



Synthesis and Characterization of Bis (3-Hydroxy-3-Phenyl-1-O-Carboxyphenyl Triazene) Manganese (II) Complex

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ABSTRACT

3-hydroxy-3-phenyl-1-o-Carboxyphenyltriazenes (HT) was synthesized by coupling ethanolic solution of diazonium salt of 2-aminobenzoic acid with phenylhydroxylamine in 1:1 molar proportion at 0-5°C in a refrigerator. Interaction of ethanolic solution of the ligand and aqueous solution of Manganese (II) sulphate heptahydrate formed bis (3-hydroxy-3-phenyl-1-o-carboxyphenyltriazenes) Manganese (II) monohydrate. The ligand is soluble in many organic solvents; however, it is slightly soluble in water. Similarly the Manganese (II) complex is soluble in some organic solvents and water. The molar conductance of the complex is 36.7 Ohm⁻¹Cm²Mol⁻¹ which is quite low, suggesting that the compound is non-electrolyte. The complex compound decomposed at 208°C, indicating good thermal stability. The infrared of the ligand and the complex showed bands, which are attributable to ν (N=N) stretching vibration at 1397 and 1400 Cm⁻¹s. The bands at 3425 and 3463 Cm⁻¹ are assigned to ν (O-H) vibration in the complex and the ligand respectively. The empirical formula calculation from gravimetric analysis results revealed a 1: 2 metal to ligand ratio.

Keywords: Schiff base complex, 3-hydroxy 3- phenyl-1-o-carboxyphenyltriazenes

INTRODUCTION

Triazene is the chemical compound NH₂N=NH that has also given name to the functional group consisting of an amine directly. The functional group is also called diazoamine group because it is related to a diazo group. Triazene complexes have been known for over 100 years. These classes of compounds are versatile because they have different application as chemical and biological reagents. Useful to scientists in pharmacology, synthesis, polymer technology and in the construction of novel ring system (Hartman and Dickey, 1943).

Hydraxytriazenes are well known chelating agents having been widely used as spectrophotometric and complexometric reagents for transition metal determination. Their application as analytical reagents is quite established as shown by various reviews in literature during the last many years (Purohit *et al.*, 1997). Hydraxytriazenes are widely used as ligands to coordinate various transition or inner transition metal ions due to their good stability in common solvents and the high stability of their complexes. They coordinate with the metal ions in a bidentate manner through N-OH group (ionic linkage) and triazeno group (coordinate linkage) (Singh *et al.*, 2005).

Ali *et al.* (2003) also reported the synthesis, characterization and screening of ten hydraxytriazenes for their activity against five

bacteria and fungi. One of the compounds 3-hydroxy-3-phenyl-1-o-carboxyphenyltriazenes was have MIC value of 12.5µm/ml.

This paper reports the synthesis and characterization of bis (3-hydroxy-3-phenyl -1-o-carboxyphenyltriazenes) Manganese (II) complex.

MATERIALS AND METHODS

All the reagents used in this work were of analytical grade purity. Glasswares were soaked in 4M nitric acid, washed with detergent, rinsed with distilled water and dried in an oven at 110°C. All weighing were carried out on electric metler balance model AB54. pH measurements were carried out using Jenway pH meter model 3505. Molar conductance measurements were done on a conductivity meter model cyberscan 500. IR spectral analysis was recorded on a Fourier transformed spectrophotometer model IR Genesis series Model in Nujol in the range 4000-400cm⁻¹. Melting point and decomposition temperature were determined on a straut scientific Melting point apparatus Model SMP3.

Preparation of the ligand

Nitrobenzene (12.3cm³) was reduced by ammonium chloride (22g) and Zinc dust (13.5g) at a temperature between 60-65°C to obtain phenylhydroxylamine. The diazotized product of 2-aminobenzoic acids was rapidly mixed with aqueous ethanol solution (50%) of previously

prepared phenylhydroxylamine at 0-5°C. The product was filtered under suction and distilled water was added to it to decrease the solubility of hydroxytriazenes in ethanol. The crude product

obtained was recrystallized twice from water when brownish yellow needle shaped crystals of 3-hydroxy-3-phenyl-1-*o*-carboxyphenyltriazenes separated (Ressan and Iyer, 2003).

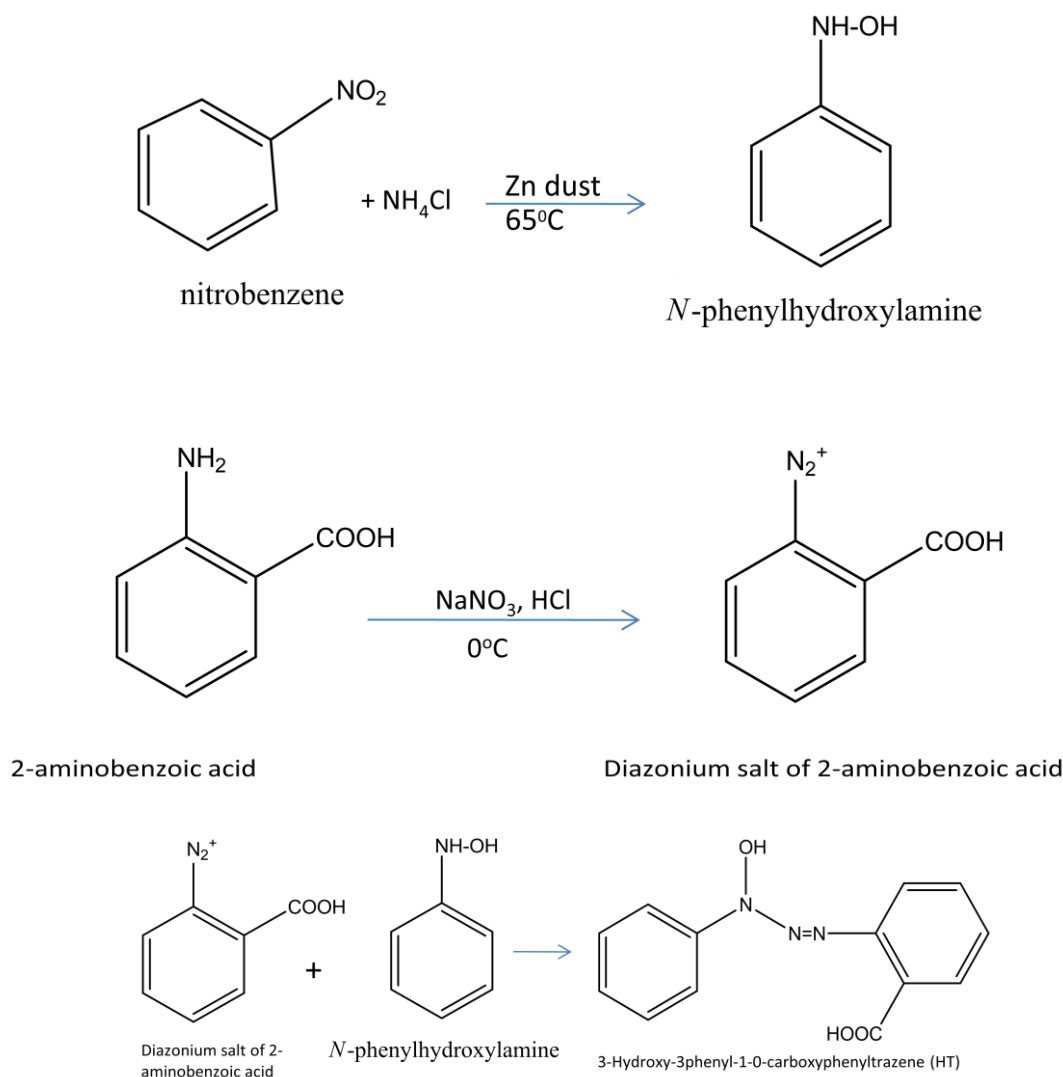
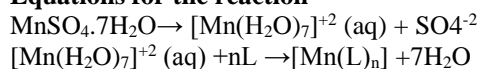


Fig. 1: Scheme for the reactions

Preparation of Manganese (II) complex

The complex was prepared by boiling aqueous solution of Manganese (II) sulphate heptahydrate (0.8450g in 20cm³ water) and ethanolic solution of the ligand (2.583g in 20cm³ ethanol). The pH of the mixture was adjusted to 4-5 with 2% sodium acetate solution to form an orange coloured solution. This was further boiled for 48 mins at 70-80 °C with constant stirring and cooled. Brown needle shaped crystals of the complex separated out which was filtered and recrystallized from 50% ethanol-water mixture (Ressan and Iyer, 2003).

Equations for the reaction



Determination of ionization Constant (pKa) of the ligand

In a 500cm³ beaker were added 90cm³ of distilled water, 100cm³ 0.2mol dm⁻³ Potassium nitrate and 10cm³ 0.4 mol dm⁻³ ligand was introduced into the solution mixture with stirring. From a burette, 10cm³ standardized sodium hydroxide was added. After each 0.5cm³ addition the cumulative volume of NaOH and the corresponding pH were recorded. The pH values were used to calculate the pKa of the ligand using the equation below (Angelici, 1971).

Determination of Stability Constant of the Metal Complex

0.4mol dm⁻³ Sodium- ligandate was added to a stirred mixture of 90cm³ distilled water, 10cm³

0.1 moldm⁻³ nitric acid, 100cm³ 0.2moldm⁻³ Potassium nitrate and 0.1 mmole of Manganese (II) sulphate contained in a 400cm³ beaker. After each addition of an aliquot (0.20cm³) of the sodium-liganate solution, the pH value was recorded from the pH meter (Angelici, 1971).

Determination of water of crystallization in the complexes

Exactly 0.2g of each of the complexes was put into an oven at 110°C for 2hrs. The net loss of weight was recorded after cooling to a constant weight and the weight loss recorded (Vogel, 1972).

RESULTS AND DISCUSSION

The ligand is brownish yellow with 49% yield while the prepared complex is brown with 78.35% yield. The melting point of the ligand is 187°C and decomposition temperature of Manganese (II) complex is 208°C which revealed that the complex is thermally stable (Table 1). The IR spectrum of the ligand and the complex compound shows band at 1397 and 1400cm⁻¹ which are attributable to ν (N=N) stretching vibration respectively. The bands at 3425 -3463cm⁻¹ are assignable to ν (O-H) vibrations in the complex and the ligand respectively. This provides evidence for the presence of water of crystallization

(Table 2). The percentage of Mn⁺², ligand and water of crystallization in the complex were 10.51%, 83.49% 6.0% and respectively, which supported the molecular formular (MnL₂).H₂O (Table 3). The potentiometric analysis of the complex suggested 1: 2 metal to ligand ratio. The ligand is soluble in many organic solvent however its solubility in ethanol and methanol is very high but it is slightly soluble in water. Similarly, the Manganese (II) complex is soluble in common organic solvents and water (Table 4). This is due to the fact that the complex has low polarity and have similar attractive forces therefore dissolved in the mention solvents which have both polar and non polar ends (Satya *et al.*, 2006). The molar conductance value of the complex in 1x 10⁻³ M DMSO solution is 36.7 ohm⁻¹cm² mol⁻¹ is quite low, suggesting that the compound is non-electrolytic in nature (Geary, 1971; Parnau *et al.*, 2004) (Table 5). The larger the negative value of Gibbs free energy the greater the stability of the complex (Satya *et al.*, 2006). The change in Gibbs free energy of the complex is 44,000.01Jmol⁻¹ suggesting good thermal stability (Table 6). The empirical formula calculation from gravimetric analysis results revealed a 1: 2 metal to ligand ratio.

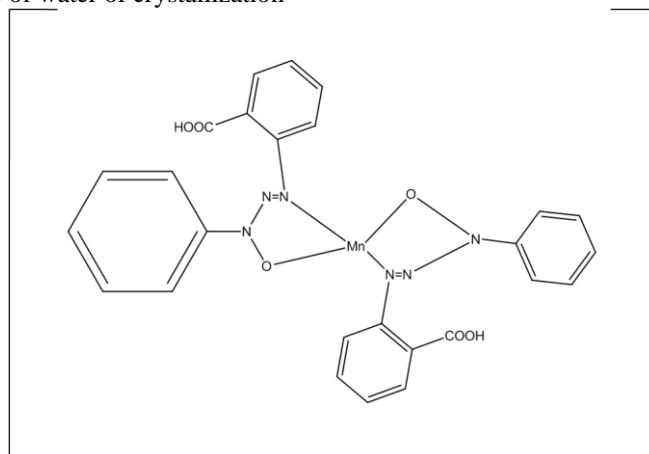


Fig. 2: Proposed structure of the Manganese (II) complex

Table 1: Some properties of the ligand and the complex

	Colour	Yield (%)	Decomposition Temp (°C)
Ligand	Brownish yellow	49	-
[MnL ₂].H ₂ O	Brown	78.35	208

L= 3-hydroxy-3-phenyl -1-o-Carboxyphenyltriazeno

Table 2: Infrared data for the ligand and the complex

	ν (N=N)	ν (M-O)	ν (M-N)	ν (O-H)
Ligand	1397	-	-	3463
[MnL ₂].H ₂ O	1400	509	606	3425

Table 3: Empirical formula calculation for Mn(II) Complex

	Manganese	ligand	Water of crystallization
Percentage composition	10.51	83.49	6.0
Moles	10.51/55	83.49/257	6.0/18
	0.19	0.32	0.33
Mole ratio	0.19/0.19	0.32/0.19	0.33/0.19
Ratio	1	2	1

Table 4: Solubility of the ligand and its complex in some common solvents

Solvents	Ligand	Manganese(II) Complex
Water	SS	S
Acetone	SS	SS
Methanol	S	S
Ethanol	S	S
Benzene	S	S
Diethyl ether	S	S
DMSO	S	S

Key: S-Soluble SS-Slightly Soluble

Table 5: Molar Conductance of the complex in 1×10^{-3} M DMSO solution

	Specific Conductance (K)	Molar conductance ($\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$)
$[\text{MnL}_2] \cdot \text{H}_2\text{O}$	3.67	36.7

Table 6: Stability constant and Gibbs free energy of the metal complex

complex	K_f	$\Delta G \text{ Jmol}^{-1}$
$[\text{MnL}_2] \cdot \text{H}_2\text{O}$	1.14×10^8	-45.00

CONCLUSION

The ligand 3-hydroxy-3-phenyl-1-o-carboxyphenyltriazenes and the Manganese (II) complex were successfully prepared and characterized. Both the ligand and complex were soluble in many polar and non polar solvents. Spectroscopic studies and elemental analysis results established a 1: 2 metal to ligand ratio.

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