

Synthesis and Characterization of Bisdithiocarbamates from Weak Nitrogen Bases and its Metal Complexes

ABSTRACT

In the present study, the disodium salts of bisdithiocarbamates have been prepared from urea, thiourea, dithiooxamide and 1,3-diaminopropane and characterized by elemental analysis, electronic, infrared (IR) spectroscopy and thermogravimetric analysis (TGA) with a view to prepare multidentate ligands. Water-soluble UBDT (ureabisdithiocarbamate) possessed good chelating ability for various metal ions. Metal complexes of this bisdithiocarbamate were synthesized with Co (II), Ni (II), Zn (II), Pb (II) and Hg (II) and characterized by elemental and spectral analysis. The nature of metal complexes were amorphous and intractable solid.

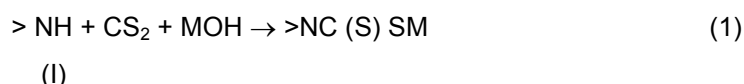
Keywords: *Bisdithiocarbamates; Bridging or Chelating Ligands; Multidentate Ligands; and Thermogravimetric Analysis (TGA).*

1. INTRODUCTION

Sulfur and nitrogen containing ligands are potentially important due to their anticancer, antiviral and antifungal activities as well as widespread industrial applications in the vulcanization of rubber [1-4].

The dithiocarbamate derivatives have long been known for their coordinating ability to act as unidentate, bidentate, chelating or bridging ligands, [5-14] widely used as analytical reagents [5,15-17] and for solvent extraction[18-21]. Dithiocarbamate derivatives have been found to be useful as iniferters [22-24] and also for photoinitiation of polymerization[25]. Recently compounds containing dithiocarbamoyl group have been used as iniferters for modification of solid surfaces by "living" free radical polymerization [26-28]. The bis(N-cyclohexyl-dithiocarbamato) nitrido technetium-99m complex [$^{99m}\text{TcN}(\text{CHDTC})_2$] (CHDTC:N-cyclohexyl dithiocarbamato) has been used as a potential brain perfusion imaging agent [29]. Dithiocarbamates are also showing characteristic photoluminescence properties in lanthanides complexes [30].

The dithiocarbamates are generally prepared from amino compounds, carbon disulphide and alkali metal hydroxides according to equation 1.



Where I, is usually a primary or secondary amine. However, hydrazine, [30,31] heterocyclic bases, [32-39] amino acids [40,41] monoethanol amine and diethanol diamine [42] have been employed for synthesis of dithiocarbamates. Thang *et al.* [44] reported synthesis of functional dithiocarbamates by heating bis (thiocarbonyl) disulfide with an azo compound. Metal complexes dithiocarbamates used in pesticides,[45] as antimicrobial agents [46] and in medicinal chemistry [47]. Dithiocarbamate functionalized chelating resins have been used for complexation [48] and analysis of various metal ions[49-54].

Anionic sulfur containing as dithiocarbamate ligands generally produces multinuclear products with transition metal ions, in absence of halides, which are commercially important chemicals [55].

Multidentate ligands may form chelate rings, which have enhanced stability (chelate effect) as compared to the stability of a similar system with none or fewer rings [5b].

Although dithiocarbamates have been extensively studied, a few reports appeared on bisdithiocarbamates [24,56-58].

The present study reports preparation of disodium salts of bisdithiocarbamates from urea, thiourea dithiooxamide and 1,3-diaminopropane, to act as multidentate ligands. The complexation behaviour of these bisdithiocarbamates towards various transition metal ions, namely Co(II), Ni (II), Cu(II), Zn (II), Hg(II) and Pb(II) has been investigated.

2. EXPERIMENTAL DETAILS

2.1 Materials

Urea (U) and thiourea (TU) were obtained from Loba Chemie Ltd., India. Dithiooxamide (DTO) and 1,3-diaminopropane (DAP) were obtained from J. T. Baker Chemical Co. Phillipsburg, NJ and E. Merck (India) Ltd., Bombay respectively. Encore, R. Johnson group, India, supplied carbon disulfide. Qualigens (Glaxo), India, supplied sodium hydroxide, acetone and other solvents. Acetates of Co (II), Ni (II), Zn (II), Hg (II) and Pb (II) , Cobalt (II) chloride and cobalt (II) sulfate were from E. Merck, India and EDTA (A.R. Qualigens, Glaxo, India). All the chemicals used were of analytical grade and were used without further purification.

2.2 Preparation of Bisdithiocarbamates (BDTs)

The bisdithiocarbamates of urea (UBDT), thiourea (TUBDT), dithiooxamide (DTOBDT) and 1,3-diaminopropane (DAPBDT) were prepared according to the literature method [22] with slight modification. A mixture of 6 g (0.1 mol) of urea or 7.4 g (0.1 mol) of thiourea, 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 in respective preparations. In case of DTOBDT 12 g (0.1 mol) of dithiooxamide was dissolved in 150 mL of ethanol and 8 g (0.2 mol) of NaOH was dissolved in 50 mL of water. For preparation of DAPBDT 7.4 mL (0.076 mol) of 1, 3- diaminopropane dissolved in the 37.5 mL of ethanol was mixed with an aqueous solution of 8 g (0.2 mol) of NaOH in 50 mL of water. In every case, the mixture was stirred magnetically until it became homogeneous. Then the temperature of this mixture was maintained below 10°C by external cooling and 12 mL (0.2 mol) of carbon disulfide was added through a dropping funnel over a period of 30 minutes. The reaction mixture turned orange in half an hour. It was then allowed to stand at room temperature for several days with intermittent stirring until the carbon disulphide layer completely disappeared. 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 crystallized into colourless crystals. However, DTOBDT was brown in colour. The crystalline products were washed with acetone and recrystallised from water. The products were water-soluble and did not melt up to 360°C.

2.3 Preparation of Metal Complexes of Ureabisdithiocarbamates

Metal complexes of Ureabisdithiocarbamates were prepared by mixing of aqueous solutions of ligands and metal salts in equimolar ratio. Aqueous solutions of 0.64 g (2.5 mmol) UBDT and 2.5 mmol of metal salts were mixed in respective preparations. The products precipitated as beautifully coloured fine powders instantaneously. For the coagulation of fine particles in every case, the mixture was stirred magnetically for 10 min then kept overnight at room temperature, filtered, washed thoroughly with water and dried.

In every case, the filtrate and washings were collected in a conical flask and the residual metal ions were estimated by complexometric titration with EDTA. The yields of the complexed resin were calculated using equation (2).

$$\text{Yield} = A / (L + M_o - M_r) \quad (2)$$

where A is the observed yield of the metal complex, L, the weight of the polymeric ligand used in g, M_o and M_r the initially used and residual weights of metal ions respectively, in g.

2.4 Measurements

IR spectra of bisdithiocarbamates were recorded on a Perkin- Elmer spectrometer model 1430 in 4000-600 cm^{-1} range using KBr as dispersant. UV-visible spectra were recorded on a Unicam spectrometer model UV-2-100. Elemental analyses were done on a Carlo Erba 1108 Elemental analyzer. Sulfur was quantitatively determined by oxidizing the bisdithiocarbamates with alkaline potassium permanganate and gravimetric determination as barium sulfate. The metal contents were determined by decomposition of coordination polymers with conc. HNO_3 and titrating against EDTA. Hg Was estimated gravimetrically as HgS after decomposition of the complex with concentrated HNO_3 .

3. RESULTS AND DISCUSSION

3.1 Characterization of Multidentate Ligands

Disodium salts of bisdithiocarbamates were prepared from urea, thiourea, dithiooxamide and 1, 3-diaminopropane. All the products were soluble in water and insoluble in organic solvents. The yields of recrystallised products and analytical data are given in Table 1.

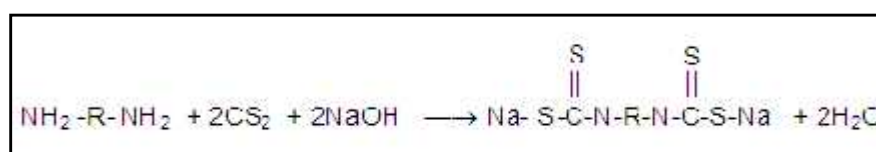
Table 1 Analytical and Elemental Data of Bisdithiocarbamates

^a For each compound the upper values represent results obtained experimentally and the lower values in parentheses show theoretical analysis.

^b % Yield of the recrystallised products. ^c pH of 0.1 M aqueous solutions.

	MOLECULAR FORMULA	YIELD ^b %	pH ^c	Elemental Analysis ^a			
				% C	%H	%N	%S
UBDT	C ₃ H ₂ N ₂ S ₄ ONa ₂ .3H ₂ O	88	11	11.9 0 (11.61)	2.51 (2.58)	8.96 (9.02)	40.82 (41.20)
TUBDT	C ₃ H ₂ N ₂ S ₅ Na ₂ .3H ₂ O	85	10.5	10.86 (11.04)	2.05 (2.45)	8.01 (8.58)	49.85 (49.05)
DAPBDT	C ₅ H ₈ N ₂ S ₄ Na ₂ .4H ₂ O	87	10	17.70 (17.54)	4.23 (4.67)	7.89 (8.18)	37. 92 (37.42)
DTOBDT	C ₄ H ₂ N ₂ S ₆ Na ₂ .4H ₂ O	74	8	12.69 (12.37)	2.08 (2.57)	7.83 (7.21)	49.71 (49.48)

In the present study, synthesis of bisdithiocarbamates is reported, from urea, thiourea, and dithiooxamide has been reported, which are diamide and thioamides respectively.



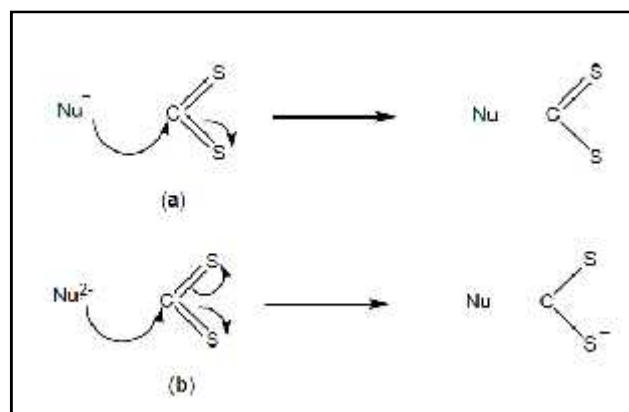
Where R = -CO- for urea, -CS- for thiourea, -(CS)₂- or dithiooxamide and (CH₂)₃ for 1,3-diaminopropane.

Amides and thioamides are much less basic than amines and are the least reactive carboxylic acid derivatives, mainly, because of the extra resonance capability of the nitrogen lone electron pair.

The resonance energy of delocalized system is lost on protonation of the nitrogen atom [65]. Probably because of the low reactivity, reports on direct synthesis of dithiocarbamate derivatives of amides could not be found. It is suggested that despite its weakness as base, urea may act as a nucleophile in presence of hydroxide ion by loss of a proton.

In presence of sodium hydroxide, interaction of an amine with carbon disulfide in 1:1 ratio produces dithiocarbamates and that of a diamine in 2:1 ratio produces bisdithiocarbamates[8].

Nucleophiles (Nu) attack of carbon disulphide as shown in scheme 3.1.



Scheme 3.1.: Nucleophiles (Nu) attack of carbon disulphide

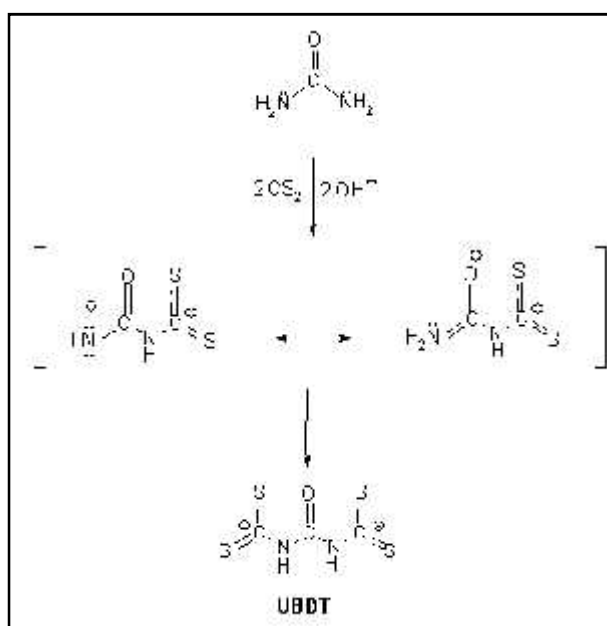
Sometimes basic and nucleophilic strengths are opposite to each other. Nucleophiles, which have unshared electron pair on the α -atom immediately adjacent to the nucleophilic centre appear to be unusually strong donors, certainly in relation to their weak basicity owing to the inductive effect of the adjacent heteroatom. The origin of this hyperactivity appears to lie in interactions between the unshared electron pairs on adjacent atoms, which result in rising of the HOMO energy and enhancement of 'soft' base behaviour [63,64]. The resulting anion being stabilized by delocalization in scheme 3.1.

Analogous mechanism can be extended for thiourea and dithiooxamide also. However, for thiourea and dithiooxamide resonance stabilization of anionic species formed in presence of NaOH is not possible to an extent as that for urea, because overlap of 3p orbital's of sulfur atom (of thioamide group) with 2 p orbitals of carbon atom is comparatively less efficient. The lower reactivity of thiourea and dithiooxamide is reflected by the greater reaction time required for them.

Based on reaction time, the reactivity order for these compounds can be given as:

1,3-diaminopropane > urea > thiourea > dithiooxamide.

The tentative mechanism proposed for formation of bisdithiocarbamate using urea as model compound is presented in scheme 3.2.



Scheme 3.2. Tentative mechanism for bisdithiocarbamates formation from urea

The canonical form of dithiocarbamate shown in following resonating structure Fig.1.

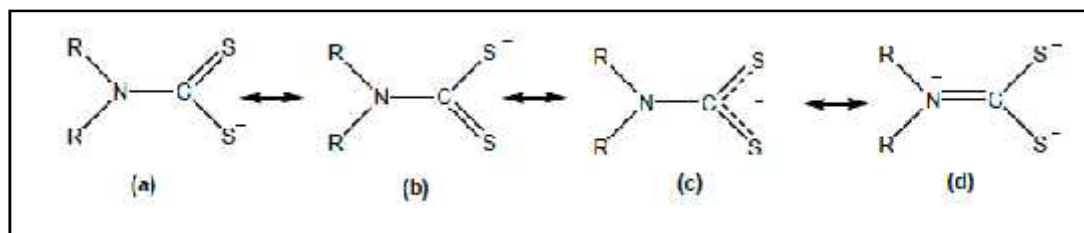


Fig.1.: Canonical form of Dithiocarbamate

3.2 Characterization of Ureabisdithiocarbamate metal complexes

An (aqueous) solution of metal salt is added slowly a solution of the UBDDTC ligands in 1:1 ratio are shown in following equation. The yield colour and elemental analysis for various metal complexes of UBDDTC are reported in Table 2.

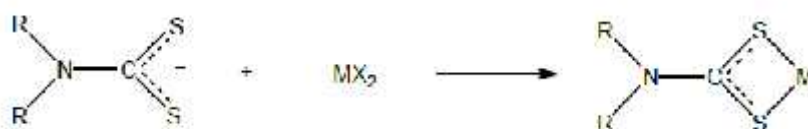


Table 2 Physical and Analytical Data of Coordination Polymers of UBDDTC^a

Complex	MOLECULAR FORMULA	COLOR	MELTING POINT ^o C	YIELD %	Elemental Analysis found (Calculated)				
					C %	H %	N %	S %	METAL %
CuAcUBDDTC	C ₁₄ H ₁₆ N ₄ O ₁₀ Na ₂ Cu ₃ (L ₂ Ac ₄ Na ₂ Cu ₃)	Seacres t green	210 ^b	61	18.7 (18.8)	1.82 (1.79)	5.9 (6.2)	28.2 (28.7)	20.6 (21.3)
CoAcUBDDTC	C ₁₆ H ₂₀ N ₄ O ₁₄ Na ₂ Co ₃ (L ₂ Ac ₆ Na ₂ Co ₃)	Dark purple	220 ^b	57	18.9 (19.2)	2.32 (2.00)	5.8 (5.6)	25.4 (25.6)	16.9 (17.7)
CoCl ₂ UBDDTC	C ₆ H ₄ N ₄ O ₂ Na ₂ Co ₃ Cl 6	Light purple	180 ^b	53	7.9 (8.4)	0.93 (0.46)	6.0 (6.6)	29.09 (30.01)	19.2 (20.0)

								)	
CoSO ₄ UBDT	C ₆ H ₄ N ₄ O ₁₀ Na ₂ Co ₃ H ₂ O(SO ₄) ₂	Light purple	220 ^b	56	6.9 (7.6)	1.50 (1.69)	5.8 (5.9)	32.15 (32.97)	18.3 (18.7)
NiAcUBDT	C ₁₆ H ₂₀ N ₄ O ₁₄ Na ₂ Ni ₃ L ₂ Ac ₆ Na ₂ Ni ₃	Light green	180 ^b	52	18.9 (19)	1.9 (2.0)	5.0 (5.6)	26.46 (25.70)	16.7 (17.4)
ZnAcUBDT	C ₁₆ H ₂₀ N ₄ O ₁₄ Na ₂ Zn ₃ L ₂ Ac ₆ Na ₂ Zn ₃	White	>360 ^o C	60	18.1 (18.8)	2.1 (1.9)	4.9 (5.5)	26.8 (25.1)	18.2 (18.9)
HgAcUBDT	C ₁₆ H ₂₀ N ₄ O ₁₄ Na ₂ Hg ₂ L ₂ Ac ₆ Hg ₂ Na ₂	Brown	>360	35	16.0 (15.7)	1.9 (1.6)	3.98 (4.58)	20.6 (20.9)	33.3 (32.8)
PbAcUBDT	C ₁₄ H ₁₆ N ₄ O ₁₀ Na ₂ Pb ₃ L ₂ Ac ₄ Na ₂ Pb ₃	White	>360	57	12.4 (12.6)	1.8 (1.2)	4.73 (4.23)	20.2 (19.3)	45.8 (46.1)

a L = -SSCNHCONHCSS, Ac = CH₃COO⁻

b Does not melt but darken at the temperature mentioned

All the complexes were stable at room temperature, unaffected by atmospheric oxygen and moisture and were insoluble in water as well as common organic solvents. The complexes appeared to be amorphous even on microscopic examination. The complexes did not melt on heating up to 360°C, however, many of them became black above 200°C.

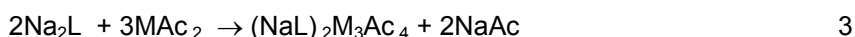
The metal complexes were dissolved in minimum quantity of concentrated nitric acid by heating and the solutions were cooled and diluted with double distilled water. Presence of sodium in the complexes was authenticated by flame photometry of these solutions. However, for mercury (II) complexes, solid reappeared on dilution of nitric acid solution, so flame photometry could not be done with these complexes. The anions viz., acetate, chloride or sulphate ions were detected qualitatively in the respective solutions of various complexes in dilute nitric acid.

The dithiocarbamate complexes have been reported to be usually crystalline compounds, soluble in organic solvents and have well defined melting points. Although the results of elemental analysis for bisdithiocarbamates in present study were reproducible within the experimental error but close agreement with the theoretical calculation based on assumed structures could not be obtained. This observation alongwith amorphous morphology and insoluble nature suggested the polymeric structure for these complexes, an obvious expectation for the multidentate ligands. The deviation of observed results of elemental analysis from the theoretical analysis may be due to the polymeric nature because the terminal units have different composition than that of the repeat units. Further the possibility of structural defects also exists.

As the analytical results of copper complex were comparatively most convincing, it was used as the model compound for further studies. Solution of UBDT and Cu (II) acetate were mixed in different molar ratios and yields of the complexes precipitated were measured. It was found that the yield was highest in 1:1 metal to ligand ratio

and colour of the complex was sea crest green. In all the other cases yields were lower. With lower proportion of Cu(II) ions green coloured complexes were obtained but with higher proportion of Cu(II) ions, complexes had slightly varying shades of light blue colour..

The stoichiometry of the Cu(II) complex formation on the basis of elemental analysis can be represented schematically by equation 3.



where L= -SSCNHCONHCSS-, Ac = CH₃COO-

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

3.3 IR spectral analysis of ligands

The IR spectra of bisdithiocarbamates of urea, thiourea, dithiooxamide and 1,3-diaminopropane are depicted in Figure 2. Assignments of these bands are based on literature data . For bisdithiocarbamates, three main regions are of interest in the infrared spectrum.

Firstly, the 3400 -3100 cm⁻¹, the broad bands in this region appear due to $\nu_{\text{N-H}}$ of dithiocarbamate ligand and $\nu_{\text{O-H}}$ from water molecules associated with the ligand [67-70].

Secondly, the 1450-1550 cm⁻¹ region which is associated primarily with the “ thioureide ” band due to $\nu_{\text{C-N}}$ vibration of the S₂C=NR₂ ligand.

Thirdly, the 950-1050 cm⁻¹ region which is associated with $\nu_{\text{(C-S)}}$ vibrations.[67-70]

A perusal of (Fig. 2 a) made it evident that the symmetric and asymmetric stretching vibrations of -NH₂ 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 strong absorption due to the stretching vibration of strongly H-bonded carbonyl group (amide I) at 1689 cm⁻¹ shifted to 1696 cm⁻¹ with reduction in intensity and was overlapped by δ OH from absorbed water molecules. The amide II vibration, which appears in urea at 1630.7 cm⁻¹ and shifted to 1660 cm⁻¹ as a shoulder in UBDT. The thioamide III band of urea at 1466 cm⁻¹ shifts to slightly lower frequency at 1460 cm⁻¹ in UBDT, which confirmed that nitrogen electron pair is conjugated to dithiolate group. The bands at 1019 and 861 cm⁻¹ can be ascribed to the ν_{as} and ν_{s} of the CS₂ groups.

For DTOBDT (Fig. 2 b) a new strong and sharp peak appeared at 1001 cm⁻¹ and the strong peaks observed for DTO at 835 and 710 cm⁻¹ appeared with reduced intensities in bisdithiocarbamate at 881.34 and 777.50 cm⁻¹, respectively. This suggested the decreased interaction of CS₂ groups with the nitrogen lone pair and consequently increased double bond character of thiocarbonyl groups.

IR spectrum of bisdithiocarbamate from propanediamine (DAPBDT) has also been shown in (Fig. 2 c). All three three region ($\nu_{\text{N-H}}$ and $\nu_{\text{O-H}}$, thioureide band due to $\nu_{\text{C-N}}$ vibration of the S₂C=NR₂ and $\nu_{\text{(C-S)}}$ vibrations) peaks are observed.

The intense bands of thiourea due to NH_2 stretching (3387 , 3282 and 3183 cm^{-1}) appeared with reduced intensity in thioureabisdithiocarbamate TUBDT (Fig. 2 d) as a broad band incorporating absorption due to absorbed water molecules also. Similarly, the band for thioamide I ($\nu\text{ CS} + \delta\text{NH}_2$) at 1620 cm^{-1} merged with the broad band for $\nu\text{ C} = \text{N}$, at 1450 cm^{-1} with a shoulder at 1406 cm^{-1} in TUBDT. These bands were sharp in thiourea and observed at higher frequencies (1479 and 1414 cm^{-1}) Thus a greater single bond character was indicated for $\text{C}-\text{N}$ bond in TUBDT. The thioamide III band of thiourea at 1084 cm^{-1} is reduced in intensity in TUBDT. A sharp band due to $\nu\text{ C} = \text{S}$ appeared at 866 cm^{-1} with a shoulder at 902.6 cm^{-1} in TUBDT. All these observations confirmed the dithiocarbamylation of thiourea as well as considerable electron delocalization within the molecule as discussed for UBDT.

Separate absorption from the free $-\text{NH}_2$ groups was not apparent in any case. The observation along with the analytical data, support the dithiocarbamylation of both the $-\text{NH}_2$ groups. Appearance of broad bands near 3400 , 1600 and 650 cm^{-1} signified the presence of water molecules in bisdithiocarbamates [67-71].

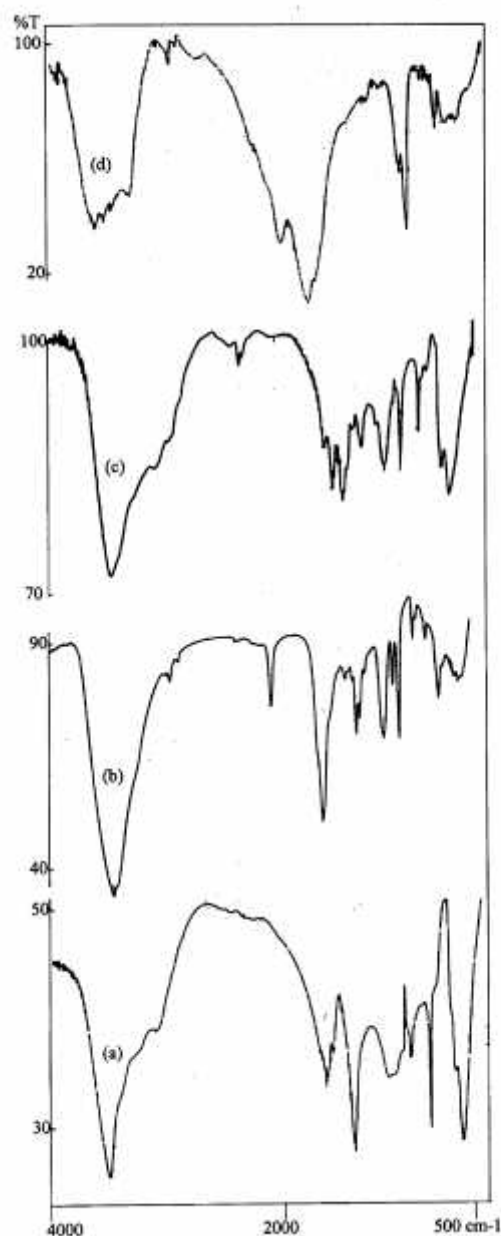


Fig. 2: IR Spectra of Bisdithiocarbamates. (a) UBDT (b) DTOBDT (c) DAPBDT (d) TUBDT

3.4 IR spectral analysis of metal complexes of UBDT

The IR spectral data of metal complexes are depicted in (Fig. 3-5). The most characteristic feature of the dithiocarbamate complexes is their Infrared (IR) spectra and generally shows three characteristic bands. They exhibit a strong absorption band between 1450 and 1550 cm^{-1} which attributed to $\nu(\text{C-N})$ vibration [3-5]. This band is referred to as the thioureide from the thioureide form of the dithiocarbamate. This band lies between the $\nu(\text{C-N})$ band at 1250 - 1350 cm^{-1} and the $\nu(\text{C=N})$ band at 1640 - 1690 cm^{-1} range. For UBDT a very intense band is observed at 1459.6 cm^{-1} indicating a sufficient double bond order for C—N, as thioureide band is characteristic of dithiocarbamate intermediate between a C=N band (1690 - 1640 cm^{-1}) and a C—N band (1360 — 1250 cm^{-1}). When compared with the position reported for propanediamine dithiocarbamate

(1479.4 cm^{-1}), this band has been observed at a lower frequency suggesting greater single bond character, which further substantiates the involvement of canonical structures (d) presented in Fig. 1.

The thioureide band characteristic of dithiocarbamates at 1459.6 cm^{-1} splits upon complexation in all the cases with a wide separation of almost 100 cm^{-1} in every case except for lead complexes. It is suggested that in UBDT due to electron delocalization —C—N (A) and —C—N (B) bands are coordinated to metal ion in canonical forms (Fig. 1) and become nonequivalent resulting in appearance of two distinct IR bands.[67-72]

The ν (CN) for the thioamides appear at about 1500 cm^{-1} and the ν (CN) for the UBDT under consideration is observed at about 1459 cm^{-1} was consistent with extensive electron delocalization rendering bond between nitrogen and carbonyl carbon equivalent to that between nitrogen and dithioate carbon. However, splitting of this band by more than 100 cm^{-1} is suggestive of coordination through carbon as well as oxygen.

The band at 1696 cm^{-1} in UBDT involves significant contribution from NH bending vibrations besides $\nu(\text{C}=\text{O})$. This band either disappears or appears as a shoulder on broad thioamide II band suggesting coordination through nitrogen and carbonyl oxygen both. [67-71]

A band at 1018.6 cm^{-1} has medium intensity and is broad, it may be assigned to asymmetric C—S stretching and an intense sharp band at 860.7 cm^{-1} may be assigned to symmetric C-S stretching. On complexation in most of the complexes the bands corresponding 1018.6 cm^{-1} band of UBDT appears with greatly decreased intensity, disappear in cobalt (II) acetate, cobalt (II) sulphate, and nickel (II) acetate complexes. Zinc (II) acetate complex is shifted downward with weak absorption. In lead (II) acetate and mercuric (II) acetate complexes this band is shifted to slightly higher wave number with medium absorption in Hg (II) Ac UBDT and weak band show in Pb (II) Ac UBDT. However, the band at 860.7 cm^{-1} although experiences a downward shift but appears as a sharp band with slightly decreased intensity on complexation except for Ni (II) acetate complex where it is broader. [67-71]

The intense bands due to carbonyl stretching overlapped by $\delta\text{ OH}$ from water molecules almost disappears in all the complexes. Thus, all these observations lead to conclude that all the donor atoms, viz., O, N, and S are involved in coordination. Presence of water molecules in all the complexes is ruled out because the bands associated with water molecules are not observed in the IR spectra.

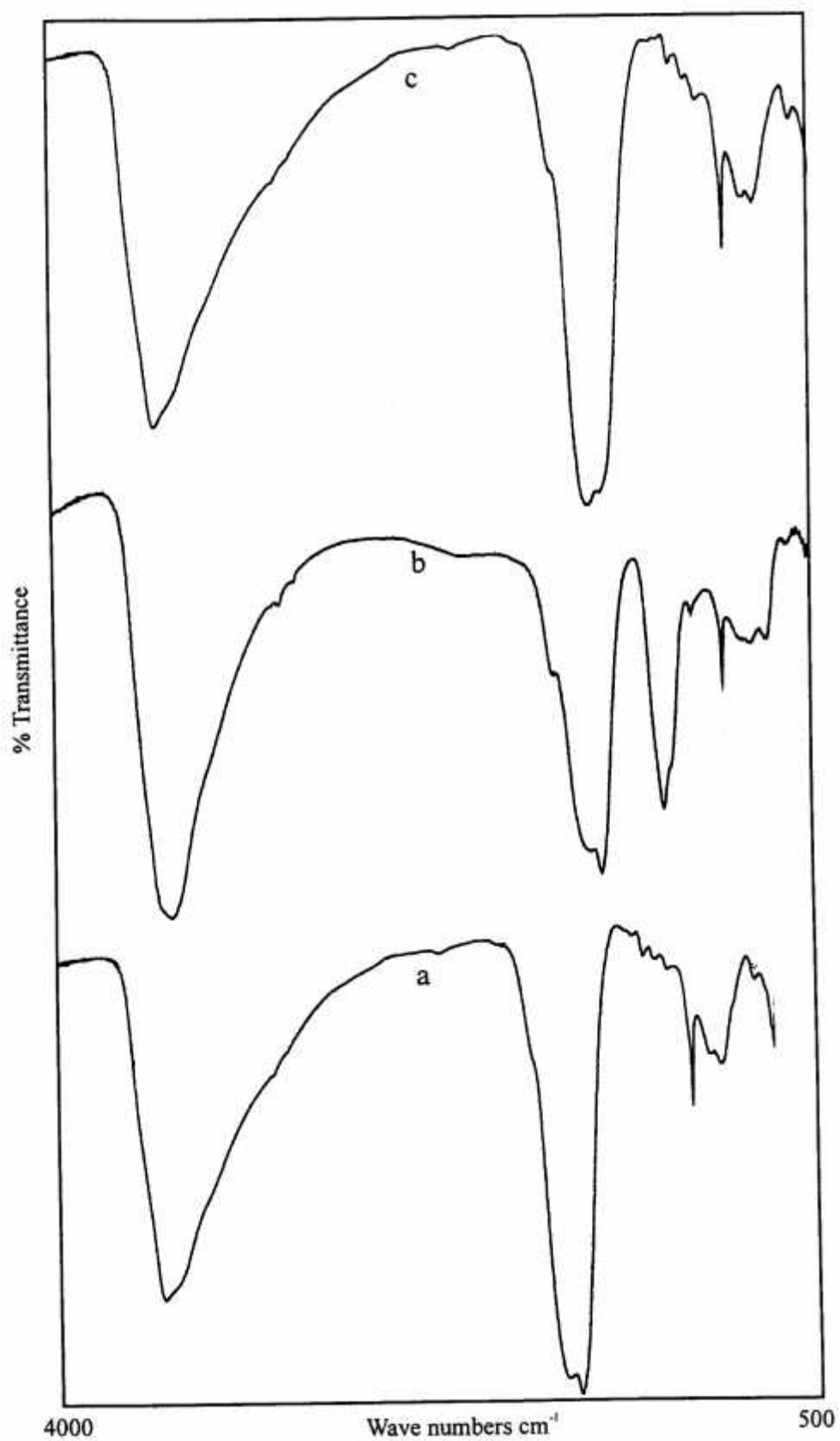


Fig. 3: IR Spectra of (a) Co Ac UBDT (b) Co Cl_2 UBDT (c) Co SO_4 UBDT

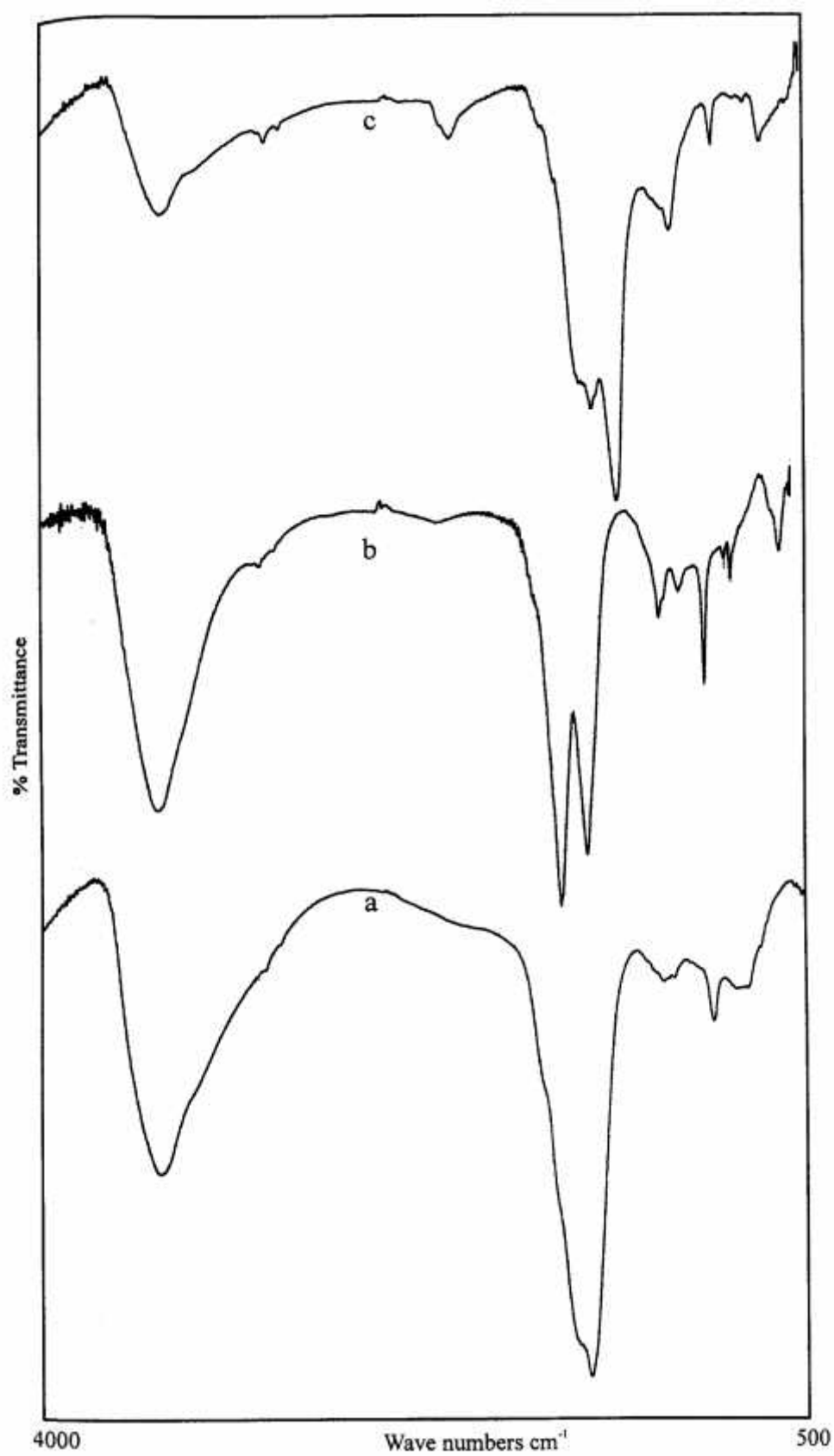


Fig. 4: IR Spectra of (a) Zn Ac UBDT (b) Ni Ac UBDT (c) Hg Ac UBDT

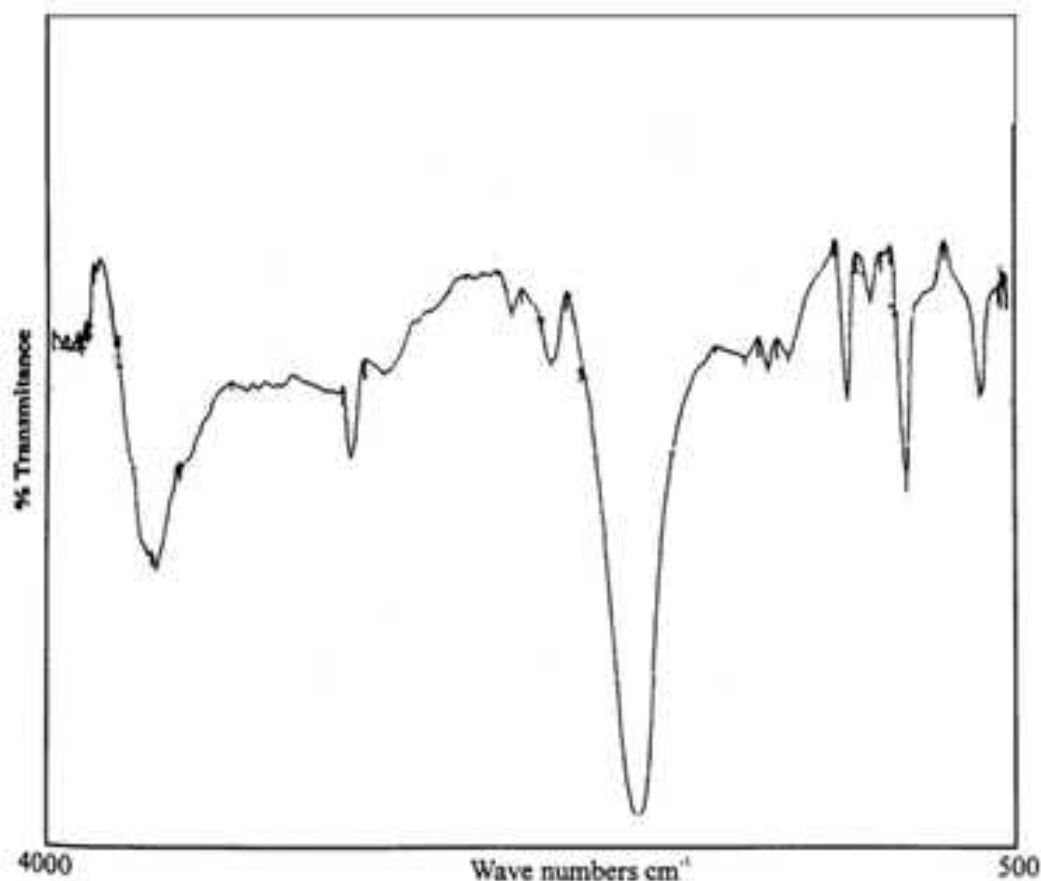


Fig. 5: IR Spectra of Pb Ac UBDT

3.4 Electronic spectral analysis of ligands

The water-soluble salts of dithiocarbamates show two UV absorption bands of high intensity, near 250 nm and at about 290 nm. [74] Takami *et al.* [74] reported unambiguous assignment for these bands based on their study of the decomposition of N-mono substituted dithiocarbamates in alkaline solutions. Petrov *et al.* [75] reported the uv spectra of ethylene-1,2-bisdithiocarbamates (EDTC). Three very intense bands at about 207, 260 and 285 nm, and one of low intensity at about 340 nm. All of them showed blue shift with increasing of the solvent polarity. The 340 nm band was ascribed to an $n \rightarrow \pi^*$ transition, while the bands at about 260 and 285 nm were attributed to $\pi \rightarrow \pi^*$ transitions. [75]

For UBDT a prominent absorption band at 233 nm ($\log \epsilon$ 3.45) may be ascribed to $\pi \rightarrow \pi^*$ transition of carbonyl group. The $\pi \rightarrow \pi^*$ transitions associated with conjugated nitrogen (N-C-S) and conjugated sulfur (S-C-S) observed at 284 nm ($\log \epsilon$ 2.18) and 297 nm ($\log \epsilon$ 1.34), respectively. The low absorption intensities as compared to those reported in literature for dithiocarbamates, may be ascribed to the symmetrical structure of molecule. For symmetrical molecules many of the electronic transitions especially the $n \rightarrow \pi^*$ transitions are forbidden because of several restrictions. [76]

Similarly for TUBDT also an intense band due to $\pi \rightarrow \pi^*$ transition of thiocarbonyl group was observed at 232 nm ($\log \epsilon$ 4.3). The $n \rightarrow \pi^*$ transition due to nitrogen conjugation was observed at 246 nm ($\log \epsilon$ 4.4). The absorption assigned to $\pi \rightarrow \pi^*$ transitions of $S = C = S$ appeared at 271 nm ($\log \epsilon$ 4.1) with a shoulder at 295 nm ($\log \epsilon$ 1.6). The $\log \epsilon$ values for TUBDT are higher than those for UBDT except for the $\pi \rightarrow \pi^*$ transition of

thiocarbonyl group. This is probably the reflection of lesser conjugation in TUBDT molecule because of the less efficient overlap of 3p orbitals of sulphur with 2p orbitals of carbon atom, hence the molecule may not be strictly coplanar and the symmetry restrictions may not be applicable as discussed for UBDT.

3.6 Electronic spectral analysis of UBDT metal complexes

Dithiocarbamates absorb strongly in UV-vis region of the spectrum [14]. Three types of absorption bands are expected which are attributed to: intraligand transitions which may be $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of the N-C-S and the S-C=S groups [52]. Two other expected transitions are the metal-ligand charge transfer (MLCT) and d-d transition. [3] The electronic spectral data for various metal complexes of UBDT are presented in Table 3.

Table 3 : Electronic spectra of UBDT metal complexes

LIGAND/COMPLEXES	Ligand transition band $n \rightarrow \pi^*$ nm	$3A_{2g} \rightarrow 3T_{1g}(P)$ V_3 nm	$3A_{2g} \rightarrow 3T_{1g}(F)$ V_2 nm
Co (II)Ac UBDT	323 376 393	506 516	812 843
Co (II)Cl₂ UBDT	382 395 421	462 473 505	
Co (II)SO₄ UBDT	390 415	471 506	810 840
Ni (II)Ac UBDT	391	522	657 720
Pb (II)Ac UBDT	394 407	450 498	
Zn (II)Ac UBDT	391 403	449 499	

Dithiocarbamate complexes can assume four structural geometries (Fig.6) :

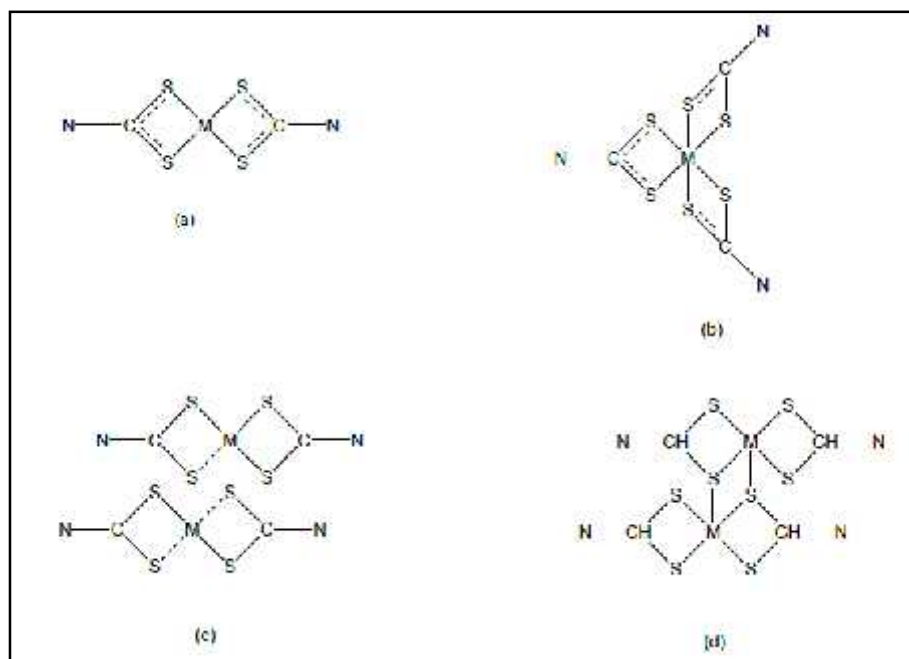


Fig.6: Dithiocarbamate complexes structural geometries

- (a) The square planar coordination geometry
- (b) The octahedral coordination geometry
- (c) The four coordinate dimer
- (d) The five coordinate dimer

The octahedral and square planar geometries are the most common structural arrangements. For various Co (II) complexes, the ν_3 band from absorption characteristic of octahedral geometry is observed in all the cases and the double peak entails the splitting of ${}^4T_{1g}$ (P) state. The weak bands due ${}^4T_{1g} \rightarrow {}^4T_{2g}$ transition are observed for cobalt (II) acetate and sulphate complexes but not for chloride complex. The ν_1 band arising from ${}^4T_{1g}$ (F) $\rightarrow$ ${}^4T_{1g}$ (P) transition range are not observable due to instrumental limitation.

The UBDT complex with nickel (II) acetate shows bands with maxima and shoulder. These bands are in accordance with the octahedral geometry and correspond to the transitions $3A_{2g} \rightarrow 3T_{1g}$ (F) and $3A_{2g} \rightarrow 3A_{1g}$ (F) respectively. The spectrum showed an upward trend above 1100 nm indicating that a band may be present in near infra-red region, which could not be located due to instrumental limitations. This band may correspond to ${}^3A_{2g} \rightarrow {}^3T_{2g}$ (F), (ν_1) transition.

3.7 Thermogravimetric analysis

A multi step decomposition pattern is evident from the thermogravimetric curves of ligands depicted in figures 7.

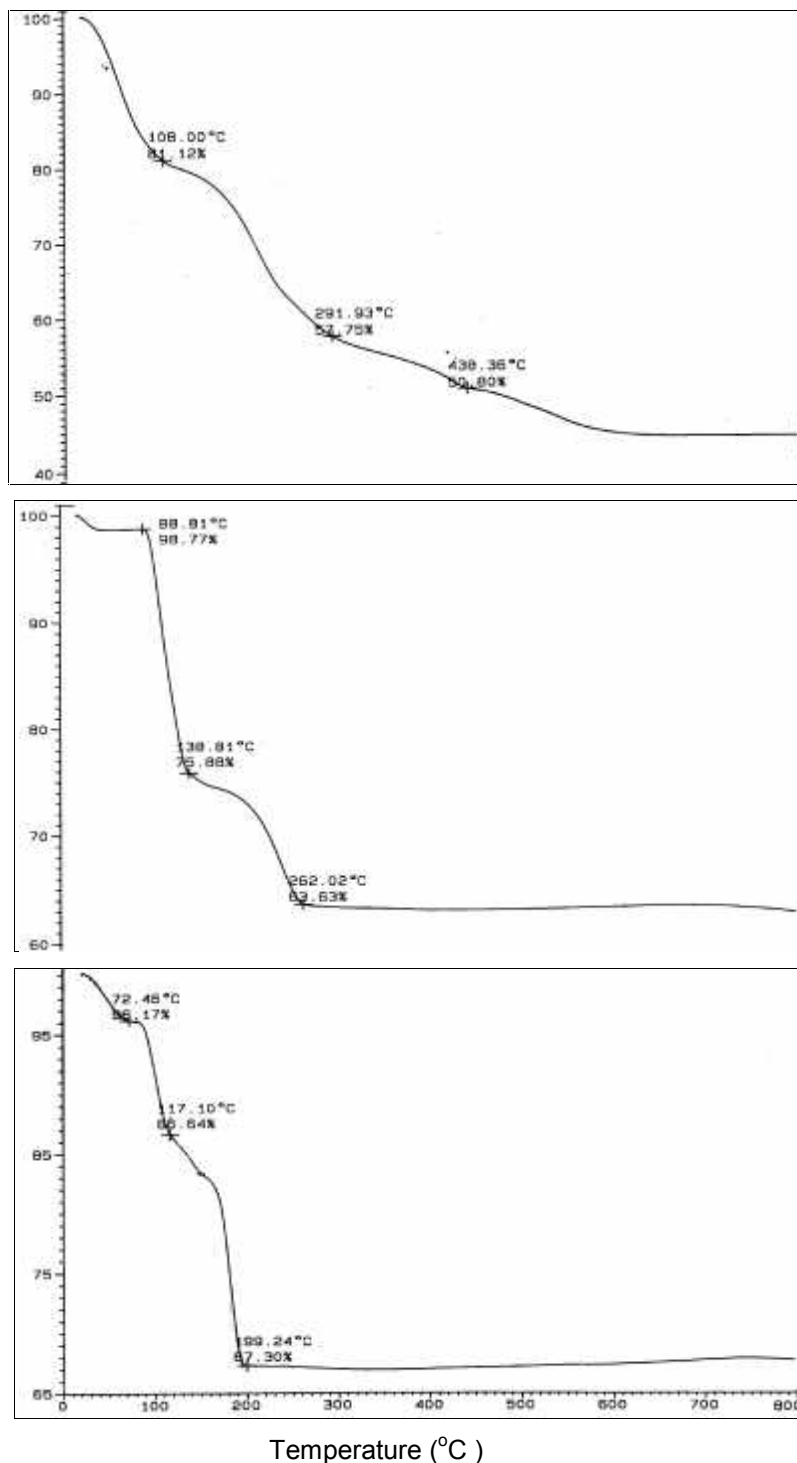


Fig. 7: T.G.A Curve of (a) UBDT (b) TUBDT (c) DTOBDT

The kinetic parameters for thermal decomposition of ligands, calculated using the method proposed by Fuoss *et al.* [59] are depicted in Table 4.

Table 4.

Kinetic Parameters for Bisdithiocarbamates Calculated using Fuoss, Salyer and Wilson method. ^[59]

Compound	Decomposition steps		Temperature at inflection point	Weight Loss	ΔE^*	Z
	Temperature range	Weight loss in temperature range				
	$^{\circ}\text{C}$	%	$^{\circ}\text{C}$	%	kJmol^{-1}	min^{-1}
UBDT	0-75	5	50	2.50	5.75	0.564
	75 -150	12	100	9.75	30.24	4.49×10^3
	150-199	15.7	185	27.00	244.78	1.16×10^{25}
DAPBDT	0-100	3	110	8.50	22.72	263.94
	100-150	23	120	18.00	87.38	2.7×10^{11}
	150-262	11.37	240	33.50	228.72	2.03×10^{23}
DTOBDT	0-100	9	50	6.75	9.83	4.41
	100-295	24	190	27.25	19.09	15.28
	295-438	6.95	215	31.50	50.02	5.4×10^3
	438-500	5	545	53.25	139.08	1.9

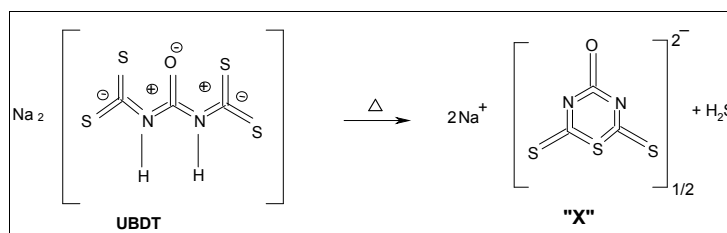
For UBDT and DAPBDT the initial weight losses in first step below 100°C , were 3.83 and 1.23 % , respectively, which were ascribed to the loss of solvent molecules occluded in the crystal lattice. Presence of traces of solvent molecules, viz., acetone and ethanol is inferred from the appearance of corresponding signals in $^1\text{H-NMR}$ spectrum. For UBDT and DAPBDT two quite steep decomposition steps were observed above 100°C and the residues left above 200 and 262°C respectively, were stable up to 800°C .

Based on general TG patterns and the amount of residues left the decreasing order of stability can be described as follows:

UBDT > DAPBDT > DTOBDT

For UBDT, DAPBDT and DTOBDT weight losses (16.80 , 22.89 and 18.88 %) in the first major decomposition step above 100°C corresponded to the calculated weights (17.41, 23.5 and 18.55 %) for the loss of three and four water molecules, respectively, which is in agreement with their stoichiometries obtained from analytical data. Chevire and Metzner [78] demonstrated that the corresponding sulphines (S-oxides) were formed on oxidation of various dithiocarbamates, which have moderate stability. When left at room temperature they decomposed to thiocarbamates. However, "X" could not be a sulphine as it was quite stable.

An aromatized six membered cyclic structure has been inferred to account for the high thermal and chemical stability of this compound. Scheme 2 tentatively represents the formation of "X" upon heating UBDT.



Scheme 3.3. Formation of heterocyclic compound for 'X' obtained on heating UBBDT.

The thermal decomposition pattern for DTOBBDT is gradual and spread over a wider temperature range than that observed for UBBDT or DAPBBDT suggesting a complex decomposition behaviour. In every step probably the different reactions are too close together and only one inflection is apparently present and the values of E^* and Z obtained are averages over those components.

Ichihara *et al.* [79] concluded that linear heating TG at constant rate (LHTG) does not necessarily mean that the decomposition reaction is a single elementary process. If a material decomposes with several consecutive reactions and the differences of activation energies are small, mass loss observed in LHTG will become a single step change.

The residual weight 50.8% after III decomposition step, *i.e.*, at 438.36° C, corresponds nearly to that calculated for Na_2S_5 (50.5%). Fabretti *et al.* [61] carried out TGA for sodium salts of 4-phenylpiperdinedithiocarbamate and N-phenylpiperazine dithiocarbamate in air and observed that residue is Na_2S_5 which then undergoes oxidation to Na_2O and / or Na_2SO_4 . In the present study, TGA was carried out in an inert atmosphere hence further weight loss may be due to partial decomposition of Na_2S_5 .

Generally the higher value of E^* suggests higher stability but there lie some more inherent physical and chemical factors which may cause a variation in this trend.[80] Higher value of E^* and lower values of Z (frequency factor) favour the reaction to proceed slower than normal. The negative value of entropy of activation indicated that the activated complex has a more ordered or more rigid structure than the reactants and the reaction is slower than the normal.[80] The very low value for E^* in first step for UBBDT and DAPBBDT supports the inference for loss of solvents. The next step corresponding to loss of water molecules showed slightly higher value of E^* . The lower E^* values obtained for DTOBBDT is in conformity with the lowest stability proposed for it.

4.CONCLUSION

Bisdithiocarbamates were prepared from urea, thiourea and dithiooxamide. Which are the least reactive derivatives of carboxylic acid. A tentative mechanism involving nucleophilic attack by the anionic species, formed in the presence of strong alkali NaOH, on the CS_2 has been proposed. Due to the low reactivity of these weak nitrogenous bases, longer reaction time was required. Spectral analysis and conductivity measurements suggested efficient electron delocalization within the molecules of various bisdithiocarbamates. These BDTCS were thermally quite stable. UBBDT yielded a heat resistance product upon heating, for which a resonance stabilized cyclic structure has been proposed. All these BDTCS were water-soluble with good complexing ability for various metal ions. Polymeric nature of the metal complexes was inferred based on amorphous and intractable nature.

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COMPETING INTERESTS

Authors have declared that no competing interest exist.

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