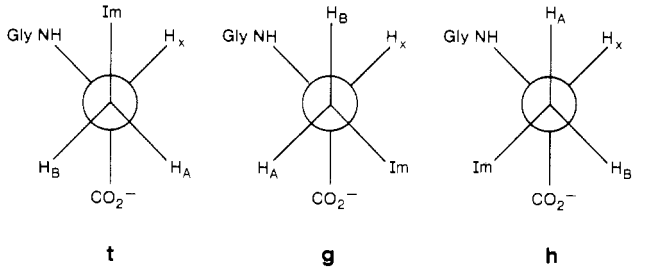


Figure 2. Staggered rotamers along the C_α–C_β bond of the histidine residue of Gly-His.

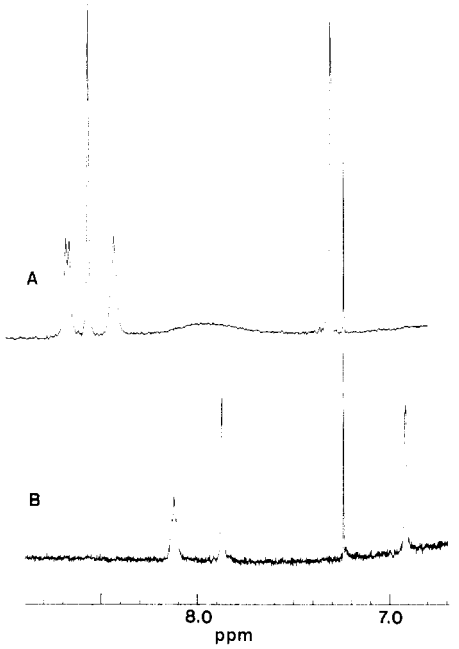


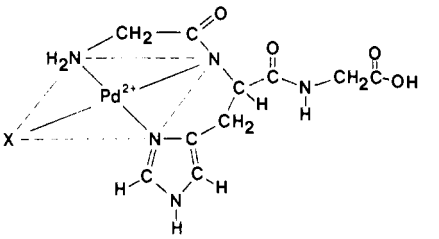
Figure 3. High-frequency regions of the 400-MHz ^1H NMR spectra of (A) 0.030 M Gly-His-Gly in H_2O solution at pH 2.91 and (B) 0.030 M Gly-His-Gly plus 0.030 M K_2PdCl_4 in H_2O solution at pH 2.98. Both solutions contain 0.154 M NaCl.

At pD above 6.9, additional resonances that are quite broad appear in the spectrum, indicating a change in the nature of the complex. It has not been possible to characterize the high-pH complexes from the NMR data.

Glycyl-L-histidylglycine. The titration curve for a solution containing 0.005 M K_2PdCl_4 and 0.005 M Gly-His-Gly does not show a sharp end point as observed in the analogous experiment with Gly-His. The solution pH is 2.5 initially, 3.5 after the addition of 1 equiv of base, 5.0 after the addition of 2 equiv, and 9.5 after the addition of 3 equiv.

The peptide proton region of the ^1H NMR spectrum of a pH 2.91 solution of Gly-His-Gly is shown in Figure 3A. The doublet at 8.72 ppm is due to the proton on the histidyl peptide nitrogen, and the unresolved triplet at 8.48 ppm is due to the glycine peptide proton. The resonances at 8.58, 7.31, and 7.244 ppm are due to the histidyl C2–H and C4–H protons and external $CHCl_3$, respectively. The same region for a pH 2.98 solution containing equimolar K_2PdCl_4 is shown in Figure 3B. The absence of the doublet for the histidyl peptide proton indicates Pd(II) binding to the deprotonated histidyl peptide nitrogen. The triplet at 8.12 ppm indicates the glycine peptide nitrogen is still protonated. This triplet is observed up to pH 6. As we found for Gly-His, the C2–H and C4–H resonances of Gly-His-Gly experience a large shift to lower frequency upon complexation, consistent with binding of Pd(II) to the imidazole 1-nitrogen. The coupling constants for the histidyl $CHCH_2$ spin system (Table I) indicate the population of conformation h (Figure 2) to be 74% for the complexed ligand.

The methylene protons of the glycine residue of Pd(II)-complexed Gly-His-Gly give an AB pattern[9] that shifts 0.30 ppm to lower frequency as the pD is increased from 1.5 to 7, indicating titration of the carboxylic acid group in the complex. Above pH 7, additional resonances that are quite broad appear in the spectra, indicating a change in the complex. The above data indicate that Pd(II) is bonded to the amino, deprotonated histidyl peptide, and imidazole 1-nitrogens while the glycine peptide nitrogen and the carboxylate group are protonated in the complex that forms at low pH (structure **2**). As the pH



2

is increased, the carboxylic acid is titrated with the total consumption of 2 equiv of base at pH 5. The triplet for the glycine peptide proton (Figure 3) of both free and complexed Gly-His-Gly also shifts to lower frequency as the carboxylic acid is titrated from which pK_A values of 3.7 and 3.0 were calculated[9] for the complexed and free ligand.

In conclusion, this study has shown that the imidazole 1-nitrogen of histidine in peptides is a strong binding site for Pd(II). In the Gly-His complex, Pd(II) binds to the amino, deprotonated peptide, and imidazole 1-nitrogens, while the carboxylic acid group is free. In contrast, simple dipeptides bind Pd(II) through the amino and deprotonated peptide nitrogens and the carboxylate group. In the Gly-His-Gly complex, Pd(II) also binds to the amino nitrogen, deprotonated peptide nitrogen, and imidazole 1-nitrogen donor set, in preference to binding to the amino nitrogen, two deprotonated peptide nitrogens, and the carboxylate oxygen as is the case with other tripeptides. The strength of the complexes formed with the amino nitrogen, deprotonated peptide nitrogen, and imidazole 1-nitrogen donor set is further indicated by the complete formation of the complexes by pH 2.2, a somewhat lower pH than for Pd(II) complexes of simple peptides.

Acknowledgment. The authors gratefully acknowledge the financial support provided by the Natural Sciences and Engineering Research Council of Canada and by an Alberta Heritage Foundation for Medical Research Fellowship (A.A.I.).

Registry No. Gly-His, 2489-13-6; Gly-His-Gly, 7758-33-0; Pd, 7440-05-3.

Contribution from the Division of Natural Sciences, University of California, Santa Cruz, California 95064

Kinetic Investigation of the Equilibrium between Mono- and Bis(1,10-phenanthroline)copper(I) in Aqueous and Sodium Dodecyl Sulfate Solution

H. Leslie Hodges* and Marco A. de Araujo

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As part of our continuing investigation of the oxidation of $Cu(phen)_2^+$ by inorganic reagents in micellar solution[1,2] we

have studied the effect of SDS micelles on the ligand association

$$Cu(phen)X_2^+ + phen \underset{k_{-p}}{\overset{k_p}{\rightleftharpoons}} Cu(phen)_2^+ + 2X \quad (1)$$

where X is presumably coordinated water.[3] Under pseudo-first-order conditions ([phen] >> [Cu(phen)X_2]), the equilibrium can be characterized by an experimental rate constant

$$k_{obsd} = k_p[phen] + k_{-p} \quad (2)$$

Although very little work has been done on substitution mechanisms of tetrahedral transition-metal complexes, for most octahedral species ligand substitution is controlled by the rate of water elimination from the metal (Eigen–Wilkins mechanism).[4] The forward rate of reaction 1 should be extremely rapid for a substitution-labile d^{10} system such as Cu(I). However, our electron-transfer work has shown that the reaction is slow enough to monitor on the stopped-flow time scale. In this study we report the association and dissociation rate constants for (1) in aqueous and micellar SDS solution.

Experimental Section

Reagents. The synthesis of $Cu(phen)_2HSO_4$ has been described previously.[1] Sodium dodecyl sulfate (>99% pure) was purchased from British Drug House and used without further purification. All other chemicals were of reagent grade, and deionized water was used throughout.

Kinetics. The basic stopped-flow instrumentation and anaerobic methods are reported elsewhere.[1] Studies were done in a nonbinding sodium cacodylate buffer (0.1 M, pH 6) to avoid any possible anion coordination to the copper which might interfere with the reactions being studied. For micellar work, [SDS] = 0.1 M and $[Na^+]_t$ = 0.2 M. In aqueous solution $[Na^+]_t$ was adjusted to 0.2 M with Na_2SO_4 (μ_t = 0.25 M).

Formation or loss of $Cu(phen)_2^+$ was monitored at 410 nm (aqueous) or 440 nm (micellar). Studies were done under pseudo-first-order conditions with Cu(I) as the limiting reagent. In aqueous solution $Cu(phen)_2HSO_4$ (2.5×10^{-5} M) dissociates approximately 30%, allowing the forward rate of (1) to be monitored simply by addition of excess phenanthroline. In SDS solution, it is necessary to generate the monophenanthroline species in situ because Cu(I) is almost exclusively in the bischelated form. This was done by mixing stoichiometric amounts of CuCl and phenanthroline. For all studies plots of log $(A - A_\infty)$ were linear for 90–95% of each reaction. Each k_{obsd} is an average of at least four independent runs.

Spectral Studies. The binding constant for the micellar association of $Cu(phen)_2^+$ was determined by monitoring spectral changes at 440 nm as a function of [SDS] under an argon atmosphere ($[Cu(phen)_2^+] = 1 \times 10^{-4}$ M, [phen] = 2×10^{-3} M). For calculations we have used cmc = 0.94×10^{-3} M, determined at [NaCl] = 0.2 M.[5] The molar extinction coefficients of aqueous and micellar $Cu(phen)_2^+$ at 440 nm were determined to be 3700 and 5700 M^{-1} cm^{-1}, respectively.

Results

Ligand Binding and Dissociation (Aqueous). Addition of excess phenanthroline to an aqueous solution containing phenanthroline and Cu(I) in a 2:1 ratio causes an increase in absorbance at 410 nm, indicating that equilibrium 1 has shifted to more complete formation of the bischelated species. Absorbance–time data indicate that the rate of this reaction has a first-order dependence on Cu(I). A plot of k_{obsd} vs. [phen] over a 6-fold range is shown in Figure 1. The limited solubility of the ligand prevents studies at higher concentrations. From eq 2, a least-squares fit of the data gives $k_p = (6.2 \pm 0.2) \times 10^4$ M^{-1} s^{-1}. The y intercept, which in principle allows a determination of k_{-p}, is zero within experimental error.

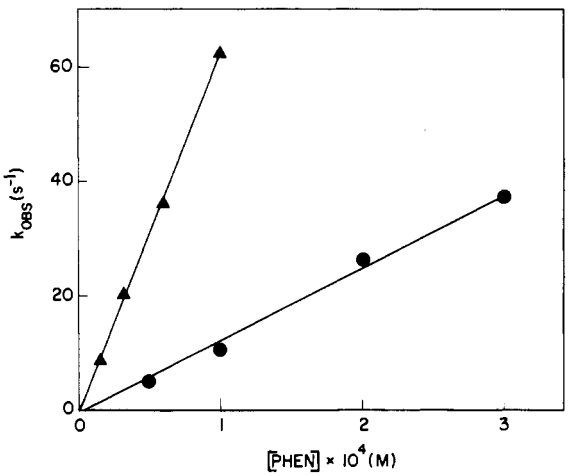

Figure 1. Plot of k_{obsd} as a function of phenanthroline for the reaction between $Cu(phen)^+$ and phenanthroline at pH 6, T = 25 °C, and $[Cu(I)]_t = 2.5 \times 10^{-5}$ M: (▲) aqueous; (●) 0.1 M SDS.

The value of k_{-p} can be obtained from a ligand-assisted dechelation reaction. Addition of acac to an aqueous solution of $Cu(phen)_2^+$ containing excess phenanthroline results in a complete loss of absorbance at 410 nm due to the formation of the colorless $Cu(acac)_2^-$ complex. Under pseudo-first-order conditions with excess acac, the reaction is first order with respect to Cu(I) and is independent of acac concentration (2.1×10^{-4} M ≤ [acac] ≤ 25×10^{-4} M) with $k_{obsd} = 0.20 \pm 0.2$ s^{-1}. This suggests that the reverse of reaction 1 is the rate-determining step and is followed by a fast reaction beween acac and $Cu(phen)X_2^+$ to ultimately form $Cu(acac)_2^-$:

$$Cu(phen)X_2^+ + 2acac \xrightarrow{k_l} Cu(acac)_2^- + phen + 2X \quad (3)$$

Making a steady-state assumption on $Cu(phen)X_2^+$, we obtain

$$-d[Cu(phen)_2^+]/dt = k_l k_{-p}[acac][Cu(phen)_2^+]/k_p[phen] + k_l[acac] \quad (4)$$

In the limit of high [acac], $k_{obsd} = k_{-p}$. The same results are obtained when EDTA is used as the competing ligand. The value of the equilibrium constant, calculated from $k_p/k_{-p} = (3.1 \pm 0.2) \times 10^5$ M^{-1}, is in excellent agreement with that of $K_p = (3.04 \pm 0.05) \times 10^5$ M^{-1} obtained in separate redox experiments.[1b]

Cu(I)–Micelle Association. In studying the effects of SDS micelles on (1) it is important to establish the extent of Cu(I) association:

$$Cu(phen)_2^+ + M \rightleftarrows Cu(phen)_2\text{–}M^+ \quad (5)$$

The micellar association is characterized by a binding constant

$$K/N = [Cu(phen)_2\text{–}M^+]/[Cu(phen)_2^+](C - cmc) \quad (6)$$

where [M] = $(C - cmc)/N$ is the concentration of micelles, N is the aggregation number, and C is the detergent concentration. We have repeated earlier spectral work monitoring the formation of $Cu(phen)_2\text{–}M^+$ at 440 nm, this time in the presence of excess phenanthroline to eliminate any spectral contributions from the monochelated form. From the total concentration of $Cu(phen)_2^+$

$$[Cu]_t = [Cu]_W + [Cu]_M \quad (7)$$

and the total absorbance change at 440 nm

(1) (a) Ponganis, K. V.; de Araujo, M. A.; Hodges, H. L. *Inorg. Chem.* **1980**, *19*, 2704. (b) de Araujo, M. A.; Hodges, H. L. *Inorg. Chem.*, in press.
(2) The following nomenclature will be used through this paper: phen = 1,10-phenanthroline, SDS = sodium dodecyl sulfate; cmc = critical micelle concentration; EDTA = ethylenediaminetetraacetic acid; acac = acetylacetonate ion.
(3) Addition of SO_4^{2-} to a solution of $Cu(phen)_2^+$ shows no spectral changes indicative of anion coordination to Cu(I), as we see with halide ion.[1]
(4) Eigen, M.; Wilkins, R. G. In "Mechanisms of Inorganic Reactions"; Gould, R. F., Ed.; American Chemical Society: Washington, D.C., 1965; Adv. Chem. Ser. No. 49, p 55.
(5) Emerson, M. F.; Holzer, A. *J. Phys. Chem.* **1967**, *71*, 1898.

$$A_t = \epsilon_W[Cu]_W + \epsilon_M[Cu]_M \quad (8)$$

eq 6 can be rearranged

$$K/N(C - \text{cmc}) = \frac{[Cu]_t - (A_t - \epsilon_M[Cu]_t)/(\epsilon_W - \epsilon_M)}{(A_t - \epsilon_M[Cu]_t)/(\epsilon_W - \epsilon_M)} = Y \quad (9)$$

Here the subscripts W and M denote aqueous and micellar quantities, respectively. All terms on the right side of eq 9 are known, and a plot of Y vs. C – cmc should yield a straight line. As shown in Figure 2, this is the case and a least-squares fit of the data yields $K/N = (1.05 \pm 0.04) \times 10^4$ M^{-1}.

Ligand Binding and Dissociation (Micellar). Addition of excess phenanthroline to a 1:1 mixture of phenanthroline and Cu(I) in 0.1 M SDS solution results in absorbance changes that are first order in both reactants. From the slope of the data plotted in Figure 1, $k_{pM}(app) = (1.3 \pm 0.3) \times 10^4$ M^{-1} s^{-1}. This value is reported as an apparent rate constant since only the total (not the micellar) concentration of phenanthroline is known. The rate constant is artificially high since there is a concentrating effect for reagents that partition favorably in the micelle.

Addition of either excess acac or EDTA to $Cu(phen)_2^+$–M in the presence of excess phenanthroline results in a complete loss of absorbance at 440 nm. Micellar dechelation is 100-fold slower than the aqueous process. The reaction is independent of ligand concentration with a rate constant $k_{-p} = (2.0 \pm 0.2) \times 10^{-3}$ s^{-1}. Aqueous and micellar rate and equilibrium constants are compared in Table I.

Discussion

Aqueous Chemistry. For substitution reactions of metal complexes that follow the Eigen–Wilkins mechanism (water exchange is rate limiting), the second-order rate constant is given by

$$k = K_{os}k_{ex} \quad (10)$$

where K_{os} is the equilibrium constant for formation of the precursor complex and k_{ex} is the first-order rate constant for loss of water from the inner coordination sphere of the metal. Usually k is within a factor of 10 of k_{ex}. The rate constant for maleic acid association with aquocopper(I), $k = 2 \times 10^9$ M^{-1} s^{-1}, is in keeping with the high values observed for substitution-labile metal centers.[6] Since the rate constant for phenanthroline substitution determined in this work is several orders of magnitude smaller than the anticipated value, it appears that the water exchange is not rate limiting.

In the chelation of Cu(II) by rigid macrocycles, slow association rates are observed because the metal is forced to undergo simultaneous multiple desolvation rather than stepwise exchange as it would with a flexible chelate.[7] Although the rigidity of the phenanthroline ring prevents stepwise chelation, other metal–phenanthroline complexations seem to fit the Eigen–Wilkins mechanism. The rate constant for the formation of $Fe(phen)_3^{2+}$ from the bis(phenanthroline) complex, $k_1 = 6.3 \times 10^5$ M^{-1} s^{-1},[8] is close to that for the Fe(II) water exchange, $k_{ex} = 3.2 \times 10^6$ s^{-1}.[9] Similarly, for the formation of $Ni(phen)_2^{2+}$ from $Ni(phen)^{2+}$, $k_1 = 4.0 \times 10^3$ M^{-1} s^{-1} [8] and $k_{ex} = 2.5 \times 10^4$ s^{-1}.[9]

We offer a tentative explanation for our slow rate on the basis of a change in metal geometry. For a dissociative mechanism, the octahedral iron(II) and nickel(II) phenanthroline complexes go from six- to four-coordinate species, which can be accommodated in a tetrahedral fashion by the ligand and solvent molecules remaining in the coordination sphere. The tetrahedral $Cu(phen)_2^{2+}$ complex, however, would have to pass through a two-coordinate state, which the remaining phenanthroline ligand could not accommodate with a linear geometry. If an associative mechanism were operative, an increase in the metal coordination would destroy the tetrahedral arrangement, which is highly favored for Cu(I) complexes. We cannot distinguish between these two possibilities, but in either case, the rate-determining step would involve a transition to a less stable Cu(I) geometry.

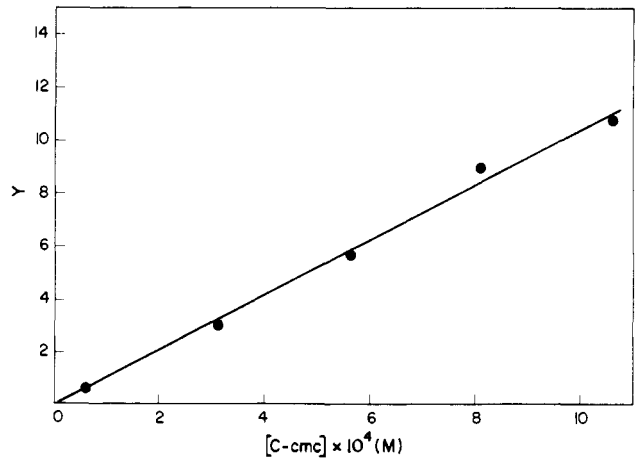

Figure 2. Plot of Y vs. C – cmc for the association of $Cu(phen)_2^+$ with SDS micelles (see text): $[Cu(phen)_2^+] = 1 \times 10^{-4}$ M; $[phen] = 2 \times 10^{-3}$ M; pH 6 (cacodylate); $T = 25$ °C.

Table I. Rate Constants for the Mono- and Bis(phenanthroline)copper(I) Equilibrium[a]

	aqueous	micellar[b]	approx rate const ratio (aqueous:micellar)
k_p, M^{-1} s^{-1}	$(6.2 \pm 0.2) \times 10^4$	$(1.3 \pm 0.3) \times 10^4$ [c]	5:1
k_{-p}, s^{-1}	$(2.0 \pm 0.2) \times 10^{-1}$ [d]	$(2.0 \pm 0.2) \times 10^{-3}$ [e]	100:1
K_p, M^{-1}	$(3.1 \pm 0.2) \times 10^5$	$(6.5 \pm 0.9) \times 10^6$ [c]	1:20

[a] All studies at pH 6.0 (cacodylate), $T = 25$ °C, $[Na^+]_t = 0.2$ M, and $[Cu(I)]_t = 2.5 \times 10^{-5}$ M. [b] [SDS] = 0.1 M. [c] Apparent values; see text. [d] Added [phen] = 4×10^{-4} M. [e] Added [phen] = 4×10^{-3} M.

The stepwise formation constants for the association of phenanthroline with Cu(I) have not been previously reported. From the aqueous rate data (Table I) and the overall stability constant ($\beta_2 = 10^{5.8}$ [10]), we calculate values of $10^{10.3}$ and $10^{5.5}$ for the first and second phenanthroline binding constants, respectively, at pH 6.

Micellar Chemistry. The partition coefficient, P, for the distribution of $Cu(phen)_2^+$ between aqueous and micellar phases is related to the binding constant by the expression[11]

$$K/N = \bar{V}P \quad (11)$$

where $\bar{V} = 0.251$ M^{-1} is the partial molar volume of the surfactant monomer in the micelle.[12] From the value of the binding constant we calculate $P = 4 \times 10^4$. This partition coefficient will have both electrostatic and hydrophobic components:

$$P = P_{es}P_{hy} \quad (12)$$

(6) Meyerstein, D. *Inorg. Chem.* **1975**, *14*, 1716.
(7) Cabbiness, D. K.; Margerum, D. W. *J. Am. Chem. Soc.* **1970**, *92*, 2151.
(8) Irving, H.; Mellor, D. H. *J. Chem. Soc.* **1962**, 5222.
(9) Swift, T. J.; Connick, R. E. *J. Chem. Phys.* **1962**, *37*, 307.
(10) James, B. R.; Williams, R. J. P. *J. Chem. Soc. A* **1961**, 2007.
(11) Berezin, I. V.; Martinek, K.; Yatsimirskii, A. K. *Russ. Chem. Rev. (Engl. Transl.)* **1973**, *42*, 787.
(12) Calculated from $\bar{V} = \bar{v}(M_r(SDS))/1000$, where $\bar{v} = 0.87$ g^{-1} cm^3, from: Tanford, C.; Nozaki, Y.; Reynolds, J. A.; Marino, S. *Biochemistry* **1974**, *13*, 2369.

The electrostatic contribution can be estimated from

$$P_{es} = e^{-Ze\psi/kT} \quad (13)$$

where Z is the ionic charge, e is the electronic charge, and ψ is the surface potential of the micelle.[11] The surface potential is sensitive to added salt and has not been determined for our exact experimental conditions, but it does not appear to change substantially once the NaCl concentration exceeds 0.025 M.[13] Using $\psi = -84$ mV, determined for SDS micelles at [NaCl] = 0.1 M,[13] we calculate $P_{es} = 27$ and $P_{hy} = 1.5 \times 10^3$ for $Cu(phen)_2^+$ binding to SDS micelles at 25 °C. Even if P_{es} is only approximate, it is apparent that the strong micellar binding of $Cu(phen)_2^+$ comes primarily from hydrophobic rather than electrostatic factors.

There is limited data available on how micelles influence metal ion complexation. In systems where there is little reagent association with the micelle, aqueous and micellar ligation rates are similar. For example, the rates of several ligand association and dissociation reactions of cobalamin in SDS solution show little difference from those in water.[14] On the other hand, when the reagents concentrate at the micelle surface, as in the reaction between Ni(II) and PADA (pyridine-2-azo-*p*-dimethylaniline), the micellar rate (SDS) is several orders of magnitude faster than the aqueous rate.[15] However, when corrections are made for the actual micellar concentrations of reagents and hydrogen ion (the association is pH dependent) the calculated second-order rate constant is very close to the value obtained in bulk solution.[13] Similar results have recently been reported for Ni(II) complexation with 2,2′-bipyridyl and 4,4′-dimethyl-2,2′-bipyridyl.[16]

There is strong binding between SDS micelles and $Cu(phen)_2^+$ (and presumably $Cu(phen)^+$ as well), but the 5-fold inhibition of the phenanthroline association rates is in marked contrast to the rate enhancement seen for the Ni(II)–chelate reactions.[13,15,16] If the actual micellar concentration of phenanthroline were known, the inhibition would be even more substantial. Micelles are known to inhibit the association reaction of a ligand with a dissociable proton by increasing the concentration of hydrogen ion at the micelle surface.[13] Although previous electron-transfer studies with $Cu(phen)_2^+$ have shown that (1) is independent of pH over the range $6 \leq pH \leq 8$,[1] we are currently investigating the reaction over a wider pH range.

We have previously suggested the possibility of ion-pair complex formation between the copper species and the detergent head groups.[1] The stability of such a complex, Cu(L)*, would be enhanced by strong hydrophobic interactions between phenanthroline and the detergent tails. The rate constant for any subsequent reaction of $Cu(phen)_2^+$ or $Cu(phen)^+$, whether it is electron transfer, ligand association, or water exchange, would be modified by the ion-pair equilibrium constant, K^*:

$$Cu(L)^* \rightleftarrows Cu(L) \qquad K^* \quad (14)$$

$$Cu(L) \rightarrow \text{products} \quad (15)$$

Thus, SDS micelles may inhibit the reactions of $Cu(phen)_2^+$ and $Cu(phen)^+$ by forming nonreactive complexes. Since aquonickel(II) has no ligands for strong hydrophobic interactions, the association reaction would not be similarly inhibited. A possible explanation for why the ligand dissociation of $Cu(phen)_2^+$ is strongly inhibited by SDS micelles while that for the similar $NiPADA^{2+}$ complex is unaffected is that the latter complex is only loosely bound to the micelle surface. Studies now in progress over a wider range of detergent concentration and with a nonionic detergent should help resolve some of these questions.

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Registry No. $Cu(phen)_2^+$, 17378-82-4.

Contribution from the Department of Chemistry, Northern Michigan University, Marquette, Michigan 49855

π-Donor Complexes of Heteroaromatic Boron–Nitrogen Compounds with Iodine

John E. Frey,* Georgianna M. Marchand, and Rodney S. Bolton

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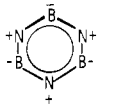
Borazine, $B_3N_3H_6$, is isoelectronic and isostructural with benzene; for this reason it is expected to behave as an aromatic system with the planar ring structure I. Although its physical properties and spectra are consistent with such an interpretation, its chemical reactivity for the most part is that expected for a cyclic aminoborane with the puckered ring structure II.[1]



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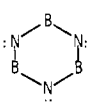

II

Evidence for aromatic chemical behavior in borazine derivatives comes from the study of weak electron donor–acceptor complexes. Champion et al.[2] report a π-donor complex between hexamethylborazine and tetracyanoethylene with an absorption maximum at 461 nm and a stability constant of 0.7 L/mol. Mellon and Lagowski,[3] however, report an absorption maximum at 320 nm for the same complex, leaving the evidence for the characteristics of the complex in doubt. Muszkat and Kirson[4] present evidence of π-complex formation between several triphenylborazines and tetracyanoethylene without making it clear whether the bonding interaction involves the borazine ring or the attached phenyl groups. Dewar and Rogers[5] present spectral evidence for π-complex formation between tetracyanoethylene and several heteroaromatic compounds containing B–N bonds but report no stability constant values.

The objective of this work is to obtain chemical evidence for π-complex formation involving B–N aromatic systems from stability constant values. Our method is similar to that of Eubanks and Lagowski,[6] who sought to determine whether substituted aminoboranes behave as lone-pair, or n, donors

(13) James, A. D.; Robinson, B. H. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 10.
(14) Fendler, J. H.; Nome, F.; Van Woert, H. C. *J. Am. Chem. Soc.* **1974**, *96*, 6745.
(15) Holzwarth, J.; Knoche, W.; Robinson, B. H. *Ber. Bunsenges. Phys. Chem.* **1978**, *82*, 1001.
(16) Reinsborough, V. C.; Robinson, B. H. *J. Chem. Soc., Faraday Trans. 1* **1979**, *75*, 2395.

(1) Mellon, E. K.; Lagowski, J. J. *Adv. Inorg. Chem. Radiochem.* **1963**, *5*, 259.
(2) Champion, N. G. S.; Foster, R.; Mackie, R. K. *J. Chem. Soc.* **1961**, 5060.
(3) Mellon, E. K.; Lagowski, J. J. *Nature (London)* **1963**, *199*, 997.
(4) Muszkat, K. A.; Kirson, B. *Isr. J. Chem.* **1964**, *2*, 57.
(5) Dewar, M. J. S.; Rogers, H. J. *J. Am. Chem. Soc.* **1962**, *84*, 395.
(6) Eubanks, I. D.; Lagowski, J. J. *J. Am. Chem. Soc.* **1966**, *88*, 2425.

0020-1669/82/1321-3239$01.25/0