

## Synthesis of oxygen bridged complexes of Cu(II) or Ni(II)-salicylaldoxime with alkali metal salts of some organic acids and studies on their antimicrobial activities

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### ABSTRACT

The copper(II) and nickel(II)-salicylaldoxime,  $M_a(\text{salox})_2$  have been used as a complex ligand in the synthesis of a number of oxygen bridge complexes of the general formula  $M_a(\text{salox})_2 \cdot (M_bL)_2$ ,  $M_a(\text{salox})_2$  acting as a bidentate complexing agent, coordinating through two oximino oxygens to alkali metal salt ( $M_bL$ ) (where  $M_b = \text{Li, Na or K}$ ;  $L =$  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 test bacteria, e.g. *E. coli*, *S. aureus* and fungi, e.g. *C. albicans*.

**Key words :** Alkali metal, salicylaldoxime, infrared spectra, biological activity.

### INTRODUCTION

Salicylaldoxime is an important ligand containing both a O-H(phenolic) and an oxime group at the ortho position. The formation of oxygen bridge complexes from salicylaldoxime is well established<sup>1-7</sup>. Salicylaldoxime was used first as a ligand for complexation of metal ions by F. Ephraim as early as 1930. X-ray structural reports on the square planar complexes of the divalent metals Ni(II), Pd(II) & Pt(II) were published shortly after that in 1935. Phenolic oximes find extensive use in industry, mainly as extractants for copper<sup>8</sup> but also as anticorrosives in protective coatings<sup>9</sup>.

Keeping this view in mind, we thought that it would be of interest to study the reactions of copper(II) and nickel(II) metal chelates with alkali metal salts of some organic acids. We have selected Cu(II) or Ni(II)-salicylaldoxime, i.e.  $\text{Cu}(\text{salox})_2$  and  $\text{Ni}(\text{salox})_2$  as "metal complex ligands".

### EXPERIMENTAL

#### Materials

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. Salicylaldoxime was used also of BDH A.R. quality.

#### Preparation of transition metal chelates, $M_a(\text{salox})_2$

Ethanol solution of 0.1 mole of copper(II) acetate or nickel(II) acetate was taken in a conical flask and then 0.2 mole of salicylaldoxime was added. The whole content was refluxed with continuous stirring on magnetic hot plate for 30 minutes at 80°C. Green or steel grey precipitate of transition metal chelate was separated out. It was filtered, washed with absolute ethanol and dried in an electric oven at 80°C.

### Preparation of alkali metal salts of organic acids, $M_bL$

95% ethanolic solution of 0.01 mole of organic acid and 0.01 mole of alkali metal hydroxide were mixed. The mixture was refluxed on magnetic hot plate for 1-1½ hours 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 (adducts), $[M_a(\text{salox})_2.(M_bL)_2]$

0.001 mole of copper(II) or nickel(II)-salicylaldoxime,  $\text{Cu}(\text{salox})_2$  or  $\text{Ni}(\text{salox})_2$  was taken in absolute alcohol and 0.002 mole of alkali metal salt of organic acid (8-hydroxy-quinoline 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 hours. A characteristic colour adduct was precipitated in room temperature. But some adducts are precipitated in hot condition or reactions start quickly. The precipitate was filtered, washed thoroughly with absolute ethanol, dried in an electric oven at 80°C.

## RESULTS AND DISCUSSION

Some physical properties and analytical data of the metal chelates and their adducts are listed in Table-1. From the results, it is evident that the adducts have characteristic colour and are different from the metal chelates. All the adducts show high melting/decomposition temperatures which indicate their greater stability.

### Molar conductivities

Molar conductivities (in  $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ ) of compounds were measured in DMSO at 30°C at a concentration of  $10^{-3}$  M (Table-1). The compounds show low values (2.0 - 11.0  $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ ) of molar conductivities, indicating that they are covalent in nature.

### Infrared spectra

Infrared spectra of metal chelates and their adducts were recorded in KBr phase between 4000-400  $\text{cm}^{-1}$  with the help of FTIR spectrophotometer, Shimadzu model-8201PC. Selected IR absorption bands of the compounds are given in Table-2.

The strong absorption bands at 3450 & 3435  $\text{cm}^{-1}$  in the infrared spectra of metal chelates,  $\text{Cu}(\text{salox})_2$  &  $\text{Ni}(\text{salox})_2$  respectively have been assigned to -OH stretching. The presence of these bands and two other bands, i.e. at 2401  $\text{cm}^{-1}$  and 2377-2200  $\text{cm}^{-1}$  in the metal chelates point out to presence of strong intramolecular hydrogen bonding. In the oxygen bridged complexes, the intensity of the band at 3450  $\text{cm}^{-1}$  & 3435  $\text{cm}^{-1}$  have reduced to 3429-3195  $\text{cm}^{-1}$  & 3391-3022  $\text{cm}^{-1}$  respectively, and other bands in the region of 2402-2356  $\text{cm}^{-1}$  suggest the strong intramolecular hydrogen bonding in the oxygen bridged complexes.

The metal complexes,  $\text{Cu}(\text{salox})_2$  and  $\text{Ni}(\text{salox})_2$  as ligands exhibit the  $\nu_{\text{C-O}}(\text{phenolic})$  at 1538  $\text{cm}^{-1}$ , which shifted upto 36  $\text{cm}^{-1}$  on oxygen bridged complex formation, indicating the coordination through the phenolic oxygen. This shift is expected due to maintenance of a ring current arising from electron delocalization in the chelating ring. The major shift of  $\nu_{\text{C-O}}(\text{phenolic})$  to lower energy by  $\sim 36$   $\text{cm}^{-1}$  in complexes certainly indicates the presence of phenoxo bridge.

The characteristic absorption bands of  $\nu_{\text{C=N}}/\nu_{\text{C=C(aromatic)}}$  stretching vibration observed at 1648/1598  $\text{cm}^{-1}$  and 1651  $\text{cm}^{-1}$  in  $\text{Cu}(\text{salox})_2$  and  $\text{Ni}(\text{salox})_2$  respectively. So, appreciable shifts after the formation of oxygen bridged complexes of  $\text{Cu}(\text{salox})_2$  and  $\text{Ni}(\text{salox})_2$  with alkali metal salts of some organic acids.

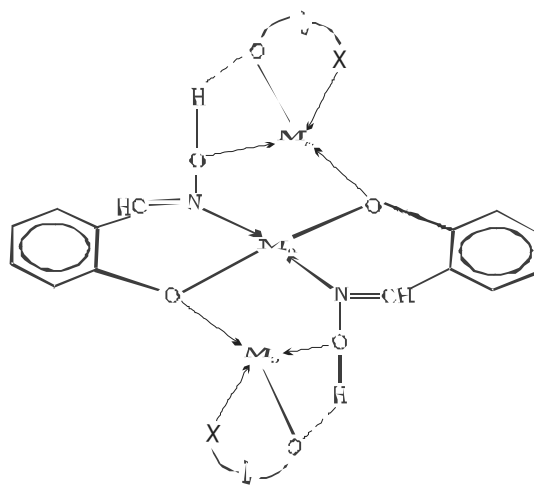


Fig. 1:

Table 1: Colour, decomp. temp., molar conductance, magnetic moments &amp; elemental analysis of the complexes

Compound	Colour	Decomp. temp.(°C)	Molar cond. ( $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ )	Magnetic moment (in BM)	C	H	N	M <sub>a</sub>	M <sub>b</sub>
					% Analysis Found/ (Calc.)				
Cu(salox) <sub>2</sub> .(Li8HQ) <sub>2</sub>	Blackish green	245d	6.4	1.82	60.82 (60.91)	3.75 (3.81)	8.58 (8.76)	9.89 (10.07)	2.10 (2.22)
Cu(salox) <sub>2</sub> .(Na8HQ) <sub>2</sub>	Light green	238m	7.0	1.78	57.24 (57.35)	3.52 (3.58)	8.18 (8.36)	9.35 (9.48)	6.70 (6.87)
Cu(salox) <sub>2</sub> .(K8HQ) <sub>2</sub>	Yellowish green	250m	5.8	1.90	57.65 (54.74)	3.35 (3.42)	7.86 (7.98)	8.97 (9.05)	10.90 (11.12)
Cu(salox) <sub>2</sub> .(Li1N2N) <sub>2</sub>	Light brown	270d	8.5	2.15	58.72 (58.83)	3.38 (3.46)	7.92 (8.07)	9.03 (9.16)	1.88 (2.02)
Cu(salox) <sub>2</sub> .(Na1N2N) <sub>2</sub>	Orange brown	238md	10.5	1.85	54.63 (54.73)	3.15 (3.22)	7.39 (7.51)	8.35 (8.52)	6.03 (6.17)
Cu(salox) <sub>2</sub> .(K1N2N) <sub>2</sub>	Deep brown	285d	7.5	2.10	53.76 (53.86)	3.05 (3.17)	7.25 (7.39)	8.26 (8.38)	10.18 (10.30)
Ni(salox) <sub>2</sub> .(Li8HQ) <sub>2</sub>	Light green	260md	10.0	-	60.55 (60.69)	3.73 (3.79)	8.75 (8.85)	9.09 (9.28)	1.95 (2.12)
Ni(salox) <sub>2</sub> .(Na8HQ) <sub>2</sub>	Parrot green	285d	8.5	—	57.62 (57.77)	3.55 (3.61)	8.39 (8.42)	8.65 (8.83)	6.83 (6.92)
Ni(salox) <sub>2</sub> .(K8HQ) <sub>2</sub>	Deep green	290d	9.0	-	55.02 (55.12)	3.35 (3.44)	7.84 (8.04)	8.32 (8.42)	11.05 (11.19)
Ni(salox) <sub>2</sub> .(Li1N2N) <sub>2</sub>	Reddish brown	>300	11.0	-	59.05 (59.24)	3.41 (3.48)	8.06 (8.13)	8.45 (8.52)	1.95 (2.03)
Ni(salox) <sub>2</sub> .(Na1N2N) <sub>2</sub>	Deep brown	>300	9.8	-	56.55 (56.61)	3.25 (3.33)	7.59 (7.70)	8.05 (8.14)	6.18 (6.38)
Ni(salox) <sub>2</sub> .(K1N2N) <sub>2</sub>	Deep brown	290d	7.8	-	54.05 (54.20)	3.05 (3.19)	7.35 (7.44)	7.55 (7.80)	10.25 (10.36)

The  $\nu_{N-O}$  band of  $Cu(salox)_2$  at  $1148\text{ cm}^{-1}$  show a appreciable change in oxygen bridged complexes which are observed between  $1217-1110\text{ cm}^{-1}$  and another band at  $1216\text{ cm}^{-1}$  remain unaffected in most of the oxygen bridged complexes. The  $\nu_{N-O}$  band of  $Ni(salox)_2$  at  $1219\text{ cm}^{-1}$  splits into two absorption bands which are observed between  $1092-1214\text{ cm}^{-1}$  in the oxygen bridged complexes. This is probably due to the presence of symmetric and asymmetric stretching band of N-O of oxime group.

In all the present complexes, the bands with medium to strong absorption in the far infrared region  $510-588\text{ cm}^{-1}$  and  $460-505\text{ cm}^{-1}$  tentatively assigned to  $\nu_{M-O}$  and  $\nu_{M-N}$  modes<sup>10</sup> respectively. These bands are not present in salicylaldehyde. While in neutral transition metal chelates,

$Cu(salox)_2$  and  $Ni(salox)_2$  at region  $465-476\text{ cm}^{-1}$  and  $570-613\text{ cm}^{-1}$ . 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 at higher wave number. The above data confirm the coordination of oxygen atoms of phenolic group and oximino group to alkali metal in all the oxygen bridged complexes.

#### Electronic absorption spectra

Electronic absorption spectra of metal chelates and their adducts 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 - 2. Electronic absorption bands are observed between

**Table 2: IR & electronic absorption bands of CuEA, NiEA and their complexes**

Compound	IR absorption bands (in $\text{cm}^{-1}$ )					Diffuse reflectance (in nm)
	$\nu_{O-H/O-H\dots O}$	$\nu_{C-O}$	$\nu_{C=N}$	$\nu_{N-O}$	$\nu_{M-O/M-N}$	
$Cu(salox)_2$	3150,2401	1538	1648, 1598	1216, 1148	613,585, 476	326,348,382,391
$Cu(salox)_2.(Na8HQ)_2$	3429,3195, 2359	1541, 1500	1605, 1549	1217, 1112	545,510, 460	319,355,391,430
$Cu(salox)_2.(K1N2N)_2$	3220,2361	1535	1651, 1590	1216, 1110	565,519, 480	328,362,391,412,427
$Ni(salox)_2$	3435,2377, 2200	1538	1651	1219	570,465	358,391,405,416,423
$Ni(salox)_2.(Li8HQ)_2$	3350,3022, 2402	1502	1605, 1589	1216, 1118	548,505, 470	348,398
$Ni(salox)_2.(Na1N2N)_2$	3391,3250 2356	1513	1601, 1593	1214, 1153, 1092	588,529, 485	358,420

**Table 3: Antibacterial and antifungal activity of the adducts**

Compound	Minimum Inhibitory conc. (in $\mu\text{gml}^{-1}$ )		
	<i>E. coli</i>	<i>S. aureus</i>	<i>C. albicans</i>
$Cu(salox)_2.(Na8HQ)_2$	35	20	30
$Cu(salox)_2.(K1N2N)_2$	35	20	30
$Ni(salox)_2.(Li8HQ)_2$	25	40	30
$Ni(salox)_2.(Na1N2N)_2$	25	20	30

352-490 nm in the metal chelates,  $\text{Cu}(\text{salox})_2$  and  $\text{Ni}(\text{salox})_2$  show that there is charge transfer as well as d-d transition.

The spectra of all the oxygen bridged complexes also gave similar type of bands in the region of 319-398 nm and 405-430 nm. This suggests square planar geometry in all the complexes and so there is no change in stereo-chemistry of after complex formation. This is supported by the magnetic moment value of the complexes. The electronic absorption bands located in the region 319-398 nm may be attributed to arise due to charge transfer. However, the possibility of peak in the region 405-430nm.

The absorption bands of medium intensity in  $\text{Ni}(\text{salox})_2$  in the region 351-490 nm in electronic spectra, suggests the square planar structure of  $\text{Ni}^{2+}$  with the coordination number 4. The absorption bands of oxygen bridged complexes derived from  $\text{Ni}(\text{salox})_2$  is found in the region of 348–423 nm, suggesting the same square planar geometry of  $\text{Ni}(\text{salox})_2$  with coordination number 4 in all the complexes.

### Magnetic moment

Magnetic moment of metal chelates and their adducts have been measured by Can Faraday magnetic susceptibility balance at 30°C. The magnetic moment 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  $\text{Cu}(\text{salox})_2$  has been found to be 1.78 BM, suggesting their square planar geometry with coordination number 4, while the magnetic moments of oxygen bridged complexes are in between 1.78 to 2.15 BM corresponds to the presence of one unpaired electron. Therefore, the stereo-chemistry of  $\text{Cu}(\text{salox})_2$  unit in the complexes remain almost same. Very low values (approaching to zero) of magnetic moment ( $\mu_{\text{eff}}$ ) of  $\text{Ni}(\text{salox})_2$  and its oxygen bridged complexes,

suggesting their diamagnetic nature. This observation also suggests their square planar geometry with coordination number 4 for  $\text{Ni}^{2+}$  ion.

### Microbiological studies

Minimum inhibitory concentration(MIC) values (in  $\mu\text{gml}^{-1}$ ) of some of the prepared oxygen bridged complexes of  $\text{Cu}(\text{salox})_2$  and  $\text{Ni}(\text{salox})_2$  have been examined by serial dilution method<sup>12</sup> for activity against some bacteria, viz. *E. coli*, *S. aureus* and fungi, viz. *C. albicans*. The results are summarized in Table - 3.

The results of antibacterial and antifungal activity evaluation revealed that four of the bimetallic complexes,  $\text{Cu}(\text{salox})_2 \cdot (\text{Na8HQ})_2$ ,  $\text{Cu}(\text{salox})_2 \cdot (\text{K1N2N})_2$ ,  $\text{Ni}(\text{salox})_2 \cdot (\text{Li8HQ})_2$  and  $\text{Ni}(\text{salox})_2 \cdot (\text{Na1N2N})_2$ , were relatively potential inhibitor of the growth of both the test bacteria and one fungi.

The MIC values of  $\text{Cu}(\text{salox})_2 \cdot (\text{Na8HQ})_2$  and  $\text{Cu}(\text{salox})_2 \cdot (\text{K1N2N})_2$  at a concentration of 35  $\mu\text{gml}^{-1}$  while  $\text{Ni}(\text{salox})_2 \cdot (\text{Li8HQ})_2$  and  $\text{Ni}(\text{salox})_2 \cdot (\text{Na1N2N})_2$  at a concentration of 25  $\mu\text{gml}^{-1}$  for *E. coli*. The MIC values of  $\text{Cu}(\text{salox})_2 \cdot (\text{K1N2N})_2$ ,  $\text{Ni}(\text{salox})_2 \cdot (\text{Li8HQ})_2$  and  $\text{Cu}(\text{salox})_2 \cdot (\text{Na8HQ})_2$ ,  $\text{Ni}(\text{salox})_2 \cdot (\text{Na1N2N})_2$  at the concentration 40  $\mu\text{g ml}^{-1}$  and 20  $\text{mgml}^{-1}$  respectively for *S. aureus*. The MIC values of all the four bimetallic complexes at the same concentration 30  $\mu\text{gml}^{-1}$  for fungi *C. albicans*.

### Structure & Bonding

The bonding between the transition metal chelates,  $\text{M}_a(\text{salox})_2$  and the alkali metal is most likely to occur by dative bonding via the phenolic and oximino oxygen atoms, which has been supported by the infrared, electronic absorption spectral studies and magnetic moment measurements. The probable structures of the newly prepared oxygen bridged complexes,  $\text{M}_a(\text{salox})_2 \cdot (\text{M}_b\text{L})_2$  may be produced schematically as such (Fig. 1).

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