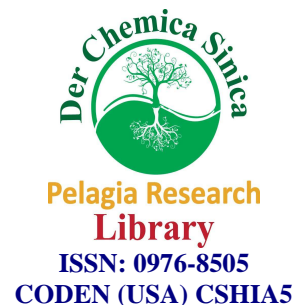




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Studies of Schiff base derived from Sulphadiazine and 2-hydroxy, 1-naphthaldehyde / benzoyl acetone for gravimetric determination of the Cu(II)

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ABSTRACT

Compounds containing the sulphonamide group have long been used as drugs for diseases like cancer, tuberculosis, diabetes, malaria and leprosy etc. It has now been observed that some of these drugs show increased biological activity when administered in the form of metal complexes. The present work deals with the synthesis and preliminary characteristics of various ligands. Here all the ligands are Schiff bases. Schiff bases derived by the condensation 2-hydroxy, 1-naphthaldehyde or benzoylacetone with Sulphadiazine. After synthesis of such Schiff bases as ligands, Cu(II) ion introduced with them by chelation. The chemical and physical properties of metal chelates will be evaluated.

Key words: ligands, sulphonamide, complexes, chelation, sulpha drugs.

INTRODUCTION

Compounds containing the sulphonamide group have long been used as drugs for diseases. It has now been observed that some of these drugs show increased biological activity when administered in the form of metal complexes[1-8].

A number of references are now available to show that the condensation products of sulpha drugs with aldehydes, ketones or their derivatives are biologically very active, besides having good complexing ability. their activity has also been shown to increase on complexation with metal ions.[9-10]

Large numbers of organic compounds like phenones, hydrazones, pheno-neoximes, chalconeoximes etc. have been used reagent for gravimetric and spectrophotometric determination [11-20]. Literature survey reveals that no work has been done Schiff base derived from sulfa drugs as a gravimetric reagent.

It was, considered of interested to synthesisze metal (II) derivatives of Schiff bases derived by the condensation 2-hydroxy, 1-naphthaldehyde or benzoylacetone with some of the welknown sulpha drugs.

Schiff bases are widely employed in synthetic organic and inorganic chemistry. They were reported to show diverse biological activity [20-24] and have many applications as ligands in coordination chemistry of transition metals[25-28].

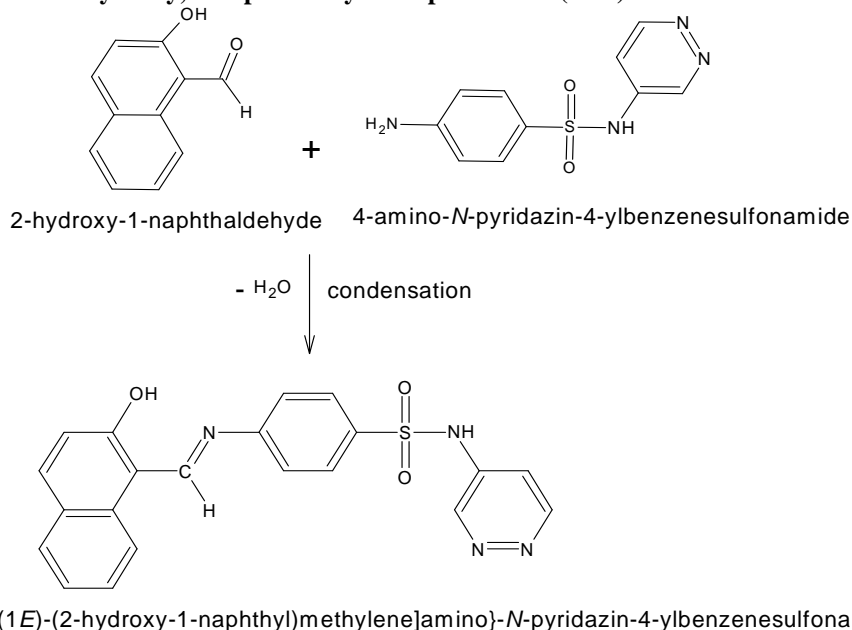
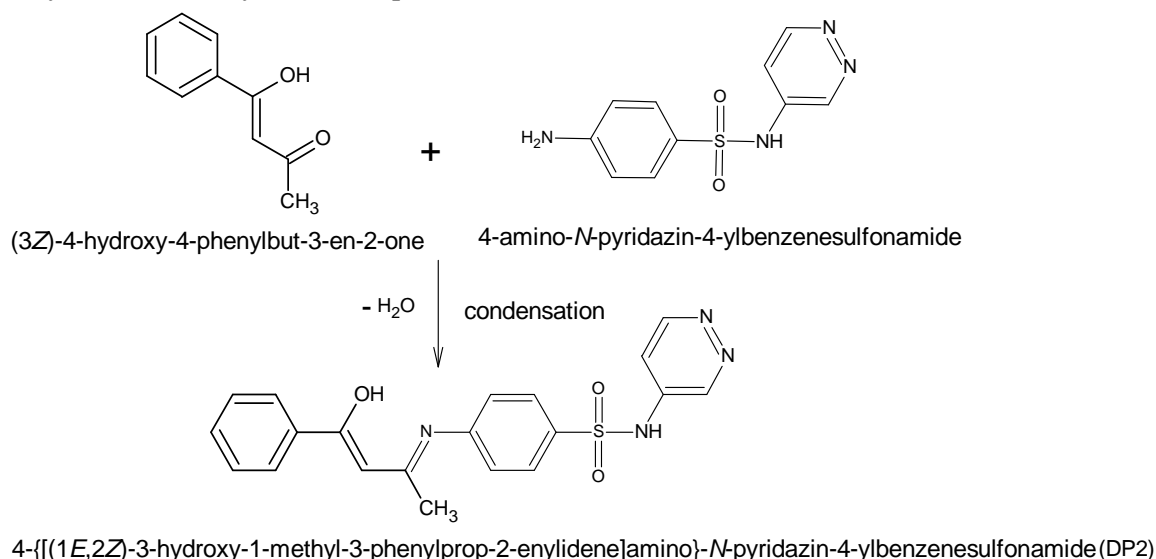
Our present work is studies on schiff bases derived from sulfa drugs and 2-hydroxy, 1-naphthaldehyde/ benzoyl acetone as gravimetric reagent for Cu(II).

MATERIALS AND METHODS

2.1 Synthesis of ligands.

All the chemicals used were of analytical grade (Sigma Aldrich Company) which was used without further purification. The melting points were determined on standard melting point apparatus.

The ligand was prepared by refluxing equimolar amount of 2-hydroxy, 1-naphthaldehyde/benzoylacetone and sulphadiazine. Ethanol/methanol. The reaction mixture was refluxed for 5 hours on water bath. On cooling, crystals of schiff base separated out with filtration, wash with alcohol, dried and recrystallised from appropriate solvent. (Table 2.1) The melting point was determined on standard melting point apparatus.

2.1.1 Synthesis of 2-hydroxy, 1-naphthaldehyde Sulphadiazine (DP1)**2.1.2 Synthesis of benzoylacetone Sulphadiazine (DP2)**

2.2 Gravimetric determination of the Metals

2.2.1 Preparation of metal chelates:

The pure ligands were used in the synthesis of metal complexes. Each ligand was purified with alcohol and ether, filtered and dried. The dried ligand sample was used for the preparation of metal complex.

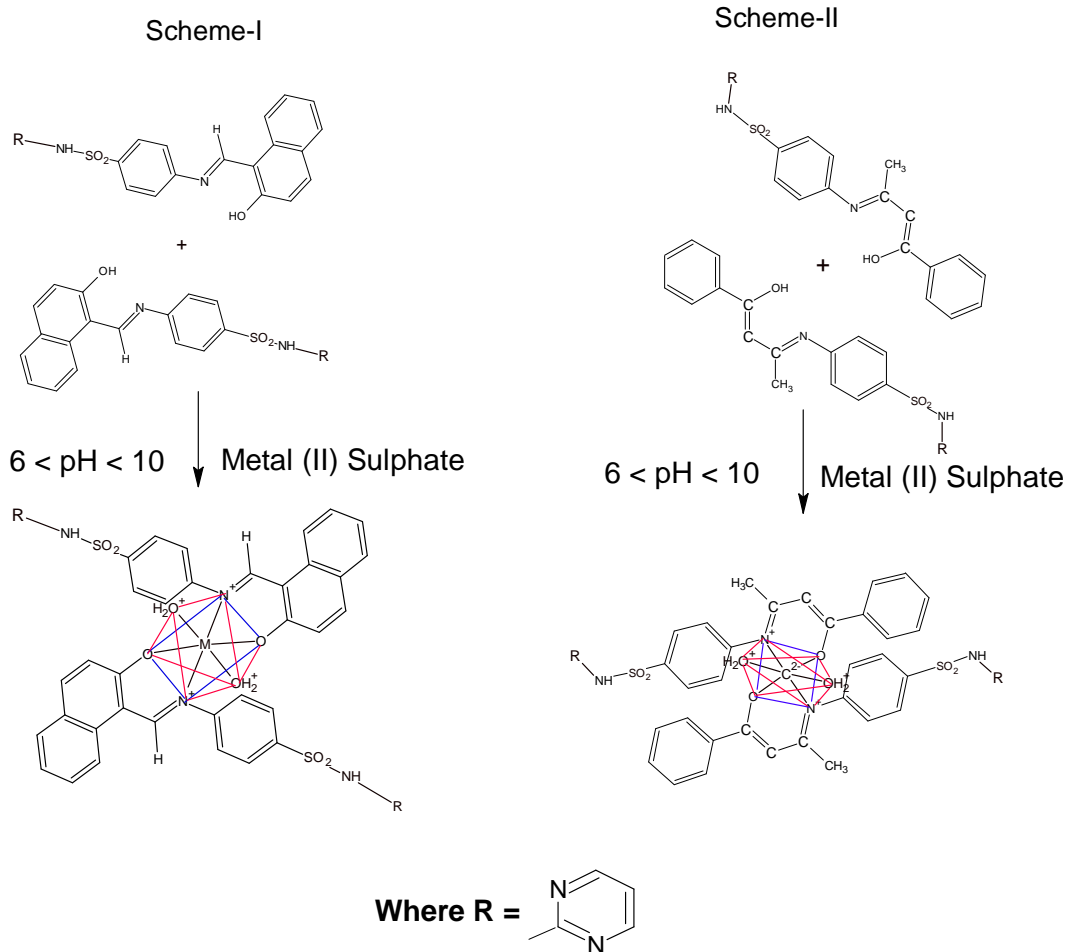
The synthesis of metal complex comprises the two steps:

- Preparation of 0.05 M solution of each metal salt.
- Preparation of metal complexes of ligands DP3 and DP4.

2.2.2 Preparation of 0.05 M solution of each metal salt.

Copper metal salts were used in forms of sulphates. Accurate quantities of sulphates of Cu (II) were dissolved in distilled water with few drops of concentrate sulphuric acid to prepare 100 ml, 0.05 M stock solution. From this stock solution 10 ml of the metal sulphate solution were used in formation metal complex.

SCHEME: 2.1



2.2.3 Gravimetric determination of copper with 2-hydroxy, 1-naphthaldehyde sulphadiazine. (DP3)

10 ml. 0.05 M cupric sulphate solution neutralized and then the pH of the solution was adjust between 3.0 to 4.0 using ammonium hydroxide solution. The solution was the diluted to 150 ml. and warmed up to 70°C. In this a reagent 2-hydroxy,1-naphthaldehyde sulphadiazine methanolic solution was added drop wise when brown precipitate of copper- bis-2-hydroxy,1-naphthaldehyde sulphadiazine was obtained. After complete precipitation, the precipitate digested for half an hour. The precipitate was filtered through counterpoised whatman filter papers and washed, dried at 120° for an hour and weighed as copper bis 2-hydroxy,1-naphthaldehyde sulphadiazine. The results are shown below.

- (1) 10ml. 0.05 M cupric sulphate solution gave 0.4497gm. copper-bis-2-hydroxy,1- naphthaldehyde sulphadiazine
 (2) 0.4497gm. copper-bis 2-hydroxy,1-naphthaldehyde sulphadiazine contains
 $\text{Cu}+2 = 0.03159\text{gm}$ (observed)
 (3) 10 ml.0.05 M cupric sulphate solution contains 0.03178 gm $\text{Cu}+2$ (Theoretical)
 Error = -0.00018 gm $\text{Cu}+2$
i.e. error = 0.60 %

2.2.4. Gravimetric determination of copper with benzoylacetone sulphadiazine. (DP4)

10 ml. 0.05 M cupric sulphate solution neutralized and then the pH of the solution was adjust between 3.0 to 4.0 using ammonium hydroxide solution. The solution was the diluted to 150 ml. and warmed up to 70°C. In this a reagent benzoylacetone sulphadiazine methanolic solution was added drop wise when brown precipitate of copper-bis-benzoylacetone sulphadiazine was obtained. After complete precipitation, the precipitate digested for half an hour. The precipitate was filtered through counterpoised whatman filter papers and washed, dried at 120° for an hour and weighed as copper bis benzoylacetone sulphadiazine. The results are shown below.

RESULTS

- (1) 10ml. 0.05 M cupric sulphate solution gave 0.4497 gm. copper-bis- benzoyl acetone sulphadiazine
 (2) 0.4497 gm. copper-bis benzoylacetone sulphadiazine contains
 $\text{Cu}+2 = 0.03170\text{ gm}$ (observed)
 (3) 10ml.0.05 M cupric sulphate solution contains 0.03178 gm $\text{Cu}+2$ (Theoretical)
 Error = -0.00008 gm $\text{Cu}+2$
i.e. error = 0.25 %

3.0 Characterization of ligands and Metal Chelates.

The present part deals with the characterization of ligands (i.e. DP1, DP2) and Metal Chelates. (DP3, DP4)

- I. Elemental analysis
- II. IR spectral studies

3.1 ELEMENTAL ANALYSIS.

The general properties of ligands are:

Melting points (°C) of all the compounds were measured by capillary method. All the mp's were uncorrected. The C, H and N elements of all the samples were measured by Elemental analyzer Thermofinigan flash1101 EA. The C, H, and N contents of all DP1, DP2, DP3 and DP4 derivatives are shown in Tables 3.1,3.2 The data are consistent with the predicted structures of ligands.

3.2 INFRARED SPECTROSCOPY :

The infrared spectra of selected ligands of the 2-hydroxy,1-naphthaldehyde sulphathiazole, benzoylacetone sulphathiazole,copper bis 2-hydroxy,1-naphthaldehyde sulphathiazole copper-bis benzoylacetone sulphathiazole shown below.

Sr.	Group	IR frequencies (Cm^{-1})
1.	- OH	3200-3600 Broad
2.	- C=N / -C=C-	1500 - 1600
3.	- C-H Stretching (Aromatic)	3000-3100
4.	Tertiary Amines	2300-2400
5.	O=S=O	1335-1375;1155-1170

RESULTS AND DISCUSSION

* The yields of 2-hydroxy, 1-naphthaldehyde sulphadiazine (DP1) and benzoyl acetone sulphadiazine (DP2) 83% and 82% respectively, copper bis 2-hydroxy,1-naphthaldehyde sulphadiazine(DP3) 99.22% and copper-bis benzoyl acetone sulphadiazine (DP4) 99.77 % respectively(TABLE-2.1,3.1).

* Schiff bases derived from sulfa drugs and 2-hydroxy, 1-naphthaldehyde and benzoyl acetone reacts with copper metal ion shows error 0.60 % and 0.25 % respectively.

* The colour of 2-hydroxy, 1-naphthaldehyde sulphadiazine (DP1) and benzoyl acetone sulphadiazine (DP2) dark yellow and pale yellow respectively. The colour of copper bis 2-hydroxy, 1-naphthaldehyde sulphadiazine(DP3) and copper-bis benzoylacetone sulphadiazine (DP4) greenish blue and pale bluish gray respectively.

Table: 2.1 The structures of Schiff base and Physical properties of the ligands.

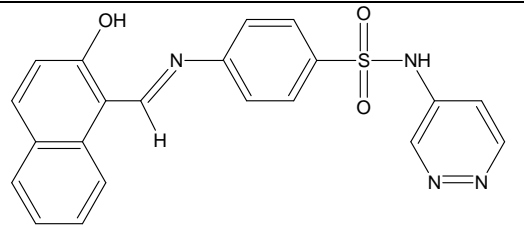
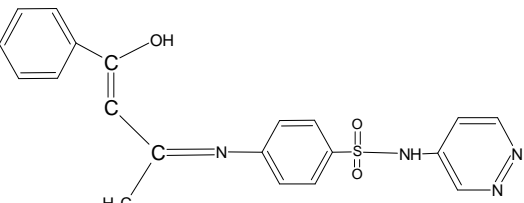
Structure	Name	Mol.wt	MP ⁰ C	Yield %
	DP1	404.443	220	85
	DP2	394.448	197	85

Table 3.1: Characterization of Ligands

Ligand No.	Molecular Formula	Mol. Wt gm/ Mole	Yield %	Elemental Analysis					
				% C		% H		% N	
				Cal.	Found	Cal.	Found	Cal.	Found
DP1	C ₂₁ H ₁₆ N ₄ O ₃ S	404.443	83	62.36	62.32	3.99	3.93	13.85	13.80
DP2	C ₂₀ H ₁₈ N ₄ O ₃ S	394.448	82	60.90	60.77	4.60	4.49	14.20	14.17

Table 3.2: Characterization of Metal Chelates . [CuL₂(H₂O)₂]

Metal Complexes	Molecular formula	M.Wt Gm/mole	%Error in Yield	% Metal analysis		Elemental analysis					
				%C		%H		%N			
				Cal.	Found	Cald.	Found	Cald.	Found	Cald.	Found
DP3	C ₄₂ H ₃₄ CuN ₈ O ₈ S ₂	906.446	99.22	7.01	7.0	55.65	55.6	3.78	3.7	12.36	12.3
DP4	C ₄₁ H ₄₁ CuN ₈ O ₈ S ₂	901.491	99.77	7.05	7.0	54.62	54.5	4.58	4.5	12.43	12.4

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REFERENCES

- [1] J.A. Vaichulish, U.S. Patent **1966**, 3, 271, 251; *chem., Abstr.*, **1966**, 65 19938e .
- [2] H. Dietrich, swiss Patent,**1968**, 440, 279 ; *chem., Abstr.*, **1968**, 69 19038q .
- [3] L.H. Schmidt *Ann. Rev. microbiol.***1969**, 23, 427.
- [4] G. Tarbini *Int. cong. Chemotherapy proc*, **1976**, V(2),909.
- [5] D. R. Williams, *chem. Rev.***1972**, 72,203.
- [6] A. Frust and R.T. Haro, *Prog. Exp. Tumor Res*,**1969**, 12,102.
- [7] G.D.Tiwari and M.N. Mishra. *Curr. sci.* **1980**, 49, 8.
- [8] M.J. Kharodawala and A.K. Rana, *Asian.J. chem.***2002**, 14 703.
- [9] G.T. Morgan, and H.D. Kdrew,; *J. Chem. Soc*, **1920**, 117, 1456.
- [10] H.F.Walton,; "Principles and methods of Chemical Analysis". Prentice Hall **1952**, 85.
- [11] F. Fegal,; "Chemistry of Specific, Selective and Sensitive Reagents" Academic Process **1949**, 2.
- [12] L.E. Godyeki, and R.E. Rundle; *Act Cryst.* **1953**, 6 ,487.
- [13] B.B.Fox; J. R. Halland, and R.A.; Plowman, *Australian J. Chem.* **1962**, 5
- [14] Morgan et al. *J. chem. Soc.*; **1920**,1457; **1921**,704; **1922**,2882; **1924**, 1731 **1925**,913.
- [15] Yoe and Sarver, *Organic reagents in Inorganic analysis*; Blackiston, Philadelphia ,**1940**
- [16] Willkinstand and Quagliano; *Chemistry of coordination compounds*, Reinhold Publication N.Y. **1956**.
- [17] Diehl, D.; *Chem. Rev.***1937**, 21,39.
- [18] Werner, Ber; **1901**, 34 ,2854.
- [19] Ramberg, Ber; **1910**,43,580; **1913**,46,3886.

[20] Feigl, et al.; *Ber* **1923**, 56,2083; **1925**, 58, 2294.

[21] Morgan, and Yang, *J. Chinese Chem. Soc*; **1936**,4 ; 27.C.A. **1936.**, 30 , 2925; *Rising. J.Biol, Chem.*, **1933**, 99,755.

[22] Heober and Levy, *Ann* **1932**, 500,14.

[23] C. Spinu, M. Pleniceanu, C. Tigae, *Turk. J. Chem.*, **2008**, 32, 487.

[24] Temel, H. Hosgoren, *Transition Met. Chem.*, **2002**, 27, 609.

[25] H. Temel, S. Ilhan, M. Sekerci, R. Ziyadanogullari, *Spectrosc. Letters*, **2002**, 35, 219.

[26] H. Temel, M. Sekerci, *Synth. React. Inorg. Met.-Org. Chem.*, **2001**, 31, 849.