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PORPHYRINS

30.* MASS SPECTROMETRIC STUDY OF ETHANE- AND ETHYLENE-BIS-PORPHYRINS

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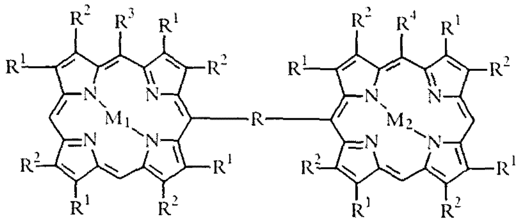
The mass spectral behavior of 1,2-di(mesoetioporphyrinyl-1)- and 1,2-di(mesooctaethylporphyrinyl)ethanes and ethylenes, their Cu and Ni complexes, as well as Ni Schiff bases of 1,2-di(mesooctaethylporphyrinyl)ethane complexes, under ionization by electron impact and bombardment by accelerated atoms, was studied. Peaks of molecular ions, for which the basic decomposition pathways were established on the basis of an analysis of the parent and daughter ions, were observed in the electron impact mass spectra of all these compounds.

The synthesis and production of bis-porphyrins is one of the directions of modern porphyrin chemistry under intensive development. A detailed analysis of the literature on covalently bonded bis-porphyrins was presented in Dolphin's review [2], from which it follows that a study of such structures is of exceptional interest for the creation of catalytic systems in order to detect simple molecules of the O_2, CO, CO_2, and NO_x types, and to establish processes of reversible binding of oxygen and the primary event of photosynthesis.

Beginning with the first studies of the synthesis of ethane-bis-porphyrins and chlorins [3, 4], the use of electron impact mass spectrometry to confirm the structure of the dimers obtained encountered definite difficulties, associated with the detection of the peaks of the molecular ions $M^{\cdot +}$. The obscurity of the origin of the most intense peaks of ions belonging to monomer derivatives of the corresponding porphyrins and their mesomethyl-substituted analogs in the mass spectra of these dimers gives rise to the need to establish the basic principles of their breakdown under electron impact for a reliable identification of compounds of this class.



I - XVIII

I, II, XIII, XVIII $R^1 = CH_3$, $R^2 = C_2H_5$; III—IX, XII, XIV—XVI $R^1 = R^2 = C_2H_5$; X $R^1 = R^2 = C_3H_7$; XI, XVII $R^1 = CH_3$, $R^2 = CH_2CH_2COOC_2H_5$; I—XI A = CH_2CH_2; XII A = CH_2OCH_2; XIII—XVII A = =CH=CH; XVIII A = CH=N—$(CH_2)_6$—N=CH; I, III $M_1 = 2H$, $M_2 = Cu$; II, IV, XII, XV $M_1 = M_2 = Cu$; V, VII $M_1 = 2H$, $M_2 = Ni$; VI, VIII, IX, XI, XVI $M_1 = M_2 = Ni$; X, XIII, XIV, XVII, XVIII $M_1 = M_2 =$ =2H; VII, VIII $R^3 = CH{=}NCH_3$, $R^4 = H$; IX $R^3 = R^4 = CH{=}NCH_3$. R^3 and R^4 = H are not indicated.

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*For Communication 29, see [1].

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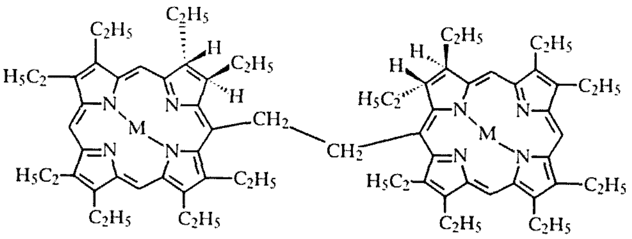


XIX - XX

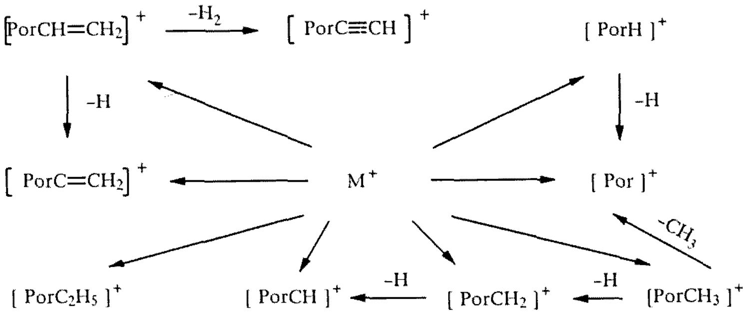
XIX M = 2 H, XX M = Cu

Thanks to the new methods of synthesis of ethane- and ethylene-bis-porphyrins [5-11] and chlorins [12] that we discovered, it was possible to produce a whole series of porphyrin dimers I-VI, X, XI, XIII-XVI and chlorin dimers XIX, XX. Moreover, formylation of the dimers V and VI, followed by treatment of the reaction products with a 25% aqueous solution of $MeNH_2$ by the method of [13], yielded a series of Schiff bases VII-IX, while the reaction of excess meso-(N,N'-dimethyliminomethylene iodide)etioporphyrin-I [14] with 1,6-hexanediamine yielded the dimer product XVIII.

Peaks of the $M^{\cdot +}$ ions are observed in the electron impact mass spectra of all the compounds studied, I-XVII (Table 2); their intensity, however, does not exceed 5%. Exceptions are the ethylene-bis-porphyrins XIII, XIV, and XVII, in the mass spectra of which the peaks of the $M^{\cdot +}$ ions have significant intensity. A comparison of the mass spectra of ethane-bis-porphyrins I-IX shows that the stability of complexes with two metal atoms in the porphyrin rings to electron impact is an order of magnitude higher than in analogous complexes with a metal atom in one porphyrin ring. On the contrary, metallocomplexes of ethylene-bis-porphyrins XV, XVI are significantly less stable to electron impact in comparison with their demetallated analog XIV.

The most intense peaks in the mass spectra of the compounds I-XVII studied are due to the ions* $[PorCH_3]^+$ and $[PorH]^+$. An analysis of the parent and daughter ions in the mass spectra of compounds IV, XIII, and XIV showed that at least part of these ions are formed directly in the breakdown of $M^{\cdot +}$ ions. Scheme 1 presents the main pathways of decomposition of the $M^{\cdot +}$ ions of the ethane- and ethylene-bis-porphyrins studied.

Scheme 1



The possible mechanism of the formation of $[PorCH_3]^+$ and $[PorCH_2]^+$ ions in the spectra of the compounds studied is evidently analogous to the rearrangement process (scheme 2) studied in the breakdown of the Schiff bases of mesoformylporphyrins [15, 16] and meso(2-methylbutenyl-1)porphyrins [17]. In the mass spectrum of compound XII, the ions $[PorCH_2OCH_3]^+$, $[PorCH_2OH]^+$ and $[PorCHO]^+$ are analogs of the ions $[PorC_2H_5]^+$ and $[PorCH=CH_2]^+$, respectively. The mass spectra of ethane- and ethylene-bis(etioporphyrins) and -(octaethylporphyrins) also contain peaks of ions due to stripping of methyl and ethyl radicals from the ions shown in scheme 1. The octaethyl esters of dimer derivatives of coproporphyrins XI, XVII are characterized by the presence in the mass spectra of peaks of ions associated with stripping of the radicals OC_2H_5, $COOC_2H_5$, and $CH_2COOC_2H_5$, respectively. The mass spectra of the Schiff bases VII-IX also contain peaks of the ions $[PorCH_3-NH_2CH_3]^+$, the mechanism of formation of which was described earlier [16].

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*Here in the text and tables and on the scheme, Por denotes the radical of the corresponding porphyrin.

TABLE 1. Characteristic Ions in the Mass Spectra of Compounds I-XVII

Compound	m/z (rel. %)*									
	M^+	$[PorC_2H_5]^+$	$[PorCHCH_2]^+$	$[PorCCH_2]^+$	$[PorCCH]^+$	$[PorCH_3]^+$	$[PorCH_2]^+$	$[PorCH]^+$	$[PorH]^+$	$[Por]^+$
I	1043 (0,8)	567 (4)	565 (2)	—	—	553 (100)	552 (18)	551 (5)	539 (34)	538 (15)
		506 (3)	504 (2)			492 (77)	491 (10)	490 (3)	478 (22)	477 (10)
II	1104 (5)	567 (7)	565 (2)	—	—	553 (100)	552 (25)	551 (3)	539 (61)	538 (14)
III	1155 (0,2)	623 (6)	621 (4)	—	—	609 (100	608 (12)	607 (8)	595 (36)	594 (11)
		562 (3)	560 (1)			548 (84)	547 (6)	546 (5)	534 (28)	533 (11)
IV	1216 (4)	623 (20)	621 (6)	—	—	609 (100)	608 (63)	607 (12)	595 (92)	594 (18)
V	1150 (2)	618 (3)	616 (3)	—	—	604 (45)	603 (24)	602 (4)	590 (8)	589 (5)
		562 (2)	560 (3)			548 (100)	547 (18)	546 (5)	534 (40)	533 (5)
VI	1206 (0,5)	618 (7)	616 (9)	—	—	604 (100)	603 (16)	602 (11)	590 (37)	589 (11)
VII*2	1191 (0,02)	659 (0,4)	657 (0,1)	—	—	645 (3)	644 (0,4)	643 (0,1)	631 (0,7)	630 (1)
		562 (5)	560 (2)			548 (100)	547 (14)	546 (3)	534 (62)	533 (13)
VIII	1247 (0,3)	659 (0,9)	657 (0,4)	—	—	645 (13)	644 (5)	643 (1)	631 (3)	630 (3)
		618 (20)	616 (30)			604 (100)	603 (13)	602 (13)	590 (17)	589 (9)
IX*3	1288 (0,1)	659 (3)	657 (2)	—	—	645 (14)	644 (15)	643 (4)	631 (8)	630 (10)
X	1319 (0,4)	674 (1)	672 (0,6)	—	—	660 (100)	659 (17)	658 (5)	646 (9)	645 (7)
XI	1670 (0,2)	850 (15)	848 (7)	—	—	836 (100)	835 (9)	834 (7)	822 (75)	821 (9)
XII*4	1232 (3)	—	—	—	—	609 (100)	608 (25)	607 (14)	595 (30)	594 (8)
XIII	980 (64)	—	504 (11)	503 (8)	502 (5)	492 (67)	491 (41)	490 (33)	478 (100)	477 (21)
XIV	1092 (45)	—	560 (3)	559 (2)	558 (2)	548 (100)	547 (25)	546 (7)	534 (27)	533 (13)
XV	1214 (2)	—	621 (5)	620 (2)	619 (1)	609 (100)	608 (26)	607 (13)	595 (68)	594 (14)
XVI	1204 (1)	—	616 (3)	615 (1)	614 (3)	604 (100)	603 (11)	602 (8)	590 (30)	589 (9)
XVII	1556 (45)	—	792 (36)	791 (14)	790 (17)	780 (34)	779 (41)	778 (27)	766 (100)	765 (10)

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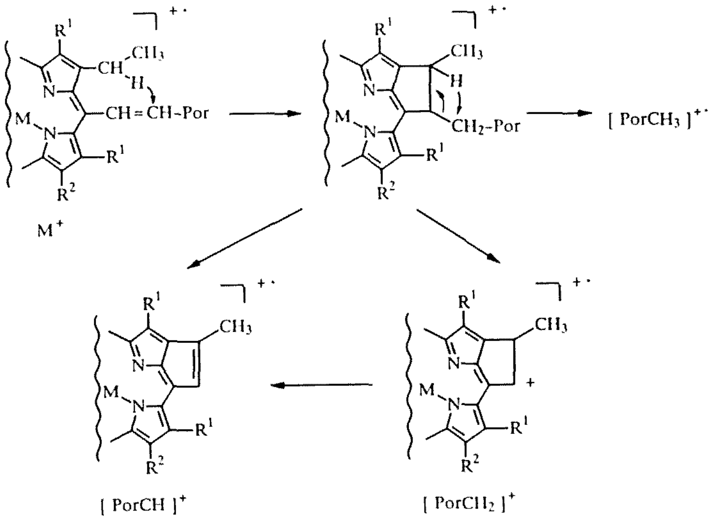
*In the spectra of compounds I-IV, XII, XV and V-IX, XI, XVI the values of m/z are given for the isotopes ^{63}Cu and ^{58}Ni, respectively.

*2Compound VII and Schiff base isomeric to it with a substituent in the β-position of the porphyrin ring have identical mass spectra.

*3m/z 616 (100).

*4In the spectrum of compound XII, the ions $[PorCH_2OCH_3]^+$ 639 (0.6), $[PorCH_2OH]^+$ 625 (48), and $[PorCH{=}O]^+$ 623 (15) are analogs of the ions $[PorC_2H_5]^+$ and $[PorCHCH_2]^+$.

Scheme 2

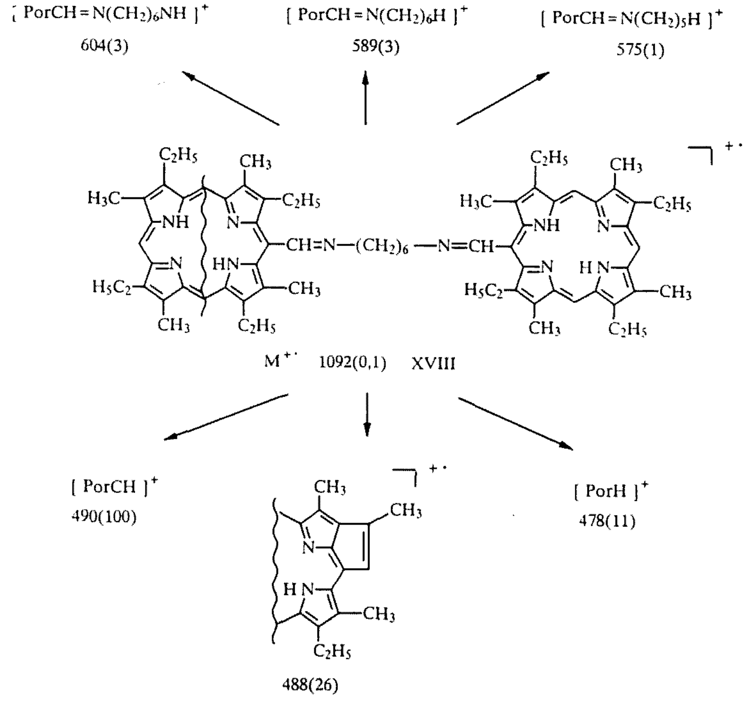


Low-intensity peaks of the ions $M^{\cdot +}$ 1098(4)* and 1220(1) were observed in the electron impact mass spectra of the chlorins XIX and XX, respectively.

The peaks of the doubly charged ions characteristic of the mass spectra of substituted porphyrins [18] are also present in the spectra of all the compounds I-XVII studied, in the form of the ions $[PorC_2H_5]^{2+}$, $[PorCH{=}CH_2]^{2+}$, $[PorCH_3]^{2+}$, and $[PorH]^{2+}$. The peaks of the doubly charged ions M^{2+} are present only in the spectra of ethylene-bis-porphyrins XIII, XIV, and XVII.

To confirm the proposed pathways of decomposition of $M^{\cdot +}$ ions of compounds I-XII (scheme 1), we obtained the electron impact mass spectrum of meso,meso-bis(N,N-hexamethyleneformaldiminethioporphyrinyl-I) (XVIII). It was found that increasing the length of the bridge between the two porphyrin rings has virtually no effect on the general patterns of decomposition established for $M^{\cdot +}$ ions of the ethane- and ethylene-bis-porphyrins studied (scheme 1), and the basic peak in the spectrum of compound XVIII corresponds to the ions of meso-substituted monomeric etioporphyrins (scheme 3).

Scheme 3



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*Here in the text and on scheme 3 the values of *m/z* and the intensity (in parentheses) are given.

TABLE 2. Characteristic Peaks of the Ions in the Mass Spectra of BAA of Compounds II, IV, V, VII, IX, XIII, XIV, and XVI

Compound	m/z (rel, %)						
	$[M+H]^+$	$[PorCHCH_2+H]^+$	$[PorCCH_2]^+$	$[PorCH_3+H]^+$	$[PorCH_2]^+$	$[PorH+H]^+$	$[Por]^+$
II	1105 (29)	566 (29)	—	—	552 (100)	—	538 (51)
IV	1217 (23)	622 (44)	—	—	608 (80)	—	594 (75)
V	1151 (57)	617 (5) 561 (12)	—	—	603 (100) 547 (51)	—	589 (9) 533 (27)
VII	1192 (18)	658 (5) 558 (10)	—	—	644 (21) 547 (100)	—	630 (6) 533 (29)
IX	1289 (16)	658 (4)	—	—	644 (100)	—	630 (18)
XIII	981 (100)	—	503 (11)	493 (11)	491 (25)	479 (26)	—
XIV	1093 (67)	—	559 (8)	549 (100)	547 (80)	535 (43)	—
XVI	1205 (2)	—	615 (5)	605 (100)	603 (48)	591 (25)	—

The mass spectra obtained in the ionization of certain ethane- and ethylene-bis-porphyrins by bombardment with accelerated atoms (BAA) (Table 2), in addition to the peaks of the protonated molecular ions, contain the peaks of the ions $[PorCHCH_2 + H]^+$, $[PorCH_2]^+$, $[Por]^+$ (ethane-bis-porphyrins) and $[PorC{=}CH_2]^+$, $[PorCH_3 + H]^+$, $[PorCH_2]^+$, $[PorH + H]^+$ (ethylene-bis-porphyrins). It is interesting to note that although ethane-bis-porphyrins are characterized by the presence of intense peaks of the $[PorCH_2]^+$ ions in the mass spectra, the formation of $[PorCH_3{+}H]^+$ ions in the mass spectra is more probable for ethylene-bis-porphyrins.

Thus, as a result of a study of the mass spectra of dimer compounds I-XX it was established that despite the low intensity of the peaks of $M^{+\cdot}$ ions of ethane-bis-porphyrins in the electron impact mass spectra, the latter, just like the mass spectra obtained in ionization by bombardment with accelerated atoms, are sufficiently informative to establish the structure of these compounds, and the peaks of the ions $[PorC_2H_5]^+$, $[PorCH_3]^+$ and $[PorH]^+$ in the electron impact mass spectra and the peaks of the ions $[PorCH_2 + H]^+$, $[PorCH_2]^+$ and $[Por]^+$ in the BAA mass spectra can be used to determine the porphyrin rings in the dimers. The BAA spectra, together with the spectra of metastable ions and the picture of the isotope distribution (calculated and experimental), permit an estimation of the contribution to the characteristic peaks of the ions formed in thermal decomposition and under the action of electron impact, respectively. In the mass spectra of the compounds that we studied, the contributions of such ions (for example, $[PorCH_3]^+$ and $[PorH]^+$) to the intensity of the peaks proved basically comparable.

EXPERIMENTAL

The electron impact mass spectra were obtained on a Finnigan MAT-90 double-focusing instrument with energy of ionizing electrons 70 eV by the method of direct introduction. The temperature of evaporation of the samples was 280-340°C, and the temperature of the ionization chamber was 200°C. The BAA mass spectra were obtained on the same instrument, using xenon atoms with energy 7-8 kV. A mixture of dithioerythritol and dithiothreitol in a 1:3 ratio ("magic bullet") was selected as the matrix. The use of glycerin as a matrix did not lead to satisfactory results. The investigated dimer was applied to the surface of the matrix, and then moistened with trifluoroacetic acid. Metastable ions were analyzed in the first and second field-free spaces; the former proved to be more informative both for the parent and for the daughter ions.

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