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THERMOGRAVIMETRIC AND INFRARED STUDIES OF TETRAMERIC ZIRCONIUM(IV) COMPOUNDS DERIVED FROM OXOZIRCONIUM(IV) CHLORIDE AND IMIDAZOLE, MORPHOLINE AND THEIR DERIVATIVES

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ABSTRACT

Oxozirconium chloride reacts with imidazole, morpholine and their derivatives in acetone medium in the presence of triethylorthoformate to form white amorphous compounds with a high melting point. IR and thermogravimetric measurements as well as analytical data indicate their polymeric formulation in the solid state where the structure is derived from the basic tetrameric dodecahedral structure of the parent $ZrOCl_2 \cdot 8H_2O$ formulated as $[Zr_4(OH)_8(H_2O)_{16}]Cl_8$. The unidentate imidazole or morpholine ligands appear to replace some of the coordinated H_2O molecules and deprotonate some other H_2O molecules forming compounds of the type $[Zr_4(OH)_{12}(H_2O)_{12-n}L_n]Cl_4$ where $n = 1$ for L = 1-MeIm, 1-EtIm, 1-ViIm, 2-iPrIm, 2-PhIm; $n = 2$ for L = Im, 2-MeIm, 4-MeMorph and $n = 4$ for L = Morph. Thermogravimetric studies indicate the stepwise loss of water molecules and the ligands forming complex intermediates with increase in temperature. The stoichiometry of decomposition products is calculated. Based on initial decomposition temperature, an order of thermal stability for the complexes is proposed.

INTRODUCTION

The chemistry of zirconium(IV) is of interest in view of the fact that this ion may form [1] a wide variety of complexes with coordination numbers 4 to 8, and 12. The geometry and coordination number around Zr in these compounds appear to be determined by various factors, such as the nature of the donor atoms, the charge on the ligand, the stoichiometry of the reactants in the preparative process, the size and the chelating ability of the ligands, vapour pressure, temperature and other physical characteristics during compound formation. The strongly bound oxygen(s) of various oxo metal compounds of the types MO^{n+} and MO_2^{n+} found among the early transition elements of groups IV, V and VI provide additional means for studying the complexes of these oxycations, beyond those normally available for the study of transition metal complexes. Selbin and Holmes [2] have observed the metal–oxygen multiple bond stretching frequency in the range

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900–1100 cm^{-1} for MoO^{3+}, MoO_2^{2+}, WO_2^{2+}, VO^{2+} and UO_2^{2+} but found no evidence for TiO^{2+} or ZrO^{2+} mononuclear species in certain so-called titanyl or zirconyl compounds. Some polymeric form of zirconium(IV) seems to predominate both in solution and in the solid state. This idea receives support from NMR measurements of hydration numbers in solution [3] and the X-ray crystal structure [4,5] of $ZrOCl_2 \cdot 8H_2O$ in the solid state, which is actually $[Zr_4(OH)_8(H_2O)_{16}]Cl_8$. The zirconium atoms in this compound lie in a distorted square, linked by pairs of hydroxo bridges and also bound to water molecules, so that the Zr atom is coordinated by eight oxygen atoms in a distorted dodecahedral arrangement (D_{2d}) with Zr–OH (bridging) of 214.2 pm and $Zr-OH_2$ (terminal) of 227.2 pm.

In spite of this convincing proof, a number of workers have reported that $ZrOCl_2 \cdot 8H_2O$ forms monomeric complexes with various ligands. Thus, $ZrOCl_2$ was shown to form [6] 1:1 addition compounds with pyridine derivatives, quinoline, isoquinoline, Me_2NPh and Et_2NPh; 1:2 complexes with DMF, $AcNH_2$, AcNHMe, $AcNMe_2$, $BzNH_2$ and 1:4 complexes with $HCONH_2$ and urea. Benzimidazole and its derivatives also form [7] 1:2 and 1:4 adducts with $ZrOCl_2$. Monomeric complexes of pyridine-*N*-oxide [8] and quinoline-*N*-oxide [9] with zirconyl perchlorate were also reported. A number of monomeric zirconyl complexes with 1, 10-phenanthroline-*N*-oxide (phen-NO) were also reported [10] where the stoichiometric formulae are of the type $[ZrO(phenNO)X_2]$ (X = Cl, Br, NCS, NO_3), $[ZrO(phenNO)_2]I_2$ and $[ZrO(PhenNO)_3](ClO_4)_2$. In all these compounds a weak IR band at 950–980 cm^{-1} was invariably assigned to $\nu(Zr{=}O)$. This assignment is surprising in view of the fact that there is no evidence for the existence of a Zr=O group in oxozirconium(IV) compounds.

Continuing our earlier work on imidazoles [11–15] and in view of the interesting chemistry of oxozirconium(IV) compounds, we chose to study the interaction of oxozirconium(IV) chloride with imidazole or morpholine ligands under anhydrous conditions with the hope of obtaining simple, monomeric, addition complexes, as reported in the literature [6–10]. Our investigations show that the complexes synthesised are far from simple and differ considerably from the literature reports. The complexes seem to have a polymeric structure that is derived from the tetrameric structure $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ [4,5] with each Zr atom having a coordination number of eight.

EXPERIMENTAL

Materials

$ZrOCl_2 \cdot 8H_2O$ (Riedel) was reagent grade and used as supplied. Imidazole, morpholine and their derivatives were used as supplied by BASF, Ludwigshafen, West Germany.

TABLE 1

Analytical data for oxozirconium complexes

Complex	Empirical formula	Mol. wt.	Element (%) found (calc.)				
			Zr	C	H	N	Cl
$[Zr_4(OH)_{12}(H_2O)_{10}(Im)_2]Cl_4$	$Zr_4C_6H_{40}N_4O_{22}Cl_4$	1027.05	35.4 (35.5)	6.9 (7.0)	3.7 (3.9)	5.0 (5.4)	13.9 (13.8)
$[Zr_4(OH)_{12}(H_2O)_{11}(1\text{-MeIm})]Cl_4$	$Zr_4C_4H_{40}N_2O_{23}Cl_4$	991.01	36.9 (36.8)	5.0 (4.8)	3.9 (4.0)	2.7 (2.8)	14.1 (14.3)
$[Zr_4(OH)_{12}(H_2O)_{11}(1\text{-EtIm})]Cl_4$	$Zr_4C_5H_{42}N_2O_{23}Cl_4$	1005.04	36.5 (36.3)	5.7 (5.9)	4.0 (4.2)	2.6 (2.8)	14.3 (14.1)
$[Zr_4(OH)_{12}(H_2O)_{11}(1\text{-ViIm})]Cl_4$	$Zr_4C_5H_{40}N_2O_{23}Cl_4$	1003.02	36.0 (36.3)	5.9 (6.0)	4.0 (4.0)	2.8 (2.8)	13.9 (14.1)
$[Zr_4(OH)_{12}(H_2O)_{10}\ (2\text{-MeIm})_2]Cl_4$	$Zr_4C_8H_{44}N_4O_{22}Cl_4$	1055.09	34.9 (34.5)	9.2 (9.1)	3.9 (4.2)	5.0 (5.3)	13.5 (13.4)
$[Zr_4(OH)_{12}(H_2O)_{11}(2\text{-iPrIm})]Cl_4$	$Zr_4C_6H_{44}N_2O_{23}Cl_4$	1019.06	35.6 (35.8)	7.0 (7.0)	4.1 (4.3)	2.8 (2.7)	14.1 (13.9)
$[Zr_4(OH)_{12}(H_2O)_{11}(2\text{-PhIm})]Cl_4$	$Zr_4C_9H_{42}N_2O_{23}Cl_4$	1053.09	34.2 (34.6)	10.0 (10.2)	4.1 (4.0)	2.4 (2.6)	13.0 (13.4)
$[Zr_4(OH)_{12}(H_2O)_8(Morph)_4]Cl_4$	$Zr_4C_{16}H_{64}N_4O_{24}Cl_4$	1203.29	30.2 (30.3)	16.0 (15.9)	5.2 (5.3)	4.2 (4.6)	11.9 (11.8)
$[Zr_4(OH)_{12}(H_2O)_{10}(4\text{-MeMorph})_2]Cl_4$	$Zr_4C_{10}H_{54}N_2O_{24}Cl_4$	1093.15	33.1 (33.3)	10.7 (10.9)	5.0 (4.9)	2.6 (2.5)	13.0 (12.9)

TABLE 2

Prominent IR bands (cm^{-1}) of some oxozirconium complexes

Complex	ν(OH)	δ(Zr-O-H)	H–O–H def.	Ligand bands [a]					
				ν(C–H)	Ring str.	Ring C–H bend + C–N str.	C–H in-plane def.	C–H out-of-plane def.	Ring def.
Imidazole	–	–	–	3030m 2934m	1550m 1492m 1451m	1278s	1101w 1058s	760s 740m	664s 620s
$[Zr_4(OH)_8(H_2O)_{16}]Cl_8$	3400br		1630br, sh	–	–	–	–	–	–
$[Zr_4(OH)_{12}(H_2O)_{10}(Im)_2]Cl_4$	3400br	1100m	1620sh	2880sh 2820m	1580s 1500sh 1440br	1320m 1260m	1070m 1050s	760br 690w	660w 625m
$[Zr_4(OH)_{12}(H_2O)_{11}(1\text{-MeIm})]Cl_4$	3400br	1115m	1625sh	2910m 2870sh	1565s 1510sh 1430m	1285s 1250w	1090m 1070m	750br 700m	650s 635w
$[Zr_4(OH)_{12}(H_2O)_{11}(1\text{-EtIm})]Cl_4$	3400br	1110m	1610sh	3015m 3005sh	1585s 1490m 1460sh	1290m 1260m	1080m 1040s	780s 730m	670m 620m
$[Zr_4(OH)_{12}(H_2O)_{11}(1\text{-ViIm})]Cl_4$	3400br	1100m	1620sh	3025m 2990m	1590m 1490m 1445m	1275s	1085w 1065s	770br 715m	665s 610m
$[Zr_4(OH)_{12}(H_2O)_{10}(2\text{-MeIm})_2]Cl_4$	3400br	1120m	1615sh	3010m 2920sh	1575s 1505m	1280s 1260w	1105w 1055m	790br 720w	655s 620s
$[Zr_4(OH)_{12}(H_2O)_{11}(2\text{-iPrIm})]Cl_4$	3400br	1115m	1615sh	2980m 2915sh	1500s 1465m 1420m	1310s 1265w	1085w 1030s	780s 745w	680m 610m
$[Zr_4(OH)_{12}(H_2O)_{11}(2\text{-PhIm})]Cl_4$	3400br	1110m	1625sh	3000m 2930sh	1530s 1490sh 1420m	1300s	1095w 1060s	795s 730m	690s 630m

[a] ν(N–H) of ligand is obscured under the broad and strong ν(O–H) of the zirconium tetramer.

Analyses

The C, H and N microanalyses were either from CDRI, Lucknow or from Technical University, Munich. Zirconium was determined gravimetrically as ZrO_2 after slow decomposition of complexes with HNO_3 and then heating at 1000°C in an electrical muffle furnace up to constant weight. The chloride content was estimated by decomposition of the complex by oxidative fusion with Na_2O_2 and NaOH followed by extraction with water, acidification by dilute HNO_3 and then precipitation as AgCl by addition of $AgNO_3$. The analytical data are presented in Table 1.

IR measurements

The IR spectra of the complexes were recorded as KBr disk (or polyethylene pellets) either in the 4000–400 cm^{-1} region using a Perkin Elmer 377 instrument or in the 4000–200 cm^{-1} region using a Perkin Elmer 983 instrument. The important IR frequencies are presented in Table 2 and IR spectra of $[Zr_4(OH)_8(H_2O)_{16}]Cl_8$ and $[Zr_4(OH)_{12}(H_2O)_{10}(Im)_2]Cl_4$ are shown in Fig. 1.

Thermogravimetric measurements

Thermal measurements in static air were carried out using a Netzsch simultaneous thermal analyser (model 429) fitted with a potentiometric recorder. The equipment records T, TG and DTA simultaneously. The rate of heating was 10°C min^{-1}. The thermal parameters for the decomposition of the complexes are shown in Table 3. Figures 2 and 3 show TG and DTA curves for $[Zr_4(OH)_{12}(H_2O)_{10}(Im)_2]Cl_4$ and $[Zr_4(OH)_{12}(H_2O)_{11}(1\text{-}Vilm)]Cl_4$, respectively.

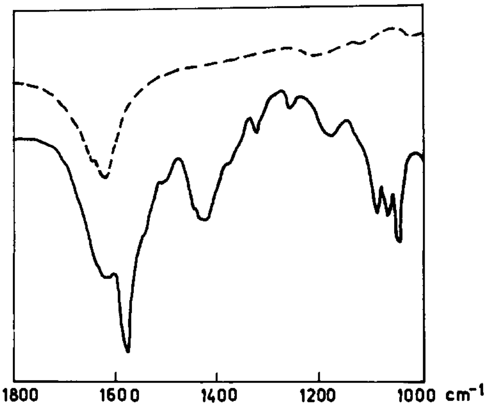


Fig. 1. IR spectra of: zirconyl octahydrate, $[Zr_4(OH)_8(H_2O)_{16}]Cl_8$ (— — —); oxozirconium-(IV) imidazole complex $[Zr_4(OH)_{12}(H_2O)_{10}(Im)_2]Cl_4$ (———).

TABLE 3

Thermal decomposition parameters of oxozirconium complexes

Starting material	Initial decomposition temp. (°C)	TG data			Species formed	DTA peak (°C)
		Temp. range (°C)	Weight loss (%)			
			Obs.	Calc.		
$[Zr_4(OH)_{12}(H_2O)_{10}(Im)_2]Cl_4$ (mol. wt. = 1027.05); Im = Imidazole (mol. wt. = 68.07)						
$[Zr_4(OH)_{12}(H_2O)_{10}(Im)_2]Cl_4$	30	30–108	12.01	12.26	$Zr_4(OH)_{12}(H_2O)_3(Im)_2Cl_4$	120(endo)
$Zr_4(OH)_{12}(H_2O)_3(Im)_2Cl_4$		108–196	19.11	21.12	$Zr_4O_2(OH)_8(Im)_2Cl_4$	
$Zr_4O_2(OH)_8(Im)_2Cl_4$		196–310	32.75	32.91	$Zr_4O_4(OH)_4(Im)_{0.75}Cl_4$	270(exo)
$Zr_4O_4(OH)_4(Im)_{0.75}Cl_4$		310–416	39.31	41.38	$Zr_4O_6Cl_4$	365(exo)
$Zr_4O_6Cl_6$		416–592	43.68	44.8	$Zr_4O_6Cl_3$	520(exo)
						580(endo)
$Zr_4O_6Cl_3$		592–680	46.41	47.76	$Zr_4O_6Cl_2$	
$[Zr_4(OH)_{12}(H_2O)_{11}(1\text{-}MeIm)]Cl_4$ (mol. wt. = 991.01); 1-MeIm = 1-Methyl imidazole (mol. wt. = 82.09)						
$[Zr_4(OH)_{12}(H_2O)_{11}(1\text{-MeIm})]Cl_4$	30	30–100	12.09	12.79	$Zr_4(OH)_{12}(H_2O)_4(1\text{-MeIm})Cl_4$	
$Zr_4(OH)_{12}(H_2O)_4(1\text{-MeIm})Cl_4$		100–155	21.77	21.89	$Zr_4O(OH)_{10}(1\text{-MeIm})Cl_4$	130(endo)
$Zr_4O(OH)_{10}(1\text{-MeIm})Cl_4$		155–300	33.06	33.55	$Zr_4O_4(OH)_4(1\text{-MeIm})_{0.25}Cl_4$	
$Zr_4O_4(OH)_4(1\text{-MeIm})_{0.25}Cl_4$		300–470	46.77	46.41	$Zr_4O_6Cl_2$	420(exo)
						470(exo)
$Zr_4O_6Cl_2$		470–800	50.00	50.35	$4(ZrO_2)$	520(endo)

$[Zr_4(OH)_{12}(H_2O)_{11}(1\text{-}ViIm)]Cl_4$ (mol. wt. = 1003.02); 1-ViIm = 1-Vinyl imidazole (mol. wt. = 94.10)						
$[Zr_4(OH)_{12}(H_2O)_{11}(1\text{-}ViIm)]Cl_4$	45	45–146	17.85	17.94	$Zr_4(OH)_{12}(H_2O)(1\text{-}ViIm)Cl_4$	120(endo)
$Zr_4(OH)_{12}(H_2O)(1\text{-}ViIm)Cl_4$		146–373	35.71	36.39	$Zr_4O_4(OH)_4Cl_4$	
$Zr_4O_4(OH)_4Cl_4$		373–520	47.60	47.05	$Zr_4O_6Cl_2$	410(exo) 490(exo)
$Zr_4O_6Cl_2$		520–800	50.00	50.94	$4(ZrO_2)$	556(endo) 760(exo) 790(endo)
$[Zr_4(OH)_{12}(H_2O)_{11}(2\text{-}iPrIm)]Cl_4$ (mol. wt. = 1019.06); 2-iPrIm = 2-isoPropyl imidazole (mol. wt. = 110.14)						
$[Zr_4(OH)_{12}(H_2O)_{11}(2\text{-}iPrIm)]Cl_4$	30	30–200	19.19	19.43	$Zr_4(OH)_{12}(2\text{-}iPrIm)Cl_4$	
$Zr_4(OH)_{12}(2\text{-}iPrIm)Cl_4$		200–448	38.84	37.38	$Zr_4O_4(OH)_4Cl_4$	440(endo)
$Zr_4O_4(OH)_4Cl_4$		448–600	41.71	40.92	$Zr_4O_6Cl_4$	
$[Zr_4(OH)_{12}(H_2O)_{11}(2\text{-}PhIm)]Cl_4$ (mol. wt. = 1053.09); 2-PhIm = 2-Phenyl imidazole (mol. wt. = 144.17)						
$[Zr_4(OH)_{12}(H_2O)_{11}(2\text{-}PhIm)]Cl_4$	30	30–210	18.78	18.80	$Zr_4(OH)_{12}(2\text{-}PhIm)Cl_4$	
$Zr_4(OH)_{12}(2\text{-}PhIm)Cl_4$		210–270	34.53	35.99	$Zr_4O_2(OH)_8Cl_4$	
$Zr_4O_2(OH)_8Cl_4$		270–600	43.17	42.83	$Zr_4O_6Cl_4$	480(endo)
$[Zr_4(OH)_{12}(H_2O)_{10}(4\text{-}MeMorph)_2]Cl_4$ (mol. wt. = 1093.15); 4-MeMorph = 4-Methyl morpholine (mol. wt. = 101.12)						
$[Zr_4(OH)_{12}(H_2O)_{10}(4\text{-}MeMorph)_2]Cl_2$	55	55–170	18.48	18.11	$Zr_4O(OH)_{10}(4\text{-}MeMorph)_2Cl_4$	120(endo)
$Zr_4O(OH)_{10}(4\text{-}MeMorph)_2Cl_4$		170–320	31.90	31.40	$Zr_4O_2(OH)_8(4\text{-}MeMorph)_{0.75}Cl_4$	350(exo)
$Zr_4O_2(OH)_8(4\text{-}MeMorph)_{0.75}Cl_4$		320–750	42.0	44.92	$Zr_4O_6Cl_4$	470(exo)

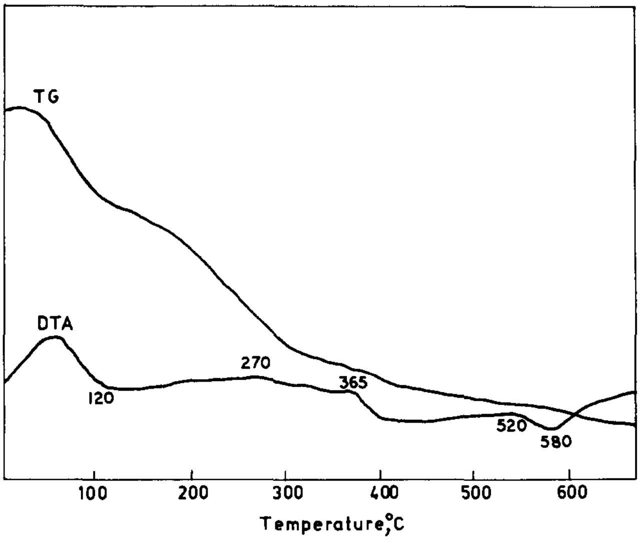


Fig. 2. TG and DTA curves for $[Zr_4(OH)_{12}(H_2O)_{10}(Im)_2]Cl_4$.

Synthesis of complexes

The complexes synthesised were of the type $[Zr_4(OH)_{12}(H_2O)_{12-n}L_n]Cl_4$ and were prepared by the reaction of $ZrOCl_2 \cdot 8H_2O$ and the ligand taken in the appropriate stoichiometric ratio by a general method. A typical method of synthesis is detailed below for the imidazole complex.

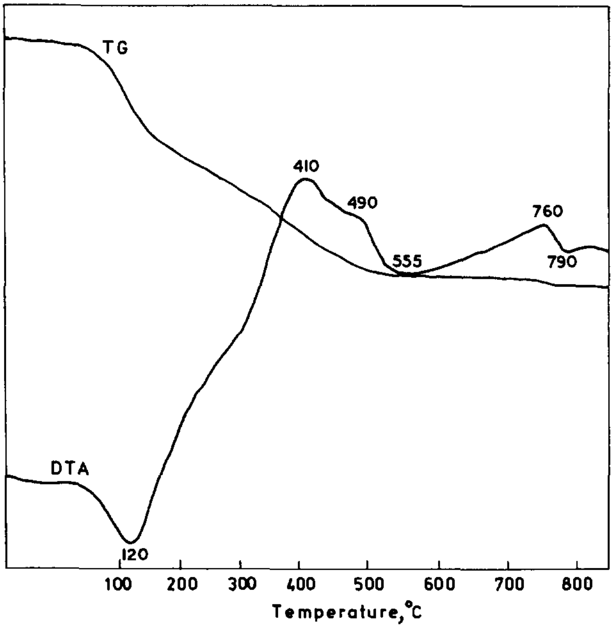
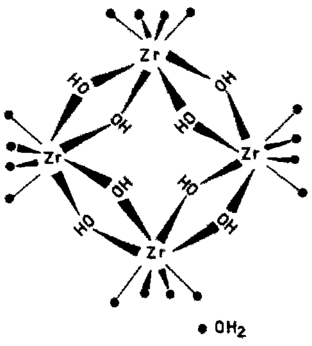


Fig. 3. TG and DTA curves for $[Zr_4(OH)_{12}(H_2O)_{11}(1\text{-ViIm})]Cl_4$.

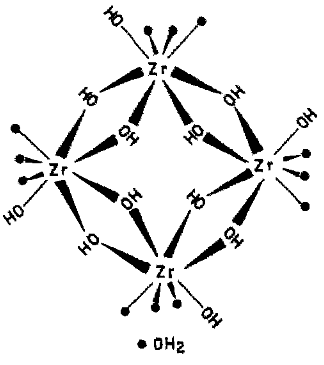
$ZrOCl_2 \cdot 8H_2O$ tetramer, 0.642 g (2 mmol), was taken in a mixture of dry acetone (5 ml) and triethylorthoformate (5 ml) and stirred vigorously for 30 min, and then cooled in an ice-bath for 15 min with stirring. To this cooled solution was added imidazole (0.272 g, 4 mmol) in acetone (5 ml) with continuous stirring. The clear solution slowly turned turbid and in about 2–3 min a powdery white compound separated out. The stirring was continued for a further 60 min in order to ensure completion of the reaction. This compound was then slowly brought to room temperature and filtered through a glass sintered frit, washed repeatedly with acetone followed by small aliquots of ether and dried in vacuo.

RESULTS AND DISCUSSION

All complexes reported in this paper were prepared by the interaction of $ZrOCl_2 \cdot 8H_2O$ in acetone (to which triethylorthoformate was added for dehydration) and the ligands in ice-cold conditions. In some cases, the compounds were formed almost immediately and for others they appeared after stirring for some time. All the compounds synthesized are reported in Table 1 along with their characterising data. They are all white and amorphous with a melting point greater than 250°C. Detailed and repeated analysis of the analytical data provide no evidence for the formation of simple, monomeric adducts with differing M : L ratios. The analytical data of these complexes agreed very well with the formula which was based on the structure [4,5] of tetrameric $[Zr_4(OH)_8(H_2O)_{16}]Cl_8$ (I) with double hydroxo bridges between each adjacent pair of Zr atoms. The analytical data show the Zr : Cl ratio to be 4 : 4 and not 4 : 8 as in $[Zr_4(OH)_8(H_2O)_{16}]Cl_8$, which shows that at some stage of complexation, four water molecules are deprotonated to give four extra hydroxo groups which are bonded terminally forming compounds of the type $[Zr_4(OH)_{12}(H_2O)_{12}]Cl_4$ which presumably



(I)



(II)

has a tetrameric structure with eight coordination around each Zr atom. This compound may be formulated as $[Zr_4(OH)^b_8(OH)^t_4(H_2O)_{12}]Cl_4$ (**II**). From this basic structure either 1, 2 or 4 water molecules are replaced by an appropriate number of neutral ligands (imidazole, morpholine or their derivatives), forming the observed complexes $[Zr_4(OH)_{12}(H_2O)_{12-n}L_n]Cl_4$ where $n = 1$, 2, or 4. The formation of eight-coordinate complexes with Zr–OH–Zr bridges is as expected for a moderately large cation (ionic radius of $Zr^{4+} = 74$ pm) with a rather high charge number.

Based upon the observation that the $[H^+]$ of $ZrOCl_2 \cdot 8H_2O$ (1 mmol) in acetone + triethylorthoformate (TEOF) was 1.7 M, the pH of imidazole (2 mmol) in acetone was 8.4, and after complexation and separation of the coordination complex the pH of the solution was 4.4 (the usual corrections were made for pH determination in non-aqueous solvents); the reaction then presumably proceeds in the sequence

$$[Zr_4(OH)_8(H_2O)_{16}]Cl_8 \xrightarrow[\text{(TEOF)}]{\text{Acetone}} [Zr_4(OH)_{12}(H_2O)_{12}]Cl_4 + 4HCl$$

$$[Zr_4(OH)_{12}(H_2O)_{12}]Cl_4 + nL \rightarrow [Zr_4(OH)_{12}(H_2O)_{12-n}L_n]Cl_4 + nH_2O$$

Zaitsev [16] has proved on chemical grounds that three distinguishable hydroxides of Zr can be obtained where the four-membered Zr atoms of the following three types may exist: (a) the freshly prepared α-hydroxide formulated as $Zr_4(OH)^b_8(OH)^t_8(H_2O)_x$ with adjacent pairs of Zr atoms joined by a double hydroxo bridge, (b) the β-hydroxide, $Zr_4O_2(OH)^b_4(OH)^t_8(H_2O)_y$ where the Zr atoms are joined alternatively by double hydroxo and oxo-bridges, and (c) the γ-hydroxide, $Zr_4O_4(OH)^t_8(H_2O)_z$ where the Zr atoms are joined only by oxo-bridges. The β- and γ-hydroxides were obtained by ageing of the α-hydroxide. No structural evidence in favour of the proposed structures were provided. However, the structure of the α-form, $Zr_4(OH)^b_8(OH)^t_8\ (H_2O)_x$ is reasonable on the basis of the structure of $ZrOCl_2 \cdot 8H_2O$ which is $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ (**I**). The compounds synthesised in our work are believed to be intermediate between the $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ and the α-hydroxide, $Zr_4(OH)^b_8(OH)^t_8(H_2O)_x$ in that they contain four chloride ions in addition to the ligands joined to the Zr atoms in place of either 1, 2 or 4 H_2O molecules. These complexes are highly insoluble in common organic solvents, precluding the measurement of conductivities and molecular weight. A comparative analysis of the IR spectra in the range 4000–200 cm^{-1} for the parent $ZrOCl_2 \cdot 8H_2O$ and the synthesised complexes are identical to each other except for the extra bands obtained in the latter cases corresponding to the various vibrational modes of the ligand. In none of the cases did we find a band in the 835–925 cm^{-1} region corresponding to $\nu(Zr{=}O)$, as has been observed by some workers [17–19], indicating clearly the absence of the ZrO^{2+} moiety.

In these complexes, a band is located in the range 1100–1115 cm^{-1} due to $\delta(Zr{-}O{-}H)$ [20,21] favouring the double hydroxo-bridge structure as proposed. The broad but strong band centred at 3400 cm^{-1} in all the complexes is assigned [22,23] to the $\nu(OH)$ of both the coordinated water and the coordinated (bridging or terminal) hydroxo groups. The bending mode, $\delta(OH)$, for the water molecule appears at 1615–1630 cm^{-1} in all the complexes, whereas for the bridged hydroxo groups [20–24] they are at 1100–1115 cm^{-1} and for the terminal hydroxo groups at 920 cm^{-1} as a weak to medium intensity band. The $\nu(Zr–O)$ appears in the range 220–300 cm^{-1} for the coordinated H_2O, terminal hydroxo and bridged hydroxo groups [25]. In addition, all important bands of the ligands are also seen for these complexes (Fig. 1, Table 2), and are also appropriately assigned [26].

The thermal decomposition of the complexes was studied in the temperature range of 30 to ca. 700°C. From the weight loss the stoichiometries of the resultant intermediate species are assigned. They seem to be non-stoichiometric species. These compounds lose coordinated H_2O in several steps, followed by the loss of OH (in multiples of two OH as H_2O molecules, leaving one oxygen at a time attached to the Zr atom), L and some of the Cl^- ions. In most cases investigated up to about the end of the thermal decomposition at ca. 600°C, no evidence was found for the formation of ZrO_2 as the end product. However, in some cases at still higher temperatures ZrO_2 seems to be formed. Somes workers [27–29] have reported the formation of ZrO_2 at around 500°C from the so-called monomeric complexes of $ZrOCl_2$ with 2-methylaminopyridine-*N*-oxide, dibenzylsulphoxide, 4-cyanopyridine, etc. and they also assign a weak band at 970–980 cm^{-1} to $\nu(Zr{=}O)$. These results seem somewhat unconvincing in view of the known tetrameric structures of the so-called zirconyl complexes. It is also reasonable to expect ZrO_2 to be formed at higher temperatures in view of the fact that the Zr content in complexes is estimated as ZrO_2 by ignition of several zirconyl salts at around 1000°C [30]. Considering the stoichiometry of the intermediate species formed during thermal decomposition processes, the following general mechanism seems to hold good.

$$Zr_4(OH)_{12}(H_2O)_{12-n}L_nCl_4 \xrightarrow{A} Zr_4(OH)_{12}L_nCl_4$$

$$\xrightarrow{B} Zr_4O_6Cl_4 \xrightarrow{C} Zr_4O_6Cl_2 \xrightarrow{D} ZrO_2$$

However, it is seen that in some cases the decomposition process proceeds up to stage B forming $Zr_4O_6Cl_4$, in some others up to stage C forming $Zr_4O_6Cl_2$ 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 zirconium oxide species such as $Zr_4O_6Cl_4$ or $Zr_4O_6Cl_2$ is available in the literature [31]. Considering the initial decomposition temperature as a rough guide for determining the thermal stability of complexes, the following stability order is proposed for the complexes investigated: $[Zr_4(OH)_{12}(H_2O)_{11}(1\text{-MeIm})]Cl_4 < [Zr_4(OH)_{12}(H_2O)_{10}(Im)_2]Cl_4 \approx [Zr_4(OH)_{12}(H_2O)_{11}$-

$(2\text{-iPrIm})]Cl_4 \approx [Zr_4(OH)_{12}(H_2O)_{11}(2\text{-PhIm})](Cl_4 < [Zr_4(OH)_{12}(H_2O)_{11}\text{-}(1\text{-ViIm})]Cl_4 < [Zr_4(OH)_{12}(H_2O)_{10}(4\text{-MeMorph})_2]Cl_4$.

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