

CHAPTER

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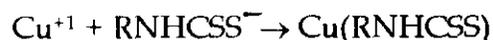
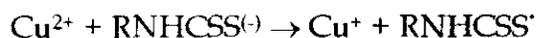
Summary and Conclusion

In the present study aimed at looking at the nature of interaction between copper(II) and dithiocarbamates derived from primary amines (N-monosubstituted dithiocarbamates, $\text{RNHCS}_2^{(-)}$ or RHDtc), a series of both alkyl and aryl substituted RHDtc are synthesised and their interaction with copper(II) investigated in detail. The reaction was carried out in various solvents like water ethanol, THF and DMF to know the effect of the solvent on the reaction. During the investigation a number of copper dithiocarbamate complexes were isolated which were analysed and studied by appropriate physicochemical methods. Many of the compounds are found to possess novel structures, never reported for copper dithiocarbamates so far. With a view to redox stabilise copper(II) ions various polymer supported RHDtc were developed and nature of species formed investigated.

Interaction of copper(II) with RHDtc was studied in aqueous medium by the controlled addition of cupric chloride solution to the dithiocarbamate solution. The dithiocarbamates generated and used in the present study are $\text{EtHNCS}_2^{(-)}$ (Et = C_2H_5 -), $\text{BuHNCS}_2^{(-)}$ (Bu = $n\text{-C}_4\text{H}_9$ -) $\text{BzHNCS}_2^{(-)}$ (Bz = $\text{C}_6\text{H}_5\text{CH}_2$ -) $\text{PhHNCS}_2^{(-)}$ (Ph = C_6H_5 -) $\text{pTHNCS}_2^{(-)}$ (pT = $\text{CH}_3\text{-}\langle\bigcirc\rangle$ -), $\text{pCHNCS}_2^{(-)}$ (pC = $\text{Cl-}\langle\bigcirc\rangle$ -) $\text{mCHNCS}_2^{(-)}$ (mC = $\langle\bigcirc\rangle$ -), $\text{pAHNCS}_2^{(-)}$ (pA = $\text{CH}_3\text{O-}\langle\bigcirc\rangle$ -) and $\text{CmHNCS}_2^{(-)}$ (Cm = HOOC-CH_2 -).¹ The reaction was monitored by stopping the addition of the salt solution by maintaining various Cu(II) : RHDtc molar ratios in the

reaction mixtures. The solid obtained was isolated and purified. The filtrate obtained in each case was also analysed by extraction and separation.

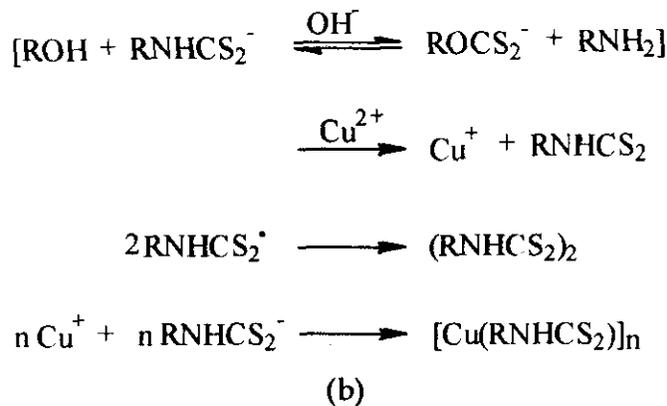
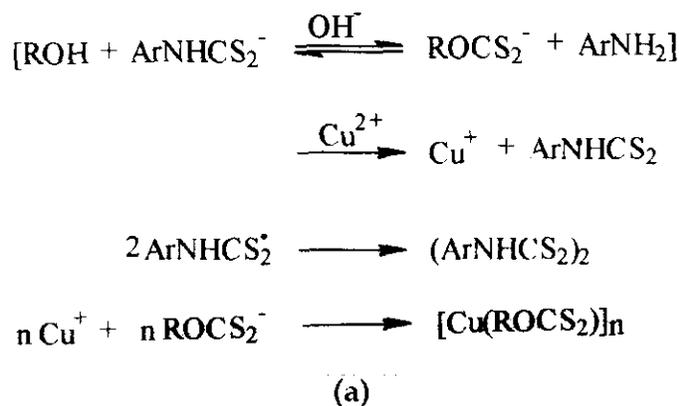
The results of the studies show that whatever may be the nature of the substituent on nitrogen atom, whether alkyl, aryl, aralkyl or aryl with electron withdrawing or electron donating groups, all N-monosubstituted dithiocarbamates almost always undergo oxidation induced by $\text{Cu}^{2+}(\text{aq})$ ions, thus clearly establishing the basic difference between N,N-disubstituted Dtc and N-monosubstituted Dtc with respect to their behaviour towards $\text{Cu}^{2+}(\text{aq})$ ions. While N,N-disubstituted Dtc are known to form dimeric bis complexes like $[\text{Cu}(\text{Et}_2\text{Dtc})_2]_2$ with $\text{Cu}^{2+}(\text{aq})$ ions RHDtc or ArHDtc get oxidised to form the corresponding N,N'-disubstituted thiuram disulphide, Cu^{2+} getting reduced to Cu(I) in the process. The excess Dtc ions present in the aqueous solution get coordinated to Cu(I) forming polymeric dithiocarbamates $[\text{Cu}(\text{Dtc})]_n$. Based on spectral, chemical and analytical data a structure analogous to that of cuprous acetate is proposed for these polymers. It is seen that for the quantitative reaction of Cu^{2+} with RHDtc a stoichiometry 1:2 is necessary. Based on this and also on the other observations made a suitable reaction mechanism could be proposed for the metal-RHDtc interaction.



Various RHDtc ions were generated *in situ* in ethanol medium also which were treated with ethanolic solution of Cu(II) ions by the same procedure as in aqueous medium. The products of interaction were isolated, purified and analysed. The Dtc⁻ generated in ethanol medium, on interaction with $\text{Cu}^{2+}(\text{aq})$, does undergo one-electron redox process, but the nature of the complex formed is seen to be different. It is seen that the nature of the product is decided by the substituent on the nitrogen atom of Dtc moiety.

Aliphatic N-substituted dithiocarbamates produce the polymeric cuprous complexes of the corresponding dithiocarbamate $[\text{Cu}(\text{RNHCS}_2)]_n$ while aryl substituted species studied, yield polymeric cuprous xanthate $[\text{Cu}(\text{CH}_3\text{CH}_2\text{OCS}_2)]_n$ in the alcohol medium. Steric factors and coordinating ability of the Dtc and xanthate, seem to be deciding which Cu(I) cluster, dithiocarbamate or xanthate, should be formed. However, in the cases of both alkyl and aromatic substituents, the oxidation products are the same, N,N'-substituted thiuram disulphide of the corresponding dithiocarbamate.

Based on this observations the following mechanism are proposed for the (a) metal-RHDtc and (b) metal-ArHDtc interaction in ethanol.



The results of the present study suggest that the literature reports of having isolated copper(II) complexes of dithiocarbamates derived from primary amines (N-monosubstituted dithiocarbamates) are incorrect. The

reported formation of Cu(II) complexes of RHDtc was checked and it was found that the redox process was invariably occurring in such system also as indicated above. The EPR inactivity and diamagnetic character of these complexes are attributed to the reduced state of copper and not due to the antiferromagnetic interaction and superexchange as suggested by these workers. They have wrongly reported a metal-ligand ratio of 1:2 for these complexes because they might have probably analysed a mixture of solid thiuram disulphide and the copper(I) complex and not the pure complex.

The effect of a reaction medium with reduced polarity on the redox reaction was studied by allowing the Cu^{2+} ions and dithiocarbamates to interact in solvents like dimethyl formamide and/or tetrahydrofuran. The dithiocarbamates studied are $\text{EtHNCS}_2^{(-)}$, $\text{BuHNCS}_2^{(-)}$, $\text{BzHNCS}_2^{(-)}$, $\text{pTHNCS}_2^{(-)}$, $\text{pCHNCS}_2^{(-)}$, $\text{mCHNCS}_2^{(-)}$, $\text{mTHNCS}_2^{(-)}$ ($\text{mT} = \text{C}_6\text{H}_4$), $\text{oTHNCS}_2^{(-)}$ ($\text{oT} = \text{C}_6\text{H}_4$), $\text{oCHNCS}_2^{(-)}$ ($\text{oC} = \text{C}_6\text{H}_3(\text{Cl})$), $\text{oAHNCS}_2^{(-)}$ ($\text{oA} = \text{C}_6\text{H}_3(\text{OCH}_3)$), $\text{PzHNCS}_2^{(-)}$ ($\text{Pz} = \text{C}_5\text{H}_4\text{N}(\text{CH}_3)_2$) and $\text{PAHNCS}_2^{(-)}$ ($\text{PA} = \text{HOOC}-\text{CH}_2-\text{C}_6\text{H}_4$).

The products were isolated, purified and analysed. The N-monosubstituted dithiocarbamates, which undergo redox reaction in aqueous medium forming their respective disulphides and polymeric cuprous dithiocarbamates, are seen not redox stabilised in THF or DMF medium also. But the complexes formed are found to possess different structures and stereochemistries which are dictated by the nature of N-substituent of the dithiocarbamate. Oligomers (dimers and tetramers) which are expected to have novel structures are isolated (Table 4.1⁵) summaries the dithiocarbamates studied in the present investigations and the number of monomeric units in their respective oligomeric copper(I) complexes.

Cu(I) complexes of N-alkyl Dtc are seen to form dimers. N-aryl Dtc with substituent at the ortho position also yield dimers. If there is no substituent at the ortho position of the phenyl ring tetramers are formed.

Based on spectral and other analytical data cuprous acetate type planar dimeric structure with coordination number two for Cu(I) is proposed for these dimers. Through sulphur bridges between dimers, planar tetramers can be formed with coordination number three and T shaped geometry for Cu(I). This is found to be so for $[\text{Cu}(\text{PhHNS}_2)]_4$, $[\text{Cu}(\text{mTHNS}_2)]_4$, etc. No Cu(I) dithiocarbamate with dimeric structure or planar tetrameric structure has been reported so far. The results of the study show that there is a relation between ν_{CN} and degree of oligomerisation of Cu(I) Dtc. Dithiocarbamate with greater CN double bond character (hence, higher ν_{CN}) tend to form dimers. The double bond character prevents free rotation about this bond so that it becomes impossible to attain a stable conformation with the four N-substituents as far apart as possible avoiding steric repulsion between them. Hence the formation of tetrameric species is prevented. Dtc with lower double bond character which allows rotation about CN bond exist as tetramers. Cu(BzHNDtc) though essentially a monoalkyl Dtc with double bond character for the CN bond, exists as tetramer because of the possible free rotation about N-CH₂Ph single bond keeping the four phenyl groups far apart avoiding steric repulsion.

Since planar bis(N-monosubstituted dithiocarbamate)nickel(II) complexes are known to undergo electrophilic substitution at the nitrogen atom, benzylation using benzoyl chloride in basic medium was attempted on the various copper(I) complexes isolated. Here the nature of the N-substituent was found to influence the reactivity of the dithiocarbamates. Only dimers and the tetramer $[\text{Cu}(\text{BzHDtc})]_4$ most probably with an isotactic stereochemistry can undergo benzylation. Benzylation does not bring about any steric strain in these molecules. Resistance of the tetramers and polymers towards benzylation which can be explained only on the basis of steric factors, supports the structures proposed for the dimers, tetramers and polymers. Dimers of N-aryl Dtc were demetallated when benzylation was attempted. This may be because of the poor coordinating ability of Dtc with a phenyl group and electron withdrawing-COC₆H₅ group on N, towards

copper(I). The benzoylated molecules are found to be tetrameric. To avoid steric strain the molecules must be having closed cubane structure of tetrameric $[\text{Cu}(\text{Et}_2\text{NCS}_2)]_4$.

There are some aliphatic and aromatic dithiocarbamates with substituents on specific positions of Ar or R, which failed to produce polymeric Cu(I) dithiocarbamates on interaction with Cu^{2+} in aqueous medium. The present study brings light on the nature of the N-substituent which prevents polymerisation. If the N-substituent is an aromatic ring presence of substituent groups at ortho or meta position prevents polymerisation. In the case of non aromatic ring, substituents at both the ortho position or meta position or one meta and one ortho position on opposite sides of the ring are necessary to prevent polymerisation. In case of N-alkyl substituent if both the α -hydrogen atoms with respect to Dtc moiety are substituted polymerisation is prevented. Steric factors brought about by the cuprous acetate type planar dimeric structure for these cuprous dithiocarbamates, linked by further sulphur bridges to form tetramers and staggered linear polymers, are therefore seem to impose the above restrictions for polymerisation to occur.

The redox process, on interaction of RHDtc with copper(II) involves the formation of neutral dithiocarbamate radicals which get dimerised to thiuram disulphide and also the simultaneous formation of cuprous dithiocarbamates which acquire stable geometry by cluster formation. With a view to redox stabilise copper(II) on interaction with RHDtc, the dithiocarbamate function was anchored to a polymer matrix and complexation attempted. Three polymer-supported ligands, $\text{P}^*-\text{NH}(\text{CH}_2)\text{NHCS}_2^{(-)}$, $\text{P}^*-\text{O}-\text{C}_6\text{H}_4-\text{NHCS}_2^{(-)}$ and $\text{P}^*-\text{O}-\text{C}_6\text{H}_3(\text{S}_2\text{CHN})-\text{NHCS}_2^{(-)}$, were prepared and allowed to interact with aqueous cupric chloride solution in the molar ratio 4:1 and the reacted polymer beads were washed, dried and probed mainly by EPR in the solid state at room temperature. The well-resolved EPR spectra suggested the formation of cupric complexes. Thus the redox behaviour of copper(II) is found to be drastically affected in the

presence of polymer bound primary amine derived dithiocarbamates; the Cu(II) state is seen redox stabilised. Immobilisation of the RHDtc function on the polymer support makes it impossible for the Cu(I) RHDtc that would be formed during the redox reaction to attain stability through cluster formation. It also prevents the neutral dithiocarbamate radicals, the oxidation product of the redox reaction, from coming close together and combining to form thiuram disulphide. The kinetic factors introduced by immobilisation of RHDtc, viz., high activation energy and energy barrier for the reaction path, inhibit the redox process and as a result the copper(II) complexes of the polymer bound RHDtc are formed. On interaction with Cu(II) ion the polymer bound dithiocarbamates are found to form two types of Cu(II) complexes, planar bis(dithiocarbamato)copper(II) complexes and planar diaquomonodithiocarbamatocopper(II) cation. Attempts to generate various mixed ligand copper(II) complexes involving one polymer bound dithiocarbamate ligand as one of the ligating species and either a Schiff base, β diketone or 8-hydroxyquinoline as other gave no positive result. Instead the planar bis(dithiocarbato)copper(II) complexes are always seen to be formed. This shows that the formation constants of the anticipated mixed ligand complexes are lower than those of both the Cu(II) chelates used and the planar bisdithiocarbamatocopper(II) complexes formed.

All the copper(I) complexes under the present study contain only sulphur-coordinated copper. However, the disposition of sulphur atoms around the metal ion might be different for the dimers, tetramers and polymers. To determine the effect of the stereochemistry of the complex and the nature of the N-substituent on the thermal behaviour, the phenomenological, kinetic and mechanistic aspects of thermal decomposition of seventeen different dimeric, tetrameric and polymeric Cu(I) dithiocarbamate complexes were studied. The thermogravimetric analyses of N-monosubstituted dithiocarbamatocopper(I) complexes show that most of these complexes undergo either two stage or three stage decomposition, quite

a few of them like $[\text{Cu}(\text{EtHNCS}_2)]_n$ decomposing completely in a single stage. The initial decomposition temperatures of the complexes as seen in the range of 106-165°C. Polymeric complexes are found to be thermally more stable than the oligomeric complexes. This could be attributed to the stability attained by the polymers through a large number of metal-metal and metal-sulphur bonds formed during polymerisation. The higher thermal stability of polymeric N-alkyldithiocarbamatecopper(I) complexes with bulkier groups suggests that the first stage of decomposition of the metal chelates may be occurring by the cleavage of CS bond and not MS bond. In the case of N-aryl substituted complexes also the first state of thermal decomposition occurs by the cleavage of CS bond. This is clearly indicated by the nature of the moieties evolved during the first decomposition stage. In the case of amino acid-derived dithiocarbamate complexes, the decomposition pattern is found to be interesting and entirely different. The decomposition seems to be initiated by the cleavage of the C-C or C-N bonds and not C-S bond.

The observed values of activation energy in different stages of thermal decomposition of the present complexes are in the range 48 to 350 kJ mol^{-1} and the values of entropy of activation in the range 52 to -260 J mol^{-1} . But no definite trend is observed either in the value of entropy of activation or in the values of activation energy among the different stages of thermal decomposition of the same complex. It is seen that $[\text{Cu}(\text{Ph HNCS}_2)]_n$ is the only complex with a positive value of entropy of activation. The values of entropy of activation indicate that the activated complex has a more ordered structure than the reactant. It is found that system requiring lower entropy of activation, whether positive or negative need higher energy of activation for its thermal decomposition.

Definite trends are found in the values of both E and ΔS for the first stage of thermal decomposition of the complexes. These are discussed in details. Activation energy is found to be always higher for the polymer with a less negative value of ΔS than for the corresponding oligomers. It is also

found that among polymeric N-alkyldithiocarbamatocopper(I) complexes, the larger the volume occupied by the R group the higher the value of E and the less negative the value of ΔS . Among the N-aryl dithiocarbamatocopper(I) complexes also the polymers require higher activation energy than the oligomers for the first stage of thermal decomposition. $[\text{Cu}(\text{oAHNCS}_2)]_2$ is the only oligomeric complex that is found to have a comparatively high value of activation energy. This could be due to the non-planarity of the molecule (as indicated by IR data). Among the polymeric complexes $[\text{Cu}(\text{PhHNCS}_2)]_n$ is found to require the maximum activation energy for the first stage thermal decomposition. The very low values of E for the first stage decomposition of aminoacid derived dithiocarbamate complexes of copper(I) indicate that the Dtc moiety may be strongly bound to the metal in the chelate thereby weakening the C-N or C-O bonds which undergo cleavage.

The various stages of thermal decomposition of the N-monosubstituted dithiocarbamatocopper(I) complexes are found to follow different mechanisms. Though the mechanisms for the second and third stages of thermal decomposition are not found to be directly influenced by the original geometry and stereochemistry of the complexes, these factors seem to influence the mechanism of the first stage of thermal decomposition of the complexes. While the polymeric complexes are generally found to have different mechanisms for their decomposition, all the oligomeric complexes except $[\text{Cu}(\text{oAHNCS}_2)]_2$, during the first stage of their decomposition follow the same mechanism, viz., random nucleation with one nucleus on each particle representing Mampel model. This could be attributed to the planarity of these oligomeric complexes.

In a nut-shell, the complexation characteristics of RHDtc with Cu(II) which is different from that of R_2Dtc under normal conditions, is drastically altered by restricting the mobility of the N-substituent group, by changing the chemical nature and size of the R group and by varying the reaction medium.

Various types of complexes, diaquodithiocarbamatocopper(II), bis(dithiocarbamato)copper(II), dimeric and tetrameric copper(I) complexes and polymeric cuprous complexes can be generated as desired by suitably varying the factors mentioned above. Many of these complexes are found to be differing in their thermal behaviour and chemical properties like electrophilic substitution. Some of these copper complexes are expected to mimic some important biological functions.

Extensive synthetic work has been undertaken in order to clarify the active site structures and the origins of the special properties of biosystems like copper proteins. These studies are based on the premise that the chemistry of copper proteins is largely dependent on the coordination structure of the active sites. Accordingly the synthesis, characterisation, and reactivity of low molecular weight copper complexes with ligands designed to mimic structurally the copper sites in proteins have been a major topic in current bioinorganic chemistry. This would help, to a large extent, to gain insight into the structures and functions of active sites of proteins. The present dimeric and tetrameric copper(I) complexes with novel structure and stereochemistry are, most probably, suitable candidates for mimicking the functions of biosystems like superoxide dismutases and type III copper proteins. In the dimeric and tetrameric complexes there are two copper centres in close proximity and, at the same time, connected by Dtc function. Dithiocarbamate ligands are well known for their ability to mediate magnetic interaction between metal centres by superexchange mechanism. These ligands are also noted for their ability to stabilise metal ions in their unusual oxidation states. Because of these structural features, the dimers and tetramers or their partially oxidised products are expected to be very good models in biomimetic chemistry. Studies on these lines are envisaged.

