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# A thermal analysis study of dialkyldithiocarbamato nickel(II) and copper(II) complexes

B.F. Ali[a], W.S. Al-Akramawi[b], K.H. Al-Obaidi[a,*], A.H. Al-Karboli[c]

[a] Chemistry Department, Al al-Bayt University, P.O. Box 130155, Mafraq, Jordan
[b] Chemistry Department, Applied Sciences University, Amman, Jordan
[c] Chemistry Department, University of Baghdad, Baghdad, Iraq

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## Abstract

A TG, DTG, and DSC study of $Ni[S_2CN(C_3H_5)_2]_2{\cdot}H_2O$ and $Cu[S_2CN(C_3H_5)_2]_2$ has been reported together with the associated thermal decomposition mechanisms. These mechanisms are rationalized in terms of the structure of the complexes and the nature of the intermediate products and final residues. The thermal analysis to NiS occurs by initial elimination of $S_2CN(C_3H_5)_2$, $C_3H_5$ and subsequent loss of $C_3H_5$–N=C=S. While the pyrolysis to CuS occurs via $Cu[S_2CN(C_3H_5)_2][SCN–C_3H_5]$ and by sequential elimination of $S_2CN(C_3H_5)_2$ followed by elimination of RCN. These dithiocarbamate complexes, thus provide a source for metal sulfide materials such as NiS and CuS.

*Keywords:* Thermal analysis; Dithiocarbamato complexes

## 1. Introduction

Dithiocarbamate complexes containing variously substituted dithiocarbamato groups have been investigated extensively from several aspects. These studies were to explain the role of these compounds in vulcanization, high pressure lubricant agents, fungicides and pesticides [1–4]. The thermochemistry of metal dithiocarbamate has been extensively reported and reviewed [5–10]. But relatively little is known about metal diallyldithiocarbamates such as $Ni[S_2CN(C_3H_5)_2]_2$, $Cu[S_2CN(C_3H_5)_2]_2$ and some of their derivatives of the general formula $M[S_2CN(C_3H_5)_2]_2L$; $M = Ni$ or Cu, $L = Ph_3P$, $Ph_3As$, py) which were prepared recently [11]. These may be considered as analogous to the complexes appeared in the literature [5,12–14]. Dithiocarbamate complexes were considered the most promising species to provide single-source materials for bulk metal sulfides [15]. For example SnS and $SnS_2$ have been deposited from $(Et_2NCS_2)_2(RS)Sn$ and $(Et_2NCS_2)_4Sn$ ($R = Cy$, $CH_2CF_3$), respectively [5]. Moreover, MS ($M = Zn$, Cd) have also been deposited thermally from $M[S_2CN(Me)CH_2CH_2CH_2NMe_2]_2$ [16].

In the present work, a thermal analysis study of $Ni[S_2CN(C_3H_5)_2]_2{\cdot}H_2O$ and $Cu[S_2CN(C_3H_5)_2]_2$ is presented and the associated thermal decomposition mechanisms are proposed.

## 2. Experimental

### 2.1. Physical measurements

Infrared (IR) spectra were recorded as KBr plates using unicam SP3-300 (PYUNICAM) spectrophotometer, and elemental analyses were conducted on MOD 1106 (CARLOERBA STRUMENTZIONE) elemental microanalyzer. Electronic spectra were recorded on Shimadzu spectrophotometer. Magnetic measurements were performed on Bruker BM6 instrument using Faraday method. Thermal analysis studies were performed on Mettler TA 3000 thermogravimetric analyser using dynamic nitrogen atmosphere.

### 2.2. Preparation of the complexes

Sodium diallyldithiocarbamato ligand was prepared from diallylamine in similar manner to that reported for sodium dialkyl-dithiocarbamates [17]. The prepared ligand was treated with appropriate metal salt to give the required

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[*] Corresponding author.
*E-mail address:* bfali@alalbayt.aabu.edu.jo (K.H. Al-Obaidi).

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Ni and Cu complexes. These were fully characterized by IR, NMR, UV-Vis, magnetic measurements, and elemental studies. For Ni[$S_2CN(C_3H_5)_2]_2 \cdot H_2O$ (diamagnetic); (found: C 40.1, H 4.9, N 6.6; $NiS_4C_{14}H_{22}N_2O$, calc.: C 40.7, H 5.3, N 6.7%); The IR spectrum shows the characteristic stretching frequencies of $\nu_{(\text{allylic C–H})}$ and $\nu_{(\text{C–N})}$ (in $cm^{-1}$) at 2945(w) and 1516(s), respectively. The UV-Vis spectrum; $\lambda_{max}$ at 16,129 and 21,700 $cm^{-1}$.

For Cu[$S_2CN(C_3H_5)_2]_2$ ($\mu_{eff} = 1.3$ B.M.); (Found: C 41.9, H 5.2, N 6.8; $CuS_4C14H_{20}N_2$, calc.: C 42.1, H 5.0, N 7.0%); The IR spectrum shows the characteristic stretching frequencies of $\nu_{(\text{allylicC–H})}$ and $\nu_{(\text{C–N})}$ (in $cm^{-1}$) at 2945(w) and 1500(s), respectively. The UV-Vis spectrum; $\lambda_{max}$ at 15,527 $cm^{-1}$.

## 3. Results and discussion

### 3.1. Thermal decomposition studies

The selected compounds were placed into dried Schlenk tube against a dry $N_2$ flow at atmospheric pressure. The compounds were then heated to the desired temperature under static $N_2$.

#### 3.1.1. Thermal analysis of Ni[$S_2CN(C_3H_5)_2]_2 \cdot H_2O$

The TG of the complex Ni[$S_2CN(C_3H_5)_2]_2 \cdot H_2O$ (Fig. 1), shows the formation of the unhydrous complex by 172 °C, which indicates the loss of the water of hydration; between 232 and 360 °C further decomposition leads to $NiS_2CN(C_3H_5)$ (observed mass loss: 49.8; theoretical 50.7%) and finally a species of mass corresponding to NiS by 600 °C (observed residual mass: 22.5; theoretical 23.2%). These findings are consistent with the DTG curve which indicates that the progressive mass loss was started at 172 °C, and the rate of reaction increases as the temperature exceeds over 230 °C, reaching its maximum at 282 °C.

This is in good agreement with the DSC measurement. The DSC curve for this complex shows a melting at 113 °C followed by the second process of an exothermic reaction at 150–280 °C. A further exothermic changes commences at 298 °C, maximizes at 307 °C, and terminates at 335 °C, followed by a broad one at 365–440 °C.

The presence of more than one exothermic peak in the DSC curve, reveals that the pyrolysis occurs in several steps before reaching stable intermediate species (Fig. 1, Table 1).

To rationalise the above findings we propose the following:

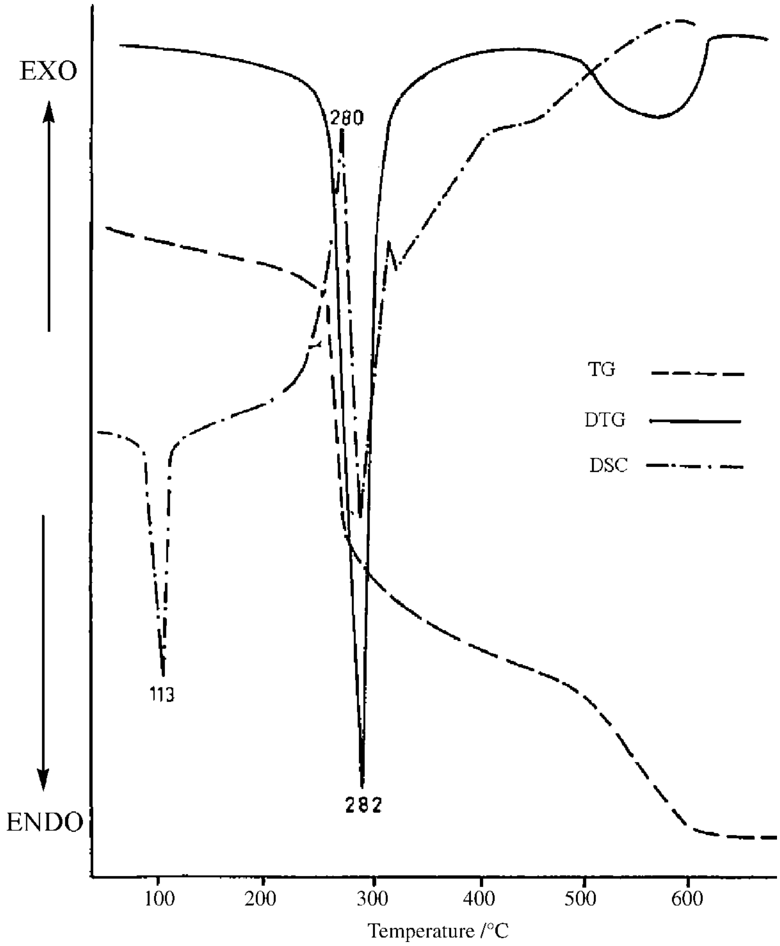


Fig. 1. TG/DTG/DSC curves for Ni[$S_2CN(C_3H_5)_2]_2 \cdot H_2O$.

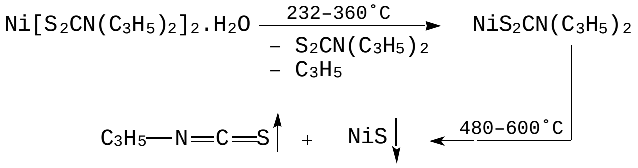
Table 1
TG/DTG/DSC studies for $Ni[S_2CN(C_3H_5)_2]_2{\cdot}H_2O$ and $Cu[S_2CN(C_3H_5)_2]_2$ under nitrogen atmosphere

| Specification | $Ni[S_2CN(C_3H_5)_2]_2{\cdot}H_2O$ | | | $Cu[S_2CN(C_3H_5)_2]_2$ | | |
|---|---|---|---|---|---|---|
| | First stage | Second stage | Third stage | First stage | Second stage | Third stage |
| Temperature range of decomposition, T (°C) | 230–360 | 400–600 | – | 200–260 | 260–415 | 440–720 |
| DTG peak, T (°C) | 282 | 560 | – | 242 | 300 | 525 |
| DSC peak, T (°C) | (113)[a] | | – | (110)[a] | | |
| | +280, −298 | +450, −477 | | (118,154)[b] | | |
| | +307, −355 | | | +250, −267 | +310, −345 | – |
| Percentage mass loss | | | | | | |
| Calculated | 50.7 | 23.2 | – | 17.9 | 42.3 | 16.5 |
| Found | 49.8 | 22.5 | | 16.8 | 41.6 | 15.7 |

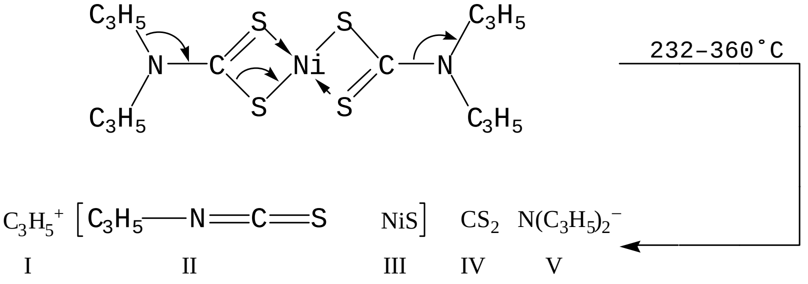
[a] Fusion temperatures.
[b] Exothermic temperatures without mass loss.

The decomposition of $Ni[S_2CN(C_3H_5)_2]_2$ appears to proceed by the sequential elimination of $S_2CN(C_3H_5)_2$ and $C_3H_5$. After this stage, the $NiS_2CNC_3H_5$ remaining will readily further decomposes to form NiS and $(C_3H_5)$–N=C=S, provided the temperature is in the range 480–600 °C, at which point the volatility of $C_3H_5$–N=C=S causes its separation from the NiS residue.

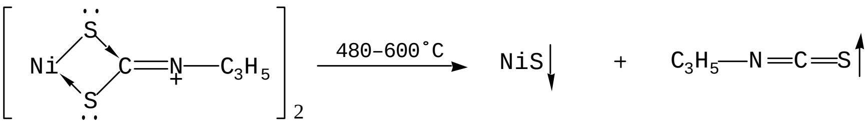
Based on the thermal analysis data, the thermal decomposition chemistry of $Ni[S_2CN(C_3H_5)_2]_2$ may be expressed as follows:



The thermal analysis data suggests that the proposed mechanism for the decomposition of $Ni[S_2CN(C_3H_5)_2]_2$ is in good agreement with the general pyrolysis of dithiocarbamato metal complexes [5,18,19]. The following diagram represents a detailed description of the mechanism and the species resulted in the first step of decomposition:



The process was then continues by the dimerisation of species II in the presence of NiS to give the stable intermediate $[(C_3H_5)NCS_2Ni]_2$ in situ, which then further decomposes in the second step of the decomposition to leave NiS by 600 °C. This step can be represented as follows:



### 3.1.2. Thermal analysis of $Cu[S_2CN(C_3H_5)_2]_2$

The TG curve (Fig. 2) shows an initial decomposition below 170 °C with a partial loss of mass that does not exceed 2%. After this process, the decomposition of the complex proceeds in essentially three stages (Fig. 2, Table 1). The first stage of decomposition between 200 and 242 °C shows a mass loss of 16.8% which correlates with the loss of $(C_3H_5)S$ (theoretical 17.9%). The second stage resulting in a further 41.6% weight loss between 300 and 445 °C that is consistent with the elimination of $S_2CN(C_3H_5)_2$ (theoretical 42.3%). The third stage of decomposition at 525–720 °C resulting in the loss of 15.7% and is probably a result of the loss of $(C_3H_5)CN$ (theoretical 16.5%). The mass remaining at this stage (24%) is in good agreement with the final product being CuS (theoretical 23.4%).

The TG results were confirmed by the data from the DSC curve of $Cu[S_2CN(C_3H_5)_2]_2$ which shows an endothermic peak of the fusion of the complex at 110 °C, followed by many exothermic processes operating in the range 118–154 °C without observed mass loss. Furthermore, another exothermic processes occurred as shown by the peaks between 175 and 198 °C and the peaks at 250 and 310 °C,

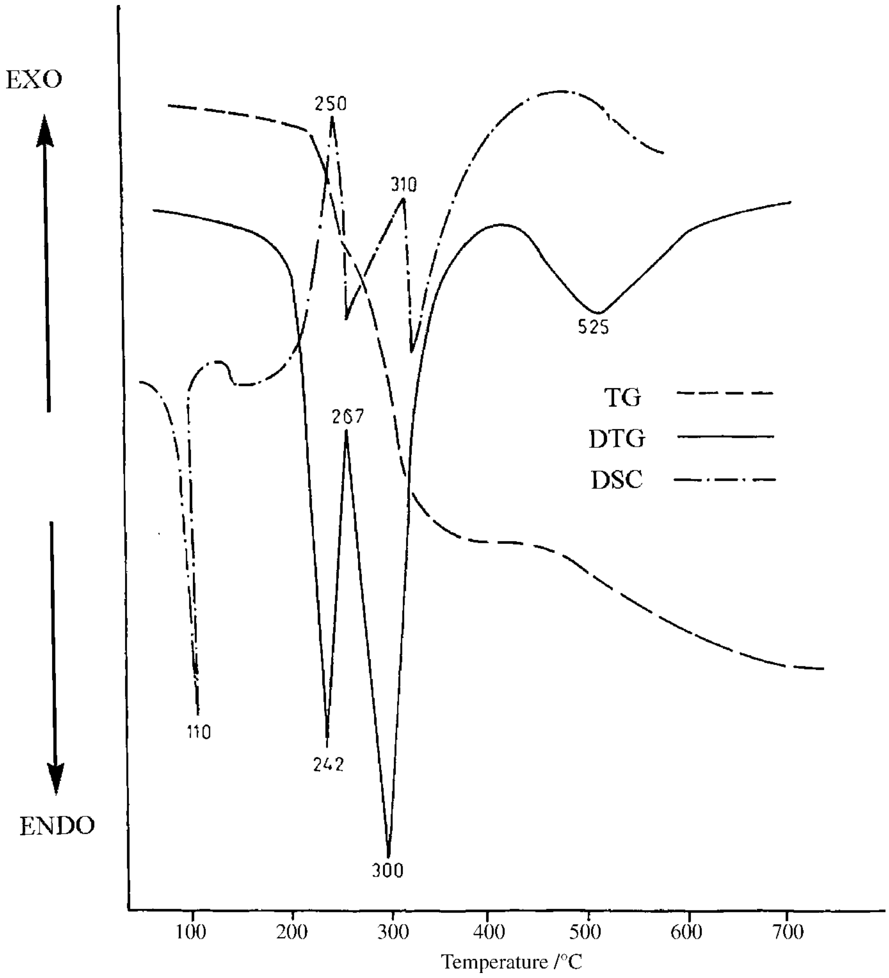
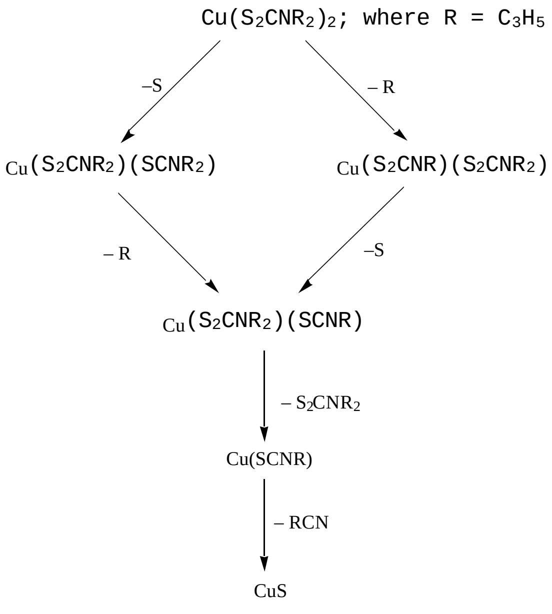


Fig. 2. TG/DTG/DSC curves for $Cu[S_2CN(C_3H_5)_2]_2$.

then the curve reaches the base line at 345 °C. Finally, the curve shows a continuous exothermic change above 360 °C.

Moreover, these findings are consistent with the DTG curve which shows three peaks at 242, 300 and 525 °C confirming the three stages of decomposition and the progressive mass loss observed in the TG curve as the temperature exceeds over 170 °C.

Thermal analysis results, suggests that the mechanism of decomposition of $Cu[S_2CN(C_3H_5)_2]_2$ occur in several steps before reaching stable intermediate species (Fig. 2, Table 1). Therefore, the mechanism of decomposition of the copper complex can be proposed to occur as follows: the first stage is the formation of $Cu[S_2CN(C_3H_5)_2(SCNR)]$ by the loss of allyl and sulfur groups, followed by complete loss of $S_2CN(C_3H_5)_2$, to form the intermediate $Cu[SCN(C_3H_5)]$. Finally the formation of copper sulfide is reached by the elimination of $(C_3H_5)CN$. The suggested mechanism for the thermal pyrolysis of copper diallyl complex can therefore be represented as follows:



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