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Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

Publication details, including instructions for authors and subscription information:

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Published online: 09 May 2007.

To cite this article: S. C. Chaudhry, Champa Verma, S. S. Bhatt & Neeraj Sharma (2007) Synthesis and Characterization of Oxozirconium(IV) Aryloxides, *Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry*, 37:4, 249-253

To link to this article: <http://dx.doi.org/10.1080/15533170701316494>

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Synthesis and Characterization of Oxozirconium(IV) Aryloxides

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Oxozirconium(IV) aryloxides of the composition $ZrO(OAr)_2$ and $ZrOCl(OAr)$ (where $OAr = OC_6H_4Cl-2$ and $OC_6H_4NO_2-4$) have been synthesized by reacting anhydrous zirconyl chloride with the respective phenols in the presence of triethylamine in pre-determined molar ratios. The double aryloxides of the composition $Na_2[ZrO(OAr)_4]$ have also been synthesized by reacting $ZrO(OAr)_2$ with a bimolar amount of the corresponding $NaOAr$. The complexes have been characterized by elemental analyses, conductance, cryoscopy, IR and 1H NMR studies. The thermal behavior of the compounds has been explored and discussed.

Keywords oxozirconium(IV), aryloxides, thermal behavior

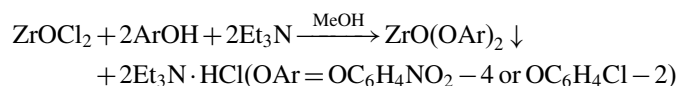
INTRODUCTION

Compared to the well-documented chemistry of zirconium(IV) complexes, only scattered references are available on the synthesis and applications of oxozirconium(IV) complexes.^[1–3] Fathima and coworkers^[4] very recently have investigated the effects of zirconium oxychloride and zirconium oxalate on the thermal and enzymatic stability of collagen and found that the former provide better enzymatic stability than the latter. Reports have also appeared about the synthesis of long fibers of $ZrTiO_4$ through sol-gel processes using titanium sulfate and zirconium oxychloride octahydrate as starting materials without any organic components.^[5] A new inorganic ion-exchanger based on zirconium(IV) triethylammoniumphosphate has been synthesized from a solution of $ZrOCl_2$ and $(C_2H_5)_3NH \cdot H_2PO_4$ by Singh and coworkers.^[6] The use of zirconium oxychloride for the preparation of zirconium alkoxides is known to have been exploited several decades ago by Bradley and coworkers.^[7] To our knowledge, zirconium aryloxide analogues seem to have been rather

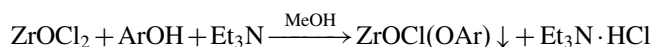
unexplored. In view of these interesting reports, the present study describes the synthesis of new oxozirconium(IV) aryloxides using zirconyl chloride and some phenols.

RESULTS AND DISCUSSION

The reaction of anhydrous oxozirconium(IV) dichloride with phenols in the presence of triethylamine in 1:2:2 molar ratios proceeds smoothly to form $ZrO(OAr)_2$ and a quantitative amount of $Et_3N \cdot HCl$ as follows:



However, when equimolar amounts of the reactants are mixed, formation of aryloxides of composition $ZrOCl(OAr)$ takes place as follows:



The most notable feature of the reactions is that the desired products are obtained as insoluble solids while $Et_3N \cdot HCl$ formed during the reaction remained in solution. The stoichiometric composition of the isolated solids was established by chemical analysis given in Table 1. The compounds of the composition $ZrO(OC_6H_4Cl-2)_2$ and $ZrOCl(OC_6H_4Cl-2)$ are white solids, while those with 4-nitrophenol are bright yellow solids. All of them are high-melting and insoluble in methanol, chloroform, acetonitrile, dichloromethane etc. but are fairly soluble in nitrobenzene. Molar conductance values of millimolar solutions of these compounds in nitrobenzene are too low ($1.64\text{--}2.98 \text{ ohm}^{-1}\text{cm}^2\text{mole}^{-1}$) to be considered as (1:1) electrolytes. Molecular weight determinations of $ZrO(OAr)_2$ compounds in nitrobenzene indicate that these compounds are polymeric in nature in this solvent as the average experimental values are more than twice the molecular weight of monomeric $ZrO(OAr)_2$.

1H NMR Spectra

In the proton NMR spectra of the oxozirconium(IV) aryloxides under investigation the signals at δ 4.32 and 4.78 ppm assigned to the phenolic OH group of 4-nitrophenol and

Received 11 January 2007; accepted 5 February 2007.

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TABLE 1
Analytical data of oxozirconium(IV) aryloxides

Complex (empirical formula)	Formula weight	Yield (%)	Decomp. temp. (°C)	Colour and physical state	Elemental analysis % found (Calc.)				Λ_M^a in PhNO ₂	Mol. Wt in PhNO ₂ found (Calc.)
					Zr	Cl	C	H		
ZrO(OC ₆ H ₄ NO ₂ -4) ₂ (C ₁₂ H ₈ N ₂ O ₇ Zr)	383	75	240	Bright yellow solid	23.80 (23.79)	–	37.69 (37.60)	2.12 (2.09)	2.9	940 (383)
ZrOCl(OC ₆ H ₄ NO ₂ -4) (C ₆ H ₄ ClNO ₄ Zr)	281	70	255	Bright yellow solid	32.05 (32.37)	12.60 (12.62)	25.59 (25.62)	1.40 (1.42)	2.8	–
ZrO(OC ₆ H ₄ Cl-2) ₂ (C ₁₂ H ₈ Cl ₂ O ₃ Zr)	362	72	270	White solid	25.35 (25.17)	19.40 (19.48)	39.71 (39.77)	2.15 (2.20)	1.6	968 (362)
ZrOCl(OC ₆ H ₄ Cl-2) (C ₆ H ₄ ClO ₂ Zr)	270	78	300	White solid	33.69 (33.74)	26.25 (26.27)	26.60 (26.66)	1.50 (1.48)	2.7	–
Na ₂ [ZrO(OC ₆ H ₄ NO ₂ -4) ₄] (C ₂₄ H ₁₆ N ₄ Na ₂ O ₁₁ Zr)	705	80	215	Mustard yellow	12.81 (12.93)	–	40.82 (40.85)	2.23 (2.26)	12.8	–
Na ₂ [ZrO(OC ₆ H ₄ Cl-2) ₄] (C ₂₄ H ₁₆ Cl ₄ Na ₂ O ₅ Zr)	663	82	242	Brown	14.15 (14.04)	21.39 (21.41)	43.40 (43.43)	2.38 (2.41)	10.8	–

^aIn $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$.

2-chlorophenol, respectively, are missing. The absence of these signals suggests the deprotonation of this group during the course of the reaction. Formation of the desired aryloxides is also indicated by the moderate to slight downfield shift of the signals due to aromatic ring protons in the range δ 7.06–8.15 and 6.67–7.2 ppm for 4-nitrophenol and 2-chlorophenol, respectively, by about 0.10–0.35 ppm on complex formation. These shifts have been attributed to the delocalization of electrons from the aromatic ring to zirconium as $\text{ArO}=\text{Zr}$. A similar explanation has been given in reports of Clark and coworkers^[8] for tantalum(V) phenoxides.

IR Spectra

An examination of the IR spectra of the complexes prepared in the present studies, has revealed that the bands at 1275–1180 cm^{-1} due to $\nu_{\text{ring}}(\text{CO})$ modes, comparatively, are at the lower frequency region than those of the pure phenols. The resulting shift is understood in terms of bonding from the phenolic oxygen to zirconium. This is further substantiated by the appearance of new bands at 760–720 and 620–590 cm^{-1} in these

aryloxides attributed to bridging $\text{Zr} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{Zr}$ groups^[9] and $\nu(\text{Zr}-\text{O})$ modes,^[10,11] respectively. Bands at 380–360 cm^{-1} in the complexes $\text{ZrOCl}(\text{OAr})$ indicates the presence of chloro ligand presumed to occupy bridging sites.^[10] A medium intensity band at 980–860 cm^{-1} in complexes $\text{ZrO}(\text{OAr})_2$ and $\text{ZrOCl}(\text{OAr})$ has been attributed to characteristic $\nu(\text{Zr}=\text{O})$ mode. Similar assignment has been made earlier also in majority of oxozirconium(IV) complexes.^[1–3,9,12,13]

Based upon the limited analytical, conductance, molecular weight determinations, ^1H NMR and IR spectral studies, a polymeric structure shown below is proposed for $\text{ZrO}(\text{OAr})_2$ (Figure 1): Similar types of structures containing infinite chains of ZrO_5 squares pyramids have been reported earlier also in case of alkali and alkaline earth metal zirconates.^[14]

For $\text{ZrOCl}(\text{OAr})$, the likely structure proposed is given below in Figure 2.

Thermal Studies

The thermal behavior of these complexes has been investigated using TG/DTA. Thermogravimetric data included in Table 2, show that the compounds $\text{ZrO}(\text{OAr})_2$ are less thermally stable than $\text{ZrOCl}(\text{OAr})$ as is indicated by their initial decomposition temperatures (IDTs). All the complexes have displayed single-stage, continuous decomposition patterns,

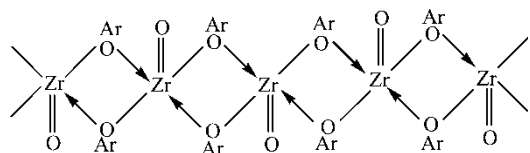


FIG. 1. Suggested structure of $\text{ZrO}(\text{OAr})_2$.

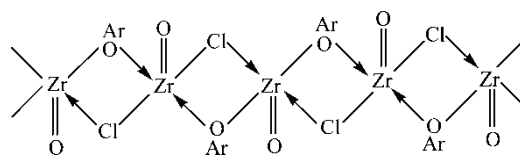
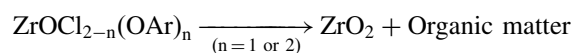


FIG. 2. Suggested structure of $\text{ZrOCl}(\text{OAr})$.

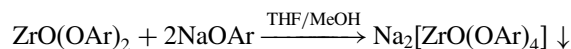
and these decompositions are exothermic as indicated by their respective DTA curves. The observed weight loss for the respective complexes has been rationalized in terms of the formation of ZrO_2 as the ultimate residue in each case, thus indirectly giving further support to the stoichiometric composition of the complexes:



It is, however, difficult to comment precisely on the type of intermediates being formed during the course of thermal decomposition.

Double Aryloxides

Although there are reports in the literature^[15,16] concerning the formation of several divalent metal oxozirconium(IV) oxalates, $\text{MZrO}(\text{C}_2\text{O}_4)_2 \cdot x\text{H}_2\text{O}$ (where $\text{M}=\text{Ba}, \text{Ca}, \text{Mg}, \text{Pb}, \text{Cd}$), yet no information is available on double salts of alkali metal oxozirconium(IV) aryloxides. Therefore, having synthesized and characterized compounds of the composition $\text{ZrO}(\text{OAr})_2$, it was interesting to explore the possibility of formation of double aryloxides by reacting them with alkali metal phenoxides. For this purpose conductometric titrations of $\text{ZrO}(\text{OAr})_2$ versus sodium salts of the phenols used in the present studies, have been carried out in nitrobenzene at $25 \pm 0.1^\circ\text{C}$. The conductance/composition curves shown in Figure 3, reveal breaks at 2:1 molar ratio $\text{NaOAr}/\text{ZrO}(\text{OAr})_2$ which are suggestive of the formation of compounds of 2:1 stoichiometry. This led to the synthesis of $\text{Na}_2[\text{ZrO}(\text{OAr})_4]$ as shown by the reaction below.



The elemental analyses of the complexes (Table 1) agreed well with their stoichiometric compositions. The molar conductance values of millimolar solutions of these complexes in nitrobenzene indicated their appreciable electrolytic nature. Interestingly, the thermal investigations of these complexes suggested that incorporation of sodium aryloxide in $\text{ZrO}(\text{OAr})_2$ yielding $\text{Na}_2[\text{ZrO}(\text{OAr})_4]$ and leads to a significant increase in the stability of the resulting products as is indicated by the increased IDTs of these complexes. Further, unlike the parent oxozirconium(IV) aryloxides, the decomposition of corresponding double aryloxides display both exothermic and endothermic peaks (Table 2). The final residue in all these cases, however, is Na_2ZrO_3 as has also been reported in the literature during thermal decomposition studies of divalent metal oxozirconium(IV) oxalates.^[12,13]

TABLE 2
Thermoanalytical data of the Oxozirconium(IV) aryloxides

Compound	Initial decomp. temp. (°C)	Temp. range TG (°C)	% TG mass loss found (Calc.)	DTA peak temperature (°C) (nature of decomposition)
ZrO(OC ₆ H ₄ NO ₂ -4) ₂	55.0	55.0–488.3	67.75 (67.80)	326.6 (–)
ZrOCl(OC ₆ H ₄ NO ₂ -4)	57.6	57.6–642.4	56.12 (56.00)	302.3 (–) 625.3 (–)
ZrO(OC ₆ H ₄ Cl-2) ₂	40.2	40.2–706.0	66.05 (66.0)	363.4 (–)
ZrOCl(OC ₆ H ₄ Cl-2)	54.0	54.0–460.1	53.80 (53.87)	350.1 (–) 455.9 (–)
Na ₂ [ZrO(OC ₆ H ₄ NO ₂ -4) ₄]	80.1	80.1–606.6	73.75 (73.80)	90.5 (+) 335.1 (–)
Na ₂ [ZrO(OC ₆ H ₄ Cl-2) ₄]	70.5	70.5–492.0 492.0–760.2	71.40 (71.90)	315.2 (–) 618.3 (–)

(–) exothermic and (+) endothermic peak and calculated for ZrO₂.

EXPERIMENTAL

Materials

Zirconium oxychloride was first purified by a literature method^[17] and then dried in a vacuum oven at 200 °C to make it anhydrous. The purity of the sample was checked by metal and chlorine analysis. The 4-Nitrophenol was used after recrystallization from THF while 2-chlorophenol was distilled before use.

Analysis and Physical Measurements

Zirconium in the complexes was determined as ZrO₂ and chlorine by Volhard's method. Carbon and hydrogen microanalyses were performed on a Coleman CHN analyzer. The IR spectra (4000–200 cm⁻¹) were recorded in KBr discs and Nujol mulls on a Beckmann IR 4250 spectrophotometer and ¹H NMR spectra on a JEOL JNM PMX 60 SI spectrometer

using CDCl₃/TFA (80:20) as solvent. Molecular weights were determined cryoscopically in nitrobenzene using a Beckmann thermometer while conductance measurements in the same solvent were made on an Elico conductivity bridge (CM Type 82 T) using 10⁻³ M solutions at 25°C. Thermograms were recorded on a Shimadzu simultaneous DT-40 DT-TG thermal analyzer, heating rate: 20°C min⁻¹, sample size: 5–10 mg, reference: Al₂O₃, thermocouple: Pt/Pt- Rh 10%.

Preparation of Oxozirconium(IV) Diaryloxides ZrO(OAr)₂ (where OAr = OC₆H₄NO₂-4, OC₆H₄Cl-2)

To a solution of zirconium oxychloride (3.01 g, 16.9 mmol) dissolved in methanol (40 mL) was added 4-nitrophenol (4.70 g, 33.8 mmol) dissolved in the same solvent (30 mL). To the resulting solution was then added triethylamine (3.41 g, 33.8 mmol) when a bright yellow solid separated out. The reaction mixture was stirred vigorously at room temperature for about 3–4 hours and left overnight. The yellow solid was separated by filtration, washed 2–3 times with methanol and finally dried under vacuum. Yield of ZrO(OC₆H₄NO₂-4)₂, 4.84 g (75%).

The filtrate was evaporated to dryness to look for the byproduct. The quantitative amount of triethylamine hydrochloride identified by its mp: 260°C (lit.^[18] 261°C) was isolated. A similar procedure was adopted for the synthesis of ZrO(OC₆H₄Cl-2)₂ by reacting the components viz. ZrOCl₂, 2-chlorophenol and triethylamine in 1:2:2 molar ratio.

Preparation of Monochloro Oxozirconium(IV) ZrOCl(OAr) Aryloxides (where OAr = OC₆H₄NO₂-4, OC₆H₄Cl-2)

In a typical reaction for the preparation of ZrOCl(OC₆H₄NO₂-4), a solution of 4-nitrophenol (2.32 g, 16.8 mmol)

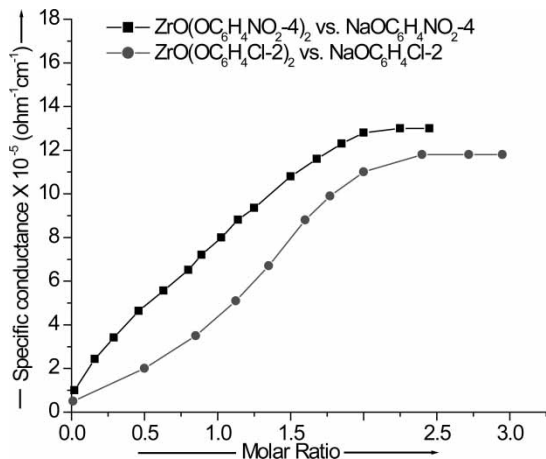


FIG. 3. Conductance composition curves of ZrO(OAr)₂ vs. NaOAr.

dissolved in methanol (30 mL) was mixed with a solution of zirconium oxychloride (3.00 g, 16.8 mmol) dissolved in the same solvent (40 mL) followed by the addition of triethylamine (1.69 g, 16.8 mmol). The reaction mixture was stirred at room temperature for about 3–4 hours, when a bright yellow solid separated out. The solid so obtained was filtered, washed 2–3 times with methanol and finally dried under vacuum. Yield of $ZrOCl(OC_6H_4NO_2-4)$, 3.36 g (72%).

From the filtrate, the quantitative amount of triethylamine hydrochloride identified by its mp: 260°C (lit.^[18] 261°C) was isolated by evaporation to dryness. A similar procedure was adopted for the synthesis of $ZrOCl(OC_6H_4Cl-2)$ by reacting the components viz. $ZrOCl_2$, 2-chlorophenol and triethylamine in 1:1:1 molar ratio.

Preparation of Double Phenoxides, $Na_2[ZrO(OAr)_4]$ ($OAr = OC_6H_4NO_2-4$ or OC_6H_4Cl-2)

A typical procedure adopted for the preparation of double phenoxides of the composition $Na_2[ZrO(OC_6H_4NO_2-4)_4]$ consists of mixing a solution of $NaOC_6H_4NO_2-4$, (1.0 g, 6.2 mmol) in a mixture of tetrahydrofuran/methanol (1:1) (20 mL) with a suspension of $ZrO(OC_6H_4NO_2-4)_2$, (1.20 g, 3.1 mmol) in the same solvent mixture (20 mL). The reaction mixture was vigorously stirred for 4–5 hours at room temperature when solids appeared to go into solution. The resulting solution was then refluxed for about 2 hours to ensure the completion of reaction. The volume of the solution was then reduced to about one third of its original volume by evaporation under vacuum. The remaining concentrated solution was treated with petroleum ether (bp: 60°C) when a colored solid compound was obtained which was separated by filtration, washed with ether (bp: 32°C) and finally dried under vacuum. The stoichiometric composition of the product was established by elemental analyses (Table 1). Yield of $Na_2[ZrO(OC_6H_4NO_2-4)_4]$, 1.76 g (80%). A similar procedure was adopted for the preparation of the double phenoxide of the composition $Na_2[ZrO(OC_6H_4Cl-2)_4]$.

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