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Zirconium(IV) Complexes of *Schiff* Bases

J. Uttamchandani and **R. N. Kapoor***

Department of Chemistry, University of Delhi, Delhi-110007, India

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Zirconium(IV) *Schiff* base derivatives have been synthesised by reacting zirconium isopropoxide with monofunctional bidentate *Schiff* bases in different stoichiometric ratios. The resulting derivatives of the type Zr(O-*Isopr*)$_3$(*SB*) and Zr(O-*Isopr*)$_2$(*SB*)$_2$, where *SB*$^-$ is the anion of the corresponding *Schiff* base *SBH*, have been isolated in almost quantitative yields. Their molecular weights have been determined ebullioscopically and their ir spectra recorded.

[Keywords: Schiff bases, complexes; Zirconium(IV) complexes]

Zirkonium(IV)-Komplexe von Schiff-Basen

Es wurden Zirkonium(IV)—*Schiff*-Basen-Derivate in verschiedenen stöchiometrischen Zusammensetzungen über die Reaktion von Zirkonium-isopropoxid mit monofunktionellen zweizähnigen *Schiff*-Basen synthetisiert. Die Komplexe vom Typ Zr(O-*Isopr*)$_3$(*SB*) und Zr(O-*Isopr*)$_2$(*SB*)$_2$ [*SB*$^-$ als Anion der *Schiff*-Base *SBH*] wurden in fast quantitativer Ausbeute erhalten. Es werden Strukturen vorgeschlagen, die auf ebullioskopisch bestimmten Molekulargewichten und den IR-Spektren basieren.

Introduction

Schiff base complexes of zirconium(IV) have been synthesised from zirconium tetrachloride[1, 2] and zirconyl chloride[3–9], but little attention has been paid to the reactions of *Schiff* bases with zirconium alkoxides. The reactions of zirconium isopropoxide with certain *Schiff* bases have been studied and the resulting complexes have been found to possess interesting properties[10–13]. ZrBr$_4$ reacts with *o*- and *p*-toluidine in *Et*O*Ac* to give products of the type Zr(*R*NH$_2$)$_4$Br$_4$[14] (where *R* = *o*-*Me*C$_6$H$_4$ or *p*-*Me*C$_6$H$_4$). In earlier publications from these laboratories, the reactions of Al[15], Ti[16] and Ta[17] alkoxides with *Schiff* bases have been reported. In the present paper we wish to report the synthesis and

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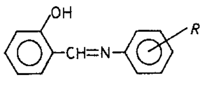
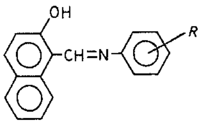
properties of zirconium isopropoxide complexes with the monofunctional bidentate *Schiff* bases derived from condensation of salicylaldehyde and 2-hydroxy-naphthylcarbaldehyde with *o*- resp. *p*-toluidine: 2-[*N*-(2- resp. 4-methylphenyl)-iminomethyl]-phenol (**1** resp. **2**) and 1-[*N*-(2- resp. 4-methylphenyl)-iminomethyl]-2-naphthol (**3** resp. **4**).



1: $R = o\text{-}CH_3$
2: $R = p\text{-}CH_3$



3: $R = o\text{-}CH_3$
4: $R = p\text{-}CH_3$

Experimental

Zirconium isopropoxide was prepared by the ammonia method[18] and recrystallized from isopropanol. *Schiff* bases were synthesised[15–17] by the usual methods and recrystallized from absolute alcohol. Benzene (BDH) was dried over sodium wire followed by azeotropic fractionation in the presence of ethanol. Isopropanol (BDH) was dried over sodium and then fractionated over aluminium isopropoxide. All the reactions were carried out under anhydrous conditions.

Table 1. *Reactions of zirconium isopropoxide with monofunctional bidentate Schiff bases*

Schiff Base	Mol. ratio Alkoxide: *Schiff* Base	Refluxing time (h.)	Products	Analysis %	
				Found (Calcd.)	
				Zr	N
1	1:1	5	$Zr(C_3H_7O)_3(C_{14}H_{12}NO)$	19.0 (19.1)	2.8 (2.9)
1	1:2	10	$Zr(C_3H_7O)_2(C_{14}H_{12}NO)_2$	14.7 (14.5)	4.2 (4.4)
2	1:1	9	$Zr(C_3H_7O)_3(C_{14}H_{12}NO)$	19.3 (19.1)	2.7 (2.9)
2	1:2	12	$Zr(C_3H_7O)_2(C_{14}H_{12}NO)_2$	14.6 (14.5)	4.2 (4.4)
3	1:1	7	$Zr(C_3H_7O)(C_{18}H_{14}NO)$	18.8 (19.3)	2.4 (2.6)
3	1:2	8	$Zr(C_3H_7O)_2(C_{18}H_{14}NO)_2$	12.7 (12.5)	3.7 (3.8)
4	1:1	8	$Zr(C_3H_7O)_3(C_{18}H_{14}NO)$	17.5 (17.3)	2.5 (2.6)
4	1:2	12	$Zr(C_3H_7O)_2(C_{18}H_{14}NO)_2$	12.6 (12.5)	3.6 (3.8)

Zirconium was estimated as zirconium dioxide, and nitrogen by the *Kjeldahl*'s method. C and H analyses were carried out at the University of Jammu, Jammu. Isopropanol was estimated by oxidation with normal dichromate solution in 12.5% sulphuric acid[19].

Molecular weights were determined in a semimicro ebulliometer (Gallenkamp) using thermistor sensing. Infrared spectra were recorded on a Perkin-Elmer-621 using KBr pellets.

The general procedure to synthesize the desired complexes was as follows:

A benzene solution of zirconium isopropoxide (0.7-1.2 g; ~ 50 ml benzene) was mixed with the proper amount of the aldehyde (molar ratio 1:1 or 1:2) and the clear solution was refluxed under a fractionating column. Refluxing was continued for 5-12 h. during which time the binary benzene—isopropanol azeotrope was collected, followed by the distillation of some of the benzene. In all cases 95 ± 5% of the theoretical amount of isopropanol was found in the azeotrope. The excess of benzene was removed under reduced pressure and the compound was dried at 40 °C/0.5 mm for 3 h.

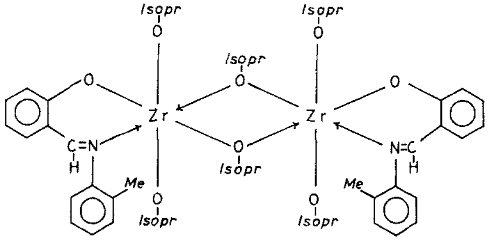
For details of the elemental analyses of the isolated complexes see Table 1.

Results and Discussion

Zirconium isopropoxide reacts with the *Schiff* bases **1-4** in 1:1 and 1:2 mole ratios in anhydrous benzene, giving soluble products as indicated below:

$$\mathrm{Zr(O\text{-}\mathit{Isopr})_4\mathit{Isopr}\text{-}OH} + \mathit{SBH} \rightarrow \mathrm{Zr(O\text{-}\mathit{Isopr})_3(\mathit{SB})} + 2\,\mathit{Isopr}\text{-}\mathrm{OH}$$
$$\mathrm{Zr(O\text{-}\mathit{Isopr})_4\mathit{Isopr}\text{-}OH} + 2\,\mathit{SBH} \rightarrow \mathrm{Zr(O\text{-}\mathit{Isopr})_2(\mathit{SB})_2} + 3\,\mathit{Isopr}\text{-}\mathrm{OH}$$

(where SB^- represents the anion of the corresponding monofunctional bidentate *Schiff* base *SBH*).

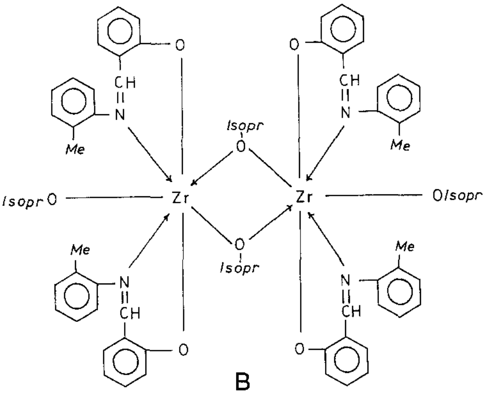


A

These reactions are quite facile and the resulting compounds could be isolated in almost quantitative yields. Zirconium(IV)—*Schiff* base complexes are pale-yellow to dark yellow solids, soluble in benzene, isopropanol, and chloroform. The complexes are susceptible to hydrolysis. Some of these compounds could be recrystallized from benzene or isopropanol or isopropanol-benzene mixture. These derivatives decompose when attempted to distill under reduced pressure.

The reactions appear to proceed only up to a 1:2 molar ratio. Even on prolonged refluxing (36 h.) 1:3 or 1:4 reaction mixtures, replacement of a third isopropoxy group by the *Schiff* base was not observed. This is probably due to steric factors.

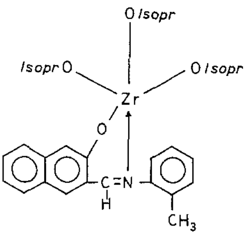
Plausible structures are given for the products **A** and **B** obtained in the reactions with **1** in 1:1 and 1:2 molar ratios, respectively.



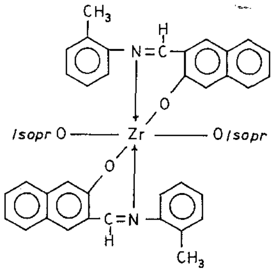
B

These derivatives have been found to be dimeric in boiling benzene, the dimerization probably takes place through the bridging isopropoxy groups and the zirconium atoms appear to be hexa- and hepta-coordinated as shown in **A** and **B**.

Products obtained in the reactions of zirconium isopropoxide with **3** in 1:1 and 1:2 molar ratios might possess the following **C** and **D** structures. These derivatives are monomeric in boiling benzene.



C



D

The monomers **C** and **D** are likely to be penta- and hexacoordinated with regard to the central metal atom. In the complexes of zirconyl chloride with thiosemicarbazones, zirconium exhibits coordination number five[3]. *Tandon et al.*[10–13] have studied the reactions of zirconium isopropoxide with certain *Schiff* bases and in the resulting derivatives metal possess coordination number 5-8.

Infrared Spectra

In the spectra of the *Schiff* bases, a strong band is observed in the 1,617-1,615 cm^{-1} region, which can be assigned to $\nu C{=}N$. In the zirconium derivatives, this band appears at almost the same position. This is consistent with the observations of *Sarma* and *Bailar*[20] who have reported no shift in $\nu C = N$ frequency even after complexation. However, some workers have reported a shift of $\nu C{=}N$ frequency either to a higher[21] or lower[22, 23] wave number.

The strong band in the region 1,308-1,282 cm^{-1} in the *Schiff* bases is attributed to the phenolic C—O stretch in view of the previous assignment[3, 24]. A number of absorption bands appeares in the region 1,340-1,280 cm^{-1} in the case of *Schiff* base complexes which could not be assigned.

The disappearance of the weak and broad bands in the region 3,300-3,100 cm^{-1} in the complexes of *Schiff* bases (due to —OH group) suggest that the *ortho*—OH group of the base has taken part in the bond formation.

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