

BINUCLEAR ALKALI METAL COMPLEXES WITH Ni(II) & Cui(II) METAL CHELATES OF 1,4-DIHYDROXYNAPHTHAQUINONE (NAPHTHAZARIN)

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Some noble complexes of the type $M_a(Nz).2H_2O.M_bL$, where $M_a = Ni(II)$ or $Cui(II)$; $M_b = Li, Na$ or K , $Nz = 1, 4$ -Dihydroxynaphthquinone (Naphthazarin), $L =$ deprotonated *o*-nitrophenol (ONP) or 1-nitroso-2-naphthol (1N2N) have been synthesized and 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 polymeric octahedral structure. IR spectral studies revealed that in the adducts, transition metal is joined to the alkali metal by phenolate bridges and two water molecules are coordinated with transition metal.

INTRODUCTION

Naphthazarin, like other hydroxyquinolines has been extensively used in technology as mordant dyes and dye intermediates [1]. It present in plant systems like other hydroxyl-quinolines and it provides potential binding sites for metal ions. A large number of these complexes containing both transition and non-transition metal ions and a variety of hydroxyquinones ligand systems have been reported [2-7]. With a view to extend the investigation of oxygen bridge complexes, we have selected Ni(II) and Cui(II) metal chelates of naphthazarin.

EXPERIMENTAL

AnalaR 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, 1, 4-Dihydroxynaphthaquinone(Naphthazarin) was prepared by reported method [8].

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 $\{M_a(Nz).2H_2O\}$; $[M_a(Nz).2H_2O.M_bL]$:

0.001mole of transition metal chelate, $M_a(Nz).2H_2O$ 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 $80^\circ C$. The adduct got precipitated immediately. It was filtered, washed with the solvent and dried in an electric oven at $100^\circ C$.

RESULTS & DISCUSSION

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

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

Compound	Colour	Decomp. Temp. ($^\circ C$)	Molar cond. ($ohm^{-1} cm^2 mol^{-1}$)	Magnetic moment in (BM)	% Analysis Found/ (Calc.)				
					C	H	N	M_a	M_b
Ni(THL) ₂ .2H ₂ 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) ₂ .2H ₂ 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) ₂ .2H ₂ 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) ₂ .2H ₂ O.Li1N2N	Blackish green	>300	7.6	3.22	59.32 (59.28)	3.76 (3.70)	2.26 (2.16)	9.16 (90.6)	1.20 (1.08)
Ni(THL) ₂ .2H ₂ 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) ₂ .2H ₂ 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) ₂ .2H ₂ 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) ₂ .2H ₂ 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) ₂ .2H ₂ 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) ₂ .2H ₂ 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) ₂ .2H ₂ 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) ₂ .2H ₂ 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)

Naphthazarin is blackish brown shining powder (M.pt. 192°C, Trans. temp. 180°C), insoluble in water but soluble in alcohol and benzene. The colour of the adducts formed are different with respect to the metal chelates. The decomposition temperatures of the adducts are higher than their respective metal chelates and ligand, which give first sight indication for the formation of polymeric adducts.

Conductivities : Molar conductivities of all these complexes were measured in DMF at 302 K at a concentration of 10^{-3} M. A value of Ca. $35-40 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ appears characteristic of 1 : 1 electrolyte [9], 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 (4.9 to 15.2) of molar conductivities of these complexes would seem to indicate neutral complexes and non-electrolyte nature.

Infrared spectra : Infrared spectral measurements were made in Nujol mull/KBr phase for the ligand (Naphthazarin), its metal chelates and their adducts between $4000-400 \text{ cm}^{-1}$ 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)₂.2H₂O, Ni(THL)₂.2H₂O and their oxygen bridged complexes

Compound	IR absorption bands (in 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) ₂ .2H ₂ O	3371	1624	1583	1292	854, 733	486, 422	670, 530, 460, 335, 330, 260
Ni(THL) ₂ .2H ₂ O.LiONP	3358	1624	1584	1292	845, 733	550, 451	665, 450, 345, 262
Ni(THL) ₂ .2H ₂ O.NaONP	3424	1639	1626, 1583	1293	772	430	668, 452, 340, 265
Ni(THL) ₂ .2H ₂ O.K1N2N	3402	1612	1531	1249	835, 756	448, 424	575, 500, 305, 260
Cu(THL) ₂ .2H ₂ O	3352	1658	1591	1277	842, 725	540, 443, 420	655, 490, 350, 285, 260
Cu(THL) ₂ .2H ₂ O.NaONP	3416	1660	1593	1269	850, 775	470, 409	660, 485, 345, 265
Cu(THL) ₂ .2H ₂ O.K1N2N	3451	1622	1597	1282	841, 746	522, 424	660, 485, 355, 285, 260

In the spectra of naphthazarin (Nz), absence of $-\text{OH}$ absorption band in the region $3500-1800 \text{ cm}^{-1}$ suggests that there is strong hydrogen bonding. This has been confirmed by Flett [10]. It is apparent that in every case where a hydroxyl ($-\text{OH}$) group is not adjacent to a carbonyl group, a band is observed at about 3350 cm^{-1} , which may be associated with the $-\text{OH}$ vibration. A hydroxy group in the o-position gives rise to no such band, but shifts the second carbonyl band to lower frequency, clearly, hydrogen bonding is responsible. The absence of the hydroxyl band and shifting to 1621 cm^{-1} of $\text{C}=\text{O}$ frequency indicate very marked weakening of the OH and C = O bond frequencies. The band is attributed to the

chelated hydroxyl group of the quinone (C=O H-O) and indicates the presence of intramolecular hydrogen bonding in the naphthazarin.

In the spectra of metal chelates, Ni(Nz).2H₂O and Cu(Nz).2H₂O, the OH absorption band of ligand(Nz) is missing because hydrogen atom of -OH(phenolic) group has replaced by transition metal (Ni or Cu) atom.

From the IR spectra, it is observed that the C=O frequency of Ni(Nz).2H₂O at 1560 cm⁻¹ shows lower shifts to 1543-1550 cm⁻¹ region in its alkali metal adducts and corresponding C=O frequency of Cu(Nz).2H₂O at 1556 cm⁻¹, again shows lower shift to 1535 cm⁻¹ region in the adducts. The characteristics absorption band of ν_{C-O} (phenolic) stretching vibration observed at 1255 cm⁻¹ and 1260 cm⁻¹ in Ni(Nz).2H₂O and Cu(Nz).2H₂O shows again higher shifts(4-16 cm⁻¹) in the 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 756-771 cm⁻¹ which suggests formation of oxo-bridge in the adducts. Broad O-H peaks at 3332-3425 cm⁻¹ and rocking δH_2O in the region 837-851 cm⁻¹, indicate the two water molecules are coordinated with Ni(II) or Cu(II) metal. H₂O molecules loss at a temperature ~ 140°C which indicates strong association. Further in the low frequency region, the bands observed at region 567-416 cm⁻¹ suggest bonding between the metal chelates and alkali metal has most likely occurred by dative bonding via oxygen atom of C-O (phenolic). So, we infer that in the alkali metal adducts the phenolate group in the chelates bridges the alkali metal salts and form a polynuclear structure. It also appears from the structure the carbonyl oxygens of metal chelates in the polymeric structure, now becomes free.

Magnetic property : Magnetic measurements were taken on Cahn-Faraday electronic balance at 295K. The values are given in Table - 1.

The octahedral complexes of Ni(II) are always paramagnetic but the possibility of diamagnetic complexes can not be ruled out. In most of the complexes the room temperature magnetic moment values of the octahedral Ni(II) complexes are observed between 2.90-3.40 BM depending the magnitude of orbital contribution [11]. Tetrahedral Ni(II) complexes are paramagnetic and their room temperature magnetic moment values are usually higher than the spin only values expected for two unpaired electrons (3.4 to 4.2 BM), in some cases lower magnetic moment values have also been reported [12-13]. The high magnetic moment values of the complexes are due to orbital contribution and are the functions of temperature. In the present investigation, the alkali metal adducts of Ni(Nz).2H₂O possess room temperature magnetic moment values between 3.05 to 3.19 BM which are close to the reported values for most of octahedral Ni(II) complexes. Thus the octahedral geometry of Ni(Nz).2H₂O retain in the alkali metal adducts.

Cu(II) whose magnetic moment values lie between 1.75 to 2.20 BM are termed as magnetically dilute complexes and their magnetic moment values are independent of temperature. The magnetic moment values of the planar Cu(II) complexes occur in the vicinity of spin only value (1.73 BM) while the room temperature magnetic moment values of octahedral Cu(II) complexes occur between 1.88 to 2.20 BM. The magnetic moment of both Cu(Nz).2H₂O and its alkali metal adducts have been found to be 1.24 and in the range 1.85-2.10 BM respectively. Thus it is clear that the complexes are magnetically dilute and they have octahedral structure [14-15].

Electronic spectra : Electronic spectra of Ni(Nz).2H₂O and Cu(Nz).2H₂O and their alkali metal adducts were recorded on SHIMAZU UV-VIS 160A spectrophotometer in Nujol mull/paraffin solvent. The observed bands in electronic spectra are given in Table - 3.

The electronic spectra of the Ni(Nz).2H₂O complexes in Nujol mull display bands in region 260-330 nm due to charge transfer. The band at 670 nm are assigned to the first & second spin allowed transition ${}^3A_{2g} \rightarrow {}^3T_{1g(F)}$ and ${}^3A_{2g} \rightarrow {}^3T_{2g(F)}$ respectively, characteristic of Ni(II) in an octahedral environment. The ${}^3A_{2g(F)} \rightarrow {}^3T_{1g(P)}$ transition could not be observed owing to a very strong charge transfer band falling into the visible region [16]. The spectra of binuclear adducts are identical and the bands usually observed in the region 450-670 nm may be also assigned ${}^3A_{2g} \rightarrow {}^3T_{1g(F)}$ and ${}^3A_{2g} \rightarrow {}^3T_{2g(F)}$. The lower energy bands (800-1000 nm) could not be recorded in the adducts due to limitations of the instrument. Hence, the nature of absorption bands of alkali metal adducts suggest their octahedral structures, this fact is also supported by magnetic measurements.

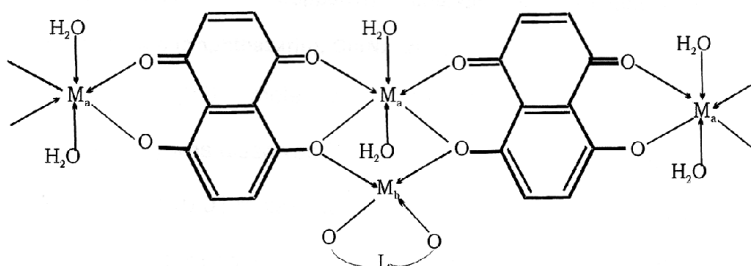
In Cu(II) complexes, charge transfer bands also appear in the region 255-345 nm. Sacconi *et al* [17] have examined spectra of a number of Cu(II) and found that the ligand field absorption bands in the region 600-1250 nm, shift to higher wavelength as the environment about the copper atoms, tends from octahedral/tetragonal/planar to tetrahedral. The electronic spectra of the Cu(Nz).2H₂O was recorded and a broad peak at 670 nm has been observed. In the spectra of alkali metal adducts of Cu(Nz).2H₂O, the band in region 650-675 nm, assigned spin allowed transition ${}^2E_g \rightarrow {}^2T_{2g}$, suggests no change in stereochemistry *i.e.* octahedral geometry of Cu(II) chelates of naphthazarin.

Table – 3. Major diffuse reflectance bands (in nm) for Ni(Nz).2H₂O & Cu(Nz).2H₂O and their alkali metal adducts.

Compound	Diffuse Reflectance (in nm)
Ni(Nz).2H ₂ O	670, 460, 330, 290, 260
Ni(Nz).2H ₂ O. Na(1N2N)	670, 505, 310, 260
Ni(Nz).2H ₂ O. K(1N2N)	660, 500, 300, 255
Ni(Nz).2H ₂ O. K(ONP)	670, 450, 320, 250
Cu(Nz).2H ₂ O	670, 340, 290, 260
Cu(Nz).2H ₂ O. Li(1N2N)	650, 342, 305, 265
Cu(Nz).2H ₂ O. Na(ONP)	665, 341, 301, 355
Cu(Nz).2H ₂ O. K(ONP)	675, 330, 260

STRUCTURE & BONDING

On the basis of above mentioned fact a polymeric octahedral structure has been proposed for the adducts, only a portion of it is given below (Fig. 1) :



(where M_a = Ni or Cu; M_b = Li, Na or K; ML = deprotonated ONP or 1N2N)

Fig. 1

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