

Spectral studies of the newly synthesized azomethine derivatives of zirconium(IV)

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Abstract. Equimolar and bimolar reactions of zirconium isopropoxide with bibasic tridentate azomethine (AZH_2) having the donor system ONO have been carried out and derivatives of the type $Zr(OPr^i)_2(AZ)$ and $Zr(AZ)_2$ [Where AZ^{2-} is the anion of the azomethine molecule] have been isolated. The labile nature of the isopropoxy groups in 1:1 derivatives has been shown by carrying out exchange reactions with equimolar amount of 2-methylpentane-2,4-diol. All the newly synthesized derivatives have been characterized on the basis of elemental analysis, conductance measurements, molecular weight determinations and infrared, ultraviolet, visible and proton magnetic resonance spectral studies.

Keywords. Zirconium (IV) complexes; azomethine derivatives; Schiff bases; spectral studies; UV spectra,

1. Introduction

The organic derivatives of metals and metalloids with the ligands having both nitrogen and oxygen as potential donors in the same molecule such as oximes (Chakravarty 1974), hydroxylamines (Singh *et al* 1974) and azomethines (Prashar and Tandon 1971; Prasad and Tandon 1975; Singh and Tandon 1978) continue to provide interesting facets in the field of coordination chemistry. Out of these ligands, azomethines have received considerable attention in recent years. The high reactivity, specificity and biological importance of the azomethines give impetus to the study of their chemistry as well as the preparation of their metal derivatives.

We have earlier reported the synthesis and important physical properties of a number of azomethine complexes of some of the IVth group elements such as silicon, germanium, tin and titanium (Singh and Tandon 1975, 1979a, b and Sharma *et al* 1979). However zirconium(IV) complexes of bibasic tridentate azomethines have been studied only marginally (Sharma *et al* 1980). Several new azomethine derivatives of zirconium have been synthesized during the course

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Table 1. Reactions of zirconium isopropoxide with azomethines.

Zr(OPr) ₄ ·Pr ^t OH (g)	Schiff base (SBH ₂) (g)	Molar ratio	Product, Yield (g) and Nature	M.P. (°C)	Pr ^t OH (g) Found (Calcd.)	Analysis (%)		Molecular weight Found (Calcd.)
						Zr Found (Calcd.)	N Found (Calcd.)	
1·10	C ₁₀ H ₁₂ NO ₃ 0·52	1:1	Zr(OPr) ₂ (C ₁₀ H ₁₁ NO ₂), (1·10), Light yellow solid, soluble in benzene	178	0·50 (0·51)	23·61 (23·59)	3·59 (3·62)	800 (386)
0·98	C ₁₀ H ₁₂ NO ₃ 0·92	1:2	Zr(C ₁₀ H ₁₁ NO ₂) ₂ , (1·14), Light yellow solid, soluble in benzene	235	0·76 (0·76)	20·51 (20·46)	6·31 (6·28)	460 (445)
0·97	C ₁₁ H ₁₃ NO ₃ 0·34	1:1	Zr(OPr) ₂ (C ₁₁ H ₁₂ NO ₂), (0·75), Light yellow solid, soluble in benzene	114	0·38 (0·37)	22·83 (22·77)	3·48 (3·49)	790 (400)
1·31	C ₁₁ H ₁₃ NO ₃ 1·30	1:2	Zr(C ₁₁ H ₁₂ NO ₂) ₂ , (1·58), Yellow solid, soluble in benzene	135	1·01 (1·02)	19·25 (19·30)	5·89 (5·91)	492 (473)
1·18	C ₁₁ H ₁₃ NO ₃ * 0·51	1:1	Zr(OPr) ₂ (C ₁₁ H ₁₂ NO ₂)*, (1·12), Light yellow foamy solid, soluble in benzene	135	0·56 (0·57)	22·83 (22·77)	3·52 (3·49)	791 (400)
0·99	C ₁₁ H ₁₃ NO ₃ * 0·98	1:2	Zr(C ₁₁ H ₁₂ NO ₂) ₂ * (1·20), Yellow solid, sparingly soluble in benzene	254	0·75 (0·77)	19·35 (19·30)	5·88 (5·91)	465 (473)
1·24	C ₁₂ H ₁₇ NO ₃ 0·66	1:1	Zr(OPr) ₂ (C ₁₂ H ₁₅ NO ₂), (1·32), Yellow solid, soluble in benzene	210	0·56 (0·58)	22·09 (22·01)	3·32 (3·38)	822 (414)
0·93	C ₁₂ H ₁₇ NO ₃ 0·99	1:2	Zr(C ₁₂ H ₁₅ NO ₂) ₂ , (1·20), Greenish yellow solid, soluble in benzene	196	0·71 (0·72)	18·25 (18·19)	5·54 (5·58)	523 (501)
0·66	C ₉ H ₁₁ NO ₃ 0·27	1:1]	Zr(OPr) ₂ (C ₉ H ₁₀ NO ₂), (0·62), Light yellow solid, soluble in benzene	149	0·30 (0·31)	25·10 (25·03)	3·80 (3·84)	724 (364)
1·01	C ₉ H ₁₁ NO ₃ 0·82	1:2	Zr(C ₉ H ₁₀ NO ₂) ₂ , (1·05), Light yellow solid, soluble in benzene	83	0·76 (0·78)	22·78 (22·72)	6·92 (6·97)	424 (401)

0.99	$C_8H_{17}NO_2$ 0.44	1:1	Zr(OPr) ₄ (C ₈ H ₁₅ NO ₂), (0.96), Light yellow solid, soluble in benzene	120	0.45 (0.46)	24.02 (24.10)	3.65 (3.70)	801 (378)
0.85	$C_9H_{17}NO_2$ 0.76	1:2	Zr(C ₉ H ₁₅ NO ₂) ₂ , (0.94), Light yellow solid, soluble in benzene	89	0.64 (0.66)	21.28 (21.22)	6.55 (6.52)	486 (429)
1.32	$C_{14}H_{15}NO_2$ 0.78	1:1	Zr(OPr) ₄ (C ₁₄ H ₁₃ NO ₂), (1.48), Yellow solid, sparingly soluble in benzene	189	0.60 (0.62)	20.82 (20.70)	3.12 (3.18)	.. (436)
0.80	$C_{14}H_{15}NO_2$ 0.95	1:2	Zr(C ₁₄ H ₁₃ NO ₂) ₂ , (1.13), Yellow solid, sparingly soluble in benzene	210	0.61 (0.62)	16.85 (16.77)	5.10 (5.13)	.. (545)
1.04	$C_{15}H_{17}NO_2$ 0.65	1:1	Zr(OPr) ₄ (C ₁₅ H ₁₅ NO ₂), (1.21), Brownish yellow solid, sparingly soluble in benzene	185	0.48 (0.48)	20.36 (20.25)	3.10 (3.11)	.. (450)
1.20	$C_{15}H_{17}NO_2$ 1.51	1:2	Zr(C ₁₅ H ₁₅ NO ₂) ₂ , (1.78), Brownish yellow solid, sparingly soluble in benzene	234	0.92 (0.93)	15.98 (15.90)	4.79 (4.88)	.. (573)

of the present investigations. Azomethines derived by the condensation of 2,4-pentanedione, *o*-hydroxyacetophenone, salicylaldehyde or 2-hydroxy-1-naphthaldehyde with 3-hydroxy-1-propyl or 1-hydroxy-2-butylamines have been used in the synthesis of new compounds described herein.

2. Experimental

2.1. Materials and methods

All the chemicals and methods used during the present investigations are the same as reported earlier (Gupta and Tandon 1973; Bradley *et al* 1952). For the preparation of azomethine complexes of zirconium(IV), zirconium isopropoxide was taken in 100 ml R.B. flask containing 40 ml of dry benzene and the calculated amount of the azomethine was added. The contents were refluxed using a fractionating column and the isopropanol liberated in the reaction was removed azeotropically with benzene. The progress of the reaction was ascertained by the estimation of isopropanol in the azeotrope. The solvent was removed and the product dried under vacuum. The details of their syntheses, analyses and physical properties are depicted in table 1.

2.2. Exchange reactions of diisopropoxy zirconium azomethine derivatives with 2-methylpentane-2,4-diol

To a benzene solution of diisopropoxy zirconium complex, an equimolar amount of 2-methylpentane-2,4-diol was added and the contents were refluxed (8-10 hr). The rest of the experimental procedure is the same as described above. The products were dried under reduced pressure and characterized on the basis of elemental analysis.

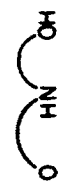
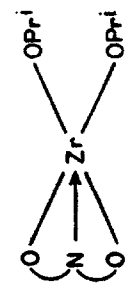
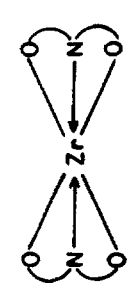
3. Results and discussion

The resulting new derivatives are yellow solids, mostly soluble in benzene, chloroform, DMF and DMSO and nonelectrolytes in DMF. $Zr(OPr)_2(AZ)$ type of products are highly hydrolyzable in nature, whereas, $Zr(AZ)_2$ type are quite stable in the open atmosphere. The 1:1 and 1:2 products are dimeric and monomeric respectively, indicating a stable hexa-coordinated environment for the central zirconium atom.

The replacement products, *i.e.*, $Zr(C_6H_{12}O_2)(AZ)$ are coloured solids, soluble in chloroform and monomeric in nature. These are, however, quite stable in the open atmosphere.

The complexes are characterized on the basis of their IR spectra in the 4000-200 cm^{-1} region recorded on a Perkin-Elmer 577 spectrophotometer. The disappearance of a band at 3300-3150 cm^{-1} due to $\nu OH/\nu NH$ in the spectra of complexes indicates coordination of oxygen as well as nitrogen atoms of the azomethine group. Further, the C=N stretching frequency in the free ligand is observed at $1620 \pm 5 cm^{-1}$ and its shift towards a lower frequency ($\sim 1600 cm^{-1}$) in all the metal complexes suggests that coordination has taken

Table 2. PMR spectral data of the ligands and their corresponding zirconium complexes in δ (ppm) with TMS as the internal standard

Compound	No.	R	a	b	c	d	e	f	g	h	i	j	k
	I	$-\text{CH}_2\text{CH}_2\text{CH}_2-$ e f e	6.68-7.60 ^m	2.40 ^s	3.0	15.8	3.65 ^e	1.80 ^e
	II	$-\text{CH}-\text{CH}_2-$ g f CH_2-CH_3 h i	6.42-7.45 ^m	2.30 ^s	2.90	16.4	..	3.63 ^s	3.63 ^s	1.6 ^{e'}	0.9 ^f
	III	$-\text{CH}_2\text{CH}_2\text{CH}_2-$ e e e	6.80-7.80 ^m	2.50 ^s	4.2	2.0 ^{e'}	4.30	1.55
	IV	$-\text{CH}-\text{CH}_2-$ g f CH_2-CH_3 h i	6.60-8.0 ^m	2.85 ^s	4.10 ^s	4.10 ^s	1.90	1.30 ^s	4.52	1.30 ^s
	V	$-\text{CH}_2\text{CH}_2\text{CH}_2-$ e f e	6.80-7.70 ^m	2.50 ^s	4.2 ^s	2.46
	VI	$-\text{CH}-\text{CH}_2-$ g f CH_2-CH_3 h i	6.70-7.90 ^m	2.75 ^s	4.0 ^s	4.0 ^s	1.65	1.5 ^f

m = Complex multiplet, *s* = singlet, *t* = triplet, *q* = quartet and *q'* = quintet. * = Overlap with each other. *Opr^s = OCH(CH₃)_s

