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THERMAL PROPERTIES OF SOME METAL CHELATES OF DI-ISOBUTYLDITHIOCARBAMIC ACID

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The thermal properties of some metal chelates of di-isobutyldithiocarbamic acid have been investigated in an inert atmosphere, with a view to applying them to gas-chromatographic separation. In spite of the slight decomposition occurring during volatilization, most of the metal chelates may be successfully separated by gas-chromatography on short nonpolar glass capillary or fused silica columns. There is no clear correlation between the gas-chromatographic behaviour and the thermal stability of the metal chelates studied here.

As early as 1908, Delepine reported that di-isobutyldithiocarbamate chelates of nickel/II/ and copper/II/ sublime in vacuum without decomposition [1]. Quantitative sublimation data for copper/II/ dithiocarbamates [2,3] have indicated that the di-isobutyl derivative exhibits the greatest degree of volatility of dithiocarbamates containing the dialkyl group.

The relative volatility of metal chelates makes them particularly suitable for gas-chromatographic separation. With this in view, the present study discusses the thermal properties of some metal di-isobutyldithiocarbamate chelates in an inert atmosphere, as determined by TG/DTG and DSC. This study on the thermal properties continues the investigation on the gas-chromatographic behaviour of metal chelates of different dialkyldithiocarbamic acids being carried out in our laboratory [4-6].

EXPERIMENTAL

Preparation of metal chelates

The metal chelates were prepared as previously described [6].

Instruments

The metal chelates were analyzed with Perkin Elmer atomic absorption spectrophotometers models 272 and 403.

Simultaneous TG/DTG curves were obtained on a Mettler TA 3000 TG 50 thermobalance, using a dynamic nitrogen furnace atmosphere (150 ml/min) with a heating rate of 20 degree/min. Sample weights ranged from 10.5 to 11.0 mg. DSC curves were recorded on a Mettler TA 3000 DSC 20 system for samples of ca. 3 mg under a dynamic nitrogen atmosphere (150 ml/min), with heating rates of 5 and 10 degree/min. Ultrapure indium /purity > 99.999%/ was used for calorimetric and temperature calibration.

The gas-chromatograph was a Carlo Erba instrument /Fractovap model 2900/ equipped with a flame ionization detector. Glass capillary and fused silica columns coated with OV-101 /4 m x 0.32 mm i.d./ were used.

RESULTS AND DISCUSSION

The TG data /Table 1/ for the metal chelates indicate that no weight loss occurred below 200°. Except for arsenic/III/ and mercury/II/ chelates, there is one major weight change in the TG curves, due to volatilization. Although slight decomposition occurs during TG heating in a nitrogen atmosphere, volatilization is the dominant effect.

The DSC data for the metal chelates are given in Table 2. Examples of typical TG/DTG and DSC curves for the metal di-isobutyldithiocarbamate chelates are shown in Figs 1 and 2. The DSC curves contain two endothermic peaks, a sharp one as an indication of melting and a broad one as an indication of vaporization. The determination of heats of sublimation in an inert atmosphere did not succeed because of the slight decomposition

occurring during vaporization. The DSC measurements should be carried out in vacuum.

Table 1
TG/DTG data for the metal chelates

Metal	Weight loss, %	Temperature range, C^{O}	DTG peak temp., C^{O}
Ni/II/	93	240-420	390
Cu/II/	94	200-400	330
Zn/II/	100	210-405	375
Cd/II/	80	225-400	358
Hg/II/	83	200-370	335
	17	370-450	425
Pb/II/	84	210-420	365
Cr/III/	93	250-440	417
Fe/III/	91	225-415	343
Co/III/	95	240-405	372
In/III/	85	235-420	380
As/III/	90	235-330	317
	10	330-395	360

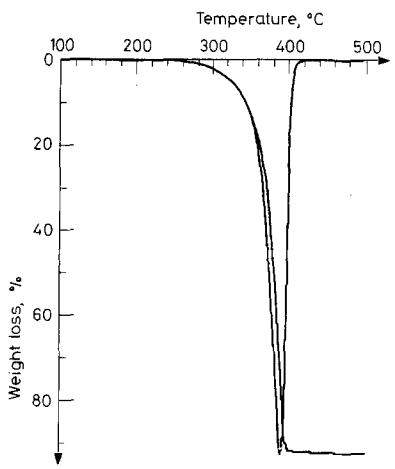

Fig. 1. TG/DTG curve for nickel/II/ di-isobutyldithiocarbamate chelate.

Table 2
DSC data for the metal chelates

Metal	M.p., °C	Other peaks*, °C	Heat of fusion, kJ/mol
Ni/II/	178	322[a], 378[b]	27.19 ± 0.55
Cu/II/	148	260 , 306	23.74 ± 0.22
Zn/II/	114	300 , 361	29.68 ± 0.49
Cd/II/	166	285 , 328	26.20 ± 0.48
Hg/II/	95	260 , 315	28.85 ± 0.18
		420↑, 440↑	
Pb/II/	100	300 , 356	15.44 ± 0.40
Cr/III/	198	370 , 399	26.18 ± 0.51
Fe/III/	170	220↑, 267↑	32.34 ± 0.62
		284 , 323	
Co/III/	212	315 , 359	29.41 ± 0.69
In/III/	172	300 , 360	31.02 ± 0.56
As/III/	129	250 , 295	25.87 ± 0.18
		360↑, 380↑	

*All peaks endothermic except those indicated /↑/

[a]Onset temperature

[b]Peak temperature

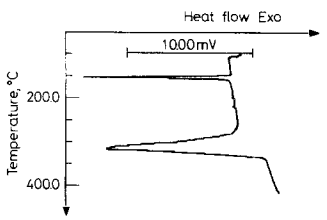

Fig. 2. DSC curve for copper/II/ di-isobutyldithiocarbamate chelate

In spite of only partial volatility, most of the metal chelates studied here may be successfully separated by gas--chromatography on short nonpolar glass capillary or fused

silica columns /Fig. 2/. Only arsenic/III/ and iron/II/ chelates showed decomposition during the gas-chromatographic separation. The detailed gas-chromatographic investigation of the metal di-isobutyldithiocarbamate chelates will be described in another article [7].

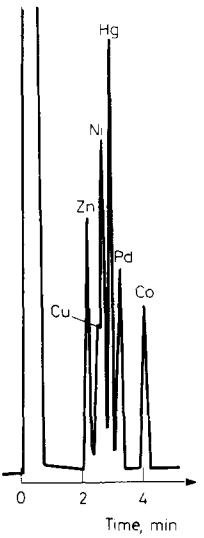

Fig. 3. Gas-chromatographic separation of zinc/II/, copper/II/, nickel/II/, mercury/II/, palladium/II/ and cobalt/III/ di-isobutyldithiocarbamate chelates on fused silica column coated with OV-101. Conditions: inj./det. 275°, oven 150° /0 min/ - 260° /1 min/, heating rate 30°/min, N_2: 8 ml/min.

There is no clear correlation between the gas-chromatographic behaviour and the thermal stability of the metal chelates studied here. From the above thermal data it is not seen, for example, that the zinc/II/ chelate is one of the most critical salts with respect to decomposition on the gas-chromatographic column. From the thermal behaviour of the metal chelates, however, their possible chromatographic characteristics can be predicted.

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ZUSAMMENFASSUNG - Die thermischen Eigenschaften einiger Metallchelate der Di-isobutyl-dithiocarbaminsäure wurden in einer inerten Atmosphäre hinsichtlich der Möglichkeiten ihrer gaschromatographischen Trennung untersucht. Trotz der während der Verflüchtigung eintretenden geringfügigen Zersetzung kann der grösste Teil der Metallchelate durch Gaschromatographie erfolgreich in kurzen nichtpolaren Glaskapillarkolonnen oder in mit geschmolzenem SiO_2 bedeckten Kolonnen getrennt werden. Es besteht keine eindeutige Korrelation zwischen dem gaschromatographischen Verhalten und der thermischen Stabilität der untersuchten Metallchelate.

Резюме - В инертной атмосфере исследованы термические свойства некоторых хелатов диизобутилкарбаминовой кислоты с ионами металлов с целью их газохроматографического разделения. Несмотря на их незначительное разложение во время испарения, большинство хелатов можно успешно разделить газовой хроматографией на короткой неполярной стеклянной капиллярной колонке или на колонке из плавленного кварца. Не наблюдалось ясной корреляции между газхроматографическим поведением изученных соединений и их термоустойчивостью.