Triazoles as Complexing Agents: Synthesis & Characterisation of Cobalt(II), Nickel(II), Copper(II), Copper(II), Zinc(II) & Cadmium(II) Complexes with 4-Amino-5-mercapto-3-n-propyl-s-triazole & 5-Mercapto-3-n-propyl-4-salicylidineamino-s-triazole

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Complexes of Co(II), Ni(II), Cu(I), Cu(II), Zn(II) and Cd(II) with 4-amino-5-mercapto-3-n-propyl-s-triazole (AMPT) and 5-mercapto-3-n-propyl-4-salicylidineamino-s-triazole (MPST) have been synthesized and characterized by elemental analyses, reflectance and IR spectral data and magnetic susceptibility measurements. It is proposed that AMPT acts as a bidentate S, N donor and MPST acts as a terdentate S, N, O donor in the present complexes. Thermal stabilities of the complexes are also reported. The properties of the complex compounds suggest that they are polymeric in nature.

Chemistry of s-triazoles has been reviewed by Kroger et al.3,4 A series of 3-alkylaryl)-4-amino-5-mercapto-s-triazoles have been prepared3,4 and their analgetic and anti-inflammatory activities have been determined5. Some studies6,7 on the complex forming ability of s-triazoles with various metal ions have been also reported. The ligand derived from benzaldehyde and 4-amino-3-ethyl-5-mercapto-s-triazole has been reported to form complexes with some metal ions. Prompted by the above observations, we thought it of interest to synthesize and characterize 4-amino-3-propyl-5-mercapto-s-triazole (AMPT) and 5-mercapto-3-n-propyl-4-salicylidineamino-s-triazole (MPST), and their complexes with Co(II), Ni(II), Cu(II), Cu(II), Zn(II) and Cd(II).

Materials and Methods
All the chemicals used were of AR grade. Ethanol and ether were dried by usual procedure and were distilled prior to use. Salicylaldehyde was purchased from M/s Sarabhai Chemicals. Bivalent metal acetates [in case of Zn(II), zinc sulphate] were used for preparing complexes. Metals were analysed using standard methods. Sulphur was determined by fusing the compounds in a nickel crucible with NaOH pellets and Na2O2 and precipitating it as BaSO4.

4-Amino-5-mercapto-3-n-propyl-s-triazole (AMPT) (I)
It was prepared by the method given by Pujari et al., m.p. 104° (70%); IR(nujol): 3260, 3140 (vN - H), 2585 (vS - H), 1620 (conjugated vC = N), 1560 (vC - N), 1120 (vC = S); PMR(acetone-d6): 1.00 (3H, t, CH3 -), 1.78 (2H, m, CH3CH2CH2), 2.75 (2H, t, CH3CH2CH2), 5.24 (2H, s, NH2, disappeared in D2O exchange), 12.40 (1H, br, s, S - H, disappeared on D2O exchange).

5-Mercapto-3-n-propyl-4-salicylidineamino-s-triazole (MPST) (II)
It was prepared by refluxing a mixture of 4-amino-5-mercapto-3-n-propyl-s-triazole and salicylaldehyde in equimolar ratio in absolute ethanol containing a few drops of piperidine for about an hour. The volume was reduced and reaction mixture was kept at room temperature. The product so obtained was filtered and crystallized from ethanol, m.p. 155° (60%); IR(nujol): 3100, 3060 (vN = H or aromatic vC = H), 2590w (vS = H)
complexes of the types $ML_2H_3Cu(I)$, with AMPT as the ligand. Reactions of metal $Co(II)$, $Ni(II)$, $Zn(II)$ and $Cd(II)$ and 1:1 complex with data indicate the formation of 1:2 complexes with metal complexes are given in Table 1. The analytical Results and Discussion complex separated as a green solid. The $Cu(II)$ (-SH) forms and hence give characteristic thione bands in their IR spectra. A broad band around 3100 cm$^{-1}$ due to ($N \equiv CH$) indicates the thione form while a very weak band in the region 2560-2550 cm$^{-1}$ suggests thiol form of the ligands. Another band at 1120 for AMPT and 1115 cm$^{-1}$ for MPST is assigned to $v(C = S)$ mode. The high intensity bands at 1620 and 1290 cm$^{-1}$ (MPST) are assigned to $v(N = CH)$ and phenolic $C \equiv O$ vibrations respectively. The findings from IR have been further confirmed by PMR data.

Preparation of complexes with AMPT

Aqueous solution of the metal acetate in case of $Co(II), Ni(II), Cu(II)$ and metal sulphate in case of $Zn(II)$ (0.05 M) was treated with hot aqueous solution of AMPT in 1:2 and 1:3 molar ratios. The solution was made alkaline with sodium carbonate solution. In the case of $Co(II)$, a pink coloured complex was formed in the beginning which remained stable up to $pH$ 6.5. On raising the $pH$, the pink coloured complex gradually changed to blue which was stable above $pH$ 7.0. $Ni(II)$ complex was formed immediately and separated as a green mass. $Cu(II)$ complex appeared as a blue mass which reduced to $Cu(I)$ and the resultant complex settled down as a white amorphous mass. $Zn(II)$ and $Cd(II)$ complexes were colourless. The solids so obtained were filtered, washed repeatedly with hot distilled water, ethanol, ether and dried in vacuo.

Preparation of complexes with MPST

Aqueous solution of $Co(II), Ni(II), Cu(II)$ or $Cd(II)$ acetate or $Zn(II)$ sulphate was refluxed on a water-bath in 1:1 molar ratio. A reddish-brown coloured complex separated as a green solid. The $Cu(II)$ complex was obtained. $Ni(II)$ complex separated as a green solid. The $Cu(II)$ complex separated as a dark-green mass. $Zn(II)$ and $Cd(II)$ formed dull white complexes. The products so obtained were filtered, washed several times with hot distilled water, ethanol and dried in vacuo.

The following changes have been observed in the IR spectra of complexes (i) The band around 2550 cm$^{-1}$ due to ($S \equiv H$) is absent in the spectra of the complexes indicating deprotonation of thiol group and formation of metal-sulphur bond$^{1,2}$, which is further confirmed by the appearance of a band in the region 380-340 cm$^{-1}$, (ii) lowering of $v(C = S) = (1100-1075$ cm$^{-1}$) indicates that coordination takes place through sulphur atom, (iii) $v(N = CH)$ for metal-MPST complexes appears in the region 1605-1590 cm$^{-1}$ suggesting the coordination through amino nitrogen atom and formation of metal-nitrogen bond$^{1,3}$, which is further confirmed by appearance of a band in the region 520-480 cm$^{-1}$. Phenolic $C \equiv O$ vibration appears in the region 1330-1310 cm$^{-1}$ in metal complexes. The presence of intramolecular hydrogen bonding in the ligand MPST is indicated by a sharp peak at 3120 cm$^{-1}$, which disappears in the $M(MPST)_2$ complexes (M = Co, Ni, Cu and Cd) and a broad band, due to intermolecular association, appears in the region 3210-3240 cm$^{-1}$. Thus, the formation of a coordinate bond between oxygen of the OH group and the metal is inferred. The above account clearly indicates the bidentate (N and S donor atoms) and terdentate (N, S and O as donor atoms) nature of AMPT and MPST respectively.

The presence of coordinating water in complexes containing water molecules is indicated by a broad band around 3400 cm$^{-1}$ and somewhat weaker bands around 850 and 700 cm$^{-1}$ assigned to OH stretching, rocking and wagging vibrations$^{1,3}$ respectively. Thermal analyses of Co(MPST)$_2$, $Ni(MPST)_2$ and $Cd(MPST)_2$ have been carried out up to 950°C. In case of Co(MPST)$_2$, $Ni(MPST)_2$ and $Cd(MPST)_2$, three water molecules were lost in three clear steps corresponding to minima of endothermic peaks observed at 75°C (DTG), 180°C (DTA) and 200°C (DTG curve). The respective mass losses, theoretical (observed) are: 4.80% (4.90%), 9.65% (9.61%) and 14.47% (14.61%). In the second stage of decomposition, the anhydrous complex is converted to $Co_2O_3$ at 690°C which is indicated by endothermic peaks in DTG and DTA curves. The formation of $Co_2O_3$ is indicated by endothermic peaks in DTG and DTA curves at 835°C. The thermal degradation of the complex can be depicted as follows.

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### Table I — Characterisation Data of the Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>Found (calc.) %</th>
<th>M</th>
<th>C</th>
<th>H</th>
<th>S</th>
<th>(B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂H₂N₄S(AMPT)</td>
<td>Shining white</td>
<td>38.8 6.05</td>
<td>20.21</td>
<td>3.84</td>
<td></td>
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<tr>
<td>C₂H₂N₄S₂Co</td>
<td>Blue</td>
<td>15.26</td>
<td>(15.75)</td>
<td>(32.17)</td>
<td>(4.82)</td>
<td>(17.16)</td>
<td></td>
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<tr>
<td>C₂H₂N₄S₂Co·2H₂O</td>
<td>Pink</td>
<td>15.02</td>
<td>31.55</td>
<td>5.21</td>
<td>15.25</td>
<td>4.69</td>
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<tr>
<td>C₂H₂N₄S₂Ni·2H₂O</td>
<td>Green</td>
<td>14.70</td>
<td>29.52</td>
<td>4.91</td>
<td>15.54</td>
<td>3.12</td>
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<tr>
<td>C₂H₂N₄S₂Cu</td>
<td>White</td>
<td>29.50</td>
<td>26.66</td>
<td>4.27</td>
<td>14.01</td>
<td></td>
<td></td>
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<tr>
<td>C₂H₂N₄S₂Zn</td>
<td>White</td>
<td>17.06</td>
<td>32.34</td>
<td>4.60</td>
<td>17.50</td>
<td></td>
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<tr>
<td>C₂H₂N₄S₂Cd</td>
<td>White</td>
<td>25.28</td>
<td>28.24</td>
<td>4.17</td>
<td>14.88</td>
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<tr>
<td>C₂H₂N₄S₂(MPST)</td>
<td>Light yellow</td>
<td>54.25</td>
<td>5.09</td>
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<tr>
<td>C₂H₂N₄S₂Co·3H₂O</td>
<td>Reddish brown</td>
<td>16.87</td>
<td>39.25</td>
<td>4.26</td>
<td>4.45</td>
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<tr>
<td>C₂H₂N₄S₂Co·2H₂O</td>
<td>Brown</td>
<td>10.78</td>
<td>48.85</td>
<td>4.34</td>
<td>4.92</td>
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<tr>
<td>C₂H₂N₄S₂Ni·3H₂O</td>
<td>Green</td>
<td>16.31</td>
<td>40.02</td>
<td>4.55</td>
<td>3.20</td>
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<tr>
<td>C₂H₂N₄S₂Ni</td>
<td>Green</td>
<td>9.84</td>
<td>48.14</td>
<td>4.19</td>
<td>2.95</td>
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<tr>
<td>C₂H₂N₄S₂Cu·H₂O</td>
<td>Dark green</td>
<td>10.44</td>
<td>48.08</td>
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<tr>
<td>C₂H₂N₄S₂Cu</td>
<td>Green</td>
<td>10.89</td>
<td>49.02</td>
<td>4.15</td>
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<tr>
<td>C₂H₂N₄S₂Zn·H₂O</td>
<td>Yellowish</td>
<td>17.40</td>
<td>42.25</td>
<td>4.09</td>
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<tr>
<td>C₂H₂N₄S₂Co·H₂O</td>
<td>White</td>
<td>27.83</td>
<td>38.29</td>
<td>3.60</td>
<td></td>
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<tr>
<td>C₂H₂N₄S₂Cd·H₂O</td>
<td>White</td>
<td>17.66</td>
<td>45.56</td>
<td>4.12</td>
<td></td>
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</table>

**Note:**
- In case of Cu(MPST)_2, organic part starts decomposing at 170°C. The formation of CuS and SO₂ is indicated by an exothermic peak in DTG curve at 575°C [mass loss: 72.75% (73.88%)]. Finally, the compound is converted into CuO as indicated by endothermic peaks in DTG and DTA curves at 910°C [mass loss: 86.43% (87.88%)]. The thermal degradation of the compound may be represented as follows:
  
  \[
  \text{Cu(MPST)}_2 \xrightarrow{170°C} \text{CuS} + \text{SO}_2 \xrightarrow{910°C} \text{CuO}
  \]

  *Thermogram of Cd(MPST)_2 is almost identical with that of Cu(MPST)_2. The thermal degradation of this complex is indicated as given below:

  \[
  \text{Cd(MPST)}_2 \xrightarrow{200°C} \text{CdS} + \text{SO}_2 \xrightarrow{905°C} \text{CdO}
  \]

**Magnetic measurements and electronic spectra**

Due to the insolubility of metal complexes, it was not possible to study their solution spectra. Therefore, only mull spectra in the region 200-1700 nm have been studied.

**Co(II) complexes**

Cobalt(II) forms blue and pink coloured complexes with AMPT of compositions Co(AMPT)_2 and Co(AMPT)_2·2H₂O respectively. The complexes formed with MPST are brown and reddish-brown having the compositions Co(MPST)_2·3H₂O and Co(MPST)_2·2H₂O. Except for Co(AMPT)_2, the µ_eff. values of Co(II) complexes (Table I) are within the range...
green and yellowish-green coloured complexes with as expected for a complex. The electronic spectrum of Cu(AMPT) showed absorption bands at 8,550 and 17,370 cm\(^{-1}\) which may be assigned to the transitions \(^4A_2 \rightarrow ^4T_{1g}\) \(P_{(x^2-y^2)}\) and \(^4A_2 \rightarrow ^4T_{2g}\) \(P_{(xy, xz, yz)}\) respectively in a \(T_d\) field. The above electronic transitions coupled with the observed magnetic moment value of 3.84 B.M. indicated tetrahedral nature of Cu(AMPT) complex.

The electronic spectra of other Co(II) complexes showed absorption bands in the regions 7690-8300, 11000-11500 and 23000-25000 cm\(^{-1}\) which may be assigned to the transitions \( ^3T_{1g} \rightarrow ^3T_{2g}\) \(P_{(x^2-y^2)}\), \( ^3T_{1g} \rightarrow ^3T_{2g}\) \(P_{(xy, xz, yz)}\) and \( ^3T_{1g} \rightarrow ^3T_{2g}\) \(P_{(x^2-y^2)}\) respectively in an octahedral field. The octahedral geometry for Co(AMPT)\(_2\).2H\(_2\)O, Co(MPST)\(_3\).3H\(_2\)O and Cu(MPST)\(_2\) is confirmed by the observed magnetic moments.

**Ni(II) complexes**

Ni(II) forms green coloured complexes with AMPT and MPST having the compositions Ni(AMPT)\(_2\).2H\(_2\)O, Ni(MPST)\(_3\).3H\(_2\)O and Ni(MPST)\(_2\). Their magnetic moment values (Table 1) are within the range (2.80-3.50 B.M.) expected for spin-free octahedral Ni(II) complexes.

The electronic spectra of above-mentioned Ni(II) complexes showed absorption bands in the regions 7690-8300, 11000-11500 and 23000-25000 cm\(^{-1}\) which may be assigned to the transitions \( ^3A_2 \rightarrow ^3T_{1g}\) \(P_{(x^2-y^2)}\), \( ^3A_2 \rightarrow ^3T_{2g}\) \(P_{(xy, xz, yz)}\), \( ^3A_2 \rightarrow ^3T_{1g}\) \(P_{(x^2-y^2)}\) and \( ^3A_2 \rightarrow ^3T_{2g}\) \(P_{(xy, xz, yz)}\) respectively. The electronic spectral data coupled with the magnetic moment data favour octahedral geometry for Ni(II) complexes.

**Copper complexes**

Cu(AMPT) complex is colourless and diamagnetic as expected for a \(d^8\) ion. Copper(I) formed dark-green and yellowish-green coloured complexes with MPST having the compositions Cu(MPST)\(_2\).H\(_2\)O and Cu(MPST)\(_2\). The electronic spectra of Cu(MPST)\(_2\).H\(_2\)O and Cu(MPST)\(_2\) showed one broad absorption band in the visible region around 17000 cm\(^{-1}\) which has been attributed to \( ^2E \rightarrow ^2T_{2g}\) transition. The electronic spectra coupled with magnetic and thermal studies indicate square-planar and octahedral geometries for Cu(MPST)\(_2\).H\(_2\)O and Cu(MPST)\(_2\) complexes respectively.

**Zn(II) and Cd(II) complexes**

Zn(II) and Cd(II) form 1:2 complexes with AMPT having the composition M(AMPT)\(_2\), where M = Zn or Cd. With MPST, they form complexes of the types Zn(MPST)\(_2\).H\(_2\)O, Cd(MPST)\(_2\).H\(_2\)O and Cd(MPST)\(_2\). The complexes are colourless and diamagnetic. On the basis of 1:2 stoichiometry and known coordination preferences, tetrahedral geometry for M(AMPT)\(_2\) (M = Zn or Cd) and M(MPST)\(_2\).H\(_2\)O (M = Zn or Cd) complexes, and octahedral geometry for Cd(MPST)\(_2\) complex can be proposed. Thermal study of Cd(MPST)\(_2\) also supports its octahedral geometry.

The properties of these complexes like insolubility in non-coordinating solvents, their insubility up to 280°C, IR, electronic and magnetic studies indicate that they may be polymeric in nature.

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**References**