



Synthesis, spectral and thermal properties of complexes derived from 2-(2-hydroxyphenylimino) methyl-6-methoxyphenol

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ABSTRACT

New metal complexes derived from schiff base ligand resulted from condensation of *o*. Vanillin and *o*. amino phenol. The ligand characterize by ¹HNMR, ¹³C NMR mass and IR. The ligand acts as tridentate coordinating with Cu(II), Co(II) and Cd(II) Via azomethine nitrogen and two enolic hydroxyl oxygen after displacement of hydrogen. The thermodynamic parameters ΔE , ΔH , ΔS and ΔG have been calculated from Tg data by Coat- Redfern method.

Keywords: Schiff base, Coat -Redfern.

INTRODUCTION

The condensation of primary amines with aldehydes and ketones give imines (Schiff base) which contain an azomethine group .Schiff base are capable of forming coordinate bonds with many of metal ions through azomethine group phenolic group and others [1,2]. Schiff base and their metal complexes have exhibited biological activity, catalytic activity , anticorrosion inhibitor [3,4] .etc.

There are several report on the thermal stability of Schiff base complexes. most complexes show high stability compared with corresponding ligand .

EXPERIMENTAL SECTION

2.1 : Material : *o*-aminophenol ,metal acetate salts from Fluka ,*o*-vanillin from Himedia , all solvents used were of analytical grade and were used without further purification .

2.2 :Measurements : IR spectra were measured using KBr discs on a SHIMIDZU-84005. El-mass spectrum of the ligand was recorded on Agilent.

¹HNMR and ¹³C NMR were recorded on a Bruker (400 MHz for HNMR and 100 MHz for ¹³C NMR) using DMSO-d₆ as a solvent.

Thermal analyses measurements (Tg and DTG) were recorded on a Rheometric Scientific Inc.1998. nitrogen flow rate 10 cm³/min and heating rate 10 c/min.

The physical properties of the ligand and metal complexes are given in Table 1.

Table 1: physical properties of compounds

compounds	Physical state	m.p °C	Yield %
R	Yellow Crystal	192- 193	64
RCu	Green powder	> 300	77
RCo	Brown powder	> 300	85
RCd	Brown powder	> 300	80

2.3 :Preparation :**2.3.1 : Preparation of the ligand :**

A solution of 10 mmole of *o*-aminophenol in 25 ml ethanol was added to 10 mmole of *o*-vanillin in 25 ml ethanol, the resulting solution was refluxed for 3hrs .The solid Orange , product which obtain was filleted off washed with ethanol and dried in air .Yield 74 % .M.p 192-193 °C .

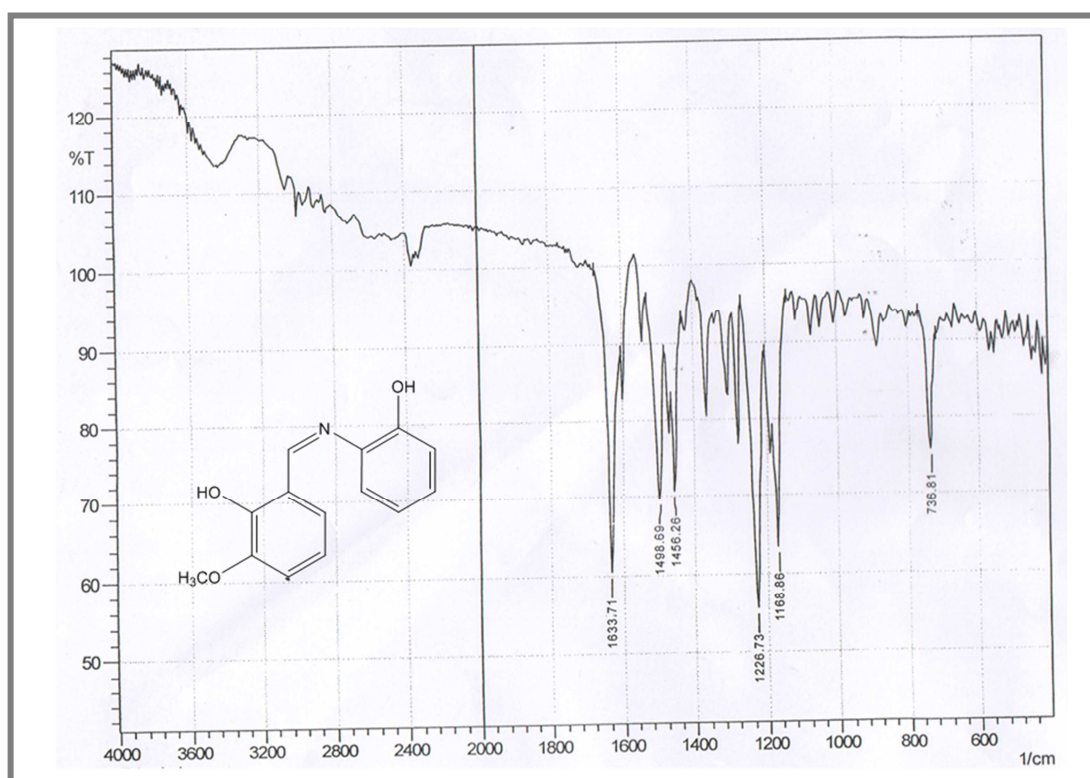
2.3.2 : synthesis of metal complexes :

Metal complexes were synthesized by adding the hot solution of the ligand (2mmole) in ethanol to a hot solution of metal acetate (2 mmole).The resulting mixture was then refluxed for 2 hours .The complexes which separated was filtered hot and washed with ethanol and then with diethyl ether and dried in air.

IR Spectra :

The ligand showed a strong band at 1633.7 cm^{-1} attributed to stretching vibration of azomethine group ,this band shifted to lower wave number in Co II ,Cu II and Cd II complexes by 13, 30 and 38 cm^{-1} respectively which indicated the coordination of azomethine nitrogen on complexation [2,4].

The ligand show a broad band at $\nu (3550.4) \text{ cm}^{-1}$ characteristic of stretching vibration of OH group , this band disappear in all complex spectra (Fig 1,2) suggests the linkage of phenolic oxygen with metals after deprotonation also a strong band at $\nu 1226.73 \text{ cm}^{-1}$ [5,6] in the IR spectrum of the ligand attributed to $\nu \text{ C-O (phenolic)}$ gets shifted to a lower wave number in the complexes by 15- 48 cm^{-1} and this is indicative of bonding through phenolic oxygen [7].

**Figure 1: IR Spectrum of R**

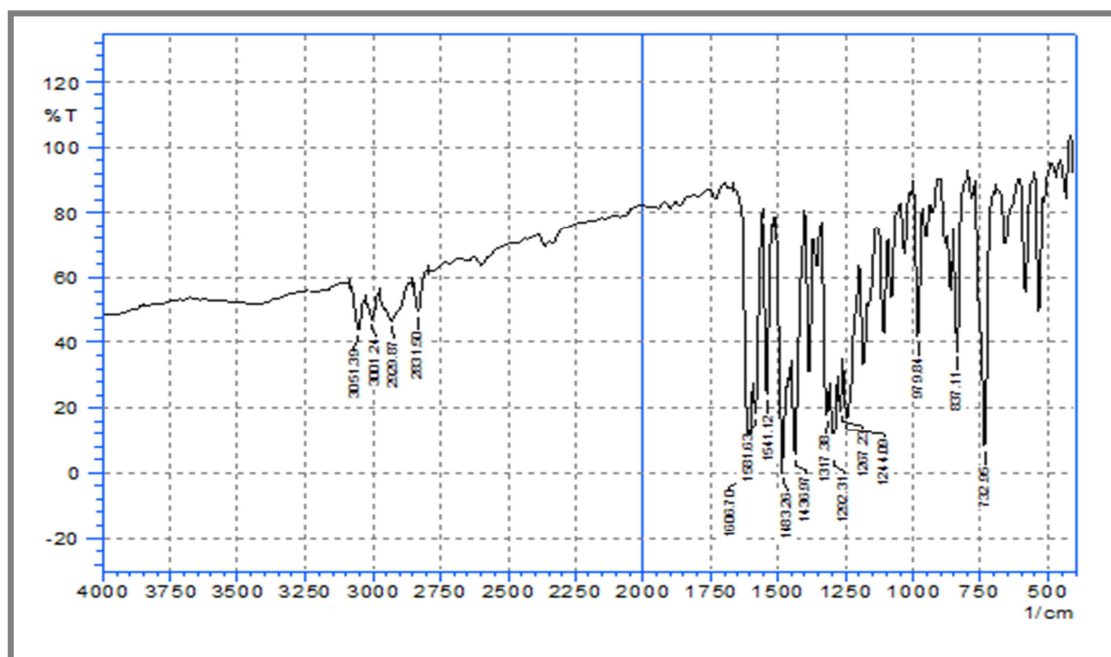
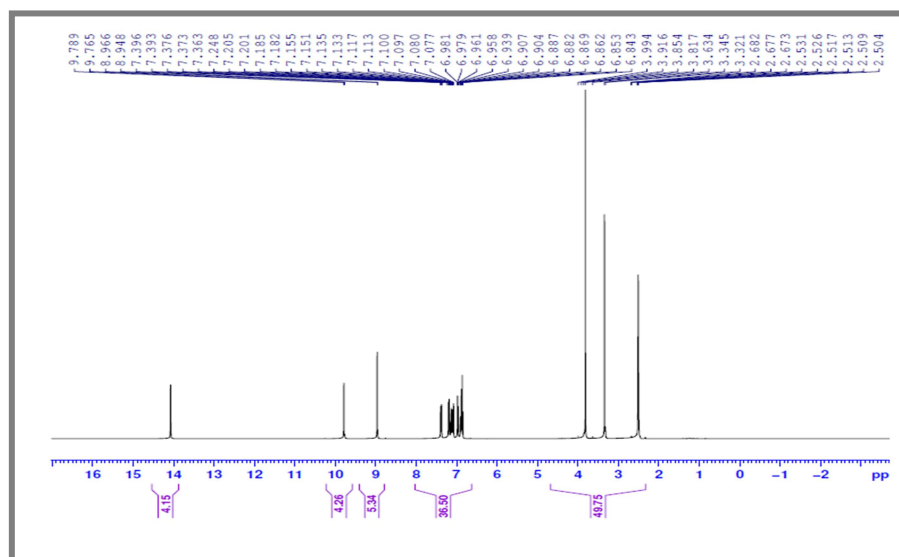


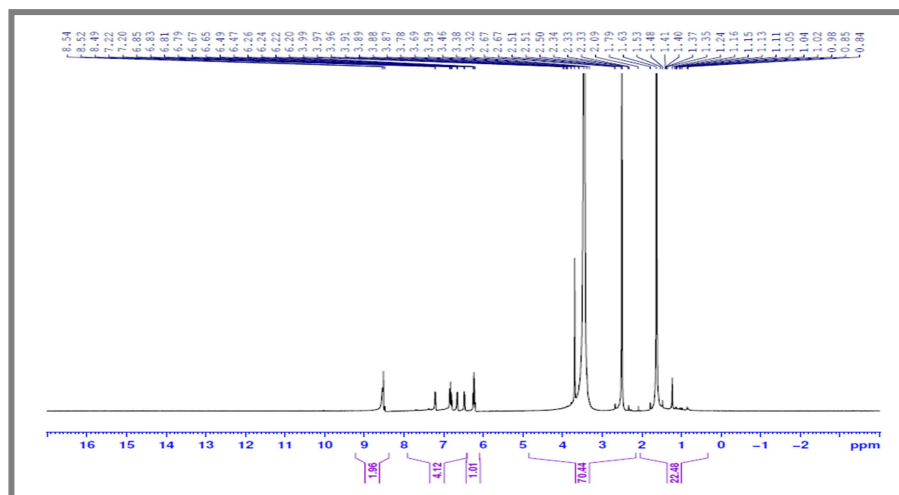
Figure 2: IR Spectrum of RCu

¹H NMR :

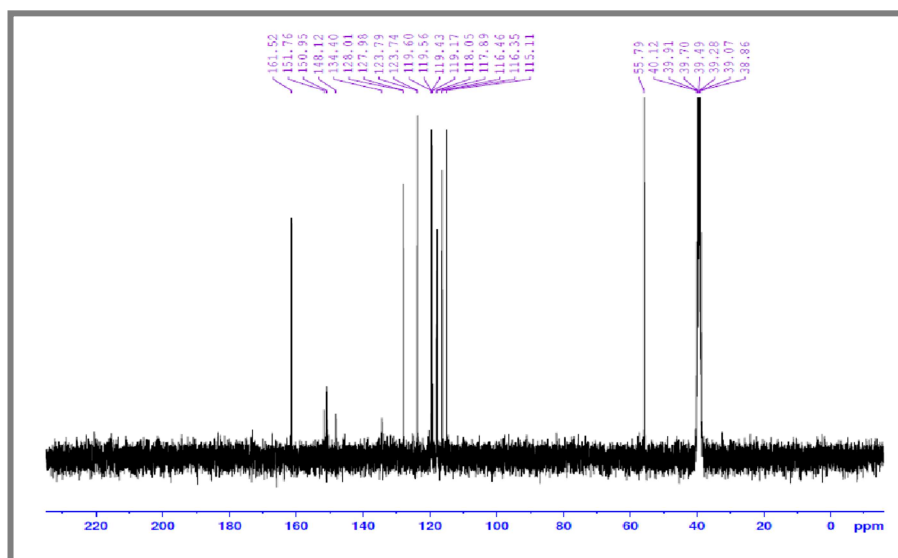
¹H NMR spectrum of the ligand show three singlet signal one of them at δ 8.94 ppm (1H) attributed to azomethine (-CH=N-) proton [9,10] and the other signal at δ 9.78 and 14.1 ppm due two phenolic protons .the multiple signal in the rang δ 6.84 – 7.39 ppm attributed to aromatic protons [7] also a singlet signal at δ 3.84 ppm due to methoxy protons [3,4] (Fig 3).

The ¹H NMR spectrum in DMSO-d₆ of diamagnetic complex (Cd complex) (Fig 4) , spectrum shows a singlet signal at 8.4 ppm assigned to the proton of the (-HC=N-) which shifted to higher field ,this is probably due to the involvement of C=N to form a M← N linkage [6,8] .The totally absente of the two singlet signals in the spectrum of the complex confirms that the two phenolic groups involvement in complex formation.

Figure 3: ¹H NMR Spectrum of R

Figure 4: ^1H NMR Spectrum of RCd **^{13}C NMR :**

^{13}C NMR spectral data of the free ligand was shown in (Fig 5) . The peak at δ 161.52 ppm is assigned to azomethine carbon [6]. The two phenol carbons appear at 150.95 and 151.76, The peak at 148.12 ppm attributed to C-N carbon . The aromatic carbons appear at 115-134 ppm, The peak at 55.79 is assigned to the carbon of methoxy group.[4]

Figure 5: ^{13}C NMR Spectrum of R**El-mass :**

The mass spectrum of the ligand (Fig 6) shows the exact molecular ion at $m/z = 243.3$ with relative abundance 100% (base peak) . This peak undergoes fragmentation to produce stable peak at 225.3 by losing of water molecule [4] . The peak at $m/z=196.2$ corresponds to the ion $[\text{C}_{13}\text{H}_{10}\text{ON}]^+$.

Thermal analysis :

The thermal investigations were carried out from room temperature to 800°C with a heating rate of $10^\circ\text{C}/\text{min}$ in nitrogen atmosphere.

The thermal degradation of RCo complex proceeds in three different stages (Fig 7) . the first decomposition process takes place between 80 and 140°C with 2.13% weight loss (theoretical 2.47%) (DTG max 110°C) which assigned to the loss of half molecule of water . The second step lies in the temperature rang $150 - 220^\circ\text{C}$ (DTG max 170°C) with mass loss 14.65% (theoretical 14.83%) corresponds to the loss of $3\text{H}_2\text{O}$ coordinated [11] . The third step lies in the temperature range $230-600^\circ\text{C}$ (DTG 370°C) corresponds to the loss of $\text{C}_{14}\text{H}_{11}\text{NO}_2$, found 60.53% (cal. 61.81%) [12].

In Tg curve of RCu no mass loss in the range 25 – 150 °C which indicate the absences of any lattice water molecule. the first step of loss in the range 150 - 210 °C with mass loss 5.41% (theoretical 5.59%) indicate the presence of one coordinated water molecule . The second step take place at 380 – 405 °C range of temperature and in fast rate to give the final residue 28.45% which may be attributed to CuO polluted with C atoms [13] (theoretical 25.98 °C).

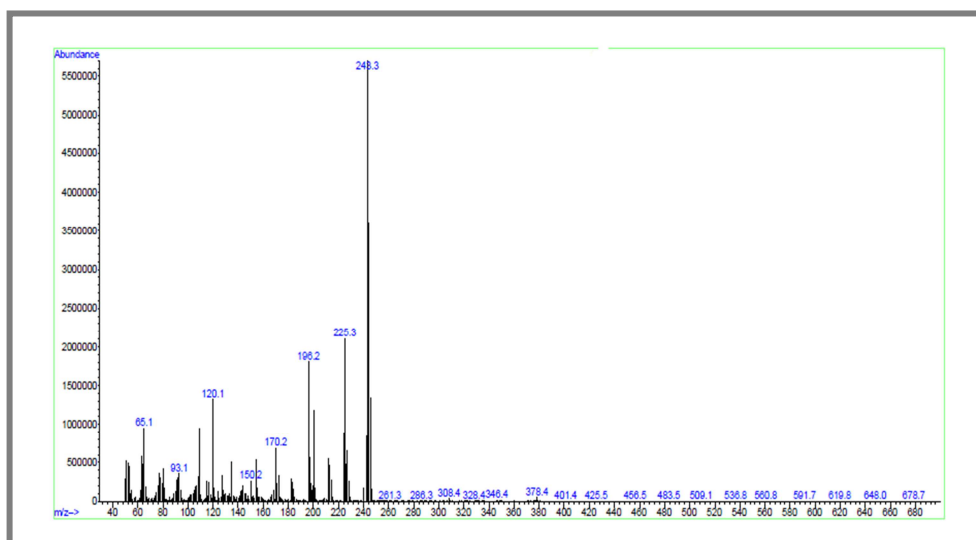


Figure 6: Mass Spectrum of R

For RCd complex the first mass loss in the range 40 – 135 °C found 14.41% (theoretical 14.69%) which prove the presence of four lattice water molecules. The second step of decomposition in the rang 150 – 205 °C found 11.1% (theoretical 11.22%) indicate the presence of three coordinated water molecules the final product 26.5% (theoretical 26.61%) with agreement with CdO.

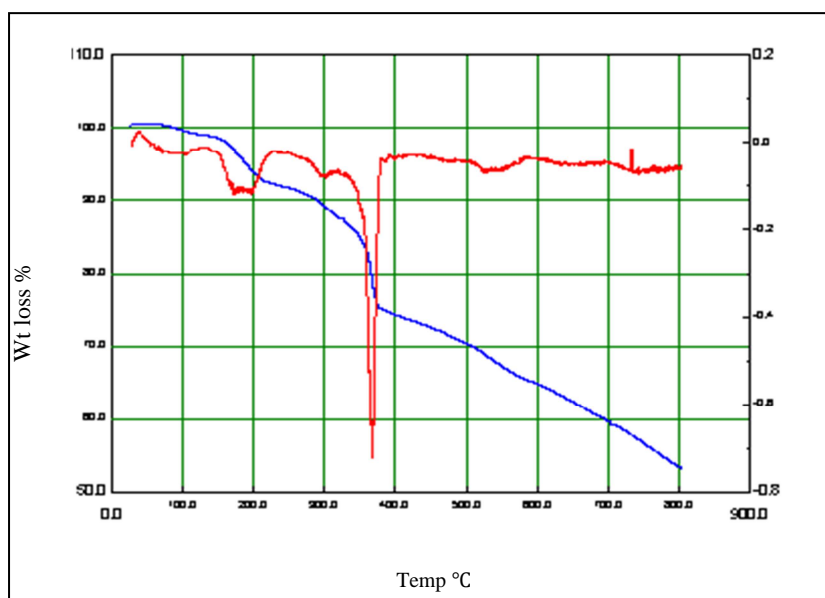
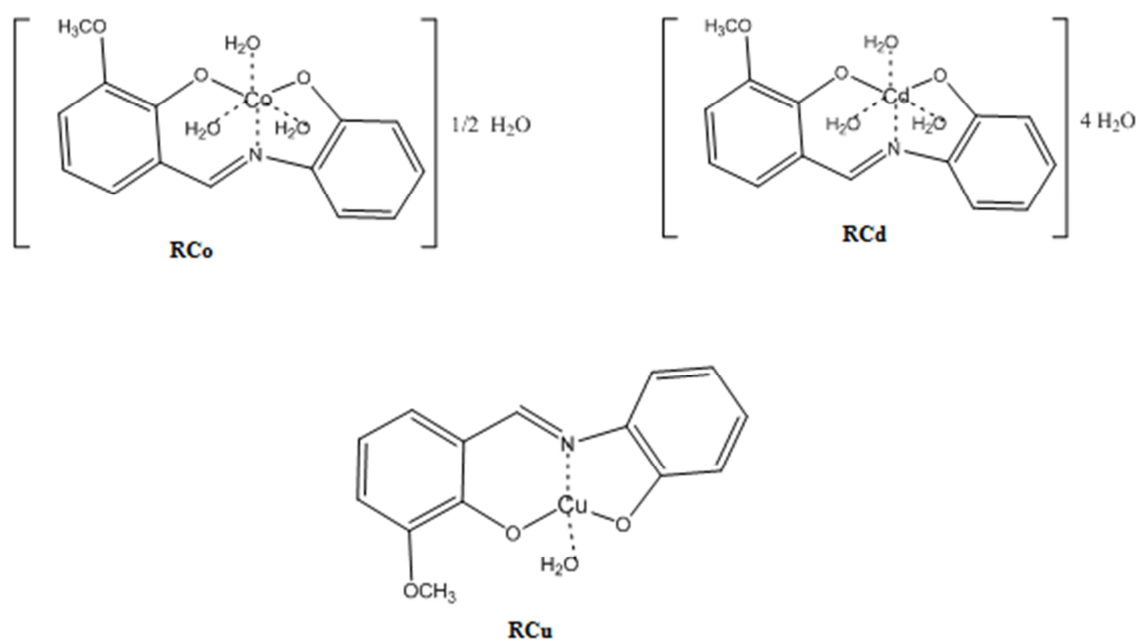


Fig.7: TG and DTG Curve of complex RCo

Based on the thermal and spectral data (IR,HNMR), the following structure are proposed for complexes.



The thermodynamic parameters (ΔE , ΔH , ΔG and ΔS) were calculated by the Coat – Redfern method (equation 1) [14 -16] and the result were collected in (Table 2) The positive ΔH show endothermic decomposition of the complexes . The negative value of Δs indicate that the complexes has more ordered structure . The positive values of ΔG indicate the non-spontaneous character of the all decomposition steps .

$$\log \left[\frac{\log \frac{W_f}{W_f - W}}{T^2} \right] = \log \left[\frac{AR}{\theta E} \left(1 - \frac{2RT}{E} \right) \right] - \frac{E}{2.303 RT} \quad \dots\dots\dots (1)$$

Table 2 : Thermal decomposition data and Kinetic parameter calculated from Coat - Redfern method of the complexes

Comp.	stage	TG rang	DTG max	Mass loss%		Assign-ment	A (S ⁻¹)	E	ΔH	ΔS	ΔG
				found	Calcu.						
RCo	I	80-140	110	2.13	2.47	1/2 H ₂ O	3.6×10^9	60.82	57.64	-0.102	96.76
	II	150-220	170	14.65	14.83	3 H ₂ O	3.1×10^{10}	99.54	95.86	-0.047	116.77
	III	230-600	370	60.53	61.81	C ₁₄ H ₁₁ NO ₂	3.07×10^9	39.90	34.55	-0.222	177.8
RCu	I	150-210	195	5.41	5.59	H ₂ O	1.3×10^4	89.7	-85.2	0.151	120.2
	II	380-405	400	67.35	69.87	C ₁₄ H ₁₁ NO ₂	1.9×10^5	465.2	-459.53	-0.423	170.1
RCd	I	40-135	95	14.41	14.69	4 H ₂ O	2.75×10^4	50.1	-47.31	0.113	90.2
	II	150-205	185	11.1	11.22	3 H ₂ O	1.06×10^4	98.2	-93.61	0.088	136.7
	III	285-578	375	46.5	47.60	C ₁₄ H ₁₁ NO ₂	4.03×10^6	154.1	-150.3	0.104	175.9

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