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Novel complexes of metal surfactants with substituted phenylthiourea and their thermogravimetric properties

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Abstract : Binuclear macrocyclic metal complexes represent an important and integral class of organic compounds which are well recognised for their multifaceted biological properties and medicinal relevance. They are no doubt the transition metal complexes which have opened new vistas of research in present era of chemistry. Related studies to them would be of immense importance to synthetic chemist, medicinal scientists as well as in pharmaceutical industry. For the same, copper soaps (derived from common fatty acids) were complexed with nitrogen and sulphur donor ligand (special reference to substituted phenylthiouea). These novel complexes were characterised by IR, NMR, ESR spectral and elemental studies. TGA analysis was studied in detail. Thermogravimetric analysis is a thermal analysis technique which measures the amount of rate of change in weight of a material as a function of temperature or time in controlled atmosphere. TGA measurements are used primarily to determine composition of soap and to predict their thermal stability up to elevated temperature.

Keywords : Copper Caprylate, Copper Oleate, Copper Palmitate, Copper Stearate, Substituted Phenylthiourea, TGA analysis.

Introduction

The synthesis of binuclear macrocyclic complexes has been the cornerstone of synthetic organic chemistry. Moreover invention of newer, cheaper and more potent analogs of molecule with already well recognised biological activities form a key part of research in pharmaceutical field. Brining about modifications by manipulating the parent structure serves to enhance the activity and overcome with adverse effects[1]. In this perspective, metal complexes of N and S chelating ligands have attracted considerable attention because of their interesting physicochemical properties[2–5] and pronounced biological and pharmacological activities. Transition metal complexes with organic ligands have been and are still viewed as promising pharmaceutical agents. It is hope that metal complexes may be behaved as therapeutics. The presence of nitrogen and sulphur atoms in the complexes give mutative ability to co-ordination sites to link directly with the transition metal ions which have attracted the chemists to prepare novel metal chelate due to their importance in antimicrobial, antiinflammatory, anitcancerous, antihelmitic, antifungal, analgesic, anticonvulsant, antituberculous applications.

Above said class of surfactants also play a vital role in various fields such as rubber industries, paints, varnishes, water proofing and repellence, protection of crops, stabilisation of nylon thread, preservation of wood, lubrication[6–15] etc.

Now, we discuss a brief summary of TGA technique. Thermogravimetric analysis is a method of thermal analysis in which changes in physical and chemical properties of material are measured as a function of temperature (with constant heat rate) or with function of time (with constant temperature or constant mass loss). This analysis covers a wide spectrum of thermoanalytical techniques. Therefore, it can be used to evaluate the thermal stability of a material. In a desired temperature range, if species is thermally stable, there is no observed mass change. Negligible mass loss corresponds to a little or no slope of TGA trace. All these indicate that material is no longer thermally stable. Because the TGA is performed in air, the oxygen reacts with the organic material which eventually degrades the material completely, with 100% mass loss. It is important to link the thermal stability to the gas in which TGA is performed. TGA can provide important information about physical phenomenon such as second

order phase transitions including vaporization, sublimation, absorption, adsorption, and desorption. Similarly important information can be gained for chemical phenomenon including chemisorptions, desolvation (especially dehydration), decomposition and solid gas reactions (oxidation and reduction).

The thermogravimetric analysis system combines thermogravimetry and differential thermal analysis and is widely used in the fields of gas/solid interactions, fuels, catalysis, polymers and chemical synthesis. TGA is commonly used to determine selected characteristics of materials that exhibit either mass loss or gain due to decomposition, oxidation or loss of volatile such as moisture. But no doubt it provides complimentary information and describes the process more precisely, save analysis time and avoid variations in experimental conditions between samples[16–18].

Common applications of TGA are

- Material characterization through analysis of characteristics decomposition patterns.
- Studies of degradation mechanisms and reaction kinetics.
- Determination of organic content in simple.
- Determination of inorganic (e.g. ash) content in simple, which may be useful for collaborating predicted material structures or simply used as a chemical analysis. It is an especially useful technique for the study of polymeric materials, including thermoplastics, thermosets, elastomers, composites, plastic films, fibres, coating and paints.

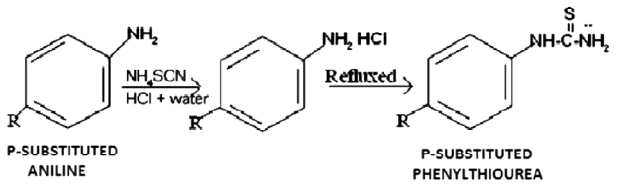
Overall interesting literature survey creates zeal to study the elemental analysis, spectral data and TGA features of copper soaps derived from fatty acids for their maximum possible benefits in agriculture medicine and industries. Hence, in view of past significant results and in continuation of our comprehensive studies on copper complexes which sulphur and nitrogen donating ligands, we report here the preparation of some novel copper complexes.

Experimental

All chemical used were of A.R. grades. All solvent were purified by standard procedures. Purity was checked by TLC the melting were determined by electric melting point apparatus and in corrected. Complexes of copper soaps with phenylthiourea as nitrogen and sulphur donor ligands were synthesised in following manner :

p-Substituted phenylthiourea :

According to Scheme 1 (0.1 mole) of *p*-substitutes aniline was heated in a 250 ml three necked flask with stirrer, dropping funnel, reflux condenser with a mixture of 9 ml (6 *N* HCl) and 25 ml water at temperature 32 °C on water bath till aniline hydrochloride is formed. Resulting solution is now cooled to room temperature and 7.6 g (0.1 mole) of NH_4SCN is added to it. Now, the reaction is refluxed for four hours on water bath. After cooling the solid separated out was filtered, washed with cold water dried and recrystallized with ethanol.



Scheme 1. Synthesis of Substituted Phenylthiourea from *p*-substituted aniline.

Copper surfactants :

Copper surfactants were prepared by mixing one gm of fatty acid into 25 ml ethyl alcohol, shake the mixture in hot water bath and then add one drop of phenolphthalein. A saturated solution of KOH in another beaker was prepared then it was added into fatty acid solution drop by drop until the light pink color appears. Now again in another beaker prepare a saturated solution of $CuSO_4$ (about 2–3 g in 5 ml H_2O) and mix it into above solution with stirring till the blue colored soap is formed. Filtered and washed with warm water and 10% ethyl alcohol then dried and recrystallised with hot benzene (Scheme 2).

$RCOOH$	+	C_2H_5OH	+	$CuSO_4$	$\longrightarrow$	$(RCOOH)_2Cu$
Fatty acid		Ethanol		Copper Sulphate		Copper Surfactant

Scheme 2. Synthesis of Copper Surfactants.

Complexation of copper surfactants with ligands :

The purified copper palmitate derived from palmitic acid was refluxed with the ligands, substituted benzothiazole and substituted phenylthiourea in 1 : 2 ra-

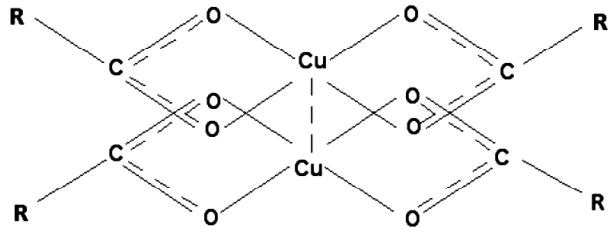


Fig. 1. Structure of synthesised copper surfactants.

Here, R = $C_{17}H_{35}$ for Copper Stearate, R = C_7H_{15} for Copper Caprylate and R = $C_{17}H_{33}$ for copper oleate.

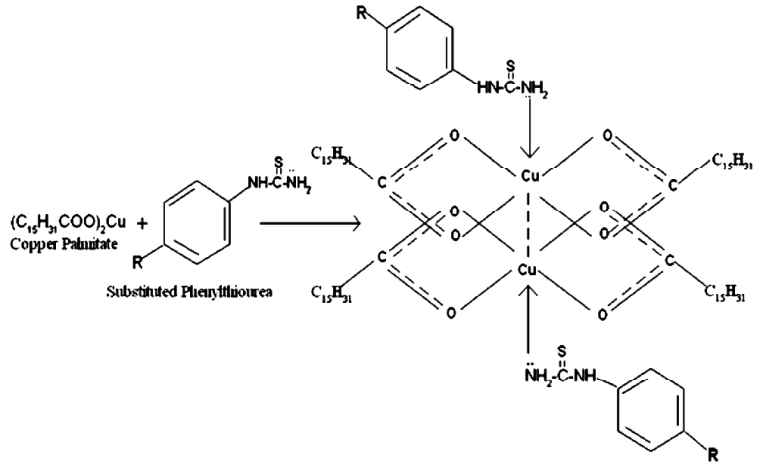
tio using ethyl alcohol as a solvent for one and half hour, it was than filtered hot, dried, recrystallised and purified in hot benzene. In general all the complexes are solid, powdered in nature. They are insoluble in water but soluble in organic solvent.

Results and discussion

TGA analysis was employed to study the kinetics of thermal decomposition of three complexes namely $CS(PTU)_{Br}$, $CC(PTU)_{Br}$, $CO(PTU)_{Br}$. The samples were sent to IIT Mumbai for thermal analysis. TGA curves were obtained by Perkin-Elmer Diamond model. Thermal behaviour of complexes was studied at nitrogen atmosphere. The results were obtained as plot of % weight vs time or temperature. The controlled atmosphere includes either the (oxygen/air) or inert conditions. To measure weight loss or gain, TGA uses heat to force reactions and physical changes in materials.

The thermal behaviour of Cu^{II} complexes including stability ranges, percentage of weight loss, percentage of residue obtained after decomposition process using thermogravimetry has been studied. Two complexes $CO(PTU)_{Br}$ and $CC(PTU)_{Br}$ undergo decomposition in one stage, which show about 90.5% decomposition (Figs. 3, 4 respectively).

The thermal decomposition of $CS(PTU)_{Br}$ (Fig. 2) was made in temperature interval from room temperature to 900 °C in stream of nitrogen. The initial weight of complex was 17.925 mg. The TGA curve was obtained at heating rate of 10 °C min^{-1}. It is evident that this copper complex decomposes in three stages by presence of three breaks in TGA graph. The sequential occurrence of thermal decomposition of stage I and stage II has occurs at 141 °C to 320 °C to 700 °C the loss of masses of about 44% and 15.29% for stage I and II respectively are recorded by the loss of parent ketone $[(C_{17}H_{35})_2CO]$ in two stages. The third step lies in range of 700 °C to 900 °C and corresponds to the loss of ligand ($C_7H_7N_3O_2S$). Mass loss of 11% accounts for the loss of one molecule of ligand into volatile matter, leaving the final residue.



Here, R = NO_2

Scheme 3. Synthesis of Complexes.

NOTE :
Complex of substituted Phenylthiourea with Copper stearate - $CS(PTU)_{Br}$
Complex of substituted Phenylthiourea with Copper caprylate - $CC(PTU)_{Br}$
Complex of substituted Phenylthiourea with Copper oleate - $CO(PTU)_{Br}$

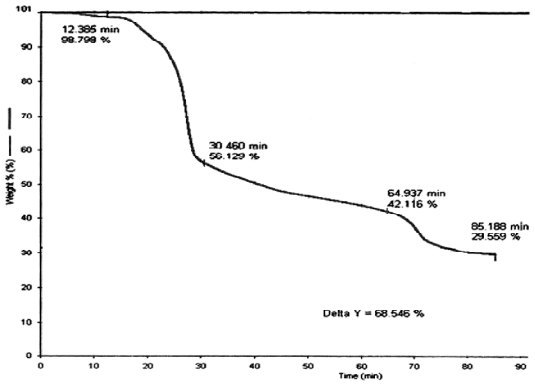


Fig. 2. TGA plot for $CS(PTU)_{Br}$.

The decomposition of $CO(PTU)_{Br}$ (Fig. 3) was recorded in temperature range 35 °C to 500 °C in nitrogen atmosphere. The curve indicates that decomposition is fairly rapid as it increases with temperature. $CO(PTU)_{Br}$ shows a one stage decomposition with weight loss of 91%. It accounts for loss of parent ketone and two ligand molecules. Beyond 360 °C a plateau indicates the formation of CuO. The percentage of cupric oxide (8.44%) found by TGA data was in good agreement with theoretical data (9.66%).

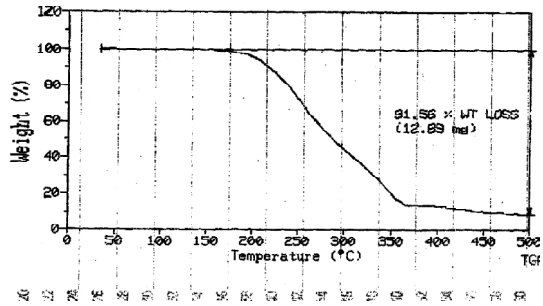


Fig. 3. TGA plot for $CO(PTU)_{Br}$.

The decomposition of $CC(PTU)_{Br}$ (Fig. 4) was recorded in temperature range ambient to 1110 °C. The complex is stable upto 100 °C as indicated by plateau in TGA curve. The total weight loss at the end (92.95%) corresponds to elimination of saturated fatty acid as parent ketone $[(C_7H_{15})_2CO]$ with loss of two molecules of ligand and carbon dioxide. The weight of residue corresponds to formation of cupric oxide. Hence, the complex finally decomposes to parent ketone, ligand, cupric oxide and carbon dioxide.

Similar interpretations can be made for $CC(PTU)_{Br}$ (Fig. 5). The complex TGA graph varied from range 30 °C

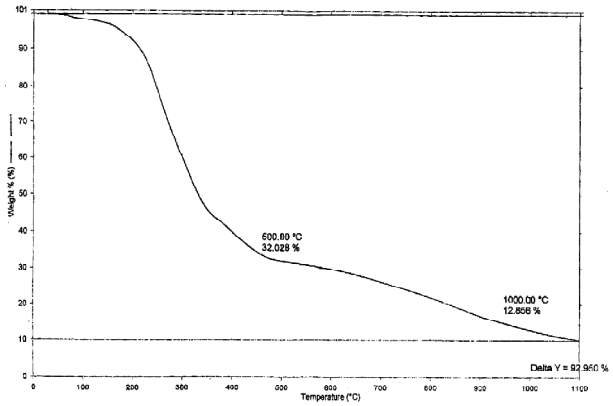


Fig. 4. TGA plot for $CC(PTU)_{Br}$.

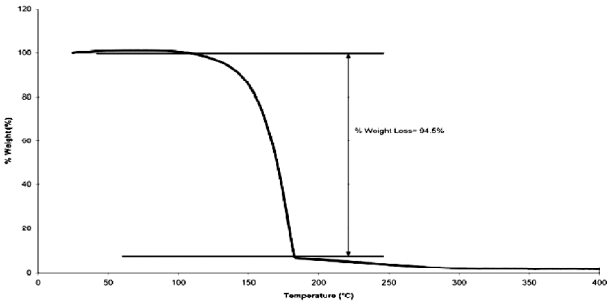


Fig. 5. TGA plot for $CC(PTU)_{Br}$.

to 400 °C. The complex is stable upto 100 °C as indicated by plateau. The total weight loss observed was around 94.5%.

Conclusion

The thermal behaviour for four Cu^{II} complexes namely $CS(PTU)_{Br}$, $CC(PTU)_{Br}$, $CO(PTU)_{Br}$ was studied by TGA technique. Two complexes $CC(PTU)_{Br}$, $CO(PTU)_{Br}$ were found to undergo decomposition in one stage while $CS(PTU)_{Br}$ undergoes decomposition in three stages. TGA results of synthesized copper(II) complexes are useful primarily to determine the composition of soaps and to predict their thermal stability up to elevated temperatures. The use of thermogravimetric data is mainly for evaluating kinetic parameters of solid state reactions involving weight loss (or gain).

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