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Spectroscopic and Thermal Characterization of Gliclazide, Glibenclamide and Glimeperide Complexes with Transition and Inner Transition Metals

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ABSTRACT

Metal complxes of Gliclazide, Glibenclamide and Glimeperide drugs were prepared and characterized based on elemental analysis, FT-IR, Molar conductance and thermal analysis (TGA and DTG) technique. From elemental analysis data, the complexes were proposed to have general formulae $(GLZ)_2Co2H_2O$, $(GLZ)_2Cu$, $(GLB)_2Co2H_2O$, $Cu(GLB)_2$, $(GLM)_2Hg$ and $(GLM)_2La2H_2O$. The molar conductance data reveal that all the metal complexes are non-electrolytic, IR spectra shows that GLZ, GLB and GLM are coordinated to metal ions in a neutral bidentate manner from the ESR spectra and XRD-spectra. It is found that the geometrical structures of these complexes are tetrahedral Cu(II) ,Hg(II) and octrahedral Co(II), La(II). The thermal behavior of these complexes studied using thermogravimetric analysis (TGA and DTG) techniques. The results obtained shows that the hydrated complexes lose water molecules of hydration followed immediately by decomposition of the anions and ligand molecules in the successive unseparate steps. Thermogravimetric analysis was carried out to study the decomposition and various kinetic parameters. Freeman Carroll and Sharp Wentworth method have been applied for calculation of kinetic parameters. While data from freeman Carroll method have been used to determine various thermodynamic parameters such as order of reactions, energy of activation, frequency factor, entropy change, free energy change and apparent entropy change and order of reaction..

Key words: FTIR Spectra, TGA, DTG, Gliclazide, Glibenclamide, Glimeperide.

INTRODUCTION

Gliclazide, Glibenclamide and Glimeperide, are bi substituted urea derivatives can exist in keto and enolic form when dissolved in an organic solvent and react with various metal ions to form intensely coloured metal complexes that provide the basis for their use as a sensitive reagent.

The thermal degradation study of complexes has become a subject of recent interest. It is important property of complexes, which decides the thermal stability and processability of the complexes. The study of thermal behaviour of complexes in air at different temperature provides important information about its practical applicability.

Iqbal S.A. *et.al*[1]*.,* (2005) synthesized the metal complexes of gliclazide characterized by FTIR, elemental analysis and TGA-DTG parameters. The thermal analysis (TGA) was performed at the heating rate of 10°C/min. in nitrogen atmosphere.

Wilma Cyril *et.al*[2]*.,* (2011) studied kinetics and Thermal decomposition of Cu(II) complex of of hydroxyl quinoline-5-sulphonic acid

Thermal data have been analyzed by Freeman Carroll and Sharp-Wentworth method.

Thermal analysis (TGA and DTG) is a typical analytical technique to describe the relationship between physico-chemical changes and temperature.[1-2] In order to synthesize complexes having practical applications. There is a need to investigate the effect of heat on complexes in order to establish thermal stability.

Iqbal and coworkers[3-4] have synthesized and characterized complexes of tolbutamide and glibenclamide by FTIR, elemental analysis and TGA-DTA technique.

Thermal studies of complexes were carried out to determine their mode of decomposition, the activation energy (Ea), order of reaction (n), frequency factor(Z), entropy change (S), Free energy (ÄF) and apparent entropy change (*S). Thermal decomposition curves were discussed with careful attention of minute details. The freeman Carroll and Sharp-Wentworth methods have been used to calculate thermal activation energy and thermal stability.

However, very little work has been carried out on the synthesis and characterization and thermal degradation studies of the metal complexes of gliclazide, glibenclamide and glimeperide.

Hence in this work we prepare complexes of Cu(II), Co(II), Hg(II) and La(II) transition and inner transition metals with gliclazide, glibenclamide and glimeperide drug molecule. The solid complexes were characterized using different physico-chemical methods, like elemental analysis (C, H, N, S and metal content), IR and thermal analysis (TGA and DTG)

EXPERIMENTAL

Materials and reagents

All chemicals used were of analytical reagent grade (A.R.) and of highest purity. They included gliclazide, glibenclamide and glimeperide (Zim laboratories, Nagpur), Copper(II) Chloride , Lanthanum(II) Chloride heptahydrate (Hi media Lab, Mumbai) organic solvents used are absolute ethyl alcohol, DMF. These solvents were spectroscopic pure from BDH, hydrogen peroxide, hydrochloric and nitric acid (E.Merck) were used. De-ionized water was used in all preparations.

Instruments

Molar conductance of solid complexes in DMF was measured using Systronics conductivity meter, elemental microanalyses of the isolated solid complexes for C,H,N were performed at CDRI, Lucknow, using (HMS-932CLECO) Vario elemental analyzers. Infrared spectra were recorded on Perkin-Elmer, FTIR type 1650 spectrophotometer in wave number 400-4000 cm^{-1}. The spectra were recorded as KBr pellets.

The thermogravimetric (TG and DTG) analysis was carried out in dynamic nitrogen atmosphere (20 $ml.min^{-1}$) with a heating rate of 10°C/min. using shimatzu TGA-50H Thermal Analyzer at IIT Bombay (Mumbai) Electronic spectra recorded at Qualichem Laboratory, Nagpur.

Synthesis of metal complexes

Metal complexes or synthesized by adding metal salt solution in appropriate solvent to the solution of the ligand. The mixture was refluxed for 3-4 hours. Then the precipitate of metal complexes was obtained. It was filtered, washed and dried in vacuum desiccators.

All selected metals forms 1:2 complexes with gliclazide, glibenclamide and glimeperide, were confirmed by Jobs method of continuous variation[5] as modified by Turner and Anderson[6].

Estimation of metals in complexes

An accurately weighed portion of the different complexes ranged from 10 to 30 mg was placed in Kjeldhal flask. A measured volume of concentrated nitric acid ranged from 5 to 10 ml was

added initially to the powdered complexes to start the fast wet oxidation digestion. This mixture had been digested with some drops of H_2O_2 solution using a gradual heating. This treatment was conducted until most of the powdered complexes were dissolved and the remaining solution had the colour of the corresponding metal salt. This solution was then diluted upto a 50 ml. with distilled water and the metal content was determined by titration against standard EDTA solution at a suitable pH value using the suitable indicator.

RESULTS AND DISCUSSION

Composition and structures of metal complexes

The isolated solid complexes of Cu(II), Co(II) ions with GLZ ligand, and GLB ligand while Hg(II), La(II) ions with GLM ligands were subjected to elemental analysis (C, H, N, S. and metal content), I.R., Molar conductance, thermal analysis (TG and DTG) to support the tentative structure. The results of elemental analysis listed in table (1) suggest the formulae $[Co(GLZ)_2]2H_2O$, $[Cu(GLZ)_2]$, $[Co(GLB)_2]2H_2O$, $[Cu(GLB)_2]$, $[Hg(GLM)_2]2H_2O$ and $[La(GLM)_2]2H_2O$ for respective complexes.

Table 1: Analytical and physical data of gliclazide, glibenclamide,and glimeperide metal complexes

Complexes	Colour	% (Yield)	m.p. (°C)	Elemental Analysis ($\Omega^{-1}Mole^{-1}cm^{-1}$)					Molar cond.
				C	H	N	S	M	'Am'
$[C_C\ (C_{15}H_{20}N_3O_3S)_2Cu$	Blue	74	189	49.67 (46.25)	5.12 (5.65)	8.12 (11.86)	6.05 (9.14)	7.18 (8.61)	13.18
$(C_{15}H_{20}N_3O_3S)_2Co.2H_2O$	Pink	70	195	48.91 (45.25)	5.42 (5.00)	9.10 (10.50)	6.66 (8.00)	6.20 (6.75	18.56
$(C_{23}H_{27}O_5ClN_3S)_2Cu$	Blue	76	205	48.41 (52.62)	4.80 (5.15)	7.42 (8.00)	5.62 (6.10)	5.43 (5.81)	24.51
$(C_{23}H_{27}O_5ClN_3S)_2Co2H_2O$	Blue	75	188	49.40 (51.11)	5.33 (5.83)	6.91 (7.84)	6.32 (6.32)	5.00 (5.00)	18.88
$(C_{24}H_{33}N_4O_6S)_2Hg$	White	65	189	49.08 (50.47)	4.02 (5.57)	8.02 (9.81)	6.18 (6.41)	12.46 (14.08)	22.1
$(C_{24}H_{33}N_4O_6S)_2La2H_2O$	White	64	188	50.12 (50.91)	4.92 (5.50)	9.26 (9.90)	7.23 (6.99)	9.01 (10.07)	30.10

Table 2: I.R. Spectra (4000-400cm^{-1}) of the GLZ, GLB, GLM and their metal complexes

Compounds	γ (OH) Enolic	γ (NH)	γ (SO_2) Asym	γ (SO_2) Sym	γ (C=O) Amide	γ (m-O)
Gliclazide	3100-3320 Br.	-	1375 sh.	1100 sh.	1460 sh.	-
$(C_{15}H_{20}N_3O_3S)_2Cu$	3220-3320 br.	3100 br.	1365 sh.	1120 sh.	1481 sh.	530 m.
$(C_{15}H_{20}N_3O_3S)_2Co.2H_2O$	3220-3363 br.	3024 br.	1340.8 m.	1160.6 sh.	1481 sh.	577 m.
Glibenclamide	3280-3310	-	1305 sh.	1160 w.	1480 sh.	-
$(C_{23}H_{27}O_5ClN_3S)_2Cu$	3280-3320 br.	3060 br.	1315 m.	1160 w.	1460 w.	530 m.
$(C_{23}H_{27}O_5ClN_3S)_2Co2H_2O$	3283.6-3363.6 br.	2945.7 br.	1340 m.	1160 sh.	1481 w.	577.0 m.
Glimeperide	3100-3400	-	1375 sh.	1100 sh.	1460 sh.	-
$(C_{24}H_{33}N_4O_6S)_2Hg$	3163.2-3384 br.	2931.0 br.	1348 m.	1161 w.	1440 w.	588.6 m.
$(C_{24}H_{33}N_4O_6S)_2La2H_2O$	3289.6-3381 br.	2932.0 br.	1358.7 m.	1216 br.	1432.8 w.	670.8 br.

Table 3: ESR spectral data of Cu(II), Co(II), Hg(II), La(II) complexes of gliclazide, glibenclamide and glimeperide

Compounds	Temp.	g_{11}	g_1	g_{av}	$A_1 \times 10^{-4}$ (cm^{-1})	g_{11}/A_{11} (cm.)	α^2	G
$(C_{15}H_{20}N_3O_3S)_2Cu$	RT[a]	2.20	2.09	2.11	184.33	119	0.7793	2.93
	LNT[b]	2.18	2.05	2.10	182.03	119	0.7628	3.27
$(C_{15}H_{20}N_3O_3S)_2Co.2H_2O$	RT[a]	2.16	2.05	2.27	184.22	117	0.7768	3.11
	LNT[b]	2.14	2.03	2.25	183.11	116	0.7755	3.07
$(C_{23}H_{27}O_5ClN_3S)2Cu$	RT[a]	2.27	2.04	2.25	184.22	119	0.7792	3.25
	LNT[b]	2.22	2.03	2.24	183.03	118	0.7631	3.08
$(C_{23}H_{27}O_5ClN_3S)2Co2H_2O$	RT[a]	2.19	2.04	2.27	185.23	118	0.7765	2.99
	LNT[b]	2.16	2.05	2.25	183.02	118	0.7762	3.22
$(C_{24}H_{33}N_4O_6S)_2Hg$	RT[a]	2.21	2.05	3.38	184.35	119	0.7760	3.05
	LNT[b]	2.16	2.03	2.27	182.04	118	0.7758	2.93
$(C_{24}H_{33}N_4O_6S)_2La2H_2O$	RT[a]	2.22	2.07	2.37	182.03	121	0.7792	2.94
	LNT[b]	2.16	2.08	2.42	182.05	118	0.7629	3.25

Where, g_{11},g, and G = are the EPR parameters A_{11}=reduced absorbances α^2=bonding parameters

Molar conductance

The complexes were dissolved in DMF and the molar conductivities of 10^{-3}M of their solutions at 298 K are measured. It is concluded from results listed in table (1) that the complexes are found to have molar conductance values of 13.18 to 30.15Ù$^{-1}$ mole^{-1} am^{-2} indicating that all the metal complexes are non-electrolytes.

IR spectral studies

The IR data of the spectra of GLZ, GLB, GLM ligand and there complexes are listed in table (2). The IR spectra of the complexes are compared with those of the free GLZ, GLB, GLM ligands in order to determine the coordination sites that may be involved in complexation[7-14]. The tautomeric equilibrium depends on the extent of conjugation, nature and position of the substituent, polarity of the solvent etc.

Electronic spectral studies

In the ESR spectrum, from the observed 'g' values of Cu(II), Co(II), Hg(II), La(II) complex. It is evident that the unpaired electron is predominantly in dx^2-y^2 orbital with the possibly of same d_2^2 character being mixed with it because of low symmetry. The 'g_1' value is less than 2.3 indicater a larger percentage of covalency. The G value less than 4, concludes the interaction between metal centres. The ratio g_{11}/A_{11}=119 cm. suggests the square planar geometry and the ratio 121 suggested the octahedral geometry(Rosenberg *et.al*[15],1999). The observations were recorded in table 3.

Magnetic susceptibility studies

The room temperature magnetic moment of the complexes was found to be 4.66 B.M. which corresponds to the presence of Co(II), La(II) in octahedral geometry. Zayed *et al* [16]., (2000) Cotton *et al.,*[17] (1999)

In addition to that, the Cu(II), complex is found to have magnetic moment value of 4.62 B.M. which indicates the presence of Cu(II) complex with tetrahedral structure.

Thermal analysis (TGA and DTG)

In the present investigation, the weight losses for each complex were calculated within corresponding temperature ranges. The obtained data are listed in table 4. All complexes are thermally decomposed in three decomposition steps within the temperature range of 50-600°C .The TGA/DTA curves for the complexes are shown in Fig. (a) to (d)

The thermoanalytical data are presented in table 4. In studying the decomposition kinetics[18-26], three methods mentioned in the

Table 4 Thermogravimetric data of Glibenclamide-Cu complex by Sharp-Wentworth[28-29] method

Temp. (°C)	°K Temp (T)	$\frac{100}{T}$	% Mass Loss	Change in Wt. 'c' grams	1-c	$-\frac{dc}{dt}$	log(dc/dt)	log(1-c)	log (dc/dt)/1-c	Weight % (%)
30	303	3.30033	0.638	0.00006	0.99994	0.00009	-4.05164	-0.00003	-4.05187	99.362
50	323	3.09598	1.106	0.00010	0.99990	0.00012	-3.92395	-0.00004	-3.92435	98.894
70	343	2.91545	1.534	0.00014	0.99986	0.00017	-3.77705	-0.00006	-3.77758	98.466
90	363	2.75482	2.148	0.00019	0.99981	0.00020	-3.69867	-0.00008	-3.69939	97.852
110	383	2.61097	2.635	0.00024	0.99976	0.00022	-3.65637	-0.00010	-3.65724	97.365
130	403	2.48139	2.958	0.00027	0.99973	0.00024	-3.61347	-0.00012	-3.61444	97.042
150	423	2.36407	3.275	0.00030	0.99970	0.00027	-3.56881	-0.00013	-3.56987	96.725
170	443	2.25734	3.629	0.00033	0.99967	0.00030	-3.52480	-0.00014	-3.52596	96.371
190	463	2.15983	4.017	0.00036	0.99964	0.00033	-3.48241	-0.00016	-3.48368	95.983
210	483	2.07039	4.432	0.00040	0.99960	0.00038	-3.42467	-0.00017	-3.42605	95.568
230	503	1.98807	5.031	0.00046	0.99954	0.00042	-3.38055	-0.00020	-3.38209	94.969
250	523	1.91205	5.594	0.00051	0.99949	0.00050	-3.30383	-0.00022	-3.30551	94.406
270	543	1.84162	6.593	0.00060	0.99940	0.00057	-3.24715	-0.00026	-3.24909	93.407
290	563	1.77620	7.556	0.00069	0.99931	0.00059	-3.23207	-0.00030	-3.23429	92.444
310	583	1.71527	7.969	0.00072	0.99928	0.00061	-3.21413	-0.00031	-3.21645	92.031
330	603	1.65837	8.324	0.00076	0.99924	0.00063	-3.19810	-0.00033	-3.20052	91.676
350	623	1.60514	8.648	0.00078	0.99922	0.00065	-3.18558	-0.00034	-3.18808	91.352
370	643	1.55521	8.917	0.00081	0.99919	0.00067	-3.17559	-0.00035	-3.17817	91.083
390	663	1.50830	9.138	0.00083	0.99917	0.00068	-3.16753	-0.00036	-3.17016	90.862
410	683	1.46413	9.32	0.00085	0.99915	0.00069	-3.16117	-0.00037	-3.16384	90.680
430	703	1.42248	9.467	0.00086	0.99914	0.00070	-3.15540	-0.00037	-3.15812	90.533
450	723	1.38313	9.598	0.00087	0.99913	0.00071	-3.14976	-0.00038	-3.15250	90.402
470	743	1.34590	9.725	0.00088	0.99912	0.00072	-3.14431	-0.00038	-3.14708	90.275
490	763	1.31062	9.849	0.00089	0.99911	0.00073	-3.13884	-0.00039	-3.14164	90.151
510	783	1.27714	9.974	0.00091	0.99909	0.00889	-2.05090	-0.00039	-2.05276	90.026

Table 5: Thermogravimetric data of Glibenclamide-Cu complex by Freeman and Carroll[26-27] method

Temp (°C)	% Mass Loss	Change in Wt. (gm.)	Time in Sec.	dw/dt	log wr = wc-w dw/dt	log wr	T (K)	1/T (K-1)	(Log dt/dt) /(log wr	(1/T)/ Log wr	α = g wt/wc	α = 1- ^{n}/1-n	$T^3 \times 10^{-7}$ (1-α)$^{1-}$	gα/T3	1/T x 10^{-3} x10^{7}	log g(α)/T^3
30	4.049	0.0002057	90	0.0004250	-3.37170	0.003171	-2.498866	303	0.003300	1.3493	-0.001321	0.06093	0.0628	2.7818	0.001376	3.300330	-86.884856
50	8.566	0.0004352	150	0.0004479	-3.34880	0.002941	-2.531500	323	0.003096	1.3229	-0.001223	0.12891	0.1378	3.3698	0.005272	3.095975	-51.943202
70	9.243	0.0004696	210	0.0004567	-3.34030	0.002907	-2.536609	343	0.002915	1.3169	-0.001149	0.13910	0.1496	4.0354	0.005155	2.915452	-41.678647
90	9.451	0.0004802	270	0.0004616	-3.33570	0.002896	-2.538191	363	0.002755	1.3142	-0.001085	0.14223	0.1532	4.7832	0.004555	2.754821	-34.742302
110	9.558	0.0004856	330	0.0004679	-3.32990	0.002891	-2.539007	383	0.002611	1.3115	-0.001028	0.14384	0.1551	5.6182	0.003970	2.610966	-29.397927
130	9.686	0.0004921	390	0.0004797	-3.31900	0.002884	-2.539985	403	0.002481	1.3067	-0.000977	0.14577	0.1573	6.5451	0.003503	2.481390	-25.051013
150	9.926	0.0005043	450	0.0005039	-3.29770	0.002872	-2.541826	423	0.002364	1.2974	-0.000930	0.14938	0.1615	7.5687	0.003188	2.364066	-21.370558
170	10.413	0.0005291	510	0.0005484	-3.26090	0.002847	-2.545584	443	0.002257	1.2810	-0.000887	0.15671	0.1702	8.6938	0.003067	2.257336	-18.105713
190	11.314	0.0005749	570	0.0006259	-3.20350	0.002801	-2.552623	463	0.002160	1.2550	-0.000846	0.17027	0.1863	9.9253	0.003196	2.159827	-15.099361
210	12.884	0.0006546	630	0.0007092	-3.14920	0.002722	-2.565170	483	0.002070	1.2277	-0.000807	0.19389	0.2151	11.2679	0.003701	2.070393	-12.245875
230	14.603	0.0007420	690	0.0008170	-3.08780	0.002634	-2.579336	503	0.001988	1.1971	-0.000771	0.21976	0.2475	12.7264	0.004275	1.988072	-9.935268
250	16.81	0.0008541	750	0.0013404	-2.87280	0.002522	-2.598228	523	0.001912	1.1057	-0.000736	0.25298	0.2908	14.3056	0.005143	1.912046	-7.922182
270	27.221	0.0013831	810	0.0021815	-2.66120	0.001993	-2.700455	543	0.001842	0.9855	-0.000682	0.40965	0.5243	16.0103	0.013415	1.841621	-4.172467
290	44.295	0.0022506	870	0.0026006	-2.58490	0.001126	-2.948599	563	0.001776	0.8767	-0.000602	0.66660	1.0864	17.8454	0.040583	1.776199	-0.785237
310	53.398	0.0027132	930	0.0027506	-2.56060	0.000663	-3.178407	583	0.001715	0.8056	-0.000540	0.80359	1.6014	19.8155	0.064941	1.715266	0.552733
330	56.805	0.0028863	990	0.0028234	-2.54920	0.000490	-3.309794	603	0.001658	0.7702	-0.000501	0.85487	1.8933	21.9256	0.073819	1.658375	0.953780
350	58.409	0.0029678	1050	0.0028782	-2.54090	0.000409	-3.388795	623	0.001605	0.7498	-0.000474	0.87900	2.0680	24.1804	0.075177	1.605136	1.073373
370	59.567	0.0030266	1110	0.0029243	-2.53400	0.000350	-3.456336	643	0.001555	0.7331	-0.000450	0.89643	2.2169	26.5848	0.074753	1.555210	1.121916
390	60.531	0.0030756	1170	0.0029769	-2.52620	0.000301	-3.521876	663	0.001508	0.7173	-0.000428	0.91094	2.3609	29.1434	0.073794	1.508296	1.141126
410	61.616	0.0031307	1230	0.0030311	-2.51840	0.000246	-3.609834	683	0.001464	0.6976	-0.000406	0.92727	2.5535	31.8612	0.074314	1.464129	1.174889
430	62.737	0.0031877	1290	0.0030755	-2.51210	0.000189	-3.724443	703	0.001422	0.6745	-0.000382	0.94414	4.2660	34.7429	0.115930	1.422475	1.741538
450	63.667	0.0032349	1350	0.0031104	-2.50720	0.000141	-3.849694	723	0.001383	0.6513	-0.000359	0.958135	0.0000	37.7933	1.267597	1.383126	4.446279
470	64.399	0.0032721	1410	0.0031412	-2.50290	0.000104	-3.982297	743	0.001346	0.6285	-0.000338	0.96915	3.3603	41.0172	0.079398	1.345895	1.250144
490	65.042	0.0033048	1470	0.0031720	-2.49870	0.000071	-4.145757	763	0.001311	0.6027	-0.000316	0.97883	3.7101	44.4195	0.081756	1.310616	1.260916
510	65.68	0.0033372	1530	0.0032094	-2.49360	0.000039	-4.408124	783	0.001277	0.5657	-0.000290	0.98843	#REF!	48.0049	#REF!	1.277139	#REF!

Table 6: Thermogravimetric data of Metal complexes of GLZ, GLB and GLM drugs with corresponding to heating rate of 10°C/min

Complexes	Decomposition Temp. (°C)	%Wt. loss	Ea(Kj/mole) F.C.	W.W	ΔS*	ΔF (Kj/mole)	Z (Kj/mole)	S*	n
$(C_{15}H_{20}N_3O_3S)_2Cu$	30-150	9.926	32.87	31.37	-28.85	-8.708	281.2	-44.2681	0.9
	150-350	58.408	51.21	51.01	-64.65	-27.29569	269.8		
	350-510	65.68	110.30	109.23	-112.5	-69.9772	252.7		
$(C_{15}H_{20}N_3O_3S)_2Co.2H_2O$	30-150	5.815	33.67	32.66	-33.98	-10.26227	322.8	-48.5380	1.01
	150-350	51.027	55.14	54.38	-82.07	-34.66047	268.3		
	350-510	69.718	109.37	108.38	-116.8	-72.65703	252.3		
$(C_{23}H_{27}O_5ClN_3S)_2Cu$	30-150	10.413	29.77	28.68	-24.59	-7.421	284.3	-43.2123	0.98
	150-350	58.409	67.76	66.14	-67.76	-29.94992	263.0		
	350-510	65.042	114.2	113.92	-116.50	-72.4653	252.0		
$(C_{23}H_{27}O_5ClN_3S)_2Co2H_2O$	30-150	11.414	33.45	33.12	-33.98	-10.26249	257.6	-39.804	0.98
	150-350	33.869	85.94	85.00	-69-18	-30.5608	257.6		
	350-510	45.139	137.5	138.00	-101.2	-42.6701	248.3		
$(C_{24}H_{33}N_4O_6S)_2Hg$	30-150	2.577	52.66	52.16	-43.48	-13.12178	269.2	-44.2381	0.99
	150-350	61.536	85.94	85.13	-82.05	-39.54421	269.2		
	350-510	81.344	138.23	138.14	-102.2	-43.09237	257.6		
$(C_{24}H_{33}N_4O_6S)_2Hg$	30-150	2.577	52.66	52.16	-43.48	-13.12178	269.2	-44.2381	0.99
	150-350	61.536	85.94	85.13	-82.05	-39.54421	269.2		
	350-510	81.344	138.23	138.14	-102.2	-43.09237	257.6		

literature were used in each case the least square plots were drawn. The first few points that did not fall on straight line were discarded. These types of deviations of points are reported in literature by several research workers. This is explained as due to the failure of obeying as first order kinetics always by the solids in their decomposition in the early stages.

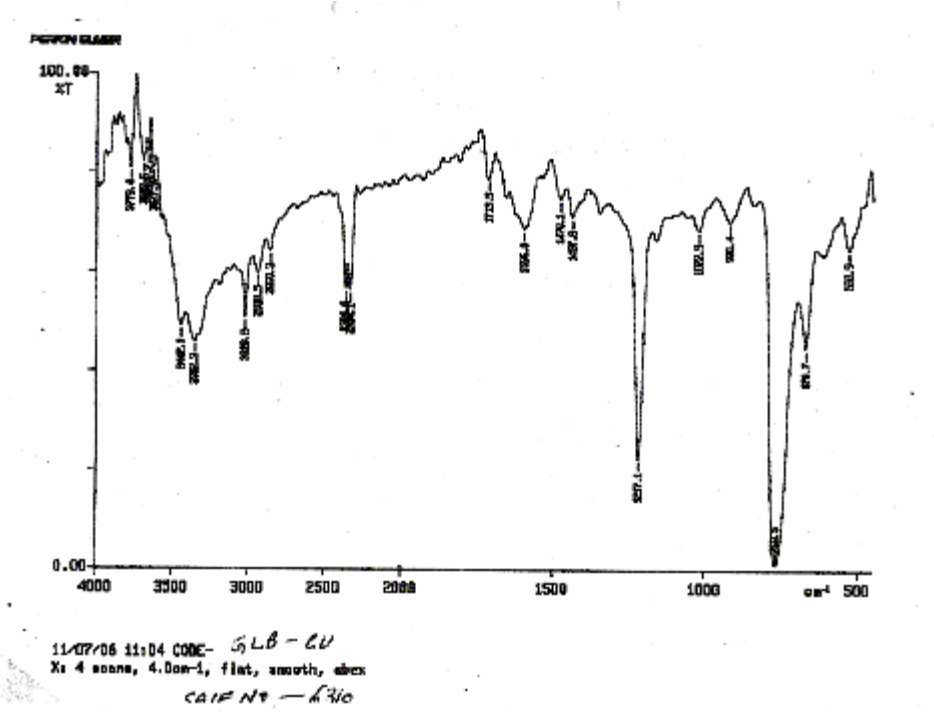


Fig. 1: The FT-IR of Cu-glibenclamide complex

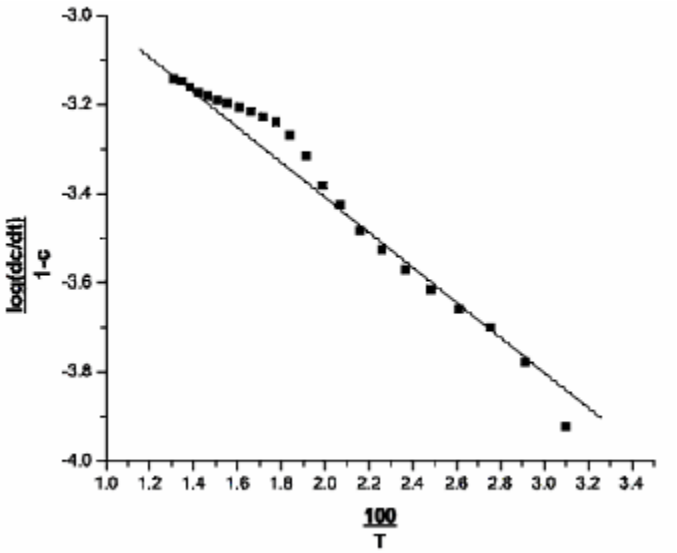


Fig. 2: Determination of activation energy by SW method

Theoretical Consideration

To provide further evidence regarding the degradation system of analyzed compounds we derived the TG curves by applying an analytical method proposed by *Freeman-Carroll*[27-28] and *Sharp-Wentworth*[29-30].

Freeman-Carroll Method[26-27]

The straight line equation derived by Freeman and Carroll, which is in the form of

Where, = rate of change of weight with time
Wr = Wc-W
W_c = Wt. loss at completion of reaction
W = Total wt. loss upto time 't'

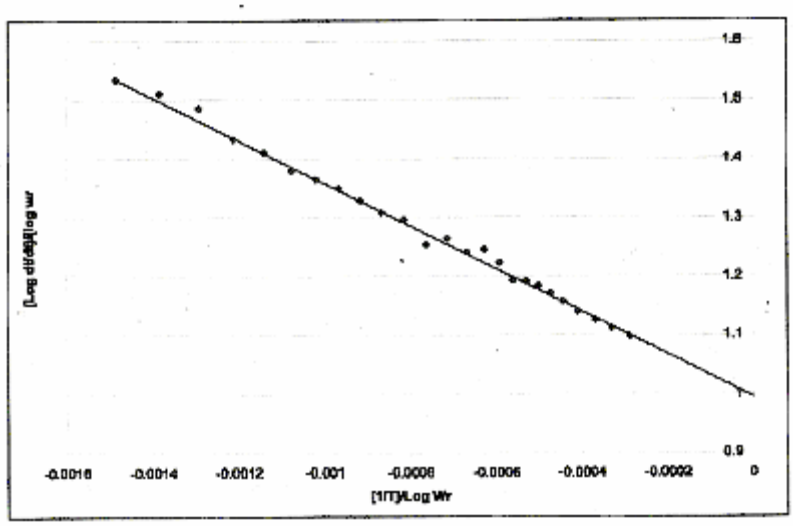


Fig. 3: Determination of order of reaction and activation energy by FC method

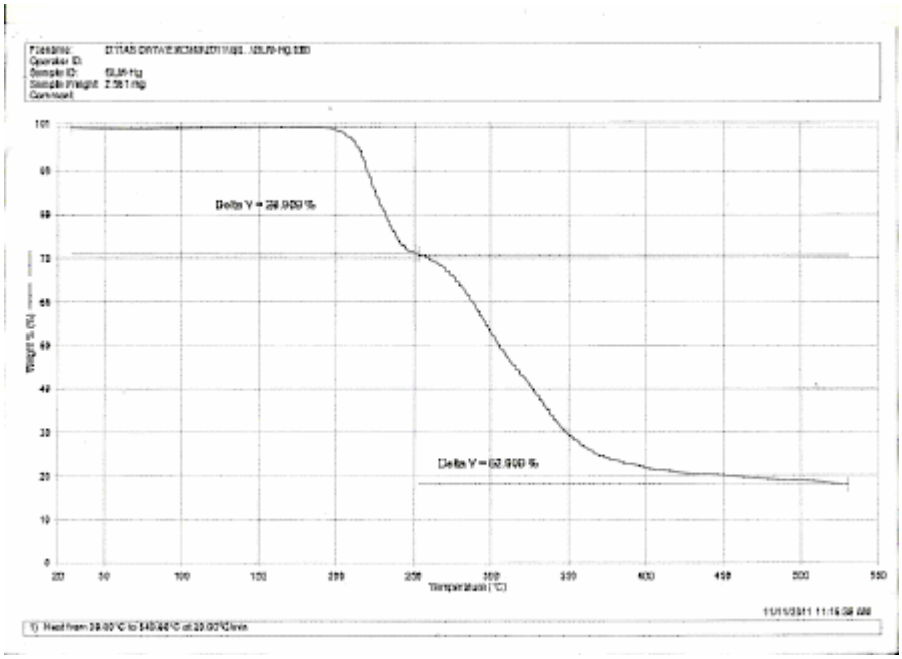


Fig. 4: TGA Curve of GLM-Hg complex

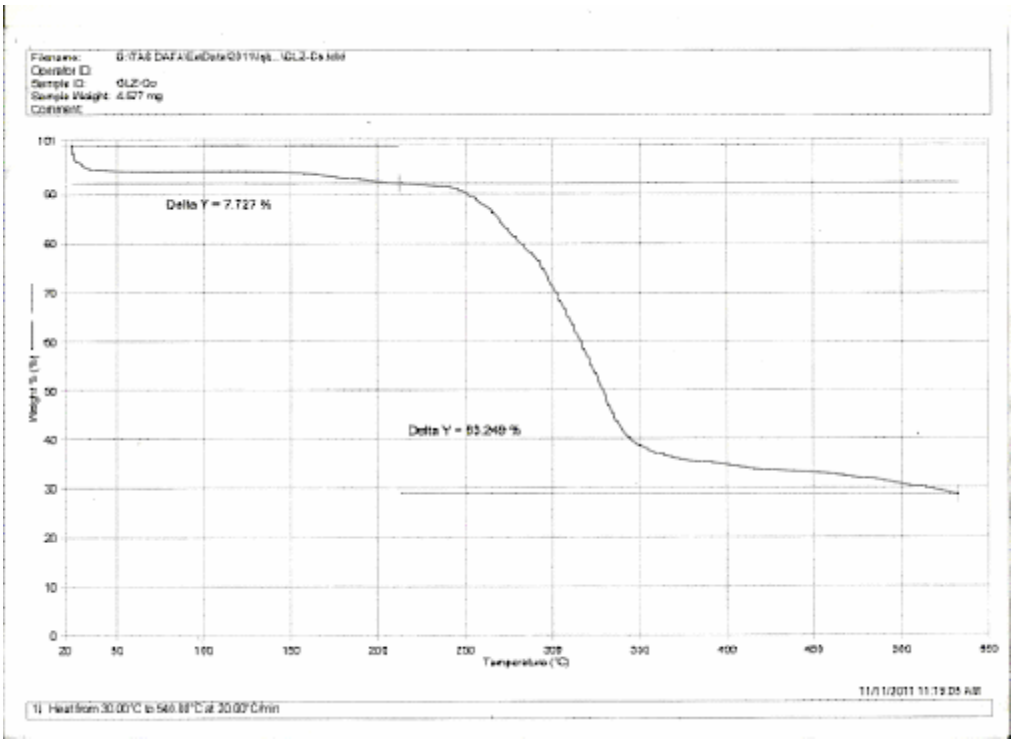


Fig. 5: TGA Curve of GLZ-Co Complex

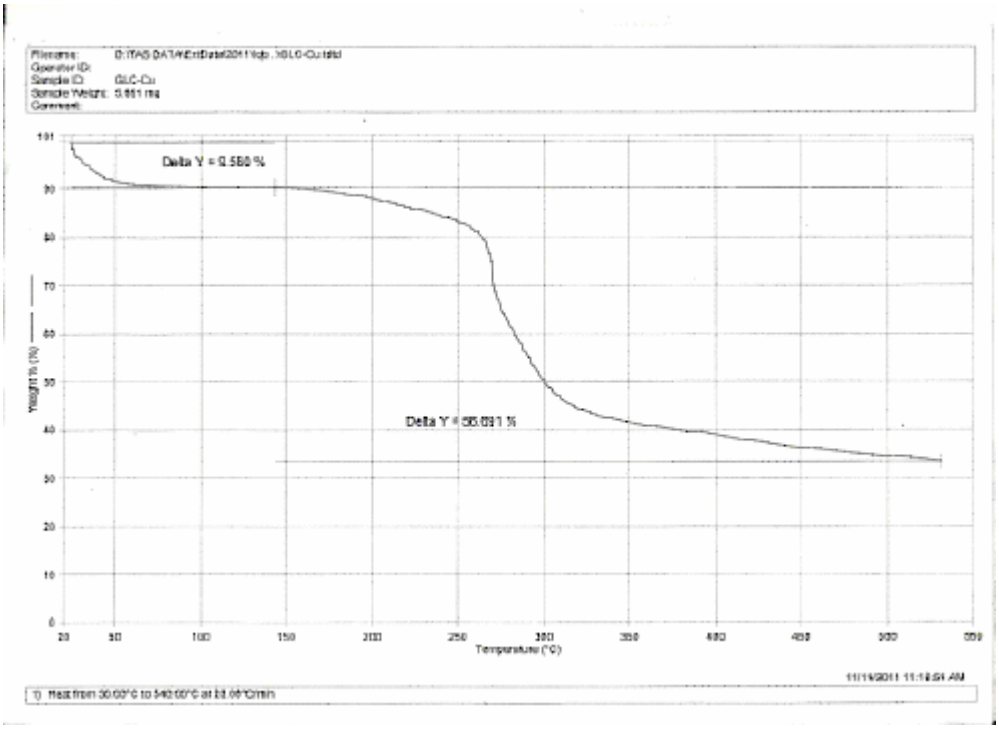


Fig. 6: TGA Curve of GLZ-Cu Complex

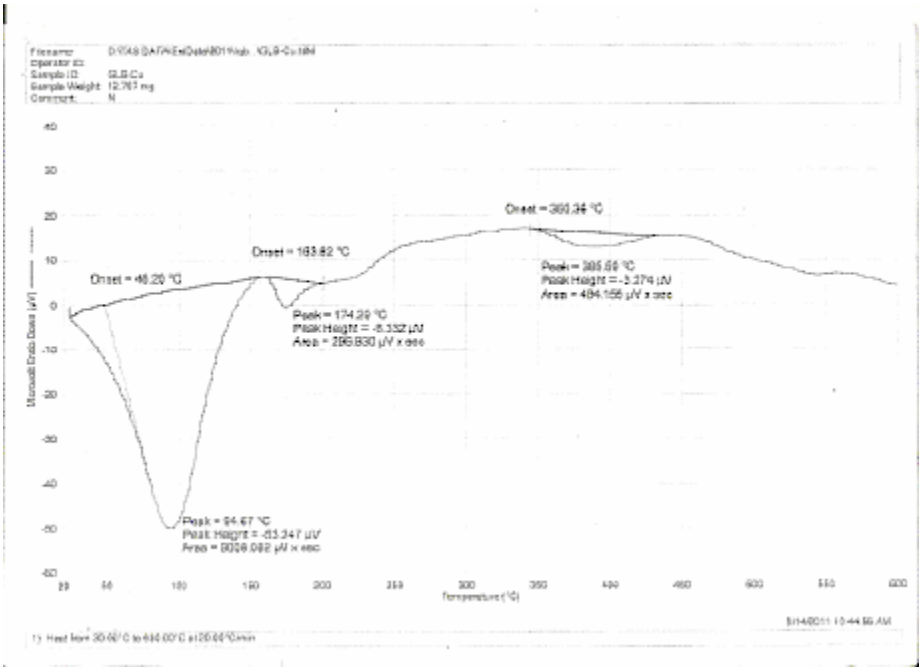


Fig. 7: DTG Curve of GLB-Cu Complex

E_a = Energy of activation
n = Order of reaction

The plot between the term Vs gives a straight line from which slope can be calculated, also we obtained energy of activation (Ea) and intercept on Y-axis as order of reaction (n). The change in entropy (ΔS), frequency factor (Z), apparent entropy (S*) can also be calculated by further calculation.

Sharp-Wentworth Method[28-29]

Using the equation derived by Sharp and Wentworth

$$\frac{\Delta \log \frac{dc}{dT}}{(1-c)} = \frac{\log A}{B} - \frac{Eq}{2.303\,R}.\frac{1}{T}$$

Where,

$\frac{dc}{dT}$ = Rate of change of fraction of weight with change in temperature.

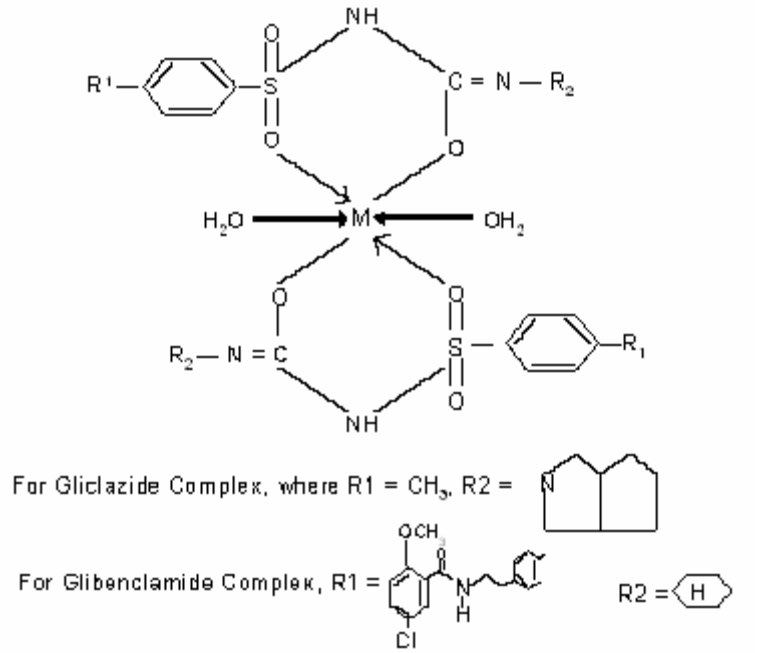
β = Linear heating rate $\frac{dT}{dt}$

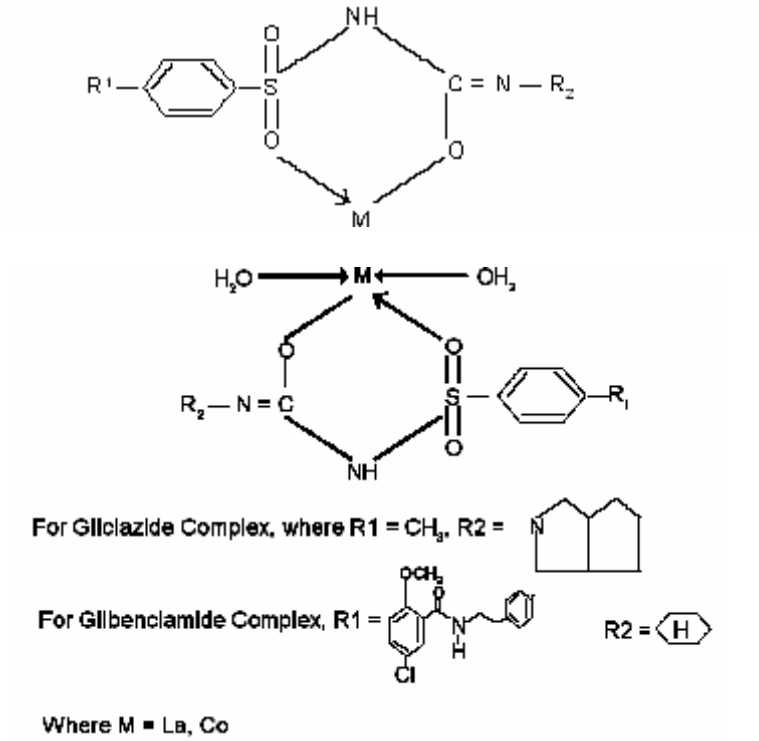
by plotting the graph between

$$\frac{\Delta \log \frac{dc}{dT}}{(1-c)} \quad Vs = \frac{1}{T},$$

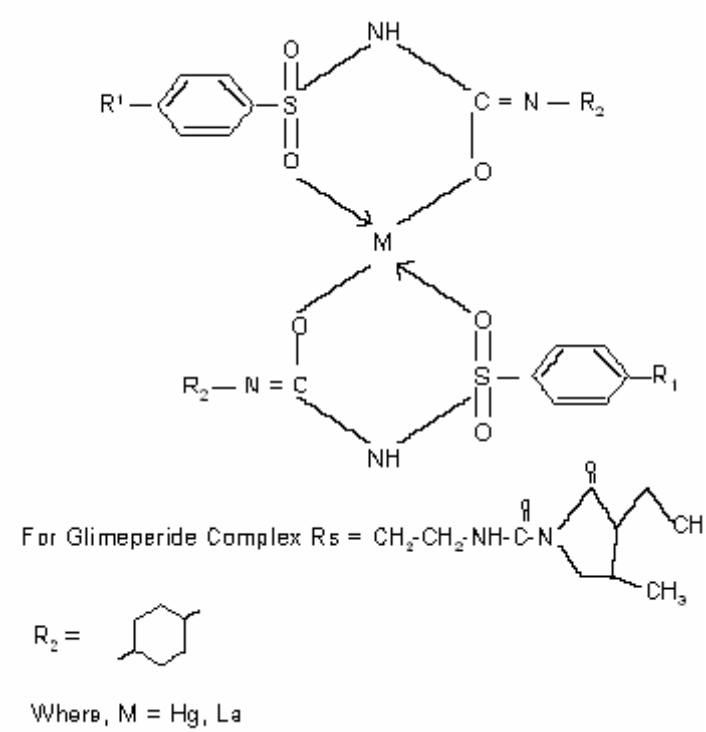
We obtained the straight line which gives energy of activation (Ea) from its slope.

The thermodynamic activation parameters of decomposition process of dehydrate complexes namely activation energy (Ea), enthalpy (ΔH), Entropy (ΔS) and Gibb's free energy change of decomposition (ΔG°) are evaluated graphically by employing Free man-Carroll and Sharp-Wentworth relation. The data are summarized in table 6 the activation energies of decomposition are found to be in the range 29.70 to 204.7 KJ.Mole^{-1}. The high value of activation energies reflect the thermal stability of complexes. The entropy of activation is found to have negative values in all the complexes


For Gliclazide Complex, where R1 = CH3, R2 =
For Glibenclamide Complex, R1 =
R2 =
Where M = Fe, Co


For Gliclazide Complex, where R1 = CH3, R2 =
For Glibenclamide Complex, R1 =
R2 =
Where M = La, Co

Structure 1



Structure 2

which indicate that decomposition reactions process with lower rate than the normal ones[31-35].

DISCUSSION

The complexes of Cu,Hg,La and Co were synthesized with oral hypoglycemic agents i.e. gliclazide,glibenclamide and glimeperide the formulae suggested for the complexes are well supported by the Jobs method of continuous variation as modified by Turner and Anderson,moreover,the formulae of the complexes further gets supports from the analytical data.

The structure of the complexes are supported from variety of spectroscopic technique like I.R,Electronic spectra,TGAmethod whose results are summarized in Tables-2,3,4,5 and 6 respectively.All the complexes prove to be formed in 2:1 ligand metal ratio The complexes are formed after enolisation of the drugs which is indicative by the presence of only metal oxygen bonds and not the metal nitrogen. The Cu and Hg complexes shows tetrahedral structures while La and Co complexes shows octahedral structures in which the six co-ordination is fulfilled by two water molecule in which the oxygen of the water is vertically joining to the metal atom, above and below the plane of the molecule.

Thus on the bases of analytical data and spectroscopic studies the following structure-I and II may be assighn for the Cu,Hg and La, Co complexes respectively.

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