

Synthesis Characterization and Spectral Studies of Bisdithiocarbamate of Urea and its Metal Complexes

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Abstract- A novel disodium salt of Bisdithiocarbamates of urea (UBDT) and its metal complexes, Co(II)UBDT, Ni(II)UBDT, Cu(II)UBDT and Cd(II)UBDT were prepared and characterized by Elemental Analysis, Conductivity Measurements, Infrared Spectroscopy, Electronic Spectroscopy and NMR Spectroscopy. Water-soluble UBDT possessed good chelating ability for various metal ions. Its complexes, Co (II), Ni (II), Cu (II) and Cd (II) are amorphous, intractable solid having polymeric structure. The ligand as well as the complex was found to possess high thermal stability.

Index Terms - Synthesis, Bisdithiocarbamates, Metal Complexes and Characterization.

I. INTRODUCTION

Dithiocarbamates are S, N containing ligands, which display a rich and varied coordination chemistry with a wide range of transition and main group metal complexes. The chemistry of these compounds has aroused special interest because of the analytical purpose, as well as their industrial applicability [1-3]. Their metal complexes present striking structural features and have diversified applications, such as high pressure lubricants in industry, fungicides and pesticides, and also as accelerators in vulcanization [4]. Dithiocarbamates have also found important use in medicine as anti-alcoholic drug [5], anticancer [6], and recently as co-adjuvant in AIDS treatment [7]. This is related to their strong metal binding capacity, hence could act as inhibitors of enzymes [8]. Thermo analytical methods are of great interest due to their wide applicability in the industrial processes that involves the thermal decomposition reactions of solids [9, 10]. Hence research in this area has gained increased attention [11].

II. EXPERIMENTAL METHOD & MATERIALS

Urea (U) was obtained from Loba Chemie Ltd., India. Encore, R. Johnson group, India, supplied carbon disulfide. Qualigens (Glaxo) supplied sodium hydroxide, acetone. Acetates of Co (II), Ni (II), Cu (II), Cd (II), are purchased from E. Merck, India. All the chemicals used were of analytical grade and were used without further purification.

A Preparation of Disodium Salt of Bisdithiocarbamate from UREA (UBDT)

The Bisdithiocarbamates of urea (UBDT) were prepared, from 0.1M Urea, 0.2M Sodium hydroxide and 0.2M carbon disulfide in water with constant stirring below 10°C. 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 colored mixture was warmed at 50°C for 1 h, and then cooled to room temperature. The product slowly crystallized into colorless crystals. The crystalline products were washed with acetone and recrystallised from water. The crystals of UBDT are water-soluble and did not melt up to 360°C.

B. Preparation of Metal Complexes of UREA Bisdithiocarbamate

Metal complexes of various bisdithiocarbamates of urea were prepared by mixing an aqueous solutions of ligand (UBDT) and metal salts of Ni, Cu, Co, Cd in equimolar ratio. The metal complexes are precipitated as fine powder instantaneously. For the coagulation of fine particles in every case, the mixture was stirred magnetically for 30minutes then kept overnight at room temperature, filtered, washed thoroughly with water and dried. The metal complexes are amorphous solids insoluble in water and common organic solvents.

III. PHYSICAL MEASUREMENTS

IR spectra of bisdithiocarbamates of urea were recorded on a Perkin-Elmer spectrometer model 1430 in the range of 4000-600 cm^{-1} using KBr pellets. UV-visible spectra were recorded on a Unicam spectrometer model UV-2-100. $^1\text{H-NMR}$ spectra were recorded on a Bruker DRX-300 FT-NMR spectrometer in CDCl_3 solutions. The synthesized ligand UBDT and its complexes were subjected to elemental analysis using Perkin Elmer elemental 2380 model. Sulfur was quantitatively determined by oxidizing the bisdithiocarbamates with alkaline potassium permanganate and gravimetric determination as barium

sulfate. The molar conductivity of solution of the synthesized complexes was determined using digital conductivity meter model-DI 9009.

IV. RESULTS AND DISCUSSION

Disodium salt of bisdithiocarbamates of urea (UBDT) and its metal complexes were prepared are stable at room temperature unaffected by atmospheric oxygen and moisture, insoluble in water and in common organic solvents. The complexes are amorphous and do not melt up to 360°C however decomposes above 200°C. The yields of recrystallised products and analytical data are given in Table-1.

A. Conductance Measurements

The molar conductance of 0.1M aqueous solution of UBDT was found to be 188Smol⁻¹Cm², indicating its electrolytic nature [22].

B. IR Spectral Analysis

Bisdithiocarbamates of urea (UBDT) shows three main regions in the infrared spectrum [12-16]. The broad band in the region 3400-3100 cm⁻¹ appear due to ν (N-H) and ν (O-H) of water molecules associated with the ligand. The 1450-1550cm⁻¹ band due to ν (C-N) vibration of the S₂C=NR₂ & the 950-1050 cm⁻¹ region which is associated with ν (C-S) vibrations in the ligand [14].

IR spectra of UBDT 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 1689cm⁻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 1630.7cm⁻¹ 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.

C. IR Spectral Analysis of Metal Complexes of UBDT

The IR spectral data of metal complexes of UBDT shows very intense band at 1459.6cm⁻¹ indicating a sufficient double bond order for C–N, as thioureide band is characteristic of dithiocarbamate intermediate between a C=N band (1690-1640cm⁻¹) and a C–N band (1360 – 1250cm⁻¹). The thioureide band characteristic of dithiocarbamates at 1459.6cm⁻¹ splits upon complexation in all the cases with a wide separation of almost 100cm⁻¹ in complexes suggested that in UBDT due to electron delocalization –C–N (A) and –C–N (B) bands are equivalent but on coordination metal ion contribution of the canonical forms (*scheme-1*) becomes greater and these two bands become non-equivalent resulting in appearance of two distinct IR bands. [23-24]

The band at 1696 cm⁻¹ in UBDT involves significant contribution from NH bending vibrations besides ν (C = O).

TABLE I
PHYSICAL AND ANALYTICAL DATA OF UBDT ^a AND METAL COMPLEXES

Molecular formula	color	M.P (°C)	Yield %	Elemental Analysis found (Calculated) %				
				C	H	N	S	M
C ₃ H ₂ N ₂ S ₄ ONa ₂ ·3H ₂ O	Yellowish Orange	135	88	11.90 (11.61)	2.51 (2.58)	8.96 (9.02)	40.82 (41.20)	--
C ₁₅ H ₂₀ N ₄ O ₁₄ Na ₂ Co ₃ (L ₂ Ac ₆ Na ₂ Co ₃)	purple	220 ^b	57	18.9 (19.2)	2.32 (2.00)	5.8 (5.6)	25.4 (25.6)	16.9 (17.7)
C ₁₅ 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 (19.0)	1.90 (2.0)	5.0 (5.6)	26.46 (25.70)	16.7 (17.4)
C ₁₄ H ₁₈ N ₄ O ₁₀ Na ₂ Cu ₃ (L ₂ Ac ₄ Na ₂ Cu ₃)	Seacrest green	210 ^b	61	18.7 (18.8)	1.82 (1.79)	5.9 (6.2)	28.2 (28.7)	20.6 (21.3)
C ₁₅ H ₂₀ N ₄ O ₁₄ Na ₂ Cd ₃ L ₂ Ac ₆ Na ₂ Zn ₃	yellow	>360	65	16.1 (15.8)	2.1 (1.6)	4.9 (4.5)	25.8 (25.1)	18.2 (19.3)

L & a = -SSCNHCONHCSS; Ac = CH₃COO⁻; b= decomposes without melting

A broad band at 1018.6cm^{-1} with medium intensity, is due to absorbance of asymmetric C—S stretching and a intense sharp band at 860.7cm^{-1} may be assigned to symmetric C—S stretching frequencies. On complexation in most of the complexes the bands corresponding 1018.6cm^{-1} band of UBDT appears with greatly decreased intensity, disappeared in cobalt (II) acetate and nickel (II) acetate complexes. Zinc (II) acetate complex is shifted downward with weak absorption.

The intense bands due to carbonyl stretching overlapped by δOH from water molecules almost disappear 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. The IR spectra of other bisdithiocarbamates can also be interpreted on similar grounds. The characteristic peaks due to dithiocarbamyl groups were observed in every case.

D. NMR Spectral Analysis

A broad signal was observed in 4.9 to 5ppm range due to -NH- proton in ^1H -NMR spectrum of UBDT. ^{13}C - NMR spectrum exhibited a single signal at 164.5ppm. It is freak that instead of two signals for C = O and CS_2 carbons only one signal was observed indicating resonance nature hence, it is suggested because of extensive conjugation, only one signal was observed for UBDT[17]. Additional support was obtained from electronic spectroscopy, conductivity measurements. NMR spectra of metal complexes could not be recorded due to insoluble in nature.

E. Electronic Spectral Studies

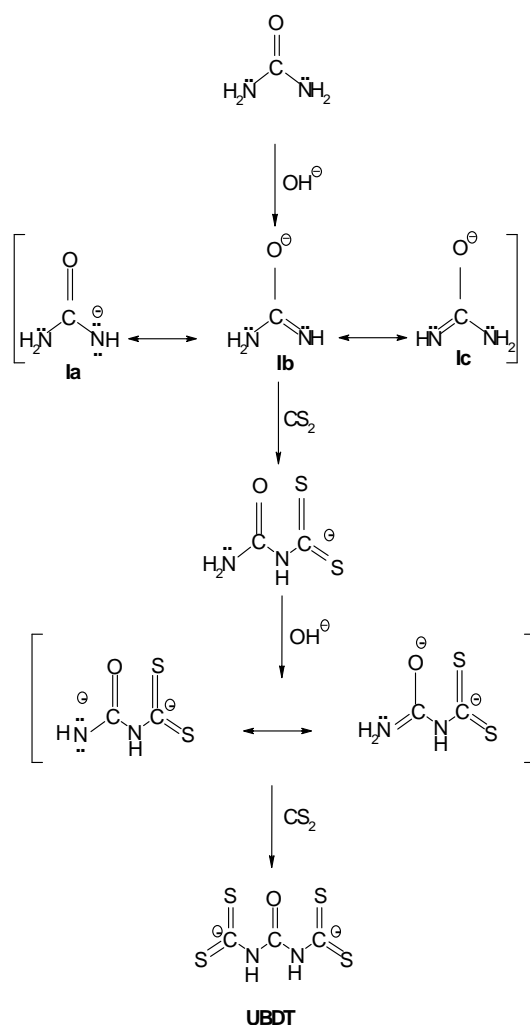
For UBDT a prominent absorption band at 233 nm ($\log \epsilon$ 3.45) may be ascribed to $\pi \rightarrow \pi^*$ transition of carbonyl group. The $\pi \rightarrow \pi^*$ transitions associated with conjugated nitrogen (N-C-S) and conjugated sulfur (S-C-S) observed at 284 nm ($\log \epsilon$ 2.18) and 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. [18, 19]

In the Cu (II) complex a broad asymmetric absorption band observed in $15000\text{-}10500\text{cm}^{-1}$ region with maxima at 12453cm^{-1} is consistent with the distorted octahedral geometry [18-21].

For 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 $^4\text{T}_{1g}(\text{P})$ state. The weak bands due $^4\text{T}_{1g} \rightarrow ^4\text{T}_{2g}$ transition are observed for cobalt (II) acetate.

The UBDT complex of nickel (II) acetate shows bands with maxima at 25575cm^{-1} , 13888cm^{-1} , and shoulder at 15220cm^{-1} . 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 spectrum showed an upward trend above 1100nm (10000cm^{-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 $^3\text{A}_{2g} \rightarrow ^3\text{T}_{2g}(\text{F})$, (ν_1) transition.



Scheme.1-Tentativemechanismfor bisdithiocarbamates formation from urea

TABLE -II
ELECTRONIC SPECTRA OF UBBDT METAL COMPLEXES

Ligand/Complexes	Ligand transition band		$3A_{2g} \rightarrow 3T_{1g}(P)$ V_3 $17000-22000 \text{ cm}^{-1}$		$3A_{2g} \rightarrow 3T_{1g}(F)$ V_2 $11000- 17000 \text{ cm}^{-1}$	
	$n \rightarrow \pi^*$		(nm)	(cm^{-1})	(nm)	(cm^{-1})
	(nm)	(cm^{-1})				
CoAcUBBDT	323	30959	506	19762	812	12315
	376	26595	516	19379	843	11862
	393	25445				
NiAcUBBDT	391	25575	522	19157	657	15220
					720	13888
CuAcUBBDT	405	24691				
	425	23529			805	12453
CdAcUBBDT	391	25505	459	22271		
	403	24822	490	20042		

CONCLUSIONS

Novel bisdithiocarbamates was prepared from urea, a tentative mechanism involving nucleophilic attack by the anionic species, formed in the presence of strong alkali Sodium hydroxide, on the CS_2 has been proposed in Scheme I. 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 bisdithiocarbamates. UBBDT and metal complexes of UBBDT are thermally quite stable and heat resistance. BDTs were water-soluble with good complexing ability for various metal ions. The thermal stability of the ligand UBBDT has increased by complexation with metal ions due to formation of ring (chelate) structure which provides additional stability to the complexes. Polymeric nature of the metal complexes was inferred based on amorphous and intractable nature. Further studies of bisdithiocarbamates, its metal complexes and biological activity are in progress.

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