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Synthesis and structure of a mixed ligand copper(II) compound based on a distorted $\{CuN_2O_3\}$ square pyramid

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The synthesis, spectra, thermal study and crystal structure of a mixed ligand copper(II) compound viz. $[Cu(biq)(acac)(NO_3)]$ **1** (biq = 2,2′-biquinoline, acac = acetylacetonate) are reported. The $\{CuN_2O_3\}$ coordination sphere is made up of two oxygen atoms of an unique acac ligand, an oxygen of the nitrate group and one N atom of biq ligand which form the basal plane $\{CuNO_3\}$ of a square pyramid. A second nitrogen atom of the biq ligand occupies the apical position resulting in a distorted square pyramidal $\{CuN_2O_3\}$ polyhedron. In the crystal structure, each neutral square pyramidal copper(II) species is linked with two symmetry related molecules with the aid of intermolecular C–H···O hydrogen bonding interactions. A study of fifteen mixed ligand copper(II) acetylacetonates reveals that in this series of compounds, **1** exhibits maximum deviation of the $\{CuN_2O_3\}$ polyhedron from square pyramidal towards trigonal bipyramidal geometry.

Keywords: Copper(II), Acetylacetonate, 2,2′-biquinoline, Square pyramid, Hydrogen bonding

Mixed ligand copper(II) polypyridyl compounds have been extensively studied due to their diverse interactions with DNA, interesting DNA cleavage properties and enzymatic, structural or reactive roles in biological processes as well as for the development of anticancer agents[1-8]. Extended π-conjugated polypyridyl ligands such as dipyrido[3,2-*d*:2′,3′-*f*]quinoxaline, dipyrido [3,2-*a*:2′,3′-*c*]phenazine, have been investigated widely for the development of DNA intercalative agents[8-9]. The synthesis of transition metal compounds bearing sterically demanding 2,2′-biquinoline ligand and its substituted analogues have been carried out to investigate the steric effect of the ligand on the photochemistry of ruthenium compounds and for the development of DNA binding agents as well as in the dye sensitized solar cells[10-15]. Copper(II) displays a wide range of coordination geometries allowing for a greater flexibility to construct framework materials[8,16,17]. Copper(II) compounds containing substituted N-donors such as 6,6′-substituted 2,2′-bipyridine, 2,9-substituted 1,10-phenanthroline etc. produce a strain on the square planar geometry causing distortion[15,18-21]. In the literature, several reports describing the synthesis and the structures of mixed ligand copper(II) acetylacetonate compounds of the type [Cu(L–L)(acac)(X)] are reported (Table 1) where L–L = 2,2′-bipyridine, 1,10-phenanthroline, 2,9-dimethyl-1,10-phenanthroline, 4,4′-dimethyl-2,2’-bipyridine, 2-(4-chlorophenyl)imidazo[4,5-f]1,10-phenanthroline, 2-(4-pyridine)oxazo[4,5-f]1,10-phenanthroline), 2-(2-nitrophenyl)imidazo[4,5-f]1,10-phenanthroline, acac = acetylacetonate and X = monoanion[13,20-27]. Interestingly the chemistry of copper(II) acetylacetonates containing 2,2′-biquinoline (biq) has not been studied. However, considerable research has been focused on the structure and properties of the homoleptic and heteroleptic copper(I) compounds with 2,2′-biquinoline (Table 1) and its derivatives[14,15,28-32]. In view of this we have undertaken this study to investigate the effect of incorporating a 2,2′-biquinoline ligand in the coordination sphere of copper(II) containing acac ligand. This has resulted in the synthesis, spectral and structural characterization of a new mixed ligand copper(II) compound viz. $[Cu(biq)(acac)(NO_3)]$ **1**, the details of which are described herein.

Materials and Methods

$Cu(NO_3)_2{\cdot}3H_2O$, 2,2′-biquinoline, acetylacetone were purchased from SRL (India) and TCI (Japan) chemicals. The solvents of reagent grade were used without any further purification. The infrared (IR) spectra of the solid samples diluted with KBr were recorded on a Shimadzu (IR Prestige–21) FT-IR

Table 1 — List of structurally characterized acetylacetonates/biquinolines of copper

No.	Compound	Space group	*Trans* basal angles (°)	τ	Coordination sphere	Ref
1	$[Cu(biq)(acac)(NO_3)]$	$P\bar{1}$	178.11, 164.96	0.219	$\{CuN_2O_3\}$	this work
2	$[Cu(bpy)(acac)Br]\cdot H_2O^*$	$P\bar{1}$	169.88, 163.71 166.81, 160.80 168.47, 165.37 164.12, 163.82	0.103 0.100 0.051 0.005	$\{CuN_2O_2Br\}$	23
3	$[Cu(phen)(acac)Cl]$	$P\bar{1}$	164.40, 158.42	0.099	$\{CuN_2O_2Cl\}$	24
4	$[Cu(4\text{-}PDOP)(acac\text{-}Cl)(MeOH)](NO_3)$	$P\bar{1}$	173.63, 167.90	0.096	$\{CuN_2O_3\}$	25
5	$[Cu(dmph)(acac)(NO_3)]$	$P\bar{1}$	175.04, 169.50	0.092	$\{CuN_2O_3\}$	20
6	$[Cu(phen)(acac)Br]$	$P\bar{1}$	164.56, 160.14	0.074	$\{CuN_2O_2Br\}$	22
7	$[Cu(phen)(acac)(NCS)]$	$P\bar{1}$	163.00, 159.62	0.056	$\{CuN_3O_2\}$	21
8	$[Cu(phen)(acac)(C_2N_3)]\cdot 2H_2O$	$P\bar{1}$	171.80, 168.73	0.051	$\{CuN_3O_2\}$	26
9	$[Cu(bpy)(acac)Cl][Cu(bpy)(acac)(H_2O)]Cl\cdot H_2O^\$$	$P\bar{1}$	167.69, 165.14 163.62, 163.25	0.043 0.006	$\{CuN_2O_3\}$ $\{CuN_2O_2Cl\}$	23
10	$[Cu(o\text{-}NPIP)(acac)(NO_3)]$	$P\bar{1}$	172.61, 170.49	0.035	$\{CuN_2O_3\}$	13
11	$[Cu(p\text{-}CPIP)(acac)(CH_3OH)](NO_3)$	$P\bar{1}$	171.30, 169.50	0.030	$\{CuN_2O_3\}$	13
12	$[Cu(phen)(acac)(NO_3)]\cdot H_2O$	$C2/c$	169.84, 166.13	0.061	$\{CuN_2O_3\}$	20
13	$[Cu(Me_2bipy)(acac)(NCS)]$	$C2/c$	167.59, 162.73	0.081	$\{CuN_3O_2\}$	21
14	$[Cu(bpy)(acac)(H_2O)]NO_3\cdot H_2O^\$$	$P2_1/n$	169.60, 164.95 169.33, 168.48	0.078 0.014	$\{CuN_2O_3\}$	22
15	$[Cu(4\text{-}PDOP)(acac)(NO_3)]$	$P2_1/c$	167.73, 166.03	0.028	$\{CuN_2O_3\}$	25
16	$[Cu(Me_2bipy)(acac)]ClO_4$	$P2_1/c$		-	$\{CuN_2O_2\}^\#$	21
17	$[Cu(acac)_2]$	$P2_1/n$		-	$\{CuO_4\}^\#$	27
18	$[Cu(biq)Cl_2]$	$C2/c$		-	$\{CuN_2Cl_2\}^§$	29
19	$[Cu(biq)_2](BF_4).biq$	$P2/n$		-	$\{CuN_4\}^§$	31
20	$[Cu(dmbiq)_2](BF_4).CH_2Cl_2$	$P2_1/c$		-	$\{CuN_4\}^§$	28
21	$[Cu(biq)_2](ClO_4).biq$	$P2/n$		-	$\{CuN_4\}^§$	14
22	$[Cu(biq)(PCH_2N(CH_2CH_2)_2O)_3)I]$	$P\bar{1}$		-	$\{CuN_2PI\}^§$	30
23	$[Cu(biq)_2](ClO_4)$	$P2_1$		-	$\{CuN_4\}^§$	14
24	$[Cu(biq)(bpy(Mes)_2)](BF_4)$	$P2_12_12_1$		-	$\{CuN_4\}^§$	32

*four unique Cu(II); $^\$$ two unique Cu(II); $^\#$ square planar; § tetrahedral

Abbreviations: acac = acetylacetone; biq = 2,2′-biquinoline; bpy = 2,2′-bipyridine; phen = 1,10-phenanthroline; acac-Cl = 3-chloroacetylacetone; 4-PDOP = 2-(4-pyridine)oxazo[4,5-f]1,10-phenanthroline; dmph = 2,9-dimethylphenanthroline; *o*-NPIP = 2-(2-nitrophenyl)imidazo[4,5-f]1,10-phenanthroline); *p*-CPIP = 2-(4-chlorophenyl)imidazo[4,5-f]1,10-phenanthroline; Me_2bipy = 4,4′-dimethyl-2,2′-bipyridine; dmbiq = 6,7-dihydro dibenzo-[*b,j*][1,10]phenanthroline; $PCH_2N(CH_2CH_2)_2O)_3$ = phosphane derived from morpholine; $bpy(Mes)_2$ = 6,6′-dimesityl-2,2′-bipyridine.

spectrometer from 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1}. The microanalyses (C, H, and N) were performed on an Elementar Variomicro Cube CHNS Analyser. UV-visible absorption spectra were recorded using Agilent 8453 UV/Vis spectrophotometer at room temperature using 1 cm × 1 cm quartz cells. TG–DTA experiment was performed in air atmosphere in alumina crucible at a heating rate of 10 °C/min in the temperature range 40 to 800 °C on a STA–409 PC simultaneous thermal analyser from Netzsch. Powder X-ray diffraction (XRD) pattern were recorded on a Bruker D8 advance powder diffractometer using Cu-Kα radiation at the Central Sophisticated Instrumentation Facility (CSIF), BITS Pilani (KK Birla Goa Campus).

Synthesis of $[Cu(biq)(acac)(NO_3)]$ 1

2,2′-Biquinoline (0.106 g, 0.41 mM), acetylacetone (0.041 g, 0.41 mM) and $Cu(NO_3)_2\cdot 3H_2O$ (0.100 g, 0.41 mM) were added to 50 mL of ethanol:water (5:1) in a 100 mL round bottom flask. The mixture was stirred under reflux for 5 h. The reaction mixture was allowed to cool to room temperature and filtered to isolate green crystals of **1** in ~40 % yield.

Anal. for $CuC_{23}H_{19}N_3O_5$ (480.95) calcd (%): C 57.43, H 3.99, N 8.73; found (%): C 57.17, H 4.57, N 8.89; IR data (KBr, cm^{-1}): 3078 w, 2922 w, 2742 w, 2468 m, 2293 s, 1980 m, 1951 m, 1724 m, 1618 m, 1587 s, 1510 s, 1454 s, 1433 m, 1381 m, 1363 m, 1340 w, 1290 s, 1213 s, 1180 m, 1161 m, 1145 m, 1136 m, 1099 s, 1016 s, 993 w, 968 m, 937 m, 867 w, 827 s, 783 s, 771 s, 752 s, 657 m, 619 w, 588 m, 489 m, 478 m, 447 m, 420 m, 395 w.

Single crystal X-ray crystallography

Single crystals suitable for XRD were grown by slow evaporation from aqueous ethanol solution at room temperature. Preliminary examination and XRD data collection at 293(2) K were performed on a Bruker D8 Quest Eco X-ray diffractometer using monochromated Mo*Kα* (λ= 0.7107 Å) radiation. The collected frames were integrated, scaled, merged and absorption correction performed using the program package APEX3 (Bruker 2019) to determine unit cell. The structure was solved with SHELXS and refined against F^2 by weighted full-matrix least-squares using SHELXL[33]. 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. Technical details of data acquisition and selected crystal refinement results are listed in Table 2.

Results and Discussion

Synthesis, spectral and thermal studies

Compound **1** was prepared by reacting $Cu(NO_3)_2{\cdot}3H_2O$ with acetylacetone (acac) and 2,2′-biquinoline (biq) in 1:1:1 molar ratio in an aqueous alcoholic medium. The product analysed satisfactorily and was further characterized by spectral and single crystal studies. The phase purity of the bulk sample was determined by powder XRD measurements (Supplementary Data, Fig. S1) by comparison of the experimental pattern with the theoretical pattern calculated from single crystal structure.

Compound **1** exhibits a low intensity *d–d* ($dz^2 \rightarrow dx^2{-}dy^2$) band at 789 nm[34] and a low intensity MLCT band at 553 nm (see inset, Supplementary Data, Fig. S2). The bands at 312 nm, 327 nm and 340 nm can probably be attributed to the N(π) → Cu(II) LMCT transition, indicating coordination of the biq ligand even in solution, which are comparable to other copper(II) polypyridyl compounds[8]. The IR spectrum of **1** (Fig. 1) displays several bands indicating the presence of organic moieties. The intense bands at 1587 and 1510 cm^{-1} can be attributed to the carbonyl vibration of the acetylacetonate ligand and monodentate binding of the nitrate group, respectively[35].

Table 2 — Crystal data and structure refinement for [Cu(biq)(acac)(NO_3)] **1**

Empirical formula	$CuC_{23}H_{19}N_3O_5$
Formula weight	480.95
T (K)	293(2)
λ (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Crystal size (mm^3)	0.118 × 0.087 × 0.058
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} (mg/m^3)	1.525
μ (Mo Kα) (mm^{-1})	1.084
F (000)	494
θ range (°)	2.662 to 26.89°
Index ranges	$-13 \leq h \leq 13$, $-13 \leq k \leq 13$, $-13 \leq l \leq 13$
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	1.053
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 (e.$Å^{-3}$)	0.313 and -0.279

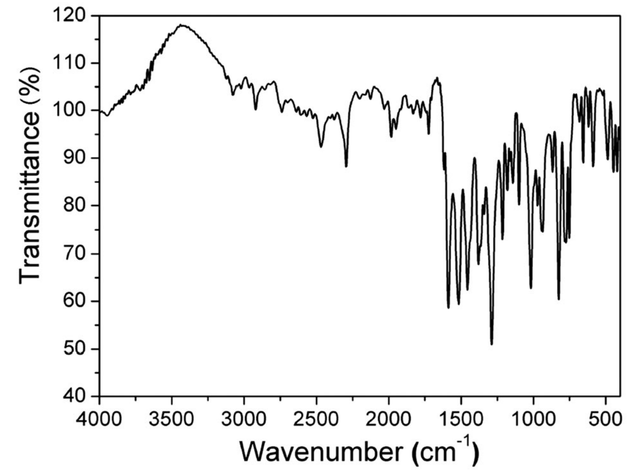

Fig. 1 — Infrared spectrum of [Cu(biq)(acac)(NO_3)] **1**

The TG curve of **1** (Supplementary Data, Fig. S3) is parallel to the X-axis till ~200 °C indicating its high thermal stability. In the temperature region (200–324 °C) continuous mass loss amounting to ~31%, is observed which can be attributed to the loss of acetylacetone and nitrate (calculated weight loss ~32%). This is followed by the complete loss of all organics at around 520 °C. The DTA curve exhibits exothermic events at 205 °C, 309 °C and 476 °C which can account for the mass losses.

Description of the crytsal structure of 1

Compound **1** crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ with all atoms located in general position. The structure of **1** consists of an unique copper(II), each of a crystallographically independent acetylacetonate anion, a nitrate anion and a 2,2′-biquinoline accounting for a neutral compound of composition [Cu(biq)(acac)(NO_3)] (Fig. 2). The geometric parameters of acac and biq are in the normal range (Supplementary Data, Table S1). Unlike the NO_3^- anion which functions as a monodentate ligand, biq and acac exhibit bidentate bonding forming five and six membered chelate rings, respectively, with the central metal. The five-membered ring (Cu1, N1, N2, C9, C10) is nearly planar, while the six-membered ring (Cu1, O1, O2, C19, C20, C21) formed by acac ligand exhibits an envelope conformation (Supplementary Data, Fig. S4). In compound **1** the central Cu(II) exhibits penta coordination, which is observed in several mixed ligand copper(II)-acetylacetonates (Entry no. 1 to 15 in Table 1).

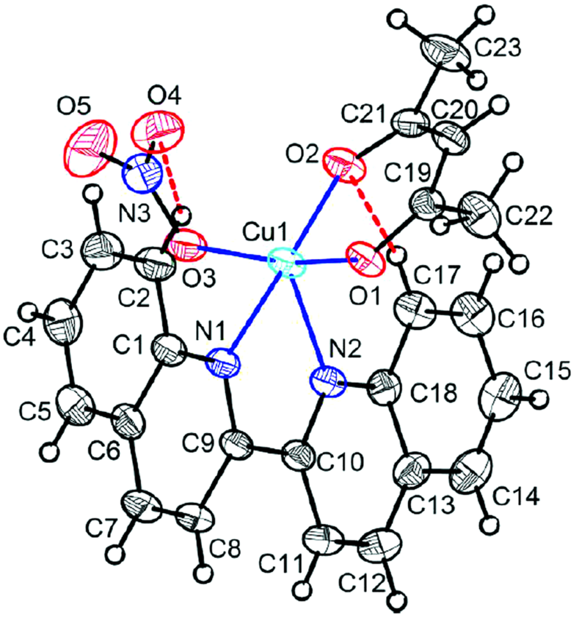

Fig. 2 — Crystal structure of [Cu(biq)(acac)(NO_3)] **1** showing penta coordination around copper. Thermal ellipsoids are drawn at 30% probability level expecting the H-atoms which are shown as spheres of arbitrary radii. Intramolecular hydrogen bonds are shown as broken red lines

The {CuN_2O_3} coordination sphere is made up of two oxygen atoms of the unique acac ligand, an oxygen of the nitrate group and one N atom of biq ligand which form the basal plane {$CuNO_3$} of a square pyramid. A second nitrogen atom of the biq ligand occupies the apical position to complete the square pyramid (Supplementary Data, Fig. S4). The Cu–N bond distances (Cu1–N1 = 2.030(2); Cu1–N2 = 2.259(2) Å) are elongated as compared to the Cu–O bond lengths which vary from 1.939(19) to 2.009(2) Å (Table 3). The O–Cu–O, N–Cu–N and O–Cu–N bond angles range between 77.36(9)° and 178.11(9)°. The variations of these from the ideal values for the *cis* and *trans* angles (Fig. S5) reveal that the {CuN_2O_3} polyhedron deviates from ideal square-pyramid geometry.

Two of the oxygen atoms of the nitrate anion viz. O3 and O4 and an oxygen of the acac ligand function as H-acceptors while three H atoms (H2, H11, H17) attached to the C of biq and one hydrogen atom (H22B) attached to the methyl group of acac function as H-donors (Table 4), resulting in a total of four C–H···O hydrogen bond interactions of which two are intramolecular (Fig. 2). O4 acts as a double acceptor unlike O2 and O3 each of which accepts single hydrogen. Each neutral [Cu(biq)(acac)(NO_3)] molecule is linked to two symmetry related molecules with the aid of C11–H11···O3^{i} and C22–H22B···O4^{ii} interactions (Symmetry code: i =1-x, 1-y, -z; ii =2-x, -y, 1-z) (Fig. 3) resulting in a one-dimensional hydrogen bond network. Additionally, **1** exhibits $\pi\cdots\pi$ stacking interactions (Supplementary Data, Fig. S6). Based on an analysis of the short ring interactions in **1** using the program Platon[36], the ring centroid distances

Table 3 — Selected bond lengths and bond angles for **1**

Bond lengths (Å)			
Cu1–O1	1.9385(19)	Cu1–N1	2.030(2)
Cu1–O2	1.9181(19)	Cu1–N2	2.259(2)
Cu1–O3	2.009(2)		
Bond angles (°)			
N1–Cu1–N2	77.36(9)	O2–Cu1–N2	104.45(9)
O1–Cu1–O3	164.96(9)	O1–Cu1–N2	105.44(8)
O2–Cu1–N1	178.11(9)	O3–Cu1–N2	88.92(9)
O1–Cu1–N1	87.22(8)	O2–Cu1–O1	92.77(8)
O3–Cu1–N1	91.71(9)	O2–Cu1–O3	87.81(9)

Table 4 — Hydrogen-bonding parameters (Å, °) for $[Cu(biq)(acac)(NO_3)]$ **1**

D–H····A	D–H	H····A	*d*(D····A)	∠D– H····A	Symmetry code
C2–H2···O4	0.93	2.50	3.231(4)	136	x, y, z
C17–H17···O2	0.93	2.34	3.183(4)	151	x, y, z
C11–H11···O3	0.93	2.58	3.241(4)	129	1-x, 1-y, -z
C22–H22B···O4	0.96	2.45	3.379(5)	163	2-x, -y, 1-z

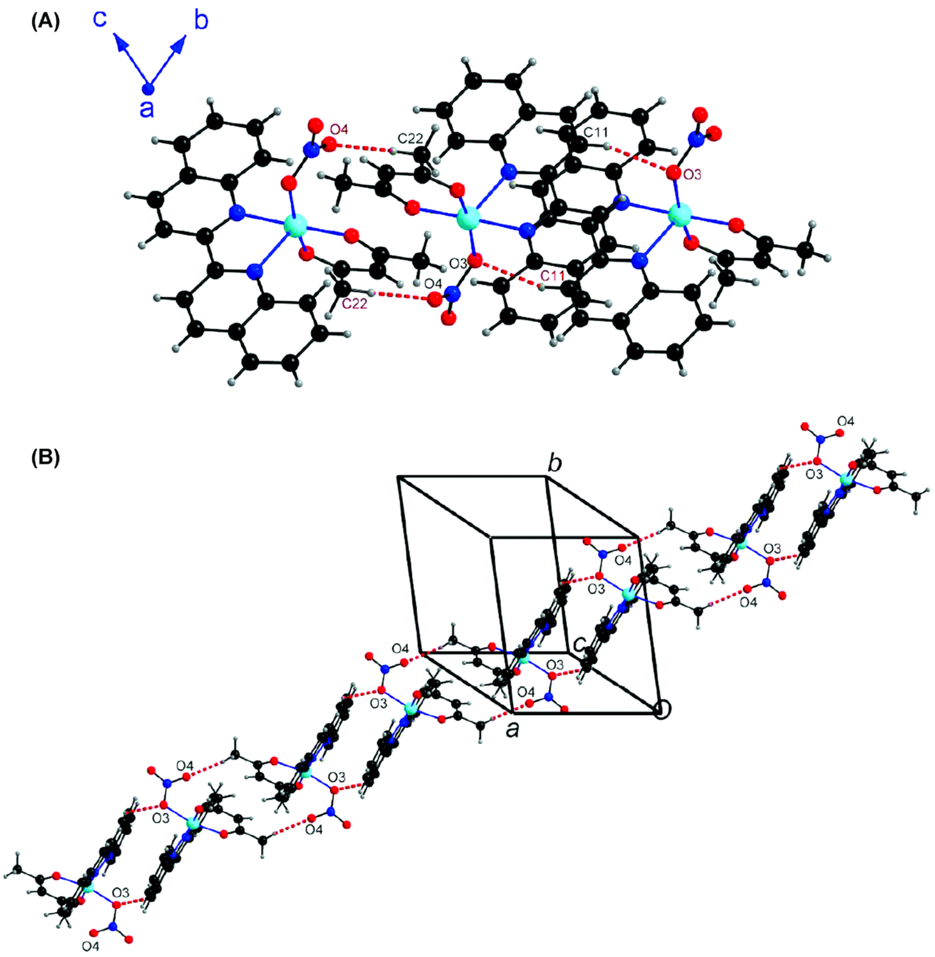

Fig. 3 — (A) H-bonding scheme around $[Cu(biq)(acac)(NO_3)]$ 1 showing that each molecule of 1 is linked to two neighbours with the aid of C11–H11···O3[i] and C22–H22B···O4[ii] interactions shown in red and (B) symmetry codes: i = 1-x,1-y,-z; ii = 2-x,-y,1-z; A view of the one-dimensional hydrogen bond network in 1 showing the stacking of the aromatic rings of the biq ligand (See Fig. S6) in adjacent molecules

(Cg···Cg) between the adjacent pyridine rings of biq are found to be of the order of ~ 4.0 Å (Supplementary Data, Table S2). The shortest Cg···Cg distance observed is 3.5541(4) Å. Since stacking interactions can exist at very long Cg···Cg distances[37], the observed data reveal that the structure is further stabilized by $\pi\cdots\pi$ stacking.

Distortion of $\{CuN_2O_3\}$ square pyramid in mixed ligand copper(II) acetylacetones

It is well documented that Cu(II) can exhibit variable coordination numbers ranging from 4 to 6 resulting in irregular polyhedra which deviate from regular geometries. For five coordinate Cu(II) compounds a trigonal bipyramid geometry (D_{3h} symmetry) or a square pyramid (C_{4v}) are the two extreme possibilities[38]. However, many compounds adopt geometries which are in between these two extremes. For five coordinated Cu(II) compounds, Addison et al.[39] defined an angular structural parameter τ given by the equation $\tau = \beta - \alpha / 60$ as an index of trigonality. In this relation α and β are the *trans* angles of the square base and the larger angle is considered as β. The value of τ is 0 for a perfect square pyramid whose *trans* angles are straight angles and 1 for trigonal bipyramid geometry. The values in between 0 and 1 indicate a deviation of the square pyramid towards trigonal bipyramid.

The observed *trans* angles in **1** (O2–Cu1–N1 = 178.11(9)°; O1–Cu1–O3 = 164.96(9)°) (Table 3), correspond to a τ value of 0.219, which indicates that the irregular coordination geometry of copper(II) as being ~22% along the pathway of distortion from square pyramidal to trigonal bipyramidal geometry. A comparative study of fifteen mixed ligand copper(II) acetylacetonates reveals that the τ value of 0.219 in **1** corresponds to significant distortion in this group of compounds. A survey of the Cambridge Structural Database[40] (CSD), reveals many examples of structurally characterized mixed ligand copper(II) acetylacetonates[13, 20-27] which are listed in Table 1 in addition to seven biquinoline compounds of copper[14,28-32]. In these compounds, the central metal exhibits coordination numbers of 4 and 5. All the copper(I) compounds are tetrahedral (entry nos. 19 to 24). Two four coordinate compounds of copper(II) other than [Cu(biq)Cl_2] adopt square planar geometry. All the compounds in Table 1 excepting the last two entries crystallize in centrosymmetric space groups. It is interesting to note that in the series of mixed ligand copper(II) acetylacetonates, the title compound exhibits the maximum τ value of 0.219, which is twice more than the τ value of the other compounds. Although the structural deviation is affected by many factors like the type of the bidentate ligands, the axial and equatorial bond distances, by definition the value of τ depends on the magnitude of the *trans* angles of the square base. The fifteen square pyramidal compounds in Table 1 exhibit some common structural features like a bidentate acac ligand, a bidentate N-donor ligand and an axial ligand which can be solvent or a halide anion. The formation of these compounds can be considered as having occurred due to the displacement of a bidentate acac ligand in the square planar [Cu(acac)$_2$] compound in the presence of the axial ligand. The trend in the observed τ values can be understood by knowing if the bidentate N-donor occupies the square base of the square pyramid or if one of the corners of the square is bonded to the monodentate ligand. A majority of the compounds in Table 1 except entry nos 1 and 5 contain either solvent / anion coordinated in the apical position and exhibit smaller τ values.

It is interesting to note that in **1**, biq coordinates to the copper(II) centre protruding up and down the basal plane with one of the nitrogen (N2) in the apical position exhibiting the longest bond distance (Cu–N2 = 2.259(2) Å) which is not observed in the other mixed ligand copper(II) acetylacetonates except [Cu(dmph)(acac)(NO_3)] (dmph=2,9-dimethylphenanthroline). Like in **1**, one N-atom of the dmph ligand occupies the basal plane while the second N occupies the axial position, which can account for the τ value of 0.092. In their study, Addison et al.[39] had also predicted that for a positive value of τ the apical bond of the fifth ligand is elongated. In the entry nos. 2, 3 and 6 the bidentate N-donor occupies the basal plane while the halide ion (X) occupies the axial position. However, the Cu–X distances in these compounds are considerably longer (for example Cu–Br distance in entry no. 2 is 2.708 Å while Cu–Cl bond length is 2.471 Å in entry no. 3) which can explain the deviation in these structures by ~10% accompanied by τ values of 0.100 and 0.099 indicating the importance of axial bond distances.

Conclusions

In this study, we describe the synthesis and spectral characterization of a mixed ligand copper(II) compound [Cu(biq)(acac)(NO_3)] **1** (biq = 2,2′-biquinoline, acac = acetylacetonate) containing bidentate acetylacetonate. The crystal structure of **1** exhibits considerable deviation from square pyramidal geometry. A comparative study of fifteen mixed ligand penta-coordinated copper compounds has been performed and the angular structural parameter τ has been analysed for this series of compounds. The analysis reveals that compound **1**, which is a new addition to the list of structurally characterized mixed ligand copper(II) acetylacetonates, exhibits the maximum deviation of 22% along the pathway of distortion from square pyramidal towards trigonal bipyramidal geometry.

Supplementary Data

Deposition Number 2026457 (for **1**), contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachin-formationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures. Supplementary data associated with this article are available in the electronic form at http://nopr.niscair.res.in/jinfo/ijca/IJCA_60A(04)499-505_SupplData.pdf.

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