

### COPPER (I) DITHIOCARBAMATES

THE formation of dithiocarbamate complexes of transition metals, which have different oxidation states, is often accompanied by redox reactions<sup>1</sup>. Thus, Mn(II), Fe(II) and Co(II) are oxidized to trivalent states<sup>2</sup>, whereas permanganate and dichromate are readily reduced to lower oxidation states<sup>3</sup>. In the case of copper only Cu(II) dithiocarbamates have so far been reported. In the present work, the isolation of dithiocarbamate-copper(I), diethyldithiocarbamate-copper(I), dibenzyl-dithiocarbamate-copper(I) and morpholyldithiocarbamate-copper(I) and some of their characteristics have been reported.

The Cu(I)-dithiocarbamates were prepared by the addition of aqueous dithiocarbamate solutions to aqueous solutions of trithiourea-copper(I) perchlorate. The molar ratio of dithiocarbamates to Cu(I) was kept normally at 2 : 1. Greyish-brown precipitates were immediately formed, which were filtered, washed with water and air-dried. The analytical data are given in Table I.

TABLE I

Name of the compound	Found %					Required %				
	Cu	C	H	N	S	Cu	C	H	N	S
Dithiocarbamate-copper(I) (CH <sub>2</sub> NS <sub>2</sub> Cu)	40.16	7.86	1.32	8.81	40.68	40.82	7.71	1.29	9.00	41.39
Diethyldithiocarbamate-copper(I) (C <sub>5</sub> H <sub>10</sub> NS <sub>2</sub> Cu)	30.46	27.93	4.66	6.56	29.71	30.00	28.36	4.76	6.61	30.28
Dibenzyl-dithiocarbamate-copper(I) (C <sub>15</sub> H <sub>14</sub> NS <sub>2</sub> Cu)	18.46	54.11	4.22	4.23	19.62	18.22	53.61	4.20	4.17	19.09
Morpholyldithiocarbamate copper(I) (C <sub>5</sub> H <sub>8</sub> NOS <sub>2</sub> Cu)	28.36	28.62	3.62	6.11	27.87	28.15	26.60	3.57	6.20	28.41

All the compounds were diamagnetic in conformity with the Cu(I) oxidation state. Attempts to get single crystals of the compounds by dissolving in solvents such as methylene chloride, chloroform, carbon tetrachloride, benzene, acetone, resulted in the disproportionation of the greyish-brown dithiocarbamate into Cu(O) and black Cu(II) dithiocarbamates. After filtering off the Cu(O), the solution on evaporation gave Cu(II)-dithiocarbamates which were characterized by chemical analysis and paramagnetic behaviour. From this, one would note that, whereas some S-ligands such as thiourea, thiocyanate and mercapto groups stabilize the Cu(I)-oxidation state, others such as thiosemicarbazide and dithiocarbamates favour the formation of Cu(II). The electronic factors which are responsible for this reversal of behaviour warrant theoretical study.

The infrared spectra of the complexes indicate three bands which are characteristic of 'thiouride' band near 1500 cm<sup>-1</sup>, NC<sub>2</sub> band near 1140 cm<sup>-1</sup> and C = S band near 1000 cm<sup>-1</sup>. Though it

is difficult from the spectral frequencies to predict the stereochemistry of copper in the complexes, the presence of single band around 1000 cm<sup>-1</sup> suggests that the dithiocarbamates are chelating in all the complexes<sup>4</sup>. The far-infrared spectra of the compounds gave a strong band around 340 cm<sup>-1</sup> which is attributed to the Cu-S stretching frequency<sup>5</sup>.

As indicated earlier, dissolution of Cu(I)-dithiocarbamates in solution led to very fast disproportionation. The electronic spectra of the filtered solutions with CHCl<sub>3</sub> as solvent, gave three intense bands around 430, 300 and 270 mμ which are characteristic of the dithiocarbamate ligand moiety<sup>6,7</sup> in Cu(II)-complexes.

The thermal behaviour of Cu(II)-dithiocarbamates was studied on recording Stanton thermobalance. The temperatures of incipient decomposition of dithiocarbamate-copper(I) was 110° and for other complexes around 190° which are slightly higher than the corresponding Cu(II)-complexes<sup>8</sup>. All the compounds gave CuO as the final product around

750° via the formation of Cu<sub>2</sub>S and basic copper sulphates.

The X-ray powder pattern of the Cu(I)-complexes gave very diffuse lines because of the non-crystallinity of the preparation. However, the lines of Cu metal and of Cu(II)-dithiocarbamates were not seen in the pattern, thus confirming the homogeneity of the complexes.

Department of Chemistry, M. R. UDUPA,  
Indian Institute of Technology, G. ARAVAMUDAN,  
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