Table I. Summary of Stability Constants and Stoichiometry of Model Complexes[a]

Iron(III) chelate[b]	Sulfhydryl compd[b]	Formulation of complex	Molar extinction coeff at min % dev of *K*	*K*
$Fe^{III}HEDTA$	H_2S	$[Fe^{III}HEDTA]_2S^{2-}$	8900 (490 nm)	4.4×10^6
$Fe^{III}HEDTA$	Mercaptoethanol	$Fe^{III}HEDTA \cdot SR^-$	3100 (530 nm)	6.0
$Fe^{III}HEDTA$	L-Cysteine	$Fe^{III}HEDTA \cdot SCy^-$	3320 (530 nm)	15.2
$Fe^{III}EDTA$	L-Cysteine	$Fe^{III}EDTA \cdot SCy^-$	3300 (530 nm)	8.6
$Fe^{III}HEDTA$	Ethyl mercaptan	$Fe^{III}HEDTA \cdot SEt^-$	3200 (530 nm)	3.9

[a] Temperature 25 ± 1°; $\mu = 0.2\ M$, KCl. [b] Approximate ranges of concentration: H_2S, 10^{-4}–10^{-2} *M*; mercaptoethanol, 10^{-2}–1 *M*; L-cysteine, 10^{-3}–10^{-1} *M*; ethyl mercaptan, 10^{-2}–10^{-1} *M*.

spin iron(III) in the model thiol complex.[8] No signal near $g = 2$ due to an iron–sulfur species was detected upon cooling the $Fe^{III}HEDTA$-H_2S system to 4° K.[9]

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Registry No. $[Fe^{III}HEDTA]_2S^{2-}$, 39459-79-5; $Fe^{III}HEDTA \cdot SCH_2CH_2OH^-$, 39452-75-0; $Fe^{III}HEDTA \cdot SCy^-$, 39452-77-2; Fe^{III}-$EDTA \cdot SCy^-$, 39452-76-1; $Fe^{III}HEDTA \cdot SEt^-$, 39452-74-9.

(8) T. Castner, Jr., G. S. Newell, W. C. Holton, and C. P. Slichter, *J. Chem. Phys.*, **32**, 668 (1960).

(9) J. C. M. Tsibris and R. W. Woody, *Coord. Chem. Rev.*, **5**, 417 (1970).

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The Ligand Pentaammine(pyrazine)ruthenium(II). Aqueous Complexes of Nickel(II), Copper(II), and Zinc(II)

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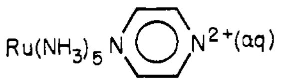
Association quotients for aqueous complexes of the bipositive ligand pentaammine(pyrazine)ruthenium(II) with nickel(II), copper(II), and zinc(II) have been determined by spectrophotometry, using the bathochromic shift of the ruthenium(II)-pyrazine electron-transfer band. For nickel(II) the association quotient is $17 \pm 2\ M^{-1}$ while the parameters ΔH and ΔS are -6 ± 0.8 kcal/mol and -15 ± 3 cal deg^{-1} mol^{-1}, respectively, at 25°, $\mu = 1.5\ M$, and pH 3.9–6. For the copper(II) adduct those quantities are $32 \pm 3\ M^{-1}$, -4.3 ± 0.5 kcal/mol, and -7 ± 2 cal deg^{-1} mol^{-1}, respectively, at 25° and $\mu = 1.0\ M$. For zinc(II) the association quotient is $3.1 \pm 0.5\ M^{-1}$ with ΔH and ΔS equal to -4.3 ± 0.5 kcal/mol and -12 ± 3 cal deg^{-1} mol^{-1} at 25° and $\mu = 2.0\ M$. The rate constants for formation and dissociation of the nickel(II) complex were also determined, yielding for k_1, $\Delta H^{\ddagger}{}_1$, and $\Delta S^{\ddagger}{}_1$ the values $(1.1 \pm 0.1) \times 10^3\ M^{-1}\ sec^{-1}$, 10 ± 1 kcal/mol, and -11 ± 3 cal deg^{-1} mol^{-1}, respectively, at 25° and $\mu = 1.0\ M$. For the reverse reaction k_{-1}, $\Delta H^{\ddagger}{}_{-1}$, and $\Delta S^{\ddagger}{}_{-1}$ were found to be $66 \pm 5\ sec^{-1}$, 16 ± 1 kcal/mol, and 4 ± 3 cal deg^{-1} mol^{-1}, respectively. The results are related to the basicity of the pentaammine(pyrazine)ruthenium(II) complex.

Introduction

An especially interesting property of the aqueous ion pentaammine(pyrazine)ruthenium(II), Ru(pz) (I), is that, when



I

protonated at the free electron pair of pyrazine, the complex has a pK_a value of 2.6.[1,2] In comparison, the pK_a of the free, aqueous pyrazinium ion is only 0.6.[3] On protonation of Ru(pz), the metal-to-ligand ($\pi^* \leftarrow t_{2g}$) electron transfer band of the complex is shifted to lower energy. Both the energy shift and the increased pK_a of pyrazine when coordinated to ruthenium(II) have been attributed to increased metal-to-ligand back-donation in the protonated complex, relative to the unprotonated ion.[2,4]

We have found that Ru(pz) can associate with several aqueous, first-row transition metal ions to form binuclear complexes. The existence of these complexes demonstrates that the basicity of pyrazine in the Ru(pz) moiety is sufficient to balance the repulsion between the two positively

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(1) P. Ford, D. F. P. Rudd, R. Gaunder, and H. Taube, *J. Amer. Chem. Soc.*, 90, 1187 (1968).

(2) D. K. Lavallee and E. B. Fleischer, *J. Amer. Chem. Soc.*, 94, 2583 (1972).

(3) R. M. Acheson, "An Introduction to the Chemistry of the Heterocyclic Compounds," Interscience, New York, N. Y., 1960, p 299.

(4) H. E. Toma and J. M. Malin, submitted for publication in *Inorg. Chem.*

charged metal centers. The Ru(pz) ligand has special utility because spectrophotometric studies can be made of its complexes with metal ions that do not absorb light at convenient wavelengths. In this article we present determinations of the association quotients of the Ru(pz) complexes of aqueous nickel(II), copper(II), and zinc(II). An investigation of the kinetics of formation of the Ni^{II}-Ru(pz) adduct is also described.

Experimental Section

Materials and Methods. The ion pentaammine(pyrazine)ruthenium(II) was prepared in aqueous solution as described by Ford, *et al.*,[1] but using only a tenfold excess of the ligand. Although the ages of the Ru(pz) stock solutions did not affect the results, new solutions at *ca.* 10^{-4} *M* concentration of Ru(pz) were prepared periodically and stored in darkness. All operations involving the Ru(pz) complex were carried out in an atmosphere of argon. Reagents were transferred using hypodermic syringes. The extinction coefficients for the aqueous Ru(pz) complex were computed from Shepherd and Taube's value of ϵ_{467} 1.34×10^4 M^{-1} cm^{-1}, at 25°.[5]

Solutions of aqueous nickel(II) perchlorate were obtained by dissolution of nickel carbonate (Carlo Erba, reagent grade) in stoichiometric amounts of perchloric acid solution. Solutions of copper(II) and zinc(II) perchlorate were prepared similarly. The concentration of nickel(II) was determined spectrophotometrically using the $Ni(CN)_4{}^{2-}$ absorption peak, ϵ_{267} 1.16×10^4 M^{-1} cm^{-1}.[6] The concentration of copper(II) in stock solutions was found by precipitation of copper as cuprous thiocyanate.[7] The concentration of zinc(II) was determined by EDTA titration using Eriochrome Black T as indicator.[8]

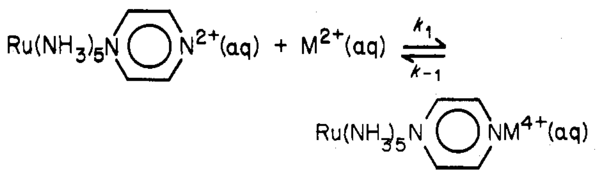
In determining the association quotients pH 3.9 or higher was obtained by adding lithium hydroxide solution while monitoring with a Beckman Expandomatic pH meter. Ionic strength was maintained by the addition of lithium perchlorate. Doubly distilled water was used in the experiments, the second distillation being made from basic permanganate solution.

Instruments. Absorbance measurements were taken using a Cary Model 14 spectrophotometer. In the stopped-flow experiments a Durrum Model D-110 instrument was employed. The cell compartments of the two spectrophotometers were thermostated to within ±0.5°.

Results

Equilibrium Measurements. Association of Ru(pz) with aqueous nickel(II), copper(II), or zinc(II) results in a shift of the electron-transfer absorption band, observed at 467 nm in Ru(pz), to longer wavelengths. By superimposing spectra taken at identical Ru(pz) concentrations, but with varying amounts of M(II), the metal ion, in large excess, plots featuring isosbestic points were constructed. The plot for the Cu^{II}-Ru(pz) association is shown in Figure 1. Similar plots were obtained using aqueous zinc(II) and nickel(II). By working at high values of [M(II)] it was possible to find the energy at maximum absorption, E_{et}, in the three binuclear species. These data are given in Table I.

Because of the isosbestic behavior and the high ratios of [M(II)] to [Ru(pz)] which were used (*ca.* 10^3:1), the calculations of association quotients refer to formation of adducts of 1:1 stoichiometry, as shown in



$$\mathrm{Ru(NH_3)_5NC_4H_4N^{2+}(aq) + M^{2+}(aq) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ru(NH_3)_5NC_4H_4NM^{4+}(aq)} \qquad (1)$$

where $k_1/k_{-1} = Q$, the association quotient.

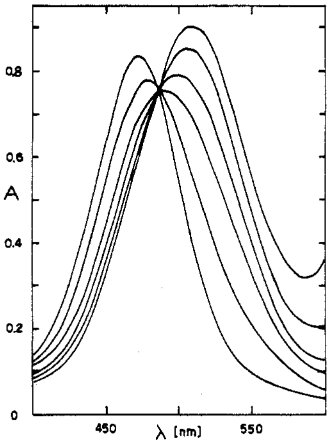


Figure 1. Variation in the visible spectrum of Ru(pz) with the concentration of copper(II). [Cu^{2+}(aq)] = 0, 0.012, 0.039, 0.079, 0.157, and 0.315 *M* for peaks moving from left to right. Conditions: [Ru(pz)] = 7.7×10^{-5} *M*, pH 4-6, 25°, $\mu = 1$ *M*.

Table I. Association Parameters and Electron-Transfer Absorption Band Energies for the Species Ru(pz)M^{II}(aq)

M	Q, M^{-1}	ΔH, kcal/mol	ΔS, cal deg^{-1} mol^{-1}	E_{et},[a] kK
Ni(II)[b]	17 ± 2	−6 ± 0.8	−15 ± 3	20.3
Cu(II)[c]	32 ± 3	−4.3 ± 0.5	−7 ± 2	19.7
Zn(II)[d]	3.1 ± 0.5	−4.3 ± 0.5	−12 ± 3	20.5

[a] E_{et} for Ru(pz) is 21.4 kK. [b] $\mu = 1.5$ *M*, 25°. [c] $\mu = 1.0$ *M*, 25°. [d] $\mu = 2.0$ *M*, 25°.

The calculations were made employing the equation

$$A/[\mathrm{Ru_T}] = \epsilon_c - B/Q \qquad (2)$$

which is easily derived,[9] where

$$B = A/[\mathrm{M(II)}][\mathrm{Ru_T}] - \epsilon_{\mathrm{Ru}}/[\mathrm{M(II)}]$$

A is the measured absorbance, [Ru_T] is the sum of the concentrations of free Ru(pz) and of the binuclear complex, [M(II)] is the concentration of the metal ion, and ϵ_{Ru} and ϵ_c are the molar extinction coefficients of Ru(pz) and of the binuclear complex, respectively. By plotting the quantity $A/[Ru_T]$ *vs.* *B*, obtained at wavelengths where the binuclear species absorbs more strongly than Ru(pz), values of *Q* were calculated from the slopes while the ordinate intercepts yielded ϵ_c. Plots of eq 2, obtained at various temperatures for the association of aqueous Ru(pz) with nickel(II), copper(II), and zinc(II), are given in Figures 2-4, respectively. In Table I are listed the association quotients, thermodynamic parameters, and electron-transfer band maxima associated with formation of the complexes.

The data for the nickel(II) and zinc(II) complexes were obtained at $\mu = 1.5$ and 2.0 *M*, respectively, in order to extend the range of M(II) concentrations which could be used. For nickel(II), equilibrium data were also taken at $\mu = 1.0$ *M*, yielding $Q = 24.2 \pm 2$ and 14 ± 1.5 M^{-1}, respectively, at 10 and 25°. Thus, *Q* was found to be slightly smaller at the lower ionic strength, as expected for reactants of the charge types employed. Within experimental error, the values of ΔH and ΔS were unaffected by the variation in μ.

Kinetics of Formation and Dissociation of the Binuclear Ion Ru(pz)Ni^{II}(aq). On mixing solutions of Ru(pz) with

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(5) R. E. Shepherd and H. Taube, *Inorg. Chem.*, 12, 1392 (1973).

(6) D. A. Margerum and B. A. Zabin, *J. Phys. Chem.*, 66, 2214 (1962).

(7) A. I. Vogel, "A Textbook of Quantitative Inorganic Analysis," Longmans, Green and Co., London, 1961, p 496.

(8) H. Flaschka, "EDTA Titrations," Pergamon Press, Oxford, 1959, p 75.

(9) The treatment is similar to that given by B. R. Baker, N. Sutin, and T. J. Welch, *Inorg. Chem.*, 6, 1948 (1967).

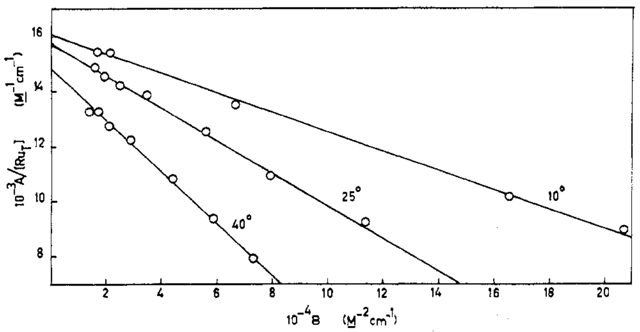

Figure 2. Plot of $10^{-3}A/[\mathrm{Ru_T}]$ *vs.* $10^{-4}B$ for the $\mathrm{Ni^{II}}$-Ru(pz) association at three temperatures. Conditions: pH 5, $\mu = 1.5\ M$, 500 nm.

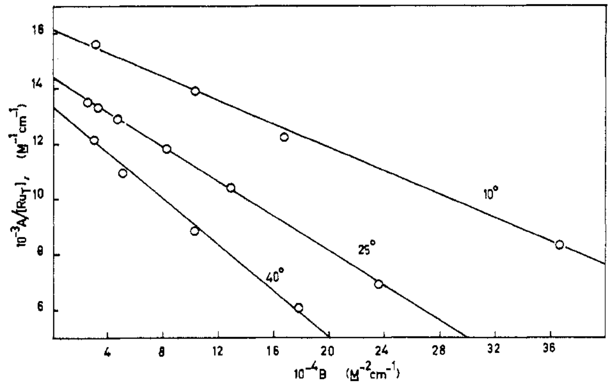

Figure 3. Plot of $10^{-3}A/[\mathrm{Ru_T}]$ *vs.* $10^{-3}B$ for the $\mathrm{Zn^{II}}$-Ru(pz) association. Conditions: pH 5-6, $\mu = 2.0\ M$, 500 nm.

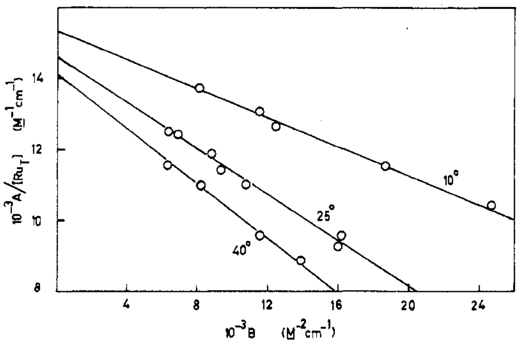

Figure 4. Plot of $10^{-3}A/[\mathrm{Ru_T}]$ *vs.* $10^{-3}B$ for the $\mathrm{Zn^{II}}$-Ru(pz) association. Conditions: pH 5-6, $\mu = 2.0\ M$, 500 nm.

excess aqueous nickel(II) in a stopped-flow apparatus it was possible to measure the rate of formation of the binuclear species. Pseudo-first-order rate constants, k_{obsd}, describing the rate of approach of the system to equilibrium, were obtained from plots of ln $|A_\infty - A_t|$ *vs.* t, where A_∞ and A_t are the measured absorbances at equilibrium and at time equals t. k_{obsd} is related to k_1 and k_{-1}, the specific rates of formation and dissociation, respectively, by eq 3. Plots of k_{obsd}

$$k_{\mathrm{obsd}} = k_1[\mathrm{Ni(II)}] + k_{-1} \qquad (3)$$

vs [Ni(II)] at several temperatures are given in Figure 5. The calculated activation parameters $\Delta H^{\ddagger}_1$ and $\Delta S^{\ddagger}_1$ for the forward reaction are 10 ± 1 kcal/mol and −11 ± 3 cal deg^{-1} mol^{-1}, respectively. For the reverse reaction $\Delta H^{\ddagger}_{-1}$ and $\Delta S^{\ddagger}_{-1}$ are 16 ± 1.5 kcal/mol and 4 ± 3 cal deg^{-1} mol^{-1}, respectively. Calculated values of k_1 and k_{-1} at 25° are $(1.1 \pm 0.1) \times 10^3\ M^{-1}$ sec^{-1} and 66 ± 5 sec^{-1}, respectively. From the relationship $Q = k_1/k_{-1}$, the quantities Q, ΔH, and ΔS are found from the kinetic parameters to be $16.7\ M^{-1}$, −6 kcal/mol, and −15 cal deg^{-1} mol^{-1}, respectively. Agreement with the results of the static measurements is very good.

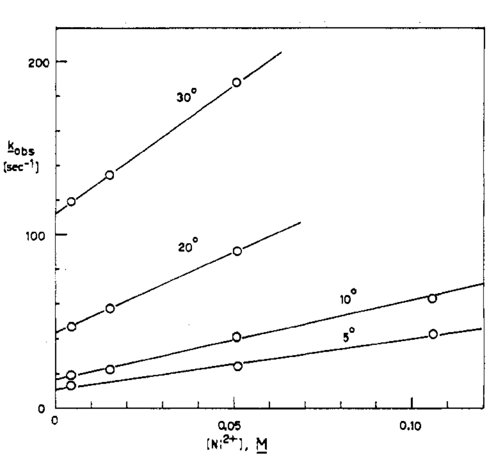

Figure 5. Plot of k_{obsd} *vs.* the concentration of aqueous nickel(II) at several temperatures. Conditions: pH 5-6, $\mu = 1.0\ M$, 500 nm.

Discussion

Table I presents the central result of this work, which is that the bipositive Ru(pz) ligand forms relatively stable complexes with the aqueous ions of nickel(II), copper(II), and zinc(II). For example, the association quotient for the $\mathrm{Ni^{II}}$-Ru(pz) reaction is greater than the known value for the nickel(II)-pyrazine association, $10 \pm 1\ M^{-1}$.[10] This is consistent with the augmented basicity of Ru(pz), relative to pyrazine.

The values of ΔS in Table I are negative, as expected for aqueous reactions in which like charges are brought together.[11] In each case the driving force for complexation is provided by a small but favorable enthalpy change. The origins of these changes are of special interest.

Values of ΔH and ΔS for the aqueous nickel(II)-pyrazine reaction are −3.2 ± 0.5 kcal/mol and −6 ± 2 cal deg^{-1} mol^{-1}, respectively.[10] In comparison, ΔH for the $\mathrm{Ni^{II}}$-Ru(pz) association is more negative by *ca.* 3 kcal/mol. This may be due mainly to a stronger σ bond between nickel(II) and Ru(pz).

However, an interesting contribution to the enthalpy of complexation is perhaps related to the degree of $d\pi$-$p\pi$ back-donation in the Ru(pz) moiety. The increasing bathochromic shift in the metal-to-ligand electron-transfer band in a series of complexes of the kind $\mathrm{Ru(NH_3)_5L^{2+}}$ or $\mathrm{Fe(CN)_5L^{3-}}$ (where L is a pyridine- or pyrazine-related ligand) can be correlated with increasing back-bonding stabilization of the complexes.[12] Since similar electron-transfer band shifts are seen on formation of the binuclear complexes described here, an increase in back-bonding stabilization within the Ru(pz) moiety may contribute to their stability. Lavallee and Fleischer[2] have advanced a similar argument for stabilization of the ion $\mathrm{Ru(pz)H^+}$.

The change in stabilization accompanying a given spectral shift of this type has not been assessed for ruthenium(II) complexes. However, for complexes of the type $\mathrm{Fe(CN)_5L^{3-}}$, increments of back-bonding stabilization are estimated at *ca.* 1 kcal/mol per kilokayser of shift.[13] Assuming that the factor for pentacyanoferrate(II) complexes is similar to

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(10) J. M. Malin and R. E. Shepherd, *J. Inorg. Nucl. Chem.*, **34**, 3203 (1972).

(11) F. J. C. Rossotti in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience, New York, N. Y., 1960, Chapter 1.

(12) H. E. Toma and J. M. Malin, *Inorg. Chem.*, 12, 1039 (1973).

(13) H. E. Toma and J. M. Malin, work in progress.

that for pentaammineruthenium(II) species, we can use the data in Table I to estimate the contribution of the back-bonding interaction to the measured enthalpy of adduct formation. For the nickel(II) and zinc(II) complexes this contribution would be *ca.* 1 kcal/mol while for the copper(II) species it would be *ca.* 1.7 kcal/mol. Thus, the effect of induced back-donation may be a significant fraction of the measured values of ΔH.

The observation that the copper(II) complex, which exhibits the largest spectral shift of the three systems studied, has a less negative enthalpy of association than the nickel(II) complex shows that the induced back-bonding effect is not predominant. The lack of a trend in the measured ΔH values for the nickel(II), copper(II), and zinc(II) reactions is probably due to other factors, *e.g.*, variations in solvation energy and in crystal field stabilization.

Kinetics of the Ru(pz)-$\mathrm{Ni^{II}}$ Reaction. Although the kinetics of many complexation reactions of aqueous nickel(II) have been studied,[10,14-18] the reaction with Ru(pz) is the first to be reported using a bipositive, monodentate ligand. The specific rate of formation of the binuclear species, $k_1 = (1.1 \pm 0.1) \times 10^3\ M^{-1}\ \mathrm{sec}^{-1}$ ($\mu = 1.0\ M$, 25°), is slightly lower than those which have been measured for neutral or positively charged ligands. In an Eigen-Wilkins mechanistic scheme,[15] the lower rate constant would be reflected in a diminished value of K_0, the outer-sphere association constant. Allowing for this charge effect, the rate of complex formation is close to rates which are known for a large number of reactions in which loss of a water molecule from the inner coordination sphere of $\mathrm{Ni^{II}(aq)}$ is rate determining.[15-18] The enthalpy of activation for the forward reaction, 10 ± 1 kcal/mol, falls within the range (9-14 kcal/mol) which has been established for water-exchange-controlled complex formation by $\mathrm{Ni^{II}(aq)}$. The entropy of activation, -11 ± 3 cal $\mathrm{deg^{-1}\ mol^{-1}}$, is negative as expected considering the charge types of the reactants.[19]

The rate constant k_{-1} and activation parameters for the dissociation step are given in the Results. Moore and Wilkins[20] have shown that the rates of dissociation of nickel(II) complexes of nitrogen bases can be correlated with the $\mathrm{p}K_{\mathrm{HL}}$ values of the leaving ligands using the equation $\log k_{-1} = 1.58 - 0.21(\mathrm{p}K_{\mathrm{HL}})$, which is valid at 8°. For the Ru(pz) ligand, the $\mathrm{p}K_{\mathrm{HL}}$ of which is *ca.* 2.6, k_{-1} is calculated from the equation to be 11 sec^{-1}. Our data yield k_{-1} equals 13 sec^{-1}, in good agreement with the predicted value. The enthalpy of activation, $\Delta H^{\ddagger}_{-1}$, is 16 ± 1 kcal/mol, a value which falls within the range of energies and enthalpies of activation established by various workers[14,16-18,20] for dissociation of aqueous nickel(II) complexes of aromatic N heterocycles.

Conclusion

Rate and equilibrium measurements have demonstrated that the Ru(pz) ligand can form binuclear complexes with aqueous nickel(II), copper(II), and zinc(II) which are relatively stable, despite their fairly high positive charge. The complexes are detected conveniently by a bathochromic shift in the electron-transfer absorption ($\pi^* \leftarrow t_{2g}$) of the Ru(pz) moiety. This shift, which also is seen in the Ru(pz)$\mathrm{H^+}$ ion, indicates that back-donation from Ru(II) to pyrazine is increased in the complexes, relative to Ru(pz). This effect is evidently a stabilizing one, but it does not predominate in determining the relative association quotients of the complexes.

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Registry No. Ru(pz), 19471-65-9; nickel, 7440-02-0; copper, 7440-50-8; zinc, 7440-66-6.

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[14] G. A. Melson and R. G. Wilkins, *J. Chem. Soc.*, 4208 (1962).

[15] M. Eigen and R. G. Wilkins, *Advan Chem. Ser.*, No. 49, 55 (1965); M. Eigen and L. DeMayer in "Techniques of Organic Chemistry," Vol. VIII, Part II, A. Weissberger, Ed., Interscience, New York, N. Y., 1963, p 895.

[16] K. Kustin and J. H. Swinehart in "Inorganic Reaction Mechanisms," J. O. Edwards, Ed., Wiley, New York, N. Y., 1970, p 107.

[17] R. G. Wilkins, *Accounts Chem. Res.*, 3, 408 (1970).

[18] P. K. Chattopadhyay and J. F. Coetzee, *Inorg. Chem.*, 12, 113 (1973).

[19] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961, p 145.

[20] P. Moore and R. G. Wilkins, *J. Chem. Soc.*, 3454 (1964).