

**SYNTHESIS, CHARACTERIZATION & ANTIMICROBIAL STUDIES OF BIMETALLIC COMPLEXES OF CU (II) & NI (II)-PYRIDINE-2-ALDOXIME WITH MG & CA METAL SALTS OF SOME ORGANIC ACIDS**Birendra Kumar<sup>\*1</sup>, Poonam<sup>2</sup>, Vijay Kumar Gupta<sup>1</sup> Asha Kumari<sup>3</sup> and Kanchan Kumari<sup>4</sup><sup>1</sup>PG Deptt. of Chemistry, Maharaja College (VKSU), Ara - 802301 (India).<sup>2</sup>Research Scholar, VKSU, Ara - 802301 (India).<sup>3</sup>Deptt. of Chemistry, Patna Science College (PU), Patna - 800005 (India).<sup>4</sup>Deptt. of Zoology VKSU.**\*Corresponding Author: Birendra Kumar**

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**ABSTRACT**

The Cu(II) and Ni(II)-pyridine-2-aldoxime,  $M_a(\text{pyox})_2$  have been used as a complex ligand for the synthesis of a number of bimetallic complexes of the type  $[M_a(\text{pyox})_2.M_bL_2]$ .  $M_a(\text{pyox})_2$  acting as a bidentate complexing agent, coordinating through O-atoms of oximino groups to Mg or Ca-metal salt ( $M_bL_2$ ; where  $M_b = \text{Mg}$  or  $\text{Ca}$ ,  $L = o$ -nitrophenol or 2,4-dinitrophenol). Stereochemistry of the complexes have been studied by elemental analysis, spectral data, conductance and magnetic moment measurements. Antimicrobial efficiency of the compounds has been screened against five different micro-organism. The antimicrobial results evidently show that the activity of the ligand/complex ligands became more pronounced when coordinated to the metal ions.

**KEYWORDS:** Bimetallic complexes, Cu (II)/Ni(II) chelates, Pyridine-2-aldoxime, Organic acids, Spectral data & Antimicrobial activity.

**INTRODUCTION**

Pyridine-2-aldoxime is an important ligand having a nitrogen heterocycle and an oximino group at ortho position. It has already been studied for the spectrophotometric estimation of iron in the ferrous state.<sup>[1]</sup> Coordination ability of pyridine-2-aldoxime with transition and non-transition metals have been extensively studied.<sup>[2-8]</sup> In this communication, we have taken Cu(II) & Ni(II)-pyridine-2-aldoxime [ $M_a(\text{pyox})_2$ ] as complex ligands and synthesized several bimetallic complexes with Mg & Ca metal salts of some organic acids.

**Experimental: 1. Synthesis of Cu(II) & Ni(II) metal chelates of pyridine-2-aldoxime, [ $M_a(\text{pyox})_2$ ]:** Ethanolic solution of 0.1 mole of Cu(II) acetate or Ni(II) acetate were taken in a conical flask and then 0.2 mole of pyridine-2-aldoxime was added. The mixture was refluxed on magnetic hot plate at 80°C for nearly half an hour with continuous stirring, green or steel grey precipitate of Cu(II) or Ni(II) chelate was separated out. It was filtered and washed with absolute ethanol and dried in an electric oven at 100°C.

**2. Synthesis of Mg & Ca metal salts of some organic acids,  $M_bL_2$ :** 95% Ethanolic solution of the organic acid (*o*-nitrophenol or 2,4-dinitrophenol) and  $\text{Mg}(\text{OH})_2$  or  $\text{Ca}(\text{OH})_2$  in 2 : 1 molar proportion were mixed. The

mixture was refluxed on magnetic hot plate with constant stirring at 80°C for nearly one hour. On cooling the solution, characteristic colour precipitate got separated. It was filtered, washed with absolute ethanol and finally dried in an electric oven at 100°C.

**3. Synthesis of Bimetallic complexes, [ $M_a(\text{pyox})_2.M_bL_2$ ]:** 0.001 mole of Cu(II) or Ni(II)-pyridine-2-aldoxime [ $M_a(\text{pyox})_2$ ] was taken in absolute ethanol and 0.001 mole of Mg or Ca metal salt of organic acid (*o*-nitrophenol or 2,4-dinitrophenol) was added with constant stirring. The whole contents were refluxed on magnetic hot plate at 80°C for 1-2 hours with continuous stirring. A characteristic colour precipitate of the complex was separated out. It was filtered, washed thoroughly with absolute ethanol and dried in an electric oven at 100°C.

**RESULTS AND DISCUSSION**

Colours, melting points, molar conductances, magnetic moment values and analytical data of the metal chelates and the bimetallic complexes are given in Table - 1. All the complexes are characteristic colours and are different from the metal chelates. They show high melting/decomposition temperatures indicating their high stabilities. Molar conductance values of the complexes were measured in DMSO at 28°C at a concentration of  $10^{-3}$  M. The low values (2.1 - 7.8  $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ ) of

molar conductances, indicate that they are non-electrolyte in nature.<sup>[9]</sup>

region 4000-400  $\text{cm}^{-1}$  in KBr phase with the help of Perkin Elmer IR spectrophotometer. Pertinent IR data for these compounds are shown in Table - 2.

**Infrared spectra:** Infrared spectra of the metal chelates and their bimetallic complexes have been recorded in the

**Table 1: Colour, decomp. temp., molar conductance, magnetic moments & elemental analysis of the compounds.**

Compound	Colour	M.Pt./Deco. temp.( $^{\circ}\text{C}$ )	Molar cond. ( $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ )	Magnetic moment (in BM)	% Analysis Found/(Calc.)				
					C	H	N	$M_a$	$M_b$
Cu(pyox) <sub>2</sub>	Green	198m	2.1	1.78	47.02	3.14	18.10	20.64	1.85
					(47.13)	(3.27)	(18.33)	(20.78)	-
Cu(pyox) <sub>2</sub> .[Mg(ONP) <sub>2</sub> ] <sub>2</sub>	Brown	250dm	4.0	1.82	47.43	2.74	12.15	6.90	5.14
	green				(47.68)	(2.87)	(12.36)	(7.01)	(5.36)
Cu(pyox) <sub>2</sub> .[Mg(DNP) <sub>2</sub> ] <sub>2</sub>	Brown	265d	6.4	1.98	39.64	1.94	15.21	5.63	4.21
	green				(39.77)	(2.02)	(15.47)	(5.85)	(4.47)
Cu(pyox) <sub>2</sub> .[Ca(ONP) <sub>2</sub> ] <sub>2</sub>	Leaf	275d	7.5	1.85	45.83	2.51	11.80	6.55	8.30
	brown				(46.08)	(2.77)	(11.95)	(6.77)	(8.53)
Cu(pyox) <sub>2</sub> .[Ca(DNP) <sub>2</sub> ] <sub>2</sub>	Dark	280d	7.8	2.10	38.49	1.88	14.87	5.52	6.88
	green				(38.66)	(1.97)	(15.03)	(5.68)	(7.16)
Ni(pyox) <sub>2</sub>	Steel grey	240m	2.6	--	47.77	2.61	12.15	6.32	5.18
					(47.89)	(3.32)	(18.62)	(19.52)	-
Ni(pyox) <sub>2</sub> .[Mg(ONP) <sub>2</sub> ] <sub>2</sub>	Greenish brown	265d	4.6	--	47.77	2.61	12.15	6.32	5.18
					(47.93)	(2.88)	(12.42)	(6.51)	(5.38)
Ni(pyox) <sub>2</sub> .[Mg(DNP) <sub>2</sub> ] <sub>2</sub>	Brown	260d	7.8	--	39.83	1.90	15.41	5.23	4.27
					(39.95)	(2.03)	(1.94)	(5.43)	(4.49)
Ni(pyox) <sub>2</sub> .[Ca(ONP) <sub>2</sub> ] <sub>2</sub>	Golden	278d	6.0	--	46.24	2.61	11.81	6.12	8.40
	brown				(46.32)	(2.79)	(12.01)	(6.29)	(8.58)
Ni(pyox) <sub>2</sub> .[Ca(DNP) <sub>2</sub> ] <sub>2</sub>	Ash	265d	7.6	--	38.79	1.88	14.96	5.04	6.98
	brown				(38.82)	(1.98)	(15.10)	(5.27)	(7.19)

**Table 2: Infrared & electronic absorption spectral data of some of the prepared compounds.**

Compound	IR absorption bands (in $\text{cm}^{-1}$ )			Diffuse reflectance (in nm)	
	$\nu_{\text{C=N}}$	$\nu_{\text{N-O}}$		$\nu_{\text{M-OM-N}}$	
Cu(pyox) <sub>2</sub>	1650, 1598	1216 1127, 1098		580, 510	340, 435
Cu(pyox) <sub>2</sub> .[Mg(ONP) <sub>2</sub> ] <sub>2</sub>	1608, 1569	1217 1094		536, 511, 469	355, 362, 391, 420, 430
Cu(pyox) <sub>2</sub> .[Mg(DNP) <sub>2</sub> ] <sub>2</sub>	1603, 1565	1216 1131, 1080		563, 513, 465	326, 358, 391, 470
Cu(pyox) <sub>2</sub> .[Ca(ONP) <sub>2</sub> ] <sub>2</sub>	1603, 1571	1216 1095		575, 512, 465	366, 391, 404, 430, 456
Ni(pyox) <sub>2</sub>	1645, 1604	1216 1051		520	315, 405
Ni(pyox) <sub>2</sub> .[Mg(DNP) <sub>2</sub> ] <sub>2</sub>	1609, 1529	1216 1083		575, 516, 470	319, 340, 358, 391, 427
Ni(pyox) <sub>2</sub> .[Ca(ONP) <sub>2</sub> ] <sub>2</sub>	1605, 1518	1217 1095		525, 502, 469	358, 391, 416, 430, 448
Ni(pyox) <sub>2</sub> .[Ca(DNP) <sub>2</sub> ] <sub>2</sub>	1627, 1519	1216 1065		560, 518, 468	362, 420

**Table 3: Antimicrobial activity of some of the prepared compounds.**

Organism	Cu (pyox) <sub>2</sub> .	Ni (pyox) <sub>2</sub> .	Inhibition zone(mm) of the compound					
			Cu(pyox) <sub>2</sub> . [Mg(ONP) <sub>2</sub> ] <sub>2</sub>	Cu(pyox) <sub>2</sub> . [Mg(DNP) <sub>2</sub> ] <sub>2</sub>	Cu(pyox) <sub>2</sub> . [Ca(ONP) <sub>2</sub> ] <sub>2</sub>	Ni(pyox) <sub>2</sub> . [Mg(DNP) <sub>2</sub> ] <sub>2</sub>	[Ni(pyox) <sub>2</sub> . [Ca(ONP) <sub>2</sub> ] <sub>2</sub>	[Ni(pyox) <sub>2</sub> . [Ca(DNP) <sub>2</sub> ] <sub>2</sub>
<i>E. coli</i>	++	+	+++	+++	+++	++	++	++
<i>S. aureus</i>	+	+	++	++	++	++	+	++
<i>C. albicans</i>	-	+	++	++	++	++	+	++
<i>A. flavus</i>	-	-	+	+	+	+	+	+
<i>P. aeruginosa</i>	+	+	-	-	-	+	+	+

The characteristic absorption bands of  $\nu_{\text{C=N}}$ / $\nu_{\text{C=C}}$  observed at 1650/1598  $\text{cm}^{-1}$  and 1645/1604  $\text{cm}^{-1}$  Cu(pyox)<sub>2</sub> and Ni(pyox)<sub>2</sub> respectively, show appreciable shifts after the formation of the complexes. Assignment of the band at 1650/1645  $\text{cm}^{-1}$  to the conjugated (C=N) stretch seemed to be more probable and this is in

agreement with the assignment previously made for this vibration in the complexes.

The  $\nu_{\text{N-O}}$  band of Cu(pyox)<sub>2</sub> at 1127  $\text{cm}^{-1}$  shows appreciable change in the bimetallic complexes which are observed between 1131 -1080  $\text{cm}^{-1}$  and another band

at  $1216\text{ cm}^{-1}$  remain unaffected or slightly changed in its complexes. The  $\nu_{\text{N-O}}$  band of  $\text{Ni}(\text{pyox})_2$  at  $1051\text{ cm}^{-1}$  shifts towards higher energy side ( $1165 - 1095\text{ cm}^{-1}$ ) on complexation, but another band at  $1216\text{ cm}^{-1}$  remain unaffected in its bimetallic complexes. Above observations indicate the coordination of Mg or Ca metal through the oxygen atoms of the oximino group.

In all the bimetallic complexes, the bands with medium to strong absorption in the far infrared region  $575 - 500\text{ cm}^{-1}$  and  $470 - 460\text{ cm}^{-1}$  tentatively assigned to  $\nu_{\text{M-O}}$  and  $\nu_{\text{M-N}}$  modes<sup>[10]</sup> respectively. These bands are not present in pyridine-2-aldoxime. In metal chelates,  $\text{Cu}(\text{pyox})_2$  and  $\text{Ni}(\text{pyox})_2$ , these bands are observed in the region  $580 - 510\text{ cm}^{-1}$ . These assignments are based on the assumption<sup>[11]</sup> that since oxygen is more electronegative than nitrogen, the M - O bond tends to be more ionic than the M - N bond. Consequently M-O vibrations are expected to appear to higher wave number. These observations indicate coordination of oximino oxygen atoms to Mg or Ca metal in all the complexes.

**Electronic spectra:** Electronic spectra of the metal chelates and their bimetallic complexes were recorded on Systronic double beam UV-VIS spectrophotometer - 2202 in methanol. The bands observed in electronic spectra of the metal chelates and their bimetallic complexes are given in Table - 2.

The electronic absorption bands of  $\text{Cu}(\text{pyox})_2$  and  $\text{Ni}(\text{pyox})_2$  observed in the region  $340 - 315\text{ nm}$  and  $505 - 435\text{ nm}$  show that there is charge transfer and d-d transition. The spectra of all bimetallic complexes of  $\text{Cu}(\text{pyox})_2$  also gave similar type of bands in the region of  $391-319\text{ nm}$  and  $470-404\text{ nm}$ . This indicates that there is no change in stereochemistry of the complexes. This is also supported by the magnetic moment data. The electronic absorption bands located in the complexes in the region  $319 - 391\text{ nm}$  may be attributed due to charge transfer.

The electronic absorption bands of medium intensity in  $\text{Ni}(\text{pyox})_2$  observed at  $362 - 391\text{ nm}$  suggest the square planar of  $\text{Ni}(\text{II})$  with C.No. 4. The absorption bands of all the bimetallic complexes are found in the region  $319 - 448\text{ nm}$ , suggesting the same stereochemistry of the metal chelate in the bimetallic complexes. No absorption band has been found in the region of  $700 - 1200\text{ nm}$ , further confirms that the C. No. of  $\text{Ni}(\text{II})$  in the bimetallic complexes has not been raised, i.e., square planar geometry with C. No. 4.

**Magnetic moment:** Magnetic moment of the metal chelates and the complexes have been measured by Can Faraday magnetic susceptibility balance at  $28^\circ\text{C}$ . The magnetic moment values are shown in Table-1. The magnetic moment of  $\text{Cu}(\text{pyox})_2$  has been found to be  $1.78\text{ BM}$ , suggesting its square planar geometry(C.No. 4). The magnetic moment values of the complexes found in the range  $1.82 - 2.10\text{ BM}$ , which corresponds to the

presence of one unpaired electron. This indicates that stereochemistry of the metal chelate remain almost same in the complexes. Very low values(nearly zero) of magnetic moments of  $\text{Ni}(\text{pyox})_2$  and its bimetallic complexes, suggesting their diamagnetic nature, and also their square planar geometry(C.No. 4).

### Structure and bonding

On the basis of above discussions, bimetallic complexes of the type  $[\text{M}_a(\text{pyox})_2.\text{M}_b\text{L}_2]$ . can be presumed to have the structure as shown in Fig.1. The structure is strongly supported by analytical data, magnetic moment measurements and spectral data.

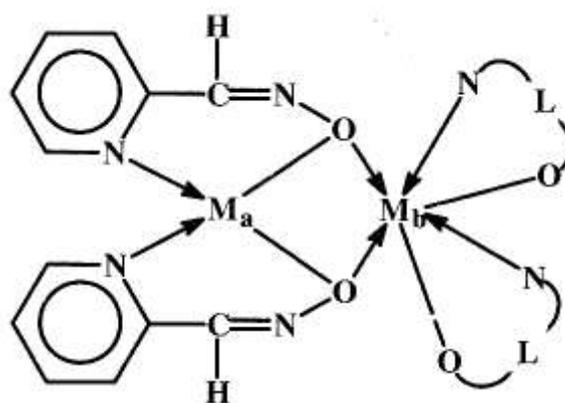


Fig. 1

(Where  $\text{M}_a = \text{Cu}(\text{II})$  or  $\text{Ni}(\text{II})$ ,  $\text{M}_b = \text{Mg}$  or  $\text{Ca}$  &  $\text{L} = o$ -nitrophenol or 2,4-dinitrophenol).

**Microbial studies:** Zone of inhibition of the synthesized compounds against a number of gram positive and gram negative pathogens bacteria and fungus were recorded in suitable medium for 24 and 48 hours at a concentration of  $0.5\mu\text{g/mL}$  and  $1\mu\text{g/mL}$  at  $30^\circ\text{C}$  for 24 hours for bacteria and  $26^\circ\text{C}$  for fungi using Serial Dilution Method.<sup>[14]</sup> The inhibition zone of the compounds were recorded in Table - 3. The antimicrobial results evidently show that the activity of the ligand/complex ligands became more pronounced when coordinated to the metal ions. It is however, not possible to make out exactly which metal ion is playing more antimicrobial role against one or other bacterial species but, it is definitive that metal ions do play a significant role in enhancing the antimicrobial activity of the ligand on chelation. From results, it is evident that most of the complexes have shown significant activity against *S.aureus*, *E.coli* and *C.albicans*.

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