

## **Synthesis and Characterization of Bisdithiocarbamates from Weak Nitrogen Bases and Its Metal Complexes**

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### **Authors' contributions**

*This work was carried out in collaboration between all authors. Authors ST and AB designed the study, performed experiment, characterization and wrote the protocol. Authors KVR, KK and VN help in the editing and formatting the manuscript. All authors read and approved the final manuscript.*

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### **ABSTRACT**

In the present study, disodium salts of bisdithiocarbamates have been prepared from urea, thiourea, dithioamide 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

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measurements, magnetic measurements and thermogravimetric analysis (TGA). Electronic spectra and magnetic measurements indicate that the complexes have contained octahedral geometry.

*Keywords: Bisdithiocarbamates; bridging or chelating ligands; multidentate ligands; thermo gravimetric analysis (TGA).*

## 1. INTRODUCTION

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

The chemistry of dithiocarbamate complexes can be seen in a great number of metal ions because of their striking structural features and diversified applications in industrial and biological activities [7,8]. The various applications that can be cited are in chemical process, such as vulcanization, or as accelerators in rubber industry [9], & many more like in the areas of analytical chemistry [10], photochemistry [11] organic synthesis [12], agriculture [13], antimicrobial activity [14,15] pharmaceutical industry [16] medicine [17,18] and electrochemical sensors [19].

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

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, including 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 are widely applied 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 on lanthanide dithiocarbamate complexes is based on their thermal and photoluminescence properties. Their potential utility as precursors is applicable in a number of

processes like, for the fabrication of lanthanide sulfide nanoparticles, thin films, fluorescent labeling reagents, imaging agents, and emitter materials in organic light-emitting diodes [29]. Moreover, several books and reviews have appeared in literature on the synthesis, characterization of dithiocarbamates *and related* compounds [30-48]. A review was published by Graeme Hogarth [36] focused on the chemistry and biological activity of dithiocarbamate complexes. 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 dithioamide and 1,3-diaminopropane) and their Co(II), Ni (II), Cu(II), Zn (II) and Pb(II) complexes with urea.

## 2. EXPERIMENTAL DETAILS

### 2.1 Materials

Urea (U) and thiourea (TU) were obtained from LobaChemie Ltd., India. Dithioamide (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), dithioamide (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 than add NaOH (8 g or 0.2 mol) dissolved in 50 mL of water.

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 color 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 colored 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 colorless crystals within 3-4 days, but in case of DTOBDT the color was brown. The crystalline products were washed with acetone and recrystallised from water.

### 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 colored 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. After filtration, and washing thoroughly with water followed by drying, the pure products were obtained.

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 (1).

$$\text{Yield} = A / (L + M_o - M_r) \quad (1)$$

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 in a Perkin- Elmer's spectrometer model 1430 in 4000-600  $\text{cm}^{-1}$  range using KBr as dispersant. UV-visible spectra were recorded on a Unicam spectrometer model UV-2-100. Elemental analysis was done in a Carlo Erba 1108 Elemental analyzer. Sulfur was then quantitatively determined by oxidizing the bisdithiocarbamates with alkaline potassium permanganate followed by gravimetric determination as barium sulfate. The metal contents were then determined by decomposition of coordination polymers with conc.  $\text{HNO}_3$  and titrating against EDTA.

## 3. RESULTS AND DISCUSSION

### 3.1 Characterization of Multidentate Ligands

In general disodium salts of bisdithiocarbamates were prepared from urea, thiourea, dithiooxamide and 1, 3- diaminopropane and it was found that all the products were soluble in water and insoluble in organic solvents. The yields and analytical data are given in Table 1.

In the present study, syntheses of bisdithiocarbamates with diamide and thioamide gave the following equation (2).



Where R = -CO- for urea, -CS- for thiourea, -(CS)<sub>2</sub>- or dithiooxamide and (CH<sub>2</sub>)<sub>3</sub> for 1,3-diaminopropane.

Amides and thioamides are much weaker bases than amines and they are inactive carboxylic acid derivatives, due to the extra resonance capability provided by the nitrogen lone electron pair. The resonance energy of delocalized system is lost due to protonation of the nitrogen atom [50]. It is suggested that despite its weakness as a base, urea may act as a nucleophile in the presence of hydroxide ion by the loss of a proton. The typical attack of Nucleophile (Nu) on carbon disulphide is shown as in scheme 3.1.

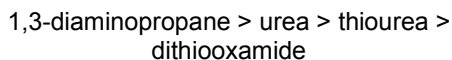
Sometimes basic and nucleophilic strengths are opposite to each other. Nucleophiles, which have unshared electron pair on the  $\alpha$ - atom immediately adjacent to the nucleophilic center appear to be unusually strong donors, though

they show weak basicity owing to the inductive effect of the adjacent heteroatom. The origin of this hyperactivity appears to lie in the 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 is described in scheme 3.1.



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

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 3 p 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 mainly due to the longer reaction time required to prepare them. Based on reaction time, the reactivity order for these compounds can be given as:



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

### 3.2 Characterization of Ureabisdithiocarbamate Metal Complexes

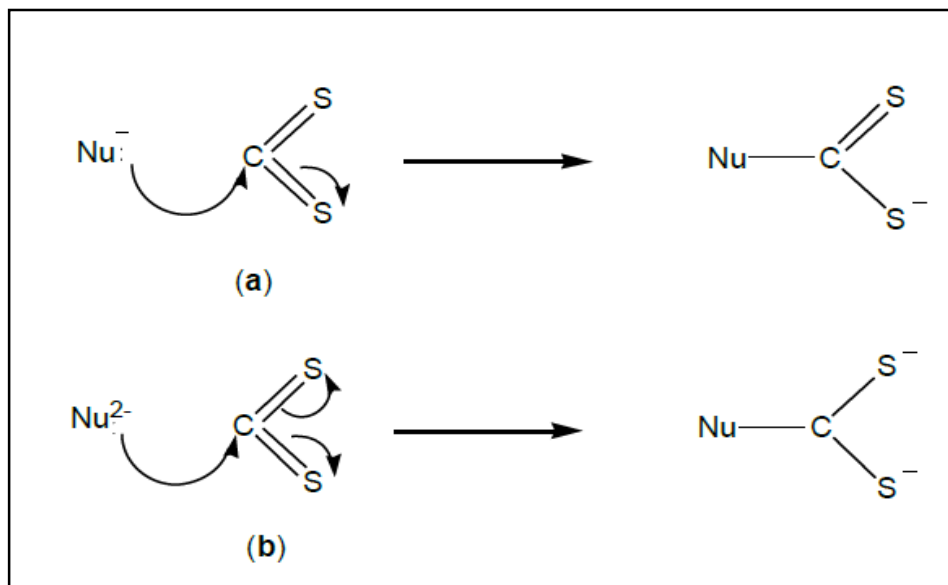
An (aqueous) solution of metal salt is added slowly in a solution of the UBDTC ligands in 1:1 ratio are shown in following equation (3).

All the complexes were stable at room temperature, appeared to be amorphous with good resistance to atmospheric conditions like oxygen, carbon dioxide and moisture and were insoluble in water as well as in common organic solvents. The complexes did not melt on heating up to 360°C, however, many of them became black above 200°C. The sodium ions present in the complexes was confirmed by flame photometry.

### 3.3 IR Spectral Analysis of Ligands

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

First, the 3400 -3100  $\text{cm}^{-1}$ , the broad bands in this region appear due to  $\nu_{\text{N}-\text{H}}$  of dithiocarbamate ligand and  $\nu_{\text{O}-\text{H}}$  from water molecules.



Scheme 3.1 Nucleophiles (Nu) attack of carbon disulphide

**Table 1. Analytical and elemental data of bisdithiocarbamates**

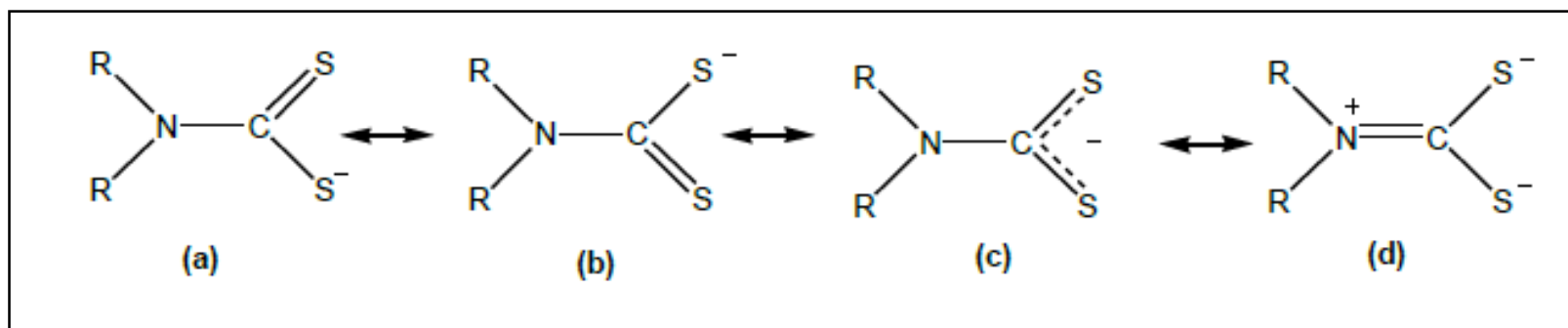
Ligand	Molecular formula	Yield <sup>b</sup> %	pH <sup>c</sup>	Elemental analysis <sup>a</sup>			
				% C	%H	%N	%S
UBDT	C <sub>3</sub> H <sub>2</sub> N <sub>2</sub> S <sub>4</sub> ONa <sub>2</sub> .3H <sub>2</sub> O	88	11	11.90 (11.61)	2.51 (2.58)	8.96 (9.02)	40.82 (41.20)
TUBDT	C <sub>3</sub> H <sub>2</sub> N <sub>2</sub> S <sub>5</sub> Na <sub>2</sub> .3H <sub>2</sub> O	85	10.5	10.86 (11.04)	2.05 (2.45)	8.01 (8.58)	49.85 (49.05)
DAPBDT	C <sub>5</sub> H <sub>8</sub> N <sub>2</sub> S <sub>4</sub> Na <sub>2</sub> .4H <sub>2</sub> O	87	10	17.70 (17.54)	4.23 (4.67)	7.89 (8.18)	37.92 (37.42)
DTOBDT	C <sub>4</sub> H <sub>2</sub> N <sub>2</sub> S <sub>6</sub> Na <sub>2</sub> .4H <sub>2</sub> O	74	8	12.69 (12.37)	2.08 (2.57)	7.83 (7.21)	49.71 (49.48)

<sup>a</sup> For each compound the upper values represent results obtained experimentally and the lower values in parentheses show theoretical analysis. <sup>b</sup> % Yield of the recrystallised products. <sup>c</sup> pH of 0.1 M aqueous solutions

**Table 2. Physical and analytical data of coordination polymers of UBDT a**

Complex	Molecular formula	Colour	Melting point <sup>c</sup>	Yield %	Elemental analysis found (calculated)				
					C %	H %	N %	S %	Metal %
CoAcUBDT	C <sub>16</sub> H <sub>20</sub> N <sub>4</sub> O <sub>14</sub> Na <sub>2</sub> Co <sub>3</sub> (L <sub>2</sub> Ac <sub>6</sub> Na <sub>2</sub> Co <sub>3</sub> )	Dark purple	220 <sup>b</sup>	57	18.9 (19.2)	2.32 (2.00)	5.8 (5.6)	25.4 (25.6)	16.9 (17.7)
CoCl <sub>2</sub> UBDT	C <sub>6</sub> H <sub>4</sub> N <sub>4</sub> O <sub>2</sub> Na <sub>2</sub> Co <sub>3</sub> Cl <sub>6</sub>	Light purple	180 <sup>b</sup>	53	7.9 (8.4)	0.93 (0.46)	6.0 (6.6)	29.09 (30.01)	19.2 (20.0)
CoSO <sub>4</sub> UBDT	C <sub>6</sub> H <sub>4</sub> N <sub>4</sub> O <sub>10</sub> Na <sub>2</sub> Co <sub>3</sub> H <sub>2</sub> O(SO <sub>4</sub> ) <sub>2</sub>	Light purple	220 <sup>b</sup>	56	6.9 (7.6)	1.50 (1.69)	5.8 (5.9)	32.15 (32.97)	18.3 (18.7)
NiAcUBDT	C <sub>16</sub> H <sub>20</sub> N <sub>4</sub> O <sub>14</sub> Na <sub>2</sub> Ni <sub>3</sub> L <sub>2</sub> Ac <sub>6</sub> Na <sub>2</sub> Ni <sub>3</sub>	Light green	180 <sup>b</sup>	52	18.9 (19)	1.9 (2.0)	5.0 (5.6)	26.46 (25.70)	16.7 (17.4)
ZnAcUBDT	C <sub>16</sub> H <sub>20</sub> N <sub>4</sub> O <sub>14</sub> Na <sub>2</sub> Zn <sub>3</sub> L <sub>2</sub> Ac <sub>6</sub> Na <sub>2</sub> Zn <sub>3</sub>	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 <sub>14</sub> H <sub>16</sub> N <sub>4</sub> O <sub>10</sub> Na <sub>2</sub> Pb <sub>3</sub> L <sub>2</sub> Ac <sub>4</sub> Na <sub>2</sub> Pb <sub>3</sub>	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 = CH<sub>3</sub>COO<sup>-</sup>; b Does not melt but darken at the temperature mentioned



**Fig. 1. Canonical form of dithiocarbamate**

Second, the 1450-1550  $\text{cm}^{-1}$  region which is associated with the "thioureide" band due to  $\nu_{\text{C-N}}$  vibration of the  $\text{S}_2\text{C=NR}_2$  ligand.

Third, the 950-1050  $\text{cm}^{-1}$  region for  $\nu_{(\text{C-S})}$  vibrations.

Infrared spectra of the ligands were observed as a peak in all the three regions i.e ( $\nu_{\text{N-H}}$  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.

In Fig. 2a (UBDT) the N-H absorptions appeared at 3467  $\text{cm}^{-1}$ . The strong absorption bands at 1696  $\text{cm}^{-1}$  are due to the stretching vibration of strongly H-bonded carbonyl group (amide I). The vibration of amide II appears at 1660  $\text{cm}^{-1}$  as a shoulder. The bands obtained at 1019 and 861  $\text{cm}^{-1}$  are due to the presence of  $\nu_{\text{as}}$  and  $\nu_{\text{s}}$  of the  $\text{CS}_2$  groups.

For Fig. 2b (DTOBDT) N-H absorptions at 3425  $\text{cm}^{-1}$ , N-H &  $\nu_{\text{C=O}}$  peak appeared at 1646  $\text{cm}^{-1}$  and thioureide band at 1001  $\text{cm}^{-1}$  and 881 respectively.

In Fig. 2c (DAPBDT) the N-H absorptions appeared at 3451  $\text{cm}^{-1}$ . The strong absorption bands at 1640 and 1628  $\text{cm}^{-1}$  are due to the stretching vibration of carbonyl group. The bands obtained at 997 and 849  $\text{cm}^{-1}$  are due to the presence of  $\nu_{\text{as}}$  and  $\nu_{\text{s}}$  of the  $\text{CS}_2$  groups.

In Fig. 2d (TUBDT) the N-H absorptions appeared at 3387  $\text{cm}^{-1}$ . The band for thioamide was obtained at 1602  $\text{cm}^{-1}$ . A sharp band due to  $\nu_{\text{C=S}}$  also appeared at 866  $\text{cm}^{-1}$ .

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

### 3.4 IR Spectral Analysis of Metal Complexes in UBDT

The general characteristic feature of the dithiocarbamate complexes is their Infrared (IR) spectrum which shows the presence of three characteristic bands. They exhibit a strong absorption band between 1450 and 1550  $\text{cm}^{-1}$  which attributed to  $\nu_{(\text{C-N})}$  vibration [53-57]. This band is referred to as the thioureide form of the dithiocarbamate. The band lies between  $\nu_{(\text{C-N})}$  band at 1250 -1350  $\text{cm}^{-1}$  and the  $\nu_{(\text{C=N})}$  band at 1640-1690  $\text{cm}^{-1}$  range.

The thioureide band characteristic of dithiocarbamates at 1459  $\text{cm}^{-1}$  splits upon complex formation in all the cases with a wide separation of almost 100  $\text{cm}^{-1}$  except for lead complexes. It is suggested that in UBDT due to electron delocalization  $-\text{C}=\text{N}$  (A) and  $-\text{C}-\text{N}$  (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].

The  $\nu_{(\text{CN})}$  for the thioamides appear at about 1500  $\text{cm}^{-1}$  and the  $\nu_{(\text{CN})}$  for the UBDT under consideration is observed at about 1459  $\text{cm}^{-1}$  with extensive electron delocalization. This bond is found between nitrogen and carbonyl carbon in amides while in the case of thioamides is found between nitrogen and dithioate carbon. However, splitting of this band by more than 100  $\text{cm}^{-1}$  suggests coordination through carbon as well as oxygen.

The band at 1696  $\text{cm}^{-1}$  in UBDT is due to NH bending vibrations besides  $\nu_{(\text{C=O})}$ . This band either disappears or appears as a shoulder on broad thioamide II band suggesting coordination between nitrogen and carbonyl oxygen [53-57].

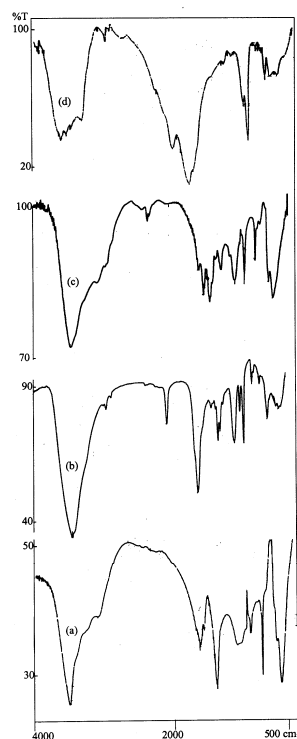
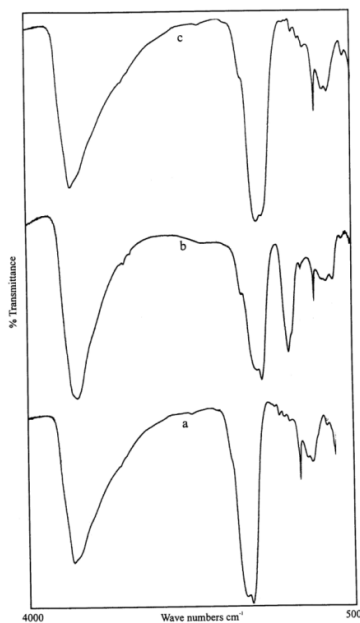


Fig. 2. IR Spectra of Bisdithiocarbamates (a) UBDT (b) DTOBDT (c) DAPBDT (d) TUBDT

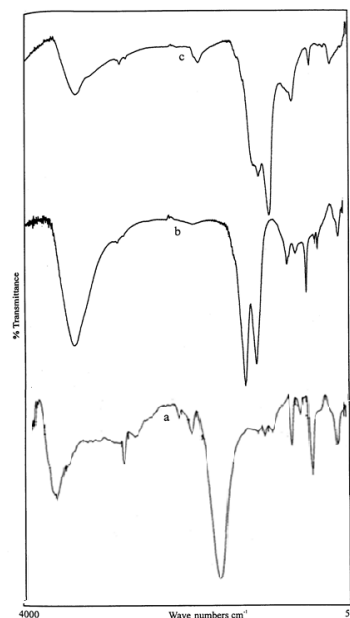
At  $1018\text{ cm}^{-1}$ , a band having medium intensity and broad in nature was found, indicating that it may be due to asymmetric C—S stretching. While an intense sharp band obtained at  $860\text{ cm}^{-1}$  may be due to symmetric C-S stretching. On complexation in most of the complexes the bands corresponding  $1018\text{ cm}^{-1}$  band of UBDT appears with decreased intensity. In case of cobalt (II) acetate, cobalt (II) sulphate, and nickel (II) acetate complexes it disappears. Zinc (II) acetate complex is shifted downward with weak absorption. In lead (II) acetate complexes this band is shifted to slightly higher wave number with medium absorption. The band at  $860\text{ cm}^{-1}$  although experiences a downward shift appears as a sharp band with slightly decreased intensity on complexation except in the case of Ni (II) acetate complex where it is broader [53-57].



**Fig. 3. IR Spectra of (a) Co Ac UBDT (b) Co Cl<sub>2</sub> UBDT (c) Co SO<sub>4</sub> UBDT**

The intense bands obtained due to carbonyl stretching are seen overlapped by  $\delta$  OH from water molecules which almost disappear in all the complexes. Presence of water molecules is ruled out, because the bands associated with water molecules are not observed in all the complexes.

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



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

### 3.5 NMR Spectral Studies

The formation of Bisdithiocarbamates ligands is further confirmed by the observation of a broad signal in 4.9 to 5 ppm range due to —NH— proton in <sup>1</sup>H- NMR spectrum of UBDT.

<sup>13</sup>C- NMR spectrum exhibits a single signal at 164.5 ppm in UBDT, DAPBDT is 164.1, TUBDT is 164.3 and DTOBDT signals were observed at 109 and 29.7 ppm. Kaur et al. [58] reported that a resonance signal at ~171 ppm for substituted phenyldithiocarbamate signals due to methylene carbons in 28-40 ppm range, and a <sup>13</sup>C-NMR signal for CS<sub>2</sub> group at 164.2 ppm was observed.

### 3.6 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. Takami et al. [59] reported unambiguous assignment for these bands based on their study of the decomposition of N-mono substituted dithiocarbamates in alkaline solutions. Petrov et 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 UBBDT 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 TUBBDT 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 TUBBDT are higher than those for UBBDT except for the  $\pi \rightarrow \pi^*$  transition of thiocarbonyl group. This is probably the reflection of lesser conjugation in TUBBDT 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 UBBDT.

### 3.7 Electronic Spectral Analysis and Magnetic Susceptibility Measurement of UBBDT 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.

The broad bands observed in the range (30959-24813)  $\text{cm}^{-1}$  are due to  $\pi\text{-}\pi^*$  or  $n\text{-}\pi^*$  within the dithiocarbamate group. The  $\nu_1$  band arising from  ${}^4\text{T}_{2g} \rightarrow {}^4\text{T}_{1g}(\text{p})$  in transition 8000-10000  $\text{cm}^{-1}$  range are not observable due to instrumental limitation.

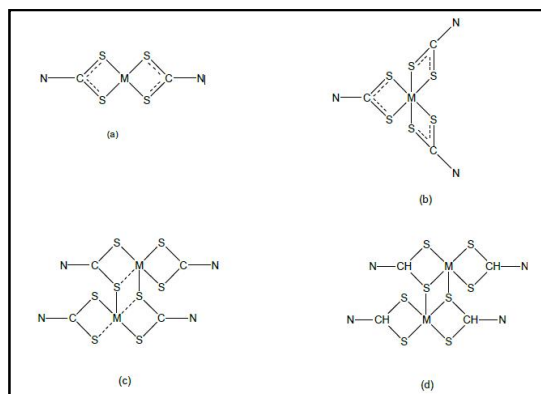
The electronic spectral data for various Co (II) complexes of UBBDT are data presented in Table 3. The  $\nu_3$  band from absorption characteristic of octahedral geometry is observed in all the cases and the double peak entails the splitting of  ${}^4\text{T}_{1g}(\text{p})$  state. The weak bands due  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$  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].

**Table 3. Electronic spectral analysis and magnetic susceptibility measurement of UBBDT metal complexes**

S. no	Metal complexes	Ligand transition band		${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$		${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$		$\mu_{\text{eff}}(\text{B.M})$
		$n \rightarrow \pi^*$		$\nu_3$ 17000-22000 $\text{cm}^{-1}$		$\nu_2$ 11000- 17000 $\text{cm}^{-1}$		
		nm	$\text{cm}^{-1}$	Nm	$\text{cm}^{-1}$	nm	$\text{cm}^{-1}$	
1.	Co (II)Ac UBBDT	323	30959	506	19762	812	12315	4.57
		376	26595	516	19379	843	11862	
		393	25445					
2.	Co (II)Cl <sub>2</sub> UBBDT	382	26178	462	21645			4.80
		395	25364	473	21141			
		421	23752	505	19801			
3.	Co (II)SO <sub>4</sub> UBBDT	390	25641	471	21231	810	12345	4.50
		415	24096	506	19762	840	11904	
4.	Ni (II)Ac UBBDT	391	25575	522	19157	657	15220	2.80
						720	13888	
5.	Pb (II)Ac UBBDT	394	25380	450	22222			
		407	24570	498	20080			
6.	Zn (II)Ac UBBDT	391	25575	449	22271			
		403	24813	499	20040			



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  $13888\text{ cm}^{-1}$ ,  $25575\text{ cm}^{-1}$  and at  $15220\text{ cm}^{-1}$ , which were assigned to  ${}^3A_{2g} \rightarrow {}^3T_{2g}$  (FT) ( $\nu_1$ ),  ${}^3A_{2g} \rightarrow {}^3T_{1g}$  (F) ( $\nu_2$ ) and  ${}^3A_{2g} \rightarrow {}^3T_{1g}$  (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,  $\mu_{\text{eff}}$  values shows that they are diamagnetic as expected [63].



**Fig. 5. 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

Mostly 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 electronic spectrum data showed an upward trend above  $\text{nm}(\text{cm}^{-1})$  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), ( $\nu_1$ ) transition [63].

Dithiocarbamate complexes can assume four structural geometries (Fig. 5).

### 3.8 Thermogravimetric Analysis

A multi-step decomposition pattern is evident from the thermogravimetric curves of ligands depicted in Fig. 6.

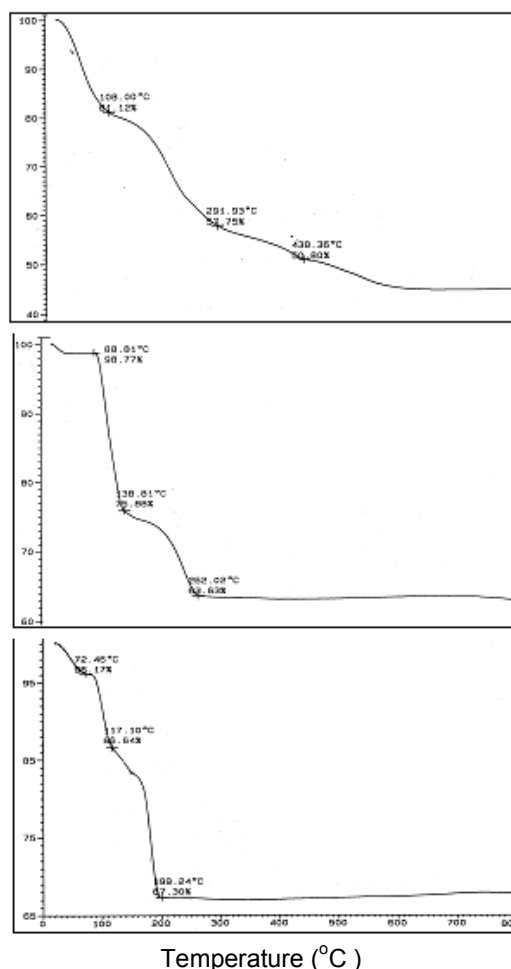
The kinetic parameters for thermal decomposition of ligands, calculated using the method proposed by Fuoss et al. [64] are depicted in Table 4.

For UBDT, DAPBDT and DTOBDT the initial weight losses in first step below  $100^\circ\text{C}$ , 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  $100^\circ\text{C}$  and the residues left above 200 and  $262^\circ\text{C}$  respectively, were stable up to  $800^\circ\text{C}$ . In case DTOBDT residue left near  $500^\circ\text{C}$ .

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

$$\text{UBDT} > \text{DAPBDT} > \text{DTOBDT}$$



**Fig. 6. T.G.A Curve of (a) UBDT; (b) DAPBDT; (c) DTOBDT**

**Table 4. Kinetic parameters for Bisdithiocarbamates calculated using Fuoss et al. [64] method**

Compound	Decomposition steps		Temperature at inflection point	Weight Loss	$\Delta E^*$	Z
	Temperature range	Weight loss in temperature range				
	$^{\circ}\text{C}$	%				
UBDT	0-100	5	50	2.50	5.75	0.564
	100 -150	12	100	9.75	30.24	$4.49 \times 10^3$
	150-199	15.7	185	27.00	244.78	$1.16 \times 10^{25}$
DAPBDT	0-100	3	110	8.50	22.72	263.94
	100-150	23	120	18.00	87.38	$2.7 \times 10^{11}$
	150-262	11.37	240	33.50	228.72	$2.03 \times 10^{23}$
DFOBBDT	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	$5.4 \times 10^3$
	438-500	5	545	53.25	139.08	1.9

The thermal decomposition pattern for DFOBBDT 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  $438.36^{\circ}\text{C}$ , corresponds nearly to that calculated for  $\text{Na}_2\text{S}_5$  (50.5%). Fabretti et al. [65] carried out TGA for sodium salts of 4-phenyl piperidine dithiocarbamate and N-phenylpiperazine dithiocarbamate in air and observed that residue is  $\text{Na}_2\text{S}_5$  which then undergoes oxidation to  $\text{Na}_2\text{O}$  and / or  $\text{Na}_2\text{SO}_4$ . In the present study, TGA was carried out in an inert atmosphere hence further weight loss may be due to partial decomposition of  $\text{Na}_2\text{S}_5$ .

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 thenormal [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 DFOBBDT is in conformity with the lowest stability proposed for it.

#### 4. CONCLUSION

Bisdithiocarbamates were prepared from urea, thiourea, diaminopropane and dithiooxamide respectively. A tentative mechanism involving nucleophilic attack by the anionic species, formed in the presence of strong alkali NaOH, on the  $\text{CS}_2$  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.

## REFERENCES

- Sharma M, Sharma A, Sachar R. Synthesis and Characterization of the Adducts of Morpholinedithiocarbamate Complexes of Oxovanadium (IV), Nickel (II), and Copper (II) with Piperidine and Morpholine. *E-Journal of Chemistry*. 2012;9(4):1929-40. Available:<http://www.ejchem.net>
- Zedan SW. Binuclear Complexes of Co(II),Ni(II), Cu(II) & Zn(II) With Mixed Ligand triethylenetetraamine dithiocarbamate & glycine. *College of Basic Education Researchers Journal*. 2010;10(2):530-42.
- Mamba SM. Synthesis, characterization and applications of dithiocarbamate transition metal complexes, University of Johannesburg; 2011.
- Yu X, Wang N, He H, Wang L. Theoretical investigations of the structures and electronic spectra of Zn(II) and Ni(II) complexes with cyclohexylamine-N-dithiocarbamate. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*. 2014;122(25): 283-287.
- RegulacioMD, Tomson N, Stoll SL. Dithiocarbamate Precursors for Rare-Earth Sulfides. *Chem. Mater*. 2005; 17: 3114-21.
- Pitchaimani P, Lo KM, Elango KP. Synthesis, spectral characterization, crystal structures and catalytic activity of a series of lanthanide(III) azepane dithiocarbamate complexes. *Polyhedron*. 2013;54:60–66.
- Onwudiwe DC, Ajibade PA, Omondi B. Synthesis, spectral and thermal studies of 2,2'-bipyridyl adducts of bis(N-alkyl-N-phenyldithiocarbamato)zinc(II). *J. Mol. Struct*. 2011;987:58–66.
- Buttrus NH, AL-Omari AF. New trinuclear complexes of Co(II),Ni(II),Cu(II) and Zn(II) with thiolotriazole, dithiocarbamate indium (III) and their biological study. *National Journal of Chemistry*. 2010;37:101-110.
- Nieuwenhuizen PJ, Ehlers AW, Haasnoot JG, Janse SR, Reedijk J, Baerends EJ. The mechanism of zinc (II)-dithiocarbamate-accelerated vulcanization uncovered; theoretical and experimental evidence. *J. of the American Chemical Society*. 1999;121(1):163-168.
- Orescanin V, Mikelic L, Roje V, Lulic S. Determination of lanthanides by source excited energy dispersive X-ray fluorescence (EDXRF) method after preconcentration with ammonium pyrrolidine dithiocarbamate (APDC). *Analytica Chimica Acta*. 2006;570:277–282.
- Kolomeetsa AV, Plyusnina VF, Grivina VP, Larionovc SV. Photochemical processes for dithiocarbamate metal complexes. *Photochemistry of Ni(II)(n-Bu<sub>2</sub>NCS<sub>2</sub>)<sub>2</sub> complex in CCl<sub>4</sub>*. *Journal of Photochemistry and Photobiology A: Chemistry*. 2011;220:164–172.
- Henckens A, Colladet K, Fourier S, Cleij TJ, Lutsen L, Vanderzande D. Synthesis of 3,4-diphenyl-substituted poly(thienylenevinylene), low-bandgap polymers via the dithiocarbamate route. *Macromolecules*. 2005;38:19–26.
- Rafin C, Veignie E, Sancholle M, Postal D, Len C, Villa P. Synthesis and antifungal activity of novel bisdithiocarbamate derivatives of carbohydrates against *Fusarium oxysporum* f. sp. lini. *J. Agric. Food Chem*. 2000;48:5283-5287.
- Odola AJ, Woods JAO. Synthesis, characterization and antimicrobial activity studies of new Nickel(II) mixed ligand complexes of disubstituted dithiocarbamates with ethylsalicylaldiminate. *Archives of Applied Science Research*. 2011;3(4):463-70.
- Desai RM, Shah MK, Shah MK. Preparation and Antimicrobial Screening of Cu (II), Ni (II), Zn (II) Cd (II) Complexes. *E-Journal of Chemistry*. 2006; 3(3): 137-41. Available:<http://www.e-journals.net>
- Odola J, Woods JAO. New nickel(II) mixed ligand complexes of dithiocarbamates with Schiff base. *Journal of Chemical and Pharmaceutical Research*. 2011;3(6):865-871.
- Manav N, Mishra AK, Kaushik NK. *In vitro* antitumour and antibacterial studies of some Pt(IV) dithiocarbamate complexes. *E-Journal of Chemistry*. 2006;3(3):137-141. Available:<http://www.e-journals.net>.
- Mansouri-Torshizia H, Saeidifar M, Divsalar A, Saboury AA. Interaction studies between a 1,10-phenanthroline adduct of palladium(II) dithiocarbamate anti-tumor complex and calf thymus DNA. A synthesis spectral and *In vitro* study. *Spectrochimica Acta Part A*. 2010;77:312–318.
- Shakhsher ZM, Odeh IMA, Rajabi IMS, KhatimK. Optical sensing properties of

- dithiocarbamate-functionalized microspheres, using a polyvinylpyridine-polyvinylbenzyl chloride copolymer. *Sensors*. 2010;10:8953-8962.
20. Lou W, Chen M, Wang X, Zhang Y, Liu W. Thermolysis of dialkyldithiophosphates in porous anodic alumina template: A versatile route to produce semiconductor metal sulfide nanowires. *Chemistry Letters*. 2006;35:850-857.
  21. Beer D, Berry N, Drew MGB, Fox OD, Padilla-Tosta ME, Patell S. Self-assembled dithiocarbamate-copper(II) macrocycles for electrochemical anion recognition. *Chemical Communications*. 2001;199-203.
  22. Siddiqi KS, Nami SAA, Chebude Y. Template synthesis of symmetrical transition metal dithiocarbamates. *Journal of the Brazilian Chemical Society*. 2006;17:107-110.
  23. Mthethwa T. Synthesis of hexadecylamine capped CdS nanoparticles using heterocyclic cadmium dithiocarbamates as single source precursors. *Polyhedron*. 2009;28:2977-2982.
  24. Onwudiwe DC, Ajibade PA. ZnS, CdS and HgS Nanoparticles via Alkyl-Phenyl Dithiocarbamate Complexes as Single Source Precursors. *Int. J. Mol. Sci*. 2011;12:5538-5551.
  25. Vickers MS, Cookson J, Beer PD, Bishop PT, Thiebaut B. Dithiocarbamate ligand stabilised gold nanoparticles. *J. Mater. Chem*. 2006;16:209-215.
  26. Nyamen LD, Pullabhotla VSR, Nejo AA, Ndifon P, Revaprasadu N. Heterocyclic dithiocarbamates: Precursors for shape controlled growth of CdS nanoparticles. *New J. Chem*. 2011;35:1133-1139.
  27. Nabipour H. Synthesis of a new dithiocarbamate cobalt complex and its nanoparticles with the study of their biological properties. *Int. J. Nano. Dim*. 2011;1(3):225-32.
  28. Ajibade PA, Ejelonu BC. Group 12 dithiocarbamate complexes: Synthesis, spectral studies and their use as precursors for metal sulfides nanoparticles and nanocomposites. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*. 2013;113:408-14.
  29. Regulacio MD, Pablico MH, Vasquez JA, Myers PN, Stoll SL. Luminescence of Ln(III) dithiocarbamate complexes (Ln) La, Pr, Sm, Eu, Gd, Tb, Dy). *Inorg. Chem*. 2008;47:1512-1523.
  30. Thorn GD, Ludwig RA. *The dithiocarbamates and related compounds*, Amsterdam, Elsevier Publishing Co; 1962.
  31. Coucouvanis D. Chemistry of the dithioacid and 1, 1-dithiolate complexes. *Prog. Inorg. Chem*. 1970;11:233-371.
  32. Coucouvanis D. The chemistry of the dithioacid and 1, 1-dithiolate complexes, 1968-1977. *Prog. Inorg. Chem*. 1979;26: 301-469.
  33. Bond AM, Martin RL. Electrochemistry and redox behavior of transition-metal dithiocarbamates. *Coord. Chem. Rev*. 1984;54:23-98.
  34. Hill JO, Magee RJ, Liesegang J. Photoelectron spectroscopy of metal dithiocarbamate, xanthate and dithiophosphate complexes: a review comments on inorganic chemistry. *A Journal of Critical Discussion of the Current Literature*. 1985;5(1):1-27.
  35. Cvek B, Dvorak Z. Targeting of Nuclear Factor-kB and Proteasome by Dithiocarbamate Complexes with Metals. *Current Pharmaceutical Design*. 2007;13: 1-13.
  36. Hogarth G. Metal-dithiocarbamate complexes: Chemistry and biological activity. *Mini-Reviews in Medicinal Chemistry*. 2012;12(12):1202-15.
  37. Kanchi S, Singh P, Bisetty K. Dithiocarbamates as hazardous remediation agent: A critical review on progress in environmental chemistry for inorganic species studies of 20<sup>th</sup> century. *Arabian Journal of Chemistry*. 2014;7:11-25.
  38. Trifunovic SR, Markovic Z, Andjelkovic K, Sabo T, Minic D. The synthesis and characterization of nickel(II) and copper(II) complexes with the polydentate dialkyl dithiocarbamic acid ligand 3-dithiocarboxy-3-aza-5-aminopentanoate. *J. Serb. Shem. Soc*. 2002;67(2):115-122.
  39. Gheibi N, Saboury AA, Mansuri-Torshizi H, Haghbeen K, Moosavi-Movahedi AA. The inhibition effect of some n-alkyl dithiocarbamates on mushroom tyrosinase. *J. Enzyme Inhib. Med Chem*. 2005; 20(4):393-399.
  40. Singh N, Bhattacharya S. Synthesis and characterization of some triorgano, diorgano, mono-organotin and a triorganolead heteroaromatic dithiocarbamate complex. *Journal of Organometallic Chemistry*. 2012;700(1): 69-77.

41. Onwudiwe DC, Arfin T, Strydom CA. Fe(II) and Fe(III) complexes of N-ethyl-N-phenyl dithiocarbamate: Electrical conductivity studies and Thermal properties. *Electrochimica Acta*. 2014;127:283-289.
42. Singh SK, Kumar V, Drew MGB, Singh N. Syntheses, crystal structures and photoluminescent properties of new heteroleptic Ni(II) and Pd(II) complexes of ferrocene functionalized dithiocarbamate and dipyrromethene ligands. *Inorganic Chemistry Communications*. 2013;37:151-154.
43. Yu X, Wang N, He H, Wang L. Theoretical investigations of the structures and electronic spectra of Zn(II) and Ni(II) complexes with cyclohexylamine-N-dithiocarbamate. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*. 2014;122:283-287.
44. Mohamed GG, Ibrahim NA, AttiaHAE. Synthesis and anti-fungicidal activity of some transition metal complexes with benzimidazole dithiocarbamate ligand. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*. 2009;72(3):610-615.
45. Tiwari S, Bajpai A. Metal ion extraction by dithiocarbamate function supported on polyacrylamide. *Reactive and Functional Polymers*. 2005;64(1):47-54.
46. Halimehiani AZ, Marjani K, Ashouri A, Amani V. Synthesis and characterization of transition metal dithiocarbamate derivatives of 1-aminoadamantane: Crystal structure of (N-adamantylidithiocarbamate)nickel(II). *Inorganica Chimica Acta*. 2011;373(1):282-285.
47. Shi Y, Chu W, Wang Y, Du J, Qin X, Zhang C. Synthesis, characterization and cytotoxicity of the Au(III) complexes with cyclic amine-based dithiocarbamate ligands. *Inorganic Chemistry Communications*. 2013;30:178-181
48. Dawood ZF, Mohammed TJ, Sharif MR. New nickel (II) complexes with benzilbis (semicarbazone) and dithiocarbamate ligands. *Iraqi Journal of Veterinary Sciences*. 2009;23(2):135-141.
49. Kobayashi N, Fujisawa T. The reactions of sodium diethyldithiocarbamate and tetraethylthiuram disulfide with mercury (II) Chloride. *Bull. Chem. Soc.* 1976; 49(10):2780-2789.
50. Norman ROC, Coxon JM. Principles of Organic Synthesis. 3<sup>rd</sup> ed. ELBS with Chapman & Hall Ltd.: London. 1993;49.
51. March J. Advanced Organic Chemistry. 2<sup>nd</sup> ed. McGraw-hillKogakusha, Ltd.: Tokyo. 1977; 338.
52. Silverstein RM, Bassler GC, Morrill TC. Spectrometric Identification of Organic Compound. 4<sup>th</sup> ed. John Wiley & Sons: New York. 1981;130.
53. Nakamoto K. Infrared Spectra of Inorganic and Coordination Compounds. 5<sup>th</sup> ed. Wiley Interscience: New York. 1968;167.
54. Brown DA, Glass WK, Burke MA. The general use of i.r. spectral criteria in discussions of the bonding and structure of metal dithiocarbamates. *Spectrochim. Acta*. 1976;32A:137-143.
55. Bellamy L, The infrared spectra of complex molecules. John Wiley & Sons: New York. 1964;298.
56. Vogel AI, Furniss BS. Vogel's textbook of practical organic chemistry, 5<sup>th</sup> ed. Longman Scientific and Technical, Wiley: New York; 1989.
57. Kemp W. Organic Spectroscopy, 3<sup>rd</sup> ed. Macmillan Press Ltd: Hong Kong London; 1991.
58. Kaur J, Marwaha SS, Sodhi GS. Organomercury(II)-dithiocarbamate complexes: Synthesis, characterization and fungicidal activity. *J. Ind. Chem. Soc.* 1999;76:185-190.
59. Takami F, Wakahara S, Maeda T. The UV spectra and dissociation constants of some dithiocarbamates. *Tetrahedron Lett.* 1971; 28:2645-2648.
60. Petrov I, Simonovska B. The UV spectra of ethylene-1, 2-bisdithiocarbamates. *J. Molecular Struct.* 1986;142:167-170.
61. Lever ABP. Electronic spectra of some transition metal complexes. *J Chem Edu.* 1968; 45(11):711-12.
62. Shriver DW, Atkins PW. Inorganic chemistry, electronic spectra of TM complexes. 4<sup>th</sup> ed. Freeman, New York; 2006.
63. Verhagen JAW, Beretta M, Spek LA, Bouwman E. New nickel complexes with an S-4 coordination sphere; synthesis, characterization and reactivity towards nickel and iron compounds. *Inorg. Chim. Acta*. 2004;357:2687-2693.
64. Fuoss RM, Salyer IO, Wilson HS. Evaluation of rate constants from

- thermogravimetric data. J. Polym. Sci. Part A. 1964;2(7):3147-3151.
65. Fabretti AC, Forghieri F, Giusti A, Preti C, Tosi G. The syntheses and properties of cobalt(II), nickel(II) and copper(II) complexes with some heterocyclic dithiocarbamates. Inorg. Chim. Acta. 1984;86:127-131.
66. Kausbik NK, Bhushan B, Sharma AK. Studies on this N[(chlorophenyl)di thiocarbamato] complexes of Au(III) and As (III). Thermochemica Acta. 1985;93:105-108.
67. Sharma AK. Thermal behaviour of metal-dithiocarbamates. Thermochemica Acta. 1986;104:339-372.

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