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Double Alkoxides of Niobium and Tantalum with Aluminium and Gallium

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Double isopropoxides of niobium and tantalum with aluminium and gallium with general formulae, $[MM'(OPr^i)_8]$ and $[MM'_2(OPr^i)_{11}]$ have been prepared by refluxing their isopropoxides in isopropanol in molar ratio 1:1 and 1:2. These are soluble in organic solvents and are distilled under reduced pressure. The mono derivatives are dimeric with considerable dissociation, while bis-products are monomeric in refluxing benzene. IR and in some cases NMR spectra have been reported and discussed.

Introduction

Synthesis of apparently covalent volatile double alkoxides of lanthanons with aluminium[1] and gallium[2] has aroused the interest in this newly developed area of double alkoxides. This work was latter extended to the synthesis of double alkoxides of zirconium[3] and hafnium[4] with aluminium. The present paper describes the preparation and properties of analogous niobium and tantalum derivatives.

Results and Discussion

Niobium and tantalum double isopropoxides of the type, $[MM'(OPr^i)_8]$ and $[MM'_2(OPr^i)_{11}]$ (where M, Nb or Ta; M', Al or Ga) were prepared by refluxing an isopropanol solution of $M(OPr^i)_5$ and $M'(OPr^i)_3$ for about 5–6 hr in various molar ratios. These reactions can be represented by the following equations:

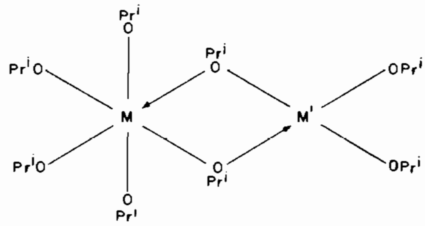
$$M(OPr^i)_5 + M'(OPr^i)_3 \xrightarrow{Pr^iOH} [MM'(OPr^i)_8]$$

$$M(OPr^i)_5 + 2M(OPr^i)_3 \xrightarrow{Pr^iOH} [MM'_2(OPr^i)_{11}]$$

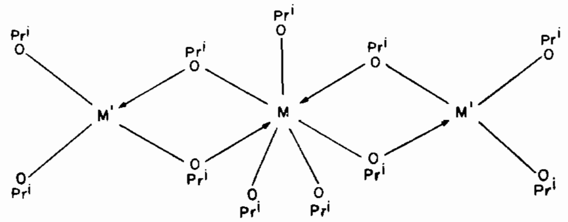
(M: Nb or Ta; M': Al or Ga)

The final end product of the reactions in the molar ratio 1:3 and 1:4 was found to be $[MM'_2(OPr^i)_{11}]$ and unreacted $M(OPr^i)_3$. The mono-derivatives are viscous pastes while the bis-derivatives are viscous liquids; both are soluble in benzene and isopropanol. All these products were purified by distillation under reduced pressure at a constant temperature. The gallium derivatives appear to be more succeptible to hydrolysis in comparison to aluminium derivatives.

Molecular weights of $[MM'(OPr^i)_8]$ and $[MM'_2(OPr^i)_{11}]$ in refluxing chloroform indicate that both are monomeric. However, in benzene solution, the 1:1 compound shows some tendency of association exhibiting average degree of complexity between 1.5 and 1.9. On the basis of the structures suggested for zirconium[3] and hafnium[4] derivatives, the following plausible structures can be postulated for these compounds having coordination number 6 and 7 for niobium and tantalum in mono- (I) and bis-derivatives (II) respectively.



I ; M = Nb or Ta , M' = Al or Ga.
$MM'(OPr^i)_8$



II ; M = Nb or Ta , M' = Al or Ga.
$MM'_2(OPr^i)_{11}$

Infrared spectra of these compounds exhibit all the characteristic frequencies for isopropyl groups. Strong broad bands in the regions 1170–1070 cm^{-1} and 1030–1000 cm^{-1} and a broad band in the range of

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630–560 cm^{-1} may be assigned to ν(C–O) and ν(M″–O) vibrations respectively in accord with previously published[5] infrared studies on metal alkoxides (Table I). As these ν(M″–O) bands are broad, it was not possible to distinguish between ν(M–O) and ν(M′–O) band which are probably overlapping with each other.

In order to elucidate the above proposed structures, the proton n.m.r. spectra of $[NbAl(OPr^i)_8]$, $[TaGa_2(OPr^i)_{11}]$ and $[NbGa_2(OPr^i)_{11}]$ were taken in carbon tetrachloride at room temperature. The methyl resonance in general shows only one doublet with τ values at 8.9, 9.2 and 9.1 (from T.M.S. respectively) (J = 6 Cps in every case) indicating that CH_3 resonance at room temperature could not be distinguished between the bridging and terminal isopropoxy groups due to a rapid interchange between them. However, in the spectra of $[NbAl(OPr^i)_8]$ and $[TaAl(OPr^i)_8]$, a resolution was obtained particularly in the case of niobium (Fig. 1). The spectra were taken with a 90 MHz nmr spectrometer in $CDCl_3$ (courtesy, Laboratorium fur Anorg. Chemie Eidgen. Technische Hochschule CH-8006, Universitatstrasse-6, Zürich, Switzerland) with Fourier transform technique. The proton ratios of the bridged isopropoxy, terminal isopropoxy on Al and on M (M = Nb and Ta) have been observed almost in 1 : 1 : 2. The data are given in Table II.

TABLE I. Infrared Spectra.

Compound	ν(C–O)	ν(M″–O)
$NbAl(OPr^i)_8$	1160,1125,980	560br
$NbGa(OPr^i)_8$	1170,1130,1010	590br
$TaAl(OPr^i)_8$	1170,1130,1010	580br
$TaGa(OPr^i)_8$	1140,1070,1000	630
$NbAl_2(OPr^i)_{11}$	1160,1120,980	560
$NbGa_2(OPr^i)_{11}$	1140,1070,1010	585
$TaAl_2(OPr^i)_{11}$	1170,1135,1029,1010	590,570
$TaGa_2(OPr^i)_{11}$	1130,1070,1040,1010	630

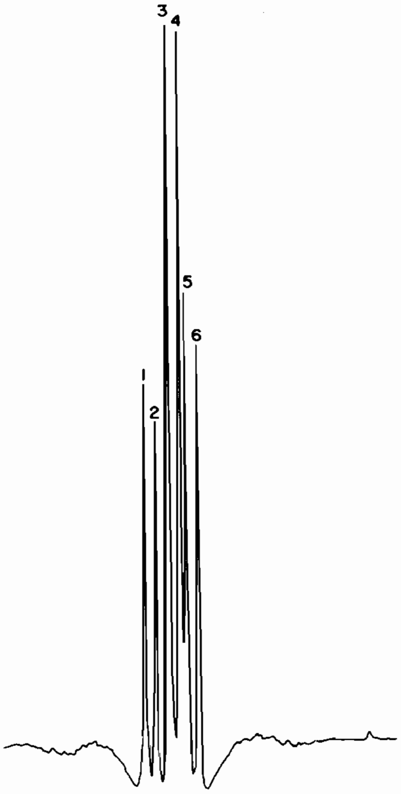

Figure 1. N.m.r. spectra of $NbAl(OPr^i)_8$.

Experimental

All glass apparatus with standard quick-fit joints was used throughout the experiments. Stringent precautions were taken to exclude moisture.

Anhydrous niobium and tantalum pentachlorides (Fluka AG, Buchs SC) and gallium trichloride (Dr. Theodor Schuchardt) and aluminium isopropoxide (N.C.L. Poona) were used. Benzene (B.D.H.) and

TABLE II. Methyl Proton Peaks of Double Alkoxides of Nb and Ta with Aluminium in Hz from Tetramethylsilane.

Compound Structure	Isopropoxy group on Al		Isopropoxy group on M		Bridging isopropoxy	
	A	B	C	D	E	F
I	1.0937	1.1621	1.1979	1.2662	1.3411	1.4127
M = Nb	Separation =	6.1523 Hz	Separation =	6.1523 Hz	Separation =	6.4453 Hz
		0.0684 δ		0.0683 δ		0.0716 δ
I	1.0904	1.1588	1.1881	1.2565	1.3476	1.4160
M = Ta	Separation =	6.1541 Hz	Separation =	6.1524 Hz	Separation =	6.1524 Hz
		0.0684 δ		0.0684 δ		0.0684 δ

TABLE III. Reactions of Niobium and Tantalum with Aluminium and Gallium Isopropoxides in Molar Ratio 1 : 1 in Isopropanol.

Reactants		B.P. °C/mm, yield (%)	State, solubility and possible compound	Analysis, (Calc.) Found			Molecular weights in benzene	Molar complexity
				Mixed oxides	Aluminium	Alkoxy		
$Nb(OPr^i)_5$ 1.095 g	$Al(OPr^i)_3$ 0.5882 g	105°/0.2, viscous mass (83)	Colourless viscous paste soluble in Pr^iOH and C_6H_6. $NbAl(OPr^i)_8$	20.99 (20.23)	4.61 (4.56)	79.61 (79.77)	875.0 (592.7) 886.0 in Pr^iOH	1.5
$Ta(OPr^i)_5$ 1.206 g	0.5253 g	107°/0.2, viscous paste (76)	Colourless viscous paste, soluble in Pr^iOH and C_6H_6. $TaAl(OPr^i)_8$	31.20 (30.55)	3.99 (3.97)	69.32 (69.45)	1075.5 (680.7)	1.6
$Nb(OPr^i)_5$ 0.708 g	$Ga(OPr^i)_3$ 0.4375 g	120°/0.2, viscous mass (72)	Colourless viscous mass soluble in Pr^iOH and C_6H_6. $NbGa(OPr^i)_8$	26.15 (25.61)	Gallium 11.01 (10.97)	73.68 (74.39)	1145.5 (635.4)	1.7
$Ta(OPr^i)_5$ 1.281 g	0.6294 g	144° C/0.2, viscous mass (89)	Colourless viscous mass soluble in C_6H_6 and Pr^iOH. $TaGa(OPr^i)_8$	34.51 (35.66)	9.67 (9.63)	66.20 (65.34)	1572.0 (723.5)	1.9

TABLE IV. Reactions of Niobium and Tantalum with Aluminium and Gallium Isopropoxides in Molar Ratio 1 : 2 in Pr^iOH.

Reactants		B.P. °C/mm, yield (%)	State, solubility and possible compound	Analysis, (Calc.) Found			Molecular weights in benzene	Molar complexity
				Mixed oxides	Aluminium	Alkoxy		
$Nb(OPr^i)_5$ 2.2625 g	$Al(OPr^i)_3$ 2.4583 g	115°/0.2, viscous liquid (80)	Colourless viscous liquid soluble in Pr^iOH and C_6H_6. $NbAl_2(OPr^i)_{11}$	18.73 (18.44)	6.79 (6.72)	81.03 (81.56)	790 (797)	0.99
$Ta(OPr^i)_5$ 1.1470 g	0.9945 g	118°/0.2, viscous liquid (88.5)	Colourless viscous liquid soluble in Pr^iOH and C_6H_6. $TaAl_2(OPr^i)_{11}$	26.84 (26.53)	6.10 (6.10)	66.18 (67.37)	782 (885)	0.89
$Nb(OPr^i)_5$ 0.495 g	$Ga(OPr^i)_3$ 0.625 g	126°/0.2, viscous liquid (60)	Colourless viscous liquid soluble in Pr^iOH and C_6H_6. $NbGa_2(OPr^i)_{11}$	26.64 (26.35)	15.86 (16.79)	73.60 (73.65)	799 (882)	0.91
$Ta(OPr^i)_5$ 0.9789 g	0.9579 g	153°/0.2, viscous liquid which solidified on keeping over-night (73)	Colourless viscous liquid soluble in Pr^iOH and C_6H_6. $TaGa_2(OPr^i)_{11}$	33.16 (32.95)	14.40 (14.36)	67.57 (67.05)	940 (970)	0.97

Isopropyl alcohol (B.D.H.) were dried by usual techniques.

Preparations of Niobium, Tantalum and Gallium Isopropoxides

Gallium isopropoxide was prepared by the sodium method[6] (b.p. 130° C/0.3 mm). Niobium and tantalum isopropoxides were prepared by the ammonia method[7] and purified by sublimation (110–140° C bath/0.2 mm).

Niobium, tantalum, aluminium and gallium were estimated as mixed oxides of the metals present after ignition of the precipitated hydroxides.

Separation of aluminium and gallium from niobium and tantalum was carried out by precipitating aluminium and gallium as oxinates in the presence of H_2O_2 and ammonia[8] (instead of ammonium acetate), when niobium and tantalum present did not appear to interfere in quantitative precipitation of aluminium or gallium.

Reliable methods could not however be evolved for the estimation of niobium and tantalum in the filtrate.

The alkoxy groups were estimated by oxidation with potassium dichromate[9].

A semimicro Gallenkamp ebulliometer with thermistor sensing was used for molecular weight determinations.

Reaction of Niobium Isopropoxide with Aluminium Isopropoxide in Molar Ratio 1:1 and 1:2 in Isopropanol.

Niobium isopropoxide (1.095 g) and aluminium isopropoxide (0.588 g) were mixed together in 1:1 molar ratio in isopropanol (~50 ml) and refluxed for about 4–5 hr. After cooling, the excess solvent was distilled off and the product obtained was finally dried under reduced pressure (0.5 mm) over a bath temperature 40–5° C. On subjecting the compound to distillation, a viscous mass was obtained at 105° C/0.2 mm. The data for this reaction as well as that of tantalum isopropoxide with aluminium isopropoxide and of niobium and tantalum isopropoxides with gallium isopropoxide are given in Table III.

Reaction of Niobium Isopropoxide with Aluminium Isopropoxide in Molar Ratio 1:2

Niobium isopropoxide (2.262 g) and aluminium isopropoxide (2.458 g) were mixed together in 1:2 molar ratio in isopropanol (~50 ml) and refluxed for about 5 hr. After cooling the excess solvent was distilled off and the product obtained was dried finally under reduced pressure (0.5 mm) over a warm bath (40–50° C). On distillation, a colourless viscous liquid was obtained at 115° C/0.2 mm. Other data of this reaction and that of tantalum isopropoxide with aluminium isopropoxide and niobium and tantalum with gallium isopropoxide are given in Table IV.

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