



## Synthesis and Antimicrobial Activities of Complexes of Cu(II) and Ni(II)-pyridine-2-aldoxime & Alkaline Earth Metal Salts

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The copper(II) and nickel(II)-pyridine-2-aldoxime,  $M_a(\text{pyox})_2$  have been used as a complex ligand for the synthesis of a number of oxygen bridged complexes of the general formula  $M_a(\text{pyox})_2 \cdot M_bL_2$ ,  $M_a(\text{pyox})_2$  acting as a bidentate complexing agent, coordinating through two oximino oxygens to alkaline earth metal salt ( $M_bL_2$ ) (where  $M_b = \text{Mg, Ca, Sr or Ba}$ ;  $L = \text{deprotonated 8-hydroxyquinoline or 1-nitroso-2-naphthol}$ ). The structure has been substantiated by infrared, electronic absorption spectra and magnetic moment measurements. Most of the compounds have shown significant activity against *E. coli*, *S. aureus* and *C. albicans*.

**Key Words:** Oxygen bridged complexes, Alkaline earth metal, Pyridine-2-aldoxime, Infrared spectra, Biological activity.

### INTRODUCTION

Pyridine-2-aldoxime is an important ligand containing both an aromatic nitrogen heterocyclic and an oxime group at the *ortho* position. The formation of oxygen bridged complexes from pyridine-2-aldoxime is well established<sup>1-7</sup>. Pyridine-2-aldoxime has already been studied for the spectrophotometric estimation of iron in the ferrous state<sup>8</sup>. Acid dissociation constants of pyridine-2-aldoxime and its affinity for various metal ions were determined by means of potentiometric titrations<sup>9</sup>.

Thus it is worthwhile to study the reactions of copper(II) and nickel(II) metal chelates with alkaline earth metal salts of some organic acids. We have selected Cu(II) or Ni(II)-pyridine-2-aldoxime *i.e.*,  $\text{Cu}(\text{pyox})_2$  and  $\text{Ni}(\text{pyox})_2$  as 'metal complex ligands'.

### EXPERIMENTAL

Copper(II) acetate and nickel(II) acetate were used of E. merck quality. The organic acids were used; 8-hydroxyquinoline and 1-nitroso-2-naphthol of BDH A.R. quality. Pyridine-2-aldoxime was used of BDH A.R. quality.

**Preparation of transition metal chelates,  $M_a(\text{pyox})_2$ :** Ethanolic solution of 0.1 mol of copper(II) acetate or nickel(II) acetate were taken in a conical flask and then 0.2 mol of pyridine-2-aldoxime was added. The content was refluxed with continuous stirring on magnetic hot plate for 0.5 h at 80 °C, green or steel grey precipitate of copper(II) or nickel(II) chelate was

separated out. It was filtered, washed with absolute ethanol and dried in an electric oven at 100 °C.

**Preparation of alkaline earth metal salts of organic acids,  $M_bL_2$ :** 95 % Ethanolic solution of 0.02 mol of 8-hydroxyquinoline or 1-nitroso-2-naphthol and 0.01 mol of alkaline earth metal hydroxide were mixed. The mixture was refluxed on magnetic hot plate for 1.0-1.5 h with continuous stirring at 80 °C. On cooling the resulting solution, a characteristic colour precipitate was obtained. It was filtered, washed with pure solvent and dried in an electric oven at 100 °C.

**Preparation of oxygen bridged complexes  $[M_a(\text{pyox})_2 \cdot M_bL_2]$ :** 0.001 mol of copper(II) or nickel(II)-pyridine-2-aldoxime [ $\text{Cu}(\text{pyox})_2$  or  $\text{Ni}(\text{pyox})_2$ ] was taken in absolute alcohol and 0.001 mol of alkaline earth metal salt of organic acid (8-hydroxyquinoline or 1-nitroso-2-naphthol) was added with constant stirring. The whole contents were refluxed on a hot plate at 80 °C with constant stirring for 1-2 h. A characteristic colour oxygen bridged complex was precipitated in room temperature. The precipitate was filtered, washed thoroughly with absolute ethanol, dried in an electric oven at 100 °C.

### RESULTS AND DISCUSSION

The physical properties and analytical data of the metal chelates and their oxygen bridged alkaline earth metal complexes are listed in Table-1. It is evident that the oxygen bridged complexes have characteristic colours and are different from the metal chelates. All the oxygen bridged complexes show

TABLE-1  
PHYSICO-CHEMICAL CHARACTERISTICS OF OXYGEN BRIDGED COMPLEXES OF Cu(II) AND Ni(II)

Compound	Colour	m.p. (°C)	Conductivity (ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> )	$\mu_{\text{eff}}$ (BM)	Elemental analysis (%): Found (calcd)				
					C	H	N	M <sub>a</sub>	M <sub>b</sub>
Cu(pyox) <sub>2</sub>	Green	198	2.0	1.78	47.03(47.13)	3.30(3.36)	18.19(18.33)	20.62(20.78)	–
Cu(pyox) <sub>2</sub> ·Mg(8HQ) <sub>2</sub>	Reddish brown	260d	6.4	1.82	58.20(58.27)	3.48(3.56)	13.46(13.59)	10.09(10.28)	3.80(3.90)
Cu(pyox) <sub>2</sub> ·Ca(8HQ) <sub>2</sub>	Reddish brown	295d	7.5	1.98	56.73(56.83)	3.35(3.47)	13.09(13.26)	9.85(10.02)	6.13(6.31)
Cu(pyox) <sub>2</sub> ·Sr(8HQ) <sub>2</sub>	Yellowish green	>300	9.0	1.76	52.71(52.85)	3.15(3.23)	12.25(12.33)	9.16(9.32)	12.75(12.86)
Cu(pyox) <sub>2</sub> ·Ba(8HQ) <sub>2</sub>	Golden yellow	>300	8.5	1.86	49.16(49.26)	2.97(3.01)	11.39(11.50)	8.55(8.69)	18.61(18.79)
Cu(pyox) <sub>2</sub> ·Mg(1N2N) <sub>2</sub>	Blackish brown	250d	7.5	2.05	56.85(56.99)	3.15(3.26)	12.36(12.46)	9.29(9.42)	3.45(3.61)
Cu(pyox) <sub>2</sub> ·Ca(1N2N) <sub>2</sub>	Deep green	270d	7.8	1.98	56.53(55.69)	3.12(3.19)	12.09(12.18)	9.15(9.21)	5.63(5.80)
Cu(pyox) <sub>2</sub> ·Sr(1N2N) <sub>2</sub>	Deep green	280d	9.0	2.15	51.91(52.09)	2.90(2.98)	11.25(11.39)	8.46(8.61)	11.75(11.86)
Cu(pyox) <sub>2</sub> ·Ba(1N2N) <sub>2</sub>	Deep brown	>300	7.5	1.95	48.66(48.80)	2.71(2.79)	10.55(10.67)	7.85(8.07)	17.31(17.45)
Ni(pyox) <sub>2</sub>	Steel grey	240	2.5	DM	47.81(47.88)	3.28(3.32)	18.51(18.62)	19.40(19.52)	–
Ni(pyox) <sub>2</sub> ·Mg(8HQ) <sub>2</sub>	Greenish brown	265d	8.5	DM	58.65(58.73)	3.55(3.59)	13.55(13.70)	9.48(9.57)	3.80(3.96)
Ni(pyox) <sub>2</sub> ·Ca(8HQ) <sub>2</sub>	Deep green	>300	9.0	DM	57.18(57.26)	3.45(3.50)	13.29(13.36)	9.25(9.34)	6.23(6.36)
Ni(pyox) <sub>2</sub> ·Sr(8HQ) <sub>2</sub>	Yellowish brown	275d	7.5	DM	53.12(53.23)	3.19(3.25)	12.36(12.42)	8.59(8.68)	12.85(12.95)
Ni(pyox) <sub>2</sub> ·Ba(8HQ) <sub>2</sub>	Yellowish green	250d	6.0	DM	48.68(48.80)	2.75(2.79)	10.58(10.67)	7.88(8.07)	17.33(17.45)
Ni(pyox) <sub>2</sub> ·Mg(1N2N) <sub>2</sub>	Deep brown	>300	8.5	DM	57.21(57.39)	3.25(3.28)	12.36(12.55)	8.03(8.17)	3.56(3.63)
Ni(pyox) <sub>2</sub> ·Ca(1N2N) <sub>2</sub>	Greenish brown	250d	7.8	DM	55.91(56.08)	3.15(3.21)	12.15(12.27)	8.42(8.57)	5.66(5.84)
Ni(pyox) <sub>2</sub> ·Sr(1N2N) <sub>2</sub>	Reddish brown	265d	6.0	DM	52.35(52.44)	2.95(3.00)	11.35(11.47)	7.92(8.01)	11.78(11.96)
Ni(pyox) <sub>2</sub> ·Ba(1N2N) <sub>2</sub>	Greenish brown	>300	7.5	DM	48.95(49.10)	2.75(2.81)	10.59(10.74)	7.12(7.30)	17.68(17.55)

d = Decomposition; DM = Diamagnetic; 8HQ = 8-hydroxyquinoline; 1N2N = 1-Nitroso-2-naphthol.

high melting/decomposition temperatures which indicate their high stability.

**Molar conductivities:** Molar conductivities (ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>) of compounds were measured in DMSO at 30 °C at a concentration of 10<sup>-3</sup> M (Table-1). The compounds show low values (2.0-9.0 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>) of molar conductivities, indicating that they are covalent in nature.

**Infrared spectra:** Infrared spectra of metal chelates [Ni(pyox)<sub>2</sub> and Cu(pyox)<sub>2</sub>] and their oxygen bridged complexes were recorded in KBr phase between 4000-400 cm<sup>-1</sup> with the help of FTIR spectrophotometer, Shimadzu model-8201PC. Selected IR absorption bands of the compounds are given in Table-2.

TABLE-2  
KEY IR BANDS (cm<sup>-1</sup>) OF OXYGEN BRIDGED COMPLEXES OF Cu(II) AND Ni(II)

Compound	v(C=N)	v(N-O)	v(M-O)/ v(M-N)
Cu(pyox) <sub>2</sub>	1650,1598	1216,1127,1098	580,510
Cu(pyox) <sub>2</sub> ·Mg(8HQ) <sub>2</sub>	1608,1569	1217,1094	535,511,469
Cu(pyox) <sub>2</sub> ·Sr(8HQ) <sub>2</sub>	1603,1575	1216,1132	570,513,485
Cu(pyox) <sub>2</sub> ·Ca(1N2N) <sub>2</sub>	1602,1568	1218,1093	553,509,469
Cu(pyox) <sub>2</sub> ·Ba(1N2N) <sub>2</sub>	1603,1571	1216,1135,1095	575,512,485
Ni(pyox) <sub>2</sub>	1645,1604	1216,1051	520
Ni(pyox) <sub>2</sub> ·Ca(8HQ) <sub>2</sub>	1615,1603	1216,1160	516,485
Ni(pyox) <sub>2</sub> ·Ba(8HQ) <sub>2</sub>	1605	1216,1155	535,500,469
Ni(pyox) <sub>2</sub> ·Mg(1N2N) <sub>2</sub>	1627	1216,1100	560,518,460
Ni(pyox) <sub>2</sub> ·Sr(1N2N) <sub>2</sub>	1614,1595	1215,1156,1050	513,495

The characteristics absorption bands of v(C=N)/v(C=C)<sub>arom.</sub> observed at 1650/1598 and 1645/1604 cm<sup>-1</sup> in Cu(pyox)<sub>2</sub> and Ni(pyox)<sub>2</sub>, respectively, show appreciable shifts after the formation of oxygen bridged complexes. Assignment of the band ca. 1650/1645 cm<sup>-1</sup> 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 v(N-O) band of Cu(pyox)<sub>2</sub> at 1127 cm<sup>-1</sup> shows appreciable change in oxygen bridged complexes which are observed

between 1135-1060 cm<sup>-1</sup> and another band at 1216 cm<sup>-1</sup> remain unaffected or slightly changed in the oxygen bridged complexes. The v(N-O) band of Ni(pyox)<sub>2</sub> at 1051 cm<sup>-1</sup> shifts towards higher energy side (1160-1100 cm<sup>-1</sup>), except Ni(pyox)<sub>2</sub>·Sr(1N2N)<sub>2</sub> on complexation, but another band at 1216 cm<sup>-1</sup> remain unaffected in its oxygen bridged complexes. Above observations indicate the coordination of alkaline earth metals through the oximino oxygen atoms.

In all the oxygen bridged complexes, the bands with medium to strong absorption in the far infrared region 575-500 and 495-460 cm<sup>-1</sup> tentatively assigned to v(M-O) and v(M-N) modes<sup>10</sup>, respectively. These bands are not present in the pyridine-2-aldoxime, while in neutral metal chelates, Cu(pyox)<sub>2</sub> and Ni(pyox)<sub>2</sub> they are observed in the region 580-510 cm<sup>-1</sup>. These assignments are based on the assumption<sup>11</sup> that since oxygen atom 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. The above data confirm the coordination of oxygen atoms of oximino group to alkaline earth metals in all the oxygen bridged complexes.

**Electronic absorption spectra:** Electronic absorption spectra of metal chelates and their oxygen bridged complexes were recorded on Systronic double beam UV-Vis spectrophotometer 2202 in methanol. The bands observed in electronic spectra of the compounds are listed in Table-3.

TABLE-3  
ELECTRONIC SPECTRAL BANDS OF OXYGEN BRIDGED COMPLEXES OF Cu(II) AND Ni(II)

Compound	Absorption band (nm)
Cu(pyox) <sub>2</sub>	352, 435
Cu(pyox) <sub>2</sub> ·Mg(8HQ) <sub>2</sub>	355, 362, 391, 420, 430
Cu(pyox) <sub>2</sub> ·Ca(1N2N) <sub>2</sub>	326, 358, 391, 470
Cu(pyox) <sub>2</sub> ·Ba(1N2N) <sub>2</sub>	366, 391, 409, 430, 456
Ni(pyox) <sub>2</sub>	362, 391, 423, 448, 490
Ni(pyox) <sub>2</sub> ·Ca(8HQ) <sub>2</sub>	391, 340, 358, 391, 427
Ni(pyox) <sub>2</sub> ·Ba(8HQ) <sub>2</sub>	358, 391, 416, 430, 448
Ni(pyox) <sub>2</sub> ·Sr(1N2N) <sub>2</sub>	362, 420

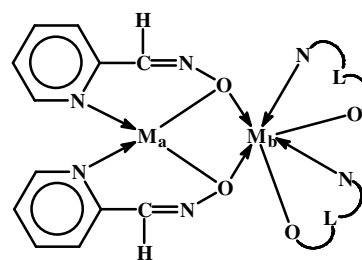
Electronic absorption bands are observed in the region of 391-352 and 490-423 nm in  $\text{Cu}(\text{pyox})_2$  and  $\text{Ni}(\text{pyox})_2$  show that there is charge transfer and  $d-d$  transition. The spectra of all oxygen bridged complexes of  $\text{Cu}(\text{pyox})_2$  also gave similar type of bands in the region of 391-326 and 470-409 nm. This suggests that there is no changes in stereochemistry of the oxygen bridged complexes after complexation. This is also supported by the magnetic moment values. The electronic absorption bands located in the region 326-391 nm may be attributed to arise due to charge transfer, however, the possibility of  $d-d$  transition for the peak in the region 409-470 nm is expected.

The absorption bands of medium intensity in  $\text{Ni}(\text{pyox})_2$  in the region 362-391 nm in electronic spectra, suggests the square planar structure of Ni(II) with C. No. 4. The absorption bands of oxygen bridged complexes are found in the region of 319-448 nm, suggesting the same square planar geometry of  $\text{Ni}(\text{pyox})_2$  with C. No. 4 in all the oxygen bridged complexes. It is clear that alkaline earth metal salts are not attached through Ni(II). No absorption bands have been found in the range of 700-1200 nm, it further confirms that the coordination number of Ni(II) in oxygen bridged complexes have not been raised, but it remains four with square planar structure.

**Magnetic moment:** Magnetic moment of metal chelates and their oxygen bridged complexes have been measured by Can Faraday magnetic susceptibility balance at 30 °C. The magnetic moment ( $\mu_{\text{eff}}$ ) values are shown in Table-1.

As a rule, the magnetic moments fall in the range 1.9-2.1 BM. The magnetic moment of  $\text{Cu}(\text{pyox})_2$  has been found to be 1.71 BM, suggesting its square planar geometry with C. No. 4, while the magnetic moments of oxygen bridged complexes are in between 1.77 to 2.18 BM which corresponds to the presence of one unpaired electron. Therefore the stereochemistry of  $\text{Cu}(\text{pyox})_2$  unit in the oxygen bridged complexes remain almost same. Very low values (approaching to zero) of magnetic moment ( $\mu_{\text{eff}}$ ) of  $\text{Ni}(\text{pyox})_2$  and its oxygen bridged complexes, suggesting their diamagnetic nature. This observation also suggests their square planar geometry with C. No. 4 for  $\text{Ni}^{2+}$  ion.

**Structure and bonding:** The probable structures and bonding of the newly prepared oxygen bridged complexes with  $\text{Cu}(\text{pyox})_2$  and  $\text{Ni}(\text{pyox})_2$  of the general formula  $\text{M}_a(\text{pyox})_2 \cdot \text{M}_b\text{L}_2$  are schematically shown in Fig. 1.



where  $\text{M}_a = \text{Cu(II)}$  or  $\text{Ni(II)}$ ,  $\text{M}_b = \text{Mg, Ca, Sr}$  or  $\text{Ba}$ ; L = deprotonated 8-hydroxyquinoline or 1-nitroso-2-naphthol; pyox = pyridine-2-aldoxime

Fig. 1

**Microbial studies:** Minimum inhibitory concentration (MIC) values ( $\mu\text{g/mL}$ ) of some of the prepared oxygen bridged alkaline earth metal complexes with  $\text{Cu}(\text{pyox})_2$  and  $\text{Ni}(\text{pyox})_2$  have been examined by serial dilution method<sup>12</sup> for activity against some bacteria, *E. coli*, *S. aureus* and fungi *C. albicans*. The results are summarized in Table-4.

TABLE-4  
ANTIMICROBIAL ACTIVITY OF SOME OXYGEN  
BRIDGED COMPLEXES OF  $\text{Cu(II)}$  AND  $\text{Ni(II)}$

Compound	Minimum inhibitory concentration ( $\mu\text{g/mL}$ )		
	<i>E. coli</i>	<i>S. aureus</i>	<i>C. albicans</i>
$\text{Cu}(\text{pyox})_2 \cdot \text{Mg(8HQ)}_2$	40	20	20
$\text{Cu}(\text{pyox})_2 \cdot \text{Ba(1N2N)}_2$	40	40	20
$\text{Ni}(\text{pyox})_2 \cdot \text{Mg(8HQ)}_2$	20	40	20
$\text{Ni}(\text{pyox})_2 \cdot \text{Ca(1N2N)}_2$	20	20	20

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