



## A comparative study of the coordination behavior of (Z)-4-[(2-(4,8-dimethylquinolin-2-yl)hydrazono) methyl] benzene-1,3-diol towards copper(II), nickel(II) and cobalt(II)-chlorides

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### Abstract

The reaction of the titled hydrazone with Co(II), Ni(II) and Cu(II)- chlorides in absence and presence of KOH afforded mononuclear and binuclear complexes. The binuclear complexes support either enhancement of the phenoxy bridging or change of the coordination behavior of the studied hydrazone. Most complexes have the preferable  $O_h$  geometry (1-4), whereas complexes 5 and 6 have  $T_d$  and square pyramid arrangements. As is evidenced from its  $\mu_{eff}$  value = 3.98 BM, complex 5 acquires a tetrahedral arrangement around the Ni(II)- ion. The hydrazone ligand has a reformed character i.e. it changes its coordination behavior towards the transition metal ions as a result of the basicity of the reaction medium. In absence of KOH, the Cu(II) and Ni(II)- complexes revealed their higher affinity for NN- donors and the ligand behaves as a neutral species. Extensive spectroscopic and analytical studies were done to support the suggested structures of the complexes.

**Keywords:** Phenolic quinolyl hydrazone complexes, Coordination behavior, Phenoxy bridging.

### Introduction

The importance of the current phenolic quinolyl hydrazone arises from incorporating the quinoline ring with the phenolic compound; 2,4-dihydroxybenzaldehyde. Phenols have antiseptic and disinfectants activities and are used in the preparation of dyes, bakelite and drugs<sup>1</sup>. On the other hand, quinoline derivatives can be used in therapeutic treatment of some diseases e.g. tuberculosis, malaria and bilharzia<sup>2,3</sup>. There is growing concern about the complexes of transition metals. Some transition metal ions constitute redox enzyme systems as they have active biological sites<sup>4</sup>. The heterocyclic hydrazones have anticancer, antitubercular and anti-inflammatory activities<sup>5-8</sup>. As a continuation of our studies of the metal complexes of some quinolyl hydrazones derived from 2,4-dihydroxybenzaldehyde<sup>9,10</sup>, the aim of the current study is to investigate the coordination behavior of (Z)-4-[(2-(4,8-dimethylquinolin-2-yl)hydrazono) methyl] benzene-1,3-diol (H<sub>2</sub>L) towards Co(II), Ni(II) and Cu(II) ions in absence and presence of KOH. This study is a comparative one considering what is similar and different about either the coordination modes of the hydrazone or the geometrical shapes of the obtained complexes in absence and presence of KOH.

### Materials and methods

**Materials:** The chemicals used in this investigation included CoCl<sub>2</sub>·6H<sub>2</sub>O, NiCl<sub>2</sub>·6H<sub>2</sub>O, CuCl<sub>2</sub>·2H<sub>2</sub>O and KOH. The other chemicals except the metal salts as well as the physical

measurements are the same as described in our previous studies<sup>9,10</sup>.

**Preparation of the phenolic quinolyl hydrazone:** The current phenolic quinolyl hydrazone was prepared as described in our reported studies<sup>9,10</sup>.

**Preparation of the metal complexes:** In this study, two different methods were used to synthesize the metal chelates under different experimental conditions:

**Complexes 1-3:** A mixture of the hydrazone, and the metal salt in the mole ratio (1:1) in ~ 60 ml methanol was heated under reflux for ~ 9-12 hrs according to the nature of each complex. The obtained solid complexes were separated on hot, filtered off, washed with methanol then ether and finally air dried.

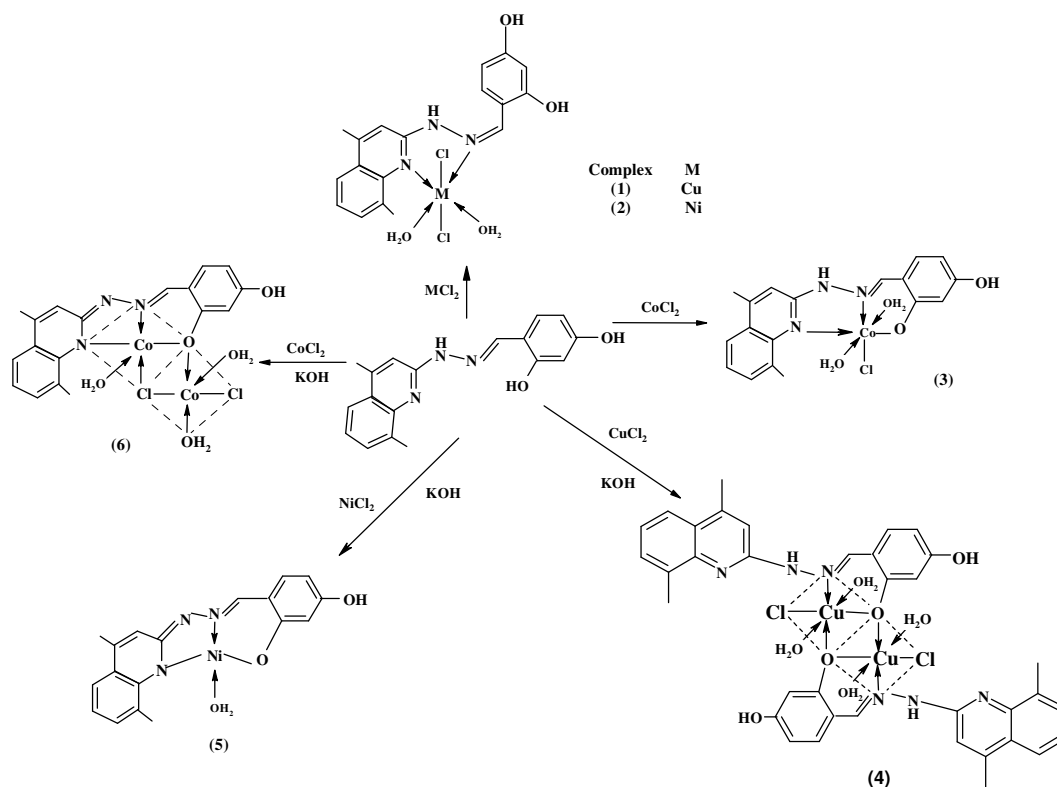
**Complexes 4-6:** A methanolic solution of KOH (1.0 mmol) was added gradually to a methanolic suspension of the hydrazone (1.0 mmol) under refluxing until the hydrazone acquires the red color. At this stage, the hydrazone acquires the anionic phenoxy form. Then, a solution of the metal salt (1.0 mmol) in 25 ml methanol was added to the above reaction mixture under refluxing for ~5-6 hrs. Meanwhile the metal chelates were precipitated, filtered off, washed with methanol then ether and finally air dried.

### Results and discussion

**Characterization of the metal complexes:** The current hydrazone has been characterized by elemental analysis, UV-

visible, IR, Mass and  $^1\text{H}$ NMR spectra as reported<sup>9,10</sup>. In an attempt for studying the ligational behavior of the current phenolic quinolyl hydrazone, it was allowed to react with Co(II), Ni(II) and Cu(II)- chlorides in absence and presence of KOH. These reactions afforded mononuclear and binuclear complexes with a variety of modes of bonding as shown in

Scheme-1. Also, the obtained complexes exhibited a structural diversity ( $\text{O}_h$ ,  $\text{T}_d$ , square pyramid). The complexes were characterized *via* elemental and thermal analyses, magnetic and conductivity measurements as well as spectral studies (UV-Vis., IR, Mass spectra). The results of elemental and thermal analyses are in good agreement with the proposed structures (Table-1).



**Scheme-1:** Mononuclear and binuclear complexes with a variety of modes of bonding.

**Table-1:** Analytical and Physical data of the complexes.

Reactants $\text{H}_2\text{L} + \text{MCl}_2 \cdot n\text{H}_2\text{O}$	Complex (F.wt)	M.F	Color	% Yield	Elemental Analysis; % Found/(Calcd)			
					C	H	N	M
$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	$[\text{Cu}(\text{H}_2\text{L})(\text{H}_2\text{O})_2\text{Cl}_2] \cdot 1\frac{1}{8}\text{H}_2\text{O}$ (498.1)	$\text{C}_{18}\text{H}_{23\frac{3}{4}}\text{N}_3\text{O}_{5\frac{1}{4}}$ $\text{Cl}_2\text{Cu}$	Dark Brown	30	43.44 (43.40)	4.73 (4.71)	8.48 (8.44)	12.75 (12.76)
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	$[\text{Ni}(\text{H}_2\text{L})(\text{H}_2\text{O})_2\text{Cl}_2] \cdot 4\frac{1}{2}\text{H}_2\text{O} \cdot \frac{1}{4}\text{MeOH}$ (562.07)	$\text{C}_{18\frac{3}{4}}\text{H}_{31}\text{N}_3$ $\text{O}_{8\frac{1}{4}}\text{Cl}_2\text{Ni}$	Yellowish Green	53	38.88 (38.99)	5.60 (5.56)	7.43 (7.47)	10.54 (10.45)
$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	$[\text{Co}(\text{HL})(\text{H}_2\text{O})_2\text{Cl}] \cdot 1\frac{3}{4}\text{H}_2\text{O} \cdot \frac{5}{8}\text{MeOH}$ (488.30)	$\text{C}_{18\frac{7}{8}}\text{H}_{26}\text{N}_3$ $\text{O}_{6\frac{3}{4}}\text{ClCo}$	Olive Green	86	45.80 (45.80)	5.40 (5.37)	8.61 (8.61)	12.17 (12.07)
$\text{CuCl}_2 \cdot 2\text{H}_2\text{O} + \text{KOH}$	$[\text{Cu}_2(\text{HL})_2(\text{H}_2\text{O})_4\text{Cl}_2] \cdot \text{MeOH} \cdot \frac{3}{4}\text{H}_2\text{O}$ (928.1)	$\text{C}_{37}\text{H}_{45\frac{1}{2}}$ $\text{N}_6\text{O}_{9\frac{3}{4}}\text{Cl}_2\text{Cu}_2$	Light Brown	40	47.90 (47.86)	4.99 (4.94)	9.05 (9.05)	13.50 (13.70)
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O} + \text{KOH}$	$[\text{Ni}(\text{L})(\text{H}_2\text{O})] \cdot \frac{3}{4}\text{H}_2\text{O} \cdot \frac{3}{4}\text{MeOH}$ (419.5)	$\text{C}_{18\frac{3}{4}}\text{H}_{21\frac{1}{2}}\text{N}_3$ $\text{O}_{4\frac{1}{2}}\text{Ni}$	Light Green	33	53.70 (53.68)	5.16 (5.16)	10.08 (10.02)	13.88 (14.06)
$\text{CoCl}_2 \cdot 6\text{H}_2\text{O} + \text{KOH}$	$[\text{Co}_2(\text{L})(\text{H}_2\text{O})_3\text{Cl}_2] \cdot \text{MeOH} \cdot \frac{3}{4}\text{H}_2\text{O}$ (593.5)	$\text{C}_{19}\text{H}_{28\frac{1}{2}}\text{N}_3$ $\text{O}_{6\frac{3}{4}}\text{Cl}_2\text{Co}_2$	Chocolate Brown	37	38.37 (38.41)	4.95 (4.50)	7.08 (7.08)	19.51 (19.85)

**Conductivity measurements:** In order to decide whether the Cl<sup>-</sup> ions are coordinated to the metal ion or situated outside the coordination sphere, the conductances of millimolar DMF solutions of the complexes were measured at room temperature (Table-2). The observed values indicate a non-electrolytic nature of all complexes. Except complex 5, the relatively high values of the molar conductance suggest a certain degree of conductivity. This may be due to partial replacement of Cl<sup>-</sup> ions by DMF molecules.

**IR spectra:** In this study, the IR spectra are aimed to investigate the coordination sites of the current hydrazone towards the different transition metal ions. For this purpose, the IR charts of the free phenolic hydrazone and its complexes were examined. The IR profile of the hydrazone is highly altered upon complexation. The complexes showed broad bands around 3435 – 3396 cm<sup>-1</sup>, strong bands in the range 1630-1613 cm<sup>-1</sup> and medium to strong bands around 1580 and 1500 cm<sup>-1</sup>, respectively. These bands may be assigned to stretches of OH, C=N (hydrazone) and C=N + C=C (quinoline ring)<sup>11</sup>, respectively, confirming that the phenolic oxygen, nitrogen of the hydrazone linkage and nitrogen of the quinoline ring are the coordination sites.

**Electronic spectra:** The electronic spectra of the studied hydrazone and its complexes were recorded as DMF solutions (Table-2). Generally, the solution electronic spectra of the complexes reflect persistence of the ligand bands with slight shifts and appearance of new weak bands in the visible region due to d-d transitions. Excluding the ligand bands, the copper (II) - complexes (1,4) display relatively less intense bands at 425 - 490 nm that arise from different d - d transitions suggesting a distorted O<sub>h</sub> environment around copper(II)- ion<sup>12</sup>. On the other hand, the electronic spectra of the nickel(II)-complexes (2,5) are highly different. Complex 2 showed two bands at 455 and 487 nm assigned to d - d transitions from <sup>3</sup>A<sub>2g</sub> (F) to <sup>3</sup>T<sub>1g</sub> (P) and <sup>3</sup>T<sub>1g</sub> (F) characteristic for O<sub>h</sub> nickel(II) - complexes. Also, the ratio ν<sub>3</sub> / ν<sub>2</sub> is ~ 1.07 supports the O<sub>h</sub> environment around the nickel(II)- ion. In contrast, complex 5 showed several irregular bands in addition to a strong band at 775 nm supporting its tetrahedral environment around the nickel(II)- ion<sup>13</sup>. In T<sub>d</sub> symmetry, the transition <sup>3</sup>T<sub>1</sub> (F) → <sup>3</sup>T<sub>1</sub> (P) occurs in the visible region (~ 13000 cm<sup>-1</sup>) and relatively strong (ε ≈ 100), therefore all the tetrahedral Ni(II)- complexes are strongly colored and tend to be blue or green<sup>13</sup>. The electronic spectra of cobalt (II)- complexes (3,6) showed the main O<sub>h</sub> bands around 450, 606 nm; <sup>4</sup>T<sub>1g</sub> (F) → <sup>4</sup>T<sub>1g</sub> (P); ν<sub>3</sub>. In addition, a shoulder and a weak band around 480, 669 nm; <sup>4</sup>T<sub>1g</sub> (F) → <sup>4</sup>A<sub>2g</sub> (F); ν<sub>2</sub>. This could be explained by either rupture of the phenoxy and chloro bridges in DMF solutions, or an axial attack<sup>14</sup> of DMF molecules (complex 6).

**Magnetic susceptibility measurements:** The μ<sub>eff</sub> values of the Cu(II)- complexes (1,4); 1.95 and 1.44 BM support the presence of one unpaired electron as expected for distorted O<sub>h</sub> Cu(II)-complexes; d<sup>9</sup>- system. The subnormal μ<sub>eff</sub> value of complex 4 suggest a dimeric structure with Cu---Cu interaction (Scheme-

1). In contrast, the Ni(II)- complexes (2,5) showed μ<sub>eff</sub> values = 3.06 and 3.98 BM in consistency to O<sub>h</sub> and T<sub>d</sub> arrangements<sup>13</sup>, respectively, since all the O<sub>h</sub> and T<sub>d</sub> Ni(II)- species are paramagnetic with two unpaired electrons. Because the ground state <sup>3</sup>T<sub>1</sub>(F) has much inherent orbital angular momentum, the magnetic moment of truly T<sub>d</sub> Ni(II)- complexes should be ~ 4-2 BM at room temperature<sup>13</sup>. On the other hand, the Co(II)-complexes (3,6) exhibited μ<sub>eff</sub> values = 4.27 and 1.60 BM suggesting the presence of three unpaired electrons and one unpaired electron, respectively. This is consistent with O<sub>h</sub> geometry<sup>15</sup> (complex 3) and square pyramid geometry (complex 6). The lower value suggests either Co---Co interaction or a strong anti-ferromagnetic exchange between the two adjacent Co(II)- ions, revealing the binuclear nature of complex 6.

**Mass spectrometry:** The mass spectrum chart of the complex (5) is depicted in Figure-1. The data extracted from the charts can be summarized as shown below:

Complex	molecular ion peak	Calcd. F.W.	Base peak
1	495.0	498.1	45.0 (Ref. 9)
5	420.0	419.5	363.05

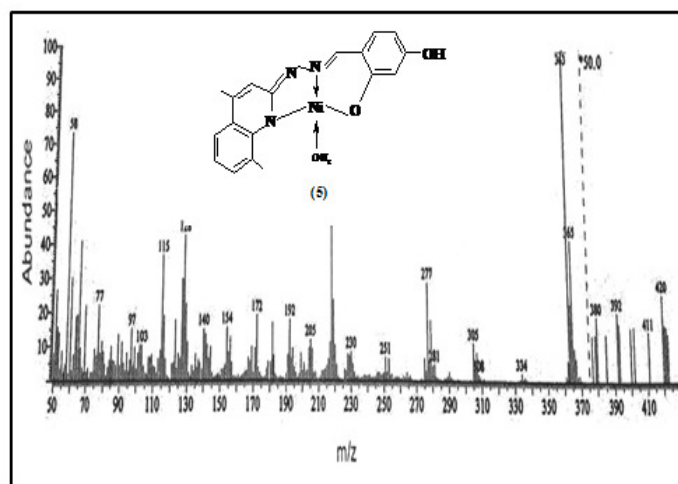
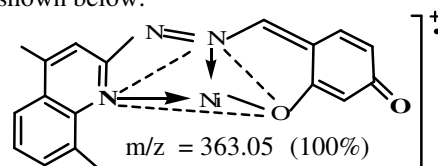


Figure-1: Mass spectrum of complex 5.

It is obvious that the molecular ion peaks agree well with the formulae weights of the complexes lending a further support of their structures. In general, the small differences between found and calculated m/z values are due to the effect of isotopes. As a general phenomenon, the observed base peaks belong to the organic ligand moiety. Fortunately and unlike all the previous reported studies<sup>9,10</sup>, the observed base peak at m/z 363.05 (complex 5) belongs to the chelated moiety not to the ligand moiety as shown below:



The highest stability of this species is due to the formation of the positively charged Quinonoid structure with extended conjugation. Surprisingly, the nickel (II) ion, in this species acquires a plane triangle shape.

**Thermal properties:** This study is aimed to decide whether water / methanol molecules are in the outer or inner coordination spheres. The TGA data (Table-3) of the complexes (1-3) exhibited an agreement with the results of elemental analysis. The thermograms are comprised of two or three regions and the following remarks were observed: i. Complex 1 loses the hydrated and coordinated water molecules in one step at the temperature range 32-292°C. This stage is accompanied by an endothermic peak. ii. On the other hand, complex 3 loses the lattice water / methanol in one step at the temperature range 24-185°C, followed by loss of the coordinated water molecules

and one HCl molecule in a second stage at the temperature range 186-414°C. In contrast, these stages are accompanied by exothermic peaks. iii. Unfortunately, complex 2 showed a confused behavior with several overlapping stages to loss lattice and coordinated water molecules in addition to one HCl molecule at the temperature range 39-299°C (Table-3). iv. Finally, the last stage of the degradation processes is the formation of the metallic residue as a final product; almost the corresponding metal oxide. The metal content is concordant with the proposed structures. In this context, the TG thermogram of complex 2 as an example was used to calculate the kinetic and thermodynamic parameters<sup>16-18</sup> for the degradation steps (Table-4). The obtained data reflect that the degradation processes are endothermic, non-spontaneous and entropically unfavorable<sup>17,18</sup>.

**Table-2:** Electronic spectral data, magnetic and conductivity of the complexes.

No.	Complexes	Electronic Spectral Bands(nm)	$\mu_{\text{eff}}$ (BM)	Conductance (Ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> )
1	[Cu(H <sub>2</sub> L)(H <sub>2</sub> O) <sub>2</sub> Cl <sub>2</sub> ].1½H <sub>2</sub> O	279, 348, 375, 438	1.95	40
2	[Ni(H <sub>2</sub> L)(H <sub>2</sub> O) <sub>2</sub> Cl <sub>2</sub> ].4½H <sub>2</sub> O.¼MeOH	268, 328, 366, 433,455, 487	3.06	35.6
3	[Co(HL)(H <sub>2</sub> O) <sub>2</sub> Cl]. 1¾H <sub>2</sub> O.⅝MeOH	280, 352, 386, 450, 480(sh)	4.27	47.0
4	[Cu <sub>2</sub> (HL) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> Cl <sub>2</sub> ].MeOH.¾H <sub>2</sub> O	275, 351, 383, 425, 495(sh)	1.44	41.3
5	[Ni(L)(H <sub>2</sub> O)].¾ H <sub>2</sub> O.¾MeOH	235, 277, 346, 407, 440(sh), 775	3.98	4.1
6	[Co <sub>2</sub> (L)(H <sub>2</sub> O) <sub>3</sub> Cl <sub>2</sub> ].MeOH.¾H <sub>2</sub> O	278, 350, 429, 606, 669	1.60	36.2

**Table-3:** Thermal behavior of the complexes.

Complex	Temperature range (°C)	% Wt. loss Found / (Calcd)	Lost molecules; Assignment	Probable residue % Found / (Calcd)
[Cu (H <sub>2</sub> L) (H <sub>2</sub> O) <sub>2</sub> Cl <sub>2</sub> ]. 1½ H <sub>2</sub> O (498.1)	32-292 293-797	9.54 (11.3) 42.06	3⅞ H <sub>2</sub> O with decomp.	(Cu <sub>2</sub> O + CuO); 48.4 (44.7)
[Ni (H <sub>2</sub> L) (H <sub>2</sub> O) <sub>2</sub> Cl <sub>2</sub> ]. 4½ H <sub>2</sub> O. ¼ MeOH (562.07)	39-74 74-121 121-220 221-299 300-567	9.05 (9.42) 4.37 15.66 4.33 (16.10) 6.96 58.70	• ¼ MeOH + 2½ H <sub>2</sub> O • 3 H <sub>2</sub> O + HCl (3 overlap stages) • Decomp.	NiO <sub>2</sub> ; 16.59 (16.12)
[Co (HL) (H <sub>2</sub> O) <sub>2</sub> Cl]. 1¾ H <sub>2</sub> O. ⅝ MeOH (488.30)	24-185 186-414 414-798	10.14 (10.55) 16.78 (14.85) 26.30	• ⅝ MeOH + 1¾ H <sub>2</sub> O • 2 H <sub>2</sub> O + HCl	Co <sub>3</sub> O <sub>4</sub> ; 46.78 (49.31)

**Table-4:** Thermodynamic and kinetic parameters for complex 2.

Complex	Stage	T (K)	A x 10 <sup>-9</sup> sec <sup>-1</sup>	E*	ΔH*	ΔG*	-ΔS*
2	1 <sup>st</sup>	333	1.575	6.032	3.269	26.463	69.653
	2 <sup>nd</sup>	367	1.873	6.372	3.326	28.655	69.018
	3 <sup>rd</sup>	461	3.992	8.161	4.335	34.13	64.631
	4 <sup>th</sup>	549	6.676	9.637	5.080	39.015	61.812

E\*, ΔH\* and ΔG\* are in k J mol<sup>-1</sup> while ΔS\* is in J mol<sup>-1</sup> K<sup>-1</sup>.

## Conclusion

This work is a comparative one in which the hydrazone ligand has a reformed character *i.e.* the hydrazone can change its coordination behavior in absence and presence of KOH. Also, mononuclear and binuclear complexes were obtained in absence and presence of KOH, respectively. Furthermore, no evidence for the formation of hydroxo- complexes and the presence of KOH in the reaction mixture enhances the phenoxy bridging leading to formation of the binuclear complexes (4,6). For cobalt(II)- complex (6), the hydrazone produces ligand field strong enough to cause spin pairing. Arguments supporting the dimeric structure (complex 4) are related to the pronounced decrease in its  $\mu_{\text{eff}}$  value (1.44 BM). The hydrazone exhibited a variety of modes of bonding *viz.* neutral NN, monobasic NO or NNO and dibasic NNO- donors with or without O- bridging.

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