

CHAPTER

3

**Interaction of Copper(II) with
Dithiocarbamates Derived from Primary
Amines: Existence of One-electron Redox
Process and Formation of Polymeric
Copper(I) Complexes**

Both N,N-disubstituted and N-monosubstituted dithiocarbamates are found to have the same ligation characteristics towards most of the metal ions. But, as mentioned earlier, there appears to be difference in the nature of their interaction with copper(II). While the complexation behaviour of secondary amine-derived dithiocarbamates with copper(II) has been intensely investigated, studies on the ligation characteristics of RHDtc towards copper(II) is almost neglected. Only very few studies have been carried out and as seen in the literature reports¹⁻⁷ there is considerable ambiguity regarding the reactivity characteristics of RHDtc towards cupric ions. While some of the early studies indicated the instability of the Cu(II) complexes having the composition $\text{Cu}(\text{RHDtc})_2$ and the presence of Cu(I) species and isothiocyanates among their decomposition products, there are later reports claiming the isolation of stable cupric complexes, $\text{Cu}(\text{RHDtc})_2$. The diamagnetic character of these so-called cupric complexes has been explained in terms of superexchange and antiferromagnetic interactions.⁷ In a few cases a magnetic moment of about 1.7 BM has been reported for some

of these complexes,⁶ notwithstanding the earlier reports of formation of only diamagnetic complexes.³

In this chapter, we discuss the interaction of copper(II) with RHDtc in some detail and attempt to throw light on the conflicting reports mentioned earlier. A series of aryl/alkyl substituted RHDtc are synthesised for the purpose and their reactions with copper(II) investigated. The nature of the products formed is studied and their characterisation made.

3.1 Experimental

3.1.1 Preparation of dithiocarbamate ligands

In the present study most of the dithiocarbamates are generated in situ in solution form, the general methods of their preparation being discussed in the previous chapter. Solid ammonium salt of dithiocarbamate derived from aniline has also been prepared by reported procedure.⁸ The brief preparative details of the various primary amine dithiocarbamates employed in the present study are as follows.

(a) *N*-ethyldithiocarbamate, (EtHNCS₂⁻)

A solution of CS₂ (1.52 g, 20 mM) in acetone (10 ml) was slowly added to a 70% aqueous solution containing 0.9 g of ethylamine (20 mM) with stirring while keeping the solution cooled in cold water. Equimolar quantity of NaOH (0.8 g) dissolved in water was then added to the above solution under stirred condition. No attempt has been made to separate the sodium salt of *N*-ethyldithiocarbamate thus formed in solid form. The yellow solution was used as such for the interaction studies.

(b) *N*-(1-butyl)dithiocarbamate, (BuHNCS₂⁽⁻⁾)

A solution of n-butylamine (1.46 g, 20 mM) was prepared in water (10 ml). CS₂ (1.52 g, 20 mM) dissolved in acetone (10 ml) was slowly added to the above solution while stirring, keeping the solution cooled in cold water. An aqueous solution of equimolar quantity of NaOH (0.8 g) was added dropwise with stirring to get an yellow solution of the sodium *N*-(1-butyl)dithiocarbamate.

(c) *N*-benzylidithiocarbamate, (B₂HNCS₂⁽⁻⁾)

Benzylamine (2.15 g, 20 mM) was dissolved in water (10 ml) containing acetone (2 ml). This solution was treated with 1.52 g of CS₂ (20 mM) and an aqueous solution of NaOH (20 mM) as described above to get a yellow solution of sodium *N*-benzylidithiocarbamate.

(d) *N*-Phenylidithiocarbamate (PhHNCS₂⁽⁻⁾)

The compound was prepared in both solution phase and in solid state.

CS₂ (2.3 g, 30 mM) was dissolved in 15 ml DMF-water mixture (2:1 v/v). Freshly distilled aniline (2.8 g, 30 mM) was added to the above solution with stirring, keeping the solution cooled in cold water. Sodium hydroxide (20 mM) dissolved in about 5 ml water was added dropwise with stirring. The solution was kept under stirred condition for about 1 min, which was then repeatedly washed with ether and the dissolved ether was removed by suction using a vacuum pump. Only freshly prepared ligand solution was used for interaction studies. Solid ammonium dithiocarbamate also was prepared from freshly distilled aniline as reported.⁸ To an ice cold mixture of aniline (0.2 M) and concentrated aqueous ammonia (0.2 M), CS₂ (0.2 M) was added dropwise with stirring. The white crystalline product

separated out was filtered, washed with a little ice cold water and several times with ether and dried over P_4O_{10} in vacuum.

(e) *N*-(4-methylphenyl)dithiocarbamate, (*p*THNCS₂⁽⁻⁾)

CS₂ (1.9 g, 25 mM) was dissolved in 15 ml DMF-water mixture (2:1 v/v). Paratoluidene (2.15 g, 20 mM) was added with stirring keeping the solution cooled in cold water. The solution was treated with an equimolar quantity of NaOH and was washed with ether as described in the case of PhHNCS₂⁽⁻⁾ to get a brownish yellow solution of sodium *N*-(4-methylphenyl)dithiocarbamate.

(f) *N*-(4-methoxyphenyl)dithiocarbamate, (*p*AHNCS₂⁽⁻⁾)

p-Anisidine (2.46 g, 20 mM) was treated with 1.9 g of CS₂ (25 mM) and the solution was washed with ether as described under Section 3.1.1d(i) to get a brown solution of sodium *N*-(4-methoxyphenyl)dithiocarbamate.

(g) *N*-(3-chlorophenyl)dithiocarbamate, (*m*CHNCS₂⁽⁻⁾)

Metachloroaniline (2.55 g, 20 mM) was treated with 1.9 g of CS₂ (25 mM) and the solution was washed with ether as described under Section 3.1.1d(i) to get a brownish yellow solution of sodium *N*-(3-chlorophenyl)dithiocarbamate.

(h) *N*-(4-chlorophenyl)dithiocarbamate, (*p*CHNCS₂⁽⁻⁾)

The procedure adopted for the preparation of the compound was similar to the one mentioned above. The solution obtained also had yellow colour.

(i) *N*-(carboxymethyl)dithiocarbamate, ($CmHNCS_2^{(-)}$)

Crystalline glycine (1.5 g, 20 mM) was dissolved in 2 M aqueous solution (20 ml) of sodium hydroxide with stirring. CS_2 (1.52 g, 20 mM) dissolved in DMF (2 ml) was added dropwise under stirred condition. The solution was kept stirred for about 1 min and washed with ether. The dissolved ether was removed by suction using a vacuum pump to get a yellow solution of sodium *N*-(carboxymethyl)dithiocarbamate.

3.1.2 Interaction of Cu(II) with RHDtc (Preparation of Cu(I) complexes)

Interaction of copper(II) with RHDtc is studied in aqueous medium by controlled addition of cupric chloride solution to an RHDtc solution in stirred condition. The addition was slow and the colour of the solution and solid was noticed throughout the addition process. The reaction was monitored by stopping the addition of the salt solution by maintaining various copper(II):RHDtc molar ratios (1:4, 1:3, 1:2 and 1:1) in the reaction mixtures. The solid obtained was filtered washed and dried. The filtrate obtained in each case was also analysed by extraction and separation. The bright yellow solids obtained in all the cases were copper(I) complexes, as explained in Section 3.2. The various copper(I) complexes obtained by the interaction of copper(II) with the corresponding primary amine dithiocarbamate ligands discussed in the present chapter are given below, along with their brief preparative details.

(a) *N*-ethyldithiocarbamatocopper(I), [$Cu(EtHNCS_2)$]

To the ligand solution of sodium *N*-ethyldithiocarbamate (20 mM), an aqueous solution of cupric chloride (10 mM) was added dropwise slowly with constant stirring. After the addition of the metal salt solution the mixture was kept stirred for about 5 min. The yellow solid obtained was

filtered, washed repeatedly and successively with water, ethanol and ether and finally dried over P_2O_5 in vacuum.

(b) *N*-(1-butyl)dithiocarbamatocopper(I), [Cu(BuHNCS₂)]

Aqueous solution of cupric chloride (10 mM) was made to react with the solution of sodium *N*-(1-butyl)dithiocarbamate (20 mM) by controlled addition. The yellow complex precipitated out was isolated in pure state and dried as described above.

(c) *N*-benzyl dithiocarbamatocopper(I), [Cu(BzHNCS₂)]

To a solution of sodium *N*-benzyl dithiocarbamate (20 mM) was added an aqueous solution of cupric chloride (10 mM). The bright yellow complex formed was isolated in pure state and dried as described under Section 3.1.2a.

(d) *N*-phenyl dithiocarbamatocopper(I), [Cu(PhHNCS₂)]

Aqueous cupric chloride solution (10 mM) was added dropwise with constant stirring to the freshly prepared solution of sodium *N*-phenyl dithiocarbamate. This resulted in the immediate precipitation of a brown complex. It was filtered, repeatedly and successively washed with water, ethanol and ether and finally dried over P_4O_{10} under vacuum. The complex was prepared also by using an aqueous solution of the solid ammonium dithiocarbamate (20 mM) and aqueous cupric chloride (10 mM) by the same method.

(e) *N*-(4-methylphenyl)dithiocarbamatocopper(I), [Cu(*p*THNCS₂)]

The solution of sodium *N*-(4-methylphenyl)dithiocarbamate (20 mM) and aqueous cupric chloride (10 mM) were allowed to interact in cold

condition. The yellow complex separated was filtered, washed and dried as described in Section 3.1.2d.

(f) *N*-(4-methoxyphenyl)dithiocarbamatocopper(I), [Cu(*p*AHNCS₂)]

The procedure employed for the preparation of the complex was similar to the one described above. A solution of sodium *N*-(4-methoxyphenyl)dithiocarbamate (20 mM) and aqueous cupric chloride solution (10 mM) were allowed to react by slow addition. The yellow complex formed was isolated and dried as described under Section 3.1.2d.

(g) *N*-(3-chlorophenyl)dithiocarbamatocopper(I), [Cu(*m*CHNCS₂)]

Aqueous solution of cupric chloride (10 mM) was added to the solution of sodium *N*-(3-chlorophenyl)dithiocarbamate (20 mM). The complex formed was brownish yellow in colour. This was filtered, washed and dried as described under Section 3.1.2d.

(h) *N*-(4-chlorophenyl)dithiocarbamatocopper(I), [Cu(*p*CHNCS₂)]

By the same procedure as in Section 3.1.2d, aqueous solution of cupric chloride (10 mM) and the solution of sodium *N*-(4-chlorophenyl)dithiocarbamate (20 mM) were allowed to react and a brownish yellow solid formed was filtered, washed and dried.

(i) *N*-(carboxymethyl)dithiocarbamatocopper(I), [Cu(*Cm*HNCS₂)]

To the solution of *N*-(carboxylate methyl)dithiocarbamate (20 mM) aqueous solution of cupric chloride (10 mM) was added dropwise with stirring to get a clear yellow solution. Acetate-acetic acid buffer solution was added dropwise with constant stirring till a bright yellow complex was

precipitated. It was filtered, washed with water and ether and finally dried over P_4O_{10} under vacuum.

3.1.3 Oxidation of RHDtc with iodine solution (Preparation of N,N' -disubstituted thiuram disulphides)

Since one of the products obtained on reaction of Cu(II) with dithiocarbamates was the oxidised form of the ligands, the various dithiocarbamates discussed in the chapter were subjected to controlled oxidation using I_2 solution to get their thiuram disulphides. The various thiuram disulphides prepared by this procedure from the corresponding dithiocarbamate ligands, discussed in Section 3.1.1, are the following.

(a) N,N' -diethylthiuram disulphide, $[EtHNC(S)S-S(S)CNHET]$

Aqueous solution of iodine (1 M) containing potassium iodide was added dropwise with constant stirring to the ligand solution of sodium N-ethylthiocarbamate (20 mM) till the brown colour of iodine just persisted. The turbid aqueous solution was extracted with chloroform. The chloroform extract was well shaken with anhydrous calcium chloride. The solvent was removed by evaporation to get reddish yellow liquid of $[EtHNC(S)S]_2$.

(b) N,N' -di(1-butyl)thiuram disulphide, $[BuHNC(S)S-S(S)CNHBu]$

Aqueous solution of iodine (1 M) containing potassium iodide was treated with the ligand solution of sodium N-(1-butyl)dithiocarbamate. The disulphide $(BuHNC(S)S)_2$ in liquid form was isolated from the turbid aqueous solution as described above.

(c) *N,N'*-dibenzylthiuram disulphide, [BzHNC(S)S-S(S)CNHBz]

Aqueous solution of iodine (1 M) was added to the ligand solution of sodium N-benzylthiocarbamate as described in Section 3.1.3a. A white solid was separated. It was filtered and recrystallised from aqueous acetone to get colourless crystals of *N,N'*-dibenzylthiuramdisulphide.

(d) *N,N'*-diphenylthiuram disulphide, [PhHNC(S)S-S(S)CNHPh]

The ligand solution of sodium N-phenylthiocarbamate (20 mM) was treated with a 1 M aqueous solution of iodine till the oxidation was complete as evidenced from the appearance of faint brown colour to the solution. The white solid of (PhHNC(S)S)₂ separated was filtered and purified as described under Section 3.1.3c.

(e) *N,N'*-di(4-methylphenyl)thiuram disulphide, [pTHNC(S)S-S(S)CNHpT]

The ligand solution of sodium N-(4-methylphenyl)dithiocarbamate (20 mM) on treatment with 1 M aqueous iodine solution formed a white solid which was separated and purified as described above.

(f) *N,N'*-di(4-methoxyphenyl)thiuram disulphide, [pAHNC(S)S-S(S)CNHpA]

The ligand solution of sodium N-(4-methoxy phenyl)dithiocarbamate (20 mM) was treated with aqueous 1 M iodine solution and a white solid of the thiuram disulphide formed was separated and purified as described under Section 3.1.3c.

(g) *N,N'*-di(3-chlorophenyl)thiuram disulphide, [mCHNC(S)S-S(S)CNHmC]

The ligand solution of sodium N-(3-chlorophenyl)dithiocarbamate (20 mM) and 1 M aqueous of iodine were allowed to interact to get a white solid and it was separated and purified as described under Section 3.1.3c.

(h) *N,N'*-di(4-chlorophenyl)thiuram disulphide, [pCHNC(S)S-S(S)CNHpC]

Sodium N-(4-chlorophenyl)dithiocarbamate solution (20 mM) was treated with 1 molar aqueous solution of iodine to get a white solid and it was separated and purified as described under Section 3.1.3c.

(i) *N,N'*-di(carboxymethyl)thiuram disulphide, [CmHNC(S)S-S(S)CNHCm]

Aqueous solution of iodine (1 M) was added dropwise to the ligand solution of N-(carboxylate methyl)dithiocarbamate (20 mM). The dropwise addition of iodine solution under stirred condition continued till the brown colour of iodine just persisted. An acetate-acetic acid buffer was added dropwise with stirring till a white solid got precipitated. It was filtered and reprecipitated from ether. On keeping, the compound was found to be acquiring pale yellow colour indicating some extent of decomposition.

Analytical and spectral methods employed for the characterisation of the products of interaction, both between Cu(II) ions and ligands and between iodine and ligands, are briefly mentioned in Chapter 2.

3.2 Results and discussion

3.2.1 Redox process in aqueous medium

The general preparative methods employed for metal complexes of dithiocarbamates ($RR'NCS_2^{(-)}$) derived from secondary amines involved interaction of either an alcoholic or aqueous solution of the $RR'Dtc$ with the metal salt solution. The nature of the solvent does not appear to give any complication in these cases and the products obtained are found to be the

same in both aqueous and alcohol media. In the present case of the interaction of RHDtc with copper(II) ions, some preliminary investigations, however, showed strong solvent dependency (discussed later). So in all cases, water solutions of both the metal ion and the RHDtc were employed and the reaction studied in aqueous conditions, for better comparison. No difference in reaction or reaction products was observed when a solution of either sodium or ammonium salt of the RHDtc was employed or when the dithiocarbamates generated *in situ* in aqueous condition was used. So in all the cases, the RHDtc were generated in solution in required quantity only just before reacting with copper(II) salt solution.

A variety of alkyl and aryl substituted primary amine dithiocarbamates are considered in the present study (Table 3.1) to monitor any possible effect due to the N-substituent on the nature of interaction and product formation. The various types of primary amines used and the nature of RHDtc generated are tabulated in Table 3.1.

Table 3.1. Various primary amines used to generate Dtc and the corresponding copper complexes

Amine used (RNH ₂)	N-substituent (R)	Dithiocarbamate generated in situ (RHDtc)	Cu(RHDtc)* formed
Ethylamine	C ₂ H ₅ (Et)	EtHNCS ₂ ⁻	Cu(EtHNCS ₂)
n-Butylamine	n-C ₄ H ₉ (Bu)	BuHNCS ₂ ⁻	Cu(BuHNCS ₂)
Benzylamine	C ₆ H ₅ -CH ₂ (Bz)	BzHNCS ₂ ⁻	Cu(BzHNCS ₂)
Aniline	C ₆ H ₅ (Ph)	PhHNCS ₂ ⁻	Cu(PhHNCS ₂)
p-Toluidine	p-CH ₃ -C ₆ H ₄ (pT)	pTHNCS ₂ ⁻	Cu(pTHNCS ₂)
p-Chloroaniline	p-Cl-C ₆ H ₄ (pC)	pCHNCS ₂ ⁻	Cu(pCHNCS ₂)
m-Chloroaniline	m-Cl-C ₆ H ₄ (mC)	mCHNCS ₂ ⁻	Cu(mCHNCS ₂)
p-Anisidine	p-CH ₃ O-C ₆ H ₄ (pA)	pAHNCS ₂ ⁻	Cu(pAHNCS ₂)
Glycine	HOOC-CH ₂ (Cm)	CmHNCS ₂ ⁻	Cu(CmHNCS ₂)

*Composition, empirical formula

The nature of the anion of the copper(II) salt does not seem to affect the products formed and hence in all the cases a solution of cupric chloride was employed.

The addition of copper(II) solution to a solution of known quantity of RHDtc was done dropwise with smooth stirring. When the green coloured cupric chloride solution makes contact with the ligand solution a brown colouration appeared which turned into yellow solid. The yellow precipitate keeps forming on further addition of the copper(II) solution. Interaction of $\text{RHNC}_2\text{S}_2^-$ with Cu(II) was tried monitoring by varying Cu(II):Dtc compositions (1:4, 1:3, 1:2, 1:1, 2:1) and in all the cases the yellow solid separated out was found to be having the same composition and structure. On the continuous addition of copper salt solution, the yellow solid was found to be continuously forming till the metal:ligand ratio was 1:2. The same observation was seen during the reverse addition also. Further addition of the Cu^{2+} does not yield any precipitate and the excess metal salt added was found to be remaining unreacted in the reaction mixture. The yellow product obtained was found to be insoluble in all solvents. In all the dithiocarbamates studied the solids obtained by the reaction were yellow in colour and exhibited same insoluble character. Observations were the same when aqueous solution of solid ammonium dithiocarbamate was treated with the copper(II) solution. Even though the addition process clearly indicated an optimum 1:2 (metal:ligand) stoichiometry for the reaction, quantitative filtration of the yellow products always showed a yield less than what was expected for this anticipated 1:2 metal-ligand composition. The elemental analysis of the yellow complexes conclusively showed 1:1 metal-ligand ratio amounting to a composition $\text{Cu}(\text{RHDtc})$ (Table 3.2).

Table 3.2. Analytical data for polymeric *N*-monosubstituted dithiocarbamato-copper(I) complexes

Complex	Colour	Found (Calculated) (%)				
		Carbon	Hydrogen	Nitrogen	Sulphur	Copper
[Cu(EtHNCS ₂) _n] (C ₃ H ₆ NS ₂ Cu)	Yellow	19.4 (19.6)	3.4 (3.3)	7.5 (7.6)	33.5 (34.9)	34.9 (34.6)
[Cu(BuHNCS ₂) _n] (C ₅ H ₁₀ NS ₂ Cu)	Yellow	28.0 (28.3)	5.1 (4.8)	6.8 (6.6)	30.8 (30.3)	29.7 (30.0)
[Cu(BzHNCS ₂) _n] (C ₈ H ₈ NS ₂ Cu)	Yellow	38.8 (39.1)	3.5 (3.3)	5.5 (5.7)	26.7 (26.1)	25.2 (25.8)
[Cu(PhHNCS ₂) _n] (C ₇ H ₆ NS ₂ Cu)	Yellow	35.7 (36.2)	2.5 (2.6)	5.9 (6.0)	26.4 (27.7)	27.3 (27.4)
[Cu(pTHNCS ₂) _n] (C ₈ H ₈ NS ₂ Cu)	Brownish yellow	38.7 (39.1)	3.6 (3.3)	5.8 (5.7)	27.0 (26.1)	26.0 (25.8)
[Cu(pCHNCS ₂) _n] (C ₇ H ₅ NS ₂ ClCu)	Brownish yellow	31.1 (31.6)	2.2 (1.9)	5.5 (5.3)	23.6 (24.1)	24.7 (23.9)
[Cu(mCHNCS ₂) _n] (C ₇ H ₅ NS ₂ ClCu)	Brownish yellow	31.3 (31.6)	1.8 (1.9)	5.1 (5.3)	23.9 (24.1)	23.3 (23.9)
[Cu(pAHNCS ₂) _n] (C ₈ H ₈ NOS ₂ Cu)	Yellow	36.0 (36.7)	3.2 (3.1)	5.0 (5.3)	22.9 (24.5)	24.6 (24.3)
[Cu(CmHNCS ₂) _n] (C ₃ H ₄ NO ₂ S ₂ Cu)	Yellow	16.4 (16.8)	1.9 (1.9)	6.7 (6.5)	29.4 (30.0)	30.4 (29.7)

This was rather surprising because the actual reaction was found to be completed only when the metal : ligand ratio was 1:2 whether the addition was ligand to metal or vice versa. Since RHDtc ion is monoanionic such a 1:1 composition for the complex is an indication of the formation of Cu(I) species rather than Cu(II).

The electronic spectra of all the complexes formed also did not show any characteristic low energy absorptions (d-d transitions) expected for Cu(II)

complexes but gave only intense high energy bands attributable to charge transfer transitions. Further all the complexes isolated were EPR inactive and showed diamagnetic character indicating conclusively the reduced state (+1) of the copper.

To find out the nature of the ligand moiety in the Cu(I) complexes, solid state IR spectra of all the complexes were taken. All the compounds showed highly characteristic peaks of dithiocarbamate moiety (RHDtc) assignable to $\nu(\text{NH})$ ($\sim 3200 \text{ cm}^{-1}$), $\nu(\text{CN})$ ($\sim 1500 \text{ cm}^{-1}$ for aliphatic species and $\sim 1350 \text{ cm}^{-1}$ for aromatic species) and $\nu(\text{CS})$ ($\sim 1000 \pm 70 \text{ cm}^{-1}$) quite agreeable to reported values.⁹

The observed reduction of copper(II) to Cu(I) on reaction with RHDtc naturally necessitates an associated oxidation process. The species which is expected to undergo oxidation is the RHDtc ion. It is known that the dithiocarbamate anion can sometimes get converted to neutral dithiocarbamate radical, R_2NCS_2 , which often dimerises to stable thiuram disulphide, $\text{R}_2\text{NC}(\text{S})\text{S}(\text{S})\text{CNR}_2$ (tds). To find out whether tds were formed as by-products, the filtrates, and the yellow complexes after washing with water were extracted with CHCl_3 . In the case of CmDtc, ether was used for extraction because of its insolubility in CHCl_3 . The extracts were shaken with anhydrous CaCl_2 and then evaporated to get white solid which on crystallisation from aqueous acetone, gave colourless plate-like crystals. In the case of CmDtc generated from glycine, the white solid was recrystallised from ether. In the cases of EtHDtc and BuHDtc, evaporation of the CHCl_3 extract gave reddish yellow viscous liquids. All the compounds were analysed for their elemental content and the data showed composition expected for the thiuram disulphide of RHDtc (Table 3.3).

Table 3.3. Analytical data for *N,N'*-disubstituted thiuram disulphides

Compound	Colour (State)	Found (Calculated) (%)			
		Carbon	Hydrogen	Nitrogen	Sulphur
EtHNC(S)-S-S(S)CNHEt (C ₆ H ₁₂ N ₂ S ₄)	Reddish yellow (liquid)	29.5 (29.9)	5.3 (5.0)	11.2 (11.6)	52.9 (53.4)
BuHNC(S)-S-S(S)CNHBu (C ₁₀ H ₂₀ N ₂ S ₄)	Reddish yellow (liquid)	40.1 (40.5)	7.0 (6.8)	9.2 (9.4)	43.6 (43.6)
BzHNC(S)-S-S(S)CNHBz (C ₁₆ H ₁₆ N ₂ S ₄)	White (solid)	53.0 (52.7)	4.4 (4.4)	8.0 (7.7)	34.9 (35.2)
PhHNC(S)-S-S(S)CNHPh (C ₁₄ H ₁₂ N ₂ S ₄)	White (solid)	50.2 (49.9)	3.8 (3.6)	7.9 (8.3)	38.0 (38.2)
pTHNC(S)-S-S(S)CNHpT (C ₁₆ H ₁₆ N ₂ S ₄)	White (solid)	52.3 (52.7)	4.6 (4.4)	7.6 (7.7)	34.7 (35.2)
pCHNC(S)-S-S(S)CNHpC (C ₁₄ H ₁₀ N ₂ S ₄ Cl ₂)	White (solid)	41.0 (41.4)	2.6 (2.5)	6.7 (6.9)	31.2 (31.7)
mCHNC(S)-S-S(S)CNHmC (C ₁₄ H ₁₀ N ₂ S ₄ Cl ₂)	White (solid)	41.5 (41.4)	2.7 (2.5)	7.0 (6.9)	30.9 (31.7)
pAHNC(S)-S-S(S)CNHpA (C ₁₆ H ₁₆ N ₂ O ₂ S ₄)	White (solid)	48.1 (48.4)	4.0 (4.1)	6.9 (7.1)	32.0 (32.4)

The compounds were further characterised by IR and ¹H-NMR and electronic spectral measurements. A typical IR spectrum of one of the tds (BuHNC(S)S-S(S)CNHBu) is shown in Figure 3.1a.

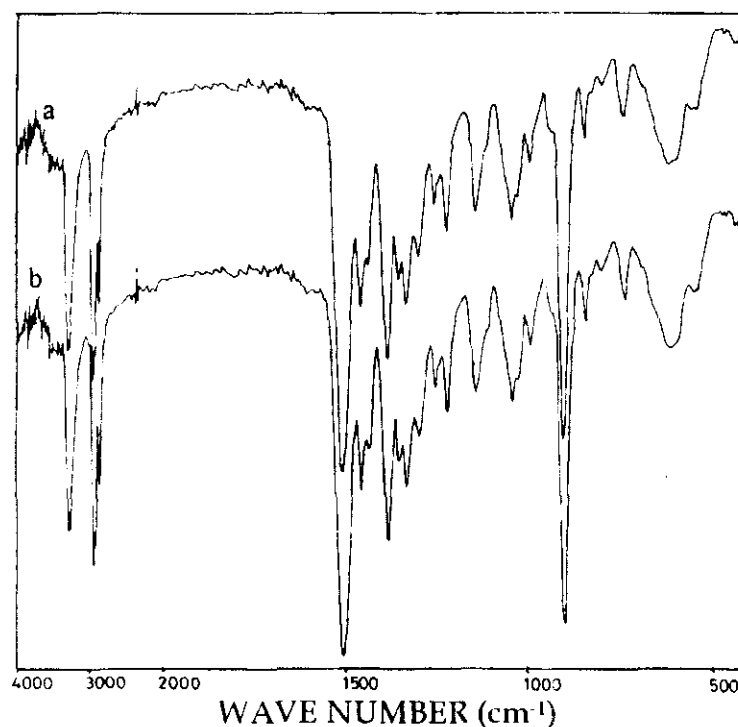


Figure 3.1. IR spectrum of thiuram disulphide obtained by interaction of (a) Cu(II) with BuHDtc and (b) iodine oxidation of BuHDtc

Some of the characteristic bands observed for various tds are tabulated in Table 3.4.

Table 3.4. The most important IR frequencies (cm^{-1}) of the thiuram disulphides and their assignments

Complex	$\nu(\text{NH})$	$\nu(\text{CN})$	$\nu(\text{CS})$
EtHNC(S)-S-S-(S)CNHEt	3250	1550	1047, 925
BuHNC(S)-S-S-(S)CNHBu	3260	1505	940, 900
BzHNC(S)-S-S-(S)CNHBz	3300	1500	960, 920
PhHNC(S)-S-S-(S)CNHPh	3202	1344	100, 932
pTHNC(S)-S-S-(S)CNHpT	3150	1335	1020, 950
pCHNC(S)-S-S-(S)CNHpC	3210, 3160	1327	1008, 922
mCHNC(S)-S-S-(S)CNHmC	3222, 3175	1328	993, 960
pAHNC(S)-S-S-(S)CNHpA	3210	1333	1028, 1008

The absorptions in the range $1550\text{-}1450\text{ cm}^{-1}$ (at 1505) corresponding to $\nu(\text{CN})$ and peaks in the range $1000 \pm 70\text{ cm}^{-1}$ for $\nu(\text{CS})$ (at 940 and 900 cm^{-1}) and $\nu(\text{NH})$ band in the range of $3300\text{-}3100\text{ cm}^{-1}$ (at 3260 cm^{-1}) agreed quite well with those of the thiuram disulphide. The $\nu(\text{CN})$ for thiuram disulphide of N-monoaryl dithiocarbamate, for example, $(\text{PhHDtc})_2$ and $(\text{pTHDtc})_2$ have comparatively low values 1344 and 1335 cm^{-1} respectively. This is in agreement with the observation that presence of aryl group on N of Dtc moiety reduces the double bond character of the CN bond due to the withdrawal of some electron density on N towards the benzene ring.¹⁰

The $^1\text{H-NMR}$ spectra were recorded in the range $0\text{-}10\ \delta$ in CDCl_3 . The compounds gave absorptions characteristic of the R group and also the NH proton. A typical spectrum of $(\text{PhHNC(S)S(S)CNHPh})$ is shown in Figure 3.2a.

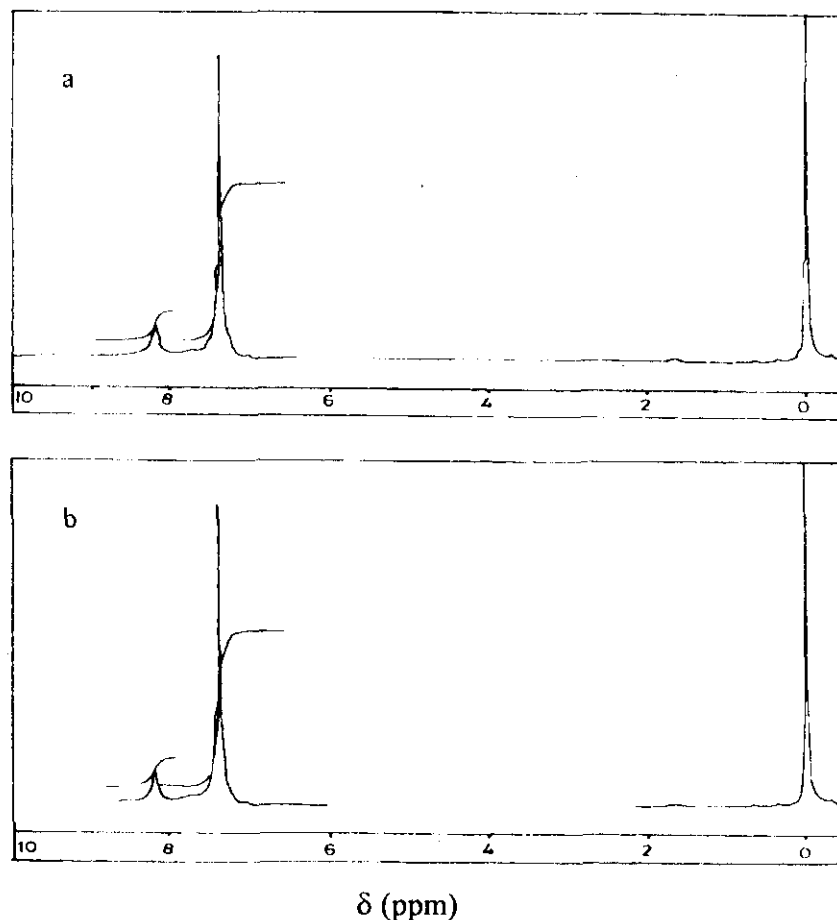


Figure 3.2. The $^1\text{H-NMR}$ spectra of thiuram disulphide obtained by interaction of (a) Cu(II) and (b) iodine solution, with PhHDtc^-

The δ values of protons of the various thiuram disulphides are given in Table 3.5.

Table 3.5. ¹H-NMR spectral data of thiuram disulphides

Compound	Solvent	δ (ppm)			
		NH	ArH	CH ₂	CH ₃
(EtHNCS ₂) ₂	CDCl ₃	7.4	-	-	1.5
(BuHNCS ₂) ₂	CDCl ₃	7.3	-	3.5, 1.7	1.0
(BzHNCS ₂) ₂	CDCl ₃	6.1	7.4	4.6	-
(PhHNCS ₂) ₂	CDCl ₃	8.2	7.4	-	-
(pTHNCS ₂) ₂	CDCl ₃	7.8	7.3	-	2.4
(pCHNCS ₂) ₂	CDCl ₃	8.5	7.3	-	-
(mCHNCS ₂) ₂	CDCl ₃	8.3	7.3	-	-
(pAHNCS ₂) ₂	CDCl ₃	8.4	7.3	-	3.7

As can be seen, the NH proton absorptions are found to be varying with the nature of the R group. The general trend is quite expected of the inductive, mesomeric and anisotropic effects. The ¹H-NMR spectra of (PhHDtc)₂ gave a multiplet around 7.392 δ and singlet at 8.176 δ with intensity ratio 5:1. The low field peaks centred at 7.392 δ are indicative of aryl protons while the peak at 8.176 δ can be considered to be due to NH proton. The signals due to aryl protons of (pTHDtc)₂ and (BzHDtc)₂ occur at about 7.323 δ and 7.426 δ respectively. The peaks at 7.831 δ in the spectrum of (pTDtc)₂ corresponds to δ (NH). The NH protons are more deshielded in (ArHDtc)₂ than in (RHDtc)₂. This is the consequence of the paramagnetic field felt at the NH proton due to the interatomic π -electron ring current in the neighbouring aryl ring. The δ (CH₂) of (BzHDtc)₂ at 4.644 ppm shows

that these protons are more deshielded than those of CH₂ attached to NCS₂ moiety in (EtHDtc)₂ and (BuHDtc)₂. This again is due to the anisotropic effect of the interatomic ring current in the adjacent phenyl ring.

Electronic spectra of these compounds were also recorded and these show two absorptions, one at ~ 45000 cm⁻¹ and the other in the range 36000-40000 cm⁻¹ (Table 3.6).

Table 3.6. *Electronic spectral data of the N,N'-disubstituted thiuram disulphides (chloroform solution)*

Complex	Electronic spectral bands ($\pi \rightarrow \pi^*$) (cm ⁻¹)	
Cu(EtHNCS ₂)	44642	39682
Cu(BuHNCS ₂)	44843	39370
Cu(BzHNCS ₂)	44642	39682
Cu(PhHNCS ₂)	44444	37174
Cu(pTHNCS ₂)	44642	37174
Cu(pCHNCS ₂)	44642	36764
Cu(mCHNCS ₂)	45871	35842
Cu(pAHNCS ₂)	45662	35971
Cu(CmHNCS ₂)*	44843	37037

*Spectra recorded in methanol-ether mixture

These two absorptions are quite characteristic of thiuram disulphides.¹¹ Electronic spectrum of a typical disulphide, N,N'-diphenyl thiuram disulphide, obtained by Cu²⁺(aq) oxidation of N-phenyl dithiocarbamate is shown in Figure 3.3a.

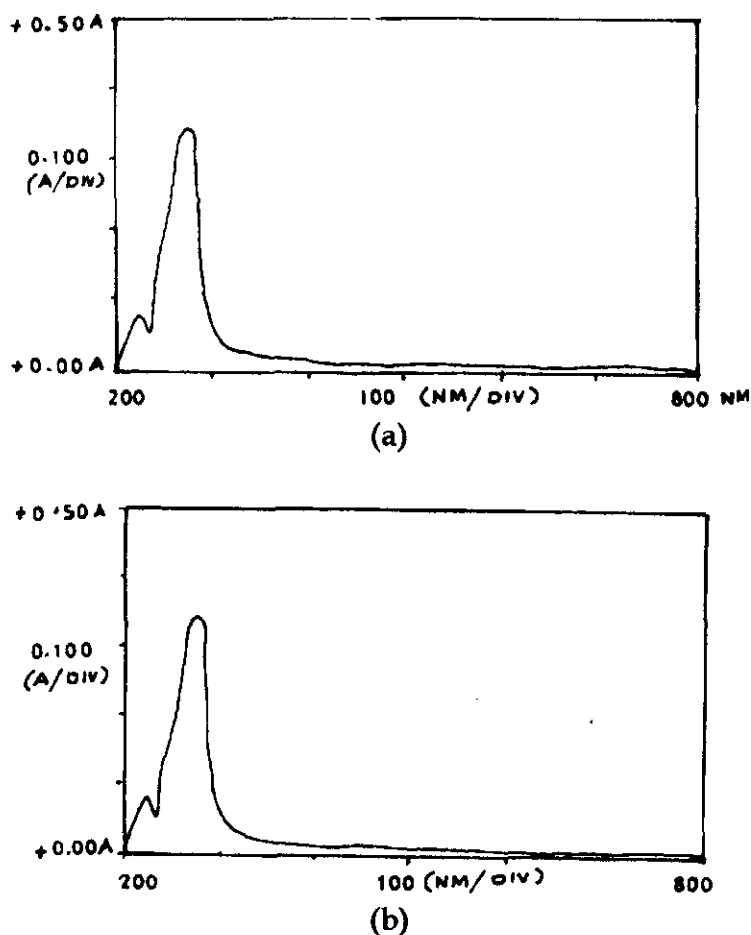


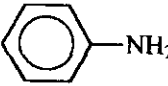
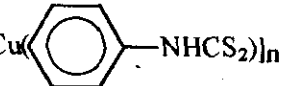
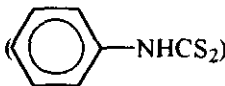
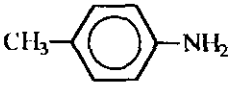
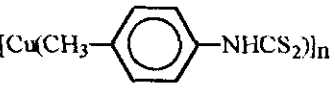
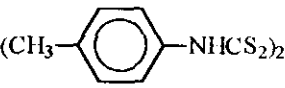
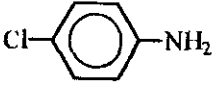
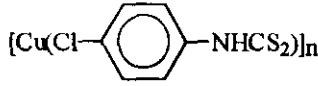
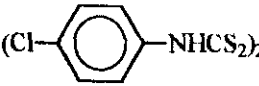
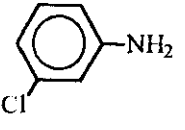
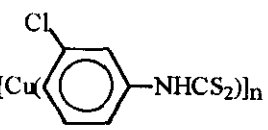
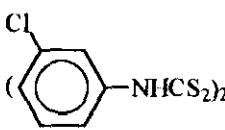
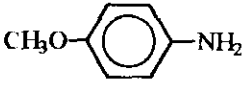
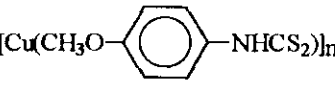
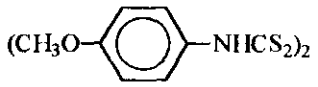
Figure 3.3. *Electronic spectra of N,N' -diphenyl thiuram disulphide formed by oxidation of N -phenyl dithiocarbamate by (a) $\text{Cu}^{2+}_{(aq)}$ and (b) iodine solution*

Since it was expected that the organic compounds obtained by the interaction of Dtc with Cu(II) to be thiuram disulphides, preparation of thiuram disulphide was attempted by iodine oxidation of the dithiocarbamate ligands to confirm their authenticity. The preparative details and purification procedures are already discussed in Section 3.1.3. These iodine oxidised products gave NMR, IR and electronic spectra identical to those given by the compounds obtained by the reaction of copper(II) with RHDtc. The IR spectrum of the disulphide formed in the reaction of Cu(II) with BuHDtc, for example, along with the spectrum of the authentic sample of disulphide prepared by I_2 oxidation are given in Figure 3.1. The $^1\text{H-NMR}$ and electronic spectra of $\text{PhHNC(S)S-S(S)CNHPh}$ formed by oxidation of

PhNHCS₂⁽⁻⁾ with I₂, along with the spectra of the Cu(II) oxidised product are given in Figures 3.2 and 3.3, respectively.

The cuprous complexes of various RHDtc and their corresponding disulphides formed during the interaction of Cu²⁺(aq) with RHDtc derived from aliphatic as well as aromatic primary amines, in aqueous medium are summarised in Table 3.7.

Table 3.7. Products of interaction between Cu²⁺(aq) and RNHCS₂⁻ and ArNHCS₂⁻ in aqueous medium

Primary amine from which Dtc is derived	Products of interaction	
	Complex	Disulphide
Et-NH ₂	[Cu(EtNHCS ₂) _n]	(EtNHCS ₂) ₂
n-But- NH ₂	[Cu(n-ButNHCS ₂) _n]	(n-ButNHCS ₂) ₂
Ph-CH ₂ -NH ₂	[Cu(Ph-CH ₂ -NHCS ₂) _n]	(Ph-CH ₂ -NHCS ₂) ₂
	[Cu()] _n	
	[Cu()] _n	() ₂
	[Cu()] _n	() ₂
	[Cu()] _n	() ₂
	[Cu()] _n	() ₂
HO ₂ C-CH ₂ -NH ₂	[Cu(HO ₂ C-CH ₂ -NHCS ₂) _n]	(HO ₂ C-CH ₂ -NHCS ₂) ₂

The simultaneous formation of a copper complex of the composition CuRHDtc and the corresponding thiuram disulphide as evidenced from the chemical and spectral data throws enough light on the nature of the reaction

involved when Cu(II) is made to react with RHDtc or ArHDtc. The reaction, as clearly evident, is essentially a redox one. Cu(II) acts as an oxidising agent to the dithiocarbamate and consequently the latter reduces the metal ion to its +1 state. The formation of the yellow compounds CuRHDtc and the thiuram disulphide can, therefore, be explained as follows:

When Cu(II) is added slowly to a solution of RHDtc or ArHDtc, the metal ion acts as a one-electron oxidant to the dithiocarbamate dictated by their redox potential values. The anionic dithiocarbamate, in that process gets oxidised to its neutral radical species. It is possible for this neutral radical to combine (dimerise) to form the thiuram disulphide. The copper(I) formed in the reaction can interact simultaneously with excess of the dithiocarbamate anion present to form a complex of the composition Cu(RHDtc). The reaction involved can be summarised as follows.



The dimerisation (3.3) of RNHCSS[·] can happen either in presence of the metal or by combining in free form. This could not be, however, verified in the present study.

3.2.2 Interaction of Cu²⁺ with RHDtc generated in ethanol medium

Since there are reports of dithiocarbamates (both N-monosubstituted and N,N-disubstituted) being prepared in alcohol medium, an attempt was made to study the interaction of Cu²⁺ ions with Dtc⁻ generated in ethanol medium without attempting to isolate the sodium salt of the ligand in solid form. The primary amines like aniline, p-toluidine, p- and m-chloroanilines, p-anisidine, ethylamine, n-butylamine and benzylamine were used for the preparation of the corresponding RHDtc in ethanol medium. A solution of the amine in ethanol was treated with CS₂ in equimolar amounts and an

equivalent amount of sodium hydroxide dissolved in minimum amount of water was added with stirring. Ethanolic solution of calculated amount of CuCl_2 required for 1:2 metal-ligand molar ratio was added dropwise with stirring to the ligand solution. Dtc derived from the aromatic amines formed orange coloured precipitates and those from aliphatic amines gave yellow precipitates during the addition process. These precipitates were filtered, washed with water and ether and dried in air. The filtrates in the case of aliphatic RHDtc were extracted with chloroform. The chloroform extracts were washed with water dried by shaking with anhydrous CaCl_2 and evaporated to get reddish yellow liquid in the case of EtHDtc and BuHDtc. The chloroform extract of the filtrate in the case of BzHDtc, on evaporation, gave a white solid. Evaporation, under reduced pressure, of filtrates from aromatic ArHDtc resulted in the separation of white solids in all cases. Elemental analysis (Table 3.8) and IR studies of the complexes gave some very interesting results.

Table 3.8. Analytical data for the Cu(I) complexes formed by the interaction of copper(II) with *N*-monosubstituted dithiocarbamates generated in ethanol

RHDtc treated with Cu(II) in ethanol	Complex	Colour	Found (Calculated) (%)				
			Carbon	Hydrogen	Nitrogen	Sulphur	Copper
$\text{EtHNCS}_2^{(-)}$	$[\text{Cu}(\text{EtHNCS}_2)]_n$ ($\text{C}_4\text{H}_9\text{NS}_2\text{Cu}$)	Yellow	18.9 (19.6)	3.5 (3.3)	7.9 (7.6)	34.2 (34.9)	34.1 (34.6)
$\text{BuHNCS}_2^{(-)}$	$[\text{Cu}(\text{BuHNCS}_2)]_n$ ($\text{C}_5\text{H}_{10}\text{NS}_2\text{Cu}$)	Yellow	27.9 (28.3)	5.1 (4.8)	6.5 (6.6)	28.8 (30.3)	28.9 (30.0)
$\text{BzHNCS}_2^{(-)}$	$[\text{Cu}(\text{BzHNCS}_2)]_n$ ($\text{C}_8\text{H}_9\text{NS}_2\text{Cu}$)	Yellow	38.6 (39.1)	3.3 (3.3)	5.4 (5.7)	26.5 (26.1)	26.0 (25.8)
$\text{PhHNCS}_2^{(-)}$	$[\text{Cu}(\text{CH}_3\text{CH}_2\text{OCS}_2)]_n$ ($\text{C}_3\text{H}_5\text{OS}_2\text{Cu}$) _n	Orange	19.2 (19.5)	3.0 (2.7)	-	33.8 (34.7)	33.9 (34.4)
$\text{mCHNCS}_2^{(-)}$	$[\text{Cu}(\text{CH}_3\text{CH}_2\text{OCS}_2)]_n$ ($\text{C}_3\text{H}_5\text{OS}_2\text{Cu}$)	Orange	18.9 (19.5)	2.9 (2.7)	-	34.5 (34.7)	33.9 (34.4)
$\text{pCHNCS}_2^{(-)}$	$[\text{Cu}(\text{CH}_3\text{CH}_2\text{OCS}_2)]_n$ ($\text{C}_3\text{H}_5\text{OS}_2\text{Cu}$)	Orange	19.9 (19.5)	2.7 (2.7)	-	35.0 (34.7)	34.2 (34.4)
$\text{pTHNCS}_2^{(-)}$	$[\text{Cu}(\text{CH}_3\text{CH}_2\text{OCS}_2)]_n$ ($\text{C}_3\text{H}_5\text{OS}_2\text{Cu}$)	Orange	19.2 (19.5)	3.1 (2.7)	-	34.0 (34.7)	33.8 (34.4)
$\text{pAHNCS}_2^{(-)}$	$[\text{Cu}(\text{CH}_3\text{CH}_2\text{OCS}_2)]_n$ ($\text{C}_3\text{H}_5\text{OS}_2\text{Cu}$)	Orange	19.7 (19.5)	2.6 (2.7)	-	33.9 (34.7)	33.7 (34.4)

It was quite surprising to find that all the complexes formed by various ArHDtc had the same percentage composition of elements (C = 19.6%, H = 2.8 %, S = 34.4%, Cu = 34%). This agrees quite well with the formula $\text{Cu}(\text{C}_3\text{H}_6\text{OS}_2)$, expected for cuprous xanthate, $\text{Cu}(\text{EtOCS}_2)$. IR spectra were also the same for all the complexes derived from various ArHDtc with absorption characteristic of xanthates. The spectra of the bright orange coloured complex isolated in the case of $\text{PhHNCS}_2^{(6)}$ is given in Figure 3.4.

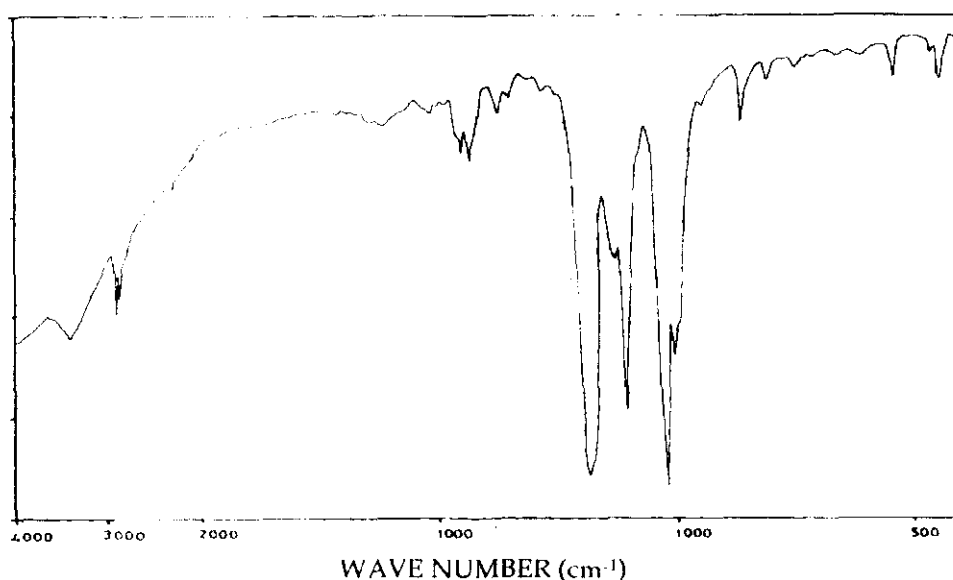


Figure 3.4. IR spectrum of cuprous xanthate

The four absorptions found at 1192, 1120, 1030 and 548 cm^{-1} for the complexes are characteristic of RO- CS_2 group. Each of these 'xanthate' bands arises primarily from combination of the $\nu(\text{C}=\text{S})$, $\nu(\text{C}=\text{O})$, $\nu(\text{C}-\text{O})$ and $\nu(\text{R}-\text{O})$ modes of xanthates, respectively.^{9,12} To prove the identity of the complex the Cu(I) complexes of xanthate was prepared separately by interacting $\text{Cu}^{2+}(\text{aq})$ with ethanolic sodium ethyl xanthate in the molar ratio 1:2. The orange coloured compound formed by the action of Cu^{2+} solution on sodium salt of ethyl xanthate in ethanolic solution had the same IR spectrum (Figure 3.4) and the same composition of elements as the above compounds (C = 19.93%, H = 2.83%, S = 34.21% and Cu = 33.99%). This confirms the formation of cuprous xanthate during the interaction of Cu^{2+} with ArHDtc generated in ethanol medium. The compound was found to be diamagnetic and EPR

silent as expected. The high insolubility in all solvents suggests its polymeric nature.

Since Cu(II) is getting reduced to Cu(I) on interaction with RHDtc/ArHDtc generated in ethanol medium also, some species must be oxidised which in the present case may be dithiocarbamate or xanthate or both the species. IR and $^1\text{H-NMR}$ spectra of the compounds isolated from the filtrates were exactly identical to the spectra of compounds obtained by the iodine or Cu^{2+} oxidation of the RHDtc ligands as described in Section 3.1.3. Since dithiocarbamates are known to be oxidised by iodine to thiuram disulphides, the byproducts of the interaction of Cu^{2+} with ArHDtc are thiuram disulphide of the corresponding dithiocarbamate and not the disulphide of xanthate. IR spectrum of the disulphide prepared by the oxidation of ethanolic solution of sodium ethyl xanthate by iodine solution and the spectrum of the product, *N,N'*-diphenyl thiuram disulphide, formed by oxidation of *N*-phenyl dithiocarbamate by iodine solution or ethanol solution of cupric ions are given in Figure 3.5.

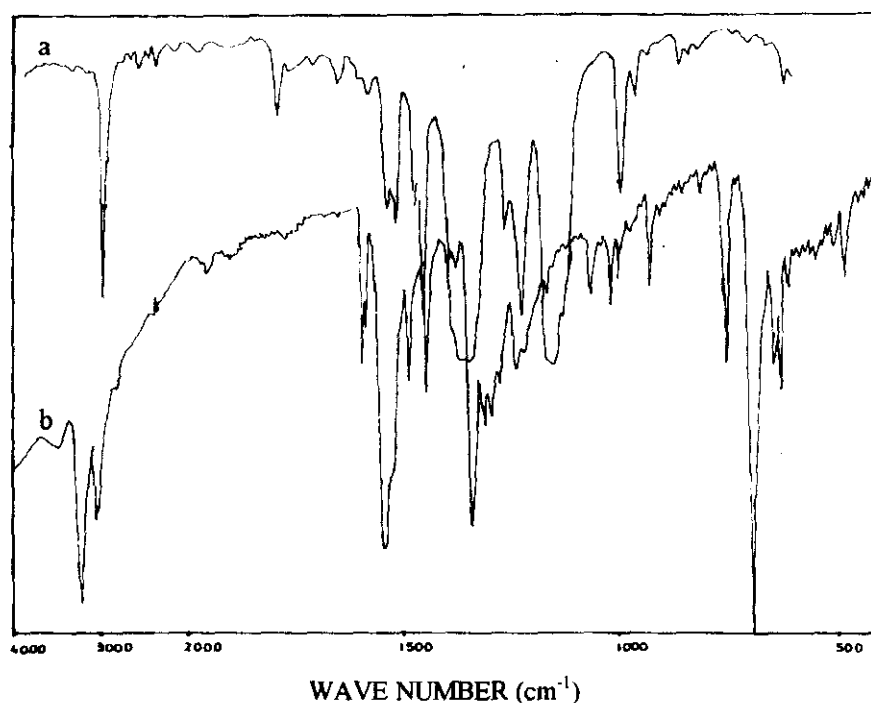
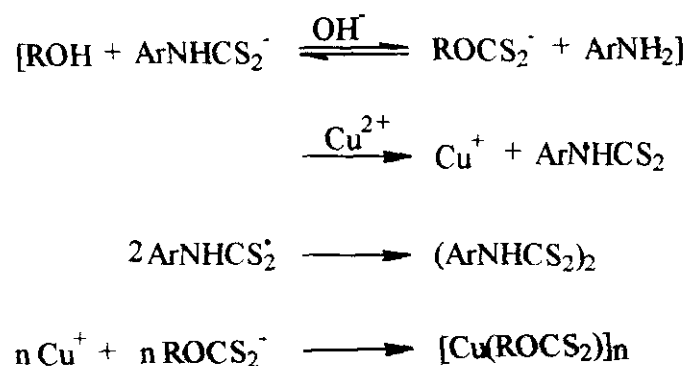


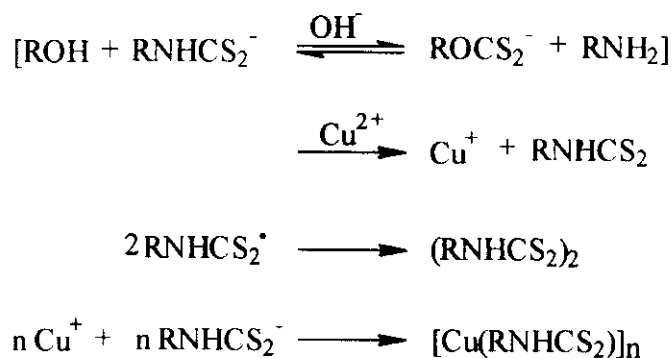
Figure 3.5. IR spectra of disulphides generated by (a) oxidation by iodine of sodium ethylxanthate and (b) oxidation of *N*-phenyl dithiocarbamate by iodine or Cu^{2+} in ethanol

From the above data it is clear that during the Cu^{2+} interaction with ArHDtc generated in ethanol medium, it is not xanthate that is getting oxidised, but the dithiocarbamate that undergoes the oxidation to the corresponding $\text{N,N}'$ -disubstituted thiuram disulphide. Based on these observations the reactions involved can be summarised as follows.



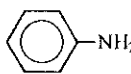
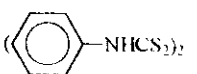
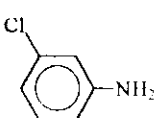
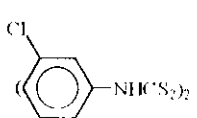

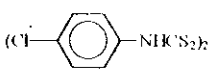
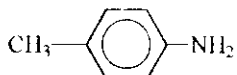
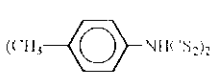
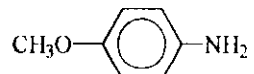
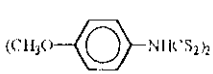
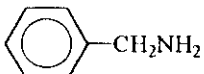
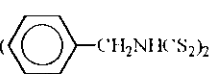
The formation of cuprous xanthate on interaction of Cu^{2+} with aromatic dithiocarbamate generated in ethanol medium in the molar ratio 1:2 (metal : ligand), necessitates the presence of unreacted amine in the reaction mixture. This is found to be quite so in the present case. The amine was isolated from the mother liquor after the separation of the disulphide by ether extraction and identified by both carbylamine and dye tests.¹³

The yellow complexes formed by the RHDtc derived from aliphatic primary amines in ethanol medium, on the other hand, are identified to be the same polymeric $[\text{Cu}(\text{RNHCS}_2)]_n$ obtained during the interaction studies in aqueous medium; IR and electronic spectra of the yellow complexes were identical to those of the corresponding polymeric $[\text{Cu}(\text{RNHCS}_2)]_n$. The disulphides are also of the respective Dtc ligand and not of the xanthate. This is proved by iodine oxidation of the ligand and comparing the IR spectra with that of the byproduct isolated during the interaction with Cu^{2+} in ethanol medium. The spectra were exactly identical. The reactions can be represented as



The cuprous complexes and disulphides formed during the interaction of Cu^{2+} with various aliphatic and aromatic primary amine dithiocarbamates generated in ethanol medium are summarised in Table 3.9.

Table 3.9. *Products of interaction between Cu^{2+} and RNHCS_2^- and ArNHCS_2^- generated in ethanol medium*

Amine used for the generation of Dtc in ethanol medium	Products of interaction with Cu^{2+}	
	Cu containing products	Oxidised organic products
	$[\text{Cu}(\text{EtOCS}_2)]_n$ (orange)	 (white solid)
	$[\text{Cu}(\text{EtOCS}_2)]_n$ (orange)	 (white solid)
	$[\text{Cu}(\text{EtOCS}_2)]_n$ (orange)	 (white solid)
	$[\text{Cu}(\text{EtOCS}_2)]_n$ (orange)	 (white solid)
	$[\text{Cu}(\text{EtOCS}_2)]_n$ (orange)	 (white solid)
	$[\text{Cu}(\text{Ph-CH}_2\text{-NHCS}_2)]_n$ (orange)	 (white solid)
$\text{CH}_3\text{-CH}_2\text{-NH}_2$	$[\text{Cu}(\text{EtNHCS}_2)]_n$ (yellow)	$(\text{EtNCS}_2)_2$ (Reddish yellow liquid)
$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-NH}_2$	$[\text{Cu}(\text{n-ButNHCS}_2)]_n$ (yellow)	$(\text{n-ButNHCS}_2)_2$ (Reddish yellow liquid)

In the case of aromatic primary amines studied, sterically it may be more favourable for the smaller ligand, xanthate to form Cu(I) clusters than for Dtc, while in the case of aliphatic primary amines both steric factors and coordinating ability of the ligand are favourable for the dithiocarbamate to form copper(I) clusters.

3.2.3 Structural aspects of Cu(I) RHDtc complexes

The high insolubility of all the Cu(I) RHDtc complexes (prepared in aqueous as well as ethanolic medium) in all solvents prevented any study in solution. No single crystals also could be grown because of this difficulty. However, the solid state EPR, IR and electronic spectral studies were carried out along with magnetic susceptibility measurements for the structural characterisation of the complexes.

The IR spectra of the complexes give some useful information on the nature of bonding of RHDtc with the Cu(I) ion. The important IR absorptions frequencies of the complexes are presented in Table 3.10.

Table 3.10. The most important IR frequencies (cm^{-1}) of the Cu(RHDtc) complexes generated in aqueous medium and their assignments (KBr discs)

Complex	$\nu(\text{NH})$	$\nu(\text{CN})$	$\nu(\text{CS})$
Cu(EtH ₂ NHCS ₂)	3270	1472	1002, 962
Cu(BuH ₂ NHCS ₂)	3270	1480 ₄	930, 900
Cu(BzH ₂ NHCS ₂)	3298	1475	928, 900
Cu(PhH ₂ NHCS ₂)	3270	1348, 1328	956, 900
Cu(pTHNHCS ₂)	3265	1344	794, 960
Cu(pCHNHCS ₂)	3250	1340	958, 940
Cu(mCHNHCS ₂)	3250	1348, 1326	966, 940
Cu(pAHNHCS ₂)	3220	1352, 1334	1028, 1008
Cu(CmH ₂ NHCS ₂)	3408,* 3230	1505	982, 948

* $\nu(\text{OH})$

In the case of copper(I) complexes derived from aliphatic primary amine dithiocarbamates $\text{Cu}(\text{EtHNCS}_2)$, $\text{Cu}(\text{BuHNCS}_2)$, $\text{Cu}(\text{BzHNCS}_2)$ and $\text{Cu}(\text{CmHNCS}_2)$ strong peaks seen at 1472, 1484, 1475, 1505 cm^{-1} , respectively are typical of $\nu(\text{CN})$ vibration of dithiocarbamates. In the free ligand, ammonium derivative of a typical N-alkyl substituted dithiocarbamate, $\text{BuHNCS}_2\text{NH}_4$, this vibration is seen at 1480 cm^{-1} . The increase in this bond energy is expected of S-coordinated dithiocarbamate species. The bands observed at 962, 1002; 900, 930; 900, 928; 897, 948 cm^{-1} for the above four complexes are attributable to $\nu(\text{CS})$ vibrations. The corresponding vibration in the free ligand $\text{BuHNCS}_2\text{NH}_4$ appears at 924, 942 cm^{-1} . This decrease in CS bond order on complexation is as expected for S-coordination of Dtc moiety. IR spectra of N-aryl substituted ($\text{Cu}(\text{PhHNCS}_2)$, $\text{Cu}(\text{pTHNCS}_2)$, $\text{Cu}(\text{pCHNCS}_2)$, $\text{Cu}(\text{mCHNCS}_2)$ and $\text{Cu}(\text{pAHNCS}_2)$) show strong or moderately strong peaks due to $\nu(\text{CN})$ at 1328, 1348; 1344; 1340; 1326, 1348 and 1334, 1352 cm^{-1} , respectively. In ammonium salt of $\text{PhHNCS}_2^{(-)}$, a typical dithiocarbamate ligand derived from aromatic primary amine, the $\nu(\text{CN})$ vibration occurs at 1395 cm^{-1} . Thus the CN bond order of ArHDtc decreases on complexation with Cu(I) unlike in the case of RHDtc. This decrease in $\nu(\text{CN})$ on S-coordination of Dtc has been reported for ArHDtc complexes of Pd(II) also.⁸ The IR bands of the above complexes at 1020, 956; 968, 932; 958, 940; 966, 900 and 1020, 970 cm^{-1} respectively can be attributed to CS vibrations. The corresponding vibration in the free ligand $\text{PhHNCS}_2\text{NH}_4$ occurs at 1028 and 998 cm^{-1} . As expected for S-coordination of Dtc the $\nu(\text{CS})$ frequency is lowered on complexation of ArHDtc with Cu(I). According to Ugo-Bonati criterion¹⁴ the appearance of only one unsplit band in the region of $\nu(\text{CS})$ absorption ($\sim 1000 \pm 70 \text{ cm}^{-1}$) correspond to symmetrical bidentate coordination of Dtc. If Dtc behaves as a monodentate ligand this peak splits and more than one absorption is observed, the separation between the peaks being more than 20 cm^{-1} . It is also reported¹⁵ that unsymmetric bidentate coordination also results in multiple bands in this region, the greater the

asymmetry in the coordination of two sulphur atoms the larger is the separation between the peaks. The multiplicity of peaks in the region $\sim 1000 \pm 70 \text{ cm}^{-1}$ (Figure 3.6) is indicative of possible unsymmetric bidentate coordination of RHDtc to Cu(I) in the present complexes.

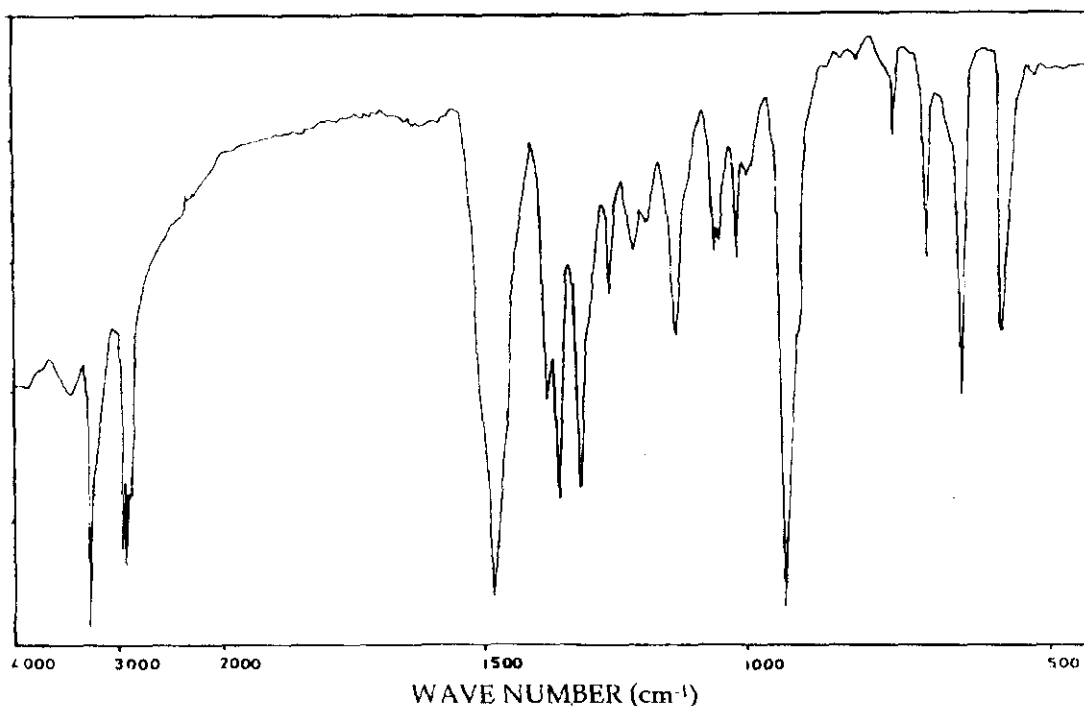


Figure 3.6. The IR spectrum of a typical CuRHDtc complex, $\text{Cu}(\text{BuHNCS}_2)$

All the complexes gave moderately strong peak around 3200 cm^{-1} characteristic of NH stretching vibration.

The electronic spectrum of a typical complex, $\text{Cu}(\text{BuHNCS}_2)$ is shown in Figure 3.7. The absence of any low energy absorption due to d-d transition indicates the reduced state (+1) of copper. The fact that weak absorptions

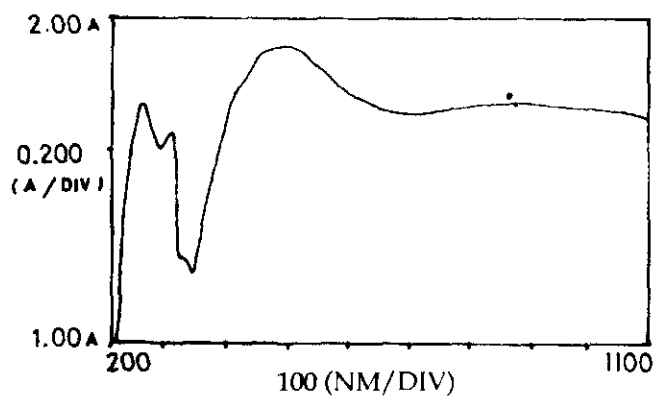


Figure 3.7. Electronic spectrum of the complex, $\text{Cu}(\text{BuHNCS}_2)$

due to d-d transitions are not observed in the spectra cannot be taken as a conclusive evidence for the Cu(I) state because of the possibility of high intensity charge transfer absorption around this region masking the d-d absorptions. However, as mentioned earlier, both the diamagnetic nature and EPR inactivity confirm the reduced state of copper. In Table 3.11 the electronic spectral data for the various Cu(RHDtc) complexes are given.

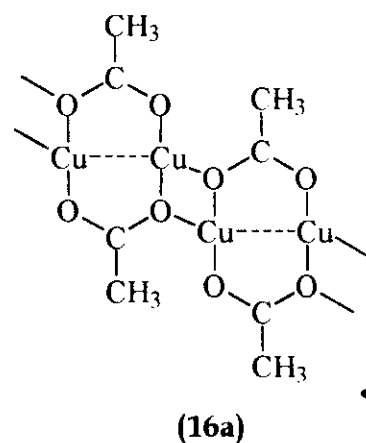
Table 3.11. Electronic spectral data of the polymeric Cu(I) RHDtc complexes formed in aqueous medium (as nujol mull) and their assignments

Complex	Band I (cm ⁻¹) ($\pi \rightarrow \pi^*$ centred at NCS)	Band II (cm ⁻¹) ($\pi \rightarrow \pi^*$ centred at CS ₂)	CT band (cm ⁻¹)
Cu(EtHNCS ₂)	40485	33333	21691
Cu(BuHNCS ₂)	40326	33449	21930
Cu(BzHNCS ₂)	40160	33557	21834
Cu(PhHNCS ₂)	40816	33333	21008
Cu(pTHNCS ₂)	39983	33333	22371
Cu(pCHNCS ₂)	39682	33222	21691
Cu(mCHNCS ₂)	39682	33333	21843
Cu(pAHNCS ₂)	40000	34602	23980
Cu(CmHNCS ₂)	40482	33557	20876

As can be seen the effect due to R group on the absorption is marginal and no correlation of the data with the nature of R group was possible. However, as compared to the absorption peaks in the spectra of RHNC(S)S-S(S)NHR (tds) all the Cu(I) complexes showed an additional intense peak at 20000-24000 cm⁻¹ which could be assigned to

MLCT [$M(d) \rightarrow L(\pi^*)$] transition. The other two peaks around 33000 and 40000 cm^{-1} in the spectra of the complexes are comparable to the values obtained for the thiuram disulphides (33000 and 45000 cm^{-1} , respectively). The origin of these bands are assigned to intraligand transition ($\pi-\pi^*$). The 33000 cm^{-1} band is assigned to electronic transition centred at CS_2 while 40000 cm^{-1} band is due to transition centred at NCS of dithiocarbamate.¹⁶

Even though structural features of $\text{Cu}(\text{RHDtc})$ could not be probed in further detail, some insight into the molecular disposition of the complexes could be gathered by examining the reported structural features of $\text{Cu}(\text{I})$ acetate complex $[\text{Cu}(\text{CH}_3\text{COO})]_n$. The complex is known to exist in polymeric forms in solid state.¹⁷ The structure of $\text{Cu}(\text{I})$ acetate in the solid state is given in (16a).



In structure (16a) $\text{Cu}(\text{I})$ takes 3 coordination and a T-shaped geometry. Since S and O donors have comparable ligation modes, an analogous coordination feature can be envisaged in COO and CSS moieties. However, the C-substituents in the acetate and in dithiocarbamates are different (CH_3 - and RHN- , respectively) which could modulate the coordinating abilities of these species to a certain extent. Based on the reported polymeric nature of $[\text{Cu}(\text{CH}_3\text{COO})]_n$ and the present $[\text{Cu}(\text{RHDtc})]_n$ complexes along with the spectral evidences obtained, a structure comparable to $\text{Cu}(\text{I})$ acetate complex could be proposed for our polymeric complexes also. Given in Figure 3.8 is the tentative structure for the present complexes.

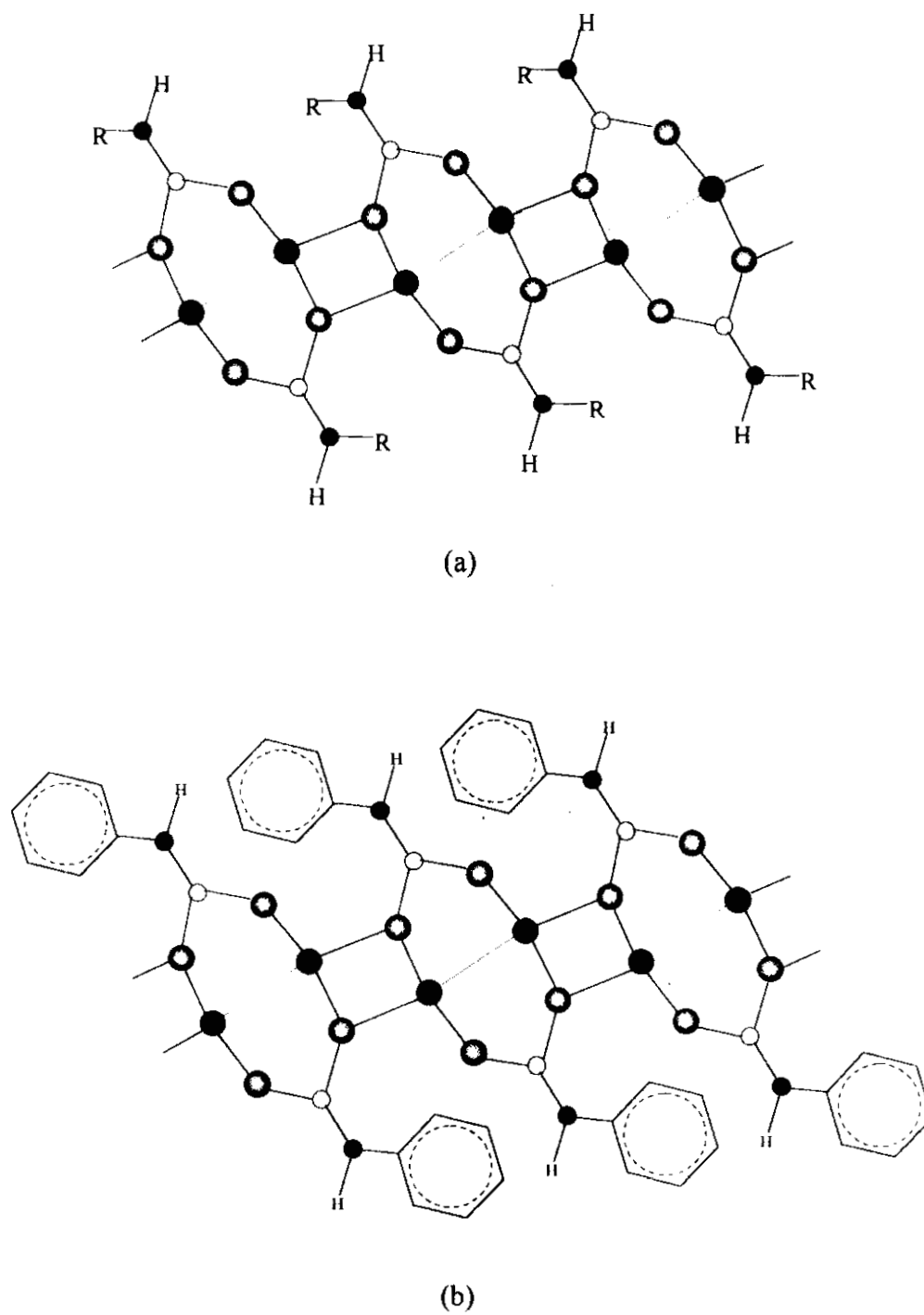


Figure 3.8. Tentative structures for (a) $[\text{Cu}(\text{RHDtc})]_n$ and (b) $[\text{Cu}(\text{ArHDtc})]_n$

The following supportive evidences for the proposed structure are worth mentioning here.

- (i) The $\nu(\text{NH})$ absorption observed for the present polymeric complexes is around 3200 cm^{-1} . This band is a little higher in energy as compared to that in free RHDtc or their thiuram disulphides or even higher than oligomeric (dimeric and tetrameric) Cu(I) complexes (discussed in detail in Chapter 4) [$\nu(\text{NH})$: $(\text{BuHNCS}_2\text{NH}_4)$ - 3084 cm^{-1} ; $(\text{BuHNC}(\text{S})\text{S}(\text{S})\text{CNHBu})$ - 3260 cm^{-1} ; $[\text{Cu}(\text{BuHNCS}_2)]_2$ - 3229 cm^{-1} and $[\text{Cu}(\text{BuHNCS}_2)]_n$ - 3292 cm^{-1}]. Further the band is found to be sharp and comparatively strong in intensity. This is indicative of the absence of any H-bonding within the complexes unlike in the free ligand or in their oligomeric species where the possibility of hydrogen bonding exists because of the nature of the overall structural disposition (for details, see Chapter 4).
- (ii) It is reported that the nature of $\nu(\text{CS})$ vibration could give an indication of the mode of linkage of S atoms of Dtc to the metal.⁶ As mentioned earlier, the $\nu(\text{CS})$ band in Dtc is known to appear around $1000 \pm 70 \text{ cm}^{-1}$. If the Dtc is symmetrically bonded to a metal centre in a bidentate manner it is seen that the above band stays unsplit. But if the S-ligation mode becomes unsymmetric it is observed that the band gets split. In all the present complexes one could clearly observe the band splitting (Figure 3.6) indicating such an unsymmetric bonding behaviour, quite in agreement with the proposed structure.
- (iii) We have attempted some electrophilic substitution on various CuRHDtc complexes, including the ones discussed in this chapter and it is seen that the polymer complexes mentioned here strongly resist such reaction (benzoylation). The details are discussed in Chapter 4. Such an inactivity of these complexes towards benzoylation could be explained in terms of the steric crowding caused by the disposition of the N-substituent in the above structure.

- (iv) We have also noted the inability of some of the RHDtc ligands to form polymeric Cu(RHDtc) complexes in aqueous condition. In the case of N-monoaryl substituted Dtc, the presence of substituent at ortho or meta position of the phenyl ring prevents the formation of polymeric complexes. If the N-substituent is an alkyl group, presence of two substituents on the α -carbon atom hinders the formation of the polymeric complex. Details are discussed in Chapter 4. The inability of such RHDtc ligands to form polymeric Cu(RHDtc) complexes could be explained by the steric crowding caused by the N-substituent in the proposed structure.

In the proposed structure, Cu(I) has a coordination number 3 with T-shaped geometry. No such structural features have been reported for any Cu(I) dithiocarbamate so far (either N-monosubstituted or N,N-disubstituted).

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