Mass Spectrometric Study on Several Metal Dialkyldithiocarbamate Chelates

M.-L. RIEKKOLA

Division of Analytical Chemistry, Department of Chemistry, University of Helsinki, SF-00100 Helsinki 10, Finland

The mass spectra of several metal dialkyldithiocarbamate chelates have been determined with samples introduced by direct inlet probe (ionization energies 23 and 75 eV) and from an interfaced gas chromatograph (23 eV). The general fragmentation pathways are given. The gas phase stability was found to decrease in the metal order $\text{Ni} > \text{Pd} > \text{Cu} > \text{Zn} > \text{Cd} > \text{Pb} > \text{Hg} > \text{Se}$ for bis (dithiocarbamates) and $\text{Rh} > \text{Cr} > \text{Co} > \text{Fe} > \text{In} > \text{As}$ for tris (dithiocarbamates). The effect of the length and shape of the nonfluorinated alkyl group on the gas phase stability is apparent in the ligand order $\text{DEDTC} > \text{DPDTC} > \text{DIBDTC} = \text{DBDTC}$. Fluorination of diethyldithiocarbamates decreases the gas phase stability. Gas chromatography-mass spectrometry provides an excellent means of verifying that metal chelates elute without decomposition under specified conditions.

Mass spectra have been reported for a number of metal dialkyldithiocarbamate chelates.^{1–13} Normally a direct inlet probe has been used for the sample introduction.

As long ago as 1908 Delépine¹⁴ reported that di-isobutyldithiocarbamates of nickel(II) and copper(II) sublime in vacuum and thus are volatile. Since the late seventies the volatility of many metal dialkyldithiocarbamates has been exploited for the development of a method allowing determination of metals by gas chromatography. The compounds have been successfully eluted from both packed¹⁵ and capillary columns.^{16,17} It has been noted, too, that fluorination of diethyldithiocarbamates greatly enhances the volatility.¹⁸

Since 1965 β -diketonate chelates have been found very promising for gas chromatographic determinations, too.¹⁹ A combination gas chromatograph-mass spectrometer (GC-MS) has recently been used to study volatile chromium(III) β -diketonate chelates with geometrical isomers.²⁰

The aim of the present work was to study the gas chromatographic behaviour, gas phase stability and influence of the alkyl substituents of several metal dialkyl-substituted (diethyl- (DEDTC), dipropyl- (DPDTC), dibutyl- (DBDTC), di-isobutyl- (DIBDTC) and di (tri-fluoroethyl)- (FDEDTC)) dithiocarbamate chelates by GC-MS, employing a falling needle injector²¹ and short nonpolar glass capillary column in the gas chromatograph. The general fragmentation pathways were compared with those for samples introduced to the MS by direct inlet probe.

EXPERIMENTAL

Materials. The nonfluorinated and fluorinated dialkyldithiocarbamate chelates were prepared and purified according to methods described previously.^{16,17,22} The metal chelates investigated are listed in Table 1.

Instrumentation. A glass capillary column coated with OV-101 liquid phase (4 m $\times$ 0.30 mm I.D.) was prepared from borosilicate glass (Duran 50), using a slight modification of the method described by Grob and Grob.²³ A Carlo Erba Fractovap Series 2300 gas chromatograph, equipped with a falling needle injector (Chrom-pack), was connected to a Jeol D 100 mass spectrometer. The capillary column was inter-

Table 1. Metal *N,N*-dialkyldithiocarbamates studied.

Ligand	Metals
DEDTC	Ni(II), Pd(II), Pt(II), Cu(II), Zn(II), Cd(II), Hg(II), Pb(II), Se(II), Cr(III), Fe(III), Co(III), Rh(III), In(III), As(III)
DPDTC	Ni(II), Pd(II), Cu(II), Zn(II), Cd(II), Hg(II), Pb(II), Se(II), Cr(III), Fe(III), Co(III), Rh(III), In(III), As(III)
DBDTC	Ni(II), Pd(II), Cu(II), Zn(II), Cd(II), Hg(II), Pb(II), Cr(III), Fe(III), Co(III), Rh(III), In(III), As(III)
DIBDTC	Ni(II), Pd(II), Cu(II), Zn(II), Cd(II), Hg(II), Pb(II), Cr(III), Fe(III), Co(III), Rh(III), In(III), As(III)
FDEDTC	Ni(II), Pd(II), Cu(II), Zn(II), Cd(II), Hg(II), Pb(II), Co(III)

faced into the ion source by a Pt/Ir capillary tube (30 cm × 0.30 mm O.D. × 0.15 mm I.D.). A helium separator was not used.

Helium was used as the carrier gas. Samples of the investigated chelates were dissolved in methylene chloride. The injection port and interface temperatures were 250 and 250 °C for metal FDEDTC chelates and 275 and 275 °C, respectively, for DEDTC, DPDTC, DBDTC and DIBDTC chelates. The oven temperatures were 160–200 °C for bis(chelates) and 170–210 °C for tris(chelate) of FDEDTC acid, 200–250 °C for bis(chelates) and 210–260 °C for tris(chelates) of DEDTC acid, and 210–260 °C for bis(chelates) and 220–270 °C for tris(chelates) of DPDTC acid, 230–265 °C for bis(chelates) and 240–275 °C for tris(chelates) of DBDTC acid, and 205–255 °C for bis(chelates) and 215–265 °C for tris(chelates) of DIBDTC acid. Heating rate was 30 °C/min.

The ionization energy of the mass spectrometer was 23 and 75 eV when samples were introduced by direct inlet probe and 23 eV when the gas chromatograph was used. The accelerating voltage was 3 kV and the ion multiplier voltages were 1–1.6 kV. Temperatures of the ion source were within the range 160 °C to 230 °C depending on the volatility of the chelate. The resolution of the instrument was 1200 with a 10 % valley (main slit 250 μm, β-slit 1 mm and collector slit 50 μm).

RESULTS AND DISCUSSION

The molecular ion peaks were detected for almost all dialkyldithiocarbamate chelates introduced by direct insertion probe, but in greatly varying relative abundances. The chelates of the nontransition metals In(III), As(III) and Se(II) were exceptional in displaying no parent molecular ions.

The 10 eV mass spectra of dimethyldithiocarbamates of In(III) and Cr(III) have been reported by Schreiner and Hauser.⁴ They found that the parent molecular ion peak of the indium chelate was virtually absent, whereas the molecular ion of the chromium chelate was present with large intensity. It was concluded that the $p\pi$ to $d\pi$ bonding between the sulfur and Cr(III) with t_{2g}^3 subshell leads to stronger metal-sulfur bonds for the chromium chelate. The relatively intense molecular ion peaks found for all chromium chelates in the present study are supportive of their interpretation.

The ions of highest mass number observed by solid probe method for the arsenic(III) chelates were the direct fragments of molecular ions of general formula $(AsL_2)^+$. Similar results have been obtained for As(III) diethyldithiocarbamate⁵ and recently for As(III) tetramethylenedithiocarbamate.¹⁰ However, for freshly extracted As(DEDTC)₃ the molecular ion peak has been observed.³ The structure of As(DEDTC)₃ is a distorted trigonal antiprism with one of the As–S bonds in each ligand practically covalent and the other one more ionic.²⁴

The absence of molecular ions of Se(DEDTC)₂ and Se(DPDTC)₂ can be attributed to electron impact or thermal or pyrolytic decomposition. Se(DEDTC)₂ forms an asymmetric planar chelate, where in both ligands one of the Se–S bonds is much longer than the other leading to probable instability of the compound. It has been inferred that the sulfur to central atom bonding is based mainly on p-orbitals, perhaps with some s-orbital contribution.²⁵ The structure of Se(DPDTC)₂ can be assumed to be similar since the structure of metal dialkyldithiocarbamates is only slightly changed upon the lengthening of the alkyl group.²⁶ The interpretation of the fragmentation pattern in terms of the solid-state structure, it may be noted, assumes the similarity of the solid- and vapour-state structures.

Fig. 1. Proposed general fragmentation pattern for metal dialkyldithiocarbamate chelates (L =ligand and M =metal).

Mass spectra were recorded for all the present metal chelates with sample introduction by direct inlet probe and ionization energies of 23 and 75 eV. Under these conditions no major fragmentation differences were found. Although intensities of the mass spectra recorded by GC-MS were decreased relative to those recorded with direct inlet probe (23 eV), the same fragmentation patterns were observed, with the exception of Se(II), As(III) and Fe(III) dialkyldithiocarbamates. These compounds decomposed in the injector, the capillary column, or the interface, resulting in more than one peak in the total ion chromatogram. Dipropylthiocarbamate of Se(II) has been found to have two gas chromatographic peaks¹⁷ and di-isobutylthiocarba-

mates of Fe(III) and As(III) to decompose during gas chromatographic elution.²⁷

The proposed general fragmentation pathways for metal dialkyldithiocarbamates are given in Fig. 1. In addition to the fragment ions of Fig. 1, the following ions may be formed $(R-1)^+$, $(R-2)^+$, CS^+ (m/e 44), CS_2^+ (m/e 76), $RNH=CH_2$, $(L-1)^+$. For arsenic and selenium chelates, thiuram disulfide $(L_2)^+$ ions were detected, too. The major peaks are in essential agreement with those reported by Krupčík *et al.* for various nickel(II) and zinc(II) dialkyldithiocarbamates.⁹

The primary fragmentation process for tris(chelates) is the loss of dithiocarbamate ligand. Ligand-deficient species $(RhL_2)^+$, $(CrL_2)^+$, $(CoL_2)^+$ and $(FeL_2)^+$ appear in quite high abundance, though for Fe(III) chelates only with the solid probe introduction.

The intensities of molecular ions and the ligand loss give information about gas phase stabilities of the chelates. Under the conditions of electron impact fragmentation the order of stability decreases as follows: $Ni > Pd > Cu > Zn > Cd > Pb > Hg \gg Se$ for bis(dithiocarbamates) and $Rh > Cr > Co > Fe \gg In > As$ for tris(dithiocarbamates). From the stability order it can be concluded that nontransition metals form more labile chelates with dithiocarbamic acids than do transition metals. The mass spectra of Pt(II) were determined only for diethyl derivative. According to these few results, platinum lies between palladium and copper in the stability order.

It has been noted earlier that nickel chelates are more stable than those of zinc.⁹ And dimethyl- and diethylthiocarbamates of rho-

Fig. 2. Mass spectrum of $Zn(FDEDTC)_2$ recorded by GC-MS.

dium and chromium have been found to be more stable than the respective iron and cobalt chelates.⁸ These findings are in agreement with the stability order above. Zn(DEDTC)₂ has been reported to occur as dimer in the gas phase.¹ In agreement with Krupčik *et al.*⁹ no ions appeared in the spectra of zinc chelates at *m/e* ratios higher than the isotopic cluster of molecular ions.

The influence of the alkyl group on the gas phase stability for the nonfluorinated dialkyl-dithiocarbamates is revealed in the following order: DEDTC>DPDTC>DIBDTC≈DBDTC. Thus the prolongation of the alkyl chain and the increasing molecular weight apparently decrease the stability.

Fluorination of diethyldithiocarbamates does

Table 2. Prominent ions and their relative intensities in the spectra of (a) metal di(trifluoroethyl)-dithiocarbamates and (b) nonfluorinated dialkyl-dithiocarbamates recorded by GC-MS (23 eV) (L=ligand and M=metal).

(a)

Chelate	[ML ₃] ⁺	[ML ₂] ⁺	[ML] ⁺	[L] ⁺	[R ₂ NCS] ⁺	[RNCS] ⁺	[H ₂ CNCS] ⁺	R ⁺
Ni (FDEDTC) ₂	—	28	9	3	100	10	5	19
Pd (FDEDTC) ₂	—	28	10	4	100	8	7	18
Cu (FDEDTC) ₂	—	28	15	10	100	6	7	14
Zn (FDEDTC) ₂	—	21	18	32	100	19	13	19
Cd (FDEDTC) ₂	—	15	8	72	100	10	11	17
Hg (FDEDTC) ₂	—	5	—	60	100	7	8	21
Pb (FDEDTC) ₂	—	2	53	7	100	9	10	14
Co (FDEDTC) ₃	10	92	9	35	100	8	9	41

(b)

Chelate	[ML ₂] ⁺	[ML] ⁺	[L] ⁺	[R ₂ NCS] ⁺	[R ₂ N] ⁺	[RNHCS] ⁺	[H ₂ NCS] ⁺	R ⁺
Ni (DEDTC) ₂	100	28	5	100	46 ^a	57	29	?
Ni (DPDTC) ₂	100	27	3	96	47	95	31	61
Ni (DBDTC) ₂	100	9	6	50	37	61	20	55
Ni (DIBDTC) ₂	100	4	1	20	17	32	3	70
Pd (DEDTC) ₂	93	40	3	56	100 ^a	79	28	?
Pd (DPDTC) ₂	89	39	19	42	100	38	22	18
Pd (DBDTC) ₂	77	32	5	24	69	38	27	100
Pd (DIBDTC) ₂	100	71	5	25	29	17	5	78
Pt (DEDTC) ₂	49	13	8	75	81 ^a	100	42	?
Cu (DEDTC) ₂	45	6	6	100	16 ^a	56	22	?
Cu (DPDTC) ₂	34	8	11	75	23	66	34	100
Cu (DBDTC) ₂	31	4	3	48	9	38	12	100
Cu (DIBDTC) ₂	36	5	2	30	7	32	3	100
Zn (DEDTC) ₂	42	15	22	100	28 ^a	59	43	?
Zn (DPDTC) ₂	36	22	24	100	20	61	28	81
Zn (DBDTC) ₂	28	10	20	80	7	60	25	100
Zn (DIBDTC) ₂	31	22	11	88	3	25	4	100
Cd (DEDTC) ₂	28	13	56	100	65 ^a	54	60	?
Cd (DPDTC) ₂	7	7	92	67	50	53	34	100
Cd (DBDTC) ₂	3	3	97	29	42	32	26	100
Cd (DIBDTC) ₂	1	2	53	26	7	31	7	100
Hg (DEDTC) ₂	2	4	100	100	56 ^a	43	84	?
Hg (DPDTC) ₂	1	2	90	70	46	44	38	100
Hg (DBDTC) ₂	1	1	91	32	40	31	24	100
Hg (DIBDTC) ₂	1	2	75	28	12	29	8	60

Table 2. Continued.

(b)

Chelate	[ML ₃] ⁺	[ML ₂] ⁺	[ML] ⁺	[L] ⁺	[R ₂ NCS] ⁺	[R ₂ N] ⁺	[RNHCS] ⁺	[H ₂ NCS] ⁺	R ⁺
Pb (DEDTC) ₂	—	15	86	25	100	45 ^a	81	56	?
Pb (DPDTC) ₂	—	3	85	32	82	43	75	46	100
Pb (DBDTC) ₂	—	3	73	97	29	42	32	26	100
Pb (DIBDTC) ₂	—	1	70	100	48	41	50	14	90
Cr (DEDTC) ₃	56	100	7	7	44	50 ^a	90	42	?
Cr (DPDTC) ₃	52	100	6	5	37	18	50	36	71
Cr (DBDTC) ₃	40	70	6	21	30	10	38	25	100
Cr (DIBDTC) ₃	41	63	2	29	28	6	32	10	100
Co (DEDTC) ₃	13	100	17	8	28	24 ^a	92	19	?
Co (DPDTC) ₃	13	100	4	7	14	9	58	17	40
Co (DBDTC) ₃	6	100	8	5	40	8	85	15	30
Co (DIBDTC) ₃	9	100	2	5	3	2	6	2	19
Rh (DEDTC) ₃	64	36	3	14	100	70 ^a	93	57	?
Rh (DPDTC) ₃	56	28	2	9	50	38	30	48	80
Rh (DBDTC) ₃	42	20	1	7	49	27	18	33	70
In (DEDTC) ₃	—	40	42	66	100	75 ^a	80	51	?
In (DPDTC) ₃	—	32	47	59	86	51	78	40	100
In (DBDTC) ₃	—	1	3	100	23	20	41	8	85
In (DIBDTC) ₃	—	2	3	100	11	11	19	5	82

^a[R₂N]⁺ + [H₂CNCS]⁺.

not change the fragmentation pattern, in agreement with a recent similar observation for Ni(FDEDTC)₂.¹² But whereas the volatility increases markedly,¹⁸ the gas phase stability decreases upon fluorination. Ni(DEDTC)₂ has a more prominent molecular ion than Ni(FDEDTC)₂ also in the published spectra¹¹ indicating greater stability for the nonfluorinated compound. The spectra were determined using solid probe and 70 eV ionization energy. The volatility of β -diketonates also increases as the ligands become more extensively fluorinated.¹⁹ But mass spectrometric detection has recently given indication of an inverse relationship between volatility and gas phase stability for some fluorinated Cr(III) β -diketonate chelates.²⁰

The intensity of the ions in the high mass region decreases with the lengthening of the alkyl substituent, in agreement with an earlier report.⁹ The base peak varies with the alkyl group. The (R₂NCS)⁺ ion is the most abundant ion for almost all diethyl- and di(trifluoroethyl)dithiocarbamates and it is also quite prominent for other dialkyldithiocarbamates. However, the base peaks for dipropyl-, dibutyl- and di-isobutyl-dithiocarbamates are very often alkyl ions in the

low mass region. Furthermore, there are other prominent peaks for cadmium, lead and mercury chelates corresponding to (ML)⁺ or (L)⁺ ions. The electron impact induced loss of (L-H)⁺ is observed with higher intensity than ion (L)⁺ for nonfluorinated dialkyldithiocarbamates of Ni(II), Pd(II) and Pt(II). This pattern is also evident in the published spectra of some nickel dithiocarbamate chelates.⁹

Gas chromatography-mass spectrometry provides an excellent means of verifying that metal chelates elute without decomposition under specified conditions. Clearly all the fluorinated metal chelates of Table 1 are successfully eluted by gas chromatography. The use of Fe(III), As(III) and Se(II) chelates is not practical for gas chromatographic separations, and the labile Hg(II) and In(III) dialkyldithiocarbamates require very carefully selected conditions. Selective metal detection may be achieved by combining capillary gas chromatography with mass fragmentation and choosing stable ion fragments which are specific for the metal chelate studied.

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