Tetrameric Zirconium(IV) Complexes Obtained from the Reactions of Oxozirconium(IV) Chloride & N-Furfurylidenearylamines

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Oxozirconium(IV) chloride reacts with the bidentate Schiff bases (SB), N-furfurylidenearylamines, to form compounds with high melting points (> 250°C). The analytical data along with the infrared and thermogravimetric measurements show their formulation as tetramers of the type \([Zr_4(OH)_{12}(H_2O)_{12-2n}(SB)_n]Cl_4\) where \(n = 1\) for N-furfurylidene-o-toluidine, N-furfurylidene-m-toluidine, N-furfurylidene-p-toluidine, and N-furfurylidene-o-anisidine, and \(n = 2\) for N-furfurylidene-o-anilide, N-furfurylidene-p-anisidine and N-furfurylidene-p-phenetidine in the solid state. The structures appear to be derived from the basic tetrameric dodecahedral structure of the parent compound ZrOCl₂·8H₂O, formulated as \([Zr_4(OH)_{12}(H_2O)_{16}]Cl_8\).

The thermogravimetric studies indicate formation of complex intermediate species after loss of water molecules and the Schiff base ligands with increase in temperature.

Selbin and Holmes¹ have observed metal-oxygen multiple bond stretching frequency in the range 900-1100 cm⁻¹ for MoO³⁺, MoO₂⁻, MoO₃⁺, VO₂⁻, VO₂²⁻ and UO₂²⁺, but found no evidence for the existence of TiO²⁺ or ZrO²⁺ mononuclear species in certain so-called tita­nyl or zirconyl compounds. Some polymeric form of zirconium(IV) predominates, both in solution and in solid state, as is clear from the NMR measurements of hydration numbers in solution² and the X-ray crystal structure of ZrOCl₂·8H₂O in solid state³,⁴, which is actually a tetramer \([Zr_4(OH)_{12}(H_2O)_{16}]Cl_8\). In spite of this convincing proof, a number of workers have reported that ZrOCl₂·8H₂O forms monomeric complexes⁵,⁶ with various ligands (L) of the type ZrOCl²⁻·nL. Monomeric complexes of pyridine N-oxide⁷, quinoline N-oxide⁸ and phenanthroline N-oxide⁹ were also reported, where even a weak IR band at 950-980 cm⁻¹ was assigned to v(Zr = O). Several tridentate Schiff base ligands (H₂L) were also shown to form monomeric ZrO(HL)₂ type complexes¹⁰⁻¹³, the infrared spectra of which showed a medium intensity band at 889-920 cm⁻¹ attributed to v(Zr = O). This assignment is surprising in view of the fact that X-ray crystallographic evidence shows the absence of Zr = O group in the starting material, viz., ZrOCl₂·8H₂O, of these oxozirconium(IV) complexes.

This paper reports complexes synthesised by the reaction of ZrOCl₂·8H₂O and the bidentate Schiff bases, N-furfurylidenearylamines, obtained by the condensation of aromatic amines (aniline or substituted anilines) and freshly distilled 2-furan carboxaldehyde. Interest in this type of ligand arises due to the fact that furan derivatives undergo interesting reaction with electrophilic and nucleophilic reagents¹⁴ and that 2-furan carboxaldehyde behaves as a true aromatic aldehyde. An earlier report¹⁵ from this laboratory reported the complexes of these bidentate Schiff bases with dioxouranium(VI). The complexes prepared in the present study are of the type \([Zr_4(OH)_{12}(H_2O)_{12-2n}(SB)_n]Cl_4\) where \(n = 1\) for SB (structure I) = N-furfurylidene-o-toluidine (FoTol), N-furfurylidene-m-toluidine (FmTol) and N-furfurylidene-o-anisidine (FoAnis); and \(n = 2\) for SB = N-furfurylidene-p-anisidine (FpAnis) and N-furfurylidene-p-phenetidine (FpPhen).

\[
R.H = N-\text{Me; } o-, m-, p- \text{Me; } o-, p- \text{OMe; } P- \text{OEt.}
\]

Materials and Methods
ZrOCl₂·8H₂O (Riedel) was of reagent grade and used as supplied. 2-Furancarboxaldehyde (BDH) was distilled prior to its use. The aromatic amines were BDH reagent grade chemicals and used as such. The C, H and N microanalyses were carried out on a Carlo Elba analyser at CDRI, Lucknow. Zr was determined gravimetrically as ZrO₂ after decomposition of the complexes with HNO₃ and then heating at 1000°C in an electric muffle furance up to...
constant weight. Chloride was estimated by decomposition of the complex by oxidative fusion with Na₂O₂ and NaOH, followed by extraction with water, acidification by dil HNO₃ and finally precipitation as AgCl by addition of AgNO₃ solution. The IR spectra were recorded as KBr disc or polyethylene pellets in 4000-200 cm⁻¹ region using a Perkin Elmer 983 instrument at RSIC, Madras.

The thermal measurements in static air were carried out using a Shimadzu DT-30 thermal analyser, which records TG, DTG and DTA simultaneously. The rate of heating was 10°C min⁻¹. Melting points were taken in sealed capillaries and are uncorrected.

**Synthesis of complexes**

All the complexes were prepared by a general method by the reaction of ZrOCl₂.8H₂O with the Schiff bases taken in appropriate stoichiometric ratio. A typical method of synthesis is detailed below for the N-furfurylideneaniline complex.

Aniline (0.37 ml, 4 mmol) and freshly distilled 2-furancarboxaldehyde (furfural) (0.38 ml, 4 mmol) were condensed in a mixture of dry acetone (5 ml) and triethylorthoformate (TEOF) (5 ml) by stirring for 30 min in an ice-bath. To this red Schiff base formed in situ, was added a solution of ZrOCl₂.8H₂O (0.64 g, 2 mmol) in acetone and TEOF (5 ml), and stirring continued for further 15 min, when the colour changed to red-brown, and a solid was formed. Stirring was continued for a further period of 60 min in order to ensure the completion of the reaction. The red-brown solid was collected on a glass-frit, washed repeatedly with small aliquots of acetone followed by ether and dried in vacuo.

**Results and Discussion**

The new complexes listed in Table 1 were obtained by the interaction of ZrOCl₂.8H₂O in acetone (to which triethylorthoformate was added for dehydration) and the Schiff base under ice-cold condition. All of them are red-brown solids, with melting points > 250°C. Detailed and repeated analysis of the compounds prepared with varying M:SB ratios provided no evidence for the formation of simple, monomeric adducts. The analytical data of the complexes correspond to the formula based on the structure of tetrameric [Zr₄(OH)₈(H₂O)₁₆]Cl₄ (structure II) of ZrOCl₂.8H₂O, the starting material for all the reported coordination complexes. However, the analytical data show the Zr:Cl ratio to be 1:1 and not 1:2 as in [Zr₄(OH)₈(H₂O)₁₆]Cl₄, indicating that at some stage of complexation, possibly four water molecules are deprotonated to give four extra –OH groups yielding compounds of the type [Zr₄(OH)₁₂(H₂O)₁₀]Cl₄, which possess presumably a tetrameric structure with eight coordination around each Zr atom. From this basic structure either 2 or 4 water molecules are replaced by 1 or 2 bidentate Schiff base ligand forming the observed complexes [Zr₄(OH)₁₂(H₂O)₁₀–₂n(SB)ₙ]Cl₄ where n = 1 or 2.

The concentration of H⁺ in acetone and triethylorthoformate solution of ZrOCl₂.8H₂O (~1 mmol) was 1.7 M, the pKₐ of the Schiff base, N-furfurylideneaniline (~2 mmol) in acetone was 4.23; after complexation and separation of the coordination

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula (Mol. wt)</th>
<th>Found (Calc.), %</th>
</tr>
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<tbody>
<tr>
<td>Zr₄(OH)₁₂(H₂O)₁₀[FA]₂Cl₄</td>
<td>Zr₄C₁₂H₂₂N₂O₁₆Cl₄ (1197.25)</td>
<td>Zr 29.9 C 21.9 H 3.8 N 1.9 Cl 11.6</td>
</tr>
<tr>
<td>Zr₄(OH)₁₂(H₂O)₁₀[FTol]Cl₄</td>
<td>Zr₄C₁₂H₂₂N₂O₁₆Cl₄ (1076.11)</td>
<td>Zr 33.2 C 13.0 H 4.1 N 1.1 Cl 12.5</td>
</tr>
<tr>
<td>Zr₄(OH)₁₂(H₂O)₁₀[FmTol]Cl₄</td>
<td>Zr₄C₁₂H₂₂N₂O₁₆Cl₄ (1076.11)</td>
<td>Zr 33.4 C 12.7 H 3.8 N 1.2 Cl 12.7</td>
</tr>
<tr>
<td>Zr₄(OH)₁₂(H₂O)₁₀[FpTol]Cl₄</td>
<td>Zr₄C₁₂H₂₂N₂O₁₆Cl₄ (1076.11)</td>
<td>Zr 33.9 C 13.4 H 4.0 N 1.3 Cl 13.2</td>
</tr>
<tr>
<td>Zr₄(OH)₁₂(H₂O)₁₀[FpAnis]Cl₄</td>
<td>Zr₄C₁₂H₂₂N₂O₁₆Cl₄ (1092.11)</td>
<td>Zr 33.9 C 13.4 H 4.0 N 1.3 Cl 13.2</td>
</tr>
<tr>
<td>Zr₄(OH)₁₂(H₂O)₁₀[FpPhen]Cl₄</td>
<td>Zr₄C₁₂H₂₂N₂O₁₆Cl₄ (1257.29)</td>
<td>Zr 29.9 C 22.2 H 3.9 N 1.9 Cl 11.3</td>
</tr>
<tr>
<td>Zr₄(OH)₁₂(H₂O)₁₀[FpPhen]Cl₄</td>
<td>Zr₄C₁₂H₂₂N₂O₁₆Cl₄ (1285.35)</td>
<td>Zr 28.1 C 24.1 H 3.9 N 1.9 Cl 11.4</td>
</tr>
</tbody>
</table>

*All compounds are red-brown in colour; †M.P. of all compounds > 250°C;
‡Abbreviations used: FA = N-furfurylideneaniline, FTol = N-furfurylidenetoluidine, FAnis = N-furfurylideneanisidine, FPhen = N-furfurylidenephenetidine; o, m and p stand for ortho, meta and para.
complex the pH of the solution was 2.74 (corrections were made for pH determination in non-aqueous solvents). The pH-metric titration of 50 cm$^3$ 0.01 M ZrOCl$_2$.8H$_2$O in the above solvent against the Schiff base (0.1 M) in acetone showed an inflexion point at a mean volume of 2.5 cm$^3$ corresponding to Zr:SB ratio of 2:1 in the complex formed in solution phase. These observations show that the reactions presumably proceed as follows:

\[
\begin{align*}
\text{Acetone} & \rightarrow [\text{Zr}_4(\text{OH})_{12}]^8\text{Cl}_4^{+} \\
(\text{H}_2\text{O})_{12} & + 4\text{HCl} \\
[\text{Zr}_4(\text{OH})_{12}](\text{H}_2\text{O})_{12} & |\text{Cl}_4 + n\text{SB} \rightarrow [\text{Zr}_4(\text{OH})_{12}](\text{H}_2\text{O})_{12} - 2n(\text{SB})_n + 2n\text{H}_2\text{O}
\end{align*}
\]

Similar tetrameric coordination complexes of zirconium(IV) with bidentate Schiff bases seem to have been extracted in the liquid-liquid extraction of zirconium(IV) by N-salicylidene-p-toluidine and N-salicylidene-p-phenetidine in benzene as the diluent.

On the basis of chemical evidence alone, Zaitsev has shown that the freshly prepared α-hydroxide, Zr$_4(\text{OH})_{8}^8$ (OH)$_8^8$ (H$_2$O)$_8$ contained a four-membered ring of Zr atoms where adjacent pairs of Zr atoms were joined by double hydroxo bridge giving rise to a structure analogous to the structure of ZrOCl$_2$.8H$_2$O which is actually $[^4\text{Zr}(\text{OH})_{8}^8](\text{H}_2\text{O})_{16}^8$ (structure II). The Schiff base complexes of ZrOCl$_2$.8H$_2$O synthesised presently seem to be intermediate between the $[\text{Zr}_4(\text{OH})_{8}^8](\text{H}_2\text{O})_{16}^8$ and the α-hydroxide, Zr$_4(\text{OH})_{8}^8$ (OH)$_8^8$ (H$_2$O)$_8$ in that they contain four chloride ions in addition to the ligands joined to the Zr atoms in place of either 2 or 4 H$_2$O molecules, yielding complexes of the type $[\text{Zr}_4(\text{OH})_{12}](\text{H}_2\text{O})_{12} - 2n(\text{SB})_n|\text{Cl}_4$ where $n = 1$ or 2 (structure III). These complexes are highly insoluble in common organic solvents precluding the measurements of conductivities and molecular weights and growth of single crystals for X-ray structure determination. IR spectra in the range 4000-200 cm$^{-1}$ of the parent ZrOCl$_2$.8H$_2$O and the synthesised complexes are identical except for the extra bands observed in the latter cases corresponding to the various vibrational modes of the ligands. In none of the cases, did we find a band in the region 835-925 cm$^{-1}$ corresponding to ν(Zr-O), as has been reported by some workers indicating clearly the absence of the ZrO$_2^+$ moiety.

In these complexes, a band is located at ~1150 cm$^{-1}$ due to the bending mode, δ(Zr-O-H)18,19. The broad but strong band centered at 3,400 cm$^{-1}$ in all the complexes is assigned to the ν(OH) of both the coordinated water and the coordinated (bridging and terminal) hydroxo groups. The bending mode δ(OH), for the water molecules appears at 1615-1630 cm$^{-1}$ in all the complexes whereas for the bridged hydroxo groups this mode occurs at 1100-1115 cm$^{-1}$; for the terminal hydroxo groups it occurs at 920 cm$^{-1}$ as a weak to medium intensity band. The ν(Zr-O) appears in the range 220-300 cm$^{-1}$. In addition, all important bands of the ligands are also assigned. The IR spectra of the solid Schiff bases reported here have been shown to exhibit a fairly intense band around 1625 cm$^{-1}$ due to ν(C=O), which shifts in these complexes to the region 1580 cm$^{-1}$ confirming the coordination of the azomethine group.25,26 The band involving the metal and the furan oxygen, ν(Zr-O), appears at 460-480 cm$^{-1}$ indicating the coordination of the furan ring oxygen. Examples of such ring oxygen and ring sulphur coordination of the furfural and thiophene-2-aldehyde derivatives are known.15,28 The important IR bands are presented in Table 2.

The thermal decomposition of the complexes was studied in the temperature range 30-800°C. The complexes initially lose water in one or more steps by about 150°C followed by the loss of Schiff base ligand and the OH groups (in multiples of two OH as H$_2$O molecules leaving one oxygen at a time attached to Zr Atom) and the Cl$^-$ ions. In some cases, formation of ZrO$_2$ was not seen up to the end of the thermal decomposition, although in some other cases, ZrO$_2$ was the ultimate end product formed at 500-600°C. Considering the stoichiometry of the intermediate species formed during thermal decomposition processes, we propose the following general mechanism for the thermal decomposition of the complexes:

\[
\begin{align*}
\text{A} & \rightarrow [\text{Zr}_4(\text{OH})_{12}](\text{H}_2\text{O})_{8}(\text{SB})_2\text{Cl}_4 \rightarrow \text{Zr}_4\text{O}_2(\text{OH})_8(\text{SB})_2\text{Cl}_4 \\
\text{B} & \rightarrow \text{Zr}_4\text{O}_2(\text{OH})_4(\text{SB})_n\text{Cl}_4 \rightarrow \text{Zr}_4\text{O}_6\text{Cl}_n (n = 4,3, or 2) \\
\text{C} & \rightarrow \text{ZrO}_2 \\
(x = 1.5, 1.25, 0.75)
\end{align*}
\]
Table 2 - Prominent IR Bands (cm\(^{-1}\)) in Oxozirconium(IV) Chloride Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\nu(Zr-O))</th>
<th>(\nu(OH))</th>
<th>(\delta(Zr-O-H))</th>
<th>(H-O-H)</th>
<th>Ligand bands</th>
</tr>
</thead>
<tbody>
<tr>
<td>([Zr_4(OH)<em>4(H_2O)</em>{10}]Cl_4)</td>
<td>275m</td>
<td>3400br</td>
<td>1630br, sh</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>([Zr_4(OH)_{12}(H_2O)_8]Cl_4)</td>
<td>245m</td>
<td>3380br</td>
<td>1625sh</td>
<td>1575br</td>
<td>1560br</td>
</tr>
<tr>
<td>([Zr_4(OH)<em>{12}(FA)</em>{12}]Cl_4)</td>
<td>440br*</td>
<td>1115br</td>
<td>1540br</td>
<td>1155m</td>
<td>140w</td>
</tr>
<tr>
<td>([Zr_4(OH)<em>{12}(FA)</em>{12}]Cl_4)</td>
<td>260m</td>
<td>3350br</td>
<td>1150m</td>
<td>1580br</td>
<td>1540br</td>
</tr>
<tr>
<td>([Zr_4(OH)<em>{12}(FA)</em>{12}]Cl_4)</td>
<td>240w</td>
<td>465m*</td>
<td>1150m</td>
<td>1580br</td>
<td>1510s</td>
</tr>
<tr>
<td>([Zr_4(OH)<em>{12}(FA)</em>{12}]Cl_4)</td>
<td>280m</td>
<td>3410br</td>
<td>1112m</td>
<td>1580br</td>
<td>1510s</td>
</tr>
<tr>
<td>([Zr_4(OH)<em>{12}(FA)</em>{12}]Cl_4)</td>
<td>230m</td>
<td>460m*</td>
<td>1140w</td>
<td>1180m</td>
<td></td>
</tr>
<tr>
<td>([Zr_4(OH)<em>{12}(FA)</em>{12}]Cl_4)</td>
<td>300m</td>
<td>3400br</td>
<td>1120m</td>
<td>1585br</td>
<td>1510s</td>
</tr>
</tbody>
</table>

*Zr – O where ‘O’ is the oxygen of furan ring.

The scheme of thermal decomposition, as reported by us, is only tentative, since in case of any single coordination complex it has not been possible to observe all the stable complex intermediate species, as stated in the scheme of decomposition, by following temperature-isolation technique. Thus, tentative stoichiometries have only been assigned based upon calculations from TG curves. Similar observations in respect of thermal behaviour of other tetrameric zirconium(IV) complexes have already been reported by us. However, it is seen that in some cases the decomposition process proceeds up to stage C forming \(Zr_4O_6Cl_4\) or \(Zr_4O_6Cl_3\) or \(Zr_4O_6Cl_2\) and in two cases it proceeds up to the end (stage D) forming \(ZrO_2\) as the ultimate end product. Evidence for the formation of halogenated oxide species such as \(Zr_4O_6F_4\), \(Zr_4O_6F_3\) or \(Zr_4O_6F_2\) is available in the literature. The thermal decomposition behaviour (TG, DTA) of zirconium(IV) complexes of N-furfurylideneaniline has been shown in Fig. 1. The DTA curve shows only an endothermic peak at 120°C and it assumes exothermic nature, thereafter. The endothermic peak may be ascribed to the decomposition of the complex and exothermic peak at 450°C may be the highest point in the process of decomposition of the complex. Considering the initial decomposition temperature as a rough guide for determining the thermal stability of complexes, we propose the following stability order for the complexes investigated:

\[
[Zr_4(OH)_{12}(H_2O)_{10}(FA)_{12}]Cl_4 < [Zr_4(OH)_{12}(H_2O)_{8}(FA)_{12}]Cl_4 < [Zr_4(OH)_{12}(H_2O)_{8}(FA)_{12}]Cl_4
\]

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References