ELECTRONIC SPECTRA OF COPPER AND ZINC COMPLEXES OF PORPHYRINS CONTAINING ETHOXYCARBONYL SUBSTITUENTS

G. V. Ponomarev, R. P. Evstigneeva, and N. A. Preobrazhenskii

Copper and zinc complexes of porphyrins containing ethoxycarbonyl substituents have been synthesized and their absorption spectra in the visible region have been studied. A connection has been shown between the α/β ratio of the absorption bands and the order of substitution of electronegative groups in the porphyrins.

The electronic spectra of the metalloporphyrins are closely connected with their thermodynamic stability and depend on the nature of the metal, the properties of the porphyrin itself, and the solvent used
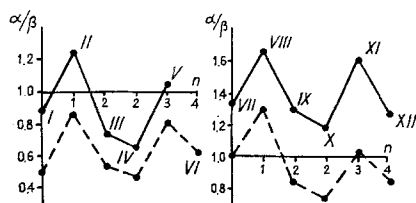
α/β Ratio as a function of the number of ethoxycarbonyl groups (n) in the spectra of the metal complexes of the porphyrins: —————for spectra in chloroform; ———————for spectra in pyridine.

[1,2]. The study of the capacity of the metalloporphyrins for forming complexes with additional ligands and the investigation of their photooxidation-photoreduction reactions and other questions of the chemical and physical nature of the porphyrins require a detailed consideration of their spectra. In the present work, we studied the spectra in the visible region of the copper and zinc complexes of porphyrins containing a regularly changing number of electronegative substituents (ethoxycarbonyl groups).

As we have shown previously, the introduction of an ethoxycarbonyl group into the porphyrin molecule causes a bathochromic shift of each of the four porphyrin bands by 6-8 nm [3] and of the Soret band by 450 cm^{-1} [4]. Regular changes of the position of the absorption maxima as a function of the number of ethoxycarbonyl groups are also found in the spectra of their metal complexes (see table).

The influence of the position of the ethoxycarbonyl groups in a porphyrin on λ_{max} of their complexes is leveled out in comparison with the initial porphyrins but, nevertheless, the α-band (the longest-wave peak) is more sensitive to a change in the chemical structure of a porphyrin than the β-band.

Furthermore, a bathochromic shift, also of about 8-12 nm, is observed for one and the same complex when chloroform is replaced by pyridine in the case of both the zinc and the copper complexes, which is apparently due to additional coordination of the metal with the solvent.

One of the characteristic features of the metal complexes is the dependence of the intensity of the long-wave peaks on the nature of the metal. Thus, for example, it is known that if the α/β ratio is greater than 1 the copper complex of a given porphyrin is more stable. Where the zinc complexes are more stable, almost always $\alpha/\beta < 1$.

It has been observed that in a number of carboxylated porphyrins it is also possible to obtain an idea of the internal structure of the porphyrins i.e. an idea of the mutual arrangement of the ethoxycarbonyl groups, from the ratio of the intensities of the α- and β-peaks, and, consequently, to deduce correctly the type of spectrum of the porphyrin itself and also to predict beforehand the type of spectrum of the metal complex when one solvent is replaced by another.
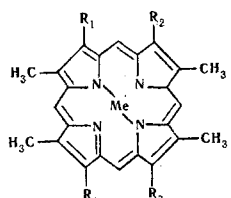
From the figures given it can be seen that the metal complexes of porphyrins having one ethoxycarbonyl group or two arranged in opposite pyrrole rings have an α/β ratio considerably greater than unity in chloroform for the copper complexes and also $\alpha/\beta > 1$ when the chloroform is replaced by pyridine. Even in the corresponding zinc complexes, the ratio $\alpha/\beta > 1$ in chloroform.

Thus, we can state with certainty that if a metal complex, copper or zinc, of a porphyrin has a ratio $\alpha/\beta > 1$ in chloroform, the porphyrin must have the "rhodo" type of spectrum in the visible region. The only exception to this rule is triethoxycarbonylporphyrin, which has the "etio" type of spectrum because of the exceptional symmetry of the three carboxy groups. If even one of them is replaced by another, related, group, for example a formyl group, the spectrum becomes of the "rhodo" type [5].

In considering the complexes of the porphyrins having two ethoxycarbonyl groups in adjacent pyrrole rings, a greater similarity of the intensity of the bands is found in complexes III and IX, diethoxycarbonylporphyrins, and in VI and XII, tetraethoxycarbonylporphyrins, which have the ethoxycarbonyl groups directed toward one another, than in complexes of the two diethoxycarbonylporphyrins (III, IX and IV, X), differing in the location of the ethoxycarbonyl groups.

As can be seen from the figure, an interesting feature of the metal complexes is the regular change in the α/β ratio by a definite amount when one solvent is replaced by another, this being 0.3-0.5 for the copper complexes and 0.2-0.4 for the zinc complexes when chloroform is replaced by pyridine.

Characteristics of the Metal Complexes of the Porphyrin Series Synthesized

Compound	Substituents	Mp °C	R_f	in pyridine I (α)	in pyridine II (β)	in chloroform I (α)	in chloroform II (β)	Empirical formula	Found % C	Found % H	Found % N	Calc. % C	Calc. % H	Calc. % N
I	$R_1=R_2=R_3=R_4=H$* $Me=Zn$	>300	0.22**	582; 570 (497) (6.33)	544 (13.68)	571; 560 (8,10) (9.05)	533 (10.5)	$C_{24}H_{20}N_4Zn$	67.28	4.86	12.89	67.03	4.69	13.03
II	$R_1=CO_2C_2H_5$ $R_2=R_3=R_4=H$ $Me=Zn$		0.08**	594 (12.91)	553 (14.9)	584 (15.2)	543 (12.2)	$C_{27}H_{24}N_4O_2Zn$	64.52	5.11	11.99	64.60	4.83	11.18
III	$R_1=R_2=CO_2C_2H_5$ $R_3=R_4=H$ $Me=Zn$	>300	0.19	603 (10.3)	560 (16.5)	596 (9.10)	553 (12.3)	$C_{30}H_{28}N_4O_4Zn$	62.72	4.90	9.77	62.77	4.91	9.76
IV	$R_1=R_4=CO_2C_2H_5$ $R_2=R_3=H$ $Me=Zn$	>300	0.19	602 (6.94)	560 (16.1)	594 (10.0)	553 (12.7)	$C_{30}H_{28}N_4O_4Zn$	62.84	4.45	10.00	62.77	4.91	9.76
V	$R_1=R_2=R_3=CO_2C_2H_5$ $R_4=H$ $Me=Zn$	>300	0.07	614 (12.7)	567 (15.85)	608 (12.5)	562 (11.7)	$C_{33}H_{32}N_4O_6Zn$	61.70	4.61	8.70	61.35	5.00	8.67
VI	$R_1=R_2=R_3=R_4=CO_2C_2H_5$ $Me=Zn$	>300		620 (8.03)	573 (13.2)			$C_{36}H_{36}N_4O_8Zn$	60.10	5.08	7.90	60.21	5.04	7.78
VII	$R_1=R_2=R_3=R_4=H$ $Me=Cu$	>300	0.63**	563 (10.10)	529 (10.10)	554; 563 (13.32) (12.2)	523 (10.20)	$C_{24}H_{20}N_4Cu$	66.84	4.69	13.28	67.35	4.71	13.09
VIII	$R_1=CO_2C_2H_5$ $R_2=R_3=R_4=H$ $Me=Cu$	157—159	0.29**	581 (14.0)	540 (10.6)	578 (17.9)	534 (10.7)	$C_{27}H_{24}N_4O_2Cu$	64.80	5.20	11.36	64.86	4.84	11.20
IX	$R_1=R_2=CO_2C_2H_5$ $R_3=R_4=H$ $Me=Cu$	>300	0.61	590 (11.0)	550 (12.61)	585 (14.9)	542 (11.5)	$C_{30}H_{28}N_4O_4Cu$	63.15	4.71	9.83	62.98	4.93	9.79
X	$R_1=R_4=CO_2C_2H_5$ $R_2=R_3=H$ $Me=Cu$	>300	0.61	588 (10.08)	549 (14.7)	582 (14.5)	541 (12.3)	$C_{30}H_{28}N_4O_4Cu$	62.96	5.24	9.75	62.98	4.93	9.79
XI	$R_1=R_2=R_3=CO_2C_2H_5$ $R_4=H$ $Me=Cu$	>300	0.17	604 (14.2)	558 (13.3)	595 (14.2)	550 (8.80)	$C_{33}H_{32}N_4O_6Cu$	61.74	4.95	8.85	61.53	5.01	8.70
XII	$R_1=R_2=R_3=R_4=CO_2C_2H_5$ $Me=Cu$	>300	0.08	609 (11.45)	565 (13.1)	598 (9.18)	559 (7.45)	$C_{36}H_{36}N_4O_8Cu$	60.58	5.00	7.79	60.39	5.05	7.82
XIII	$R_1=CO_2C_2H_5 R_3=CHO$ $R_2=R_4=H$ $Me=Cu$	>300	0.35	601 (13.3)	555 (8.9)	594 (13.3)	547 (7.39)	$C_{28}H_{24}N_4O_3Cu$	63.48	4.67	10.30	63.69	4.58	10.60
XIV	$R_1=CO_2C_2H_5; R_3=CH=NOH$ $R_2=R_4=H$ $Me=Cu$			590 (13.0)	488 (10.7)			$C_{28}H_{25}N_5O_3Cu$						
XV	$R_1=R_2=CO_2C_2H_5$ $R_3=CHO; R_4=H$ $Me=Cu$	>300	0.25	597 (11.62)	555 (11.12)	590 (11.62)	545 (8.37)	$C_{31}H_{28}N_4O_5Cu$	62.17	4.93	9.54	62.05	4.70	9.33
XVI	$R_1=R_2=CO_2C_2H_5$ $R_3=CH=NOH$ $R_4=H$ $Me=Cu$			593 (12.45)	552 (13.85)			$C_{31}H_{29}N_5O_5Cu$						
XVII	$R_1=R_2=R_3=R_4=CO_2C_2H_5$ meso-CHO, $Me=Cu$	>300	0.05	650; 612 (6.13) (12.5)	567 (9.68)	650; 608 (4.72) 9.19	565 (5.9)	$C_{37}H_{36}N_4O_9Cu$	59.86	5.27	7.84	59.70	4.88	7.52
XVIII	$R_1=R_2=R_3=R_4=CO_2C_2H_5$ meso-CH=NOH, $Me=Cu$			612 (14.05)	565 (12.65)			$C_{37}H_{37}N_5O_9Cu$						

*In the complexes of tetramethylporphyrin (I, VII), splitting of the α-band is found.
**In kerosine.

EXPERIMENTAL

The metal complexes of the porphyrins were obtained by boiling the corresponding porphyrins with an excess of copper or zinc acetate in chloroform until the spectrum of the initial porphyrin could no longer be detected in a sample. Then the solvent was distilled off and the residue was washed with water and methanol to eliminate unchanged copper or zinc acetate and was recrystallized from chloroform or a mixture of chloroform and petroleum ether, depending on the solubility of the complex obtained. The spectra in the visible region were recorded on an SF-10 or SF-2M spectrophotometer. Ascending paper chromatography on Whatman No. 1 was carried out in the following systems: a) kerosine; b) 1:2 mixture of chloroform and petroleum ether. The oximes of the corresponding formylporphyrins were obtained by heating them with hydroxylamine hydrochloride in pyridine at 100°C for 5 min. The results of analysis and the spectral data are given in the table.

REFERENCES

1. J. N. Phillips, in: Comprehensive Biochemistry, Eds. M. Florkin and E. H. Stotz. Elsevier, Amsterdam, N.Y. London, 9, 51, 1963.

2. J. F. Falk, Porphyrins and Metalloporphyrins, Amsterdam, 28, 1964

3. G. V. Ponomarev, R. P. Evstigneeva, and N. A. Preobrazhenskii, ZhOKh, Collection III, Synthesis of Natural Compounds, Their Analogs and Fragments [in Russian], 227, 1965.

4. V. M. Mamaev, G. V. Ponomarev, and R. P. Evstigneeva, KhGS [Chemistry of Heterocyclic Compounds], 3, 861, 1967.

5. G. V. Ponomarev, R. P. Evstigneeva, V. N. Stromnov, and N. A. Preobrazhenskii, KhGS [Chemistry of Heterocyclic Compounds], 2, 628, 1966