Nickel(II) and palladium(II) compounds theoretically have either two unpaired electrons (μ = 2.83 Bohr magnetons) or none (μ = 0.0 Bohr magnetons). The susceptibilities of bis-(α-benzildioximato-N,N′)-nickel(II)[5] and bis-(2,3-butanedionedioximato-N,N′)-nickel(II)[5,6] are recorded in the literature, but the data for the latter compound are not in agreement. Our values for the susceptibilities of the nine metal(II) complexes are given below in Table I. For the two compounds investigated previously, our values are only slightly more negative than those of Cambi and Szegö.

Experimental

Materials.—The bis-(*vic*-dioximato-N,N′)-metal(II) complexes, with the exception of the bis-(α-benzildioximato-N,N′)-metal(II) complexes, were prepared in 5–20 g. batches by precipitation from aqueous solutions, using procedures more or less linearly scaled up from the usual analytical methods in which these reagents are used.[7–10] The two alicyclic *vic*-dioximes which were not available commercially, were synthesized according to published directions.[11,12]

The low solubility of α-benzildioxime in water and the usual solvents prevented the preparation of its metal(II) complexes by precipitation from aqueous solution. The precipitations were carried out, instead, in acetone, into which the reagent was introduced by means of a Soxhlet extractor and to which an aqueous-alcoholic solution of the metal chloride was added very slowly from a dropping funnel.

Special low-cobalt nickel chloride obtained from J. T. Baker Co. was used in the preparation of the bis-(*vic*-dioximato-N,N′)-nickel(II) complexes. Commercially available palladium chloride was carefully purified as described previously.[9b] Demineralized water was used throughout to keep the products free from iron contamination. Other materials were of reagent grade.

The precipitated and dried bis-(*vic*-dioximato-N,N′)-metal(II) complexes were very difficult to handle, chiefly because of their tendency to pick up static charges. This condition was improved somewhat by recrystallization from 1,2-dichlorobenzene (nitrobenzene in the case of the bis-(1,2-cycloheptanedionedioximato-N,N′)-nickel(II)), which served to increase particle size. The recrystallization also darkened the usual brilliant colors of these complexes. All nine complexes were analyzed for metal content, to make sure that the recrystallization process had not changed their fundamental nature.

Magnetic Measurements.—A Gouy magnetic balance was employed for securing all magnetic data. This system[13] was composed principally of a Consolidated Engineering Corporation 23-104A electromagnet, its rectifier power supply, a damped Ainsworth semimicro balance and a potentiometer-galvanometer circuit for measuring coil current. Double-length sample tubes of 0.75-cm. internal diameter were used, the lower half containing dry air. The tubes were calibrated with a 30% nickel chloride solution. All data presented are averages of six or more individual measurements, at various currents, for each of at least two tube fillings. The densities of the crystalline compounds were estimated by the liquid displacement pycnometer method. Corrections were made for the amount of air remaining in the packed columns. The data are believed accurate and precise only to within 2–3%, because of the difficulty met in packing the tubes uniformly.

Summary.—Since all nine bis-(*vic*-dioximato-N,N′)-metal(II) complexes studied were found to be diamagnetic, they presumably all have square coplanar structures (dsp^2) similar to that found by Godycki and Rundle[14] for bis-(2,3-butanedionedioximato-N,N′)-nickel(II).

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The Acid—Base Equilibria of Porphyrins. Nonsimultaneous Dissociation of Two Protons Upheld

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RECEIVED AUGUST 16, 1954

Walter[1] has reported studies of the spectral changes of a solution of the dipotassium salt of deuteroporphyrin IX dimethyl ester disulfonic acid ($DPE(SO_3K)_2$), on adding increasing quantities of dilute hydrochloric acid. He employed the method of continuous variations (see below), and concluded from his studies that the monocation of this porphyrin was never present in sufficient quantity to make an important contribution to the observed spectra.

A year previously an extensive study of the basicities of porphyrins had been published by Neuberger and Scott.[2] Walter was not aware of this work, which included the measurement of pK'_1 and pK'_2 of $DPE(SO_3H)_2$ by spectrophotometric titration.

Considering only the charges on the nitrogen atoms, these constants were defined as

$$K_1 = \frac{[\text{mono-cation}][\text{H}^+]}{[\text{di-cation}]}$$

$$K_2 = \frac{[\text{free base}][\text{H}^+]}{[\text{mono-cation}]}$$

Values found for $DPE(SO_3H)_2$ were $pK'_1 \simeq 0.3$; $pK'_2 \simeq 4.7$.

Provided it is accepted that a porphyrin monocation, if formed, will have a characteristic spectrum, then Walter's interpretation of his results would also require, as he pointed out, that $K'_1 \simeq K'_2$. This would not only contradict the values already found, but would also deny the existence of the distinctive spectra observed by Treibs,[3] and by Stern and Molvig,[4] and confirmed by Neuberger and Scott. It might in addition be taken to imply a tri-molecular reaction, and the nature of the error of previous workers[5] in reaching this conclusion has already been explained.[2]

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The method of continuous variations was devised by Job[6] for the identification of complexes, whose formation may be represented by the equation[7]

$$\mathrm{A} + n\mathrm{B} \rightleftharpoons \mathrm{AB}_n \qquad (1)$$

This method was later extended and rationalized by Vosburgh and Cooper,[7] to include further reactions of the type

$$\mathrm{AB}_n + q\mathrm{B} \rightleftharpoons \mathrm{AB}_{(n+q)} \qquad (2)$$

They proved that, by plotting the differences in absorption spectra, $\Delta(D)$, at different wave lengths as the ratio of A to B is increased in a particular way, the maxima of $\Delta(D)$ will all occur at the same value of B, regardless of the wave length, provided that the reaction is confined to formation of one new species, as in equation 1. A necessary requirement for fulfillment of the above conditions is that the family of curves representing $\Delta(D)$ at different wave lengths should cross at ($\Delta(D) = 0$, $B = 0$) and also at ($\Delta(D) = 0$, B = maximum). If the curves cross the line $\Delta(D) = 0$ at any other value of B, then more than one complex has been formed and implications of equation 2 must be considered. Normally, only when equation 1 is applicable can a *unique* value be found for n. Walter has not fully appreciated these requirements. When allowance is made for them and for a second error, his work leads to diametrically opposite conclusions, as will now be shown.

Vosburgh and Cooper proved that, under conditions of equation 1

$$n = X/(1 - X) \qquad (3)$$

when a volume, X (<1), of a solution of B is added to a volume $1 - X$ of an equimolar solution of A. But it must be realized that the method of continuous variations can naturally only give information on equilibria which can occur within the concentration range, whose upper limit is fixed by the molar concentration of A or B. In the present case A represents the porphyrin, and B represents H^+, both at a concentration of 0.001 M. As X approaches unity, the pH will therefore approximate to 3. By reference to Fig. 6, curve 3 in the paper of Neuberger and Scott, it may be seen that at this pH $\mathrm{DPE(SO_3H)_2}$ shows a nearly pure mono-cation spectrum. It may also be seen that, as the pH is lowered below 2, very great changes take place in the spectrum, indicating an equilibrium involving a further proton and a nitrogen atom of the resonating ring. It is well known that changes in the ionization state of atoms outside the resonating ring provoke no change in the spectrum, and are accordingly spectrophotometrically inoperable. Therefore the spectral changes observed by Walter can only refer to the over-all equilibrium

$$\text{Porphyrin} + n(\mathrm{H}^+) \rightleftharpoons \text{Porphyrin mono-cation } (\textit{i.e.} >\mathrm{NH}^+) \qquad (4)$$

Walter obtained maxima or minima for $\Delta(D)$ at $X = 0.667$, giving $n = 2$, and indicating, therefore, an equilibrium involving two protons. But his curves do not fulfill the required conditions since they may be extrapolated to coincide roughly at ($\Delta(D) = 0$, $B \simeq 0.35$). As has been explained, this means that more than one stable ionic species is being formed. The fact that there was no change in the spectrum whatsoever, as X was increased from 0 to 0.3, indicates that the first equilibrium, corresponding to equation 1, is spectrophotometrically inoperable. Some atom or group outside the resonating ring must therefore be accepting a proton. This could, conceivably,[8] be one of the sulfonate ions reacting thus

$$\mathrm{DPE(SO_3^-)_2} + \mathrm{H}^+ \rightleftharpoons \mathrm{DPE(SO_3^-)(SO_3H)} \qquad (5)$$

When this group is approximately 50% titrated ($X = 0.33$), a second equilibrium becomes evident, since this time a change of spectrum is involved. This will be

$$\mathrm{DPE(SO_3^-)(SO_3H)} + \mathrm{H}^+ \rightleftharpoons (\mathrm{H}^+)\mathrm{DPE(SO_3^-)(SO_3H)} \qquad (6)$$

The first sulfonic acid group to ionize will be stronger than the second, both for statistical[9] reasons, and because the negative charge of the first sulfonate ion is balanced at lower pH by the positive charge on the nitrogen atom. The second sulfonic acid group will also be further weakened owing to the proximity of the charge on the first sulfonate ion. Addition of (5) and (6) gives the predicted over-all equilibrium 4, with n equal to 2.

It should be emphasized that the foregoing conclusions in no way imply any inconsistency in the method of Vosburgh and Cooper. This is, in fact, a special case of their equation 13, which related $\Delta(D)$ to the other variables where there are two equilibria involved. The special condition is that $\epsilon_1 = \epsilon_3$, the extinction coefficients of A and AB_n, in their four component system. Under such conditions the stepwise addition of the protons can only be recognized by the fact that the curves cannot be extrapolated to cross $\Delta(D) = 0$ at both limits of X.

Walter's illustration of the spectra of the di-cation and the free base are most misleading, since these are not the limits between which $\Delta(D)$ was varied in his measurements. This can be seen by noting that his curve for the di-cation is labeled pH 0.70. The minimum pH attainable under the conditions of his measurements has been shown to be pH 3. Furthermore, Walter himself made the observation that "the species $\mathrm{PH_4^{++}}$ (di-cation) is a sufficiently strong acid that the complete titration curve could not be observed in water, ..." This is in entire agreement with our finding that $pK'_1 \simeq 0.3$. It may therefore be concluded that all porphyrins so far investigated ionize as bases by one-proton steps. Walter's results correctly interpreted only serve to corroborate this conclusion.

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[8] NOTE ADDED IN PROOF.—This supposes there was no basic impurity present. Walter (private communication, 1954) now considers that his $\mathrm{DPE(SO_3K)_2}$ contained free alkali, so that (5) would become simply $\mathrm{OH^-} + \mathrm{H^+} \rightleftharpoons \mathrm{H_2O}$.

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