the constants for dissociation of the two possible histamine proton cations. A plot of $\bar{n}$ against the negative logarithm of the free unprotonated histamine concentration, p[hn], permitted selection of temporary formation constants. Final values of the constants were obtained by successive approximation.

Metal chloride solutions, made up from reagent grade materials and dissolved in HCl, were diluted with an excess of 0.1 N KCl to give a total ionic strength of 0.135 upon titration. Approximately 1.3 M histamine solutions were added from a 5-ml. buret. The titration cell contained a hydrogen electrode in addition to the glass and calomel electrodes. The cell was flushed with hydrogen, which had been purified and presaturated with water vapor, and was mounted in a water-bath at 25°. A Leeds and Northrup Type 7663 pH meter, previously calibrated against the hydrogen electrode, was used. Solutions of 0.05 M phthalate, pH 4.01, were employed as reference buffer.

Histamine was obtained from the Nutritional Biochemical Corporation, Cleveland, Ohio. It was purified by repeated extraction with dry benzene which yielded a product of m.p. 84.5–86.5° (lit. 86°, sealed tube). Histamine solutions were standardized by potentiometric titration. The metal chloride solutions were standardized by electrodeposition[7] upon platinum electrodes.

Results

In Table I, $\bar{n}$ values are shown at selected intervals over the range of the titrations.

TABLE I

AVERAGE NUMBER OF HISTAMINE MOLECULES BOUND PER CENTRAL METAL ION AT VARIOUS FREE HISTAMINE CONCENTRATIONS, 25°

p[hn]	Cu II	$\bar{n}$ Ni II	Co II
10.5	0.13		
10.0	.28		
9.5	.53		
9.0	.80		
8.0	1.02	0.07	
7.0	1.30	.45	
6.0	1.72	.97	0.22
5.0	1.95	1.52	0.70
4.0	1.99	2.02	1.30
3.0	2.03	2.55	1.95
2.5		2.80	2.20
2.25		2.95	2.35
2.15		2.90	

Copper here takes up a maximum of two histamine molecules, whereas a value of three is approached by nickel. At lower p[hn], $\bar{n}$ values for cobalt became erratic, possibly due to secondary reactions.[2]

Logarithms of the consecutive formation constants are given in Table II. The third constant for cobalt was obtained by extrapolation of its formation curve; the slope of the nickel curve was used as a guide.

TABLE II

CONSECUTIVE FORMATION CONSTANTS FOR THE HISTAMINE COMPLEXES, 25°

	Cu II	Ni II	Co II
log k_1	9.55	6.88	5.27
log k_2	6.48	5.03	3.68
log k_3		3.09	2.03

Theoretical formation curves, as predicted by the mass action law and constructed in terms of these

(7) A. I. Vogel, "Textbook of Quantitative Inorganic Analysis. Theory and Practice." Longmans, Green and Co., London, New York, 1951, pp. 518, 523, 524.

constants, superimpose upon the experimetal plots. The formation curves for the nickel and cobalt complexes are similar to those of ethylenediamine.[6] However, the stabilities of the histamine complexes decrease more rapidly with increasing substitution upon the central ion. This effect is particularly pronounced in the copper system, for which Eichler and Meyer[4] have estimated a much lower first constant.

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Magnetic Studies of Nickel(II) and Palladium(II) Complexes with Some vic-Dioximes[1,2]

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In connection with current studies being made in this Laboratory of the fundamental nature and analytical applications of the reaction of the vic-dioximes with metal ions it became necessary to know the magnetic susceptibility of several of the bis-(vic-dioximato-N,N')-metal(II) complexes. The compounds studied were the nickel(II) and palladium(II) complexes of α-benzildioxime, α-furildioxime, 2,3-butanedionedioxime (dimethylglyoxime), 1,2-cycloheptanedionedioxime and the nickel(II) complex of 1,2-cyclohexanedionedioxime.

TABLE I

MAGNETIC DATA FOR THE BIS-(vic-DIOXIMATO-N,N')-METAL(II) COMPLEXES AT 20°

Compound	Metal, % Calcd.	Obsd.	Density, g./ml.	Molar susceptibility, $\chi_M \times 10^6$
I[a]	20.32	20.47	1.715	−108
II	17.21	17.30	1.703	−134
III	15.90	15.88	1.619	−173
IV	11.81	11.87	1.747	−193
V	10.92	10.97	1.509	−262
VI	31.67	31.6	1.931	−121
VII	25.59	25.5	1.692	−191
VIII	19.57	19.5	1.832	−210
IX	18.23	18.2	1.534	−296

[a] I, bis-(2,3-butanedionedioximato-N,N')-nickel(II); II, bis-(1,2-cyclohexanedionedioximato-N,N')-nickel(II); III, bis-(1,2-cycloheptanedionedioximato-N,N')-nickel(II); IV, bis-(α-furildioximato-N,N')-nickel(II); V, bis-(α-benzildioximato-N,N')-nickel(II); VI, bis-(2,3-butanedionedioximato-N,N')-palladium(II); VII, bis-(1,2-cycloheptanedionedioximato-N,N')-palladium(II); VIII, bis-(α-furildioximato-N,N')-palladium(II); IX, bis-(α-benzildioximato-N,N')-palladium(II).

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-butanedione-dioximato-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 (dsp²) similar to that found by Godycki and Rundle[14] for bis-(2,3-butanedionedioximato-N,N')-nickel(II).

(14) L. E. Godycki and R. E. Rundle, *Acta Cryst.*, **6**, 487 (1953).

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The Acid—Base Equilibria of Porphyrins. Non-simultaneous Dissociation of Two Protons Upheld

BY JOHN J. SCOTT

Walter[1] has reported studies of the spectral changes of a solution of the dipotassium salt of deuteroporphyrin IX dimethyl ester disulfonic acid (DPE(SO₃K)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(SO₃H)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(SO₃H)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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(13) Described fully in Atomic Energy Commission Report, ISC-250, "Magnetic and Spectrophotometric Studies of Nickel(II) Complexes with some vic-Dioximes," by Roy W. Vander Haar and Charles V. Banks.

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