



## Spectroscopic, Thermal and Powder X-ray diffraction studies of bis-(benzoylacetato)cobalt(II) and nickel(II) complexes

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### ABSTRACT

Two Bis-(benzoylacetato)cobalt(II) and nickel (II) complexes has been synthesized and their characterization has been done on the basis of CHN analyses, IR, UV-Vis, X-ray powder pattern techniques. The cobalt(II) complexes has triclinic crystal system with unit cell dimensions,  $a = 6.499$ ;  $b = 5.300$ ;  $c = 11.327$  and  $\alpha = 86.754$ ;  $\beta = 111.279$ ;  $\gamma = 98.620$ , whereas the nickel (II) complex has monoclinic system with  $a = 12.8142$ ;  $b = 5.1697$ ;  $c = 9.2825$  and  $\beta = 141.849$ . The thermal decomposition steps of the complexes have been studied by thermogravimetric and differential thermal analyses. Thermodynamic parameters like activation energy ( $E_a^*$ ),  $\Delta H$ ,  $\Delta S$  and  $\Delta G$  for each decomposition of the complexes in the solid state were evaluated by following some standard methods and useful conclusions were drawn. The  $\Delta G$  and  $\Delta S$  of the systems were found to be negative, indicating the reactions were thermodynamically allowed.

**Key words:** Activation energy, X-ray powder pattern, thermal properties, cobalt(II) and nickel(II) complexes.

### INTRODUCTION

Benzoylacetone is a  $\beta$ -diketone analog, a bidentate ligand with O, O'-donor sets. In spite of having good complexing ability towards variable metal ions,  $\beta$ -diketones have immense analytical applications [1]. Some of rare-earth  $\beta$ -diketone complexes were known to be promising high- optical density recording materials for blue optoelectronics [2]. Moreover, they were good ligand precursors for the synthesis of Schiff base ligands and organometallic complexes. In an effort to synthesize Schiff base complexes by following multicomponent reaction scheme, Bis-(benzoylacetato)cobalt(II) and nickel(II) complexes were formed. As the synthesis of the single crystals for these complexes were found unsuccessful, powder pattern XRD technique was employed to determine their tentative crystal systems. The present work will give spectroscopic details and thermodynamic parameters ( $E_a^*$ ,  $\Delta H$ ,  $\Delta S$  and  $\Delta G$ ) evaluations.

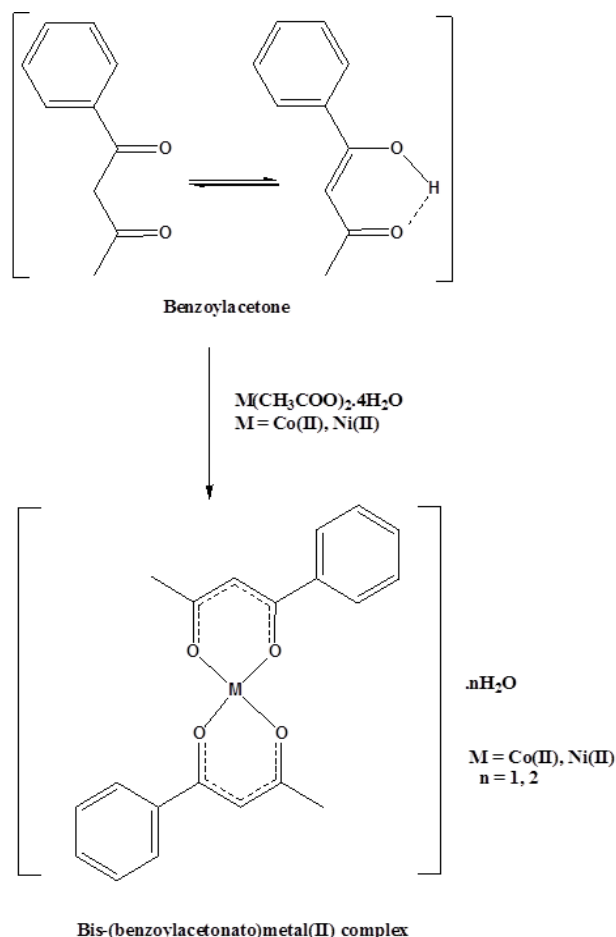
### EXPERIMENTAL SECTION

All the reagents were of analytical reagent grade. They were used as received without further purifications. The purity of the prepared complexes was checked by TLC method. Elemental analyses were carried out in Perkin Elmer 2400 Series II CHN analyzer. The amount of cobalt present in the cobalt(II) complex was estimated by normal decomposition method followed by complexometric EDTA titration. The nickel percentage was estimated by gravimetric analysis using DMG. Infra red spectra were recorded in Shimadzu FTIR-8400 spectrometer in solid using KBr discs. Electronic spectra were recorded in Perkin-Elmer Lamda 35 UV/VIS Spectrometer. The magnetic susceptibility measurements were carried out with a Sheerwood Magnetic Susceptibility Balance (MSB) at room temperature and diamagnetic corrections were made using Pascal's constants. Thermal analyses were carried out on a Perkin Elmer STA 6000 Thermal Analyzer at  $10^\circ\text{C min}^{-1}$  within the temperature range  $25-900^\circ\text{C}$  under nitrogen atmosphere. The powder XRD patterns were recorded in PAN-analytical diffractometer with  $\text{CuK}\alpha$  radiation of wavelength  $1.54060 \text{ \AA}$  operating at a voltage of 40kV and a current of 20 mA. The scanning rate was maintained

$1.6^\circ \text{ mm}^{-1}$  over  $2\Theta$  range of  $5-50^\circ$  employing the reflection mode for scanning. The crystal lattice parameters were determined using a set of programs, called P-Index, which was based on least squares approach.

#### *Synthesis of the Bis-(benzoylacetonato)cobalt(II) complex*

Benzoylacetone (324 mg, 2mmol) was dissolved in 10 ml methanol and to it 10 ml methanolic solution of cobalt acetate tetrahydrate ( 248 mg, 1mmol) was added and the reaction mixture was heated to refluxed for several hours in presence of 1 mmol (248 mg) of 4,4'-diaminodiphenylsulfone. An orange red coloured precipitate complex obtained. Yield: 318 mg ( $\approx 80\%$ ). Anal. Calcd. for  $\text{C}_{20}\text{H}_{20}\text{CoO}_5$  (M.W. 399.24 g/mol): C, 60.11; H, 4.50; Co, 14.75. Found: C, 59.40; H, 4.04; Co, 14.55.  $\mu_{\text{eff}} = 3.62$  B.M.



**Figure 1. Schematic representation for the synthesis of the Bis(benzoylacetonato)cobalt(II) and nickel(II) complexes** *Synthesis of the Bis-(benzoylacetonato)nickel(II) complex*

The procedure for the synthesis of the nickel(II) complex was similar to above described procedure except for the addition of cobalt acetate tetrahydrate, nickel acetate tetrahydrate ( 247 mg, 1 mmol) in 10 ml methanol was added. A green coloured precipitate complex obtained. Yield: 323 mg ( $\approx 80\%$ ). Anal. Calcd. for  $\text{C}_{20}\text{H}_{22}\text{NiO}_6$  (M.W. 417.04 g/mol): C, 57.55; H, 5.27; Ni, 14.07. Found: C, 58.67; H, 5.64; Ni, 14.92.  $\mu_{\text{eff}} = 2.64$  B.M.

## RESULTS AND DISCUSSION

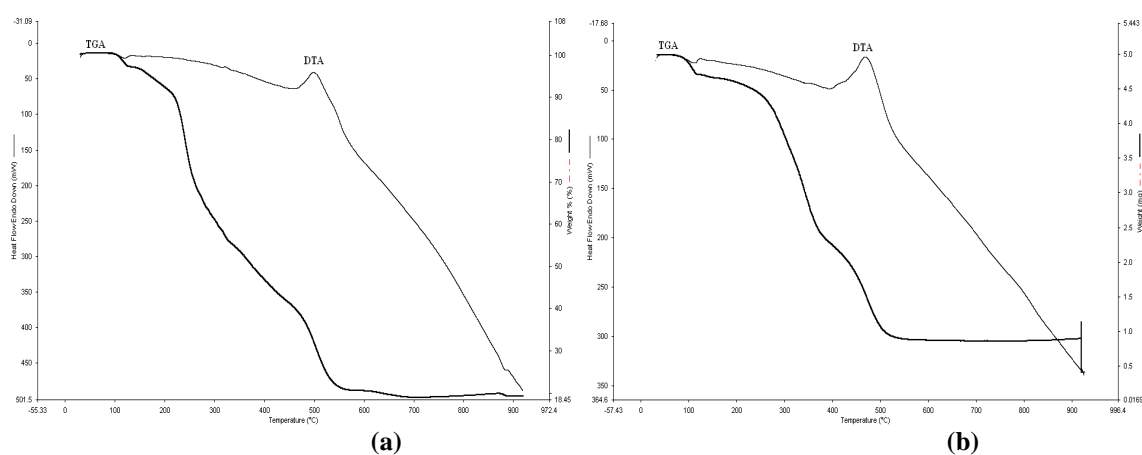
The prepared Bis-(benzoylacetonato)cobalt(II) and nickel(II) complexes were soluble in acetonitrile,  $\text{CHCl}_3$ , DMSO, DMF and stable in air. The IR spectrum of the free ligand exhibit  $\nu(\text{C}=\text{O})$  band *ca.*  $1598 \text{ cm}^{-1}$  which is much lower than that for conjugated ketones[3]. This much lowering is due to the intramolecular hydrogen bonding established by resonance as the  $\beta$ -diketones exists as a mixture of ketonic and enolic forms in equilibrium with each other [4]. In the IR spectra of the cobalt(II) and nickel(II) complexes, the  $\nu(\text{C}=\text{O})$  band shifts towards the lower frequency range  $1592-1593 \text{ cm}^{-1}$  respectively, indicating coordination of the ligand to the respective metal ions through the O-atoms[5]. The bands appearing around  $516-435 \text{ cm}^{-1}$  has been assigned to the  $\nu(\text{M}-\text{O})$  [6]. Bands at *ca.*  $3479-3375 \text{ cm}^{-1}$  may be assigned to the  $\nu(\text{O}-\text{H})$  for lattice water molecules. The electronic spectra of the cobalt(II) and nickel(II) complexes in DMF exhibit broad absorption bands *ca.*  $17,699$  and  $15,748 \text{ cm}^{-1}$

corresponding to the  ${}^4A_2 \rightarrow {}^4T_1(P)$  and  ${}^3T_1(F) \rightarrow {}^3T_1(P)$  transitions respectively, suggesting a tetrahedral or a pseudo-tetrahedral structure for the complexes [7, 8], Table I. The room temperature magnetic moment value ( $\mu_{\text{eff}}$ ) 3.62 B.M. for the cobalt(II) complex is intermediate between values for tetrahedral and square planar structures and it may be the result from a spin equilibrium between low and high spin Co(II) states [9]. On the other hand, the nickel(II) complex shows  $\mu_{\text{eff}} = 2.64$  B.M. value which is too small for high spins ( $S = 1$ ) and too large for low spin ( $S = 0$ ) nickel complexes, which may be arise due to an antiferromagnetic interaction or by spin equilibrium between low and high spin states [10].

**Table I. Spectroscopic data of the Benzoylacetone, cobalt(II) and nickel(II) complexes**

Compound	IR data ( $\nu$ in $\text{cm}^{-1}$ )			Electronic absorption data ( $\nu$ in $\text{cm}^{-1}$ )	
	$\nu(\text{O-H})$	$\nu(\text{C=O})$	$\nu(\text{M-O})$	Bands	Assigned Transitions
Benzoylacetone	3109-3006	1598	-----	-----	-----
Cobalt(II) complex	3375	1592	516	17,699	${}^4A_2 \rightarrow {}^4T_1(P)$
Nickel(II) complex	3479	1593	435	15,748	${}^3T_1(F) \rightarrow {}^3T_1(P)$

The TGA-DTA thermograms of the complexes were shown in figure 2. The general decomposition of the cobalt(II) and nickel (II) complexes proceeds with two main decomposition steps, Table II. The first step was the removal of lattice water molecules, which occurs at the temperature range 30-125°C.

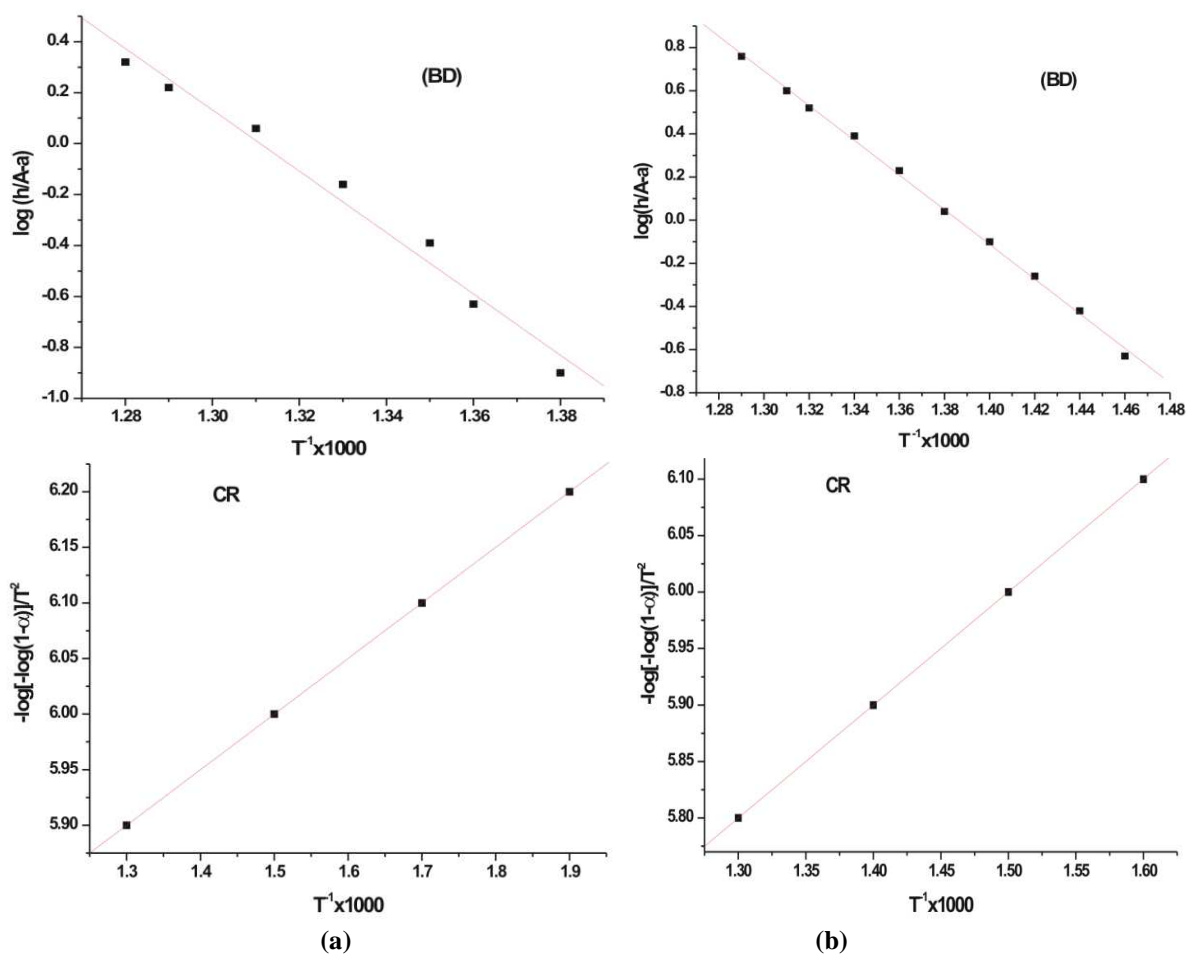


**Figure 2. TGA-DTA curves of (a) cobalt(II) complex, (b) nickel(II) complex**

The weight loss associated with this state 0.158 mg and 0.215 mg is very close to the theoretical calculated values of 0.214 mg and 0.290 mg corresponding to the loss of one and two water molecules from the cobalt(II) and nickel(II) complexes, respectively. A simultaneous weight loss curve was observed in the temperature range 125-573 and 116-542°C, corresponding to the loss of two ligand molecules representing weight loss of  $\approx 3.618$  mg and 3.800 mg and its calculated value is  $\approx 3.614$  mg and 3.639 mg respectively for cobalt(II) and nickel(II) complexes. The final thermal product obtained *ca.* 600-700°C was metal oxides (CoO, NiO respectively).

**Table II. Thermal data of the cobalt(II) and nickel(II) complexes (where, L= benzoylacetone)**

Compound	Decomposition Reaction Steps	TG Temp. range (°C)	TG Weight loss (mg)	DTA peak (°C)	Assignments
Cobalt(II) complex	1(a) $\text{CoL}_2 \cdot \text{H}_2\text{O} \rightarrow \text{CoL}_2$	30-125	0.158	111 (endo)	$-\text{H}_2\text{O}$
	1(b) $\text{CoL}_2 \rightarrow \text{CoO}$	125-573	3.618	503 (exo)	$-2(\text{C}_{10}\text{H}_8\text{O}_2)$
Nickel(II) complex	1(a) $\text{NiL}_2 \cdot 2\text{H}_2\text{O} \rightarrow \text{NiL}_2$	30-116	0.214	111 (endo)	$-2\text{H}_2\text{O}$
	1(b) $\text{NiL}_2 \rightarrow \text{NiO}$	116-542	3.800	471 (exo)	$-2(\text{C}_{10}\text{H}_8\text{O}_2)$



**Figure 3. Kinetics diagrams of the Coats and Redfern(CR) and Borchardt and Daniels (BD) equations for the (a) cobalt(II) ; (b) nickel (II) complexes.**

The thermodynamic parameters of decomposition steps of the complexes namely activation energy were evaluated graphically by employing the Coats-Redfern method [11] for TG curves and Borchardt and Daniels method [12] for DTA curves, Figure 3. The entropy of activation ( $\Delta S$ ), enthalpy of activation ( $\Delta H$ ) and the free energy change ( $\Delta G$ ) were calculated. The values of kinetic parameters are summarized in Table III. From the TG curves the activation energies of decomposition were found to be in the range 15-35  $\text{kJmol}^{-1}$ . The values suggest that the complexes were thermally stable. The  $\Delta G$  is negative for reaction for which  $\Delta H$  and  $\Delta S$  is negative.

**Table III. Kinetic parameters of the cobalt(II) and nickel(II) complexes (where, L= benzoylacetone).**

Compound	Decomposition Reaction Steps	$E_a^*$ ( $\text{kJmol}^{-1}$ )		$\Delta H$ ( $\text{kJmol}^{-1}$ )	$\Delta S$ ( $\text{KJmol}^{-1}$ )	$\Delta G$
		TG	DTA(exo)			
Cobalt(II) complex	1(a) $\text{CoL}_2 \cdot \text{H}_2\text{O} \rightarrow \text{CoL}_2$	--	--	--	--	--
	1(b) $\text{CoL}_2 \rightarrow \text{CoO}$	15	-156	-2.82	-3.63	-2.58
Nickel(II) complex	1(a) $\text{NiL}_2 \cdot 2\text{H}_2\text{O} \rightarrow \text{NiL}_2$	--	--	--	--	--
	1(b) $\text{NiL}_2 \rightarrow \text{NiO}$	35	-117	-2.83	-3.80	-2.23

The reaction for which  $\Delta G$  and  $\Delta S$  is negative is considered as favourable or as spontaneous reaction. i.e., the complexes were thermally unstable and kinetically stable [13, 14]. The entropy of activation was found to have negative values in all the complexes which indicate that the decomposition reactions proceed with a lower rate than normal ones.

X-ray powder diffraction methods are crucial techniques involved in material chemistry. The powder XRD diffraction patterns of the complexes were shown in figure 4. The crystallite sizes of the complexes were calculated by following Debye-Scherrer equation.

$$D = 0.9 \lambda / \beta \cos \theta \text{----(1)}$$

Where,

- D = Crystallite Size  
 $\lambda$  = wavelength of X-ray diffraction  
 $\beta$  = FWHM of observed peaks  
 $\Theta$  = Angle of diffraction

The crystallite size of the cobalt(II) and nickel(II) complexes were found to be 87.8 nm and 31.5 nm respectively. The cobalt(II) complexes has triclinic crystal system having  $a = 6.499$ ;  $b = 5.300$ ;  $c = 11.327$  and  $\alpha = 86.754$ ;  $\beta = 111.279$ ;  $\gamma = 98.620$ . On the other hand, the nickel (II) complex is monoclinic in nature with  $a = 12.8142$ ;  $b = 5.1697$ ;  $c = 9.2825$  and  $\beta = 141.849$ .

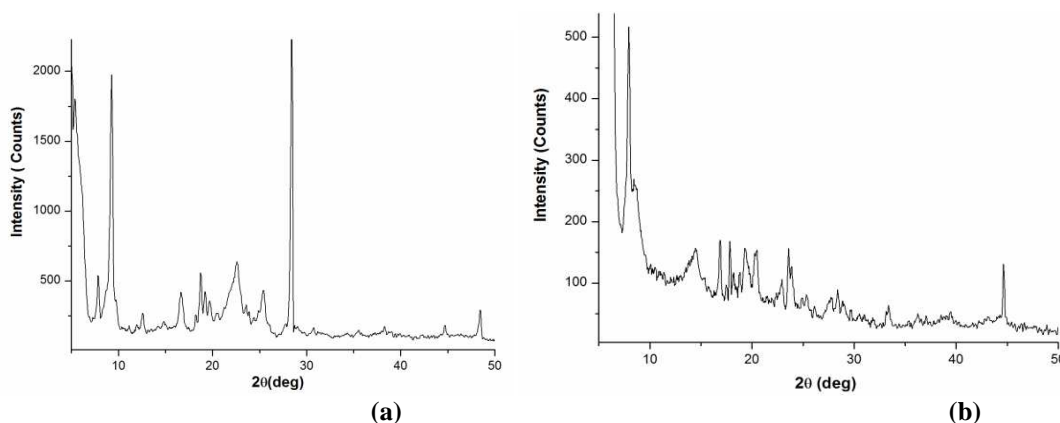


Figure 4. X-ray powder diffraction patterns of the (a) cobalt(II) complex; (b) nickel(II) complex

### CONCLUSION

In conclusion, two mononuclear Bis-(benzoylacetonato)cobalt(II) and nickel(II) complexes having molecular formula  $[\text{Co}(\text{C}_{10}\text{H}_9\text{O}_2)_2] \cdot \text{H}_2\text{O}$  and  $[\text{Ni}(\text{C}_{10}\text{H}_9\text{O}_2)_2] \cdot 2\text{H}_2\text{O}$  were synthesized and characterized by elemental analyses, spectroscopic (IR, UV-VIS) and X-ray powder diffraction studies. The electronic spectral study and magnetic moment values strongly suggests tetrahedral coordination around the respective cobalt(II) and nickel(II) ions. Thermal study of the complexes suggests the decomposition reaction processes were thermodynamically allowed.

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