Copper (I) complexes of 2-thiouracil

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Copper complexes obtained from the reactions between 2-thiouracil and cupric hydroxide in different solvents have been investigated. Mononuclear or polynuclear complexes of Cu(I) have been obtained depending on the reaction conditions. Hydroxo complexes of copper(I) have been obtained at pH around 3.5. 2-Thiouracil acts as mono- or bidentate ligand in complexes. [Cu(H2TU)2OH], [Cu3(H2TU)6(OH)5] and [Cu3(H2TU)4-(HTU)(OH)2] have been obtained from the aqueous ethanolic, aqueous and dioxan solutions, respectively. Oligomeric structures of polynuclear complexes are suggested to be via the bridging of copper atoms through electron donating atoms of bidentate thiouracil. The complex, [Cu3(H2TU)4(HTU)(OH)2], reacts with concentrated HCl to give [Cu3(H2TU)4Cl3], in which its trinuclear structure is preserved. The properties and structure of [Cu3(H2TU)4Cl3] are different from those of [Cu(H2TU)2Cl], which is synthesized from cuprous chloride. Spectral, thermal, magnetic studies and elemental analyses for the complexes have been carried out.

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2-Thiouracil [2,3-dihydro-2-thioxo-(1H)pyrimidin-4-one], [H2TU], is one of the components of transfer ribonucleic acid. H2TU and its substituted thiouracils have shown therapeutic effects, such as anti-tumour and anti-thyroid activities1-3. 2-Thiouracil exhibits several tautomeric forms which allow several coordination routes for metals and also provides hydrogen bonding sites to give highly stable compounds4.

Most of the transition metal complexes5,6 of 2-thiouracil have been obtained at neutral pHs and involve the deprotonated ligand (HTU-) in the complexes of the type, Me(HTU)2, or a dimer or a polynuclear polymer Me2(TU)n with N, S bridging. At higher pHs (e.g., 7.5-10.5) equimolar mixture of Pb(II) or Cd(II) with H2TU, Me2(TU)2 dimers have been isolated6.

Studies of the compositions and structures of copper 2-thiouracil complexes have been subject of many investigations. Oxidation state of copper in complexes has been dependent on the kind of reaction medium and working conditions. In neutral or alkaline solutions, Cu(II) complexes are obtained. Refluxing tetraamine Cu(II) and H2TU in dioxane solution gives two Cu(II) complexes: brown [Cu(HTU)(OH)(H2O)2.3H2O]7 and green [Cu(HTU)(OH)]8. Mixed ligand complexes of glycine or histidine with H2TU contain Cu(II) which is in contradiction with the diamagnetic properties of complexes. This phenomenon has been explained by dimerization of Cu(II) complexes9,10, which is supported by the presence of band at 27,780 cm⁻¹ in their electronic spectra9,10.

However, copper(II) reacts with H2TU in neutral aqueous solution to give an acidic solution with simultaneous formation of Cu(I) complexes6,12. Redox between Cu(II) and H2TU gives Cu(I) and the disulphide of H2TU, namely, bis(4-hydroxy-2-pyrimidinyl) disulphide. The disulphide disproportionates in acidic solution to give sulfinic acid and H2TU6, 12-15. Disulphide formation has also been shown by x-ray photoelectron spectrometry16.

\[
\begin{align*}
R-SH & \leftrightarrow R-S^- + H^+ \quad (pK_a = 7.46 \, (25^\circ C) (Ref. \, 6)) \quad (1) \\
2 \, R-SH + 2 \, Cu^{2+} & \rightarrow R-S-S-R + 2 \, Cu^+ + 2 \, H^+ \quad (2) \\
2 \, R-S-S-R + 2 \, H_2O & \rightarrow R-SO_2H + 3 \, R-SH \quad (3)
\end{align*}
\]

Thus, the acidity of solution is important to catalyze the redox reaction. This acidity can be achieved by self ionization of H2TU or more effectively via acid addition. In warm acidic (6% HCl) solution, cupric acetate reacts to give a cyclic tetramer [Cu4(HTU)4] along with [Cu2(H2TU)3Cl2], in which coppers are at cuprous state17.

In organic solvents the complexation can give Cu(I) complexes in different yields along with Cu(II) complexes. Although CuCl2 reacts with H2TU to give the Cu(I) complex [Cu(H2TU)2Cl], in refluxing acetone-methanol mixture, only the Cu(II) complex, [Cu(HTU)Cl]2, is obtained in refluxing methanol17.
The binding modes of thiouracil in complexes have been reported to be thione sulfur alone or along with N(3) for H₂TU ligand. For deprotonated ligand, coordination to metal ion through carbonyl oxygen have also been reported. Thus, various complexation routes are possible depending on the reaction conditions and oxidation state of copper.

In the present study, we have investigated the reaction between 2-thiouracil (H₂TU) and cupric hydroxide Cu(OH)₂. The structures of the complexes have been elucidated by spectroscopic studies, magnetic susceptibility measurements, elemental analyses and DTA/TGA data. Single crystals could not be obtained for X-ray studies.

Experimental
Copper hydroxide was prepared starting from copper sulphate and dried under vacuum. 2-Thiouracil and other chemicals were reagent grade (Fluka). Copper hydroxide was prepared from a reaction between 2-thiouracil (H₂TU) and cupric sulphate and dried under vacuum. 2-Thiouracil was dissolved in distilled water and 10% NH₃ solution was added dropwise with vigorous stirring until blue color disappeared. The copper(II) hydroxide formed was filtered, washed with distilled water of pH 9.5-10; and dried in vacuo over concentrated sulfuric acid.

To prepare copper hydroxide, CuSO₄.5H₂O (50 g) and other chemicals were reagent grade (Fluka). Copper hydroxide was prepared starting from copper sulphate and dried under vacuum. 2-Thiouracil was dissolved in hot water and NaOH (10%) solution was added to get the dark blue hexaammine copper complex. To this, Cu(OH)₂ (20 mmol) was added. The suspension (pH: 4.09) was refuxed for 2 hr and filtered hot. The greenish light yellow precipitate (complex I) was washed with hot EtOH : water (4:5) and finally dried in vacuo. Yield 3.0 g (44%). [Cu(H₂TU)₂OH], m.p. 230°C (decomp).

IR(KBr, ν/cm⁻¹): 3432 (O-H str, m, br), 3086,3051(C-H / N-H str, m), 1704 (C=O str, m), 1636 (O=C-N bend, s), 1625 (amide II, m), 1562 (thioamide I, s), 1215 (N-C-S bend, s), 1176 (s), 1158 (m) (ν N-C-S), 837 (m), 822 (sh) (ν CS), 547 (amide IV, s). ¹H NMR (200 MHz, δ, ppm): 7.40 (H(6), d, 1H), 5.81 (H(5), d, 2H), 3.33 [Cu(H₂TU)₂, 1.2%]; 308 [m -Cu, 19%], 307 [CuOH₂, 26%], 292 [Cu₂H₂O, 4%], 128 [H₂TU, 68%], 69 [128-HNCS, 100%].

Preparation of the complexes
Complex (I) [Cu(H₂TU)₂(OH)]

H₂TU (5.1 g, 40 mmol) was dissolved in 90 mL of warm ethanol: water (4:5, ν/ν, pH:5.42) and 1.94 g Cu(OH)₂ (20 mmol) was added. The suspension (pH: 4.09) was refuxed for 2 hr and filtered hot. The greenish light yellow precipitate (complex I) was washed with hot EtOH : water (4:5) and finally dried in vacuo. Yield 3.0 g (44%). [Cu(H₂TU)₂OH], m.p. 230°C (decomp).

IR(KBr, ν/cm⁻¹): 3432 (O-H str, m, br), 3086,3051(C-H / N-H str, m), 1704 (C=O str, m), 1636 (O=C-N bend, s), 1625 (amide II, m), 1562 (thioamide I, s), 1215 (N-C-S bend, s), 1176 (s), 1158 (m) (ν N-C-S), 837 (m), 822 (sh) (ν CS), 547 (amide IV, s). ¹H NMR (200 MHz, δ, ppm): 7.40 (H(6), d, 1H), 5.81 (H(5), d, 2H), 3.33 [Cu(H₂TU)₂, 1.2%]; 308 [m -Cu, 19%], 307 [CuOH₂, 26%], 292 [Cu₂H₂O, 4%], 128 [H₂TU, 68%], 69 [128-HNCS, 100%].

Complex (II) [Cu₂(H₂TU)₂(OH)₃]

H₂TU (4 g, 31 mmol) was dissolved in hot water (150 mL) (pH:4.15) and Cu(OH)₂ (1.40 g, 14.3 mmol) was added (pH:3.33). The mixture was heated at 80-85°C for 2 hrs. The low density portion of the suspension was separated from the small amount of high density portion by decantation and filtered hot. It was washed with hot water and then with acetone. The light yellow compound (II) was isolated in 48% yield (1.6 g), [Cu₂(H₂TU)₆(OH)₅], m. pt.: 245°C (decomp).

IR(KBr, ν/cm⁻¹): 3440 (O-H str, m, br), 3110, 3084(N-H/C-H m, br), 1701 (C=O, str, m), 1647 (O=C-N bend, s), 1628 (amide II, s), 1534 (thioamide I, s), 1200 (N-C-S bend, m), 1159 (thioamide III, νC=N, s), 827 (thioamide II, νC=S, s), 837 (thioamide IV, νC=S, s), 761 (thioamide V, νC=O, s), 548 (amide VI, νC=O, s). ¹H NMR(200 MHz, δ, ppm): 12.35 (NH, b, 2H), 7.43 (H(6), d, 1H), 5.86 (H(5), d, 1H) J=7.5 ppm. ¹³C NMR (50 MHz, ppm): 176.1 (C(2)), 161.1 (C(4)), 105.4 (C(5)), 142.2 (C(6)).
141.96 [C(6)]. Mass (70 ev, m/z (%)): 1106.7 [M-H-Cu, 0.5%], 1022.0 [M-H-Cu-5OH, 0.8], 765.5 [4Cu3H2TU. HTU, 1.1], 385.0 [3H2TU, 2.3], 208.8 [H2TUCuOH, 1.7], 191.2 [H2TUCu, 1.7].

Complex (III) [Cu3(H2TU)4 (HTU) (OH)]

H2TU (5.1 g, 40 mmol) and Cu(OH)2 (1.94 g, 20 mmol) was suspended in 100 mL dioxane and refluxed for 5 hrs at 95-103°C. The low-density light yellow solid part was separated from high-density greenish particles (complex I) by decantation; filtered, washed with hot dioxane and dried in vacuo. The filtrate was reddish-yellow in colour. The light yellow compound (III) [Cu3(H2TU)4 (HTU) (OH)] was obtained in 37% (2.1 g) yield; m. pt.: 270-271°C (decomp.).

IR(KBr, ν/cm-1): 3474 (O-H str, s, br), 3089 (NH, b, 6H), 7.42 [H(6)d, 4H], 7.66 [H(6)], 5.85 [H(5), d, 2H]. 1H-NMR (200 MHz, DMSO-d6): 12.33 (NH, b, 6H), 7.48 [H(6)d, 4H], 7.66 [H(6)], 5.93 [H(5), d, 2H]. 3Cu, 0.5% [Cu3H2TU, 1.7], 636.5 [2Cu4H2TU, 1.5], 591.9 [2Cu4H2TU, 1.1], 384.4 [3H2TU, 0.6], 190.7 [3Cu, 0.5], 127.1 [HTU, 60.6], 113 (100%).

Complex (IV) [Cu3(H2TU)4 Cl3]

III was treated with conc. HCl at room temperature, left to stand overnight, diluted with distilled water, filtered, washed with water until the washings become chloride-free and finally dried in vacuo. Complex IV [Cu3(H2TU)4 Cl3] was obtained quantitatively as pale yellow solid; m. pt. 281°C (decomp.).

IR(KBr, ν/cm-1): 3491 (O-H str, s, br), 3078 (N-H str, s, br), 1703 (C=O str, s, br), 1678 (O-C str, s), 5.85 [H(5), d, 2H]. 1H-NMR (200 MHz, DMSO-d6): 12.33 (NH, b, 6H), 12.48 (OH, b, 2H), 7.44 [H(6)d, 4H], 5.88 [H(5), d, 4H]. 3Cu, 0.5% [Cu3H2TU, 1.7], 636.5 [2Cu4H2TU, 1.5], 591.9 [2Cu4H2TU, 1.1], 384.4 [3H2TU, 0.6], 190.7 [3Cu, 0.5], 127.1 [HTU, 60.6], 113 (100%).

Complex (V) [Cu3(H2TU)4 Cl3]

H2TU (5.1 g, 40 mmol) was heated in 100 mL water (pH 4.59) to give a white slurry. To this, Cu3Cl3(1.98 g, 20 mmol) in 60 mL water was added to get a mixture of pH 2.56. The mixture was heated at about 90°C for 2 hrs and filtered hot. The precipitate was washed with 100 mL hot water and dried in vacuo to get 2.72 g (19%) of [Cu(H2TU)2 Cl] (V) as greenish-yellow solid, m. pt. 276°C (decomp.).

IR(KBr, ν/cm-1): 3474 (O-H str, s, br), 3084(s) (C-H/N-H str, s, br), 1704 (C-O str, s), 1679 (O-C=N bending, s), 1623 (C-O, m), 1553 (thioamide I, s), 1208 (N-C=S, s), 1170(m) (thioamide III, N-C-S), 832 (thioamide IV, C=S, m), 542 (amide VI, m). 1H-NMR (200 MHz, δ, DMSO-d6): 12.30 (NH, b, 6H), 7.48 [H(6)d, 4H], 7.66 [H(6)], 5.93 [H(5), b, 2H]. 13C NMR (50MHz, ppm, DMSO-d6): 174.3 [C(2)], 159.7, [C(4)], 105.8 [C(5)], 141.4 [C(6)]. Mass (70 ev, m/z(%)): 798.3 [M-H-Cu, 0.8%], 781.2 [M-H-Cu-OH, 0.8], 764.5 [M-H-Cu-2OH, 1], 636.5 [2Cu4H2TU, 1.5], 591.9 [2Cu4H2TU, 1.1], 384.4 [3H2TU, 0.6], 190.7 [3Cu, 0.5], 127.1 [HTU, 60.6], 113 (100%).

Results and discussion

2-Thiouracil reacts with copper (II) hydroxide to give several copper (I) complexes, depending on the solvent composition. During the complexation process, the reaction medium becomes more acidic and due to the redox reactions between copper (II) and thiouracil, copper (I) complexes are formed. The oxidation product is thiouracil disulphide which was not isolated since it decomposes into sulfinic acid and thiouracil6,12-15.

Reaction of thiouracil and copper (II) hydroxide gives only one mononuclear hydroxido complex under specific conditions, but under different conditions, polynuclear complexes have been obtained. The hydroxido complexes of copper (I) have been isolated even at low pHs to indicate strong stabilization of hydroxido group via coordination to copper (I).

Effect of solvent on the complexation pathway

Composition of the solvent affects the bonding modes in the complexes. In aqueous solutions or in non-aqueous solvents the reactants give several polynuclear complexes with oligomeric structures, while in aqueous ethanol, the mononuclear complex
NOTES

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Table 1—Analytical and other physicochemical data of complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Found (Calc.) (%)</th>
<th>( \Lambda_\text{m}^a ) (DMSO)</th>
<th>( \lambda ) (nm) (e\text{_{max}})</th>
<th>Effective magnetic moment (BM) (293 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cu(H₂TU)₂OH] (I)</td>
<td>C 28.9 (28.5)</td>
<td>H 2.3 (2.7)</td>
<td>N 16.3 (16.6)</td>
<td>Cu 18.0 (18.9)</td>
</tr>
<tr>
<td>[Cu₅(H₂TU)₆(OH)₅] (II)</td>
<td>C 25.0 (24.6)</td>
<td>H 2.3 (2.45)</td>
<td>N 14.5 (14.4)</td>
<td>Cu 27.5 (27.1)</td>
</tr>
<tr>
<td>[Cu₃(H₂TU)₄-HTU(OH)₂ (III)</td>
<td>C 28.5 (27.8)</td>
<td>H 2.2 (2.4)</td>
<td>N 15.7 (16.2)</td>
<td>Cu 22.2 (22.1)</td>
</tr>
<tr>
<td>[Cu₃(H₂TU)₄Cl₃] (IV)</td>
<td>C 23.3 (23.7)</td>
<td>H 1.98 (2.0)</td>
<td>N 13.4 (13.8)</td>
<td>Cu 24.2 (23.5)</td>
</tr>
<tr>
<td>[Cu(H₂TU)₂Cl] (V)</td>
<td>C 26.3 (27.0)</td>
<td>H 2.10 (2.3)</td>
<td>N 15.2 (15.8)</td>
<td>Cu 18.1 (17.9)</td>
</tr>
</tbody>
</table>

\( ^a \text{ Millimolar conductivity in DMSO at 20}\^\circ\text{C}. \)

(I), [Cu(H₂TU)₂OH], is obtained. In aqueous solution (pH 3.33), with 1 : 2 molar ratio of Cu:H₂TU, five copper nuclei containing complex (II), [Cu₅(H₂TU)₆(OH)₅], is formed via coordination with six thiouracil ligands. In non-aqueous medium, as in dioxane, the reaction proceeds to give three copper nuclei containing complex (III), [Cu₃(H₂TU)₄-HTU(OH)₂], in which deprotonated ligand is involved.

Stability and reactions of complexes

Greenish light yellow complex (I) and light yellowish-green complex (II) are stable on heating up to 80°C. However, when complex II which is contaminated with H₂TU is heated at 80°C in air, it gives a dark green complex (IIa). Complex IIa does not have a definite composition and its colour becomes more intense by increase the heating time. The EPR data for complex IIa suggests oxidation to Cu(II) which is consistent with its magnetic susceptibility measurements. In the spectrum of IIa in DMSO, two splittings with g value of 2.157 and with hyperfine splitting constant \( a_{\text{iso}} \) 60 ± 1.0 gauss become stronger when the DMSO solution was left to stand for 5 days giving a g value of 2.159 and \( a_{\text{iso}} \) 70 ± 1.0 gauss. At 3100 G, strong full-field transition in solid IIa was observed with g value of 2.159 and anisotropic hyperfine splitting constant 227.5 ± 0.8 gauss. Increase in hyperfine splitting constant was possibly due to restriction in tumbling movements.

Complex III reacts with conc. HCl to give the chloro complex IV, [Cu₃(H₂TU)₃Cl₃], by the substitution of HTU⁻ and OH⁻ groups with chloride (Eq. 4). In this reaction, trinuclear structure of III is not changed.

\[
\text{[Cu₃(H₂TU)₄-HTU(OH)₂]} + 3\text{HCl} \rightarrow \text{[Cu₃(H₂TU)₃Cl₃]} + \text{H₂TU} + 2\text{H₂O} \quad \text{(4)}
\]

The elemental and spectral properties of complex IV are entirely different than those of an authentic sample of [Cu(H₂TU)₂Cl] (V), which has been synthesized from H₂TU and cuprous chloride. Syntheses of complex V and other complexes obtained from cupric chloride have been reported. We now report additional data for complex V.

Some analytical and physicochemical data of complexes are given in Table 1. All the complexes are amorphous. Besides complexes I and V, the other complexes are insoluble in common organic solvents as well as in water which can be attributed to the polynuclear chain structure. They are slightly soluble in DMSO at room temperature. The very low molar conductivity (S cm² mol⁻¹) values in DMSO at 20°C indicate the non-electrolyte character of the complexes.

Spectral properties of the complexes

Strong IR absorption bands of 2-thiouracil appearing at 1707 and 1684 cm⁻¹, which are assigned to ν (C=O) stretching and ν (C=C) stretching or to ν (O=C-N) bending vibrations shift in the complexes to different extents. Band broadening and shift to lower wave numbers suggest coordination through...
N(3) along with the presence of lactim OH which have been observed in the spectra of Complexes II, III and IV. In addition, the presence of ν (C=O) band at around 1707 cm⁻¹ and ν (NH) at around 3100 cm⁻¹ for the ligand indicates the contributions of the lactam and lactim forms of H₂TU in these complexes. The ν(Cu-S) bands in the far IR region at 260-235 cm⁻¹ indicate the coordination through sulfur atom. In the UV region, intense sulfur to metal charge transfer bands appearing at around 290-300 nm supporting this conclusion (Table 1). Shifts of thioamide I-IV bands indicate the contributions to the bonding via (C=S) and N(3)⁹. Thioamide III band (~1156 cm⁻¹) of thiouracil raises to higher frequencies at around 1170 cm⁻¹ while the thioamide IV band (ν Cu=S) (~837 cm⁻¹) of H₂TU is lowered to 820-830 cm⁻¹.

In non-aqueous medium, H₂TU deprotonates and thiolactim anion is involved in the coordination to
Complex overall weight loss of 58.87% is observed. Magnetic susceptibility measurements, NMR data between molecular units of complexes 11, common solvents may be due to the polymerization atoms of thiouracil. The insolubility of complexes in possibly takes place through two electron donating C(2) of tiolactim form of H2TU. In 1H NMR spectra, additional peak is observed at around 169 ppm for belonging to C(4) of lactim form. For peaks around 152 ppm appear for (C-S) bands are assigned to coordination through sulfur atoms of both C=S and thiolactim. 13C and 1H-NMR data also support these observations. In the 13C NMR spectra, additional peaks around 152 ppm appear for II, III and IV belonging to C(4) of lactim form. For III, an additional peak is observed at around 169 ppm for C(2) of tiolactim form of H2TU. In 1H NMR spectra, the N-H and C-OH protons of lactam and lactim forms appear as unresolved broad peaks in most complexes.

Thus, in the formation of oligomeric structure in II, III and IV, the bridging between copper(I) atoms possibly takes place through two electron donating atoms of thiouracil. The insolubility of complexes in common solvents may be due to the polymerization between molecular units of complexes.

Magnetic susceptibility measurements, NMR data showing the absence of band at around 360 nm, which is characteristic for dimeric copper(II) complexes 11, support the presence of copper(I) in the complexes. Magnetic moments of complexes vary from -0.8 to +0.8 B.M. Copper(I) is reported to give complexes in which it has planar trigonal coordination as in chloro forms appear as unresolved broad peaks in most images as shown by SEM images (Fig. 1).

Overall 80.54% weight loss has been observed up to 500°C.

In the chloro complex IV, [Cu3(H2TU)6Cl3 ], loses 3.90% of its weight on heating up to 181.1°C, which corresponds to the loss of one HCl molecule (theoret. 4.51%). The main step is between 271.5°C and 366.6°C with a peak at 321.6°C. The overall weight loss of 61.88 % corresponds to the residue mainly consisting of Cu3Cl6 (theoret. 36.7 %).

All the compounds show entirely different surface images as shown by SEM images (Fig. 1).

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Thiouacil itself has a very simple decomposition pattern with one decomposition step between 254-370°C. The hydroxoo complexes show weight loss of water up to nearly 240°C. Complex II, [Cu3(H2TU)6(OH)5], loses 7.94% of its weight up to 233.9°C corresponding to the loss of five water molecules (theoret. 7.69%). The second decomposition step is between 233.9-339°C (36.14%) with an exothermic peak at 309°C. Up to 600°C, an overall weight loss of 58.87% is observed.

Complex III, [Cu3(H2TU)6(HTU)(OH)2], loses 12.9% of its weight between 197.8°C and 243.1°C (exo.) corresponding to the loss of six water molecules (theoret. 12.06%). The main decomposition of complex III occurs between 243.1°C and 383.3°C, with two exothermic peaks at 313°C and 333.1°C. Other decomposition steps are seen at 370°C and 366.6°C with overall 80.54% weight loss has been observed up to 500°C. Thermal analysis

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