

NOTE

Synthesis and Characterization of Manganese(II) Complexes of Schiff Base Derived from Pyrazinamide

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A new ligand have been synthesized by the interaction of pyrazinamide with salicylaldehyde in 1 : 1 molar proportion carried out in ethanol-water mixture. The metal complex of Mn(II) with the ligand have been prepared and characterized using physicochemical methods such as elemental analysis, conductometric studies, magnetic susceptibility, IR and electronic spectral data. It has been found that the complex is non-electrolytic in nature. Spectral measurements showed that the ligand was coordinated to the metal ion through azomethine group. The magnetic moment, electronic spectral data indicate octahedral geometry of the metal complex.

Key Words: Manganese(II), Schiff base, Pyrazinamide.

Pyrazinamide is the most common antitubercular drug. A detailed survey of literature reveals that a large number of drugs have been used to synthesize the complexes with many transition metals¹⁻⁶ with a view to enhance their bacteriostatic action. Considering the importance of drugs and their complexes it has been desired necessary to synthesize and study the metal complexes of pyrazinamide with transition metals. The present paper describes the synthesis and characterization of manganese(II) with pyrazinamide.

All chemicals used were of AR grade. Pure sample of pyrazinamide (m.f. $C_5H_5N_3O$, m.w. 123.11) was obtained from Dr. Reddy's Laboratories, Hyderabad.

The elemental microanalyses of C, H and N were carried out with Thomas and Coleman Analyzer Carlo Erba 1106 while the metal content in the complex was determined by standard methods. The molar conductance value of the complex was measured in dimethyl sulphoxide (DMSO) using Systronics digital conductivity meter. Ligand-metal ratio was calculated using the same instrument. IR spectra were obtained from CDRI Lucknow (instrument used: Perkin-Elmer FTIR spectrophotometer). Magnetic susceptibility measurements were received from CAT, Indore (instrument used: vibrating sample magnetometer).

Synthesis of ligand: A mixture of pyrazinamide (1 mol) and salicylaldehyde (1 mol) was refluxed for 3 h in a 250 mL round bottom flask. Light yellow crystalline solid was separated by filtration, washed with alcohol and dried. (Yield 34%). The product obtained was soluble in acetone-water mixture (1 : 1).

Ligand-metal ratio: 20 mL of the ligand (0.02 M) was diluted to 200 mL using 50% acetone and titrated against $MnCl_2 \cdot 4H_2O$ (0.01 M) solution prepared in 50% acetone. Conductance was recorded after each addition of metal salt. Graph is

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plotted between corrected conductance and volume of metal salt added. From the equivalence point in the graph, it has been concluded that the complex formation of the ligand with Mn metal takes place in the ratio of 2 : 1 (L : M). Stability constant and free energy change were also calculated by using Job's method of continuous variation⁷ modified by Turner and Anderson⁸.

Synthesis of pyrazinamide-Mn(II) complex: 1.13 g (2 mol) of the ligand was dissolved in 100 mL of acetone-water mixture (1 : 1) and added slowly to a solution of 0.49 g (1 mol) of manganese chloride solution (solvent acetone-water mixture 1 : 1). The mixture was refluxed for 3 h, cooled and filtered. A white coloured crystalline complex was separated. The complex was washed with acetone, dried and weighed (yield 26%).

TABLE-1
ANALYTICAL AND PHYSICAL DATA OF THE LIGAND AND ITS METAL COMPLEX

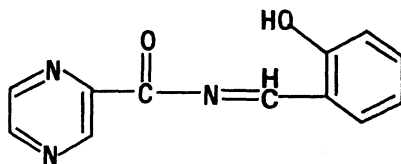
Compound, m.f. (m.W.)	Colour	Yield (%)	m.p. °C	Elemental analysis %:					Stability constant log K (L/mol)	Free energy change ΔF (kcal/mol)
				Found (Calcd.)						
				C	H	N	M	H ₂ O		
Ligand, C ₁₂ H ₉ N ₃ O ₂ (227.22)	Light yellow	34.0	194	63.99 (63.43)	3.02 (3.99)	18.00 (18.49)	—	—	—	—
Pyrazinamide-Mn complex (C ₁₂ H ₈ N ₃ O ₂) ₂ Mn·2H ₂ O	White	26.0	216	54.02 (53.04)	3.01 (2.96)	15.01 (15.46)	9.9 (10.11)	6.01 (6.63)	12.088	17.03

Analytical data and conductometric studies suggest 2 : 1 (L : M) ratio for pyrazinamide-Mn complex. The complex is insoluble in water and other common organic solvents but soluble in DMSO. The low value of molar conductance (9.2 ohm⁻¹ cm² mol⁻¹) suggests non-electrolytic nature of the complex.

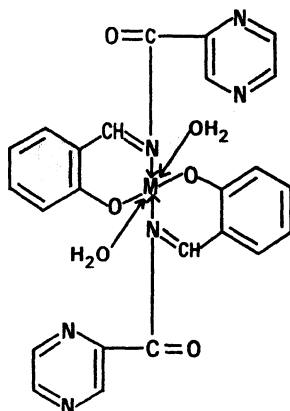
The IR spectral band at 1165 ± 20 cm⁻¹ due to pyrazine ring remain unchanged indicating the non-involvement of pyrazine ring nitrogen in complexation⁹⁻¹¹. The bands at 1713 and 1601 cm⁻¹ are attributed to $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{N})$ vibrations in the Schiff base (ligand). Aromatic ring frequency appears both in the ligand and complex at 1973 cm⁻¹. The absence of $\nu(\text{OH})$ and shifting of $\nu(\text{C}=\text{N})$ to higher frequency in the spectra of complex suggest the deprotonation of phenolic group and subsequent coordination of phenolic oxygen and azomethine nitrogen to the metal. Coordinated water and chelate ring frequency at 3415 and 1380 cm⁻¹ respectively has been observed in the case of complex. New bands at 541 and 669 cm⁻¹ appeared in the spectra of complex which are assigned to $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{O})$ linkages indicating the involvement of azomethine group in coordination^{12, 13}.

The manganese(II) complexes of pyrazinamide have effective magnetic moment value in the range 5.6–5.8 B.M. which is very close to the calculated value and corresponds to a high spin state of the metal ion. The electronic spectra of the Mn(II) complex of pyrazinamide¹⁴ display three bands at 24,390, 22,220 and 16,666 cm⁻¹ which can be assigned to ${}^4\text{E}_g(\text{G}) \leftarrow {}^6\text{A}_{1g}$, ${}^4\text{T}_{2g}(\text{G}) \leftarrow {}^6\text{A}_{1g}$ and ${}^4\text{T}_{1g}(\text{G}) \leftarrow {}^6\text{A}_{1g}$ transitions, respectively, suggesting an octahedral environment¹⁵ around the manganese ion.

On the basis of the above studies the following structure can be proposed for pyrazinamide-Mn complex.



1. Schiff base of pyrazinamide



2. Pyrazinamide-Mn complex (M = Mn)

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