SYNTHESIS, THERMAL STABILITY AND KINETIC STUDIES OF COPPER(II) AND COBALT(II) COMPLEXES DERIVED FROM 4-AMINOBENZOHYDRAZIDE AND 2-MERCAPTOBENZOTHIAZOLE

Maged S. Al-Fakeh[a, b]*

Complexes of divalent transition metal ions Cu(II) and Co(II) of the formula [M(ABZH)(MBTH)Cl₂(H₂O)₂], (M= Cu(II) and Co(II), ABZH=4-Aminobenzohydrazide (L₁) and MBTH = 2-mercaptobenzthiazole (L₂)) have been synthesized and characterized. The structure of the two compounds has been assigned based on elemental analysis, electronic spectral, FT-IR, magnetic measurements and XRD. The thermal properties of copper(II) and cobalt(II) metal complexes in dynamic air have been analyzed via thermogravimetry (TG) and differential thermogravimetry(DTG). The kinetic analyses of the thermal decomposition for the two compounds were calculated by the Coats-Redfern and Horowitz-Metzger methods. The obtained kinetic parameters display the kinetic compensation effect.

* Corresponding Author
  E-Mail: alfakehmmaged@yahoo.com , m.alfakeh@qu.edu.sa
[a] Department of Chemistry, College of Science, Qassim University, Buraydah, Qassim, Kingdom of Saudi Arabia
[b] Taiz University, Taiz, Yemen

INTRODUCTION

The coordination complexes comprise of a central ion or atom, which is usually metallic, and a surrounding array of ions or bound molecules, that are in turn known as complexing agents or ligands.[1,2] Many transition metals for example, copper(II) and cobalt(II) form coordination compounds. The name coordination indicates the coordinate covalent bonds between the ligands and the central ion or atom in the complexes. Cu(II), Co(II) and other transition metals mainly occur in solution as coordination compounds.[3] This class of complexes is useful in a wide variety of ways such as in bio-inorganic chemistry, analysis, homogeneous catalysis and many other applications. Copper and cobalt are metals with very high thermal and electrical conductivity, form complex ions, alloys, and has natural properties that destroy a wide range of microorganisms and they are used many applications.[4-6] Chemistry of heterocyclic complexes is a developing field of biology and chemistry because of many applications of the organic complexes of heterocyclic rings in medicine, pharmacy, agriculture and other fields. Anthranilic acid (4-aminobenzoic acid) is a compound, in which carboxyl group and amino are bounded to aromatic ring and its derivatives are known to have biological activity, additionally it has many applications such as used in dyes, corrosion inhibitors and for the synthesis of compounds, fluorescent and radio protective properties.[7-9] Moreover, in recent years, 4-aminobenzoic acid have attracted interest as ligand in transition metal compounds, which is apparent by many publications.[10,11] 2-Mercaptobenzothiazoles have been used as bactericide, fungicide and herbicide in agriculture, as antimicrobial agents[12,13] and also having interesting biological activities, it finds an important role in industrial and pharmaceutical applications.[14-16]

Stability of complexes in aqueous solution are indicated by its Gibbs free energy, standard electrode potential, rate constant or activation energy for substitution reactions and bond dissociation energy. The thermodynamic stability of compounds indicates its propensity to exist under equilibrium conditions. Although there are large number of studies of thermal analysis on Schiff base metal compounds, few papers have been published on calculation of the thermodynamic and kinetic parameters of their decomposition.[17,18]

EXPERIMENTAL

Material and methods

High purity 4-aminobenzoic acid, 2-mercaptobenzthiazole and hydrazine hydrate were supplied by Merck and Sigma Aldrich. CuCl₂.2H₂O and CoCl₂.6H₂O were of AR grade.

Synthesis of 4-aminobenzohydrazide(ABZH) ligand (1)

4-Aminobenzoic acid (1.4 g, 1mmol) was dissolved in distilled water (30 mL) in a 250 mL conical flask, then 0.5 ml of hydrazine hydrate was added to conical flask with stirring and the mixture was refluxed for 14 h. After cooling of the mixture, the white product was filtrated, washed with ethanol and dried under vacuum at room temperature overnight. M.p.: 218 °C. The FT-IR spectral data displayed absorption at (1628 cm⁻¹, for $\nu_{C=O}$), (3034 cm⁻¹, for ν_{C-H}, aromatic), (1560 cm⁻¹, for $\nu_{C=C,Ar}$) and (3428-3236 cm⁻¹ for ν_{NHNH2}).

Synthesis of copper(II) and cobalt(II) complexes

Synthesis of the mixed ligand complexes of Cu(II) and Co(II) with 4-aminobenzohydrazide (**L₁**) and 2-mercaptobenzthiazole (**L₂**) follows the same procedure.

Table 1. Pysical properties of the complexes.

Compound	Mol. formula (M.Wt)	Color	Found (Calcd. %)				Mp. °C
			C	H	N	S	
[Cu(ABZH)(MBTH)Cl₂(H₂O)₂]	$C_{14}H_{18}N_4S_2CuCl_2O_3$ 488.92	Light brown	35.75 34.39	3.92 3.71	11.83 11.46	14.02 13.11	252
[Co(ABZH)(MBTH)Cl₂(H₂O)₂]	$C_{14}H_{18}N_4S_2CoCl_2O_3$ 484.30	Dark green	35.04 34.71	3.98 3.75	11.95 11.57	13.78 13.23	226

Synthesis of [Cu(ABZH)(MBTH)Cl₂(H₂O)₂] is typical. An ethanolic solution (20 mL) of **L₁** (1mmol) was added to a hot ethanolic solution (15 mL) of CuCl₂.2H₂O (1.74 g, 1mmol) and to it an ethanolic solution (20 mL) of **L₂** (1.70 g, 1mmol) was added dropwise. The resultant product was stirred for 30 min and filtered. Light-brown precipitate was collected, washed with ethanol, and then dried over P₂O₅.

Physical measurements for complexes

Analysis of carbon, hydrogen, nitrogen and sulphur were carried out by using Analyischer Funktions test. Details of physical measurements have been reported earlier.[19]

RESULTS AND DISCUSSION

The 4-aminobenzohydrazide ligand was synthesized by the substitution reaction of 4-aminobenzoic acid and hydrazine hydrate, in presence of the ethanol as a solvent. The prepared two complexes were found to react in molar ratio; 1:1:1, metal:ABZH:MBTH. The copper(II) and cobalt(II) complexes are air stable. The syntheses of the two compounds are supported by the elemental analysis and melting points (Table 1).

FT-IR results

The Fourier-transform infrared spectroscopy recorded absorption at (1628 cm⁻¹, for $v_{C=O}$), (3034 cm⁻¹, for $v_{C-H,Ar}$), (1560 cm⁻¹, for $v_{C=C,Ar}$.) and (3428-3236 cm⁻¹ for v_{NHNH2}) (Figure 1). The FT-IR spectrum for 4-aminobenzohydrazide displays the stretching vibration at 3210-3400 cm⁻¹ for asymmetric and symmetric (NHNH₂) and evanescence band at 1685 cm⁻¹, which belong to stretching vibration, of CO group of ester.[20] The MBTH ligand consists of three centers capable of chelation either to the two sulfur atoms or to one of the sulfurs and the nitrogen atom and appears to be in the range 3148-3170 cm⁻¹. Absorption shown at 764, 766 cm⁻¹ and 1634, 1638 cm⁻¹ for v_{C-S} and $v_{C=N}$ by cobalt (II) and copper(II) compounds, respectively, indicated that the metal ions are coordinated to one amino and the sulfur centre.[21] Furthermore, the bands found in the region of 3196-3204 cm⁻¹ are due to the v_{OH} stretching vibrations of the coordinated H₂O for both the complexes. M-O and M-N bonding are demonstrated by the presence of a band at 539-548 cm⁻¹ and 436-442 cm⁻¹ regions, respectively.

UV spectra and magnetic measurements

The UV spectra of the cobalt(II) and copper(II) complexes were determined in DMSO solution. The band observed in the case of two ternary compounds of 4-aminobenzohydrazide and 2-mercaptobenzthiazole the region of 238-242 nm may be assigned to a (π→π*) transition due to molecular orbital energy levels originating, in the ABZH ligand. For the cobalt(II) and copper(II) compounds another band is recorded in the region of 325-329 nm and has been ascribed to an intra-ligand transition for the MBTH.
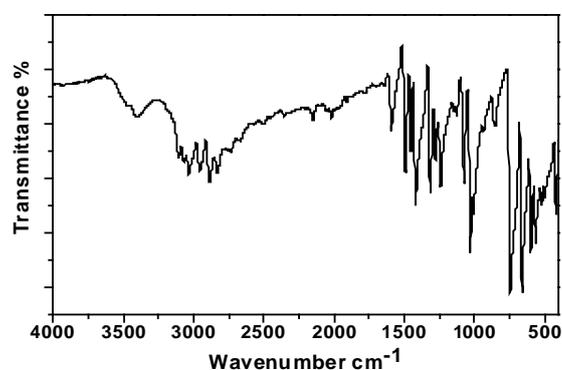
Figure 1. FT-IR spectrum of the Cu(II) complex.

In Co(II) compound a *d-d* band was observed in the 505 nm. The magnetic moment value for this complex was found to be 4.23 BM, which is in agreement with the octahedral environment around Co(II) ion.[22] The magnetic moment value of 1.87 B.M for the Cu(II) compound indicates a octacoordination around copper(II) and a *d-d* transition band showed at 475 nm.[23] The suggested structures for ABZH mixed ligand compounds are shown in Figure 2 and 3.
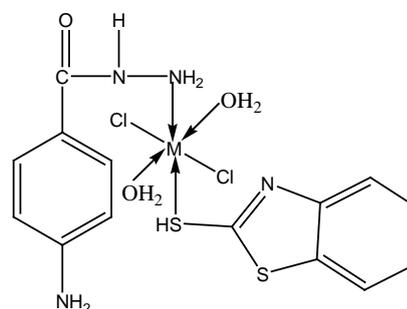
Figure 2. Structure of the two complexes; M= Cu(II) or Co(II).

The thermal decomposition details of the copper(II) and cobalt(II) complexes are presented in Table 2. The two compounds are thermally stable and their, thermal decompositions are multi-stage processes. The compounds were subjected to a TG analysis from (50-700 °C) in dynamic air.

Figure 3. A proposed view of coordination round Cu(II).

The thermogravimetry (TG, DTG and DTA) curves of the Cu(II) complex are given in Figure 4. They showed that the thermal decomposition of the compound involves four stages. The first stage is a dehydration process happening in the temperature range of 48 to 145 ºC. The mass loss (calcd. 7.36 %, found 7.19 %) indicates a loss of $2H_2O$. For this step (DTG minimum at 89 ºC) an endothermic peak is showed in the DTA curve at 92 ºC.
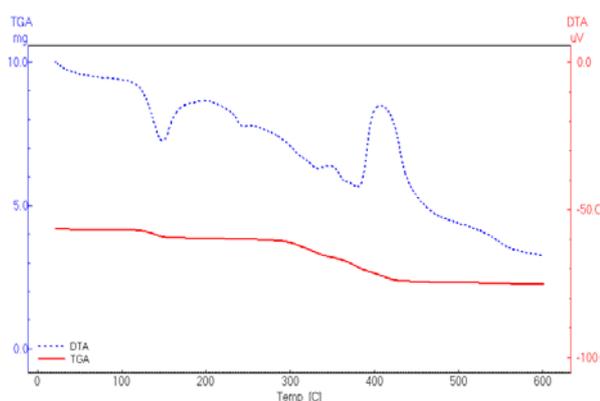

Figure 4. TG, DTG and DTA of the Copper(II) complex.

The second, third and fourth steps (147-700 ºC) represents a mass loss of 77.62 % and appears in the DTG curve as three peaks at 182, 347 and 438 ºC with the corresponding three exothermic peaks in DTA curve at 184, 349 and 440 ºC. At about 700 ºC, the final stable residue is copper oxide. CuO. The theoretical mass loss should be 16.26 %, the found one was 15.94 %.

A four-steps decomposition was observed in the thermo-gravimetric curve of the Co(II) complex. This occurs in the temperature ranges 45-123, 125-250, 252-410 and 412-700 ºC. The first step in the TG curve shows a loss amounting of 7.44 % corresponds to the release of the $2H_2O$ molecules. For this step a differential thermogravimetry (DTG) peak at 85 ºC and an exothermic peak at the position at 87 ºC in DTA trace were recorded. The 2ⁿᵈ, 3ʳᵈ and 4ᵗʰ steps agree to the decomposition of the rest of ligands. It is manifested on the DTG curve as three peaks at 174, 390 and 496 ºC and the DTA trace furnishes an exothermic DTA effect at 176, 392 and 498 ºC. The final stable residue is CoO (calcd.15.47 %, found 14.89 %).

Kinetic analysis for the compounds

Non-isothermal kinetic studies, of the two compounds were accomplished applying two different procedures, the Coats-Redfern[24] and the Horowitz-Metzger[25] methods (Figures 5-10). The kinetic parameters were calculated given by the two equations and are listed in Table 3.

Table 2. Thermal decomposition data for two complexes.

Complex	Step	TG/DTG			Mass loss, %
		T_i	T_m	T_f	
1	1ˢᵗ	48	89	145	7.36
	2ⁿᵈ	147	182	243	14.50
	3ʳᵈ	245	347	380	30.12
	4ᵗʰ	382	438	700	31.92
2	1ˢᵗ	45	85	123	7.44
	2ⁿᵈ	125	174	250	13.63
	3ʳᵈ	252	390	410	31.20
	4ᵗʰ	412	496	700	32.54

Table 3. Kinetic parameters for the two compounds.

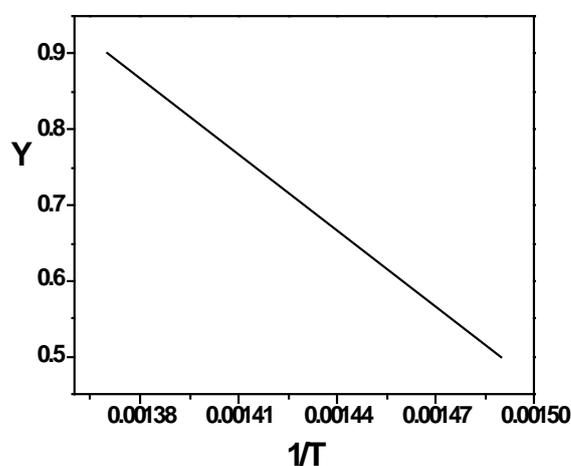| Metal	Step	Coats-Redfern equation			
		r	*n*	*E*	*Z*
Cu(II)	1ˢᵗ	0.9984	0.00	52.15	10.70×10^2
		0.9979	0.33	57.00	11.45×10^2
		0.9977	0.50	60.01	12.06×10^2
		0.9976	0.66	62.26	12.52×10^2
		0.9971	1.00	67.86	13.65×10^2
		0.9955	2.00	86.53	17.51×10^2
Co(II)	1ˢᵗ	0.9995	0.00	34.23	6.91×10^2
		1.0000	0.33	50.40	10.29×10^2
		0.9998	0.50	60.86	12.23×10^2
		0.9997	0.66	71.32	14.35×10^2
		0.9987	1.00	97.94	19.72×10^2
		0.9957	2.00	116.49	23.42×10^2

Figure 5. Coats-Redfern plots for [Co(ABZH)(MBTH)Cl₂(H₂O)₂].
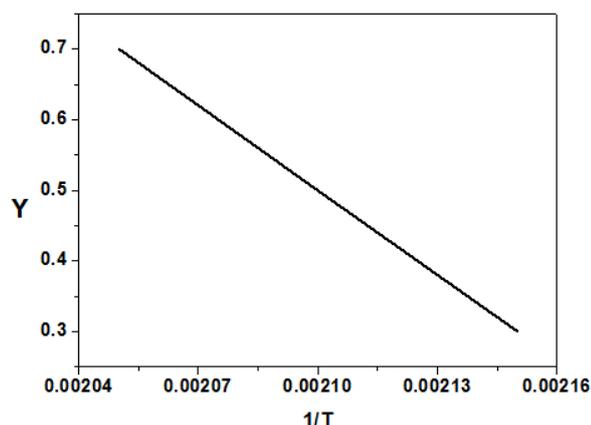
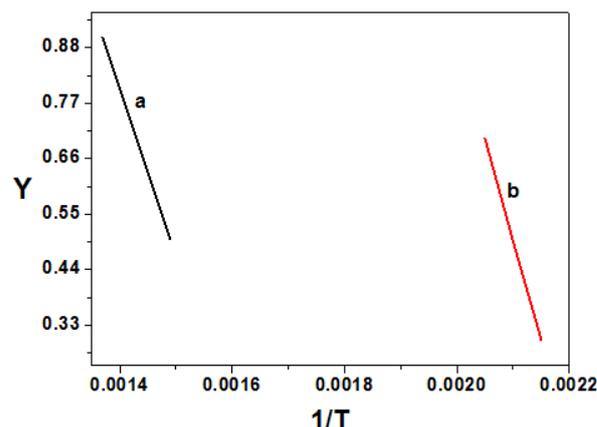**Figure 6.** Horowitz-Metzger plots for [Co(ABZH)(MBTH)Cl₂(H₂O)₂].

Figure 7. Coats-Redfern plots for [Cu(ABZH)(MBTH)Cl₂(H₂O)₂].

Figure 8. Horowitz-Metzger plots for the compound [Cu(ABZH)(MBTH)Cl₂(H₂O)₂].

Thermodynamic parameters for the compounds

The activation variables ΔH^*, ΔS^* and ΔG^*, for the decomposition steps of the two compounds are listed in Table 4. Negative ΔS^* numbers of the both steps of decomposition of the compounds suggest that the activated compound is more highly ordered by than the reactants and the reaction rates are low than normal.[26] The more ordered nature is due to the polarization of bonds in the activated complex, which happens to be charge transfer electronic transition (CTET).[27] The difference in of ΔG^* and ΔH^*
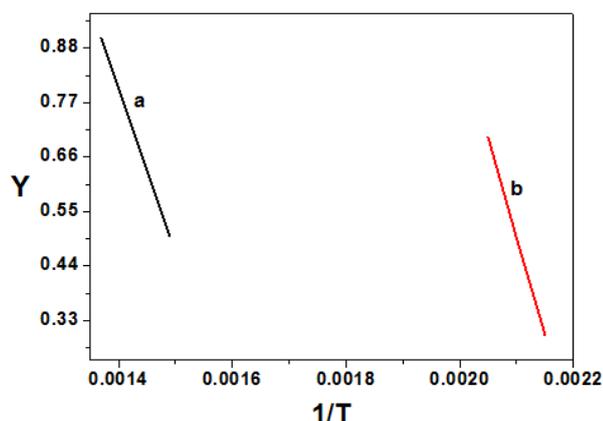

Figure 9. Coats-Redfern plots for (a) the Co(II) complex and (b) the Cu(II) complex.

Figure 10. Horowitz-Metzger plots for (1) the Co(II) complex and (2) the Cu(II) complex.

of the two complexes indicate to the effect of the suggested structure of the Cu(II) or Co(II) complexes on their thermal stability.[28] The positive numbers of ΔG^* indicate the decomposition reaction is not spontaneous. The stability of metal complexes is decided by two different considerations such as thermodynamic and kinetic stabilities.

Table 4. Thermodynamic parameters for the compounds.

Metal	Step	ΔS^*	ΔH^*	ΔG^*
Cu(II)	1st	-190.69	48.24	137.86
		-190.12	53.09	142.44
		-189.69	56.10	145.25
		-189.38	58.35	147.35
		-188.66	63.95	152.62
		-186.59	82.62	170.31
Co(II)	1st	-197.31	28.63	161.41
		-194.00	55.80	175.36
		-192.56	55.26	184.85
		-191.23	65.72	194.42
		-188.59	92.34	219.26
		-187.16	110.89	236.84

ΔH^*, ΔG^* are in kJ mol^{-1} and ΔS^* in kJ mol^{-1} K^{-1}

Decomposition rate and stabilities of the two complexes

The decomposition rates of the two compounds in dynamic air have been deduced from plotting α (fraction decomposition) against temperature of decomposition for

the first step as depicted in Figure 11. Taking the temperature of maximum decomposition rate (DTG maximum temperature) as a criterion, the stabilities of the complexes could be correlated. Accordingly, in the following are the decomposition rate and the stability orders of the two compounds (the decomposition rate is based on the temperature of the inflection point and the stability order on the initial temperature of the first step of the anhydrous compounds).

Co(II) complex (685°C) > Cu(II) complex(475°C) (Decomposition rate).

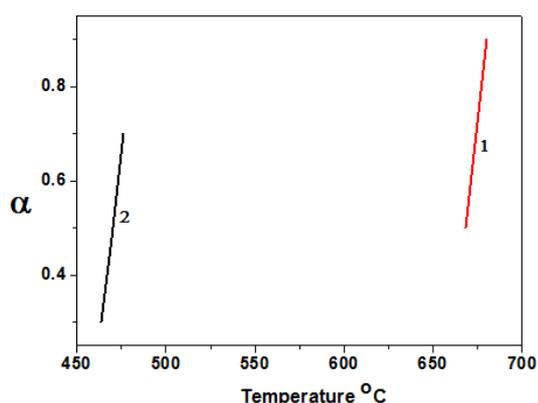Cu(II) complex (450°C) > Co(II) (650°C) (sequence of stability).

Figure 11. Fraction decomposed (α) and temperature plots of the (1) Cobalt(II) and(2) Copper(II)complexes.

The steepness of the curves (α against temperature) indicates that the copper(II) and cobalt(II) compounds decompose by different decomposition rates depending on the respective metal ion. The observed differences in the thermal stability of the two compounds for the same ligand may be ascribed also to the nature of the central metal ion. The effective electric field strength F^* of the metal ion may affect the stabilities of the compounds. F^* can be calculated from the relation

$$F^* = Z_{eff}/r_c^2 \tag{1}$$

where Z_{eff} and r_c are effective charge and ionic radius of the cation present, respectively.[29,30] Increase of F^* of the metal ion leads to an increase in thermal stability of the compounds. For their mixed ligand complexes with 4-aminobenzohydrazide and 2-mercaptobenzthiazole in dynamic air, the F^* values run in the direction Cu(II) complex > Co(II) complex which, is in good correspond with the Irving-Williams series.[29,30]

Kinetic compensation effect

The kinetic compensation effect (KCE), means that the reduction in rate, which is predictable from an increase in activation energy does not show for the given set of reactions. KCE, which was noted in many non iso-thermal methods is seen to be valid here. It was recorded that for the particular process, the value of energy (E) conforms to a

linear relationship to ln Z (Eqn. 2), where E = energy, a and b are constants.

$$\ln Z = a\text{E} + b \tag{2}$$

The application of this equation to the Co(II) and Cu(II) mixed ligand compounds are shown Figures 12 and 13.
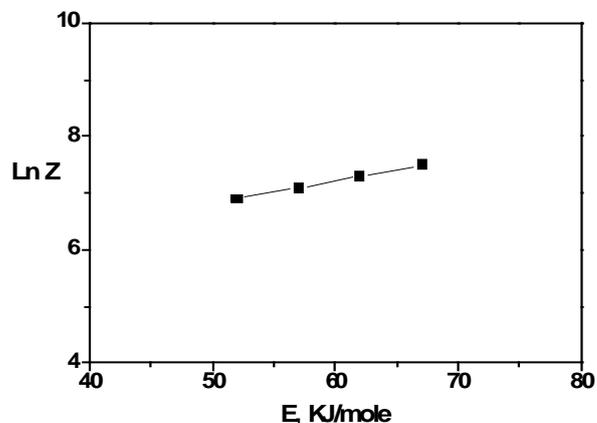

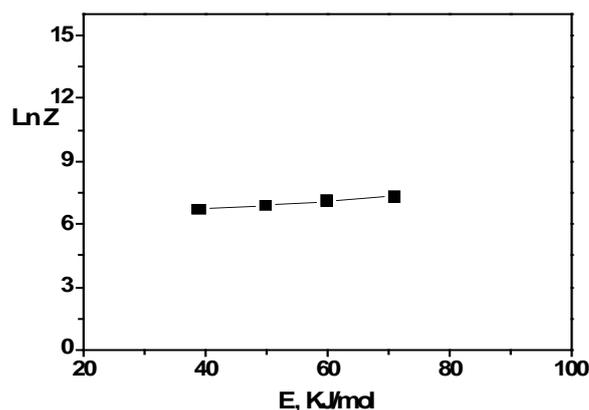**Figure 12.** Kinetic compensation effect in Cu(II) complex.

Figure 13. Kinetic compensation effect in Co(II) complex.

XRD for the copper(II) and cobalt(II) complexes

The XRD patterns were recorded for two the complexes. The crystal details for all compounds correspond to the crystal system triclinic for copper(II) complex and monoclinic system for cobalt(II) complex. XRD of compounds are shown in Figure 14 and 15.

Table 5. XRD data of the two complexes.

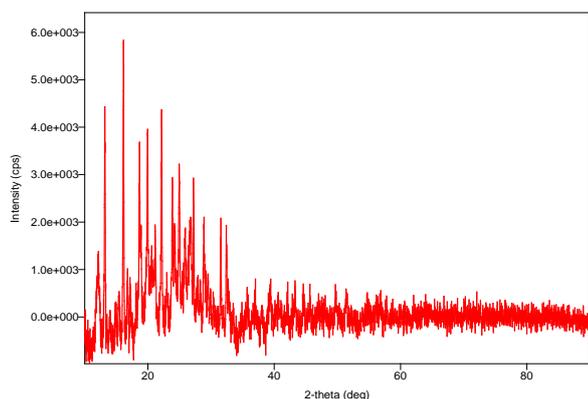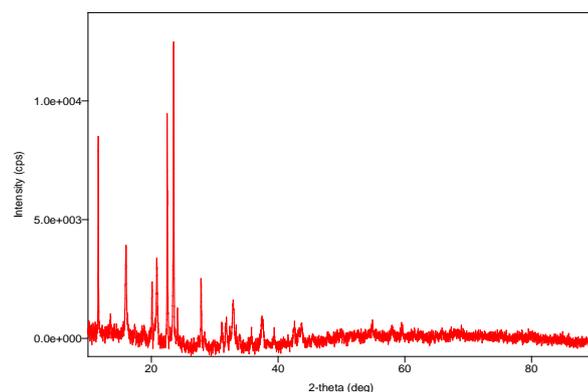| Parameters	Co complex	Cu complex
C.S	monoclinic	triclinic
a (Å)	7.433	6.126
b (Å)	8.528	10.745
c (Å)	3.675	5.981
α (°)	90.00	82.31
β (°)	99.28	107.34
γ (°)	90.00	102.58
V, (Å³)	229.9	365.4

Figure 14. XRD of Cu(II) complex.

Figure 15. XRD of Co(II) complex,

Scherrer's equation (eqn. 2) was used to appreciate the particle size, of the two compounds.

$$D = \underline{K}\lambda/\beta\cos\theta \qquad (3)$$

The elementary cell parameters for the Cu and Co-compounds are listed in Table 5.

CONCLUSION

In this article we report on the kinetics, of the thermal decompositionand the accompanying compensation effect; for a Cu(II) and Co(II), ABZH and MBTH mixed ligand complexes. Also, it is supposed that dehydration of the compounds including water happen within an active reaction interface. The (KCE) is excellent for the thermal decomposition of the two compounds indicating the effect of the change of compound mass on the evaluated values of activation energy and preexponential factor. The copper(II) and cobalt(II) complexes are found to possess a triclinic and monoclinic crystal system, respectively.

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