Synthesis and Structural Characterization of Mixed Ligand Copper(II) Polypyridyl Compounds

DISSERTATION

Submitted in Partial Fulfillment of

The Degree of M.Sc. (Physical Chemistry)

BY

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To
School of Chemical Sciences
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STATEMENT

I hereby declare that the results presented in this dissertation entitled, ‘Synthesis and Structural Characterization of Mixed Ligand Copper(II) Polypyridyl Compounds’ is based on the result of investigations carried out by me at the School of Chemical Sciences, Goa University under the guidance of Dr. Megha S. Deshpande and the same has not been submitted elsewhere for the award of a degree or diploma.

Ms. Amrita A. Naik

CH-18-050

CERTIFICATE

This is to certify that the dissertation entitled, ‘Synthesis and Structural Characterization of Mixed Ligand Copper(II) Polypyridyl Compounds’ is the research work carried out by Ms. Amrita A. Naik under my supervision in partial fulfillment of the requirements for the award of the degree of Master of Science in Physical Chemistry at the School of Chemical Sciences, Goa University.

Dr. Megha S.Deshpande

ACKNOWLE DGEMENTS

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Last but not the least, I would like to express my sincere gratitude to the Dean of the School of Chemical Sciences, Goa University for this opportunity and support all the way.

LIST OF ABBREVIATIONS

Formula	**Name**	**Code**	**Molecular weight**
$Cu(NO_3)_2.3H_2O$	copper(II) nitrate trihydrate		241.6
$C_{14}H_{12}N_2$	2,9-dimethyl-1,10 phenanthroline	dmp	208.27
$C_{18}H_{12}N_2$	2,2’-biquinoline	biq	256.31
$C_3H_4O_4$	malonic acid	mal	104.06
$C_5H_8O_2$	acetyl acetone	acac	100.12

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INTRODUCTION

One of the major aspects of coordination chemistry is to study about the interaction of a central metal atom with its surrounding atoms, ions or molecules. Polypyridyl ligands have a great importance since they are used as chelating agents because they form stable complexes with transition metals. This field is very important with respect to an understanding of fundamental factors governing various properties of transition metal compounds. Based on all these properties, synthesis of different coordination compounds with desired properties by ligand tailoring has become a fascinating research field. These ligands can be neutral, cationic or anionic in nature. They change the chemical behavior of a metal. The term ligand is derived from the Latin word 'ligare' which means 'to bind'. Ligands acts as monodentate, bidentate, tridentate, tetradentate or multidentate. The ligand which has one donor atom and coordinates to central metal in a compound is a monodentate ligand. Examples are NH_3, Cl^-, H_2O etc. The ligand which has more than one donor atoms which coordinates to central metal atom is called polydentate or multidentate ligand. Examples are ethylene diamine, oxalate, triethylenetetramine etc.

Mixed ligand compounds are different from that of the traditional compounds as they have at the least two different kinds of ligands attached to the same metal ion in a compound. The presence of two or more different ligands in a compound increases variations in properties. Mixed metal polypyridine coordination compounds with judicious choice of the ligands, such as 2,2'-bipyridine (bpy) or 1,10-phenanthroline (phen), etc. coordinates to the centered metal ion generates diverse supramolecular 1D, 2D, or 3D hydrogen bonded network structures. Polypyridines form compounds with metals in their lower oxidation states[7]. These are the examples of classic chelating ligands and serve as reservoirs of electrons for the metal. The properties of metal ions are changed using different polypyridyl ligands. Polypyridyl ligands being multi-dentate ligands play a significant role in modern coordination chemistry. We can tune the properties of the ligands by modification which further modifies the properties of the metal polypyridyl compounds. The compounds are reasonably stable to light, electricity and heat, because the bonds between the central metal and polypyridyl ligands are very strong. These compounds possess specific optical, electrochemical properties; moreover, some of these exhibits a strong absorption band in the visible light range, namely the metal-to-ligand charge transfer (MLCT). The MLCT absorption band, emission wavelength, and emission lifetime can be easily varied by the introduction of various substituents with different electronic properties to the polypyridyl ligands. Metal polypyridyl compounds are well known for being coordinately saturated, substitutionally inert and displaying unique redox properties. Furthermore, their exceptional photophysical and photochemical features have allowed them to be employed in a wide range of applications. Copper(II) ions are the second most abundant transition metals in human bodies which is found either at the active sites or as structural components of a number of enzymes. These metals compounds have been found to exhibit anticancer and antimicrobial activities. The ligands like 1, 10-phenanthroline (phen) and 2,2'-bipyridine (bpy) are strong field bidentate ligands that form stable compounds with many first row transition metals. These ligands as well as some of their derived compounds exhibit antimicrobial properties. Copper(II) polypyridyl compounds found to be useful as chemical probes of DNA in view of their relevance to various biochemical and biomedical application[1-3].

In the present work, we report the synthesis of the mixed ligand copper(II) polypyridyl compounds of the type [Cu(N–N)(O–O)(L)](L) and [Cu(N–N)(O–O)(L)] where N–N = polypyridyl ligand, O–O = malonic acid / acetyl acetone, L = anion / water. Here, we mainly used the strain inducing polypyridyl ligands such as 2,9-dimethyl 1, 10-phenanthroline, 2,2’-biquinoline etc. to see the effect on the geometry and structural properties of the copper(II) compounds.

EXPERIMENTAL DETAILS

MATERIALS AND METHODS

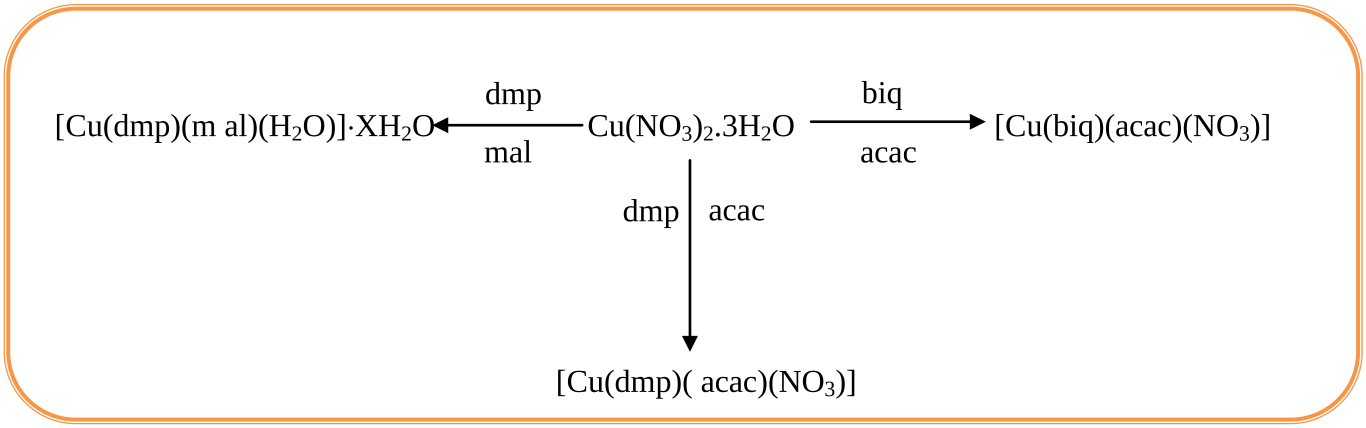
All the chemicals used in the research work was of AR grade and used as received. Double distilled water was used as a solvent. The reactions were repeated out two to three times to check its reproducibility. The products obtained were qualitatively analyzed. The compounds were characterized by IR, UV−vis spectroscopy and X-ray powder diffraction measurements. The compounds **1** and **2** were structurally characterized by single crystal X-ray crystallography. The IR spectra of the samples were recorded in the region 4000-400 cm^{-1} using Shimadzu IR prestige 21 FTIR spectrophotometer. UV−vis absorption spectra were carried out on Agilent 8453 UV/Vis spectrophotometer at room temperature using 1 cm × 1 cm quartz cells. X-Ray powder patterns were recorded using Rigaku Miniflex diffractometer with Cu K radiation Ni filter step 0.02° (10-80).

Single crystal X−ray Crystallography

Bluish green coloured single crystals of **1** and **2** suitable for X–ray diffraction were grown by slow evaporation from aqueous ethanol solution at room temperature. Crystal of appropriate dimension was mounted on Cryoloops (0.4–0.5 mm). Preliminary examination and X−ray diffraction data collection for **1** at100 (2) K and **2** at293(2) K were performed on a Bruker D8 Quest Eco X−ray diffractometer using monochromated Mo $K\alpha$ (λ= 0.7107 Å) radiation. The collected frames were integrated, scaled, merged and performed absorption correction using the program package APEX3 (Version 2018.1). The structure was solved by SHELXS and refined against F^2 by weighted full−matrix least−squares using SHELXL. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to carbon were placed at calculated positions and refined using a riding model. Structure was checked using IUCR check CIF tools in PLATON.

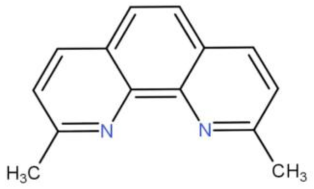
SYNYHESES

Scheme for the synthesis of mixed ligand copper(II) polypyridyl compounds:

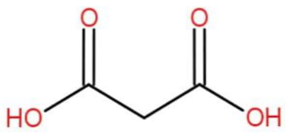


Structure of different ligands used in the present work:

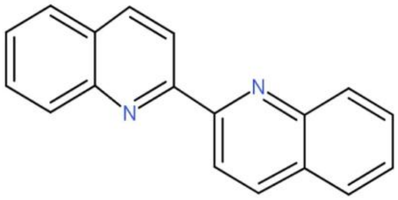
1. 2, 9-dimethyl-1,10 phenanthroline



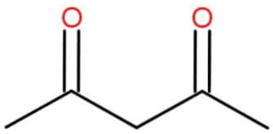
2. Malonic acid



3. 2, 2’-biquinoline



4. Acetyl acetone



Synthesis of [Cu(dmp)(mal)(H_2O)]·2H_2O (1)

Compound **1** was synthesized by reacting $Cu(NO_3)_2.3H_2O$ (0.150 g, 0.620 mM), 2,9-dimethyl-1,10 phenanthroline (0.129 g, 0.620 mM) and malonic acid (0.0645 g, 0.620 mM) in a 1:1:1 molar ratio in ethanol/water mixture (1:1) and refluxed for four hour. Bluish green colored solution was obtained which was kept for crystallization. Bluish green colored crystals suitable for single crystal X-ray crystallography were obtained. Compound was characterized by using IR spectroscopy, X-ray powder diffraction measurements and structurally characterized by single crystal X-ray crystallography.

Yield : 50 %; Anal. calcd for $CuC_{17}N_2O_7H_{20}$ (427.89): C 47.71, H 4.72, N 6.54 %; found: C 47.92, H 4.90, N 6.70 %; I.R. (KBr cm^{-1}): 408 m, 435 m, 549 s, 588 m, 655 m, 682 w, 719 m, 732 m, 777 m, 794 w, 812 w, 837 w, 862 s, 943 s, 950 s, 972 m,1031 s, 1157 s, 1224 s, 1251 s, 1276 s, 1296 s, 1327 s, 1365 s, 1433 s, 1504 s, 1556 m, 1591 s, 1666 s, 1786 m, 1838 m, 1880 m, 1973 m, 2063 m, 2144 w, 2243 w, 2520 w, 2538 w, 2646 w, 2924 br, 3356 br

Synthesis of [Cu(biq)(acac)(NO_3)] (2)

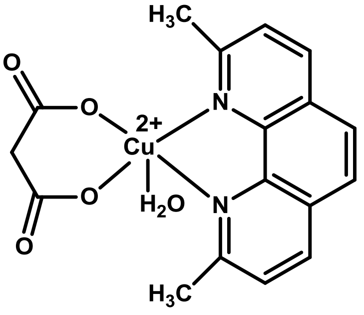
Compound **2** was synthesized by refluxing $Cu(NO_3)_2.3H_2O$(0.150 g, 0.620 mM), 2 ,2'-biquinoline (0.159 g, 0.620 m M) and acetyl acetone (70 µL, 0.620 mM) in a 1:1:1 molar ratio in ethanol/water mixture (5:1) for four hours. Purple colored solution was obtained and it was kept for crystallization. Green colored crystals suitable for single crystal X-ray crystallography were obtained. Compound was characterized by using IR spectroscopy, X-ray powder diffraction measurements and structurally characterized by single crystal X-ray crystallography.

Yield : 40 %; Anal. calcd for $CuC_{23}H_{20}N_3O_5$ (480.95): C 57.31, H 4.19, N 8.72 %; found: C 57.17, H 4.57, N 8.89 %; I.R. (KBr cm^{-1}): 395 w, 420 m, 447 m, 478 m, 489 m, 588 m, 619 w, 657 m, 752 s, 771 s, 783 s, 827 s, 867 w, 937 m, 968 m, 993 w, 1016 s, 1099 s, 1136 m, 1145 m, 1161 m, 1180 m, 1213 s, 1290 s, 1340 w, 1363 m, 1381 m, 1433 m, 1454 s, 1510 s, 1587 s, 1618 m, 1724 m, 1951 m, 1980 m, 2293 s, 2468 m, 2742 w, 2922 w, 3078 w

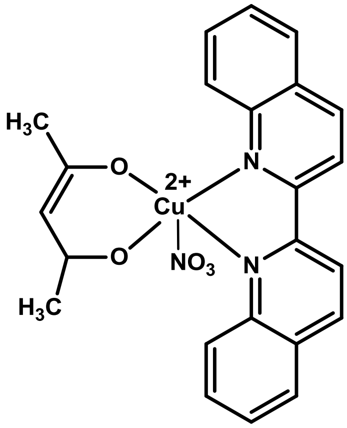
Synthesis of [Cu(dmp)(acac)(NO_3)] (3)

Compound **3** was synthesized by refluxing $Cu(NO_3)_2.3H_2O$ (0.150 g, 0.620 mM), 2,9-dimethyl-1,10 phenanthroline (0.129 g, 0.620 m M) and acetylacetone (63μL, 0.620 mM) in a 1:1:1 molar ratio in ethanol/water mixture (1:1) for four hours. Brown colored solution was obtained and it was kept for crystallization. Dark green colored crystals suitable for single crystal X-ray crystallography were obtained. Compound was characterized by using IR spectroscopy, X-ray powder diffraction measurements and structurally characterized by single crystal X-ray crystallography. Yield :50 %

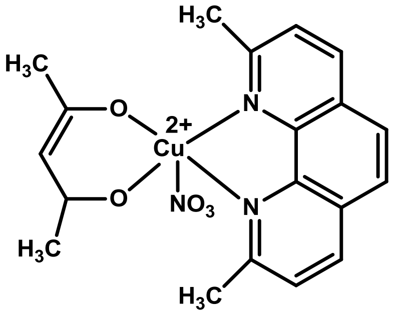
MOLECULR STRUCTURES OF SYNTHESIZED MIXED LIGAND COPPER(II) POLYPYRIDYL COMPOUNDS:



1



2



3

RESULTS AND DISCUSSIONS

1. [Cu(dmp)(mal)(H_2O)]·2H_2O (1)

Synthesis and characterization:

Compound **1** was synthesized by reacting $Cu(NO_3)_2{\cdot}3H_2O$, 6,6'–dimethyl–1, 10–phenanthroline (dmp) and malonic acid (mal) in a 1:1:1 molar ratio. Bluish green colored single crystals suitable for X-ray crystallography were obtained by slow evapouration of aqueous ethanol solution. Compound **1** was characterized by UV–Vis, Infrared spectroscopy, elemental analysis, powder X–ray diffraction (PXRD) measurements and by single crystal X–ray crystallography. The IR spectrum of **1** (Figure 2) shows asymmetric and symmetric stretching bands of the carboxylate groups at 1666 and 1365 cm^{-1} respectively. These frequencies significantly shifted to lower value when compared with the IR spectrum of malonic acid which has intense bands at 1737 and 1706 cm^{-1} due to ν_{as}(COO), 1418 and 1398 cm^{-1} bands due to symmetric stretches of carboxylate groups. This significant lowering of the frequencies indicates the coordination of malonate to the copper ion. For **1**, the medium intensity band at around 950 cm^{-1} attributes to the bending vibration, d(O–C–O) of the carboxylate group. The compound shows strong broad band at 3356 cm^{-1} due to O–H stretching vibrations as well as the H-bonding interactions between the water molecules. Compound **1** displays medium intensity band in the region 2825–2930 cm^{-1} could be attributed to CH_3 asymmetric and symmetric stretching vibrations. Also the strong intensity bands observed at 1224 cm^{-1} for **1** may be due to in-plane C–H bending. The absorption spectrum of **1**in DMSO solvent is as shown in Figure 3. The very strong absorption band observed in the UV region (275 nm) is ascribed to the intraligand π–π* transitions.

Compound **1** exhibit a d–d ($dz^2 \rightarrow dx^2\!-\!dy^2$) band at 695 nm with very low molar absorptivity, assigned to an LMCT transition. A very low intensity MLCT band observed at 456 nm.

Single crystal X-ray crystallography:

Compound **1** crystallizes in the triclinic crystal system in space group $P\bar{1}$. Details of the crystal parameters, data collection conditions and refinement parameters for **1** were summarized in Table 1. Compound crystallizes with two lattice water molecules. The Cu(II) atom is coordinated to bidentate 2,9-dimethyl-1,10 phenanthroline ligand through the nitrogen atoms and to the malonic acid through the oxygen atoms as shown in Figure 1. Selected bond lengths and angles with the relevant hydrogen bonds are listed in Table 2.

The copper(II) compound is distorted by the incorporation of dmp ligand that clash with malonate when assembled around the copper(II) centre. The coordination environment around the copper(II) ion is best described as five coordinated distorted square pyramidal. The distortion of the square pyramidal geometry is manifest in lengthening of the bonds between the copper(II) ion and the ligands (Figure 1 and Table 2). The dmp ligand binds to the copper(II) ion through N1 and N2, with the angle between N1−Cu1−N2 is 79.38(4)° significantly deviated from the ideal 90° (Figure 1). N2 of the dmp and O2 of the malonate ligand are at approximately 90° angle with each other, whereas the N1 and O3 situated at 100.54(4)° angle with each other. The N1 atom of the dmp ligand occupy the apical position with Cu1−N1 bond distance 2.2453(10) Å, and two oxygen atoms of malonate (O1 and O2), O5 of the water molecule and N2 of the dmp ligand forms the basal plane. The sterically bulky dmp ligand protruding up and down to this basal plane. The bond lengths of dmp ligand (Cu1−N(1), 2.2453(11) Å; Cu1−N(2), 2.0030(11) Å) where Cu1−N(1) bond length significantly lengthened (Figure 1). This steric effect results in the rearrangement of the ligands around the copper(II) centre. Malonate acts as a bi-dentate ligand which binds to the copper(II) centre through O1 and O2, with the bond length observed are Cu1–O(1), 1.9442(9) and Cu1–O(2), 1.9481(9) respectively and the angle between O1–Cu1–O2 is 92.14(4)° (Figure 1 and Table 2). The five-membered chelate ring formed by Cu1, N1, N2, C11 and C12 is nearly planar; however the six-membered chelate ring formed by Cu1, O1, O2, C15, C16, C17, has an envelope conformation (Figure 1) As anticipated, this deviation may be due to the presence of bulky methyl group on the periphery of the dmp ligand which prevent it from occupying the basal position. Water molecule O5W coordinated to the copper(II) ion completing CuN_2O_3 chromophore with Cu1–O5 bond distance 1.9927(9)Å. The bulky methyl groups of the dmp ligand do not provide sufficient protection of the copper(II) center to impede coordination by the water molecule.

PXRD measurements:

In order to see the crystalline phase purity of the bulk samples, powder X–ray diffraction (PXRD) measurements are carried out (Figure 4). The experimental PXRD patterns and simulated from single crystal structures are uniform, with all major peaks matches well with the simulated patterns indicating crystalline phase purity.

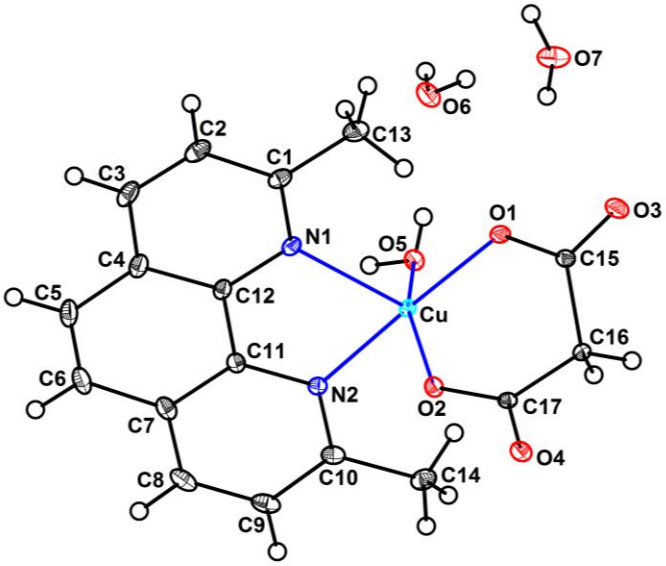


Figure 1. Crystal structure of **[Cu(dmp)(mal)(H_2O)].2H_2O (1)** showing the atom labels (Thermal ellipsoids are drawn at 30 % probability level).

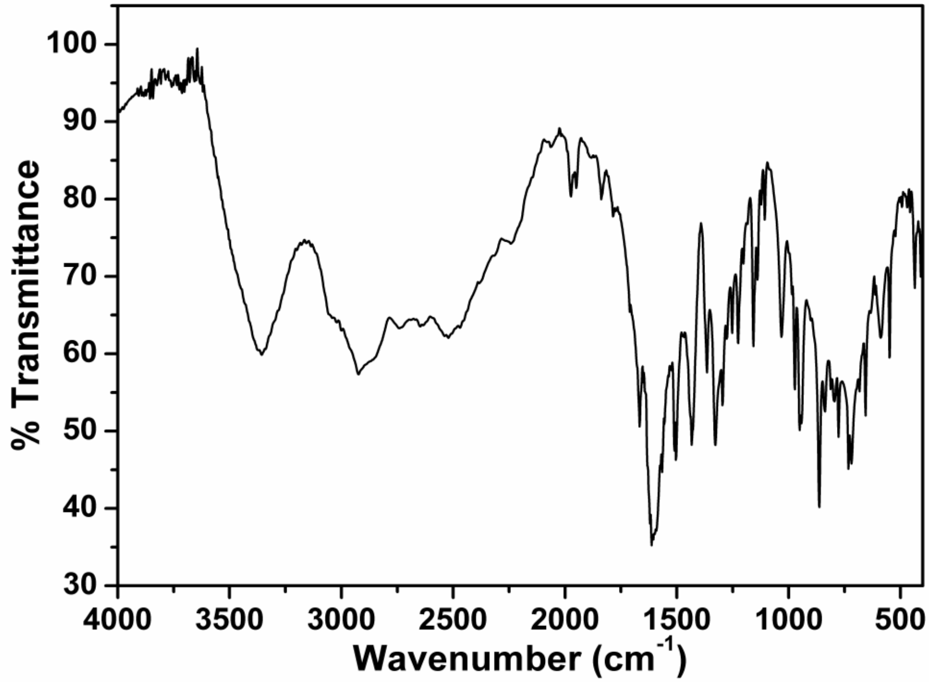


Figure 2. IR data of **[Cu(dmp)(mal)(H_2O)].2H_2O (1).**

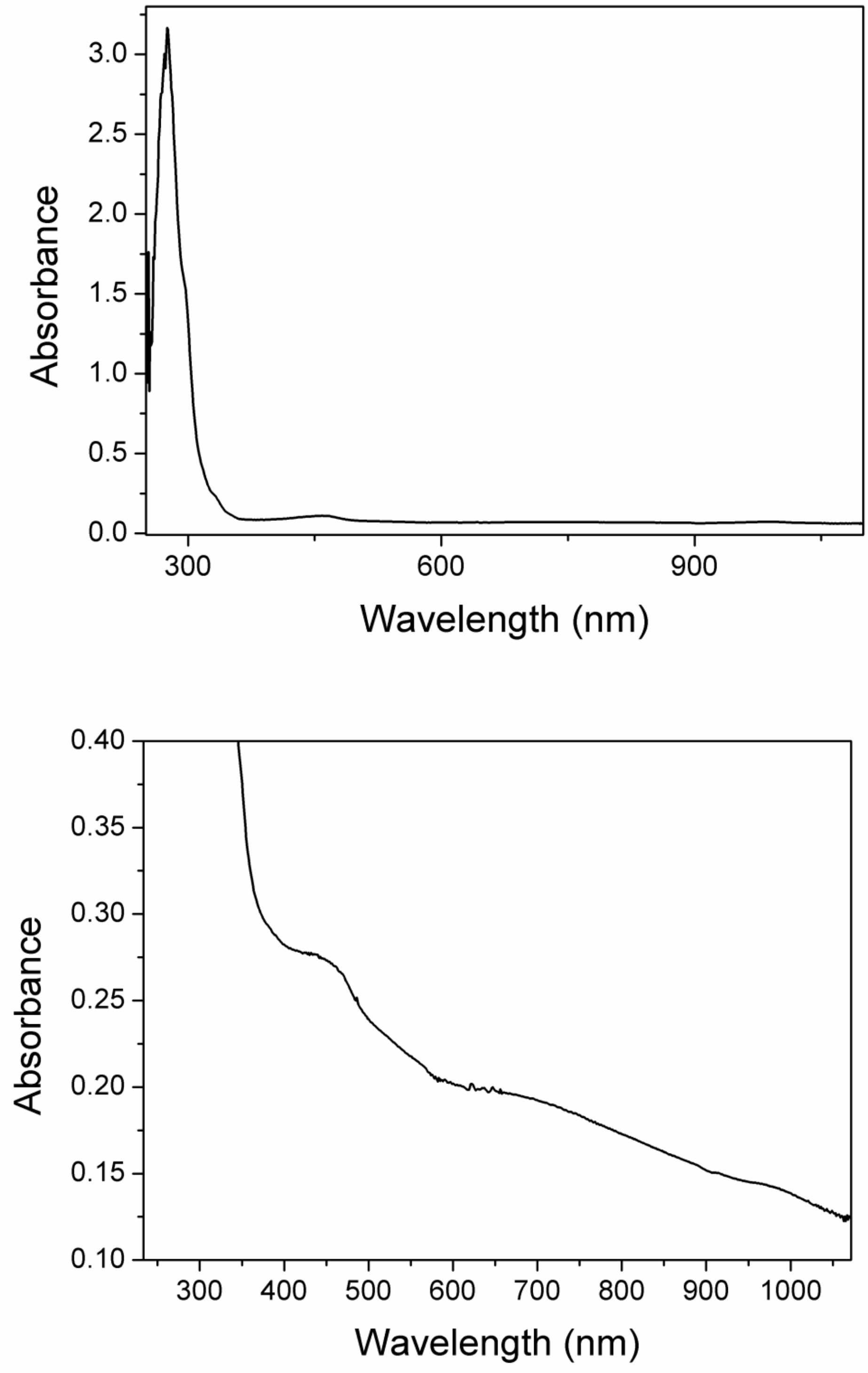


Figure 3 . UV-visible absorption spectrum of **[Cu(dmp)(mal)(H_2O)].2H_2O (1)** in DMSO solvent.

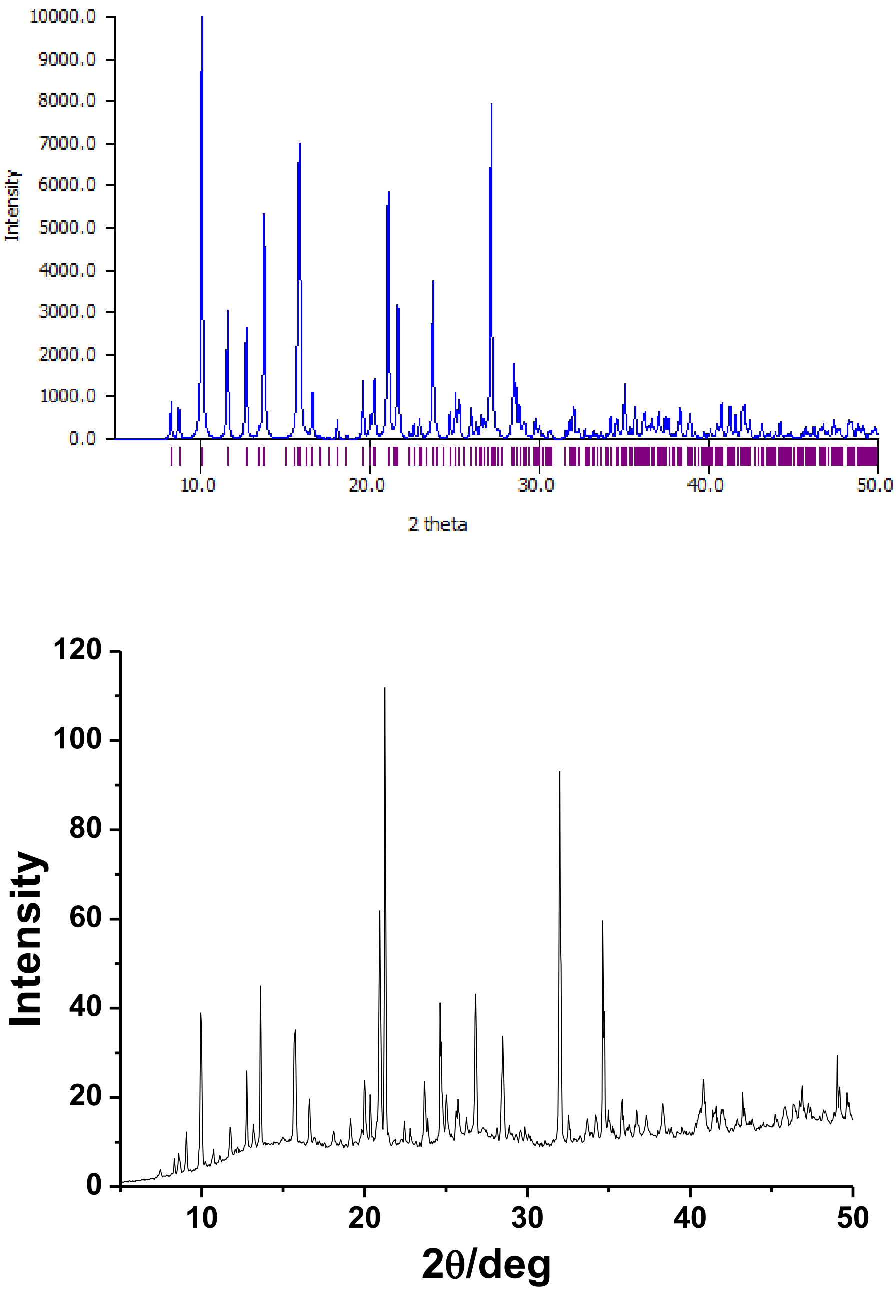


Figure 4. The X-ray powder pattern of **[Cu(dmp)(mal)(H_2O)].2H_2O (1);** (a) simulated from single crystal data and (B) powder of **1**.

Table 1. Crystal data and structure refinement for **[Cu(dmp)(mal)(H_2O)]·2H_2O** (**1**).

Empirical formula	$CuC_{17}H_{20}N_2O_7$
Formula weight	427.89
T (K)	100(2) K
λ (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
a, Å	7.8182(5)
b, Å	10.5916(6)
c, Å	11.3559(7)
α,°	106.136(2)
β,°	100.692(2)
γ,°	95.264(2)
V, Å^3	877.33(9)
Z	2
d_{calc}(g/cm^3)	1.620
μ (MoKα) (mm^{-1})	1.289
F (000)	442
θ range (°)	3.106 to 28.319°
Reflections collected/unique	12650/4331 [R(int) = 0.0159]
Completeness to θ	99.2 %
Refinement method	Full–matrix least–squares on F^2
Absorption correction	Semi–empirical from equivalents
Data/restraints/parameters	4331/2/270
GOF on F^2	1.062
R_1, wR_2 [I>2σ(I)]	R_1 = 0.0216, wR_2 = 0.0595
R_1, wR_2 (all data)	R_1 = 0.0225, wR_2 = 0.0603
Largest diff. peak and hole	0.399 and -0.371 e.Å^{-3}

Table 2. Selected bond lengths (Å) and bond angles (°) for **[Cu(dmp)(mal)(H_2O)]·2H_2O(1)**.

Bond lengths (Å)	
Cu–O1	1.9442(9)
Cu–O2	1.9481(9)
Cu–O5	1.9927(9)
Cu–N2	2.0035(11)
Cu–N1	2.2453(10)
Bond angles (°)	
O1–Cu–O2	92.14(4)
O1–Cu1–O5	88.32(4)
O2–Cu1–O5	156.16(4)
O1–Cu1–N2	175.36(4)
O2–Cu1–N2	89.86(4)
O5–Cu1–N2	88.15(4)
O1–Cu1–N1	104.34(4)
O2–Cu1–N1	100.56(4)
O5–Cu1–N1	102.41(4)
N2–Cu1–N1	79.38(4)
C15–O1–Cu1	123.91(8)
C1–N1–Cu1	132.93(9)
C12–N1–Cu1	108.33(8)
C17–O2–Cu1	125.05(8)
C10–N2–Cu1	123.92(9)
C11–N2–Cu1	116.10(8)

2. [Cu(biq)(acac)(NO_3)] (2)

Synthesis and characterization:

Compound **2** was synthesized by reacting $Cu(NO_3)_2{\cdot}3H_2O$, 2,2'-biquinolyl (biq) and acetyl acetone (acac) in a 1:1:1 molar ratio. Green coloured single crystals suitable for X–ray crystallography were obtained by slow evapouration of aqueous ethanol solution. Compound was characterized by UV-visible, infrared spectroscopy, powder X–ray diffraction (PXRD) measurements and by single crystal X–ray crystallography.

The IR spectrum of **2** (Figure 6) displays medium intensity bands in the region 2825–2930 cm^{-1} could be attributed to CH_3 asymmetric and symmetric stretching vibrations. The strong intensity bands observed at 1213 and 1381 cm^{-1} are due to in-plane C–H bending. The band observed at 3078 cm^{-1} could be assigned to the aromatic –CH stretching vibrations. Two strong bands observed at 1587 and 1510 cm^{-1} that can be assigned to ν(C=O) and ν(C=C) respectively. The ν(Cu–O) vibrations observed at 447 cm^{-1}. The band observed at 1724 cm^{-1} could be assigned to the monodentate coordination of the nitrate group.

The absorption spectra of **2** in DMSO solvent are as shown in Figure 7. The very strong absorption band observed in the UV region (265 nm) is ascribed to the intraligand π–π^* transitions. Compound **2** exhibit a d–d ($dz^2 \rightarrow dx^2{-}dy^2$) band at 789 nm with very low molar absorptivity, assigned to an LMCT transition. A very low intensity MLCT band observed at 553 nm. An intense bands observed at 312 nm, 327 nm and 340 nm are attributed to the N(π) → Cu(II) LMCT transition, indicates the coordination of the biq ligand even in solution, which are comparable to the other copper(II) polypyridyl compounds.

Single crystal X-ray crystallography:

Compound **2** crystallizes in the triclinic crystal system in space group $P\bar{1}$. Details of the crystal parameters, data collection conditions and refinement parameters for **2** were summarized in Table 3. The Cu(II) atom is coordinated by bidentate 2,2'-biquinolyl ligand through the nitrogen atoms and to the acetyl acetone through the oxygen atoms as shown in Figure 5. Selected bond lengths and angles with the relevant hydrogen bonds are listed in Table 4.

The copper(II) compound is distorted by the incorporation of biq ligand that clash with acac when assembled around the copper(II) centre. The coordination environment around the copper(II) ion is best described as five coordinated distorted square pyramidal. The distortion of the square pyramidal geometry is manifest in lengthening of the bonds between the copper(II) ion and the ligands (Figure 5 and Table 4). The 2,2'–biquinoline binds to the copper(II) ion through N1 and N2, with the angle between N(1)–Cu–N(2) is 77.36(9)° significantly deviated from the ideal 90° (Figure 5). The N2 atom of the biq ligand occupy the apical position with Cu1–N2 bond distance 2.259 Å, and two oxygen atoms of acac (O1 and O2), O3 of the nitrate anion and N1 of the biq ligand forms the basal plane. The sterically bulky biq ligand protruding up and down to the basal plane. The quinoline rings of the biq ligand are planar, with the bond lengths (Cu1–N1, 2.030 (2) Å; Cu1–N2, 2.259 (2) Å) significantly lengthened (Table 4) when compared with the compound having 1,10-phenanthroline ligand (Cu1–N1, 2.022(3) Å; Cu1–N2, 2.005(3)). The bond length of biq ligand Cu1–N2, 2.259(2) Å is slightly longer reveals the increased strain induced between the acac and biq ligand. This steric effect results in the rearrangement of the ligands around the copper(II) centre. Acetyl acetone acts as a bi-dentate ligand which binds to the copper(II) centre through O1 and O2, with the bond length observed are Cu1−O(1), 1.9385 (2) Å and Cu1−O(2), 1.9181(2) Å respectively. The angle between O(1)−Cu1−O(2) is 92.77(9)° (Table 4). The five-membered nearly planar chelate ring formed by Cu, N1, N2, C9 and C10; however the six-membered chelate ring formed by Cu, O1, O2, C19, C20, C21 has an envelope conformation (Figure 5). As anticipated, this deviation may be due to the steric effect of the bulky biq ligand which prevents biq ligand to occupy the basal position (Figure 5). Nitrate anion coordinated to the copper(II) ion completing CuN_2O_3 chromophore with Cu1–O3 bond distance 2.009(2) Å. The quinolone moiety of the sterically bulky biq ligand do not provide sufficient protection of the copper(II) center to impede coordination by the nitrate counterion.

PXRD measurements:

In order to see the crystalline phase purity of the bulk samples, powder X−ray diffraction (PXRD) measurements are carried out (Figure 8). The experimental PXRD patterns and simulated from single crystal structures are uniform, with all major peaks matches well with the simulated patterns indicating crystalline phase purity.

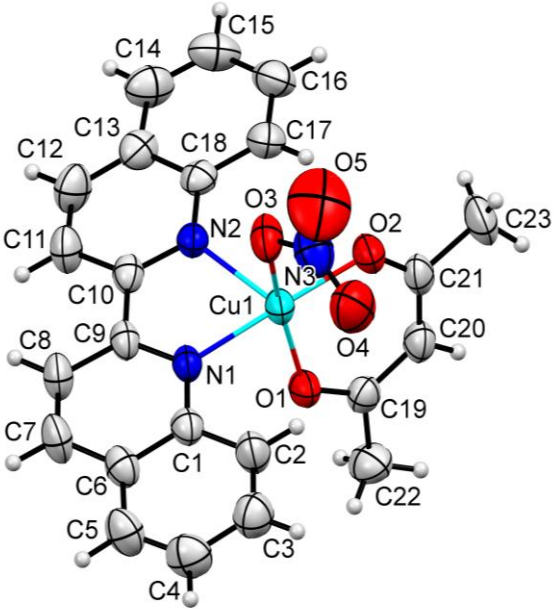


Figure 5. Crystal structure of **[Cu(biq)(acac)(NO_3)] (2)** showing the atom labels (Thermal ellipsoids are drawn at 30 % probability level).

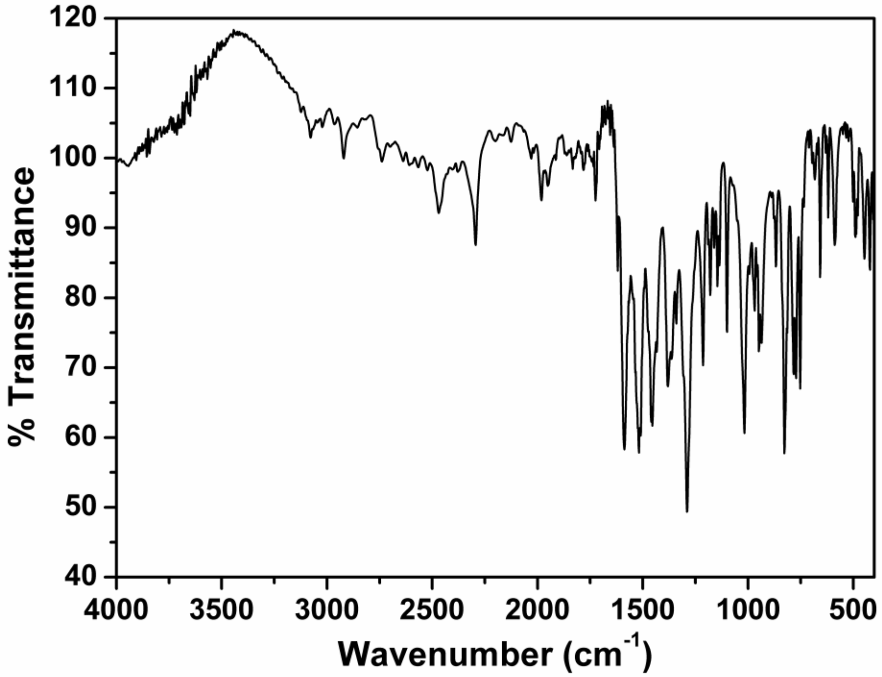


Figure 6. IR spectrum of **[Cu(biq)(acac)(NO_3)](2)**.

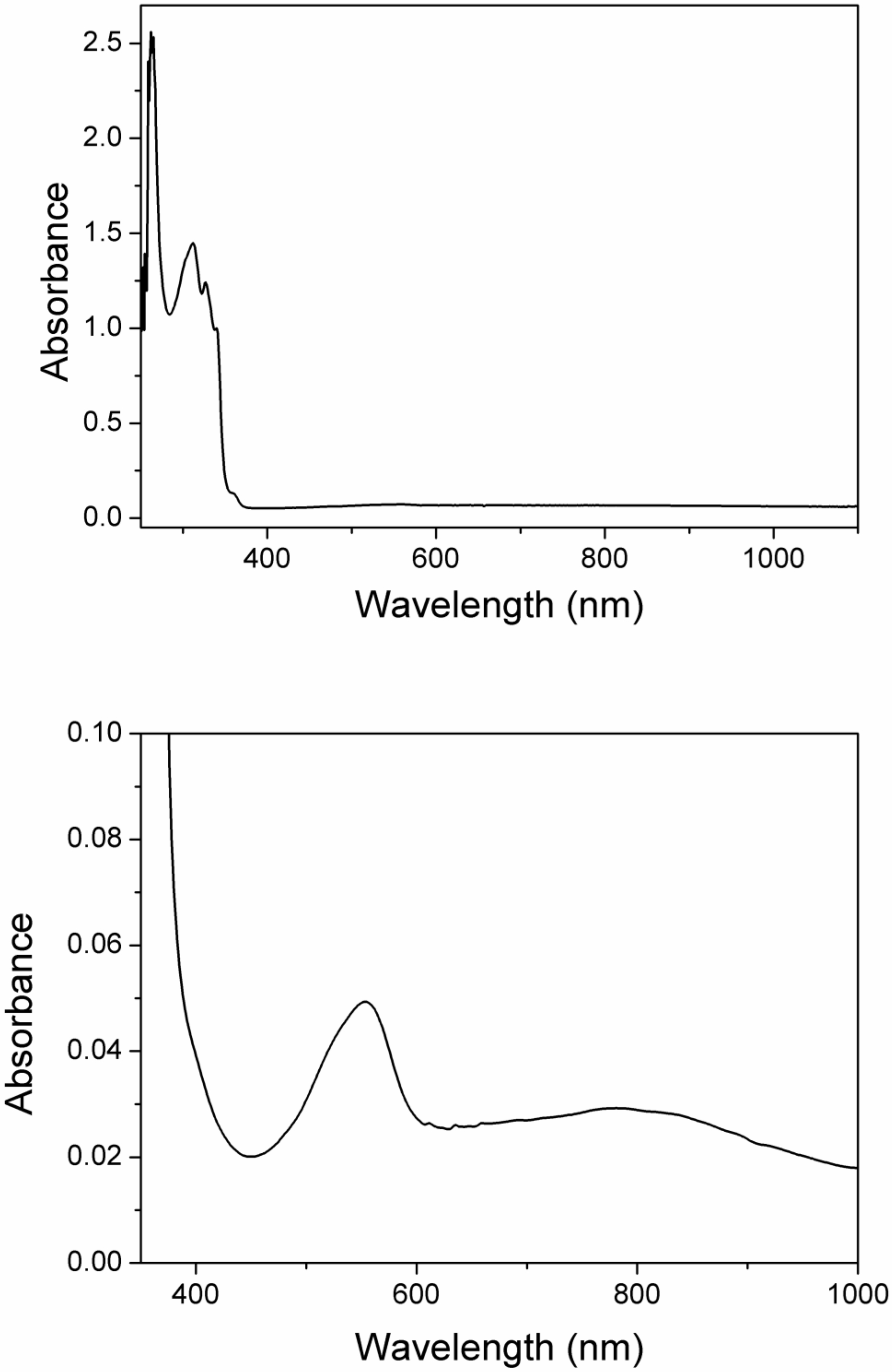


Figure 7. UV-vis absorption spectrum of **[Cu(biq)(acac)(NO$_3$)](2)** in DMSO solvent.

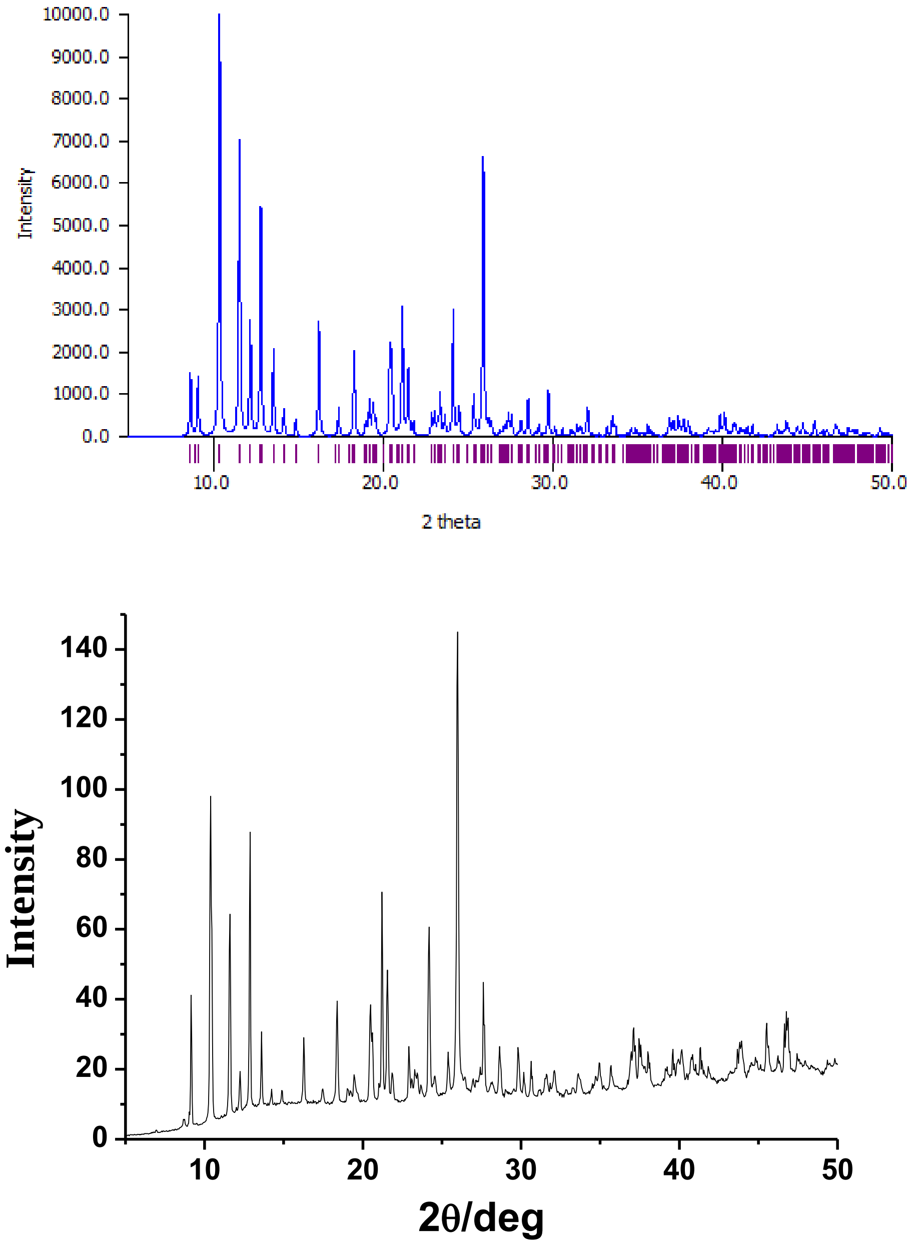


Figure 8. The X-ray powder pattern of **[Cu(biq)(acac)(NO$_3$)](2)**; (a) simulated from single crystal data and (B) powder of **2**.

Table 3. Crystal data and structure refinement for **[Cu(biq)(acac)(NO_3)] (2)**.

Empirical formula	$CuC_{23}H_{19}N_3O_5$
Formula weight	480.95
T (K)	293(2) K
λ (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
a, Å	10.3125(11)
b, Å	10.4418(10)
c, Å	10.4761(12)
α,°	70.104(4)
β,°	89.718(4)
γ,°	81.335(3)
V, Å^3	1047.33(19)
Z	2
d_{calc}(g/cm^3)	1.525
μ (MoKα) (mm^{-1})	1.084
F (000)	494
θ range (°)	2.662 to 26.889°
Reflections collected/unique	14134/4504 [R(int) = 0.0387]
Completeness to θ	99.8 %
Refinement method	Full–matrix least–squares on F^2
Absorption correction	Semi–empirical from equivalents
Data/restraints/parameters	4504/0/295
GOF on F^2	1.052
R_1, wR_2 [I>2σ(I)]	R_1 = 0.0404, wR_2 = 0.0890
R_1, wR_2 (all data)	R_1 = 0.0705, wR_2 = 0.1048
Largest diff. peak and hole	0.313 and -0.279 e.Å^{-3}

Table 4. Selected bond lengths (Å) and bond angles (°) for **[Cu(biq)(acac)(NO_3)](2).**

Bond length (Å)	
Cu1–N1	2.030(2)
Cu1–N2	2.259(2)
Cu1–O1	1.9385(19)
Cu1–O2	1.9181(19)
Cu1–O3	2.009(2)
Bond angles (°)	
N1–Cu1–N2	77.36(9)
O2–Cu1–N1	178.11(9)
O1–Cu1–N1	87.22(8)
O3–Cu1–N1	91.71(9)
O2–Cu1–N2	104.45(9)
O1–Cu1–N2	105.44(8)
O3–Cu1–N2	88.92(9)
O2–Cu1–O1	92.77(8)
O2–Cu1–O3	87.81(9)
O1–Cu1–O3	164.96(9)
C19–O1–Cu1	125.32(19)
C21–O2–Cu1	126.55(19)
C9–N1–C1	119.6(2)
C9–N1–Cu1	117.85(19)
C1–N1–Cu1	122.55(17)
C10–N2–C18	118.8(2)
C10–N2–Cu1	110.87(18)
C18–N2–Cu1	129.95(18)

3. [Cu(dmp)(acac)(NO_3)] (3)

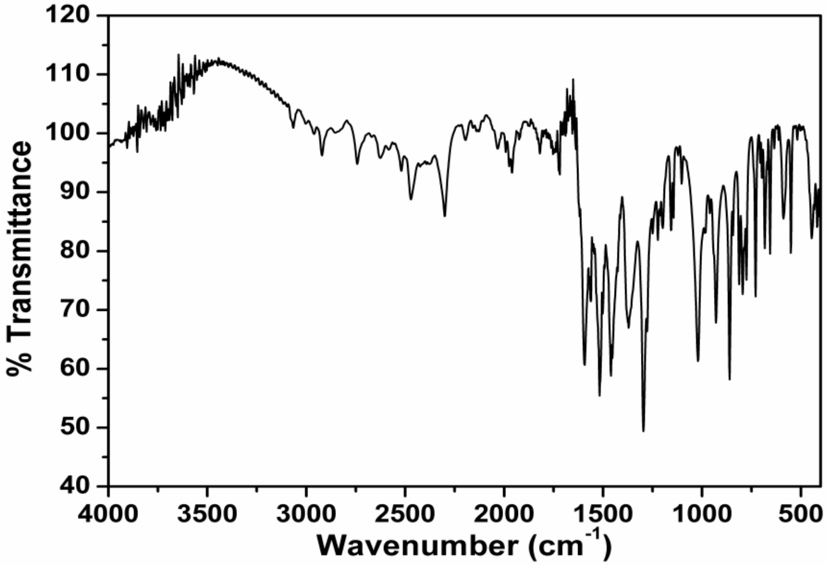


Figure 9. IR spectrum of [Cu(dmp)(acac)(NO_3)](3)

CONCLUSIONS

Mixed ligand copper(II) polypyridyl compounds with strain inducing polypyridyl ligand have been synthesized and characterized by infrared, UV-vis spectroscopy and powder X-ray powder diffraction measurements and by single crystal X-ray crystallography. The strain inducing polypyridyl ligands, 2,9-dimethyl-1,10 phenanthroline and 2,2'-biquinolyl along with chelating agents like malonic acid and acetyl acetone form stable copper(II) compounds under normal synthetic route. The presence of strained polypyridyl ligands modify the arrangement of the ligands around the copper(II) center which results in the distorted square pyramidal geometry. DNA cleavage and antimicrobial activity studies on these compounds are in progress.

REFERENCES

1. Santini, C.; Pellei, M.; Gandin, V.; Porchia, M.; Tisato, F.; Marzano, C., Advances in copper complexes as anticancer agents. *Chem Rev,* **2013,** 114, 815-862.

2. Chikira, M.; Tomizawa, Y.; Fukita, D.; Sugizaki, T.; Sugawara, N.; Yamazaki, T.; Sasano, A.; Shindo, H.; Palaniandavar, M.; Antholine, W. E., DNA-fiber EPR study of the orientation of Cu(II) complexes of 1,10-phenanthroline and its derivatives bound to DNA: mono(phenanthroline)-copper(II) and its ternary complexes with amino acids. *J Inorg Biochem* **2002,** 89, 163-173.

3. Selvakumar, B.; Rajendiran, V.; Uma Maheswari, P.; Stoeckli-Evans, H.; Palaniandavar, M., Structures, spectra, and DNA-binding properties of mixed ligand copper(II) complexes of iminodiacetic acid: the novel role of diimine co-ligands on DNA conformation and hydrolytic and oxidative double strand DNA cleavage. *J Inorg Biochem* **2006,** 100, 316-330.

4. Gupta, T.; Dhar, S.; Nethaji, M.; Chakravarty, A. R., Bis(dipyridophenazine)copper(II) complex as major groove directing synthetic hydrolase. *Dalton Trans* **2004**, 12, 1896-1900.

5. Dhar, S.; Chakravarty, A. R., Photosensitizer in a molecular bowl: steric protection enhancing the photonuclease activity of copper(II) scorpionates. *Inorg Chem* **2005,** 44, 2582-2584.

6. Dhar, S.; Nethaji, M.; Chakravarty, A. R., DNA cleavage on photoexposure at the d-d band in ternary copper(II) complexes using red-light laser. *Inorg Chem* **2006,** 45, 11043-11050.

7. Deshpande, M. S.; Kumbhar, A. S.; Näther, C., Stabilization of acyclic water tetramer in a copper(II) malonate framework structure. *Dalton Trans.* **2010,** 39, 9146–9152.

8. Dhar, S.; Reddy, P. A.; Chakravarty, A. R., Intramolecular nucleophilic activation promoting efficient hydrolytic cleavage of DNA by (aqua)bis (dipyridoquinoxaline) copper(II) complex. *Dalton Trans* **2004**, 5, 697-698.

9. Paulovicova, A.; El-Ayaan, U.; Fukuda, Y., Synthesis, characterization and X-ray crystal structures of two five-coordinate ternary copper(II) complexes containing acetylacetonate with 1,10-phenanthroline and 2,9-dimethyl phenanthroline. *Inorg. Chim. Acta* **2001,** 321, 56–62.

10. Madalan, A. M.; Kravtsov, V. C.; Pajic, D.; Zadro, K.; Simonov, Y. A.; Stanica, N.; Ouahab, L. e.; Lipkowski, J.; Andruh, M., Chemistry at the apical position of square-pyramidal copper(II) complexes: synthesis, crystal structures, and magnetic properties of mononuclear Cu(II), and heteronuclear Cu(II)–Hg(II) and Cu(II)–Co(II) complexes containing [Cu(AA)(BB)]+ moieties (AA = acetylacetonate, salicylaldehydate; BB = 1,10-phenanthroline, Me_2bipy = 4,4'-dimethyl-2,2'-bipyridine). *Inorg. Chim. Acta* **2004,** 357, 4151–4164.

11. Potapov, A. S.; Khlebnikov, A. I.,Synthesis of mixed-ligand copper(II) complexes containing bis(pyrazol-1-yl)methane ligands. *Polyhedron* **2006,** 25, 2683–2690.

12. Ramakrishan, S.; Palaniandavar. M., Mixed-ligand copper(II) complexes of dipicolylamine and 1,10-phenanthrolines: The role of diimines in the interaction of the complexes with DNA. *J. Chem. Sci.* **2005,** 117, 179–186.

13. Denat, F.; Gros, C. P., Introduction to the nitrogen ligands themed issue. *New J. Chem.,* **2016,** 40, 5643–5643.

14. Cotton, F. A., Chemical Applications of Group Theory. Wiley Inter-Science Publications, Third Edition **1999**.

15. West, A. R., Solid State Chemistry and its Applications. John Wiley & Sons, Inc. Publications, Wiley Student Edition.

16. Silverstein, R. M.; Webster, F. X., Spectrometric Identification of Organic Compounds. John Wiley and Sons, Inc. Publications, Sixth Edition.

17. Svehla, G., Vogel’s Qualitative Inorganic Analysis. Pearson Publications, Seventh Edition **2011**.