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# Synthesis and Characterisation of Metal chelates of (5-(2,3-dimethyl-1-phenyl-3-pyrazolin-5-one-4-ylazo)-1H-pyrimidine-2,4-dione)

VIDYA V G and V SADASIVAN

University College, M G Road, Palayam, Thiruvananthapuram- 695 034, Kerala, (India)

Corresponding Author Email:- [vg\\_vidya@yahoo.co.in](mailto:vg_vidya@yahoo.co.in)

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### Abstract

An azo dye UAAP and Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes were synthesized and characterized using elemental analysis, mass spectra, UV- Vis, fluorescence spectra, ESR spectrum, IR spectra, NMR spectra, NLO property, molar conductance and magnetic measurements. The spectral and analytical data reveal that UAAP act as both bidentate and tridentate ligand. The molar conductance data reveal that complexes Co(II), Cu(II) and Zn(II) are nonelectrolytic and Mn(II), Ni(II) 1:2 electrolyte in nature. Based on all data structures were proposed for UAAP and complexes. The UAAP and metal complexes were screened for antimicrobial activity, antioxidant study, DNA cleavage analysis and anticancerous investigation.

*Key words:* Azo dye, Uracil, NLO

### Introduction

The chemistry of pyrimidines is extensively investigated as they are well known for their widespread potential activities and medicinal application<sup>1,2,3,4</sup>. They have the most important role in structure and function of nucleic acids. The pyrimidine derivatives are of interest due to its potential important in genetics and its related fields<sup>9</sup>. Due to their potent biological character and presence of their moieties in various vitamins, they are used in area of drugs and agriculture<sup>5</sup>. 5-substituted 1H-pyrimidine-2,4-dione

were reported to be important core structure of diverse therapeutics. The transition metal complexes of azodyes derived from 4-amino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one have been studied extensively due to their wide applications in various fields<sup>6</sup>.

This paper deals with synthesis and characterisation of some new complexes of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with the azo dye [5-(2,3-dimethyl-1-phenyl-3-pyrazolin-5-one-4-ylazo)-1H-pyrimidine-2,4-dione] derived from 1H-pyrimidine-2,4-dione and diazotised 4-amino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one.

## Experimental

### *Preparation of UAAP :*

About 5 g of 4-aminoantipyrine dissolved in 25 ml 1:1 HCl and cooled to 0°C. To this an ice cold solution of 1.8 g sodium nitrite was added slowly with stirring. The reaction mixture was allowed to remain in ice bath for 30 minutes for the completion of reaction. The presence of excess of HNO<sub>2</sub> was tested with starch iodide paper and was destroyed by adding urea. 2.75 g of uracil was dissolved in 45 ml 10% NaOH solution. After making solution clear, cooled to below 5°C. The cold diazotised solution of 4-aminoantipyrine was added to this with vigorous stirring. The colour of the solution turned yellow. A yellow solid product was separated slowly. The mixture was allowed to stand for 30 minutes. The product obtained was filtered under suction, washed well with cold water and dried over anhydrous calcium chloride. The product was recrystallized from DMF. Yield was 86%.

### *Preparation of complexes :*

The complexes of 5-(2,3-dimethyl-1-phenyl-3-pyrazolin-5-one-4-yl azo)-1H-pyrimidine-2,4-dione [UAAP] with Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes were prepared by the following general method. A methanolic solution of the corresponding metal salt Mn(Ac)<sub>2</sub>.4H<sub>2</sub>O, Co(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O, NiCl<sub>2</sub>.6H<sub>2</sub>O, CuCl<sub>2</sub>.2H<sub>2</sub>O and Zn(Ac)<sub>2</sub>.2H<sub>2</sub>O (0.01 mole) was added to a solution of UAAP (0.01 mole) in methanol. The metal salt to ligand molar ratio was kept in 1:1. The resulting mixture was stirred and refluxed for 3-4 hours. The solution thus obtained is concentrated to get solid complex. It was filtered off washed with ethanol, dried and kept in a dessicator over anhydrous CaCl<sub>2</sub>. Yield was 75-79%.

C, H, N and S contents of ligands and complexes were determined by microanalytical methods. About 0.2 g of the complex was digested with concentrated sulphuric acid and perchloric acid. The resulting clear solution was evaporated to dryness and residue was extracted with distilled water. This aqueous solution after neutralization was used as such for estimation of metal ions.

Molar conductivities of newly synthesized complexes in nitrobenzene and methanol were

determined at room temperature using Systronics direct reading conductivity meter. The magnetic susceptibility of the complexes were recorded at room temperature on a Sherwood Scientific magnetic susceptibility balance. The electronic absorption spectral measurements of the ligands and complexes in methanol were recorded on Perkin-Elmer Lambda 25 UV-Visible spectrophotometer in the range 200 to 800 nm. The IR spectra of the ligands and complexes were recorded on a Perkin-Elmer spectrum 65 infrared spectrometer using KBr pellets in the region 400-4000 cm<sup>-1</sup>. The proton NMR spectra of the ligands and the complexes were recorded in DMSO on a 400 MHz FTNMR instrument using TMS as reference material. The ESI mass spectra of ligands and their zinc complexes were recorded on FTMS mass spectrometer. The X band ESR spectra of three copper complex was recorded in solid, solution and in frozen state on a Varian E-112 spectrometer using TCNE as reference. The fluorescence spectral measurements of UAAP and complexes in methanol were recorded on a JASCO-750 fluorescence spectrometer. The cyclic voltammograms of cobalt(II) complex was recorded on a BAS CV-50W voltammetric analyser. UAAP and Mn(II) complex were evaluated for their nonlinear optical activity.

The ligands and complexes were subjected to antimicrobial study and were screened against microbes by adapted qualitative diffusimetric methods. The ligands and their selected metal complexes were studied for their antioxidant activity by DPPH assay. UAAP and Co metal complex were studied for the cleavage efficiency compared to that of control. Cobalt complex were evaluated for the anticancer studies against human cervical cancer cell line, SiHa and human breast cell line, SkBr<sub>3</sub>.

### *Analyses and physico-chemical studies of complexes:*

## Results and Discussion

All complexes are stable at room temperature. The complexes are soluble in DMF, DMSO and partially soluble in methanol. The microanalytical data of the complexes are presented in Table 1. The analytical data are in good agreement with the theoretical values.

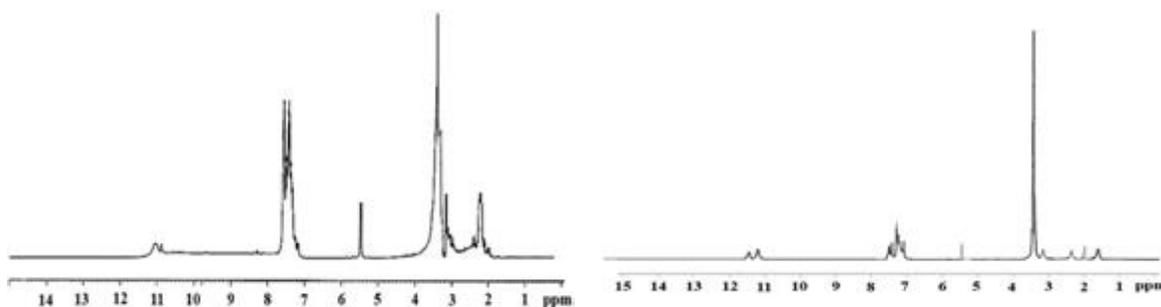
Table 1. Analytical data of Ligand UAAP and its complexes

| Complex                                    | Colour | Mol. Wt | %M    |       | % C   |       | %H   |      | % N   |       | %Cl  |      |
|--|--------|---------|-------|-------|-------|-------|------|------|-------|-------|------|------|
|  |        |         | Cal   | Exp   | Cal   | Exp   | Cal  | Exp  | Cal   | Exp   | Cal  | Exp  |
| UAAP                                       | Yellow | 326     | -     | -     | 57.20 | 57.69 | 4.29 | 4.86 | 22.76 | 22.00 | -    | -    |
| [Mn(UAAP) <sub>2</sub> ](OAc) <sub>2</sub> | Brown  | 825     | 6.01  | 6.03  | 48.14 | 48.15 | 5.97 | 5.98 | 25.09 | 25.10 | -    | -    |
| [Co(UAAP)(NO <sub>3</sub> ) <sub>2</sub> ] | Red    | 509     | 11.57 | 11.58 | 33.00 | 33.01 | 2.55 | 2.56 | 22.01 | 22.00 | -    | -    |
| [Ni(UAAP) <sub>2</sub> ] Cl <sub>2</sub>   | Brown  | 782     | 10.61 | 10.58 | 42.98 | 42.97 | 3.30 | 3.29 | 14.32 | 14.30 | 7.17 | 7.18 |
| [Cu(UAAP) <sub>2</sub> ] Cl <sub>2</sub>   | Brown  | 787     | 8.30  | 8.32  | 42.72 | 42.73 | 3.31 | 3.32 | 10.68 | 10.67 | 9.02 | 9.03 |
| [Zn(UAAP) <sub>2</sub> ](OAc) <sub>2</sub> | yellow | 835     | 9.34  | 9.45  | 45.90 | 45.89 | 3.80 | 3.81 | 17.20 | 17.19 | -    | -    |

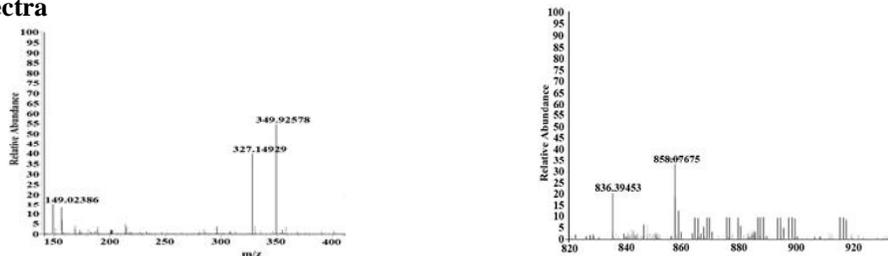
**<sup>1</sup>H-NMR spectra :**

The <sup>1</sup>H-NMR spectra of UAAP and its Zn(II) complex were recorded in d<sup>6</sup>-DMSO on a 400 MHz FTNMR spectrometer using TMS as reference material. The NMR data of UAAP and its Zn(II) complex are

presented in Table 2. A slight downfield shift was noted in all signals of the complex compared to that of UAAP. Additional peaks are at δ 1.64 ppm (3H, s) and other at δ 2.03 ppm (3H, s) appears in the <sup>1</sup>H-NMR of complex are due to the CH<sub>3</sub> group of coordinated acetate ions.

Fig. 1 <sup>1</sup>H NMR of UAAP<sup>1</sup>H NMR of [Zn(UAAP)<sub>2</sub>](OOCCH<sub>3</sub>)<sub>2</sub>Table 2 <sup>1</sup>H NMR signals of the ligands

| UAAP (δ ppm)    | [Zn(UAAP) <sub>2</sub> ](OOCCH <sub>3</sub> ) <sub>2</sub> (δ ppm) | Assignments              |
|-----------------|--|--------------------------|
| 11.02 (s)       | 11.22 (s)  | N-H proton               |
| 10.99 (s)       | 11.10 (s)  |                          |
| 7.57 – 7.72 (m) | 7.17 - 7.81 (m)  | Aryl proton              |
| 5.47 (s)        | 5.28 (s)   | Vinyl proton             |
| 2.23 (s)        | 2.31 (s)   | C-CH <sub>3</sub> proton |
| 3.15 (s)        | 3.26 (s)   | N-CH <sub>3</sub> proton |
| -               | 2.03 (s) 1.64 (s)  | CH <sub>3</sub> COO      |

**Mass spectra**Fig. 2 Mass spectra of UAAP and [Zn(UAAP)<sub>2</sub>](CH<sub>3</sub>COO)<sub>2</sub>

The mass spectrum of UAAP consists of a peak corresponds to the species  $[(C_{15}H_{14}N_6O_3)Na]^+$  at  $m/z$  349 and  $[C_{15}H_{14}N_6O_3]^+$  at  $m/z$  327. These are assignable to  $[M + Na]^+$  and  $[M + 1]^+$  peaks. The co-occurrence of the two peaks undoubtedly express the molecular formula of the azo dye UAAP as  $C_{15}H_{14}N_6$ . Mass spectrum of Zn(II) complex shows a molecular ion peak at  $m/z$  836 corresponds to molecular ion species  $[Zn(UAAP)_2(CH_3-COO)_2]^-$  and its stoichiometry is again confirmed by the presence of another peak at  $m/z$  858 assignable to its  $(M+Na)$  species, which is  $[Zn(UAAP)_2(CH_3COO)_2Na]^+$ . A peak at  $m/z$  469 is due to the detachment of one azo component, two pyrimidine ring and two acetate group from zinc complex, which corresponds to species  $[C_{22}H_{22}N_6O_2Zn]$ . A peak at  $m/z$  440 is due to the existence of zinc ion bonded to two pyrazolone ring, that corresponds to species  $[C_{22}H_{22}N_4O_2Zn]$ . From the mass spectra it can be confirmed that two ligand molecules are coordinated to Zn(II) along with two acetate ions which is confirmed from its non electrolytic behavior. The mass spectra is shown in Fig.2.

#### Infrared spectra :

The important IR spectral bands of the ligand

5-(2,3-dimethyl-1-phenyl-3-pyrazolin-5-one-4-ylazo)-1H-pyrimidine-2,4-dione (UAAP) and its complexes are listed in Table 3. In the IR spectrum of UAAP, band at  $1455\text{cm}^{-1}$  corresponds to  $\nu_{N=N}$  was shifted to lower frequency range  $1409\text{-}1419\text{ cm}^{-1}$  indicating the coordination of  $-N=N-$  group to metal ion<sup>7</sup>. The  $\nu_{C=O}$  band of pyrazolone ring is shifted from  $1677\text{ cm}^{-1}$  to lower value in the range  $1647\text{-}1670\text{ cm}^{-1}$ <sup>8</sup>. The involvement of  $>C=O$  on pyrimidine ring is indicated by the shift in  $\nu_{C=O}$  from  $1748\text{ cm}^{-1}$  to  $1704 - 1737\text{ cm}^{-1}$ <sup>9</sup>. The appearance of new band around  $520\text{ cm}^{-1}$  and  $440\text{ cm}^{-1}$  are assignable to  $\nu_{M-O}$  and  $\nu_{M-N}$  stretching frequency in complexes<sup>10,11</sup>. The IR spectral evidence indicates that UAAP is acting as neutral bidentate ligand in  $[Cu(UAAP)_2Cl_2]$  and  $[Zn(UAAP)_2(OOC-CH_3)_2]$  complexes. In this case the coordination to the metal ion is through the azo group and carbonyl group on pyrimidine ring. UAAP acts as neutral tridentate ligand in  $[Mn(UAAP)_2](OOC-CH_3)_2$ ,  $[Co(UAAP)(NO_3)_2]$  and  $[Ni(UAAP)_2]Cl_2$  complexes where the coordination to metal ion is through the azo group and carbonyl group of both pyrimidine ring and pyrazolone ring.

Table 3 IR data of complexes of UAAP

| UAAP | $[Mn(UAAP)_2](OOCCH_3)_2$ | $[Co(UAAP)(NO_3)_2]$ | $[Ni(UAAP)_2]Cl_2$ | $[Cu(UAAP)_2Cl_2]$ | $[Zn(UAAP)_2](OOCCH_3)_2$ | Band assignments         |
|------|---------------------------|----------------------|--------------------|--------------------|---------------------------|--------------------------|
| 3397 | 3389                      | 3389                 | 3392               | 3393               | 3396                      | $\nu_{NH}$               |
| 3224 | 3218                      | 3231                 | 3220               | 3221               | 3225                      |                          |
| 2933 | 2933                      | 2932                 | 2933               | 2933               | 2933                      | $\nu_{CH}$ aromatic      |
| 1748 | 1735                      | 1737                 | 1738               | 1724               | 1708                      | $\nu_{C=O}$ (pyrimidine) |
| 1677 | 1670                      | 1650                 | 1660               | 1677               | 1677                      | $\nu_{C=O}$ (pyrazolone) |
| 1455 | 1419                      | 1419                 | 1419               | 1419               | 1409                      | $\nu_{N=N}$              |
| 823  | 809                       | 862                  | 860                | 860                | 823                       | $\nu_{CH}$ bend          |
| -    | 526                       | 520                  | 527                | 529                | 520                       | $\nu_{M-O}$              |
| -    | 410                       | 438                  | 436                | 441                | 443                       | $\nu_{M-N}$              |

**Molar conductance :**

The molar conductance at room temperature was determined using  $10^{-3}$ M solutions of the complexes in methanol and nitrobenzene. The molar conductance data are presented in Table 4. The molar conductance value of newly prepared Co(II), Cu(II) and Zn(II) complexes are observed in the range 5 - 14  $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$  in methanol and 2 - 10 in nitrobenzene revealing their nonelectrolytic nature. Mn(II) and Ni(II) complexes show molar conductance values 180 and 200  $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$  in methanol and 45 and 53  $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$  in nitrobenzene suggesting them as 1 : 2 electrolytes<sup>12</sup>.

**3.4.5 Magnetic behaviour :**

Magnetic measurements were conducted to obtain the electronic structure and oxidation states of the central metal ion and symmetry of the complexes in certain cases. The effective magnetic moment values

of the complexes are also given in Table 4. The present  $[\text{Mn}(\text{UAAP})_2](\text{CH}_3\text{COO})_2$  complex shows a magnetic moment value of 5.90 BM. The value is very close to spin-only value of high spin octahedral complex<sup>13,14</sup>. The present  $[\text{Fe}(\text{UAAP})_2]\text{Cl}_3$  complex shows a magnetic moment value of 6.12 BM, indicates that Fe(III) is in a high spin octahedral environment<sup>15</sup>. The magnetic moment value of  $[\text{Fe}(\text{UAAP})_2\text{SO}_4]$  is 4.52 BM which indicates Fe(II) is in high spin octahedral state<sup>16</sup>. The magnetic moment value of  $[\text{Co}(\text{UAAP})(\text{NO}_3)_2]$  complex is 2.37 BM<sup>15,16</sup>. The value is very close to reported five coordinate species<sup>17</sup>. The measured magnetic moment value of  $[\text{Ni}(\text{UAAP})_2]\text{Cl}_2$  complex is 2.86 BM. This value is in the range expected for an octahedral Ni(II) complex<sup>18</sup>. The effective magnetic moment value of  $[\text{Cu}(\text{UAAP})_2\text{Cl}_2]$  complex is 1.99 BM. This value agrees with an octahedral geometry for Cu(II) ion.

Table 4 Molar conductance and magnetic moment values of UAAP complexes

| Complex   | Concentration x $10^{-3}$ M | Conductance ( $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ) |              | Magnetic moment (BM) |
|---|-----------------------------|---|--------------|----------------------|
|   |                             | methanol  | nitrobenzene |                      |
| $[\text{Mn}(\text{UAAP})_2](\text{CH}_3\text{COO})_2$ | 8.25                        | 180   | 45           | 5.90                 |
| $[\text{Co}(\text{UAAP})(\text{NO}_3)_2]$             | 5.09                        | 10  | 9            | 2.37                 |
| $[\text{Ni}(\text{UAAP})_2]\text{Cl}_2$               | 7.81                        | 200   | 53           | 2.86                 |
| $[\text{Cu}(\text{UAAP})_2\text{Cl}_2]$               | 7.86                        | 12  | 2            | 1.99                 |
| $[\text{Zn}(\text{UAAP})_2](\text{CH}_3\text{COO})_2$ | 8.35                        | 14  | 10           | Diamagnetic          |

**Electronic spectra**

The electronic spectral data of different complexes of UAAP are studied. The electronic spectra of UAAP recorded in methanolic solution consists of two maxima at 430 nm and 310 nm corresponding to  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  transition respectively. The newly synthesised Mn(II) complex exhibit intense bands around 426 nm and a very weak shoulder around 545 nm. The intense peak may be due to ligand absorption and weak shoulder due to overlapping of spin forbidden d-d transition with the ligand absorption. In Co(II) complex there appears three bands at 735nm, 640nm and 539 nm due to three transitions and the fourth band appears at 420 nm that refers to ligand

metal charge transfer band which resembles those of five coordinate Co(II) complex<sup>19,20</sup>. The Ni(II) complex of UAAP displays four absorption bands at 425 nm 472 nm, 620 nm and 740 nm corresponds to intraligand  $n \rightarrow \pi^*$ ,  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$ ,  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$  and  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$  transitions in an octahedrally coordinated Ni(II) ion<sup>21</sup>. The electronic spectra of Cu(II) complex of UAAP shows a broad band around 429 nm corresponds to intraligand  $n \rightarrow \pi^*$  transition in UAAP. A very weak shoulder centred around 459 nm may be due to d-d transitions in Jahn –Teller distorted octahedral Cu(II) centre<sup>22</sup>.

### ESR spectrum

In the ESR spectrum of synthesised Cu(II) complex, there is absorption around 3200G, which is characteristics of  $\text{Cu}^{2+}$  species. The absence of half field peak around 1600 G rules out Cu-Cu interaction in this complex<sup>23</sup>. The ESR spectra of Cu(II) complex at 77 K is shown in fig. 3. The spectrum recorded at liquid nitrogen temperature (77K) shows four well resolved peaks with low intensities in low field region and one intense field at the high field region. The  $G$  value is calculated using the relation,

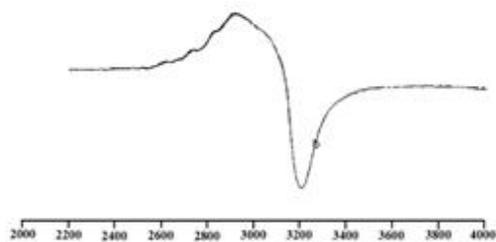
$$G = \frac{g_{\parallel} - 2.0027}{g_{\perp} - 2.0027}$$

If  $G > 4$ , local tetragonal axes are aligned parallel or only misaligned. That is the exchange coupling is negligible. This complex has  $G = 6.4$  to assign tetragonally distorted geometry<sup>24</sup>. It is possible to measure the sigma bond parameter  $\alpha^2$ , where  $\alpha$  is the coefficient of the ground state  $d_{x^2-y^2}$  orbital, from the approximate expression.

$$\alpha^2 = -\frac{A_{\parallel}}{0.036} + (g_{\parallel} - 2.0027) + \frac{3}{7}(g_{\perp} - 2.0027) + 0.04$$

$A_{\parallel}$  is hyperfine splitting constant expressed in  $\text{cm}^{-1}$ . The perpendicular component shows no hyperfine splitting and hence  $A_{\perp}$  is zero<sup>25</sup>. The calculated  $\alpha^2$  value is 0.78 which indicates the presence of covalent bonding between ligand and Cu(II) ion<sup>26</sup>.

Cu(II) complex shows  $g$  value 2.44 and  $g_{\perp}$  value 2.07, both are greater than  $g_e$  (2.0027). This observation indicates that the unpaired electrons are in  $d_{x^2-y^2}$  orbital of Cu(II) ion<sup>27</sup>. The  $g_{\text{avg}}$  value calculated is 2.19.



Magnetic field strength (Gauss)→

Fig. 3 ESR of  $[\text{Cu}(\text{UAAP})_2\text{Cl}_2]$

### Cyclic voltammetry :

The cyclic voltammogram of the Co(II) complex in MeCN in the potential range +1.50 V to -1.50 V shows a well-defined redox process corresponding to formation of Co(II)/Co(I) couple. Voltammogram displays a reduction peak at  $E_{pc} = -0.680$  V with an associated peak at  $E_{pa} = -0.782$  V. This couple is found to be reversible with  $\Delta E_p = 0.102$  V. the ratio of anodic to cathodic peak current is  $\approx 1$  corresponding to one electron process. The complex also shows a quasi-reversible peak due to oxidation couple Co(II)/Co(III) at  $E_{pc} = +0.782$  V with an associated peak at  $E_{pa} = +0.727$  V. the peak separation of this couple is 0.055 V. the ratio of anodic to cathodic peak current is 1 corresponding to one electron process. Analysis of electrochemical studies proved that this Co(II) complex is more towards its electrochemical behavior. The tapering of peak on either side is due to ligand oxidation. Cyclic voltammetry is given in Fig. 6<sup>28,29</sup>.

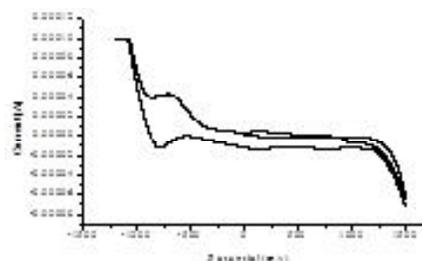


Fig. 4 CV of  $[\text{Co}(\text{UAAP})(\text{NO}_3)_2]$  complex

### Non linear optical property (NLO) :

The NLO property of ligand and complexes were studied in powder form by Kurtz and Perry technique. The well powdered sample was filled in capillary tube having 0.8 mm thickness. The NLO responses of these samples were recorded using KDP as reference filled in similar capillary tube. The experimental arrangement for nonlinear optical property utilize a Quanter ADCR II Nd/YAG laser with 4.9 mJ pulse at a repetition rate of 5Hz. The selected wavelength is 1064 nm. After the selection of wavelength laser beam is split into two parts one to generate second harmonic signal in sample and other to generate second harmonic signal in reference (KDP). An output of 532 nm measured in 90° geometry using

KDP as standard. The efficiency of NLO activity of compounds are expressed in % as

$$\% \text{ Efficiency} = \frac{\text{signal of sample}}{\text{signal of KDP}} \times 100$$

The second harmonic generation efficiency of UAAP and complexes were determined. The efficiency of sample was compared with microcrystalline powder of (potassium dihydrogen phosphate) KDP. UAAP shows 5 SHG/mV and complexes shows in range 5.1-7 SHG/mV compared to 11 SHG/mV for KDP. The percentage efficiency of UAAP is 45.45% and for complexes it is in range 46.36 -63.63% with respect to KDP. The UAAP shows 0.5 times activity as that of KDP and complexes shows enhanced activity compared to UAAP. Though the present investigated azo dye ligand possesses a pathway of conjugated electrons, the NLO activity is low and may be due to absence of electron pull and electron push substituents on aromatic rings. The presence of electron acceptor groups on both sides of azo compound causes reduction in second order nonlinearity. Hence we conclude that substituents play an important role in charge transfer through the molecule. Therefore the substituents require a special attention in designing azo dye ligands for non linear optical property.

#### 3.4.11 Fluorescence spectroscopy :

UAAP,  $[\text{Mn}(\text{UAAP})_2](\text{CH}_3\text{COO})_2$  and  $[\text{Ni}(\text{UAAP})_2]\text{Cl}_2$  exhibit fluorescence in the range 350-700 nm in methanol solution at room temperature. These are assigned as intraligand ( $\pi \rightarrow \pi^*$ )

fluorescence<sup>30,31</sup>. It is interesting that Mn(II) and Ni(II) complexes of UAAP azo dye shows higher intensity than that of free ligand. The emission spectra is less pronounced for other complexes. Metal ions can enhance the fluorescence emission of azo dye. The fluorescence spectra of UAAP,  $[\text{Mn}(\text{UAAP})_2](\text{CH}_3\text{COO})_2$  and  $[\text{Ni}(\text{UAAP})_2]\text{Cl}_2$  are given in Fig 7<sup>32,33,34</sup>.

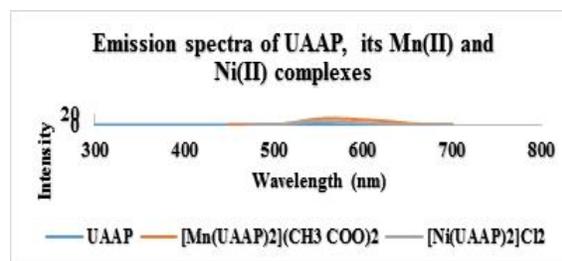


Fig. 7 Fluorescence spectra of UAAP,  $[\text{Mn}(\text{UAAP})_2](\text{CH}_3\text{COO})_2$  and  $[\text{Ni}(\text{UAAP})_2]\text{Cl}_2$

UAAP when excited at 430 nm shows two emission bands at 515 nm and 568 nm.  $[\text{Mn}(\text{UAAP})_2](\text{CH}_3\text{COO})_2$  shows emission at 571 nm and  $[\text{Ni}(\text{UAAP})_2]\text{Cl}_2$  at 554 nm when excited respectively at 426 and 472 nm. The increase in intensity of complexes can be due to the formation of a metal to ligand ratio of 1:2 resulting in larger molecule formation and due to interaction between the metal and ligand upon coordination. The photoluminescence data of ligand and its complexes are given in Table 5.

Table 5. Photoluminescence data of UAAP and its complexes

| Compound  | $\lambda_{\text{excitation}}$ (nm) | $\lambda_{\text{emission}}$ (nm) | Intensity of emission | Stokes shift |
|---|------------------------------------|----------------------------------|-----------------------|--------------|
| UAAP  | 430                                | 568/515                          | 1.231.58              | 13885        |
| $[\text{Mn}(\text{UAAP})_2](\text{CH}_3\text{COO})_2$ | 426                                | 571                              | 11.4                  | 145          |
| $[\text{Ni}(\text{UAAP})_2]\text{Cl}_2$               | 472                                | 554                              | 6.81                  | 82           |

#### Biological Activity :

The *in vitro* antimicrobial activity of UAAP and metal complexes have been tested to ascertain the effectiveness of metal complexes in comparison with ligand. The screening data obtained and results are shown in Fig. 8. From the results it is interesting to

observe that UAAP is less active where as its complexes are comparatively active for all the tested microorganism. This suggest that the coordination have played a significant role in enhancement of activity but they are not as potent as standard drugs used.

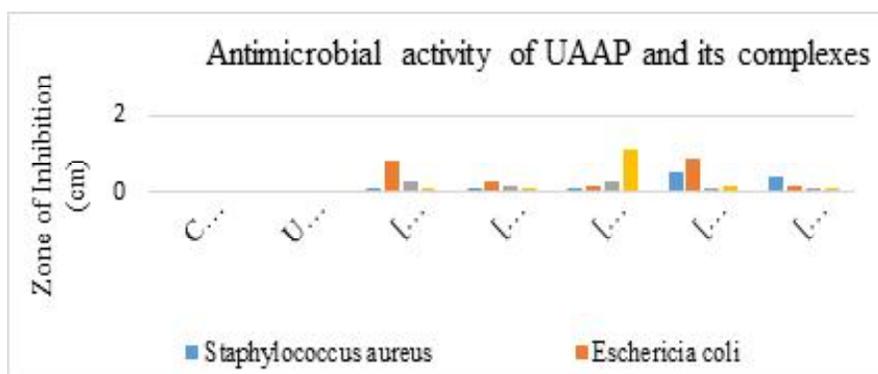


Fig. 6. Graphical representation of antimicrobial activity of UAAP and its complexes

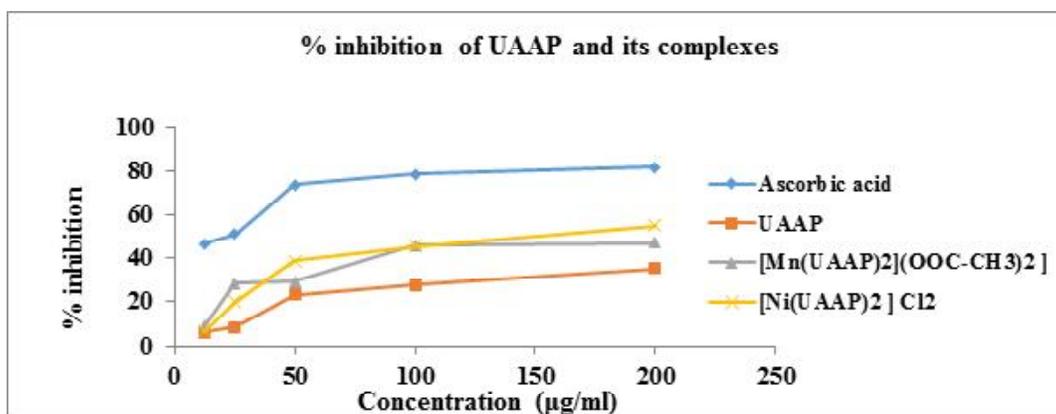


Fig. 7. % inhibition of UAAP and its complexes

The antioxidant activity of UAAP and complexes were done and their % inhibition values also found. Results indicate that UAAP and complexes does not have any antioxidant activity whereas  $[\text{Mn}(\text{UAAP})_2](\text{CH}_3\text{COO})_2$  and  $[\text{Ni}(\text{UAAP})_2]\text{Cl}_2$  complexes exhibits some activity due to presence of metal moiety during complexation and is given in fig.7. Other complexes does not give any  $\text{IC}_{50}$  value<sup>35</sup>.

The ability of UAAP and  $[\text{Co}(\text{UAAP})(\text{NO}_3)_2]$  to effect DNA cleavage has been investigated and the result obtained is shown in Fig. 8. Control DNA does not show any apparent cleavage of pUC 18 DNA. For UAAP and  $[\text{Co}(\text{UAAP})(\text{NO}_3)_2]$  complex no bands were observed in respective lane which can be due to absence of DNA cleavage. Another reason for absence of bands may due to the complete degradation of DNA into small pieces. It can be expected due to hydrolytic cleavage<sup>36</sup>.

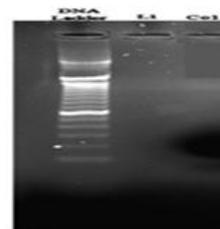


Fig. 8. DNA cleavage activity of UAAP and  $[\text{Co}(\text{UAAP})(\text{NO}_3)_2]$ .

L1-UAAP, Co1- $[\text{Co}(\text{UAAP})(\text{NO}_3)_2]$

The anticancer activity of  $[\text{Co}(\text{UAAP})(\text{NO}_3)_2]$  shows high percentage cell death under the condition studied against Human breast cell line-SKBR3 and cervical cell line SiHa. In most cases activity remained almost same with increase in concentration of test samples. All complexes shows increased activity. Image of control and activity is shown in Fig. 9.

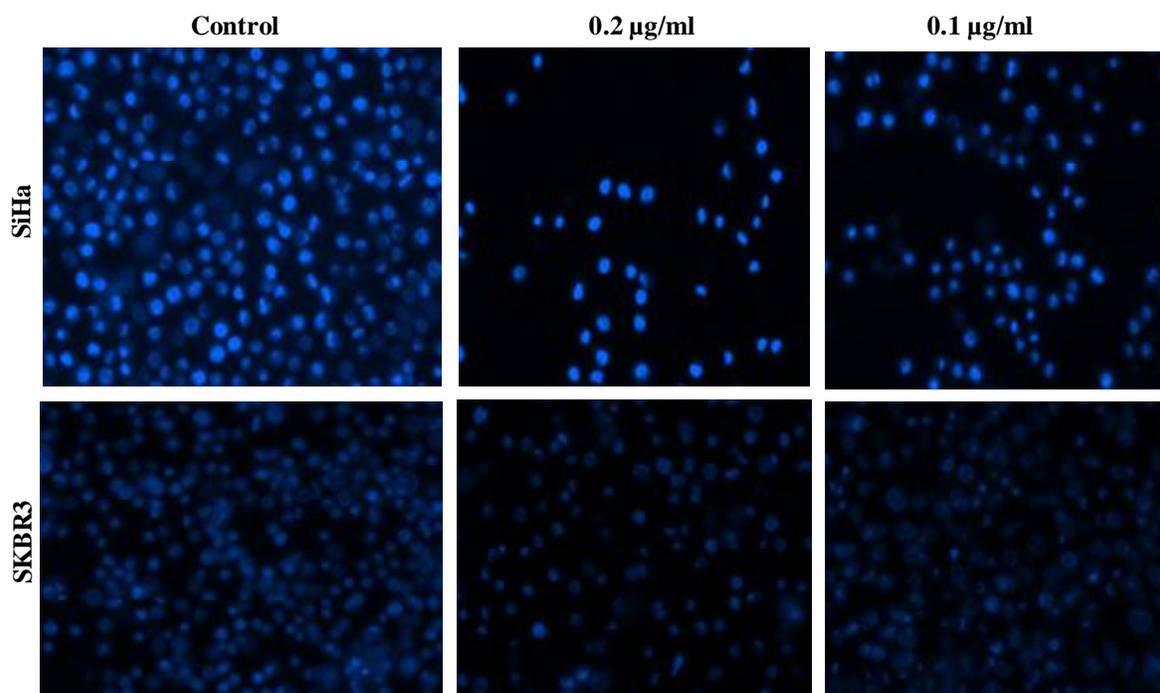


Fig. 9 Image of control,  $[\text{Co}(\text{UAAP})(\text{NO}_3)_2]$  for SiHa and SKBR3

#### Coordination number and geometry :

Analytical data shows that the metal to ligand ratio of UAAP complexes are 1:2 for all except in Co(II) complex which shows 1:1. The mass spectrum of Zn(II) complex agrees with the proposed stoichiometry. The molar conductance values suggest that Co(II), Cu(II), and Zn(II) are nonelectrolytes but Mn(II) and Ni(II) complexes are 1:2 electrolyte. The shift of  $^1\text{H}$  NMR signals towards lower field in the Zn(II) complex indicates the chelation of ligand group. The infrared spectra indicates that the ligand UAAP is acting as neutral bidentate towards Cu(II) and Zn(II) and also as neutral tridentate towards Mn(II), Co(II) and Ni(II) complexes. The coordinating centres are azo nitrogen, carbonyl group on pyrazolone ring and carbonyl group of pyrimidine moiety. From IR spectra it can be suggested that acetate and nitrate anions are coordinated in monodentate fashion. All complexes exhibit octahedral geometry except for Co(II) complex which shows five coordinate square pyramidal geometry. This is more evidenced from the electronic spectra and magnetic moment values.

#### Conclusion

Five new complexes of (5-(2,3-dimethyl-1-phenyl-3-pyrazolin-5-one-4-ylazo)- $^1\text{H}$ -pyrimidine-2,4-dione) with Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) were prepared and characterized by elemental analysis, molar conductance,  $^1\text{H}$ NMR, mass, IR, ESR, electronic spectral studies, cyclic voltammetry and magnetic susceptibility measurements. Mass spectral data of Zn(II) complex supports the proposed stoichiometry. IR data reveals the neutral bidentate and tridentate nature of the ligand, the presence of coordinated water and the involvement of anions in coordination. Conductance values also support various electrolytic and non-electrolytic behaviour of the complexes. Electronic spectra and magnetic moment value suggest octahedral geometry for all complexes except for Co(II) which has square pyramidal geometry. The Mn(II) and Ni(II) complexes show enhanced fluorescence. The NLO activity of complexes are higher compared to UAAP. UAAP and metal complexes were screened for antimicrobial activity, antioxidant study, DNA cleavage

analysis and anticancerous investigation. The results reveal that the metal complexes are active against the microbes compared to UAAP. Complexes are found to be more active against two bacteria *E. coli*, *S. aureus* and two fungi *A. niger*, *C. albicans* compared to UAAP. Antioxidant activity was less prominent for complexes and UAAP. Anticancer study and DNA cleavage of [Co(UAAP)(NO<sub>3</sub>)<sub>2</sub>] was done and shows good anticancerous activity against two cell lines. This work may be extended to study the single crystal data of the new ligand and complexes.

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### Conflict of interest :

The authors declare that they have no conflict of interest.

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