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GAS CHROMATOGRAPHIC SEPARATION OF SOME DIALKYLDITHIO-CARBAMATES OF NICKEL(II)

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SUMMARY

The possibility of separating some nickel(II) bis(dialkyldithiocarbamates) by gas chromatography in a packed column with SE-30 as the stationary phase has been studied. In order to prove the structure of nickel(II) bis(N,N-diethyldithiocarbamate) in the gaseous phase, its mass spectrum is presented.

The thermal behaviour of nickel(II) bis(dialkyldithiocarbamates) was studied by means of thermal analysis. It was found that it is possible to apply gas chromatography to compounds that are solids at the temperature of separation.

The peaks of nickel(II) bis(dialkyldithiocarbamates) are symmetrical and their shape does not differ from those of hydrocarbons chromatographed under similar conditions.

INTRODUCTION

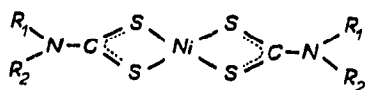
Dithiocarbamates are widely used in agriculture, medicine and rubber chemistry¹. They are usually analyzed on the basis of their decomposition to amines and carbon disulphide by mineral acids¹. Direct spectrophotometry of dithiocarbamates can be used if there is no interfering absorption from other components of the material being analyzed¹. Column and thin-layer chromatography have been applied to the separation and determination of some dithiocarbamates of metals^{1–3}. Gas chromatography (GC) has also been used for the analysis of some S-alkyl-N,N-dialkyldithiocarbamates⁴. The best method for S-alkyl-N,N-dialkyldithiocarbamates and S-alkyl-N-monoalkyldithiocarbamates was a combination of gas chromatography with mass spectrometry (GC-MS)^{5,6}.

In a previous paper, we discussed the analysis of the bis(N,N-diethyldithiocarbamates) of some divalent metals by GC⁷. This paper deals with some problems that occurred in the GC of some nickel(II) bis(N,N-dialkyldithiocarbamates).

EXPERIMENTAL

Nomenclature

The structure of bis(N,N-dialkyldithiocarbamates) of nickel(II) can be written as



All of the bis(*N,N*-dialkyldithiocarbamates) of nickel(II) so far investigated exhibit a monomeric planar structure in the solid state⁸⁻¹³. The compounds used in this study are listed in Table I.

TABLE I

BIS(*N,N*-DIALKYLDITHIOCARBAMATES) OF NICKEL(II) STUDIED

<i>Systematic name</i>	<i>Abbreviation</i>	<i>Mol. wt.</i>
Nickel(II) bis(<i>N,N</i> -dimethyldithiocarbamate)	(DMDTC) ₂ Ni(II)	299.99
Nickel(II) bis(<i>N,N</i> -diethyldithiocarbamate)	(DEDTC) ₂ Ni(II)	355.23
Nickel(II) bis(<i>N,N</i> -dipropyldithiocarbamate)	(DPDTC) ₂ Ni(II)	411.33
Nickel(II) bis(<i>N,N</i> -diisopropyldithiocarbamate)	(DIPDTC) ₂ Ni(II)	411.33
Nickel(II) bis(<i>N,N</i> -dibutyldithiocarbamate)	(DBDTC) ₂ Ni(II)	467.44
Nickel(II) bis(<i>N,N</i> -diisobutyldithiocarbamate)	(DIBDTC) ₂ Ni(II)	467.44
Nickel(II) bis(pentamethylenedithiocarbamate)	(PMDTC) ₂ Ni(II)	379.25

Preparation of bis(N,N-dialkyldithiocarbamates) of nickel(II)

The chelates listed in Table I were prepared by adding a solution of nickel chloride to a solution of a sodium salt of *N,N*-dialkyldithiocarbamic acid in the absence of oxygen¹. The products formed were re-crystallized from different organic solvents [ethanol, chloroform, benzene or a mixture of benzene and acetone (1:3)]. The elemental analyses of the compounds prepared show good agreement with the theoretical values, except for (DMDTC)₂Ni(II) (Table II).

Gas chromatography

A Packard Instruments gas chromatograph (Becker Model 419) equipped with a flame ionization detector (FID) and a W + W Electronic Model 101 recorder was used. The glass column was 200 cm in length with an I.D. of 3 mm packed with 3% SE-30 coated on 60-80 mesh Chromosorb W-HP (Supelco, Bellefonte, Pa., U.S.A.).

Combined gas chromatography-mass spectrometry

A Varian-MAT 111 gas chromatograph-mass spectrometer was used to obtain the mass spectra of (DEDTC)₂Ni(II). The gas chromatograph was fitted with a 150 mm × 2 mm I.D. stainless-steel column packed with 3% SE-30 coated on 100-120-mesh Chromosorb W-HP. The flow-rate of helium carrier gas was 15 ml/min. The temperature was programmed from 190 to 270° at the rate of 6°/min, the injection block was maintained at 270° and the temperature of the splitting-type carrier gas separator and ionization source was 270°. The ionization energy was 70 eV and the trap current was 270 μA.

Thermal analysis

Thermogravimetric curves of the compounds listed in Table I were obtained

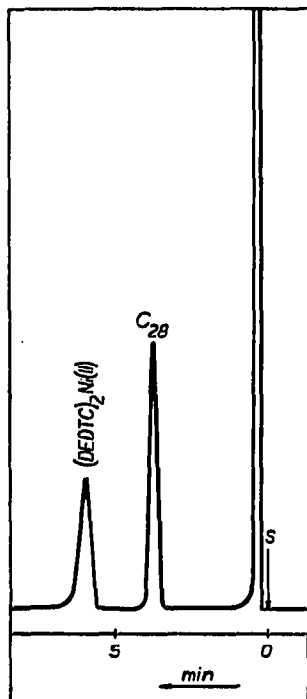


Fig. 1. Gas chromatographic separation of octacosane (C_{28}) and nickel(II) bis(N,N-diethyldithiocarbamate) at 270° . Operating conditions: pressure of nitrogen, 2.0 atm; hydrogen flow-rate, 30 ml/min; air flow-rate, 400 ml/min; on-column injection.

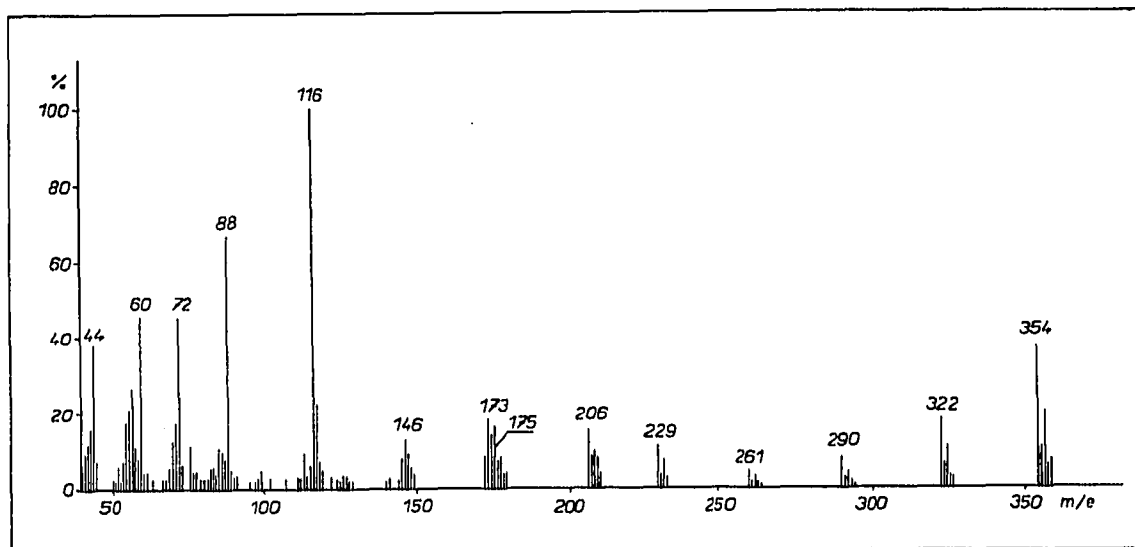


Fig. 2. Mass spectrum of nickel(II) bis(N,N-diethyldithiocarbamate). The ordinate represents the relative intensities of the fragment ions. Details are given in Table III.

TABLE II
RESULTS OF ELEMENTAL ANALYSES

Compound	C		H		N		S		Ni (calculated)
	Found	Calculated	Found	Calculated	Found	Calculated	Found	Calculated	
(DMDTC) ₂ Ni(II)	28.6	24.0	4.6	4.3	8.6	9.3	37.3	42.8	19.6
(DEDTC) ₂ Ni(II)	33.8	33.8	5.4	5.7	7.6	7.9	34.9	36.1	16.5
(DPDTC) ₂ Ni(II)	41.2	40.9	6.9	6.9	6.4	6.8	29.2	31.2	14.3
(DIPDTC) ₂ Ni(II)	41.4	40.9	6.8	6.9	6.5	6.8	29.5	31.2	14.3
(DBDTC) ₂ Ni(II)	46.7	46.2	8.2	7.8	5.8	6.0	25.7	27.4	12.6
(DIBDTC) ₂ Ni(II)	46.5	46.2	7.8	7.8	5.2	6.0	25.5	27.4	12.6
(PMDTC) ₂ Ni(II)	38.3	38.0	5.5	5.3	7.2	7.4	33.2	33.8	15.5

TABLE III
IONS OF PRINCIPAL ISOTOPIC PEAKS FOR (DEDTC)₂Ni(II)

<i>m/e</i>	<i>Ion</i>	<i>m/e</i>	<i>Ion</i>
354	M ⁺	146	[(C ₂ H ₄) ₂ NCS ₂] ⁺
322	[M - S] ⁺	116	[(C ₂ H ₃) ₂ NCS] ⁺
290	[M - S ₂] ⁺	88	[C ₂ H ₅ NHCS] ⁺
261	[M - C ₂ H ₅ S ₂] ⁺	72	[(C ₂ H ₃) ₂ N] ⁺
229	[M - C ₂ H ₅ S ₃] ⁺	60	[NH ₂ CS] ⁺
206	[M - (C ₂ H ₃) ₂ NCS ₂] ⁺		

with a Mettler Thermoanalyzer 2 using *ca.* 7.0 mg of sample and a heating rate of 6°/min in a flow of pure nitrogen (7 l/h). For differential thermal analysis (DTA) curves, a Pt-Pt/Rh thermocouple with alumina as standard was used.

RESULTS AND DISCUSSION

As has been shown in our previous work⁷, it is possible to analyze (DEDTC)₂Ni(II) by gas chromatography. It can be seen from Fig. 1 that the peak for (DEDTC)₂Ni(II) is symmetrical and similar to that obtained for a C₂₈ hydrocarbon. The mass spectrum proved that the peak represents (DEDTC)₂Ni(II). As the mass spectra of nickel(II) bis(N,N-dialkyldithiocarbamates) have not been published, the

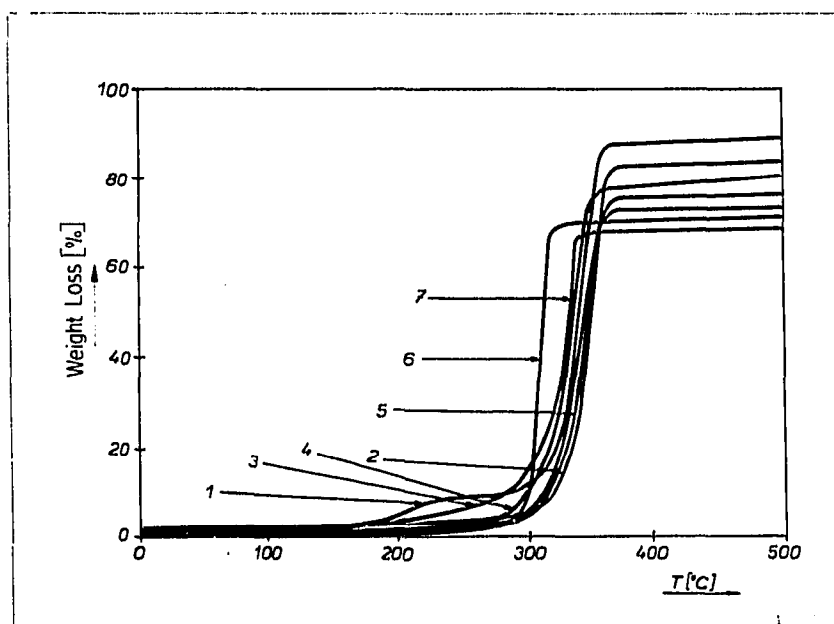


Fig. 3. Thermograms of the nickel(II) bis(N,N-dialkyldithiocarbamates) listed in Table I. 1 = Di-methyl; 2 = diethyl; 3 = di-*n*-propyl; 4 = diisopropyl; 5 = diisobutyl; 6 = pentamethylene; 7 = di-*n*-butyl.

spectrum of $(\text{DEDTC})_2\text{Ni}(\text{II})$ is given in Fig. 2. As was found for copper(II) bis(N,N-diethyldithiocarbamate)¹⁴, $(\text{DEDTC})_2\text{Ni}(\text{II})$ also yielded peaks for the molecular ions. The ions of the other principal isotopic peaks are presented in Table III.

In a more detailed study of the thermal behaviour of $(\text{DEDTC})_2\text{Ni}(\text{II})$, we found that it appears to be sufficiently stable at the temperature used for the GC analysis¹⁵. The volatilization of bis(N,N-dialkyldithiocarbamates) of nickel(II) at the temperature used (270°, see Fig. 1) under thermoanalytical conditions was found to be not greater than about 10% (Fig. 3).

The DTA curves showed that below 270° only some of the nickel(II) bis(N,N-dialkyldithiocarbamates) exhibited an endothermic peak corresponding to the temperature of the melting point. It is surprising that those compounds which are supposed to be in the solid state at 270° [$(\text{DMDTC})_2\text{Ni}(\text{II})$, $(\text{DIPDTC})_2\text{Ni}(\text{II})$ and $(\text{PMDTC})_2\text{Ni}(\text{II})$] could be separated by gas chromatography. The gas chromatographic separation of $(\text{DIPDTC})_2\text{Ni}(\text{II})$ and $(\text{DIBDTC})_2\text{Ni}(\text{II})$ is shown in Fig. 4. Both peaks are almost identical when the same amounts (5 μg) were injected. The broken line in Fig. 4 represents the peak for $(\text{DPDTC})_2\text{Ni}(\text{II})$. The relative positions of the peaks in Fig. 4 did not change significantly with a change in the operating temperature (Fig. 5).

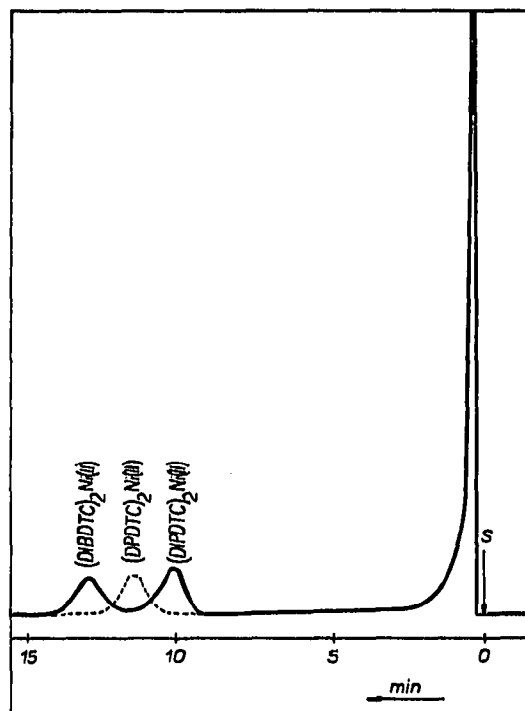
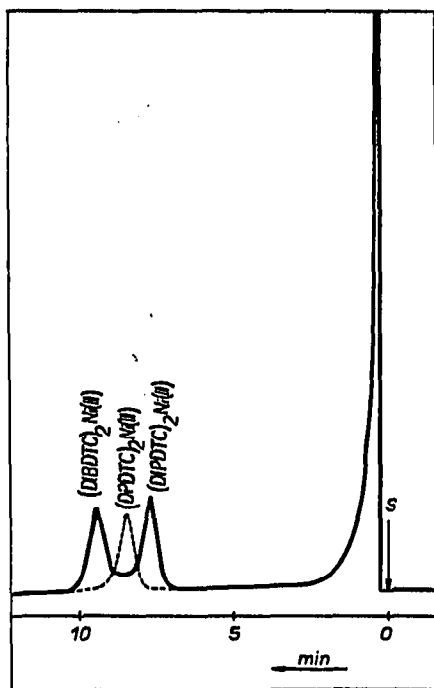


Fig. 4. Gas chromatographic separation of nickel(II) bis(N,N-diisopropylidithiocarbamate), nickel(II) bis(N,N-dipropylidithiocarbamate) and nickel(II) bis(diisobutylidithiocarbamate) at 270°. Pressure of nitrogen 2.0 atm.

Fig. 5. Gas chromatographic separation of compounds shown in Fig. 4 at 250°. Pressure of nitrogen, 3.5 atm.

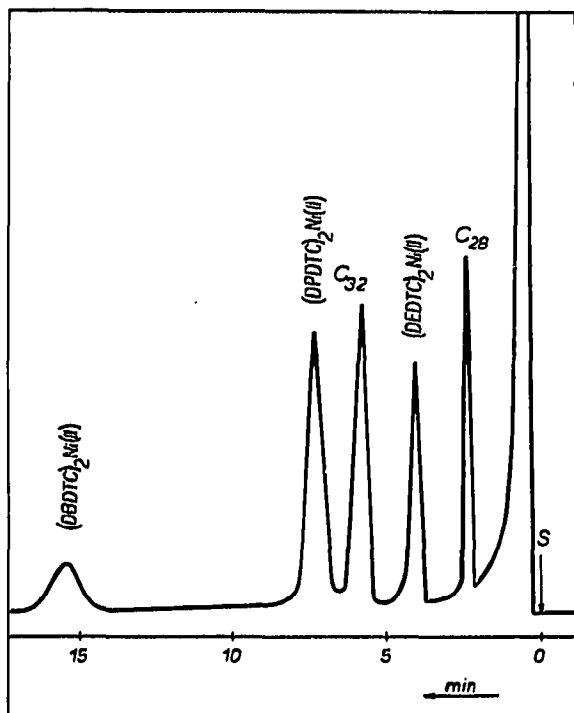


Fig. 6. Gas chromatographic separation of hydrocarbons (C_{28} , C_{32}) and nickel(II) bis(N,N-dialkyl-dithiocarbamates) (diethyl, di-*n*-propyl, di-*n*-butyl) at 270° . Pressure of nitrogen, 3.0 atm.

Fig. 6 represents the GC separation of hydrocarbons (C_{28} , C_{32}), $(DEDTC)_2Ni(II)$, $(DPDTC)_2Ni(II)$ and $(DBDTC)_2Ni(II)$. $(PMDTC)_2Ni(II)$ is eluted together with $(DBDTC)_2Ni(II)$ under the conditions used at temperatures of 240 – 270° .

For $(DEDTC)_2Ni(II)$, $(DPDTC)_2Ni(II)$ and $(DBDTC)_2Ni(II)$, the Kováts retention indices were measured (Table IV). It was found that an increase in the alkyl chain corresponding to one CH_2 group increased the index by less than 100 units.

TABLE IV

KOVÁTS INDICES OF $(DEDTC)_2Ni(II)$, $(DPDTC)_2Ni(II)$ AND $(DBDTC)_2Ni(II)$ OBTAINED AT 270°

Dithiocarbamate	Kováts index
$(DEDTC)_2Ni(II)$	3044
$(DPDTC)_2Ni(II)$	3297
$(DBDTC)_2Ni(II)$	3606

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