

Synthesis and Characterization of Transition Metal Complexes with 7-(R)-2-Amino-2-(4-hydroxyphenyl)acetamido]-3-methyl-3-cephem-4-carboxylic Acid Monohydrate

J.H. DESHMUKH[†] and M.N. DESHPANDE*

Department of Chemistry, NES Science College, Nanded-431 605, India
E-mail: deshmukhjitu@rediffmail.com

7-(R)-2-Amino-2-(4-hydroxyphenyl)acetamido]-3-methyl-3-cephem-4-carboxylic acid monohydrate (AMCC) is a active chelating agent due to presence of different donor atoms. When this chelating agent is treated with Fe²⁺, Co²⁺ and Cu²⁺ metal ion solution at specific pH it produces different metal ion complexes, after purification they were characterized by physical and chemical methods. To determine the nature of bonding in the complexes infrared, UV-Visible, ESR spectra are used. TGA-DTA gives information regarding effect of temperature in the decomposition of complexes. XRD and other parameters are used for determining probable geometry of metal complexes.

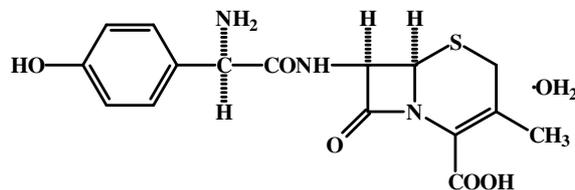
Key Words: Synthesis, Transition metal complexes, 7-(R)-2-Amino-2-(4-hydroxyphenyl)acetamido]-3-methyl-3-cephem-4-carboxylic acid monohydrate.

INTRODUCTION

The literature survey indicates that the number of macromolecules containing different donor atoms are well known chelating agents¹. It is also proved that the some of the metal complexes have a certain physiological activities². The study reveals that some of the metal complexes are inhibitors to tumor growth³ and they are used in cerebrovascular⁴ disease. Some metal complexes are active against bacterial⁵ and fungal growth^{6,7}. Some antibacterial drugs have chelating tendency⁸.

In this work, 7-(R)-2-amino-2-(4-hydroxyphenyl) acetamido]-3-methyl-3-cephem-4-carboxylic acid monohydrate (AMCC, **1**) is used as a chelating agent to synthesize some transition metal complexes. The complexing agent contains –NH₂, COOH and amide group. Many research papers revealed that the compounds containing –NH₂, –COOH, phenolic and amide group have ability to form coordinate bond with metal ion. The complexes show a wide range of biological activities⁹⁻¹³.

[†]Department of Chemistry, Yeshwant Mahavidyalaya, Nanded-431 602, India.



7-(R)-2-Amino-2-(4-hydroxyphenyl) acetamido]-3-methyl-3-cephem-4-carboxylic acid monohydrate (AMCC)

EXPERIMENTAL

Complexing agent is obtained from Dey's Medical Stores, Kolkata and its purity is confirmed by mixed melting point and TLC. All the chemical used are of AR grade.

Preparation of [Fe(AMCC)₂] complex: 25 mL 0.1 M alcoholic solution of FeCl₂ is taken in round bottom flask. 50 mL 0.1 M of complexing agent solution in alcohol is transferred to round bottom flask, pH of solution is maintained. The reaction mixture is refluxed for 2 h in round bottom flask using air condenser. The obtained precipitate is filtered through Whatman filter paper. The complex was purified by washing with ethyl alcohol. The product is dried and yield is recorded.

Preparation of [Co(AMCC)₂].H₂O complex: 25 mL of 0.1 M alcoholic cobalt chloride solution were mixed with 50 mL of 0.1 M (AMCC). The pH of reaction mixture is maintained at 7.2 by adding alcoholic ammonia solution drop by drop. The reaction mixture is refluxed for 3 h using water condenser. The obtained precipitate were filtered and washed with ethyl alcohol. The precipitate of complex is dried and yield is recorded.

Preparation of [Cu(AMCC)Cl].H₂O complex: 0.1 M, 25 mL of alcoholic copper chloride solution is mixed with 25 mL of 0.1 M chelating agent solution in the round bottom flask. The pH of reaction mixture is adjusted at 6.9 by adding alcoholic ammonia. The reaction mixture is refluxed for 3 h using water condenser. The obtained product is filtered through Whatman filter paper. The complex was purified by washing with ethyl alcohol.

The physico-chemical parameters were estimated by known methods¹³.

RESULTS AND DISCUSSION

The physico-chemical parameters of synthesized metal complexes indicates that the metal complexes are stable. The analytical data indicates that the two chelating agent (AMCC) molecules react with Fe²⁺ and Co²⁺ metal ion. The M:L ratio of Fe²⁺ and Co²⁺ metal ion chelates are 1:2 and M:L ratio Cu²⁺ metal complex is 1:1 (Table-1). The molecular formula of the complexes are [Fe(AMCC)₂].H₂O, [Co(AMCC)₂].H₂O and [Cu(AMCC)Cl].H₂O. The value of magnetic susceptibility indicates that the complexes are paramagnetic. Molar conductance of prepared complexes was measured in non-electrolytic solvent. The value of molar conductance indicates that the complexes are non-electrolytic.

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

Metal complex (m.w.)	Colour (d.p. °C)	Yield (%) (M:L ratio)	Molar conductance (S cm ² mol ⁻¹)	μ_{eff} (BM)	Elemental analysis (%): Found (Calcd)			
					C	H	N	S
[Fe(AMCC) ₂].H ₂ O (798)	Brown (268)	72 (1:2)	10.76	3.01	48.31 (48.12)	3.96 (4.26)	10.23 (10.52)	8.28 (8.02)
[Co (AMCC) ₂].H ₂ O (800.9)	Dark brown (257)	65 (1:2)	9.11	4.02	47.43 (47.94)	4.41 (4.24)	10.14 (10.48)	7.62 (7.99)
[Cu(AMCC)Cl].H ₂ O (479)	Dark green (242)	80 (1:1)	8.20	2.09	39.69 (40.08)	3.88 (3.75)	8.64 (8.76)	6.51 (6.68)

d.p. = Decomposition temperature.

Thermal analysis study: TGA-DTA study of prepared complexes were obtained using TA-instrument-model SDT-2960 from Shivaji University, Kolhapur. The temperature range is from room temp to 1000 °C. Thermal analysis data of the complexes are given in Table-2.

TABLE-2
THERMAL ANALYSIS DATA OF METAL COMPLEXES

Complexes	Total mass losses		Temperature (°C)	Loss (%)
	Theoretical	Experimental		
[Fe(AMCC) ₂].H ₂ O	79.95	80.20	Room-90	2.76
			90-242	9.28
			242-375	42.10
			375-750	26.06
			750-1000.	19.00 (Residue) 20.05 (Calcd.)
[Co(AMCC) ₂].H ₂ O	90.65	90.82	Room-95	2.5
			95-350	24.48
			350-600	46.45
			600-850	17.39
			850-1000	9.1 (Residue) 9.35 (Calcd.)
[Cu(AMCC)Cl].H ₂ O	83.41	84.28	Room-98	3.63
			98-210	8.18
			210-350	20.00
			350-650	39.53
			650-780	13.14
780-1000	15.46 (Residue) 16.59 (Calcd.)			

TGA study of [Fe(AMCC)₂].H₂O metal complex: The decomposition of [Fe(AMCC)₂].H₂O takes place in 5 stages. At temperature 90 °C there is 2.76 % loss. This loss may be due to the lattice water, the peak is endothermic¹⁴. The second peak is obtained in temperature range 90-242 °C. In this temperature range mass loss corresponds to 9.28 %. Further the complex decomposes between 242-375 °C,

in this temperature range most of the organic part of a complex is decomposed. Mass loss in this temperature range corresponds to 42.10 %. Then 26.06 % loss of the complex observed in the temperature range 375-750 °C indicates loss of remaining part of organic moiety. After 750 °C there is no change in graph due to conversion of complex into corresponding residue as Fe₂O₃. This result matches with the theoretical result. The weight of observed residue is 19 % while theoretical weight of residue is 20.05 %.

Thermal study of [Co(AMCC)₂]-H₂O metal complex: This complex decomposes in 5 stages. At 95 °C, 2.5 % mass loss is observed. This loss may be due to the loss of lattice water. The result matches with theoretical results. In the temperature range between 95-350 °C, 24.48 % and in the range 350-600 °C, 46.45 % loss is observed indicating loss of most of the part of ligand from complex. Then in 600-850 °C temperature range the decomposition of complex corresponds to 17.39 % loss due to loss of remaining organic part. After 850 °C temperature, there is no change in graph indicating the formation of cobalt oxide. The weight of cobalt oxide residue obtained from the graph is 9.1 % and the theoretical loss is 8.9 %¹⁵.

TGA-DTA study of [Cu(AMCC)Cl]-H₂O complex: Endothermic peak is observed at 98 °C. This may be due to loss of lattice water molecule which is 3.63 %. This water molecule is present outside the coordination sphere. Thermal decomposition of [Cu(AMCC)Cl]H₂O complex is in the range 98-210 °C. In this temperature range 8.18 % loss is obtained. Further in the temperature range 210-350 °C there is loss of 20 % indicates loss of some organic part of complex. In the temperature range of 350-650 °C, the remaining part loss corresponds to 39.53. Then 13.14 % loss of the metal complex is observed in the temperature range 650-780 °C it is due to loss of remaining organic part of the complex. Above 780 °C straight line graph is obtained indicate the formation of CuO.

Infrared spectra: The IR spectra of chelating agent 7-[(R)-2-amino-2-(4-hydroxyphenyl)acetamido]-3-methyl-3-cephem-4-carboxylic acid monohydrate (AMCC) show peak due to -NH₂, phenolic -OH, carboxylic acid, carbonyl groups, also the tertiary nitrogen and ring sulphur. Band observed at 3501 cm⁻¹ due to the presence of ν(-NH₂) group. The band at 3199 cm⁻¹ is due to presence of (NH) amide group. The compound contains two ν(C=O) groups, of which one carbonyl group has bending, therefore two bands at 1756-1685 cm⁻¹ are obtained. The ν(C-N) stretching is also observed at 1119 cm⁻¹. The IR spectral data of the chelating agent and prepared metal complex are given in Table-3.

TABLE-3
CHARACTERISTIC IR BANDS OF LIGAND AND ITS COMPLEX

Compound	ν(N-H) of NH ₂	ν(N-H) amide	ν(C=O) carbo.	ν(C=O) bending	ν(C-N)	ν(M-N)	ν(M-O)
(AMCC)	3501	3199	1685	1756	1119	-	-
[Fe(AMCC) ₂]-H ₂ O	3421	3197	1617	1668	1088	546	469
[Co(AMCC) ₂]-H ₂ O	3401	3191	1610	1662	1087	558	465
[Cu(AMCC)Cl]-H ₂ O	3430	3128	1608	1732	1114	569	460

IR spectra of $[\text{Fe}(\text{AMCC})_2]\text{H}_2\text{O}$ is compared with infrared spectra of ligand (AMCC), there are certain shifts in the bands. The $-\text{NH}_2$ band is shifted towards 3421 cm^{-1} indicating involvement in coordination¹⁶. The amide band is also slightly shifted at 3197 cm^{-1} due to coordination. The band stretching vibration in complex due to carbonyl $\nu(\text{C}=\text{O})$ group observed at $1668\text{--}1617\text{ cm}^{-1}$, respectively. The band at 1119 cm^{-1} in ligand due to $\nu(\text{C}-\text{N})$ stretching vibration is shifted and appear at 1088 cm^{-1} in complex indicate participation in co-ordinate bond formation. The new bands found in the IR spectra of Fe^{2+} metal ion complex at $546\text{--}469\text{ cm}^{-1}$ due to new bonding *i.e.*, $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{O})$ ¹⁷.

IR of $[\text{Co}(\text{AMCC})_2]\text{H}_2\text{O}$ complex is different than IR spectra of complexing agent. In complex broad band appears at 3401 cm^{-1} due to stretching of $\nu(\text{NH}_2)$ group and 3191 cm^{-1} is due to $\nu(\text{NH})$ stretching of amide group, these bands in ligand were at $3501\text{--}3199\text{ cm}^{-1}$, respectively. This indicates that both groups are involved in coordination. The ligand exhibit bands at $1685\text{--}1756\text{ cm}^{-1}$ due to $\nu(\text{C}=\text{O})$ vibration stretching and are shifted in complex to lower frequency region at $1662\text{--}1610\text{ cm}^{-1}$ showing coordination¹⁸. The presence of new bands at $558\text{--}465\text{ cm}^{-1}$ are due to $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{O})$ bond.

The IR spectra of $[\text{Cu}(\text{AMCC})\text{Cl}]\text{H}_2\text{O}$ complex is also different than the IR of chelating agent. In Cu^{2+} complex peaks are obtained due to shifting of $\nu(-\text{NH}_2)$ group at 3430 cm^{-1} and $\nu(\text{N}-\text{H})$ of amide group stretching is at 3128 cm^{-1} . This shifting in band attributed to involvement in co-ordination. The intense band observed at $1732\text{--}1608\text{ cm}^{-1}$ assigned to stretching vibration of $\nu(\text{C}=\text{O})$ group. The new bands at $569\text{--}460\text{ cm}^{-1}$ is due to presence of $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{O})$. Bonding observed at 287 cm^{-1} due to formation of co-ordinate bond between $\text{M}-\text{Cl}$ ¹⁹.

Electronic spectral study: The electronic spectra of the AMCC and its complexes were recorded in the Table-4. The electronic spectra of ligand exhibit bands at 28169 , 30487 and 35087 cm^{-1} due to $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$ transitions.

The Fe^{2+} complex display two bands at $13908\text{--}29069\text{ cm}^{-1}$ assignable to ${}^5\text{T}_{2g} \rightarrow {}^5\text{E}_g$ and charge transfer transitions, respectively. This suggests an octahedral geometry around the Fe^{2+} ion in the complex and having magnetic moment $3.01\text{--}3.15\text{ BM}$.

TABLE-4
ELECTRONIC SPECTRAL DATA METAL COMPLEXES

Compound	Wavelength	Transition	Magnetic Moment in BM
$[\text{Fe}(\text{AMCC})_2]\text{H}_2\text{O}$	13908, 29069	${}^5\text{T}_{2g} \rightarrow {}^5\text{E}_g$, charge transfer transition	3.01
$[\text{Co}(\text{AMCC})_2]\text{H}_2\text{O}$	12626, 15898, 22172	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}$, ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$, ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$	4.02
$[\text{Cu}(\text{AMCC})\text{Cl}]\text{H}_2\text{O}$	19600, 21598, 22573	${}^4\text{A}_2 \rightarrow {}^4\text{T}_1(\text{p})$, two charge transfer transition	2.09

The Co^{2+} complex shows three absorption bands. These bands are at 12626, 15898 and 22172 cm^{-1} may be assigned to ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}$, ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$ and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ transitions assigned to octahedral arrangement of the ligand atoms around the central Co^{2+} ion which is further confirmed by magnetic moment between 4.02-5.14 BM^{20} .

The Cu^{2+} complex exhibit three intense peaks at 19600, 21598 and 22573 cm^{-1} may be assigned to ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1(\text{P})$ and two charge transfer transitions, respectively, respectfully suggest an tetrahedral geometry around central Cu^{2+} ion in the complex. Further it is supported by magnetic moment value 2.09 BM .

Electron spin resonance spectral study: The ESR spectrum of the Fe^{2+} , Co^{2+} and Cu^{2+} 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. $g_s \times H_s = g_{\parallel} \times H_{\parallel}$ and g_s

$H_s = g_{\perp} H_{\perp}$. From g_{\parallel} and g_{\perp} , g_{av} value can be calculated by $g_{\text{av}} = \frac{1}{3}(g_{\parallel} + 2g_{\perp})$. The calculated value of g_{\parallel} , g_{\perp} and g_{av} from ESR spectrum of the Fe^{2+} , Co^{2+} and Cu^{2+} complexes are listed in the Table-5.

TABLE-5
ESR SPECTRAL DATA OF Fe^{2+} , Co^{2+} and Cu^{2+} COMPLEXES

Complexes	g_{\parallel}	g_{\perp}	g_{av}
$[\text{Fe}(\text{AMCC})_2]\text{H}_2\text{O}$	1.81	2.41	2.21
$[\text{Co}(\text{AMCC})_2]\text{H}_2\text{O}$	1.95	2.36	2.22
$[\text{Cu}(\text{AMCC})\text{Cl}]\text{H}_2\text{O}$	1.90	2.20	2.10

The ESR spectra of Fe^{2+} complex show two peaks, one intense peak at high field and the other less intensity at low field. The table reveals that g_{\perp} , g_{\parallel} and g_{av} for Fe^{2+} complexes is, 2.41, 1.81 and 2.21, respectively. g_{av} value for the complex is found to be less than 2.3 which indicates the presence of covalence between metal ion and ligand in the Fe^{2+} complex²¹. ESR spectrum Co^{2+} complex reveals that, g_{\perp} , g_{\parallel} and g_{av} value for complex are 2.36, 1.95 and 2.22, respectively. The g_{av} value is found to be less than 2.3, indicating the complex compound has covalent character. From the ESR spectrum of Cu^{2+} complex the g_{av} parameter has only one value *i.e.*, 2.10. This value is less than 2.3. Therefore the complex compound is covalent²¹.

X-Ray diffraction study: The X-ray diffraction pattern for Fe^{2+} , Co^{2+} and Cu^{2+} complexes has been determined between 2θ range from 100-800 and data has been summarized in the following Tables 6-8:

Conclusion

On the basis of crystal lattice parameters, analytical and spectral data, Fe^{2+} , Co^{2+} complexes exhibit octahedral structure where as Cu^{2+} exhibit tetrahedral structure as shown in the following figure:

TABLE-6
CELL DATA AND CRYSTAL LATTICE PARAMETERS FOR [Fe(AMCC)₂]H₂O
a(Å) = 10.2138 ± 0.0628; b(Å) = 17.4182 ± 0.2461; c(Å) = 13.4951 ± 0.04992; Volume (Å)³ =
12298.32; D_{cal} = 0.8616 g/cm³; D_{obs} = 1.0392 g/cm³; Standard deviation = 1.25 %; Z = 8;
α = 90°, β = 87.1°, γ = 90°; Crystal system = Monoclinic Porosity (%) = 17.09

I/Io	D _{obs}	D _{cal}	h	k	l
16	4.4211230	4.3337540	0	4	0
8	4.5912320	4.6001210	1	2	-2
2	2.3059380	2.3063420	3	5	2
100	12.998958	12.997634	0	0	1
3	5.6432220	5.6478650	1	2	0
5	5.3162430	5.3249870	2	2	0
9	4.3786740	4.3899870	1	3	3
2	2.4089640	2.4123870	3	5	2

The table reveals that complex have monoclinic crystal system.

TABLE-7
CELL DATA AND CRYSTAL LATTICE PARAMETERS FOR [Co(AMCC)₂]H₂O
a(Å) = 21.685360 ± 0.019767; b(Å) = 23.224180 ± 0.070931; c(Å) = 27.445560 ± 0.121237;
Volume (Å)³ = 13822.26; D_{cal} = 0.7695 g/cm³; D_{obs} = 1.0241 g/cm³; Standard deviation =
0.0030561 = 0.3 %; Z = 8; Crystal system = Orthorhombic;
α = 90°, β = 90°, γ = 90°; Porosity (%) = 24.86

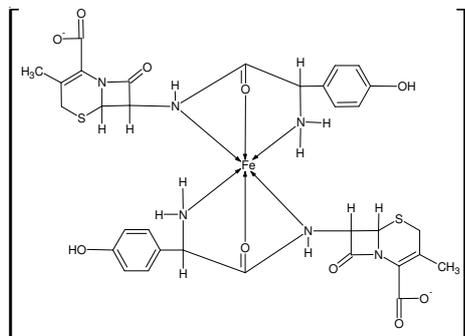
I/Io	D _{obs}	D _{cal}	h	k	l
40	4.218508	4.212842	5	1	1
62	3.961926	3.962494	4	4	0
70	3.440960	3.450936	6	2	0
78	3.115265	3.115308	5	3	5
100	2.411530	2.409485	9	0	0
81	2.214781	2.213118	8	6	1
89	2.096155	2.096775	9	2	-6
73	1.948603	1.947885	10	4	4

From cell data and crystal lattice parameter it is clear that complex has orthorhombic crystal system.

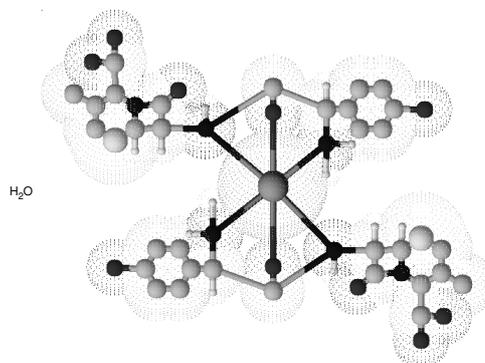
TABLE-8
CELL DATA AND CRYSTAL LATTICE PARAMETERS FOR [Cu(AMCC)Cl]H₂O
a(Å) = 21.668460 ± 0.015622; b(Å) = 23.269650 ± 0.056269; c(Å) = 27.419440 ± 0.062121;
Volume (Å)³ = 13825.34; D_{cal} = 0.9202 g/cm³; D_{obs} = 1.0683 g/cm³; Standard deviation =
0.0025966 = 0.25 %; Z = 16; Crystal system = Monoclinic;
α = 90°, β = 89.9°, γ = 90°; Porosity (%) = 13.86

I/Io	D _{obs}	D _{cal}	h	k	l
32	4.086094	4.086602	3	2	-5
48	3.961926	3.964444	4	4	0
61	3.440960	3.449074	6	2	0
74	3.310913	3.319386	5	3	4
89	2.975044	2.974217	7	2	1
85	2.548492	2.546396	8	3	1
100	2.270120	2.267212	9	3	-2
76	2.064732	2.063589	10	3	2
91	1.821968	1.820779	7	9	6
59	1.643877	1.643181	9	7	9

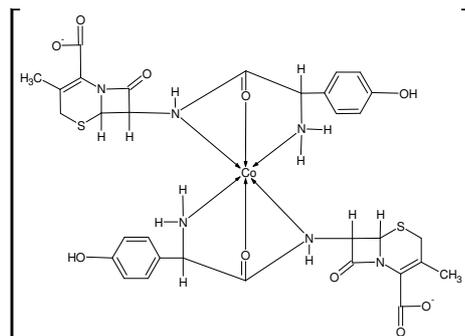
Cell data and Crystal lattice parameter of Cu²⁺ complex indicates that it has monoclinic crystal system.

Proposed structure of $[\text{Fe}(\text{AMCC})_2]\cdot\text{H}_2\text{O}$ complex

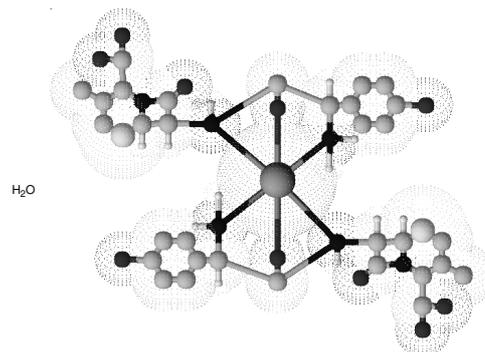
Molecular formula: $\text{C}_{32}\text{H}_{32}\text{N}_6\text{O}_{11}\text{S}_2\text{Fe}$
Molecular weight = 798



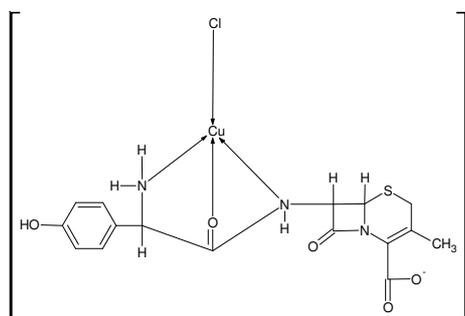
3D view of $[\text{Fe}(\text{AMCC})_2]\cdot\text{H}_2\text{O}$ complex

Proposed structure of $[\text{Co}(\text{AMCC})]\cdot\text{H}_2\text{O}$ complex

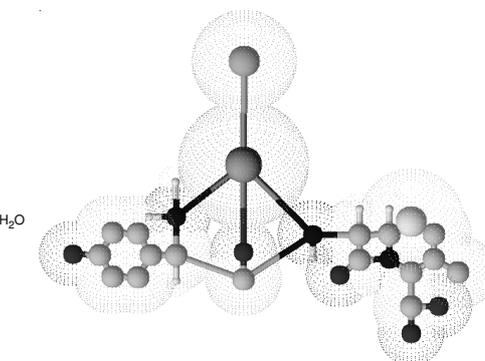
Molecular formula: $\text{C}_{32}\text{H}_{32}\text{N}_6\text{O}_{11}\text{S}_2\text{Co}$
Molecular weight = 800.9



3D view of $[\text{Co}(\text{AMCC})]\cdot\text{H}_2\text{O}$ complex

Proposed structure of $[\text{Cu}(\text{AMCC})\text{Cl}]\cdot\text{H}_2\text{O}$ complex

Molecular formula: $\text{C}_{16}\text{H}_{17}\text{N}_3\text{O}_6\text{S}\cdot\text{ClCu}$
Molecular weight = 479



3D view of $[\text{Cu}(\text{AMCC})\text{Cl}]\cdot\text{H}_2\text{O}$ complex

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REFERENCES

1. M. Tumer, H. Koksall, S. Serin and S. Patat, *Synth. React Inorg. Met.-Org. Chem.*, **27**, 59 (1997).
2. H. Sigel and R.B. Martin, *Chem. Rev.*, **82**, 385 (1982).
3. F.P. Dwyer, E. Mayhe, E.M.F. Roe and A. Shulama, *Br. J. Cancer*, **19**, 195 (1965).
4. V. Zappia and M. De Rosa, US Patent, 4772463 (1988).
5. A. Maiti, A.K. Guha and A. Gosh, *J. Inorg. Biochem.*, **41**, 13 (1998).
6. N.K. Kaushik and A.K. Mishra, *Indian J. Chem.*, **42A**, 276 (2003).
7. M.J. Sevilla, M.D. Moragues and F. Uruburu, *Antonie van Leeuwenhoek*, **54**, 75 (1988).
8. B. Kalluraya, R. Chimbalkar and P. Gunaga, *Indian J. Hetrocycl. Chem.*, **6**, 103 (1996).
9. A. Sebastiyana and D. Venkappayya, *J. Indian Chem. Soc.*, **67**, 584 (1990).
10. N. Raman and S. Ravichandran, *Asian J. Chem.*, **14**, 1766 (2002).
11. N. Raman and S. Ravichandran, *Asian J. Chem.*, **15**, 255 (2003).
12. N. Raman and R. Vimalaramani and Thangaraja, *Indian J. Chem.*, **43A**, 2357 (2004).
13. A.J. Vogel, Quantitative Inorganic Analysis, Longman. ELBS, London, edn. 3 (1962).
14. D. Nicholls, Comprehensive Inorganic Chemistry, Pergamon, Press New York, p. 1089 (1978).
15. P.K. Panchal, D.H. Patel and M.N. Patel, *Synth. React. Inorg. Met.-Org. Chem.*, **34**, 7 (2004).
16. K.P. Srivastava and N.K. Ojha, *Asian J. Chem.*, **19**, 355 (2007).
17. K. Nakamoto, Infrared Raman Spectra of Inorganic and Coordination Compounds, Wiley, New York, edn. 5 (1997).
18. N.B. Colthup, L.H. Daly and S.E. Wiberly, Introduction to Infrared and Raman Spectroscopy, Academic Press, New York, edn. 2 (1975).
19. M. Goldstein and D. Unworth, *Inorg. Chem. Acta*, **4**, 37 (1970).
20. R.L. Dutta and A. Syamal, Elements of Magnetochemistry, Affiliaed East-West Press Pvt. Ltd., edn. 2 (1993).
21. B.N. Figgis, Introduction to Ligand Fields, Wiley Eastern Ltd., New Delhi, India, p. 305 (1976).

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