PORPHYRINS

27.* SYNTHESIS OF METAL COMPLEXES OF CIS-1,2-
BIS(OCTAETHYL-5-PORPHYRINYL)ETHYLENE AND
THEIR TRANSFORMATION INTO THE TRANS ISOMERS

G. V. Ponomarev

The synthesis of the Cu, Ni, and Zn complexes of cis-1,2-bis(octaethyl-5-porphyrinyl)ethylene has been carried out and their transformation into the corresponding trans isomers has been investigated under various conditions. The crystal and molecular structure of the Ni complex of trans-1,2-bis(octaethyl-5-porphyrinyl)ethylene was determined by x-ray structural analysis. It was shown that the Zn and Ni complexes of the cis isomer were readily converted into the trans isomers in chloroform. A stepwise introduction of Ni atoms into the trans dimer was discovered on heating it with Ni(OAc)₂ in DMF. The conversion of the Zn complex of the cis dimer into the trans dimer was facilitated on adding pyridine.

It was shown recently that the reductive dimerization of Cu and Ni complexes of meso-formyloctaethylporphyrin under the conditions of the McMurry reaction [2], i.e., treatment of the porphyrins in dimethoxyethane (1:1.5) in the presence of Zn–Cu couple leads, not to the expected trans-ethylenes (Ia) and (Ib) [3], but to a mixture of trans (Ia) or (Ib) and cis dimers (IIa) or (IIb) [4]. Complexes of trans-bis(meso-tetraphenyl-2-porphyrinyl)ethylene are formed exclusively in the dimerization of the Zn and Cu complexes of β-formyl-meso-tetraphenylporphyrin under similar conditions, viz., by the action of TiCl₃/LiAlH₄ in boiling THF [5, 6]. The dimerization of the Ni complex of 2-formyl-3,7,8,12,13,17,18-heptaethylporphyrin with TiCl₃ in dimethoxyethane [4] gives bis(hepta-ethyl-2-porphyrinyl)-carbinol. The reductive dimerization according to McMurry’s method leads to its own set of products in each actual case.

The purpose-directed preparation of the individual trans-dimer (III) [7] and the cis-dimer (IV) [8] from bis-1,2-(octaethyl-5-porphyrinyl)ethane (V) discovered by us enabled investigation of the process of introducing metal atoms into these dimers for the first time. Complex formation in such rigidly bound dimers as the cis-dimer is of considerable interest for creating model photosynthetic "special" pairs since a strong π,π-interaction of the closely placed porphyrin rings is possible in them. The distance between the copper atoms is 3.36 Å and the porphyrin macrocycles are practically plane-parallel (the angle between them is 1.9°) according to the data of the x-ray structural analysis (XSA) of the Cu complex (IIa) [4]. When introducing metal atoms into the dimer (IV) approach is only possible from the outer sides of the porphyrin rings.

The preparation of the complexes was effected by the procedure traditional for porphyrins, i.e., by heating the appropriate dimers (III) or (IV) with an excess of metal acetate in a chloroform–methanol mixture or in DMF.

The metal-complexes of the trans dimer (III) with Cu, Ni, and Zn, viz., (Ia), (Ib), and (Ic), respectively, were formed at the rate usual for porphyrins in quantitative yield. The complexes (Ia) and (Ic) were poorly soluble in chloroform and other solvents traditional for porphyrins, particularly after forming crystals. They were obtained as very fine crystals, and their solubility in chloroform was sufficient only for investigating electronic spectra. The complex (Ib) had a significantly higher solubility in chloroform. We succeeded in selecting conditions for crystallizing it from a chloroform–methanol mixture and obtained crystals of size 0.05 × 0.10 × 0.15 mm suitable for XSA, which was carried out in the Department of Applied

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The complex (Ib) is a centrosymmetric molecule with a distance between the copper atoms of 10.07 Å and the distance between the parallel planes passing through the nitrogen atoms in each of the porphyrins is 4.27 Å. The parameters of the complex are close to those of the Ni complex of the ethane-bisporphyrin (VI) [10]. The overall shape of the complex is shown in Fig. 1a, and a computer representation of bond directions in the molecule relative to the bridge double bond is given in Figs. 1b, 1c. It follows from these figures that the porphyrin macrocycle is not planar in the dimer. The dihedral angle between the