NOTES

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References


Imido Derivatives of Zirconium(IV)

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Various imido derivatives of zirconium(IV) have been obtained by reacting zirconium(IV) isopropoxide with acetamide, benzamide and nicotinamide in different stoichiometric ratios in anhydrous benzene under reflux. These imido derivatives can be represented by the general formula (PrO)_4-Zr(NHCOR)_n where n = 1-4 and R = CH_3, C_6H_5, C_6H_4N. These complexes seem to be highly polymeric as indicated by their insoluble nature in common organic solvents. The complexes have been characterised on the basis of elemental analysis and infrared spectral data.

Metal alkoxides have been used as the starting materials for the preparation of a variety of metal organic compounds. Recently a number of complexes of alkyl halides and alkoxides of tin(IV) with amides have been reported. We report here the results of our study on the reactions of zirconium(IV) isopropoxide with acetamide, benzamide and nicotinamide on which no previous work appears to have been done.

The reactions of zirconium isopropoxide with the amides in different molar ratios (1:1, 1:2, 1:3 and 1:4) in anhydrous benzene under reflux yielded mixed imido isopropoxy/imido derivatives, (PrO)_3 Zr(NHCOR), (PrO)_2 Zr(NHCOR)_2, (PrO)Zr(NHCOR)_3 and Zr(NHCOR)_4 respectively (where R = CH_3, C_6H_5, C_6H_4N) in quantitative yields (85-95%) (Eq. 1).

\[ \text{Zr}({\text{OPr}})_4 + \text{PrOH} + n\text{RCONH}_2 \rightarrow \text{Zr}({\text{OPr}})_4 \cdot n\text{RCONH}_2 \]

The progress of reaction was checked by estimating the liberated isopropanol at different intervals of time. In the case of reaction of the zirconium alkoxide and benzamide in molar ratio 1:4 it was observed that the release of one molecule of isopropanol was very rapid. Further release of isopropanol was slow and increased with time in a regular manner.

It therefore seems likely that on mixing Zr(OPr)_4, PrOH and amide a complex Zr(OPr)_4 + nRCONH_2 is formed immediately releasing one molecule of isopropanol. This is followed by substitution of isopropanoxy group(s) by imido group(s) resulting in the formation of mixed imido isopropanoxy and finally imido derivatives of zirconium(IV) according to the following mechanism:

All the products are colourless solids. They rapidly hydrolyse in air like the parent zirconium(IV) isopropoxide. They are virtually insoluble in common organic solvents. The high insolubility of these derivatives suggests their polymeric nature. They are presumably polymeric due to intermolecular bridging of isopropanoxy group(s) or inter/intramolecular hydrogen bonding of NH group(s). Attempts to distil these compounds under reduced pressure were unsuccessful. Polymeric metal-alkoxides are usually solids of low volatility. The involatile nature of these derivatives can be due to their polymeric nature as indicated by their insolubility in common organic solvents and the presence of the bridging isopropanoxy group(s) revealed in the IR spectra (in case of imido-isopropanoxy derivative). Some of the complexes have characteristic melting points (Table 1).

In the complexes of various metal halides with amides it is generally observed that metal is bonded through oxygen of the carbonyl group. However, in the present study the synthetic and infrared studies indicate that the zirconium atom is bonded to nitrogen atom of the amides. The bond between zirconium and nitrogen appears to be fairly strong as indicated by the fact that the reverse reaction between zirconium(IV) imido derivatives and isopropanol does not take place even on prolonged refluxing.
TABLE 1 — REACTIONS OF ZIRCONIUM(IV) ISOPOXIDE WITH ACETAMIDE, BENZAMIDE AND NICOTINAMIDE IN ANHYDROUS BENZENE

<table>
<thead>
<tr>
<th>Molar ratio Zr(PrO)3:PrOH:OH</th>
<th>Reflux time (hr)</th>
<th>Product</th>
<th>PrOH(g)</th>
<th>Found (calc.)</th>
<th>m.p. (°C)</th>
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</thead>
<tbody>
<tr>
<td>Zr(PrO)3Zr(NHCOCH3)</td>
<td>1:1 12</td>
<td>(PrO)2Zr(NHCOCH3)</td>
<td>0.42</td>
<td>27.84</td>
<td>4.25</td>
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<tr>
<td></td>
<td></td>
<td>(PrO)Zr(NHCOCH3)</td>
<td>0.40</td>
<td>28.20</td>
<td>8.50</td>
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<td></td>
<td>1:2 14</td>
<td>(PrO)2Zr(NHCOCH3)</td>
<td>0.41</td>
<td>28.04</td>
<td>8.60</td>
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<tr>
<td></td>
<td></td>
<td>(PrO)Zr(NHCOCH3)</td>
<td>0.99</td>
<td>28.83</td>
<td>12.72</td>
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<tr>
<td></td>
<td>1:3 20</td>
<td>(PrO)Zr(NHCOCH3)</td>
<td>0.99</td>
<td>28.13</td>
<td>12.95</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zr(NHCOCH3)</td>
<td>1.63</td>
<td>27.74</td>
<td>17.12</td>
</tr>
<tr>
<td></td>
<td>1:4 20</td>
<td>Zr(NHCOCH3)</td>
<td>1.64</td>
<td>28.22</td>
<td>17.32</td>
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<tr>
<th>Molar ratio Zr(PrO)3:PrOH:OH</th>
<th>Reflux time (hr)</th>
<th>Product</th>
<th>PrOH(g)</th>
<th>Found (calc.)</th>
<th>m.p. (°C)</th>
</tr>
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<tr>
<td>Zr(PrO)3Zr(NHCONC6H5)</td>
<td>1:1 10</td>
<td>(PrO)2Zr(NHCONC6H5)</td>
<td>0.35</td>
<td>22.74</td>
<td>3.66</td>
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<tr>
<td></td>
<td></td>
<td>(PrO)Zr(NHCONC6H5)</td>
<td>0.78</td>
<td>20.64</td>
<td>6.35</td>
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<tr>
<td></td>
<td>1:2 16</td>
<td>(PrO)2Zr(NHCONC6H5)</td>
<td>0.78</td>
<td>20.30</td>
<td>6.20</td>
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<td>(PrO)Zr(NHCONC6H5)</td>
<td>0.66</td>
<td>17.72</td>
<td>8.23</td>
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<tr>
<td></td>
<td>1:3 16</td>
<td>Zr(NHCONC6H5)</td>
<td>0.66</td>
<td>17.78</td>
<td>8.23</td>
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<tr>
<td></td>
<td>1:4 16</td>
<td>Zr(NHCONC6H5)</td>
<td>0.45</td>
<td>15.79</td>
<td>9.82</td>
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<td>(0.48)</td>
<td>(15.96)</td>
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<table>
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<tr>
<th>Molar ratio Zr(PrO)3:PrOH:OH</th>
<th>Reflux time (hr)</th>
<th>Product</th>
<th>PrOH(g)</th>
<th>Found (calc.)</th>
<th>m.p. (°C)</th>
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<tr>
<td>Zr(PrO)3Zr(NHCONC6H5)</td>
<td>1:1 10</td>
<td>(PrO)2Zr(NHCONC6H5)</td>
<td>0.46</td>
<td>23.80</td>
<td>7.16</td>
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<td>(PrO)Zr(NHCONC6H5)</td>
<td>0.46</td>
<td>23.41</td>
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<td></td>
<td>1:2 16</td>
<td>(PrO)2Zr(NHCONC6H5)</td>
<td>0.43</td>
<td>20.76</td>
<td>12.36</td>
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<td></td>
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<td>(PrO)Zr(NHCONC6H5)</td>
<td>0.43</td>
<td>20.79</td>
<td>12.39</td>
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<tr>
<td></td>
<td>1:3 28</td>
<td>(PrO)Zr(NHCONC6H5)</td>
<td>0.74</td>
<td>17.70</td>
<td>16.34</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>(0.75)</td>
<td>(17.75)</td>
<td>(16.35)</td>
</tr>
<tr>
<td></td>
<td>1:4 30</td>
<td>Zr(NHCONC6H5)</td>
<td>0.88</td>
<td>15.80</td>
<td>19.46</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>(0.88)</td>
<td>(15.84)</td>
<td>(19.43)</td>
</tr>
</tbody>
</table>

Amides in general exhibit structurally two resonance forms, lactam(I) and lactim(II).

Free primary amides show two strong, usually broad bands (due to Fermi resonance) around 3365-60 and 3190-60 cm⁻¹ due to antisymmetric and symmetric stretching vibrations respectively of the NH group. These bands appear as weak and broad absorptions in the present imido complexes in the regions 3365-40 and 3170-40 cm⁻¹. Weak absorption indicates replacement of one of the hydrogen atoms of the NH₂ group resulting in the formation of imido derivatives. The observed lowering in νN-H and its broad nature may be due to association involving hydrogen bonding and complexation (C = O...NH) in the insoluble nature of these derivatives may in part be due to hydrogen bonding referred to above.

Comparison of the spectra of the free amides and the imido derivatives show that the position and nature of νC=O bands are similar to those of parent amide(s). This indicates non-involvement of lactim(II) form in the reactions and suggests that in these imido derivatives substitution is at the NH₂ group of form I.

The strong to medium intensity bands with a negative shift in the regions 1565-50 (a), 1620-1595 (b) and 1610-1586(n) and 1370-65 (a), 1395 (b) and 1390 cm⁻¹ (n) can be assigned to NH bending vibrations and C–N stretching vibrations in the complexes of acetamide (a), benzamide (b) and nicotinamide (n), respectively.

Bands of strong to medium intensity observed in the mixed isoproxy imido complexes in the regions 1150–1135 and 1022–1005 cm⁻¹ can be assigned to the bridging and the terminal isoproxy group vibrations, respectively. However, in the complex of nicotinamide it is difficult to assign the bands in the region 1020–25 cm⁻¹ exclusively to the bridging isoproxy group(s) as this is the region where ring breathing vibrations of the pyridine also occur. New bands below 600 cm⁻¹ in the complexes may be due to νZr–O and νZr–N modes.

The ν M–N vibrations in the case of Schiff base complexes of titanium and zirconium have been found in the region 600–500 cm⁻¹. Vibrations around 620 cm⁻¹ can also be due to in-plane bending of the O=C–N group and out-of-plane bending of the C=O groups. The low frequency modes observed thus could not be assigned properly.

All the preparative work was carried out in strictly dry atmosphere because of the moisture-sensitive nature of the compounds. Benzene, isopropanol and other solvents were dried as reported earlier. Zirconium (IV) isopropanoxide supplied by ‘Alfa’ Chemicals was recrystallised from benzenone. Acetamide (BDH) was distilled under reduced pressure. Benzamide and nicotinamide (BDH) were recrystallised from ethanol and dried in vacuo for 4 hr.
IR spectra of acetamide complexes were recorded on Specord 75 in nujol phase whereas those of other compounds were recorded on a perkin-Elmer grating infrared spectrophotometer model 577 in KBr.

The imido and imidoisopropoxy derivatives of zirconium(IV) were obtained by heating Zr(OPr)₄, Pr₄OH with amide in benzene under reflux. Typically, acetamide (0.249 g) was added to Zr(OPr)₄, Pr₄OH (1.37 g) in dry benzene (70 ml). The mixture was refluxed for 12 hr, during which time liberated isopropanol was collected in the form of a benzene-isopropanol azoetope at 72°C. The excess of benzene was removed from the insoluble product by fractionalation at 80°C. The white insoluble product obtained was washed first with ethanol (3 × 1.5 ml) to remove traces of unreacted acetamide, if any, present and finally washed with dry benzene (3 × 2 ml). The complex was dried to constant weight under reduced pressure (10⁻² torr) at room temperature. [Zr(OPr)₄], Zr(NHCOCH₃)₂, yield 90%. [Found: Zr, 27.84; N, 4.25. Calc. : Zr, 27.87; N, 4.97%]. Isopropanol in the azoetope: [Found: 0.420 g; Calc. for replacement of two moles, 0.423 g]. The details of other reactions are summarised in Table 1.

Zirconium was determined after ignition to dioxide and nitrogen was determined by the kjeldahl's method. The imido and imidoisopropoxy derivatives of zirconium(IV) were obtained by heating Zr(OPr)₄, Pr₄OH with amide in benzene under reflux. Typically, acetamide (0.249 g) was added to Zr(OPr)₄, Pr₄OH (1.37 g) in dry benzene (70 ml). The mixture was refluxed for 12 hr, during which time liberated isopropanol was collected in the form of a benzene-isopropanol azoetope at 72°C. The excess of benzene was removed from the insoluble product by fractionalation at 80°C. The white insoluble product obtained was washed first with ethanol (3 × 1.5 ml) to remove traces of unreacted acetamide, if any, present and finally washed with dry benzene (3 × 2 ml). The complex was dried to constant weight under reduced pressure (10⁻² torr) at room temperature. [Zr(OPr)₄], Zr(NHCOCH₃)₂, yield 90%. [Found: Zr, 27.84; N, 4.25. Calc. : Zr, 27.87; N, 4.97%]. Isopropanol in the azoetope: [Found: 0.420 g; Calc. for replacement of two moles, 0.423 g]. The details of other reactions are summarised in Table 1.

Zirconium was determined after ignition to dioxide and nitrogen was determined by the kjeldahl's method. Isopropanol was estimated by oxidation with normal sulphuric acid and back titration of the excess dichromate iodometrically.

Thanks are due to Prof. R. N. Kapoor, Chemistry Department, University of Delhi, for helpful discussions. Thanks are also due to Prof. R. C. Kapoor, Head, Department of Chemistry, University of Jodhpur, for providing laboratory facilities and the UGC, New Delhi for a research fellowship to one of us (KRN).

References


Synthesis & Characterisation of New Molybdenum(VI) Complexes

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Some new molybdenum (VI) complexes of triazene 1-oxides of composition MoO₂L₂ are reported. Evidences suggest cis-dioxo structure for them.

The recognition of molybdenum as an active site in many biosystems has given a new impetus to the synthesis and study of new molybdenum compounds in different oxidation states. During the course of our study of the transition metal complexes of triazene 1-oxides (I, X = H, OCH₃, OC₂H₅), new molybdenum compounds were synthesised and studied using these ligands, since very little work is reported on molybdenum complexes. For convenience the ligand system (I) has been abbreviated as (R-C₆H₄X) and the complex as (R-C₆H₄X)₂MoO₄.

The ligands used here were synthesised by a general method. The molybdenum complexes were prepared as follows: one mol equivalent of molybdenum (ammonium molybdate) was dissolved in minimum quantity of water by adding a few drops of ammonia solution. This was added to a clear solution of 2 mol equivalent of ligand in methanol with stirring. The solution was acidified with conc. HNO₃ to pH 3-4. An orange coloured solution was formed which on cooling gave yellow-orange crystals. The crude product was recrystallised from methanol and dried in vacuo. Characterisation data of the complexes are presented in Table 1.

All the molybdenum complexes are stable in air and soluble in many organic solvents. These complexes are diamagnetic and monomeric in methanol