The spectrum in pyridine solution was similar but the C=O stretching frequency appeared at 1673 cm.$^{-1}$.

Nuclear magnetic resonance spectra were carried out on Varian high resolution spectrometers at 40, 56.4, and 60 Mc./sec. Spectra in organic solvents are calibrated with respect to tetramethylsilane as an internal reference.

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The Thermodynamics of Complexes Formed with 2,2′-Bipyridine and Transition Metal Ions

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The thermodynamic quantities of formation have been measured for the Mn(II), Ni(II), Cu(II), and Zn(II) complexes formed with 2,2′-bipyridine. The Bjerrum potentiometric titration technique was used to measure ΔF. ΔH was measured using an adiabatic calorimeter and a titration method analogous to the ΔF determination. The sequential decrease of ΔF during stepwise complex formation is shown to be primarily an entropy effect within experimental error. The stability of the Cu(II) complexes is lower than those of ethylenediamine. A correlation between the thermodynamic and spectroscopic stabilization energies is made for the Ni(II) complex.

Introduction

The ability of 2,2′-bipyridine to complex with transition metals has been known for many years. The work prior to 1954 has been reviewed by Brandt, *et al.*[3] The similarity of bipyridine to other biologically important heterocyclic nitrogen ligands such as the porphyrins and purines has promoted an interest in the study of the bonding in metal complexes.[4-6]

Recent work in the thermodynamics of bipyridine complexes has been reported by various workers.[7-11] Due to the lack of comparable data obtained by a single method under identical conditions of temperature and ionic strength, a comparison of the thermodynamics for a group of transition metal ions has really not been possible. In order to better understand the bonding a study of a series of related metals similar to that reported for ethylenediamine is desirable. Irving[11] has used a partition method to obtain the formation curves for several of the transition metal ions with bipyridine.

Both the free energies and heats of formation of a series of transition metal ions with bipyridine were determined at 25° in a 1 M $NaClO_4$ solution. By keeping the concentrations of reacting species below 0.01 M and maintaining a constant ionic strength the activities of the ions may be considered to be proportional to the concentrations. The concentrations of all of the reacting species were determined by measuring $[H^+]$ and calculating the stoichiometry of the reaction.

The enthalpies of formation were measured by direct calorimetry rather than by a temperature dependency study in the potentiometric determination of the equilibrium constants.

Experimental

Reagents.—2,2′-Bipyridine and the metal perchlorates were obtained from the G. F. Smith Company. The bipyridine was purified by recrystallizing from petroleum ether to a melting point of 69.0–70.0°. Its base strength was checked by titration against standard $HClO_4$ in

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ethanol. All solutions were made with boiled distilled water and were made 1 *M* in $NaClO_4$ with anhydrous $NaClO_4$. Stock solutions of Mn(II), Ni(II), Cu(II), and Zn(II) perchlorates were analyzed for the respective metal ions.

Determination of Stability Constants.—All determinations were made at 25.00 ± 0.05° with a Beckman GS pH meter. The KCl solution in the reference electrode of the pH meter was replaced by a saturated NaCl solution to prevent the precipitation of $KClO_4$ in the fiber. A series of standard $HClO_4$ solutions was used to calibrate the electrodes to read $[H^+]$ rather than activities. Thus $pH = -\log [H^+]$ in the discussion below.

A solution of $HClO_4$ was first titrated with bipyridine, all concentrations being millimolar. For this titration

$$HB^+ \overset{K_a}{\rightleftharpoons} H^+ + B$$

$$pK_a = pH + \log \frac{C_H - [H^+]}{C_B - C_H + [H^+]}$$

where C_H and C_B represent the total concentration of hydrogen ions and bipyridine and $[H^+]$ the concentration of hydrogen ions determined by the corrected pH meter reading.

Repeating the titration with a metal ion, C_M, gave

$$[B] = \frac{K_a(C_H - [H^+])}{[H^+]}$$

and

$$\bar{n}_m = \frac{C_B - (C_H - [H^+])(1 + (K_a/[H^+]))}{C_m}$$

where [B] represents the concentration of free bipyridine and $\bar{n}_m$ represents the average number of ligand molecules per metal ion at any point in the titration.

The stepwise equilibrium constants were calculated and refined from the formation curve by the Bjerrum procedures. An IBM 704 computer was used in the calculations.

Calorimetry.—A dewar calorimeter based on a design proposed by Schlyter[12] was used. Bead thermistors (Veco No. 31A18) in a Maier bridge arrangement gave a temperature sensitivity of $\pm 1 \times 10^{-4}$ degree. A calibrated heater was used to determine the heat capacity of the calorimeter and contents. The calorimeter was equipped with a thermostated buret for enthalpy titrations. Standard heats of neutralization of $HClO_4$ with NaOH and the heat of dilution of HCl were measured to standardize the calorimeter.[13]

The calorimeter and contents were allowed to equilibrate in a constant temperature bath maintained to ±0.005°. A typical experiment consisted of titrating a 125 ml. solution of 0.0001 *M* $HClO_4$ with 5 ml. amounts of 0.002 *M* bipyridine. The titration was repeated with 0.001 *M* metal perchlorate being added to the $HClO_4$ solution. The enthalpic titrations were carried out under the same conditions as the potentiometric titrations. Several runs were made with each system.

A number of Joule calibrations were made during the enthalpy titrations to determine the heat capacity in calories per degree of the calorimeter and contents. The bridge was balanced and the detecting galvanometer switched into the circuit on its most sensitive scale. No external galvanometer damping was used in the course of the determinations. Readings in mm. of scale deflection were taken at 30-sec. intervals until a constant drift of the galvanometer was maintained. The heater was turned on for 60 sec., a new drift observed, and the readings extrapolated to the mid-point of the heating cycle. The difference gave a measure of the temperature change. Using an arbitrary sensitivity of 1×10^{-4} degree/mm. the heat capacity of the calorimeter and contents was calculated. For a heat of reaction, the temperature change was measured in the same manner. This heat of reaction was given by $Q = C_{p(avg)}\Delta T$. $C_{p(avg)}$ was determined by calibrations before and after an addition of titrant. Values averaged around 150 cal. per degree for a typical experiment involving 125 ml. of solution. Since the temperature sensitivity of the thermistors was $\pm 1 \times 10^{-4}$ degree, this permitted heats to be measured to ±0.02 cal. Thus for quantities of heat involving 1 cal. or more, the calorimeter could be expected to show about 2% precision.

Several 5 ml. additions of ligand were made in the course of an enthalpy titration. The individual values in cal. per ml. of ligand were converted to kcal. per mole of ligand by dividing through by $\Delta\bar{n}_m C_m$ where $\Delta\bar{n}_m$ represents the change in the number of ligands per metal ion as determined by earlier potentiometric studies, and C_m represents the concentration of metal ion in all of its forms. The data were analyzed according to standard procedures.[14,15] Since a constant ionic strength was maintained, no correction was necessary for heats of dilution. Because the temperature of the titrant was slightly different from the temperature of the calorimeter a correction was made to each observed heat to account for this difference. For this purpose the heat capacity of 1 ml. of 1 *M* $NaClO_4$ was taken as 0.918 cal. per degree. With a 0.005° uncertainty in temperature readings, this factor caused an error of 0.005 cal. per ml. of titrant.

The information used to calculate ΔH values was: (1) Concentrations and volumes of all reagents. (2) Temperature change on addition of the titrant. (3) Heat capacity; determination by a plot of *Cp vs.* volume of solution in the calorimeter. (4) Temperature of both the bath and the calorimeter.

Data on several runs are given in Table I.

Results and Discussion

Table II contains the formation constants of the complexes of Mn(II), Ni(II), Cu(II), and Zn(II). Table III gives the ΔF_i, ΔH_i, and ΔS_i data on each of the complexes. The values of ΔH/step are average values. Within the limits of the experiment, no difference could be detected

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TABLE I

HEATS OF COMPLEX FORMATION WITH BIPYRIDINE

System	mmoles $HClO_4$	mmoles $M(ClO_4)_2$	mmoles bipy added	q_{cal}	$\Delta\bar{n}_m$
H-bipy	0.1012	0.0000	0.0180	0.064	...
			.0210	.047	...
			.0420	.067	...
			.1280	.086	...
Cu(II)-bipy	.1012	.0247	.0106	.132	0.432
			.0105	.117	.424
			.0106	.069	.193
Ni(II)-bipy	.0000	.0518	.0112	.387	.215
			.0103	.136	.200
			.0102	.238	.196
			.0103	.150	.197
			.0131	.156	.254
			.0089	.127	.173
			.0105	.267	.202
Mn(II)-bipy	.0000	.0235	.0168	.049	.748
			.0103	−.023	.438
			.0106	.098	.452
Zn(II)-bipy	.0000	.0279	.0101	.040	.361
			.0110	.174	.395
			.0104	.042	.373
			.0103	.044	.370
			.0098	.216	.353

TABLE II

FORMATION CONSTANTS FOR BIPYRIDINE COMPLEXES AT 25° IN 1 M $NaClO_4$

$$M^{++} + B \overset{k_1}{\rightleftharpoons} MB^{++}$$

$$MB^{++} + B \overset{k_2}{\rightleftharpoons} MB_2^{++}$$

$$M^{++} + 2B \overset{\beta_2}{\rightleftharpoons} MB_2^{++}$$

	log k_1	log k_2	log β_2	log k_3	log β_3
Mn(II)	4.06	3.78	7.84	3.63	11.47
Ni(II)	6.80	6.46	13.26	5.20	18.46
Cu(II)	6.94	5.74	12.68	...	...
Zn(II)	4.89	4.58	9.47	4.27	13.74

Acid dissociation constant of protonated ligand: pK_a = 4.334.

in the stepwise ΔH_i values as $\bar{n}_m$ increased from 0 to 3.

For a closer look at the stability constants it is instructive to examine the ratios of the successive formation constants. The stepwise constants tend to decrease as complex ion formation proceeds. From statistical considerations this is expected since the number of sites in the central metal ion for ligand attachment becomes progressively less. Also, since relatively small waters of hydration are being replaced by more bulky organic ligands, steric factors operate to decrease the tendency for subsequent ligand addition. For many of the systems studied heretofore, the values of log k_n/log $k_{(n+1)}$ have been positive and nearly equal.

Below are calculated the ratios of the first two sets of stability constants for the bipyridine complexes.

	log k_1/ log k_2	log k_2/ log k_3
Mn(II)	1.07	1.02
Ni(II)	1.07	1.24
Cu(II)	1.21	...
Zn(II)	1.07	1.07

The ratios of five out of the seven tested are clearly constant, as would be expected from the discussion above. However, it is worthwhile to examine the case of log k_1/log k_2 for Cu(II) and log k_2/log k_3 for Ni(II). In the former case, the high ratio indicates that the second stability constant for Cu(II) is much lower than for the other three metals. It indicates that the second mole of bipyridine goes on with considerable more difficulty than the first. Such a result is not surprising when one remembers that the Jahn-Teller effect for Cu(II) complexes often is the overriding factor influencing stability. This causes the Cu(II) ion to depend on the tetragonality of the ligand field for its stability, and makes it very sensitive to the rigid geometrical requirements of bipyridine. The Ni(II) ion appears to have an unusually low k_3 with bipyridine. This again may indicate a change in geometry in going from the four-coördinate to the six-coördinate species.

Figure 1 shows a comparison between log k_1 for bipyridine and ethylenediamine. The pK_a values for the latter, 7.49 and 10.17, show it to be a much stronger base than bipyridine. Nevertheless, the magnitude of the stability constants is of the same order for Mn(II), Ni(II), and Zn(II). The stability of the Cu(II) complex differs notably between the two ligands. This may be due either to a specific Cu(II)-primary amine interaction which enhances the stability with respect to the rest of the transition metal series, or to complications arising from hydrolysis of the Cu(II) ion in the pH region in which complexation with the ethylenediamine occurs.

An examination of the literature for stepwise enthalpies of complexation reveals that successive values of ΔH_i are roughly constant.[16] This is not too surprising when one considers the thermochemical cycle given by Grinberg and

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(16) F. J. C. Rossotti, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, ed., Interscience, New York, N. Y., 1960.

TABLE III[a]

THERMODYNAMIC DATA FOR BIPYRIDINE COMPLEXES IN KCAL./MOLE

	$-\Delta F_1$	$-\Delta F_2$	$-\Delta F_3$	$-\Delta H$/step	ΔS_1, e.u.	ΔS_2, e.u.	ΔS_3, e.u.
Mn(II)	5.53	5.16	4.95	4.30	4.1	2.9	2.2
Ni(II)	9.27	8.81	7.09	8.03	4.0	2.5	−3.3
Cu(II)	9.47	7.83	...	8.33	3.8	−1.7	...
Zn(II)	6.67	6.25	5.82	5.27	4.7	3.3	1.8

[a] All measurements at 25° in 1 *M* $NaClO_4$ medium.

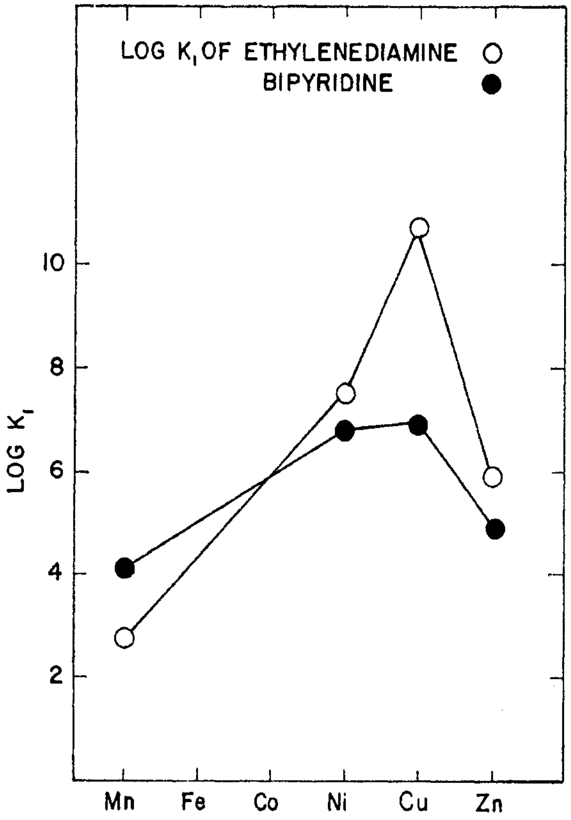

Fig. 1.—Log k_1 of bipyridine and ethylenediamine complexes; ethylenediamine data from reference 14.

Yatsimirskii.[17] The addition of an uncharged ligand to a completely hydrated metal must be very similar to the addition of a ligand to a partially complexed species. The charge of the ion has not changed so the main contributing effect which is constant will be the difference between the heat of vaporization of the ligand and of the displaced water. However, it is still anticipated that by using very precise calorimetry one should be able to measure a difference as complexation increases. Such a difference might be expected with Cu(II) because of geometry problems.

A plot of ΔH may be made as a function of atomic number. Figure 2 gives ΔH in kcal./mole for each metal–ligand bond. Taking a baseline between Mn(II) and Zn(II), one can calculate the crystal field stabilization energy (CFSE) for the Cu(II) and Ni(II) complexes. Mn(II) and Zn(II), having half-filled and filled d-electron shells, respectively, are not stabilized by crystal fields. Yet, they do indicate the trend in covalent and electrostatic contributions to the enthalpies. Cu(II) and Ni(II) show a CFSE of 3.28 and 3.20 kcal./mole, respectively, for the mono-complex. Because the stabilization increases with additional ligands, the tris-bipyridine complex of Ni(II) would show a CFSE of 9.6 kcal./mole for the reaction $[Ni(H_2O)_6]^{+2} + 3bipy \rightleftharpoons [Ni(bipy)_3]^{+2} + 6H_2O$. One may compare this value with that

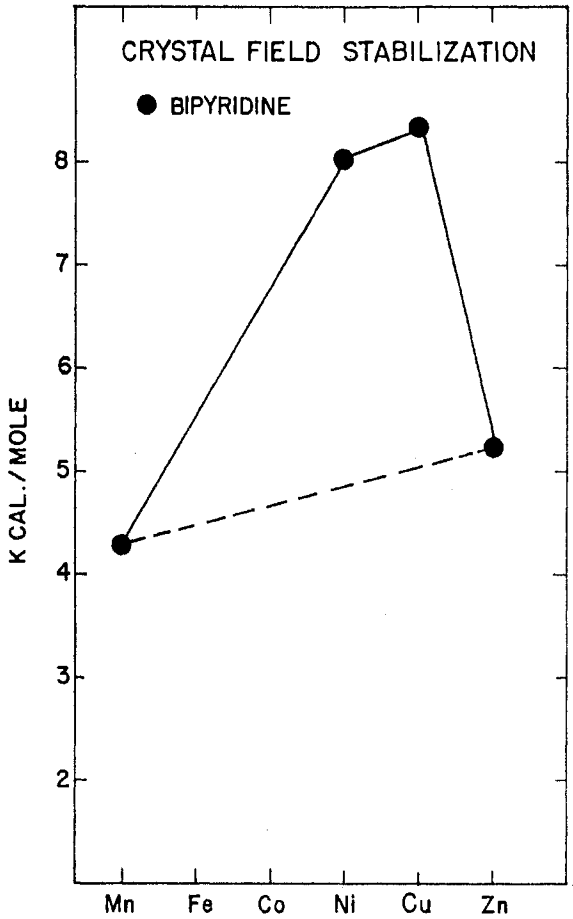

Fig. 2.—ΔH_1 of formation of bipyridine complexes.

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(17) A. A. Grinberg and K. B. Yatsimirskii, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 239 (1952).

obtained from spectroscopy,[18] leading to a stabilization with respect to water of 10.6 kcal./mole, in good agreement with the thermodynamic value.

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Metal Halide Complexes of *o*-Quinones. I. Preparation and Preliminary Characterization[1]

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Twenty-one representative complexes formed by the action of metal halides on phenanthrenequinone and chrysenequinone have been prepared from non-aqueous solution. The compounds are intensely colored, highly unstable in polar solvents, and occur in stoichiometric ratios of quinone:metal equal to 1:1, 2:1, and 3:1. A preliminary classification is proposed.

Introduction

Certain quinones have been reported to react with metal halides in non-aqueous solution to form intensely colored complexes. Pfeiffer[3] lists several complexes formed by various *o*-quinones and refers to the early work in this field. Meyer[4] reported the preparation of phenanthrenequinone complexes of zinc, mercury(II), iron(III), aluminum, and tin(IV) chlorides, while Knox and Innes[5] prepared phenanthrenequinone complexes containing halides of the zinc group. No further work on complexes of this sort has been reported and nothing is known of their structure and chemical nature. We intend to rectify this lack of information by a study of the electron-donor properties of these and related quinones.

The preparation of these complexes depends upon the availability of the metal halide in the pure, anhydrous form and the existence of a suitable solvent for both halide and quinone. The most practical solvent we have tested is glacial acetic acid. If anhydrous halide is available, hot, saturated solutions of the components are mixed and allowed to cool. The complex generally crystallizes rapidly. The method has a distinct disadvantage if the halide is significantly hygroscopic, as is generally the case. However, solutions of many anhydrous bromides can be prepared easily by direct bromination of the metal in methanol.[6] These solutions can be used for the preparation of the complexes by substitution of glacial acetic for most of the methanol after concentration of the latter solvent by evaporation. Addition of hot acetic acid solution to the quinone produces considerable darkening of the solution, and crystallization usually takes place at once. If not, excess solvent can be removed by boiling or, preferably, distilling under vacuum.

Four *o*-quinones were tested by these procedures: 9,10-phenanthrenequinone (I) (abbreviated phenqu), 1,2-chrysenequinone (II) (abbreviated chryqu), acenaphthenequinone (III), and 2-nitrophenanthrenequinone.

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[1] Taken from a thesis submitted to the University of New Hampshire for the degree of Doctor of Philosophy by Paul J. Crowley. Supported in part by the U. S. Atomic Energy Commission.

[2] To whom communications should be addressed.

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