

MASS SPECTROMETRY OF  
FLUORINATED METAL  $\beta$ -DIKETONATES  
AND  
MONOTHIO- $\beta$ -DIKETONATES

by

Mark Lindsay John Reimer

B.Sc.(Hons.), University of Manitoba, 1981

A Thesis

Submitted to the Faculty of Graduate Studies  
in partial fulfillment of the requirements  
for the degree of  
Doctor of Philosophy

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### 3. Mass Spectra of Monothio- $\beta$ -diketonates

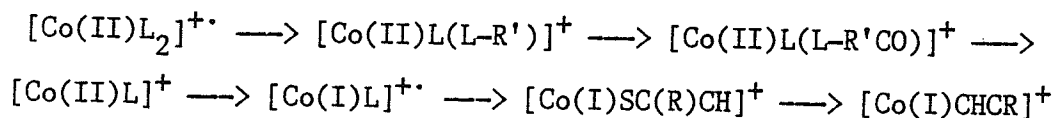
#### (a) Co(III) Monothio- $\beta$ -diketonates

Relative abundance data for the six Co(III) monothio- $\beta$ -diketonates studied appear in Tables 42 and 43. Plots of the EI mass spectra are depicted in Figures 91-96. The results of a linked-scanning, metastable investigation of **Co-14b** were used in the elucidation of fragmentation pathways. There are no published reports concerning the mass spectra of these complexes, although several trifluoromethyl-substituted Co(III) monothio- $\beta$ -diketonates have been examined (145,147).

Suggested decomposition pathways for the Co(III) monothio- $\beta$ -diketonate complexes possessing a pentafluoroethyl- ( $R' = C_2F_5$ ; Table 42) or heptafluoropropyl- ( $R' = C_3F_7$ ; Table 43) substituent are shown in Scheme 62. The absence of an abundant molecular ion in cobalt chelates of this type has been rationalized (145,147) by assuming that the complexes undergo thermal degradation in the ion source to give the reduced cobalt complex  $Co(II)L_2$  and the OE' neutral  $L'$ . However, the present results contradict this assumption, at least insofar as the penta- and hepta-fluoro compounds are concerned. Weak but detectable  $[Co(III)L_3]^+$  and  $[Co(III)L_2(L-F)]^+$  abundances in several of the complexes suggest a measure of stability in the molecular ion. Supporting this argument are the fragments  $[Co(III)FL(L-CF_3)]^+$  (all complexes) and  $[Co(III)FL(L-C_2F_5)]^+$  (**Co-14b** and **Co-15b** only),

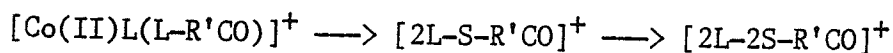
presumably formed by successive eliminations of  $\text{CF}_2$  from the  $\text{EE}^+$  ion  $[\text{Co(III)L}_2]^+$  (see Scheme 63). The cobalt +3 oxidation state may be stabilized in these species through the influence of the strongly electron-withdrawing  $\text{C}_2\text{F}_5$  and  $\text{C}_3\text{F}_7$  groups.

Reduction of the metal in  $[\text{Co(III)L}_2]^+$  results in the  $\text{OE}^+$  species  $[\text{Co(II)L}_2]^+$ , which in turn can lose either a  $\text{F}^{\cdot}$  radical to yield  $[\text{Co(II)L(L-F)}]^+$ , or an  $\text{R}^{\cdot}$  radical to give  $[\text{Co(II)L(L-R')}]^+$  (confirmed by a metastable transition). Schemes 64 and 65 illustrate proposed mechanisms for the reaction sequence



Alternative decomposition routes emanating from  $[\text{Co(II)L(L-R')}]^+$  are shown in Scheme 66 and involve the elimination of the  $\text{EE}^0$  neutrals  $\text{CO}$ ,  $\text{S}$ ,  $\text{COS}$  and  $\text{RC}_2\text{H}$ . From a mechanistic standpoint, the loss of  $\text{COS}$  is comparable to the loss of  $\text{CO}_2$  in  $\text{Co(III)}$   $\beta$ -diketonates (see Scheme 35).

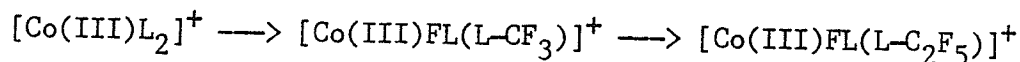
All of the chelates exhibit metal-free peaks at high  $m/z$  values. These ions have been attributed to the losses of  $\text{CoS}$  and  $\text{S}$  in the sequence



as shown in Scheme 67. However, metastable evidence indicates that  $[2\text{L-2S-R'CO}]^+$  is a daughter of  $[\text{Co(II)L(L-R'CO)}]^+$ , suggesting that the reaction may also follow a concerted mechanism. Loss of  $\text{MetS}$  has been

previously documented in the mass spectra of trifluoromethyl-substituted monothio- $\beta$ -diketone complexes of Ni(II), Pd(II), Pt(II), Fe(III), Ru(III) and Co(III) (146,147).

An examination of metal-fluorine bond formation in these complexes results in an interesting dichotomy. While fluorine transfer in



can be rationalized on the basis of the hard acceptor characteristics of Co(III), the process is completely suppressed along other fragmentation routes. Hard/Soft Acid/Base theory suggests three possible reasons for this behavior: (i) after metal reduction ( $[\text{Co(III)L}_2]^+ \longrightarrow [\text{Co(II)L}_2]^{+ \cdot}$ ), fluorine transfer to the borderline acid Co(II) center is not favored; (ii) the highly electronegative  $\text{C}_2\text{F}_5$  and  $\text{C}_3\text{F}_7$  groups have a strong affinity for the hard fluorine (especially in light of the weak acceptor characteristics of Co(II)), and (iii) the introduction of a metal-bonded sulfur atom into the chelate ring results in further softening of the metal center and hence a lowering of the probability for fluorine migration. Clearly then, the observance (or absence) of metal-fluorine bonded fragments in the mass spectra of these compounds is indicative of the associated electronic environment within each given chelate structure.

Table 42. 70 eV-EI mass spectra of compounds Co-13b, Co-14b and Co-15b.

	Co-13b			Co-14b			Co-15b		
R =	-C <sub>6</sub> H <sub>5</sub>			-C <sub>4</sub> H <sub>3</sub> S			-C <sub>10</sub> H <sub>7</sub>		
R' =	-C <sub>2</sub> F <sub>5</sub>			-C <sub>2</sub> F <sub>5</sub>			-C <sub>2</sub> F <sub>5</sub>		
ION	%RA	m/z	%TIC	%RA	m/z	%TIC	%RA	m/z	%TIC
[CoL <sub>3</sub> ] <sup>+</sup>	0.6	(902)	0.2	-	(920)	-	-	(1052)	-
[CoL <sub>2</sub> ] <sup>+</sup> (a)	100.0	(621)	37.3	63.0	(633)	12.9	100.0	(721)	21.9
[CoL(L-F)] <sup>+</sup>	1.3	(602)	0.5	1.5	(614)	0.3	2.0	(702)	0.4
[CoFL(L-CF <sub>3</sub> )] <sup>+</sup> (b)	4.9	(571)	1.8	13.0	(583)	2.7	16.0	(671)	3.5
[CoFL(L-R')] <sup>+</sup>	-	(521)	-	1.0	(533)	0.2	<sup>b</sup> 2.8	(621)	0.6
[CoL(L-R')] <sup>+</sup> (c)	0.9	(502)	0.3	<sup>a</sup> 1.6	(514)	0.3	1.2	(602)	0.3
[CoL(L-R'CO)] <sup>+</sup> (d)	6.8	(474)	2.5	<sup>c</sup> 2.5	(486)	0.5	<sup>c</sup> 3.5	(574)	0.8
[CoL] <sup>+</sup> (e)	17.0	(340)	6.3	<sup>c,d</sup> 29.0	(346)	5.9	12.0	(390)	2.6
[CoSC(R)CH] <sup>+</sup>	5.9	(193)	2.2	8.1	(199)	1.7	12.0	(243)	2.6
[CoCHCR] <sup>+</sup>	3.1	(161)	1.2	5.8	(167)	1.2	5.0	(211)	1.1
[2L-S-R'CO] <sup>+</sup>	0.9	(383)	0.3	1.6	(395)	0.3	3.1	(483)	0.7
[2L-2S-R'CO] <sup>+</sup>	2.8	(351)	1.0	<sup>d</sup> 6.8	(363)	1.4	2.3	(451)	0.5
[HL] <sup>+</sup>	8.5	(282)	3.2	13.0	(288)	2.7	23.0	(332)	5.0
[L] <sup>+</sup> (f)	50.0	(281)	18.7	100.0	(287)	20.5	78.0	(331)	17.1
[L-F] <sup>+</sup>	5.3	(262)	2.0	5.0	(268)	1.0	7.0	(312)	1.5
[L-S] <sup>+</sup>	-	(249)	-	<sup>f</sup> 88.0	(255)	18.0	4.7	(299)	1.0
[L-2F] <sup>+</sup>	<sup>e</sup> 10.3	(243)	3.8	<sup>e</sup> 20.0	(249)	4.1	15.0	(293)	3.3
[L-CF <sub>2</sub> ] <sup>+</sup>	1.9	(231)	0.7	11.0	(237)	2.3	-	(281)	-

Table 42. (continued).

[HL-R'] <sup>+</sup>	9.9 (163)	3.7	15.0 (169)	3.1	25.0 (213)	5.5
[RCSCH] <sup>+</sup>	12.0 (134)	4.5	18.0 (140)	3.7	29.0 (184)	6.4
[RCS] <sup>+</sup>	9.4 (121)	3.5	18.0 (127)	3.7	19.0 (171)	4.2
[RCCH] <sup>+</sup>	6.3 (102)	2.4	17.0 (108)	3.5	46.0 (152)	10.1
[R] <sup>+</sup>	4.3 ( 77)	1.6	34.0 ( 83)	7.0	18.0 (127)	3.9
[CF <sub>3</sub> ] <sup>+</sup>	5.0 ( 69)	1.9	12.0 ( 69)	2.5	31.0 ( 69)	6.8

<sup>a</sup> Identified metastable transitions are indicated by superscripts which relate the daughter ion to its precursor as labelled in column 1.

Table 43. 70 eV-EI mass spectra of compounds Co-16b, Co-17b and Co-18b.

	Co-16b			Co-17b			Co-18b		
R =	-C <sub>6</sub> H <sub>5</sub>			-C <sub>4</sub> H <sub>3</sub> S			-C <sub>10</sub> H <sub>7</sub>		
R' =	-C <sub>3</sub> F <sub>7</sub>			-C <sub>3</sub> F <sub>7</sub>			-C <sub>3</sub> F <sub>7</sub>		
ION	%RA	m/z	%TIC	%RA	m/z	%TIC	%RA	m/z	%TIC
[CoL <sub>3</sub> ] <sup>+</sup>	0.5(1052)	0.2	0.4(1070)	0.1	- (1202)	-	-		
[CoL <sub>2</sub> (L-F)] <sup>+</sup>	0.1(1033)	-	0.1(1051)	-	- (1183)	-	-		
[CoL <sub>2</sub> ] <sup>+</sup>	71.0 (721)	21.6	44.0 (733)	15.7	100.0 (821)	34.8			
[CoL(L-F)] <sup>+</sup>	1.4 (702)	0.4	1.1 (714)	0.4	1.7 (802)	0.6			
[CoFL(L-CF <sub>3</sub> )] <sup>+</sup>	7.3 (671)	2.2	0.8 (683)	0.3	5.1 (771)	1.8			
[CoL(L-R')] <sup>+</sup> (a)	0.7 (552)	0.2	1.1 (564)	0.4	1.2 (652)	0.4			
[CoL(L-R'CO)] <sup>+</sup> (b)	<sup>a</sup> 6.5 (524)	2.0	<sup>a</sup> 1.5 (536)	0.5	<sup>a</sup> 4.6 (624)	1.6			
[CoLCHCR] <sup>+</sup>	0.5 (492)	0.2	0.5 (504)	0.2	1.3 (592)	0.5			
[CoL] <sup>+</sup> (c)	15.0 (390)	4.6	17.0 (396)	6.1	8.8 (440)	3.1			
[CoSC(R)CH] <sup>+</sup>	6.2 (193)	1.9	2.9 (199)	1.0	9.8 (243)	3.4			
[CoCHCR] <sup>+</sup>	3.5 (161)	1.1	3.3 (167)	1.2	2.9 (211)	1.0			
[2L-2S-R'CO] <sup>+</sup>	<sup>b</sup> 2.6 (401)	0.8	<sup>b</sup> 3.6 (413)	1.3	2.6 (501)	0.9			
[HL] <sup>+</sup>	15.0 (332)	4.6	5.2 (338)	1.9	13.0 (382)	4.5			
[L] <sup>+</sup>	100.0 (331)	30.4	100.0 (337)	35.7	33.0 (381)	11.5			
[L-F] <sup>+</sup>	3.2 (312)	1.0	1.7 (318)	0.6	3.8 (362)	1.3			
[L-S] <sup>+</sup>	0.5 (299)	0.2	37.0 (305)	13.2	3.3 (349)	1.1			
[L-2F] <sup>+</sup>	<sup>c</sup> 14.0 (293)	4.3	<sup>c</sup> 15.0 (299)	5.4	15.0 (343)	5.2			
[HL-R'] <sup>+</sup>	22.0 (163)	6.7	7.1 (169)	2.5	12.0 (213)	4.2			



Table 43. (continued).

[CRCHS] <sup>+</sup>	20.0 (134)	6.1	12.0 (140)	4.3	20.0 (184)	7.0
[RCS] <sup>+</sup>	16.0 (121)	4.9	9.6 (127)	3.4	15.0 (171)	5.2
[RCCH] <sup>+</sup>	8.1 (102)	2.5	9.0 (108)	3.2	26.0 (152)	9.1
[CF <sub>3</sub> ] <sup>+</sup>	14.0 ( 69)	4.3	6.2 ( 69)	2.2	7.5 ( 69)	2.6

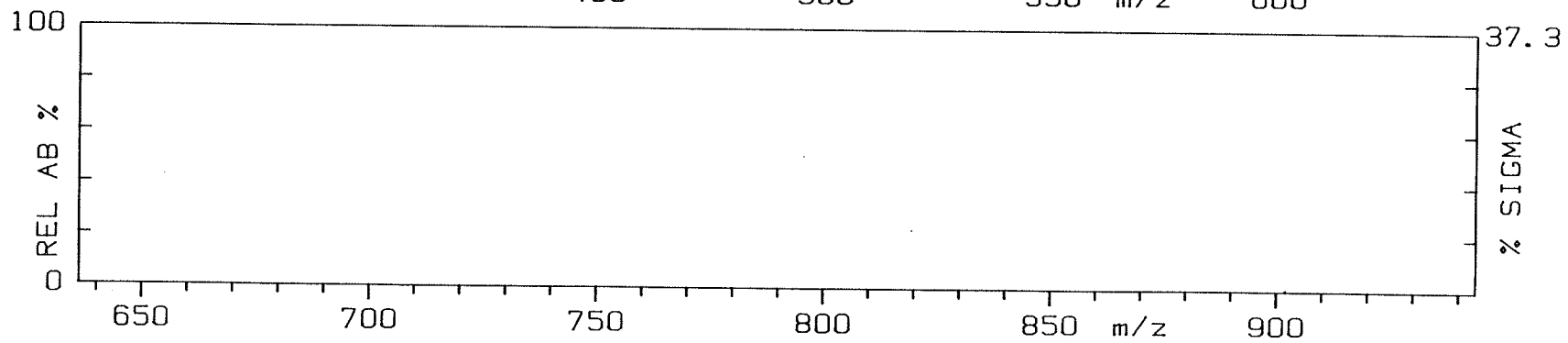
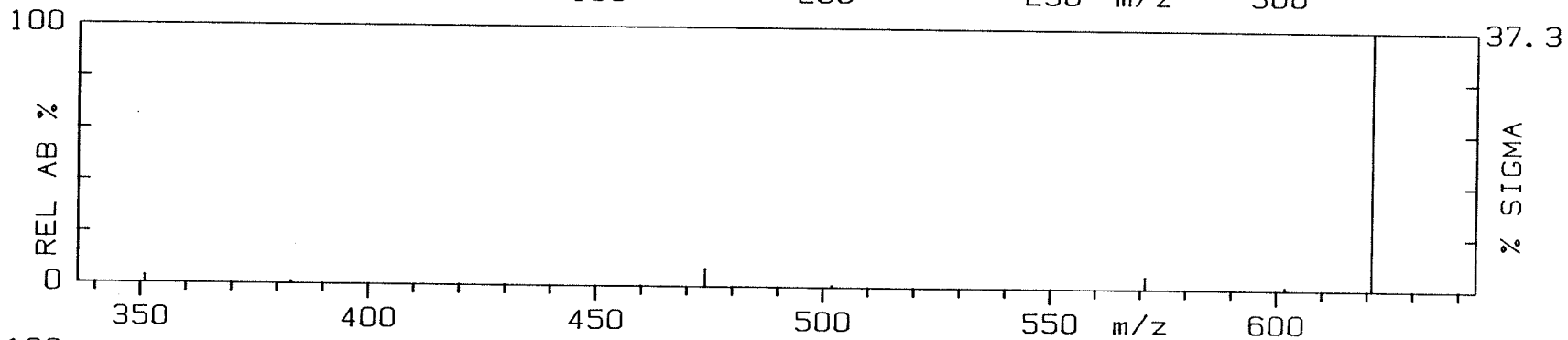
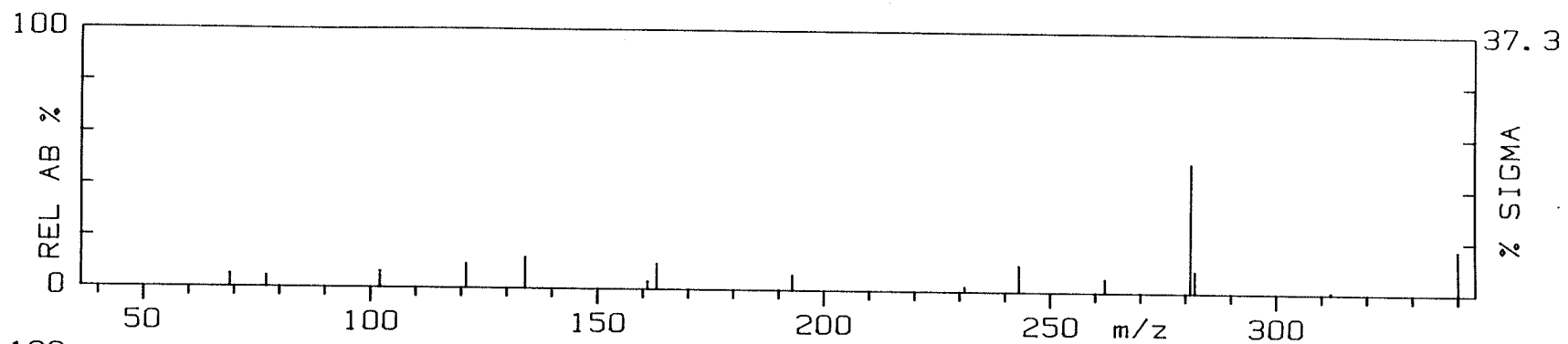
<sup>a</sup> Identified metastable transitions are indicated by superscripts which relate the daughter ion to its precursor as labelled in column 1.

**Figure 91.**

Normalized 70 eV-EI mass spectrum of  
tris[1,1,1,2,2-pentafluoro-5-mercapto-5-phenyl-pent-4-en-3-onato]Co(III)  
{Co-13b}.

$m/z$   $[M]^{+•} = 902$ ,  $[L]^+ = 281$

CO-13B 70EV.

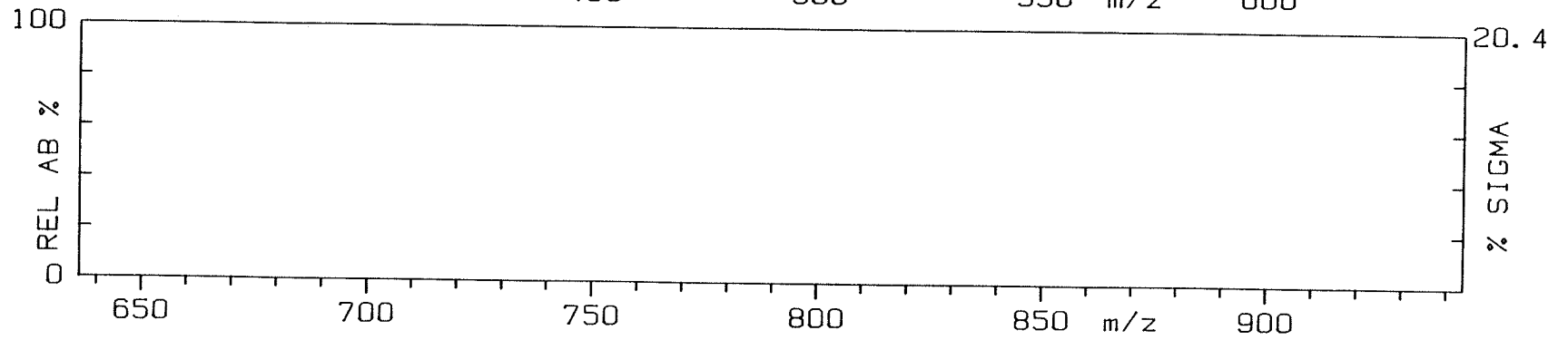
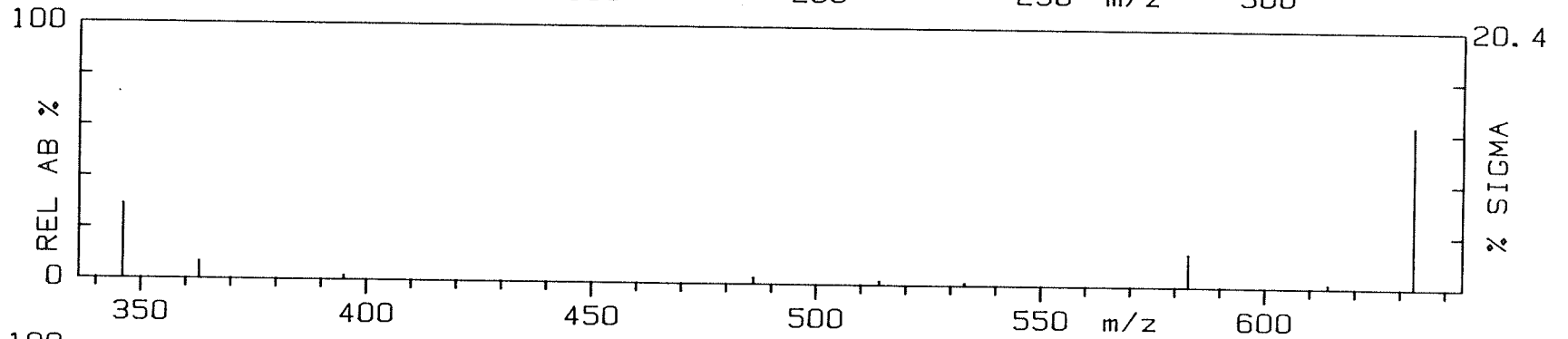
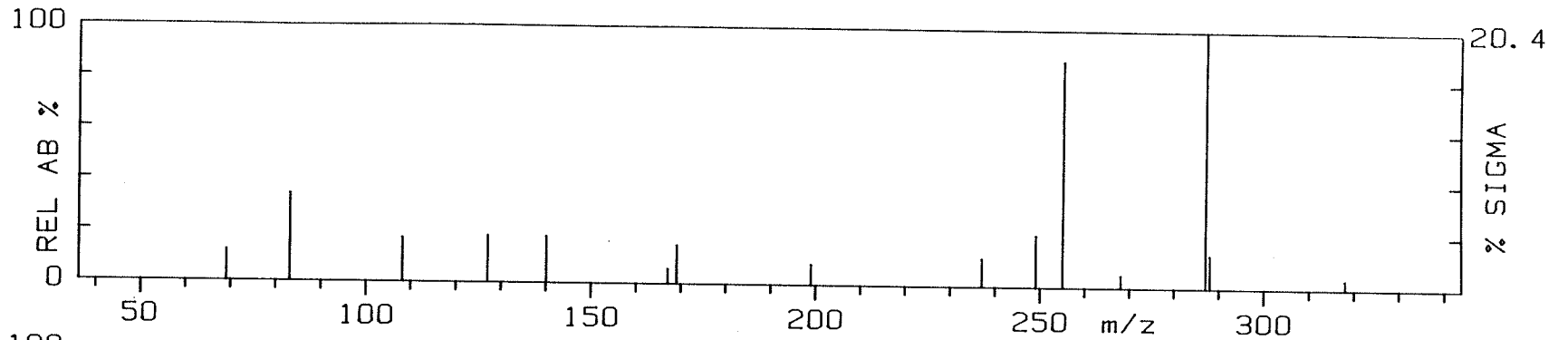


**Figure 92.**

Normalized 70 eV-EI mass spectrum of  
tris[1,1,1,2,2-pentafluoro-5-mercapto-5-(2'-thienyl)-  
pent-4-en-3-onato]Co(III) (Co-14b).

$m/z$   $[M]^{+}$  = 920,  $[L]^{+}$  = 287

CO-14B 70EV.

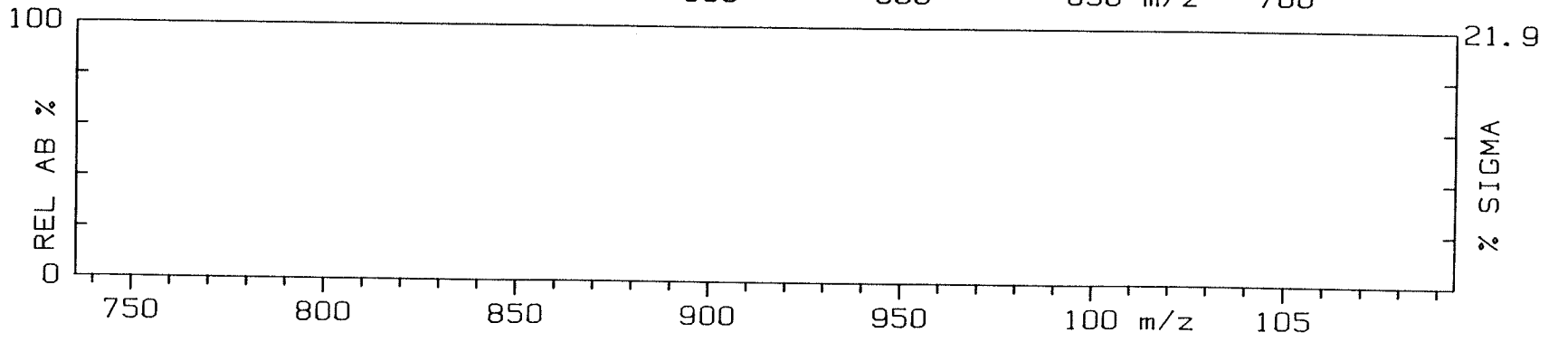
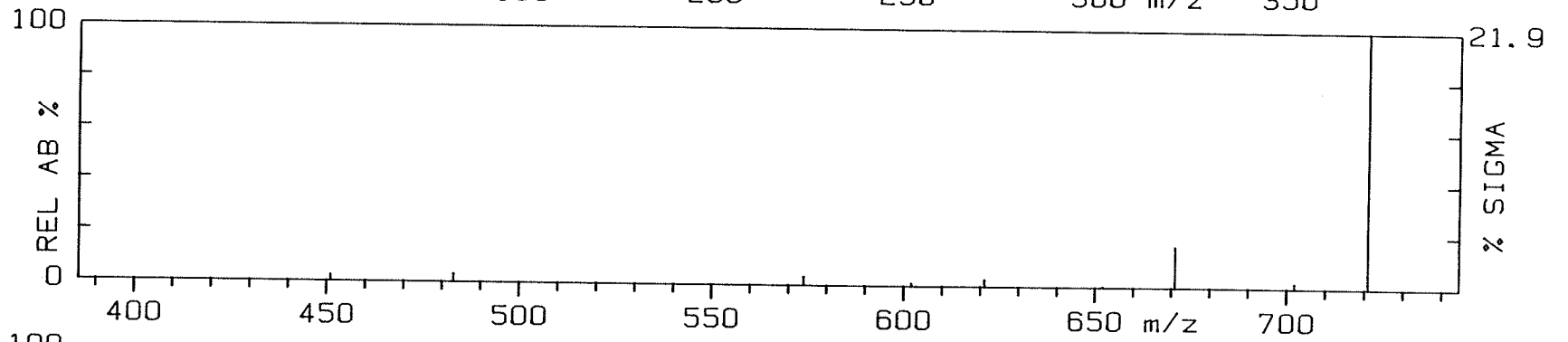
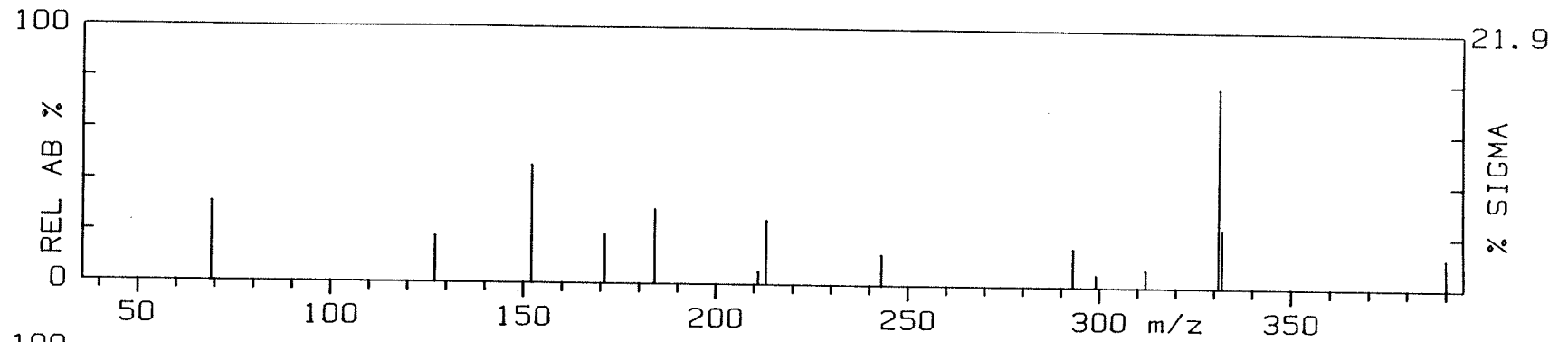


**Figure 93.**

Normalized 70 eV-EI mass spectrum of  
tris[1,1,1,2,2-pentafluoro-5-mercapto-5-(2'-naphthyl)-  
pent-4-en-3-onato]Co(III) (Co-15b).

$m/z$   $[M]^{+•} = 1052$ ,  $[L]^+ = 331$

CO-15B 70EV.



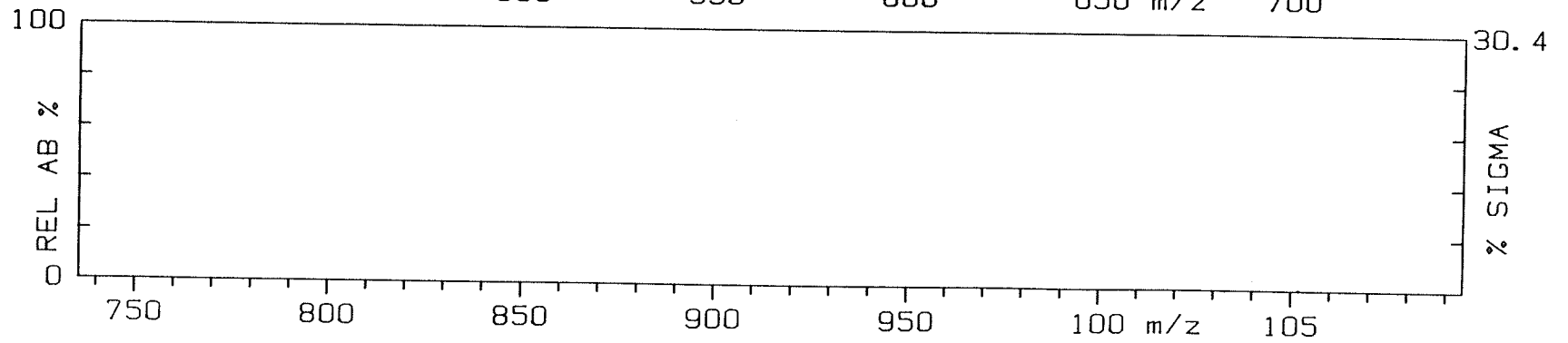
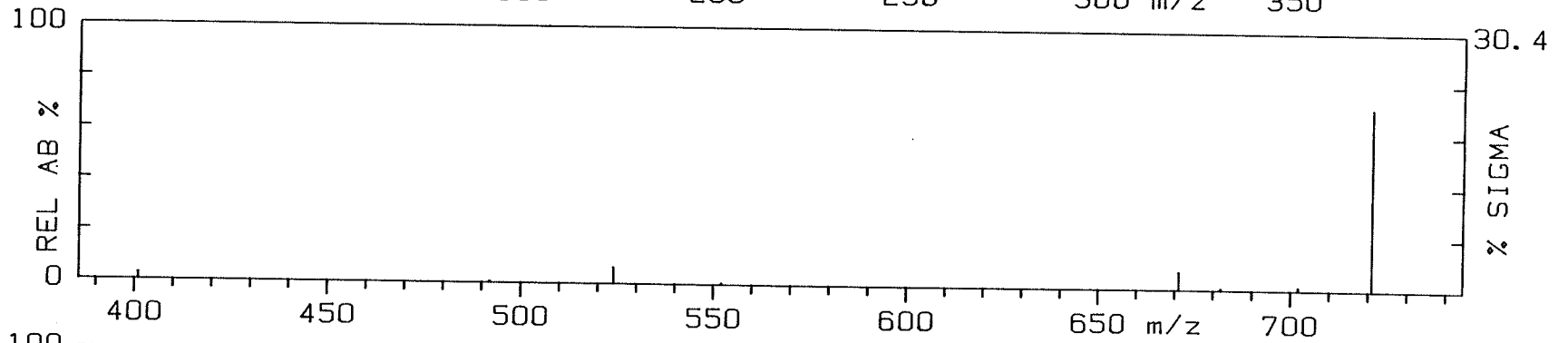
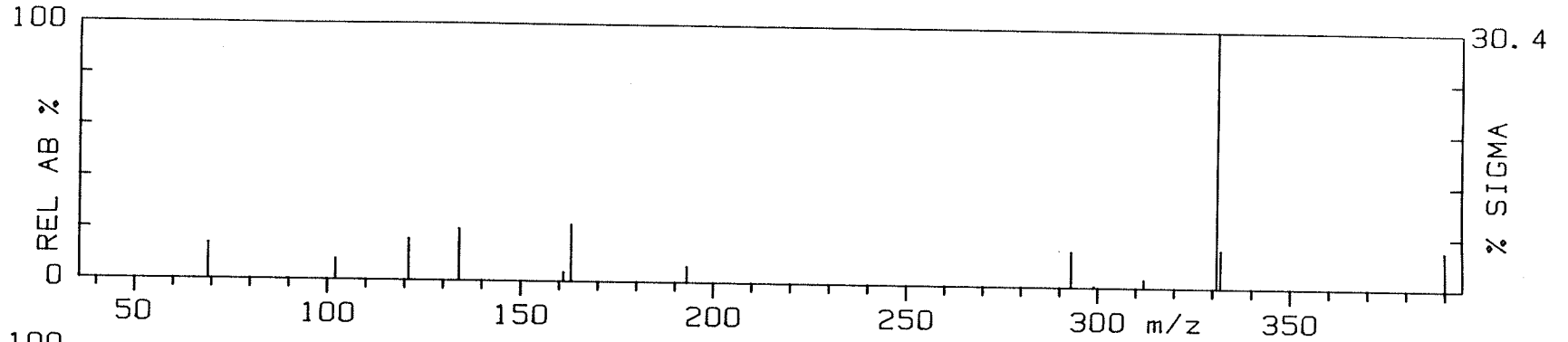
**Figure 94.**

Normalized 70 eV-EI mass spectrum of  
tris[1,1,1,2,2,3,3-heptafluoro-6-mercapto-6-phenyl-  
hex-5-en-4-onato]Co(III) (Co-16b).

$m/z$   $[M]^{+}$  = 1052,  $[L]^{+}$  = 331



CO-16B 70EV.

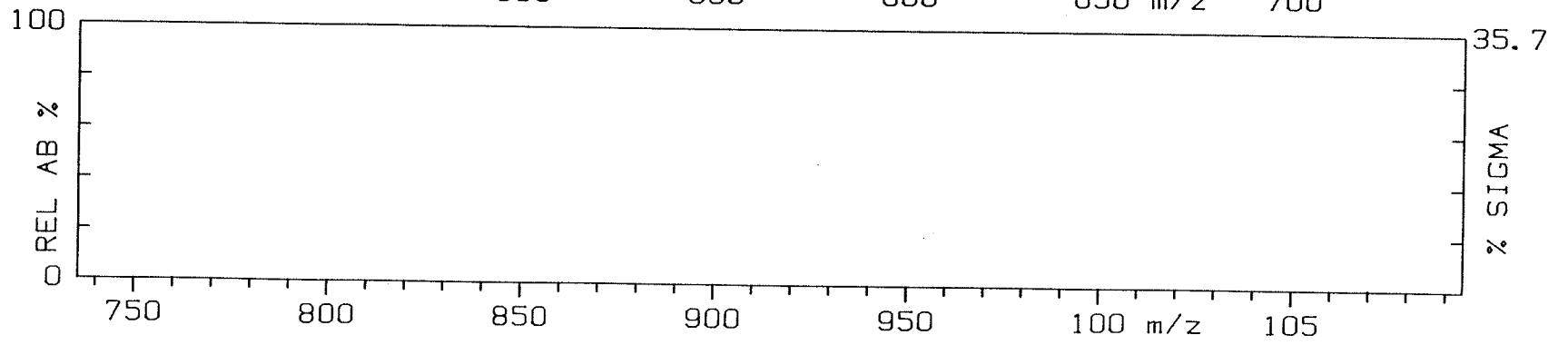
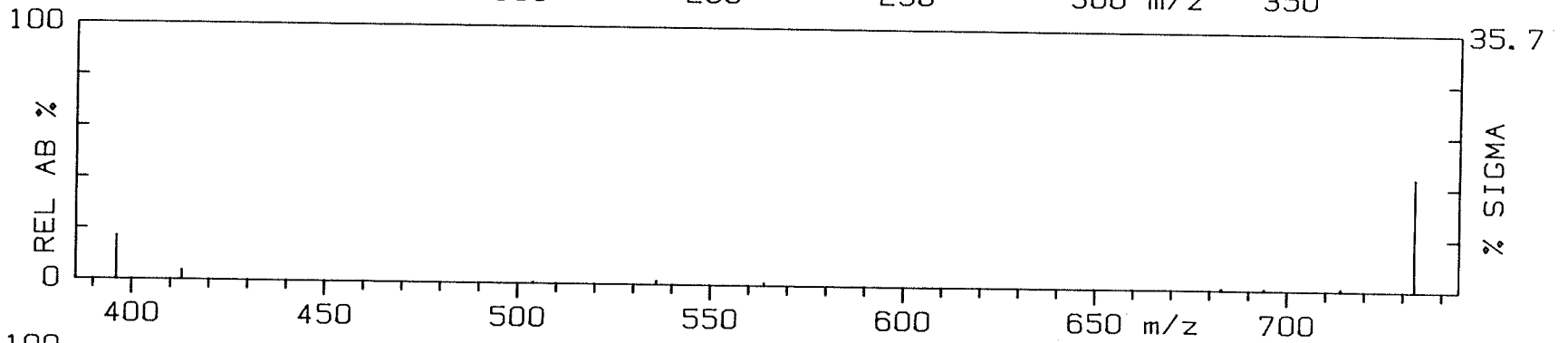
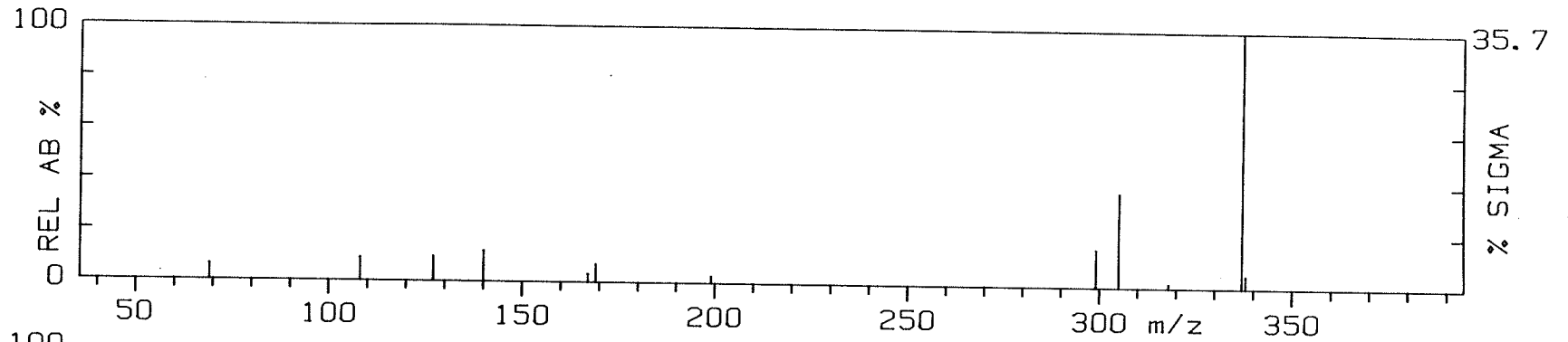


**Figure 95.**

Normalized 70 eV-EI mass spectrum of  
tris[1,1,1,2,2,3,3-heptafluoro-6-mercapto-6-(2'-thienyl)-  
hex-5-en-4-onato]Co(III) (Co-17b).

$m/z$   $[M]^+$  = 1070,  $[L]^+$  = 337

CO-17B 70EV.

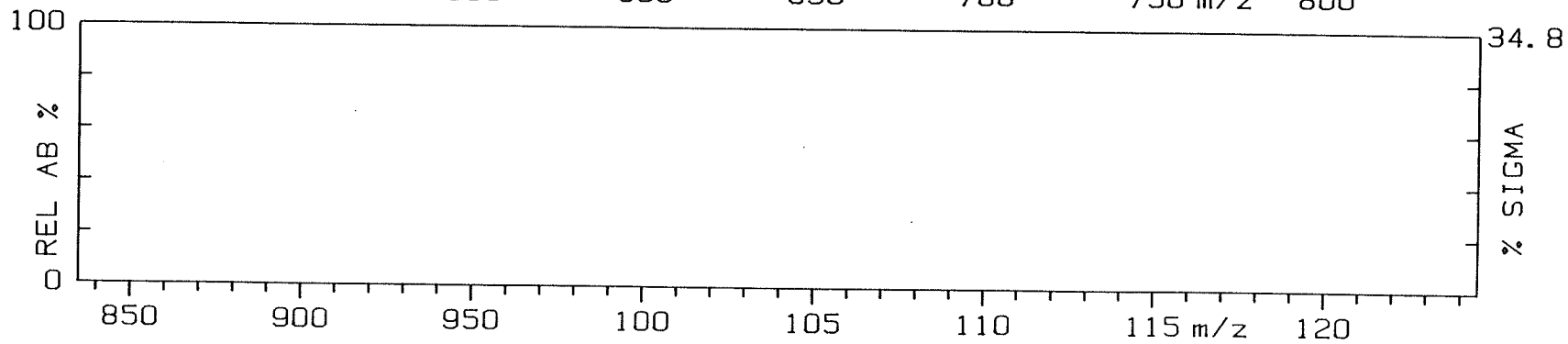
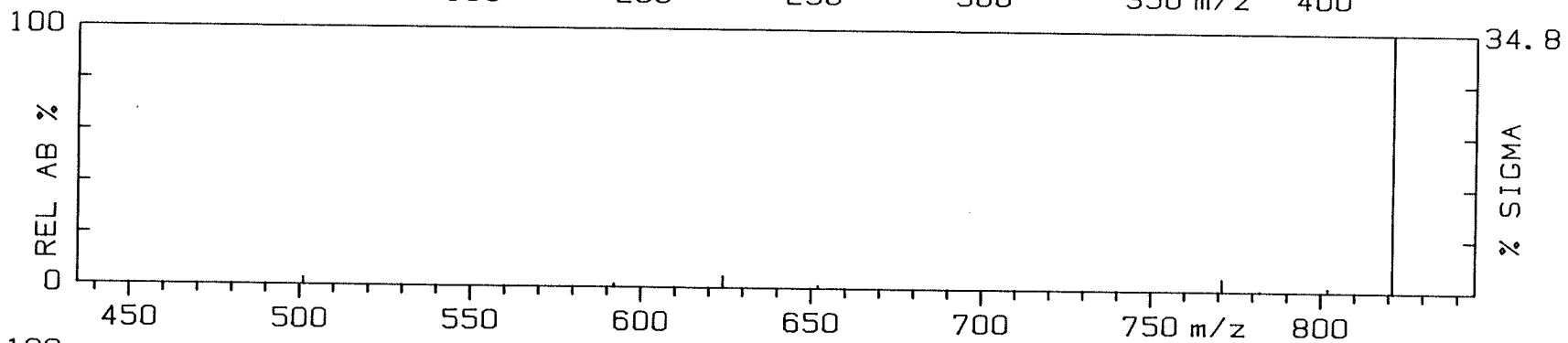
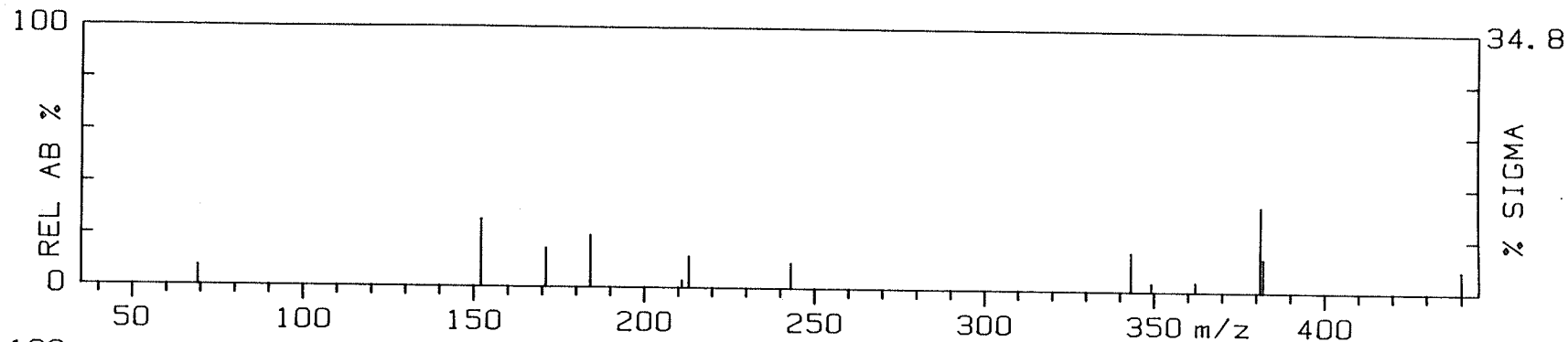


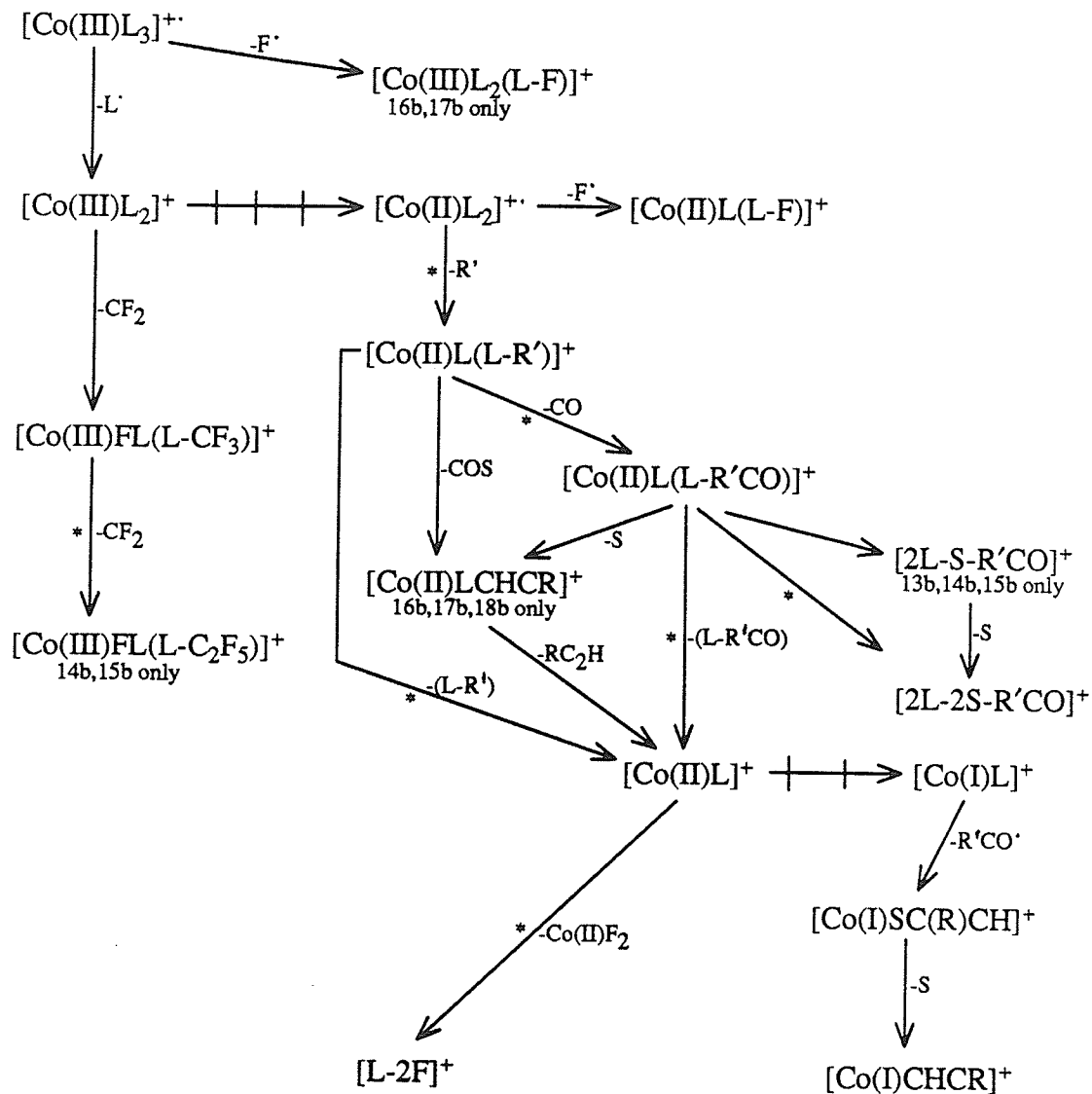
**Figure 96.**

Normalized 70 eV-EI mass spectrum of  
tris[1,1,1,2,2,3,3-heptafluoro-6-mercapto-6-(2'-naphthyl)-  
hex-5-en-4-onato]Co(III) (Co-18b).

$m/z$   $[M]^{+•} = 1202$ ,  $[L]^+ = 381$

CO-18B 70EV.

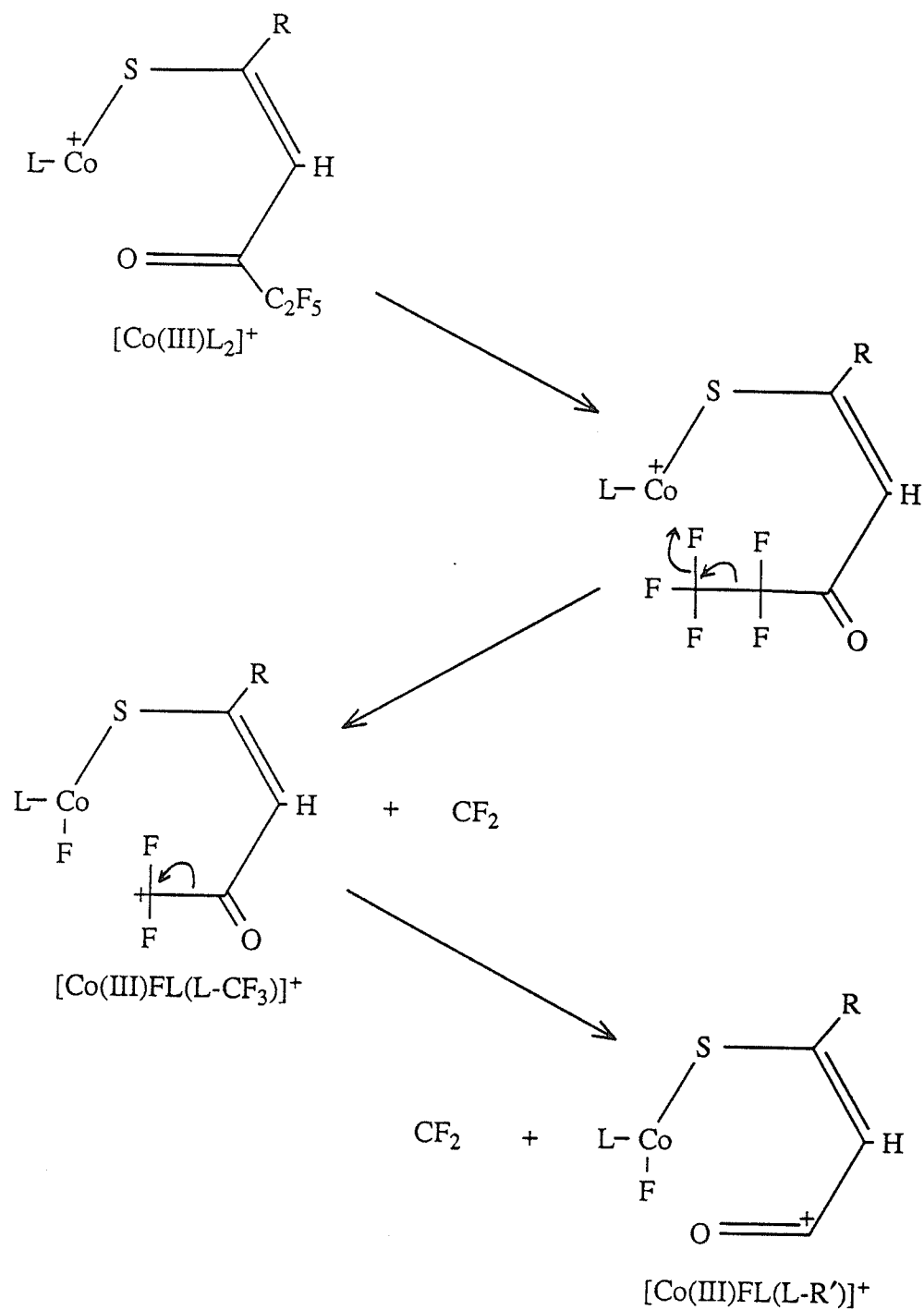




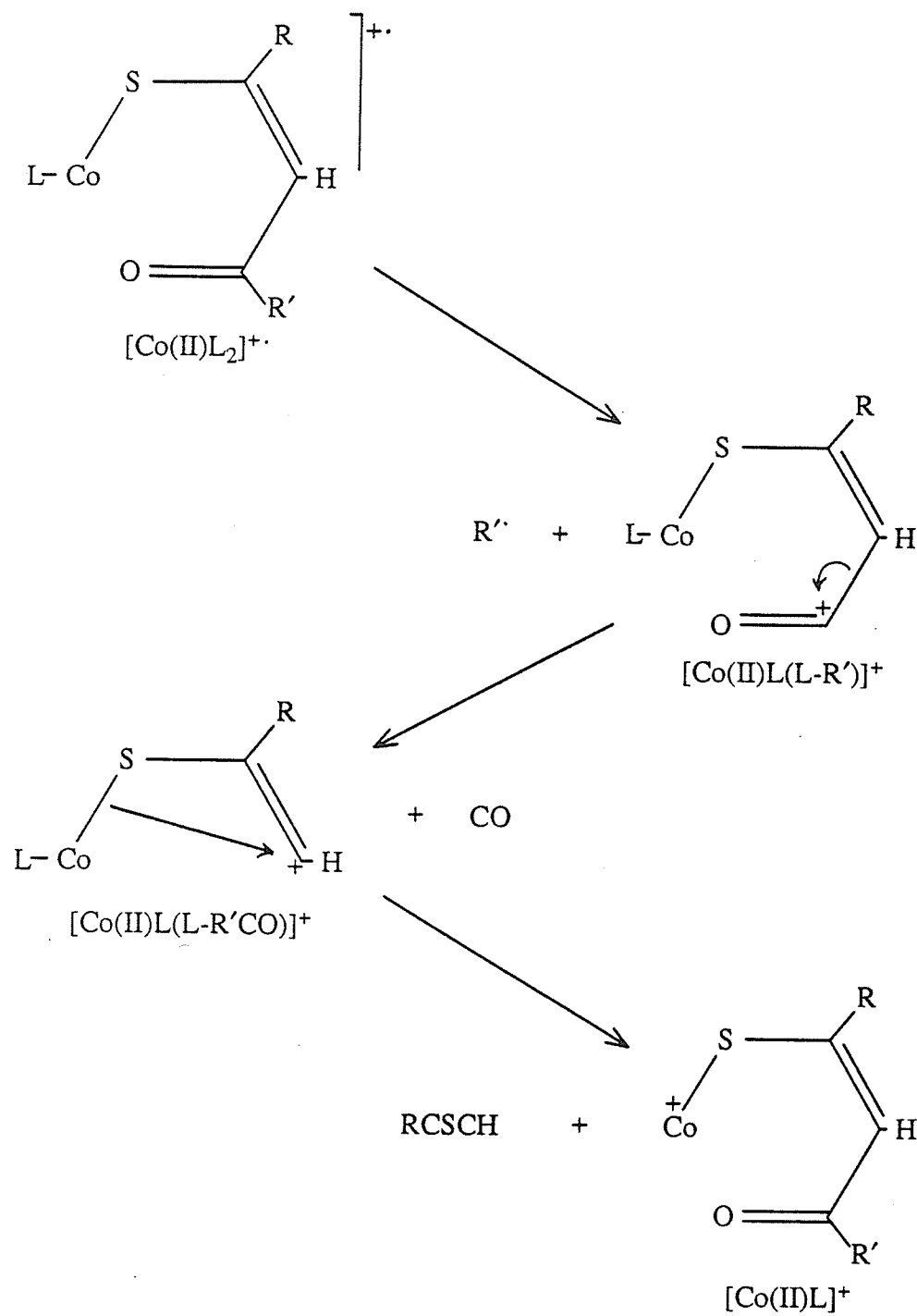
\* process confirmed by the observation of a metastable transition in at least one of the complexes.

$\text{+\text{+\text{+}}}$  reaction step in which a change in metal oxidation state is proposed.

**Scheme 62.** Proposed fragmentation pathways for Co(III) monothio- $\beta$ -diketonates where  $\text{R}' = \text{C}_2\text{F}_5$  (Co-13b, -14b and -15b) or  $\text{C}_3\text{F}_7$  (Co-16b, -17b and -18b). Pathways are common to all complexes except where noted.

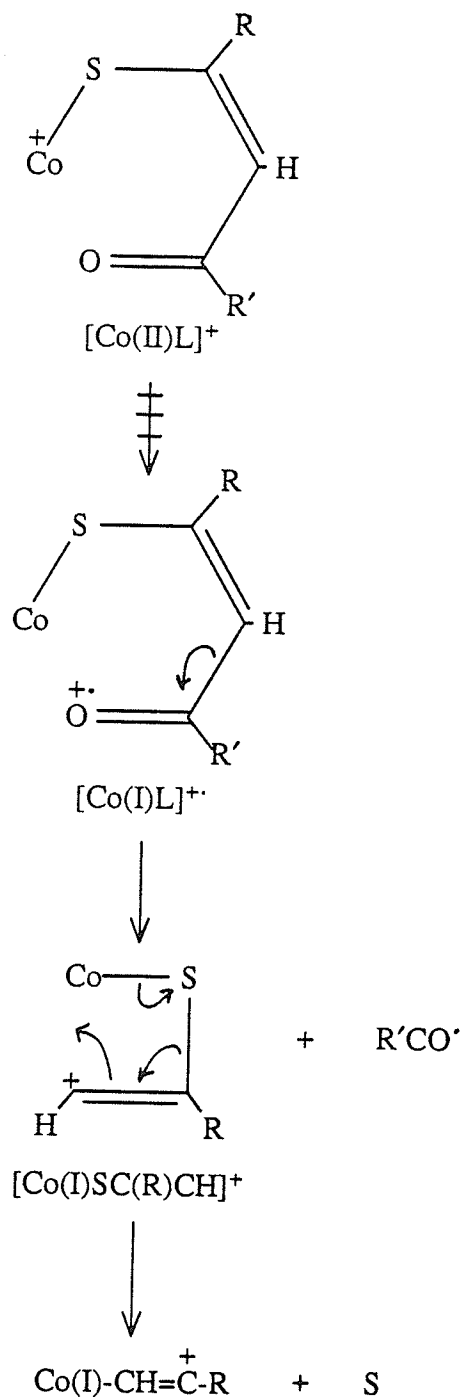


**Scheme 63.** Suggested mechanism for the formation of  $[Co(III)FL(L-CF_3)]^+$  and  $[Co(III)FL(L-R')]^+$  in **Co-14b** and **-15b**.

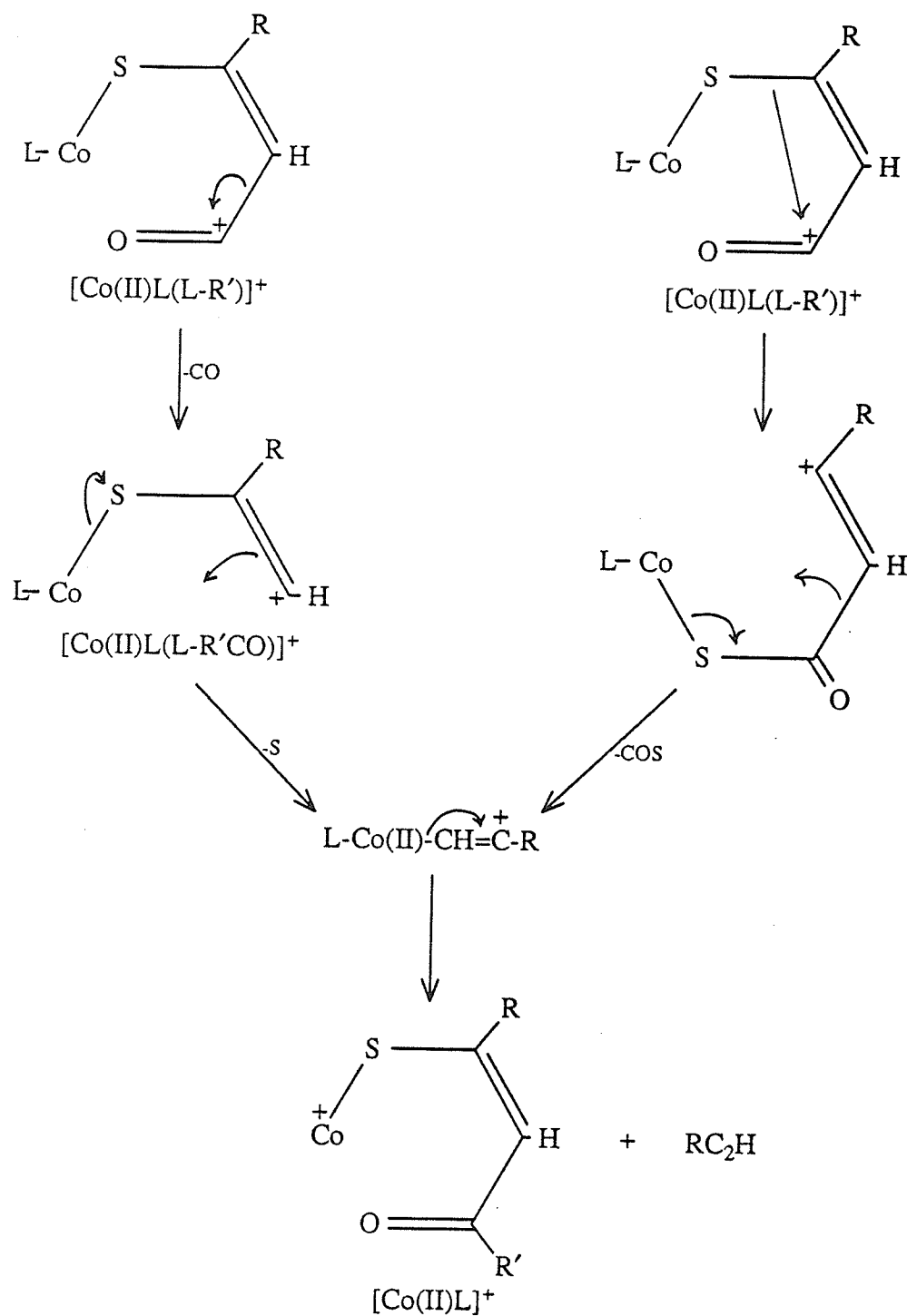


**Scheme 64.** Suggested mechanism for the formation of  $[Co(II)L(L-R')]^+$ ,  $[Co(II)L(L-R'CO)]^+$  and  $[Co(II)L]^+$  in **Co-13b**, **-14b**, **-15b**, **-16b**, **-17b** and **-18b**.

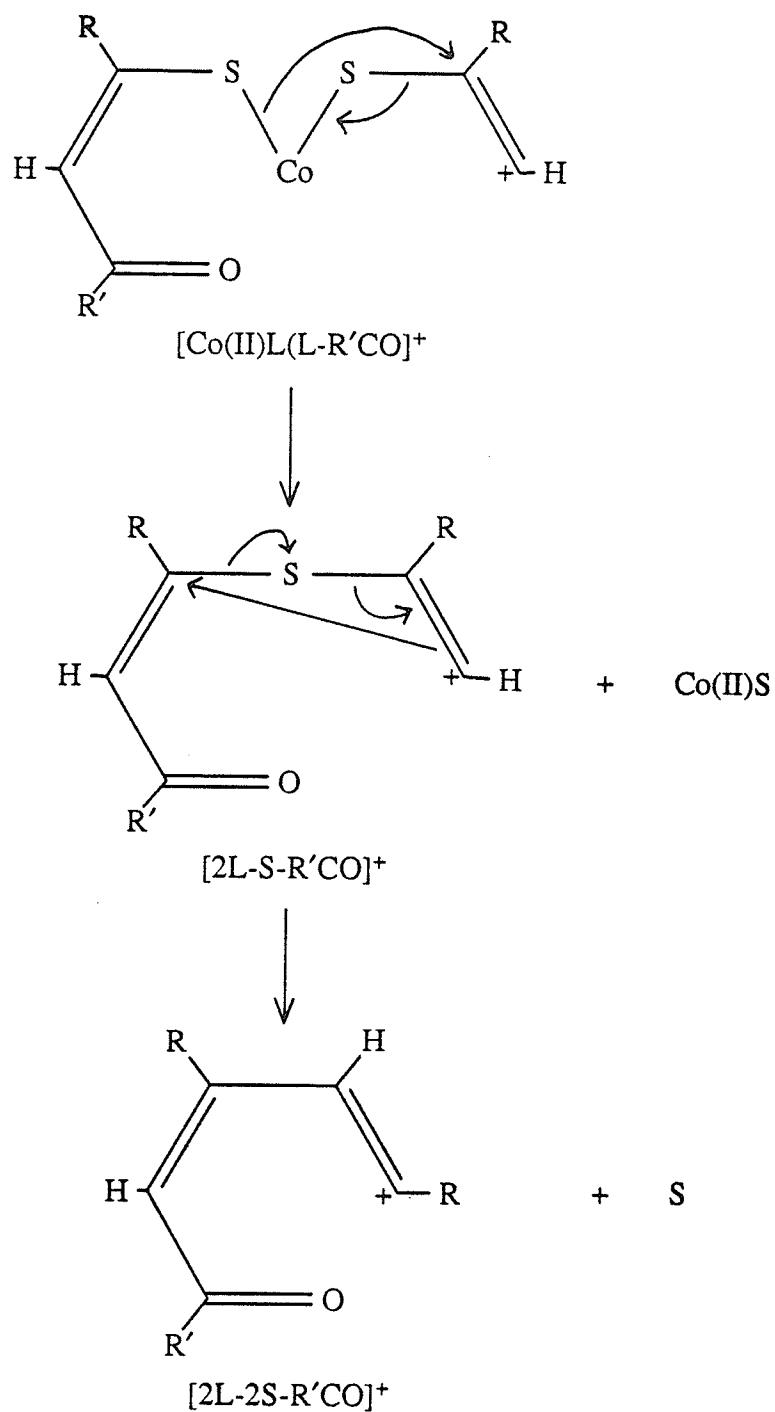




**Scheme 65.** Suggested mechanism for the formation of  $[\text{Co(I)L}]^+$ ,  $[\text{Co(I)SC(R)CH}]^+$  and  $[\text{Co(I)CHCR}]^+$  in **Co-13b**, **-14b**, **-15b**, **-16b**, **-17b** and **-18b**.



**Scheme 66.** Suggested mechanism for the formation of  $[\text{Co(II)LCHCR}]^+$  in Co-16b, -17b and -18b.



**Scheme 67.** Suggested mechanism for the formation of  $[\text{2L-S-R'CO}]^+$  and  $[\text{2L-2S-R'CO}]^+$  in Co-13b, -14b, -15b, -16b, -17b and -18b.

(b) Ni(II) Monothio- $\beta$ -diketonates

Relative abundance data for the eleven Ni(II) monothio- $\beta$ -diketonates studied appear in Tables 44-47. Plots of the EI mass spectra are shown in Figures 97-107. A linked-scanning, metastable analysis of **Ni-5b** was performed. Das and Livingstone (143) have reported the mass spectra of **Ni-3b** and **Ni-8b**.

Suggested decomposition pathways for the Ni(II) monothio- $\beta$ -diketonate complexes possessing a trifluoromethyl substituent ( $R' = CF_3$ ; Tables 44 and 45) are shown in Scheme 68. The molecular ion is the most abundant metal-containing species in each of the spectra, while  $[L]^+$  is normally the most abundant metal-free ion. Metastable evidence indicates that  $[L]^+$  arises from the molecular ion through the elimination of the neutral fragment Ni(I)L (Scheme 69(a)). The ligand likely adopts a resonance-stabilized cyclic structure as shown in Scheme 69(b).

Several other novel decompositions emanating from the molecular ion are evident in these spectra. For instance, loss of a sulfur atom from  $[M]^{+}$  in complex **Ni-5b** results in the  $OE^{+}$  ion  $[Ni(II)L(L-S)]^{+}$  (see Scheme 70). By contrast, **Ni-3b** exhibits a weak signal due to  $[Ni(II)SL]^{+}$ , which corresponds to the retention of a sulfur atom and the elimination of the  $OE'$  neutral  $RC=CHCOR'$  from the molecular ion. A mechanism for this process as well as other canonical forms of the product ion are proposed in Scheme 71.

All of the complexes give a peak corresponding to the ion  $[Ni(II)(L-H)]^{+}$ ; its formation by the loss of HL from  $[Ni(II)L_2]^{+}$  (Scheme 72) is supported by a metastable transition. A similar process (hydrogen transfer from a ligand to the oxygen atom of the other ligand) was suggested by Livingstone and co-workers (146,147) in their study of trifluoromethyl-substituted monothio- $\beta$ -diketonates of Ni(II) and Pt(II). One of the canonical forms of  $[Ni(II)(L-H)]^{+}$  shown in Scheme 72 involves the nickel +1 oxidation state. This form may be favored for complexes possessing an electron-releasing R group; the release of electrons to the adjacent sulfur-bound carbon atom should increase the electron density on the sulfur atom, thereby promoting the Ni(I) state.

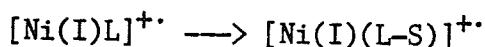
The suggested mechanisms for the formation of ions  $[Ni(I)SC(R)CH]^{+}$ ,  $[Ni(I)SCR]^{+}$  and  $[Ni(I)]^{+}$  are shown in Scheme 73. The elimination of the  $OE'$  neutral  $R'CO'$  from  $[Met(I)L]^{+}$  to give  $[Met(I)SC(R)CH]^{+}$  was first proposed in Scheme 65 for the decomposition of Co(III) monothio- $\beta$ -diketonates. The subsequent loss of  $RC(S)=CH$  would appear to be the

more preferred pathway to  $[\text{Ni(I)}]^+$ ; the expulsion of  $\text{CH}^\cdot$  from  $[\text{Ni(I)SC(R)CH}]^+$ , although proposed in the decomposition of similar  $\text{Co(III)}$  monothio- $\beta$ -diketonates (145), entails both the breaking of a bond and the energetically-unfavorable separation of an electron pair. The elimination of  $\text{L}^\cdot$  from  $[\text{Ni(I)L}]^+$  is also a possible route to the formation of  $[\text{Ni(I)}]^+$ .

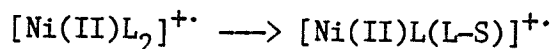
Many of the remaining fragmentation pathways given in Scheme 68 have been described previously:

<u>Fragmentation</u>	<u>Scheme</u>
$[\text{Ni(II)L}_2]^+ \longrightarrow [\text{Ni(II)L(L-R')}]^+$	64
$[\text{Ni(II)L(L-R')}]^+ \longrightarrow [\text{Ni(II)L(L-R'CO)}]^+$	64
$[\text{Ni(II)L(L-R'CO)}]^+ \longrightarrow [\text{Ni(II)L}]^+$	64
$[\text{Ni(I)SC(R)CH}]^+ \longrightarrow [\text{Ni(I)CHCR}]^+$	65
$[\text{Ni(II)L(L-R')}]^+ \longrightarrow [\text{Ni(II)LCHCR}]^+$	66
$[\text{Ni(II)LCHCR}]^+ \longrightarrow [\text{Ni(II)L}]^+$	66
$[\text{Ni(II)L(L-R'CO)}]^+ \longrightarrow [\text{Ni(II)LCHCR}]^+$	66
$[\text{Ni(II)L(L-R'CO)}]^+ \longrightarrow [2\text{L-2S-R'CO}]^+$	67

The mechanism responsible for the loss of sulfur in the reaction



is essentially the same as that depicted in Scheme 70 for



Suggested decomposition pathways for the  $\text{Ni(II)}$  monothio- $\beta$ -diketonates possessing pentafluoroethyl ( $\text{R}' = \text{C}_2\text{F}_5$ ; Table 46) or

heptafluoropropyl ( $R' = C_3F_7$ ; Table 47) substituents are shown in Scheme 74. As was observed for the trifluoromethyl derivatives, the most abundant nickel-containing and nickel-free ions are  $[Ni(II)L_2]^+$  and  $[L]^+$ , respectively. The mechanisms underlying many of the ion-decomposition reactions illustrated in Scheme 74 are known:

<u>Fragmentation</u>	<u>Scheme</u>
$[Ni(II)L]^+ \longrightarrow [L-2F]^+$	32
$[Ni(II)L_2]^+ \longrightarrow [Ni(II)L(L-R')]^+$	64
$[Ni(II)L(L-R')]^+ \longrightarrow [Ni(II)L(L-R'CO)]^+$	64
$[Ni(II)L(L-R'CO)]^+ \longrightarrow [Ni(II)L]^+$	64
$[Ni(I)L]^+ \longrightarrow [Ni(I)SC(R)CH]^+$	65
$[Ni(I)SC(R)CH]^+ \longrightarrow [Ni(I)CHCR]^+$	65
$[Ni(II)L(L-R')]^+ \longrightarrow [Ni(II)LCHCR]^+$	66
$[Ni(II)L(L-R'CO)]^+ \longrightarrow [Ni(II)LCHCR]^+$	66
$[Ni(II)LCHCR]^+ \longrightarrow [Ni(II)L]^+$	66
$[Ni(II)L(L-R'CO)]^+ \longrightarrow [2L-2S-R'CO]^+$	67
$[Ni(II)L_2]^+ \longrightarrow [L]^+$	69
$[Ni(II)L_2]^+ \longrightarrow [Ni(II)L(L-S)]^+$	70
$[Ni(I)L]^+ \longrightarrow [Ni(I)(L-S)]^+$	70
$[Ni(II)L_2]^+ \longrightarrow [Ni(II)SL]^+$	71
$[Ni(II)L_2]^+ \longrightarrow [Ni(II)(L-H)]^+$	72
$[Ni(I)SC(R)CH]^+ \longrightarrow [Ni(I)]^+$	73

Scheme 75 outlines a proposed mechanism for the formation of  $[Ni(II)L(L-F-HF)]^+$  in complexes **Ni-16b** and **Ni-17b**. A metastable transition in the spectrum of **Ni-16b** supports the loss of HF from

$[\text{Ni(II)L(L-F)}]^+$ . The absence of  $[\text{Ni(II)L(L-F-HF)}]^+$  in the pentafluoroethyl derivatives may be related to the R' chain length; a product ion possessing a sterically-favorable five-membered ring is generated when  $\text{R}' = \text{C}_3\text{F}_7$ , while a more strained, four-membered ring is required for  $\text{R}' = \text{C}_2\text{F}_5$ .

Fluorine migration to the metal is more prevalent in the  $\text{C}_2\text{F}_5^-$  and  $\text{C}_3\text{F}_7^-$ -substituted chelates than it is in the  $\text{CF}_3$  derivatives, which is perhaps attributable to a hardening of the metal center by the highly electronegative perfluoroethyl and perfluoropropyl groups. A proposed mechanism for the formation of the fluorine transfer ions  $[\text{Ni(III)FL(L-CF}_3)]^+$  and  $[\text{Ni(III)FL(L-C}_2\text{F}_5)]^+$  in complex **Ni-18b** is given in Scheme 76. A similar reaction sequence was suggested earlier for the Ni(II)  $\beta$ -diketonates (see Scheme 42).

The fragments corresponding to  $[\text{NiHL}]^+$  can be rationalized by Schemes 77-79, which include mechanisms that were first proposed for the appearance of  $[\text{NiHL}]^+$  in Ni(II)  $\beta$ -diketonates (see Schemes 44-46). The majority of the arguments set forth at that time apply to the present situation as well, especially those pertaining to the influence of the aryl substituents upon the rates of  $[\text{NiHL}]^+$  formation. An averaging of the %TIC for each of the three R groups in Tables 46 and 47 establishes the following order of  $[\text{NiHL}]^+$  abundances:  $\text{R} = 2\text{-thienyl} (0\%) < \text{phenyl} (0.2\%) < 2\text{-naphthyl} (0.8\%)$ . Compared to  $\text{R} = \text{phenyl}$ , it appears that the extensive, electron-releasing  $\pi$ -system of the naphthyl substituent (Scheme 79) allows for a more facile hydrogen-to-metal transfer.



**Table 44.** 70 eV-EI mass spectra of compounds Ni-3b, Ni-5b and Ni-7b.

ION	Ni-3b			Ni-5b			Ni-7b		
	%RA	m/z	%TIC	%RA	m/z	%TIC	%RA	m/z	%TIC
R=		-C <sub>6</sub> H <sub>5</sub>			-C <sub>6</sub> H <sub>4</sub> F			-C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub>	
R'=		-CF <sub>3</sub>			-CF <sub>3</sub>			-CF <sub>3</sub>	
[NiL <sub>2</sub> ] <sup>+</sup> (a)	81.8	(520)	29.6	61.2	(556)	15.8	72.1	(580)	16.4
[NiL(L-F)] <sup>+</sup>	1.9	(501)	0.7	2.4	(537)	0.6	-	(561)	-
[NiL(L-S)] <sup>+</sup>	-	(488)	-	15.1	(524)	3.9	-	(548)	-
[NiL(L-R')] <sup>+</sup>	1.5	(451)	0.5	<sup>a</sup> 0.2	(487)	0.1	21.1	(511)	4.8
[NiL(L-R'CO)] <sup>+</sup> (b)	0.7	(423)	0.3	2.6	(459)	0.7	0.6	(483)	0.1
[NiLCHCR] <sup>+</sup>	0.4	(391)	0.1	-	(427)	-	0.5	(451)	0.1
[NiSL] <sup>+</sup>	0.7	(321)	0.3	<sup>a</sup> 0.1	(339)	-	-	(351)	-
[NiLH] <sup>+</sup>	1.2	(290)	0.4	<sup>a</sup> 0.2	(308)	0.1	-	(320)	-
[NiL] <sup>+</sup> (c)	6.3	(289)	2.3	<sup>a,b</sup> 14.3	(307)	3.7	23.3	(319)	5.3
[NiL-H] <sup>+</sup>	1.9	(288)	0.7	<sup>a</sup> 12.5	(306)	3.2	8.7	(318)	2.0
[NiL-F] <sup>+</sup>	0.3	(270)	0.1	<sup>c</sup> 0.1	(288)	-	-	(300)	-
[NiL-S] <sup>+</sup>	2.2	(257)	0.8	-	(275)	-	-	(287)	-
[NiSC(R)CH] <sup>+</sup> (d)	9.2	(192)	3.3	<sup>c</sup> 14.8	(210)	3.8	11.7	(222)	2.7
[NiSCR] <sup>+</sup>	2.4	(179)	0.9	4.7	(197)	1.2	6.7	(209)	1.5
[NiCHCR] <sup>+</sup>	5.9	(160)	2.1	9.5	(178)	2.5	9.3	(190)	2.1
[Ni] <sup>+</sup>	9.9	( 58)	3.6	<sup>d</sup> 37.3	( 58)	9.7	10.9	( 58)	2.5
[2L-2S-R'CO] <sup>+</sup>	0.4	(301)	0.1	4.2	(337)	1.1	14.5	(361)	3.3
[HL] <sup>+</sup>	2.5	(232)	0.9	-	(250)	-	0.8	(262)	0.2
[L] <sup>+</sup> (e)(f)	100.0	(231)	36.2	<sup>a</sup> 100.0	(249)	25.9	<sup>a</sup> 100.0	(261)	22.7

Table 44. (continued).

[L-S] <sup>+</sup>	- (199)	-	<sup>e</sup> 0.1 (217)	-	15.0 (229)	3.4
[L-S-CF <sub>2</sub> ] <sup>+</sup>	4.5 (149)	1.6	15.9 (167)	4.1	36.2 (179)	8.2
[RCSCH] <sup>+</sup> (g)	17.8 (134)	6.4	<sup>b,c</sup> 33.6 (152)	8.7	<sup>f</sup> 32.2 (164)	7.3
[RC <sub>3</sub> O] <sup>+</sup>	5.2 (129)	1.9	10.0 (147)	2.6	9.3 (159)	2.1
[RCS] <sup>+</sup>	7.6 (121)	2.8	14.8 (139)	3.8	13.9 (151)	3.2
[RCCH] <sup>+</sup>	4.9 (102)	1.8	<sup>g</sup> 11.8 (120)	3.1	37.1 (132)	8.4
	2.3 ( 89)	0.8	- (107)	-	- (119)	-
	- ( 87)	-	7.3 (105)	1.9	10.7 (117)	2.4
[R] <sup>+</sup>	3.6 ( 77)	1.3	- ( 95)	-	- (107)	-
[R'] <sup>+</sup>	3.6 ( 69)	1.3	14.4 ( 69)	3.7	5.2 ( 69)	1.2

<sup>a</sup> Identified metastable transitions are indicated by superscripts which relate the daughter ion to its precursor as labelled in column 1.

Table 45. 70 eV-EI mass spectra of compounds Ni-8b and Ni-9b.

ION	Ni-8b			Ni-9b		
	%RA	m/z	%TIC	%RA	m/z	%TIC
	R =	-C <sub>4</sub> H <sub>3</sub> S			-C <sub>4</sub> H <sub>2</sub> SCH <sub>3</sub>	
	R' =	-CF <sub>3</sub>			-CF <sub>3</sub>	
[NiL <sub>2</sub> ] <sup>+</sup>	84.7	(532)	18.9	100.0	(560)	30.2
[NiL(L-F)] <sup>+</sup>	2.1	(513)	0.5	3.0	(541)	0.9
[NiL(L-R')] <sup>+</sup>	4.0	(463)	0.9	4.9	(491)	1.5
[NiL(L-R'CO)] <sup>+</sup>	1.5	(435)	0.3	1.0	(463)	0.3
[NiLCHCR] <sup>+</sup>	1.5	(403)	0.3	0.8	(431)	0.2
[NiHL] <sup>+</sup>	0.8	(296)	0.2	1.5	(310)	0.5
[NiL] <sup>+</sup>	11.3	(295)	2.5	6.5	(309)	2.0
[NiL-H] <sup>+</sup>	1.9	(294)	0.4	2.9	(308)	0.9
[NiL-S] <sup>+</sup>	3.3	(263)	0.7	3.8	(277)	1.2
[NiSC(R)CH] <sup>+</sup>	7.1	(198)	1.6	2.6	(212)	0.8
[NiSCR] <sup>+</sup>	2.8	(185)	0.6	1.7	(199)	0.5
[NiCHCR] <sup>+</sup>	9.6	(166)	2.1	2.2	(180)	0.7
[Ni] <sup>+</sup>	9.0	( 58)	2.0	8.3	( 58)	2.5
[2L-2S-R'CO] <sup>+</sup>	1.3	(313)	0.3	-	(341)	-
[HL] <sup>+</sup>	5.4	(238)	1.2	11.2	(252)	3.4
[L] <sup>+</sup>	100.0	(237)	22.3	46.6	(251)	14.1
[L-S] <sup>+</sup>	80.8	(205)	18.0	54.6	(219)	16.5
[HL-R'] <sup>+</sup>	4.8	(169)	1.1	6.2	(183)	1.9

Table 45. (continued).

$[\text{L-S-CF}_2]^+$	12.4 (155)	2.8	11.3 (169)	3.4
$[\text{RCSCH}]^+$	25.2 (140)	5.6	17.2 (154)	5.2
$[\text{RC}_3\text{O}]^+$	7.0 (135)	1.6	5.7 (149)	1.7
$[\text{RCS}]^+$	13.7 (127)	3.1	13.7 (141)	4.1
$[\text{RCCH}]^+$	14.4 (108)	3.2	13.5 (122)	4.1
$[\text{R}]^+$	- ( 83)	-	5.6 ( 97)	1.7
$[\text{R}']^+$	18.3 ( 69)	4.1	8.5 ( 69)	2.6
$[\text{CSCH}]^+$	24.6 ( 57)	5.5	- ( 57)	-

Table 46. 70 eV-EI mass spectra of compounds Ni-13b, Ni-14b and Ni-15b.

ION	Ni-13b			Ni-14b			Ni-15b		
	%RA	m/z	%TIC	%RA	m/z	%TIC	%RA	m/z	%TIC
	R =	-C <sub>6</sub> H <sub>5</sub>		-C <sub>4</sub> H <sub>3</sub> S			-C <sub>10</sub> H <sub>7</sub>		
	R' =	-C <sub>2</sub> F <sub>5</sub>		-C <sub>2</sub> F <sub>5</sub>			-C <sub>2</sub> F <sub>5</sub>		
[NiL <sub>2</sub> ] <sup>+</sup> (a)	66.9	(620)	14.9	95.6	(632)	19.5	71.2	(720)	23.7
[NiL(L-F)] <sup>+</sup>	-	(601)	-	1.6	(613)	0.3	1.2	(701)	0.4
[NiFL(L-CF <sub>3</sub> )] <sup>+</sup>	3.8	(570)	0.8	10.8	(582)	2.2	1.5	(670)	0.5
[NiL(L-R')] <sup>+</sup>	1.6	(501)	0.4	5.6	(513)	1.1	1.9	(601)	0.6
[NiL(L-R'CO)] <sup>+</sup>	0.9	(473)	0.2	1.4	(485)	0.3	0.5	(573)	0.2
[NiLCHCR] <sup>+</sup>	0.8	(441)	0.2	1.7	(453)	0.3	0.9	(541)	0.3
[NiSL] <sup>+</sup>	0.9	(371)	0.2	0.6	(377)	0.1	-	(421)	-
[NiHL] <sup>+</sup>	0.5	(340)	0.1	0.2	(346)	-	1.3	(390)	0.4
[NiL] <sup>+</sup>	8.3	(339)	1.8	15.8	(345)	3.2	3.0	(389)	1.0
[NiL-H] <sup>+</sup>	1.3	(338)	0.3	1.6	(344)	0.3	2.5	(388)	0.8
[NiL-S] <sup>+</sup>	1.8	(307)	0.4	3.4	(313)	0.7	1.8	(357)	0.6
[NiSC(R)CH] <sup>+</sup>	23.7	(192)	5.3	16.9	(198)	3.5	18.5	(242)	6.1
[HL-R'] <sup>+</sup>	12.0	(163)	2.7	9.7	(169)	2.0	4.1	(213)	1.4
[NiCHCR] <sup>+</sup>	8.9	(160)	2.0	15.7	(166)	3.2	8.1	(210)	2.7
[Ni] <sup>+</sup>	15.5	(58)	3.5	-	(58)	-	5.6	(58)	1.9
[2L-2S-R'CO] <sup>+</sup>	0.6	(351)	0.1	1.8	(363)	0.3	0.3	(451)	0.1
[HL] <sup>+</sup> (b)	6.7	(282)	1.5	6.7	(288)	1.4	2.8	(332)	0.9
[L] <sup>+</sup> (c)	<sup>a,b</sup> 100.0	(281)	22.3	<sup>a</sup> 100.0	(287)	20.4	100.0	(331)	33.2
[L-F] <sup>+</sup>	2.5	(262)	0.5	1.7	(268)	0.3	0.9	(312)	0.3

Table 46. (continued).

[L-S] <sup>+</sup>	0.6 (249)	0.1	<sup>c</sup> 86.2 (255)	17.6	1.4 (299)	0.5
[L-2F] <sup>+</sup>	6.8 (243)	1.5	6.5 (249)	1.3	3.2 (293)	1.0
[L-CF <sub>2</sub> ] <sup>+</sup>	4.9 (231)	1.1	5.7 (237)	1.2	1.1 (281)	0.4
[L-57] <sup>+</sup>	5.0 (224)	1.1	2.5 (230)	0.5	1.9 (274)	0.6
[L-S-CF <sub>2</sub> ] <sup>+</sup>	- (199)	-	5.3 (205)	1.1	- (249)	-
[RCSCH] <sup>+</sup>	23.1 (134)	5.1	31.3 (140)	6.4	30.4 (184)	10.1
[RC <sub>3</sub> O] <sup>+</sup>	8.2 (129)	1.8	8.3 (135)	1.7	4.7 (179)	1.5
[RCS] <sup>+</sup>	13.7 (121)	3.0	16.7 (127)	3.4	8.0 (171)	2.7
[R'] <sup>+</sup>	15.7 (119)	3.5	4.9 (119)	1.0	0.6 (119)	0.2
[RCO] <sup>+</sup>	3.8 (105)	0.8	4.1 (111)	0.8	1.3 (155)	0.4
[RCCH] <sup>+</sup>	16.8 (102)	3.7	20.1 (108)	4.1	19.9 (152)	6.6
[R] <sup>+</sup>	9.0 ( 77)	2.0	- ( 83)	-	2.9 (127)	1.0
[CF <sub>3</sub> ] <sup>+</sup>	58.0 ( 69)	12.9	9.4 ( 69)	1.9	2.0 ( 69)	0.7
[CSCH] <sup>+</sup>	28.9 ( 57)	6.4	- ( 57)	-	- ( 57)	-

<sup>a</sup> Identified metastable transitions are indicated by superscripts which relate the daughter ion to its precursor as labelled in column 1.

Table 47. 70 eV-EI mass spectra of compounds Ni-16b, Ni-17b and Ni-18b.

	Ni-16b			Ni-17b			Ni-18b		
R =	-C <sub>6</sub> H <sub>5</sub>			-C <sub>4</sub> H <sub>3</sub> S			-C <sub>10</sub> H <sub>7</sub>		
R' =	-C <sub>3</sub> F <sub>7</sub>			-C <sub>3</sub> F <sub>7</sub>			-C <sub>3</sub> F <sub>7</sub>		
ION	%RA	m/z	%TIC	%RA	m/z	%TIC	%RA	m/z	%TIC
[NiL <sub>2</sub> ] <sup>+</sup> (a)	91.5	(720)	28.2	100.0	(732)	23.2	80.0	(820)	20.3
[NiL(L-F)] <sup>+</sup> (b)	2.4	(701)	0.7	2.8	(713)	0.7	2.4	(801)	0.6
[NiL(L-S)] <sup>+</sup>	-	(688)	-	-	(700)	-	2.4	(788)	0.6
[NiL(L-F-HF)] <sup>+</sup>	<sup>b</sup> 1.3	(681)	0.4	1.8	(693)	0.4	-	(781)	-
[NiFL(L-CF <sub>3</sub> )] <sup>+</sup>	-	(670)	-	0.8	(682)	0.2	14.0	(770)	3.5
[NiFL(L-C <sub>2</sub> F <sub>5</sub> )] <sup>+</sup>	-	(620)	-	-	(632)	-	2.4	(720)	0.6
[NiL(L-R')] <sup>+</sup> (c)	2.8	(551)	0.9	7.6	(563)	1.8	2.4	(651)	0.6
[NiL(L-R'CO)] <sup>+</sup>	<sup>c</sup> 2.8	(523)	0.9	<sup>c</sup> 2.8	(535)	0.7	0.7	(623)	0.2
[NiLCHCR] <sup>+</sup>	-	(491)	-	3.0	(503)	0.7	2.4	(591)	0.6
[NiSL] <sup>+</sup>	1.2	(421)	0.4	0.7	(427)	0.2	-	(471)	-
[NiHL] <sup>+</sup>	0.7	(390)	0.2	0.2	(396)	-	4.3	(440)	1.1
[NiL] <sup>+</sup>	8.1	(389)	2.5	15.3	(395)	3.6	3.8	(439)	1.0
[NiL-H] <sup>+</sup>	1.2	(388)	0.4	1.3	(394)	0.3	-	(438)	-
[NiL-S] <sup>+</sup>	2.7	(357)	0.8	3.0	(363)	0.7	1.9	(407)	0.5
[NiSC(R)CH] <sup>+</sup>	25.6	(192)	7.9	17.6	(198)	4.1	24.0	(242)	6.1
[NiCHCR] <sup>+</sup>	11.0	(160)	3.4	14.4	(166)	3.3	10.5	(210)	2.7
[Ni] <sup>+</sup>	13.8	( 58)	4.3	7.2	( 58)	1.7	14.0	( 58)	3.5

Table 47. (continued).

[2L-2S-R'CO] <sup>+</sup>	0.7 (401)	0.2	2.3 (413)	0.6	1.0 (501)	0.3
[HL] <sup>+</sup>	- (332)	-	1.1 (338)	0.3	- (382)	-
[L] <sup>+</sup>	<sup>a</sup> 100.0 (331)	30.9	83.0 (337)	19.3	100.0 (381)	25.3
[L-S] <sup>+</sup>	- (299)	-	71.8 (305)	16.7	2.7 (349)	0.7
[L-2F] <sup>+</sup>	5.9 (293)	1.8	7.2 (299)	1.7	3.2 (343)	0.8
[R'] <sup>+</sup>	- (169)	-	5.6 (169)	1.3	- (169)	-
[RCSCH] <sup>+</sup>	21.3 (134)	6.6	28.4 (140)	6.6	32.0 (184)	8.1
[RC <sub>3</sub> O] <sup>+</sup>	6.9 (129)	2.1	9.7 (135)	2.3	- (179)	-
[RCS] <sup>+</sup>	9.8 (121)	3.0	13.0 (127)	3.0	14.0 (171)	3.5
[RCO] <sup>+</sup>	1.6 (105)	0.5	3.8 (111)	0.9	5.5 (155)	1.4
[RCCH] <sup>+</sup>	6.1 (102)	1.9	16.4 (108)	3.8	26.0 (152)	6.6
[R] <sup>+</sup>	3.3 ( 77)	1.0	- ( 83)	-	8.4 (127)	2.1
[CF <sub>3</sub> ] <sup>+</sup>	5.2 ( 69)	1.6	9.0 ( 69)	2.1	38.0 ( 69)	9.6

<sup>a</sup> Identified metastable transitions are indicated by superscripts which relate the daughter ion to its precursor as labelled in column 1.

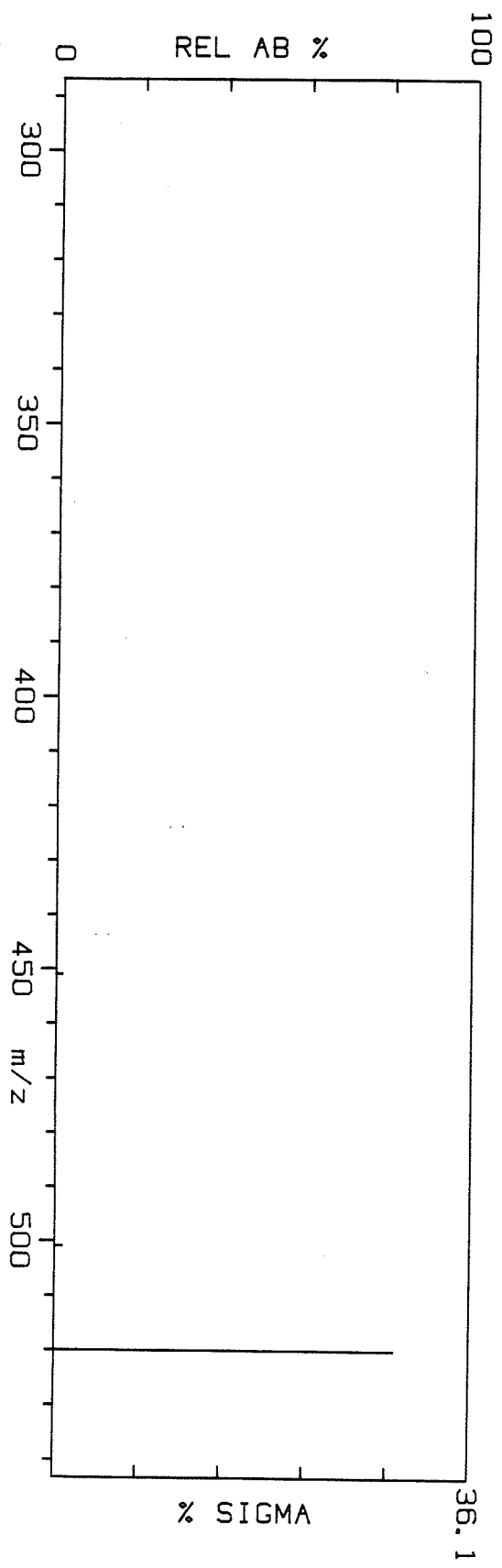
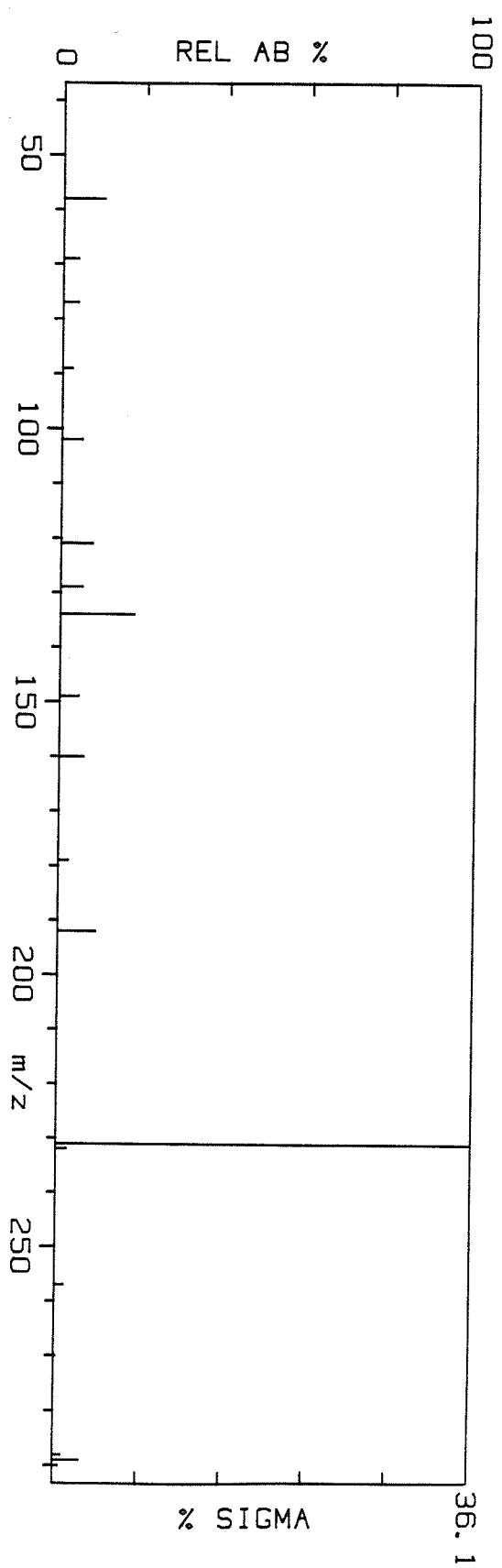


**Figure 97.**

Normalized 70eV-EI mass spectrum of  
bis[1,1,1-trifluoro-4-mercapto-4-phenyl-but-3-en-2-onato]Ni(II)  
{Ni-3b}.

$m/z$   $[M]^{+}$  = 520,  $[L]^{+}$  = 231

NI-38 70EV.

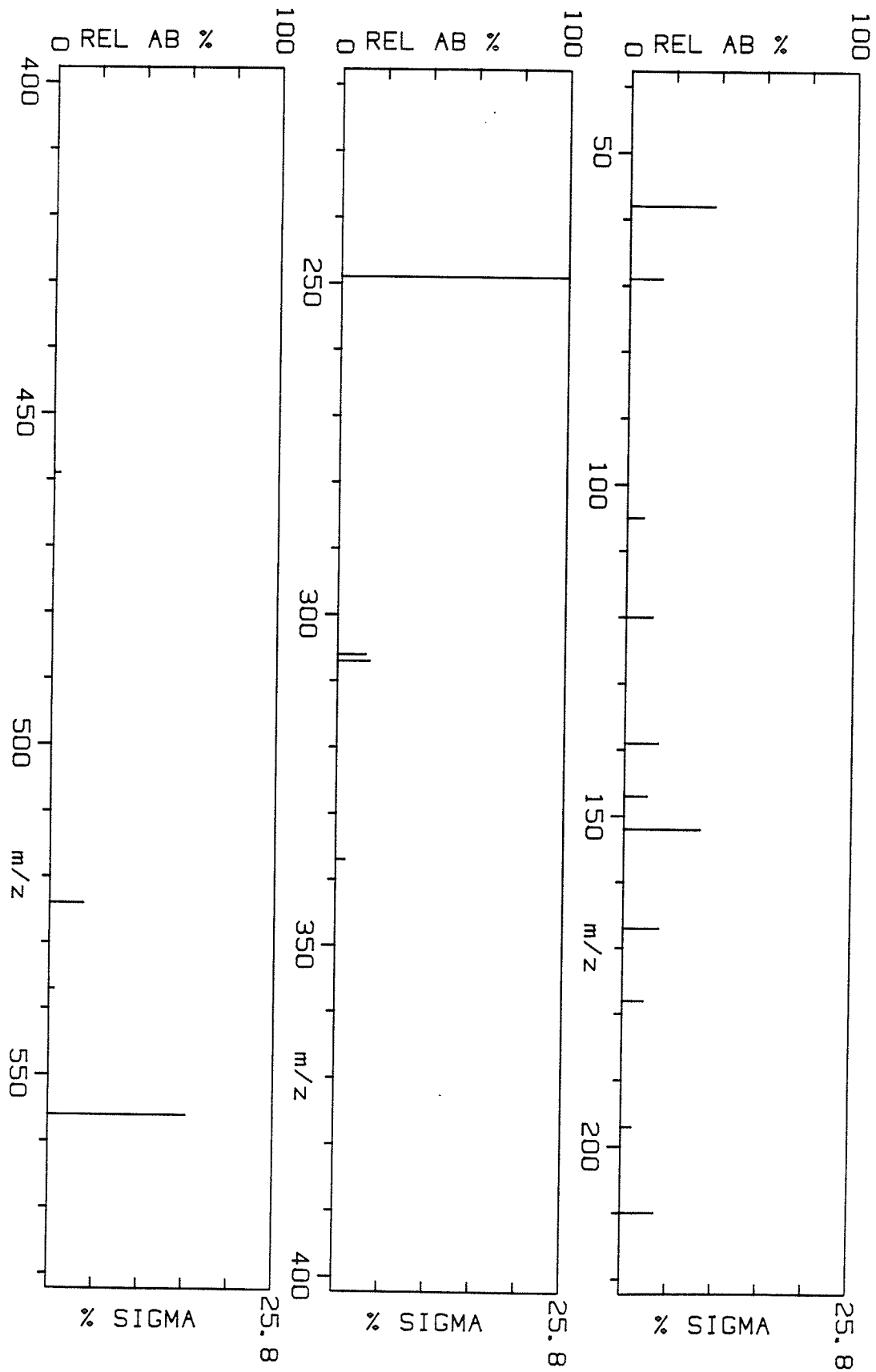


**Figure 98.**

Normalized 70 eV-EI mass spectrum of  
bis[1,1,1-trifluoro-4-mercapto-4-(4'-fluorophenyl)-  
but-3-en-2-onato]Ni(II) (Ni-5b).

$m/z$   $[M]^{+}$  = 556,  $[L]^{+}$  = 249

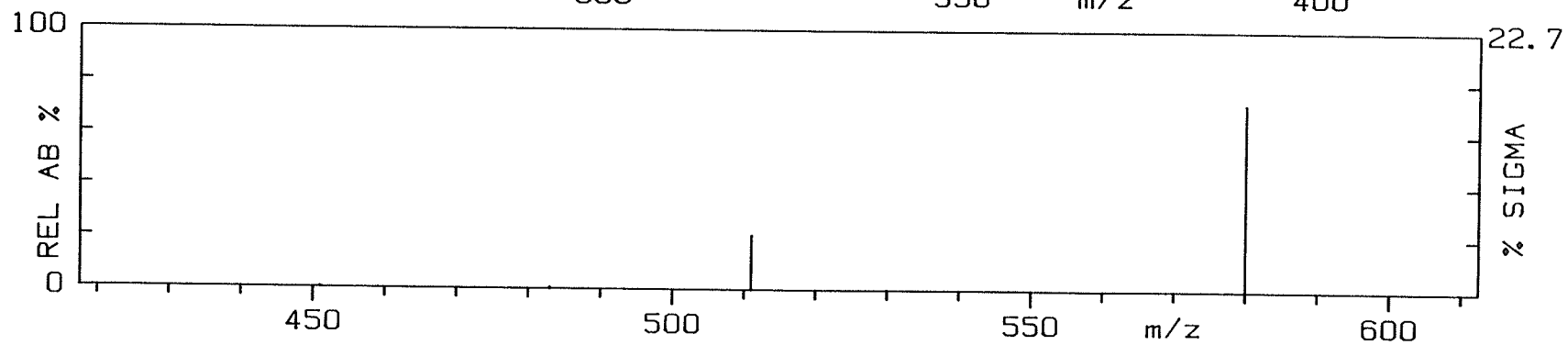
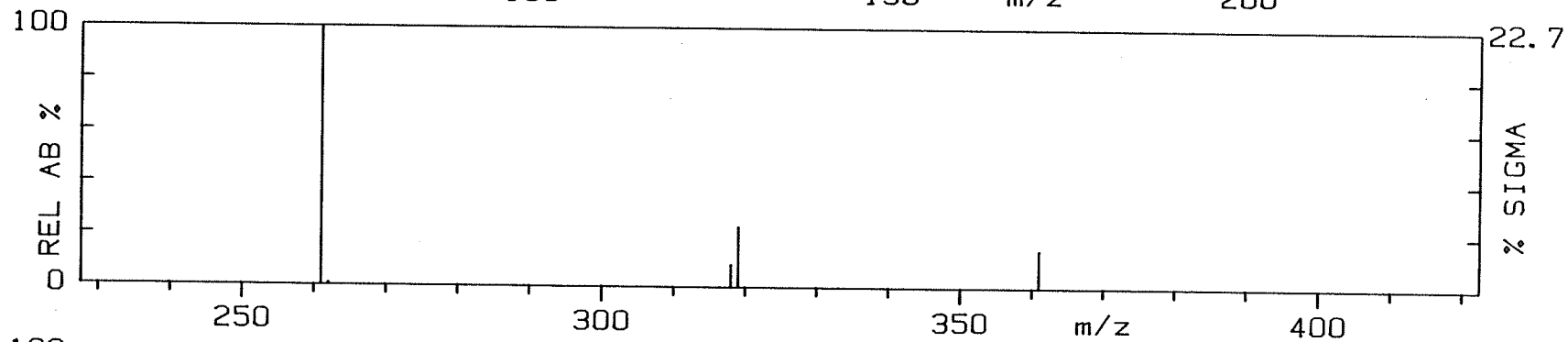
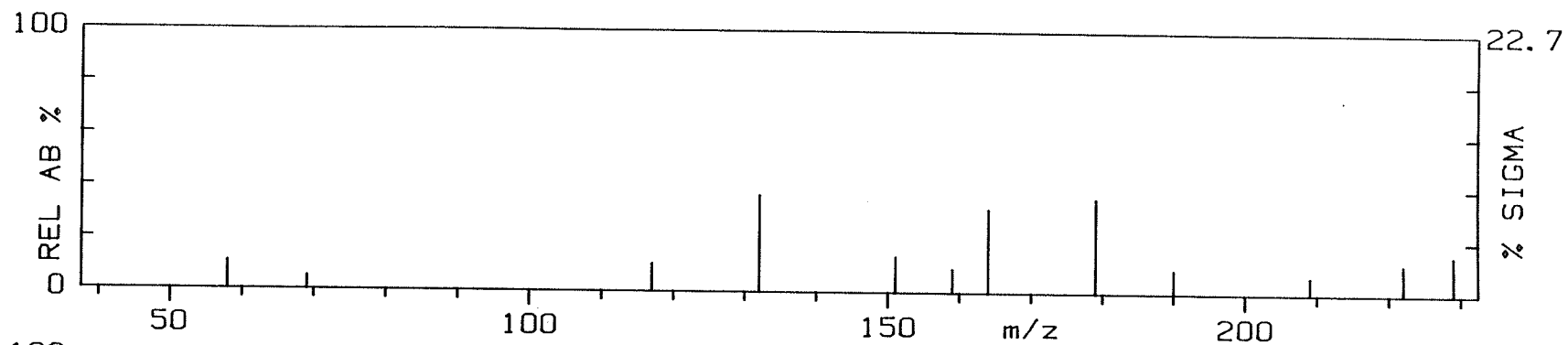
NI-58 70EV.



**Figure 99.**

Normalized 70 eV-EI mass spectrum of  
bis[1,1,1-trifluoro-4-mercapto-4-(4'-methoxyphenyl)-  
but-3-en-2-onato]Ni(II) (Ni-7b).  
 $m/z$   $[M]^+$  = 580,  $[L]^+$  = 261

NI-7B 70EV.

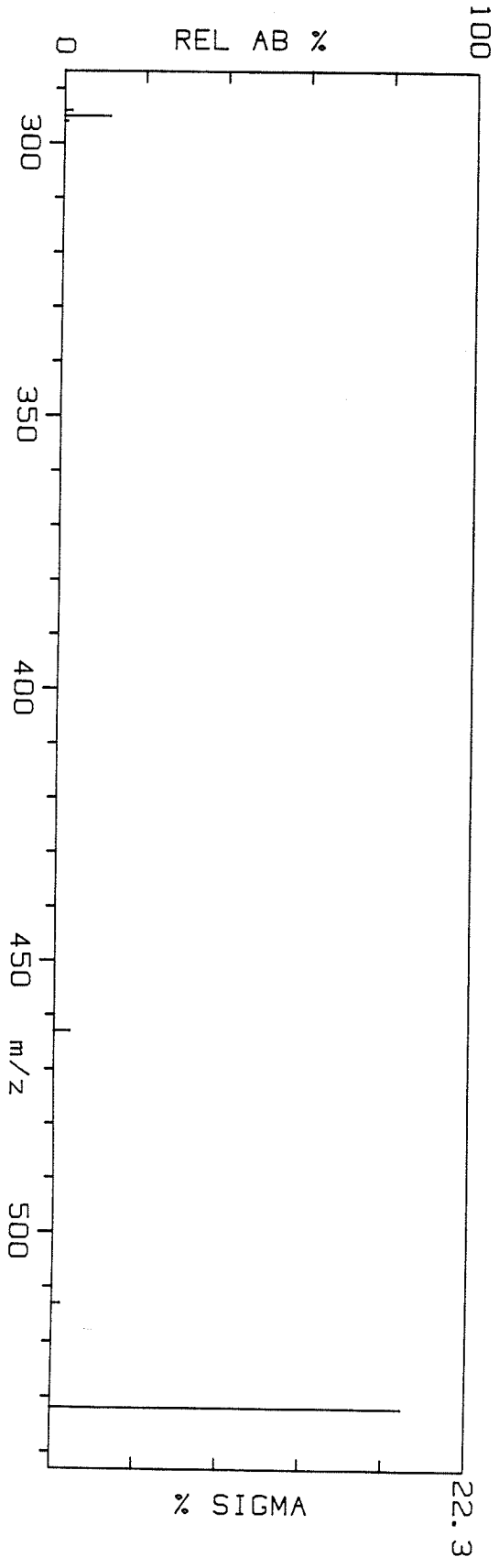
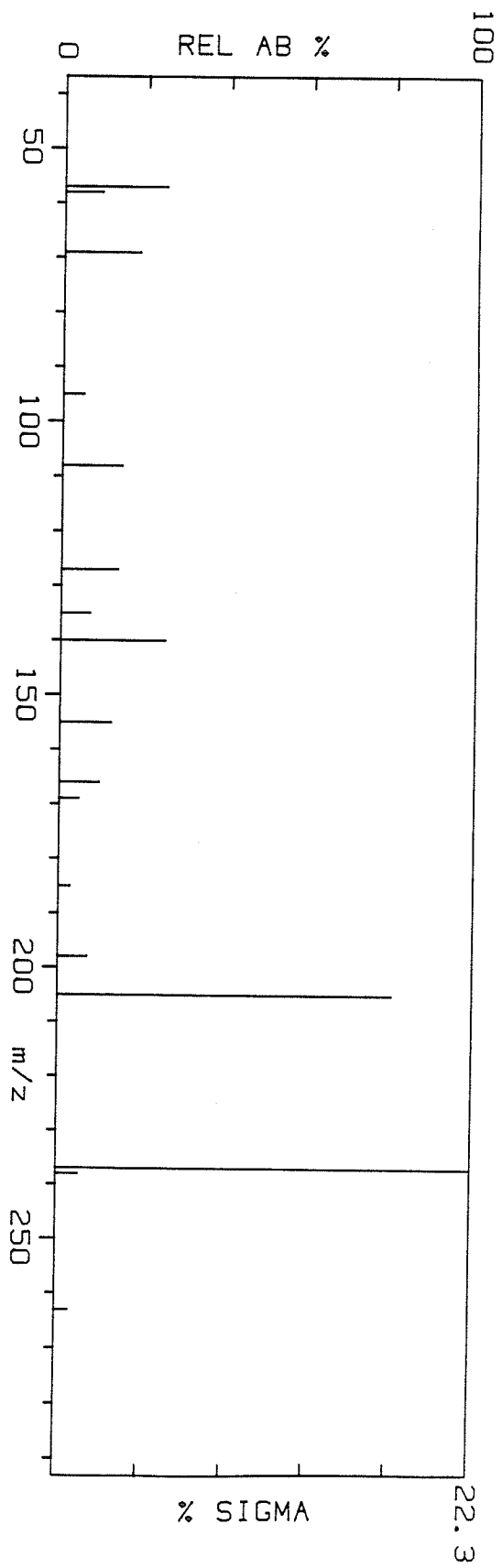


**Figure 100.**

Normalized 70 eV-EI mass spectrum of  
bis[1,1,1-trifluoro-4-mercapto-4-(2'-thienyl)-but-3-en-2-onato]Ni(II)  
{Ni-8b}.

$m/z$   $[M]^{+\cdot} = 532$ ,  $[L]^+ = 237$

NI-88 70EV.



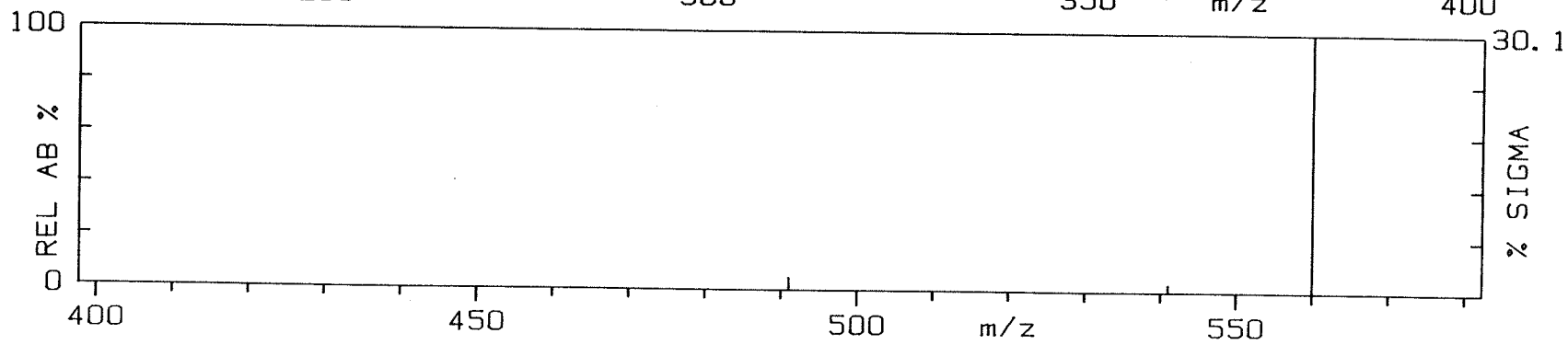
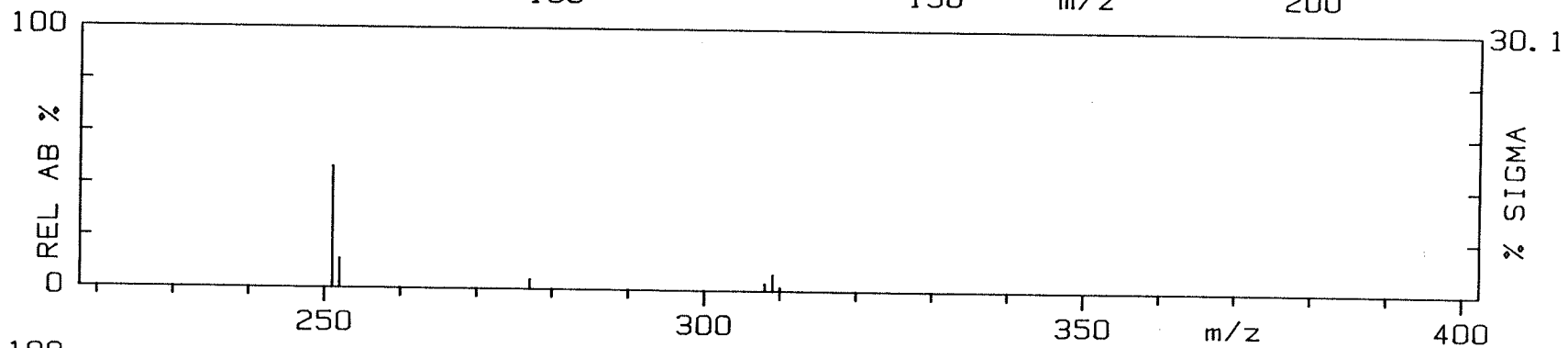
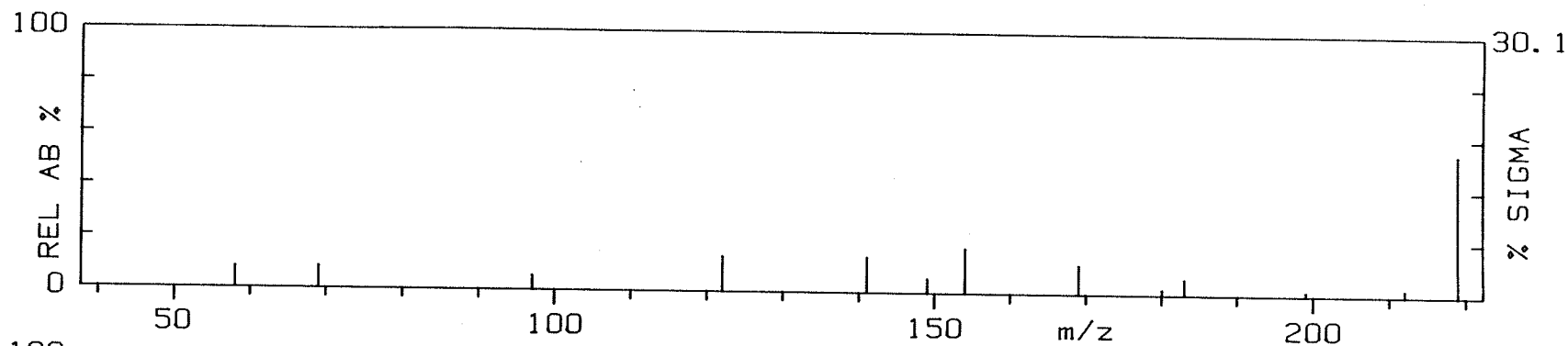


**Figure 101.**

Normalized 70 eV-EI mass spectrum of  
bis[1,1,1-trifluoro-4-mercapto-4-(5'-methyl-2'-thienyl)-  
but-3-en-2-onato]Ni(II) (**Ni-9b**).

$m/z$   $[M]^{+•} = 560$ ,  $[L]^+ = 251$

NI-9B 70EV.

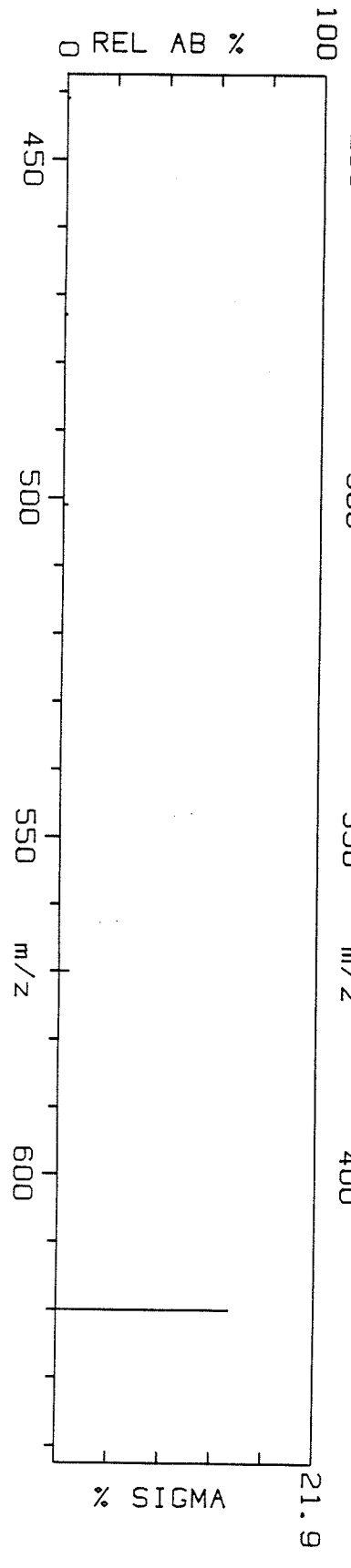
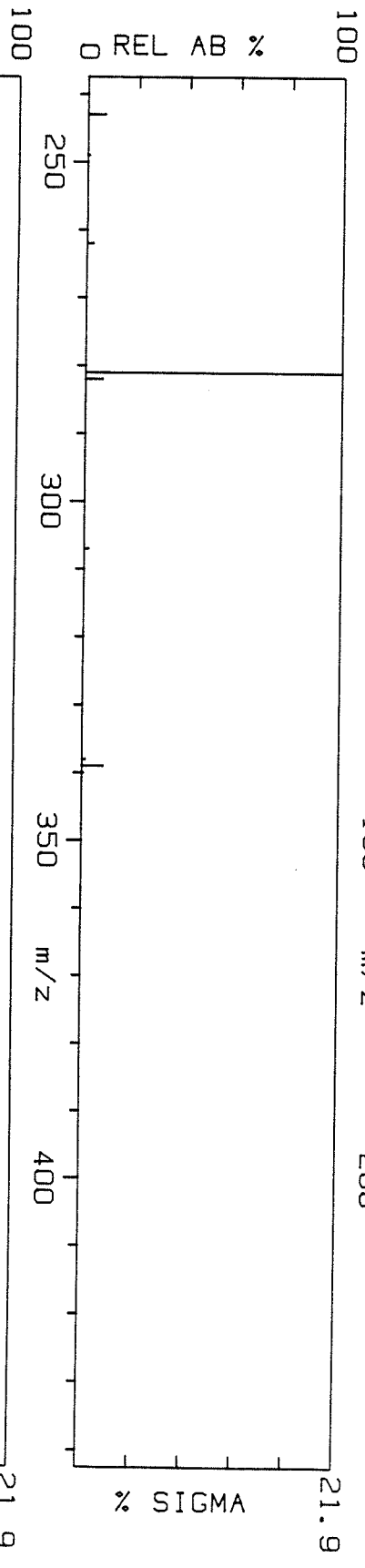
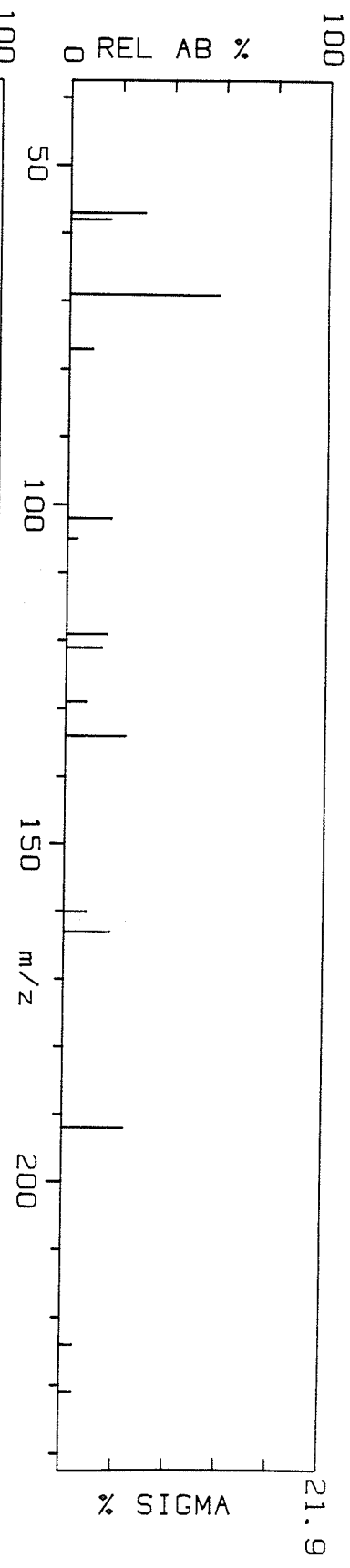


**Figure 102.**

Normalized 70 eV-EI mass spectrum of  
bis[1,1,1,2,2-pentafluoro-5-mercapto-5-phenyl-pent-4-en-3-onato]Ni(II)  
(Ni-13b).

$m/z$   $[M]^{+}$  = 620,  $[L]^{+}$  = 281

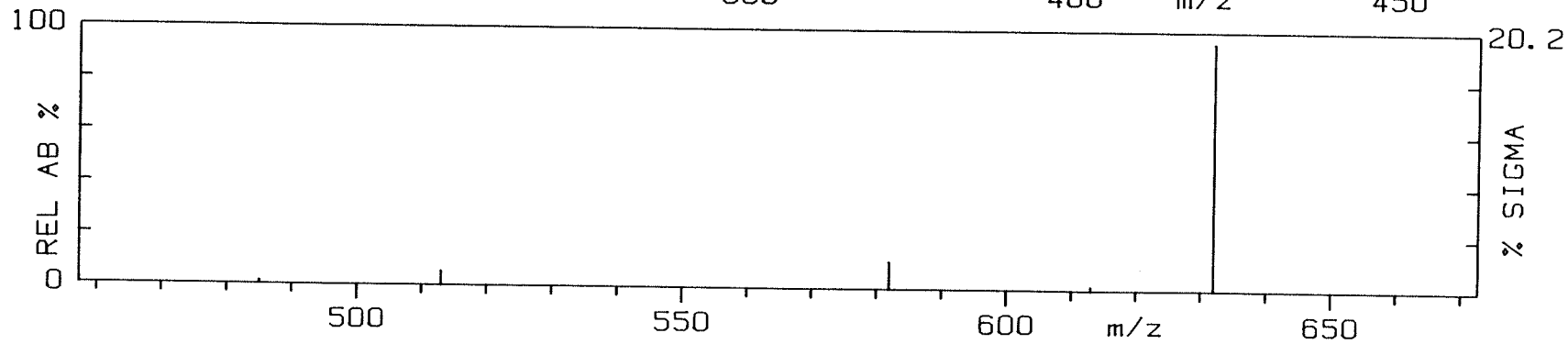
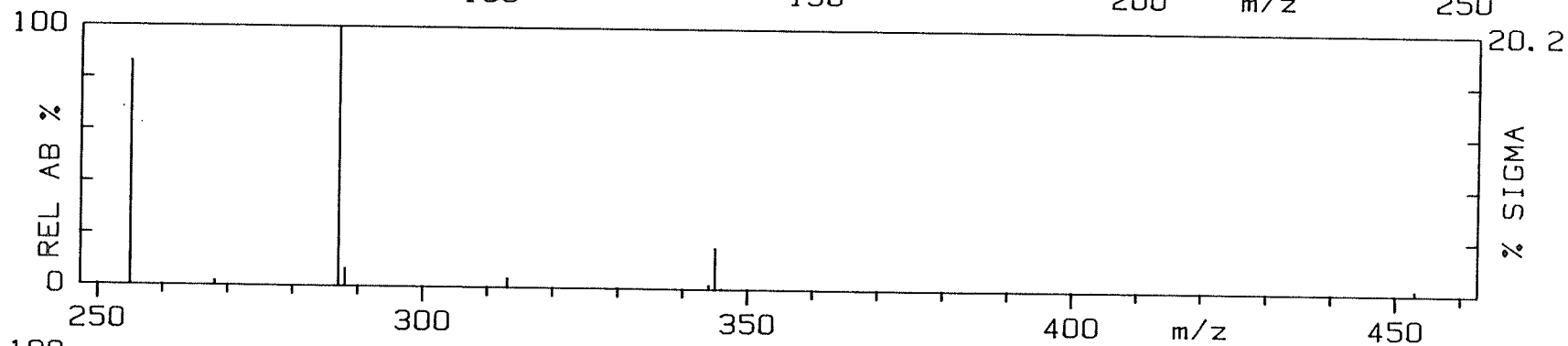
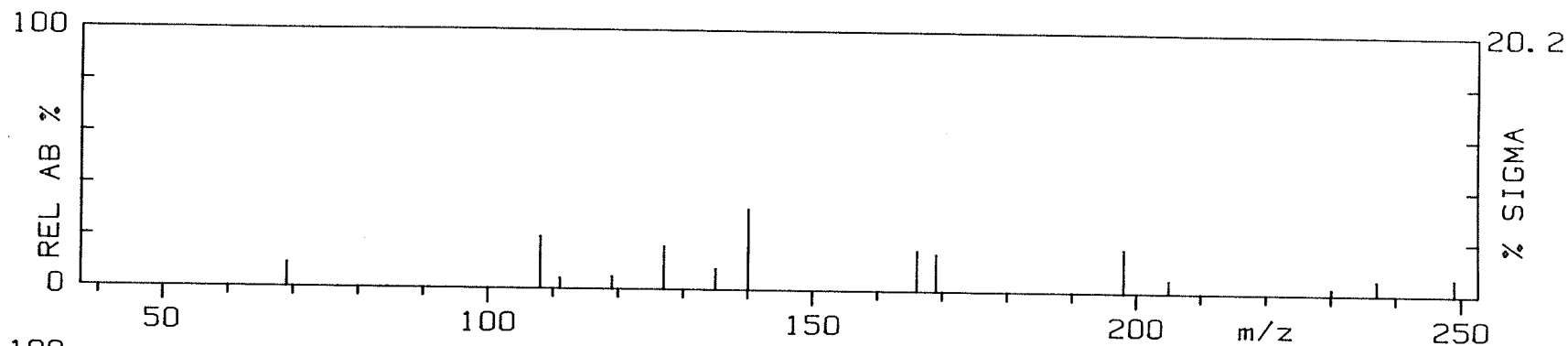
NI-138 70EV.



**Figure 103.**

Normalized 70 eV-EI mass spectrum of  
bis[1,1,1,2,2-pentafluoro-5-mercapto-5-(2'-thienyl)-  
pent-4-en-3-onato]Ni(II) (Ni-14b).  
 $m/z$   $[M]^{+}$  = 632,  $[L]^{+}$  = 287

NI-14B 70EV.

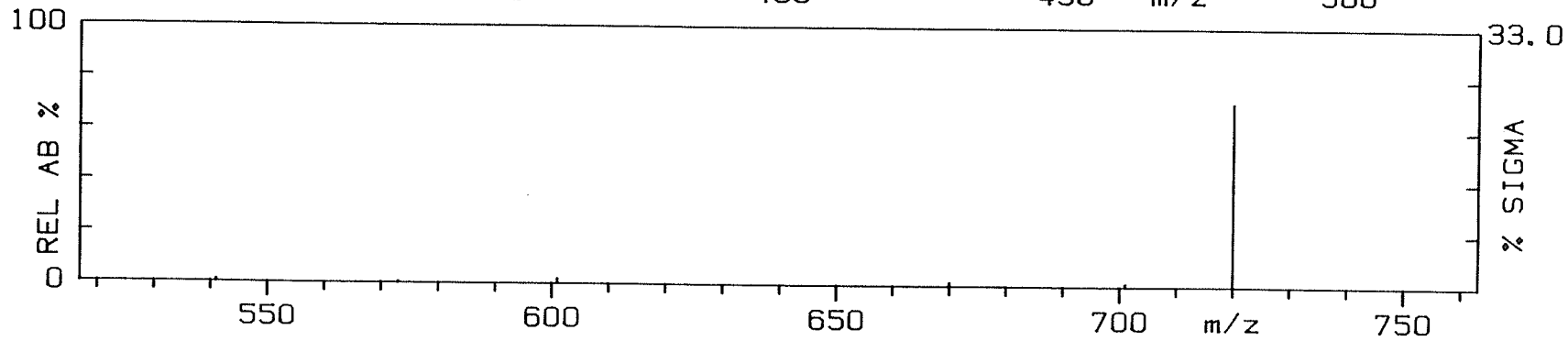
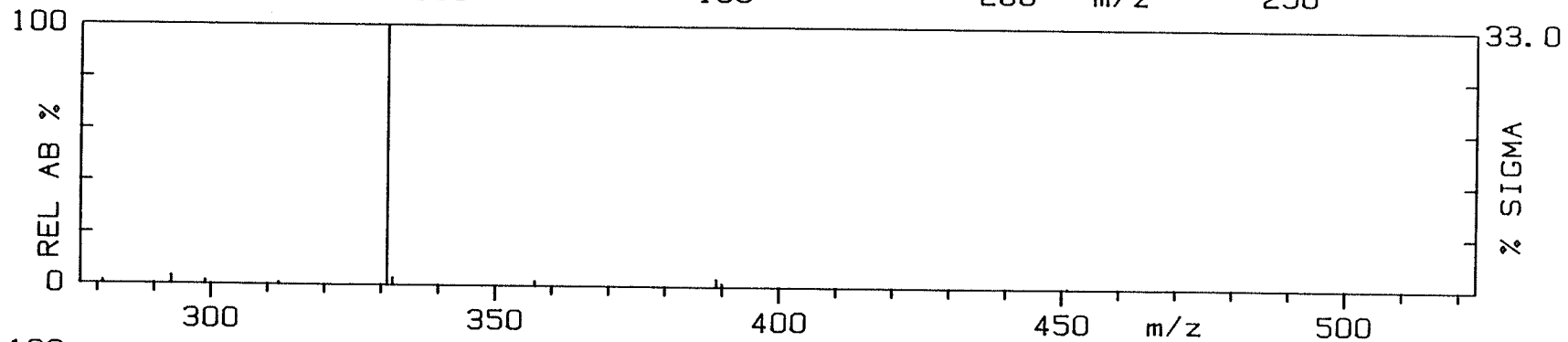
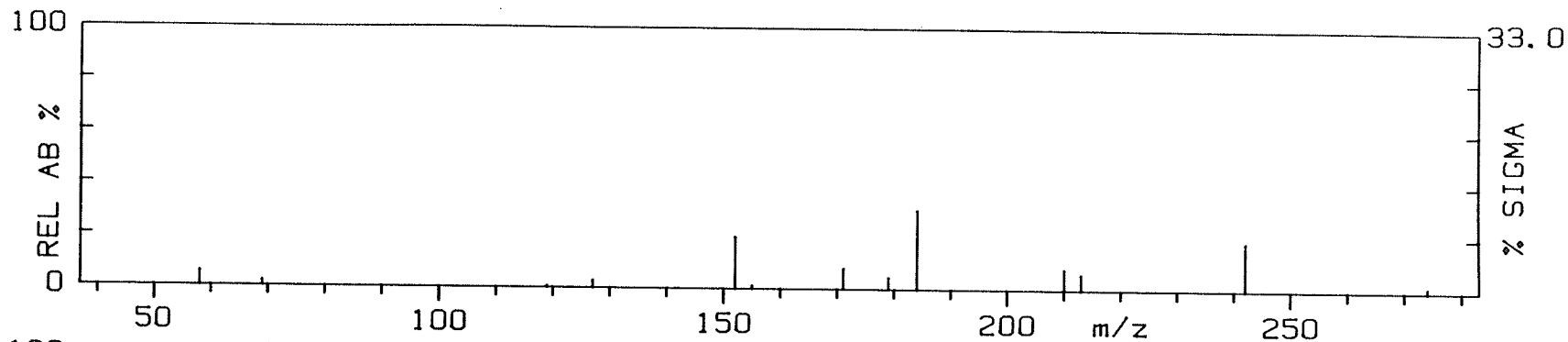


**Figure 104.**

Normalized 70 eV-EI mass spectrum of  
bis[1,1,1,2,2-pentafluoro-5-mercapto-5-(2'-naphthyl)-  
pent-4-en-3-onato]Ni(II) (Ni-15b).

$m/z$   $[M]^{+•} = 720$ ,  $[L]^+ = 331$

NI-15B 70EV.



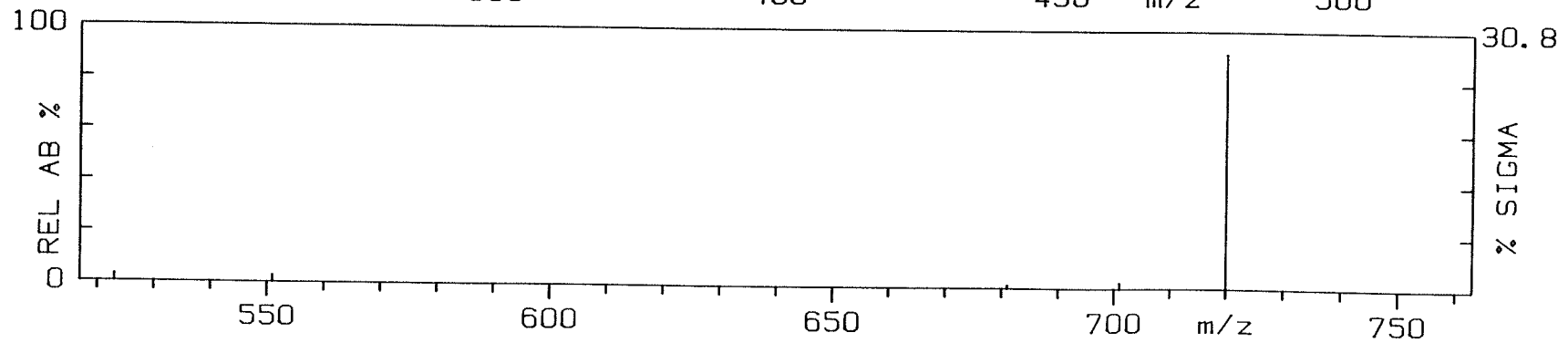
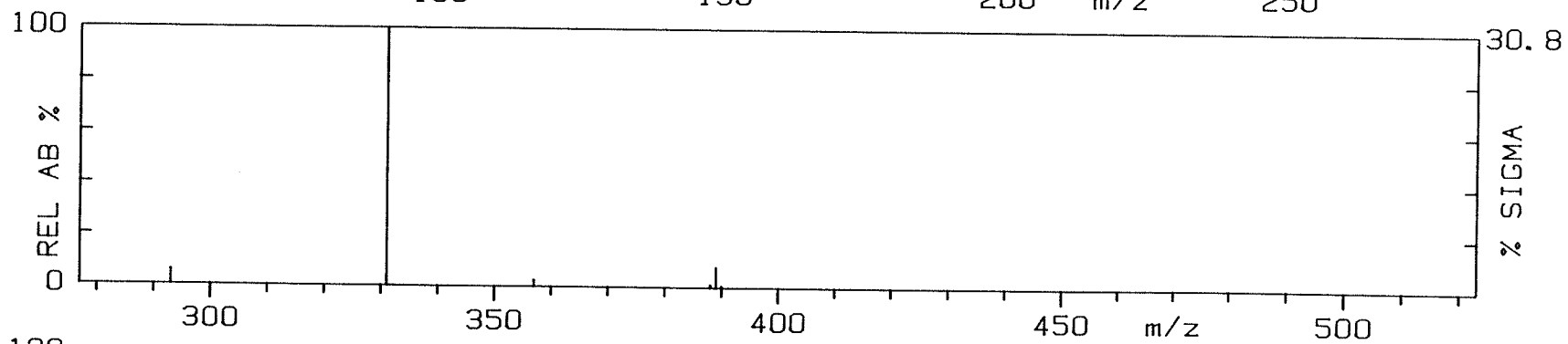
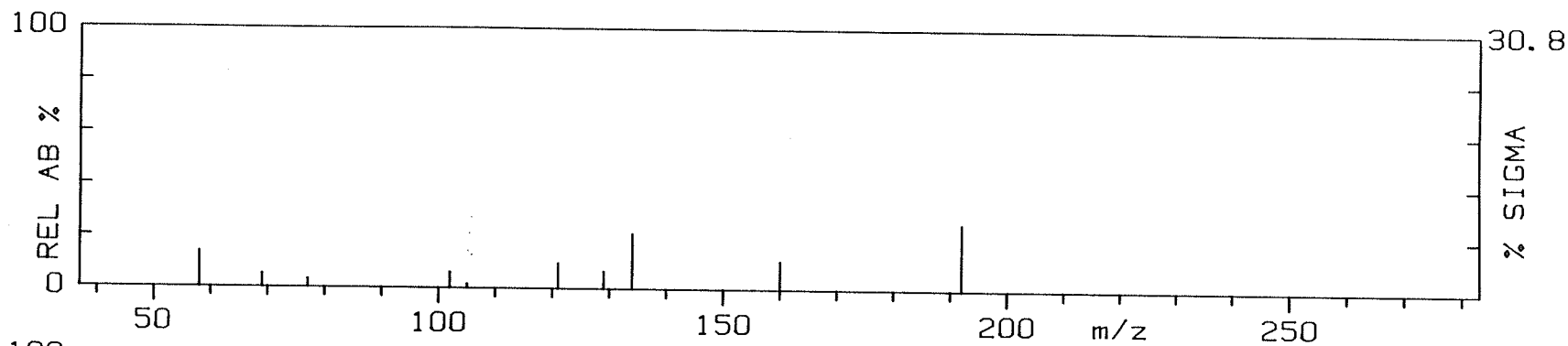


**Figure 105.**

Normalized 70 eV-EI mass spectrum of  
bis[1,1,1,2,2,3,3-heptafluoro-6-mercapto-6-phenyl-  
hex-5-en-4-onato]Ni(II) (Ni-16b).

$m/z$   $[M]^{+\cdot} = 720$ ,  $[L]^+ = 331$

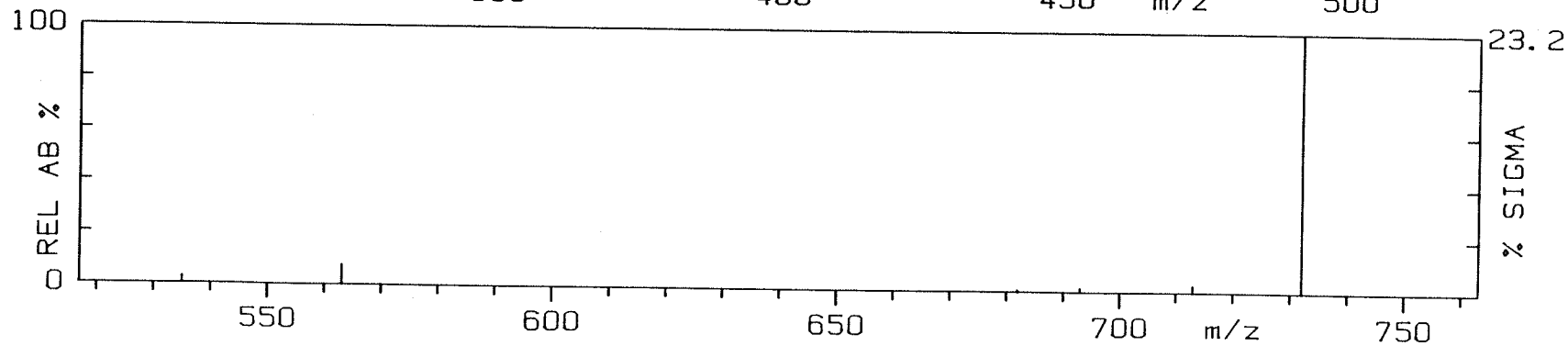
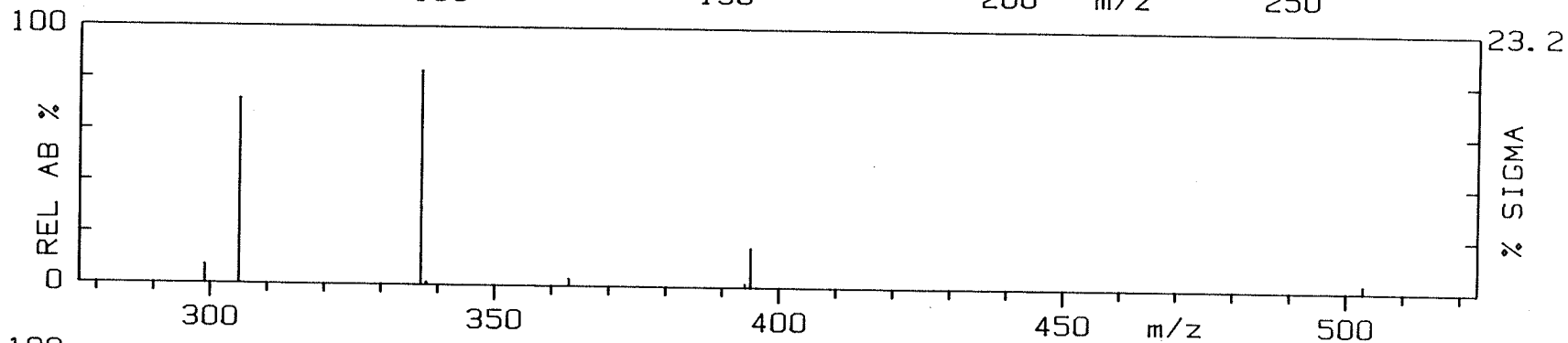
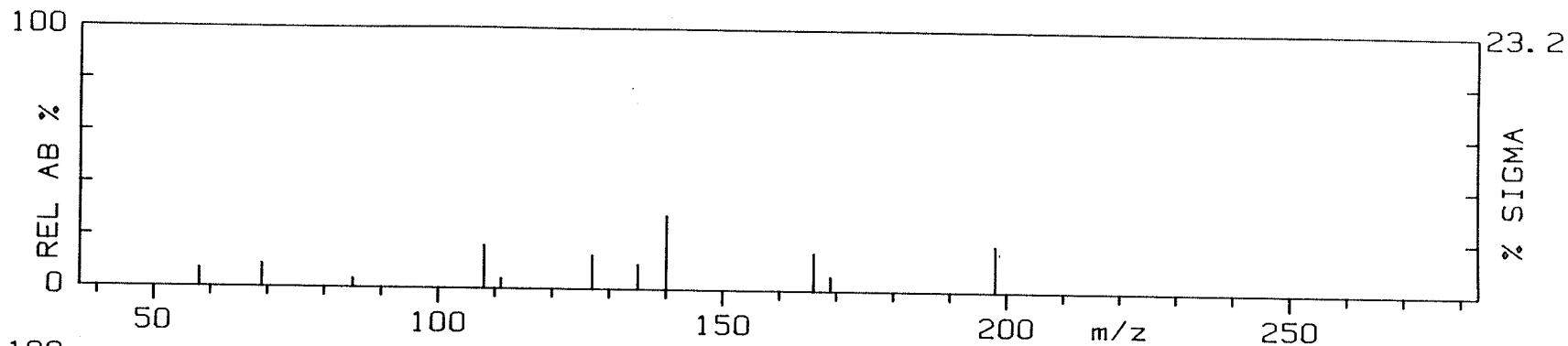
NI-16B 70EV.



**Figure 106.**

Normalized 70 eV-EI mass spectrum of  
bis[1,1,1,2,2,3,3-heptafluoro-6-mercapto-6-(2'-thienyl)-  
hex-5-en-4-onato]Ni(II) (Ni-17b).  
 $m/z$   $[M]^{+•} = 732$ ,  $[L]^+ = 337$

NI-17B 70EV.

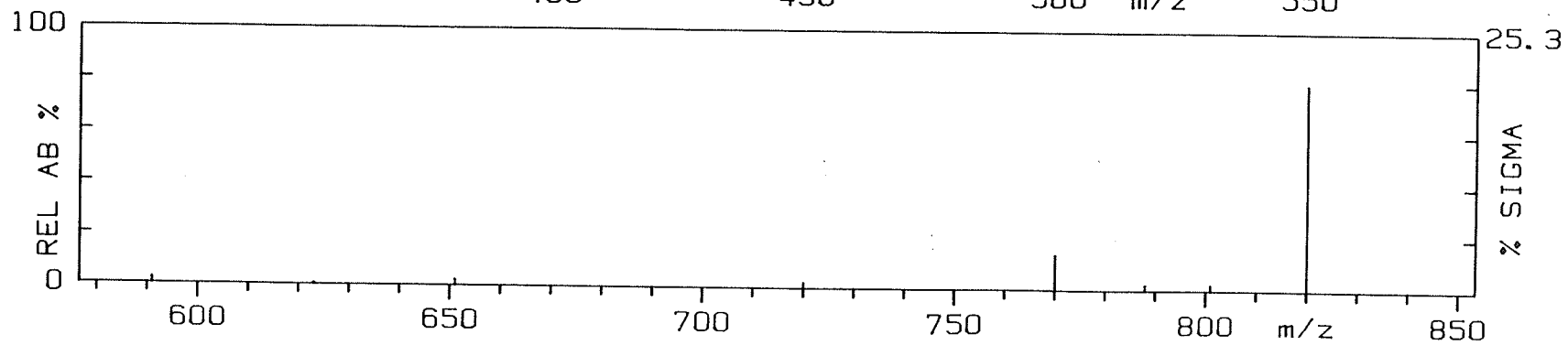
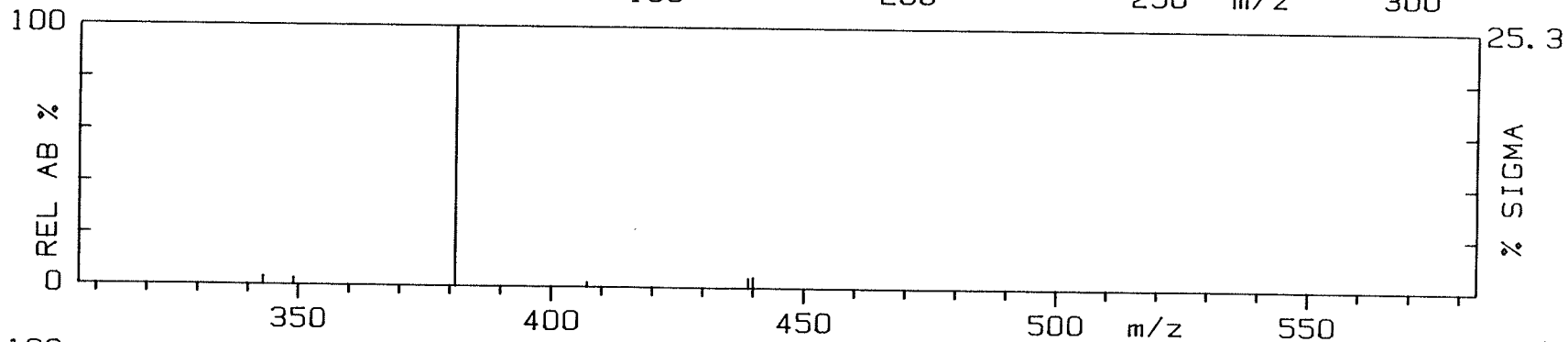
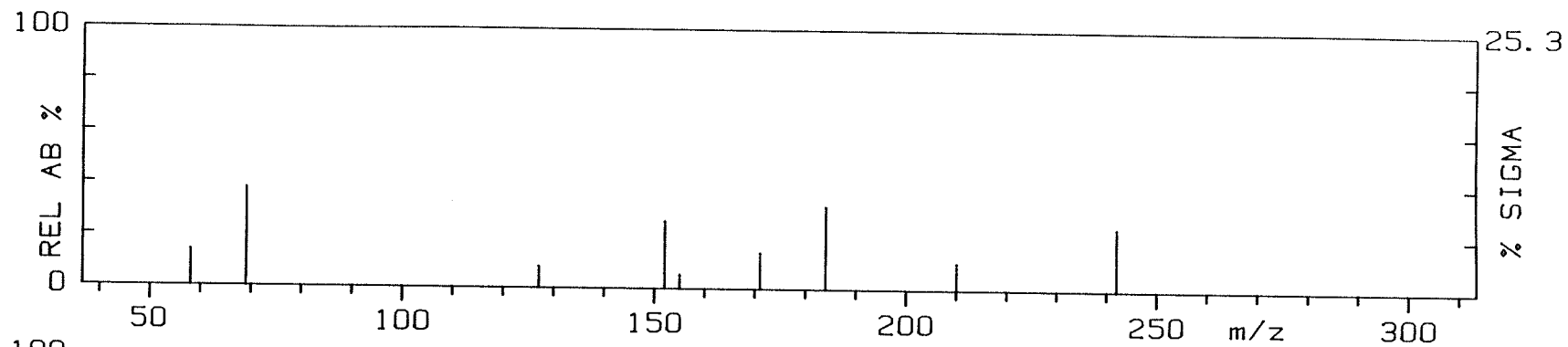


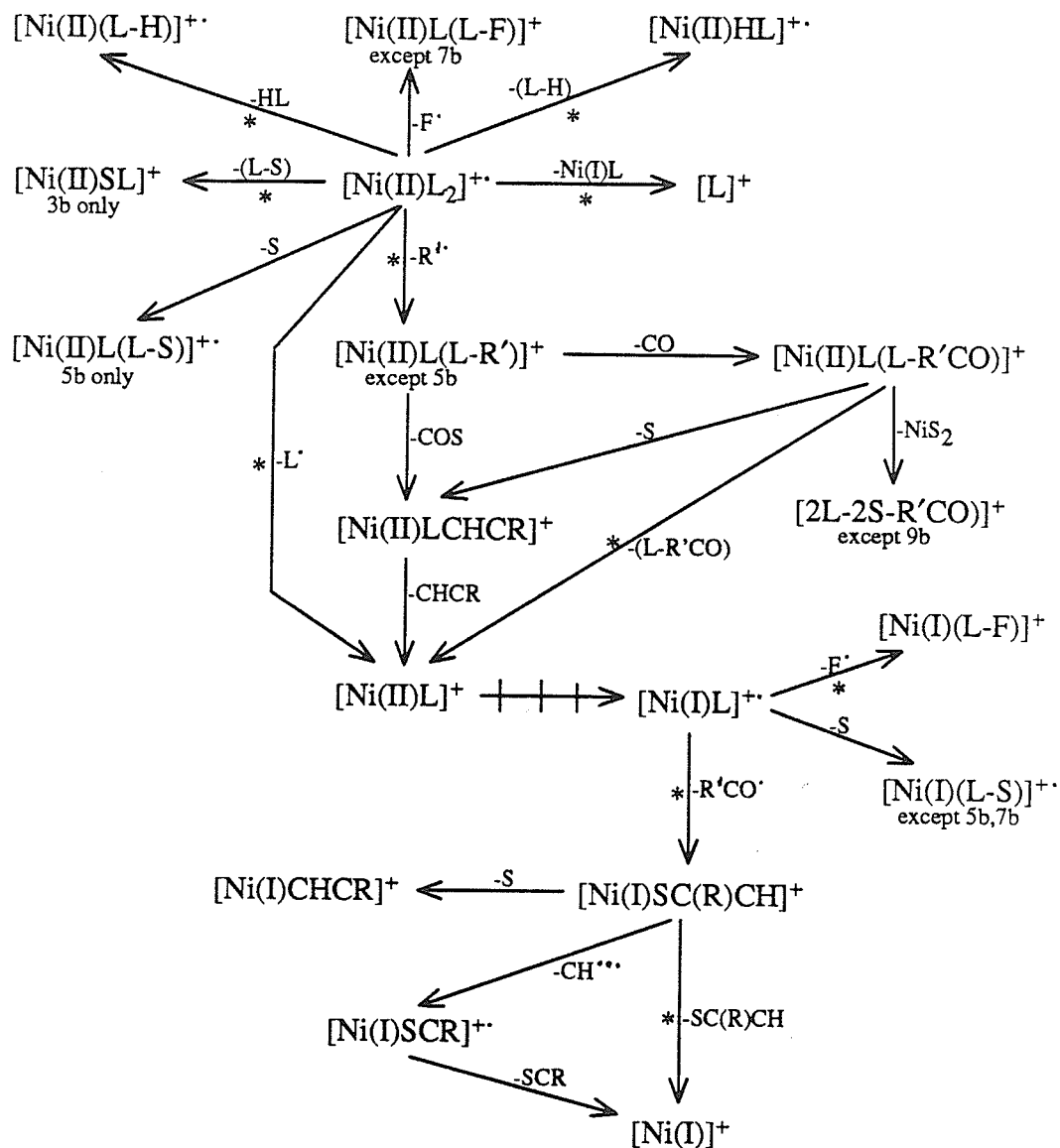
**Figure 107.**

Normalized 70 eV-EI mass spectrum of  
bis[1,1,1,2,2,3,3-heptafluoro-6-mercapto-6-(2'-naphthyl)-  
hex-5-en-4-onato]Ni(II) {Ni-18b}.

$m/z$   $[M]^{+}$  = 820,  $[L]^{+}$  = 381

NI-18B 70EV.

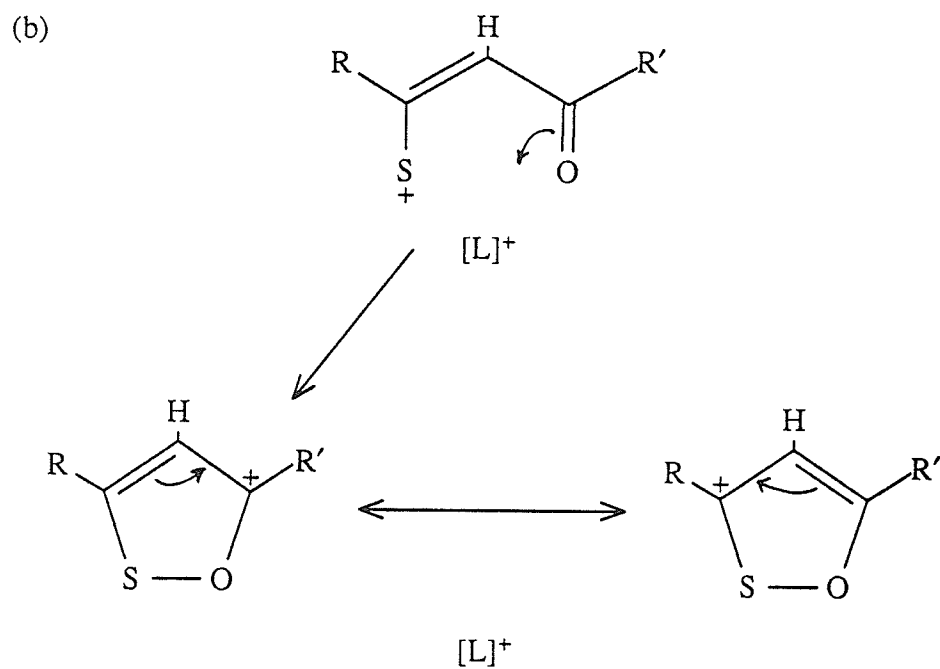
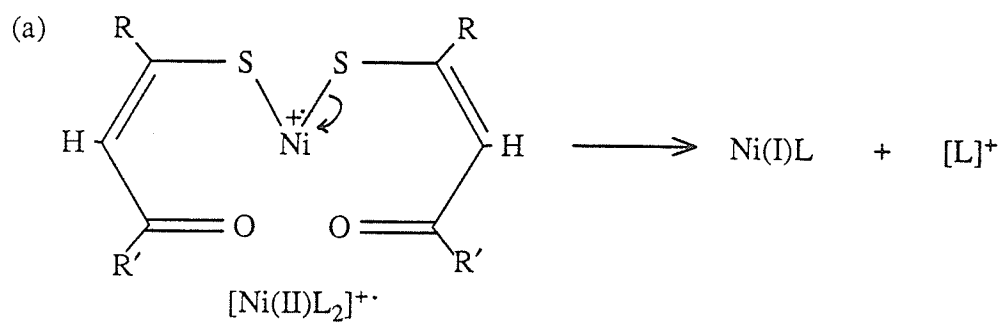




\* process confirmed by the observation of a metastable transition in at least one of the complexes.

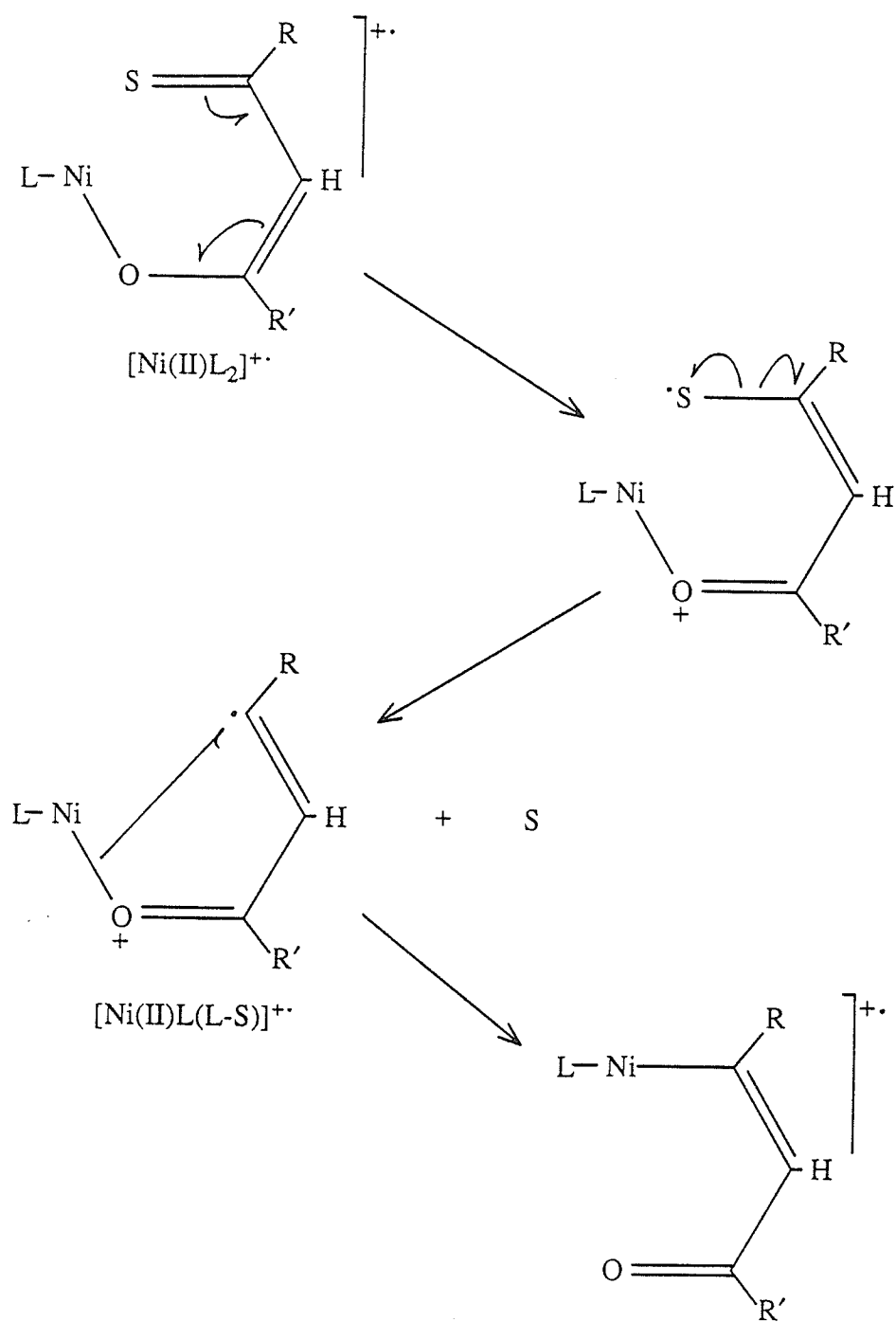
→ reaction step in which a change in oxidation state is proposed.

**Scheme 68.** Proposed fragmentation pathways for Ni(II) monothio- $\beta$ -diketonates where  $R' = \text{CF}_3$  (Ni-3b, -5b, -7b, -8b and -9b). Pathways are common to all complexes except where noted.

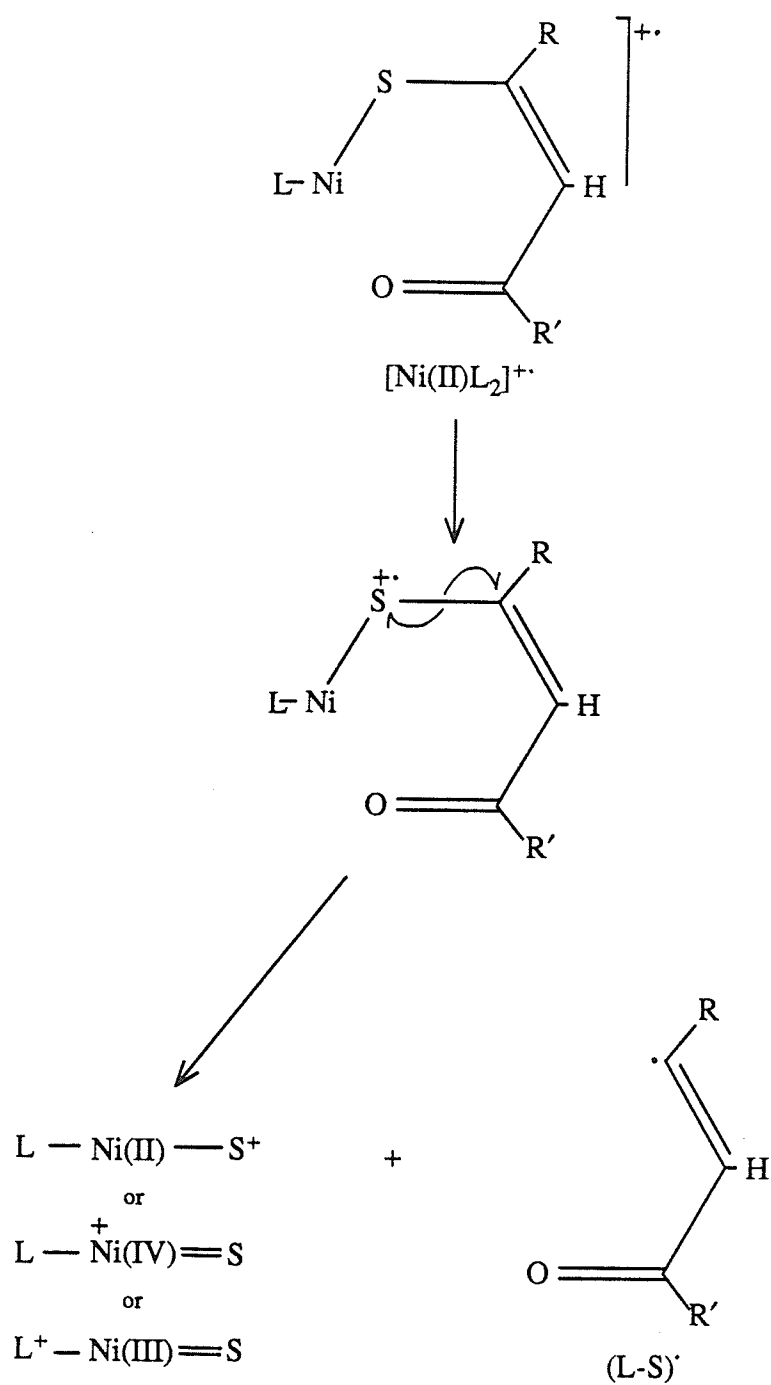


**Scheme 69.** (a) Suggested mechanism for the formation of  $[\text{L}]^+$  from  $[\text{Ni}(\text{II})\text{L}_2]^{2+}$  in Ni-3b, -5b, -7b, -8b and -9b.  
 (b) Proposed resonance-stabilized forms of  $[\text{L}]^+$ .

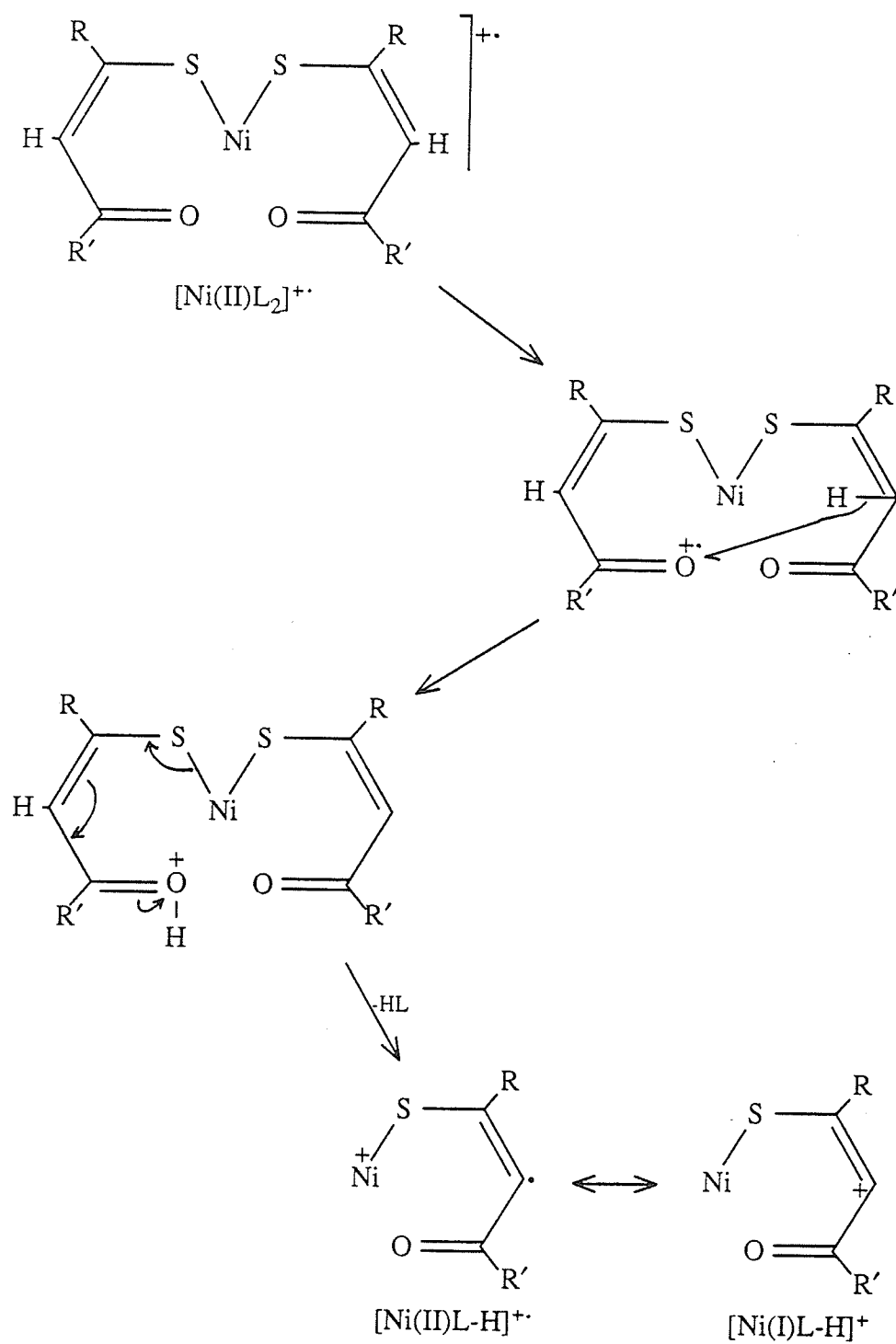




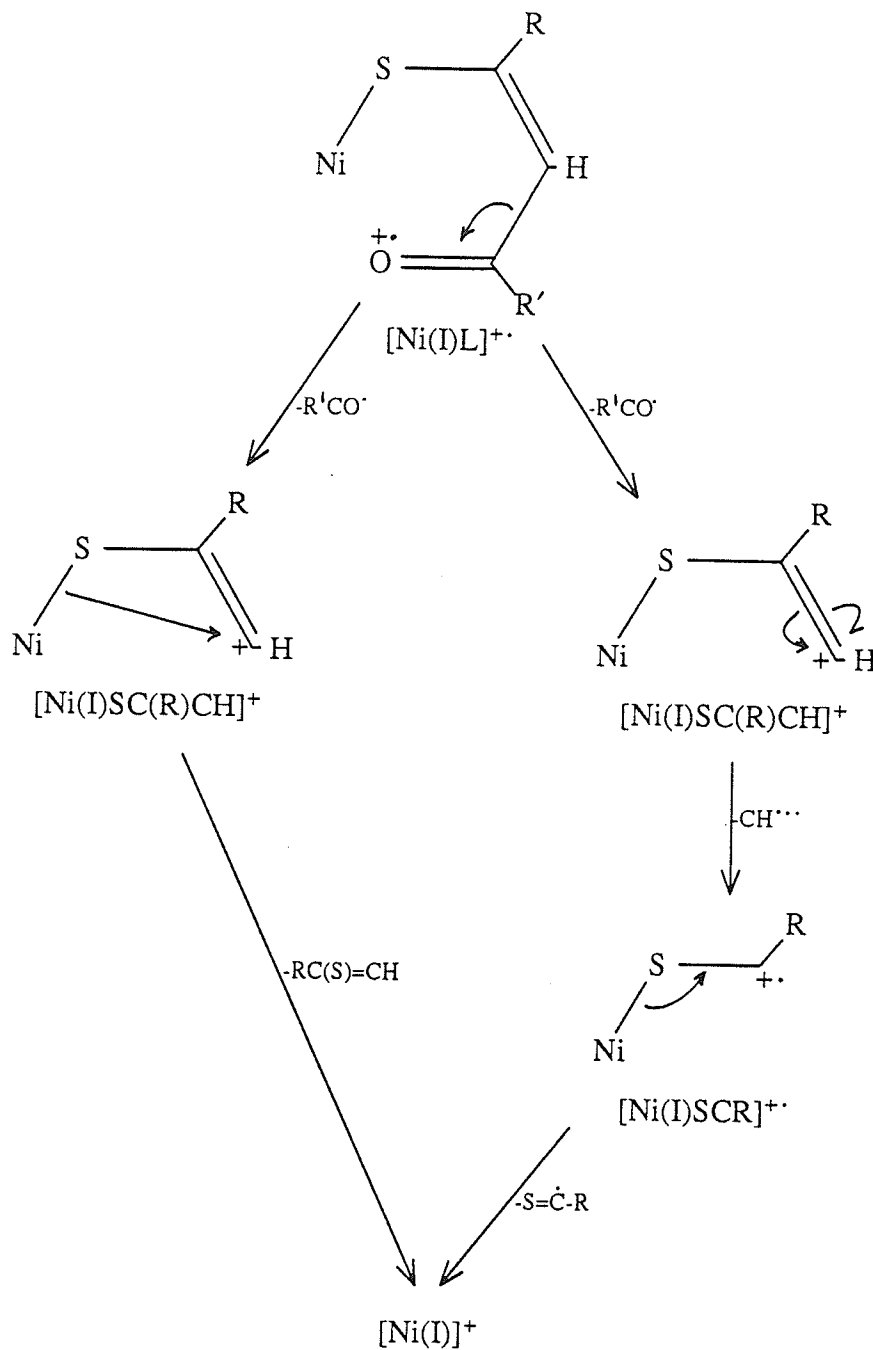
**Scheme 70.** Suggested mechanism for the formation of  $[\text{Ni(II)L(L-S)}]^+$  in Ni-5b.



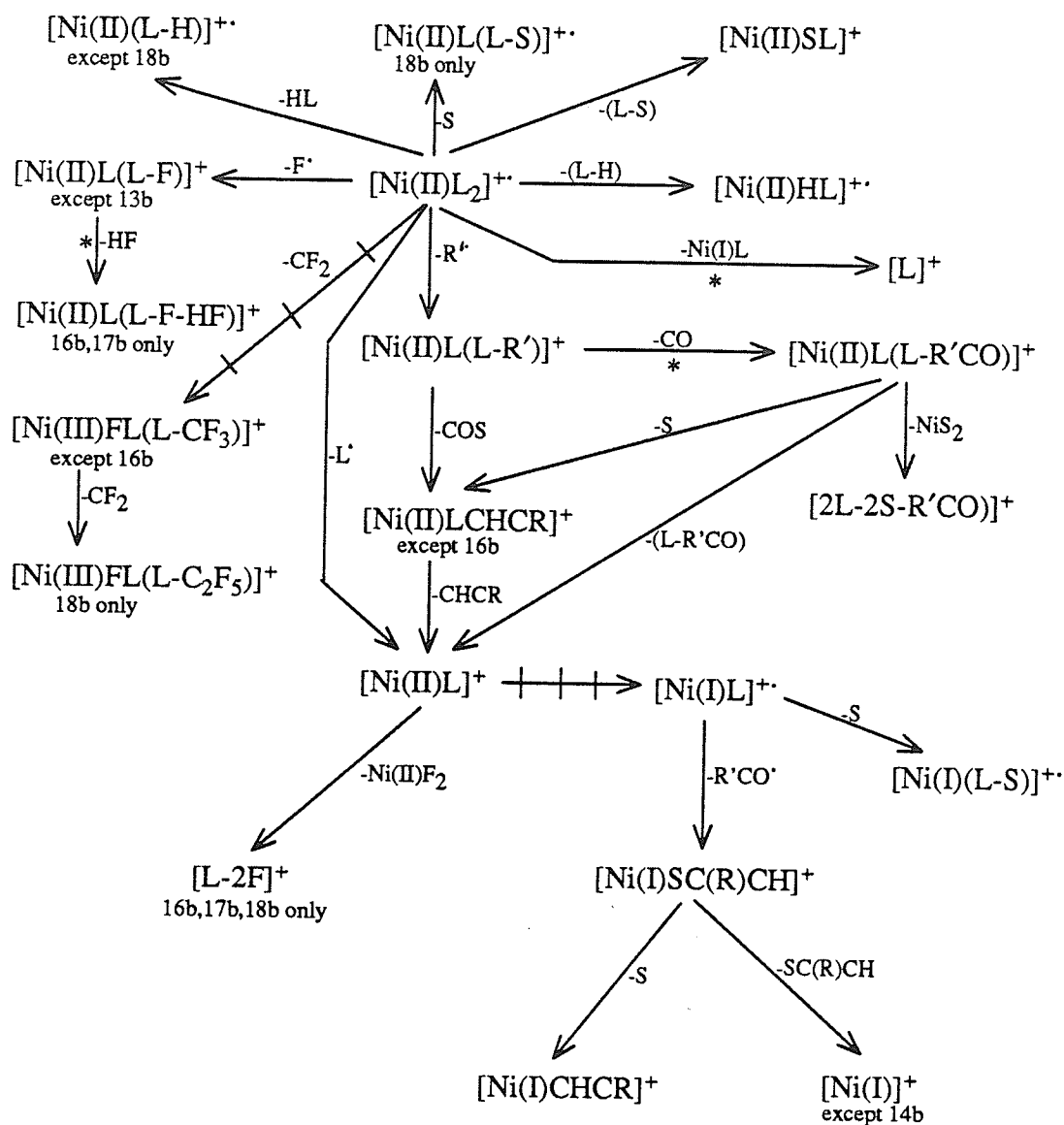
**Scheme 71.** Suggested mechanism for the formation of  $[\text{NiSL}]^+$  in **Ni-3b**.



**Scheme 72.** Suggested mechanism for the formation of  $[\text{Ni}(\text{L-H})]^+$  in Ni-3b, -5b, -7b, -8b and -9b.

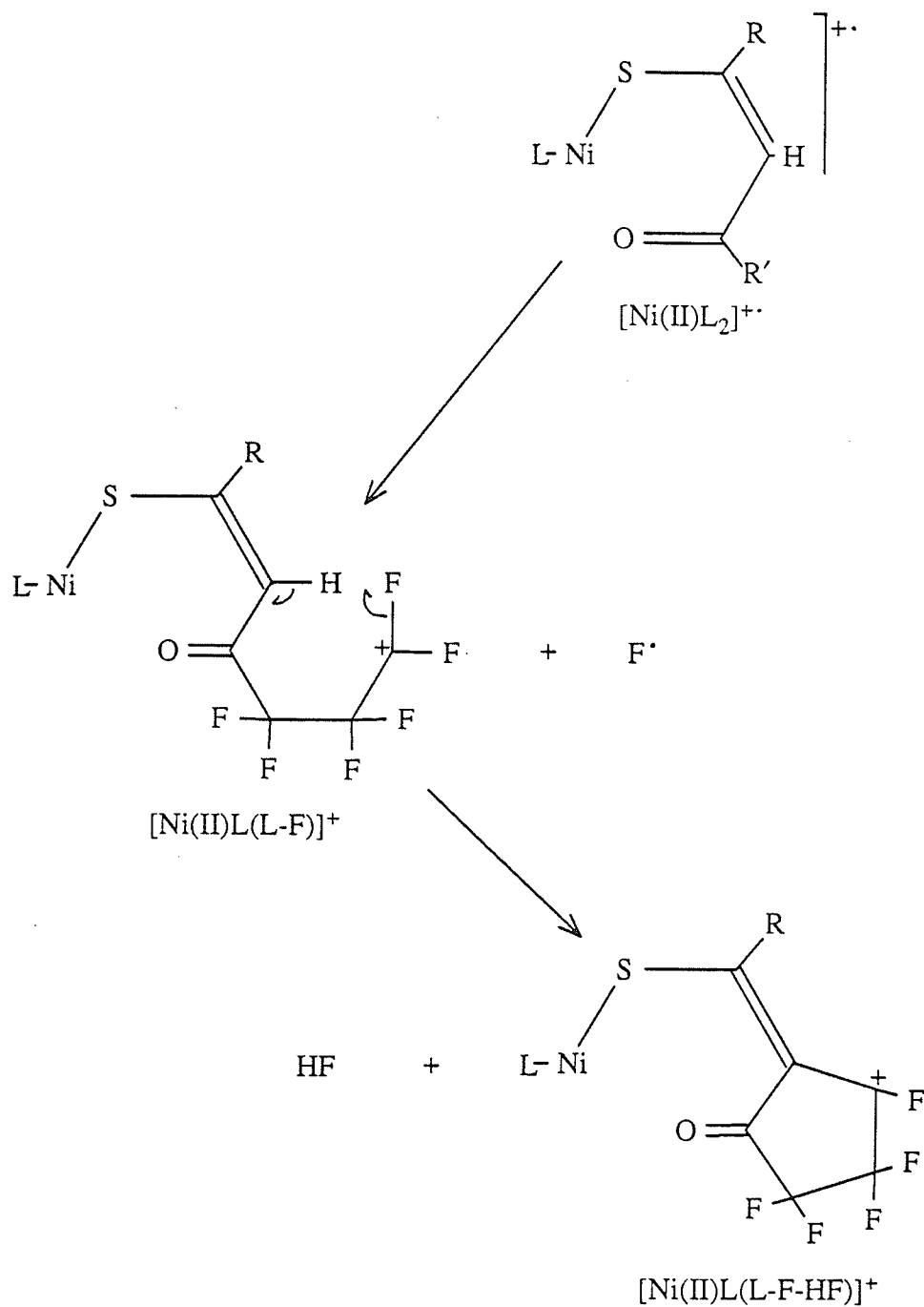


**Scheme 73.** Suggested mechanism for the formation of  $[\text{Ni(I)SC(R)CH}]^+$ ,  $[\text{Ni(I)SCR}]^{+\bullet}$  and  $[\text{Ni(I)}]^+$  in **Ni-3b**, **-5b**, **-7b**, **-8b** and **-9b**.

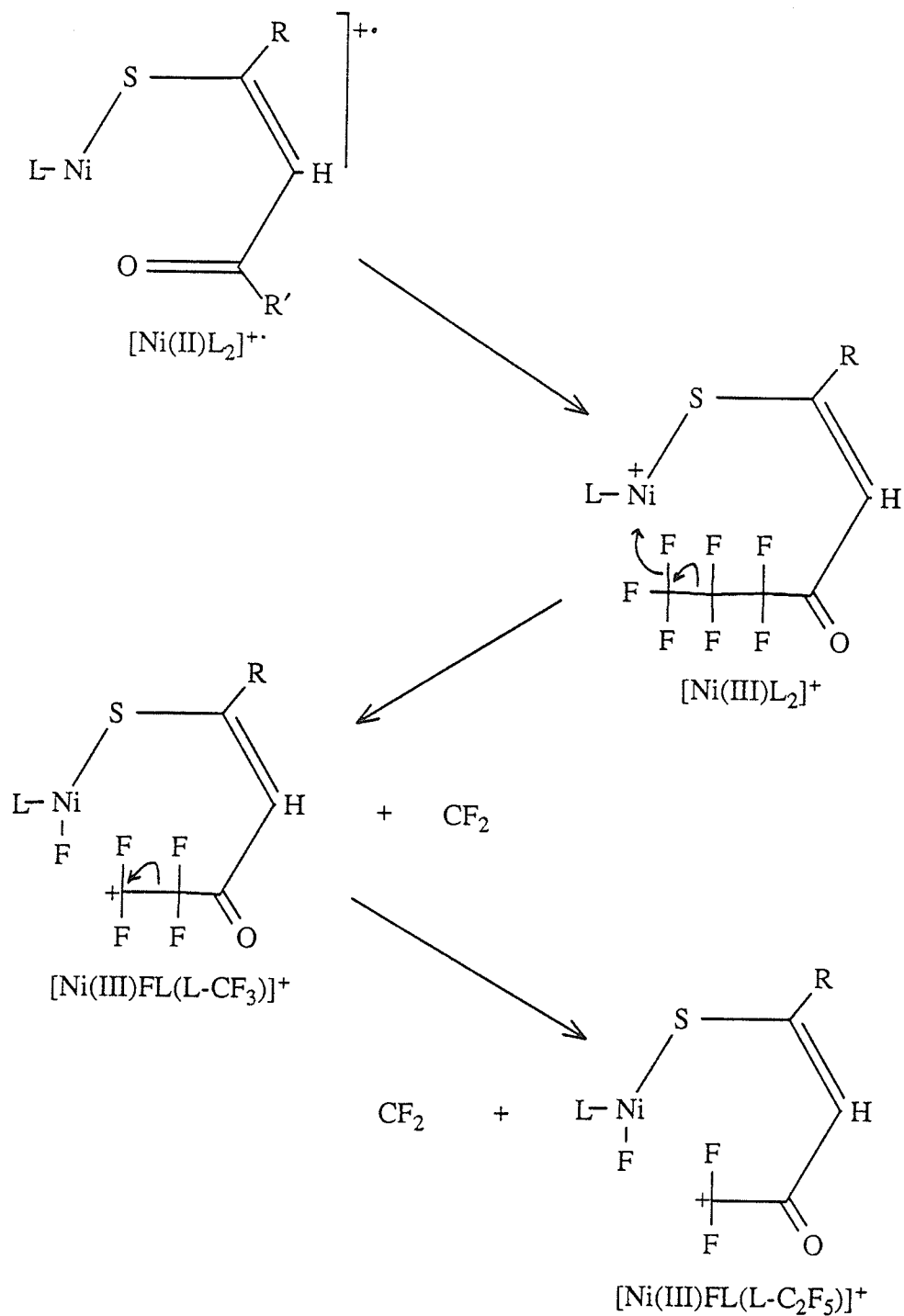


$\text{|||} \rightarrow$  reaction step in which a change in oxidation state is proposed.

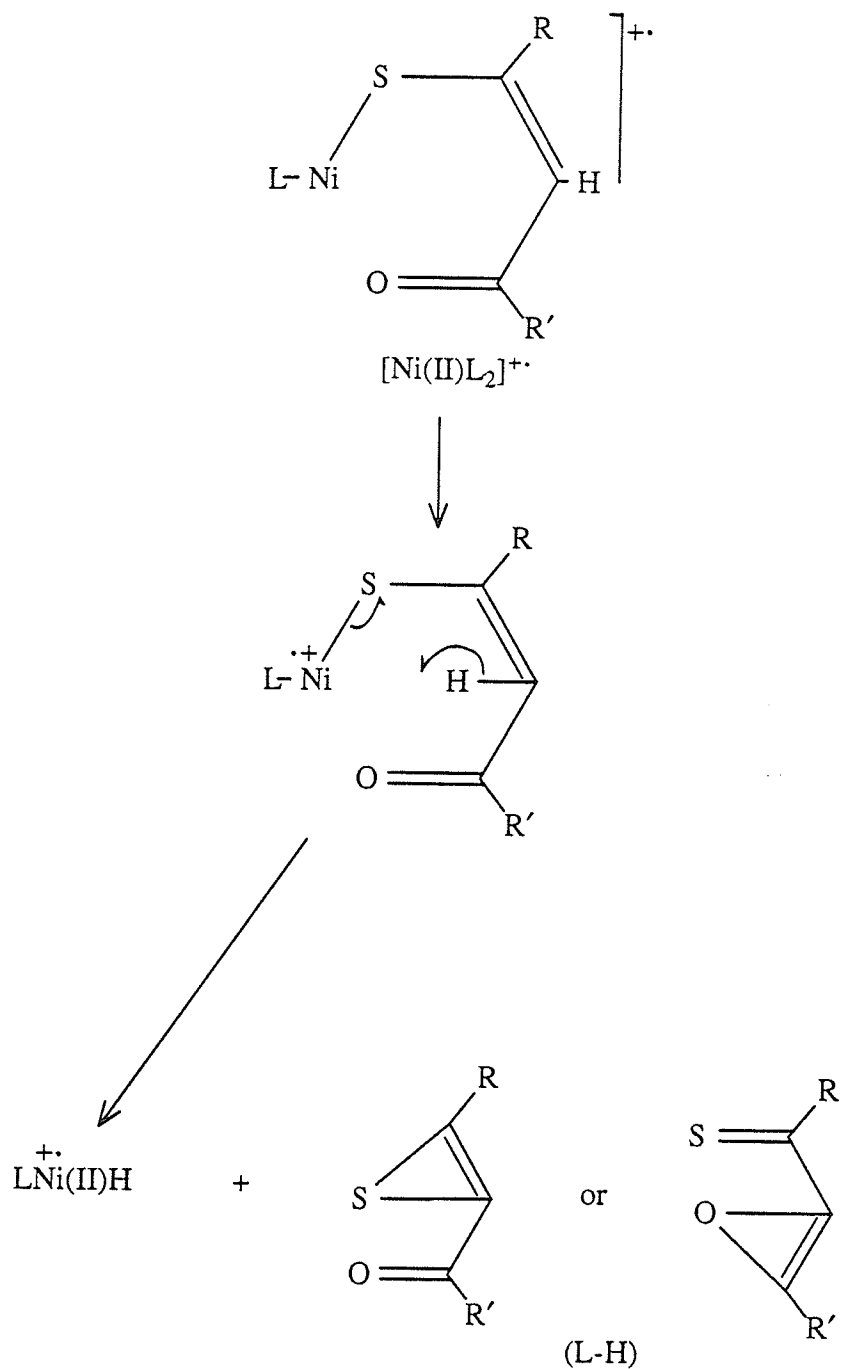
**Scheme 74.** Proposed fragmentation pathways for Ni(II) monothio- $\beta$ -diketonates where  $\text{R}' = \text{C}_2\text{F}_5$  (**Ni-13b**, **-14b** and **-15b**) or  $\text{C}_3\text{F}_7$  (**Ni-16b**, **-17b** and **-18b**). Pathways are common to all complexes except where noted.



**Scheme 75.** Suggested mechanism for the formation of  $[Ni(II)L(L-F)]^+$  and  $[Ni(II)L(L-F-HF)]^+$  in Ni-16b and -17b.

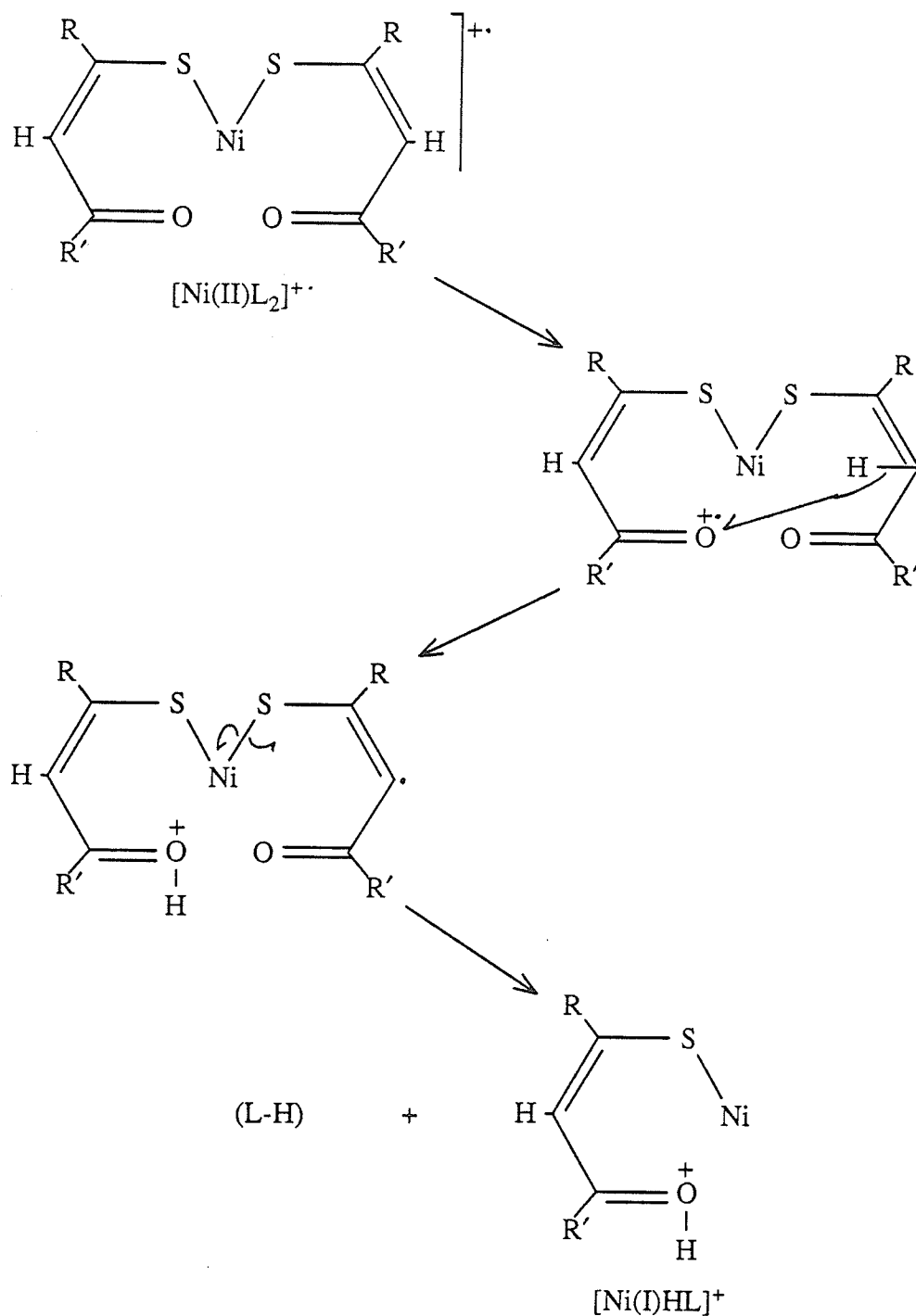


**Scheme 76.** Suggested mechanism for the formation of  $[\text{Ni(III)FL(L-CF}_3)]^+$  and  $[\text{Ni(III)FL(L-C}_2\text{F}_5)]^+$  in **Ni-18b**.

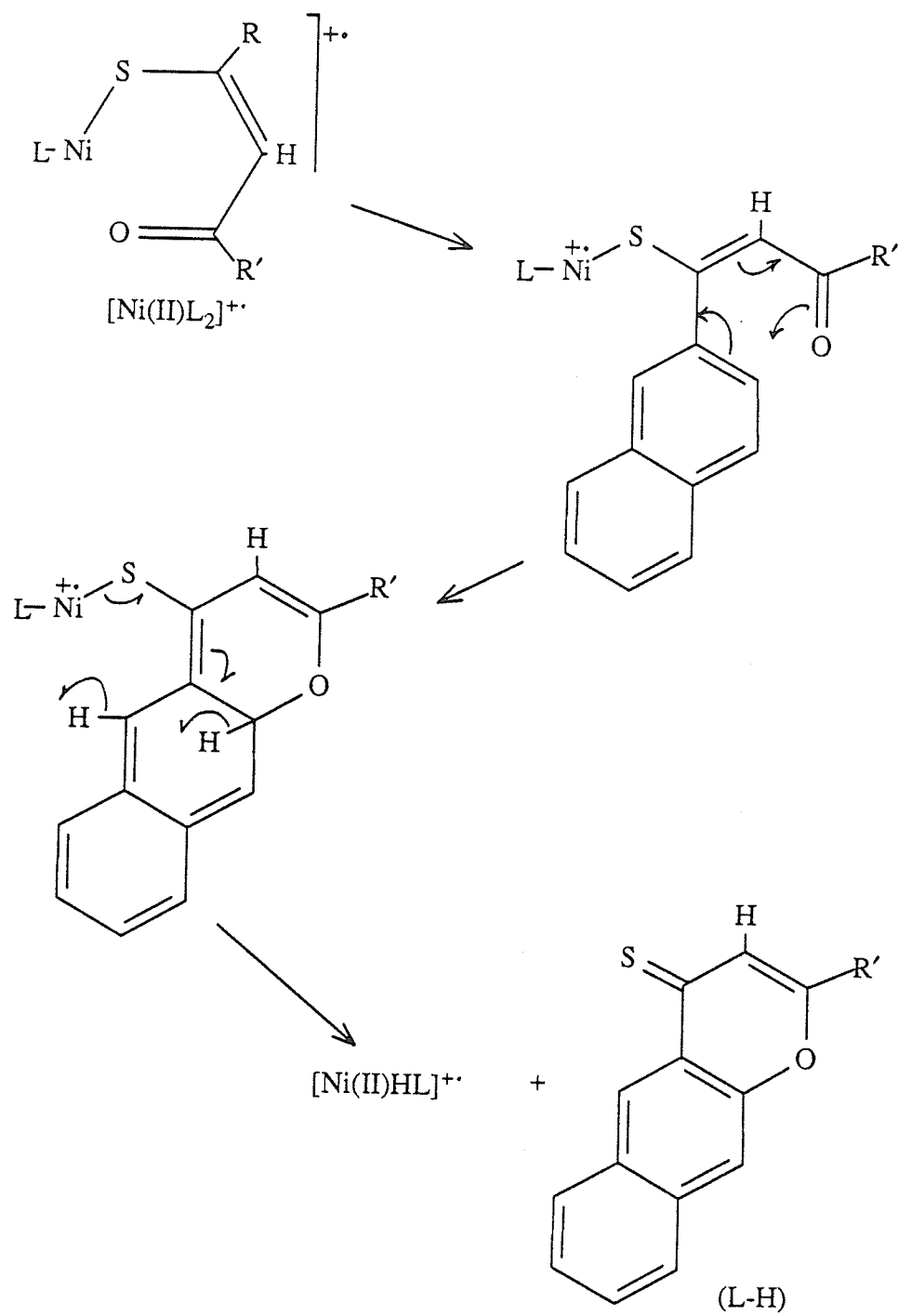


**Scheme 77.** Suggested mechanism for the formation of  $[\text{Ni(II)HL}]^+$  (involving hydrogen transfer from the bridging ligand to the metal) in Ni-13b, -14b, -15b, -16b, -17b and -18b.





**Scheme 78.** Suggested mechanism for the formation of  $[\text{Ni(I)HL}]^+$  (involving hydrogen transfer from the bridging ligand to the other ligand) in Ni-13b, -14b, -15b, -16b, -17b and -18b.



**Scheme 79.** Suggested mechanism for the formation of  $[\text{Ni}(\text{II})\text{HL}]^{+}$  in Ni-15b and -18b.

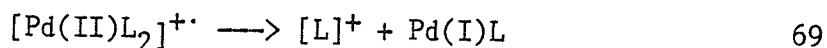
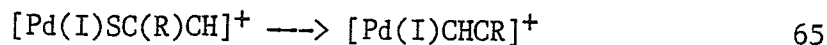
(c) Pd(II) Monothio- $\beta$ -diketonates

Relative abundance data for the nine Pd(II) monothio- $\beta$ -diketonates studied appear in Tables 48-50. Plots of the EI mass spectra are presented in Figures 108-116. A linked-scanning, metastable analysis of Pd-7b was performed. The mass spectrum of Pd-3b has received prior mention in the literature (144).

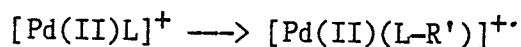
Contamination due to metal-ligand exchange in the ion source was once again in evidence. Signals corresponding to  $^{58}\text{Ni}$ -chelated ions were observed in many of the spectra. However in general, they did not pose any difficulties insofar as spectral interpretation and abundance calculations were concerned.

Suggested decomposition pathways for the Pd(II) monothio- $\beta$ -diketonates possessing a trifluoromethyl substituent ( $\text{R}' = \text{CF}_3$ ; Table 48) are given in Scheme 80. In many instances, the pathways are confirmed by metastable transitions. The molecular ion is the most abundant metal-containing species in all three spectra. Evidence of fluorine-to-metal migration is lacking, although this is not surprising in light of the soft acid character of Pd(II). Some of the fragmentations parallel those discussed for the Co(III) and Ni(II) monothio- $\beta$ -diketonates:

<u>Fragmentation</u>	<u>Scheme</u>
$[\text{Pd}(\text{II})\text{L}_2]^+ \longrightarrow [\text{Pd}(\text{II})\text{L}(\text{L}-\text{R}')]^+$	64
$[\text{Pd}(\text{I})\text{L}]^+ \longrightarrow [\text{Pd}(\text{I})\text{SC}(\text{R})\text{CH}]^+$	65



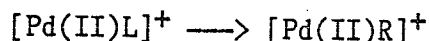
The Pd(I) designation proposed in two of the above mechanisms is not a common palladium oxidation state. In fact, the absence of a bare  $[\text{Pd(I)}]^+$  metal ion attests to the relative instability of the univalent state. An alternative mechanism for the formation of  $[\text{PdSC(R)CH}]^+$  and  $[\text{PdCHCR}]^+$  involving Pd(II) is shown in Scheme 81. The formation of the  $\text{OE}^+$  fragment  $[\text{Pd(II)SC(R)CH}]^+$  from the  $\text{EE}^+$  ion  $[\text{Pd(II)L}]^+$  is not expected to be a favored process, although Das and Livingstone (144) suggested a similar decomposition:



in their study of trifluoromethyl-substituted palladium monothio- $\beta$ -diketonates.

A mechanism for the formation of the novel species  $[\text{Pd(II)(L-H-R')}]^+$  is illustrated in Scheme 82. This type of fragmentation was first observed by Livingstone and Moore (147) in the mass spectrum of bis(1,1,1-trifluoro-4-mercapto-4-(2'-naphthyl)-but-3-en-2-onato)Pt(II). Interestingly however, the  $[\text{Met(II)(L-H-R')}]^+$  ion is not reported in the analogous Pd(II) complexes (144,147).

The presence of  $[\text{PdR}]^+$  in the spectra of Pd-3b and Pd-7b indicates a migration of the aryl group to the metal. Two possible mechanisms for the reaction

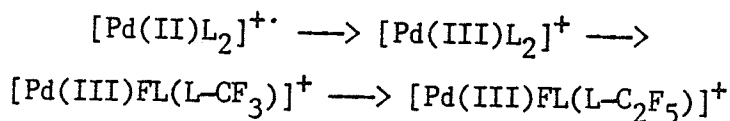


are given in Scheme 83. One route involves the cleavage of a palladium-sulfur bond, the other the breaking of a Pd-O bond. Based on relative bond strengths, the latter mechanism should be the more favored. The strong binding preference of palladium for sulfur is due in large part to the formation of metal-ligand  $\pi$  bonds by overlap of filled  $d\pi$  orbitals ( $d_{xy}$ ,  $d_{yz}$  and  $d_{xz}$ ) on the metal with empty  $d\pi$  orbitals in the valence shells of sulfur (178).

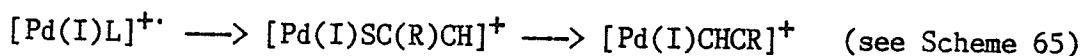
Suggested ion-fragmentation routes for the Pd(II) monothio- $\beta$ -diketonates possessing a pentafluoroethyl ( $R' = C_2F_5$ ; Table 49) or heptafluoropropyl ( $R' = C_3F_7$ ; Table 50) substituent are presented in Scheme 84. Several of the decompositions have been described previously:

<u>Fragmentation</u>	<u>Scheme</u>
$[Pd(II)L_2]^+ \longrightarrow [Pd(II)L(L-R')]^+$	64
$[Pd(I)L]^+ \longrightarrow [Pd(I)SC(R)CH]^+$	65
$[Pd(I)SC(R)CH]^+ \longrightarrow [Pd(I)CHCR]^+$	65
$[Pd(II)L_2]^+ \longrightarrow [L]^+ + Pd(I)L$	69
$[Pd(II)L_2]^+ \longrightarrow [Pd(II)L(L-S)]^+$	70
$[Pd(I)L]^+ \longrightarrow [Pd(I)(L-S)]^+$	70
$[Pd(III)L_2]^+ \longrightarrow [Pd(III)FL(L-CF_3)]^+$	76
$[Pd(III)FL(L-CF_3)]^+ \longrightarrow [Pd(III)FL(L-C_2F_5)]^+$	76
$[Pd(II)L_2]^+ \longrightarrow [Pd(II)HL]^+$	77-79
$[Pd(II)L_2]^+ \longrightarrow [Pd(II)(L-H-R')]^+$	82
$[Pd(II)L(L-R')]^+ \longrightarrow [Pd(II)L]^+$	83

The application of Scheme 76 to the successive elimination of two  $\text{CF}_2$  neutrals from  $[\text{Pd(II)L}_2]^+$  requires a unit increase in the oxidation state of palladium:



In contrast to nickel, however, the +3 state is virtually unknown in palladium complexes. The strong electron-withdrawing influence of the  $\text{C}_2\text{F}_5$  and  $\text{C}_3\text{F}_7$  groups may aid in stabilizing the trivalent Pd structures. As well, the reaction sequence



can be described by the alternative mechanism shown in Scheme 81, which is based upon a Pd(II) oxidation state.

The hydrogen transfer mechanisms presumed to be at work in the formation of  $[\text{PdHL}]^+$  ions were outlined in the treatment of Ni(II) monothio- $\beta$ -diketonates (see Schemes 77-79). The importance of the R substituent in "ortho" hydrogen transfer (Scheme 79) can be seen in Tables 49 and 50; a comparison of the average %TIC carried by the three R groups reveals a clear trend in  $[\text{PdHL}]^+$  stabilities (average %TIC in parentheses): R = 2-thienyl (0.2) < phenyl (0.3) < 2-naphthyl (0.8). This relationship affirms the earlier assertion concerning the electron-releasing abilities of the aryl substituents and their considerable influence upon rates of  $[\text{MetHL}]^+$  formation.

Most of the Pd(II) monothio- $\beta$ -diketonates studied exhibit a number of metal-free peaks at  $m/z$  values greater than  $[L]^+$ . These ions have been assigned the structures  $[2L-S]^+$ ,  $[2L-S-R']^+$ ,  $[2L-S-R'CO]^+$  and  $[2L-S-2R'CO]^+$  and are believed to arise through the loss of Pd(II)S from the molecular ion as depicted in Scheme 85. Livingstone and Moore (147) have described a similar reaction sequence for various divalent and trivalent metal chelates of 1,1,1-trifluoro-4-mercapto-4-(2'-naphthyl)-but-3-en-2-one. However, their claim of a "unique" status for the 2-naphthyl substituent with regard to the abundance of high-mass, metal-free ions is not corroborated by the present data.

Table 48. 70 eV-EI mass spectra of compounds Pd-3b, Pd-7b and Pd-8b.

ION	Pd-3b			Pd-7b			Pd-8b		
	%RA	m/z	%TIC	%RA	m/z	%TIC	%RA	m/z	%TIC
	R =	-C <sub>6</sub> H <sub>5</sub>		-C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub>		-C <sub>4</sub> H <sub>3</sub> S			
	R' =	-CF <sub>3</sub>		-CF <sub>3</sub>		-CF <sub>3</sub>			
[PdL <sub>2</sub> ] <sup>+</sup> (a)	74.1	(568)	22.8	63.3	(628)	15.4	52.0	(580)	12.5
[PdL(L-R')] <sup>+</sup>	17.0	(499)	5.2	<sup>a</sup> 8.0	(559)	1.9	16.6	(511)	4.0
[PdL] <sup>+</sup> (b)	11.8	(337)	3.6	<sup>a</sup> 14.1	(367)	3.4	8.9	(343)	2.1
[PdL-H-R'] <sup>+</sup>	14.1	(267)	4.3	12.7	(297)	3.1	7.8	(273)	1.9
[PdSC(R)CH] <sup>+</sup>	15.0	(240)	4.6	<sup>b</sup> 9.1	(270)	2.2	12.2	(246)	2.9
[PdCHCR] <sup>+</sup>	5.1	(208)	1.6	-	(238)	-	6.1	(214)	1.5
[PdR] <sup>+</sup>	7.4	(183)	2.3	<sup>b</sup> 2.8	(213)	0.7	-	(189)	-
[2L-S] <sup>+</sup> (c)	-	(430)	-	2.8	(490)	0.7	1.6	(442)	0.4
[2L-S-R'CO] <sup>+</sup> (d)	-	(333)	-	<sup>c</sup> 6.5	(393)	1.6	4.5	(345)	1.1
[2L-S-2R'CO] <sup>+</sup>	-	(236)	-	<sup>d</sup> 16.7	(296)	4.1	8.3	(248)	2.0
[HL] <sup>+</sup>	6.3	(232)	1.9	22.4	(262)	5.4	15.6	(238)	3.7
[L] <sup>+</sup> (e)	100.0	(231)	30.8	<sup>a</sup> 100.0	(261)	24.3	58.4	(237)	14.0
	-	(209)	-	3.9	(239)	0.9	-	(215)	-
[L-S] <sup>+</sup> (f)	-	(199)	-	11.8	(229)	2.9	100.0	(205)	24.0
[HL-R'] <sup>+</sup>	6.0	(163)	1.8	17.8	(193)	4.3	11.4	(169)	2.7
[L-S-CF <sub>2</sub> ] <sup>+</sup>	5.5	(149)	1.7	20.5	(179)	5.0	13.4	(155)	3.2
[RCSCH] <sup>+</sup>	30.3	(134)	9.3	<sup>b,e</sup> 28.2	(164)	6.9	23.0	(140)	5.5
[RC <sub>3</sub> O] <sup>+</sup>	4.1	(129)	1.3	6.0	(159)	1.5	3.9	(135)	0.9
[RCS] <sup>+</sup>	8.0	(121)	2.5	18.5	(151)	4.5	16.4	(127)	3.9



Table 48. (continued).

[RCO] <sup>+</sup>	4.7 (105)	1.4	7.5 (135)	1.8	4.6 (111)	1.1
[RCCH] <sup>+</sup>	5.2 (102)	1.6	<sup>f</sup> 22.2 (132)	5.4	17.9 (108)	4.3
[RCH <sub>2</sub> ] <sup>+</sup>	- (91)	-	8.8 (121)	2.1	5.6 (97)	1.3
[R] <sup>+</sup>	5.8 (77)	1.8	- (107)	-	6.8 (83)	1.6
[R'] <sup>+</sup>	4.1 (69)	1.3	7.5 (69)	1.8	22.3 (69)	5.3

<sup>a</sup> Identified metastable transitions are indicated by superscripts which relate the daughter ion to its precursor as labelled in column 1.

**Table 49.** 70 eV-EI mass spectra of compounds Pd-13b, Pd-14b and Pd-15b.

ION	Pd-13b			Pd-14b			Pd-15b		
	%RA	m/z	%TIC	%RA	m/z	%TIC	%RA	m/z	%TIC
	R =	-C <sub>6</sub> H <sub>5</sub>		-C <sub>4</sub> H <sub>3</sub> S		-C <sub>10</sub> H <sub>7</sub>			
	R' =	-C <sub>2</sub> F <sub>5</sub>		-C <sub>2</sub> F <sub>5</sub>		-C <sub>2</sub> F <sub>5</sub>			
[PdL <sub>2</sub> ] <sup>+</sup>	100.0	(668)	37.6	99.0	(680)	14.8	48.0	(768)	7.8
[PdL(L-F)] <sup>+</sup>	3.2	(649)	1.2	4.4	(661)	0.7	1.5	(749)	0.2
[PdFL(L-CF <sub>3</sub> )] <sup>+</sup>	7.2	(618)	2.7	13.0	(630)	1.9	2.6	(718)	0.4
[PdFL(L-C <sub>2</sub> F <sub>5</sub> )] <sup>+</sup>	-	(568)	-	4.4	(580)	0.7	-	(668)	-
[PdL(L-R')] <sup>+</sup>	20.0	(549)	7.5	44.0	(561)	6.7	23.0	(649)	3.7
[PdHL] <sup>+</sup>	0.6	(388)	0.2	1.5	(394)	0.2	4.4	(438)	0.7
[PdL] <sup>+</sup>	6.2	(387)	2.3	13.0	(393)	1.9	16.0	(437)	2.6
[PdL-H-R'] <sup>+</sup>	6.6	(267)	2.5	13.0	(273)	1.9	13.0	(317)	2.1
[PdSC(R)CH] <sup>+</sup>	6.2	(240)	2.3	19.0	(246)	2.8	15.0	(290)	2.4
[PdCHCR] <sup>+</sup>	-	(208)	-	8.8	(214)	1.3	8.8	(258)	1.4
[2L-S] <sup>+</sup>	0.4	(530)	0.2	6.0	(542)	0.9	9.0	(630)	1.5
[2L-S-R'] <sup>+</sup>	3.3	(411)	1.2	2.3	(423)	0.3	2.7	(511)	0.4
[2L-S-R'CO] <sup>+</sup>	4.7	(383)	1.8	14.0	(395)	2.1	17.0	(483)	2.8
[L+31] <sup>+</sup>	1.2	(312)	0.5	6.4	(318)	1.0	2.7	(362)	0.4
[HL] <sup>+</sup>	3.8	(282)	1.4	9.3	(288)	1.4	24.0	(332)	3.9
[L] <sup>+</sup>	31.0	(281)	11.6	68.0	(287)	10.1	100.0	(331)	16.2
[L-S] <sup>+</sup>	0.8	(249)	0.3	100.0	(255)	14.9	12.0	(299)	1.9
[2L-S-2R'CO] <sup>+</sup>	6.6	(236)	2.5	39.0	(248)	5.8	40.0	(336)	6.5
[R+116] <sup>+</sup>	3.8	(193)	1.4	15.0	(199)	2.2	5.8	(243)	0.9

Table 49. (continued).

$[\text{HL-R}']^+$	10.4 (163)	3.9	24.0 (169)	3.6	33.0 (213)	5.4
$[\text{SC(R)CH}]^+$	14.0 (134)	5.3	36.0 (140)	5.4	72.0 (184)	11.7
$[\text{RCS}]^+$	8.8 (121)	3.3	27.0 (127)	4.0	27.0 (171)	4.4
$[\text{RCO}]^+$	6.3 (105)	2.4	8.6 (111)	1.3	16.0 (155)	2.6
$[\text{RCCH}]^+$	7.9 (102)	3.0	42.0 (108)	6.3	96.0 (152)	15.6
$[\text{R}]^+$	4.4 ( 77)	1.7	15.0 ( 83)	2.2	14.0 (127)	2.3
$[\text{R}']^+$	4.1 (119)	1.5	10.4 (119)	1.6	3.1 (119)	0.5
$[\text{CF}_3]^+$	4.7 ( 69)	1.8	27.0 ( 69)	4.0	9.9 ( 69)	1.6

Table 50. 70 eV-EI mass spectra of compounds Pd-16b, Pd-17b and Pd-18b.

ION	Pd-16b			Pd-17b			Pd-18b		
	%RA	m/z	%TIC	%RA	m/z	%TIC	%RA	m/z	%TIC
R =	-C <sub>6</sub> H <sub>5</sub>			-C <sub>4</sub> H <sub>3</sub> S			-C <sub>10</sub> H <sub>7</sub>		
R' =	-C <sub>3</sub> F <sub>7</sub>			-C <sub>3</sub> F <sub>7</sub>			-C <sub>3</sub> F <sub>7</sub>		
[PdL <sub>2</sub> ] <sup>+</sup>	84.0 (768)	17.1	33.0 (780)	6.0	83.8 (868)	12.4			
[PdL(L-F)] <sup>+</sup>	5.9 (749)	1.2	2.6 (761)	0.5	2.4 (849)	0.4			
[PdL(L-S)] <sup>+</sup>	1.1 (736)	0.2	1.1 (748)	0.2	- (836)	-			
[PdFL(L-CF <sub>3</sub> )] <sup>+</sup>	1.1 (718)	0.2	1.1 (730)	0.2	6.0 (818)	0.9			
[PdL(L-R')] <sup>+</sup>	40.0 (599)	8.1	30.0 (611)	5.5	40.7 (699)	6.0			
[PdHL] <sup>+</sup>	1.5 (438)	0.3	1.1 (444)	0.2	5.9 (488)	0.9			
[PdL] <sup>+</sup>	19.0 (437)	3.9	14.0 (443)	2.5	17.6 (487)	2.6			
[PdL-S] <sup>+</sup>	2.9 (405)	0.6	4.0 (411)	0.7	- (455)	-			
[PdL-H-R'] <sup>+</sup>	32.0 (267)	6.5	18.0 (273)	3.3	15.6 (317)	2.3			
[PdSC(R)CH] <sup>+</sup>	27.0 (240)	5.5	26.0 (246)	4.7	15.8 (290)	2.3			
[PdCHCR] <sup>+</sup>	9.9 (208)	2.0	15.0 (214)	2.7	9.5 (258)	1.4			
[2L-S] <sup>+</sup>	1.2 (630)	0.2	9.8 (642)	1.8	7.5 (730)	1.1			
[2L-S-R'] <sup>+</sup>	4.9 (461)	1.0	2.2 (473)	0.4	3.2 (561)	0.5			
[2L-S-R'CO] <sup>+</sup>	8.0 (433)	1.6	15.0 (445)	2.7	16.5 (533)	2.4			
[L+31] <sup>+</sup>	2.2 (362)	0.4	9.1 (368)	1.7	1.2 (412)	0.2			
[HL] <sup>+</sup>	9.3 (332)	1.9	13.0 (338)	2.4	22.7 (382)	3.4			
[L] <sup>+</sup>	100.0 (331)	20.3	58.0 (337)	10.5	100.0 (381)	14.8			
[L-S] <sup>+</sup>	1.7 (299)	0.3	100.0 (305)	18.2	11.5 (349)	1.7			
[2L-S-2R'CO] <sup>+</sup>	- (236)	-	- (248)	-	40.5 (336)	6.0			

Table 50. (continued).

[R+116] <sup>+</sup>	6.1 (193)	1.2	20.0 (199)	3.6	3.3 (243)	0.5
[HL-R'] <sup>+</sup>	18.0 (163)	3.7	32.0 (169)	5.8	32.3 (213)	4.8
[SC(R)CH] <sup>+</sup>	53.0 (134)	10.8	45.0 (140)	8.2	67.1 (184)	9.9
[RC <sub>3</sub> O] <sup>+</sup>	- (129)	-	- (135)	-	10.2 (179)	1.5
[RCS] <sup>+</sup>	18.0 (121)	3.7	27.0 (127)	4.9	26.2 (171)	3.9
[RCO] <sup>+</sup>	12.0 (105)	2.4	6.9 (111)	1.3	10.7 (155)	1.6
[RCCH] <sup>+</sup>	14.0 (102)	2.8	37.0 (108)	6.7	82.1 (152)	12.1
[R] <sup>+</sup>	7.5 ( 77)	1.5	4.7 ( 83)	0.9	9.7 (127)	1.4
[CSCHCO] <sup>+</sup>	- ( 85)	-	- ( 85)	-	21.1 ( 85)	3.1
[CF <sub>3</sub> ] <sup>+</sup>	11.0 ( 69)	2.2	24.0 ( 69)	4.4	10.0 ( 69)	1.5

**Figure 108.**

Normalized 70 eV-EI mass spectrum of  
bis[1,1,1-trifluoro-4-mercapto-4-phenyl-but-3-en-2-onato]Pd(II)  
(Pd-3b).  
 $m/z$   $[M]^{++} = 568$ ,  $[L]^+ = 231$

PD-38 70EV.

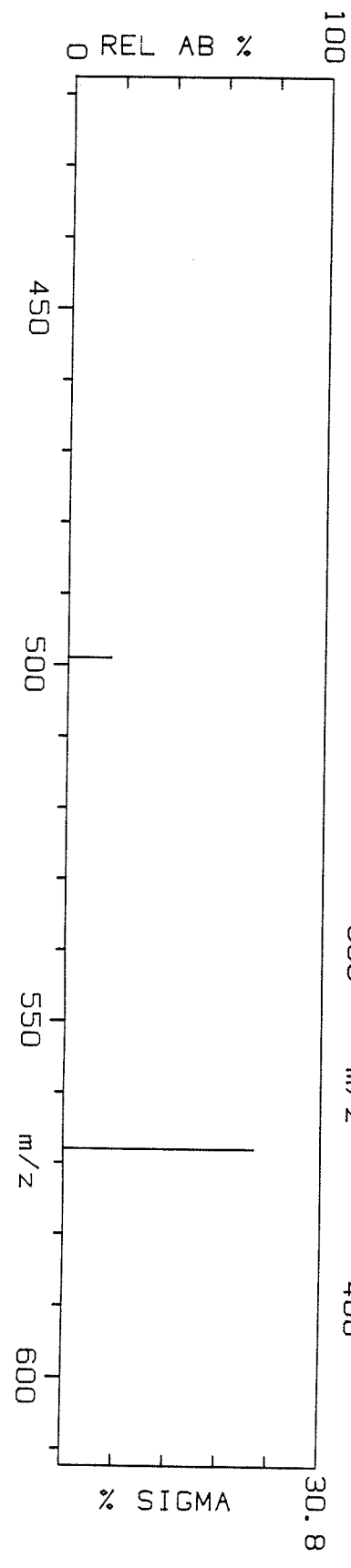
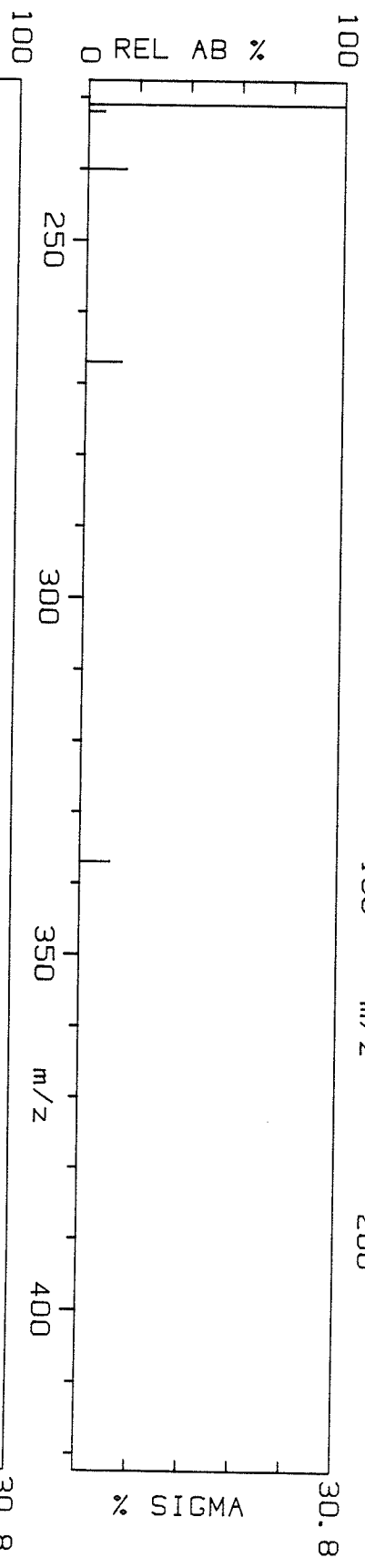
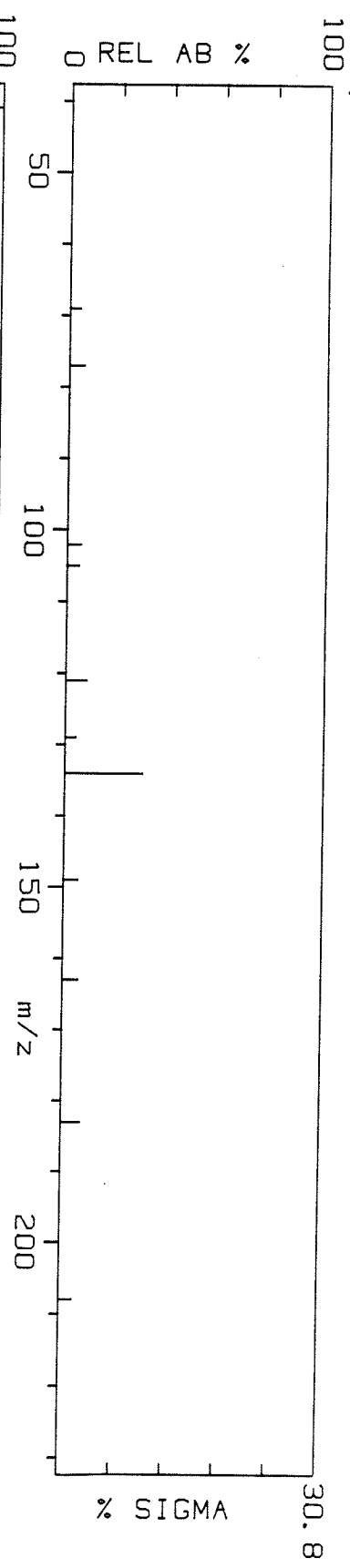


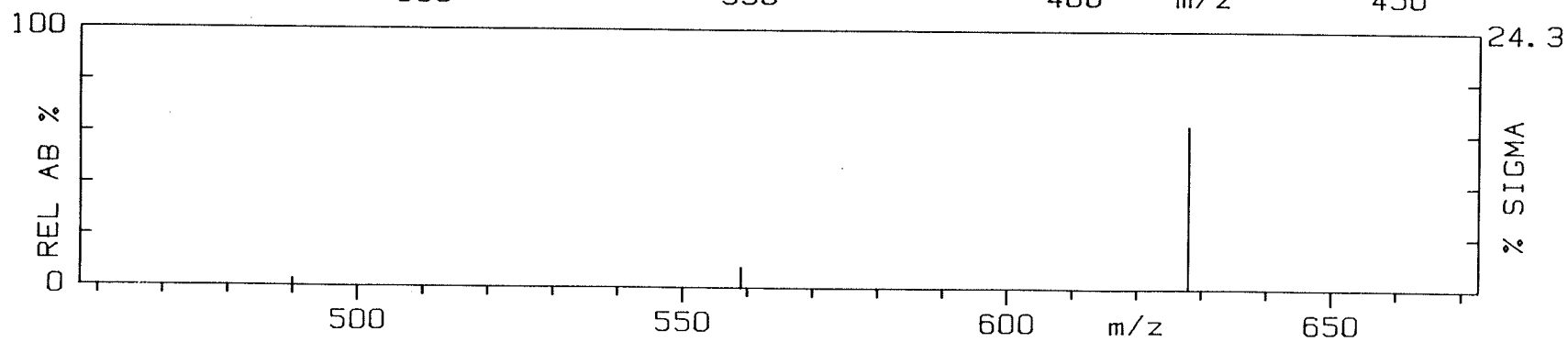
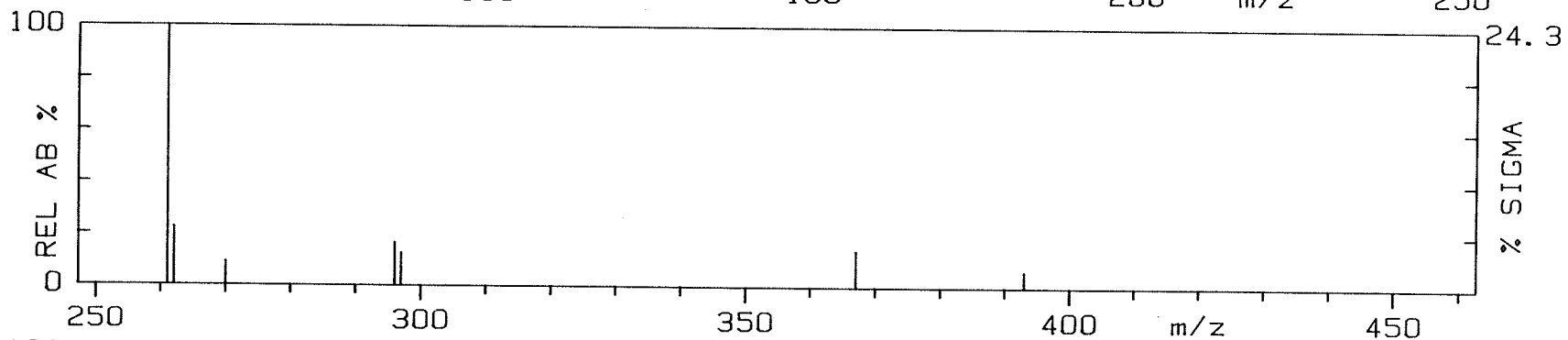
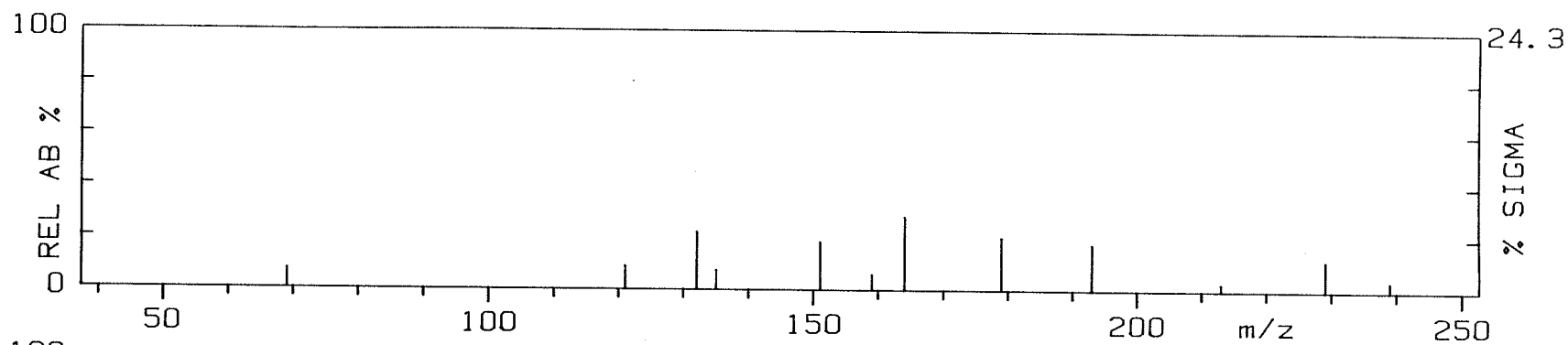
Figure 109.

Normalized 70 eV-EI mass spectrum of  
bis[1,1,1-trifluoro-4-mercapto-4-(4'-methoxyphenyl)-  
but-3-en-2-onato]Pd(II) {Pd-7b}.

$m/z$   $[M]^+$  = 628,  $[L]^+$  = 261



PD-7B 70EV.

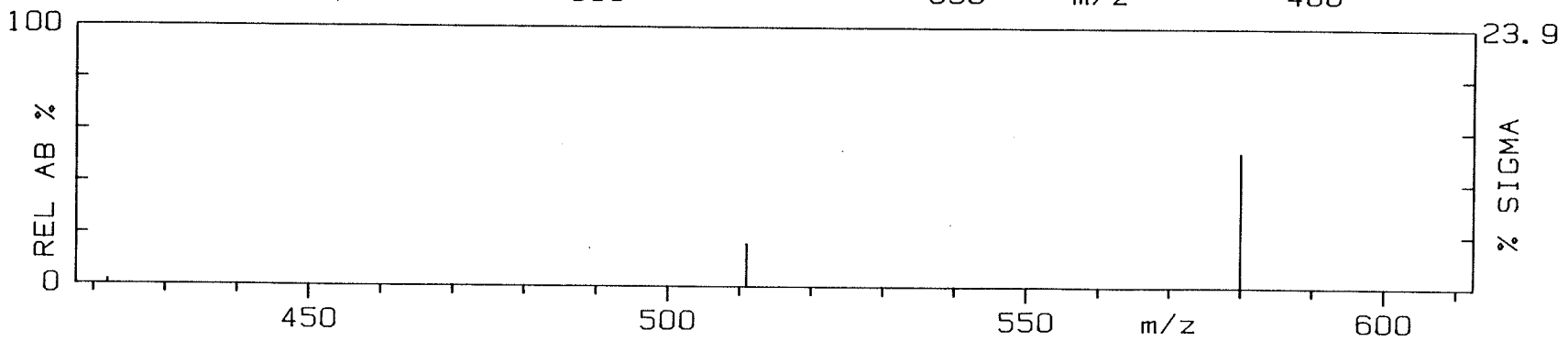
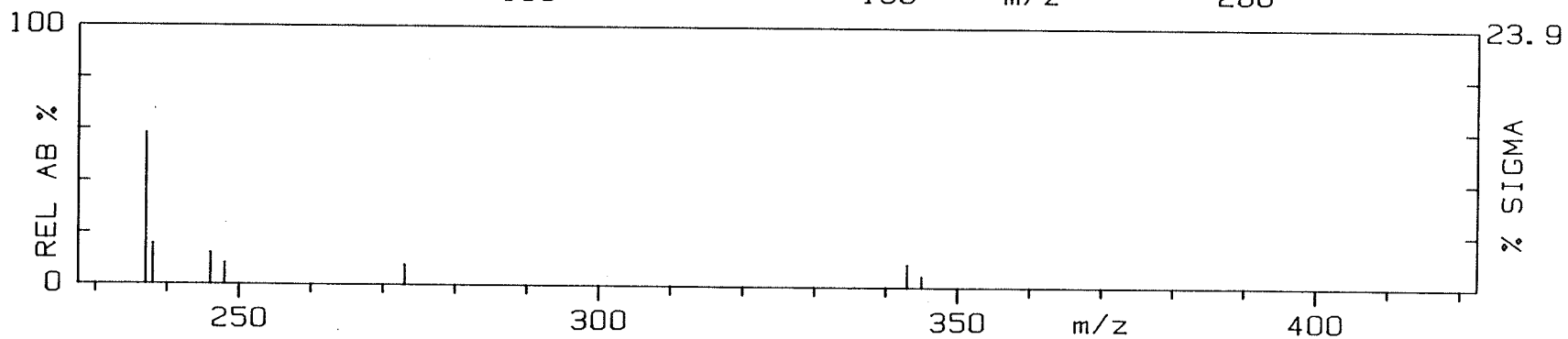
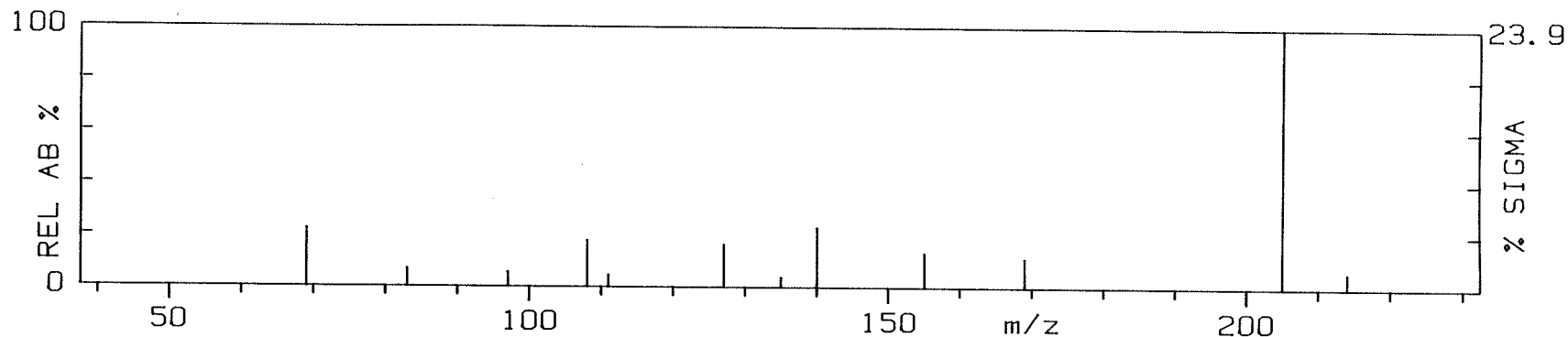


**Figure 110.**

Normalized 70 eV-Ei mass spectrum of  
bis[1,1,1-trifluoro-4-mercapto-4-(2'-thienyl)-but-3-en-2-onato]Pd(II)  
{Pd-8b}.

$m/z$   $[M]^+$  = 580,  $[L]^+$  = 237

PD-8B 70EV.

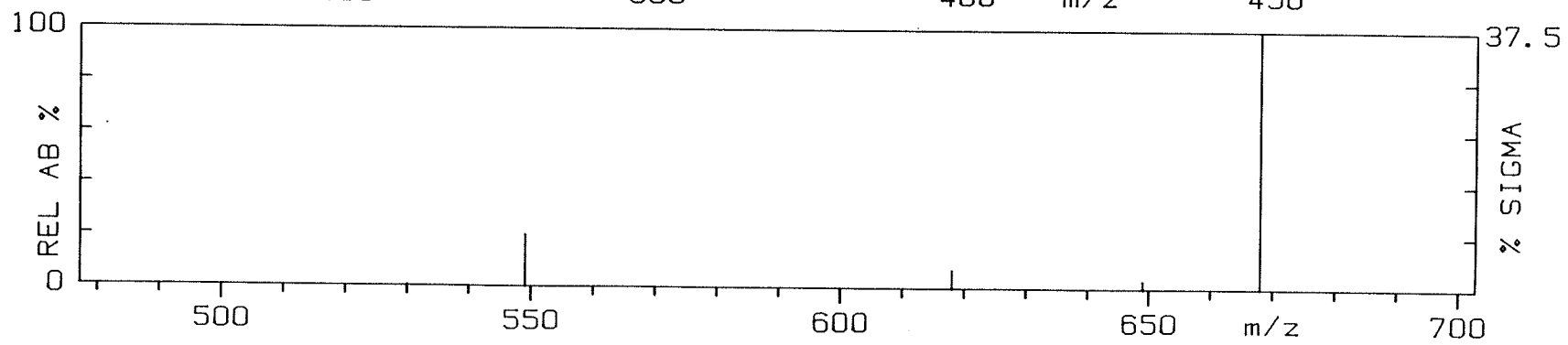
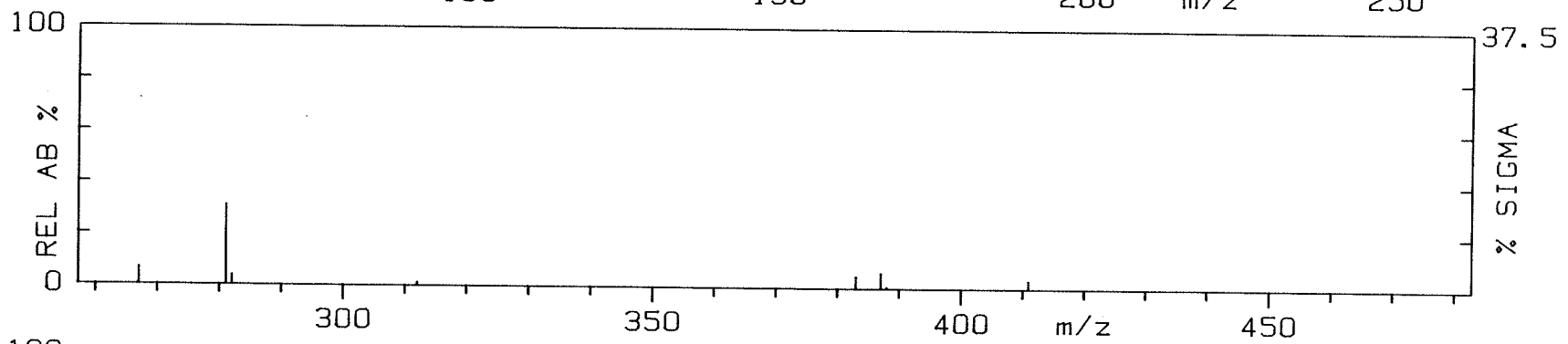
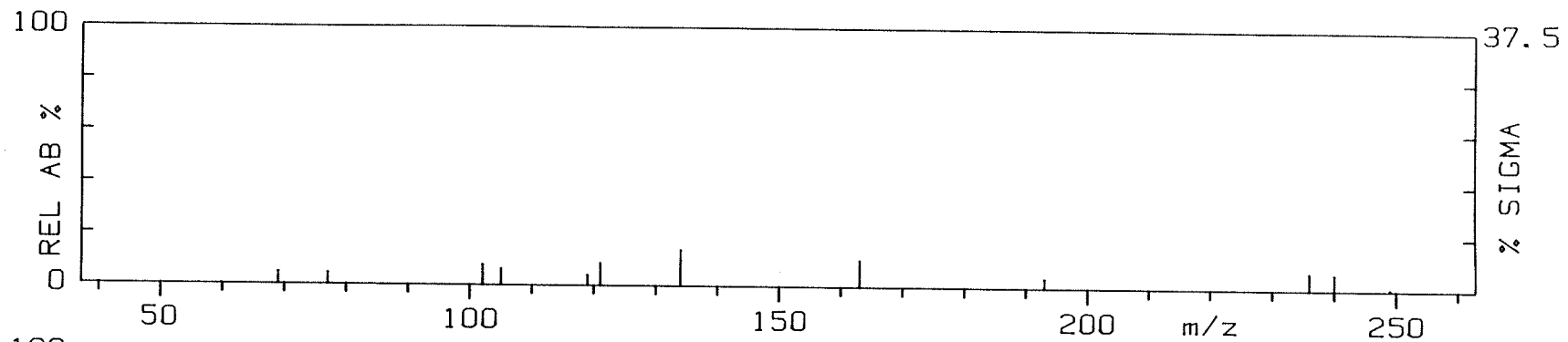


**Figure 111.**

Normalized 70 eV-EI mass spectrum of  
bis[1,1,1,2,2-pentafluoro-5-mercapto-5-phenyl-pent-4-en-3-onato]Pd(II)  
{Pd-13b}.

$m/z$   $[M]^+$  = 668,  $[L]^+$  = 281

PD-13B 70EV.

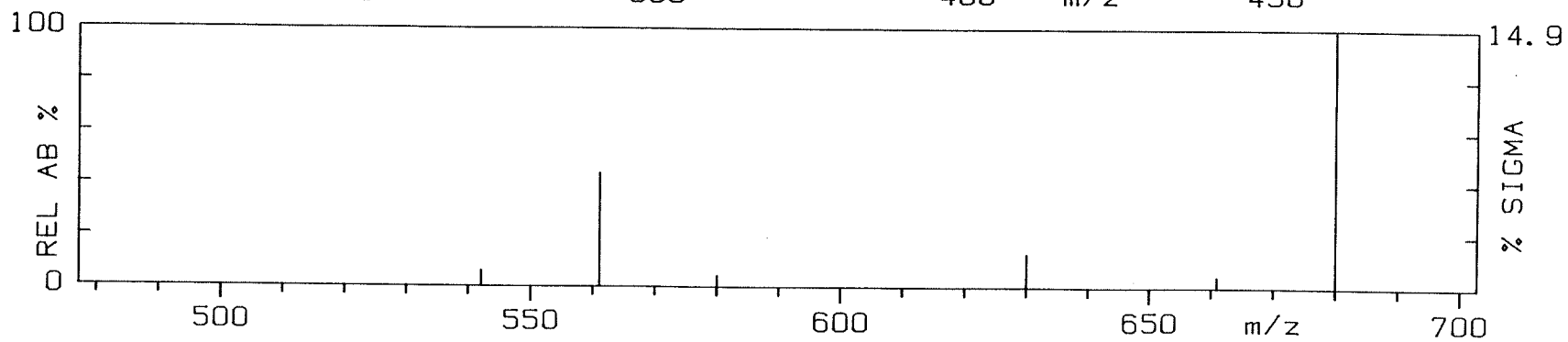
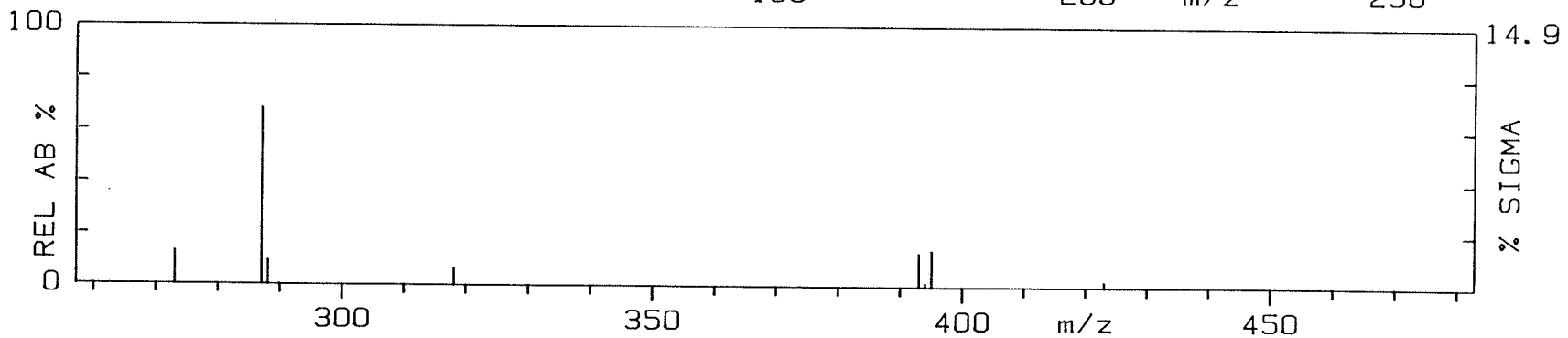
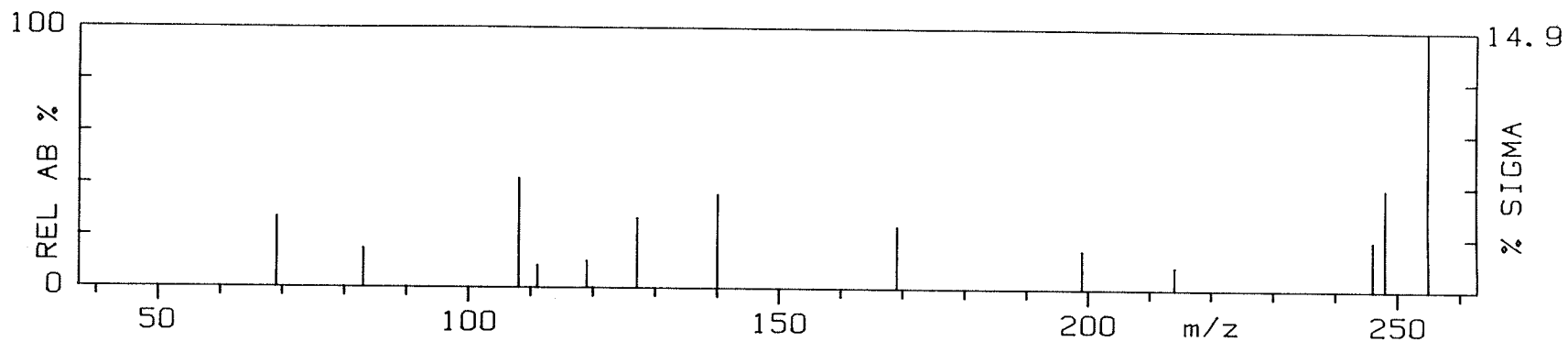


**Figure 112.**

Normalized 70 eV-EI mass spectrum of  
bis[1,1,1,2,2-pentafluoro-5-mercapto-5-(2'-thienyl)-  
pent-4-en-3-onato]Pd(II) (Pd-14b).

$m/z$   $[M]^+$  = 680,  $[L]^+$  = 287

PD-14B 70EV.



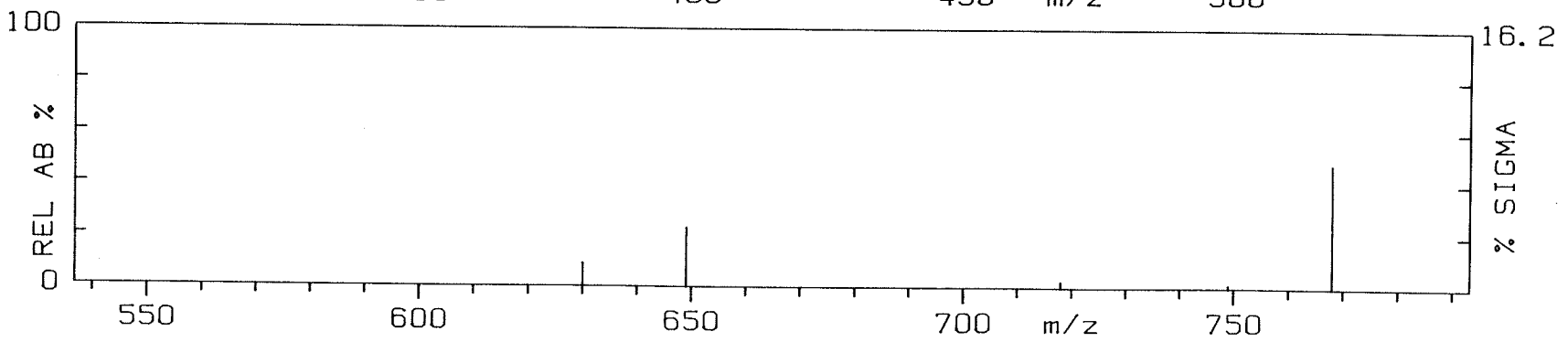
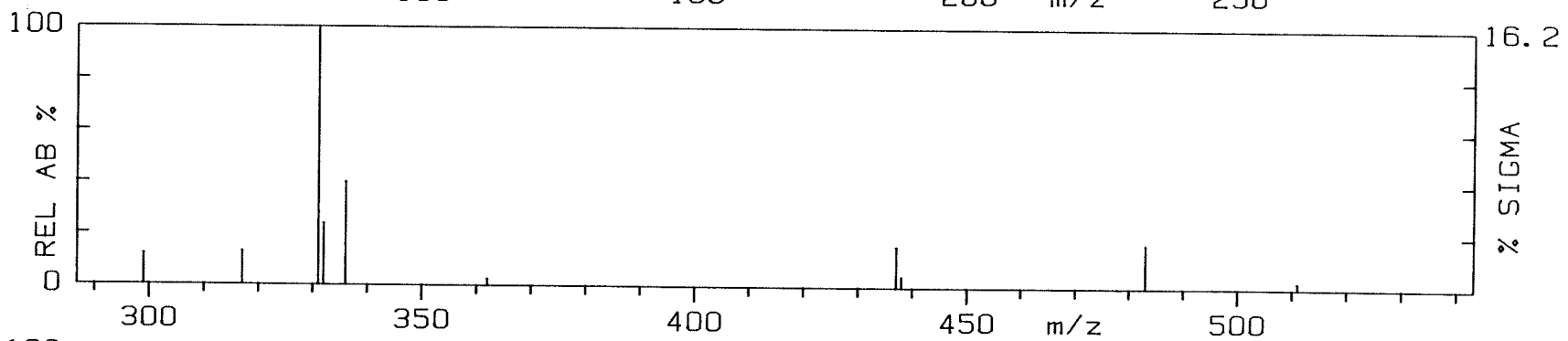
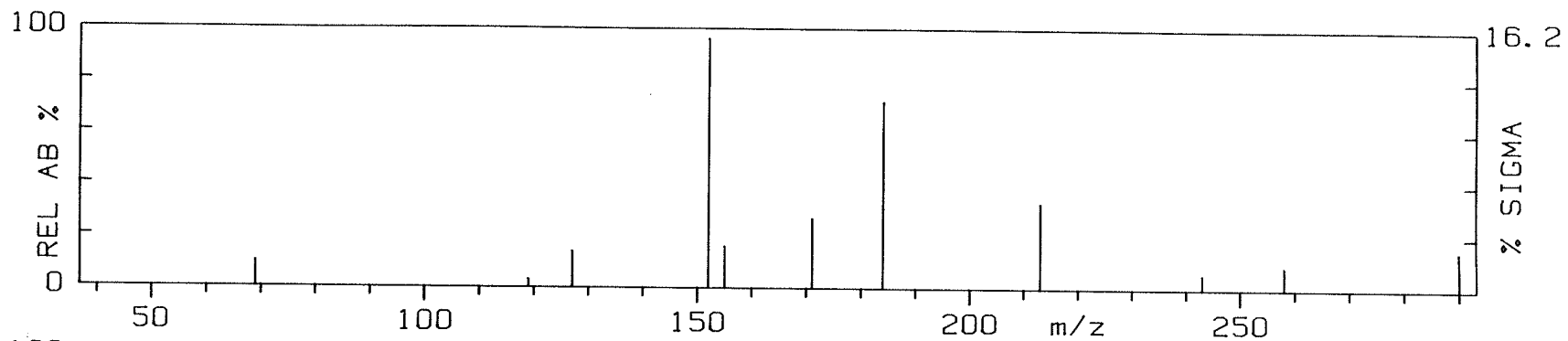
**Figure 113.**

Normalized 70 eV-EI mass spectrum of  
bis[1,1,1,2,2-pentafluoro-5-mercapto-5-(2'-naphthyl)-  
pent-4-en-3-onato]Pd(II) (Pd-15b).

$m/z$   $[M]^{+•} = 768$ ,  $[L]^+ = 331$



PD-15B 70EV.

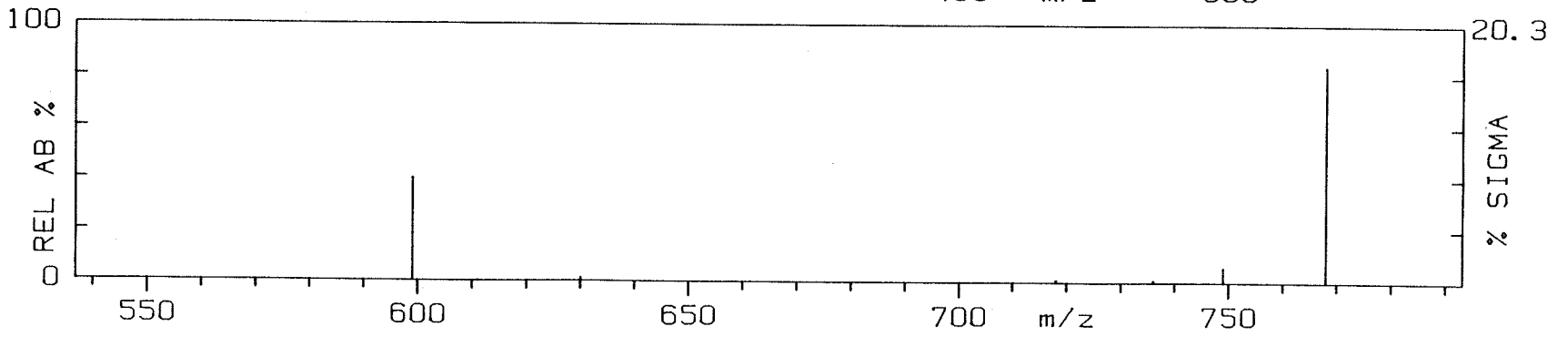
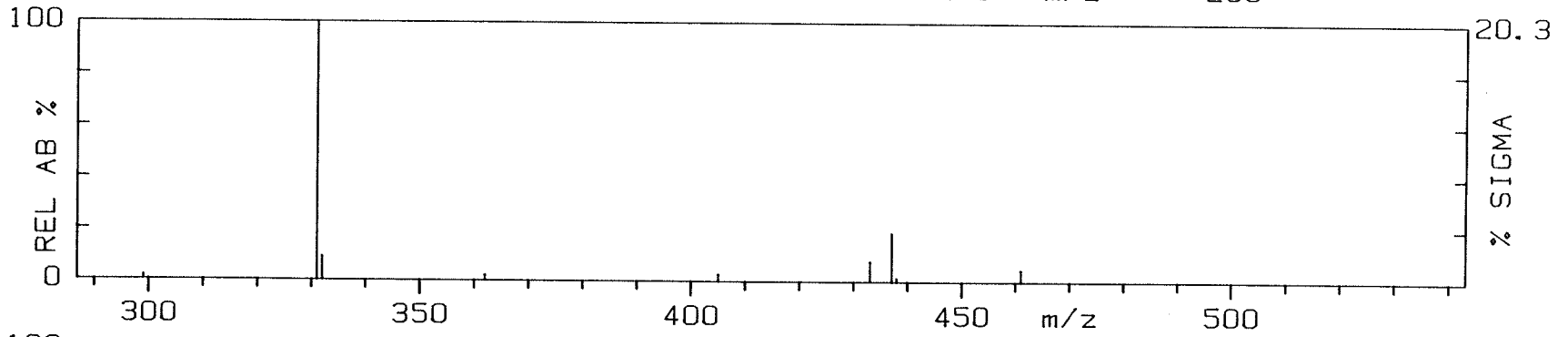
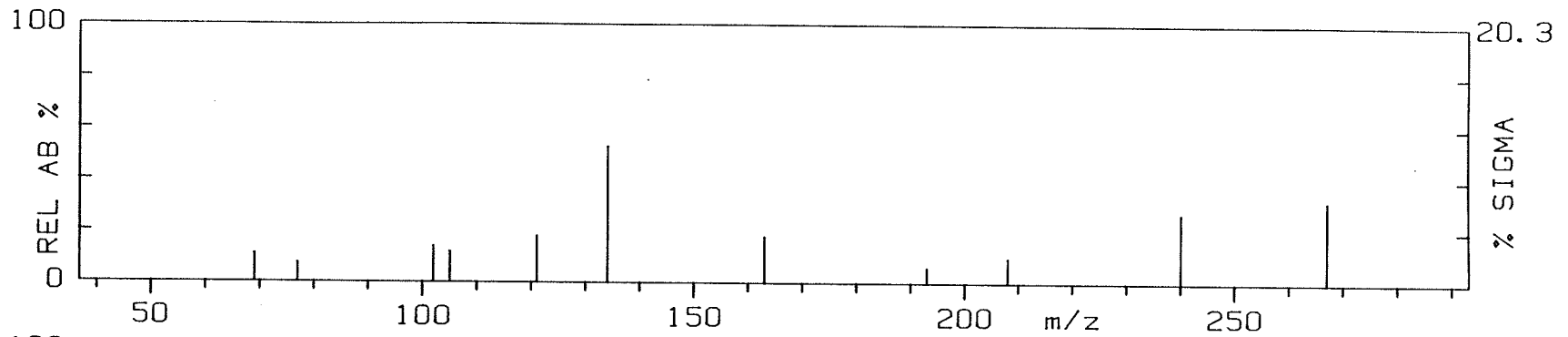


**Figure 114.**

Normalized 70 eV-EI mass spectrum of  
bis[1,1,1,2,2,3,3-heptafluoro-6-mercapto-6-phenyl-  
hex-5-en-4-onato]Pd(II) (Pd-16b).

$m/z$   $[M]^{+\cdot} = 768$ ,  $[L]^+ = 331$

PD-16B 70EV.

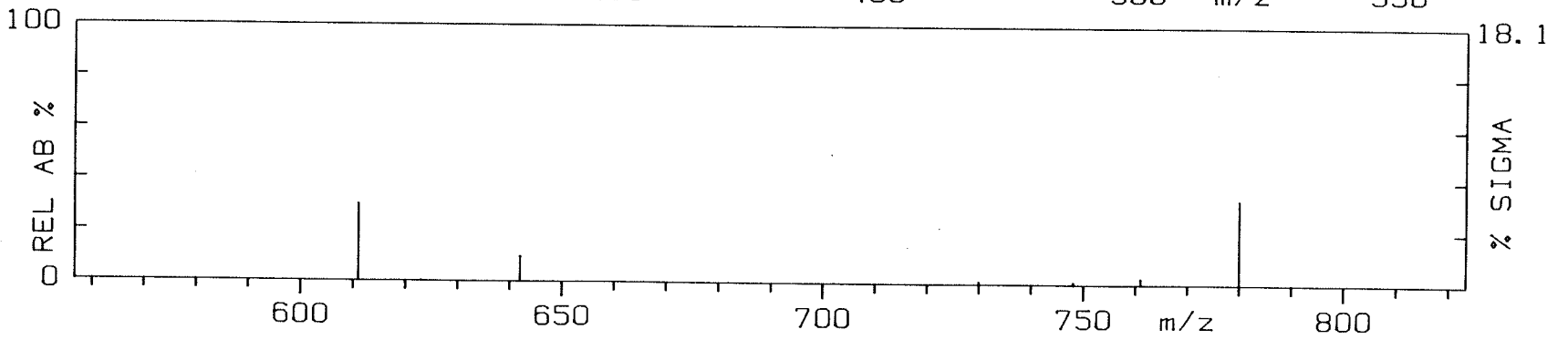
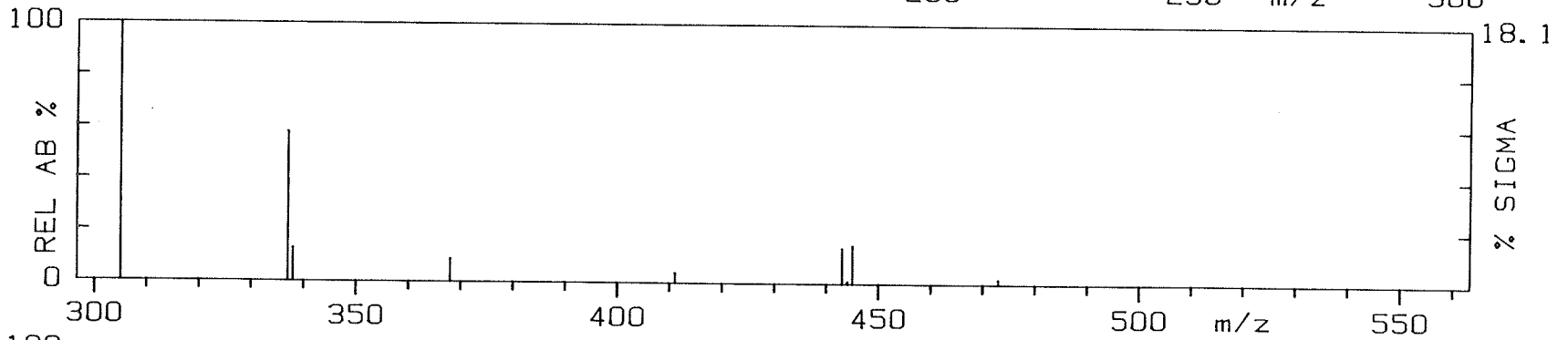
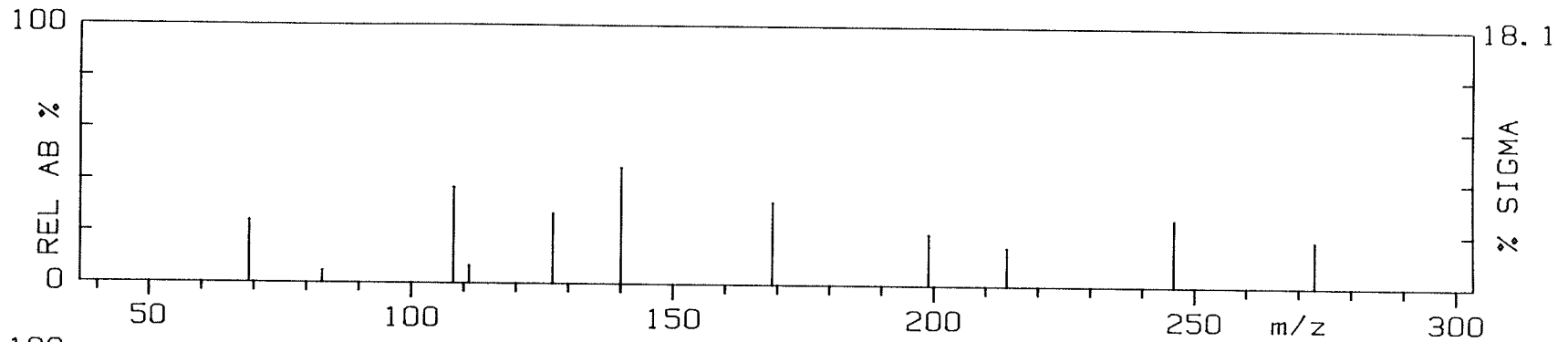


**Figure 115.**

Normalized 70 eV-EI mass spectrum of  
bis[1,1,1,2,2,3,3-heptafluoro-6-mercapto-6-(2'-thienyl)-  
hex-5-en-4-onato]Pd(II) {Pd-17b}.

$m/z$   $[M]^{+}$  = 780,  $[L]^{+}$  = 337

PD-17B 70EV.

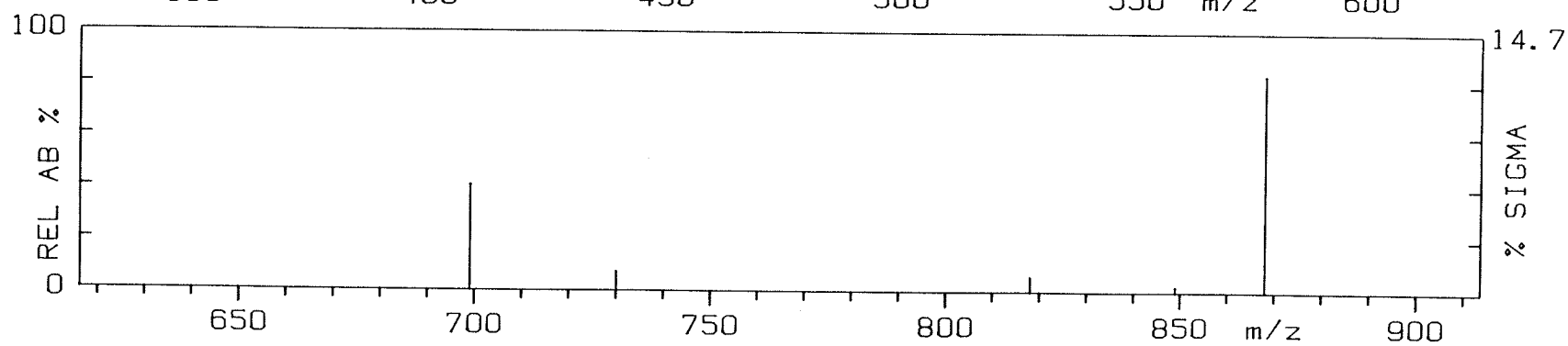
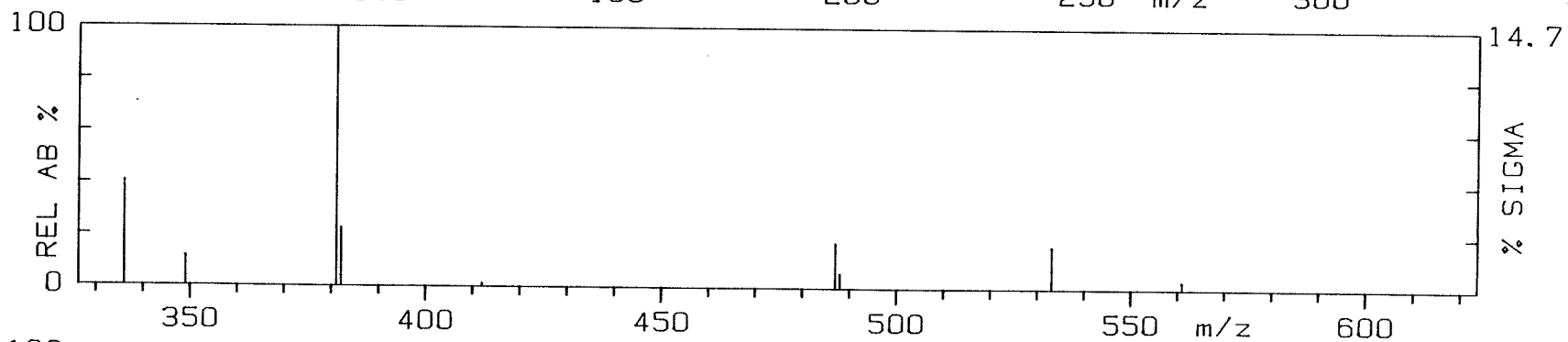
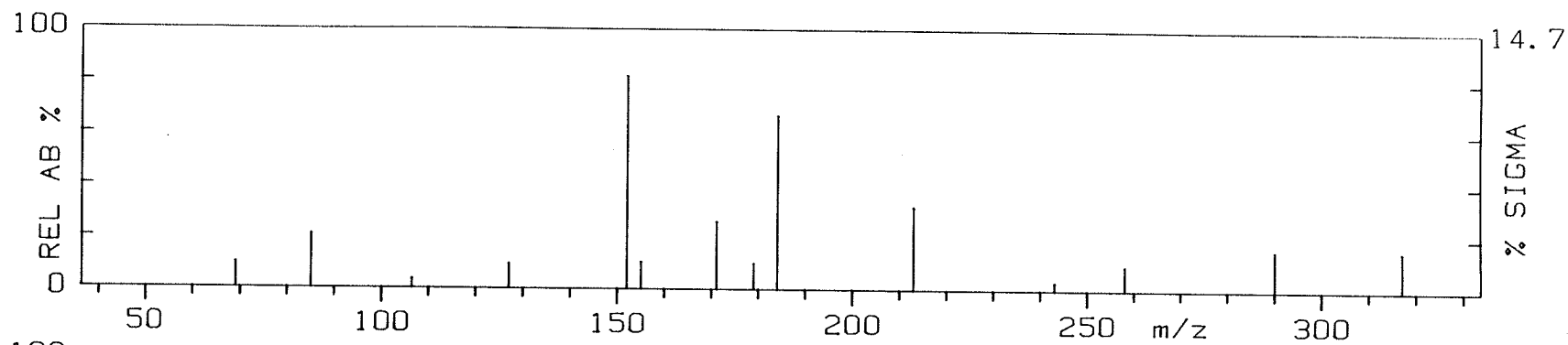


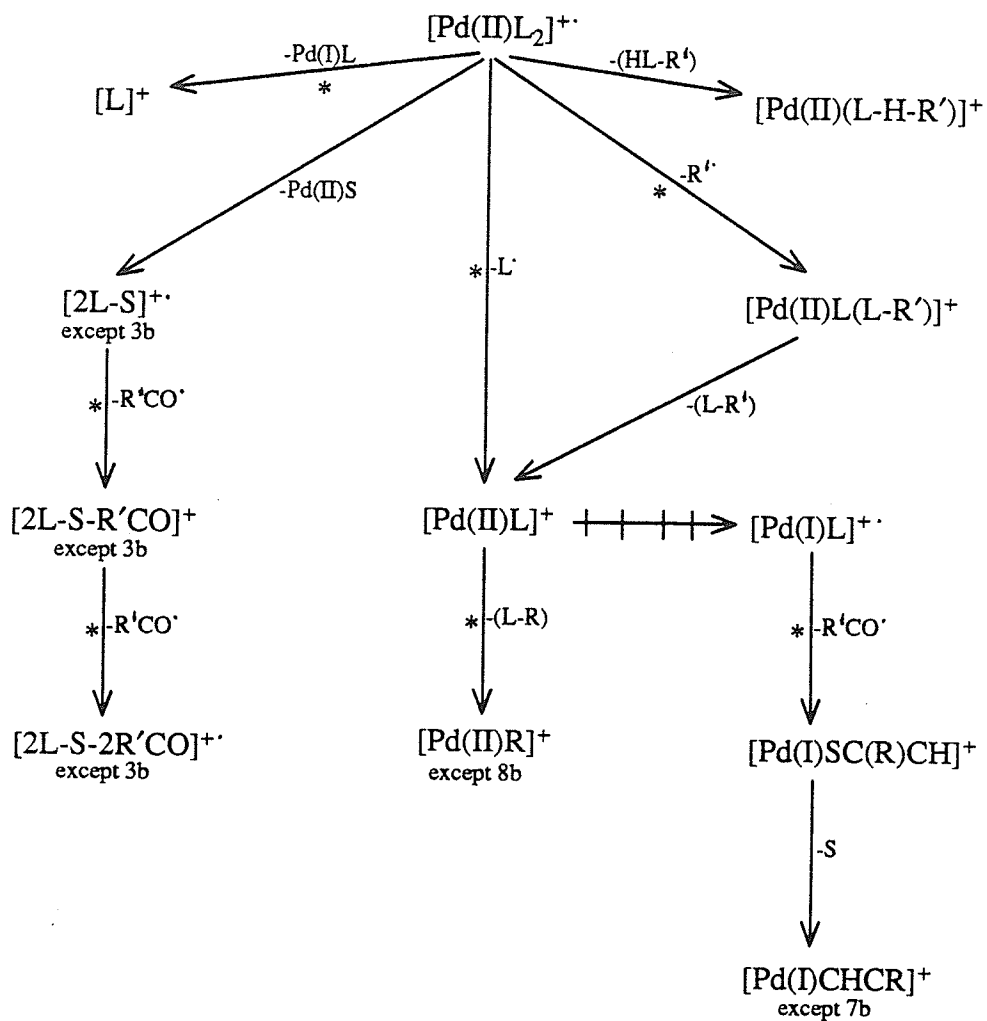
**Figure 116.**

Normalized 70 eV-EI mass spectrum of  
bis[1,1,1,2,2,3,3-heptafluoro-6-mercapto-6-(2'-naphthyl)-  
hex-5-en-4-onato]Pd(II) {Pd-18b}.

$m/z$   $[M]^{+•} = 868$ ,  $[L]^{+} = 381$

PD-18B 70EV.



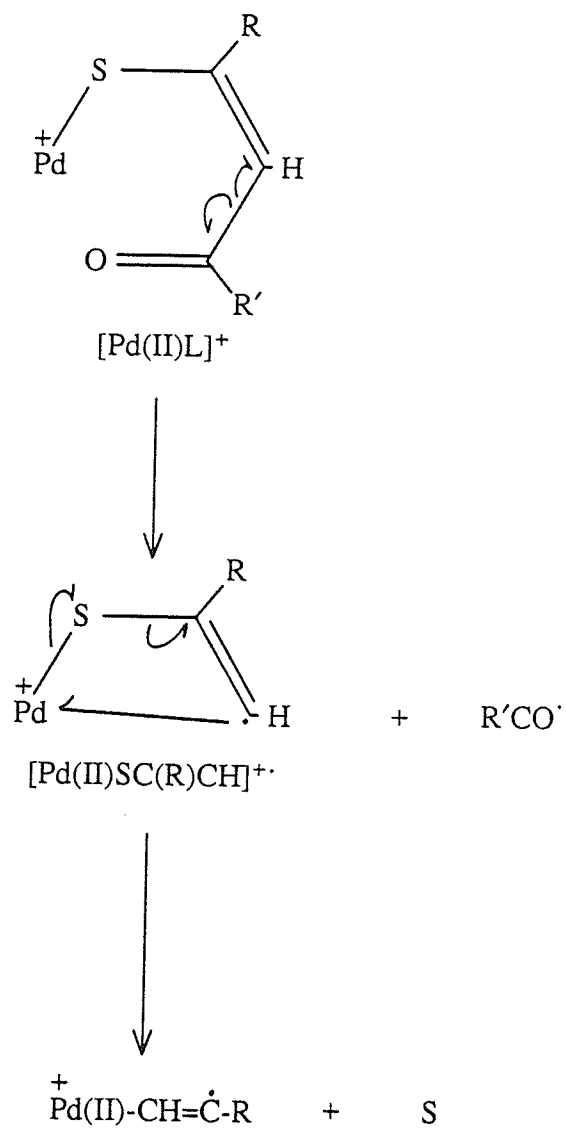


\* process confirmed by the observation of a metastable transition in at least one of the complexes.

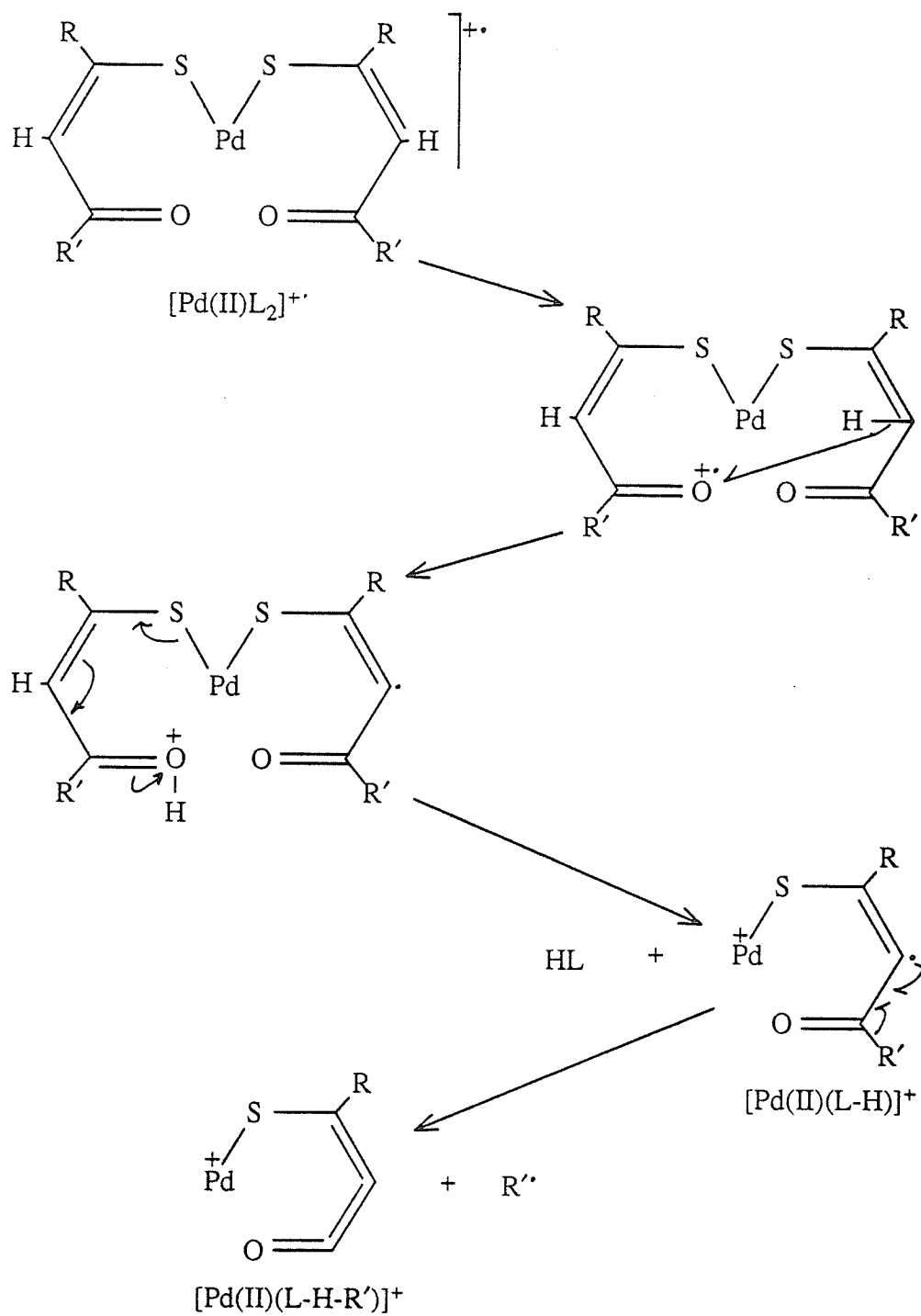
---> reaction step in which a change in metal oxidation state is proposed.

**Scheme 80.** Proposed fragmentation pathways for Pd(II) monothio- $\beta$ -diketonates where  $\text{R}' = \text{CF}_3$  (Pd-3b, -7b and -8b). Pathways are common to all complexes except where noted.

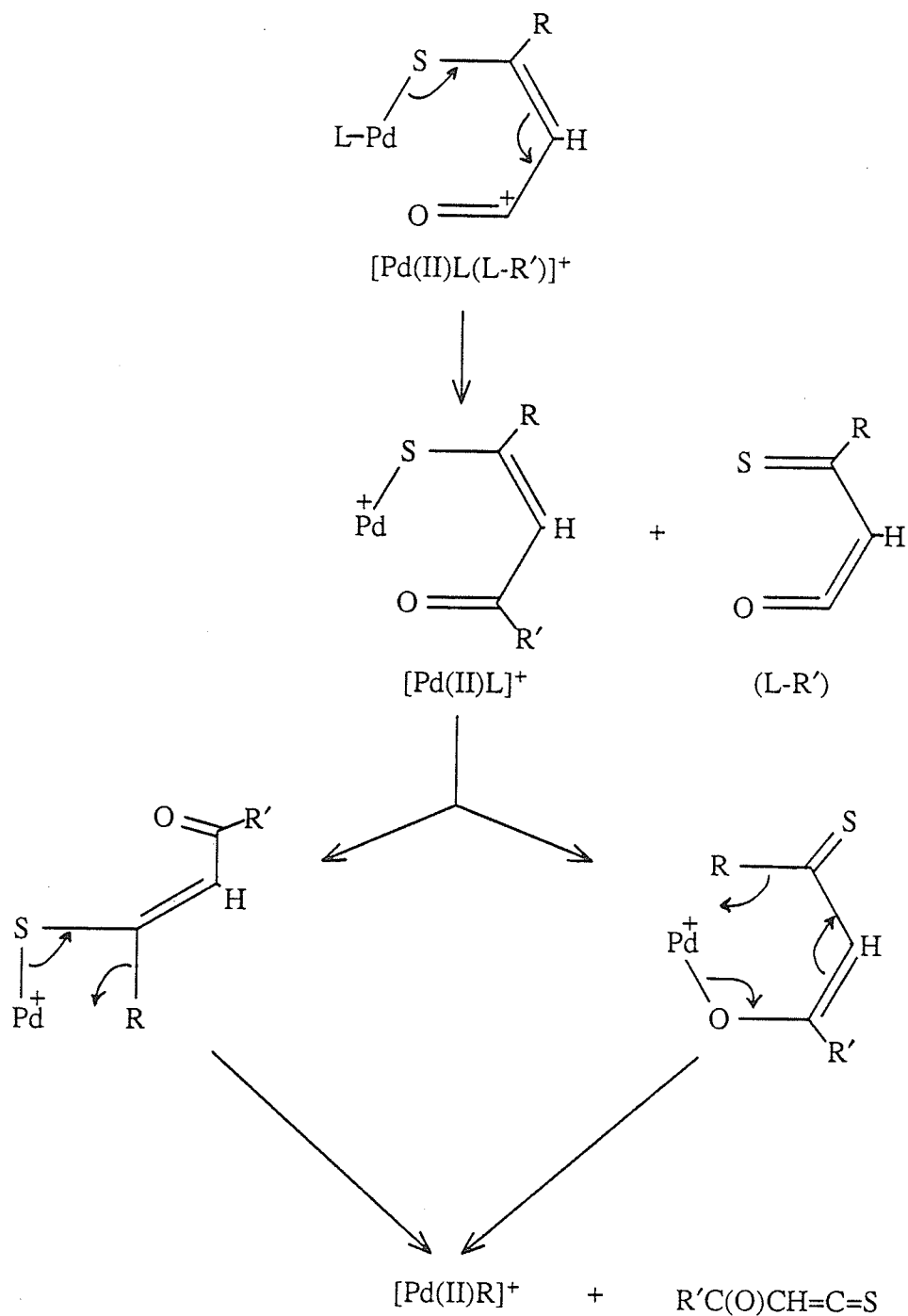




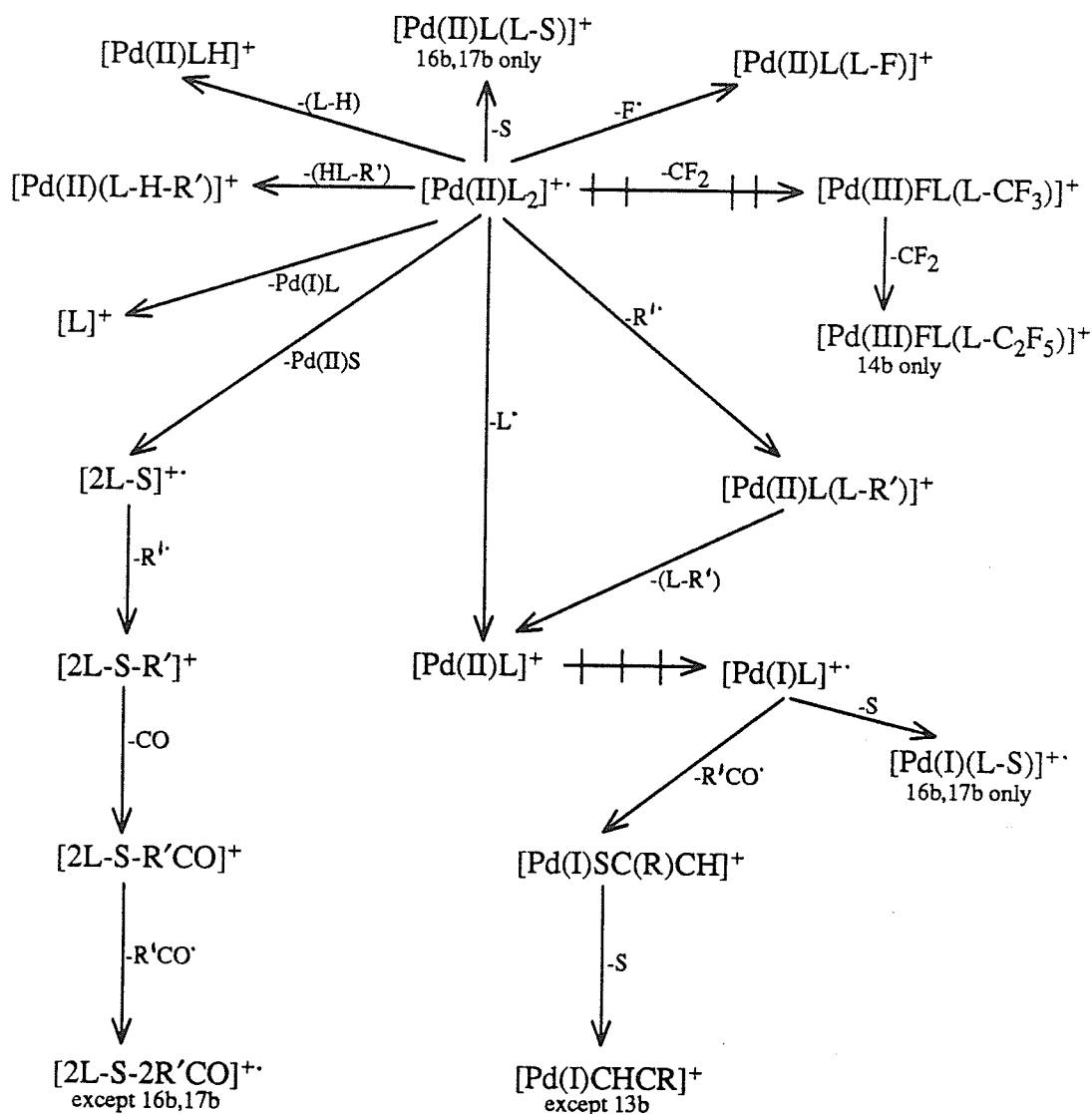
**Scheme 81.** Suggested mechanism for the formation of  $[\text{Pd(II)SC(R)CH}]^+$  and  $[\text{Pd(II)CHCR}]^+$  in Pd-3b, -7b and -8b.



**Scheme 82.** Suggested mechanism for the formation of  $[Pd(II)(L-H-R')]^+$  in Pd-3b, -7b and -8b.

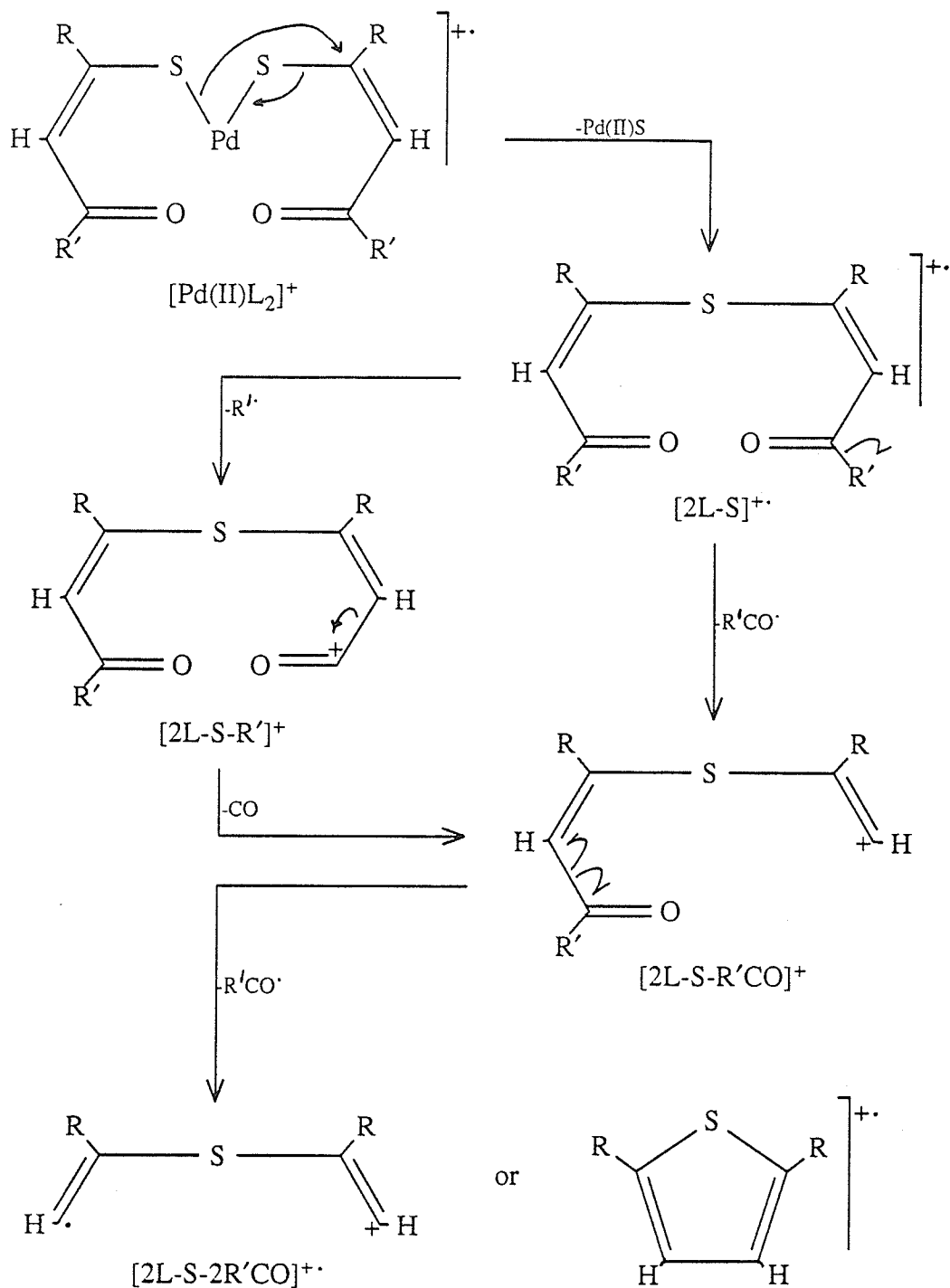


**Scheme 83.** Suggested mechanism for the formation of  $[Pd(II)L]^+$  and  $[Pd(II)R]^+$  in **Pd-3b** and **-7b**.



$\dashrightarrow$  reaction step in which a change in metal oxidation state is proposed.

**Scheme 84.** Proposed fragmentation pathways for Pd(II) monothio- $\beta$ -diketonates where  $R' = C_2F_5$  (Pd-13b, -14b and -15b) or  $C_3F_7$  (Pd-16b, -17b and -18b). Pathways are common to all complexes except where noted.

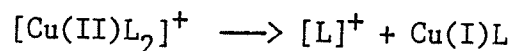


**Scheme 85.** Suggested mechanism for the formation of  $[2L-S]^{\bullet+}$ ,  $[2L-S-R']^+$ ,  $[2L-S-R'CO]^+$  and  $[2L-S-2R'CO]^{\bullet+}$  in Pd-13b, -14b, -15b, -16b, -17b and -18b.

(d) Cu(II) Monothio- $\beta$ -diketonates

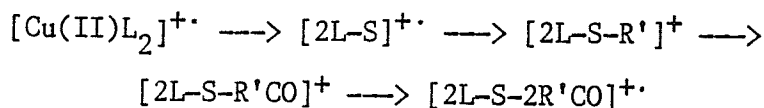
Relative abundance data for the six Cu(II) monothio- $\beta$ -diketonates studied appear in Tables 51-53. Plots of the EI mass spectra can be found in Figures 117-122. There are no previously published reports concerning the mass spectra of these complexes.

Suggested fragmentation pathways for the trifluoromethyl-substituted derivatives ( $R' = CF_3$ ; Tables 51 and 52) are presented in Scheme 86. All of the spectra are characterized by a notable lack of metal-containing ion abundance;  $[Cu(I)]^+$  is normally the most abundant copper species (usually < 4%), while  $[L]^+$  invariably constitutes the base peak. These observations, when coupled with the established reducibility of Cu(II) to Cu(I), suggest that the decomposition



is probably the dominant reaction process (see Scheme 69 for a proposed mechanism).

Scheme 87 outlines a suggested mechanism for the formation of  $[\text{Cu(I)}]^+$  from  $[\text{Cu(II)L}]^+$ . Unfortunately, all attempts at obtaining metastable evidence for the decompositions involving copper-containing ions proved futile, probably because of their low abundance. The reaction sequence



as shown in Scheme 86 has been described previously (see Scheme 85).

Suggested decomposition pathways for the pentafluoroethyl- and heptafluoropropyl-substituted  $\text{Cu(II)}$  chelates ( $\text{R}' = \text{C}_2\text{F}_5, \text{C}_3\text{F}_7$ ; Table 53) are given in Scheme 88. The fragmentations are essentially the same as those seen in the  $\text{CF}_3$ -substituted derivatives:

<u>Fragmentation</u>	<u>Scheme</u>
$[2\text{L-S-R}'\text{CO}]^+ \longrightarrow [2\text{L-2S-R}'\text{CO}]^+$	67
$[\text{Cu(II)L}_2]^+ \longrightarrow [\text{L}]^+ + \text{Cu(I)L}$	69
$[\text{Cu(II)L}_2]^+ \longrightarrow [2\text{L-S}]^+$	85
$[2\text{L-S}]^+ \longrightarrow [2\text{L-S-R}]^+$	85
$[2\text{L-S-R}]^+ \longrightarrow [2\text{L-S-R}'\text{CO}]^+$	85
$[2\text{L-S-R}'\text{CO}]^+ \longrightarrow [2\text{L-S-2R}'\text{CO}]^+$	85
$[\text{Cu(I)L}]^+ \longrightarrow [\text{Cu(I)(L-R}')]^+$	87
$[\text{Cu(I)(L-R}')]^+ \longrightarrow [\text{Cu(I)}]^+$	87

Table 51. 70 eV-EI mass spectra of compounds Cu-3b and Cu-4b.

ION	Cu-3b			Cu-4b		
	%RA	m/z	%TIC	%RA	m/z	%TIC
R =		-C <sub>6</sub> H <sub>5</sub>			-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	
R' =		-CF <sub>3</sub>			-CF <sub>3</sub>	
[CuL <sub>2</sub> ] <sup>+</sup>	0.7	(525)	0.3	2.9	(553)	1.2
[CuL(L-F)] <sup>+</sup>	-	(506)	-	0.2	(534)	0.1
[CuL] <sup>+</sup>	-	(294)	-	0.4	(308)	0.2
[CuL-R'] <sup>+</sup>	2.7	(225)	1.0	1.6	(239)	0.7
[Cu] <sup>+</sup>	10.9	( 63)	4.2	6.4	( 63)	2.7
[2L-S] <sup>+</sup>	-	(430)	-	0.6	(458)	0.3
[2L-S-R'] <sup>+</sup>	0.3	(361)	0.1	0.4	(389)	0.2
[2L-S-R'CO] <sup>+</sup>	3.1	(333)	1.2	3.6	(361)	1.5
[2L-S-2R'CO] <sup>+</sup>	5.6	(236)	2.1	7.3	(264)	3.1
[HL] <sup>+</sup>	11.4	(232)	4.4	8.3	(246)	3.6
[L] <sup>+</sup>	100.0	(231)	38.3	100.0	(245)	42.9
[HL-CH <sub>3</sub> ] <sup>+</sup>	-	(217)	-	5.9	(231)	2.5
[L-F] <sup>+</sup>	0.1	(212)	-	1.1	(226)	0.5
[L-S] <sup>+</sup>	-	(199)	-	1.3	(213)	0.6
[HL-R'] <sup>+</sup>	12.2	(163)	4.7	8.9	(177)	3.8
[L-S-CF <sub>2</sub> ] <sup>+</sup>	14.0	(149)	5.4	12.0	(163)	5.1
[RCSCH] <sup>+</sup>	25.2	(134)	9.7	14.0	(148)	6.0
[RC <sub>3</sub> O] <sup>+</sup>	4.6	(129)	1.8	2.4	(143)	1.0
[RCS] <sup>+</sup>	13.0	(121)	5.0	9.8	(135)	4.2



Table 51. (continued).

[RCO] <sup>+</sup>	9.6 (105)	3.7	6.6 (119)	2.8
[RCCH] <sup>+</sup>	8.9 (102)	3.4	5.1 (116)	2.2
[RCC] <sup>+</sup>	3.1 (101)	1.2	13.0 (115)	5.6
[RCH <sub>2</sub> ] <sup>+</sup>	6.2 ( 91)	2.4	1.3 (105)	0.6
[RCH] <sup>+</sup>	3.1 ( 90)	1.2	0.7 (104)	0.3
[RC] <sup>+</sup>	4.2 ( 89)	1.6	1.3 (103)	0.6
[CSCHCO] <sup>+</sup>	3.7 ( 85)	1.4	5.0 ( 85)	2.1
[R] <sup>+</sup>	9.3 ( 77)	3.6	6.2 ( 91)	2.7
[R'] <sup>+</sup>	9.1 ( 69)	3.5	6.8 ( 69)	2.9

Table 52. 70 eV-EI mass spectra of compounds Cu-5b and Cu-8b.

ION	Cu-5b			Cu-8b		
	%RA	m/z	%TIC	%RA	m/z	%TIC
	R =	-C <sub>6</sub> H <sub>4</sub> F			-C <sub>4</sub> H <sub>3</sub> S	
	R' =	-CF <sub>3</sub>			-CF <sub>3</sub>	
[CuL <sub>2</sub> ] <sup>+</sup>	1.5 (561)	0.6		1.2 (537)	0.5	
[CuL] <sup>+</sup>	0.3 (312)	0.1		- (300)	-	
[CuL-R'] <sup>+</sup>	1.6 (243)	0.6		3.5 (231)	1.4	
[Cu] <sup>+</sup>	6.7 ( 63)	2.5		9.3 ( 63)	3.8	
[2L-S] <sup>+</sup>	0.3 (466)	0.1		- (442)	-	
[2L-S-R'] <sup>+</sup>	0.6 (397)	0.2		- (373)	-	
[2L-S-R'CO] <sup>+</sup>	3.2 (369)	1.2		0.6 (345)	0.2	
[2L-S-2R'CO] <sup>+</sup>	6.2 (272)	2.3		2.3 (248)	0.9	
[HL] <sup>+</sup>	14.1 (250)	5.2		1.8 (238)	0.7	
[L] <sup>+</sup>	100.0 (249)	37.1		100.0 (237)	41.1	
[L-F] <sup>+</sup>	1.6 (230)	0.6		- (218)	-	
[L-S] <sup>+</sup>	0.9 (217)	0.3		11.3 (205)	4.6	
[HL-R'] <sup>+</sup>	13.2 (181)	4.9		2.9 (169)	1.2	
[L-S-CF <sub>2</sub> ] <sup>+</sup>	17.2 (167)	6.4		13.3 (155)	5.5	
[RCSCH] <sup>+</sup>	24.1 (152)	8.9		32.7 (140)	13.5	
[RC <sub>3</sub> O] <sup>+</sup>	3.9 (147)	1.4		2.9 (135)	1.2	
[RCS] <sup>+</sup>	14.0 (139)	5.2		9.6 (127)	3.9	
[RCO] <sup>+</sup>	11.1 (123)	4.1		2.3 (111)	1.0	
[RCCH] <sup>+</sup>	10.5 (120)	3.9		12.6 (108)	5.2	

Table 52. (continued).

[RCC] <sup>+</sup>	2.0 (119)	0.8	- (107)	-
[RCH <sub>2</sub> ] <sup>+</sup>	6.3 (109)	2.3	1.5 ( 97)	0.6
[RCH] <sup>+</sup>	3.6 (108)	1.3	11.3 ( 96)	4.6
[RC] <sup>+</sup>	4.5 (107)	1.7	5.1 ( 95)	2.1
[R] <sup>+</sup>	4.7 ( 95)	1.7	1.2 ( 83)	0.5
[CSCHCO] <sup>+</sup>	3.7 ( 85)	1.4	3.7 ( 85)	1.5
[R'] <sup>+</sup>	13.9 ( 69)	5.2	14.0 ( 69)	5.8

Table 53. 70 eV-EI mass spectra of compounds Cu-13b and Cu-16b.

ION	Cu-13b			Cu-16b		
	%RA	m/z	%TIC	%RA	m/z	%TIC
	R =	-C <sub>6</sub> H <sub>5</sub>		-C <sub>6</sub> H <sub>5</sub>		
	R' =	-C <sub>2</sub> F <sub>5</sub>		-C <sub>3</sub> F <sub>7</sub>		
[CuL <sub>2</sub> ] <sup>+</sup>	0.3	(625)	0.1	0.2	(725)	0.1
[CuL] <sup>+</sup>	0.5	(344)	0.2	-	(394)	-
[CuL-R'] <sup>+</sup>	6.1	(225)	2.2	0.4	(225)	0.2
[Cu] <sup>+</sup>	11.0	(63)	4.0	1.3	(63)	0.7
[2L-S] <sup>+</sup>	0.4	(530)	0.2	0.1	(630)	0.1
[2L-S-R'] <sup>+</sup>	3.0	(411)	1.1	1.1	(461)	0.6
[2L-S-R'CO] <sup>+</sup>	6.4	(383)	2.3	1.9	(433)	1.0
[2L-2S-R'CO] <sup>+</sup>	0.4	(351)	0.2	0.1	(401)	0.1
[HL] <sup>+</sup>	6.3	(282)	2.3	2.6	(332)	1.4
[L] <sup>+</sup>	100.0	(281)	36.1	100.0	(331)	54.9
[L-F] <sup>+</sup>	0.8	(262)	0.3	0.8	(312)	0.4
[L-S] <sup>+</sup>	1.1	(249)	0.4	-	(299)	-
[2L-S-2R'CO] <sup>+</sup>	11.5	(236)	4.2	3.0	(236)	1.7
[L-CF <sub>2</sub> ] <sup>+</sup>	3.2	(231)	1.2	1.1	(281)	0.6
[R'] <sup>+</sup>	7.9	(119)	2.9	3.0	(169)	1.7
[HL-R'] <sup>+</sup>	12.3	(163)	4.5	5.8	(163)	3.2
[RCSCH] <sup>+</sup>	17.9	(134)	6.5	24.4	(134)	13.4
[RC <sub>3</sub> O] <sup>+</sup>	6.1	(129)	2.2	2.2	(129)	1.2
[RCS] <sup>+</sup>	12.3	(121)	4.5	6.2	(121)	3.4

Table 53. (continued).

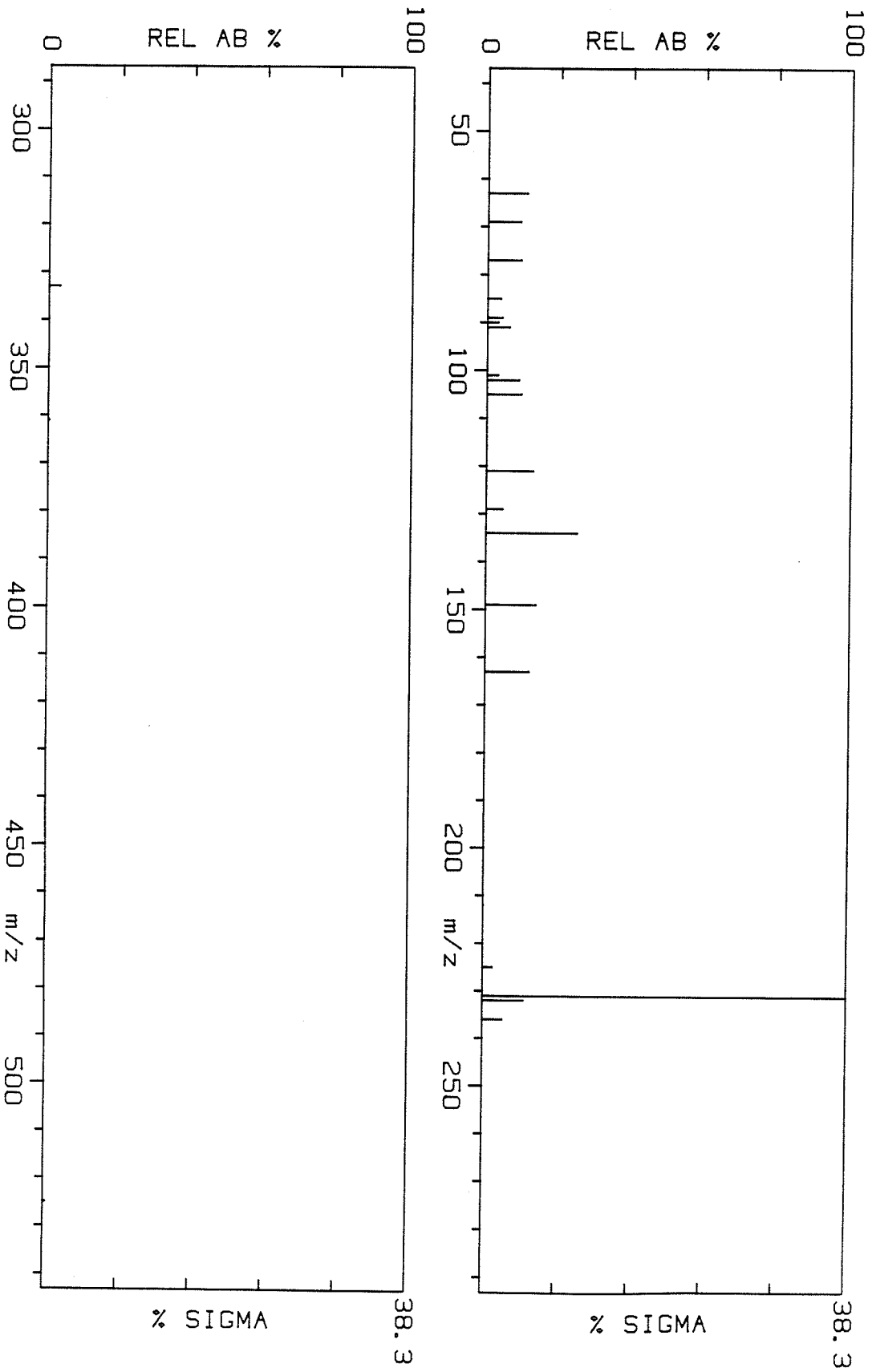
$[\text{RCO}]^+$	7.8 (105)	2.8	3.8 (105)	2.1
$[\text{RCCH}]^+$	15.3 (102)	5.6	8.1 (102)	4.5
$[\text{RCH}_2]^+$	5.0 (91)	1.8	1.8 (91)	1.0
$[\text{RCH}]^+$	3.4 (90)	1.2	2.3 (90)	1.3
$[\text{RC}]^+$	5.0 (89)	1.8	2.2 (89)	1.2
$[\text{R}]^+$	17.6 (77)	6.4	4.3 (77)	2.4
$[\text{CF}_3]^+$	14.7 (69)	5.3	5.6 (69)	3.1

**Figure 117.**

Normalized 70 eV-EI mass spectrum of  
bis[1,1,1-trifluoro-4-mercapto-4-phenyl-but-3-en-2-onato]Cu(II)  
{Cu-3b}.

$m/z$   $[M]^{+}$  = 525,  $[L]^{+}$  = 231

CU-3B 70EV.



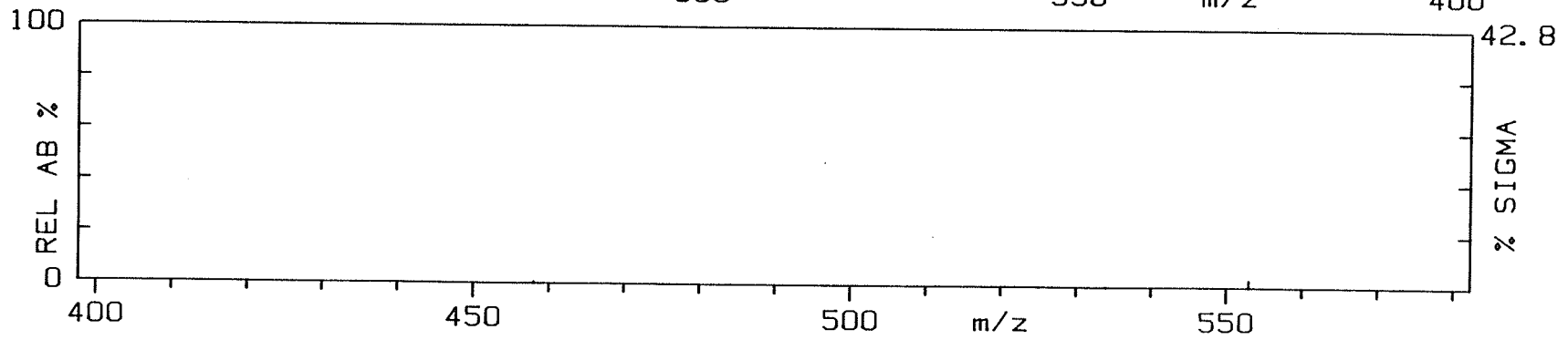
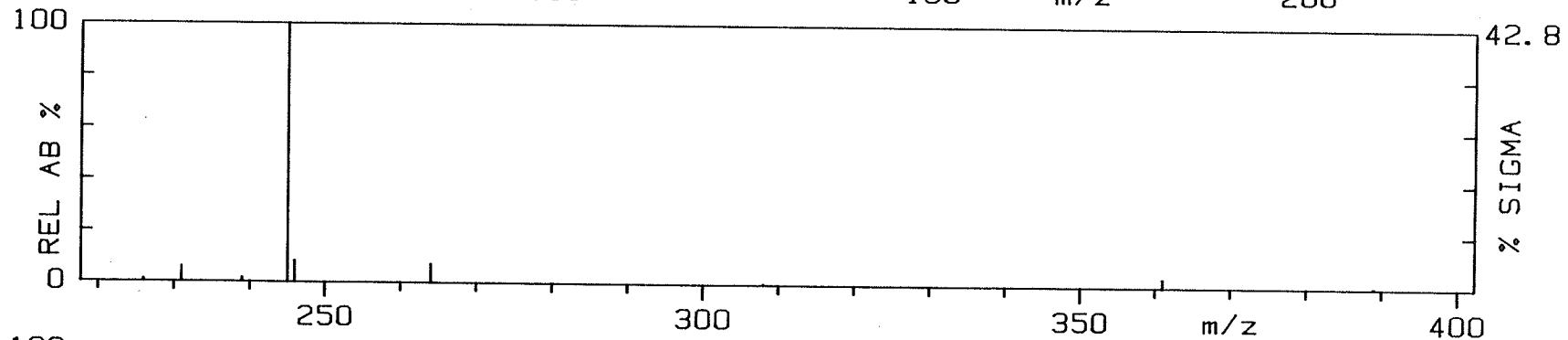
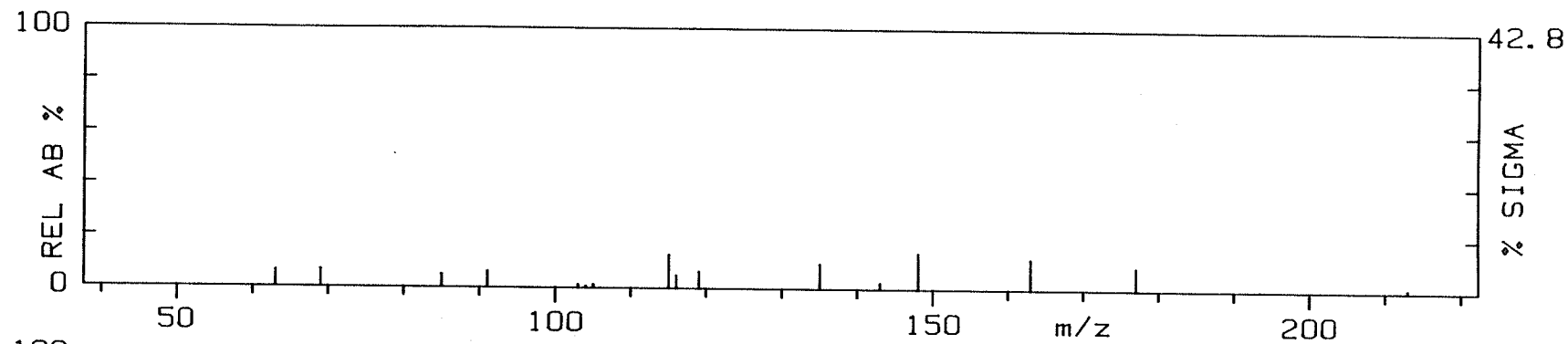
**Figure 118.**

Normalized 70 eV-EI mass spectrum of  
bis[1,1,1-trifluoro-4-mercapto-4-(4'-methylphenyl)-  
but-3-en-2-onato]Cu(II) {Cu-4b}.

$m/z$   $[M]^{++} = 553$ ,  $[L]^+ = 245$



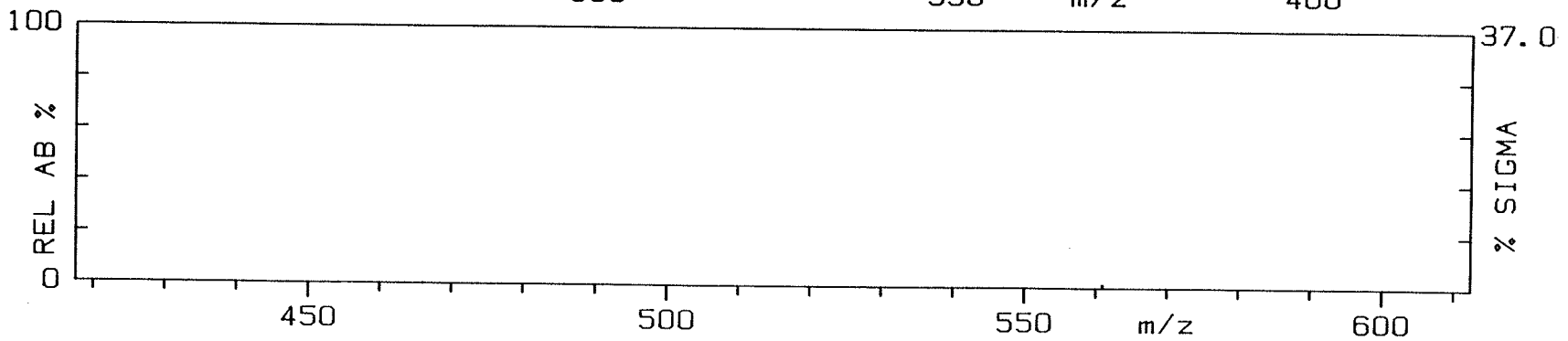
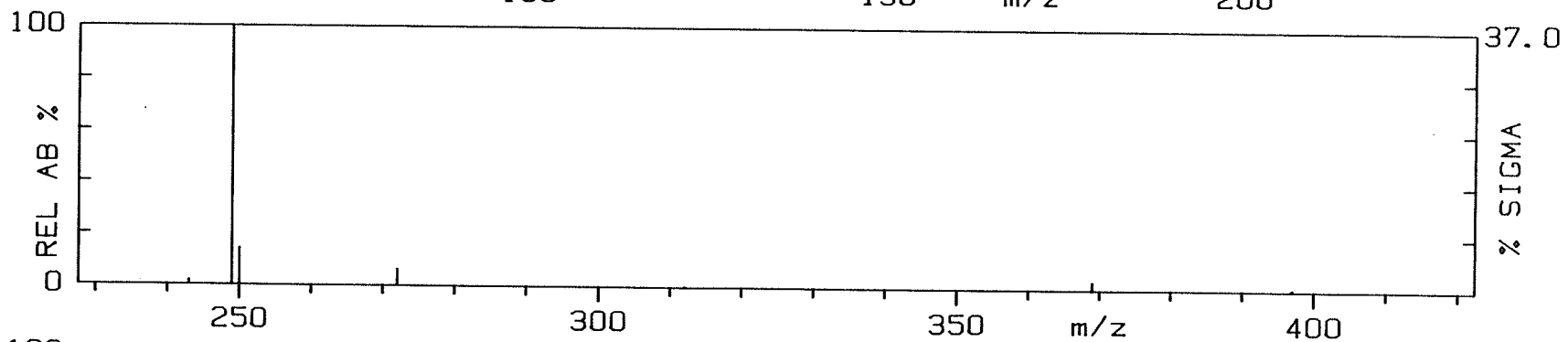
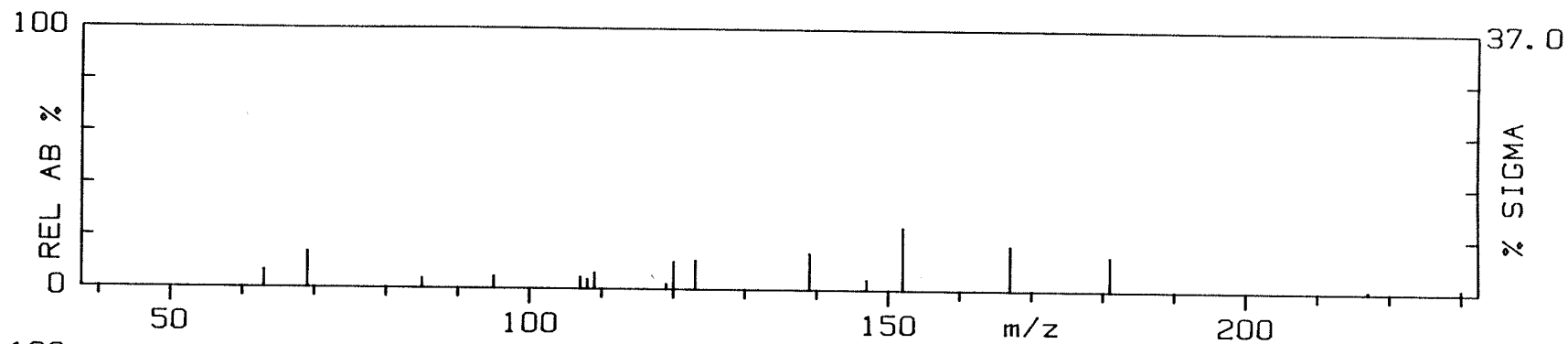
CU-4B 70EV.



**Figure 119.**

Normalized 70 eV-EI mass spectrum of  
bis[1,1,1-trifluoro-4-mercapto-4-(4'-fluorophenyl)-  
but-3-en-2-onato]Cu(II) (Cu-5b).  
 $m/z$   $[M]^{+}$  = 561,  $[L]^{+}$  = 249

CU-5B 70EV.

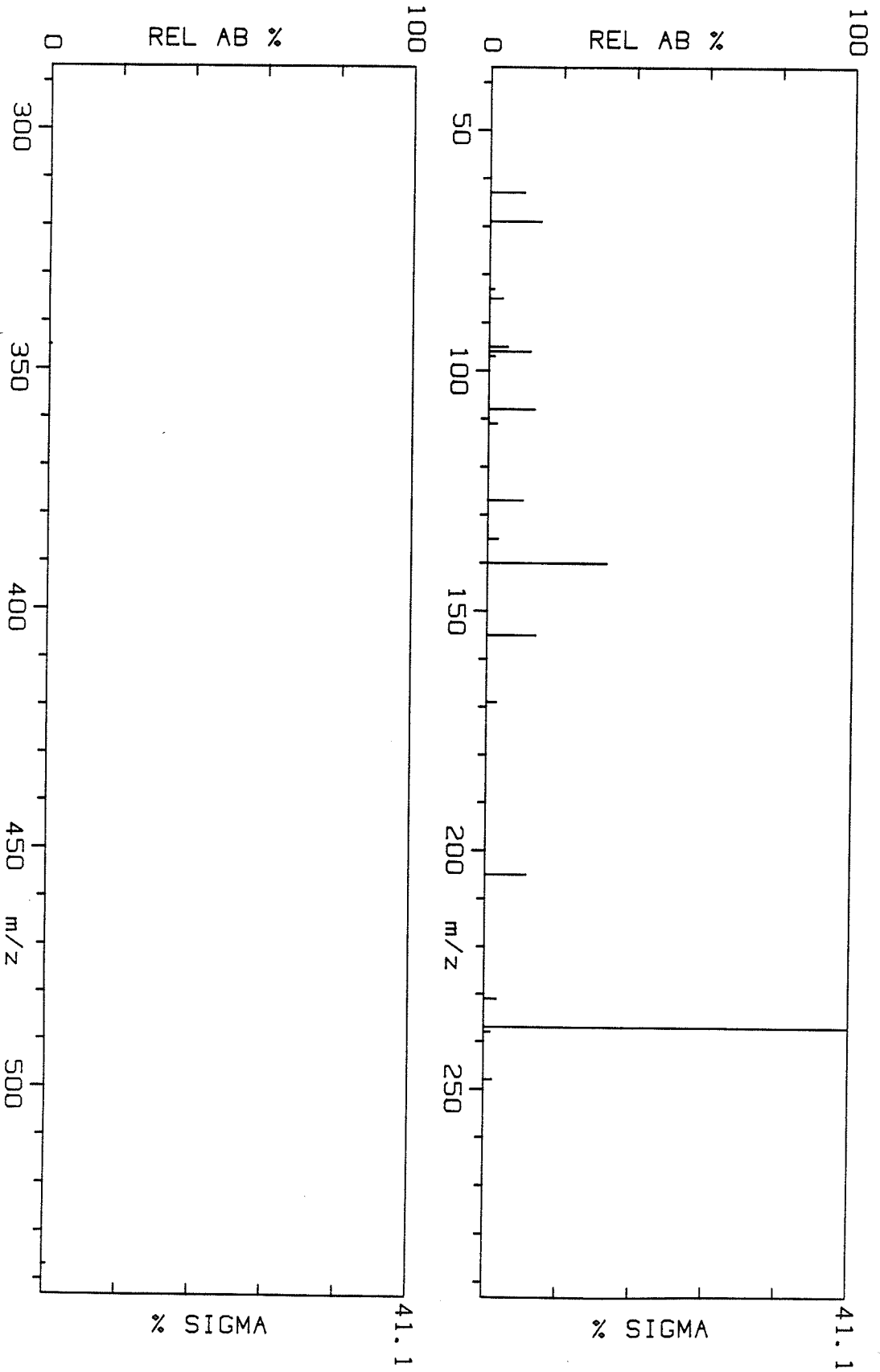


**Figure 120.**

Normalized 70 eV-EI mass spectrum of  
bis[1,1,1-trifluoro-4-mercapto-4-(2'-thienyl)-but-3-en-2-onato]Cu(II)  
{Cu-8b}.

$m/z$   $[M]^{+•} = 537$ ,  $[L]^+ = 237$

CU-88 70EV.

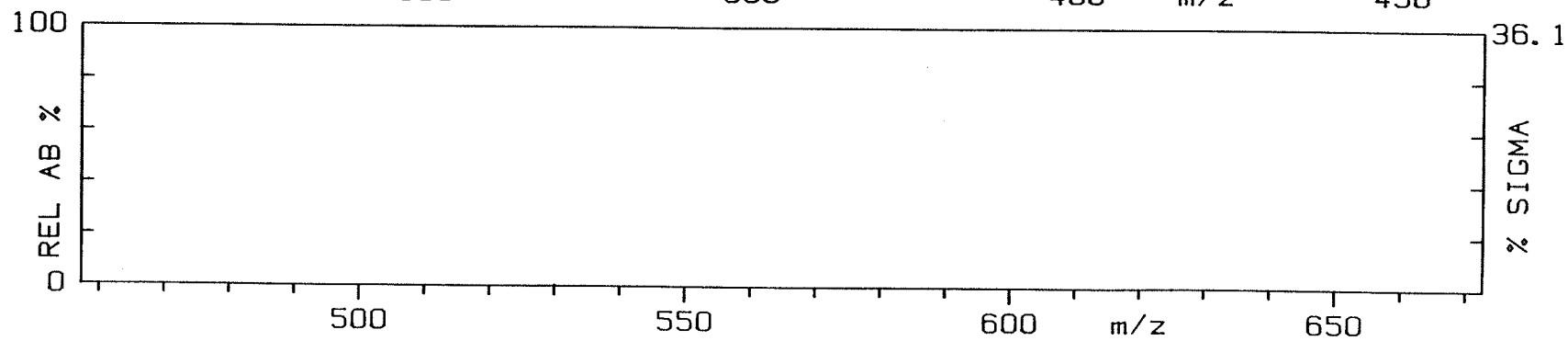
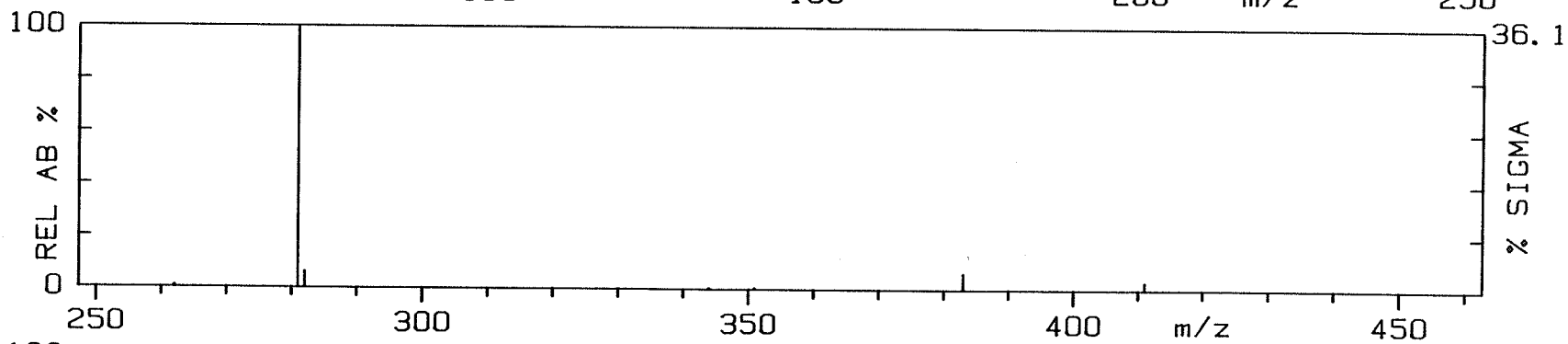
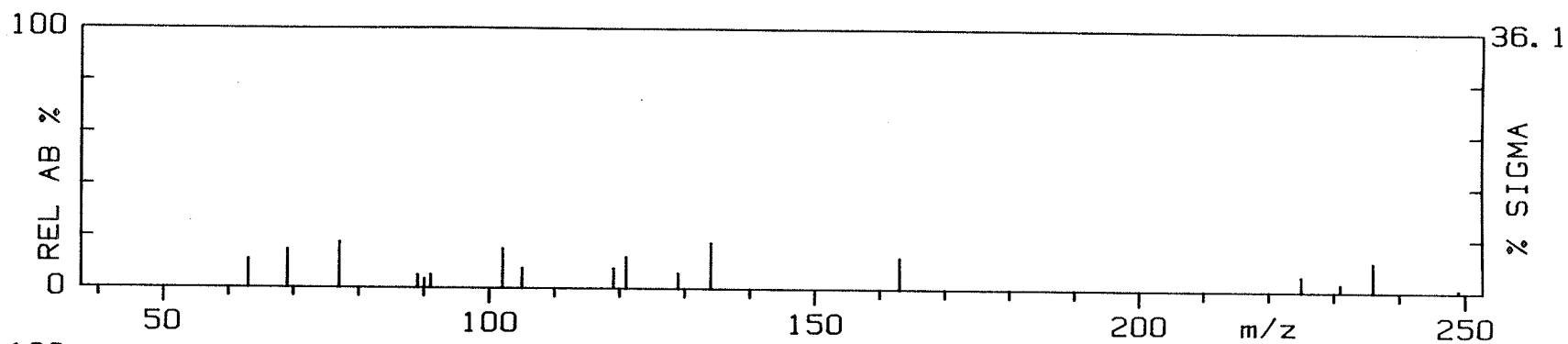


**Figure 121.**

Normalized 70 eV-EI mass spectrum of  
bis[1,1,1,2,2-pentafluoro-5-mercapto-5-phenyl-pent-4-en-3-onato]Cu(II)  
{Cu-13b}.

$m/z$   $[M]^{+}$  = 625,  $[L]^{+}$  = 281

CU-13B 70EV.



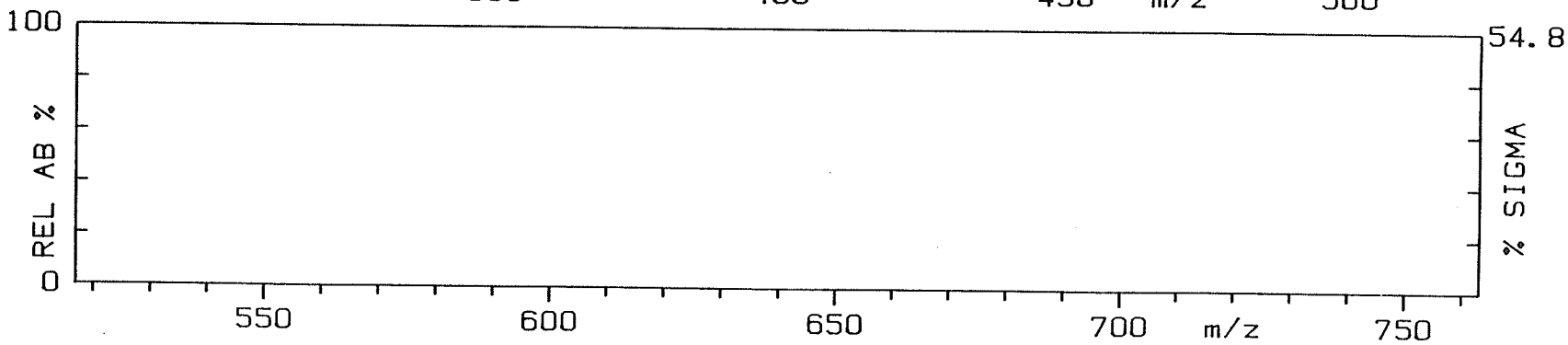
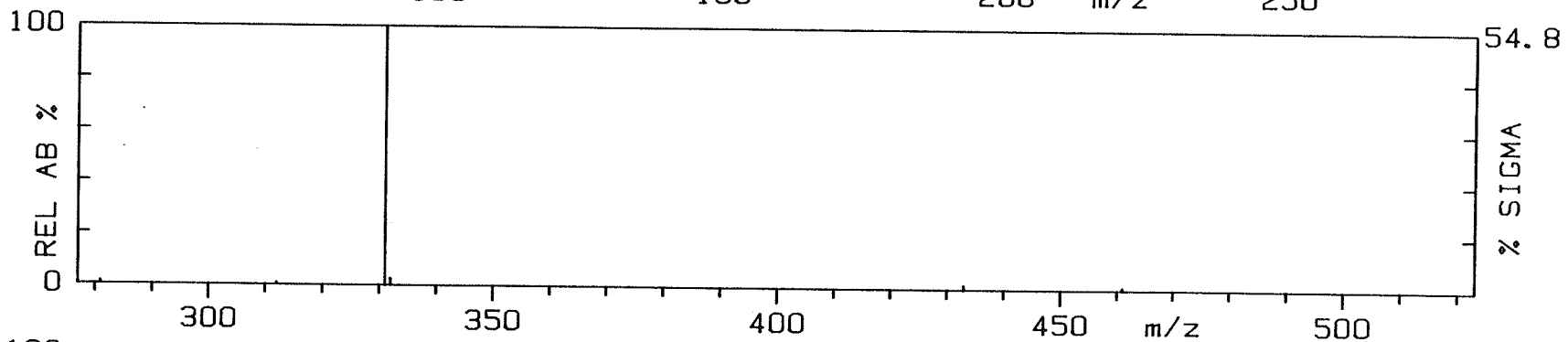
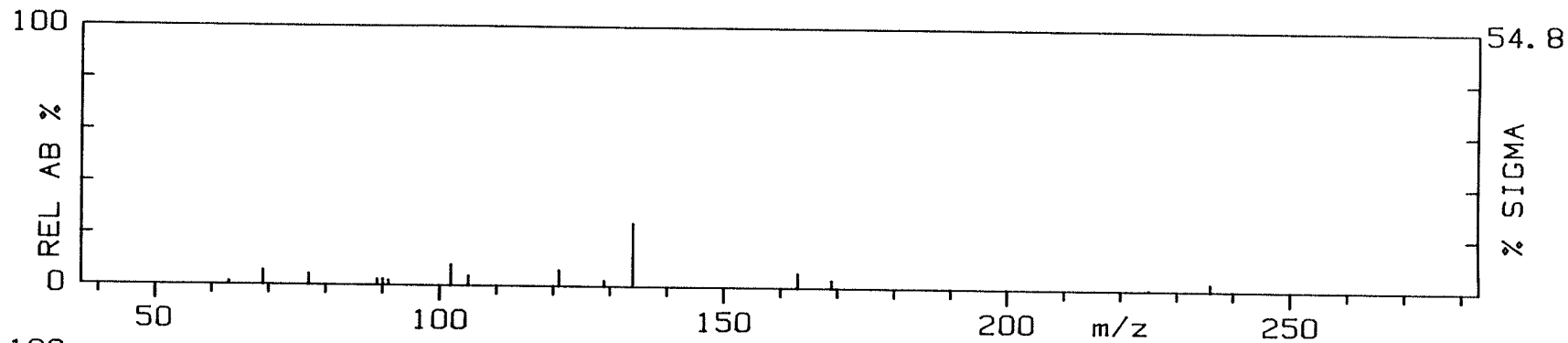
**Figure 122.**

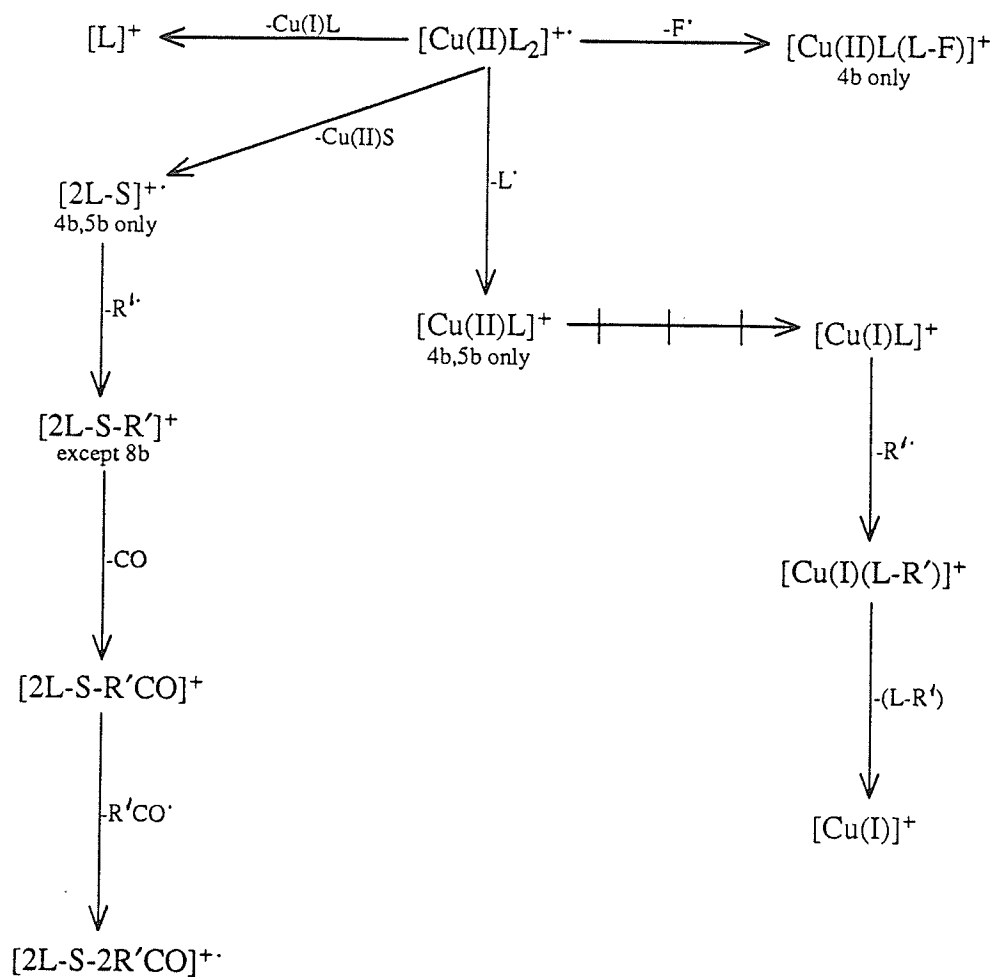
Normalized 70 eV-EI mass spectrum of  
bis[1,1,1,2,2,3,3-heptafluoro-6-mercapto-6-phenyl-  
hex-5-en-4-onato]Cu(II) (Cu-16b).

$m/z$   $[M]^{+}$  = 725,  $[L]^{+}$  = 331



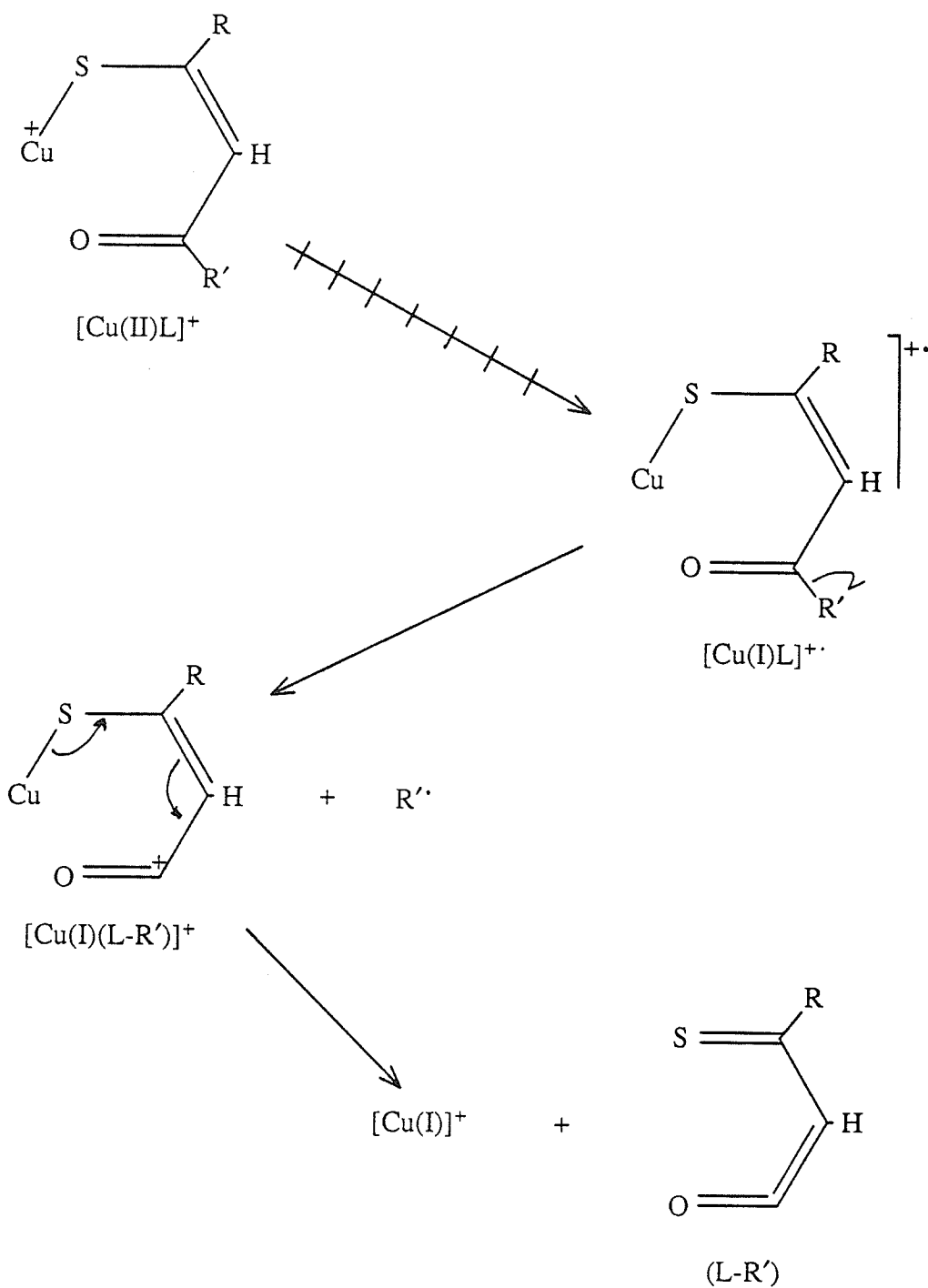
CU-16B 70EV.



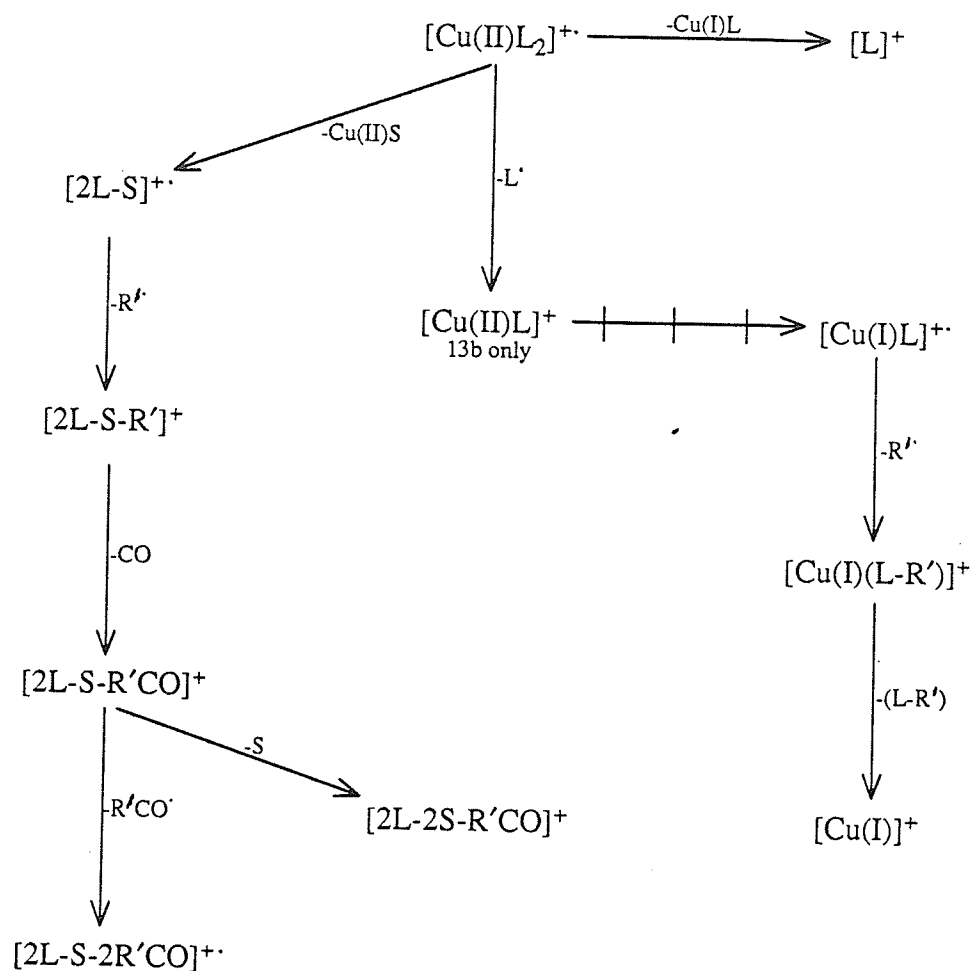


$\text{---} \rightarrow$  reaction step in which a change in metal oxidation state is proposed.

**Scheme 86.** Proposed fragmentation pathways for Cu(II) monothio- $\beta$ -diketonates where  $R' = CF_3$  (Cu-3b, -4b, -5b and -8b). Pathways are common to all complexes except where noted.



**Scheme 87.** Suggested mechanism for the formation of  $[Cu(I)]^+$  in **Cu-3b**, **-4b**, **-5b** and **-8b**.



$\text{---}$  reaction step in which a change in metal oxidation state is proposed.

**Scheme 88.** Proposed fragmentation pathways for Cu(II) monothio- $\beta$ -diketonates where  $\text{R}' = \text{C}_2\text{F}_5$  (Cu-13b) or  $\text{C}_3\text{F}_7$  (Cu-16b). Pathways are common to all complexes except where noted.

(e) Zn(II) Monothio- $\beta$ -diketonates

Relative abundance data for the five Zn(II) monothio- $\beta$ -diketonates studied appear in Tables 54 and 55. Plots of the EI mass spectra can be found in Figures 123-127. Metastable evidence was obtained through a linked-scanning study of **Zn-7b**. The mass spectra of complexes **Zn-3b** and **Zn-8b** have been obtained by Das and Livingstone (143).

Suggested ion decomposition pathways for the CF<sub>3</sub>-substituted zinc complexes (Tables 54 and 55) are given in Scheme 89. The most abundant metal-containing ions include [Zn(II)L<sub>2</sub>]<sup>+</sup>, [Zn(II)L(L-R')]<sup>+</sup>, [Zn(II)L]<sup>+</sup> and [Zn(II)F(L-R')]<sup>+</sup>; the mechanisms responsible for the formation of these and several other fragment ions shown in Scheme 89 have been discussed:

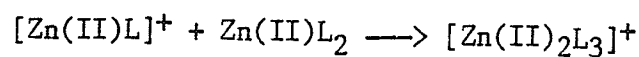
<u>Fragmentation</u>	<u>Scheme</u>
[Zn(II)L(L-R')] <sup>+</sup> → [Zn(II)LCHCR] <sup>+</sup>	66
[Zn(II)LCHCR] <sup>+</sup> → [Zn(II)L] <sup>+</sup>	66
[2L-S-R'CO] <sup>+</sup> → [2L-2S-R'CO] <sup>+</sup>	67
[Zn(II)L <sub>2</sub> ] <sup>+</sup> → [L] <sup>+</sup> + Zn(I)L	69
[Zn(II)L(L-R')] <sup>+</sup> → [Zn(II)L] <sup>+</sup>	83
[Zn(II)L <sub>2</sub> ] <sup>+</sup> → [2L-S-R'CO] <sup>+</sup>	85
[2L-S-R'CO] <sup>+</sup> → [2L-S-2R'CO] <sup>+</sup>	85

Mechanisms for the fragmentation of [Zn(II)L]<sup>+</sup> by the initial elimination of the EE<sup>0</sup> neutral CF<sub>2</sub> are illustrated in Schemes 90 and 91. The subsequent losses of either COS or HF from [Zn(II)F(L-R')]<sup>+</sup>

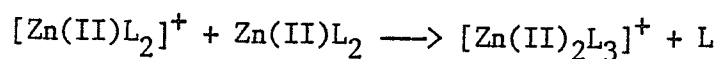
were not reported in the previous study of **Zn-3b** and **Zn-8b** (143). However, Livingstone and Moore (147) did record a similar reaction sequence in the mass spectrum of bis(1,1,1-trifluoro-4-mercapto-4-(2'-naphthyl)-but-3-en-2-onato)Zn(II). The ion  $[\text{Zn(II)F(L-R')}]^+$  can also arise via the unimolecular decomposition of either  $[\text{Zn(II)L}_2]^+$  or  $[\text{Zn(II)L(L-R')}]^+$ ; these processes, supported by metastable transitions, are described in Scheme 92.

An expansion of the experimental scan range during the mass spectral acquisition of **Zn-3b** resulted in the fortuitous observation of two Zn(II) polymer ions at  $m/z$  821 and 609, corresponding to the structures  $[\text{Zn(II)}_2\text{L}_3]^+$  and  $[\text{Zn(II)}_2\text{FL}_2]^+$ , respectively. Although the relative abundances were low (<5% of the base peak), careful examination of the isotopic envelopes revealed a good agreement between observed and calculated abundances, thus providing confirmation of the empirical formulae (see Figures 128 and 129). Polymeric ions have been observed in the mass spectra of metal acetylacetonates (105,179-181), but this appears to be the first report of such ion formation in metal monothio- $\beta$ -diketonates. In some cases, these ions are believed to be a result of the direct volatilization of the polymeric species from the solid state. However, monomeric complexes such as metal monothio- $\beta$ -diketonates can also generate polymeric ions through ion/molecule reactions in the ion source; the acute dependence of polymer ion abundance upon sample pressure in certain metal acetylacetonates is indicative of gas-phase polymerization (179,180). The precise nature of these ion/molecule reactions is not clear. For example, in the

formation of  $[\text{Zn}(\text{II})_2\text{L}_3]^+$ , a condensation reaction such as



is difficult to distinguish from a process such as



A decomposition of  $[\text{Zn}(\text{II})_2\text{L}_3]^+$  involving fluorine-to-metal migration may be responsible for the formation of  $[\text{Zn}(\text{II})_2\text{FL}_2]^+$  as shown in Scheme 93. This scheme also presents some suggested ion structures based on the premise of a bridging ligand; although not specifically illustrated, several canonical forms of both  $[\text{Zn}(\text{II})_2\text{L}_3]^+$  and  $[\text{Zn}(\text{II})_2\text{FL}_2]^+$  are probable.

Table 54. 70 eV-EI mass spectra of compounds Zn-3b, Zn-5b and Zn-7b.

ION	Zn-3b			Zn-5b			Zn-7b		
	%RA	m/z	%TIC	%RA	m/z	%TIC	%RA	m/z	%TIC
R =	-C <sub>6</sub> H <sub>5</sub>			-C <sub>6</sub> H <sub>4</sub> F			-C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub>		
R' =	-CF <sub>3</sub>			-CF <sub>3</sub>			-CF <sub>3</sub>		
[ZnL <sub>2</sub> ] <sup>+</sup> (a)	100.0	(526)	17.2	100.0	(562)	18.8	100.0	(586)	16.4
[ZnL(L-R')] <sup>+</sup> (b)	65.1	(457)	11.2	<sup>a</sup> 53.9	(493)	10.1	<sup>a</sup> 35.8	(517)	5.9
[ZnLCHCR] <sup>+</sup>	3.0	(397)	0.5	2.7	(433)	0.5	<sup>b</sup> 10.9	(457)	1.8
[ZnL] <sup>+</sup> (c)	71.8	(295)	12.3	74.4	(313)	14.0	<sup>a,b</sup> 54.6	(325)	9.0
[ZnF(L-R')] <sup>+</sup> (d)	45.5	(245)	7.8	<sup>b</sup> 47.2	(263)	8.9	<sup>*</sup> 41.8	(275)	6.9
[Zn(L-CF <sub>2</sub> -HF)] <sup>+</sup>	5.6	(225)	1.0	7.1	(243)	1.3	<sup>d</sup> 0.1	(255)	-
[ZnFCHCR] <sup>+</sup>	14.2	(185)	2.4	18.8	(203)	3.5	<sup>d</sup> 21.2	(215)	3.5
[2L-S-R'CO] <sup>+</sup>	-	(333)	-	-	(369)	-	6.0	(393)	1.0
[2L-2S-R'CO] <sup>+</sup>	1.2	(301)	0.2	-	(337)	-	7.5	(361)	1.3
[2L-S-2R'CO] <sup>+</sup>	1.3	(236)	0.2	-	(272)	-	17.5	(296)	2.9
[HL] <sup>+</sup>	6.9	(232)	1.2	3.3	(250)	0.6	8.7	(262)	1.4
[L] <sup>+</sup>	29.3	(231)	5.0	24.1	(249)	4.5	<sup>a</sup> 23.8	(261)	3.9
[L-F] <sup>+</sup>	40.7	(212)	7.0	32.4	(230)	6.1	<sup>a</sup> 21.6	(242)	3.5
[L-S] <sup>+</sup>	1.2	(199)	0.2	-	(217)	-	12.3	(229)	2.0
[L-COF <sub>2</sub> ] <sup>+</sup>	3.9	(165)	0.7	5.9	(183)	1.1	12.3	(195)	2.0
[HL-R'] <sup>+</sup>	6.9	(163)	1.2	-	(181)	-	8.9	(193)	1.5
[L-R'] <sup>+</sup>	7.2	(162)	1.2	5.4	(180)	1.0	-	(192)	-
[L-S-CF <sub>2</sub> ] <sup>+</sup>	13.1	(149)	2.2	10.3	(167)	1.9	24.4	(179)	4.0
[RCSCH] <sup>+</sup>	58.6	(134)	10.1	48.3	(152)	9.1	<sup>#</sup> 25.0	(164)	4.1



Table 54. (continued)

[RCS] <sup>a</sup>	44.6 (121)	7.7	36.1 (139)	6.8	#32.7 (151)	5.4
[RCO] <sup>a</sup>	9.5 (105)	1.6	9.4 (123)	1.8	#45.6 (135)	7.5
[RCCH] <sup>a</sup>	17.6 (102)	3.0	15.3 (120)	2.9	#36.8 (132)	6.0
[R] <sup>a</sup>	16.5 ( 77)	2.8	9.6 ( 95)	1.8	- (107)	-
[CSCHCO] <sup>a</sup>	5.0 ( 85)	0.9	10.2 ( 85)	1.9	31.4 ( 85)	5.2
[R'] <sup>a</sup>	14.3 ( 69)	2.5	17.8 ( 69)	3.3	30.2 ( 69)	5.0

<sup>a</sup> Identified metastable transitions are indicated by superscripts which relate the daughter ion to its precursor as labelled in column 1.

\* daughter ion of (a),(b) and (c).

# daughter ion of (a),(b),(c) and (d).

Table 55. 70 eV-EI mass spectra of compounds Zn-8b and Zn-9b.

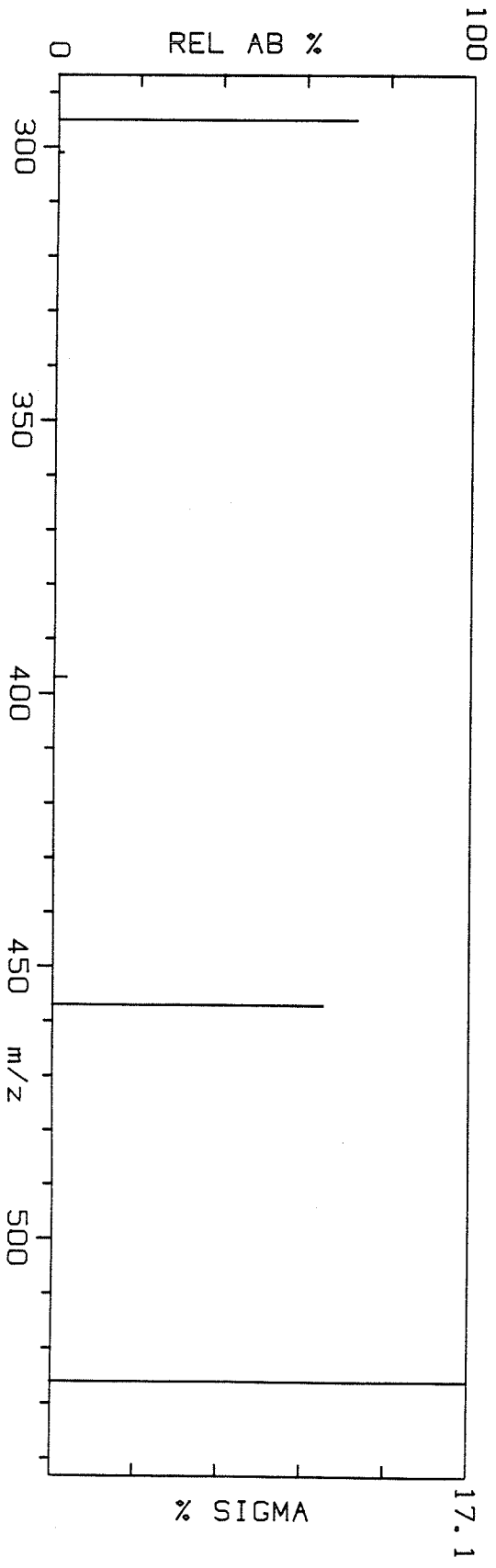
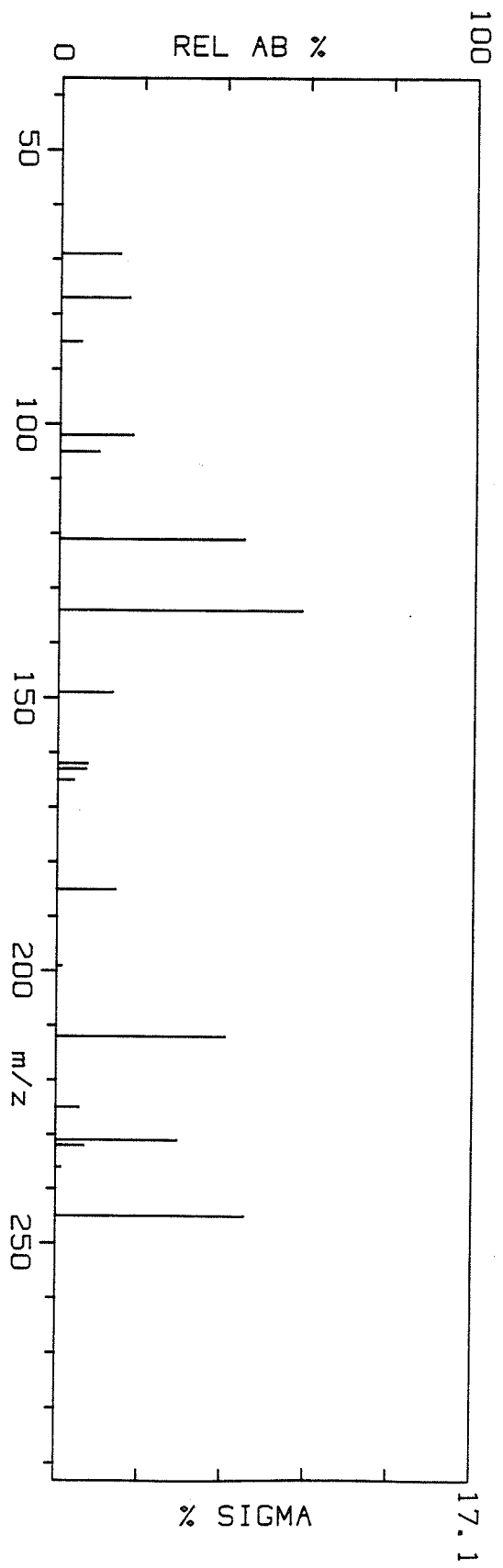
ION	Zn-8b			Zn-9b		
	%RA	m/z	%TIC	%RA	m/z	%TIC
R =		$-C_4H_3S$			$-C_4H_2SCH_3$	
R' =		$-CF_3$			$-CF_3$	
$[ZnL_2]^+$	45.9 (538)	12.7		34.7 (566)	11.6	
$[ZnL(L-R')]^+$	12.0 (469)	3.3		10.0 (497)	3.3	
$[ZnLCHCR]^+$	2.0 (409)	0.6		3.9 (437)	1.3	
$[ZnL]^+$	41.3 (301)	11.5		42.2 (315)	14.1	
$[ZnF(L-CF_3)]^+$	31.1 (251)	8.6		26.4 (265)	8.8	
$[Zn(L-CF_2-HF)]^+$	3.7 (231)	1.0		2.0 (245)	0.7	
$[ZnFCHCR]^+$	10.8 (191)	3.0		8.3 (205)	2.8	
$[2L-2S-R'CO]^+$	3.7 (313)	1.0		- (341)	-	
$[HL]^+$	2.0 (238)	0.6		7.4 (252)	2.5	
$[L]^+$	11.6 (237)	3.2		8.6 (251)	2.9	
$[L-F]^+$	7.0 (218)	1.9		4.1 (232)	1.4	
$[L-S]^+$	100.0 (205)	27.7		100.0 (219)	33.5	
$[HL-R']^+$	- (169)	-		4.5 (183)	1.5	
$[L-S-CF_2]^+$	6.7 (155)	1.9		4.4 (169)	1.5	
$[RCSCH]^+$	24.0 (140)	6.7		9.3 (154)	3.2	
$[RCS]^+$	18.8 (127)	5.2		11.2 (141)	3.8	
$[RCO]^+$	- (111)	-		3.5 (125)	1.2	
$[RCCH]^+$	14.5 (108)	4.0		7.5 (122)	2.6	
$[R]^+$	9.9 ( 83)	2.7		2.8 ( 97)	1.0	
$[CSCHCO]^+$	- ( 85)	-		4.4 ( 85)	1.5	
$[R']^+$	15.4 ( 69)	4.3		3.6 ( 69)	1.2	

**Figure 123.**

Normalized 70 eV-EI mass spectrum of  
bis[1,1,1-trifluoro-4-mercapto-4-phenyl-but-3-en-2-onato]Zn(II)  
{Zn-3b}.

$m/z$   $[M]^+$  = 526,  $[L]^+$  = 231

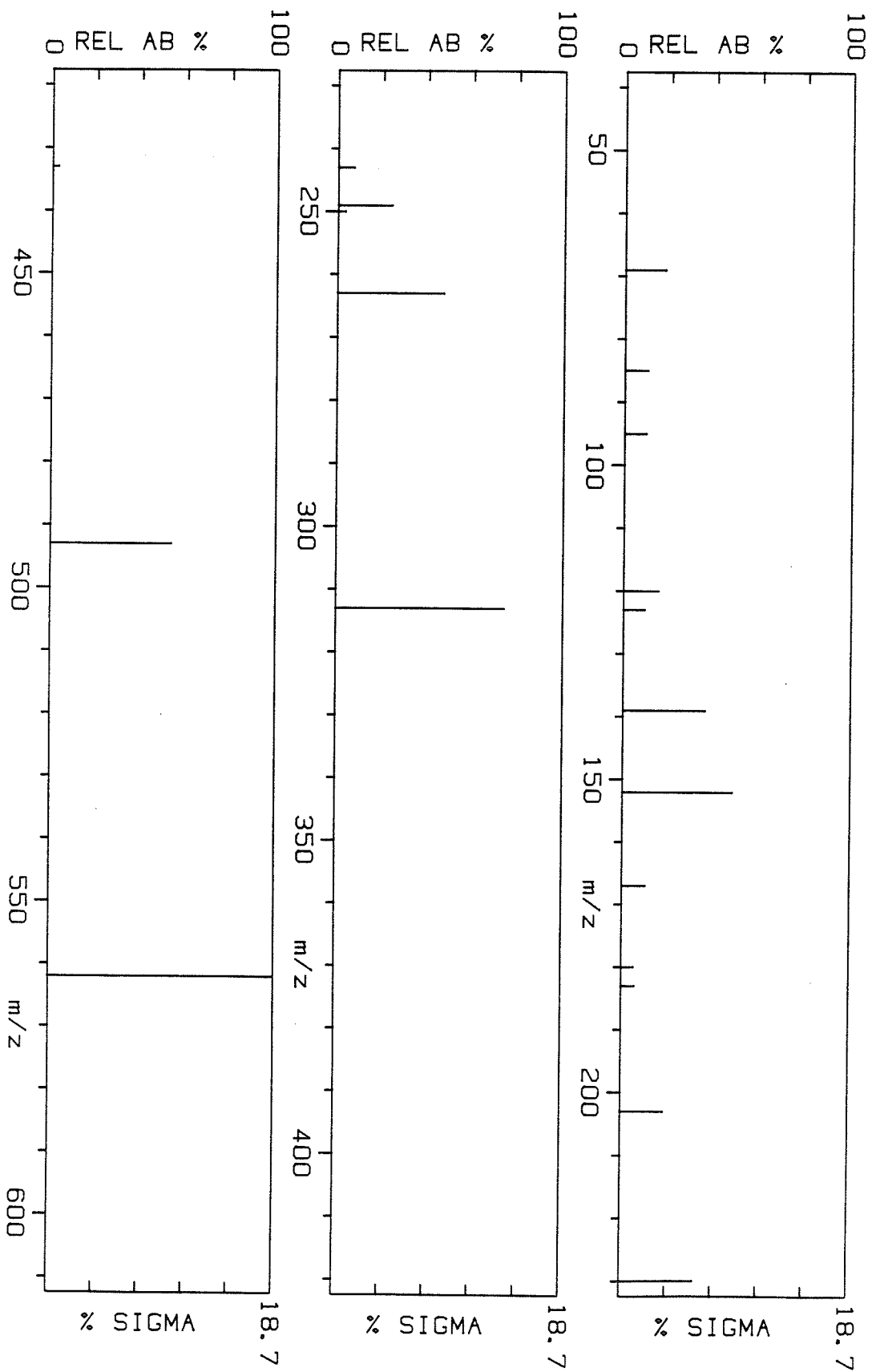
ZN-3B 70EV.



**Figure 124.**

Normalized 70 eV-EI mass spectrum of  
bis[1,1,1-trifluoro-4-mercapto-4-(4'-fluorophenyl)-  
but-3-en-2-onato]Zn(II) (Zn-5b).  
 $m/z$   $[M]^+$  = 562,  $[L]^+$  = 249

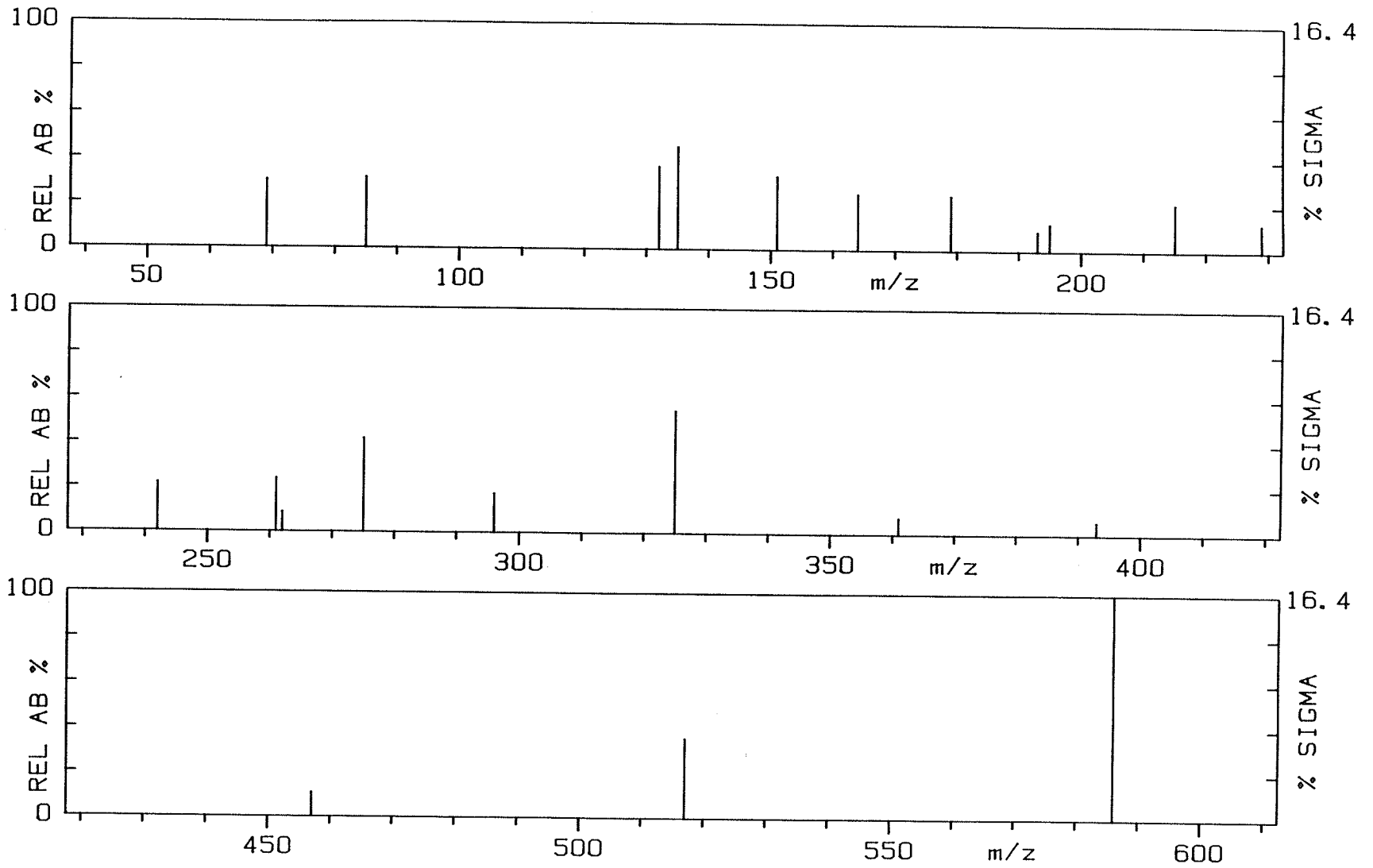
ZN-58 70EV.



**Figure 125.**

Normalized 70 eV-Ei mass spectrum of  
bis[1,1,1-trifluoro-4-mercapto-4-(4'-methoxyphenyl)-  
but-3-en-2-onato]Zn(II) (Zn-7b).  
 $m/z$   $[M]^{+}$  = 586,  $[L]^{+}$  = 261

ZN-7B 70EV.



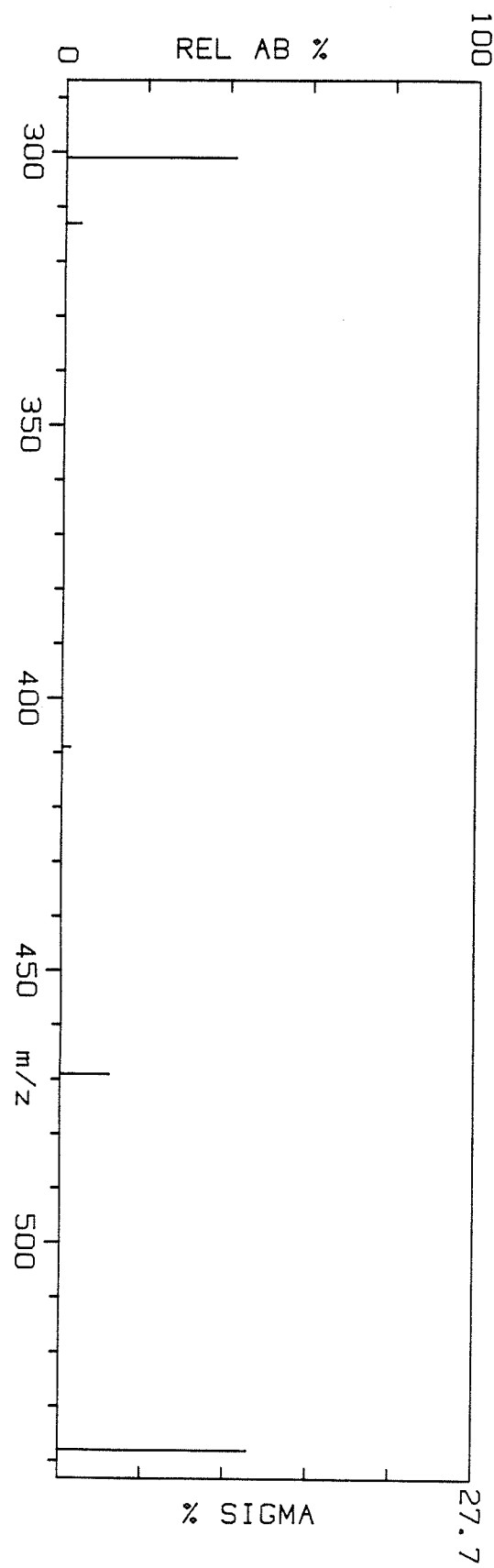
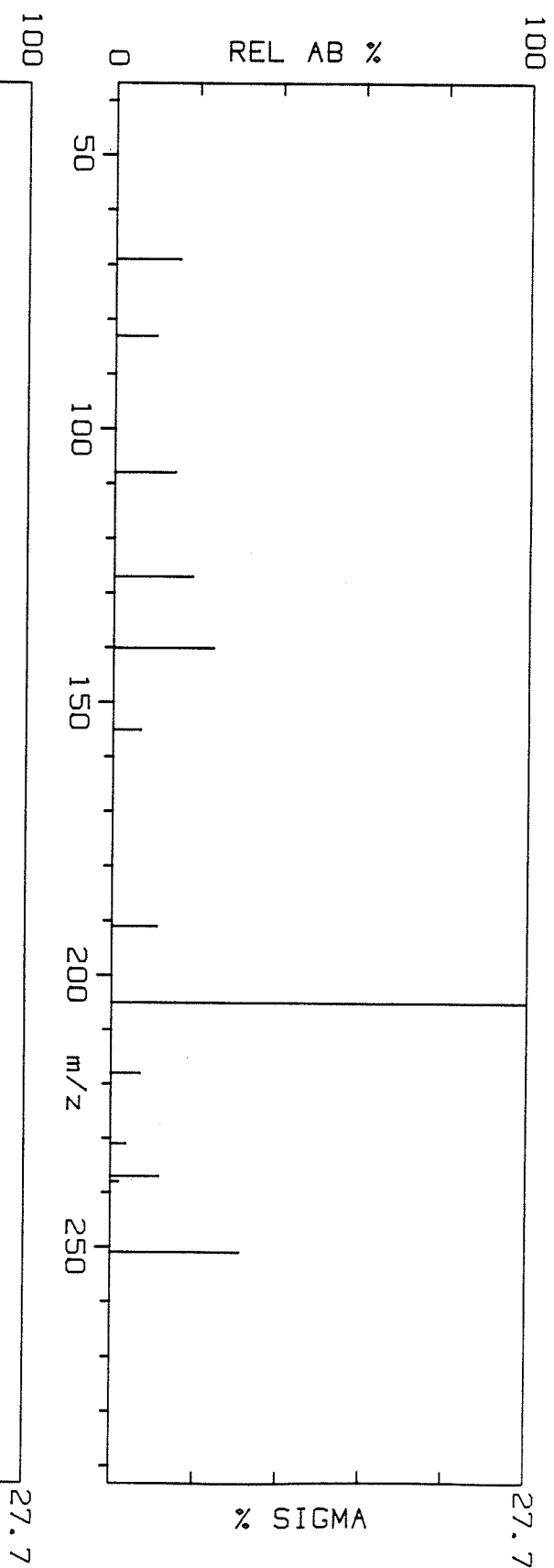


**Figure 126.**

Normalized 70 eV-EI mass spectrum of  
bis[1,1,1-trifluoro-4-mercapto-4-(2'-thienyl)-but-3-en-2-onato]Zn(II)  
{Zn-8b}.

$m/z$   $[M]^{++} = 538$ ,  $[L]^+ = 237$

ZN-88 70EV.

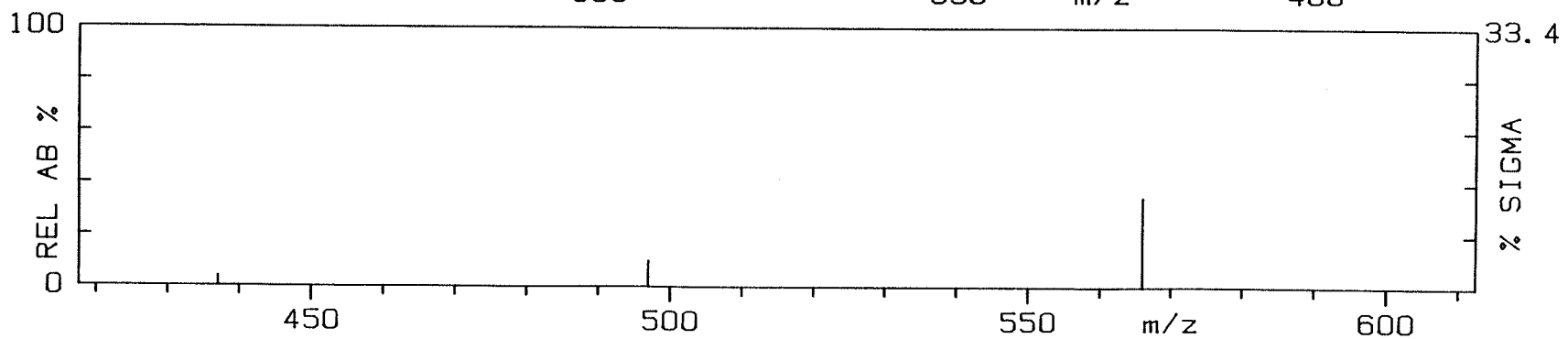
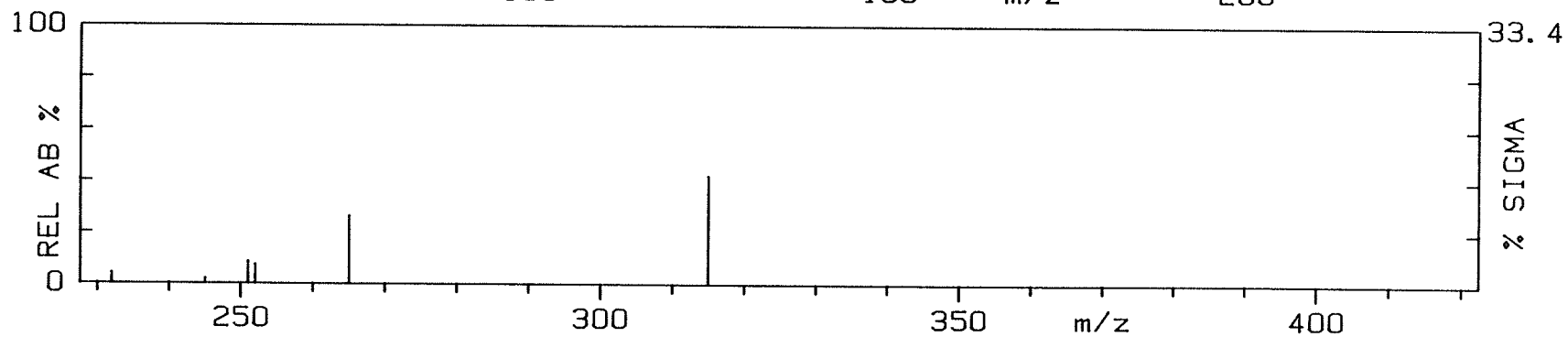
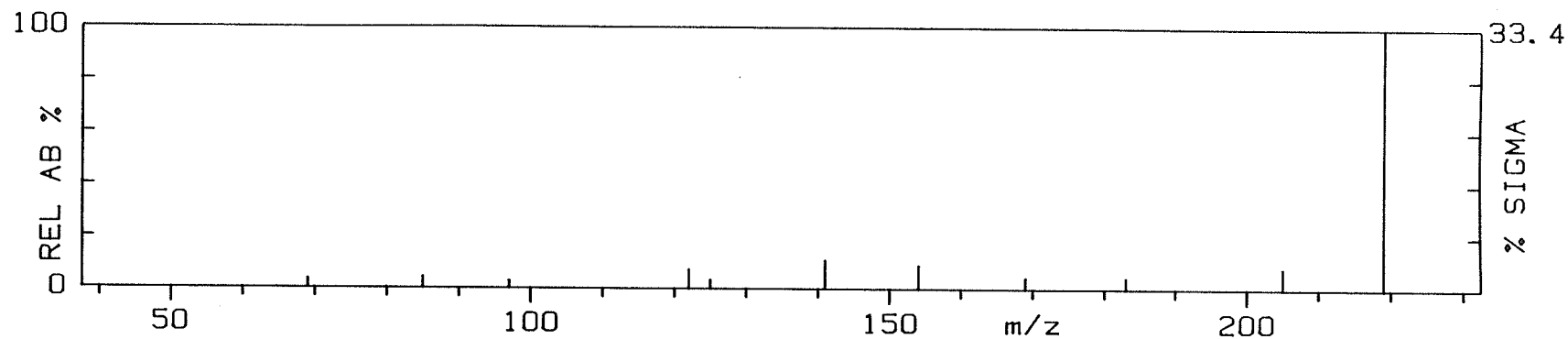


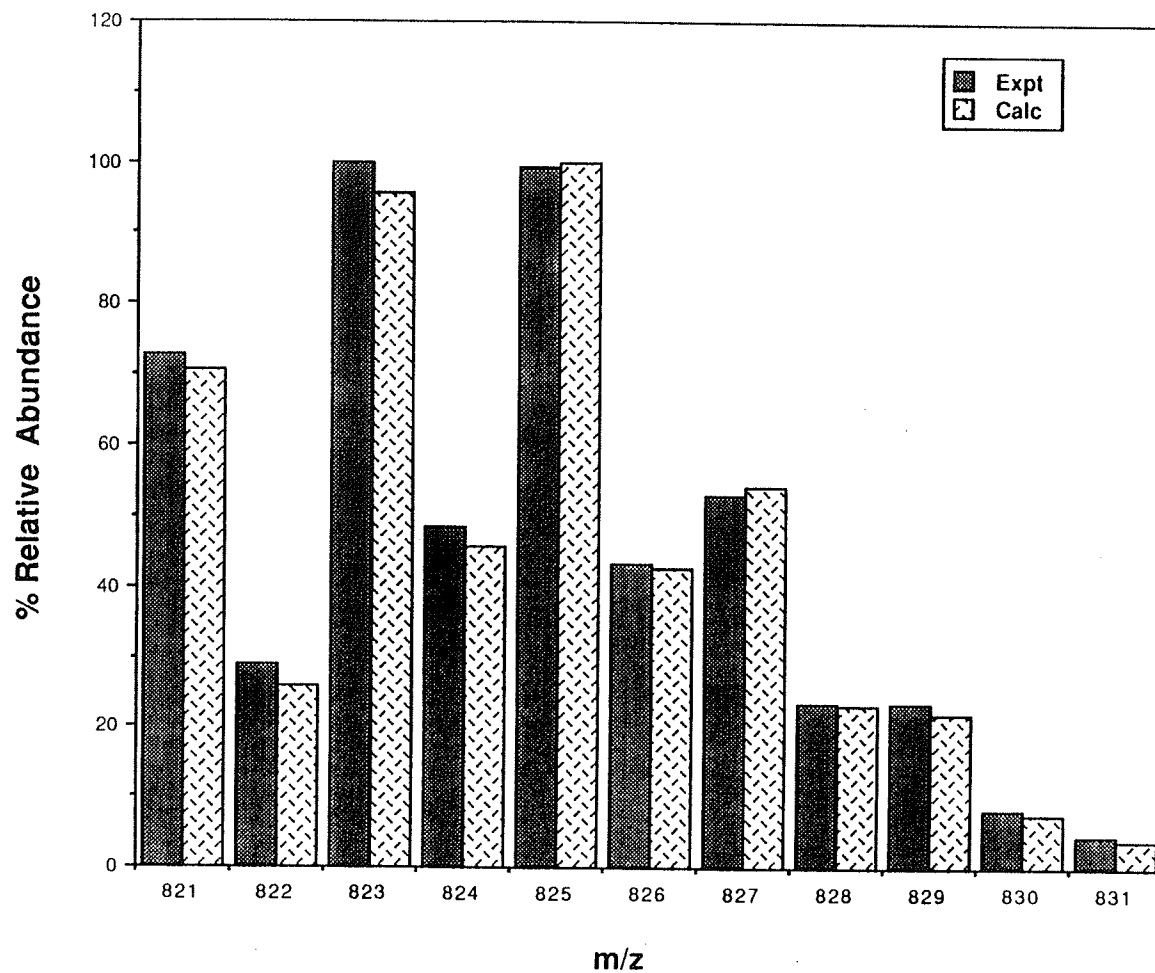
**Figure 127.**

Normalized 70 eV-EI mass spectrum of  
bis[1,1,1-trifluoro-4-mercapto-4-(5'-methyl-2'-thienyl)-  
but-3-en-2-onato]Zn(II) {Zn-9b}.

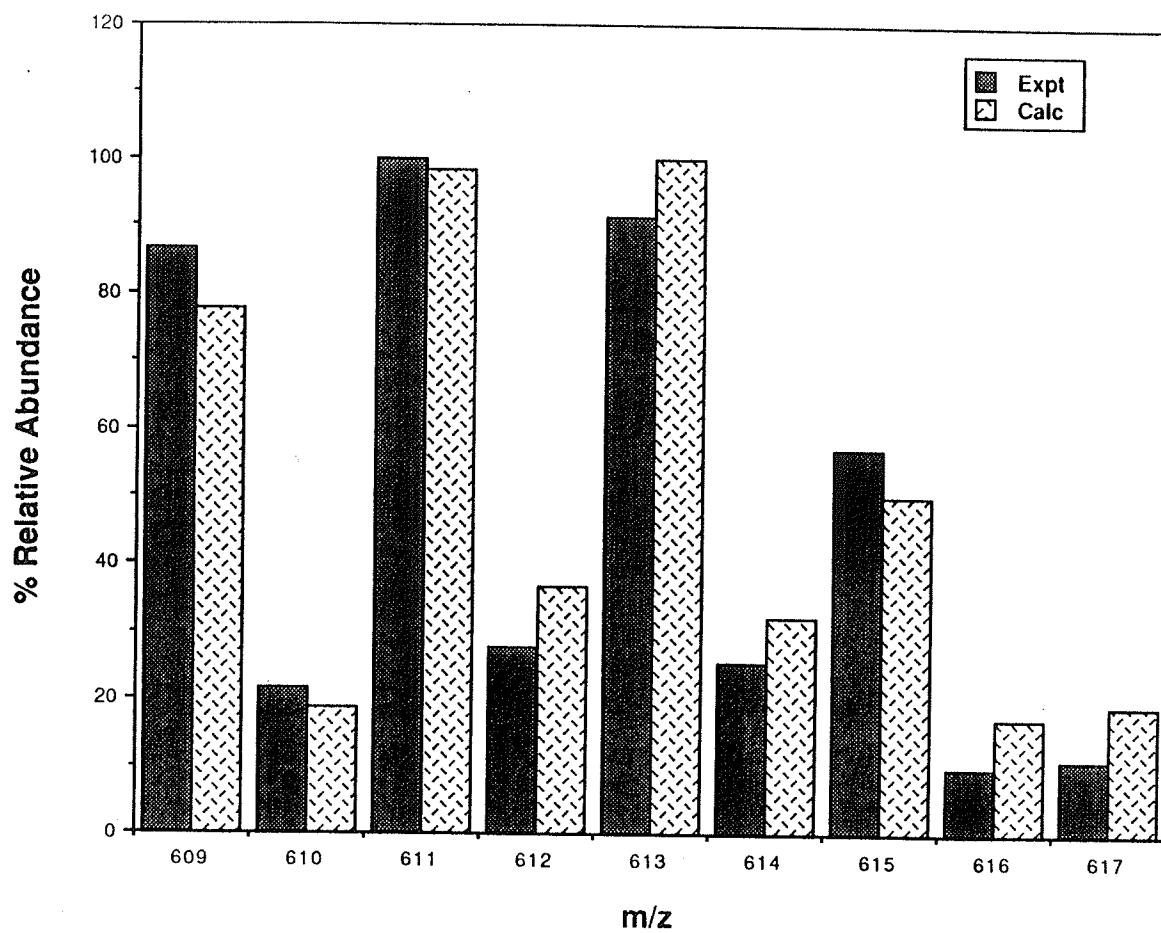
$m/z$   $[M]^{+}$  = 566,  $[L]^{+}$  = 251

ZN-9B 70EV.

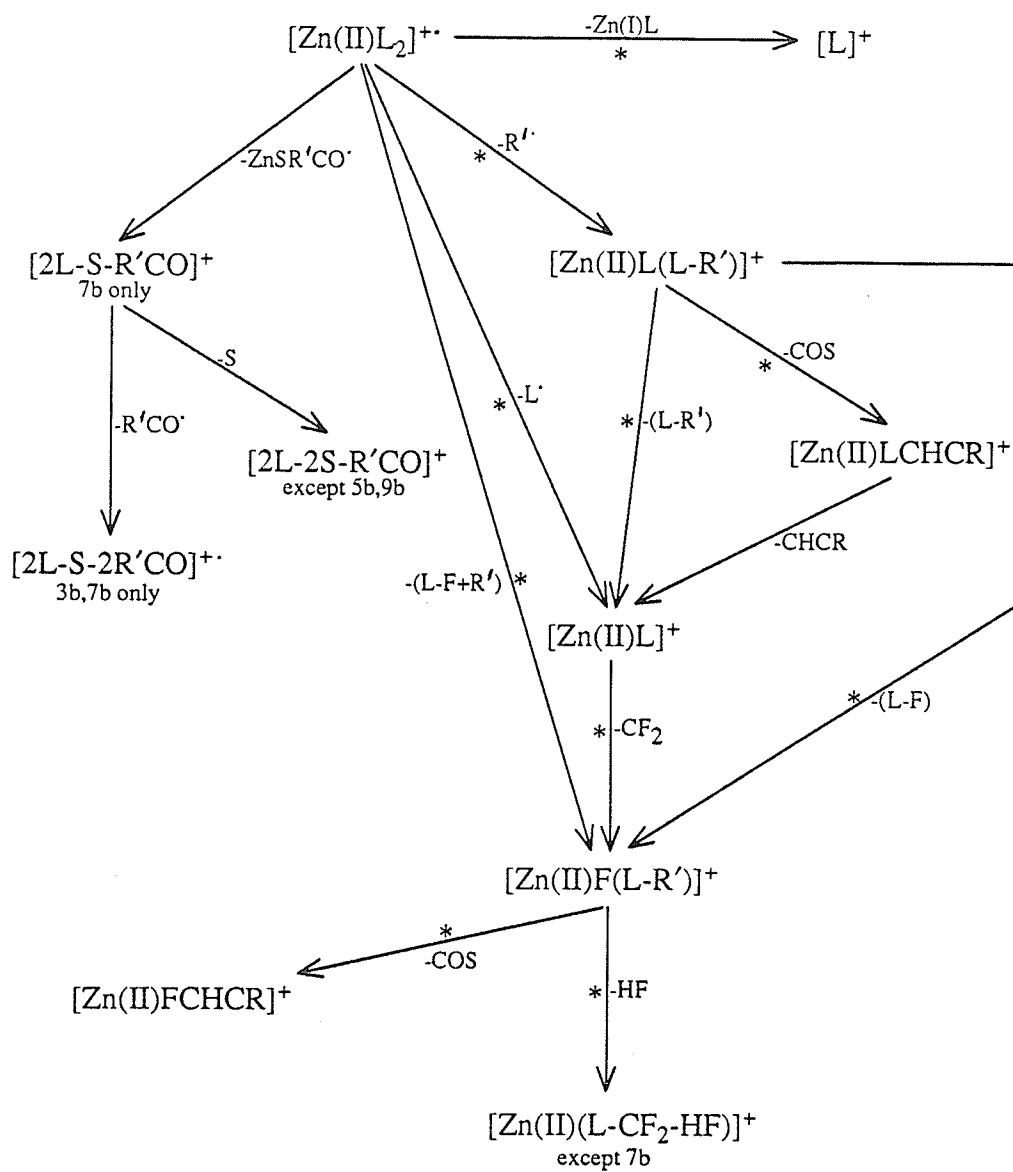




**Figure 128.** Comparison of experimental and calculated isotopic envelope distribution for the cluster ion  $[\text{Zn}(\text{II})_2\text{L}_3]^+$ .

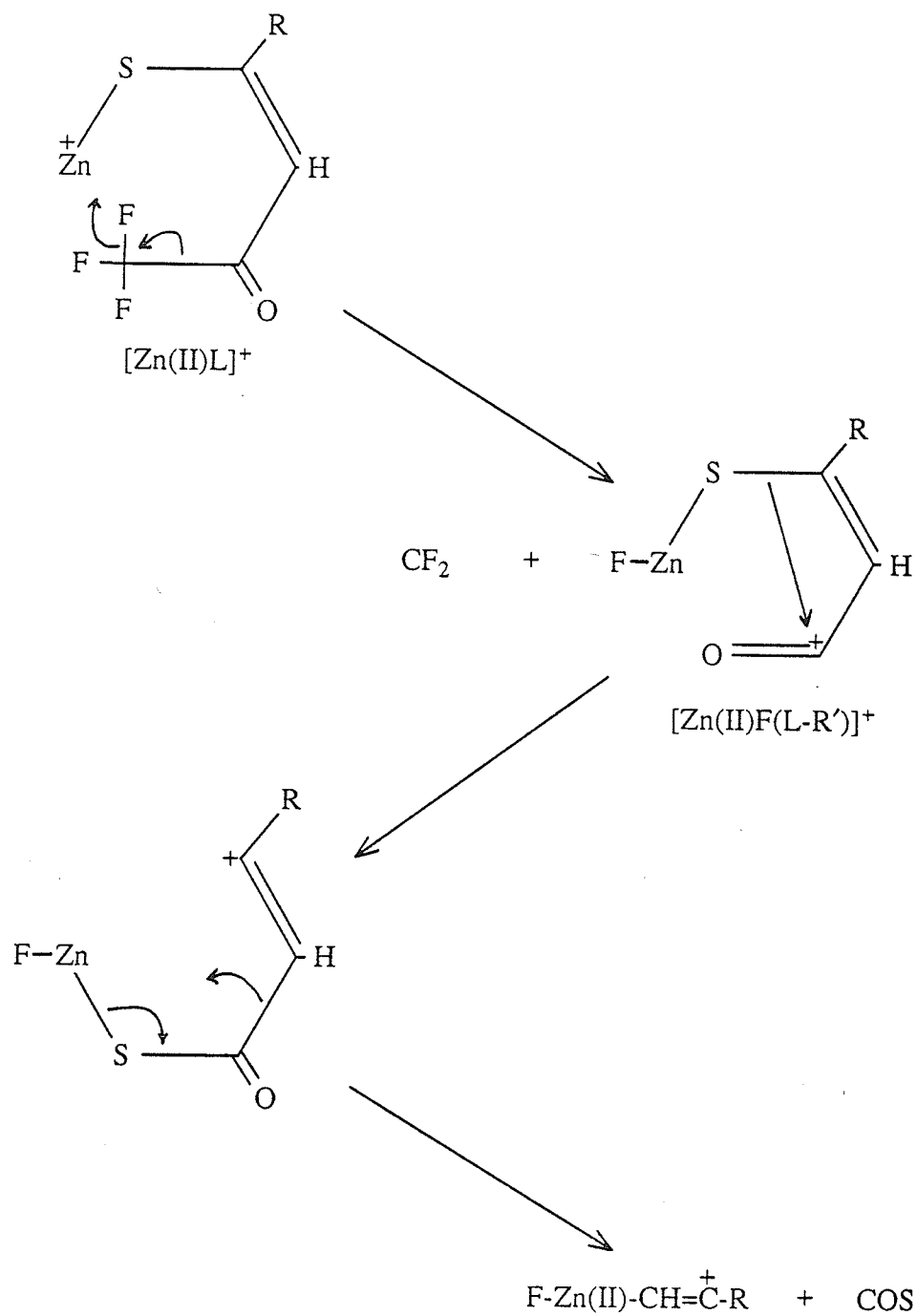


**Figure 129.** Comparison of experimental and calculated isotopic envelope distribution for the cluster ion  $[\text{Zn}(\text{II})_2\text{FL}_2]^+$ .



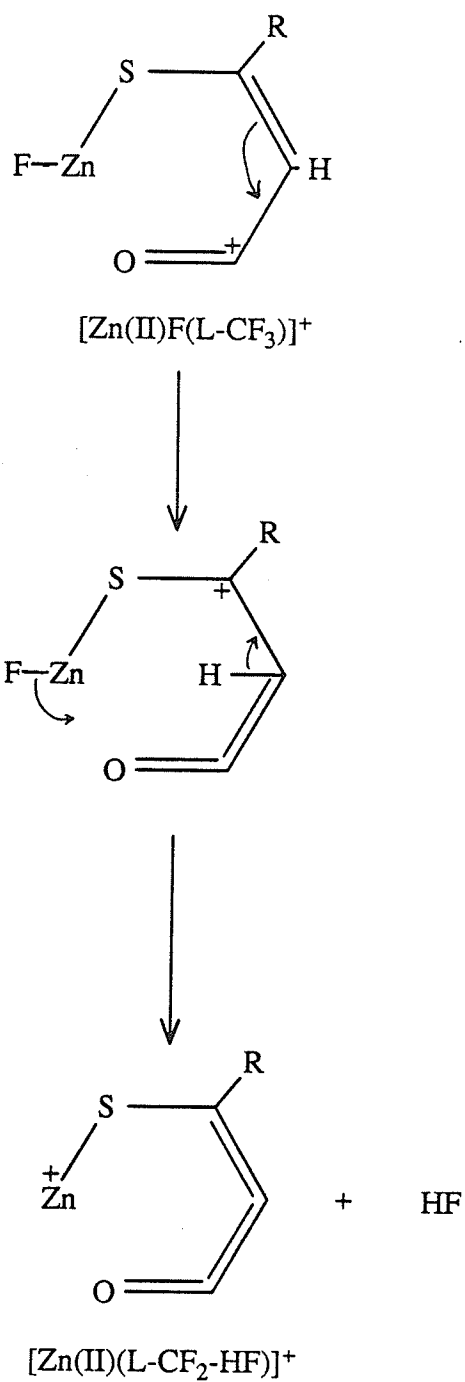
\* process confirmed by the observation of a metastable transition in at least one of the complexes.

**Scheme 89.** Proposed fragmentation pathways for Zn(II) monothio- $\beta$ -diketonates where  $R' = CF_3$  (Zn-3b, -5b, -7b, -8b and -9b). Pathways are common to all complexes except where noted.

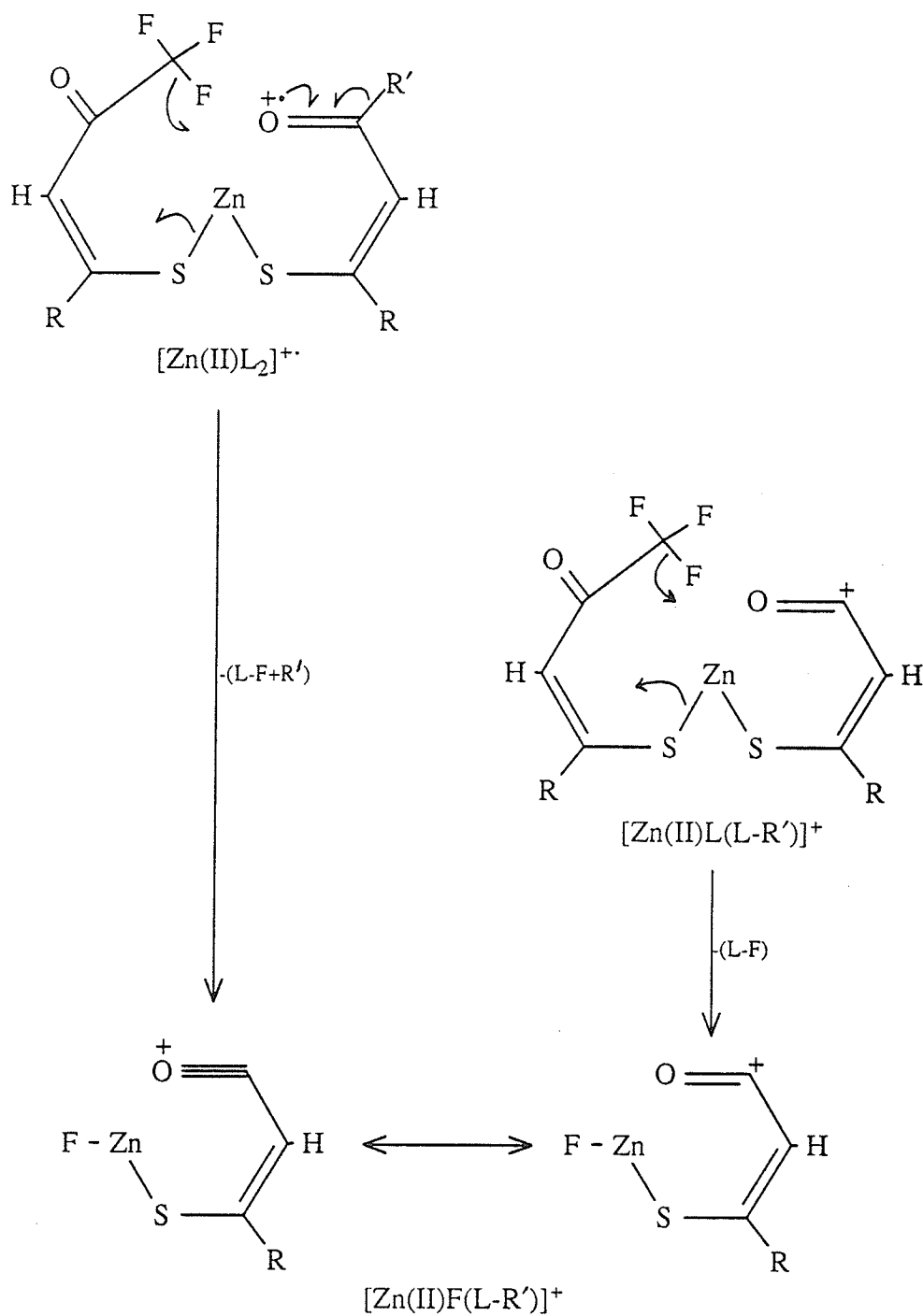


**Scheme 90.** Suggested mechanism for the formation of  $[Zn(II)F(L-R')]^+$  and  $[Zn(II)FCHCR]^+$  in Zn-3b, -5b, -7b, -8b and -9b.

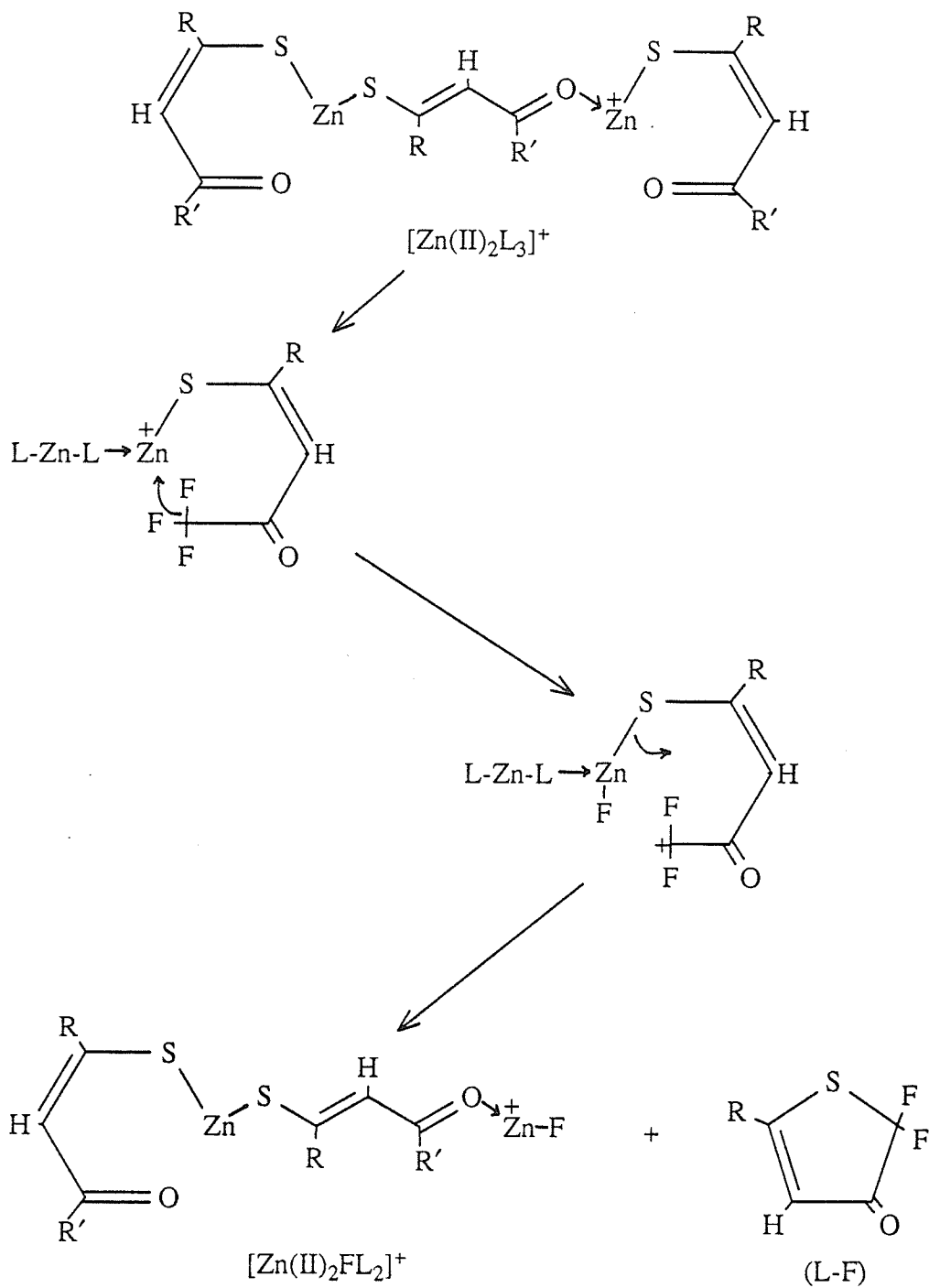




**Scheme 91.** Suggested mechanism for the formation of  $[\text{Zn(II)(L-CF}_2\text{-HF)}]^+$  in **Zn-3b**, **-5b**, **-7b**, **-8b** and **-9b**.



**Scheme 92.** Suggested mechanism for the formation of  $[Zn(II)F(L-R')]^+$  in Zn-3b, -5b, -7b, -8b and -9b.



**Scheme 93.** Suggested mechanism for the formation of  $[Zn(II)_2FL_2]^+$  from  $[Zn(II)_2L_3]^+$  in Zn-3b.

#### D. SUMMARY

The mass spectra of ninety-nine metal  $\beta$ -diketonates and monothio- $\beta$ -diketonates have been examined in this work. All of the complexes are similar in structure, but at the same time unique in composition. Their uniqueness stems from four factors: (i) the central metal, (ii) the aryl substituents (R groups), (iii) the fluorinated alkyl substituents (R' groups), and (iv) the sets of ligand donor atoms (either O,O or O,S). As the ultimate aim of this study is to assess each factor's contribution to the observed mass spectra, each will be reviewed in turn.

##### (1) The Central Metal

The seven metals used in this study were chosen, in part, for their diversity; they include main group (Al(III), Ga(III) and Zn(II)), first transition series (Co(III), Ni(II) and Cu(II)) and second transition series elements (Pd(II)). Their influence on the fragmentation patterns can be divided into two general categories: valence stability and hardness/softness. In those complexes in which the metal is resistant to a change in oxidation state (Al(III), Ga(III), Pd(II) and Zn(II)), fragmentation from the  $OE^+$  molecular ion normally proceeds through the elimination of an  $OE'$  neutral (typically  $L'$ ,  $F'$  or  $R''$ ), followed by one or more  $EE^0$  neutral losses. On the other hand, the Co(III) and Cu(II) chelates, which are readily reduced, fragment by the

elimination of two  $OE^\cdot$  radicals from  $[M]^{+}$ . This process is presumed to involve a reduction of the metal after the loss of the initial radical species. Subsequent decomposition in these complexes occurs through the loss of  $EE^0$  neutrals or, as in the case of cobalt, a third  $OE^\cdot$  radical may be lost, indicating a further reduction to the Co(I) oxidation state. In the nickel chelates, the +II state appears to dominate, although some important Ni(I) structures are proposed for the monothio- $\beta$ -diketonates.

Ions arising from fluorine-to-metal migration occur with varying frequency and abundance throughout the recorded mass spectra. A rationale for this behavior can be found in the Hard/Soft Acid/Base Principle. Upon close examination, it is apparent that the extent of fluorine transfer for a given complex parallels the established hardness of the metal acceptor involved. For example, fluorine migration is widespread in the Al(III) and Ga(III)  $\beta$ -diketonates (both classified as hard acids), but suppressed in the chelates of Pd(II), a soft acid. Ni(II), Cu(II) and Zn(II) are all borderline acids and as such exhibit only a moderate attraction for the hard fluorine base. The cobalt complexes are more difficult to categorize; although Co(III) is a hard acid and as such should bind effectively with fluorine, it is so rapidly reduced to the softer Co(II) state that relatively few Co(III)-F complexes are detected.

The existence of  $[Met(II)R]^+$  bonded species in the  $\beta$ -diketonate series also seems to be dependent upon the nature of the metal, in particular the d electron population. The only complexes not

exhibiting  $[\text{Met(II)R}]^+$  ions are those derived from aluminum, which also happens to be the only metal lacking at least a partially-filled d shell. This combined with the large abundance of  $[\text{Met(II)R}]^+$  (and related species) found in the Pd(II) spectra would suggest that metal-aryl  $\pi$ -bonding is responsible for the formation of these species. Two bonding components are central to this type of interaction: (a) the overlap of the  $\pi$ -electron density of the aryl group with a vacant  $\pi$ -type acceptor orbital on the metal atom, and (b) a "back-bond" resulting from the flow of electron density from the filled metal d orbitals into suitable  $\pi^*$  (antibonding) acceptor orbitals located on the carbon atoms.

## (2) The R (Aryl) Substituent

Of the ten aromatic or substituted-aromatic substituents used in this study, all have a pronounced influence upon the rate of formation of fluorine-transfer fragment ions. The stability of these metal-fluorine bonded species appears to directly reflect the inductive nature of the R group; the more strongly electron-withdrawing the R group, the greater the abundance of ions derived from fluorine migration. This phenomenon can be viewed as an example of the HSAB symbiotic effect, in which the introduction of hard, non-polarizable substituents into a molecule enhances the hardness of a given site (i.e. metal), thereby inducing greater hard-hard acid-base interactions. Based on observed ion stabilities (and some inferences regarding the inductive capabilities of the R groups), an approximate

ordering of the aryl substituents can be proposed: 4-methoxyphenyl < 4-methylphenyl < phenyl = 2-naphthyl < 4-chlorophenyl < 5-methyl-2-thienyl < 4-fluorophenyl < 5-chloro-2-thienyl < 2-thienyl < 2-furyl.

Resonance charge stabilization by proximal aryl groups is crucial to the formation of many ions. The lone pair resonance provided by the heterocyclic R groups (eg. 2-thienyl, 2-furyl) is particularly important in ions such as  $[\text{Pd(II)(L-O)}]^+$  (palladium  $\beta$ -diketonates),  $[\text{Zn(II)LCHCR}]^+$  (zinc  $\beta$ -diketonates) and  $[\text{Co(II)LCHCR}]^+$  (cobalt  $\beta$ -diketonates).

The nature of the R group also plays a role in the formation of ions resulting from hydrogen transfer processes. For example, there is an increase in the abundance of  $[\text{MetHL}]^+$  (Met = Ni, Cu) when R = phenyl or 2-naphthyl, indicating that ortho hydrogen transfer makes a significant contribution to the overall mechanism of H-transfer in these complexes. As well, electron-releasing aryl substituents are believed to promote the nickel +I oxidation state in  $[\text{Ni(L-H)}]^+$  ions (nickel monothio- $\beta$ -diketonates) by increasing the effective charge density on the metal-bonded sulfur atom.

### (3) The R' Substituents

Several trends become evident when differentiating between spectra on the basis of the fluoroalkyl substituents. In the  $\beta$ -diketonates, fluorine-to-metal migrations generally decrease in both number and significance with increasing fluorination of R'. It is believed that

the more highly electronegative penta- and heptafluorinated R' groups become effective competitors with the metal for the migrating fluorine. Oddly enough however, the opposite tendencies are shown in the monothio- $\beta$ -diketonates, where fluorine transfer is more common in the  $-C_2F_5$  and  $-C_3F_7$  derivatives than for their  $-CHF_2$  and  $-CF_3$  counterparts. This apparent anomaly may be attributed to the higher fluorinated groups having a greater influence in reducing the electron density on the metal-bonded sulfur (thereby hardening the metal) than in retaining the transferable fluorine. Extending this work to complexes possessing a wider variety of ring donor atoms and R' groups might help to clarify this situation.

In spectra where trivalent ion structures are proposed (especially those involving Co(III) and Ni(II)), the inductive power of the  $-C_2F_5$  and  $-C_3F_7$  groups appear to stabilize the higher valency forms by reducing the electron density in the quasi-aromatic chelate rings.

#### (4) Ligand Donor Atoms

The introduction of sulfur into the chelate ring has a marked influence on the nature of the fragmentation. For example, loss of elemental sulfur is much more common in the monothio- $\beta$ -diketonates than the loss of oxygen is in  $\beta$ -diketonates. Similarly, the retention of sulfur in Met-S bonds is observed more frequently in the thio derivatives than Met-O bonding in  $\beta$ -diketonates. And finally, while the strong attraction of sulfur for palladium has been documented (see



Part C, section 3(c)), this relationship can be seen to extend to all of the metal monothio- $\beta$ -diketonates. For instance, the appearance of  $[\text{Met(II)R}]^+$  ions in the majority of the  $\beta$ -diketonate spectra and their absence in the spectra of the monothio- $\beta$ -diketonates is indicative of the stronger Met-S bond as compared to the Met-O bond; since the mechanism proposed for the formation of  $[\text{Met(II)R}]^+$  involves the breaking of a metal-donor bond (see Scheme 26), the non-migration of R in the mass spectra of the monothio derivatives is reflective of the stronger Met-S attraction.

The elimination of neutral  $\text{Met(II)S}$  in many of the monothio- $\beta$ -diketonates leads to the formation of high mass, metal-free ions based on a ligand dimer structure ( $[\text{2L-S}]^{+}$ ,  $[\text{2L-S-R}']^{+}$ , etc.). These ion types are missing from the mass spectra of the dioxo complexes. The high abundance of  $[\text{L}]^+$  (formed by the elimination of  $\text{Met(I)L}$  from  $[\text{Met(II)L}_2]^{+}$ ) also appears to be unique to the monothio- $\beta$ -diketonates.

Fluorine transfer undergoes a pronounced decline in the (O,S) substituted complexes. The presence of the sulfur donor presumably softens the electronic environment of the metal, thereby making the migration of the hard fluorine a less-favored process. However, as was mentioned, this effect is partially negated when strongly electronegative R' substituents are present.

APPENDIX I.

Comprehensive Listing of References to  
Mass Spectral Studies of Metal  $\beta$ -diketonates

(General Form  $\text{Met}^{n+}[\text{RC}(\text{O})\text{CQC}(\text{O})\text{R}']_n$ , where Met. = metal; R,R' = alkyl,  
perfluoroalkyl or aryl; Q = H (usually); n = 2,3 or 4)

<u>LIGAND CODE* {MW}</u>	<u>METAL</u>	<u>IONIZATION MODE*</u>	<u>REFERENCE</u>
BRPDO {178}	Cr(III)	EI	113
	Pd(II)	EI	111
CLPDO {134}	Cr(III)	EI	113
DMHDO {142}	Mg(II)	EI	121
	Cu(II)	EI	121
	Zn(II)	EI	121
DPPDO {224}	Be(II)	EI	120,182
	Mg(II)	EI	120
	Al(III)	EI	109,120
	Sc(III)	EI	120
	OV(IV)	EI	120
	Cr(III)	EI	109,120
	Mn(III)	EI	120

\* (See end of Appendix I. for explanation of abbreviations)

	Fe(III)	EI	120
	Co(II)	EI NCI	120 183
	Co(III)	EI	120
	Ni(II)	EI NCI	120 149,183
	Cu(II)	EI NCI NEC	120,125 183 133
	Zn(II)	EI	120
	Y(III)	EI	120
	Th(IV)	EI	120
ETBDO {130}	Ni(II)	NCI	149
HEXDO {114}	Cu(II)	EI	121
HFDMO {296}	Mg(II)	EI	184
	Ca(II)	EI	184
	Cr(III)	LPD	139
	Mn(III)	LPD	139
	Fe(III)	LPD	139
	Co(III)	LPD	139
	Ni(II)	LPD NEC	139 134
	Cu(II)	LPD NEC	139 133
	Zn(II)	LPD	139
	Sr(II)	EI	184
	Ba(II)	EI	184
	Eu(III)	MPI	138

HFPDO {208}	Mg(II)	NEC	130,132
	Al(III)	EI	123,124,127, 128,167
		LPD	139
		NEC	130,131
	Sc(III)	NEC	131
	Ti(III)	NEC	131
	V(III)	NEC	130,131
	Cr(III)	EI	113,126,127, 124,128,167
		LPD	139
		MPI	138
		NEC	130,131
	Mn(II)	EI	167
		PCI	136
		NEC	130,132
	Mn(III)	NEC	130,131
	Fe(II)	EI	124,167
		NEC	130
	Fe(III)	EI	124,126,128,167
		NEC	130,131
	Co(II)	EI	167
		PCI	136
		LPD	139
		NEC	130,132
	Co(III)	EI	126-128
		NEC	130,131
	Ni(II)	EI	167
		PCI	136
		MPI	138
		NEC	130,132
	Cu(I)	EI	167
	Cu(II)	EI	111,121,124 123,125
		LPD	139
		PCI	136,137
		NEC	130,132

	Zn(II)	EI PCI NCI NEC	123,124,167 136 135 130,132
	Ga(III)	NEC	131
	Ru(III)	EI	185
	Rh(III)	EI	185
	In(III)	NEC	131
	Sn(II)	EI	186
	Eu(III)	EI	187
	Re(III)	EI	188
HFPHD {316}	Be(II)	EI	189
	Pd(II)	EI	142
	O <sub>2</sub> U(VI)	EI	190
HFTHD {322}	Be(II)	EI	189
	Ni(II)	NEC	134
	Cu(II)	NEC	133
	Pd(II)	EI	142
	O <sub>2</sub> U(VI)	EI	190
IOPDO {226}	Cr(III)	EI	113
MEHDO {128}	Cu(II)	EI	121
MEPDO {114}	Cr(III)	EI PLD NLD	113,119 119 119
	Cu(II)	EI	125

NTPDO {145}	Cr(III)	EI	113
	Cu(II)	EI	111
PENDO {100}	Be(II)	EI	105,111
	Mg(II)	EI	105
	Al(III)	EI	105,109,111, 112,191
		LPD	139
	Ca(II)	EI	105
	Sc(III)	EI	105
	Ti(III)	EI	112
	V(III)	EI	112
	OV(IV)	EI	105,111,119
		PLD	119
		NLD	119
		SIMS	117
	Cr(III)	EI	105,111,112, 113,121,192
		LD	119
		LPD	139
MPI		138	
SIMS		117	
Mn(II)	EI	105,114,115	
	LPD	139	
	SIMS	117	
Mn(III)	EI	112,193	
	LPD	139	
	SIMS	117	
Fe(II)	EI	114,115	
Fe(III)	EI	105,109,111,112	
	LPD	139	
	MPI	138	
	SIMS	117	
Co(II)	EI	105,111,114,115	
	MPI	138	
	NCI	183	

Co(III)	EI	105,109,111, 112,119	
	PLD	119	
	NLD	119	
	LPD	139	
	MPI	138	
	SIMS	117	
Ni(II)	EI	105,111,114,115	
	LPD	139	
	MPI	138	
	NCI	148,149,183	
	SIMS	117	
Cu(II)	EI	105,109,111, 114,121,125 115,119	
	PLD	119	
	NLD	119	
	LPD	139	
	PCI	137	
	NCI	183	
	NEC	133	
	SIMS	117	
	Zn(II)	EI	105,111,114
LPD		139	
NCI		135	
Ga(III)	EI	116,191	
Zr(IV)	EI	105	
Ru(III)	EI	185	
Rh(III)	EI	105,185	
Pd(II)	EI	111	
Cd(II)	EI	193	
In(III)	EI	116,191	
Sn(II)	EI	186	
La(III)	EI	105	
Ho(III)	EI	195	
Re(III)	EI	188	
Os(III)	EI	105	

	Ir(III)	EI	105
	Pt(II)	EI	111
	Th(IV)	EI	105
	O <sub>2</sub> U(VI)	EI	115
PFDMH {246}	Mg(II)	EI	184
	Ca(II)	EI	184
	Ni(II)	NEC	134
	Cu(II)	NEC	133
	Sr(II)	EI	184
PFPPD {266}	Be(II)	EI	189
	Pd(II)	EI	142
	O <sub>2</sub> U(VI)	EI	190
PFTPD {272}	Be(II)	EI	189
	Pd(II)	EI	142
	O <sub>2</sub> U(VI)	EI	190
PHBDO {162}	Be(II)	EI	182
	Fe(III)	EI	105
	Ni(II)	NCI	149
	Cu(II)	EI NEC	125 133
PHPDO {176}	Be(II)	EI	182
	Cu(II)	EI	125
TCPDO {202}	Al(III)	EI	168
	Cr(III)	EI	168



	Mn(II)	EI	168
	Fe(III)	EI	168
	Co(II)	EI	168
	Cu(II)	EI	168
TFBPB {294}	Y(III)	EI	196
	Ce(IV)	EI	196
	Pr(III)	EI	196
	Eu(III)	EI	196
	Dy(III)	EI	196
	Ho(III)	EI	196
	Er(III)	EI	196
	Yb(III)	EI	196
TFCYB {180}	Fe(III)	EI	140
TFDMH {196}	Mg(II)	EI	184
	Ca(II)	EI	184
	Ni(II)	NEC	134
	Cu(II)	NEC	133
	Sr(II)	EI	184
	Y(III)	EI	196
	Cd(II)	EI	194
	Ba(II)	EI	184
	La(III)	EI	196
	Ce(IV)	EI	196,197
	Pr(III)	EI	196
	Nd(III)	EI	196

	Sm(III)	EI	196
	Eu(III)	EI	196
	Gd(III)	EI	196
	Tb(III)	EI	196
	Dy(III)	EI	196
	Ho(III)	EI	196
	Er(III)	EI	196
	Yb(III)	EI	196
TFFBD {206}	Be(II)	EI	189
	Sc(III)	EI	198
	Cu(II)	EI NEC	125 133
	Y(III)	EI	198
	Pd(II)	EI	142
	O <sub>2</sub> U(VI)	EI	190
TFFPB {234}	Ga(III)	EI	141
	In(III)	EI	141
TFHDO {168}	Ni(II)	NEC	134
	Cu(II)	NEC	133
	Eu(III)	EI	187
TFMHD {182}	Ni(II)	NEC	134
	Cu(II)	NEC	133
	Cd(II)	EI	194
	Eu(III)	EI	187

TFMHP {196}	Ni(II)	NEC	134
	Cu(II)	NEC	133
	Cd(II)	EI	194
	Eu(III)	EI	187
TFMOP {246}	Ga(III)	EI	141
	In(III)	EI	141
TFMPB {230}	Ga(III)	EI	141
	In(III)	EI	141
	Pr(III)	EI	199
	Nd(III)	EI	199
	Sm(III)	EI	199
	Eu(III)	EI	199
	Gd(III)	EI	199
	Dy(III)	EI	199
	Ho(III)	EI	199
	Er(III)	EI	199
TFMPX {230}	Y(III)	EI	196
	Ce(IV)	EI	196
	Pr(III)	EI	196
	Nd(III)	EI	196
	Sm(III)	EI	196
	Eu(III)	EI	196
	Gd(III)	EI	196
	Tb(III)	EI	196
Dy(III)	EI	196	

	Ho(III)	EI	196
	Er(III)	EI	196
	Yb(III)	EI	196
TFMIF {304}	Cu(II)	EI	200
TFNBD {266}	Ni(II)	NEC	134
	Cu(II)	EI NEC	125 133
	Ga(III)	EI	141
	Cd(II)	EI	194
	In(III)	EI	141
TFNPB {230}	Y(III)	EI	196
	Ce(IV)	EI	196
	Pr(III)	EI	196
	Sm(III)	EI	196
	Eu(III)	EI	196
	Gd(III)	EI	196
	Tb(III)	EI	196
	Dy(III)	EI	196
	Yb(III)	EI	196
TFPBD {216}	Be(II)	EI	189
	Al(III)	EI	128
	Sc(III)	EI	198
	Cr(III)	EI SIMS	128 117
	Fe(III)	EI	109,128,140
	Co(III)	EI	127,128,140

	Ni(II)	NCI NEC	149 134
	Cu(II)	EI NEC	125 133
	Ga(III)	EI	141
	Y(III)	EI	198
	Pd(II)	EI	142
	Cd(II)	EI	194
	In(III)	EI	141
	Ce(IV)	EI	197
	Nd(III)	EI	199
	Sm(III)	EI	199
	Eu(III)	EI	199
	Gd(III)	EI	199
	Dy(III)	EI	199
	Ho(III)	EI	199
	Er(III)	EI	199
	Yb(III)	EI	199
	O <sub>2</sub> U(VI)	EI	190
TFPDO {154}	Be(II)	EI	189
	Al(III)	EI LPD	123,124,128,191 139
	Sc(III)	EI	198
	Cr(III)	EI LPD MPI SIMS	113,124,128 139 138 117
	Mn(II)	LPD	139
	Fe(II)	EI	124

	Fe(III)	EI LPD MPI	124,128 139 138
	Co(III)	EI LPD	127,128 139
	Ni(II)	LPD NCI	139 149
	Cu(II)	EI LPD PCI NEC	121,123,124,125 139 137 133
	Zn(II)	EI LPD NCI	123,124 139 135
	Ga(III)	EI	116,141,191
	Y(III)	EI	198
	Ru(III)	EI	185
	Rh(III)	EI	185
	Pd(II)	EI	142
	Cd(II)	EI	194
	In(III)	EI	141
	Sn(II)	EI	186
	Eu(III)	EI	187
	O <sub>2</sub> U(VI)	EI	190
TFTBD {222}	Be(II)	EI	189
	Sc(III)	EI	198
	Cr(III)	EI	175
	Mn(II)	EI	175
	Fe(III)	EI	128,140,175
	Co(II)	EI	175
	Co(III)	EI	140

	Ni(II)	EI NEC	175 134
	Cu(II)	EI NEC	125,175 133
	Zn(II)	EI	175
	Ga(III)	EI	141
	Y(III)	EI	196,198
	Pd(II)	EI	142
	In(III)	EI	141
	La(III)	EI	196
	Ce(IV)	EI	196,197
	Pr(III)	EI	196
TFTFH {254}	Cu(II)	EI	200
TMHDO {184}	Al(III)	NEC	122
	Sc(III)	NEC	122
	Cr(III)	NEC	122
	Mn(III)	LPD NEC	139 122
	Fe(III)	LPD NEC	139 122
	Co(II)	NCI NEC	183 122
	Co(III)	LPD NEC	139 122
	Ni(II)	LPD NCI NEC	139 148,149,183 122
	Cu(II)	LPD NCI NEC	139 183 122,133

Zn(II)	LPD	139
	NCI	135
	NEC	122
Ga(III)	NEC	122
In(III)	NEC	122
La(III)	MPI	138
Ce(IV)	MPI	138
Eu(III)	MPI	138
Er(III)	MPI	138
Nd(III)	EI	196
Sm(III)	EI	196,201
Eu(III)	EI	196,201
Gd(III)	EI	196,201
Tb(III)	EI	196,201
Dy(III)	EI	196
Ho(III)	EI	196
Er(III)	EI	196
Yb(III)	EI	196
O <sub>2</sub> U(VI)	EI	190



Abbreviations for Appendix I.**1. Ionization Modes**

EI = Electron Ionization  
LPD = Laser Photodissociation  
MPI = Multi-Photon Ionization  
NCI = Negative-ion Chemical Ionization  
NEC = Negative Electron Capture  
NLD = Negative-ion Laser Desorption  
PCI = Positive-ion Chemical Ionization  
PLD = Positive-ion Laser Desorption  
SIMS = Secondary-ion Mass Spectrometry

**2. Ligand Codes (listed alphabetically)**

BRPDO = 3-bromo-2,4-pentanedione  
CLPDO = 3-chloro-2,4-pentanedione  
DMHDO = 2,2-dimethyl-3,5-hexanedione  
DPPDO = 1,3-diphenyl-1,3-propanedione  
ETBDO = 4-ethoxy-2,4-butanedione  
HEXDO = 2,4-hexanedione  
HFDMO = 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione  
HFPDO = 1,1,1,5,5,5-hexafluoro-2,4-pentanedione  
HFPHD = 1,1,1,2,2,3,3-heptafluoro-6-phenyl-4,6-hexanedione  
HFTHD = 1,1,1,2,2,3,3-heptafluoro-6-(2'-thienyl)-4,6-hexanedione  
IOPDO = 3-iodo-2,4-pentanedione  
MEHDO = 2-methyl-3,5-hexanedione  
MEPDO = 3-methyl-2,4-pentanedione

NTPDO = 3-nitro-2,4-pentanedione  
PENDO = 2,4-pentanedione  
PFDMH = 1,1,1,2,2-pentafluoro-6,6-dimethyl-3,5-heptanedione  
PFPPD = 1,1,1,2,2-pentafluoro-5-phenyl-3,5-pentanedione  
PFTPD = 1,1,1,2,2-pentafluoro-5-(2'-thienyl)-3,5-pentanedione  
PHBDO = 1-phenyl-1,3-butanedione  
PHPDO = 3-phenyl-2,4-pentanedione  
TCPDO = 1,1,1-trichloro-2,4-pentanedione  
TFBPB = 1,1,1-trifluoro-4-(4'-bromophenyl)-2,4-butanedione  
TFCYB = 1,1,1-trifluoro-4-cyclopropyl-2,4-butanedione  
TFDMH = 1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedione  
TFFBD = 1,1,1-trifluoro-4-(2'-furyl)-2,4-butanedione  
TFFPB = 1,1,1-trifluoro-4-(4'-fluorophenyl)-2,4-butanedione  
TFHDO = 1,1,1-trifluoro-2,4-hexanedione  
TFMHD = 1,1,1-trifluoro-5-methyl-2,4-hexanedione  
TFMHP = 1,1,1-trifluoro-6-methyl-2,4-heptanedione  
TFMOP = 1,1,1-trifluoro-4-(4'-methoxyphenyl)-2,4-butanedione  
TFMPB = 1,1,1-trifluoro-4-(4'-methylphenyl)-2,4-butanedione  
TFMPX = 1,1,1-trifluoro-4-(3'-methylphenyl)-2,4-butanedione  
TFMTF = 5,5-bis(trifluoromethyl)-6,6,6-trifluoro-2,4-hexanedione  
TFNBD = 1,1,1-trifluoro-4-(2'-naphthyl)-2,4-butanedione  
TFNPB = 1,1,1-trifluoro-4-(2'-methylphenyl)-2,4-butanedione  
TFPBD = 1,1,1-trifluoro-4-phenyl-2,4-butanedione  
TFPDO = 1,1,1-trifluoro-2,4-pentanedione  
TFTBD = 1,1,1-trifluoro-4-(2'-thienyl)-2,4-butanedione  
TFTFH = 5,6,6,6-tetrafluoro-5-trifluoromethyl-2,4-hexanedione  
TMHDO = 2,2,6,6-tetramethyl-3,5-heptanedione

APPENDIX II.

Comprehensive Listing of References to  
Mass Spectral Studies of Metal Monothio- $\beta$ -diketonates

(General Form  $\text{Met}^{n+}[\text{RC}(\text{S})\text{CQC}(\text{O})\text{R}' ]_n$ , where Met = metal; R, R' = alkyl, perfluoroalkyl or aryl; Q = H (usually); n = 2, 3 or 4)

<u>LIGAND CODE* (MW)</u>	<u>METAL</u>	<u>IONIZATION MODE*</u>	<u>REFERENCE</u>
DFSMP {228}	Co(III)	EI	99
	Cu(II)	EI	99
	Zn(II)	EI	99
DFSPB {214}	Co(III)	EI	99
	Ni(II)	EI	99
	Cu(II)	EI	99
	Zn(II)	EI	99
DFSTB {220}	Co(III)	EI	99
	Ni(II)	EI	99
	Cu(II)	EI	99
	Zn(II)	EI	99
DPSPO {240}	Fe(III)	EI	202
	Co(III)	EI	202

\* (See end of Appendix II. for explanation of abbreviations)

	Ni(II)	EI NCI	48,202 149
	Zn(II)	EI	202
HFSP0 {224}	Ni(II)	EI	203
	Pd(II)	EI	204
	Pt(II)	EI	204
PSBEO {178}	Fe(III)	EI	202
	Co(III)	EI	202
	Ni(II)	EI NCI	48,202 149
	Zn(II)	EI	202
SPENT {116}	Co(II)	EI	205
	Co(III)	EI	205
	Ni(II)	EI NCI	48,205 148,149
	Zn(II)	EI	205
	Pd(II)	EI	205
	Cd(II)	EI	205
	Pt(II)	EI	205
	Pb(II)	EI	205
TFSBP {310}	Co(III)	EI	145
	Rh(III)	EI	145
	Pd(II)	EI	144
	Pt(II)	EI	144

TFSFP {250}	Co(III)	EI	145
	Rh(III)	EI	145
TFSMH {212}	Fe(III)	EI	146
	Co(III)	EI	146
	Ni(II)	EI	146
	Cu(II)	EI	146
	Zn(II)	EI	146
	Ru(III)	EI	146
	Rh(III)	EI	146
	Pd(II)	EI	146
TFSMP {246}	Fe(III)	EI	206
	Co(III)	EI	145
	Ni(II)	EI	143
	Zn(II)	EI	143
	Ru(III)	EI	206
	Rh(III)	EI	145
	Pd(II)	EI	144
TFSMX {198}	Fe(III)	EI	146
	Co(III)	EI	146
	Ni(II)	EI	146
	Cu(II)	EI	146
	Zn(II)	EI	146
	Ru(III)	EI	146
	Rh(III)	EI	146
	Pd(II)	EI	146

TFSNB {282}	Cr(III)	EI	207
	Fe(III)	EI	147
	Co(III)	EI	147
	Ni(II)	EI	147
	Zn(II)	EI	147
	Ru(III)	EI	147
	Rh(III)	EI	147
	Pd(II)	EI	147
	Pt(II)	EI	147
TFSNP {277}	Pd(II)	EI	144
	Pt(II)	EI	144
TFSPB {232}	Cr(III)	EI	207
	Fe(III)	EI	206
	Co(III)	EI	145
	Ni(II)	EI NCI	143 149
	Zn(II)	EI	143
	Ru(III)	EI	206
	Rh(III)	EI	145
	Pd(II)	EI	144
	Pt(II)	EI	144
TFSPB {170}	Co(III)	EI	145
	Ni(II)	EI NCI	143, 203 149
	Zn(II)	EI	143
	Rh(III)	EI	145

	Pd(II)	EI	144
	Pt(II)	EI	144
TFSTB {238}	Cr(III)	EI	207
	Fe(III)	EI	206
	Co(III)	EI	145
	Ni(II)	EI	48,143
	Zn(II)	EI	143
	Ru(III)	EI	206
	Rh(III)	EI	145
	Pd(II)	EI	144
	Pt(II)	EI	144
TMSHO {200}	Ni(II)	EI NCI	48 148,149

Abbreviations for Appendix II.**1. Ionization Modes**

EI = Electron Ionization  
 NCI = Negative-ion Chemical Ionization

**2. Ligand Codes (listed alphabetically)**

DFSMP = 1,1-difluoro-4-mercapto-4-(4'-methylphenyl)-  
 but-3-en-2-one

DFSPB = 1,1-difluoro-4-mercapto-4-phenyl-but-3-en-2-one

DFSTB = 1,1-difluoro-4-mercapto-4-(2'-thienyl)-but-3-en-2-one

DPSPO = 1,3-diphenyl-3-mercapto-prop-2-en-1-one

HFSPO = 1,1,1,5,5,5-hexafluoro-4-mercapto-pent-3-en-2-one

PSBEO = 1-phenyl-3-mercapto-but-2-en-1-one

SPENT = 4-mercapto-pent-3-en-2-one

TFSBP = 1,1,1-trifluoro-4-mercapto-4-(4'-bromophenyl)-  
 but-3-en-2-one

TFSFP = 1,1,1-trifluoro-4-mercapto-4-(4'-fluorophenyl)-  
 but-3-en-2-one

TFSMH = 1,1,1-trifluoro-4-mercapto-6-methyl-hept-3-en-2-one

TFSMP = 1,1,1-trifluoro-4-mercapto-4-(4'-methylphenyl)-  
 but-3-en-2-one

TFSMX = 1,1,1-trifluoro-4-mercapto-5-methyl-hex-3-en-2-one

TFSNB = 1,1,1-trifluoro-4-mercapto-4-(2'-naphthyl)-but-3-en-2-one

TFSNP = 1,1,1-trifluoro-4-mercapto-4-(4'-nitrophenyl)-  
 but-3-en-2-one

TFSPB = 1,1,1-trifluoro-4-mercapto-4-phenyl-but-3-en-2-one

TFSPO = 1,1,1-trifluoro-4-mercapto-pent-3-en-2-one

TFSTB = 1,1,1-trifluoro-4-mercapto-4-(2'-thienyl)-but-3-en-2-one

TMSHO = 2,2,6,6-tetramethyl-5-mercapto-hept-4-en-3-one



APPENDIX III.

The following is a listing of the BASIC program used for the plotting of normalized mass spectra. The program was run on a Zenith Z-100 microcomputer with graphic output to a Hewlett Packard 7470A plotter. Development of this program was by J.B. Westmore, with refinements by M.L.J. Reimer.

```

10 CLS: LOCATE 1,8
20 PRINT"***** PLOT MASS SPECTRA *****"
30 REM
40 REM
100 LOCATE 6,13: PRINT"This program plots normalized mass spectra (400 peaks"
110 LOCATE 7,20: PRINT"maximum) using the HP 7470A plotter."
150 GOSUB 1550: REM - CONTINUE
180 REM
190 REM
300 GOSUB 1000: REM - LOAD MASS SPECTRA
340 CLS: INPUT"What do you want to title the plot?: ", TITLE$
350 GOSUB 2500: REM - NORMALIZE, FIND HIGHEST MASS AND % SIGMA
360 GOSUB 3000: REM - INITIALIZE PLOTTING PARAMETERS
370 GOSUB 3500: REM - PLOT GRIDS
380 GOSUB 4000: REM - DRAW TICKS
390 GOSUB 4500: REM - TITLE AND LABEL AXES
400 GOSUB 5000: REM - DRAW PEAKS
500 REM
520 REM
990 CLS: SCREEN 0,1: PRINT "THIS IS THE END OF THE PROGRAM. ENTER 'RUN' IF YOU W
ANT TO PLOT ANOTHER SPECTRUM": SCREEN 0,0: END
992 REM
994 REM
1000 REM - LOAD MASS SPECTRA
1005 CLS: DIM MZ(400): DIM RI(400)
1020 GOSUB 7000: REM - READ DATA FILE
1200 REM - CHECK DATA
1205 CLS: LOCATE 1,1: PRINT SNAME$: PRINT SDATE$
1210 FOR J = 1 TO K
1220 REM - PRINT COLUMN HEADINGS
1230 G = (J-.9)/50: IF G-INT(G)<.01 THEN AA = 4: BB = 2: CC = 1: GOSUB 1900
1240 REM - PRINT COLUMN HEADINGS
1250 G = (J+31.1)/50: IF G-INT(G)<.01 THEN AA = 1: BB = 28: CC = 27: GOSUB 1900
1260 REM - PRINT COLUMN HEADINGS
1270 G = (J+15.1)/50: IF G-INT(G)<.01 THEN AA = 1: BB = 56: CC = 55: GOSUB 1900
1280 LOCATE ,CC: PRINT USING"##"; J: PRINT USING"#####.##"; MZ(J): PRINT USING
"#####.##"; RI(J)
1290 IF J=50 OR J=100 OR J=150 THEN GOSUB 1400: GOSUB 1550: REM - ALL CORRECT?
1300 NEXT J
1310 GOSUB 1550: REM - CONTINUE
1390 RETURN
1392 REM
1394 REM
1550 REM - CONTINUE
1560 LOCATE 20,33: PRINT "Press any key to continue."
1570 Q$ = INKEY$: IF Q$ = "" THEN 1570
1590 RETURN
1592 REM
1594 REM
1900 REM - PRINT COLUMN HEADINGS
1910 LOCATE AA,BB: PRINT "I      m/z      pk. ht": PRINT
1940 RETURN
1942 REM
1944 REM

```

```

1950 REM - CLEAR CORNER OF SCREEN
1960 FOR I = 20 TO 24
1970 LOCATE I,28: PRINT SPC(51)
1980 NEXT I
1990 RETURN
1992 REM
1994 REM
2500 REM - FIND HIGHEST MASS AND % SIGMA
2510 HIMASS = 40: SIG = 0: BIGPK = 0
2520 FOR J = 1 TO K
2530 IF HIMASS < MZ(J) THEN HIMASS = MZ(J)
2540 IF BIGPK < RI(J) THEN BIGPK = RI(J)
2550 NEXT J
2560 FOR J = 1 TO K: RI(J) = RI(J)*100/BIGPK: SIG = SIG + RI(J): NEXT J
2570 SIG = 10000/SIG: SIG$ = STR$(SIG)
2580 SIG$ = LEFT$(SIG$,5):SIG$ = RIGHT$(SIG$,4)
2590 RETURN
2592 REM
2594 REM
3000 REM - INITIALIZE PLOTTING PARAMETERS
3010 MINPLOT = 40
3020 IF HIMASS > 550 THEN 3100
3030 MAXPLOT = (INT(HIMASS/20) + 1) * 20: GRID = 2: RIFACTOR = 24
3040 MIDPLOT = (MINPLOT+MAXPLOT)/2: MFACTOR = 7850*2/(MAXPLOT-MINPLOT):GOTO 3490
3100 FRACT = HIMASS/30 - INT(HIMASS/30): GRID = 3: RIFACTOR = 15
3110 IF FRACT > .7 THEN MAXPLOT = INT(HIMASS/30)*30+70 ELSE MAXPLOT = INT(HIMASS
/30)*30+40
3120 MIDPLOT1 = (MAXPLOT + 2*MINPLOT)/3: MIDPLOT2 = (2*MAXPLOT + MINPLOT)/3
3130 MFACTOR = 7850 * 3/(MAXPLOT - MINPLOT)
3490 RETURN
3492 REM
3494 REM
3500 REM - DRAW GRIDS
3510 LPRINT"IN:SP1;VS2;"
3520 IF GRID = 2 THEN GOSUB 3600: REM - DRAW TWO GRIDS
3530 IF GRID = 3 THEN GOSUB 3700: REM - DRAW THREE GRIDS
3590 RETURN
3592 REM
3594 REM
3600 REM - DRAW TWO GRIDS
3610 LPRINT"PA950,1100;PD9000,1100,9000,3500,950,3500,950,1100;PU;"
3620 LPRINT"PA950,4000;PD9000,4000,9000,6400,950,6400,950,4000;PU;"
3690 RETURN
3692 REM
3694 REM
3700 REM - DRAW THREE GRIDS
3710 LPRINT"PA950,1100;PD9000,1100,9000,2600,950,2600,950,1100;PU;"
3720 LPRINT"PA950,3000;PD9000,3000,9000,4500,950,4500,950,3000;PU;"
3730 LPRINT"PA950,4900;PD9000,4900,9000,6400,950,6400,950,4900;PU;"
3790 RETURN
3792 REM
3794 REM
4000 REM - DRAW TICKS

```

```
4010 IF GRID = 2 THEN GOSUB 4100
4020 IF GRID = 3 THEN GOSUB 4200
4090 RETURN
4092 REM
4094 REM
4100 REM - TICKS FOR TWO GRIDS
4110 YI = 480: LPRINT"PA950,4000;TL0.7,0;": GOSUB 4300: REM - DRAW RI TICKS
4120 LPRINT"PA950,1100;": GOSUB 4300: REM - DRAW RI TICKS
4130 LPRINT"PA9000,4000;TL0,0.7;": GOSUB 4300: REM - DRAW RI TICKS
4140 LPRINT"PA9000,1100;": GOSUB 4300: REM - DRAW RI TICKS
4150 MFCTR = MFACTOR*10: P = (MAXPLOT - MINPLOT)/20
4160 XAXIS = 4000: DD = 0: LPRINT"TL0,0.7;"
4170 GOSUB 4400: REM - DRAW M/Z TICKS
4180 XAXIS = 1100: DD = P: GOSUB 4400: REM - DRAW M/Z TICKS
4190 RETURN
4192 REM
4194 REM
4200 REM - TICKS FOR THREE GRIDS
4210 YI = 300: LPRINT"PA950,4900;TL0.7,0;": GOSUB 4300: REM - DRAW RI TICKS
4225 LPRINT"PA950,3000;": GOSUB 4300: REM - DRAW RI TICKS
4230 LPRINT"PA950,1100;": GOSUB 4300: REM - DRAW RI TICKS
4235 LPRINT"TL0,0.7;PA9000,4900;": GOSUB 4300: REM - DRAW RI TICKS
4240 LPRINT"PA9000,3000;": GOSUB 4300: REM - DRAW RI TICKS
4245 LPRINT"PA9000,1100;": GOSUB 4300: REM - DRAW RI TICKS
4250 MFCTR = MFACTOR*10: P = (MAXPLOT - MINPLOT)/30
4260 XAXIS = 4900: DD = 0: LPRINT"TL0,0.7;": GOSUB 4400: REM - DRAW M/Z TICKS
4270 XAXIS = 3000: DD = P: GOSUB 4400: REM - DRAW M/Z TICKS
4280 XAXIS = 1100: DD = 2*P: GOSUB 4400: REM - DRAW M/Z TICKS
4290 RETURN
4292 REM
4294 REM
4300 REM - DRAW RI TICKS
4310 FOR J = 1 TO 4: LPRINT"PR0,":YI;":YT;": NEXT J
4390 RETURN
4392 REM
4394 REM
4396 REM
4400 REM - DRAW M/Z TICKS
4410 FOR J = 0 TO P: KK = (J + DD - 1)/5
4420 IF KK - INT(KK) < .1 THEN LPRINT"TL0,1.2;"
4430 LPRINT"PA":1050 + MFCTR*J,XAXIS;":XT;TL0,0.7;"
4440 NEXT J
4450 RETURN
4490 REM
4492 REM
4500 REM - TITLE AND LABEL AXES
4510 LPRINT"PU:DT.;DI1,0;PA1250,6600;LB"TITLE$".:DT ;"
4550 IF GRID = 2 THEN GOSUB 4600
4560 IF GRID = 3 THEN GOSUB 4700
4590 RETURN
4592 REM
4594 REM
4600 REM - LABEL FOR TWO GRIDS
4610 Q1 = INT((MIDPLOT+1)/50): Q2 = INT((MAXPLOT+1)/50)
```

```

4620 LPRINT"PA";950+MFCTR;"3750;LB50 ;"
4630 MFCTR = MFACTOR*50: XB = .8: YH = 3750
4640 FOR J = 2 TO Q1: GOSUB 4800: NEXT J: REM - LABEL M/Z AXIS
4645 GOSUB 4900: REM - LABEL m/z, RI AND % SIGMA
4650 YH = 850: XB = .6 + (P+1)/5
4660 FOR J = Q1 TO Q2: GOSUB 4800: NEXT J: REM - LABEL M/Z AXIS
4665 GOSUB 4900: REM - LABEL m/z, RI AND % SIGMA
4690 RETURN
4692 REM
4694 REM
4700 REM - LABEL FOR THREE GRIDS
4710 Q1 = INT((MIDPLOT1+1)/50): Q2 = INT((MIDPLOT2+1)/50)
4715 Q3 = INT((MAXPLOT+1)/50)
4720 LPRINT"PA";950+MFCTR;"4650;LB50 ;"
4730 MFCTR = MFACTOR*50: XB = .8: YH = 4650
4740 FOR J = 2 TO Q1: GOSUB 4800: NEXT J: REM - LABEL M/Z AXIS
4745 GOSUB 4900: REM - LABEL m/z, RI AND % SIGMA
4750 YH = 2750: XB = .6 + (P+1)/5
4760 FOR J = Q1 TO Q2: GOSUB 4800: NEXT J: REM - LABEL M/Z AXIS
4765 GOSUB 4900: REM - LABEL m/z, RI AND % SIGMA
4770 YH = 850: XB = .6 + (2*P+1)/5
4780 FOR J = Q2 TO Q3: GOSUB 4800: NEXT J: REM - LABEL M/Z AXIS
4785 GOSUB 4900: REM - LABEL m/z, RI AND % SIGMA
4790 RETURN
4792 REM
4794 REM
4800 REM - LABEL M/Z AXIS
4810 IF J - XB < 0 THEN 4890
4820 MZ = .001+50*J: MZ$ = STR$(MZ): MZ$ = LEFT$(MZ$,4): MZ$ = RIGHT$(MZ$,3)
4830 LPRINT"PA";900+MFCTR*(J-XB);", ";YH;";LB";MZ$;" ;"
4890 RETURN
4892 REM
4894 REM
4900 REM - LABEL m/z, RI AND % SIGMA
4910 LPRINT"PA";900+MFCTR*(J-XB-1.6);", ";YH;";LBm/z ;"
4920 LPRINT"PA770,";YH+200;";LB0 ;"
4930 LPRINT"PA550,";YH+100*RIFACTOR+200;";LB100 ;"
4940 LPRINT"DT%;DI0,1;PA820,";YH+55*RIFACTOR-425;";LBREL AB %;"
4950 LPRINT"DTA;PA9250,";YH+55*RIFACTOR-325;";LB% SIGMA;DT ;DI1,0;"
4960 LPRINT"PA9050,";YH+100*RIFACTOR+200;";LB"SIG$" ;"
4990 RETURN
4992 REM
4994 REM
5000 REM - DRAW PEAKS
5010 IF GRID = 2 THEN GOSUB 5100: REM - DRAW A PEAK
5020 IF GRID = 3 THEN GOSUB 5200: REM - DRAW A PEAK
5030 LPRINT"SP0:"
5090 RETURN
5092 REM
5094 REM
5100 REM - DRAW A PEAK (2 GRIDS)
5120 FOR J = 1 TO K: RI = RI(J) * RIFACTOR
5130 IF MZ(J) > MIDPLOT THEN Y0 = 1100: Y1 = 1100+RI: X0 = 1050+(MZ(J)-MIDPLOT)*M
FACTOR: GOTO 5160

```

```
5140 Y0 = 4000: Y1 = 4000+RI: X0 = 1050+(MZ(J)-MINPLOT)*MFACTOR
5160 GOSUB 5400
5170 PRINT MZ(J), RI(J): NEXT J
5190 RETURN
5192 REM
5194 REM
5200 REM - DRAW A PEAK (3 GRIDS)
5210 LPRINT"PA";X0;" ";Y0;" ";PD";X0;" ";Y1;" ";PU;"
5220 FOR J = 1 TO K: RI = RI(J) * RIFACTOR
5230 IF MZ(J) > MIDPLOT2 THEN Y0 = 1100: Y1 = 1100+RI: X0 =1050+(MZ(J)-MIDPLOT2)
*MFACTOR: GOTO 5270
5240 IF MZ(J) > MIDPLOT1 THEN Y0 = 3000: Y1 = 3000+RI: X0 =1050+(MZ(J)-MIDPLOT1)
*MFACTOR: GOTO 5270
5250 Y0 = 4900: Y1 = 4900+RI: X0 = 1050+(MZ(J)-MINPLOT)*MFACTOR
5270 GOSUB 5400
5280 PRINT MZ(J), RI(J): NEXT J
5290 RETURN
5292 REM
5294 REM
5400 REM - DRAW A PEAK
5410 LPRINT"PA";X0;" ";Y0;" ";PD";X0;" ";Y1;" ";PU;" : RETURN
5490 REM
5492 REM
7000 REM - READ A SEQUENTIAL DATA FILE
7010 CLS: SCREEN 0,1: PRINT "PLACE A DATA DISC IN DISC DRIVE":
7020 SCREEN 0,0: PRINT "Press any key to continue."
7030 Q$ = INKEY$: IF Q$ = "" THEN 7030
7040 PRINT "The following is a list of data files on disc:": PRINT
7050 FILES "*.MSD"
7060 PRINT : PRINT "What is the name of the file you want to recall?"
7070 PRINT : INPUT"          (no extension necessary)?": ", NFILE$
7080 NN$ = NFILE$ + ".MSD"
7090 OPEN "I", #1, NN$
7100 INPUT#1, SNAME$, SDATE$, NFILE$, K
7120 FOR I = 1 TO K: INPUT#1, MZ(I), RI(I): NEXT I
7130 CLOSE #1
7190 RETURN
```

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