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Cu(I).Cu(III) Mixed Valence Complexes of Thiuram Disulfides of Triethylenetetramine Based Schiff Bases

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Mixed valence Cu(I).Cu(III) complexes of thiuram disulphide formed from triethylenetetramine (trien) based Schiff bases have been isolated and characterized. Schiff bases are formed with salicylaldehyde, cinnamaldehyde, acetophenone, benzophenone and acetyl acetone. The complexes are characterized by elemental and thermal analysis, IR, UV-Visible, XPES studies. Magnetic studies indicate diamagnetic nature of the complexes.

Key Words: Thiuram disulphides, Complexes, Mixed valence Cu(I).Cu(III), Schiff bases of triethylenetetramine.

INTRODUCTION

Thiuram disulphides are the thiocarbamyl esters of dialkyldithiocarbamic acids. Both dithiocarbamates and thiuram disulphides are significant on account of their biological activity[1]. They find extensive applications as fungicides, rubber vulcanization accelerators, agents of alcoholism therapy[2-4] and as arrestors of human immuno deficiency virus infections such as AIDS[5]. Here we report the isolation and characterization of mixed valence Cu(I).Cu(III) thiuram disulphides of Schiff bases derived from triethylenetetramine.

EXPERIMENTAL

All reagents used were of analytical grade and used without further purification. The disulphides were prepared by simultaneous addition of 0.02 mol of triethylenetetramine (trien) and 0.04 mol of aldehyde/ketone to 0.02 mol of copper sulphate in 10 mL of distilled water. After vigorous stirring 0.04 mol of CS_2 were added stirred well and then added 0.04 mol of NaOH in water. Solution was stirred vigorously for 0.5 h with addition of 40 mL of rectified spirit. The brown complexes obtained were filtered and dried in air. 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 $BaSO_4$. TG/DTA plots were recorded either in air/nitrogen atmosphere, using NETZSCHSTA 409C/CD thermal analyzer with a heating rate of 10 ºC/min. Magnetic susceptibility studies were carried out using vibrating magnetometer EG & GPARC Model 155.

UV-Visible absorption spectra were recorded as mull using Varian Cary Spectrophotometer 5E-UV-Vis-NIR. IR spectra were recorded in KBr using Bruker IFS 66V FT IR spectrometer. X-Ray photoelectron spectrum of the acetophenone complex was recorded in Cu-2P, S-2P and N-1S regions using VG-ESCA LAB MKII ESCA/ Auger Spectrometer.

RESULTS AND DISCUSSION

The elemental and thermal analysis data (Tables 1 and 2) indicated the composition $[Cu_2(SB(n))(CS_2)_2(OH)](OH)_3.xH_2O$ where $SB(n)H_2$ refers to Schiff base formed from trien and aldehyde/ketone. x = 2, n = 1 for salicylaldehyde complex; x = 1, n = 2 for cinnamaldehyde and x = 1, n = 3 for acetophenone complex and x = 0, n = 4 for benzophenone complex. The acetyl acetone complex has a composition $[Cu_2(SB(5)\text{-}2H)(CS_2)_2(OH)]OH.6H_2O$ where (SB(5)-2H) represents Schiff base less 4H. In all the cases Schiff base formation involves one trien molecule and two aldehydes/ketones. The complexes are insoluble in common solvents like $CHCl_3$, alcohol, DMSO, DMF. TG and DTA data (Table-2) indicates two stages. The first stage corresponds to loss of water and CS_2 while second stage leads to formation of CuO.

TABLE-1
PHYSICAL CHARACTERISTICS, ANALYTICAL, MAGNETIC AND UV-VISIBLE DATA ON COMPLEXES

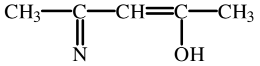
Complex (Magnetism)	Colour	Elemental analysis (%): Found (Calcd.)			λ_{max} (nm)
		Cu	N	S	
$[Cu_2SB(1)(CS_2)_2(OH)](OH)_3.2H_2O$	Brown	17.57	7.07	17.06	265sh, 362,
(Diamagnetic)		(17.29)	(7.62)	(17.41)	425sh
$[Cu_2SB(2)(CS_2)_2(OH)](OH)_3.H_2O$	Brown	17.56	7.17	18.01	273, 343sh, 435
(Diamagnetic)		(17.24)	(7.60)	(17.36)	
$[Cu_2SB(3)(CS_2)_2(OH)](OH)_3.H_2O$	Brown	16.98	7.98	17.10	260, 420sh
(Diamagnetic)		(17.82)	(7.85)	(17.95)	
$[Cu_2SB(4)(CS_2)_2(OH)](OH)_3$	Brown	16.17	7.37	15.20	242, 283, 355sh
(Diamagnetic)		(15.51)	(6.84)	(15.62)	
$[Cu_2(SB(5)\text{-}2H)(CS_2)_2(OH)](OH).6H_2O$	Brown	16.98	7.19	18.00	279, 460
(Diamagnetic)		(17.47)	(7.70)	(17.60)	

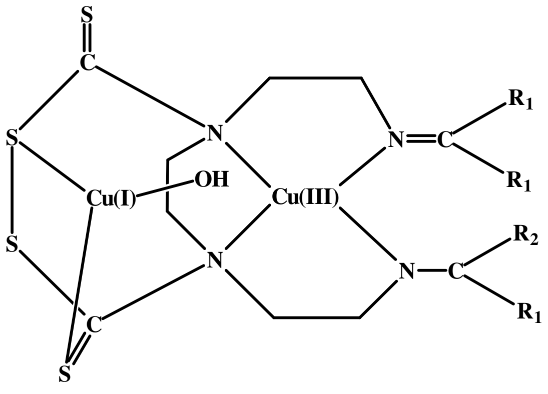
The magnetic susceptibility of the complexes are negative indicating diamagnetic nature. The XPES in Cu(2P) region gives two peaks at 933.3 and 952.5 eV corresponding to $2P_{3/2}$ and $2P_{1/2}$ spin orbit coupled states. The peak at 933.3 eV on deconvolution gives two symmetrical peaks at 931.6 and 935 eV which may be assigned to Cu(I) and Cu(III), respectively. The sulphur 2P region shows two peaks at 161.8 and 168.75 eV corresponding to one S being in different environment from the other three. The N (1S) shows two symmetrical peaks around 399.6 corresponding to the nitrogen environment in trien.

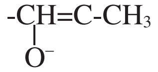
TABLE-2
TG/DTA DATA ON COMPLEXES

Complex (DTA peaks (-endo, +exo)	Medium	Loss of water + CS_2		Formation of CuO	
		Temp. (°C)	% Loss	Temp. (°C)	% Loss
$[Cu_2SB(1)(CS_2)_2(OH)](OH)_3.2H_2O$ (-66, +93.1, +274.5, -750, +934)	N_2	50-190	18.4 (15.24)*	200-840	22.5 (21.61)
$[Cu_2SB(2)(CS_2)_2(OH)](OH)_3.H_2O$ (-60, +125, -376.9, -588, -866)	N_2	50-190	14.6 (12.75)*	200-850	21.55 (22.0)
$[Cu_2SB(3)(CS_2)_2(OH)](OH)_3.H_2O$ (-100, - 484.9, +750, +840)	Static air	50-175	23.0 (23.84)	200-930	21.0 (22.30)
$[Cu_2SB(4)(CS_2)_2(OH)](OH)_3$ (+107.8, -500, +763.9)	Static air	75-115	18.0 (18.55)	150-900	20.0 (19.42)
$[Cu_2(SB(5)-2H)(CS_2)_2(OH)](OH).6H_2O$ (-170, -466.7, +1087)	Static air	50-180	26.0 (25.30)*	200-1050	21.0 (21.87)

The UV-Visible spectra of the complexes show one or two peaks in the region 240-285 nm which is assigned to ligand transitions and one or two peaks in the region 350-445 nm confirming the presence of Cu(III) in square planar geometry (Table 1).

IR spectra of the complexes show strong bands in the region 1630-1640 cm^{-1} and may be assigned to ν(C=N) of Schiff base. A peak around 3420 cm^{-1} correspond to OH stretching. No peak is seen around 1700 cm^{-1} in the acetyl acetone Schiff base complex. This may be inferred as ionization of enolic OH and coordination through O^- of the  $CH_3-\underset{N}{\underset{\|}{C}}-CH=\underset{OH}{\underset{|}{C}}-CH_3$ moiety. All the complexes exhibit peak around 760 cm^{-1} corresponding to ν_{cs} and at 617 or 618 cm^{-1} corresponding to ν_{s-s}. Based on the above informations the complexes are assumed to be thiuram complexes with two -S-S- sulphur atoms, one -C=S- sulphur and one OH tetrahedrally surrounding Cu(I) and 4 N atoms forming a square plane around Cu(III) with the remaining OH as counter ions or in weak interactions with Cu(III). The complex is tentatively assigned the following structure:



$R_1 = [C_6H_4(OH)]$ R_2 = H for the salicylaldehyde complex.
$R_1 = [C_6H_5CH{=}CH]$ R_2 = H for the cinnamaldehyde complex.
$R_1 = C_6H_5$ $R_2 = CH_3$ for the acetophenone complex.
$R_1 = C_6H_5$ $R_2 = C_6H_5$ for the benzophenone complex.
R_1 =  $R_1 = -\underset{\displaystyle O^-}{\underset{|}{C}}H{=}C{-}CH_3$ $R_2 = CH_3$ for acetyl acetone complex.

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