Reactions of Tetra(isopropoxy)hafnium Isopropanol with Semicarbazones

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The reactions of tetra(isopropoxy)hafnium isopropanol, Hf(OPr')4Pr'OH, with monobasic bidentate (LH, L'H and L"H) and dibasic tridentate (L'"H2 and L'""H2) semicarbazones in different molar ratios have been carried out in refluxing benzene. Products of the types Hf(OPr')4-L(n) where n = 1 to 4, Hf(OPr')4-2n(L) where n = 1 to 2, have been obtained. These have been characterised on the basis of elemental analyses, UV and IR spectral studies. The present hafnium complexes show coordination numbers varying from five to eight.

There is a growing interest in the chemistry of transition metal complexes of semicarbazones due to their use as insecticides¹, stabilizers², analytical reagents³,⁴, and biologically active compounds⁵,⁶. Semicarbazones also behave as N, O donors to form a variety of complexes⁷,⁸. In most of the cases semicarbazones react in keto form⁹, but recently it has been shown that they coordinate in enol form after deprotonation¹¹,¹². The recent interest in Hf(IV) chemistry is mainly due to its marked tendency to form compounds with higher coordination numbers.

During the present investigation the reactions of tetra(isopropoxy)hafnium isopropanol with semicarbazones have been studied. The following semicarbazones (I) have been used in the present studies.

\[
\begin{align*}
\text{R}_1 & = \text{C}_6\text{H}_5, \\
\text{R}_2 & = \text{H}; \\
\text{L'H}: & \text{R}_1 = \text{C}_4\text{H}_2\text{O}, \\
& \text{R}_2 = \text{H}; \\
\text{L"H}: & \text{R}_1 = \text{C}_6\text{H}_5, \\
& \text{R}_2 = \text{CH}_3; \\
\text{L'"H}_2: & \text{R}_1 = \text{HOCH}_2\text{H}_4, \\
& \text{R}_2 = \text{H}; \\
\text{L'""H}_2: & \text{R}_1 = \text{HOCH}_2\text{H}_4. \\
\end{align*}
\]

HfCl₄ (Alpha product) was used without any further purification for the synthesis of tetra(isopropoxy)hafnium isopropanol. Solvents were dried by the standard methods¹³. Semicarbazones were synthesised by the condensation of semicarbazide hydrochloride with benzaldehyde, furfuraldehyde, acetophenone, salicylaldehyde and vanillin. All experimental manipulations were carried out under strictly anhydrous conditions.

Hafnium was estimated gravimetrically as HfO₂. Isopropanol was estimated by the literature method¹⁵. Nitrogen was estimated by Kjeldahl's method. Infrared spectra of the compounds were recorded in nujol-mull on a Perkin-Elmer 621 spectrophotometer in the range 4000-200 cm⁻¹ using a cesium iodide cell. Electronic spectra of the complexes were recorded on a Perkin-Elmer 554 spectrophotometer using dimethyl sulfoxide as a solvent. Nuclear magnetic resonance spectra of complexes could not be recorded due to their insufficient solubilities.

Reactions of Hf(IV) complexes

Reactions of tetra(isopropoxy)hafnium isopropanol with monobasic semicarbazones were carried out in 1:1, 1:2, 1:3 and 1:4 molar ratios while reactions of dibasic semicarbazones were carried out in 1:1 and 1:2 molar ratios. The results are summarised in Table 1.

Tetra(isopropoxy)hafnium isopropanol was dissolved in benzene and different semicarbazones were added in appropriate molar ratios. The reaction mixture was refluxed and the progress of reaction was followed by estimating the liberated isopropanol in the azeotrope. The excess of solvent was removed under reduced pressure, products were recrystallised from benzene-hexane mixture (10:1) and finally dried at 0.4 mm/30°C/2 hr.

The reactions of tetra(isopropoxy)hafnium isopropanol with monobasic semicarbazones were carried out in stoichiometric ratios 1:1 to 1:4 molar ratios can be represented by the following equation,

\[
\text{Hf(OPr')}_4\text{Pr'OH} + n\text{LH} \rightarrow \text{Hf(OPr')}_4 \cdot n(\text{L}) + (n + 1)(\text{Pr'OH})
\]

where \(n = 1, 2, 3 \) and 4; \(L = \text{L'H}, \text{L"H} \) and \(L'"H \)

The replacement of three moles of the isopropoxy group of Hf(OPr')₄ was quite facile; however, the replacement of fourth isopropoxy group was achieved only on prolonged refluxing (~ 100 hr) in benzene.

The reactions of tetra(isopropoxy)hafnium isopropanol with dibasic semicarbazones (LH₂) in stoichiometric ratios 1:1 and 1:2 can be represented by the following equation,

\[
\text{Hf(OPr')}_4\text{Pr'OH} + n\text{LH}_2 \rightarrow \text{Hf(OPr')}_4 \cdot 2n(\text{L}) + (2n + 1)(\text{Pr'OH})
\]

where \(n = 1, 2; \text{LH}_2 = \text{L'"H}_2 \) and \(\text{L'""H}_2 \)

Most of the complexes are light yellow solids and insoluble in common organic solvents probably due to polymerization. The physical properties and elemental analyses of the compounds are given in Table 1.

In the infrared spectra of ligands the bands observed
Table 1 — Characterisation Data of Hafnium Complexes

<table>
<thead>
<tr>
<th>Molar ratio of reactants</th>
<th>Refluxing time (hr)</th>
<th>Product, colour, m.p. (°C)</th>
<th>Found (Calc.), %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>PrOH Hf N</td>
<td>PrOH Hf N</td>
</tr>
<tr>
<td>1:1</td>
<td>6</td>
<td>Hf(OPr)₂L₂, White, 201-5</td>
<td>0.18 34.29 7.85</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>Hf(OPr)₂L₂, White, 230-33</td>
<td>(0.19) (34.46) (8.11)</td>
</tr>
<tr>
<td>1:2</td>
<td>14</td>
<td>Hf(OPr)₂L₃, White, 218-23</td>
<td>0.24 23.16 13.17</td>
</tr>
<tr>
<td></td>
<td>93</td>
<td>HfL₄, Light yellow, 236-38</td>
<td>0.20 20.67 19.80</td>
</tr>
<tr>
<td>1:1</td>
<td>5</td>
<td>Hf(OPr)₂L₄, Light yellow, 175-79</td>
<td>(0.19) (35.14) (8.27)</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>Hf(OPr)₂L₅, Light yellow, 207-11</td>
<td>0.14 29.36 13.40</td>
</tr>
<tr>
<td>1:3</td>
<td>12</td>
<td>Hf(OPr)₂L₆, Light yellow, 198-202</td>
<td>(0.16) (29.70) (13.98)</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>HfL₇, Yellow, 220-24</td>
<td>0.17 22.95 20.01</td>
</tr>
<tr>
<td>1:1</td>
<td>8</td>
<td>Hf(OPr)₂L₇, Brown, 280-85</td>
<td>0.17 32.89 7.46</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>Hf(OPr)₂L₈, Brown, 300</td>
<td>(0.18) (33.55) (7.89)</td>
</tr>
<tr>
<td>1:3</td>
<td>22</td>
<td>Hf(OPr)₂L₉, Brown, &gt;300</td>
<td>0.20 22.88 16.06</td>
</tr>
<tr>
<td></td>
<td>95</td>
<td>HfL₆, Dark Brown, &gt;300</td>
<td>0.24 19.80 18.50</td>
</tr>
<tr>
<td>1:1</td>
<td>10</td>
<td>Hf(OPr)₂L₁₀, Yellow, 249-54</td>
<td>(0.17) (37.39) (8.51)</td>
</tr>
<tr>
<td></td>
<td>34</td>
<td>HfL₇, Yellow, 285-90</td>
<td>0.15 32.98 15.29</td>
</tr>
<tr>
<td>1:1</td>
<td>8</td>
<td>Hf(OPr)₂L₁₀, Light yellow, 210-15</td>
<td>(0.16) (33.49) (15.77)</td>
</tr>
<tr>
<td></td>
<td>38</td>
<td>HfL₈, Light yellow, 224-29</td>
<td>0.31 29.72 13.66</td>
</tr>
</tbody>
</table>

in the regions 1735-1670, 1650-1615 and 1595-1470 cm⁻¹ are assigned to ν(C=O) (amide-I), ν(C=N) (azomethine) and ν(C=N + δNH) (amide-II) vibrations respectively. The spectra of the complexes exhibit no change in the frequencies of first two bands, indicating thereby the non-coordination of carbonyl oxygen and azomethine nitrogen to the hafnium atom. The presence of amide-I band in the spectra of the complexes excludes the possibility of the presence of enol form of these ligands even in the complexes. The bonding of secondary amide-nitrogen to metal atom after deprotonation is indicated by the absence of the band due to νNH vibration (3360-3260 cm⁻¹) in the spectra of the complexes. However, there is no significant shifting of the 1595-1470 cm⁻¹ band (amide-II vibration) because of the presence of NH₂ group which along with the carbonyl group gives the amide-II vibration.

The ν(NH₂) mode which occurs in the semicarbazones in the region 3470-3400 cm⁻¹ shows a downward shift of 100-50 cm⁻¹ in complexes indicating the participation of the group in coordination, resulting in the formation of a four-membered chelate ring. The four-membered chelate rings in the copper complex of semicarbazones have been reported earlier by Gingras et al.¹⁶. In the infrared spectra of dibasic semicarbazones, ν(OH) (hydrogen bonded) (phenolic) vibration appears in the region 3180-3150 cm⁻¹. This band disappears in the spectra of corresponding complexes indicating bonding of phenolic oxygen to the hafnium atom, resulting in the formation of seven-membered chelates. The shift of ν(C−O) (phenolic) band occurring at 1320-1245 cm⁻¹ in these ligands to higher frequencies in the complexes (1365-1330 cm⁻¹) confirms the metal-oxygen (phenolic) bonding¹⁷.

New bands occurring in the regions 590-570 and 470-400 cm⁻¹ in the complexes can be assigned tentatively to ν(Hf-N)¹⁸,¹⁹ and ν(Hf-O)²⁰-²² vibrations. The isopropoxy group shows its characteristic bands in the regions 1390-1365, 1170-1160 and 1330-1120 cm⁻¹.
The electronic spectra of the complexes recorded in dimethyl sulphoxide show a charge-transfer band in the region 35300-33700 cm\(^{-1}\).

On the basis of the elemental analyses and spectral evidences, structures II and III are tentatively proposed for the complexes with monobasic (L, L' H, L'H) and dibasic (L''H\(_2\), L'''H\(_2\)) ligands respectively. Hafnium exhibits coordination numbers 5, 6, 7 and 8 in the complexes, Hf(OPr\(_3\))\(_{4-d}\)L\(_d\)as n varies from 1 to 4.

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References
1 Samuel I G & Herbert L G H, U S Pat Appl, 2 (1945) 479, 574.