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.
Received 15 June 2010, revised 28 August, accepted 8 September 2010.

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 manipulations ² 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.⁶⁻⁷ Triazine based herbicides have gained world wide recognition. The major problems experienced due to herbicides is the contamination of soil, surface water and possible ground water with their residuals. Systematic studies of residual triazine and related compounds are necessary.⁸ 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.⁹⁻¹³ 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-mercaptopo-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-mercaptopo-6-methyl-5-oxo-1,2,4-triazine (ammot) was prepared by reported literature method.¹⁷

2.3.1. 4-(4-Fluorobenzalideamino)-3-mercaptopo-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-Acetyl furanlideamino)-3-mercaptopo-6-methyl-5-oxo-1,2,4-triazine (afmmot)
A mixture of afmmot (4.74 g, 30 mmol) and 2-acetyl furan (3.32 g, 30 mmol) in ethanol (40 mL) was boiled under reflux for
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\textsubscript{10}H\textsubscript{10}N\textsubscript{4}O\textsubscript{2}S: C, 47.99; H, 4.02; N, 22.38 %).

2.3.3.2. Metal Complexes of \textit{fmmot}

The hot ethanolic solutions of the \textit{fmmot} (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(\textit{fmmot})OAc.3H\textsubscript{2}O: m.p. >276, (Found: C, 35.72; H, 3.69; N, 12.88; Co, 13.33 % Calcd. for C\textsubscript{12}H\textsubscript{18}N\textsubscript{4}O\textsubscript{7}SCo: C, 33.86; H, 3.71; N, 12.15; Ni, 14.11 %).

Ni(\textit{fmmot})OAc.3H\textsubscript{2}O: m.p. >253, (Found: C, 33.80; H, 3.69; N, 12.15; Ni, 14.12 % Calcd. for C\textsubscript{12}H\textsubscript{18}N\textsubscript{4}O\textsubscript{7}SNi: C, 33.86; H, 3.71; N, 12.15; Ni, 14.11 %).

Cu(\textit{fmmot})OAc.3H\textsubscript{2}O: m.p. >290, (Found: C, 38.67; H, 3.22; N, 13.86; Cu, 15.73 % Calcd. for C\textsubscript{12}H\textsubscript{18}N\textsubscript{4}O\textsubscript{7}SCu: C, 38.66; H, 3.24; N, 13.87; Cu, 15.73 %).

Zn(\textit{fmmot})OAc.3H\textsubscript{2}O: m.p. >266, (Found: C, 35.33; H, 3.86; N, 12.66; Zn, 14.76 % Calcd. for C\textsubscript{12}H\textsubscript{18}N\textsubscript{4}O\textsubscript{7}SZn: C, 35.35; H, 3.87; N, 12.68; Zn, 14.79 %).

2.3.3.3. Metal Complexes of \textit{afmmot}

The hot ethanolic solutions of the \textit{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(\textit{afmmot})OAc.3H\textsubscript{2}O: m.p. >288, (Found: C, 34.19; H, 4.28; N, 13.23; Co, 13.87 % Calcd. for C\textsubscript{12}H\textsubscript{18}N\textsubscript{4}O\textsubscript{7}SCo: C, 34.21; H, 4.30; N, 13.29; Co, 13.98 %).

Ni(\textit{afmmot})OAc.3H\textsubscript{2}O: m.p. >240, (Found: C, 34.19; H, 4.29; N, 13.29; Ni, 13.85 % Calcd. for C\textsubscript{12}H\textsubscript{18}N\textsubscript{4}O\textsubscript{7}SNi: C, 34.23; H, 4.30; N, 13.30; Ni, 13.94 %).

Cu(\textit{afmmot})OAc.3H\textsubscript{2}O: m.p. >256, (Found: C, 36.88; H, 3.59; N, 14.29; Cu, 16.19 % Calcd. for C\textsubscript{12}H\textsubscript{18}N\textsubscript{4}O\textsubscript{7}SCu: C, 36.97; H, 3.61; N, 14.37; Cu, 16.29 %).

Zn(\textit{afmmot})OAc.3H\textsubscript{2}O: m.p. >246, (Found: C, 35.58; H, 4.21; N, 13.00; Zn, 15.30 % Calcd. for C\textsubscript{12}H\textsubscript{18}N\textsubscript{4}O\textsubscript{7}SZn: C, 33.69; H, 4.24; N, 13.09; Zn, 15.28 %).

2.3.3.4. Metal Complexes of \textit{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 \textit{fmmot} (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(\textit{afmmot})\textsubscript{2}H\textsubscript{2}O: m.p. >282, (Found: C, 40.42; H, 3.69; N, 18.80; Co, 9.89 % Calcd. for C\textsubscript{20}H\textsubscript{22}N\textsubscript{8}O\textsubscript{6}SZn: C, 40.47; H, 3.73; N, 18.89; Cu, 9.93 %).

Ni(\textit{afmmot})\textsubscript{2}H\textsubscript{2}O: m.p. >280, (Found: C, 40.39; H, 3.69; N, 18.78; Ni, 9.80 % Calcd. for C\textsubscript{20}H\textsubscript{22}N\textsubscript{8}O\textsubscript{6}SNi: C, 40.47; H, 3.73; N, 18.89; Ni, 9.89 %).

Cu(\textit{afmmot})\textsubscript{2}H\textsubscript{2}O: m.p. >230, (Found: C, 42.68; H, 3.19; N, 19.87; Cu, 11.27 % Calcd. for C\textsubscript{20}H\textsubscript{22}N\textsubscript{8}O\textsubscript{6}SCu: C, 42.71; H, 3.22; N, 19.94; Cu, 11.30 %).

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 \textit{fmmot} and \textit{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
theoretical and experimental composition of \textit{fbmmot} and \textit{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 10–3M dimethyl formamide are in the range 1.5–3.6 ohm –1 cm2 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 \textit{fbmmot} and \textit{afmmot} showed a band at 1700 cm–1 and 1698 cm–1, respectively, which was assigned for ν(C=O) 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 \textit{fbmmot} and \textit{afmmot} exhibited characteristic bands due to ν(C=O) and ν(N=CH-/ -N=CCH3) 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 band due to ν(N=CH-/ -N=CCH3) showed -5-10 cm–1 shift21–23 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 ~1100 cm–1 in the IR spectra of Schiff bases was assigned to ν(C=S).18 This band disappeared in the spectra of metal complexes and a new band appeared at ~750 cm–1, which is assigned to ν(C-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

A 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 water 23 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 \textit{fbmmot} and \textit{afmmot} show singlet at δ 8.7 and 2.2 ppm.

### Table 1 IR Spectral data of Schiff bases and metal complexes (cm–1) (KBr/Nujol mulls).

<table>
<thead>
<tr>
<th>Sr. no.</th>
<th>Compound</th>
<th>ν(C=O)</th>
<th>ν(N=CH/N=CCH3)</th>
<th>ν(C=S)/(C-S)</th>
<th>ν(NH)</th>
<th>ν(M-N)</th>
<th>ν(M-S)</th>
<th>ν(OAc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C6H7N4OSF (\textit{fbmmot})</td>
<td>1700</td>
<td>1599</td>
<td>1110</td>
<td>3154</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>2</td>
<td>C6H8N4OS (\textit{afmmot})</td>
<td>1698</td>
<td>1607</td>
<td>1127</td>
<td>3225</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>3</td>
<td>Co(fbmmot)OAc.3H2O (C6H7N4CoO4SF)</td>
<td>1698</td>
<td>1608</td>
<td>751</td>
<td>–</td>
<td>535</td>
<td>346</td>
<td>1720</td>
</tr>
<tr>
<td>4</td>
<td>Co(fbmmot)2H2O (C6H7N4CoO3SF)</td>
<td>1697</td>
<td>1610</td>
<td>750</td>
<td>–</td>
<td>539</td>
<td>338</td>
<td>–</td>
</tr>
<tr>
<td>5</td>
<td>Ni(fbmmot)OAc.3H2O (C6H7N4NiO4SF)</td>
<td>1695</td>
<td>1611</td>
<td>753</td>
<td>–</td>
<td>502</td>
<td>352</td>
<td>1733</td>
</tr>
<tr>
<td>6</td>
<td>Ni(fbmmot)2H2O (C6H7N4NiO3SF)</td>
<td>1695</td>
<td>1612</td>
<td>753</td>
<td>–</td>
<td>502</td>
<td>357</td>
<td>–</td>
</tr>
<tr>
<td>7</td>
<td>Cu(fbmmot)OAc.3H2O (C6H7N4CoUO4SF)</td>
<td>1697</td>
<td>1610</td>
<td>750</td>
<td>–</td>
<td>492</td>
<td>350</td>
<td>1750</td>
</tr>
<tr>
<td>8</td>
<td>Cu(fbmmot)2H2O (C6H7N4CoUO3SF)</td>
<td>1697</td>
<td>1610</td>
<td>768</td>
<td>–</td>
<td>490</td>
<td>348</td>
<td>–</td>
</tr>
<tr>
<td>9</td>
<td>Zn(fbmmot)OAc.3H2O (C6H7N4ZnO4SF)</td>
<td>1696</td>
<td>1612</td>
<td>730</td>
<td>–</td>
<td>525</td>
<td>340</td>
<td>1736</td>
</tr>
<tr>
<td>10</td>
<td>Zn(fbmmot)2H2O (C6H7N4ZnO3SF)</td>
<td>1697</td>
<td>1611</td>
<td>731</td>
<td>–</td>
<td>538</td>
<td>362</td>
<td>–</td>
</tr>
<tr>
<td>11</td>
<td>Co(fbmmot)OAc.3H2O (C6H7N4CoO4S)</td>
<td>1699</td>
<td>1614</td>
<td>753</td>
<td>–</td>
<td>505</td>
<td>357</td>
<td>1722</td>
</tr>
<tr>
<td>12</td>
<td>Co(fbmmot)2H2O (C6H7N4CoO3S)</td>
<td>1698</td>
<td>1612</td>
<td>753</td>
<td>–</td>
<td>515</td>
<td>361</td>
<td>–</td>
</tr>
<tr>
<td>13</td>
<td>Ni(fbmmot)OAc.3H2O (C6H7N4NiO4S)</td>
<td>1697</td>
<td>1614</td>
<td>754</td>
<td>–</td>
<td>492</td>
<td>348</td>
<td>1733</td>
</tr>
<tr>
<td>14</td>
<td>Ni(fbmmot)2H2O (C6H7N4NiO3S)</td>
<td>1696</td>
<td>1618</td>
<td>750</td>
<td>–</td>
<td>480</td>
<td>349</td>
<td>–</td>
</tr>
<tr>
<td>15</td>
<td>Cu(fbmmot)OAc.3H2O (C6H7N4CuO4S)</td>
<td>1692</td>
<td>1619</td>
<td>753</td>
<td>–</td>
<td>512</td>
<td>343</td>
<td>1748</td>
</tr>
<tr>
<td>16</td>
<td>Cu(fbmmot)2H2O (C6H7N4CuO3S)</td>
<td>1695</td>
<td>1622</td>
<td>751</td>
<td>–</td>
<td>511</td>
<td>367</td>
<td>–</td>
</tr>
<tr>
<td>17</td>
<td>Zn(fbmmot)OAc.3H2O (C6H7N4ZnO4S)</td>
<td>1692</td>
<td>1617</td>
<td>757</td>
<td>–</td>
<td>488</td>
<td>365</td>
<td>1735</td>
</tr>
<tr>
<td>18</td>
<td>Zn(fbmmot)2H2O (C6H7N4ZnO3S)</td>
<td>1694</td>
<td>1622</td>
<td>748</td>
<td>–</td>
<td>492</td>
<td>348</td>
<td>–</td>
</tr>
</tbody>
</table>
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 4T₁g(F)-4T₂g(F) (ν₁) and 4T₁g(F)-4T₂g(P) (ν₃) transitions, respectively. These bands are the characteristic of octahedral Co(II) complexes. However, ν₂ band is not observed because of its proximity to strong ν₃ transition. The nickel complexes exhibited three bands in the region 9998–10952 cm⁻¹, 16584–17763 cm⁻¹, 22753–24601 cm⁻¹ for ν₁, ν₂ and ν₃, respectively. These bands are assigned to the transitions 3A₂g(F)-3T₂g(F) (ν₁), 3A₂g(F)-3T₁g(F) (ν₂) and 3A₂g(F)-3T₁g(P) (ν₃),

Table 2 ¹H NMR spectral data of metal complexes.

<table>
<thead>
<tr>
<th>Sr. no.</th>
<th>Metal complexes</th>
<th>¹H NMR (DMSO-d₆)/ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>fbmmot (C₅H₅N₄OSF)</td>
<td>2.5 (s, 3H, -CH₃), 7.1–8.4 (m, 4H, Ar-H)</td>
</tr>
<tr>
<td>2</td>
<td>afmmot (C₅H₅N₄O₂S)</td>
<td>2.5 (s, 3H, -CH₃), 6.3–7.6 (m, 3H, Ar-H)</td>
</tr>
<tr>
<td>3</td>
<td>Zn(fbmmot)OAc.3H₂O (C₁₁H₁₁N₈O₃S⁻F⁻)</td>
<td>2.5 (s, 3H, Triazine-CH₃), 9.2 (s, 1H, -N=CH-), 7.2–8.2 (m, 4H, Ar-H), 2.4(s,3H, CH₃COO⁻)</td>
</tr>
<tr>
<td>4</td>
<td>Zn(fbmmot)₂H₂O (C₁₀H₁₀N₄O₄S⁻F⁻)</td>
<td>2.5 (s, 3H, Triazine-CH₃), 9.2 (s, 1H, -N=CH-), 7.1–8.3 (m, 4H, Ar-H)</td>
</tr>
<tr>
<td>5</td>
<td>Zn(afmmot)OAc.3H₂O (C₁₀H₁₀N₈O₃S⁻F⁻)</td>
<td>2.5 (s, 3H, Triazine-CH₃), 2.3 (s, 1H, -N=C-CH₃), 6.5–7.6 (m, 3H, Ar-H), 2.4(s,3H, CH₃COO⁻)</td>
</tr>
<tr>
<td>6</td>
<td>Zn(afmmot)₂H₂O (C₁₃H₁₇N₈O₄S⁻F⁻)</td>
<td>2.5 (s, 3H, Triazine-CH₃), 2.3 (s, 3H, -N=C-CH₃), 6.5–7.6 (m, 3H, Ar-H)</td>
</tr>
</tbody>
</table>

Table 3 Electronic Spectral data of metal complexes.

<table>
<thead>
<tr>
<th>Sr. no.</th>
<th>Metal complexes</th>
<th>Electronic spectra</th>
<th>B.M./µ eff</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Co(fbmmot)OAc.3H₂O (C₁₃H₁₇N₄CoO₆SF)</td>
<td>10940, 20553</td>
<td>4T₁g(F)-4T₂g(F) (ν₁), 4T₁g(F)-4T₂g(P) (ν₃)</td>
</tr>
<tr>
<td>2</td>
<td>Co(fbmmot)₂H₂O (C₁₀H₁₀N₄CoO₄S⁻F⁻)</td>
<td>10945, 20533</td>
<td>4T₁g(F)-4T₂g(F) (ν₁), 4T₁g(F)-4T₂g(P) (ν₃)</td>
</tr>
<tr>
<td>3</td>
<td>Ni(fbmmot)OAc.3H₂O (C₁₁H₁₁N₈NiO₃SF)</td>
<td>10952,16584, 22753</td>
<td>1A₂g(F) – 3T₂g(F) (ν₁), 1A₂g(F) – 3T₁g(F) (ν₂), 1A₂g(F)– 3T₁g(P) (ν₃)</td>
</tr>
<tr>
<td>4</td>
<td>Ni(fbmmot)₂H₂O (C₁₀H₁₀N₈NiO₄S⁻)</td>
<td>10940, 16584, 23270</td>
<td>1A₂g(F) – 3T₂g(F) (ν₁), 1A₂g(F) – 3T₁g(F) (ν₂), 1A₂g(F)– 3T₁g(P) (ν₃)</td>
</tr>
<tr>
<td>5</td>
<td>Cu(fbmmot)OAc.3H₂O (C₁₁H₁₄N₄CuO₄SF)</td>
<td>18555</td>
<td>3B₁g–5A₁g</td>
</tr>
<tr>
<td>6</td>
<td>Cu(fbmmot)₂H₂O (C₁₀H₁₁N₄CuO₄S⁻F⁻)</td>
<td>18559</td>
<td>3B₁g–5A₁g</td>
</tr>
<tr>
<td>7</td>
<td>Co(fbmmot)OAc.3H₂O (C₁₁H₁₁N₈CoO₄S⁻)</td>
<td>9949, 18666</td>
<td>4T₁g(F)-4T₂g(F) (ν₁), 4T₁g(F)-4T₂g(P) (ν₃)</td>
</tr>
<tr>
<td>8</td>
<td>Co(fbmmot)₂H₂O (C₁₀H₁₀N₈CoO₄S⁻)</td>
<td>9930, 18583</td>
<td>4T₁g(F)-4T₂g(F) (ν₁), 4T₁g(F)-4T₂g(P) (ν₃)</td>
</tr>
<tr>
<td>9</td>
<td>Ni(fbmmot)OAc.3H₂O (C₁₁H₁₁N₈NiO₄S⁻)</td>
<td>10100, 17561, 24538</td>
<td>1A₂g(F) – 3T₂g(F) (ν₁), 1A₂g(F) – 3T₁g(F) (ν₂), 1A₂g(F)– 3T₁g(P) (ν₃)</td>
</tr>
<tr>
<td>10</td>
<td>Ni(fbmmot)₂H₂O (C₁₀H₁₀N₈NiO₄S⁻)</td>
<td>9998, 17763, 24601</td>
<td>1A₂g(F) – 3T₂g(F) (ν₁), 1A₂g(F) – 3T₁g(F) (ν₂), 1A₂g(F)– 3T₁g(P) (ν₃)</td>
</tr>
<tr>
<td>11</td>
<td>Cu(fbmmot)OAc.3H₂O (C₁₁H₁₄N₄CuO₄S⁻)</td>
<td>17655</td>
<td>3B₁g–5A₁g</td>
</tr>
<tr>
<td>12</td>
<td>Cu(fbmmot)₂H₂O (C₁₀H₁₁N₄CuO₄S⁻)</td>
<td>17568</td>
<td>3B₁g–5A₁g</td>
</tr>
</tbody>
</table>
respectively, consistent with their well defined octahedral configuration.\textsuperscript{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.\textsuperscript{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 \(\mu_{\text{eff}}\) \((5.0–4.3\ \text{BM}), (3.2–2.8\ \text{BM})\) and \((1.8–1.7\ \text{BM})\), 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.\textsuperscript{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 decomposition\textsuperscript{14} observed is almost similar therefore only two complexes Ni(fbmmot)OAc.3H\(_2\)O and Zn(fbmmot)\(_2\)2H\(_2\)O 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.3H\(_2\)O 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 2 Thermoanalytical curves of Ni(fbmmot)OAc.3H\(_2\)O and Zn(fbmmot)\(_2\)2H\(_2\)O.
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 substituent 26–27 (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(fbmmot).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 the formation of Zn(triazine). 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 geometries 28 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-mercaptop-6-
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.

Acknowledgements

Kiran Singh is highly thankful to Chairman, Department of Chemistry, Kurukshetra University Kurukshetra for providing necessary laboratory facilities. Thanks are also due to SAIF, Punjab University Chandigarh, for providing C, H, N analyses and spectral data.

References