

Metal Chelates of Zirconium (IV) with anti-Tubercular Isonicotinic and hydrazide drug

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Abstract

Isonicotinic acid hydrazide (INH) forms stable solid complexes at various pH with Zr (IV) salts having general formula $[\text{Zr}(\text{INH})_2\text{A}_2]\text{X}_2$ ($\text{A} = \text{H}_2\text{O}/\text{OH}/\text{Py}/\text{SO}_4$; $\text{X} = \text{NO}_3/\text{Cl}$). Trans-octahedral configuration of complexes have been assigned using analytical, conductometric, magnetic moment, IR and electronic spectral studies and ligand acts as bidentate (N, O) donor.

Key words : anti-Tubercular drug, Zr (IV) – chelates.

Introduction

Isonicotinic acid hydrazide is a very common anti-Tubercular drug used as chelating agent for Zirconium (IV) ions. Our special interest is discrete ZrO^{++} group as persistent species in solution which existence in certain are lacking reported by several workers¹⁻⁴. However, ZrO^{++} group is said to be present in several complexes of the type $[\text{ZrOX}_2\text{L}_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{NO}_3, \text{NCS}$), $[\text{ZrOL}_4]\text{I}_2$ and $[\text{ZrOL}_6](\text{ClO}_4)_2$ where L represents several oxygen donor ligands⁵⁻⁸ and a number of Schiff base complexes⁹⁻¹⁰ of the type $[\text{ZrO}(\text{HL})_2]$, $[\text{ZrOCIL}]$ and $[\text{ZrOL}_2]$. Hence, this aspect of study is very interesting and the present work is under taken to investigate structure, bonding and stereochemical preferences of spherically symmetrical d^0 -configuration

of Zr (IV) which may display a great variety of coordination geometries.

Experimental

Isonicotinic acid hydrazide (INH) was obtained from E. Merck company and used after crystallization and its purity was checked spectroscopically. All chemicals used were of AR grade or CP grade. The metal chelates were prepared using a general method. Methanolic solution of metal salts. $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$, $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ or $\text{ZrCl}_4 \cdot 8\text{H}_2\text{O}$ were mixed with methanolic solution ligand in molar ratio 1:2. The mixture was stirred on magnetic stirrer at 100°C for 1 hr. and pH of the mixture was adjusted as desired using $\text{NaOH}(2\text{N})/\text{Py}$ and corresponding acid of the same salt. The volume of the mixture was evaporated to 10 ml and the solid obtained after cooling was

washed with ice cold methanol and dried in a vacuum desiccator over anhydrous CaCl_2 . The physical and analytical data of complexes are given in Table-1.

Elemental analyses were performed by microanalysis division, RSIC, CDRI, Lucknow. IR Spectra of ligands and complexes were recorded on a Perkin-Elmer Model-577 spectro photometer in the range of 4000-200 cm^{-1} as KBr pellets. The electronic spectra were recorded with Ziess (Jena) Model of automatic recording system. Magnetic measurements were made on Gouy balance using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as calibrant. The molar conductance of complexes (10^{-3}M) were measured in DMF using Wiss-Wekstatter Weithem obb type LBR conductivity meter.

Results and Discussion

Isonicotinic acid hydrazide (INH) forms stable complexes with Oxozirconium (IV) and Zirconium (IV) salts at various pH. All solid products are thermally stable upto 300°C and did not melt. However, loss in weight above 85°C was observed for each hydrated complexes (S. No. 1 & 5). Elemental analysis and conductance measurement data (Table 1) support our formulation. The ionic nature of nitrate and chloride revealed by conductance data is further supported by the chemical analysis of their Na_2CO_3 extract and infrared spectral data. All Zirconium (IV) complexes were found to be diamagnetic as expected for d^0 -configuration. Electronic spectra of complexes display a very strong band in the region 27400-26315 cm^{-1} which may be due to charge transfer besides the ligand bands. However, no absorption is observed above 25000 cm^{-1}

indicating d^0 -configuration of all Zr (IV) complexes¹¹ and octahedral configuration may be tentatively assumed following previous literature¹²⁻¹⁴.

Infrared spectra :

The IR bands of interest the ligand (INH) and complexes are discussed here. A comparison of infrared spectra of the ligand complexes indicate the following:

- (i) The characteristic IR bands observed in the spectrum of the ligand (INH) at 3400, 3310, 3210, 1680 and 1560 cm^{-1} are assigned to νNH_2 , $\nu_{\text{asym}}(\text{N-H})$, $\nu_{\text{sym}}(\text{N-H})$, amide band I and amide band II respectively. The νNH_2 of free ligand red shift to lower frequency $\sim 100 \text{ cm}^{-1}$ on complexation. This indicate bonding of the ligand through amino nitrogen of hydrazine residue¹⁵⁻¹⁷. The red shift (20-25 cm^{-1}) of band observed at 1640 cm^{-1} due to NH_2 deformation associated with OCN bending on coordination also support the formation of Zr – N bond. The pronounced shifting of $\nu\text{C-N} + \nu\text{N-N}$ frequency by 20-30 cm^{-1} towards lower frequency in complexes as compared to free ligand also suggest involvement of amino nitrogen of the ligand in coordination.
- (ii) The νCO of the ligand observed at 1680 cm^{-1} as strong band red shift to lower frequency (30-40 cm^{-1}) on complexation indicating bonding through oxygen atom of carbonyl group of ligand. Bonding through carbonyl oxygen decreases CO bond order and increase in CN bond order substantiated by splitting of band at 1255 cm^{-1} into two components (1195-1210 cm^{-1}) and (1380-1395 cm^{-1}) in the spectra of complexes. The

latter components might be due to sym (C=N) developed on complexation in the spectra of complexes.

- (iii) The absence of a band in the region 835-955 cm^{-1} due to $\nu\text{Zr}=\text{O}$ stretch in the present Zr (IV) complexes (S. No. 5 & 6) suggest their formulation as $[\text{Zr}(\text{OH}_2)(\text{ligand})_2]\text{X}_2$ ($\text{X} = \text{Cl}/\text{NO}_3$) and not as $[\text{ZrO}(\text{H}_2\text{O})(\text{ligand})_2]\text{X}_2$. The presence of a broad band at 3440 cm^{-1} and appearance of new medium intensity band at 1135 cm^{-1} due to the $\delta\text{Zr}-\text{OH}$ bending mode also support the proposed structure and in agreement with previous workers³.
- (iv) The presence of anions in the complexes are identified by non-ligand bands at 1350 (s) and 815 (m) for ionic nitrate¹⁸ and at 1010 (m), 970 (m), 940 (m) and 603 (m) due to monodentate sulphate group¹⁹.
- (v) New non-ligands bands in far IR spectra at 510-480 cm^{-1} ($\nu\text{Zr}-\text{O}$), 470-440 cm^{-1}

($\nu\text{Zr}-\text{N}$) are in good agreement with previous literature²⁰.

On the basis of correlation of the experimental and other physico-chemical data allow to assign an octahedral stereochemistry to all reported complexes:

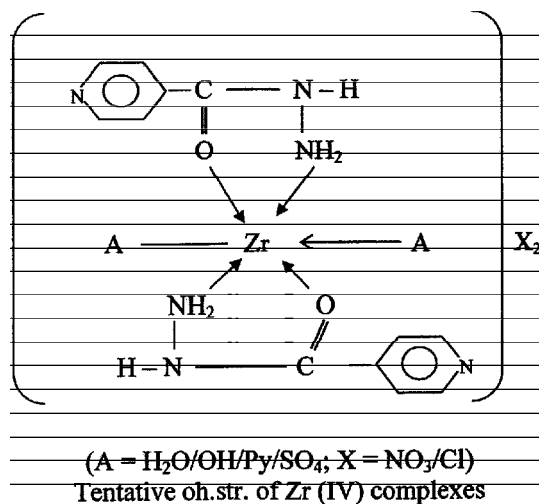


Table 1. Analytical and Physical data of complexes

S. No.	Complex (pH of isolation, colour)	Mol. conductance ($\pi^{-1} \text{ cm}^2 \text{ mol}^{-1}$)	Analysis (%) Found/(Cal)			
			C	H	N	Zr
1.	$[\text{Zr}(\text{INH})_2(\text{SO}_4)_2] \cdot 3\text{H}_2\text{O}$ (4, cream)	10.60	23.23 (23.55)	4.20 (4.25)	13.82 (13.74)	15.01 (14.92)
2.	$[\text{Zr}(\text{INH})_2(\text{H}_2\text{O})_2](\text{NO}_3)_4$ (4, light yellow)	310.10	20.70 (20.77)	3.40 (3.46)	22.20 (29.21)	13.42 (13.15)
3.	$[\text{Zr}(\text{INH})_2(\text{Py})_2](\text{NO}_3)_4$ (7, cream)	315.62	34.30 (34.23)	3.10 (3.11)	21.99 (21.78)	11.92 (11.82)
4.	$[\text{Zr}(\text{INH})_2(\text{H}_2\text{O})_2]\text{Cl}_4$ (4, light yellow)	320.12	28.54 (28.44)	4.80 (4.74)	16.62 (16.59)	18.25 (18.01)
5.	$[\text{Zr}(\text{INH})_2(\text{OH})_2]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (8, light yellow)	168.92	28.32 (28.45)	5.23 (5.13)	16.50 (16.59)	17.89 (18.01)
6.	$[\text{Zr}(\text{INH})_2(\text{OH})_2](\text{NO}_3)_2$ (8, faint yellow)	172.23	27.53 (27.51)	3.01 (3.05)	21.45 (21.40)	17.45 (17.43)

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