

## Preface

**N**-substituted carbamodithioates, popularly known as dithiocarbamates, form a class of compounds which find extensive use in chemical industry. These compounds are widely used as vulcanisation accelerators, floatation agents, fungicides, pesticides, radiation protectors, antioxidants and photostabilisers of polymers. They find use in organic synthesis and inorganic qualitative analysis in addition of their practical application in medicine and biology. In spite of the fact that these compounds have been extensively studied owing to their interesting ligation characteristics and possible wide applications, there is a relatively unattended aspect of dithiocarbamate coordination chemistry—ligation characteristics of dithiocarbamates towards an important transition metal ion,  $\text{Cu}^{2+}$  especially with those derived from primary amines. While most of the metal ions show comparable ligation characteristics with both *N,N*-disubstituted and *N*-monosubstituted dithiocarbamates, copper(II) appears to be exhibiting unusual and ambiguous reactivity characteristics towards *N*-monosubstituted dithiocarbamates. Only a few literature reports are available on the interaction of these dithiocarbamates with copper(II) and we find some of them unreasonable, conflicting and quite often contradictory. Whereas early studies indicated the instability of  $\text{Cu(II)}$  complexes of *N*-monosubstituted dithiocarbamates and their instantaneous decomposition by some unknown mechanism, most of the later workers have claimed and reported the isolation of their cupric complexes.

We probe in detail, in the present investigation, the nature of interaction between copper(II) and *N*-monosubstituted dithiocarbamates. A variety of reaction conditions were tried to study their effects on the reaction. A series of *N*-monosubstituted dithiocarbamates with various *N*-substituents, like alkyl, aryl, aralkyl, heterocyclic and aryl with electron donating or electron withdrawing groups were generated and used. A variety of reaction medium like water, ethanol, tetrahydrouran and dimethyl formamide were employed. The reaction was carried out even on polymer support by immobilising the monosubstituted dithiocarbamate on it. Several very interesting observations were noted. Many of the conflicting literature reports on the subject could be reexamined in detail and discuss the chemistry involved in them quite convincingly. During the course of this investigation we could isolate a wide variety of copper complexes which were studied extensively by various analytical techniques. Many of these compounds are found to possess novel structure and interesting stereochemistry, never reported so far for copper dithiocarbamate complexes. Being buried in an entirely *S* surrounded "cavity" with the possibility of 2, 3 or 4 coordination the soft  $\text{Cu(I)}$  ions in these complexes is expected to show interesting reactivity properties. Besides probing some electrophilic substitution reaction, attempts were also made to investigate on their thermal decomposition characteristics which showed some interesting dissociation properties.

The structures of most of these copper(I) *N*-monosubstituted dithiocarbamates are seen to be very unique and hence they are expected to be very good candidates for mimicking several important biological functions.

It is hoped that the results of the present study would go a long way in understanding the functioning of biosystems like copper proteins and related metalloenzymes.