Thermochimica Acta, 8 (1974) 439–446

THERMAL STUDIES ON NICKEL(II) AND COPPER(II) COMPLEXES OF MONOETHANOL- AND DIETHANOL-DITHIOCARBAMIC ACIDS

BOOKHARI ANNUAR, J. O. HILL AND R. J. MAGEE

Department of Inorganic and Analytical Chemistry, La Trobe University, Bundoora, Victoria 3083 (Australia)

(Received 13 August 1973)

ABSTRACT

Thermoanalytical data (TG/DTA) have been obtained for bis-monoethanoldithiocarbamato nickel(II) and bis-diethanoldithiocarbamato nickel(II) and copper-(II) complexes. A thermal decomposition mechanism is proposed for bis-monoethanoldithiocarbamato nickel(II).

INTRODUCTION

Although the formation of disubstituted dithiocarbamates by the reaction of a secondary amine and carbon disulphide is well established, the reaction between aminoalcohols and carbon disulphide is not well known and few investigations have been reported.

Haas and Schwarz[1] prepared ammonium diethanoldithiocarbamate and proposed it as a new reagent for the spectrophotometric determination of molybdenum and uranium. The only reference to a monoethanolamine derivative is that by Nathsen[2]. This author claimed that the product formed in the reaction between ethanolamine and carbon disulphide reacts with metal ions to give characteristic precipitates.

In the present work, the reaction between monoethanolamine and carbon disulphide and diethanolamine and carbon disulphide was investigated and complexes with copper and nickel isolated and characterised. Thermal studies (TG/DTA) on the complexes were carried out and the thermal decomposition products analysed mass spectrophotometrically. No thermoanalytical data exists in the literature for such complexes.

EXPERIMENTAL

Preparation of the mono- and di-ethanol-dithiocarbamate complexes of copper and nickel

For the mono-derivatives, the procedure of Nathsen[2] was examined and found unsatisfactory. The following procedure was developed. CS_2 was added slowly with stirring to a small excess of ethanolamine in cold water. The viscous product which formed was kept in ice for 2 hours. It was not possible to isolate the viscous product as a solid or as the sodium salt, and it was used directly to form the nickel and copper complexes. The green nickel complex was recrystallised from ethanol. The yellow copper(I) complex was not stable.

For the di-ethanol complexes, the procedure of Haas and Schwarz[1] was used to prepare ammonium diethanol-dithiocarbamate. The nickel and copper complexes were prepared by reacting the reagent in aqueous solution with nickel chloride and copper sulphate solutions, respectively. Both complexes were re-crystallised from ethanol. The analytical data for the mono- and the di-ethanol-dithiocarbamate complexes are shown in Table 1.

TABLE 1

ANALYTICAL DATA FOR MONOETHANOL- AND DIETHANOL-DITHIOCARBAMATE DERIVATIVES

Complex	*Formula*	*M. pt. (°C)*		*C*	*H*	*N*	*S*
(Mono-Etol-DTC)$_2$Ni	$(HOC_2H_4NHCS_2)_2Ni$	170	Found	22.2	4.0	8.4	38.8
			Calcd.	21.8	3.6	8.5	38.7
(Di-Etol-DTC)$_2$Ni	$[(HOC_2H_4)_2NCS_2]_2Ni$	220	Found	28.7	4.9	6.8	30.4
			Calcd.	28.6	4.8	6.7	30.6
(Di-Etol-DTC)$_2$Cu	$[(HOC_2H_4)_2NCS_2]_2Cu$	172	Found	28.6	4.9	6.6	30.2
			Calcd.	28.3	4.8	6.6	30.2

TG/DTA data

Simultaneous TG/DTA thermograms (temperature range ambient to 900 °C) were obtained using a Stanton Thermobalance (Model TR01) with the Stanton DTA Attachment (Model STA 661), employing an air atmosphere and a heating rate of 4 °C per minute.

Mass spectral data

Mass spectra were obtained using a 12 inch radius 60° magnetic sector quadrupole mass spectrometer constructed by the Department of Physical Chemistry, La Trobe University.

RESULTS AND DISCUSSION

From investigations carried out by the authors using infrared, ultraviolet, visible and magnetic measurements and reported elsewhere[3], it was concluded that both nickel complexes have a square planar structure, while the structure of the copper diethanol-dithiocarbamate complex was square pyramidal. From the infrared studies, there was also evidence of intra-molecular hydrogen bonding in the nickel mono-ethanol-dithiocarbamate and polymolecular association of hydroxyl groups in the nickel and copper diethanol-dithiocarbamates.

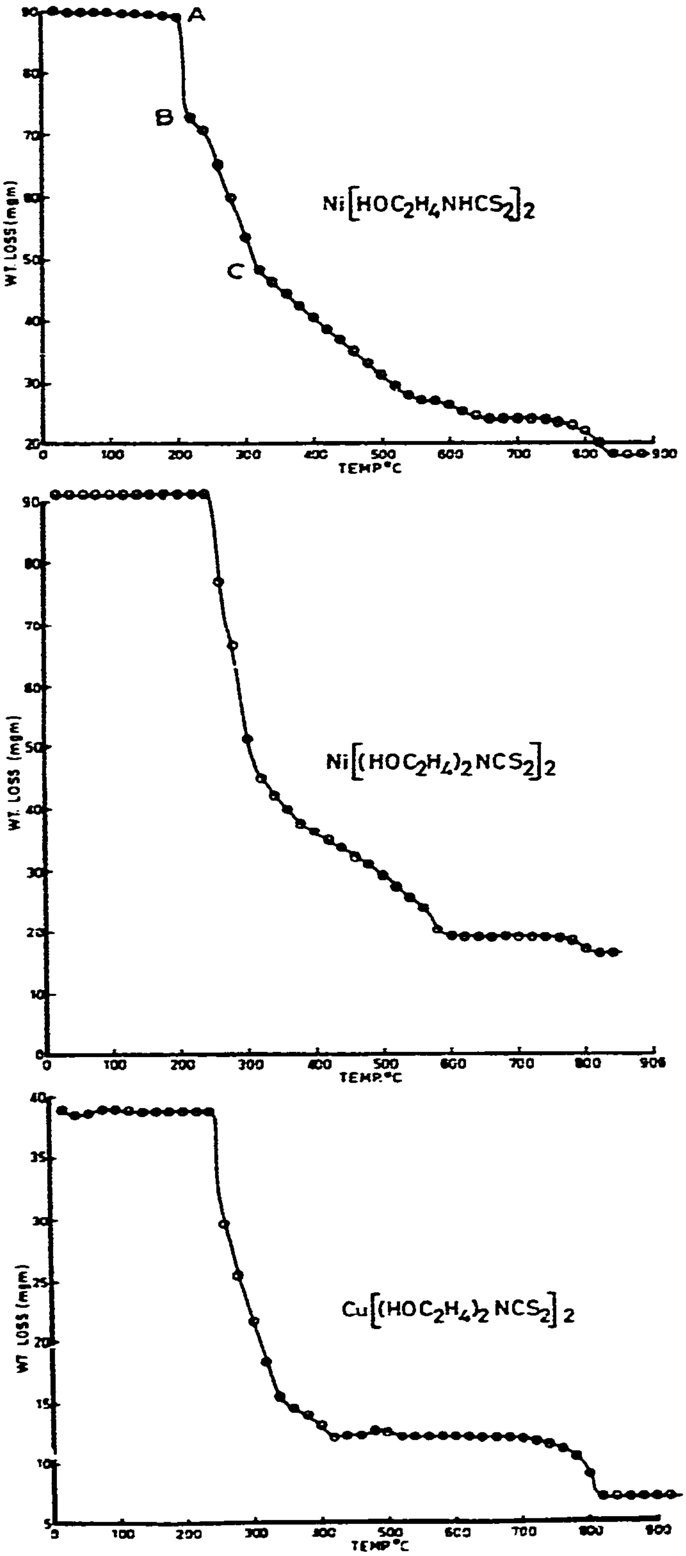

Fig. 1. TG curves of nickel monoethanol-dithiocarbamate, nickel diethanol-dithiocarbamate and copper diethanol-dithiocarbamate.

If intra-molecular hydrogen bonding and polymolecular association of hydroxyl groups is present, it would seem that it might be reflected in the thermal decomposition modes of the complexes.

Thermogravimetric data

The TG curves for all three complexes are reproduced in Fig. 1 and are fundamentally similar, but differ from the non-stepwise TG curve of the alkyldithiocarbamates, e.g., Fe(III) diethyl-dithiocarbamate[4]. Further, Lyalikov and Kitovskaya[5] have suggested that a step-wise thermal decomposition mode is characteristic of dithiocarbamate complexes with cyclic structures, i.e., where interaction occurs between substituent groups on the nitrogen atom.

For the three complexes studied, the rate of initial decomposition (210–215°C: $Ni[HOC_2H_4NHCS_2]_2$; 250–300°C: $Ni[(HOC_2H_4)_2NCS_2]_2$ and $Cu[(HOC_2H_4)_2NCS_2]_2$) is rapid, but relaxation of the primary decomposition is apparent at a lower temperature for nickel(II) monoethanol-dithiocarbamate than for nickel(II) and copper(II) diethanol-dithiocarbamates, thus reflecting the presence of an additional C_2H_4OH grouping in the latter two complexes.

The stable intermediate formed at 660°C (nickel(II) monoethanol-dithiocarbamate) and at 600°C (nickel(II) diethanol-dithiocarbamate) was found from the calculated weight loss to be nickel sulphide. All complexes yielded the metallic oxide as the final non-degradable residue.

DTA data

The DTA curves of the three complexes are reproduced in Fig. 2(i), (ii) and (iii). The data show that the complexes begin to decompose just prior to melting; the

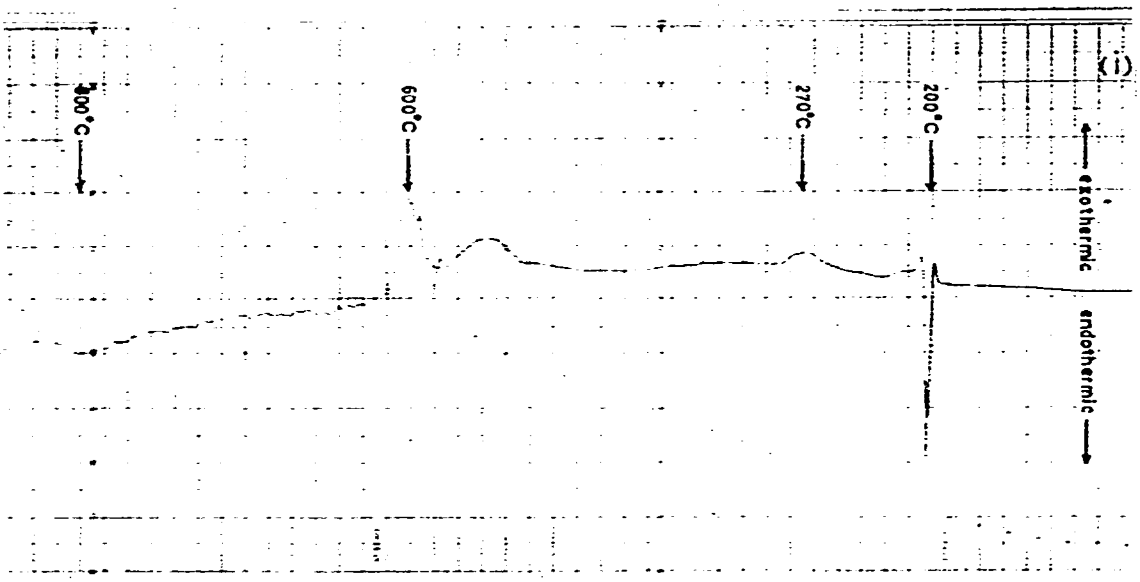

Fig. 2.

Fig. 2. DTA curves of (i) nickel monoethanol-dithiocarbamate. (ii) nickel diethanol-dithiocarbamate and (iii) copper diethanol-dithiocarbamate.

melting point is indicated by a sharp endothermic peak. For the two nickel complexes, a stable intermediate first appears at about 600 °C, whereas for the copper complex the corresponding intermediate appears at about 500 °C. In all three cases, these stable intermediates decompose to a final non-degradable residue at about 800 °C.

The DTA curve of copper(II) diethanol-dithiocarbamate, Fig. 2(iii), shows a unique endothermic peak at 200 °C which may indicate the formation of a monomeric species. The DTA curve of nickel(II) diethanol-dithiocarbamate, Fig. 2(ii), with the appearance of a strong exothermic peak at approximately 300°C, confirms that this complex degrades by a different mechanism from nickel(II) monoethanol-dithiocarbamate and copper(II) diethanol-dithiocarbamate.

Mass spectral data

Mass spectra for nickel(II) mono- and diethanol-dithiocarbamates and copper(II) diethanol-dithiocarbamate are reproduced in Fig. 3(i), (ii), (iii). The mass spectra of nickel(II) monoethanol-dithiocarbamate and copper(II) diethanol-dithiocarbamate show strong peaks at m/e = 76 characteristic of carbon disulphide, whereas this peak is markedly absent in the mass spectrum of nickel(II) diethanol-dithiocarbamate which reinforces the DTA evidence for a unique thermal decomposition mechanism for this complex.

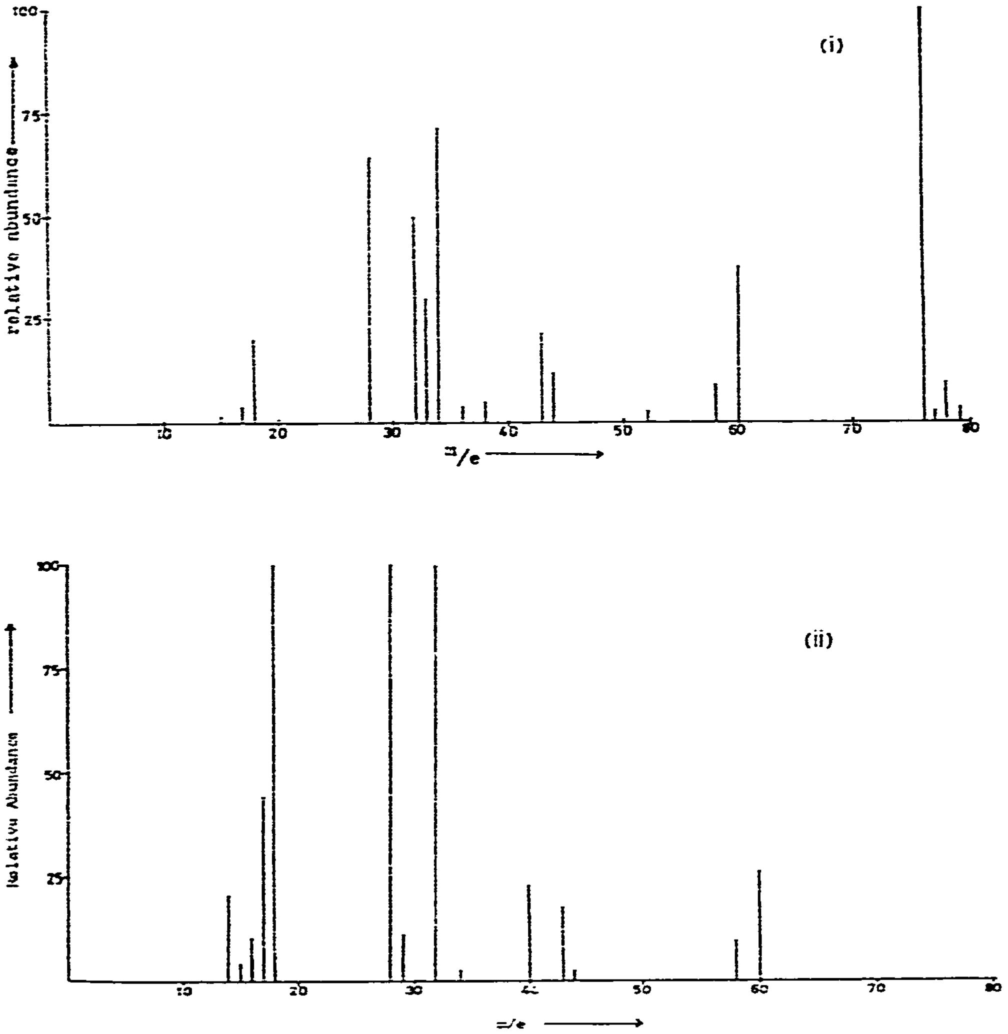

Fig. 3.

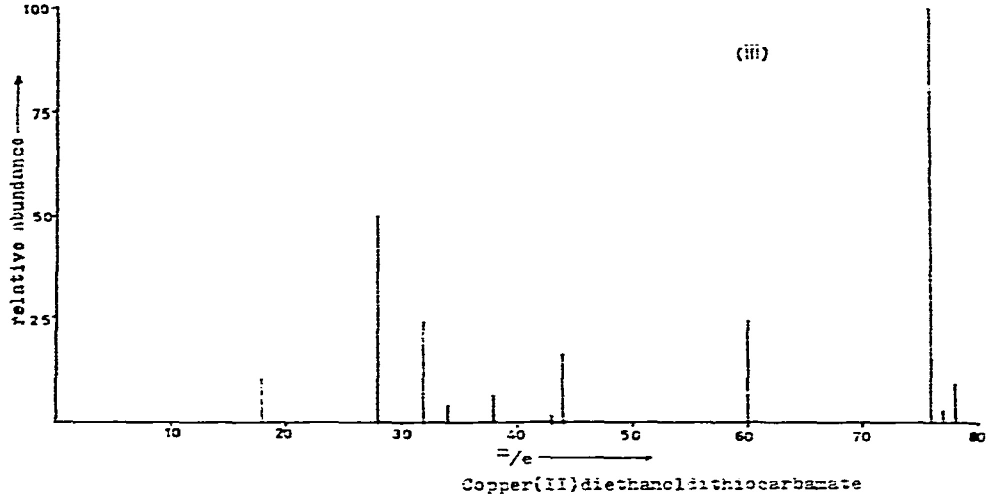

Fig. 3. Mass spectra of (i) nickel monoethanol-dithiocarbamate and (ii) nickel diethanol-dithiocarbamate. (During this recording there was some trouble with an air leak.) (iii) Copper diethanol-dithiocarbamate.

Thermal decomposition mechanisms

It is highly speculative to give a detailed thermal decomposition mechanism for each complex in the absence of complete crystal structure data. Further, although mass spectral analysis identifies the gaseous fragments of the thermal degradation, the different heating rates associated with TG/DTA analyses and mass spectral analysis modify the decomposition mode of the complex: the more abrupt heating rate associated with the mass spectral analysis eliminates step-wise decomposition. Such divergent analytical conditions between TG/DTA and MS therefore render any proposed thermal decomposition mechanism approximate. It is, however, evident from the mass spectral data that each complex thermally degrades by a different mechanism and the following thermal decomposition mechanism is suggested for nickel(II) monoethanol-dithiocarbamate (Fig. 4, Fig. 3(i)). Upon melting, (200 °C), intra-molecular hydrogen bonding is destroyed and the complex decomposes rapidly (region AB Fig. 1), yielding ethanolamine (m/e = 60), and the evolution of carbon disulphide (m/e = 76) (region BC Fig. 1). The intermediate nickel(II) species formed at

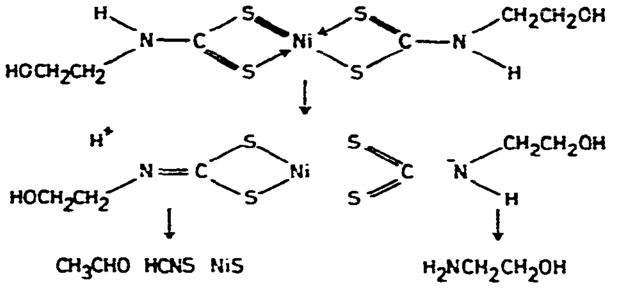

Fig. 4. Thermal decomposition mechanism of nickel monoethanol-dithiocarbamate.

C (Fig. 1), $HOCH_2CH_2NCS_2Ni$ degrades slowly to NiS (m/e = 44), acetaldehyde (m/e = 43) and thiocyanic acid HCNS (m/e = 58). The final non-degradable residue is NiO. It is not possible to propose an unambiguous thermal decomposition mechanism for nickel(II) and copper(II) diethanol-dithiocarbamates with the thermoanalytical data presented herein.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge Mr. John F. Smith, Department of Physical Chemistry, La Trobe University for kindly providing the mass spectral analysis data, and one of us (B. A.) thanks the National University of Malaysia, Kuala Lumpur for financial support.

REFERENCES

1 W. Haas and T. Schwarz, *Microchim. Ichnoanal. Acta*, (1963) 253.
2 B. Nathsen, *Search*, 2 Feb. 1971.
3 B. Annuar, J. O. Hill and R. J. Magee, *J. Inorg. Nucl. Chem.*, in press.
4 G. D'Ascenzo and W. W. Wendlandt, *J. Inorg. Nucl. Chem.*, 32 (1970) 2431.
5 Y. S. Lyalikov and M. I. Kitovskaya, *J. Therm. Anal.*, 4 (1972) 271.