International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN: 0974-4290
Vol.8, No.3, pp 1310-1318, 2015

Thermodynamic and Decomposition Kinetic Studies of Cobalt Schiff base Complexes of 2,4 –pentanedione with diamines and semicarbazide

P. Sravanthi, C. Chandrakala, K. S. Nagaraja, B. Jeyaraj*

Department of Chemistry, Loyola Institute of Frontier Energy (LIFE),
Loyola College, Chennai – 600 034, India

Abstract: Three Cobalt (II) Schiff base complexes, 4,4’-(propane-1,3-diyl)-bis(azan-1-yl-1-yldene)dipent-2-en-2-onato)cobalt(II) [CADP], 4,4’-(butane-1,4-diyl)-bis(azan-1-yl-1-yldene) dipent-2-en-2-onato)cobalt(II) [CADB], (3,5-dimethyl-1H-pyrazole-1-carboxamide) cobalt (II) [CAS] were synthesized using 2, 4– pentanedioneligandwith1,3 – diaminopropane, 1,4 –diaminobutane and semicarbazide. They were characterized by IR, Mass, Ultra-violet spectroscopy, CHN and Magnetic studies. The thermogravimetry (TG) and Differential thermoanalysis (DTA) of the Co(II) complexes were carried out in the range of 30 – 600 °C. Thermodynamic parameters like activation energy (E_a), entropy (ΔS^*), enthalpy (ΔH^*) and Gibbs free energy (ΔG^*) for each decomposition step of the complexes in the solid state were evaluated by following standard methods i,e; Coats – Redfern (CR) and Horowitz – Metzger (HM) and useful conclusions were drawn. CADP and CADB decomposed in two steps whereas CAS decomposed in three steps. The thermal decomposition of the complexes followed first order kinetics.

Keywords: Schiff base Cobalt complex, Spectral Analysis, Thermogravimetric analysis, Kinetics of decomposition.

Introduction:

The presence of backbone in the Schiff base ligands i.e., nitrogen, sulphur and oxygen donor atoms, acting as a good chelating agent readily co-ordinates with wide range of transition and non-transition metal ions yielding stable and intensively coloured complexes [1]. Some of them exhibit interesting physical and chemical properties. The chemistry of semicarbazide and diamine ligands of transition and non-transition metalions has been an extremely active area of research primarily because of the beneficial structural, electrochemical and good biological activities. Recent years witnessed a growing interest in the chemistry of semicarbazides owing to their ligational properties achieved through available coordination sites. They form an important class of biological active ligands and provide models for metal-ligand bonding sites in several enzymes[2].In this paper we report the synthesis, characterization, thermodynamic and kinetic studies of univalent bidentate Schiff base ligands derived from 2,4 – pentanedione and 1,3-diaminopropane or 1,4-diaminobutane or semicarbazide. The ligands have both oxygen and nitrogen donor sites. A proton is liberated from the ligand coordinating with the metal ion in tetrahedral manner [3,4] and the thermal decomposition behavior of the complexes was investigated with the aim to examine the kinetics of non-isothermal decomposition using model –free isoconversional methods [5].

Experimental Section:

Reagents:

All commercially obtained reagent grade chemicals were used without further purification except for the ligands, which were recrystallized.

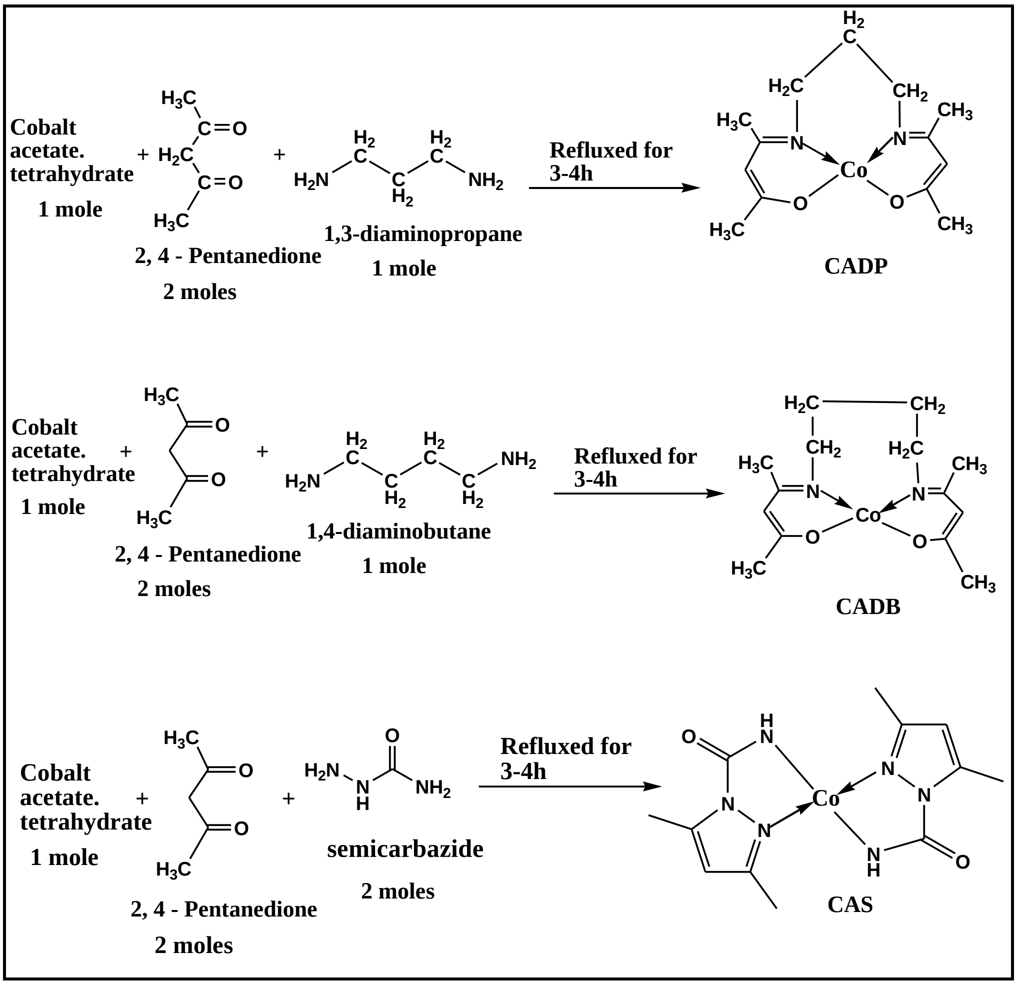
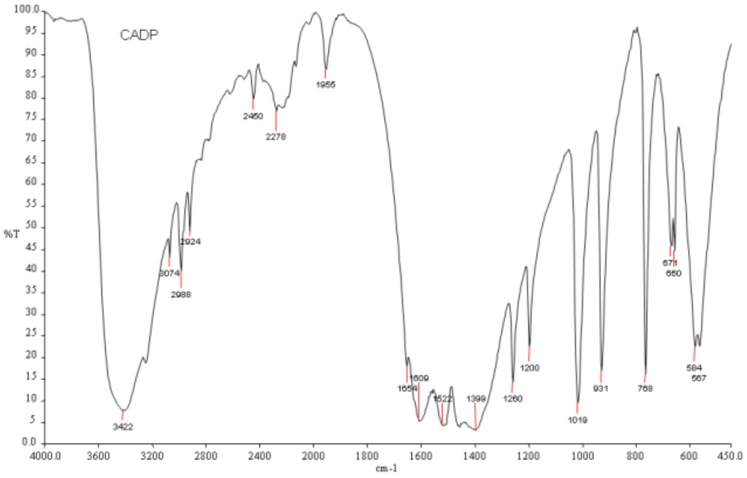


Figure 1: Reaction scheme of CADP, CADB and CAS complexes

Synthesis of the complexes:



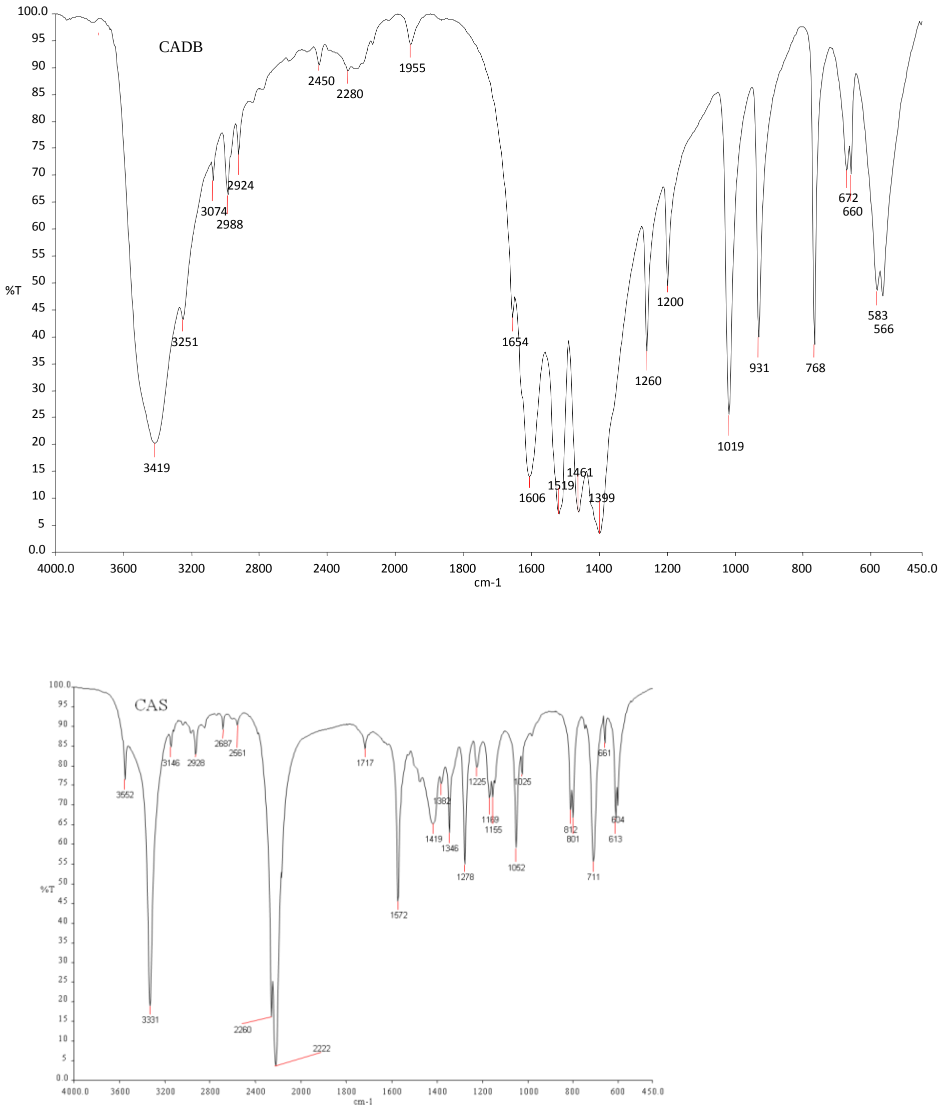


Figure 2: FT-IR Spectra of CADP, CADB and CAS

The synthesis was carried out in a one-pot synthesis [6]. Aqueous solution of cobalt(II) acetate tetrahydrate (1.24g, 0.00497mol), ethanolic solution of 2, 4 - pentanedione (2ml, 0.02mol) and1, 3-diamino propane (0.7 ml, moles?) or 1,4-diaminobutane (0.8 ml, moles?) or semicarbazide hydrochloride (2.2g, 0.0197mol) were added in a RBF and refluxed for 2-3 hr. Volume of the resulting solution was reduced to half and the solution was left overnight. The resulting pinkish flakes for CADP and CADB and the blue colour crystalline compound for CAS were filtered under suction, washed with ethanol and dried under fused anhydrous calcium chloride. The products were recrystallized in dichloromethane and ethanol in 1:3 ratios. The melting points and CHN analysis of these complexes are represented in Table. 1. The higher M.P. of CAS is due to the intermediate bonding between C=N and N-H groups.

Table: 1 Data Analysis of the complexes

Complex	Molecular Formula	Melting Point (°C)	Colour	Analysis		
				C%	H%	N%
CADP	$C_{13}H_{22}N_2O_2Co$	177	Pink	52.53(53.53)	7.46(7.40)	9.42(9.42)
CADB	$C_{14}H_{24}N_2O_2Co$	176	Pink	54.02(54.01)	7.77(7.71)	9.00(9.00)
CAS	$C_{12}H_{16}N_6O_2Co$	193	Blue	42.99(42.98)	4.81(4.77)	25.07(25.07)

Results and Discussion:

Infrared Spectroscopy:

Co-ordination of the Schiff bases through the azomethine nitrogen atom is expected to reduce the electrondensity in the azomethine bond thus lowering the υ(C=N) frequency. Hence the υ(C=N) is found at1572

-1606 cm^{-1} after complexation. This bond also shows azine formation (C=N-N=C) supporting the formation of enolic structure in CAS[7]. The broad band due to υ(OH) is absent in the spectra indicating the deprotonation of the Schiff base prior to co-ordination. υ(C-O) at1278 - 1399 cm^{-1} in the complexes suggests that the other co-ordinating atom is carbonyl group oxygen. Binding of the metal to the ligand through nitrogen and oxygen is further supported by new bands 566 – 583 cm^{-1} and 604 – 672 cm^{-1}which are assigned to υ(M-N) and υ (M-O) respectively in all the complexes. The position of υ (N-H) in the complexes is at 3332 – 3422cm^{-1}[8].

Ultraviolet – Visible Spectroscopy:

The electronic spectrum of the complexes (fig. 3) in ethanol showed lower energy bands at 554 – 557 nm in all the three complexes. In CAS complex the band at 590 nm may be due to $^1A_{1g} \rightarrow {}^1T_{1g}$ transition, characteristic of the distorted tetrahedral cobalt Co(II) center. The other band at 622 nm is assigned to $^1A_{1g} \rightarrow {}^1T_{2g}$ transition [9 -11]. In CADP and CADB the co-ordination sphere is same (CoN_2O_2) whereas in CAS it is different Co(N_4).

Magnetic Measurements:

Magnetic hysteresis measurements performed on CAS complex is presented in the fig 4. The room temperature M – H curve is linear with the field and has no coercivity and remenance [12].The effective magnetic moment (μ_{eff}) of the Cobalt (II) complex is found to be 3.87 BM suggesting tetrahedral arrangement of ligand molecules around the metal atom. Thus both the UV-Visible and magnetic studies indicate the tetrahedral co-ordiantion and Co^{2+} ion.

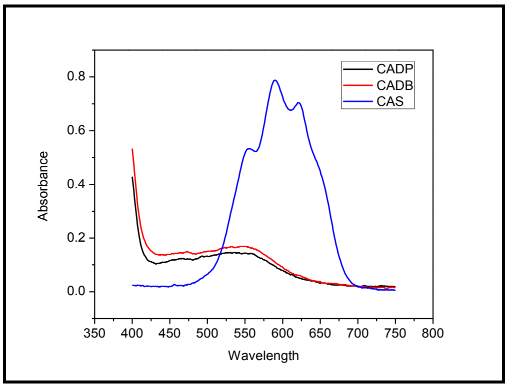


Figure 3: UV-Visible Spectroscopy of complexes

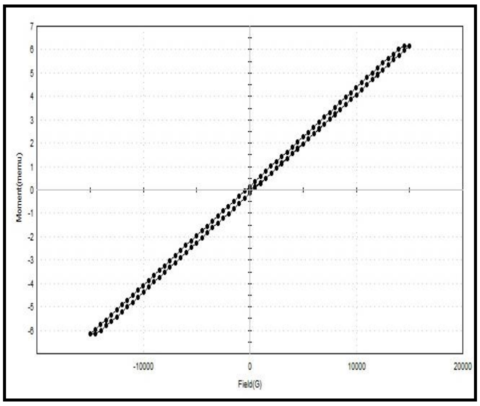
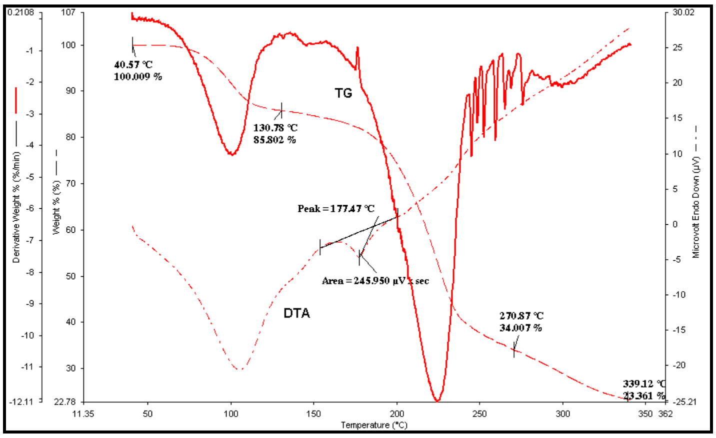


Figure 4: Magnetic Studies of CAS complex at Room Temperature.

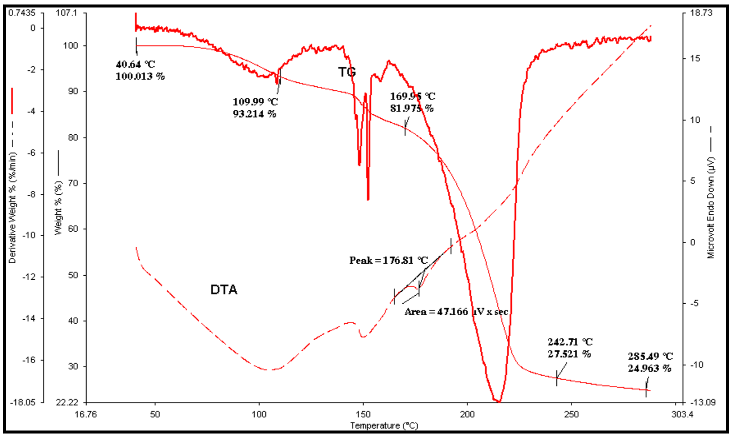
Mass Spectroscopy:

The electronic mass spectra of the three complexes CADP, CADB and CAS show the molecular ion peaks at m/z = 297, 311, 335amu corresponding to the species, which confirms the proposed formula. It also showed peaks at 241, 252, 276 corresponding to the loss of two ligand moieties. The intensities of these peaks gave idea of the stabilities of the fragments.

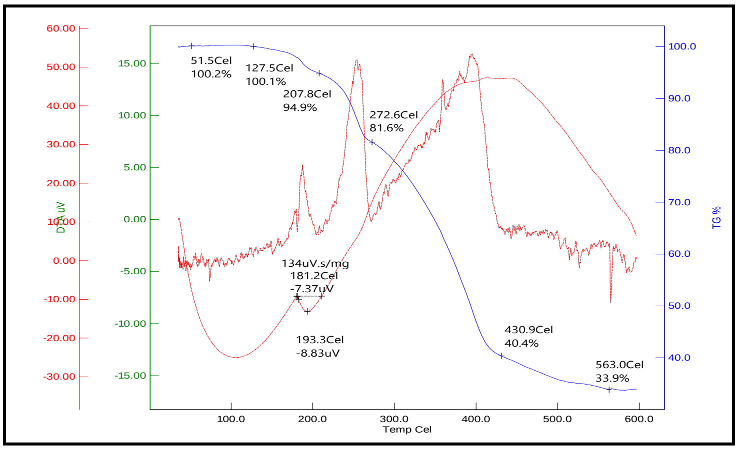
Thermogravimetric Studies:



CADP



CADB



CAS

Figure 5: Thermogravimetric Analysis of complexes in N_2 atmosphere at 10 °C

From the TG curve of the three complexes (fig 5), it is seen that while CADB and CADP show two steps mass loss, CAS show three steps. The first step weight loss of the complexes is observed at 130 ºC in

CADP and at 169 ºC in CADB. The DTA peak of CADP and CADB complexes shows endothermic peak at the range of 130 – 270 ºC corresponding to the weight elimination of the organic moiety. The second step of the thermal decomposition for which kinetic parameters were under taken occurs in the range of 270-339 ºC which is endothermic with the loss of oxygen atom and formed cobalt oxide 550 ºC. In CAS complex, TG shows no weight loss up to 150 ºC indicating no water molecule is coordinated to the complex. The second step from 207 – 272 ºC, an exothermic peak may be attributed to the loss of azo-semicarbazide groups. The final step occurs in the range of 272 – 563 ºC. In this step all organic residues are removed leaving cobalt nitride as the final product [13-15].

According to decomposition temperatures in the II stage follows CAS > CADP > CADB. CADB has seven membered ring and unstable. CADP has six membered ring which is more stable. CAS has five membered ring and the extra stability is due to the intermolecular hydrogen bonding between C=O and the N-H groups of the neighboring molecules. The CADP and CADB have Vander walls forces and no hydrogen bonding is present.

Kinetic Studies:

The present investigation show the general behavior of the complexes in terms of stability ranges, peak temperatures and kinetic parameters values which are presented in the tables - 2,3. The suitable stages were selected to study the decomposition kinetics of the complexes. Various methods exist for studying the thermal decomposition of complexes. In this work, Coats – Redfern (CR) and Horowitz – Metzger (HM) (Ref) methods are utilized.

Table 2: Thermogravimetric parameters of CADP, CADB, and CAS

compound	Decomposition Stage	DTA Peak Temp °C	TG range °C	DTG peak	Mass loss %
CADP	II	177	130 -270	230	34
	Residue				CoO
CADB	II	176	169 - 242	215	27
	Residue				CoO
CAS	II	193	127 - 271	201,262	81
	III	206	272 - 430	369	40
	Residue				Co_2N

Table 3: Decomposition Kinetic parameters of CADP, CADB and CAS

compound	steps	n	Method	E_a kJ mol^{-1}	A s^{-1}	ΔS* Jk^{-1} mol^{-1}	ΔH* $kJmol^{-1}$	ΔG* kJ mol^{-1}
CADP	2	0.947	A	80.13	1.1	-128	1.83	27.62
			CR	15.24	$8.2*10^{-3}$	-211.39	1.89	46.72
			HM	15.15	339.54	-103.82	1.9	25.81
CADB	2	0.938	A	5.886	5.25	-132.91	1.8	23.96
			CR	38.11	0.297	-162.78	1.87	33.93
			HM	0.030	0.217	-165.38	1.82	34.55
CAS	2	1	A	0.430	1.137	-150.445	2.108	36.047
			CR	77.91	160.872	-138.001	2.113	31.387
			HM	14.34	223.499	-106.541	2.094	24.926
	3	0.983	A	1.26	1.34	-145.373	3.291	54.284
			CR	29.28	$5.9*10^{-3}$	-209.515	3.263	79.717
			HM	5.976	21.738	-122.21	2.1026	28.892

Coats – Redfern method:

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{(1-n)T^2}\right] = \ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT} \quad \text{For } (n\neq 1)$$

$$\ln\left[-\frac{\ln(1-\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT} \quad \text{For } (n=1)$$

Horowitz – Metzger (HM) method:

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{1-n}\right] = \frac{\ln\left(ART_s^2\right)}{\beta E} - \frac{E}{RT_s} + \frac{E\theta}{RT_s^2} \quad \text{For } (n\neq 1)$$

$$\frac{\ln[-\ln(1-\alpha)] = \ln\left(ART_s^2\right)}{\beta E} - \frac{E}{RT_s} + \frac{E\theta}{RT_s^2} \quad \text{For } (n=1)$$

Where, α= Fraction of material decomposed,
n = Order of the decomposition reaction,
R = Gas constant (8.314 J mol^{-1} K^{-1}),
β = Heating Rate,
$\theta = T - T_s$, T_s is the temperature at the DTG peak,
T = temperature corresponding to weight loss.

The plots are drawn against left hand side against 1/T for CR and θ for HM methods giving slope from which activation energy (E) is calculated and the Pre-exponential factor (A) is determined from the intercept. Thermodynamic parameters were calculated;

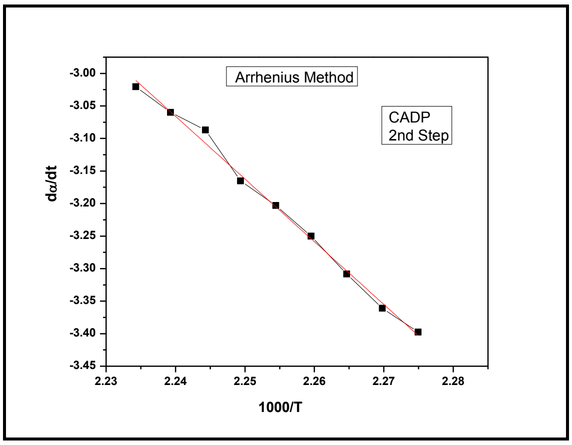
Entropy of Activation: $\Delta S^* = R\ln\left(\frac{Ah}{kT_s}\right)$

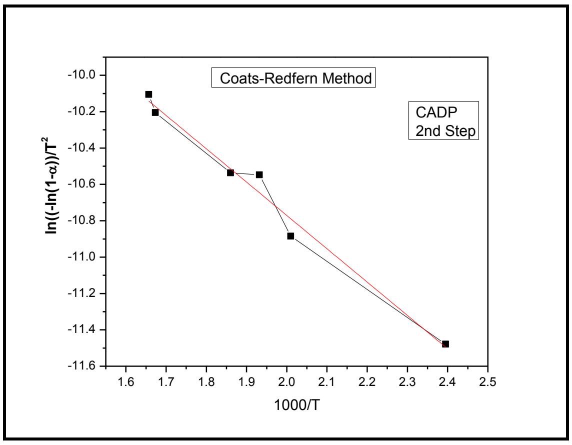
Enthalpy of Activation: $\Delta H^* = E - RT_s$

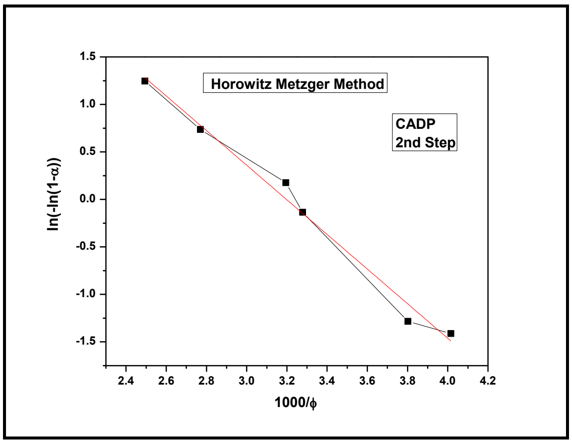
Gibbs free energy of Activation: $\Delta G^* = \Delta H^* - T_s\Delta S^*$

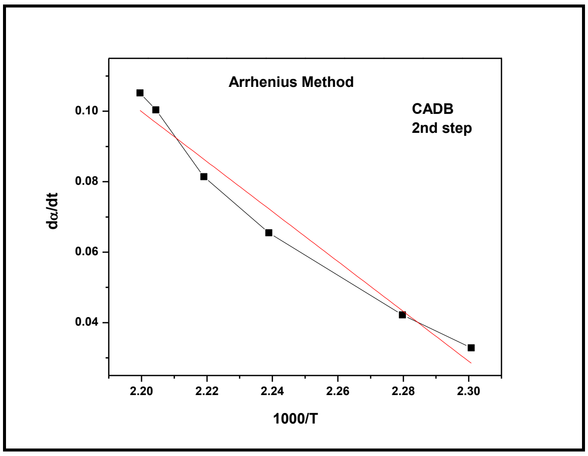
Where h = Planck's constant ($6.626*10^{-34}$ J s)
k = Boltzmann constant ($1.38*10^{-23}$ J K^{-1})

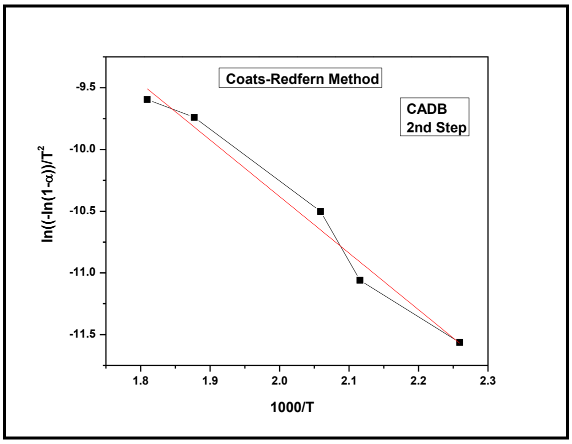
The kinetics and thermodynamic data obtained by the two methods are comparable. The correlation coefficients (r) of the Arrhenius plots of the decomposition steps were found in the range of 0.979 – 0.999, showing a good fit with linear function. The kinetic data obtained from TG curves, showed the activation energies of decomposition to be in the range of 0.03 –80 $kJmol^{-1}$ illustrating the thermal stability of the complexes. The corresponding values of the entropy of activation, ΔS^* were in the range of -103.82 to -211.39 Jk^{-1} mol^{-1}. The ΔS^* value of the complexes were found to be negative. This indicates that the activated complex is more ordered than the reactants and/or the reactions are slow. The enthalpy of activation, ΔH^* and Gibbs free energy ΔG^* values are in the range 1.8-3.29 kJ mol^{-1} and 23.96 – 79.71 kJ mol^{-1} representing endothermic pathway in the thermal decomposition steps [16, 17].

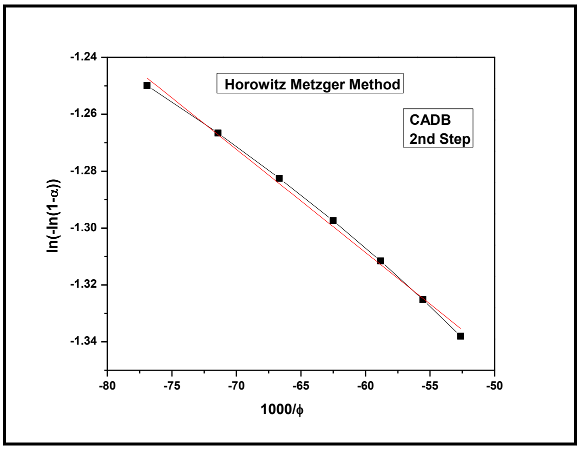












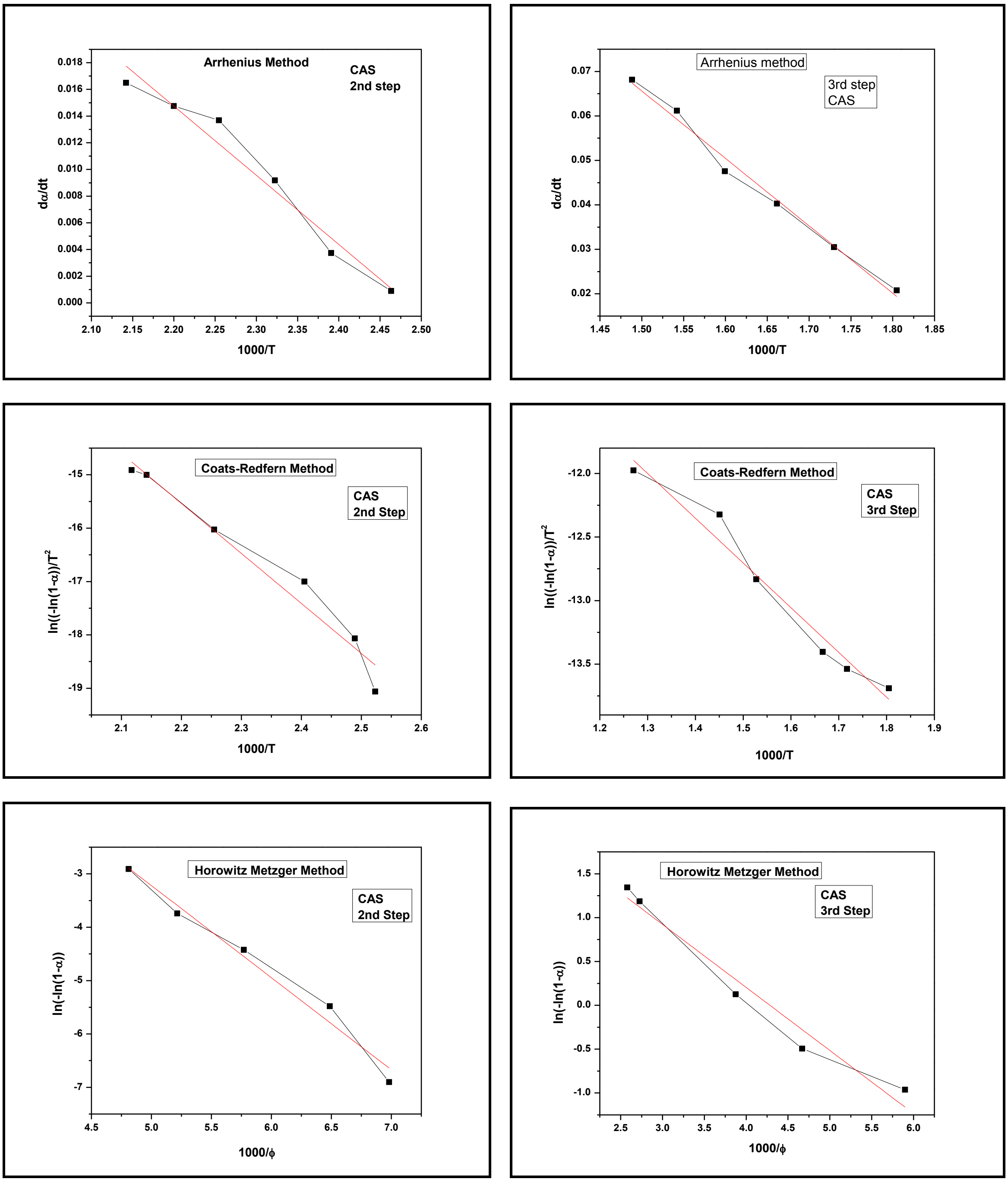


Figure 6: Kinetic data curves of CADP, CADB and CAS

Conclusion:

In this studystable complexes of Co(II) with bidentate ligands, CADP, CADB and CAS- were synthesized and characterized by analytical and spectral techniques. M – H curve of CAS was linear with the field and has no coercivity and remenance. The kinetics was evaluated by TG-Transpiration technique. In CADP and CADB, DTG showed exothermic two peaks whereas CAS showed two endothermic peaks. The decomposition kinetics of all the complexeswas investigated by evaluating the dynamic thermogravimetric data in single heating rate 10 °C/min.Also, the thermal study revealed thermal stability of all the three synthesized metal complexes and indicated that all the decomposition steps were non-spontaneous processeswhich followed standard methods like CR and HM. In CADP the activation energy for both the methodswere comparable, whereas for CADB and CAS, CR method gave higher results when compared to HM method. The activation energies of the second step follow the order CAS>CADB>CADP.

References:

1. Shakir. M, Abbasi. A, Azam. M, A. U. Khan., Synthesis, spectroscopic studies and crystal structure of the Schiff base ligand L derived from condensation of 2-thiophenecarboxaldehyde and 3,3′-diaminobenzidine and its complexes with Co(II), Ni(II), Cu(II), Cd(II) and Hg(II): Comparative DNA binding studies of L and its Co(II), Ni(II) and Cu(II) complexes., Spectrochim. Acta A., 2011, 79, 1866–1875.
2. Chikate R. C., PadhyeS. B., Transition metal quinone–thiosemicarbazone complexes 3: Spectroscopic characterizations of spin-mixed iron (III) of naphthoquinone–thiosemicarbazones, Spectrochim.Acta A., 2007, 66, 1091–1096.
3. Sallam. S. A., Orabi. A. S., El-Shetary. B. A., Lentz. A., Copper, nickel and cobalt complexes of Schiff-bases derived from β-diketones, Transit. Metal Chem., 2002, 27, 447-453.
4. Nagajothi. A., Kiruthika. A., Chitra. S., Parameswar. K., Synthesis and characterization of Tetradentate Co(II) Schiff Base Complexes : Antimicrobial & DNA Cleavage Studies, Int. J. Res. Pharm. Biomed. Sci. 2012, 3, 1768-1778.
5. Mahfouz. R. M., Al-Ahmari. S., Al-Fawaz. A., Al-Othman. Z., Warad. I. K., Siddiqui. M. R. H., Kinetic Analysis for Non-isothermal Decomposition of Unirradiated and γ-Irradiated Indium Acetyl Acetonate, Mater. Res., 2011, 14, 7-10.
6. Kumar. S., Kumar. N., Synthesis and biological activity of acetylacetone thiosemocarbazone and their metallic complexes, Int. Cur. Pharm. J. 2013, 2, 88 – 91.
7. Raman. N., Ravichandran. S., Thangaraja. C, Copper(II), Cobalt(II), nickel(II) and zinc(II) complexes of Schiff base derived from benzyl-2,4-dinitrophenylhydrazone with aniline, J. Chem. Sci., 2004, 116, 215-219.
8. Chandar. S. C. N., Santha kumar. K., Arumugham. M. N., Metallosurfactant Schiff base cobalt(III) coordination complexes. Synthesis, characterization, determination of CMC values and biological activities, Transit. Metal Chem., 2009, 34, 841-848.
9. Khan. S, Bhar. K., Roy. S, Ramachandran. K., Ghosh. B. K., Syntheses, structures and molecular properties of two mononuclear cobalt(III) halide complexes containing a tetradentate N-donor Schiff base, Indian J. Chem., 2011, 50A, 1429 – 1435.
10. Chakrabortya. J, Bhubon Singh. R. K., Samantaa. B., Choudhurya. C. R., Deya. S. K., Talukdera. P., Borahb. M. J., Mitraa. S., Two New Quadridentate Schiff Base Complexes of Nickel(II) and Cobalt(III): Synthesis, Structure and Spectral Characterisation, Z. Naturforsch., 2006, 61b, 1209 – 1216.
11. Mazhar–ul-Haque, SakhawatHussain. M., Cobalt(III) and chromium(III) complexes of thiosemicarbazide: the crystal structure of Λ-*cis*-*tris*(thiosemicarbazide)cobalt(III) chloride trihydrate., Transit. Metal Chem., 1994, 9, 95-98.
12. Ozkaya. T., Baykal. A., Koseoglu. Y., Kavas. H., Synthesis of Co3O4 nanoparticles by Oxidation-Reduction method and its magnetic characterization, Cent. Eur. J.Chem., 2009, 7, 410-414.
13. Li. X., Wu. Y., Gu. D., Gan. F., Thermal decomposition kinetics of nickel(II) and cobalt(II) azo barbituric acid complexes, Thermochim Acta., 2009, 493, 85–89.
14. Curtis. S. D. A., Kurdziel. K., Materazzi. S., Vecchio. S., Crystal structure and thermoanalytical study of cobalt(II) and nickel(II) complexes with 2,2′-bis-(4,5-dimethylimidazole), Thermochim Acta., 2010, 510, 75–81.
15. M. Y. El-Sayed. M. Y., S. M. El-Megharbel. S.M., Spectral and Kinetic Studies of Thermal Decomposition of Ni^{II} hexanoate Complex $Ni_2(cap)_4$., Life Sci. J., 2012, 9, 1143-1151.
16. Kurtoglu. G., Avar. B., Zengin. H., Kose. M., Sayin. K., Kurtoglu. M., A novel azo-azomethine based fluorescent dye and its Co(II) and Cu(II) metal chelates , J. Mol. Liq., 2014, 200B, 105–114.
17. Mohammadi. K., Rastegari. M., New tetradentate Schiff bases of 2,2-dimethyl-1,3-diaminopropane and acetylacetone derivatives and their vanadyl complexes, Spectrochim. Acta A., 2012, 97, 711–716.

*****