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## **Studies on A Novel S-Triazine Based ONO Donor Heterocyclic Ligand and its Transition Metal(II) Complexes**

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**Abstract:** A series of metal(II) complexes of a novel ONO donor type ligand 4,6-bis(antipyrin-4-ylamino)-N-phenyl-2-amino-1,3,5-triazine with general formula  $ML(NO_3)_2 \cdot H_2O$  [ where M= Cu(II), Ni(II), Co(II) and Zn(II) ] have been synthesized. The structural features of the ligand and the metal complexes have been characterized by micro analytical data, magnetic susceptibility measurements, molar conductance, IR, UV-VIS,  $H^1$  NMR spectral techniques. Cyclic voltammogram of copper(II) complex reveals that the redox process is irreversible one. The free ligand and their metal complexes have been screened for their in vitro biological activity against bacteria *E.Coli*, *Pseudomonas aeruginosa*, *Bacillus subtilis* and *Vibrio.sp* and the fungi *Candida albican* by well diffusion method and reveal that the metal(II) complexes have increased activity than that of free ligand.

**Keywords:** s-triazine, 4-amino antipyrine, metal(II) complexes and biological activity.

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### **1. INTRODUCTION**

Triazines and their derivatives have been widely studied in terms of synthetic methodologies and their promising biological activities. Among them 1,3,5-triazine possessing threefold symmetry was chosen as the scaffold because they allow for versatile modifications uncomplicated by regiochemical concerns and have proven themselves to be useful biological targets.<sup>1-3</sup> Several derivatives of s-triazine show antibacterial, antimicrobial<sup>4</sup>, and herbicidal activities. Amino substituted s-triazine derivatives are associated with number of pronounced antibacterial activities against gram positive and gram negative organism. 4-Aminoantipyrine is known for the variety of its clinical applications such as anti-inflammatory, analgesic, antipyretic<sup>5,6</sup> and several chemotherapeutic agents<sup>7</sup>. Compounds possessing pyrazole nuclei showed significant antihelmintic as well as antimicrobial activities<sup>8-11</sup>. Hence the present work deals with the synthesis of rationally designed a multidentate s-triazine based ligand with pyrazolone moiety and the biological activity of metal (II) complexes.

### **2. EXPERIMENTAL**

#### **2.1. Materials and Physical Measurements**

The solvents used in the reactions were dried as per standard procedures. The UV-vis spectra was recorded using a JASCO V-530 Spectrophotometer. The metal content of the complexes was estimated by incinerating them in to oxides<sup>12</sup>. FT-IR spectra was recorded on a SHIMADZU FT-IR spectrophotometer using KBr discs.  $H^1$  NMR spectrum was recorded in a Bruker DRX-300, 300 MHz NMR spectrometer, using TMS as reference. Magnetic susceptibility measurements were performed at room temperature using Sherwood MSB Mark 1, Gouy Balance UK. Cyclic voltammetry measurement was carried out with an electrochemical analyzer using a three-electrode cell containing a reference SCE, Pt wire auxiliary electrode, and glassy carbon working electrode with tetrabutylammoniumperchlorate (TBAP) as supporting electrolyte.

#### **2.2. Synthesis of 4,6-bis(antipyrin-4-ylamino)-N-phenyl-2-amino-1,3,5-triazine (BAPT)**

2-Amino antipyrine (20 mmol) in THF was refluxed with 2-phenylamino-4,6-dichloro-1,3,5-triazine (10 mmol) in THF for 6 hrs in presence of  $NaHCO_3$ . The resulting mixture was poured

into ice cold water and the pale yellow solid separated was filtered, recrystallised from hot ethanol, and dried in vacuum.

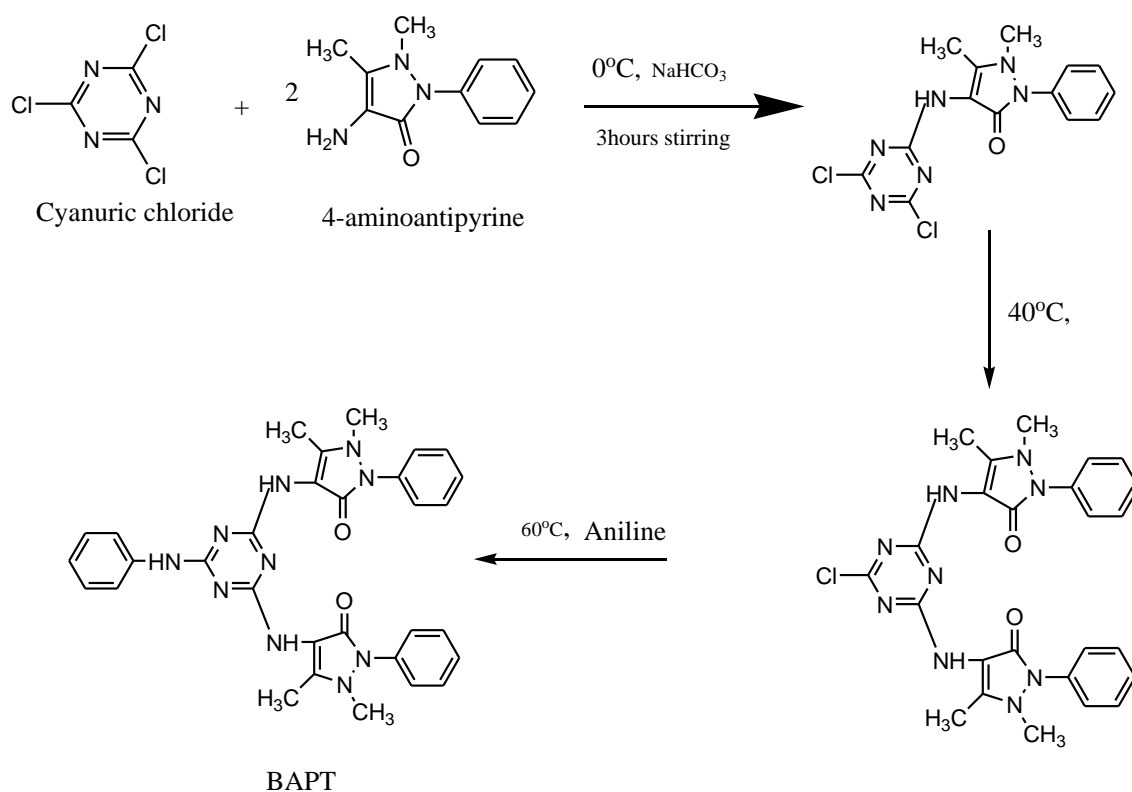
IR,  $\nu_{\max}$  (KBr) $\text{cm}^{-1}$  1666( $\nu_{\text{C=O}}$ ), 1756( $\nu_{\text{C=N}}$ ),  $^1\text{H}$  NMR (in DMSO  $\delta/\text{ppm}$ ) 6.9-7.5  $\delta$  (5H,m, for aromatic ring protons), 1.25 $\delta$  (6H, s, =C-CH<sub>3</sub>), 2.14 $\delta$  (6H, s, N-CH<sub>3</sub>), 3.2 $\delta$  (1H, -NH-Ph) and 3.95 $\delta$  (2H, s, 3.95 $\delta$  -NH-pyrazole).

### 2.3. Synthesis of Metal (II) Complexes

The solution of BAPT in ethanol (10 mmol) was refluxed with metal(II) nitrates (10 mmol) in ethanol for 2 hrs. The characteristic colored complex precipitated was filtered, washed with ethanol and dried in vacuum.

### 3. RESULT AND DISCUSSION

All the complexes are intensely coloured and stable at room temperature. The metal(II) complexes are soluble in common organic solvents. Analytical and molar conductance data of ligand and metal(II) complexes are given in table-1. The molar conductance of complexes in DMF solution is in the range 101-120  $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ , which is a characteristic of 1:1 electrolytic nature<sup>13</sup> of the complexes.



**Fig 1.** Scheme for synthesis of ligand

**Table 1.** Physical properties and analytical data of ligand and its metal(II) complexes

Compound	Colour	M. Pt ( $^\circ\text{C}$ )	Elemental analysis Found (calculated) %					Molar conductance $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$
			M	C	N	H	O	
BAPT	Light brown	>260	-	64.30 (64.81)	24.11 (24.39)	5.03 (5.20)	5.64 (5.57)	-
[Cu(BAPT)(NO <sub>3</sub> )(H <sub>2</sub> O)](NO <sub>3</sub> )	Green	>360	8.51 (8.10)	46.91 (47.69)	21.21 (21.55)	4.04 (4.15)	17.93 (18.47)	104.9
[Co(BAPT)(NO <sub>3</sub> )(H <sub>2</sub> O)](NO <sub>3</sub> )	Blue green	>360	7.82 (7.44)	47.10 (46.92)	20.93 (21.18)	4.14 (4.28)	19.59 (20.18)	118.4
[Ni(BAPT)(NO <sub>3</sub> )(H <sub>2</sub> O)](NO <sub>3</sub> )	Brown	>360	7.70 (7.40)	46.52 (46.92)	20.86 (21.19)	4.15 (4.28)	20.33 (20.17)	101.2

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[Zn(BAPT)(NO <sub>3</sub> )(H <sub>2</sub> O)](NO <sub>3</sub> )	White	>360	8.41 (8.17)	46.31 (46.53)	20.88 (21.01)	4.09 (4.25)	20.22 (20.00)	103.4
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### 3.1. IR Spectral Studies

The IR spectra of the compound BAPT shows band at 1576cm<sup>-1</sup> corresponds to the  $\nu(\text{C}=\text{N})$  stretching modes of the triazine ring<sup>14</sup>. A sharp band at 1666cm<sup>-1</sup> is the characteristic of (C=O) stretching mode<sup>15</sup> is shifted to 1643–1618cm<sup>-1</sup> region indicating the coordination of -C=O of the pyrazolone moiety of the ligand to the M(II) ion.

In the case of complexes the strong absorption bands that appear around 1576 cm<sup>-1</sup> correspond to the  $\nu(\text{C}=\text{N})$  stretching vibrations of the triazine rings of the ligand exhibit a shifts as well as splitting indicating the involvement of s- triazine nitrogen in coordination<sup>16</sup>. Apart from that new bands appeared around 1384 cm<sup>-1</sup> and 1017 cm<sup>-1</sup> characteristics of nitrate group<sup>17</sup> in coordination. The weak bands appeared in the complexes around 400-430 cm<sup>-1</sup> and 587 cm<sup>-1</sup> region can be assigned to  $\nu(\text{M}-\text{N})$  and  $\nu(\text{M}-\text{O})$  vibration<sup>18</sup> respectively and confirm the interaction between the metal and the ligand. The high frequency region of the IR spectra shows an unresolved absorption band in the region 3200-3600 cm<sup>-1</sup> which comprised of stretching modes of coordinated water

Compound	$\nu_{\text{C}=\text{O}}$	$\nu_{\text{C}=\text{N}}$	$\nu_{\text{NO}_3^-}$	$\nu_{\text{M}-\text{O}}$	$\nu_{\text{H}_2\text{O}}$
BAPT	1666	1576	-	-	-
[Cu(BAPT)(NO <sub>3</sub> )(H <sub>2</sub> O)](NO <sub>3</sub> )	1637	1505	1384	588	3560
[Co(BAPT)(NO <sub>3</sub> )(H <sub>2</sub> O)](NO <sub>3</sub> )	1613	1547 1518	1384, 1017	587	3396
[Ni(BAPT)(NO <sub>3</sub> )(H <sub>2</sub> O)](NO <sub>3</sub> )	1643	1510	1384	586	3396
[Zn(BAPT)(NO <sub>3</sub> )(H <sub>2</sub> O)](NO <sub>3</sub> )	1660	1503	1384	587	3586

molecules and NH group<sup>19</sup>.

**Table 2.** IR stretching frequencies (cm<sup>-1</sup>) for the ligand and metal(II) complexes

### 3.2. Electronic Spectra and Magnetic moment

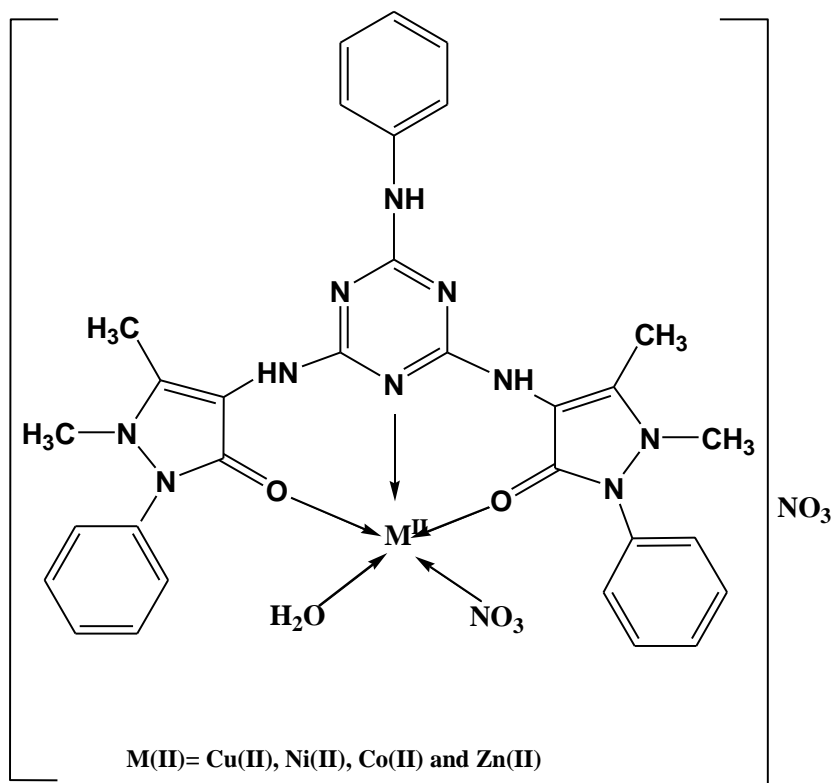
The UV–Vis spectra of the complexes were recorded in DMF and characterized by several spectral regions. The absorption bands for the ligand in the region of 26525 cm<sup>-1</sup> and 37037 cm<sup>-1</sup> are due to  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  transition (INCT transition)<sup>18,20,21</sup>. The electronic spectral data of the complexes are given in Table-3. The electronic spectrum of Cu(II) complex exhibits two absorption bands around 16920 cm<sup>-1</sup> and 19880 cm<sup>-1</sup> which may be tentatively assigned to the transition  ${}^2\text{B}_1 \rightarrow {}^2\text{A}_1$  ( $\nu_1$ ) and  ${}^2\text{B}_1 \rightarrow {}^2\text{E}_g$  ( $\nu_2$ ) respectively for a square pyramidal geometry<sup>22-24</sup>. The electronic spectrum of Ni(II) complex appears bands at 10132 cm<sup>-1</sup>, 13017 cm<sup>-1</sup>, and 17605 cm<sup>-1</sup> due to the transitions  ${}^3\text{B}_1(\text{F}) \rightarrow {}^3\text{E}(\text{F})$ ,  ${}^3\text{B}_1(\text{F}) \rightarrow {}^3\text{A}_2(\text{P})$  and  ${}^3\text{B}_1(\text{F}) \rightarrow {}^3\text{E}(\text{P})$  respectively consistent with five-coordinate square pyramidal geometry for nickel(II) complexes<sup>26, 27,28,29</sup>.

The Co(II) complex displayed two absorption bands at 11750 cm<sup>-1</sup> and 17650 cm<sup>-1</sup> which can be assigned to the transitions  ${}^4\text{A}_2 \rightarrow {}^4\text{B}_1$  and  ${}^4\text{A}_2 \rightarrow {}^4\text{E}(\text{P})$  respectively which are characteristic of square pyramidal geometry<sup>30,31</sup>. The magnetic moment of Cu(II) complex is 1.74BM (Table-2) also suggestive of the five coordinate square pyramidal geometry<sup>32</sup>. Cobalt(II) and Nickel(II) complexes have magnetic moment values 3.11 BM and 2.84 BM respectively<sup>33</sup> also further confirms the square pyramidal geometry. From all the above spectral and analytical data, the following structure (Fig-2) has been proposed for the metal(II) complexes.

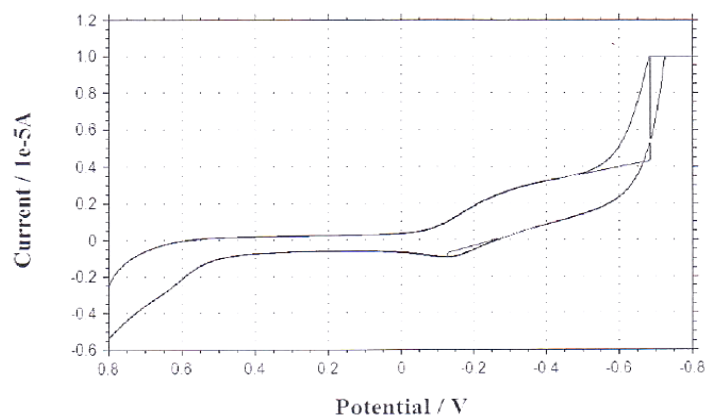
**Table 3.** Electronic spectral data(cm<sup>-1</sup>) of ligand and metal(II) complexes

Compound	$\lambda_{\max}$ (cm <sup>-1</sup> )	Band assignment	Geometry	Magnetic moment $\mu_{\text{eff}}$ (BM)
Ligand	26525 37037	$n \rightarrow \pi^*$ INCT $\pi \rightarrow \pi^*$ INCT	-	-
[Cu(BAPT)(NO <sub>3</sub> )(H <sub>2</sub> O)](NO <sub>3</sub> )	16920 19880 23041	${}^2B_1(F) \rightarrow {}^2A_1(v_1)$ ${}^2B_1 \rightarrow {}^2E_g(v_2)$ INCT	Square pyramidal	1.74
[Ni(BAPT)(NO <sub>3</sub> )(H <sub>2</sub> O)](NO <sub>3</sub> )	10132 13017 17605	${}^3B_1(F) \rightarrow {}^3E(F)$ ${}^3B_1(F) \rightarrow {}^3A_2(P)$ ${}^3B_1(F) \rightarrow {}^3E(P)$	Square pyramidal	2.84
[Co(BAPT)(NO <sub>3</sub> )(H <sub>2</sub> O)](NO <sub>3</sub> )	11750 17605	${}^4A_2 \rightarrow 4B_1$ ${}^4A_2 \rightarrow 4E(P)$	Square pyramidal	3.11

### 3.3. Electrochemical Behaviour



**Fig 2.** Proposed structure of the metal(II) complexes



**Fig 3.** Cyclic Voltammogram of the Cu(II) complex

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Cyclic voltammogram of copper(II) complex(Fig-3) displays a pair of oxidation-reduction peaks at -0.683V and-0.127V. The redox peak potential separation ( $\Delta E_p$ ) of 556 mV suggests that the Cu(II)/Cu(I) redox couple was irreversible<sup>34</sup> in nature. The ratio of anodic to cathodic peak currents ( $I_{pc}/I_{pa} \approx 1$ ) corresponding to a simple one electron process. The irreversibility observed for the reductive response of the complex may be due to a short-lived reduced state of the metal(II) ion or due to the oxidative degradation of the ligand<sup>35</sup>.

### 3.4. Antimicrobial Activity

All the newly synthesized ligand and the metal(II) complexes were screened for their antibacterial activity. The microorganisms employed for antibacterial studies were *Bacillus subtilis*, *E.Coli* and *Pseudomonas aeruginosa* and *Vibrio.sp* and the organism used for antifungal studies was *candida albicans*. Antimicrobial studies were assessed by well diffusion method. Amikacin and Ketoconazole were taken as the standard for antibacterial and antifungal studies respectively.

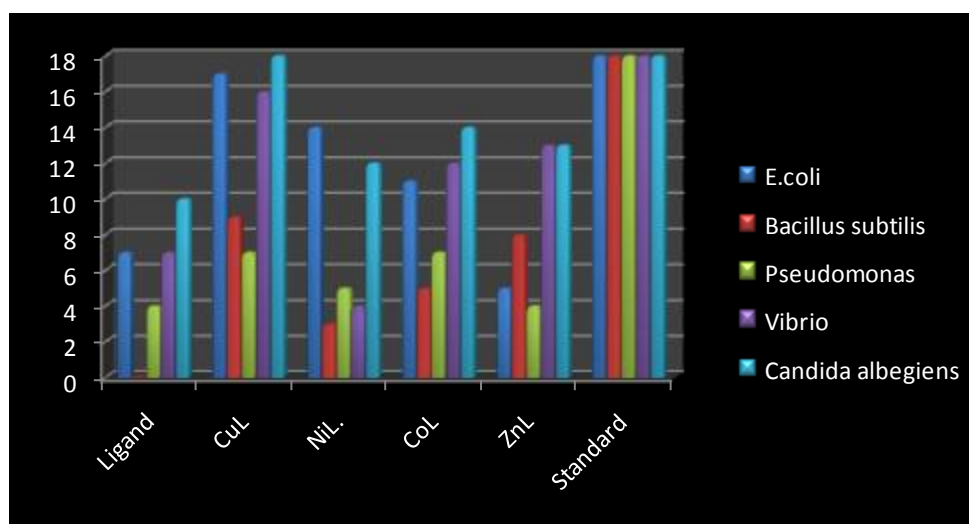


Fig 4. Antimicrobial activity of the ligand and metal(II) complexes

Table 4. Zone of inhibition in mm

	<i>E.coli</i>	<i>Bacillus subtilis</i>	<i>Pseudomonas.sp</i>	<i>Vibrio.sp</i>	<i>Candida albicans</i>
Ligand	7	0	4	7	10
[Cu( BAPT)(NO <sub>3</sub> )(H <sub>2</sub> O)](NO <sub>3</sub> ) (CuL)	17	9	7	16	18
[Ni( BAPT)(NO <sub>3</sub> )(H <sub>2</sub> O)](NO <sub>3</sub> ) (NiL)	14	3	5	4	12
[Co( BAPT)(NO <sub>3</sub> )(H <sub>2</sub> O)](NO <sub>3</sub> ) (CoL)	11	5	7	12	14
[Zn( BAPT)(NO <sub>3</sub> )(H <sub>2</sub> O)](NO <sub>3</sub> ) (ZnL)	5	8	4	13	13
Standard	18	18	18	18	21

The antimicrobial activity data clearly illustrates that the metal complexes have significant antibacterial activity against tested organism. All complexes displayed a high order of antibacterial activity than the ligand. From Table-4 it is concluded that the Cu(II) complex showed higher activity whereas the other M(II) complexes exhibit moderate activity. Cu(II) complex has significant activity against *E.Coli* and *Candida albicans* which is similar to the standard. From the Fig-4 it is clear that all the compounds have displayed maximum activity against *E.Coli* and *Candida albicans* and a moderate activity against other bacteria. Overton's concept and Chelation theory explains the increased microbial toxicity of the complexes than the ligand.

#### 4. CONCLUSION

A novel ONO tridentate donor s-triazine based ligand and its transition metal(II) complexes have been synthesized and characterized. From the spectral and analytical data all the M(II) complexes are tentatively assigned as square pyramidal geometry. Cyclic voltammogram of copper(II) complex reveals that the redox process is irreversible one. The antimicrobial studies clearly illustrate that the metal(II) complexes have significant antimicrobial activity against tested organism and found to be showing comparable activity against some bacteria compared to standard antibiotic drugs. The produced compounds possess good microbial toxicity due to presence of two pharmacologically active s-triazine, and pyrazolone nuclei.

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