

**SYNTHESIS, CHARACTERIZATION & ANTIMICROBIAL STUDIES OF BIMETALLIC COMPLEXES OF Ni(II) & Cu(II)-PYRIDINE-2-ALDOXIME WITH Rb & Cs METAL SALTS OF SOME ORGANIC ACIDS**

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A number of bimetallic complexes of the type  $[M_a(\text{pyox})_2.(M_bL)]$ , where  $M_a = \text{Ni(II)}$  or  $\text{Cu(II)}$ ,  $M_b = \text{Rb}$  or  $\text{Cs}$ ,  $\text{pyox} = \text{pyridine-2-aldoxime}$ ,  $L = \text{deprotonated o-nitrophenol, 2,4-dinitrophenol}$  have been synthesized.  $[M_a(\text{pyox})_2]$  have been used as a complex ligand for the synthesis. It acts as a bidentate complexing agent, coordinating through oxygen atoms of oximino groups to Rb or Cs metal. 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-organisms. The antimicrobial results evidently show that the activity of the ligand/complex ligands became more pronounced when coordinated to the metal ions..

## **I**NTRODUCTION

**P**yridine-2-aldoxime is an important ligand having a nitrogen heterocycle and an oximino group at ortho position. It has already been studied for the spectro-photometric estimation of iron in the ferrous state [1]. Coordination ability of pyridine-2-aldoxime with transition and non-transition metals have been extensively studied [2-8]. In this communication, we have taken Ni(II) & Cu(II)-pyridine-2-aldoxime  $[M_a(\text{pyox})_2]$  as complex ligands and synthesized a number of new bimetallic complexes with Rb & Cs metal salts of some organic acids(o-nitrophenol & 2,4-dinitrophenol).

## **E**XPERIMENTAL

**P**reparation of Ni(II) & Cu(II) metal chelates of pyridine-2-aldoxime,  $[M_a(\text{pyox})_2]$  :

Ethanol solution of 0.1 mole of Ni(II) acetate or Cu(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, steel grey or deep green precipitate of Ni(II) or Cu(II) chelate was separated out. It was filtered and washed with absolute ethanol and dried in an electric oven at 100°C.

**Preparation of Rb & Cs metal salts of some organic acids,  $M_bL$**  : Equimolar proportions of RbOH or CsOH and organic acid(o-nitrophenol or 2,4-dinitrophenol) and were mixed. The mixture was refluxed on magnetic hot plate with constant stirring at 60-70°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 80°C

**Preparation of Bimetallic complexes,  $[M_a(pyox)_2.M_bL]$**  : 0.001 mole of Ni(II) or Cu(II)-pyridine-2-aldoxime  $[M_a(pyox)_2]$  was taken in absolute ethanol and 0.001 mole of Rb or Cs 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 70-80°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.

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

Compound	Colour	M.Pt./Deco. Temp. (°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 (47.13)	3.14 (3.27)	18.10 (18.33)	20.64 (20.78)	1.85 –
[Cu(pyox) <sub>2</sub> .RbONP]	Brown green	250dm	4.0	1.82	47.43 (47.68)	2.74 (2.87)	12.15 (12.36)	6.90 (7.01)	5.14 (5.36)
[Cu(pyox) <sub>2</sub> .RbDNP]	Brown green	265d	6.4	1.98	39.64 (39.77)	1.94 (2.02)	15.21 (15.47)	5.63 (5.85)	4.21 (4.47)
[Cu(pyox) <sub>2</sub> .CsONP]	Leaf brown	275d	7.5	1.85	45.83 (46.08)	2.51 (2.77)	11.80 (11.95)	6.55 (6.77)	8.30 (8.53)
[Cu(pyox) <sub>2</sub> .CsDNP]	Dark green	280d	7.8	2.10	38.49 (38.66)	1.88 (1.97)	14.87 (15.03)	5.52 (5.68)	6.88 (7.16)
[Ni(pyox) <sub>2</sub> ]	Steel grey	240m	2.6	–	47.77 (47.389)	2.61 (3.32)	12.15 (18.62)	6.32 (19.52)	5.18 –
[Ni(pyox) <sub>2</sub> .RbONP]	Greenish brown	265d	4.6	–	47.77 (47.93)	2.61 (2.88)	12.15 (12.42)	6.32 (6.51)	5.18 (5.38)
[Ni(pyox) <sub>2</sub> .RbDNP]	Brown	260d	7.8	–	39.83 (39.95)	1.90 (2.03)	15.41 (1.94)	5.23 (5.43)	4.27 (4.49)
[Ni(pyox) <sub>2</sub> .CsONP]	Golden brown	278d	6.0	–	46.24 (46.32)	2.61 (2.79)	11.81 (12.01)	6.12 (6.29)	8.41 (8.58)
[Ni(pyox) <sub>2</sub> .CsDNP]	Ash brown	265d	7.6	–	38.79 (38.82)	1.88 (1.98)	14.96 (15.10)	5.04 (5.27)	6.98 (7.19)

## RESULTS & DISCUSSION

**C**olours, 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 thermal stabilities. Molar conductance values of the complexes were measured in DMSO at 30°C at a concentration of  $10^{-3}$  M. The low values ( $2.1 - 10.5 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ) of molar conductances, indicate that they are non-electrolyte or covalent in nature [9].

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

**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> .RbONP]	1608, 1569	1217 1094	536, 511, 469	355, 362, 391, 420, 430
[Cu(pyox) <sub>2</sub> .RbDNP]	1603, 1565	1216 1131, 1080	563, 513, 465	326, 358, 391, 470
[Cu(pyox) <sub>2</sub> .CsONP]	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> .RbDNP]	1609, 1529	1216 1083	575, 516, 470	319, 340, 358, 391, 427
[Ni(pyox) <sub>2</sub> .CsONP]	1605, 1518	1217 1095	525, 502, 469	358, 391, 416, 430, 448
[Ni(pyox) <sub>2</sub> .CsDNP]	1627, 1519	1216 1065	560, 518, 468	362, 420

The characteristic absorption bands of  $\nu_{\text{C=N}}/\nu_{\text{C=C}}$  observed at  $1645/1604 \text{ cm}^{-1}$  and  $1650/1598 \text{ cm}^{-1}$  [Ni(pyox)<sub>2</sub>] and [Cu(pyox)<sub>2</sub>] respectively, show appreciable shifts ( $1650 - 1618/1602 - 1605$  &  $1659 - 1655/1606 - 1596$ ) after the complexation. Assignment of the band at  $1645/1650 \text{ cm}^{-1}$  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 [Ni(pyox)<sub>2</sub>] at  $1051 \text{ cm}^{-1}$  shifts towards higher energy side ( $1160 - 1117 \text{ cm}^{-1}$ ) on complexation, but another band at  $1216 \text{ cm}^{-1}$  remain unaffected or slightly changed in its complexes. The  $\nu_{\text{N-O}}$  band of [Cu(pyox)<sub>2</sub>] at  $1127 \text{ cm}^{-1}$  shows appreciable change in the complexes which are observed between  $1150 - 1110 \text{ cm}^{-1}$  and another band at  $1216 \text{ cm}^{-1}$  remain unaffected in its complexes. Above observations indicate the coordination of Rb or Cs metal through the oxygen atoms of the oximino group.

The bands in the region  $519 - 450$  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 [10] respectively. These bands are not present in pyridine-2-aldoxime. In metal chelates, Cu(pyox)<sub>2</sub> and Ni(pyox)<sub>2</sub>, these bands are observed in the region  $580 - 510 \text{ cm}^{-1}$ . These assignments are based on the assumption [11] 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 Rb or Cs 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 nm and 505-435 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 nm and 470-404 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 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 nm suggest the square planar of Ni(II) with C. No. 4. The absorption bands of all the bimetallic complexes are found in the region 319-448 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 nm, further confirms that the C. No. of Ni(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°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 BM, suggesting its square planar geometry (C. No. 4). The magnetic moment values of the complexes found in the range 1.82-2.10 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 & 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.

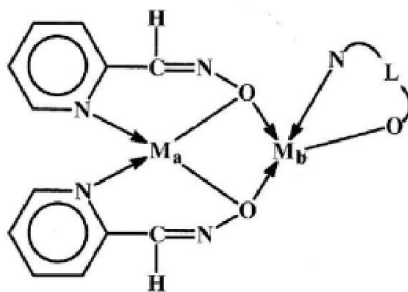


Fig. 1

where  $\text{M}_a = \text{Cu}(\text{II})$  or  $\text{Ni}(\text{II})$ ,  $\text{M}_b = \text{Rb}$  or  $\text{Cs}$  &  $\text{L} = \text{o-nitrophenol}$  or  $2,4\text{-dinitrophenol}$

**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°C for 24 hours for bacteria and 26°C for fungi using Serial Dilution Method [12]. 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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