Inorganica Chimica Acta, 14 (1975) 49–51
© Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Coordination Complexes Containing Multidentate Ligands. VII*. Mass Spectral Studies on Some Open-chain Tetradentate Thioether Chelates

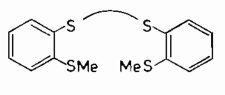
C.A. McAULIFFE**, S. G. MURRAY and R. D. SEDGWICK
Department of Chemistry, University of Manchester Institute of Science and Technology, P. O. Box 88, Manchester M60 IQD, U.K.

Received December 17, 1974

The mass spectra of six open-chain tetradentate thioether ligands are reported; two containing all aliphatic linkages, 1,2-bis(2-methylthioethylthio)ethane and 1,3-bis(2-methylthioethylthio)propane, and four containing both aliphatic and aromatic linkages, 1,2-bis(o-methylthiophenylthio)ethane, 1,3-bis(o-methylthiophenylthio)propane, 1,4-bis(o-methylthiophenylthio)butane, and cis-1,2-bis(o-methylthiophenylthio)ethylene. The fragmentation patterns are illustrated and discussed with respect to differences between the ligands and the fragments derived from different ligands. The completely aliphatic ligands exhibit a complex fragmentation of α-cleavages with and without hydrogen atom migration; the formation of heterocyclic intermediates in those containing aromatic groups is dependent on the number of methylene groups in the aliphatic chain. An unusual feature of the latter type of ligand is the formation of ion m/e = 91 (C_7H_7) directly from m/e = 155 ($C_7H_7S_2$).

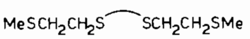
Introduction

We have been engaged for some time in synthesising new chelating ligands, particularly those containing heavy donor atoms, and we have begun to study the fragmentation patterns of some of these chelates.[2,3] Our synthetic work has now included the preparation of some linear ("open-chain") tetrathioether chelates of types (I) and (II). A series of ligands such as this allows us to investigate the way in which variation of chelate backbone affects the stereochemistry and spectrochemistry of the resulting complexes formed from these ligands. Moreover the current interest in metal ion catalysed S-dealkylation reactions,[4,5] and the well established biological significance of S-alkylation,[6] suggests to us that mass spectral studies of these chelates are of particular interest.



(I)

Ia	- $(CH_2)_2$-
Ib	- $(CH_2)_3$-
Ic	- $(CH_2)_4$-
Id	cis-CHCH-



$MeSCH_2CH_2S\frown SCH_2CH_2SMe$

(II)

IIa	- $(CH_2)_2$-
IIb	- $(CH_2)_3$-

Experimental

The synthesis of the chelates will be reported in due course.[7]

The spectra were obtained using an A.E.I. MS902 mass spectrometer at 70 eV linked to a DS 30 Data System.

Results and Discussion

Ligands of Type (I)

In all cases the initial fragmentation of the parent ion is an α-cleavage of the aliphatic chain both with and without rearrangement *via* hydrogen atom migration (Figure), except for ligand Id where the rearrangement mechanism is inhibited, presumably because of the presence of the double bond. Such facile cleavage of sulphur–carbon bonds in non-terminal thioether groups has already been observed in the nickel(II) catalysed bis-S-dealkylation of bis(*o*-diphenylarsinophenylthio)alkanes.[4] Above m/e = 169 the major fragments are P–155 and P–156 from the initial fragmentation of the parent ions. The major components of the spectra of Ia–c are contained in Table I showing that the patterns of these compounds are generally the same. The Figure diagrammatically represents the fragmentation of Ib. The spectrum of Ia follows this general pattern with the notable lack of m/e = 169. This suggests that this ion originates from the (P–155) ion by olefin loss from the aliphatic chain. A similar genesis in the case of Ia would require the loss of $\cdot CH_2$.

---

[*] For Part VI see ref. 1.

[**] Address correspondence to this author.

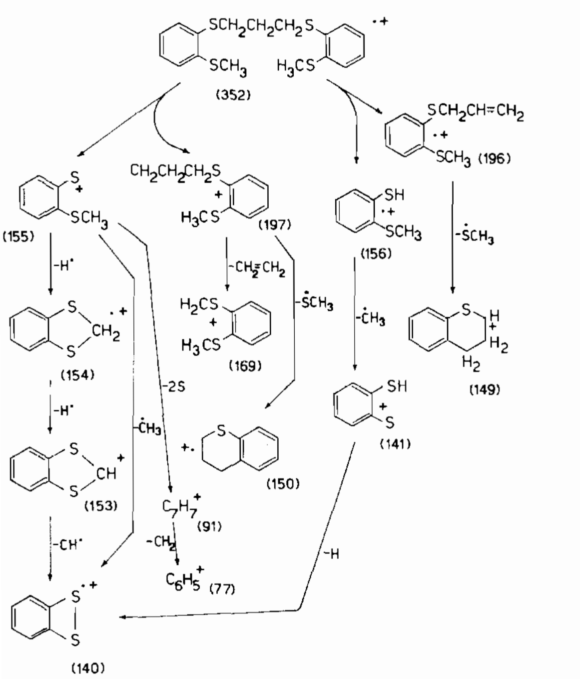
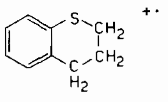


TABLE I. Relative Intensities.

m/e	I(a)	I(b)	I(c)	Fragment	
366	13.9	–	–	$C_{13}H_{22}S_4$	P^+
352	–	100.0	–	$C_{17}H_{20}S_4$	
338	–	–	21.9	$C_{16}H_{18}S_4$	
183	22.7	–	–	$C_{11}H_{15}S_2$	$(P–155)^+$
197	–	83.5	–	$C_{10}H_{13}S_2$	
211	–	–	100.0	$C_9H_{11}S_2$	
182	21.5	–	–	$C_{11}H_{14}S_2$	$(P–156)^+$
196	–	13.3	–	$C_{10}H_{12}S_2$	
210	–	–	0.8	$C_9H_{10}S_2$	
169	0.0	17.5	13.5	$C_8H_9S_2$	
156	14.1	23.4	26.7	$C_7H_8S_2$	
155	75.9	37.6	13.7	$C_7H_7S_2$	
154	11.5	46.7	22.1	$C_7H_6S_2$	
153	23.3	77.6	17.5	$C_7H_5S_2$	
150	0.0	13.6	0.0	$C_9H_{10}S$	
149	0.0	39.2	0.7	C_9H_9S	
141	3.5	7.5	8.1	$C_6H_5S_2$	
140	11.2	10.5	5.4	$C_6H_4S_2$	
135	17.5	6.5	2.5	C_8H_7S	
134	11.1	4.4	2.8	C_8H_6S	
122	5.9	9.1	3.1	C_7H_6S	
121	7.5	11.5	4.5	C_7H_5S	
109	9.8	14.4	7.5	C_6H_5S	
91	100.0	82.6	34.8	C_7H_7	
78	3.3	7.5	3.1	C_6H_6	
77	11.3	17.5	8.4	C_6H_5	
65	5.2	6.5	3.8	C_5H_5	

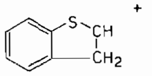
This unlikely event does not occur, nor does the symmetrical cleavage of the parent ion which would also generate m/e = 169. The P–155 ion, as might be expected, readily undergoes loss of $CH_2{=}CH_2$ to give m/e = 155.

Differences in the spectra appear linked to the length of the aliphatic chain. In the spectrum of Ib two intense peaks appear at m/e = 150 and 149 and are absent in Ia and Ic. Stability of these ions may be due to ring formation giving a six membered ring as in (III), and

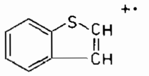


(III) m/e = 150

the ions m/e = 149, 148, 147 are derived from this by hydrogen loss. We assign heterocyclic structures (IV) and (V) to the ions m/e = 135 and 134, respectively.



(IV) m/e = 135



(V) m/e = 134

Since Ic does not give this type of ion this lends support to this proposal, since from Ic the products would contain the unfavourable seven membered ring. Also worthy of note is the intensity of the parent ion in the spectrum of Ib, suggesting an enhanced stability compared with Ia, c, d.

The fragmentation of Id appears to be quite different to those of Ia–c, the major fragments being shown in Table II. The basic pattern appears to be an α-cleavage with hydrogen atom transfer to give m/e = 181 as base peak. The other major ions are m/e = 166, resulting from loss of $\cdot CH_3$ from m/e = 181, a process which does not occur in the breakdown of Ia–c, and m/e = 134. There is very little m/e = 155 and m/e = 91, both major fragments in Ia–c.

The origin of m/e = 91[8] (C_7H_7) originally presented us with some problems, but by a metastable scanning procedure it was found that the major precursor of the fragment was the ion m/e = 155 and no intermediate step in the process 155→91 appears to occur. This is most unusual, since to undergo this pro-

TABLE II.

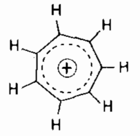
m/e	Relative Intensity	Fragment
336	39.6	$C_{16}H_{16}S_4$
181	100.0	$C_9H_9S_2$
166	36.1	$C_8H_6S_2$
134	6.1	C_8H_6S

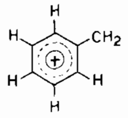
TABLE III.

m/e	Relative Intensity	Fragment
II(a)		
242	0.3	$C_8H_{18}S_4$
194	4.8	$C_7H_{14}S_3$
168	21.2	$C_5H_{12}S_3$
134	25.2	$C_5H_{10}S_2$
108	12.7	$C_3H_8S_2$
107	7.0	$C_3H_7S_2$
86	10.9	C_4H_6S
84	9.6	C_4H_4S
75	100.0	C_3H_7S
74	16.1	C_3H_6S
61	16.9	C_2H_5S
60	6.1	C_2H_4S
59	8.3	C_2H_3S
47	17.9	CH_3S
45	11.8	CHS
44	11.4	CS
41	17.7	C_3H_5
40	14.5	C_3H_4
II(b)		
256	10.4	$C_9H_{20}S_4$
208	13.3	$C_8H_{16}S_3$
182	18.3	$C_6H_{14}S_3$
181	12.0	$C_6H_{13}S_3$
134	4.4	$C_5H_{10}S_2$
133	6.8	$C_5H_9S_2$
108	4.0	$C_3H_8S_2$
107	5.6	$C_3H_7S_2$
106	5.7	$C_3H_6S_2$
87	3.4	C_3H_7S
75	100.0	C_3H_7S
74	11.8	C_3H_6S
61	23.7	C_2H_5S
60	8.4	C_2H_4S
59	12.5	C_2H_3S
47	26.0	CH_3S
46	10.5	CH_2S
45	18.5	CHS
41	32.6	C_3H_5

cess the m/e = 155 ion must lose two sulphur atoms only.[9]

The fragmentation pattern for Ia–c below m/e = 91 showed a larger peak for m/e = 77 (C_6H_5) than for m/e = 65 (C_5H_5). This suggests that m/e = 91 is not the tropylium ion (VI) but is the benzyl ion (VII).


(VI)


(VII)

The tropylium ion readily loses HC≡CH to give an intense ion m/e = 65,[10] whereas the benzyl ion would be more likely to give m/e = 77 by loss of $\cdot CH_2$.

Ligands of Type II

The major fragments of IIa and IIb are shown in Table III. The fragmentation process consists mainly of α-fission with and without rearrangement by hydrogen atom migration. The base peak in both spectra is m/e = 75, presumably formed by cleavage of $CH_3SCH_2CH_2^{+\cdot}$ from the parent ions. However, with these ligands there does not appear to be a single distinct formation of a daughter ion which in turn gives rise to recognisable fragments as in type I ligands. Rather, there are many different cleavage reactions occurring because of the presence of several aliphatic chains.

Acknowledgement

One of us (SGM) is grateful to the Science Research Council for the award of a Research Studentship.

References

1 Part VI. S.T. Show and C.A. McAuliffe, *J. Organomet. Chem., 77* (1974) 401.
2 K.K. Chow and C.A. McAuliffe, *J. Organomet. Chem., 59* (1973) 247.
3 W. Levason, C.A. McAuliffe and R.D. Sedgwick, *J. Organomet. Chem., 84* (1975) 239.
4 C.A. McAuliffe, *Inorg. Chem., 12* (1973) 2477.
5 T.N. Lockyer, *Aust. J. Chem., 27* (1974) 259.
6 S.K. Shapiro and F. Schlenk, Ed., "Transmethylation and Methionine Biosynthesis," The University of Chicago Press, Chicago and London, 1965.
7 C.A. McAuliffe and S.G. Murray, manuscript in preparation.
8 A. Tatematsu, S. Inoue and T. Goto, *Tet. Letts.,* 4609 (1966).
9 J. D. Madsen, C. Nolde, S.-O. Lawesson, G. Schroll. J.H. Bowie and D.H. Williams, *J. Chem. Soc. (B),* 951 (1966).
10 S. Meyerson, *J. Am. Chem. Soc., 85* (1963) 3340.