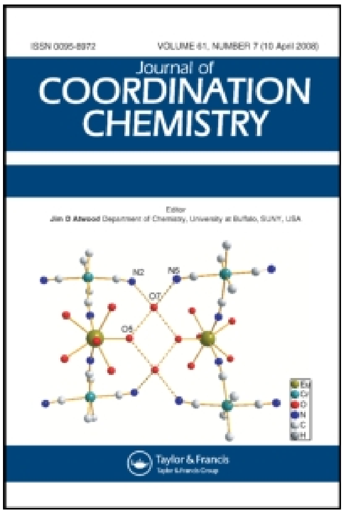

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Synthesis and spectral characterization of Cu(II) complexes of some thio-Schiff bases of acyl pyrazolone analogues

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Synthesis and spectral characterization of Cu(II) complexes of some thio-Schiff bases of acyl pyrazolone analogues

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A series of tridentate pyrazolone-based thio-Schiff bases were synthesized by the interaction of 4-acyl/aroyl pyrazolones with thiosemicarbazide in an ethanolic medium. All of these ligands were characterized on the basis of elemental analysis, infrared (IR), ^{1}H- and ^{13}C-NMR data. Nuclear magnetic resonance (NMR) suggests the amine-one form of ligand in solution at room temperature. Copper Schiff-base complexes, [Cu(L)(H_2O)], have been prepared by the interaction of the aqueous solution of copper sulfate pentahydrate with hot ethanolic solution of the appropriate ligand. The resulting complexes have been characterized by elemental analysis, metal content determination, molar conductance, fast atom bombardment mass spectra, magnetic measurements, thermogravimetric analysis (TGA), IR, and electronic spectral studies. Thermal stability, heat capacity, and activation energy of thermal degradation for these complexes were determined by TGA, differential thermal analysis, and differential scanning calorimetry. Suitable structures are proposed for these complexes.

Keywords: Acyl pyrazolone; Copper complexes; Thio-Schiff base; Thiosemicarbazone

1. Introduction

The interest in sulfur donor chelating agents has grown very rapidly. Most of the early investigations on these systems were centered on their use as analytical reagents. Interest in complexes of these ligands now covers a full gamut of areas ranging from general metal–sulfur bonding and electron delocalization in transition metal complexes to potential biological activity and practical application in fields as diverse as rubber technology and agriculture. Complexes of transition metals containing ligands with N, S or N, S, and O donors are known to exhibit interesting stereochemical, electrochemical, and electronic properties [1, 2]. Derivatives of semicarbazones and thiosemicarbazones are among the most widely studied nitrogen and oxygen/sulfur donors [3, 4]. Particularly, thiosemicarbazones have emerged as an important class of sulfur ligand for transition metal ions. The real impetus toward developing their coordination chemistry was their physicochemical properties and significant biological activities [5, 6]. Compounds containing a thiosemicarbazone component have shown broad spectrum chemotherapeutic properties, including antimalarial [7],

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antitumor [8], antibacterial [9], antitrypanosomal [10], and antiviral [11] activities. Thiosemicarbazones and their metal complexes have attracted attention because of their wide ranging biological activities, analytical applications, specific structures, and chemical properties [12–27]. Thiosemicarbazones usually react as chelating ligands by bonding through the sulfur and the hydrazinic nitrogen through ligand deprotonation. Metal complexes of first and second raw transition elements are of interest of many researchers [28, 29], especially those involving $[MoO]^{+2}$ or $[MoOS]^{+2}$ core are studied to mimic xanthine oxidase [30, 31].

The coordination behavior of Schiff bases of acyl pyrazolones is of interest of many researchers including us [32–35]. However, there are scanty reports on thio-Schiff bases of this class of ligands, especially thiosemicarbazones which are potentially tridentate ligands having NSO donors. Moreover, the interesting pharmacological properties of the thio-Schiff bases are believed to be due to the presence of sulfur. We have synthesized and characterized the thio-Schiff-base ligands of acyl pyrazolones and mononuclear Cu(II) complexes $[CuL(H_2O)]$.

2. Experimental

2.1. *Materials*

All the chemicals used in this study were of the best quality. Pyrazolones (3-methyl-1-(3′-chloro phenyl)-2-pyrazolin-5-one and 3-methyl-1-(4′-methyl phenyl)-2-pyrazolin-5-one) were gifted from Nutan Dye Chem Pvt. Ltd., Sachin, Surat, and used after crystallization from alcohol. 1,4-Dioxane was obtained from Sisco Chem Pvt. Ltd., Mumbai, and used as supplied. Thiosemicarbazide obtained from Loba Chemie Pvt. Ltd., Mumbai, was used without purification. Absolute ethanol was obtained from Baroda Chemical Industries Ltd., Baroda. Calcium hydroxide and acetyl chloride were supplied by Suvidhinath Laboratories, Baroda. Benzoyl chloride was obtained from Gayatri Minerals & Chemicals, Baroda. Sodium acetate was obtained from Qualigens Fine Chemicals, Mumbai. Copper(II) sulfate was supplied by Suvidhinath Laboratories, Baroda. The solvents used in this study were purified by the following standard procedures.

2.2. *Instruments*

Elemental analyses (C, H, and N) were performed on a model 2400 Perkin Elmer elemental analyzer. Infrared (IR) spectra were recorded on a Perkin Elmer Fourier transform IR (FT-IR) spectrum RX 1 spectrometer as KBr pellets. Nuclear magnetic resonance (NMR) spectra were recorded on an AVANCE-II-500 Bruker FT-NMR instrument at Central Salt & Marine Chemicals Research Institute (CSMCRI), Bhavnagar, Gujarat, India. Electronic spectra were recorded on a Perkin Elmer Lambda 35 UV-Vis spectrometer. Specific conductivities of the complexes were measured on an Elico CM 180 conductivity meter. Room temperature magnetic susceptibilities were measured by a Gouy balance using Hg(II) tetrathiocyanato cobaltate(II) as a calibrant. Diamagnetic corrections were estimated from Pascal tables. Fast atom bombardment (FAB) mass spectra were recorded on a JEOL SX

102/DA-6000 at room temperature using *m*-nitro benzyl alcohol as a matrix. A simultaneous TG/DTA (thermogravimetry/differential thermal analysis) was carried out on a SII EXSTAR6000 TG/DTA 6300. The experiments were performed in N_2 at a heating rate of 10°C min^{-1} in the temperature range 25–560°C using an Al_2O_3 crucible. The sample sizes ranged in mass from 4.5 to 10 mg. The differential scanning calorimetry (DSC) was recorded using DSC 2920, TA Instrument, USA. The DSC curves were obtained at a heating rate of 5°C min^{-1} in N_2 over the temperature range of 25–400°C using an aluminum crucible.

2.3. *Synthesis of ligands*

2.3.1. Preparation of 4-acetyl-3-methyl-1-(3′-chloro phenyl)-2-pyrazolin-5-one. 3-Methyl-1-(3′-chloro phenyl)-2-pyrazolin-5-one (AMC) (20.85 g, 0.1 mol) was dissolved in a hot dioxane (80 cm^3) in a flask equipped with a stirrer, separating funnel, and reflux condenser. Calcium hydroxide (14.81 g, 0.2 mol) was added to this solution, followed by acetyl chloride (10 mL) added dropwise with caution, as this reaction was exothermic. During this addition, the whole mixture was converted into a thick paste. After complete addition, the reaction mixture was refluxed for 2 h, and then poured into a cold dilute hydrochloric acid (200 cm^3, 2 mol). Thus, the colored crystals obtained were separated by filtration, washed with acidified water, and dried [35, 36]. Yield 74.92%, m.p. 72°C.

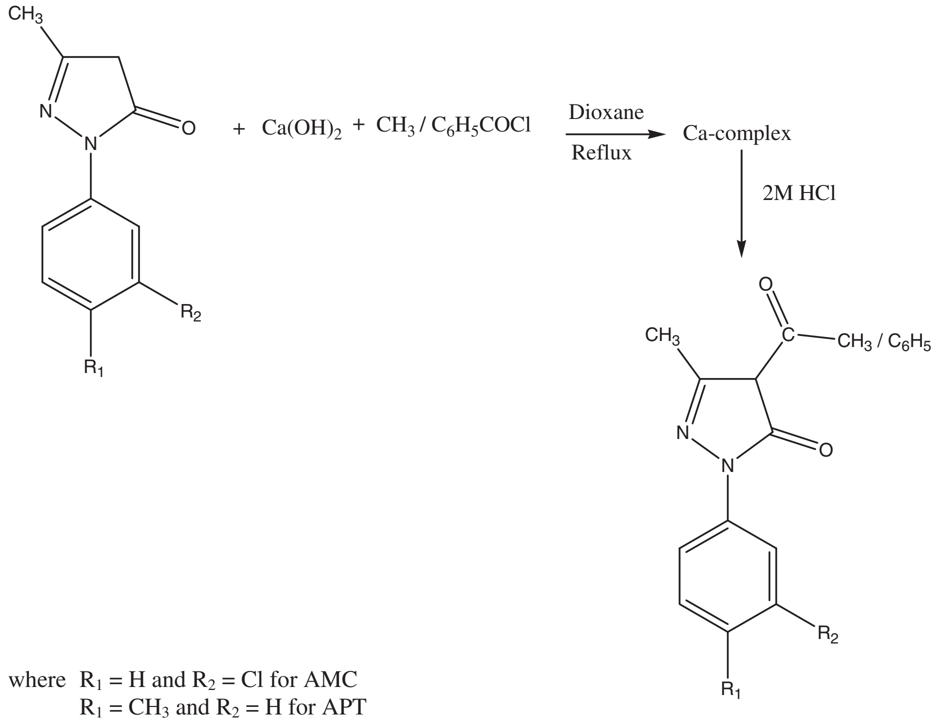
2.3.2. Preparation of 4-acetyl-3-methyl-1-(4′-methyl phenyl)-2-pyrazolin-5-one. 4-Acetyl-3-methyl-1-(4′-methyl phenyl)-2-pyrazolin-5-one (APT) was prepared analogously from 3-methyl-1-(4′-methyl phenyl)-2-pyrazolin-5-one (20.1 g, 0.1 mol) and yellow crystals were obtained. Yield 75.19%, m.p. 91°C.

2.3.3. Preparation of 4-benzoyl-3-methyl-1-(4′-methyl phenyl)-2-pyrazolin-5-one. 4-Benzoyl-3-methyl-1-(4′-methyl phenyl)-2-pyrazolin-5-one (BPT) was prepared analogously from 3-methyl-1-(4′-methyl phenyl)-2-pyrazolin-5-one (20.1 g, 0.1 mol) and instead of acetyl chloride, benzoyl chloride (10 mL) was used; yellow crystals were obtained. Yield 75.99%, m.p. 106°C. The synthesis of these compounds is summarized in scheme 1.

2.3.4. Preparation of thiosemicarbazones (AMC-TS, APT-TS, and BPT-TS). An identical procedure was used in the preparation of all the thiosemicarbazones (scheme 2). The thiosemicarabazones were prepared by refluxing 1 : 1 mole ratio of 4-acetyl/benzoyl-2-pyrazolin-5-one and thiosemicarbazide in ethanol for 2 h. The thiosemicarbazones thus obtained were filtered and dried [37].

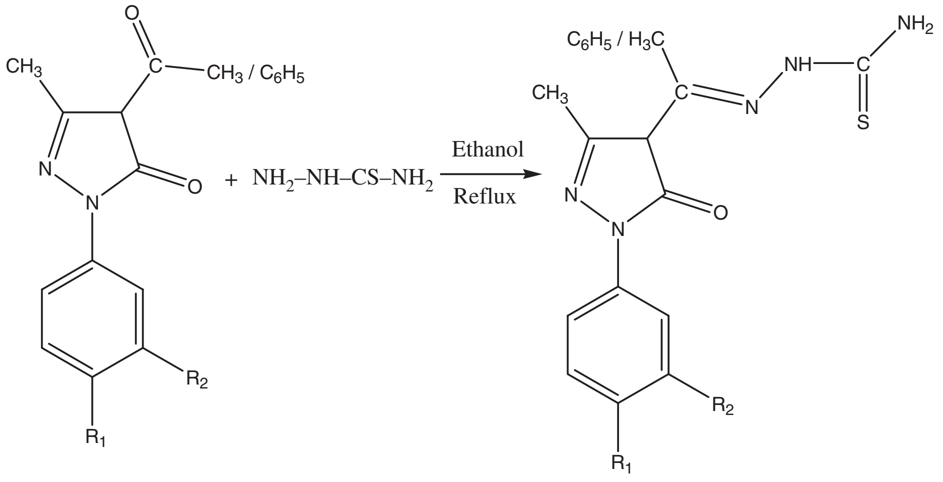
The physical properties are given in table 1. All the data were in good agreement with the proposed structure.

2.3.5. Preparation of Cu(II) complexes. The following general procedure was used in the synthesis of copper complexes (scheme 3). Copper sulfate pentahydrate was dissolved in minimum hot ethanol. The hot ethanolic ligand solution in slight excess over the metal was added dropwise with constant stirring. To the resultant mixture,



where $R_1 = H$ and $R_2 = Cl$ for AMC
$R_1 = CH_3$ and $R_2 = H$ for APT

Scheme 1. Preparation of acetyl/benzoyl pyrazolones. $R_1 = H$ and $R_2 = Cl$ for AMC; $R_1 = CH_3$ and $R_2 = H$ for APT.



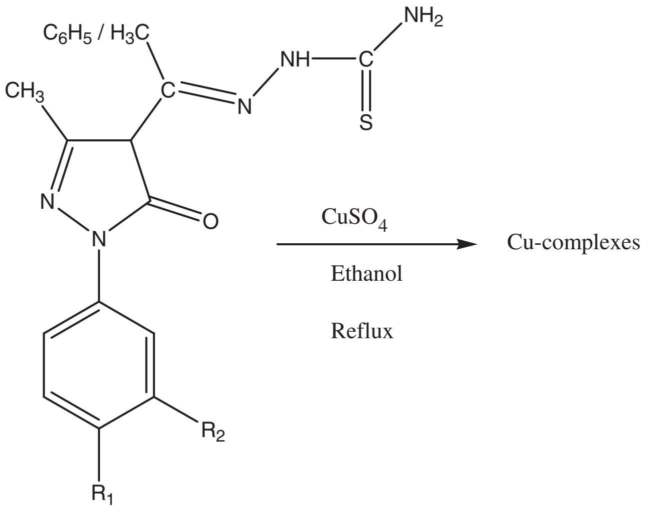
where $R_1 = H$ and $R_2 = Cl$ for AMC-TS
$R_1 = CH_3$ and $R_2 = H$ for APT-TS and BPT-TS

Scheme 2. Preparation of ligands. R1 = H and R2 = Cl for AMC-TS; R1 = CH3 and R2 = H for APT-TS and BPT-TS.

Table 1. Melting point, elemental analysis (C, H, and N) and yield of the ligands.

		Elemental analysis (%)[a]			
Ligands	m.p. (°C)	Carbon	Hydrogen	Nitrogen	Yield (%)
AMC-TS	200	48.20 (48.22)	4.30 (4.98)	21.30 (21.62)	74.92
APT-TS	205	55.05 (55.42)	5.49 (5.64)	22.80 (23.08)	75.19
BPT-TS	214	62.79 (62.44)	5.19 (5.24)	18.26 (19.16)	75.99

[a] Calculated values are given in parentheses.



Scheme 3. Preparation of Cu(II) complexes.

2 g of sodium acetate was added and the mixture was refluxed for 1 h. The resulting solution was then concentrated to half of its original volume and cooled. The product obtained was filtered and washed several times with hot water and finally with ethanol and dried at 45°C. The yields of the complexes were almost quantitative. The physical properties of complexes are depicted in table 2.

3. Results and discussion

3.1. *Characterization of the ligands*

3.1.1. IR spectra. The important absorption frequencies for the ligands are listed in table 3. All show a sharp band at $\sim$1590 cm^{-1} due to ν(C=N) coordinated + ν(C=O). There is some contribution from aromatic vibrations and also azomethine ν(C=N) at $\sim$1620 cm^{-1}. The ligands show a band at $\sim$3300 cm^{-1} due to ν(N–H). The band for ν(N–N) is observed at $\sim$950 cm^{-1} [38].

The ligands show very complicated spectra, especially in the 1500–1650 cm^{-1} region from the presence of C=O, –NH$_2$, and more than one C=N. Therefore, the correct

Table 2. Analytical data and physical properties of complexes.

Complexes	Color	Yield (%)	m.p. (°C)	M^a(%)	Molar conductance, Λ_M	Effective magnetic moments, μ_{eff} (B.M.)
[Cu(AMC-TS) · (H_2O)]	Green	86.61	< 250	15.25 (15.75)	24.0	1.71
[Cu(APT-TS) · (H_2O)]	Green gold	72.27	248	15.88 (16.55)	12.0	1.72
[Cu(BPT-TS) · (H_2O)]H_2O	Garland	47.71	242	14.61 (14.27)	4.0	1.68

^{a}Calculated values are given in parentheses.

Table 3. Important IR frequencies (cm^{-1}) of ligands.

Ligands	ν(N–H)	ν(C=N) coordinated + ν(C=O)	ν(C=N) azomethine	ν(C=S)		ν(C=S) + δ(NH) + $\xi(NH_2)$	ν(N–N)
AMC-TS	3305 (w, s)	1587	1616	766 (s, s)	464 (w, s)	1286 (s, s)	965
APT-TS	3314 (w, s)	1581	1613	767 (s, s)	475 (w, s)	1285 (s, s)	952
BPT-TS	3306 (w, s)	1570	1620	758 (s, s)	471 (w, s)	1283 (s, s)	932

assignments to the observed bands in this region are difficult; tentative assignments based on the previous work are given in table 3.

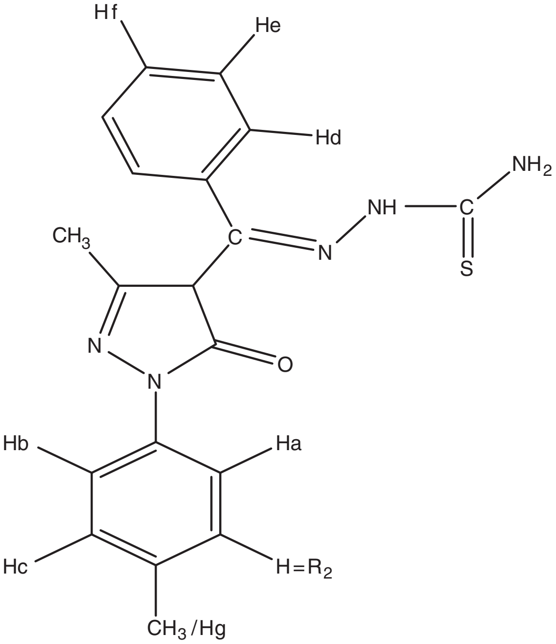
C=S having proton adjacent is relatively unstable and tends to change to a stable C–S by enethiolization [39]. The IR spectra of ligands show intense bands at ~760 cm^{-1} and a weak band at ~470 cm^{-1}, assigned to C–S stretching vibrations (table 3). A strong band at ~1280 cm^{-1} due to a coupled vibration of $\nu(C{=}S) + \delta NH + \delta NH_2$ is also observed in the IR spectra.

3.1.2. ^{1}H-NMR spectra. ^{1}H-NMR spectra of ligands 1–3 are summarized in "Supplementary material." The signal due to methyl protons appeared as a singlet in the range of δ 2.0–2.3 ppm. In some cases signals of CH_3 groups overlapped and it is difficult to assign each signal to a particular methyl, and no attempt has been made for such assignment [35].

A singlet corresponding to one proton for all such ligands is observed at δ 10.04–10.08 ppm and disappears on deuterium exchange assigned to thiol group (–SH). However, when ligand exists in –NH–CS– form, this signal may be assigned to –NH. A downfield signal corresponding to one proton for all ligands is observed at δ 12.04–12.12 ppm and also disappeared when a D_2O exchange experiment was carried out. It can be assigned either to –OH or –NH, strongly deshielded because of hydrogen bonding with the other atom (N/O). Integration of this signal matches with one proton, which suggests that only one tautomeric form of the ligands exists in solution [40].

For the convenience of identification, the protons in the ligands are assigned as follows (scheme 4).

3.1.3. ^{13}C-NMR spectra. In ^{13}C-NMR spectra of APT-TS ligand, the carbons of methyl appear at δ 14.41–20.52 ppm. Carbons of benzene rings are present at δ 129.21–132.97 ppm. A total of 11 signals were observed, as expected for *p*-substituted



Scheme 4. Proton numbering scheme for interpretation of NMR.

benzene ring of pyrazolone. One signal was observed around δ 40.0 ppm, which was associated with the carbon of the heterocyclic ring. The most deshielded signal (δ 164.43) can be assigned to C=S and the next signal (δ 147.34) to C=O of the heterocyclic ring. The singlet at δ 118.10–136.64 ppm is assigned to the carbon of C–N, upfield due to the electron-donating methyl attached to it [35].

3.1.4. Mass spectra. The direct analysis in real time mass spectrometry (DART–MS) of APT-TS (figure S1 in Supplementary material) was recorded on a JEOL-AccuTOF JMS-T100LC mass spectrometer having DART source. Dry helium was used for ionization at 350°C. The molecular ion peak at $m/z = 304.15$ matches well the calculated value of 303.28.

3.2. *Characterization of Cu(II) complexes*

Cu(II) complexes of all five ligands were synthesized by the reaction of $CuSO_4$ and the respective ligands in ethanol. Molar conductivities show Λ_M values (table 2) lower than those expected for 1 : 1 electrolytes, confirming the non-electrolytic nature of complexes [41]. Magnetic moment measurements of the complexes show μ_{eff} of ~1.70 (table 2), which corresponds to one unpaired electron and is expected from mononuclear Cu(II) complexes (d^9) with some orbital contribution. The metal and C, H, and N analyses of these complexes (table 2) suggest a molecular formula $[Cu(L)(H_2O)]$, where L = deprotonated form of the respective ligand.

Table 4. Important IR frequencies (cm^{-1}) of metal complexes.

Complexes	ν(O–H)	ν(C=N) coordinated + ν(C=O)	ν(C=N) cyclic	ν(M–N)	ν(M–S)	ν(C=N) azomethine
[Cu(AMC-TS) · (H_2O)]	3444 (m, br)	1574 (s, br)	1596 (m, s)	513 (w, br)	494 (w, s)	1625 (w, s)
[Cu(APT-TS) · (H_2O)]	3445 (m, br)	1572 (s, br)	1596 (m, s)	514 (w, br)	492 (w, s)	1624 (w, s)
[Cu(BPT-TS) · (H_2O)]H_2O	3441 (m, br)	1566 (s, br)	1598 (m, s)	513 (w, br)	490 (w, s)	1624 (w, s)

Table 5. Electronic spectral data of complexes.

Complexes	d–d maxima (nm)	d–d maxima (cm^{-1})	ε (molar absorptivity)
[Cu(AMC-TS) · (H_2O)]	557.04	17952	192
[Cu(APT-TS) · (H_2O)]	571.09	17510	218
[Cu(BPT-TS) · (H_2O)]H_2O	577.02	17330	318

3.2.1. IR spectra. Spectra of the metal complexes (table 4) indicate that the ligands are tridentate, coordinating through the nitrogen of azomethine group, sulfur of mercapto, and oxygen of enol.

Bands at ~760 and ~470 cm^{-1} in spectra of the ligands, mainly due to C=S stretch, disappear on complexation. During complexation, C=S is converted into $C–S^-$. The ligand band at ~1280 cm^{-1} also disappears due to the change of $^1N–C–N^2$ to $^1N–C=N^2$. From the spectral and analytical data, the ligands are doubly charged tridentate by losing the protons from mercapto and hydroxyl.

3.2.2. Electronic spectral analysis. Electronic spectra of all the complexes were recorded in dimethylformamide (DMF), and the data are presented in table 5. For square planer Cu(II), the expected transitions are $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_g$ with respective absorptions at 505–520 and 665–650 nm. Due to Jahn–Teller (J-T) distortions, square planar Cu(II) complexes give a broad absorption between 600 and 700 nm and the peak at 505–520 nm merges with the broad band [42], and thus only one broad band is observed. All the complexes under this study exhibit a broad band in the region of 550–600 nm.

3.2.3. FAB mass spectra. Mass spectra were obtained at electron beam energy of 70 eV. The simplest event that occurs is the removal of a single electron from the molecule in gas phase by an electron of the electron beam to form a molecular ion, a radical cation (M^+). A special reference of exact masses of isotopes was taken. The FAB mass spectrum (figure S2 in Supplementary material) of [Cu(APT-TS) · (H_2O)] was recorded in *m*-nitro benzyl alcohol as a matrix. The parent ion peak can be observed at $m/z = 365$ with relative abundance 100% (table 6). This is formed by the complex, and in the place of water molecule a proton is associated. So the parent ion is $[Cu\text{-}APT\text{-}TS]^+$. A peak corresponding to ligand, $C_{14}H_{21}N_5OS$ appears at $m/z = 307$ with 51% relative abundance. Peaks at $m/z = 365$, 366, 307, and 277 with relative abundance 100%, 89%, 51%, and 63%, respectively, strongly indicate the formation of [Cu-APT-TS]. The peaks corresponding to the *m*-nitro benzyl alcohol and the associated products

Table 6. Mass spectral fragmentation of [Cu(APT-TS) · (H_2O)].

m/z (relative abundance)	Molecular formula of the fragment
365 (100%)	$[C_{14}H_{19}N_5OSCu]^+$
366 (89%)	$[C_{14}H_{20}N_5OSCu]^+$
307 (51%)	$[C_{14}H_{21}N_5OS]^+$
277 (63%)	$[C_7H_{12}N_5OSCu]^+$

Table 7. Thermoanalytical results (TG, DTG, DTA) of Cu(II) complexes.

Complexes	TG range (°C)	DTG_{max} (°C)	Peak temp. in DTA (°C)	Mass loss estimation (Calcd %)*	Assignment
[Cu(AMC-TS) · (H_2O)]	50–121 209–500	78 245	79(−) 245(−)	4.44 (4.93) 77.72 (78.26) 17.22 (16.81)	Loss of one coordinated H_2O Loss of ligand molecule Leaving CuO residue
[Cu(APT-TS) · (H_2O)]	40–210 220–550	224 360	227(−) 290(−)	4.03 (4.90) 81.66 (82.68) 12.89 (12.42)	Loss of one coordinated H_2O Loss of ligand molecule Leaving CuO residue
[Cu(BPT-TS) · (H_2O)]H_2O	40–220 255–525	100 260	52(+) and 155(−), 265(−)	6.75 (7.70) 77.0 (78.25) 13.86 (14.05)	Loss of one coordinated and one hydrated H_2O Loss of ligand molecule Leaving CuO residue

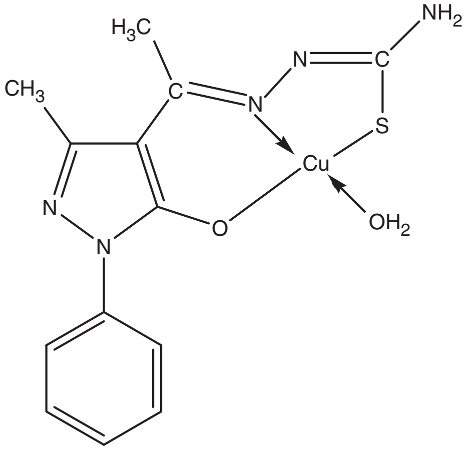
DTG, derivative thermogravimetry; (−) exothermic; (+) endothermic; (*) total mass loss.

are observed at $m/z = 136$, 137, 154, and 289 with high relative abundance. The natural abundances of ^{63}Cu and ^{65}Cu are 69.1% and 30.9%, respectively. Therefore, mass spectral peaks of copper complexes and fragment ions having at least one copper atom must exhibit isotope distribution pattern in the abundance ratio 2 : 1 [43]. All the mass spectral peaks of the complexes in this study exhibit isotope distribution patterns arising from the molecular/fragment ions containing copper (figure S2 in Supplementary material). In addition to the molecular ion peak at 366, peaks at $m/z = 428$, 483, 522, etc., are due to the combination of molecular ion with other fragments of copper and/or matrix and their fragments. The peak at $m/z = 428$ is due to $[M + Cu]^+$, also showing isotopic pattern due to the presence of copper ion, while $m/z = 522$ peak in the FAB mass spectra of the [Cu(APT-TS) · (H_2O)] is due to the combination of molecular ion with matrix, i.e., *m*-nitro benzyl alcohol.

3.3. *Thermal studies*

The thermoanalytical results of Cu(II) complexes summarized in table 7 are in good agreement with the proposed structures. The following stability order of complexes is observed:

$$[\mathrm{Cu(BPT-TS)\cdot(H_2O)]H_2O} > [\mathrm{Cu(APT-TS)\cdot(H_2O)}] > [\mathrm{Cu(AMC-TS)\cdot(H_2O)}]$$



Scheme 5. Structure of the metal complexes.

All the complexes contain coordinated water, in addition to that [Cu(BPT-TS)$\cdot$(H_2O)]H_2O contain one hydrated water. The Cu(II) complexes decomposed in several steps are summarized in table 7. The final product of the thermal decomposition CuO was determined by the elemental analysis.

4. Conclusion

This study provides a general way of synthesizing mononuclear [CuL]H_2O and [CuL(H_2O)]H_2O complexes (where L is the dianion of the ONS donor Schiff base) which can undergo reversible and facile transformations because of the combined presence of hard (O and N) and soft (S) donors in the Schiff base skeleton. Binegative Schiff bases satisfy the 2+ charge of the metal leading to the formation of uncharged complexes which are stable and easy to isolate from the reaction medium. Interaction of $CuSO_4\cdot 5H_2O$ with AMC-TS, APT-TS, or BPT-TS resulted in the formation of complexes with square planar stereochemistry: Schiff base nitrogen, enolic oxygen, and sulfur coordinate Cu(II). One coordinated water is present in all the complexes. Spectroscopic data confirm the proposed structure. From thermal study, [Cu(BPT-TS)$\cdot$(H_2O)]H_2O is more stable due to the 4-benzoyl stable resonance structure [44]. From all the structural characterizations, structure provided in scheme 5 has been proposed for metal complexes

Supplementary material

Thermodynamic data of the thermal decomposition of Cu(II) complexes, TGA, DTA, and DSC curves along with discussion and mass spectra of one ligand (APT-TS) and its

Cu(II) complexes is available as a supplementary material in the online version of this article.

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