Asian Journal of Chemistry Vol. 22, No. 8 (2010), 5961-5970

Fe(II), Co(II), Cu(II) Metal Complexes with 4-Chloro-N-furfuryl-5-sulphamoylanthranilic Acid

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4-Chloro-N-furfuryl-5-sulphamoylanthranilic acid when treated with metal ion solutions of Fe(II), Co(II), Cu(II) in non-aqueous medium using different experimental conditions, there is formation of metal complex. After the purification of metal complexes, they are characterized by analytical, thermal, magnetic, infrared, electronic and X-ray diffraction methods. The expected geometry and structure of prepared metal complexes were determined. The nature of the bonding present in the complexes is determined by ESR spectra.

Key Words: Synthesis, Fe(II), Co(II), Cu(II) Complexes, 4-Chloro-N-furfuryl-5-sulphamoylanthranilic acid, IR, ESR, UV-Visible spectral study.

INTRODUCTION

4-Chloro-N-furfuryl-5-sulphamoylanthranilic acid (Fig. 1) with molecular formula $C_{12}H_{11}N_2O_5SCl$ and molecular weight 330.74. It is diuretic drug and white crystalline powder. It is soluble in acetone, sparingly soluble in ethanol. It contains the free -COOH group, primary amine and the secondary amine. Literature survey indicates that the ligand containing functional group -COOH, $-NH_2$ are very important for analytical and biological reactions[1]. The synthesis stability study and reactivity of prepared complexes is a very interesting in field of research[2,3]. There may be interaction of metal ion with ligand containing oxygen, nitrogen, sulphur donor atoms[4,5].

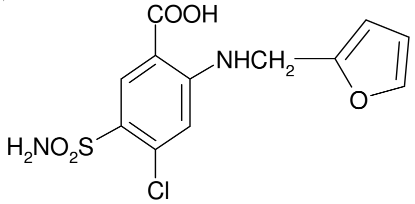

Fig. 1.

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The complexing agent 4-chloro-N-furfuryl-5-sulphamoylanthranilic acid (NFSA) is obtained from Avnetis Pharma Limited, Ankleshwar. The purity of the compound is tested by melting point and TLC.

Synthesis of *bis*-4-chloro-N-furfuryl-5-sulphamoylanthranilate Fe(II) complex: Iron chloride BDH make is used to prepare the Fe(II) metal complex. 0.1 molar solution of $FeCl_2$ is prepared in redistilled ethyl alcohol. A 0.2 M solution of 4-chloro-N-furfuryl-5-sulphamoylanthranilic acid is prepared in acetone. The ligand solution is added in Fe(II) ion solution in the round bottom flask. The pH of solution is adjusted 6.8 to 7.2 by adding alcoholic ammonia. The reaction mixture is refluxed in the water bath by using vertical water condenser and maintaining the temperature 45 to 50 ºC for 3 h. Obtained precipitate which is filtered through buchner funnel using suction pump. The complex is purified by acetone later on by ethyl alcohol. The dried complex is stored in stopper glass sample tube.

Preparation of mono chloro mono-4-chloro-N-furfuryl-5- sulphamoylanthranilate diaquo Co(II) complex: 0.1 M Alcoholic solution of cobalt chloride (BDH make) (50 mL) is mixed with 60 mL of 0.1 M ligand solution (prepared in acetone) in round bottom flask. Round bottom flask is kept in water bath. The temperature of the water bath is maintained at 60 ºC and the reaction mixture is refluxed for 6 h using vertical water condenser. The precipitate of complex is obtained and it is filtered through Buchner funnel using suction pump. The obtained product is purified by washing with acetone and ethyl alcohol. The dried complex is placed in stopper glass sample bottle.

Preparation of mono 4-chloro-N-furfuryl-5-sulphamoylanthranilate mono aquo copper chloride complex: 0.1 M 50 mL 4-chloro-N-furfuryl-5-sulphamoylanthranilic acid (NFSA) prepared in acetone were mixed with 70 mL of 0.1 M BDH make copper chloride solution prepared in redistilled ethyl alcohol. The reaction mixture is transferred to round bottom flask and is refluxed for 3 h by using vertical water condenser by keeping the round bottom flask in water bath and maintaining temperature 60 ºC. The pH of reaction mixture is kept 7.2. The precipitate of complex is filtered using the Buckner funnel and is purified by washing with ethyl alcohol and acetone.

The synthesized metal complexes were characterized by physical, chemical and spectral parameters. The physical parameters like yield, colour, decomposition point, nature and water of crystallization and molar conductance were measured and parameters are given in the Table-1. Presence of hygroscopic water is determined by keeping the known weight of complex in the previously weighed crucible in the oven and maintaining the temperature 80 to 90 ºC for 1 h. The difference in weight gives the presence of hygroscopic water. M:L ratio is determined by taking the known weight of the complex in previously weighed nickel crucible. The complex is heated slowly in beginning and later on strong flame. From the weight of residue M:L ratio is determined.

TABLE-1
ANALYTICAL DATA AND OTHER PHYSICAL PROPERTIES OF METAL COMPLEXES

Metal complex (colour)	m.w. (decomp., °C)	Yield (%) (M.L. ratio)	Molar cond. (S cm^2 mol^{-1})	μ_{eff} (BM)	Elemental analysis (%): Found (Calcd.)			
					C	H	N	S
$[Fe(NFSA)_2]$	714.94	86	14.22	4.92	39.91	2.87	7.65	9.08
(Brown)	(259)	(1:1)			(40.28)	(2.79)	(7.83)	(8.95)
$[Co(NFSA)Cl2H_2O]$	460.24	79	16.20	4.12	31.23	2.98	9.86	7.06
(Turkish blue)	(248)	(1:1)			(31.28)	(3.04)	(10.42)	(6.95)
$[Cu(NFSA)H_2O]Cl$	446.74	77	15.40	2.96	31.87	2.68	5.76	7.38
(Light leaf green)	(287)	(1:1)			(32.23)	(2.81)	(6.26)	(7.16)

Thermal study of prepared complexes: Fe(II), Co(II) and Cu(II) complexes were studied by thermogravimetric analysis from ambient temperature to 1000 °C in nitrogen atmosphere. The range of temperature and the experimental and calculated mass losses of the decomposition reaction are given in the Table-2.

TABLE-2
RESULTS OF THERMOGRAVIMETRIC ANALYSIS OF COMPLEXES OF 4-CHLORO-N-FURFURYL-5-SULPHAMOYLANTHRANILATE WITH Fe(II), Co(II), Cu(II)

Complexes	Total mass losses		Temperature (°C)	Loss (%)
	Theoretical	Expt.		
$[Fe(NFSA)_2]$	77.63	77.35	236-549 549-825 825-1000	47.38 29.97 22.65 (Residue) 22.37 (Calcd.)
$[Co(NFSA)Cl2H_2O]$	83.73	82.08	145-187 187-416 416-780 780-1000	6.89 39.21 35.98 17.08(Residue) 16.27 (Calcd.)
$[Cu(NFSA)H_2O]Cl$	82.21	81.92	135-148 148-816 816-1000	4.21 77.71 17.98 (Residue) 17.79 (Calcd.)

Thermal study of $[Fe(NFSA)_2]$ complex: The Fe(II) complex of NFSA is thermally stable up to 236 °C indicating that there is no coordinated water. The thermogram of Fe(II) complex shows sharp decomposition associated with loss of organic part beyond 236 °C. The decomposition of complex continues up to 549 °C and the loss corresponds to 47.38 % indicating decomposition of some organic part of the complex. Loss of remaining part of organic molecule occurs in the temperature range 549-825 °C corresponds to 29.97 %. Finally at 825 °C complex remains in the form of metal oxide residue[6] which is found to be 22.65 %. This value is in agreement with theoretical value of Fe(II) complex *i.e.* 22.37 %.

Thermal study of [Co(NFSA)ClH$_2$O] complex: Thermogram of Co(II) complex shows weight loss corresponding to 2 water molecule in the temperature range 145-187 ºC. The loss of water in this temperature range indicates the presence of water molecule in the coordination sphere of Co(II) complex. Decomposition reaction corresponds to an experimental mass 39.21 % occurs in the temperature range 187-416 ºC attributed loss of some organic moiety. In the temperature range 416-780 ºC remaining part of organic molecule along with chloride moiety is lost and this loss corresponds to 35.98 %. Finally (780-1000 ºC) residue is obtained corresponding to CoO as a stable residue 17.08 %.

Thermal study of [Cu(NFSA)H$_2$O].Cl complex: The TGA of Cu(II) complex indicates loss in weight in the temperature range 135-148 ºC corresponding to 4.21 % indicates the loss of coordinated water. The complex start decomposition beyond 148 ºC continues up to 816 ºC. The weight loss 77.71 % indicating loss of organic part of the complex. The ligand loss by steps resulting as stable product in the form of oxide.

Infrared spectroscopy: Infrared spectra of ligand and its metal complexes provide some information regarding the bonding in the compounds. Important absorption frequencies of ligand and complexes along with their assignments are given in the Table-3. Infrared spectra of ligand shows strong band in the region of 3284 cm^{-1} which is assigned to hydrogen bonded ν(OH) stretching vibration[7]. Ligand also shows intense band observed at 1671 cm^{-1} is attributed to the stretching vibrations ν(C=O)[8] In the IR spectrum of ligand appearance of band at 3351 cm^{-1} attributed to ν(NH$_2$)[9], Broad band due to ν(NH) stretching vibration in ligand appears at 3399 cm^{-1}.

TABLE-3
INFRARED SPECTRAL DATA OF LIGAND AND ITS METAL COMPLEXES

Compound	ν(NH$_2$)	ν(NH)	ν(O-H)	ν(O-O)	ν(C=O)	ν(C-H)	ν(M-N)	ν(M-O)
NFSA	3351	3399	3284	1496	1671	2958	-	-
[Fe(NFSA)$_2$]	3284	3390	3254	1493	1671	2958	540	490
[Co(NFSA)Cl2H$_2$O]	3500-3000	3500-3000	3200-2900	1504	1671	2958	585	425
[Cu(NFSA)H$_2$O]Cl	3287	3352	3352-3287	1497	1671	2958	583	497

In the IR spectrum of the free ligand the ν(C-O) band appears at 1496 cm^{-1}. This band in Fe(II) complex is at 1493 cm^{-1}. This indicates bonding between oxygen of ν(C-O) with metal ion. Further the ν(NH$_2$) band in ligand observed at 3351 cm^{-1}. This band in complex shifted towards lower frequency at 3284 cm^{-1} indicates participation in coordinate bond formation. The sharp intense band of ν(NH) is observed in ligand observed at 3399 cm^{-1}, this band in Fe(II) complex shifted and appears at 3390 cm^{-1}. A medium intensity broad band at 3284 cm^{-1} due to ν(O-H) in free ligand is shifted to lower frequency in complex and appear at 3254 cm^{-1} indicating participation in coordinate bond formation. Bands present in ligand at 1671 and

2958 cm^{-1} due to ν(C=O) and ν(C-H) stretching vibration, respectively remains unaffected upon complexation indicating non-involvement. The new bands observed in complex in the region 600-300 cm^{-1} particularly at 539 and 490 cm^{-1} attributable to ν(Fe-N) and ν(Fe-O) band stretching, respectively[10].

The infrared spectrum of Co(II) complex compared with ligand, the broad band observed in free ligand at 3351 cm^{-1} due to $\nu(NH_2)$ is shifted in complex and merge in the region 3500-3000 cm^{-1} indicating involvement in co-ordination. Bands present in ligand at 1671 and 2958 cm^{-1} due to ν(C=O) and ν(C-H) vibration, respectively remains unaffected upon complexation indicating non-involvement. A shift in medium intensity band is observed at 1504 cm^{-1} assigned to ν(C-O) stretching vibrations and in free ligand this band is at 1496 cm^{-1}. Similarly band observed at 3399 cm^{-1} due to ν(NH) in ligand is now shifted merge in the region 3500-3000 cm^{-1} in complex indicating involvement in coordination. Broad band in ligand at 3284 cm^{-1} due to ν(O-H) get merge in the range 3200-2900 cm^{-1}. The coordination through nitrogen and oxygen is further confirmed by the occurrence of new bands at 585 and 425 cm^{-1} in the spectra of complex assigned to ν(Co-N) and ν(Co-O) stretching vibrations, respectively[11]. The band observed at 295 cm^{-1} in far infrared region is due to ν(Co-Cl)[12,13].

The infrared spectrum of Cu(II) complex shows intense band at 1497 cm^{-1} due to ν(C-O) stretching vibration. This band in ligand observed at 1493 cm^{-1}. In free ligand $\nu(NH_2)$ band appears at 3351 cm^{-1} where as in complex this band shifted towards lower frequency appears at 3287 cm^{-1} indicating participation in coordinate bond formation. Medium intensity band in ligand appears at 1671 and 2958 cm^{-1} due to ν(C=O) and ν(C-H), respectively[14] remains intact in complex indicating non-participation in coordination. The ν(NH) stretching vibration in ligand is at 3399 cm^{-1} is shifted to lower frequency appears at 3352 cm^{-1}. New low intensity bands at 583 and 497 cm^{-1} in the spectra of complex due to ν(Cu-N) and ν(Cu-O) vibrations, respectively. The ν(OH) band is merge in the range 3352-3287 cm^{-1} indicating the presencef coordinated water. It is further supported by TGA and DTA analysis.

Electronic spectra of complexes: The electronic spectra are recorded in ultraviolet and visible region. The electronic spectra of the complexing agent 4-chloro-N-furfuryl-5-sulphamoylanthranilic acid and their complexes with Fe(II), Co(II) and Cu(II) is tabulated in the Table-4.

TABLE- 4
ELECTRONIC SPECTRAL DATA OF COMPLEXES

Compound	Wavelength	Transition	μ_{eff} (BM)
[Fe(NFSA)$_2$]	22624, 28653	${}^5T_{2g} \rightarrow {}^5E_g$, Charge transfer	4.92
[Co(NFSA)ClH$_2$O]	15625, 17094, 28490	${}^4T_{1g}(F)\rightarrow{}^4T_{2g}$, ${}^4T_{1g}(F)\rightarrow{}^4A_{2g}(F)$, ${}^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$	4.12
[Cu(NFSA)H$_2$O]Cl	22172, 27174, 37879	${}^4A_2 \rightarrow {}^4T_1$ (p), Charge transfer transitions	2.96

Ligand exhibit strong band in the range 36231-31250 cm^{-1} assigned to $\pi \rightarrow \pi^*$ transition and 30769-27700 cm^{-1} assigned to $n \rightarrow \pi^*$ transition. Fe(II) complex is d^6 system having four unpaired electrons. Due to *d-d* transition the electronic spectra of Fe(II) complex is different that of ligand. Fe(II) complex shows intense bands at 22624 and 28653 cm^{-1} assigned to $^5T_{2g} \rightarrow ^5E_g$ transition and charge transfer transition, respectively confirms the octahedral geometry of Fe (II) complex[15] magnetic moment value for complex is found to be 4.92 BM.

Electronic spectra of Co(II) complex exhibits three main absorption bands at 15625, 17094 and 28490 cm^{-1} assigned to $^4T_{1g}(F) \rightarrow ^4T_{2g}$, $^4T_{1g}(F) \rightarrow ^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow ^4T_{1g}(P)$ transitions, respectively in a high spin octahedral geometry[16,17], further supported by magnetic moment value 4.12 BM.

The electronic spectra of Cu(II) complex exhibits intense bands at 22172, 27174 and 37879 cm^{-1}. The first band attributes to $^4A_{2g} \rightarrow ^4T_1(P)$ transition and remaining two bands assigned to charge transfer transitions. The magnetic moment value is 2.96 BM attributed to tetrahedral geometry[18].

Electrons spin resonance spectroscopy of complexes: The ESR spectra of Fe(II), Co(II) and Cu(II) complexes with 4-chloro-N-furfuryl-5-sulphamoylanthranilic acid was recorded at room temperature using tetracyanoethylene radical as 'g' marker. The $g_{\parallel}$, $g_{\perp}$ and $H_{\parallel}$, $H_{\perp}$ were found out from the spectrum. From these values g_{av} is calculated by $g_{av} = \frac{1}{3}(g_{\parallel} + 2g_{\perp})$. All the values of $g_{\parallel}$, $g_{\perp}$ and g_{av} tabulated in the Table-5.

TABLE-5
ESR SPECTRAL DATA OF Fe(II), Co(II) AND Cu(II) COMPLEXES

Compounds	$g_{\perp}$	$g_{\parallel}$	g_{av}
$[Fe(NFSA)_2]$	2.37	1.78	2.17
$[Co(NFSA)Cl2H_2O]$	2.41	1.78	2.20
$[Cu(NFSA)H_2O]Cl$	2.51	1.97	2.33

The electron spin resonance spectrum of Fe(II) complex reveals that $g_{\perp}$ factor is found at 2.37 while $g_{\parallel}$ found at 1.78. The g_{av} value for Fe(II) complex is 2.17 which is less than 2.3 indicates the presence of sufficient covalency in the complex. Electron spin resonance spectrum of Co (II) complex indicates the $g_{\perp}$ factor is found at 2.41 and $g_{\parallel}$ set up at 1.78. The value of g_{av} is 2.20 which is less than 2.3 indicates the presence of sufficient covalent character in Co(II) complex of 4-chloro-N-furfuryl-5-sulphamoyl anthranilic acid[19]. In the ESR spectrum of Cu(II) complex value of $g_{\perp}$ and $g_{\parallel}$ is found at 2.51 and 1.97, respectively, g_{av} value is found to be 2.33 which is more than 2.30, attributed to the presence of ionic character in the Cu(II) complex with 4-chloro-N-furfuryl-5-sulphamoylanthranilic acid.

X-ray diffraction study: The X-ray diffractogram of the complexes were recorded in the range 200 to 800, on 2θ scale. The major refluxes were measured and corresponding *d*-value are obtained[20]. An independent indexing for each of these refluxes was obtained by least square method. The miller indices (h k 1) were calculated and refined by using back-cal program by computational method and data has been summarized in Tables 6-8.

TABLE-6
CELL DATA AND CRYSTAL LATTICE PARAMETERS FOR [Fe(NFSA)$_2$] COMPLEX

a (Å) = 21.898300 ± 0.016032 Volume (Å)^3 = 14334.26
b (Å) = 23.399780 ± 0.093451 D_{cal} = 1.3247g/ cm^3
c (Å) = 27.973860 ± 0.057719 D_{obs} = 1.3892g/ cm^3
Standard deviation = 0.0036957 % Z = 16
= 0.36 % Crystal system = Orthorhombic
α = 90º; β = 90º; γ = 90º; Porosity (%) = 4.64

I/Io	D_{obs}	D_{cal}	h	k	1
9	4.288056	4.304912	5	1	0
27	4.151308	4.151531	3	2	5
32	3.845215	3.843364	4	4	2
100	3.581998	3.576527	6	1	1
16	3.396491	3.398659	6	0	3
71	3.078964	3.081871	7	1	1
20	3.043481	3.044896	3	2	8
17	2.975110	2.965871	7	0	3
36	2.878231	2.874938	7	2	3
27	2.433285	2.433148	9	0	0
30	2.348712	2.348364	9	2	2
30	2.328537	2.329796	8	5	2

From the X-ray diffraction spectral parameters tabulated in above table reveals that Fe(II) complex have orthorhombic crystal system.

TABLE-7
CELL DATA AND CRYSTAL PARAMETERS FOR [Co(NFSA)Cl2H$_2$O] COMPLEX

a (Å) = 21.926270 ± 0.020082 Volume (Å)^3 = 14229.07
b (Å) = 23.261330 ± 0.077436 D_{cal} = 0.8590 g/cm^3
c (Å) = 27.898270 ± 0.087626 D_{obs} = 1.0732 g/cm^3
Standard deviation = 0.0032710% Crystal system = Orthorhombic
α = 90 º; β = 90 º; γ = 90 º; Porosity (%) = 19.95

I/Io	D_{obs}	D_{cal}	h	k	1
27	4.218846	4.229145	3	3	4
36	4.151308	4.143940	3	2	5
49	3.902708	3.909938	5	1	3
58	3.581998	3.580249	6	1	1
56	2.909781	2.904293	7	3	0
71	2.348583	2.350408	9	2	2
89	2.019460	2.019506	10	5	4
87	1.733027	1.731278	8	8	8
100	1.581469	1.580329	9	9	8
98	1.540000	1.538913	9	9	9
85	1.416418	1.418637	10	10	9

The cell data and crystal lattice parameters of Co(II)complex given in Table-7 indicates that the complex have orthorhombic crystal system.

TABLE-8
CELL DATA AND CRYSTAL PARAMETERS FOR [Cu(NFSA)H_2O]Cl COMPLEX

a (Å) = 21.904190 ± 0.011564
b (Å) = 23.298810 ± 0.0286865
c (Å) = 27.968810 ± 0.061355
Standard deviation = 0.0024508
= 0.24 %

Volume $(Å)^3$ = 14273.65
D_{cal} = 0.8312 g/cm^3
D_{obs} = 1.0352 g/cm^3
Z = 16
Crystal system = Orthorhombic

$\alpha = 90°$; $\beta = 90°$; $\gamma = 90°$; Porosity (%) = 19.7

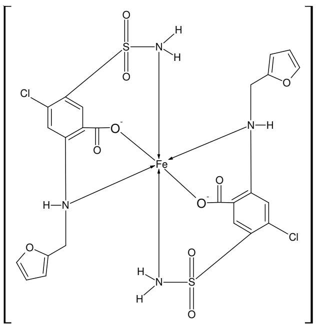
I/Io	D_{obs}	D_{cal}	h	k	l
45	4.151308	4.149209	3	2	5
34	3.802708	3.908722	5	1	3
37	3.789483	3.780624	5	3	1
53	3.682723	3.681081	5	3	2
100	3.581998	3.577073	6	0	1
92	3.936491	3.399366	6	1	3
49	3.078964	3.082432	7	1	1
24	3.008883	3.010965	3	7	1
70	2.878237	2.874784	7	2	3
53	2.817214	2.814945	6	5	2
32	2.548492	2.549525	8	0	4
32	2.478043	2.478208	5	7	4
33	2.328537	2.327731	8	5	2
31	2.521322	2.253559	9	3	3
30	2.227431	2.230568	8	6	1

From the X-ray diffraction spectrum of Cu(II) complex cell data and crystal lattice parameters of calculated and tabulated in Table-8 indicates that complex has orthorhombic crystal system.

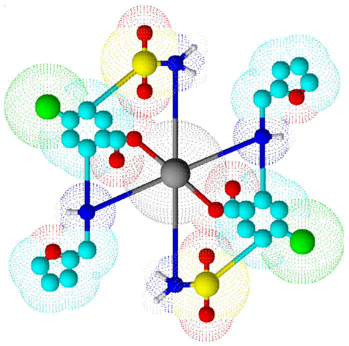
Conclusion

On the basis of crystal lattice parameters, analytical and spectral data, Fe(II), Co(II) complexes exhibit octahedral structure where as Cu(II) exhibit tetrahedral structure as shown in the following figure.

Bis 4-chloro-N-furfuryl-5-sulphamoylanthronilate iron (II) complex

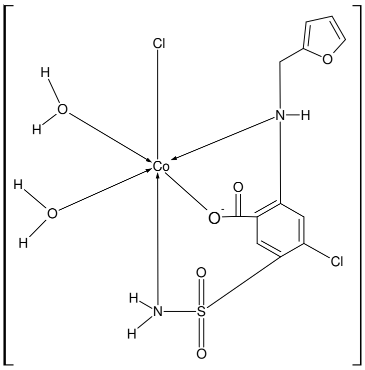


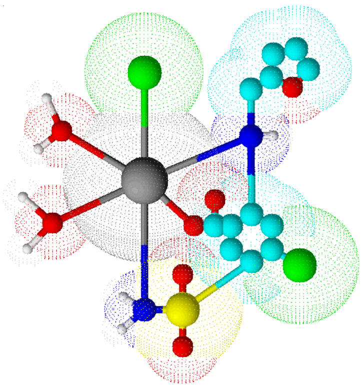
m.f. = $C_{24}H_{20}N_4O_{10}S_2Cl_2Fe$; m.w. = 714.94



3D view of [Fe$(NFSA)_2$] complex.

Monochloro mono-4-chloro-N-furfuryl-5-sulphamoylanthranilate diaquo cobalt(II) complex.

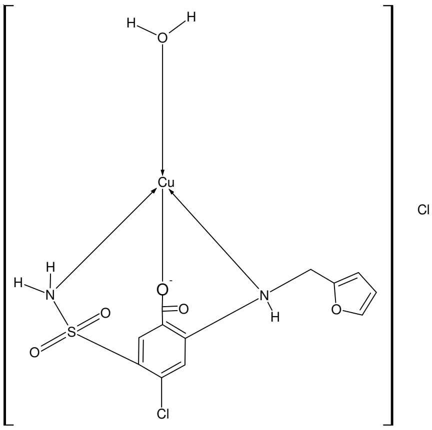


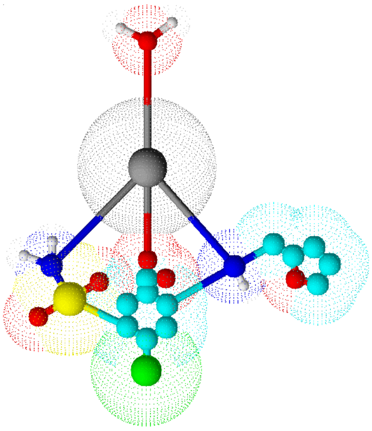


m.f. = $C_{12}H_{14}N_2O_7SCl_2Co$, m.w. = 460.24

3D view of [Co(NFSA)ClH$_2$O] complex

Mono 4-chloro-N-furfuryl-5-sulphamoyanthranilate mono aquo copper(II) chloride complex.





m.f. = $C_{12}H_{12}N_2O_6OSCl_2Cu$, m.w. = 446.74

3D view of [Cu(NFSA)H$_2$O]Cl complex

ACKNOWLEDGEMENTS

The authors thank to the Principal and Head, Department of Chemistry, Science College, Nanded for providing all necessary facilities. In addition, the authors wish to acknowledge the Principal, Yeshwant College, Nanded for encouragement.

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(*Received*: 12 September 2009; *Accepted*: 30 April 2010) AJC-8647