

BINUCLEAR ALKALI METAL COMPLEXES WITH Ni (II) & Cu (II) METAL CHELATES OF 2, 5-DIHYDROXY-1, 4-BENZOQUINONE

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A number of new heterobinuclear alkali metal complexes of general formula $M_a(BQ).2H_2O.M_bL$, where $M_a = Ni(II)$ or $Cu(II)$, $H_2BQ = 2, 5$ -dihydroxy-1, 4-benzoquinone, $M_b = Li, Na$ or K & $L =$ deprotonated 1-nitroso-2-naphthol (1N2N) or o-nitrophenol (ONP) have been synthesized and characterized with the help of elemental analysis, IR, electronic spectral data, molar conductance and magnetic moment measurements. The IR spectra suggest bonding between the $Ni(II)$ or $Cu(II)$ metal chelate and alkali metal which appear by dative bond via oxygen atoms of C–O (phenolic). The electronic spectral data and magnetic moment values indicate the octahedral geometry of the complexes.

KEYWORDS : Binuclear complexes, Alkali metal & 2, 5-Dihydroxy-1, 4-benzoquinone.

INTRODUCTION

2, 5-Dihydroxy-1, 4-benzoquinone shows chelating properties owing to the presence of hydroxyl and keto groups. The hydroxyl groups at positions 2 and 5 being highly acidic lead to the formation of anion with relative ease. Most of the hydroxy quinones are present in plant system [1] and have important analytical applications. It has been well investigated for its coordinating behaviour towards the alkali metals [2-5] and transition metals [6, 7]. Extending our investigation to synthesize a number of new heterobinuclear complexes by interacting $Ni(II)$ or $Cu(II)$ metal chelates of 2, 5-dihydroxy-1, 4-benzoquinone with alkali metal salt of some organic acids.

RESULTS AND DISCUSSION

Both $Ni(II)$ and $Cu(II)$ metal chelates and their alkali metal adducts are coloured solids and stable at room temp. The decomposition temperatures of metal chelates and their adducts

are considerably higher than the ligand (H₂BQ), show the strong bonding probably through oxygen atoms of the metal chelates to the alkali metal salts. These adducts are highly soluble in DMF but insoluble in benzene, ethanol, chloroform etc, indicates polymeric structure of the adducts. Some physical properties and analytical datas are given in Table-1.

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

Compound	Colour	Decomp. Temp. (°C)	Molar cond. (ohm ⁻¹ cm ² mol ⁻¹)	Magnetic moment (in BM)	% Analysis Found/(Calc.)				
					C	H	N	M _a	M _b
NiBQ, 2H ₂ O.LiONP	Orange	> 300	9.8	2.90	38.12 (38.16)	2.64 (2.72)	3.70 (3.81)	15.54 (15.63)	1.85 (1.98)
NiBQ, 2H ₂ O.NaONP	Reddish brown	> 300	8.5	3.00	36.57 (36.62)	2.54 (2.61)	3.55 (3.65)	14.90 (14.98)	5.84 (5.93)
NiBQ, 2H ₂ O.KONP	Yellowish brown	> 300	5.5	2.95	35.14 (35.19)	2.44 (2.60)	3.41 (3.49)	14.33 (14.42)	9.51 (9.62)
NiBQ, 2H ₂ O.Li1N2N	Yellowish brown	> 300	4.9	3.05	46.43 (46.68)	2.91 (2.98)	3.40 (3.48)	14.25 (14.30)	1.70 (1.81)
NiBQ, 2H ₂ O.Na1N2N	Reddish brown	> 300	7.8	3.10	44.89 (44.95)	2.88 (2.86)	3.27 (3.37)	13.72 (13.82)	5.38 (5.48)
NiBQ, 2H ₂ O.K1N2N	Dark red	> 300	3.8	3.24	43.27 (43.30)	2.61 (2.70)	3.15 (3.35)	13.22 (13.35)	8.78 (8.86)
Cu.BQ.2H ₂ O.LiONP	Reddish brown	292d	8.6	1.94	37.64 (37.68)	2.61 (2.65)	3.66 (3.74)	16.60 (16.75)	1.83 (1.89)
Cu.BQ.2H ₂ O.NaONP	Dull red	> 300	9.2	2.05	36.13 (36.19)	2.50 (2.55)	3.51 (3.58)	15.93 (16.01)	5.77 (5.85)
Cu.BQ.2H ₂ O.KONP	Deep brown	> 300	10.2	2.15	34.74 (34.79)	2.41 (2.49)	3.37 (3.46)	15.32 (15.42)	9.40 (9.48)
Cu.BQ.2H ₂ O.Li1N2N	Greenish brown	> 300	8.6	2.10	36.09 (36.14)	2.68 (2.76)	3.36 (3.45)	15.24 (15.32)	1.68 (1.76)
Cu.BQ.2H ₂ O.Na1N2N	Light brown	> 300	7.8	2.18	44.39 (44.44)	2.77 (2.85)	3.23 (3.30)	14.68 (14.79)	5.31 (5.38)
Cu.BQ.2H ₂ O.K1N2N	Light brown	> 300	9.1	2.15	42.81 (42.98)	2.87 (2.97)	3.32 (3.42)	14.15 (14.65)	5.69 (6.05)

Molar conductance measurement : Molar conductance of all the adducts was measured in methanol at 27°C at the concentration 10⁻³ M. The molar conductance values are given in Table-1. The value of about 35-40 ohm⁻¹ cm² mole⁻¹ is characteristic of a 1 : 1 electrolyte, whereas ideally molar conductance of a neutral complex should be zero [8]. The low molar conductance values (3.8 to 10.1 ohm⁻¹ cm² mole⁻¹) of all the adducts indicate their non-electrolyte nature.

Infrared spectra : Infrared spectral measurements were made in Nujol mull/KBr phase for the ligand (H₂BQ), Ni (II) & Cu (II) metal chelates and their alkali metal adducts between 4000-400 cm⁻¹ with the help of JASCO FT/IR spectrophotometer model 5300. Pertinent IR data for these compounds are shown in Table-2.

The absorption bands of our interests in the infrared spectrum of ligand (H₂BQ) are 3263 cm⁻¹ and 1618 cm⁻¹. The H₂BQ molecule has a sharp absorption peak in the 3263 cm⁻¹ region due to the -OH stretching vibration. The hydrogen bonded carbonyl is assigned to 1618 cm⁻¹.

Table-2. IR & electronic absorption bands of H₂BQ, CuBQ.2H₂O, NiBQ.2H₂O and their oxygen bridged complexes

Compound	IR absorption bands (in cm ⁻¹)					Diffuse reflectance (in nm)
	$\nu_{\text{O-H}}$	$\nu_{\text{C-H}}$	$\nu_{\text{C-O}}$	$\delta_{\text{H}_2\text{O}}$ rocking/ oxo-bridge	$\nu_{\text{M-O}}$	
2, 5-Dihydroxybenzoquinine (H ₂ BQ)	3263	1618	1307
NiBQ, 2H ₂ O	3331	1530	1265	818, 771	532, 418	600, 440, 370, 330, 250
NiBQ, 2H ₂ O.LiONP	3330	1571, 1529	1269	821, 774	540, 423	670, 485, 380, 340, 290, 250
NiBQ, 2H ₂ O.Na1N2N	3547, 3396	1597, 1560, 1531	1267	835, 816, 768	524, 463, 415	660, 490, 340, 300, 250
NiBQ, QH ₂ O.K1N2N	3369, 3231	1570, 1529	1267	817, 771	540, 424	665, 490, 400, 340, 255
CuBQ.2H ₂ O	3545, 3295	1535	1253	870, 825, 775	542, 424	650, 490, 320, 290, 260
Cu.BQ.2H ₂ O.LiONP	3431	1535	1255	852, 812, 762	521, 461	670, 495, 430, 340, 300, 255
Cu.BQ.2H ₂ O.NaONP	3418	1618	1285	854, 823, 755	460	660, 490, 340, 280, 250
Cu.BQ.2H ₂ O.K1N2N	3404	1550	1255	858, 810, 767	540, 463	650, 490, 430, 300, 250

The infrared spectra of H₂BQ and its divalent transition metal chelates have been reported by Bottei & Fangman [9]. They observed that the C = O peak of H₂BQ at 1618 cm⁻¹ shifted down in the region 1525-1472 cm⁻¹ due to chelation.

The infrared absorption spectra did not give any conclusive evidence concerning the end groups present in the metal chelates and adducts. The peaks in the region 3263 cm⁻¹ is shifted to higher frequency due to presence of water molecule. On this basis it can be concluded that the phenolic hydrogens present in the H₂BQ molecule released in the formation of the chelates. This is also supported by three absorption peaks in the region 1200 cm⁻¹ found in the H₂BQ, which are not found in metal chelates and adducts. This is a region that is normally assigned to the -OH bending vibration.

The broad absorption peaks have been observed at ~ 3400-3500 cm⁻¹ in all the adducts of H₂BQ with Ni (II) and Cu (II) metal chelates. The $\delta_{\text{H}_2\text{O}}$ (rocking) has been spotted in region 816-858 cm⁻¹ for all the compounds, indicates the two water molecules are co-ordinated and loss at a temperature ~ 150°C, showing strong association.

The $\nu_{\text{C-O}}$ stretch is observed in the free ligand in the region at 1307 cm⁻¹, on chelation with Ni (II) or Cu (II) metal, these bands shift to lower frequency region 1265-1253 cm⁻¹, indicating coordination through oxygen atom of the phenolic group and the shifting of the strongest absorption band of carbonyl group at 1618 cm⁻¹ to lower region 1535-1530 cm⁻¹ also suggest coordination through carbonyl oxygen atom.

In the alkali metal adducts of Ni (BQ)₂.2H₂O and Cu (BQ)₂.2H₂O metal chelates, the higher shift of $\nu_{\text{C-O}}$ stretching frequency shows the increased bond order between the C & O atoms as a result of coordination of oxygen atom of C-O (phenolic) to the alkali metals. Slight shift in $\nu_{\text{C=O}}$ stretching frequencies are also found in all the adducts probably due to change in stereochemistry of the complexes.

In the spectra of alkali metal adducts we find lower shift in the region $755\text{-}775\text{ cm}^{-1}$ which indicates the formation of oxygen bridged in the complexes. Further, in the low frequency region $463\text{-}450\text{ cm}^{-1}$, bands observed in the complexes are assigned to $\nu_{\text{M-O}}$.

Magnetic properties: Magnetic measurements were taken on Cahn-Faraday electronic balance at 22°C . The results of the magnetic measurements are given in Table-1.

The majority of the copper(II) complexes display magnetic moment values in the range of 1.75 to 2.20 BM, while 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 lies between 1.75 to 2.25 BM are termed as magnetically dilute complexes and their magnetic moment values are independent of temperature.

The magnetic moment values of Cu (BQ). $2\text{H}_2\text{O}$ has been found to be 1.25 BM at room temperature, due to antiferromagnetic nature or dimeric interaction, whereas the binuclear alkali metal adducts of Cu (BQ). $2\text{H}_2\text{O}$, display magnetic moment values between 1.98 to 2.18 BM, which clearly indicate that antiferromagnetic nature is diminished but polymeric octahedral geometry appear in their alkali metal adducts.

Magnetic moment values at room temperature of majority of octahedral Ni(II) complexes are found between 2.90-3.40 BM [10] but in the tetrahedral Ni(II) complexes magnetic moment values are usually higher than spin only value expected for two unpaired electrons (2.83 BM) [11]. In the present investigation, the magnetic moment for Ni (BQ). $2\text{H}_2\text{O}$ has been found 2.90 BM, which is very near to spin only value. The binuclear adducts of Ni (BQ). $2\text{H}_2\text{O}$ possess magnetic moment values between 2.90 to 3.24 BM at room temperature which are close to the reported values for most of the octahedral Ni(II) complexes, thus octahedral structure of Ni (BQ). $2\text{H}_2\text{O}$ retain in the alkali metal adducts.

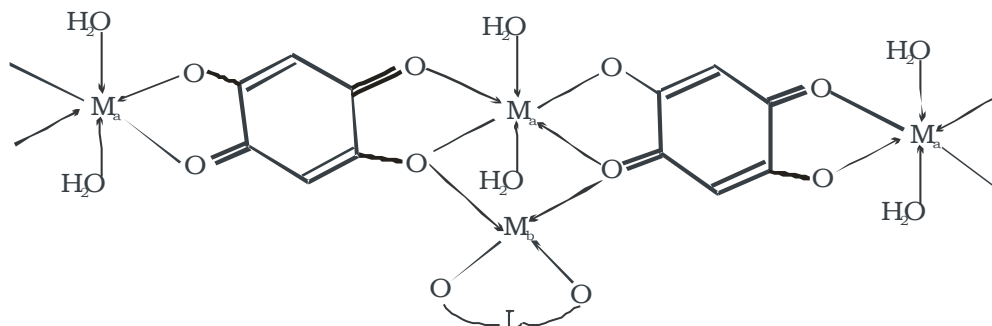
Electronic spectra : Electronic spectra were recorded on SHIMADZU UV-VIS 160A spectrophotometer in Nujol mull/paraffin solvent. The bands observed in electronic spectra of metal chelates and their adducts are given in Table-2.

The electronic spectra of Ni(BQ). $2\text{H}_2\text{O}$ and their alkali metal adducts in paraffin liquid display bands in the region 250-370 nm due to charge transfer. The bands at region 440-600 nm are assigned to the first and second spin allowed transition ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g(\text{F})}$ and ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g(\text{F})}$ respectively, characteristic of Ni (II) in an octahedral environment. The spectra of binuclear alkali metal adducts, bands also appear in region 485-670nm may be assigned to ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g(\text{F})}$ and ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g(\text{F})}$, The ${}^3\text{A}_{2g(\text{F})} \rightarrow {}^3\text{T}_{1g(\text{P})}$ 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 Cu (BQ). $2\text{H}_2\text{O}$ and its binuclear alkali metal adducts band appear in the region 250-340 nm is due to charge transfer and bands in the region 430-670 nm assigned spin allowed transition to ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$ which clearly indicates octahedral geometry of Cu(BQ). $2\text{H}_2\text{O}$ & also in its binuclear alkali metal adducts.

STRUCTURE AND BONDING

On the basis of above discussions, alkali metal adducts of the type $M_a(BQ).2H_2O.M_bL$ can be presumed to have the structure as shown in Fig. 1. The structure is strongly supported by conductivity measurements, magnetic moment data & electronic spectra.



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

Fig. 1

MATERIALS AND METHODS

Chemicals of A.R. grade have been used for synthesizing the compounds. 2, 5-Dihydroxy-1, 4-benzoquinone (H_2BQ) has been synthesized from hydroquinone by the method of Jones & Shonle [12].

Synthesis of metal chelates : 2.48 gm (0.01 mole) nickel acetate tetrahydrate was dissolved in 95% ethanol, then 1.64 gm (0.01 mole) of 2, 5-dihydroxy-1, 4-benzoquinone was added to it with continuous stirring on a hot plate of magnetic stirrer. A reddish brown colour Ni(II) metal chelate precipitated out. The precipitate was filtered, washed with solvent and then dried in an electric oven at about 100°C . Cu (II) metal chelate was also synthesized by similar procedure.

Synthesis of the adducts : 0.25 gm (0.001 mole) of Ni (II) or Cu (II) metal chelate of 2, 5-dihydroxy-1, 4-benzoquinone was taken in absolute ethanol and 0.001 mole of alkali metal salt of 1N2N or ONP was added to it. On stirring, the colour of the mixture changed. The mixture solution was refluxed at 80°C over a hot plate of magnetic stirrer for 2-3 hours. The concentrated solution was cooled when characteristic colour adducts separated out. The adducts were filtered, washed with absolute ethanol and then dried in an electric oven at 100°C .

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