

Evidence for a Chelate-Induced Changeover in the Substitution Mechanism of Aquated Copper(II). Volume Profile Analyses of Water Exchange and Complex-Formation Reactions

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The substitution behavior of aquated Cu(II) ions is strongly affected by the presence of the tren (2,2',2''-triaminotriethylamine) chelate. The kinetics and mechanism of solvent (water) exchange and of a series of complex-formation reactions of Cu(tren)H₂O²⁺ were studied in detail at pressures up to 200 MPa using ¹⁷O NMR and T-jump techniques. The water exchange rate on the pentacoordinate Cu(tren)H₂O²⁺, $k_{\text{ex}}^{298} = (2.39 \pm 0.09) \times 10^6 \text{ s}^{-1}$, is over 3 orders of magnitude slower than on the hexacoordinate Cu(H₂O)₆²⁺. The reported volumes of activation strongly support the operation of an associative interchange (I_a) mechanism, viz. $-4.7 \pm 0.2 \text{ cm}^3 \text{ mol}^{-1}$ for water exchange and between -4.7 and $-10 \text{ cm}^3 \text{ mol}^{-1}$ for complex-formation and reverse aquation reactions involving pyridine and substituted pyridines. The latter results are used to construct volume profiles for the complex-formation reactions that further illustrate the volume collapse that occurs in going to the transition state for both reactions. The results are discussed with reference to earlier data reported in the literature. It is concluded that a chelate such as tren can induce a mechanistic changeover on labile aquated metal ions.

Introduction

The intimate nature of ligand substitution reactions of divalent first row transition metal ions strongly depends on the size and electronic structure of the metal ion and the nature of the coordinated ligands. In this respect the determination of the volumes of activation for solvent exchange and complex-formation reactions of such metal ions,^{2,3} along with the construction of reaction volume profiles,⁴ have greatly assisted the elucidation of the underlying reaction mechanism. In general, a decrease in the ionic radius of the metal ion and an increase in the bulkiness of the coordinated ligands will cause a gradual changeover from a more associative (I_a) to a more dissociative (I_d) ligand interchange mechanism.⁵ Complex-formation reactions of such metal ions exhibit mechanistic behavior very similar to that of the corresponding solvent exchange reactions.³ Consequently, complex-formation data have for instance been used to resolve the nature of the water exchange mechanism of Cr(H₂O)₆²⁺.⁶

What do we know about the ligand substitution mechanism of Cu(II) ions and complexes? The Cu(H₂O)₆²⁺ ion is well known for its extreme lability ($k_{\text{ex}}^{298} = (4.4 \pm 0.1) \times 10^9 \text{ s}^{-1}$)⁷ with close to diffusion controlled rate constants.⁸ Preliminary studies showed a small positive ΔV^\ddagger value for the water

exchange process, which suggests an I_d mechanism.⁹ The extreme lability of Cu(H₂O)₆²⁺ has been ascribed to a dynamic Jahn–Teller distortion: the elongated axial bonds are weaker, and the rapid change of the axis of distortion (lifetime ca. $5 \times 10^{-12} \text{ s}$)⁷ results in an enhanced lability of all the coordinated water molecules. Simple mono-, bi-, tri- and tetradentate ligands in Cu(II) complexes typically decrease the rate of the subsequent complex-formation reactions by up to a factor of 20. Significant deviations from this pattern were observed either when steric effects inhibit the reaction or when specific interactions between the coordinated and entering ligands accelerate the complex-formation step.^{8,10,11}

The Cu(tren)²⁺ (tren = 2,2',2''-triaminotriethylamine) species represents a special case among Cu(II) complexes. The water exchange rate constant for this complex ($k_{\text{ex}}^{298} = 2.5 \times 10^5 \text{ s}^{-1}$)¹² is about 4 orders of magnitude smaller than that for Cu(H₂O)₆²⁺. This unique kinetic feature of the tren complex is even more apparent when complex-formation reactions of Cu(tren)²⁺ and Cu(nta)⁻ (nta³⁻ = nitrilotriacetate) are compared.^{10,13,14} On the basis of the structural similarity between the two tripodal ligands, one would expect analogous kinetic behavior. However, in the absence of steric effects, complex-formation reactions of Cu(nta)⁻ are thousand times faster than those of Cu(tren)²⁺. This marked difference was attributed to

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Table 1. Compositions (*m*) of the Different Samples Used in the ^{17}O NMR Studies

sample no.	[Cu $^{2+}$]	[Zn $^{2+}$]	[tren]	pH
1	0.0382		0.0396	6.9
2		0.0395	0.0395	7.1
3	0.0200		0.0200	6.4
4		0.0200	0.0200	6.3
5	0.0221		0.0214	5.8
6		0.0207	0.0191	6.1

different geometries of the two complexes, viz. distorted octahedral with two water molecules in the cis position^{10,15,16} and trigonal-bipyramidal with one coordinated water molecule,^{12–14,17} respectively. The structure of the Cu(tren) $^{2+}$ complex in solution has not been determined explicitly. X-ray crystallographic measurements of the thiocyanate salt¹⁷ show a five-coordinate trigonal bipyramidal structure. It may, therefore, be safe to assume that the complex in aqueous solution is present as Cu(tren)H $_2$ O $^{2+}$. The dependence of the reaction rates for typical complex-formation reactions on the nature of the ligand, and the reported activation parameters, suggested that ligand substitution takes place via an associative (I $_a$) instead of the usually expected dissociative (I $_d$) mechanism.¹⁴ Thus the unusual coordination geometry induced by the chelate in Cu(tren)H $_2$ O $^{2+}$ not only drastically reduces the rate of ligand substitution reactions, but presumably also brings about a mechanistic changeover from I $_d$ to I $_a$.¹⁴

We have now performed a detailed study of the effect of pressure on water exchange and complex-formation reactions of Cu(tren)H $_2$ O $^{2+}$ using ^{17}O NMR and *T*-jump techniques. These data are used to determine the volumes of activation for the different reactions, to construct reaction volume profiles, and hence to elucidate the intimate nature of the ligand substitution process.

Experimental Section

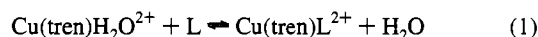
Preparation of Solutions for NMR Studies. Stock solutions of Cu(ClO $_4$) $_2$, Zn(ClO $_4$) $_2$ and tren were prepared using doubly distilled water and Cu(ClO $_4$) $_2$ ·6H $_2$ O (Fluka purum), Zn(ClO $_4$) $_2$ ·6H $_2$ O (Johnson Matthey), and tren (Fluka) as supplied. The samples were prepared by mixing appropriate stoichiometric quantities of the stock solutions with ca. 1% ^{17}O enriched water (Yeda). The pH was measured using a glass electrode, and the pH meter was calibrated using pH = 4.0 and pH = 7.0 buffer solutions (Metrohm). The compositions of the different samples are shown in Table 1.

^{17}O NMR Measurements. Variable temperature ^{17}O NMR measurements were performed at two magnetic fields using Bruker AM-400 (9.4 T, 54.2 MHz) and Bruker AC-200 (4.7 T, 27.1 MHz) spectrometers. Bruker VT-1000 temperature control units were used to stabilize the temperature, which was measured by a substitution technique.¹⁸ The samples were sealed in glass spheres, fitting into 10-mm NMR tubes, in order to eliminate susceptibility corrections to the chemical shift.¹⁹ Variable pressure NMR measurements were made up to 200 MPa on a Bruker AM-400 spectrometer equipped with a home-built probe head.²⁰ The temperature was controlled by circulating fluid from a temperature bath, and was measured using a built-in Pt-resistor. It was previously shown⁷ that ^{17}O transverse relaxation rates, $1/T_2$, obtained by line width and spin echo methods were identical for aqueous solutions of Cu $^{2+}$. The $1/T_2$ and $1/T_{2A}$ values were therefore measured directly from the line widths.

Complex-Formation Studies. All chemicals were reagent grade quality. The ligands pyridine (py), 3-methylpyridine (Mepy) and 3-chloropyridine (Clpy) (Aldrich) were used without further purification, whereas tren (Alfa Products) was distilled before use.

For the equilibrium and *T*-jump relaxation studies the Cu(ClO $_4$) $_2$ stock solution was prepared by mixing equivalent amounts of CuSO $_4$ and Ba(ClO $_4$) $_2$ (Merck) solutions. After the BaSO $_4$ precipitate was filtered off the Cu $^{2+}$ concentration was determined by using a standard iodometric method.²¹ The samples were prepared by adding various amounts of the second ligand to a stoichiometric mixture of Cu $^{2+}$ and tren solutions. The pH was controlled by adding 0.05 M MES (2-morpholinoethanesulfonic acid, Fluka) and appropriate aliquots of 1.0 M NaOH (Fluka) to the samples. The ionic strength was adjusted to 1.0 M with NaClO $_4$ (Merck). The applied concentration ranges are as follows: [Cu(tren) $^{2+}$] = (3.0–5.1) × 10 $^{-4}$ M; [L] = (3.0–30.2) × 10 $^{-3}$ M, pH = 6.34–6.47 (py); [L] = (1.45–21.8) × 10 $^{-3}$ M, pH = 6.44–6.51 (Mepy); [L] = (1.0–6.0) × 10 $^{-2}$ M, pH = 6.40 (Clpy).

Equilibrium Measurement. At ambient pressure (1 bar) the stability constants of the Cu(tren)L $^{2+}$ ternary complexes produced in reaction 1 were determined spectrophotometrically by using a HP



8452A diode-array spectrophotometer. The pH of the samples was measured with a WTW PMX 500 pH-meter equipped with an Ingold combined glass electrode. The electrode calibration for H $^+$ concentration was described elsewhere,^{11,22} such that pH means $-\log[\text{H}^+]$.

The observed spectral changes in the near-UV region are very similar to those reported for the Cu $^{2+}$ –tren–Clpy system.¹⁴ Calculations by using earlier published stability constants for the binary Cu $^{2+}$ –tren system indicate that the Cu(tren) $^{2+}$ complex is the predominant species in the applied pH region.²³ Thus, side reactions do not interfere with the ternary complex formation, and the observed spectral effects could be interpreted by considering only reaction 1 and the protolytic equilibria of L and MES. The stability constants for reaction 1 were calculated by simultaneously fitting the experimental data at 6 different wavelengths in the 300–330 nm region with the program PSEQUAD.²⁴ For these calculations the pK $_a$'s of the ligands and MES were taken from the literature.^{14,25} The equilibrium constants are given in Table 2.

Temperature-Jump Measurements. The complex formation reactions were studied at pressures up to 140 MPa by using the earlier described high-pressure joule-heating *T*-jump apparatus (rise time ~ 10 μs).²⁶ A 3 °C temperature change was achieved during an electric discharge of ~20 kV. Kinetic traces were collected in the 300–320 nm region by emulating a transient recorder with a 486 PC equipped with a TR-PC 25-8 card from Dr. Strauss System Elektronik GmbH. A few representative kinetic curves are shown in Figure 1. In all cases, first a relatively large absorbance jump was observed within the dead time of the instrument. It was attributed to a shift in the protolytic equilibria and/or the temperature dependence of the molar absorptivities of the colored species. After the jump, a single relaxation process was observed in each trace. On the basis of experiments in the absence of the pyridine ligands, the relaxation effect was assigned to reaction 1.

The rate constants for the relaxation curves were fitted with the OLIS KINFIT program.²⁷ The experimental rate constants (*k*) were calculated from the average of at least three replicate kinetic runs. The reproducibility of *k* was within 10% even for the traces with the smallest signal to noise ratios.

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Table 2. Thermodynamic and Kinetic Parameters for the $\text{Cu}(\text{tren})\text{H}_2\text{O}^{2+} + \text{L} \rightleftharpoons \text{Cu}(\text{tren})\text{L}^{2+} + \text{H}_2\text{O}$ Reaction at 25 °C, 1 bar, and $I = 1.0 \text{ M}$

parameter	ligand			ref
	Clpy	py	Mepy	
$k_{\text{on}} (\text{M}^{-1} \text{s}^{-1})$	$(4.5 \pm 0.3) \times 10^4$	$(1.3 \pm 0.1) \times 10^5$	$(1.6 \pm 0.1) \times 10^5$	a
	3.4×10^4	1.7×10^5	2.1×10^5	14
$k_{\text{off}} (\text{s}^{-1})$	$(3.3 \pm 0.2) \times 10^3$	$(1.2 \pm 0.1) \times 10^3$	$(8.1 \pm 0.3) \times 10^2$	a
	3.5×10^3	1.3×10^3	9.2×10^2	14
$\Delta V_{\text{on}}^\ddagger (\text{cm}^3 \text{mol}^{-1})$	-10.0 ± 2.0	-7.1 ± 1.0	-8.7 ± 1.1	a
$\Delta V_{\text{off}}^\ddagger (\text{cm}^3 \text{mol}^{-1})$	-4.7 ± 1.0	-8.7 ± 1.0	-7.5 ± 1.2	a
$\text{p}K_{\text{a}}$	2.85	5.64	6.14	14
$\log K^{\text{sp}}$	1.22 ± 0.01	2.09 ± 0.02	2.26 ± 0.01	a
$\log K^{\text{kin}}$	1.13	2.07	2.30	b
$\Delta \bar{V} (\text{cm}^3 \text{mol}^{-1})$	-5.3	1.6	-1.2	c
$\Delta S_{\text{on}}^\ddagger (\text{J K}^{-1} \text{mol}^{-1})$	-38.0	-60.8	-83.0	14
$\Delta S_{\text{off}}^\ddagger (\text{J K}^{-1} \text{mol}^{-1})$	-82.3	-44.0	-30.4	14

^a This work. ^b $\log K^{\text{kin}} = \log(k_{\text{on}}/k_{\text{off}})$. ^c $\Delta \bar{V} = \Delta V_{\text{on}}^\ddagger - \Delta V_{\text{off}}^\ddagger$; $\text{p}K_{\text{a}} = 6.10$ for MES.²⁵

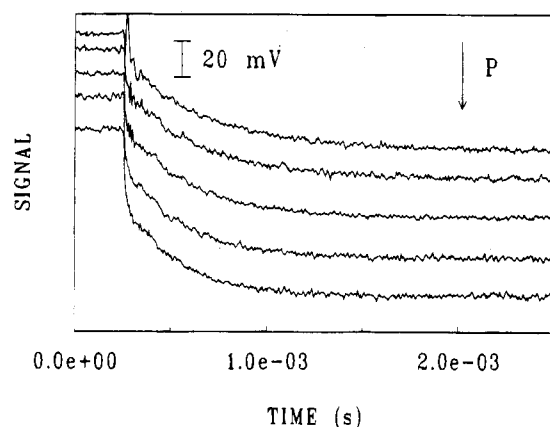


Figure 1. Typical T -jump traces for the $\text{Cu}(\text{tren})\text{H}_2\text{O}^{2+} + \text{py} \rightleftharpoons \text{Cu}(\text{tren})\text{py}^{2+} + \text{H}_2\text{O}$ reaction at pressures of 0.1, 35, 70, 105, and 140 MPa. Each curve represents the average of at least three replicate runs. $[\text{Cu}(\text{tren})^{2+}] = 5.06 \times 10^{-4} \text{ M}$, $[\text{py}] = 1.06 \times 10^{-2} \text{ M}$, $[\text{MES}] = 0.05 \text{ M}$.

Results

Water Exchange Reaction. From the measured ^{17}O NMR transverse relaxation rate and angular frequency, $1/T_2$ and ω , of each $\text{Cu}(\text{tren})\text{H}_2\text{O}^{2+}$ solution, and the corresponding values, $1/T_{2A}$ and ω_A , for the diamagnetic reference solution with Cu^{2+} replaced by Zn^{2+} , one can calculate the reduced transverse relaxation rates and chemical shifts, $1/T_{2r}$ and $\Delta\omega_r$, (eqs 2 and 3).²⁸ Here, $1/T_{2m}$ is the transverse relaxation rate in the bound

$$\frac{1}{T_{2r}} = \frac{1}{P_m} \left[\frac{1}{T_2} - \frac{1}{T_{2A}} \right] = \frac{1}{\tau_m} \frac{T_{2m}^{-2} + \tau_m^{-1} T_{2m}^{-1} + \Delta\omega_m^2}{(\tau_m^{-1} + T_{2m}^{-1})^2 + \Delta\omega_m^2} + \frac{1}{T_{2os}} \quad (2)$$

$$\Delta\omega_r = \frac{1}{P_m} (\omega - \omega_A) = \frac{\Delta\omega_m}{(1 + \tau_m T_{2m}^{-1})^2 + \tau_m^2 \Delta\omega_m^2} + \Delta\omega_{os} \quad (3)$$

water, $\Delta\omega_m$ is the chemical shift difference between bound water and bulk water (in the absence of a paramagnetic interaction with the bulk water), P_m is the mole fraction of bound water, and τ_m is the residence time of water molecules in the inner coordination sphere. The total outer sphere contributions to the reduced relaxation rate and chemical shift are represented by $1/T_{2os}$ and $\Delta\omega_{os}$.

The temperature variation of $1/T_{2r}$ at two different magnetic fields and two different Cu^{2+} concentrations are shown in Figure

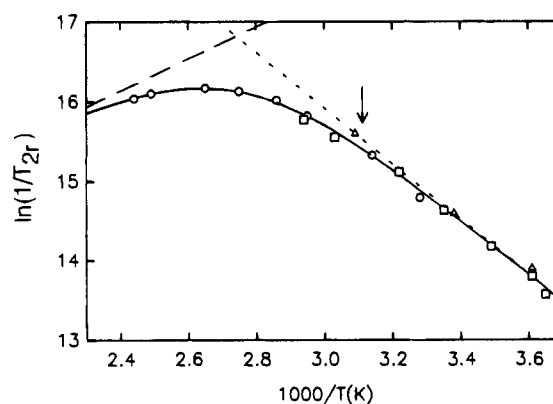


Figure 2. Reduced transverse relaxation rates of 0.0382 m $\text{Cu}(\text{tren})\text{H}_2\text{O}^{2+}$ ($\text{pH} = 6.9$) at 4.7 T (\circ) and 9.4 T (\square) and 0.020 m $\text{Cu}(\text{tren})\text{H}_2\text{O}^{2+}$ ($\text{pH} = 6.4$) at 9.4 T (\triangle). The solid curve represents the least-squares fit to the data and the long- and short-dashed lines represent $1/T_{2m}$ and k_{ex} , respectively. The arrow indicates the temperature at which variable pressure measurements were made.

2. No dependence on concentration or magnetic field is observed. The $\Delta\omega_r$ values obtained over the same temperature range are very poorly determined, but allow us to estimate that, at 9.4 T, $\Delta\omega_m$ varies from ca. $5.3 \times 10^6 \text{ rad s}^{-1}$ at 410 K to ca. $7.1 \times 10^6 \text{ rad s}^{-1}$ at 273 K. It can then be shown *a posteriori* from the treatment below that the contribution of $\Delta\omega_m$ to $1/T_{2r}$ in eq 2 is negligible (from ca. 5% at 410 K to 0.4% at 273 K—see Supplementary Material). If one also assumes that the outer-sphere contribution, $1/T_{2os}$, can be neglected, $1/T_{2r}$ is given by the much simpler eq 4. The maximum observed in the

$$\frac{1}{T_{2r}} = \frac{1}{T_{2m} + \tau_m} \quad (4)$$

temperature dependence of $1/T_{2r}$ (Figure 2) is characteristic of a changeover from the “fast exchange” limit at high temperatures, where T_{2m} is the dominant term in the denominator of eq 4, to the “slow exchange” limit at low temperatures, where τ_m is the dominant term. If there was a significant outer sphere contribution to $1/T_{2r}$, this would be visible as a changeover to positive slope at low temperatures (as can be clearly seen in an ^{17}O NMR study²⁹ of DMF exchange on Ti^{3+}): the approximation used in eq 4 is justified by the absence of such an effect.

We assume that the bound water relaxation rate, $1/T_{2r}$, has a simple exponential temperature dependence (eq 5) where

$$1/T_{2m} = 1/T_{2m}^{298} \exp\{E_m/R(1/298.15 - 1/T)\} \quad (5)$$

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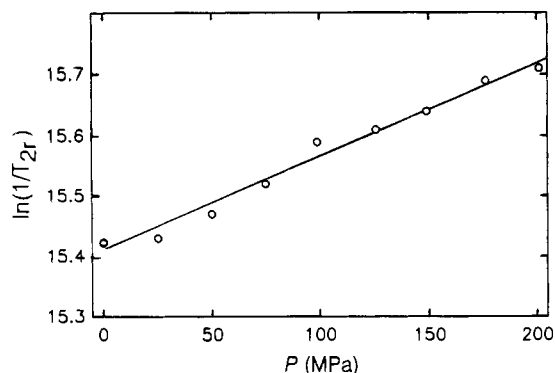


Figure 3. Pressure dependence of the reduced transverse relaxation rates in a 0.0221 *m* (pH = 5.8) solution of Cu(tren)H₂O²⁺ at 9.4 T and 320.9 K. The curve is the result of the least-squares fit to the data.

Table 3. Parameters Obtained from Least-Squares Fits of 1/T_{2r} as a Function of (a) Temperature and (b) Pressure

(a) Temperature	
k_{ex}^{298}	$(2.39 \pm 0.09) \times 10^6 \text{ s}^{-1}$
ΔH^\ddagger	$26.4 \pm 1.4 \text{ kJ mol}^{-1}$
ΔS^\ddagger	$-34.4 \pm 4.9 \text{ J K}^{-1} \text{ mol}^{-1}$
$1/T_{2m}^{298}$	$(6.8 \pm 3.8) \times 10^7 \text{ s}^{-1}$
E_m	$-16.6 \pm 5.2 \text{ kJ mol}^{-1}$
(b) Pressure	
$(k_{\text{ex}})_0^{320.9}$	$(5.58 \pm 0.05) \times 10^6 \text{ s}^{-1}$
ΔV^\ddagger	$-4.7 \pm 0.2 \text{ cm}^3 \text{ mol}^{-1}$

$1/T_{2m}^{298}$ is the rate at 298.15 K and E_m is the activation energy. The binding time (or exchange rate, k_{ex}) of water molecules in the inner sphere is assumed to obey the Eyring equation, eq 6,

$$\frac{1}{\tau_m} = k_{\text{ex}} = \frac{k_B T}{h} \exp\left\{\frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT}\right\} = \frac{k_{\text{ex}}^{298} T}{298.15} \exp\left\{\frac{\Delta H^\ddagger}{R} \left(\frac{1}{298.15} - \frac{1}{T}\right)\right\} \quad (6)$$

where ΔS^\ddagger and ΔH^\ddagger are the entropy and enthalpy of activation for water exchange and k_{ex}^{298} is the exchange rate at 298.15 K. The curve in Figure 2 is the result of a least squares fit of the data using eqs 4, 5, and 6 and four parameters: ΔH^\ddagger , ΔS^\ddagger (or k_{ex}^{298}), $1/T_{2m}^{298}$, and E_m . The fitted parameters are given in Table 3.

The pressure dependence of the reduced transverse relaxation rate, $1/T_{2r}$, at 320.9 K and 9.4 T is shown in Figure 3. At this temperature $1/T_{2r}$ is near the slow exchange limit and so is dominated by water exchange (see Figure 2): τ_m is about 90% of the denominator in eq 4 at ambient pressure. At the same time, the temperature is sufficiently high that $1/T_{2A}$ is only about 7% of $1/T_2$, so that the pressure dependence of the reference relaxation rate has only a small influence on the measured $1/T_{2r}$. The increase of $1/T_{2r}$ with pressure in Figure 3 is due to an acceleration of the water exchange process. The pressure dependence of the water exchange rate can be described by eq 7, where ΔV_0^\ddagger is the activation volume at zero pressure and

$$\frac{1}{\tau_m} = k_{\text{ex}} = (k_{\text{ex}})_0^T \exp\left\{-\frac{\Delta V_0^\ddagger}{RT} P + \frac{\Delta\beta^\ddagger}{2RT} P^2\right\} \quad (7)$$

temperature T , $(k_{\text{ex}})_0^T$ is the exchange rate at zero pressure and temperature T and $\Delta\beta^\ddagger$ is the compressibility coefficient of activation. Since the pressure dependence of $\ln(k_{\text{ex}})$ in Figure 3 is nearly linear, we assume that $\Delta\beta^\ddagger = 0$.

We performed a least-squares fit of the data in Figure 3 using eqs 4 and 7 and two fitted parameters: $(k_{\text{ex}})_0^T$ and ΔV^\ddagger . The value of $1/T_{2m}$ at 320.9 K was calculated using eq 5 with the

$1/T_{2m}^{298}$ and E_m in Table 3 and was assumed to be independent of pressure. The fitted parameters are given in Table 3. The value obtained for $(k_{\text{ex}})_0^T$ is in excellent agreement with the value, $(k_{\text{ex}})_0^{320.9} = 5.5 \times 10^6 \text{ s}^{-1}$, calculated from the variable-temperature parameters.

Ligand Substitution Reactions. The appropriate kinetic model for the interpretation of the T -jump experiments is given as follows:



$$K_B = \frac{[\text{HB}]}{[\text{H}^+][\text{B}^-]}$$



$$K_L = \frac{[\text{HL}^+]}{[\text{H}^+][\text{L}]}$$



$$K = \frac{[\text{Cu}(\text{tren})\text{L}^{2+}]}{[\text{Cu}(\text{tren})^{2+}][\text{L}]}$$

Here, B represents the basic form of the buffer (MES). Since the proton transfer reactions (eqs 8 and 9) are fast pre-equilibria prior to the complex formation, the following expression can be derived for the relaxation effect:

$$k = k_{\text{on}}(\alpha[\text{Cu}(\text{tren})\text{H}_2\text{O}^{2+}] + [\text{L}]) + k_{\text{off}} \quad (10)$$

where

$$\alpha = \frac{1 + K_L[\text{L}](1 + K_B[\text{H}^+]) + K_B[\text{B}]}{1 + K_L[\text{L}](1 + K_B[\text{H}^+]) + K_B[\text{B}](1 + K_L[\text{H}^+])}$$

Under the applied conditions, $\alpha[\text{Cu}(\text{tren})^{2+}] \ll [\text{L}]$, and eq 10 reduces to

$$k = k_{\text{on}}[\text{L}] + k_{\text{off}} \quad (11)$$

At ambient pressure, [L] was calculated by using K_L , K_B , and K listed in Table 2. In the calculations for pressures other than 1 bar, the protonation constants (K_L , K_B) were corrected on the basis of eq 12 by using previously reported reaction volumes

$$K^P = K e^{(-\Delta v/RT)\Delta p} \quad (12)$$

for the corresponding protolytic reactions: $\Delta\bar{V} = -4.4 \text{ cm}^3 \text{ mol}^{-1}$ (py),³⁰ $-3.4 \text{ cm}^3 \text{ mol}^{-1}$ (Mepy),³⁰ and $-3.9 \text{ cm}^3 \text{ mol}^{-1}$ (MES).²⁵ In eq 12, K , K^P and Δp are the stability constants at 1 bar and the actual pressure p and the difference between the two pressures, respectively. Such corrections were not made for K , in effect implying that this stability constant is pressure independent. Since the Cu(tren)L²⁺ complex always represents a negligible small fraction (always less than 5%) of the total ligand concentration, this approximation does not modify the calculated speciation and can be accepted for all practical purposes. The experimental data (supplementary Tables S1–S3) are plotted according to eq 11 in Figure 4.

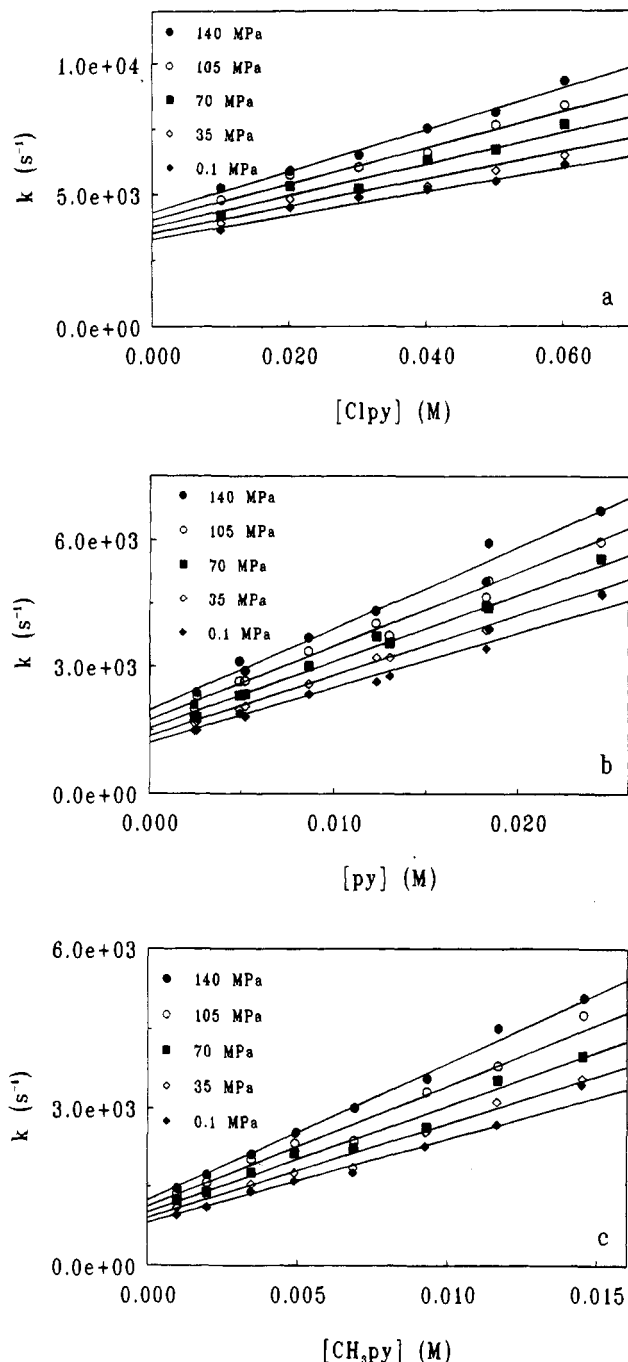


Figure 4. Kinetic data for the $\text{Cu}(\text{tren})\text{H}_2\text{O}^{2+} + \text{L} \rightleftharpoons \text{Cu}(\text{tren})\text{L}^{2+} + \text{H}_2\text{O}$ reaction at various pressures according to eq 11: (a) $\text{L} = \text{Clpy}$; (b) $\text{L} = \text{py}$; (c) $\text{L} = \text{Mepy}$.

Taking into account the pressure dependence of the rate constants, equation 11 can be rewritten in the following form:

$$k = k_{\text{on}} e^{(-\Delta V_{\text{on}}^{\ddagger}/RT)\Delta p} [\text{L}] + k_{\text{off}} e^{(-\Delta V_{\text{off}}^{\ddagger}/RT)\Delta p} \quad (13)$$

where k_{on} and k_{off} are forward and reverse rate constants at 1 bar, and $\Delta V_{\text{on}}^{\ddagger}$ and $\Delta V_{\text{off}}^{\ddagger}$ are the corresponding activation volumes assumed to be pressure-independent over the 0.1–140 MPa range. The four kinetic parameters were calculated by simultaneously fitting all data with the program NESSIE³¹ as described earlier³² (see supplementary material).

(31) Fábíán, I. NESSIE: A General Purpose Non-Linear Least Squares Fitting Program. L. Kossuth Univ., Debrecen, Hungary, 1982.

(32) Fábíán, I.; van Eldik, R. *Inorg. Chem.* **1993**, *32*, 3339.

Discussion

The water exchange rate at 298K and activation enthalpy obtained from our variable temperature ¹⁷O NMR results (Table 3) are very different from the values $k_{\text{ex}}^{298} = 2.5 \times 10^5 \text{ s}^{-1}$ and $\Delta H^{\ddagger} = 43.5 \text{ kJ mol}^{-1}$ obtained previously by Rablen et al. using ¹⁷O NMR.¹² It is difficult to account for this discrepancy, as these authors did not show their relaxation data or describe their analysis. Water exchange on $\text{Cu}(\text{tren})\text{H}_2\text{O}^{2+}$ is over 3 orders of magnitude slower than on the hexaqua ion (for $\text{Cu}(\text{H}_2\text{O})_6^{2+}$, $k_{\text{ex}}^{298} = (4.4 \pm 0.1) \times 10^9 \text{ s}^{-1}$).⁷ This is in marked contrast to $\text{Ni}(\text{H}_2\text{O})_6^{2+}$, where progressive substitution of the water by amines progressively increases the lability of the remaining water molecules by up to 2 orders of magnitude.³³ The extreme lability of $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ has been ascribed to a dynamic Jahn–Teller effect.⁷ The reduced exchange rate found for $\text{Cu}(\text{tren})\text{H}_2\text{O}^{2+}$ is consistent with this argument, as the tren ligand will restrict the degree and rapidity of distortion of the complex and so remove the dynamic Jahn–Teller effect as a labilizing effect. The negative activation volume, $\Delta V^{\ddagger} = -4.7 \text{ cm}^3 \text{ mol}^{-1}$, indicates an associatively activated exchange mechanism, most probably I_a .^{3–5}

This mechanistic conclusion is in contrast to that drawn from a variable pressure ¹H NMR study of *N,N*-dimethylformamide (DMF) exchange on $\text{Cu}(\text{Me}_6\text{tren})\text{DMF}^{2+}$ ($\text{Me}_6\text{tren} = 2,2',2''\text{-tris}(\text{dimethylamino})\text{triethylamine}$).³⁴ The positive activation volume showed that a dissociative activation mode operates for this exchange process. This mechanistic difference with water exchange on $\text{Cu}(\text{tren})\text{H}_2\text{O}^{2+}$ can be interpreted as being a result of greater steric crowding due either to the greater bulk of DMF or to the methyl groups. Stopped-flow and T-jump methods were used to study the complex-formation reactions of $\text{Cu}(\text{Me}_6\text{tren})\text{H}_2\text{O}^{2+}$ with the much smaller azide and thiocyanate ligands.³⁵ It was concluded that a dissociatively activated I_d mechanism operates for these reactions. This suggests that it is the steric effect of the methyl groups that causes the mechanistic differences, and a dissociatively activated mechanism may be predicted for water exchange on $\text{Cu}(\text{Me}_6\text{tren})\text{H}_2\text{O}^{2+}$.

We now turn to the investigated ligand substitution reactions. The ratios of the forward and reverse rate constants ($K^{\text{kin}} = k_{\text{on}}/k_{\text{off}}$) agree very well with the stability constants obtained from the independent spectrophotometric measurements (K^{sp}). This indicates the excellent internal consistency of the results presented here. The rate constants at 25 °C and ambient pressure are also in good agreement with the data published by Cayley et al.¹⁴

In general, ligand substitution reactions are visualized as a series of consecutive steps initiated by a diffusion-controlled outer sphere complex-formation between the reactants. In the case of monodentate ligands the rate determining step is always the displacement of a solvent molecule from the first coordination sphere. The second order rate constant for the complex-formation is given as $k_{\text{on}} = K_{\text{os}}k_1$, where K_{os} and k_1 are the outer-sphere stability constant and the rate constant for the replacement of a coordinated solvent molecule by the ligand in a concerted internal exchange process, respectively. It follows that the experimentally observed activation volume is the sum of the corresponding two volume components:

(33) Wilkins, R. G. *Kinetics and Mechanisms of Reactions of Transition Metal Complexes*, 2nd ed.; VCH: Weinheim, Germany, 1991; p 214.

(34) Lincoln, S. F.; Hounslow, A. E.; Pisanello, D. L.; Doddridge, B. G.; Coates, J. H.; Merbach, A. E.; Zbinden, D. *Inorg. Chem.* **1984**, *23*, 1090.

(35) Coates, J. H.; Collins, P.; Lincoln, S. F. *J. Chem. Soc., Faraday Trans.* **1979**, *75*, 1236.

$$\Delta V_{\text{on}}^{\ddagger} = \Delta \bar{V}_{\text{os}} + \Delta V_{\text{I}}^{\ddagger} \quad (14)$$

In the reactions of the pyridine ligands with $\text{Cu}(\text{tren})\text{H}_2\text{O}^{2+}$, both the leaving (H_2O) and the entering ligands are neutral and the overall process does not involve charge creation or cancellation. Consequently, the outer-sphere contribution can be neglected and $\Delta V_{\text{I}}^{\ddagger}$, which is the mechanistic indicator, equals $\Delta V_{\text{on}}^{\ddagger}$ (Table 2). In agreement with earlier suggestions¹⁴, the negative ΔV^{\ddagger} 's confirm an associative mode of activation for both the forward and reverse reactions. This is also demonstrated by the minima in the volume profiles constructed for these reactions (Figure 5). The ΔV^{\ddagger} values for the reactions in both the forward and reverse directions (Table 2) are very typical for an associative interchange mechanism.²⁻⁵ In addition, the values are close to that reported for solvent exchange on $\text{Cu}(\text{tren})\text{H}_2\text{O}^{2+}$ in Table 3. In the case of the reverse aquation reactions, significant bond formation must occur with the entering solvent (water) molecule in the transition state of the interchange step, accompanied by partial bond breakage with the leaving group. The $\Delta V_{\text{off}}^{\ddagger}$ values are of similar magnitude to ΔV^{\ddagger} for the water exchange reaction, which is in agreement with expectations for a common bond-formation step with the entering solvent molecule. The volume of activation data in Tables 2 and 3 strongly support the operation of an I_a ligand substitution mechanism for water exchange and complex-formation reactions of $\text{Cu}(\text{tren})\text{H}_2\text{O}^{2+}$.

In the case of the solvent exchange reaction we are dealing with a symmetrical process for which $\Delta \bar{V} = 0$. For the complex-formation reaction 1, however, $\Delta \bar{V}$ is not zero (see Table 2) since we are dealing with a nonsymmetrical ligand exchange process. The volume profiles in Figure 5 clearly demonstrate that the partial molar volume of the transition state is significantly smaller than either the reactant or product states, in line with an associative interchange of ligands. The $\Delta V_{\text{on}}^{\ddagger}$ and $\Delta \bar{V}$ values become more negative along the series $\text{py} > \text{Mepy} > \text{Clpy}$, whereas $\Delta V_{\text{off}}^{\ddagger}$ becomes more positive along this series. This is in agreement with the partial molar volumes of the entering ligands, viz. 52.4 (py), 61.9 (Mepy), and 74.2 (Clpy) $\text{cm}^3 \text{mol}^{-1}$, respectively, as calculated from density data. The exchange of a solvent molecule with a large entering ligand will cause a more negative reaction volume.

A complete set of kinetic and equilibrium parameters are now available for the studied complex-formation reactions (Table 2). This enables an inspection of the general thermodynamic and kinetic features of complex formation in these systems. As expected, the stability of the ternary complex increases with increasing basicity of L. In a series of I_a ligand substitution reactions with the same complex, the variation in the associative character is predominantly determined by the nucleophilicity of the entering ligand. Since the nucleophilic strength of closely related ligands most likely follows the order of the basicities, a well-defined correlation can also be envisioned between the kinetic parameters and the $\text{p}K_a$'s. The variation in the rate constants and activation entropies fulfills this expectation; k_{on} increases and $\Delta S_{\text{on}}^{\ddagger}$ becomes more negative in the $\text{Clpy} > \text{Mepy} > \text{py}$ order. On the basis of these results, one would project the least associative character and, consequently, the least negative activation volume for the reaction with Clpy. In reality, however, the most negative $\Delta V_{\text{on}}^{\ddagger}$ was found with this ligand, most probably due to its significantly higher partial molar volume as pointed out above. Alternatively, the less basic

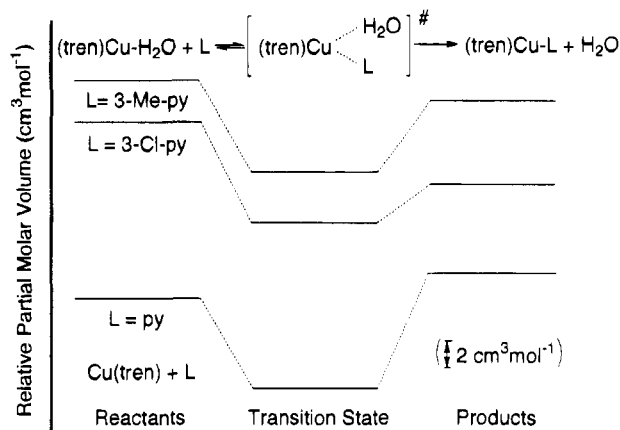


Figure 5. Volume profile for the $\text{Cu}(\text{tren})\text{H}_2\text{O}^{2+} + \text{L} \rightleftharpoons \text{Cu}(\text{tren})\text{L}^{2+} + \text{H}_2\text{O}$ reaction.

nucleophile could cause a "later" (product-like) transition state, whereas the more basic nucleophile could cause an "earlier" (reactant-like) transition state, and so account for the observed trends in $\Delta V_{\text{on}}^{\ddagger}$. Exactly the opposite trend is observed for the reverse aquation reactions: k_{off} is the slowest for the more basic and stronger nucleophiles py and Mepy, and $\Delta V_{\text{off}}^{\ddagger}$ is the smallest for the weakest nucleophile.

On the basis of the results presented here and available from previous literature, an interesting trend emerges for the kinetic properties of copper(II) complexes with tripodal tetradentate ligands. As long as the complex is octahedral, the ligand substitution reactions are fast and proceed via an I_d mechanism.¹⁰ When the strong ligand field forces the metal ion into a trigonal bipyramidal geometry, the coordination of the second ligand slows down by 3–4 orders of magnitude. Moreover, the mechanism becomes I_a . When the bulkiness of the tetradentate ligand is increased, e.g. in the $\text{Cu}(\text{Me}_6\text{tren})\text{DMF}^{2+}$ complex, the penetration of the entering ligand into the first coordination sphere is sterically hindered and an I_d activation mode becomes operative again.³⁴ In the case of trigonal bipyramidal copper(II) complexes a very large crystal field activation energy is expected for the I_d process.³⁴ Therefore, the rate of the ligand substitution reactions drops again by a factor of 10^3 . The noted variation in the kinetic behavior strongly suggests that the rate and mechanism of the related reactions can be controlled by appropriate selection of the tripodal ligand. It follows that the chelate ligand can induce a changeover in the substitution mechanism of aquated $\text{Cu}(\text{II})$, and so adds a further parameter to the steric and electronic control over ligand substitution reactions of very labile metal ions.

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Supplementary Material Available: Tables S1–S5 summarizing experimental and calculated rate constants for reaction 1 for L = py, Mepy, and Clpy as a function of [L] and pressure, measured ¹⁷O NMR linewidths, resonance frequencies, calculated reduced transverse relaxation rates, and chemical shifts at variable temperature and pressure for the $\text{Cu}(\text{tren})^{2+}$ samples and $\text{Zn}(\text{tren})^{2+}$ references and Figure S1 reporting plots of $\ln(1/T_2)$ and $-\Delta\omega/\omega_1$ versus $1/T$ (7 pages). Ordering information is given on any current masthead page.