

Letter to the Editor

Dear Sir,

Loss of a Phenyl Anion by Heterolytic Bond Cleavage in the EI Mass Spectra of Bis(salicylideneamino)alkane-Bis(diphenylboron) Chelates

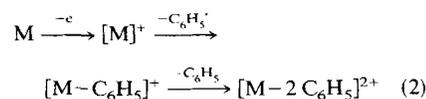
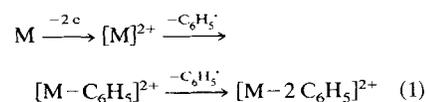
During a systematic mass spectrometric study of the structures of boron chelates we investigated the mass spectra of the bis(azomethine-diphenylboron) chelates **1-6** (bis(2,2-diphenyl-1-oxa-3-azonia-2-borata-3-naphthyl)alkanes) and the mono(diphenylboron) chelate **7** derived from aliphatic diamines.¹

The intensities of the molecular ions of **1-7** in the 70 eV mass spectra are low (see Fig. 1 for **2**) and the base peak of all spectra corresponds to the fragment ions $[M - C_6H_5]^+$ in agreement with the mass spectra of the corresponding 'monochelates' derived from aliphatic monoamines.^{2,3} Contrary to the behaviour of the monochelates, however, the mass spectra of the 'bischelates' **1-6** contain characteristic signals which can be attributed to the doubly charged ions $[M - 2C_6H_5]^{2+}$ (see Table 1).

The formation of doubly charged ions containing two boron atoms is easily recognized by intense satellite peaks due to the boron isotopes which appear at half mass units on the mass scale. By this test no doubly charged ions are formed in the mass spectrum of the monochelate **7**, and the peak at m/z 146 in this spectrum is due to singly charged fragment ions.

In the case of **2**, the formation of fragment ions $[M - C_6H_5]^+$ and $[M - 2C_6H_5]^{2+}$, respectively, has been further corroborated by high resolution mass spectrometry (MAT 311A mass spectrometer, mass resolution c. 10 000). The ion masses determined are in good agreement with those calculated for the proposed elemental compositions of the ions (see Table 2).

A priori the $[M - 2C_6H_5]^{2+}$ ions may be formed via one of the following reaction sequences:



The doubly charged molecular ions formed in reaction sequence (1) may decompose by the subsequent loss of two phenyl radicals. However, this sequence is unlikely to occur in the present case because the intermediate ions $[M]^{2+}$ and $[M - C_6H_5]^{2+}$ are either absent or of very low intensity in the mass spectra of **1-6**. In reaction sequence (2), the

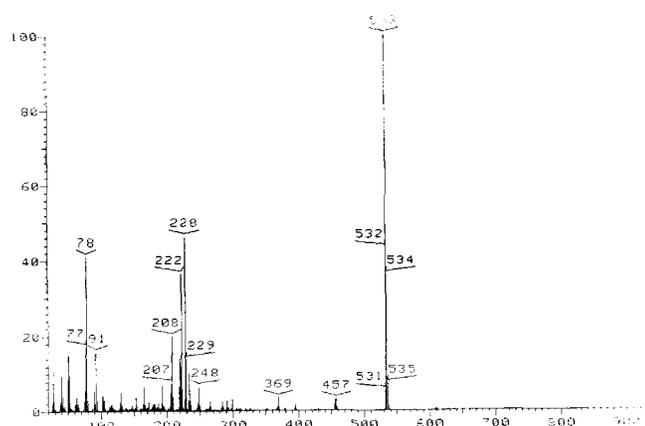
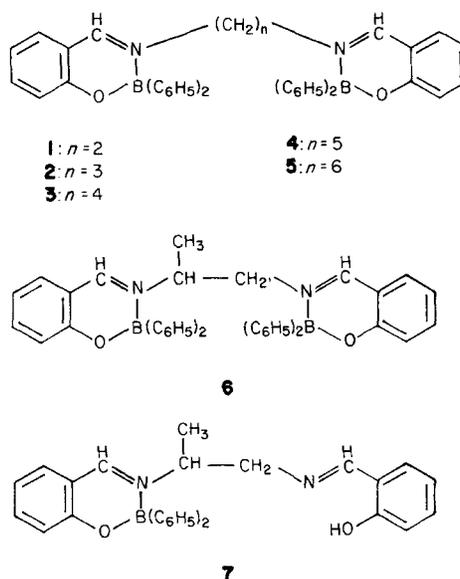


Figure 1. 70 eV mass spectrum of 1,3-bis(2,2-diphenyl-1-oxa-3-azonia-2-borata-3-naphthyl)propane (**2**), obtained on a Varian MAT 311A mass spectrometer.

Table 1. Mass numbers and relative intensities of characteristic singly and doubly charged ions in the mass spectra of **1-7**^a

Chelate		$[M]^{2+}$	$[M]^{2+}$	$[M - C_6H_5]^+$	$[M - C_6H_5]^{2+}$	$[M - 2C_6H_5]^+$	$[M - 2C_6H_5]^{2+}$
1	m/z	596	298	519	259.5	442	221
	% Rel. int.	—	1	100	1	2	41
2	m/z	610	305	533	266.5	456	228
	% Rel. int.	—	—	100	2	3	61
3	m/z	624	312	547	273.5	470	235
	% Rel. int.	—	—	100	—	—	57
4	m/z	638	319	561	280.5	484	242
	% Rel. int.	—	6	100	—	10	49
5	m/z	652	326	575	287.5	498	249
	% Rel. int.	2	—	100	—	17	56
6	m/z	610	305	533	266.5	456	228
	% Rel. int.	1	—	100	2	4	68
7	m/z	446	223	369	184.5	292	146
	% Rel. int.	—	2	66	2	2	(71)

^a Electron impact mass spectra were obtained at 70 eV on a Varian MAT CH7 mass spectrometer.

Table 2. Calculated and experimentally determined masses of $[M-C_6H_5]^+$ and $[M-2C_6H_5]^{2+}$ ions in the mass spectrum of **2**

Ion	Elemental composition	Mass	
		Calc. ^a	Exp.
$[M-C_6H_5]^+$	$C_{35}H_{31}N_2O_2^{11}B_2$	533.2584	533.2693
	$C_{35}H_{31}N_2O_2^{10}B^{11}B$	532.2612	532.2603
$[M-2C_6H_5]^{2+}$	$C_{29}H_{26}N_2O_2^{11}B_2$	228.1097	228.1107
	$C_{29}H_{26}N_2O_2^{10}B^{11}B$	227.6109	227.6103

^a Mean value including contribution of ^{13}C satellite which is not separated at a resolution of 10 000.

$[M-2C_6H_5]^{2+}$ ions arise from the singly charged fragment ions $[M-C_6H_5]^{2+}$ by loss of a phenyl anion (or phenyl radical + electron?). To establish the mechanism of formation of the $[M-2C_6H_5]^{2+}$ ions their direct metastable precursor ions in the mass spectra of **1-3** have been determined by the accelerating voltage scan technique and by the B^2/E linked scan technique with a VG 2 ZAB mass spectrometer.

The metastable precursor ion spectra of the $[M-2C_6H_5]^{2+}$ ions of **1-3** thus obtained show signals due to the process $[M-C_6H_5]^+ \rightarrow [M-2C_6H_5]^{2+} + C_6H_5^-$ as expected for reaction sequence (2). In the case of **2**, this process gives rise to the only signal observed in the B^2/E spectrum, while the B^2/E spectra of **1** and **3** contain some additional peaks of lower intensity which, however, cannot be related to the last step in reaction sequence (1) or to other meaningful fragmentation reactions. It should be noted that only in the mass spectrum of **2** is the peak group of the $[M-2C_6H_5]^{2+}$ ions free from interference by other fragment ions, while in the case of **1** and **3** fragment ions of unknown structure, but of the same masses as the relevant $[M-2C_6H_5]^{2+}$ ions, appear in the mass spectra.

Hence, the metastable precursor ion

spectra prove clearly that the $[M-2C_6H_5]^{2+}$ ions in the mass spectra of **1-3** are formed (at least in part) by a heterolytic bond cleavage in the singly charged species $[M-C_6H_5]^+$ and by loss of a phenyl anion as shown in reaction (2).

The formation of doubly charged fragment ions by a similar process of charge separation has been reported by Bel and Mandelbaum in the 70 eV mass spectra of certain bisbenzyltetrahydroisoquinolines.⁴ The bis(azomethine-diphenylboron) chelates represent a further example of this unusual fragmentation reaction. The phenyl anion (or phenyl radical + electron) lost during the fragmentation of the bischelates is not stable and not a good leaving group. Furthermore, the monochelate **7** and other monochelates^{2,3} do not form $[M-2C_6H_5]^{2+}$ ions by electron impact. This shows clearly that the $[M-2C_6H_5]^{2+}$ ions in the mass spectra of the bischelates **1-6** are formed by the loss of one phenyl group from each of the diphenylboron groups in the molecules.

We assume that the driving force of the heterolytic bond cleavage and the loss of a phenyl anion from the $[M-C_6H_5]^+$ ions is the formation of a strong B—N bond with a boron atom of coordination number 3.⁵ In fact, the absence or very low abundance of

the molecular ions of **1-7** and of other azomethine-boron chelates in the EI mass spectra³ may indicate that even the $[M-C_6H_5]^+$ ions are formed by a heterolytic bond cleavage induced in the neutral molecule by electron impact.

Yours

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