



Synthesis, Characterization and Antimicrobial studies of metal complexes of 1-[2'-Chloro-5'-Sulphophenyl]-3-Methyl-4-Azo – [2''-Carboxy-5''-Sulphonic acid]-5-Pyrazolone and Their Transition Metal Chelates

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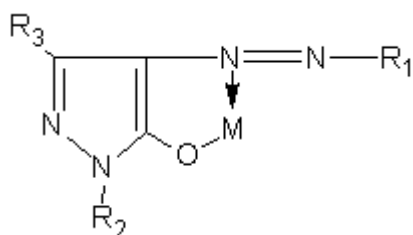
ABSTRACT

1-[2'-Chloro-5'-Sulphophenyl]-3-Methyl-4-Azo-[2''-Carboxy-5''-Sulphonic acid]-5-Pyrazolone was prepared by diazotization of 4-sulphoanthranilic acid and then coupling with 1-[2'-Chloro-5'-Sulphophenyl]-3-Methyl-5-Pyrazolone in alkaline medium. It was characterized by elemental analysis and spectral studies. The transition metal chelates of the same were prepared with Cu^{2+} , Ni^{2+} , Co^{2+} , Mn^{2+} and Fe^{3+} and characterized by IR spectral studies and physico chemical studies. The antimicrobial activity of ligand and its metal chelates were screened against various gram-positive (+) and gram-negative (−) organism. The results show that all these samples are more or less active agents against various organisms.

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Introduction

Pyrazolone ring due to its reactive 4-position undergoes coupling reaction with a number of aryl diazonium chlorides to form 4-aryldiazonium derivatives, which constitute an important class of azo dyes. These heterocyclic azo dyes are also good chelating agents. Many metal complexes of these azo dyes have been studied.^[1-7]

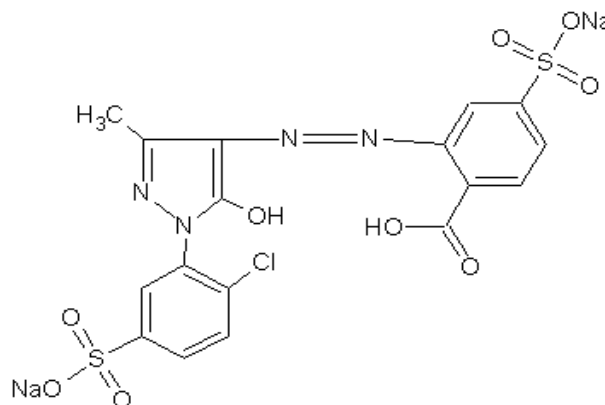
Where, R_1 = aryl group R_2 = alkyl or aryl group or hydrogen R_3 = alkyl or aryl group or hydrogen

The coordination chemistry of pyrazolone was studied due to their importance in industry, agriculture and their biological activity. In view of the above facts and in continuation of our interest in studying the ligating behavior of such compounds⁸⁻¹¹, therefore the present paper comprise the synthesise and characterize the solid complexes of the newly ligand containing the pyrazolone moieties, 1-[2'-Chloro-5'-Sulphophenyl]-3-Methyl-4-Azo-[2''-Carboxy-5''-Sulphonic acid]-5-Pyrazolone with Fe^{3+} , Cu^{2+} , Ni^{2+} , Mn^{2+} Co^{2+} and investigate their antimicrobial effects towards some Gram-positive and Gram-negative bacteria.

Synthesis of ligand HL

1-[2'-Chloro-5'-Sulphophenyl]-3-Methyl-4-Azo – [2''-Carboxy-5''-Sulphonic acid]-5-Pyrazolone (CSMACSP) was prepared by diazotization of 4-sulphoanthranilic acid (0.01 mol) and then coupling with 1-[2'-Chloro-5'-Sulphophenyl]-3-Methyl-5-Pyrazolone (0.01 mol) in alkaline medium. After the

completion of reaction, NaCl solution (10 % w/v) was added with stirring to precipitate out the solid material. It was then filtered off and crystallised from mixture of dimethyl formamide (DMF) and acetone (yield 80 %). Orange yellow crystals, soluble in water and DMF, insoluble in ethanol, methanol, acetone and chloroform. m.p. >300 °C.



1-(2'-CHLORO-5'-SULPHOPHENYL)-3-METHYL-4-AZO-(2''-CARBOXY-5''-SULPHONICACID)-5-PYRAZOLONE – REAGENT

Material and methods

All the chemicals used were of pure grade (Merck and B.D.H). The melting points of all complexes were determined by open capillary method and were uncorrected.

Synthesis of Chelates

The Cu^{2+} , Co^{2+} , Ni^{2+} , Mn^{2+} and Fe^{3+} metal ion complexes of CSMACSP have been prepared in a similar manner. The procedure is as follow.

0.01 mole corresponding ligands were dissolved in water and 0.005 mole metal salts also dissolved in minimum quantity of water. The resultant pH 3 (for Cu^{+2}), pH 9.0 (for Ni^{+2} and Co^{+2}), pH 9.5 (for Mn^{+2}) and pH 4 (Fe^{+3}) was maintained by

adding of sodium acetate and $[\text{NH}_3 + \text{NH}_4\text{Cl}]$ buffer of suitable concentration refluxed on water bath for 4 h. The solid mass was filtered. The percentage yield of chelates was in the range of 75-90 %. All the chelates were powdered well and dried at 110°C over a period of 24 h.

Measurements

The C, H and N contents of metal chelates were determined on elemental analyzer Thermofinigan 1101 Flash EA (ITALY). The metal contents were estimated using standard methods¹². The halogen content was determined by Carius method¹³. The infrared spectra (KBr) were recorded in the range $4000\text{--}600\text{ cm}^{-1}$ with a nicolet -760 spectrophotometer. A reflectance spectrum of ligand was recorded on a Beckman -DK-2A spectrophotometer using MgO as reference.

The following techniques have been used for the antimicrobial activities of these compounds. In this technique sterilized hot nutrient agar medium and 5 mm diameter paper discs of Whatman were used¹⁴⁻¹⁵. The agar medium was poured into the petri plates. After solidifications, the petri plates were stored in inverted position so that there was condensation of water in the upper lid. Solutions of test compounds in DMSO in 500 and 1000 ppm concentrations were prepared in which discs were dipped in solution of the test sample placed on seeded plates. The petri plates having these discs on the seeded agar should first be placed at low temperature for two or four hours to allow for the diffusion of chemicals before being incubated at suitable optimum temperature $28 \pm 2^\circ\text{C}$ for 24-30 hours. After the expiry of their incubation period, the zone of inhibition associated with the treated disc was measured in mm. The compounds were tested against *Bacillus subtilis*, *Staphylococcus aureus* gram-positive (+) and *Escherichia coli*, *Salmonella typhi* gram-negative (−) organism.

Results and discussion

Elemental analysis of complexes

All the five complexes were analysed for their carbon, hydrogen, nitrogen and sulphur content. The percentage of these elements were found in accordance with their molecular formula. The results obtained as tabulated below:

Chelate	Carbon % found (% calcd.)	Hydrogen % found (% calcd.)	Nitrogen % found (% calcd.)	Sulphur % found (% calcd.)
Cu (II)- CSMACSP	32.69	1.76	8.97	10.25
Ni (II)- CSMACSP	32.95	1.77	9.04	10.33
Co (II)- CSMACSP	32.92	1.77	9.03	10.33
Mn (II)- CSMACSP	33.14	1.78	9.09	10.39
Fe (III)- CSMACSP	33.09	1.78	9.08	10.38

Infrared spectra

The IR spectrum of ligand HL, The bands were observed at $3370, 1680, 1545$ and 1490 cm^{-1} . The inflexions at 1490 cm^{-1} are due to $\text{C}=\text{O}$ - group. The strong band at 1680 cm^{-1} is attributed to $\text{C}=\text{O}$ of carboxylic group of anthranilic acid. Several bands appeared between $1500\text{--}1600\text{ cm}^{-1}$ region may arise from aromatic breathing. The IR band at 1545 cm^{-1} due to $\text{N}=\text{N}$ - group.

The IR spectra of the ligand and the complexes were recorded in the form of their KBr pellets. The important absorption bands observed were as follows:

Physico chemical method:-

Many azo dyes like have been used as spectrophotometric reagent for transition metal ions. Here we report the use of 1-

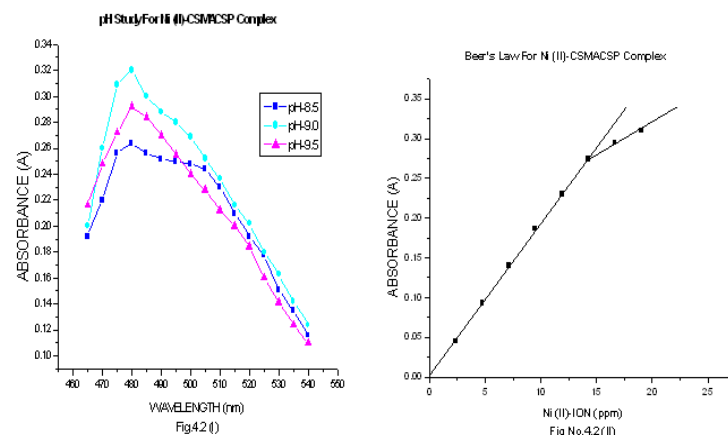
$[2'\text{-Chloro-5'-Sulphophenyl-3-Methyl-4-Azo} - [2''\text{-Carboxy-5''-Sulphonic acid}]\text{-5-Pyrazolone}$ (CSMACSP) as spectrophotometric reagent for Ni (II) and as indicator in EDTA titration of Ni (II).

The yellow coloured reagent CSMACSP is soluble in water and shows maximum absorbance at 410 nm. The reagent CSMACSP forms orange red coloured complex with Ni (II) in pH range 8.5 to 9.5. To study the effect of pH, 1 ml 0.005 M Ni (II) solution, was mixed with 3 ml 0.01 M solution of ligand in water was mixed. pH of solution was adjusted 8.5, 9.0 and 9.5 using $[\text{NH}_3 + \text{NH}_4\text{Cl}]$ buffer of suitable concentration. All solution was diluted to 25.0 ml in volumetric flask and absorbance was measured between 400 nm and 600 nm against reagent blank. Absorbance spectra shown in fig. (1) Shows that maximum absorbance is found at 480 nm in all cases. Maximum complex formation occurs at pH 9.0. Thus in all further studies pH 9.0 was used.

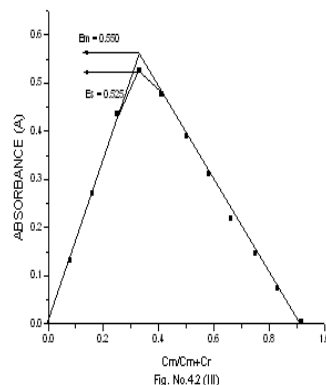
The absorbance spectra of the reagent Shows λ_{max} at 410 nm. At 480 nm where complex shows maximum absorbance [fig. S1] the reagent does not absorb much, and hence 480 nm wavelength was used in further studies.

Verification of beer's law:-

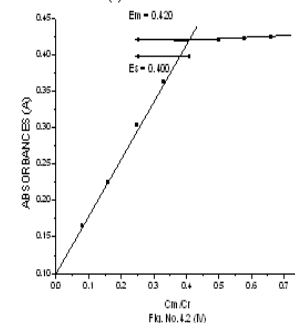
In 100 ml beakers, varying amount of 0.002 M Mn (II) solutions 0.5 ml, 1.0 ml ...5.0 ml. were taken and 3.0 ml 0.01 M reagent solutions were added to each beaker. pH of each solution was adjusted at 9.0 using $[\text{NH}_3 + \text{NH}_4\text{Cl}]$ buffer. All solution was diluted to 25.0 ml with water in volumetric flask, and absorbance was measured at 480 nm against reagent blank. The Beer's law plot is shown in fig. S2.



COMPOSITION OF Ni (II) CSMACSP COMPLEX BY JOB'S METHOD



COMPOSITION OF Ni (II) CSMACSP COMPLEX BY MOLE RATIO METHOD



Stoichiometry of Complex:

It was confirmed that only one complex was formed under the conditions. Stoichiometry was found (1:2) M: L using Job's method of continuous variation and Yoe and Jones mole ratio method. Stability constant was determined from the graphs using following formula.

Compound	- OH stretching cm^{-1}	Stretching C = O in -COOH group cm^{-1}	N = N cm^{-1}	O = H banding of - COOH cm^{-1}	C-O-H bending of OH in pyrazolone	S = O Stretching in -SO ₃ H group cm^{-1}	C-Cl Stretching cm^{-1}
CSMACSP Ligand	3590	1670	1540	1490	1390	1180,1030	790
Cu (II)-CSMACSP	-	1540	1490	-	1360	1190,1040	710
Ni (II)-CSMACSP	-	1610	1490	-	1370	1180,1030	650
Co (II)-CSMACSP	-	1550	1440	-	1370	1120,1040	650
Mn (II)-CSMACSP	-	1630	1490	-	1370	1180,1040	620
Fe (II)-CSMACSP	-	-	1440	-	1370	1240,1040	690

$$\text{Degree of dissociation} = \frac{E_m - E_s}{E_m}$$

E_m = Maximum absorbance

E_s = Absorbance found at correct Stoichiometry

$$\text{Stability constant } K_s = \frac{(1-\alpha)}{4\alpha^3 c^2}$$

C = Concentration in mol/lit.

Average stability constant found from two methods was 3.99×10^9 .

Determination of Nickel in German silver:

The standard sample (preanalysed) of German silver (0.2294 gm) was dissolved in nitric acid (1 : 2) by heating on a water-bath for 30 to 40 minutes. The solution was evaporated on a water-bath to a volume of 5 ml but not to dryness and excess of nitric acid was removed. The resulting solution was treated with deionised water. The solution was made up to 100 ml in a volumetric flask.

An aliquot of the above diluted solution (10.0 ml) was taken in a 50 ml beaker. pH of the solution was then adjusted to 9.0 using buffer solution. To this solution was diluted to 25 ml with deionised water in a volumetric flask. The absorbance was measured at 480 nm against the reagent blank. The results are tabulated below;

german solution: 0.2294 gm German silver in 250 ml stock solution.

∴ 5.0 ml stock solution contains 4.588 mg German silver; 10.0 ml aliquot contained 0.4588 mg German silver.

Reagent solution : 3.0 ml (0.01M)

pH : 9.0

Final volume : 25 ml

Wavelength : 480 nm

From the above experiment,

Absorbance was found to be 0.180, which corresponds to 0.1086 mg copper in 10.0 ml finally diluted solution of brass.

Nickel found in German silver sample = 27.67%

(Reported nickel in german silver sample = 23.44%

% Relative error = 0.9812%

¹H-NMR spectra

The NMR spectra of the ligand gave the multiplet between 7.1-8.2 δ ppm for aromatic protons, singlet at 3.5 δ ppm for -OH and singlet at 2.3 δ ppm due to the aliphatic -CH₃ group protons. Thus the structure of ligand is confirmed. The complexes are microcrystalline colored powders having melting points higher than the ligands. They are stable in air at room temperature.

Antimicrobial activity

The result indicates that the Cu (II) and Zn (II) exhibits higher activity towards most of the plant pathogenic organisms studied than the ligands

The other metal complexes did not show any significant increase in activity as compared to the ligands. The results suggest that variation in structure on coordination affects the growth of micro organisms and may result in to inhibitory or reduction in toxicology of metal ions towards some organisms¹⁶.

Conclusion

- The dye forms intense coloured complexes with Cu(II), Ni(II), Co(II), Fe(III) and Mn(II) and few other metal ions which are completely soluble in water and hence, there is no necessity of extracting the complexes, This saves costly and toxic solvents. However this reduces its selectivity.

- The dye solution and the complexes are stable over a long period.

- It is well suited as metallochromic indicator. Compared to many other metallochromic indicators which are soluble in ethanol, it is soluble in water.

- It can be used to analyse alloys and medicinal sample with fairly high accuracy.

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