



Copper Complexes of Dithiocarbamates and Thiuram Disulphides of Diethylenetriamine Based Schiff Bases

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Tetranuclear Cu(II) complexes of dithiocarbamates and Cu(I) complexes of thiuram disulphides which are derived from diethylenetriamine based Schiff bases are reported. Dithiocarbamate complexes were formed from Schiff bases of diethylenetriamine and salicylaldehyde/acetophenone while thiuram disulphide complexes were done with Schiff bases formed from diethylenetriamine and salicylaldehyde/cinnamaldehyde/acetophenone/benzophenone. The complexes have been characterized by elemental and thermal analysis, magnetic studies, IR, UV-VIS, NMR, CVM and X-ray photoelectron spectroscopic studies. Antibacterial studies on some of the Cu(I) complexes of thiuram disulphide are promising against *Klebsiella pneumonia*, *Salmonella typhi*, *Escherichia coli*, *Enterococcus faecalis*, *Pseudomonas aeruginosa*, *Proteus vulgaris*, *Staphylococcus epidermis*, methicilline resistant *Staphylococcus aureus*, ciprofloxin resistant *E. coli* and carbapennin resistant *Acetobacter baumannii*.

Key Words: Diethylenetriamine Schiff bases, Cu(II) dithiocarbamates, Cu(I) thiuram disulphides.

INTRODUCTION

Dithiocarbamates are products of the reaction between a primary or secondary amine and carbon disulphide in basic media. The stability of dithiocarbamates in solution has been studied by several authors¹⁻⁷. Oxidation of aqueous solutions of dithiocarbamates result in thiuram disulphides. Complexes of metal ions with both dithiocarbamates and thiuram disulphides gain significant importance due to their applications in medicine, agriculture, industry and analytical field⁸⁻¹⁷. Here we report the isolation, characterization and antibacterial studies of tetranuclear Cu(I) thiuram disulphide complexes of Schiff bases of diethylenetriamine.

EXPERIMENTAL

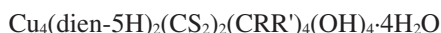
All reagents used were of analytical grade and used without purification. The disulphides were prepared by adding 0.03 mol of diethylenetriamine and 0.06 mol of aldehyde/ketone to 0.06 mol of CuSO₄ dissolved in water. To this solution 0.03 mol of CS₂ in 0.06 mol of NaOH were added. Excess alcohol was then added and stirred for 0.5 h when brown coloured complexes resulted which were filtered and dried in air. The aldehydes used were salicylaldehyde, cinnamaldehyde and ketones used were acetophenone and benzophenone. However dithiocarbamate complexes were obtained with salicylaldehyde and acetophenone when the above preparations were

repeated without the addition of alcohol, greenish brown complexes resulted which were filtered and dried immediately.

Copper in the complex was determined by optical emission spectroscopy using ICP-OES Perkin Elmer Optima 5300 DV spectrometer. Nitrogen is estimated by Kjeldhal's method and sulphur gravimetrically as BaSO₄. TG/DTA plots were recorded in N₂ atmosphere using NETZSCHSTA 409 C/CD thermal analyzer with a heating rate of 10 °C/min. Magnetic susceptibility studies were carried out using vibrating magnetometer EG and GPARC model 155. UV-Visible absorption spectra were recorded in DMSO or as mull using Varian Cary spectrophotometer 5E-UV-VIS-NIR. IR spectra were recorded in KBr using Bruker IFS 66V FTIR spectrometer, X-ray photoelectron spectrum of the complex was recorded in Cu-2P, S-2P and N-1S regions using VG-ESCA LAB MKII ESCA/Auger spectrometer. ¹H NMR spectra (400 MHz) of the DMSO soluble diamagnetic complexes were recorded in DMSO-*d*₆ by employing TMS as internal standard using JEOL MODEL: GSX. CVM of thiuram disulphide salicylaldehyde Schiff base complex was recorded in DMF medium with the addition of electrolyte tetra butyl ammonium perchlorate. The electrode used was glassy carbon. The reference electrode used was Ag/AgCl and the counter control was Pt wire. The scan rate was 10 mm/s. Conductivity of the soluble complexes was measured using simple conductivity bridge. Antibacterial activity of the complexes was tested using minimum modification of the disc diffusion method¹⁸.

RESULTS AND DISCUSSION

Elemental analysis data (Tables-1) indicate the following composition for thiuram disulphide complexes



where R = H and R' = C₆H₄OH for salicylaldehyde complexes/ R' = CHCHC₆H₅ for cinnamaldehyde complex. While R = C₆H₅ and R' = CH₃ for acetophenone complex/R' = C₆H₅ for benzophenone complex.

The two dithiocarbamates prepared are assigned the compositions



R = H, R' = C₆H₄OH for the salicylaldehyde complex and R = CH₃, R' = C₆H₅ for the acetophenone complex.

TABLE-1
ELEMENTAL ANALYSIS DATA ON THE COMPLEXES

Complexes λ_{max} (nm)	Anal: Found (Calcd.) (%)		
	Cu	N	S
$\text{Cu}_4(\text{dien-5H})_2(\text{CS}_2)_2(\text{CHC}_6\text{H}_4\text{OH})_4(\text{OH})_4 \cdot 4\text{H}_2\text{O}$ 256, 301	22.01 (21.79)	7.42 (7.2)	11.23 (10.98)
$\text{Cu}_4(\text{dien-5H})_2(\text{CS}_2)_2(\text{CHCHCHC}_6\text{H}_5)_4(\text{OH})_4 \cdot 4\text{H}_2\text{O}$ 269, 306	22.2 (21.07)	6.87 (6.96)	10.95 (10.61)
$\text{Cu}_4(\text{dien-5H})_2(\text{CS}_2)_2(\text{CCH}_3\text{C}_6\text{H}_5)_4(\text{OH})_4 \cdot 4\text{H}_2\text{O}$ 261, 295	21.14 (21.95)	7.63 (7.25)	11.85 (11.05)
$\text{Cu}_4(\text{dien-5H})_2(\text{CS}_2)_2(\text{CC}_6\text{H}_5\text{C}_6\text{H}_5)_4(\text{OH})_4 \cdot 4\text{H}_2\text{O}$ 295, 305	18.45 (18.07)	6.68 (5.97)	9.42 (9.10)
$\text{Cu}_4(\text{dien-5H})_2(\text{CS}_2)_2(\text{CHC}_6\text{H}_4\text{OH})_4(\text{OH})_6$ 323, 437, 623	23.01 (22.53)	7.92 (7.45)	10.99 (11.35)
$\text{Cu}_4(\text{dien-5H})_2(\text{CS}_2)_2(\text{CCH}_3\text{C}_6\text{H}_5)_4(\text{OH})_6$ 312, 437	22.01 (22.69)	6.96 (7.50)	11.98 (11.42)

The dithiocarbamate complexes were soluble in CHCl₃, DMSO, DMF, while the thiuram disulphide complexes were soluble only in DMSO and DMF. The conductivity measurements on all the complexes indicated non-electrolytic nature. Magnetic studies on thiuram disulphide complexes showed negative magnetic susceptibility indicating diamagnetic nature and the electronic spectra show bands around 300 and 260 nm. The XPES of acetophenone based Schiff base thiuram disulphide complex in Cu-2P region shows two peaks in the intensity ratio 2:1 at 931.7 and 951.7 eV corresponding to Cu-2P_{3/2} and 2P_{1/2} spin orbit coupled states. The value 931.7 eV

indicates Cu in +1 oxidation state¹⁹. The peak is unsymmetrical indicating Cu atoms in different environment. The S-2P region consist of two peaks in the intensity ratio 3:1 at 160.8 and 166.9 eV. A difference of 6.1 eV cannot be due to spin orbit coupling²⁰ and hence a peaks indicate two different environments of sulphur. The N-1S region at 399.6 eV shows a broad peak which on deconvolution corresponds to two peaks in the intensity ratio 1:2. This goes in accordance with the nitrogen atoms in diethylenetriamine. The cyclic voltogram of thiuram disulphide complex with salicylaldehyde indicates irreversible oxidation corresponding to Cu(I) → Cu(II) at 1.15 V in DMF against Ag/AgCl electrode. The peak is broad which perhaps indicates Cu(I) in different environment undergoing successive oxidation. On the contrary the dithiocarbamate complexes are paramagnetic and show electronic absorptions around 320, 435 and 620 nm corresponding to a distorted square planar arrangement of Cu(II).

TG/DTA data on the thiuram disulphide complexes and dithiocarbamate complexes are given in Table-2. The thiuram disulphide complexes loss water around 50 °C with a DTA showing an endotherm. The next stage corresponds to loss of ligands leading to the formation of CuS. The dithiocarbamate complexes indicate only the ligand decomposition leading to the formation of CuS. The ¹H NMR data on thiuram disulphide salicylaldehyde complex shows signals at 7.117 and 6.702 ppm corresponding to aromatic protons. A signal at 6.597 ppm almost overlap with 6.702 ppm may be assigned to a protons of CH=N group. CH₂ protons appear at 3.577 and 3.36 ppm. The peaks at 8.37 and 7.84 ppm may be assigned to OH protons. The IR spectral data on the complexes are given in Table-3. The $\nu(\text{C}=\text{S})$ stretching appears in the region 1200-1075 cm⁻¹ while $\nu(\text{C}-\text{S})$ appears around 750 cm⁻¹ in both dithiocarbamate and thiuram disulphide complexes. The S-S stretching which appears in the region 625-615 cm⁻¹ in the thiuram disulphide complexes is absent in dithiocarbamate complexes.

Antibacterial studies of salicylaldehyde and cinnamaldehyde thiuram disulphide complexes are presented in Table-4. 1.25-5.00 mg of sample have been tried for the activity. The salicylaldehyde complex is active against methicilline resistant *Staphylococcus aureus*, ciprofloxin resistant *E. coli* and carbapennin resistant *Acetobacter baumannii* against which streptomycin (standard) is inactive. The cinnamaldehyde

TABLE-2
TG AND DTA DATA ON COMPLEXES

Complexes	Water loss			Ligand decomposition leading to CuS formation	
	Loss (%)	Temp. range (°C)	DTA peak	CuS (%)	DTA peaks (°C)
$\text{Cu}_4(\text{dien-5H})_2(\text{CS}_2)_2(\text{CHC}_6\text{H}_4\text{OH})_4(\text{OH})_4 \cdot 4\text{H}_2\text{O}$	5.8 (6.17)	50-105	-55, -100	32.5 (32.8)	+1149.8, +801.9 +1029.5
$\text{Cu}_4(\text{dien-5H})_2(\text{CS}_2)_2(\text{CHCHCHC}_6\text{H}_5)_4(\text{OH})_4 \cdot 4\text{H}_2\text{O}$	6.8 (5.97)	50-100	-95	32.00 (31.68)	-281.1, -492.4
$\text{Cu}_4(\text{dien-5H})_2(\text{CS}_2)_2(\text{CCH}_3\text{C}_6\text{H}_5)_4(\text{OH})_4 \cdot 4\text{H}_2\text{O}$	6.1 (6.2)	50-110	-50	33 (32.9)	+168.4, +362.6, +655.9 +800.7, +895.2, -1255.6
$\text{Cu}_4(\text{dien-5H})_2(\text{CS}_2)_2(\text{CC}_6\text{H}_5\text{C}_6\text{H}_5)_4(\text{OH})_4 \cdot 4\text{H}_2\text{O}$	5.7 (5.1)	50-110	-50, -145	27 (27.2)	-496.7, -863.6, -1020
$\text{Cu}_4(\text{dien-5H})_2(\text{CS}_2)_2(\text{CHC}_6\text{H}_4\text{OH})_4(\text{OH})_6$	–	–	–	34.95 (33.87)	+174, -678
$\text{Cu}_4(\text{dien-5H})_2(\text{CS}_2)_2(\text{CCH}_3\text{C}_6\text{H}_5)_4(\text{OH})_6$	–	–	–	35.8 (34.2)	+112.8, +718.8, -850

–: Endotherm, +: Exotherm.

TABLE-3
 IR SPECTRAL DATA (cm⁻¹) ON Cu(II) COMPLEXES

Complexes	v(O-H)	v(C=N), v(C=C)	v(C=S)	v(C-S)	v(S-S)
Cu ₄ (dien-5H) ₂ (CS ₂) ₂ (CHC ₆ H ₄ OH) ₄ ·4H ₂ O	3428	1620, 1538, 1468	1197, 1129	760	617
Cu ₄ (dien-5H) ₂ (CS ₂) ₂ (CHCHCHC ₆ H ₅) ₄ (OH) ₄ ·4H ₂ O	3435	1631, 1491, 1450	1171	751	622
Cu ₄ (dien-5H) ₂ (CS ₂) ₂ (CCH ₃ C ₆ H ₅) ₄ (OH) ₄ ·4H ₂ O	3435	1633, 1506	1115	750	618
Cu ₄ (dien-5H) ₂ (CS ₂) ₂ (CC ₆ H ₅ C ₆ H ₅) ₄ (OH) ₄ ·4H ₂ O	3435	1637, 1511	1112	694	618
Cu ₄ (dien-5H) ₂ (CS ₂) ₂ (CHC ₆ H ₄ OH) ₄ (OH) ₆	3300	1636, 1624, 1578, 1480	1177	750	–
Cu ₄ (dien-5H) ₂ (CS ₂) ₂ (CCH ₃ C ₆ H ₅) ₄ (OH) ₆	3300	1642, 1491	1077	750	–

 TABLE-4
 ANTIBACTERIAL STUDIES

Complex	Mg/disc	Diameter of the inhibitory zone (mm)									
		KP	EC	PV	ST	EF	PA	SE	MRSA	CRE	CRA
I	1.25	8	7	–	–	–	8	8	8	–	8
I	2.50	11	10	9	10	8	10	10	12	10	9
I	5.00	13	13	13	12	10	12	13	15	12	11
II	1.25	–	8	9	–	10	8	9	10	14	11
II	2.50	9	10	12	10	13	13	11	12	–	–
II	5.00	15	15	15	12	17	13	15	–	–	–
Standard streptomycin	30 µg	15	15	15	12	17	13	15	–	–	–

I: Salicylaldehyde thiuram disulphide complex. II: Cinnamaldehyde thiuram disulphide complex.

complex shows considerable activity against *Klebsiella pneumonia*, *Salmonella typhi*, *Escherichia coli*, *Enterococcus faecalis*, *Pseudomonas aeruginosa*, *Proteus vulgaris* and *Staphylococcus epidermis*, respectively. As the concentration of the complex increases, it is seen that the diameter of the inhibitory zone also increases indicating increased activity. *Klebsiella pneumonia* (KP), *Salmonella typhi* (ST), *Escherichia coli* (EC), *Enterococcus faecalis* (EF), *Pseudomonas aeruginosa* (PA), *Proteus vulgaris* (PV), *Staphylococcus epidermis* (SE), methicilline resistant *Staphylococcus aureus* (MRSA), ciprofloxin resistant *E. coli* (CRE) and carbapennin resistant *Acetobacter baumannii* (CRA).

It is presumed that the formation of Schiff base takes place only at the primary amino groups of the diethylenediamine ligand and the introduction of the CS₂ occurs at the NH site. The dithiocarbamate complexes thus formed are unstable and we have isolated two such complexes namely salicylaldehyde dithiocarbamate complex and acetophenone dithiocarbamate complex. The dithiocarbamate complexes contain four Cu(II), two of which are surrounded by two dithiocarbamate sulphur, one nitrogen bearing the dithiocarbamate group and OH group. The other two Cu(II) are coordinated to two Schiff base nitrogens and two OH groups. The Cu(II) have tentatively a square planar arrangement. The disulphide complexes may be assigned a structure wherein two Cu(I) are tetrahedrally surrounded by one disulphide sulphur, one S=C sulphur, nitrogen of NCS₂ group and a OH group. The other two Cu(I) may be coordinated with two Schiff base nitrogen atoms and hydroxyl group. Fourth tetrahedral site may be satisfied by weak interactions with water molecules.

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