

Synthesis, Characterization and Thermal Studies of Co(II), Ni(II), Cu(II) and Zn(II) Complexes of Some Schiff Bases Derived from 4-Amino-3-mercapto-6-methyl-5-oxo-1,2,4 triazine

Kiran Singh*, Yogender Kumar and Manjeet S. Barwa

Department of Chemistry, Kurukshetra University Kurukshetra, Haryana, India-136119.

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ABSTRACT

Co(II), Ni(II), Cu(II) and Zn(II) Complexes of bidentate Schiff bases derived from the condensation of 4-amino-3-mercapto-6-methyl-5-oxo-1,2,4-triazine with 4-fluoro benzaldehyde and 2-acetyl furan were synthesized and characterized by various physico-chemical techniques. A square planar geometry was suggested for Cu(II) and octahedral geometry proposed for Co(II), Ni(II) and Zn(II). TG curves indicated that the complexes decompose in three to four steps. The presence of coordinated water in metal complexes was confirmed by thermal and IR data of the complexes.

KEY WORDS

Synthesis, Schiff bases, 1,2,4-triazine, thermal study.

1. Introduction

Triazine chemistry has attracted attention due to the utility of melamine derivatives as starting material for a variety of polymers,¹ as scavenging resins in organic manipulations² and in medicinal chemistry.³ Recent studies have shown their ability in chelating transition metal ion to form stable metal complexes.^{4–5} They provide a wide range of applications in the field of optics, herbicides and pharmaceuticals.^{6–9} Triazine based herbicides have gained world wide recognition. The major problems experienced due to herbicides are the contamination of soil, surface water and possible ground water with their residuals. Systematic studies of residual triazine and related compounds are necessary.¹⁰ Many derivatives of 1,2,4-triazine form coloured complexes with different metal ions and can be used as analytical reagent for their determination. The 1,2,4-triazine compounds are well known in natural materials and show interesting biological, pharmacological and medicinal properties.^{11–13}

Therefore, and in continuation of our previous studies on characterization of new triazine ligands and their transition metal complexes,^{14–15} the present investigation deals with the syntheses, characterization and thermal studies of Co(II), Ni(II), Cu(II) and Zn(II) complexes of some Schiff bases derived from 4-Amino-3-mercapto-6-methyl-5-oxo-1,2,4-triazine (*ammot*) with 4-fluoro benzaldehyde and 2-acetyl furan (Fig. 1).

2. Experimental

2.1. Chemicals

All the chemicals used in this investigation were of Analytical grade. The metal contents were estimated using standard gravimetric methods; cobalt was estimated as cobalt pyridine thiocyanate, nickel as nickel dimethyl glyoximate, copper as cuprous thiocyanate and zinc as zinc ammonium phosphate.¹⁶

2.2. Instrumentation

Melting points were determined in open capillaries in electrical

melting point apparatus Perfit and are uncorrected.

Carbon, hydrogen and nitrogen were estimated using Perkin-Elmer 2400 Elemental Analyzer at Punjab University, Chandigarh. The water of hydration was included in micro analysis data of the metal complexes. Electronic spectra of metal complexes were recorded in DMF on a Hitachi U-2000 spectrophotometer in the region 1100–200 nm. IR spectra were recorded in Beckman IR-20 Spectrophotometer in KBr/Nujol mulls in the range 4000–250 cm⁻¹. Proton NMR spectra were recorded in DMSO-d₆ on a Bruker ACF 300 spectrometer at 300 MHz using 'tetramethyl silane' as the internal standard. Magnetic moments were measured at IIC, IIT Roorkee on vibrating sample magnetometer (Model 155). Thermal analysis of metal complexes was carried out in atmospheric air at the heating rate of 10 °C/minute using a Perkin Elmer (Pyris Diamond) instrument reference to alumina powder at IIC, IIT Roorkee.

2.3. Syntheses

4-Amino-3-mercapto-6-methyl-5-oxo-1,2,4-triazine (*ammot*) was prepared by reported literature method.¹⁷

2.3.1. 4-(4-Fluorobenzalideamino)-3-mercapto-6-methyl-5-oxo-1,2,4-triazine (fbmmot)

A solution of *ammot* (4.74 g, 30 mmol) in ethanol (40 mL) was treated with 4-Fluorobenzaldehyde (3.72 g, 30 mmol). The reaction mixture was refluxed for four hours. After completion of the reaction, the solid crude was filtered and washed with cold ethanol, and dried on water bath and recrystallized from the same solvent. m.p. 133–135, (Found: C, 49.68; H, 3.48; N, 21.31 %. Calcd. For C₁₁H₉N₄OSF: C, 49.97; H, 3.43; N, 21.20 %).

2.3.2. 4-(2-Acetylfuranlideamino)-3-mercapto-6-methyl-5-oxo-1,2,4-triazine (afmmot)

A mixture of *afmmot* (4.74 g, 30 mmol) and 2-acetylfuran (3.32 g, 30 mmol) in ethanol (40 mL) was boiled under reflux for

* To whom correspondence should be addressed. E-mail: yogikhosya@gmail.com

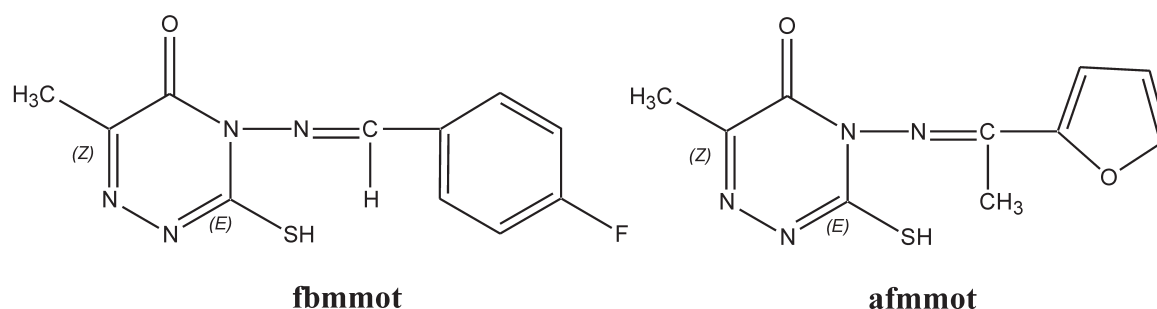


Figure 1 Structure of Schiff bases.

four hours. The light brown coloured solid so obtained after keeping over night, was filtered, washed with cold ethanol and recrystallized from ethanol.

m.p. 219–222, (Found: C, 47.91; H, 4.12; N, 22.40 % Calcd. for $C_{10}H_{10}N_4O_2S$: C, 47.99; H, 4.02; N, 22.38 %).

2.3.3. Synthesis of Metal Complexes

2.3.3.1. Metal Complexes of fbmmot

The hot ethanolic solutions of the fbmmot (0.79 g, 3 mmol) were added to the aqueous ethanolic solutions of metal acetates of Co(II) (0.74 g, 3 mmol), Ni(II) (0.74 g, 3 mmol), Cu(II) (0.63 g, 3 mmol) and Zn(II) (0.64 g, 3 mmol), which resulted in the immediate precipitation of metal derivatives. The products formed were filtered, washed with warm water, ethanol and finally with acetone and dried on water bath.

Co(fbmmot)OAc.3H₂O: m.p. >276, (Found: C, 35.72; H, 3.69 ; N, 12.88; Co, 13.33 % Calcd. for $C_{13}H_{17}N_4O_6SFCo$: C, 35.87; H, 3.93; N, 12.87; Co, 13.53 %).

Ni(fbmmot)OAc.3H₂O: m.p. >253, (Found: C, 33.80; H, 3.69 ; N, 12.15; Ni, 14.12 % Calcd. for $C_{13}H_{17}N_4O_6SFNi$: C, 33.86; H, 3.71; N, 12.15; Ni, 14.11 %).

Cu(fbmmot)OAc.H₂O: m.p. >290, (Found: C, 38.67; H, 3.22 ; N, 13.86; Cu, 15.73 % Calcd. for $C_{13}H_{13}N_4O_4SFCu$: C, 38.66; H, 3.24; N, 13.87; Cu, 15.73 %).

Zn(fbmmot)OAc.3H₂O: m.p. >266, (Found: C, 35.33; H, 3.86 ; N, 12.66; Zn, 14.76 % Calcd. for $C_{13}H_{17}N_4O_6SFZn$: C, 35.35; H, 3.87; N, 12.68; Zn, 14.79 %).

2.3.3.2. Metal Complexes of fbmmot

The aqueous ethanolic solutions of metal acetates of Co(II) (0.50 g, 2 mmol), Ni(II) (0.50 g, 2 mmol), Cu(II) (0.46 g, 2 mmol) and Zn(II) (0.44 g, 2 mmol) were treated with the hot ethanolic solutions of the fbmmot (1.05 g, 4 mmol). The solid complexes separated, were filtered, washed with warm water, ethanol and finally with acetone and dried on water bath.

Co(fbmmot)₂.2H₂O: m.p. >230, (Found: C, 44.75; H, 3.20; N, 17.28; Co, 8.68 % Calcd. for $C_{24}H_{20}N_8O_4S_2F_2Co$: C, 44.85; H, 3.13; N, 17.43; Co, 8.71 %).

Ni(fbmmot)₂.2H₂O: m.p. >238, (Found: C, 44.68; H, 3.13; N, 17.35; Ni, 9.07 % Calcd. for $C_{24}H_{20}N_8O_4S_2F_2Ni$: C, 44.67; H, 3.12; N, 17.36; Ni, 9.09 %).

Cu(fbmmot)₂: m.p. >282, (Found: C, 44.77; H, 2.73 ; N, 18.99; Cu, 10.74 % Calcd. for $C_{22}H_{16}N_8O_2S_2F_2Cu$: C, 44.78; H, 2.73; N, 18.98; Cu, 10.76 %).

Zn(fbmmot)₂.2H₂O: m.p. >260, (Found: C, 42.13; H, 3.20; N, 17.83; Zn, 10.44 % Calcd. for $C_{24}H_{20}N_8O_4S_2F_2Zn$: C, 42.14; H, 3.21; N, 17.87; Zn, 10.42 %).

2.3.3.3. Metal Complexes of afmmot

The hot ethanolic solutions of the afmmot (0.74 g, 3 mmol) were added to the aqueous ethanolic solution of metal acetates of Co(II) (0.74 g, 3 mmol), Ni(II) (0.74 g, 3 mmol), Cu(II) (0.63 g, 3 mmol) and Zn(II) (0.65 g, 3 mmol), which resulted in the immediate precipitation of metal derivatives. The products formed were filtered, washed with warm water, ethanol and finally with acetone and dried on water bath.

Co(afmmot)OAc.3H₂O: m.p. >288, (Found: C, 34.19; H, 4.28 ; N, 13.23; Co, 13.87 % Calcd. for $C_{12}H_{18}N_4O_7SCo$: C, 34.21; H, 4.30; N, 13.29; Co, 13.98 %)

Ni(afmmot)OAc.3H₂O: m.p. >240, (Found: C, 34.19; H, 4.29 ; N, 13.29; Ni, 13.85 % Calcd. for $C_{12}H_{18}N_4O_7SNi$: C, 34.23; H, 4.30; N, 13.30; Ni, 13.94 %).

Cu(afmmot)OAc.H₂O: m.p. >256, (Found: C, 36.88; H, 3.59 ; N, 14.29; Cu, 16.19 % Calcd. for $C_{12}H_{14}N_4O_5SCu$: C, 36.97; H, 3.61; N, 14.37; Cu, 16.29 %).

Zn(afmmot)OAc.3H₂O: m.p. >246, (Found: C, 35.58; H, 4.21 ; N, 13.00; Zn, 15.30 % Calcd. for $C_{12}H_{18}N_4O_7SZn$: C, 33.69; H, 4.24; N, 13.09; Zn, 15.28 %).

2.3.3.4. Metal Complexes of afmmot

The aqueous ethanolic solution of metal acetates of Co(II) (0.50 g, 2 mmol), Ni(II) (0.49 g, 2 mmol), Cu(II) (0.46 g, 2 mmol) and Zn(II) (0.48 g, 2 mmol) were treated with the hot ethanolic solutions of the fbmmot (1.00 g, 4 mmol). The solid complexes separated were filtered, washed with warm water, ethanol and finally with acetone and dried on water bath.

Co(afmmot)₂.2H₂O: m.p. >282, (Found: C, 40.42; H, 3.69 ; N, 18.80; Co, 9.89 % Calcd. for $C_{20}H_{22}N_8O_6S_2Co$: C, 40.44; H, 3.73; N, 18.88; Co, 9.93 %).

Ni(afmmot)₂.2H₂O: m.p. >280, (Found: C, 40.39; H, 3.69 ; N, 18.78; Ni, 9.80 % Calcd. for $C_{20}H_{22}N_8O_6S_2Ni$: C, 40.47; H, 3.73; N, 18.89; Ni, 9.89 %).

Cu(afmmot)₂: m.p. >230, (Found: C, 42.68; H, 3.19 ; N, 19.87; Cu, 11.27 % Calcd. for $C_{20}H_{18}N_8O_4S_2Cu$: C, 42.71; H, 3.22; N, 19.94; Cu, 11.30 %).

Zn(afmmot)₂.2H₂O: m.p. >240, (Found: C, 40.10; H, 3.65 ; N, 18.61; Zn, 10.88 % Calcd. for $C_{20}H_{22}N_8O_6S_2Zn$: C, 40.02; H, 3.69; N, 18.68; Zn, 10.90 %).

3. Results and Discussion

3.1. Chemistry

Analytical data of the metal complexes indicated the formation of 1:1 and 1:2 metal complexes of fbmmot and afmmot with Co(II), Ni(II), Cu(II) and Zn(II) metal ions. The ligands are soluble in ethanol and methanol. The elemental analysis shows that the

Table 1 IR Spectral data of Schiff bases and metal complexes (cm^{-1}) (KBr/Nujol mulls).

Sr. no.	Compound	$\nu(\text{C}=\text{O})$	$\nu(\text{N}=\text{CH}/\text{N}=\text{CCH}_3)$	$\nu(\text{C}=\text{S})/(\text{C}-\text{S})$	$\nu(\text{NH})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{S})$	$\nu(\text{OAc})$
1	$\text{C}_{11}\text{H}_9\text{N}_4\text{OSF}$ (<i>fbmmot</i>)	1700	1599	1110	3154	–	–	–
2	$\text{C}_{10}\text{H}_{10}\text{N}_4\text{O}_2\text{S}$ (<i>afmmot</i>)	1698	1607	1127	3225	–	–	–
3	$\text{Co}(\text{fbmmot})\text{OAc}\cdot 3\text{H}_2\text{O}$ ($\text{C}_{13}\text{H}_{17}\text{N}_4\text{CoO}_6\text{SF}$)	1698	1608	751	–	535	346	1720
4	$\text{Co}(\text{fbmmot})_2\cdot 2\text{H}_2\text{O}$ ($\text{C}_{24}\text{H}_{20}\text{N}_8\text{CoO}_4\text{S}_2\text{F}_2$)	1697	1610	750	–	539	338	–
5	$\text{Ni}(\text{fbmmot})\text{OAc}\cdot 3\text{H}_2\text{O}$ ($\text{C}_{13}\text{H}_{17}\text{N}_4\text{NiO}_6\text{SF}$)	1695	1611	753	–	502	352	1733
6	$\text{Ni}(\text{fbmmot})_2\cdot 2\text{H}_2\text{O}$ ($\text{C}_{24}\text{H}_{20}\text{N}_8\text{NiO}_4\text{S}_2\text{F}_2$)	1695	1612	753	–	502	357	–
7	$\text{Cu}(\text{fbmmot})\text{OAc}\cdot \text{H}_2\text{O}$ ($\text{C}_{13}\text{H}_{13}\text{N}_4\text{CuO}_4\text{SF}$)	1697	1610	750	–	492	350	1750
8	$\text{Cu}(\text{fbmmot})_2$ ($\text{C}_{22}\text{H}_{16}\text{N}_8\text{CuO}_2\text{S}_2\text{F}_2$)	1697	1610	768	–	490	348	–
9	$\text{Zn}(\text{fbmmot})\text{OAc}\cdot 3\text{H}_2\text{O}$ ($\text{C}_{13}\text{H}_{17}\text{N}_4\text{ZnO}_6\text{SF}$)	1696	1612	730	–	525	340	1736
10	$\text{Zn}(\text{fbmmot})_2\cdot 2\text{H}_2\text{O}$ ($\text{C}_{24}\text{H}_{20}\text{N}_8\text{ZnO}_4\text{S}_2\text{F}_2$)	1697	1611	731	–	538	362	–
11	$\text{Co}(\text{afmmot})\text{OAc}\cdot 3\text{H}_2\text{O}$ ($\text{C}_{12}\text{H}_{18}\text{N}_4\text{CoO}_7\text{S}$)	1699	1614	753	–	505	357	1722
12	$\text{Co}(\text{afmmot})_2\cdot 2\text{H}_2\text{O}$ ($\text{C}_{20}\text{H}_{22}\text{N}_8\text{CoO}_6\text{S}_2$)	1698	1612	753	–	515	361	–
13	$\text{Ni}(\text{afmmot})\text{OAc}\cdot 3\text{H}_2\text{O}$ ($\text{C}_{12}\text{H}_{18}\text{N}_4\text{NiO}_7\text{S}$)	1697	1614	754	–	492	348	1733
14	$\text{Ni}(\text{afmmot})_2\cdot 2\text{H}_2\text{O}$ ($\text{C}_{20}\text{H}_{22}\text{N}_8\text{NiO}_6\text{S}_2$)	1696	1618	750	–	480	349	–
15	$\text{Cu}(\text{afmmot})\text{OAc}\cdot \text{H}_2\text{O}$ ($\text{C}_{12}\text{H}_{14}\text{N}_4\text{CuO}_5\text{S}$)	1692	1619	753	–	512	343	1748
16	$\text{Cu}(\text{afmmot})_2$ ($\text{C}_{20}\text{H}_{18}\text{N}_8\text{CuO}_4\text{S}_2$)	1695	1622	751	–	511	367	–
17	$\text{Zn}(\text{afmmot})\text{OAc}\cdot 3\text{H}_2\text{O}$ ($\text{C}_{12}\text{H}_{18}\text{N}_4\text{ZnO}_7\text{S}$)	1692	1617	757	–	488	365	1735
18	$\text{Zn}(\text{afmmot})_2\cdot 2\text{H}_2\text{O}$ ($\text{C}_{20}\text{H}_{22}\text{N}_8\text{ZnO}_6\text{S}_2$)	1694	1622	748	–	492	348	–

theoretical and experimental composition of *fbmmot* and *afmmot* corresponds with molecular formula. All the metal complexes are coloured, nonhygroscopic solids stable in air, infusible at higher temperature, insoluble in water and many common organic solvents but they are soluble in DMF and DMSO. The molar conductances of the complexes measured in 10^{-3}M dimethyl formamide are in the range 1.5–3.6 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ indicating the nonelectrolytic nature. The purity of ligands and their metal complexes has been checked by TLC.

3.2. IR Spectra and Nature of Bonding

The prominent infrared spectral data of Schiff bases and their metal complexes are presented in Table 1.

The ligands *fbmmot* and *afmmot* showed a band at 1700 cm^{-1} and 1698 cm^{-1} , respectively, which was assigned for $\nu(\text{C}=\text{O})$ ^{18–19} of the 1,2,4-triazine ring. In the metal derivatives, no significant change was observed, indicating that the carbonyl oxygen is not coordinated to metal ion. The ligands *fbmmot* and *afmmot* exhibited characteristic bands due to $\nu(\text{N}-\text{H})$ and $\nu(-\text{N}=\text{CH}/-\text{N}=\text{CCH}_3)$ at 3154 , 1599 cm^{-1} and 3225 , 1607 cm^{-1} , respectively. The band due to $\nu(-\text{N}=\text{CH}/-\text{N}=\text{CCH}_3)$ showed $+5$ – 10 cm^{-1} shift^{13–15, 20–22} in the spectra of the metal complexes indicating coordination through nitrogen atom of azomethine group.

Formation of metal nitrogen bond is further supported by the presence of a band in the region 540 – 480 cm^{-1} in far IR spectra.^{23–24} A strong band observed at $\sim 1100\text{ cm}^{-1}$ in the IR spectra of Schiff bases was assigned to $\nu(\text{C}=\text{S})$.¹⁸ This band disappeared in the spectra of metal complexes and a new band appeared at $\sim 750\text{ cm}^{-1}$, which is assigned to $\nu(\text{C}-\text{S})$ and it confirms coordination through sulphur atom. Metal sulphur bond formation is further confirmed by a band in the region 380 – 340 cm^{-1} in the far IR spectra of metal complexes.²³

Broad band centered at 3200 cm^{-1} and a medium intensity band at 850 cm^{-1} in all the metal complexes except in 1:2 copper complexes confirms the presence of coordinated water²³ molecules in the metal complexes. The presence of acetate group in 1:1 metal complexes is indicated by the appearance of a strong band in the region 1750 – 1720 cm^{-1} .

3.3. ^1H NMR Spectra

The ^1H NMR spectra have been recorded for Schiff bases and their Zn (II) complexes (Table 2).

The ^1H NMR spectral data have been interpreted based on literature data.^{13–15} In the NMR spectra of complexes we have observed a shift of electron density from the ligand to metal. The ligands *fbmmot* and *afmmot* show singlet at δ 8.7 and 2.2 ppm

Table 2 ^1H NMR spectral data of metal complexes.

Sr. no.	Metal complexes	^1H NMR (DMSO- d_6)/ppm
1	<i>fbmmot</i> ($\text{C}_{11}\text{H}_9\text{N}_4\text{OSF}$)	2.5 (s, 3H, -CH ₃), 7.1–8.4 (m, 4H, Ar-H) 8.7 (s, 1H, -N=CH-), 11.1 (S, 1H, -SH)
2	<i>afmmot</i> ($\text{C}_{10}\text{H}_{10}\text{N}_4\text{O}_2\text{S}$)	2.5 (s, 3H, -CH ₃), 6.3–7.6 (m, 3H, Ar-H) 2.2 (s, 3H, -N=C-CH ₃ -), 11.6 (S, 1H, -SH)
3	Zn(<i>fbmmot</i>)OAc.3H ₂ O ($\text{C}_{13}\text{H}_{17}\text{N}_4\text{ZnO}_6\text{SF}$)	2.5(s, 3H, Triazine-CH ₃), 9.2(s, 1H, -N=CH-), 7.2–8.2 (m, 4H, Ar-H), 2.4(s, 3H, CH ₃ COO)
4	Zn(<i>fbmmot</i>) ₂ .2H ₂ O ($\text{C}_{24}\text{H}_{20}\text{N}_8\text{ZnO}_4\text{S}_2\text{F}_2$)	2.5(s, 3H, Triazine-CH ₃), 9.2(s, 1H, -N=CH-), 7.1–8.3 (m, 4H, Ar-H)
5	Zn(<i>afmmot</i>)OAc.3H ₂ O ($\text{C}_{12}\text{H}_{18}\text{N}_4\text{ZnO}_7\text{S}$)	2.5(s, 3H, Triazine-CH ₃), 2.3(s, 1H, -N=C-CH ₃), 6.5–7.6 (m, 3H, Ar-H), 2.4(s, 3H, CH ₃ COO)
6	Zn(<i>afmmot</i>) ₂ .2H ₂ O ($\text{C}_{20}\text{H}_{22}\text{N}_8\text{ZnO}_6\text{S}_2$)	2.5(s, 3H, Triazine-CH ₃), 2.3(s, 3H, -N=C-CH ₃), 6.5–7.6 (m, 3H, Ar-H)

which is assigned to azomethine proton and methyl group protons attached to azomethine carbon, respectively. These signals deshielded in the spectra of metal complexes, suggests coordination of metal ion to azomethine nitrogen atom of the ligands. In addition to this, the signals at δ 11.1 and 11.6 ppm are ascribed to SH protons. Disappearance of these SH protons signals in the spectra of metal complexes supported the deprotonation of thiol group. In the spectra of ligands multiplet signals around δ 7.1–8.4 and δ 6.3–7.6 ppm were assigned to aromatic protons. These multiplets show a slight shift upon coordination. In the spectra of 1:1 Zn complexes singlet at δ 2.4 ppm is due to methyl group of acetate ion.

3.4. Electronic Spectra

The electronic spectra of Co(II), Ni(II) and Cu(II) complexes were recorded in DMF (Table 3). The Co(II) complexes exhibited absorption bands in two principal regions, i.e. 9930–10945 cm^{-1} and 18666–20553 cm^{-1} , which are assigned to $^4\text{T}_{1g}(\text{F})$ - $^4\text{T}_{2g}(\text{F})$ (ν_1) and $^4\text{T}_{1g}(\text{F})$ - $^4\text{T}_{2g}(\text{P})$ (ν_3) transitions, respectively. These bands are the characteristic of octahedral Co(II)^{13,25} complexes. However, ν_2 band is not observed because of its proximity to strong ν_3 transition. The nickel complexes exhibited three bands in the region 9998–10952 cm^{-1} , 16584–17763 cm^{-1} , 22753–24601 cm^{-1} for ν_1 , ν_2 and ν_3 , respectively. These bands are assigned to the transitions $^3\text{A}_{2g}(\text{F})$ - $^3\text{T}_{2g}(\text{F})$ (ν_1), $^3\text{A}_{2g}(\text{F})$ - $^3\text{T}_{1g}(\text{F})$ (ν_2) and $^3\text{A}_{2g}(\text{F})$ - $^3\text{T}_{1g}(\text{P})$ (ν_3),

Table 3 Electronic Spectral data of metal complexes.

Sr. no.	Metal complexes	Electronic spectra		B.M./ μ_{eff}
		Absorption, ν_{max} / cm^{-1}	Assignment	
1	Co(<i>fbmmot</i>)OAc.3H ₂ O ($\text{C}_{13}\text{H}_{17}\text{N}_4\text{CoO}_6\text{SF}$)	10940, 20553	$^4\text{T}_{1g}(\text{F})$ - $^4\text{T}_{2g}(\text{F})$ (ν_1), $^4\text{T}_{1g}(\text{F})$ - $^4\text{T}_{2g}(\text{P})$ (ν_3)	4.3
2	Co(<i>fbmmot</i>) ₂ .2H ₂ O ($\text{C}_{24}\text{H}_{20}\text{N}_8\text{CoO}_4\text{S}_2\text{F}_2$)	10945, 20533	$^4\text{T}_{1g}(\text{F})$ - $^4\text{T}_{2g}(\text{F})$ (ν_1), $^4\text{T}_{1g}(\text{F})$ - $^4\text{T}_{2g}(\text{P})$ (ν_3)	4.5
3	Ni(<i>fbmmot</i>)OAc.3H ₂ O ($\text{C}_{13}\text{H}_{17}\text{N}_4\text{NiO}_6\text{SF}$)	10952, 16584, 22753	$^3\text{A}_{2g}(\text{F})$ - $^3\text{T}_{2g}(\text{F})$ (ν_1), $^3\text{A}_{2g}(\text{F})$ - $^3\text{T}_{1g}(\text{F})$ (ν_2), $^3\text{A}_{2g}(\text{F})$ - $^3\text{T}_{1g}(\text{P})$ (ν_3)	2.8
4	Ni(<i>fbmmot</i>) ₂ .2H ₂ O ($\text{C}_{24}\text{H}_{20}\text{N}_8\text{NiO}_4\text{S}_2\text{F}_2$)	10940, 16584, 23270	$^3\text{A}_{2g}(\text{F})$ - $^3\text{T}_{2g}(\text{F})$ (ν_1), $^3\text{A}_{2g}(\text{F})$ - $^3\text{T}_{1g}(\text{F})$ (ν_2), $^3\text{A}_{2g}(\text{F})$ - $^3\text{T}_{1g}(\text{P})$ (ν_3)	3.2
5	Cu(<i>fbmmot</i>)OAc.H ₂ O ($\text{C}_{13}\text{H}_{13}\text{N}_4\text{CuO}_4\text{SF}$)	18555	$^2\text{B}_{1g}$ - $^2\text{A}_{1g}$	1.7
6	Cu(<i>fbmmot</i>) ₂ ($\text{C}_{22}\text{H}_{16}\text{N}_8\text{CuO}_2\text{S}_2\text{F}_2$)	18559	$^2\text{B}_{1g}$ - $^2\text{A}_{1g}$	1.8
7	Co(<i>afmmot</i>)OAc.3H ₂ O ($\text{C}_{12}\text{H}_{18}\text{N}_4\text{CoO}_7\text{S}$)	9949, 18666	$^4\text{T}_{1g}(\text{F})$ - $^4\text{T}_{2g}(\text{F})$ (ν_1), $^4\text{T}_{1g}(\text{F})$ - $^4\text{T}_{2g}(\text{P})$ (ν_3)	5.0
8	Co(<i>afmmot</i>) ₂ .2H ₂ O ($\text{C}_{20}\text{H}_{22}\text{N}_8\text{CoO}_6\text{S}_2$)	9930, 18583	$^4\text{T}_{1g}(\text{F})$ - $^4\text{T}_{2g}(\text{F})$ (ν_1), $^4\text{T}_{1g}(\text{F})$ - $^4\text{T}_{2g}(\text{P})$ (ν_3)	4.3
9	Ni(<i>afmmot</i>)OAc.3H ₂ O ($\text{C}_{12}\text{H}_{18}\text{N}_4\text{NiO}_7\text{S}$)	10100, 17561, 24538	$^3\text{A}_{2g}(\text{F})$ - $^3\text{T}_{2g}(\text{F})$ (ν_1), $^3\text{A}_{2g}(\text{F})$ - $^3\text{T}_{1g}(\text{F})$ (ν_2), $^3\text{A}_{2g}(\text{F})$ - $^3\text{T}_{1g}(\text{P})$ (ν_3)	3.1
10.	Ni(<i>afmmot</i>) ₂ .2H ₂ O ($\text{C}_{20}\text{H}_{22}\text{N}_8\text{NiO}_6\text{S}_2$)	9998, 17763, 24601	$^3\text{A}_{2g}(\text{F})$ - $^3\text{T}_{2g}(\text{F})$ (ν_1), $^3\text{A}_{2g}(\text{F})$ - $^3\text{T}_{1g}(\text{F})$ (ν_2), $^3\text{A}_{2g}(\text{F})$ - $^3\text{T}_{1g}(\text{P})$ (ν_3)	2.9
11.	Cu(<i>afmmot</i>)OAc.H ₂ O ($\text{C}_{12}\text{H}_{14}\text{N}_4\text{CuO}_5\text{S}$)	17655	$^2\text{B}_{1g}$ - $^2\text{A}_{1g}$	1.8
12.	Cu(<i>afmmot</i>) ₂ ($\text{C}_{20}\text{H}_{18}\text{N}_8\text{CuO}_4\text{S}_2$)	17568	$^2\text{B}_{1g}$ - $^2\text{A}_{1g}$	1.7

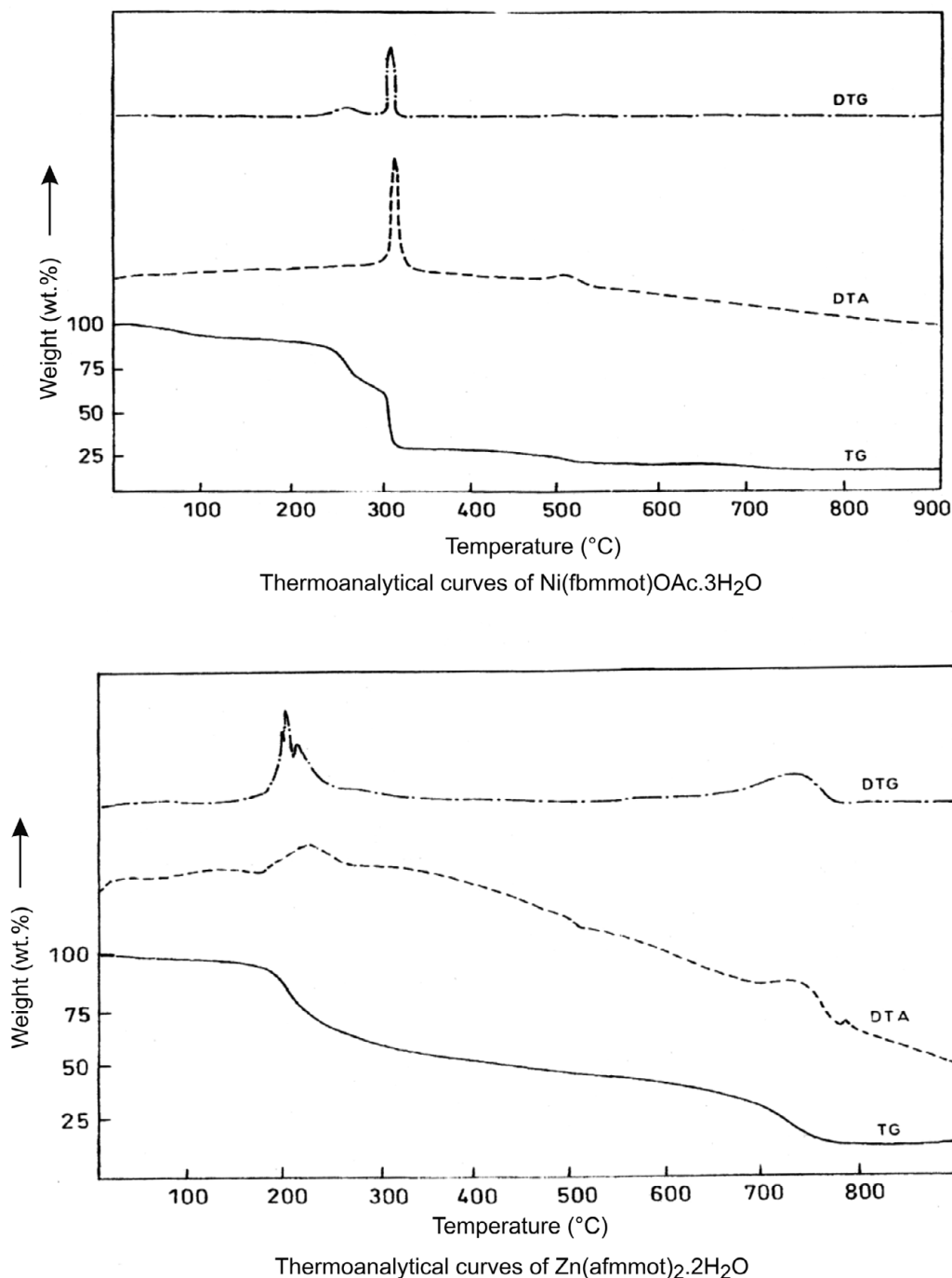


Figure 2 Thermoanalytical curves of Ni(fbmmot)OAc.3H₂O and Zn(afmmot)₂.2H₂O.

respectively, consistent with their well defined octahedral configuration.^{13–15,25}

The 1:1 and 1:2 copper complexes display a band in the region 17565–18559 cm⁻¹, attributed to ²B_{1g}–²A_{1g} transition. This band is a characteristic of square planar geometry.^{13,25}

3.5. Magnetic Measurements

The magnetic moments obtained at room temperature are given in Table 3. The magnetic measurement for Co(II), Ni(II) and Cu(II) complexes exhibit magnetic moment values μ_{eff} (5.0–4.3 BM), (3.2–2.8 BM) and (1.8–1.7 BM), respectively. These magnetic measurements show the presence of three, two and one unpaired electron in Co(II), Ni(II) and Cu(II) complexes, respectively, suggesting consistency with their octahedral and square planar environment.^{13,25}

3.6. Thermal Analysis

Thermal analyses were carried out in atmospheric air at a heating rate of 10 °C/min up to 900 °C and are shown in Fig. 2. The mode of decomposition¹⁴ observed is almost similar therefore only two complexes Ni(fbmmot)OAc.3H₂O and Zn(afmmot)₂.2H₂O are discussed here in detail. The TG curve gives information on the thermal stability and the product formed on heating. The results show that the complexes generally decompose in several thermal events, i.e. three or four decomposition steps. The first step represents a dehydration step which correlates well with the theoretical values corresponding to the elimination of the water molecules.

Ni(fbmmot)OAc.3H₂O complex decomposes in three major steps. The first step involves loss of three water molecules at 80, 125 and 195 °C corresponding to mass loss 3.43 % (calcd 3.65 %),

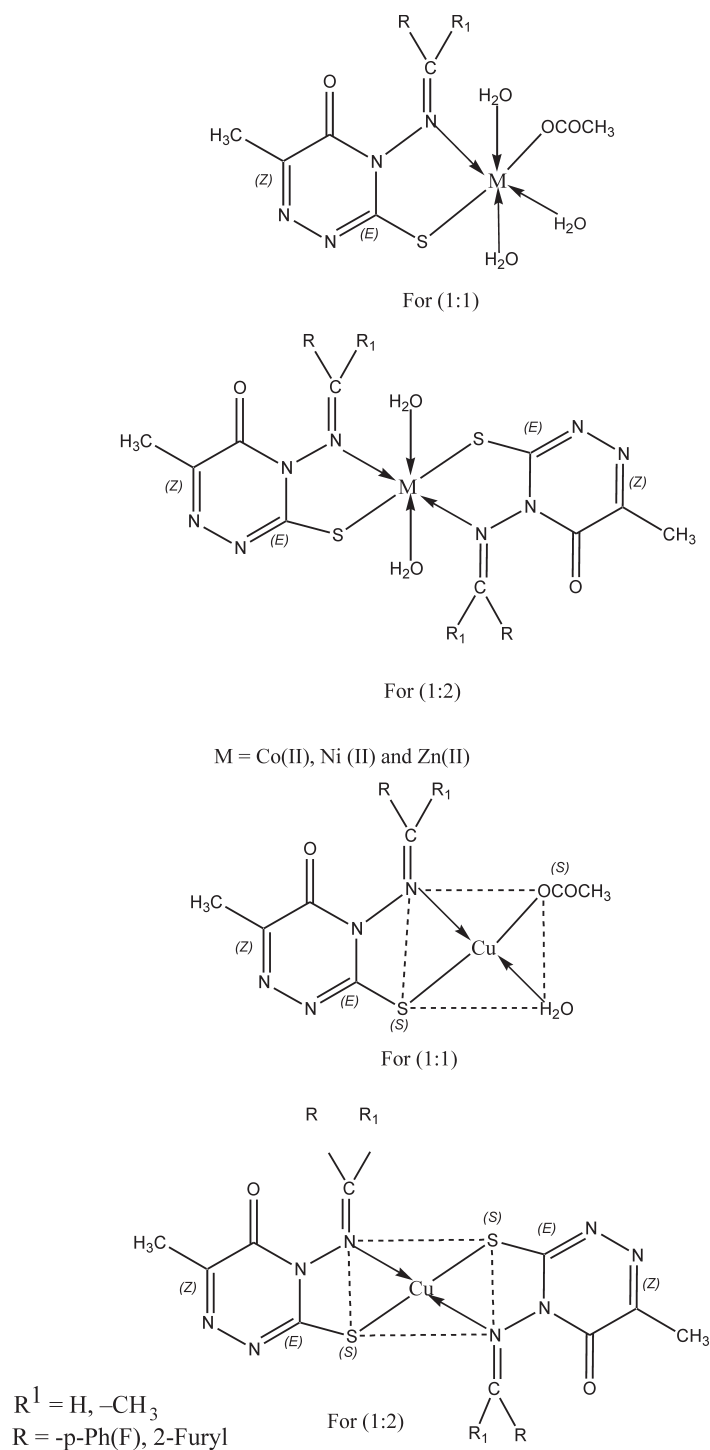


Figure 3 Proposed structures of metal complexes.

7.81 % (calcd. 8.03 %) and 11.45 % (calcd. 11.58 %) on the TG curve. The second step is accompanied by a mass loss of 49.67 % (calcd. 50.08 %) at 330 °C giving metal triazine with decomposition of the organic substituent²⁶⁻²⁷ (Fig. 2). In the temperature range 330–850 °C, the triazine decomposed with mass loss 81.21 % (calcd. 81.42 %) and finally formation of NiO took place at 850 °C. The sequence of thermal degradation of the complex Ni(*fbmmot*)OAc.3H₂O is given in Scheme 1.

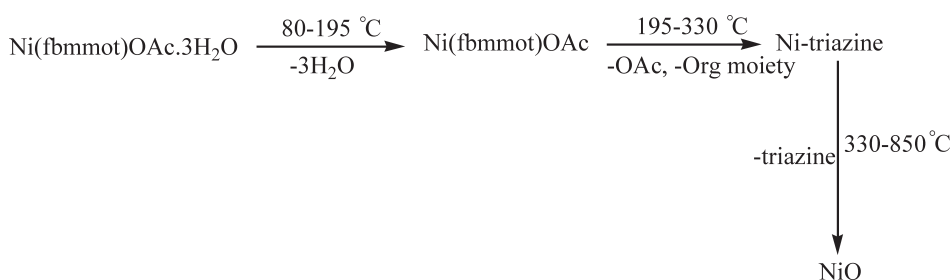
Zn(*afmmot*).2H₂O complex decomposes in four major steps. The first step involves loss of two water molecules at 96 and 164 °C with the mass loss 2.87 % (calcd. 3.08 %) and 5.89 % (calcd. 6.17 %) on the TG curve. The second step is accompanied by a mass loss of 42.97 % (calcd. 43.22 %) in the temperature range

164–364 °C, corresponds to decomposition of the organic substituent, resulting in to formation of Zn(triazine)₂. The third step involves the loss of one triazine at 672 °C with a mass loss of 67.23 % (calcd. 67.40 %) and the mass loss 85.88 % (calcd. 86.10 %) in the final step is due to decomposition the second triazine, leaving behind ZnO at 896 °C (Fig. 2; Scheme 2).

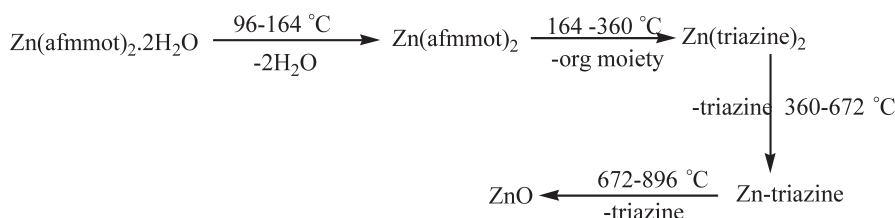
With the help of various physico-chemical techniques geometries²⁸ of the newly synthesized compounds have been proposed (Fig. 3).

4. Conclusion

In this study, the Co(II), Ni(II), Cu(II) and Zn(II) complexes with Schiff bases derived from 4-Amino-3-mercapto-6-



Scheme 1



Scheme 2

methyl-5-oxo-1,2,4-triazine with 4-fluoro benzaldehyde and 2-acetyl furan were synthesized and characterized. On the basis of different techniques, square planar geometry was suggested for Cu(II) and octahedral geometry proposed for Co(II), Ni(II) and Zn(II) complexes. TG curves indicated that the complexes decompose in three to four steps. The presence of coordinated water in metal complexes was confirmed by thermal, IR and micro analysis data of the complexes.

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