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Kinetics and Mechanisms of Ligand-Substitution Reactions at Tetrahedral Bis(diimine)copper(I) Complexes in Acetone and Methanol

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The equilibrium constants for the stepwise substitution of biquinolyl (biq) by 2,9-dimethylphenanthroline (dmp) in $Cu(biq)_2^+$ were determined in acetone and methanol solutions by UV–visible spectroscopy. The kinetics of the mixed-ligand complex formation in these two solvents were studied by means of the stopped-flow method. The formation of $Cu(biq)(dmp)^+$ follows two parallel pathways: a direct reaction via an outer-sphere encounter complex and a solvent-assisted path via an intermediate in which one biq ligand is fully dissociated. Unexpectedly, the rate behavior is quite different in these two solvents. In acetone the overall rate constant for the direct reaction, $k_{12} = K_{os}k_I$, is 1.8×10^3 M^{-1} s^{-1} with $k_I = 2.9 \times 10^2$ s^{-1}. The solvent-assisted pathway is of minor importance. In methanol k_{12} is 7 M^{-1} s^{-1} and $k_I = 1.1$ s^{-1}. The rates for the direct pathway and the solvent pathway are similar. The ligand dependence (dmp, phen) of k_I in acetone shows that an associative activation mode is preferred.

Introduction

In recent years the interest in the coordination chemistry of copper(I) has increased mainly because of its function in biological systems.[1] Nevertheless solution studies on ligand-substitution reactions at Cu(I) complexes are not numerous. Obviously they have been hampered by the air sensitivity of the complexes, kinetic lability of the complexes, and the tendency of the complexes to undergo disproportionation reactions. In particular, kinetic information is rather scarce, in contrast to Cu(II) where an impressive amount of data is known.[2] An early pulse-radiolytic investigation showed that the reaction of the Cu^+ aquaion with fumarate and maleate in aqueous solution is diffusion-controlled.[3] Therefore, it was somewhat puzzling that a much smaller rate was found for the reaction of 1,10-phenanthroline (phen) with $Cu(phen)^+(aq)$ ($k = 6.2 \times 10^4$ M^{-1} s^{-1}).[4] Later it was shown that $Cu(phen)_2^+$ in aqueous solution has a strong tendency to form oligomers.[5] In a 9/1 mixture of acetonitrile and water the dissociation kinetics of a series of complexes with phenanthrolines and catenates were measured in the presence of the decomplexing agent CN^-.[6] Furthermore, a recent publication reported the kinetics of ligand substitution on a pentacoordinated Cu(I) complex in acetonitrile.[7]

Without doubt there is still a considerable demand for fundamental information on the substitution lability of Cu(I) complexes, in particular tetrahedral Cu(I). The knowledge of substitution kinetics is desirable also for the detailed understanding of Cu(II)/Cu(I) electron-transfer reactions, as coordination geometry and often even coordination number changes in the course of the redox process. However, it is not clear to what extent substitution reactions can interfere with electron-transfer reactions.

In this paper we report a kinetic investigation of ligand-substitution reactions of $Cu(biq)_2^+$ (biq = 2,2′-biquinolyl). One attractive feature of bis(diimine)copper(I) complexes is that they show a remarkable resistence toward air oxidation and the absence of disproportionation if ortho-substituted diimine ligands are used. Preliminary experiments showed that substitution reactions at various Cu(I) complexes in acetonitrile are too fast to be studied with the stopped-flow method. Surprisingly, however, in acetone and methanol the Cu(I) complexes are much less labile. In addition to the kinetic investigation in these solvents, we have measured the equilibrium constants for various substitution reactions at bis(diimine)copper(I) complexes utilizing the UV–visible spectrophotometric method.

Experimental Section

Biq, dmp, methanol (Fluka, puriss. p.a.), and acetone (Merck, p.a.) were used as received. According to the manufacturers the concentrations of impurities which are potential ligands are as follows: H_2O, <0.05%; NH_3, <0.0001%; HCOOH, <0.0025% for methanol; and H_2O, <0.2%; CH_3COOH, <0.002% for acetone. Special care was taken to insure that these impurities did not affect the reaction. For this purpose an additional amount (over that given in guaranteed content) of each of these chemicals was added to the solvent. Kinetic test experiments clearly showed that no significant deviations of the k_{obsd} values were obtained even in the lower concentration ranges of the reagents.

$[Cu(biq)_2]ClO_4$ was prepared by mixing 2 equiv of biq with $[Cu(CH_3CN)_4]ClO_4$ in dimethylformamide (Fluka, p.a.). After the solvent was pumped off, the residue was recrystallized twice from ethanol, and dried in vacuo. The UV–visible spectrum was in agreement with that reported in ref 8. The Cu content was determined by atomic absorption: calcd, 9.40; found, 9.37. The ^1H NMR spectrum corresponds to a complex with symmetrically coordinated ligands. ^1H NMR ($CDCl_3$, 250 MHz), δ: 8.95 (d), H^3; 8.81 (d), H^4; 7.98 (d × d), H^8; 7.68 (d × d), H^5; 7.51 (d × d × d), H^7; 7.35 (d × d × d), H^6. $[Cu(dmp)_2]ClO_4$ was prepared as described in ref 8. Cu content: calcd, 11.0; found, 11.1. The UV–visible spectrum was in agreement with that reported in ref 8 and the ^1H and ^{13}C NMR spectra correspond to a symmetric complex. ^1H NMR ($CDCl_3$, 250 MHz), δ: 8.52 (d), H^4; 8.04 (s), H^5; 7.80 (d), H^3; 2.44 (s), CH_3. ^{13}C NMR ($CDCl_3$, 50.3 MHz), δ: 157.8, C^2; 143.1, C^{10a}; 137.5, C^4; 127.8, C^{4a}; 126.2 and 125.7, C^5 and C^3; 26.0, CH_3. The mixed-ligand complex $[Cu(biq)(dmp)]ClO_4$ was prepared by dissolving equimolar amounts of $[Cu(CH_3CN)_4]ClO_4$, dmp, and biq in acetonitrile. The red-purple crystals obtained after slow evaporation of the solvent were filtered off and dried in vacuo. Cu content: calcd, 10.13; found, 10.0. It was somewhat suprising that the mixed-ligand complex was obtained, since the ligand-disproportionation equilibrium, eq 3, is more rapidly established in acetonitrile than in acetone or methanol; see below. The ^1H NMR solution spectrum corresponds, therefore, to that of a mixture of $Cu(biq)_2^+$, $Cu(dmp)_2^+$, and $Cu(biq)(dmp)^+$. However, the solid-state ^{13}C NMR spectrum of $[Cu(biq)(dmp)]ClO_4$ is clearly different from that of a mixture of the 1:2 complexes; see Figure 1.

Solutions of $Cu(biq)_2^+$ containing a slight excess of biq are stable against oxidation by air and can be stored in the dark for weeks.

NMR Spectroscopy. Solution NMR spectra were measured at room temperature in $CDCl_3$ solution on Bruker WM 250 (250.13 MHz) and AC 200 (50.3 MHz) instruments for ^1H and ^{13}C, respectively. The ^{13}C solid-state NMR spectra were obtained on a Bruker AMX 400 instrument at 100.6 MHz using cross-polarization techniques and fast sample spinning (4–5 KHz) in the magic angle (CP MAS).

Equilibrium Measurements. Spectra for equilibrium constant determinations were recorded using a Kontron UVIKON 820 UV–visible spectrophotometer equipped with 1-cm cuvettes thermostated to 25.0 ± 0.2 °C. Digital data were transferred directly from the spectrophotom-

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(1) See, for example: (a) *Copper in Coordination Chemistry: Biochemical and Inorganic Perspectives*; Karlin, K. D., Zubieta, J., Eds.; Adenine: Guilderland, NY, 1983. (b) *Biological and Inorganic Copper Chemistry*; Karlin, K. D.; Zubieta, J., Eds.; Adenine: Guilderland, NY, 1986; Vols. I and II.

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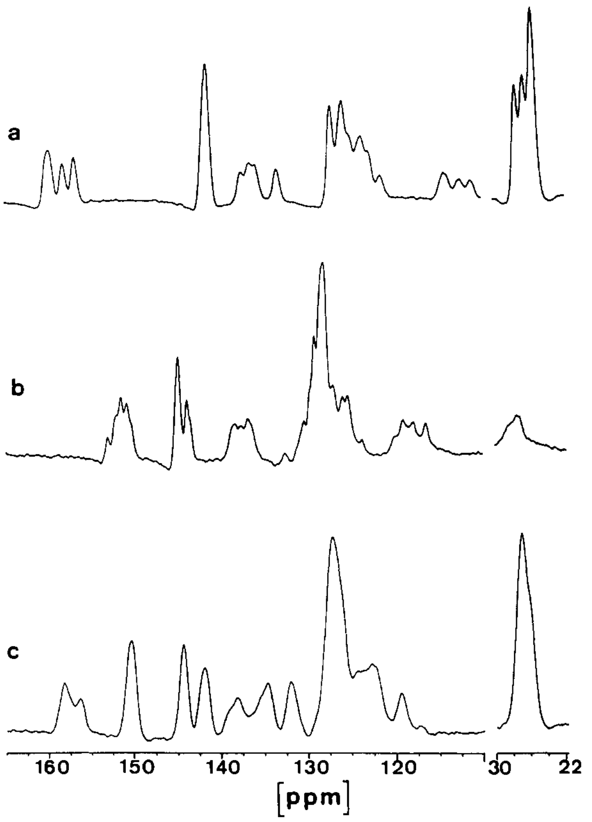

Figure 1. Solid-state ^{13}C-CP MAS NMR spectra of $[Cu(dmp)_2]ClO_4$ (a), $[Cu(biq)_2]ClO_4$ (b), and $[Cu(biq)(dmp)]ClO_4$ (c) showing the aromatic and the methyl parts only.

eter to an HP 1000 laboratory computer system. The change in the MLCT spectra of the Cu(I) complexes upon substitution of biq by dmp permitted the calculation of the equilibrium constants by use of the SPECFIT program.[9] Typically, absorbance data at wavelengths that spanned the region 400–580 nm were used. In both solvents the spectra of the complexes change in the presence of 0.1 M tetraethylammonium perchlorate. This is probably a consequence of the association of ClO_4^-. Therefore, we performed all experiments without using an inertelectrolyte. The ionic strength was defined by the total concentration of copper(I) perchlorate, $[Cu]_t$, which was not varied within an experimental series, the [Cu(I)] being between 2×10^{-5} and 5×10^{-5} M in all experiments. In these dilute solutions ion association is negligible in methanol[10] as well as in acetone.[11] In all experiments the solutions of $Cu(biq)_2^+$ contained a large excess of biq. In this way complete coordination of Cu(I) was guaranteed, and possible traces of free acids in the solvents would have been neutralized by biq.

Kinetic Measurements. A Durrum D110 stopped-flow spectrophotometer was used for the kinetic measurements. Absorbance data were digitized by two transient recorders (Maurer, TM 110 and TM 1009, Luzern, Switzerland) in a master–slave relationship.[12] This arrangement permitted data acquisition at two data rates for each reaction mixture. Digital kinetic data were analyzed by a nonlinear least-square fit of the first-order kinetic model.[12] The kinetic data were analyzed over 3–5 half-lives. Reported k_{obsd} values are the average of at least four replicates.

Results and Discussion

Equilibrium Studies. It is well-known that, in acetonitrile, the formation constants of Cu(I) complexes with α,α'-diimine ligands can be determined spectrophotometrically by utilizing the MLCT spectra.[13,14] However, in the poorly coordinating solvents, i.e., acetone and methanol, the stepwise complex formation cannot be studied because the corresponding solvated Cu^+ ions do not exist. Nevertheless, the stepwise substitution reactions eqs 1 and 2 can

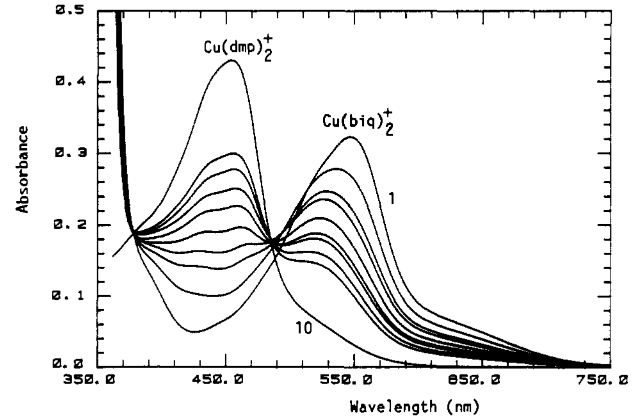

Figure 2. Equilibrium spectra of the Cu(I)/biq/dmp system in acetone at 25 °C. Concentrations (M) for curves 1–10 ($[Cu]_t$, $[biq]_t$, $[dmp]_t$): 5.00×10^{-5}, 1.86×10^{-2}, 0; 5.07×10^{-5}, 1.81×10^{-2}, 2.52×10^{-5}; 5.04×10^{-5}, 1.78×10^{-2}, 4.16×10^{-5}; 5.09×10^{-5}, 1.76×10^{-2}, 5.01×10^{-5}; 5.04×10^{-5}, 1.74×10^{-2}, 6.09×10^{-5}; 5.03×10^{-5}, 1.72×10^{-2}, 7.14×10^{-5}; 5.16×10^{-5}, 1.70×10^{-2}, 8.03×10^{-5}; 5.09×10^{-5}, 1.69×10^{-2}, 8.95×10^{-5}; 5.096×10^{-5}, 1.70×10^{-2}, 9.76×10^{-5}; 5.05×10^{-5}, 1.01×10^{-4}, 1.0×10^{-3} (spectrum of $Cu(dmp)_2^+$).

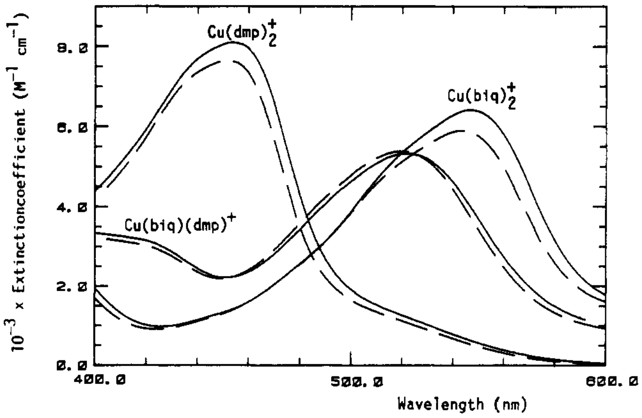

Figure 3. Spectra of $Cu(biq)_2^+$, $Cu(biq)(dmp)^+$, and $Cu(dmp)_2^+$ in acetone (—) and methanol (--).

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

	log K^c	
reacn	acetone	methanol
$Cu(biq)_2^+ + dmp = Cu(biq)(dmp)^+ + biq$	3.74	2.56
$Cu(biq)(dmp)^+ + dmp = Cu(dmp)_2^+ + biq$	3.27	1.62
$Cu(biq)_2^+ + phen = Cu(biq)(phen)^+ + biq$	2.19	
$Cu(biq)(phen)^+ + phen = Cu(phen)_2^+ + biq$	1.68	
$2Cu(biq)(dmp)^+ = Cu(biq)_2^+ + Cu(dmp)_2^+$	−0.50	−0.94
$2Cu(biq)(phen)^+ = Cu(biq)_2^+ + Cu(phen)_2^+$	−0.53	

[a] $I \approx 5 \times 10^{-5}$ M. [b] $I \approx 2 \times 10^{-5}$ M. [c] Estimated error: ±0.1 log unit.

$$Cu(biq)_2^+ + dmp \rightleftarrows Cu(biq)(dmp)^+ + biq \qquad (1)$$

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

be determined, where dmp = 2,9-dimethyl-1,10-phenanthroline. Figure 2 shows a typical series of spectra obtained by titrating a solution of $Cu(biq)_2ClO_4$ with dmp in acetone. The excess of biq is necessary in order to shift the equilibria to obtain significant concentrations of the biq-containing species. The equilibrium constants for eqs 1 and 2 were determined with the program SPECFIT;[9] cf. Table I. The spectra of the complexes are shown in Figure 3. The occurrence of the mixed-ligand complex, postulated in eqs 1 and 2, was substantiated by isolation of

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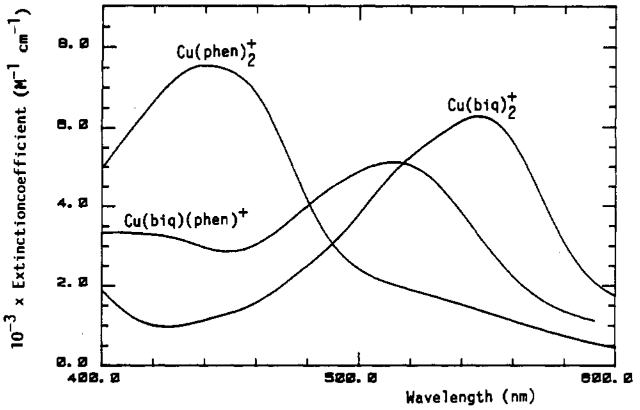


Figure 4. Spectra of $Cu(biq)_2^+$, $Cu(biq)(phen)^+$, and $Cu(phen)_2^+$ in acetone.

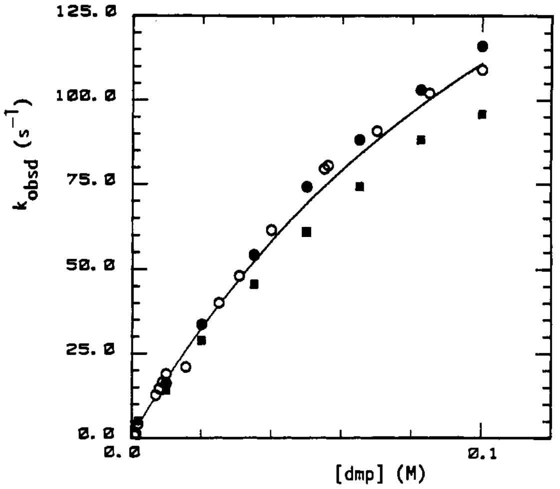


Figure 5. Dependence of the pseudo-first-order rate constants k_{obsd} (s^{-1}) on the concentration of dmp for the reaction with $Cu(biq)_2^+$, $[Cu]_t = 8 \times 10^{-5}$ M, in acetone. Various concentrations of biq are added: (○) 5×10^{-6} M; (●) 1×10^{-3} M; (■) 1×10^{-2} M.

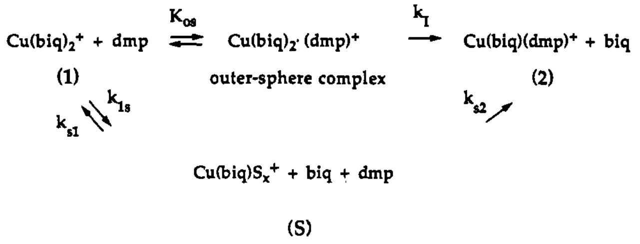
$[Cu(biq)(dmp)]ClO_4$. Its spectrum in acetone, as well as that in methanol, agrees very well with that obtained from the measurement of the substitution reactions. The ligand-disproportionation reaction, eq 3, has a half-life of approximately 10 min

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

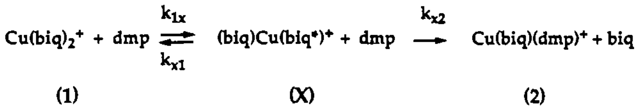
in both solvents. This easily allows the extrapolation of the absorption to time zero. Furthermore, the ligand-substitution reactions in acetone, eqs 1 and 2, were investigated with phen instead of dmp. The spectra of $Cu(phen)_2^+$ and $Cu(biq)(phen)^+$ are shown in Figure 4. The equilibrium constants are given in Table I. The stronger coordination tendency of dmp, compared with phen, is in line with the higher basicity of dmp. The equilibrium constants for the ligand-disproportionation reaction, eq 3, are close to the statistically expected value ($\log K = -0.60$).

Kinetic Studies. (A) Acetone. In contrast to the high substitution lability in acetonitrile,[15] the tetrahedral Cu(I) complexes with α,α'-diimine ligands in acetone show a relative inertness, which conveniently allows their investigation by the stopped-flow method. Under pseudo-first order conditions, the ligand-substitution reactions, eqs 1 and 2, proceed completely to the right. If the reaction is monitored at the isosbestic point of $Cu(biq)(dmp)^+$ and $Cu(dmp)_2^+$, $\lambda = 482$ nm, the mixed-ligand complex formation, eq 1, could be studied separately, although the following reaction, eq 2, proceeds with a similar rate. Within the wide range of the excess dmp, 10^{-3} to 0.1 M, the reaction shows typical saturation kinetics. The rate constants k_{obsd} approach a value which is independent of [dmp]; cf. Figure 5. This indicates a two-step process. The k_{obsd} values are independent on the added biq up to a concentration of 10^{-3} M. With [biq] = 10^{-2} M a small rate retardation is observed which is just at the limit of the reproducibility of the measurements. Thus one cannot exclude that, to a small extent, the reaction follows a solvent path via an intermediate in which one biq ligand is completely dissociated. However, the main contribution to the reaction is a pathway where in the intermediate species both biq molecules are still coordinated. A plot of $1/k_{obsd}$ against 1/[dmp] yields a straight line with a finite intercept. The form of the rate law is therefore equal to eq 4 with

Scheme I



Scheme II



biq* = unidentate biq

Table II. Rate Constants for Ligand-Substitution Reactions According to Scheme I in Acetone and Methanol at 25 °C[a]

	acetone		methanol
	dmp[b]	phen[c]	dmp[d]
k_{12}, M^{-1} s^{-1}	1.8×10^3 (0.2)	3.8×10^3 (0.6)	7 (2)
k_I, s^{-1}	2.9×10^2 (0.3)	1.6×10^3 (0.3)	1.1 (0.2)
K_{os}, M^{-1}	6.6 (1.2)	2.3 (0.5)	6.6 (1.2)
k_{1s}, s^{-1}			0.60 (0.1)
k_{s2}/k_{s1}			0.16 (0.02)

[a] Uncertainties in parentheses indicate the range of experimental values. [b] $I \approx 8 \times 10^{-5}$ M. [c] $I \approx 1 \times 10^{-4}$ M. [d] $I \approx 5 \times 10^{-5}$ M.

$$k_{obsd} = \frac{a[dmp]}{1 + b[dmp]} \qquad (4)$$

$a = 1840$ (± 200) M^{-1} s^{-1} and $b = 6.6$ (± 1.2) M^{-1}. Such behavior can be accommodated either by the upper reaction pathway shown in Scheme I or by that shown in Scheme II. The observed first-order rate constant for the reaction sequence according to Scheme I is given by the relationship shown in eq 5, i.e., of the

$$k_{obsd} = K_{os}k_I[dmp]/(1 + K_{os}[dmp]) \qquad (5)$$

form described in eq 4, with $a = k_{12} = K_{os}k_I$ and $b = K_{os}$, where K_{os} is the equilibrium constant for the outer-sphere complex formation and k_I is the interchange rate constant. The values of K_{os} and k_I are collected in Table II. The experimental value of $K_{os} = 6.6$ M^{-1} is in good agreement with that calculated with the Fuoss equation.[16] An alternative reaction pathway corresponds to Scheme II with relationship shown in eq 6. The significance

$$k_{obsd} = (k_{1x}/k_{x1})k_{x2}[dmp]/(1+(k_{x2}/k_{x1})[dmp]) \qquad (6)$$

of this pathway can be easily checked, because the rate of the opening of the biq-chelate ring, which should correspond to the maximum value for k_{obsd}, $k_{1x} = 280$ s^{-1}, should be independent of the incoming ligand. Therefore we used phen instead of dmp. The results show that for [phen] ≥ 0.1 M the k_{obsd} values are still increasing and are clearly above 280 s^{-1}; cf. Figure 6. The different reactivity of these two ligands clearly indicates that Scheme II can be discarded. For the reaction with phen, Scheme

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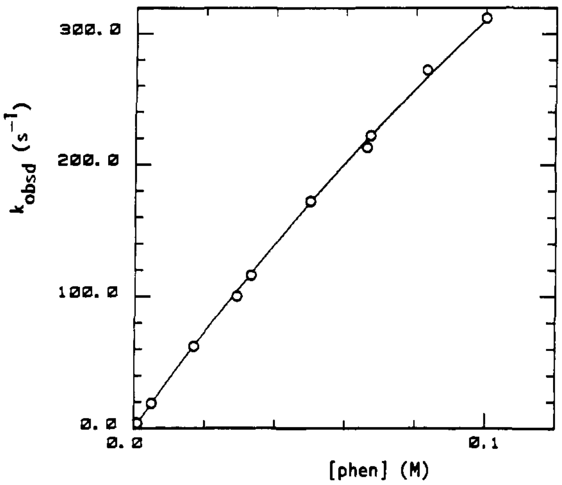

Figure 6. Dependence of the pseudo-first-order rate constants k_{obsd} (s^{-1}) on the concentration of phen for the reaction with $Cu(biq)_2^+$, $[Cu]_t = 1 \times 10^{-4}$ M, in acetone. Added $[biq] = 1 \times 10^{-3}$ M.

I upper pathway, a good fit is obtained for $K_{os} = 2.3$ M^{-1} and $k_I = 1650$ s^{-1}. If one considers the bulkiness of dmp, it is quite understandable that for phen the interchange rate constant k_I is significantly larger whereas K_{os} is slightly smaller. The ligand-dependence of k_I is indicative of an associative mechanism (I_a). Clear evidence for an associative activation mode was obtained in a kinetic study of substitution reactions with unidentate ligands at bis(diimine)copper(I) complexes.[15]

(B) Methanol. In methanol the mixed-ligand complex formation reaction, eq 1, was investigated under pseudo-first-order conditions with excess dmp. This reaction, as well as the following reaction shown in eq 2, proceeds completely to the right. Similar to the study in acetone, the mixed-ligand complex formation could be studied separately at the isosbestic point of $Cu(biq)(dmp)^+$ and $Cu(dmp)_2^+$, $\lambda = 480$ nm. As can be seen from Figure 7 the dependence of k_{obsd} on [dmp] is nonlinear in the concentration range 5×10^{-4} M < [dmp] < 0.13 M. In contrast to the results obtained in the acetone solutions, k_{obsd} is clearly dependent on the concentration of the leaving ligand biq. This shows that a solvent-assisted pathway is followed via an intermediate $Cu(biq)S_x^+$ (S = solvent) in which one biq is completely dissociated; cf. the lower path in Scheme I. The corresponding first-order rate constant is given by eq 7. However, a good fit over the whole

$$k_{obsd} = k_{1s}k_{s2}[dmp]/(k_{s1}[biq] + k_{s2}[dmp]) \qquad (7)$$

concentration range is obtained only if one assumes a parallel pathway via an outer-sphere complex. This direct ligand path constitutes the main contribution to the substitution reaction in acetone. The calculated curves in Figure 7 are based on this two-pathway reaction mechanism; cf. Scheme I with k_{obsd} equal to the sum of eqs 5 and 7. For K_{os} the value determined in acetone was used. The rate constants obtained are collected in Table II. It is most striking that the substitution reaction, via the direct ligand path ($k_{12} = K_{os}k_I$), is more than 2 orders of magnitude slower in methanol than in acetone. The contribution of the solvent path is similar to that of the direct path. It should be noted that a solvent path in acetone with rate constants of the same order of magnitude as that in methanol cannot be excluded because such a contribution to k_{obsd} would be within the error limit in that solvent.

It is somewhat surprising that $Cu(biq)_2^+$ in methanol is significantly more inert than in acetone. Probably acetone is a poorer nucleophile towards Cu^+. However, the solubility of the ligand biq in methanol is 5× smaller than in acetone, whereas the solubility of dmp is 13× larger in methanol as compared with that in acetone. The large difference in the substitution lability of $Cu(biq)_2^+$ in these two solvents shows clearly that the bulkiness of the complex is not rate determining. As mentioned earlier, the cation $Cu(biq)_2^+$ is more labile in acetonitrile than in acetone or methanol. It has also been shown[15] that the dominant pathway in acetonitrile is solvent-assisted. This is likely to be associated with its excellent solvating properties. The quotient $k_{s2}/k_{s1} = 0.16$ shows that biq is clearly preferred as an incoming ligand. This is plausible if one considers that biq can approach the coordination sphere of Cu(I) more easily than dmp. It is also in line with the above-mentioned lower solubility of biq which may favor the desolvation of biq, relative to dmp, in the course of the substitution reaction.

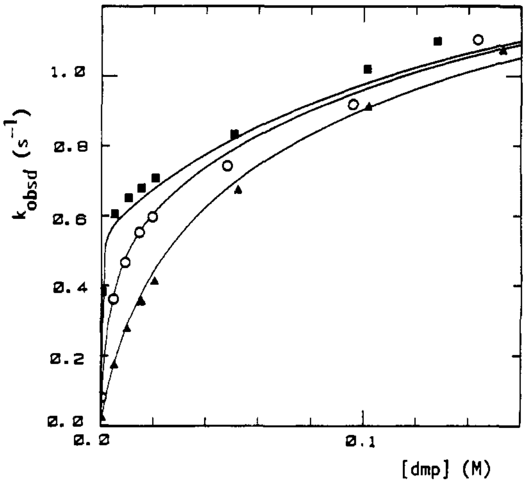

Figure 7. Dependence of the pseudo-first-order rate constants k_{obsd} (s^{-1}) on the concentration of dmp for the reaction with $Cu(biq)_2^+$, $[Cu]_t = 5 \times 10^{-5}$ M, in methanol. Various concentrations of biq are added: (■) 2×10^{-5} M; (○) 5×10^{-4} M; (▲) 2.5×10^{-3} M.

Conclusions

The mechanism of the substitution of biq by diimine ligands at Cu(I) is characterized by the same two-term rate law which is well-known for substitution reactions in square-planar and linear metal complexes. In methanol both pathways, the direct ligand path and the solvent path, are of similar importance, whereas in acetone the direct path is predominant. In the latter case the substitution reaction proceeds via an intermediate which is clearly identified as an outer-sphere complex. The subsequent rate-determining interchange is a multistep reaction. The kinetics do not allow us to analyze in detail the steps which are involved in the substitution of the chelated biq by another bidentate ligand. However, the significant difference in the k_I values for dmp (2.9×10^2 s^{-1}) and phen (1.6×10^3 s^{-1}) clearly shows that an associative activation mode (I_a) is preferred. It is somewhat surprising that the direct ligand path for dmp in acetone is clearly faster ($k_{12} = 1.8 \times 10^3$ M^{-1} s^{-1}) than that in methanol ($k_{12} = 7$ M^{-1} s^{-1}). The faster interchange rate in acetone ($k_I = 2.9 \times 10^2$ s^{-1}) relative to that in methanol ($k_I = 1.1$ s^{-1}) may be a consequence of the differences in rates of solvation and desolvation of the two ligands and their complexes. However, their relative contributions to the activation process cannot be unequivocally assessed.

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