Kinetics and mechanisms of the reactions of copper(II) with heptane-2,4,6-trione, 1-phenylhexane-1,3,5-trione and 1,5-diphenylpentane-1,3,5-trione in methanol–water (70:30 vol./vol.) solution

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Abstract

The kinetics of the reactions of copper(II) with heptane-2,4,6-trione (H_2hto), 1-phenylhexane-1,3,5-trione (H_2phto) and 1,5-diphenylpentane-1,3,5-trione (H_2dppto) in methanol–water (70:30 vol./vol.) solution at 25 °C and ionic strength 0.5 mol dm^{-3} have been investigated. The equilibrium constants for these reactions have been determined. Two possible mechanisms are discussed. The dimerization reactions of [Cu(Hhto)]$^+$ and [Cu(Hphto)]$^+$ were also investigated. A detailed mechanism is proposed which is consistent with the experimental data.

Introduction

The kinetics and mechanisms of the reactions of copper(II) with β-diketones in solution have been the subject of a number of investigations [1–8]. To date, no such investigations of the reactions of copper(II) with triketones have been carried out. However, the structures of a number of these complexes have been determined and the most studied of the triketonate magnetic exchange systems have been the copper(II) oxygen bridged 2:2 chelates in which two copper atoms are bound in relatively close proximity [9, 10]. In general, the binuclear copper triketonates have magnetic moments of approximately 0.7 BM although the 2:2 copper(II) complex of the t-butyl substituted triketone (2,2'-dimethyloctane-3,5,7-trione) and its ethylenediamine Schiff-base derivative are virtually diamagnetic at room temperature [9]. Very recently, the electron-transfer reactions of a limited range of these complexes have been the subject of a cyclic voltammetry investigation and the results have proved to be very interesting [11, 12]. For some time now we have been investigating the electron transfer reactions of iron(III) complexes of triketones with outer-sphere reducing agents [13]. We are now extending this work to copper(II) triketone complexes. Initially however, we have investigated the equilibria and kinetics of the complex formation reactions of copper(II) with a number of triketone ligands. We now report the results of these investigations.

Experimental

Stock solutions of copper(II) were prepared from reagent grade $Cu(NO_3)_2 \cdot 3H_2O$ (BDH). These solutions were standardized by reaction with excess potassium iodide. The liberated iodine was titrated with standard sodium thiosulphate solution.

Heptane-2,4,6-trione (H_2hto) was prepared according to the method of Bethell and Maitland [14]. 1-Phenylhexane-1,3,5-trione (H_2phto) and 1,5-diphenylpentane-1,3,5-trione (H_2dppto) were prepared according to Hauser and Harris [15]. Solutions of the ligands were standardized by titration with sodium hydroxide. Endpoints were determined using an iterative computer program based on the method of Gran and Johansson [16].

Methanol was purified by distillation from magnesium and iodine. Solutions were prepared using distilled water which was subsequently boiled for at least 15 min to remove dissolved gases. Methanol–water solutions (70:30 vol./vol.) were prepared by adding water (300 g) to a volumetric flask (1000 cm^3) and diluting to the mark with dry methanol. Sodium perchlorate was purified as previously described [17] and the ionic strength of all solutions was adjusted to 0.5 mol dm^{-3} using this salt.

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pH readings were made using a PTI-6 digital pH meter equipped with a Russell combination electrode. The potassium chloride in the reference compartment was replaced by 3 mol dm^{-3} sodium chloride. The pH meter was calibrated to read hydrogen ion concentration directly using perchloric acid–sodium hydroxide titrations. Endpoints were determined using the method of Johansson [18].

NMR spectra were recorded on a Jeol JNM-GX270 FT NMR spectrometer.

The kinetic data were obtained using a Hi-Tech SF20 stopped-flow mixing device interfaced to a BBC microcomputer via a Datalab DL901 transient recorder. The metal concentration was always maintained in at least six-fold excess over the ligand concentration which was $c.$ 1×10^{-4} mol dm^{-3}. The pseudo-first-order rate constants were calculated by fitting the absorbance data to eqn. (1) using a three parameter curve-fitting routine [19] in which the absorbance at time zero, A_0, the absorbance at infinity time, A_∞, and the rate constant, k, were treated as variables. Data for at least three half-lives were used in this procedure. The reported rate constants are the average of at least three determinations. The standard deviation of individual runs was less than one percent.

$$A = A_\infty(1 - \exp(-kT)) + A_0 \exp(-kT) \qquad (1)$$

Ligand and metal solutions used for kinetic studies of the complex formation reactions at $[\mathrm{H}^+] = 1.0 \times 10^{-4}$ mol dm^{-3} were buffered by the addition of 2.0×10^{-3} mol dm^{-3} tetramethylpyrazine (Aldrich). Blank experiments showed no extraneous effects due to the presence of the buffer.

The dissociation constants ($\mathrm{p}K_1$ and $\mathrm{p}K_2$) of the ligands used in this study have already been reported [20]. Due to the high values of the stability constants of the 1:1 complexes with Cu^{2+}, they could not be reliably determined using the potentiometric technique. Consequently, the stability constants of the 1:1 complexes were determined using a spectrophotometric method. Each of the metal–ligand systems was studied at three different hydrogen ion concentrations. Six or seven solutions, each having a different metal to ligand ratio were prepared at each hydrogen ion concentration. The spectrum of each of these solutions was recorded over a suitable wavelength range following which it was digitized at ten different wavelengths. Typical ligand concentrations were in the range 1.0×10^{-4} to 3.0×10^{-4} mol dm^{-3}. Metal additions were made using a micrometer syringe. The metal concentrations ranged from 2.0×10^{-5} to 1.0×10^{-3} mol dm^{-3} while the hydrogen ion concentrations were in the range 1.0×10^{-3} to 1.0×10^{-2} mol dm^{-3}. The absorbance, metal, ligand
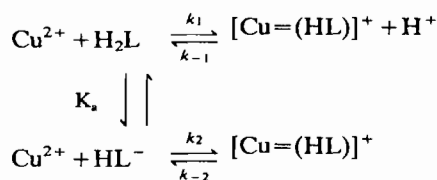
and hydrogen ions concentrations for each point (a minimum of 180 data points) were used as input for the computer program SQUAD [21]. As would be expected [20] only the 1:1 complexes are formed in the pH range used. Models containing complexes having ligand:metal ratios of 2:1 and 2:2 were rejected by SQUAD. As the pH is raised, the 1:1 complexes are smoothly converted to the 2:2 complexes [20]. However, in the case of all the ligands, even in very dilute solutions, precipitation of the 2:2 copper(II) complexes occurred when the pH was raised to values at which appreciable concentrations of this were present. Consequently, it was not possible to determine the equilibrium constants for conversion of the 1:1 to the 2:2 complexes. However, the relative insolubility did not preclude kinetic investigations which could be carried out at extremely low concentrations of the metal complex ($c.$ 5×10^{-5} mol dm^{-3}).

Results

Complex formation reactions

The equilibrium constants ($\log \beta_1$) for reaction of copper(II) with $H_2\mathrm{hto}$, $H_2\mathrm{phto}$ and $H_2\mathrm{dppto}$ are 8.99 (± 0.01), 9.01 (± 0.01) and 8.90 (± 0.01), respectively. Table 1 gives the kinetic data for reaction of Cu^{2+} with all three ligands. The presence of a strong resonance at 1.98 ppm in the NMR spectrum of heptane-3,5-dione in methanol–water (70:30 vol./vol.) confirmed that the predominant form of the ligand present was the bis-enol. This deduction is based on the assignments of Sagara et al. [22] who assigned a resonance at 1.97 pm to the terminal CH_3- of the bis-enol form. Consequently, formation of the 1:1 complexes is treated as reaction of the metal species with a H_2L ligand. Temperature-jump relaxation [23], pH jump and bromination experiments [24–26] have shown that the rate constants for ionization of these ligands are greater than 300 s^{-1}. This is considerably more rapid than any of the k_{obs} values measured for the complex formation reactions.

The usual simple mechanism for reaction of metal ions with protonated ligands is shown in Scheme 1. For this mechanism k_{obs} has the form of eqn. (2) where $[\mathrm{Cu}=(\mathrm{HL})]^+$ represents the chelated com-

$$\mathrm{Cu}^{2+} + H_2L \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\mathrm{Cu}=(\mathrm{HL})]^+ + \mathrm{H}^+$$

$$K_a \Big\updownarrow$$

$$\mathrm{Cu}^{2+} + \mathrm{HL}^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [\mathrm{Cu}=(\mathrm{HL})]^+$$

Scheme 1.

TABLE 1. Kinetic data for the reaction of Cu^{2+} with triketones in methanol–water (70:30 vol./vol.) solution at 25 °C, $I = 0.5$ mol dm^{-3} $NaClO_4$.

Ligand	$10^3 \times [Cu^{II}]$ (mol dm^{-3})	$10^3 \times [H^+]$ (mol dm^3)	k_{obs} (s^{-1})	k_{calc}^a (s^{-1})	k_{calc}^b (s^{-1})
H_2hto^c	0.594	10.0	42.6	43.3	40.8
	1.19	10.0	53.0	53.6	51.3
	0.594	6.31	33.2	31.3	30.5
	1.19	6.31	40.2	41.6	41.0
	0.594	3.98	24.1	23.7	23.6
	1.19	3.98	33.5	34.2	34.2
	0.505	3.84	23.7	21.7	21.6
	1.04	3.84	33.6	31.1	31.1
	1.49	3.84	39.5	39.0	39.1
	2.08	3.84	45.7	49.4	49.7
	2.55	3.70	53.8	57.2	57.7
	0.594	2.51	20.8	19.1	19.1
	1.19	2.51	30.2	29.6	29.9
	0.594	1.58	17.9	16.3	16.4
	1.19	1.58	27.2	27.0	27.3
	0.510	1.04	13.0	13.2	13.3
	1.02	1.04	23.1	22.7	23.0
	1.53	1.04	30.4	32.2	32.6
	2.05	1.04	46.5	41.9	42.4
	2.55	1.04	54.6	51.2	51.8
	0.594	1.00	14.2	14.6	14.8
	1.19	1.00	24.1	25.7	26.1
	0.50	0.10	18.8	16.8	16.7
	1.00	0.10	32.5	32.9	32.8
	1.50	0.10	48.6	49.0	48.9
	2.00	0.10	64.4	65.1	65.0
	2.50	0.10	81.3	81.2	81.2
	0.00	5.55	15.9	f	17.7
	0.00	11.1	30.8	f	33.5
	0.00	16.6	46.0	f	47.3
	0.00	22.2	61.0	f	60.2
H_2phto^d	1.04	10.0	12.1	12.4	11.9
	2.08	10.0	16.7	16.2	15.7
	1.04	6.31	9.50	9.27	9.12
	2.08	6.31	13.0	13.0	13.0
	1.04	3.98	7.65	7.28	7.28
	2.08	3.98	10.6	11.1	11.1
	1.04	2.51	6.47	6.06	6.10
	2.08	2.51	9.41	9.88	9.99
	0.510	2.34	4.45	3.98	3.98
	1.02	2.34	6.07	5.85	5.89
	1.53	2.34	7.82	7.73	7.80
	2.04	2.34	9.31	9.61	9.72
	2.55	2.34	11.1	11.4	11.6
	1.04	1.58	5.79	5.31	5.37
	2.11	1.58	9.50	9.32	9.44
	1.04	1.00	5.38	4.91	4.97
	2.08	1.00	8.93	8.90	9.01
	0.510	0.739	3.05	2.69	2.73
	1.02	0.739	4.95	4.69	4.75
	1.53	0.739	6.72	6.69	6.77
	2.04	0.739	8.50	8.69	8.80
	2.55	0.739	10.2	10.6	10.8
	1.00	0.10	6.23	6.18	6.18
	2.00	0.10	13.1	12.2	12.2

(continued)

TABLE 1. (continued)

Ligand	$10^3 \times [Cu^{II}]$ (mol dm^{-3})	$10^3 \times [H^+]$ (mol dm^3)	k_{obs} (s^{-1})	k_{calc}^a (s^{-1})	k_{calc}^b (s^{-1})
	3.00	0.10	18.6	18.3	18.3
	4.00	0.10	24.2	24.3	24.3
	5.00	0.10	29.8	30.4	30.3
	0.00	5.55	4.46	f	4.69
	0.00	11.1	8.80	f	8.90
	0.00	16.6	13.1	f	12.7
	0.00	22.2	15.8	f	16.3
H_2dppto^e	1.04	10.0	17.6	16.5	16.4
	2.08	10.0	21.8	21.5	21.5
	1.04	6.31	13.7	12.4	12.4
	2.08	6.31	17.7	17.5	17.5
	0.505	3.98	7.74	7.15	7.13
	1.04	3.98	9.93	9.80	9.79
	2.08	3.98	14.2	14.9	15.0
	0.505	2.51	6.09	5.53	5.53
	1.04	2.51	8.36	8.24	8.23
	2.08	2.51	12.9	13.4	13.5
	1.02	2.34	7.56	7.95	7.96
	1.53	2.34	9.72	10.5	10.6
	2.04	2.34	11.8	13.0	13.1
	2.55	2.34	14.1	15.7	15.7
	0.505	1.58	4.96	4.54	4.55
	1.04	1.58	7.44	7.32	7.33
	2.08	1.58	12.4	12.7	12.7
	0.505	1.00	4.66	4.00	4.00
	1.04	1.00	7.34	6.89	6.90
	2.08	1.00	12.7	12.5	12.5
	0.510	0.739	4.46	3.84	3.84
	1.02	0.739	7.41	6.71	6.71
	1.53	0.739	10.2	9.60	9.58
	2.04	0.739	12.8	12.5	12.5
	2.55	0.739	15.1	15.3	15.3
	1.00	0.10	12.4	11.0	11.0
	2.00	0.10	23.6	21.7	21.7
	3.00	0.10	32.7	32.4	32.4
	4.00	0.10	42.6	43.1	43.1
	5.00	0.10	52.9	53.8	53.8
	0.00	5.55	6.65	f	6.37
	0.00	11.1	13.0	f	12.5
	0.00	16.6	19.4	f	18.5
	0.00	22.2	23.4	f	24.5

^{a}On basis of Scheme 1. ^{b}On basis of Scheme 2. $^c\lambda = 315$ nm. $^d\lambda = 350$ nm. $^e\lambda = 430$ nm. ^{f}Hydrolysis.

plex, $K_f = \beta_1 = [Cu(HL)^+]/[Cu^{2+}][HL^-] = k_2/k_{-2} = k_1/(k_{-1}K_a)$, K_a is the first dissociation constant of the ligand and $[Cu^{II}]$ is the total concentration of copper(II).

$$k_{obs} = (k_1[H^+] + k_2 K_a)\{[Cu^{II}]/(K_a + [H^+]) + 1/(K_a K_f)\}$$

(2)

By fitting the data to this mechanism while keeping K_f constant, the rate constants shown in Table 2 are obtained.

TABLE 2. Summary of rate constants for formation and dissociation of the monocomplexes of Cu^{2+} with H_2hto, H_2phto and H_2dppto in methanol–water (70:30 vol./vol.) at 25 °C and $I = 0.5$ mol dm^{-3} $NaClO_4$ on the basis of Scheme 1

Rate constant (mol dm^{-3})	H_2hto	H_2phto	H_2dppto
k_1 (exp.)	$1.72(\pm 0.02) \times 10^4$	$3.59(\pm 0.04) \times 10^3$	$4.82(\pm 0.08) \times 10^3$
k_2 (exp.)	$2.81(\pm 0.11) \times 10^8$	$6.01(\pm 0.16) \times 10^7$	$1.10(\pm 0.03) \times 10^8$
k_{-1} (exp.)	$2710(\pm 8)$	$785(\pm 4)$	$1150(\pm 7)$
k_{-1} (predicted)	3277	861	1130
k_{-2} (exp.)	$0.825(\pm 0.110)$	$0.097(\pm 0.015)$	$0.192(\pm 0.050)$
k_{-2} (predicted)	0.30	0.06	0.14
R^a	4.73	3.23	4.46
R^b	7.48	5.67	4.58

[a]Calculated with hydrolysis data omitted. [b]Calculated with hydrolysis data included.

Hydrolysis of the complexes was carried out by reacting solutions of the metal ion and the ligand at a pH where there was appreciable complex formation with an excess of acid and monitoring the absorbance changes observed. The kinetic data for the hydrolysis reactions could be fitted to a straight line, eqn. (3).
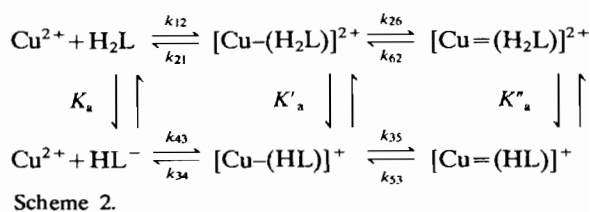
$$k_{obs} = a + b[H^+] \qquad (3)$$

The rate-law for the hydrolysis reactions is readily obtained by setting $[Cu^{II}]$ in eqn. (2) equal to zero. Thus $a = k_{-2}$ while $b = k_{-1}$. The experimental values obtained for k_{-1} and k_{-2} are shown in Table 2. The experimental values of k_{-1} are in all cases in good agreement with those calculated on the basis that $k_{-1} = k_1/K_f K_a$. With the exception of H_2dppto, the agreement between the experimental values of k_{-2} and the predicted values calculated on the basis that $k_{-2} = k_2/K_f$ is not entirely satisfactory. Indeed, in the case of H_2hto, the agreement is quite poor. This is confirmed by an examination of the R values where R is given by eqn. (4) and can be usefully used as a measure of the 'goodness of fit'. Two sets of R values were calculated (Table 2). In the first, the hydrolysis data were omitted from the fitting procedure while they were included in the second. In the case of H_2hto, the R value obtained when the hydrolysis data are included is almost twice that obtained when the hydrolysis data are omitted from the fitting procedure.

$$R = 100 \left(\frac{\sum W_i (k_{obs} - k_{calc})^2}{\sum W_i (k_{calc})^2} \right)^{1/2} \qquad (4)$$

Chopra and Jordan [27, 28] have proposed a general mechanism for reactions of metal ions with protonated ligands. In particular, they have drawn attention to a number of complex formation studies in which there are discrepancies between the directly determined equilibrium data and those derived from

kinetic measurements. They have shown that in such instances the simple mechanism shown in Scheme 1 may be inadequate and in order to overcome these difficulties they have proposed an alternative mechanism for reaction of metal ions with protonated ligands (Scheme 2). This mechanism might also be applicable to the reactions of metal ions with tri-ketones of the type under investigation, in particular the reactions involving H_2hto where the agreement between the experimental and predicted values of k_{-2} is less than satisfactory. In Scheme 2, $[Cu-(H_2L)]^{2+}$ and $[Cu(-HL)]^+$ represent species in which the ligand is bonded to the metal in a unidentate mode while $[Cu=(H_2L)]^{2+}$ and $[Cu=(HL)]^+$ represent species in which the ligand is chelated to the metal ion in a bidentate fashion. If a steady state is assumed for the monodentate intermediates represented by $[Cu-(H_2L)]^{2+}$ and $[Cu-(HL)]^+$, k_{obs} has the form of eqn. (5).

$$Cu^{2+} + H_2L \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} [Cu-(H_2L)]^{2+} \underset{k_{62}}{\overset{k_{26}}{\rightleftharpoons}} [Cu=(H_2L)]^{2+}$$

$$K_a \updownarrow \qquad\qquad K'_a \updownarrow \qquad\qquad K''_a \updownarrow$$

$$Cu^{2+} + HL^- \underset{k_{34}}{\overset{k_{43}}{\rightleftharpoons}} [Cu-(HL)]^+ \underset{k_{53}}{\overset{k_{35}}{\rightleftharpoons}} [Cu=(HL)]^+$$

Scheme 2.

$$k_{obs} = \frac{(k_{12}[H^+] + k_{43}K_a)(k_{26}[H^+] + k_{35}K'_a)}{(k_{21} + k_{26})[H^+] + (k_{34} + k_{35})K'_a}$$
$$\times \left[\frac{[Cu^{2+}]}{(K_a + [H^+])} + \frac{K''_a}{K_a K_f (K''_a + [H^+])} \right] \qquad (5)$$

For all three ligands, pK_a is approximately 8.3 [20] so that under the experimental conditions used here, $[H^+] \gg K_a$. On the basis of previous work it is not unreasonable to assume that $k_{35} \approx k_{26} \approx 10^9$ s^{-1}, the solvent exchange rate of Cu^{2+}. In the case of (salicylato)pentamminecobalt(III) the pK of the free

ligand is reduced from 13.3 to approximately 10 in the complex [29]. In view of the lower charge on the metal ion, it is unlikely that the reduction in the case of copper(II) would be greater. Consequently it seems reasonable to assume that $[H^+] \gg K'_a$ and consequently, $k_{26}[H^+] \gg k_{35}K'_a$. Introducing this simplification and letting $k_{34}K'_a = k_{21}k_{43}K_a/k_{12}$ results in eqn. (6).

$$k_{obs} = \frac{(k_{12}[H^+] + k_{43}K_a)(k_{12}/k_{21})k_{26}[H^+]}{k_{12}[H^+] + k_{43}K_a + (k_{12}/k_{21})k_{26}[H^+]}$$
$$\times \left[\frac{[Cu^{2+}]}{(K_a + [H^+])} + \frac{K''_a}{K_a K_f(K''_a + [H^+])} \right] \quad (6)$$

Making the reasonable assumption that $(k_{12}/k_{21})k_{26}[H^+] \gg (k_{12}[H^+] + k_{43}K_a)$ eqn. (6) reduces to eqn. (7).

$$k_{obs} = (k_{12}[H^+] + k_{43}K_a)$$
$$\times \left[\frac{[Cu^{2+}]}{K_a + [H^+])} + \frac{K''_a}{K_a K_f(K''_a + [H^+])} \right] \quad (7)$$

When $K''_a \gg [H^+]$, eqn. (7) reduces to eqn. (2). Provided that the values of K_a and K_f are known, eqn. (7) can be treated as having three unknown parameters, i.e. k_{12}, k_{43} and K''_a. A non-linear least-squares fit of the kinetic data gives the values for the three quantities shown in Table 3. The kinetic data for the hydrolysis reactions are included in this fitting with the copper(II) concentration in eqn. (7) set equal to zero. For all three ligands the agreement between the experimental and calculated values of k_{obs} for both the complex formation and hydrolysis reactions is excellent over the range of metal and hydrogen ion concentrations studied. The reason for the discrepancy between the fitted and experimental values of k_{-2} (Scheme 1) becomes apparent when the values obtained for K''_a are examined. In the case of H₂hto, the largest value of the hydrogen ion concentration is approximately 22% the value of K''_a and clearly shows the inadequacy of the mechanism outlined in Scheme 1 for this ligand. In the case of H₂dppto, the largest value of the hydrogen ion concentration is only 3% of the values of K''_a, so that eqn. (2) gives a good representation of the kinetic data in this case. The fact that K''_a is considerably larger than $[H^+]$ also accounts for the

relatively large uncertainty in the value of K''_a when H₂dppto is the ligand.

As expected, the R values obtained are of similar magnitude to those obtained using the mechanism in Scheme 1 but with the hydrolysis data omitted from the calculations. This supports the validity of the mechanism in Scheme 2.

The rate constant for reaction of Cu^{2+} with Hphto⁻ is less that its rate constant for reaction with either Hhto⁻ or Hdppto⁻. This is different to the results obtained for the reactions of Co^{2+} where the rates of reaction with the mono-anionic form of all three ligands were very similar [24–26]. In the case of Ni^{2+}, the reaction with H₂dppto was approximately twice as rapid as with the other two ligands.

The reductions in pK, i.e. (pK–pK'') are 7.25, 7.44 and 8.09 for H₂hto, H₂phto and H₂dppto, respectively. These are quite similar to the values obtained by Chopra and Jordan [27], e.g. 7.08 for salicylic acid and 6.21 for 5-chlorosalicylate. In the case of 3,5-dinitrosalicylate, however, the reduction is only 3.8 pK units.

Dimerization reactions

The kinetics of the conversion of the 1:1 to the 2:2 complexes can be conveniently monitored by reacting solutions containing equal quantities of Cu^{2+} and H₂L in which the pH has been adjusted to ensure complete formation of $[Cu(HL)]^+$ with solutions of sodium hydroxide. In each of the two cases investigated, an absorbance increase which was the sum of two exponentials was observed. The kinetic data for the fast step are listed in Table 4 and the rate constants are shown in Table 5. For both H₂hto and H₂phto, the faster reaction was found to be first-order in both complex and hydroxide ion concentration. The second step was independent of the complex concentration used.

Previous work has shown that the 1:2 complexes of copper(II) with heptane-3,5-dione, $[Cu(Hhpto)_2]$ exist in the keto form [30, 31]. The kinetic data for the fast step of the dimerization reaction are consistent with a mechanism shown in Scheme 3 in which a hydroxide ion removes a proton from the methine carbon of the keto form of the 1:1 complex to give the monoanion $[ML]^-$. This then reacts with

TABLE 3. Summary of parameters obtained on fitting kinetic data to mechanism in Scheme 2

|	H₂hto	H₂phto	H₂dppto
k_{12}	$1.75(\pm 0.03) \times 10^4$	$3.65(\pm 0.05) \times 10^3$	$4.83(\pm 0.09) \times 10^3$
k_{43}	$2.75(\pm 0.12) \times 10^8$	$5.86(\pm 0.19) \times 10^7$	$1.10(\pm 0.03) \times 10^8$
K''_a	$9.62(\pm 1.7) \times 10^{-2}$	$0.113(\pm 0.019)$	$0.67(\pm 0.55)$
R	4.79	3.54	4.53

TABLE 4. Kinetic data for fast step of conversion of the mononuclear 1:1 copper(II)[a] complexes of heptane-2,4,6-trione (H_2hto) and 1-phenylhexane-1,3,5-trione (H_2phto) to the dinuclear 2:2 complexes in methanol–water solution (70:30 vol./vol.) at 25 °C and $I = 0.5$ mol dm^{-3} $NaClO_4$

Ligand	$10^3 \times [OH^-]$ (mol dm^{-3})	k_{obs} (s^{-1})
H_2hto[b]	0.495	5.80
	0.990	10.5
	1.24	12.6
	1.48	15.4
	1.98	19.2
H_2phto[c]	0.945	4.97
	1.98	9.97
	3.02	14.8
	4.02	18.7
	5.01	23.0

[a][Copper(II)]$_{total}$ = 5×10^{-5} mol dm^{-3}. [b]λ = 385 nm.
[c]λ = 420 nm.

a second molecule of the 1:1 complex to give a dimeric precursor complex. Assuming a steady state for the intermediate B, k_{obs} has the form of eqn. (8).
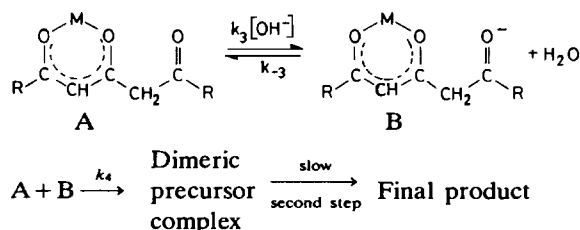
Scheme 3.

$$d[dimer]/dt = \frac{k_3 k_4 [Cu(HL)^+]^2[OH^-]}{k_{-3} + k_4[Cu(HL)^+]} \qquad (8)$$

It is apparent that depending on the relative magnitude of the various rate constants, the reaction can be first-order or second-order in $[Cu(HL)]^+$. In the present instance, due to fact that the rate constant is first-order in complex concentration and first-order in hydroxide ion concentration, the dominant term in the denominator must be that containing $[Cu(HL)]^+$. Thus eqn. (8) reduces to eqn. (9).

$$d[dimer]/dt = k_3[Cu(HL)^+][OH^-] \qquad (9)$$

Thus the slope of the plot of k_{obs} against $[OH^-]$ is equal to k_3, the rate of proton removal from the methine carbon by hydroxide ion. The values obtained here, 9.1×10^3 and 4.4×10^3 dm^3 mol^{-1} s^{-1} for $[Cu(Hhto)]^+$ and $[Cu(Hphto)]^+$, respectively, are lower than the value obtained for removal of a proton from the keto tautomer of pentane-2,4-dione by OH^-, 4.4×10^4 dm^3 mol^{-1} s^{-1} [32]. The values of k_3 are also comparable to the rate of proton loss from $[Ag(OH)_3(H_2O)]$ and k_{-5} in eqn. (10) has a value of c. 10^3 mol dm^{-3} [33].

$$[Ag(OH)_4]^- + H_2O \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}}$$

$$[Ag(OH)_3(H_2O)] + OH^- \qquad (10)$$
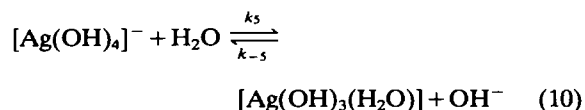
In another previous investigation, Kustin and co-workers [34] have found the rate of proton loss from the nickel(II) complex of 3,4-dihydroxyphenyl-alanine to be 1 s^{-1} and furthermore, the bimolecular rate constant for reaction of H^+ with the ionized form of this complex is several orders of magnitude lower than the diffusion-controlled limit [35, 36].

Alternative mechanisms to that outlined above might involve a pathway where the coordinated water in the $[M(HL)]^+$ species is hydrolyzed under the reaction conditions. However, simple mechanism involving such species do not give the required rate laws.

The slow second step represents a rearrangement of the dimeric precursor complex as previously demonstrated in the case of the dimerization of $[Ni(Hphto)]^+$ [24].

Discussion

The mechanism outlined in Scheme 2 accounts well for the kinetic data obtained for reactions of Cu^{2+} with all three ligands investigated. In the case of H_2phto and H_2dppto, K''_a is considerably larger than the highest hydrogen ion concentrations used and eqn. (2) is a reasonable approximation of eqn. (6). However, when H_2hto is the ligand, this is no longer true and this accounts for the relatively poor agreement between the directly determined and calculated values of k_{-2} (Table 2). Chopra and Jordan

TABLE 5. Summary of rate constants for conversion of the mononuclear 1:1 copper(II) complexes of heptane-2,4,6-trione (H_2hto) and 1-phenylhexane-1,3,5-trione (H_2phto) to the dinuclear 2:2 complexes in methanol–water (70:30 vol./vol.) solution at 25 °C and $I = 0.5$ mol dm^{-3} $NaClO_4$

k	H_2hto	H_2phto
1:1 → 2:2 (fast step)	$1.4 + 9.10 \times 10^3[OH^-]$	$1.1 + 4.41 \times 10^3[OH^-]$
1:1 → 2:2 (slow step) (s^{-1})	0.748	0.939

[27, 28] have outlined a number of other examples where the simple mechanism in Scheme 1 does not account satisfactorily for the kinetic data obtained for reaction of nickel(II) with a range of protonated ligands.

In conclusion, it would appear that a reasonable interpretation of the kinetic results would be that reaction of Cu^{2+} with the fully protonated form of all three ligands proceeds at rates that are greatly retarded compared to those predicted on the basis of the solvent exchange rate of Cu^{2+} by the Eigen–Wilkins mechanism [37]. The retardation factor is of the order of 10^4. On the other hand, reaction of Cu^{2+} with the mono-anions of all three ligands proceeds at rates comparable to those predicted by the Eigen–Wilkins mechanism.

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