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# Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

Publication details, including instructions for authors and subscription information: <u>http://www.tandfonline.com/loi/lsrt20</u>

# 2-Hydroxybenzaldehyde-(4,6-Dimethylquinolin-2-yl)-Hydrazone (HBDH), Synthesis, Characterization, and Ligational Behavior Towards Some Metals

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To cite this article: Nasser Mohammed Hosny, Mohamed Abdel-Moneim Mahmoud & Mohamed R.E. Aly (2010) 2-Hydroxybenzaldehyde-(4,6-Dimethylquinolin-2-yl)-Hydrazone (HBDH), Synthesis, Characterization, and Ligational Behavior Towards Some Metals, Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 40:7, 439-446

To link to this article: <u>http://dx.doi.org/10.1080/15533174.2010.494271</u>

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# 2-Hydroxybenzaldehyde-(4,6-Dimethylquinolin-2-yl)-Hydrazone (HBDH), Synthesis, Characterization, and Ligational Behavior Towards Some Metals

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2-Hydroxybenzaldehyde-(4,6-dimethylquinolin-2-yl)-hydrazone, and its metal complexes with Cu(II), Co(II), Ni(II), and Zn(II) have been synthesized and characterized using elemental analyses. spectral analyses (IR, UV, <sup>1</sup>H-NMR, MS), thermal analyses (TGA and DTG), conductance and magnetic measurements. The results showed that 2-hydroxybenzaldehyde-(4,6-dimethylquinolin-2-yl)hydrazone acts as mononegative tridentate ligand coordinating to the metal ions through quinoline nitrogen, azomethine nitrogen and phenolic oxygen after deprotonation. The difference between  $v_{as}$  and  $v_{as}$  stretching vibrations indicates that acetate group binds to the metal ions in a bi-dentate fashion. An octahedral stereochemistry has been suggested for all metal ions. The vibrational spectra of the ligand and its metal complexes have been calculated using semi-empirical calculations, AM1, PM3 and ZINDO/1 methods, to facilitate the assignments of the experimental spectra. Also, the optical band gap (Eg) of the metal complexes has been calculated. The optical transition energy (Eg) is direct and equals 2.40, 2.62 and 2.71 ev for Co, Ni and Cu complexes, respectively.

**Keywords** 2-hydroxybenzaldehyde-(4,6-dimethylquinolin-2-yl)hydrazone, metal complexes, spectral analyses, optical band gap

# INTRODUCTION

Aroyl hydrazones are an important class of compounds containing azomethine group. Hydrazides and their corresponding hydrazones can function as anti-tuberculoses and anti-oxidants.<sup>[1-5]</sup> The anti-tuberculoses activity of hydrazides comes from their ability to form metal chelates with transition metal ions. This category of compounds has not only pharmacological activity, but also extensive applications.<sup>[6]</sup> Polyazomethines have been widely studied for their high thermal stability, mechanical properties, electrical and magnetic properties, liquid-crystal properties, and non-linear optical properties.<sup>[7,8]</sup> Metal complexes of the polypyridine family have attracted a great deal of attention from the photochemical community.<sup>[9]</sup> Another strategy found in the literature to improve the light harvesting efficiency and sensitivity at longer wavelengths of mononuclear pyridyl metal complexes sensitizers is the introduction of phenyl groups in the chromophoric ligands.<sup>[10]</sup> The diversity of applications and in continuation to our previous work on hydrazones<sup>[11-15]</sup> has prompted us to synthesis a new series of hydrazones metal complexes containing quinoline moiety. The structure of the ligand and its metal complexes have confirmed by different physicochemical techniques. The vibrational spectra of the most important bands of the ligand and its metal complexes were calculated theoretically using semi-empirical methods to facilitate the assignments of the experimental results. Also, the optical band gap of the isolated complexes has been calculated to shed more light on the conductivity of these complexes.

# **EXPERIMENTAL**

# Reagents

All the chemicals used were of analytical grade and used without further purifications.

# Analysis and Equipment

Carbon and hydrogen contents were determined at the Microanalytical Unit of Mansoura University. The metal analyses were carried out by standard methods.<sup>[16]</sup> Molar conductance measurements of the complexes  $(10^{-3} \text{ M})$  in DMSO were carried out with a conductivity bridge YSI model 32. Infrared spectra were measured using KBr discs on a Mattson 5000 FTIR spectrometer. Calibration with the frequency reading was made with polystyrene film at Mansoura University. Electronic spectra were recorded on UV2 Unicam UV/vis. Spectrometer using 1 cm Stoppard silica cells at Mansoura University. Magnetic measurements were carried out on a Sherwood magnetic

Received 22 July 2009; accepted 15 May 2010.

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FIG. 1. Structure of the ligand (HBDH).

balance at Mansoura University. Thermal analysis measurements (TGA) were recorded on a Schimadzu model 50 instrument using 20 mg samples. The nitrogen flow rate and heating were 20 cm<sup>3</sup>/ min. and 10°C /min., respectively. The <sup>1</sup>H-NMR spectrum of the ligand was recorded in d<sub>6</sub>-DMSO on a Gemini-200 spectrometer at Cairo University. Mass spectra of the ligand were recorded on Shimadzu GC-MS-QP 1000 Ex at 70 ev mass spectrometer at Cairo University.

## **Computational Details**

Molecular geometries of all forms of the ligand and its metal complexes were optimized using molecular mechanics and the semi-empirical ZINDO/1, PM3 and AM1 methods using the hyperchem series of programs.<sup>[17]</sup> Molecular mechanics technique was used to investigate rapidly the geometries of the suggested structures of the ligand. The low lying conformers obtained from this search were then optimized at AM1, ZINDO/1 and PM3, (Polak-Ribiere) RMS 0.01kcal.

#### Preparation of the Ligand

A mixture of 2-hydrazino-4,6-dimethylquinoline (4.2 mmol, 0.8 g) and salicylaldehyde (7.6 mmol, 0.8 ml) in benzene (8 ml) was heated under reflux for 2 h then left to be cooled to ambient temperature. The orange-yellow crystals formed were filtered in vacuum, washed with petroleum ether and dried well to afford 2-hydoxybenzaldehyde-(4,6-dimethylquinolin-2-yl)-hydrazone; (1.07 g, 86 %) (Figure 1).

# **Preparation of Metal Complexes**

The metal complexes were prepared by adding equimolar amounts (1 mmol) of the metal (II) acetate in 25 ml absolute EtOH to a hot solution of the ligand (1 mmol, 0.29 gm) in 25 ml absolute EtOH. The precipitate formed was filtered immediately and washed with hot absolute EtOH to ensure the isolation of pure complexes then kept in a vacuum desiccator over fused CaCl<sub>2</sub>.

# **RESULTS AND DISCUSSION**

The reaction of Cu(II), Co(II), Ni(II), and Zn(II) acetates with the ligand (HBDH) results in the formation of [MLAc.H<sub>2</sub>O] (M = Cu(II), Co(II) Ni(II) or Zn(II); L = 2-hydoxybenzaldehyde-(4,6-dimethylquinolin-2-yl)-hydrazone]. One type of metal complexes has been formed from the reaction of 2-hydroxybenzaldehyde-(4,6-dimethylquinolin-2-yl)-hydrazone with Cu, Co, Ni and Zn acetates. The ligand is chelated to all the metal ions as mono negative tridentate after replacement of one hydrogen atom from the phenolic oxygen. Ethanol was used as a solvent in the preparation of all the metal complexes.

The formation of metal chelate may be represented by the following equation:

 $\begin{array}{l} HBDH + M(CH_{3}COO)_{2} \\ \xrightarrow{EtOH} & [M(HBDH)OAc.H_{2}O] + CH_{3}COOH \\ & (where M = Cu(II), Co(II), Ni(II) and \\ & Zn(II), OAc = CH_{3}COO^{-}) \end{array}$ 

All the complexes are quite stable in air. These complexes are generally insoluble in common organic solvents, but soluble in coordinating solvents as DMSO and DMF. The conductance measurements ( $\sim 7.0 \text{ ohm}^{-1}\text{cm}^2 \text{ mol}^{-1}$  in  $10^{-3}\text{M DMF}$ ) indicate that the complexes are essentially nonelectrolytes.<sup>[18]</sup> The elemental analyses and some physical data are collected in Table 1.

 TABLE 1

 Analytical data and physical properties of the the ligand (HBDH) and its complexes

			% Found (calcd.)		
Compound	Color	M.P. °C	С	Н	М
HL	orange-yellow	228	75.0 (74.6)	5.9 (5.5)	-
[CuL.Ac H <sub>2</sub> O]	green	>300	56.0 (55.8)	4.7 (4.7)	14.7 (14.9)
[NiL. Ac H <sub>2</sub> O]	green	>300	57.0 (56.5)	4.8 (4.7)	14.0 (13.8)
[CoL.Ac H <sub>2</sub> O]	yellow	>300	56.9 (56.5)	5.0 (4.7)	13.5 (13.9)
[ZnL.Ac H <sub>2</sub> O]	brown	>300	55.2 (55.6)	5.1 (4.6)	14.8 (15.1)



# Mass Spectra

The mass spectral fragmentation mode of (HBDH) has been investigated. The mass spectrum (Figure 2) shows an intense molecular ion peak at m/z = 291, corresponding to the molecular formula  $C_{18}H_{17}N_3O$ . The ion of m/z = 291, undergoes fragmentation to produce a stable peak at m/z = 274, by losing hydroxyl group (OH). The loss of phenyl group from the ion with m/z = 274, with rearrangement results in the formation of methyl diazoquinoline gives ion at m/z = 198. The loss of CN group from the ion at m/z = 198 gives the base peak at m/z =172. The base peak undergoes loss of ammonia molecule to give the peak at m/z = 155, followed by loosing of HCN molecule to give the ion at m/z = 128. It further undergoes loss of CH,  $C_2H_4$  and  $C_2H_2$  to give peaks at m/z = 115, 91 and 65, respectively (Scheme 1).

# <sup>1</sup>H-NMR

The <sup>1</sup>H-NMR spectrum (Figure 3) of the ligand (HBDH), in DMSO- $d_6$  shows two singlets signals in the upfieled region at 2.51 and 2.67 ppm, corresponding to the two methyl groups, C4-CH<sub>3</sub> and C6-CH<sub>3</sub> with C4-CH<sub>3</sub>being more desheielded by



FIG. 4. IR spectra of the ligand and its metal complexes.

the anisotropy of the endocyclic-nitrogen. The aromatic protons appear as multiplet in the 6.91–7.72 ppm region. Just next to the aromatic protons at 8.40 ppm the methane protons of the imine moiety appeared as singlet. The broad singlet peak in the far downfieled region in the range 10.45–11.4 ppm was assigned for the H-bonded NH and OH groups with an integration that fits for two protons.

# **IR Spectra**

The most important IR band assignments of the experimentally and theoretically calculated for the optimized structures are included in Table 2.

IR spectra of the ligand and its metal complexes are collected in Figure 4.



FIG. 3. <sup>1</sup>H-NMR spectrum of the ligand (HBDH).



SCH. 1. Fragmentation pattern of the ligand (HBDH).

The IR spectrum of the ligand shows a band at  $3420 \text{ cm}^{-1}$  assigned to  $\nu$  (OH). Also, another band is observed at  $1353 \text{ cm}^{-1}$  assigned to  $\delta$  (OH).<sup>[14]</sup> The presence of a broad band at 2853 cm<sup>-1</sup> which may be assigned to OH....O stretching vibration, indicates the possibility of intermolecular hydrogen bonding of the phenolic OH group. The bands observed at 3182, 1590 and 1580 cm<sup>-1</sup> are assigned to  $\nu$  (NH),  $\delta$  (NH) and  $\nu$  (C=N), respec-

tively. The bands located at 1611, 1032, 651 and 420 cm<sup>-1</sup>, may be assigned to  $\nu$  (C=C) + $\nu$  (C=N)<sub>Q</sub>, the ring skeletal mode, in plane and out of plane ring deformation modes, respectively.<sup>[19]</sup> These bands are of considerable importance in deciding whether the quinoline nitrogen is involved in the coordination with the metal ion.<sup>[20]</sup> The spectra of all metal complexes show a broad band located at 3430 cm<sup>-1</sup> assigned to  $\nu$  (OH) of water. The

			Õ	bserved a	nd calcul	ated wav-	enumbers	$(cm^{-1})$	of the lig	and (HBI	DH) and	its metal	complexe	ŝ			
		HB	HO			Cu complex			Co complex			Ni complex			Zn con	ıplex	
Vibration	Exp.	AMI	PM3	ZINDO/1	Exp	PM3	ZINDO/1	AM1									
$\nu(NH)$	3182	3234	3125	4782	3250	3897	4218	3206	3370	4737	3208	3320	4247	3205	3325	4259	3296
$\nu(C=N)_Q$	1611	1618	1614	1676	1620	1634	1661	1619	1607	1610	1620	1604	1605	1620	1617	1649	1639
$\nu(C=N)$	1580	1566	1570	1602	1557	1512	1634	1556	1530	1576	1554	1550	1562	1555	1566	1596	1543
ν(C−O)*	1373	1354	1446	1427	1342	1327	1361	1335	1337	1322	1338	1322	1376	1340	1347	1349	1319
Py skeletal	1032,651, 420	1053,674, 455	1043,650, 427	1081,645, 429	1038,668, 446	1035,654, 435	1039,668, 458	1038,668, 445	1025,658, 449	1031,637, 432	1038,674, 432	1034,676, 436	1024,681, 442	1038,670, 440	1042,672, 441	1075,665, 446	1026,659, 449
Q = q	uinoline ni	trogen.															

TABLE 2 alculated wavenumbers $(cm^{-1})$ of the livand (HBDH) and its metal complexes	
Observed and calculated v	



FIG. 5. Suggested structure of metal complexes.

band assigned to  $\delta$  OH of phenolic group disappeared in the spectra of metal complexes indicating the participation of this group in bonding after deprotonation. The bands at 1580 and 905  $cm^{-1}$  assigned to azomethine group v (C=N) and v (N-N), respectively, are shifted to lower wavenumber due to the decrease of electron density on the nitrogen atom, suggesting the participation of the azomethine group in bonding. On contrary, the bands assigned to quinoline ring are shifted to higher wavenumber due to the increase of electron density on the quinoline nitrogen through back donation. This behavior indicates that quinoline nitrogen is one of the active sites that take part in coordination to the metal ion.<sup>[15]</sup> Two new bands are observed at 1470 and  $\sim$  1307 cm<sup>-1</sup> assigned to  $\nu_{as}$  and  $\nu_{s}$  of the acetate group, respectively. The difference between these two bands indicates the bi-dentate nature of this group.<sup>[21,22]</sup> Several new weak bands are observed in the regions 478-487 and 526-533 cm<sup>-1</sup> assigned to  $\nu$  (M-N) and  $\nu$  (M-O), respectively.<sup>[23]</sup> On the basis of the above evidence, it could be suggested that the ligand acts as mononegative tridentate ligand coordinating to the metal ions through quinoline nitrogen, azomethine nitrogen and phenolic oxygen after deprotonation of phenolic oxygen (Figure 5).

From Table 2, it is clear that AM1 and PM3 methods agree well with the characteristic group frequencies in case of the free ligand and Zn complex, while PM3 and ZINDO/1 agree well for Co(II) and Ni(II) complexes. Also, PM3 agrees well with the experimental data for the Ni(II) complex.

The experimental data are obtained in the solid state where the calculated frequencies are estimated in the gas phase. This may be the reason for the difference observed between the calculated and experimental values.

## **Thermal Analyses**

Thermal analysis plays an important role in studying the properties of metal complexes to obtain a useful data on the thermal stability and metal–ligand bonds. The thermal analyses TGA and DTG of Zn complex were studied as a representative example to shed more light on the thermal decomposition of this category of metal complexes. The thermal measurements (TGA and DTG) were carried out within a temperature range from 25 up to 800°C. The thermograms of Zn complex show that it is stable up to 200°C. It decomposes in three steps; the first is endothermic, lies in the temperature range 200–359°C and corresponds to the loss of one coordinated H<sub>2</sub>O and acetate (mass loss is 17.1%; close to the calculated 17.8%). The second step is an endothermic, lies in temperature range 359 – 443°C and corresponds to the loss of Ph, HCN and N (mass loss is 27.6%; calculated 27.0%). The last step is an endothermic, corresponds to the loss of step is an endothermic, is a step is an endothermic, corresponds to the loss of Ph, HCN and N (mass loss is 27.6%; calculated 27.0%). The last step is an endothermic, step lies in the temperature range 443 – 575°C. The remaining is assigned to ZnO (mass loss is 19.7%; calculated 18.8%).

## **Electronic Spectra and Magnetic Moments**

The electronic spectrum of Cu(II) complex in Nujol shows a band at 18181 cm<sup>-1</sup>. The position of this band suggests the presence of distorted octahedral around Cu(II).<sup>[24]</sup> The band observed at 23256 cm<sup>-1</sup> may be LMCT transition.

The magnetic moment value is 1.80 B.M. in the range suggested for monomeric copper complexes.<sup>[14]</sup>

The electronic spectra of Co(II) complexes exhibit two bands at 15723 and 18868 cm<sup>-1</sup> assigned to  ${}^{4}T_{1g}$  (F)  $\rightarrow {}^{4}A_{2g}$  (F) and  ${}^{4}T_{1g}$  (F)  $\rightarrow {}^{4}T_{1g}$  (P) transitions, respectively.<sup>[25]</sup> The band recorded at 23148 cm<sup>-1</sup> may be attributed to LMCT.

The magnetic moment value 4.9 B.M. supports the presence of an octahedral geometry around Co(II). The ligand field parameters [B = 839,  $\beta$  = 0.86 and 10 Dq = 8390 cm<sup>-1</sup>] fall in the range suggested for octahedral geometry of Co(II).

Electronic spectrum of Ni(II) complex in Nujol shows two bands at 13054 and 22522 cm<sup>-1</sup> assigned to  ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g} (\nu_2)$ and  ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g} (P) (\nu_3)$  transitions, respectively. The presence of these bands indicates an octahedral geometry around Ni(II) ion<sup>[25]</sup>. The ligand field parameters [B = 789,  $\beta = 0.75$  and 10 Dq = 7890 cm<sup>-1</sup>] support the presence of an octahedral geometry.

The magnetic moment value 2.90 B.M. is consistent with octahedral configuration around Ni(II).

# **Optical Band Gap (Eg)**

To clarify the conductivity of the isolated complexes the optical band gap ( $E_g$ ) of Cu(II), Co(II) and Ni(II) complexes has been calculated from the following equations:  $\alpha = 1/d \ln A$  (1) where, ( $\alpha$ ) is the absorption coefficient and (d) is the width of the cell. The optical band gap ( $E_g$ ) is calculated from the relation:

 $\alpha h\nu = A (h\nu - E_g)^m$  (2), where m is equal to 1/2 and 2 for direct and indirect transition respectively, A is an energy independent constant.<sup>[26,27]</sup> The values of  $\alpha$  calculated from relation 1 was used to plot  $(\alpha h\nu)^2$  and  $(\alpha h\nu)^{1/2}$  vs. h $\nu$  from which a direct band gap was found (Figure 6), by extrapolating the linear portion of the curve to  $(\alpha h\nu)^2 = 0$ . From the curve it is clear



FIG. 6. The plots of  $(\alpha h\nu)^2$  vs h $\nu$  of Cu(II), Co(II), and Ni(II) complexes.

that the values of the direct band gap  $(E_g)$  equal 2.40, 2.62 and 2.71 ev in case of Co, Ni and Cu complexes, respectively. There is a direct relation between the atomic number of the central atoms and  $(E_g)$  values, indicating that  $(E_g)$  depends on the electronic configuration of the d orbital of the central ion. The band gap values suggest that these complexes are semi-conductors and lie in the same range of highly efficient photovoltaic materials. So, the present compounds could be considered potential materials for harvesting solar radiation in solar cell applications.<sup>[28]</sup>

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