

SYNTHESIS AND SPECTRAL CHARACTERIZATION OF (Z)-2-((2-HYDROXY-6-METHYLQUINOLIN-3-YL) METHYLENEAMINO)-5-IODOBENZOIC ACID AND THEIR METAL (II) COMPLEXES

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Article Received on
01 September 2014,

Revised on 26 Sept 2014,
Accepted on 20 Oct 2014

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ABSTRACT

The Cu(II), Co(II), Ni(II), Zn(II), Cd(II), Hg(II), Mn(II) and Fe(III) complexes of Schiff base (Z)-2-((2-hydroxy-6-methylquinolin-3-yl)methyleneamino)-5-iodobenzoic acid has been synthesized and characterized by various spectral techniques. The complexes were prepared by reacting the ligand and metal chloride of Cu(II), Co(II), Ni(II), Zn(II), Cd(II), Hg(II), Mn(II) and Fe(III) in ethanol to get a series of mononuclear complexes. The complexes were characterized by CHN analysis, conductivity measurements, magnetic susceptibility, IR, ¹H NMR, ESR, UV-Vis and X-ray powder diffraction studies. By these spectral studies it is found that Cu(II), Co(II), Ni(II), Mn(II) and Fe(III) complexes have exhibited octahedral geometry and Zn(II), Cd(II), Hg(II) complexes have exhibited tetrahedral geometry. The ligand and its metal complexes have been screened for their

antimicrobial activities. The prepared ligand shows low activity and its metal complexes shows moderate to good activity.

KEYWORDS: Methyl quinoline, 2-amino-5-iodo-bezoic acid, Schiff base and Metal complexes.

INTRODUCTION

Quinoline and its derivatives are a class of hetero aromatic compounds that have drawn much attention because of their biological and pharmaceutical activities including wide range medicinal and biological applications, such as anti-cancer ^[1], antimicrobial ^[2], HIV protease inhibitors ^[3], antileishmanial activity^[4]. Quinoline derivatives as a source of valuable drug

candidates and useful intermediates in organic chemistry^[5] thus, the synthesis of this heterocyclic nucleus is of much used in pharmacopeia in treatment of malaria^[6] and more recently tumors^[7]. Our work is concerned with complexation in aqueous- organic solvents attract study researchers participation of the organic component. As a continuation of studies concerning the effect of acid hydrazides^[8], Quinoline attract much interest in view of their DNA-binding^[9] and DNA-photo damaging properties^[10], inhibit dihydrofolate reductase exhibit an important role in clinical medicine as exemplified by the use of methotrexate in neoplastic diseases^[11], inflammatory bowel diseases^[12], rheumatoid arthriti^[13], psoriasis^[14], asthma^[15], antineoplastic activities^[16]. In view of the biological and pharmaceutical applications of 2-amino-5-iodobenzoic acid in the present investigation we thought it is worthwhile to synthesize the Schiff's bases derived from the condensation of 2-hydroxy-6-methylquinoline-3-carbaldehyde.

Experimental

MATERIALS AND METHODS

All the chemicals are purified, 2-amino-5-iodo-benzoic acid hydrazide and substituted quinoline aldehyde was synthesized and metal salts are used for AR grade.

Synthesis of Schiff base ligand (Z)-2-((2-hydroxy-6-methylquinolin-3-yl) methyl eneamino)-5-iodobenzoic acid

A mixture of 2-Amino-5-iodo-bezoic acid (1mole) and 2-hydroxy-6-methylquinoline-3-carbaldehyde (1mole) in ethanol (30ml) was refluxed in the presence of catalytic amount of acetic acid (1-2 drops) for about 7 - 8 hours on a water bath. The reaction mixture was cooled to room temperature to afford the intense yellow compound (ligand). The separated compound was collected by filtration, washed with ethanol, dried and recrystallized from ethyl alcohol. The yield obtained 85%.

Preparation of Metal Complexes

A solution of 0.01mole of metal chloride in ethanol was mixed with the ethanol solution of 0.01 mole of ligand and refluxed for 3-4 hours on water both to get clear solution. 0.5gm of excess sodium acetate was added to the reaction mixture to adjust the pH 7-8 of the solution. The reaction mixture was further, refluxed for 2 hours more. The resulting mixture was decomposed by pouring into a 100ml of distilled water with constant stirring. The suspended solid complex was allowed to settle and collected by filtration, washed with sufficient

quantity of distilled water and then with little hot ethanol to apparent dryness and dried in a vacuum over anhydrous calcium chloride in a desiccators. (Yield, 55-75%)

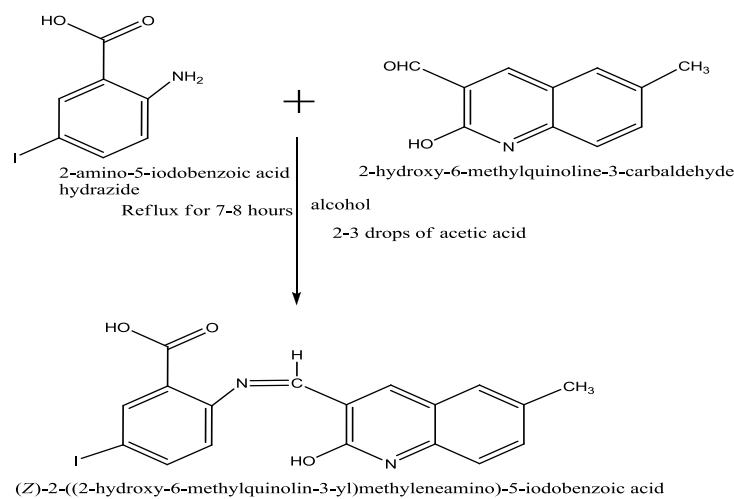


Figure-I

Physical Measurements

Infrared spectra of the ligand and its metal complexes in KBr pellets were recorded in the spectral range 3800 – 350 cm⁻¹ with Perkin Elmer Spectrum One FT-IR Spectrometer. ¹H NMR Spectra were recorded on AMX-4000 NMR Spectrometer, using TMS as internal standard and DMSO as a solvent. The Electronic Spectra were recorded on an Elico-SL-164 Double BEAM UV-Visible Spectrophotometer in the range of 200 - 1200nm in DMF. X-ray powder diffraction was recorded at department of physics Gulbarga university, Gulbarga. Magnetic susceptibility measurements were recorded on Guoy balance method. The Conductance measurements were made on an ELICO-CM-82-conductivity bridge.

RESULTS AND DISCUSSION

Nature and Stoichiometry of Ligand

All the complexes were sparingly soluble in common organic solvents but soluble in DMF, DMSO and acetonitrile. The analytical data indicates that the complexes are agree well with 1:1 metal to ligand stoichiometry for Zn(II), Cd(II) and Hg(II) and 1:2 for Cu(II), Co(II), Ni(II), Mn(II) and Fe(III) complexes shown in Table XI. The observed molar conductance values measured in DMF solution fall in the range (14-20 Ohm⁻¹ cm² mol⁻¹). These observed values of the molar conductance are well within the expected range for non-electrolytic [17].

Table I. Analytical, magnetic susceptibility, molar conductance of the ligand and its metal complexes.

| Ligand / Complex | Mol. Wt. | M.P (°C) | Yield (%) | Found /Calculated (%) | | | | | μ_{eff} B.M. | Molar conductance $\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ |
|---|----------|----------|-----------|-----------------------|---------------|-------------|-------------|------|-------------------------|---|
| | | | | M | C | H | N | Cl | | |
| [C ₁₈ H ₁₃ IN ₂ O ₃] | 432.21 | 270 | 75 | - | 50.02 (49.88) | 3.03 (3.08) | 6.48 (6.55) | - | - | - |
| [Cu(C ₃₆ H ₂₈ I ₂ N ₄ O ₈)] | 961.98 | 312 | 70 | 6.86 (6.84) | 46.70 (46.69) | 2.61 (2.56) | 6.05 (6.09) | - | 1.96 | 19 |
| [Co(C ₃₆ H ₂₈ I ₂ N ₄ O ₈)] | 957.37 | 320 | 75 | 6.40 (6.48) | 46.93 (46.68) | 2.63(2.60) | 6.08 (6.02) | - | 4.74 | 18 |
| [Ni(C ₃₆ H ₂₈ I ₂ N ₄ O ₈)] | 957.13 | 301 | 70 | 6.37 (6.35) | 46.94 (46.70) | 2.63 (2.60) | 6.08 (6.03) | - | 2.93 | 17 |
| [Mn(C ₃₆ H ₂₈ I ₂ N ₄ O ₈)] | 953.38 | 318 | 75 | 5.87 (5.92) | 46.23 (46.21) | 2.80 (2.83) | 5.99 (5.94) | - | 5.68 | 14 |
| [Fe(C ₃₆ H ₂₆ I ₂ N ₄ O ₇)Cl] | 971.72 | 340 | 70 | 5.75 (5.74) | 44.50 (44.44) | 2.70 (2.74) | 5.77(5.74) | 3.65 | 5.75 | 17 |
| [Zn(C ₁₈ H ₁₂ IN ₂ O ₃)Cl] | 532.07 | 348 | 75 | 12.29 (12.24) | 40.63 (40.60) | 2.27 (2.25) | 5.27 (5.24) | 6.66 | Diamagnetic | 16 |
| [Cd(C ₁₈ H ₁₄ IN ₂ O ₄)Cl] | 597.08 | 350 | 80 | 18.83 (18.80) | 36.21 (36.29) | 2.36 (2.33) | 4.69 (4.63) | 5.94 | Diamagnetic | 14 |
| [Hg(C ₁₈ H ₁₄ IN ₂ O ₄)Cl] | 685.26 | 372 | 80 | 29.27 (29.27) | 31.55 (31.52) | 2.06 (2.05) | 4.09 (4.10) | 5.17 | Diamagnetic | 20 |

IR Characterization of Schiff's Base Ligands

The significant IR bands for the ligand (Z)-2-((2-hydroxy-6-methylquinolin-3-yl) methyleneamino)-5-iodobenzoic acid as well as for its metal complexes and their tentative assignments are compiled and represented Table II. The broad band observed at 3435 cm^{-1} in the IR spectra of the ligand assigned to $\nu_{(\text{OH})}$, which were found to have disappeared in all their respective complexes, there by indicating the involvement of phenolic oxygen is bonding with metal ions through deprotonation. A strong sharp band observed at 1662 cm^{-1} is assigned to 2-amino -5-iodo benzoic acid hydrazide ring $\nu_{(\text{C=O})}$ which was shifted to 1-36 cm^{-1} in all complexes, indicates the involvement of 2-amino-5-iodo benzoic acid hydrazide ring carboxyl in complexation with metal ion. The band at 1599 cm^{-1} is assigned to the azomethine $\nu_{(\text{C=N})}$ group, lowering of $\nu_{(\text{C=N})}$ 1-49 cm^{-1} in the complexes as compared to its ligand, is due to reduction of double bond character carbon-nitrogen bond of the azomethine group ^[18]. The band observed at 1209 cm^{-1} , of the ligand is attributed to phenolic $\nu_{(\text{C-O})}$ in view of previous observations^[19]. This band is shifted to higher frequency and is found in the region 1209-1268 cm^{-1} (1-62 cm^{-1}) for the complexes. Thus, the low frequency skeletal vibrations due to $\nu_{(\text{M-O})}$ and $\nu_{(\text{M-N})}$ stretching provide direct evidence for complexation. In the present investigation the bands in the 555-570 cm^{-1} region for $\nu_{(\text{M-O})}$ 478 -498 cm^{-1} region for $\nu_{(\text{M-N})}$ vibration and 358-394 cm^{-1} region for $\nu_{(\text{M-Cl})}$ respectively.

Table II. IR Spectral data of the ligand and its metal complexes (cm⁻¹).

| Ligand / complex | ν_{OH} | $\nu_{\text{C=O}}$ | $\nu_{\text{C=N}}$ | $\nu_{\text{C-O}}$ | $\nu_{\text{M-O}}$ | $\nu_{\text{M-N}}$ | $\nu_{\text{M-Cl}}$ |
|---|-------------------|--------------------|--------------------|--------------------|--------------------|--------------------|---------------------|
| [C ₁₈ H ₁₃ IN ₂ O ₃] | 3435 | 1662 | 1599 | 1209 | - | - | - |
| [Cu(C ₃₆ H ₂₈ I ₂ N ₄ O ₈)] | - | 1670 | 1563 | 1234 | 555 | 478 | - |
| [Co(C ₃₆ H ₂₈ I ₂ N ₄ O ₈)] | - | 1684 | 1560 | 1260 | 566 | 494 | - |
| [Ni(C ₃₆ H ₂₈ I ₂ N ₄ O ₈)] | - | 1698 | 1574 | 1263 | 560 | 482 | - |
| [Mn(C ₃₆ H ₂₈ I ₂ N ₄ O ₈)] | - | 1692 | 1580 | 1264 | 556 | 469 | - |
| [Fe(C ₃₆ H ₂₆ I ₂ N ₄ O ₇)Cl] | - | 1683 | 1558 | 1234 | 557 | 468 | 360 |
| [Zn(C ₁₈ H ₁₂ IN ₂ O ₃)Cl] | - | 1679 | 1550 | 1224 | 552 | 498 | 358 |
| [Cd(C ₁₈ H ₁₄ IN ₂ O ₄)Cl] | - | 1689 | 1560 | 1268 | 568 | 482 | 376 |
| [Hg(C ₁₈ H ₁₄ IN ₂ O ₄)Cl] | - | 1697 | 1555 | 1240 | 570 | 485 | 394 |

Magnetic Movement and Electronic Spectra of the Complexes**1. Copper (II) Complex**

The complexes having temperature independent magnetic moments in the range of 1.74-2.2 B.M. agreeable to the spin only value. These complexes are mononuclear having no major spin-spin interactions; however no compromise can be set between the magnitude of the distortion and other variable factors. The Cu(II) complexes with this behavior indicate marked spin-exchange and strong coupling interaction between Cu(II) atoms. As the spin only value for a single unpaired electron is 1.72 B.M. The slight excess over this value for the Cu(II) complexes can be attributed to spin orbital coupling. The observed magnetic moment values for the present Cu(II) complexes is 1.90 B.M⁶⁷. This value is expected for one electron system and is in the normal range of Cu(II) complex system. As the spin only values for a single unpaired electron is 1.72 B.M. The slight excess over this value found for the Cu(II) complex can be attributed to spin orbital coupling. In view of the above observations the magnetic moment values for the present Cu(II) complexes, suggest the distorted octahedral geometry around Cu(II) ions. Electronic spectra of Cu(II) complexes exhibit a broad, low intensity shoulder band. The ²E_g and ²T_{2g} states of octahedral Cu(II) ion (d⁹) split under the influence of the tetragonal distortion and the distortion can be such as to cause the three transition viz., ²B_{1g} → ²B_{2g}, ²B_{1g} → ²E_g and ²B_{1g} → ²A_{1g}, to remain unresolved in the spectra. It is concluded that all three transition lie within the single broad band in the region 25400 – 31000 cm⁻¹, have been assigned to charge transfer bands from ligand to metal. The observation favor distorted octahedral geometry around Cu(II) complexes. A broad asymmetric band in the region 12099-16580 cm⁻¹, the symmetry being on the lower energy side ^[20]. The broadness of the band may be due to dynamic John-Teller distortion. The band maxima observed for the present Cu(II) complexes is at 12099-16580 cm⁻¹, 12745-16462 cm⁻¹ and 16049 – 18357 cm⁻¹ suggest that the complex displays coordination number six. In

addition, we have observed a high intensity band around 15640cm^{-1} that can be attributed to the ligand-metal charge transfer transition. ^[21]

2. Cobalt (II) Complex

In octahedral Co(II) complexes the ground state is ${}^4\text{T}_{1g}$ and a large orbital contribution to the magnetic moment values for various Co(II) complexes are in the range 4.11-4.78 B.M. and 4.6-5.18 B.M. for tetrahedral and octahedral complexes respectively. In present investigation the observed magnetic moment values is in the range 4.68 B.M ^[22], which indicates octahedral geometry for these Co(II) complexes. This is due to partial quenching of orbital contribution to the magnetic moment. Electronic spectra of Co(II) complex exhibits three bands in the region $9980\text{-}11365\text{cm}^{-1}$, $15420\text{-}16349\text{cm}^{-1}$ and $21051\text{-}25910\text{ cm}^{-1}$ due to the transition. ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$ (ν_1) = $9980\text{-}11365\text{cm}^{-1}$, ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$ (ν_2) = $15420\text{-}16349\text{cm}^{-1}$ and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ (ν_3) = $21051\text{-}25910\text{ cm}^{-1}$. These transitions suggest octahedral geometry ^[23]. The region at $25650\text{-}26990\text{ cm}^{-1}$ refers to the charge transfer band. These transitions suggest octahedral geometry for the Co(II) complexes. These assignments are in good agreement with the reported values ^[24].

3. Nickel (II) Complex

Ni(II) complexes exhibits the magnetic moment value of 4.70 which are well within the range of expected value for octahedral geometry around the central metal ion ^[25]. Electronic spectra of Ni(II) complexes in octahedral coordination is ${}^3\text{A}_{2g}$, the Ni(II) complexes show three transition in an octahedral field, *viz.*, ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$; ν_1 $8460\text{-}9220\text{cm}^{-1}$, ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$; ν_2 $16480\text{-}17530\text{cm}^{-1}$, ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$; ν_3 $25875\text{-}26540\text{cm}^{-1}$. The observed transition bands lie well within in the range of reported values. These values indicate considerable covalent character and support the octahedral geometry for the Ni(II) complex ^[26].

4. Manganese (II) Complex

The observed magnetic moment values for Mn(II) complex of the ligand is in the range 5.50 B.M. The electronic spectra of Mn(II) complex shows three transition, which corresponds to the following transitions, ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}(4\text{G})$; $\nu_1 = 9565\text{-}15860\text{cm}^{-1}$, ${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g(4\text{D})$; $\nu_2 = 17510\text{-}19723\text{cm}^{-1}$, ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}(4\text{D})$; $\nu_3 = 21942\text{-}24710\text{cm}^{-1}$ These values indicate considerable covalent character and support the octahedral geometry²⁷. Hence under the present study octahedral geometry is suggested for Mn(II) complex.

5. Iron (III) Complex

The observed magnetic moment values for Fe(III) exhibited the magnetic moments values of 5.72 B.M. The electronic spectra of Fe(III) complex shows three transition, which corresponds to the following transitions, $^6A_{1g} \rightarrow ^4T_{1g}$ (4G); $\nu_1 = (\nu_1) 11918-14652\text{cm}^{-1}$, $^6A_{1g} \rightarrow ^4E_g$ (4D); $\nu_2 = 14990-16874\text{cm}^{-1}$, $^6A_{1g} \rightarrow ^4T_{1g}$ (4D); $\nu_3 = 19683-20245\text{cm}^{-1}$ These values indicate considerable covalent character and support the octahedral geometry²⁸. Hence under the present study octahedral geometry is suggested for Fe(III) complex.

Table III. Electronic spectral data of ligand field parameters of Cu(II), Co(II), Ni(II) and Mn(II) metal complexes

| Complexes | $\nu_1(\text{cm}^{-1})$ | $\nu_2(\text{cm}^{-1})$ | $\nu_3(\text{cm}^{-1})$ | $Dq (\text{cm}^{-1})$ | B^1 | β | $\beta\%$ | ν_2/ν_1 | ν_3/ν_2 | LFSE k cal mol ⁻¹ |
|---|-------------------------|-------------------------|-------------------------|-----------------------|-------|---------|-----------|---------------|---------------|------------------------------|
| [Cu(C ₃₆ H ₂₈ I ₂ N ₄ O ₈)] | | 12099 – 16049 | | 1420 | - | - | - | - | - | 24.70 |
| [Co(C ₃₆ H ₂₈ I ₂ N ₄ O ₈)] | 9980 | 15420 | 21051 | 930 | 828 | 0.96 | 15.07 | 1.54 | 1.36 | 14.20 |
| [Ni(C ₃₆ H ₂₈ I ₂ N ₄ O ₈)] | 8460 | 16480 | 25875 | 912 | 837 | 0.84 | 19.91 | 1.94 | 1.57 | 30.80 |
| [Mn(C ₃₆ H ₂₈ I ₂ N ₄ O ₈)] | 9565 | 17510 | 21942 | 939 | 861 | 0.82 | 23.01 | 1.83 | 1.25 | 14.55 |
| [Fe(C ₃₆ H ₂₆ I ₂ N ₄ O ₇)Cl] | 11918 | 14990 | 19683 | 940 | 881 | 0.80 | 22.08 | 1.25 | 1.31 | 18.20 |

¹H NMR Spectra

Spectrum of ¹H NMR is DMSO-d₆ solvent used. In ligand (Z)-2-((2-hydroxy-6-methylquinolin-3-yl)methyleneamino)-5-iodobenzoic acid showed the sharp peak at δ 12.2 (S, 1H) due to OH at 2-position of phenyl ring of 2-hydroxy quinoline moiety has resonated, but in the case of Zn(II) complex which has been disappeared indicating the involvement of phenolic oxygen in the coordination *via*, deprotonation^[29, 30]. A single large peak showed at δ 8.8 (S, 1H, CH₃) due to protons of the azomethine group in ligand but in case of Zn(II) complex the peak observed at δ 8.6 (S, 1H, CH₃)^[31]. The ten aromatic protons due to quinoline and phenyl rings have resonated in region δ 7.0-8.6 (m, 14H, Ar-H) as a multiplet, in Zn (II) complex the ten aromatic protons have been observed in the region δ 7.0-8.6(m, 14H, Ar-H) as a multiplet. The Zn(II) complex suggests coordination of the phenolic -OH with metal ion.

ESR Spectrum

The ESR spectrum of the powder Cu(II) complex was recorded at room temperature using DPPH as a standard showed a broadened feature without hyperfine splitting due to the dipolar interaction from the ESR spectrum of a set of magnetic parameter $g_{||} = 2.237$, $g_{\perp} = 2.054$. The observed ESR spectrum is characteristic of distorted octahedral geometry g value

averaged to over all directions and G which is measure of extent of exchange interaction between metal ions have been calculated. In present case the value of G was found to be 4.338 according to Hathway³². If G value is greater than 4, the spin exchange interaction is negligible whereas G value is less than 4 indicate considerable interaction between metal ions in solid complex clearly indicate that Cu(II) ion in the complex is mononuclear nature of the complex.

Table IV. ESR spectral data of the Cu(II) complex.

| Complex | g_{\parallel} | g_{\perp} | g_{av} | g_{iso} | G |
|---|-----------------|-------------|----------|-----------|-------|
| [Cu(C ₃₆ H ₂₈ I ₂ N ₄ O ₈)] | 2.235 | 2.054 | 2.144 | 2.189 | 4.338 |

X-ray Powder Diffraction Studies

X-ray powder diffraction pattern for Cu(II) complex has characterized with a view to find the type of crystal system the XRD data given the table the diffractogram of Cu(II) complex consists of ten reflections in the range of 5 - 58 (2 θ value) with maxima at 2 θ = 19.76 $^{\circ}$ A. The interplanar spacing(d) has been calculated from the position of intense peaks using Bragg's equation $n\lambda=2dsin\theta$, $\lambda = 1.5406^{\circ}$ A. The observed and calculated values of d are quite consistent (Table V). The unit cell calculations have been carried out for the cubic system, the set of $h^2 + k^2 + l^2$ values of the complex were found to be 1, 4, 5, 6, 7, 9 and 14 which corresponds to the planes and absence of forbidden number its confirms the hexagonal symmetry from the above results the unit cell constants for hexagonal system were found to be $a=b=c = 11.46^{\circ}$ A for the Cu(II) complex of the ligand the complex showed broad peak indicates amorphous nature³³⁻³⁵.

Table V. X-ray powder diffraction data of Cu(II) complex of ligand.

| 2 θ | θ | $sin\theta$ | $sin^2\theta$ | $h^2+k^2+l^2$ (a) | $h^2+k^2+l^2$ (b) | $h\ k\ l$ | d-spacing | | Relative intensity (%) | a ($^{\circ}$ A) |
|------------|----------|-------------|---------------|----------------------|----------------------|-----------|-----------|--------|---------------------------|----------------------|
| | | | | | | | Cal. | Abs | | |
| 5.691 | 2.845 | 0.049 | 0.002 | 1 | 1 | 1 0 0 | 15.517 | 15.517 | 5.36 | 11.46 |
| 11.719 | 5.859 | 0.102 | 0.010 | 3.6 | 4 | 2 0 0 | 7.544 | 7.544 | 15.69 | 11.46 |
| 14.437 | 7.218 | 0.125 | 0.015 | 6.6 | 7 | 3 1 0 | 6.127 | 6.127 | 25.44 | 11.46 |
| 19.766 | 9.883 | 0.171 | 0.029 | 13.7 | 14 | 3 2 1 | 4.487 | 4.487 | 100.00 | 11.46 |
| 27.463 | 13.731 | 0.237 | 0.056 | 4.6 | 5 | 2 1 0 | 3.244 | 3.244 | 47.89 | 11.46 |
| 32.596 | 16.299 | 0.280 | 0.078 | 5.9 | 6 | 2 1 1 | 2.744 | 2.744 | 9.481 | 11.46 |
| 36.426 | 18.213 | 0.312 | 0.097 | 4.4 | 4 | 2 0 0 | 2.464 | 2.464 | 8.245 | 11.46 |
| 39.150 | 19.575 | 0.335 | 0.112 | 5.7 | 6 | 2 1 1 | 6.078 | 6.078 | 5.36 | 11.46 |
| 58.290 | 29.140 | 0.486 | 0.236 | 9.2 | 9 | 2 2 1 | 1.580 | 1.580 | 8.82 | 11.46 |

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