

Infra Red Spectral and X-ray Diffraction Study of Fe (II), Co(II), Cu (II), Metal Chelates with N¹-(5, 6-dimethoxypyrimidin-4-yl) Sulphanilamide

Jitendra H. Deshmukh*¹ and M. N. Deshpande²

¹Department of chemistry, Yeshwant Mahavidyalaya, Nanded-431602

²Head P.G. Department of chemistry, NES, Science College, Nanded-4316053

*E-mail: jitendra_deshmukh25@rediffmail.com

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ABSTRACT

N¹-(5, 6-dimethoxypyrimidin-4-yl) sulphanilamide (DMPS) forms chelates having general formula [Fe (DMPS)₂ Cl₂] H₂O, [Co (DMPS)Cl₂2H₂O] and [Cu(DMPS)ClH₂O]Cl. Infra red, electronic and X-ray diffraction study of Fe(II), Co(II), Cu(II) metal chelates.

Keywords: N¹-(5,6-dimethoxypyrimidin-4-yl)sulphanilamide, Infra red, electronic and X-ray diffraction study

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INTRODUCTION

Literature survey reveals that complexes of metal salts are more potent and less toxic in many cases as compared to the parent drug[1]. These complexes are found to be interesting due to their biological application like antifungal[2], antibacterial[3] activity. Large number of drugs has been used to synthesize the complexes with many metals with a view to enhance their therapeutic action[4-6]. In continuation of our studies on the metal complexes of N¹-(5,6 dimethoxypyrimidin-4-yl) sulphanilamide we report here Infra red, electronic and X-ray diffraction study of Fe(II), Co(II), Cu(II) metal chelates.

EXPERIMENTAL

All the chemicals used in the present study were from BDH grade. Metal salts and solvents were used of reagent grade. Metal ion solution and ligand solution in appropriate as desired and pH of resulting mixture were maintained about 6.8 to 7.1 by putting alcoholic ammonia solution. The reaction mixture was refluxed for three hours by keeping the round bottom flask on steam bath, The solid thus separated on cooling was filtered, washed and dried in vacuum desiccators over anhydrous CaCl₂. The detailed preparation of complexes were discussed in earlier papers.

RESULTS AND DISCUSSION

Infrared Spectral study

Important absorption frequencies of ligand and complexes along with their assignment are presented in the table-1. The assignments are well supported by literature survey. The comparison of IR spectrum data of Fe (II), Co (II) and Cu (II) complexes with ligand N¹-(5, 6-dimethoxypyrimidin-4-yl) sulphanilamide helps in determining bonding pattern in the complexes.

Table-1: Infrared spectral data of the ligand (DMPS) and their metal complexes

Compound	v(NH ₂)	v(NH)	v(OCH ₃)	v(M-Cl)	v(M-N)	v(M-O)
DMPS	3238	3216	1010	-	-	-
[Fe(DMPS) ₂ Cl ₂] H ₂ O	3296	3256	1010	340	459	553
[Co(DMPS) Cl ₂ 2H ₂ O]	3334	3248	1010	317	417	519
[Cu (DMPS) Cl H ₂ O] Cl	3200- 3449	3200- 3449	1010	299	432	502

IR spectra of ligand shows strong bond in the region 3238 cm⁻¹ which is assigned to v(NH₂) Stretching vibration[7]. Ligand shows band at 3116 cm⁻¹ assigned to v(NH) stretching[8]. Band at 1010 cm⁻¹ is due presence of (OCH₃) group in ligand[9].

The IR of Fe (II) complex shows strong band at 3406 cm⁻¹ assigned to presence of lattice water in the complex[10]. In the IR Spectra of Fe (II) complex, ν(NH₂) band shifted and observed at 3296 cm⁻¹ indicating formation of co-ordinate bond with metal. Similarly ν(NH) band in ligand is at 3216 cm⁻¹ which shift to higher frequency region 3256 cm⁻¹ in complex. The additional bands around 459 cm⁻¹ and 553 cm⁻¹ are assigned to ν(M-N) and ν(M-O) Stretching vibration, respectively. These bands were not observed in ligand. Co-ordination with the chlorine atom is supported by the appearance of band in the far IR region at 340 cm⁻¹ which may be assigned to ν(M-Cl) linkage[11].

IR spectra of Co (II) complex shows intense band at 3334cm⁻¹ due to ν(NH₂) band. This band in ligand observed at 3338 cm⁻¹. This band shifting indicates coordination of nitrogen with metal ion. In ligand ν(NH) observed at 3216 cm⁻¹ but Co(II) complex it is shifted towards higher frequency and appears at 3248 cm⁻¹. In the far IR spectra region of the complex, the bands at 417cm⁻¹ and 519cm⁻¹ observed can be assigned to ν(M-N) and ν(M-O) stretching vibration respectively. Strong band at 3465 cm⁻¹ indicates the presence of lattice water and ν(M-Cl) stretching vibration is observed at 317cm⁻¹.

In the IR spectra Cu (II) Complex band at 3475 cm⁻¹ is observed indicating the presence of coordinated water. ν(NH₂) and ν(NH) bands merge in the complex and appeared 3200-3449 cm⁻¹. Similarly low intense band is observed at 432 cm⁻¹ and 502 cm⁻¹ due to formation of ν(M-N) and ν(M-O) bond. Band at 299 cm⁻¹ indicates formation of coordinate bond of chlorine with metal ν(M-Cl).

Electronic spectra

The electronic spectrum deals with transitions in UV and Visible region. The electronic spectra of the complexing agent N¹⁻ (5, 6-dimethoxypyrimidin-4-yl) sulphanilamide and their metal complexes were obtained from SAIF, IIT Chennai. The ligand exhibit strong bands around 36000 cm⁻¹ with a shoulder at 33,000cm⁻¹ assigned to π→π* and n→π* transitions respectively[12]. Different absorption bands and corresponding transitions are given in the table 2.

Table-2: Electronic spectral data in cm⁻¹ and magnetic moment values of Fe (II), Co (II) and Cu (II) complexes with DMPS

Compound	Absorbance band cm ⁻¹	Transitions	Magnetic Moment (BM)
[Fe (DMPS) ₂ Cl ₂] H ₂ O	23774, 21505, 16606	No specific assignment are made	5.05
[Co(DMPS)Cl ₂ 2H ₂ O]	22779, 16339, 14925	⁴ T _{1g} (F)→ ⁴ T _{1g} (P) ⁴ T _{1g} (F)→ ⁴ A _{2g} (F), ⁴ T _{1g} (F) → ⁴ T _{2g} ,	3.85
[Cu (DMPS) Cl H ₂ O] Cl	22727, 17921, 14513	⁴ A ₂ → ⁴ T _{1g} charge transfer	2.08

Electronic spectra of Fe (II) complex have different transitions and different absorbance peaks due to presence of the metal ion in the complex. Fe (II) complex is d⁶ system having four unpaired electrons. Therefore complex is paramagnetic. Due to presence of the d-d transitions some different peaks are observed in electronic spectra of the complex than the electronic spectra of the ligand. In electronic spectra of Fe(II)complex low intensity bands 23774 cm⁻¹, 21505 cm⁻¹ and 16606 cm⁻¹ no specific assignments are made[13].Complex may acquire octahedral geometry outer hybrid orbital are used to form co-ordinate bond between donor atom of ligand and the central metal ion. The magnetic moment shown by metal complex is 5.05 BM. Electronic spectra of Co (II) complex exhibit three absorbance peaks at 22779 cm⁻¹, 16339 cm⁻¹ and 14925 cm⁻¹. These absorbance maxima due to ⁴T_{1g}(F)→⁴T_{1g}(P), ⁴T_{1g}(F)→⁴A_{2g}(F) and ⁴T_{1g}(F) → ⁴T_{2g}, transitions respectively characteristics of the octahedral geometry around Co(II)metal ion[14]. Magnetic moment is found to be 3.85 BM. Electronic spectra of Cu (II) complex have three bands at 22727 cm⁻¹, 17921cm⁻¹ and 14513cm⁻¹ indicating the transition between the ligand to copper metal ion. The geometry of the complex is tetrahedral. Magnetic susceptibility indicates the presence of one unpaired electron. The presence of above bands in electronic spectra of Cu (II) complex indicates 4A₂→⁴T_{1g} transition and also the transitions due to charge transfer. Magnetic moment for the complexes is found to be 2.08 BM.

Electron Spin Resonance study

The ESR spectrum of the Fe (II), Co (II) and Cu (II) complexes was recorded at room temperature using tetracyanoethylene radical as ‘g’ marker. The H_{\parallel} and H_{\perp} values were measured from the spectrum and used to calculate the g_{\parallel} and g_{\perp} values by using the formula are given in the table-3.

$$g_{av} = \frac{1}{3}(g_{\parallel} + 2g_{\perp})$$

ESR spectra of Fe (II) complex in polycrystalline state shows two peaks. From the observed ESR of Fe (II) complex, the ‘g’ value is 2.203 which is less than 2.3 indicating the coordinate bond between donors atoms of ligand with metal ion have partial covalent character. From ESR spectra of Co (II) complex, g_{\parallel} obtained is 1.84 and g_{\perp} is 2.36. g_{av} value for Co (II) complex is found to be 2.18 which is less than 2.3 indicating covalent character of the metal ligand bond[15].

ESR spectra of Cu (II) complex show two peaks. One of intense absorption peak at high field and the other of less intensity peak at low field. From these two peaks, g_{\parallel} and g_{\perp} have been calculated. The g_{av} value of Cu (II) is 2.34 which are more than 2.3 indicating the presence of ionic character in the complex.

Table-3: ESR spectral data of Fe(II), Co(II) and Cu(II) complexes with DMPS

ESR spectral parameters	[Fe (DMPS) ₂ Cl ₂] H ₂ O	[Co(DMPS)Cl ₂ 2H ₂ O]	[Cu (DMPS) Cl H ₂ O] Cl
g_{\parallel}	1.78	1.84	1.91
g_{\perp}	2.40	2.36	2.55
g_{av}	2.203	2.18	2.34

X-ray diffraction Study

The crystal lattice parameters of Fe (II), Co (II), Cu (II) complexes with DMPS were found out by X-ray diffraction powder method. The X-ray diffraction of complexes was recorded in the range 20° to 80° on 2θ value. The major reflexes were measured and the corresponding d-values were obtained. An independent indexing for each of these reflexes was carried out by least square method[16]. The miller indices (h k l) were calculated and refined using Back-cal program by computational method and data has been summarized in the following tables.

Table-4: Cell data and crystal lattice parameters for [Fe (DMPS)₂Cl₂] H₂O complex

$a (A^{\circ}) = 30.052210 \pm 0.035028$

Volume (A⁰)³ = 19578.25

$b (A^{\circ}) = 30.052210 \pm 0.032651$

$D_{cal} = 1.0387 \text{ g/cm}^3$

$c (A^{\circ}) = 25.031710 \pm 0.093737$

$D_{obs} = 1.2985 \text{ g/cm}^3$

Standard deviation=0.049395

Z = 16

= 4.9%

Crystal system = Hexagonal

$\alpha=90^{\circ}$

$\beta=90^{\circ}$

$\gamma=120^{\circ}$

Porosity (%) = 20

I/I ₀	D_{obs}	D_{cal}	h	k	l
11	4.362115	4.378966	6	-1	2
49	3.902708	3.919956	7	-1	1
65	3.789483	3.783258	7	-1	2
38	3.682723	3.677650	8	-3	1
32	3.533657	3.532010	7	-3	4
72	3.486692	3.467847	8	-2	2
33	3.115265	3.110134	7	-1	5
16	2.847374	2.851161	10	-3	2
51	2.455439	2.451257	9	2	3
100	2.196959	2.198960	10	3	1
28	2.049400	2.051326	6	6	7
27	1.990465	1.990256	9	6	0
19	1.882965	1.885334	9	2	9
17	1.798814	1.798980	8	8	4

16	1.662780	1.662464	10	8	1
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The cell data and crystal parameters of Fe (II) complex is given in the table indicates that the complex have hexagonal crystal system.

Table-5: Cell data and crystal lattice parameters for [Co (DMPS)Cl₂ 2H₂O] complex

a (Å) = 30.059050 ± 0.047643 Volume (Å)³ = 19552.39
 b (Å) = 30.0659050 ± 0.045038 D_{cal} = 1.2940 g/cm³
 c (Å) = 24.970650 ± 0.053964 D_{obs} = 1.3988 g/cm³
 Standard deviation = 0.0050235 Z = 32
 = 0.50% Crystal system = Hexagonal

α= 90° β= 90° γ=120° Porosity (%) = 7.49

I/Io	D _{obs}	D _{cal}	h	k	l
20	3.902708	3.921863	7	-1	1
9	3.646795	3.641020	4	-2	6
7	3.631565	3.611176	8	-2	0
25	2.675749	2.677321	5	0	8
14	2.478043	2.479616	8	-1	7
23	2.411530	2.414165	8	4	2
14	2.308712	2.309016	10	0	5
13	2.214781	2.215209	10	1	5
9	2.019460	2.022433	10	4	3
16	1.935065	1.936715	9	6	3
39	1.870411	1.871525	10	2	8
16	1.702111	1.700870	9	8	4
19	1.572922	1.569306	10	9	2

Cell data and crystal lattice parameters of Co (II) complex attributed to hexagonal crystal system.

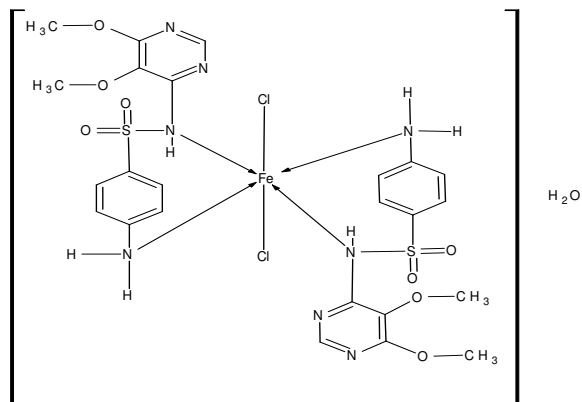
Table-6: Cell data and crystal lattice parameters for [Cu (DMPS) Cl H₂O] Cl Complex

a (Å) = 21.878380 ± 0.015787 Volume (Å)³ = 14362.44
 b (Å) = 23.412220 ± 0.041224 D_{cal} = 0.8558 g/cm³
 c (Å) = 28.039510 ± 0.054712 D_{obs} = 1.0963 g/cm³
 Standard deviation = 0.0030459 Z = 16
 = 0.3% Crystal system = Orthorhombic

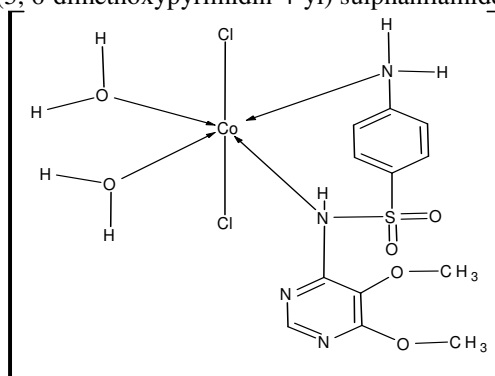
α= 90° β= 90° γ= 90° Porosity (%) = 24.05

I/Io	D _{obs}	D _{cal}	h	k	l
8	4.087049	4.098696	5	2	0
27	3.789483	3.793231	3	5	2
17	3.533657	3.528988	6	0	2
12	3.440960	3.434774	3	5	4
11	3.396491	3.397027	6	0	3
100	2.878237	2.873455	7	2	3
7	2.675844	2.680874	7	3	4
10	2.524552	2.526895	6	0	8
11	2.478043	2.477680	8	4	0
10	2.369269	2.368666	6	0	9
11	2.232888	2.232415	8	6	1
7	2.128633	2.125735	10	2	2
10	1.935064	1.935126	9	3	8

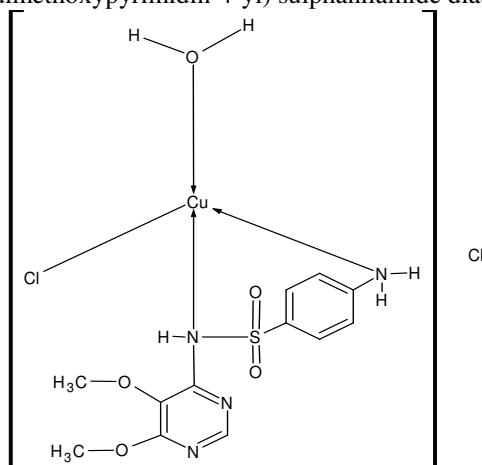
Cell data and crystal lattice parameters of Cu (II) complex indicates that complex have orthorhombic crystal system.



Mol. formula $C_{24}H_{30}N_8O_9S_2Cl_2Fe$; Mol. wt. = 765.64
Dichloro bis N^1 -(5, 6-dimethoxypyrimidin-4-yl) sulphanilamide Fe (II) complex.



Mol. Formula: $C_{12}H_{18}N_4O_6SCl_2Co$; Mol. wt. = 476.32
Dichloro N^1 -(5, 6-dimethoxypyrimidin-4-yl) sulphanilamide diaquo Co (II) Complex



Molecular Formula: $C_{12}H_{16}N_4O_5S Cl_2Cu$; Mol. wt. = 462.82
Monochloro N^1 -(5,6-dimethoxypyrimidin-4-yl) sulphanilamide aquo Cu(II) Chloride Complex.

CONCLUSION

All the complexes are paramagnetic. Electronic spectrum of each metal complexes produce intense peak at higher wave number. From the foregoing observations, the suggested chemical structures for the prepared complexes under investigation are as follows.

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Editor-in-Chief

23, 'Anukampa', Janakpuri, Opp. Heerapura Power Station,
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E-mail: ijcepr@gmail.com

Phone:0141-2810628(O), 09414202678, 07597925412(M)