Mechanism of Water Substitution in the Trigonal-bipyramidal Complex $[Cu(tren)(OH_2)]^{2+}$ (tren = 2,2',2''-triaminotriethylamine): Evidence for an Associative Mechanism

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The mechanism of substitution of water in the title complex by a series of pyridine derivatives has been studied using temperature-jump relaxation spectrophotometry. The dependence of k_f and k_b on the nature of the ligand and the values of the activation parameters offer strong support for an associative mechanism.

THE rates of water exchange [1] and ligand-substitution reactions [2,3] of the trigonal-bipyramidal complex $[Cu(tren)(OH_2)]^{2+}$ (tren = 2,2',2''-triaminotriethylamine) are unusually slow compared to the corresponding reactions [4,5] of the octahedral complexes. This has been attributed to the relatively rigid geometry of $[Cu(tren)(OH_2)]^{2+}$ which does not allow Jahn–Teller inversion to occur.[4-7] Substitution reactions of octahedral copper(II) complexes have been shown to follow a dissociative pathway.[5] In other first transition series octahedral complexes a mechanistic changeover for water exchange from associative to dissociative has been reported [8] for Mn^{2+}, Fe^{2+}, Co^{2+}, and Ni^{2+}. No studies have been made on the mechanism of substitution in five-co-ordinated copper(II) complexes.

We have studied the mechanism of substitution of water in $[Cu(tren)(OH_2)]^{2+}$ by a series of pyridine derivatives. The results provide strong evidence that the mechanism proceeds by an associative pathway.

EXPERIMENTAL

Materials and Methods.—Pyridine, 3-methylpyridine, and 4-methylpyridine (B.D.H., Poole) were redistilled in an all-glass apparatus before use. 3-Chloropyridine was obtained from Aldrich Chemical Company (Gillingham, Dorset) and used without further purification. All other chemicals were of reagent grade quality and purchased from B.D.H. unless otherwise stated.

2,2',2''-Triaminotriethylamine was separated from technical grade triethylenetetra-amine (Hopkin & Williams, Romford, Essex) in the form of the hydrochloride according to the procedure of Wilson and Rose [9] and recrystallised twice from ethanol–water before use (Found: C, 28.1; H, 8.2; N, 21.95. Calc. for tren·3HCl: C, 28.15; H, 8.30; N, 21.9%). Carbon-13 n.m.r. spectra of the salt showed only two resonance peaks which confirms that the purified tren·3HCl is free from residual triethylenetetra-amine. The salt was converted into the free base by passing through a column of Zerolite FF(ip) anion-exchange resin in the hydroxide form and standardised by titrating against standard acid using bromocresol green as indicator.

Copper(II) perchlorate was prepared by treating copper carbonate with an excess of perchloric acid and was recrystallised from water. Its solutions were standardised by atomic absorption spectroscopy.

The complex $[Cu(tren)(OH_2)]^{2+}$ was prepared by mixing copper(II) perchlorate and tren in the molar ratio 1 : 1.06. It has a stability constant [2] of 10^{19} dm^3 mol^{-1} and is effectively the only copper species present between pH 4 and 8.

Temperature-jump relaxation measurements were performed on a type SBA7 relaxation spectrophotometer (Messanlagen Studiengesellschaft MBH, Gottingen) employing a Tektronix type 535A oscilloscope. The standard sample cell (capacity 6 cm^3, light path 1 cm) was thermostatted to ± 0.1 °C using a Grant LB3 circulating water-bath. Temperatures were measured using a Comark type 1604 electronic thermometer. All the experiments employed a discharge of 30 kV corresponding to a temperature rise of 3.9 °C. The data reported refer to the final temperature of measurement, *i.e.* after electrical heating.

The concentration of $[Cu(tren)(OH_2)]^{2+}$ used in the relaxation studies was fixed at 0.436 mmol dm^{-3} and the medium was buffered at pH 6.1 with 0.04 mol dm^{-3} 2-morpholinoethanesulphonic acid buffer. The latter, purchased from Sigma Chemical Co., was the buffer of choice since it did not affect the u.v. or visible spectrum of $[Cu(tren)(OH_2)]^{2+}$ under the conditions of experiment. The concentrations of pyridine or its derivatives were varied from 5 to 25 mmol dm^{-3}. Ionic strength was maintained constant at 1.0 mol dm^{-3} by addition of sodium perchlorate.

The reaction between pyridines and $[Cu(tren)(OH_2)]^{2+}$ was followed at 305 nm for each of four temperatures in the range 10—30 °C. Each relaxation time reported is the average of five independent measurements, the standard deviation being less than 5%; the relaxation times were calculated from plots of log Δ(absorbance) against time taken from 10× enlarged photographic prints.

The pK_a of pyridine or its derivatives was determined by pH titration of a 15 mmol dm^{-3} solution with 1.0 mol dm^{-3} perchloric acid at an ionic strength of 1.0 mol dm^{-3} through addition of sodium perchlorate. These titrations were carried out in thermostatted vessels using a type PHM26 pH meter (with scale expansion) which incorporated a GK 2321C glass electrode and K401 calomel electrode (Radiometer, Copenhagen). Sodium chloride replaced potassium chloride in the salt-bridge connections of the electrodes to prevent precipitation of potassium perchlorate.

All pH measurements were corrected for activity by comparing the measured pH values of different concentrations of $HClO_4$ in 1 mol dm^{-3} $Na[ClO_4]$ with the values calculated from the acid molarity. The kinetics were analysed according to the reaction scheme below where M represents

$$M + HL^+ \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} M + L + H^+ \underset{k_b}{\overset{k_f}{\rightleftharpoons}} ML + H^+$$

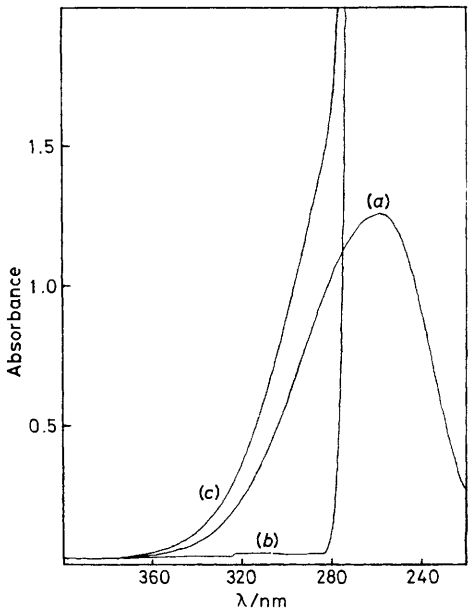
(1) (2) (3)

$[Cu(tren)(OH_2)]^{2+}$ and L represents the pyridine derivative. The step (1) $\rightleftharpoons$ (2) involving protonation was treated as a fast pre-equilibration prior to the metal–ligand reaction. The hydrogen-ion concentration was maintained constant

throughout by the buffered conditions and the large excess of L over M ensures pseudo-first-order behaviour. The values of k_f and k_b were determined from the slope and intercept of a plot of τ^{-1} against $[L]_t/(1 + K_a[H^+])$ where $[L]_t$ is the total ligand concentration and K_a is the acid stability constant of the ligand.

RESULTS

The Figure shows the spectra of $[Cu(tren)(OH_2)]^{2+}$, 3-chloropyridine, and the $[Cu(tren)]^{2+}$–3-chloropyridine complex. Similar results were obtained with the other pyridines studied. It can be seen that only the complexes absorb at 305 nm, the wavelength at which relaxation measurements are made. Neither $[Cu(tren)(OH_2)]^{2+}$ nor the pyridines show any relaxation on the time scale over which the $[Cu(tren)]^{2+}$–pyridine complexes were studied.



Ultraviolet–visible spectrum of (*a*) $[Cu(tren)(OH_2)]^{2+}$ (0.66 mmol dm^{-3}); (*b*) 3-chloropyridine (2.0 mmol dm^{-3}); and (*c*) $[Cu(tren)(OH_2)]^{2+}$ (0.66 mmol dm^{-3})–3-chloropyridine (2.0 mmol dm^{-3}) all in 2-morpholinoethanesulphonic acid buffer (0.04 mol dm^{-3}) pH 6.1 containing $Na[ClO_4]$ (1 mol dm^{-3})

TABLE 1

Values of k_f and k_b for the reaction of pyridine derivatives with $[Cu(tren)(OH_2)]^{2+}$, and pK_a values at different temperatures

Ligand	θ_c/°C	pK_a	10^{-5} k_f/dm^3 mol^{-1} s^{-1}	10^{-3} k_b/s^{-1}
Pyridine	11.9	5.869 ± 0.007	0.97	0.55
	15.2	5.822 ± 0.003	1.18	0.70
	20.0	5.720 ± 0.003	1.46	0.94
	24.9	5.638 ± 0.006	1.64	1.27
	28.7	5.590 ± 0.002	1.90	
3-Methyl-pyridine	12.2	6.403 ± 0.006	1.39	0.38
	18.1	6.240 ± 0.006	1.75	0.57
	24.1	6.146 ± 0.007	1.97	0.87
	29.5	6.049 ± 0.001	2.31	1.25
4-Methyl-pyridine	12.2	6.735 ± 0.006	1.59	0.36
	18.1	6.585 ± 0.006	2.04	0.52
	24.1	6.482 ± 0.006	2.45	0.75
	29.5	6.394 ± 0.004	2.70	1.16
3-Chloro-pyridine	15.0		0.21	2.33
	24.8		0.33	3.18
	29.1		0.42	3.96
	31.3		0.51	4.84

The plot of τ^{-1} against $[L]/(1 + K_a[H^+])$ is linear over the full concentration range (5—25 mmol dm^{-3}) of the pyridine derivatives studied. This confirms the assumed mechanism in the scheme and shows that even at high ligand concentrations only one molecule of the ligand binds to one molecule of $[Cu(tren)(OH_2)]^{2+}$. The values of k_f and k_b for ligands at different temperatures are given in Table 1 along with the pK_a values. The compound 3-chloropyridine is present as the neutral species under the conditions of the experiments and thus it was not necessary to determine the variation of its pK_a with temperature. The activation parameters for the formation and dissociation reactions are given in Tables 2 and 3 respectively.

TABLE 2

Activation parameters and rate constants at 25 °C for the formation of $[Cu(tren)]^{2+}$–pyridine complexes

Ligand	pK	10^{-5} k_f/dm^3 mol^{-1} s^{-1}	E_A	$\Delta G^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}
			kJ mol^{-1}			
3-Chloropyridine	2.85	0.35	38.19	47.04	35.71	−38.00
Pyridine	5.64	1.67	27.54	43.17	25.06	−60.76
3-Methylpyridine	6.14	2.08	20.38	42.62	17.90	−82.96
4-Methylpyridine	6.48	2.48	20.85	42.18	18.37	−79.91

TABLE 3

Activation parameters and rate constants at 25 °C for the dissociation of $[Cu(tren)]^{2+}$–pyridine complexes

Ligand	10^{-3} k_b/s^{-1}	E_A	$\Delta G^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}
		kJ mol^{-1}			
3-Chloropyridine	3.46	30.72	52.77	28.25	−82.27
Pyridine	1.33	44.48	55.13	42.01	−44.04
3-Methylpyridine	0.92	49.47	56.05	46.00	−30.36
4-Methylpyridine	0.82	44.10	56.33	41.63	−49.33

DISCUSSION

The results given in Table 1 indicate that the magnitudes of k_f and k_b for ligand-substitution reactions with $[Cu(tren)(OH_2)]^{2+}$ depend on the nature of the ligand and parallel the pK_a values of the ligands; these findings indicate an associative mechanism for substitution.[7,10]

Support for an associative mechanism comes from a comparison of the values for the activation energy for ligand substitution given in Table 2 with the corresponding value (43.4 ± 1.25 kJ mol^{-1}) for water exchange [1] in $[Cu(tren)(OH_2)]^{2+}$. If ligand substitution took place by a dissociative mechanism, water dissociation from $[Cu(tren)(OH_2)]^{2+}$ would be the rate-determining step and the activation energy for the substitution reactions would be *equal to* or *greater than* the activation energy for water exchange. The activation energies for ligand substitution are in all cases *less than* that for water exchange and hence are inconsistent with a dissociative mechanism.

Further support for an associative mechanism comes from the activation entropies. For a series of related

reactions in a given solvent, the relative values for the entropies of activation should correlate with the mechanism.[7,11] The relatively large negative values of $\Delta S^{\ddagger}$ (see Tables 2 and 3) for both formation and dissociation of the $[Cu(tren)]^{2+}$–pyridine complexes and their dependence on the nature of the ligand again favour an associative mechanism.

The associative ligand substitution in $[Cu(tren)(OH_2)]^{2+}$ is in contrast to the substitution reactions of distorted octahedral copper(II) complexes[4,5] which occur by a dissociative mechanism through the substitution of the relatively weakly bound axial water followed by Jahn–Teller inversion which places the substituted ligand in an equatorial position. The crystal structure[12] of [Cu(tren)(NCS)][SCN] shows the complex to be trigonal bipyramidal with a short Cu–NCS bond length (1.959 Å). The relatively low pK_a of the co-ordinated water molecule of $[Cu(tren)(OH_2)]^{2+}$ in solution,[13] the slow water-exchange rate,[1] and the ability of $[Cu(tren)(OH_2)]^{2+}$ to form only a single complex with ammonia [1] indicate that the trigonal-bipyramidal structure of $[Cu(tren)(OH_2)]^{2+}$ is maintained in aqueous medium. This would give the co-ordinated water equatorial character and favour associative substitution reactions. The finding that substitution of equatorial ligands in $[CuL_2(OH_2)_2]^{2+}$ (L = carbon-substituted ethylenediamines), where the waters are both axially located, occurs by an associative mechanism[14] is consistent with this conclusion. Although few studies on the mechanism of ligand substitution in five-co-ordinated transition-metal complexes have been reported, both dissociative[15–19] and associative[20–24] pathways have been found. The present report of associative ligand substitution in $[Cu(tren)(OH_2)]^{2+}$ is novel for five-co-ordinated Cu^{2+}.

It is interesting to speculate on the significance of these findings with $[Cu(tren)(OH_2)]^{2+}$ to the role of copper in the enzyme monoamine oxidase from pig plasma. Recent studies on the enzyme have established that copper is involved in the catalytic mechanism[25,26] whilst the rate of exchange of water co-ordinated to copper in the enzyme is very similar[1,26] to that found for $[Cu(tren)(OH_2)]^{2+}$. Thus, elementary steps in the catalytic cycle of the enzyme involving substitution reactions at the copper sites might also proceed *via* associative mechanisms.

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