

Figure 1. Esterification of chrysotile-asbestos by allyl alcohol: the units on the ordinate are expressed in milliequivalents of ester groups/100 g of inorganic substrate; degree of hydrolysis reported on the abscissa represents the fraction (%) of the original magnesium which was eliminated; curve A, hydrolyzed fiber; curve B, chlorinated fiber.

out the esterification. The procedure of chlorination is described in detail elsewhere.⁴ This reaction substitutes Si-Cl groups for the silanol groups generated by hydrolysis.

Results and Discussion

The results obtained in this study are summarized in Table II and in Figure 1. One can see that the degree of esterification increases gradually with the degree of hydrolysis. This result clearly shows that esterification is only possible on the siloxanic surface. One also notices that the degree of coverage is relatively constant and does not depend on the degree of hydrolysis of the fiber. The mean degree of coverage is 316 OR groups/nm² for the hydrolyzed fibers and 400 OR groups/nm² for the chlorinated ones. This result represents a relative increase of about 26%. This increase in the degree of surface coverage could result from the higher reactivity of the Si-Cl groups as compared with that of the silanol groups.

If we compare our results with the figure obtained by

Wartmann⁶ for the esterification of silica gel chloride with short chain alcohols, we see that the degree of coverage obtained here is much higher. For example, for the esterification of 1-propanol, Wartmann grafted 168 OR/100 nm². It is our opinion that the higher degree of coverage obtained with chrysotile results from the very regular quasicrystalline structure of the surface produced by hydrolysis compared with the mainly amorphous surface of synthetic silica gel.

Iler⁷ has calculated on a theoretical basis that there are between 800 and 900 OH groups/100 nm² of a silanolic surface. If we take into consideration the problem of steric hindrance introduced by the allylic ester groups, we may expect a maximum degree of substitution of 50%, i.e. between 400 and 500 OR groups/100 nm². The experimental values that we have obtained in this study are very close to this theoretical value, especially for the chlorinated fibers.

In conclusion, in this study, it has been shown that the reaction of esterification of hydrolyzed or chlorinated chrysotile is possible with an efficiency higher than that obtained for silica gel. This method is very convenient for grafting a continuous layer of organophilic groups onto the surface of phyllosilicates.

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Registry No. Chrysotile, 12001-29-5; allyl alcohol, 107-18-6.

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Notes

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Isolation of a Mixed Niobium Tantalum Alkoxide

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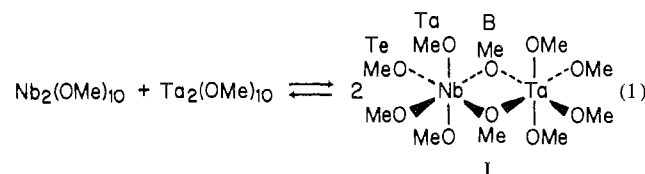
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Dimeric niobium and tantalum alkoxides have been known for a long time¹ and have been the subject of many studies² and reviews.³ Alkoxides containing both a transition metal and a group 1 or 2 metal are also well known, but there seems to be no report yet of a mixed alkoxide containing *two different transition metals*.⁴ We now wish to report the preparation and isolation as a crystalline compound of a mixed-metal alkoxide of molecular formula NbTa(OCH₃)₁₀ (I), which appears to be the first mixed transition metal alkoxide isolated.

Results and Discussions

Compound I forms when niobium pentamethoxide and tantalum pentamethoxide are mixed in octane, toluene, or acetonitrile solutions, according to eq 1. In any of these



solvents the low-temperature proton NMR spectra (Figure 1), recorded immediately after mixing, show, in addition to the signals corresponding to the symmetric starting materials, the presence of four new signals in the region of the terminal methoxy groups and one additional signal in the region of the bridging methoxy group, as would be expected for the mixed-metal alkoxide of structure I. The relative areas of these new signals remain constant when the Nb(OCH₃)₅:Ta(OC-

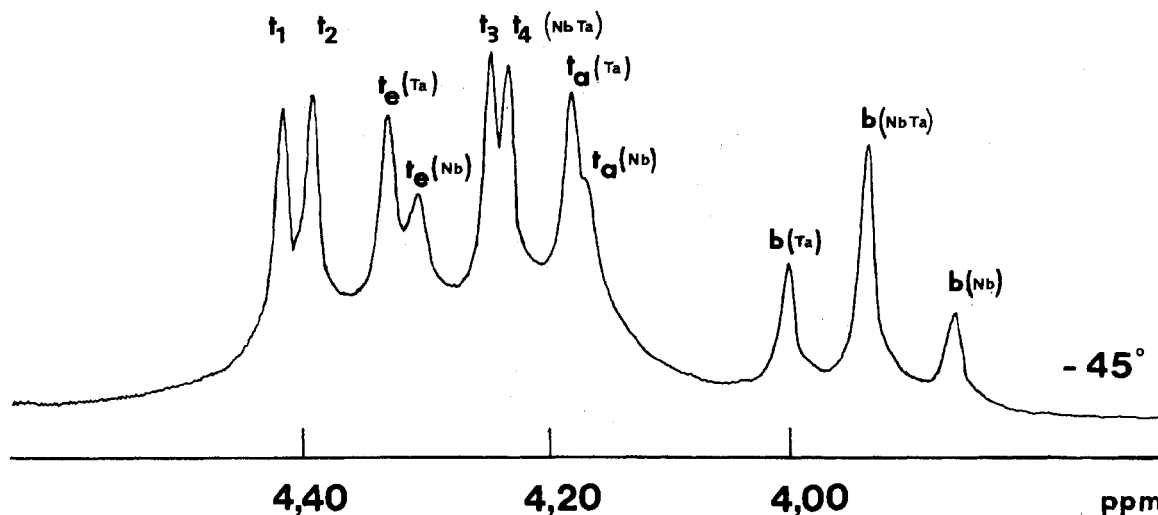


Figure 1. Proton NMR spectrum at -45°C of a mixture of niobium and tantalum pentamethoxides (0.90:1) in acetonitrile (0.03 M). Lower case letters are used to label the peaks; e.g., $t_e(\text{Nb})$ = terminal equatorial methoxy signals in the symmetric niobium dimer; $t_{1-4}(\text{NbTa})$ = terminal methoxy protons in the mixed NbTa species; b = bridging methoxy protons. (Capital letters are used to label the sites in structure I.)

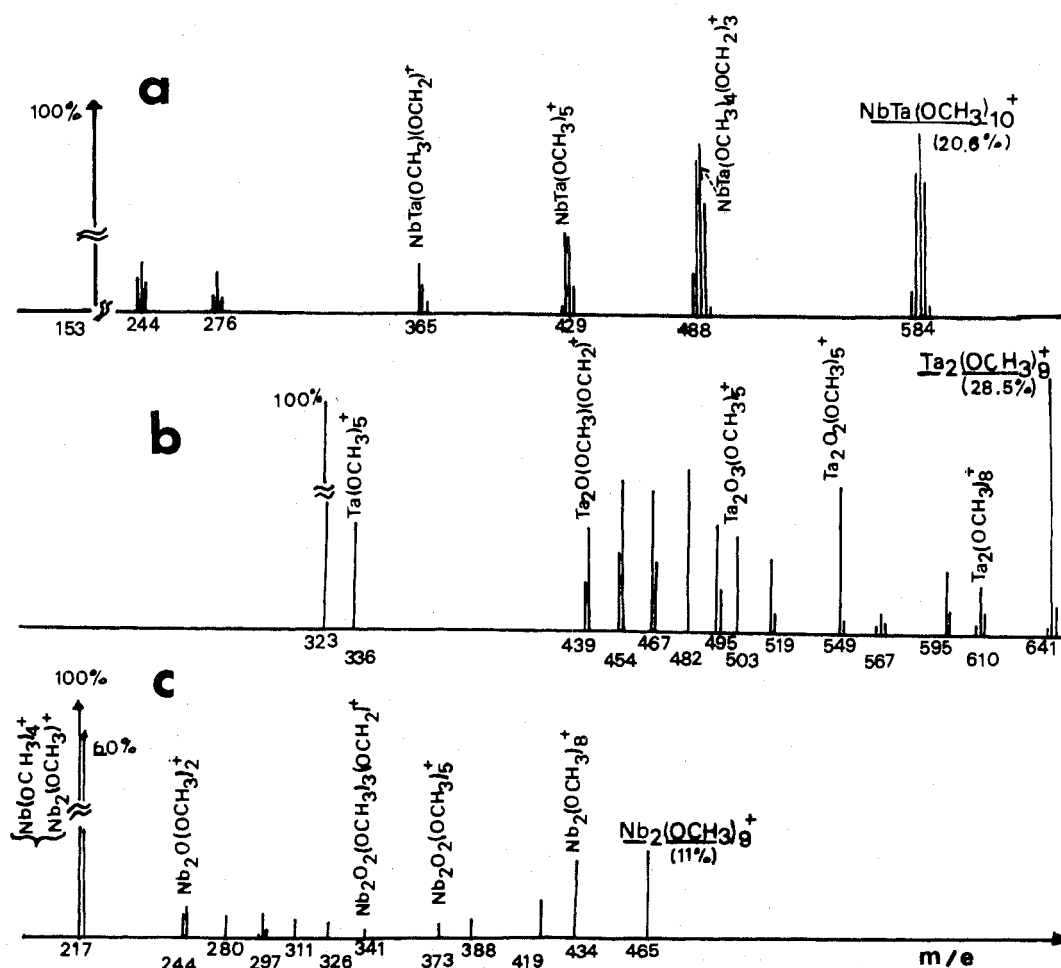


Figure 2. Comparison of the mass spectra (70 eV, 200°C) of (a) $\text{NbTa}(\text{OMe})_{10}$, (b) $\text{Ta}_2(\text{OMe})_{10}$, and (c) $\text{Nb}_2(\text{OMe})_{10}$. The assignments are tentative.

$\text{H}_3)_5$ ratio is varied. These peaks were assigned, as shown in Figure 1, on the basis of their chemical shifts and relative peak area.

The coalescence of the three bridging methoxy signals ($\sim 20^{\circ}\text{C}$ in a 0.03 M 1:1 mixture in acetonitrile) indicates that the equilibrium depicted in eq 1 between the three species is dynamic on the NMR time scale. The ulterior coalescence

of all the signals into one single peak as the temperature increases (above 35°C) shows that the methoxy groups exchange between all the nonequivalent sites of the three dimetallic alkoxide structures.

Upon cooling of equimolar mixtures of $\text{Nb}_2(\text{OCH}_3)_{10}$ and $\text{Ta}_2(\text{OCH}_3)_{10}$ in octane (0.01 M), well-shaped colorless crystals were observed to form, in conditions where neither

$\text{Nb}_2(\text{OCH}_3)_{10}$ nor $\text{Ta}_2(\text{OCH}_3)_{10}$ crystallizes. Identical crystals were also obtained from nonequimolar mixtures of the symmetric alkoxides. Their ir spectrum shows the presence of both $\nu(\text{Nb}-\text{O})$ and $\nu(\text{Ta}-\text{O})$ stretching frequencies (550 and 511 cm^{-1} , respectively).⁵

When dissolved in various solvents, the crystals give NMR spectra which are identical with those observed with equimolar mixtures of the symmetric alkoxides dissolved in the same solvent.

That the isolated solid does not consist of mixed crystals of both symmetric dimers is further borne out by mass spectral analysis. Figure 2 compares the mass spectrum of compound I with those measured on the symmetric alkoxides $\text{Nb}_2(\text{OMe})_{10}$ and $\text{Ta}_2(\text{OMe})_{10}$. The molecular ion is found at m/e 584 (20.6%) (expected for $\text{NbTa}(\text{OMe})_{10}$: 584.09). Other fragments containing both niobium and tantalum atoms were identified at m/e 582, 488, 486, 431, 429, 367, 365, and 276 (loss of CH_3OH , CH_2O , or $(\text{CH}_3)_2\text{O}$), while none of the higher mass fragments containing two tantalum atoms (m/e 641, 610, 595, 549, 519, 503, 495, 482, 467, 454, 439) or two niobium atoms (m/e 465, 434, 419, 388, 373, 326, 311, 297, 280, 264, 262, 218, 217), which are found in the spectra of the symmetric alkoxides,⁶ were detected in the spectrum of I.

The molar equilibrium distributions of the three species in solution were determined from the NMR spectra for various Nb:Ta ratios and in several solvents. Average values (10 samples examined) for the equilibrium constant $\bar{K} = [\text{NbTa}(\text{OMe})_{10}]^2/[\text{Nb}_2(\text{OMe})_{10}][\text{Ta}_2(\text{OMe})_{10}]$ are 3.1 ± 0.7 (toluene), 6.2 ± 0.3 (acetonitrile), and 5.4 ± 0.3 (octane) at -30°C . These values are close to the value of 4 which would correspond to a random association of the $\text{Nb}(\text{OMe})_5$ and $\text{Ta}(\text{OMe})_5$ monomers. This is interpreted to mean that the replacement of one niobium atom by a tantalum atom, or vice versa, in the symmetric dimers does not drastically alter their structures and suggests that tantalum may be used as a label in polynuclear niobium compounds and vice versa.

Experimental Section

All manipulations were carried out under dry nitrogen. The symmetric alkoxides were synthesized as reported in the literature.¹ Solvents were purified and dried by standard methods. NMR spectra (δ in ppm, TMS as internal standard) were recorded on JEOL C-60 HL and Varian HA-100 spectrometers equipped with a variable-temperature attachment. Quantitative evaluations of the concentrations in equilibrated mixtures were performed by cutting and weighing of Xerox copies of several spectra each time. Ir spectra were measured on Nujol mulls on a Beckman IR 12 spectrometer. Mass spectra were obtained on an AEI MS 902 apparatus under 70 eV at a source temperature of 200°C .

Crystalline Niobium Tantalum Decamethoxide (I). Niobium pentamethoxide (442 mg, 1.78 mmol) and tantalum pentamethoxide (485 mg, 1.44 mmol) were dissolved in dry octane (12 ml). Deposition of colorless crystals occurs slowly at room temperature. The crystalline product was filtered after 2 months, washed with petroleum ether, and dried under vacuum: mp 110°C ; ir (Nujol): 1160, 1100 ($\nu(\text{C}-\text{CR})$); 880, 800, 720; 550 ($\nu(\text{Nb}-\text{O})$), 511 ($\nu(\text{Ta}-\text{O})$) cm^{-1} . $\text{NbTa}(\text{OCH}_3)_{10}$ is very unstable in air. It is soluble in toluene or acetonitrile and insoluble in aliphatic hydrocarbons.

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Registry No. $\text{NbTa}(\text{OMe})_{10}$, 56348-61-9; $\text{Nb}_2(\text{OMe})_{10}$, 18533-43-2; $\text{Ta}_2(\text{OMe})_{10}$, 18533-42-1.

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Raman Spectrum of Matrix-Isolated S_2O . Evidence for the Formation of S_3 and SO_2 from S_2O

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Disulfur monoxide, once mistaken as sulfur monoxide,^{1,2} has now been well characterized.³⁻⁶ In the infrared spectrum of gaseous S_2O , Jones² observed two bands at 1165 and 679 cm^{-1} . Later, these were correctly assigned to ν_1 (S-O stretching vibration) and ν_2 (S-S stretching vibration) by Blukis and Myers.⁵ The frequency of the bending vibration, ν_3 , was first estimated from the microwave spectrum of gaseous S_2O by Meschi and Myers;⁴ however, a more precise frequency (388 cm^{-1}) was obtained from the infrared spectrum of a frozen film at 77 K.⁵ Despite the fact that the sulfur oxides are very good Raman-scattering species, the Raman spectrum of S_2O has not been reported to date. The reason for this is probably due to the fact that S_2O is not very stable, and it is usually prepared in very small quantities by passing SO_2 (or $\text{S} + \text{SO}_2$) through an electronic discharge.

The objective of the present study was to observe the Raman spectrum of matrix-isolated S_2O by preparing relatively large amounts through the direct synthesis from thionyl chloride and silver sulfide. However, in addition to obtaining the spectrum of matrix-isolated S_2O , we also obtained information on the bimolecular reaction of two S_2O molecules through changes in the spectra as a function of the M/A (matrix:active species) ratio and by limited diffusion experiments.

Disulfur monoxide, S_2O , was prepared by passing thionyl chloride, SOCl_2 , over warm Ag_2S . SOCl_2 (J. T. Baker, purified) and Ar (Matheson, 99.998%) were used without further purification. The vapor of SOCl_2 was mixed with Ar to obtain the desired matrix ratios by standard manometric procedures. Ag_2S was precipitated from aqueous AgNO_3 by adding aqueous Na_2S ; the precipitate was washed with hot distilled water several times and dried on a hot plate. Ag_2S was dried again in situ under vacuum at $\sim 200^\circ\text{C}$ for 1 hr prior to each experiment. The gaseous mixture of SOCl_2 and Ar were passed through Ag_2S contained in a horizontal Pyrex tube (1-cm o.d., 20 cm long), and the reaction products were cocondensed with Ar onto an OFHC copper cold finger (20 K) in a hydrogen Cryotip cell⁷ at the rate of 6-8 mmol/hr. The Ag_2S in the tubing was heated by a nichrome winding, and the temperature was varied from room temperature to 150°C . Because of the higher partial pressure of SOCl_2 at lower M/A (Ar: SOCl_2) ratios, a higher Ag_2S temperature was used in order to make the reaction between SOCl_2 and Ag_2S more complete. The temperature of Ag_2S was 150°C at $M/A = 25$ and 50 , 120°C at $M/A = 100$, 70°C at $M/A = 140$, and 23°C (room temperature) at $M/A = 250$ and 500 .

Raman spectra were measured using a Spex Industries