Forschung, Wissenschaft

Niobium Pentamethoxide: a Multi-facet Study of an Early Transition Metal Alkoxide *

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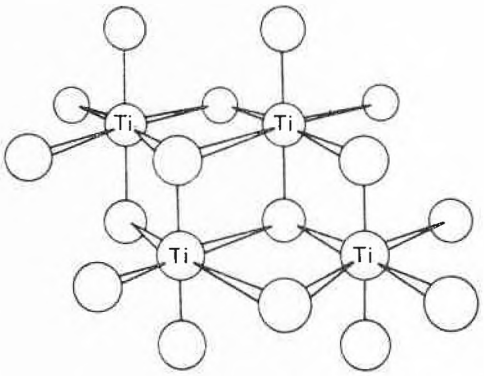
Summary

Niobium pentamethoxide, $Nb_2(OCH_3)_{10}$, was chosen as a typical early transition metal alkoxide on which to undertake a multi-facet study, including such aspects as crystal and molecular structure, exchange of methoxo groups among coordination sites, exchange mechanisms, solvation and coordination properties, for the purpose of gaining some deeper insight into the structure and behaviour of such alkoxides. The X-ray structure determination showed the presence of two different conformers in the unit cell, a moderately strained bridge, evidence for π-bonding in the Nb-O bonds, and no detectable *trans* effect. The exchange of methoxo groups among the three non-equivalent sites of structure II is rapid in solution on the NMR time scale; the terminal-bridge and terminal-terminal exchanges occur via independent processes. It is shown that, contrary to earlier conclusions, the mechanism of exchange of the bridging groups is very likely to be intermolecular. The exchange of the terminal substituents is also discussed. A mixed transition metal alkoxide, $NbTa(OCH_3)_{10}$ (V), was isolated. Evidence for the formation of a solvation cage by polar solvents is presented. The coordination chemistry of the alkoxide has also been investigated, and the ability of the most common ligands to compete with auto-association of $Nb(OCH_3)_5$ into a dimer is discussed. The exchange of methoxo groups between the non-equivalent sites of adduct VI, and between dimer and adduct, are also dynamic on the NMR time-scale.

Numerous metal alkoxides have been synthesized and their chemistry has been thoroughly reviewed by Bradley [1], Fairbrother [2], Keppert [3] and Mehrotra [4]. Structurally speaking they are primarily characterized by their strong tendency to form alkoxo bridges in order to achieve hexacoordination of the metal. Thus group IV elements will form trimeric or tetrameric structures (e.g. structure I: $[Ti(OC_2H_5)_4]_4$; only Ti and O atoms are shown) while dimerisation suffices for group V elements to reach this goal (structure II: $[Nb(OCH_3)_5]_2$; only Nb and O atoms are shown).

We were interested in having a closer look at one or other of these metal alkoxides in order to gain some deeper insight into some of their characteristic features such as their crystal and molecular structure, their structural dynamics, the mechanisms of exchange of the alkoxo groups between coordination sites, and their solvation and bridge opening reactions to form coordination complexes.



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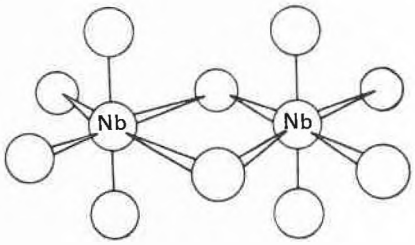

II

Niobium pentamethoxide was chosen for this purpose because of its simple dimeric structure (II) which offers the interesting feature that, for a high symmetry (D_{2h} if one considers only the niobium atoms and their surrounding oxygen atoms), it nevertheless exhibits three types of non-equivalent methoxo sites, namely, bridges (B), equatorial terminal groups (T_e) and axial terminal groups (T_a). These environments are differentiable by ^1H NMR, hence this technique represents an excellent tool for studying dynamic stereochemistry.

Crystal and molecular structure

In contrast to the many publications and reviews which have been devoted to the preparation and solution properties of numerous transition metal alkoxides, there are very few data concerning structures in the solid state. To our knowledge, the only X-ray structure determinations reported to date are those of the

* Received June 24, 1976

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polymeric vanadium oxyalkoxide $(VO(OCH_3)_3)_n$ [5] and the tetrameric titanium alkoxides $Ti_4(OCH_3)_{16}$ [6], $Ti_4(OC_2H_5)_{16}$ [7] and $Ti_4(OCH_3)_4(OC_2H_5)_{12}$ [8]. In the case of the vanadium and the methoxo titanium compounds, the precision of the structures, which were determined from film data (R = 0.17 and 0.14 respectively), does not allow one to discuss the bonding parameters with any certainty; in the latter molecule two of the methoxo groups were presumed to be largely hydrolyzed in the sample which was analyzed. In the other two titanium alkoxides, only the metal and oxygen coordinates were reported.

Both niobium and tantalum pentamethoxides were prepared initially by Bradley et al. [9]. These compounds are dimeric in non-complexing solvents [10], and this degree of aggregation persists in the vapour phase according to mass spectrometry [11]. We expected that a precise knowledge of their molecular structure would shed some light on the question of a *trans* effect, i.e. non-equivalence in the axial and equatorial methyl-oxygen bond distances.

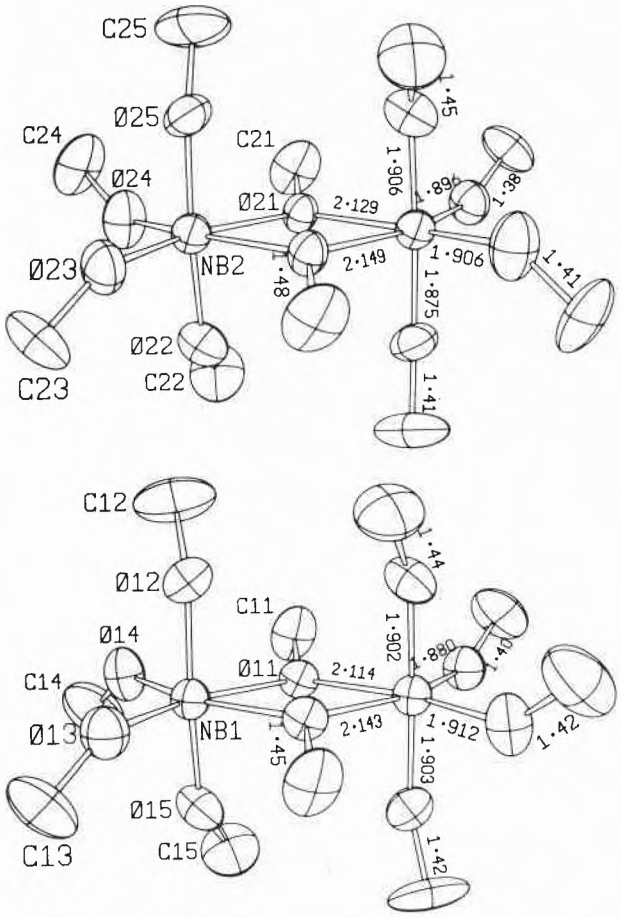


Fig. 1: A view of the two conformers of $[Nb(OCH_3)_5]_2$

$Nb_2(OCH_3)_{10}$ crystallizes in the triclinic system ($P\bar{1}$ space group) and exhibits the interesting feature of the existence of two conformers of the same molecule within the same unit cell [12] (Fig. 1). Both conformers are centrosymmetric and consist of two approximately octahedral units with a shared edge which is differentiated by a *cis* or *trans* arrangement of the equatorial methyl groups with respect to the equatorial plane. The bridging oxygens have an essentially planar configuration. Strain in the bridge is evident from the reduction of the bridge angle at niobium (70.4°) from the ideal octahedral angle of 90° and the relatively long Nb–O bridge bonds (2.13 Å *vs* 2.07 Å from the sum of the covalent radii).

The large bond angles on the terminal oxygen atoms (145.3° av.) together with the short terminal Nb-O bonds (1.90 Å *vs* 2.07 Å for the sum of the covalent radii) may be taken to indicate a significant π contribution to the bonding. The character of the terminal oxygen atoms may be described as between sp^2 and sp, which leaves two pairs of electrons in orbitals with a significant amount of p character, which may in turn interact with the vacant t_{2g} orbitals on the metal. On the other hand, contrary to some early predictions, we have found no significant difference between the axial and equatorial terminal Nb–O bond lengths for either conformer, which would mean that there is no significant *trans* effect or that such a *trans* effect is counterbalanced by some other effect.

Structural dynamics in solution

The structures of $Nb(OCH_3)_5$ and $Ta(OCH_3)_5$ in non-complexing solvents were elucidated independently in 1968 by Bradley et al. [13] and in our Laboratory [14] by means of ^1H NMR spectroscopy. It was then found that the methoxo groups exchanged rapidly among the three non-equivalent ligand sites of structure II, as evidenced by the coalescence of the three NMR signals in the variable temperature experiment shown in Fig. 2a. Both groups were able to establish the interesting fact that there were two distinct exchange rates, the faster concerning the exchange of the methoxo ligands among the terminal positions, the other relating to exchange between terminal positions and bridges. This was accomplished primarily by comparing the observed spectra (Fig. 2a) with those calculated (Fig. 2b), on the assumption that there was only one exchange process that permuted the three different sites. It is quite obvious from Fig. 2 that such a hypothesis is invalid, because there is no perceptible broadening of the bridging group signal b during the coalescence of signals t_1 and t_2, which would be the case (Fig. 2b) if the same process were responsible for the exchange among all the three types of sites. The *difference* in activation energy between the two processes was established by standard methods at *ca.* 8 ± 4 kJ. mole^{-1}. The kinetic data collected for various niobium and tantalum alkoxides are shown in Table 1.

No evidence for depolymerisation—i.e., no change in chemical shifts with temperatures for example—was found for the methoxides up to 160°. This observation contrasts with those made on higher alkoxides, since a

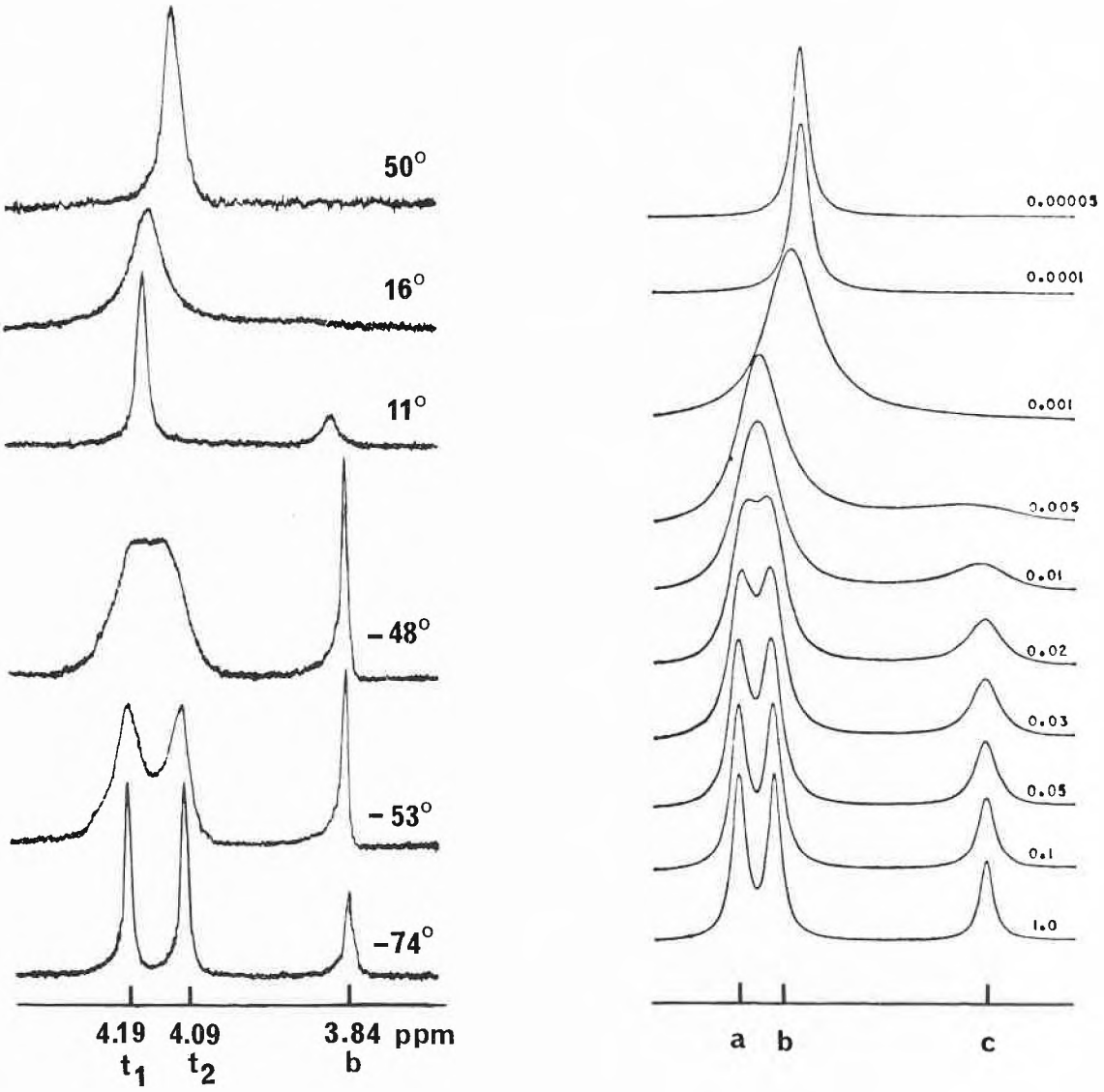


Fig. 2: a) Variable temperature proton NMR spectra measured on a 0.085 molar solution of $Nb(OCH_3)_5$ in CS_2.

b) Spectra calculated in the hypothesis of a random exchange between three sites of population ratio 2/2/1.

Table 1: Kinetic data, from NMR measurements, for various niobium and tantalum alkoxides and various solvent and dilution conditions

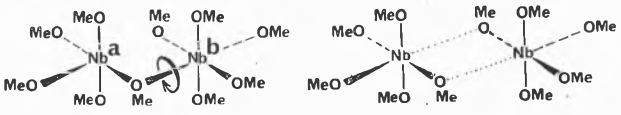
			Terminal – Terminal Exchange				*Terminal – Bridge Exchange*			
	Solvent	Dilution m.l^{-1}	*Tc*(*T*–*T*) °C	$\Delta G^{\neq}$ (kJ. mole^{-1})	E_a (kJ. mole^{-1})	$\Delta S^{\neq}$ (J.d^{-1} mole^{-1})	*Tc* (*T*–*B*) °C	$\Delta G^{\neq}$ (kJ. mole^{-1})	E_a (kJ. mole^{-1})	$\Delta S^{\neq}$ (J.d^{-1} mole^{-1})
$Nb(OMe)_5$	C_8H_{18} [13]		−46	51.0 ± 4			11 to 19	64 ±0.4	39.7 ± 4	−75.2 ± 13
	$C_6H_5CH_3$ [13]	2.25 to 0.025	−54 ± 1	50.1 ± 1.3	31.3 ± 4	−96 ± 12	9 ± 5	60.2 ± 2.1	37.6 ± 4	−87.8 ± 16.7
	CS_2 [14]	0.10	−48 ± 1	52.1 ± 1.3	34.7 ± 4	−88 ± 12	21 ± 3	61.9 ± 2.1		
	MeCN [16]	2.7 to 0.03	−32 ± 1	55.2 ± 1.3			25 ± 2	65.2 ± 2.1		
$Nb(OEt)_5$	C_8H_{18} [13]	0.1 to 0.05	−60	48.1 ± 1.3			48 to 58	68.5 ± 0.4	43.9 ± 4	−77.3 ± 1.3
$Nb(OBu^i)_5$	C_8H_{18} [13]	0.1 to 0.05	5 to 15	64.8 ± 1.3			70 to 80	70.6 ± 0.4	48.1 ± 8	−71.0 ± 25
$Ta(OMe)_5$	C_8H_{18} [13]	0.1 to 0.05	−28	54.0 ± 0.4	36 ± 2	−84 ± 8	35 to 40	64.5 ± 0.4	43.5 ± 2	−71.0 ± 6.3
	$C_6H_5CH_3$ [14]	0.5	−29 ± 1	56.0 ± 1.3	37 ± 4	−75 ± 12	30 ± 3	66.0 ± 2	46.0 ± 4	−58.5 ± 16.7
	MeCN [16]		−15 ± 1	57.7 ± 1.3			44 ± 3	69.8 ± 2		
$Ta(OEt)_5$	C_8H_{18} [13]	0.1 to 0.05	−30 to −20	54.0 ± 1.3			35 to 48	65.8 ± 0.4	49.8 ± 4	−60.6 ± 1.3
$Ta(OBu^i)_5$	C_8H_{18} [13]	0.1 to 0.05	25 to 35	69.0 ± 1.3			75 to 85	74.4 ± 0.4	41.8 ± 4	−100.3 ± 1.3

monomer-dimer equilibrium was clearly demonstrated for the isopropoxides (enthalpy of dissociation *ca.* 71 kJ.mole^{-1}), and tantalum pentatertiobutoxide has been found to be monomeric [13]. On the other hand, the activation energy for the terminal-bridge exchange is higher for the tantalum isopropoxide than for its methoxide. This suggests that the steric effect of the bulky alkoxide groups is two-fold: on one hand it weakens the bridge in the dimer and thus lowers the dissociation energies, or even opposes its formation, whilst on the other hand it slows down the motion of these groups, and thus increases the activation energies for terminal-bridge exchange.

Addition of the parent alcohols gave sharp alcohol signals in the NMR, showing that the exchange between the dimeric alkoxides and the parent alcohol is much slower than the exchange of the alkoxo groups among the sites on the metal [13,15]. This is in contrast to the behaviour of the trimeric titanium alkoxides, which showed rapid interchange with free alcohol. On the other hand, rapid exchanges with the parent alcohol were observed with the *monomeric* isopropoxides and tertiobutoxides [13].

Terminal-Bridge exchange mechanism: intra or intermolecular?

The terminal-bridge exchange process in $[Nb(OCH_3)_5]_2$ necessarily involves the rupture of one bond; however, such a process can be intra or inter-molecular: one of the *intra*molecular processes would involve the breaking of one of the branches of the bridge only, followed by a 90° rotation of one side of the molecule around the remaining bridge bond, as depicted in III, which causes one of the terminal methoxo groups to come into the appropriate position to form a new bridge.



III IV

On the other hand, an *inter*molecular process would result from a simultaneous breaking of the two bridges into identical fragments as indicated in IV.

Although earlier conclusions favoured an intramolecular exchange mechanism [13–15], the main experimental fact on which this was based was the independence of the coalescence temperature to dilution (between 2.25 and 0.025 M in toluene [14]; 2.7 and 0.03 M in acetonitrile [16] for $Nb(OCH_3)_5$, and, for $Ta(OCH_3)_5$, between 0.5 and 0.05 M in n-octane [15]). However, NMR experiments as a function of concentration *cannot* be conclusive here. A formal kinetic analysis of the problem shows that, in the case of a symmetrical dissociation into identical fragments, the lifetime of the methoxo groups in any one site of the dimer can be expressed as a function of rate constants and equilibrium constants [17].

Consider the dissociation of the dimer (D) into two identical monomeric fragments (M) followed by a recombination of two such fragments M and M*, according to (1):

$$D \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} M + M$$

and (1)

$$M + M^* \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} D^*$$

The reciprocal mean exchange lifetime τ_D of the dimer is

$\frac{1}{\tau_D} = fk_1$ (if the dissociation is rate-determining)

while

$\frac{1}{\tau_D} = fk_{-1}K$ (if recombination is the rate-determining step),

where $K = k_{-1}/k_1$ stands for the formation constant of the dimer, while f reflects the probability of exchange between the sites (if $\tau = \tau_T$, $f = 1/5$ and if $\tau = \tau_B$, $f = 4/5$).

Consequently, whatever the rate-determining step is, dilution experiments are not sufficient in this case to distinguish an *intra*molecular from an *inter*molecular mechanism.

The fact that the activation entropy is negative ($\Delta S^{\neq} = -75.5 \pm 13$ J.d^{-1}.mole^{-1} for $Nb[OCH_3]_5$ in octane) [15] cannot be considered as conclusive if one considers the values obtained for the well-established dissociative exchange mechanism of $TaCl_5.SMe_2$ ($\Delta S^{\neq} = -380 \pm 12$ J.d^{-1}.mole^{-1}; $\Delta S^{\neq} = 75.5 \pm 25$ J.d^{-1}.mole^{-1} in the case of the non-dissociative exchange in $TaCl_5.OMe_2$) [18].

A mixed transition metal alkoxide

In order to solve the problem, one has to be able to distinguish the two fragments. Labelling the methoxo groups cannot be effective, since they exchange sites rapidly and would immediately distribute equally between the two niobium atoms. One has to label the metal atoms. The way we solved the problem was to replace one of the niobium atoms by a tantalum atom. It is well-known, indeed, that niobium and tantalum are "cousins" in the Periodic Table; they have comparable radii (r_i 0.70 and 0.73 Å) and polarisabilities (10.9–10.9 Å^3) [19], while still inducing different chemical shifts to the methoxo groups that are linked to them.

Fig. 3 shows the low-temperature proton NMR spectra of a mixture of niobium pentamethoxide and tantalum pentamethoxide in acetonitrile. One now observes in the region assigned to the bridging methoxo groups, next to the signals b_{Nb} and b_{Ta} caused by the bridges in the two symmetric dimers, a new signal, b_{Nb-Ta},

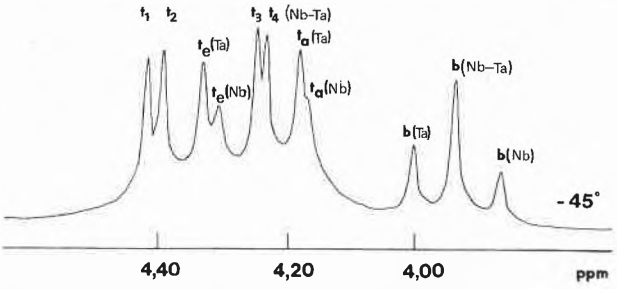


Fig. 3: Proton NMR spectrum at $-45°$ of a mixture of niobium and tantalum pentamethoxides (0.91/1) in acetonitrile (0.03 M). Labeling of the signals: examples: t_e (Nb) = terminal equatorial methoxo group in the symmetric niobium dimer: t_{1-4}(NbTa) = terminal methoxo groups in the mixed Nb–Ta species: b = bridging methoxo protons.

which we attribute to the bridging OCH_3 groups in a mixed niobium-tantalum dimer. In the same way, in the terminal OCH_3 region one finds the four new signals which are expected for the mixed dimer V. That these

(2)

V

4 + 1 signals originate from the same single molecular species was further evidenced by the fact that their relative area is independent of the ratio of the starting ingredients.

The mixed-transition metal alkoxide $NbTa(OCH_3)_{10}$, which seems to be the first of its kind to be reported, was isolated as a crystalline species. That the isolated solid does *not* consist of mixed crystals of both symmetric dimers is further borne out by their mass spectra, which exhibit the expected molecular ion (M/e = 584) and several fragments containing both niobium and tantalum atoms, while none of the mass fragments containing both niobium and tantalum atoms, while none of the mass fragments containing two niobium or two tantalum atoms, which were found in the spectra of the symmetric alkoxides, were detected [20].

The formation of the mixed dimer, according to eq. (2), ranges from 3 to 6 at $-30°$, depending on the solvent. This value is close to the random value 4, which affords one more argument for considering that the replacement of one niobium atom by a tantalum atom does not perturb the system drastically.

Equilibrium (2) is dynamic on the NMR time-scale and a most significant observation is that the exchange rate of the *bridging* methoxo groups among the three distinct species is of the same order as that between terminal and bridging positions in the symmetric niobium and tantalum dimers ($\Delta G^{\neq} = 66 \pm 4$, 64 ± 4 and 63 ± 4 kJ.mole^{-1} respectively). Since the former is necessarily *intermolecular* this provides strong evidence in support of a similar intermolecular exchange mechanism in the case of the latter [31].

Exchange of the terminal methoxo groups: dissociative or non-dissociative?

The exchange between the axial and equatorial terminal sites appears to be intramolecular, since the coalescence temperature is significantly independent of the dilution. Furthermore, in this case there is no possibility of a symmetric dissociation of type IV occurring without the simultaneous exchange of the bridging alkoxo groups, which has been shown *not* to be the case.

The question of the exchange mechanism deserves some discussion, especially since stereochemical non-rigidity is very seldom observed in octahedral complexes. On the contrary it is well established that the exchange of *monodentate* ligands on octahedrally substituted metals generally proceeds by a dissociative mechanism. In fact, the prominent examples of non-dissociative processes which have been clearly established for the exchange of monodentate ligands seem to be those of the distorted hydrophosphito complexes such as $H_2Fe[P(OR)_3]_4$ by Meakin et al [21] and of the compounds of series $M(CO)_4(EMe_3)_2$ (where M = Fe, Ru, Os; E = Si, Ge, Sn, Pb) by Graham et al. [22].

However, none of the mechanisms proposed in these cases seem to apply here: the tunnelling mechanism proposed by Meakin et al. supposes a highly distorted structure, and the exchange mechanism of Graham et al. involving cis-trans isomerisation is not possible here because of the bridge.

Nevertheless, we feel that an intramolecular non-dissociative mechanism may be plausible in the case of the early transition metal derivatives, since these metals readily accept being hepta or octa-coordinated, unlike most of the metals on which the previous studies have been made, and which lie further to the right of the transition periods. Thus one is entitled to think that the coordination sphere of niobium, tantalum and other early transition metals, where they are hexa-coordinated, is less tightly packed, less rigid, and thus would more easily allow for stereolability. For example, an *associative* mechanism has been established for the substitution of hexacoordinated niobium (V) and tantalum (V) halides by dialkylchalcogenides [18].

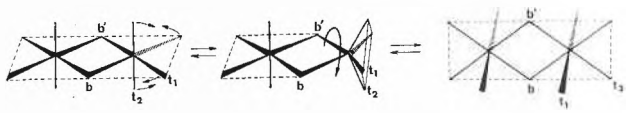


Fig. 4: A possible non-dissociative mechanism for the exchange of methoxo groups among terminal sites.

In the case of the $[Nb(OCH_3)_5]_2$ dimer, the small (70°) O–Nb–O bridge angle leaves even more room for the remaining ligands to move. In fact, one can crudely consider niobium to be pseudo-penta-coordinated by fusing the bridging ligands into one "substituent". In this way one can imagine a two-step intramolecular non-dissociative mechanism such as the one depicted

in Fig. 4: first a Berry-like pseudorotation taking the bridge as the pivot, then a 90° rotation—or turnstile—about the bridge in order to recover the initial structure. Of course the two steps would be coupled. The activation energy for such an intramolecular mechanism should not be too high, due to its fourfold character.

An alternative would consist of an intramolecular but dissociative mechanism involving the breaking of one of the less stable *bridging bonds* to give intermediate III followed by pseudo-rotation of the bonds about niobium a, which would be expected to be rapid. This mechanism would simply require that activation energies both for breaking the bridging bond and for pseudorotation be lower than that for rotation of niobium b around the remaining bridging bond. This alternative also seems to be reasonable if one considers that it needs only 8–12 more kJ. to dissociate both bridging bonds.

Still another possibility would consist of a *dissociative* mechanism which would take place inside a solvent or solvation cage, as has been invoked in the case of aluminium alkyls [23]. Let's assume that one terminal bond is dissociated but that the methoxo group is somehow maintained in the neighborhood of the molecule by such a cage. The niobium atom, then becoming pentacoordinated, would be expected to undergo a rapid non-dissociative exchange of the three remaining terminal methoxo groups. Then after a couple of such exchanges this MeO group would, with a high probability, come back onto the same niobium atom. From the standpoint of NMR, such a mechanism would appear intramolecular within this sort of "supermolecule" constituted by the complex and its solvent or solvation cage. By "solvent cage" [24] one generally implies a situation where the surrounding solvent by its viscosity slows the diffusion rates and opposes the migration of dissociation fragments, thus favoring a recombination of the same fragments. However, in the case of n-octane for example (η = 0.546 cP), the effect of such a solvent cage appears to be significant only on processes having rate constants of the order of 10^{-8} or higher. In our case the rate of exchange is much too low to allow assignment of the independence of coalescence temperature on dilution to such a solvent cage effect. On the other hand, in polar solvents such as acetonitrile, the interactions between solvent and solute are mainly dependent on the dielectric constant of the solvent, and one speaks of a "solvation cage" [24]. In this case it would be expected that, if there is a dissociation of one of the methoxo groups, this group would itself be immediately solvated and dragged out of the solvation cage.

Besides that it would seem less likely that the stronger terminal Nb–O bonds would more easily break than the weaker (longer) bridging Nb–O bonds, our best evidence so far against such a dissociative but cage-confined mechanism is that the coalescence temperature for the terminal group signals remains reasonably independent of dilution in solvents as different as octane, toluene, carbon disulfide and acetonitrile. It seems highly improbable indeed that all these various solvents, each in its own way, are able to constitute a leak-proof cage around the niobium pentamethoxide dimer.

Evidence for a solvation cage

Having three distinct probes with which to explore the surroundings of the molecule, we felt that we were in a good position to undertake a study of the solvation of niobium pentamethoxide by polar but non-complexing solvents. It should be noted that there are almost no data available on the solvation of such metal compounds.

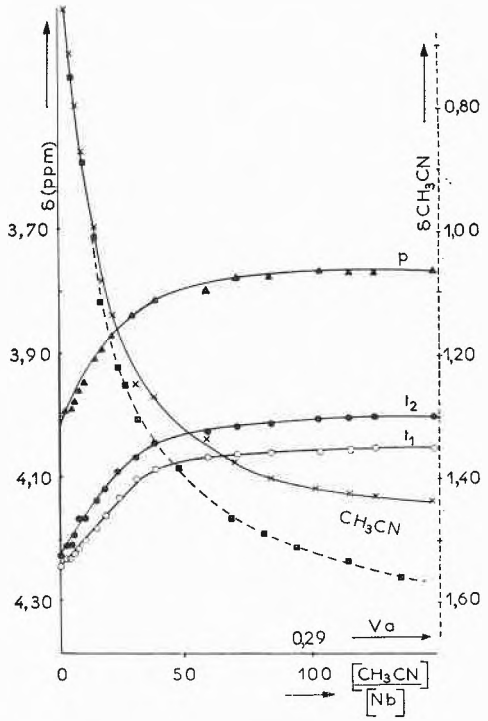


Fig. 5: Chemical shift variation at − 56°, during the addition of increasing amounts of acetonitrile to a 0.09 molar solution of $Nb(OCH_3)_5$ in toluene.

The results of these investigations [25] are summarized in Figs. 5–9. Fig. 5 is a plot of the chemical shift variations at − 56° of our three probes if one adds increasing amounts of acetonitrile to a solution of niobium pentamethoxide in toluene. It shows that a plateau is reached in these variations when about 80 to 100 molecules of acetonitrile are added, which still represents a low % volume of the polar solvent with respect to toluene. Another important point is that this levelling is practically independent of the initial dilution of the alkoxide in toluene, i.e. independent of the Nb/toluene and MeCN/toluene ratios. On the other hand, it greatly depends on the bulkiness of the polar solvent, as can be seen, for example, by comparing Figs. 5 and 6. It takes only 30 to 50 molecules of

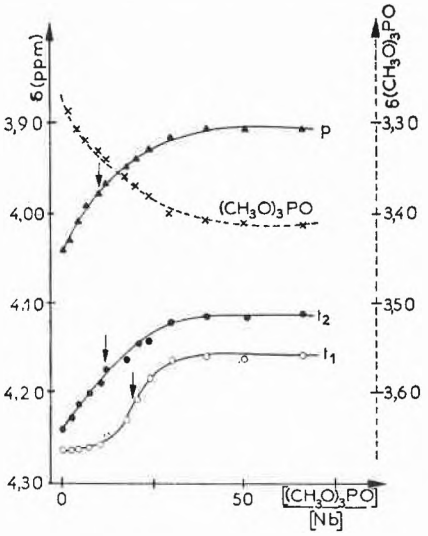


Fig. 6: Chemical shift variation at − 56°, during the addition of increasing amounts of trimethyl phosphate to a 0.1 molar solution of $Nb(OCH_3)_5$ in toluene.

trimethylphosphate per molecule of niobium pentamethoxide to reach the plateau, while 25 to 30 molecules suffice in the case of pivalonitrile. Thus we think that these figures are an indication of the number of solvent molecules which constitute the first solvation shell of the alkoxide. Still another interesting feature of these variations is the delay which is found in the variation of the chemical shift of one of the terminal sites when the solvent becomes bulky (see Fig. 6). It is tempting to assign this to a preferential solvation of one of the terminal sites.

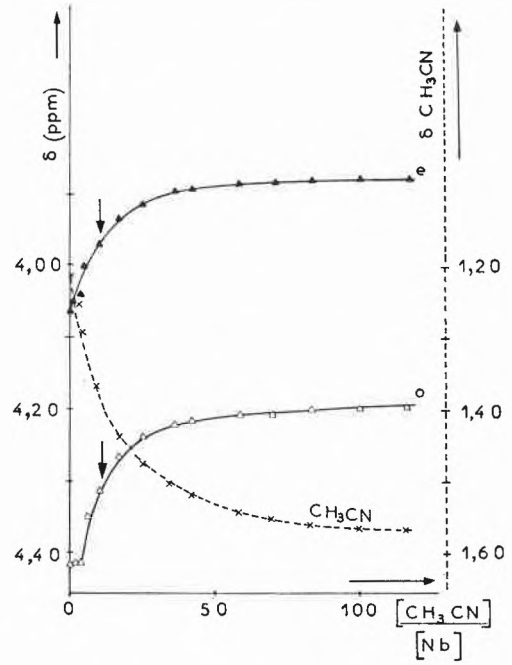
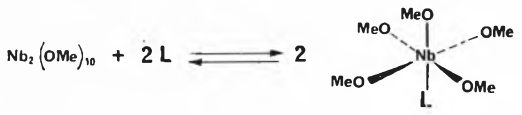


Fig. 7: Chemical shift variation at − 56°, during the addition of acetonitrile to a solution defined by the molar ratios: Nb/toluene = 0.04 and NC_5H_5/Nb = 22.

Similar observations were made for the octahedral complexes of type $Nb(OCH)_3)_5$ L, which form according to (3) in the presence of complexing polar solvents,



(3)

VI

and are illustrated in Fig. 7 for L = pyridine, and Fig. 8 for the much bulkier ligand hmpa. Again a plateau is reached for a reproducible, limited, dilution-independent number of solvent molecules. When hmpa is the solvent, about 15 molecules of solvent per niobium suffice to reach the plateau, and the delay observed in the variation of the chemical shift assigned to the methoxo site *trans* to the ligand indicates that it is solvated last. Note that equilibrium (3) is displaced to the right by addition of polar solvents, which supposes a preferential solvation of the adduct.

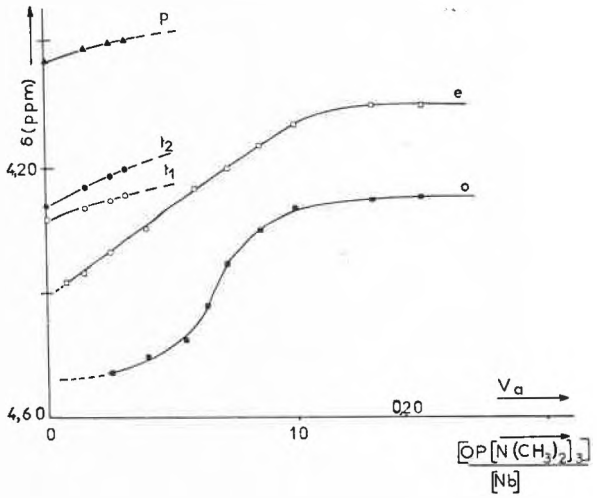


Fig. 8: Chemical shift variation at − 56°, during the addition of increasing amounts of HMPA to a 0.9 molar solution of $Nb(OCH_3)_5$.

Our major concern in this study was to establish whether or not the observed chemical shift variations can, at least predominantly, be attributed to a reaction field between the solvent molecules and the dissolved species, in other words to solvation, and not to some magnetic anisotropy effect of the solvents. Our best arguments for this are: 1) that the plateaux are reached for still low volumic fractions of the polar solvents, and are independent of the proportion of toluene; 2) that the differences in chemical shifts between the various sites of the dimer, when measured in pure solvents of widely different anisotropy, are usually still comparable to those observed in the presence of large amounts of toluene, and vary linearly with the $\varepsilon - 1/\varepsilon + 1$ ratio, as expected in the case of a field reaction [26]; 3) another striking argument was obtained through a comparison of the variations in chemical shifts with the variations of formation constants of complexes when polar solvents are added. Fig. 9 shows, indeed, that very similar

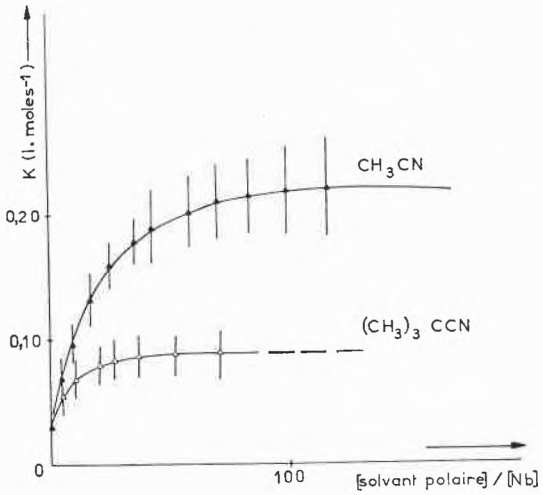


Fig. 9: Variation of the formation constant of complex $Nb(OCH_3)_5 \cdot NC_5H_5$ in toluene during the addition of increasing amounts of acetonitrile or pivalonitrile.

variations with levelling for comparable numbers of added polar solvent molecules and comparable dependence on solvent bulkiness (ca. 100 for acetonitrile and ca. 30–40 for pivalonitrile) are observed. These parallel variations of chemical shifts and equilibrium constants can hardly both arise from the magnetic anisotropy of the solvent.

Limited coordination abilities

The early transition metal alkoxides do not readily form coordination complexes but prefer to autoassociate into dimers, trimers, etc. [1–4]. Methoxo bridges (2.13 Å *vs* 2.07 Å from the sum of covalent radii) are stronger than chloro bridges (2.55 Å [27] *vs* 2.33 Å from the sum of covalent radii), presumably because the former are better π-donors. In the case of tantalum (V) methoxide, the formation of a pyridine (py) complex was however postulated as early as 1956 by Bradley et al. [10] to account for ebullioscopic weight measurements, but attempts to isolate the complex by evaporation of the solution failed.

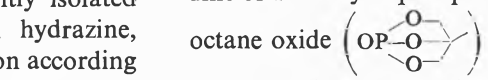
In the case of niobium pentamethoxide, the first $Nb(OCH_3)_5L$ complexes were only recently isolated (L = pyridine, α-picoline, morpholine, hydrazine, $ONMe_3$, $OP(NMe_2)_3$) [28]. Their formation according to eq. (3) can easily be detected by ^1H NMR because of the development of two new signals, in 4:1 ratio in the spectra, as expected for the octahedral structure VI. This allowed us to observe the formation of a few other 1:1 complexes, in addition to those above, but only with some other amines (NH_3, NH_2Me, $NHMe_2$, piperidine) or oxo-type ligands ($OPMe_3$ and $OAsMe_3$); but they were not isolated [29].

On the other hand, more than twenty other potential monodentate ligands were tested, including ethers (OMe_2, OEt_2, tetrahydrofuran, furan, dioxane, thioxane, acetone); amines (NMe_3, pyrrole); nitriles (MeCN, Me_3CCN, benzonitrile); sulfides (SMe_2, S_2Me_2, thiophene); phosphines (PMe_3, $P(NMe_2)_3$); phosphites ($P(OMe)_3$); phosphine sulfides ($SPMe_3$); phosphates ($OP(OMe)_3$); sulfoxides ($OSMe_2$); sulfites ($OS(OMe)_2$) and arsines ($AsMe_3$), but afforded no NMR-detectable amounts of complexes.

A range of bidentate ligands was also tested. It was shown that ethylene diamine and hydrazine probably behave as monodentate ligands, while salicylaldehyde gives monomeric $NbO(OCH_3)_2OC_6H_4CHO$ [32].

In some cases (L = $OPClMe_2$, $OPMe(SCN)_2$, $OPMeF_2$, for example), extensive redistribution of ligands between the phosphorus atom and the metal was observed to occur [32], but with monodentate ligands, at least, we never observed such other reactions as reduction, even in drastic conditions (heating for 4 months at 100° with pyridine), formation of oxoniobium derivatives [30], or further coordination, which are commonly observed in the case of niobium pentahalides [2]. To summarize, coordination complexes of $Nb(OCH_3)_5$ can form, although only a few ligands are able to compete with the bridge formation; moreover, equilibrium (3) generally lies to the right, and therefore the question of predicting which ligands are able to give complexes of type C was raised.

Which ligands will coordinate niobium pentamethoxide?

The coordination chemistry of niobium and tantalum pentamethoxides can obviously not be rationalized on the basis of the qualitative hard and soft model [31]; for example, the borderline base pyridine complexes these alkoxides, which would *a priori* be expected to behave as hard acids, while no coordination was noted with harder donors such as ethers, acetone, or methoxybisdimethylaminophosphine oxide. Nor is there any obvious relationship between the coordinative properties of the ligand and the existence of a delocalized π-system on it: pyridine and piperidine both form complexes with pentamethoxide. Steric hindrance can explain why α-picoline, unlike the other picolines, does not complex the pentamethoxide, but certainly does not account for the noncomplexing character of trimethylphosphate, quinuclidine or 1-methyl 4-phospha 3,5,8 trioxa bicyclo (2,2,2) octane oxide  compared to hexamethylphosphortriamide, or trimethylamine oxide.

More attractive is Hollebone's approach, which considers the symmetry and energy of the donor's frontier orbitals. Accordingly, ammonia, whose highest occupied molecular orbital (HOMO) is localized on the donor atom and has a most favorable symmetry ($2a_1$) is expected to be a better base than trimethylamine, whose HOMO ($4p_e$) is stabilized by *ca.* 40 kcal. A similar situation is found for dimethylether. Unfortunately our knowledge of the energy gap between the frontier orbitals is too limited to allow general predictions.

A more empirical approach was made in the case of a series of phosphoryl donors, to correlate formation

constants and charge distributions on the ligand donor atom (as evaluated from Faraday effect measurements). The charge distribution on the oxygen is related to the phosphoryl's π-bond order [29], and in turn to the $\nu(P=O)$ frequency in the infrared spectra. Thus the observation that substitution of *one* methyl or dimethylamino group in $OPMe_3$ and $OP(NMe_2)_3$ by a methoxo group suffices to completely inhibit their coordination ability, is consistent with the increase of the phosphoryl's π-bond character and with the related shift of the $\nu(P=O)$ vibration toward higher frequencies. As a practical rule it is predicted that complexation will occur, in the absence of steric or other specific constraints, for phosphoryl ligands having $\nu(P=O)$ frequencies lower than 1210 cm^{-1}.
Similar considerations explain why no sulfoxides, and only arsine oxides having $\nu(As=O)$ higher than 910 cm^{-1} gave adducts with niobium pentamethoxide.

Dynamics of the solution equilibria

Another aspect of our investigations concerns the dynamic character of the exchange processes which occur in solutions of the $M(OCH_3)_5L$ adducts. This point is illustrated in Fig. 10, where variable temperature NMR spectra are shown. Successive coalescence of all the methoxo signals (Fig. 10a) shows that not only the exchange of the methoxo groups among sites in the dimer, but also their exchange between the non-equivalent *cis* and *trans* positions in adduct VI, and finally their exchange between the dimer and the adduct, are rapid on the NMR time-scale. At the same time the exchange of the ligand between its free and its coordinated site is shown in Fig. 10b. A detailed analysis was attempted on a few chosen samples in order to decide which, among a range of 13 possible mono and bimolecular exchange processes, would be primarily responsible for the line-shape dependence in the vicinity of the five observed coalescence temperatures [16]. It was shown, for example, that, for given experimental conditions, the exchange of both the methoxo groups among sites in the complex C, and of the ligand L, according to process:

$$C^* + L \rightleftarrows C + L^* \quad (4)$$

is significantly faster than the exchange of the alkoxo groups between dimer and complex according to:

$$D + C^* \rightleftarrows D^* + C \quad (5)$$

or $$D + 2L \rightleftarrows 2C \quad (6)$$

Thus the first process can be held as primarily responsible for the observed ligand's curve shape variations, which in turn allowed us to derive for this process a complete set of kinetic parameters from the analysis of the coalescence of the ligand signals (E_a = 31.4 ± 1.3 kJ.mole^{-1}; log A_o = 7.2 ± 0.2; $\Delta G^{\neq}$ = 59.0 ± 2.1 kJ.mole^{-1}; $\Delta S^{\neq}$ = − 117 ± 21 J.d^{-1}.mole^{-1}).

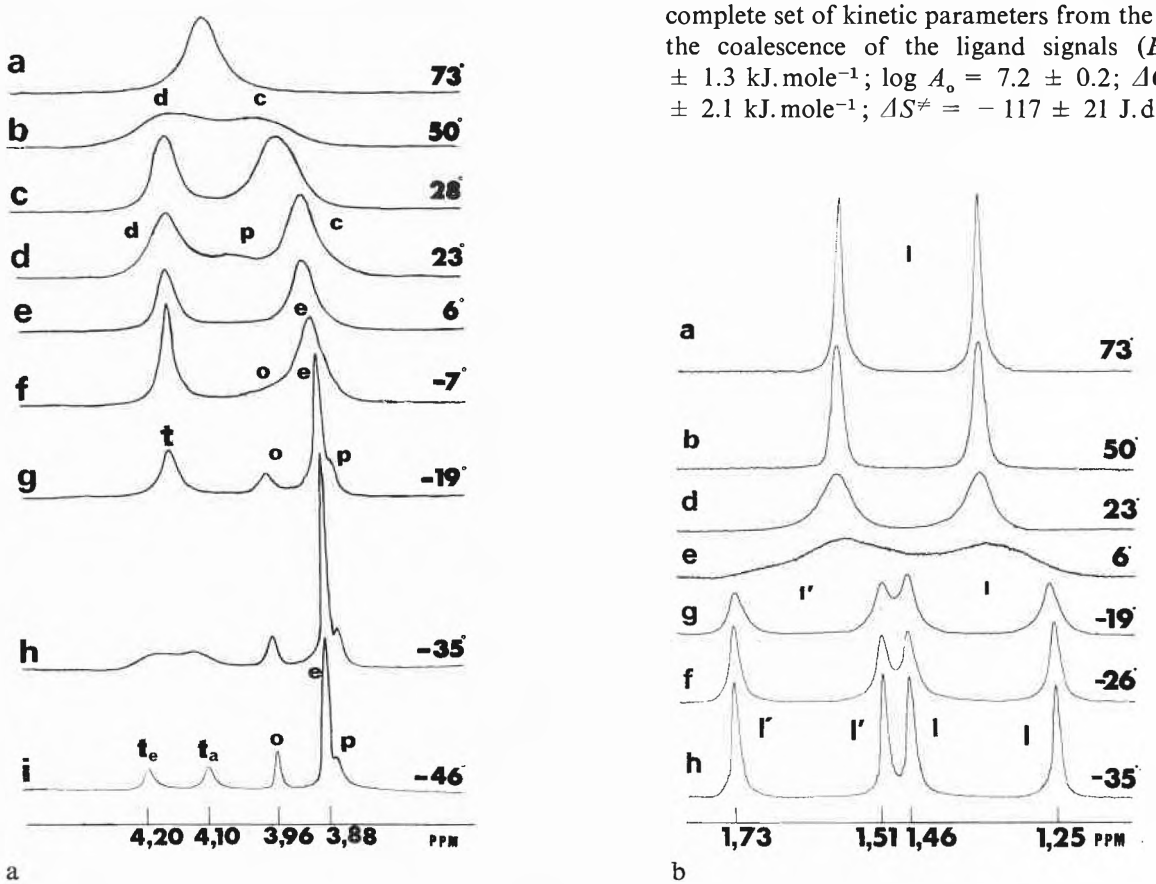


Fig. 10: Variable temperature proton NMR spectra measured on a 0.75 molar solution of $Nb(OCH_3)_5$ in acetonitrile in the presence of $OP(CH_3)_3$ (molar ratio L/Nb = 2).
a) the methoxo groups region b) the ligand resonances

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