Polyhedron Vol. 4, No. 5, pp. 845–852, 1985
Printed in Great Britain

0277–5387/85 \$3.00 + .00

SYNTHESIS OF NOVEL TERMETALLIC ISOPROPOXIDES

M. AGGRAWAL* and R. C. MEHROTRA†
Chemical Laboratories, University of Rajasthan, Jaipur 302004, India

(*Received* 2 *July* 1984; *accepted* 24 *September* 1984)

Abstract—Novel termetallic isopropoxides are reported which may be represented by the general formulae: $[(Pr^iO)_3M(\mu\text{-}OPr^i)_2Be(\mu\text{-}OPr^i)_2Al(OPr^i)_2]$, $[(Pr^iO)_2M(\mu\text{-}OPr^i)_2Be(\mu\text{-}OPr^i)_2Al(OPr^i)_2]_2$ [where M = Ti(IV), Zr(IV) and Hf(IV)] and $[(Pr^iO)_4M(\mu\text{-}OPr^i)_2Be(\mu\text{-}OPr^i)_2Al(OPr^i)_2]$ [where M = Nb(V) and Ta(V)]. Attempts to synthesize derivatives with the general formula, $[(Pr^iO)_7M_2(\mu\text{-}OPr^i)_2Be(\mu\text{-}OPr^i)_2Al(OPr^i)_2]$ [where M = Ti(IV), Zr(IV) or Hf(IV)], were unsuccessful and in all such cases a mixture of $M(OPr^i)_4$ and $[(Pr^iO)_3M(\mu\text{-}OPr^i)_2Be(\mu\text{-}OPr^i)_2Al(OPr^i)_2]$ was obtained. All these derivatives are soluble in common organic solvents and with the exception of titanium(IV) derivatives, they can be volatilised without noticeable disproportionation. These products have been characterized by elemental analyses, molecular weights, IR, ^{1}H NMR and (in representative cases) mass spectral studies also.

Amongst the interesting series of compounds with more than one metallic centre,[1] bimetallic alkoxides which were initially considered as alkoxo salts[2,3] have been shown to be coordination compounds stabilized by alkoxo bridges.[4] Special interest has been aroused in these derivatives by the exceptional stability and volatility of bimetallic alkoxides of strongly electropositive alkali, alkaline earth and lanthanide metals such as $[M\{Zr_2(OPr^i)_9\}]$,[5,6] $[M\{Ta(OR)_6\}]$,[7] $[M'\{Nb(OR)_6\}_2]$[8] and $[M'\{Al(OR)_4\}_2]$,[9] and in $[Ln\{Al(OPr^i)_4\}_3]$[10] (where M = Li, Na, K, Rb, Cs; M′ = Mg, Ca, Sr, Ba; Ln = lanthanides and R = Me, Et, Pr^i, Pr^n, Bu^n etc.) and the same has been sustained by the synthesis of soluble, monomeric, volatile bimetallic alkoxides $[M\{Al(OR)_4\}_2]$ of metals (M = Be,[11,12] Zn,[11] Cd,[11] Hg,[11] Mn,[13] Co,[14] Ni[15] and Cu[16]), the simple alkoxides of which are all insoluble, polymeric, non-volatile compounds. A novel interest in these compounds is indicated by the use of bimetallic μ-oxoalkoxides as catalysts for the polymerization of propylene oxide, lactones, oxiranes, epoxides etc.[17,18]

In view of the interest in stable derivatives[1] with more than two metallic centres, it was considered worthwhile to try to synthesize some termetallic alkoxides with bridging ligands like $[Al(OPr^i)_4]^-$ and $[Zr_2(OPr^i)_9]^-$. The strategy planned for this was to synthesize 1:1 derivatives like $[(Pr^iO)M(\mu\text{-}OPr^i)_2Al(OPr^i)_2]$ and replace the terminal isopropoxy group attached to the metal "M" with other chelating alkoxy ligands involving metals other than aluminium. It has already been reported[11] that attempts to synthesize $[(Pr^iO)M(\mu\text{-}OPr^i)_2Al(OPr^i)_2]$ derivatives (M = Be, Zn, Cd and Hg) by a reaction of the following type:

$$MCl_2 + 2KOPr^i + Al(OPr^i)_3 \rightarrow [(Pr^iO)M(\mu\text{-}OPr^i)_2Al(OPr^i)_2] + 2KCl$$

gave equimolar mixtures of insoluble $M(OPr^i)_2$ and soluble $[M\{(\mu\text{-}OPr^i)_2Al(OPr^i)_2\}]$ in all other cases except for the case of beryllium, in which a soluble and volatile product $[(Pr^iO)Be(\mu\text{-}OPr^i)_2Al(OPr^i)_2]$ was isolated as a viscous liquid.

The species $[(Pr^iO)Be(\mu\text{-}OPr^i)_2Al(OPr^i)_2]$, on interaction with isopropoxides of titanium, zirconium, hafnium, niobium and tantalum results in the formation of a number of stable novel termetallic isopropoxides which are being reported for the first time. Amongst the characteristics of these new types of derivatives are their solubility in common organic solvents and volatility (in the majority of the derivatives) on heating under reduced pressure.

EXPERIMENTAL

Stringent precautions were taken to maintain anhydrous conditions throughout the experimental work in view of the extremely hydrolysable nature of

---

* Present address: Department of Chemistry, SLP College, Morar, Gwalior 474001, India.

† Author to whom correspondence should be addressed.

the newly synthesized derivatives. The general method of synthesis is as follows.

All of these derivatives were synthesized (Table 1) by dissolving each constituent metal alkoxide $Ti(OPr^i)_4$,[19] $Zr(OPr^i)_4 \cdot Pr^iOH$,[20] $Hf(OPr^i)_4Pr^iOH$,[21] $Nb(OPr^i)_5$,[22] $Ta(OPr^i)_5$[22] $[(Pr^iO)Be(\mu\text{-}OPr^i)_2Al(OPr^i)_2]$[11] in benzene, mixing them together and refluxing the total contents for ~ 1 h in each case. As $[ClBe(\mu\text{-}OPr^i)_2Al(OPr^i)_2]$[23] is insoluble in benzene, its solution was prepared in isopropanol; on adding a benzene solution of $[K\{M_2(OPr^i)_9\}]$[6,24] (where M = Ti, Zr or Hf) to it, an exothermic reaction took place and the white insoluble product (identified as KCl) was separated out in this case by filtration. Excess solvent was stripped off under reduced pressure. With the exception of the titanium derivatives (which disproportionate), the products obtained distil unchanged on heating under reduced pressure (Table 1). All these termetallic derivatives are soluble in common organic solvents, e.g. benzene, chloroform and isopropanol.

Metal estimations (as mixed oxides) were carried out by standard methods.[25] Isopropoxy groups were estimated by dichromate oxidation[26] (Table 1).

IR and ^1H NMR spectra were recorded on a Perkin–Elmer 577 and R-32 spectrophotometer respectively. $CDCl_3$ was made anhydrous by storing over molecular sieves (type 4A) for ~ 24h. TMS was used as internal standard. Mass spectra were recorded on a JEOL DMX-300.

Molecular weights were measured in a semimicro ebulliometer (Gallenkamp) equipped with a thermistor sensor using benzene or isopropanol as solvent.

RESULTS AND DISCUSSION

During the successful synthesis of a 1 : 1 bimetallic isopropoxide of beryllium and aluminium $[(Pr^iO)Be(\mu\text{-}OPr^i)_2Al(OPr^i)_2]$, it was observed that this derivative exhibits a strong tendency to dimerize even on standing. This has been explained by the tendency of the tri-coordinate beryllium in the monomeric species to attain four-coordinate environment through dimerization.[17]

In view of the above tendency of beryllium atoms, it was conjectured that it might be possible to satisfy it by formation of new bridges with alkoxides of other metals, leading to the synthesis of stable termetallic alkoxides, with three different metals in the same molecule. This has been achieved by carrying out the reactions of the product $[(Pr^iO)Be(\mu\text{-}OPr^i)_2Al(OPr^i)_2]$ with the isopropoxides of titanium, zirconium, hafnium, niobium and tantalum resulting in the preparation of a number of stable novel termetallic isopropoxides for the first time. The results obtained are discussed under the following heads:

Termetallic isopropoxides of titanium, zirconium or hafnium with beryllium and aluminium with the general formulae $[(Pr^iO)_3M(\mu\text{-}OPr^i)_2Be(\mu\text{-}OPr^i)_2Al(OPr^i)_2]$ *and* $[\{(Pr^iO)_2M\{(\mu\text{-}OPr^i)_2Be(\mu\text{-}OPr^i)_2Al(OPr^i)_2\}_2]$

These derivatives have been synthesized as represented by the following equations:

$$[(Pr^iO)Be(\mu\text{-}OPr^i)_2Al(OPr^i)_2] + M(OPr^i)_4^* \xrightarrow{C_6H_6} [(Pr^iO)_3M(\mu\text{-}OPr^i)_2Be(\mu\text{-}OPr^i)_2Al(OPr^i)_2], \quad (1)$$
$$(T_1)$$

$$2[(Pr^iO)Be(\mu\text{-}OPr^i)_2Al(OPr^i)_2] + M(OPr^i)_4^* \xrightarrow{C_6H_6} [(Pr^iO)_2M\{(\mu\text{-}OPr^i)_2Be(\mu\text{-}OPr^i)_2Al(OPr^i)_2\}_2], \quad (2)$$
$$(T_2)$$

where M = Ti(IV), Zr(IV) or Hf(IV).

Both types of derivatives, $\mathbf{T}_1$ and $\mathbf{T}_2$, synthesized as shown above are soluble in common organic solvents (Table 1). In the case of titanium, both the 1 : 1 ($\mathbf{T}_1$) and 1 : 2 ($\mathbf{T}_2$) products are pale yellow viscous liquids which disproportionate on heating under reduced pressure into $Ti(OPr^i)_4$ (45°C/0.05 mm) and $[(Pr^iO)Be(\mu\text{-}OPr^i)_2Al(OPr^i)_2]$ (128°C/0.05 mm). By contrast, the corresponding derivatives in the cases of zirconium and hafnium, both ($\mathbf{T}_1$ and $\mathbf{T}_2$) types can be volatilised unchanged under reduced pressure to colourless viscous liquids at 139 and 137°C for the $\mathbf{T}_1$ derivatives and at 132 and 129°C for $\mathbf{T}_2$ derivatives (all at 0.05 mm pressure), the hafnium products exhibiting slightly lower boiling points compared to zirconium analogues for the both types of derivatives.

Ebullioscopic measurements indicate that the titanium derivative $\mathbf{T}_1$ like all $\mathbf{T}_2$ derivatives exhibits monomeric nature in benzene while their $\mathbf{T}_1$ type zirconium and hafnium analogues depict dimeric behaviour (Table 1); these derivatives, expectedly depict monomeric nature in isopropanol: 683 obs. (616 calc). 698 (659) and 734 (746) for titanium, zirconium and hafnium derivatives respectively.

The above observations can be easily understood on

---

*In the cases of zirconium and hafnium isopropoxides, their crystalline adducts $M(OPr^i)_4 \cdot Pr^iOH$ were taken, but for simplicity these are represented by the reactive species $M(OPr^i)_4$.

Table 1. Synthetic details of termetallic isopropoxides

Sl. no.	Reactants;* molar ratio/ reflux time (h)	Product	Volatility (°C/torr)	Yield of distilled product (g/%)	Analysis: % found (calc.) Individual metal	Mixed oxide of metals	OPr^i	Molecular weight obs. (calc.)
1	A = 1.91 g, B = 1.64 g; 1:1/1	$TiBeAl(OPr^i)_9$	†	3.52/99‡	—	25.41 (25.31)	85.94 (86.37)	632 (616)
2	A = 1.54 g, C = 1.80 g; 1:1/1	$ZrBeAl(OPr^i)_9$	139/0.05	1.91/62	13.99 Zr (13.84)	30.28 (30.23)	80.26 (80.70)	1232 (659)
3	A = 1.04 g, D = 1.50 g; 1:1/1	$HfBeAl(OPr^i)_9$	137/0.05	1.29/55	24.01 Hf (23.91)	38.19 (38.38)	70.72 (71.27)	1412 (746)
4	A = 2.57 g, D = 1.10 g; 2:1/1	$TiBe_2Al_2(OPr^i)_{14}$	†	3.64/99‡	—	24.42 (24.47)	87.18 (87.34)	963 (947)
5	A = 2.11 g, C = 1.25 g; 2:1/1	$ZrBe_2Al_2(OPr^i)_{14}$	132/0.05	1.12/58	9.31 Zr (9.21)	27.89 (27.78)	82.99 (83.51)	943 (991)
6	A = 1.88 g, D = 1.38 g; 2:1/1	$HfBe_2Al_2(OPr^i)_{14}$	129/0.05	1.18/58	16.59 Hf (16.56)	33.24 (33.63)	76.50 (76.76)	1093 (1078)
7	A = 1.68 g, E = 1.97 g; 1:1/1	$NbBeAl(OPr^i)_{10}$	112/0.05	3.3/92	—	28.47 (29.02)	81.72 (82.09)	688 (720)
8	A = 1.45 g, F = 2.12 g; 1:1/1	$TaBeAl(OPr^i)_{10}$	120/0.05	3.0/85	—	36.50 (36.75)	72.66 (73.15)	789 (808)

* A = $Pr^iOBe(\mu\text{-}OPr^i)_2Al(OPr^i)_2$; B = $Ti(OPr^i)_4$; C = $Zr(OPr^i)_4 \cdot Pr^iOH$; D = $Hf(OPr^i)_4 \cdot Pr^iOH$; E = $Nb(OPr^i)_5$; F = $Ta(OPr^i)_5$. All reactants dissolved in 30 cm^3 benzene.

† Disproportionated on heating under reduced pressure.

‡ Undistilled product.

the basis of known differences in the properties of titanium on the one hand and zirconium or hafnium on the other.

Of the termetallic isopropoxides described in Table 1 both the titanium derivatives (T_1 and T_2) disproportionate on heating under reduced pressure yielding volatile $Ti(OPr^i)_4$ (49°C/0.1 mm),[27] but the zirconium and hafnium products (both T_1 and T_2 type distil unchanged around 129–139°C/0.05 mm.

In fact, the extraordinarily low boiling point of $Ti(OPr^i)_4$ might actually facilitate the dissociation of termetallic isopropoxides, which might be represented by the following types of equilibria:

$$[(Pr^iO)_3Ti(\mu\text{-}OPr^i)_2Be(\mu\text{-}OPr^i)_2Al(OPr^i)_2] \rightleftharpoons [Pr^iOBe(\mu\text{-}OPr^i)_2Al(OPr^i)_2] + Ti(OPr^i)_4,$$

$$[(Pr^iO)_2Ti\{(\mu\text{-}OPr^i)_2Be(\mu\text{-}OPr^i)_2Al(OPr^i)_2\}_2] \rightleftharpoons 2[(Pr^iO)Be(\mu\text{-}OPr^i)_2Al(OPr^i)_2] + Ti(OPr^i)_4.$$

It appears that the extent of dissociation even in the titanium species (Table 1) is insignificantly low under ambient conditions to be detected by the traditional molecular weight measurements (which normally have an accuracy of $\pm 5\%$), but during attempts to distil these products under reduced pressure, the equilibrium is gradually shifted to the right as the comparatively more volatile titanium isopropoxide is removed by distillation.

Conversely, the higher volatility of the termetallic T_1 isopropoxides of zirconium and hafnium [e.g. b.ps for T_1:Zr derivative, 139°C/0.05 mm, Hf derivative 137°C/0.05 mm as compared to the constituent simple isopropoxides (b.ps: $Zr(OPr^i)_4$, 172°C/0.35 mm and $Hf(OPr^i)_4$, 170°C/0.35 mm][20,21] would tend to shift the equilibria preferably to the formation of termetallic species as shown below:

$$[(Pr^iO)Be(\mu\text{-}OPr^i)_2Al(OPr^i)_2] + M(OPr^i)_4 \rightleftharpoons [(Pr^iO)_3M(\mu\text{-}OPr^i)_2Be(\mu\text{-}OPr^i)_2Al(OPr^i)_2], \quad (T_1)$$

$$2[(Pr^iO)Be(\mu\text{-}OPr^i)_2Al(OPr^i)_2] + M(OPr^i)_4 \rightleftharpoons [(Pr^iO)_2M\{(\mu\text{-}OPr^i)_2Be(\mu\text{-}OPr^i)_2Al(OPr^i)_2\}_2], \quad (T_2)$$

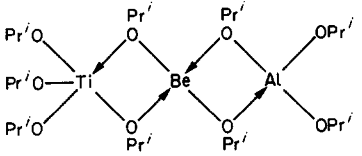
where M = Zr(IV) or Hf(IV).

The slightly higher boiling points of T_1 than T_2 derivatives may easily be understood by the observed dimeric nature of T_1.

The slightly lower boiling points of hafnium compared to zirconium ternary analogues are similar to the earlier reported[21] differences in boiling points of simple alkoxides of the two metals.

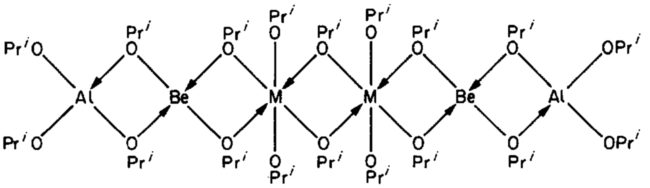
IR spectra of these derivatives mainly depict absorptions in four regions of interest, i.e. 1175–930 cm^{-1} {four or five [very strong (vs) or strong (s)] absorptions}: 850–800 cm^{-1} {two [vs, s or medium (m)] absorptions}: 770–630 cm^{-1} {three or four [vs, s or m] absorptions} and 630–530 cm^{-1} {two [vs, s, m or weak] absorptions}, which have been assigned [27–30] to ν_{OPr^i}, ν_{Be-O}, ν_{Al-O} and ν_{M-O}, are indicative of different modes of bonding. Though no definitive assignments have been made yet in general the higher ones are assignable to terminal while lower ones to bridging groups.[27–30]

On the basis of the above discussions, the following tentative structures (I–III) may be proposed for these derivatives:



Monomeric in benzene

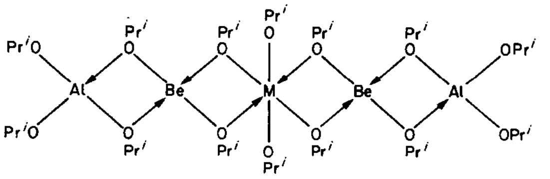
I



II

Dimeric in benzene

M = Zr(IV) or Hf(IV)



III

Monomeric in benzene

M = Zr(IV) or Hf(IV)

Table 2. PMR spectral data of termetallic isopropoxides of Ti(IV), Zr(IV), Hf(IV), Nb(V) and Ta(V) with Be(II) and Al(III)

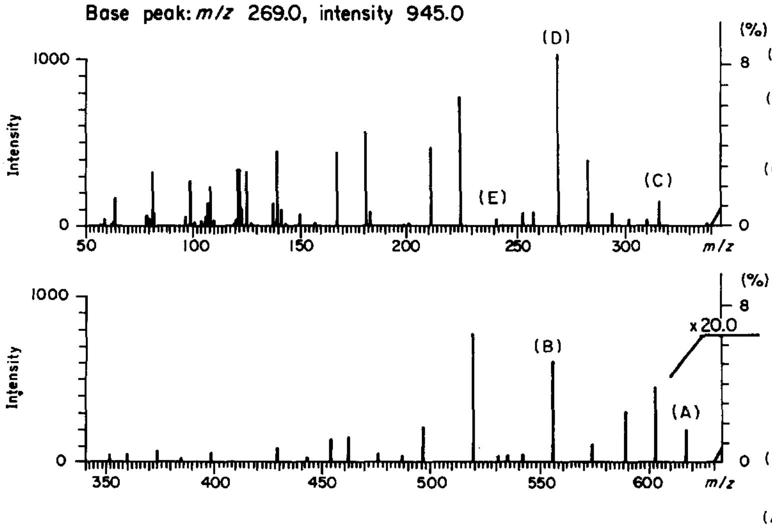
Sl. No.	Compound	Chemical shift* (δ) (ppm)
1	$TiBeAl(OPr^i)_9$	4.85m, 4H(O$\underline{CH}$-B); 4.30m, 5H(O$\underline{CH}$-T); 1.62d† (CH_3-B) and 1.52d,† ($\underline{CH}_3$-T) 54‡
2	$ZrBeAl(OPr^i)_9$	4.15m, 9H(O$\underline{CH}$-BT); 1.32d† ($\underline{CH}_3$-B), 1.15d† (CH_3-T) 54H‡
3	$HfBeAl(OPr^i)_9$	4.15m, 9H(O$\underline{CH}$-BT); 1.32d† ($\underline{CH}_3$-B), 1.08d† ($\underline{CH}_3$-T) 54H‡
4	$TiBeAl(OPr^i)_{14}$	4.20m, 14H(O$\underline{CH}$-BT); 1.40m, 84H($\underline{CH}_3$-BT)
5	$ZrBe_2Al_2(OPr^i)_{14}$	4.18m, 14H(O$\underline{CH}$-BT); 1.25d† ($\underline{CH}_3$-B), 1.10d† ($\underline{CH}_3$-T) 84H‡
6	$HfBe_2Al_2(OPr^i)_{14}$	4.15m, 14H(O$\underline{CH}$-BT); 1.25d† ($\underline{CH}_3$-B), 1.05d† ($\underline{CH}_3$-T) 84H‡
7	$NbBeAl(OPr^i)_{10}$	4.95m, 4H(O$\underline{CH}$-B); 4.35m, 6H(O$\underline{CH}$-T); 1.47d, 24H($\underline{CH}_3$-B); 1.33d, 36H(CH_3-T)
8	$TaBeAl(OPr^i)_{10}$	4.80m, 4H(O$\underline{CH}$-B); 4.17m, 6H(O$\underline{CH}$-T); 1.48d† and 1.28d† ($\underline{CH}_3$-B), 1.21d‡ and 1.14d† ($\underline{CH}_3$-T), 60H‡

* Solvent $CDCL_3$: m, multiplet; d, doublet; B, bridging; T, terminal.

† Overlapped each other and appeared to be a triplet.

‡ Integration could not be differentiated between bridging and terminal groups.

The ^1H NMR spectral data of all the products of the T_1 and T_2 (Table 2) show that as expected the spectra for zirconium and hafnium derivatives are similar in nature. In all the cases for T_1 derivatives, signals due to methine protons appear as the septets centred at 4.85 and 4.30 δ for titanium; and at 4.15 δ for zirconium as well as hafnium derivatives; these are as usual not so well defined. However, the methine protons in the spectrum for the titanium derivative T_1 (Table 2) showed rather a clear separation of almost two septets centred, as indicated above at 4.85 and 4.30 δ, with an integration ratio of ~ 4:5 in accordance with the structure I for the same. The absorptions occurring in the higher side may be assigned to terminal groups.[31–33] The relative ratio of the methyl signals (Table 2) assignable to terminal and bridging isopropoxy groups are in general (although not exact) conformity with the tentative structures suggested for the T_2 products except in the spectrum of titanium (T_2) product (Table 2) in which case a symmetrical unresolved spectrum only could be recorded. This might indicate the presence of more than one species, presumably due to dissociation of



	m/z	Raw itensity	R. intensity	Sigma (%)
	201.0	18.0	19.0	0.29
	211.0	430.6	455.6	7.05
	225.0	716.5	758.2	11.73
(E)	241.0	41.2	43.0	0.67
	253.0	69.1	73.1	1.13
	258.0	78.1	82.6	1.27
(D)	269.0	945.0	1000.0	15.47
	283.0	363.4	384.5	5.95
	294.0	68.5	72.4	1.12
	302.0	37.4	33.6	0.61
	310.0	37.0	39.1	0.60
(C)	316.0	134.4	142.2	2.20
	327.0	11.6	12.3	0.19
	338.0	17.3	18.4	0.28
	341.0	15.5	16.4	0.25
	352.0	44.8	47.4	0.73
	360.0	43.6	46.2	0.71
	374.0	65.7	69.6	1.07
	385.0	26.0	27.6	0.42
	399.0	52.6	55.7	0.86
	429.0	80.0	84.7	1.31
	443.0	27.4	28.9	0.44
	454.0	128.6	136.0	2.10
	462.0	133.7	146.7	2.27
	476.0	49.9	52.8	0.81
	487.0	40.6	42.9	0.66
	497.0	203.7	215.5	3.33
	520.0	720.7	762.5	11.80
	531.0	40.8	43.1	0.66
	535.0	39.8	42.2	0.65
	542.0	46.9	49.6	0.76
(B)	556.0	560.5	593.1	9.17
	574.0	99.8	105.6	1.63
	589.0	282.8	299.2	4.63
	603.0	419.2	443.5	6.86
(A)	617.0	9.5	10.1	0.15

Fig. 1. Mass spectrum of $[(Pr^iO)_3Ti(\mu\text{-}OPr^i)_2Be(\mu\text{-}OPr^i)_2Al(OPr^i)_2]$.

this product to some extent, even at ambient temperatures (which might not be detectable by the ebullioscopic method) may be ascribed to the steric strain produced on the central titanium atom bonded to six isopropoxy groups. Thus, the pmr spectra also support the proposed structures for these derivatives.

Mass spectral studies of the product $[(Pr^iO)_3Ti(\mu\text{-}OPr^i)_2Be(\mu\text{-}OPr^i)_2Al(OPr^i)_2]$ have been carried out and tentative assignments have been made. The mass spectral data of the derivative exhibited (Fig. 1) a weak signal of molecular ion at 617* (A) [molecular weight M = 615; (M + 2H)] and an intense signal at 556*(B) [M − 59(OPr^i)] (a usual fragment reported in isopropoxy derivatives of metals).[34–37] The identity of the termetallic product is also corroborated[37] by non-appearance of signals for the constituent alkoxides at 331* $[(Pr^iO)BeAl(OPr^i)_4]$ or at 284* $[Ti(OPr^i)_4]$. However, signals at 316*(C) [331 − 15(CH_3)], 269*(D) [(284 − 15(CH_3)] and 241*(E) [(284 − 43(Pr^i)] etc. were observed in notable intensity. These would have resulted either as fragments from termetallic species or could be due to fragmentation of products resulting from slight dissociation of the parent derivative to its constituent alkoxides. Assignments of other signals have been deliberately avoided as these would be more speculative in nature.

Attempted syntheses of the derivatives with the general formula $[(Pr^iO)_7M_2(\mu\text{-}OPr^i)_2Be(\mu\text{-}OPr^i)_2Al(OPr^i)_2]$ (*where* M = Ti(IV), Zr(IV) *or* Hf(IV)

By analogy with the derivatives of the general formulae $[K\{Zr_2(OPr^i)_9\}]$[6] or $[Mg\{Zr_2(OPr^i)_9\}_2]$[38] etc. the synthesis of the derivatives with the composition $[(Pr^iO)_7M_2(\mu\text{-}OPr^i)_2Be(\mu\text{-}OPr^i)_2Al(OPr^i)_2]$ was also attempted as represented by the following two different routes:

Instead of obtaining a single compound T_3 as represented by eqn (3) or (5), mixtures of two products were obtained in both the cases as represented by eqns (4) and (6); this was indicated by the observed apparent molecular weights of these products being almost half the theoretical values for T_3. Attempts were made to separate both constituents by dissolving them in limited amounts of isopropanol. The tetraisopropoxide isopropanolates, $M(OPr^i)_4 \cdot Pr^iOH$ (M = Zr or Hf) crystallized out in the cases of the zirconium and hafnium derivatives, eqns (4) and (6), due to their poor solubility in isopropanol; the remaining products were identified as derivatives T_1 as shown above. However, $Ti(OPr^i)_4$ could not be separated in the case of titanium derivative as it does not form a sparingly soluble isopropanolate. When the complex T_3 was heated under reduced pressure, it disproportionated and the total $Ti(OPr^i)_4$ contents distilled out 45°C/0.05 mm) followed by $[(Pr^iO)Be(\mu\text{-}OPr^i)_2Al(OPr^i)_2]$ (128°C/0.05 mm).

Termetallic isopropoxides of niobium or tantalum with beryllium and aluminium with the general formula $[(Pr^iO)_4M(\mu\text{-}OPr^i)_2Be(\mu\text{-}OPr^i)_2Al(OPr^i)_2]$

These derivatives have been synthesized by the interaction of $Nb(OPr^i)_5$ or $Ta(OPr^i)_5$ with $[(Pr^iO)Be(\mu\text{-}OPr^i)_2Al(OPr^i)_2]$ in 1 : 1 molar ratios as indicated by the equation:

$$M(OPr^i)_5 + [(Pr^iO)Be(\mu\text{-}OPr^i)_2Al(OPr^i)_2] \xrightarrow{C_6H_6} [(Pr^iO)_4M(\mu\text{-}OPr^i)_2Be(\mu\text{-}OPr^i)_2Al(OPr^i)_2],$$
$$(T_4)$$

where M = Nb(V) or Ta(V).

The derivatives T_4 could be distilled (Table 1) unchanged as colourless viscous liquids in almost quantitative (85–92%) yields at 112 and 120°C respectively at 0.05 mm for the niobium and

$$[(Pr^iO)Be(\mu\text{-}OPr^i)_2Al(OPr^i)_2] + 2M(OPr^i)_4^*$$
$$\xrightarrow{C_6H_6} \begin{array}{lr} [(Pr^iO)_7M_2(\mu\text{-}OPr^i)_2Be(\mu\text{-}OPr^i)_2Al(OPr^i)_2] & (3) \\ \qquad (T_3) & \\ [(Pr^iO)_3M(\mu\text{-}OPr^i)_2Be(\mu\text{-}OPr^i)_2Al(OPr^i)_2] + M(OPr^i)_4 & (4) \\ \qquad (T_1) & \end{array}$$

$$[Cl\ Be\ (\mu\text{-}OPr^i)_2Al(OPr^i)_2] + [K\{M_2(OPr^i)_9\}]$$
$$\xrightarrow[C_6H_6]{Pr^iOH} \begin{array}{lr} [(Pr^iO)_7M_2(\mu\text{-}OPr^i)_2Be(\mu\text{-}OPr^i)_2Al(OPr^i)_2] + KCl\downarrow & (5) \\ \qquad (T_3) & \\ [(Pr^iO)_3M(\mu\text{-}OPr^i)_2Be(\mu\text{-}OPr^i)_2Al(OPr^i)_2] + M(OPr^i)_4 + KCl\downarrow & (6) \end{array}$$

where M = Ti(IV), Zr(IV) or Hf(IV).

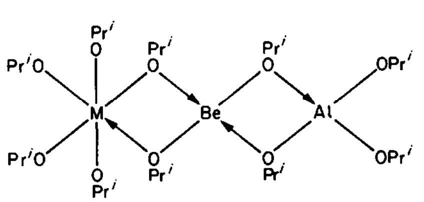
---

* See footnote to eqn (2).

tantalum derivatives. Both these derivatives are soluble in benzene in which they are monomeric.

IR spectra of these complexes are similar to those of **T**$_1$ and **T**$_2$ derivatives, showing terminal and bridging ν_{OPr^i}, $\nu_{\mathrm{Be-O}}$ and $\nu_{\mathrm{Al-O}}$ in the same regions. $\nu_{\mathrm{Nb-O}}$ and $\nu_{\mathrm{Ta-O}}$ absorptions have also been observed in the expected regions [for **T**$_4$: 560vs, 530vs; 580m, 530w for Nb(V) and Ta(V) derivatives respectively], the higher ones being assigned to terminal and the lower ones to bridging isopropoxy groups.[27–30]

On the basis of molecular weight and IR spectral data, the derivatives **T**$_4$ could be assigned the following plausible structure:



IV

M = Nb(V) or Ta(V)

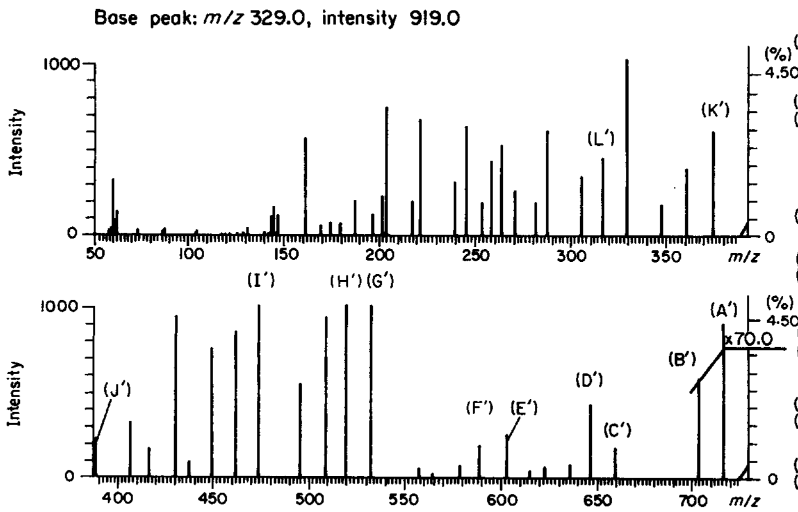
The ^{1}H NMR spectrum of [(Pr^{i}O)$_4$Nb(μ-OPr^i)$_2$Be(μ-OPr^i)$_2$Al(OPr^i)$_2$] (Table 2) appears to be in conformity with the above plausible structure. The methine signals appear in the form of two septets at δ-values of 4.95 and 4.35 in the ratio of $\sim 2:3$. Similarly the methyl signals appear in the form of two doublets centred at values of 1.47 and 1.33 in the ratio of $\sim 2:3$. For the tantalum analogue, the two septets for methine protons appeared (Table 2) at δ-values of 4.80 and 4.17 again in the ratio of $\sim 2:3$, which also corroborates with structure **IV**.

The methyl protons in the pmr spectrum of the latter tantalum product **T**$_4$, [(Pr^{i}O)$_4$Ta(μ-OPr^i)$_2$Be(μ-OPr^i)$_2$Al(OPr^i)$_2$], however, are more complicated (Table 2). Although exact integration for terminal and bridging groups was not possible individually yet the spectrum could be considered to be consisting of two doublets centred at 1.40 and 1.28 δ with considerable overlapping at 1.21 and 1.14 δ in the ratio of roughly 2 : 3. Similar differences have been recorded[39] in the ^{1}H NMR spectra of niobium and tantalum pentaisopropoxides. The spectrum of tantalum penta-isopropoxide[39] showed three doublets in the methyl portion of the spectrum and nineteen peaks (about three septets) in the methine portion of the spectrum, in contrast to that of niobium penta-isopropoxide, which gave only a broad methine signal at 4.70 δ and an averaged doublet due to methyl portions at 1.20 δ.

Mass spectral studies have also been carried out in the case of [(Pr^{i}O)$_4$Nb(μ-OPr^i)$_2$Be(μ-OPr^i)$_2$Al(OPr^i)$_2$]. The mass spectral data of this derivative exhibited (Fig. 2) a molecular ion peak at 717*(A′) [molecular weight M = 719; (M − 2H)] followed by a weak signal at 704*(B′) [M − 15(CH$_3$)] and an intense signal at 660*(C′) [M − 59(OPr^i)] which supported formation of the product.[35–38] Other notable signals can be tentatively explained as arising from the fragmentation of termetallic derivative according to the following assignments:

---

* *m*/*z* values.



	m/*z*	Raw intensity	R. intensity	Sigma (%)	
	305.0	312.6	339.9	2.72	
(L′)	316.0	406.9	442.5	3.54	
	329.0	919.7	1000.0	8.00	
	347.0	163.3	177.6	1.42	
	360.0	350.5	381.2	3.05	
(K′)	374.0	551.0	599.1	4.79	
(J′)	389.0	212.5	231.0	1.85	
	407.0	298.4	324.5	2.59	
	417.0	157.9	171.6	1.37	
	431.0	861.1	936.2	7.49	
	438.0	91.6	99.6	0.79	
	450.0	693.1	753.6	6.03	
	462.0	781.7	850.0	6.80	
(I′)	474.0	Over			
	496.0	502.2	546.0	4.37	
	509.0	860.8	936.0	7.49	
(H′)	520.0	Over			
(G′)	533.0	Over			
	558.0	55.3	60.2	0.48	
	565.0	29.4	32.0	0.25	
	579.0	69.7	75.8	0.60	
(F′)	589.0	173.6	188.8	1.51	
(E′)	603.0	230.4	250.5	2.00	
	615.0	40.8	44.3	0.35	
	623.0	64.9	70.6	0.56	
	636.0	75.6	82.2	0.65	
(D′)	647.0	388.1	422.0	3.37	
(C′)	660.0	161.9	176.0	1.40	
	680.0	6.6	7.2	0.05	
	693.0	7.0	7.6	0.06	
(B′)	704.0	7.6	8.3	0.06	
(A′)	717.0	11.7	12.7	0.10	End

Fig. 2. Mass spectrum of [(Pr^{i}O)$_4$Nb(μ-OPr^i)$_2$Be(μ-OPr^i)$_2$Al(OPr^i)$_2$].

647*(D′) [M − 59(OPr^i) − 13(CH)], 603*(E′) [647(Pr^i + 1H)], 589*(F′) [603 − 14(CH_2)], 533*(G′) [589 − 56(C_4H_8)], 520*(H′) [533 − 13(CH)], 474*(I′) [533 − 59(OPr^i)], 389*(J′) [388{Nb(OPr^i)$_5$} + 1H], 374*(K′) [388 − 14(CH_2)] and 316*(L′) [331 − 15(CH_3)] etc. It may be emphasized that the spectrum did not exhibit signals for the constituent alkoxides, i.e. at 331* for [(Pr^{i}O)Be(μ-OPr^i)$_2$Al(OPr^i)$_2$] or at 388* for Nb(OPr^i)$_5$ which corroborates the identity of T_4 and shows that the termetallic product is not merely a mixture of the constituent alkoxides.[37]

Acknowledgements—We are grateful to Dr P. Ramachandran, Director, Defence Research and Development Establishment, Gwalior for providing facilities for spectroscopic studies at this Centre. A Teacher Fellowship to one of the authors (M.A.) by the University Grants Commission is also gratefully acknowledged.

REFERENCES

1. J. C. Jeffery, A. G. Orpen, W. T. Robinson, F. G. A. Stone and M. J. Went, *J. Chem. Soc., Chem. Commun.* 1984, 396.
2. H. Meerwein, *U.S. Patent* 1929, 1, 689, 356; *Chem. Abstr.* 1929, **23**, 156.
3. H. Meerwein and T. Bersin, *Ann.* 1929, **476**, 113; *Chem. Abstr.* 1930, **24**, 586.
4. R. C. Mehrotra and A. Mehrotra, *Inorg. Chim. Acta Rev.* 1971, **5**, 127.
5. W. G. Bartley and W. Wardlaw, *J. Chem. Soc.* 1958, 422.
6. R. C. Mehrotra and M. M. Agrawal, *J. Chem. Soc.* 1967, 10; 26.
7. R. C. Mehrotra, M. M. Agrawal and P. N. Kapoor, *J. Chem. Soc.* 1968, 2673.
8. S. Govil, P. N. Kapoor and R. C. Mehrotra, *J. Inorg. Nucl. Chem.* 1976, **38**, 172.
9. R. C. Mehrotra, S. Govil, A. B. Goel, R. B. King and K. C. Nainan, *Inorg. Chim. Acta* 1978, **29**, 131.
10. R. C. Mehrotra, M. M. Agrawal and A. Mehrotra, *Synth. React. Inorg. Met.–Org. Chem.* 1973, **3**, 181.
11. M. Aggrawal, C. K. Sharma and R. C. Mehrotra, *Synth. React. Inorg. Met.–Org. Chem.* 1983, **13**, 571.
12. M. Aggrawal and R. C. Mehrotra, *Synth. React. Inorg. Met.–Org. Chem.* 1984, **14**, 139.
13. J. V. Singh, N. C. Jain and R. C. Mehrotra, *Synth. React. Inorg. Met.–Org. Chem.* 1979, **9**, 79.
14. R. C. Mehrotra and J. Singh, *J. Coord. Chem.* (in press).
15. R. C. Mehrotra and J. Singh, *Can. J. Chem.* 1984, **62**, 1003.
16. R. C. Mehrotra and J. Singh, *Z. Anorg. Allg. Chem.* (in press).
17. P. Teyssie, J. P. Bioul, L. Hocks and T. Ouhadi, *Chemtech.* 1977, 7, 192; *Chem. Abstr.* 1977, **86**, 171914.
18. M. Osgan and P. Teyssie, *Polym. Lett.* 1967, **5**, 789.
19. N. M. Cullinane and S. J. Chard, *Nature* (*London*) 1949, **164**, 710.
20. D. C. Bradley and W. Wardlaw, *J. Chem. Soc.* 1951, 280.
21. D. C. Bradley, R. C. Mehrotra and W. Wardlaw, *J. Chem. Soc.* 1953, 1634.
22. D. C. Bradley, B. N. Chakravarti, A. Chatterjee, W. Wardlaw and A. Whitley, *J. Chem. Soc.* 1958, 99.
23. M. Aggrawal and R. C. Mehrotra, under communication.
24. M. M. Agrawal, Ph.D. thesis, University of Rajasthan, Jaipur, India (1966).
25. A. I. Vogel, *A Text Book of Quantitative Inorganic Analysis*. Longman, London (1973).
26. D. C. Bradley, F. M. A. Halim and W. Wardlaw, *J. Chem. Soc.* 1950, 3450.
27. D. C. Bradley, R. C. Mehrotra and D. P. Gaur, *Metal Alkoxides*. Academic Press, New York (1978).
28. C. J. Barraclough, D. C. Bradley, J. Lewis and I. M. Thomas, *J. Chem. Soc.* 1961, 2601.
29. K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*. Wiley, New York (1963).
30. V. A. Sipachev and A. I. Grigorev, *Russ. J. Inorg. Chem.* 1972, **17**, 176.
31. J. G. Oliver and I. J. Worrall, *J. Chem. Soc.* (*A*) 1970, 845.
32. R. C. Mehrotra and A. Mehrotra, *J. Chem. Soc., Dalton Trans.* 1972, 1203.
33. S. Govil, P. N. Kapoor and R. C. Mehrotra, *Inorg. Chim. Acta* 1975, **15**, 43.
34. W. Fieggen, H. Gerding and N. M. M. Nibbering, *Rec. Trav. Chim.* 1968, **87**, 377.
35. J. G. Oliver and I. J. Worrall, *J. Chem. Soc.* (*A*) 1970, 2347.
36. A. Mehrotra, Ph.D. thesis, University of Rajasthan, Jaipur, India (1975).
37. L. G. Hubert-Pfalzgraf and J. G. Riess, *Inorg. Chem.* 1975, **14**, 2854.
38. S. Govil and R. C. Mehrotra, *Aust. J. Chem.* 1975, **28**, 2125.
39. D. C. Bradley and C. E. Holloway, *J. Chem. Soc.* (*A*) 1968, 219.

---

* *m*/*z* values.