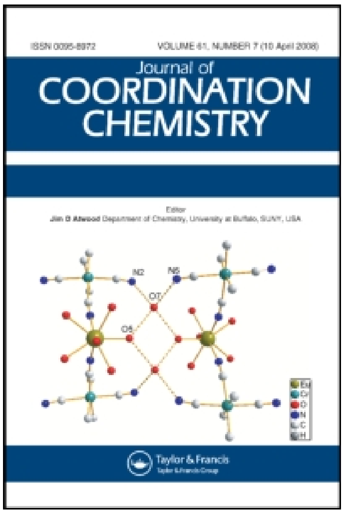

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Glycol modified *cis*-diisopropoxy-*bis* (*N*-phenylsalicylideneiminato)zirconium(IV): syntheses, characterization and low temperature transformation to nanocrystalline zirconia

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$Zr(OPr^i)_4 \cdot Pr^iOH$ reacts with *N*-phenylsalicylideneimine in anhydrous benzene in 1 : 2 molar ratio to afford $[Zr\{O(C_6H_4)CH{=}NPh\}_2\{OPr^i\}_2]$ (**1**). Further reactions of **1** with various glycols yield heteroleptic complexes of the type $[Zr\{O(C_6H_4)CH{=}NPh\}_2\{O–G–O\}]$ [where $–G– = (CH_2)_2$ (**2**), (CH_2CHCH_3) (**3**), $(CH_3CHCHCH_3)$ (**4**), $(CH_2CHC_2H_5)$ (**5**), $(CH_2)_3$ (**6**), $(CH_2CH_2CHCH_3)$ (**7**), and $(CH_2)_6$ (**8**)]. All new derivatives have been characterized by elemental analyses, FTIR and NMR (^1H and $^{13}C\{^1H\}$) studies. FAB mass spectra of **1** and **7** revealed the monomeric nature of these complexes. Complete hydrolyses and low temperature transformations of **1** and **7** using Sol-Gel technique formed tetragonal phase of ZrO_2 at 700°C, whereas transformation of tetragonal to monoclinic phase occurred at 900°C. SEM observations of these samples indicate formation of agglomerates of nanocrystalline zirconia (Scherer analysis).

Keywords: Glycol modified zirconium(IV)precursors; *cis*-diisopropoxy-*bis*(*N*-phenylsalicylideneiminato)zirconium(IV); Zirconia

1. Introduction

Interest in the chemistry of zirconium alkoxides has grown continuously due to their structural variety and coordination chemistry [1–8]. Moreover, these complexes can be used as components of coordination polymers [9–11] and as precursors for the deposition of protective and dielectric ZrO_2 coatings by Sol-Gel, MOCVD and ALD techniques [12–18].

The chemical inertness and low conductivity of ZrO_2 causes ongoing interest in applications as high dielectric materials to replace SiO_2 in metal oxide-semiconductors

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(MOS), transistors and capacitors as well as in dynamic random access memory devices [19–21]. Further applications are as catalysts [22–25], fuel cells, oxygen sensors, thermal behavior and optical coatings [26–28].

Zirconium alkoxide precursors often require modifications prior to use in Sol-Gel/MOCVD processes due to their extreme moisture sensitivity. On hydrolysis of their solution by pure water or its solution in organic solvents massive uncontrolled phase separation, *precipitation*, occurs:

$$\mathrm{Zr(OPr^i)_4 \cdot Pr^iOH + H_2O \xrightarrow{Fast} (Pr^iO)_3Zr(OH) + 2Pr^iOH}$$

$$\mathrm{(OPr^i)_3Zr(OPr^i) + (OH)Zr(OPr^i)_3 \longrightarrow (Pr^iO)_3Zr - O - Zr(OPr^i)_3 + Pr^iOH}$$

$$\mathrm{(Pr^iO)_3Zr(OH) + (OH)Zr(OPr^i)_3 \xrightarrow{Slow} (Pr^iO)_3Zr - O - Zr(OPr^i)_3 + H_2O}$$

Once the hydrolysis is initiated the above reactions occur simultaneously. In the lack of direct evidence it has been assumed that if the hydrolysis reaction is much faster than polymerization by condensation a polymeric gel is obtained. On the other hand, a gelatinous precipitate or a colloidal gel is obtained when the kinetics of the above two reactions are similar. Thus, to slow down the reactivity of zirconium isopropoxide, some of the isopropoxy ligands can be replaced by some complexing ligands such as carboxylic acids, Schiff bases, β-diketones and functional alcohols etc. [29–32].

Addition of water to solutions of modified alkoxides often result in formation of clear sols and not precipitates. It was assumed that introduction of modifying complexing ligands decreased the reactivity of precursors in hydrolysis and polycondensation reactions. However, knowledge about the structure and reactivity of zirconium precursors has strongly improved during recent years, leading to a drastic re-evaluation of Sol-Gel processes. Mixed-ligand zirconium alkoxide complexes, produced by modification of zirconium alkoxides by carboxylic acids [33], β-diketones [34, 35] and ethanolamines [36] appeared to be kinetically unhindered species; reactivity in hydrolysis-polycondensation is not decreased, but in contrast, increased by chemical modification. That is also observed for chemically modified titanium alkoxides, where recent kinetic studies reveal a facile proton-assisted $\mathrm{SN^1}$ mechanism analogous to that for acid-catalyzed hydrolysis of silicon alkoxides and not an $\mathrm{SN^2}$ mechanism, proved for the base-catalyzed hydrolysis of silicon alkoxides [37]. Thus, the Sol-Gel transformation is not a kinetically controlled hydrolysis-polycondensation, but a micellar self-assembly process directed by surface interactions enhanced by the introduced heteroligands [38].

Our recent studies on some chemically modified titanium alkoxide precursors and their partially hydrolyzed products exhibited some interesting structural variations [39, 40]. Complete hydrolysis of some of these derivatives yielded pure nanosized titania.

Herein, we report the reaction of $\mathrm{Zr(OPr^i)_4Pr^iOH}$ with *N*-phenylsalicylideneimine to give a modified precursor $\mathrm{Zr(OPr^i)_2\{OC_6H_4(CH{=}NPh\}_2}$ (**1**), which was further modified with bifunctional bidentate ligands, such as glycols in the second step for the synthesis of heteroleptic derivatives. Although **1** appears to be hydrolytically more stable than pure $\mathrm{Zr(OPr^i)_4 \cdot Pr^iOH}$ due to the presence of terminal isopropoxy groups, it undergoes fast hydrolysis. Therefore, the precursor was further modified with a variety of glycols in the second step to convert it into a relatively more stable species.

Some of these derivatives were used in a Sol-Gel process to form nanocrystalline zirconia powders, which were characterized by SEM, XRD and EDX analysis.

2. Experimental

Rigorous precautions were taken to exclude moisture during experimental manipulation. Solvents and reagents were dried by conventional methods and distilled before use. *Due precautions were taken to handle hazardous chemicals, like benzene.* $Zr(OPr^i)_4 \cdot PriOH$ [41] and *N*-phenylsalicylideneimine [42] were prepared as described. Zirconium was estimated as ZrO_2 [43] and the liberated isopropanol by the oxidimetric method [44].

IR spectra were recorded on a SHIMADZU FTIR 8400 spectrometer in dry KBr powder. NMR [^1H and $^{13}C\{^1H\}$] data were collected on a JEOL FX 300 FT NMR spectrometer in $CDCl_3$ solutions at 300.4 and 75.45 MHz frequencies for ^1H and $^{13}C\{^1H\}$ NMR, respectively. FAB mass spectra of some of the complexes were obtained on a JEOL SX 102/DA-6000 mass spectrometer using *m*-nitrobenzylalcohol matrix. Microanalyses were carried out on a Heraeus Carlo Erba 1108 analyzer. X-ray diffraction analysis was carried out on a Siemens D500 diffractometer operating with Cu-K_α radiation. Scanning electron microscopy (SEM) and EDX–analysis were performed on an EDX-coupled scanning electron microscope JSM-6400F (JEOL).

2.1. *Preparation of [$Zr\{O(C_6H_4)CH{=}NPh\}_2\{OPr^i\}_2$] (1)*

To a benzene solution of $Zr(OPr^i)_4 \cdot Pr^iOH$ (4.92 g, 12.69 mmol), 5 g (25.35 mmol) of *N*-phenylsalicylideneimine was added. The mixture was refluxed and the reaction progress was monitored by estimating liberated isopropanol. The excess solvent was stripped off under *vacuo* and a yellow solid (7.62 g) was obtained. The physical and analytical data are summarized in table 1.

2.2. *Preparation of [$Zr\{O(C_6H_4)CH{=}NPh\}_2\{OCH_2CH_2O\}$] (2)*

The weighed amount of $Zr(OPr^i)_2\{O(C_6H_4)CH{=}NPh\}_2$ (3.12 g, 5.18 mmol) was added to the required amount of ethylene glycol (0.32 g, 5.16 mmol) in benzene. The mixture was refluxed for 6 h and the liberated isopropanol was extracted azeotropically with benzene. As soon as the azeotrope showed negligible presence of Pr^iOH, the reaction was stopped and the solvent was removed under reduced pressure to give a yellow solid (2.81 g). Their physical and analytical data are summarized in table 1.

2.3. *Hydrolysis of 1 and 7 using sol-gel technique*

Compound **1** (5.24 g, 8.71 mmol) was dissolved in isopropanol (~40 mL). 1 mL mixture of water and isopropanol (1 : 1 V/V) was added to the solution and stirred for 24 h, whereby gelation occurred immediately. Afterwards, 2 mL water and isopropanol mixture were added and the mixture was stirred again for two days to complete

Table 1. Physical and analytical data for $Zr\{O(C_6H_4)CH{=}NPh\}_2(OPr^i)_2$ and gycolatobis(*N*-phenylsalicylideneiminato)zirconium(IV) complexes.

		Elemental analyses (%) found (calcd)					
Complex	Color and yield (%)	Liberated Pr^iOH	C	H	N	Zr	M.Pt. (°C)
$Zr\{O(C_6H_4)CH{=}NPh\}_2(OPr^i)_2$ (**1**)	Canary yellow (98)	2.11 (2.30)	63.5 (63.9)	5.8 (5.9)	4.6 (4.6)	15.2 (15.2)	96
$Zr\{O(C_6H_4)CH{=}NPh\}_2\{OCH_2–CH_2–O\}$ (**2**)	Dark yellow (96)	0.54 (0.62)	61.7 (61.8)	4.2 (4.4)	5.1 (5.2)	16.7 (16.8)	*
$Zr\{O(C_6H_4)CH{=}NPh\}_2\{OCH_2–CH(O)–CH_3\}$ (**3**)	Yellowish orange (97)	0.57 (0.61)	62.3 (62.4)	4.6 (4.7)	5.2 (5.0)	16.4 (16.4)	88
$Zr\{O(C_6H_4)CH{=}NPh\}_2\{CH_3–CH(O)–CH(O)–CH_3\}$ (**4**)	Yellowish orange (95)	0.54 (0.60)	63.2 (63.0)	4.7 (4.9)	5.0 (5.0)	15.9 (16.0)	89
$Zr\{O(C_6H_4)CH{=}NPh\}_2\{OCH_2–CH(O)–CH_2–CH_3\}$ (**5**)	Yellow (97)	0.54 (0.61)	62.8 (63.0)	4.8 (4.9)	4.8 (4.9)	16.0 (16.0)	98
$Zr\{O(C_6H_4)CH{=}NPh\}_2\{OCH_2–CH_2–CH_2O\}$ (**6**)	Canary yellow (96)	0.58 (0.60)	62.1 (62.4)	4.6 (4.7)	4.9 (5.0)	16.4 (16.4)	76
$Zr\{O(C_6H_4)CH{=}NPh\}_2\{OCH_2–CH_2–CH(O)–CH_3\}$ (**7**)	Dark yellow (97)	0.53 (0.57)	62.9 (63.0)	4.8 (4.9)	4.9 (5.0)	16.0 (16.0)	*
$Zr\{O(C_6H_4)CH{=}NPh\}_2\{OCH_2–(CH_2)_4–CH_2O\}$ (**8**)	Canary yellow (96)	0.56 (0.62)	64.0 (64.1)	5.3 (5.4)	4.7 (4.7)	15.2 (15.2)	69

*Sticky solids.

the hydrolysis. The resulting sol was dried in an oven at 100°C overnight. A yellow powder was obtained, which was washed three times with *n*-hexane and acetone mixture and sintered at 700°C for 2 h [C, 0.42%; H, 1.23%; N, nil and EDX analysis: Zr: 35.9%; O: 40.8%; C: 21.4%] and then at 900°C to give a white powder, which was characterized as pure ZrO_2 [C, 0.32%; H, 2.15%; N, nil and EDX analysis: Zr: 36.9%; O: 43.5%; C: 17.5%].

Compound **7** was also hydrolyzed similar to **1** and sintered at 700°C to obtain ZrO_2 [C, 0.26%; H, 1.40%; N, nil and EDX analysis: Zr: 24.8%; O: 47.5%; C: 20.3%].

3. Results and discussion

Reaction of *N*-phenylsalicylideneimine with $Zr(OPr^i)_4 \cdot Pr^iOH$ in 1 : 2 molar stoichiometry in anhydrous benzene yields $Zr\{O(C_6H_4)CH{=}NPh\}_2(OPr^i)_2$ (**1**):

$$Zr(OPr^i)_4 \cdot Pr^iOH + 2HO(C_6H_4)CH = NPh \xrightarrow{\text{benzene}} \underset{\mathbf{(1)}}{Zr\{O(C_6H_4)CH = NPh\}_2(OPr^i)_2} + 3Pr^iOH$$

Further reactions of **1** with glycols in 1 : 1 molar stoichiometry afforded heteroleptic complexes of the type $Zr\{O(C_6H_4)CH{=}NPh\}_2(O–G–O)$ (**2–8**).

$$Zr\{O(C_6H_4)CH = NPh\}_2(OPr^i)_2 + HO - G - OH \xrightarrow{\text{benzene}} \underset{\mathbf{(2–8)}}{Zr\{O(C_6H_4)CH = NPh\}_2(O - G - O)} + 2Pr^iOH$$

[where –G–=$(CH_2)_2$ (**2**), (CH_2CHCH_3) (**3**), $(CH_3CHCHCH_3)$ (**4**), $(CH_2CHC_2H_5)$ (**5**), $(CH_2)_3$ (**6**), $(CH_2CH_2CHCH_3)$ (**7**), $(CH_2)_6$ (**8**)].

All the above reactions are quite facile and quantitative yielding yellow solids with defined melting points. Progress of the above reactions was monitored by estimating liberated isopropanol in the benzene-isopropanol azeotrope by oxidimetric method. FAB mass spectral studies of two of the representative compounds $Zr\{O(C_6H_4)CH{=}NPh\}_2(OPr^i)_2$ (**1**) and $Zr\{O(C_6H_4)CH{=}NPh\}_2(OCH_2CH_2CH(O)CH_3)$ (**7**) (table 2) indicate monomers. Appearance of some molecular ion peaks at higher m/e than the molecular ion in the FAB mass spectra may be due to reassembly of molecule fragments.

3.1. *IR spectra*

IR spectra of **1**–**8** have been recorded in KBr and some relevant data are summarized in table 3. Absence of hydroxyl group absorption of *N*-phenylsalicylideneimine as well as of glycols in the IR spectra indicates deprotonation and concomitant bond formation of the ligand moieties with the zirconium. Strong absorption in the 535–554 cm^{-1} region in the spectrum of all the glycolato derivatives **2–8** is due to ν(Zr–O) [6, 7]. A significant downfield shift of ν(C=N) was observed in all the complexes as compared to the free ligand indicating chelation of the ligand, further confirmed by the appearance of a new absorption in the 432–450 cm^{-1} region attributed to ν(Zr–N) in all these complexes [6, 7].

Table 2. Fragmented molecular ions and m/e values of $Zr\{O(C_6H_4)CH{=}NPh\}_2\{OPr^i\}_2$ and $Zr\{O(C_6H_4)CH{=}NPh\}_2\{OCH_2–CH_2–CH(O)–CH_3\}$.

Complex	Fragmented ions	*m/e* value
$Zr\{O(C_6H_4)CH{=}NPh\}_2\{OPr^i\}_2$	$[Zr\{O(C_6H_4)CH{=}NPh\}_2\{OPr^i\}_2\{H_2O\}]^{+1}$	619
	$[Zr\{O(C_6H_4)CH{=}NPh\}_2\{OPr^i\}_2]^+$	600
	$[Zr\{O(C_6H_4)CH{=}NPh\}\{O(C_6H_4)CH{=}N\}\{OPr^i\}_2]^+$	523
	$[Zr\{O(C_6H_4)CH{=}NPh\}\{O(C_6H_4)CH{=}N\}\{OPr^i\}]^+$	464
	$[Zr\{O(C_6H_4)CH{=}NPh\}\{O(C_6H_4){=}N\}\{OC_2H_7\}]^+$	439
	$[Zr\{O(C_6H_4)CH{=}NPh\}\{O(C_6H_4){=}N\}\{C_2H_5\}]^+$	421
	$[Zr\{O(C_6H_4)CH{=}NPh\}\{H_2O\}\{C_2H_5\}]^+$	333
	$[Zr\{O(C_6H_4)CH{=}NPh\}]^+$	286
$Zr\{O(C_6H_4)CH{=}NPh\}_2\{OCH_2–CH_2–CH(O)–CH_3\}$	$[Zr\{O(C_6H_4)CH{=}NPh\}_2\{OCH_2–CH_2–CH(O)–CH_3\}]^+$	570
	$[Zr\{O(C_6H_4)CH{=}NPh\}\{O(C_6H_4)CH{=}NC_3H_5\}\{OCH_2–CH_2–CH(O)–CH_3\}]^+$	534
	$[Zr\{O(C_6H_4)CH{=}NPh\}\{O(C_6H_4)\}\{C_2H_7O\}]^+$	441
	$[Zr\{O(C_6H_4)CH{=}NPh\}\{O(C_6H_4)\}\{CH_5O\}]^+$	411
	$[Zr\{O(C_6H_4)CH{=}NPh\}\{C_6H_7)\}]^+$	365
	$[Zr\{O(C_6H_4)CH{=}NPh\}]^+$	286

Table 3. Some important IR absorptions of **1**–**8**.

Complex	ν(C=N)	ν(C–O)	$\nu(Zr–O)_{(glycol)}$	ν(Zr–N)
(1)	1546	990	542	440
(2)	1545	1034	548	436
(3)	1549	1032	554	440
(4)	1550	1020	550	432
(5)	1548	1036	552	446
(6)	1546	1030	550	450
(7)	1542	1025	551	434
(8)	1548	1032	535	442

*All absorptions are of strong intensity.

3.2. *NMR spectra*

^{1}H and ^{13}C{^{1}H} NMR spectra were recorded in $CDCl_3$ and the data are given in table 4. Consistent with the IR spectral observations, the hydroxyl proton resonances of free *N*-phenylsalicylideneimine (at δ 13.31 ppm) and glycols (around δ 2.0–3.5 ppm) were absent in the ^{1}H NMR spectra of all derivatives. A significant shift in the azomethine proton resonance (0.60–0.92 ppm) of *N*-phenylsalicylideneimine on complexation suggests bidentate attachment of this ligand *via* O and N in all complexes.

However, no significant shift in the CH=N carbon resonance in the ^{13}C{^{1}H} NMR spectra of all these derivatives was observed.

Table 4. ^1H and $^{13}C\{^1H\}$ NMR spectral data for **1**–**8**.

Complex	^1H NMR data (δ ppm)	$^{13}C\{^1H\}$ NMR data (δ ppm)
1	1.26 (br, 12H, CH_3); 4.52 (m, 2H, CH); 7.03 (m, 10H, N–Ph); 6.54–7.40 (m, 8H, C_6H_4); 7.93 (s, 1H, CH=N)	26.8 (CH_3); 71.7 (CH); 116.4–147.6 (all aromatic carbons); 161.5 (CH=N)
2	3.64 (br, 4H, OCH_2); 7.04 (m, 10H, N–Ph); 7.17–7.47 (m, 8H, C_6H_4); 8.02 (s, 2H, CH=N)	77.4 (OCH_2); 117.1–148.4 (all aromatic carbons); 161.1 (CH=N)
3	1.25 (br, 3H, CH_3); 3.60 (br, 2H, OCH_2); 4.38 (br, 1H, OCH); 7.04 (m, 10H, N–Ph); 7.16–7.45 (m, 8H, C_6H_4); 7.70 (s, 2H, CH=N)	24.6 (CH_3); 76.5 (OCH_2); 85.1 (OCH); 117.1–147.7 (all aromatic carbons); 161.0 (CH=N)
4	1.01 (br, 6H, CH_3); 3.66 (br, 2H, OCH); 6.97 (m, 10H, N–Ph); 7.18–7.46 (m, 8H, C_6H_4); 8.00 (s, 2H, CH=N)	22.0 (CH_3); 76.5 (OCH); 117.2–148.4 (all aromatic carbons); 161.1 (CH=N)
5	0.85 (br, 3H, CH_3); 2.17 (br, 2H, CH_2); 3.63 (br, 2H, OCH_2); 3.98 (br, 1H, OCH); 7.04 (m, 10H, N–Ph); 7.18–7.45 (m, 8H, C_6H_4); 7.97 (s, 2H, CH=N)	15.0 (CH_3); 27.2 (CH_2); 62.5 (OCH_2); 76.5 (OCH); 115.2–148.4 (all aromatic carbons); 161.1 (CH=N)
6	1.21 (m, 2H, CH_2); 4.00 (br, 4H, OCH_2); 6.92 (m, 10H, N–Ph); 7.25–7.45 (m, 8H, C_6H_4); 8.26 (s, 2H, CH=N)	24.9 (CH_2); 67.1(OCH_2); 117.2–148.4 (all aromatic carbons); 161.1 (CH=N)
7	1.25 (br, 3H, CH_3); 1.79 (m, 2H, CH_2); 3.48 (br, 2H, OCH_2); 3.70 (m, 1H, OCH); 6.94 (m, 10H, N–Ph); 7.19–7.45 (m, 8H, C_6H_4); 7.97 (s, 2H, CH=N)	22.1 (CH_3); 31.1 (CH_2); 77.4 (OCH_2); 84.1 (OCH); 116.1–144.4 (all aromatic carbons); 161.0 (CH=N)
8	1.25 {m, 4H, $CH_2(3)$}; 1.67{br, 4H, $CH_2(2)$}; 4.25 {br, 4H, $CH_2(1)$}; 7.04 (m, 10H, N–Ph); 7.15–7.45 (m, 8H, C_6H_4); 7.98 (s, 2H, CH=N)	26.2 {$CH_2(3)$}; 34.5{$CH_2(2)$}; 76.6 (OCH_2); 116.3–148.2 (all aromatic carbons); 160.9 (CH=N)

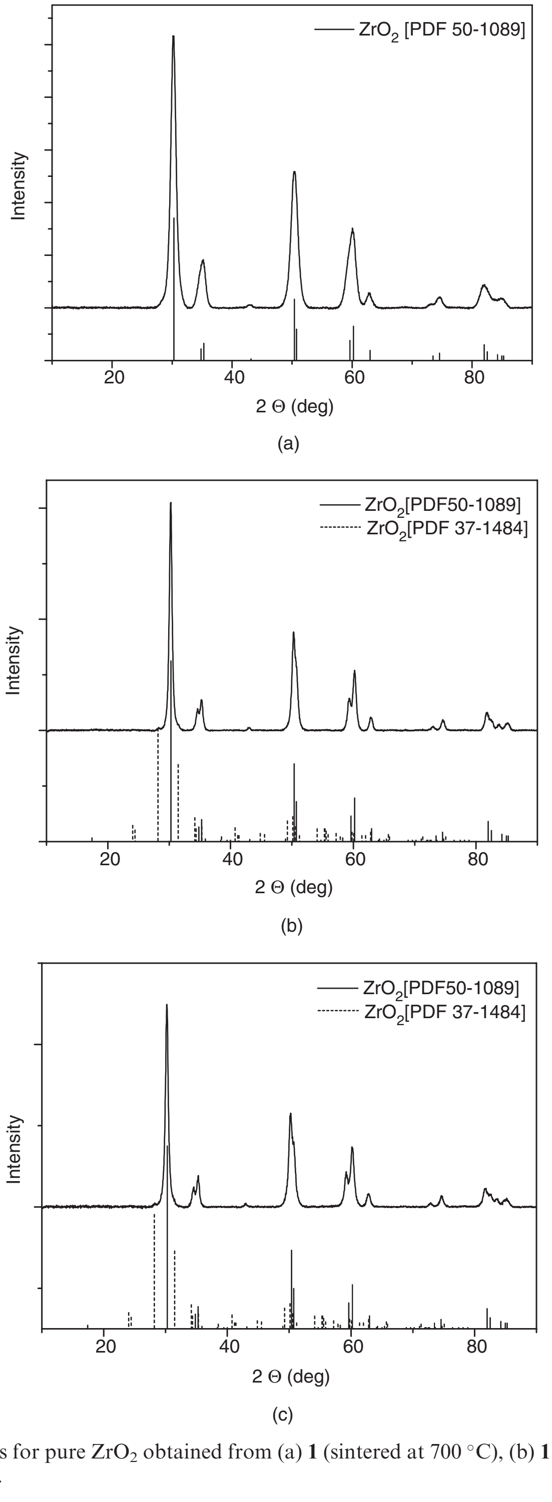

Figure 1. XRD patterns for pure ZrO_2 obtained from (a) **1** (sintered at 700 °C), (b) **1** (sintered at 900°C) and (c) **7** (sintered at 700°C).

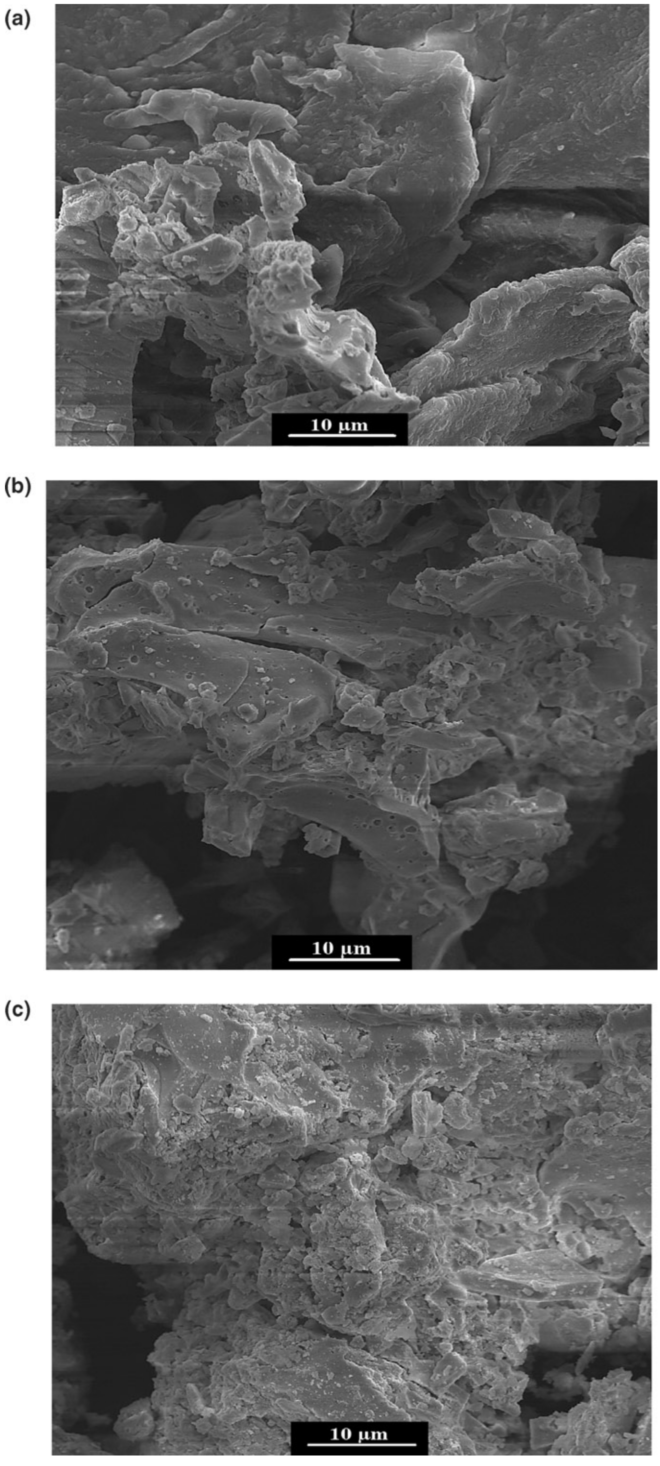

Figure 2. SEM images of pure ZrO_2 obtained from (a) **1** (sintered at 700°C), (b) **1** (sintered at 900°C) and (c) **7** (sintered at 700°C).

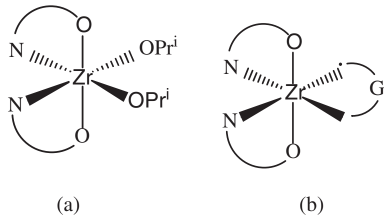

Figure 3. Proposed structures for (a) $Zr\{O(C_6H_4)CH{=}NPh\}_2(OPr^i)_2$ and (b) $Zr\{O(C_6H_4)CH{=}NPh\}_2$ (O–G–O).

Other proton and carbon resonances for *N*-phenylsalicylideneimine [45–47] and glycolate [48] moieties appeared at the expected positions and with desired multiplicities in all derivatives.

3.3. *Sol-gel process and material characterization*

Hydrolyses of two representative derivatives, $Zr\{O(C_6H_4)CH{=}NPh\}_2(OPr^i)_2$ (**1**) and $Zr\{O(C_6H_4)CH{=}NPh\}_2(OCH_2CH_2CH(O)CH_3)$ (**7**), were carried out by sol-gel methods. ZrO_2 obtained by hydrolysis of $Zr\{O(C_6H_4)CH{=}NPh\}_2(OPr^i)_2$ (**1**) was sintered at two different temperatures, 700°C and 900°C, respectively.

XRD spectra (figure 1a) of ZrO_2 (obtained from **1** and sintered at 700 °C) exhibited the formation of pure tetragonal zirconia, whereas at 900 °C traces of monoclinic ZrO_2 were formed (figure 1b), consistent with reported studies [49, 50] that tetragonal ZrO_2 formed from precipitation reactions remains stable until a critical particle size of *ca.* 30 nm is reached, where the surface energy favors the transformation to monoclinic ZrO_2. The XRD spectra of ZrO_2, obtained from $Zr\{O(C_6H_4)CH{=}NPh\}_2$ $(OCH_2CH_2CH(O)CH_3)$ (**7**), sintered at 700°C, show the formation of tetragonal ZrO_2 along with traces of monoclinic ZrO_2 (figure 1c). The fact that only the tetragonal phase of ZrO_2 is present at 700°C in the powders derived from the above zirconium precursors (**1** and **7**) appears to be consistent with the results reported earlier on the sucrose/pectin derived powders [51].

SEM images (figure 2a–c) of these oxides show formation of micro scale agglomerates of the nanocrystalline zirconia.

4. Conclusion

A series of glycolato derivatives of zirconium was synthesized and characterized. It is difficult to comment on the actual solid-state structure of the complexes without single crystal X-ray diffraction investigations. However, NMR data and IR spectra of the complexes combined with literature values of titanium analogues [34] lead to the assumption of octahedral geometry and *cis*-orientation of N,O atoms of the salicylideneimine moiety around a zirconium atom. Both glycolato and isopropoxo derivatives were transformed into zirconia, with no differences in phase formation or morphology of the obtained powders.

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