

Synthesis, characterization and spectroscopic studies of mixed-ligand Cu(II) complexes with 2,6-pyridinedicarboxylic acid and L-glutamic, succinic, malonic acids and glutamine

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Abstract

Mixed-ligand coordination complexes of copper(II) (1-4) were synthesized by solvothermal method in 1:1:1 molar ratio [metal: 2,6-pdc: amino acid = L-glutamic acid (L-glu), glutamine (gln), succinic acid (SA) and malonic acid (MA)], using 2,6-pyridinedicarboxylic acid (2,6-pdc) and amino acids as primary and secondary ligands respectively. These complexes are formulated as: 1. $[Cu_3(2,6-Hpdc)_2(2,6-pdc)(L-glu)(H_2O)_5]$ 2. $[Cu_3(2,6-pdc)_2(2,6-Hpdc)(gln)(H_2O)_5]$ 3. $[Cu_3(2,6-Hpdc)_2(2,6-pdc)(SA)(H_2O)_6]$ and 4. $[Cu_3(2,6-Hpdc)_2(2,6-pdc)(MA)(H_2O)_7]$.

All these complexes (1-4) have been characterized by elemental, FT-IR and mass spectroscopy. Mass spectroscopic data showed that the complexes (1-4) were trinuclear and chelating. The FT-IR and UV-visible spectroscopy, data confirmed the proposed octahedral geometry of the complexes.

Keywords: Cu(II) complexes, 2,6-pyridinedicarboxylic acid, IR, mass spectroscopy, synthesis, amino acid, UV.

Introduction

2,6-pyridinedicarboxylic acid (2,6-pdc) or dipicolinic acid (DPC) forms stable chelates with simple metal ions and oxo-metal cations and can display varying coordination, functioning as a multidentate ligand. Dipicolinates (dipic) mostly coordinate to transition metals by either carboxylate bridges between metal centers to form polymeric or dimeric complexes^{11,22,23,30} or by tridentate (O, N, O') chelation to one metal^{17,23}. DPC has applications in analytical chemistry^{3,16} corrosion inhibition, decontamination of nuclear reactors¹⁸ and diverse biological activities^{2,32,37}. Dipicolinate complexes have been used as electron carriers in some model biological systems as specific molecular tools in DNA cleavage¹³ and as NO scavengers⁶.

The chemistry of Cu(II) carboxylate complexes, especially with N-donor ligands, has been extensively studied^{9,26,27}. The crystal structures of copper complexes of 2-aminopyridine with carboxylate^{19,39} and oxalate⁸ are also reported in the literature. Some Cu(II) complexes possess a wide range of biological activity such as antivirals, fungicides, pesticides and even tracers, depending on the ligand-binding sites^{5,12,29,38}. Dipicolinic ligand with Cu(II)

commonly has one or two coordination modes. In one, a single planar dipic binds in the equatorial plane of a Cu(II) cation and other ligands such as H₂O or pyridine occupy the remaining sites, forming a square planar or square-pyramidal coordination geometry²⁴; or two planar dipic molecules coordinate perpendicularly, generating a distorted octahedral coordination geometry³³.

Attention of bioinorganic chemists has been directed toward the synthesis and characterization of new Cu(II) carboxylates with N-donor ligands to model the active sites in metalloenzymes³¹. The amino acids have significant importance among the chemicals since they are the "building blocks" of the living systems. This amino acid with its terminal -C(=O)-NH₂ group has the potential to form significant hydrogen bonding interactions with the double-stranded (ds) DNA and could show good DNA-binding propensity²⁰. Glutamic acid (glu), which is an endogenous amino acid, is the main stimulating neurotransmitter in the brains of mammals. Glu is the most important oxidative substrate for the intestinal mucosa and also plays a critical role in synaptic maintenance and plasticity and formation and function of the cytoskeleton⁴.

Succinic acid is a dicarboxylic acid produced as an intermediate of the tricarboxylic acid cycle (TCA) and also as one of the fermentation products of anaerobic metabolism¹⁵.

The malonate group (dianion of the propanedioic acid, malonic acid) seems a suitable candidate. The occurrence of two carboxylate groups in the 1,3-positions allows this ligand to adopt simultaneously chelating bidentate and different carboxylate bridging modes (*syn-syn*, *syn-anti* and *anti-anti* through one or both carboxylate groups)⁴⁰. Structures of 2,6-pyridinedicarboxylic acid, malonic acid, glutamic acid, succinic acid and glutamine, ligands are given in fig. 1.

This study aims first at compiling these studies related to structural characterization of complexes 1. $[Cu_3(2,6-Hpdc)_2(2,6-pdc)(L-glu)(H_2O)_5]$; 2. $[Cu_3(2,6-pdc)_2(2,6-Hpdc)(gln)(H_2O)_5]$, 3. $[Cu_3(2,6-Hpdc)_2(2,6-pdc)(SA)(H_2O)_6]$ and 4. $[Cu_3(2,6-Hpdc)_2(2,6-pdc)(MA)(H_2O)_7]$. These complexes (1-4) have been characterized by elemental, FT-IR, UV-visible spectroscopy and mass spectroscopy respectively to arrive at conclusion regarding their geometrical molecular structure as shown in fig. 2.

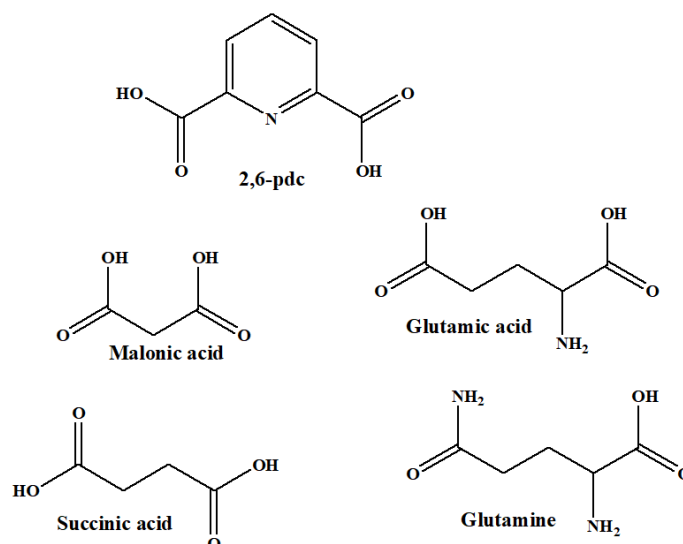


Fig. 1: Ligands used for the synthesis of the mixed-ligand complexes

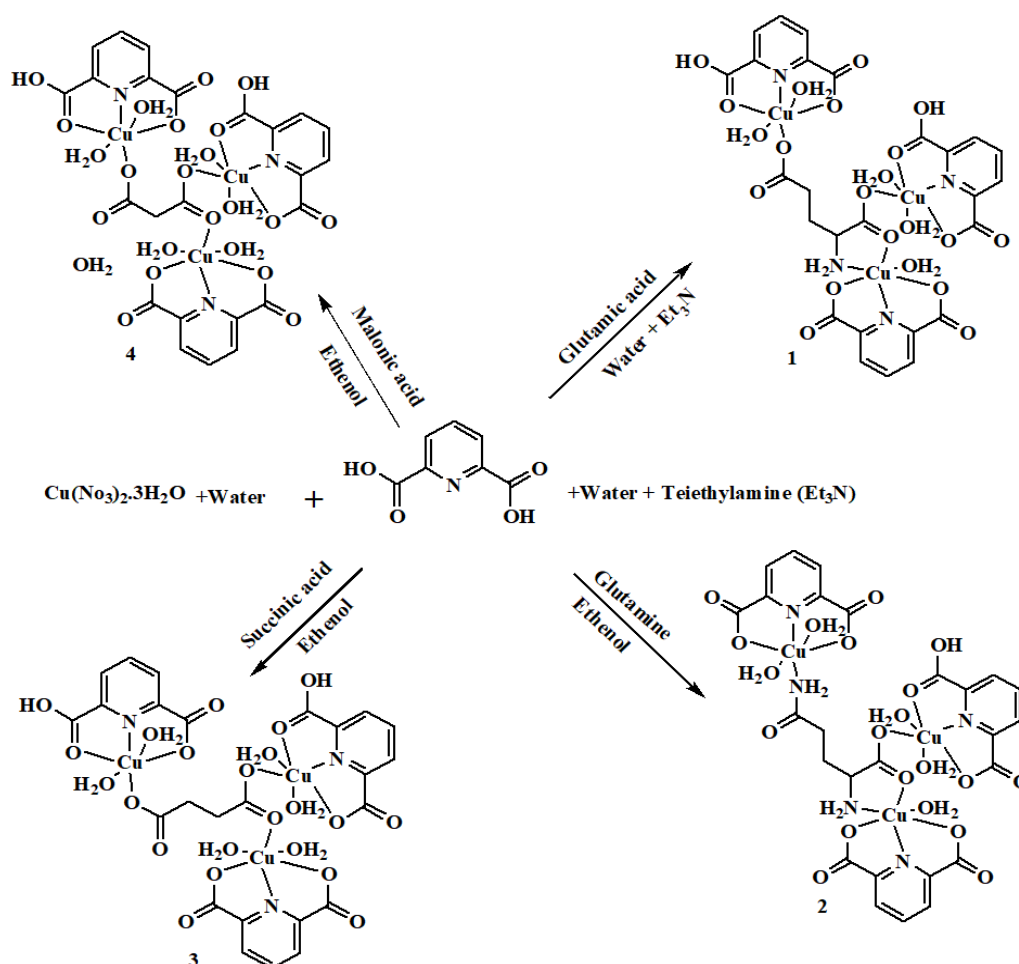


Fig. 2: Hydrothermal process for the synthesis of mixed-ligand complexes, 1-4 and their proposed geometrical molecular structures

Material and Methods

Materials: All chemicals and organic solvents were purchased commercially for the synthesis and used as such without further purification. Chemicals $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 2,6-pyridinedicarboxylic acid, glutamic acid, glutamine, succinic acid and malonic acid were purchased from Sigma

Aldrich and used without further purification. All other reagents are commercially available and used as received.

Physical Measurement: Melting points were recorded on a Perfit melting point apparatus. Elemental Analyses (C,H,N) were carried out with Thermo Finnigan, FLASH EA 1112

Elemental Analyzer. IR spectra were recorded with a FT-IR Spectrum 2 (PerkinElmer) (in KBr pellets) in the 4000-400 cm^{-1} region. The mass spectra were recorded with Waters UPLC-TQD Mass Spectrometer ESI/MS in the mass range of 150-2000 Da. The Electronic absorbance spectroscopy of all these complexes was recorded by LAMBADA-35 Spectrophotometer.

Synthesis of mixed-ligand complexes of Cu(II), 1-4:

$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.361 g, 1.5 mmol) dissolved in 12 mL deionized water. 2,6-pyridinedicarboxylic acid (0.250 g, 1.5 mmol) was dissolved in 12 mL deionized water and 9 drops Et_3N . Glutamic acid (0.220 g, 1.5 mmol) dissolved in 12 mL deionized water and 9 drops Et_3N . Glutamine (0.219 g, 1.5 mmol) was dissolved in 12 mL ethanol. Succinic acid (0.177 g, 1.5 mmol) dissolved in 12 mL ethanol. Malonic acid (0.156 g, 1.5 mmol) was dissolved in 12 mL ethanol (i.e. 1:1:1 molar ratios).

Then, these solutions were mixed with each other and sonicated for 15 mins. The mixtures (3 and 4) were placed in glass vials and put in oven for solvothermal synthesis at 90°C for 9 hrs, while complexes (1 and 2) were obtained at room temperature. The obtained solid was filtered and washed several times with small portions of alcohol/ether and then air dried at room temperature.

Characterization of $[\text{Cu}_3(2,6\text{-Hpdc})_2(2,6\text{-pdc})(\text{L-glu})(\text{H}_2\text{O})_5]$ 1:

The blue color solid (Yield: 47.00 %; mp 280°C). Anal. Calcd. for $\text{C}_{26}\text{H}_{28}\text{N}_4\text{O}_{21}\text{Cu}_3$: C, 33.81; H, 3.03; N, 6.06%; Found: C, 31.04; H, 2.74; N, 5.09%. IR data (KBr pellets, cm^{-1}) 3445, 3063, 3037, 1683, 1645, 1431, 1363, 1181, 1079, 774, 735, 684, 593, 551 and 434 cm^{-1} .

Characterization of $[\text{Cu}_3(2,6\text{-pdc})_2(2,6\text{-Hpdc})(\text{Gln})(\text{H}_2\text{O})_5]$ 2:

The blue color solid (Yield: 48.00 %; mp 302°C). Anal. Calcd. for $\text{C}_{26}\text{H}_{29}\text{N}_5\text{O}_{20}\text{Cu}_3$: C, 33.85; H, 3.14; N, 7.59%; Found: C, 30.80; H, 2.72; N, 5.46%. IR data (KBr pellets, cm^{-1}) 3445, 3063, 3038, 1683, 1645, 1431, 1363, 1269, 1181, 1079, 774, 735, 684, 593, 550 and 435 cm^{-1} .

Characterization of $[\text{Cu}_3(2,6\text{-Hpdc})_2(2,6\text{-pdc})(\text{SA})(\text{H}_2\text{O})_6]$ 3:

The blue color solid (Yield: 51.42 %; mp 300°C). Anal. Calcd. for $\text{C}_{25}\text{H}_{27}\text{N}_3\text{O}_{22}\text{Cu}_3$: C, 32.87; H, 2.95; N, 4.60%; Found: C, 32.53; H, 2.24; N, 3.49%. IR data (KBr

pellets, cm^{-1}) 3447, 3063, 3037, 1684, 1645, 1431, 1363, 1181, 1079, 915, 774, 735, 684, 593, 550 and 434 cm^{-1} .

Characterization of $[\text{Cu}_3(2,6\text{-Hpdc})_2(2,6\text{-pdc})(\text{mal})(\text{H}_2\text{O})_7]$ 4:

The blue color solid (Yield: 47.00 %; mp 302°C). Anal. Calcd. for $\text{C}_{24}\text{H}_{27}\text{N}_3\text{O}_{23}\text{Cu}_3$: C, 31.38; H, 2.94; N, 4.58%; Found: C, 31.51; H, 2.70; N, 5.14%. IR data (KBr pellets, cm^{-1}) 3446, 3063, 3037, 1683, 1645, 1431, 1363, 1181, 1079, 774, 735, 684, 593, 551 and 435 cm^{-1} .

Results and Discussion

Elemental analyses: The physical properties and analytical data of the copper (II) complexes (1-4) are summarized in table 1.

FT-IR spectra: The frequencies of IR absorption bands of these complexes 1-4 and their corresponding IR spectra are depicted in table 2 and fig. 3 and 4 respectively. The peak at 3445, 3445, 3447 and 3446 cm^{-1} can be attributed to the presence of coordinated water¹⁴. Weak bands between 3063 and 3037 cm^{-1} are attributed to $\nu(\text{C-H})$ of aromatic and methylene groups respectively. The carboxylate stretching vibration (νCOOH) for free 2,6-pdc ligand, glutamic acid, glutamine, succinic acid and malonic acid was observed at 1722 cm^{-1} , but the band for νCOOH disappeared when 2,6-pdc, glutamic acid, glutamine, succinic acid and malonic acid were coordinated to Cu(II) ion. It exhibited an asymmetric $\nu_{\text{asy}}(\text{COO}^-)$ and symmetric $\nu_{\text{sym}}(\text{COO}^-)$ carboxylate stretching vibrations at 1683-1645 and 1363 cm^{-1} for 1, 1683-1645 and 1363 cm^{-1} for 2, 1684-1645 and 1363 cm^{-1} for 3, 1683-1645 and 1363 cm^{-1} for 4.

The difference between asymmetric and symmetric carboxylate stretching frequencies ($\Delta\nu = \nu_{\text{asy}}(\text{COO}^-) - \nu_{\text{sym}}(\text{COO}^-)$) is often used to correlate the carboxylate coordination mode^{25,34,36}. The values of $\Delta\nu(\nu_{\text{asy}}-\nu_{\text{sym}})$ are 301, 301, 302 and 301 cm^{-1} for 1-4 respectively confirming the monodentate coordination modes of the carboxylic groups^{21,28}. Characteristic of $\text{C}=\text{N}$, $\text{C}=\text{C}$ of pyridine rings can be observed from 1468 to 1431 cm^{-1} . The wagging vibrations of pyridines and amino acid are observed at, 774 and 684 for 1-4 respectively. Weak bands at 593 and 434 cm^{-1} , 593 and 435 cm^{-1} , 593 and 434 cm^{-1} and 593 and 435 cm^{-1} are attributed to Cu-N and Cu-O vibrations of mixed-ligand complexes 1-4 respectively⁷.

Table 1
Analytical data and physical properties of Cu(II) complexes 1-4

E.F.of 1-4	M.W. ($^\circ\text{C}$)	Color (%)	M.P.	Yield	Elemental analyses (%) Calcd.(Found)		
					C	H	N
$\text{C}_{26}\text{H}_{28}\text{N}_4\text{O}_{21}\text{Cu}_3$ 1	922.62	blue	280	47.16	33.81 (31.04)	3.03 (2.74)	6.06 (5.09)
$\text{C}_{26}\text{H}_{29}\text{N}_5\text{O}_{20}\text{Cu}_3$ 2	921.62	blue	302	48.29	33.85 (30.80)	3.14 (2.72)	7.59 (5.46)
$\text{C}_{25}\text{H}_{27}\text{N}_3\text{O}_{22}\text{Cu}_3$ 3	912.62	blue	300	51.54	32.87 (32.53)	2.95 (2.24)	4.60 (3.49)
$\text{C}_{24}\text{H}_{27}\text{N}_3\text{O}_{23}\text{Cu}_3$ 4	917.62	blue	302	49.66	31.38 (31.51)	2.94 (2.70)	4.58 (5.14)

Table 2
FT-IR spectral data (cm⁻¹) of Cu(II) complexes, 1-4

Assignment	1	2	3	4
v(O-H) _{water}	3445(br)	3445(br)	3447(br)	3446(br)
v(C-H) _{aromatic}	3063(w)	3063(w)	3063(w)	3063(w)
v(C-H) _{aliphatic}	3037(w)	3038(w)	3037(w)	3037(w)
v(C=N)	1468(w)	1468(w)	1468(w)	1468(w)
v(C=C)	1431(m)	1431(m)	1431(m)	1431(m)
v _{asy} (COO ⁻)	1683-1645(s)	1683-1645(s)	1684-1645 (s)	1683-1645(s)
v _{sym} (COO ⁻)	1363(s)	1363(s)	1363(s)	1363(s)
Δv	301	301	302	301
v(py)	774(s)	774(s)	774(s)	774(s)
	684(s)	684(s)	684(s)	684(s)
v(Cu-N)	593(m)	593(m)	593(m)	593(m)
v(Cu-O)	434(m)	435(m)	434(m)	435(m)

w: weak, br: broad, m: medium, s: strong

Table 3
Mass fragments data of Cu(II) complexes.

Complex	Molar mass	Important mass fragmentations (m/z) values
[Cu ₃ (2,6-Hpdc) ₂ (2,6-pdc)(L-glu)(H ₂ O) ₅] 1	922.62	915 [M-7], 687.62 (M-5H ₂ O, Glu), 458.08 (M-5H ₂ O, Glu, Cu, 2,6-pdc), 228.54 (M-5H ₂ O, Glu, Cu ₂ , 2,6-Hpdc, 2,6-pdc) 165.00 (M-5H ₂ O, Glu, Cu ₃ , 2,6-pdc, 2,6-Hpdc)
[Cu ₃ (2,6-pdc) ₂ (2,6-Hpdc)(Gln)(H ₂ O) ₅] 2	921.62	915 [M-6], 686.62 (M-5H ₂ O, Gln), 458.08 (M-5H ₂ O, Gln, Cu, 2,6-pdc), 228.54 {M-5H ₂ O, Gln, Cu ₂ , (2,6-pdc) ₂ } 166 {M-5H ₂ O, Gln, Cu ₃ , (2,6-pdc) ₂ }
[Cu ₃ (2,6-Hpdc) ₂ (2,6-pdc)(SA)(H ₂ O) ₆] 3	912.62	916 [M+4], 804.62 (M-6H ₂ O), 688.62 (M-6H ₂ O, SA), 459.08 (M-6H ₂ O, SA, Cu, 2,6-Hpdc), 229.54 {M-6H ₂ O, SA, Cu ₂ , (2,6-Hpdc) ₂ }, 166 {M-6H ₂ O, SA, Cu ₃ , (2,6-Hpdc) ₂ }
[Cu ₃ (2,6-Hpdc) ₂ (2,6-pdc)(MA)(H ₂ O) ₇] 4	917.62	916 [M-1], 809.62 (M-6H ₂ O), 687.62 (M-7H ₂ O, MA), 458.08 (M-7H ₂ O, MA, Cu, 2,6-Hpdc), 228.54 {M-7H ₂ O, MA, Cu ₂ , (2,6-Hpdc) ₂ }, 165 {M-7H ₂ O, MA, Cu ₃ , (2,6-Hpdc) ₂ }

Table 4
Electronic absorption spectral data for mixed-ligand Cu(II) complex species formed in 1:1:1 molar ratio in DMSO

Solvent	Complexes	Color of solid complex	Color of complex in solvent	λ _{max} (nm)	ε(Lmol ⁻¹ cm ⁻¹)
DMSO	[Cu ₃ (2,6-Hpdc) ₂ (2,6-pdc)(L-glu)(H ₂ O) ₅] 1	Blue	Light blue	782	180
	[Cu ₃ (2,6-pdc) ₂ (2,6-Hpdc)(Gln)(H ₂ O) ₅] 2	Blue	Light blue	784	268
	[Cu ₃ (2,6-Hpdc) ₂ (2,6-pdc)(SA)(H ₂ O) ₆] 3	Blue	Light blue	785	259
	[Cu ₃ (2,6-Hpdc) ₂ (2,6-pdc)(MA)(H ₂ O) ₇] 4	Blue	Light blue	783	273

Mass spectral analysis: The mass spectral data of the Cu(II) complexes, (1-4) exhibited the main mass fragmentation peaks fig. 5 and 6 tabulated in table 3.

Mass spectrum of the complex (1) (molecular weight 922.62) gave molecular ion peaks [M-7] at m/z = 915, a peak at m/z = 687.62 assigned to (M-5H₂O, Glu), a peak at m/z = 458.08 assigned to (M-5H₂O, Glu, Cu, 2,6-pdc), a peak at m/z = 228.54 assigned to (M-5H₂O, Glu, Cu₂, 2,6-Hpdc, 2,6-

pdc) and a peak at m/z = 165 assigned to (M-5H₂O, Glu, Cu₃, 2,6-pdc, 2,6-Hpdc). The spectrum of complex (2) (molecular weight 921.62) gave molecular ion peaks [M-6] at m/z = 915, a peak at m/z = 686.62 assigned to (M-5H₂O, Gln), a peak at m/z = 458.08 assigned for (M-5H₂O, Gln, Cu, 2,6-pdc), a peak at m/z = 228.54 assigned for {M-5H₂O, Gln, Cu₂, (2,6-pdc)₂} and a peak at m/z = 166 assigned for {M-5H₂O, Gln, Cu₃, (2,6-pdc)₂}.

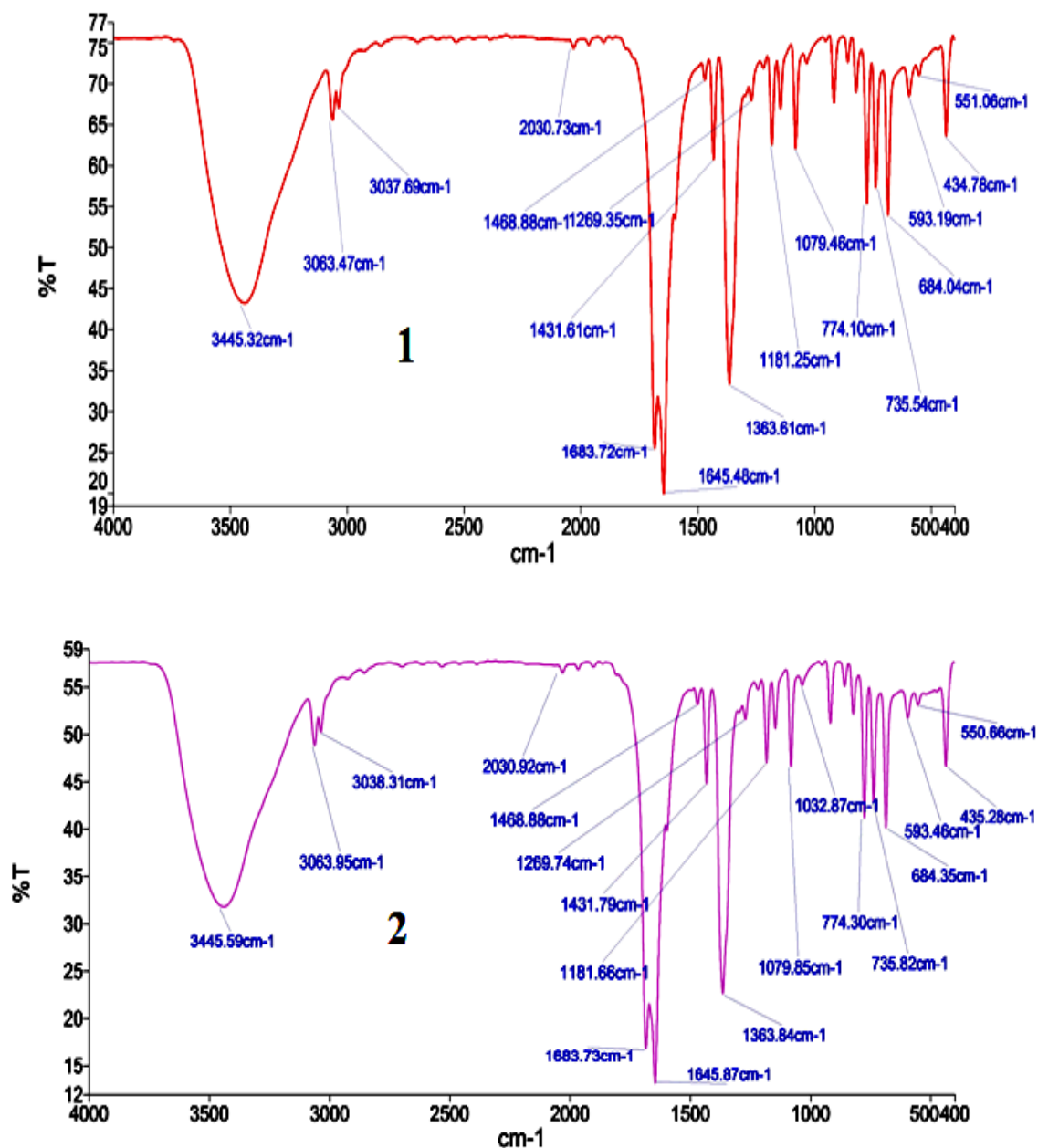


Fig. 3: FT-IR absorption bands of the complexes 1 and 2

The spectrum of complex (3) (molecular weight 912.62) gave molecular ion peaks [M+4] at $m/z = 916$, a peak at $m/z = 804.62$ assigned for (M-6H₂O), a peak at $m/z = 688.62$ assigned to (M-6H₂O, SA), a peak at $m/z = 459.08$ assigned for (M-6H₂O, SA, Cu, 2,6-Hpdc), a peak at $m/z = 229.54$ assigned for {M-6H₂O, SA, Cu₂, (2,6-Hpdc)₂} and a peak at $m/z = 166$ assigned for {M-6H₂O, SA, Cu₃, (2,6-Hpdc)₂}.

The spectrum of complex (4) (molecular weight 917.62) gave molecular ion peaks [M-1] at $m/z = 916$, a peak at $m/z = 809.62$ assigned for (M-6H₂O), a peak at $m/z = 687.62$ assigned to (M-7H₂O, MA), a peak at $m/z = 458.08$ assigned for (M-7H₂O, MA, Cu, 2,6-Hpdc), a peak at $m/z = 228.54$ assigned for {M-7H₂O, MA, Cu₂, (2,6-Hpdc)₂} and a peak

at $m/z = 165$ assigned for {M-7H₂O, MA, Cu₃, (2,6-Hpdc)₂}¹.

Electronic absorption spectroscopy: The electronic absorption spectral data for copper (II) mixed-ligand complexes 1–4 are given in table 4 and spectra are shown in fig. 7 and 8. The spectra of these complexes were measured in DMSO at 25°C by LAMBDA-35 model. The broad bands at 782 nm (light blue color), 784 nm (light blue color), 785 nm (light blue color) and 783 nm (light blue color) were observed in complexes 1–4 respectively. The bands 782–785 nm were assigned to d–d transitions. The d–d transitions in copper (II) mixed-ligand complexes (1–4), due to an 6-coordinated octahedral environment were around the copper (II) metal ions³⁵.

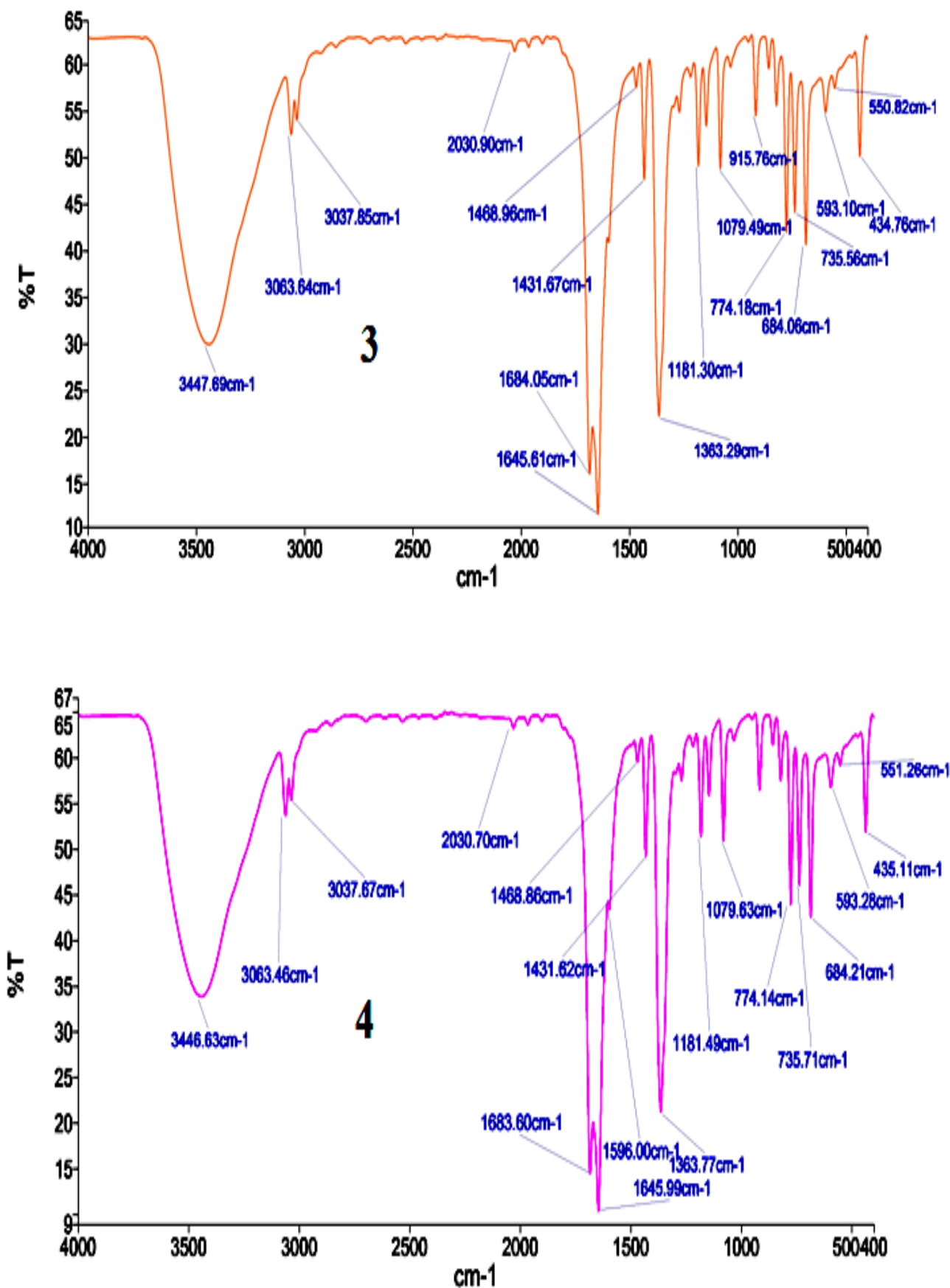


Fig. 4: FT-IR absorption bands of the complexes 3 and 4

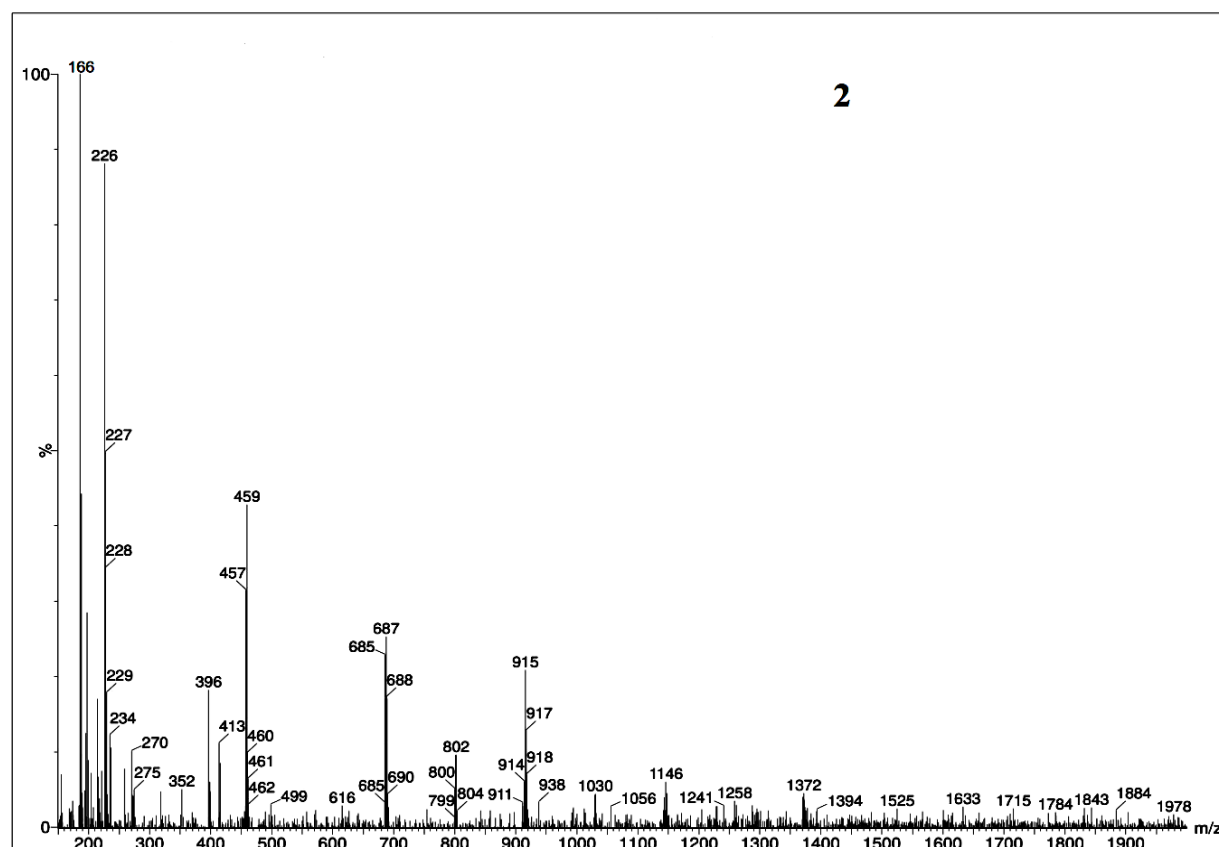
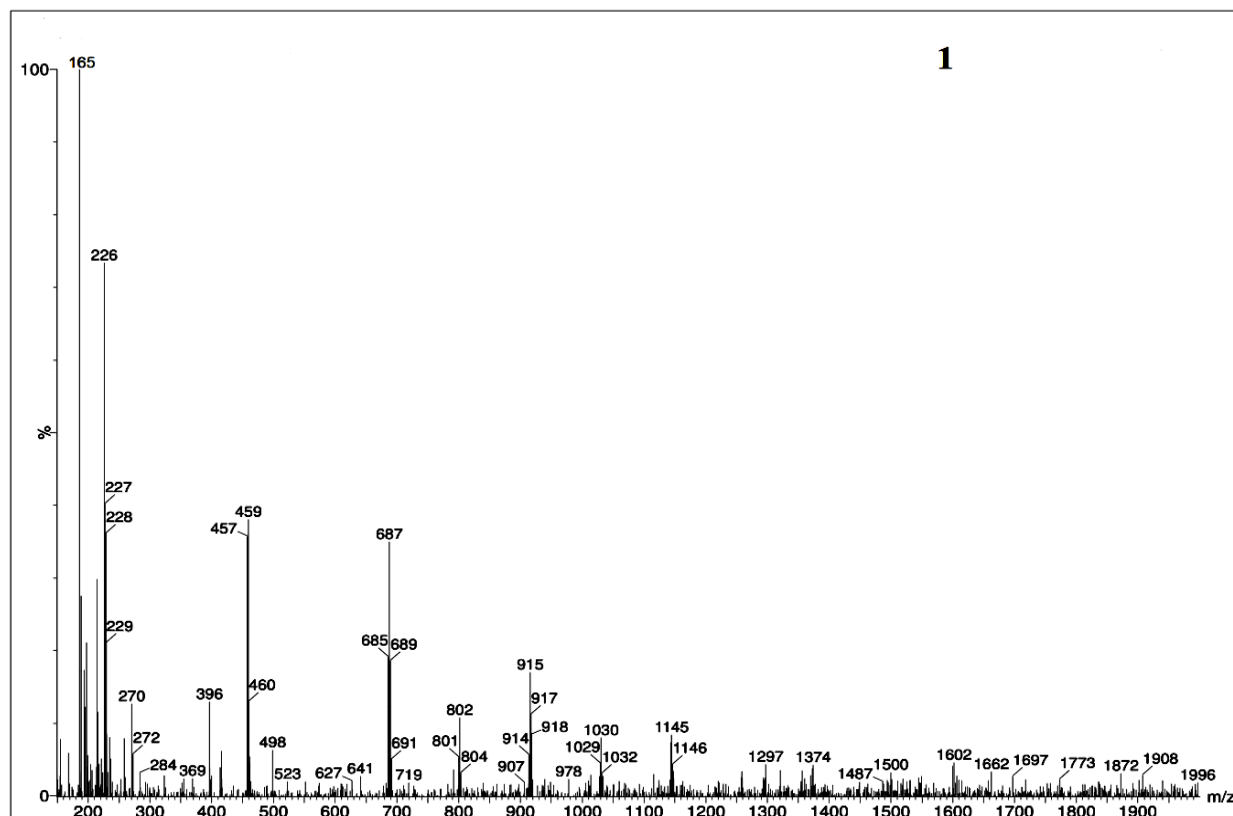


Fig. 5: Mass spectrum of mixed-ligand complexes 1 and 2

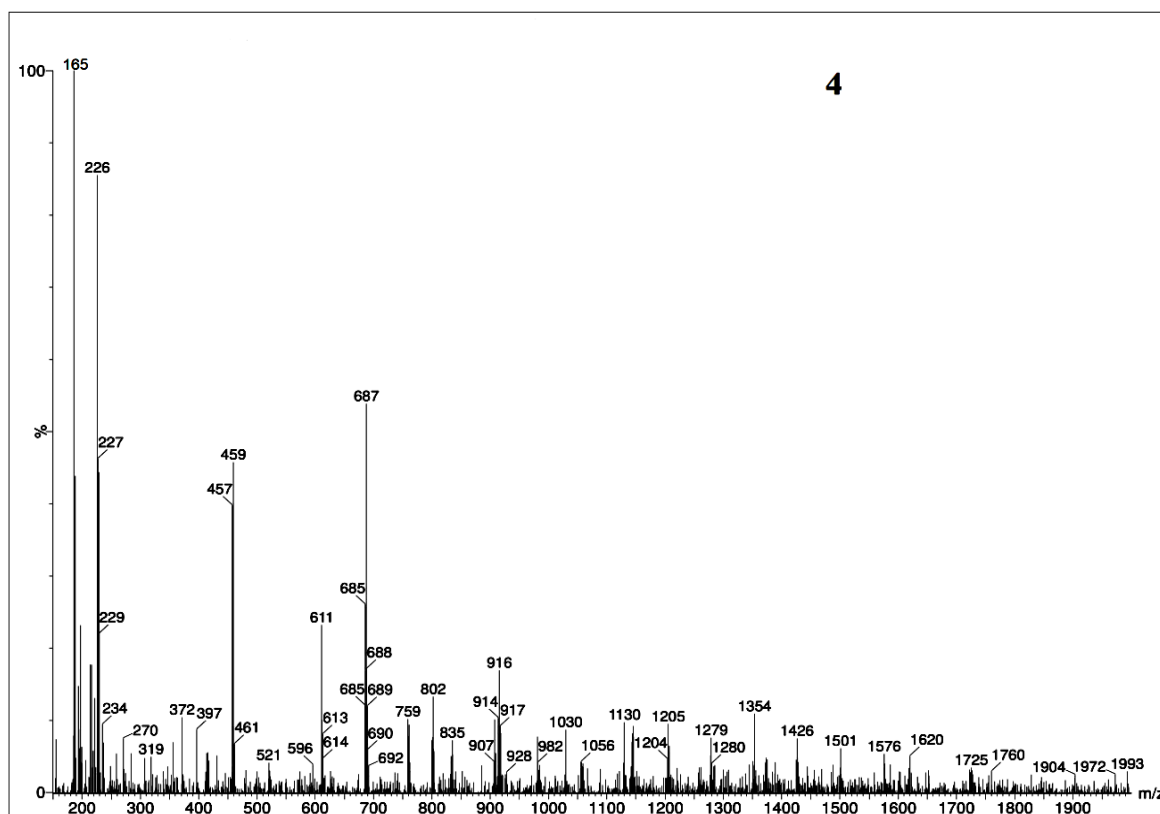
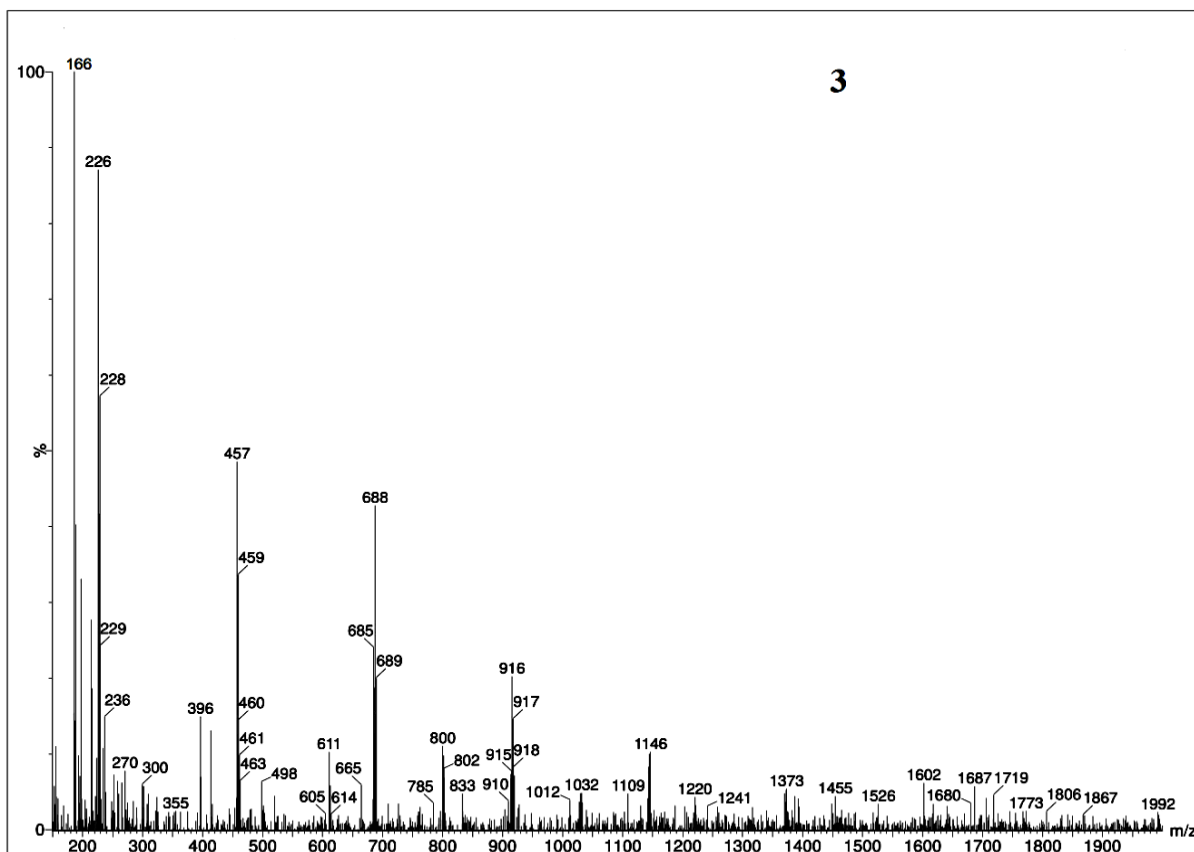


Fig. 6: Mass spectrum of mixed-ligand complexes 1 and 2

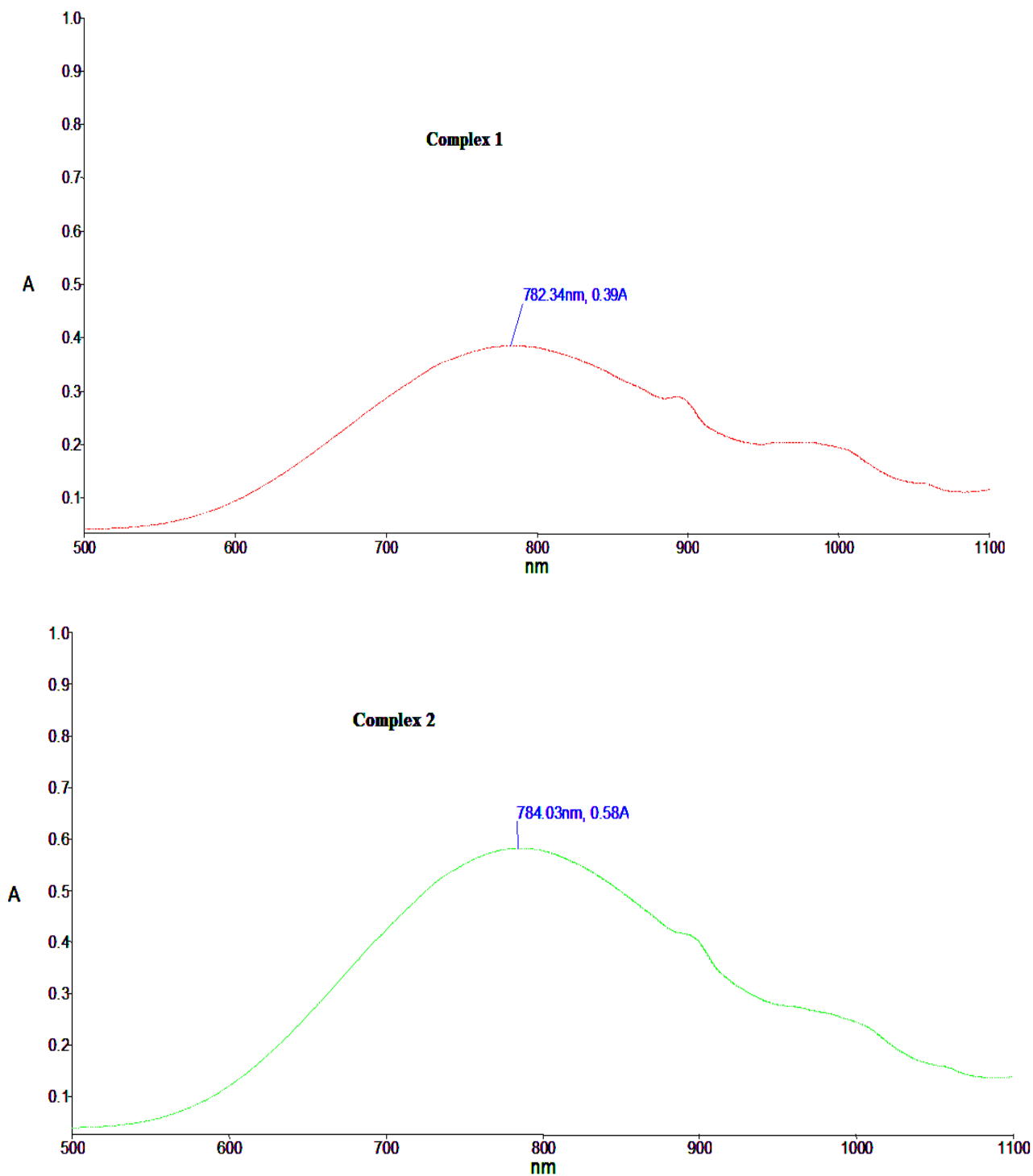


Fig. 7: Electronic spectra of mixed-ligand complexes 1 and 2

Conclusion

In this study, solvothermal syntheses, characterization and spectral studies of mixed-ligand Cu(II) complexes (1-4) have been investigated. These complexes were characterized by elemental analyses, FT-IR spectra, Mass spectra and UV-visible spectroscopy respectively. FTIR spectra suggested that the starting acids, 2,6-pyridinedicarboxylic acid glutamic acid, glutamine, succinic and malonic acid were

completely protonated and coordinated to the metal center through carboxylate O in monodentate manner.

The appearance of a lower shifted peak at 1683-1645, 1683-1645, 1684-1645, 1683-1645 cm^{-1} and a higher shifted sharp and medium bands at 774 and 684, 774 and 684, 774 and 684 cm^{-1} and 774 and 684 cm^{-1} indicated that the Cu(II) complexes 1-4 coordinate to an oxygen atom in the C=O bond.

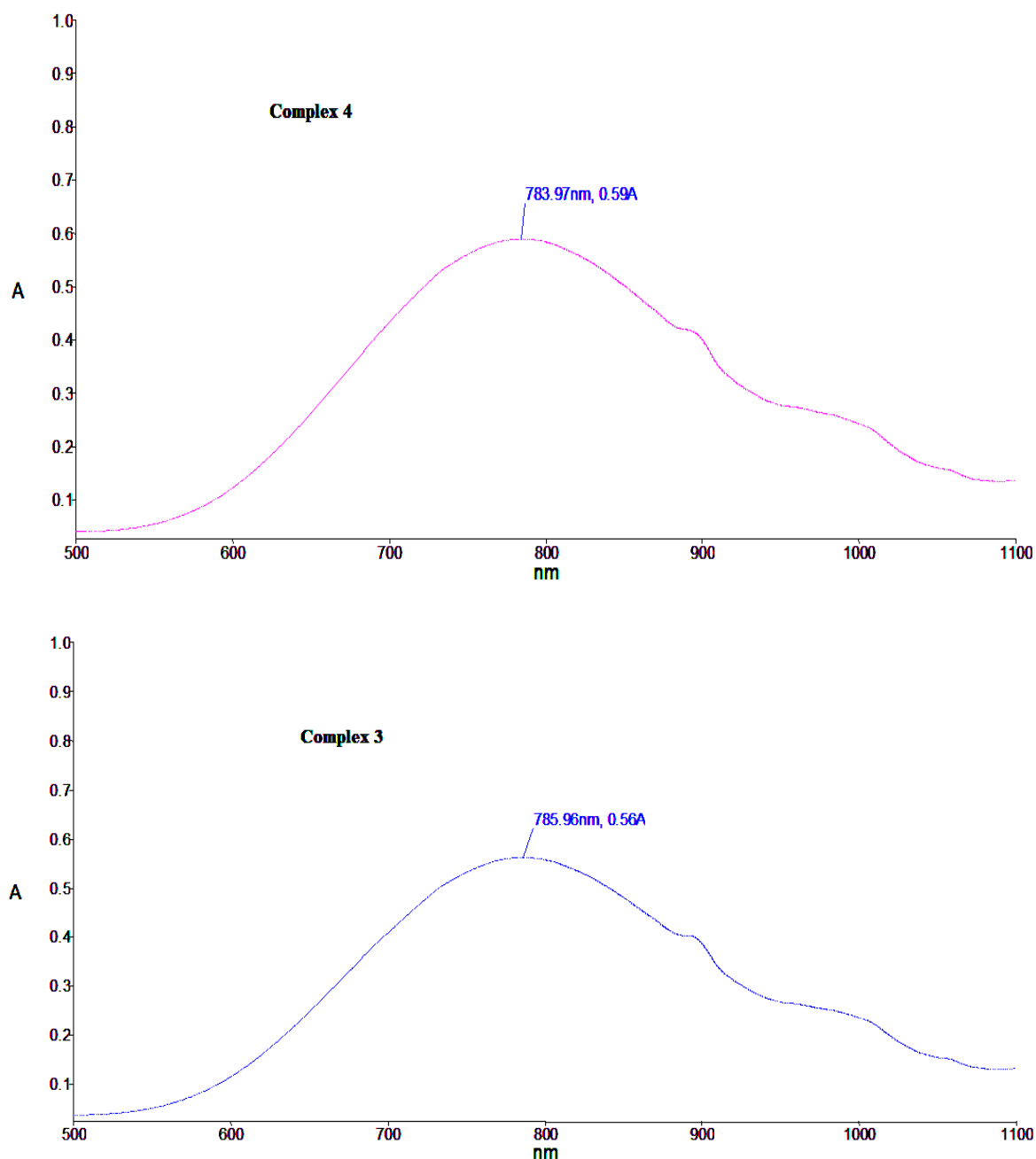


Fig. 8: Electronic spectra of mixed-ligand complexes 3 and 4

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