

THE THERMAL PROPERTIES OF SOME METAL COMPLEXES OF DIETHYLDITHIOCARBAMIC ACID

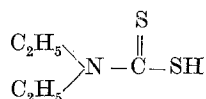
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(Received October 19, 1970)

The cobalt(II), cadmium(II), copper(II), mercury(II), nickel(II) and zinc(II) complexes of diethyldithiocarbamic acid were prepared and investigated by TG, DSC, thin-layer chromatography and gas-liquid chromatography. Heats of fusion were determined.

Diethyldithiocarbamic acid (DDC) readily forms complexes with



monovalent, divalent, and trivalent metal ions, having the general formula $M(\text{DDC})_n$, where n is the positive charge of the metal ion. D'Ascenzo and Wendlandt [1] have reported the preparation and thermal properties of hydrated forms of cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), silver(I) and mercury(II) complexes of DDC. These workers concluded that most of these metal chelates were highly volatile and therefore suggested their separation via the gas chromatographic technique. We have attempted to reproduce the preparations and thermal characteristics of these hydrated metal complexes but can find no evidence of hydrate formation and from our thermal data we do not reach the same conclusions as D'Ascenzo and Wendlandt [1] regarding the volatility of these particular metal complexes. We wish to report our studies on the preparation of these particular metal chelates and their investigation by thermogravimetry (TG), differential scanning calorimetry (DSC), thin-layer chromatography (t.l.c.) and gas-liquid chromatography (GLC).

Experimental

Thermal instrumentation

The TG curves were recorded on a Du Pont Model 950 Thermobalance using a dynamic nitrogen furnace atmosphere. Sample sizes ranged from 9.9 to 10.1 mg; a heating rate of 10° per min was employed. DSC curves were recorded on a Perkin-Elmer DSC-1B with a dynamic nitrogen atmosphere. Sample sizes ranged from 3 to 10 mg and a heating rate of 8° per min was employed. The temperature scale of the DSC was calibrated using pure Indium metal (m.p.

156°). Heats of fusion were determined by DSC using pure Indium metal as the standard (ΔH fusion 6.79 cal/g). Temperatures (DSC) represent "onset" temperatures.

Thin-layer chromatography

Samples were spotted on Kieselguhr G plates, developed in benzene/chloroform (2:1) mixtures, and detected by spraying with an aqueous solution of copper(II) chloride.

Gas chromatography

A Pye series 104 gas chromatograph fitted with a flame-ionisation detector was employed. A PTFE column (4' \times 1/8") packed with 5% SE 52 on Gas Chrom Z was used and operated between 180 and 220 °C.

Preparation of compounds

The metal complexes were prepared as previously described [1] and the samples dried at room temperature in a vacuum desiccator (water pump) for several hours.

Infrared spectra

Infrared spectra were recorded on a Perkin-Elmer 237 Spectrophotometer with samples presented in the form of Nujol mulls.

Results and discussion

The melting points and heats of fusion (determined by DSC) of the metal complexes prepared are shown in Table 1. All the complexes were obtained in an anhydrous form even when, after filtration, the samples were allowed to air-dry. Infrared spectra showed no free or hydrogen-bonded OH stretching band in any of the compounds studied, and attempts to produce a hydrated form

Table 1
Melting points (DSC) and heats of fusion of metal complexes

Compound	m.p. °C	Heat of fusion (cal/g)
Cd(DDC) ₂	250	19.4
Na[Co(DDC) ₃]	266	23.0
Cu(DDC) ₂	200	25.6
Hg(DDC) ₂	136	10.2
Ni(DDC) ₂	236	30.0
Zn(DDC) ₂	178	24.2

(by prolonged suspension in hot water, or by boiling) gave only the anhydrous form (as shown by IR, DSC and TG).

The DSC curves of the metal complexes are shown in Fig. 1. In all cases there were no deviations from the baseline, due to sublimation or vaporisation, up to the first endothermic transition (fusion). The erratic behaviour at the higher temperatures was due to vaporisation (slight) followed by decomposition. In the mercury compound, the peak at 136° was a fusion transition, while the endotherm

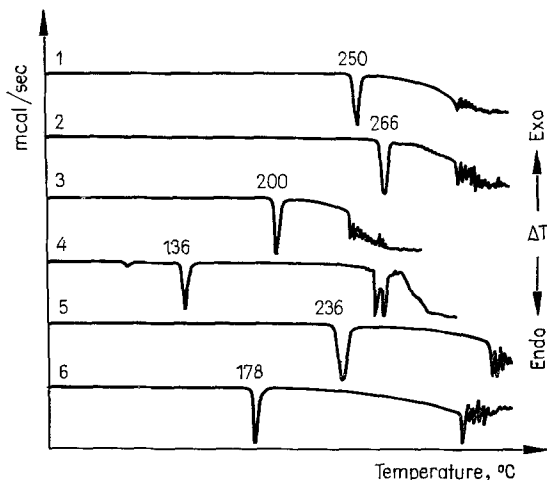


Fig. 1. DSC curves of some metal complexes of diethyldithiocarbamic acid. 1: $\text{Cd}(\text{DDC})_2$, 2: $\text{Na}[\text{Co}(\text{DDC})_3]$, 3: $\text{Cu}(\text{DDC})_2$, 4: $\text{Hg}(\text{DDC})_2$, 5: $\text{Ni}(\text{DDC})_2$, 6: $\text{Zn}(\text{DDC})_2$; atmosphere: nitrogen, 40 ml/min; sample weights: 5–7 mg; scanning rate = $8^\circ/\text{min}$

at 90° was probably due to a trace of $\text{NaDDC} \cdot \text{H}_2\text{O}$ in the sample. The DSC curves of volatile, or highly volatile, metal chelates (e.g. metal acetylacetonates and their fluorinated derivatives) generally show an increasingly marked drift (in an endothermic direction) of the baseline due to loss of the sample by volatilisation up to their melting points.

The TG curves for the DDC derivatives of $\text{Hg}(\text{II})$, $\text{Cd}(\text{II})$, $\text{Ni}(\text{II})$, and for $\text{Na}[\text{Co}(\text{DDC})_3]$ are shown in Fig. 2 and the TG data for all the complexes studied in Table 2. No mass losses occurred below 200° and, except for the nickel and zinc derivatives, the thermal stabilities of these complexes appeared to be very low as indicated by the amount of residues obtained. None of the above complexes were eluted when injected into a gas chromatograph and, in all cases, only a tailing solvent peak was observed. After several injections, the column was badly discoloured due to thermal decomposition of the samples. We have found, however, that these complexes may be easily separated by a simple thin-layer chromatographic procedure (DDC complexes of Cd, Cu, Hg, Ni, Zn had R_F values of 0.72, 0.91, 0.90, 0.85 and 0.95 respectively; $\text{Na}[\text{Co}(\text{DDC})_3]$, R_F 0.73).

Table 2
TG data for metal complexes

Compound	Temperature at max. rate of wt. loss, °C	Wt. loss range, °C	% residue at 500 °C
Cd(DDC) ₂	310	240–335	16
Na[Co(DDC) ₃]	320	200–360	12
Cu(DDC) ₂	300	220–340	18
Hg(DDC) ₂	290	200–400	–4
Ni(DDC) ₂	330	130–350	1
Zn(DDC) ₂	300	200–320	4

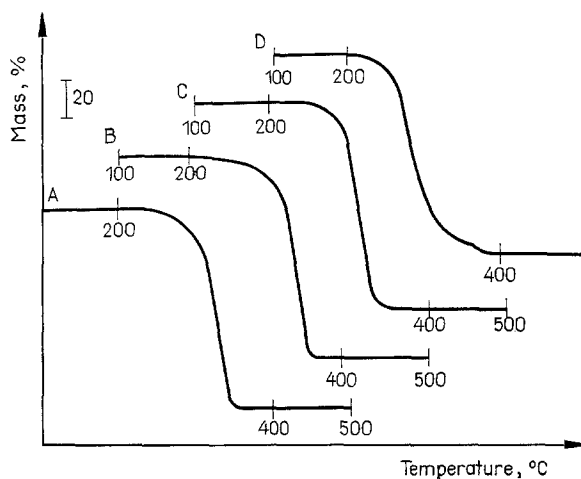


Fig. 2. TG curves of some metal complexes of diethyldithiocarbamic acid. A: Ni(DDC)₂, B: Na[Co(DDC)₃], C: Cd(DDC)₂, D: Hg(DDC)₂; atmosphere: nitrogen, 50 ml/min; sample weights 9.9–10.1 mg; scanning rate: 10°/min

The DSC and TG results show that these particular metal chelates do not form hydrates, are not significantly volatile below their melting points and undergo extensive thermal decomposition soon after fusion. The low volatility and thermal instability of these complexes would indicate that they are unsuitable compounds for analysis by gas chromatographic techniques.

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Permission to publish this paper has been given by the Government Chemist, Ministry of Technology.

Reference

1. G. D'ASCENZO and W. W. WENLANDT, *J. Thermal Anal.*, 1 (1969) 423.