Again the main reaction was the oxidation of HNF_2 to N_2F_4.

$$2OF_2 + 4KF{\cdot}HNF_2 \rightarrow 2N_2F_4 + 4KHF_2 + O_2$$

In the case of $FOClO_3$ and $KF{\cdot}HNF_2$, the mixture exploded when warmed from −196 toward −78 °C. For $FONO_2$, the reaction could be sufficiently controlled, but again N_2F_4 was formed in almost quantitative yield with NO_2, O_2, and FNO_2 as the major byproducts. It thus appears that with hypofluorites, which are powerful oxidizers, fluorination of HNF_2 to N_2F_4 and HF is favored over $XONF_2$ formation.

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Registry No. D_2, 7782-39-0; HNF_2, 10405-27-3; KF, 7789-23-3; RbF, 13446-74-7; CsF, 13400-13-0; TeF_5OF, 83314-21-0; OF_2, 7783-41-7; $FONO_2$, 7789-26-6; $FOClO_3$, 10049-03-3; HF, 7664-39-3; N_2F_4, 10036-47-2.

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Kinetics of the Consecutive Binding of Bipyridyl Ligands and of Phenanthroline Ligands to Copper(II)

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By the application of temperature-jump relaxation techniques, the kinetics of the consecutive binding of bipyridyl ligands (bpy) and of phenanthroline ligands (phen) to Cu(II) have been studied, $CuL_{i-1}{}^{2+} + L \xrightarrow{k_i} CuL_i{}^{2+}$ (i = 2, 3; L = bpy, phen). At 25 °C and ionic strength 0.5 M, the following forward rate constants have been obtained: for bpy, $k_2 = 1.5 \times 10^9$ M^{-1} s^{-1} and $k_3 = 8.6 \times 10^8$ M^{-1} s^{-1}; for phen, $k_2 = 6.9 \times 10^8$ M^{-1} s^{-1} and $k_3 = 1.8 \times 10^9$ M^{-1} s^{-1}. These rate constants are appreciably larger than those for formation of the 1:1 complexes, which were determined earlier, $k_1 = (4\text{–}5) \times 10^7$ and 6.4×10^7 M^{-1} s^{-1}, respectively. The rate enhancement in the formation of the bis and tris complexes is attributed to stacking interactions between the coordinated and the incoming ligands. Several kinetic features of these reactions are discussed.

Introduction

Complex formation processes involving Cu(II) are usually very fast, with second-order rate constants not far below the diffusion-controlled limit.[2,3] The rapidity of these reactions not only requires the application of specialized techniques for their investigation but also impedes the elucidation of mechanistic details. Several experimental studies have indicated that substitution processes at hexacoordinated Cu(II) are best described to proceed by a dissociative mechanism,[3-5] like those of various other divalent metal ions. On the other hand, associative mechanisms for Cu(II) have also been suggested.[6,7]

The high rates of substitution at $Cu(H_2O)_6{}^{2+}$ reflect the weak binding of the H_2O ligands in the axial positions of the distorted octahedron.[8] The observation that many multidentate ligands, too, react very fast with Cu^{2+} is obviously due to a rapid inversion of the Jahn–Teller distortion.[3,8] It has been reported that for $Cu(H_2O)_6{}^{2+}$ this inversion occurs with a rate of 6×10^{10} s^{-1}.[9]

A subject of wide interest is the effects of ligands already coordinated to metal ions on the kinetics of further ligand binding.[2] A variety of factors may be of importance in this context: steric and electronic effects, inhibited Jahn–Teller inversion, and specific interactions between the ligands already bound and the incoming ligand. In this paper we report on the kinetics of the consecutive binding of 2,2′-bipyridyl (bpy) and of 1,10-phenanthroline (phen) to Cu(II) to form the corresponding bis and tris complexes, $CuL_{i-1}{}^{2+} + L \rightleftharpoons CuL_i{}^{2+}$ (i = 2, 3). The rates of formation of the 1:1 complex species have been previously determined.[10,11]

Table I. Values of log K_{stab} for Complexes of bpy and phen (25 °C; I = 0.5 M)

		log K			
		bpy	ref	phen	ref
$H^+ + L = HL^+$	K_H	4.54	14	5.03	17
$Cu^{2+} + L = CuL^{2+}$	K_1	8.70^a	10	9.20	17
$CuL^{2+} + L = CuL_2{}^{2+}$	K_2	5.78	15	6.70	17
		5.70^b		6.69^b	
$CuL_2{}^{2+} + L = CuL_3{}^{2+}$	K_3	3.25^c	16	5.20	17

[a] I = 0.3 M. [b] This work; see text. [c] I = 1.0 M.

Experimental Section

Materials. Stock solutions of $CuCl_2$, KCl, bpy, and phen were prepared from "reagent grade" chemicals (Merck) without further purification. In order to solubilize bpy and phen, equivalent amounts of HCl were added. The ligand solutions were kept in the dark to avoid any possible photodecomposition. The pH of the reactant solutions was brought to the desired value (±0.01) by the dropwise addition of 1 M KOH or HCl (Baker Chemicals). The ionic strength (I) was adjusted to 0.5 M by using KCl. The chloride medium was chosen because of the UV absorption of $NO_3{}^-$ and the solubility problems encountered in the presence of $ClO_4{}^-$.

Methods. pH measurements were carried out by means of a Radiometer PHM 52 digital pH meter equipped with a Metrohm EA 125 combined electrode. The calibration procedure for converting pH values to H^+ concentrations was described elsewhere.[4] The kinetics of the complex formation reactions were studied by applying the temperature-jump relaxation technique with spectrophotometric detection.[12] The instrument used was either a conventional apparatus[12] with a lower limit of the accessible time range of 2 μs or a cable T-jump apparatus[13] with

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Table II. Rate Constants of the Stepwise Binding Reactions of bpy and phen with Cu(II)[a] (25 °C; I = 0.5 M Unless Otherwise Stated)

		bpy	phen	ref
$Cu^{2+} + L = CuL^{2+}$	k_1	5.0×10^7	6.4×10^7	11[b]
		$\sim 4 \times 10^7$		10[c]
	k_{-1}	$\sim 9 \times 10^{-2}$	4.0×10^{-2}	*d*
$Cu^{2+} + HL^+ = CuL^{2+} + H^+$	k'_1	2.6×10^5	$<5 \times 10^2$	11[b]
		2.9×10^5		10[c]
	k'_{-1}	14		10[c]
$CuL^{2+} + L = CuL_2^{2+}$	k_2	$(1.5 \pm 0.1) \times 10^9$	$(6.9 \pm 0.3) \times 10^8$	*f*
	k_{-2}	$(3.5 \pm 0.4) \times 10^3$	$(1.4 \pm 0.2) \times 10^2$	*f*
$CuL^{2+} + HL^+ = CuL_2^{2+} + H^+$	k'_2	$(2.7 \pm 0.4) \times 10^6$	$(8.4 \pm 2.2) \times 10^4$	*f*
	k_{-2}[d]	1.9×10^5	1.8×10^3	*f*
$CuL_2^{2+} + L = CuL_3^{2+}$	k_3	$(8.6 \pm 1.5) \times 10^8$	$(1.8 \pm 0.4) \times 10^9$[e]	*f*
	k_{-3}	$(4.3 \pm 1.4) \times 10^5$	1.1×10^4[d]	*f*

[a] Rate constants k_{-1}, k_{-2}, and k_{-3} in s^{-1}; all others in $M^{-1}\ s^{-1}$. [b] I = 1 M. [c] I = 0.3 M. [d] From the forward rate constant and the stability constant. [e] From the one-parameter fit. [f] This work.

a lower limit of ca. 0.1 μs. The sample solution was thermostated at 22.0 °C prior to the T jump, and then the temperature was raised by 3.0 °C by discharging the capacitor (30 kV) or the coaxial cable (70 kV).

The relaxation processes were monitored by using the UV absorption of the ligand and complex species (λ = 280–334 nm). The reaction signals were stored in a transient recorder (Datalab DL 905 or DL 920) and evaluated either by a computer (Univac 1108) or after display on a screen by means of an electronic simulator constructed by C. R. Rabl. Each relaxation time given is the average of five to seven individual measurements. The rate constants were obtained by fitting the analytical expression for $1/\tau$ to the measured values with the use of a nonlinear least-squares program that minimizes the relative deviations, $\sum[(1/\tau_{calcd} - 1/\tau_{exptl})/(1/\tau_{exptl})]^2$.

Results

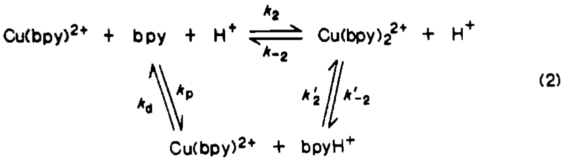
The equilibria of the systems Cu^{2+} + bpy and Cu^{2+} + phen have been extensively studied, and the respective equilibrium constants are available from the literature. The values that have been adopted for the present study are summarized in Table I. The stepwise equilibrium constants are well separated; therefore, the kinetics of each reaction step can be investigated without interference by the other steps.

Formation of the Bis Complexes. Consider the formation of the bis(bipyridyl) complex, $Cu(bpy)^{2+}$ + bpy = $Cu(bpy)_2^{2+}$. If the concentration of free unprotonated bpy is adjusted to a value close to $1/K_2$, then $[Cu(bpy)^{2+}] \simeq [Cu(bpy)_2^{2+}]$, whereas the concentrations of Cu^{2+} and $Cu(bpy)_3^{2+}$ are more than 100-fold smaller than those of the mono and bis complexes and can be neglected. In order to achieve reasonable amplitudes of the relaxation processes, the measurements have to be carried out at fairly low pH values, such that the concentrations of $bpyH^+$ and H^+ are at least of a magnitude comparable to those of the mono and bis complexes. The overall equilibrium can then be described by

$$K'_2 = \frac{[Cu(bpy)_2^{2+}][H^+]}{[Cu(bpy)^{2+}][bpyH^+]} = \frac{K_2}{K_H} \quad (1)$$

and [bpy] is to a good approximation a steady-state concentration (much smaller than those of the species in eq 1).

Since it has been established that metal ions react with both the unprotonated and the protonated bpy ligand,[10,11] the following reaction scheme was considered:



(2)

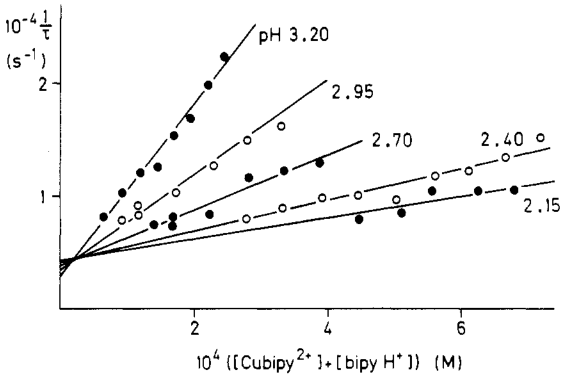


Figure 1. Kinetic data for the reaction $Cu(bpy)^{2+}$ + bpy = $Cu(bpy)_2^{2+}$ (plot according to eq 4).

Only one relaxation effect was observed under our conditions, as expected if [bpy] represents a steady state. Applying the steady-state approximation yields the following expression for the reciprocal relaxation time:[10]

$$\frac{1}{\tau} = \left(\frac{k_2 k_d}{k_p[H^+] + k_2[Cu(bpy)^{2+}]} + k'_2\right)([Cu(bpy)^{2+}] + [(bpy)H^+]) + \left(\frac{k_{-2}k_p}{k_p[H^+] + k_2[Cu(bpy)^{2+}]} + k'_{-2}\right) \times ([Cu(bpy)_2^{2+}] + [H^+]) \quad (3)$$

The kinetic studies were carried out over the following concentration range: $[Cu(II)]_o = (0.5–5) \times 10^{-4}$ M, $[bpy]_o = (1.4–8.7) \times 10^{-4}$ M, $-\log [H^+]$ = 1.98–3.20 (the index "o" denotes total concentrations of metal and ligand, respectively). The concentrations of all individual species were calculated from the total concentrations and the equilibrium constants with the help of a computer program ([bpy] = $(1.4–1.9) \times 10^{-6}$ M). The relaxation process was monitored at 320 nm. The observed relaxation times varied from 45 to 137 μs (conventional T jump).

Under our conditions $k_p[H^+]$ was always $\gg k_2[Cu(bpy)^{2+}]$ and in most experiments $[H^+] \gg [Cu(bpy)_2^{2+}]$. To a good approximation eq 3 therefore simplifies to

$$\frac{1}{\tau} = \left(\frac{k_2}{K_H[H^+]} + k'_2\right) \times ([Cu(bpy)^{2+}] + [bpyH^+]) + k_{-2} + k'_{-2}[H^+] \quad (4)$$

A plot of most of the experimental data according to eq 4 is shown in Figure 1. Although $[bpyH^+] \gg [bpy]$, the reaction with bpy is the main pathway under our conditions, as demonstrated by the $[H^+]$ dependencies of the slopes and intercepts of Figure 1. The final evaluation of the rate constants was accomplished by a computer-programmed fitting procedure. The approximation $[H^+] \gg [Cu(bpy)_2^{2+}]$ was abandoned, and k'_{-2} was replaced by k'_2K_H/K_2. Thus three quantities were left to be fitted: k_2, k_{-2},

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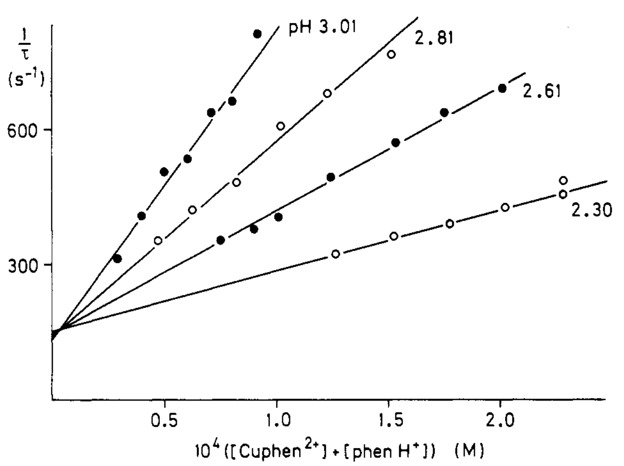

Figure 2. Kinetic data for the reaction $Cu(phen)^{2+}$ + phen = $Cu(phen)_2^{2+}$ (plot according to eq 4).

and k'_2. During this fitting procedure, the value of K_2 used to calculate the equilibrium concentrations was systematically varied until the best fit with the resulting k_2/k_{-2} was achieved. This value of K_2 is included in Table I. The rate constants obtained are summarized in Table II.

For the formation of the bis(phenanthroline) complex, the situation is completely analogous to the one just discussed for the bpy system. The experimental conditions were the following: $[Cu(II)]_0 = (0.2\text{–}3.0) \times 10^{-4}$ M, $[phen]_0 = (0.5\text{–}5.0) \times 10^{-4}$ M, $-\log [H^+] = 1.80\text{–}3.00$ ($[phen] = (1.2\text{–}2.0) \times 10^{-7}$ M); $\lambda = 312$ nm, $\tau = 1.2\text{–}3.2$ ms (conventional *T* jump). The experimental data are shown in Figure 2, and the rate constants that have been evaluated are given in Table II.

Formation of the Tris Complexes. As before, the concentrations of free unprotonated ligand were adjusted to a value close to the reciprocal stability constant, $1/K_3$. Then $[CuL_2^{2+}] \simeq [CuL_3^{2+}]$, whereas the concentrations of CuL^{2+} and Cu^{2+} are negligibly small. Because of the lower values of K_3 as compared to K_2, [L] is now correspondingly higher than in the formation of the bis complexes. [L] is not a steady state but is of comparable magnitude to the concentrations of CuL_2^{2+} and CuL_3^{2+}. If we work at high pH, such that $[LH^+] << [L]$, the only step that has to be taken into account is now

$$CuL_2^{2+} + L \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} CuL_3^{2+} \qquad (5)$$

and then

$$1/\tau = k_3([CuL_2^{2+}] + [L]) + k_{-3} \qquad (6)$$

The experiments were carried out under the following conditions.

(a) Cu(II)-bpy: $[Cu(II)]_0 = (0.4\text{–}2.0) \times 10^{-3}$ M, $[bpy]_0 = (1.5\text{–}5.6) \times 10^{-3}$ M, $-\log [H^+] = 6.1\text{–}6.3$ ($[bpy] = (1.6\text{–}8.7) \times 10^{-4}$ M); $\lambda = 335$ nm, $\tau = 0.6\text{–}1.1$ μs. Because of the very short reaction time constants, these measurements have been done by means of the cable *T*-jump technique.

(b) Cu(II)-phen: $[Cu(II)]_0 = (0.44\text{–}4.0) \times 10^{-5}$ M, $[phen]_0 = (0.18\text{–}1.1) \times 10^{-4}$ M, $-\log [H^+] = 7.3$ ($[phen] = (6.8\text{–}8.7) \times 10^{-6}$ M); $\lambda = 280$ nm, $\tau = 16\text{–}40$ μs (conventional *T* jump).

Figure 3 shows the experimental data for $Cu(bpy)_2^{2+}$ + bpy = $Cu(bpy)_3^{2+}$. The observed amplitudes were rather small, and the accuracy of the time constants is correspondingly low. The straight line in Figure 3 represents the best fit to the linear relationship (6). The slope/intercept ratio yields $\log K_3 = 3.30$, a value that agrees very well with the equilibrium constant of Table I.

The experimental data for $Cu(phen)_2^{2+}$ + phen = $Cu(phen)_3^{2+}$ are shown in Figure 4. The broken line indicates the best fit for k_3 and k_{-3} according to eq 6. The slope/intercept ratio of this line yields $\log K_3 = 5.6$, as compared to 5.2 in Table I. Replacing k_{-3} in eq 6 by k_3/K_3 gives the one-parameter best fit indicated by the solid line. The values of k_3 obtained by the two evaluations differ by 20%.

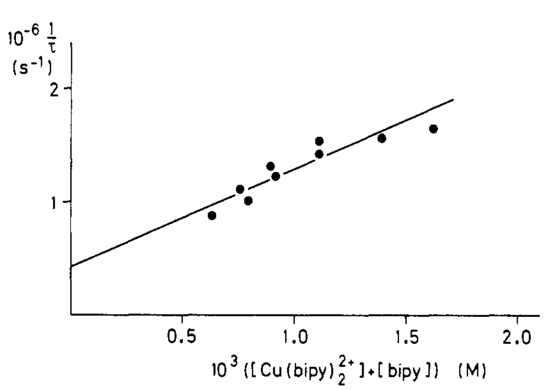

Figure 3. Kinetic data for the reaction $Cu(bpy)_2^{2+}$ + bpy = $Cu(bpy)_3^{2+}$ (plot according to eq 6; pH_c 6.1–6.3).

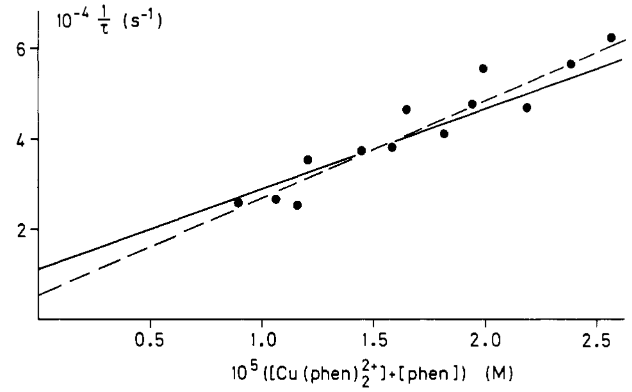

Figure 4. Kinetic data for the reaction $Cu(phen)_2^{2+}$ + phen = $Cu(phen)_3^{2+}$ (plot according to eq 6; pH_c 7.3): broken line, two-parameter best fit; solid line, one-parameter best fit.

A summary of all rate constants is presented in Table II.

Discussion

Earlier studies on the kinetics of the consecutive ligand-binding reactions of Cu(II) with bidentate ligands revealed that the formation of the 1:1 complexes usually proceeds somewhat faster (factors 2–20) than the formation of the bis complexes, CuL + L → CuL_2. This was observed, for instance, with a large number of amino acid anions, ethylenediamine, and other ligands.[2] The lower values of k_2 as compared to those of k_1 have been rationalized by taking into account statistical factors (number of H_2O ligands available for substitution),[18,19] charge effects,[18,19] steric effects,[20] and possibly a reduction in rate of the Jahn–Teller inversion in the 1:1 complexes due to the coordinated bidentate ligand.[18,19,21]

The situation is different with bpy and phen as ligands. As demonstrated by the data of Table II, the rates of formation of the bis and tris complexes (k_2 and k_3) of these ligands with Cu(II) are appreciably higher than those for formation of the 1:1 complexes (k_1).

The rate constants k_1 for bpy and phen are near 5×10^7 M^{-1} s^{-1}, clearly lower than those for some other uncharged N-donating ligands like NH_3 (2×10^8 M^{-1} s^{-1}) and imidazole (5.7×10^8 M^{-1} s^{-1}).[4] It appears very unlikely that the relatively low k_1 values in the case of bpy and phen are due to rate-controlling chelate ring closure: Since pyridine (which is of a basicity comparable to those of bpy and phen) binds to Cu^{2+} with a stability constant of ca. 400 M^{-1},[17] the ring-closure step with bpy and phen would have to be as slow as $\sim 1 \times 10^5$ s^{-1} in order to account for the observed values of k_1 if the first binding step occurs with a "normal" second-order rate constant of about 4×10^8 M^{-1} s^{-1}.

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Ruling out rate-determining ring closure, the relatively low values of k_1 can be attributed either to rather weak outer-sphere association with $Cu(H_2O)_6^{2+}$ or to a lower-than-normal rate of the first substitution step. An inspection of molecular models suggests that there may be some steric hindrance to the first inner-sphere binding step in the case of bpy and phen (from the other hetero aromatic ring).

Whatever the nature of this effect, it is expected to show up also in the formation of the bis and tris complexes. Table II reveals, however, that k_2 is larger than k_1 by factors of 30 (bpy) and 11 (phen) and that k_3 is larger than k_1 by factors of 17 (bpy) and 28 (phen). The highest rate constants observed with these uncharged ligands are in excess of 1×10^9 M^{-1} s^{-1} and are very close to the diffusion-controlled values.

With other metal ions, large rate enhancements for ligand binding have been found if part of the metal ion's aquo ligands had been replaced by (strongly basic) aliphatic amino groups. It could be proven unequivocally that the increase in rate is due to a labilization of the remaining water ligands by the coordinated amino groups.[2] In the case of aromatic N-donor ligands like bpy and phen, the labilizing effects are very small, a consequence of the π-acceptor properties of these ligands. For instance, Grant, Dodgen, and Hunt reported the following water-exchange rates (per H_2O): $k_{ex} = 3.2 \times 10^4$ s^{-1} for $Ni(H_2O)_6^{2+}$, 4.9×10^4 s^{-1} for $Ni(H_2O)_4bpy^{2+}$, and 6.6×10^4 s^{-1} for $Ni(H_2O)_2(bpy)_2^{2+}$.[22] The small increases in k_{ex} are fully compensated by the statistical factors. Therefore, a labilization effect can be ruled out in the interpretation of our data. Consistent with this view is the observation that the rate of $Cu(bpy)^{2+} + gly^- \rightarrow Cu(bpy)gly^+$ is 2.5-fold lower than that of $Cu^{2+} + gly^- \rightarrow Cu(gly)^+$.[23] Similar results have been obtained with several other ligands in place of gly^-.[7]

The most plausible explanation for the high values of k_2 and k_3 observed in the present study is the existence of a specific interaction between the coordinated and the incoming hetero aromatic ligand that leads to an increase in the stability of the outer-sphere complex. Such an effect was first considered by Rablen and Gordon in order to account for the unusual high rate of formation of the bis(2,2′,2″-terpyridine) complex of Ni(II).[24] A systematic study of this effect was carried out by Cayley and Margerum.[25] These authors investigated reactions of the type $NiL_{(1)}^{2+} + L_{(2)} \rightarrow NiL_{(1)}L_{(2)}^{2+}$, where $L_{(1)}$ and $L_{(2)}$ stand for a wide variety of heterocyclic and aromatic ligands. Appreciable rate enhancements were observed (up to a factor of 2×10^3), which were attributed to stacking interactions between the coordinated and the incoming ligand. A reaction mechanism involving stacking in the outer-sphere state and during the replacement of the first H_2O ligand was proposed.[25]

We assume that stacking interactions do account also for the high values of k_2 and k_3 (as compared to k_1) in the Cu(II) reactions considered here. Contrary to the one example given for Ni(II),[25] rate enhancements are observed in our study also with the inflexible phen as the incoming ligand. The irregular configuration of hexacoordinated Cu(II) and the general variability of the coordination configuration of Cu(II) may play a role in these reactions. The moderate variations in the rate constants for bpy and phen, $k_{2(bpy)}/k_{2(phen)} = 2$ and $k_{3(bpy)}/k_{3(phen)} = 0.5$, are not readily rationalized. The two ligands differ in the strength of their stacking interactions, in their flexibility, and in their nucleophilicity (phen forms stronger complexes (Table I) and may labilize somewhat the remaining water ligands). A delicate balance of these factors may produce the observed variations. In general, however, the rate enhancements of k_2 and k_3 over k_1, varying from 10 to 30, are of the same magnitude as those reported for similar reactions involving Ni(II).[25] They are also consistent with the self-association constants of bpy and phen in aqueous solution.[26] Enhanced stability due to intramolecular stacking is well established for certain ternary complexes of Cu(II).[27] Of relevance to the present investigation are some of the results of a quantitative study of the stacking interactions between aromatic diamines (DA) and aromatic amino acids (AA) as ligands in ternary complexes of Cu(II), published recently by Yamauchi and Odani.[28] According to these authors, the free energy of the reaction of Cu(DA)(ala) + Cu(en)(AA) $\rightleftharpoons$ Cu(DA)(AA) + Cu(en)(ala), mainly due to stacking between DA and AA in Cu(DA)(AA), is -3.4 kJ mol^{-1} for Cu(DA)(AA) = Cu(bpy)(phe), -3.6 kJ mol^{-1} for Cu(phen)(phe), -6.8 kJ mol^{-1} for Cu(bpy)(trp), and -7.9 kJ mol^{-1} for Cu(phen)(trp), where phe = phenylalanine and trp = tryptophan (large aromatic side group).

The data of Table II suggest that the stacking effect operates also in the reaction with the protonated ligands, since $k'_2 \gg k'_1$. For $phenH^+$ this ratio is surprisingly high, $k'_2/k'_1 > 170$. The second-order rate constants of the reactions with HL^+ are several orders of magnitude lower than those with the unprotonated ligands, mainly because proton loss becomes rate determining in the overall reactions with HL^+.[10,11] It may also be noticed that the reactions with $phenH^+$ are clearly slower than those with $bpyH^+$. Why? Molecular models reveal that in the inflexible $phenH^+$ the attached proton causes additional steric hindrance to the first substitution step, whereas such an effect is not expected for the flexible $bpyH^+$ (free rotation exists around the C–C bond, but a trans configuration seems to be preferred[29]).

The reverse rate constants reported here are in good or reasonable agreement with some dissociation rate data determined earlier.[30] The high value of $k_{-2(bpy)}$ is consistent also with NMR measurements that indicate very fast ligand exchange in the system $Cu(bpy)_2^{2+} + gly^- = Cu(bpy)gly^+ + bpy$.[16] The kinetic lability of our bis complexes is particularly revealing if we consider the ratio k_{-2}/k_{-1}, which is 3.9×10^4 for bpy and 3.5×10^3 for phen (Table II) but much smaller for other bidentate ligands, e.g. 15 for en,[31] 1.5 for gly^-,[19] and 2.8 for α-ala.[32] This difference is in part due to the stacking effect, which leads to an increase also in k_{-2}.[25] More important, however, are the structural features of these bis complexes: In the case of en, gly^-, and α-ala^-, the two ligands are arranged in a square-planar configuration. The bis complexes of bpy and phen, however, are of cis-octahedral structure (distorted).[33] In the latter configuration one of the two ligands will always occupy a weakly binding axial position with one donor group, and hence this ligand can dissociate at a much higher rate.

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Registry No. $Cu(bpy)^{2+}$, 16482-45-4; $Cu(phen)^{2+}$, 15891-89-1; $Cu(bpy)_2^{2+}$, 16787-11-4; $Cu(phen)_2^{2+}$, 15823-71-9; bpy, 37275-48-2; phen, 66-71-7.

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