# Synthesis, Characterization and Electrical conductivities of the Complexes of Nickel(II), Copper(II) and Zinc(II) with 2,5-diamino-3,6-dichloro-1,4-benzoquinone

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#### Abstract

Complexes of the type [M(dadb)] (M = Ni(II), Cu(II))and Zn(II)) with ligand 2,5-diamino-3,6-dichloro-1,4benzoquinone (dadb) have been synthesized and microanalysis, characterized bv magnectic susceptibility, electronic, IR, ESR spectroscopy thermogravimetric analysis techniques, (TG),differential thermal analysis (DTA), X-ray powder diffraction (XRD) and solid phase conductivity measurements.

The room temperature ESR spectra of Cu(II) complex yield  $\langle g \rangle$  values, characteristics of square planar geometry. The solid state electrical conductivities of the complexes increase as the temperature increases from 311-383 K, with a band gap of 0.11- 0.21 eV, indicating their semiconducting behaviour.

**Keywords:** DADB, complexes, Nickel, Copper, Zinc, Conductivity.

# Introduction

Benzoquinones (Bq) are the most pervasive natural products on the earth's surface and play a vital role in certain cellular function from the point of view of electron transfer reactions, which play an important role in biological systems<sup>15,16,21</sup>. They have applications in synthetic organic chemistry<sup>1,6,8</sup>. Derivatives of Bq, amino quinones obtained by the reaction of amine with various quinones are used as medicines<sup>2,7,10</sup>, herbicides<sup>23</sup> and they also show interesting redox switching properties<sup>22</sup>.

2,5-Diamino-3,6-dichloro-1,4-benzoquinone (dadb) and its derivatives have been found to be potential central nervous system antitumor agents<sup>3-5,11</sup>. The reports are available that the dadb molecule improves the resistance to repeated exposure of photoreceptor<sup>19</sup>, provides resistance to thermal oxidation of polypropylene and polyacetyle fibers<sup>24</sup> and inhibits degradation of polyolefines exposed to uv / sunlight<sup>9</sup>. The *ab initio* calculation of dadb molecule revealed that there are two parallel sets of conjugated strands which could provide a route to conduct charges<sup>17</sup> along the molecule. Our recent studies are devoted to the synthesis and characterization of metal dadb assemblies. In this communication, we describe construction of transition metal complex-based assemblies, currently of great interest due to

their potential properties such as magnetism, electrical conductivity etc.

# **Material and Methods**

All the chemicals used under present investigations were of analytical reagent grade. Solvent was dried and purified by standard methods reported in the literature<sup>14</sup>.

**Synthesis of 2,5-diamino-3,6-dichloro-1,4-benzoquinone** (**dadb**): For the synthesis of ligand dadb, ammonium chloride (0.428 g) was added to a reaction mixture of 2,3,5,6-tetrachloro-1,4-benzoquinone (0.984 g) and anhydrous sodium acetate (2.296 g) in absolute ethanol (15 ml) stirred for 15 min with constant stirring at room temperature. The color of the reaction mixture slowly changed from light yellow to dark reddish brown. The stirring was continued for 1hr and refluxed for 5hrs.

The resulting reddish brown precipitated product was filtered off, washed with cold water followed by ethanol and dried under vacuo over calcium chloride.

Yield: 80%, m.p. > 320°C; Anal. Calcd for  $C_6H_4N_2Cl_2O_2$ : C 34.78%, N 13.52%, H 1.95%; found: C 32.96%, N 12.41%, H 2.65%.UV  $\lambda_{max}$  (nm) 530, 516, 352, 348; IR (KBr, v, cm<sup>-1</sup>) 3374 (N-H), 1667 (C=O); <sup>1</sup>H NMR (DMSO-d<sub>6</sub> TMS,  $\delta$ , ppm): 8.0 (NH<sub>2</sub>); <sup>13</sup>CNMR (DMSO-d<sub>6</sub> TMS,  $\delta$ , ppm): 170.17(C<sub>1</sub> and C<sub>4</sub>), 148.86(C<sub>2</sub> and C<sub>5</sub>) and 99.53  $\delta$ (C<sub>3</sub> and C<sub>6</sub>).

Synthesis of [M(dadb)] (M = Ni(II), Cu(II) and Zn(II)): These complexes were prepared by the solution of each metal salt (2mmol) dissolved in 5ml ethanol and then adding in solution of dadb (0.414g) in 20 ml DMF. A solution of anhydrous sodium acetate (0.328g) in 5ml ethanol was added in above reaction mixture and heated for 30 min on the water bath and kept as such overnight. The reaction mixtures were filtered off, precipitated complexes were obtained, washed with water followed by ethanol and dried in vacuo.

**Analyses and physical measurements:** The complex was analysed by the elemental analysis (carbon, hydrogen and nitrogen) performed on a Elemental Analyzer model Carlo Erba 1108. Magnetic susceptibility of the powdered samples was measured at room temperature on a Cahn Faradey electro balance using [Co(NCS)<sub>4</sub>Hg] as calibrant. The diamagnetic correction was made using Pascal's constant.

Electronic absorption spectra were recorded on a UV-1700 Pharmaspec, UV-visible spectrophotometer as Nujol mulls<sup>-</sup> IR spectra were recorded on a Varian 3100 FT-IR spectrophotometer in the region 4000 $\pm$ 400 cm<sup>-1</sup> on KBR disc. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded in solvent DMSO-d<sub>6</sub> using tetramethylsilane (TMS) as internal standard on a JEOL AL 300 FT NMR spectrometer.

The room temperature E.S.R. spectra of the powdered samples were recorded on a Varian USA model 112 ESR spectrometer. The microwave frequency was calibrated using tetracyanoethylene (TCNE), g = 2.00277 as a hgi marker. The X-ray powder diffraction patterns were recorded on Rigaku DMax- B powder X-ray diffractometer with CuK $\alpha$  – radiation. The thermogravimetric analysis (TGA) was achieved on analyzer model Perkin Elmer, Diamond TG/DTA analyzer. The electrical conductivity of the metal complexes was measured over a 311 - 383 K temperature range using conventional two-probe technique on a Keithley 236 source measure unit used to measure the sample resistance.

# **Results and Discussion**

All the complexes are insoluble in both non-polar solvents like benzene, hexane etc. and organic solvents like ethanol, methanol, ether, chloroform and dichloromethane but very slightly soluble in polar solvents like DMF and DMSO. The air stable complexes decompose in the >280°C range. The complexes isolated in the present study are listed in table 1 together with some of their properties. All having a 1:1 metal ligand stoichiometry, are formed by loss of two protons from the ligand.

**Magnetic moments and electrical spectra:** The room temperature magnetic moment (Table 1) and electronic spectrum (Table 2) of Nidadb exhibit a magnetic moment

2.86 B.M. and shows UV- Vis. two bands at 18,518 and 26,737 cm<sup>-1</sup>. The first band was assigned to  ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{2g}(F)(v_1) \rightarrow {}^{3}T_{2g}(F)(v_2) \rightarrow {}^{3}T_{1g}(P)(v_3)$  while the second band may be due to charge transfer transition. The value of ligand field parameters suggests an octahedral geometry around the metal ion. The magnetic moment of Cudadb complex is 2.03 B.M. due to the presence of one unpaired electron. These complexes show a band at 23,202 cm<sup>-1</sup> due to the envelope of the  ${}^{2}B_{1g} \rightarrow {}^{2}A_{1g}$ ,  ${}^{2}B_{2g}$  and  ${}^{2}E_{g}$  transitions, usually observed for square-planar Cu(II) complexes<sup>13</sup>. The complex of Zndadb is diamagnetic. On the basis of spectral data, tetrahedral geometry is suggested for the Zn(II) complex.

**I.R. Spectra:** The important IR spectral bands and their assignment are given in table 3. The spectrum of free dadb in KBr shows band at 3376 cm<sup>-1</sup> due to the presence of NH<sub>2</sub> group. The bands at 1667, 1580, 1381, 1310, 943 and 552 cm<sup>-1</sup> are assigned to v (NH<sub>2</sub>), v(C = O), v(C – NH<sub>2</sub>) and v(ring) modes respectively<sup>17</sup>. The metal complexes of Ni(II), Cu(II) and Zn(II) show peaks 3304-3314 cm<sup>-1</sup> range due to v(NH), with a negative shift between 62–72 cm<sup>-1</sup> range, suggesting loss of one proton via enolization, consistent with coordination of the ligand nitrogen to the metal. The three intensities bands at 1599, 1647and 1655 cm<sup>-1</sup> in the complexes Nidadb, Cudadb and Zndadb respectively shifted to lower wave number when compared with the p-quinoid carbonyl absorption of the dadb (1667 cm<sup>-1</sup>), suggesting the involvement of carbonyl oxygen in the bonding.

Furthermore, the intensities bands  $v(C - NH_2)$  in metal complexes of Ni(II), Cu(II) and Zn(II) shift to a higher frequency at 1388, 1385 and 1388 cm<sup>-1</sup> respectively as compared to dadb (1382 cm<sup>-1</sup>). In the spectra of the ligand, dadb v(C - C) mode is absent, but new bands appear at 1010, 1013 and 1007 cm<sup>-1</sup> in the complexes Nidadb, Cudadb and Zndadb respectively due to v(C - C) mode.

Table 1
Analytical data and physical properties of the complexes of 2.5-diamino-2.6-dichloro-1.4-benzoquinone

Compound	Colour	Yield(%)	Found (calcd.) %			µeff(B.M.)	M.P.(°C)
			С	Н	Ν		
Dadb	Reddish	80	33.0	2.6	12.7	-	> 320
$C_6H_4N_2Cl_2O_2$	brown		(34.8)	(2.0)	(13.5)		
Nidadb	Dark black	63	25.2	2.5	7.2	2.86	270 <sup>a</sup>
C <sub>6</sub> H <sub>6</sub> N <sub>2</sub> Cl <sub>2</sub> O <sub>4</sub> Ni			(27.0)	(1.5)	(10.5)		
Cudadb	Blackish	65	24.4	1.9	8.0	2.03	280 <sup>a</sup>
$C_6H_6N_2Cl_2O_4Cu$	green		(24.9)	(1.7)	(9.7)		
Zndadb	Dark	72	27.3	2.1	8.6	dia	> 300
$C_6H_4N_2Cl_2O_3Zn$	Pink		(26.4)	(1.5)	(10.2)		

<sup>a</sup> dec.

 Table 2

 Electronic spectra data for the complex and their assignments

Compound	$\lambda_{\max}$ (cm <sup>-1</sup> )	Assignment
dadb	24510, 30120	-
Nidadb	18518, 26737, 28653	${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{2g}(F)(\nu_{1}) \rightarrow {}^{3}T_{2g}(F)(\nu_{2}) \rightarrow {}^{3}T_{1g}(P)(\nu_{3}), C.T., L$
Cudadb	23202, 29718	${}^{2}\mathrm{B}_{1\mathrm{g}} \rightarrow {}^{2}\mathrm{A}_{1\mathrm{g}}, {}^{2}\mathrm{B}_{2\mathrm{g}}, {}^{2}\mathrm{E}_{\mathrm{g}}, \mathrm{L}$
Zndadb	19881, 24096, 29498	C.T., L

Important IN spectral bands (cm <sup>-</sup> ) and then assignments						
Compound	v (NH <sub>2</sub> )	v(C = O)	$v(C - NH_2)$	v(ring)	<b>v</b> ( <b>C</b> – <b>C</b> )	
dadb	3376 s	1667 ms	1382 s	1310 m		
Nidadb	3314 s	1599 w	1388 w	1297 s	1010s	
Cudadb	3227 b	1647 w	1385 m	1289 s	1013m	
Zndadb	3304 s	1655 m	1388 m	1306 s	1007s	

 Table 3

 Important IR spectral bands (cm<sup>-1</sup>) and their assignments

S = strong, m = medium, w = weak, vs = very strong, b = broad,ms = medium strong

Table 4						
Main TG and DTA data for the complexes:						

Compounds	DTA Results T(K)	TG Results		Losses
	Peak	T range(K)	Moss Loss (%)	
		-	Found (Calcd)	
Cudadb	382 endo	366 -537	15.0 (15.03)	2H <sub>2</sub> O
	357 exo	537-613	22.0 (23.3)	2HCl
	624 exo	613-1203		Organic matter
	775 exo			
	906 exo			
Nidadb	364 exo	347-419	13.8 (12.8)	2H <sub>2</sub> O
	569 exo	419-502	10.0 (11.8)	HCl
	878 exo	502-863		Organic matter
Zndadb	441 endo	343-488	6.8 (6.4)	H <sub>2</sub> O
	599 exo	488-1093		Organic matter
	906 endo			

**ESR spectra:** The room temperature powder X-band ESR spectrum of Cudadb shows well solved parallel and perpendicular region, with parallel, perpendicular and average g = 2.2064, 2.0404 and 2.0958 respectively. The trend  $g_{\parallel}>g_{\perp}>g_{av} = 2.0023$  shows that the unpaired electron is present in the  $d_{x2-y2}$  orbital. The g-values suggest a square-planar geometry around copper (II).

**Thermal behavior:** Thermal degradation is an important tool for coordination compounds to derive their nature. The nature and number of water molecules present in the hydrated complexes may be deduced on the basis of the temperature range at which it is eliminated. The thermogravimetric analyses (TGA and DTA) of complexes were recorded in the temperature range 298 – 1473 K. The TG and DTA traces of copper complex show mass loss from 356K to 537K (the lost weight is 15.0%, calculated value is 15.03%) which is a clear indication of presence of two water molecule in the coordination sphere.

From 537K to 613K, a sharp fall in the TG curve with 22% mass loss was observed. This may be due to the elimination of two HCl moieties while the nickel complex begins to lose two lattice waters at 347K and ends at about 419K (the lost weight is 13.8%, calculated value is 12.8%) and in zinc complex loses one water at 343K and ends at about 488K (the lost weight is 6.8%, calculated value is 6.4%).

**Powder XRD:** X-ray powder diffraction study of the complexes was carried out at room temperature in order to examine the lattice dynamics. X-ray diffraction patterns of

the complexes Ni(II), Cu(II) and Zn(II) were recorded at  $2\theta$ =10-80° range as shown in fig 2. All the complexes exhibit many lines indicating the crystalline nature of these complexes<sup>17</sup>. No lines are common in the powder pattern of these complexes, suggesting that they are new entities. The ligand shows sharp peaks in comparison to metal complexes. The line broadening of the crystalline diffraction peak in the Cu(II) complexes shows higher crystallinity than that Ni(II) and Zn(II) complexes.

Solid state electrical conductivity: Solid state electrical conductivities of the pellet sample were measured in the 311 383 K range employing the convetional two probe \_ techinque on Keithly 236 source measure unit. The pellets were prepared on the pellet surface using silver paint. A sequence of increasing voltage (in +10 to -10 V range with an increase of 5V in each step) was passed and the current measured. Resistance was calculated from the I-V curve. Specific resistance was calculated from the resistance measurement using known dimension of the sample discs and converted into the specific conductance. Fig. 2 of plot log  $\sigma$  versus 1000/T over the above temperature range indicates their semiconducting behavior as their conductivity increases by increasing the temperature.

The energy band gap evaluated from the plots was found to be 0.11, 0.12 and 0.21eV for Nidadb, Cudadb and Zndadb respectively. All the complexes exhibit  $\sigma_{rt}$  in the range of 8.94 X 10<sup>-14</sup> to 1.11 X 10<sup>-13</sup> Scm<sup>-1</sup>. The conductivities of the diamagnetic and paramagnetic compounds are almost in the range of the paramagnetic complexes which indicate that the

unpaired electrons are not playing an important role in the electrical conductivity mechanism. On the basis of physicochemical studies and the foregoing discussion, the proposed structures of the complexes are shown in fig. 3.

#### Conclusion

We proposed that mesomeric stabilization by oxygen atoms in 2,5–Diamino–3,6–dichloro–1,4–benzoquinone favours the deprotonation of amino group. Accordingly, the prepared metal complexes of dadb with Ni(II), Cu(II) and Zn(II) metal ions are characterized with elemental analyses, IR spectral study, specific conductivity and thermovolumetric studies.

Thermovolumetric studies indicated that in case of Ni(II) and Cu(II) complexes, two moles and one mole of HCl

molecules are evolved quantitatively whereas in case of Zn(II) complex, no HCl gas molecules were evolved. It was interpreted that HCl molecules react with Zn(II) ions and form complex.

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Fig. 1: XRD differaction pattern of Nidadb, Cudadb and Zndadb complexes



Fig. 2: Temperature dependence of electrical conductivities for the complexes



[M(dadb)] (M = Ni(II), Cu(II) and Zn(II)) Fig. 3: Postulated structures for the metal complexes of dadb

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