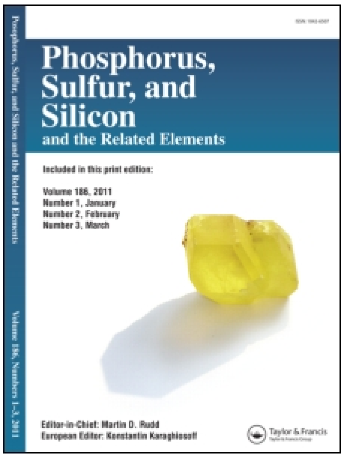

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Some Zirconium(IV) Complexes of Sterically Constrained Sulfur-Containing Schiff Bases of Heterocyclic β-Diketones: Synthetic Strategy and Structural Investigation Based Upon Spectroscopic Studies

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Zirconium(IV) Schiff base chelates having the general formula $ZrL(OPr^i)_2$ *[where* $LH_2 = RCNH(C_6H_4)SC{:}C(OH)N(C_6H_5)N{:}CCH_3$, $R = –C_6H_5$, $–C_6H_4Cl(p)$*] were synthesized by the reaction of* $Zr(OPr^i)_4.Pr^iOH$ *with sterically constrained sulfur-containing Schiff bases of heterocyclic β-diketones in a 1:1 molar ratio in dry refluxing benzene. The complexes* $ZrL(OPr^i)_2$ *were used as important precursors for the synthesis of the complexes of the type* $Zr(L)_2$*. The complexes,* $Zr(L)_2$*, were prepared by the interaction of precursor* $ZrL(OPr^i)_2$ *with sterically constrained sulfur-containing Schiff bases of heterocyclic β-diketones in a 1:1 molar ratio in dry benzene. The structures of these zirconium(IV) chelates have been discerned with the help of elemental analyses, physicochemical studies, and spectral [IR and NMR (*^1H *and* ^{13}C*)] data. A distorted trigonal bipyramidal and a distorted octahedral geometry may be assigned to zirconium(IV) chelates of the types* $ZrL(OPr^i)_2$ *and* $Zr(L)_2$*, respectively.*

Keywords Alcohol interchange reactions; spectroscopic studies; sterically constrained sulfur containing Schiff bases of heterocyclic β-diketones; $Zr(OPr^i)_4.Pr^iOH$

INTRODUCTION

There has been a tremendous development in the technological applications of hybrid materials[1–9] owing to their high performance. Macromolecules containing metals[10] constitute an important facet of hybrid materials. There is considerable current interest in the coordination chemistry of zirconium(IV).[11–15] A good deal of work has been reported on the organic derivatives of zirconium isopropoxide. ZrO_2 is an important material possessing special properties that finds applications[16–19] in various fields such as catalysts, in the making of thin films devices, as optical coatings, for its thermal behavior, and in dynamic random

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access memory devices. The rate of hydrolysis and reactivity of zirconium isopropoxide can be controlled by different modifiers possessing O, N, and/or S atoms.

In order to modify the reactivity of zirconium isopropoxide, sterically constrained sulfur-containing Schiff bases of heterocyclic β-diketones have been employed. These Schiff bases show interesting structures.[20] As an extension of our work on the incorporation of group(IV) metals into sterically hindered Schiff bases derived from heterocyclic β-diketones, we now report the encapsulation of zirconium(IV) in sterically constrained sulfur-containing Schiff bases derived from heterocyclic β-diketones, which afforded bulky metallacyclic systems possessing zirconium surrounded by oxygen, nitrogen, and sulfur. A part of the framework of these metallacyclic systems consists of N, S-orthometallated zirconium(IV) chelates.

RESULTS AND DISCUSSION

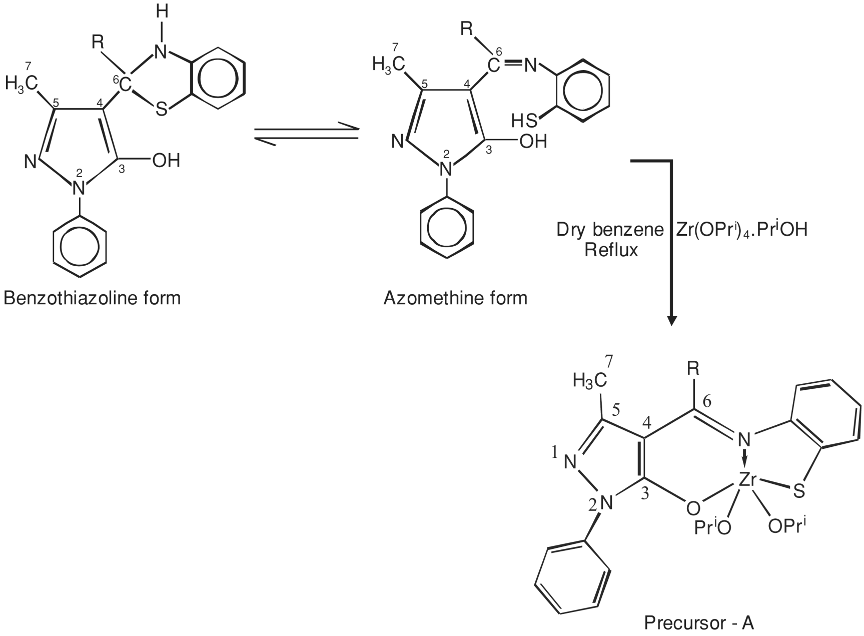
The bulky chelates of zirconium(IV) of sterically constrained sulfur containing Schiff bases of heterocyclic β-diketones possessing general formula $\mathrm{ZrL(OPr^i)_2}$, [where $\mathrm{LH_2} = \mathrm{RCNH(C_6H_4)SC{:}C(OH)N(C_6H_5)N{:}C}$ $\mathrm{CH_3}$ R = $-\mathrm{C_6H_5}$, $-\mathrm{C_6H_4Cl}$ (p)] were synthesized by the reaction of $\mathrm{Zr(OPr^i)_4.Pr^iOH}$ with sterically constrained sulfur-containing Schiff bases of heterocyclic β-diketones in a 1:1 molar ratio in dry benzene. This interaction yielded precursor A, as shown in Scheme 1.

The steric profile of precursor A for further reaction was investigated. The interaction of precursor A with another molecule of sterically constrained sulfur-containing Schiff base of heterocyclic β-diketones in a 1:1 molar ratio in dry benzene afforded bulky zirconium(IV) complexes as given in Scheme 2.

The complex $\mathrm{Zr(L_1)_2}$ may also be synthesized by the interaction of $\mathrm{Zr(OPr^i)_{4.}Pr^iOH}$ with sterically constrained sulfur-containing Schiff bases of heterocyclic β-diketones in a 1:2 molar ratio in dry benzene.

Similarly, the complex $\mathrm{Zr(L_2)_2}$ was also prepared by the reaction of $\mathrm{ZrCl_4}$ with disodium salt of the ligand in a 1:2 molar ratio in dry THF.

The progress of the reactions involving alkoxide was followed by estimating the liberated isopropanol in the azeotrope by oxidimetric method. These reactions were completed in ~10 h of refluxing. After removing the excess solvent under reduced pressure, brown-colored



Where

R = $-C_6H_5$ Complex $[ZrL_1(OPr^i)_2]$

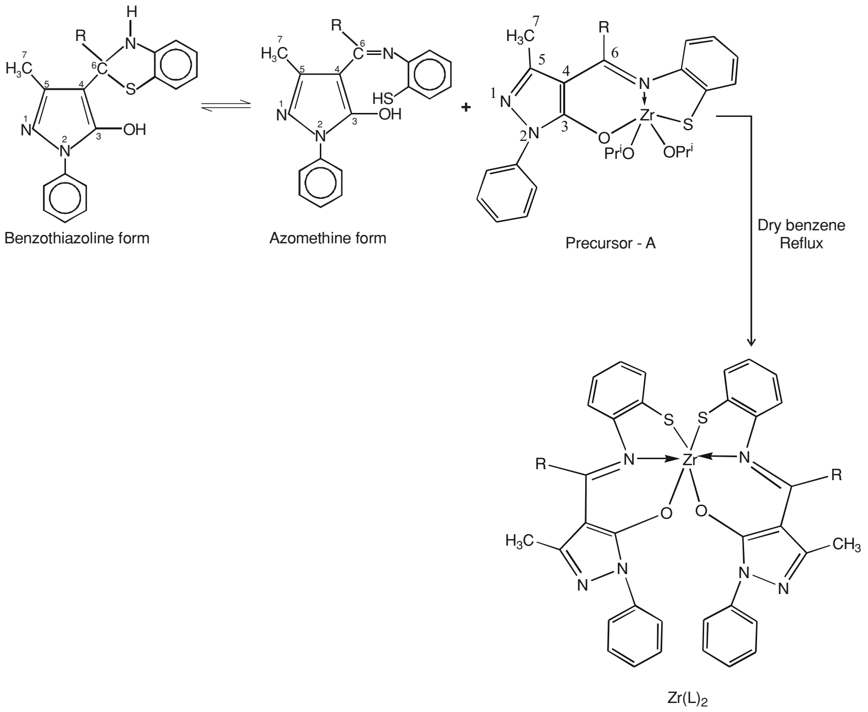
R = $-C_6H_4Cl(p)$ Complex $[ZrL_2(OPr^i)_2]$

SCHEME 1

solids were isolated, which were recrystallized from a chloroform and pet.-ether mixture. Molecular weight measurements reveal their monomeric nature.

It is quite interesting to investigate the alcohol interchange reactions in some of the bis alkoxy derivatives (precursor A). It has been observed that one of the isopropoxy groups of precursor A was substituted by a tert.butoxy group (a larger alcoholic functionality) when treated with an excess of tert.-butanol in dry refluxing benzene, as outlined in Scheme 3.

Even upon prolonged refluxing of the reaction contents, the second isopropoxy group could not be substituted by tert.-butanol.



Where

R = $-C_6H_5$ Complex $[Zr(L_1)_2]$

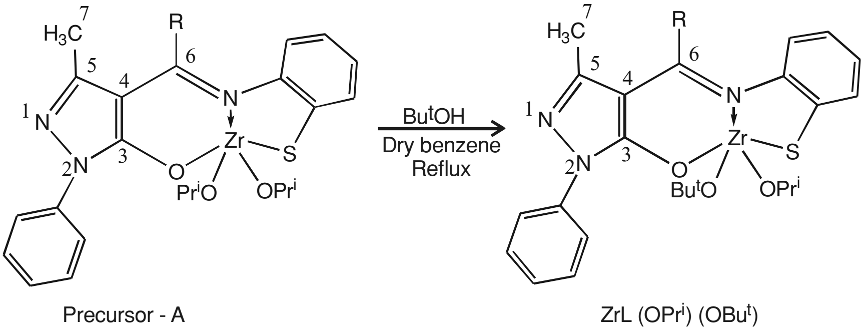
R = $-C_6H_4Cl(p)$ Complex $[Zr(L_2)_2]$

SCHEME 2

Spectroscopic Studies

IR Spectra

The broad bands present in the IR spectra of the sterically constrained sulfur-containing Schiff bases in the region 3400 cm^{-1} and 3300 cm^{-1} due to νOH and νNH, respectively,[20–21] were found to be absent in the spectra of the corresponding zirconium(IV) complexes. In the IR spectra of the complexes of the types $ZrL(OPr^i)_2$, $[ZrL(OPr^i)(OBu^t)]$, and $Zr(L)_2$, a medium intensity band observed in the region 540–560 cm^{-1} supports the formation of Zr-O bond.[13,14] Another band present in the region ~1090 cm^{-1} may be assigned to Zr-O (isopropoxy)



Where

R = $-C_6H_5$ Complex $ZrL_1(OPr^i)(OBu^t)$

R = $-C_6H_4Cl(p)$ Complex $ZrL_2(OPr^i)(OBu^t)$

SCHEME 3

stretching[15] in the IR spectra of zirconium(IV) complexes of the types $ZrL(OPr^i)_2$ and $[ZrL(OPr^i)(OBu^t)]$. A medium intensity band observed in the region 425–435 cm^{-1} may be attributed to $\nu Zr \leftarrow N$ bond.[13] The sterically constrained sulfur-containing Schiff bases of heterocyclic β-diketones exist in benzothiazoline form in the free state and rearranges to azomethine form during complex formation. This may be corroborated by the presence of a band in the IR spectra of zirconium(IV) complexes in the region 1600–1615 cm^{-1} which may be due to >C=N-.[22]

^{1}*H NMR Spectra*

The ^{1}H NMR spectra of zirconium(IV) complexes of sterically constrained sulfur-containing Schiff bases derived from heterocyclic β-diketones of the types $ZrL(OPr^i)_2$, $[ZrL(OPr^i)(OBu^t)]$, and $Zr(L)_2$ and their parent ligands were recorded in $CDCl_3$, and TMS was used as an internal reference. The observed values of ^{1}H NMR chemical shifts were summarized in Table I. The ^{1}H NMR spectra of these zirconium(IV) complexes exhibited expected multiplicity of peaks. The broad singlets present in the ^{1}H NMR spectra of the sulfur-containing Schiff bases in the region δ 5.20–6.42 ppm may be attributed to >NH/–SH protons. The signals of >NH/–SH protons were found to be absent in the ^{1}H NMR

TABLE I ^{1}H NMR Data of $ZrL((OPr^i)_2$, $ZrL(OPr^i)(OBu^t)$, and $Zr(L)_2$ Types of Complexes

Ligands and Complexes	$\mathrm{R\underline{\overline{CNH(C_6H_4)S}}\overline{C{:}C(OH)N(C_6H_5)N{:}C}CH_3}$, $[LH_2]$			$(CH_3)_3C\text{-}OH$, $[Bu^tOH]$		Isopropoxy	
	>NH/SH	Ring methyl	Ring phenyl/terminal phenyl/ $-C_6H_4Cl(p)$ / Thiophenol ring	OH	CH_3	CH	CH_3
L_1H_2	5.20(bs)	1.92 (s)	6.55–8.05 (m)				
$ZrL_1(OPr^i)_2$	—	1.81 (s)	6.55–7.90 (m)			4.33 (sep.)$_{unr.}$	1.26 (d)$_{unr.}$
Bu^tOH				3.45(bs)	1.28(s)		
$ZrL_1(OPr^i)(OBu^t)$	—	1.78 (s)	6.56–7.90 (m)	—	*	4.33 (sep.)$_{unr.}$	1.25 (d)$_{unr.}$
$Zr(L_1)_2$	—	1.83 (s)	6.55–7.96 (m)				
L_2H_2	6.42 (bs)	2.10 (s)	6.54–7.86 (m)				
$ZrL_2\ (OPr^i)_2$	—	1.78 (s)	6.55–7.88 (m)			4.32 (sep.)$_{unr.}$	1.21 (d)$_{unr.}$
$ZrL_2(OPr^i)(OBu^t)$	—	1.71 (s)	6.55–8.07 (m)		*	4.32 (sep.)$_{unr.}$	1.24 (d)$_{unr.}$

Note : Where (bs) = broad singlet, (s) = singlet, (d) = doublet, (m) = multiplet, (sep.) = septet, unr. = unresolved.

*merge with methyl of isopropoxy group.

$[LH_2] = \mathrm{R\underline{\overline{CNH(C_6H_4)S}}\overline{C{:}C(OH)N(C_6H_5)N{:}C}CH_3}$

$R = -C_6H_5, -C_6H_4Cl\ (p)$

TABLE II ^{13}C **NMR Data of** $ZrL(OPr^i)_2$**,** $ZrL(OPr^i)(OBu^t)$**, and** $Zr(L)_2$ **Types of Complexes**

	$RC\boxed{NH(C_6H_4)S}C\boxed{:C(OH)N(C_6H_5)N:}CCH_3$, [$LH_2$]						$(CH_3)_3C\text{-}OH$, [Bu^tOH]		Isopropoxy	
Ligands and Complexes	C_3	C_4	C_5	C_6	C_7	Ring phenyl/ Terminal $-C_6H_5$/ $-C_6H_4Cl$ (p) / Thiophenol ring	CO	CH_3	CH	CH_3
L_1H_2	161.15	104.18	137.28	191.80	15.75	115.21–148.58				
$ZrL_1(OPr^i)_2$	163.37	107.26	137.95	187.60	16.01	115.18–148.59			64.28	24.84
Bu^tOH							68.31	30.89		
$ZrL_1(OPr^i)(OBu^t)$	163.59	107.54	137.91	187.74	16.37	115.29–148.72	69.07	31.21	63.94	25.31
$Zr(L_1)_2$	162.30	105.57	137.34	191.65	15.70	155.22–148.58				
L_2H_2	160.48	103.92	137.64	190.13	15.43	115.16–148.99				
$ZrL_2\ (OPr^i)_2$	163.89	107.60	136.71	186.97	16.08	115.20–148.57			64.97	24.86
$ZrL_2(OPr^i)(OBu^t)$	162.75	105.67	136.98	191.16	15.12	114.92–148.42	68.45	30.69	64.20	24.77
$Zr(L_2)_2$	161.05	104.02	137.35	190.02	15.70	115.14–148.97				

spectra of zirconium(IV) complexes, which indicates deprotonation of >NH/–SH protons and formation of Zr—O bond. The disappearance of hydroxyl protons of tert-butanol in the complex [ZrL(OPr^i)(OBu^t)] indicates the formation of Zr—O bonds through tert-butanol. In the ^{1}H NMR spectra of the complexes of the types ZrL(OPr^i)$_2$ and [ZrL(OPr^i)(OBu^t)], methyl and methine protons of isopropoxy groups appended to zirconium appeared in the region δ 1.21–1.26 ppm and δ 4.32–4.33 ppm, respectively. Methyl protons of the tert-butoxy group merged with methyl protons of the isopropoxy group in the ^{1}H NMR spectra of the complex [ZrL(OPr^i)(OBu^t)]. The aromatic protons of the sterically constrained sulfur-containing Schiff bases[20] of heterocyclic β-diketones and the corresponding complexes were present as a complex pattern in the region δ 6.54–8.07 ppm.

^{13}C NMR Spectra

The ^{13}C NMR spectra of the sterically constrained sulfur-containing Schiff bases of heterocyclic β-diketones and their corresponding complexes of the types ZrL(OPr^i)$_2$, [ZrL(OPr^i)(OBu^t), and Zr(L)$_2$ were recorded in CDCl$_3$/CDCl$_3$ and DMSO-d$_6$ solution and are summarized in Table II. A comparative study of the ^{13}C NMR spectra of zirconium(IV) complexes and their parent ligands furnished useful information in diagnosing the nature of bonding and discerning plausible structures of these complexes. In the ^{13}C NMR spectra of the free Schiff bases, the C$_6$ carbon signal was observed in the region δ 190.13–191.80 ppm. In the ^{13}C NMR spectra of zirconium(IV) complexes, the C$_6$ carbon signal experiences some shift in its position, which clearly shows that >C$_6$ =N– is involved in bonding. In the ^{13}C NMR spectra of zirconium(IV) complexes of the types ZrL(OPr^i)$_2$ and [ZrL(OPr^i)(OBu^t)], signals of methyl carbons and methine carbon of the isopropoxy group appended to zirconium were observed at δ 24.77–25.31 ppm and δ 63.94–64.97 ppm, respectively. The replacement of one of the isopropoxy group in the complex ZrL(OPr^i)$_2$ by higher alcohol like tert-butanol to yield the product [ZrL(OPr^i)(OBu^t)] is also supported by ^{13}C NMR spectral evidence. In the ^{13}C NMR spectra of the complex [ZrL(OPr^i)(OBu^t)], signals of CO and –CH$_3$ of the tert-butoxy group appeared at δ 68.45–69.07 ppm and δ 30.69–31.21 ppm, respectively.

The molecular weight measurements reveal the monomeric nature of these complexes. On the basis of physicochemical and spectral evidence, the plausible structure in Figure 1 may be suggested for precursor A, ZrL(OPr^i)$_2$.

The complexes ZrL(OPr^i)$_2$ (Precursor A) contain penta-coordinated zirconium centers, and a distorted trigonal bipyramidal geometry may

TABLE III Synthetic and Analytical Data of $ZrL(OPr^i)_2$, $ZrL(OPr^i)$, (OBu^t) and $Zr(L)_2$ Types of Complexes

	Reactants in g (mmol)								Yield	
Complex Formula	$Zr(OPr^i)_4.Pr^iOH$/ $ZrL(OPr^i)_2$	LH_2	Bu^tOH	Liberated Pr^iOH Found (Calc.)	$-OPr^i$ % Found (Calc.)	%Zr Found (Calc.)	m.p. (in °C)	Mol. wt. Found (Calc.)	Found (Calc.) (in g)	(in %)
$ZrL_1(OPr^i)_2$ [$C_{29}H_{31}N_3O_3SZr$]	$Zr(OPr^i)_4.Pr^iOH$ 1.60 g (4.12 mmol)	1.59 g (4.12 mmol)		0.73 (0.74)	19.90 (19.94)	15.40 (15.39)	84	610.10 (592.48)	2.09 (2.45)	85
$ZrL_1(OPr^i)(OBu^t)$ [$C_{30}H_{33}N_3O_3SZr$]	$ZrL_1(OPr^i)_2$ 1.10 g (1.85 mmol)		0.30 g 4.04 mmol (excess)	0.10 (0.11)	9.72 (9.74)	15.06 (15.04)	93	620.01 (606.49)	1.00 (1.12)	89
$Zr(L_1)_2$ [$C_{46}H_{34}N_6O_2S_2Zr$]	$ZrL_1(OPr^i)_2$ 0.91 g (1.53 mmol)	0.59 g (1.53 mmol)		0.17 (0.18)	—	10.64 (10.63)	107	863.50 (857.66)	1.15 (1.32)	87
$ZrL_2(OPr^i)_2$ [$C_{29}H_{30}N_3O_3SZrCl$]	$Zr(OPr^i)_4.Pr^iOH$ 1.22 g (3.14 mmol)	1.32 g (3.14 mmol)		0.56 (0.57)	18.80 (18.84)	14.55 (14.54)	78	630.70 (626.98)	1.71 (1.98)	86
$ZrL_2(OPr^i)(OBu^t)$ [$C_{30}H_{32}N_3O_3SZrCl$]	$ZrL_2(OPr^i)_2$ 1.35 g (2.15 mmol)		0.35 g (4.72 mmol) (excess)	0.11 (0.12)	9.20 (9.21)	14.24 (14.23)	112	647.50 (640.99)	1.20 (1.38)	86
$Zr(L_2)_2$ [$C_{46}H_{32}N_6O_2S_2ZrCl_2$]	$ZrL_2(OPr^i)_2$ 1.12 g (1.76 mmol)	0.74 g (1.76 mmol)		0.20 (0.21)	—	9.87 (9.85)	132	930.00 (926.66)	1.46 (1.65)	88

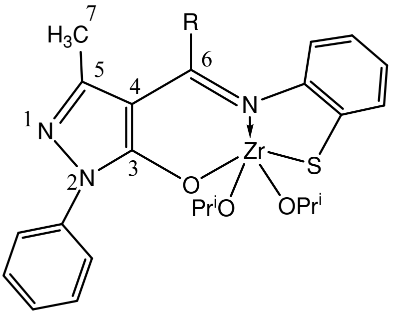


FIGURE 1 Proposed structure of precursor A complex [$ZrL(OPr^i)_2$]. Where R = $-C_6H_5$ Complex [$ZrL_1(OPr^i)_2$]. R = $-C_6H_4Cl(p)$ Complex [$ZrL_2(OPr^i)_2$]

be suggested for these complexes. The central zirconium is surrounded by three heteroatoms—oxygen, nitrogen and sulfur—in these metallacyclic systems, a part of the framework of which is made up of N,S-orthometallated zirconium(IV) chelates. As a consequence of this, there is formation of a six-membered ring and a five-membered ring. These metallacyclic systems possess a Zr←N bond. Because of the presence of two isopropoxy groups on zirconium, these complexes, $ZrL(OPr^i)_2$, are used as important precursors for the synthesis of complexes of the type $Zr(L)_2$.

The physicochemical studies and spectroscopic data suggest the plausible structure in Figure 2 for the complexes of the type $Zr(L)_2$.

A distorted octahedral geometry[23] may be discerned for these complexes. Zirconium is encapsulated in the sterically constrained sulfur-containing Schiff bases of heterocyclic β-diketones, which resulted in the formation of metallacyclic systems, in which central zirconium is surrounded by O, N, and S atoms. A part of the framework of this metallacyclic system consists of N,S-orthometallated zirconium(IV) chelates. These zirconium(IV) complexes possess Zr←N bonds.

CONCLUSION

Synthetic strategy has been devised to encapsulate zirconium(IV) in sterically constrained sulfur-containing Schiff bases, which afforded complexes of the type $Zr(L)_2$. For the preparation of $Zr(L)_2$, precursor A, $ZrL(OPr^i)_2$ was synthesized by the interaction of $Zr(OPr^i)_4.Pr^iOH$ and the Schiff base in a 1:1 molar ratio in dry benzene. The interaction of precursor A, $ZrL(OPr^i)_2$ with a sterically constrained sulfur-containing Schiff base of heterocyclic β-diketone, LH_2, in a 1:1: molar ratio yielded

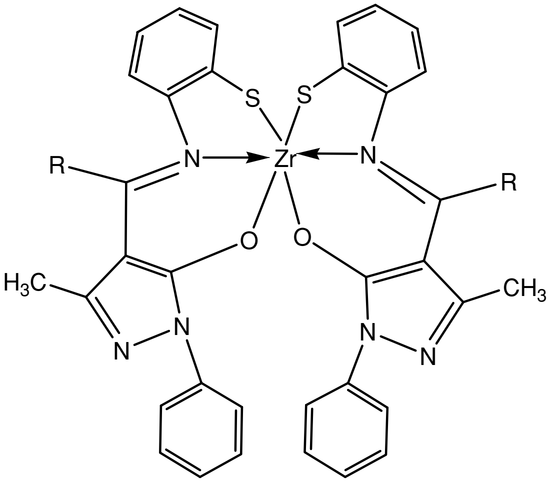


FIGURE 2 Proposed structure of complex $Zr(L)_2$. Where R = $-C_6H_5$ Complex $[Zr(L_1)_2]$. R = $-C_6H_4Cl(p)$ Complex $[Zr(L_2)_2]$

the encapsulated complex $Zr(L)_2$. The complex $Zr(L_1)_2$ may also be prepared by the interaction of $Zr(OPr^i)_4$ Pr^iOH with sterically constrained sulfur-containing Schiff base in a 1:2 molar ratio in dry benzene.

EXPERIMENTAL

The whole experimental work was carried out under strictly anhydrous conditions. The solvents such as benzene, THF, and pet-ether were dried over sodium. Isopropanol and tert-butanol were dried over sodium followed by aluminium isopropoxide, whereas choloroform was dried over fused calcium chloride. Methanol was dried over magnesium turnings in the presence of iodine crystals. Sterically constrained sulfur-containing Schiff bases of heterocyclic β-diketones were prepared by reported method.[20] $Zr(OPr^i)_4.Pr^iOH$ was prepared by reported method.[24] Zirconium was estimated as ZrO_2,[25] and the liberated isopropanol in the azeotrope was estimated by oxidimetric method. Molecular weight measurements of zirconium(IV) complexes of the types $ZrL(OPr^i)_2$, $[ZrL(OPr^i)(OBu^t)]$, and $Zr(L)_2$ were carried out cryoscopically in benzene solution. IR (4000–400 cm^{-1}) spectra of the samples were recorded on SHIMADZU, FTIR 8400 spectrophotometer, and samples were prepared as KBr pellets.

Synthesis of $Zr(OPr^i)_2[C_6H_5C{:}N(C_6H_4)SC{:}C(O)N(C_6H_5)N{:}CCH_3]$

To a benzene solution of $Zr(OPr^i)_4.Pr^iOH$ (1.60 gm, 4.12 mmol.), a benzene solution of stoichiometric amount of sterically constrained sulfur containing Schiff base of heterocyclic β-diketone, L_1H_2 [where $L_1H_2 = C_6H_5CNH(C_6H_4)SC{:}C(OH)N(C_6H_5)N{:}CCH_3$] (1.59 gm, 4.12 mmol.) was added. The reaction contents were refluxed for ~10 h, and the liberated isopropanol was fractionated off azeotropically with benzene. After the completion of the reaction and removal of the excess solvent in vacuo, a light brown coloured solid product was isolated which was recrystallised from chloroform and pet.-ether mixture. The physical and analytical data are summarized in Table III.

Synthesis of $Zr[C_6H_5C{:}N(C_6H_5)SC{:}C(O)N(C_6H_5)N{:}CCH_3]_2$

To a benzene solution of $Zr(OPr^i)_2$ $[C_6H_5C{:}N(C_6H_4)SC{:}C(O)N(C_6H_5)N{:}CCH_3]$ (0.91 g, 1.53 mmol) was added a benzene solution of the required amount of sterically constrained sulfur-containing Schiff base of heterocyclic β-diketone, L_1H_2 [where $L_1H_2 = C_6H_5CNH(C_6H_4)SC{:}C(OH)N(C_6H_5)N{:}CCH_3$] (0.59 g, 1.53 mmol). The reaction was completed in ~10 h of refluxing, and the liberated alcohol in the azeotrope was estimated by oxidimetric method. The excess solvent was removed under reduced pressure. A brown-colored solid was obtained, which was recrystallized from chloroform pet.-ether mixture. The physical and analytical data are summarized in Table III.

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