



## SYNTHESIS, CHARACTERIZATION AND APPLICATIONS OF METAL COMPLEXES OF 5-NITROSALICYLIDENE 4-AMINO 3-MERCAPTO-1, 2, 4-TRIAZINE- 5-ONE

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### ABSTRACT

Transition metal complexes of Cu(II), Ni(II), Co(II) with 5- Nitro salicylidene 4- amino 3 -mercapto 1,2,4 triazine-5-one have been synthesized and characterized by analytical and spectral techniques. All metal complexes form ML type of complexes. Based on analytical data, IR spectra and magnetic moments Co (II), Ni (II) are assigned octahedral geometries while Cu (II) a square planar geometry. In all these complexes azomethine nitrogen, carbonyl oxygen and phenolic oxygen are involved in bond formation.

**Key Words:** Triazines, Schiff base, antibacterial studies, octahedral geometry.

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### INTRODUCTION

Nitrogen containing heterocyclic compounds like triazoles, triazines, imines and amines forms good Schiff bases with aldehydes like substituted and unsubstituted benzaldehyde, salicylaldehyde. These Schiff bases are known to form complexes with transition metals and lanthanides. These compounds forms complexes by involving azomethine linkage and phenolic oxygen.<sup>1,2</sup> Some of these complexes are found to possess antibacterial and antifungal activity.

The development of new ligands is a very important step in the development of metal complexes. These metal complexes have unique properties and novel reactivities. The nature of these groups like steric properties, electronic properties, and the geometric properties affect the metal orbitals and thus affect its properties. In catalytic systems small change in electron donating property of the ligand or the size of the substituents on the ligand play an important role in enantioselectivity and efficiency of a ligand or its complex. One such group is the nitro group in a ligand which acts as a strong electron withdrawing group and due to its steric effects has played an important role in asymmetric cyclopropanation and allylic alkylation reactions.<sup>3</sup> Many reports have been reported on metal complexes containing nitro group on the ligand.<sup>4-6</sup>

In the present note we have undertaken the synthesis and characterization of Ni (II), Co (II) and Cu (II) complexes of 5-nitrosalicylidene-4-amino-3-mercapto-1, 2, 4-triazine-5-one (nitroSAMT) and their possible anti-bacterial activity has been explored.

### EXPERIMENTAL

The metal content of these complexes were estimated using Varian AA 55B atomic absorption spectrometers, infrared spectrum was recorded on ABB BOMEM FT-IR spectrophotometer, carbon hydrogen nitrogen and sulfur were analyzed on Thermo Flash EA 1112 series CHN analyzer, magnetic susceptibilities were determined using Sherwood Scientific Magnetic Susceptibility meter (UK), electronic spectra of complexes in DMF on GBC model UV visible spectrophotometer, and Thermogravimetric analysis was carried out by TGA analyzer SII EXSTAR 6000.

#### Synthesis of ligand

The ligand was synthesized in two steps.<sup>7</sup> In the first step 0.76 g of 50% glyoxylic acid was taken in minimum amount of water. To this a solution of 1.07 g of thiocarbonylhydrazide in 12 ml of water was

added, and mixture was refluxed for 1 hour, the resultant yellowish white precipitate was filtered, dried, and recrystallized from hot water. The M.P: 213 °C. Yield: 75%. In the second step, to a solution of 0.1 mol of 4-amino-3-mercapto-1,2,4-triazine-5-one in 10 ml of ethanol, and 0.1 mmol of 5-Nitrosalicylaldehyde was refluxed for 4 hours, filtered, washed with water, dried. The yellow colored compound was recrystallized from absolute alcohol, The yellow colored 5-Nitrosalicylidene-4-amino-3-mercapto-1,2,4-triazine-5-one (Nitro-SAMT) was dried in a desiccator. MP: 251 °C. Yield: 83%.

#### Synthesis of complexes

To a hot solution of 0.002 mol solution of nitroSAMT in 20 ml alcohol, a 0.002 mol of transition metal salts in minimum amount of water was added and refluxed for 2 hours. The complexes were filtered, washed with alcohol, ether and dried in a desiccator.

#### Biological Tests

The synthesized complexes of Nitro-SAMT were screened for their *invitro* antibacterial activity against pathogenic strains of gram negative bacteria such as *E.Coli*, *Pseudomonas aeruginosa*, *salmonella typhi* and *shigella flexneri* using plate technique. The bacterial were cultured (15 mm dia) in previously sterilized Mueller Hinton agar medium in a petri dish. The ligand and its complexes solutions in DMF were placed on cultured agar medium and incubated for a period of 24 hrs at 37 °C. Nicotinic acid was used as reference material. After the incubation period the plates were observed for zones of inhibition (in mm).

## RESULTS AND DISCUSSION

#### Analytical

The analytical results show that the cobalt (II), nickel (II) and copper (II) forms ML type of complexes with nitro-SAMT ligand. Co (II), Ni (II) and Cu (II) complexes shows presence of coordinated water molecules.

#### Infrared spectra

The ligands shows infra red band at 2900 cm<sup>-1</sup> indicating the absorptions  $\nu$ (C-H). The ligand also shows the presence of four thioamide bands I, II, III and IV at 1550, 1270, 900, 800 cm<sup>-1</sup> respectively, indicating the presence of thioamide moiety in the ligand molecule [8]. No systematic shift was observed due to these bands in the complexes. The band at around 1700 cm<sup>-1</sup>, corresponding to  $\nu$ (C=O) of the carbonyl group, in the ligand is found altered in the complexes. These indicate the possibility of carbonyl group participating in the bonding. The bands at 1650 and 1600 cm<sup>-1</sup> in the ligand and the complexes corresponds to that of  $\nu$ (C=N) of the azomethine linkage<sup>9</sup>, and the shift in frequency to lower wave number side indicates the coordination of the nitrogen of this group with the metal ions. In complexes the band at 1300 cm<sup>-1</sup>, due to the phenolic group is shifted to higher wave number side indicating the involvement of phenolic oxygen in the formation of coordination bond with the metal. The broad band at around 3500 cm<sup>-1</sup> and 890 cm<sup>-1</sup>, corresponding to  $\nu$ (O-H) in case of Cu(II), Co(II) and Ni(II) complexes indicates the presence of coordinated water molecules in the complex.<sup>10</sup> This also indicates that the nitro group is not involved in bond formation.

#### NMR spectra

The <sup>1</sup>H NMR spectra of the free ligands and complexes have been recorded in CDCl<sub>3</sub>. The ligands exhibit singlets at 11.58. These signals in the spectra of the complexes remain as such, suggesting the non participation of sulphur in the coordination. The singlet at 8.1 ppm (-CH=N-) in the ligand is altered to that in the complex at 8.54 ppm. In the spectra of the ligands, multiplets due to aromatic protons appear in the range  $\delta$  6.24–8.76 ppm. These resonance signals remain unchanged in the spectra of the complexes, suggesting their non-involvement in bonding. The peak corresponding to -OH at 12.85 ppm in the free ligand is not observed in the complexes. This clearly shows the deprotonation of -OH during the formation of the complex.

#### Magnetic susceptibility

The magnetic susceptibility results indicate NitroSAMT complexes of Co (II), Ni (II), Cu (II) are paramagnetic. Nickel (II) being a d<sup>8</sup> in octahedral field contains two unpaired electrons and hence shows paramagnetism. The value of 2.7 BM is close to the theoretical value and reported value<sup>11-14</sup> of 2.83 for

octahedral nickel (II) complexes. Co (II) being a  $d^7$  system, its complexes show paramagnetism equivalent to three unpaired electrons of octahedral geometry. Since the orbital contribution of tetrahedral Co(II) is much less than that of octahedral complexes, tetrahedral Co(II) complexes have generally lower values of magnetic moments, as compared to that of octahedral complexes. This high degree of orbital contribution for octahedral complexes is due to the three fold degeneracy of  ${}^4T_{1g}$  ground state. The observed value of 3.87BM is close to the theoretical calculated values of 3.83 BM for octahedral Co (II) complexes. Cu (II) being a  $d^9$  system shows paramagnetism in square planar complexes. The value of 1.91BM is close to theoretical value of 1.73 BM for Cu (II) octahedral complexes. The results of analysis are shown in Table 1.

#### Electronic spectra

In the case of six coordinate octahedral and pseudo-octahedral Ni(II) complexes the three spin allowed transitions from  ${}^3A_{2g}(F)$  to  ${}^3T_{2g}(F)$ ,  ${}^3T_{1g}(F)$  and  ${}^3T_{1g}(P)$  generally fall within the region  $7000-13000\text{ cm}^{-1}$ ,  $11000-20000\text{ cm}^{-1}$  and  $19000-27000\text{ cm}^{-1}$  respectively. The ratio of the frequencies of the second to the first transitions would be around 1.8<sup>15</sup>. The first transition corresponding to  ${}^3A_{2g}(F)$  to  ${}^3T_{2g}(F)$  is not recorded in the electronic spectra. The assignment of the transition was calculated. For high spin octahedral complexes of Co(II), three transitions are expected in the electronic spectra and they are  ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ ,  ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$ , and  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$  in the order of increasing energies. The first transition was not recorded but the position was calculated from the second transition. For high spin octahedral complexes of Cu(II), only one transition  ${}^2E_{1g}(F) \rightarrow {}^2T_{2g}(F)$  is expected, and that is observed in the spectrum.

#### Molar conductance

The results of molar conductance which are less than  $30\ \mu\text{S}$  in DMF solutions, indicates that all the formed complexes are non electrolytes, electrically neutral and non ionic in nature<sup>16,17</sup>. The results are as shown in Table 1.

#### Thermogravimetric analysis

TGA analysis of Ni (II), Cu(II) and Co (II) complexes shows a weight loss starting from around  $100\ ^\circ\text{C}$  and ending at around  $300\ ^\circ\text{C}$ . The loss in weight from  $100\ ^\circ\text{C}$  to  $150\ ^\circ\text{C}$  indicates presence of water of coordination in Ni (II) and Co (II). The weight loss from  $200\ ^\circ\text{C}$  to  $250\ ^\circ\text{C}$  and from  $250\ ^\circ\text{C}$  to  $300\ ^\circ\text{C}$  in Ni(II), Co(II) and Cu(II) NitroSAMT complexes indicates the evaporation and decomposition of organic ligand respectively<sup>18-20</sup>.

#### Antibacterial tests

Cu(II), Co(II) and Ni(II) complexes of Nitro-SAMT showed more zone of inhibition compared to the free schiff base indicating that these complexes possess more antibacterial activity against pathogenic strains of gram negative bacteria such as *E.Coli*, *Pseudomonas aeruginosa*, *salmonella typhi* and *shigella flexneri*<sup>21,22</sup>.

### CONCLUSIONS

On the basis of above analytical, magnetic, molar conductance, electronic and infra red spectral data and keeping in view of the preferred geometries, octahedral structures have been proposed for Co(II), Ni(II) complexes of Nitro-SAMT, and square planar for Cu(II) complexes. Cu(II), Ni(II) and Co(II) complexes exhibits antibacterial activity against gram negative bacteria such as *E.Coli*, *Pseudomonas aeruginosa*, *salmonella typhi* and *shigella flexneri*. Further studies on the catalytic and biological applications are in progress.

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Table-1: Analytical data, molar conductance and magnetic susceptibility data for complexes.

Complex	Analytical data Found (calculated)					Molar conductance ( $\mu$ S)	Magnetic Susceptibility(B M)
	M	C	N	H	S		
$C_{10}H_6N_5O_3S$	-	41.07 (41.09)	23.94 (23.97)	2.00 (2.05)	10.99 (10.96)	-	-
$C_{10}H_6ClCuN_5O_4S$	15.9 (15.8)	29.79 (29.93)	19.88 (19.95)	1.50 (1.49)	7.90 (7.98)	25.2	1.91 (1.73)
$C_{10}H_6ClN_5NiO_4S$	14.72 (14.82)	30.19 (30.29)	20.10 (20.19)	1.48 (1.51)	8.11 (8.08)	11.3	2.75 (2.83)
$C_{10}H_6ClCoN_5O_4S$	14.80 (14.87)	30.25 (30.28)	20.22 (20.18)	1.49 (1.51)	8.05 (8.07)	11.2	3.87 (3.87)

Table-2: Infrared band positions of NitroSAMT complexes of some transition metals.

Ligand	Ni(II), Co(II), Cu(II)	Assignment
-	3500B	$\nu$ (O-H) water
3000m	2900m	$\nu$ (C-H)
1700s	1700s	$\nu$ (C=O)
1650m	1630m	$\nu$ (C=N)
1550s	1540	Thioamide I
1450s	1500m	Thioamide II
1200s	1200w	Thioamide III

750s	720w	Thioamide IV
-	900	Characteristic of coordinated water
700m	700	Aromatic ring
-	440w	v (M-N)
-	490w	v (M-O)
-	560w	v (M-S)

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