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Mechanism of water exchange on five-coordinate copper(II) complexes †

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The effects of temperature and pressure on the water exchange reaction of the five-coordinate complexes $[Cu(tmpa)(H_2O)]^{2+}$ and $[Cu(fz)_2(H_2O)]^{2-}$ (tmpa = tris(2-pyridylmethyl)amine; fz = ferrozine = 5,6-bis(4-sulfonatophenyl)-3-(2-pyridyl)-1,2,4-triazine) were studied by employing ^{17}O NMR spectroscopy. The former compound shows a solvent exchange rate constant k_{ex} of $(8.6 \pm 0.4) \times 10^6$ s^{-1} at 298 K and ambient pressure, within a factor of three of that for the corresponding process for $[Cu(tren)(H_2O)]^{2+}$ (tren = 2,2′,2″-triaminotriethylamine). The activation parameters $\Delta H^\#$, $\Delta S^\#$ and $\Delta V^\#$ for the reaction are 43.0 ± 1.5 kJ mol^{-1}, $+32 \pm 6$ J K^{-1} mol^{-1} and -3.0 ± 0.1 cm^3 mol^{-1}, respectively. For $[Cu(fz)_2(H_2O)]^{2-}$, k_{ex} is $(3.5 \pm 2.6) \times 10^5$ s^{-1} at 298 K and ambient pressure, which is about an order of magnitude less than for $[Cu(tren)(H_2O)]^{2+}$. The $\Delta H^\#$, $\Delta S^\#$ and $\Delta V^\#$ values for the water exchange are 25.9 ± 2.2 kJ mol^{-1}, -52 ± 7 J K^{-1} mol^{-1} and -4.7 ± 0.2 cm^3 mol^{-1}. The activation volume is modestly negative for both reactions and therefore implies an associative interchange (I_a) mechanism. The results are discussed in reference to data for water exchange reactions of Cu(II) complexes available from the literature.

Introduction

In contrast to other divalent first row transition metal aqua ions, the aquated Cu(II) ion is extremely labile[1–4a] towards water exchange; k_{ex}^{298} is $(4.4 \pm 0.1) \times 10^9$ s^{-1}. This lability is a dynamic consequence of Jahn–Teller (J–T) distortion.[5] The tetragonal distorted geometry of aqua copper(II) has been observed in the solid state by employing X-ray[6–8] and neutron diffraction[9] techniques. Water exchange on aqua copper(II) occurs mainly at the more distant, labilised axial position, but due to the J–T inversion a given bound water molecule inverts several times before it exchanges with a bulk water molecule. The lifetime of this J–T inversion is about 5×10^{-12} s, in the time region of a single vibration.[3] The influence of J–T distortion is not restricted to water exchange on the aquated Cu(II) ion; substitution on six-coordinate copper species is also generally very fast. Steric effects give rise to decreased lability, while specific interactions between the coordinated ligand and the incoming nucleophile enhance the substitution process.[10–12] In all cases ligand substitution occurs *via* a dissociative interchange (I_d) mechanism.

The indubitable influence of the J–T effect on the reactivity of copper(II) ions was indirectly shown in the case of the $[Cu(tren)]^{2+}$ ion (with tren = 2,2′,2″- triaminotriethylamine), a trigonal bipyramidal species with the water molecule located in an axial position. Water exchange is characterized by a k_{ex}^{298} of $(2.39 \pm 0.09) \times 10^6$ s^{-1}, *i.e.* about 5000 times smaller than for the $[Cu(H_2O)_6]^{2+}$ ion.[13] The activation entropy of -34 ± 5 J K^{-1} mol^{-1} and the activation volume of -4.7 ± 0.2 cm^3 mol^{-1} were taken to indicate that water exchange occurs *via* an associative interchange (I_a) mechanism. Recently, Lu *et al.* found that $[Cu(tren)]^{2+}$ reacts with 4,5-diazofluoren-9-one in ethanol to form a distorted six-coordinate complex.[14] The bond lengths between the central atom and the two nitrogens of the bidentate ligand are reported to be 2.027 and 2.995 Å.[14] The structure of the complex illustrates that six-coordination (even though it is distorted) can also be found in the ground state in Cu(II) complexes of tren. An associative substitution process has also been reported for substitution of water in $[Cu(tren)(H_2O)]^{2+}$ by neutral or anionic nucleophiles.[13,15,16]

The six methyl groups of Me$_6$tren (2,2′,2″-tris(dimethylamino)triethylamine) have a dramatic influence on the lability of the coordinated molecule in the fifth position of the trigonal bipyramidal copper(II) complex of Me$_6$tren.[17] Compared with $[Cu(tren)(H_2O)]^{2+}$, the lability is reduced by a factor of about 10^5.[16,18–20] Due to the steric hindrance afforded by three of the donor groups of the tetradentate ligand, an associative substitution process is no longer possible. Interestingly, very recently, it has been reported[21] that water exchange on the five-coordinate, (presumed trigonal bipyramidal) $Cu(terpy)(H_2O)_2^{2+}$ ion (terpy = 2,2′:6′,2″-terpyridine) is characterised by $k_{ex}^{298} = 6.6 \times 10^8$ s^{-1}, indicating that markedly lower labilisation of coordinated water is not obligatory in five-coordinate Cu(II) complex species.

The immense difference in reactivity between $[Cu(tren)(H_2O)]^{2+}$ and $[Cu(Me_6tren)(H_2O)]^{2+}$ complexes, challenged us to investigate the kinetics of solvent exchange and substitution processes of additional five-coordinate copper(II) complexes, in order to obtain a better understanding of steric and electronic influences on the reactivity of copper complexes in examples where J–T distortion is absent, or is greatly reduced. An investigation of the kinetics of substitution of the coordinated water on $[Cu(Me_3tren)(H_2O)]^{2+}$ (Me$_3$tren = 2,2′,2″-tris(monomethylamino)-triethylamine) by pyridine,[22] demonstrated a modest lability reduction due to steric influences. The mechanism of the pyridine for water exchange is quite similar to that for $[Cu(tren)(H_2O)]^{2+}$. We have now focused on the kinetics of solvent exchange on two other five-coordinate copper(II)

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† In memory of Manuela Körner (05.04.1970–08.04.2000).

Electronic supplementary information (ESI) available: line widths and chemical shifts as a function of temperature and pressure for water exchange on $[Cu(tmpa)(H_2O)]^{2+}$, $[Cu(tmpa)(OH)]^{+}$, $[Cu(Me_3tren)(H_2O)]^{2+}$ and $[Cu(fz)_2(H_2O)]^{2-}$. See http://www.rsc.org/suppdata/dt/b1/b107458j/

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Table 1 Composition of the different samples used in the ^{17}O NMR studies

Sample	[Complex]/M	pH
$[Cu(tmpa)(H_2O)]^{2+}$	0.018	4.56
$[Zn(tmpa)(H_2O)]^{2+}$	0.018	6.25
$[Cu(tmpa)(H_2O)]^{2+}$	0.0067	5.04
$[Zn(tmpa)(H_2O)]^{2+}$	0.0067	6.26
$[Cu(tmpa)(OH)]^{2+}$	0.015	11.1
$[Cu(fz)_2(H_2O)]^{2-}$	0.020	8.0
$[Cu(fz)_2(H_2O)]^{2-}$	0.026	8.52

complexes. The results for water exchange on $[Cu(tmpa)(H_2O)]^{2+}$ (tmpa = tris(2-pyridylmethyl)amine) and $[Cu(fz)(H_2O)]^{2-}$ (fz = ferrozine = 5,6-bis(4-sulfonatophenyl)-3-(2-pyridyl)-1,2,4-triazine) and our observations on related systems are reported herein. The coordination geometry of the former complex species has been firmly established in aqueous solution as trigonal bipyramidal.[23] The ferrozine complex is square pyramidal,[24] a geometry exhibited in other Cu(II) complexes.[25]

Following the completion of this project, experimental and theoretical evidence has been presented that strongly suggests that aquated copper(II) prefers a five-coordinate state rather than the traditionally accepted six-fold coordination.[4b] This only marginally affects the water exchange rate constant on aquated Cu(II) which was determined based on the assumption that six water molecules were coordinated. This finding therefore implies that partial substitution of water on aquated Cu(II) by chelating ligands prevents the rapid geometrical interconversion proposed on five-coordinate aquated Cu(II), and leads to a considerably reduced water lability.

Experimental

Materials

Tmpa was prepared according to the procedure of Karlin and coworkers[26] and characterized by ^1H, ^{13}C NMR spectroscopy and elemental analysis. The data were in accordance with those published earlier.[26]

All chemicals used in solution preparation were reagent grade quality. Stock solutions of $Cu(NO_3)_2\cdot 6H_2O$ (Merck) and $Zn(NO_3)_2\cdot 4H_2O$ (Merck) were prepared in doubly distilled water. Solutions of $[Cu(tmpa)(H_2O)]^{2+}$ and $[Zn(tmpa)(H_2O)]^{2+}$ were prepared by mixing stoichiometric amounts of $Cu(NO_3)_2\cdot 6H_2O$ and $Zn(NO_3)_2\cdot 4H_2O$ with tmpa. The ionic strength was adjusted with KNO_3 to $I = 0.10$ M. The $[Cu(fz)_2(H_2O)]^{2-}$ complex was prepared *in situ* using weighed amounts of $CuSO_4\cdot 5H_2O$ (Merck) and double the equimolar concentration of fz (Aldrich). The complex was fully characterized by UV/Vis, IR, EA, ICP, EPR spectroscopy and electrochemistry, of which the details are reported elsewhere.[24]

The samples for the water exchange experiments were prepared by mixing the appropriate amounts of the metal salts with tmpa and fz in ^{17}O enriched (*ca.* 1%) water (Yeda). The pH was measured by employing a Mettler Toledo Delta 350 pH meter equipped with a Mettler Toledo combined glass electrode (InLab 422). The electrode calibration for H^+ concentration has been described elsewhere,[12,27] such that pH means $-\log[H^+]$. The compositions of the different samples are shown in Table 1.

^{17}O NMR Measurements

The ^{17}O NMR spectra were recorded on a Bruker AVANCE DRX 400WB spectrometer operating at a resonance frequency of 54.24 MHz. At atmospheric pressure the measurements were performed on a commercial 5 mm Bruker broadband probe thermostatted with a Bruker B-VT 3000 variable temperature unit.

Variable pressure experiments up to 150 MPa were performed on a homemade high pressure probehead.[28] The ^{17}O NMR experiments were performed unlocked but the sample was shimmed on the corresponding proton FID, so that significant line broadening due to field inhomogeneity caused by the high pressure probe was excluded. The temperature was controlled with a Pt-100 resistor as described elsewhere[28] and remained constant within ±0.5 K. Transverse relaxation rates, $1/T_2^{Cu}$ and $1/T_2^{Zn}$, were obtained directly from the linewidths according to $1/T_2 = \pi\Delta\nu_{1/2}$.

Results

Potentiometric titrations of the ligand and the copper(II) complex carried out at 293 K and at an ionic strength of 0.10 M (KNO_3)[29] show that the $[Cu(tmpa)(H_2O)]^{2+}$ complex significantly dissociates only in strong acidic media at a pH below 1. The pK_a value of the coordinated water is 7.40 ± 0.03. Based on these thermodynamic data the solutions for the NMR studies were prepared in a way that either only the aqua or the hydroxo species are present in solution (see Table 1). Experiments on the hydroxo species show that exchange cannot be observed. Therefore, the kinetic observations refer only to water exchange on the aqua complex. For the $[Cu(fz)_2(H_2O)]^{2-}$ complex, the pH was selected to ensure that the coordinated ligand is fully deprotonated and thus the complex carries an overall $2-$ charge. In this case the pK_a value of the coordinated water molecule is expected to be significantly higher than for the $2+$ charged tmpa complex.

The water exchange rates of $[Cu(tmpa)(H_2O)]^{2+}$ and $[Cu(fz)_2(H_2O)]^{2-}$ were determined by ^{17}O NMR spectroscopy from measurements of the transverse relaxation times and the chemical shift of the paramagnetic complex (T_2^{Cu}, ω_{Cu}) and the diamagnetic reference (T_2^{Zn}, ω_{Zn}). For $[Cu(tmpa)(H_2O)]^{2+}$ the corresponding Zn complex and in the case of $[Cu(fz)_2(H_2O)]^{2-}$ pure water was used as a reference. From these experimental values, together with the mole fraction of bound water, P_m, the reduced transverse relaxation rate ($1/T_{2r}$) and the reduced chemical shift $\Delta\omega_r$ can be calculated for each temperature and pressure. According to Swift and Connick[30,31] T_{2r} and $\Delta\omega_r$ are related to T_{2m}, the transverse relaxation time of coordinated water in the absence of chemical exchange, the exchange rate k_{ex} (= $1/\tau_m$) and the shift difference between coordinated water and bulk water, $\Delta\omega_m$, by eqns. (1) and (2).

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

$$\Delta\omega_r = \frac{1}{P_m}(\omega_{Cu} - \omega_{Zn}) = \frac{\Delta\omega_m}{(\tau_m/T_{2m} + 1)^2 + \tau_m^2\Delta\omega_m^2} + \Delta\omega_{os} \quad (2)$$

The total outer-sphere contributions on T_{2r} and $\Delta\omega_r$ arising from long-range interaction of the paramagnetic unpaired electron of the copper complex with the water outside the first coordination sphere are represented by T_{2os} and ω_{os}.

No significant shift difference between the signal for the paramagnetic copper species and the reference signal, $\Delta\omega_r$, was obtained. The contribution of $\Delta\omega_m$ and $1/T_{2os}$ to $1/T_{2obs}$ was found to be negligible, so that eqn. (1) reduces to eqn. (3).

$$\frac{1}{T_{2r}} = \frac{1}{T_{2m} + \tau_m} \quad (3)$$

We assumed an Arrhenius-type temperature dependence on $1/T_{2m}$ (eqn. (4)) with $1/T_{2m}^{298}$ as the rate at 298.15 K and E_m as the activation energy. For the exchange rate, k_{ex}, or the reciprocal residence time of the bound water molecule, $1/\tau_m$, a temperature dependence according to the Eyring equation (5) is assumed.

$$1/T_{2\mathrm{m}} = 1/T_{2\mathrm{m}}^{298} \exp\{E_\mathrm{m}/R(1/298.15 - 1/T)\} \qquad (4)$$

$$\frac{1}{\tau_\mathrm{m}} = k_\mathrm{ex} = \frac{k_\mathrm{B}T}{h}\exp\left\{\frac{\Delta S^{\#}}{R} - \frac{\Delta H^{\#}}{RT}\right\} = \frac{k_\mathrm{ex}^{298}T}{298.15}\exp\left\{\frac{\Delta H^{\#}}{R}\left(\frac{1}{298.15} - \frac{1}{T}\right)\right\} \qquad (5)$$

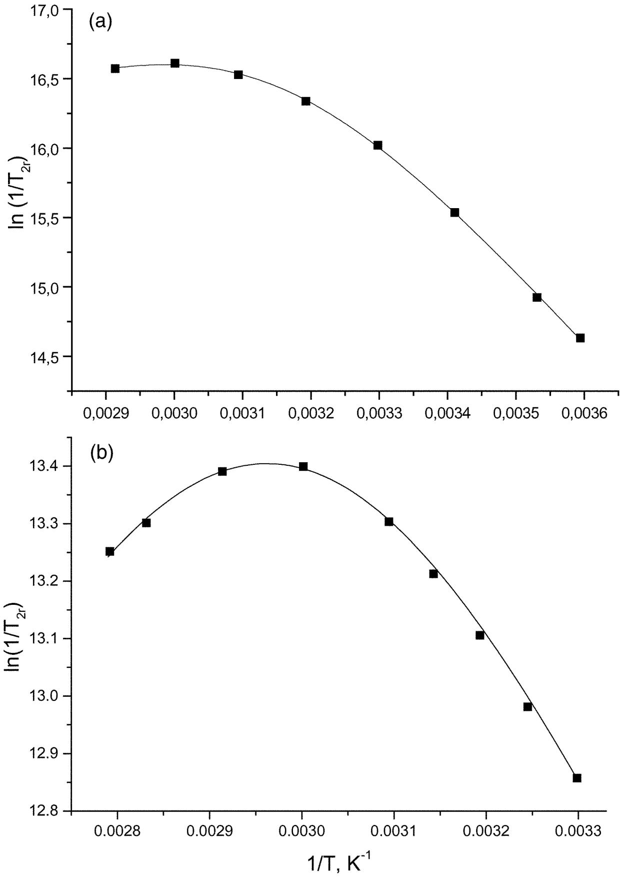

Fig. 1 Temperature dependence of the reduced transverse relaxation rate of (a) $[\mathrm{Cu(tmpa)(H_2O)}]^{2+}$ (concentration = 0.018 M) and (b) $[\mathrm{Cu(fz)_2(H_2O)}]^{2-}$ (concentration = 0.020 M).

A non-linear least-squares fit (see Fig. 1) to eqns. (3) to (5) yields the parameters given in Table 2. The pressure dependences of the reduced transverse relaxation rate, $1/T_{2\mathrm{r}}$, at 297.6 K are shown in Fig. 2.

We performed a least-squares fit of the data in Fig. 2 using eqns. (3), (4) and (6). $1/T_{2\mathrm{m}}^{297.6}$ was calculated using eqn. (4)

$$\frac{1}{\tau_\mathrm{m}} = k_\mathrm{ex} = k_\mathrm{ex}^\circ \exp\left\{-\frac{\Delta V^{\#}}{RT}P\right\} \qquad (6)$$

with $1/T_{2\mathrm{m}}^{298}$ and E_m in Table 2 and was assumed to be independent of pressure. The fitted parameters are given in Table 2. The values obtained for k_ex° (ambient pressure at 297.6 K) are in good agreement or consistent with the corresponding values k_ex° from the temperature dependence study. Further details of the experimental data and other parameters may be found in the ESI.

Discussion

The rate constants for water exchange on $[\mathrm{Cu(tmpa)(H_2O)}]^{2+}$ and $[\mathrm{Cu(fz)_2(H_2O)}]^{2-}$ (Table 3) are within a factor of three and ten of that for the corresponding process on $[\mathrm{Cu(tren)(H_2O)}]^{2+}$. In aqueous solution the copper complexes of the tetradentate ligands tmpa and tren and of two bidentate fz ligands contain a coordinated water molecule to form a five-coordinate geometry around the metal center. The similar rate constants for these systems indicate that the five-coordinate geometry of the complex ion is responsible for a very similar rate reduction from that for water exchange on the aquated copper(II) ion. Further, it is implied that, at least for these examples, the lability of the water molecule is not highly sensitive to the specific nature of the ligand, and also not to the organisation of the components of the complex ion. There is variation in the effect of different solvent exchange labilities for a common complex ion: in the case of $[\mathrm{Cu(tren)(solv)}]^{2+}$ only minor differences in reactivity are observed, whereas there is a substantial difference in the case of $[\mathrm{Cu(Me_6tren)(solv)}]^{2+}$ (see Table 3). Solvent exchange studies using the complex ions of Me$_6$tren in $\mathrm{CH_3CN}$ have been extended to Mn(II) and Co(II), and interesting kinetic and mechanistic information emerged which could be explained in terms of the different d orbital occupancies and other factors.[20]

Table 2 Parameters obtained from least-squares fits of $1/T_{2\mathrm{r}}$ as a function of (a) temperature and (b) pressure

	$[\mathrm{Cu(tmpa)(H_2O)}]^{2+}$	$[\mathrm{Cu(fz)_2(H_2O)}]^{2-}$
(a) Temperature		
$k_\mathrm{ex}^{298}/\mathrm{s}^{-1}$	$(8.6 \pm 0.4) \times 10^6$	$(3.5 \pm 2.6) \times 10^5$
$\Delta H^{\#}/\mathrm{kJ\ mol^{-1}}$	43.0 ± 1.5	25.9 ± 0.3
$\Delta S^{\#}/\mathrm{J\ mol^{-1}\ K^{-1}}$	$+32 \pm 6$	-52 ± 7
$(1/T_{2\mathrm{m}}^{298})/\mathrm{s}$	$(4.3 \pm 0.7) \times 10^7$	$(4.9 \pm 1.2) \times 10^6$
$E_\mathrm{m}/\mathrm{kJ\ mol^{-1}}$	-15 ± 3	-28 ± 3
(b) Pressure		
$k_\mathrm{ex}^{297.6}/\mathrm{s}^{-1}$	$(8.81 \pm 0.04) \times 10^6$	
$k_\mathrm{ex}^{313.2}/\mathrm{s}^{-1}$		$(6.92 \pm 0.05) \times 10^5$
$\Delta V^{\#}/\mathrm{cm^3\ mol^{-1}}$	-3.0 ± 0.1	-4.7 ± 0.2

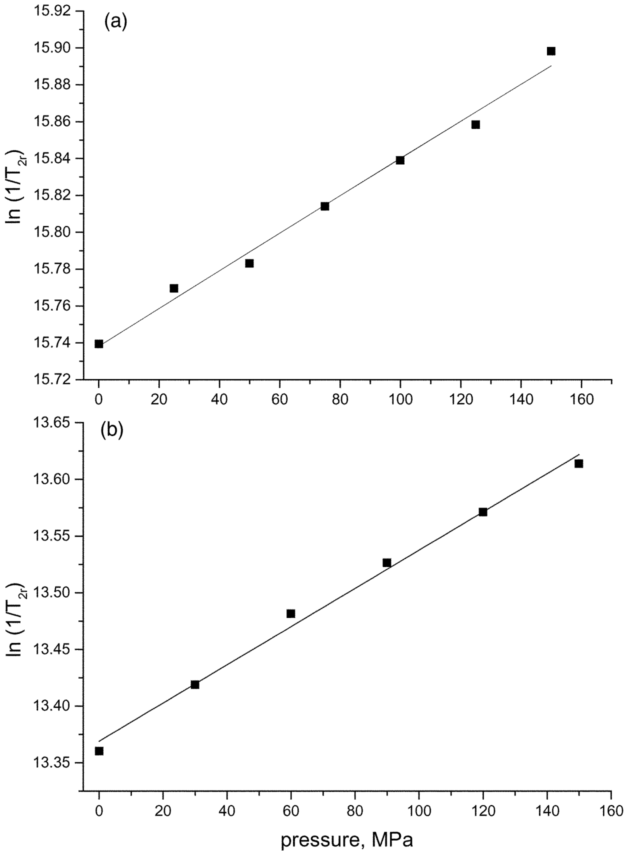

Fig. 2 Pressure dependence of the reduced transverse relaxation rate of (a) $[\mathrm{Cu(tmpa)(H_2O)}]^{2+}$ (concentration = 0.0067 M at 297.6 K) and (b) $[\mathrm{Cu(fz)_2(H_2O)}]^{2-}$ (concentration = 0.020 M at 313.2 K).

While the rate constants for water exchange on $[\mathrm{Cu(tren)(H_2O)}]^{2+}$ and $[\mathrm{Cu(tmpa)(H_2O)}]^{2+}$ are rather similar, the

Table 3 Rate and activation parameters for solvent exchange reactions on Cu(II) complexes

Complex	k_{ex}^{298}/s^{-1}	$\Delta H^{\#}$/kJ mol^{-1}	$\Delta S^{\#}$/J mol^{-1} K^{-1}	$\Delta V^{\#}$/cm^3 mol^{-1}	Ref.
$[Cu(H_2O)_6]^{2+}$	$(4.4 \pm 0.1) \times 10^9$	11.5 ± 0.3	-21.8 ± 0.9	$+2.0 \pm 1.5$	3,4
$[Cu(tmpa)(H_2O)]^{2+}$	$(8.6 \pm 0.4) \times 10^6$	43.0 ± 1.5	$+32 \pm 6$	-3.0 ± 0.1	[a]
$[Cu(tren)(H_2O)]^{2+}$	$(2.4 \pm 0.1) \times 10^6$	26.4 ± 1.4	-34 ± 5	-4.7 ± 0.2	13
$[Cu(tren)(CH_3CN)]^{2+}$	$(1.7 \pm 0.2) \times 10^6$	45 ± 4	$+26 \pm 16$		5
$[Cu(Me_6tren)(DMF)]^{2+}$	555 ± 39	43.3 ± 1.1	-47 ± 3	$+6.5 \pm 0.2$	19,20
$[Cu(fz)_2(H_2O)]^{2-}$	$(3.5 \pm 2.6) \times 10^5$	25.9 ± 2.2	-52 ± 7	-4.7 ± 0.2	[a]

[a] This work.

individual thermal activation parameters show substantial differences, reflecting through $\Delta H^{\#}$ an apparently much stronger oxygen to copper bond in the latter complex ion. This can be rationalized in terms of the lower pK_a of the coordinated water in $[Cu(tmpa)(H_2O)]^{2+}$ (7.4 compared to the value of 9.4 in $[Cu(tren)(H_2O)]^{2+}$)[13,32] if this ground state property can be related to the transition state. A corollary of the difference in $\Delta H^{\#}$ is that the difference in the $\Delta S^{\#}$ values extends to a difference in sign, albeit the magnitude of the difference (Table 3) is not enormous. The activation enthalpy of the $[Cu(fz)(H_2O)]^{2-}$ complex has nearly the same value as that for the tren complex, whereas the activation entropy is more negative. When the values are similar this may be coincidental, as the exchanging water molecules are from complex ions of the same coordination numbers but of different geometries. Furthermore, the non-exchanging ligand(s) can contribute to a very different electron density at the site of bond breakage. It is worthwhile to emphasise that extracting the thermal activation parameters from the primary NMR spectroscopic data requires calculating five parameters out of eight data pairs, *i.e.* the values may mask a greater uncertainty than is reported.

The entropy of activation in a solvent exchange process consists in effect of both intrinsic and solvational components; hence solvent exchange, diagnosed as occurring by a common mechanism (determined principally by a common intrinsic component) for two ions, may indeed have very different solvation changes accompanying the exchange process. This leads, therefore, to notably different $\Delta S^{\#}$ values. Thus, in principle, there is transparent virtue in measuring $\Delta V^{\#}$, at least if this parameter characterizes the intrinsic component in solvent exchange.[33] That is, when positive it represents the increase in volume when the exchanging water molecule is departing from the metal ion coordination sphere, and when negative it represents the decrease in volume as a water molecule undergoes the influence of the charged coordinated metal ion. The mechanism of water exchange can, for the two title complex ions, as a first approximation, be assigned as associative interchange (I_a) based on the $\Delta V^{\#}$ values in Table 3, with slightly less associative character in the case of the tmpa complex ion compared to tren. The same trend on $\Delta H^{\#}$ and $\Delta S^{\#}$ observed for the fz and tren complexes results in the same activation volume of -4.7 cm^3 mol^{-1} for these systems (Table 3). Other authors[20] have pointed to the value of $\Delta V^{\#}$ as a far better mechanistic indicator than $\Delta S^{\#}$, and the literature contains other examples where the signs of $\Delta V^{\#}$ and $\Delta S^{\#}$ are opposite in solvent exchange reactions and even in other contexts. The value of attempting to use $\Delta S^{\#}$ in mechanistic interpretation has been queried.[20] An argument advanced to support a dubious value is that in addition to the contribution to $\Delta S^{\#}$ from solvent rearrangement in the second coordination sphere, a second possible contribution to this parameter arises from vibrational and rotational changes within the *first* coordination sphere.[19,20] On the other hand, it may also be argued that a measured activation volume may not only represent an intrinsic volume change as described above, but also contains contributions from changes in volume of the coordinated non-exchanging water molecules or other ligands, and of water molecules in the second coordination sphere. In addition, it has been pointed out that the outer sphere line broadening caused by a paramagnetic ion may affect the value of $\Delta V^{\#}$ as a result of the effect of pressure on the viscous flow and the compressibility of the solvent.[34] Fortunately, these effects fall within the experimental uncertainty of the measurements in the case of water as solvent.[34]

The $\Delta V^{\#}$ values reported for solvent exchange on $[Cu(tren)(H_2O)]^{2+}$, $[Cu(tmpa)(H_2O)]^{2+}$ and $[Cu(fz)_2(H_2O)]^{2-}$ in Table 3 confirm the associative nature of the exchange mechanism as characterized by a more compact transition state than either the reactant or product states. Although the magnitude of these values suggests the operation of an associative interchange (I_a) mechanism, as argued above, the possible operation of a limiting A mechanism is not ruled out. At present the overall volume reduction expected for the associative entrance of a water molecule into a trigonal bipyramidal or a square pyramidal structure is not known as in the case of octahedral complexes. In addition, the possible formation of a pseudo-octahedral intermediate[14,35] would be accompanied by a significant volume collapse due to the coordination of a solvent molecule, which will be partly offset by a volume increase as a result of J–T distortion of the pseudo-octahedral state. Thus the resulting volume of activation for a limiting A mechanism in such systems may indeed be a relatively small negative number. Hence while $\Delta V^{\#}$ values of the magnitude reported here would customarily be interpreted as indicative of an I_a mechanism, an A mechanism in these cases is not necessarily ruled out. It may be speculated that water exchange on the tmpa complex occurs by a "*cis*" mechanism whereby the entering water molecule loosely associates with the complex center with simultaneous weakening of the bound water molecule. Clearly both cannot occupy the same location hence neither will be attached with the metal–oxygen bond at 90° to the equatorial plane during the actual interchange. In the case of water exchange from the fz complex a comparable exchange process could occur, or a "*trans*" exchange can take place with the incoming molecule entering at the opposite unoccupied position, with subsequent loss of the exchanging water molecule. The latter method of exchange could be more favourable energetically: the magnitudes of the enthalpies of activation (Table 2) are not inconsistent with this. It also correlates with the much more negative activation entropy for the fz complex compared to the tmpa complex, although we have expressed reservations about the reliability of interpretations based only on the latter parameter.

The body of accumulated results points to rates of water exchange on five-coordinate Cu(II) complexes being several orders of magnitude lower than exchange on aquated Cu(II). One notable exception is $Cu(terpy)(H_2O)_2^{2+}$ (*vide supra*).[21] An explanation may reside in two factors: the first is that the complex ion is not actually five-coordinate, and a second is that an unusual degree of reactivity arises from the presence of the terpyridine ligand that gives rise to a water exchange rate constant for a five-coordinate complex that approaches that for the aquated Cu(II) ion. In the solid state mono-terpy complexes of Cu(II) possess five-coordinate, trigonal bipyramidal geometry. It has been assumed that this geometry and coordination number is preserved in solution. Confirmatory experiments would be needed to firmly establish this. A dramatic labilising effect of terpyridine was noted for the associative nucleophilic substitution of water in a series of amine substituted Pt(II) complexes of the type $Pt^{II}(NNN)(H_2O)$.[36] It was concluded that the pyridine chelate rings in terpyridine can communicate electronically, become part of the π-conjugated system, increasing the electophilic character of the metal and thereby inducing a more rapid nucleophilic attack by the entering nucleophile. This would then account for the higher exchange rate constant found for the five-coordinate $Cu(terpy)(H_2O)_2^{2+}$ complex.[21]

Conclusions

Rates of water exchange on five-coordinate complexes of copper(II) are drastically reduced from the rate of exchange on aquated copper(II) ions, since the dynamic consequences of Jahn–Teller distortion are absent. The rates of exchange on the five-coordinate systems depend less on the particular ligand and appear not to be very markedly influenced by the particular five-coordinate geometry. Apparently $Cu(terpy)(H_2O)_2^{2+}$ is an exception, in that water exchange is very rapid. The mechanism of water exchange is of associative character in all examples studied to date. The overall charge on the complex does not seem to have a specific effect on the water exchange mechanism. In the case of the anionic fz complex, the charge on the chelate is far removed from the metal center and may therefore not have a drastic effect on the substitution kinetics of the complex. We are investigating other similar systems, although some are bedevilled by experimental difficulties. For example, water exchange on $[Cu(Me_3tren)(H_2O)]^{2+}$ is accessible in the time window of the ^{17}O line broadening approach to the kinetics. However, the temperature dependence of $1/T_{2r}$ is in the region of very slow exchange with a dominating outer sphere contribution, even at high temperatures, thus preventing extraction of reliable kinetic parameters.

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