

BIMETALLIC ALKOXIDES OF NIOBIUM

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Abstract—The formation of the I–III group metal alkoxoniobates has been studied using the physicochemical analysis method, namely the investigation of solubility isotherms for the $M(OR)_n-Nb(OR)_5-ROH$ systems ($M = Li, Ba, Sc, La$; $R = 2Et, Pr^i$). The crystallization of the following complexes has been observed: $LiNb(OEt)_6$ (I), $[LiNbO(OEt)_4(EtOH)]_2$ (II), $[BaNbO(OEt)_5(EtOH)_{1.5}]_4$ (III), $BaNb_2(OPr^i)_{12}(Pr^iOH)_2$ (IV) and $LaNb_2(OPr^i)_{13}$ (V). It has been found that the bimetallic isopropoxide of Sc and Nb does not exist in the solid state. The oxo complexes II and III are formed on storage (or more rapidly on refluxing) of the solutions of non-oxo compounds in alcohols in the presence of dry air and are, in fact, the products of these compounds oxidation by oxygen. The structure of II is built of dimeric molecules with the metal–oxygen core analogous to that of $Ti_4(OMe)_{16}$. The molecule of III is constructed around the $[Ba_4O_4]$ cubane-like unit, whose oxygen vertices are occupied by the oxo atoms of $NbO(OEt)_5$ octahedra. The structures of the molecules of IV, V and recently studied $Nb(OPr^i)_5$ are based on the common motif featuring the M_2O_2 four-membered cycles in edge sharing octahedra. All the observed $[NbMNb]$ units are non-linear, the molecule of V being asymmetric, for the central $[LaO_6]$ octahedron is sharing simultaneously an edge with one $[NbO_6]$ octahedron and a face with the other. The conditions leading to the formation of oxo groups and the influence of the latter on the complexation process have been discussed. The literature data on the existence of *3d* transition metals alkoxoniobates have not been confirmed. It has been found that interaction of Nb and Co or Ni isopropoxides takes place only due to preliminary microhydrolysis or pyrolysis and leads to formation of oxoalkoxoniobates.

The bimetallic alkoxides of niobium attract considerable attention due to their application as precursors in the synthesis of mono-, di- or trivalent metal niobates, ferro- or piezo-electric, resonator materials, etc.^{1,2} The study of composition and structure of the complexes present in solutions of two alkoxides in organic solvents is considered as one of the most important steps of investigation of

the mechanism of mixed oxides sol–gel preparation. The quality of the final materials is to a great extent dependent on the processes taking place in the initial solutions of alkoxides, namely complex formation, partial decomposition, etc.

Numerous alkoxoniobates of general composition $M[Nb(OR)_6]_n$, where $M = Li-Cs$,^{3a} Mg–Ba,^{3b} Al, Ga,^{3c} Cr, Fe (II and III), Co, Ni, Cu^{3d,e} have been described. These compounds were prepared by reaction of two alkoxides in the alcohol solution or by metathesis of MCl_n ($M = 3d$ metal)

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with KNb(OR)_6 as crystalline samples or viscous liquids, highly soluble in alcohols and hydrocarbons, which permits their use in the sol-gel preparation of oxide materials. The data on their structures are scarce, being limited to only two examples, namely LiNb(OEt)_6 ⁴ and $\text{Pb}_6\text{Nb}_4\text{O}_4(\text{OEt})_{24}$.⁵ The structure of the former is based on a polymeric helix formed by $[\text{LiO}_{4/2}]$ tetrahedra and $[\text{NbO}_2\text{O}_{4/2}]$ octahedra. The core of the lead oxoethoxoniobate represents an octahedral cluster $[\text{Pb}_6(\mu_3\text{-O})_4(\mu_3\text{-OR})_4]$ (*cf.* Ref. 6), whose four oxocapped faces are additionally coordinated by the $[\text{Nb(OR)}_5]$ groups.

The present paper deals with the study of conditions of formation of Li, Ba, Sc and La alkoxoniobates [using the isothermic sections of solubility diagrams in the three-component $\text{M(OR)}_n\text{-Nb(OR)}_5\text{-ROH}$ systems] and the preparative, physicochemical and X-ray structural investigation of the properties. The reaction of formation of 3d metal isopropoxide complexes with $\text{Nb(OPr}^i)_5$ has been re-examined to check the applicability of these species for sol-gel technology. The complexes formed have been assumed to represent oxoalkoxoniobates containing M-O-Nb bridges. These species may be considered as true precursors of oxide phases with homogeneous distribution of two metals on the molecular level.

EXPERIMENTAL

All manipulations were carried out under dry argon. EtOH and Pr^iOH were distilled over Ca(OEt)_2 and $\text{Al(OPr}^i)_3$ respectively, the water content in the products used not exceeding 0.02% according to Fischer titration. Nb(OR)_5 , “ $\text{La(OPr}^i)_3$ ”, “ $\text{Sc(OPr}^i)_3$ ”, $\text{Ni(OPr}^i)_2$ and $\text{Co(OPr}^i)_2$ were prepared by anodic oxidation of metals in alcohols (in the presence of LiCl or $[\text{Bu}_4\text{N}]\text{Br}$ as conductive additives).⁷⁻⁹ Nb(OEt)_5 was then distilled and $\text{Nb(OPr}^i)_5$ sublimed *in vacuo* (10^{-1} mm), at 160 and 100°C respectively. Nb(OEt)_5 has an unlimited solubility in ethanol, while the solubility of $\text{Nb(OPr}^i)_5$ in Pr^iOH is about 15 wt% at 20°C.¹⁰ Lanthanum and scandium “isopropoxides” were purified by recrystallization [the composition of their needle-shaped crystals corresponds, as it has been shown in Ref. 11, to the formulae $\text{M}_5\text{O(OPr}^i)_{13} \cdot n\text{Pr}^i\text{OH}$]. “ $\text{Sc(OPr}^i)_3$ ” is in fact insoluble in Pr^iOH at room temperature, while the solubility of

“ $\text{La(OPr}^i)_3$ ” samples may vary in quite a wide range (from 0 to 30 wt%) being strongly dependent on the conditions of their preparation and storage.⁸

Barium and lithium ethoxides, obtained on dissolution of metals in EtOH, crystallize as $\text{LiOEt} \cdot 2\text{EtOH}$ and $\text{Ba(OEt)}_2 \cdot 4\text{EtOH}$ solvates respectively, their solubility at 20°C being equal to 16.0% for LiOR and 30.2% for Ba(OR)_2 .^{12,13}

Barium isopropoxide has been obtained only in the form of isopropanol solutions [on the storage of the latter the solvate $\text{BaO}_n(\text{OPr}^i)_{2-2n} \cdot x\text{Pr}^i\text{OH}$ is crystallized; its X-ray single crystal structure has not yet been solved],¹⁴ solubility isotherms were studied by the analytical method. The equilibrium was achieved by isothermic saturation of Nb(OR)_5 solutions by different solid phases. IR spectra were recorded in Nujol or hexachlorobutadiene mulls using a Perkin-Elmer 580 spectrometer, mass spectra were registered on a MEI MS-30 mass spectrometer (direct probe introduction, 70 eV ionizing potential).

Synthesis of bimetallic complexes

LiNb(OEt)_6 is precipitated as a fine crystalline powder from solution containing equivalent amounts of two ethoxides (*cf.* its elemental analysis and IR spectral characteristics in Table I). The crystals are readily soluble in EtOH, THF and benzene (36.2, 21.6 and 11.7% respectively). Its powder diffraction data correspond to the orthorhombic unit cell with the parameters given in Ref. 4 ($a = 17.704$, $b = 18.736$, $c = 21.267$ Å, space group *Pbca*). In the mass spectrum mainly the ions, corresponding to fragmentation of LiOR and Nb(OR)_5 have been observed, while in some cases the peaks corresponding to bimetallic fragments ($m/z = 362$ and 330) were detected.

The rectangular crystals of $[\text{LiNbO(OEt)}_4(\text{EtOH})]$ (II)* are slowly precipitated (the solutions turning yellowish brown at the same time) in a poor yield (5–10%) from the concentrated (20–30%) solutions of I subjected to a prolonged refluxing (10–15 h) in a dry oxygen atmosphere. The elemental analysis data of this product indicate an easy loss of solvating alcohol, the crystals at the same time turning non-transparent. In the IR spectrum of II, along with the bands coinciding with those present in the spectrum of I, appears a new weak band at about 3170 cm^{-1} (OH . . . O).

The complex III is formed with an ~80% yield on storage of orange yellow solutions of barium and niobium ethoxides in EtOH (Ba:Nb = 1:1) with $\leq 45\%$ concentration. Preliminary refluxing of solutions for 15–30 min significantly speeds up the crystallization. If the synthesis is carried out in

*The X-ray single crystal data for this complex were first interpreted as corresponding to a product of partial hydrolysis of I, “[$\text{LiNb(OEt)}_5(\text{OH})_2$].”^{15a}

Table 1. Elemental analysis data, IR spectra

Complex	Analysis found (Calc.), %				IR (v. cm ⁻¹)
	M	Nb	C	H	
LiNb(OEt) ₆ (I)	1.8 (1.8)	25.5 (25.1)	38.8 (38.9)	8.5 (8.1)	2972 s, 2925 m, 1450 w, 1380 vs. 1368 sh, 1160 s, 1110 vs. 1070 vs. 900 s, 560 s, 500 m, 415 w
LiNbO(OEt) ₄ (EtOH) (II)	2.3 (2.0)	26.9 (27.2)	33.1–34.7 (35.1)	7.0–7.8 (7.6)	all lines of I + 3170 w
BaNbO(OEt) ₄ (EtOH) _{1.5} (III)	25.8 (25.4)	16.9 (17.1)	29.4 (28.9)	6.1 (6.3)	3200–3400 m, 2975 s, 2930 s, 2860 m, 1460 m, 1380 s, 1150 vs. 1110 vs. 1062 vs., 900 s, 720 vs. 525 s, 415 w
BaNb ₂ (OPr ⁱ) ₁₂ (iPrOH) ₂ (IV)	11.8 (11.9)	15.8 (16.2)	42.1 (43.8)	8.2 (8.5)	
LaNb ₂ (OPr ⁱ) ₁₃ (V)	12.9 (12.7)	16.0 (17.0)	41.3 (42.8)	8.1 (8.3)	2960 m, 2930 s, 2855 w, 1475 m, 1380 m, 1165 s, 1130 vs. 1020 m, 985 m, 960 m, 860 sh, 840 m, 585 s, 450–70 bs

complete isolation from oxygen (in pure N₂ or He atmosphere) the yield of **III** decreases drastically. The composition of the crystals after washing with alcohol and drying *in vacuo* corresponded to the formula BaNbO(OEt)₅(EtOH)_{1.5}. The solubility of the latter is about 3% in alcohol and 27% in benzene at 20°C. The residue obtained by evaporation of benzene solutions represented a viscous liquid.

Similar results were obtained on attempts to prepare the “Ba[Nb(OEt)₆]₂” complex, described by Mehrotra.^{3b} The evacuation of barium and niobium ethoxides solutions with Ba:Nb = 1:2 ratio leads to a viscous liquid. However, the freezing of these solutions never resulted in crystallization. In the mass spectra only the fragments of [Nb(OR)₅] have been found, which contradicts the data of Ref. 3b on the existence of Ba[Nb(OEt)₆]₂ in the gaseous phase and possibility of its distillation.

[BaNb₂(OPrⁱ)₁₂(PrOH)₂] (**IV**) precipitates with a quantitative yield from the solutions of two alkoxides (Ba:Nb = 1:2) in alcohol in the form of tiny rhomboids. Compound **IV** is practically insoluble in alcohol (<1%) at room temperature and easily loses the solvating alcohol molecules at 20°C (this process is followed by amorphization of the samples). The product described by Mehrotra and coworkers in Ref. 3b was formed probably due to desolvation of **IV**. Crystals are readily soluble in benzene and THF. The mass spectrometric data of **IV** show that in the gaseous phase only Nb(OR)₅ is

present. The IR spectrum of the product of desolvation of **IV** turned out to be a combination of Nb(OR)₅ and “Ba(OR)₂” spectra.

The LaNb₂(OPrⁱ)₁₃ complex (**V**) crystallizes as thin needles from solutions containing two alkoxides in La:Nb = 1:(1–3) molar ratio. The concentrations of the parent solutions varied in a rather wide range from 5 to 30% of the complex, being dependent upon the technique employed for achievement of equilibrium. From solutions with average concentration ≤10% the product with the lowest solubility and the melting point ~160°C precipitates, while from the parent solutions of ~20% concentration (obtained by saturation of ~12% solutions of “La(OR)₃” with solid Nb(OR)₅) the most soluble samples with the melting point ~150°C are crystallized.^{15b} All samples of **V** (irrespective of their melting points) are readily soluble in hydrocarbon solvents.

Such variability of physicochemical properties, in particular the solubility in alcohol, is characteristic of samples of a number of simple and bimetallic alkoxides (see, e.g. Refs 8 and 9) and shows their non-uniformity in either molecular or chemical composition (coexistence of species of different molecular complexity or so-called “coordination polymerism”, the presence of admixtures of oxo-compounds, solvates, etc.). The single crystal for the X-ray diffraction study has been chosen from the crystalline sample with the melting point of 160°C.

The powder prepared by crushing of this sample turned out to be amorphous, so no powder diffraction pattern could be registered.

The interaction of Nb(OPrⁱ)₅ with Co and Ni isopropoxides

In the present work we tried to reproduce the synthesis of transition metal alkoxoniobates, such as Co[Nb(OPrⁱ)₆]₂ and Ni[Nb(OEt)₆]₂ by interaction of corresponding alkoxides or by metathesis of MCl₂ with MⁱNb(OR)₆ under the conditions described in Ref. (3e). On refluxing of the mixture of solid M(OPrⁱ)₂ [reddish violet Co(OR)₂ and dark violet Ni(OR)₂] with the alcohol solutions of Nb(OPrⁱ)₅ of 5–30% concentration, no dissolution of M(OR)₂ has been observed after 24 h. However, on introduction of water (~0.1% solution in alcohol) into the reaction mixture or using partially hydrolysed green samples of “Ni(OPrⁱ)₂” (see Ref. 9)* the dissolution of M(OR)₂ with the formation of yellowish green (M = Ni) or blue (M = Co) solutions took place after about 15–30 min of refluxing. Viscous residues infinitely soluble in alcohol, benzene or hexane remained on evaporation of these solutions *in vacuo*. In their mass spectra only Nb(OPrⁱ)₅ fragmentation products have been detected. On interaction of MCl₂ solutions (0.02 mol in 50 ml of PrⁱOH) with NaNb(OPrⁱ)₆ (0.04 mol in 100 cm³ of alcohol/benzene mixture) under reflux for 2–3 h both cobalt and nickel alkoxides precipitated quantitatively in the form of M(OR)₂ (the precipitates according to the X-ray powder data in both cases contained NaCl). Thus, it has been shown that under the conditions previously described^{3e} the formation of crystalline “M[Nb(OPrⁱ)₆]₂” complexes did not take place.

RESULTS AND DISCUSSION

The structures of alkoxoniobates

The crystals of **III** are formed of tetrameric octanuclear molecules [Ba₄Nb₄(μ₄-O)₄(μ₃-OR)₄(μ-OR)₈(OR)₈(ROH)₆] (R = Et) occupying a special position on the two-fold symmetry axis (Fig. 1).¹⁶ The structure is built around a distorted cubane with Ba and oxo atoms in its alternating vertices. Each oxo atom is bonded to one Nb atom and has a distorted tetrahedral surrounding [the bond angles vary from 96.0 to 144.2° at O(1) and from 96.2 to 146.6° at O(2)]. Two symmetrically independent Nb atoms with octahedral coordination are addition-

ally attached to the cubane core via two μ₂- and one μ₃-OR groups each, the two other OR groups being terminal. Each Ba atom is coordinated by three μ₄-oxo atoms, two μ₃-OR, two μ₂-OR and solvating alcohol molecules, one in the case of Ba(1), and two in the case of Ba(2). As a result, Ba(2) is non-coordinated, whereas Ba(1) has only eight ligands. All the active hydrogen atoms of alcohol molecules take part in hydrogen bonding: two of the three symmetrically independent ROH molecules form the H bond with the oxygen atoms of terminal OR groups [O(13)...O(7') 2.57(3) and O(15)...O(12') 2.66(3)Å] and one with μ₂-OR [O(14)...O(10) 2.58(3)Å]. In general, the cubane-like core of molecule **III** is analogous to that of recently studied [Ba₄Ti₄O₄(OPrⁱ)₁₆(PrⁱOH)₃₋₄].¹⁷

The Ba—O bond lengths in the molecule of **III** (2.64–3.05 Å) do not differ significantly from those in the known structures of inorganic compounds thus indicating their predominantly ionic character. The Nb—O(oxo) bond distances [1.82(1) and 1.83(1) Å] are close to the shorter bond of an asymmetric Nb...O—Nb bridge in the molecule of Nb₈O₁₀(OEt)₂₀ (1.81–1.85 Å),¹⁸ while the Nb—O(Et) distances (1.96–2.07 Å) are almost equal to the longer bond of this bridge. It should be emphasized that the Nb—O(R) bond length in **III** is practically independent of the character of OR group bonding (terminal, μ₂- or μ₃-bridging). The Nb—O—C bond angles are slightly more sensitive to the type of bonding of the OR group. They are significantly increased for terminal groups [146–158.4°; the corresponding angles at O(7) and O(12) are decreased probably due to participation of these atoms in H bonding], but practically coincide for μ₂- and μ₃-bridging ligands (123.2–131.4° and 125.7–129.3° respectively). All the OR groups around the Nb atoms can be considered, therefore, in the first approximation as terminal and thus the molecule of **III** as a whole can be represented as a complex formed of the ion pairs [Ba(ROH)_{1,5}]₄²⁺[NbO(OR)₅]₄²⁻.

Taking into consideration the possibility of formation of oxoethoxoniobates in the case of lithium and the recent publication on the structure of **I**,⁴ in the present work we decided to propose a different interpretation for the structure of **II** considered previously as the hydroxyl-containing product of partial hydrolysis of **II**, namely “[LiNb(OEt)₅(OH)]₂”.¹⁵ Earlier, it has been stated that the structure of **II** is built of tetranuclear molecules containing two [NbO₆] octahedra and two [LiO₄] tetrahedra [their metal–oxygen framework is very close to that of Ti₄(OMe)₁₆ or W₄(OEt)₁₆]. One of the terminal oxygen-containing ligands, which had no ethyl radical, was considered as an OH

* Just such samples were used in Ref. 3e.

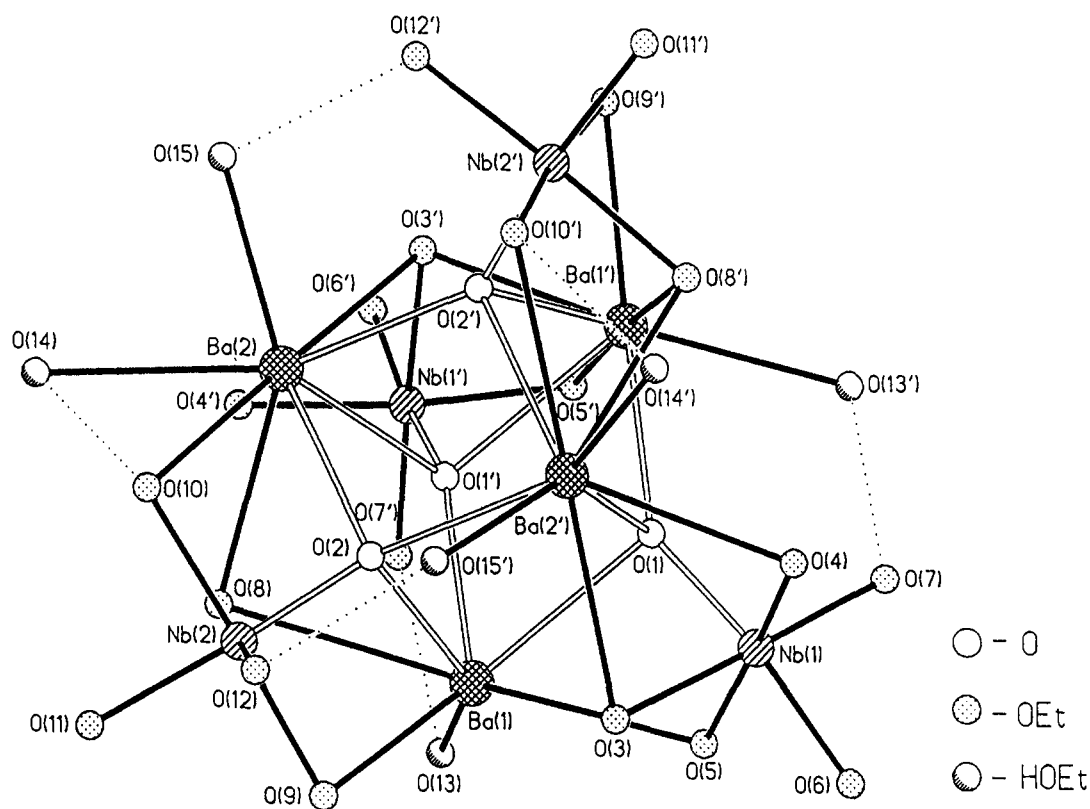
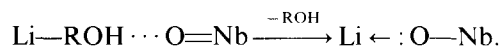


Fig. 1. The molecular structure of $[\text{BaNbO}(\text{OEt})_5(\text{EtOH})_{1.5}]_4$ (III).

group. In our new interpretation of the structure of **II** we suggest that the rather short Nb—O(5) distance (1.695 Å) should be considered to be a double Nb=O bond. In order to keep the molecule of **II** electroneutral, it is necessary to consider one of the ligands, earlier described as an OR group, as a solvating alcohol molecule. The active H atoms in the structure of **II** have not been located objectively (as well as in the molecules of other oxoalkoxides). However, the very short O(5) . . . O(6') contact [2.68(2) Å] can serve as an indication of existence of an intermolecular hydrogen bonding between the active

hydrogen atom H[O(6')] of the alcohol molecule (coordinated by Li atom) and the multiply bonded oxygen atom O(5). The latter interpretation of the structure of complex **II** clarifies the reason for the observed difference in the Nb—O(1) and Nb—O(1') distances [2.118(4) and 2.319(5) Å respectively]: thus the elongation of the Nb—O(1') bond turns out to be a result of the "niobyl" O(5) atom *trans* influence. The molecule of **II** should therefore be formulated as $[\text{Li}_2\text{Nb}_2\text{O}_2(\mu_3\text{-OR})_2(\mu\text{-OR})_4(\text{OR})_2(\text{ROH})_2]$ (Fig. 2). If such an interpretation is accepted, it should be supposed that the desolvation of **II** is to be followed by formation of an oxobridge between the two metal atoms:



The $\text{Ba}[\text{Nb}(\text{OPr}^i)_6]_2(\text{Pr}^i\text{OH})_2$ molecule (**IV**) is a fragment of a chain made up of three octahedra.^{19*} The central $[\text{BaO}_6]$ octahedron is sharing two neighbouring edges with the peripheral $[\text{NbO}_6]$ ones (Fig. 3). The Ba atom has a distorted octahedral coordination formed by four oxygen atoms of $\mu\text{-OR}$ groups (Ba—O 2.651–2.729 Å) and two oxygen atoms which belong obviously to solvating alcohol molecules [Ba—O 2.725(6) and 2.740(5) Å†]. Short intramolecular contacts O(8) . . . O(14)

* The same structure has been simultaneously determined in the group of Prof. L. G. Hubert-Pfalzgraf, University of Nice, France.²⁶

† The determined Ba—O distances are very close to those found in the $[\text{BaZr}_2(\text{OPr}^i)_{10}]_2$ molecule which also contains octahedral Ba atoms (2.551–2.895 Å).²⁰ In general, it should be noted that the parameters change regularly with the changes in the Ba atom coordination number: the observed distances are 2.509 and 2.576 Å for coordination numbers 4 and 5 in $\text{Ba}_2(\text{OCPh}_3)_4$ (THF)₃,²¹ and 2.724–2.852 Å for 7, 8 and 9 respectively in $[\text{BaTiO}(\text{OR})_4 \cdot 7/8\text{ROH}]_4$, R = Pr,¹⁷ $\text{BaTi}_4(\text{OEt})_{18}$,²² and $[\text{BaNbO}(\text{OEt})_5(\text{EtOH})_{1.5}]$.¹⁹

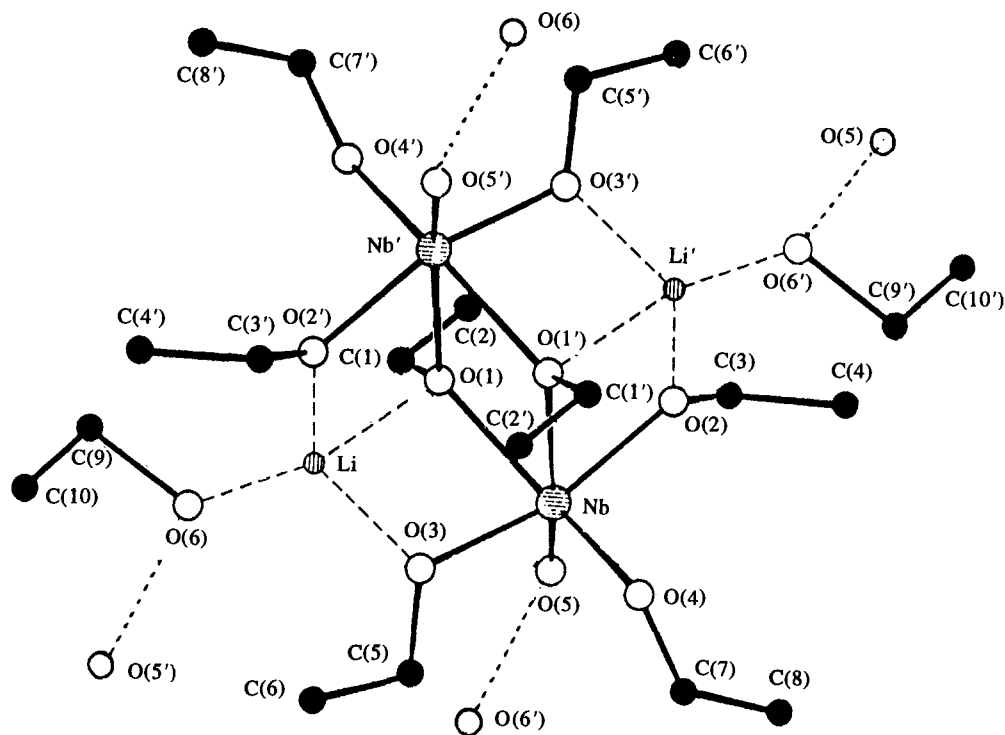


Fig. 2. The molecular structure of $[\text{LiNbO}(\text{OEt})_4(\text{EtOH})]_2$ (II).

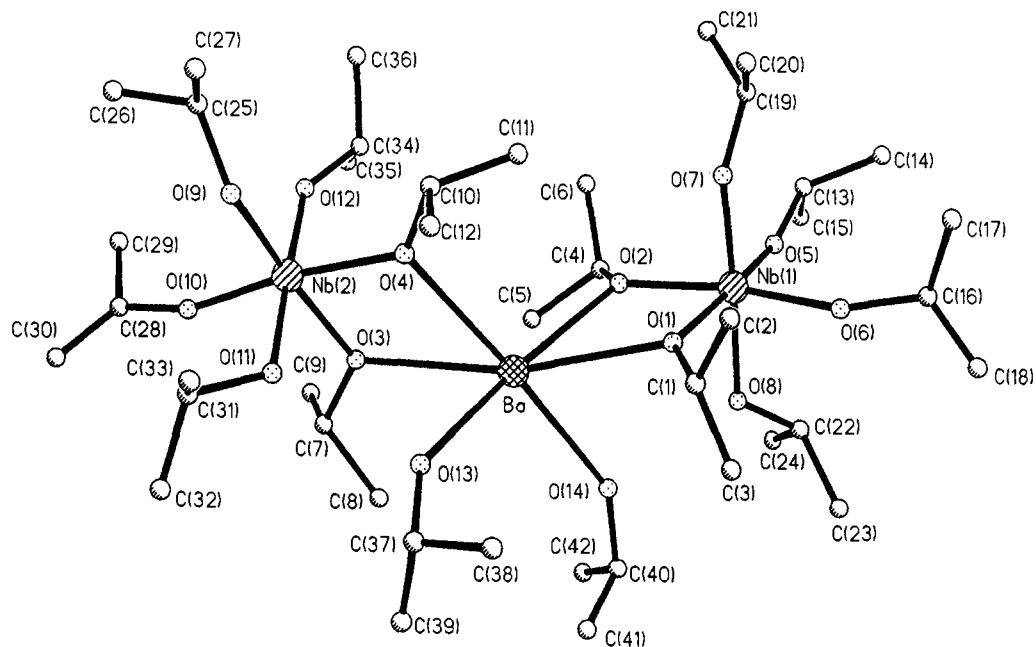


Fig. 3. The molecular structure of $[\text{BaNb}_2(\text{OPr})_{12}(\text{PrOH})_2]$ (IV).

2.62(1) Å and O(11) ... O(13) 2.64(1) Å should correspond to rather strong H bonding. The existence of the latter is proved also by the characteristics of O(8) and O(11) surrounding: Nb(1)—O(8) and Nb(2)—O(11) bonds [2.051(6)

and 2.025(5) Å respectively] are noticeably longer than those corresponding to other terminal OR groups (1.889–1.913 Å) and do not differ in principle from those for Nb— μ -OR (2.005–2.042 Å); the Nb—O—C bond angles at O(8) 125.3(5)° and

O(11) 123.7(5)[°] are significantly smaller than those for other terminal groups (143.2–161.9[°]).

In the structures of dimeric molecules of solvates $[M(OPr^i)_4(Pr^iOH)]_2$, $M = Sn, Zr, Hf, Ce$,^{23–25} both axial OR groups are participating in H bonding (over and below the equatorial plane). Therefore for the latter compounds no significant difference has been observed in the bonding parameters for two axial OR groups. In contrast to this situation in the molecule of **IV**, the Nb(1)—O(7) and Nb(1)—O(8) distances are 1.889(6) and 2.051(6) Å respectively, and the corresponding angles Nb(1)O(7)C(20) and Nb(1)O(8)C(22) are 156.0(7) and 125.3(5)[°], thus reflecting the influence of asymmetric H bonding.

It seems probable that the ethoxo analogue of **IV** cannot exist in the solid state because of low stability of the $[BaO_6]$ octahedron formed by OEt ligands which have much smaller volume than OPrⁱ groups. This assumption can be confirmed by comparison of the structures of molecules **III** and **IV**; in the former the Ba atoms coordinating oxo and ethoxo groups have coordination numbers 8 and 9.

The $LaNb_2(OR)_{13}$ molecule (**V**) is an asymmetric cyclolinear chain in which the strongly distorted central coordination octahedron of the La atom is sharing a face with $[Nb(1)O_6]$ and an edge with $[Nb(2)O_6]$ octahedra (Fig. 4).¹⁹ It is of interest that in both molecules **IV** and **V** the trimetal chain is non-linear: the NbLaNb and NbBaNb angles are 136.2(1)° and 137.4(1)° respectively. The analogous metal-oxygen core has been found in the structure

of $Al_3(OPr^i)_4Cl_5$,²⁷ in contrast to numerous other trinuclear molecules with linear M_3 arrays, such as $Pb_3(OBu^t)_6$, $MM'_2(OBu^t)_6$ ($M = Sr, Ba, Cd, Eu, Sn, Pb$; $M' = Ge, Sn, Pb$).²⁸

The La— μ -OR distances for the “common edge” turned out to be noticeably shorter than for the “common face” [2.465(6) and 2.455(7) in comparison with 2.501(7)–2.556(6) Å] and in their turn much longer than that for the only La—OR terminal group [2.164(7) Å]. The La—O—Nb angles are quite naturally somewhat larger for edge-sharing fragment [110.9(5) and 111.0(2)°] than for the face-sharing one [96.5(2), 96.6(2) and 95.4(3)°], the latter being close to those found in the known structures of $U_2(OBu^t)_9$ and $U_2(OPr^i)_{10}$ (97 and 111°).²⁹ The Nb— μ -OR distances do not display such regular difference for either of the Nb atoms (2.009–2.087 Å), while the terminal Nb(2)—OR are slightly, but regularly longer than Nb(1)—OR bonds (1.898–1.921 and 1.859–1.880 Å). In comparison with the structures of $Nb(OR)_5$ dimers ($R = Me, Pr^i$)^{19,30} the structure of **V** has a number of peculiarities. Thus, for the Nb(2) environment {which can be considered as a subunit of $[Nb(OR)_5]_2$ structure} the sum of “axial” bonds lengths is smaller than for “equatorial” ones, though no distinct correlations between bond lengths and angles have been observed. Indeed, the bond angles at two axial atoms, O(10) and O(12), differ significantly [165.1(1) and 135.1(9)°], the same can be observed for the angles at the equatorial O(13) and O(11) atoms [144.8(8) and

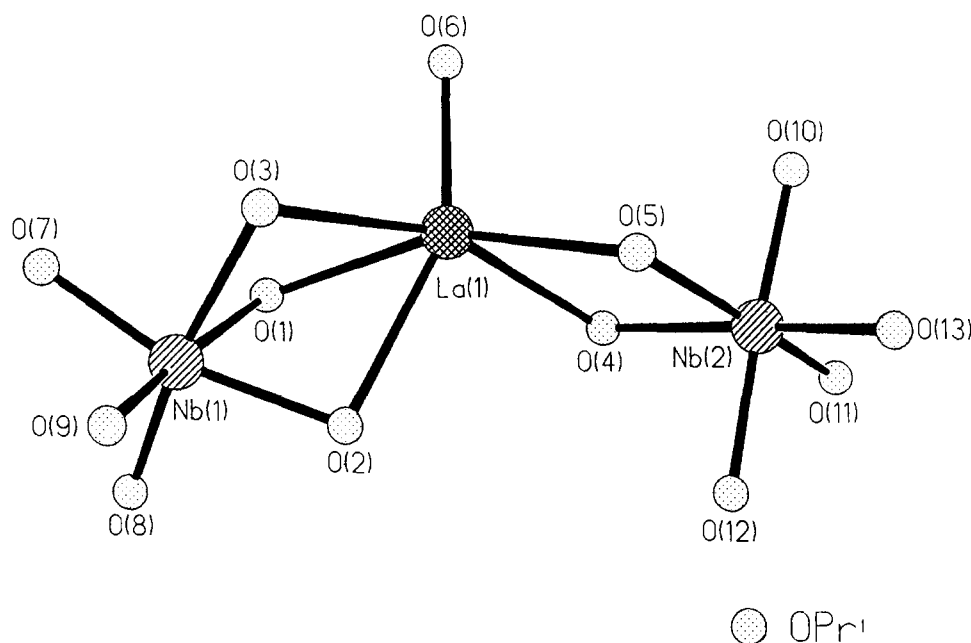


Fig. 4. The molecular structure of $[LaNb_2(OPr^i)_{13}]$ (**V**).

166.0(1)° respectively]. It cannot be excluded, that the latter difference is caused by different coordination of bridging O(4) and O(5) atoms, situated in *trans* positions to the O(13) and O(11) atoms [the sum of bond angles is equal to 360° at the O(4) atom, and 353° at the O(5) atom, indicating a noticeably non-planar environment of the latter]. The coordination geometry of the O(1), O(2) and O(3) atoms is also displaying some deviations from planarity (the corresponding sums of bond angles being 355, 359 and 357°). Some geometric characteristics of the La atom coordination in **V** are close to those observed in the structure of $\text{La}_3(\text{O-Bu}^t)_9(\text{Bu}^t\text{OH})_2$.³¹ It may be assumed, that the described molecule **V** might be considered as one of the possible isomers of the $\text{LaNb}_2(\text{OPr}^i)_{13}$ complex. The octahedral coordination of all three metal atoms in this isomer makes this form the most stable. One can imagine, however, the molecular forms with a different distribution of bridging and terminal ligands, such as $[(\text{RO})_4\text{Nb}(\mu\text{-OR})_2]_2\text{La}(\text{OR})$ for example, which may account for the variability of the properties of the samples of **V**.

In conclusion we would like to mention the results of the single crystal X-ray study of $\text{Nb}(\text{OPr}^i)_5$. In spite of the presence of only monomeric molecules in the gaseous phase, its crystals are built of dimers (two octahedra sharing a common edge) (Fig. 5).¹⁹ Their shape and the geometric par-

ameters of the niobium–oxygen core almost coincide with those of the known structure of $\text{Nb}(\text{OME})_5$.³⁰ The peculiar features of such structures are much smaller sums of axial in comparison with the sums of equatorial bond lengths (3.788 and 4.042–4.035 Å), which is due to different contribution of π component to the interaction of metal and oxygen atomic orbitals.^{32a} The much larger Nb–O–C bond angles for axial oxygen atoms in comparison with the corresponding angles at the equatorial O atoms (160.2–164.0 and 141.3–142.8° respectively) are in agreement with this conclusion.

The conditions of alkoxoniobate formation

The formation of $\text{LiNb}(\text{OEt})_6$ (**I**) complex has been observed both in the solution and in the solid state on the basis of the solubility data in $\text{LiOEt-Nb}(\text{OEt})_5\text{-EtOH}$ system at 20°C (Fig. 6). Its composition in solution was derived from the extrapolation of the crystallization curve of $\text{LiOR} \cdot 2\text{ROH}$ up to its intersection with the $\text{LiOR-Nb}(\text{OR})_5$ edge of this triangle. Lithium ethoxoniobate is congruently soluble in alcohol and has a wide area of crystallization.

In the $\text{Ba}(\text{OEt})_2\text{-Nb}(\text{OEt})_5\text{-EtOH}$ system the formation of bimetallic complexes has not been detected. Only the alkoxides of barium, solvated $\text{Ba}(\text{OEt})_2 \cdot 4\text{EtOH}$, and unsolvated $\text{Ba}(\text{OEt})_2$, are

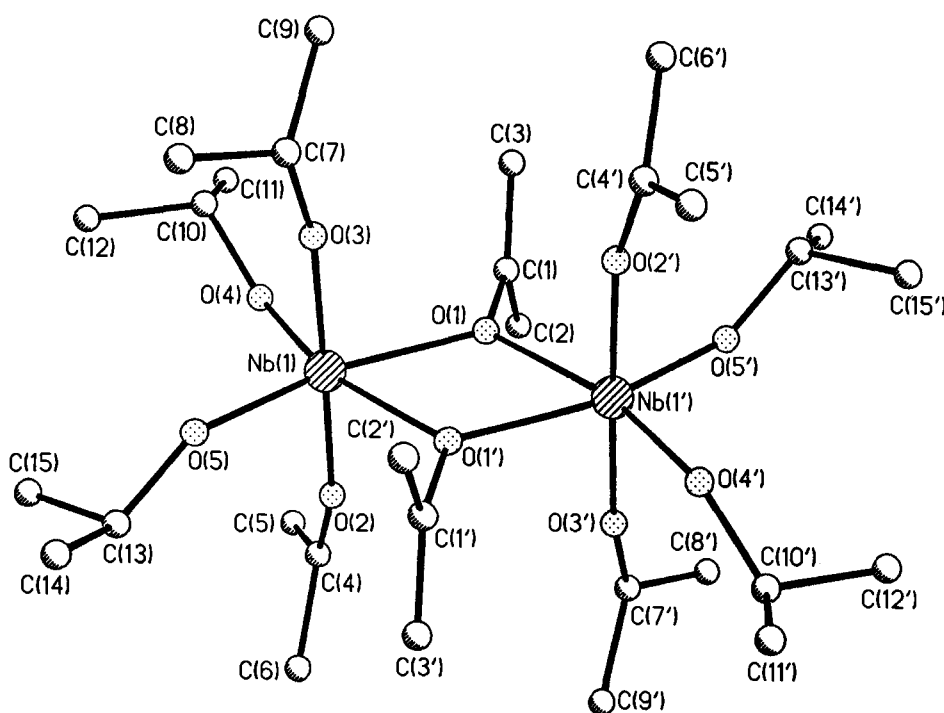


Fig. 5. The molecular structure of $[\text{Nb}(\text{OPr}^i)_5]_2$.

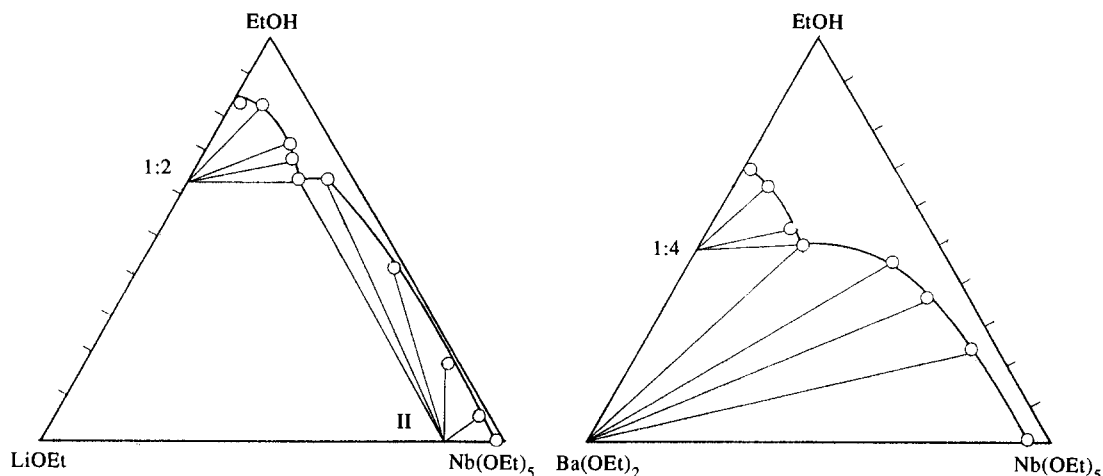


Fig. 6. Solubility isotherms (20°C) for LiOEt-Nb(OEt)₅-EtOH and Ba(OEt)₂-Nb(OEt)₅-EtOH systems.

crystallized from this system (see Fig. 6). The latter was prepared by reaction of barium metal with stoichiometric amounts of alcohol in benzene. It should be mentioned that the products of Ba(OEt)₂ · 4EtOH desolvation possessing the same elemental composition, but containing probably some microamounts of oxo ligands in their structure (formed in the course of solvolysis), have somewhat higher solubility: up to 30% in liquid Nb(OEt)₅ [as compared with 5–6% for Ba(OEt)₂ samples free of oxo groups]. Although no complexes precipitated from this system, the complex formation probably takes place in solution. On the basis of refraction coefficient, viscosity and electric conductivity measurements in the isomolar series* the formation of the Ba:Nb = 1:2 complex has been postulated (Fig. 7). The crystalline complex of the BaNb₂(OPrⁱ)₁₂(PrⁱOH)₂ (IV) stoichiometry precipitates from solutions of two isopropoxides in alcohol (Fig. 8).

The "Sc(OPrⁱ)₃"-Nb(OPrⁱ)₅-THF solubility isotherm shows the absence of complexes in the solid state, but does not exclude their formation in solution, for the solubility of scandium isopropoxide slightly increases in the presence of Nb(OPrⁱ)₅. The investigation of "La(OPrⁱ)₃"-Nb(OPrⁱ)₅-PrⁱOH isotherm (see Fig. 8) demonstrates irreproducibility of the solubility values for different samples of the complex LaNb₂(OR)₁₃ (V) formed in the solid state.

* The determination of the mentioned parameters was carried out in the Nb-rich area, for, as it has been shown in the present work, at the Ba:Nb ≥ 1:1 ratio the decomposition of bimetallic species with the formation of oxoalkoxoniobates takes place and, therefore, there is no sense in the application of the isomolar series method.

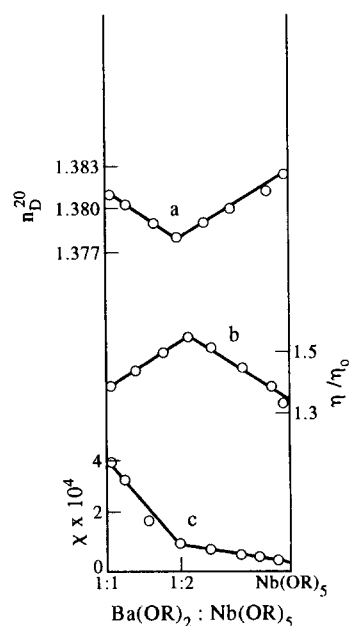


Fig. 7. Refraction coefficient (n_D^{20}), viscosity (η/η_0) and electric conductivity (χ , $\Omega^{-1} \text{ cm}^{-1}$) in Ba(OEt)₂-Nb(OEt)₅ system, the isomolar series Ba(OR)₂+Nb(OR)₅/[EtOH] = 0.04.

The upper liquidus curve corresponds to the least soluble samples (m.p. 160°C), the lower one, to the most soluble ones (m.p. 150°C). The curves corresponding to the dissolution of components have their metastable continuation into the area corresponding to the dissolution of the complex.

The crystallization of oxo complexes such as [LiNbO(OEt)₄(EtOH)]₂ and [BaNbO(OEt)₅(EtOH)_{1.5}]₄ (III) from coloured solutions containing ethoxoniobates is apparently associated

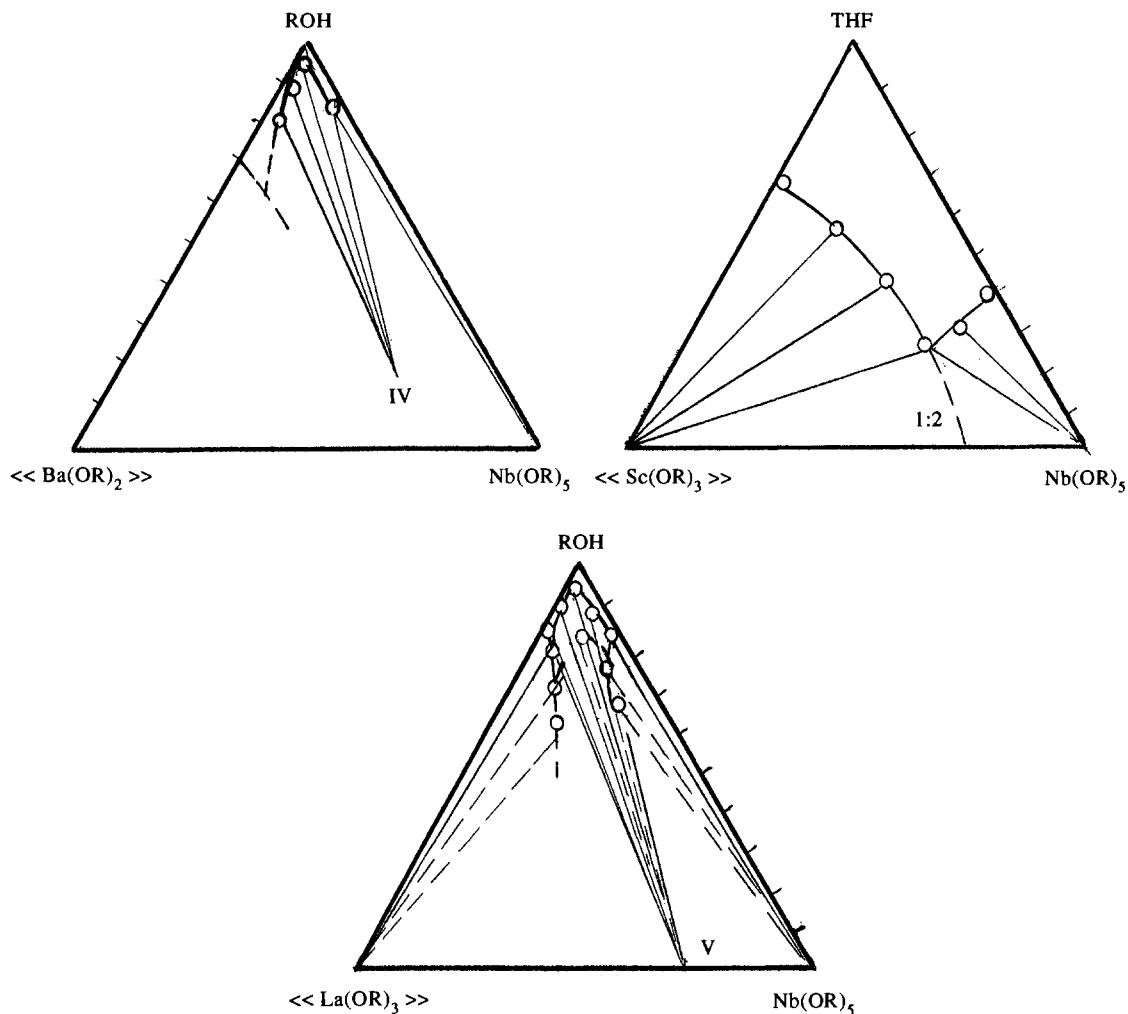


Fig. 8. Solubility isotherms (20°C) for “Ba(OR)₂”-Nb(OR)₅-ROH and “M(OR)₃”-Nb(OR)₅-L systems (M = Sc, La; R = Prⁱ, L = ROH, THF).

with the uncontrollable oxidation of the latter by the traces of oxygen (either dissolved in ROH or present in the atmosphere). Oxidation proceeds much faster if the solutions are refluxed in an atmosphere of oxygen (while the introduction of micro-amounts of water does not lead to the formation of **II**). Under the conditions of complete isolation from air, even after a prolonged refluxing, the formation of **II** (in contrast to **III**) does not take place.

The presence of oxo ligands in the molecules of numerous mono- and bi-metallic alkoxides has been recently established with the help of X-ray single crystal studies. The presence of solvating alcohol in their molecules was often misleading, for the elemental analysis data corresponded to “true” alkoxides. The authors of the review³² associated such an “inexplicable” appearance of oxo ligands in the metal atoms coordination sphere with the possibility of alkoxide decomposition via elimination of ethers. Such transformations have been

indeed observed for some niobium and especially molybdenum alkoxides, exhibiting a propensity to formation of Mo=O terminal groups.³³ However, in the course of the investigation of calcium oxoethoxide Ca₆O₂(OEt)₈(EtOH)₁₄³⁴ or barium alkoxides¹⁴ we have proved that the formation of oxoalkoxides in these cases is caused by oxidation of RO⁻ ions by oxygen. Primary products of this reaction contain —OOR and —OOH groups. The decomposition of the latter proceeds via formation of coloured radicals, which are finally responsible for the observed characteristic colouration.

It can be supposed that this process of uncontrolled oxidation occurs predominantly in the excess of alkaline, alkaline earth or rare earth metal alkoxide in respect to the composition of the complex (Fig. 7c), the “Meerwein Salt”, formed by neutralization of an acidic alkoxide [Nb(OR)₅ in this case] by a basic one. In fact, the solutions with Ba : M ~ 1 : 1 ratio (M = Nb, Ti) are readily

oxidized forming $\text{BaMO}(\text{OR})_n \cdot x\text{ROH}$,* while from the solutions with $\text{Ba}:\text{M} \sim 1:2$ ratio the $\text{BaM}_2(\text{OR})_n \cdot m\text{ROH}$ complexes without oxo ligands are crystallized.

This regularity can be as well illustrated by the chemistry of bimetallic isopropoxozirconates with different $\text{M}:\text{Zr}$ ratio. Compare, for example, $\text{K}_4\text{Zr}_2\text{O}(\text{OR})_{10}$ [unexpectedly formed in the reaction of KH with $\text{Zr}(\text{OR})_4(\text{ROH})$] and such complexes as $\text{LiZr}_2(\text{OR})_9(\text{ROH})$, $\text{Ba}_2\text{Zr}_4(\text{OR})_{20}$ and $\text{Ba}[\text{Zr}_2(\text{OR})_9]_2$.³²

It is necessary to make a special emphasis on the interaction of crystalline oxoethoxoniobates with alcohol. On their dissolution or crystallization the equilibrium values of **II** or **III** solubilities can never be reached. Their transition into alcohol solution (which takes place usually on heating or via mechanical destruction of crystals) is accompanied by a solvolytic decomposition of polynuclear molecules. Only a minor part of the fragments present in the solution contain oxo groups and may re-associate into the initial structures on crystallization. Therefore, while the majority of the known crystalline oxoalkoxides such as $\text{Ti}_7\text{O}_4(\text{OEt})_{20}$,³⁵ $\text{Nb}_8\text{O}_{10}(\text{OEt})_{20}$,¹⁸ $\text{Ca}_6\text{O}_2(\text{OEt})_8 \cdot 14\text{EtOH}$,³⁴ $\text{Pb}_6\text{O}_4(\text{OPr}^i)_4$ ⁵ and $\text{BaTiO}(\text{OPr}^i)_4 \cdot 7/8\text{Pr}^i\text{OH}$ ¹⁷ are practically insoluble in ROH at room temperature, the concentrations of mother liquors after their crystallization are usually very high. This circumstance provides apparently the basis for the possibility of obtaining alkoxo compounds without oxo ligands, namely **IV** and **V**, from solutions that already contain an oxo compound such as Ba or La "isopropoxides". The important condition necessary for their crystallization is the presence in the solution of the excess of an acidic component, $\text{Nb}(\text{OR})_5$.

In conclusion it is necessary to consider the problem of $\text{Nb}(\text{OR})_5$ complex formation with the $3d$ metal alkoxides and the existence of corresponding bimetallic complexes. The attempt to reproduce the synthesis of this compound under the conditions described by Mehrotra and coworkers^{3c} was unsuccessful. It turned out that the formation of complexes of $\text{Nb}(\text{OPr}^i)_5$ with, for example, $\text{Ni}(\text{OPr}^i)_2$ or $\text{Co}(\text{OPr}^i)_2$ takes place only under the conditions

of microhydrolysis or pyrolysis of $\text{M}(\text{OR})_2$, accompanied apparently by formation of oxoalkoxides being rather more reactive than polymeric $\text{M}(\text{OR})_2$.

Earlier, the analogous observations have been made by us in the case of the complex formation of $\text{Al}(\text{OPr}^i)_3$ with the isopropoxides of Ni^{II} , Cr^{III} and Fe^{III} . Instead of crystalline " $\text{Ni}[\text{Al}(\text{OR})_4]_2$ ", " $\text{Cr}[\text{Al}(\text{OR})_4]_3$ " or " $\text{Fe}[\text{Al}(\text{OR})_4]_3$ ", we have obtained only the mixtures of two corresponding alkoxides, the latter reacted with each other only in the presence of traces of water forming the oxo complexes (coloured viscous liquids).^{36†} Of great interest are in this sense the recent data on interaction of Zn isopropoxide with Nb or Ta isopropoxides obtained by the group of Professor Hubert-Pfalzgraf. It has been found that $\text{Zn}(\text{OPr}^i)_2$ can participate in this reaction only in the form of freshly obtained $\text{Zn}[\text{N}(\text{SiMe}_3)_2]$ alcoholysis product. Dried $\text{Zn}(\text{OPr}^i)_2$ samples did not react even with 130-fold excess of $\text{M}(\text{OR})_5$ by refluxing for more than 48 h. The heterometallic product obtained by the abovementioned route turned out to be an oxo-compound of the $[\text{ZnTa}_5\text{O}_2(\text{OPr}^i)_8]_2$ composition.³⁷

In general, the consideration of the reliable literature data on the composition of alkoxides of the $\text{M}_m\text{M}'_n(\text{OR}')_p$ type, where $\text{R} = \text{Alk}$ (i.e. those with known crystal structures) leads to the following conclusion: the "true" bimetallic alkoxides not containing any ligands other than OR groups can exist only in the case when one of the metals (M) is an alkali metal, magnesium, alkaline earth or rare earth metal, and when the $\text{M}:\text{M}'$ ratio does not exceed that which corresponds to the composition of complex with maximal contents of acidic component. The excess of the basic component gives rise to bimetallic oxo complexes. The analogous results are obtained on interaction of two alkoxides of metals with electronegativities higher than those of metals mentioned above.

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* While the crystallization of the isopropoxo analogue of **III** has not been observed, the evacuation of the corresponding solutions gives powders of the $\text{BaNbO}(\text{OPr}^i)_5$ composition.

† The analogous negative result has been recently obtained in the study of $\text{Zr}(\text{OPr}^i)_4(\text{Pr}^i\text{OH})$ reaction with $\text{M}(\text{OPr}^i)_2$, $\text{M} = \text{Co}, \text{Ni}$, which should lead in accordance with³⁸ to " $\text{M}[\text{Zr}_2(\text{OR})_9]_2$ ".

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