

A Case study :

Synthesis and characterization of Cu (II) complexes of dithiocarbamates with different substituents

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ABSTRACT

The ligands, disodium diethylenetriamine bis(dithiocarbamate), diendtc and disodium triethylenetetramine bis(dithiocarbamate), triendtc have been prepared and Cu(II) complexes of these ligands along with pyrrolidine dithiocarbamate are synthesized. These Cu(II) dithiocarbamate complexes are characterized by elemental analysis, IR, UV, and ESR. The electronic spectra of Cu(II) dithiocarbamate complexes are indicative of square planar (D_{2h}) symmetry which is supported by ESR spectra of these complexes. The ESR Spectra are also indicative of substantial distortion in Cu(diendtc) and Cu(triendtc) complexes

KEY WORDS : Cu (II) Complexes, Elemental analysis, IR, UV and ESR spectra

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Synthesis of the ligands:

Ammonium pyrrolidine dithiocarbamate:

Pyrrolidtc of AR grade was obtained from LOBA chemical.

Synthesis of disodium diethylenetriamine bis (dithiocarbamate), diendtc:

This was prepared by reacting 50 ml diethylenetriamine (18ml, 1M) with 50ml NaOH (6g, 1M) and CS_2 (18ml, 2M) in distilled methanol under ice-cold condition. The NaOH solution was first added to diethylenetriamine slowly through constant stirring. The CS_2 solution was finally added dropwise under constant stirring. The white precipitate thus formed, was filtered in a Buchner funnel and washed several times with methanol and dried in air. Yield \approx 78 per cent.

Preparation of disodium triethylenetetramine bis(dithiocarbamate), triendtc:

The disodium triethylenetetramine bis (dithiocarbamate) was prepared by reacting 50 ml triethylenetetramine (22.5ml, 1M) in distilled methanol, under ice cold condition using similar procedure as described above. Yield \approx 70 per cent.

Synthesis of copper complexes with the ligands:

Bis (pyrrolidine dithiocarbamate) Cu(II), Cu (pyrrolidtc)₂:

It was prepared by adding methanolic solution of

pure cupric acetate (recrystallised, 0.1M) to methanolic solution of ammonium pyrrolidine dithiocarbamate (0.2M). The brown coloured precipitate of *Cu (pyrrolidtc)₂* was obtained which was filtered in a Buchner funnel, washed several times with methanol and finally dried in a dessicator. Yield \approx 65 per cent. It was then recrystallised from methanol-dichloromethane (1:3) mixture.

Diethylenetriamine bis(dithiocarbamate) Copper (II), Cu (diendtc):

This brownish yellow complex was prepared by the reaction between methanolic solution of cupric acetate (0.1M) and disodium salt of the ligand (0.1M) in water-methanol (1:3) mixture, through constant stirring employing similar procedure as described above. Yield \approx 40 per cent.

Triethylenetetramine bis (dithiocarbamate) copper(II), Cu(triendtc):

The brown coloured complex was obtained by the reaction of methanolic solution of cupric acetate (0.1M) with disodium salt of the ligand (0.1M) in water-methanol (1:1) mixture employing similar procedure as described above. Yield \approx 30 per cent.

Physical measurements:

Elemental analysis:

Determination of sulphur⁷⁹:

About 300mg of Cu-complex of the ligand was taken

in a 500 ml beaker, added 4ml of conc. HCl and 2—3 drops of conc. HNO₃. It was digested twice, latter only with conc. HCl. Dissolved the contents of the beaker with 50ml water, heated and filtered. Added about 2 per cent BaCl₂ solution till the complete precipitation of sulphur as BaSO₄. Filtered the contents with ashless Sartorius(393) filter paper and then burnt it in a silica crucible, the amount of sulphur was calculated from BaSO₄.

Determination of Cu⁷⁹:

Cu was determined volumetrically. About 200 mg of the Cu –complex was digested with conc. HCl twice in a 500 ml beaker. Added, about 20ml water and heated for about 2 minutes. It was then filtered, kept in a volumetric flask and made the volume upto 100 ml. About 10ml of solution was pipetted out in a conical flask and titrated it with standard thio solution, standardised with CuSO₄ solution, using starch as indicator.

ESR spectra:

The magnetically dilute isomorphous powdered samples of the Cu- complexes of Cu (pyrroldtc)₂, Cu (diendtc) and Cu(triendtc) were prepared by dissolving a mixture of 2:98 Cu(II) sulphate and zinc sulphate in aqueous methanolic solution to which equimolar amount of ligands(pyrroldtc, diendtc and triendtc)are added, the light brown precipitates so obtained were filtered and dried. The ESR spectra were recorded with JEOL-JES-FA200 (X—band). electron spin resonance (ESR) spectrometer at room temperature.

Electronic spectra :

The electronic spectra of the Cu(II) dithiocarbamate complexes were recorded with a Shimadzu(model: UV—1700) UV—VIS spectrophotometer in the range 400—800 using dichloromethane and dimethylsulphoxide as solvents.

IR Spectra :

The IR spectra (4000—250cm⁻¹) were recorded with

a FT-IR Shimadzu spectrophotometer (Mode:IR-Prestige21)with DRS(diffuse reflectance solid)technique mixing with KBr. The low frequency 400-250cm⁻¹ IR spectra were taken separately to find out Cu-S IR bands.

Electronic spectra :

Electronic spectra of Cu(II) complexes of pyrroldtc, diendtc and triendtc were taken in the visible region(400-800) using different solvents. In Cu(Pyrroldtc)₂, the solvent was dichloromethane, while in Cu(diendtc) and Cu(triendtc), dimethylsulphoxide was taken as solvent. In all the cases, the solutions were in dilute conditions. In the visible region, the complexes were found to show two bands as shown in the Table 1.

Complexes	$\lambda_{max}(nm), \nu. (cm^{-1})$	
Cu(pyrroldtc) ₂	433.5nm, (23,068 cm ⁻¹)	637.5nm, (15,686 cm ⁻¹)
Cu(diendtc)	431nm, (23,201 cm ⁻¹)	675nm, (14,814 cm ⁻¹)
Cu(triendtc)	432nm, (23,148cm ⁻¹)	636nm, (15,723 cm ⁻¹)

The electronic spectra of Cu(pyrroldtc)₂, Cu(diendtc) and Cu(triendtc) are shown in the Fig. 4. The energy level sequence in copper dithio complexes are found to be xy>z²>x²>xz>yz, in agreement with Hitchman’s angular overlap model.⁸⁰ The two bands observed in the spectra of the complexes are assigned as crystal field (d-d) transitions i.e. d_{xz} → d_{xy}(²A₂→²B₁) and d_{yz}(²A₂→²B₂) which are allowed in D_{2h} symmetry and are in agreement with other CuS₄ systems.

ESR Spectra:

The ESR spectra of the Cu dithio complexes under study, magnetically diluted in isomorphous Zn(II) matrix showed hyperfine lines. For this, the complexes were prepared from a methanolic solution of copper(II) sulphate and zinc sulphate mixture (2:98 ratio). The spin hamiltonian parameters were calculated and given in the Table 2 while the ESR spectra of powered cu(II)dithio complexes are shown in the Fig. 1 to 4.

Complexes	Decomposition temperature (°C)	Analysis % ; found/(cald.)	
		S	Cu
Cu (pyrroldtc) ₂	~260	35.60 (36.10)	16.77 (17.93)
Cu(diendtc)	~190	40.35 (40.44)	19.09(20.06)
Cu(triendtc)	~165	35.2 (35.60)	16.9(17.66)

Complexes	$\nu (C...N)$	$\nu (C...S)$	$N_{i(CS)} + \delta_{SCS}$	$\nu_{(Cu-S)}$
Cu(pyrroldtc) ₂	1497·91	1001·35	532·86	366·23
Cu (diendtc)	1507·04	1000·61	537·67	393·48
Cu(triendtc)	1502·58	1000·93	539·23	378·06

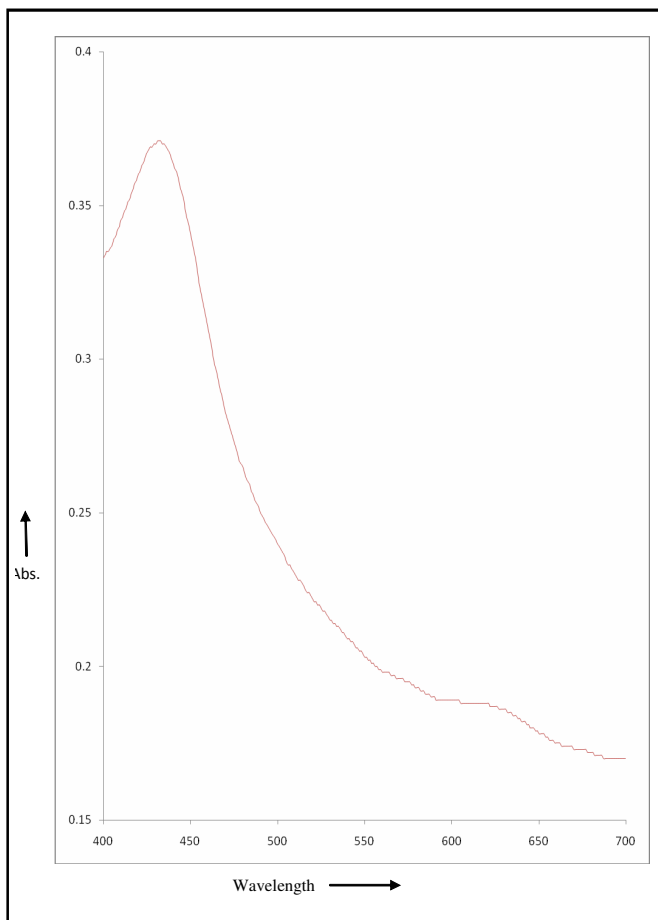


Fig. 1 : Electronic spectrum of Cu(diendtc)

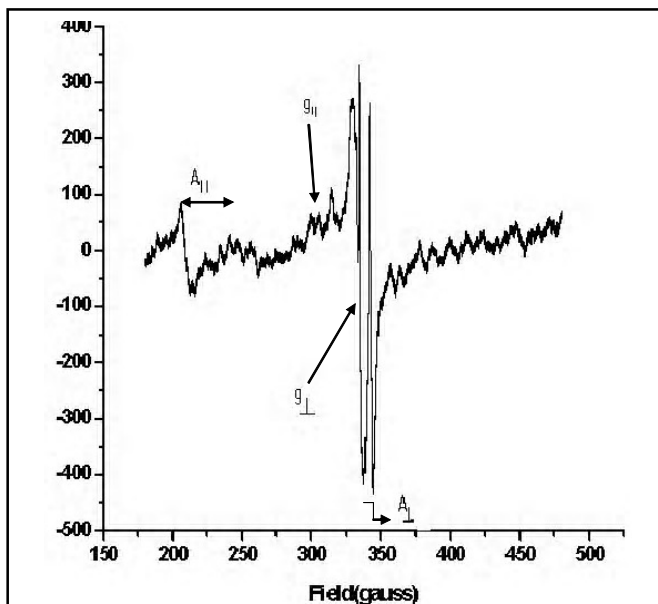
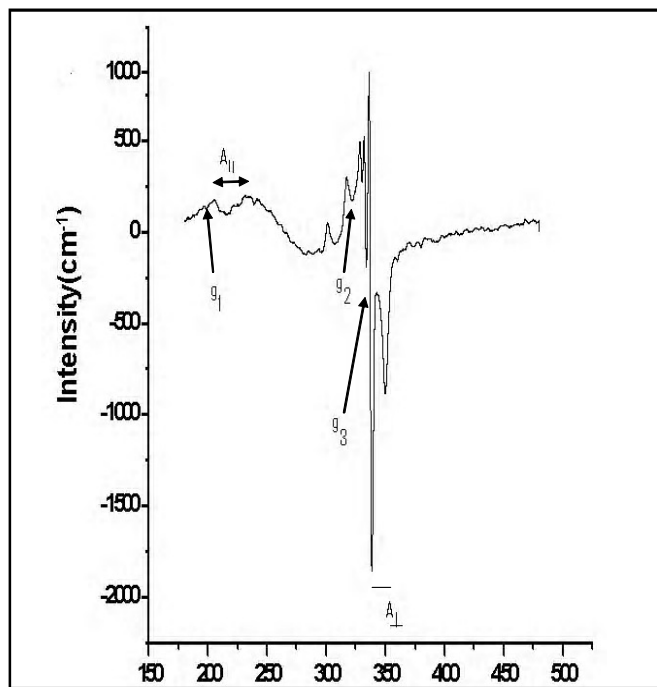
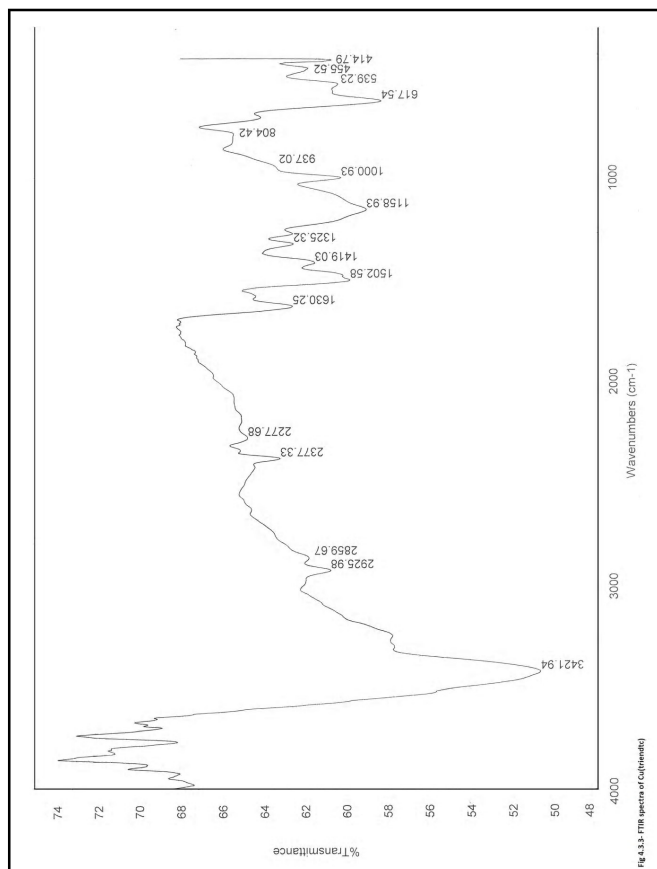
Fig. 2 : Electronic spectrum of Cu (pyrroldtc)₂

Fig. 3 : ESR spectrum of Cu(diendtc)

Fig. 4 : FTIR spectrum of Cu(triendtc),(4000-400 cm^{-1})

IR spectra:

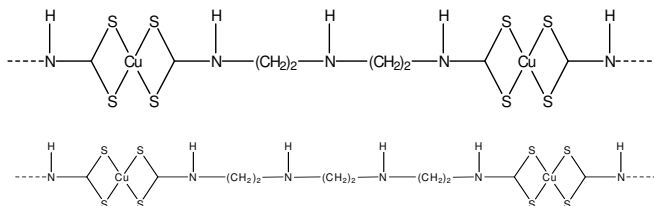
In the IR spectrum of Cu(pyrroldtc)₂, the band observed at 1497.9 cm^{-1} was assigned to which was

intermediate between $\nu_{(C=N)}$ (1640-1690) cm^{-1} and $\nu_{(C-N)}$ (1250—1350 cm^{-1}) indicating partial double bond

character in the C—N bond. For diendtc and triendtc derivative, $\nu_{(C-N)}$ were observed at 1507.04 and 1502.58 cm^{-1} , respectively. The lower frequency in the first one could be explained on the basis of less electron releasing ability of the pyrrolidine ring toward C—N bond. The bands observed at 1000.35, 1001.61 and 1000.93 cm^{-1} , respectively for pyrroldtc, diendtc and triendtc were assigned to $\nu_{(C-S)}$ mode. Appearance of single band in this region was indicative of bidentate chelating nature of the dithiocarbamate ligand. The bands at 532.86, 537.67 and 539.23 cm^{-1} were assigned to the $\nu_{(CS)} + \nu_{(SCS)}$ vibrations for $\text{Cu}(\text{pyrroldtc})_2$, $\text{Cu}(\text{diendtc})$ and $\text{Cu}(\text{triendtc})$, respectively. The bands at 366.23, 393.48 and 378.79 cm^{-1} for , respectively pyrroldtc, diendtc and triendtc derivatives were assigned to $\nu_{(Cu-S)}$ mode of vibration.⁵⁴ The important IR frequencies are given in the Table 2.

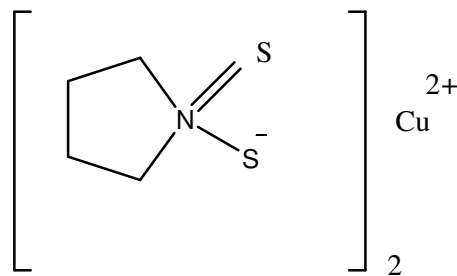
Concluding remarks:

From the solubility of Cu-complexes of dithiocarbamates , it is observed that $\text{Cu}(\text{pyrroldtc})_2$ is



soluble in dichloromethane while $\text{Cu}(\text{diendtc})$ and $\text{Cu}(\text{triendtc})$ are soluble in highly polar dimethylsulphoxide and it is indicative of their polymeric structure and may be, respectively represented as:

While the structure of $\text{Cu}(\text{pyrroldtc})_2$ can be represented as:



From IR spectral data, it is observed that the $\text{Cu}(\text{II})$ complexes of dithiocarbamates behave as bidentate chelates due to presence of only band in the range 1090-940 cm^{-1} region, while delocalisation of electrons are observed over S-C-S atoms.

The ESR spectra of the complexes are indicative of distortion from the ideal site symmetries. In the $\text{Cu}(\text{pyrroldtc})_2$ complex , the bonding parameters \hat{a}^2 , \hat{a}_1^2 and \hat{a}^2 are being calculated which indicate covalency in the metal-ligand bond. In $\text{Cu}(\text{diendtc})$ and $\text{Cu}(\text{triendtc})$, appearance of three g values *i.e.* g_1 , g_2 and g_3 indicates substantial distortion in their structures.

The electronic spectra of the complexes indicate square planer (D_{2h}) symmetry of the complexes.

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