3132 *Inorg. Chem.* **1992,** *31,* 3132–3137

Lewis-Base-Catalyzed Diimine-Ligand-Substitution Reactions at Copper(I)

Urs M. Frei and Gerhard Geier*

Laboratorium für Anorganische Chemie, ETH Zürich, CH-8092 Zürich, Switzerland

Received December 4, 1991

Substitutions of 2,2′-biquinoline (biq) in $Cu(biq)_2^+$ by 2,9-dimethylphenanthroline (dmp) and 1,10-phenanthroline (phen), in acetone, were found to be catalyzed by Lewis bases, L. The catalyzed pathway involves an intermediate mixed-ligand complex $Cu(biq)L^+$, in which L is rapidly replaced by the incoming diimine ligand. The individual rate constants for L = iodide and acetonitrile were evaluated. Analysis of the respective rate constants, together with the equilibrium constants, clearly shows that the better nucleophile, iodide, is the more efficient catalyst. The ligand dependences of the rate constants indicate that the mechanism of ligand-substitution reactions at tetrahedral Cu(I) is associative (I_a). On the basis of the effect of acetonitrile-assisted substitution reactions in acetone, an attempt was made to obtain an approximate value of the corresponding rate constants in the pure solvent by extrapolation from low acetonitrile concentrations. The result agrees with the observation that substitution reactions at Cu(I) in acetonitrile are generally too fast for the stopped-flow time scale. The solvent-assisted pathway represents an important contribution to diimine-substitution reactions in acetonitrile, whereas in acetone this pathway is of minor importance.

Introduction

After the development of methods for studying fast reactions in solution, numerous kinetic investigations of complex-formation reactions with the Cu^{2+} aqua ion were performed.[1] However, the situation with respect to Cu^+ is quite different and our knowledge of its substitution lability is still limited. Solution studies have been hampered by air sensitivity and the tendency of Cu^+ to undergo disproportionation reactions.

The first kinetic study of complexation of Cu^+ with maleate and fumarate in aqueous solution showed that these reactions are diffusion controlled.[2] A slower rate was reported for $Cu(phen)_2^+$ formation.[3] However, Cu(I)–phen complexes have a strong tendency to form oligomeric species in aqueous solution.[4] In a recent investigation,[5] we found that the substitution lability of tetrahedral bis(diimine)copper(I) ions is strongly dependent on the solvent used. In methanol and acetone, the substitution of 2,2′-biquinoline (biq) in $Cu(biq)_2^+$ by 2,9-dimethyl-1,10-phenanthroline (dmp) or phen can easily be followed by stopped-flow techniques whereas, in acetonitrile, these reactions are too fast for this method. We also found that the substitution reactions in acetone are accelerated by addition of acetonitrile. It turns out that, within a broad concentration range of acetonitrile, no complexes containing this potential ligand can be detected under equilibrium conditions; i.e., it merely acts as a catalyst.

This paper reports an investigation of the influence of acetonitrile on the kinetics and mechanism of ligand substitution in $Cu(biq)_2^+$ by dmp and phen. In addition, we describe the effect of iodide, which accelerates the diimine-substitution reactions much more strongly. To improve our knowledge of the interaction between the bis(diimine)copper(I) ion and acetonitrile, we also measured some equilibrium constants and the kinetics of the dissociation of $Cu(dmp)_2^+$ in acetonitrile solutions.

Experimental Section

$[Cu(biq)_2]ClO_4$ and $[Cu(biq)(dmp)]ClO_4$ were prepared as described earlier.[5] $[Cu(CH_3CN)_4]ClO_4$ was prepared by adding an excess of Cu powder to $[Cu(H_2O)_6](ClO_4)_2$ dissolved in acetonitrile. The suspension was stirred for 3 h and filtered. Evaporation of the colorless solution yielded white crystals of $[Cu(CH_3CN)_4]ClO_4$, which were filtered off and dried in vacuo. The copper content was determined by atomic absorption spectrometry or by complexometric titration after oxidizing the sample with nitric acid. Tetraethylammonium iodide (TEAI), tetraethylammonium perchlorate (TEAP), biq, and dmp were used as received from Fluka. Acetonitrile, Fluka puriss., was further purified by distillation over calcium hydride, followed by fractional distillation over phosphorus(V) oxide. Fluka does not mention that their acetonitrile contains ca. 3×10^{-3} mol/L acrylonitrile, which is not removed by the above purification procedure. However, for the experiments described here, the same results were obtained using either this solvent or Merck Uvasol acetonitrile, which did not contain acrylonitrile.

Solutions of $Cu(biq)_2^+$ and $Cu(dmp)_2^+$ that contain a slight excess of biq and dmp, respectively, are stable against oxygen and can be stored in the dark for weeks. Acetonitrile solutions containing only copper(I) perchlorate were prepared fresh daily from $[Cu(CH_3CN)_4]ClO_4$. The exact Cu(I) content was determined spectrophotometrically as $Cu(dmp)_2^+$ ($\epsilon = 7790\ M^{-1}\ cm^{-1}$ at $\lambda = 456$ nm, 0.1 M TEAP, 25 °C). Solutions of mercury(II) perchlorate in acetonitrile were prepared by diluting a saturated aqueous solution of $Hg(ClO_4)_2$ at pH 1 with acetonitrile. The results of the kinetic experiments were not influenced by variation of the water content. No attempt was made to handle anhydrous $Hg(ClO_4)_2$ solutions.

The ionic strength in acetonitrile was maintained at 0.1 M with TEAP. No inert electrolyte was added in acetone to avoid ion-pairing. Nevertheless, the ionic strength was constant within an experimental series and defined by the total concentration of copper(I) perchlorate. It was shown that ion-pair formation is negligible in dilute solutions of $[Cu(dmp)_2]ClO_4$ in acetone[6] and acetonitrile.[7] The same is true for $[Cu(CH_3CN)_4]ClO_4$[8] and TEAP[9] in acetonitrile.

Equilibrium Measurements. Spectra for the determination of equilibrium constants were recorded using a Kontron Uvikon 820 UV–visible spectrophotometer equipped with 1-cm cuvettes thermostated at 25.0 ± 0.2 °C. Digital data were transferred directly from the spectrophotometer to an HP 1000 laboratory computer system. The spectra of the complexes permitted the calculation of the equilibrium constants by use of the SPECFIT program.[10] Typically, absorbance data at 50 wavelengths, spanning the region 380–580 nm, were used. The free ligands, biq and dmp, do not absorb at $\lambda > 360$ nm. The electrolyte TEAP contains traces of chloride ion. Analysis by ion chromatography yielded a concentration

---

(1) Margerum, D. W.; Cayley, G. R.; Weatherburn, D. C.; Pagenkopf, G. K. In *Coordination Chemistry, Vol. 2*; Martell, A. E., Ed.; ACS Monograph 174; American Chemical Society: Washington, DC, 1978; pp 77–80.

(2) Meyerstein, D. *Inorg. Chem.* **1975**, *14*, 1716.

(3) Hodges, H. L.; de Araujo, M. A. *Inorg. Chem.* **1982**, *21*, 3236.

(4) Lee, C. W.; Anson, F. C. *Inorg. Chem.* **1984**, *23*, 837.

(5) Frei, U. M.; Geier, G. *Inorg. Chem.* **1992**, *31*, 187.

(6) Miyoshi, K.; Tominaga, T.; Yamamoto, Y. *Chem. Lett.* **1973**, 47.

(7) Miyoshi, K. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 426.

(8) Yeager, H. L.; Kratochvil, B. *J. Phys. Chem.* **1969**, *73*, 1963.

(9) Yeager, H. L.; Kratochvil, B. *J. Phys. Chem.* **1969**, *73*, 471.

(10) (a) Gampp, H.; Maeder, M.; Meyer, C. J.; Zuberbühler, A. D. *Talanta* **1985**, *32*, 95. (b) Gampp, H.; Maeder, M.; Meyer, C. J.; Zuberbühler, A. D. *Talanta* **1985**, *32*, 257.

0020-1669/92/1331-3132$03.00/0

Table I. Logarithms of Equilibrium Constants[a] for Ligand-Substitution Reactions in Acetonitrile and Acetone at 25 °C

reaction		acetonitrile[b] L = biq	acetonitrile[b] L = dmp	acetone L = dmp[c]	acetone L = I^- [d]
$Cu^+ + L = CuL^+$	K_1	4.4 (0.1)	7.2 (0.3)		
$CuL^+ + L = CuL_2^+$	K_2	4.4 (0.1)	7.0 (0.3)		
$Cu(biq)_2^+ + L = Cu(biq)L^+ + biq$	K_4		3.1 (0.3)	3.74 (0.05)	≈1.2
$Cu(biq)L^+ + L = CuL_2^+ + biq$	K_5		2.6 (0.3)	3.27 (0.05)	≈0.8
$2Cu(biq)L = Cu(biq)_2^+ + CuL_2^+$	K_6		−0.6 (0.3)	−0.5 (0.05)	≈−0.3

[a] Uncertainty in parentheses. [b] $I = 0.1$ M (TEAP). [c] Reference 5; $I \approx 5 \times 10^{-5}$ M. [d] The ionic strength was not constant, $[CuClO_4]_t = 6 \times 10^{-5}$ M, and $2 \times 10^{-5} \leq [TEAI]_t \leq 5 \times 10^{-4}$ M.

range of $0.01 \leq [Cl^-] \leq 0.07$ mol %. Careful checks were made to see whether the presence of Cl^- interfered with the equilibrium measurements in CH_3CN. For this purpose the influence of variable $[Cl^-]$ was determined for different $[Cu]_t$ and $[biq]_t$ by measuring the concentration of $Cu(biq)_2^+$ directly from the spectra at 546 nm. The stability constants used for the chloro complexes are given elsewhere.[11] Comparison of the calculated and experimental absorbances at 546 nm showed that the influence of Cl^- in the concentration range used is small and does not exceed the experimental error given in Table I. In the Cu(I)/dmp system, the influence of Cl^- is even smaller and falls within the experimental margin of error.

Kinetic Measurements. A Durrum D110 stopped-flow spectrophotometer was used for the kinetic measurements. The previously described procedure for data acquisition and evaluation of the k_{obsd} values was used.[5] Reported k_{obsd} values are the average of at least four replicates. For the investigation of the Lewis-base assistance of the diimine-substitution reactions, a solution of $[Cu(biq)_2]ClO_4$ (typically ca. 10^{-4} M) was mixed with a solution of the excess component, dmp or phen, which established pseudo-first-order conditions. Both starting solutions contained the nucleophile L = CH_3CN or I^- and excess biq to prevent the formation of mixed-ligand complexes of the type $Cu(biq)L_x^+$. The $Cu(biq)_2^+$ solutions with excess biq yielded identical absorption spectra in the presence and absence of CH_3CN, which indicates that in the equilibrium state no detectable amounts of mixed-ligand complexes are formed under the experimental conditions used. Iodide solutions, which were saturated with biq ([biq] = 0.0018 M), contained approximately 5% Cu(biq)I. However, this small amount of mixed-ligand complex did not interfere with the reactions under observation because it reacted to form $Cu(biq)(dmp)^+$ within the mixing time of the experiments. Therefore, under the concentration conditions used, the nucleophile L = I^- or CH_3CN can be considered as being coordinated only in short-lived intermediates.

Results

Equilibrium Studies. (A) The Copper(I)/biq/dmp System in Acetonitrile. The stepwise complex formation of Cu^+ with NN = biq and dmp in acetonitrile, eqs 1 and 2, was investigated by

$$Cu^+ + NN \rightleftharpoons Cu(NN)^+ \qquad (1)$$

$$Cu(NN)^+ + NN \rightleftharpoons Cu(NN)_2^+ \qquad (2)$$

spectrophotometric titrations.[12,13] Figure 1 shows a typical series of spectra which were obtained by titrating a solution containing a constant [biq] with $CuClO_4$. The stability constants K_1 and K_2 were calculated using the program SPECFIT;[10] cf. Table I. The spectra of the complexes are shown in Figure 2. The direct spectrophotometric determination of K_1 and K_2 with NN = dmp is only approximate because the coordination tendency of this ligand is so strong. However, an exact equilibrium constant for eq 3,

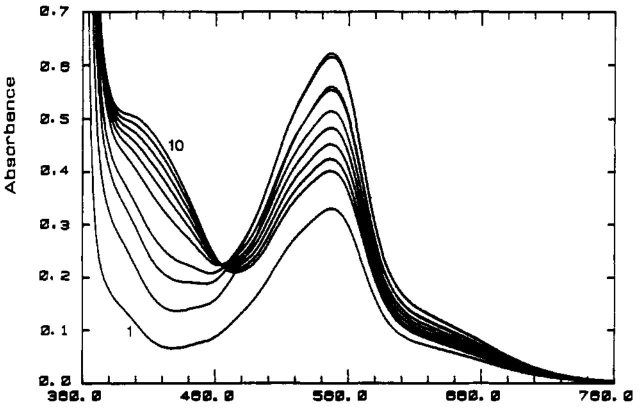


Figure 1. Equilibrium spectra of the Cu(I)/biq system in acetonitrile (I = 0.1 M (TEAP), 25 °C). $[biq]_t = 3.02 \times 10^{-4}$ M. Curves 1–10 are for $[Cu]_t = 6.35 \times 10^{-5}$, 1.31×10^{-4}, 1.95×10^{-4}, 2.56×10^{-4}, 4.10×10^{-4}, 5.17×10^{-4}, 6.18×10^{-4}, 7.22×10^{-4}, 8.40×10^{-4}, and 9.57×10^{-4} M.

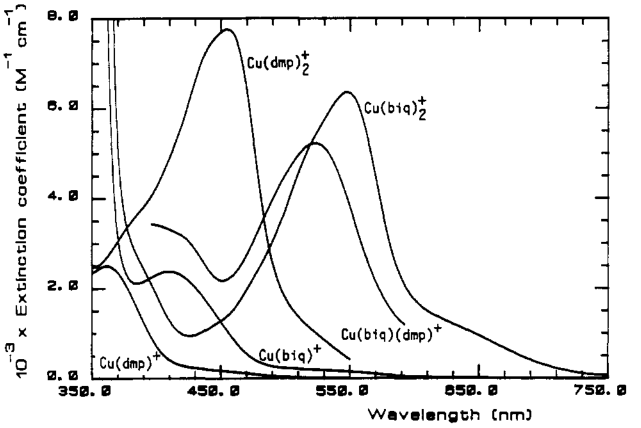


Figure 2. Spectra of $Cu(biq)^+$, $Cu(biq)_2^+$, $Cu(dmp)^+$, $Cu(dmp)_2^+$, and $Cu(biq)(dmp)^+$ (calculated) in acetonitrile (I = 0.1 M (TEAP), 25 °C).

$$Cu(dmp)_2^+ + Cu^+ \rightleftharpoons 2Cu(dmp)^+ \qquad (3)$$

$K_3 = K_1/K_2$, could be determined and gave log $K_3 = 0.18 \pm 0.05$. Moreover, the equilibrium constants for the reactions 4 and 5,

$$Cu(biq)_2^+ + dmp \rightleftharpoons Cu(biq)(dmp)^+ + biq \qquad (4)$$

$$Cu(biq)(dmp)^+ + dmp \rightleftharpoons Cu(dmp)_2^+ + biq \qquad (5)$$

K_4 and K_5, respectively, could be determined; cf. Figure 3 and Table I. The overall stability constant for $Cu(dmp)_2^+$ was calculated from the relation log β_2(dmp) = log β_2(biq) + log K_4 + log K_5 = 14.5 ± 0.3. Thus the values of K_1 and K_2 could be obtained in combination with K_3; cf. Table I. The calculated spectrum for the mixed-ligand complex $Cu(biq)(dmp)^+$ in Figure 2 agrees very well with that of a solution of $[Cu(biq)(dmp)]ClO_4$ in acetone. In acetonitrile, the spectrum of $[Cu(biq)(dmp)]ClO_4$ could not be obtained because the ligand-disproportionation reaction (6) reaches an equilibrium state within the time required

$$2Cu(biq)(dmp)^+ \rightleftharpoons Cu(biq)_2^+ + Cu(dmp)_2^+ \qquad (6)$$

to dissolve the sample. In acetone, however, the half-life of reaction 6 is approximately 10 min, which easily allows the extrapolation to time zero.[5] The equilibrium constant for reaction 6 is similar in both solvents and agrees fairly well with the statistically expected value (log K = −0.6).[14] It is notable that

---

(11) Ahrland, S.; Nilsson, K.; Tagesson, B. *Acta Chem. Scand.* **1983**, *A37*, 193.

(12) Ayranci, H.; Daul, C.; Zobrist, M.; von Zelewsky, A. *Helv. Chim. Acta* **1975**, *58*, 1732.

(13) Atkins, C. E.; Park, S. E.; Blasak, J. A.; Mc Millin, D. R. *Inorg. Chem.* **1984**, *23*, 569.

(14) De Witt, R.; Watters, J. I. *J. Am. Chem. Soc.* **1954**, *76*, 3810.

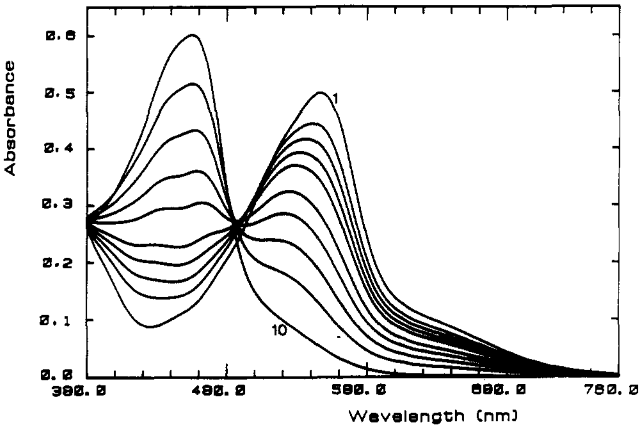


Figure 3. Equilibrium spectra of the Cu(I)/biq/dmp system in acetonitrile (I = 0.1 M (TEAP), 25 °C). $[\mathrm{Cu}]_t = 8.05 \times 10^{-5}$ M; $[\mathrm{biq}]_t = 1.63 \times 10^{-3}$ M. Curves 1–10 are for 0, 2.64×10^{-5}, 4.09×10^{-5}, 5.44×10^{-5}, 6.71×10^{-5}, 9.03×10^{-5}, 1.08×10^{-4}, 1.28×10^{-4}, 1.54×10^{-4}, and 4.57×10^{-4} M $[\mathrm{dmp}]_t$.

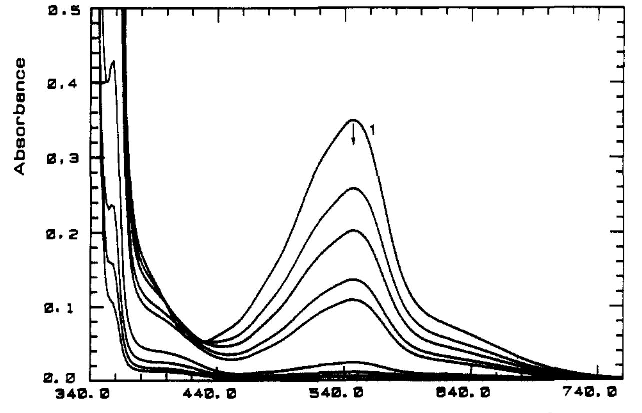


Figure 4. Equilibrium spectra of the Cu(I)/biq/I⁻ system in acetone (25 °C). $[\mathrm{Cu}]_t = 5.90 \times 10^{-5}$ M; $[\mathrm{biq}]_t = 2.13 \times 10^{-4}$ M. Curves 1–9 are for 0, 2.20×10^{-5}, 4.23×10^{-5}, 6.66×10^{-5}, 7.94×10^{-5}, 1.82×10^{-4}, 2.68×10^{-4}, 3.74×10^{-4}, and 5.31×10^{-4} M $[\mathrm{I}^-]_t$.

the equilibrium constants for substitution reactions 4 and 5 are of the same orders of magnitude in acetonitrile and acetone.

The stability constants for the Cu(I) complexes with biq in acetonitrile are comparable with those obtained from a potentiometric study, i.e. $\log K_1 = 4.0$ and $\log K_2 = 4.15$.[15] A previous spectrophotometric study of the dmp complexes gave an order of magnitude of the stability constants as $\log K_1 \approx 6$ and $\log K_2 \approx 5$.[13] The reason for the disagreement with our values is probably the absence of an inert electrolyte in the earlier study.

(B) The Copper(I)/biq/Iodide System in Acetone. The interpretation of the acceleration of the diimine-substitution reaction by iodide (see kinetic studies) required some knowledge of the equilibria in the Cu(I)/biq/I⁻ system. Therefore, ligand-substitution reactions 7 and 8 were studied spectrophotometrically.

$$\mathrm{Cu(biq)_2}^+ + \mathrm{I}^- \rightleftharpoons \mathrm{Cu(biq)I} + \mathrm{biq} \qquad (7)$$

$$\mathrm{Cu(biq)I} + \mathrm{I}^- \rightleftharpoons \mathrm{CuI_2}^- + \mathrm{biq} \qquad (8)$$

A typical series of spectra is shown in Figure 4. It should be noted that $\mathrm{CuI_2}^-$ does not absorb in the wavelength range used here. In these experiments, no inert electrolyte was present and the concentrations of the ionic species were not kept constant ($[\mathrm{Cu}]_t = 5.9 \times 10^{-5}$ M; $2 \times 10^{-5} < [\mathrm{I}]_t < 5 \times 10^{-4}$ M). For the analysis of the data, it was assumed that no other complexes, e.g. $\mathrm{CuI_3}^{2-}$ and $\mathrm{Cu(biq)I_2}^-$, were present under these experimental conditions. A similar assumption was made in an analogous study in acetone with $\mathrm{Cu(phen)_2}^+$ and NCS⁻.[16] Comparison of the overall equilibrium constant in acetone ($\log K_7 + \log K_8 = 2$) with that in acetonitrile ($\log \beta_2(\mathrm{CuI_2}^-) - \log \beta_2(\mathrm{Cu(biq)_2}^+) = -2.63$)[11] clearly shows that coordination of I⁻ is much stronger in acetone because of the smaller dielectric constant of this solvent. It should also be mentioned that ion-pair formation of $[\mathrm{Cu(dmp)_2}]\mathrm{ClO_4}$ in acetone[6] and acetonitrile,[7] as well as that of tetraethylammonium iodide in acetone,[17] is negligible within the range of concentrations used.

Kinetic Studies. (A) Copper(I)–Diimine Complexes in Acetonitrile. Preliminary experiments showed that the rates of the complex-formation reactions of solvated Cu⁺ with biq, phen, and dmp and those of substitution reactions 4 and 5 are too fast to study with our stopped-flow apparatus. Nevertheless, it was possible to obtain some information on the substitution lability of Cu(I) in acetonitrile by monitoring the dissociation of $\mathrm{Cu(dmp)_2}^+$ according to eqs 9 and 10. In a 20–1000-fold excess

$$\mathrm{Cu(dmp)_2}^+ + M^{z+} \underset{k_2}{\overset{k_{-2}}{\rightleftharpoons}} \mathrm{Cu(dmp)}^+ + \mathrm{dmp} + \mathrm{M}^{z+} \qquad (9)$$

$$\mathrm{Cu(dmp)}^+ + \mathrm{dmp} + \mathrm{M}^{z+} \xrightarrow{k_\mathrm{M}} \mathrm{Cu(dmp)}^+ + \mathrm{M(dmp)}^{z+} \qquad (10)$$

of $[\mathrm{M}^{z+}]$, M^{z+} = Cu⁺ or Hg²⁺, the rate is independent of the nature and concentration of M^{z+}. With Hg²⁺, the overall reaction (11) goes completely to the right. Reactions 9 and 10 could be

$$\mathrm{Cu(dmp)_2}^+ + \mathrm{Hg}^{2+} \rightarrow \mathrm{Cu}^+ + \mathrm{Hg(dmp)_2}^{2+} \qquad (11)$$

observed independently from the dissociation of the second dmp ligand by monitoring the reactions at λ = 456 nm, where the absorbances of $\mathrm{Cu(dmp)}^+$ and Cu⁺ are negligible. It was shown experimentally that $k_\mathrm{M}[\mathrm{M}^{z+}] \gg k_{-2}$ and that the rate law is given by eq 12, with $k_\mathrm{obsd} = k_{-2}$. A linear plot gave the value $k_{-2} = 3.8 \pm 0.2$ s⁻¹.

$$v = -\mathrm{d}[\mathrm{Cu(dmp)_2}^+]/\mathrm{d}t = k_\mathrm{obsd}[\mathrm{Cu(dmp)_2}^+] \qquad (12)$$

This result is in good agreement with an ¹H and ¹³C NMR study which gave $k_{-2} = 4.5$ s⁻¹.[18] A decomplexation study of $\mathrm{Cu(dmp)_2}^+$ with CN⁻ in acetonitrile/water (9:1) solvent gave a very similar value of $k_{-2} = 4.8$ s⁻¹.[19] From $K_2 = 1 \times 10^7$ M⁻¹, we calculated $k_2 = 4\ (\pm 2) \times 10^7$ M⁻¹ s⁻¹. The kinetics of the dissociation of $\mathrm{Cu(dmp)}^+$ could not be studied using a method analogous to that expressed by eqs 9 and 10, because the rates proved to be dependent on $[\mathrm{M}^{z+}]$. The large contribution of the $[\mathrm{M}^{z+}]$-dependent pathway did not allow us to evaluate the rate constant for the direct dissociation. Thus, at present, $k_2 = 4 \times 10^7$ M⁻¹ s⁻¹ represents the only available value for the substitution lability of Cu(I) in acetonitrile.

(B) Ligand Substitutions of Bis(diimine)copper(I) Complexes in Acetone/Acetonitrile Mixtures. It was shown earlier that, in acetone, the kinetics of reactions 13 and 14 for NN = dmp and

$$\mathrm{Cu(biq)_2}^+ + \mathrm{NN} \rightleftharpoons \mathrm{Cu(biq)(NN)}^+ + \mathrm{biq} \qquad (13)$$

$$\mathrm{Cu(biq)(NN)}^+ + \mathrm{NN} \rightleftharpoons \mathrm{Cu(NN)_2}^+ + \mathrm{biq} \qquad (14)$$

phen could be studied by means of the stopped-flow method.[5] Substitution reaction 13 proceeds via two parallel pathways: a direct path via an outer-sphere complex as an intermediate and a solvent-assisted path which, however, is of minor importance; cf. upper two pathways in Scheme I. Reactions 13 and 14 are

---

(15) Leupin, P. Dissertation No. 819, Université de Fribourg, 1980.

(16) Kitagawa, S.; Munakata, M. *Kinki Daigaku Rikogakubu Kenkin Hokoku* **1986**, *22*, 73.

(17) Evans, D. F.; Thomas, J.; Nadas, J. A.; Matesich, M. A. *J. Phys. Chem.* **1971**, *75*, 1714.

(18) Ochsenbein, U. Dissertation No. 828, Université de Fribourg, 1981.

(19) Albrecht-Gary, A. M.; Saad, Z.; Dietrich-Buchecker, C. O.; Sauvage, J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3205.

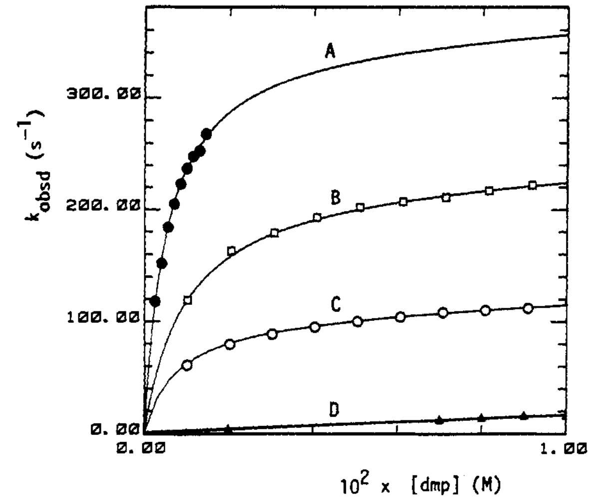


Figure 5. Dependence of the pseudo-first-order rate constants k_{obsd} (s^{-1}) on the concentration of dmp for the reaction with $Cu(biq)_2^+$ in acetone in the presence of acetonitrile at 25 °C (biq excess = 1×10^{-3} M): (A) [CH_3CN] = 3 M, $[Cu]_t = 2.5 \times 10^{-5}$ M; (B) [CH_3CN] = 2 M, $[Cu]_t = 1 \times 10^{-4}$ M; (C) [CH_3CN] = 1 M, $[Cu]_t = 1 \times 10^{-4}$ M; (D) data from ref 5, no acetonitrile added. The curves are calculated (eq 15).

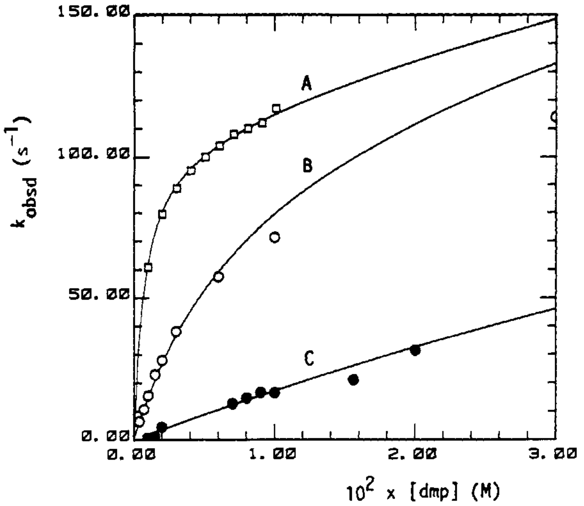
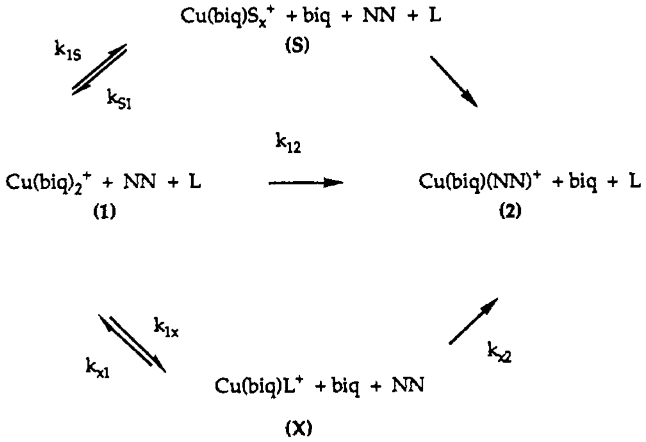


Figure 6. Dependence of the pseudo-first-order rate constants k_{obsd} (s^{-1}) on the concentration of dmp for the reaction with $Cu(biq)_2^+$ in acetone in the presence of 1 M CH_3CN and variable concentrations of biq at 25 °C: (A) biq excess = 1×10^{-3} M, $[Cu]_t = 1 \times 10^{-4}$ M; (B) biq excess = 1×10^{-2} M, $[Cu]_t = 4 \times 10^{-5}$ M; (C) data from ref 5, no CH_3CN added, biq excess $\leq 1 \times 10^{-3}$ M. The curves are calculated (eq 15) with the values of the best fit for both biq concentrations; cf. Table II.

Scheme I



accelerated by adding acetonitrile. The overall reaction goes completely to the right. In the present study, we investigated the influence of acetonitrile on reaction 13 for NN = dmp and phen by monitoring the system at the isosbestic point given by Cu(biq)(NN)$^+$ and $Cu(NN)_2^+$ (λ = 482 nm for NN = dmp, λ = 480 nm for NN = phen). An example with dmp is given in Figure 5, where the rates increase with increasing [CH_3CN]. For a given [CH_3CN], a limiting value for k_{obsd} is reached with increasing [dmp]. In the corresponding kinetic study in pure acetone, saturation is observed at much larger [dmp] (>0.1 M).[5] Saturation kinetics are indicative of a pathway involving an intermediate. To characterize this intermediate, X, the concentration of the added excess biq was varied. Figure 6 clearly shows that, for a fixed [CH_3CN], the rates decrease with increasing [biq]. This indicates that one can exclude intermediates in which both biq ligands are coordinated or a biq ligand is bound as a unidentate ligand. Most likely, the intermediate X contains only one biq ligand, the other being completely dissociated; cf. Cu(biq)$(CH_3CN)_x^+$, lower pathway in Scheme I. The intermediate X is not detectable under equilibrium conditions (see Experimental Section). Therefore, a steady-state assumption can be applied for it. Consequently, in the presence of CH_3CN, ligand-substitution reaction 13 under pseudo-first-order irreversible conditions ([NN], [biq], [CH_3CN] ≫ $[Cu]_t$) can be described by the rate law given in eq 15.

$$k_{obsd} = k_{obsd(12)} + k_{obsd(1X2)} = k_{12}[NN] + k_{1X}k_{X2}[NN]/(k_{X1}[biq] + k_{X2}[NN]) \quad (15)$$

Since relatively small concentrations of NN were used throughout this work, the rates of the direct path ($1 \rightarrow 2$, middle pathway in Scheme I) can be described by the term $k_{obsd(12)} = k_{12}[NN]$ with $k_{12} = 1.8 \times 10^3$ M^{-1} s^{-1}.[5] Under the experimental conditions used (cf. Figures 5 and 6), the solvent-assisted path contributes less than 1% to k_{obsd} for [biq] = 10^{-3} M, and therefore, the corresponding term has been omitted in eq 15. Thus the value for the acetonitrile-assisted pathway ($k_{obsd(1X2)}$) can be calculated by subtracting $k_{obsd(12)}$ from the experimental k_{obsd}. For evaluation of the rate constants (cf. Table II), the reciprocal form of $k_{obsd(1X2)}$ was used according to eq 16, where $q = 1/k_{1X}$ and $p = k_{X1}[biq]/k_{1X}k_{X2}$.

$$1/k_{obsd(1X2)} = q + p/[NN] \quad (16)$$

For [biq] = 10^{-2} M, a small rate retardation is observed which is just at the limit of the reproducibility of the measurements (cf. curve B in Figure 6 and uncertainty for k_{1X}, Table II). Here the solvent path is no longer completely negligible.[5]

The increasing values of k_{1X} with increasing [CH_3CN] suggest that the step $1 \rightarrow X$ is first order in [$Cu(biq)_2^+$] and [CH_3CN]. However, experimental first-order rate constants k_{1X} are not exactly proportional to [CH_3CN]. Calculated second-order rate constants k_{1X} and the values for k_{X2}/k_{X1} show slight deviations for the various [CH_3CN]. This is not surprising if one considers the range of [CH_3CN] used, namely 1–3 M. The assumption of a constant medium may not be valid. To account for this uncertainty, we calculated the curves in Figure 5 with the parameters for each individual [CH_3CN] as given in Table II. A mean value for the second-order rate constant k_{1X} was calculated from the experiments with the lower [CH_3CN].

The accelerating effect of acetonitrile led us to tentatively conclude that extrapolation from acetonitrile containing acetone to pure acetonitrile as a solvent could be of interest for the understanding of the pronounced substitution lability in acetonitrile (see part A). Under the assumption of first-order dependence in [CH_3CN], one can calculate $k_{obsd} \approx 2 \times 10^3$ s^{-1} for [dmp] = 10^{-2} M and [biq] = 10^{-3} M. A reaction with such a large rate constant is too fast for the stopped-flow time scale, in agreement with experiments showing that reactions 13 and 14, in acetonitrile, are completed within the deadtime of the apparatus. Of course, this agreement does not definitely prove the validity of the extrapolation of kinetic rate constants.

A consequence of the acetonitrile-assisted path $1 \rightarrow X \rightarrow 2$ is that the first step (cf. k_{1X} in Scheme I) represents the substitution

Table II. Rate Constants[a] for the Catalytic Pathway for the Reaction $Cu(biq)_2^+ + dmp \rightarrow Cu(biq)(dmp)^+ + biq$ in the Presence of Unidentate Ligands L in Acetone at 25 °C

L	$[biq]_t$, M	$[L]_t$, M	k_{1X}, s^{-1}	k_{X2}/k_{X1}	k_{1X}, $M^{-1}\,s^{-1}$
CH_3CN[b]	1×10^{-3} [d]	1	108 (3)	1.23 (0.03)	108 (3)
	1×10^{-2} [d]	1	92 (27)	1.75 (0.6)	92 (27)
	1×10^{-3}	2	227 (3)	1.06 (0.02)	113 (2)
	1×10^{-3}	3	357 (3)	1.94 (0.02)	119 (2)
I^- [c]	1.8×10^{-2}	2×10^{-4}	123 (30)	55 (21)	$6\ (\pm 2) \times 10^5$

[a] Estimated error in parentheses. [b] Ionic strength is defined by $[Cu(NN)_2ClO_4]_t$ ($\approx 5 \times 10^{-5}$ M). [c] Ionic strength is defined by $[Cu(NN)_2ClO_4]_t$ ($\approx 5 \times 10^{-5}$ M) and $[TEAI]_t$ ($= 2 \times 10^{-4}$ M). [d] The best fit for both biq concentrations yields $k_{1X} = 105\ s^{-1}$ and $k_{X2}/k_{X1} = 1.4$; cf. Figure 5.

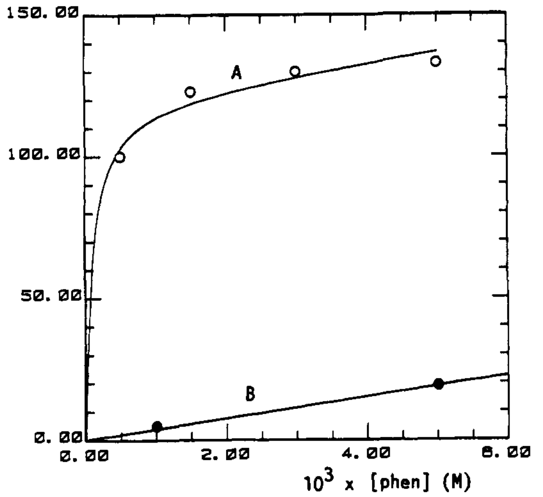


Figure 7. Dependence of the pseudo-first-order rate constants k_{obsd} (s^{-1}) on the concentration of phen for the reaction with $Cu(biq)_2^+$ in acetone at 25 °C: (A) $[CH_3CN] = 1$ M, biq excess $= 4.6 \times 10^{-4}$ M, $[Cu]_t = 5 \times 10^{-5}$ M, calculated curve (eq 15); (B) data from ref 5, no CH_3CN added.

of biq by CH_3CN and should be independent of the entering ligand NN. Therefore, we examined substitution reaction 13 with NN = phen. The experimental data were analyzed in an analogous way. The resulting values are $k_{1X} = 120 \pm 15\ s^{-1}$ and $k_{X2}/k_{X1} = 5 \pm 2$. The calculated curve in Figure 7 is based on eq 15 and also takes $k_{12} = 3.8 \times 10^3\ M^{-1}\,s^{-1}$ into account.[5] The resulting k_{1X}(phen) is in very good agreement with k_{1X}(dmp) for the same $[CH_3CN]$. This shows that the formation of the intermediate X is indeed independent of NN.

Finally, it must be mentioned that the number x of coordinated CH_3CN ligands in the intermediate complex $Cu(biq)(CH_3CN)_x^+$ cannot be determined from the kinetics. The simplest case with $x = 1$ seems probable and would be analogous to the recently determined structure of $[Cu(dmp)(CH_3CN)]ClO_4$.[20]

(C) Ligand Substitutions of Bis(diimine)copper(I) Complexes in the Presence of Iodide in Acetone. Another consequence of the acetonitrile-assisted path is the possibility of accelerating reaction 13 by addition of another nucleophile L. A good candidate is iodide in acetone, because it forms much stronger complexes than CH_3CN and dmp can easily substitute I^- in Cu(biq)I; cf. Table I. The kinetics were monitored at λ = 482 nm. Figure 8 shows that the presence of small $[I^-]$ accelerates reaction 13. Due to the strong coordination tendency of I^-, one has to increase the excess concentration of biq in order to minimize the concentration of the mixed-ligand complex Cu(biq)I. Thus, it was not possible to vary the biq concentration in a rigorous way. Therefore, one cannot definitely exclude the occurrence of Cu(biq)(biq*)I as an intermediate X where biq* is unidentate. However, X is unlikely to have such a structure, as it is bulkier than $Cu(biq)_2^+$ and could not account for the large catalytic effect. The rate parameters are listed in Table II. The relatively large uncertainty for k_{1X} is a consequence of the large excess concentration of biq. As already mentioned, one cannot exclude the possibility that, to a small extent, the reaction follows a solvent path; cf. upper path in Scheme I.[5]

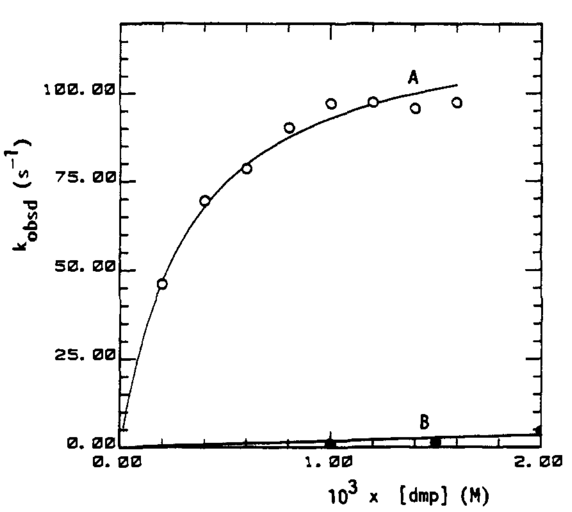


Figure 8. Dependence of the pseudo-first-order rate constants k_{obsd} (s^{-1}) on the concentration of dmp for the reaction with $Cu(biq)_2^+$ in acetone in the presence of I^- at 25 °C: (A) $[I^-]_t = 2 \times 10^{-4}$ M, $[Cu]_t = 2 \times 10^{-5}$ M, biq excess $= 1.8 \times 10^{-3}$ M, calculated curve (eq 15); (B) data from ref 5, no I^- added.

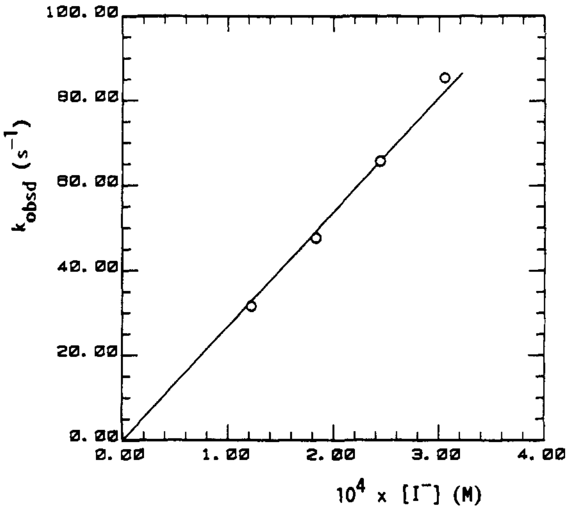


Figure 9. Resolution of k_{I^-} ($M^{-1}\,s^{-1}$) from the dependence of k_{obsd} (s^{-1}) on the concentration of I^- in acetone at 25 °C. $[Cu]_t = 1 \times 10^{-5}$ M; $I = 5 \times 10^{-3}$ M (TEAP).

The proposed mechanism for the Lewis-base-catalyzed pathway (cf. Scheme I) could be tested otherwise, namely by investigating the step 1 → X separately. Thus we measured the kinetics of reaction 7 by monitoring it at the absorption maximum of $Cu(biq)_2^+$ (λ = 546 nm). Since Cu(biq)I and CuI_2^- do not absorb at this wavelength, the decrease of absorbance corresponds directly to the formation of the Cu(biq)I complex. For pseudo-first-order irreversible conditions ($[I^-] \gg [Cu(biq)_2^+]$), the rate law is described by $k_{obsd} = k_{I^-}[I^-]$. The results are shown in Figure 9. From the slope of the straight line one obtains $k_{I^-} = (2.7 \pm 0.5) \times 10^5\ M^{-1}\,s^{-1}$. The agreement with $k_{1X} = 6 \times 10^5\ M^{-1}\,s^{-1}$ is satisfactory if one considers the different experimental conditions used: reaction 7 was investigated at constant ionic strength, $I = 5 \times 10^{-3}$ M (TEAP), whereas the iodide-catalyzed reaction (13) was studied in the presence of 2×10^{-4} M tetraethylammonium iodide (it is known that the activity of I^- is decreased significantly in the presence of tetraethylammonium ions due to ion-pair formation[17]).

---

(20) Munakata, M.; Maekawa, M.; Kitagawa, S.; Matsuyama, S.; Madusa, H. *Inorg. Chem.* **1989**, *28*, 4300.

Table III. Rate and Equilibrium Constants of Ligand-Substitution Reactions with Bis(diimine)copper(I) Complexes in Acetone at 25 °C

reaction	k, $M^{-1}\,s^{-1}$	log K	ionic strength, M
$Cu(dmp)^+ + dmp \rightarrow Cu(dmp)_2^+$	4×10^7 [a]	7.0[a]	0.1[a]
$Cu(biq)_2^+ + dmp \rightarrow Cu(biq)(dmp)^+ + biq$	1.8×10^3 [b]	3.7[b]	$\approx 5 \times 10^{-5}$
$Cu(biq)_2^+ + phen \rightarrow Cu(biq)(phen)^+ + biq$	3.8×10^3 [b]	2.2[b]	$\approx 5 \times 10^{-5}$
$Cu(biq)_2^+ + CH_3CN \rightarrow Cu(biq)(CH_3CN)^+ + biq$	1×10^2 [c]	≈ -4.4[d]	$\approx 5 \times 10^{-5}$
$Cu(biq)_2^+ + I^- \rightarrow Cu(biq)I + biq$	6×10^5 [e]	≈ 1.2	$\approx 2 \times 10^{-4}$
$Cu(biq)I + dmp \rightarrow Cu(biq)(dmp)^+ + I^-$	2×10^6 [f]	≈ 2.5	$\approx 2 \times 10^{-4}$
$Cu(biq)(CH_3CN)^+ + dmp \rightarrow Cu(biq)(dmp)^+ + CH_3CN$	$\approx 3 \times 10^6$ [g]		$\approx 5 \times 10^{-5}$
$Cu(biq)(CH_3CN)^+ + phen \rightarrow Cu(biq)(phen)^+ + CH_3CN$	$\approx 1 \times 10^7$ [h]		$\approx 5 \times 10^{-5}$

[a] In acetonitrile [b] Reference 5. [c] Equal to k_{1X}; cf. Table II. [d] Value for acetonitrile solution; cf. Table I. [e] Equal to k_{1X}; cf. Table II. [f] Equal to k_{X2}; calculated with $k_{X2}/k_{X1} = 55$ and k_{X1} from $k_{1X}/k_{X1} = 16$; cf. Table I and footnote *e*. [g] Equal to k_{X2}; calculated with $k_{X2}/k_{X1} = 1.4$ and $k_{X1} = 2.5 \times 10^6\ M^{-1}\,s^{-1}$; cf. footnotes *c* and *d*. [h] Equal to k_{X2}; calculated with $k_{X2}/k_{X1} = 5$ and $k_{X1} = 2.5 \times 10^6\ M^{-1}\,s^{-1}$; cf. footnotes *c* and *d*.

Discussion

As mentioned in a recent investigation,[5] we found that, in acetone, substitution reactions of $Cu(biq)_2^+$ with bidentate diimine ligands, eq 13, follow two parallel pathways: a direct ligand path and a solvent-assisted path (cf. upper two pathways in Scheme I). The present investigation shows that these substitution reactions are subject to Lewis-base catalysis. Potential unidentate ligands L promote the reaction by replacing one biq ligand, forming an intermediate mixed-ligand complex $Cu(biq)L_x^+$. Afterwards, L is rapidly substituted by a diimine ligand. This sequence is more favorable than the direct reaction, **1** → **2** in Scheme I. Every rate constant could be evaluated for the catalyzed pathway **1** ⇌ X → **2**. These values are given in Table III. For $L = I^-$, the experimental value for k_{1X} is $6 \times 10^5\ M^{-1}\,s^{-1}$. For the reverse reaction, one obtains $k_{X1} = k_{1X}/K_7 = 3.9 \times 10^4\ M^{-1}\,s^{-1}$, because the equilibrium constant for **1** ⇌ X is identical with that for reaction 7, log $K \approx 1.2$. Using the quotient $k_{X2}/k_{X1} = 55$, we calculate $k_{X2} = 2 \times 10^6\ M^{-1}\,s^{-1}$. The catalytic effect of I^- is obvious from a comparison with the much smaller rate constant for the direct pathway, $k_{12} = 1.8 \times 10^3\ M^{-1}\,s^{-1}$. The main reason for the lower efficiency of $L = CH_3CN$ as catalyst is the much smaller value for the second-order rate constant k_{1X} ($1 \times 10^2\ M^{-1}\,s^{-1}$). This is understandable if one takes into account that, in contrast to the case where $L = I^-$, for $L = CH_3CN$ the reaction **1** → X is endergonic. The corresponding equilibrium constant can be estimated by assuming the value in pure acetonitrile, $-\log K_2 = -4.4$ (cf. Table I). Under this assumption, one can calculate the rate constant for the exergonic direction, $k_{X1} = 2.5 \times 10^6\ M^{-1}\,s^{-1}$. By utilizing the quotient $k_{X2}/k_{X1} = 1.4$, one obtains $k_{X2} = 3 \times 10^6\ M^{-1}\,s^{-1}$. It is not surprising that the substitution of CH_3CN by dmp is faster than that of I^-, because the former is a better leaving group. However, this slower rate for I^- does not affect the catalytic activity, because the quotient k_{X2}/k_{X1} is actually more relevant. For $L = I^-$, the more favorable value, namely $k_{X2}/k_{X1} = 55$, is due to the fact that the forward step, X → **2**, is exergonic, whereas the reverse step, X → **1**, is endergonic. On the other hand, for $L = CH_3CN$ both rate constants correspond to exergonic reactions.

A prerequisite for establishing the catalytic effect, as found in this work, is that acetone be a poorly coordinating solvent, a possible solvent-assisted pathway therefore being of minor importance. The Lewis-base-induced pathway provides a kind of substitute for this pathway. This can be recognized by looking at the role of $L = CH_3CN$. The extrapolation of the concentration dependence of the kinetics to pure acetonitrile yields for k_{1X} a value of $\approx 2 \times 10^3\ s^{-1}$. In this solvent, the rate constant for the reaction of $Cu(dmp)(CH_3CN)_x^+$ with dmp is $k_2 = 4 \times 10^7\ M^{-1}\,s^{-1}$. Thus, it is obvious that the solvent-assisted pathway makes a very significant contribution to substitution reactions similar to eqs 13 and 14. This substitution lability actually prevents the application of the stopped-flow method.

It is probable that in noncoordinating solvents, similar Lewis-base-induced substitution reactions are possible. In an ^1H, ^{13}C, and ^{63}Cu NMR study, Schlaepfer and Ochsenbein[18] found that, in chloroform, the ligand-exchange reactions of some bis(diimine)copper(I) complexes are faster in the presence of acetonitrile or pyridine. Palmer and Wild,[21] in a synthetic study of tetrahedral Au(I) complexes with bidentate phosphines, found that, in dichloromethane, the rates of ligand-redistribution reactions are dependent on the type of counterion. With hexafluorophosphate, the reactions are very slow whereas, with bromide, a significant acceleration occurs. Bromide obviously behaves as a better nucleophile toward Au(I).

The occurrence of Lewis-base-induced ligand-substitution reactions at tetrahedral Cu(I) suggests that an associative activation mode is preferred. It is obvious that a five-coordinate transition-state complex is much more easily formed with a unidentate ligand than with a rigid bidentate ligand. A closer look at the various rate constants in Table III shows that the type of ligand dependence is in line with an I_a mechanism. The reactions of $Cu(biq)_2^+$ with bidentate ligands, too, may indicate an associative mechanism, as the reaction with phen is faster than that with bulkier dmp.

All the above mentioned rate constants are clearly smaller than those found for the complex formation of Cu^+ with fumarate and maleate in aqueous solution, where these reactions are diffusion controlled.[2] It is interesting to compare the substitution lability of these tetrahedral Cu(I) complexes with that of similar complexes of the d^{10} center Hg(II). The reactions of $Hg(bpy)^{2+}$ and $Hg(phen)_2^{2+}$ with the OH^- ion in aqueous solution are nearly diffusion controlled[22] whereas the comparable reaction of $Cu(biq)_2^+$ with the I^- ion in acetone is almost 4 orders of magnitude slower. Formation of $Cu(dmp)_2^+$ in acetonitrile ($k_2 = 4 \times 10^7\ M^{-1}\,s^{-1}$) is also much slower than the corresponding diffusion-controlled formation of $Hg(bpy)_2^{2+}$ and of $Hg(phen)_2^{2+}$ in aqueous solution.[22] The extreme substitution lability of Hg(II) is probably a consequence of the fact that coordination expansion is easily possible for the transition state and the ground state of Hg(II). Thus with phen and bpy even 1:3 complexes exist[22] whereas similar Cu(I) complexes with coordination number 6 are not known. On the other hand, Cu(I) complexes with the unusual coordination number 5 have been known for a few years, in particular with N-ligand atoms.[23] Very recently, the structure of a complex with a quinquedentate ligand was determined in the solid state and in solution.[24] This shows that an associative activation mode for substitution reactions with tetrahedral Cu(I) complexes is not unusual even if this activation mode is less feasible than with Hg(II).

Acknowledgment. We are greatly indebted to Prof. L. M. Venanzi for helpful discussions. This work was supported by grants from the Swiss National Science Foundation (Project Nos. 20-5223.87 and 20-26219.89).

---

(21) Palmer, J. A. L.; Wild, S. B. *Inorg. Chem.* **1983**, *22*, 4054.
(22) Gross, H.; Geier, G. *Inorg. Chem.* **1987**, *26*, 3044.
(23) Goodwin, J. A.; Wilson, L. J.; Stanbury, D. M.; Scott, R. A. *Inorg. Chem.* **1989**, *28*, 42.
(24) Coggin, D. K.; Gonzáles, J. A.; Kook, A. M.; Stanbury, D. M.; Wilson, L. J. *Inorg. Chem.* **1991**, *30*, 1115.