

Synthesis and characterization of some monofunctional bidentate Schiff bases derived from cinnamaldehyde and β -triazoles, and their Co(II), Ni(II), Cu(II) and Zn(II) complexes

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MS received 30 June 1997; revised 27 March 1998

Abstract. A new series of complexes of Co(II), Ni(II), Cu(II) and Zn(II) with Schiff bases derived from the condensation of cinnamaldehyde with 4-amino-5-mercapto- β -triazole and 4-amino-5-mercapto-3-methyl- β -triazole have been synthesized. The complexes are characterized by elemental analyses, ¹H NMR, IR, electronic spectra and magnetic susceptibility measurements. The spectroscopic studies reveal that Schiff base acts as bidentate ligand with N, S donor set. Thermal studies of the complexes are also reported.

Keywords. Metal complexes; Schiff base complexes; bidentate ligands.

1. Introduction

Schiff bases are an important class of ligands in coordination chemistry and find extensive applications in different spheres¹⁻⁵. As compared to metal complexes of Schiff bases derived from salicylaldehyde or 2-hydroxy-1-naphthaldehyde and β -triazoles, complexes of cinnamalideneamino- β -triazoles have received very little attention. In view of this, it was considered of interest to synthesize and characterize their Co(II), Ni(II), Cu(II) and Zn(II) complexes. Due to insolubility in common organic solvents and infusibility at higher temperature, complexes are considered to be polymeric in nature.

2. Experimental

All the chemicals and solvents used were of Analar grade. Cinnamaldehyde was obtained from Sisco-Chem Industries. Metal acetates were purchased from Albright and Wilson (Mfg) Ltd., England. Metal contents were estimated using standard methods⁶.

2.1 Preparation of ligands

4-Amino-5-mercapto- β -triazole and 4-amino-5-mercapto-3-methyl- β -triazole were prepared by a known method⁷.

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2.2 Synthesis of Schiff bases

4-Cinnamalideneamino-5-mercapto-*s*-triazole (CMT) and 4-cinnamalideneamino-5-mercapto-3-methyl-*s*-triazole (CMMT) were synthesized by the condensation of cinnamaldehyde with 4-amino-5-mercapto-*s*-triazole and 4-amino-5-mercapto-3-methyl-*s*-triazole, respectively, using ethanol (40ml) as solvent. The reaction mixtures were refluxed for 3-5 h. On cooling the reaction mixture, light yellow small crystals started separating out. The product was then filtered. It was washed with ethanol and ether. The ligand was dried on a water bath.

2.3 Preparation of metal complexes

Warm aqueous ethanolic solution of the metal acetate was treated with ethanolic solution of the Schiff bases in 1:1 and 1:2 molar ratios, which resulted in immediate precipitate formation which was allowed to settle. It was washed with distilled water, ethanol and ether, and finally dried under vacuum. The yield of the complexes varied from 70–80%. The complexes obtained were solid and non-hygroscopic. Their purity was checked by TLC. The analytical data (table 1) indicated general formulae (MLOAc). $n\text{H}_2\text{O}$ and $\text{ML}_2 \cdot n\text{H}_2\text{O}$ in 1:1 and 1:2 molar ratios, respectively (OAc = CH_3COO^- , $n = 1$ for Cu(II), $n = 3$ for Co(II), Ni(II) and Zn(II) in 1:1 ratio and $n = 2$ for Co(II), Ni(II) and Zn(II) in 1:2 ratio). With Cu(II) in 1:2 ratio the complex formed was found to be anhydrous.

2.4 Physical measurements

Carbon, hydrogen and nitrogen were estimated by Semimicro Analyzer, LG-VEB Labogerate and Orthopadic, Leipzig. Infrared spectra of the complexes were recorded on a Perkin-Elmer 842 spectrophotometer in the region $4000\text{--}350\text{ cm}^{-1}$. Diffused reflectance spectra were recorded on a Cary 2390 in the $300\text{--}1800\text{ nm}$ region at the Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Chennai (RSIC, IIT). ^1H NMR spectra were taken using TMS as the internal standard on a 90 MHz Perkin-Elmer R-32 spectrometer. Thermal studies were carried out in an atmosphere of air using a Stanton Redcroft Instrument (USIC, University of Roorkee, Roorkee) and specimens were heated at the rate of 10° per min in the temperature range $0\text{--}800^\circ\text{C}$. Heated alumina was used as standard. EPR spectra of the solid copper complexes were recorded at RSIC, IIT, Chennai using Varian E-4 (X-band) spectrometer which was operated at 9.5 GHz .

3. Results and discussion

The analytical results are tabulated in table 1. The structure given in figure 1 is based on elemental analyses, IR, ^1H NMR, electronic spectra and magnetic measurements.

3.1 Infrared spectra

The broad band in the region $\sim 3350\text{--}3100\text{ cm}^{-1}$ in the infrared spectra of 1:1 and 1:2 complexes is assigned to the $\nu(\text{OH})$ vibration of coordinated water except in Cu(II) 1:2 complexes. A strong band at $1650\text{--}1610\text{ cm}^{-1}$ in the IR spectra of all the free ligands assigned to $\nu(-\text{N}=\text{CH})$ is lowered by $20\text{--}35\text{ cm}^{-1}$ in the spectra of complexes, indicating coordination through azomethine nitrogen of Schiff bases (8, 9). The ligands CMT and CMMT showed characteristic $\nu(\text{NH})$ and $\nu(\text{SH})$ bands around 3140 and 2650 cm^{-1} . Another band around 1100 cm^{-1} is assigned to $\nu(\text{C-S})$. The deprotonation

Table I. Analytical and physical data for the complexes

Compounds	Colour	Analysis % Found (Calcd.)				
		M	C	H	N	S
$C_{11}H_{10}N_4S$ (CMT)	Light yellow	---	57.40(57.39)	4.20(4.34)	24.20(24.34)	13.90(13.91)
$Co(C_{11}H_9N_4S)OAc \cdot 3H_2O$	Purple	14.12(14.69)	38.51(38.51)	5.01(4.48)	13.84(13.96)	8.05(7.98)
$Co(C_{13}H_{12}N_4SO_2) \cdot 3H_2O$						
$Co(C_{22}H_{18}N_8S_2) \cdot 2H_2O$	Grey	11.24(10.69)	47.24(47.74)	3.81(3.97)	21.01(20.25)	11.90(11.57)
$Ni(C_{11}H_9N_4S)OAc \cdot 3H_2O$	Light green	14.78(14.65)	38.11(38.93)	4.67(4.49)	13.80(13.97)	8.11(7.99)
$Ni(C_{13}H_{12}N_4SO_2) \cdot 3H_2O$						
$Ni(C_{22}H_{18}N_8S_2) \cdot 2H_2O$	Light green	10.53(10.62)	46.98(47.76)	3.36(3.98)	20.53(20.26)	12.15(11.58)
$Cu(C_{11}H_9N_4S)OAc \cdot H_2O$	Brown	16.92(17.19)	42.62(42.21)	3.65(3.78)	15.04(15.15)	8.70(8.65)
$Cu(C_{13}H_{12}N_4SO_2) \cdot H_2O$						
$Cu(C_{22}H_{18}N_8S_2)$	Brick red	12.60(12.18)	51.14(50.61)	3.50(3.45)	21.80(21.47)	12.60(12.27)
$Zn(C_{11}H_9N_4S)OAc \cdot 3H_2O$	Light yellow	16.24(16.04)	38.63(38.29)	4.27(4.41)	13.52(13.74)	7.52(7.85)
$Zn(C_{13}H_{12}N_4SO_2) \cdot 3H_2O$						
$Zn(C_{22}H_{18}N_8S_2) \cdot 2H_2O$	Light yellow	11.89(11.68)	47.32(47.19)	3.65(3.93)	20.24(20.02)	11.76(11.44)
$C_{12}H_{12}N_4S$ (CMMT)	Light yellow	---	58.75(59.06)	4.98(4.91)	23.06(22.95)	13.50(13.11)
$Co(C_{12}H_{11}N_4S)OAc \cdot 3H_2O$	Purple	14.45(14.19)	41.11(40.49)	4.62(4.82)	13.76(13.49)	7.61(7.71)
$Co(C_{14}H_{14}N_4SO_2) \cdot 3H_2O$						
$Co(C_{12}H_{11}N_4S) \cdot 2H_2O$	Light purple	10.64(10.13)	50.11(49.57)	5.10(4.50)	20.22(19.28)	11.64(11.02)
$Ni(C_{12}H_{11}N_4S)OAc \cdot 3H_2O$	Green	14.05(14.15)	40.80(40.51)	4.90(4.82)	13.67(13.50)	7.90(7.71)
$Ni(C_{14}H_{14}N_4SO_2) \cdot 3H_2O$						
$Ni(C_{12}H_{11}N_4S) \cdot 2H_2O$	Light green	10.80(10.10)	50.56(49.59)	4.70(4.50)	19.85(19.28)	11.44(11.02)
$Cu(C_{12}H_{11}N_4S)OAc \cdot H_2O$	Brown	15.98(16.56)	43.74(43.80)	3.98(4.17)	14.92(14.60)	8.50(8.34)
$Cu(C_{14}H_{14}N_4SO_2) \cdot H_2O$						
$Cu(C_{12}H_{11}N_4S)$	Yellow green	12.40(11.56)	53.19(52.40)	4.52(4.00)	20.65(20.38)	12.26(11.64)
$Zn(C_{12}H_{11}N_4S)OAc \cdot 3H_2O$	Light yellow	15.62(15.51)	39.94(39.86)	4.68(4.74)	13.76(13.28)	13.40(13.16)
$Zn(C_{14}H_{14}N_4SO_2) \cdot 3H_2O$						
$Zn(C_{12}H_{11}N_4S) \cdot 2H_2O$	Light yellow	11.85(11.13)	50.40(49.03)	4.80(4.42)	19.45(19.06)	10.60(10.59)

Table 1. (Continued)

Compounds	Colour	Analysis % Found (Calcd.)				
		M	C	H	N	S
$C_{13}H_{14}N_4S$ (CEMT)	Light yellow	---	60.21(60.46)	5.30(5.42)	21.45(21.70)	12.60(12.40)
$Co(C_{13}H_{13}N_4S)OAc \cdot 3H_2O$	Purple	14.20(13.73)	42.30(41.96)	5.50(5.12)	12.87(13.05)	7.50(7.46)
$Co(C_{15}H_{16}N_4SO_2) \cdot 3H_2O$						
$Co(C_{13}H_{13}N_4S)_2 \cdot 2H_2O$	Light purple	10.05(9.67)	51.70(51.23)	5.06(4.92)	18.59(18.39)	10.79(10.51)
$Ni(C_{13}H_{13}N_4S)OAc \cdot 3H_2O$	Light green	14.20(13.69)	42.08(41.98)	5.40(5.13)	13.20(13.06)	7.30(7.46)
$Ni(C_{15}H_{16}N_4SO_2) \cdot 3H_2O$						
$Ni(C_{13}H_{13}N_4S)_2 \cdot 2H_2O$	Light green	9.80(9.64)	51.44(51.25)	5.04(4.92)	18.70(18.39)	10.90(10.51)
$Cu(C_{13}H_{13}N_4S)OAc \cdot H_2O$	Green	16.50(15.98)	45.48(45.27)	4.31(4.52)	14.26(14.08)	8.50(8.04)
$Cu(C_{13}H_{13}N_4S)_2$	Dirty green	11.28(11.00)	53.90(54.02)	4.90(4.50)	19.45(19.38)	10.78(11.08)
$Zn(C_{13}H_{13}N_4S)OAc \cdot 3H_2O$	Light yellow	15.70(15.01)	41.50(41.34)	4.90(5.05)	12.60(12.86)	7.40(7.35)
$Zn(C_{15}H_{16}N_4SO_2) \cdot 3H_2O$						
$Zn(C_{13}H_{13}N_4S)_2 \cdot 2H_2O$	Light yellow	11.14(10.62)	50.45(50.70)	4.90(4.87)	18.40(18.20)	10.35(10.40)
$C_{14}H_{16}N_4S$ (CMPT)	Light yellow	---	62.05(61.76)	5.70(5.88)	20.78(20.58)	11.80(11.76)
$Co(C_{14}H_{15}N_4S)OAc \cdot 3H_2O$	Light purple	13.70(13.29)	43.90(43.35)	5.37(5.41)	12.80(12.64)	7.42(7.22)
$Co(C_{16}H_{18}N_4SO_2) \cdot 3H_2O$						
$Co(C_{14}H_{15}N_4S)_2 \cdot 2H_2O$	Light purple	9.80(9.24)	52.53(52.75)	5.80(5.33)	17.12(17.58)	10.30(10.04)
$Ni(C_{14}H_{15}N_4S)OAc \cdot 3H_2O$	Light green	13.70(13.25)	43.90(43.37)	5.20(5.42)	12.43(12.65)	7.20(7.23)
$Ni(C_{16}H_{18}N_4SO_2) \cdot 3H_2O$						
$Ni(C_{14}H_{15}N_4S)_2 \cdot 2H_2O$	Light green	9.40(9.21)	52.45(52.77)	5.71(5.34)	17.97(17.59)	10.08(10.05)
$Cu(C_{14}H_{15}N_4S)OAc \cdot H_2O$	Yellowish green	15.24(15.43)	46.80(46.65)	4.75(4.85)	13.68(13.60)	7.90(7.77)
$Cu(C_{16}H_{18}N_4SO_2) \cdot H_2O$						
$Cu(C_{14}H_{15}N_4S)_2$	Dirty green	10.78(10.49)	55.20(55.48)	4.90(4.95)	18.67(18.49)	10.90(10.56)
$Zn(C_{14}H_{15}N_4S)OAc \cdot 3H_2O$	Light yellow	14.66(14.54)	43.08(42.72)	5.70(5.34)	12.81(12.46)	6.97(7.12)
$Zn(C_{16}H_{18}N_4SO_2) \cdot 3H_2O$						
$Zn(C_{14}H_{15}N_4S)_2 \cdot 2H_2O$	Light yellow	10.42(10.16)	52.40(52.22)	7.98(5.28)	17.22(17.40)	9.65(9.94)

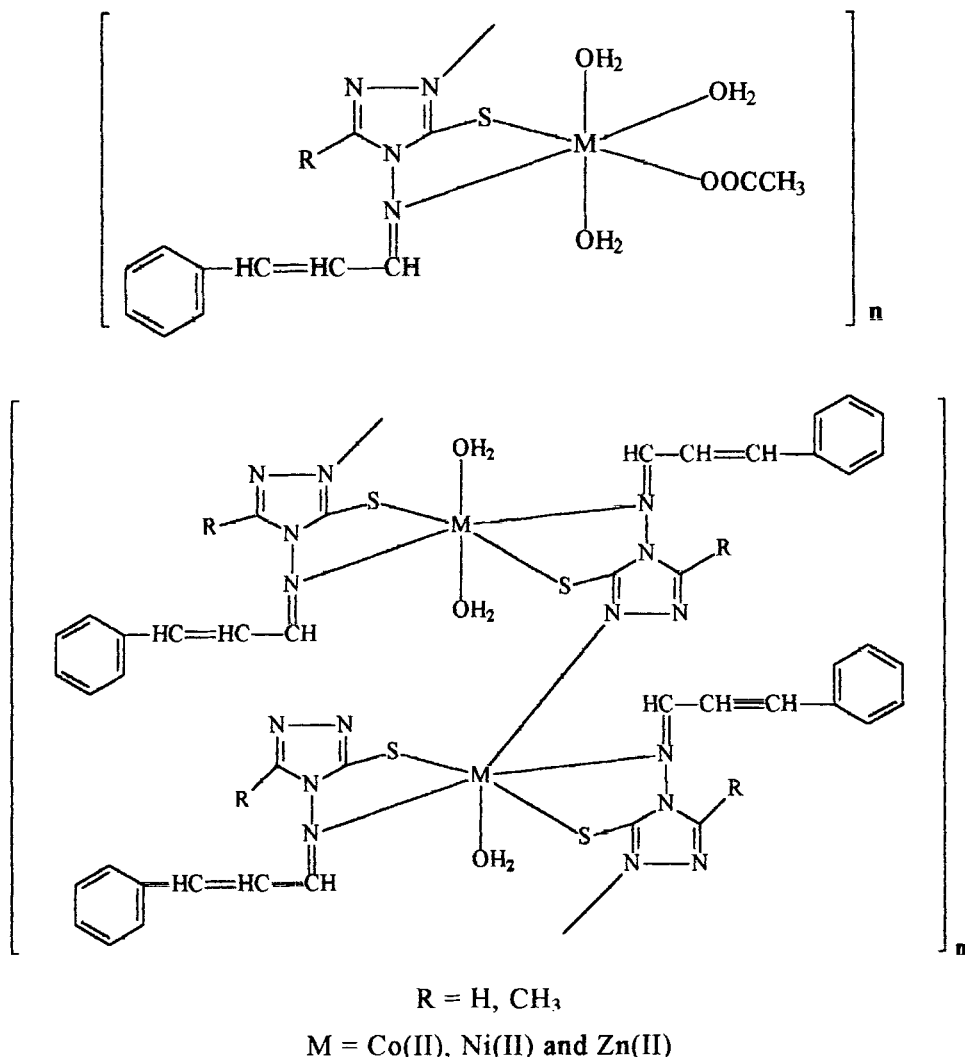


Figure 1. Structures of the metal complexes in 1:1 and 1:2 molar ratio

of thiol group and complexation through sulphur is indicated by the absence of band around $\sim 2650\text{ cm}^{-1}$ (due to $\nu(\text{SH})$) in the spectra of complexes. Metal-sulphur bond^{10,11} formation is further confirmed by a band around $400\text{--}360\text{ cm}^{-1}$ in the far IR region. A new band appears at 795 cm^{-1} $\nu(\text{C-S})$, indicating the coordination through sulphur atom. Formation of metal-nitrogen bond^{12,13} is supported by the presence of an IR band in the region $550\text{--}480\text{ cm}^{-1}$. A strong band in the region $1750\text{--}1730\text{ cm}^{-1}$ has been assigned to $\nu(\text{OOCCH}_3)$ in 1:1 (metal:ligand) complexes. The above discussion indicates bidentate (N and S donor atoms) nature of ligands.

3.2 Electronic spectra

The electronic spectra of the Co(II) complexes showed absorption band in the regions $8000\text{--}10000$ and $18000\text{--}20000\text{ cm}^{-1}$ for ν_1 and ν_3 transitions [${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})(\nu_1)$, ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})(\nu_3)$] suggesting octahedral geometry¹⁴. The ν_2 transition is not

observed in these cases e.g. $\text{Co}(\text{C}_{12}\text{H}_{11}\text{N}_4\text{S})\text{OAc}\cdot 3\text{H}_2\text{O}$ showed absorption bands at 9500 and 18200 cm^{-1} for ν_1 and ν_3 transitions, respectively. The magnetic moment values for the Co(II) complexes at room temperature were found to be in the range of 2.2–2.8 BM, indicating d^7 low spin six-coordinated complexes e.g. the magnetic moment for the $\text{Co}(\text{C}_{11}\text{H}_9\text{N}_4\text{S})_2\cdot 2\text{H}_2\text{O}$ showed value 2.78 BM.

Nickel (II) complexes exhibit three absorption bands in the regions 7000–13000, 13000–19000 and 20000–27000 cm^{-1} for ν_1 , ν_2 and ν_3 transitions [${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$ (ν_1), ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$ (ν_2) and ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$ (ν_3)], respectively. The electronic spectrum of $\text{Ni}(\text{C}_{11}\text{H}_9\text{N}_4\text{S})\text{OAc}\cdot 3\text{H}_2\text{O}$ showed three spin-allowed bands at 8400, 15600 and 22200 cm^{-1} for ν_1 , ν_2 and ν_3 transitions, respectively, indicating octahedral geometry¹². The magnetic moment values for the Ni(II) complexes at room temperature were found to be in the normal range (2.8–3.5 BM)¹⁵ e.g. $\text{Ni}(\text{C}_{11}\text{H}_9\text{N}_4\text{S})_2\cdot 2\text{H}_2\text{O}$ showed magnetic moment value of 2.81 BM.

In Cu(II) complexes, a single band observed around 18500 cm^{-1} was assigned to the transition ${}^2\text{E}_g \rightarrow {}^3\text{T}_{2g}$, which is characteristics of square-planar geometry^{14,16}. Cu(II) complexes exhibited magnetic moment value in the normal range 1.70–2.20 BM e.g. $\text{Cu}(\text{C}_{11}\text{H}_9\text{N}_4\text{S})_2$ showed magnetic moment of 1.7 BM.

Zinc(II) complexes are diamagnetic as expected for the d^{10} configuration.

3.3 ${}^1\text{H}$ NMR spectra

The ${}^1\text{H}$ NMR spectra of CMMT and its 1:1 and 1:2 zinc complexes were recorded in TFA (table 2). The signal due to SH proton of ligand appears at δ 4.71 and disappeared in the spectra of the corresponding zinc(II) complexes. The signal at δ 9.98 ppm due to azomethine proton ($-\text{N}=\text{CH}-$) is shifted in the spectra of its 1:1 and 1:2 Zn(II) complexes and was observed at δ 10.21 and 10.30 ppm, respectively. It indicates chelation of the ligand through sulphur and azomethine nitrogen.

3.4 EPR spectra

EPR spectrum of $\text{Cu}(\text{C}_{11}\text{H}_9\text{N}_4\text{S})_2$ has been discussed. The g_{\parallel} and g_{\perp} values have been found to be 2.18 and 2.04 respectively. The g_{ave} was calculated to be 2.09. The greater value of g_{\parallel} as compared to g_{\perp} indicates the presence of the unpaired electron in dx^2-y^2 orbital.

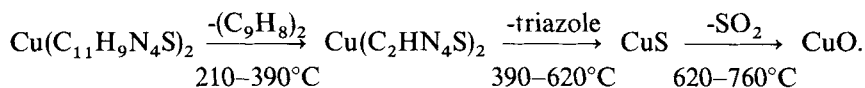
3.5 Thermal studies

Thermal behaviour of the complexes are almost, the same. Hence only $\text{Cu}(\text{C}_{11}\text{H}_9\text{N}_4\text{S})_2$ and $\text{Ni}(\text{CMMT})\text{OAc}\cdot 3\text{H}_2\text{O}$ are discussed in detail. The anhydrous copper(II) complex

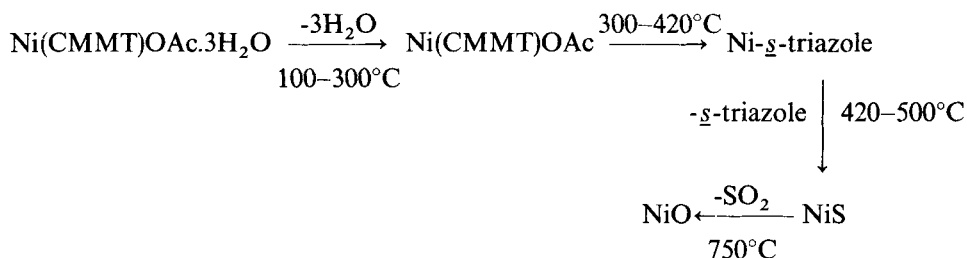
Table 2. ${}^1\text{H}$ NMR spectral data (δ ppm) of 4-cinnamalideneamino-5-mercapto-3-methyl-*s*-triazole (CMMT) and its Zn^{+2} complexes.

Compound	SH	Aromatic	Alkyl	$-\text{CH}=\text{N}-$	$-\text{O}-\text{C}-\text{CH}_3$ O
CMMT	4.71 <u>s</u>	6.94–7.38	1.74 <u>s</u> ($-\text{CH}_3$) 4.66–4.69 broad peak ($-\text{CH}=\text{CH}-$)	9.98 <u>d</u>	—
$\text{CMMTZn}(\text{OAc})\cdot 3\text{H}_2\text{O}$	—	7.03–7.45 (m, 7H)	1.9 <u>s</u> ($-\text{CH}_3$)	10.21 <u>d</u>	2.33
$(\text{CMMT})_2\text{Zn}\cdot 2\text{H}_2\text{O}$	—	7.13–7.45 m, 7H	1.77 <u>s</u> ($-\text{CH}_3$)	10.30 <u>d</u>	—

is almost stable up to 210°C and then the organic part partially starts decomposing giving metal-triazole at 390°C with a mass loss of 45.20% on TG curve (44.48% theoretically). In the temperature range 400–620°C, all the organic part decompose as indicated by the DTA curve with a mass loss of 82.14% (82.44% theoretically) and formation of CuS took place at 620°C. Finally at 760°C, CuO is obtained as the end product requiring the mass loss of 84.2% (84.74% theoretically). The thermal degradation of the Cu(C₁₁H₉N₄S)₂ is given below,



Thermal degradation of Ni (CMMT) OAc.3H₂O follows the following course,



Acknowledgements

We are grateful to the University Grants Commission, New Delhi and in particular the Department for laboratory facilities and one of us (AKS) is thankful for financial assistance.

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