

# Coordination Compounds of Anthraquinone Dioxime (AQD) with Cobalt(II), Nickel(II) and Copper(II)

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**Summary:** The present research deals with the synthesis and structural studies of anthraquinone dioxime complexes having general formula  $[M(L)_2]$  where L stands for anthraquinone dioxime and M for Cu(II), Co(II), and Ni(II). All compounds were characterized by elemental and metal ion analysis and various spectroscopic techniques such as ultraviolet/visible, NMR and infrared spectra. Disappearance of peak around  $3000-3400\text{ cm}^{-1}$  in the I.R. spectra was considered to be a diagnostic test for the formation of complexes. The Uv-visible spectra show the  $D_{4h}$  symmetry of the complexes according to the expectation. This structure is further supported by conductance and magnetic data.

## Introduction

The most significant early event in the area of transition metal chemistry of oxime is the reaction between nickel salts and dimethylglyoxime ( $H_2\text{dmg}$ ). The details are given in the literature [1-6].

Later on chelating agents having both amino and oxime group attracted attention of various researchers [7-16]. Their chemistry has fundamental bearings on areas related to molecular structures, stability, catalytic activity, analytical chemistry, unidirectional conduction properties, superconducting molecular systems and biochemical models [17].

Oximes have been used for the determination of several metal ions present in various materials. The complexes formed with metal ions are usually extracted into organic solvents enabling spectrophotometric determination of trace elements [18,19]. Kuse *et al.*, [19] investigated sixteen compounds as analytical reagents for Nickel(II) and concluded that

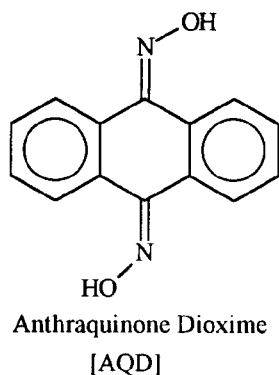
$\alpha$ -furildioxime and  $\alpha$ -benzildioxime are particularly useful for the extraction of Nickel(II) in the organic solvents.  $\alpha$ -furildioxime has also been found the best reagent for the spectrophotometric determination of Nickel(II) in rocks and alloys by Bodart [20] and in the body fluid by atomic absorption spectrometry [21]. Liardon and Ryan [22] used benzildioxime as a reagent for the extraction of Nickel(II) from sea water. These are used for the estimation of tin, rhenium, copper, rhodium and cobalt separately and in the presence of each other [23]. The chemistry of these ligands has also been systematically studied by Aqil Khan to explore additional possibilities of complexation [24].

Much of the current interest in transition metal chelates of substituted glyoximes is centered on their use as chemical models for biological systems such as  $B_{12}$ , which is involved in many biological activities [25] and its importance is due to its ability to form alkyl derivative with cobalt-to-

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carbon sigma bond [26], which is generally difficult to synthesize and are unstable unless the transition metals are in lower oxidation states. In the present work coordination compounds of cobalt(II), nickel(II) and copper(II) salts using anthraquinone dioxime (AQD) has been reported.



### Results and Discussion

The ligand AQD behaves as a bidentate ligand and bears resemblance to DMG in terms of chromophoric environment. AQD is characterized by its melting point, analytical data, mass spectra.  $^1\text{H}$  and  $^{13}\text{C}$ -NMR spectra (Fig. 2 and 3). The proton NMR spectra show two peaks around 7 ppm and 10 ppm indicating the aromatic and alcoholic proton, whereas  $^{13}\text{C}$  shows the aromatic carbon around 120

ppm and carbon attached to the nitrogen with double bond around 170 ppm. The mass spectra (Fig. 4) confirms the ligand by showing molecular weight at 238.

A summary of I.R bands of solid complexes as KBr pellets, in the selected region has been given in Table-3. The similarities of the infrared spectra of AQD complexes with those of HDMG and  $\text{BF}_2\text{DMG}$  indicates the formation of H-bond [27]. Blinc and Hadzi [27] made the following assignments:  $\nu_{\text{O-H}}$  2300-2900 and  $\nu_{\text{C=N}}$  1500-1600  $\text{cm}^{-1}$ .

The Nickel(II) complexes of AQD is yellow in color and quite stable in nature. The elemental analysis (Table-1) shows the attachment of two ligand moieties with the metal ion. The magnetic moment has a very low value and the conductance data (Table-2) shows the non electrolytic behavior. The electronic absorption spectra of the complex in the visible region is typical to planar nickel(II). The  $^1\text{A}_{2g}$  to  $^1\text{A}_{2g}$  transition in a  $d^8$  system of  $D_{4h}$  (Table-4) symmetry was independent of the solvent and is identical in shape to that observed in  $[\text{Ni}(\text{C},\text{C-TetraMeen})_2]^{+2}$ , and nickel complexes of diazacyclooctane and diazacycloheptane, where square planar geometry has been demonstrated [28]. By the use of molecular models, the most favourable conformation of the square-planar bis-complex of AQD can be envisioned with the benzene rings in the chair boat conformation. The unreactivity of

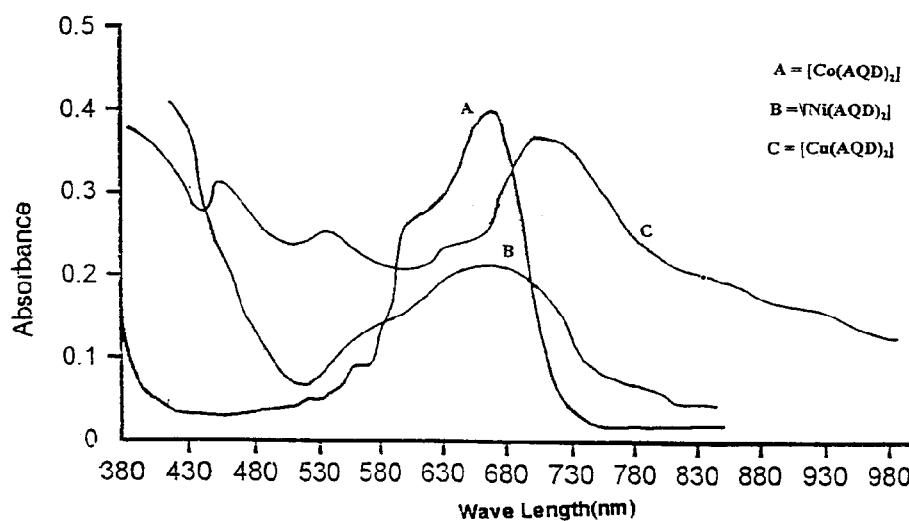


Fig. 1: Absorption spectra AQD complexes with Cobalt(II), Nickel(II) and Copper(II)

Table-1: Analytical data of AQD and its complexes

Ligand	Colour	Dec. pt. °C	C%	N%	H%	Cation %
AQD	Off-white	245	70.4 (70.60)	11.70 (11.70)	4.50 (4.20)	-
[Ni(AQD) <sub>2</sub> ]	Yellow	218	64.12 (63.31)	10.83 (10.55)	2.89 (3.01)	12.00 (11.06)
[Cu(AQ) <sub>2</sub> ]	Apple green	224	63.41 (62.74)	10.64 (10.46)	2.81 (2.99)	12.60 (11.87)
[Cu(AQD) <sub>2</sub> ]	Light Pink	222	63.90 (63.28)	11.73 (10.55)	3.24 (3.01)	10.48 (11.11)

Theoretical percentages are given in parentheses.

Table-2: Conductance and magnetic susceptibility data of AQD complexes

Compound	Temp. K°	$\Lambda$ (mho mol <sup>-1</sup> cm <sup>3</sup> )	$10^6 \chi_m^{conf}$ (cgsu)	$\mu_{eff}$ (B.M.)
[Ni(AQD) <sub>2</sub> ]	298	3.6 Non-elec	836	0.40
[Cu(AQD) <sub>2</sub> ]	298	5.3 Non-elec	1118.9	1.64
[Co(AQD) <sub>2</sub> ]	298	21.6 Non-elec	3022.4	2.69

$\mu_{eff} = 2.04 \sqrt{\chi_m T}$  (B.M.)

[Ni(AQD)<sub>2</sub>] complex arises from strong field induced in the xy-plane by the ligand coupled with

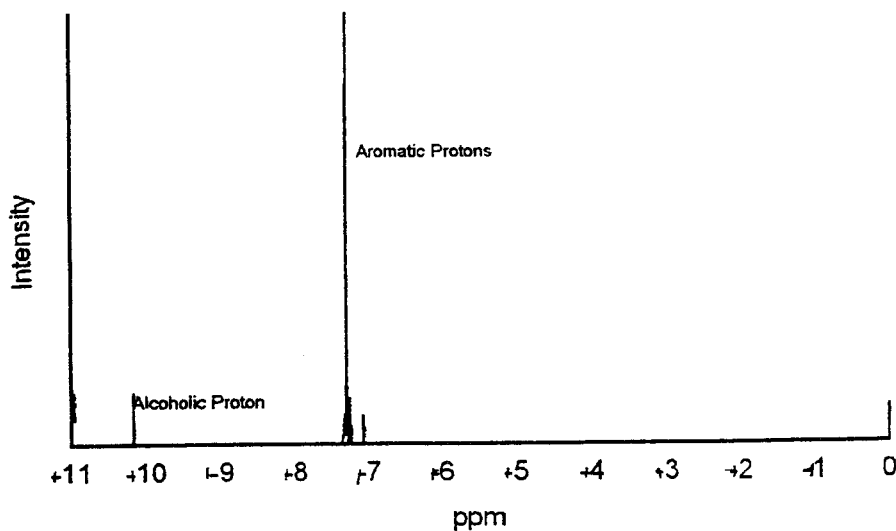


Fig. 2: Proton NMR spectra of AQD

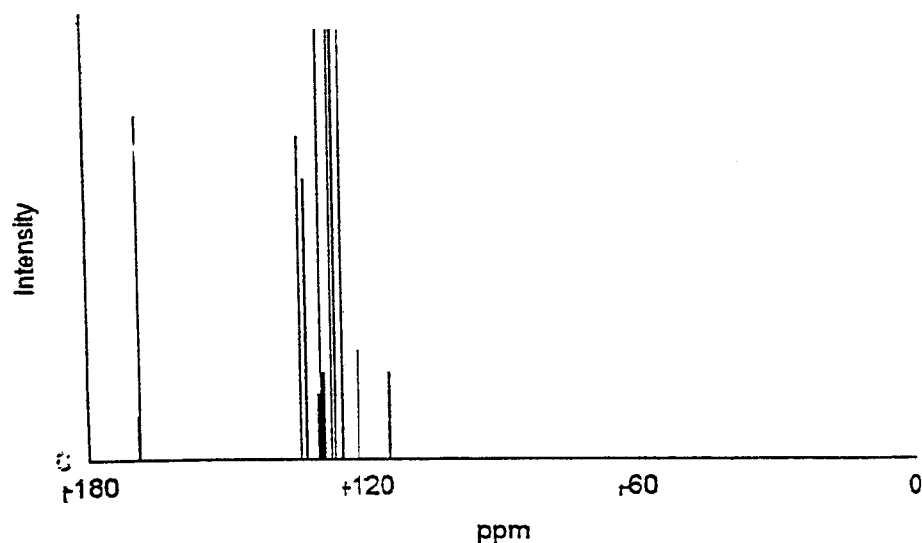


Fig. 3: Carbon 13 NMR spectra of AQD

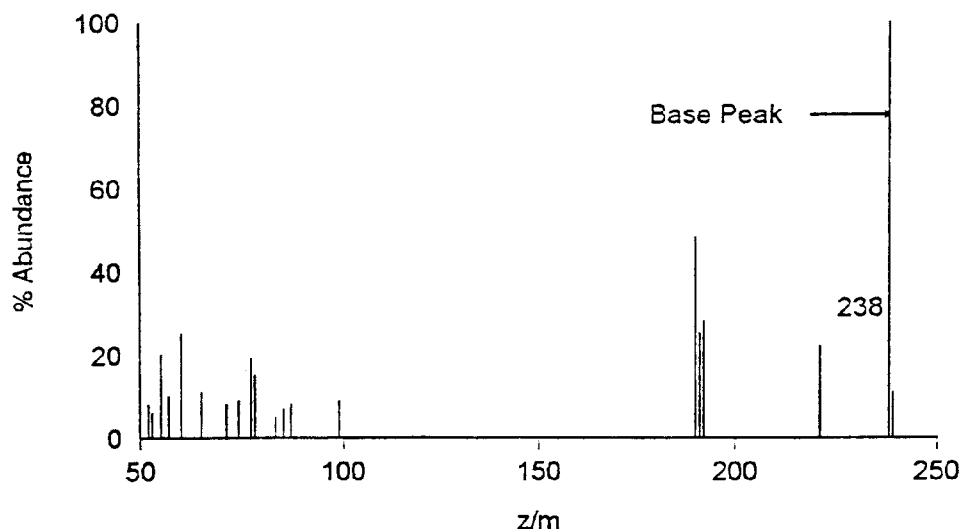


Fig. 4: Mass Spectra of AQD

Table-3: IR data of AQD and its complexes

Compound	$\nu_{OH}$	$\nu_{N=C}$	Aromatic ring	Significant bands
AQD	3100vs	1640s	1600s, 1570s, 1500s, 1450s	1100, 760s, 750s, 600s, 400s
[Ni(AQD) <sub>2</sub> ]	3000b, 3110w	1640s	1600s, 1570s, 1500s, 1450s	1100, 760, 750s, 600s, 400s
[Cu(AQD) <sub>2</sub> ]	3000b, 2950 m	1640s	1600sb, 1570s, 1450s	1100, 760w, 750w, 600s, 400s
[Co(AQD) <sub>2</sub> ]	3000b, 3100m	1640s	1600sb, 1570w, 1450s	1100, 760w, 600s, 400s

s Sharp; vs very sharp; b broad; m medium; w weak

Table-4: UV-visible spectra of AQD complexes

Complex	$\lambda_{max}$	$\nu(\text{cm}^{-1})$	$\epsilon_{max} (\text{M}^{-1}\text{cm}^{-1})$
[Ni(AQD) <sub>2</sub> ]	500 nm	17800	85.5
[Cu(AQD) <sub>2</sub> ]	670 nm	16600	427.2
[Co(AQD) <sub>2</sub> ]	640 nm	15600	277.7

crystal field stabilization energy for the  $d^8$  system, and thus prevents incoming axial ligands from effectively interacting with the filled  $dz^2$  orbital [29].

The blue coloration in [Cu(AQD)<sub>2</sub>] complex and the absorption maximum in the visible spectrum (Fig. 1) is quite similar to that of [Cu(diamine)<sub>2</sub>]<sup>2+</sup> [28]. The spectral data (Table-4) indicates that the ligand distortion is extremely high and that the inductive effect greatly predominates over steric effect in this complex [30]. The magnetic moment, conductance and the visible spectrum, all favour the distorted square-planar complex.

The cobalt(II) complex is light pink in colour. The elemental analysis (Table-1) shows the

attachment of two ligand moieties with the metal ion. The magnetic moment of the complex is 2.69 B.M. (Table-2), which again favours the square-planar geometry. The spectral data of such complex is complicated and much study has not been carried out, although it might be expected that the unpaired electron would occupy  $dz^2$  orbital.

## Experimental

### Materials

Analytical grade salts of Nickel(II), Cobalt(II), Copper(II) were used without further purification. The nonaqueous solvents used in synthetic work were distilled twice.

### Preparation of the ligand

1 gram of anthraquinone mixed with 8.4 gram of hydroxylamine dissolved in 50 mL of pyridine (dry) and was heated for 8 hours. The contents were, then, poured into 100 mL of dilute H<sub>2</sub>SO<sub>4</sub>. The precipitate formed was filtered and washed several times with water and dried under vacuum at 35°C. Light yellow powder of anthraquinone dioxime (m.p. 245°C) was obtained (95%).

### Preparation of the complexes

The complexes of Nickel(II), Copper(II) were prepared by using the same general procedure. The

required amount of the salt was dissolved in minimum amount of the specific dry solvent. The salt was then dehydrated by stirring its solution with an appropriate amount of 2,2-dimethoxypropane for about 4-5 hours [31,32] to ensure complete removal of water from the salt. For the preparation of complexes 2:1 ligand to metal ratio was maintained. The ligand was dissolved in hot dry methanol-ethanol mixture/dimethyl-formamide (DMF). This solution was added to the metal salt solution slowly with constant stirring. The change in colour of solution indicated the formation of the complex. The complexes were formed after reducing the volume of the solution under vacuum at 40°C. The product obtained was filtered through a sintered glass crucible, washed several times with acetone and then dried under vacuum at low temperature.

#### Instrumentation

Cations were determined by usual methods whereas C, H, and N elemental analysis were performed through the courtesy of H.E.J. Research Institute of Chemistry, University of Karachi on Carloerba MOD 1106.

The magnetic moments of the solid complexes at room temperature were determined by the Gouy method. A double ended Gouy tube was calibrated using  $\text{Hg}[\text{Co}(\text{SCN})_4]$  as standard, Pascal's constants were used to the observed molar susceptibilities of crystalline complexes for the diamagnetism of the ligand and the anions involved [33].

The electrolytic conductance measurement of the complexes were determined by conductivity bridge made by Mullard Inc. England. The conductivity cell was properly calibrated. The observed conductivity was corrected for the specific conductance of the pure solvent used [34].

The Infra-red absorption spectra of the solid complexes as KBr discs were obtained on I.R. Spectrometer Model SP-3 100 PYE Unicam A.M.

Visible and ultraviolet spectra of the complexes in different solvents were obtained on JASCO UNIDEC-1 recording spectrophotometer using set matched 1 cm quartz cells. The absorption spectra were always recorded using freshly prepared solutions (Fig. 1).

The  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  data for the ligand were obtained by NMR spectrophotometer Model JNM-PMX at 300 MHz. All the spectra for proton and  $^{13}\text{C}$  were measured relative to tetramethylsilane (TMS) as an external standard in DMSO (Fig. 2 and 3).

The mass spectra of the ligand were recorded with MA-312 mass spectrometer at H.E.J. Research Institute of Chemistry, University of Karachi (Fig. 4).

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