Synthesis and Characterisation of Transition Metal Complexes of 2-hydroxy-1-Naphthylaldehyde { 4-((2-hydroxynaphthalen-1-yl) methylene Thiosemicarbazone (2H1NATSC) and Its Biological Activity

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Abstract

Synthesis of 2-hydroxy-1-Naphthylaldehyde Thiosemicarbazone(2H1NATSC), Melting point, Elemental analysis, X-RD, X-ray diffraction pattern withpowder X-ray diffraction was studied. NMR, A spectrophotometric method for the determination of palladium (II) and molybdenum (V) with 2-hydroxy-1-naphthyaldehyde thiosemicarbazone (2H1NATSC) is reported. The reagent forms 1:1 coloured complexes with Pd(II) and Mo(V) at pH 6 & 5. The colour development of palladium &molybdenum complex is instantaneous and shows absorption maximum at 400 nm & 395 nm respectively.Effect of the diverse ion have been studied. Stability constant of the complex, Dissociation constant and Change in free energy are determined. Composition of the metal and ligand has been determined by Job's variation and mole ratio methods. The optimum conditions for complete colour development have been established by studying parameters like effect of medium, reagent concentration, time period have been studied. Applications of this (2H1NATSC) for antimicrobial activity have been performed.

Keywords : Pd(II),Mo(II), 2H1NATSC, Specrophotometry,Antimicrobial sample

INTRODUCTION

The coordination chemistry of nitrogen-sulphur donor ligands such as substituted thiosemicarbazides [1], thiosemicarbazones [2-4]. Thiosemicarbazides & thiosemicarbazones forms a metal complex with transition metal ions. Metal ions are a key factor for organization of biochemical molecules. thiosemicarbazones have variable bonding modes, promising biological implications and structural diversity [5]. Metal complex of salicyaldehyde thiosemicarbazones was studied [6]. Transition metal complexes of thiosemicarbazones has attention due to their potentially chemotherapeutic properties of both ligands and complexes on antitumor and antibacterial agents [7]. Diabasic tridentate thiosemicarbazones with ONS donors are of immense importance because they posses a wide spectrum of medicinal properties [8]. They has remarkable antineoplastic activity against a variety of tumors [9], antifungal [10] and antibacterial activities [11].The derivatives of thiosemicarbazones are chemical and pharmacological importance because they possess a number of different biological anticancer, antiviral, antibacterial, antifungal activity, etc.[12]. Pharmacological potential of thiosemicarbazone as antitumor agent is one of the most promising areas of its research [13]. Thiosemicarbazones represents a class of N,S-donor ligands important in coordination chemistry. These ligands have great versatility, manifested by the existence of two forms (thione-thiol), and the ability to bind metal ions in the neutral or anionic

form, acting as monodentate or bidentate ligands [16-21]. thiosemicarbazones and their complexes to be antifungal, antibacterial, antiviral, anti-inflammatory and chemotherapeutic agents, potentially useful for inhibiting the activities of cancer cells [22-32]. The cytotoxicity of these ligands is enhanced by coordination to metal ions such as copper, zinc, platinum and palladium. This activity is explained not only by the metals' ability to influence lipophilicity but also the mechanism of action within the cell [33-41]. Substitution on the C2 position can also affect the coordination and biological properties.

Palladium complexes used as starting materials to prepare polymers, agrochemicals , pharmaceuticals, flavors and fragrance. They have also been used for the total synthesis of natural products and nanocompounds .Series of palladium complexes have been synthesized that has good activity against tumour cell. Synthesis of Cu(II) and Pd(II) complexes with 8-propyl2-hydroxytricyclo tridecan-13-one-thiosemicarbazone and 8-furyl-2-hydroxytricyclo tridecan-13-one-thiosemicarbazone [42].

Molybdenum complexes attract much interest due to their importance in biochemistry, catalysis, medicine and materials [43-45].Number of molybdenum compounds supported by the transition metals and organic ligands have been synthesized and characterized [46]. Some potential applications of the molybdenum complexes have also been investigated [47].

EXPERIMENTAL WORK

Materials and methods

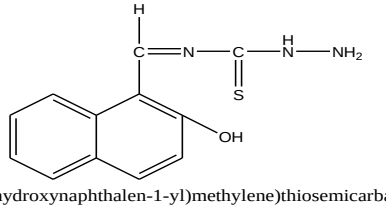
An Elico UV-visible spectrophotometer model UV-SL 164 equipped with 1 cm quartz cell is used for spectrophotometric measurements. An Elico pH meter LI-610 is used for pH measurements. The chemicals used are of analytical reagent grade. Perkins Elmer 221 IR spectrophotometer using KBr pellets techniques is used for IR studies. X-RD was taken on PW 3710 diffractometer using CuK_2 radiation has been taken on the instrument BRUKER AC 300 F NMR spectrophotometer 33 HZ with $CDCl_3$ solvent. Elemental analysis and antimicrobial activity was done in laboratory approved by Central Government for AGMARK.

Synthesis and Characterisation of 2H1NATSC

Synthesis of 2H1NATSC

2-hydroxy-1-Naphthylaldehyde Thiosemicarbazones (2H1NATSC) was prepared by conducting 2-hydroxy-1-Naphthylaldehyde andThiosemicarbazide in methanol medium for six hours.

The structure of the reagent is



4-((2-hydroxynaphthalen-1-yl)methylene)thiosemicarbazide

Characterisation of 2H1NATSC

Elemental Analysis of 2H1NATSC

The elemental analysis of 2H1NATSCwas done in laboratory approved by Central Government for AGMARK. It showsthe result of elemental analysis in **Table 1**

X-RD of 2H1NATSC

X-RD spectra of 2H1NATSC was taken on PW 3710 diffrctometer using CuK_2 radiation (Y= 1.54056 A^0). The X-RD diffraction of 2H1NATSC was recorded at angle 20 from 10.565 to 36.995. The data of X-ray diffraction of 2H1NATSC were presented in **Table 2**. And X-ray spectrum in **Fig 1**. For the determination of structure Hesse-Lipson procedure is used [65].

Absorption Spectra of 2H1NATSC

The absorption spectra of 2H1NATSC was recorded against a blank solution containing buffer (pH=5) and is shown in **Figure 2.** Absorption spectra was recorded in the wave length range 220-520 nm. The complex shows an absorption maximum at 330 nm. At 330 nm wavelength the molar absorptivity of 2H1NATSC is 1.4423 x 10^4 $L.mol^{-1}$. Cm^{-1}.

Infrared Spectra of 2H1NATSC

IR spectra of 2H1NATSC was taken in the range of 4000 cm^{-1} to 200 cm^{-1} on Perkin Elmer 221 IR Spectrophotometer using KBr pellet technique. The characteristic bands observed are as in **Table 3. Figure 3** shows IR spectra of 2H1NATSC

NMR Spectra of 2H1NATSC

NMR spectra of 2H1NATSC has been taken from Government of Central Instrumentation laboratory. Instrument used BRUKER AC 300F NMR spectrophotometer 300 HZ with $CDCl_2$ solvent. The characteristic chemical shift and the type of proton given in **Table 4.** The NMR spectra of 2H1NATSC is as shown in **Fig 4.** From NMR spectra and the table it is observed that the aromatic proton tallies with the structure of 2H1NATSC

Antimicrobial Activity of 2H1NATSC

Antimicrobial activity of 2H1NATSC has done in the laboratory approved by Central Government through AGMARK. The result are noted in **Table 5.**

Physico-chemical Characteristic of Pd(II)-2H1NATSC and Mo(VI)-2H1NATSC

Physico-chemical and Analytical Characteristic of Pd(II)-2H1NATSC and Mo(VI)-2H1NATSC was studied and given in **Table 6**.

RESULTS AND DISCUSSION

Table No.1 Elemental Analysis of 2H1NATSC

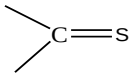
Sr.No.	Chemical Analysis	Percentage Found	Percentage Expected
1	Carbon	56.01	58.75
2	Hydrogen	05.63	04.52
3	Sulphur	12.98	13.07
4	Nitrogen	18.04	17.13
5	Oxygen	07.34	06.52

Table No.2 XRD for 2H1NATSC (Powder method)

2θ	hkl	Sin^2 Observed	Sin^2 Calculated	$d(A^0)$ Observed	$d(A^0)$ Calculated
10.565	100	0.00847	0.00729	8.3666	9.0210
12.185	100	0.01126	0.00729	7.2576	9.0210
12.705	100	0.01224	0.00729	6.9617	9.0210
16.190	110	0.02011	0.02013	5.4702	5.4254
16.315	110	0.02013	0.02015	5.4285	5.4254
16.970	111	0.02177	0.02780	5.2205	4.6191
19.080	111	0.02746	0.02780	4.6476	4.6191
19.665	200	0.02915	0.02916	4.5107	4.5105
20.750	200	0.03242	0.02916	4.2772	4.5105
21.660	200	0.03530	0.02916	4.0995	4.5105
23.660	210	0.04202	0.04202	3.7573	2.7573
24.045	210	0.04338	0.04202	3.6980	3.7573
24.395	210	0.04463	0.04202	3.6457	3.7573
24.485	211	0.04675	0.04968	3.6325	3.4556
25.760	211	0.04968	0.04968	3.4556	3.4556

26.310	211	0.05179	0.04968	3.3846	3.4556
26.435	211	0.05227	0.04968	3.3688	3.4556
27.685	211	0.04653	0.04968	3.2195	3.4556
29.660	220	0.06551	0.08061	3.0095	2.7129
30.090	220	0.06737	0.08061	2.9674	2.7129
36.995	222	0.10065	0.11225	2.4279	2.3093

Table No.3 Infrared spectra of 2H1NATSC

Sr.No.	Frequency Wavenumber	Expected Element
1	850	Other olefins C-H
	910	
	1040	
2	1200	
	1250	
	1330	
	1430	
3	1480	
	1570	-NH
4	1570	
	1620	NH_2, medium
5	1700	Benzene ring strong
6	1970	
	2010	N=C=S
	2220	
7	2300	
	2600	$-NH_2$, =NH, medium

	2660		
8	2780		
	2900		Aromatic homolytic compound
	3060		
	3180		
9	3060		
	3180		Disubstituted
	3380		
10	3410		Free OH, -OH strong

Table No.4 NMR Data of 2H1NATSC

Sr.No.	Types of Proton	Groups	Chemical Shift (ppm)
1	Secondary proton	R_2-CH_2	1.20271
			1.19653
			1.17891
			1.17403
			1.15596
			1.14973
2	Alcoholic proton	HC-OH	3.65200
			3.64624
			3.62835
			3.62232
			3.60455
			3.59973
			3.58161
			3.57547

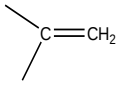
3	Vinylic proton		4.58358

Table No.5 Antimicrobial activity of 2H1NATSC

Sr.No.	Antimicrobial	Activity
1	Klebsiella pneumonia	Nil
2	Vibriaecholerease	Nil
3	Salmonallatyphi	Nil

Table No.6 Physico-chemical and Analytical characteristic of Pd(II)-2H1NATSC and Mo(VI)-2H1NATSC

Sr.No.	Characteristics	Results	
		Pd(II)-2H1NATSC	Mo(VI)-2H1NATSC
1	Absorption spectra	400 nm	395 nm
2	Molar absorptivity ($L.mole^{-1}.cm^{-1}$)	1.7303×10^{4}	8.6382×10^{3}
3	Sandell'ssemsivity (mg/cm^{-2})	0.006150	0.0111064
4	pH range (optimum)	6	5
5	Reagent required for maximum complexation	2.0 ml	2.0 ml
6	pKa	5.9347×10^{8}	6.2916×10^{8}
7	Beer's Law validity range (ppm)	4.681×10^{-6} M to 4.681×10^{-5} M	9.84×10^{-6} M to 9.84×10^{-5} M
8	Composition of complex (M;L) obtained in Job's and mole ratio method	1:2	1:2
9	Degree of dissociation	0.065714	0.10023
1	Stability constant	9.39082×10^{8}	2.32376×10^{10}

10	Change in free energy	-51.19 KJ/mol	-51.14 KJ/mol
11	Dissociation constant	1.064866 $x10^{-9}$	4.303359 $x10^{-11}$

Table No.7 Tolerance limit of diverse ions in the determination of Palladium and Molybdenium

Sr.No.	Metal ion	Salt	Interference	
			Palladium (II)	Molybdenium (VI)
1	Cr (II)	$K_2Cr_2O_7$	11.71	07.06
2	Ti (II)	$TiCl_2$	None	None
3	Fe (III)	Amm. Ferrous Sulphate	04.96	00.59
4	Citrate	Citric acid	03.37	00.59
5	Sn (II)	$SnCl_2$	05.06	01.65
6	Pb (II)	$Pb(NO_3)_2$	-----	00.82
7	Mg (II)	$MgCl_2$	03.47	00.59
8	Co (II)	$CoSO_4$	04.86	01.76
9	Hg (II)	$HgCl_2$	06.15	01.41
10	CH_3COO^-	CH_3COONa	None	02.16
11	SCN	NH_4SCN	None	None

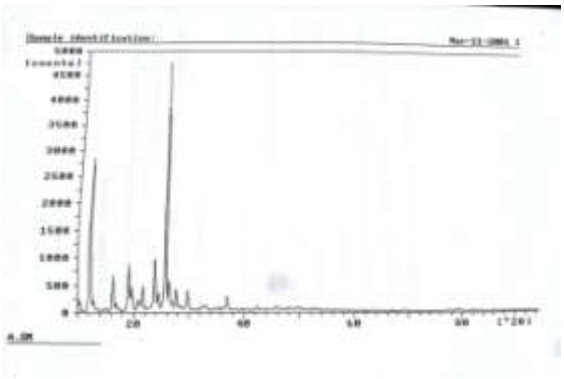


Fig 1 X-RD Spectra of 2H1NATSC

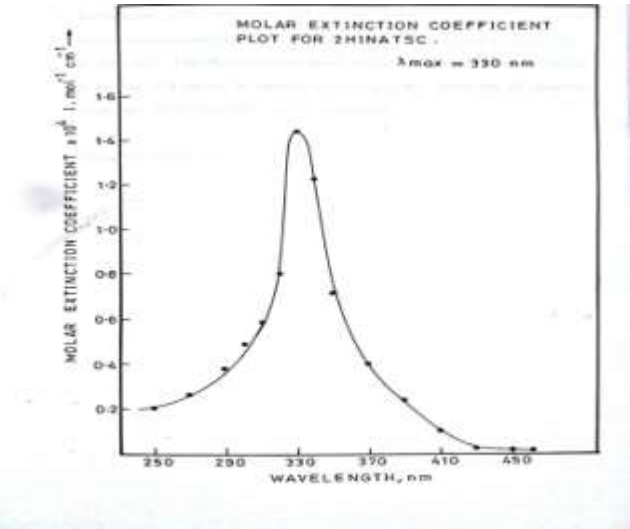


Figure 2 AbsorptionSpectra of 2H1NATSC

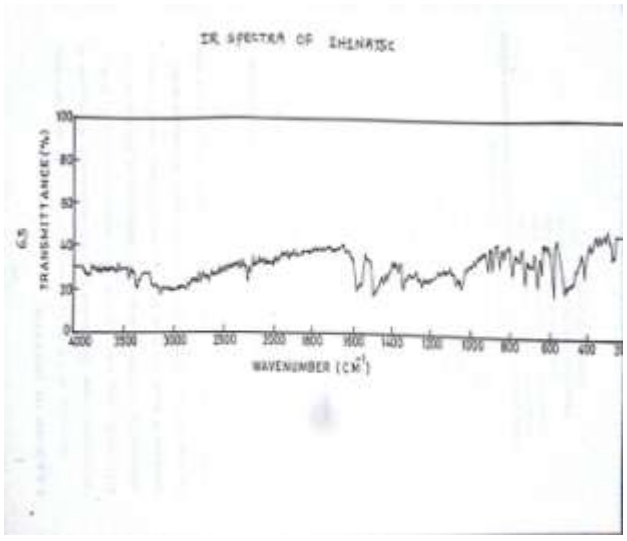
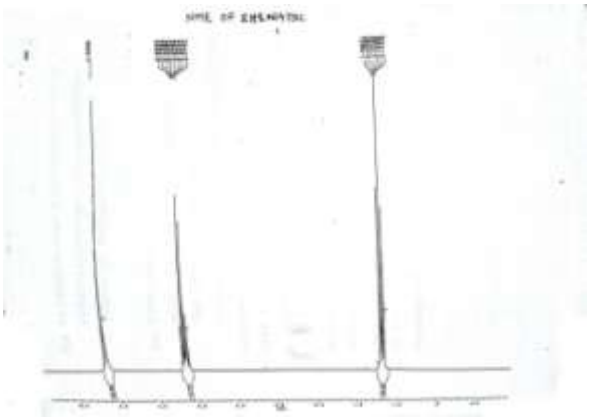
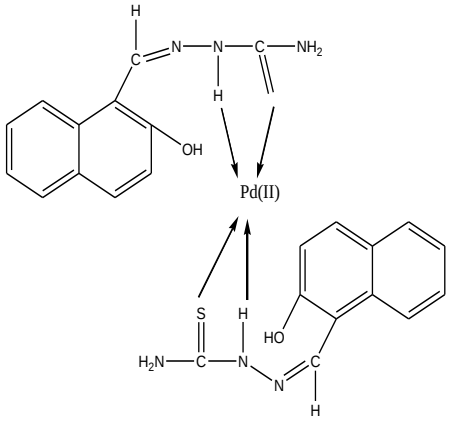


Figure 3 IR Spectra of 2H1NATSC



Structure of Pd (II)-2H1NATSC



Structure of Mo(VI)-2H1NATSC

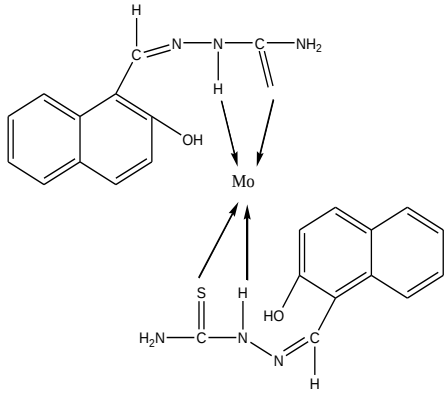


Figure 4 NMR Spectra of 2H1NATSC

CONCLUSIONS

2-hydroxy-1-Naphthylaldehyde Thiosemicarbazone **(**2H1NATSC) is suitable reagent for the determination of Pd (II) and Mo(VI) . 2H1NATSC shows the absorption at 330 nm and molar extinction

coeffieicent 1.4423 x10^4 L. $mol^{-1}cm^{-1}$. The value of elemental analysis is matches with the expected value. 2H1NATSC shows colour complex with Pd(II) and Mo(VI). It shows 1:2 complex with Pd (II) and Mo (VI). Antimicrobial activities give good results**.**

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