International Journal of Engineering Technology Science and Research
IJETSR
www.ijetsr.com
ISSN 2394 – 3386
Volume 5, Issue 1
January 2018

Ni (II), Cu (II) and Zn (II) Complexes of Benzoxazine Schiff Base: Geometry Optimization and Non-isothermal Kinetic Parameters

N. Kavitha[1]
Department of Chemistry, University College for Women,
Osmania University, Koti, Hyderabad, Telangana State, India.
P.V. Anantha Lakshmi[2]*
Department of Chemistry, University College of Technology,
Osmania University, Hyderabad, Telangana State, India

ABSTRACT

Thermogravimetric analysis is a simple, widely used technique which gives information from a thermogram. In the present study thermal stabilities of Ni (II), Cu (II) and Zn (II) complexes of HMOPE-HBO were measured by TGA analysis. The Kinetic parameters such as energy of activation (E_a), enthalpy (aH), entropy(aS) and free energy changes (aG) have been determined by the thermogravimetric data obtained. The kinetic and thermodynamic parameters for the degradation of the complexes were calculated by using Coats-Redfern integration method involving thirteen different kinetic models.

The stability of the ligand and its complexes were also evaluated from the molecular orbital structures from which the quantum chemical parameters were calculated using the energies of HOMO and LUMO.

KEY WORDS

Thermogravimetric analysis, kinetic parameters, energy of activation, HOMO-LUMO energies.

I. INTRODUCTION

TGA is a thermal analysis method which measures the amount and rate of change in weight of a compound as a function of time or temperature in a controlled atmosphere. It is used to determine the composition, thermal stability and kinetics of decomposition. TGA is used to analyze % wt. loss at a given temperature, at a final temperature % of undecomposed compound and temperature of degradation of compound at all steps.

Kinetic analysis of thermal decomposition process is the subject of interest for many researchers. The kinetic parameters are useful in the determination of rate constants, activation energies, pre exponential factors and reaction orders. Kinetics is the key point to frame the mechanism for thermal decompositions, where selection of a correct reaction model is a crucial point in kinetic analysis. There are various methods for the study of kinetics of non-isothermal reactions such as statistical methods, pre exponential factors, Coats-Redfern method and iso-conventional model free methods.

Benzoxazines are importantN-heterocyclic compounds with wide range of biological activity and used for the synthesis of many pharmaceutical compounds such as antifungal [1],antimicrobial[2], anti-thrombotic and cardiovascular agents[3],normolipemic agents [4],inotropic chronotropic and coronary vasodilating agents, antirheumatic agents[5], neuroprotective agents,estrogen receptor β agonists, anti-mycobacterial agents and antidiabetic agents.Benzoxazines and their Schiff bases are found to be biologically active.

3-acetyl-4-hydroxy-6-methyl-2H-pyran-2-one (AHMPO)(dehydroacetic acid) isone of the oxygen heterocyclic compounds which is an excellent chelating agent possessing fungicidal, bactericidal, herbicidal

International Journal of Engineering Technology Science and Research
IJETSR
www.ijetsr.com
ISSN 2394 – 3386
Volume 5, Issue 1
January 2018

and insecticidal activities [6, 7] and is also a versatile starting material for the synthesis of avariety of heterocyclic compounds [8, 9].

In view of the importance of the Hydrazones, synthesis of the Schiff base 3-(2-(1-(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)ethylidene)hydrazinyl)-2H-benzo[b][1,4] oxazin-2-one (HMOPE-HBO)[10,11,12] derived from AHMPO and HBO and synthesis and characterization of its Ni(II), Cu (II) and Zn(II) complexes have been performed and reported from our laboratory[12].

Thermogravimetric analysis of HMOPE-HBO Ni (II), Cu (II) and Zn (II) metal complexes was performed by recording TGA /DTG and DSC curves. The heating rates were controlled at 10 °C min^{-1} under nitrogen atmosphere and the weight loss was measured from ambient temperature to 350 °C. From this, the percentage weight loss in all the complexes was obtained which showed loss of lattice water molecules and was in agreement with the calculated values.

In the present study we are interested in exploring the Kinetic and thermodynamic parameters for the degradation of the complexes by using Coats-Redfern integration method involving thirteen kinetic models and also to study the stability of the ligand and its complexes from quantum chemical parameters which are calculated using the energies of HOMO and LUMO structures.

2. EXPERIMENTAL

2.1 THERMAL DECOMPOSITION KINETICS

The change in the reaction rate (α) is used to study the solid state reaction kinetics:

$\alpha = w_0 - w_t / w_0 - w_f$

Where, w_0, w_t and w_f are initial sample weight, sample weight at time t and final weight of the sample respectively.

The kinetic and thermodynamic parameters of the thermal degradation of the complexes i.e., activation energy (E_a), enthalpy (ΔH), entropy(ΔS) and free energy changes (ΔG) were evaluated graphically from DTG curves by employing the most popular Coats-Redfern relation: [13, 14]

$$\ln [g(\alpha)/T^2] = \ln (AR/\beta E_a) - E_a/RT$$

T= temperature, A= pre-exponential term, R= gas constant, E_a= activationenergy, β = heating rate

Plotting the left hand side of the equation, which includes g(α) verses 1/T gives E_a, A from the slope and intercept respectively. The model that gives the best linear fit is selected as the chosen model and other parameters ΔH, ΔS and ΔG were calculated by using the relations: [15, 16]

$\Delta H = E_a - RT$, $\Delta S = R [\ln (Ah/kT) - 1]$ and $\Delta G = \Delta H - T\Delta S$, where k is Boltzmann's constant and h is the plank's constant.

Various reaction models and rate equations obtained using g (α) are depicted in Table 1.

2.2 MOLECULAR ORBITAL STRUCTURES OF HMOPE-HBO AND ITS COMPLEXES

The molecules were built with the Perkin Elmer Chem Bio Draw and optimized geometry using the Perkin Elmer Chem Bio 3D software. Stability of the ligand and its complexes were studied from quantum chemical parameters which were calculated using the energies of HOMO and LUMO structures.

International Journal of Engineering Technology Science and Research
IJETSR
www.ijetsr.com
ISSN 2394 – 3386
Volume 5, Issue 1
January 2018

Table 1. Rate equations

	Reaction Model	g(α)
Nucleation Models		
1	Power Law	$a^{1/4}$
2	Power Law	$a^{1/3}$
3	Power Law	$a^{1/2}$
4	Avrami-Erofeev	$[-\ln(1-\alpha)]^{1/4}$
5	Avrami-Erofeev	$[-\ln(1-\alpha)]^{1/3}$
6	Avrami-Erofeev	$[-\ln(1-\alpha)]^{1/2}$
Diffusion Models		
7	One dimensional diffusion	α^2
8	Diffusion control (Janders)	$[1-(1-\alpha)^{1/3}]^2$
9	Diffusion control (Crank)	$1-(2/3)\ \alpha-(1-\alpha)^{2/3}$
Reaction order & contraction models		
10	Maple first order	$-\ln(1-\alpha)$
11	Second order	$(1-\alpha)^{-1}-1$
12	Contracting cylinder	$1-(1-\alpha)^{1/2}$
13	Contracting sphere	$1-(1-\alpha)^{1/3}$

3. RESULTS AND DISCUSSION

3.1. EVALUATION OF KINETIC PARAMETERS FROM THERMAL DEGRADATION STUDIES

According to CR equation, if a correct model is selected for the reaction, the plot will be linear with high correlation coefficient.

The Kinetic and Thermodynamic parameters of thermal decomposition of HMOPE-HBO complexes are obtained from the model that gives the best linear fit (correct model) and is represented in Table 2.

Figs.1, 2 and 3 shows the plots of $\ln[g(\alpha)/T^2]$ Verses 1/T for different models of Ni (II), Cu (II) and Zn (II) complexes respectively. It shows that all models show linear trend with correlation coefficient values greater than 0.9.

Table 2. Kinetic and Thermodynamic parameters of thermal decomposition of HMOPE-HBO complexes

Complexes	E_a(J.mol^{-1})	A(S^{-1})	ΔH(J.mol^{-1})	ΔS(J.mol^{-1}.K^{-1})	ΔG(J.mol^{-1})
Ni(II)	5.56×10^{4}	2.07×10^{7}	5.28×10^{4}	-9.9×10^{1}	8.61×10^{4}
Cu(II)	6.59×10^{4}	1.86×10^{10}	6.31×10^{4}	-4.9×10^{1}	7.94×10^{4}
Zn(II)	4.41×10^{4}	2.6×10^{6}	4.14×10^{4}	-1.22×10^{2}	8.18×10^{4}

International Journal of Engineering Technology Science and Research
IJETSR
www.ijetsr.com
ISSN 2394 – 3386
Volume 5, Issue 1
January 2018

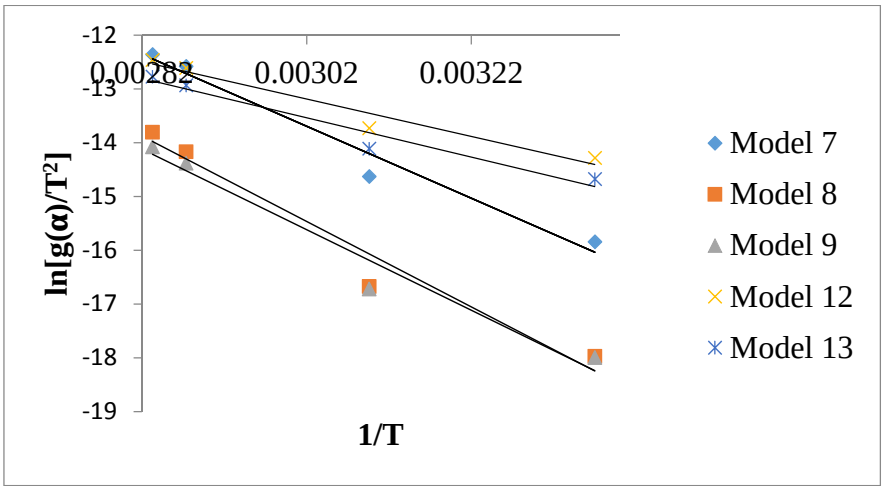

Fig 1: plots of ln[g(α)/T^2] Verses 1/T for different models using α values of Ni (II) complex.

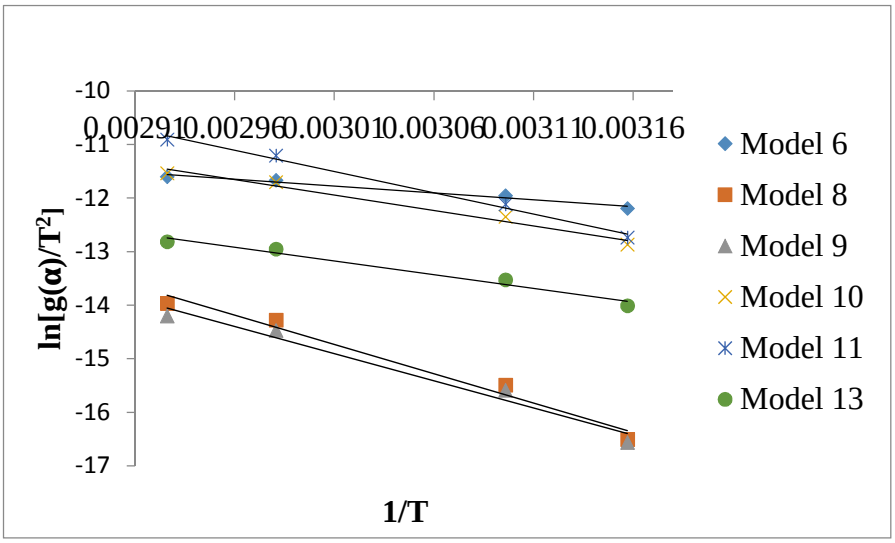

Fig 2: plots of ln[g(α)/T^2] Verses 1/T for different models using α values of Cu (II) complex.

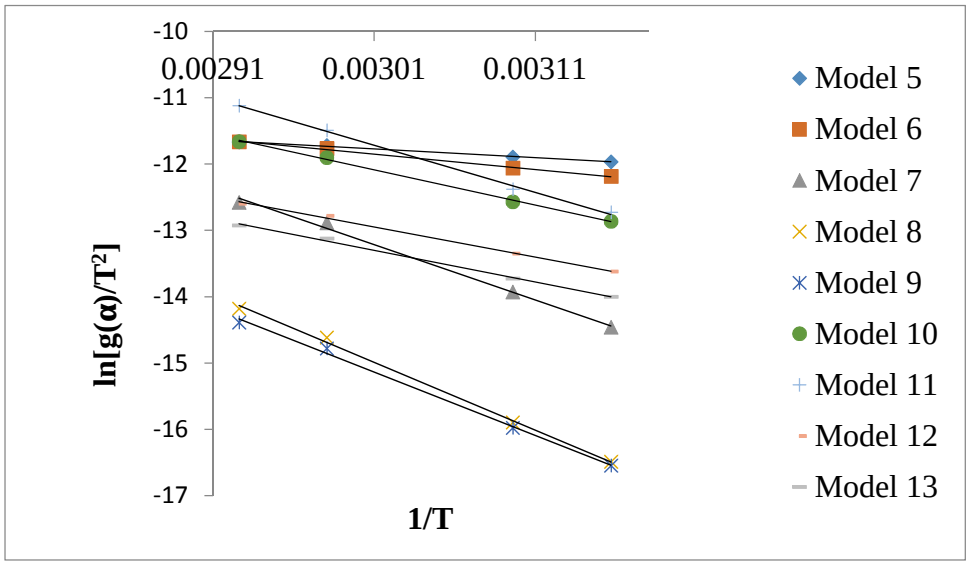

Fig 3: plots of ln[g(α)/T^2 Verses 1/T for different models using α values of Zn (II) complex.

International Journal of Engineering Technology Science and Research
IJETSR
www.ijetsr.com
ISSN 2394 – 3386
Volume 5, Issue 1
January 2018

From the above data obtained the following can be illustrated:

1. The positive values of ΔH refer to the endothermic nature of the decomposition processes [17].

2. The Gibbs free energy of activation ΔG is used to determine the spontaneity of the reaction. All the complexes show positive values of ΔG indicating that they are endergonic and are non-spontaneous processes [18, 19].

3. The negative values of ΔS indicate a more ordered activated complex than reactants or the reactions are slow [20].

4. The high values of the activation energy E_a illustrates to the high thermal stability of the complexes.

3.2. STABILITY EVALUATION OF HMOPE-HBO COMPLEXES AND QUANTUM CHEMICAL PARAMETERS

The geometrical structures of the metal complexes were obtained by optimizing their bond lengths andbond angles. The geometrical structures of the ligand, Ni (II), Cu (II) and Zn (II) complexes are presented in [Fig.4]. Selected geometric parameters- bond lengths and bond angles of the metal complexes are tabulated in Tables3-5.Molecular orbital structures (HOMO & LUMO) for the ligand and metal complexes are presented in [Fig.5]. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are the two main orbitals that take part in the chemical stability, where the HOMO represents the ability to donate an electron (electron donor) and LUMO represents the ability to obtain an electron (electron acceptor).

Quantum chemical parameters of the ligand and its complexes are obtained from calculations such as energies of HOMO and LUMO (E_{HOMO} and E_{LUMO}), ΔE, HOMO-LUMO energy gap, η, absolute hardness, χ, absolute electro negativities, σ, absolute hardness, ω, global electrophilicity, S, global softness, ΔN_{max}, additional electronic charge, Pi, chemical potentials using the following equations:[21]

$\Delta E = E_{LUMO} - E_{HOMO}$	(1)
$\text{¡} = -\frac{(E_{HOMO} + E_{LUMO})}{2}$	(2)
$\text{¦} = \frac{(E_{LUMO} - E_{HOMO})}{2}$	(3)
$\pm = \frac{1}{\text{¦}}$	(4)
$Pi = -\text{¡}$	(5)
$S = \frac{1}{2\text{¦}}$	(6)
$\mu = \frac{Pi^2}{2\text{¦}}$	(7)
$\Delta N_{max} = \frac{-Pi}{\text{¦}}$	(8)

International Journal of Engineering Technology Science and Research
IJETSR
www.ijetsr.com
ISSN 2394 – 3386
Volume 5, Issue 1
January 2018

The energy gap ΔE between HOMO and LUMO is the important stability parameter. The smaller theΔE value, more is the reactivity of the compound [22, 23]. From the above results, Zn (II) complex is found to be more stable and less reactive compared to the ligand and other complexes.

The Quantum chemical parameters calculated for the ligand and its complexes are given in Table.6

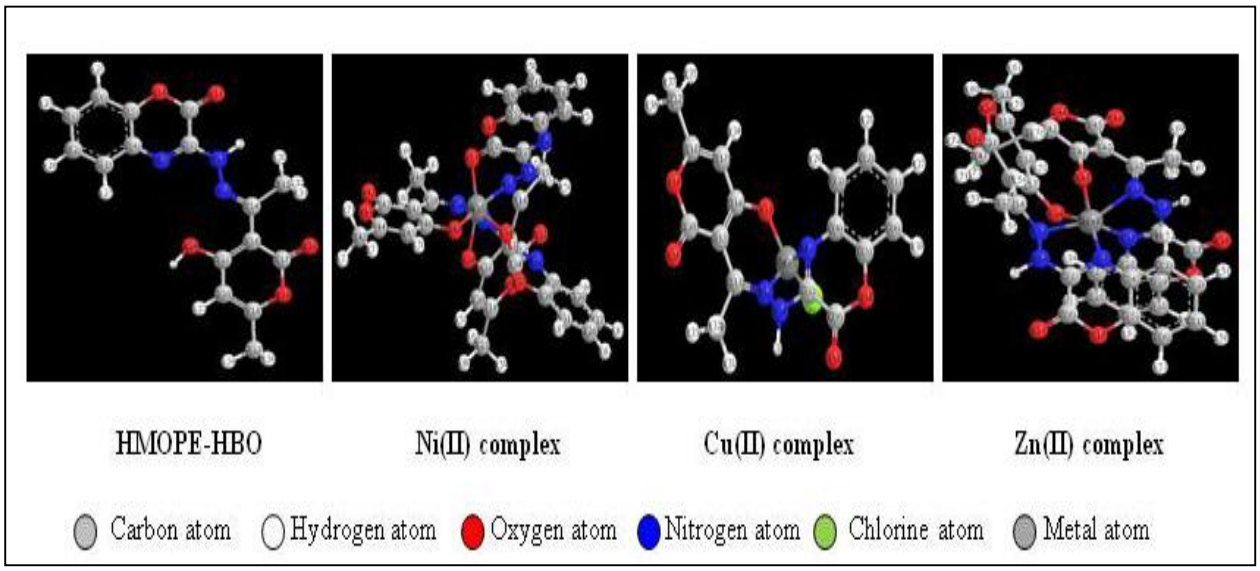

Fig 4: Molecular structures with atomic numbering for ligand and complexes

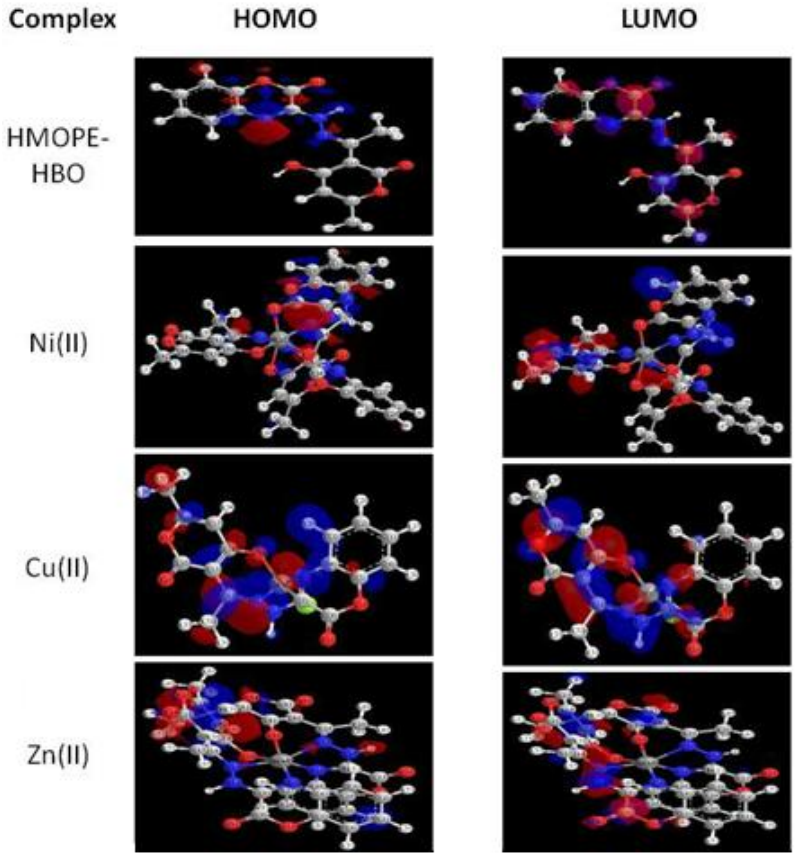

Fig 5: Molecular orbital structures (HOMO & LUMO) for ligand and complexes

International Journal of Engineering Technology Science and Research
IJETSR
www.ijetsr.com
ISSN 2394 – 3386
Volume 5, Issue 1
January 2018

Table 3. Selected bond lengths and bond angles of Ni (II) complex

Bond Lengths (Å)	
Ni(25)-N(38)	1.7879
Ni(25)-O(36)	1.7986
Ni(25)-O(11)	1.8142
Ni(25)-N(13)	1.9469
O(24)-Ni(25)	1.9339
Ni(25)-O(49)	1.7921
Bond angles (°)	
N(38)-Ni(25)-O(36)	145.2056
N(38)-Ni(25)-O(11)	99.5325
N(38)-Ni(25)-O(49)	112.9023
N(38)-Ni(25)-O(24)	65.6825
N(38)-Ni(25)-N(13)	82.2022
O(36)-Ni(25)-O(11)	111.2488
O(36)-Ni(25)-O(49)	81.6328
O(36)-Ni(25)-O(24)	87.1535
O(36)-Ni(25)-N(13)	85.9038
O(11)-Ni(25)-O(49)	93.8487
O(11)-Ni(25)-O(24)	160.0168
O(11)-Ni(25)-N(13)	82.7079
O(49)-Ni(25)-O(24)	80.7884
O(49)-Ni(25)-N(13)	164.8889
O(24)-Ni(25)-N(13)	107.1852

Table 4. Selected bond lengths and bond angles of Cu (II) complex

Bond Lengths (Å)	
Cu(25)-N(12)	1.3243
Cu(25)-N(7)	1.3338
Cu(25)-Cl(26)	2.1613
Cu(25)-O(23)	1.8079
Bond angles (°)	
N(12)-Cu(25)-N(7)	108.2092
N(12)-Cu(25)-Cl(26)	109.9135
N(12)-Cu(25)-O(23)	107.8207
N(7)-Cu(25)-Cl(26)	112.5181
N(7)-Cu(25)-O(23)	110.0861
Cl(26)-Cu(25)-O(23)	108.1920

International Journal of Engineering Technology Science and Research
IJETSR
www.ijetsr.com
ISSN 2394 – 3386
Volume 5, Issue 1
January 2018

Table 5. Selected bond lengths and bond angles of Zn (II) complex

Bond Lengths (Å)	
N(13)-Zn(49)	1.9576
O(24)-Zn(49)	1.9289
O(48)-Zn(49)	1.9096
N(37)-Zn(49)	1.9511
N(31)-Zn(49)	1.9503
N(7)-Zn(49)	1.9606
Bond Angles (°)	
N(13)-Zn(49)-O(24)	70.3305
N(13)-Zn(49)-O(48)	81.7722
N(13)-Zn(49)-N(37)	147.6467
N(13)-Zn(49)-N(7)	80.7185
N(13)-Zn(49)-N(31)	141.9798
O(24)-Zn(49)-O(48)	99.7905
O(24)-Zn(49)-N(37)	117.4590
O(24)-Zn(49)-N(7)	138.9916
O(24)-Zn(49)-N(31)	89.5020
O(48)-Zn(49)-N(37)	66.1217
O(48)-Zn(49)-N(7)	104.2021
O(48)-Zn(49)-N(31)	134.6331
N(37)-Zn(49)-N(7)	102.6191
N(37)-Zn(49)-N(31)	70.1955
N(7)-Zn(49)-N(31)	96.4933

Table 6. Quantum chemical parameters of HMOPE-HBO and its complexes

	HOMO	LUMO	ΔE	χ	η	σ	Pi	S	ω	ΔN
HMOPE-HBO	-6.897	-3.718	3.179	5.307	1.589	0.629	-5.307	0.314	8.861	3.339
Ni(II) complex	-3.667	-2.562	1.105	3.114	0.552	1.809	-3.114	0.904	8.778	5.637
Cu(II) complex	-5.370	-3.010	2.360	4.190	1.180	0.847	-4.190	0.423	7.439	3.550
Zn(II) complex	-4.259	-0.803	3.456	2.531	1.728	0.578	-2.531	0.289	1.853	1.464

4. CONCLUSIONS

1. In the present study the Kinetic parameters: E_a, ΔH, ΔS and ΔG of Ni (II), Cu (II) and Zn (II) complexes of HMOPE-HBO ligand have been determined by the TGA data by using Coats-Redfern method, which concludes that the decomposition processes of complexes is endothermic in nature as ΔH values are positive, all the complexes show positive values of ΔG indicating that they are non-spontaneous processes, the negative values of ΔS indicate a more ordered activated complex than reactants, the high values of the activation energy E_a shows high thermal stability of the complexes.

2. Further, in this study the stability of the ligand and its complexes were also evaluated from the molecular orbital structures from which the quantum chemical parameters were calculated using the HOMO and LUMOenergies. The results showed that Zn (II) complex is found to be more stable and less reactive compared to the ligand and other complexes as it has high HOMO-LUMO energy gap ΔE.

ACKNOWLEDGEMENTS

We are thankful to the DST-FIST Program of India (SR/FST/CSI-213/2010) for providing the infrastructural facilities, Department of Chemistry, University College for Women, Osmania University, Hyderabad.

REFERENCES

[1] Fringuelli, R.,Pietrella, D.,Schiaffella, F.,Guarraci, A., Perito, S.,Bistonib, F., andVecchiarellib, A."Anti-candida albicansproperties ofNovel benzoxazineanalogues",Bioorgan. Med. Chem., 2002, 10, 1681-1686.
[2] Alper-Hayta, S.,Aki-Sener, E.,Tekiner-Gulbas, B.,Yildiz, I.,Temiz-Arpaci, O.,Yalcin, I.,and Altanlar,N."Synthesis, antimicrobial activity and QSARs of new benzoxazine-3-one",Eur. J. Med. Chem., 2006, 41, 1398-1404.
[3]Siddiquia, N., Alia, R.,ShamsherAlama, M., and Ahsana, W. "Pharmacological profile of benzoxazines: A short review", J. Chem. Pharm. Res., 2010, 2, 309-316.
[4]Depreux, P., Moussavi, Z., Lesieur, D., and Sauzieres."N-arylpiperazinyl derivatives of 2,3-dihydro benzoxazin[1,4]-3-ones synthesis and normolipemic activity", J. Farmaco., 1993, 48, 1079-1089.
[5] Mizar, P., and Myrboh, B."Synthesis of substituted 4-(3-alkyl-1,2,4-oxadiazol-5-ylmethyl)-3,4-dihydro-2H-1,4-benzoxazines and 4-(1H-benzimidazol-2-ylmethyl)-3,4-dihydro-2H-1,4-benzoxazines",Tetrahedron Lett. 2006, 47, 7823-7826.
[6] Schleiffenbaum, B.,Spertini, O.,and Tedder Thomas, F. "Soluble L-selectin is present in human plasma at high levels and retains functional activity", J. Cell. Biol., 1992, 119, 229-238.
[7] Stanley, V. G., Woldesenbet, S., and Cassandra, G. "Sensitivity of Escherichia Coli 0157:H7 strain 932 to selected anticoccidial drugs in broiler chicks", Poultry Sci., 1996, 75, 42.
[8] Achut, S. M., Amarnath, N. J., Sarika, M.J., and Trimbak, K.C."Synthesis, characterization and thermal study of some transition metal complexes of an asymmetrical tetradentate Schiff base ligand", J. Serb. Chem. Soc., 2010, 75, 349-359.
[9]Levai, A., and Jeko, J. Monatshefte fur.Chemie. 2006,137, 339-345.
[10] Loev, B., Jones, H., Brown, R.E., Huang, F.C., Khandwala, A., Leibowitz, M.J., and Goldman, P.S."[1,4] Benzoxazine-2,3-diones as antiallergic agents",J. Med. Chem., 1985, 28, 24-27.
[11]Haribabu, V.,Anantha Lakshmi, P.V.,and Jayatyaga Raju, V. "3d transition metal complexes of 3-hydrazino-benzoxazine-2-one: Synthesis, characterization and antifungal activity ",Der Pharma Chemica, 2011, 3, 413-421.
[12] Kavitha, N., and Anantha Lakshmi, P.V. "Synthesis, characterization, thermal and molecular modeling studies of transition metal complexes Supported by ONN/ONO Tridentate Schiff base hydrazone",Der Pharma Chemica, 2016, 8, 184-197.
[13]Ebrahimi-kahrizsangi, R., andAbbasi, M.H. "Evaluation of reliability of Coats–Redfern method for kinetic analysis of non-isothermal TGA", Trans. Nonferrous Met. Soc. China, 2008, 18 217-221.
[14]Coats, A.W., and Redfern, J.P. Kinetic Parameters from Thermogravimetric Data,Nature, 1964, 201, 68-69.
[15]Sivakumar, P.,Parthiban, K.S., Vinoba, M., andRenganathan, S. "Optimization of extraction process and kinetics of Sterculiafoetida seed oil and its process augmentation for biodiesel production",Ind. Eng. Chem. Res. 2012, 52, 8992-8998.
[16] Hanna El-Borary, A., Mogda El-Salamony, A., and AblaHathout, A. "Macrocyclic [N5] transition metal complexes: synthesis, characterization and biological activities",Incl. Phenom Macrocycl. Chem., 2016, 86, 153.
[17]El. Grammal, O.A."Synthesis, characterization, molecular modeling and antimicrobial activity of 2-(2-(ethylcarbamothioyl)hydrazinyl)-2-oxo-N-phenylacetamide copper complexes",SpectrochimActa A, 2010, 75, 533.
[18] Borsato, D., Galvan, D., Pereira, J.L., Orives, J.R., Angilelli, K.G., and Coppo, R.L. "Kinetic and thermodynamic parameters biodesel oxidation with synthetic anti-oxidants: simplexcentroid mixture design",J. Braz. Chem. Soc., 2014, 25, 1984-1992.
[19]Maravalli, P.B., and Goudar, T.R. "Thermal and spectral studies of 3-N-methyl-morpholino-4-amino-5-mercapto-1, 2, 4-triazole and 3-N-methyl-piperidino-4-amino-5-mercapto-1, 2, 4-triazole complexes of Co (II), Ni (II) and Cu (II)",Thermochem. Acta, 1999, 325, 35-41.

[20]Shabi, M."Coordination behavior of new bis(tridentate ONO, ONS and ONN) donor hydrazones towards some transition metal ions: Synthesis, spectral, thermal, antimicrobial and antitumor studies",J. Mol. Str., 2017, 1128, 79-93.

[21]El. Sonbati, A.Z., Diab, M.A., El. Bindary, A.A., Abou-Dobara, M.I., and Seyam, H.A."Molecular docking, DNA binding, thermal studies and antimicrobial activities of Schiff base complexes", J.Mol. Liq. 2016, 218, 434-456.

[22]El. Ghamaz, N.A., Diab, M.A., El. Bindary, A.A., El-Sonbati, A.Z., and Seyam, H.A. "Geometrical structure and optical properties of antipyrine Schiff base derivatives", J.Mater. Sci. Semicond.Process, 2014, 27, 521-531.

[23] El. Ghamaz, N.A., Diab, M.A., El. Bindary, A.A., and Morgan, Sh.M."Supramolecular spectroscopic and thermal studies of azodye complexes",Spectrochim. Acta A, 2014, 127, 310-328.