Synthesis, analytical, spectral and x-ray diffraction studies of
Co(II), Fe(II) and Mn(II) complexes with Glimepiride,[1-s[[p-[2-(3-ethyl-4-methyl-2-oxo-3-pyrroline-1carboxamido) ethyl]phenyl] sulphonyl]-3-(trans-4-methylcyclohexayl)urea an oral antidiabetic agent

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Abstract

Metal complexes of Glimepiride-an oral antidiabetic drug were prepared and characterized based on elemental analysis, FT-IR, NMR and powdered X -Ray Diffraction techniques. From elemental analysis data, the complexes were proposed to have general formulae $(C_{24}H_{31}N_4O_6S)_2Co.2H_2O$, $(C_{24}H_{31}N_4O_6S)_2Fe.2H_2O$ and $(C_{24}H_{31}N_4O_6S)_2Mn.2H_2O$. The IR spectra shows that Glimepiride is coordinated to metal ions in a neutral bidentate manner. From the IR spectra and XRD-spectra, it is found that the geometrical structures of these complexes are octahedral. The XRD data was used to calculate various parameters like crystal system, volume, density, porosity, particle size etc. which shows that the complexes of Co(II), Fe(II) and Mn(II) have octahedral structure.

Key words: *Crystal structure, IR, Glimepiride, , metal complex, NMR and X-ray diffration.*

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1. INTRODUCTION

Diabetes mellitus, is a prolong and the most common metabolic disease, which is only controllable by taking medicines continually but it is not curable, therefore patient should continue the therapy for life. NIDDM or type II diabetic patients can vary considerably in their ability to secrete insulin. The most widely used hypoglycemic drugs for treating type II (non-insulin-dependent) *diabetes mellitus* are sulfonyl-urea derivatives. Glimepiride a sulfonyl-urea derivative is known to improve hypoglycemic effect. It is [1-[[p-[2-(3-ethyl-4-methyl-2-oxo-3-pyrroline1carboxamido) ethyl] phenyl] sulphonyl]-3- (trans-4-methylcyclohexayl) urea having molecular formula $C_{24}H_{33}N_4O_6S$. It works by stimulating the production and release of insulin from the pancreas. Glimepiride is extensively metabolized in the liver and readily absorbed from the gastrointestinal tract. The metabolites having no significant hypoglycemic effects.

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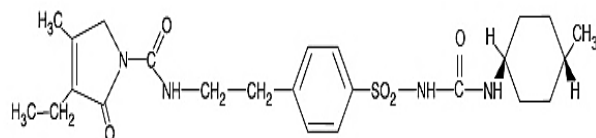
Polyfunctional ring compounds and synthesis of their metal complexes which have various biological activities and include hetero atom, have been formed in organic synthesis and coordination chemistry [1],[2],[3,4],[5],[6].Glimepiride is bisubstituted urea derivative which can exist in keto and enolic forms when dissolved in an organic solvent and react with various metal ions to form intensely colored metal complexes that provide the basis for their use as a sensitive reagent. Many transition and inner transition metal complexes have been synthesized for analytical and commercial applications many of medicinal use [7],[8],[9].

The synthesis and characterization of Glimepiride with new metal complexes is of great importance for understanding the drug–metal ion interaction and for their potential pharmacological use. Literature survey reveals that the transition and inner transition metal complexes generally shows tetrahedral, octahedral geometry [10],[11]. The synthesis and characterization of the glimepiride metal complexes is reported in this paper. Different spectroscopic techniques such as infrared spectroscopy, ^{1}H-NMR, ele-

mental analysis and X-Ray diffraction techniques have been used for their characterization.

Structure of Glimepiride

2. EXPERIMENT

All the chemicals used for the preparation of complexes are of Hi-media, AR grade and E-Merck quality. Metal complexes are synthesized by adding metal salt solution in appropriate solvent to the solution of the ligand. The mixture was refluxed for 3-4 hours, whereby the precipitate of metal complexes was obtained. It was filtered, washed and dried in vacuum desiccators. All selected metals form 1:2 complexes with Glimepiride which was further confirmed by Job's method [12] of continuous variation as modified by Turner and Anderson [13].

2.1 ligand-metal ratio
(a) Mono-Variation method

The ligand-metal ratio of complex formation was determined by conductometric titration using mono-variation method on Systronics coductivity meter using dip type electrode. . Conductivity water was obtained by distilling laboratory de-ionized water over potassium permanganate. Pure Glimepiride m.p. 206°C, 0.005 M, was diluted to 100 ml as required and titrated conductometrically against metal salt solution at 30±1°C. Results were plotted in the form of a graph which indicate ligand metal ratio as 2:1 (L_2M).

(b)Job's method of continuous variation (as modified by Turner and Anderson)

0.002 M and 0.005 M solutions of ligand glimepiride and metal salt were prepared in DMF and ethanol respectively. The solution of metal salt and ligand were mixed in varying proportions as under:

Metal (ml) 0 1 2 3 4 5 6 7 8 9 10 11 12

Ligand (ml) 12 11 10 9 8 7 6 5 4 3 2 1 0

pH of the solution was adjusted to 6.5. The absorbance was measured at 630 nm. From these values the stability constant (log k) and free energy (ΔF), were also calculated (Irving and Rossotti). The absorbance was recorded in table 1 and 2 and job's plot is given as fig. 1a, 1b, fig. 2a, 2b and fig.3a, 3b. It is evident from the graph that absorbance increases up to molar composition of metal to the ligand and after that it decreases, indicating 1:2 stoichiometry of the complex.

2.2 Synthesis of metal complexes

Metal complexes were 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 form 1:2 complexes with glimepiride, were confirmed by Job's method of continuous variation as modified by Turner   and   Anderson[13].

Table 1   **GLIMEPIRIDE WITH COBALTOUS CHLORIDE**

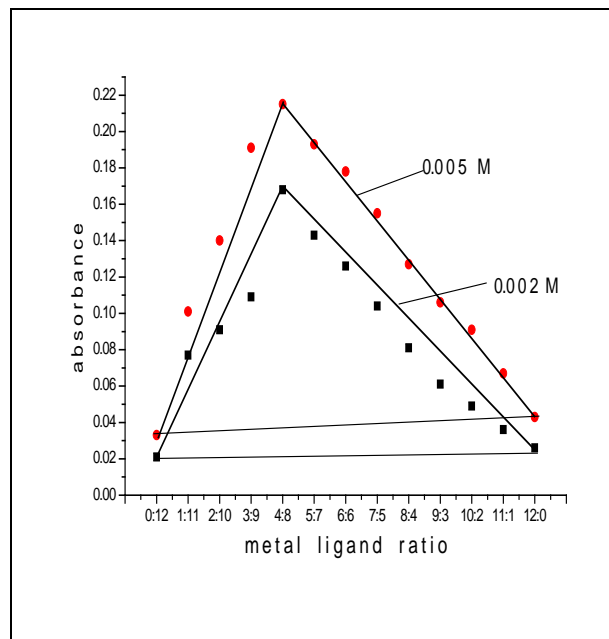Glimepiride-0.002M, 0.005 M   Cobaltous chlorides - 0.002 M. 0.005M
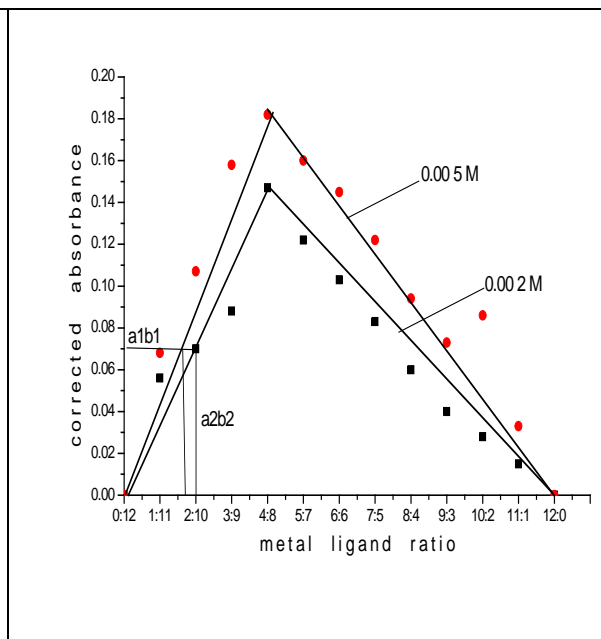
Solvent: Ethanol   Temperature: 30±1^{0}C

Wavelength: 630 nm   pH: 5.9

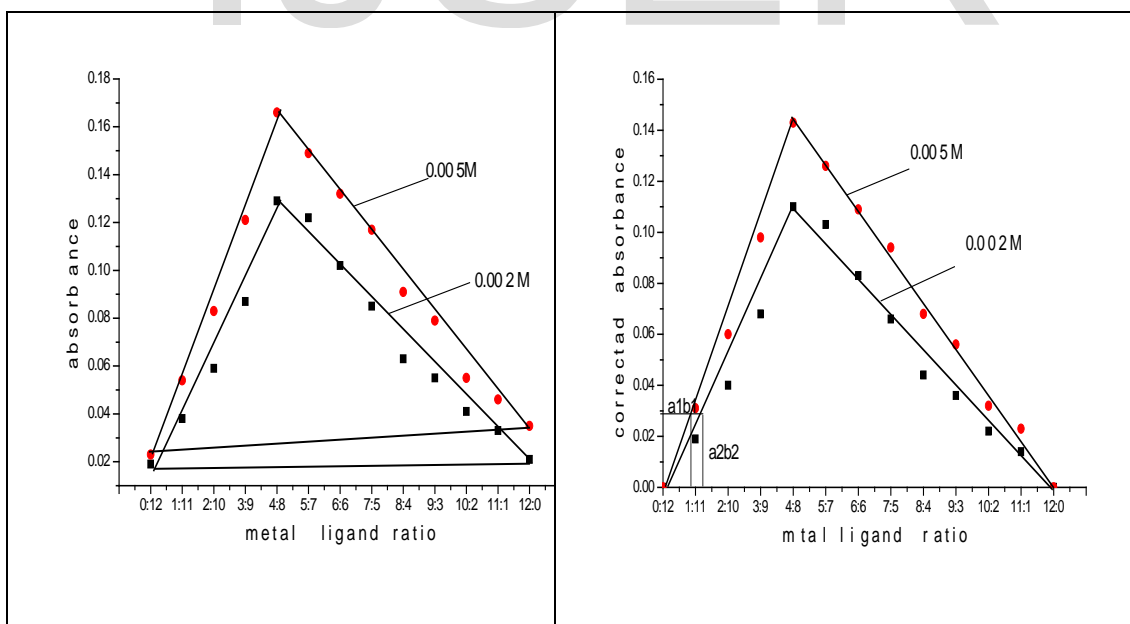| S.No.	Metal :Ligand Ratio	Absorbance		Corrected Absorbance	
		0.002M	.005M	0.002M	0.005M
0	0:12	0.021	0.042	0.00	0.00
1	1:11	0.048	0.079	0.027	0.037
2	2:10	0.071	0.097	0.05	0.095
3	3:9	0.084	0.124	0.063	0.082
4	4:8	0.119	0.186	0.098	0.144
5	5:7	0.099	0.169	0.078	0.127
6	6:6	0.082	0.143	0.061	0.101
7	7:5	0.062	0.127	0.041	0.085
8	8:4	0.053	0.109	0.032	0.067
9	9:3	0.047	0.087	0.026	0.045
10	10:2	0.033	0.064	0.012	0.022
11	11:1	0.029	0.044	0.008	0.006
12	12:0	0.00	0.00	0.00	0.00

Fig: 1a   **Fig: 1b**

Table 2 **GLIMEPIRIDE WITH MANGANESE CHLORIDE**

Glimepiride-0.002M, 0.005M   Manganese chloride-0.002 M,0.005 M

Solvent: Ethanol   Temp.: 30 ± 1^0C

Wavelength: 630 nm   pH: 5.9

S.No.	Metal :Ligand Ratio	Absorbance		Corrected Absorbance	
		0.002M	.005M	0.002M	0.005M
0	0:12	0.019	0.023	0.00	0.00
1	1:11	0.038	0.054	0.019	0.031
2	2:10	0.059	0.083	0.04	0.06
3	3:9	0.087	0.121	0.068	0.098
4	4:8	0.129	0.166	0.11	0.143
5	5:7	0.122	0.149	0.103	0.126
6	6:6	0.102	0.132	0.083	0.109
7	7:5	0.085	0.117	0.066	0.094
8	8:4	0.063	0.091	0.044	0.068
9	9:3	0.055	0.079	0.036	0.056
10	10:2	0.041	0.055	0.022	0.032
11	11:1	0.033	0.046	0.014	0.023
12	12:0	0.00	0.00	0.00	0.00

Fig: 2a

Fig: 2b

Table 3   GLIMEPIRIDE WITH FERROUS SULPHATE

Glimepiride-0.002M, 0.005M	Ferrous Sulphate- 0.002M.0.005M
Solvent: Ethyl alcohol	Temperature: 30±1^{0}C
Wavelength: 630 nm	pH: 5.9

S.No.	Metal :Ligand Ratio	Absorbance		Corrected Absorbance	
		0.002M	.005M	0.002M	0.005M
0	0:12	0.01	0.021	0.00	0.00
1	1:11	0.031	0.053	0.021	0.032
2	2:10	0.058	0.079	0.048	0.058
3	3:9	0.084	0.097	0.074	0.076
4	4:8	0.114	0.153	0.104	0.132
5	5:7	0.097	0.129	0.087	0.108
6	6:6	0.074	0.104	0.064	0.083
7	7:5	0.059	0.086	0.049	0.065
8	8:4	0.046	0.062	0.036	0.041
9	9:3	0.037	0.042	0.027	0.021
10	10:2	0.029	0.033	0.019	0.012
11	11:1	0.026	0.03	0.016	0.03
12	12:0	0.00	0.00	0.00	0.00
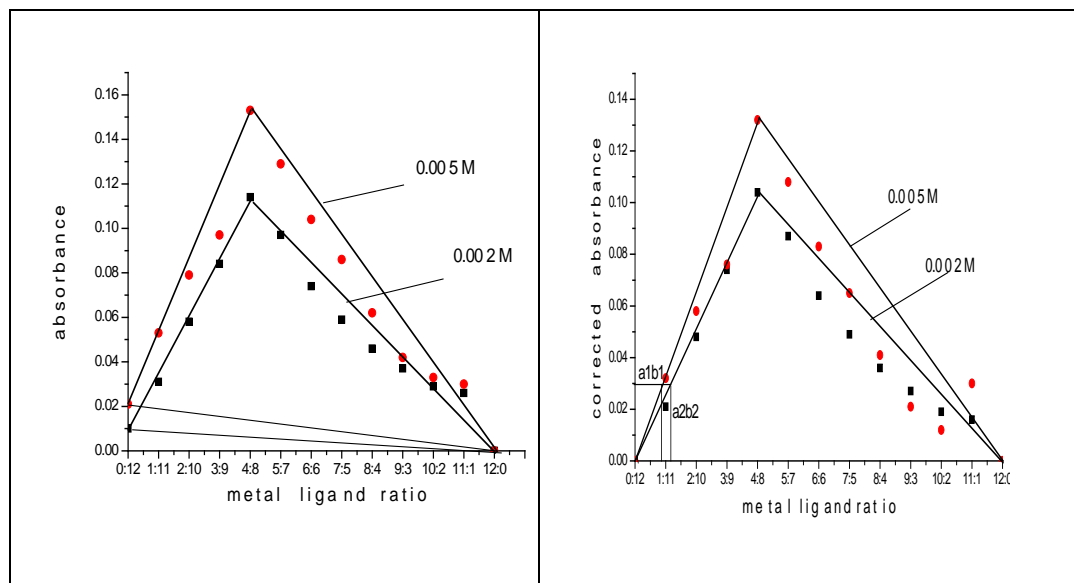
Fig: 3a

Fig: 3b

The elemental analysis of the isolated complexes was carried out using Elementer Vario EL III Analyzer at STIC Kerala, India. The IR spectrum of the ligand as well as of

3. RESULTS

the complex was recorded on Perkin Elmer Spectrometer at CDRI, Lucknow and ^{1}H-NMR spectra of the ligand and isolated complex was recorded on a Bruker DRX-300 Spec

trometer at CDRI Lucknow and $CDCl_3$ was used as a solvent and X-Ray diffractrogram from Punjab University, Chandigarh. From stoichiometry and analytical data, the composition of the complex comes out to be $((C_{24}H_{31}N_4O_6S)_2M. 2H_2O$, which favours 2:1 (L_2M) ratio. The tentative structure (I) has been assigned to complex on the basis of analytical data and IR, NMR and X-ray

3.1 Table 4: Physico-chemical characteristics of Glimepiride complexes

S. No	Composition of metal complex	Metal ligand ratio	%Yield	M.P.(oC)	Log k	-ΔF
1	(C24H31N4O6S)2Co.2H2O	1:2	54	210	11.52	-16.236
2	(C24H31N4O6S)2Mn.2H2O	1:2	61	216	9.821	-13.842
3	(C24H31N4O6S)2Fe.2H2O	1:2	64	211	10.251	-14.445

3.2 Table 5: Analytical data of Glimepiride complexes

S. No.	Metal Complex	%C	%H	%N	%S	% metal
1	$(C_{24}H_{31}N_4O_6S)_2Co.2H_2O$	48.24 (49.70)	6.14 (4.86)	11.36 (7.75)	9.15 (5.80)	16.68 (17.33)
2	$(C_{24}H_{31}N_4O_6S)_2Mn.2H_2O$	44.31 (42.70)	5.62 (4.86)	11.10 (9.70)	7.91 (7.21)	18.08 (17.96)
3	$(C_{24}H_{31}N_4O_6S)_2Fe.2H_2O$	44.13 (42.80)	5.74 (4.86)	11.12 (9.90)	7.82 (6.77)	8.06 (7.76)

3.3 Infrared spectral studies of the complexes

IR spectra [14],[15],of the ligand and the isolated complexes were recorded in the range 4000-450cm^{-1}. Assignments of the infra-red spectral bands are based on literature.
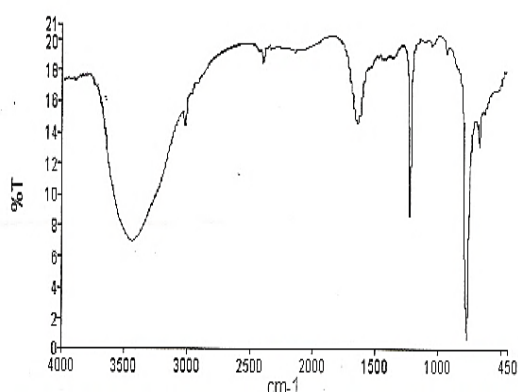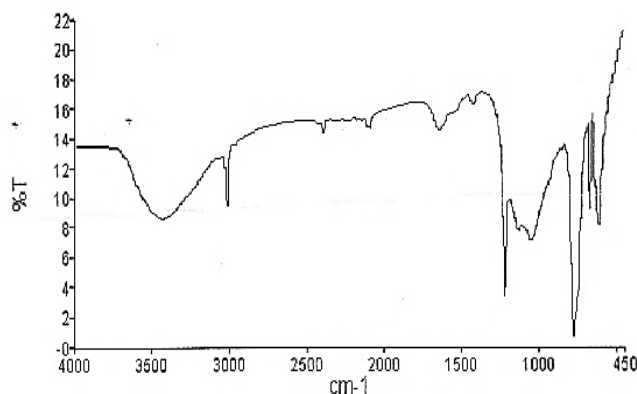

Fig.4 FT-IR of Glimepiride-Co complex

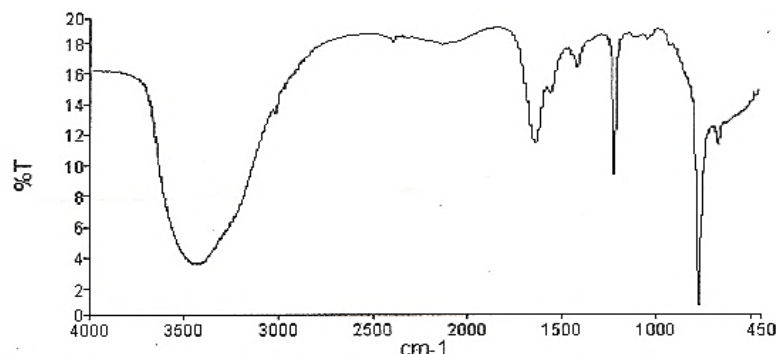Fig.5 FT-IR of Glimepiride-Fe complex

Fig.6 FT-IR of Glimepiride-Mn complex

The proposed structure for the isolated complex is also supported by IR absorption bands and characterized by the absorption of carbonyl (C=O) group at 1703 cm^{-1},1635 cm^{-1},1637 cm^{-1} and 1642 cm^{-1} in the ligand and its Co(II), Mn(II)

and Fe(II) complexes respectively. Also the NH group observed at 3288 cm^{-1} in the ligand glimepiride just disappeared in all the three metal complexes. The next IR band of structural significance of the ligand appears at 1152cm^{-1} which may be assigned to -SO_2N which got shifted downward at1130 cm^{-1} in manganese and cobalt Glimepiride complexes while in Iron-Glimepiride complex it just appears at 1129cm^{-1} respectively. The chelate ring frequencies are observed at 1050±10 cm^{-1}.The shift of the C=O and S=O by decreased frequencies in the complex indicates that these groups are involved in the complexation. The linkage through amide -O- and sulphone –O atom was further supported by the appearance of a band in the far IR region at 670 cm^{-1}in the Co(II),669 cm^{-1}Mn(II) and   668cm^{-1}in Fe(II) complexes that may be assignable   to M-O frequency[16].

Additional band in the complex region of Mn(II),Fe(II) and Co(II) at 1447cm^{-1}, 1417cm^{-1} and 1442cm^{-1} compared with IR

spectra of the free ligand has tentatively been assigned to six member enolic ring structure modified to chelate ring formation in the complexes[17],[18]. A strong band in the region of 3560cm^{-1}in Co, 3525cm^{-1} in Fe complex and at 3555cm^{-1} in Mn-glimepiride complex shows the presence of co-ordinated water molecule. The proposed structure for the isolated complex is also supported by IR absorption and has been reported by Rao, Bellamy and Weissberger[19],[20],[21].

3.4 H^1-NMR Studies

We have observed imides (NH) proton around (δ8.35) in the spectrum of the ligand that has disappeared in the spectra of the complexes molecule due to formation of M-O bond. This also confirms the deprotonation of imide NH group through enolisation.

Table 6: H^{1}NMR Assignments of Glimepiride and its complexes

Ligand / Complexes	Assignment
Pure Drug glimepiride $C_{24}H_{33}N_4O_6S$	δ1.11-1.45(sCH$_2$), δ2.92-2.87(s, CH$_3$ group attached to benzene)δ1.71-1.96(sCH$_2$),δ3.01-3.16(dNH),δ3.78(O-CH),δ 6.44(aromatic) , δ7.32-7.44(d, benzene), δ7.877.96(aromatic), δ8.36-8.351(s, 1H, NHCO), δ10.308 (ketonic CO group)
$(C_{24}H_{31}N_4O_6S)_2Co2H_2O$	δ1.601-1.007(s,CH$_3$),δ 2.503(s,CH$_3$gp attached to benzene), δ3.354(s,solvent),
$(C_{24}H_{31}N_4O_6S)_2Fe2H_2O$	δ0.455(s,CH$_3$), δ1.11-1.44(d,CH$_2$), δ1.71-1.96(q,CH$_3$)), δ2.731(s,CH$_3$gp attached to benzene), δ2.820-2.883(q,3H,NH), δ3.314(s,solvent), 4.022(s,2H,NH), 7.446(d,benzene), 8.366(d, aromatic)
$(C_{24}H_{31}N_4O_6S)_2Mn2H_2O$	δ0.851(s. CH$_3$), δ1.294(s,CH$_3$), δ1.488-1.557(q,CH$_3$), δ 2.501(s,CH$_3$gp attached to benzene), δ3.322(s,solvent),δ 4.027(s,2H,NH)

3.5 X-ray diffraction study of Glimepiride complexes

The X-ray diffraction of Co (II), Mn (II) and Fe (II) complexes with glimepiride were obtained and summarized in following tables. All reflections has been indexed for h, k, l values using reported literature[22],[23],[24] and full proof suit XRD software v.2.0by using foolproof suite XRD software the d-values of metal complexes were obtained. The X-ray diffraction pattern of Co (II), Mn(II) and Fe (II) complexes has been determined 2θ range from 14.007 to 78.9473°, Diffractogram (Fig-7, 8, 9) and data has been summarized in the following tables:

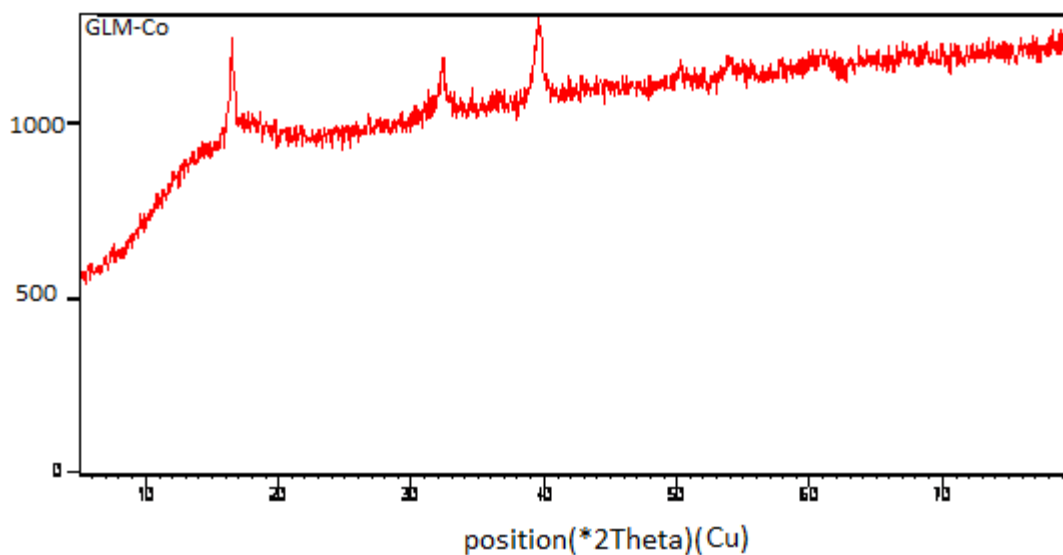Fig. 7: X-ray diffractrogram of GLM-Co Complex

Table 7: Cell data and crystal parameter of GLM-Co complex

a(Å) = 21.243
b(Å) = 24.242
c(Å) = 27.134
α=90°, β=89.4°, γ=90°
Particle size = 7.694microns
Standard deviation = 0.0032%
Space group = Pmmm

Volume Å= 13968.661 cm^3
Dcal=1.85432g/cm^3
Dobs= 1.81431g/cm^3
Density = 0.08472 gm/cm^3
Porosity (%) = 2.157%
Crystal system = Monoclinic
Mass of unit cell=1.9650×10^{-25}

2θ	I/I_0	$D_{(obs)}$	$D_{(cal)}$	h	k	l
14.0017	8.81	6.32518	6.27742	3	0	2
16.5081	67.17	5.37004	5.35343	1	4	2
32.3607	35.90	2.76657	2.76595	4	6	5
39.5899	59.14	2.27647	2.27436	5	9	0
50.2873	100.00	1.81444	1.81431	11	1	5
53.9992	89.02	1.69816	1.69710	4	12	7
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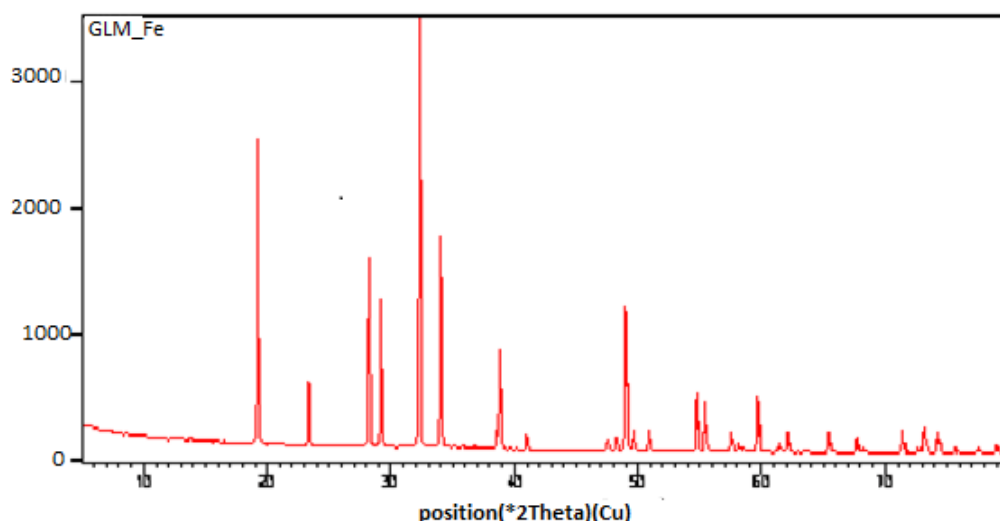Fig. 8: X-ray diffractrogram of GLM-Fe Complex

Table 8: Cell data and crystal parameter of GLM-Fe complex

a(Å) = 21.40260 Volume A=14205.604 cm^3
b(Å) = 24.21780 D cal=2.76891g/cm^3
c(Å) = 27.70890 Dobs= 2.76888g/cm^3
α=90°, β=89.4°, γ=90° Density = 0.0818gm/cm^3
Particle size = 9.89 microns Porosity (%) = 1.083%
Standard deviation = 0.038% Crystal system = Monoclinic
Space group = Pmmm Mass of unit cell=1.952×10^{-25}

| 2θ	I/I0	D(obs)	D(cal)	h	k	l
19.2125	73.55	4.61599	4.61619	3	4	0
23.3264	15.40	3.81038	3.81319	1	6	2
28.1963	44.55	3.16236	3.16493	2	4	7
29.1512	34.68	3.06090	3.06504	0	7	6
32.3051	100.00	2.76891	2.76888	1	6	8
34.0269	49.62	2.63263	2.62851	1	4	10
35.8330	0.54	2.50397	2.50228	1	4	10
40.9501	3.54	2.20212	2.20162	8	6	2
47.5074	2.94	1.91233	1.91212	3	8	10
48.1981	3.75	1.88653	1.88649	10	6	1
49.6365	5.21	1.83518	1.83513	1	1	15
50.8675	5.11	1.79362	1.79337	4	10	9
52.8642	0.45	1.73048	1.73056	7	2	13
54.7365	14.17	1.67563	1.67553	3	11	10
55.3883	12.06	1.65744	1.65758	7	1	14
57.5222	4.88	1.60092	1.60101	11	5	8
58.1333	2.11	1.58554	1.58558	3	1	17
58.4667	1.43	1.57729	1.57756	8	2	14
59.6532	13.27	1.54872	1.54862	0	7	16
61.4272	2.57	1.50818	1.50824	14	0	3
62.0922	5.22	1.49362	1.49366	5	13	9
63.5900	1.03	1.46200	1.46199	3	16	3
65.4150	5.05	1.42555	1.42551	2	16	6
67.6842	3.59	1.38318	1.38318	0	1	20
68.2238	0.95	1.37355	1.37346	10	11	9
71.3860	5.37	1.32027	1.32048	4	12	15
72.6097	1.46	1.30100	1.30105	13	1	13
73.1149	6.32	1.29325	1.29329	16	4	3
74.6626	5.31	1.27671	1.27655	10	15	3
75.6626	1.71	1.25591	1.25585	16	5	5
77.4692	1.42	1.23107	1.23116	2	2	1
78.9473	2.45	1.21169	1.21172	4	11	6
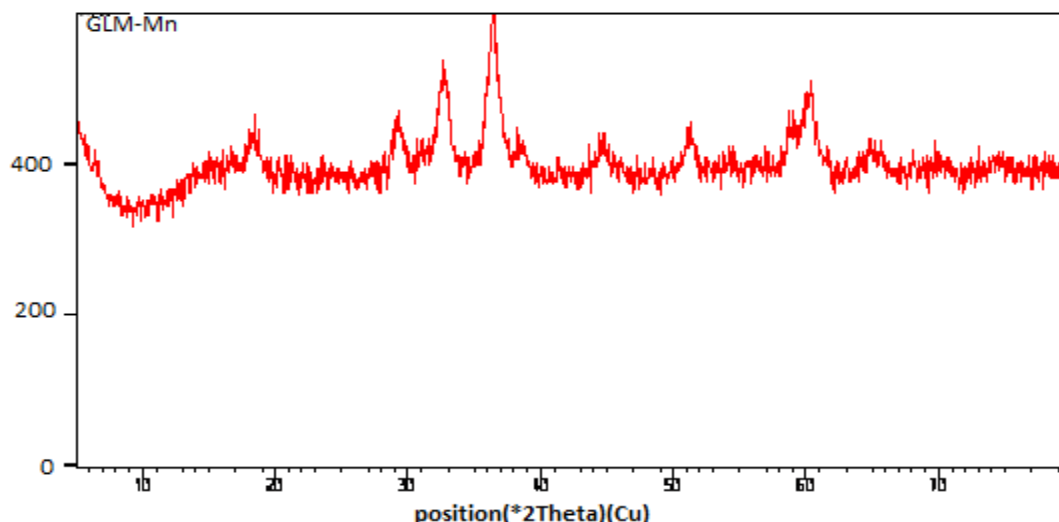
Fig. 9: X-ray diffractrogram of GLM-Mn Complex

**Table 9: Cell data and crystal parameter of GLM-Mn complex**

a(Å) = 21.2798   Volume Å= 14205.604 cm^3
b(Å) = 24.2431   D cal=2.46855g/cm^3
c(Å) = 27.5362   Dobs= 2.47068g/cm^3
α =90°, β =89.4°, γ=90°   Density = 0.08771gm/cm^3
Particle size = 4.12microns   Porosity (%) = 0.086%
Standard deviation = 0.026%   Crystal system = Monoclinic
Space group = Pmmm   Mass of unit cell=2.0156×10^{-25}

2θ	I/I$_0$	D$_{(ods)}$	D$_{(cal)}$	h	k	l
18.3427	25.74	4.83688	4.84051	3	1	4
29.2588	33.99	3.05242	3.05129	6	2	4
32.7446	61.53	2.73501	2.65359	3	3	9
36.3638	100.00	2.44855	2.47068	5	8	0
51.2428	24.42	1.78283	1.78149	2	7	13
58.8296	24.91	1.56972	1.56972	8	2	14
60.1321	53.15	1.53337	1.53764	0	5	11

X-ray diffraction studies also confirm the complexes and formation of new bonds. glimepiride showed sharp peaks at the diffraction angle of 2θ at 13.52°, 18.23°, and 21.18° with peak intensities of 1216.66, 1293, and 1667.11, respectively, suggesting the crystalline nature of drug. Glimepiride shows a number of peaks while no. of peaks in $(C_{24}H_{31}N_4O_6S)_2Co.2H_2O$,$(C_{24}H_{31}N_4O_6S)_2Fe.2H_2O$ and $(C_{24}H_{31}N_4O_6S)_2Mn.2H_2O$ are 6, 7 and 37 respectively . Thus indicating that complexes formed are a well kit one moreover, in the X-ray pattern of Glimepiride-metal complexes all the reflections present are new ones and the patterns are fairly strong. On com

paring the pattern obtained with available Literature, it is evident that the pattern is not in good agreement with available information and thus confirms the formation of totally new compounds. The X-ray pattern have been indexed by using computer Software (FPSUIT 2.0V) and applying interactive trial and error methods keeping in mind the characteristics of the various symmetry system, till a good fit was obtained between the observed and the calculated 2Sinθ value. The unit cell parameters were calculated from the indexed data, from cell data and crystal lattice parameters of system. $(GLM)_2Co.2H_2O$ and $(GLM)_2Mn.2H_2O$ and $(GLM)_2Fe2H_2O$ complexes attributed to Monoclinic crystal system.

R1 =

R2 =
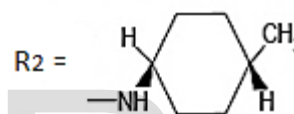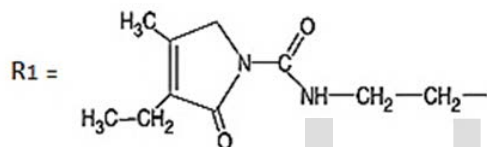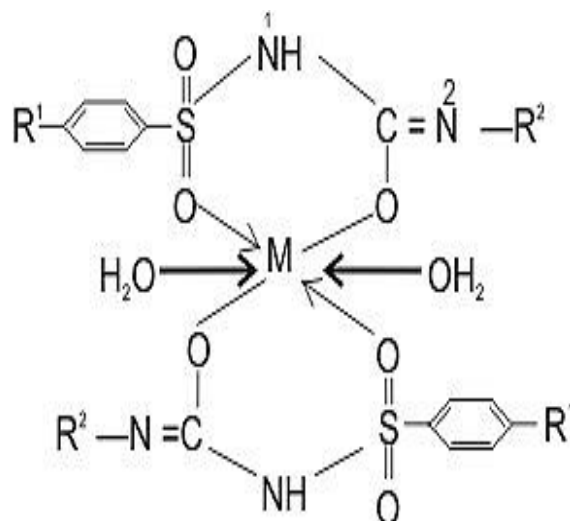
M=Co, Mn, F

Proposed Structure 1

DISCUSSION

For supporting the proposed structure of Co(II), Fe(II) and Mn(II) complexes of glimepiride, initially Job's method of continuous variation as modified by Turner and Anderson (table 1, 2, 3 and fig.1 a, b, fig 2a & b and fig 3a & b) was conducted which indicates 2:1 ligand metal ratio of the complexes. Moreover, stability constant and free energy change was also calculated. Analytical data agrees to the molecular formula $(C_{24}H_{31}N_4O_6S)_2Co.2H_2O$, $(C_{24}H_{31}N_4O_6S)_2Fe.2H_2O$ and $(C_{24}H_{31}N_4O_6S)_2Mn.2H_2O$. For determining the proposed structure on the basis of stoichiometry and analyzing the complexes, advanced Spectrophotometric methods like IR, NMR (table 6 and fig 4, 5 ,6) were conducted which suggest the co-ordination of the metal atom with enolic oxygen of the carbonyl group on one side and oxygen of the sulphonyl group from the other side. These observations were further supported from the IR and NMR values of M-O and the appearance of N-H linkage in NMR. A detailed study of X-ray diffraction (table 7,8,9) also supports the complex formation and various values like particle size, porosity, and volume of unit cell, density as well as the crystal system was evaluated and discussed. Moreover looking to the higher electronegativity of the oxygen as compared to nitrogen, N^2 enolisation is strongly supported.

CONCLUSION

The differences in melting point of all these complexes as compared to glimepiride suggested that a new product was formed. The shift peaks in IR region as well as new signals around at δ 3.00 due to deshielding of N-bearing proton in H^{1}NMR further confirmed the drug metal complexation. The final proof of metal incorporation in glimepiride was obtained by the estimating of metals from these complexes by Atomic absorption spectroscopy.

REFERENCE

[1] S.N. Pandeya, D. Sriram, G. Nath and E.De.Clereq, *Arzneim-forsch/Drug Re.*, 50:55 (2000).

[2] B.S. Hollo, K.A. Poojary and B. Kollurya, II, *.Farmaco* (1996), 793

[3] M. Kidwai, P. Sapra, P. Mishra; R.K. Saxena and M. Singh Bioorg. *Med. Chem*. 9, (2001), 217

[4] M. Kumar and S.Ahmad, *Orient J,Chem*, 26(4),1455-1459 (2010).

[5] H.K. Reddy, D.P. Seshaiah and A.V.Reddy, *Orient. J. Chem*, 27(3), (2011), 1125-1131

[6] B.H. Mehta and S.A. Dagaonkar., Proceeding of 13th, Australia Symposium on analytical chemistry, Darwin Northern, Australia (1995).

[7] R.N. Pandey, D.P. Singh, Priya and R.K.Singh, *Orient .J. Chem*, 2**6**(4), (2010), 1513-1516

[8] K.Jamuna., D. Harikishore., B.N.Kumar and D.K.Ramana., *Orient.J.Chem.*, 27(3), (2011), 1141-1147

[9] Bal Krishan and Iqbal, S.A, *Orient.J.Chem*, 28(4,) (2012), 1883-1888

[10] Sharma, S, Iqbal, S.A, and Budhani P, *Orient. J. Chem*, 26(1) (2010), 287-300

[11] Sharma, R.N, Sharma, K.P., and Dixit, S.N, *Orient. J.Chem*, 26(1), (2010), 283-86

[12] Job, P, Ann. Chim, ,10, (1928), 113

[13] Turner, S.E. and Anderson, R.C, *J. Am. Chem. Soc,* 71 (1949), 912

[14] Chohan, Zahid H. Praveen M. and Ghaffer A., Synth. React. Inorg. Met. Org.Chem 28, (1998), 1973.

[15] A. Scott, Standard Methods of Chemical Analysis, Van Nostrand, p. 634 (1960).

[16] F.A. Cotton, Modern Co-ordination Chemistry, *Inter Science Pub.Ed.* (1963).

[17] K. Nakamotto Infrared spectra of Inorganic and Co-ordination compounds John Wiley and Son's New York Ed. (1963).

[18] Weissberger, A., "Chemical Application of Spectroscopy" Vol. IX, Inter Sci. Pub. N. Y, (1956),

[19] C.N. Rao., "Chemical Applications of Infra-red Spectroscopy", Academic Press New York, (1963).

[20] L. J. Bellamy, "The Infra-red Spectra of complex molecules", Methuen and Co. ltd, London, (1964)

[21] Khalil, O.M., and Reefat, H.M., *Orient. J. Chem*, 27(9): 1581-1590 (2011).

[22] Bhadja, D.R. and Parsania, P.H, *Orient. J. Chem*, 27(4): 1699-1707 (2011).