

## **BINUCLEAR ALKALI METAL COMPLEXES WITH Ni(II) & Cui(II) METAL CHELATES OF 3-HYDROXY-2-METHYL-1, 4-NAPHTHAQUINONE(THIocol)**

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A number of complexes of the type  $M_a(THL)_2 \cdot 2H_2O \cdot M_bL$ , where  $M_a = Ni(II)$  or  $Cu(II)$ ;  $M_b = Li, Na$  or  $K$ , THL = 3-Hydroxy-2-methyl-1, 4-naphthaquinone (Thiocol), L = deprotonated o-nitrophenol (ONP) or 1-nitroso-2-naphthol (1N2N) have been synthesized by treating Ni(II) or Cui(II) metal chelate with alkali metal salt of organic acid (ONP or 1N2N) in ethanolic medium. The complexes were characterized by elemental analysis, molar conductance, magnetic moment measurements, IR, UV-VIS spectral data. On the basis of experimental data, these complexes were found to be octahedral in geometry and non-electrolyte nature.

### **INTRODUCTION**

Thiocol found in many plant systems [1] and has important analytical applications. It provides a potential binding sites for the metal ions. It has been well investigated for its coordinating behaviour towards the transition and non-transition metal ions [2-8]. With a view to extend the investigation of oxygen bridge complexes, we have selected Ni(II) and Cui(II) metal chelates of Thiocol.

### **EXPERIMENTAL**

AnalalaR quality of o-nitrophenol (ONP), 1-nitroso-2-naphthol (1N2N), nickel (II) acetate and cupric chloride were used for the preparation of metal chelates and adducts. Ligand, 3-Hydroxy-2-methyl-1, 4-naphthaquinone (Thiocol) was prepared by the method of Burton [9].

**Preparation of Ni(II) or Cui(II) metal chelates :** 0.01 mole of 1, 4-Dihydroxynaphthaquinone was dissolved in 100 ml of ethanol. To this was added 0.01 mole nickel (II) acetate or cupric chloride in 50 ml warm distilled water. The mixture solution was refluxed for one hour on hot plate of magnetic stirrer.

**Preparation of adduct of alkali metal salt of organic acid ( $M_bL$ ) with transition metal chelate  $\{M_a(THL)_2 \cdot 2H_2O\}$ ;  $[M_a(THL)_2 \cdot 2H_2O \cdot M_bL]$  :**

0.001mole of transition metal chelate,  $M_a(\text{THL})_2 \cdot 2\text{H}_2\text{O}$  was taken in absolute ethanol in a conical flask and 0.001 mole alkali metal salt of 1-nitroso-2-naphtho/o-nitrophenol was added to it, slight excess of alkali metal salt was added. On stirring, the colour of mixture solution changed. It was further refluxed for 2-3 hours on hot plate of magnetic stirrer at  $80^\circ\text{C}$ . The adduct got precipitated immediately. It was filtered, washed with the solvent and dried in an electric oven at  $100^\circ\text{C}$ .

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

Compound	Colour	Decomp. 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	Ma	Mb
Ni(THL) <sub>2</sub> ·2H <sub>2</sub> O·LiONP	Reddish brown	>300	9.8	3.22	54.80 (54.75)	3.66 (3.58)	2.40 (2.28)	9.65 (9.56)	1.24 (1.14)
Ni(THL) <sub>2</sub> ·2H <sub>2</sub> O·NaONP	Reddish brown	>300	8.5	3.25	53.42 (53.36)	3.60 (3.49)	2.30 (2.22)	9.40 (9.32)	3.76 (3.65)
Ni(THL) <sub>2</sub> ·2H <sub>2</sub> O·KONP	Reddish brown	>300	5.5	3.28	52.10 (52.03)	3.50 (3.41)	2.24 (2.17)	9.18 (9.09)	6.13 (6.04)
Ni(THL) <sub>2</sub> ·2H <sub>2</sub> O·Li1N2N	Blackish green	>300	7.6	3.22	59.32 (59.28)	3.76 (3.70)	2.26 (2.16)	9.16 (9.06)	1.20 (1.08)
Ni(THL) <sub>2</sub> ·2H <sub>2</sub> O·Na1N2N	Blackish green	>300	8.4	3.09	57.92 (57.85)	3.69 (3.61)	2.19 (2.11)	8.92 (8.84)	3.56 (3.46)
Ni(THL) <sub>2</sub> ·2H <sub>2</sub> O·K1N2N	Blackish green	>300	3.8	3.16	56.56 (56.49)	3.60 (3.53)	2.16 (2.06)	8.75 (8.63)	5.84 (5.74)
Cu(THL) <sub>2</sub> ·2H <sub>2</sub> O·LiONP	Dark brown	>300	8.6	2.14	54.36 (54.31)	3.60 (3.55)	2.34 (2.26)	10.32 (10.28)	1.21 (1.13)
Cu(THL) <sub>2</sub> ·2H <sub>2</sub> O·NaONP	Reddish brown	>300	9.2	2.15	52.99 (52.94)	3.52 (3.46)	2.28 (2.20)	10.10 (10.02)	3.76 (3.62)
Cu(THL) <sub>2</sub> ·2H <sub>2</sub> O·KONP	Deep brown	>300	9.2	2.19	51.76 (51.64)	3.46 (3.38)	2.24 (2.15)	9.85 (9.77)	6.05 (5.99)
Cu(THL) <sub>2</sub> ·2H <sub>2</sub> O·Li1N2N	Greenish brown	>300	8.6	1.85	58.92 (58.84)	6.69 (3.68)	2.18 (2.14)	9.80 (9.74)	1.14 (1.07)
Cu(THL) <sub>2</sub> ·2H <sub>2</sub> O·Na1N2N	Greenish brown	270d	15.2	2.18	57.48 (57.43)	3.65 (3.59)	2.14 (2.09)	9.58 (9.51)	3.50 (3.44)
Cu(THL) <sub>2</sub> ·2H <sub>2</sub> O·K1N2N	Greenish brown	>300	9.1	2.20	56.15 (56.09)	3.56 (3.50)	2.12 (2.04)	9.36 (9.29)	5.76 (5.59)

## RESULTS & DISCUSSION

Some of the physical properties of Thiocol, its metal chelates and new adducts formed are listed in Table-1.

Thiocol is bright yellow shining powder, melting point  $173^\circ\text{C}$ . The adducts are of characteristic colours. They are generally slightly soluble in methanol, ethanol, DMF but

insoluble in benzene, chloroform etc. The decomposition temperatures of the adducts are higher than their respective metal chelates and ligand. The higher decomposition temperatures show the strong bonding probably through oxygen atom of the metal chelates to the alkali metal salts.

**Conductivities :** Molar conductivities of all these complexes were measured in methanol at 303 K at a concentration of  $10^{-3}$  M. A value of ca.  $35\text{-}40\text{ ohm}^{-1}\text{ cm}^2\text{ mole}^{-1}$  appears characteristic of 1 : 1 electrolyte [10], whereas ideally molar conductivity of a neutral complex should be zero. From result (Table-1), it is observed that none of the value approach either ideal or 1 : 1 electrolyte. Low values (3.8 – 10.1) of molar conductivities of these complexes would seem to indicate neutral complexes and covalent nature.

**Infrared spectra :** Infrared spectral measurements were made in Nujol mull/KBr phase for the ligand (Thioco), its metal chelates and their adducts between  $4000\text{-}400\text{ cm}^{-1}$  with the help of JASCO-FT/IR spectrometer model 5300. Selected absorption bands in different regions are given in Table-2.

**Table 2. IR and electronic absorption bands of THL, Cu(THL)<sub>2</sub>.2H<sub>2</sub>O, Ni(THL)<sub>2</sub>.2H<sub>2</sub>O and their oxygen bridged complexes**

Compound	IR absorption bands (in $\text{cm}^{-1}$ )						Diffuse reflectance (in nm)
	$\nu_{\text{O-H}}$	$\nu_{\text{C=O}}$ (free)	$\nu_{\text{C=O}}$ (bonded)	$\nu_{\text{C-O}}$	$\delta_{\text{H}_2\text{O}}$ rocking/ oxo-bridge	$\nu_{\text{M-O}}$	
3-Hydroxy-2-methyl-1,4-naphthaquinone (THL)	3347	1670	1630	1290	...	...	
Ni(THL) <sub>2</sub> .2H <sub>2</sub> O	3371	1624	1583	1292	854, 733	486, 422	670, 530, 460, 335, 330, 260
Ni(THL) <sub>2</sub> .2H <sub>2</sub> O.LiONP	3358	1624	1584	1292	845, 733	550, 451	665, 450, 345, 262
Ni(THL) <sub>2</sub> .2H <sub>2</sub> O.NaONP	3424	1639	1626, 1583	1293	772	430	668, 452, 340, 265
Ni(THL) <sub>2</sub> .2H <sub>2</sub> O.K1N2N	3402	1612	1531	1249	835, 756	448, 424	575, 500, 305, 260
Cu(THL) <sub>2</sub> .2H <sub>2</sub> O	3352	1658	1591	1277	842, 725	540, 443, 420	655, 490, 350, 285, 260
Cu(THL) <sub>2</sub> .2H <sub>2</sub> O.NaONP	3416	1660	1593	1269	850, 775	470, 409	660, 485, 345, 265
Cu(THL) <sub>2</sub> .2H <sub>2</sub> O.K1N2N	3451	1622	1597	1282	841, 746	522, 424	660, 485, 355, 285, 260

The moderately strong band present in thiocol at  $3347\text{ cm}^{-1}$  is attributed to the stretching-OH vibration frequency. The free carbonyl and the hydrogen bonded carbonyl are assigned to  $1630\text{ cm}^{-1}$ . Attempts have been made to assign peak shifts due to chelation of formerly hydrogen bonded carbonyl.

The infrared spectra of Ni(THL)<sub>2</sub>.2H<sub>2</sub>O and Cu(THL)<sub>2</sub>.2H<sub>2</sub>O have been reported by Bottei & McEachern [11]. They observed that the C = O peak of lawsone at  $1632\text{ cm}^{-1}$  shifted down in the region  $1500\text{-}1600\text{ cm}^{-1}$  due to chelation.

The –OH stretching frequency of thiocol is missing in the Ni(THL)<sub>2</sub>.2H<sub>2</sub>O & Cu(THL)<sub>2</sub>.2H<sub>2</sub>O complexes because hydrogen atom of –OH group is replaced by Ni or Cu atom from all the transition metal chelates.

From the IR spectra, it is observed that the C=O frequency of Ni(THL)<sub>2</sub>.2H<sub>2</sub>O at 1583 cm<sup>-1</sup> shows higher shifts to 1584-1626 cm<sup>-1</sup> region in its alkali metal adducts and the corresponding C=O frequency of Cu(THL)<sub>2</sub>.2H<sub>2</sub>O at 1591 cm<sup>-1</sup>, again shows higher shift to 1593 -1597 cm<sup>-1</sup> region in its adduct. The characteristics absorption band of  $\nu_{C-O}$  (phenolic) stretching vibration observed at 1292 cm<sup>-1</sup> and 1277 cm<sup>-1</sup> in Ni(THL)<sub>2</sub>.2H<sub>2</sub>O and Cu(THL)<sub>2</sub>.2H<sub>2</sub>O shows again higher shifts in the alkali metal adduct which indicate increased bond order between the C and O atoms as a result of coordination of oxygen atom to the alkali metal. A new band appears at region 725-775 cm<sup>-1</sup> suggests formation of oxo-bridge in the adducts. The broad O–H peaks at 3352-3451 cm<sup>-1</sup> and rocking  $\delta_{H_2O}$  in the region 835 - 854 cm<sup>-1</sup>, showing the two water molecules are coordinated with Ni(II) or Cu(II) metal. H<sub>2</sub>O molecules loss at a temperature ~ 150°C which indicates strong association. Further in the low frequency region, the bands observed at region 409-550 cm<sup>-1</sup> suggest bonding between the metal chelates and alkali metal which generally appear by dative bonding via oxygen atom of C–O (phenolic).

**Magnetic property** – Magnetic measurements were taken on Cahn-Faraday electronic balance at 295K. The results of the magnetic measurements are given in Table-1. In most of the octahedral Ni(II) complexes, the magnetic moment values at room temperature are found between 2.90-3.40 BM [15], but in the tetrahedral Ni(II) complexes magnetic moment values are usually much higher than spin only value expected for two unpaired electrons (2.83 BM) [12].

In the present investigation, the magnetic moment for Ni(THL)<sub>2</sub>.2H<sub>2</sub>O has been found 2.78 BM, which is very close to spin only value. The binuclear adducts of Ni(THL)<sub>2</sub>.2H<sub>2</sub>O possess magnetic moment values between 3.09-3.28 BM. at room temperature, which are fall in range of octahedral Ni(II) complexes.

The majority of the copper (II) complexes display magnetic moment values in the range of 1.75 to 2.20 BM, while the magnetic moment values of some Cu(II) complexes are substantially below the spin only value (1.73 BM) and remarkably temperature dependent. The complexes, which have magnetic moment values lower than the spin only value, are termed as magnetically subnormal complexes. Copper (II) complexes whose magnetic moment values lie between 1.75 and 2.20 BM are termed as magnetically dilute complexes and their magnetic moment values are independent of temperature [13].

The magnetic moment values of Cu(THL)<sub>2</sub>.2H<sub>2</sub>O has found to be 1.23 BM at room temperature (22°C), due to antiferromagnetic or dimeric interaction and the magnetic moment values of the binuclear alkali metal adducts of Cu(THL)<sub>2</sub>. 2H<sub>2</sub>O display higher magnetic moment values (2.15-2.20 BM), which clearly indicate that antiferromagnetic nature is diminished, but simple octahedral geometry appears in the adducts.

**Electronic spectra** : Electronic spectra were recorded on SHIMADZU UV-VIS 160A spectrophotometer in Nujol mull/paraffin solvent. The band observed in electronic spectra of Ni(II) and Cu(II) metal chelates and their binuclear alkali metal adducts are shown in Table-2.

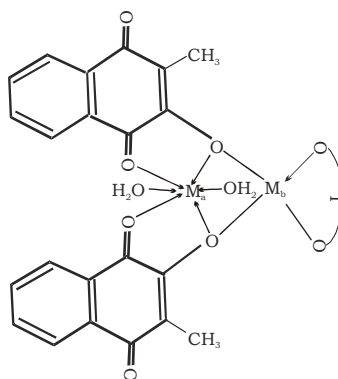
The electronic spectra of Ni(THL)<sub>2</sub>.2H<sub>2</sub>O and its binuclear alkali metal adducts in paraffin liquid display bands in the region 260 - 345 nm due to charge transfer. In Ni(THL)<sub>2</sub>.2H<sub>2</sub>O, and at region 460-670 nm assigned to the first and second spin allowed transition  ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$  and  ${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$  respectively characteristic of Ni(II) octahedral complexes. The spectra of binuclear alkali metal adducts, bands also appear in region 450-670nm may be assigned to

${}^3A_{2g} \rightarrow {}^3T_{1g(F)}$  and  ${}^3A_{2g} \rightarrow {}^3T_{2g(F)}$ , The  ${}^3A_{2g(F)} \rightarrow {}^3T_{1g(P)}$  transition could not be observed owing to a very strong charge transfer falling in the visible region. Lower energy bands could not be recorded due to limitations of the instrument. Hence, the nature of absorption band in the alkali metal adducts indicates that octahedral structure.

Study of the spectra of  $\text{Cu}(\text{THL})_2 \cdot 2\text{H}_2\text{O}$  and its binuclear alkali metal adducts band appear in the region from 260-350 nm is due to charge transfer and bands in the region 485-665 nm assigned spin allowed transition to  ${}^2E_g \rightarrow {}^2T_{2g}$  which clearly indicates octahedral geometry of  $\text{Cu}(\text{THL})_2 \cdot 2\text{H}_2\text{O}$  and also in its binuclear alkali metal adducts.

## STRUCTURE AND BONDING

All these observations put together project the following probable structure for these complexes where in transition metal exhibits coordination number six while alkali metal four (Fig. 1).



(where  $M_a = \text{Ni}$  or  $\text{Cu}$ ,  $M_b = \text{Li}$ ,  $\text{Na}$  or  $\text{K}$ ,  $L = \text{deprotonated ONP}$  or  $1\text{N}2\text{N}$ )

Fig. 1.

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