

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

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

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

Summary

Interaction of $ZrOCl_2 \cdot 8H_2O$, $[Zr_4(OH)_8(H_2O)_{16}]Cl_8 \cdot 12H_2O$, with the heterocyclic aldimines (PyAlA) and heterocyclic ketimines (AcPyA) in Me_2CO in the presence of $HC(OEt)_3$ yields white amorphous compounds of the type $[Zr_4(OH)_{12}(H_2O)_8(PyAlA)_2]Cl_4$ and $[Zr_4(OH)_{12}(H_2O)_{10}(AcPyA)]Cl_4$. 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 MO_n^{+} and MO_2^{+} in early transition elements⁽³⁾, but there is no evidence for the existence of TiO^{2+} or ZrO^{2+} 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 $ZrOCl_2 \cdot 8H_2O$ which is actually a tetramer, $[Zr_4(OH)_8(H_2O)_{16}]Cl_8 \cdot 12H_2O$. In spite of this, monomeric complexes, $ZrOCl_2 \cdot nL$, have been reported^(7–9) in which a weak i.r. band at 950–980 cm^{-1} has been assigned to $\nu(Zr=O)$. 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 *p*-anisidine or *p*-phenetidine). The complexing agents were obtained by condensing aromatic amines with 2-pyridinecarboxaldehyde or 2-acetylpyridine, respectively. The complexes have the $[Zr_4(OH)_{12}(H_2O)_8(PyAlA)_2]Cl_4$ and $[Zr_4(OH)_{12}(H_2O)_{10}(AcPyA)]Cl_4$ stoichiometry. The complexing agents react with UO_2X_2 to form dimeric complexes⁽¹⁰⁾ of the type $[UO_2(OH)(PyAlA)Cl]_2$ and $[UO_2(OH)(H_2O)(AcPyA)_{0.5}Cl]_2$ and with ThX_4 forming monomeric complexes⁽¹¹⁾ of the type $[Th(PyAlA)X_4]$ and $[Th(AcPyA)X_4]$ ($X = NO_3$ 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 HNO_3 and then igniting to 1000°C and finally weighing as ZrO_2 . Thiocyanate was determined by the alkaline oxidative fusion method: oxidation of sulphur to sulphate and then weighing as $BaSO_4$.

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*-, *m*- or *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 $PhNH_2$ (0.37 cm^3 , 0.004 mol) and 2-pyridinecarboxaldehyde (0.43 cm^3 , 0.004 mol) in Me_2CO (10 cm^3) and $HC(OEt)_3$ (10 cm^3) 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 $ZrOCl_2 \cdot 8H_2O$ (0.64 g, 0.002 mol) in dry Me_2CO and $HC(OEt)_3$ with constant stirring. The yellowish-brown precipitate which formed was collected, washed with small aliquots of Et_2O and finally dried *in vacuo*.

$[Zr_4(OH)_{12}(H_2O)_{10}(AcPyA)]Cl_4$ (A = aniline, *o*-, *m*- or *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 metal-to-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.

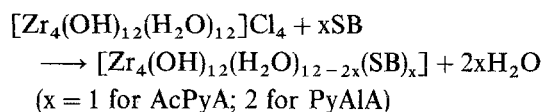
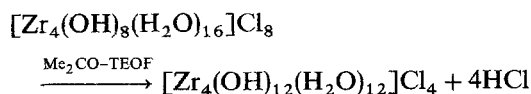
* Author to whom all correspondence should be directed.

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

Compound	Mol formula (Mol. wt)	Found (Calcd.)%					Λ_M in MeOH (mho cm ² mol ⁻¹)
		Zr	C	H	N	Cl	
A in [Zr ₄ (OH) ₁₂ (H ₂ O) ₈ (PyAlA) ₂]Cl ₄							
Aniline	Zr ₄ C ₂₄ H ₄₈ N ₄ O ₂₀ Cl ₄ (1219)	29.6 (29.9)	23.5 (23.6)	3.9 (3.9)	4.4 (4.6)	11.4 (11.6)	320.10
<i>o</i> -Toluidine	Zr ₄ C ₂₆ H ₅₂ N ₄ O ₂₀ Cl ₄ (1247)	29.0 (29.2)	25.2 (25.0)	4.1 (4.2)	4.3 (4.5)	11.3 (11.4)	309.9
<i>m</i> -Toluidine	Zr ₄ C ₂₆ H ₅₂ N ₄ O ₂₀ Cl ₄ (1247)	29.2 (29.2)	24.8 (25.0)	4.2 (4.2)	4.3 (4.5)	11.2 (11.4)	315.6
<i>p</i> -Toluidine	Zr ₄ C ₂₆ H ₅₂ N ₄ O ₂₀ Cl ₄ (1247)	29.0 (29.2)	25.1 (25.0)	4.4 (4.2)	4.2 (4.5)	11.1 (11.4)	295.17
<i>o</i> -Anisidine	Zr ₄ C ₂₆ H ₅₂ N ₄ O ₂₂ Cl ₄ (1279)	28.3 (28.5)	24.3 (24.4)	4.0 (4.1)	4.4 (4.4)	11.1 (11.1)	276.39
<i>p</i> -Anisidine	Zr ₄ C ₂₆ H ₅₂ N ₄ O ₂₂ Cl ₄ (1279)	28.4 (28.5)	24.4 (24.4)	4.2 (4.1)	4.5 (4.4)	10.8 (11.1)	385.68
<i>p</i> -Phenetidine	Zr ₄ C ₂₈ H ₅₆ N ₄ O ₂₂ Cl ₄ (1307)	27.7 (27.9)	25.6 (25.7)	4.3 (4.3)	4.1 (4.3)	10.7 (10.8)	270.90
Aniline							
Aniline	Zr ₄ C ₁₃ H ₄₄ N ₂ O ₂₂ Cl ₄ (1087)	33.4 (33.6)	14.4 (14.3)	4.0 (4.0)	2.7 (2.5)	12.9 (13.0)	—
<i>o</i> -Toluidine	Zr ₄ C ₁₄ H ₄₆ N ₂ O ₂₂ Cl ₄ (1101)	33.2 (33.1)	15.3 (15.2)	4.3 (4.2)	2.6 (2.5)	12.9 (12.9)	—
<i>m</i> -Toluidine	Zr ₄ C ₁₄ H ₄₆ N ₂ O ₂₂ Cl ₄ (1101)	33.0 (33.1)	15.3 (15.2)	4.0 (4.2)	2.7 (2.5)	12.6 (12.9)	—
<i>p</i> -Toluidine	Zr ₄ C ₁₄ H ₄₆ N ₂ O ₂₂ Cl ₄ (1101)	33.2 (33.1)	15.1 (15.2)	4.2 (4.2)	2.6 (2.5)	12.8 (12.9)	—
<i>o</i> -Anisidine	Zr ₄ C ₁₄ H ₄₆ N ₂ O ₂₃ Cl ₄ (1117)	32.6 (32.7)	15.0 (15.0)	4.3 (4.1)	2.2 (2.5)	12.5 (12.7)	—
<i>p</i> -Anisidine	Zr ₄ C ₁₄ H ₄₆ N ₂ O ₂₃ Cl ₄ (1117)	32.5 (32.7)	15.2 (15.0)	4.0 (4.1)	2.3 (2.5)	12.7 (12.7)	—
<i>p</i> -Phenetidine	Zr ₄ C ₁₅ H ₄₈ N ₂ O ₂₃ Cl ₄ (1131)	32.3 (32.2)	16.0 (15.9)	4.1 (4.2)	2.5 (2.5)	12.7 (12.5)	—

The Zr:Cl ratio in [Zr₄(OH)₈(H₂O)₁₆]Cl₈ 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, and yielding complexes formulated as [Zr₄(OH)₈^b(OH)₄^t(H₂O)₁₂]Cl₄. 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 ZrOCl₂·8H₂O 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:



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, Zr₄(OH)₈^b(OH)₈^t(H₂O)_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 [Zr₄(OH)₈^b(H₂O)₁₆]⁸⁺. The aldimine and ketimine complexes described in this paper seem to be intermediate between the [Zr₄(OH)₈(H₂O)₁₆]⁸⁺ and the α -hydroxide, [Zr₄(OH)₈^b(OH)₈^t(H₂O)_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 molecules, yielding complexes of the type [Zr₄(OH)₈^b(OH)₄^t(H₂O)_{12-2x}(SB)_x]Cl₄, where x = 1 for the ketimines AcPyA and 2 for aldimines PyAlA.

A comparative i.r. spectral analysis in the 4000–200 cm⁻¹ range show the starting material ZrOCl₂·8H₂O and the product complexes to be identical except for the extra bands in the latter corresponding to

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 loss (%)		Species formed	DTA peak (°C)
			Obsd.	Calcd.		
$[\text{Zr}_4(\text{OH})_{12}(\text{H}_2\text{O})_8(\text{L}^1)_2]\text{Cl}_4$	40	40–150	14.96	14.76	$\text{Zr}_4\text{O}_2(\text{OH})_8(\text{L}^1)_2\text{Cl}_4$	110 (endo)
$[\text{Zr}_4(\text{OH})_{12}(\text{H}_2\text{O})_8(\text{L}^1)_2]\text{Cl}_4$			39.90	39.34	$\text{Zr}_4\text{O}_6(\text{L}^1)_{0.75}\text{Cl}_4$	
			61.65	59.64	$4(\text{ZrO}_2)$	400 (exo)
$[\text{Zr}_4(\text{OH})_{12}(\text{H}_2\text{O})_8(\text{L}^2)_2]\text{Cl}_4$	40	40–110	16.45	14.43	$\text{Zr}_4\text{O}_2(\text{OH})_8(\text{L}^2)_2\text{Cl}_4$	80 (endo)
$[\text{Zr}_4(\text{OH})_{12}(\text{H}_2\text{O})_8(\text{L}^2)_2]\text{Cl}_4$			47.86	47.73	$\text{Zr}_4\text{O}_6(\text{L}^2)_{0.25}\text{Cl}_4$	
			61.32	60.54	$4(\text{ZrO}_2)$	425 (exo)
$[\text{Zr}_4(\text{OH})_{12}(\text{H}_2\text{O})_8(\text{L}^3)_2]\text{Cl}_4$	40	40–130	17.95	18.21	$\text{Zr}_4\text{O}_2(\text{OH})_8(\text{L}^3)_{1.75}\text{Cl}_4$	90 (endo)
$[\text{Zr}_4(\text{OH})_{12}(\text{H}_2\text{O})_8(\text{L}^3)_2]\text{Cl}_4$			43.21	44.58	$\text{Zr}_4\text{O}_6(\text{L}^3)_{0.5}\text{Cl}_4$	
			62.50	61.51	$4(\text{ZrO}_2)$	420 (exo)
$[\text{Zr}_4(\text{OH})_{12}(\text{H}_2\text{O})_8(\text{L}^4)_2]\text{Cl}_4$	40	40–105	16.00	18.08	$\text{Zr}_4\text{O}_2(\text{OH})_8(\text{L}^4)_{1.75}\text{Cl}_4$	85 (endo)
$[\text{Zr}_4(\text{OH})_{12}(\text{H}_2\text{O})_8(\text{L}^4)_2]\text{Cl}_4$			48.00	49.55	$\text{Zr}_4\text{O}_6(\text{L}^4)_{0.25}\text{Cl}_4$	
			64.00	62.36	$4(\text{ZrO}_2)$	420 (exo)
$[\text{Zr}_4(\text{OH})_{12}(\text{H}_2\text{O})_{10}(\text{L}^1)]\text{Cl}_4$	40	40–120	15.3	16.55	$\text{Zr}_4(\text{OH})_{12}(\text{L}^1)\text{Cl}_4$	100 (endo)
$[\text{Zr}_4(\text{OH})_{12}(\text{H}_2\text{O})_{10}(\text{L}^1)]\text{Cl}_4$			23.25	24.38	$\text{Zr}_4\text{O}_2(\text{OH})_8(\text{L}^1)_{0.75}\text{Cl}_4$	
			39.78	40.02	$\text{Zr}_4\text{O}_6(\text{L}^1)_{0.25}\text{Cl}_4$	
			56.92	54.74	$4(\text{ZrO}_2)$	
$[\text{Zr}_4(\text{OH})_{12}(\text{H}_2\text{O})_{10}(\text{L}^2)]\text{Cl}_4$	40	40–110	12.60	13.07	$\text{Zr}_4(\text{OH})_{12}(\text{H}_2\text{O})_2(\text{L}^2)\text{Cl}_4$	90 (endo)
$[\text{Zr}_4(\text{OH})_{12}(\text{H}_2\text{O})_{10}(\text{L}^2)]\text{Cl}_4$			24.56	24.38	$\text{Zr}_4\text{O}_2(\text{OH})_8(\text{L}^2)_{0.75}\text{Cl}_4$	
			39.68	40.46	$\text{Zr}_4\text{O}_6(\text{L}^2)_{0.25}\text{Cl}_4$	
			47.25	45.25	$\text{Zr}_4\text{O}_6\text{Cl}_4$	
$[\text{Zr}_4(\text{OH})_{12}(\text{H}_2\text{O})_{10}(\text{L}^3)]\text{Cl}_4$	40	40–105	11.93	11.28	$\text{Zr}_4(\text{OH})_{12}(\text{H}_2\text{O})_3(\text{L}^3)\text{Cl}_4$	90 (endo)
$[\text{Zr}_4(\text{OH})_{12}(\text{H}_2\text{O})_{10}(\text{L}^3)]\text{Cl}_4$			25.18	24.40	$\text{Zr}_4\text{O}_2(\text{OH})_8(\text{L}^3)_{0.75}\text{Cl}_4$	
			39.76	40.97	$\text{Zr}_4\text{O}_6(\text{L}^3)_{0.25}\text{Cl}_4$	
			58.38	56.00	$4(\text{ZrO}_2)$	
$[\text{Zr}_4(\text{OH})_{12}(\text{H}_2\text{O})_{10}(\text{L}^4)]\text{Cl}_4$	40	40–115	11.13	11.14	$\text{Zr}_4(\text{OH})_{12}(\text{H}_2\text{O})_3(\text{L}^4)\text{Cl}_4$	105 (endo)
$[\text{Zr}_4(\text{OH})_{12}(\text{H}_2\text{O})_{10}(\text{L}^4)]\text{Cl}_4$			21.15	19.09	$\text{Zr}_4\text{O}_2(\text{OH})_8(\text{L}^4)\text{Cl}_4$	
			41.75	41.39	$\text{Zr}_4\text{O}_6(\text{L}^4)_{0.25}\text{Cl}_4$	
			57.34	56.49	$4(\text{ZrO}_2)$	

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