

CHAPTER

4

Interaction of Copper(II) with Dithiocarbamates Derived from Primary Amines: Formation of Dimeric and Tetrameric Copper(I) Complexes

4.1 Introduction

The effect of the nature of the solvents employed on the redox reaction between Cu(II) and primary amine dithiocarbamates is partly evident from the discussion made in the previous chapters. The solvents of interest are water, alcohol, dimethyl formamide and tetrahydrofuran. The ability of the substituent on nitrogen atom of the RR'Dtc ligand (derived from secondary amine) to dictate the course of the reaction or to decide the stereochemistry and structure of the reaction products as demonstrated by selecting dithiocarbamates with various substituents on nitrogen, alkyl, aralkyl, aryl and aryl with electron donating or electron withdrawing groups has been mentioned.¹ Preliminary studies by us indicated that neither the nature of the reaction mediums nor any of the N-substituents could redox stabilise the Cu²⁺; the redox reaction was always found to be occurring in the case of RHDtc (derived from primary amines). The nature of the N-substituent can be expected to exert significant influence in deciding the stereochemistry of the resulting complexes. In the present chapter it is intended to discuss the nature of interaction between copper(II) and various

RHDtc in selected solvents and isolation and characterisation of the complexes formed. It was found that while in aqueous condition RHDtc formed polymeric copper(I) complexes, the nonaqueous solvents help the formation of a variety of oligomeric copper(I) complexes with interesting structural features.

Unlike RR'Dtc, the monosubstituted RHDtc are expected to show substitution property by which the H moiety could be replaced with an appropriate R' moiety. The ligation of the RHDtc onto a metal can substantially change the electron density distribution of the ligand by which the H can be made more substitution (electrophilic) labile. The already present R group also can modulate this property. In the case of a few bis-nickel(II) complexes of RHDtc such a property has been already demonstrated but no reference has been so far made on their copper complexes. In the present work, some of the copper(I) complexes have been subjected to electrophilic substitution with benzoyl chloride under controlled conditions. The complexes formed are separated, characterised and the data obtained are discussed.

4.2 Experimental

4.2.1 Preparative details

(a) RHDtc ligands

The following ligands were considered for the interaction with copper(II) in non-aqueous solvents: (i) ammonium N-phenyl dithiocarbamate ($\text{PhHNCS}_2\text{NH}_4$), (ii) sodium N-(3-chlorophenyl) dithiocarbamate (mCHNCS_2Na), (iii) sodium N-ethyldithiocarbamate (EtHNCS_2Na), (iv) sodium N-(1-butyl)dithiocarbamate (BuHNCS_2Na), (v) sodium N-benzyl dithiocarbamate (BzHNCS_2Na), (vi) sodium N-(4-methyl phenyl)dithiocarbamate (pTHNCS_2Na), and (vii) sodium N-(4-chlorophenyl) dithiocarbamate (pCHNCS_2Na).

The preparative details are already discussed in Chapter 3 but care was taken to use minimum amount of water during the preparation. Large amount of non-aqueous solvents like THF or DMF was added to this to mask any affect due to slight water present in the system.

Ammonium N-phenyl dithiocarbamate was prepared in the solid state as described under Section 3.1.1d. All the other ligands were prepared *in situ* in solution condition as described under Section 3.1.1.

(b) Oligomeric Cu(I) complexes

Interaction of copper(II) with RHDtc was studied in non-aqueous medium by controlled addition of cupric chloride solution to an RHDtc solution in stirred condition. The reaction products were isolated by extraction and separation. The reddish brown or brown complexes obtained in all the cases were copper(I) complexes as mentioned in Section 4.2. These species formed are seen to be different from those obtained in aqueous condition both in terms of colour and solubility characteristics. The various copper(I) complexes obtained along with their preparative details are given below.

(i) N-phenyldithiocarbamatocopper(I), $[Cu(PhHNCs_2)]_4$

Solid ammonium N-phenyl dithiocarbamate (3.7 g, 20 mM) was dissolved in DMF (20 ml). Cupric chloride (10 mM) dissolved in sufficient quantity of DMF was slowly added to the ligand solution dropwise with stirring. The reddish solution formed was mixed well with chloroform (20 ml) to extract the complex. The solution was repeatedly washed with water till all the DMF was completely removed from the solution. The chloroform solution on evaporation gave a reddish brown complex. It was repeatedly washed with methanol and finally with ether and dried over P_4O_{10} in vacuum.

(ii) *N*-(3-chlorophenyl)dithiocarbamatocopper(I), $[\text{Cu}(\text{mCHNCS}_2)]_4$

The ligand solution of *N*-(3-chlorophenyl)dithiocarbamate (20 mM) was mixed well with DMF (50 ml). A solution of cupric chloride (10 mM) in DMF was slowly added dropwise with constant stirring. A red solution formed was mixed with chloroform (20 ml). This solution was repeatedly washed with water till all the DMF was completely removed from the solution. The chloroform solution was evaporated to get a reddish brown complex. The complex was repeatedly washed with methanol and finally with ether and dried over P_4O_{10} in vacuum.

(iii) *N*-ethyldithiocarbamatocopper(I), $[\text{Cu}(\text{EtHNCS}_2)]_2$

To the ligand solution of sodium *N*-ethyldithiocarbamate (20 mM), THF (50 ml) was added and stirred well. Cupric chloride solution (10 mM) in THF was added dropwise with constant stirring to the ligand to get a brown solution. The brown solution formed was kept aside for sometime for the removal of THF by evaporation. On evaporation, at one stage an aqueous layer appeared at the bottom which was separated and discarded. The THF layer on complete evaporation gave a brownish yellow solid. It was repeatedly washed with methanol and finally with ether and dried over P_4O_{10} in vacuum.

(iv) *N*-(1-butyl)dithiocarbamatocopper(I), $[\text{Cu}(\text{BuHNCS}_2)]_2$

An aqueous solution of the ligand solution of *N*-(1-butyl)dithiocarbamate (20 mM) in minimum quantity of water was mixed well with THF (50 mM). Cupric chloride solution (10 mM) dissolved in sufficient quantity of THF was added dropwise with constant stirring. On evaporation of the brown solution an aqueous layer appeared at the bottom and it was discarded. Complete evaporation of the THF layer gave a brownish yellow complex. It was repeatedly washed with methanol and finally with ether and dried over P_4O_{10} in vacuum.

(v) *N*-benzylthiocarbamatocopper(I), [Cu(BzHNCS₂)]₄

To the concentrated solution of *N*-benzyl dithiocarbamate prepared (20 mM) about five times its volume of THF (75 ml) was added and stirred well. A solution of cupric chloride in THF (10 mM) was added dropwise under stirred condition. The solution was evaporated. The aqueous layer appeared at the bottom was discarded. The evaporation was allowed to continue to get a brownish yellow solid. The compound obtained was repeatedly washed with methanol, then with ether and dried over P₄O₁₀ in vacuum.

(vi) *N*-(4-methylphenyl)dithiocarbamatocopper(I), [Cu(pTHNCS₂)]₄

A concentrated solution of sodium *N*-(4-methylphenyl) dithiocarbamate (20 mM) in aqueous DMF was mixed with about five times its volume of THF (75 ml). Cupric chloride solution in THF (10 mM) was added dropwise with constant stirring. A brownish yellow complex was isolated from the above solution as described above.

(vii) *N*-(4-chlorophenyl)dithiocarbamatocopper(I), [Cu(pCHNCS₂)]₄

A concentrated solution of sodium *N*-(4-chlorophenyl) dithiocarbamate (20 mM) in aqueous DMF was stirred well with THF (75 ml). Cupric chloride solution in THF (10 mM) was added dropwise to this under stirred condition. A reddish brown complex was isolated by the above procedure which was repeatedly washed with methanol and ether and dried in vacuum.

4.2.2 Benzoylation reaction of Cu(RHDtc) complexes

The Cu(RHDtc) complexes considered for benzoylation reaction are the following: (i) *N*-ethylthiocarbamatocopper(I), (ii) *N*-(1-butyl)dithiocarbamatocopper(I), (iii) *N*-benzylthiocarbamatocopper(I), (iv) *N*-phenylthiocarbamatocopper(I), (v) *N*-(3-methylphenyl)dithiocarbamatocopper(I), (vi) *N*-(4-chlorophenyl)dithiocarbamatocopper(I), (vii) *N*-(3-chlorophenyl)

dithiocarbamatocopper(I), (viii) N-(4-methylphenyl)dithiocarbamato-copper(I), (ix) N-(2-methylphenyl)dithiocarbamatocopper(I), (x) N-(2-methoxyphenyl)dithiocarbamatocopper(I), (xi) N-(2-chlorophenyl)dithiocarbamatocopper(I).

The preparative details of (i) to (viii) complexes are already discussed in Section 3.1.2 and 4.1.1b. The compounds (ix) to (xi) are prepared in aqueous condition as per the procedure discussed later in Section 4.3.5. Two procedures were employed for benzoylation reaction.

- (a) The appropriate copper complex (1 mM) was suspended in distilled water (20 ml) taken in a stoppered bottle. This was treated with 0.1 M NaOH solution (1 ml) and 1 mM of benzoyl chloride. The bottle was closed air-tight and kept under magnetic stirring for about half an hour. The suspended solid complex was filtered, washed with water, methanol and ether. The complexes were purified by reprecipitation from benzene solution, followed by washing with ether and drying over P_4O_{10} in vacuum.
- (b) Benzoylation was also carried out by the method reported for Ni(II) complexes of RHDtc.² 1 mM of the complex in acetone (20 ml) was treated with 2 mM of triethylamine and 2 mM of benzoyl chloride. The reaction mixture was stirred for one hour at room temperature and poured into large amount of water in a breaker while stirring. The solid separated at the bottom was washed with ether and purified by recrystallisation from benzene.

4.3 Results and discussion

4.3.1 Nature of reaction between Cu^{2+} and RHDtc in nonaqueous solvents

It is seen in the studies discussed in Chapter 3 that the copper(II) invariably undergoes redox reaction with RHDtc in aqueous condition. Since the redox potential of the Cu(II)/Cu(I) system is known to depend on the solvent used,³ it is probable that Cu(II) may be redox-stabilised on changing

the solvent conditions. With this in view different solvents were chosen for the reaction studies which included dimethyl formamide and tetrahydrofuran. As in the interaction studies in aqueous medium, the metal-ligand molar ratio was kept at 1:2 since this stoichiometry is required whether it is a redox process or direct complexation between cupric ions and dithiocarbamates. Some of the interesting observations noticed are the following.

At the point of addition of the metal ion solution to the bulk of the ligand solutions, a reddish or reddish brown colouration appeared and, unlike in the case of the interaction in aqueous medium, precipitation of any yellow solid was not observed. Throughout the addition of the metal ion solution the brown colour persisted. All the complexes isolated after careful removal of the solvent were brown or reddish brown in colour. All of them are freely soluble in chloroform, tetrahydrofuran, dimethyl formamide and dimethyl sulphoxide, unlike the yellow complexes separated in aqueous condition. The high insolubility of polymeric Cu(I) dithiocarbamates (yellow complexes) reported in Chapter 3 and the solubility of bis (dithiocarbamato) copper(II) complexes of RR'Dtc (made from secondary amines) in organic solvents made us initially doubt that the new brown compounds could be cupric complexes. Moreover, as it is known that copper(II) complexes can appear red or brown when there is a strong charge transfer band spreading into the visible region, the colour of the complexes also does not rule out the possibility of the metal being in the Cu(II) oxidation state with a metal-ligand molar ratio of 1:2, although the yield of the complexes were always less than that expected for this composition. The elemental analysis of all the complexes were carried out. Analytical data of the brown complexes separated out from DMF/THF medium are given in Table 4.1.

Table 4.1. Analytical data for oligomeric *N*-monosubstituted dithiocarbamate-copper(I) complexes formed in DMF/THF medium

Complex	Colour	Found (Calculated) (%)				
		Carbon	Hydrogen	Nitrogen	Sulphur	Copper
Cu(EtHNCS ₂) (C ₃ H ₆ NS ₂ Cu)	Brown	19.2 (19.6)	3.6 (3.3)	7.3 (7.6)	35.4 (34.9)	33.7 (34.6)
Cu(BuHNCS ₂) (C ₅ H ₁₀ NS ₂ Cu)	Brown	27.8 (28.3)	5.2 (4.8)	6.2 (6.6)	31.1 (30.3)	28.9 (30.0)
Cu(BzHNCS ₂) (C ₈ H ₈ NS ₂ Cu)	Yellowish brown	38.7 (39.1)	3.4 (3.3)	5.8 (5.7)	25.8 (26.1)	25.1 (25.8)
Cu(PhHNCS ₂) (C ₇ H ₆ NS ₂ Cu)	Brown	36.1 (36.2)	2.8 (2.6)	6.3 (6.0)	26.5 (27.1)	28.0 (27.4)
Cu(pTHNCS ₂) (C ₈ H ₈ NS ₂ Cu)	Yellowish brown	39.5 (39.5)	3.1 (3.3)	5.4 (5.7)	27.0 (26.1)	25.3 (25.8)
Cu(pCHNCS ₂) (C ₇ H ₅ NS ₂ Cu)	Brown	31.0 (31.6)	1.8 (1.9)	5.5 (5.3)	24.3 (24.1)	23.2 (23.9)
Cu(mCHNCS ₂) (C ₇ H ₅ NS ₂ Cu)	Dark brown	31.8 (31.6)	2.0 (1.9)	4.9 (5.1)	24.5 (24.1)	22.9 (23.9)

The percentage composition of the complexes suggests the general formula Cu(RHDtc) and not Cu(RHDtc)₂. This composition indicates the existence of the metal as Cu(I) species rather than as Cu(II), as in the case of polymeric Cu(RHDtc) complexes discussed in the previous chapter.

The nature of the ligand moiety in these complexes is revealed by their IR spectra. All the compounds showed 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 in agreement with reported values for dithiocarbamates.⁴

Electronic spectral data of the complexes recorded in Nujol mull are given in Table 4.2.

Table 4.2. *Electronic spectral data for Cu(RHDtc) complexes generated in THF/DMF medium.*

Complex	Band I ($\pi \rightarrow \pi^*$) (cm^{-1})	Band II ($\pi \rightarrow \pi^*$) (cm^{-1})	Band III (M \rightarrow LCT) (cm^{-1})
Cu(EtHNCS ₂)	40120	33200	23930
Cu(BuHNCS ₂)	40000	34602	24038
Cu(BzHNCS ₂)	40322	33333	21929
Cu(PhHNCS ₂)	40650	33557	24570
Cu(pTHNCS ₂)	39840	33222	23866
Cu(pCHNCS ₂)	39840	34364	20080
Cu(mCHNCS ₂)	40000	34602	24038

The two bands observed in the electronic spectra of all RHDtc ligands (band I and band II) are at about 40000 and 33000 cm^{-1} , respectively and these bands are seen retaining their positions in our complexes without much change. As mentioned earlier, these are due to the intraligand transitions centred at the NCS and CS₂ moieties, respectively, of the ligand.⁵ In addition to these bands an intense broad band centred around 21000-24000 cm^{-1} occurred in all the complexes. No low energy transitions (d-d) characteristic of copper(II) complex could be detected in those complexes, though the possibility of masking such an absorption by broad-intense band around 24000 cm^{-1} could be doubted. These complexes were found to be EPR silent and again, magnetic moment measurements showed them to be diamagnetic, indicating copper to be in the reduced state (+1) with d^{10} configuration.

These data suggest that the redox reaction exists in the interaction of Cu²⁺ with RNHCS₂⁽⁻⁾ or ArNHCS₂⁽⁻⁾ in DMF or THF medium also. But the

colour and solubility characteristics of the resulting complexes are entirely different from those isolated in aqueous medium. While the polymeric complexes reported in Chapter 3 were yellow in colour and insoluble in all solvents including DMF, DMSO and THF, the present complexes are soluble brown/reddish brown species. This suggests a clear structural and stereochemical change in these complexes as compared to the polymeric copper(I) complexes mentioned earlier.

The chemical nature of the byproducts of the reaction (isolated from the respective filtrates exactly as described in Chapter 3 is easily established by examining their IR spectra. The identity between the vibrational spectra of these compounds and those of the compounds obtained by the iodine oxidation of the respective ligands establishes that *N,N'*-disubstituted thiuram disulphides are the byproducts of the redox reaction, as in aqueous medium. Hence the reactions which are found to occur in aqueous medium also represent the redox process taking place in DMF or THF medium (Eqn. (1), (2) and (3) under Section 3.2.1). As in aqueous condition, the Cu(II) acts as a one-electron oxidants to RHDtc. The anionic dithiocarbamate is oxidised to a neutral radical species, Cu(II) getting reduced to Cu(I). The Cu(I) is complexed with the excess RHDtc present to form Cu(RHDtc) and the neutral radicals dimerise to form thiuram disulphide.

4.3.2 *Dimeric and tetrameric species*

Because of the appreciable solubility and low molecular weight characteristics, the molecular mass determination of the present complexes were carried out in nitrobenzene. The mass values of the various Cu(RHDtc) are tabulated in Table 4.3 and shows some interesting features.

Table 4.3. *The dithiocarbamates used in DMF and THF medium and the molecular mass of the corresponding Copper(I) complexes*

RHDtc	Molecular mass of Cu(RHDtc) (in nitrobenzene)	Nature of the complex
EtHNCS ₂ ⁻	396 (368)	[Cu(EtHNCS ₂) ₂] ₂
BuH NCS ₂ ⁻	446 (423)	[Cu(BuH NCS ₂) ₂] ₂
BzHNCS ₂ ⁻	477 (492)	[Cu(BzHNCS ₂) ₄]
PhHNCS ₂ ⁻	964 (927)	[Cu(Ph HNCS ₂) ₄]
pTHNCS ₂ ⁻	1005 (983)	[Cu(pTHNCS ₂) ₄]
pCHNCS ₂ ⁻	1061 (1065)	[Cu(pCHNCS ₂) ₄]
mCHNCS ₂ ⁻	1080 (1065)	[Cu(mCHNCS ₂) ₄]

While two of the complexes, Cu(EtHNCS₂) and Cu(BuHNCS₂) show dimeric nature all the others are found to be tetrameric. Attempts were made to grow single crystals for carrying out X-ray diffraction studies of these oligomeric complexes for finding out their molecular structure. But normal methods could not yield any good crystal. The structural features of case complexes were probed by various spectroscopic methods. IR spectra of the complexes were recorded, the spectral data are tabulated in Table 4.4.

Table 4.4. *Most relevant IR absorption frequencies for Cu(RHDtc) complexes generated in THF/DMF medium.*

Complex	$\nu(\text{NH})$	$\nu(\text{CN})$	$\nu(\text{CS})$
Cu(EtHNCS ₂)	3228	1500	957
Cu(BuHNCS ₂)	3292	1495	930
Cu(BzHNCS ₂)	3230	1485	1025, 922
Cu(PhHNCS ₂)	3200	1348	1000, 968
Cu(pTHNCS ₂)	3250	1350	968, 938
Cu(pCHNCS ₂)	3200	1378	1008, 958
Cu(mCHNCS ₂)	3200	1374	1042, 970

There is a close similarity between the spectra of the present complexes and those of the polymeric dithiocarbamates formed in aqueous medium (discussed in Chapter 3). As seen in the case of the polymeric complexes, there are absorption characteristic of both NH and Dtc functions in the spectra of the oligomers also. In spite of the similarity there are remarkable differences also. In the case of the dimeric complexes $[\text{Cu}(\text{EtHNCS}_2)]_2$ and $[\text{Cu}(\text{BuHNCS}_2)]_2$ strong peaks seen at 1500 and 1495 cm^{-1} , respectively are typical of $\nu(\text{CN})$ vibration of RHDtc. In the corresponding polymeric complexes their vibration occur at lower frequencies, 1472 and 1484 cm^{-1} , respectively. A comparison of the position of $\nu(\text{CN})$ absorptions in the spectra of $[\text{Cu}(\text{BuHNCS}_2)]_n$ and $[\text{Cu}(\text{BuHNCS}_2)]_2$ is shown in Figure 4.1.

Absorptions at 957 and 920 cm^{-1} in the spectra of $[\text{Cu}(\text{EtHNCS}_2)]_2$ and $[\text{Cu}(\text{BuHNCS}_2)]_2$, respectively are attributed to $\nu(\text{CS})$ vibration. There is a markable difference in the nature of $\nu(\text{CS})$ absorption in the dimeric and the corresponding polymeric complexes (Figure 4.2). While the $\nu(\text{CS})$ band

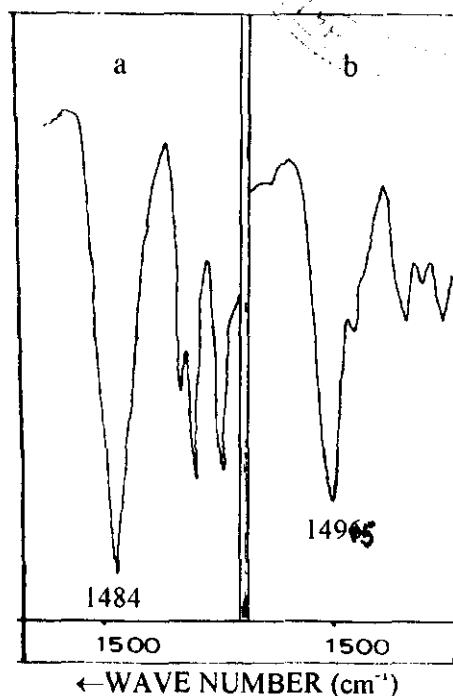


Figure 4.1. IR spectra in the region of $\nu(\text{CN})$ absorption of Bu (a) $[\text{Cu}(\text{EtNHCS}_2)]_n$ and (b) $[\text{Cu}(\text{BuNHCS}_2)]_2$

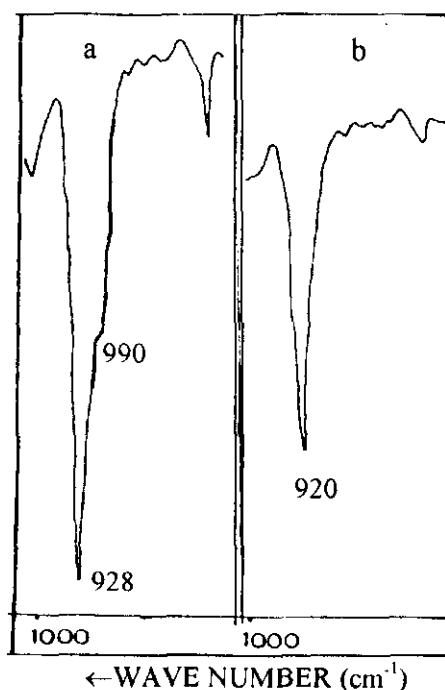


Figure 4.2. IR spectra in the region of $\nu(\text{CS})$ absorption of Bu (a) $[\text{Cu}(\text{EtNHCS}_2)]_n$ and (b) $[\text{Cu}(\text{BuNHCS}_2)]_2$

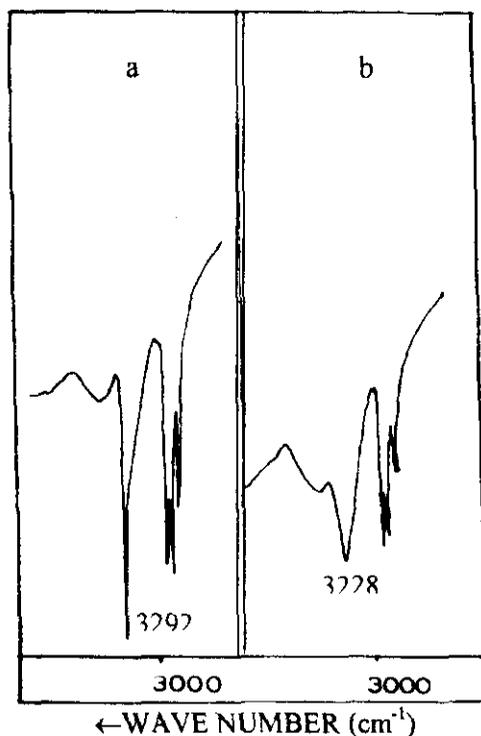


Figure 4.3. IR spectra in the region of $\nu(\text{NH})$ absorption of Cu (a) $[\text{Cu}(\text{EtNHCS}_2)]_n$ and (b) $[\text{Cu}(\text{BuNHCS}_2)]_2$

remains unsplit in the dimer at 920 cm^{-1} , it is splitted and occurs at a slightly higher position at 930 cm^{-1} in the polymers. The unsplit band is an indication of symmetric coordination of the two S atoms to Cu(I) in the dimeric complex. Band at $\sim 3228\text{ cm}^{-1}$ in the spectra of both $[\text{Cu}(\text{EtNHCS}_2)]_2$ and $[\text{Cu}(\text{BuNHCS}_2)]_2$ is attributed to $\nu(\text{NH})$ vibration. In the polymeric $[\text{Cu}(\text{BuNHCS}_2)]_n$ this band is sharp and intense occurring at a higher position (3292 cm^{-1}). In the dimer this band is rather broad (Figure 4.3).

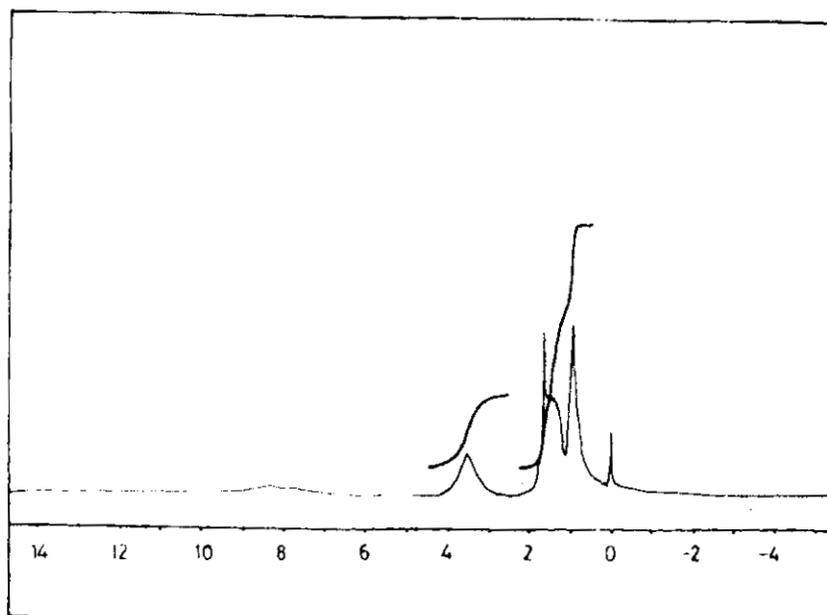
IR spectra of the tetrameric complexes $([\text{Cu}(\text{BzHNCS}_2)]_4, [\text{Cu}(\text{PhHNCS}_2)]_4, [\text{Cu}(\text{pTHNCS}_2)]_4, [\text{Cu}(\text{pCHNCS}_2)]_4$ and $[\text{Cu}(\text{mCHNCS}_2)]_4)$ show strong or moderately strong peaks due to $\nu(\text{CN})$ at 1485, 1348, 1350, 1378 and 1374 cm^{-1} respectively. All the tetramers except $[\text{Cu}(\text{BzHNCS}_2)]_4$, which is essentially a N-alkyl Dtc, show $\nu(\text{CN})$ absorption at low frequency due to the conjugation of nitrogen lone pair with the pi-electron system of the phenyl ring. A comparison of the $\nu(\text{CN})$, $\nu(\text{NH})$ and $\nu(\text{CS})$ vibration of the oligomeric and the corresponding polymeric Cu(I) RHDtc complexes are given in Table 4.5.

Table 4.5. A comparison of $\nu(\text{CN})$ and $\nu(\text{NH})$ vibration of polymeric and oligomeric Copper(I) dithiocarbamates

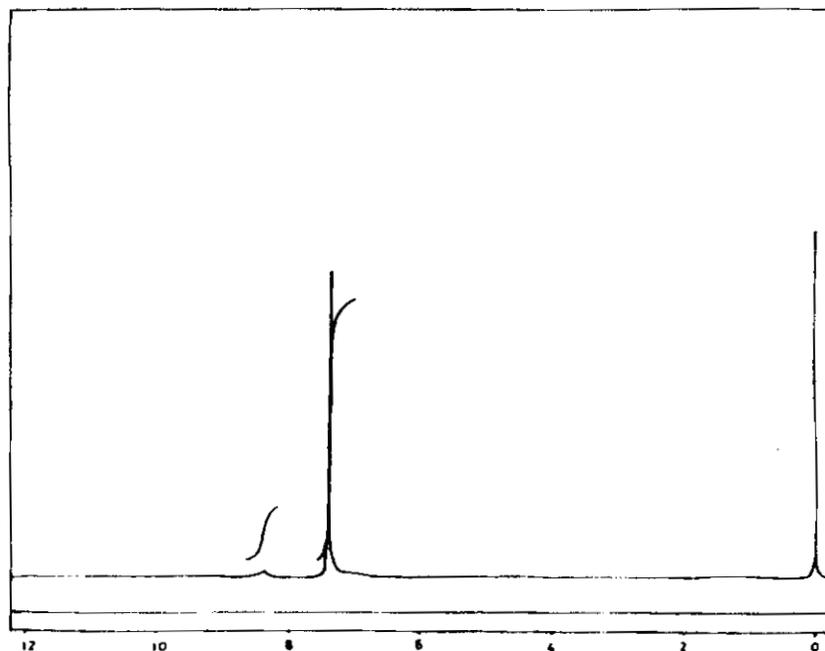
Complex	$\nu(\text{NH})$ (cm^{-1})		$\nu(\text{CN})$ (cm^{-1})		$\nu(\text{CS})$ (cm^{-1})	
	Polymer	Oligomer	Polymer	Oligomer	Polymer	Oligomer
CuEtHNCS ₂	3270	3228 (dimer)	1472	1500 (dimer)	1002, 962	957
CuBuHNCS ₂	3292	3228 (dimer)	1480 4	1495 (dimer)	930, 900	930
CuBzHNCS ₂	3298	3230 (tetramer)	1475	1485 (tetramer)	1020, 928	1025, 922
CuPhHNCS ₂	3270	3200 (tetramer)	1345	1348 (tetramer)	1020, 956	1000, 968
CuPt HNCS ₂	3265	3250 (tetramer)	1344	1350 (tetramer)	974, 960	968, 933
Cu P _c HNCS ₂	3250	3200 (tetramer)	1340	1378 (tetramer)	958, 940	1008, 958
CuMcHNCS ₂	3250	3200 (tetramer)	1348	1374 (tetramer)	966, 920	1042, 970

In all the four tetrameric complexes just as in the case of dimers, $\nu(\text{NH})$ stretching vibration occurs at a lower frequency indicating the existence H-bonding involving NH protons. As seen in the spectra of polymers multiple bands are observed in the region of $\nu(\text{CS})$ absorption of tetramers. This is indicative of possible unsymmetric bidentate coordination of RHDtc to Cu(I) in the tetrameric complexes.^{6,7}

The present complexes, unlike in the case of $[\text{Cu}(\text{RHDtc})]_n$ generated in aqueous condition, could be analysed for ¹HNMR spectra because of their solubility. It is interesting to note that the ¹HNMR spectra of all these soluble complexes appear as sharp bands in the normal expected region which clearly rules out presence of any copper(II) species. A few typical spectra are presented in Figure 4.4.



(a)



(b)

Figure 4.4. ^1H NMR spectra of (a) $[\text{Cu}(\text{BuHNCS}_2)]_2$ and (b) $[\text{Cu}(\text{PhHNCS}_2)]_4$

The assignments of the bands for all the complexes for which ^1H NMR were recorded are given in Table 4.6.

Table 4.6. ¹HNMR data for Cu(RHDtc) complexes generated in THF/DMF medium.

Complex	Solvent	δ (ppm)			
		NH	Ar-H	CH ₂	CH ₃
[Cu(EtHNCS ₂) ₂] ₂	CDCl ₃	8.40	-	3.50	0.94
[Cu(BuHNCS ₂) ₂] ₂	CDCl ₃	8.32	-	3.51, 1.54	0.93
	DMSO-d ₆	10.40	-	3.48, 1.6, 1.36	0.92
[Cu(BzHNCS ₂) ₄]	CDCl ₃	7.90	7.26	4.73	-
	DMSO-d ₆	10.9	7.30	4.73	-
[Cu(PhHNCS ₂) ₄]	CDCl ₃	8.41	7.38	-	-
[Cu(pTHNCS ₂) ₄]	CDCl ₃	7.75	7.23	-	2.35
[Cu(pCHNCS ₂) ₄]	CDCl ₃	8.50	7.33	-	-
[Cu(mCHNCS ₂) ₄]	CDCl ₃	8.40	7.25	-	-

The δ_{NH} values of the complexes [Cu(EtHNCS₂)₂]₂, [Cu(BuHNCS₂)₂]₂, [Cu(BzHNCS₂)₄], [Cu(PhHNCS₂)₄], [Cu(pTHNCS₂)₄], [Cu(pCHNCS₂)₄] and [Cu(mCHNCS₂)₄] are observed at 8.4, 8.3, 7.9, 8.4, 7.8, 8.5 ppm, respectively. The δ values of the aromatic protons in [Cu(BzHNCS₂)₄], [Cu(PhHNCS₂)₄], [Cu(pTHNCS₂)₄], [Cu(pCHNCS₂)₄] and [Cu(mCHNCS₂)₄] are found at 7.6, 7.38, 7.23 and 7.33 ppm, respectively. This shows that the NH protons are highly deshielded more than even the aromatic protons. This can be explained by the electron flow from nitrogen to the CS₂ moiety as shown in (2c) along with H-bonding as evidenced by IR spectra. In the case of Cu(I) ArHDtc the anisotropic effect of the ring current in the adjacent phenyl ring also contributes to the deshielding. Compared to other Cu(I)RHDtc complexes whose ¹HNMR spectra were measured, the δ_{NH} value of [Cu(pTHNCS₂)₄] is slightly lower, occurring at 7.8 ppm. This can be attributed to the +I effect of the CH₃ group which can shield the proton to some extent. A comparison of the δ_{NH} values of thiuram disulphides and the corresponding oligomeric complexes shows that the NH protons of the

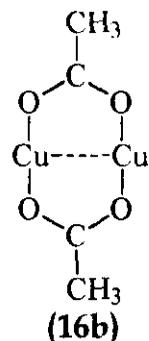
complexes and tds are deshielded to almost the same extent in the case of ArHDtc (Table 4.7). This shows that in these complexes the deshielding of NH proton is due to anisotropic effect and H-bonding only and not due to any additional electron flow from nitrogen towards Cu(I) on complexation. We have already seen that, as indicated by IR spectra, the CN bond order does not increase on complexation of ArHDtc with Cu(I) (Section 3.2.3). But in the case of Cu(RHDtc) complexes with N-alkyl substituent, the NH protons are more deshielded than those of the corresponding tds.

Table 4.7. Comparison of the ^1H NMR spectral data (δ_{NH}) of thiuram disulphides and Cu(I) complexes of some RHDtc ligands.

Ligand	δ_{NH}	
	Thiuram disulphide	Cu(I) complex
EtHDtc	7.4	8.4
BuHDtc	7.2	8.3
BzHDtc	6.4	7.9
PhHDtc	8.2	8.4
pTHDtc	7.8	7.8
pCHDtc	8.3	8.5
mCHDtc	8.3	8.4

This can be explained as due to deshielding caused by the electron flow from the ligand to metal on coordination as evidenced by the increase in $\nu(\text{CN})$ frequency of RHDtc on complexation with Cu(I) (Section 3.2.3). In Dtc complexes with a symmetric bonding mode to the metal, a correlation between $\delta(\text{NH})$ and $\nu(\text{CN})$ is found to exist.⁸ In the present complexes, only $[\text{Cu}(\text{EtHNCS}_2)]_2$ and $[\text{Cu}(\text{BuHNCS}_2)]_2$ are found to have such a coordination as indicated by their IR spectra and a correlation exists between their $\delta(\text{NH})$ and $\nu(\text{CN})$. In $[\text{Cu}(\text{EtHNCS}_2)]_2$ complex with a $\nu(\text{CN})$ frequency of 1500 cm^{-1} , $\delta(\text{NH})$ is found to be 8.4 ppm while in $[\text{Cu}(\text{BuHNCS}_2)]_2$ which has a $\nu(\text{CN})$ frequency of 1480 cm^{-1} , $\delta(\text{NH})$ is found to have a lower value, 8.3 ppm.

An insight into the molecular structure of the dimeric complexes could be gathered by examining the reported structural features of Cu(I) acetate complex $[\text{Cu}(\text{CH}_3\text{COO})_2]_2$. Cu(I) acetate is reported to be existing in the gaseous state as a dimer.⁹ The structure of the dimeric molecule is presented in (16b).



In structure (16b) Cu(I) takes 2 coordination with linear geometry. Because of the possibility of comparable ligation modes of S and O (Section 3.2.3), based on the reported dimeric nature of Cu(I) acetate and the present Cu(EtHDtc) and Cu(BuHDtc) complexes along with the spectral evidences, a structure comparable to (16b) could be proposed for the dimeric complexes. In Figure 4.5 the tentative structures for the dimeric complexes are given.

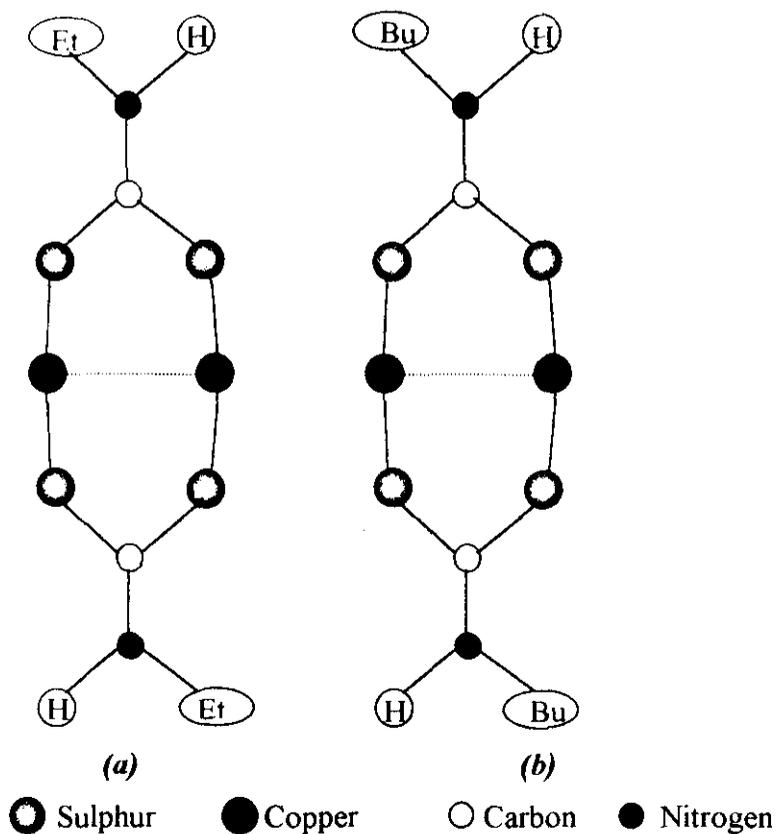


Figure 4.5. Possible structures of (a) $[\text{Cu}(\text{EtHNCS}_2)]_2$ and (b) $[\text{Cu}(\text{BuHNCS}_2)]_2$

It is to be noted that the polymeric complexes $[\text{Cu}(\text{RHDtc})]_n$ possess the repeating units of this dimeric structure (Figure 3.8). In the proposed structures the bonding mode of RHDtc is symmetric which explains the presence of unsplit bands in the IR spectra of $[\text{Cu}(\text{EtHNCS}_2)]_2$ and $[\text{Cu}(\text{BuHNCS}_2)]_2$ in the region of $\nu(\text{CS})$ absorption (Figure 4.2b). The dimeric complexes are stabilised by intermolecular hydrogen bonding as evident from the IR and ^1H NMR spectra [$\nu(\text{NH})$ absorptions are not sharp and occur at lower frequencies as compared to the polymeric complexes and their protons are highly deshielded as indicated by high δ values]. The overall structural disposition of the planar dimers as shown in Figure 4.5. is conducive for such an intermolecular hydrogen bonding. To our knowledge no dimeric copper(I) dithiocarbamate complexes have been reported so far, even though dimeric Au(I) complexes of N,N-dialkyl Dtc are known.¹⁰

The nature of the $\nu(\text{CS})$ vibration in the tetrameric complexes could give an indication of the mode of linkage of S atom of RHDtc to Cu(I) (Table 4.4). In the spectra of all these complexes $[\text{Cu}(\text{BzHNCS}_2)]_4$, $[\text{Cu}(\text{PhHNCS}_2)]_4$, $[\text{Cu}(\text{pTHNCS}_2)]_4$, $[\text{Cu}(\text{pCHNCS}_2)]_4$ and $[\text{Cu}(\text{mCHNCS}_2)]_4$ one could clearly observe the band splitting in the region of $\nu(\text{CS})$ absorption, as seen, for example, in the IR spectra of $[\text{Cu}(\text{BzHNCS}_2)]_4$ (Figure 4.6).

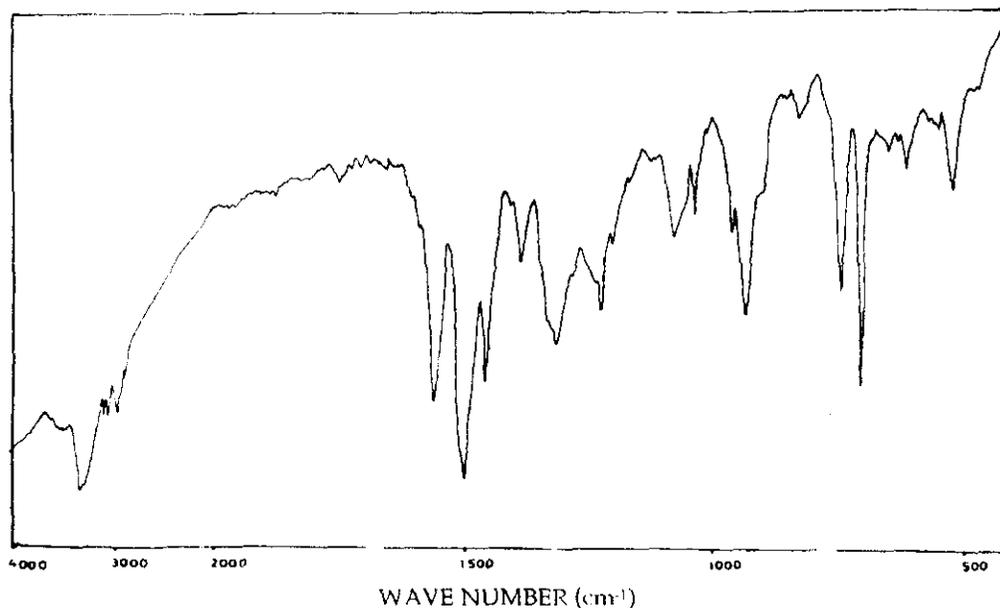


Figure 4.6. IR spectra of $[\text{Cu}(\text{BzHNCS}_2)]_4$.

This band splitting indicates an unsymmetric bonding behaviour of RHDtc to Cu(I). A structure which is quite in agreement with this spectral feature and which can explain the existence of H-bonding involving NH protons, as evidenced by the IR and ^1H NMR spectral data of the tetramers (Table 4.5), is proposed (Figure 4.7).

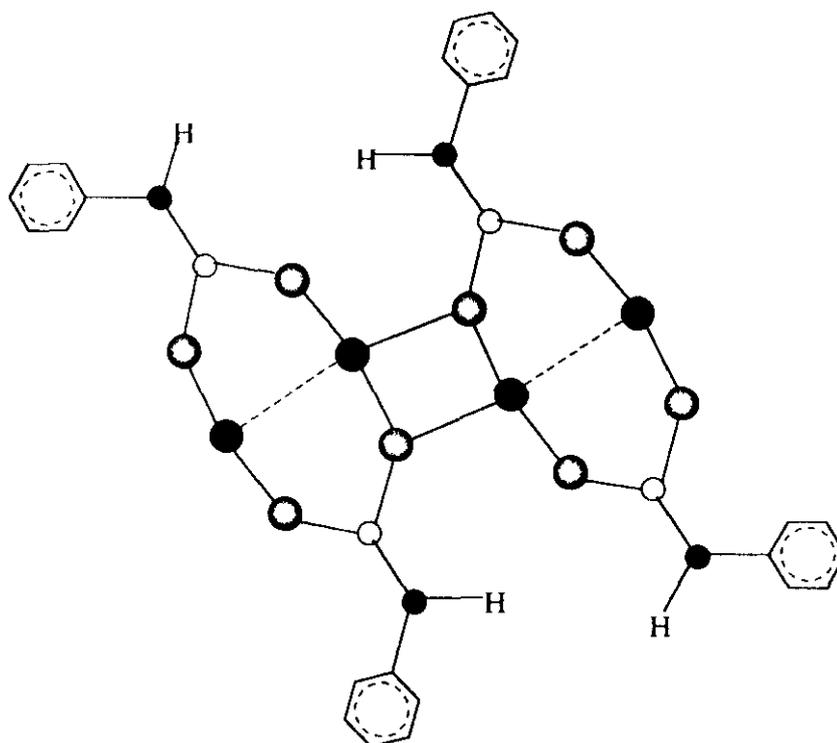


Figure 4.7. Possible structure of $[\text{Cu}(\text{ArHNCS}_2)]_4$

Two dimeric units (Figure 4.5) join together through two sulphur bridges to form the planar tetramer.

The comparison of $\nu(\text{CN})$ vibrations of the tetramers and the polymers given in Table 4.5 shows that in the polymer $\nu(\text{CN})$ vibration always occurs at a lower frequency compared to that of the tetramers. This indicates that the N-substituent remains slightly out of plane of CS_2 moiety because of the steric strain in polymers (Figures 3.8). This weakens the CN bonds in the polymers

because of the breakage of conjugation to a small extent. The spectral data indicate that the tetramers (as well as the dimers) should have a stereochemistry devoid of such a strain. In the proposed structure given above, the phenyl rings are far apart avoiding steric strain, quite in agreement with the spectral behaviour. Supportive evidence for this structure is obtained from the reactivity of these tetrameric complexes towards benzoylation reaction (discussed in Section 4.3.4). These complexes are found to strongly resist benzoylation. If these tetrameric complexes had the closed cubane structure of $[\text{Cu}(\text{Et}_2\text{Dtc})]_4$ complex, benzoylation should have been possible. But because of the steric strain that would be introduced on benzoylation, these complexes with the planar tetrameric structure resists such a reaction. $[\text{Cu}(\text{BzHNCS}_2)]_4$ is the only tetrameric complex which is found to undergo benzoylation. This can be due to the possible free rotation about N-CH₂Ph single bond keeping the four phenyl groups far apart avoiding steric hindrance. This is illustrated in Figure 4.8.

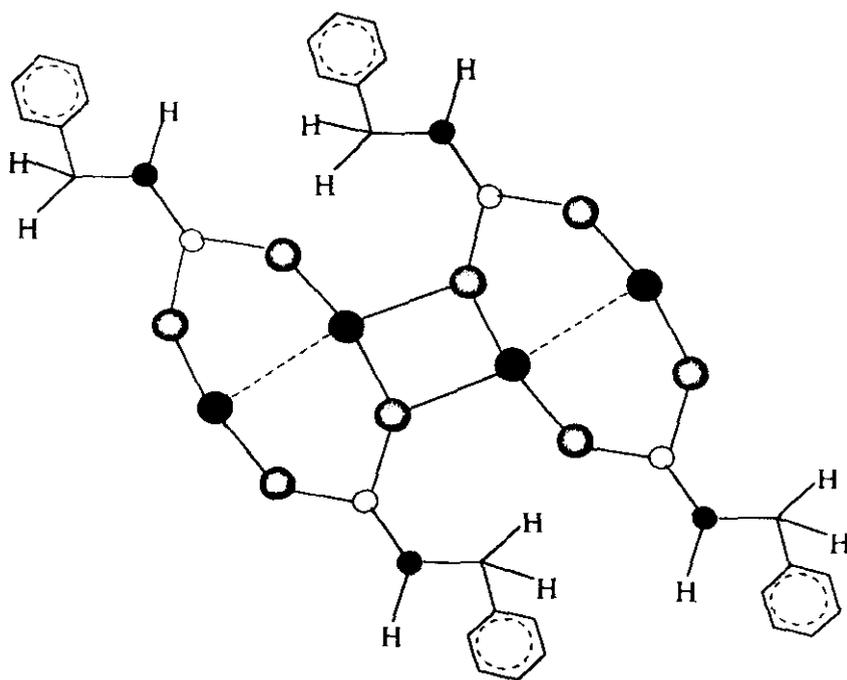


Figure 4.8. Stereochemistry (probable) of $[\text{Cu}(\text{BzHNCS}_2)]_4$

This stereochemistry does not bring about any steric crowding in the benzoylated complex.

The tendency for tetramer formation should be greater than for dimerisation, the number of the number of metal-sulphur and metal-metal bonds in the tetramer being greater. The tetramers are also stabilised by intermolecular hydrogen bonding between the planar tetramers. If the structures were of closed cubane type,¹¹ similar to that of $[\text{Cu}(\text{Et}_2\text{NCS}_2)]_4$, the extent of intermolecular hydrogen bonding would have been less. *N,N*-disubstituted Dtc are not found to form planar tetramers, instead they form tetramers with closed cubane structure having the four Cu(I) atoms at the four corners of a distorted tetrahedron. This can be attributed to two factors: (i) in the *N,N*-disubstituted Dtc there is no possibility of stabilisation by intermolecular hydrogen bonding between the planar tetramers and (ii) steric crowding brought about by the presence of two substituents on nitrogen makes the planar tetrameric structures impossible. There are reports¹² that size and structural characteristics of the substituents on nitrogen appear to play an important role in determining the degree of polymerisation of $\text{Cu}(\text{R}_2\text{Dtc})$ complexes since oligomers as well as higher polymers were found, when their molecular mass were determined. Nothing has been mentioned so far about the nature of these polymeric complexes and the role played by the *N*-substituents in deciding their degree of polymerisation. The results of the present study make us suggest 'a cuprous acetate-type' planar linear polymeric structure for these *N,N*-disubstituted dithiocarbamatecopper(I) complexes also. The bulkier substituents favour tetramers with closed cubane structure to avoid steric repulsion while smaller *N*-substituents like H and methyl group facilitate the formation of planar polymers.

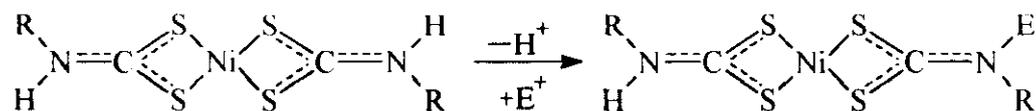
It is instructive to consider why *N*-monoalkyl Dtc do not form planar tetramers instead of forming only planar dimers, while *N*-monoaryl Dtc form only planar tetramers. The answer to this question lies in the difference in the

CN bond order of these complexes. While the $\nu(\text{CN})$ for N-monoalkyl Dtc complex is about 1500 cm^{-1} , that for N-monoaryl Dtc complex it is only about 1350 cm^{-1} (Table 4.5). This increased double bond character of the C-N bond of the Dtc moiety of the planar complexes prevents the rotation about this bond so that the attainment of a conformation for the tetramer with the four alkyl groups as far apart as possible, avoiding steric repulsion is not easy. This keeps the Cu(I) complexes of N-monoalkyl Dtc in the dimeric state. But benzyl Dtc, BzNHCS_2^- , essentially a monoalkyl Dtc, forms a tetrameric copper(I) complex. This may be due to the possibility of free rotation about N- CH_2Ph single bond keeping the four phenyl groups far apart avoiding steric repulsion. This has been illustrated in Figure 4.8.

It is worth considering why the copper(I) complexes of all the N-monosubstituted Dtc mentioned above form polymeric complexes in aqueous medium. In polar solvents like water and alcohol, the NH nitrogen will be strongly hydrogen bonded to the solvent. This is also evident when $^1\text{H NMR}$ of $\text{Cu}(\text{RHDtc})$ complexes are recorded in polar and nonpolar solvents. The $\delta(\text{NH})$ values were found to be shifted downfield (high δ) in polar solvents (Table 4.6). In this conditions the hybridisation of NH nitrogen will have greater sp^3 character making it possible for the complex to acquire the strain free conformation required for polymer formation by rotation about C-N bond (Figure 3.8). Once polymerisation has occurred, the complex gets precipitated from the aqueous medium and no more N-H hydrogen bonding with the solvent. The N atom returns to the almost trigonal hybridisation with some double bond character for the CN bond making the polymer planar. In the case of the polymers of N-monoalkyl Dtc this introduces some steric strain. This may be the reason why $[\text{Cu}(\text{RNHCS}_2)]_n$, especially $[\text{Cu}(\text{BuNHCS}_2)]_n$ which has the maximum strain among these complexes have a tendency to decompose within a few days, while all oligomeric and N-monoaryl substituted polymeric complexes stay stable, without getting oxidised to Cu^{2+} in air.

4.3.3 Electrophilic substitution of the NH Proton of the N-monosubstituted dithiocarbamatocopper(I) complexes

It is known that square planar d^8 bis(N-monosubstituted dithiocarbamate)metal(II) complexes, with excess tertiary phosphine easily form dithiocarbamate complexes of the type $[M(S_2C=NR)(PR_3)_2]$.¹³ Nickel complexes of N-monosubstituted dithiocarbamates, $Ni(S_2CNHR)_2$ are also known to react with electrophiles E^+ according to Scheme 4.1.² By varying the relative ratio of the complex and the electrophile both mono and disubstituted complexes have been synthesised.



Scheme 4.1.

Selecting electrophiles with strong electron withdrawing groups carbodithioato derivatives of weak nitrogen nucleophiles have been synthesised. For example, $Ni[S_2CN(OCR')R]_2$ ($R' = CH_3$ or C_6H_5) have been synthesised by acylation or benzylation using acetic anhydride or benzoyl chloride in presence of triethylamine.² In an attempt to study the reactivity of NH proton of N-monosubstituted dithiocarbamatocopper(I) complexes towards electrophilic substitution, both Schotten-Baumann reaction and the reaction method mentioned above for Ni(II) complexes were tried on various copper(I) complexes developed, both with oligomeric and polymeric nature. The complexes were obtained after the reaction as red solid in the case of $[Cu(EtHNCS_2)]_2$, $[Cu(BuHNCS_2)]_2$ and $[Cu(BzHNCS_2)]_4$. The elemental analysis of these complexes revealed the substitution as expected. The data are presented in Table 4.8.

Table 4.8. Analytical data for the copper(II) complexes formed by the benzoylation of *N*-monosubstituted dithiocarbamatocopper(I) complexes

Complex	Colour	Found (Calculated) (%)				
		Carbon	Hydrogen	Nitrogen	Sulphur	Copper
Cu[EtCOC ₆ H ₅)NCS ₂] (C ₁₀ H ₁₀ NOS ₂ Cu)	Red	40.8 (41.7)	3.7 (3.5)	5.1 (4.9)	21.8 (22.3)	21.7 (22.1)
Cu[BuCOC ₆ H ₅)NCS ₂] (C ₁₂ H ₁₄ NOS ₂ Cu)	Red	44.5 (45.6)	4.8 (4.5)	4.7 (4.4)	19.6 (20.3)	19.8 (20.1)
Cu[BzCOC ₆ H ₅)NCS ₂] (C ₁₅ H ₁₂ NOS ₂ Cu)	Red	50.9 (51.5)	3.6 (3.5)	3.8 (4.0)	17.9 (18.4)	18.0 (18.2)

It is found that even though both the methods of benzoylation were tried, only the complexes mentioned above were benzoylated. The response of the various Cu(I) dithiocarbamates towards the benzoylation reaction attempted are presented in Table 4.9.

Table 4.9. Reactivity of Copper (I) dithiocarbamates towards benzoylation

Complex	Benzoylation condition	Nature of reaction (Product)
[Cu(RHDtc)] _n	(a) and (b)	No reaction
[Cu(ArHDtc)] _n	(a) and (b)	"
[Cu(ArHDtc)] ₄	(a) and (b)	"
[Cu(BzHDtc)] ₄	(b)	Benzoylated [Cu(S ₂ Cn(COC ₆ H ₅)Bz)] ₄
[Cu(EtHDtc)] ₂	(b)	Benzoylated [Cu(S ₂ CN(COC ₆ H ₅)Et)] ₄
[Cu(BuHDtc)] ₂	(b)	Benzoylated [Cu(S ₂ CN(COC ₆ H ₅)Bu)] ₄
[Cu(ArHDtc)] ₂	(a) and (b)	Demetallated (not characterised)

The benzoylated complexes gave IR spectra different from their parent unbenzoylated species. There were characteristic dithiocarbamate peaks in addition to some new absorption peaks (Table 4.10). The spectral values of the unbenzoylated complexes are also presented for comparison.

Table 4.10. The most relevant IR frequencies (cm^{-1}) of the benzoylated and unbzoylated complexes and their molecular masses

Compound	$\nu(\text{NH})$ (cm^{-1})	$\nu(\text{CN})^*$ (cm^{-1})	$\nu_{\text{C=S}}$ (cm^{-1})	$\nu_{\text{C=O}}$ (cm^{-1})	Molecular mass
$\text{Cu}[\text{S}_2\text{CN}(\text{COC}_6\text{H}_5)\text{Et}]$	-	1388	983, 955	1705	1117 (1155)
$[\text{Cu}(\text{EtHNCS}_2)]_2$	3270	1498	1002, 962	-	396 (368)
$\text{Cu}[\text{S}_2\text{CN}(\text{COC}_6\text{H}_5)\text{Bu}]$	-	1390	978, 928	1705	1341 (1263)
$[\text{Cu}(\text{BuHNCS}_2)]_2$	3270	1484	930, 900	-	446 (423)
$\text{Cu}[\text{S}_2\text{CN}(\text{COC}_6\text{H}_5)\text{Bz}]$	-	1378	940, 900	1705	143 (1399)
$[\text{Cu}(\text{BzHNCS}_2)]_4$	3298	1485	1020, 928	-	477 (492)

*The strongest and broadest peak in the region $1550\text{-}1300\text{ cm}^{-1}$ is assigned to $\nu(\text{CN})$.

The absence of NH absorption and the presence of a strong band at 1705 cm^{-1} are clear indication of complete benzoylation of the complex. $\nu(\text{CN})$ are found at lower frequencies in the benzoylated products because of the electron withdrawing COC_6H_5 group attached to N atom. In the place of the unsplit peak in the $\nu(\text{CS})$ region of $\text{Cu}(\text{EtNHCS}_2)$ and $\text{Cu}(\text{BuNHCS}_2)$, multiplets are observed in the spectra of benzoylated products. This is expected because, in the absence of NH hydrogen, no more hydrogen bonding is possible and the hydrogen bond stabilised planar dimeric structures in these two complexes and the planar tetrameric structure in $\text{Cu}(\text{BzNHCS}_2)$ would be converted to the tetrameric closed cubane structure similar to that of $[\text{Cu}(\text{Et}_2\text{NCS}_2)]_4$ (Figure 4.9).¹¹ The molecular weight determinations showed that these benzoylated complexes are tetrameric.

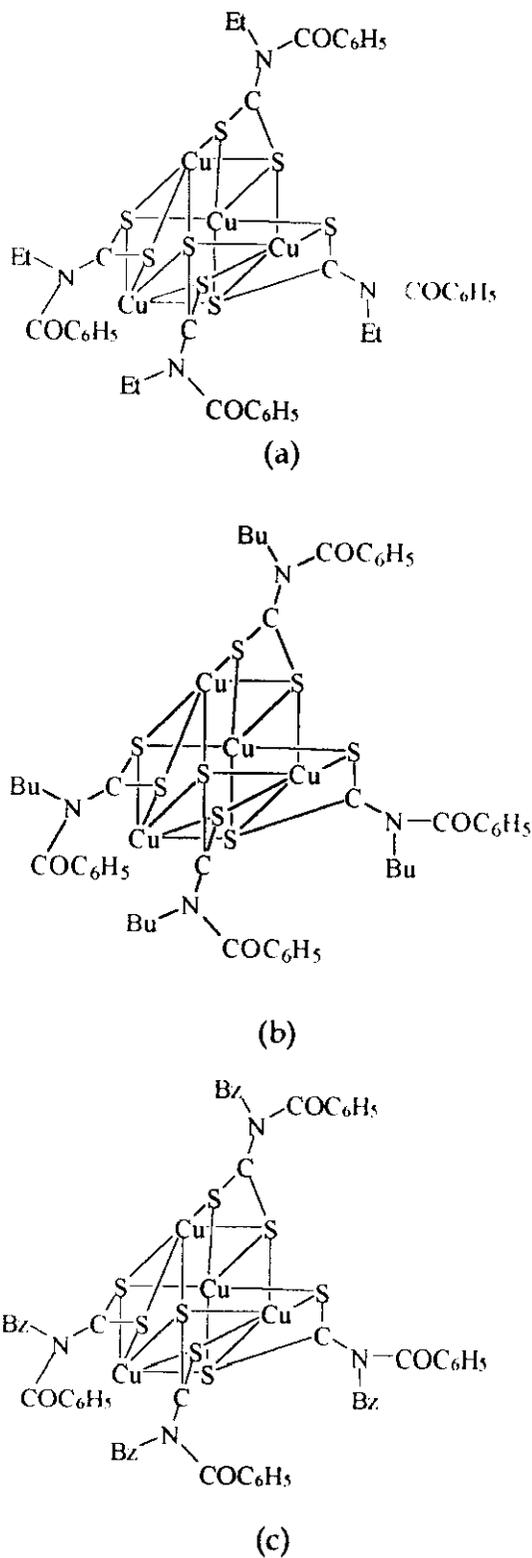


Figure 4.9. Probable structure of (a) $[Cu(S_2CN(COC_6H_5)Et)]_4$, (b) $[Cu(S_2CN(COC_6H_5)Bu)]_4$ and (c) $[Cu(S_2CN(COC_6H_5)Bz)]_4$

In this context it is noteworthy to consider the following aspects of the benzoylation reaction. Among the N-mono substituted Dtc complexes tried for benzoylation, all the N-alkyl substituted Dtc, $\text{Cu}(\text{EtNHCS}_2)$, $\text{Cu}(\text{BuNHCS}_2)$ and $\text{Cu}(\text{BzNHCS}_2)$ were benzoylated. None of the N-monoaryl Dtc on the other hand could be benzoylated. This is in contrast to bis planar N-mono substituted dithiocarbamate nickel(II) complexes where both N-alkyl and N-aryl Dtc were benzoylated. This observation conclusively proves the structures assigned to these complexes as indicated. If the reduced nucleophilicity of the N-aryl N atom were responsible for the inertness of tetrameric N-monoaryl Dtc complexes of Cu(I) towards benzoylation, Ni(II) complexes also would not have been benzoylated. This indicates that the real cause is a steric one, which also is the reason why polymeric complexes of even N-alkyl Dtc are not getting benzoylated. Only in the case of dimers benzoylation can take place without any steric hindrance. Both in tetramers of N-monoaryl substituted Dtc and all the polymeric Dtc, benzoylation will cause steric hindrance. In the case of $\text{Cu}(\text{BzNHCS})$, even though a tetramer, may be having isotactic stereochemistry which allows benzoylation without any steric hindrance. It is seen that dimers of N-aryl Dtc were getting demetallated when benzoylation was attempted by us. Poor coordinating ability of Dtc, with a phenyl group and electron withdrawing $-\text{COC}_6\text{H}_5$ group on N, towards copper(I) may be considered responsible for this behaviour.

4.3.4 Oligomeric CuRHDtc species from aqueous medium

The N-monosubstituted dithiocarbamates studied so far are those which form oligomeric Cu(I) complexes in non-aqueous solvents like DMF and THF and form polymeric complexes in aqueous medium. However, while attempting to synthesise polymeric Cu(I) complexes of a few

N-monosubstituted dithiocarbamates, we found some interesting observations. Some monosubstituted dithiocarbamates were not capable of forming polymeric copper(I) complexes in aqueous medium. These dithiocarbamates are essentially those derived from *m*-toluidine ($m\text{THNCS}_2^-$), *o*-toluidine ($o\text{THNCS}_2^-$), *o*-chloroaniline ($o\text{CHNCS}_2^-$), *o*-anisidine ($o\text{AHNCS}_2^-$), 4-aminoantipyrine (PzHNCS_2^-) and phenylalanine (PAHNCS_2^-). The preparation of the ligands and their reaction with Cu^{2+} are briefly described below.

The ligand PAHNCS_2^- was also prepared by the procedure as described under Section 3.1.1(i). Crystalline phenylalanine (20 mM) was dissolved in 2 molar aqueous solution of NaOH (20 ml) with stirring. 20 mM CS_2 dissolved in DMF (2 ml) was added dropwise under stirred condition. The solution was washed with ether and any dissolved ether was removed by suction. All the other ligands were prepared as discussed under Section 3.1.1(e). CS_2 (25 mM) in DMF-water mixture (2:1 v/v) was added to the corresponding amine (20 mM) with stirring keeping the solution cooled in cold water. An equimolar quantity of aqueous NaOH was added to the solution and stirred. The solution was repeatedly washed with ether and dissolved ether was removed by suction.

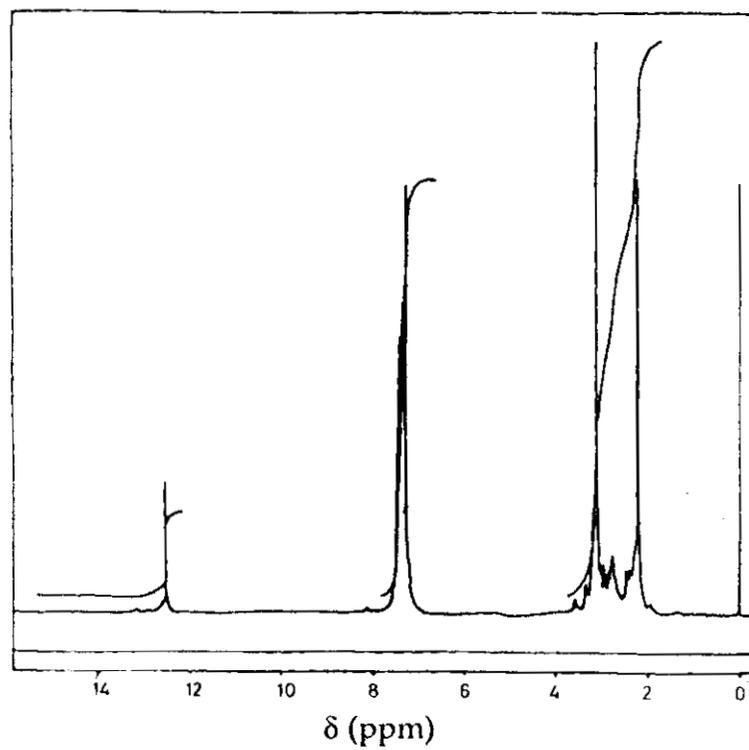
The ligands except PAHNCS_2^- were treated with Cu^{2+} (aq) in the molar ratio 2:1 as described in Section 3.1.2(a). The solids precipitated were filtered, washed successively with methanol and ether and dried over P_4O_{10} under vacuum. PAHNCS_2^- was treated with Cu^{2+} (aq) in the molar ratio 2:1 as described under Section 3.1.2(i). The brown solid formed was filtered washed with THF and then ether and finally dried over P_4O_{10} under vacuum. On the addition of Cu^{2+} (aq) ions to the ligand we were expecting the formation of yellow complexes as in the case of other complexes mentioned in

the previous chapter. Instead, the solid precipitated was brown in colour. All the complexes were similar in colour and also solubility characteristics to those of the oligomeric complexes produced during the interaction studies in DMF or THF medium. These complexes are brown and soluble in chloroform, THF and DMF. Elemental analysis (Table 4.11.) suggests a metal ligand ratio of 1:1 in agreement with the composition Cu(RHDtc).

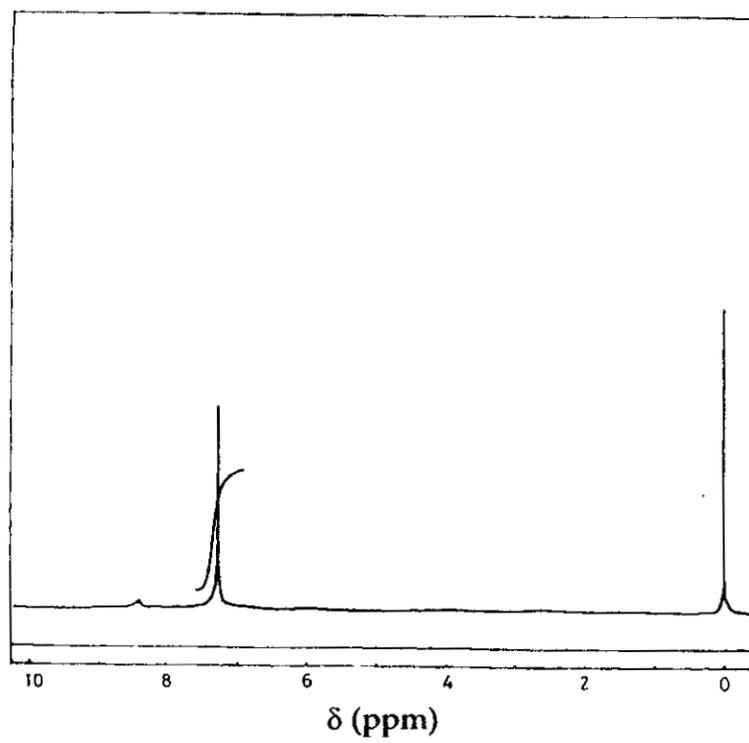
Table 4.11. Analytical data for oligomeric *N*-monosubstituted dithiocarbamate-copper(I) complexes formed in aqueous medium

Complex	Colour	Found (Calculated) (%)				
		Carbon	Hydrogen	Nitrogen	Sulphur	Copper
[Cu(MtHNCS ₂) ₄] (C ₈ H ₈ NS ₂ Cu)	Brown	38.9 (39.1)	3.6 (3.3)	6.0 (5.7)	25.9 (26.1)	25.1 (25.8)
[Cu(oTHNCS ₂) ₂] (C ₈ H ₈ NS ₂ Cu)	Dark brown	38.4 (39.1)	3.2 (3.3)	5.4 (5.7)	26.0 (26.1)	25.3 (25.8)
[Cu(oCHNCS ₂) ₂] (C ₇ H ₅ NS ₂ Cu)	Yellowish brown	31.0 (31.6)	2.1 (1.9)	5.1 (5.3)	24.8 (24.5)	23.5 (24.3)
[Cu(oAHNCS ₂) ₂] (C ₈ H ₈ NS ₂ Cu)	Brown	35.9 (36.7)	3.3 (3.1)	5.0 (5.3)	24.8 (24.5)	23.5 (24.3)
[Cu(PzHNCS ₂) ₂] (C ₁₂ H ₁₂ N ₃ S ₂ OCu)	Brown	41.8 (42.0)	3.8 (3.5)	11.7 (12.3)	19.0 (18.8)	18.1 (18.6)
[Cu(pAHNCS ₂) ₂] (C ₁₀ H ₁₀ N ₂ SO ₂ Cu)	Brown	40.1 (39.5)	3.4 (3.3)	4.3 (4.6)	20.6 (21.1)	20.4 (20.9)

The complexes are EPR inactive and are found to be diamagnetic suggesting the reduced state of copper(I). The ¹HNMR spectra recorded in the normal range of chemical shift values again suggests Cu(I) state. Two representative ¹HNMR spectra of [Cu(PzHNCS₂)₂] and [Cu(oCHNCS₂)₂] are presented in Figure 4.10.



(a)



(b)

Figure 4.10. $^1\text{H NMR}$ spectra of (a) $[\text{Cu}(\text{PzHNCs}_2)]_2$ and (b) $[\text{Cu}(\text{oCHNCs}_2)]_2$

Electronic spectra of the complexes show the two characteristic intraligand $\pi\text{-}\pi^*$ transitions of Dtc ligand at about 40000 and 33000 cm^{-1} along with the $\text{L}\leftarrow\text{M}$ C.T. band spreading to the visible region (Table 4.12).

Table 4.12. *Electronic spectral data for oligomeric Cu(RHDtc) complexes generated in aqueous medium*

Complex	Band I ($\pi\rightarrow\pi^*$) (cm^{-1})	Band II ($\pi\rightarrow\pi^*$) (cm^{-1})	Band III (M \rightarrow LCT) (cm^{-1})
Cu(mTHNCS ₂)	39682	33222	21505
Cu(oTHNCS ₂)	40160	33333	21786
Cu(oCHNCS ₂)	40000	33150	21160
Cu(oAHNCS ₂)	39840	33333	21276
Cu(PzHNCS ₂)	40160	33333	24271
Cu(PAHNCS ₂)	40240	33050	23560

Absorptions characteristic of N-monosubstituted Dtc are present in the IR spectra of the present complexes (Table 4.13).

Table 4.13. *The most important IR frequencies (cm^{-1}) of oligomeric N-monosubstituted dithiocarbamatecopper(I) complexes formed in aqueous medium and their assignments.*

Complex	$\nu(\text{NH})$	$\nu(\text{CN})$	$\nu(\text{CS})$
Cu(mTHNCS ₂)	3200	1340	975, 940
Cu(oTHNCS ₂)	3250	1490	975, 955
Cu(oCHNCS ₂)	3240	1495	975, 960
Cu(oAHNCS ₂)	3325	1500	1020, 970
Cu(PzHNCS ₂)	3250	1488	1020, 985
Cu(PAHNCS ₂)	3425,* 3260, 1600**	1480	960, 920

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

$\nu(\text{NH})$ is observed in the range of 3260-3200 cm^{-1} for all the complexes except $\text{Cu}(\text{oADtc})$ which has a higher value of 3325 cm^{-1} . This can be attributed to the fact that the $-\text{OCH}_3$ group which projects out of the plane of the molecule prevents intermolecular hydrogen bonding. The IR spectra of these complexes show that the $\nu(\text{CN})$ occurs at about 1500 cm^{-1} in $\text{Cu}(\text{PAHDtc})$ and $\text{Cu}(\text{PzHDtc})$ and in the range of 1350-1300 cm^{-1} in the N-aryl substituted complex $\text{Cu}(\text{mTHDtc})$. Though $\text{Cu}(\text{oADtc})$, $\text{Cu}(\text{oTHDtc})$ and $\text{Cu}(\text{oCHDtc})$ are N-aryl substituted Dtc, the $\nu(\text{CN})$ in them occurs at about 1500 cm^{-1} . In the case of these ortho substituted complexes, because of steric factors, the planar phenyl ring may remain out of plane of the NCS_2 moiety to some extent breaking the extended conjugation. This can prevent the electron flow from N to the benzene ring raising the energy of CN stretching vibration.

Molecular masses of these complexes were determined cryoscopically in nitrobenzene and the values are tabulated in Table 4.14.

Table 4.14. RHDtc generated in aqueous medium and the molecular masses of the corresponding oligomeric Cu(I) dithiocarbamates

RHDtc	Molecular mass (Calculated)	Nature of complex species
mTHNCS_2^-	944 (982)	$[\text{Cu}(\text{mTHNCS}_2)]_4$
oTHNCS_2^-	538 (492)	$[\text{Cu}(\text{oTHNCS}_2)]_2$
oCHNCS_2^-	563 (532)	$[\text{Cu}(\text{oCHNCS}_2)]_2$
oAHNCS_2^-	558 (523)	$[\text{Cu}(\text{oAHNCS}_2)]_2$
PzHNCS_2^-	671 (684)	$[\text{Cu}(\text{PzHNCS}_2)]_2$
PAHNCS_2^-	641 (608)	$[\text{Cu}(\text{PAHNCS}_2)]_2$

The molecular masses suggest dimeric state for $\text{Cu}(\text{PzHDtc})$, $\text{Cu}(\text{PAHDtc})$ and all the ortho substituted complexes and tetrameric nature for $\text{Cu}(\text{mTHDtc})$. Having double bond character for C-N bond as indicated

by $\nu(\text{CN})$ values ($\approx 1500 \text{ cm}^{-1}$) it is not possible for $\text{Cu}(\text{PzHDtc})$, $\text{Cu}(\text{PAHDtc})$, $\text{Cu}(\text{oTHDtc})$, $\text{Cu}(\text{oAHDtc})$ and $\text{Cu}(\text{oCHDtc})$ to attain the desired conformation for tetramer formation by rotation about C-N. This is illustrated in Figure 4.11.

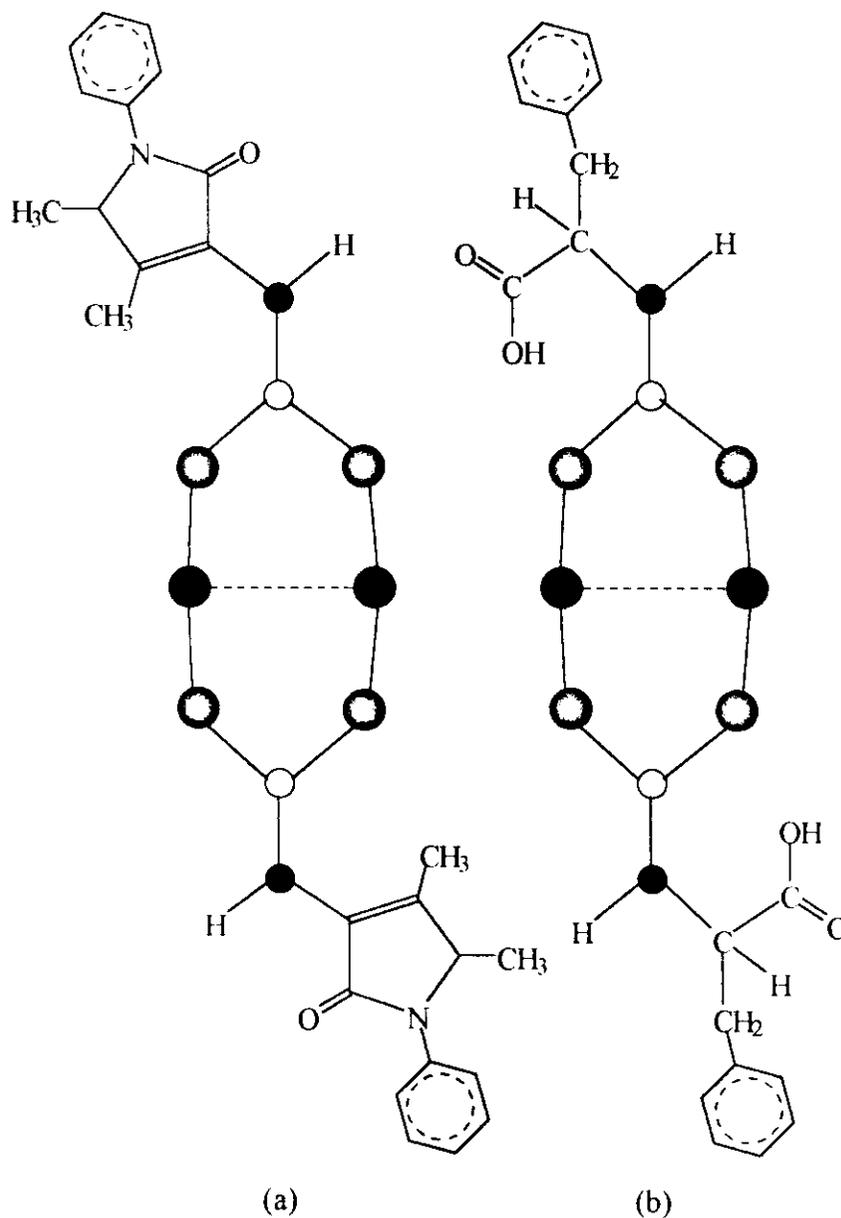


Figure 4.11. Tentative structures of (a) $[\text{Cu}(\text{PzHDtc})]_2$ and (b) $[\text{Cu}(\text{PAHDtc})]_2$

It is evident from the above observations and the results discussed in Section 4.3.2 that there is a relation between CN bond order in RHDtc and the number of monomeric units in their respective oligomeric copper(I) complexes, as illustrated in Table 4.15.

Table 4.15. *N*-monosubstituted Dtc and the number of monomeric units in their corresponding oligomeric Cu(I) Dtc.

Dithiocarbamate (Empirical formula)	Nature of oligomers	ν_{CN} , cm^{-1}
Cu(EtHDtc)	Dimer	1500
Cu(BuHDtc)	Dimer	1495
Cu(PzHDtc)	Dimer	1488
Cu(PhHDtc)	Tetramer	1348
Cu(^{mT} MtHDtc)	Tetramer	1340
Cu(^{mC} MeHDtc)	Tetramer	1378
Cu(^{pC} PeHDtc)	Tetramer	1374
Cu(^{oT} OtHDtc)	Dimer	1492
Cu(^{oC} OeHDtc)	Dimer	1500
Cu(^{oA} OaHDtc)	Dimer	1495

If the CN bond order is such that it allows free rotation about the C-N bond, the tetramers are formed. If the CN bond order is more, as indicated by higher $\nu(\text{CN})$ frequency, rotation about the C-N bond is restricted and the complex remains as dimer.

While most of the primary amine derived dithiocarbamates prefer to form polymeric Cu(RHDtc) in aqueous condition the reason why the Cu(RHDtc) [Cu(mTHNCS₂), Cu(oTHNCS₂), Cu(oCHNCS₂), Cu(oAHNCS₂), Cu(PzHNCS₂) and Cu(PAHNCS₂)] do not form polymeric complexes even in aqueous medium is worth discussing. From the present study, it can be generalised that the following conditions prevent polymer formation.

- (i) In the case of ArNHCS_2^- , substitution at the ortho or meta position of the phenyl group prevents polymerisation of resulting CuArHDtc . If the substituent is a single atom (like Cl) at meta position, polymerisation is possible. If the substituent is at the para position of the phenyl moiety, irrespective of its size and nature, polymeric CuRHDtc species are always found to be formed.
- (ii) In the case of RNHCS_2^- , when two substituents are present at the α -carbon atom (with respect to the Dtc moiety) polymerisation is prevented. Therefore, Dtc of any α -amino acid other than glycine is not capable of forming polymeric CuRHDtc .
- (iii) In the case of non-aromatic ring as the N-substituent, substitution at both the ortho or metapositions or at one ortho and one meta on the opposite sides of the ring also seem to prevent polymerisation.

All the above observation can be well explained if these Cu(I) polymers possess a structure analogous to that of cuprous acetate, a polymer of planar dimeric units, linked by sulphur bridges into a staggered linear polymer (Figure 4.12).

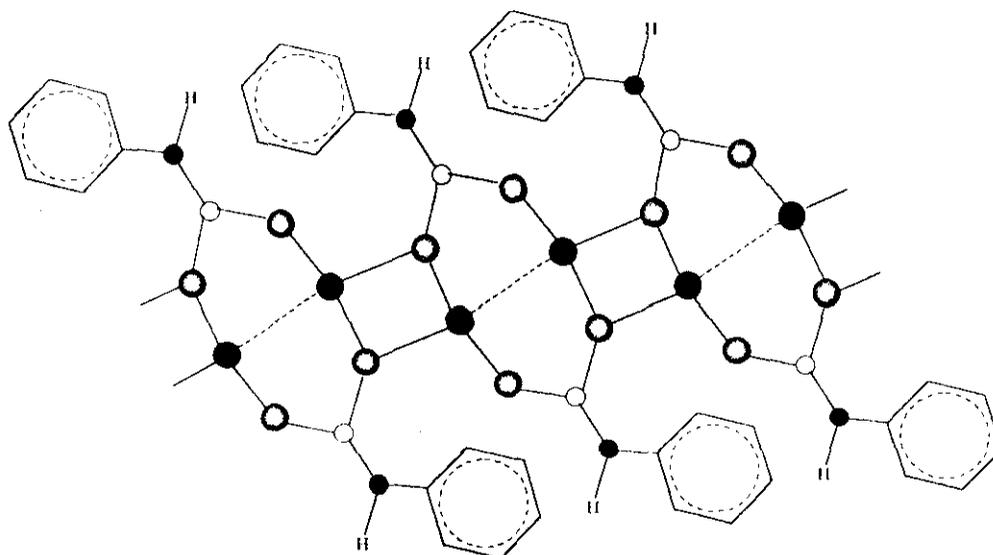


Figure 4.12. Stereochemical configuration of $[\text{Cu}(\text{Dtc})]_n$, the isotactic form

Only if the substituents on N are arranged in an isotactic fashion polymer can be stable without steric hindrance. If there are substituents at the ortho or meta position it will cause steric hindrance with S atom and NH of Dtc respectively. Rotation of the aryl ring about N-C α bond so as to avoid steric repulsion is not favoured because of the breakage of conjugation. In the case of non aromatic ring, where there is no conjugation of the nitrogen lone pair of electrons with aryl pi-electrons, rotation about N-C α is possible and hence, substitution at both the ortho or meta positions or one ortho and one meta on the opposite sides of the ring is required to prevent polymerisation like in the case of [Cu(PzDtc)]₂. If the N-substituent is an alkyl group, in the presence of two substituents (or more) at the α position, just as in α -amino acids except glycine, rotation about N-C α bond cannot avoid steric repulsion and polymer formation is impossible.

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