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# Synthesis and Spectral Studies of ZrO(II) Complexes with Aroylhydrazones

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Complexes of zironium(IV) with aroylhydrazones have been prepared in methanolic medium. The complexes have the stoichiometry of the type $ZrOCl_2L_2$. These are yellow to orange amorphous substances and are soluble in methanol, ethanol and DMF. The spectral data suggest that the oxygen of carbonyl group and nitrogen of azomethine group are involved in coordination. These ligands behaves as bidentates and a coordination number of seven has been proposed for zirconium in these complexes.

## INTRODUCTION

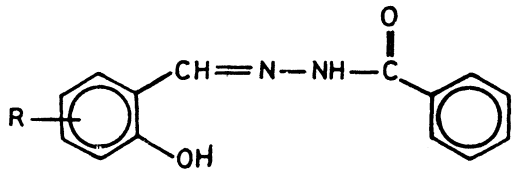
The hydrazides have been successfully tried for the complexation and have been shown to coordinate through the C=O and the terminal —NH groups[1–6]. The hydrazones containing C=O and C=N coordinating sites are the reaction products of hydrazides with aldehydes or ketones[7]. The *ortho* hydroxy aldehydes or ketones yield the bases containing the active group —OH in addition to the C=O and C=N coordinating groups. The previous examples manifest that these bases show varied behaviour depending the involvement of active and coordination sites[8–11]. The present work describes the synthesis and spectral properties of ZrO(II) complexes with the following hydrazones (Structures I–VI).

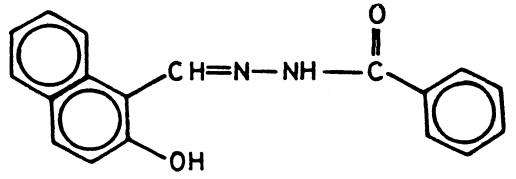
## EXPERIMENTAL

$ZrOCl_2 \cdot 8H_2O$ was of Fluka made, benzoyl hydrazide, various substituted salicyloyldehydes and the aroyl hydrazones were prepared according to the literature procedure.

### Preparation of the Complexes

A methanolic solution of $ZrOCl_2 \cdot 8H_2O$ (0.01 mol) and that of the ligands (0.02 mol) in the same solvent were mixed. The reaction mixture was refluxed on water bath for 2–3 h. Yellow coloured amorphous complex was separated by adding ether. The complex was filtered and washed with ether. The complex was dried in vacuum over fused calcium chloride.




VI.

## RESULTS AND DISCUSSION

The complexes are yellow coloured amorphous substances, soluble to a limited extent in nitrobenzene, chloroform, tetrahydrofuran, dioxan and highly soluble in ethanol, methanol, DMF and DMSO. The elemental analysis agrees with 1:2 stoichiometry of the type $ZrOCl_2L_2$ (Table 1). The molar conductance values of the complexes in DMF at the concentration of $10^{-3}$M are given in Table 1. These values are too low to account for any electrolytic behaviour[12].

TABLE-I
ELEMENTAL ANALYSIS AND CONDUCTIVITY DATA OF THE COMPLEXES

| Empirical formulae | % Analyses, Found (Calcd.) | | | $\Lambda_m$ ohm$^{-1}$ cm$^2$ mol$^{-1}$ |
|---|---|---|---|---|
| | Zr | N | Cl | |
| $ZrOCl_2(C_{14}H_{12}N_2O_2)_2$ | 14.4 (14.2) | 9.3 (8.7) | 10.0 (11.1) | 32.5 |
| $ZrOCl_2(C_{15}H_{14}N_2O_2)_2$ | 14.5 (13.6) | 8.4 (8.2) | 10.1 (10.6) | 32.4 |
| $ZrOCl_2(C_{15}H_{14}N_2O_2)_2$ | 14.1 (13.6) | — | 10.2 (10.6) | 36.1 |
| $ZrOCl_2(C_{15}H_{14}N_2O_2)_2$ | 13.9 (13.6) | — | 9.9 (10.6) | 33.0 |
| $ZrOCl_2(C_{14}H_{11}ClN_2O_2)_2$ | 12.0 (12.5) | 8.3 (7.7) | 8.9 (9.2) | 45.6 |
| $ZrOCl_2(C_{18}H_{14}N_2O_2)_2$ | 12.2 (12.0) | 8.8 (7.4) | 8.4 (9.3) | 26.3 |

The important IR frequencies of the ligands and their zirconium complexes along with their assignments are summerised in Table 2.

TABLE-2
IMPORTANT INFRARED FREQUENCES ($cm^{-1}$) OF ZrO(II) COMPLEXES AND THEIR ASSIGNMENTS

| Complex | ν(NH) | ν(OH) | ν(C=O) | ν(C=N) | ν(C—O) | ν(Zr=O) | ν(Zr—N)/ ν(Zr—O) |
|---|---|---|---|---|---|---|---|
| I | 3175s | 2800 br | 1625s | 1610s | 1295s | 900s | 545vs<br>425s |
| II | 3150b | 2800 br | 1620s | 1600s | 1295s | 905s | 545s<br>425s |
| III | 3150m | 2800 br | 1620s | 1600s | 1295s | 905s | 525b<br>455w |
| IV | 3150b | 2800 br | 1625s | 1600s | 1298s | 910s | 525s<br>420b |
| V | 3175b | 2800 br | 1620s | 1600sh | 1300b | 900s | 545s<br>440s |
| VI | 3150s | 2800 br | 1625s | 1600s | 1300s | 920s | 555s<br>440s |

It is established that the hydrazones are capable of exhibiting keto-enol tautomerism, however, one of the form is retained in complexes[13]. In the complexes under present investigation the spectral observations suggest that the hydrazones exist in the keto form. The following evidences may be advanced in support of the above conclusion.

The medium intensity band in the region 3275–3200 $cm^{-1}$ attributable to the secondary NH stretching vibrations[14] of the ligands is observed in the region 3175–3150 $cm^{-1}$ for the complexes. In the ligands the high intensity band in the region 1675–1650 $cm^{-1}$ is ascribed to ν(C=O) and another band in the region 1625–1600 $cm^{-1}$ to the ν(C=N) vibration in view of previous assignments[15]. We observe a clear resolution of these bands in the complexes too. The high intensity band around 1625 $cm^{-1}$ is assigned to ν(C=O) and other one in the region 1610–1600 $cm^{-1}$ to ν(C=N) vibration. The shifting of the both ν(C=O) and ν(C=N) to the lower frequency indicates the coordination of both the groups *viz.*, ν(C=O) and ν(C=N) to the zirconium moiety through oxygen and nitrogen respectively.

The broad weak band in the region 2750–2700 $cm^{-1}$ attributable to the intra molecular hydrogen bonded —OH[16] is retained in the complexes suggesting that the *o*-hydroxy group has not taken part in the bond formation. The phenolic (C—O) stretch does not show any shift to the higher frequency (Table 2), indicating that the OH group has not undergone deprotonation during the reaction.

The comparative study of infrared spectra of hydrazones and zirconium complexes, have made us to assign as strong band in the region 920–900 $cm^{-1}$ to ν(Zr=O) (oxocation bond).

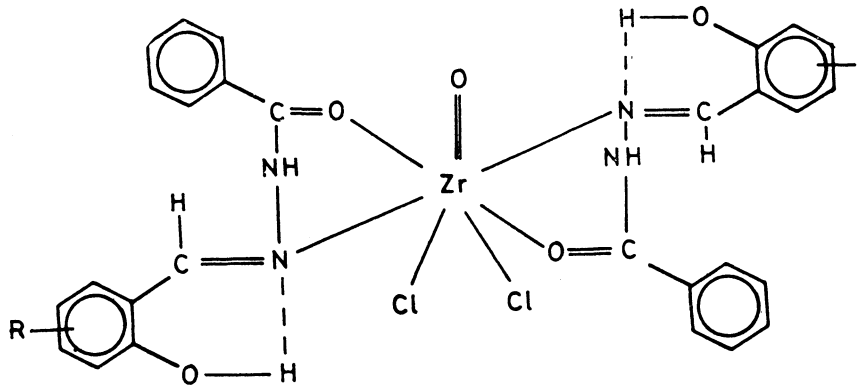
The (M—L), (M—O) and (M—Cl) vibration modes are generally found to occur[18] between 600–250 $cm^{-1}$. However, in these complexes we are observing the bands in the region 575–480, 460–420 $cm^{-1}$ and are assigned to ν(M—L) and ν(M—O) vibrations respectively[17, 18].

The pmr spectra of the ligands is characterised by four signals at 7.1, 7.7, 8.1

and 8.8 ppm and they have been attributed to the various protons of phenyl ring of the aldehyde part, phenyl protons of the hydrazide part, protons of NH + CH and the OH protons respectively.

In the corresponding complexes all the signals show a shift to the lower field and appear at 7.4, 7.8, 8.5 and 9.35 ppm respectively. This indicates that the ligands behaves as bidentate in these complexes.

On the basis of these studies the following structures for these complexes has been suggested in which zirconium exhibits the coordination number seven.

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