1.40, N:O = 1.22 Å., ∠CON = 105° and ∠O: N:O = 135°[13]; tetrahedral angles were assumed within the methyl group. With these parameters the principal moments of inertia of the configuration in which the C, N and O nuclei are coplanar (Fig. 2) are 41.9, 103.8 and 142.1 a.w. − Å.[2], and the reduced moments of inertia for internal rotation are 2.8 (methyl rotation) and 10.5 (skeletal rotation).[14] The rotational entropy is calculated for the limiting case of free internal rotation and is corrected for the change of the moments of inertia with the angle of the internal skeletal rotation (Table V).

TABLE V

STANDARD ENTROPY OF METHYL NITRATE VAPOR (298.2°, 1 ATM.)

	$S^0_{298.2}$		$S^0_{298.2}$
Translation	38.92	Liquid (0–298°)[10]	51.81
Rotation	24.88	Vaporization	27.20
Vibration (ν_{1-16})	2.79	Compression	−3.15
Free internal rotation(2)	9.38	Vapor imperfection	0.03
	75.97		75.89

The entropy of methyl nitrate has been measured by Gray and Smith,[10] but the heat and entropy of vaporization are available only from vapor pressure data over a limited temperature range.[15] The published vapor pressure equation corresponds to $\Delta S^{298.2}_{evap} = 27.40$ e.u. and $\Delta C_p = -12.6$ cal. mole^{-1}. When, as a precaution, C_p (vapor) is calculated from the spectroscopic data and subtracted from the observed heat capacity of the liquid[10] it is found that

(13) The value of ∠O:N:O = 135° is adopted by analogy with nitric acid (vapor): cf. the discussion by H. Cohn, C. K. Ingold and H. G. Poole, J. Chem. Soc., 2284 (1952).

(14) K. S. Pitzer and W. D. Gwinn, J. Chem. Phys., 10, 428 (1942).

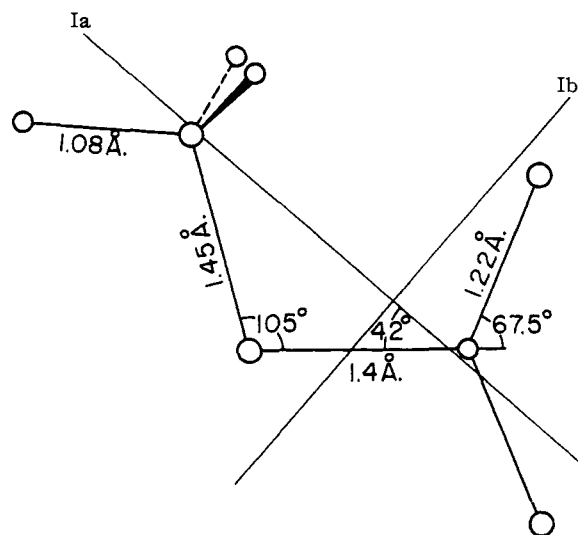(15) J. S. McKinley-McKee and E. A. Moelwyn-Hughes, Trans. Faraday Soc., 48, 247 (1952).

Fig. 2.—Methyl nitrate in the planar configuration and the principal axes of inertia.

ΔC_p should lie between −18.0 and −21.4 cal. mole^{-1} (at 298°), the second value being for the case of free internal rotation. Either of these values can be used in a vapor pressure equation without seriously disturbing the agreement with the experimental data. For consistency we have chosen the value corresponding to free rotation and fitted an equation to the experimental points in the mid and upper section of the pressure range where the measurements are presumably most accurate: This treatment yields $\Delta H^{298}_{evap} = 8110$ cal. (Berthelot correction of 54 cal.[16]) and $\Delta S^{298}_{evap} = 27.20$ e.u. The entropy of compression to the standard state is corrected for vapor imperfection using the modified Berthelot equation.[16]

(16) Based on $T_c = 520°K$. and $P_c = 65$ at (estimated).

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NOTES

Complexes of Histamine with Co[II], Ni[II] and Cu[III]

By B. L. MICKEL AND A. C. ANDREWS

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Metal complexes of histamine, 4(5)-(2-aminoethyl)-imidazole, have been reported,[2-5] but this information has been largely qualitative. It might be expected that histamine forms chelate complexes

(1) Portion of a dissertation presented by B. L. Mickel as partial fulfillment of the requirement for the degree Doctor of Philosophy in chemistry at Kansas State College, 1955. This investigation was supported by a research grant G 3920 from the National Institutes of Health, Public Health Service.

(2) W. Zimmermann, Z. physiol. Chem., 186, 260 (1930).

(3) F. Axmacher, Biochem. Z., 284, 339 (1936).

(4) O. Eichler and G. Meyer, Naturwissenschaften, 35, 934 (1948).

(5) R. W. Cowgill and W. M. Clark, J. Biol. Chem., 198, 33 (1952).

through the aminoethyl nitrogen and the basic 3-nitrogen of the imidazole nucleus, and that the 1-nitrogen makes no contribution to bond formation. In its reactions with the ions Co[II], Ni[II] and Cu[II], histamine has been here considered, mathematically, to behave as an aliphatic diamine. The apparent fulfillment of ordinary coördination numbers permits the calculation of formation constants in terms of this complexing mechanism.

Experimental

The potentiometric technique of Bjerrum,[6] as applied to ethylenediamine, was used. The average number of histamine molecules bound per central ion, $\bar{n}$, was calculated conventionally in terms of total reactant concentrations and

(6) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941, pp. 198–219.

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}	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.	Metal, % 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).

(1) Work was performed in the Ames Laboratory of the Atomic Energy Commission.

(2) No. XVI in a series on "Chemistry of the vic-Dioximes." Recent papers in this series are: (a) No. XII, Anal. Chem., 23, 1730 (1951); (b) No. XIII, Anal. Chim. Acta, 7, 291 (1952): (c) No. XIV, J. Org. Chem., 18, 267 (1953), (d) No. XV, Anal. Chim. Acta, 10, 129 (1954).

(3) Partially abstracted from a dissertation submitted by Roy W. Vander Haar to the Graduate Faculty of Iowa State College in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1952.

(4) Partially abstracted from a dissertation submitted by Raymond P. Vander Wal to the Graduate Faculty of Iowa State College in partial fulfillment of the requirements for the degree of Master of Science, 1954.