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Kinetics of Ligand Exchange Reactions of Copper(II) Complexes of Pyridine-2-Aldehyde-2′-pyridylhydrazone

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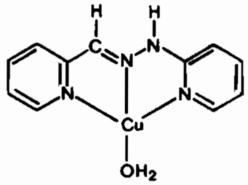
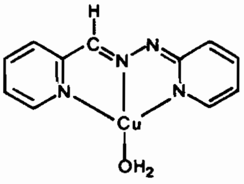
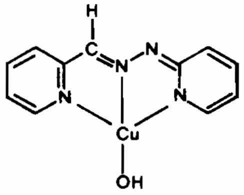
The kinetics of the reactions of the copper(II) complexes of pyridine-2-aldehyde-2′-pyridylhydrazone (PAPHY) with ethylenediaminetetraacetic acid (EDTA) and triethylenetetramine (trien) have been studied at 25 °C and 0.1 ionic strength. The reaction is first order in copper complex and first order in the incoming ligand. The rate constant is pH dependent reaching a maximum at pH 7.5 and 9 for EDTA and trien respectively. The rate determining step in the reaction with trien is the loss of a water molecule from the CuPAPHY complexes. The rate determining step in the reaction with EDTA occurs after the coordination of the EDTA to the complex. The effect of deprotonation of the ligand in the copper complex on the rate of exchange of the coordinated water molecules is discussed.



I CuPAPHY^{2+}



II CuPAPY^{+}



III CuPAPYOH

Introduction

The effect of coordinated ligands on the rate of exchange of water molecules in the first coordination sphere of a metal complex with the bulk solvent is a topic which has received much attention [1]. The evidence available suggests that both the nature of the metal ion and of the ligand are important in determining the rate of solvent exchange. The electron donating ability of the ligand has been suggested [2] as the major influence of the ligand on the rate of water exchange, but unfortunately reliable data on the electron donating ability of most ligands is lacking. This work was begun in an attempt to test the effect of the electron donating ability of the ligand by using the copper(II) complexes of the ligand pyridine-2-aldehyde-2′-pyridylhydrazone (PAPHY). PAPHY forms a number of different complexes with copper(II) [3, 4], a simple 1:1 complex, CuPAPHY^{2+}(I), a complex in which a proton has been removed from the imino nitrogen, CuPAPY^{+}(II), a complex in which a hydroxide ion is bound to the deprotonated copper complex, CuPAPYOH(III), and a complex containing two mol of PAPHY for each copper, $Cu(PAPHY)_2(ClO_4)_2$ [3–5]. The complexes I, II and III are represented here as being four coordinate – however in aqueous solution the copper will probably be five or six coordinate.

It was hoped that complexes I and II would provide an opportunity to study the effect of the electron donating ability of the ligand, without altering the metal ion or the atoms coordinated to the metal. Removal of the imino proton from the CuPAPHY^{2+} complex results in delocalisation of the electrons within the ligand and it was reasoned that this delocalisation could cause a change in electron donating ability of the pyridine nitrogens. Such a change in the ligand should be reflected in a change in the rate of water exchange.

Using the stopped flow technique it was not possible to study reactions of monodentate ligands such as ammonia with CuPAPHY, the spectral changes were too small or the reactions were too fast to measure. However it was possible to study ligand exchange reactions of the type

$$\text{CuPAPHY} + \text{L} \rightarrow \text{CuL} + \text{PAPHY}$$

where L is a multidentate ligand. The results reported here are for the ligands triethylenetetramine (trien) and ethylenediaminetetraacetic acid (EDTA). The results obtained for the reaction with trien indicate that the rate determining step is the loss of the first water molecule from the metal complex so that the effects of deprotonation on the water exchange rate can be measured. The reaction with EDTA is slower and the rate determining step occurs after the coordination of the EDTA to the CuPAPHY molecule.

Experimental

PAPHY (Aldrich Chemical Co.) was recrystallised from ethanol. The trien was purified by precipitating the hydrochloride salt and recrystallising from water–ethanol mixtures. The trien was standardized by a spectrophotometric mol ratio method using standard copper(II) solutions. EDTA was standardized by titration with zinc. Copper perchlorate was prepared from copper carbonate and perchloric acid and was recrystallised from water. A stock solution was standardized by a spectrophotometric mol ratio method with EDTA. All other chemicals were reagent grade and were used without further purification. Stock copper PAPHY solutions were prepared by dissolving a weighed amount of PAPHY in water and adding a stoichiometric amount or a slight excess of standard copper perchlorate solution. These solutions were freshly prepared each day. Solutions for the kinetic runs were prepared by dilution of this stock solution with buffer and sodium perchlorate solutions to give a solution of the desired pH and concentration. Buffers used were sodium borate, boric acid pH 7.5–11, NaH_2PO_4/Na_2HPO_4 pH 5–7.5 and sodium acetate/acetic acid pH 3.7–5. No effects due to the different buffers were observed. pH measurements were taken at room temperature using either a Pye Model 292 or a Radiometer PHM 28 pH meter, and a combination electrode. The ionic strength was adjusted to 0.1 with sodium perchlorate.

The reactions were monitored with a Durrum Gibson stopped flow apparatus at various wavelengths but mainly at 450 nm. The temperature was controlled to 25 ± 0.1 °C. The oscilloscope traces were photographed using either Polaroid Film (University of Queensland) or 35 mm film (Victoria University). The data was obtained using 35 mm film by tracing on to graph paper, the polaroid film data was measured directly off the film. Most reactions were studied under pseudo first order conditions. The computer programs used to calculate the rate constants from the least squares slope of the straight line obtained by plotting $-\ln(A - A_\infty)$ against time have been described [6]. The reaction between CuPAPHY and trien had to be studied under second order equal conditions; appropriate modifications to the computer program were made. Each rate constant is the average of at least three determinations. Hydrogen ion concentrations were calculated using $\log [H^+] = pH - 0.11$ [7]. The protonation and stability constants used in this study are as follows: PAPHY and CuPAPHY, $pK_1 = 5.71$, $pK_2 = 2.87$ $\log K_{CuL} = 11.6$, $pK_{1CuL} = 5.96$, $pK_{2CuL} = 8.74$ [5]; trien, $pK_1 = 9.95$, $pK_2 = 9.31$, $pK_3 = 6.86$, $pK_4 = 3.66$ $\log K_{CuL} = 20.2$ [8, 9]; EDTA, $pK_1 = 9.60$; $pK_2 = 6.22$, $pK_3 = 2.67$, $pK_4 = 1.99$, and $\log K_{CuL} = 18.8$ [10, 11].

Results

The exchange reaction between CuPAPHY and trien is thermodynamically favourable at every pH studied. The reaction between CuPAPHY and EDTA however does not proceed to completion above pH 12 so that the maximum pH studied was 11.5. The rate expression for the reactions with EDTA and trien is given by equation 1

$$-\frac{d[CuPAPHY]}{dt} = k_{obs}[CuPAPHY]_T[L]_T \qquad (1)$$

where T refers to the total analytical concentration of the copper complex and the substituting ligand L. The reaction rate was very pH dependent and the reaction rate–pH profile is shown in Figure 1.

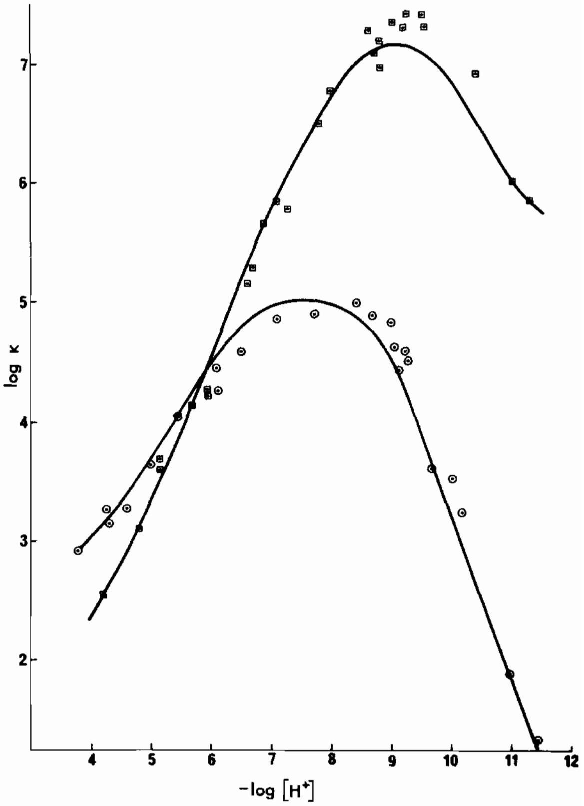


Figure 1. Plot of the observed rate constants for reaction of CuPAPHY with trien □ and EDTA ⊚ as a function of hydrogen ion concentration. The solid lines are calculated on the basis of the resolved rate constants in Table III.

TABLE I. Second Order Rate Constants for the Reaction CuPAPHY + Trien.

10^5[Cu(PAPHY)]$_T$ M	10^4[trien]$_T$ M	pH	k_{obs} M^{-1} sec^{-1}
5.0	23.25	4.20	3.56×10^2
0.95	2.4	4.80	1.25×10^3
2.68	4.8	5.10	4.8×10^3
5.0	23.25	5.15	4.9×10^3
0.95	2.4	5.16	3.9×10^3
0.95	2.4	5.67	1.4×10^4
0.95	0.96	5.92	1.87×10^4
0.95	2.4	5.98	1.75×10^4
0.95	2.4	6.60	1.45×10^5
2.5	2.3	6.70	1.95×10^5
2.68	4.8	6.88	4.6×10^5
0.95	2.4	7.11	6.9×10^5
0.95	2.4	7.22	6.00×10^5
0.95	0.96	7.79	3.1×10^6
0.95	0.099	7.97	5.96×10^6
0.95	0.099	8.60	1.9×10^7
2.5	0.205	8.70	1.2×10^7
1.5	1.5	8.78	1.5×10^7
0.95	0.96	8.80	9.2×10^6
0.95	0.099	9.00	2.2×10^7
2.5	0.205	9.18	2.0×10^7
2.5	0.205	9.23	2.5×10^7
2.5	0.205	9.50	2.5×10^7
1.5	1.5	9.52	2.0×10^7
2.5	0.205	10.38	8.1×10^6
2.5	2.3	11.00	9.90×10^5
2.5	2.3	11.30	7.15×10^5

TABLE II. Second Order Rate Constants for the Reaction CuPAPHY + EDTA.

10^5[Cu(PAPHY)]$_T$ M	10^4[EDTA] M	pH	k_{obs} M^{-1} sec^{-1}
7.5	22.2	3.77	8.12×10^2
8.0	36.9	4.25	1.84×10^3
7.5	22.2	4.30	1.40×10^3
7.5	22.2	4.60	1.90×10^3
4.0	36.9	5.00	4.44×10^3
2.5	22.2	5.45	1.26×10^4
2.5	22.2	6.10	2.86×10^4
0.85	1.12	6.11	1.88×10^4
2.5	22.2	6.50	3.84×10^4
1.25	9.83	7.10	7.3×10^4
0.85	1.12	7.72	7.95×10^4
1.25	9.83	8.42	9.9×10^4
1.25	9.83	8.68	7.7×10^4
1.25	9.83	9.00	6.9×10^4
1.25	9.83	9.05	4.3×10^4
1.25	9.83	9.12	2.75×10^4
1.25	9.83	9.22	4.0×10^4
1.25	9.83	9.28	3.2×10^4
1.25	9.83	9.68	4.2×10^4
0.96	8.2	10.03	3.42×10^3
1.25	9.83	10.18	1.8×10^3
1.25	9.83	10.98	7.5×10^1
1.25	9.83	11.42	2.2×10^1

The reaction between (CuPAPHY)$_T$ and trien is so fast in the pH range 8 to 11 that second order equal concentration conditions had to be used. Table I lists the experimental conditions and the observed rate constants. Even under the second order equal conditions, the half life of the reaction was of the order of 10^{-2} s^{-1} and the rate constants under these conditions should be considered to be less accurate than the constants obtained under pseudo first order conditions. The CuPAPHY reaction with EDTA was in general slower than the reaction with trien. The fact that k_{obs} is greater for EDTA than trien below pH 6 is due to the different protonation constants of the two ligands. The experimental conditions for the EDTA reaction and the results obtained are given in Table II.

The rate constants for the reactions of the copper PAPHY complexes with trien and EDTA were resolved into individual proton dependent terms to fit equation 2, using a non-linear least squares regression program [12]. Charges and coordinated water molecules of the species in equation 2 have been omitted for reasons of clarity.

$$\begin{gathered}
k_{obs}[CuPAPHY]_T[L]_T = \\
= k_L^{CuPAPHY}[CuPAPHY][L] + \\
+ k_{HL}^{CuPAPHY}[CuPAPHY][HL] + \\
+ k_{H_2L}^{CuPAPHY}[CuPAPHY][H_2L] + \\
+ k_{H_3L}^{CuPAPHY}[H_3L] + \\
+ k_L^{CuPAPY}[CuPAPY][L] + \\
+ k_{HL}^{CuPAPY}[CuPAPY][HL] + \\
+ k_{H_2L}^{CuPAPY}[CuPAPY][H_2L] + \\
+ k_{H_3L}^{CuPAPY}[CuPAPY][H_3L] + \\
+ k_L^{CuPAPYOH}[CuPAPYOH][L] + \\
+ k_{HL}^{CuPAPYOH}[CuPAPYOH][HL] + \\
+ k_{H_2L}^{CuPAPYOH}[CuPAPYOH][H_2L] + \\
+ k_{H_3L}^{CuPAPYOH}[CuPAPYOH][H_3L] \qquad (2)
\end{gathered}$$

In deriving equation 2, the fully protonated ligand H_4L was assumed to be unreactive. Preliminary analysis of the data indicated that the terms involving $k_L^{CuPAPHY}$, $k_{H_2L}^{CuPAPYOH}$ and $k_{H_3L}^{CuPAPYOH}$ could be neglected under all the conditions used as these rate constants would have to be greater than 10^{11} M^{-1} sec^{-1} to contribute significantly to the observed rate. The concentrations of the various species were calculated using the program COMICS [13]. Only the terms pertinent to the given system were included in

TABLE III. Resolved Rate Constants (M^{-1} sec^{-1}) for the Reactions at 25 °C, $\mu = 0.1$.

Rate Constant (M^{-1} sec^{-1})	EDTA	trien
$k_{HL}^{CuPAPHY}$	$(7.2 \pm 0.5) \times 10^4$	
$k_{H_2L}^{CuPAPHY}$	$(8.7 \pm 0.5) \times 10^2$	$(1.2 \pm 0.2) \times 10^6$
$k_{H_3L}^{CuPAPHY}$	–	$(2.1 \pm 0.2) \times 10^2$
k_{L}^{CuPAPY}	$(9 \pm 1) \times 10^3$	$(2.6 \pm 0.2) \times 10^8$
k_{HL}^{CuPAPY}	$(1.1 \pm 0.3) \times 10^5$	$(1.2 \pm 0.2) \times 10^8$
$k_{H_2L}^{CuPAPY}$		$(7.6 \pm 0.5) \times 10^5$
$k_{L}^{CuPAPYOH}$		$(3.3 \pm 0.3) \times 10^5$

the least squares analysis. These terms were determined from a number of preliminary analyses of the data using the non-linear regression program. The resolved rate constants are given in Table III.

The solid lines in figure 1 were calculated using the resolved rate constants and equation 2.

Discussion

A number of general observations can be made concerning the rates of the reactions reported here.

1. The increasing rate observed with both trien and EDTA as the pH is raised from 4 to 8 can be attributed to the decreasing number of protons associated with the incoming ligand. The differences in the slopes of the pH profiles simply indicate differences in the protonation constants of these ligands.

2. The decrease in the rate at higher pH can be attributed to the formation of the CuPAPYOH species which is much less reactive kinetically.

3. The fact that the maximum in the pH profile of the EDTA reaction occurs at about pH 7.5 compared to about pH 9.5 for the trien reaction suggests that the species $EDTA^{4-}$ is much less reactive than $HEDTA^{3-}$.

4. Multidentate ligand exchange reactions generally involve a series of steps, consisting of bond breakage by the leaving ligand with the vacated coordination position being occupied by a water molecule, and bond formation, with the displacement of a water molecule by the incoming ligand. The CuPAPHY–trien reactions are very much faster than the CuPAPHY–EDTA reactions, despite the favourable electrostatic attraction between the reactants for the latter. This means that the rate determining step in the ligand exchange must occur much earlier on in the exchange process for trien than for EDTA.

5. The reaction of trien with the CuPAPHY complexes is extremely rapid. The CuPAPHY complexes have up to three coordination positions occupied by water molecules which could be taken by the incoming ligand before bond breakage between the copper and the PAPHY must occur. The fact that the incoming ligand can be strongly chelated to the metal before bond breakage by the leaving group must occur is probably a necessary condition for such rapid ligand exchange reactions. Comparable rate constants to those observed here have been reported for the ligand exchange reactions of $Cu(NTA)^-$ (NTA = nitrotriacetic acid) with $H_2tetren^{2+}$ (tetren = tetraethylenepentamine) ($k = 2.1 \times 10^8$ M^{-1} sec^{-1}) [14], $Cu(dien)^{2+}$ (dien = diethylenetriamine) with tetren ($k = 1.02 \times 10^8$ M^{-1} sec^{-1}) [15] and $PbNTA^-$ with NTA^{3-} ($k = 6.6 \times 10^7$ M^{-1} sec^{-1}) [16]. Each of these complexes has water molecules which may be displaced by the incoming ligand before bond breakage by the leaving ligand must occur. This is not a sufficient condition however as there are many examples where such ligand exchange reactions are much slower *e.g.* CuPAPHY + EDTA.

$CuPAPHY^{2+}$

The resolved rate constants given in Table III indicate that the reaction of I with H_2trien^{2+} is very rapid and is only six times slower than the reaction of Cu^{2+} (aq) with H_2trien^{2+} ($k_{H_2trien}^{Cu} = 7.5 \times 10^6$ M^{-1} sec^{-1}) [17]. The reaction between Cu^{2+} (aq) and H_2trien proceeds via a mechanism in which dissociation of a water molecule from the $Cu(H_2O)_6^{2+}$ ion is rate determining [17]. In view of the value of the rate constants it seems likely that a similar rate determining step applies to the reaction with $CuPAPHY^{2+}$. The number of water molecules bound to the copper in $Cu(PAPHY)^{2+}$ is not known, four, five and six coordinate CuPAPHY complexes are known in the solid state and non aqueous solvents [3, 4]. For the purposes of the arguments to be presented here, we shall assume that the copper is six coordinate with three coordinated water molecules. Different assumptions will give different numerical results but will not affect the main conclusions.

We can use the substitution rate constant for the H_2trien^{2+} reaction to calculate the value of the water exchange rate constant of $Cu(PAPHY)(H_2O)_3^{2+}$ provided that a value of the equilibrium constant for outer sphere complex formation is known or can be calculated. The calculation of a value for K_{os} using the usual equation [18]

$$K_{os} = (4/3\pi N a^3 e^b) 10^{-3} \tag{3}$$

for species such as H_2trien^{2+} is complicated by the fact that a, the centre to centre distance between the metal and ligand, does not correspond to the charge separation between the metal and a protonated nitrogen. Rorabacher [19] has proposed a modified form of the expression

$$K_{os} = 4/3\pi N a^3 \exp\left(\frac{-Z_m Z_L e_0^2}{a' \epsilon k T}\right) \tag{4}$$

where a' is the centre to centre distance between the metal ion and the protonated nitrogen. There is still the problem that the values of a and a' are not known, usually the physically reasonable values of a = 5–7 Å are used The best estimate for K_{os} for H_2-trien^{2+} and CuPAPHY^{2+} can probably be obtained from the rates of the reaction of H_2trien^{2+} with Cu^{2+} (aq) and the known rate of water exchange for Cu-$(H_2O)_6^{2+}$ (k = 2 × 10^9 sec^{-1}) [14, 20] which gives K_{os} = 0 0038 M^{-1} Using this value and taking into account the decrease in the number of water molecules available for exchange [21] we calculate a value of 6 × 10^8 sec^{-1} for water exchange of Cu(PAPHY) $(H_2O)_3^{2+}$ Such a value of the water exchange rate constant is consistent with the behaviour of other copper(II) complexes The fast water exchange rate for $Cu(H_2O)_6^{2+}$ can be understood in terms of Jahn–Teller distortion and rapid interconversion of the axial and equatorial ligands Coordination of a multidentate ligand to copper could inhibit this rapid interconversion and slow the rate of water exchange, but a consideration of the results obtained for the rates of formation of *bis* and ternary copper complexes [22] shows that the effect is to slow the rate but it is not large, generally less than a factor of ten, except in the case of Cu(tren)$(H_2O)^{2+}$ (tren = *tris*(2-aminoethyl)-amine) [23]

The rate of attack of H_3trien^{3+} on CuPAPHY^{2+} (k = 2 1 × 10^2 M^{-1} sec^{-1}) is much less than the rate for H_3trien^{3+} on $Cu(H_2O)_6^{2+}$ (k = 1 6 × 10^4 M^{-1} sec^{-1}) [17] and much less than would be predicted from the increase in electrostatic repulsion The reduction is probably due to a requirement that the incoming ligand be chelated to the metal ion before dissociation of the leaving ligand can occur H_3trien^{3+} cannot be chelated without the loss of a proton Proton loss has been postulated as rate determining in the reaction of $Cu(H_2O)_6^{2+}$ with H_3trien^{3+} [17]

The reaction of EDTA with CuPAPHY^{2+} is much slower than the reaction with trien despite the favourable electrostatic attraction in the case of EDTA The rate step must therefore occur after the loss of the water molecule from CuPAPHY^{2+} Attempts to determine the rate determining step by examining the possible sequence of intermediates and relating the observed rate constant to the stability of the intermediate and the predicted rate constant for the rate determining step are frustrated by a lack of knowledge of the stability of the ternary complexes formed by CuPAPHY^{2+} It seems likely however that the EDTA is at least bidentate The dissociation rate constant for a carboxylate group bound to copper is high, and EDTA is known to coordinate to metal ions with the carboxylate group as the first group bound to the metal [24, 25]. Chelation is therefore necessary to slow the rate of dissociation of the ligand from the mixed complex

The stability of a mixed Cu(PAPHY) (EDTA) complex, with the EDTA acting as a bidentate ligand (N and O coordination) can be estimated to be ~10^6 from the following data The stability constant for the reaction Cu(terpy)$^{2+}$ + n-butylamine is $10^{4\ 71}$ and for the reaction Cu(dpa)$^{2+}$ + n-Butylamine K = $10^{3\ 76}$ (dpa = dipicolylamine) [26], both ligands are structurally similar to PAPHY The stability constant for the mixed complex between Cu(bipy)$^{2+}$ (bipyridyl) and glycinate is $10^{7\ 92}$ [27] If we assume that Cu-PAPHY^{2+} will form ternary complexes of comparable stability to those of Cu(terpy)$^{2+}$ and Cu(dpa)$^{2+}$ then the stability of the mixed complex between Cu-PAPHY^{2+} and a bidentate EDTA molecules should be greater than 10^4 (due to the chelate effect) Bipyridyl is a bidentate ligand and should form more stable ternary complexes than a tridentate ligand such as PAPHY, the stability constant should therefore be less than 10^8 The data available only gives the rate constant for the reaction HEDTA^{3-} + CuPAPHY^{2+} and the effect of protonation of the EDTA molecule on the stability of the proposed intermediate is unknown If we assume that the rate constant for the reaction EDTA^{4-} with CuPAPHY is 10^6 M^{-1} sec^{-1}, (a large increase due to the increased electrostatic attraction is not expected) then as the observed rate constant k is given by the product of the stability of the mixed complex and the rate constant for the rate determining step, k_{rds} must be about 1 sec^{-1} Such a rate probably corresponds to the breaking of a Cu–PAPHY bond but no information is available to confirm this point It is possible that the EDTA acts as a tridentate in the reaction intermediate with a corresponding increase in stability and a decrease in the value of k_{rds} As data is not available on the rate of opening of chelate rings in complexes like CuPAPHY^{2+} and as there is considerable uncertainty in the value of the stability constants for the intermediates a detailed interpretation is not possible

CuPAPY

The reaction of II with trien is also so fast that it is probable that water loss from the II is rate determining The decrease in the rate of the reaction with H-trien$^+$ compared to trien is expected from the results of similar systems A decrease by a factor of five has been observed for similar reactions involving the exchange of polyamine ligands coordinated to copper [15] The factor of about two observed here is attributed to the reduced electrostatic repulsion between the CuPAPY$^+$ complex and Htrien$^+$ compared with the +2 charged copper polyamine complexes

The rate of water exchange can be calculated for the CuPAPY$^+$ complex The calculated value of K_{os} for the Cu^{2+} + H_2trien^{2+} reaction is 0 0038 Assuming a value of 5 Å for the value of a in equation 4, the value of a' is 6 5 Å Using these values for a and a', a value of K_{os} = 0 03 for the CuPAPY$^+$, H_2trien^{2+} outer sphere complex is calculated Assuming the complex contains three water molecules and given the rate constant for $CuPAPY^+$ + H_2trien^{2+}, the water exchange rate constant for $CuPAPY^+$ is 5×10^7 sec^{-1}. The value of K_{os} for the reaction of unprotonated trien with $CuPAPY^+$, should be 0.3 (assuming a value of a = 5 Å). This value predicts a rate of substitution of 1.5×10^7 M^{-1} sec^{-1}, a factor of ten less than the observed rate constant. This suggests that either the calculated water exchange rate is not correct or that the attack of unprotonated trien on II is enhanced by the internal conjugate base mechanism described by Rorabacher [28]. Rate enhancement by a factor of one hundred has been reported for the reaction of tetren with $Cudien^{2+}$ [15].

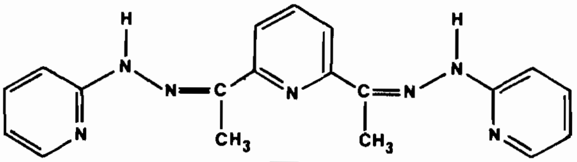
The resolved rate constants for the reaction with EDTA show rates which are very much slower than the rates for trien and a large increase in the rate for $HEDTA^{3-}$ compared to $EDTA^{4-}$ ($k_{HL}^{CuP}/k_L^{CuP} = 12$). Increased protonation in the reaction intermediates giving rise to an increase in the rate of reaction indicates that the proton is on the leaving group during the rate determining step. If the proton in the reaction intermediate is associated with the most basic site, then this will be the nitrogen of the PAPY ligand only if the EDTA is coordinated to the metal via both nitrogens. The pK_a of an uncoordinated iminodiacetate group of EDTA would be expected to be one or two orders of magnitude greater than the pK_a (5.96) of the PAPY ligand. However the stable form of the intermediate could be a species in which the EDTA is bound to the $CuPAPY^+$ via only one nitrogen and the proton on the iminodiacetate group but the kinetically active form of this intermediate has the proton of the PAPY ligand. In view of this uncertainty it is not possible to be more precise about the nature of the intermediate.

CuPAPYOH

The reaction of III with trien is about 1000 times slower than the reaction of II with trien. The reaction of III with EDTA was too slow to observe. This decrease in rate constant for the hydroxy complex is much greater than the decrease observed with copper polyamine exchange reactions [15]. Since the trien is unchanged, electrostatic differences due to changes in the charge of the complex are not important and the decrease must be due to the less rapid loss of the coordinated hydroxide from III compared to the loss of the coordinated water from II.

Water Exchange Rates

The substitution reactions of trien have allowed the calculation of water exchange rate constants for the species $Cu(PAPHY)\ (H_2O)_3^{2+}$ ($k^{-H_2O} = 6 \times 10^8$ s^{-1}) and $CuPAPY(H_2O)_3^{2+}$ (k^{-H_2O} = 5×10^7 s^{-1}). These calculations are based upon certain assumptions, which have already been stated. The numerical values would be changed if the number of water molecules bound to the copper is less than three but the relative values of the rate constants would be the same provided the coordination number of the copper in the two complexes is the same. The deprotonation of the PAPHY ligand with its consequent delocalisation of electrons throughout the ligand has resulted in a significant decrease in the rate of water exchange on the copper. A large number of different factors have been shown to influence the rates of water exchange of nickel complexes [29] but deprotonation of the ligand bound to the metal has not previously been shown to influence water exchange rates. It can be argued that delocalisation of the π electrons results in a change in the electron donating ability of the ligand compared to its protonated form and that the decrease in the electron density on the metal is responsible for the decrease in the water exchange rate. However recent crystallographic evidence suggests that little or no change occurs in the electronic structure of pyridylhydrazones either upon complex formation or deprotonation [31]. This crystallographic evidence does suggest an alternative explanation for the observed effects. The ligand H_2-dapp(IV)



IV

coordinated to cobalt(II) and zinc(II) is almost planar [30] as is PAPHY in the complex $Co(PAPHY)Cl_2$ [31]. Upon deprotonation of the zinc complex of IV large changes occur in the conformation of IV due to rotation about the bonds joining the side chains to the central pyridine rings. The situation is complicated by the fact that the deprotonated zinc complex is dimeric with (IV) acting as a bridging ligand but similar twists (about the N–N bond) have been reported in one side chain of the deprotonated form of the copper(II) complex 2,6-diacetylpyridine-*bis*-(picolinoylhydrazone) [32]. If changes in the structure of the complexes studied here occur on deprotonation then this would be reflected in the water exchange rates.

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