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CHEMISTRY OF DITHIOCARBAMATE DERIVATIVES OF AMINO ACIDS. PART IV. THERMAL BEHAVIOUR OF NICKEL (II) COMPLEXES

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ABSTRACT

Thermal decomposition in nitrogen of nickel(II) complexes with dithiocarbamate of α-amino acids (glycine, DL-alanine, DL-valine and DL-leucine) has been studied Decomposition takes place in four well-defined steps corresponding to (i) loss of one ligand, (ii) formation of alkyl derivatives of 2,5-dioxopiperazine, (iii) formation of stoichiometric nickel sulphide, (iv) formation of non-stoichiometric nickel sulphide The corresponding compounds have been characterized by chemical analysis, X-ray diffraction and infrared spectroscopy

INTRODUCTION

Sharma has recently reviewed [1] the thermal behaviour of compounds containing metal-dithiocarbamates, this review clearly concludes that a great confusion exists on the decomposition paths of these compounds, as well as on the nature of intermediate and final compounds, this author suggesting that further investigations are needed to clarify insight in this field, using different metal cations and different dithiocarbamates

The aim of this paper is to assist in this elucidation Complexes of nickel(II) with dithiocarbamates derived from α-amino acids have been synthesized [2,3] and now we report their decomposition in an inert atmosphere Due to the huge number of compounds prepared so far, in this report, decomposition of four compounds are included, two from linear amino acids and two from branched ones, that is, $Ni(S_2C–NH–CH(R)–COOH)_2$, R = $-H$ (glycine, gly), $-CH_3$ (DL-alanine, ala), $-CH(CH_3)_2$ (DL-valine, val) and $-CH_2–CH(CH_3)_2$ (DL-leucine, leu)

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EXPERIMENTAL

Synthesis of the complexes has been described elsewhere [2,3], and it is carried out according to

$$\begin{aligned}&2Ba(S_2C\text{-}NH\text{-}CH(R)\text{-}COO)\\&\quad + Ni^{2+} \xrightarrow[(2)\ HCl]{(1)\ Et_2O} Ni(S_2C\text{-}NH\text{-}CH(R)\text{-}COOH)_2\end{aligned} \tag{1}$$

Characterization has been performed by chemical analysis, IR, V–UV and ^1H-NMR spectroscopic methods, magnetic measurements and optical rotatory dispersion [2,3]

Thermogravimetric (TG) curves have been obtained in flowing nitrogen (45 cm^3 min^{-1}) in a Perkin–Elmer TGS-2 instrument coupled to a data station, the heating rate was 12° C min^{-1}

Differential thermal analysis (DTA) was performed in a Perkin–Elmer 1700 instrument, using alumina to dilute the samples, with a heating rate of 12° C min^{-1} in flowing nitrogen (45 cm^3 min^{-1})

Infrared spectra of the successive decomposition residues at increasing temperatures were recorded in a double-beam Beckman Acculab 10 apparatus, using KBr pellets

Thermal decomposition to obtain the intermediates was carried out in flowing nitrogen, in order to achieve experimental conditions as close as possible to those used in TG and DTA, in a Heraeus ROK 3/60 tubular furnace

X-Ray diffraction diagrams have been recorded in a Philips PW 1030 instrument, using Ni-filtered Cu K_α radiation ($\lambda = 154\ 05$ pm) and standard conditions

Finally, chemical analyses were determined in Instituto de Química Bio-Orgánica (Barcelona, CSIC), using standard methods

RESULTS AND DISCUSSION

TG and DTA profiles for all four samples have been included in Figs 1–4 Summarized data are listed in Table 1

Decomposition takes place at 200–210° C, and a good fit between experimental and theoretical data for decomposition to NiS is observed

From the curves in Figs 1–4, decomposition of these complexes can be assumed to take place in four steps

Step 1 This step would correspond to the 145–215° C range for gly and ala derivatives, and 180–195° C for val and leu derivatives A net step is observed in the TG profile of the second couple of compounds in this temperature range A sharp endothermic effect is recorded in these temperature ranges in the DTA diagrams of all four samples

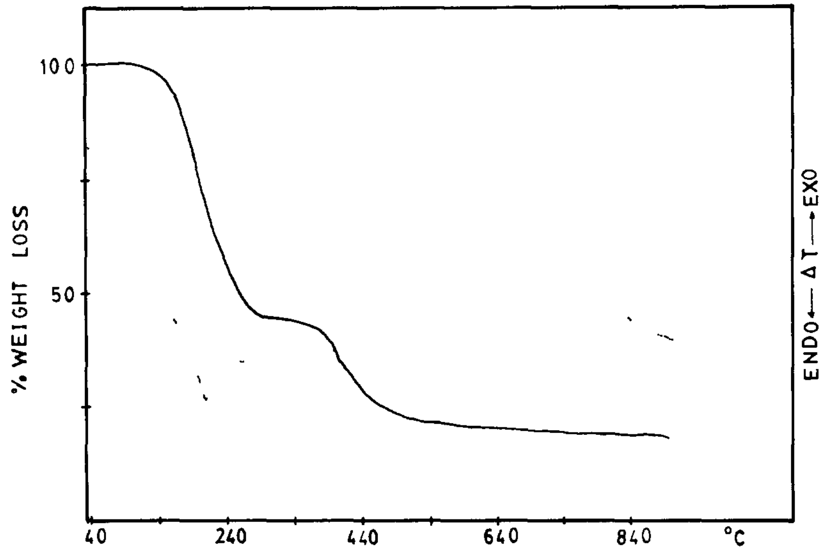


Fig 1 TG (solid line) and DTA (dotted line) profiles for Ni(dtc-gly)$_2$

The infrared spectra of the residues after heating at temperatures just above the endothermic effect (180–215 °C) show an intense absorption at 1550 cm^{-1} due to the carboxylate stretching mode, while the absorption at 1700 cm^{-1}, recorded in the spectra of the parent complexes and due to the C=O stretching mode of carboxylic acid (–COOH), is absent, (Fig 5) Other absorption bands are only slightly altered This behaviour is similar to that observed previously with other dithiocarbamate complexes [1,4–6]

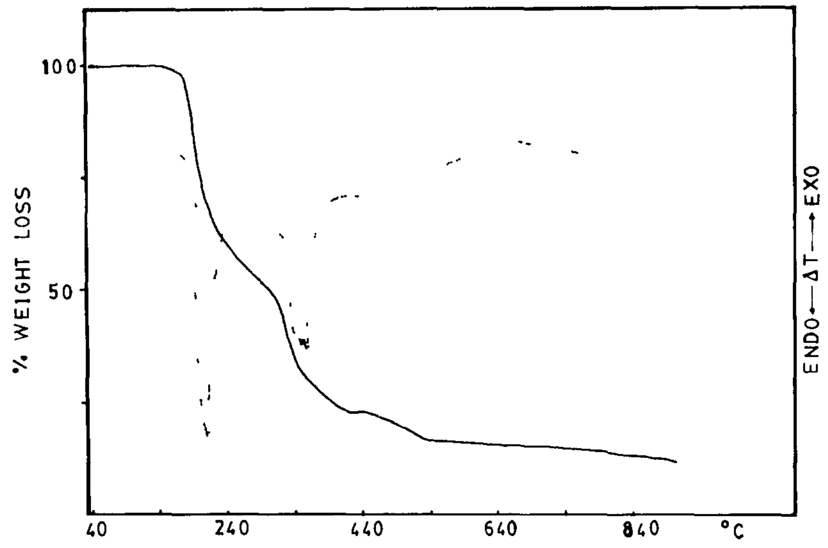


Fig 2 TG (solid line) and DTA (dotted line) profiles for Ni(dtc-DLala)$_2$

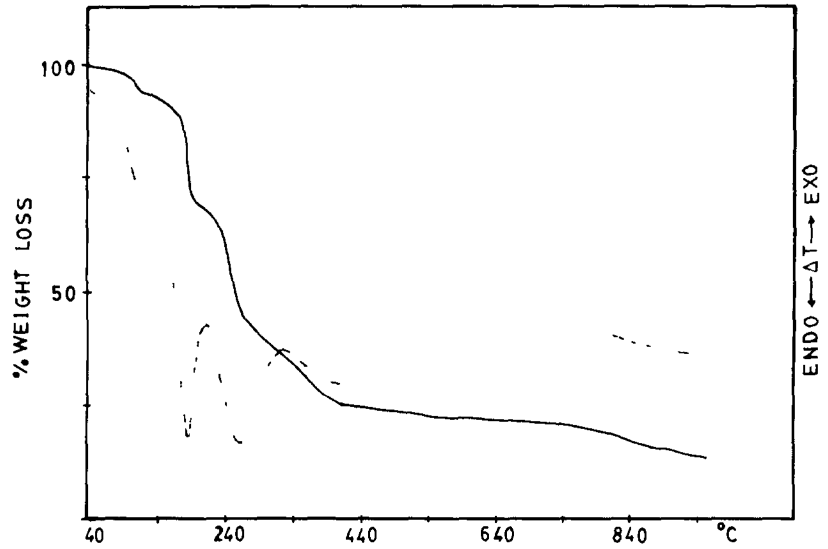


Fig 3 TG (solid line) and DTA (dotted line) profiles for Ni(dtc-DLval)$_2$

So, taking into account the IR data and weight loss percentages included in Table 1, this first step may be due to the process

$$\mathrm{Ni(S_2C{-}NH{-}CH(R){-}COOH)_2} \xrightarrow{180\text{-}215\,^\circ\mathrm{C}} \mathrm{Ni(S_2C{-}NH{-}CH(R){-}COO)}$$

$$+\ \mathrm{HS_2C{-}NH{-}CH(R){-}COOH} \quad (2)$$

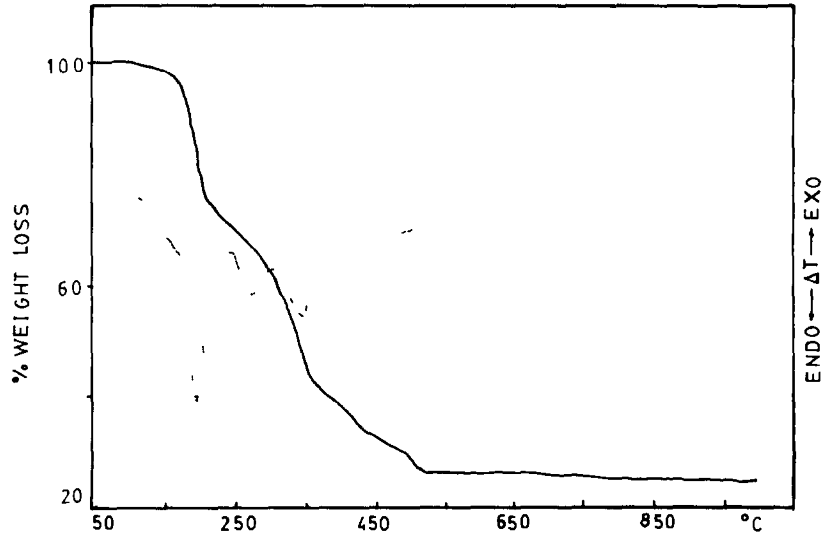


Fig 4 TG (solid line) and DTA (dotted line) profiles for Ni(dtc-DLleu)$_2$

TABLE 1

Summary of TG/DTA data for the complexes

Compound	Decomposition temperature (° C)	Decomposition range (° C)	TG (% wt loss)	DTA peak (° C)
Ni(dtc-gly)$_2$	200	100–540	24 8 (25 3) [a]	146, 206, 265
Ni(dtc-DLala)$_2$	210	100–540	23 3 (23 4)	211, 364
Ni(dtc-DLval)$_2$	200	100–740	21 0 (20 6)	93, 180, 262
Ni(dtc-DLleu)$_2$	210	100–740	19 1 (19 2)	128, 192, 274 351, 559

[a] Calculated values in parentheses

Obviously the presence of free dithiocarbamic acid cannot be checked without doubt, and it is probably simultaneously decomposed

Step 2 This corresponds to the temperature range 265–365 °C, where two endothermic effects are recorded, although overlapped in the case of the alanine derivative

When decomposition was carried out in the tubular furnace to collect the residues, sublimation of a yellowish-white product, which condenses on the cold part of the tube, was observed This solid has been characterized by

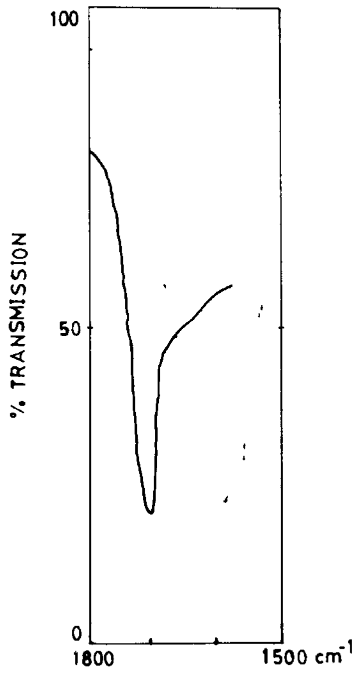
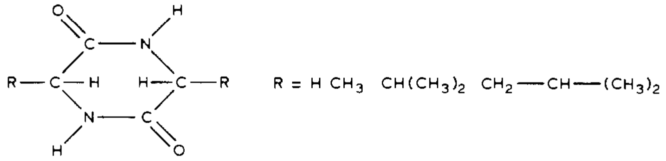


Fig 5 IR spectra ($\nu_{C=O}$ region) of Ni(dtc-DLval)$_2$ (solid line) and residue after heating in nitrogen at 215 °C (dotted line)

chemical analysis and infrared spectroscopy, and, as will be shown below, is an alkyl derivative of 2,5-dioxopiperazine



Main infrared features of this compound are recorded at 3200–3180 cm^{-1} with a shoulder at 3080–3040 cm^{-1} (N–H stretching mode of amine), 1460 cm^{-1} (deformation of the lactame group) and medium intensity bands at 850–800 cm^{-1} due to skeletal deformation modes of the N–H group The strongest band, due to $\nu_{C=O}$, is recorded at 1700 (solid obtained from the glycine compound), 1690 (ala), 1660 (val) and 1670 cm^{-1} (leu) These data, for dioxopiperazine residues obtained from the four complexes, have been summarized in Table 2 Chemical analysis data in Table 3 show a good fit between the experimental and the expected values

TABLE 2

Main IR spectroscopy features for the 2,5-dioxopiperazine alkyl derivatives (cm^{-1})

Substituent	ν(NH)	ν(CH)	ν(CONH)	δ(C–CH_3)	δ(N–H)	γ(NH)
-H	3190	2980	1700	–	1350	850
	3150	2900				800
	3020	2870				
-CH_3	3200	2980	1685	1460	1330	850
	3080	2830		1450		830
	3060	2800				
–$CH(CH_3)_2$	3200	2960	1665	1460	1350	850
	3100	2920		1450		810
	3040	2870				
-$CH_2CH(CH)_3)_2$	3190	2950	1670	1460	1360	850
	3090	2920		1440		820
	3040	2860				

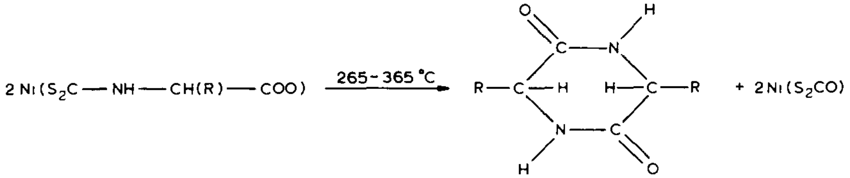
TABLE 3

Analytical data for 2,5-dioxopiperazine derivatives

Substituent	C (%)	N (%)	H (%)
-H	40 85 (42 10) [a]	23 76 (24 56)	4 92 (5 26)
-CH_3	49 82 (60 70	19 07 (19 72)	6 97 (7 04)
-$CH(CH_3)_2$	59 04 (60 60)	13 60 (14 14)	8 71 (9 09)
-$CH_2CH(CH_3)_2$	62 46 (63 71)	12 01 (12 39)	9 81 (9 73)

[a] Calculated values in parentheses

With these data, this second step can be written as



i e leading to the alkyl derivatives of 2,5-dioxopiperazine and nickel dithiocarbonate

Step 3 This step is not too well defined, as no sharp peaks nor steps are recorded in the DTA and TG curves, respectively However, taking into account literature data on decomposition of other metal dithiocarbamates [1,8–10], it can be safely assumed that a further step exists, leading to formation of nickel sulphide, NiS For our complexes, after heating at 410 °C, a black residue identified by X-ray diffraction (file 2-1280 from JCPDS) as NiS is obtained So, step 3 can be written as

$$Ni(S_2CO) \xrightarrow{\geqslant 410\,^\circ C} NiS + S{=}C{=}O$$

Formation of SCO can be only tentatively assumed, from weight loss data, X-ray diffraction and infrared spectroscopy data above, and reports in the literature [7]

Step 4 Between 410 and 700 °C a flat TG curve is obtained in all cases However, an ill-defined exothermic effect is recorded around 650 °C in the DTA diagrams This effect may be due to formation of a non-stoichiometric nickel sulphide, which would take place with negligible weight loss, furthermore, this behaviour is well known to be shown by metallic sulphides when heated in an inert atmosphere [1,4,5,8–10] An X-ray diffraction study of this final residue exhibited peaks due to stoichiometric NiS, in addition to others, not recorded in the JCPDS files, and these may be ascribed to non-stoichiometric sulphides, after decomposition above 650 °C.

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