

BIFUNCTIONAL TETRADENTATE ALDIMINE AND KETAMINE DERIVATIVES OF ZIRCONIUM(IV)

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ABSTRACT

Zirconium(IV) isopropoxide isopropanolate has been found to undergo 1:1 and 1:2 molar reactions with bifunctional tetradentate Schiff bases derived by the condensation of salicylaldehyde, 2-hydroxy-1-naphthaldehyde, 2,4-pentanedione or 2-hydroxyacetophenone with 1,2-propylenediamine and 1,3-propylenediamine. In the resulting derivatives, the central zirconium atom appears to be hepta- and octa-coordinated as indicated by their molecular weights determined ebullioscopically in boiling benzene or chloroform. The isopropoxy groups of the bisisopropoxy zirconium Schiff base derivatives have been found to undergo replacement reactions with 2-methylpentane-2,4-diol and the resulting complexes are hydrolytically stable. All the newly synthesized derivatives have been characterized by elemental analysis, molecular weight and conductance measurements and I.R., U.V. and ^1H NMR spectral studies.

INTRODUCTION

In previous communications, from these laboratories, reactions of zirconium(IV) isopropoxide isopropanolate with a few monofunctional bidentate¹ and bifunctional tridentate² Schiff bases have been reported. During the course of the present investigations, reactions of zirconium(IV) isopropoxide isopropanolate with bifunctional tetradentate Schiff bases (SBH_2) have been studied and several new derivatives have been synthesized for the first time. The results of these investigations are discussed in the present paper.

EXPERIMENTAL

All the chemicals of analytical grade were used. Zirconium(IV) isopropoxide isopropanolate was prepared by the ammonia method³. Schiff bases were synthesized by the condensation of aldehyde/ketone with diamine in the alcohol medium. These were further purified by recrystallization from the same solvent. The following ligands were prepared:

- (I) $\text{N,N}'$ -1,2-propylene *bis*(salicylaldimine), ($\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}_2$), Yellow solid, melts at room temperature (20°C).
- (II) $\text{N,N}'$ -1,3-propylene *bis*(salicylaldimine), ($\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}_2$)*, Yellow solid, m.p. 52.5°C .
- (III) $\text{N,N}'$ -1,2-propylene *bis*(2-hydroxy-1-naphthalaldimine), ($\text{C}_{23}\text{H}_{22}\text{N}_2\text{O}_2$), Yellow solid, m.p. 185°C .
- (IV) $\text{N,N}'$ -1,3-propylene *bis*(2-hydroxy-1-naphthalaldimine), ($\text{C}_{23}\text{H}_{22}\text{N}_2\text{O}_2$)*, Yellow solid, m.p. 216°C .
- (V) $\text{N,N}'$ -1,2-propylene *bis*(2,4-pentanedioneimine), ($\text{C}_{13}\text{H}_{22}\text{N}_2\text{O}_2$), Colourless solid, m.p. 89°C .
- (VI) $\text{N,N}'$ -1,3-propylene *bis*(2,4-pentanedioneimine), ($\text{C}_{13}\text{H}_{22}\text{N}_2\text{O}_2$)*, Straw coloured solid, m.p. $46-47^\circ\text{C}$.

(VII) $\text{N,N}'$ -1,2-propylene *bis*(2-hydroxyacetophenoneimine), ($\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_2$), Yellow solid, m.p. 95°C .

(VIII) $\text{N,N}'$ -1,3-propylene *bis*(2-hydroxyacetophenoneimine), ($\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_2$)*, Yellow solid, m.p. 128°C .

Preparation of metal complexes

Zirconium(IV) isopropoxide isopropanolate was taken in anhydrous benzene and the requisite amount of the Schiff base in 1:1 and 1:2 molar ratio was added. The contents were refluxed over a fractionating column and the isopropanol liberated in the reaction was collected azeotropically with benzene. The progress of the reaction was ascertained by the estimation of isopropanol⁴ periodically in the azeotrope. On its completion (12-14 h), the solvent was removed and the products were dried under vacuum. Analyses of the compounds for Zr, C, H and N agreed with the theoretical values within the limits of experimental errors.

Replacement reactions of $\text{Zr}(\text{OPr}^i)_2$ (SB) type of complexes with 2-methylpentane-2,4-diol.

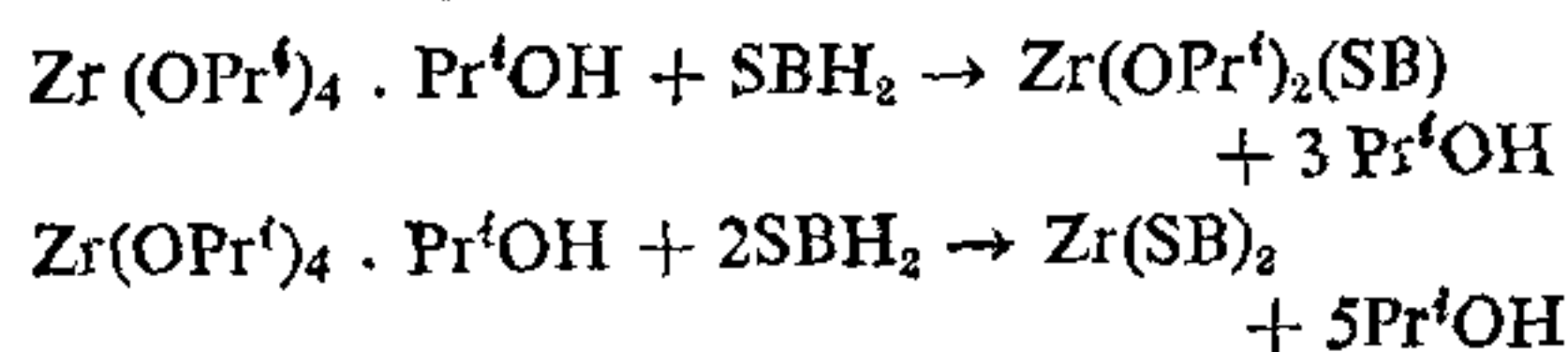
$\text{Zr}(\text{OPr}^i)_2$ (SB) type of complexes were dissolved in anhydrous benzene (50 ml) and 2-methylpentane-2,4-diol ($\text{C}_8\text{H}_{14}\text{O}_2$) added in equimolar ratio. The rest of the experimental procedure was same as described above.

Zirconium was estimated as its oxide, nitrogen by the Kjeldahl's method and isopropanol by oxidimetric method using normal $\text{K}_2\text{Cr}_2\text{O}_7$ in 12.5% sulphuric acid⁴. The IR, UV, and ^1H NMR spectra, molecular weight determinations and conductivity measurements were carried out as described previously⁵.

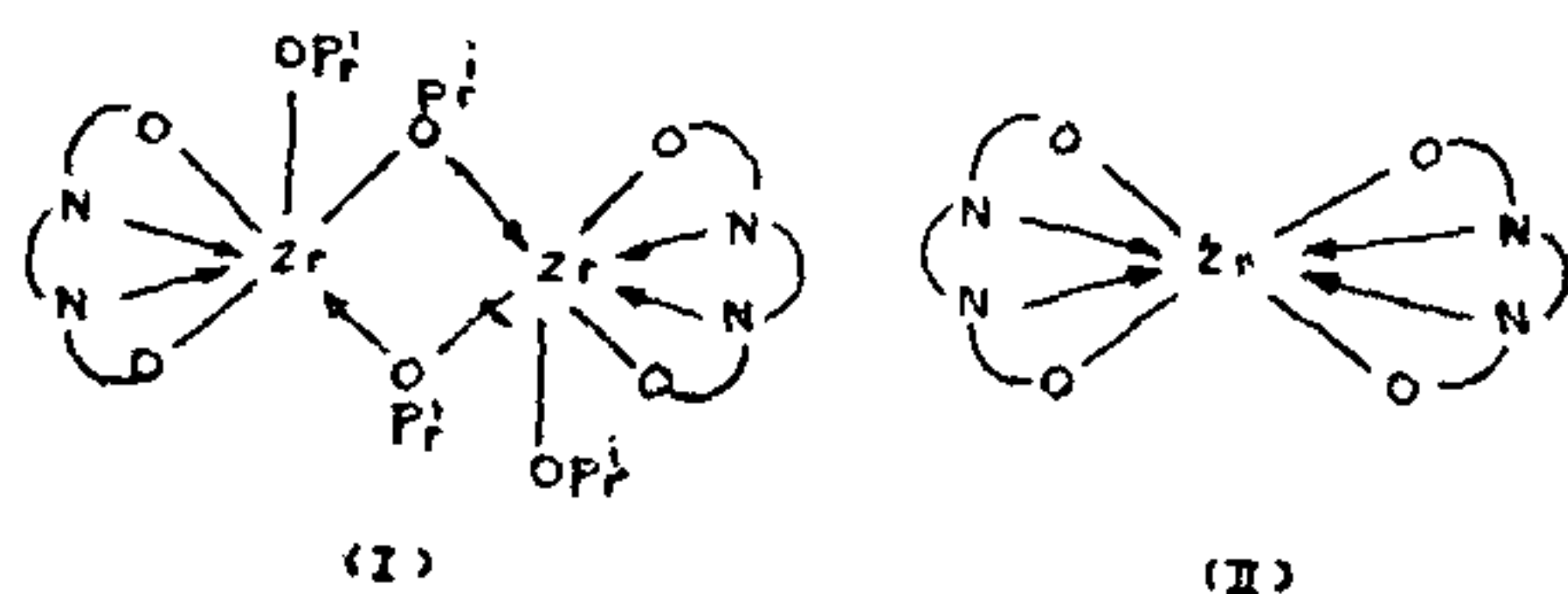
RESULTS AND DISCUSSION

$\text{Zr}(\text{OPr}^i)_2$ (SB) and $\text{Zr}(\text{SB})_2$ type of products were obtained by the reactions of $\text{Zr}(\text{OPr}^i)_4$. Pr^iOH and

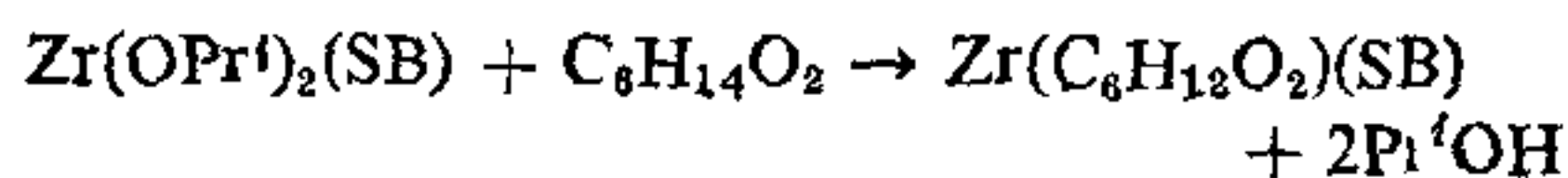
SBH₂ in 1:1 and 1:2 molar ratios respectively. These reactions may be represented as follows:



All the resulting derivatives are coloured solids, mostly soluble in chloroform and DMF and non-electrolytes in dry DMF. The determinations of molecular weights of 1:1 and 1:2 complexes show them dimeric and monomeric in nature respectively. Thus, in the complexes of the type Zr(OPrⁱ)₂(SB) and Zr(SB)₂, the metal atoms have probably a hepta- and octa-coordinated state as represented by the structures (I) and (II):



(where HONNOH represents the Schiff base molecule)
The replacement reaction of Zr(OPrⁱ)₂(SB) type of derivatives with 2-methylpentane-2,4-diol (C₈H₁₄O₂) can be represented by the following equation:



These are also monomeric in nature, quite soluble in chloroform and DMF and behave as non-electrolytes.

Infrared spectral studies

The IR spectra of the Schiff bases as well as the corresponding zirconium complexes have been recorded and some important features may be summarised as follows:

Strong bands in the region, 3100–2900 cm⁻¹ present in the Schiff bases, may be assigned to the hydrogen

bonded νOH or νNH. These bands disappear in the corresponding zirconium complexes thereby indicating the chelation of metal atom to both the oxygen and nitrogen atoms. Further, a strong band is observed at 1270 ± 10 cm⁻¹ and which is due to the phenolic C–O stretching vibrations. In the resulting derivatives, a shift of this band to the higher frequency (1300 ± 5 cm⁻¹) indicates the bonding of the Schiff base and the metal atom through the phenolic oxygen^{6,7}.

All the Schiff bases show a strong and sharp band at 1625 ± 10 cm⁻¹ and which may be assigned to the νC=N. In the zirconium complexes, this band appears at around 1600 cm⁻¹ and the shift of this band to the lower frequency indicates that the nitrogen of the azomethine linkage gets coordinated to zirconium atom. Several medium to strong intensity bands in the regions 590 ± 10 and 540 ± 10 cm⁻¹ may be assigned to ν(Zr–O) and ν(Zr–N) respectively⁸.

Ultraviolet spectra

The absorption spectral measurements of the solutions of Schiff bases and their zirconium complexes in chloroform have been carried out with a Toshniwal Spectrophotometer using 1 cm quartz cell in the range of 600–250 nm. In almost all the cases studied, two very important bands appear around 318 and 250 nm in the U.V. region.

¹H Nuclear magnetic resonance spectral studies

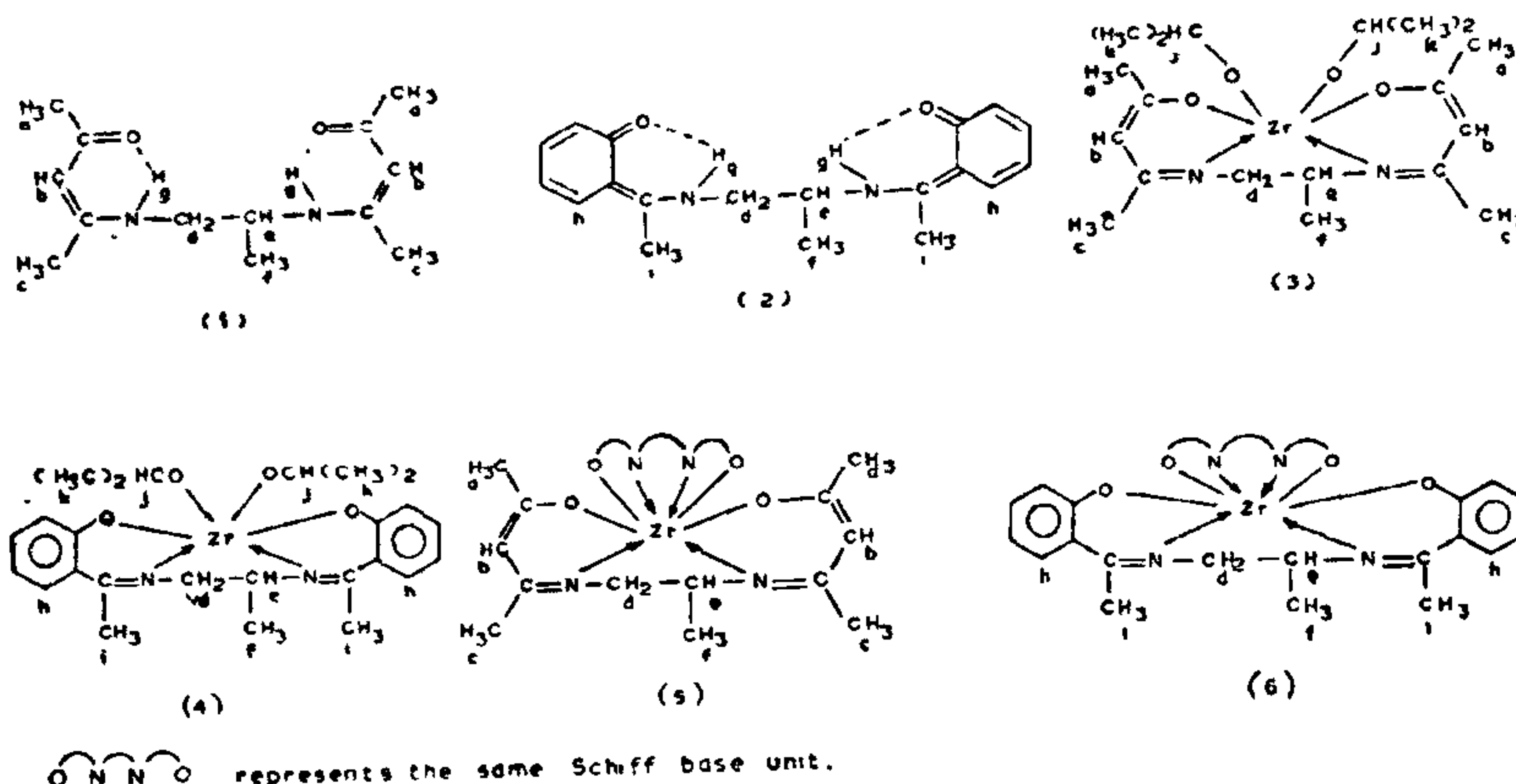
The ¹H NMR spectra of N,N'-1,2-propylene bis(2,4-pentanedioneimine)(1), N,N'-1,2-propylene bis(2-hydroxyacetophenoneimine) (2), and their corresponding zirconium complexes (3), (4), (5) and (6) have been recorded in benzene or CDCl₃. The chemical shift values (δ) for different protons are recorded in Table I. A comparison of the two spectra leads to the following conclusions and this is in conformity with the structures proposed for these complexes.

The ¹H NMR spectra, however, show preference for the ketamine structures over other equilibrium forms for the ligands (1) and (2) as well as for the Schiff

TABLE I
¹H NMR spectral data (δ ppm) of the Schiff bases and their zirconium complexes

Compound No.	a	b	c	d	e	f	g	h	i	j	k
(1)	1.63 ^s	4.50 ^s	1.25 ^s	2.35	2.80	0.46 ^d	10.80
(2)	4.05	4.55	1.74 ^d	16.20	7.50 ^s	2.65 ^d
(3)	1.63 ^s	4.80 ^s	1.35 ^s	2.70	3.22 ^{s'}	0.60 ^d	4.52	1.1
(4)	4.15	4.70 ^{s'}	2.0 ^d	..	8.20 ^{s'}	2.98 ^d	4.50	0.95
(5)	1.65 ^s	4.75 ^s	1.30 ^s	2.68	3.0 ^{s'}	0.60 ^d
(6)	4.40	5.0 ^{s'}	1.90 ^d	..	7.90 ^{s'}	2.85 ^d

s = singlet, d = doublet, s' = sextet and c' = complex multiplet,



bases derived by the condensation of β -diketones with alkyl or arylamines or diamines as reported in the literature^{7,8}. The 10.80 and 16.20 ppm peaks due to the hydrogen bonded NH protons of the ligands (1) and (2) respectively disappear in compounds (3), (4), (5) and (6) indicating their chelating nature.

In compounds (3), (4), (5) and (6), the methine, methylene and methyl proton signals are shifted downfield as compared to the ligands indicating the coordination of nitrogen of the ligand moiety to the zirconium atom.

New proton signals at 4.52, 4.50 and 1.1, 0.95 ppm in compounds (3) and (4) are due to methine and methyl protons respectively of the isopropoxy groups and which do not appear in the corresponding ligands.

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MECHANISM OF UREA ADDUCT FORMATION

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ABSTRACT

The energy of activation required for penetration of $-\text{CH}_2-$ group into urea lattice has been calculated by the Lennard-Jones potential energy expression method, and compared with the experimental value for the same by urea adduct experiments using dodecane at 45° and 60° C. There has been a fair agreement between the two values.

MUCH research has already been done¹ on the mechanism of separation of straight chain hydrocarbons from branch chain ones by the formation of

urea adducts. It has been postulated that separation by urea adduct formation takes place by a process of penetration of the urea crystals by the hydrocarbon chains. Support has been drawn for this conclusion from x-ray studies² of urea adducts formed from hydrocarbons of different chain lengths.

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