

1 *Research Paper*

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

4 **ABSTRACT**

In the present study, disodium salts of bisdithiocarbamates have been prepared from urea, thiourea, dithiooxamide and 1,3-diaminopropanewith carbon disulfide under strong alkaline medium of a sodium hydroxide solution. All ligands possessed good chelating ability for various metal ions. Metal complexes of urea bisdithiocarbamates was synthesized with Co (II), Ni (II), Zn (II), and Pb(II). The nature of metal complexes was amorphous and solid. The prepared ligands and complexes were characterized by elemental analysis, electronic, infrared (IR) spectroscopy, conductivity measurements, magnetic measurements and thermogravimetric analysis (TGA). Electronic spectra and magnetic measurements indicate that the complexes have contained octahedral geometry.

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6 **Keywords:** *Bisdithiocarbamates; Bridging or Chelating Ligands; Multidentate Ligands; Thermo*
7 *gravimetric Analysis (TGA).*

1. INTRODUCTION

Dithiocarbamates are the half amides of dithiocarbonic acids and can act as monodentate, bidentate chelating or bidentate bridging ligands [1]. Dithiocarbamates are highly versatile mono-anionic chelating ligands which form stable complexes with all transition elements and also the majority of main group, lanthanide and actinide elements [2-6].

The chemistry of dithiocarbamate complexes have been reported to a great number of metal ions because of their striking structural features and diversified applications in ~~the field of~~ industrial and biological applications [7,8]. The various applications in chemical process, such as vulcanization accelerators in rubber industry [9], in the areas of analytical chemistry [10], photochemistry [11] organic synthesis [12], agriculture [13], antimicrobial activity [14,15] pharmaceutical industry [16] medicine [17,18] electrochemical sensors [19].

Dithiocarbamates possess interesting electrochemical and optical properties due to their redox behavior and strong coordination ability [20]. ~~The optical and electrochemical properties of dithiocarbamates can effectively be used for practical applications [21, 22].~~

A developing interest in the area of dithiocarbamate chemistry is focused on the functionalization of their backbone. Even though this area is still in its early stages, interesting potential applications have been already noted ~~which include~~ the functionalization of gold nanoparticles, precursors for nanomaterials, stepwise build-up of multimetallic arrays, and the synthesis of dithiocarbamate containing supramolecular systems [23, 24]. More recently ~~nanomaterial dithiocarbamate complexes based nanoparticles with a size ranging between 1 and 100 nm were synthesized, which exhibited a broad spectrum of applications~~ in catalysis, electronic, optical and magnetic materials because of their unique chemical and physical properties. Besides, they are also used in light emitting devices, solar cells and bio-imaging [25 -28].

The studies of lanthanide dithiocarbamate complexes on their thermal and photoluminescence properties become more interesting because of their potential utility as precursors for the fabrication of lanthanide sulfidenanoparticles, thin films, fluorescent labeling reagents, imaging agents, and emitter materials in organic light-emitting diodes [29]. ~~In recent past, several books and reviews appeared in literature on the synthesis, characterization of dithiocarbamates and Related Compounds [30- 48].~~ A review published by Graeme Hogarth [36] focused on the chemistry and biological activity of dithiocarbamate coordination compounds, while a critical review reported by Kanchi et al [37] highlighted a wide range of applications of dithiocarbamates (DTCs) in environmental samples. The present study reports a detailed study on the synthesis and characterization of disodium salts of bisdithiocarbamates (from urea, thiourea dithiooxamide and 1,3-diaminopropane) and their Co(II), Ni (II), Cu(II), Zn (II) and Pb(II) complexes.

2. EXPERIMENTAL DETAILS

2.1 Materials

Urea (U) and thiourea (TU) were obtained from LobaChemie 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) and Pb (II), cobalt (II) chloride and sulfate were purchased from E. Merck, India and EDTA (A.R. Qualigens, Glaxo, India). All the chemicals with analytical grade were directly 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 literature methods [49] 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. However, in case of DTOBDT 12 g (0.1 mol) of dithiooxamide was dissolved in 150 mL of ethanol. To the resultant solution, NaOH (8 g or 0.2 mol) dissolved in 50 mL of water was added.

For preparation of DAPBDT, 7.4 mL (0.076 mol) of 1, 3- diaminopropane and 37.5 mL of ethanol were 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 kept below 10°C by external cooling and 12 mL (0.2 mol) of carbon disulfide was slowly dropped over 30 minutes. The mixture gradually turned from colorless to orange in half an hour. Then the mixture was 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, and heated at 50°C for 1 h, and then cooled to room temperature. The product was slowly crystallized into colourless crystals within 3 -4 days, (the color for DTOBDT was brown). The crystalline products were washed with acetone and recrystallised from water. The purified products were water-soluble.

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 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. Then 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. HNO₃ and titrating against EDTA.

RESULTS AND DISCUSSION

2.1 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 and analytical data are given in Table 1.

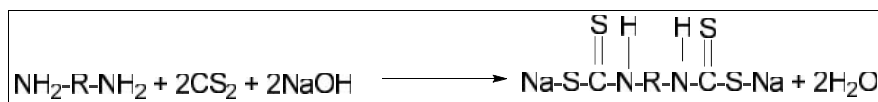
Table 1 Analytical and Elemental Data of Bisdithiocarbamates

Ligand	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	11.90 (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)

^aFor 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.

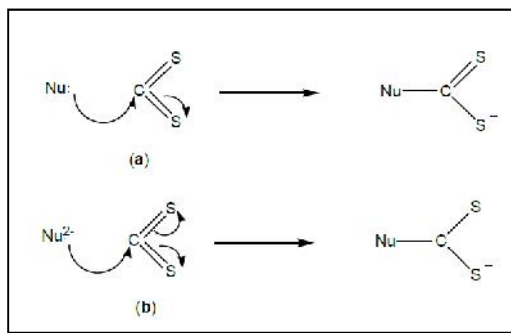
In the present study, syntheses of bisdithiocarbamates with diamide and thioamide structures from urea, thiourea, and dithiooxamide were reported respectively.



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

Amides and thioamides are much weaker bases than amines and they are inactive carboxylic acid derivatives. Due to their extra resonance capability of the nitrogen lone electron pair. The resonance energy of delocalized system is lost on protonation of the nitrogen atom[50]. 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. Nucleophiles (Nu) attack of carbon disulphide was shown in scheme 3.1.

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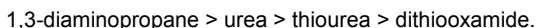


Scheme 3.1.: Nucleophiles (Nu) attack of carbon disulphide

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 center 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 behavior [51,52]. The resulting anion being stabilized by delocalization was described in scheme 3.1.

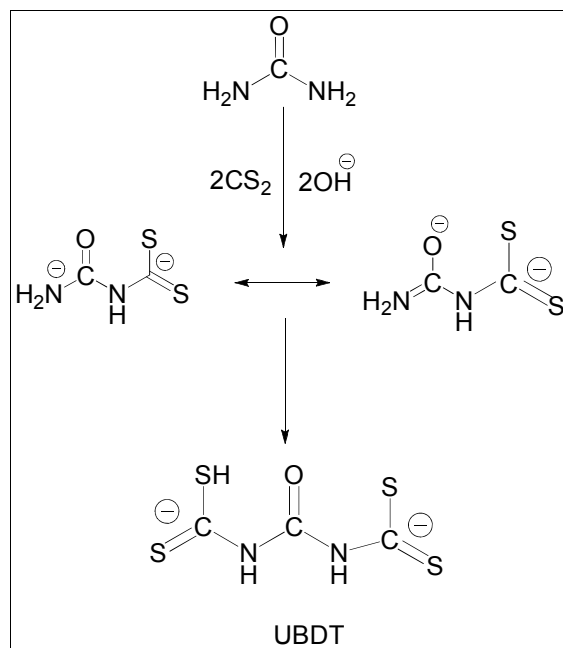
Analogous mechanism can be extended for thiourea and dithiooxamide also. However, for thiourea and dithiooxamide resonance stabilization of anionic species formed in presence of NaOH is not possible to an extent as that for urea, because overlap of 3p orbital's of sulfur atom (of thioamide group) with 2 p orbital's 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:



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

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Scheme 3.2. Tentative mechanism for bisdithiocarbamates formation from urea

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

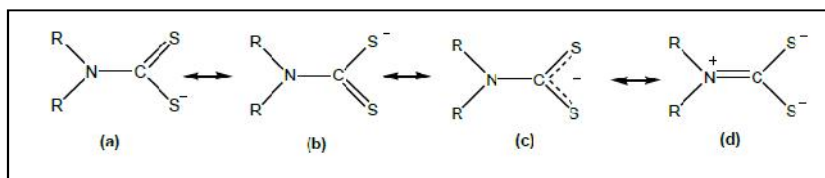
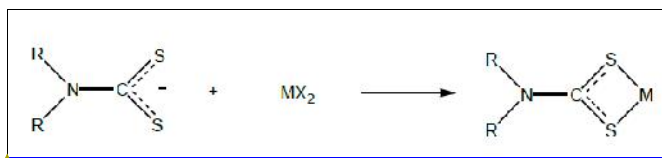


Fig.1.: Canonical form of Dithiocarbamate

2.2 Characterization of Ureabisdithiocarbamate metal complexes

An (aqueous) solution of metal salt is added slowly in a solution of the UBDTC ligands in 1:1 ratio are shown in following equation.



The yield colour and elemental analysis for various metal complexes of UBDT are reported in Table 2.

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166 **Table 2 Physical and Analytical Data of Coordination Polymers of UBDT ^a**

Complex	Molecular Formula	Colour	Melting point ^c	Yield %	Elemental Analysis found (Calculated)				
					C %	H %	N %	S %	Metal %
CoAcUBDT	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 UBDT	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	60	18.1 (18.8)	2.1 (1.9)	4.9 (5.5)	26.8 (25.1)	18.2 (18.9)
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)

167

168 ^a L = -SSCNHCONHCSS, Ac = CH₃COO⁻169 ^b Does not melt but darken at the temperature mentioned

170

171 All the complexes were stable at room temperature, unaffected by atmospheric oxygen and
 172 moisture and were insoluble in water as well as common organic solvents. The complexes appeared
 173 to be amorphous even on microscopic examination. The complexes did not melt on heating up to
 174 360°C, however, many of them became black above 200°C.

175 The metal complexes were dissolved in minimum quantity of concentrated nitric acid by heating and
 176 the solutions were cooled and diluted with double distilled water. Presence of sodium in the
 177 complexes was authenticated by flame photometry of these solutions. The anions viz., acetate,
 178 chloride or sulphate ions were detected qualitatively in the respective solutions of various complexes
 179 in dilute nitric acid.

180 **2.3 IR spectral analysis of ligands**

181 The IR spectra of bisdithiocarbamates of urea, thiourea, dithiooxamide and 1, 3-
 182 diaminopropane are depicted in Figure 2. Assignments of these bands are based on literature data
 183 [53-57]. For bisdithiocarbamates, three main regions are of interest in the infrared spectrum.

184 Firstly, the 3400 -3100 cm⁻¹, the broad bands in this region appear due to ν_{N-H} of
 185 dithiocarbamate ligand and ν_{O-H} from water molecules associated with the ligand.

186 Secondly, the 1450-1550 cm⁻¹ region which is associated primarily with the "thioureide"
 187 band due to ν_{C-N} vibration of the S₂C=NR₂ ligand.

188 Thirdly, the 950-1050 cm⁻¹ region which is associated with ν_(C-S) vibrations.

189 A perusal of (Fig. 2 a) made it evident that the symmetric and asymmetric stretching
 190 vibrations of -NH₂ groups of urea observed at 3447 and 3348 cm⁻¹ merged into a single band at
 191 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 $\delta\text{ OH}$ from absorbed water molecules. The amide II vibration, which appears in urea at 1630 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 CS_2 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 and 777 cm^{-1} , respectively. This suggested the decreased interaction of CS_2 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 region ($\nu_{\text{N-H}}$ and $\nu_{\text{O-H}}$, thioureide band due to $\nu_{\text{C-N}}$ vibration of the $\text{S}_2\text{C=NR}_2$ 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 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.

Appearance of broad bands near 3400 , 1600 and 650 cm^{-1} signified the presence of water molecules in bisdithiocarbamates [53-56].

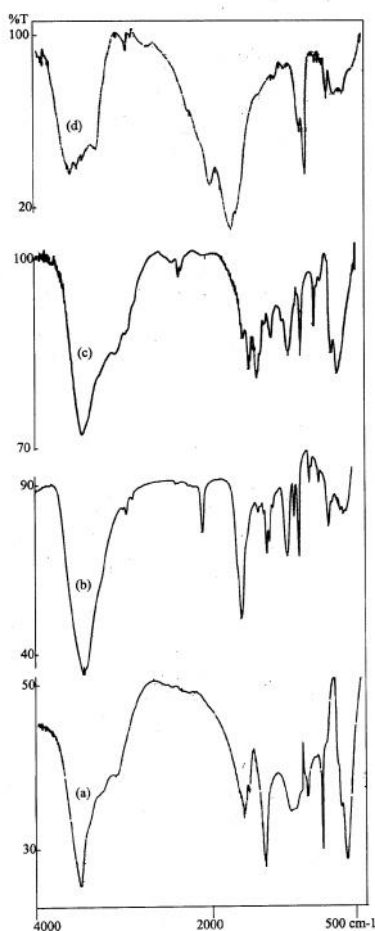


Fig. 2: IR Spectra of Bisdithiocarbamates (a) UBDT (b) DTOBDT (c) DAPBDT (d) TUBDT

2.4 IR spectral analysis of metal complexes of UBDT

The IR spectral data of metal complexes are depicted in (Fig. 3& 4). 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 ν (C-N) vibration [53-57]. This band is referred to as the thioureide form of the dithiocarbamate. This band lies between the ν (C-N) band at 1250 - 1350 cm^{-1} and the ν (C= N) band at 1640 - 1690 cm^{-1} range.

The thioureide band characteristic of dithiocarbamates at 1459 cm^{-1} splits upon complex formation 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 [53-57].

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

237 The band at 1696 cm^{-1} in UBDT involves significant contribution from NH bending vibrations
238 besides $\nu(\text{C}=\text{O})$. This band either disappears or appears as a shoulder on broad thioamide II band
239 suggesting coordination through nitrogen and carbonyl oxygen both[53-57].

240 A band at 1018 cm^{-1} has medium intensity and is broad, it may be assigned to asymmetric
241 C—S stretching and an intense sharp band at 860 cm^{-1} may be assigned to symmetric C-S stretching.
242 On complexation in most of the complexes –the bands corresponding 1018 cm^{-1} band of UBDT
243 appears with greatly decreased intensity. In case of cobalt (II) acetate, cobalt (II) sulphate, and nickel
244 (II) acetate complexes it is disappear. Zinc (II) acetate complex is shifted downward with weak
245 absorption. In lead (II) acetate complexes this band is shifted to slightly higher wave number with
246 medium absorption. However, the band at 860 cm^{-1} although experiences a downward shift but
247 appears as a sharp band with slightly decreased intensity on complexation except for Ni (II) acetate
248 complex where it is broader [53-57].

249 The intense bands due to carbonyl stretching overlapped by δ OH from water molecules
250 almost disappear in all the complexes. Presence of water molecules is ruled out, because the bands
251 associated with water molecules are not observed in all the complexes.

252 All these observations lead to conclude that all the donor atoms, viz., O, N, and S are involved in
253 coordination.

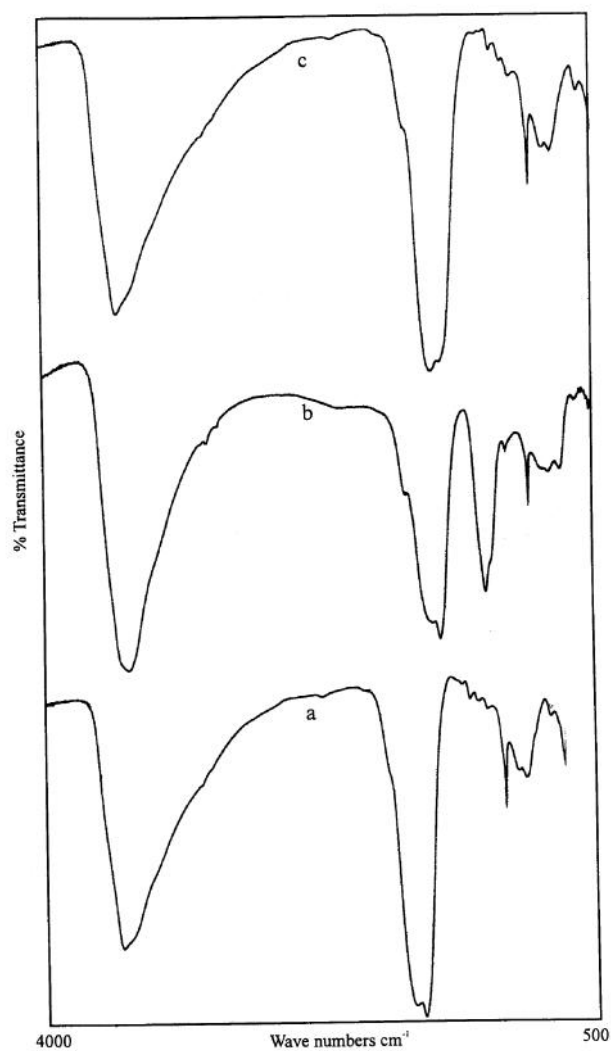


Fig. 3: IR Spectra of (a) Co Ac UBDT (b) Co Cl₂ UBDT (c) Co SO₄ UBDT

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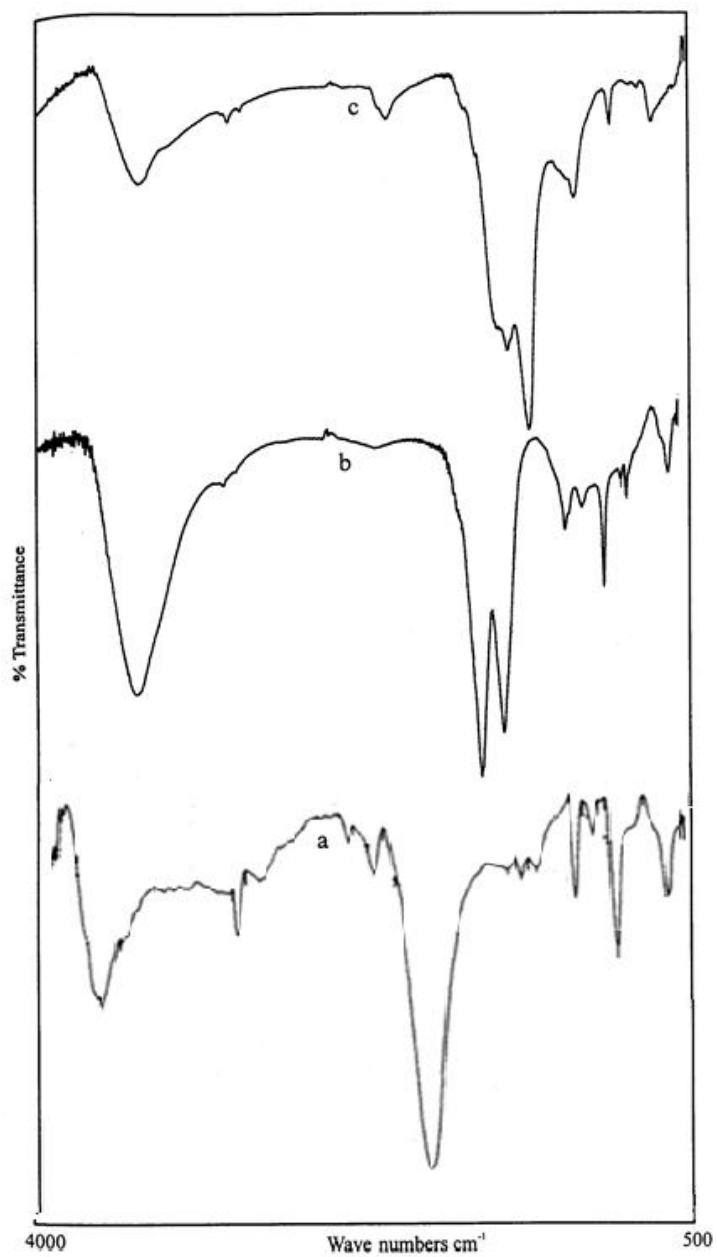


Fig. 4: IR Spectra of (a) Pb Ac UBDT (b) Zn Ac UBDT (c) Ni Ac UBDT

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2.5 NMR spectral studies

Bisdithiocarbamate formation is further substantiated by the observation of a broad signal in 4.9 to 5 ppm range due to $-\text{NH}-$ proton in ^1H - NMR spectrum of UBDT. ^{13}C - NMR spectrum exhibits a single signal at 164.5 ppm. It is strange that instead of two signals expected for $\text{C}=\text{O}$ and CS_2 carbons only one signal was observed. Kaur et al.[58] reported a resonance signal at ~ 171 ppm for substituted phenyldithiocarbamate. For bisdithiocarbamate derived from 1,3-diaminopropane besides the signals due to methylene carbons in 28-40 ppm range, a ^{13}C -NMR signal for CS_2 group at 164.2 ppm was observed. In case of DTOBDT the ^{13}C - NMR signals were observed at 109.5 and 29.7 ppm.

2.6 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. Takamiet al. [59] reported unambiguous assignment for these bands based on their study of the decomposition of N-mono substituted dithiocarbamates in alkaline solutions. Petrovet al.[60] 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 are reported. 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.

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 [61].

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 $\text{S}=\text{C}=\text{S}$ 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.

2.7 Electronic Spectral Analysis and Magnetic Susceptibility Measurement of UBDT Metal Complexes

The electronic spectra of the complexes were recorded as 10^{-3}M solution in DMSO and the results were presented in Table 3.

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The broad bands observed in the range (30959-24813) cm^{-1} are due to $\pi\text{-}\pi^*$ or $n\text{-}\pi^*$ within the dithiocarbamate group. The ν_1 band arising from ${}^4\text{T}_{2g}\rightarrow{}^4\text{T}_{1g}(\text{p})$ in transition 8000-10000 cm^{-1} range are not observable due to instrumental limitation.

Table 3 Electronic Spectral Analysis and Magnetic Susceptibility Measurement of UBDT Metal Complexes

S.No	Metal Complexes	Ligand transition band		${}^3\text{A}_{2g}\rightarrow{}^3\text{T}_{1g}(\text{P})$		${}^3\text{A}_{2g}\rightarrow{}^3\text{T}_{1g}(\text{F})$		$\mu_{\text{eff}}(\text{B.M})$
		$n \rightarrow \pi^*$		ν_3 17000-22000 cm^{-1}		ν_2 11000- 17000 cm^{-1}		
		nm	cm^{-1}	Nm	cm^{-1}	nm	cm^{-1}	
1.	Co (II)Ac UBDT	323 376 393	30959 26595 25445	506 516	19762 19379	812 843	12315 11862	4.57
2.	Co (II)Cl ₂ UBDT	382 395 421	26178 25364 23752	462 473 505	21645 21141 19801			4.80
3.	Co (II)SO ₄ UBDT	390 415	25641 24096	471 506	21231 19762	810 840	12345 11904	4.50
4.	Ni (II)Ac UBDT	391	25575	522	19157	657 720	15220 13888	2.80
5.	Pb (II)Ac UBDT	394 407	25380 24570	450 498	22222 20080			
6.	Zn (II)Ac UBDT	391 403	25575 24813	449 499	22271 20040			

The electronic spectral data for various Co (II) complexes of UBDT are data presented in Table. The ν_3 band from absorption characteristic of octahedral geometry is observed in all the cases and the double peak entails the splitting of ${}^4\text{T}_{1g}(\text{p})$ state. The weak bands due ${}^3\text{A}_{2g}\rightarrow{}^3\text{T}_{1g}(\text{F})$ transition are observed for cobalt (II) acetate and sulphate complexes but not for chloride complex. The magnetic moment values of Co(II) complexes are (4.57, 4.80 and 4.50 B.M) also correspond to an octahedral geometry of the complex [62].

The magnetic moment of Ni(II) complex (2.80 B.M) which indicates the presence of two electrons and have a octahedral geometry. The electronic spectra of UBDT complex with nickel (II) acetate show the presence of three band in the region at 13888 cm^{-1} , 25575 cm^{-1} and at 15220 cm^{-1} , which were assigned to ${}^3\text{A}_{2g}\rightarrow{}^3\text{T}_{2g}(\text{F})$ (ν_1), ${}^3\text{A}_{2g}\rightarrow{}^3\text{T}_{1g}(\text{F})$ (ν_2) and ${}^3\text{A}_{2g}\rightarrow{}^3\text{T}_{1g}(\text{P})$ respectively this show that the geometry of the complex is octahedral. The Zn(II) and Pb(II) complexes are not well resolved, so it is not interpreted, μ_{eff} values shows that they are diamagnetic as expected [63].

Mostly these bands are in accordance with the octahedral geometry and correspond to the transitions ${}^3\text{A}_{2g}\rightarrow{}^3\text{T}_{1g}(\text{F})$ and ${}^3\text{A}_{2g}\rightarrow{}^3\text{A}_{1g}(\text{F})$ respectively. The electronic spectrum data showed an upward trend above nm(cm^{-1}) 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 [63].

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

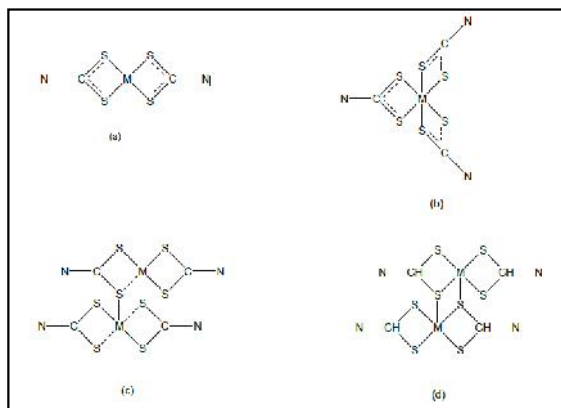


Fig.6: Dithiocarbamate complexes structural geometries

(a) The square planar coordination geometry

(b) The octahedral coordination geometry

(c) The four coordinate dimer

(d) The five coordinate dimer

3.7 Thermogravimetric analysis

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

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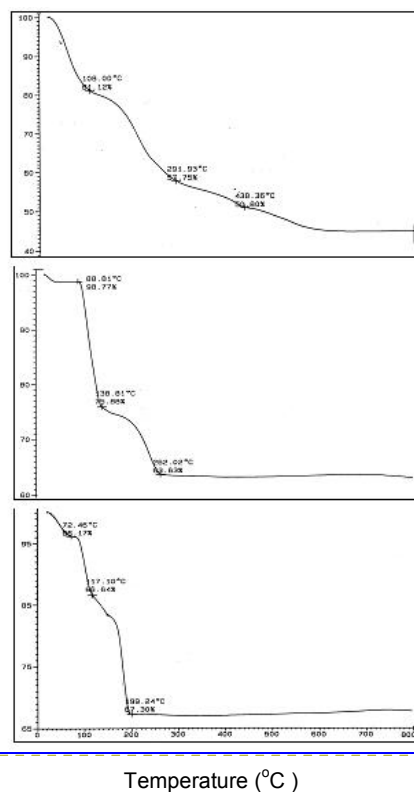


Fig. 7: T.G.A Curve of (a) UBDT (b) DAPBDT(c) DTOBDT

The kinetic parameters for thermal decomposition of ligands, calculated using the method proposed by Fuosset *al.* [64] are depicted in Table 4.

Table 4. Kinetic Parameters for Bisdithiocarbamates Calculated using Fuoss et.al method

Compound	Decomposition steps		Temperature at inflection point °C	Weight Loss %	ΔE^* kJmol ⁻¹	Z min ⁻¹
	Temperature range °C	Weight loss in temperature range %				
UBDT	0-100	5	50	2.50	5.75	0.564
	100 -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, DAPBDT and DTOBDT the initial weight losses in first step below 100°C, were 2.50, 8.50 and 6.75 % , respectively, which were ascribed to the loss of solvent molecules occluded in the crystal lattice.

For UBDT and DAPBDT two steep decomposition steps were observed above 100°C and the residues left above 200 and 262°C respectively, were stable up to 800°C. In case DTOBDT residue left near 500°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

The thermal decomposition pattern for DTOBDT is gradual and spread over a wider temperature range than that observed for UBDT or DAPBDT suggesting 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.

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.* [65] 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 .

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 [66]. Higher value of E^* and lower values of Z (frequency factor) favor 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 [67]. The very low value for E^* in first step for UBDT and DAPBDT 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 DTOBDT is in conformity with the lowest stability proposed for it.

4. CONCLUSION

Several bisdithiocarbamates were prepared from urea, thiourea and dithiooxamide respectively. 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 stable. UBDT 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 exists.

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