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Metal Complexes of Porphyrin Dimers with Ether and C=C Bonds

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A novel synthesis of a heterometallic complex of ether-bonded porphyrin–chlorin has been performed; metal complexes of α-hydroxyethyl-substituted porphyrins were found to form 2,3-bis-metallporphyrinbut-2-enes in the presence of trifluoroacetic acid; the dimers of two different types exhibited essentially distinct fragmentation in plasma desorption mass spectrometry (PDMS).

Covalently-bonded dimeric porphyrins and their metal complexes are useful models for the study of energy transfer, as oxygen activation models and for the selective design of catalysts. Our last paper was devoted to the synthesis of bis-metal complexes of ether-bonded porphyrin-chlorin dimers.[1] Insertion of two different metals into the dimer molecule could potentially create new models.

In this paper we present a first synthesis of metal complexes of this type. Attempts at step-by-step metal insertion into dimer **3a**,[2] based upon the difference in complex-forming ability of porphyrin and chlorin moieties,[1] were found to be too cumbersome. Thus, we initially prepared copper α-hydroxyethylporphyrin **1b**, which was then treated with chlorin **2b** in the presence of 1 mol of *N*,*N*-dimethylaminopyridine. The resulting copper complex **3b** was treated with zinc acetate to give zinc-copper hetero-complex **3c**. The electronic absorption spectrum of hetero-metal dimer showed bands at 528 and 564 nm, which correspond to a copper–porphyrin moiety, and a 617 nm band, which represents a zinc–chlorin moiety. The general structure of the dimer was confirmed by mass spectrometry.†

In the course of synthesis of dimer **3b** we found that, unlike free base porphyrin **1a**, its metal complex in the presence of even trace amounts of trifluoroacetic acid rapidly converted into symmetric 2,3-bis-copper-porphyrin-but-2-ene **4a**.‡ Similar dimerization of *meso*-substituted methoxypor-phyrin leading to 1,2-ethylene-bis-porphyrin formation was described earlier.[4] An explanation was proposed based upon the ability of *meso*-methoxyporphyrins to form stabilised carbocations on protonation with trifluoroacetic acid in chloroform or dichloroethane solutions; these carbocations in trufluoroacetic media in the absence of nucleophilic agents could undergo various transformations until they finally end up as dimeric porphyrins.

A study of the reaction discovered has shown that it is common to α-hydroxy-substituted porphyrin metal complexes. The copper complex of porphyrin **1b** (as chloroform solution) was shown to transfer into dimer **4a** with a yield of 80% in the presence of trifluoroacetic acid.‡

†Copper complex **1b** was obtained from hydroxyporphyrin **1a**[3] by treatment with copper acetate at 20 °C for 5 min to yield 88%, m.p. 302–304 °C (decomp.), λ_{max} ($CHCl_3$)/nm, ($\varepsilon/10^3$ dm^3 mol^{-1} cm^{-1}): 398 (350), 525 (12.7), 563 (22.6), *m/z* (%): 612 ($M^{\cdot+}$, 100), 580 (75), 564 (60).

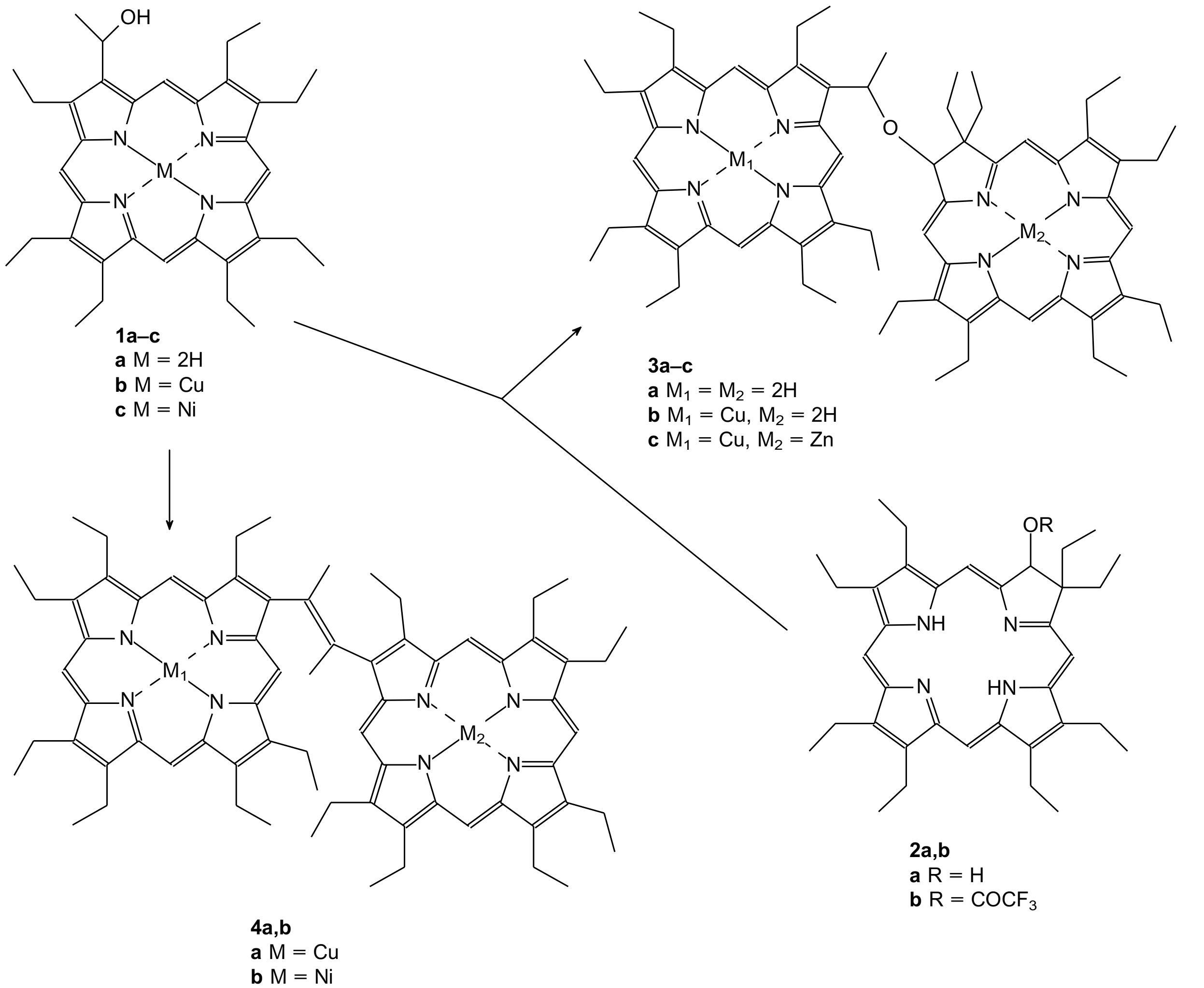
Dimer **3b** was prepared in 35% yield, m.p. 234–236 °C, λ_{max} ($CHCl_3$)/nm ($\varepsilon/10^3$ dm^3 mol^{-1} cm^{-1}): 402 (236), 497 (13.4), 525 (13.2), 563 (18.8), 613 (3.6), 642 (31.5), *m/z* (%): 1147 ($M^{\cdot+}$, 100), 594 (105), 580 (110), 534(105).

Zinc–copper dimer **3c** was prepared in 94% yield, m.p. 160–162 °C, λ_{max} ($C_2H_4Cl_2$)/nm ($\varepsilon/10^3$ dm^3 mol^{-1} cm^{-1}): 399 (207), 528 (16.0), 564 (24.2), 617 (29.5), *m/z* (%): 1211 ($M^{\cdot+}$, 100), 600 (45), 572 (50).

‡ Characteristic data for the dimer **4a**: m.p. 156-158 °C, λ_{max} ($CHCl_3$)/nm ($\varepsilon/10^3$ dm^3 mol^{-1} cm^{-1}): 408 (178), 413 (205), 529 (18.3), 565 (29.7), *m/z* (%): 1189 ($M^{\cdot+}$, 100), 1160 (50), 621(40).

§ Nickel complex **1c** was prepared by heating hydroxyporphyrin **1a** with nickel acetate in acetic acid at 50 °C for 3 h to give 53%, m.p. 296–298 °C (decomp.), λ_{max} ($CHCl_3$)/nm ($\varepsilon/10^3$ dm^3 mol^{-1} cm^{-1}): 394 (122), 518 (10.3), 553 (25.0), *m/z* (%): 607 ($M^{\cdot+}$, 100).

Dimer **4b** was obtained in 72% yield, m.p. 198–202 °C, λ_{max} ($CHCl_3$)/nm ($\varepsilon/10^3$ dm^3 mol^{-1} cm^{-1}): 399 (127), 407 (130), 523 (15.6), 567 (35.6), *m/z* (%): 1179 ($M^{\cdot+}$, 100), 1151 (40), 618 (50), ^{1}H NMR δ (ppm): 10.48 (1H, s, *meso*-H), 9.80 (1H, s, *meso*-H), 9.69 (1H, s, *meso*-H), 9.65 (1H, s, *meso*-H), 9.57 (1H, s, *meso*-H), 9.45 (1H, s, *meso*-H), 9.08 (1H, s, *meso*-H), 9.01 (1H, s, *meso*-H), 3.4-4.2 (28H, m, C*H*$_2$CH$_3$), 1.52 (6H, s, CH$_3$), 0.8–2.1 (42H, m, CH$_2$C*H*$_3$).



Nickel complex **4b**[§] was prepared by the same procedure.

Electron absorption spectra of dimers **4a** and **4b** have a specific Soret band split into two maxima of approximately equal intensity, which indicates considerable macrocycle interaction. The presence of eight *meso*-proton resonances in the ^{1}H NMR spectrum of **4b** also confirms the rearrangement of electron density between the porphyrin rings.

The C=C dimers synthesised were found to exhibit unusual behaviour in their ^{252}Cf PDMS spectra.[¶] Usually, the most abundant $M^{\cdot+}$ and less intense MH^+ signals are recorded in PDMS spectra in the region of porphyrin molecular mass.[6] The molecular weights of compounds **1**–**4** were unambigously determined by the average mass of the $M^{\cdot+}$ ion, which was the most abundant sharp signal with the highest m/z value (Fig. 1). Fragment ions of starting monomers **1a**–**c** and **2a**, as well as of dimers **3** and **4** were represented by characteristic series of regularly spaced (14 m/z units apart) abundance-oscillating signals in the range of m/z 400–650, which corresponded to ethyl substituent cleavage of monomeric porphyrin. For monomer **1** and **2a** spectra these signals appeared to arise close to the $M^{\cdot+}$ peak and usually constituted not more than 80% of its abundance, Fig. 1(*a*). Fragment ion signals of ether-bonded porphyrin dimers **3a**–**c** were removed from the molecular ion peak, Fig. 1(*b*). These fragmentation patterns in the PDMS spectra were observed for all previously synthesised ether-bonded dimers.[1,2,7]

Fragmentation of newly synthesised **3** and **4** dimers reflects the distinctions between the type of chemical linkage between the macrocycles, Fig. 1(*b,c*). As a consequence of insufficient ether-bond stability between the macrocycles, abundant fragment ions with "retained" dimeric structure were not recorded for the **3a**–**c** dimers, Fig. 1(*b*). This typical spectrum, which is inherent in porphyrin dimers with either an ether or an ester bond between macrocycles, has been discussed in the literature.[8,9] For the C=C dimers **4a,b**, which are more chemically stable relative to the above-mentioned ether/ester-linked dimers, one more characteristic set of peaks was observed in the PDMS spectra, Fig. 1(*c*). The signals were found to be regularly spaced in the m/z scale close to the molecular ion and constituted about 40% of its abundance. These ions correspond to ethyl-substituent fragmentation of the unbroken dimeric structure. Hence, the fragmentation pattern of the PDMS spectra for porphyrin dimers of different species was found to be characteristic and represents differences in the stability of the chemical linkage between the macrocycles.

¶ Mass spectra were obtained on a time-of-flight (TOF) biochemical mass spectrometer BC MS[5] (SELMY, Sumy, Ukraine), with resolution $m/\Delta m$ at full width at half-maximum (FWHM) 500 on $(CsI)_2Cs^+$ ion. Samples were applied onto a gilded disc as chloroform solutions (1 nmol), accelerating voltage was +10 kV.

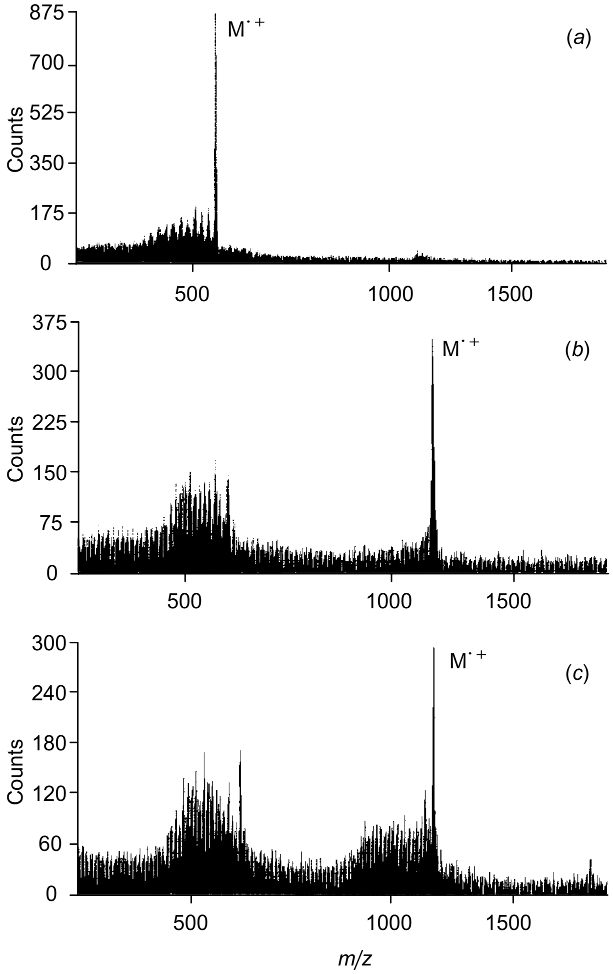


Fig. 1 Mass spectra of compounds (*a*) **2a**; (*b*) **3c** and (*c*) **4b**.

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