also observed in both the complexes in the region 900-725. Similar behaviour of the other metal complexes with \( \alpha \)-phenanthroline was observed by Schilt and Taylor\(^2\). The corresponding germanium and tin derivatives, \( B(OMMe)\_3 \) (\( M = \text{Ge and Sn} \)) could not be obtained by the above route\(^3\). Recently, we synthesized \( \text{tris(tributylstan}-\text{nyl)borate} \) by an alternative route\(^4\) involving the reaction

\[
\begin{align*}
\text{C}_6\text{H}_{15} & \\
2\text{B(OH)}_3 + 3(\text{Me}_3\text{Sn})_2\text{O} & \rightarrow 2\text{B(OSnMe)}_3 + 3\text{H}_2\text{O} \quad \ldots \ldots (1)
\end{align*}
\]

Tris(tributyl-germyl)borate could also be synthesized easily by the above method. The corresponding reaction between bis(tributyl-germanium) oxide and boronic acid appears to be quite slow. However, tris(tributyl-germyl)borate \( B(\text{OGeMe})_3 \), could be easily obtained by the interaction between \( \text{Me}_3\text{GeO} \) and boronic acid. This reaction did not appear to proceed at all in case of silicon even after 24 hr of refluxing.

Thus, the reactivity of bis(tributyl-metall)oxide with boronic acid (or oxide) decreases in the following order: \( \text{Sn} > \text{Ge} > \text{Si} \).

B-O-Sn linkage is readily cleaved by chloro-silanes and chloro-germanes and, therefore, the reaction offers a convenient route for synthesis of tris(tributyl-silyl) and -germyl)borates (Eq. 2). The reactions of tris(tributyl-stannyl)borate with trimethylchloro-silane or -germane are exothermic and the products are obtained in quantitative yields. Fractional distillation gave pure products (PMR) as tris(tributyl-silyl) or -germyl)borate distils at a lower temperature than tributyl-tin chloride: \( \text{B(O(SnBu)}_3 + 3\text{Me}_3\text{MCl} \rightarrow \text{B(OMMe)}_3 + 3\text{BuSnCl} \) \ldots \ldots (2) \]

\( M = \text{Si and Ge} \)

IR spectral absorptions of tris(tributyl-silyl, -germyl and -stannyl)borates in the range 3600-400 cm\(^{-1}\) with tentative assignments have been tabulated in Table 1.

The \( v_{as} \) (B-O-M) frequencies showed a gradual decrease in going from silicon (1325 cm\(^{-1}\)) via germanium (1315 cm\(^{-1}\)) to tin (1300-1285 cm\(^{-1}\)). The tentative assignment of \( v_{as} \) (B-O-M) in the range 1305-1285 finds support from the following two observations:

(i) During the preparation of tris(tributylstannyl)borate from bis(tributyltin)oxide, the strong absorption at 740 cm\(^{-1}\) due to \( \nu_{as} \) (Sn-O-Sn) disappears completely and a strong peak appears at 1300-1285 cm\(^{-1}\).

\begin{table}[h]
\centering
\begin{tabular}{ccc}
\hline
\text{Tentative} & \text{B(OSiMe)}_3 & \text{B(OGeMe)}_3 & \text{B(OSnMe)}_3 \\
\text{assignments} & & & \\
\hline
\text{2970 s} & 2975 m & 2975 m & \text{vSiCH}_3 \\
\text{2900 w} & 2920 m & 2920 m & \text{vSiCH}_3 \\
\text{1410 s} & 1400 m & 1400 \text{w(ab)} & \text{vSiCH}_3 \\
\text{1370 vs} & 1345 \text{vs} & 1345 \text{vs(ab)} & \text{vSi(BO)}_3 \\
\text{1325 vs} & 1315 \text{vs} & 1300-1285 \text{vs(br)} & \text{vSi(BO-M)} \\
\text{1257 vs} & 1240 \text{vs} & 1188 s & \text{vSi(BO-M)} \\
\text{883 vs} & \text{883 vs} & \text{883 vs} & \text{vBO-M} \\
\text{842 vs} & 821 \text{vs}, 725 \text{s} & 775-65 \text{vs(br)} & \text{vBO-M} \\
\text{755 vs} & 755, 685 \text{w} & 685 s & \text{vSi(BO-M)} \\
\text{677 w} & 609 \text{vs} & 532 vs & \text{vSi(BO-M)} \\
\text{618 w} & 568 w & 507 w & \text{vSi(BO-M)} \\
\hline
\end{tabular}
\caption{IR DATA OF TRIS(tributyl-silyl, -germyl and -stannyl)borates}
\end{table}
cm⁻¹. In other respects, the spectra of tris(trimethylgermyl)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 trimethylpeak positions in bis(trimethylmetal)oxide and tris(trimethylmetal)borates (where metal = Si, Ge and Sn) are given below:

<table>
<thead>
<tr>
<th>Compound</th>
<th>δM(Hz)</th>
<th>Compound</th>
<th>δM(Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Me₃Si)₃O</td>
<td>-3.6</td>
<td>B(OSiMe₃)₂</td>
<td>-4.8</td>
</tr>
<tr>
<td>(Me₃Ge)₃O</td>
<td>-18.5</td>
<td>B(OGeMe₃)₂</td>
<td>-19.2</td>
</tr>
<tr>
<td>(Me₃Sn)₃O</td>
<td>-14.2</td>
<td>B(OSnMe₃)₂</td>
<td>-12.2</td>
</tr>
</tbody>
</table>

*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(trimethylmetal)oxides.

Reaction between bis(trimethylgermanium)oxide and boric anhydride—Boric anhydride (0.58 g, 0.83 mmole) was added to bis(trimethyl-germanium)oxide (0.611 g, 2.44 mmole). The mixture was kept aside for 1 h; the white solid goes in solution slowly to give bis(trimethylgermyl)borate, which distills at 75°/6 mm (Found: B, 2.61). Tris(trimethylgermyl)borate and tris(trimethylgermyl)germane were distilled before use.

Reaction between tris(tributyl-stannyl)borate and tris(trimethylstannyl)borate were synthesized by the known methods reported earlier. Tris(tributyl-stannyl)borate (2.42 g, 2.61 mmole) was added drop by drop to tris[(tributyl-stannyl)borate; the distillation under reduced pressure. Molecular weights of magnesium and calcium, derived from isopropanol or by sublimation! could not be determined due to low solubility.

**Double Isopropoxides of Hf(IV) with Alkaline Earth Metals**

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Volatile double isopropoxides, M[H₄(OPr)₄]₃ and MΗ₆(OPr)₃, 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 laboratories. 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[H₄(OPr)₄]₃ have been synthesized by dissolving the alkaline earth metals in the solution of hafnium isopropoxide isopropanolate, H[(OPr)₄]₄PriOH in isopropanol in 1:4 molar ratio in accordance with Eq. (1).

\[ M + 4H[(OPr)₄]₄PriOH \rightarrow M[H₄(OPr)₄]₃ + H₂ \uparrow \]  

\( M = \text{Mg, Ca, Sr or Ba} \)

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(OPr)₄PrOH in 1:3 molar ratio in isopropanol in the presence of small amounts of HgCl₂, resulted in the formation of the product, MΗ₄(OPr)₃ (Eq. 2).

\[ M + 3H[(OPr)₄]₄PriOH \rightarrow M[H₄(OPr)₄]₃ + H₂ \uparrow \]  

\( M = \text{Mg, Ca, Sr or Ba} \)

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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