THERMAL STABILITY AND STRUCTURAL STUDIES OF SOME MIXED LIGAND COMPLEXES

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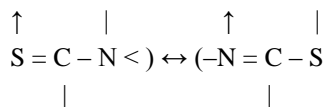
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INTRODUCTION

The paper entitled, "Thermal Stability and Structural Studies of Some Mixed Ligand Complexes", embodies the thermogravimetric studies of some complexes of 2, 5-dimercapto-1, 3, 4- thiadiazole ($DMTDH_2$) and 2-Amino-5-mercapto-1, 3, 4-thiadiazole (AMTDH) with Zn(II), Cd(I) and Hg(II). For derivatographic studies some complexes have been prepared and characterized by elemental analysis, I.R. and electrical conductance value.

The complexes are of the composition M(DMTDH), (where $M = Zn^{2+}$ and Cd^{2+}); M(DMTD) β- pic ($M = Zn^{2+}$ and Cd^{2+}); M(DMTDH) nH_2O ($M = Cd^{2+}$, Zn^{2+} and Hg^{2+} n = 1, 2, 4); Hg ($DMTDH_2$) Cl_2; Zn (DMTD) $(NH_3)_2$; $M(AMTD)_2$ (where $M = Zn^{2+}$, Cd^{2+}, Hg^{2+}) and Hg (AMTD)Cl.

From elemental analysis, electrical conductance value and I.R. spectral studies the above compositions have been tentatively suggested. In M(DMTD) nH_2O, ($M = Cd^{2+}$, Zn^{2+} and Hg^{2+} and n= 1, 2, 4) aquo type complexes both the protons of the ligand molecule are deprotonated and ligand coordinates as dianionic molecules. In these complexes thioamide group is bonded as bidentate bridging group in resonating form as –

$$\underset{\displaystyle |}{\overset{\displaystyle \uparrow \qquad\quad |}{S = C - N <}}) \leftrightarrow (\underset{\displaystyle |}{\overset{\displaystyle \uparrow \qquad |}{-N = C - S}}$$

The similar bending pattern is also present in M (DMTD) (β - pic) ($M = Zn^{2+}$ or Cd^{2+}) and Zn (DMTD) (NH_3). In case of bisligated complexes $M(DMTDH)_2$ ($M = Zn^{2+}$, Cd^{2+}) the ligand is bonded as bidentate molecule only and one thioamide group is free in these complexes. In $M(AMTD)_2$ ($M = Zn^{2+}$, Cd^{2+} and Hg^{2+}) complexes, the ligand is bounded to metal ions as monoaniomic molecule and it acts as bidentate molecules. The donor atoms are thioamide group nitrogen and sulphur atom of the ligand in these complexes.

The T.G. graphs of three complexes have been examined thoroughly and different steps of dissociation and decomposition of complexes with increasing temperature and the derivatographic data have been complied in tables – X, XI and XII. The attempts have also

been made to substantiate the product formed from calculation of percentage weight loss at required temperature. In some cases the last decomposition product obtained are either metal sulphide or metal oxide. In case of mercury complexes the residue obtained does not correspond to the weight required for HgS or HgO.

The different kinetic as well as thermodynamic parameters such as kinetic order, activation energy, entropy change, free energy change etc. have been determined with the help of Freeman-Carroll method and presented in the end of this chapter in tabular form. From the study of kinetic and thermodynamic parameters it is inferred that the each steps of decomposition is exothermic in nature. The reaction rate calculated by Freeman Carroll method is of zero or first orders. The complexes have high activation energy and low entropy change. In Cd(II) and Zn(II) complexes the conversion of complexes into their metallic sulphide or oxide takes place. In Hg(II) complex it has been observed that the product gets sublimed and weight of residual substances is less than that the weight of expected metal sulphide or oxide.

$\mathcal{E}$XPERIMENTAL, RESULT AND RESULT

(A) 2,5 – Dimercapto – 1, 3, 4 – thiadiazole :

2, 5 – Dimercapto – 1, 3, 4 – thiadiazole is formed in good yield by reaction of CS_2 with hydrazine hydrate (98%) in pyridine medium at reflux temperature.

$$NH_2 - NH_2 + CS_2 \xrightarrow[\text{Reflux temp}]{\text{Pyridine}}$$

(2,5−Dimercapto−1,3,4−thiadiazole)
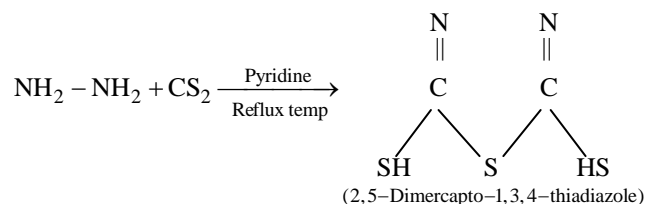
The compound is obtained as Pyridinium salt from which the free ligand is prepared by acidifying the pyridinum salt with dilute hydrochloric acid.

$\mathcal{P}$ROCEDURE :

$\boxed{\text{H}}$ydrazine hydrate (20 mL) and CS_2 (72.0 gm) were refluxed in pyridine (200 mL) for one hour. The clear yellow solution was evaporated in a stream of air to about half of the original volume, when spontaneous crystallization occurred. The product (88.0 g; 96% yield) crystallized from a small volume of water as pale yellow rods (m.p. 176-177°C) consisting of the pyridinium salt of 2, 5 dimercapto 1, 3, 4-thiadiazole.

Found for $C_7H_2N_3S_2$:-

|	C	H	N	S
Found	36.46	3.19	18.56	42.13
Calculated	36.71	3.08	18.30	41.91

The pyridine salt (9.2 gm) crystallized above was dissolved in water (100 mL) and acidified it with conc. HCl (20 mL) colourless rods of 2,5 dimercapto-1, 3, 4, thiadiazole were obtained (5.44 gm; 90% yield) m.p. 169 – 169.5°C

Found for $C_2H_2N_2S_3$:-

	C	H	N	S
Found	16.92	1.42	18.53	63.78
Calculated	16.80	1.34	18.70	64.00

(B) 2– Amino – 5 – mercapto – 1, 3, 4 – thiadiazole :

It was prepared by the reaction between thiosemicarbazide and carbon disulphide in pyridine.

$$CS_2 + H_2S.NH.CSNH_2 \longrightarrow$$

(Thiosemicarbazide)

(2−Amino −5 mercapto−1, 3, 4−thiadiazole)

$$+ H_2S$$
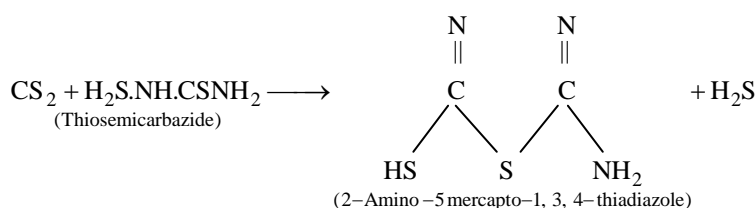
𝒫ROCEDURE :

Thiosemicarbazide (37.20 g) and carbondisulphide (48 gm) were mixed and mixture was refluxed with pyridine (300 mL) on a steam bath for two hours. Then the pyridine was removed in vacuo and the residue was crystallized from water (500 mL) as long, pale yellow rods (43.20 g; 82% yield), m.p. 233-234°C (decomp).

Found for $C_2H_3N_3S_2$:-

	C	H	N	S
Found	17.92	2.32	31.34	48.23
Calculated	18.02	2.25	31.50	48.05

SOURCE OF CHEMICAL REQUIRED :

Hydrazine hydrate, carbon disulphide, thiosemicarbazide and other organic chemicals were obtained from E, Merck, BDH or IDPL. Organic solvents used were usually of E. Merck extra pure grade or BDH laboratory grade chemicals.

Metal salts used for preparation of complexes were either E. Merck extra pure chemicals or BDH Analar grade chemicals.

For electrical conductance measurement the solvents were purified by standard method.

METHODS OF ANALYSIS :

Elemental Analysis : The analytical results of carbon, hydrogen and nitrogen present in the ligands as well as in the metal complexes were obtained from CDRI (Lucknow).

Sulphur : An accurately weighed quantity (225-300 mg) of the powdered compound was placed in a 750 mL capacity round bottomed flask containing (3-4.5 drops of liquid bromine and 30-45 mL conc. HNO_3. The mouth of the flask was covered with a conical funnel. The content of the flask was slowly refluxed for an hour over sand bath to a small volume. The process was repeated by the addition of the same amount of liquid bromine and conc. HNO_3 till the solution was clear. The insoluble residue, if any was removed by diluting the solution with excess of water and filtering it while hot. The solution was cooled and transferred into a beaker. The sulphate formed due to oxidation of sulphur was precipitated by adding $BaCl_2$ solution. The precipitate obtained was digested by heating for half an hour and kept overnight. The precipitate of $BaSO_4$ was filtered on what man No. 42 filter paper, washed well with water till no white precipitate of AgCl with $AgNO_3$ solution was formed. Now it was dried, ignited in a porcelain crucible to a constant weight of $BaSO_4$. The percentage Sulphur in the compound was estimated from the weight of $BaSO_4$ obtained in the experiment.

Estimation of metal ions :

"Standard method" of the estimation of the metal ions as described below:

Zinc : After the decomposition of the complexes with conc. HNO_3 and $HClO_4$, the Zinc content of the complexes was precipitated as Zinc oxinate Zn $(C_9H_6ON)_2$ from the neutral solution (neutral solution made by using Na_2CO_3 and acetic acid). The precipitate was filtered, washed with water and dried at 110-115°C and weighed as $Zn(C_2H_6ON)_2$.

Cadmium : After the decomposition of the Cd(II) complexes with conc. HNO_3 and $HClO_4$, the cadmium present in the complexes was precipitated as cadmium oxinate $Cd(C_9H_6ON)_2$ from the buffered solution (Na_2CO_3 and acetic acid at pH- 5.5).

Mercury : It was estimated as HgS by the procedure suggested by Volhard. About (150-300 mg of the accurately weighed mercury complex was taken in 375 mL pyrex beaker

covered with a watch glass. It was decomposed by repeated evaporation with conc. HNO_3 and perchloric acid mixture on a sand bath. This decomposed complex was finally treated with 30-32.50 mL of conc. HCl and evaporated to small volume. It was finally diluted with water to a clear solution. The solution was neutralized with Na_2CO_3 and treated with slight excess of freshly prepared ammonium sulphide solution (7.5 – 15 mL). To the precipitated sulphide 15% Analar NaOH solution was added until the dark liquid began to lighten. Then it was heated to boiling and more NaOH solution was added till the liquid was perfectly clear. Now solid NH_4NO_3 (7.5 gm for each 150 mL) was added to this clear solution and boiled to expel NH_3 completely. During this process HgS is reprecipitated as black precipitate. It was allowed to settle. The clear liquid was decanted through a sintrered glass crucible and the precipitate was washed by decantation with hot water until the wash water gave no precipitate with $AgNO_3$ solution. The precipitate was then transferred to the crucible, dried at 110°C and weighed as HgS.

𝒫HYSICAL MEASUREMENTS

Electrical conductance value :

The electrical conductance value of complexes in DMF solution were measured at room temperature. The molar electrical conductance values were calculated from specific conductance value. The value is almost qualitative.

Infrared spectra

The IR spectra were recorded on perkin-Elmer 137 and 221 spectrophotometer in KBr disc at CDRL Lucknow. Some IR spectra were recorded as Nujol Mull in the range $4000 – 625$ cm^{-1}.

Magnetic Susceptibility :

Magnetic susceptibility of the complexes was measured on a Gouy balance at room temperature. In present work, the field strength was determined by using mercury cobaltous thiocynate HgCO $(NCS)_4$. The value of field strength was calculated from the equation

$$H_{max} = \sqrt{(2.1m/1.019 \times \psi g \times W)}$$

where W = Weight of Substance in gm,

ψg = gram susceptibility of

l = length of column in cm

m = change in wt. in mg

Hg]Co$(NCS)_4$] at room temperature

The value of maximum field strength $H_{(max)}$ was found to be 8.75×10^3 Gauss.

Now the mole susceptibility of the substances was calculated from the expression :

$$\mu_M = 21 \text{ mM}/1.019 \times H^2_{max} \times w$$

where, M = Molecular weight of the complex in gm for one metal atom.

$$\mu_M \text{ (corrected} = \mu_M + \text{Diamagnetic correction.}$$

The μ_{eff} was calculated making diamagnetic correction using Pascal's constants.

$$\mu_{eff} = 2.839 \sqrt{\psi_M (\text{corrected}) \times T}$$

where T = absolute temperature.

Thermogravimetric analysis :

The thermogravimetric studies of complexes were made on thermogravimetric balance manufactured by steel authority of India Ltd. Ranchi. The thermal loss of complexes were made in static air with heating rate of 10°C per minute. The complexes were heated in static air upto temperature 650°C. From TG Loss the DTG curve were plotted. The DTG curve indicated the different stage of thermal loss in complexes. The TG studies were made in static air with heating rate 10°C per minute.

Evaluation of various thermodynamic parameters

The various thermodynamic parameters like entropy change, activation energy, free energy change, frequency factor etc. can be evaluated from thermogravimetric studies for different stages of dissociation and decomposition occurring during thermal loss. There are different approach and method developed for the evaluating thermodynamic parameters.

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