



New aryloxide derivatives of monochlorotris(acetylacetonato)zirconium(IV)

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ABSTRACT

A series of tris(acetylacetonato)zirconium(IV) aryloxides of composition $Zr(acac)_3(OAr-X)$ [where $acac =$ acetylacetonato anion; $OAr-X=OC_6H_2Cl-2,4,6$; $OC_6H_3Cl-2,6$; $OC_6H_3Cl-2,4$; OC_6H_4Cl-2 , and OC_6H_4Cl-4] have been synthesized from the reaction of $ZrCl(acac)_3$ with one equivalent of the substituted phenol in the presence of diethyl amine. These complexes have been characterized by using elemental analyses, molecular weight determinations, molar conductance measurements and thermo analytical (TG/DTA) studies. Based on limited analytical, physico chemical, spectroscopic and molecular modeling technique, a capped trigonal prismatic geometry has been proposed for these complexes. The addition of sodium aryloxides to CCl_4+MeOH solution of the monomeric $Zr(acac)_3(OAr-X)$ derivatives have afforded the complexes of composition $Na[Zr(acac)_3(OAr-X)_2]$, which have also been characterized.

Keywords: Zirconium(IV), aryloxides, acetylacetonate, chlorophenols, molecular modeling, TG/DTA

INTRODUCTION

Literature survey reveals a voluminous documentation on the chemistry of zirconium (β -diketonates(1,2), alkoxides (3,4), mixed β -diketonato-alkoxo complexes (5), and their wide applications in material sciences for making thin films by sol-gel (6,7), MOCVD processes involving the hydrolysis of M-OR bonds (8,9), and as catalyst in polymerization (10-12). Surprisingly, little efforts seem to have been made on the synthesis of the closely related aryloxo complexes of zirconium (IV). Therefore, in continuation of previous on going research on the synthesis of zirconium (IV) complexes, we report here the synthesis of monochlorotris(acetylacetonato) aryloxides. An attempt has also been made to propose a suitable geometry for these complexes using molecular modeling technique.

MATERIALS AND METHOD

Zirconium tetrachloride (Fluka) was purified by sublimation in a vacuum and substituted chlorophenols (s.d.fine) were used as such without further purification. The purity of

phenols was checked by their melting point and chlorine estimation. Monochlorotris (acetylacetonato) zirconium (IV) was synthesized by the reported method (16), of reacting $ZrCl_4$ and acetylacetone using benzene as solvent under reflux. Zirconium in the complexes was determined gravimetrically as ZrO_2 and chlorine by Volhard's method. Carbon and hydrogen microanalyses were performed on a Coleman CHN analyzer. The conductance measurements in nitrobenzene were made on an NDC-732 Elico Digital conductivity bridge and molecular weights were determined by Rast's Camphor method. Infrared spectra (KBr) were recorded from $4000-200\text{ cm}^{-1}$ with Perkin Elmer FTIR spectrophotometer and 1H NMR spectra on a Jeol JNM PMX 60 SI using CCl_4 as solvent. Thermo grams were recorded on a Shimadzu simultaneous DT-40 DT-TG thermal analyzer, heating rate: $10\text{ }^\circ\text{C min}^{-1}$; sample size 5-10 mg; reference Al_2O_3 ; thermocouple: Pt/Pt-Rh 10%.

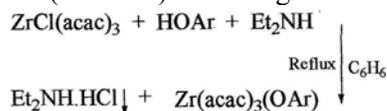
Preparation of tris(acetylacetonato) zirconium(IV) aryloxides, $[Zr(acac)_3(OAr-X)]$ ($OAr-X=OC_6H_2Cl-2,4,6$; $OC_6H_3Cl-2,6$; $OC_6H_3Cl-2,4$; OC_6H_4Cl-2 , and OC_6H_4Cl-4)

To a solution of $\text{ZrCl}(\text{acac})_3$ (1.5g, 3.5 mmol) was added a mixture solution of substituted chlorophenols (2,4,6-TCP= 0.699g, 3.5 mmol ; 2,4-DCP= 0.577g, 3.5 mmol ; 2,6-DCP= 0.577g, 3.5 mmol; 2-CP= 0.455g, 3.5 mmol and 4-CP = 0.455g, 3.5 mmol) and diethylamine (0.2584g, 3.5 mmol) in benzene with continuous stirring followed by refluxing in separate experiments. Diethylamine hydrochloride ($\text{Et}_2\text{NH}\cdot\text{HCl}$) formed during course of reaction was removed by filtration. From the filtrate, the respective compounds of composition, $\text{Zr}(\text{acac})_3(\text{OAr-X})_2$, were extracted with the addition of petroleum ether and dried under vacuum.

Preparation of $\text{Na}\{\text{Zr}(\text{acac})_3(\text{OAr-X})_2\}$. To a solution of $\text{Zr}(\text{acac})_3(\text{OAr-X})$ [OAr-X = 2,4,6-TCP= 1.0g, 1.17 mmol; 2,4-DCP=1.0g, 1.817 mmol; 2,6-DCP=1.0g, 1.817 mmol; 2-CP = 1.0g, 1.938 mmol and 4-CP = 1.0g, 1.938 mmol] in CCl_4 ; was added $\text{Na}(\text{OAr-X})$ of corresponding phenols (2,4,6-TCP= 0.3753g,1.17 mmol; 2,4-DCP=0.3662g, 1.817 mmol; 2,6-DCP=0.3662g, 1.817 mmol; 2-CP = 0.2919g, 1.938 mmol and 4-CP = 0.2919g, 1.938 mmol) in methanol by stirring. The mixture solution was refluxed after stirring for ~6h to ensure completion of the reaction. The solvent was then removed under vacuum and from the remaining concentrated solution, the complexes were extracted by the addition of petroleum ether.

RESULTS AND DISCUSSION

The reaction of $\text{ZrCl}(\text{acac})_3$ with equimolar amounts of substituted chlorophenols in the presence of diethylamine as HCl acceptor afforded the formation of complexes in good yields (70-80 %) according to the equation as:



The stoichiometric compositions of the compounds isolated were established by the elemental analyses (Table-I). These complexes were yellow to brown in colour and soluble in CCl_4 . The low molar conductance values of millimolar solution of these compounds in

nitrobenzene are suggestive of their non-ionic nature. The molecular weight determination of these complexes by Rast's Camphor method indicates them to be monomers.

Formation of the new complexes has been inferred from comparison of IR spectra with those of free phenol as reported for zirconium acetylacetonates¹⁷. Complete absence of the band in the region $3450\text{-}3000\text{ cm}^{-1}$ is indicative of deprotonation of phenol during the reaction. The occurrence of strong bands at $1600\text{-}1580\text{ cm}^{-1}$ and $1450\text{-}1370\text{ cm}^{-1}$ region in the complexes has been assigned to asymmetric $\nu_{\text{C=O}}$ and symmetric $\nu_{\text{C=O}}$ modes of the co-ordinated acetylacetonato molecules. The most important and strong band present at $1260\text{-}1225\text{ cm}^{-1}$ in different substituted phenols assigned to $\nu_{\text{C-O}}$ mode is significantly lowered ($1200\text{-}1159\text{ cm}^{-1}$) suggesting a considerable contribution from a structure of type $\text{M}^{\text{---}}\text{O}^{\text{---}}\text{C}$ wherein drainage of electron density from the ring to metal through (C-O) bond occurs. Co-ordination from phenolic oxygen of corresponding phenols have been confirmed by the appearance of entirely new bands in the region $592\text{-}562\text{ cm}^{-1}$ has been assigned to terminal $\nu_{\text{Zr-O}}$ mode. The band at $360\text{-}340\text{ cm}^{-1}$ region assigned to $\nu_{\text{Zr-Cl}}$ mode present in $\text{ZrCl}(\text{acac})_3$ is missing in the synthesized complexes.

The ^1H NMR spectra of the complexes did not show any signal which could be assigned to phenolic OH groups, thereby suggesting their formation. The signals due to aromatic protons observed in the region δ 6.62-7.35 ppm in pure phenol have been found to undergo very small downfield shifts and have appeared in the region δ 6.69-7.26 ppm. The signals at δ 5.36 and 2.14 ppm observed in $\text{ZrCl}(\text{acac})_3$ due to ethylenic protons and methyl protons of acetylacetonato group almost remain unaltered on complex formation. The integration of signals of protons due to acetylacetonato and aryloxy ligands agreed well to their proposed formation and this is also in accordance with earlier observations (15, 18).

Molecular modeling

Molecular modeling of transition metal compounds is complicated by the partially

filled d-orbitals of the metal ions that are responsible for the multifarious structures of coordination compounds with a large variety of possible coordination numbers and geometries. For a molecular modeling technique to be useful and to achieve widespread application, it must readily and reliably reproduce molecular properties that closely resemble experimentally determined data. Therefore in the present endeavor, this technique has been used to propose the structure for the various complexes isolated in the present studies using Hyper Chem 7.5. Structures of complexes of $Zr(acac)_3(OAr-X)$ were drawn in the workspace.

The initial strained structure related to the most probable geometry of each metal complex was drawn and related to the minimum strain energy using Hyper Chem 7.5 (student evaluation). The geometry of the complex was energetically optimized through molecular mechanics applying MM^+ force field in vacuo with the Polka-Ribiere algorithm and RMS gradient 0.01 kcal/mole followed by molecular dynamics the molecular dynamics simulation was done upto 1000K (for both relaxation time 1 ps) followed by molecular mechanics calculation again and the process was repeated five times to ensure that the true energy minimum had been reached. The strain energy was noted after each calculation and then the structures with minimum strain energy have been selected as most probable geometry of the complexes. Thus, based upon limited analytical, conductance, IR and 1H NMR spectral studies, molecular weight determinations, earlier reports in literature¹⁹ and from minimization of the energies by drawing and molecular modeling of the complexes of different compositions on Hyper Chem, in case of complexes of composition $Zr(acac)_3(OAr-X)$ with coordination no. 7, out of three possible geometries possible (pentagonal bipyramidal, capped octahedral and capped trigonal prismatic) only capped

trigonal prismatic geometry has been found to be the most probable with capping from one of the rectangular faces of the prism have been found.

Double aryloxides

In the course of present study, we have also investigated the reactivity of the complexes towards alkali metal aryloxides i.e. $NaOAr-X$ with an objective of ascertaining their ability to form double aryloxides. The conductometric titrations of the isolated complexes against respective $NaOAr-X$ have shown increase in conductivity of millimolar solution of the complexes on the addition of solution of $NaOAr-X$. Conductance-composition curves show discontinuities at 1: 1 stoichiometry. This lead to synthesis of complexes of composition $Na [Zr(acac)_3(OAr-X)_2]$ by the following reaction:

The complexes were creamish to yellow in colour having solubility in $CHCl_3$. The molar conductance values of millimolar solutions of these complexes in nitrobenzene indicates their appreciable electrolytic nature (Table-2). Formation of these complexes has been supported from the IR spectra of the complexes by the appearance of all bands characteristic of phenolic bonding in the region 1245-1129, 932, 661 cm^{-1} .

Thermal decomposition data of $ZrCl(acac)_3$ and its complexes with substituted chlorophenols, $Zr(acac)_3(OAr-X)$ obtained from TGA and DTA curves given in Table-3 shows that these complexes decompose into two steps with the formation of $ZrO(acac)_2$ as the most probable intermediate in the first step and ZrO_2 as the final residual product in the second step. The decrease in the final decomposition temperatures ($\sim 78-83^\circ C$) of the complexes in comparison to parent

ZrCl(acac)₃ indicates their potential use as precursors for making thin films of ZrO₂. The DTA peaks shows that decompositions are exothermic in nature. The mechanism, energy of activation (ΔE^*) and frequency factor (A) of non-isothermal decomposition of the complexes have been evaluated from TG data using Coats-Redfern equation (Table-3). All the complexes have been found to decompose by R3 (Phase Boundary Reaction: spherical symmetry) mechanism. The values of activation energies (ΔE^*) for the complexes suggest a direct relation between activation energy and thermal stability (IDT) of the complexes.

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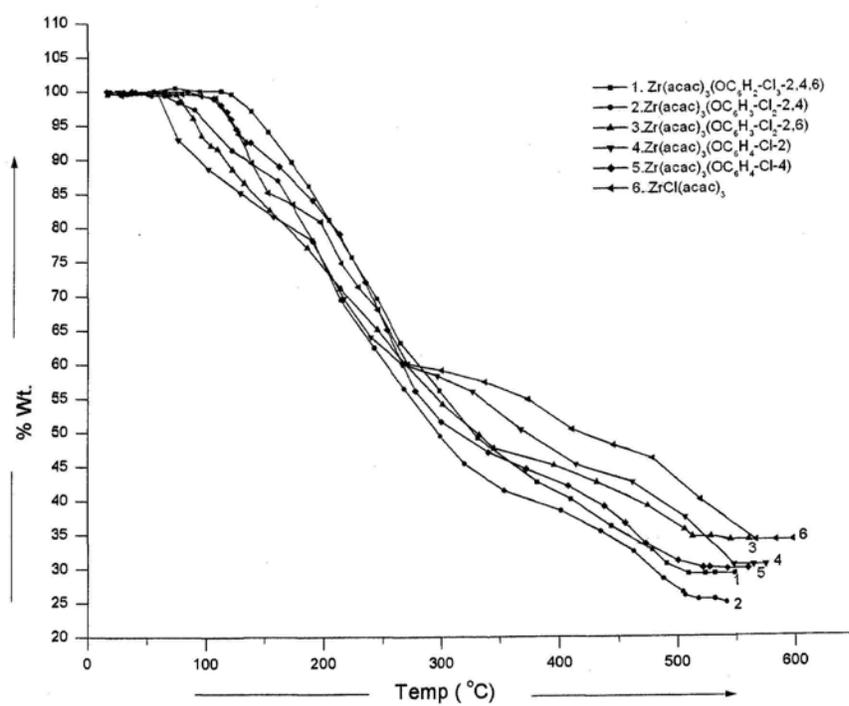
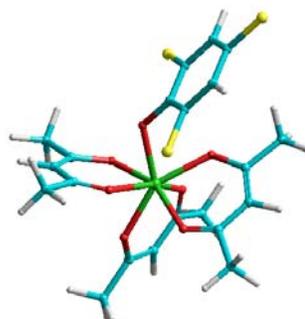


Fig.1. TGA curves of complexes

Table 1. Analytical data of tris(acetylacetonato)zirconium(IV) aryloxides

Compound	Colour	% Analysis		Melting Point (°C)	Molar cond.in PhNO ₂ (Ω ⁻¹ cm ² mole ⁻¹)	Molecular weight Found (Calc.)
		Zr Found (Calc.)	Cl Found (Calc.)			
ZrCl(acac) ₃	Creamish	21.46 (21.52)	8.27 (8.37)	160-162	0.223	403.8 (423.7)
Zr(acac) ₃ (OC ₆ H ₂ Cl-2,4,6)	Orange	15.24 (15.29)	18.16 (18.21)	152-155	1.848	550.81 (584.65)
Zr(acac) ₃ (OC ₆ H ₃ Cl-2,6)	Yellow	16.68 (16.57)	12.80 (12.90)	110-118	1.526	527.47 (550.2)
Zr(acac) ₃ (OC ₆ H ₂ Cl-2,4)	Yellow	16.71 (16.57)	12.83 (12.90)	124-130	1.742	518.09 (550.2)
Zr(acac) ₃ (OC ₆ H ₄ Cl-2)	Pale yellow	17.75 (17.68)	6.74 (6.88)	85-94	1.826	499.87 (515.76)
Zr(acac) ₃ (OC ₆ H ₄ Cl-4)	Brown	17.52 (17.68)	6.69 (6.88)	120-158	1.6457	480.43 (515.76)

Table 2. Analytical data of double phenoxides of tris(acetylacetonato)zirconium(IV)

Compound	Colour	%Elemental analysis Found (Reqd.)		Molar cond.in PhNO ₂ (Ω ⁻¹ cm ² mole ⁻¹)	Molecular weight Found (Calc.)
		Cl	Zr		
Na[Zr(acac) ₃ (OC ₆ H ₂ Cl-2,4,6) ₂]	Yellow	26.37 (26.48)	11.31 (11.34)	7.82	789 (804.1)
Na[Zr(acac) ₃ (OC ₆ H ₃ Cl-2,4) ₂]	Creamish	19.25 (19.30)	12.36 (12.39)	7.23	705.6 (735.65)
Na[Zr(acac) ₃ (OC ₆ H ₃ Cl-2,6) ₂]	Creamish	19.23 (19.30)	12.38 (12.39)	6.94	711.9 (735.65)
Na[Zr(acac) ₃ (OC ₆ H ₄ Cl-2) ₂]	Pale yellow	10.61 (10.65)	13.67 (13.68)	7.03	645.8 (666.32)
Na[Zr(acac) ₃ (OC ₆ H ₄ Cl-4) ₂]	Light brown	10.64 (10.65)	13.65 (13.68)	8.36	651.4 (666.32)

Table 3. Thermoanalytical data of the complexes

Compound	IDT (°C)	FDT (°C)	Stages of Decomp.	Product of Decomp.	% Mass Loss Found (Reqd.)	Kinetic Parameters*	
						Frequency factor A (sec ⁻¹)	Energy of Activation E _a (KJ Mol ⁻¹)
ZrCl(acac) ₃	109.7587.9		IInd Stage	ZrO(acac) ₂	28.04(27.96)	5.37 x 10 ⁻⁶	17.814
Zr(acac) ₃ (OC ₆ H ₂ Cl-2,4,6)	122.4509.9		IInd Stage	ZrO ₂	43.12(42.96)	0.84 x 10 ⁻⁶	28.832
			IInd Stage	ZrO(acac) ₂	47.90(47.79)		
Zr(acac) ₃ (OC ₆ H ₃ Cl-2,6)	75.8 511.1		IInd Stage	ZrO ₂	32.00(31.13)	1.91 x 10 ⁻⁶	23.080
			IInd Stage	ZrO(acac) ₂	44.49(44.53)		
Zr(acac) ₃ (OC ₆ H ₂ Cl-2,4)	77.4 505.3		IInd Stage	ZrO ₂	33.09(33.08)	2.13 x 10 ⁻⁶	22.879
			IInd Stage	ZrO(acac) ₂	44.52(44.52)		
Zr(acac) ₃ (OC ₆ H ₄ Cl-2)	69.6 505.5		IInd Stage	ZrO ₂	33.07(33.08)	2.17 x 10 ⁻⁶	22.849
			IInd Stage	ZrO(acac) ₂	41.00(40.82)		
Zr(acac) ₃ (OC ₆ H ₄ Cl-4)	113.9507.4		IInd Stage	ZrO ₂	35.29(35.29)	0.94 x 10 ⁻⁶	27.628
			IInd Stage	ZrO(acac) ₂	40.89(40.82)		
			IInd Stage	ZrO ₂	36.00(35.29)		