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Synthesis, FTIR, NMR, Mass spectral, X-ray crystallographic & Thermal Studies of Hg(II) Complex of *N, N*-dimethylbiguanide

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ABSTRACT

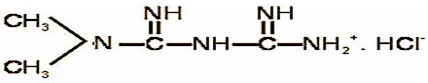
Metal chelate of antidiabetic drug is synthesized and characterized by using various spectroscopic tools like elemental analyses, IR, NMR, mass spectra, thermal analyses (TGA) and X-ray powder diffraction techniques. The nonvariation conductometric titration method indicated the ionic nature of the complex and LM_2 structure type. Complex was assigned tetrahedral geometry based on the spectral data and was found to have chemical formula $[(C_4H_{10}N_5)(HgCl)_2]$ (Scheme-I). Crystallographic parameters have been calculated from powder X-ray diffraction analysis. The thermal and kinetic behaviour of the complex has been studied using Thermogravimetric analysis, which indicates that water molecules of crystallization together with anions are removed in the first step. Calculation of thermodynamic parameters has been done and their relative thermal stabilities of the complex is also discussed. Thermal stability and activation energy have been calculated by F. C and S. W methods. F. C method and TG curves have been used to determine thermodynamic specification viz. free energy change (ΔF), entropy change (ΔS).

Keywords: Antidiabetic drugs, Complex, Spectroscopy, Therma land X-ray crystallographic.

INTRODUCTION

Metal ions play indispensable role in various biological processes and their deficiency is the root causes of many diseases[1]. Well-known examples of such diseases are pernicious anemia resulting from iron deficiency. Millions of people suffer from diabetes mellitus, a progressive health complication characterized by long-lasting hyperglycaemia and disorders of carbohydrate[2-4]. Zinc-insulin has been proved to be a very effective medicine in the treatment of diabetes and till date, a number of treatment methods have been developed to control the blood glucose level in diabetic patient[5-6]. Insulin-enhancing properties have been markedly shown by vanadium-containing compounds and they also show anti-diabetic effects both *In vivo* and *In vitro*[7-8]. Discovery of oral hypoglycemic drugs which has been takes place to avoid the daily pain of hypodermic syringe. Transition metals, whose ability to form coordination compounds and chelate are of great biological importance. In past few years greater number of sulphonyl-urea complexes has been synthesized because of their high complex formation

tendency. Literature report that the Sulphonyl-urea are effective for Type-2 diabetes[2-4]. Complexation of sulphonyl-urea with lighter transition metals has been studied in detail by Yoshinaga and Yamamotto[9-10]. by Iqbal *el at.,* and other had studied the complexation of sulphonyl-urea and biguanidine[11-12]. Therefore, to further explore the immense potential of metal complexes, we have synthesized metformin-mercury complex and characterized by various techniques. Mercury-metformin complex characterization and synthesis has been reported in the present paper.



Structure of ligand (metformin)

EXPERIMENTAL

Metal-Ligand Ratio

1.565 g of metformin, diluted to 200 mL and mercuric chloride solution in same solvent was papered. They were conductometrically titrated at 30±1°C and graph was designed from the results which indicates that complex is in 2:1 ratio.

Job's method[13] of continuous variation as modified by Turner and Anderson[14] was used for further confirmation of metal-ligand ratio (Table 1 and Fig. 1a & 1b) using absorbance as index property. Values of log k and -ΔF have been calculated.

Table 1: Job's method as modified by Turner and Anderson

S. No.	M:L Ratio	Absorbance		Corrected Absorbance	
		0.002M	0.005M	0.002M	0.005M
1	0:12	0.009	0.014	0.00	0.00
2	1:11	0.022	0.029	0.013	0.015
3	2:10	0.033	0.058	0.024	0.043
4	3:9	0.053	0.071	0.041	0.055
5	4:8	0.052	0.099	0.040	0.080
6	5:7	0.088	0.109	0.073	0.091
7	6:6	0.113	0.144	0.100	0.124
8	7:5	0.127	0.157	0.111	0.134
9	8:4	0.159	0.186	0.141	0.161
10	9:3	0.105	0.139	0.085	0.115
11	10:2	0.085	0.103	0.064	0.073
12	11:1	0.041	0.067	0.019	0.034

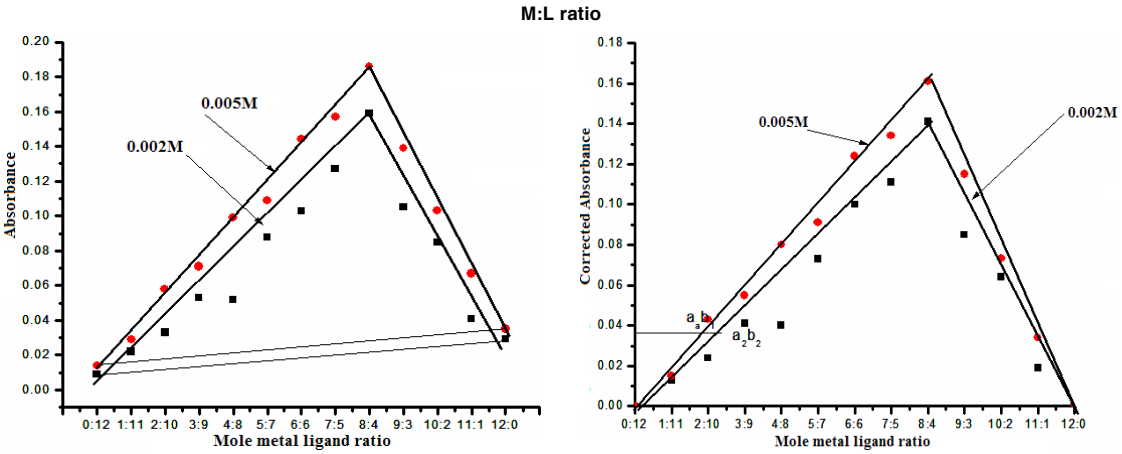


Fig. 1a and 1b-Graphs of Job's method of continuous variation to find out M:L ratio

Preparation

All the chemicals used in this study were of analytical grade.1.656 g. of "metformin" and 0.677 g metal salt were dissolved distinctly in 90% ethanol. Drug solution was added gradually to the metal salt with constant stirring (pH 5.5). A white coloured precipitate was obtained. The solution was reflux for 3 hours. After that the solution was cooled and

filtered. The complex formed was purified by ethanol and dried and finally weighed (Yield, 60%).

RESULT

Physico-chemical properties of complex

Molecular formula, Mol.wt, Colour, Yield, Stability constant, Free Energy Change, of the complex $[(C_4H_{10}N_5)(HgCl)_2]$, has been found to be 601.08, White, 55.63%,12.64; -17.19 respectively. Melting ponit: 276°C, C,7.98(7.65), H,1.66(2.05), N,11.64(11.50), Metal, 33.27(33.50), Cl,11.62(11.85).

Infra-red spectral studies

The Infrared spectra of prepared complex was obtained within the range 4000-400 cm^{-1}. Spectral bands have been assigned to their corresponding groups after comparing with the data available in literature[15-20]. Infrared spectra shows prominent peaks due to presence of ν(Metal-Nitrogen) 500±10 cm^{-1}, ν(C-N-C) 670±10 cm^{-1}, ν(-Nitrogen-Hydrogen bond) 1426±10 cm^{-1}, ν(-N-H) 1630±10 cm^{-1}, (amine salt) 2380±20 cm^{-1}, ν(C-H) 3020±20 cm^{-1}, ν(N-H bond) 3275±10 cm^{-1}, ν(N-H bond) 3520±10 cm^{-1}.

^{1}H-NMR Studies

^{1}H-NMR spectrum was obtained on a Bruker AM-200 Spectrometer by using d_6-Dimethylsulphoxide. A singlet has been found to be around δ=8.74 due to the presence of imide (-NH) proton of the ligand and spectral peak has been found to be less broad in complex, which confirms the loss of proton of imide -NH group through enolization. Assignment of complex as molecular formula $[(C_4H_{10}N_5)(HgCl)_2]$, (molecular weight=601) δ 7.207(s, amine salt), δ 6.788 (s,1H,Carbon-NH-Carbon, J = 2.014 Hz), δ 2.912 (s,6H,2 methyl group J = 3.134 Hz) δ 2.49(s), δ 3.369(s) Residual solvent & water of solvent of the DMSO-d_6 respectively. Literature also supports above spectra data for complex formation.[21-22]

Mass spectral studies

Molecular mass analysis also gives the exact mass of the complex. It gives information about the molecular assembly of coordination compounds[23-24]. The assignments of complex as molecular formula $[(C_4H_{10}N_5)(HgCl)_2]$,(Mol.Wt.=601), mass over charge ratio at 601 is due to $[(C_4H_{11}N_5)(HgCl)_2]^+$. or $(M_2L)^+$. Peak at 130 shows the presence of $[C_4H_{11}N5]^+$., base peak ion having 100% relative abundance at m/z 316 due to$[C_3H_6N_2HgCl]^+$., m/z 88 due to $[C_3H_9N_3]^+$ fragment ion.

X-Ray diffraction studies

From the literature, it is found to be that X-ray crystallography confirm the prepared complex and establishment of new bonds[25-29]. X-ray diffraction lines (Table 2 and Fig. 2) have been indexed and the unit cell parameters has been calculated. The data shows orthorhombic crystal structure and thus confirms the same structure for Hg(II)- complex. The Scherrer formula $Dhkl=\kappa\lambda/\beta hkl\ cos\theta$, has been used to calculate the particle size and found to be 6.31 micron. Porosity of the complex get calculate by formula $\frac{d_{true}-d_{obs}\times 100}{d_{tru}}$ and found to be 0.171 and unit cell volume is 14025.41 is find out by Volume(abcsinβ)Å where a,b and c are lattice parameters. Moreover, density of the complex has been calculated by $D=\frac{Weight}{Volume}$ is found 0.04419 g/cm^3 for synthesized complex. Space group for prepared complex is Pmmm and α=90°, β=90°, γ=90°.

Thermal analysis

Metformin complex was degraded in two degradation steps with the variation of temperature from 20-600°C. The first degradation is due to loss of water molecule and second step is due to the loss of organic constituents (Table 3). The complete Thermogravimetrically analysis is shown in Figure 3.

The thermoanalytical data have been obtained by F-C and S-W method are presented in Table 4 & 5. Kinetics methods reported in the literature have been used to study decomposition[30].

Freeman-Carroll[31] and Sharp-Wentworth.[32] were used to find out kinetic parameter (Table 4).

The straight-line have been obtained by equation derived by F.C method, which is in the form of $\frac{\Delta log\frac{dw}{dt}}{\Delta log\ Wr}=n-\frac{E_a}{2.303R}\cdot\frac{\Delta\frac{1}{T}}{\Delta log\ Wr}$ Where, $\frac{dw}{dt}$= rate of change of mass with time, Wr=Wc-W, Wc=Weight loss when the reaction complete, W=Total weight

loss with time 't', E_a=Activation energy, n=Order of reaction. Graph has been plotted by using the values of $\frac{\Delta log \frac{dw}{dT}}{\Delta \log Wr}$ and values of $\frac{\Delta \frac{1}{T}}{\Delta \log Wr}$ which gives a straight line from which slope and other parameters were calculated.

Various thermodynamic parameter like activation energy, Gibbs free energy and entropy of the synthesized complex were evaluated by using the S.W equation.

$\frac{\Delta log \frac{dc}{dT}}{(1-c)} = log \frac{A}{B} - \frac{Eq}{2.303\,R} \cdot \frac{1}{T}$, where, $\frac{dw}{dt}$ = Rate of change of weight loss with change of temperature. By plotting the graph between the values of $\frac{\Delta log \frac{dc}{dT}}{(1-c)}$ and values of $\frac{1}{T}$..

A straight line was obtained and various parameters were calculated[33-34].

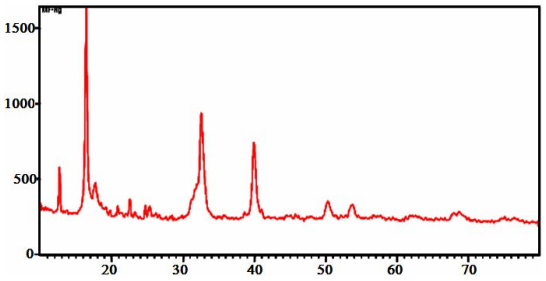


Fig. 2. X-ray difractogram of metformin-mercurycomplex

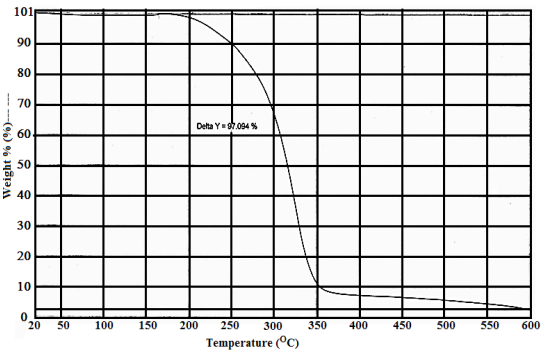
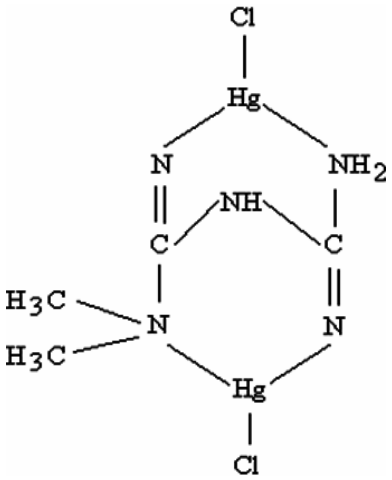


Fig. 3. TGA Curve of metformin-mercury complex



Scheme I. Proposed Structure (scheme-I) for metformin mercury complex

Table 2: X-ray measurement of complex

Pos. [°2Th.]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]	Area [cts*°2Th.]
12.7240	0.2175	6.95731	21.84	62.76
16.4612	0.2509	5.38524	100.00	331.62
17.7016	0.3346	5.01057	16.05	70.97
19.8348	0.2175	4.47624	2.59	7.46
20.8349	0.2007	4.26360	5.00	13.28
22.5976	0.2342	3.93484	9.06	28.03
24.6988	0.2509	3.60466	6.54	21.70
25.3489	0.3680	3.51367	5.84	28.41
32.5464	0.2676	2.75121	46.93	166.00
39.8827	0.3346	2.26043	35.12	155.29
50.4146	0.4349	1.81016	7.61	43.75

Table 3: TGA data of prepared complex

Complex	Decay Temperature (°C)	Percentage Wt. loss	Activation energy(Kj/mole) S.W.	F.C.	ΔS* (Kilo jule/mole)	ΔF (Kilo jule/mole)	Order of reaction(n)
$[(C_4H_{10}N_5)(HgCl)_2]$.	40-600	100	101.92	98.01	-77.80	-31.80	0.99

Table 4: Thermogravimetric analysis of prepared complex by S-W method

Temp. (°C)	°K Temp (T)	1000 T	% Mass Loss	Change in Wt. 'c' grams	1-c	dc\dt	log(dc/dt)	log (1-c)	log(dc/dt)/1-c	Weight % (%)
30	303	3.300330033	0.145	1.53526E-05	0.999984647	3.79845E-05	-4.420394158	-6.6676E-06	-4.420462023	99.855
50	323	3.095975232	0.366	3.87521E-05	0.999961248	6.1908E-05	-4.208252974	-1.68301E-05	-4.208416058	99.634
70	343	2.915451895	0.603	6.38456E-05	0.999936154	7.37825E-05	-4.132046763	-2.77287E-05	-4.132310593	99.397
90	363	2.754820937	0.727	7.69748E-05	0.999923025	7.58789E-05	-4.119878962	-3.3431E-05	-4.120196113	99.273
110	383	2.610966057	0.753	7.97276E-05	0.999920272	7.16119E-05	-4.145014573	-3.46267E-05	-4.145345072	99.247
130	403	2.481389578	0.714	7.55983E-05	0.999924402	7.0442E-05	-4.152168544	-3.28332E-05	-4.152482465	99.286
150	423	2.364066194	0.701	7.42219E-05	0.999925778	1.22768E-05	-4.910915314	-3.22353E-05	-4.911279839	99.299
170	443	2.257336343	0.151	1.59879E-05	0.999984012	7.5646E-05	-4.121214227	-6.9435E-06	-4.121280117	99.849
190	463	2.159827214	0.722	7.64454E-05	0.999923555	0.00024489	-3.611029211	-3.32011E-05	-3.611305279	99.278
210	483	2.070393375	2.349	0.000248712	0.999751288	0.000592139	-3.227576192	-0.000108028	-3.228379129	97.651
230	503	1.988071571	5.71	0.000604575	0.999395425	0.001025183	-2.989198562	-0.000262643	-2.991006849	94.29
250	523	1.912045889	9.968	0.001055412	0.998944588	0.001680167	-2.774647454	-0.000458602	-2.777578944	90.032
270	543	1.841620626	16.367	0.001732938	0.998267062	0.002630128	-2.580023112	-0.000753258	-2.584501893	83.633
290	563	1.776198934	25.659	0.002716775	0.997283225	0.004394131	-2.357126983	-0.001181486	-2.363548211	74.341
310	583	1.715265866	42.784	0.00452997	0.99547003	0.007219195	-2.141511235	-0.00197181	-2.151256362	57.216
330	603	1.658374793	70.322	0.007445693	0.992554307	0.008994178	-2.046038533	-0.003245722	-2.061386988	29.678
350	623	1.605136437	88.463	0.009366462	0.990633538	0.009256755	-2.033541236	-0.004086973	-2.052768415	11.537
370	643	1.555209953	91.85	0.009725078	0.990274922	0.009308811	-2.031105798	-0.004244219	-2.051052442	8.15
390	663	1.508295626	92.511	0.009795065	0.990204935	0.009337287	-2.029779283	-0.004274913	-2.049857772	7.489
410	683	1.464128843	92.813	0.00982704	0.99017296	0.009358241	-2.028805781	-0.004288938	-2.048940805	7.187
430	703	1.422475107	93.026	0.009849593	0.990150407	0.009389407	-2.027361852	-0.00429883	-2.047529181	6.974
450	723	1.383125864	93.331	0.009881886	0.990118114	0.009423156	-2.025803624	-0.004312994	-2.046022183	6.669
470	743	1.34589502	93.665	0.00991725	0.99008275	0.009456963	-2.024248293	-0.004328506	-2.044524353	6.335
490	763	1.31061599	94.001	0.009952826	0.990047174	0.009499548	-2.022297044	-0.004344111	-2.042626955	5.999
510	783	1.277139208	94.42	0.00999719	0.99000281	0.009548364	-2.020071021	-0.004363573	-2.040469986	5.58
530	803	1.245330012	94.902	0.010048224	0.989951776	-0.000502411	#NUM!	-0.004385961	#NUM!	5.098

Table 5: Thermogravimetric analysis of prepared complex by F.C. method

Temp. (°C)	% Mass Loss	Change in Wt. (gm.)	Time in Sec.	dw/dt	log dw/dt	wr= wc-w	log wr	T(K)	1/T(K^{-1})	(Log dt/dt) /(log wr	(1/T)/ Log wr	α= wt/wc	gα=1-(1-α) 1-n/1-n	T3 x 10^{-7}	gα/T3 x 10^{7}	1/T x 10^{-3}	log g (α)/T3	Weight % (%)
30	0.145	0.00002	90	0.000038	-4.420	0.01003	-1.9986	303	0.00330	2.212	-0.0017	0.0015	0.0015	2.7818	0.0000	3.3003	-202.4396	99.855
50	0.366	0.00004	150	0.000062	-4.208	0.01001	-1.9996	323	0.00310	2.105	-0.0015	0.0039	0.0039	3.3698	0.0000	3.0960	-143.2349	99.634
70	0.603	0.00006	210	0.000074	-4.132	0.00998	-2.0007	343	0.00292	2.065	-0.0015	0.0064	0.0064	4.0354	0.0000	2.9155	-108.8517	99.397
90	0.727	0.00008	270	0.000076	-4.120	0.00997	-2.0013	363	0.00275	2.059	-0.0014	0.0077	0.0077	4.7832	0.0000	2.7548	-88.4310	99.273
110	0.753	0.00008	330	0.000072	-4.145	0.00997	-2.0014	383	0.00261	2.071	-0.0013	0.0079	0.0080	5.6182	0.0000	2.6110	-74.7441	99.247
130	0.714	0.00008	390	0.000070	-4.152	0.00997	-2.0012	403	0.00248	2.075	-0.0012	0.0075	0.0076	6.5451	0.0000	2.4814	-64.8662	99.286
150	0.701	0.00007	450	0.000012	-4.911	0.00997	-2.0011	423	0.00236	2.454	-0.0012	0.0074	0.0074	7.5687	0.0000	2.3641	-56.3048	99.299
170	0.151	0.00002	510	0.000076	-4.121	0.01003	-1.9986	443	0.00226	2.062	-0.0011	0.0016	0.0016	8.6938	0.0000	2.2573	-64.3705	99.849
190	0.722	0.00008	570	0.000245	-3.611	0.00997	-2.0012	463	0.00216	1.804	-0.0011	0.0076	0.0076	9.9253	0.0000	2.1598	-42.6774	99.278
210	2.349	0.00025	630	0.000592	-3.228	0.00980	-2.0088	483	0.00207	1.607	-0.0010	0.0248	0.0251	11.2679	0.0001	2.0704	-28.4656	97.651
230	5.71	0.00060	690	0.001025	-2.989	0.00944	-2.0249	503	0.00199	1.476	-0.0010	0.0602	0.0620	12.7264	0.0003	1.9881	-19.0796	94.29
250	9.968	0.00106	750	0.001680	-2.775	0.00899	-2.0461	523	0.00191	1.356	-0.0009	0.1050	0.1108	14.3056	0.0008	1.9120	-13.5188	90.032
270	16.367	0.00173	810	0.002630	-2.580	0.00832	-2.0801	543	0.00184	1.240	-0.0009	0.1725	0.1889	16.0103	0.0020	1.8416	-9.2876	83.633
290	25.659	0.00272	870	0.004394	-2.357	0.00733	-2.1348	563	0.00178	1.104	-0.0008	0.2704	0.3142	17.8454	0.0048	1.7762	-6.0004	74.341
310	42.784	0.00453	930	0.007219	-2.142	0.00552	-2.2582	583	0.00172	0.948	-0.0008	0.4508	0.5958	19.8155	0.0136	1.7153	-2.8812	57.216
330	70.322	0.00745	990	0.008994	-2.046	0.00260	-2.5846	603	0.00166	0.792	-0.0006	0.7410	1.3328	21.9256	0.0450	1.6584	-0.0247	29.678
350	88.463	0.00937	1050	0.009257	-2.034	0.00068	-3.1664	623	0.00161	0.642	-0.0005	0.9322	2.6194	24.1804	0.1010	1.6051	1.6033	11.537
370	91.85	0.00973	1110	0.009309	-2.031	0.00032	-3.4906	643	0.00156	0.582	-0.0004	0.9678	3.3216	26.5848	0.1209	1.5552	1.9077	8.15
390	92.511	0.00980	1170	0.009337	-2.030	0.00025	-3.5966	663	0.00151	0.564	-0.0004	0.9748	3.5489	29.1434	0.1187	1.5083	1.8495	7.489
410	92.813	0.00983	1230	0.009358	-2.029	0.00022	-3.6552	683	0.00146	0.555	-0.0004	0.9780	3.6742	31.8612	0.1128	1.4641	1.7435	7.187
430	93.026	0.00985	1290	0.009389	-2.027	0.00020	-3.7020	703	0.00142	0.548	-0.0004	0.9802	3.7737	34.7429	0.1065	1.4225	1.6351	6.974
450	93.331	0.00988	1350	0.009423	-2.026	0.00017	-3.7790	723	0.00138	0.536	-0.0004	0.9834	3.9374	37.7933	0.1025	1.3831	1.5557	6.669
470	93.665	0.00992	1410	0.009457	-2.024	0.00013	-3.8828	743	0.00135	0.521	-0.0003	0.9870	4.1571	41.0172	0.1000	1.3459	1.4947	6.335
490	94.001	0.00995	1470	0.009500	-2.022	0.00010	-4.0205	763	0.00131	0.503	-0.0003	0.9905	4.4468	44.4195	0.0992	1.3106	1.4496	5.999
510	94.42	0.01000	1530	0.009548	-2.020	0.00005	-4.2921	783	0.00128	0.471	-0.0003	0.9949	5.0132	48.0049	0.1039	1.2771	1.4538	5.58

DISCUSSION

Scheme I is given for synthesized complex and confirmed by analytical, spectral and other methods. Job's method of continuous variation as modified by Turner and Anderson was conducted to confirm ligand-metal ratio which indicate the formation of complex in 1:2. Analytical data confirm the molecular formula $[(C_4H_{10}N_5)(HgCl)_2]$. The proposed structure was further confirmed by spectroscopic tools viz Infrared, Nuclear Magnetic Resonance, UV-Vis and mass studies etc. The Infrared spectral specification shows that coordinate bond is formed by the replacement of hydrogen. Moreover, nuclear magnetic resonance studies strongly support the formation of complex. Mass spectral results and values are further supporting the coordination of mercury with nitrogen atom of the drug. X-ray studies also confirms the complex formation and various parameters also have been find out. S.W and F-C methods have been used to determine E_a, Kinetic parameters viz. change of entropy, ΔF and order of reaction (n).

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Conflict of Interests

There is no conflict of interests for this article publication.

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