CHROM. 11,553

ANALYSIS OF DIVALENT METAL DIALKYLDITHIOCARBAMATES BY GAS CHROMATOGRAPHY AND MASS SPECTROMETRY

Department of Analytical Chemistry, Faculty of Chemical Technology, Slovak Technical University, 880 37 Bratislava (Czechoslovakia)

P. A. LECLERCQ

Laboratory of Instrumental Analysis, Eindhoven University of Technology, Eindhoven (The Netherlands)

and

J. GARAJ and J. MASARYK

Department of Analytical Chemistry, Faculty of Chemical Technology, Slovak Technical University, 880 37 Bratislava (Czechoslovakia)

SUMMARY

The influence of various gas chromatographic supports, coated with SE-30 as stationary phase, on the qualitative and quantitative analysis of Ni(II) and Zn(II) dithiocarbamates was investigated. Retention indices were correlated with the structures of the compounds studied. Cu(II), Co(II) and Cd(II) dialkyldithiocarbamates decomposed during analysis under the applied conditions. Special emphasis was given to the quantitative analysis of Ni(II) and Zn(II) bis(N,N-dialkyldithiocarbamates).

Basic conditions were established for the separation of Ni(II) bis(N,N-dialkyldithiocarbamates) on glass capillary columns coated with polydimethylsiloxane stationary phases (OV-101 and SE-30). The main problem in the successful analysis of these compounds in glass capillary columns was found to be adsorption on the column wall.

Electron-impact positive-ion mass spectra of Ni(II) and Zn(II) bis(N,N-dialkyldithiocarbamates) are discussed in detail. From the mass spectra of these compounds, general fragmentation pathways were derived. All of the dithiocarbamates studied showed molecular ions, the intensity of which decreased with increasing size of the alkyl substituent.

INTRODUCTION

Successful analyses of metal chelates containing a dialkyldithiocarbamate ligand by gas chromatography have been recently published[1–6]. We have previously described the separation of nickel and zinc bis(N,N-diethyldithiocarbamates)[1]. Zn(II), Cd(II), Pb(II), Hg(II), Ni(II), Pd(II) and Pt(II) bis(N,N-diethyldithiocarbamates) have

been analysed by gas chromatography[3,4]. The separation of a mixture of Ni(II), Zn(II) and Cd(II) bis(N,N-diethyldithiocarbamates) was also described by Tavlaridis and Neeb[5]. For the determination of metals in water, Tavlaridis and Neeb proposed the gas chromatographic analysis of chelates containing a di(trifluoroethyl)dithiocarbamate ligand[6]. Fluorinated diethyldithiocarbamates are more volatile and show better thermal stability above 473 °K than do the corresponding diethyldithiocarbamates. A mixture of Zn, Ni, Cd, Sb and Bi bis[N,N-di(trifluoroethyl)dithiocarbamates] has been successfully analysed by gas chromatography.

For the analysis of metal dithiocarbamates by gas chromatography, columns packed with non-polar stationary phases (silicone greases and elastomers) on silanized support materials based on Chromosorbs have been used exclusively[1-6].

The mass spectra of metal N,N-dialkyldithiocarbamates have not yet been studied systematically[2,7-16], and only a few mass spectral data have been reported on some dithiocarbamates of the bivalent metals Cu[7], Zn[7,12,13] and Ni[2,14]. Detailed fragmentation patterns are not found in the literature.

The aim of the present work was to study the problems encountered in analyses of divalent metal dialkyldithiocarbamates by gas chromatography. Special emphasis is given to the quantitative analysis of Ni(II) and Zn(II) bis(N,N-dialkyldithiocarbamates).

Another objective of the work was to explore the basic conditions for the separation of Ni(II) bis(N,N-dialkyldithiocarbamates) by capillary column gas chromatography. Finally, the mass spectra of Ni(II) and Zn(II) bis(N,N-dialkyldithiocarbamates) are discussed in detail.

EXPERIMENTAL

Preparation of divalent metal dialkyldithiocarbamates

Dialkyldithiocarbamate chelates of divalent metals were prepared using the procedure described previously[2]. The chelates used are listed in Table I. The purity of the compounds obtained was checked by elemental analysis and mass spectrometry.

Gas chromatography

A Carlo Erba (Milan, Italy) gas chromatograph (Fractovap Model 2300) equipped with a flame-ionization detector (FID) and a stream splitter, allowing the use of capillary columns, was used.

Glass packed columns of length 60–200 cm and I.D. 3 mm were used. The support materials applied are listed in Table II. Glass capillary columns coated with OV-101 and SE-30 as stationary phases were prepared according to a previously described procedure[17]. The glass capillary columns used are listed in Table III. Capillary columns were coated using the dynamic plunger method[17] and the modified static method[19].

Nitrogen was used as the carrier gas in all experiments. Samples of dithiocarbamates were dissolved in chloroform (1 mg in 1 ml). n-Alkanes were dissolved in n-hexane (1 mg in 1 ml). Solutions were injected with a 10-μl Hamilton microsyringe.

Peak asymmetry was measured at one tenth of the peak height[20]. Retention times were measured with a stop-watch. A digital integrator (Autolab, Model 6300) was used to measure peak areas for quantitation.

TABLE I

DIVALENT METAL BIS(N,N-DIALKYLDITHIOCARBAMATES) STUDIED

Systematic name	Abbreviation
Copper(II) bis(N,N-diethyldithiocarbamate)	$Cu(DEDTC)_2$
Cadmium(II) bis(N,N-diethyldithiocarbamate)	$Cd(DEDTC)_2$
Cobalt(II) bis(N,N-diethyldithiocarbamate)	$Co(DEDTC)_2$
Nickel(II) bis(N,N-diethyldithiocarbamate)	$Ni(DEDTC)_2$
Zinc(II) bis(N,N-diethyldithiocarbamate)	$Zn(DEDTC)_2$
Nickel(II) bis(N,N-dimethyldithiocarbamate)	$Ni(DMDTC)_2$
Nickel(II) bis(N,N-dipropyldithiocarbamate)	$Ni(DPDTC)_2$
Nickel(II) bis(N,N-dipentyldithiocarbamate)	$Ni(DPEDTC)_2$
Nickel(II) bis(N,N-dibutyldithiocarbamate)	$Ni(DBDTC)_2$
Nickel(II) bis(N,N-dihexyldithiocarbamate)	$Ni(DHDTC)_2$
Nickel(II) bis(N,N-diheptyldithiocarbamate)	$Ni(DHPDTC)_2$
Nickel(II) bis(N,N-dioctyldithiocarbamate)	$Ni(DODTC)_2$
Nickel(II) bis(N,N-diisopropyldithiocarbamate)	$Ni(DIPDTC)_2$
Nickel(II) bis(N,N-diisobutyldithiocarbamate)	$Ni(DIBDTC)_2$
Nickel(II) bis(N,N-methylisopropyldithiocarbamate)	$Ni(MIPDTC)_2$
Zinc(II) bis(N,N-dimethyldithiocarbamate)	$Zn(DMDTC)_2$
Zinc(II) bis(N,N-dipropyldithiocarbamate)	$Zn(DPDTC)_2$
Zinc(II) bis(N,N-dibutyldithiocarbamate)	$Zn(DBDTC)_2$
Zinc(II) bis(N,N-dipentyldithiocarbamate)	$Zn(DPEDTC)_2$
Zinc(II) bis(N,N-diisopropyldithiocarbamate)	$Zn(DIPDTC)_2$
Zinc(II) bis(N,N-diisobutyldithiocarbamate)	$Zn(DIBDTC)_2$
Zinc(II) bis(N,N-methylisopropyldithiocarbamate)	$Zn(MIPDTC)_2$

TABLE II

SUPPORTS USED

Support	Mesh range	Source
Gas-Chrom P sil.*	100–120	Carlo Erba (Milan, Italy)
Chromosorb W sil.*	80–100	Carlo Erba
Chromosorb P sil.*	80–100	Carlo Erba
Chromaton N AW HMDS	80–100	Lachema (Brno, Czechoslovakia)
Chezasorb AW HMDS	60– 80	Lachema
Chromosorb G AW DMCS	80–100	Packard-Becker (Delft, The Netherlands)
Chromosorb W	80–100	Carlo Erba
Gas-Chrom Q	100–120	Carlo Erba

* Silanization procedure is not known.

Mass spectrometry

Electron-impact positive-ion mass spectra were obtained on an AEI (Manchester, Great Britain) MS-12 single focussing mass spectrometer under the following conditions: electron energy, 70 eV; trap current, 0.500 mA; ion accelerating voltage, 4 kV; and source temperature, 520 °K. The compounds were admitted via a solid insertion probe. Spectra were obtained at probe temperatures within the ranges 420–470 °K for the nickel chelates and 390–450 °K for the zinc chelates.

TABLE III

GLASS CAPILLARY COLUMNS

Column No.	Length (m)	Stationary phase	Coating procedure	Etching	
				Time (h)	Temperature (°K)
1	31.4	10% OV-101	Dynamic	2	623
2	22.6	15% OV-101	Dynamic	4	623
3	19.0	30% OV-101	Dynamic	16	623
4	22.0	20% OV-101	Dynamic	20	623
5	24.9	20% OV-101	Dynamic	19	623
6	24.0	0.25% SE-30	Static	19	623
7*	21.6	0.25% SE-30	Static	5 min	623
8	22.6	0.50% SE-30	Static	17	605

* Column 7 was etched dynamically as proposed by Franken et al.[18].

RESULTS AND DISCUSSION

Qualitative analysis on packed columns

It was obvious from the results of preliminary experiments, and also from published data[3,4], that analyses under the given conditions (non-polar silicone stationary phases and the stated temperature) are considerably affected by the support material. The influence of support materials on the qualitative analysis was monitored by the retention times observed for Ni(DEDTC)$_2$ relative to n-octacosane (Table IV). It was assumed that the retention time of the latter would not be affected by the support.

TABLE IV

RELATIVE RETENTION TIMES (r) AND ASYMMETRY COEFFICIENTS (As) OF Ni (DEDTC)$_2$ FOUND AT 533 °K ON VARIOUS SUPPORTS COATED WITH SE-30 STATIONARY PHASE

$r = t'_{R,x}/t'_{R,C_{28}}$, where $t'_R = t_R - t_M$, x represents Ni(DEDTC)$_2$ and C_{28} represents n-octacosane; $As = 100a/b$, where a is the distance between the perpendicular from the top of the peak to the leading edge and b is the distance between the perpendicular from the top and the descent edge, measured at one tenth of the peak height[20].

Support	Concentration of SE-30 (%)	As	r	Column length (m)
Chromosorb G AW DMCS	2	83	1.68	1.10
Gas-Chrom P sil.	3	86	1.68	0.55
Gas-Chrom P sil.	1	46	1.74	1.95
Chromaton N AW HMDS	3	93	1.75	0.55
Chromosorb W sil.	3	92	1.81	0.55
Chezasorb AW HMDS	3	71	1.81	0.55

The support, owing to its polarity, increases the polarity of the non-polar coated packing material. Consequently, the relative retention time (r in Table IV) increases with increasing polarity of the support. Accordingly, the most suitable support for the separation of dialkyldithiocarbamates is Chromosorb G AW DMCS. The relative retention time decreases with increasing amount of stationary phase (for Gas-Chrom P the relative retention time decreased from 1.74 to 1.68 when the amount

of the stationary phase decreased from 3 to 1%). In addition, as a result of the effect of the support material, the peaks become non-symmetrical (apart from the partition processes, adsorption phenomena also become manifest), making accurate quantitative analysis more difficult.

Fig. 1 shows that for the analysis of Ni(DEDTC)$_2$ the least suitable support material is Chezasorb AW HMDS. It follows further (Table IV) from the asymmetry coefficient that the packing obtained by coating Gas-Chrom P sil. with 1% of SE-30 is not suitable for the analysis of Ni(DEDTC)$_2$.

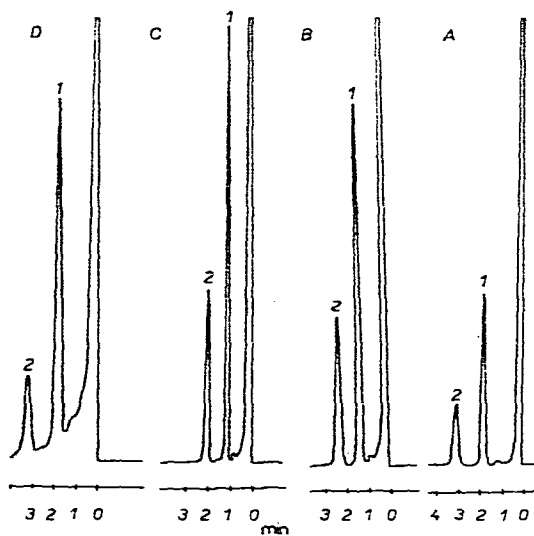Fig. 1. Peak shapes of (1) n-octacosane and (2) Ni(DEDTC)$_2$ obtained on columns packed with various silanized supports coated with 3% of SE-30. Column length, 0.55 m. (A) Gas-Chrom P sil.; (B) Chromaton N AW DMCS; (C) Chromosorb W sil.; (D) Chezasorb AW HMDS.

In agreement with the observations during thin-layer chromatography of dithiocarbamates[21], Zn(II) bis(N,N-dialkyldithiocarbamates) gave less symmetrical gas chromatographic peaks than the corresponding nickel chelates. Consequently, the analysis of zinc dialkyldithiocarbamates is more difficult and the conditions must be selected more carefully than when nickel dithiocarbamates are to be analysed.

Peaks obtained from Zn(DEDTC)$_2$ are more symmetrical than those from Zn(DMDTC)$_2$ (Table V) or Zn(DPDTC)$_2$ (Fig. 2).

TABLE V

ASYMMETRY COEFFICIENTS (As) OF Zn(DMDTC)$_2$ AND Zn(DEDTC)$_2$ PEAKS OBTAINED ON VARIOUS SUPPORTS COATED WITH SE-30 STATIONARY PHASE AT 513 °K
Asymmetry coefficients calculated as in Table IV.

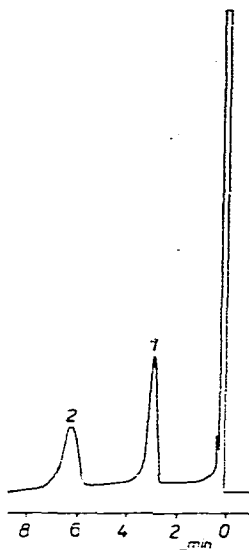| Support	As	
	Zn(DMDTC)$_2$	Zn(DEDTC)$_2$
Chromosorb G AW DMCS	66	91
Gas-Chrom Q	61	76
Chromosorb W sil.	50	66

Fig. 2. Separation of (1) Zn(DEDTC)$_2$ and (2) Zn(DPDTC)$_2$ on a column packed with Gas-Chrom Q coated with 3% of SE-30 at 513 °K and 245.5 kPa.

For the analysis of Zn(II) bis(dialkyldithiocarbamates) the least polar packing was used (Fig. 3). The dashed peaks represent substances chromatographed separately. Under the given conditions, Zn(MIPDTC)$_2$ and Zn(DEDTC)$_2$ could not be separated.

Nickel and zinc dialkyldithiocarbamates were characterized by their retention times relative to *n*-octacosane and by their retention indices. Table VI gives the rel-
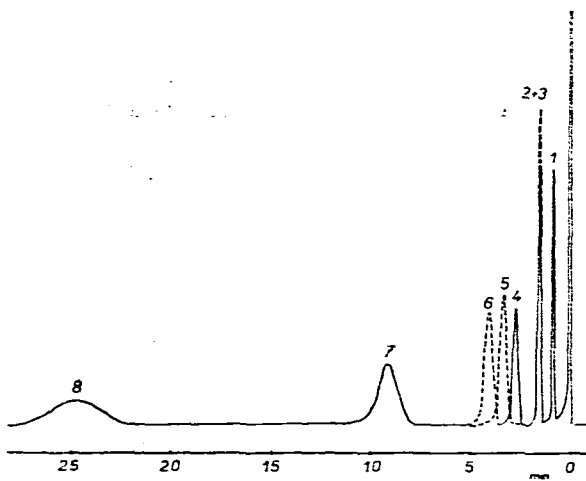

Fig. 3. Separation of Zn(II) bis(N,N-dialkyldithiocarbamates) on a column packed with Chromosorb G AW DMCS coated with 2% of SE-30 at 503 °K and 147.3 kPa. 1, Zn(DMDTC)$_2$; 2+3, Zn (DEDTC)$_2$ + Zn(MIPDTC)$_2$; 4, Zn(DIPDTC)$_2$; 5, Zn(DPDTC)$_2$; 6, Zn(DIBDTC)$_2$; 7, Zn(DBDTC)$_2$; 8, Zn(DPEDTC)$_2$.

TABLE VI

RELATIVE RETENTION TIMES (r) AND KOVÁTS RETENTION INDICES (I) OF NICKEL(II) AND ZINC(II) DIALKYLDITHIOCARBAMATES OBTAINED ON GAS-CHROM Q COATED WITH 3% OF SE-30

$$r = t'_{R.x}/t'_{R.C_{23}}.$$

$$I = 100z + 200 \cdot \frac{\log t'_{R.x}/t'_{R.z}}{\log t'_{R.z+z}/t'_{R.z}}$$

where z is the carbon number of the n-alkane eluted in front of a dialkyldithiocarbamate x and $t'_R = t_R - t_M$.

Alkyl group in ligand	Ni(II) at 543 °K		Zn(II) at 515 °K	
	r	I	r	I
Methyl	1.08	2833	0.59	2548
Ethyl	1.66	3007	0.67	2728
Propyl	3.22	3277	1.79	3013
Isopropyl	2.84	3229	1.52	2951
Butyl	7.52	3618	4.63	3358
Isobutyl	3.71	3332	2.06	3086
Pentyl	17.57	3969	12.05	3706

ative retention times and Kováts retention indices for zinc and nickel dialkyldithio-carbamates as measured on Gas-Chrom Q coated with 3% of SE-30.

Kováts retention indices were used to calculate the increments corresponding to four CH$_2$ groups:

$$\Delta I_{4CH_2} = I_{n+1} - I_n$$

where n is the number of carbon atoms in the alkyl group linked to the nitrogen atom in the dithiocarbamate ligand. Table VII shows that the increments corresponding to four CH$_2$ groups differ considerably from the expected value of 400 (ref. 22) and that their value increases with increasing number of carbon atoms in the ligand. The deviation from the expected value is connected with the electronegativity of the nitrogen atom in the dithiocarbamate ligand and the inductive effect of the alkyl group. As can be seen by comparison of the results obtained with Zn(II) and Ni(II) bis(N,N-

TABLE VII

DIFFERENCES IN INCREMENTS OF FOUR CH$_2$ GROUPS CALCULATED FROM KOVÁTS RETENTION INDICES (I)

ΔI_{4CH_2}*	Ni	Zn
$I_{ethyl} - I_{methyl}$	174	180
$I_{propyl} - I_{ethyl}$	270	285
$I_{butyl} - I_{propyl}$	341	345
$I_{pentyl} - I_{butyl}$	351	348
$I_{isobutyl} - I_{isopropyl}$	103	135

* $\Delta I_{4CH_2} = I_{n+1} - I_n$, where n represents the number of carbon atoms of the alkyl group linked to the nitrogen atom in the dithiocarbamate ligand.
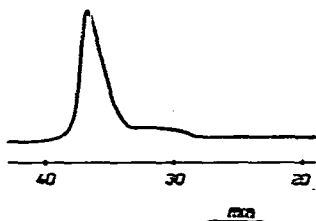
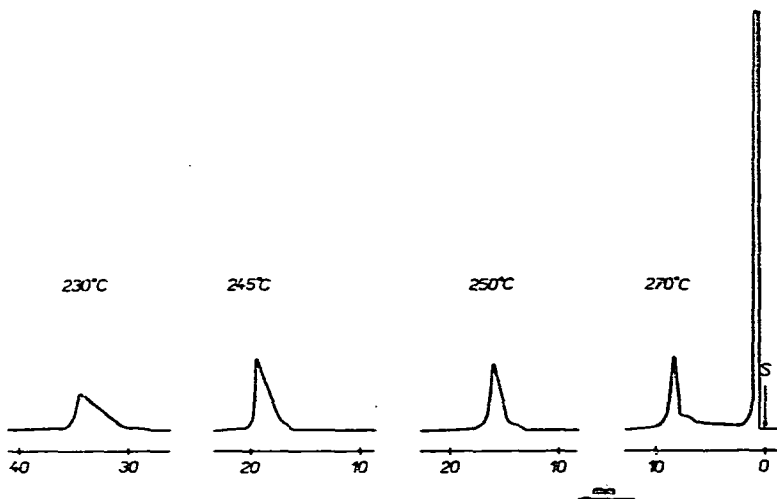Fig. 4. Peak shape of Cu(DEDTC)$_2$ chromatographed on Gas-Chrom P sil. coated with 3% of SE-30 at 503 °K.

Fig. 5. Peak shapes of Cd(DEDTC)$_2$ chromatographed on Gas-Chrom P sil. coated with 3% of SE-30.

dialkyldithiocarbamates) (Table VII), the central atom does not have a substantial effect on the ΔI_{4CH_2} values.

In contrast to published data[3-6], Cu(DEDTC)$_2$ and Cd(DEDTC)$_2$ decomposed during the gas chromatographic analysis (Figs. 4 and 5). Cd(DEDTC)$_2$ also decomposed when chromatography was carried out at temperatures below the melting point (Fig. 5). Similar decomposition was also observed during the gas chromatography of Co(DEDTC)$_2$.

Dimeric structures of Zn(II) and Cd(II) chelates[3,4] could not be detected under the conditions used.

Quantitative analysis on packed columns

The effect of the support material on the quantitative analysis of dithiocarbamates was tested by analysing standard solutions of Ni(DEDTC)$_2$ and Zn(DMDTC)$_2$ by the calibration graph method using the technique involving washing out the sample with a plug of solvent.

The calibration graph obtained for Ni(DEDTC)$_2$ on Gas-Chrom Q coated with 2% of SE-30 is shown in Fig. 6. The equations, calculated using the least-
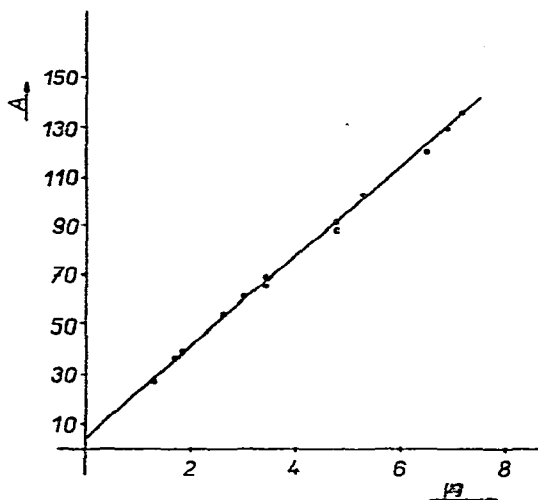
Fig. 6. Calibration graph for Ni(DEDTC)$_2$ obtained on Gas-Chrom Q coated with 2% of SE-30. Peak area (A) *versus* amount of Ni(DEDTC)$_2$ injected.

squares method, of the calibration graphs obtained for Ni(DEDTC)$_2$ analysed on columns packed with various supports are given in Table VIII. It follows that the most suitable packing materials for the quantitative analysis of Ni(DEDTC)$_2$ are those involving Gas-Chrom Q and Chromosorb G AW DMCS as supports, as the calibration graphs pass through the origin.

TABLE VIII

EQUATIONS FOR CALIBRATION GRAPHS OBTAINED FOR Ni(DEDTC)$_2$ CHROMATO-GRAPHED ON VARIOUS SUPPORTS COATED WITH 3% OF SE-30

Support	Equation[*]
Chromosorb W sil.	$y = -2.92 + 4.94\,x$
Gas-Chrom Q	$y = 0.099 + 2.78\,x$
Chromosorb G AW DMCS	$y = -0.022 + 2.92\,x$
Gas-Chrom P sil.	$y = -3.50 + 3.90\,x$
Chromaton N AW HMDS	$y = -8.15 + 9.81\,x$

[*] y is the peak area ($\times$ 1000 digits) and x (μg) the amount of Ni(DEDTC)$_2$ injected.

Quantitative analyses of Zn(II) dialkyldithiocarbamates require much more careful selection of high-quality supports, such as Chromosorb G AW DMCS, Gas-Chrom Q and Chromosorb W sil. Zn(DMDTC)$_2$ (Ziram) was chosen as the test compound.

The equations for the calibration graphs for Zn(DMDTC)$_2$, obtained in a manner similar to that used for Ni(DEDTC)$_2$, are given in Table IX. A comparison of the results in Tables VIII and IX shows that in the quantitative analysis of Zn(DMDTC)$_2$ a considerably greater systematic error than with Ni(DEDTC)$_2$ occurs.

Table IX indicates that the systematic error of the determination decreases with decreasing separation temperatures.

TABLE IX

EQUATIONS FOR CALIBRATION GRAPHS OBTAINED FOR Zn(DMDTC)₂ CHROMATO-GRAPHED ON VARIOUS SUPPORTS COATED WITH 3% OF SE-30

Support	Column temperature (°K)	Equation*
Chromosorb G AW DMCS	503	$y = -16.9 + 20.0\,x$
Chromosorb G AW DMCS	493	$y = -\ 8.3 + 13.2\,x$
Gas-Chrom Q	503	$y = -17.1 + 15.4\,x$
Chromosorb W sil.	493	$y = -51.3 + 50.8\,x$

* y is the peak area ($\times$ 1000 digits) and x (μg) the amount of Zn(DMDTC)₂ injected.

Capillary column gas chromatography

Metal capillary columns, coated with a non-polar stationary phase, have a high activity[23]. Glass capillary columns offer certain possibilities for the analysis of metal chelates by gas chromatography, as the surface of glass, after suitable modification, can be rendered sufficiently inert[24]. Glass capillary columns were prepared as previously described[17].

For practical reasons, a carrier gas velocity of *ca.* 50 cm/sec was used, which is approximately five times higher than the optimal velocity.

The quality of the capillary columns was tested by means of the Golay equation[25] for *n*-octacosane, and by determining the coefficient of asymmetry for the peak of Ni(DEDTC)₂.

A plot of H versus $\bar{u}$ for three capillary columns coated with a silicone phase is given in Fig. 7, which shows that the best column is that coated by the static method[19] using a 0.25% solution of SE-30. The column coated with a 0.5% solution of SE-30 is less efficient, possibly because the layer of the phase is twice as thick. The mode of coating (static or dynamic) under the given conditions does not appear to affect substantially the quality of the capillary columns (columns 1 and 2, Fig. 7).

Golay equations calculated for columns 3, 6 and 8 (Table III) can be written as $H = B/\bar{u} + C\bar{u}$:

Column 8: $H = 0.267/\bar{u} + 0.0029\bar{u}$

Column 6: $H = 0.218/\bar{u} + 0.00296\bar{u}$

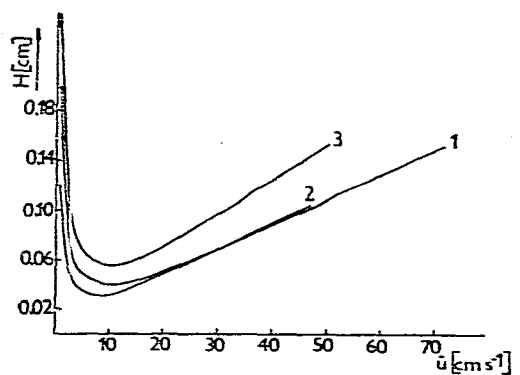Column 3: $H = 0.197/\bar{u} + 0.00207\bar{u}$

Fig. 7. Dependence of the height equivalent to a theoretical plate (H) on the mean carrier gas (nitrogen) velocity obtained for three capillary columns. Column: (1) No. 3; (2) No. 6; (3) No. 8.

It follows from these equations and from Fig. 7 that the quality of the columns is considerably affected by the resistance towards mass transfer, which manifests itself mainly at high carrier gas velocities. This resistance has its origin in the heterogeneity of the wall surface of the glass capillary columns (after etching with hydrogen chloride, crystals of sodium chloride are formed on the surface of the wall). With substances that require high carrier gas velocities, the limiting factor in the use of etched glass capillary columns is this resistance towards the mass transfer.

Another factor that affects the quality of the glass columns, apart from the sodium chloride crystals, are the silanol groups, formed during the process of etching as a result of the reaction of glass with hydrogen chloride. The silanol groups make the peak asymmetry of $Ni(DEDTC)_2$ more pronounced.

Table X shows the asymmetry coefficients, capacity ratios and relative retention times measured on capillary columns for n-octacosane and $Ni(DEDTC)_2$. It is obvious from the relative retention times that the analysis of $Ni(DEDTC)_2$ on capillary columns is affected also by other factors in addition to the distribution coefficient. The asymmetry coefficients show that $Ni(DEDTC)_2$ exhibits tailing on all columns examined except column 7. The main cause of this tailing is the adsorption of $Ni(DEDTC)_2$ on the glass surface. It follows from the asymmetry coefficient for column 7 ($As = 161$) that the applied temperature of the analysis (501 °K) is not high enough [the melting point of $Ni(DEDTC)_2$ is 508 °K] because, in order to convert the substance into the gaseous state, the heat of melting, in addition to the heat of evaporation, must be supplied. As these two phenomena do not occur fast enough, the elution peak is non-symmetrical and appears overloaded.

TABLE X

ASYMMETRY COEFFICIENTS (As), CAPACITY FACTORS (k), EFFICIENCY [No. OF PLATES, n, AND n/m] AND RELATIVE RETENTION TIMES (r) OF $Ni(DEDTC)_2$ OBTAINED AT 529 °K

Column	Compound	As	k	n	n/m	r
1	$Ni(DEDTC)_2$	38	21.9	16760	533	1.66
	C_{28}	—	13.2	20420	650	
2	$Ni(DEDTC)_2$	40	21.7	7960	352	1.70
	C_{28}	—	12.75	8550	378	
3	$Ni(DEDTC)_2$	89	37.5	11360	598	1.65
	C_{28}	—	22.6	12500	657	
4	$Ni(DEDTC)_2$	45	47.75	11930	540	1.70
	C_{28}	—	28.0	16250	740	
6	$Ni(DEDTC)_2$	54	13.0	13670	570	1.83
	C_{28}	—	7.1	16780	700	
7*	$Ni(DEDTC)_2$	161	18.7	19320	895	1.63
	C_{28}	—	11.3	37450	1734	

* Measured at 501 °K.

We have found that the value of the parameter C for a column etched by the dynamic method is about half of that for a column etched in the static manner. The value of C for columns etched statically is 0.002 sec. For column 7 (etched dynamically for 5 min at 625 °K), a value of $C = 0.001$ sec was found and thus the highest efficiency (plates per metre, Table X) for $Ni(DEDTC)_2$ was found for this column.
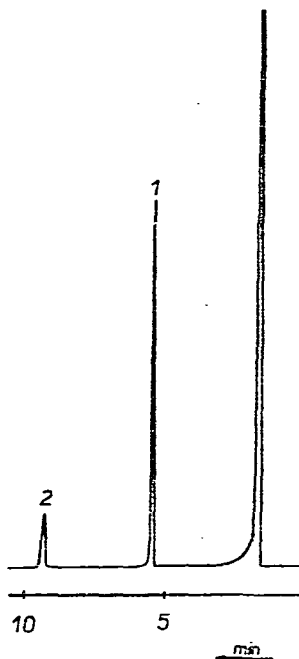
Fig. 8. Separation of (1) *n*-octacosane and (2) Ni(DEDTC)₂ on a glass capillary column (column No. 1) at 543 °K and a mean carrier gas (nitrogen) velocity of 42 cm/sec.

The separation of Ni(DEDTC)₂ and *n*-octacosane on capillary column 1 is shown in Fig. 8.

Fig. 9 shows a chromatogram of a mixture of Ni(DMDTC)₂, Ni(DEDTC)₂, Ni(DPDTC)₂, Ni(DIPDTC)₂, Ni(DBDTC)₂, Ni(DIBDTC)₂ and Ni(DPEDTC)₂ on a capillary column coated with OV-101 as stationary phase at 543 °K. Dashed peaks represent substances chromatographed separately.
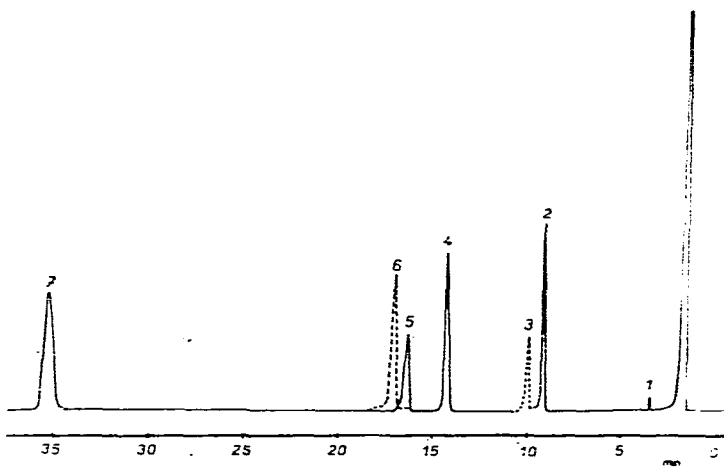

Fig. 9. Separation of Ni(II) bis(N,N-dialkyldithiocarbamates) on a glass capillary column (column No. 1) at 543 °K and a mean carrier gas (nitrogen) velocity of 42 cm/sec. 1, Ni(DMDTC)₂; 2, Ni(DEDTC)₂; 3, Ni(MIPDTC)₂; 4, Ni(DIPDTC)₂; 5, Ni(DPDTC)₂; 6, Ni(DIBDTC)₂; 7, Ni(DBDTC)₂.
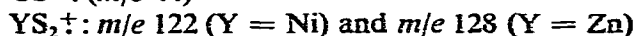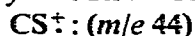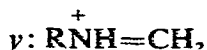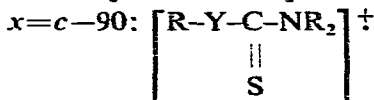
Mass spectrometry of nickel(II) and zinc(II) bis(N,N-dialkyldithiocarbamates)

The mass spectra of a number of N,N-dialkyldithiocarbamato complexes of various metals have been reported[2,7-16]. Only few analyses of fragmentation patterns have been attempted, notably for tris(N,N-dimethyldithiocarbamates) of Cr, In[8], Fe, Co, Ru and Rh[9]; for tris(N,N-diethyldithiocarbamates) of Cr, Fe, Co, Ru, Tl[9] and As[10]; for various trisdithiocarbamato complexes of As, Sb and Bi[10]; for halobis(dialkyldithiocarbamates) of As, Sb, Bi[11] and Fe[9]; and for tetrakisdihalobis- and diphenylbis(N,N-diethyldithiocarbamates) of Sn(IV)[16]. Mass spectral data on some bis(N,N-dialkyldithiocarbamates) of Cu[7], Zn[7,12,13] and Ni[2,14] and for monoalkyl- and dialkyldithiocarbamates of Na, [$S_2CN(CH_3)_2$]$_2$ and [$S_2CN(C_2H_5)_2$]$_2$ have been published[9,12].

Of the Zn(II) bis(N,N-dialkyldithiocarbamate) series, mass spectra of only the permethyl[12,15] and the perethyl compounds[7,13] have been reported. The mass spectrum of Ni(II) bis(N,N-diethyldithiocarbamate)[2] and the negative-ion mass spectra of the perethyl-, per-*n*-propyl- and per-*n*-butyldithiocarbamate derivatives of Ni(II)[14] are the only data that have been presented to date on Ni(II) bis(N,N-dialkyldithiocarbamates).

As we had many homologues available, we decided to investigate in detail the electron-impact (positive-ion) mass spectra of all of the Ni(II) and Zn(II) bis(N,N-dialkyldithiocarbamates) listed in Table I.

From the mass spectra of these compounds, we derived a rationale for a general fragmentation scheme, as presented in Fig. 10. Although alternative pathways are possible for the genesis of a number of ions, metastable transitions support the formation of the major ions in this scheme. In addition to these fragment ions, the following ions may be formed via various pathways:

$h-1$: $(R-1)=\overset{+}{N}=C=S$

r: $(M-CS_2-H\cdot)^+$

s: $CS_2^{+\cdot}$ (m/e 76)

$t-1$: $(R-1)^{+\cdot}$

$t-2$: $(R-2)^+$

u: R_2N^+

$$w=q-R: \left[R-N=C\overset{\diagup Y}{\underset{\diagdown S}{}} \right]^{+\cdot}$$

$w-32$: $[R-N=C=Y]^{+\cdot}$

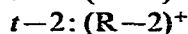$$x=c-90: \left[\begin{array}{c} R-Y-C-NR_2 \\ \parallel \\ S \end{array} \right]^{+\cdot}$$

y: $R\overset{+}{N}H=CH_2$

$y-2$: $R\overset{+}{N}\equiv CH$

$CS^{+\cdot}$: (m/e 44)

$YS_2^{+\cdot}$: m/e 122 (Y = Ni) and m/e 128 (Y = Zn)

(M) $L-Y-L$ ⁷⁺

$- R\cdot$ $- S$

(a) $L-Y-S-\overset{+}{\underset{\underset{S}{||}}{C}}-\overset{.}{N}-R$ (b) $L-Y-S-\overset{\bullet}{\underset{}{C}}=\overset{+}{N}\overset{R}{\underset{R}{<}}$

$- S$ $- R\cdot$ $- S$

(c) $L-Y-S-C\equiv\overset{+}{N}-R$ (o) $L-Y-\overset{\bullet}{C}=\overset{+}{N}\overset{R}{\underset{R}{<}}$

$- RCN$ (l) $- S$ $- R\cdot$
$- RCN$

(d) $L-Y-S^+ \rightarrow (n)$ $\ast$ (m) $L-Y-C\equiv\overset{+}{N}-R$

$- S$ (k) $- RCN$ $- S$

(e) $L-Y^+$ (p) $\overset{R}{\underset{R}{>}}N-\underset{\underset{S}{||}}{C}-Y-C\equiv\overset{+}{N}-R$

$- Y$ $- S$ $- RCN$

(f) L^+ (q) $\overset{R}{\underset{R}{>}}N-\underset{\underset{S}{||}}{C}-Y^+$ (z)

$- S$ $- Y$

(g) $\overset{R}{\underset{R}{>}}\overset{+}{N}=C=S$ $\ast$
(l) $\overset{R}{\underset{H}{>}}N-\underset{\underset{S}{||}}{C}-S-Y-S-C\equiv\overset{+}{N}-R$

$- R\cdot$ $- S$ (n) $\overset{R}{\underset{H}{>}}N-\underset{\underset{S}{||}}{C}-S-Y-S^+$

(h) $R-\overset{+}{\underset{\bullet}{N}}=C=S$ (i) $\overset{R}{\underset{H}{>}}\overset{+}{N}=C=S$ (j) $\overset{R}{\underset{R}{>}}\overset{+}{N}=C$ (k) $\overset{R}{\underset{H}{>}}N-\underset{\underset{S}{||}}{C}-S-Y^+$

$- HNCS$

(t) R^+ (v) $H_2N=C=S$
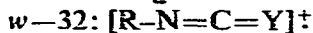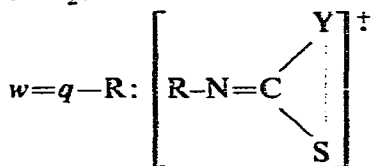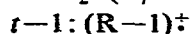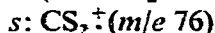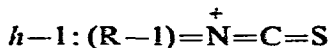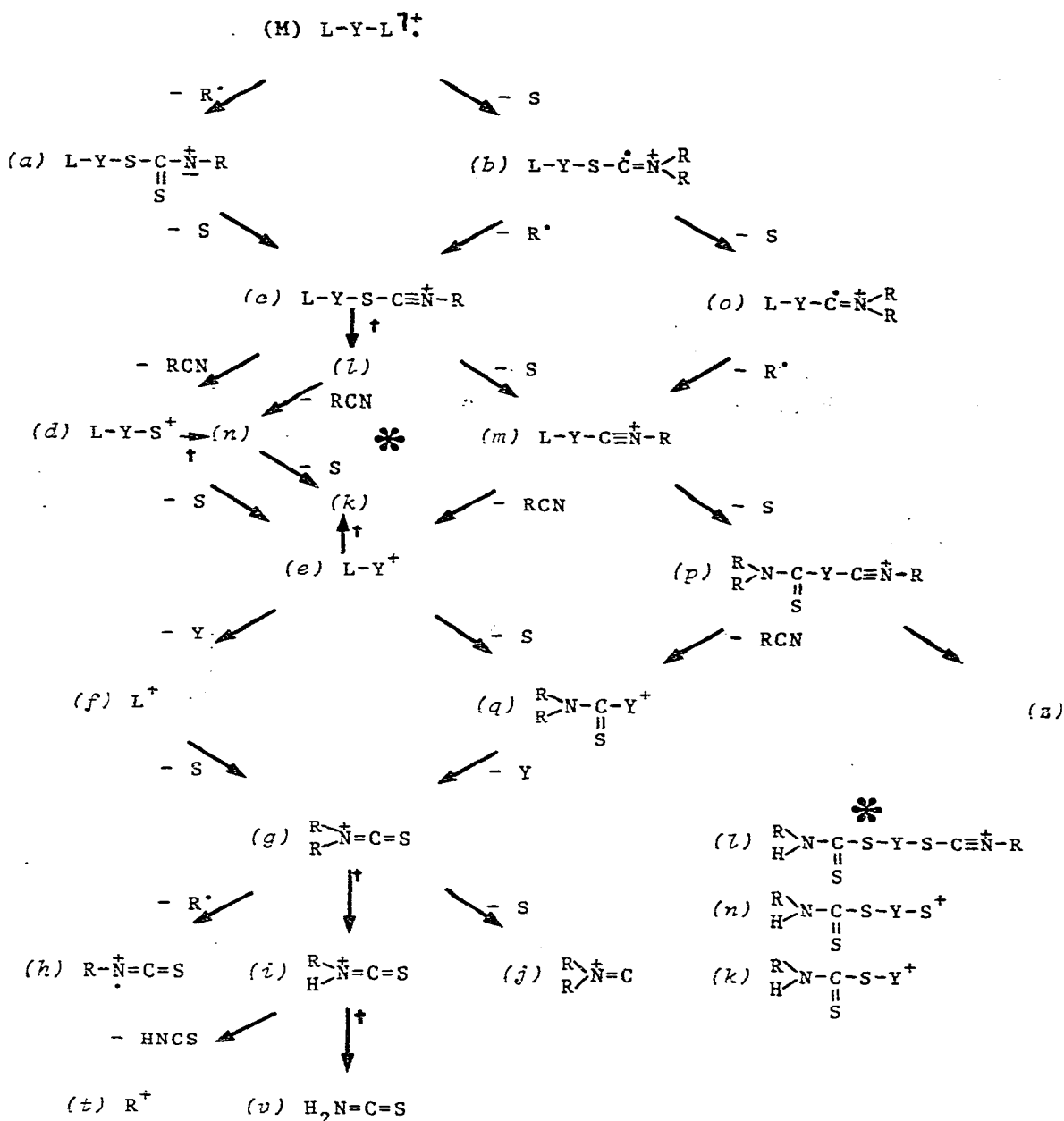
Fig. 10. Proposed fragmentation pathways of Ni(II) and Zn(II) bis(N,N-dialkyldithiocarbamates).

$Y = Zn$ or Ni; $L = $ ligand $= \overset{R}{\diagdown}N-\underset{\underset{S}{||}}{C}-S$; $R = $ alkyl group. †All horizontal and vertical arrows depict the loss of an olefinic molecule, $R-1$. All diagonal arrows from left to right indicate the loss of a molecule of S. Diagonal arrows from right to left represent losses as indicated. Note: the Y(MIPDTC)$_2$ complexes yield two series of fragment ions.

Although structures of the fragments are given, it should be borne in mind that many isomeric and mesomeric structures are possible. The molecular ion M, for example, can be represented as follows:

$$\left[\begin{array}{c} R \\ R \end{array}\!N\overset{S}{\underset{S}{\cdots}}\!\!\overset{S}{\underset{S}{\cdots}}\!\!N\begin{array}{c} R \\ R \end{array}\right]^{\overset{+}{\bullet}} \longleftrightarrow \left[\begin{array}{c} R \\ R \end{array}\!N\!-\!\overset{}{\underset{S}{C}}\!-\!S\!-\!Y\!-\!S\!-\!\overset{}{\underset{S}{C}}\!-\!N\begin{array}{c} R \\ R \end{array}\right]^{\overset{+}{\bullet}} \longleftrightarrow \left[\begin{array}{c} R \\ R \end{array}\!N\!-\!\overset{S}{\underset{S}{C}}\!\!\overset{S}{\underset{S}{\cdots}}\!C\!-\!N\begin{array}{c} R \\ R \end{array}\right]^{\overset{\pm}{}}$$
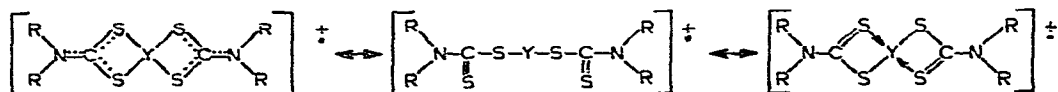
In all instances characteristic isotopic clusters appear for the Y-containing ions (M,$a,b,c,d,e,k,l,m,n,o,p,q,r,w,x,z$). Moreover, e, q and f appear in clusters -2 to $+4$ a.m.u. Especially for more highly substituted compounds, alkyl fragment series are abundant (m/e 57, 55, 43, 41). The electron-impact mass spectra of Ni(II) and Zn(II) bis(N,N-dialkyldithiocarbamates) are summarized in Tables XI and XII, respectively (full spectra are available on request from P.A.L.). In these tables, only the most abundant peaks from the isotopic clusters are included, corresponding to ^{58}Ni- and ^{64}Zn-containing ions, respectively. Above mass 100, the intensities of the ions omitted in Tables XI and XII are generally less than 2% of that of the base peak, with the following exceptions. Table XI: Ni(DMDTC)$_2$, $y = 56^0/_{00}$; Ni(DHPDTC)$_2$, $z = 102^0/_{00}$. Table XII: Zn(DPDTC)$_2$, $m = 22^0/_{00}$; Zn(MIPDTC)$_2$, $n = 27^0/_{00}$; Zn-(DMDTC)$_2$, $q = 27^0/_{00}$. Moreover NiS$_2^+$ (m/e 122) occurs in the spectra of Ni-(DMDTC)$_2$, $72^0/_{00}$; Ni(DEDTC)$_2$, $110^0/_{00}$; Ni(MIPDTC)$_2$, $205^0/_{00}$; and Ni(DPDTC)$_2$, $25^0/_{00}$. ZnS$_2^+$ (m/e 128) in found only in the spectrum of Zn(DEDTC)$_2$, $89^0/_{00}$. Fig. 10 is redrawn for nickel and zinc complexes in Figs. 11 and 12, respectively, indicating the major fragmentation pathways for these classes of compounds. Pathways confirmed by metastable decompositions are indicated.

Discussion of mass spectra

From Tables XI and XII and Figs. 11 and 12, different fragmentation patterns appear for Ni(II) and Zn(II) chelates. The molecular ions M of nickel derivatives are more abundant than those of zinc. Because the relative intensities of the molecular ions reflect the bond strengths of the YS$_4$ coordination cores, this indicates that complexes of nickel are more stable than those of zinc. Owing to the lower relative intensities of the molecular ions, the primary fragmentation products of the zinc complexes are less abundant than the corresponding nickel fragment ions. However, the formation of ions a, c, d and f is clearly favoured with zinc derivatives over nickel derivatives. In the spectra of the nickel complexes, ions b, $e+1$, w and the cluster around q are relatively more abundant than in the zinc bis(dialkyldithiocarbamate) spectra. Ions g, h, i, s, u, v and the clusters of t and y are the most abundant fragment ions in all instances.

In general, the intensity of the ions in the high mass region decreases predictably with increasing size of n-alkyl substituents, per-pentyl compounds being anomalous. The isopropyl and isobutyl derivatives of nickel bis(dithiocarbamates) fragment much more easily than the n-alkyl derivatives. With zinc bis(dialkyldithiocarbamates) this effect is less evident.

TABLE XI

RELATIVE INTENSITIES (%₀) OF MAJOR IONS (ABOVE m/e 40) IN THE MASS SPECTRA OF Ni(II) BIS(N,N-DIALKYLDITHIOCARBAMATES)

Terms in parentheses represent coincident ions. Superscripts: $^{+2}$ = 2 a.m.u. higher; $^{+1}$ = 1 a.m.u. higher; $^{-1}$ = 1 a.m.u. lower; $^{-2}$ = 2 a.m.u. lower. ? = Not measured.

Compound	M	b	e	e+1	f	g	h−1	h	i	j	k	m	n	o
Ni(DMDTC)₂	671	204	406	96	62^{+1}	*1000*	109	273	54	122	119^{-1}	86	10^{-1}	89
Ni(DEDTC)₂	742	134	225	260	140^{-2}	915	68	61	*1000*	—	147^{-1}	59	134^{-1}	53
Ni(MIPDTC)₂*	375	92	269	303	67^{+1}	750	35 (u)	99 251	31 707	48	12^{-1} 129^{-1}	2 80	2^{-1} 61	31
Ni(DPDTC)₂	469	113	124	115	67^{-1}	503	(u)	37	571	27	38^{-1}	18	6	18
Ni(DIPDTC)₂	219	90	58	43	8	271^{+1}	(u)	529	298	37	21^{-1}	8	7^{+1}	—
Ni(DBDTC)₂	425	82	64	57	52^{+1}	249	56	49	411	93	(f+1)$^{-1}$	5	1^{-1}	7
Ni(DIBDTC)₂	301	79	76	18	52^{+1}	121	41	72	306	28	(f+1)$^{-1}$	3	2^{-1}	5
Ni(DPEDTC)₂	751	219	78	28	45^{+1}	253	33	39	406	195	13	4^{+2}	7	7
Ni(DHDTC)₂	255	56	19	16	44^{+1}	253	39	28	237	278	—	6^{+2}	—	2
Ni(DHPDTC)₂	158	16	4	40	31	182	40	5	149	504	7	—	—	—
Ni(DODTC)₂	42	8	—	3	9	61	23	2	31	283	2	—	9	—

* Upper row corresponds to ions containing more methyl than isopropyl groups and the lower row to the opposite situation.

TABLE XII

RELATIVE INTENSITIES (%₀) OF MAIN IONS (ABOVE m/e 40) IN THE MASS SPECTRA OF Zn(II) BIS(N,N-DIALKYLDITHIOCARBAMATES)

Notes as in Table XI.

Compound	M	a	b	c	d	e	f	g	h−1	h	i	j
Zn(DMDTC)₂	168	7	4	4	42	91	243	*1000*	431	301	81	270
Zn(DEDTC)₂	140	18	—	8	85	100	218	724	386	781	861	66
Zn(MIPDTC)₂*	161	— 16	4^{-1}	— 18	66	81	110	237	106 (u)	50 849	13 643	34
Zn(DPDTC)₂	121	9	11^{-1}	28	63	91	118	287	(u)	119	248	99
Zn(DIPDTC)₂	34	9	—	7	14	52	30	59	(u)	499	183	—
Zn(DBDTC)₂	23	1	5^{-1}	3	11	18	33	83	52	546	267	177
Zn(DIBDTC)₂	43	—	6^{-1}	32	31	82	56	137	58	198	156	74
Zn(DPEDTC)₂	56	—	14^{-1}	9	28	46	48	175	23	39	123	348

* Upper row corresponds to ions containing more methyl than isopropyl groups and the lower row to the opposite situation.

The occurrence of the [Zn(DEDTC)₂]₂ dimer in the gas phase has been reported[13]: the ion 2M had an intensity of 1% relative to M in the mass spectrum. In contrast to these findings, we could not detect any ions above the isotopic cluster of M (under the conditions applied, all ions with an intensity higher than 0.01% of the base peak were detected). In the low mass region, alkyl (m/e 43, 57, ..., t) and alkenyl (m/e 41, 55, ..., t−2) ions are prominent. The intensity of HNR⁺ ions, as reported for perethyl compounds[10], in which case this ion coincides with CS⁺ at m/e 44, is higher

p	q−2	q−1	q	s	t−2	t	u	v	w	x	y−2	y	m/e 57	m/e 55	m/e 43	m/e 41
79	71	87	187	203	?	?	812	70	138	74	390	(u)	128^{+1}	$(j)^{+1}$	106	115
117	60	236	161	127	?	?	610	943	140	27	162	101	$(y)^{+1}$	110^{+1}	218^{+1}	102^{+1}
—	49	237	174	129	?	?	502	60	51	22	397	52	104^{+1}	169^{+1}	(t)	(t−2)
50					588	1000			274	29	40	(u)				
64	51	92	101	27	398	1000	272	318	50	28	74	54	72^{+1}	26^{+1}	(t)	(t−2)
14	—	17	35	650	736	1000	206	809	14^{+1}	—	105	188	280	89	(t)	(t−2)
31	48	47	40	75	198	1000	191	199	49	21	81	75	(t)	(t−2)	103	598
33	35	69	61	26	191	1000	98	78	60	6	84	33	(t)	(t−2)	89	558
32	56	32	33	57	234	866	229	115	48	69	101	104	20	178	1000	632
11	9	10	6	13	108	418	105	104	29	26	141	242	269	448	1000	801
—	10	12	6	741	163^{+1}	58	184	98	14	12	412	671	714	981	1000	805
—	1	2	—	282	60^{+1}	12	67	15	—	8	199	803	508	315	1000	491

k	s	t−2	t	u	v	y−2	y	m/e 57	m/e 55	m/e 43	m/e 41
4	336	?	?	641	50	801	(u)	$(j−1)^{-1}$	23	204	60
20	260	?	?	201	1000	252	85^{+1}	50^{-1}	120	812^{+1}	344^{+1}
—	95	?	?	436	48	587	90	166^{+1}	261^{+1}	(t)	(t−2)
46		723	1000			58	(u)				
14	50	760	1000	115	231	132	147	167^{+1}	58	(t)	(t−2)
15	115	680	1000	196	364	47	60	147^{+1}	38	(t)	(t−2)
—	63	124	174	123	48	63	90	(t)	(t−2)	51	1000
23	60	476	532	21	93	118	65	(t)	(t−2)	502	1000
5	91	299	398	53	80	104	109	48	258	780	1000

than that of the alkyl ions (at 1 a.m.u. lower) for the lower alkyl derivatives. These ions are included in Tables XI and XII under m/e 57 and 43 with the superscript $^{+1}$. Prominent peaks in the spectra of $Zn(DMDTC)_2$ and $Zn(DEDTC)_2$ have earlier been ascribed to ions a, c, d, e, f, g, h−1, h, i, l, r, s, u and v[7,12], but fragmentation pathways were indicated only for a, d, e, f, g and h[12]. The fragmentation pathways of the ligand in the mass spectra of sodium (N,N-dialkyldithiocarbamates) have also been reported[9,12] and are in agreement with the fragmentation of f(+1) in Fig. 10. The de-
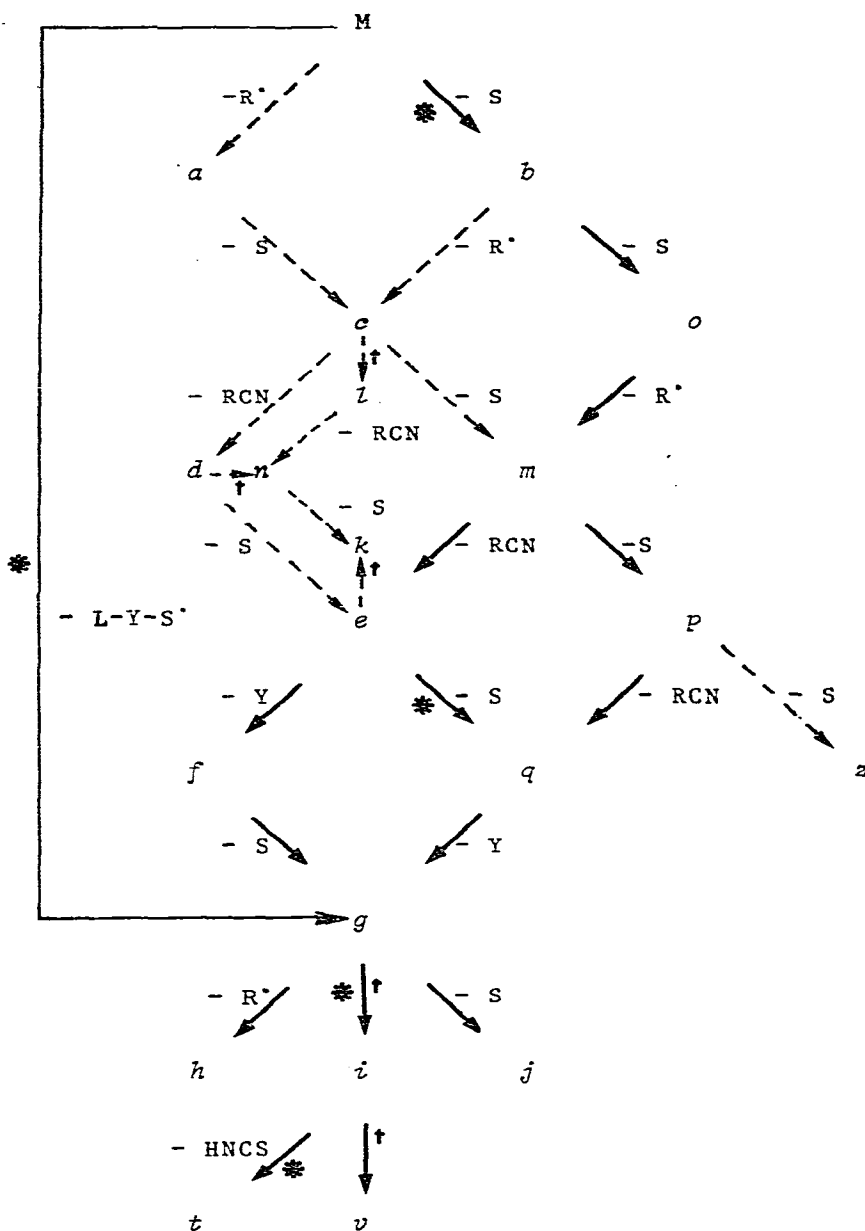
Fig. 11. Main fragmentation pathways of Ni(II) bis(N,N-dialkyldithiocarbamates). Main pathways are represented by full arrows and minor routes by dotted arrows. * Confirmation by metastable transitions (a metastable was also observed for the decomposition of e: $e - H_2S \to q - 2$). For further explanation, see Fig. 10.

compositions $f + 1 \to s$, $g \to u$ and $h \to h - 1$ were proposed[9] for the genesis of s, u and h (not included in Fig. 10).

It is interesting to compare the spectra of the nickel and zinc chelates with those of tri- and tetravalent metal derivatives[8–10,16]. The primary fragmentation process is

M

- R·

- S

a

b

- S

- R·

- S

c

o

- RCN

l

- S

- R·

- RCN

d - n

m

- S

- S

k

- RCN

- S

e

p

- Y

- S

- RCN

- S

f

q

z

- S

- Y

g

- R·

* ↑
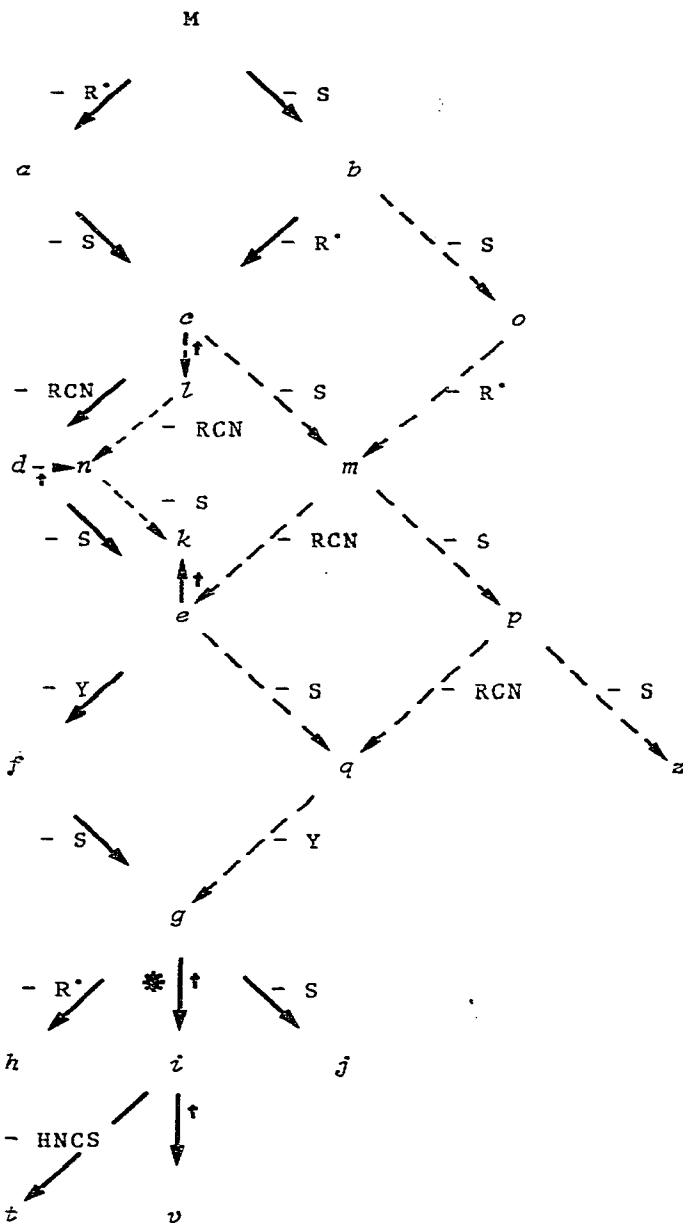
- S

h

i

j

- HNCS

t

v

Fig. 12. Main fragmentation pathways of Zn(II) bis(N,N-dialkyldithiocarbamates). Main pathways are represented by full arrows and minor routes by dotted arrows. * Confirmation by metastable transitions. For further explanation, see Fig. 10.

usually ligand loss, yielding abundant $[L-Y-L]^+$ ions. Important secondary fragmentations involve the loss of S_2, CS_2 and/or YS [often CS_2^+ (s) is the base peak]. S^+ is common, as are Y^+, $Y_mS_n^+$ and YSC^+. None of these ions is found in the mass spectra of the nickel and zinc analogues with the exception of YS_2^+, which is found in the spectra of the lower alkyldithiocarbamates of Ni- and $Zn(DEDTC)_2$, as noted earlier.

ACKNOWLEDGEMENT

REFERENCES

1 J. Masaryk, J. Krupčík, J. Garaj and M. Košik, *J. Chromatogr.*, 115 (1975) 256.
2 J. Krupčík, J. Garaj, Š. Holotík, D. Oktavec and M. Košik, *J. Chromatogr.*, 112 (1975) 189.
3 T. J. Cardwell, D. J. Desarro and P. C. Uden, *Anal. Chim. Acta.*, 85 (1976) 415.
4 M. Ahmad and A. Aziz, *J. Chromatogr.*, 152 (1978) 542.
5 A. Tavlaridis and R. Neeb, *Naturwissenschaften*, 63 (1976) 146.
6 A. Tavlaridis and R. Neeb, *Z. Anal. Chem.*, 282 (1976) 17.
7 J. F. Villa, D. A. Chatfield, M. M. Bursey and W. E. Hatfield, *Inorg. Chim. Acta*, 6 (1972) 332.
8 P. J. Hauser and A. F. Schreiner, *Inorg. Chim. Acta*, 9 (1974) 113.
9 K. W. Given, B. M. Mattson, G. L. Miessler and L. H. Pignolet, *J. Inorg. Nucl. Chem.*, 39 (1977) 1309.
10 G. E. Manoussakis, E. D. Micromastoras and C. A. Tsipis, *Z. Anorg. Allg. Chem.*, 403 (1974) 87.
11 C. A. Tsipis and G. E. Manoussakis, *Inorg. Chim. Acta*, 18 (1976) 35.
12 F. I. Onuska and M. E. Comba, *J. Ass. Offic. Anal. Chem.*, 59 (1976) 622.
13 J. F. Villa, M. M. Bursey and W. E. Hatfield, *Chem. Commun.*, (1971) 307.
14 I. W. Fraser, J. L. Garnett, I. K. Gregor and K. J. Jessop, *Org. Mass Spectrom.*, 10 (1975) 69.
15 W. R. Benson and J. N. Damico, *J. Ass. Offic. Anal. Chem.*, 51 (1968) 347.
16 G. K. Bratspies, J. F. Smith, J. D. Hill and R. J. Magee, *Thermochim. Acta*, 19 (1977) 335, 349 and 361.
17 J. Krupčík, M. Kristin, M. Valachovičová and S. Janiga, *J. Chromatogr.*, 126 (1976) 147.
18 J. J. Franken, G. A. F. M. Rutten and J. A. Rijks, *J. Chromatogr.*, 126 (1976) 117.
19 J. Bouche and M. Verzele, *J. Gas Chromatogr.*, 6 (1968) 501.
20 D. M. Ottenstein, *Advan. Chromatogr.*, 3 (1966) 137.
21 E. Brandšteterová, unpublished results.
22 E. Kováts, *Advan. Chromatogr.*, 1 (1965) 229.
23 J. Krupčík, K. Tesařik, O. J. Liška, J. Němec and Y. P. Duchesne, *Chromatographia*, 5 (1972) 252.
24 G. A. F. M. Rutten and J. A. Luyten, *J. Chromatogr.*, 74 (1972) 177.
25 L. S. Ettre, *Open Tubular Columns in Gas Chromatography*, Plenum Press, New York, 1965.