

Application of thermogravimetric analysis for characterisation of bisdithiocarbamate of urea and its copper (II) complex

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Abstract

A novel disodium salt of bisdithiocarbamate of urea (UBDT) and its Cu(II) complex Cu(II)UBDT were prepared and characterised by elemental analysis, IR, electronic and NMR spectroscopy, conductivity measurements and thermogravimetric analysis (TGA). Water-soluble UBDT possessed good chelating ability for various metal ions. Its copper (II) complex, Cu(II)UBDT was amorphous, intractable solid having polymeric structure. The ligand as well as the complex was found to possess high thermal stability. UBDT cyclised on heating to yield a heterocyclic compound (“X”, probably highly stabilised by resonance) which also showed coordinating tendency for various metal ions.

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1. Introduction

Sulphur and nitrogen containing compounds act as multi-dentate ligands and usually produce coordination polymers with high thermal stability [1–4] and sometimes electrical conductivity due to presence of heteroaromatic rings [4,5]. Dithiocarbamates are S, N containing ligands, which display a rich and varied coordination chemistry providing a wide range of transition and main group metal complexes many of which have important chemical and biological properties [6]. It has been found although dithiocarbamates have been extensively studied a few reports appeared on bisdithiocarbamates [7,8]. Metal dithiocarbamates in general and Cu(II) dithiocarbamates in particular have been the subject of number of investigations by X-ray photoelectron spectroscopy (XPS). Because XPS investigation did not always give coincident results, problem of chemical instability under XPS condition was suggested [9]. Thermogravimetric analysis (TGA) is a useful technique not only to evaluate the thermal stability of the various substances but also to establish the structure of insoluble and infusible compounds [10]. Thermal analysis had more than 11 decades of history, and today it has become an essential tool for material research and

development. By the conventional thermal analysis, such as differential thermal analysis (DTA), thermogravimetry (TG) and thermomechanical analysis (TMA), only macroscopic change can be detected. However, microscopic information, such as chemical and crystal structure can be obtained by three-dimensional thermal analysis, e.g. thermophotometry by FT-IR, EGA by mass spectrometry (MS), thermo-analytical X-ray diffraction, etc. [11].

The conventional thermal analytical methods have been applied more commonly for inorganic materials for interpretation of the kinetics and mechanisms of thermal decompositions of solids [12]. Physical transformations, crystallisation mechanisms, enthalpies of hydration are also popular in the fields of metal complexes and polymeric materials. Reports generally appear on thermal stability, pyrolysis and combustion behaviour of such materials. For structural analysis of polymers TG is generally coupled with MS [13]. However, TG-MS is not useful for those materials which do not undergo complete degradation into volatile products upon heating.

Despite a great deal of reports on structural features of dithiocarbamate compounds, the first thermochemical results appeared only in 1969 [14].

A limited number of reviews including thermal data and solution thermochemistry of metal dithiocarbamate complexes and related compounds were published [15–17].

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Usually the dithiocarbamates are prepared from aliphatic amines. In present communication a novel bisdithiocarbamate prepared from urea is reported. Urea, a diamide, was employed with a view to prepare multidentate ligand, which may form chelate rings on complexation, which have enhanced stability (chelate effect) as compared to the stability of a similar system with none, or fewer rings [18a].

2. Experimental

2.1. Materials

Urea (U) was obtained from Loba Chemie Ltd., India. Carbon disulphide was supplied by Encore R. Johnson group, India. Sodium hydroxide, acetone and other solvents were supplied by Qualigens (Glaxo), India. Cu(II) acetate was analytical quality product of E. Merck, India. All the chemicals used were of analytical grade and were used without further purification.

2.2. Preparation of bisdithiocarbamate from urea (UBDT)

The ligand was prepared according to the literature method with slight modification [7]. A mixture of 6 g (0.1 mol) of urea, 8 g (0.2 mol) of sodium hydroxide and 80 ml of water were placed in a two-necked flask fitted with an air condenser and stirred magnetically until it became homogenous. Then the temperature of this mixture was maintained below 10 °C by external cooling and 15.2 g (0.2 mol) of carbon disulphide was added through a dropping funnel over a period of 30 min, then the stirring was continued for 15 h at room temperature. The orange coloured mixture was transferred to an evaporating dish, warmed at 50 °C for 1 h, and then cooled to room temperature. The product slowly crystallised into colourless crystals, which were washed with acetone and recrystallised from water. The yields of crude and recrystallised products were 23 g (90%) and 22.5 g (88%), respectively. The colourless crystalline product was freely soluble in water, insoluble in organic solvents and did not melt up to 360 °C. Anal. calc. for (C₃H₂N₂S₄ONa₂·3H₂O): C, 11.61%; H, 2.58%; N, 9.02%; S, 41.29%. Found: C, 11.9%; H, 2.51%; N, 8.96%; S, 40.82%.

2.3. Preparation of copper (II) complex of bisdithiocarbamate of urea (Cu(II)UBDT)

Aqueous solutions of UBDT 0.64 g (2.5 mmol) and Cu(II) acetate 0.5 g (2.5 mmol) were mixed and the product

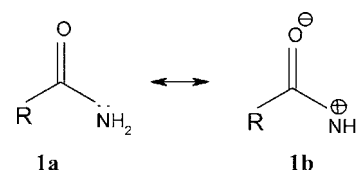
precipitated as a very fine powder instantaneously. For the coagulation of fine particles, the mixture was stirred magnetically for 10 min and then kept overnight at room temperature, filtered, washed thoroughly with water and dried. The product was sea-crest green amorphous solid, insoluble in water and common organic solvents. The yield was 0.67 g (61% of the reactants). It turned black above 210 °C but did not melt up to 360 °C. Anal. calc. for (C₁₄H₁₆O₁₀N₄S₈Na₂Cu₃): C, 18.82%; H, 1.79%; N, 6.27%; S, 28.68%; Cu, 21.34%. Found: C, 18.70%; H, 1.82%; N, 5.98%; S, 28.18%; Cu, 20.60%.

2.4. Measurements

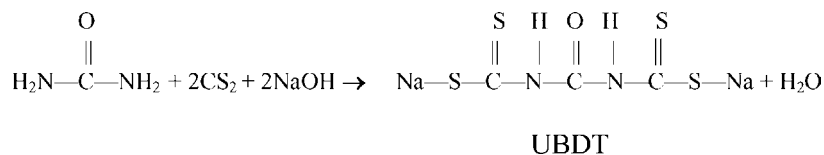
IR spectra were recorded on a Perkin-Elmer spectrometer model 1430 in 4000–600 cm⁻¹ range using KBr as dispersant. UV-Vis spectra were recorded on a Unicam spectrometer model UV-2-100. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker DRX-300 FT-NMR spectrometer (Bruker Instruments, Billerica, MA) in CDCl₃ solutions. Elemental analyses were done on a Carlo Erba 1108 Elemental analyser. Thermogravimetric analyses were carried out on a Perkin-Elmer thermal analyser TGS-4 in N₂ atmosphere at a heating rate of 10 °C min⁻¹. Sulphur in various products was determined by oxidising them with alkaline potassium permanganate followed by gravimetric determination as barium sulphate. The quantitative determination of metal content in the complex was done by complexometric method using EDTA [19].

3. Results and discussion

Bisdithiocarbamates are generally prepared from amines. Urea is a diamide. Amides are the least reactive derivatives of carboxylic acids and much less basic than amines mainly because of the extra resonance capability of the nitrogen lone electron pairs. However, a prolonged reaction of urea with



carbon disulphide in presence of sodium hydroxide yielded the disodium salt of bisdithiocarbamate (UBDT).



(1)

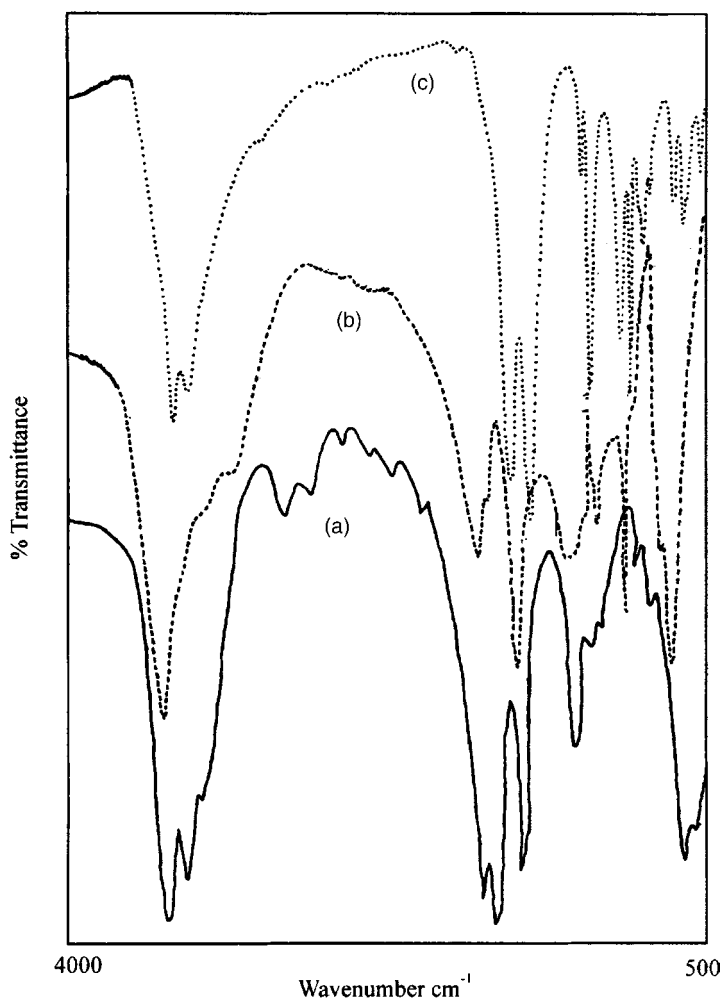


Fig. 1. IR spectra of (a) urea, (b) bisdithiocarbamate of urea (UBDT) and (c) copper (II) complex of UBDT (Cu(II)UBDT).

Formation of UBDT was evidenced by electronic, IR and NMR spectroscopy and TGA.

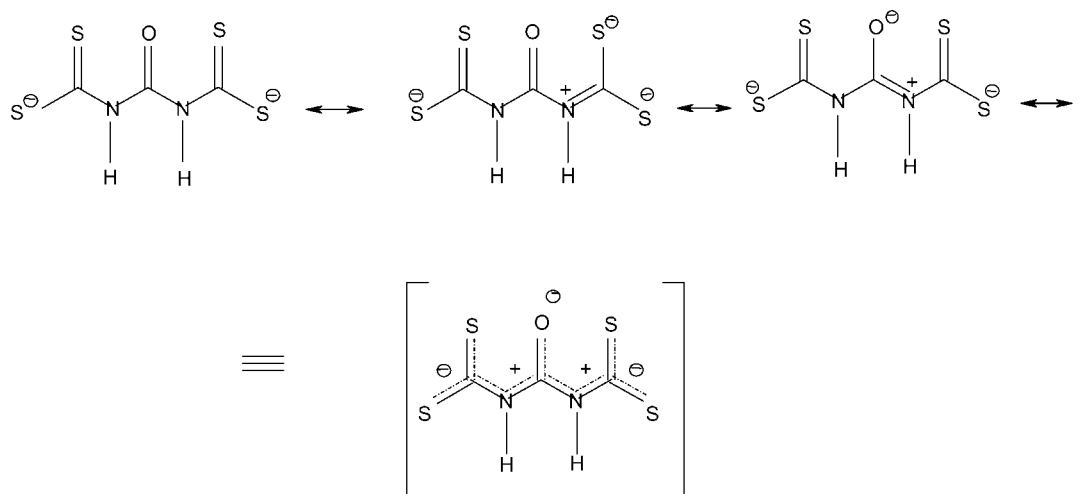
3.1. IR spectral analysis of ligand

The IR spectra of urea, UBDT and the copper (II) complex are depicted in Fig. 1. Assignments are based on literature data [20]. The symmetric and asymmetric stretching vibrations of NH_2 groups of urea observed at 3447 and 3348 cm^{-1} merged into a single band at slightly higher wave number at 3467 cm^{-1} on dithiocarbamylation. The thioamide III band of urea at 1466 cm^{-1} shifted to slightly lower frequency at 1460 cm^{-1} in UBDT, which confirms that nitrogen electron pair is conjugated to dithiolate group, as shown in Scheme 1. The bands at 1019 and 861 cm^{-1} can be ascribed to the ν_{as} and ν_{s} of the S–C–S groups. Appearance of broad bands at 3467 , 1697 and 650 cm^{-1} signify the presence of water molecules in UBDT [21]. This also supports the stoichiometry with three water molecules inferred from analytical data.

3.2. NMR spectral analysis of ligand

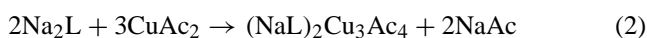
Bisdithiocarbamate formation is further substantiated by the observation of a broad signal in 4.9 – 5.5 ppm range due to $-\text{NH}-$ proton in ^1H NMR spectrum of UBDT. ^{13}C NMR spectrum exhibited a single signal at 164.5 ppm. Kaur et al. [22] reported a resonance signal at ~ 171 ppm for substituted phenyldithiocarbamate. For reference purpose, we synthesised bisdithiocarbamate from 1,3-diaminopropane and recorded its ^{13}C NMR spectrum. Besides the signals due to methylene carbons in 28 – 40 ppm range, a ^{13}C NMR signal for CS_2 group was observed at 164.2 ppm.

The ligand was freely soluble in water and pH of aqueous solution was ~ 10.5 . Its complex with Cu(II) was obtained simply on mixing of aqueous solutions of ligand and copper (II) acetate. Presence of sodium in the ligand and the complex was authenticated by flame photometry. The stoichiometry of the complex formation based on elemental analysis can be represented schematically



Scheme 1. Some of the possible resonating structures of UBTD dianion.

by Eq. (2).



where $\text{L} = \text{--SSCNHCONHCSS--}$ and $\text{Ac} = \text{CH}_3\text{COO--}$.

The yield of the complex became quantitative on considering this stoichiometry.

3.3. IR spectral analysis of complex

Presence of water molecules in the complex was ruled out because the bands associated with water molecules were not observed in its IR spectrum (Fig. 1). The coupled vibration (amide I) involving main contribution from ν_{CO} and δ_{NH} was observed in the complex at considerably lower frequency at 1519 cm^{-1} , indicating involvement of carbonyl oxygen in coordination with Cu(II). Similarly the intense absorption due to thioamide III with major contribution from $\text{C}=\text{N}$ at 1460 cm^{-1} lowered down to 1400 cm^{-1} on complexation supporting coordination through nitrogen [23]. The region $950\text{--}1050\text{ cm}^{-1}$ associated with CSS vibration is used effectively in differentiation between monodentate and bidentate dithiocarbamate ligands [24]. The application of the Ugo–Bonati criterion for the number of bands observed in $950\text{--}1050\text{ cm}^{-1}$ region to determine the nature of the coordination of the ligand is well documented [25]. Changing the geometry of a dithiocarbamate group from bidentate to monodentate shifts many important bands by $10\text{--}20\text{ cm}^{-1}$ and additional bands occur when unsymmetrical bidentate bonding is present and extent of splitting increases as the bonding becomes more unsymmetrical [23].

For the Cu(II) complex of UBTD three bands were observed at 1058 , 894 and 815 cm^{-1} , respectively. The upward shifting of the ligand band due to $\nu_{\text{as}}\text{CS}_2$ at 1019 cm^{-1} and splitting of $\nu_{\text{s}}\text{CS}_2$ at 861 cm^{-1} is a definite indication of unsymmetrical bidentate coordination from CS_2 group.

A polymeric structure (Fig. 2) is proposed for the complex based on stoichiometry, bonding behaviour inferred from IR spectroscopy, amorphous nature and insolubility.

Additional support for this structure was obtained from electronic spectroscopy, conductivity measurements and TGA.

3.4. Electronic spectral analysis

It is well known that water-soluble salts of dithiocarbamates show two UV absorption bands of fairly high intensity near 250 and 290 nm . The shorter wavelength band has been associated with the nitrogen conjugation and the longer wavelength to sulphur conjugation (Scheme 1). For UBTD the prominent absorption band at 233 nm ($\log \epsilon\ 3.45$) may be ascribed to $\pi \rightarrow \pi^*$ transition of carbonyl group,

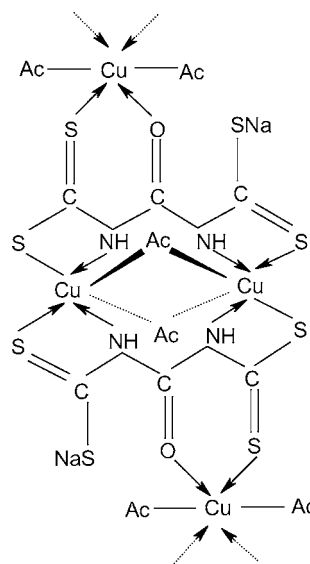


Fig. 2. Proposed structure for Cu(II)UBTD.

observed at a higher wavelength, as compared to that of urea (<200 nm), because of extended conjugation. The extended conjugation is further evinced by the bathochromic shift of $n \rightarrow \pi^*$ transitions associated with conjugated nitrogen and conjugated sulphur observed at 284 nm ($\log \epsilon$ 2.18) and 297 nm ($\log \epsilon$ 1.34), respectively. However, it is interesting to note that absorption intensities are low as compared to those reported in literature for dithiocarbamates [22]. The ligand UBDT is a symmetrical molecule and more so due to extended conjugation resulting in forced coplanarity of all the atoms constituting the molecule, yielding a symmetrical structure (Scheme 1). It is known that symmetrical molecules have more restrictions on their electronic transitions than have less symmetrical molecules. Therefore, many of the electronic transitions especially the $n \rightarrow \pi^*$ transitions are forbidden [26]. It is observed that the corresponding bands in the Cu(II) complex are more intense as the symmetry of the ligand is disturbed on complexation. In the complex, a broad asymmetric absorption band observed in 15,000–10,500 cm^{-1} with maxima at 12,453 cm^{-1} is consistent with the distorted octahedral geometry of six coordinate complex [27]. Huheey et al. [28] attributed breadth of the absorption mainly to the fact that the complex is not a rigid and static structure. Rather the metal ligand bonds are constantly vibrating with the result that an absorption peak is integrated over a collection of molecules with slightly different molecular structures and Δ_0 values. Such ligand motions will be exaggerated through molecular collisions in solution. Hence, the proposed structure for Cu(II)UBDT complex with two types of copper atoms with different environments seems to be justified (Fig. 2). The envelope of this band is unsymmetrical, seeming to encompass several overlapping transitions [18b].

3.5. Conductivity measurements

The molar conductance of 0.1 M aqueous solution of UBDT was found to be 188 $\text{S mol}^{-1} \text{cm}^2$ indicating the electrolytic behaviour. However, the value of conductance is lower than the expected value for univalent–divalent electrolyte (240 $\text{S mol}^{-1} \text{cm}^2$) [29]. Further, increase in the conductance value with increasing dilution is an indication of weak electrolytic nature.

3.6. Thermogravimetric analysis of UBDT

3.6.1. Several methods are prevalent

The TG curves for the ligand and the complex are presented in Fig. 4. For the ligand the initial weight loss of 3.83% below 100 °C is ascribed to the loss of solvent molecules occluded in the crystal lattice. Presence of traces of solvent molecules, viz. acetone and ethanol was inferred from the appearance of corresponding signals in ^1H NMR spectrum also. Two-stage decomposition was observed above 100 °C. The total weight loss above 100 °C up to 200 °C is 28.9%, which corresponded to the loss of three

water molecules (calc. 17.41%) and one molecule of hydrogen sulphide (calc. 10.96%). The final product is quite stable up to 800 °C. To determine the nature of this product, the ligand was heated under nitrogen atmosphere and hydrogen sulphide was detected qualitatively among the volatile products. Heating was continued isothermally at 360 °C for 4 h and the white crystalline residue so obtained was hygroscopic in nature and soluble in water, and has good complexing ability for various transition metal ions. Another sample of UBDT was heated similarly under nitrogen atmosphere and the residue obtained (“Y”) was off white, hygroscopic powder. Its aqueous solution also readily formed complexes with metal ions. The IR spectra of these compounds “X” and “Y” are depicted in Fig. 3. These spectra are quite similar to that of original compound, UBDT except for some new bands observed in 2400–2000 cm^{-1} region. Absorption due to stretching vibration of $-\text{N}=\text{C}=\text{O}$, $-\text{N}=\text{C}=\text{N}-$, $-\text{S}-\text{C}\equiv\text{N}$ and $-\text{N}=\text{C}=\text{S}$ groups are expected in this region [20]. Two bands observed at 972.1 and 846.6 cm^{-1} were assigned to the vibrations of $-\text{S}-\text{C}-\text{S}-$ group. Downward shift of these bands as compared to those of UBDT indicated increased single bond character. Broad absorption bands due to water molecules were observed at 3471.6, 1691.5 and near 600 cm^{-1} [30]. Presence of sodium in these compounds was detected by flame photometry. “X” and “Y” were stable towards oxidation by alkaline potassium permanganate even on heating for a prolonged period. Repeated experiments conducted to determine sulphur in “X” and “Y” gave abnormal and variable results.

Organic compounds with heteroatoms often produce cyclic compounds on heating. From the TG, DTG and GC/MS studies on the thermal behaviour of some alkyl-*N*-aryldithiocarbamates, Szafranek and Szafranek [31] inferred degradation through cyclic intermediates, ArNCS and RSH were the main products and ArNH_2 and CS_2 were the minor ones. They identified symmetrical thiourea formed by an intermolecular reaction of isothiocyanates [31].

A cyclic structure is proposed for “X” and “Y”. The high thermal and chemical stability of this compound can be accounted for because of resonance stabilised six membered cyclic system. Some of the several possible resonating structures are presented in Scheme 2. The molar conductance for “X” (UBDT heated in presence of air at 360 °C for 4 h) 226 $\text{S mol}^{-1} \text{cm}^2$ and “Y” (UBDT heated under flow of nitrogen gas at 360 °C for 4 h) 234 $\text{S mol}^{-1} \text{cm}^2$ approached quite close to the theoretical value for univalent–divalent electrolytes supporting highly polar structure suggested for this compound.

In the electronic absorption spectrum of “X” three absorption bands were observed in UV range, at 258 nm ($\log \epsilon$ 2.32), 292 nm ($\log \epsilon$ 2.06) and 304 nm ($\log \epsilon$ 1.97). For “Y”, the absorption bands were observed at 265 nm ($\log \epsilon$ 3.07), 285 nm ($\log \epsilon$ 2.40) and 295 nm ($\log \epsilon$ 2.35). It seems that the $\pi \rightarrow \pi^*$ transition from carbonyl group of UBDT experienced a bathochromic shift, a definite proof for enhanced electron delocalisation. The position of $n \rightarrow \pi^*$ transition

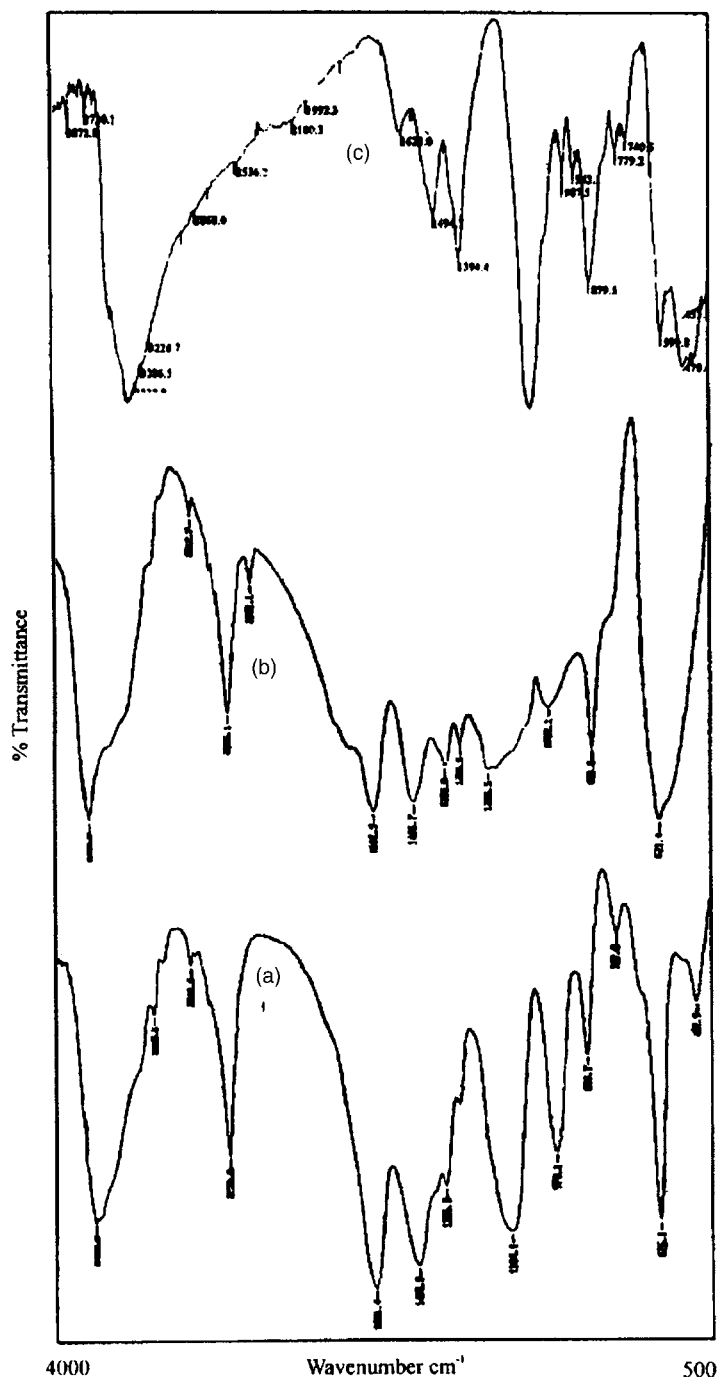


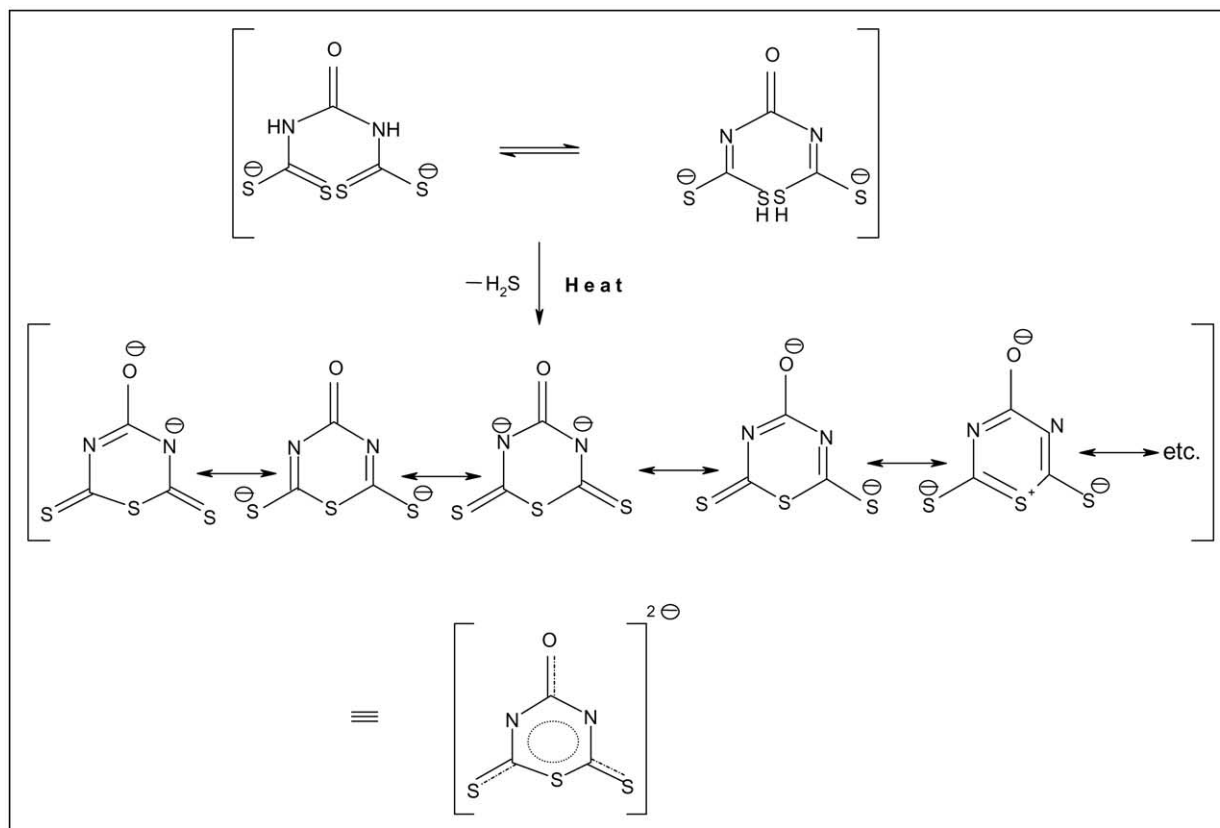
Fig. 3. IR spectra of heated samples (a) “X” (UBDT heated in air), (b) “Y” (UBDT heated under flow of nitrogen) and (c) Cu(II)UBDT heated in air.

due to nitrogen and sulphur were not much affected, but the absorption intensities were increased due to enhanced transition probability, perhaps as a result of better availability of lone electron pairs on N and S atoms (cf. Scheme 1).

3.7. Thermogravimetric analysis of Cu(II)UBDT

A gradual and slow weight loss was observed in the entire temperature range up to 800 °C for the complex (Fig. 4).

The nature of the curve for the complex in Fig. 4 clearly evidenced that the decomposition is quite complicated and several reactions and/or concurrent processes overlap [32]. Thermal decomposition behaviour with consecutive reactions by TG pointed out that even a single step mass loss obtained in linear heating TG at constant rate (LHTG) does not necessarily mean that decomposition reaction is a single elementary process. If a material decomposes with several consecutive reactions and the differences of activation energies



Scheme 2. Some of the possible resonating structures for the "X".

are small, mass loss observed in LHTG will become a single step change. Although controlled rate TG (CRTG) is a useful tool, it is difficult to analyse results of CRTG kinetically for decomposition involving consecutive reaction because the rate of mass loss for each reaction is not constant.

Some polymeric materials, especially coordination polymers are difficult to characterise completely by conventional methods because of their insoluble and infusible nature. These materials may have broad polydispersity, different stoichiometry at chain terminals and structural defects may also exist. These phenomena are outwardly manifested by the amorphous nature of such materials. In such cases, it is rather difficult to resolve consecutive steps and/or concurrent process. Here TG data can only be discerned semiquantitatively as a support for establishing a possible structure. Broad DTG peaks were observed at 80, 240 and 440 °C (Fig. 5). The total weight loss up to 800 °C was 27.25%, which corresponded to the percentage weight of acetate moieties (calc. 26.44%) according to the proposed stoichiometry. On the basis of gradual weight loss, it is inferred that all the acetate species were not lost in a single step. This observation further supported the polymeric nature proposed for this complex. The weight gain by intermediate products, more clearly visible as negative inflection in normalised DTG curve (Fig. 5) was

probably the result of absorption of some gaseous products by solid residue. The complex was heated at 400 °C under flow of dry nitrogen gas for 5 h. The IR spectrum of the residue is depicted in Fig. 3 along with those of "X" and "Y". The position and intensities of most of the IR absorption bands are affected on heating the complex. However, the presence of CO, NH and CSS groups and their coordination to copper was evinced on perusal of this spectrum. It is suggested that the loss of acetate moieties was accompanied by the rearrangement within the units of polymeric structure and the six membered ring structures were largely intact. The importance of the size of chelate rings in stabilisation of complexes has been frequently observed [33]. Because complete characterisation of this complex was not possible logical speculations may find support from the trends observed for related compounds.

A perusal of literature relevant with TGA of dithiocarbamate complexes revealed that generally these complexes either volatilise leaving negligible amount of residue or decompose to yield metal sulphide. D'Ascenzo and Wendlndt [34] reported iron (III) diethyldithiocarbamate as a volatile metal chelate. Iron (III) pyrrolidyl and piperidyl dithiocarbamates were also reported to be volatile [35]. However, mixed-ligand diethyldithiocarbamates with

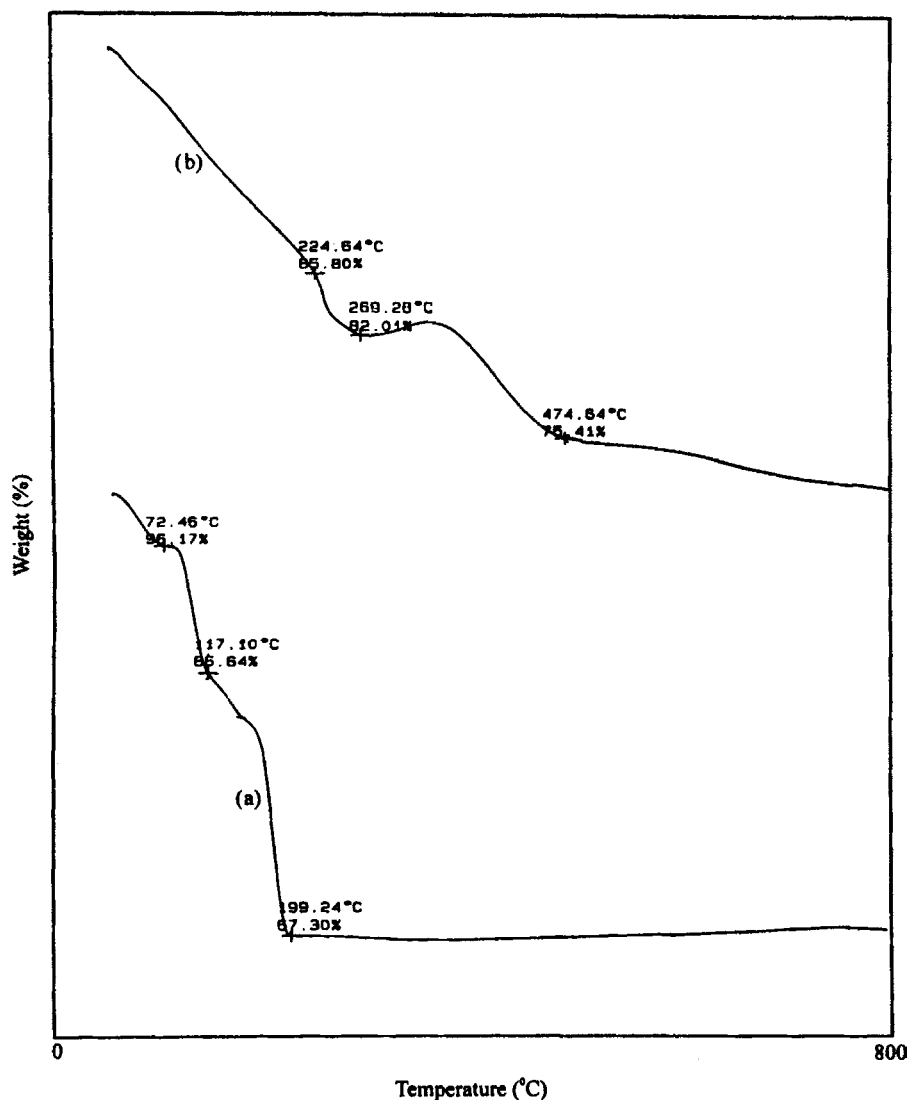


Fig. 4. Thermogravimetric curves of (a) UBDT and (b) Cu(II)UBDT.

different chelating ligands were found to be non-volatile with 17.4–55% residual weights [36]. Iron (III) dimethyl and diethyl dithiocarbamates decomposed in a single step at $\sim 250^\circ\text{C}$ yielding Fe_2S_3 as residues. Phenylmethyl, ethylmethyl and *iso*-propylmethyl dithiocarbamates iron (III) complexes were non-volatile and had a complex decomposition behaviour inferred from a uniformly slow decomposition in entire temperature range up to 900°C [35]. Criado et al. [37] observed a multi-step decomposition path for complexes of Pt(II) with dithiocarbamates derived from α -amino acids. The overlapping steps led to formation of metallic platinum. On the contrary, Sharma [38] reported that decomposition of dithiocarbamate complexes of Pt(II) yielded non-stoichiometric platinum sulphide.

Bell et al. [39] studied complexes of zinc dialkyldithiocarbamates with bidentate nitrogen ligands. On the basis of TG studies, they showed that 2,2'-bipyridyl complexes

decompose by loss of ligand followed by evaporation of zinc dialkyldithiocarbamates, whereas phenanthroline and substituted phenanthroline complexes undergo more complex decomposition and the residue at 500°C corresponds to zinc sulphide. They proposed that intermediate mass loss corresponds to loss of tetra-alkylthiuram monosulphide, $\text{R}_2\text{NC}(\text{S})\text{SC}(\text{S})\text{NR}_2$, alternatively, to loss of $\text{R}_2\text{NC}(\text{S})\text{SC}(\text{S})\text{NR}_2 + \text{CS}_2$ or $\text{RSNH}_2 + \text{RNCS}$ through two competing reactions as reported for decomposition of $\text{Sn}(\text{S}_2\text{CNR}_2)_2$ ($\text{R} = -\text{C}_2\text{H}_5$) [40].

Mathew et al. [41] investigated the thermal decomposition of metal complexes of dithiocarbamate functions supported on crosslinked polyacrylamides in different structural environments. The residual weights obtained at 700 – 800°C were generally 20–30% and in a few cases nearly 40%.

In the present case, the ligand as well as the complex appears to be thermally quite resistant with 63.7 and 72% residue weights respectively even up to 800°C .

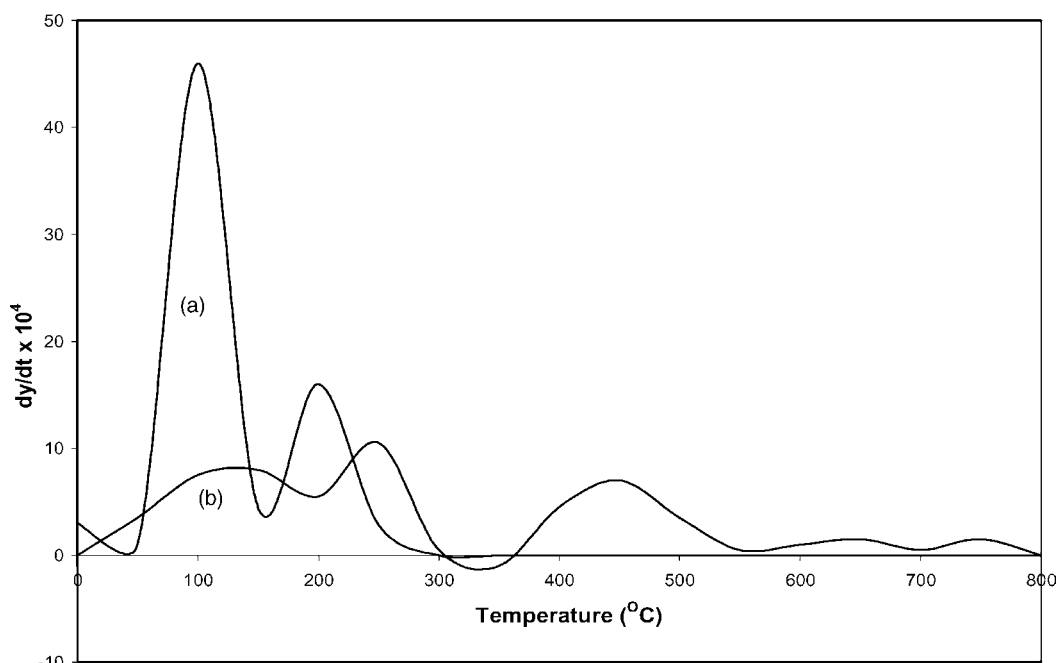


Fig. 5. Normalized DTG curves for (a) UBDT and (b) Cu(II)UBDT.

3.8. Evaluation of kinetic parameters of UBDT and Cu(II)UBDT

The heat resistance of UBDT and Cu(II)UBDT is further substantiated by kinetic parameters calculated by the method proposed by Fuoss et al. [42], used for the calculation of entropy of activation, ΔE^* for thermal degradation at inflection temperature obtained from normalised DTG curves (Fig. 5). Bajpai and Simon [10] compared the method by Fuoss et al. [42] with those by Freeman and Carroll [43], Broido [44] and Dave and Chopra [45] for evaluation of kinetic parameters of dimeracid-based metal containing polyesters using TGA. They demonstrated that slightly different results were obtained from these methods. However, Fuoss method seemed to be easiest, most direct and may have higher precision as well as it is subject to no mathematical approximations. Following equations were used for calculation of kinetic parameters.

$$\Delta E^* = - \left(\frac{RT_i^2}{W_i} \right) \left(\frac{dW}{dT} \right)_i \quad (3)$$

where T_i and W_i are the temperature and weight at inflection point on TG curve, $(dW/dT)_i$ is the corresponding slope and R is the universal gas constant. Frequency factor, Z and entropy, ΔS^* were calculated using following equations.

$$Z = - \frac{\beta}{W_i} \left(\frac{dW}{dT} \right)_i \exp \left(\frac{\Delta E^*}{RT_i} \right) \quad (4)$$

$$\Delta S^* = 2.303R \log \left(\frac{Zh}{kT_i} \right) \quad (5)$$

where β is the heating rate, h is Planck's constant and k is the Boltzmann constant. The total weight loss up to the DTG peak temperature and corresponding kinetic parameters are listed in Table 1. In case of the ligand the first two values of ΔE^* are low supporting the inference for loss of solvents and water molecules. The third value is higher suggestive

Table 1
Kinetic parameters for UBDT and it Cu(II)UBDT calculated by Fuoss, Salyer and Wilson method [42]

Compound	Peak temperature (°C)	Weight loss (%)	ΔE^* (kJ mol ⁻¹)	Z (min ⁻¹)	ΔS^* (JK ⁻¹ mol ⁻¹)	ΔG^* (kJ mol ⁻¹)
UBDT	50	2.5	5.8	0.56	1223.7	401.1
	100	9.7	30.2	4.5×10^3	-1080.9	433.4
	185	27.0	244.8	1.1×10^{25}	-40.7	263.4
Cu(II)UBDT	353	4.2	5.6	0.4	-1229.8	439.8
	513	16.7	36.5	8.6×10^2	-1109.9	605.9
	673	19.5	48.6	7.6×10^2	-1112.7	797.3
	683	20.5	57.5	3.7×10^3	-1085.4	798.8

of covalent bond fission. Similarly the ΔE^* values for the complex are in general low indicating loss of loosely held species only. The entropy value obtained by calculation at lower temperature for the ligand and the complex are very low supporting their ordered structures, as inferred from other studies. With increasing temperature ΔS^* for the ligand increases, i.e. structure becomes more disordered. The planar urea bisdithiocarbamate molecules with polar groups may fit into crystal lattice through hydrogen bonding forming an ordered structure. For the compound "X" such hydrogen bonding interactions may not be present, as loss of both the hydrogen atoms as hydrogen sulphide has been inferred.

For the complex, also the entropy increases with increase in temperature. However, increase in randomness to a much lower extent was, conclusively an evidence of the proposal that an ordered polymeric structure is intact even upon heating of the complex.

Acknowledgements

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