

cm⁻¹. In other respects, the spectra of tris(trimethyltin)oxide are quite similar. (ii) During the cleavage or insertion reaction of B-O-Sn linkage, the peak in the region 1300-1285 cm⁻¹ disappears completely.

The trimethyl-metal peak positions in bis(trimethyl-metal)oxide and tris(trimethylmetal)borates (where metal = Si, Ge and Sn) are given below:

Compound	δ _M (Hz)*	Compound	δ _M (Hz)
(Me ₃ Si) ₂ O	-3.5	B(OSiMe ₃) ₃	-4.8
(Me ₃ Ge) ₂ O	-18.5	B(OGeMe ₃) ₃	-19.2
(Me ₃ Sn) ₂ O	-14.2	B(OSnMe ₃) ₃	-12.2

*Values taken from literature *Angew. Chem.* (internat. edn), **4** (1965), 201.

The PMR spectra of these derivatives show only a singlet for methyl protons thus indicating the purity of the products. The chemical shifts of these peaks appear to be in the same range as for the corresponding bis(trimethyl-metal)oxides.

Tris(tributyl-stannyl)borate and tris(trimethylstannyl) borate were synthesized by the known methods reported earlier⁶. Trimethylchlorosilane and trimethylchloro-germane were distilled before use.

Reaction between bis(trimethyl-germanium)oxide and boric anhydride—Boric anhydride (0.58 g, 0.83 mmole) was added to bis(trimethyl-germanium)oxide (0.611 g, 2.44 mmoles). The mixture was kept aside for 1 hr; the white solid goes in solution slowly to give tris(trimethyl-germyl)borate, which distils at 75°/6 mm (Found: B, 2.8. C₉H₂₇O₆Ge₃ requires B, 2.6%).

Reaction between tris(tributyl-stannyl)borate and trimethylchlorosilane—An exothermic reaction was observed when trimethylchlorosilane (1.00 g, 9.21 mmoles) was added drop by drop to tris(tributylstannyl)borate (2.42 g, 2.61 mmoles). Distillation of the mixture gave tris(trimethyl-silyl)borate, b.p. 62-64°/6 mm (0.42 g, 49% yield) as the first fraction; tributyl-tin chloride (2.52 g, 98% yield) appeared as the second fraction at 97°/0.3 mm.

Reaction between tris(tributyl-stannyl)borate and trimethylchloro-germane—Trimethylchloro-germane (1.07 g, 7.05 mmoles) was added drop by drop to tris(tributyl-stannyl)borate (2.07 g, 2.23 mmoles). Reaction was exothermic, distillation gave tris(trimethylgermyl)borate, b.p. 78°/6 mm (0.49 g, 53%) as the first fraction and tributyl-tin chloride as the second fraction, b.p. 100°/0.3 mm (1.86 g, 85% yield).

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Double Isopropoxides of Hf(IV) with Alkaline Earth Metals

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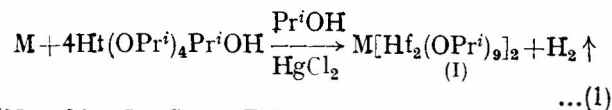
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Volatile double isopropoxides, M[Hf₂(OPrⁱ)₂], and MHf₃(OPrⁱ)₁₄, have been synthesized by the reaction of hafnium isopropoxide isopropanolate and alkaline earth metals in different stoichiometric ratios.

A NUMBER of volatile double alkoxides of hafnium with alkali metals, aluminium and gallium were synthesized in our laboratories¹. These double alkoxides are soluble in organic solvents. However, alkoxides of alkaline earth metals and magnesium are insoluble in organic solvents and in view of this, it was considered of interest to make a study of double alkoxides of hafnium with these metals.

Alkaline earth metal isopropoxides are insoluble in isopropanol, and the rate of dissolution of these isopropoxides is extremely slow in the alcohol even in the presence of mercuric chloride catalyst. The rate of dissolution is markedly enhanced by the addition of hafnium isopropoxide, yielding finally double isopropoxides which are soluble in isopropanol and can be volatilized without decomposition under reduced pressure.

Products of the type M[Hf₂(OPrⁱ)₂] have been synthesized by dissolving the alkaline earth metals in the solution of hafnium isopropoxide isopropanolate, Hf(OPrⁱ)₄ PrⁱOH, in isopropanol in 1:4 molar ratio in accordance with Eq. (1).



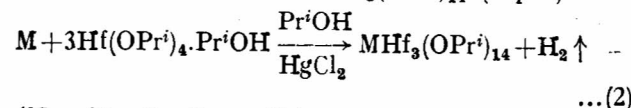
(M = Mg, Ca, Sr or Ba)

Catalytic amount of mercuric chloride was used to facilitate the reaction.

All these products are white crystalline solids, soluble in isopropanol, benzene and in common organic solvents. These could be purified by recrystallization from isopropanol or by sublimation/distillation under reduced pressure.

Molecular weights of magnesium and calcium derivatives were determined in benzene; the former shows monomeric behaviour while the later is dimeric.

Reactions of alkaline earth metals with Hf(OPrⁱ)₄ PrⁱOH in 1:3 molar ratio in isopropanol in the presence of small amount of HgCl₂, resulted in the formation of the product, MHf₃(OPrⁱ)₁₄ (Eq. 2).



(M = Mg, Ca, Sr or Ba)

These products are also white crystalline solids, less soluble in isopropanol, benzene and in other common organic solvents as compared to products of the type (I). These can be volatilized under reduced pressure. Molecular weights of II could not be determined due to low solubility.

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TABLE 1 — REACTIONS OF $\text{Hf}(\text{OPri})_4 \cdot \text{PriOH}$ WITH ALKALINE EARTH METALS (Mg, Ca, Sr or Ba)

Reactants (g)		Reaction time (hr)	b.p. ($^{\circ}\text{C}/0. \text{ mm}$) and yield (%)	Product	Found (Calc.) (%)		
Metal	$\text{Hf}(\text{OPri})_4 \cdot \text{PriOH}$				Metal	Hf	Isopropoxy
1:4 MOLAR RATIO							
Mg (0.09)	4.63	65	165/0.1 (55)	$\text{Mg}[\text{Hf}_2(\text{OPri})_9]_2$	1.34 (1.33)	39.56 (39.62)	59.21 (59.05)
Ca (0.09)	4.12	165	S. 180-90/0.1 (40)	$\text{Ca}[\text{Hf}_2(\text{OPri})_9]_2$	2.16 (2.20)	39.42 (39.26)	57.96 (58.44)
Sr (0.25)	5.33	10	S. 180-5/0.05 (60)	$\text{Sr}[\text{Hf}_2(\text{OPri})_9]_2$	4.64 (4.66)	38.20 (38.28)	57.70 (57.06)
Ba (0.25)	3.47	20	S. 230-40/0.05 (35)	$\text{Ba}[\text{Hf}_2(\text{OPri})_9]_2$	7.14 (7.17)	37.35 (37.28)	54.95 (55.55)
1:3 MOLAR RATIO							
Mg (0.03)	1.78	60	180/0.1 (60)	$\text{Mg Hf}_3(\text{OPri})_{14}$	1.74 (1.73)	38.58 (38.61)	59.82 (59.65)
Ca (0.08)	2.97	170	S. 190-5/0.05 (50)	$\text{Ca Hf}_3(\text{OPri})_{14}$	2.84 (2.83)	38.01 (38.17)	59.12 (59.98)
Sr (0.19)	3.12	15	S. 210-20/0.1 (40)	$\text{Sr Hf}_3(\text{OPri})_{14}$	6.10 (6.04)	36.87 (36.91)	56.94 (57.05)
Ba (0.26)	2.71	25	S. 250-60/0.05 (30)	$\text{Ba Hf}_3(\text{OPri})_{14}$	9.15 (9.13)	35.82 (35.71)	55.35 (55.16)

The NMR spectra (Varian-60) of I and II exhibited only a single methyl doublet suggesting rapid interchange between bridging and terminal isopropoxy groups.

All the manipulations were carried out under anhydrous conditions.

Hafnium isopropoxide isopropoxide was prepared by ammonia method² from anhydrous HfCl_4 .

Isopropoxy group was estimated by the oxidation of potassium dichromate³. Hafnium, magnesium, calcium, strontium and barium were estimated gravimetrically as HfO_2 , $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$, SrSO_4 and BaSO_4 respectively.

Reaction of magnesium with $\text{Hf}(\text{OPri})_4 \cdot \text{PriOH}$ in molar ratios 1:4 — Magnesium (0.09 g) was dissolved in a solution of $\text{Hf}(\text{OPri})_4 \cdot \text{PriOH}$ (4.63 g) in isopropanol (~ 40 ml) in the presence of HgCl_2 (0.01 g) as catalyst, by refluxing for 65 hr. The white crystals appeared after leaving overnight. Excess of the solvent was removed and the product dried under reduced pressure. The white crystalline solid $\text{Mg}[\text{Hf}_2(\text{OPri})_9]_2$ obtained could be distilled at $165^{\circ}/0.1$ mm in 55% yield.

Analyses of this product and the details of other similar reactions are given in Table 1.

Reaction in molar ratio 1:3 — Magnesium (0.03 g) was dissolved in the solution of $\text{Hf}(\text{OPri})_4 \cdot \text{PriOH}$ (1.78 g) in isopropanol (≈ 40 ml) in presence of HgCl_2 (0.008 g) as catalyst. This mixture was refluxed for about 60 hr. After leaving this solution overnight, a white crystalline product appeared. Excess of the solvent was removed and the residue was dried *in vacuo* to give a white crystalline product, $\text{MgHf}_3(\text{OPri})_{14}$, which could be distilled at $180^{\circ}/0.1$ mm in 60% yield.

Details of this and other similar reactions are given in Table 1.

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Solvent Extraction Behaviour of Tris(oxalato)Co(III) with Long-chain Amines: Part II — Extraction from Hydrochloric & Sulphuric Acid Solutions

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Extraction of tris(oxalato)Co(III) anion into long-chain amines, viz. primene JMT, Amberlite LA-2, tri-*n*-hexylamine and triisooctylamine, in xylene, toluene, CCl_4 or nitrobenzene as diluents from hydrochloric and sulphuric acid solutions has been studied. In dilute solutions of the amines, the extraction follows the order primary > tertiary > secondary from HCl solutions, while the order primary \approx secondary > tertiary is followed for extraction from H_2SO_4 solutions. On the other hand, for concentrated solutions of the same amines (2%), the order of extraction is reversed. The results indicate that salts of Amberlite LA-2 and triisooctylamine are monomers, whereas primene JMT and tri-*n*-hexylamine form aggregates to a certain extent. Nitrobenzene (as diluent) is found to increase the extraction, except in the case of primene JMT whereas carbon tetrachloride decreases the extraction in all the cases.

IN continuation of our work¹ on extraction of tris(oxalato)Co(III) anion by several long-chain amines from essentially perchloric acid solutions,