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## Complexes of *meso*-tetrametalloacenylporphyrins with Zn<sup>II</sup> ion and their stability constants with imidazole

N. M. Loim,\* N. V. Abramova, R. Z. Khaliullin, and V. I. Sokolov

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,  
28 ul. Vavilova, 117813 Moscow, Russian Federation.  
Fax: 007 (095) 135 5085

Recently we have obtained the first representatives of a novel class of porphyrins containing metallocenyl groups (ferrocenyl, ruthenocenyl, and cymantrenyl) in *meso*-positions.<sup>1-3</sup> A direct bond of the macroheterocycle skeleton to the metallocenyl fragments with their specific geometry and reactivity opens up new possibilities for obtaining porphyrins and their metallocomplexes with useful practical properties.

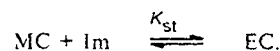
The constants of equilibrium of the formation of the extraligand complexes are important characteristics of porphyrin metallocomplexes, determining their behavior in various processes. In this work, complexes of the Zn<sup>II</sup> ion with tetracyantrenylporphyrin (**1**), tetraferrocenylporphyrin (**2**), and tetraruthenocenylporphyrin (**3**) are first described, and the stability constants ( $K_{st}$ ) of extraligand metallocomplexes **1a**–**3a** with imidazole (Im) have been determined.

Complexes **1a**–**3a** were obtained by interaction of porphyrins **1**–**3** with zinc acetate or zinc chloride in DMF in 85–90% yield and characterized by <sup>1</sup>H NMR, electronic and mass spectra (FAB). UV spectra (CHCl<sub>3</sub>),  $\lambda_{max}/nm$ : **1a** – 464, 559, 595, and 643; **2a** – 436, 618, and 673; **3a** – 438, 599, and 647. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>),  $\delta$ : **1a** – 9.67 (s, 8 H,  $\beta$ -H): 5.79 (m, 8 H, Cp); 5.30 (m, 8 H, Cp); **2a** – 9.84 (s, 8 H,  $\beta$ -H): 5.37 (m, 8 H, Cp); 4.80 (m, 8 H, Cp); 4.07 (s, 20 H, Cp); **3a** – 9.79 (s, 8 H,  $\beta$ -H): 5.71 (m, 8 H, Cp); 5.05 (m, 8 H, Cp); 4.40 (s, 20 H, Cp). MS (FAB),  $m/z$ : **1a** – 1181 [M+H]<sup>+</sup>; **2a** – 1108 [M<sup>+</sup>]; **3a** – 1292 [M<sup>+</sup>].

Samples **1a**–**3a** used for determination of  $K_{st}$  were additionally purified by column chromatography on Al<sub>2</sub>O<sub>3</sub> (Brockmann II activity, benzene), reprecipitated from saturated solutions in benzene or chloroform with cooled hexane, and dried *in vacuo*. The  $K_{st}$  values for the extraligand complexes of compounds **1a**–**3a** with Im and that for zinc tetraphenylporphyrinate (**4**) (taken as

the standard) were obtained by the method of spectrometric titration in benzene at two wavelengths and at 25 °C on a Specord UV-VIS instrument.

The formation of extracomplexes (EC) is accompanied by a bathochromic shift of all absorption bands of the porphyrin chromophore and by a change in their relative intensities. As the metallocomplex (MC) : Im ratio changes in the range from 1 : 0.1 to 1 : 500, several isobestic points are observed in the spectra of the mixtures. They are indicative of the formation of monoligand EC in the solution and existence of an equilibrium of the type:



The obtained value of  $K_{st} = (3.0 \pm 0.6) \cdot 10^4$  for compound **4** at 550 and 570 nm is in good agreement with the data reported previously for the EC of **4** with related extraligands.<sup>4,5</sup> The  $K_{st}$  values  $(3.8 \pm 0.9) \cdot 10^4$  and  $(3.0 \pm 0.7) \cdot 10^4$  for complexes **2a** (at 436 and 684 nm) and **3a** (at 647 and 667 nm), respectively, appeared to be close to each other and to that of **4**. In contrast to this, the stability of the extraligand complex **1a** with Im exceeds the above mentioned values of  $K_{st}$  by two orders of magnitude and equals  $(7.7 \pm 0.5) \cdot 10^6$  (at 586 and 650 nm).

Thus, as could be expected, the stability of complexes of the donor extraligand with the acceptor Zn atom in the studied metalloporphyrins increases as the electron-withdrawing character of *meso*-substituents increases and principally corresponds to the increase in the values of  $\sigma_p$  constants for these substituents: –0.05 (Fc),  $\pm 0.05$  (Ph), 0.04 (Rc), and 0.17 (Cy).<sup>6,7</sup>

Hence, the transfer of the electron influence of the *meso*-substituents in the metallocomplexes studied occurs mainly according to the induction mechanism, which implies a predominant mutually perpendicular orientation of the planes of the porphyrin cycle and of the aromatic ring. This geometry for the series of *meso*-arylporphyrins and their metallocomplexes was established by both X-ray analysis and computational methods.<sup>8,9</sup> There are no X-ray structural data for metallocenylporphyrins. Nevertheless, the analysis of the molecular structure using the Stewart—Briegleb model and calculations using the MM<sup>+</sup> method allow one to draw a conclusion that the Cp-ring plane of the metallocenyl fragments in stable conformers of these compounds makes an angle of 45–60° with the plane of the macrocycle. The above value of the angle does not exclude a partial direct conjugation of the *meso*-metallocenyl substituents with the  $\pi$ -system of the porphyrin cycle.

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