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Oxozirconium(IV) Complexes with Schiff Base of 2-Aminopyridine

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A series of new oxozirconium(IV) complexes with a Schiff base derived from 2-aminopyridine, *i.e.*, 2-N-[benzalidene] aminopyridine (BAPy) has been synthesized. Analytical, spectral and conductance studies revealed that complexes have the general composition $Zr(OH)_2X_2 \cdot nL$ ($X = Br^-$, I^-, or NCS^-, $n = 4$; $X = NO_3^-$, $n = L$; $L = BAPy$) after trapping one water molecule. Zr-atom is 8-coordinated in these complexes. Antifungal studies on the representative have been done successfully.

INTRODUCTION

Oxocation complexes are of great interest for most of the workers because of their ample atomic size and high positive formal charge so that they fulfil the optimum conditions for high coordination[1]. These metals can be considered as hard acids according to the definition of Pearson[2]. In the recent past a number of workers[3–10] have reported a series of complex compounds formed by dioxouranium(VI), oxozirconium(IV) and oxovanadium(IV) with nitrogen donor ligands including Schiff bases. In this present communication we wish to report the investigations on high coordination compounds of oxozirconium(IV) metal with 2-N-[benzalidene] aminopyridine (BAPy).

The ligand was found to be neutral monodentate (N-coordinating) and led to the formation of high coordination compounds having the general composition $Zr(OH)_2X_2 \cdot nL$ ($X = Br^-$, I^- or NCS^-, $n = 4$; $X = NO_3^-$, $n = 2$; $L = BAPy$). These complexes are generally soluble in common organic solvents and are quite stable.

EXPERIMENTAL

All the reagents were used as supplied by B.D.H. and Merck. Zirconyl iodide, isothiocyanate and bromide were prepared by reported methods[11].

IR spectra were recorded on Perkin-Elmer infrared spectrophotometer Model 521 KBr/CSI in the range 4000–200 cm^{-1}. Nitrogen was estimated in the laboratory by Kjeldahl's method. All other physico-chemical measurements were done according to the reported method[6].

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The ligand was prepared as follows: A solution of distilled aromatic aldehyde (benzaldehyde) (1 mmole) in absolute alcohol (50 mL) was mixed with corresponding amine, *i.e.*, 2-amino pyridine (1.1 mmole) in the same solvent and the mixture was refluxed for 3–4 h. On cooling yellow product was obtained which was recrystallized in the same solvent and dried *in vacuo* over anhydrons $CaCl_2$.

Preparation of complexes: The respective metal salt solutions were treated with ligand solution in required molar concentrations (1 : 2 or 1 : 4). In some cases complexes were isolated immediately in cold while in some cases in hot solutions after refluxing the resulting solutions for 2–3 h at 60–80°C. The solvent used was ethanol or isopropanol. The complexes were collected, washed with solvent and finally with anhydrons ether and dried *in vacuo* over $CaCl_2$.

RESULTS AND DISCUSSION

The interaction of BAPy with oxozirconium(IV) salts results in the formation of $Zr(OH)_2X_2\cdot nL$ ($X = Br^-$, I^- or NCS^-, n = 4; $X = NO_3^-$, M = 2; L = BAPy). It was inferred on the basis of elemental analyses, conductance, mol. wt. and IR data that zirconyl ion forms complexes in $Zr(OH)_2X_2\cdot nL$ form after trapping one water molecule as mentioned above.

The elemental analyses of these complexes are given in Table-1. These complexes are quite stable and can be stored at room temperature (*ca.* 25°C) except the iodide one which decomposes to sticky mass after a few weeks. All are sufficiently soluble in common organic solvents.

TABLE-1
ANALYTICAL AND CONDUCTANCE DATA OF OXOZIRCONIUM(IV) COMPLEXES OF 2-N-[BENZALIDENE] AMINO PYRIDINE (BAPy)

Complex	Colour	m.p. (°C)	Analysis found (calcd.) %			m.w. found (calcd.)	Λ_m ohm^{-1} cm^2 mole^{-1}
			M	N	Anion		
$Zr(OH)_2Br_2\cdot 4BAPy$	yellow	212	9.1 (10.6)	14.4 (13.1)	16.9 (18.7)	849 (853)	3.8
$Zr(OH)_2I_2\cdot 4BAPy$	chocolate brown	218	7.9 (8.2)	11.3 (10.1)	21.2 (22.9)	1102 (1107)	3.9
$Zr(OH)_2(NCS)_2\cdot 4BAPy$	yellow	218	8.6 (9.4)	12.3 (11.5)	10.2 (11.9)	958 (969)	4.2
$Zr(OH)_2(NO_3)_2\cdot 2BAPy$	yellow	211	14.2 (15.6)	10.9 (9.6)	14.7 (15.8)	572 (581)	4.1

Electrical conductance values for these complexes were recorded in $PhNO_2$ medium and it was inferred that the complexes are essentially non-electrolyte which is in general agreement with previous observations[11–14]. The ratio of molecular weights to be calculated is 0.98 which shows that these complexes are monomeric in nature.

Infrared spectra: The IR spectra of the complexes when compared with those of the ligand shows a considerable shift in ν(C═N) azomethine absorption to lower frequency indicating a decrease in the stretching force constant of (C=N) as a consequence of the coordination through azomethine nitrogen, the double bond character between carbon and nitrogen is reduced[12–15]. The strong bands observed at *ca.* 1575–1570 cm^{-1} and 1055–1050 cm^{-1} are tentatively assigned to antisymmetric and symmetric ν(C=C) and ν(C—N) of pyridine ring which remain practically unchanged in frequency and band intensities, revealing non-involvement of pyridine nitrogen and metal bond. Some new medium and weak intensities bands are observed in the range 450–420 cm^{-1} in the complexes where the ligand has no absorptions. These bands are tentatively assigned to ν(M—N) stretching modes[16, 17]. In these complexes, the presence of coordinated water was suggested by a very broad absorption around 3400 cm^{-1} in their infrared spectra. Bands at *ca.* 920 and 980 cm^{-1} may be attributed to rocking and wagging modes of the coordinated water. The partial IR data is given in Table-2.

TABLE-2

PARTIAL IR DATA (cm^{-1}) FOR OXOZIRCONIUM(IV) COMPLEXES OF 2-N-[BENZALIDENE] AMINO PYRIDINE (BAPy)

Complex	ν(C=N) (azomethine)	Pyridine ring breathing and deformation bands		ν(M—N)
		ν(C=C)	ν(C—N)	
BAPy	1600 (s)	1570 (m)	1050 (m)	—
$Zr(OH)_2(NO_3)_2\cdot(BAPy)_2$	1550 (s)	1575 (s)	1050 (m)	450 (m)
$Zr(OH)_2I_2\cdot(BAPy)_4$	1545 (s)	1575 (sh)	1055 (sh)	430 (m)
$Zr(OH)_2Br_2\cdot(BAPy)_4$	1550 (s)	1570 (m)	1055 (sh)	440 (m)
$Zr(OH)_2\cdot(NCS)_2\cdot(BAPy)_4$	1545 (s)	1570 (m)	1050 (m)	440 (m)

Configuration of complexes: It is revealed from the electrical conductance and molecular weight studies that in halo and isothiocyanato complexes Zr-atom is eight-coordinated as these anions are covalently bonded, as it is clear from IR data that after trapping water molecule these complexes have the general formula $Zr(OH)_2X_2\cdot4BAPy$ ($X = Br^-, I^-$ or NCS^-). In case of $Zr(OH)_2(NO_3)_2\cdot2BAPy$, Zr-atom is again eight-coordinated as nitrate ion is bidentate in nature in these complexes. Bidentate nature of nitrate ion is confirmed from IR studies.

Antifungal studies: Antifungal activity of a representative complex was done successfully. The radial growth and paper disc methods were used to evaluate antifungal activity[18]. The activity was checked on *Peronaspora* sp. and *Albugo* sp.: two-fungi which were grown on PDA culture on living host tissue, *i.e.*, *Brassica compestris*. Inoculation was made from infected inflorescence of *Brassica* sp. in petriplates containing PDA medium. 10 mm paper discs dipped in solution of complex in DMF in varied concentrations[19, 20] were put on petriplates before inoculating them with the fungus. The plates containing unamended PDA were maintained as control. The inoculated plates were incubated at 25 ± 1°C for 5 days. The radial growths of the fungal colonies were measured on 6th day and the data were statistically analysed. Table-3 shows the effect of concentrations of the complex on the mean radial growth (in cm.) of fungus. The control petriplate which does not contain any paper disc of complex solution shows the radial growth of 4.0–4.5 cm for fungal colonies.

TABLE-3
EFFECT OF BARIED CONCENTRATION OF OXOZIRCONIUM(IV) COMPLEXES ON THE MEAN RADIAL GROWTH (IN cm) OF FUNGAL COLONIES

Compound	*Peronaspora* sp.			*Albugo* sp.		
	30 mg/ 10 mL	20 mg/ 10 mL	10 mg/ 10 mL	30 mg/ 10 mL	20 mg/ 10 mL	10 mg/ 10 mL
$Zr(OH)_2(NO_3)_2 \cdot 2BAPy$	1.6	2.3	3.7	1.4	2.5	3.9

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