Tetrameric zirconium(IV) complexes with bidentate ligands

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Oxozirconium(IV) chloride reacts with several heterocyclic bidentate ligands, 2,2'-bipyridyl (Bipy), 1,10-phenanthroline (Phen), 2-(2'-pyridyl) benzimidazole (PBH), 3,5-dimethyl-1 (2'-pyridyl) pyrazole (DMPP) and bidentate Schiff bases obtained by condensing salicylaldehyde with aromatic amines, to form tetrameric complexes where the four zirconium atoms are connected in a ring by four pairs of hydroxy bridges. Each Zr atom has eight-coordinated dodecahedral structure as is the case with the parent compound ZrOCl₂. The compounds are formulated as \([\text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_8(\text{L})_4]X_8\) (L = bidentate ligand) and \([\text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_14(\text{DMPP})]X_8\) (X = Cl, NCS). The analytical data, conductance, IR, Raman and NMR spectra and the thermogravimetric measurements characterise the complexes. The thermogravimetric measurements show that the complexes lose H₂O followed by ligands finally forming ZrO₂ as the end product.

The study of oxozirconium(IV) complexes is of interest in view of conflicting claims about their stoichiometry. Although metal-oxygen multiple bond stretching frequencies are observed in the range 900-1100 cm⁻¹ in the IR spectra of complexes of oxo-metal ions such as MoO₃⁺, MoO₂⁻⁺, WO₂⁺, VO₂⁺ and UO₂⁻⁺, no such vibrational mode attributable to the presence of v(M=O) are found in several oxometal(IV) compounds such as TiO₂⁺ and ZrO₂⁺. Such compounds are actually polymeric in solid state and in solution. X-ray crystal structure of ZrOCl₂.8H₂O in solid state and NMR measurements of hydration numbers in solution confirm the tetrameric structure, \([\text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_8]^{8+}\), in which four zirconium atoms are connected in a ring by four pairs of OH⁻ bridges and each zirconium atom is dodecahedrally coordinated to eight oxygen atoms. The eight-coordinated dodecahedral structure for zirconium is in agreement with its rather large size and the high charge. However, despite of the dodecahedral classification, many workers have reported the formation of monomeric complexes of oxozirconium(IV) chloride with unidentate and multidentate ligands starting material is seen in the IR spectra near 1000 cm⁻¹ which might have been the source of erroneous interpretation.

In continuation of our earlier work on oxozirconium(IV) compounds, we report here complexes obtained by the reaction of ZrOCl₂.8H₂O with a variety of bidentate ligands like 2,2'-bipyridyl (Bipy), 1,10-phenanthroline (Phen), 2-(2'-pyridyl)benzimidazole (PBH), 3,5-dimethyl-1-(2'-pyridyl)pyrazole (DMPP) and Schiff bases (containing N, O donor set) derived by the condensation of appropriate aromatic amines with salicylaldehyde. These complexes are tetrameric, similar to those reported earlier.

Materials and Methods
Salicylaldehyde (Sarabhai M Chemicals, India) was distilled prior to its use. ZrOCl₂.8H₂O (Riedel), 2,2'-bipyridyl (Bipy), 1,10-phenanthroline (Phen) (BDH, reagent grade) and 2-(2'-pyridyl)benzimidazole (PBH) (Ega-Chemie, Germany) were used as supplied. 3,5-Dimethyl-1-(2'-pyridyl)pyrazole (DMPP) was prepared and characterised as reported. Zirconium was estimated volumetrically by EDTA titration using xylene orange as the indicator following a modified literature method. Zirconium was estimated volumetrically by EDTA titration using xylene orange as the indicator following a modified literature method. For the IR spectra were recorded as KBr discs in 4000-400 cm⁻¹ region using Nicolet 20 SXC FTIR spectrophotometer. The Raman spectra was obtained from RSIC, IIT, Madras. The ¹H and...
$^{13}$C NMR spectra of some of the complexes were recorded at IIT, Delhi.

The thermal measurements were carried out in static air with a Shimadzu DT-30 thermal analyser, which records T, TG, DTG and DTA simultaneously. The rate of heating was $10^\circ$C min$^{-1}$. Melting points were taken in sealed capillaries and are uncorrected. Conductances in solutions were measured using a Systronics conductivity meter 304.

**Synthesis of complexes**

All the complexes were prepared by a general method involving reaction of ZrOCl$_2$.8H$_2$O or ZrO(NCS)$_2$ (in solution) with the ligands taken in 1:2 ratio. ZrO(NCS)$_2$ was obtained as light red solution, by the metathesis of ZrOCI$_2$.8H$_2$O with KNC in 1:2 ratio in acetone and filtering off the KCl formed. A typical method of synthesis is given below for the $[Zr_4(OH)_8(H_2O)_8(PBH)_4]Cl_8$ complex.

ZrOCI$_2$.8H$_2$O (0.322 g, 1 mmole) was dissolved in a mixture of acetone (5 ml) and triethylorthoformate (TEOF) (2 ml) and cooled to 0-4°C. To this was added the ligand PBH (0.39 g, 2 mmole) dissolved in warm acetone (5 ml), with constant stirring. Immediately a white precipitate was obtained. The mixture was stirred for further 1 hr, and filtered (G-3 crucible), washed with acetone followed by ether and finally dried *in vacuo*.

Although the chloro complexes were readily obtained, prolonged stirring was required for the corresponding thiocyanato complexes. For the complex of the ligand DMPP, prolonged stirring and refluxing (~ 24 hr) was necessary. The thiocyanato complex of the ligand DMPP was obtained only after further extraction with ether.

**Results and Discussion**

All the complexes except those of DMPP and Schiff bases are colourless solids (Table 1). The DMPP complexes are brown, whereas the Schiff base complexes are yellow to brown in colour. All complexes have melting points > 240°C. The analytical data of the complexes (Table 1) do not agree with simple mononuclear composition and

| Table 1—Analytical Data of Oxozirconium(IV) Complexes$^{ab}$ |
|------------------|------------------|------------------|
| **Compound**     | **Colour**       | **Found (Calc.) %** |
|                  | Zr   | C    | H    | N    | Cl/S  |
| [Zr$_4$(OH)$_8$(H$_2$O)$_8$(PBH)$_4$]Cl$_8$ | White | 20.6 | 32.9 | 3.6 | 9.4 | 16.1 |
|                  |      | (21.3) | (33.7) | (3.5) | (9.8) | (16.6) |
| [Zr$_4$(OH)$_8$(H$_2$O)$_8$(PBH)$_4$](NCS)$_8$ | White | 19.8 | 36.0 | 2.9 | 14.7 | 12.8 |
|                  |      | (19.3) | (35.6) | (3.2) | (14.8) | (13.5) |
| [Zr$_4$(OH)$_8$(H$_2$O)$_8$(DMPP)]Cl$_8$ | Brown | 30.3 | 9.6 | 4.1 | 3.5 | 22.9 |
|                  |      | (30.1) | (9.9) | (3.9) | (3.5) | (23.5) |
| [Zr$_4$(OH)$_8$(H$_2$O)$_8$(DMPP)](NCS)$_8$ | Brown | 25.0 | 15.4 | 3.2 | 10.8 | 18.2 |
|                  |      | (26.2) | (15.5) | (3.4) | (11.0) | (18.4) |
| [Zr$_4$(OH)$_8$(H$_2$O)$_8$(Bipy)$_4$]Cl$_8$ | White | 24.0 | 30.8 | 3.5 | 7.6 | 18.1 |
|                  |      | (23.5) | (30.9) | (3.6) | (7.2) | (18.3) |
| [Zr$_4$(OH)$_8$(H$_2$O)$_8$(Bipy)$_4$](NCS)$_8$ | White | 20.7 | 33.6 | 3.3 | 12.9 | 15.1 |
|                  |      | (21.0) | (33.3) | (3.2) | (12.9) | (14.8) |
| [Zr$_4$(OH)$_8$(H$_2$O)$_8$(Phen)$_4$]Cl$_8$ | White | 22.2 | 34.8 | 3.2 | 6.6 | 17.3 |
|                  |      | (22.1) | (34.9) | (3.4) | (6.8) | (17.2) |
| [Zr$_4$(OH)$_8$(H$_2$O)$_8$(Phen)$_4$](NCS)$_8$ | White | 19.8 | 36.4 | 3.2 | 12.2 | 14.3 |
|                  |      | (19.9) | (36.8) | (3.0) | (12.3) | (14.0) |
| [Zr$_4$(OH)$_8$(H$_2$O)$_8$(H-Sal-Anis)$_4$]Cl$_8$ | Yellow | 19.9 | 36.6 | 4.3 | 2.8 | 15.4 |
|                  |      | (19.8) | (36.6) | (4.1) | (3.0) | (15.5) |
| [Zr$_4$(OH)$_8$(H$_2$O)$_8$(H-Sal-Anis)$_4$](NCS)$_8$ | Brown | 17.8 | 37.9 | 3.5 | 8.3 | 12.5 |
|                  |      | (18.1) | (38.1) | (3.8) | (8.3) | (12.7) |
| [Zr$_4$(OH)$_8$(H$_2$O)$_8$(H-Sal-Tol)$_4$]Cl$_8$ | Yellow | 19.6 | 37.5 | 4.2 | 3.2 | 15.6 |
|                  |      | (20.5) | (37.9) | (4.3) | (3.2) | (16.0) |
| [Zr$_4$(OH)$_8$(H$_2$O)$_8$(H-Sal-o-ClAn)$_4$]Cl$_8$ | Brick Red | 19.2 | 33.7 | 3.6 | 3.1 | 22.8 |
|                  |      | (19.7) | (33.6) | (3.4) | (3.0) | (23.0) |

$^a$ All the compounds melt above 240°C.

$^b$ Abbreviations used: PBH = 2-(2'-pyridyl)benzimidazole; DMPP = 3,5-dimethyl-1(2'-pyridyl) pyrazole; Bipy = 2-2'-bipyridyl; Phen = 1,10-phenanthroline; H-Sal-Anis = p-anisidine salicylideneimine; H-Sal-Tol = p-toluidine salicylideneimine; H-Sal-o-ClAn = o-chloroaniline salicylideneimine.

$^c$ Conductance in DMSO.
actually seem to correspond to the composition based on the tetrameric structure, of
\[ \text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}, \ \left[ \text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{16}\right]\text{Cl}_8 \]. The complexes are formed by the replacement of two water molecules from each of the four zirconium atoms in the tetramer by a bidentate ligand. The reaction of the ligand DMPP with
\[ \left[ \text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{16}\right]\text{Cl}_8 \]
leads to the compound
\[ \left[ \text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{14}\text{DMPP}\right]\text{Cl}_8 \]. In all the cases corresponding thiocyanato complexes were also synthesised and characterised. Most of the complexes are highly insoluble in common organic solvents precluding X-ray structure determination, molecular weight determination and conductivity measurement. Conductances of only some complexes in DMF or DMSO could be obtained (Table 1) and the values obtained are similar to the values for the parent compound ZrOCl\(_2\) \(8\text{H}_2\text{O} \) or \( \left[ \text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{16}\right]\text{Cl}_8 \), suggesting similar ionic nature.

IR spectra in the range 4000-400 cm\(^{-1}\) of the parent ZrOCl\(_2\) \(8\text{H}_2\text{O} \) and the complexes reported are identical except for the extra bands observed indicating coordination of the ligands and the thio-cyanate ion (in thiocyanato complexes). In none of the complexes we could find a band in the region 880-980 cm\(^{-1}\) corresponding to \( \nu(Zr=O) \) as has been reported indicating clearly the absence of Zr\(^{2+}\) moiety. In the IR spectra of all the complexes a strong band located at \( \sim 1175 \text{ cm}^{-1} \) has been assigned to \( \delta(Zr-\text{O-H}) \). The broad but strong band centred at 3400 cm\(^{-1}\) is assigned to \( \nu(\text{OH}) \) mode of both the coordinated water and the coordinated bridging hydroxo groups. The band in the region 1600 cm\(^{-1}\) may also be assigned to \( \delta(H-\text{OH}) \) of coordinated water molecules, whereas a weak band in the region 1101-1124 cm\(^{-1}\) assigned to bending modes of bridging hydroxo groups.

Two strong and sharp bands at \( \sim 2040 \) and \( \sim 750 \text{ cm}^{-1} \) in the IR spectra of all the thiocyanato complexes, assignable to \( \nu(C=N) \) and \( \nu(C-S) \) respectively, clearly suggest the ionic nature of NCS groups. The \( \delta(\text{NCS}) \) observed at \( \sim 475 \text{ cm}^{-1} \) also supports the ionic formulation. In the complexes of Bipy, Phen, PBH and DMPP, the ligands are coordinated to the metal ion in a bidentate fashion through the two ring nitrogens. A strong band in the region 1590-1600 cm\(^{-1}\) in the spectra of the Schiff base complexes, assignable to \( \nu(C=N) \) suggests coordination through the nitrogen of the azomethine group (the \( \nu(C=N) \) mode in the free ligands appear at \( \sim 1635 \text{ cm}^{-1} \)). A sharp band at \( \sim 1260 \text{ cm}^{-1} \) is assigned to \( \nu(C-O) \) of the coordinated C–OH groups. The IR spectra of the Schiff bases and their complexes exhibit broad and weak bands in the region 3058-3376 and at \( \sim 1290 \text{ cm}^{-1} \) assignable to \( \nu(\text{OH}) \) and \( \delta(\text{OH}) \) respectively suggest the Schiff bases co-ordinate to the metal ion as a bidentate neutral ligand and not as deprotonated anions.

Raman spectra of only two complexes \( \left[ \text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{16}(\text{PBH})_4(\text{NCS})_8 \right] \) and \( \left[ \text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{14}(\text{DMPP})\text{Cl}_8 \right] \) could be obtained. Bands in the region \( \sim 3350 \) (broad band due to \( \nu(\text{OH}) \), 3060 (aromatic str.), 1600-1620 (sharp band due to azomethine \( \nu(C=N) \), 1440-1485 (aromatic C–C str.) 1550-1560 cm\(^{-1}\) (pyridine ring vibration) and 985-1020 cm\(^{-1}\) (pyridine ring breathing) are observed in the Raman spectra of both the complexes. The \( \delta(Zr-\text{OH}) \) in both the complexes appears at \( \sim 1145 \text{ cm}^{-1} \). In addition, other bands at \( \sim 620-660 \) and \( \sim 700-770 \text{ cm}^{-1} \) (aliphatic and aromatic C–H str.) are also observed, similar to the IR bands.

The \(^1\text{H} \) and \(^{13}\text{C} \) NMR spectra of only three complexes, viz. \( \left[ \text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{16}(X)_8 \right] \) \( (X=\text{Cl} \) and NCS) and \( \left[ \text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{14}(\text{Phen})_4(\text{NCS})_8 \right] \) could be recorded. Almost similar signals are obtained for the ligands and complexes. Except for somewhat down field shift of signals in \(^1\text{H} \) and \(^{13}\text{C} \) NMR spectra, indicating coordination of ligands to the metal ion, the \(^1\text{H} \) and \(^{13}\text{C} \) NMR profiles do not reveal any characteristic feature.

The thermal behaviour of all the complexes has been studied in the temperature range of 30° to 800°C. The thiocyanato complexes appear to be more stable than the corresponding chloride complexes. In the case of the chloride complexes, one endothermic peak appears at 90-100°C, thereafter the DTA curve shows an exothermic behaviour and an exothermic peak is obtained at 500-510°C. Throughout the course of heating, as seen from the TG curve, the gradual mass loss with increasing temperature precludes any clear cut assignment of the intermediate species. In the thiocyanato complexes, the first endothermic peak appears at 360-440°C and thereafter the DTA curve shows an exothermic behaviour. Finally a sharp exothermic peak is obtained at 600°C. In all the cases the final product obtained is identified as ZrO\(_2\). However, the thermal behaviour of Schiff base complexes follows a different pattern, being endothermic in nature throughout the process. The final product here also is identified as ZrO\(_2\) at \( \sim 470°C \). The analysis of the TG and DTG curves clearly show that in all the cases, the complexes lose all the water molecules in one or more steps followed by the loss of ligands and the OH.
groups (in multiples of two OH as H₂O molecules).

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References