



Cobalt(II), copper(II) and zinc(II) complexes of di-2-pyridyl ketone-4-methoxybenzhydrazone: Preparation and characterization

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Received 19 August 2022; accepted 21 October 2022

A new aroylhydrazone ligand, di-2-pyridyl ketone-4-methoxybenzhydrazone (DKMBH·H₂O) and its three complexes with cobalt(II), copper(II) and zinc(II), labelled Co(DKMB)Cl (1), Cu(DKMB)Cl (2), and Zn(DKMB)Cl (3) have been prepared and structurally studied. The spectroscopic techniques like IR, UV-Vis, MS, and ¹H NMR, as well as CHN analysis and thermal analysis, have been used to physico-chemically characterize the synthesized compounds. The IR and ¹H NMR analyses have made clear that the aroylhydrazone remains in the amido form in the solid state. The IR spectral measurements further support the tridentate character of the NNO donor aroylhydrazone. In all complexes, pyridine nitrogen, azomethine nitrogen, and iminolate oxygen of the tridentate aroylhydrazone are involved to coordinate to the metal centre.

Keywords: ¹H NMR spectrum, Aroylhydrazone, IR spectrum, Mass spectrum, Metal complex, NNO donor, UV-Vis spectrum

One of the most difficult, alluring, and demanding areas of research in contemporary inorganic chemistry is coordination chemistry. The coordination compounds with intriguing ligand systems and a variety of donor sites, including NO, NNO, ONO, and NNS, provide exciting applications in a number of fields. Due to their simplicity of synthesis, denticity, easily tailorable electrical characteristics and ability to create a wide range of complexes of structural, industrial, and biological importance^{1,2}, hydrazones stand out among other nitrogen oxygen donor ligands. The hydrazones are multifaceted and readily accessible. Depending on the nature of the initial materials used for their synthesis, these ligands can have different functionalities and denticities. Hydrazones have a number of advantages over imines, including simplicity in preparation, enhanced hydrolytic stability, and a propensity towards crystallinity. Since they have these advantageous characteristics, hydrazones have long been the subject of intense research⁴⁻⁶. Particularly, the presence of both nucleophilic and electrophilic nature; for instance, the nitrogen atoms in hydrazones are nucleophilic, whilst the carbon atom exhibits both types of nature⁷. When functional groups are introduced in the system,

hydrazones will form materials with distinct chemical and physical properties. The coordination mode of the ligand will be impacted by the structural changes of the groups attached to the hydrazone, enabling flexible coordination modes with transition metal ions and leading to a variety of coordination geometries, including tetrahedral, square planar, octahedral and square pyramidal⁸⁻¹² arrangements. The condensation of aromatic hydrazides with carbonyl compounds results in the formation of aroylhydrazones, which are important class of hydrazones with adaptable ligand systems and having a -C=N-N- functional moiety. In the absence of other donor atoms, aroylhydrazones coordinate to the metal through carbonyl oxygen and amine nitrogen and act as a bidentate ligands¹³. In hydrazones, amido-iminol tautomerism is prominent and plays a significant part in determining the coordination mode of ligand. Specifically, the overall charge on the ligand is defined by amido-iminol tautomerism. In the solid state, hydrazones often take the amido form, but in solution, they tend to exist as an equilibrium mixture of the amido and iminol forms^{14,15}. Hydrazones can combine to the metal centre through either in the neutral amido or in the anionic iminolate forms. These compounds are multidentate chelating

agents with exciting ways of ligation for a wide spectrum of metal ions due to their availability of several possible donor sites and amido-iminol tautomerization⁸. Enolate oxygen, azomethine nitrogen, and the hetero atom located in the carbonyl moiety serve as the potential coordination sites for NNO donor aroylhydrazones. In this study, we discuss the synthesis of a novel aroylhydrazone and its cobalt(II), copper(II) and zinc(II) complexes, which were characterized by various analytical and spectroscopic methods.

Experimental Section

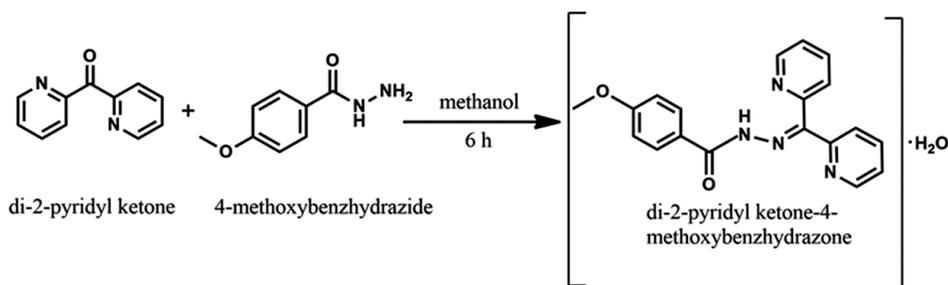
Starting materials

All of the chemicals and solvents used are commercially accessible and were used without further purification. Cobalt(II) chloride hexahydrate (SRL), copper(II) chloride dihydrate (SRL), zinc chloride (SRL), 4-methoxybenzhydrazide (Sigma Aldrich) and di-2-pyridyl ketone (Sigma Aldrich) were used as supplied. The solvent, methanol was obtained from SRL and used directly.

Synthesis of di-2-pyridylketone-4-methoxybenzhydrazone (DKMBH·H₂O)

Di-2-pyridyl ketone (1 mmol, 0.1840 g) dissolved in 10 mL methanol was combined with 4-Methoxybenzhydrazide (1 mmol, 0.1662 g) dissolved in 10 mL of methanol, and the mixture was then refluxed for 6 hours. A few drops of acetic acid have been added to the boiling solution. The resulting solution was light yellowish. After letting the resultant solution sit at room temperature and slowly evaporating, the colourless crystalline product was separated, filtered, and dried. Scheme 1 depicts the synthesis of aroylhydrazone monohydrate (DKMBH·H₂O).

For DKMBH·H₂O: Yield: 74.0% (0.2591 g). Colour: Colourless. Anal. Calc. for C₁₉H₁₈N₄O₃ (M.W.: 350.16 g mol⁻¹) C, 65.13; H, 5.18; N, 15.99%. Found: C, 65.22; H, 5.20; N, 15.38%.



Scheme 1 — Synthesis of di-2-pyridyl ketone-4-methoxybenzhydrazone (DKMBH·H₂O).

Synthesis of metal(II) complexes

Synthesis of [Co(DKMB)Cl] (1)

Methanolic solutions di-2-pyridyl ketone (1 mmol, 0.1840 g) and 4-methoxybenzhydrazide (1 mmol, 0.1662 g) were mixed and refluxed for 6 h. To this, methanolic solution of CoCl₂·6H₂O (0.2379 g, 1 mmol) was added and the resulting brown colored solution was refluxed for further 6 hours. The resulting brown colored product was filtered and dried (Scheme 2).

For [Co(DKMB)Cl] (1): Yield: 72.0% (0.3070 g), Colour: Brown, Anal. Calc. for C₁₉H₁₅N₄O₂CoCl (M.W.: 426.40 g mol⁻¹) C, 53.60; H, 3.55; N, 13.16%. Found: C, 52.84; H, 3.51; N, 13.22%, Λ_M (DMF): 34 ohm⁻¹cm² mol⁻¹.

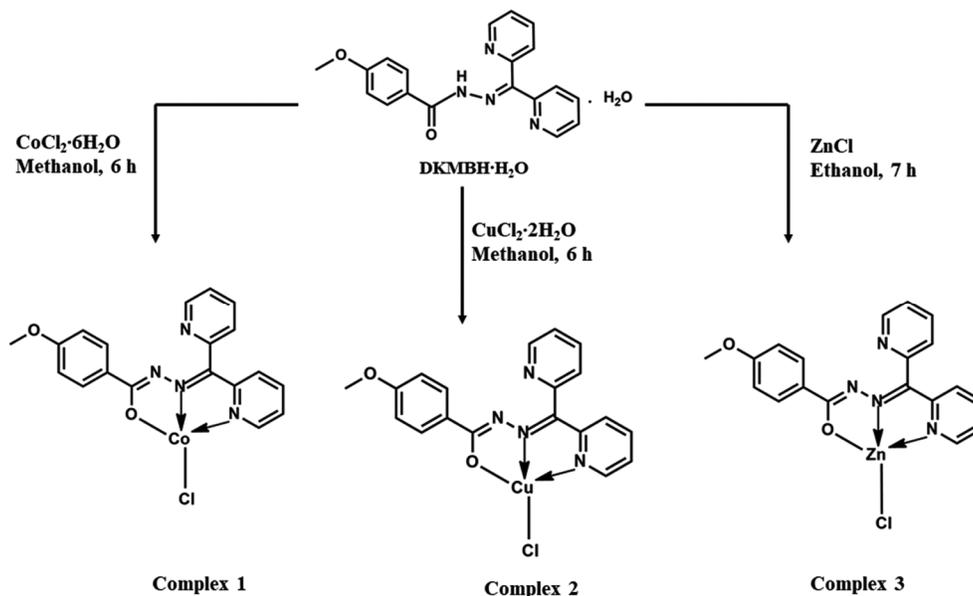
Synthesis of [Cu(DKMB)Cl] (2)

Methanolic solutions of 4-methoxybenzhydrazide (1 mmol, 0.1662 g) and di-2-pyridyl ketone (1 mmol, 0.1840 g) were mixed and refluxed for 6 h. To this, methanolic solution of CuCl₂·2H₂O (0.1704 g, 1 mmol) was added and the resulting green colored solution was refluxed for 6 hours. The resulting green colored product obtained was filtered and dried (Scheme 2).

For [Cu(DKMB)Cl] (2): Yield: 68.0% (0.2930 g), Colour: Green, Anal. Calc. for C₁₉H₁₅N₄O₂CuCl (M.W.: 429.50 g mol⁻¹) C, 53.03; H, 3.51; N, 13.02%. Found: C, 52.97; H, 3.61; N, 12.93%, Λ_M (DMF): 31 ohm⁻¹cm² mol⁻¹.

Synthesis of [Zn(DKMB)Cl] (3)

Methanolic solutions of 4-methoxybenzhydrazide (1 mmol, 0.1662 g) and di-2-pyridyl ketone (1 mmol, 0.1840 g) were mixed and refluxed for 6 hours. To this, methanolic solution of ZnCl₂ (0.1362 g, 1 mmol) was added and the resulting yellow colored solution was refluxed for 6 hours. The yellow colored product obtained was filtered and dried (Scheme 2).



Scheme 2 — Synthesis of complexes 1, 2 and 3.

For [Zn(DKMB)Cl] (**3**): Yield: 61.0% (0.2640 g), Colour: Yellow, Anal. Calc. for $\text{C}_{19}\text{H}_{15}\text{N}_4\text{O}_2\text{ZnCl}$ (M.W.: $432.80 \text{ g mol}^{-1}$) C, 52.80; H, 3.49; N, 12.96%. Found: C, 53.48; H, 3.57; N, 12.33%, Λ_M (DMF): $28 \text{ ohm}^{-1}\text{cm}^2 \text{ mol}^{-1}$.

Physical measurements

Various spectroscopic methods have been used to characterize the synthesized aroylhydrazone and metal complexes. C, H, and N analyses have been performed using the Vario ELCube elemental analyzer. FT-IR spectra of the ligand and complexes were recorded in the range $4000\text{--}400 \text{ cm}^{-1}$ on a Perkin-Elmer Spectrum-II FT-IR Spectrometer by ATR technique. UV-Visible spectra of the compounds were recorded on a Shimadzu UV-2600 UV-Vis spectrometer and measurements were taken in the $200\text{--}800 \text{ nm}$ range. Thermal studies were carried out on a Perkin-Elmer STA 6000 analyzer under nitrogen atmosphere with 2-5 mg of the sample in the temperature range of $35\text{--}950 \text{ }^\circ\text{C}$ with a heating rate of $10^\circ\text{C min}^{-1}$. ^1H NMR spectrum of the aroylhydrazone was recorded using the instrument Brücker Advance 500 MHz using CDCl_3 as solvent. Mass spectra were recorded using the Brücker maXis mass spectrometer using methanol as solvent. The ionization technique used was Electron Spray Ionization (ESI). Time of flight (TOF) analyzer was used for the detection.

Results and Discussion

Di-2-pyridyl ketone-4-methoxybenzhydrazone and its three metal(II) complexes have prepared and

structural properties have been studied by analytical techniques like elemental analysis, molar conductivity measurements, and FT-IR, electronic, NMR, and mass spectra.

The aroylhydrazone and its three metal(II) complexes prepared are soluble in common solvents such as methanol, ethanol, DMF and DMSO. They are stable towards air at room temperature. The chemical composition of the ligand and its complexes are determined using the results acquired from elemental analysis. The molar conductivity measurements are performed in DMF ($1 \times 10^{-3} \text{ M}$) solution and the values are low for all complexes which reveal that these complexes are non-electrolyte in nature¹⁶.

IR spectra

The prominent IR spectral peaks of aroylhydrazone and its metal(II) complexes in the region $4000\text{--}400 \text{ cm}^{-1}$ have been provisionally ascribed and depicted in Fig. 1. At 3450 and 1674 cm^{-1} , strong bands associated with $\nu(\text{N-H})$ and $\nu(\text{C=O})$ are seen, which suggest the presence of the amido form of the aroylhydrazone in solid state¹⁷. Due to the interaction between the amino group of the hydrazide part and keto group of the carbonyl compound, a new band is observed at 1610 cm^{-1} . The additionally formed band corresponds to the azomethine $\nu(\text{C=N})$ bond which confirms the condensation between hydrazide and carbonyl part¹⁸. The O-H stretching vibration of lattice water molecule is observed as overlapped with

N-H stretching vibration. In order to identify the binding tendency of ligand to the metal centre, notable vibrational bands of the aroylhydrazone is correlated with the metal complexes. On complexation, the $\nu(\text{C}=\text{O})$ and (N-H) bands vanished from the complexes, implying that coordination occurred through the enolate form of the ligand, which is formed during the tautomerization. The additional bands at 1400, 1369, and 1362 cm^{-1} in the complexes 1, 2, and 3 are a result of (C-O) stretching. The emergence of new bands suggests that the C=O of the amido group underwent iminolization, resulting in the formation of the $-\text{C}=\text{N}-\text{C}=\text{N}$ moiety¹⁹. The shift of (C=N) band towards lower frequency in all of the complexes provides evidence that azomethine nitrogen is coordinated to the metal center^{20,21}. The iminolization of the aroylhydrazone in these complexes is demonstrated by the elimination of strong bands attributable to $-\text{C}=\text{O}$ stretching vibrations and the formation of new bands in the 1575–1630 cm^{-1} region as a result of asymmetric stretching vibration of the newly formed C–N bond^{22,23}. On the basis of spectral analysis, it is confirmed that DKMBH·ligand is coordinated to the metal *via* iminolite oxygen, azomethine and pyridyl nitrogens in all complexes.

Electronic spectra

The electronic spectral bands of aroylhydrazone and its metal(II) complexes in DMF solution are compiled in Fig. 2. The electronic spectra of DKMBH·H₂O and its complexes exhibited various $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions attributed the carbonyl group, the pyridyl rings of the hydrazone and

azomethine chromophore. For aroylhydrazone, the bands responsible for the $\pi-\pi^*$ and $n-\pi^*$ transitions are observed at 275, 330 and 395 nm^{25,26}. In contrast to the metal free ligand, the complexes featured a broad band in the 400–420 nm range, which may be referred to charge transfer transitions²⁷. In the instance of metal complexes, absorption maximum value of the intraligand bands suffered bathochromic shift; this is apparently due to the conjugation that followed complexation. In addition to intraligand and charge transfer transitions, complexes 1 and 2 displayed *d-d* transitions in the 548–670 nm region. In complex 1, the electronic configuration of Co^{2+} is $(e)^4 (t_2)^3$. ${}^4\text{T}_2(\text{F}) \leftarrow {}^4\text{A}_2$, ${}^4\text{T}_1(\text{F}) \leftarrow {}^4\text{A}_2$ and ${}^4\text{T}_1(\text{P}) \leftarrow {}^4\text{A}_2$ are the three anticipated transitions²⁸. But in practice the Co(II) complex showed only two bands at 592 and 669 nm. The observed bands belonging to ${}^4\text{T}_1(\text{F}) \leftarrow {}^4\text{A}_2$ and ${}^4\text{T}_1(\text{P}) \leftarrow {}^4\text{A}_2$ transitions^{29,30} [Figs 2(a) and 2(b)], however the other transition, which is in the near IR

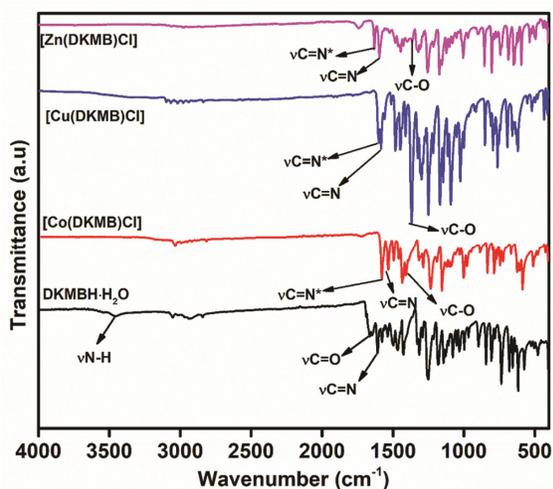


Fig. 1 — FT-IR spectra of DKMBH·H₂O, [Co(DKMB)Cl], [Cu(DKMB)Cl] and [Zn(DKMB)Cl].

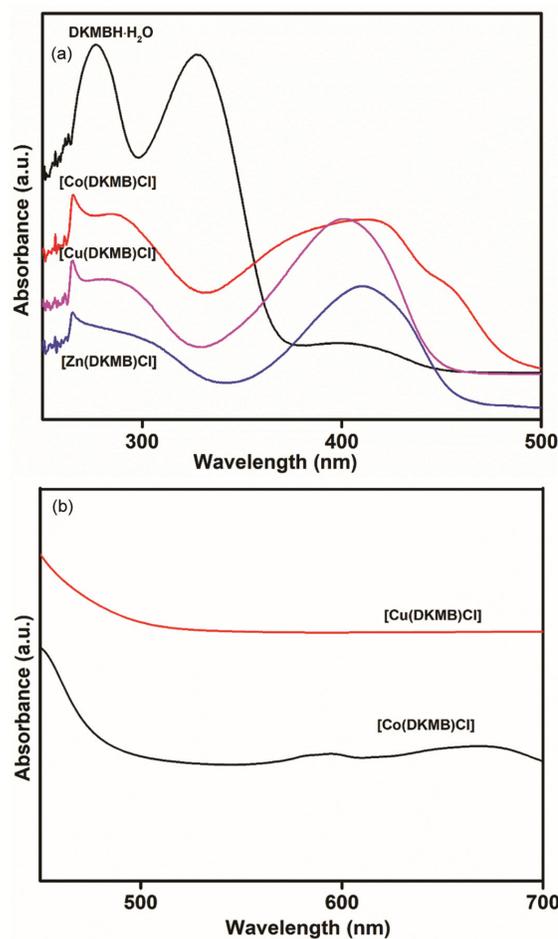


Fig. 2 — (a) Electronic spectra of DKMBH·H₂O, [Co(DKMB)Cl], [Cu(DKMB)Cl], [Zn(DKMB)Cl] and (b) Expanded (500–700 nm) electronic spectra of [Co(DKMB)Cl] and [Cu(DKMB)Cl].

region, is not seen because the spectrophotometer being used cannot detect it. For complex 2, a broad band seen at 647 nm assigned to the *d-d* transition of Cu^{2+} complex. Specific to Cu(II) complexes with d^9 configuration, Jahn-Teller distortion is supposed to occur which further divide the 2E_g and ${}^2T_{2g}$ levels. The splitting of energy levels ultimately resulted in three spin allowed transitions, ${}^2A_{1g} \leftarrow {}^2B_{1g}$, ${}^2B_{2g} \leftarrow {}^2B_{1g}$, ${}^2E_g \leftarrow {}^2B_{1g}$ ²⁸. These theoretical presumptions, however, are generally not seen in practice due to the incredibly small energy difference between the d levels, and these bands typically appear to overlap and are difficult to resolve into discrete bands. The convergence of ${}^2A_{1g} \leftarrow {}^2B_{1g}$, ${}^2B_{2g} \leftarrow {}^2B_{1g}$, ${}^2E_g \leftarrow {}^2B_{1g}$ transition can be attributed to the existence of a broad band in Cu(II) complex. The ligand to metal charge transfer transition occurred between enolate oxygen and Cu(II) ion is accountable for the intense band seen at 405 nm³⁰⁻³³. In addition to intraligand transitions, compound 3 also features a distinctive band at 410 nm that can be associated to metal to ligand charge transfer transition happened between Zn(II) and enolate oxygen³⁴.

Thermal analyses

Thermal studies were performed to evaluate the presence of lattice water and to learn more about the thermal properties of the aroylhydrazone and its metal complexes. Selected TGA curves are presented in Fig. 3. TGA studies were conducted in the temperature range 35-950 °C in nitrogen environment at a heating rate of 10°C/min.

Thermogram of hydrated aroylhydrazone was recorded in the range 35-950 °C. As anticipated, mass loss up to 120°C showed the existence of water. The TGA curve for the ligand demonstrates the first stage of decomposition between 50 and 120 °C, which is accompanied by the loss of one water molecule³³ with 2.90% of the total weight of the complex (calculated. 5.1%). A marginal decomposition was encountered in the temperature range 250-412°C which refers to the partial collapse of ligand. The decomposition continues until the complete collapse of ligand. Thermograms of anhydrous metal complexes were also assessed in the range 35-950°C. As predicted, there was no mass loss up to 280°C, confirming the absence lattice water. All complexes are stable up to 260°C and above which they displayed two stages of decomposition due to the complete collapse of

ligand moiety. And the further decomposition continues until the metallic residue was formed.

¹H NMR spectra

The ¹H NMR spectrum of the prepared aroylhydrazone was acquired on Brücker Advance 500 MHz instrument. CDCl_3 served as solvent and TMS served as the internal standard. Proton NMR spectra generally offers the insights regarding various type of hydrogen atoms present in the organic compound and the arrangement. The ¹H NMR spectrum of the aroylhydrazone, DKMBH·H₂O is represented in the Fig. 4.

Aromatic protons are identified as multiplets in the region 7.2-8.0 ppm. Methoxy proton is responsible for the sharp singlet observed at 3.820 ppm. Two identical protons near to the ring nitrogen are found to be the source of two doublets seen at 8.7 and 8.5 ppm. An iminolic analog of the aroylhydrazone is accountable for a singlet in the downfield zone with a chemical shift value of 15.33 ppm³⁵.

Mass spectra analysis

The formation of aroylhydrazone (DKMBH·H₂O) and metal(II) complexes are further confirmed from mass spectrometry analysis. The mass spectra of synthesized aroylhydrazone, DKMBH·H₂O and its complexes were recorded using electron spray ionization technique. The mass spectra of the ligand and its metal complexes are displayed in the Fig. 5 (a, b, c and d). The (M+1) peak at *m/z* 351 confirms the expected aroylhydrazone. And also contains the fragmentation peak at *m/z* 333 by losing

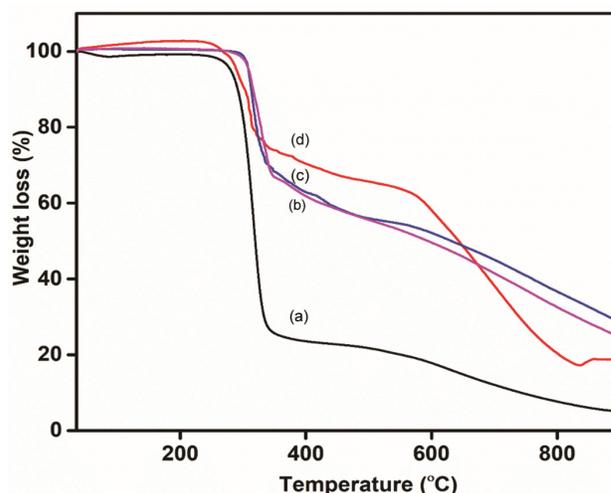
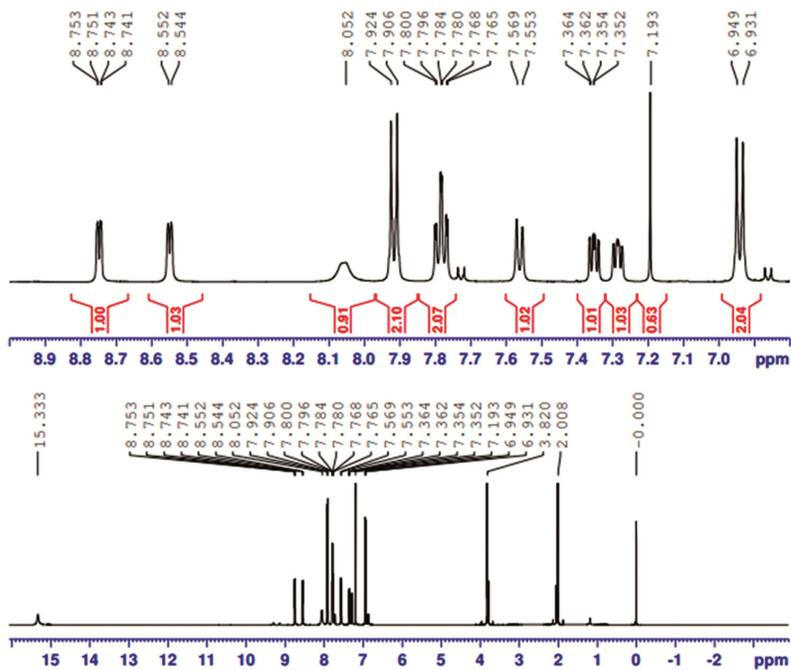
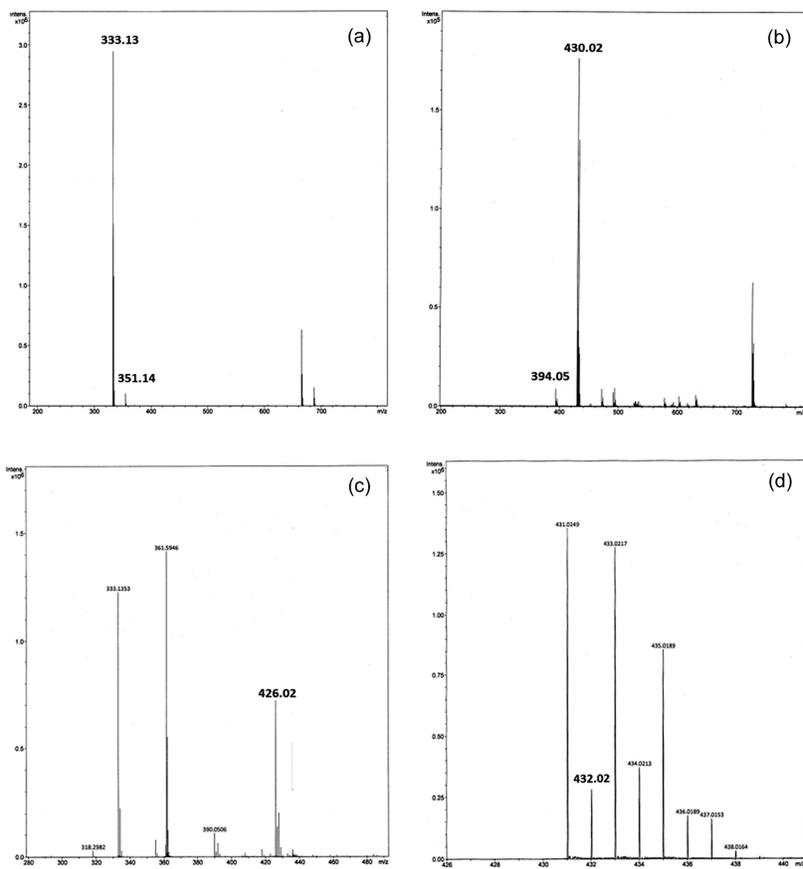


Fig. 3 — TG profile of (a) DKMBH·H₂O; (b) [Zn(DKMB)Cl], (c) [Cu(DKMB)Cl] and (d) [Co(DKMB)Cl].

Fig. 4 — ^1H NMR spectrum of DKMBH·H₂O.Fig. 5 — Mass spectra of (a) DKMBH·H₂O; (b) [Cu(DKMB)Cl]; (c) [Co(DKMB)Cl] and (d) [Zn(DKMB)Cl].

water molecule. The mass spectrum of Cu(II) complex 2 showed a distinct peak at m/z 430.02 ($M+1$) which coincides with the molecular weight of proposed structure, (Mw: 429.50 g/mol). The complex 2 also displayed a fragmentation peak at m/z 394.04 corresponds to $C_{19}H_{15}N_4O_2Cu$ by losing one chlorine atom. The mass spectrum of Co(II) complex 1 shows a peak at m/z 426.02 (M^+) which exactly agree with molecular weight predicted from analytical data, (Mw: 426.40 g/mol). The Zn(II) complex 3 exhibit peak at m/z 432 (M^+) matches with the anticipated molecular weight, (Mw: 432.80 g/mol). The mass spectra of the aroylhydrazone and its metal complex further provide the confirmation for the formation of the compounds.

Conclusion

In the present paper, the synthesis and systematic characterization of a new aroylhydrazone ligand, di-2-pyridyl ketone-4-methoxybenzhydrazone, and three of its cobalt(II) (1), copper(II) (2) and zinc(II) (3) complexes have been carried out. The synthesized complexes have been characterized by various analytical and spectroscopic methods such as; elemental analysis, molar conductivity measurements, thermal analysis, IR, UV-Vis spectroscopy, NMR, and mass spectrometry. Aroylhydrazone, $C_{19}H_{18}N_4O_3$ present in an amido form, which is apparent from IR spectral data. Based on spectral analysis, it is confirmed that the aroylhydrazone ligand is coordinated to the metal via iminolate oxygen, azomethine and pyridyl nitrogens in all complexes. The electronic spectra of metal complexes exhibit a bathochromic shift in the maximum absorption value of the intraligand bands, which is apparently due to the conjugation that followed complexation. In addition to intraligand and charge transfer transitions, complexes displayed d-d transitions. Furthermore, it fortifies the complexation. The thermal analysis clearly figured out the existence of water in aroylhydrazone and the absence of lattice water among all complexes. The iminolic analogue of aroylhydrazone is supported by a singlet observed in the downfield zone of 1H NMR spectrum. Moreover, the mass spectra of the aroylhydrazone and its metal complex further confirm the formation of the compounds. The aroylhydrazone and its three metal complexes showed distinct peaks which coincide with the molecular weight predicted from analytical data. The analytical and spectral studies help us to conclude that all complexes are monomeric in nature. In all

complexes, aroylhydrazone binds to the metal centre in a tricoordinate deprotonated form.

Acknowledgement

Nishana L. K. is grateful to the Central University of Kerala for the fellowship and Lab facilities.

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