878. *The Negative Ions of Some Porphin and Phthalocyanine Derivatives, and their Electronic Spectra.*

By J. W. Dodd and N. S. Hush.

The reactions between sodium and a number of metal complexes of porphins, tetra-azaporphins, tetrabenzoporphin, and phthalocyanine are discussed. In tetrahydrofuran or 1,2-dimethoxyethane solution, two successive reduction stages are observed; these are assigned to the formation of mono- and di-negative ions of the complexes. In the reaction between free-base porphin, or phthalocyanine, and sodium, the initial product is a disodium salt. Copper and nickel tend to be replaced in their complexes, but this process is slower than the concurrent anion-formation. Zinc and magnesium are not replaced in this way. Quantitative experiments between zinc tetraphenylporphin and sodium are described, and are taken as a model for the other porphyrins. The electronic spectra of solutions of typical reduction products are given, the theoretical interpretation of which will be published separately.

The vital role played by porphyrin derivatives in photosynthesis, and in many other biological processes, is well known.[1] Clearly, it is important to investigate the products of the simplest reduction and oxidation steps, corresponding to addition of electrons to, or

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[1] " Hæmatin Enzymes," ed. Falk, Lemberg, and Morton, Pergamon, 1961.

removal of electrons from, the porphyrin system. Calvin and Androes [2] have suggested that such ions may occur as intermediates in photosynthetic processes. The formation of negative ions from a number of porphin, tetra-azaporphin, tetrabenzoporphin, and phthalocyanine complexes has therefore been investigated,[3] and is briefly reported here. The electronic spectra of solutions of representative anions are also given.

The study of the electronic structures of porphyrin–metal complexes is of considerable theoretical interest in its own right. The observed strong electronic transitions have their origin in ligand excitations which are only slightly perturbed by the metal ion. This is unusual in co-ordination compounds. As Gouterman has shown,[4] the influence of the metal on band frequencies and intensities can be interpreted by means of a second-order perturbation theory. An extension of this approach to include the ions of porphyrin complexes should provide more information about the metal–ligand bonding. The effect of the metal on the absorption-band frequencies of various aetioporphin and tetraphenylporphin derivatives is summarised in Table 1.

TABLE 1.

The influence of various metals on the absorption bands of some porphin derivatives in solution.

	Copper ætioporphin IV Zinc ætioporphin I	Zinc ætioporphin I Disodium ætioporphin I	Zinc tetraphenylporphin Disodium tetraphenylporphin
$\Delta\nu$ in metal complex	400	700	700
$\Delta\nu$ in mononegative ion	500	800	800

$\Delta\nu$ is the average frequency difference, in cm.$^{-1}$, between corresponding absorption bands in any two metal complexes. For example, a given band in copper aetioporphin IV is *ca.* 400 cm.$^{-1}$ higher than the corresponding band in zinc aetioporphin I. For the radical-ions of these complexes, the difference is 500 cm.$^{-1}$.

Metal–porphyrin complexes exhibit a symmetry close to D_{4h}, as the recent X-ray work of Fleischer on ætioporphin [5] and tetraphenylporphin [6] derivatives has shown. The complete X-ray structure and analysis of a free-base porphin has not yet been reported, but that of phthalocyanine was published by Robertson [7] in 1936. A typical free-base porphin has a strong absorption band at about 25,000 cm.$^{-1}$ (the Soret band), and four visible bands. The intensities of the latter are greatly enhanced by nitrogen substitution of the four methine bridge atoms, or by conversion into a tetrabenzoporphin or into a phthalocyanine. With a change in point-group symmetry from D_{2h} to D_{4h}, upon conversion of the free base to a metal complex, the four visible bands are replaced by two others, and a Soret band remains. The formation of negative ions from such a metal complex is accompanied by further spectral changes, especially in the visible region. Table 2 lists all the porphyrins from which such reduction products were prepared, together with the accompanying colour changes. The spectra of an aetioporphin,[8] its copper [8] and zinc [3] complexes, $\alpha\beta\gamma\delta$-tetraphenylporphin and its zinc complex,[9] tetra-azaporphin,[10] its octamethyl nickel complex,[11] and its octaphenyl magnesium complex,[3] tetrabenzoporphin and its zinc complex,[12] and phthalocyanine and its copper complex [10] are all given in the available literature. It is hoped to publish elsewhere the anion spectra which are not reported here.

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[2] Calvin and Androes, *Science*, 1962, **138**, 867.
[3] Dodd, Ph.D. Thesis, Bristol, 1963.
[4] Gouterman, *J. Chem. Phys.*, 1959, **30**, 1139.
[5] Fleischer, *J. Amer. Chem. Soc.*, 1963, **85**, 146.
[6] Fleischer, *J. Amer. Chem. Soc.*, 1963, **85**, 1353.
[7] Robertson, *J.*, 1936, 1195.
[8] Erdman and Corwin, *J. Amer. Chem. Soc.*, 1946, **68**, 1885.
[9] Dorough, Miller, and Huennekens, *J. Amer. Chem. Soc.*, 1951, **73**, 4315.
[10] Ficken and Linstead, *J.*, 1952, 4846.
[11] Baguley, France, Linstead, and Whalley, *J.*, 1955, 3521.
[12] Gouterman, *J. Mol. Spectroscopy*, 1961, **6**, 138.

TABLE 2.

Solutions of the porphyrin derivatives examined, and their colours.

Porphyrin	Parent complex	Mononegative ion	Dinegative ion
Ætioporphin I	Orange		
Disodium ætioporphin I	Pink	Yellow-green	(Purple)
Zinc ætioporphin I	Pink	Green	Crimson
Zinc ætioporphin III	Pink	Green	Crimson
Copper ætioporphin IV	Cherry	Green	(Turquoise)
Tetraphenylporphin	Pink		
Disodium tetraphenylporphin	Green	Yellow-green	(Blue)
Zinc tetraphenylporphin	Pink	Green	Amber
Magnesium octaphenyltetra-azaporphin	Emerald	Grey	Brown
Nickel octamethyltetra-azaporphin	Purple	Indigo	Brown
Zinc tetrabenzoporphin	Green	Amber	Blue-green
Phthalocyanine	Turquoise		
Disodium phthalocyanine	Turquoise	Blue	Indigo
Copper phthalocyanine	Blue	Blue	Indigo

The above colours refer to *ca.* 10^{-4}M-solutions of the anions in 2-methyltetrahydrofuran. In such solutions, ion-pairing with sodium ions is likely to occur to a certain extent, but the effects of this on the spectra are probably very limited. The same solvent was used for all the parent porphin complexes, except nickel octamethyltetrazaporphin and the phthalocyanines, which dissolved only in 1-chloronaphthalene.

RESULTS AND DISCUSSION

Anion formation was complicated by the versatile nature of the porphyrin molecule. The initial product in the reaction between sodium and a free-base porphin, or phthalocyanine, was the disodium salt. Further, there was a tendency for sodium to replace copper in both its aetioporphin and phthalocyanine complexes. This was more noticeable for solutions in 1,2-dimethoxyethane than for those in tetrahydrofuran. Nickel in its octamethyltetra-azoporphin complex was less easily replaced, whilst magnesium and zinc were not replaced at all in the reduction of the tetrabenzoporphin or porphin complexes listed in Table 2. For this reason, the spectra of the negative ions given in Figs. 1—4 are those of the magnesium complex of octaphenyltetra-azaporphin and of the zinc complexes of tetraphenylporphin, aetioporphin I, and tetrabenzoporphin. In each of these cases, two successive reduction products were identified. The spectra of the phthalocyanine negative ions (Fig. 5) refer to ions of the copper complex, in which the replacement of copper by sodium was not apparent until the second reduction stage had been reached.

In the reactions between sodium and the free bases aetioporphin I and tetraphenylporphin, only one reduction product could be distinguished from the disodium salt. Eventually the spectral bands of this product became very diffuse, with increasing absorption in the ultraviolet region. This was thought to indicate progressive saturation of the porphin ring. It is well known that solvolysis reactions occur in the corresponding reduction of aromatic hydrocarbons.[13] Similar changes in the spectra of the reduction products of the zinc–porphin complexes were much less marked. In the case of the phthalocyanines, distinct third and fourth reduction stages were noted upon prolonged contact with sodium. The corresponding spectra are given in Fig. 6. These final two reduction products, which have not yet been characterised, were common to both phthalocyanine and its copper complex.

In order to characterise the first and second reduction products, known amounts of the only readily available porphin, zinc tetraphenylporphin, were treated with one and two atoms of sodium, in separate experiments. The results, given in the Experimental section, indicate that the products are at the oxidation level of mono- and di-negative ion, respectively. The observed spectra of the two species (Fig. 1) agree well with those given by Closs and Closs [14] for these ions. The behaviour of zinc tetraphenylporphin was taken as

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[13] Hoijtink and Zandstra, *Mol. Phys.*, 1960, **3**, 371.

[14] Closs and Closs, *J. Amer. Chem. Soc.*, 1963, **85**, 818.

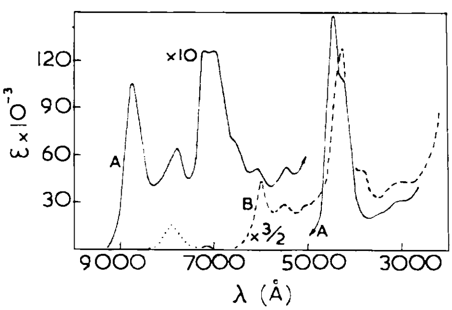

FIG. 1.

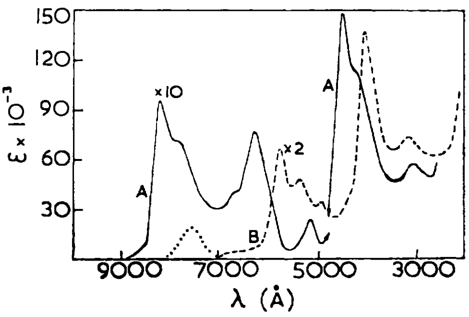

FIG. 2.

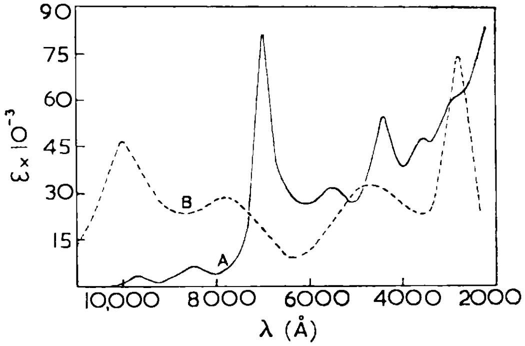

FIG. 3.

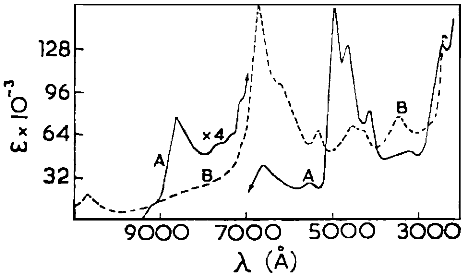

FIG. 4.

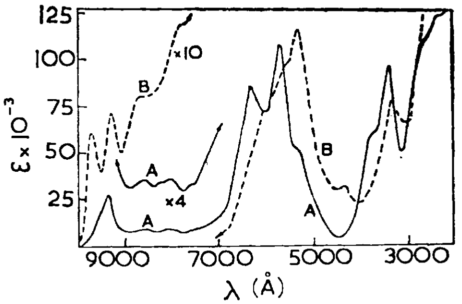

FIG. 5.

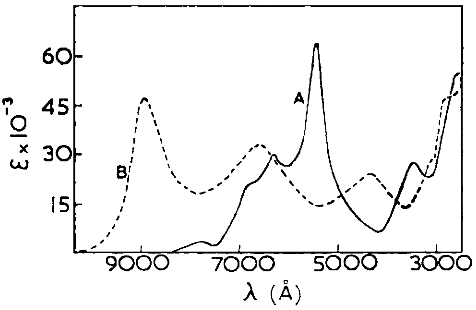

FIG. 6.

Electronic spectra of reduction products of some porphyrin derivatives (ϵ is the molar extinction coefficient). FIG. 1. Zinc tetraphenylporphin (A) mono- (B) di-negative ion. FIG. 2. Zinc ætioporphin I (A) mono- (B) di-negative ion. FIG. 3. Magnesium octaphenyltetrazaporphin (A) mono- (B) di-negative ion. FIG. 4. Zinc tetrabenzoporphin (A) mono- (B) di-negative ion. FIG. 5. Copper phthalocyanine (A) mono- (B) di-negative ion. FIG. 6. Phthalocyanine (A) third reduction product (B) fourth reduction product.

being typical of that of the other porphyrin systems, given in Table 2, for which two distinct and successive reduction products were observed. Electron spin resonance measurements indicated that radical-ions were produced in these reactions. However, since the porphyrins were only available in very limited quantities, it was not possible to isolate a given reduction stage (see the Experimental section). Thus, characterisation on the basis of paramagnetic properties was, of necessity, precluded.

Upon exposure of solutions of the dinegative ion of zinc–porphin complexes to a controlled flow of dry oxygen, the parent compounds were regenerated in *ca.* 75% yield. Similarly, a copper complex was recovered in 60% yield, whilst the free bases, which had been reacted with excess of sodium, were recovered in less than 50% yields. No " foreign " bands persisted in the spectra of these oxidised species, although the general level of absorption into the ultraviolet region increased. Since the concentration of the parent complex at the beginning of a reduction experiment was known, the extinction coefficients of the mononegative-ion bands could be calculated. It was assumed that no solvolytic side-reactions had occurred up to that point. The extinction coefficients for the dinegative-ion stage were corrected by a factor based on the above recoveries of the parent porphyrins. The disodium salts were prepared independently by treating the free-base porphyrins with sodium methoxide in an appropriate solvent; corrections could then be made for the presence of these salts in solutions of a reduced free-base porphyrin or of its copper complex. In the above way, the spectra of the individual reduction products were elucidated (see Figs. 1—6).

Closs and Closs [14] have reported anions of zinc tetraphenylporphin derivatives, with spectra very similar to those shown in Fig. 1. By means of both quantitative experiments and paramagnetic measurements, they showed that these species were due to mono- and di-negative ions. The spectrum of a " phlorin " complex, produced by direct protonation of the dinegative ion, was also given. This had a single strong band in the visible region, at a frequency very close to that of the lowest energy band in Fig. 1(B) (dotted line). This and the corresponding band for zinc aetioporphin [Fig. 2(B)] are, therefore, to be regarded with some reserve. The antisymmetric molecular orbital (A.S.M.O.) theory which has been developed [3] only accounts for the bands at higher frequencies in the spectra of the di-negative porphin ions.

Shablya and Terenin [15] have reported similar reactions between sodium and magnesium phthalocyanine, and have ascribed the initial reduction product to a radical-ion. The direction of the frequency shift on going from the first to the second reduction stage, as well as the actual location of the bands, is in agreement with Fig. 5. A third reduction product is also described by these authors.

Detailed analysis of the relevant data from Figs. 1—5 shows that the oscillator strength of the most intense band in the spectra of the anions is similar to that of the Soret band of the parent porphin complex. On conversion of the radical-ions to the dinegative ions, the absorption bands are shifted to higher frequencies in the porphin and tetra-azaporphin derivatives, and to lower frequencies in the tetrabenzoporphin and phthalocyanine derivatives. The negative-ion spectra of the latter pair of compounds are richer in fine-structure than those of the former pair. All these facts are consistent with the general predictions of the A.S.M.O. theoretical treatment,[3] which will be published elsewhere. In this treatment, the negative-ion spectra are interpreted on the basis of π^*–π^* and π–π^* transitions involving the upper two bonding orbitals only. However, in the case of the porphin neutral molecules, a better correlation has been established by considering transitions from filled orbitals of lower energy. Further, the interpretation of the dinegative-ion spectra was consistent with the assumption that the ground state is always a singlet. Since the lowest empty orbital in these porphyrin molecules is doubly degenerate, or only slightly split, a triplet ground state might have been expected for the dinegative ions. However, configurational interaction leads to a larger lowering of the ground state for the singlet than

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[15] Shablya and Terenin, *Optika i Spektroskopiya*, 1960, **9**, 533.

for the triplet. Because of the degeneracy of the lowest non-bonding orbitals, third and fourth reduction steps might be expected; however, the theoretical treatment was not extended beyond the dinegative-ion stage.[3]

EXPERIMENTAL

The purity of each porphyrin sample was checked by comparison of its spectrum with that given in the literature. 2-Methyltetrahydrofuran was purified by initial distillation, followed by 50 hr.'s reflux distillation over sodium–potassium alloy. In the final stages of the latter process, the formation, *in situ*, of the coloured anthracene dinegative ion was used as a criterion of dryness. Sodium azide was recrystallised three times from distilled water before use.

Solutions of the anions were prepared by reaction of the porphyrin (*ca.* 0·001 g.) with an excess of sodium metal in very dry, purified 2-methyltetrahydrofuran (5 ml.).[3] The sodium metal was obtained as a pure film by the thermal decomposition of sodium azide. A quartz optical cell, of 1 mm. path length, was sealed to the reaction vessel. The latter was evacuated to below 10^{-4} mm. for 3 hr. before the reaction was allowed to take place, in order to remove final traces of water vapour.

It was not practicable to handle less than 0·003 g. of sodium azide in the above process. Since the molecular weight of any porphyrin in Table 2 is between six and ten times greater than that of the azide, quantitative experiments were not possible with the very limited amounts of porphyrins available. The exception was zinc tetraphenylporphin, 0·2 g. of which was prepared by means of a method based on that of Ball, Dorough, and Calvin.[16] Benzaldehyde and pyrrole (in the ratio 2 : 1 by volume), in pyridine, were caused to react, in an autoclave, with a slight excess of zinc acetate. The reaction mixture was kept at 200° for 40 hr. The product was obtained in 99% purity by repeated chromotography, first in chloroform over alumina, and finally in benzene over silica (Hopkin and Williams M.F.C. grade). Samples of this zinc salt (0·050 g.) were treated separately with one and two mols. of sodium in very dry 2-methyltetrahydrofuran. The molar conversion was 95% for the first reduction product [Fig. 1(A)] and 84% for the second [Fig. 1(B)]. These values are based on the extinction-coefficient data of Closs and Closs,[14] which are probably more accurate than ours, since they isolated salts of the anions in a pure crystalline form. The somewhat low conversion values may be due to side-reactions between the solvent and either the anions or the sodium film. Since the zinc was not replaced by sodium, the products are ascribed to mono- and di-negative ions, respectively.

All the spectra were measured with a Beckman DK.2 ratio-recording spectrophotometer, and are shown (Figs. 1—6) with a wavelength scale, in order to facilitate comparison with the spectra in the literature. In order to clarify the weak absorption in the visible region, some of the bands have been scaled up by the magnification factors shown on the Figures.

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DEPARTMENT OF CHEMISTRY, THE UNIVERSITY, BRISTOL 8.
[Present address (J. W. D.): ACETATE AND SYNTHETIC FIBRES LABORATORY,
COURTAULDS LIMITED, COVENTRY.]

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[16] Ball, Dorough, and Calvin, *J. Amer. Chem. Soc.*, 1946, **68**, 2278.