

TABLE VI
FIRST- AND SECOND-ORDER RATE CONSTANTS FOR AQUEOUS
SOLUTION AND 25°

	k_1 , sec. ⁻¹	k_2 , M ⁻¹ sec. ⁻¹
Pt(C ₂ O ₄) ₂ ⁻² -C ₂ O ₄ ⁻²	10 ⁻⁹	4 × 10 ⁻⁷
<i>trans</i> -Pt(NH ₃) ₂ Cl ₂ -C ₂ O ₄ ⁻²	~10 ⁻⁵	~7 × 10 ⁻³
Systems summarized by Gray ^{3d}	10 ⁻⁴ -10 ⁻⁵	10 ⁻¹ -10 ⁻⁴ ^a

^a Excluding OH⁻, which is a very weakly biphilic reagent.

is with oxalate as a bidentate ligand, can account for the extremely low rates observed.

It is of interest to compare the first- and second-order rate constants for the oxalate-bisoxalatoplatinate(II) exchange with values obtained under similar conditions for substitution of monodentate groups in platinum(II) complexes. Table VI summarizes our values, those obtained by Banerjee, *et al.*,^{3b} for oxalate replacement of a chloride in *trans*-Pt(NH₃)₂Cl₂, and those accumulated by Gray^{3d} for monodentate substitution in a series of complexes (where the group *trans* to that being replaced was ammonia, a secondary amine, or chloride). Both the constants for the bisoxalatoplatinate(II) exchange are of the order of 10⁻⁴ times the average constants quoted by Gray. The observations can be explained in terms of the mechanism we have proposed, considered to proceed through reactions 1, 2, and 3, if ~0.01% of the bisoxalatoplatinate(II) ion is in the form of intermediate I and this is as reactive as one of the above monodentate platinum(II) complexes.

The proposed mechanism requires that intermediate III react rapidly with free oxalate. There is considerable evidence in the literature^{3b,3d,19,20} to indicate that aquoplatinum(II) complexes react rapidly enough with ligands to be intermediates in reactions exhibiting first-order behavior, and it is reasonable to assume that diaquo complexes are at least equally reactive. The invariance of k_1 with ionic strength does seem to rule out the possibility that the first-order term corresponds to a rate-determining nucleophilic attack of the complex by nitrate ion. Our results give no information on whether the first-order term (equivalent to equilibrium between intermediates I and III in the mechanism) involves solvent participation or proceeds by SN1-type elimination of oxalate from intermediate I. However, the arguments of Gray and Olcott¹⁹ favoring solvent participation in exchange reactions involving complexes of the type Pt(dien)X are probably relevant in the case of the oxalate-bisoxalatoplatinate(II) exchange. From Debye-Hückel considerations reactions between ions of similar sign of charge would be expected to be accelerated by increasing ionic strength. This could explain why the second-order reaction (for which we proposed reaction 2 and/or reaction 4 to be rate-determining) is accelerated by increases in ionic strength.

(19) H. B. Gray and R. J. Olcott, *Inorg. Chem.*, **1**, 481 (1962).

(20) T. S. Elleman, J. W. Reishus, and D. S. Martin, Jr., *J. Am. Chem. Soc.*, **80**, 536 (1958).

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Imidazole Complexes of Nickel(II), Copper(II), Zinc(II), and Silver(I)

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The site of complex formation of the imidazole molecule has been determined to be the pyridine nitrogen by comparing data on the N-methylimidazole complex with the imidazole complex of Ag(I). The preparation and characterization of a dual system of imidazole and imidazolate complexes is presented for Ni(II), Cu(II), Zn(II), and Ag(I). Total heats of formation of these complexes have been determined.

Introduction

The bonding of imidazole with transition metal ions is of interest because of this ligand's close relationship with biological systems of a more complex nature involving histidine residues. The literature contains free energy data obtained by potentiometric studies on these systems.¹⁻⁴ These data indicate that imidazole forms some of the most stable complexes of all heterocyclic-N ligands. This is corroborated by the high

acid association constant of imidazole. Although the acidity of the hydrogen bound at the pyrrole nitrogen⁵ in the imidazole ring (hereafter referred to as the "pyrrole hydrogen") is very weak, with a pK_a value of 14.52,⁶ metal imidazoles were known as early as 1877.^{7,8} The formation of the compound Hg(C₃H₃N₂)(ClO₄)·H₂O was reported by Brooks and Davidson.⁹ Martin and Edsall¹⁰ reported that Cu(II) and Ni(II) induced the ionization of the pyrrole hydrogen in glycyl- and his-

(1) J. T. Edsall, G. Felsenfeld, D. S. Goodman, and F. R. N. Gurd, *J. Am. Chem. Soc.*, **76**, 3054 (1954).

(2) B. L. Mickel and A. C. Andrews, *ibid.*, **77**, 5291 (1955).

(3) A. C. Andrews, T. D. Lyons, and T. D. O'Brien, *J. Chem. Soc.*, 1776 (1962).

(4) W. L. Koltun, R. N. Dexter, R. E. Clark, and F. R. N. Gurd, *J. Am. Chem. Soc.*, **80**, 4188 (1958).

(5) The imino nitrogen in the imidazole ring is referred to as the "pyrrole nitrogen" and the other nitrogen the "pyridine nitrogen." This nomenclature is rather arbitrary.

(6) H. Walba and R. W. Isensee, *J. Org. Chem.*, **21**, 702 (1956).

(7) G. Wyss, *Ber.*, **10**, 1365 (1877).

(8) A. Windaus and F. Kopp, *ibid.*, **38**, 1166 (1905).

(9) P. Brooks and N. Davidson, *J. Am. Chem. Soc.*, **82**, 2118 (1960).

(10) R. B. Martin and J. T. Edsall, *ibid.*, **82**, 1107 (1960).

tidylhistidines. Recent studies on 2,2'-biimidazole by Holmes, *et al.*,¹¹ and on benzimidazole by Goodgame and Cotton¹² again indicate the ionization of the pyrrole hydrogen in complex formation.

Several studies have been made on the imidazole ring to determine, if possible, which nitrogen is involved in the binding to a transition metal ion. Li, *et al.*,¹³ determined the constants of imidazole and N-methylimidazole with Cu(II). By their similarity the bonding site was assumed to be the pyridine nitrogen. Gold and Gregor¹⁴ determined the formation constants with Ag(I); the pyrrole nitrogen was thought to be involved in the binding because the formation constants of metal imidazole complexes compared well with those of the corresponding metal-ammonia complexes. N.m.r. results on the ligand¹⁵ indicate that the pyrrole hydrogen exchanges rapidly with the solvent (H₂O) and also with the nitrogen at the 3-position. This amidine tautomerism had earlier been studied by Raman spectra.¹⁶ Indirect structural determination of imidazole, however, indicates the C-N bonds are non-equivalent.¹⁷

Since enthalpic determinations by calorimetry had not been made on imidazole complexes, it was thought that this simple and direct method should provide some additional information on the metal-ligand bond energies. A semiadiabatic calorimeter was used in the measurements.

Experimental

Reagents.—Solutions of reagent grade Ni(II), Cu(II), Zn(II), and Ag(I) nitrates and HNO₃ (Baker and Adamson) were prepared and standardized by conventional methods. Imidazole (ImH) (Eastman) was recrystallized from benzene and sublimed under vacuum. N-Methylimidazole (ImCH₃) was supplied by Eastman and redistilled at a pressure of approximately 3 mm. All solutions except in the studies of Ag(I) were made up to be 0.16 M in KNO₃ (Baker and Adamson); Ag(I) complexes were studied in a medium of 1 M KNO₃.

Calorimetry.—A thermometric titration type calorimeter was designed to measure heats of reaction on the order of 0.5 cal. The calorimeter, similar to the one reported by Schlyter¹⁸ and Atkinson and Bauman,¹⁹ consists of an inner glass beaker and outside brass jacket, a thermistor bridge, an electrical heater, a thermostated buret, and a glass stirrer. The stirrer was driven by a 3600-r.p.m. synchronous motor geared down to 180 r.p.m. The hollow shaft of the stirrer also served as an air cooler for the calorimeter. The whole calorimeter was immersed in a water bath; the bath temperature was maintained at 25 ± 0.003°.

To achieve the required sensitivity, a thermistor (Veco number 31A18, 1000 ohms) was used in one arm of a simple Wheatstone bridge. The other three arms consisted of three 300-ohm precision resistances, and the thermistor was shunted by a resistance such that the bridge would be approximately balanced at 25°.

The output of the bridge was connected to a Leeds and Northrup 7553 Type K-3 potentiometer, which was used to balance the bridge potential at bath temperature. The unbalanced potential resulting from temperature change was amplified by a d.c. μ volt-indicating amplifier (Leeds and Northrup) and was recorded by a potentiometric chart recorder (Minneapolis-Honeywell). The potentiometer and amplifier were also used in measuring the current through the bridge and the heater.

The total heat capacity of the calorimeter and its contents was calibrated by the electric heater (made of No. 38 manganin wire, resistance 46.04 ohms) and represented as cal./cm. chart width. For dilute solutions in 0.16 M potassium nitrate the heat capacity could be represented by the equation

$$i_B C = 0.01916 + 0.05110V$$

where i_B is the bridge current in ma., C the heat capacity of the calorimeter and contents in cal./cm. of chart width, and V the volume of solution in ml.

The heat of reaction was calculated from the equation

$$Q = C\Delta l + \Delta V C'(T_c - T_b)$$

where C is the heat capacity of the calorimeter and contents in cal./cm., Δl the recorder response in cm., ΔV the volume in ml. of titrant added, C' the heat capacity of the titrant in cal./ml., and T_c and T_b the initial temperature of the calorimeter contents and the temperature of the titrant, taken as the bath temperature. The heats of dilution could be neglected.

Since there was an uncertainty in measuring T_c by the thermistor because of the drifting of its resistance with time and the so-called "thermistor jumps," it was necessary to minimize $T_c - T_b$. This was done by considering the heat-transfer equation

$$q_t + q_s + K(T_b - T_c) = C dl/dt$$

where q_t and q_s are the rate of energy dissipation of the thermistor and stirrer, respectively, K the heat-transfer coefficient of the calorimeter, and dl/dt is the slope of the curve recorded by the recorder. When thermal equilibrium is reached, $dl/dt = 0$ and $T_b - T_c = (q_t + q_s)/K$.

In designing a calorimeter for fast reactions, it is more important to reduce the time required to approach thermal equilibrium than to minimize the rate of heat loss. K was measured to be 1 cal./deg. min. if the annular space of the calorimeter was not evacuated. This would give $T_b - T_c = -0.005^\circ$ approximately at $dl/dt = 0$. It was estimated that this temperature difference corresponded to 5 cm. on the recorder chart. The position of the recording pen was noted at thermal equilibrium. Then the temperature of the calorimeter contents was lowered slightly so that the pen moved approximately 5 cm. to the left of the equilibrium position before titrant was added. In this way no correction was necessary for temperature difference between the titrant and the calorimeter contents.

To check the accuracy of the calorimeter, ΔH of neutralization of 0.0493 M NaOH with 0.0546 M HNO₃ was measured. Five additions with 1 ml. of acid in each addition gave an average value of -13.8 ± 0.2 kcal./mole. Papee and co-workers²⁰ reported a value of $\Delta H = -13.5 \pm 0.05$ kcal./mole for neutralization of strong acid with strong base at infinite dilution.

Enthalpic titrations were carried out by adding ligand solution (approximately 0.1 M) by means of a thermostated buret into the calorimeter in 1-ml. portions. The initial solution in the calorimeter was 50 ml. at known acid and metal ion concentration. After each addition of titrant, several electrical heat capacity calibrations were made and the temperature of the calorimeter returned to the bath temperature by the passage of precooled air through the hollow shaft of the stirrer. An identical potentiometric titration was made separately to determine the $\bar{n}$ value of each point of the enthalpic titration. $\bar{n}$ is the average number of bound ligand molecules per metal ion.

(11) F. Holmes, K. M. Jones, and E. G. Torrible, *J. Chem. Soc.*, 4790 (1961).

(12) M. Goodgame and F. A. Cotton, *J. Am. Chem. Soc.*, **84**, 1543 (1962).

(13) N. C. Li, J. M. White, and E. Doody, *ibid.*, **76**, 6219 (1954).

(14) D. H. Gold and H. P. Gregor, *J. Phys. Chem.*, **64**, 1461 (1960).

(15) R. J. Gillespie, A. Grimison, J. H. Ridd, and R. F. M. White, *J. Chem. Soc.*, 3228 (1958).

(16) D. N. Shirogin and I. K. Syrkin, *Izv. Akad. Nauk SSSR, Ser. Fiz.*, **9**, 225 (1945).

(17) D. Garfinkel and J. T. Edsall, *J. Am. Chem. Soc.*, **80**, 3807 (1958).

(18) K. Schlyter, *Trans. Roy. Inst. Tech., Stockholm*, **132** (1959).

(19) G. Atkinson and J. E. Bauman, *Inorg. Chem.*, **1**, 900 (1962).

(20) H. M. Papee, W. J. Canady, and K. J. Laidler, *Can. J. Chem.*, **34**, 1677 (1956).

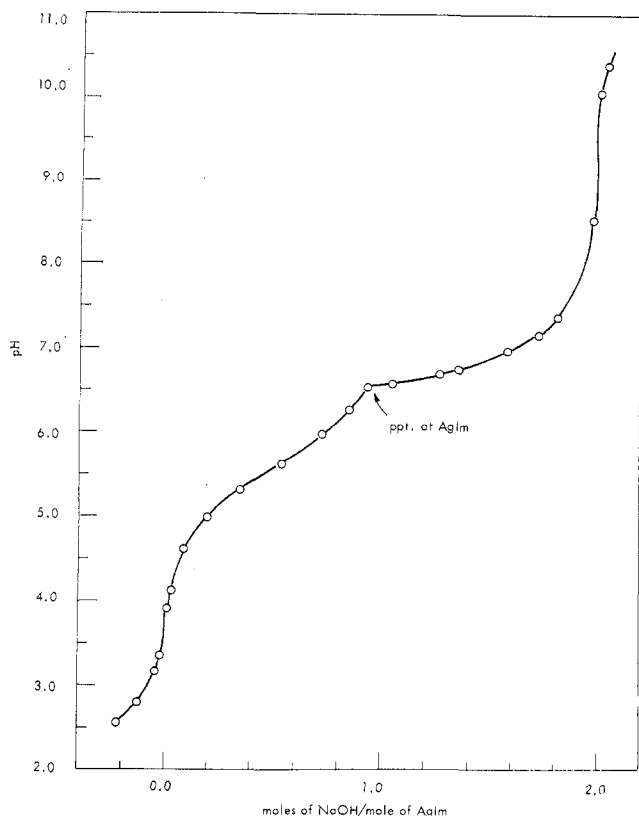


Fig. 1.—Titration of silver imidazolate with NaOH: 0.1196 g. of AgIm in 50 ml. of 0.08044 *N* HNO₃ vs. 0.0945 *N* NaOH.

The total heat of complex formation was measured by adding metal nitrate solution (approximately 0.05 *M*) into 50 ml. of ligand solution in the calorimeter. The ligand solution had been buffered by adding nitric acid to a pH such that no metal imidazolate or metal hydroxide would form. The free ligand concentration was approximately 0.05 *M*. In the case of Ni(II) and Zn(II), the heat per mole of metal ion added dropped as more metal nitrate solution was added. In these cases the apparent molar heat of complex formation was plotted against the number of moles of metal ion added. Extrapolation to zero metal ion concentration gave the total heat of complex formation.

Potentiometry.—Stability constants of Ag(I) with imidazole and *N*-methylimidazole were obtained by pH measurement. A Metrohm E-388 pH meter with a combination electrode (20-01-20X) was used.

Preparation of Solid Complexes.—Ag(C₃H₃N₂)₂NO₃ was prepared by dissolving 1.2 g. of AgNO₃ in 35 ml. of 95% ethanol to which 2 g. of imidazole was added. The solution was evaporated at room temperature until crystals began to appear and then cooled to 0°, filtered, washed with methanol, and dried at room temperature under vacuum. Silver was analyzed gravimetrically as AgCl.

Anal. Calcd. for Ag(C₃H₃N₂)₂NO₃: Ag, 35.24. Found: Ag, 35.38, 35.44.

Ag(C₃H₃N₂)₂ was prepared by dissolving equimolar AgNO₃ and imidazole in distilled water. NaOH solution was added dropwise until a pH of approximately 10 was reached. The precipitate formed was filtered, washed with ethanol, and dried at room temperature under vacuum. Silver was analyzed by dissolving the compound in excess nitric acid and then precipitating as AgCl.

Anal. Calcd. for Ag(C₃H₃N₂): Ag, 61.66. Found: Ag, 61.28, 61.44.

Zn(C₃H₃N₂)₂ was prepared by adding NaOH solution (0.13 *M*) to a solution of 1.8 g. of Zn(ClO₄)₂, 1 ml. of 0.1 *M* HClO₄, and 16 ml. of 0.625 *M* imidazole until a white precipitate was formed. The precipitate was filtered and dried under vacuum. Carbon,

hydrogen, and nitrogen analyses were made by Galbraith Laboratories.

Anal. Calcd. for Zn(C₃H₃N₂)₂: C, 36.1; H, 3.04; N, 28.1. Found: C, 35.8; H, 3.12; N, 27.1.

Cu(C₃H₃N₂)₂ was prepared by dissolving 4 g. of imidazole in 100 ml. of 0.05 *M* Cu(NO₃)₂, to which NaOH solution (0.1 *M*) was added dropwise until a reddish purple precipitate appeared. The precipitate was filtered, washed with ethanol, and dried at 80° *in vacuo*.

Anal. Calcd. for Cu(C₃H₃N₂)₂: C, 36.4; H, 3.06. Found: C, 36.63; H, 3.38.

Ni(C₃H₃N₂)₂ was prepared by dissolving 5 g. of imidazole and 3 g. of Ni(NO₃)₂·6H₂O in 100 ml. of water. The lavender precipitate formed was filtered, and NaOH solution (0.1 *M*) was added to the filtrate to give a yellow precipitate. A comparison of the infrared spectrum of the yellow precipitate with that of copper imidazolate showed that the yellow precipitate was an imidazolate.

Anal. Calcd. for Ni(C₃H₃N₂)₂: C, 37.37; H, 3.14. Found: C, 36.63; H, 3.15.

Cd(C₃H₃N₂)₂ was prepared in the same manner as Ni(C₃H₃N₂)₂.

Infrared spectra of all metal imidazolates were obtained with a Perkin-Elmer Model 137 Infracord. The Nujol mull technique was used in sample preparation; absorption bands due to the Nujol medium were excluded by comparing with the corresponding fluorolube spectrum.

Results

Ionization of Pyrrole Hydrogen in Imidazole Complexes of Metal Ions.—Figure 1 shows the titration curve of silver imidazolate with NaOH. The same titration curve can be obtained by dissolving equimolar AgNO₃ and imidazole in excess acid and titrating with NaOH. The first end point corresponds to the neutral-

TABLE I

ABSORPTION FREQUENCIES (CM. ⁻¹) IN METAL IMIDAZOLATES ^a				
Ni(Im) ₂	Cu(Im) ₂	Zn(Im) ₂	Cd(Im) ₂	Ag(Im)
1580 (w)	1600 (w)	1590 (w)	1590 (w)	...
1480 (s)	1480 (s)	1480 (s)	1480 (s)	1480 (s)
1460 (s)	1460 (s)	1460 (s)	1460 (s)	1460 (s)
1320 (sh)	1320 (sh)		1320 (m)	1300 (w)
1310 (m)	1310 (m)	1310 (w)		
...	1280 (w)	1270 (w)	1280 (m)	1280 (w)
1240 (m)	1240 (m)	1230 (m)	1250 (s)	1240 (w)
				1230 (m)
1180 (m)	1170 (m)	1160 (m)	1170 (m)	1170 (m)
	1110 (sh)		1110 (s)	1110 (sh)
1090 (vs)	1090 (vs)	1080 (vs)	1090 (vs)	1100 (sh)
				1090 (s)
				1086 (s)
1057 (m)	1046 (w)			
976 (w)	970 (w)	972 (w)	968 (m)	964 (w)
960 (w)	952 (s)	952 (s)	946 (s)	946 (w)
933 (m)				
918 (w)				
880 (w)	880 (w)	880 (w)	...	860 (m)
830 (s)	837 (s)	833 (m)	843 (m)	830 (s)
821 (sh)	828 (sh)	823 (m)	835 (m)	
			828 (m)	
			822 (m)	
	787 (s)	...	...	777 (s)
770 (sh)	757 (s)	757 (s,b)	762 (s)	759 (s)
743 (s,b)	750 (s)		759 (s)	748 (vs)
			748 (s)	
670 (s)	669 (s)	668 (s)	668 (s)	663 (s)

^a s, strong; m, medium; w, weak; sh, shoulder; b, broad; v, very.

ization of the excess free acid. The abscissa is the number of moles of NaOH added (in addition to that required to neutralize free HNO_3) per mole of silver imidazolate. At a pH of 6.53, corresponding to a NaOH:AgIm ratio of 0.97, a white precipitate begins to form. Also there is an abrupt change of the slope of the titration curve indicating the ionization of the pyrrole hydrogen in the silver imidazole complex. The pH rises sharply again at a molar ratio NaOH:AgIm of 2. This represents the end point of the N-H ionization. The precipitate was isolated after the titration and was confirmed as silver imidazolate by its infrared spectrum.

Table I contains infrared absorption frequencies of some transition metal imidazoles prepared in this laboratory. It is to be noted that the N-H stretching band normally appearing at $3150\text{--}3400\text{ cm}^{-1}$ for imidazolyl complexes is missing in all metal imidazoles as expected.

The solubility product of silver imidazolate at 25° was calculated using the equation

$$K_{\text{AgIm}} = [\text{Ag}^+][\text{Im}^-] = K_a[\text{Ag}^+][\text{ImH}]/[\text{H}^+]$$

where $K_a = [\text{H}^+][\text{Im}^-]/[\text{ImH}]$ is the acid dissociation constant of the pyrrole hydrogen. At the point of the onset of precipitation shown in Fig. 1, the amount of AgIm formed is negligible and the following material balances hold

$$\begin{aligned} [\text{H}^+]_T &= [\text{H}^+] + 2[\text{HImH}^+] + [\text{ImH}] + [\text{Ag}(\text{ImH})^+] + \\ &\quad 2[\text{Ag}(\text{ImH})_2^+] + [\text{Na}^+] - [\text{OH}^-] \\ &= [\text{H}^+] + [\text{H}^+][\text{ImH}]/K + [\text{ImH}]_T + \\ &\quad [\text{Na}^+] - [\text{OH}^-] \quad (1) \end{aligned}$$

$$\begin{aligned} [\text{Ag}^+]_T &= [\text{Ag}^+] + [\text{Ag}(\text{ImH})^+] + [\text{Ag}(\text{ImH})_2^+] \\ &= [\text{Ag}^+](1 + K_1[\text{ImH}] + K_1K_2[\text{ImH}]^2) \quad (2) \end{aligned}$$

where $[\text{H}^+]_T$, $[\text{ImH}]_T$, and $[\text{Ag}^+]_T$ are the total acid concentration, total imidazole concentration, and total silver concentration, respectively, $[\text{Na}^+]$ is the sodium ion concentration resulting from the addition of sodium hydroxide, and K is the acid dissociation constant of the protonated imidazole

$$K = \frac{[\text{H}^+][\text{ImH}]}{[\text{HImH}^+]}$$

Since the pH is 6.53 at this point, $[\text{ImH}]$ was calculated to be $1.90 \times 10^{-4} M$ from eq. 1, taking $\log K$ as 7.09.²¹ $[\text{Ag}^+]$ was then calculated to be $7.86 \times 10^{-3} M$ from eq. 2, taking K_1 and K_2 to be $10^{3.05}$ and $10^{3.83}$, respectively (Table IV). Therefore, $K_{\text{AgIm}} = 10^{-14.52}$. $[\text{Ag}^+][\text{ImH}]/[\text{H}^+] = 10^{-13.8} M$.² This value is only approximate since the K_a value used in the calculation is for a medium of $0.5 M \text{ KNO}_3$, and K_1 and K_2 are formation constants in $1.0 M \text{ KNO}_3$. Similarly the solubility product of zinc imidazolate at 25° was calculated to be $10^{-22.8} M$.³

Imidazole and N-Methylimidazole Complexes of Ag(I).—The formation curve of Ag(I) with N-methylimidazole at 25.6° in $1 M \text{ KNO}_3$ medium is shown in Fig. 2. The formation constants $\log K_1$ and $\log K_2$ at

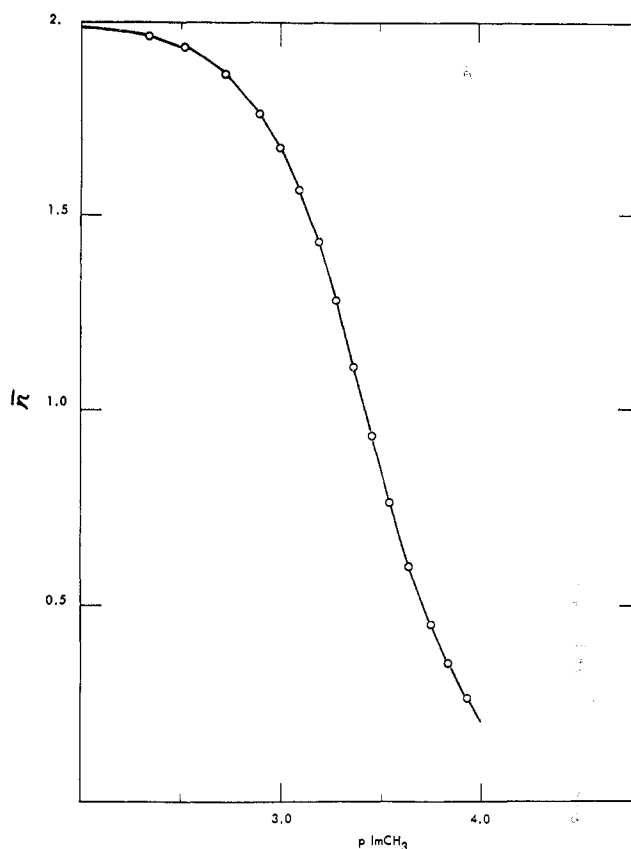


Fig. 2.—Formation curve of Ag(I)-N-methylimidazole: —, curve calculated for $\log K_1 = 2.983$, $\log K_2 = 3.867$; O, experimental points.

25.6° were calculated to be 2.98 and 3.87, respectively, by taking $\log K_1K_2 = -2 \log [\text{ImCH}_3]_{\text{at } n=1} = 6.850$ and calculating K_2 from the equation

$$K_2 = (K_1K_2(2 - \bar{n})[\text{ImCH}_3]^2 - \bar{n})/(\bar{n} - 1)[\text{ImCH}_3]$$

at every point where $\bar{n} > 1$ and then taking the average. These equations can be derived readily from the equilibrium relationships and the definition of $\bar{n}$. Formation constants for Ag(I)-imidazole complexes at 25° and $1.0 M \text{ KNO}_3$ medium were calculated similarly to be 3.05 and 3.83, respectively. Enthalpy changes for the formation of $\text{Ag}(\text{ImH})_2^+$ and $\text{Ag}(\text{ImCH}_3)_2^+$ in $1.0 M \text{ KNO}_3$ solution at 25° were measured to be $-15.7 \pm 0.2 \text{ kcal./mole}$ in both cases.

Thermodynamic Data of Imidazole Complexes of Cu(II), Ni(II), Zn(II), and Ag(I).—Enthalpic titration data of Cu(II), Ni(II), Zn(II), and Ag(I) with imidazole are listed in Table II. The number of ligand molecules per metal ion, $\bar{n}$, is calculated from the corresponding potentiometric titration curve and $\Delta \bar{H}$ is calculated from the equation

$$\Delta \bar{H} = (\Sigma Q - Q')/\bar{n}M$$

where ΣQ is the sum of the heats evolved in the titration (kcal.), Q' is the heat of neutralization of the acid (kcal.), $\bar{n}$ is the average number of ligands per metal ion, and M is the total number of moles of metal ion in solution.

Although in principle the stepwise enthalpy changes

TABLE II: ENTHALPIC TITRATION DATA OF Cu(II), Ni(II), Zn(II), AND Ag(I) WITH IMIDAZOLE AT 25°

Soln. I: Cu(II) ^a 50 ml. of 0.00465 M HNO ₃ + 0.00690 M Cu(NO ₃) ₂ Titrant: 0.0846 M imidazole					Soln. II: Ni(II) ^a 50 ml. of 0.00465 M HNO ₃ + 0.00576 M Ni(NO ₃) ₂ Titrant: 0.0846 M imidazole					Soln. III: Zn(II) ^a 50 ml. of 0.00465 M HNO ₃ + 0.00672 M Zn(NO ₃) ₂ Titrant: 0.0846 M imidazole					Soln. IV: Ag(I) ^b 50 ml. of 0.00924 M AgNO ₃ + 10 ml. of 0.03132 M HNO ₃ Titrant: 0.0862 M imidazole				
ImH added, mmoles	Q, cal.	$\bar{n}$	$-\Delta H$, kcal./mole	ImH added, mmoles	Q, cal.	$\bar{n}$	$-\Delta H$, kcal./mole	ImH added, mmoles	Q, cal.	$\bar{n}$	$-\Delta H$, kcal./mole	ImH added, mmoles	Q, cal.	$\bar{n}$	$-\Delta H$, kcal./mole	ImH added, mmoles	Q, cal.	$\bar{n}$	$-\Delta H$, kcal./mole
0.0444	0.412	0	...	0.0840	0.786	0	...	0.0931	0.842	0	...	0.129	1.10	0	...	0.104	0.928	0	...
0.0588	0.563	0	...	0.0961	0.892	0	...	0.0964	0.861	0	...	0.104	0.928	0	...	0.099	0.865	0.04	...
0.0607	0.564	0	...	0.0367	0.509	0.04	...	0.0855	0.429	0.08	...	0.099	0.865	0.04	...	0.172	1.17	0.42	6.9
0.0592	0.563	0	...	0.130	0.625	0.42	5.5	0.174	0.463	0.44	3.7	0.172	1.17	0.42	6.9	0.182	1.24	0.77	7.3
0.0839	0.646	0.210	7.8	0.145	0.630	0.80	5.6	0.171	0.440	0.82	3.6	0.182	1.24	0.77	7.3	0.160	1.17	1.11	7.3
0.0865	0.640	0.456	7.7	0.267	0.825	1.38	5.3	0.169	0.449	1.18	3.6	0.160	1.17	1.11	7.3	0.152	1.12	1.40	7.5
0.0842	0.682	0.700	7.6	0.292	0.616	1.90	5.0	0.191	0.422	1.72	...	0.152	1.12	1.40	7.5	0.191	1.22	1.72	7.8
0.119	0.802	1.05	7.3	0.296	0.360	2.31	4.6	0.171	0.429	0.89	7.7	0.191	1.22	1.72	7.8	0.171	0.629	0.89	7.7
0.129	0.874	1.40	7.3	0.280	0.227	2.67	4.3	0.213	0.236	0.96	7.7	0.171	0.629	0.89	7.7	0.213	0.236	0.96	7.7
0.142	0.873	1.76	7.2	0.283	0.154	2.99	4.0	0.170	0.039	0.97	7.7	0.213	0.236	0.96	7.7	0.170	0.039	0.97	7.7
0.169	0.913	2.17	7.1	0.285	0.087	3.31	3.7												
0.197	0.867	2.69	6.9																
0.169	0.492	2.91	6.6																
0.253	0.523	3.30	6.3																
0.252	0.345	3.52	6.2																
0.254	0.223	3.74	6.0																
0.254	0.085	3.96	5.7																

^a Medium 0.16 M KNO₃. ^b Medium 1.00 M KNO₃.TABLE III
TOTAL HEATS AND ENTROPIES OF FORMATION AT 25°^{a,b}

Complex	Molar ionic strength	ΔF , ^c kcal./mole	ΔH , ^b kcal./mole	ΔS , ^j e.u.
HImH ⁺	0.16, KNO ₃	-9.7 ^d	-9.1 ⁱ	+2
Ni(ImH) ₆ ⁺²	0.16, KNO ₃	-15.5 ^e	-18.4	-10
Cu(ImH) ₄ ⁺²	0.16, KNO ₃	-17.2 ^d	-23.0	-20
Zn(ImH) ₄ ⁺²	0.16, KNO ₃	-12.6 ^f	-16.2	-12
Ag(ImH) ₂ ⁺	1.0, KNO ₃	-9.4 ^g	-15.7	-21
Ag(ImCH ₃) ₂ ⁺	1.0, KNO ₃	-9.4 ^g	-15.6	-21

^a ImH = imidazole; ImCH₃ = N-methylimidazole.^b Data refer to the reaction of $M^{+m} + nL \rightarrow ML_n^{+m}$ in aqueous solution at the ionic strength indicated. ^c ΔF data were calculated from the corresponding stability constants. ^d B. L. Mickel and A. C. Andrews, *J. Am. Chem. Soc.*, **77**, 5291 (1955). ^e N. C. Li, T. L. Chu, C. T. Fujii, and J. M. White, *ibid.*, **77**, 859 (1955). ^f W. L. Koltun, R. N. Dexter, R. E. Clard, and F. R. N. Gurd, *ibid.*, **80**, 4188 (1958). ^g This work. ^h ΔH data were obtained by calorimetry, error estimated to be ± 0.2 kcal./mole. ⁱ Wadso reported a value -8.79 ± 0.04 kcal./mole: I. Wadso, *Acta Chem. Scand.*, **16**, 479 (1962). ^j Calcd. from ΔF and ΔH , error estimated to be ± 1 e.u.

can be calculated from the enthalpic titration curve and the known stability constants, the difficulty in solving a large number of simultaneous equations makes this impractical unless data of higher precision are available. Only the first step enthalpy changes for Cu(II), Ni(II), and Zn(II) imidazole complexes were calculated. These are -7.6, -5.8, and -3.8 kcal./mole, respectively. Two stepwise enthalpy changes for Ag(I) imidazole complexes were calculated to be -7.3 and -8.4 kcal./mole, respectively.

Table III contains thermodynamic data for the formation of the over-all complexes.

Discussion

The Ag(I) formation constants of imidazole and N-methylimidazole are listed in Table IV. Ag(I) formation constants of pyridine and β -picoline are also listed for comparison.

TABLE IV
Ag(I) FORMATION CONSTANTS OF IMIDAZOLE, N-METHYLIMIDAZOLE, PYRIDINE, AND β -PICOLINE AT 25°

	log K ₁	log K ₂
Imidazole	3.05 (1.0 M KNO ₃)	3.83 (1.0 M KNO ₃)
N-Methylimidazole	3.00 ^a (1.0 M KNO ₃)	3.89 ^a (1.0 M KNO ₃)
Pyridine ^b	2.38 (inf. dil.)	4.35 (inf. dil.)
β -Picoline ^b	2.35 (inf. dil.)	4.35 (inf. dil.)

^a Obtained by extrapolating data at 27° (log K₁ = 2.94, log K₂ = 3.82) and 25.6° (log K₁ = 2.98, log K₂ = 3.87). ^b Data from Table II, R. K. Murmann and F. J. Basolo, *J. Am. Chem. Soc.*, **77**, 3483 (1955).

It can be seen that the effect of the methyl group in N-methylimidazole is very similar to the effect observed by comparing β -picoline to pyridine. A recent study on the N-alkyl substituted 2-methyl-2-amino-3-butanone oximes showed that the heats of protonation as well as the heats of complex formation with Cu(II) and Ni(II) of these N-alkyl derivatives were lowered by at least 1-2

kcal./mole as compared with the unsubstituted ligand.²² Since an alkyl group substituted at a binding site decreases the heats of complex formation, the identical heats of formation of bisimidazoylsilver(I) and bis-N-methylimidazoylsilver(I) favors the conclusion that the pyridine nitrogen rather than the imino nitrogen is the binding site in the formation of imidazolyl complexes.

On the other hand, although the free energy data appear to be very similar for imidazole-metal ion complexes and the corresponding ammonia-metal ion complexes, the ligational enthalpies are quite different. The first step ligational enthalpies were found to be -7.6 and -5.8 kcal./mole, respectively, for the formation of Cu(II) and Ni(II) complexes of imidazole, while the corresponding enthalpy changes for the formation of the metal-ammonia complexes were reported to be -5.6 and -4.0 kcal./mole, respectively.²³ Therefore, the argument¹⁵ that the pyrrole nitrogen is the bonding site based on a comparison of imidazole-metal ion association constants and ammonia-metal ion association constants cannot be favored.

Some of our early attempts to prepare Cu(II) imidazolate and Ni(II) imidazolate failed because of the formation of the metal hydroxide. This difficulty was solved by considering the equations

$$\begin{aligned} M^{+2} + 2Im^- &= MIm_2(s) \\ [M^{+2}][Im^-]^2 &= K_a^2[M^{+2}][ImH]^2/[H^+]^2 \\ &= K_a^2[M^{+2}][OH^-]^2[ImH]^2/K_w^2 \end{aligned}$$

where K_a is the acid dissociation constant of the pyrrole hydrogen and K_w the ionization constant of water. If $K_{M(OH)_2}$ is the solubility product of the metal imidazolate, it can be seen that if $K_a^2 K_{M(OH)_2} [ImH]^2 / K_w^2 > K_{MIm_2}$ where K_{MIm_2} is the solubility product of the metal imidazolate, the imidazolate will form instead of the hydroxide. Therefore, Cu(II) and Ni(II) imidazolates were prepared in aqueous solution at high imidazole concentration. The solubility products of $CuIm_2$ and $NiIm_2$ have not been calculated, because the free metal ion concentration cannot be calculated within a reasonable error when the free ligand concentration is very high.

It is interesting to note that the ionization of the pyrrole hydrogen changes the monodentate imidazole molecule into the bidentate imidazolate anion. This in turn raises the possibility of the formation of a polymeric compound as illustrated in Fig. 3. The last structure shown is only schematic. It is to be noted that the two nitrogen atoms in the ring are actually indistinguishable. This kind of polymeric structure was assumed for the complex $Hg(Im)(ClO_4) \cdot H_2O$ ⁹ and the benzimidazolato complex of Co(II), $Co(C_7H_5N_2)_2$.¹² X-Ray diffraction indicated that zinc imidazolate is an infinite polymer in which the metal ion is tetra-

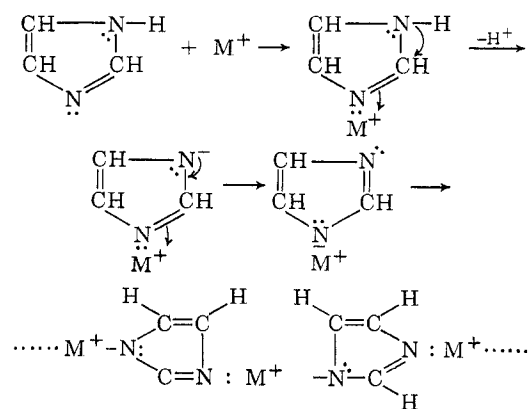


Figure 3.

hedrally surrounded by four ligand molecules, and each bidentate ligand molecule links two metal ions.²⁴

The characteristics of the metal-nitrogen bond in metal imidazolates are expected to be intermediate between the metal pyrrolate type bond and the metal-pyridine type bond. The similarity between the bonding in metal imidazolates and some important biological systems such as hemoglobin and chlorophyll is interesting.

Data listed in Table II indicate that in general the trend of the stepwise enthalpy changes is parallel to the trend of the stepwise stability constants. As $\bar{n}$ increases, $\Delta\bar{H}$ decreases in the case of Ni(II) and Cu(II) but increases in the case of Ag(I). The Zn(II) titration was terminated at a low $\bar{n}$ value because of the precipitation of zinc imidazolate at higher $\bar{n}$ during the enthalpic titration.

Negative values of $\log K_1/K_2$ for various silver(I)-ammines have been attributed to the special stability of the linear sp-hybridized bonds in the literature.²⁵ The increase in heats as $\bar{n}$ increases for Ag(I)-imidazole complexes seems to support this argument. However, the decrease in heats for Cu(II) and Ni(II)-imidazole complexes was not observed in the Cu(II) and Ni(II)-ammonia systems.²³ It is tentatively assumed that this decrease in heats is due to the steric hindrance of the ligand molecules and the decreasing contribution of π -bonding as $\bar{n}$ increases. Leussing and Hansen²⁶ reported that for the Cu(II)-pyridine system, $-\Delta H/\bar{n}$ was constant for the first four steps. It is felt that unless stepwise constants of complex formation in the gaseous phase as well as in aqueous solution are available, it is unjustified to give any rigorous interpretation.

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(24) See I. Lindquist, footnote 16a in ref. 12.

(25) J. Bjerrum, *Chem. Rev.*, **46**, 381 (1950).

(26) D. L. Leussing and R. C. Hansen, *J. Am. Chem. Soc.*, **79**, 4207 (1957).

(22) R. K. Murmann, private communication.

(23) K. B. Yatsimirskii and P. M. Milyukov, *Zh. Fiz. Khim.*, **31**, 842 (1957).