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NEW COMPLEXES OF Co-meso-(TETRAPYRIDIN-4-YL)PORPHINE

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New unsymmetrical complexes have been obtained from Co-meso-(tetrapyridin-4-yl)porphine. As the ligands to the central cobalt carbon atom we have investigated a number of aliphatic, aromatic, and heterocyclic amines. The compounds synthesized have been characterized by IR and electron spectroscopy.

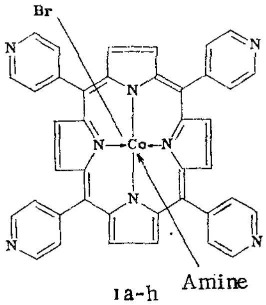
The diverse unique properties of the metalloporphyrins possessing substituents capable of exerting an appreciable influence on the electronic system of porphyrin are opening up great possibilities for the search for new and effective catalysts for medical and technical purposes [1, 2]. The formation of complexes of the metalloporphyrins is at the basis of the important vital processes of respiration, photosynthesis, and enzymatic catalysis [3]. One of the clear examples of enzymatic catalysts is vitamin B_{12}, which is based on an octahedral cobalt complex with a modified porphyrin ring.

In the light of what has been said above, the synthesis of complexes of cobalt porphyrins with the aim of obtaining biologically active compounds is acquiring particular significance.

There is information on the formation of complexes in cobalt porphyrins [4-8], most of which have not been isolated in the crystalline state. A number of complexes based on Co-etioporphyrin have been obtained and isolated [9] and have been characterized by elementary analysis and electron spectroscopy.

The present work set itself the aim of obtaining complexes from Co-meso-(tetrapyridin-4-yl)porphine (CoTPyP) which is capable through the pyridine nitrogens of forming various derivatives, including water-soluble derivatives, the catalytic and biological properties of which may be of great interest. Only one example of a pentacoordinated zinc complex of tetrapyridylporphine with pyridine is known from the literature [10, 11].

As the ligands to the central cobalt atom we investigated a number of aliphatic, aromatic, and heterocyclic amines (n-butylamine, sec-butylamine, tert-butylamine, pentylamine, cyclohexylamine, piperidine, aniline, and pyridine).



Ia-h

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TABLE 3. Amine Derivatives of meso-(Tetrapyridin-y-yl)-porphinobromocobalt (III)

Compound	Amine	Electronic absorption spectrum, nm†	IR spectrum, cm^{-1}*
Ia	n-Butylamine	434, 550, 587 sh.	558 ν(M–L); 1275; 1370, 1465 $\delta(CH_2, CH_3)$; 2865, 2875 $\nu_s(CH_2, CH_3)$; 2935, 2960 $\nu_{as}(CH_2, CH_3)$; 3225 $\nu(NH_2)$
Ib	2-Aminobutane	436, 552, 590	555 ν(M–L); 1375, 1460 $\delta(CH_2, CH_3)$; 2860, 2870 $\nu_s(CH_2, CH_3)$; 2930, 2960 $\nu_{as}(CH_2, CH_3)$; 3220 $\nu_s(NH_2)$; 3300 $\nu_{as}(NH_2)$
Ic	tert-Butylamine	436, 550, 558 sh.	560 ν (M–L); 1375, 1460 $\delta(CH_3)$; 2870 $\nu_s(CH_3)$; 2960 $\nu_{as}(CH_3)$; 3225 $\nu_s(NH_2)$; 3305 $\nu_{as}(NH_2)$
Id	Pentylamine	432, 548, 585 sh.	550 ν(M–L); 735; 1375, 1460 $\delta(CH_2, CH_3)$; 2860, 2870 $\nu_s(CH_2, CH_3)$; 2930, 2960 $\nu_{as}(CH_2, CH_3)$; 3220 $\nu_s(NH_2)$; 3310 $\nu_{as}(NH_2)$
Ie	Cyclohexylamine	435, 552, 588 sh.	1362, 1447 $\delta(CH_2)$; 2860 $\nu_s(CH_2)$; 2930 $\nu_{as}(CH_2)$; 3210 $\nu_s(NH_2)$; 3300 $\nu_{as}(NH_2)$
If	Pyridine	438, 553, 590 sh.	692 ρ(CH); 1610 ν(CC), β(CCH)
Ig	Aniline	438, 554, 589 sh.	560 ν(M–L); 696, 765, 810 ρ(CH); 1500 ν(CC); 3270 $\nu_s(NH_2)$; 3360 $\nu_{as}(NH_2)$
Ih	Piperidine	437, 551, 588 sh.	550 ν(M–L); 1448 $\delta(CH_2)$, 2866 $\nu_s(CH_2)$; 2930 $\nu_{as}(CH_2)$

Compound	Found, %				Empirical formula.	Calculated, %				Yield, %
	C	H	Br	N		C	H	Br	N	
Ia	63,5	4,4	9,4	15,0	$C_{44}H_{35}BrCoN_9$	63,8	4,2	9,7	15,2	81,6
Ib	63,6	4,0	9,5	15,3	$C_{44}H_{35}BrCoN_9$	63,8	4,2	9,7	15,2	81,0
Ic	63,4	4,1	9,2	15,5	$C_{44}H_{35}BrCoN_9$	63,8	4,2	9,7	15,2	40,8
Id	63,8	4,1	9,2	14,7	$C_{45}H_{37}BrCoN_9$	64,1	4,4	9,5	14,9	79,3
Ie	64,5	4,0	9,1	14,4	$C_{46}H_{37}BrCoN_9$	64,6	4,3	9,4	14,7	82,0
If	64,5	3,2	9,4	15,0	$C_{45}H_{29}BrCoN_9$	64,7	3,5	9,6	15,1	60,7
Ig	64,8	3,6	9,2	14,7	$C_{46}H_{31}BrCoN_9$	65,1	3,7	9,4	14,9	41,0
Ih	63,9	4,0	9,2	15,2	$C_{45}H_{35}BrCoN_9$	64,3	4,2	9,5	15,0	80,5

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*The tables give the wave numbers of the bands that are absent from the spectrum of CoTPyP.

†In the spectrum of CoTPyP, the corresponding bands are located at 412, 530, and 560 nm.

In the process of investigation we used different variants of the coordination of the amines with the simultaneous oxidation of Co^{2+} to Co^{3+}. Thus, the interaction of a chloroformic–methanolic mixture of Co-porphyrin with a tenfold excess of the amine and subsequent treatment of the mixture with 48% HBr gave a low yield of product (0.5-1%). When a solution of the Co-tetrapyridylporphine in the corresponding amine was treated with 48% HBr, the yield rose to 40%. A good result was obtained by adding the metalloporphyrin to a solution of the hydrobromide of the amine in the corresponding amine, which permitted the avoidance of the hydrobromation of the pyridinium nitrogen atoms of the Co-tetrapyridylporphine.

It is interesting to note that the yield of products (Ia-c) in the series n-butylamine, sec-butylamine, and tert-butylamine amounted to 81.6%, 81%, and 40.8%, respectively. Since the basicity of the amines rises in this sequence, we tend to explain the lowering of the yield of the unsymmetrical complex by the influence of the steric factor. The complexes obtained, unlike the starting material, were readily soluble in organic solvents (chloroform, methanol, ethanol).

The compounds (Ia-h) synthesized were characterized by the results of elementary analysis and infrared and electron absorption spectroscopy (Table 1).

The presence of the ligands in the samples synthesized was shown by a comparison of the IR spectra of the complexes with the spectrum of the initial Co-tetrapyridylporphine. The IR spectra of the compounds obtained contained new bands that were absent from the spectrum of Co-tetrapyridylporphine, and their frequencies were close to or coincided with the frequencies of the IR absorption bands of the corresponding ligands (see Table 1).

We also made attempts to split out the ligands under conditions of a high vacuum (10^{-4} torr) and gentle heating (50-60°C) of the initial complexes. The ligands eliminated in this way were deposited directly on a KBr support, cooled with liquid nitrogen and placed with a vacuum cryostat, which made it possible to obtain their IR spectra. In all cases, these experiments proved successful, and the ligand IR spectra obtained showed the absence of any chemical transformations whatever of the complex amines during the reaction.

The identification from their IR spectra of the complexes with such ligands as butylamine, pentylamine, cyclohexylamine, and piperidine presented no difficulties, since the Co-tetrapyridylporphine molecule has no saturated groups and the corresponding region of the spectrum (in particular, the region of the stretching vibrations of CH_2, CH_3, NH, and NH_2 groups) contains no absorption bands. In the case of the complex with pyridine, the absorption was somewhat complicated, since the majority of the bands of the coordinated pyridine were masked by the bands of the porphyrin itself, which contains four pyridine residues. However, in this case as well, the detection in the spectrum of two new absorption bands (see Table 1) displaced in the expected direction relative to the bands of free pyridine confirmed the formation of the TPyP-pyridinobromocobalt (III).

The coordination of the amines effected through the unshared pair of electrons of the nitrogen appreciably changes only the direct environment of the nitrogen atom itself. Because of this, in the coordination of amines appreciable changes in the vibrational frequencies are observed mainly for the bands of the stretching and deformation vibrations of NH and NH_2 groups, while the electronic structure of the remainder of the molecule is practically unaffected. In examples known from the literature [12], on the coordination of amines the frequencies of the stretching vibrations $\nu_{NH_2(NH)}$ decrease. A similar pattern was observed in our case (see Table 1).

In the 500-600 cm^{-1} region, the initial CoTPyP has a broad structured band of low intensity which, on passing to the complexes (Ia-h) [with the exception of the TPyP-pyridinobromocobalt(III) (If)] changed its form and the position of its maximum and increased appreciably in intensity. It may be assumed that this is connected with the appearance in this region of the spectrum of a new band superposed on the CoTPyP band and, apparently, corresponding to the vibration of a Co—N complex. The complex pattern of the spectrum in this region does not provide the possibility of an unambiguous assignment of the band to the metal—ligand vibrations, although the fact that in the complex $[Co(NH_3)_6]^{3+}$ the analogous vibration is located at 502 cm^{-1} [13] is evidence in favor of this assignment. In the case of the complex with pyridine (If), in which the nitrogen atom is included in a rigid aromatic system, according to the literature [14] the M—L vibrations should be considerably lower. So far as concerns the two new bands in the TPyP-pyridinobromocobalt complex (III) they represent ν(CC) and β(CCH) bands shifted as the result of coordination; $\nu_{11}\rho(CH)$ in free pyridine is located at 1580 and 702 cm^{-1} [15]. Such shifts are observed in pyridine complexes known from the literature [16] and, in particular, in $CoPy_2Br_2$.

It is known that the addition of ligands to metalloporphyrin molecules is also accompanied by appreciable changes in the electronic absorption spectra [17], both hypsochromic [18] and bathochromic [19] band shifts being observed. In the case of the complexes obtained, as can be seen from Fig. 1 and Table 1, coordination leads to a bathochromic shift both of the Soret band and of the bands in the visible region of the spectrum by approximately 25 nm.

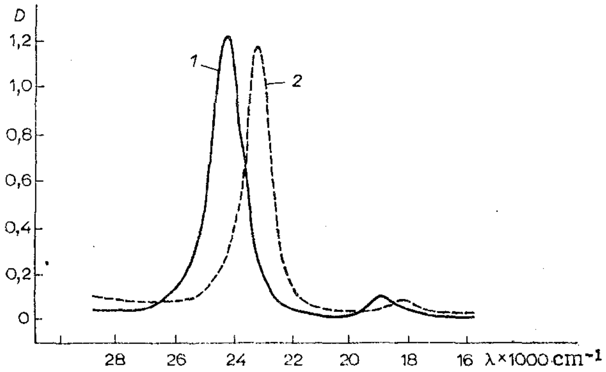

Fig. 1. Electronic absorption spectra in the 350-700 nm region: 1) CoTPyP; 2) $BrCoTPyPNH_2C_5H_{11}$ (Id) in chloroform.

EXPERIMENTAL

The IR spectra of the samples in the 400-3600 cm^{-1} region were measured on a UR-20 spectrophotometer in the form of tablets with KBr or of mulls in paraffin oil.

Electronic spectra in the 350-800 nm region were obtained on a Specord UV-Vis spectrophotometer using carefully dried chloroform as solvent.

Amine Derivatives of meso-(Tetrapyridin-4-yl)porphinobromocobalt(III). With cooling to 0°C, 20 ml of 48% HBr was added to 80 ml of the corresponding amine. Then 0.4 g (0.6 mmole) of Co-tetrapyridylporphine was added in small portions. The mixture was heated in the boiling water bath under reflux for 75 min. After cooling to room temperature, it was poured into water (1 liter) and extracted with chloroform (3 × 200 ml), and the chloroform extract was washed with water (3 × 100 ml) and dried (Na_2SO_4). After elimination of the solvent, the residue was crystallized from a mixture of chloroform and ether to form violet plates. The constants of the compounds synthesized are given in Table 1.

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