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## Studies on novel *o*-hydroxyacetophenone substituted triazine based ligand and its metal complexes

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### ABSTRACT:

A novel design of triazine based ligand with *o*-hydroxyacetophenone nucleus (L) has been synthesized. A series of metal(II) complexes of general formula [ML.H<sub>2</sub>O][where M = Cu(II), Ni(II), Co(II) and Zn(II)] have been obtained. UV-Visible, magnetic susceptibility, Infrared, <sup>1</sup>H NMR, Mass and electron spin resonance (ESR) techniques have been used to elucidate the structures of metal complexes. Spectroscopy and other data show octahedral geometry for metal(II) complexes. The fluorescence spectra of all the complexes revealed the photoactive nature of the complexes. The ligand was found to exhibit better second harmonic generation (SHG) efficiency compared to that of urea and KDP. The ligand and its metal complexes were screened for their antibacterial and antifungal activities. This study revealed the increased antimicrobial activity exhibited by the ligand.

**Keywords:** Triazine, *o*-hydroxyacetophenone, fluorescence, SHG, Antimicrobial activity.

## 1. INTRODUCTION

S-triazine and its derivatives display a wide range of pharmacological properties including antibacterial, antiviral, antimalarial, anti-inflammatory activities and exhibit promising anticancer, anti-leukemia and anti-HIV activities.<sup>[1-3]</sup> Extensively  $\pi$ -conjugated materials have attracted much interest in the recent past due to their excellent semiconducting properties.<sup>[4,5]</sup> 1,3,5-triazine are important class of  $\pi$ -conjugated heterocycles with nitrogen atoms in the six-membered ring each with a lone-pair of electrons pointing outside the ring.

1,3,5-triazine derivatives are of great interest due to their importance as drug precursors and additives for stabilizing light emission in OLEDs.<sup>[6-8]</sup> Triazine chemistry has attracted attention due to the utility of its derivatives as starting materials for a variety of polymer as scavenging resins in organic manipulations and in medicinal chemistry.<sup>[9-11]</sup> They provide a wide range of applications in the field of optics, herbicides and pharmaceuticals.<sup>[12]</sup>

Transition metal ions with different oxidation states have a strong role in bio-inorganic chemistry and redox enzyme

systems and may provide the basis of models for active sites of biological systems.<sup>[13]</sup> Transition metal complexes with potential bio activity are the focus of extensive investigations. 2-Hydroxyacetophenone is an important bioactive ligand for a wide variety of applications such as antimetagenic activity in *salmonella typhi* and acts as an analytical reagent for the gravimetric and colorimetric estimation of transition metals.<sup>[14]</sup> Acetophenone is used in consumer fragrances and as an industrial solvent. In general, acetophenones may serve as a novel group of useful therapeutics against mycobacteria.<sup>[15]</sup> Some acetophenone derivatives have antimicrobial activity while others are used as herbicides.<sup>[16,17]</sup>

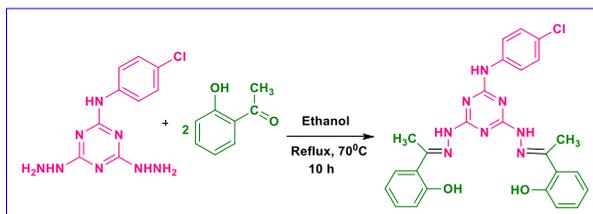
Review of literature reveal that the synthesis and characterization of metal complexes of dihydrazino-s-triazine with 2-hydroxyacetophenone have not been reported earlier. The electron-rich hydrazine group will have a greater stabilizing effect on the electron deficient s-triazine ring, while providing significant chelating centers.<sup>[18]</sup> Interesting structural features, NLO properties and biological activities of such compounds were key factors to carry out this investigation. In this study, we have designed the ligand with nitrogen and oxygen containing  $N_3O_2$  chromophore, with dianionic character. The compounds have been synthesized by condensing dihydrazino-s-triazine with 2-hydroxyacetophenone to get  $N_3O_2$  chromophore. Fluorescence, nonlinear optical property, biological activity of the ligand and its metal complexes were also examined.

## 2. MATERIALS AND METHOD

All chemicals were obtained from Aldrich Chemical & Co. and used without purification. All solvents including acetonitrile, dichloromethane (DCM), dimethylformamide (DMF), dimethylsulfoxide (DMSO), ethanol (ETOH) and ethyl acetate (ETOAC) were of analytical grade and were procured from SD fine chemicals Limited (India) and were used without purification. Fluorescence spectra were obtained on ELICO SL174 spectrofluorometer using DMSO as solvent. The IR spectra in KBr disc were recorded on a SHIMADZU FT-IR spectrophotometer. <sup>1</sup>H NMR spectrum was recorded in  $CDCl_3$  using a Bruker DRX-300, 300 MHz NMR spectrometer. EI mass was recorded by JEOL-GCMATE-2. The synthesized compound was screened for biological activity through the well-diffusion method. The SHG conversion efficiency of the compound was determined by the modified version of powder technique.

### Synthesis of 2-(4-chlorophenyl)amino-4,6-bis(2-(hydroxyacetopheno)hydrazinyl)-1,3,5-triazine (CPHAHT)

A solution of 2-hydroxyacetophenone (2.34 g, 10 mmol) in ethanol (10 ml) was mixed with 2-(4-chlorophenyl)amino-4,6-dihydrazinyl-1,3,5-triazine (CPHT) (1.33 g, 5 mmol) in ethanol (15 ml) and refluxed for 10 h at 70°C. [The method of synthesis of CPHT<sup>[20]</sup> is discussed in chapter II]. Gradually yellow precipitate was separated out on cooling. The precipitate was filtered and recrystallized from ethanol. Yield: 76%; (Scheme 1)



**Scheme 1.Synthesis of ligand (CPHAHT)**

### Synthesis of metal(II)complexes

The metal complexes were synthesized by the addition of hot solution of the appropriate metal(II) chlorides (1 mmol) ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{ZnCl}_2$ ) in 25 ml of ethanol to the hot ethanolic solution of the ligand (CPHAHT) (1mmol). The resulting mixture was stirred for 2 h and the complex precipitated were collected by filtration, washed with ethanol and dried in vacuum. Yield: 71-75%

### 3. Results and Discussion

The metal(II) complexes of copper(II), cobalt(II), nickel(II) and zinc(II) of  $[\text{ML} \cdot \text{H}_2\text{O}]$  type were obtained in good yield through the reaction of (CPHAHT) with the corresponding metal salts. The ligand and its metal(II) complexes were characterized through electronic absorption, IR, NMR, Mass, ESR spectral data and the corresponding structure is depicted. The molar conductance of the metal(II) complexes was measured to determine the charge of the metal(II) complexes and implies that all the complexes are non-electrolytes. Spectral, mass and conductance data suggest that the molecular formula  $[\text{ML} \cdot \text{H}_2\text{O}]$  for copper(II), cobalt(II), nickel(II) and zinc(II) complexes. The magnetic moment of the complexes is

in consistent with octahedral geometry around central metal ion.

### Mass spectral studies

The mass spectra of the ligand (CPHAHT) and copper(II) complex were recorded and compared. Mass spectrum of the ligand (CPHAHT) shows a molecular ion peak at  $m/z$  503 (Calculated); found: 521 ( $\text{M} + \text{H}_2\text{O}$ ) and the molecular ion peak for cobalt(II) complex is observed at  $m/z$  577 ( $\text{M} + 1$ ) confirms the stoichiometric composition of the metal(II) complexes as being of the  $[\text{ML} \cdot \text{H}_2\text{O}]$  type.

### Electronic Absorption Spectral Studies

The electronic spectrum of the ligand exhibits a strong peak in the UV range, centered at  $38910 \text{ cm}^{-1}$  and  $47169 \text{ cm}^{-1}$  due to charge transfer bands. The electronic spectrum of copper(II) complex shows two bands at  $22351 \text{ cm}^{-1}$  ( $\epsilon$ ,  $210 \text{ M}^{-1} \text{ cm}^{-1}$ ) and  $11737 \text{ cm}^{-1}$  ( $\epsilon$ ,  $78 \text{ M}^{-1} \text{ cm}^{-1}$ ) which were assigned to intra ligand charge transfer (ILCT) band and  ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$  transition respectively. The magnetic moment value of 1.90 B.M for copper(II) complex supports octahedral geometry for copper(II) ion. The cobalt(II) complex exhibits three transitions at  $9608 \text{ cm}^{-1}$  ( $\epsilon$ ,  $127 \text{ M}^{-1} \text{ cm}^{-1}$ ),  $15851 \text{ cm}^{-1}$  ( $\epsilon$ ,  $184 \text{ M}^{-1} \text{ cm}^{-1}$ ) and  $19046 \text{ cm}^{-1}$  ( $\epsilon$ ,  $221 \text{ M}^{-1} \text{ cm}^{-1}$ ) attributed to  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$ ,  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$  and  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$  transitions respectively characteristic of distorted octahedral geometry. The magnetic moment of cobalt(II) complex is 4.75 B.M also confirms the octahedral geometry. The electronic spectrum of nickel(II) complex exhibits three d-d bands at  $10010 \text{ cm}^{-1}$  ( $\epsilon$ ,  $68 \text{ M}^{-1} \text{ cm}^{-1}$ ),  $13349 \text{ cm}^{-1}$  ( $\epsilon$ ,  $105 \text{ M}^{-1} \text{ cm}^{-1}$ ) and  $23849 \text{ cm}^{-1}$  ( $\epsilon$ ,  $131 \text{ M}^{-1} \text{ cm}^{-1}$ ) which can be assigned to  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$ ,  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$

and  ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$  transitions respectively. The magnetic moment for nickel(II) complex is 2.95 B.M. It is well within the range expected for octahedral geometry around the central metal ion.

### Infrared spectral studies

In IR spectrum, the ligand (CPHAHT) shows a broad band centered at  $3186\text{ cm}^{-1}$  which is characteristic of  $\nu(\text{OH})$ . This band disappears in all the complexes, which can be attributed to the involvement of phenolic  $-\text{OH}$  in coordination. The involvement of deprotonated phenolic moiety in complexes is confirmed by the shift of  $\nu(\text{C}-\text{O})$  stretching band observed at  $1212\text{ cm}^{-1}$  in the free ligand to a lower frequency to the extent of  $10\text{--}20\text{ cm}^{-1}$ . The shift of  $\nu(\text{C}-\text{O})$  band at  $1212\text{ cm}^{-1}$  to a lower frequency suggests the weakening of  $\nu(\text{C}-\text{O})$  and formation of stronger  $\text{M}-\text{O}$  bond. In IR spectrum, the bands around  $1420$  and  $1644\text{ cm}^{-1}$  for the ligand (CPHAHT) attributed to the  $\nu(\text{C}=\text{N})$  groups are shifted to  $1407$  and  $1636\text{ cm}^{-1}$ . The strong sharp band that appears at  $1644\text{ cm}^{-1}$  is due to exocyclic  $\nu(\text{C}=\text{N})$  stretching vibration. The band at  $1420\text{ cm}^{-1}$  is characteristic of triazine moiety and the band at  $958\text{ cm}^{-1}$  is due to  $\nu(\text{N}-\text{N})$  stretching. The IR spectra of metal(II) complexes show significant variations when compared with the free ligand spectrum. The  $\nu(\text{C}=\text{N})$  mode of ligand is found to shift to the lower frequency suggesting that the coordination of nitrogen atom to the central metal ion. The broad band at around  $3400\text{ cm}^{-1}$  for the complexes suggests the existence of coordinated water in all the complexes. The  $\nu(\text{C}=\text{N})$  shifts to lower frequency also indicates stronger  $\text{M}-\text{N}$  bonding. Thus a

band observed between  $418\text{--}458\text{ cm}^{-1}$  is attributed to  $\nu(\text{M}-\text{N})$  stretching vibrations. In addition, a band observed between  $510\text{--}537\text{ cm}^{-1}$  which is assigned to the interaction of phenolic oxygen to the metal atom, i.e., the stretching vibrations of  $\nu(\text{M}-\text{O})$  respectively. The bands at  $910$ ,  $887$ ,  $853$  and  $860\text{ cm}^{-1}$  are due to  $\nu(\text{N}-\text{N})$  stretching modes of  $\text{Cu(II)}$ ,  $\text{Co(II)}$ ,  $\text{Ni(II)}$  and  $\text{Zn(II)}$  complexes respectively. The shift of this band to a lower value also indicates the coordination of nitrogen atom to the metal ion.

### NMR spectral studies

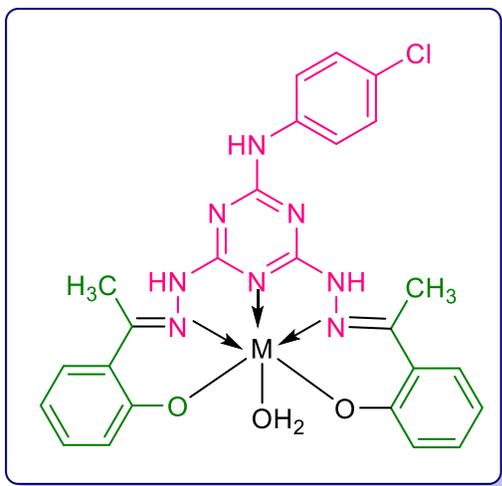
The  ${}^1\text{H}$  NMR spectra of ligand was recorded in DMSO using tetramethylsilane (TMS) as internal standard. The  ${}^1\text{H}$  NMR spectrum of ligand (CPHAHT) peaks at  $2.57\text{--}2.65\text{ ppm}$  ( $\delta$ ) is due to six methyl protons. Aromatic protons have resonated in the range  $6.93\text{--}7.90\text{ ppm}$  ( $\delta$ ). The two singlets at  $11.5\text{ ppm}$  ( $\delta$ ) ( $2\text{H}$ , s,  $=\text{N}-\text{NH}$ ) and  $12.1\text{ ppm}$  ( $\delta$ ) ( $1\text{H}$ , s,  $\text{NH}$  substituted benzene ring) correspond to  $-\text{NH}$  protons.

### ESR spectral studies

The ESR spectrum of copper(II) complex was recorded in DMSO. The 'g' tensor values of the copper(II) complex can be used to derive the ground state. The observed spectral parameters of the complex show  $g_{\parallel} > g_{\perp}$  value is characteristic of an octahedral geometry. The  $g_{\parallel} > g_{\perp} > g_e$  ( $2.0027$ ) observed for the complex reveals that the unpaired electron is localized in the  $d_{x^2-y^2}$  orbital of the copper(II) ions. The  $g_{\parallel}/A_{\parallel}(169.6\text{ cm})$  ratio suggests the distorted octahedral geometry. As the value  $g_{\parallel}$  value is found to be lesser than  $2.3$  the metal-ligand bonds must be covalent in nature. It is clear that  $K_{\parallel} < K_{\perp}$  is for in-plane  $\pi$  bonding and

$K_{\parallel} > K_{\perp}$  for out of plane  $\pi$  bonding. The copper complex is in good agreement with the relation  $K_{\parallel} > K_{\perp}$  which indicates the presence of out of plane  $\pi$  bonding.

On the basis of the above physico-chemical evidences, the following structure has been assigned for the metal complexes of  $[M(L)H_2O]$  type. (Fig.1)



M = Cu(II), Co(II), Ni(II) and Zn(II)

**Fig.1. Proposed structure of metal(II) complexes**

### Fluorescence studies

The fluorescent properties of ligand and its metal complexes were studied in DMSO. A significant difference in the positions of emission maxima of ligand and its metal complexes indicates the complexation process. The metal complexes show broad emission bands indicating the charge transfer nature of the transitions. They exhibit strong fluorescence with high quantum yield compared to ligand. This can be better explained by electronic charge transfer processes. The pronounced shift in the emission of metal complexes clearly indicates that the dipole moment of the excited state is higher compared to that in the ground state. In such cases, relative to

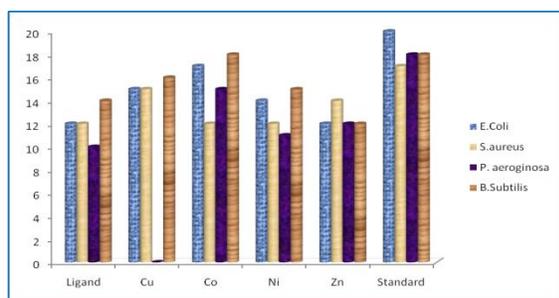
the ground state  $S_0$ , the excited state  $S_1$  will be energetically stabilized and a significant red shift of the fluorescence will be observed.

### NLO property

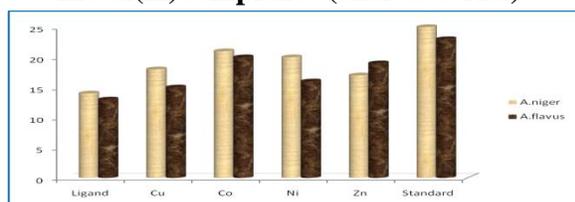
The efficiency of the ligand was compared with microcrystalline powder of KDP and urea. The ligand exhibits 3.2 times greater SHG efficiency with respect to KDP and 0.73 times greater with respect to urea.

### Biological activity

The ligand and its metal complexes were screened for their antibacterial and antifungal activities. All the compounds were tested against both Gram positive (*Staphylococcus aureus*, *Bacillus subtilis*) and Gram negative (*Pseudomonas aeruginosa*, *Escherichia coli*) bacteria. Amikazin and ketoconazole have been used as standard reference compounds for antibacterial and antifungal activities respectively. Biological study reveals that the complexes exhibit higher antimicrobial activity than the ligand. Such an enhanced activity can be explained on the basis of chelation theory. The cobalt complex is found to be more effective against *E. coli* with the zone of inhibition 17 mm and more than 50% inhibition of mycelia growth against *A. niger*. Biospectrum of ligand (CPHAHT) and its metal(II) complexes are presented in **Fig.2.a and b**.



**Fig.2 (a) Biospectrum of ligand and its metal(II) complexes (antibacterial)**



**Fig.2 (b) Biospectrum of ligand and its metal(II) complexes (antifungal)**

#### 4. Conclusion

The metal(II) complexes of Cu(II), Co(II), Ni(II) and Zn(II) obtained from 2-(4-chlorophenyl)amino-4,6-bis(2-(hydroxyacetopheno)hydrazinyl)-1,3,5-triazine (CPHAHT) were synthesized and characterized by spectral and analytical methods. The spectral and analytical data confirm the bonding of ligand to metal(II) ions and the octahedral geometry of metal(II) complexes. The ligand exhibits appreciable nonlinear optical property in comparison with KDP and urea, hence the compound can be studied for optical sensing material for further applications. Ligand and its metal(II) complexes are fluorescent in nature. Most of the metal chelates show better antimicrobial activity than ligand, particularly Co(II) complex has higher antimicrobial activity compared to other complexes.

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