissociated (~12% in 0.14 *M* solution) octahedral isomers in dynamic equilibrium. The isomer in which the ligand molecules are cis and occupy nonequivalent positions is largely predominant (94% of the 2:1 compounds). Partial dissociation of these 2:1 adducts occurs in acetonitrile according to $NbOCl_3 \cdot 2OSMe_2 \rightleftharpoons NbOCl_3 \cdot OSMe_2(MeCN) + OSMe_2$. The formation of the 1:1 $NbOCl_3$·ligand adduct, which is probably coordinated by an additional molecule of acetonitrile, was established by stepwise ligand addition experiments. The interconversion of all the species present in the solution is rapid, causing the coalescence of the signals in the nmr above 60°.

Although more than 30 niobium(V) and tantalum(V) oxohalide complexes of general formula $MOX_3 \cdot L$ and $MOX_3 \cdot 2L$ have been isolated so far, there is still surprisingly little information available on their structures.[1] To our knowledge, only in the case of $NbOCl_3 \cdot 2CH_3CN$ has an X-ray study recently been performed.[2] The other data are restricted to some ir measurements. Thus a monomeric structure was postulated for complexes $NbOCl_3 \cdot 2L$, with L = $OPPh_3$ and $OP(NMe_2)_3$, on the basis of the presence of an absorption band attributed to the ν(Nb=O) vibrations,[3,4] while a polymeric structure involving eight-coordinated niobium was suggested for $NbOCl_3 \cdot 2L$, with L = $OSMe_2$ and $OSPh_2$, on the basis of the absence of an absorption which could be attributed to this vibration.[5] The data on the structure of such compounds in solution are even scarcer and limited to some cryoscopic and ebulliometric molecular complexity measurements[6,7] and to a preliminary nmr study of the $NbOCl_3 \cdot 2OP(NMe_2)_3$ adduct.[8]

The present series of papers is intended to provide structural information, including information on the stereolability and dissociation processes, on molecular early transition metal derivatives. This first paper is devoted to low-temperature nmr study of the compound $NbOCl_3 \cdot 2OSMe_2$ and to its dissociation in solution.

Experimental Details

The 2:1 adduct $NbOCl_3 \cdot 2OSMe_2$ was prepared from $NbOCl_3$ and dimethyl sulfoxide according to the literature[5] and was carefully purified by recrystallization. All the reactions and manipulations were carried out in an atmosphere of oxygen-free dry nitrogen. The solvents were carefully dried.

The nmr spectra were recorded on a JEOL C-60 HL spectrometer; the infrared spectra were measured on a Perkin-Elmer Model 577 instrument. Molecular weights were determined with a KNAUER vapor pressure osmometer.

Results and Discussion

A molecular weight evaluation for compound $NbOCl_3 \cdot 2OSMe_2$ in acetonitrile, using vapor tension osmometry, gave 380 (a monomeric structure would require 371.5). Conductivity measurements show that $NbOCl_3 \cdot 2OSMe_2$ is a nonelectrolyte in acetonitrile ($\Lambda = 17\ \Omega^{-1}\ cm^2$ for a 10^{-3} *M* solution).

The infrared spectrum of compound $NbOCl_3 \cdot 2OSMe_2$ (Nujol mull) presents a broad, complex band in the region where the ν(S=O) and ν(Nb=O) vibrations are expected to be found. This broad band, extending from 900 to 950 cm^{-1}, contains at least four maxima at 915, 930, 938 (sh), and 950 cm^{-1}. There may be an additional less pronounced shoulder at *ca.* 920 cm^{-1}. The two absorptions at 915 and 930 cm^{-1} could be attributed to a splitting of the ν(S=O) vibration[9] as was observed by Lappert when the two ligand molecules are in cis positions in the octahedral complex $SnCl_4 \cdot 2OSMe_2$.[10]

The definite presence of a shoulder at 938 cm^{-1} might then be assigned to the ν(Nb=O) vibration, although the band at 950 cm^{-1} is still in the region where ν(Nb=O) is expected to be found, and, moreover, the ν(Nb=O) vibration could be masked by the ν(S=O) band at 930 cm^{-1}.[11] Thus the infrared spectrum cannot, in our opinion, provide any evidence for the *absence* of a ν(Nb=O) vibration band.

Low-Temperature Nmr of $NbOCl_3 \cdot 2OSMe_2$. A typical ^1H nmr spectrum measured on a 0.09 *M* solution of the adduct in deuterioacetonitrile at −40° is shown in Figure 1. It consists of five signals in the region expected for $OSMe_2$ resonances. Increasing the dilution affects significantly the relative peak areas, except for peaks 2 and 4 which always keep nearly equal area. Peak 5 is the most affected by dilution, being shifted toward higher fields while its area increases most. This indicates that several molecular species are present. Addition of an excess of the ligand results in further variations of the relative peak areas, except for peaks 2 and 4, and causes a large increase in intensity of peak 5 which could thus be attributed to the free ligand. The presence of peak 5 in the solution of pure $NbOCl_3 \cdot 2OSMe_2$ means that the complex is partially dissociated (~15% in the 0.09 *M* solution). It will be shown below that peak 1 can be assigned to an $NbOCl_3 \cdot OSMe_2$ adduct.

The fact that only a single peak is observed when the spec-

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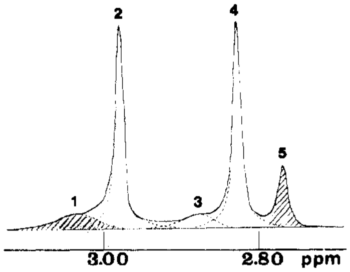
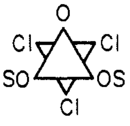


Figure 1. Proton nmr spectrum of a 0.09 *M* solution of $NbOCl_3 \cdot 2OSMe_2$ in acetonitrile at −40°. Hatched areas of peaks 1 and 5 are equal within 10%.

tra are measured above 60° shows that all the species present in the solution are in rapid dynamic equilibrium.

The above results, together with the molecular weight and conductometric measurements, are consistent with the view that $NbOCl_3 \cdot 2OSMe_2$ in acetonitrile solution is a mixture of partially dissociated fast interconverting molecular complexes, which supposes that niobium is hexacoordinated. The geometrical isomers I-III, where OS = $OSMe_2$, may then be



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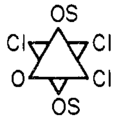

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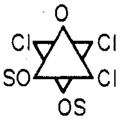

III

present. Isomer III in which the two ligand molecules occupy nonequivalent positions would account for the two consistently equal signals 2 and 4. Signals 2 and 4 are tentatively assigned to the ligand molecules which are trans to the oxygen atom or to a chlorine atom, respectively, on the basis that the ligand molecule which is trans to the best π donor is expected to be the most shielded. For the same reason, signal 3, which is close to signal 4, would arise from isomer I rather than from isomer II. Furthermore, it is known that the stablest geometrical isomers for octahedral complexes of the type $MX_4 \cdot 2L$, where L is an oxo ligand, are those in which the ligands are trans to a better π donor rather than trans to each other, unless they are forced in the other way by steric repulsions.[12] Attempts to obtain from $NbCl_5 \cdot OSMe_2$ a reference chemical shift for an $OSMe_2$ molecule coordinated trans to chlorine were prevented by the immediate formation of the $NbOCl_3 \cdot 2OSMe_2$ adduct[5] when the ligand was added to a solution of $NbCl_5$ in acetonitrile even at −40°.

Stepwise Addition of Dimethyl Sulfoxide to a Niobium Oxochloride Solution. Experiments in which the ligand was added stepwise to a solution of $NbOCl_3$ in deuterioacetonitrile were undertaken in order to elucidate the dissociation process. The evolution of the low-temperature nmr spectra is shown on Figure 2 for a 0.14 *M* solution of $NbOCl_3$ and for increasing values of the $R = OSMe_2{:}Nb$ ratio. Figure 3 represents the variation in relative concentrations of species assumed to correspond to signals 1, 2 and 4, 3, and 5, as evaluated from the quantitative analysis of the nmr spectra as a function of R in the composition domain $0 < R < 3$.

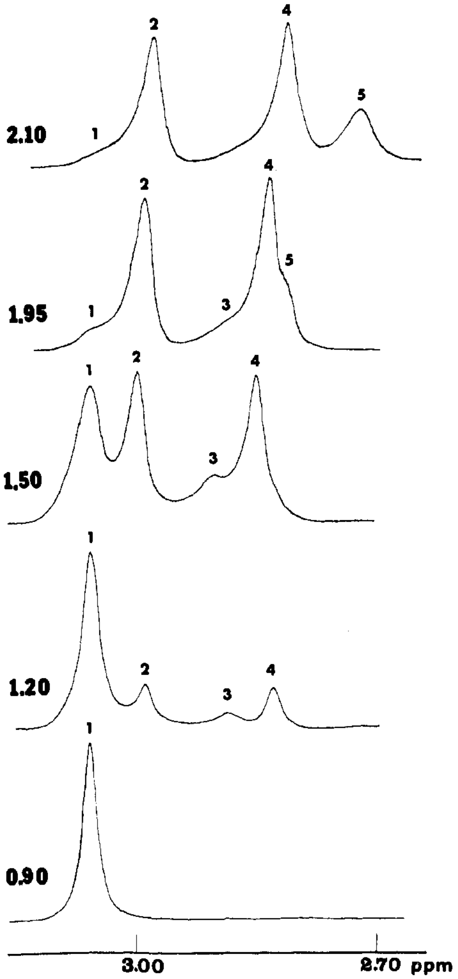

Figure 2. Proton nmr spectra measured at −40° in deuterioacetonitrile for various $R = OSMe_2{:}NbOCl_3$ ratios.

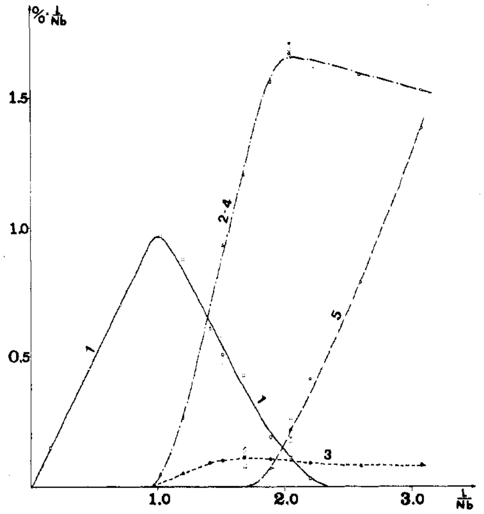

Figure 3. Relative areas of the nmr signals as a function of $R = OSMe_2{:}NbOCl_3$.

The following reproducible observations were made. (i) For $R < 1$ only one signal, 1, is present, for which the chemical shift does not vary significantly upon addition of the ligand. No free ligand is detected. (ii) For $R > 1$ and up to $R = 3.0$, three more signals, 2, 3, and 4, develop simultaneously while peak 1 decreases in intensity. (iii) Signal 1 goes through maximum intensity for $R = 1$ and becomes indetectably small for $R > 2.3$. (iv) The signal corresponding to the free ligand, 5, becomes detectable only when $R > 1.7$. (v) The spectra measured for $R = 2$ are identical with those measured for solutions of the pure crystalline isolated adduct $NbOCl_3 \cdot 2OSMe_2$ at the same dilution.

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(vi) No new signals were detected for the higher R ratios.
(vii) Signals 2 and 4 remain of consistently equal area (±4%) throughout the experiments.

These experiments demonstrate the formation of an intermediate species for the ligand to metal ratio of 1:1. Our efforts to isolate this compound from the solution have failed so far: the only compound which crystallizes out of this solution is the 2:1 adduct, even for $R < 1$. However, the fact that no absorption assignable to a ν(Nb-O-Nb) vibration could be found in the 770-cm^{-1} region,[13] the well-established tendency of niobium to achieve at least hexacoordination, and the fact that a well-defined crystalline molecular 2:1 compound $NbOCl_3 \cdot 2MeCN$[2] is known and readily forms upon dissolution of $NbOCl_3$ in acetonitrile make it reasonable to assume that one molecule of acetonitrile is still coordinated to niobium in a $NbOCl_3 \cdot OSMe_2(MeCN)$ complex. Thus the stronger donor $OSMe_2$, when added, would displace the acetonitrile molecules stepwise from the initially formed $NbOCl_3 \cdot 2MeCN$ adduct. It is worth noting also that no 1:1 adduct between $NbOCl_3$ and an oxo ligand has ever been reported.

Four geometric isomers would *a priori* be possible for an octahedral $NbOCl_3 \cdot OSMe_2(MeCN)$ compound. The fact that only one signal is observed in the spectra down to −40° could mean that one of these isomers is strongly favored but is more likely to mean that the isomers are rapidly interconverting in the solution, due to a fast exchange of the weaker ligand MeCN between the coordination sphere of the metal and the solvation sphere of the adduct. Well-resolved spectra could not be obtained at lower temperatures for these solutions. Attempts to provide direct evidence for the coordination of MeCN, for example by allowing equimolar amounts of $NbOCl_3$, $OSMe_2$, and CH_3CN to react, were precluded by the insolubility of $NbOCl_3$ in noncoordinating solvents such as chloroform or methylene dichloride. It is noteworthy that in these solvents dimethyl sulfoxide reacts only at higher temperatures with the undissolved $NbOCl_3$ and that, independently of the amount of dimethyl sulfoxide present, only the 2:1 adduct could be identified in the supernatant.

On the basis of the preceding experiments peak 1 of Figure 1 was assigned to the 1:1 $OSMe_2$-metal adduct, the dissociation reaction being

$$NbOCl_3 \cdot 2OSMe_2 \rightleftharpoons NbOCl_3 \cdot OSMe_2(MeCN) + OSMe_2$$

It is noteworthy that allowing a mixture of equimolar amounts of $NbOCl_3$ and $NbOCl_3 \cdot 2OSMe_2$ to react gave the same spectra as the reaction of equimolar amounts of $NbOCl_3$ and $OSMe_2$.

The fact that signals 2 and 4 remain of consistently equal area all through these experiments, while the relative areas of the other signals vary significantly, further establishes that they belong to the same molecular species and supports their assignment to isomer III.

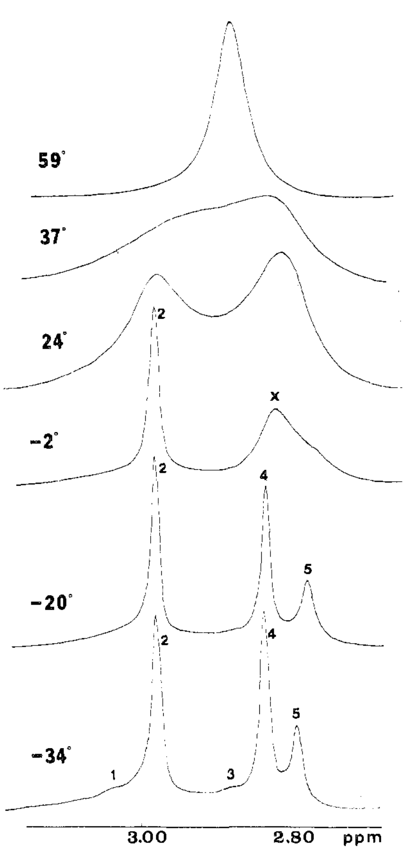

Figure 4. Temperature dependence of the proton spectra for a 0.09 M solution of $NbOCl_3 \cdot 2OSMe_2$ in deuterioacetonitrile.

Variable-Temperature Nmr. The temperature dependence of the proton spectra of $NbOCl_3 \cdot 2OSMe_2$ in a deuterioacetonitrile solution (0.09 M) is illustrated in Figure 4. The coalescence of the signals to a single peak above 59° shows that all the species present in the solution undergo a rapid dynamic interchange. The observation that peak 4 broadens faster than peak 2 would also be in agreement with some labilizing effect on the $OSMe_2$ trans to chlorine. No accurate line shape analysis was undertaken since the various signals have widely different and probably temperature-dependent intensities. On the other hand, the low solubility of the compound prevented us from obtaining significant data on the variation of the coalescence temperatures as a function of the dilution. No splitting due to the diastereotopic character of the methyl groups was detected; such splitting would be temperature independent unless there is a rapid inversion at sulfur.

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Registry No. $NbOCl_3 \cdot 2OSMe_2$, 36509-34-9.

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