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Synthesis, characterization and thermal studies of copper (ii) complexes of 2,2′ – bipyridyl and 1,10-phenanthroline

Nandababu Singh Laishram

Department of Chemistry, D.M. College of Science, Imphal (Manipur)- 795001,

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ABSTRACT

Copper (II) acetate and copper (II) dichloroacetate complexes of 2,2′- bipyridyl (L^1) and 1, 10- phenanthroline (L^2) were synthesized. They were characterized b·y elemental analyses, IR spectra, thermal analyses, magnetic moment measurement and electronic spectral data.

They were found to have the following compositions:

$[CuL^1_2(OAc)_2]\cdot 2H_2O$, $[CuL^2_2(OAc)_2]\cdot 4H_2O$, $[CuL^1_2(DCA)_2]\cdot 2H_2O$ *and* $[CuL^2_2(DCA)_2]\cdot 2H_2O$ *where* L^1*=2,2′- bipyridyl (bipy),* L^2 *= 1, 10- phenanthroline (Phen), OAc = acetate and DCA = dichloroacetate respectively.*

The complexes were found to be six co-ordinated and possess octahedral geometry. Thermal parameters such as activation energy (Ea), enthalpy change (ΔH) and entropy change (ΔS) for dehydration and decomposition reactions of the complexes, were evaluated. The order of stability of the complexes (with respect to Ea*) was also compared.*

Key words : Copper (II) salts, 2,2′- bipyridyl, 1,10-phenanthroline, IR spectral data and thermal analyses.

INTRODUCTION

On extensive literature survey, it was found that works on 2,2′-bipyridyl and 1,10-phenanthroline complexes of copper (II) salts such as copper (II) acetate and copper (II) dichloroacetate, were very less. Although similar types of works on copper (II) complexes of the above mentioned ligands had been reported earlier [1-8], in the present cases the compositions of complexes differ from that of earlier ones.

Till now, to the best of my knowledge, no one has done thermal studies (investigations) of these complexes in the solid state in detail.

The main aim of the present work is to synthesize and characterize the copper (II) acetate and copper (II) dichloro acetate complexes of 2,2′-bipyridyl and 1,10-phenanthroline and further to carry out thermal studies (both TGA and DTA) of these complexes in solid state and also to evaluate thermal parameters like activation energy ((Ea*), enthalpy change (ΔH) and entropy change (ΔS) with the help of standard methods [9-11]. Stability order of complexes with respect to Ea* (from TGA curve) have been drawn.

EXPERIMENTAL SECTION

Copper (II) acetate (AR Grade) was used as received. Copper (II) dichloro acetate was freshly prepared by nutralizing dichloroactic acid (AR Grade) with copper oxide and on subsequent crystallization of the filtrate obtained at room temperature. 2,2′-Bipyridyl (AR Grade) and 1,10-phenanthroline (AR Grade) were used as received.

Ethylalcohol and ether were dried by using standard procedures [12].

Synthesis of Metal complexes :

$[Cu(bipy)_2(OAc)_2]\cdot 2H_20$ (1) and $[Cu(phen)_2(OAc)_2]\cdot 4H_20$ (2):-

In order to synthesize complex (1), 25 ml ethanolic solution of copper (II) acetate (4 mmol) was added to 15 ml of ethanolic solution of 2,2′- bipyridyl (8 mmol) with constant stirring. The resulting mixture was treated with ether and thereby the complex existed in oily state which was separated out in light blue coloured solid form after vigorous stirring with a glass rod. It was filtered, washed with dry ether and dried over fused calcium chloride in a dessiccator. Yield : *ca.75%.*

Complex (2) was also synthesized in the same way as mentioned in case of complex (1). However, here in case of complex (2), the light blue complex separated out immediately just after the adolition of ether. Yield:*ca.80%.*

$[Cu(bipy)_2(DCA)_2]\cdot 2H_20$ (3) and $[Cu(phen)_2(DCA)_2]\cdot 2H_20$ (4) :

Complex (3) was obtained by mixing 35 ml ethanolic solution of $Cu(DCA)_2$ (3 mmol) with 20 ml ethanolic solution of 2, 2′-bipyridyl (6 mmol). When ether was added drop by drop to the resulting blue coloured solution with constant stirring, light blue complex separated out immediately. It was filtered, washed with either and dried over fused calcium chloride in a dessiccator. Yield: *ca.85%.*

Complex (4) was also synthesized in a similar manner. It was obtained as light blue coloured complex compound. Yield : *ca:85%.*

Copper was estimated gravimetrically using standard procedure [13], and C, H and N analyses were done by Perkin-Elmer 240C and Carlo Erba 1106 elemental analysers. Results of elemental analyses have been shown in table-1. Thermal investigations (both IGA and DTA) were carried out on a Shimadzu Thermal Analyzer DT-30 under a dynamic nitrogen atmosphere, with a heating rate of $10^{O}C\ min^{-1}$ and α- alumina as a standard reference substance. Activation energy (Ea*) was evaluated from the TGA curve using the equation of Horowitz and Metzger [9] and from the DTA curve using that of Borchardt and Daniels [10]. ΔH was evaluated from the DTA curve using the relation [10], $\Delta H = KA$, where K is the heat transfer co-efficient (cell constant or calibration constant, here the cell is platinum crucible and its constant, K was evaluated using indium metal as a calibrant), and A is the total area under the particular DTA curve measured with a compensating planimeter with optical tracer of Fuji Corora 027. ΔS was calculated from the relation [11], $\Delta S = \Delta H/Tm$, Tm being the DTA peak temperature in Kelvin. Infrared and far-i.r. spectra were recorded with Beckman IR 20A and Perkin-Elmer 783 spectrophotometers in KBr and polythene powder discs. Electronic spectra were recorded with Beckman DU-6 spectrophotometer using dimethylformamide (DMF) as reference solvent. The effective magnetic moments were evaluated from magnetic susceptibility measurements with EG and G PAR 155 vibrating sample magnetometer at room temperature.

RESULTS AND DISCUSSION

From elemental analyses, magnetic moment values and electronic spectral data (Table-1), IR spectral data (Table -2) and thermal analyses data (Table-3), it has been confirmed that both copper (II) acetate and copper (II) dichloroacetate form complexes with 2,2′-bipyridyl (bipy) and 1,10-phenanthroline (phen) having the formulae : $[Cu(bipy)_2(OAc)_2]\cdot 2H_20$ (1) and $[Cu(phen)_2(OAc)_2]\cdot 4H_20$ (2), $[Cu(bipy)_2(DCA)_2]\cdot 2H_20$ (3) and $[Cu(phen)_2(DCA)_2]\cdot 2H_20$ (4) respectively (as shown in Table – 1). All of them possess octahedral geometry.

Elemental analyses, Magnetic moment and Electronic spectra:

Elemental analyses results of complexes (1) to (4) as shown in table -1, prove that the bidentate ligands-2, 2′-bipyridyl and 1,10-phenanthroline are co-ordinated with copper in their corresponding complexes. The magnetic moment values of the complexes ranges from 2.00 to 2.14 B.M., which supports their octahedral geometry [14]. Further, the electronic spectral data (Table-1) also supports their octahedral geometry [15].

Infrared Spectral Studies :

The Key IR spectral data of complexes (1) to (4), are shown in table-2. In case of complexes (1) to (4), the ν(OH) bands appear in the range 3370-3510 cm^{-1} which supports the presence of lattice water molecules in all the complexes [16]. For complexes (1) to (4), $\nu_a\ (COO^-)$ (overlapped with δ(HOH)) appear in the range 1510-1772 cm^{-1} and that of $\nu_s\ (COO^-)$ appear in the range 1390-1455cm^{-1} (Table -2).

TABLE – 1 Elemental analyses, magnetic moment and electronic spectral data of 2,2′-bipyridyl (bipy) and 1,10-phenanthroline (phen) complexes of Cu(II).

Complex compounds	Colour	Elemental Analyses: Found (Calcd.)%				μ_{eff} (B.M.)	λ_{max} (nm)
		Cu	C	H	N		
(1) [Cu L^1_2(OAc)$_2$]·2H$_2$O	Light blue	12.20(11.98)	54.43 (54.35)	4.89(4.91)	10.61 (10.57)	2.12	666
(2) [Cu L^2_2(OAc)$_2$]·4H$_2$O	Light blue	10.50(10.34)	54.83 (54.73)	4.78(4.89)	9.02(9.12)	2.04	685
(3) [Cu L^1_2(DCA)$_2$]·2H$_2$O	Light blue	9.48 (9.51)	43.23(43.12)	3.25(3.29)	8.40(8.38)	2.03	672
(4) [Cu L^2_2(DCA)$_2$]·2H$_2$O	Light blue	8.81 (8.87)	46.89(46.93)	3.00(3.07)	7.78(7.82)	2.00	-

Here, L^1 = 2,2′- bipyridyl (bipy), L^2 = 1, 10- phenanthroline (phen), OAc = Acetate and DCA = dichloroacetate.

TABLE – 2 Key IR Spectral data (cm^{-1}) of Metal Complexes

Metal complexes	ν(OH)	δ(HOH) + ν_a (COO$^-$)	ν_s (COO$^-$)	ν(Cu-N)	ν (Cu-O)
(1) [Cu L^1_2(OAc)$_2$]·2H$_2$O	3510 (br) 3370(br)	1510(ms) 1570 (s)	1390(vs)	523(w) 499(w)	310(s) 295(vw)
(2) [Cu L^2_2(OAc)$_2$]·4H$_2$O	3420(br)	1772(vw) 1718(br) 1700(vw)	1455(ms)	520(br) 505(w)	300(w) 292(w)
(3) [Cu L^1_2(DCA)$_2$]·2H$_2$O	3440(br)	1710(ms) 1640(s,br)	1450(s)	450(w) 410(w)	350(w) 290(w)
(4) [Cu L^2_2(DCA)$_2$]·2H$_2$O	3430(br)	1710 (vs) 1630 (w) 1590 (w)	1430(s)	445 (br) 400 (w)	365(w) 340(w)

Here, v= very, s=strong, m=medium, br=broad and w=weak

Appearance of ν(M-O) in the range 290-365cm^{-1} for the complexes (1) to (4), establishes the fact that both acetato (CH_3COO^-) and dichloroacetato (Cl_2CHCOO^-) groups are directly co-ordinated with the copper atom in their corresponding complexes [17]. Again, for the complexes (1) to (4), the ν(Cu-N) bands appear in the range 400-523 cm^{-1}, which supports the co-ordination of both 2, 2′- bipyridyl and 1,10-phenanthroline through their N-donor atoms with the copper atom in their corresponding complexes [17-19].

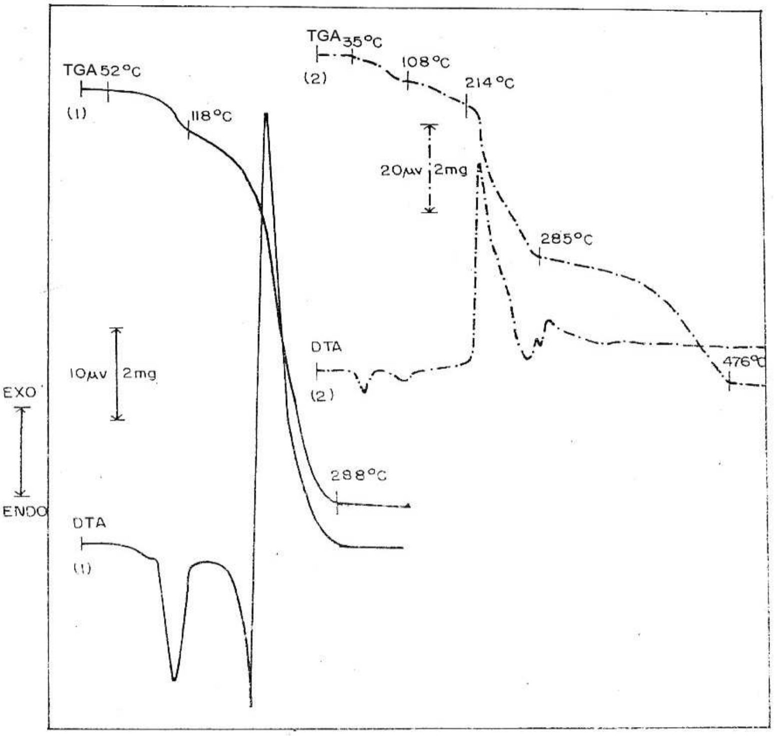

Fig. 1: Thermal curves of [Cu(bipy)$_2$ (OAc)$_2$]·2H$_2$O (1) (-) sample mass 12.2 mg and [Cu(phen)$_2$ (OAc)$_2$]·4H$_2$O (2) (—) sample mass 11.7 mg.

Thermal Analyses Studies :

When the complex (1) is heated under non-isothermal condition, mass loss in the TGA curve corresponds to two molecules of lattice water and it occurs in the temperature range 52-118^{O}C (Fig. 1) showing the presence of two lattice water molecules in complex (1). The corresponding DTA curve is endothermic in nature and its peak appears at 76^{O}C. On further heating, the anhydrous complex $[Cu(bipy)_2(OAc)_2]$ is converted into $Cu(OAc)_2$ in the temperature range 118-288^{O}C (Fig. 1).

The corresponding DTA curve shows two peaks – one endothermic and other exothermic in nature and appear at 195 and 228^{O}C respectively (Fig. 1). The values of ΔH and ΔS for dehydration are 41 KJmol^{-1} and 117 JK^{-1}mol^{-1} respectively. For the second step of decomposition, the value of Ea* from TGA curve is 110 KJmol^{-1} as shown in table- 3.

On heating, complex (2) loses the four lattice water molecules in two steps in between 35-108 ^{O}C and 108-214^{O}C and each step corresponds to two molecules of water. This establishes the fact that complex (2) contains four molecules of lattice water. The DTA peaks are endothermic and appear at 102 and 143^{O}C (Fig. 1). On further heating, the complex $[Cu(phen)_2(OAc)_2]$ is converted into $Cu(OAc)_2$ in two steps via the formation of the intermediate $[Cu(phen)(OAc)_2]$ in the temperature ranges 214-285^{O}C and 285-476^{O}C. The corresponding. DTA peak for the step 2(c) appears at 233^{O}C and is exothermic in nature (Fig. 1). The intermediate complex $[Cu(phen)(OAc)_2]$ was isolated by keeping the rate of heating at 1^{O}C min^{-1} and characterized by usual procedure. The values of Ea*, ΔH and ΔS for the step 2 (c) and Ea* (from TGA) for the state 2(d) are evaluated and given in table-3 as shown below.

TABLE-3 Thermal parameters of 2,2′ - bipyridyl (L^1) and 1, 10- phenanthroline (L^2) complexes of Cu(II) (values are to the nearest whole number).

Decomposition reactions	**Temperature range (^{O}C)**	**DTA peak temperature (^{O}C)**		**Ea*(KJmol^{-1})^a**		**Enthalpy^a change, Δ H (KJmol^{-1})**	**Entropy^a change, ΔS(JK^{-1} mol^{-1})**
		Endo	**Exo**	**TGA**	**DTA**		
1(a)$[Cu\ L^1_2(OAc)_2]\cdot 2H_2O \longrightarrow$ $[Cu\ L^1_2(OAc)_2]$	52-118	76	-	-	-	41	117
(b))$[Cu\ L^1_2(OAc)_2] \longrightarrow$ $Cu\ (OAc)_2$	118-288	195	228	110	-	-	-
2(a)$[Cu\ L^2_2(OAc)_2]\cdot 4H_2O \longrightarrow$ $[Cu\ L^2_2(OAc)_2]\cdot 2H_2O$	35-108	102	-	-	-	-	-
(b)$[Cu\ L^2_2(OAc)_2]\cdot 2H_2O \longrightarrow$ $[Cu\ L^2_2(OAc)_2]$	108-214	143	-	-	-	-	-
(c)$[Cu\ L^2_2(OAc)_2] \longrightarrow$ $[Cu\ L^2\ (OAc)_2]$	214-285	-	233	119	64	102	202
(d)$[Cu\ L^2\ (OAc)_2] \longrightarrow$ $Cu(OAc)_2$	285-476	-	-	128	-	-	-
3(a)$[Cu\ L^1_2(DCA)_2]\cdot 2H_2O \longrightarrow$ $[Cu\ L^1_2(DCA)_2]$	24-135	87^b,107	-	-	-	31	86
(b)$[Cu\ L^1_2(DCA)_2] \longrightarrow$ $Cu\ (DCA)_2$	135-205	154	-	177	-	32	75
4(a)$[Cu\ L^2_2(DCA)_2]\cdot 2H_2O \longrightarrow$ $[Cu\ L^2_2(DCA)_2]$	25-150	150	-	-	-	-	-
(b)$[Cu\ L^2_2(DCA)_2] \longrightarrow$ $Cu\ (DCA)_2$	150-330	288	167	51	-	-	-

^{a} *In some cases thermodynamic paremeters are not possible to evaluate due to some irregular nature of the TGA and DTA curves.*
^{b} *DTA peak temperature used for the evaluation of entropy change.*

On heating, the mass loss in the TGA curves of the complexes (3) and (4), corresponds to two molecules of water in each case. This also proves the presence of two lattice water molecules in each of complexes (3) and (4). The mass loss occurs, for complexes (3) and (4), in the ranges 24-135 ^{O}C and 25-150^{O}C respectively. Endothermic DTA peaks for steps 3(a) and 4(a) appear at 87, 107^{O}C and 150^{O}C respectively (Fig. 2).

The enthalpy and entropy changes for dehydration of step 3(a) are 31 KJmol^{-1} and 86 JK^{-1} mol^{-1} respectively (Table-3). On further heating under non-isothermal condition, the complexes $[Cu(bipy)_2(DCA)_2]$ of step 3 (b) and $[Cu(phen)_2(DCA)_2]$ of step 4(b) are converted into $Cu(DCA)_2$ in a single step with the loss of two molecules of ligands in the temperature ranges 135-205^{O}C and 150-330^{O}C respectively. The corresponding endothermic DTA peaks appear at 154^{O}C and 288^{O}C respectively and exothermic DTA peak for step 4(b) appear at 167^{O}C. Activation energy for the decompositions steps 3(b) and 4(b) are 177 and 51 KJmol^{-1} respectively and ΔH and Δ S values for the step 3(b) are 32KJmol^{-1} and 75 JK^{-1}mol^{-1} respectively as shown in table-3.

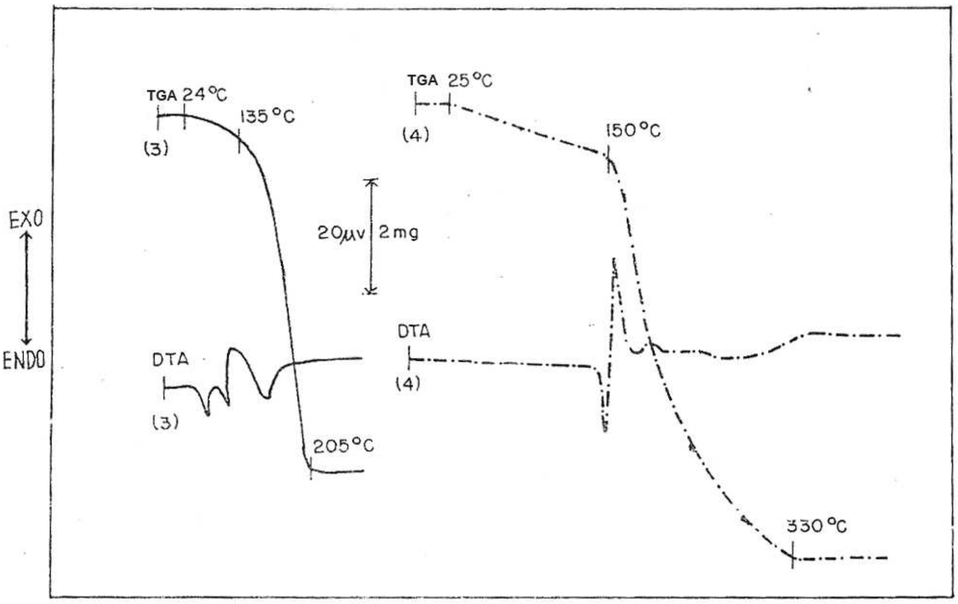

Fig. 2 : Thermal curves of [Cu(bipy)$_2$(DCA)$_2$] . 2H$_2$O (3) (——) sample mass 9.4 mg and [Cu(phen)$_2$(DCA)$_2$] · 2H$_2$O (4) (—·—·) sample mass 12.0mg.

From the values of activation energy (Table-3) for the conversions [Cu(bipy)$_2$(OAc)$_2$] $\xrightarrow{step\ 1(b)}$ Cu(OAc)$_2$ and [Cu(phen)$_2$(OAc)$_2$] $\xrightarrow{step\ 2(c)}$ [Cu(phen)(OAc)$_2$] $\xrightarrow{step\ 2(d)}$ Cu(OAc)$_2$, it has been found that compound [Cu(bipy)$_2$(OAc)$_2$] is less stable than compound [Cu(phen)$_2$(OAc)$_2$] showing that bipy is a weaker ligand than phen. This is in conforming with the spectrochemical series. However, the reverse trend is observed in case of the decomposition of dichloroacetato copper (II) complexes with bipy and phen. That is, in these complexes bipy serves as a stronger ligand than phen, which is evident from the values of activation energy (with respect to the expulsion of ligands)- 177 and 51 KJmol^{-1} for the steps 3(b) and 4(b) respectively. This may be due to the steric effect caused by the presence of more bulkier phenanthroline and dichloroacetate groups.

CONCLUSION

Copper (II) acetate and copper (II) dichloroacetate form octahedral complexes with 2,2'- bipyridyl (bipy) and 1,10-phenanthroline (phen). Further, the thermal stability order (w.r.t. Ea* of TGA) of the anhydrous forms of copper (II) acetate complexes of 2,2'- bipyridyl and 1,10-phenanthroline follows the trend:

[Cu(phen)$_2$(OAc)$_2$] > [Cu(bipy)$_2$(OAc)$_2$].

However, the thermal stability order of the anhydrous forms of copper (II) dichloroacetate complexes with 2,2'-bipyridyl and 1,10-phenanthroline, is found to be in a reverse trend:

[Cu(bipy)$_2$(DCA)$_2$] > [Cu(phen)$_2$(DCA)$_2$]

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REFERENCES

[1] B.J. Hathaway, N.Ray, D. Kennedy, N.O'. Brien and B.Murphy, *Acta cryst.*, **1980**, B36, 1371-1377.

[2] S. Tyagi and B.J. Hathaway, *J. Chem. Soc. Dalton Trans.*, **1983**, 199-203.
[3] L. H. Abdel-Rahman and L.P. Battaglia, *Polyhedron*, **1996**, 15 (2), 327-334.
[4] Z.W. Mao, F.W. Heinemann, G. Liehr and R.V. Eldik, *J. Chem. Soc. Dalton Trans.*, **2001**, 3652-3662.
[5] J.P. Zhang, Y.Y.Lin, Y.Q. Weng and X.M. Chen, *Inorganica Chimica Acta*, **2006**, 359, 3666-3670.
[6] N. Turkel and C. Sahin**,** *Chem. Pharm.Bull.,***2009**, 57(7), 694-699.
[7] R.Chaudhary and Shelly, *Res.J.Chem. Sci.*,**2011**, 1(5), 1-5.
[8] V.K. Yadav, N. Kumari and Lallan Mishra, *Indian J. Chem.*, **2011**, 50A(8), 1035-1042.
[9] H.H. Horowitz and G. Metzger, *Anal.Chem.*, **1963**, 35, 1464.
[10] H.J. Borchardt and F.Daniel, *J. Am. Chem.Soc.*, **1957**, 79,41-46.
[11] L.K. Singh and S.Mitra, *J. Chem.Soc. Dalton Trans.*, **1987**, 2089-2094.
[12] A.I. Vogel, A Text Book of Practical organic Chemistry**,** 4th Edition., ELBS and Longmanns, London, **1980**, 269 and 272.
[13] A.I. Vogel, A Text Book Quantitative Inorganic Analysis, 3rd Edition., ELBS and Longmanns, London, **1968**, 497.
[14] F.A. Cotton, G.Wilkinson, C.A. Murillo and M.Bochmann, Advanced Inorganic Chemistry, 6th Edition., John Wiley & Sons (Asia) Pte. Ltd., Singapore, **2003**, 855 and 867.
[15] A.B.P. Lever, Inorganic Electronic Spectroscopy, 2nd Edition., American Elsevier, New York, **1984**, 557-558.
[16] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Co-ordination Compounds (Part B), 5th Edition., John Wiley and Sons Inc, New York, **1997**, 54, 271-272.
[17] S.A. Aly*, J. Chem. Pharm. Res.*, **2011**, 3(6), 1028-1036.
[18] A.H.A. Ahmed, S.A. Mahmood, R.M. Mohamed and M.A. Mohammed, *J.Chem. Pharm.Res.*, **2010**, 2(3), 120-126.
[19] Y. Harinath, D.H.K. Reddy, B.N. Kumar, K.Lakshmi and K. Seshaiah, *J.Chem.Pharm.Res.*, **2011**, 3(1), 698-706.