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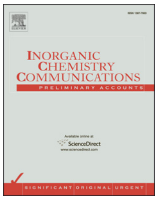

Feature article

A novel dinuclear zirconium (IV) complex derived from $[Zr(acac)_4]$ and a pentadentate Schiff base ligand: Synthesis, characterization and catalytic performance in synthesis of indole derivatives

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ABSTRACT

$[Zr(acac)_4]$ underwent ligand exchanges with pentadentate Schiff base ligand of N,N′-bis(3-salicylidenaminopropyl)amine. Full characterization of this complex was accomplished with elemental analyses, spectroscopic studies (^{1}H NMR, ^{13}C NMR, FT-IR, UV–vis) and X-ray structure analysis. X-ray crystallography indicated that this complex had a dinuclear structure in which each seven coordinated zirconium atom adopted a distorted pentagonal bipyramid geometry that was joined to the second zirconium by a μ-oxo bridge. The catalytic activity of the prepared complex was investigated in the synthesis of indole derivatives under mild conditions. The results revealed that although in this complex Zr (IV) was surrounded by seven other atoms, it could still catalyze indole condensation reaction and lead to plausible yields of products.

Contents

Introduction. The chemistry of zirconium is highly dominated by compounds in oxidation state (IV) [1]. A high charge-to-size ratio ($Z^2/r = 22.22\ e^2m^{-10}$) of the zirconium (IV) ion gives it a marked preference for higher coordination numbers [2] including 7 and 8. The common starting materials for zirconium (IV) complexes are $ZrCl_4$, $ZrOCl_2 \cdot 8H_2O$, and $[Zr(acac)_4]$. $ZrCl_4$ is prone to easy hydrolysis [3], and $ZrOCl_2 \cdot 8H_2O$ has a tetrameric structure which leads to tetrameric complexes with double hydroxo bridges [4]. Among them, $[Zr(acac)_4]$ is stable [1], and low toxic (LD50 {$[Zr(acac)_4]$ oral rat} = 719 mg/kg). This compound can undergo partial or total exchange of acac with other suitable ligands and produce various complexes.

Schiff base ligands represent one of the most widely utilized and versatile ligands in metal coordination chemistry. Many Schiff base complexes have potential biological interest and are utilized as almost successful models of biological compounds [5]. Besides, their use in catalytic reactions has been well regarded [6]. On the other hand, the relatively large size and high charge of the Zirconium (IV) give it strong coordination ability with oxygen- and nitrogen-containing Schiff base ligands [2]. Recently, some investigations have been reported on the salen-type of Schiff bases and Zr (IV) derived from $ZrCl_4$ [7] and $ZrOCl_2 \cdot 8H_2O$ [8], resulting in the synthesis of monoclear metal complexes [9]. However, there are few studies on dinuclear complexes with Schiff base ligands of N_xO_y and zirconium (IV) [10].

Indole derivatives have attracted great interest due to ring system that is the most widely distributed heterocycle found in nature. Indole core presents in many natural products, pharmaceuticals, and agrochemicals [11]. They are also effective in the prevention of cancer due to their ability to modulate certain cancer causing estrogen metabolites [12]. Indole can readily undergo electrophilic substitution reaction with the oxygen atom of carbonyl compounds in the present of a suitable

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catalyst bis and tris (1H-indole-3-yl) methanes [2]. Different compounds are known to catalyze this reaction [13].

In the present study, synthesis and characterization of a new and stable Zr (IV) complex **1** obtained by the ligand exchange of Schiff base ligand of N,N′-bis(3-salicyliden-aminopropyl)amine with [Zr(acac)$_4$] is reported. A single-crystal X-ray structure of this compound proves that the complex is a centrosymmetric dinuclear unit in the solid state consisting of two mononuclear zirconium containing ligands that are joined by a μ-oxo bridge. Each monomeric unit exhibits distorted pentagonal bipyramidalgeometry. The catalytic activity of this complex is investigated in the reaction of indole condensation with different aldehydes in different solvents.

Experimental. ***General information***. Diethylenetriamine, salicylaldehyde, zirconium (IV) acetylacetonate, methanol and chloroform were purchased from Merck Chemical Company and utilized without any more purification.

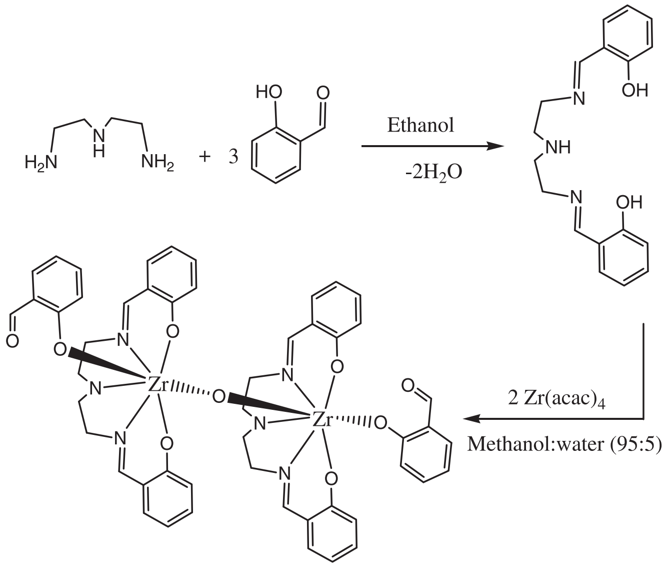
Instrumentation. Infrared spectra were recorded as KBr pellets using Unicam Mattson 1000 FT-IR. Elemental analysis (C, H, N) was performed using a Heraeus Elemental Analyzer CHN-O-Rapid (Elemental-Analysesysteme, GmbH, West Germany). ^{1}H and ^{13}C NMR spectra were obtained in CDCl$_3$ solutions with a Bruker T-NMR 250 (250 MHz) spectrometer. A digital melting point measuring device (Electrotermal 9100) was used. A double beam spectrophotometer (Shimadzu, UV-240) was used for the UV–vis absorption determination.

Preparations. *H$_2$saldien*. The pentadentate Schiff base ligand of N, N′-bis(3-salicyliden-aminopropyl)amine was synthesized similar to Coleman et al. [14] by 1:3 condensation reaction of diethylenetriamine (dien) and salicylaldehyde (sal) in absolute ethanol at room temperature for 15 min. The volume of the solution was reduced until an oil remained which was identified via NMR and FT-IR [14].

1·2CHCl$_3$·MeOH. Zr (IV) complex **1** was prepared by treatment of prepared ligand with [Zr(acac)$_4$] in molar ratio 2:1, respectively, in methanol according to Scheme 1.

A solution of H$_2$saldien (0.311 g, 1 mmol) in methanol:water (95:5) (10 mL) was added to a suspension of [Zr(acac)$_4$] (0.24 g, 0.5 mmol) in methanol: water (5 mL). A light yellow compound separated immediately. Stirring was continued for further 3 h. Then, it was filtered and washed with methanol and dried at room temperature. Finally, the obtained product was recrystallized in chloroform. Yield: 95%.

General procedure for the condensation of indoles with aldehyde compounds catalyzed by complex. Indole (0.234 g, 2 mmol) was added to a solution of the aldehyde compound (1 mmol) and complex (0.026 g, 0.02 mmol) in acetonitrile (0.5 mL). The mixture was stirred at 50 °C for an appropriate time, as monitored by TLC. The isolated yields were measured by using TLC plates and products were characterized by ^{1}H NMR and ^{13}C NMR.



Scheme 1. Preparation of **1**.

X-ray crystallography. The selected crystals of Zr (IV) were covered with perfluorinated oil and mounted on the top of a glass capillary under a flow of cold gaseous nitrogen. The orientation matrix and the unit cell dimensions were determined from 4000 reflections (Stoe IPDS 2 T (Zr (IV) complex) graphite-monochromated Mo-Kα radiation (λ = 71.073 pm); see also Table 5. The intensities were corrected for Lorentz and polarization effects. In addition, absorption corrections were applied for Zr (IV) complex (numerical). The structures were solved by direct methods using *SIR-92* and were refined against F^2 by full-matrix least-squares using the program *SHELXL-97*. (See Table 1.)

Results and discussion. The Schiff base complex crystallized as a stable light yellow crystal which decomposed at 267 °C. It was soluble in acetonitrile, dichloromethane and chloroform. Analytical and physical data for 1·2CHCl3·MeOH complex is given in Table 2.

IR. A sharp band at 1634 cm^{-1} due to υ (C═N) (azomethine) in free ligand, shifts to lower wavenumber, and appears at 1628 cm^{-1}. It depicts the involvement of azomethine nitrogen in coordination [15]. A rather sharp band at 1317 cm^{-1} is assigned to the phenolic C–O strength of the coordinated ligands [1]. The C–O stretching vibration in free ligand is observed at 1278 cm^{-1}. This frequency shifts in the complex towards lower or higher values as a result of coordination of the oxygen to the metal ion [16]. Besides, lowering a wavenumber related to stretching vibration of carbonyl group from 1668 cm^{-1} [23] to 1665 cm^{-1}, depicts the presence of intramolecular hydrogen bonding in this compound. Bands at 570–540 and 525–430 cm^{-1} might be assigned to Zr–O and Zr–N bonds [17] and a band at 714 cm^{-1} represents Zr–O–Zr bond [22a].

UV. Table 3 provides electronic spectra of the prepared zirconium complex along with its assignments. The electronic absorption spectrum which was measured in CHCl$_3$ at room temperature exhibits three bands. Two bands between 257 and 350 nm are due to π → π* and n → π* ligand transitions. Appearance of a lower intensity band at 379 nm is due to ligand to metal charge transfer (LMCT) transition [18]. The presence of a weak shoulder at 288 nm is indicative of an intramolecular hydrogen bonding [19]. In addition, no other absorption bands correspondent to d-d transitions are seen that is in agreement with d^0 configuration of zirconium (IV).

Table 1
Crystallographic data of 1·2CHCl$_3$·MeOH.

Compound	**1**·2CHCl$_3$·MeOH
Empirical formula	$C_{53}H_{54}Cl_6N_6O_{10}Zr$
Formula mass	1330.16
Crystal size/mm	0.22 × 0.19 × 0.15
Crystal system	Tetragonal
Space group	$I4_1/a$
a, b, c/pm	2930.3(1), 2930.3(1), 1260.1(1)
α, β, γ/°	90, 90, 90
Volume/pm^3·10^6	10,992(1)
Z	8
$D_{calcd.}$/g·cm^{-3}	1.608
Absorp. correction	Empirical (X-red32/X-area (Stoe))
μ/cm^{-1} (Mo-Kα)	7.35
Temp./K	100
$2\theta_{max}$/°	51.76
Index range (h, k, l)	−35 → 31,−22 → 35,−14 → 15
Reflections collected	14,737
Uniq. reflect.	5313
R_{int}	0.0327
Reflect. with $F_o > 4\sigma(F_o)$	3674
Parameters	362
R_1	0.035
wR_2 (all data)	0.0824
Max.residual electron density/(e·pm^{-3})·10^{-6}	0.662

a) $w = 1/[\sigma2(Fo2) + (0.0492 \cdot P)^2]$; $P = [\max(Fo2, 0) + 2.Fc2]/3$.

Table 2
Analytical and physical data for **1**.

Compound formula	Formula weight	Yield/(%)	Color	Decomposition temperature/(°C)
$C_{53}H_{54}Cl_6N_6O_{10}Zr$	1330.16	95	Light yellow	267
	%C	%H	%N	%Zr[a]
Found (calculated)	47.02	3.89	6.30	13.44
	(47.85)	(4.06)	(6.32)	(13.71)

[a] Zr was estimated by slow decomposition of complex with conc. HNO_3 (AR) and then weighing as ZrO_2 after igniting to 1000 °C [1].

NMR. The ^1H NMR spectrum of the H_2saldien ligand exhibits the following signals [19]. 13.02 (s, 2H, OH), 8.50 (s, 2H, – CH=N –), 6.40–7.10 (m, 8H, aromatic), 2.5–4 (complex multiplet, 8H, CH_2). The ^1H NMR spectrum of **1**, however, shows the disappearing of phenolic signal and downfield shift (9.66 ppm) of azomethine signal indicates the coordination of phenolic oxygen and azomethine nitrogen to Zr atom. A signal at 9.99 (s, 2H, – CHO) indicates the presence of aromatic aldehyde. The signal related to – NH at 5–6 ppm, is not located here probably due to the coordination of nitrogen of the Schiff base to zirconium, and producing a tertiary amine. Furthermore, ^1H NMR spectrum depicts no signal correspondent to acac groups [1], which indicates all acac groups were exchanged with other ligands. Other signals i.e. those due to aromatic and CH_2 protons appear nearly at the same position as the free ligand.

The ^{13}C NMR spectrum of **1** is in agreement with ^1H NMR. In the complex, signals due to azomethine carbon are observed at 165.64 ppm that are shifted downfield compared to free Schiff base ligand, suggesting the involvement of the nitrogen lone pair in coordination with metal ion [20]. It also exhibits the signals corresponding to aromatic aldehyde at 192.77 ppm. Besides, signals related to acac groups are not seen due to their exchanges with ligand atoms.

Crystal structure analysis of 1·2CHCl₃·MeOH. Light yellow crystals of **1**·$2CHCl_3$·MeOH, suitable for X-ray diffraction studies, were obtained. The compound crystallizes in the tetragonal space group $I4_1/a$ with eight molecules in the unit cell. An ORTEP view of **1** is shown in Fig. 1.

It is noteworthy to mention that **1** has a centrosymmetric dinuclear structure. The coordination sphere of the Zr1 can be described as distorted pentagonal-bipyramidal. Pentadentate Schiff base ligand coordinates to zirconium from all its five donor atoms. Besides, as Zr (IV) is characterized by its high affinity for oxygen [21], each Zr is also bound to two other oxygen atoms. One of them is the oxygen atom of salicylaldehyde. Another oxygen which is considered as the μ-oxo bridge is presumably sourced from a water molecule (or hydroxide) of solvent [23a], as the solvent of the reaction is methanol containing 5% water. It can be assumed that the reaction yields to $[(sal)Zr(saldien)OH_2]^{1+}$ or [(sal)Zr(saldien)OH] intermediates. In the next step, the remained $acac^-$ groups make a basic condition and get intermediates to dimerize and form a μ-oxo bridge. To our knowledge only two examples of Zr compounds with a single Zr – O – Zr bridge and distorted pentagonal-bipyramidal coordination sphere were described [22]. The distance Zr1–O5 of 196.04(3) pm in **1** is in good agreement with the measured values of the two corresponding compounds (196 pm, mean value) [22]. O5 lies on a center of inversion and occupies one apical position of the pentagonal bipyramid. On the second apical position O3 from the corresponding phenolate molecule of the salicylaldehyde is located. The Zr – N bonds between Zr1 and the neutral N atoms N1, N2, and N3 show typical long bond lengths between 243.2(3) and 244.8(2) pm. Neutral aza-crownethers bonded to Zr(IV) exhibit values of 246 pm (average) [22a].

Catalytic activity studies. As it has been mentioned, high charge-to-size ratio of the zirconium (IV) ion gives it a marked preference for coordination number of 8. Since in our prepared complex, zirconium (IV) has the coordination number of 7 which two coordinated atoms are electronegative oxygens; hence, the complex can be considered as a Lewis acid. Therefore, its catalytic activity was investigated in the reaction of indole condensation with different derivatives of benzaldehyde.

In the first step, the reaction of indole with benzaldehyde was chosen as a model (Scheme 2) in various solvents (Table 4). The reaction was carried out within 45 min that led to 79% yield. Increasing the time of the reaction up to 60 min gave 80% yield; therefore, 45 min was chosen as the optimized time of running the reaction. Moreover, Based on the optimized solvent, the procedure was applied in acetonitrile, to a variety of benzaldehyde derivatives to investigate the reaction scope. Results are summarized in Table 5.

As shown in Table 5, 4-$NO_2C_6H_5$ with the electron-withdrawing group affords higher yield of product (82%) compared to benzaldehyde (79%). However, 2-$NO_2C_6H_5$ leads to a low yield (70%) that is probably due to the strict hindrance of the nitro group in ortho position with the groups surrounding the zirconium (IV). Besides, 4-MeC_6H_5 with the electron-donating group leads to low yield of product (59%).

Table 3
UV–vis data for 1.

1	λ_{max} (nm) (ε (×10^5), M^{-1}, cm^{-1})	Assignment
	257, 2.299	$\pi \rightarrow \pi^*$
	350, 2.429	$n \rightarrow \pi^*$
	379, 1.263	LMCT

Table 4
Yields of condensation of indole with benzaldehyde in various solvents.

Entry	Solvent	Yield/(%)[a]
1	CH_3CN	79
2	CH_3Cl	71
3	CH_2Cl_2	70
4	MeOH[b]	–
5	EtOH[b]	–
6	AcOEt[b]	–
7	n-C_6H_{14}[b]	–

The reactions were run at 50 °C, in 45 min, and the molar ratio of aldehyde/indole/catalyst was 100:200:2 in 0.5 mL solvent.

[a] Isolated yield.

[b] Catalyst was not soluble in solvent.

Table 5
Condensation of indole with different derivatives of benzaldehyde.

Entry	Benzaldehyde compounds	Isolated yield/(%)[a]
1	X = H	79
2	X = 4-NO_2	82
3	X = 2-NO_2	70
4	X = 4-Br	67
5	X = 4-OMe	64
6	X = 4-OH	63
7	X = 4-Me	59

The reactions were run at 50 °C, in 45 min, and the molar ratio of aldehyde/indole/catalyst was 100:200:2 in 0.5 mL CH_3CN.

[a] All products were identified by their spectroscopic data and their comparison with known samples [2].

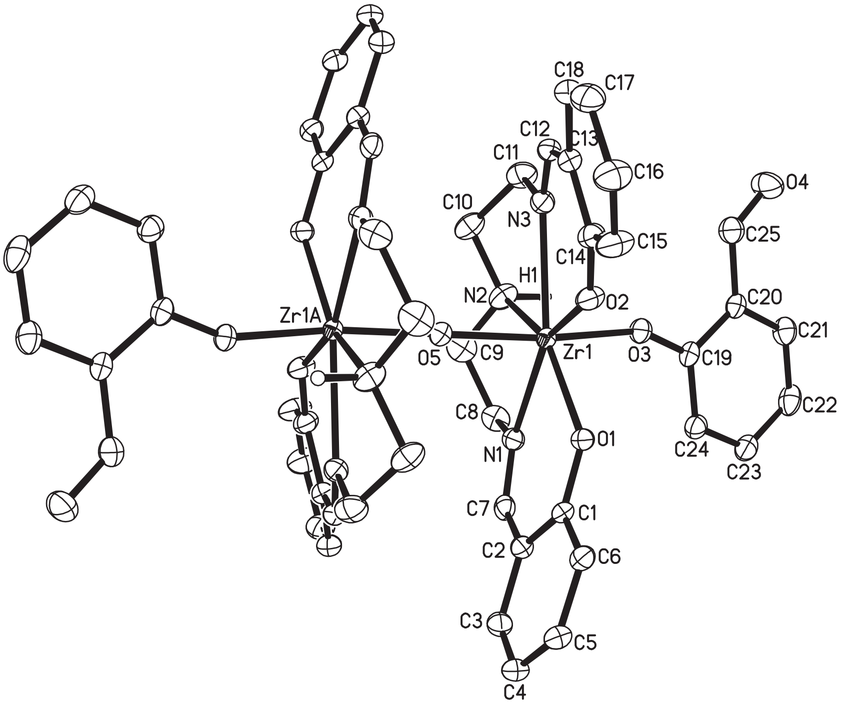


Fig. 1. Molecular structure of 1(thermal ellipsoids are at the 30% probability level). Selected bond lengths/pm and angles/°:Zr1-O5 196.04(3), Zr1-O2 205.7(2), Zr1-O3 208.5(2), Zr1-O1 209.4(2), Zr1-N2 243.2(3), Zr1-N3 243.7(3), Zr1-N1 244.8(2); Zr1-O5-Zr1a 180, O1-Zr1-O2 77.09(8),O1-Zr1-N2 150.21(8), O1-Zr1-N1 77.81(8), N1-Zr1-N2 68.33(9), N1-Zr1-N3 136.56(9), N2-Zr1-N3 68.28(9), O3-Zr1-O5 162.30(6), O1-Zr1-O3 92.24(8).

Hence, it can be concluded that Zr complex plays a Lewis acid role; giving rise to zirconium interaction with the oxygen atom of aldehyde and promoting the condensation reaction of indoles with aldehydes. It is noteworthy that on the one hand, the prepared dinuclear complex is composed of two ions of zirconium (IV) that increases its Lewis acidic sites. On the other hand, each zirconium (IV) is surrounded by 7 other groups which decrease its availability for the reaction. Therefore, although the prepared catalyst could catalyze the reaction, the obtained yields were not higher than 82%.

Conclusions. A new dinuclear complex of Zr (IV) with N_3O_2 pentadentate Schiff base ligand was prepared and characterized. Crystal structure of the complex was determined. In the crystal structure, zirconium atoms have distorted pentagonal bipyramidal geometries. This complex had potential Lewis acid properties, so it was used as the catalyst in the reaction of indole condensation. In this way, the catalyzed reaction of indole condensation with 4-$NO_2C_6H_5$ depicted the plausible yield (82%) in acetonitrile.

Acknowledgment

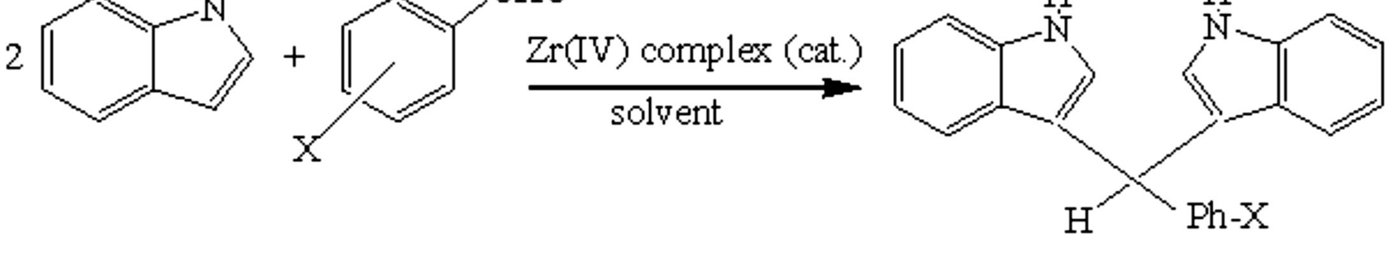
This work was supported by the K.N. Toosi University of Technology.

Appendix A. Analytical data

^{1}H NMR ($CDCl_3$, TMS, ppm): $\delta = 9.68$ (s, 4H, CH═N), 6.45–7.64 ppm (m, 24H, Ar-H and Ar-CHO), 2.6–3.55 ppm (complex multiplet, about 16H, CH_2). ^{13}CNMR ($CDCl_3$, TMS, ppm): $\delta = 192.75$ ppm (Ar-CHO), 165.64 ppm (HC═N), 115.90–122.82 ppm (Aromatic Ar-H and Ar-CHO), 61.61 ppm (−CH_2-N−), 48.59 ppm (−CH_2-C═N−). IR (KBr, cm^{-1}): υ(C═N) 1628, υ (phenolic C−O) 1317, υ (C═O) 1665, υ(Zr−O and Zr−N) 570–540 and 525–430, υ(Zr−O−Zr) 714 cm^{-1}. UV–vis spectrum in $CHCl_3$ [λ_{max} (nm)]: 257, 350, 379. $C_{53}H_{54}Cl_6N_6O_{10}$-Zr(1330.16): calcd. C 47.85, H 4.06, N 6.32, Zr 13.71% ; found C 47.02, H 3.89, N 6.30, Zr 13.44%.

Appendix B. Supplementary material

The crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication number CCDC 945942. Copies of the data can be obtained, free of charge, by application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; Email: data_request@ccdc.cam.ac.uk or via the internet: http://www.ccdc.cam.ac.



Scheme 2. Condensation of indole with benzaldehyde compounds catalyzed by 1.

uk/products/csd/request. Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.inoche.2013.12.011.

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