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Spectral Analysis Of The New Ternary Complexes Of Cu (II) Ion With Ciprofloxacin And Different Amino Acids.

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ABSTRACT

Complexes of Cu(II) with ciprofloxacin drug and different amino acids are synthesized and characterized by different types of analytical methods such as elemental analysis and spectral analysis like UV-Visible, IR and ESR analysis. The general formula [Cu(dap)(L)].xH_2O are found for the ternary chelate complexes. From the analytical and spectral data the stoichiometry has been found to be 1:1:1 for all the complexes.

Keywords: Ciprofloxacin, spectral analysis, ternary complexes.

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INTRODUCTION

The mixed-ligand complexes play an important role in biological processes[1-2].The numbers of transition metal complexes are involved in storage,transport and catalytic processes[3].Copper is an essential element, present in large number of enzymes.Because its role in facilitating iron uptake.Copper deficiency can often produce anemia like symptoms[4].Amino acids containing –NH2 and –COOH groups are well known for their tendency to form complexes and metals and have good significance in biological and pharmaceutical fields.They are also involved in all the metabolic enzymatic activities of living organism[5-7].Fluoroquinolones behaved as bidantate ligand binding to the metallic ion through the carboxylate and carbonyl oxygens[8]. Ciprofloxacin is a synthetic,broad spectrum fluoroquinolone antibacterial agent [9].It is the second generation quinolone currently marketed in USA,which is rapidly and nearly completely absorbed on oral administration[10].The chemical structure of ciprofloxacin is shown in figure 1.

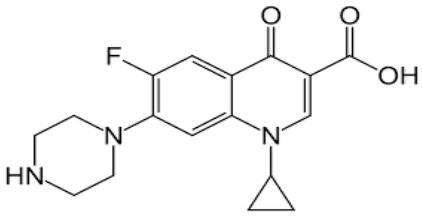

Figure 1. Ciprofloxacin drug

Hence, the present paper deals with the systematic study of Cu(II) complexes with drug ciprofloxacin as primary ligand and different amino acids as secondary ligand.

EXPERIMENTAL SECTION

Materials

All the chemicals used in present study were AR grade.The metal is used as sulphate.Pure drug sample is obtained from pharmaceutical industries.The pure sample of amino acids were obtaind from S.D. Fine Mumbai.The solutions of all reagents were prepared in double distilled water having pH 6.80-6.90.

Method

Firstly prepared Cu(II) hydroxide by precipitation method.For precipitation 0.2 M sodium hydroxide solution is added to 25 ml aqueous solution of copper sulphate with constant stirring.After precipitation, precipitate is filtered and washed by cold distilled water until all sulphate was removed.

Precipitated copper hydroxide take into different beakers and added to equimolar amount of drug and different amino acids as powder form.The mixture was heated on water bath for 2-4 hours,then filter the hot solution and concentrate on water bath.Obtained complexes are blue in colour,which are separated by slow evaporation and recrystallized with double distilled water.The pH of solution is kept 7.Complexes are dried in vaccum at 70oC.

RESULT AND DISCUSSION

Elemental analysis

The elemental data of synthesized complexes are tabulated in table 1.On the basis of the following data we can observe that these complexes have stoichiometry 1:1 metal to ligand ratio.

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Table 1: Elemental analysis data of synthesized complexes.

S.N.	Name of complexes	Molecular formula of complexes	Elemental analysis (%)							Molecular weight
			C%	H%	N%	O%	S%	F%	M(Cu) %	
1.	Ciprofloxacin	$C_{17}H_{18}FN_3O_3$	61.65 %	5.43 %	12.69 %	14.50 %	--	5.71%	--	330.9
2.	[Cu(cipro)(arg)].6H_2O	$C_{23}H_{32}N_7O_5F$	41.09 % (41.00)	6.55 % (5.90)	14.59 % (14.28)	26.20 % (26.15)	--	2.81% (2.09)	8.73% (8.70)	671.59
3.	[Cu(cipro)(val)].4H_2O	$C_{22}H_{29}N_4O_5F$	45.62 % (44.09)	6.39 % (6.33)	9.67% (9.05)	24.88 % (24.48)	---	3.26% (3.24)	10.14 % (10.0 2)	578.59
4.	[Cu(cipro)(pro)].8H_2O	$C_{22}H_{27}N_4O_5F$	40.70 % (40.59)	6.62 % (6.58)	8.63% (8.61)	32.06 % (32.00)	---	2.91% (2.87)	9.04% (9.41)	648.59
5.	[Cu(cipro)(threo)].5H $_2$O	$C_{21}H_{27}N_4O_6F$	42.31 % (40.97)	5.70 % (5.00)	9.40% (9.33)	29.55 % (28.4)	---	3.17% (3.14)	9.85% (9.56)	595.59
6.	[Cu(cipro)(ala)].6H_2O	$C_{20}H_{25}N_4O_5F$	40.91 % (40.80)	6.30 % (6.29)	9.54% (9.52)	30.00 % (29.00)	---	3.22% (3.10)	10.00 %(9.9 0)	586.59
7.	[Cu(cipro)(glu)].7H_2O	$C_{22}H_{27}N_4O_7F$	41.60 % (41.52)	6.46 % (6.40)	8.82% (8.74)	30.88 % (30.80)	---	2.97% (2.90)	9.24% (9.06)	634.59
8.	[Cu(cipro)(phen)].6H_2 O	$C_{26}H_{29}N_4O_5F$	47.08 % (47.12)	6.18 % (6.09)	8.45% (8.34)	26.56 % (26.49)	---	2.85% (2.59)	8.85% (8.69)	662.59
9.	[Cu(cipro)(tryp)].4H_2 O	$C_{28}H_{30}N_5O_5F$	51.88 % (51.04)	5.86 % (5.79)	10.80 % (10.73)	19.45 % (19.39)	----	2.91% (2.84)	9.06% (9.01)	647.59
10.	[Cu(cipro)(tyro)].5H_2 O	$C_{26}H_{29}N_4O_6F$	47.23 % (47.12)	5.90 % (5.89)	8.47% (8.96)	26.64 % (26.25)	---	2.86% (2.78)	8.88% (8.46)	660.59
11.	[Cu(cipro)(gly)].7H_2O	$C_{19}H_{23}N_4O_5F$	38.60 % (38.25)	6.26 % (6.13)	9.48% (9.39)	32.50 % (32.00)	---	3.20% (30.1 4)	9.93% (9.80)	590.59

UV-Visible spectral analysis

In the UV-Visible spectrum of all mixed-ligand complexes two close peaks are obtained in the uv region with λmax at 315 nm, which indicate the π-π* transition in all complexes.Also a band occur at 30248 cm-1 may be assigned to charge-transfer transition[11].UV-Visible spectral data of complexes are given in table 2.

ISSN: 0975-8585

Table 2: UV-Visible spectral data of synthesized copper complexes.

S.N.	Name of complexes	λmax	Absorbance	Wave no. (cm-1)	Energy (eV)	Frequency (THz)	Ɛmax (M-1 cm-1)
1.	Ciprofloxacin	278		35971.22	4.4599	107	
2.	[Cu(cipro)(arg)].6H_2O	635	2.844	15748.03	1.9525	472	28.40
3.	[Cu(cipro)(val)].4H_2O	628	0.025	15903.31	1.9718	476	2.50
4.	[Cu(cipro)(pro)].8H_2O	600	0.111	16666.67	2.0664	499	11.10
5.	[Cu(cipro)(threo)].5H_2O	656	0.117	15243.90	1.8900	456	11.0
6.	[Cu(cipro)(ala)].6H_2O	615	0.624	16260.16	2.0160	487	62.40
7.	[Cu(cipro)(glu)].7H_2O	626	0.405	15974.44	1.9806	478	40.50
8.	[Cu(cipro)(phen)].6H_2O	620	0.168	16129.03	1.9997	483	16.80
9.	[Cu(cipro)(tryp)].4H_2O	616	0.114	16233.77	2.0127	486	11.40
10.	[Cu(cipro)(tyro)].5H_2O	640	0.154	15625.00	1.9373	468	15.40
11.	[Cu(cipro)(gly)].7H_2O	658	0.144	15188.34	1.8820	455	14.40

IR spectral studies

The assignment of the bands are based on similar studies of drug-based metal complexes [12-13].In the IR spectrum of free ciprofloxacin ligand,we observed that the vibrations those at 1628 , 1507 and 1473 cm^{-1} are assigned to vibration absorption of –CH_2 on the benzene ring.The 1721 and 3403 cm^{-1} stretching vibrations are attributed to carbonyl and hydroxyl in a carboxyl group, respectively.The 1396 and 941 cm^{-1} vibrations corresponding to the bending of –OH and around 740 cm^{-1} indicates the absorption peak of secondary amine [14].

Some vibrational bands which are present in free ligand are also appear in their complexes ,because of structural similarities.The M-O band occur at 755 cm^{-1} for Cu(II) complexes.The ν(OH) band at 3529 cm^{-1} ciprofloxacin shifted to 3413 cm^{-1} in complexes.The disappearence of the band at 1474 cm^{-1} in ciprofloxacin due to –COOH group suggests that the coordination was through o-atom of the carboxylic group[15].It can be observed in the spectrum of all the metal complexes that the peak at 3403 cm^{-1} shows negative shift compared with the spectrum of ciprofloxacin.The diappearence of peak 1721 cm^{-1} assigned to the association between copper metal ion and carbonyl group.ν C=O band shows positive shift from the ciprofloxacin.In all the metal complexes peaks at 802-896 cm^{-1} confirm the presence of co-ordinated water molecule.The IR spectral data of complexes are given in table 3.

Table 3: IR spectral data of copper complexes.

S.N.	Name of complexes	vNH2	vC=O	vC-O	πC=O	vMN	MO	C-W
1.	Ciprofloxacine	3093	1622	1323	----	---	----	-----
2.	[Cu(cipro)(arg)].6H2O	3290	1550	1386	----	456	326	850
3.	[Cu(cipro)(val)].4H2O	3286	1565	1396	556	417	330	817
4.	[Cu(cipro)(pro)].8H2O	3203	1510	1380	530	486	340	850
5.	[Cu(cipro)(threo)].5H2O	3296	1523	1356	518	461	323	812
6.	[Cu(cipro)(ala)].6H2O	3250	----	1388	520	455	390	852
7.	[Cu(cipro)(glu)].7H2O	3290	1454	1302	549	443	310	800
8.	[Cu(cipro)(phen)].6H2O	3263	1581	1392	596	461	350	896
9.	[Cu(cipro)(tryp)].4H2O	3279	1572	1338	572	----	300	852
10.	[Cu(cipro)(tyro)].5H2O	3232	1545	1390	561	464	375	804
11.	[Cu(cipro)(gly)].7H2O	3288	1593	1375	555	449	315	858

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ESR spectral studies

The ESR spectra of the complexes are given in table 4, which indicate that the complexes are paramagnetic in nature with one unpaired electron (d^9 configuration).The trend $g_{II}>g_{I}$ observed that suggest the unpaired electron is localized in dx2-y2 orbital[15].The observed AII and higher gII values indicate that there is slight distortion from planarity[16].

Table 4: ESR spectral data of copper complexes.

S.N.	Name of complexes	ESR parameters				
		g_{II}	g_{I}	g_{av}	A_{II}	A_{I}
1.	[Cu(cipro)(arg)].6H_2O	2.4	2.0	2.1	230	19.34
2.	[Cu(cipro)(val)].4H_2O	2.2	2.0	2.0	180	22.19
3.	[Cu(cipro)(pro)].8H_2O	2.4	2.0	2.1	440	41.32
4.	[Cu(cipro)(threo)].5H_2O	2.4	2.1	2.2	420	83.25
5.	[Cu(cipro)(ala)].6H_2O	2.5	2.0	2.1	540	44.25
6.	[Cu(cipro)(glu)].7H_2O	2.3	2.0	2.1	150	11.62
7.	[Cu(cipro)(phen)].6H_2O	2.3	2.0	2.1	160	61.62
8.	[Cu(cipro)(tryp)].4H_2O	2.4	2.0	2.2	220	81.62
9.	[Cu(cipro)(tyro)].5H_2O	2.3	2.0	2.1	160	81.62
10.	[Cu(cipro)(gly)].7H_2O	2.5	2.0	2.2	250	91.62

Magnetic measurement

The magnetic moment data of the complexes are presented in table 5.These values are closer to those reported in some similar type of complexes[17].The magnetic moment values suggesting the paramagnetic nature of complexes with the presence of unpaired electron in the outer orbital of the metal ion.

Table 5: Magnetic measurement data of copper complexes.

S.N.	Name of complexes	Mol. Wt.	Magnetic susceptibility	Molar magnetic susceptibility	μ_{eff}
1.	[Cu(cipro)(arg)].6H_2O	671.59	2.16E-06	0.001450	1.8
2.	[Cu(cipro)(val)].4H_2O	578.59	1.80E-06	0.001041	1.5
3.	[Cu(cipro)(pro)].8H_2O	648.59	1.76E-06	0.001141	1.6
4.	[Cu(cipro)(threo)].5H_2O	595.59	1.90E-06	0.001131	1.6
5.	[Cu(cipro)(ala)].6H_2O	586.59	1.10E-06	0.000645	1.2
6.	[Cu(cipro)(glu)].7H_2O	634.59	2.12E-06	0.001345	1.7
7.	[Cu(cipro)(phen)].6H_2O	662.59	1.91E-06	0.001265	1.7
8.	[Cu(cipro)(tryp)].4H_2O	647.59	1.34E-06	0.000867	1.4
9.	[Cu(cipro)(tyro)].5H_2O	660.59	1.29E-06	0.000852	1.4
10.	[Cu(cipro)(gly)].7H_2O	590.59	1.35E-06	0.007972	1.3

CONCLUSION

The new ternary complexes of Cu(II) metal ion with drug ciprofloxacin and different amino acids were synthesized and characterized.The prepared ternary complexes are characterized by elemental analysis,UV-Visible and IR spectra as well as magnetic measurement.Based on analytical and spectral data ,the stoichiometry has been found to be 1:1:1 for all the complexes.Magnetic measurement and ESR spectral data explain the paramagnetic nature of the complexes.

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