Tetrameric zirconium(IV) compounds derived from oxozirconium(IV) chloride and heterocyclic aldimines and ketimines

Chitta R. Panda, Vivekananda Chakravortty and Kailash C. Dash*

Department of Chemistry, Utkal University, Vani Vihar, Bhubaneswar-751004, India

Summary

Interaction of $\text{ZrOCl}_2:8\text{H}_2\text{O}$, $[\text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{16}]\text{Cl}_8$ ·12H₂O, with the heterocyclic aldimines (PyAlA) and heterocyclic ketimines (AcPyA) in Me₂CO in the presence of HC(OEt)₃ yields white amorphous compounds of the type $[\text{Zr}_4(\text{OH})_{12}(\text{H}_2\text{O})_8(\text{PyA1A})_2]\text{Cl}_4$ and $[\text{Zr}_4(\text{OH})_{12}(\text{H}_2\text{O})_{10}(\text{AcPyA})]\text{Cl}_4$. Presumably these compounds have a tetrameric dodecahedral structure, derived from the parent. The analytical data, i.r., electrical conductance and t.g. measurements all favour the tetrameric formulation. The t.g. studies also indicate the intermediacy of complex species, which lose water and the Schiff base ligands, with increase in temperature.

Introduction

Zirconium(IV) complexes exhibit a wide range of coordination numbers: 4 to 8 and also 12^(1,2). The M-O multiple bond stretching frequency in the 900-1100 cm⁻¹ range has been identified in compounds of the type MOⁿ⁺ and MO_2^{n+} in early transition elements⁽³⁾, but there is no evidence for the existence of TiO²⁺ or ZrO²⁺ mononuclear species in certain so-called titanyl or zirconyl compounds. A polymeric form of zirconium(IV) predominates, both in solution and in solid state, as is clear from n.m.r. measurements of hydration numbers in solution⁽⁴⁾ and the solid state structure^(5,6) of ZrOCl₂·8H₂O which is actually a tetramer, $[Zr_4(OH)_8(H_2O)_{16}]Cl_8 \cdot 12H_2O$. Inspite of this, monomeric complexes, ZrOCl₂ nL, have been reported⁽⁷⁻⁹⁾ in which a weak i.r. band at 950-980 cm⁻¹ has been assigned to v(Zr=O). This is surprising in view of the x-ray evidence, which confirms the absence of Zr=O group in the starting material.

This paper is concerned with the complexes prepared by reaction of $ZrOCl_2 \cdot 8H_2O$ with the bidentate heterocyclic aldimines (PyAlA) and the ketimines (AcPyA) (PyAl = 2-pyridinecarboxaldehyde; AcPy = 2-acetylpyridine; A = aniline, o-, m- or p-toluidine, o- or panisidine or p-phenetidine). The complexing agents were obtained by condensing aromatic amines with 2-pyridinecarboxaldehyde or 2-acetylpyridine, respectively. The complexes have the [Zr₄(OH)₁₂(H₂O)₈(PyAlA)₂]Cl₄ and [Zr₄(OH)₁₂(H₂O)₁₀(AcPyA)]Cl₄ stoichiometry. The complexing agents react with UO₂X₂ to form dimeric complexes⁽¹⁰⁾ of the type [UO₂(OH)(PyAlA)Cl]₂ and [UO₂(OH)(H₂O)(AcPyA)_{0.5}Cl]₂ and with ThX₄ forming monomeric complexes⁽¹¹⁾ of the type [Th(PyAlA)X₄] and [Th(AcPyA)X₄] (X = NO₃ or NCS).

Experimental

Reagent grade $ZrOCl_2 \cdot 8H_2O$ (Riedel) was used as supplied. 2-Pyridinecarboxaldehyde (Fluka), 2-acetyl-

pyridine (Koch-Light) and the aromatic amines (BDH) were distilled prior to use. Zirconium was estimated by slowly decomposing the complexes with AR HNO₃ and then igniting to 1000° C and finally weighing as ZrO₂. Thiocyanate was determined by the alkaline oxidative fusion method: oxidation of sulphur to sulphate and then weighing as BaSO₄.

The electrical conductivity, i.r. spectra and t.g. measurements were made as described $earlier^{(10)}$.

 $[Zr_4(OH)_{12}(H_2O)_8(PyAlA)_2]Cl_4$ (A = aniline, o-, mor p-toluidine, o- or p-anisidine or p-phenetidine)

These complexes were prepared by reacting $ZrOCl_2 \cdot 8H_2O$ with the Schiff bases, taken in 1:2 stoichiometric ratio. A typical method is given below for $[Zr_4(OH)_{12}(H_2O)_8(PyAlAnil)_2]Cl_4$.

The aldimine Schiff base was first prepared in situ by stirring a mixture of PhNH₂ (0.37 cm³, 0.004 mol) and 2pyridinecarboxaldehyde (0.43 cm³, 0.004 mol) in Me₂CO (10 cm³) and HC(OEt)₃ (10 cm³) for 15 min followed by heating under reflux for 60 min. The mixture was then brought to room temperature and to this reddish solution was added ZrOCl₂·8H₂O (0.64g, 0.002 mol) in dry Me₂CO and HC(OEt)₃ with constant stirring. The yellowish-brown precipitate which formed was collected, washed with small aliquots of Et₂O and finally dried *in vacuo*.

 $[Zr_4(OH)_{12}(H_2O)_{10}(AcPyA)]Cl_4$ (A = aniline, o-, mor p-toluidine, o- or p-anisidine, or p-phenetidine)

These compounds were prepared by the same procedure, using 2-acetylpyridine instead of 2-pyridinecarboxaldehyde. The white complexes were collected, washed, dried and characterised in the usual way.

Results and discussion

Analytical data and other characterising data for the zirconium complexes are given in Table 1. They are sparingly soluble in methanol and insoluble in most common organic solvents, precluding molecular weight determination. The electrical conductance measurements of the aldimine complexes of zirconium in MeOH solution were consistent with them being 1:4 electrolytes. Conductance measurements for the ketimine complexes could not be made due to their insolubility. The aldimine complexes are brown and the ketimine complexes pale white. All have m.ps higher than 250° C. Careful repeated analysis of the compounds prepared with varying metalto-Schiff base ratios provide no evidence for the formation of simple, monomeric complexes. The analytical data correspond to the formulae based on the tetrameric structure^(5,6), $[Zr_4(OH)_8(H_2O)_{16}]Cl_8$, with double hydroxo-bridges between each adjacent pair of zirconium atoms.

^{*} Author to whom all correspondence should be directed.

288 C. R. Panda, V. Chakravortty and K. C. Dash

Table 1. Analytical and other characterising data of aldimine and ketimine complexes of oxozirconium(IV).

| Compound | Mol formula | Found (Calcd.)% | | | | | A _w in MeOH | |
|---|--|-----------------|--------|-------|-------|--------|-------------------------------------|--|
| - | (Mol. wt) | Zr C H | | Ĥ | Ν | Cl | $(\text{mho cm}^2 \text{mol}^{-1})$ | |
| A in $[Zr_4(OH)_{12}(H_2O)_8(PyAlA)_2]Cl_4$ | | | | | | | | |
| Aniline | $Zr_4C_{24}H_{48}N_4O_{20}Cl_4$ | 29.6 | 23.5 | 3.9 | 4.4 | 11.4 | 320.10 | |
| | (1219) | (29.9) | (23.6) | (3.9) | (4.6) | (11.6) | | |
| o-Toluidine | $Zr_4C_{26}H_{52}N_4O_{20}Cl_4$ | 29.0 | 25.2 | 4.1 | 4.3 | 11.3 | 309.9 | |
| | (1247) | (29.2) | (25.0) | (4.2) | (4.5) | (11.4) | | |
| <i>m</i> -Toluidine | $Zr_4C_{26}H_{52}N_4O_{20}Cl_4$ | 29.2 | 24.8 | 4.2 | 4.3 | 11.2 | 315.6 | |
| | (1247) | (29.2) | (25.0) | (4.2) | (4.5) | (11.4) | | |
| <i>p</i> -Toluidine | Zr ₄ C ₂₆ H ₅₂ N ₄ O ₂₀ Cl ₄ | 29.0 | 25.1 | 4.4 | 4.2 | 11.1 | 295.17 | |
| | (1247) | (29.2) | (25.0) | (4.2) | (4.5) | (11.4) | | |
| o-Anisidine | $Zr_4C_{26}H_{52}N_4O_{22}Cl_4$ | 28.3 | 24.3 | 4.0 | 4.4 | 11.1 | 276.39 | |
| | (1279) | (28.5) | (24.4) | (4.1) | (4.4) | (11.1) | | |
| p-Anisidine | $Zr_4C_{26}H_{52}N_4O_{22}Cl_4$ | 28.4 | 24.4 | 4.2 | 4.5 | 10.8 | 385.68 | |
| | (1279) | (28.5) | (24.4) | (4.1) | (4.4) | (11.1) | | |
| p-Phenetidine | $Zr_4C_{28}H_{56}N_4O_{22}Cl_4$ | 27.7 | 25.6 | 4.3 | 4.1 | 10.7 | 270.90 | |
| | (1307) | (27.9) | (25.7) | (4.3) | (4.3) | (10.8) | | |
| Aniline | $Zr_4C_{13}H_{44}N_2O_{22}Cl_4$ | 33.4 | 14.4 | 4.0 | 2.7 | 12.9 | - | |
| | (1087) | (33.6) | (14.3) | (4.0) | (2.5) | (13.0) | | |
| o-Toluidine | $Zr_4C_{14}H_{46}N_2O_{22}Cl_4$ | 33.2 | 15.3 | 4.3 | 2.6 | 12.9 | - | |
| | (1101) | (33.1) | (15.2) | (4.2) | (2.5) | (12.9) | | |
| <i>m</i> -Toluidine | $Zr_4C_{14}H_{46}N_2O_{22}Cl_4$ | 33.0 | 15.3 | 4.0 | 2.7 | 12.6 | - | |
| | (1101) | (33.1) | (15.2) | (4.2) | (2.5) | (12.9) | | |
| <i>p</i> -Toluidine | $Zr_4C_{14}H_{46}N_2O_{22}Cl_4$ | 33.2 | 15.1 | 4.2 | 2.6 | 12.8 | | |
| | (1101) | (33.1) | (15.2) | (4.2) | (2.5) | (12.9) | | |
| o-Anisidine | $Zr_4C_{14}H_{46}N_2O_{23}Cl_4$ | 32.6 | 15.0 | 4.3 | 2.2 | 12.5 | | |
| | (1117) | (32.7) | (15.0) | (4.1) | (2.5) | (12.7) | | |
| p-Anisidine | $Zr_4C_{14}H_{46}N_2O_{23}Cl_4$ | 32.5 | 15.2 | 4.0 | 2.3 | 12.7 | _ | |
| - | (1117) | (32.7) | (15.0) | (4.1) | (2.5) | (12.7) | | |
| <i>p</i> -Phenetidine | $Zr_4C_{15}H_{48}N_2O_{23}Cl_4$ | 32.3 | 16.0 | 4.1 | 2.5 | 12.7 | _ | |
| - | (1131) | (32.2) | (15.9) | (4.2) | (2.5) | (12.5) | | |

The Zr:Cl ratio in $[Zr_4(OH)_8(H_2O)_{16}]Cl_8$ is 4:8, whereas this ratio for the complexes under consideration is 4:4. This clearly shows that at some stage of complexation four H₂O molecules are being deprotonated to give four extra hydroxo(-OH) groups, bonded terminally, complexes formulated and yielding as $[Zr_4(OH)_8^b(OH)_4^t(H_2O)_{12}]Cl_4$. From this basic structure, either four or two water molecules are replaced by two bidentate aldimine Schiff base ligands, or one bidentate ketimine ligand giving rise to the observed stoichiometries. We made similar observations at an earlier stage for the tetrameric oxozirconium(IV) complexes with unidentate nitrogen ligands imidazoles and morpholines⁽¹²⁾ and with bidentate furfural-based Schiff base ligands⁽¹³⁾.

pH measurements of the metal salt, the ligand and the complexes in acetone-triethylorthoformate (TEOF) mixture have been made to substantiate the proposed hydroxo-bridged tetrameric structure. The concentration of H⁺ in the above solution of the starting material $ZrOCl_2 \cdot 8H_2O$ was 1.7 M, the pH of the aldimine PyAlA (A = aniline) was 5.8 and that of the ketimine AcPyA (A = aniline) was 4.1 while after complexation and separation of the product complex the pH of the solution was 4.1 and 3.55, respectively (usual corrections for pH determination in non-aqueous medium were made). These observations suggest that the reactions presumably proceed as follows:

$$[Zr_4(OH)_8(H_2O)_{16}]Cl_8$$

$$\xrightarrow{Me_2CO-TEOF} [Zr_4(OH)_{12}(H_2O)_{12}]Cl_4 + 4HCl$$

$$\begin{split} & [Zr_4(OH)_{12}(H_2O)_{12}]Cl_4 + xSB \\ & \longrightarrow [Zr_4(OH)_{12}(H_2O)_{12-2x}(SB)_x] + 2xH_2O \\ & (x = 1 \text{ for AcPyA}; 2 \text{ for PyAlA}) \end{split}$$

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 using benzene as the diluent⁽¹⁴⁾.

Based solely on chemical analysis, Zaitsev⁽¹⁵⁾ has shown that the freshly prepared α -hydroxide, $Zr_4(OH)_8^b(OH)_8^t(H_2O)_x$, contains a four-membered ring of zirconium atoms with adjacent pairs of metal atoms joined by a double hydroxo-bridge, giving rise to a structure analogous to the tetrameric structure of "zirconyl chloride octahydrate"^(5,6), which is actually $[Zr_4(OH)_8^b(H_2O)_{16}]^{8+}$. The aldimine and ketimine complexes described in this paper seem to be intermediate between the $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ and the α -hydroxide, $[Zr_4(OH)_8^b(OH)_8^t(H_2O)_x]$ (where b stands for bridging and t for terminal -OH groups) in that they contain four chloride ions in addition to the ligands joined to the zirconium atoms in place of either four or two H₂O yielding complexes of molecules, the type $[Zr_4(OH)_8^b(OH)_4^i(H_2O)_{12-2x}(SB)_x]Cl_4$, where x = 1 for the ketimines AcPyA and 2 for aldimines PyAlA.

A comparative i.r. spectral analysis in the $4000-200 \text{ cm}^{-1}$ range show the starting material $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and the product complexes to be identical except for the extra bands in the latter corresponding to

Transition Met. Chem., 13, 287–290 (1988)

Table 2. Prominent IR absorption bands (cm⁻¹) of some aldimine and ketimine complexes of oxozirconium(IV).

| Compound | $[Zr_4(OH)]$ | ,(H ₂ O), |] ^{4 ÷} | Ligand | | | |
|--|-------------------|----------------------|---------------------------------------|------------|--------------------|-----------|-------|
| | v(Zr-O) | v(ÔH) | $\delta(\text{Zr}-\text{O}-\text{H})$ | H—O—H def. | $\nu(\breve{C}=N)$ | ν(C==C) | v(CN) |
| A in $[Zr_4(OH)_{12}(H_2O)_8(PyAlA)_2]Cl_4$ | | | | | · | | |
| Aniline | 450w ^a | 3250br | 1120m | 1630s | 1625s | 1520s | 1155m |
| <i>m</i> -Toluidine | 470mª | 3250br | 1110m | 1600s | 1595s | 1500s | 1170m |
| p-Anisidine | 470mª | 3250br | 1105m | 1640sh | 1625s | 1570m | 1180m |
| <i>p</i> -Phenetidine | 445w ^a | 3250br | 1110m | 1625sh | 1615s | 1585m, br | 1172m |
| A in $[Zr_4(OH)_{12}(H_2O)_{10}(AcPyA)]Cl_4$ | | | | | | | |
| Aniline | 300m | 3200br | 1100m | 1630sh | 1620s | 1560sh | 1160m |
| | 250m | | | | | | |
| | 500m ^a | | | | | | |
| o-Toluidine | 280m | 3200br | 1115m | 1610sh | 1600s | 1500sh | 1170m |
| | 235m | | | | | | |
| | 510m ^a | | | | | | |
| <i>p</i> -Toluidine | 270m | 3200br | 1110m | 1620sh | 1590s | 1500sh | 1165m |
| • | 240m | | | | | | |
| | 515m ^a | | | | | | |
| <i>p</i> -Anisidine | 260m | 3200br | 1115m | 1620sh | 1620s | 1530s | 1185m |
| - | 230m | | | | | | |
| | 470mª | | | | | | |
| <i>p</i> -Phenetidine | 265m | 3200br | 1110m | 1610sh | 1605s | 1520s | 1180m |
| | 245m | | | | | | |
| | 485mª | | | | | | |
| | | | | | | | |

 $^{a}v(M-N)$ where N is the nitrogen of azomethine group.



Figure 1. T.g., d.t.g. and d.t.a. curves of the coordination complex $[Zr_4(OH)_{12}(H_2O)_8(PyAlAnil)_2]Cl_4$.

the various vibrational modes of the complexing agents (Table 2). In no case was a band observed in the 835–925 cm⁻¹ region corresponding to v(Zr=0), indicating the absence of the ZrO^{2+} group. The broad but strong band centred at 3200 cm^{-1} in all the complexes are assigned⁽¹⁶⁾ to v(OH) of both the coordinated water and the coordinated (bridging or terminal) hydroxo groups. The bending mode, $\delta(\text{OH})$, for the water molecule appears at 1615–1635 cm⁻¹ in all the complexes, whereas for bridged hydroxo-groups⁽¹⁶⁻¹⁸⁾ they are at 1100–1115 cm⁻¹ and for the terminal hydroxo groups at 920 cm⁻¹ as a weak to medium intensity band. v(Zr=-0) appear in the 220–300 cm⁻¹ range for coordinated H₂O, terminal hydroxo and bridged-hydroxo groups⁽¹⁹⁾. The

aldimine and ketimine Schiff base v(C=N) bands are located at *ca*. 1590–1620 cm⁻¹, lowered on coordination, due to bonding of the nitrogen. The v(C-N) bands in the complexes are located at 1170–1175 cm⁻¹ and the v(M-N) (where N is nitrogen of the azomethine group), expected to occur at 525–425 cm^{-1(20,21)} are observed at *ca*. 500 cm⁻¹.

Thermogravimetric analysis

The t.g. analysis of the complexes clearly shows the presence of water molecules whose loss, in all the cases, is supported by the appearance of endothermic peaks at *ca*. 100° C (Figure 1). All the complexes start to decompose at 40° C with the loss of H₂O, OH groups in multiples of two OH as H₂O molecules (leaving one oxygen), the ligands and Cl⁻ ions. The loss of ligands occurs in a stepwise manner with the formation of one or more intermediate products, stoichiometries of which have been calculated (Table 3). Based on stoichiometries of the intermediate species formed during the thermal decomposition process, the following general scheme can be proposed.

$$\begin{bmatrix} Zr_4(OH)_{12}(H_2O)_{12-2x}(SB)_x \end{bmatrix}Cl_4 \xrightarrow{A} Zr_4O_2(OH)_8(SB)_YCl_4$$
(x = 1 for AcPyA; 2 for PyAlA)
$$\begin{array}{c} (y = 1 \text{ or } 0.75 \text{ for } AcPyA; \\ 2 \text{ or } 1.75 \text{ for } PyAlA) \\ B \downarrow \\ ZrO_2 \xleftarrow{C} Zr_4O_6(SB)_zCl_2 \\ (z = 0.25 \text{ for } AcPyA; 0.75, \\ 0.5 \text{ or } 0.25 \text{ for } PyAlA) \end{array}$$

During the process of loss of ligands from the tetrameric oxozirconium(IV) complexes with double hydroxo bridge, Zr—O—Zr type species are obtained. Evidence for the formation of halogenated oxide species such as $Zr_4O_6Cl_4$, $Zr_4O_6Cl_3$ or $Zr_4O_6Cl_2$ is also available in the literature⁽²²⁾.

Transition Met. Chem., 13, 287–290 (1988)

Table 3. Thermal decomposition parameters of some aldimine and ketimine complexes of oxozirconium(IV).

| Compound | Initial dec. Temp. (°C) | T.g. data Temp. range (°C) | Weight Obsd. | loss (%) Calcd. | Species formed | DTA peak (°C) |
|---------------------------------------|----------------------------------|-------------------------------------|-----------------|--------------------|---|---------------|
| $[Zr_4(OH)_{1,2}(H_2O)_8(L^1)_7]Cl_4$ | (m.w. = | 1219); $L^1 = 1$ | PyAlAnil (1 | m.w. = 182 |) | |
| $[Zr_4(OH)_{12}(H_2O)_8(L^1)_2]Cl_4$ | 40 | 40-150 | 14.96 | 14.76 | $Zr_4O_2(OH)_8(L^1)_2Cl_4$ | 110 (endo) |
| | | 150-390 | 39.90 | 39.34 | $Zr_4O_6(L^1)_{0.75}Cl_4$ | |
| | | 390-600 | 61.65 | 59.64 | $4(ZrO_2)$ | 400 (exo) |
| $[Zr_4(OH)_{12}(H_2O)_8(L^2)_2]Cl_4$ | (m.w. = | 1247); $L^2 = 1$ | PyAlm-Tol | (m.w. = 19) | 96) | |
| $[Zr_4(OH)_{12}(H_2O)_8(L^2)_2]Cl_4$ | 40 | 40 - 110 | 16.45 | 14.43 | $Zr_4O_2(OH)_8(L^2)_2Cl_4$ | 80 (endo) |
| | | 110-390 | 47.86 | 47.73 | $Zr_4O_6(L^2)_{0.25}Cl_4$ | |
| | | 390-600 | 61.32 | 60.54 | $4(ZrO_2)$ | 425 (exo) |
| $[Zr_4(OH)_{12}(H_2O)_8(L^3)_2]Cl_4$ | (m.w. = | 1279); $L^3 = 1$ | PyAlp-Anis | m.w. = 2 | 12) | |
| $[Zr_4(OH)_{12}(H_2O)_8(L^3)_2]Cl_4$ | 40 | 40-130 | 17.95 | 18.21 | $Zr_4O_2(OH)_8(L^3)_{1.75}Cl_4$ | 90 (endo) |
| | | 130-380 | 43.21 | 44.58 | $Zr_4O_6(L^3)_{0.5}Cl_4$ | |
| | | 380-600 | 62.50 | 61.51 | $4(ZrO_2)$ | 420 (exo) |
| $[Zr_4(OH)_{12}(H_2O)_8(L^4)_2]Cl_4$ | (m.w. = | 1307); $L^4 = 1$ | PyAlp-Phe | m(m.w. = 2) | 226) | |
| $[Zr_4(OH)_{12}(H_2O)_8(L^4)_2]Cl_4$ | 40 | 40-105 | 16.00 | 18.08 | $Zr_4O_2(OH)_8(L^4)_{1.75}Cl_4$ | 85 (endo) |
| | | 105-380 | 48.00 | 49.55 | $Zr_4O_6(L^4)_{0.25}Cl_4$ | |
| | | 380-600 | 64.00 | 62.36 | $4(ZrO_2)$ | 420 (exo) |
| $[Zr_4(OH)_{12}(H_2O)_{10}(L^1)]Cl_4$ | (m.w. = | 1087); $L^1 = L^2$ | AcPyAnil (; | m.w. = 196 | 5) | |
| $[Zr_4(OH)_{12}(H_2O)_{10}(L^1)]Cl_4$ | 40 | 40-120 | 15.3 | 16.55 | $\operatorname{Zr}_4(\operatorname{OH})_{12}(L^1)\operatorname{Cl}_4$ | 100 (endo) |
| | | 120-180 | 23.25 | 24.38 | $Zr_4O_2(OH)_8(L^1)_{0.75}Cl_4$ | |
| | | 180-385 | 39.78 | 40.02 | $Zr_4O_6(L^1)_{0.25}Cl_4$ | |
| _ | | 385-600 | 56.92 | 54.74 | $4(ZrO_2)$ | |
| $[Zr_4(OH)_{12}(H_2O)_{10}(L^2)]Cl_4$ | (m.w. = | 1101); $L^2 = L^2$ | AcPyp-Tol | (m.w. = 21) | (0) | |
| $[Zr_4(OH)_{12}(H_2O)_{10}(L^2)]Cl_4$ | 40 | 40-110 | 12.60 | 13.07 | $Zr_4(OH)_{12}(H_2O)_2(L^2)Cl_4$ | 90 (endo) |
| | | 110–195 | 24.56 | 24.38 | $Zr_4O_2(OH)_8(L^2)_{0.75}Cl_4$ | |
| | | 195-370 | 39.68 | 40.46 | $Zr_4O_6(L^2)_{0.25}Cl_4$ | |
| | | 370-425 | 47.25 | 45.25 | $Zr_4O_6Cl_4$ | |
| | | 425-600 | 59.84 | 55.31 | $4(ZrO_2)$ | |
| $[Zr_4(OH)_{12}(H_2O)_{10}(L^3)]Cl_4$ | (m.w. = | 1117); $L^3 = I$ | AcPyp-Ani | s (m.w. = 2 | (26) | 00 (1) |
| $[Zr_4(OH)_{12}(H_2O)_{10}(L^3)]Cl_4$ | 40 | 40-105 | 11.93 | 11.28 | $Zr_4(OH)_{12}(H_2O)_3(L^3)Cl_4$ | 90 (endo) |
| | | 105-230 | 25.18 | 24.40 | $Zr_4O_2(OH)_8(L^3)_{0.75}Cl_4$ | |
| | | 230390 | 39.76 | 40.97 | $Zr_4O_6(L^3)_{0.25}Cl_4$ | |
| | | 390600 | 58.38 | 56.00 | $4(ZrO_2)$ | |
| $[Zr_4(OH)_{12}(H_2O)_{10}(L^4)]Cl_4$ | (m.w. = | 1131); $L^4 = L^4$ | AcPyp-Phe | m (m.w. = 1) | $\frac{240}{2}$ | 105 (1) |
| $[Zr_4(OH)_{12}(H_2O)_{10}(L^4)]Cl_4$ | 40 | 40115 | 11.13 | 11.14 | $Lr_4(OH)_{12}(H_2O)_3(L^-)Cl_4$ | 105 (endo) |
| | | 115-195 | 21.15 | 19.09 | $Zr_4O_2(OH)_8(L^{-})Cl_4$ | |
| | | 195-405 | 41.75 | 41.39 | $2r_4O_6(L^-)_{0.25}Cl_4$ | |
| | | 405-600 | 57.34 | 56.49 | $4(2rO_2)$ | |

Acknowledgements

Grateful thanks are due to Council of Scientific and Industrial Research (CSIR), New Delhi for financial support for this work. VC thanks the CSIR for the award of a Research Associateship and KCD thanks UGC for the award of a National Fellowship.

References

- ⁽¹⁾T. E. MacDermott, Coord. Chem. Rev., 11, 1 (1973).
- ⁽²⁾N. N. Greenwood and A. Earnshaw, Chemistry of the
- Elements, Pergamon, Oxford, 1984. ⁽³⁾ J. Selbin and L. H. Holmes, Jr., J. Inorg. Nucl. Chem., 24,
- 1111 (1962). ⁽⁴⁾ A. Fratiollo, G. A. Vidalich and F. Nako, *Inorg. Chem.*, **12**, 470 (1973).
- ⁽⁵⁾ A. Clearfield and P. A. Vaughan, Acta Crystallogr., 9, 555 (1956).
- ⁽⁶⁾ T. C. W. Mak, Can. J. Chem., 46, 3493 (1968).
- ⁽⁷⁾ N. S. Biradar and A. L. Locker, *Curr. Sci.*, 43, 5761 (1974).
 ⁽⁸⁾ A. K. Srivastava, R. K. Agarwal, M. Srivastava and T. N.
- Srivastava, J. Inorg. Nucl. Chem., 43, 2144 (1981).
- ⁽⁹⁾ A. Syamal and D. Kumar, Synth. React. Inorg. Met-Org. Chem., 10, 63 (1980).
- ⁽¹⁰⁾C. R. Panda, V. Chakravortty and K. C. Dash, J. Less Common Mets. 135, 77 (1987).

- ⁽¹¹⁾C. R. Panda, V. Chakravortty and K. C. Dash, J. Less Common Mets., submitted for publication.
- ⁽¹²⁾C. R. Panda, V. Chakravortty and K. C. Dash, *Thermochim.* Acta, **109**, 303 (1987).
- ⁽¹³⁾C. R. Panda, V. Chakravortty and K. C. Dash, *Ind. J. Chem.*, accepted for publication.
- ⁽¹⁴⁾C. R. Panda, V. Chakravortty and K. C. Dash, Solv. Ext. Ion. Exchange, 3, 857 (1985).
- ⁽¹⁵⁾L. M. Zaitsev, Russ J. Inorg. Chem., 11, 900 (1966).
- ⁽¹⁶⁾C. J. Hardy, B. O. Field and D. Scargill, J. Inorg. Nucl. Chem., 28, 2408 (1966).
- ⁽¹⁷⁾K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, 2nd edit, Wiley, New York, 1970.
- ⁽¹⁸⁾ Yu. Ya. Kharitnov and L. M. Zaitsev, Russ. J. Inorg. Chem., 13, 476 (1968).
- ⁽¹⁹⁾K. C. Malhotra, A. Kumar and S. C. Chaudhury, Ind. J. Chem., 18A, 3807 (1958).
- ⁽²⁰⁾G. Gupta, R. Sharma and R. N. Kapoor, *Transition Met. Chem.*, 3, 282 (1978).
- ⁽²¹⁾ B. Khera, A. K. Sharma and N. K. Kaushik, Polyhedron, 2, 1177 (1983).
- ⁽²²⁾ J. W. Mellor, A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Longmans, London, 1963, Vol. 7.

(Received 28 August 1987)

TMC 1768