# Reactions of Metal Ions with Triketones. Part 3.[1] Kinetics and Mechanisms of the Reactions of Nickel(II) and Cobalt(II) with 1-Phenylhexane-1,3,5-trione in Methanol–Water (70:30 v/v) Solution

## James Walsh and Michael J. Hynes *
Chemistry Department, University College, Galway, Ireland

The kinetics and mechanisms of the reactions of nickel(II) and cobalt(II) with 1-phenylhexane-1,3,5-trione ($H_2$phto) to form the 1:1 and 2:2 complexes have been investigated in methanol–water (70:30 v/v) solutions at 25 °C and ionic strength 0.5 mol dm$^{-3}$ NaClO$_4$. The rate constants for 1:1 complex formation with $H_2$phto ($k_{HL}$) and with Hphto$^-$ ($k_L$) have been determined. For Ni$^{2+}$, $k_{HL}$ = 3.48 and $k_L$ = 5.14 × 10$^4$ dm$^3$ mol$^{-1}$ s$^{-1}$ while for Co$^{2+}$, $k_{HL}$ = 0.6 and $k_L$ = 1.26 × 10$^6$ dm$^3$ mol$^{-1}$ s$^{-1}$. The conversion of the 1:1 into the 2:2 complexes takes place via a two-step mechanism, the first of which is second order in complex concentration and first order in hydroxide-ion concentration, while the second step is first order in complex concentration. The rate constants for Ni$^{2+}$ are 1.99 × 10$^7$ dm$^3$ mol$^{-1}$ s$^{-1}$ and 0.34 s$^{-1}$ while for Co$^{2+}$ they are 3.12 × 10$^7$ dm$^3$ mol$^{-1}$ s$^{-1}$ and 0.16 s$^{-1}$. Mechanisms are proposed which account for the kinetic data.

An interesting property of 1,3,5-triketones and their diamine Schiff-base derivatives is their ability to chelate two metal ions relatively close together. By varying the end groups of the triketones and the use of the Schiff-base derivatives, different ligand environments can be readily created. To date, most of the investigations of metal–triketone metal complexes have been concerned with the solid-state structures and magnetic properties of these species.[2,3] We have recently shown that in methanol–water (70:30 v/v) solution both mononuclear (1:1) and binuclear (2:2) complexes are formed.[4] However, the π system of the dianions with its preference for a planar configuration apparently precludes terdentate co-ordination by the ligands to a single metal ion. The stability constants of some of these species have been determined[4] and the kinetics and mechanisms of the reactions of Ni$^{II}$ and Co$^{II}$ with heptane-2,4,6-trione ($H_2$hpto) have been investigated.[1] Additionally, the transformation of the 1:1 complexes to the 2:2 complexes has been reported.[1]

As part of our continuing studies in this area we now report the results of investigations into the kinetics and mechanisms of the reactions of nickel(II) and cobalt(II) with 1-phenylhexane-1,3,5-trione ($H_2$phto).

## Experimental

Stock solutions of Ni$^{II}$ and Co$^{II}$ were prepared from their nitrates (BDH). These solutions were standardised by titration with ethylenediaminetetra-acetate. 1-Phenylhexane-1,3,5-trione was prepared according to the method of Hauser and Harris.[5] Stock solutions of the ligand were standardised by titration with standard sodium hydroxide. End-points were determined using an iterative computer program based on the method of Gran and Johansson.[6]

Methanol was purified by distillation from magnesium and iodine. All solutions were prepared using distilled water which had been boiled for 15 min. Methanol–water solutions (70:30 v/v) were prepared by adding water (300 cm$^3$) to a 1 000-cm$^3$ volumetric flask and diluting to the mark with distilled methanol. The mole fraction of methanol in this solution is 0.508. Sodium perchlorate purified as previously described[7] was used to adjust the ionic strength of all solutions to 0.5 mol dm$^{-3}$. The pH was measured using a Pye model 290 pH meter

equipped with a Pye Ingold E$_0^7$ combined electrode. The KCl in the electrode compartment was replaced by 3 mol dm$^{-3}$ NaCl. pH Readings were converted into hydrogen-ion concentration as described by Agrawal.[8] Solutions of perchloric acid and sodium hydroxide were used to adjust the pH values of solutions. Cacodylic acid [Me$_2$As(O)OH], N-(2-hydroxyethyl)-piperazine-N'-ethane-2-sulphonic acid (hepes), 2,6-dimethyl-pyridine-3-sulphonic acid, and HCl–HN(CH$_2$CH$_2$OH)$_2$ were used to control the pH. These were shown not to interfere with the reactions at the concentrations used.

Rate constants were measured using an Applied Photophysics stopped-flow device interfaced to a BBC micro-computer via a Datalab DL901 transient recorder. Pseudo-first-order rate constants were calculated as previously described.[1]

The kinetics of ionization of the ligand was investigated using a pH-jump technique. A slightly acidic solution of 5 × 10$^{-4}$ mol dm$^{-3}$ H$_2$phto was mixed in the stopped-flow apparatus with a series of HCl–HN(CH$_2$CH$_2$OH)$_2$ buffers at the same ionic strength and having pH values varying from zero to two pH units above the p$K$ of the ligand (8.39[4]). Blank experiments revealed no contributions due to external effects.

Most of the reactions were followed by observing an absorbance increase at around 400 nm as wavelengths in this region afforded the largest absorbance changes. However, in order to test the wavelength independence of the kinetic data, a number of runs were made at other wavelengths. No wavelength dependence was observed.

The conversion of the 1:1 into the 2:2 complexes was monitored by treating solutions of the 1:1 complexes with standard sodium hydroxide solutions and observing an absorbance increase around 430 nm. These reactions were found to be biphasic. A second-order reaction was followed by a slower first-order reaction. In view of the fact that it was not possible to obtain stable infinity values at the end of the initial second-order phase, the time-lag method recently reported by Espenson[9] was used to determine the second-order rate constants over a range of substrate and hydroxide-ion concentrations.

Hydrolysis reactions were carried out by treating solutions containing the metal and the ligand at the appropriate pH with standard perchloric acid solutions and observing the absorbance changes at a suitable wavelength.

All reactions were carried out at 25.0 ± 0.1 °C.

**Table 1.** Observed rate constants for the reaction of $Ni^{II}$ and $Co^{II}$ with 1-phenylhexane-1,3,5-trione ($H_2$phto) in methanol–water (70:30 v/v) solution at 25 °C and $I = 0.5$ mol dm$^{-3}$ NaClO$_4$

| Metal | $10^3[M]$/mol dm$^{-3}$ | $[H^+]$/mol dm$^{-3}$ | $k_{obs.}$/s$^{-1}$ | $k_{calc.}$/s$^{-1}$ |
|---|---|---|---|---|
| $Ni^{II}$ | 1.19 | $1.36 \times 10^{-5}$ | 0.09 | 0.09 |
| | 2.38 | $1.36 \times 10^{-5}$ | 0.14 | 0.12 |
| | 3.57 | $1.36 \times 10^{-5}$ | 0.15 | 0.14 |
| | 4.76 | $1.36 \times 10^{-5}$ | 0.17 | 0.17 |
| | 5.96 | $1.36 \times 10^{-5}$ | 0.20 | 0.19 |
| | 1.19 | $1.36 \times 10^{-6}$ | 0.24 | 0.24 |
| | 2.38 | $1.36 \times 10^{-6}$ | 0.42 | 0.43 |
| | 3.57 | $1.36 \times 10^{-6}$ | 0.60 | 0.62 |
| | 4.76 | $1.36 \times 10^{-6}$ | 0.78 | 0.81 |
| | 5.95 | $1.36 \times 10^{-6}$ | 0.95 | 0.99 |
| | 1.19 | $1.36 \times 10^{-7}$ | 1.86 | 1.85 |
| | 2.38 | $1.36 \times 10^{-7}$ | 3.72 | 3.64 |
| | 3.57 | $1.36 \times 10^{-7}$ | 5.50 | 5.44 |
| | 4.76 | $1.36 \times 10^{-7}$ | 7.20 | 7.23 |
| | 5.95 | $1.36 \times 10^{-7}$ | 9.00 | 9.00 |
| | 5.95 | $6.10 \times 10^{-6}$ | 0.30 | 0.32 |
| | 5.95 | $9.60 \times 10^{-6}$ | 0.22 | 0.23 |
| $Co^{II}$ | 1.25 | $1.36 \times 10^{-5}$ | 6.36 | 6.20 |
| | 2.50 | $1.36 \times 10^{-5}$ | 6.90 | 6.68 |
| | 3.75 | $1.36 \times 10^{-5}$ | 7.11 | 7.01 |
| | 5.00 | $1.36 \times 10^{-5}$ | 7.52 | 7.41 |
| | 6.25 | $1.36 \times 10^{-5}$ | 7.98 | 7.81 |
| | 1.25 | $4.28 \times 10^{-6}$ | 10.5 | 11.4 |
| | 2.50 | $4.28 \times 10^{-6}$ | 15.1 | 16.1 |
| | 3.75 | $4.28 \times 10^{-6}$ | 21.1 | 20.8 |
| | 5.00 | $4.28 \times 10^{-6}$ | 25.5 | 25.5 |
| | 6.25 | $4.28 \times 10^{-6}$ | 31.5 | 30.2 |
| | 1.25 | $1.36 \times 10^{-6}$ | 7.10 | 7.95 |
| | 2.50 | $1.36 \times 10^{-6}$ | 8.50 | 9.38 |
| | 3.75 | $1.36 \times 10^{-6}$ | 10.0 | 10.8 |
| | 5.00 | $1.35 \times 10^{-6}$ | 12.0 | 12.2 |
| | 6.25 | $1.35 \times 10^{-6}$ | 14.0 | 13.6 |
| | 6.25 | $5.91 \times 10^{-6}$ | 10.7 | 10.4 |
| | 6.25 | $9.23 \times 10^{-6}$ | 9.60 | 9.50 |

**Table 2.** Rate constants for the dimerisation of $[Ni(Hphto)]^+$ in methanol–water (70:30 v/v) solution at 25 °C and $I = 0.5$ mol dm$^{-3}$ NaClO$_4$

| $10^4[Ni(Hphto)]^+$/ mol dm$^{-3}$ | $10^3[NaOH]$/ mol dm$^{-3}$ | $10^{-7} \times$ Second-order rate constant/dm$^3$ mol$^{-1}$ s$^{-1}$ |
|---|---|---|
| 2.5 | 5 | 2.11 |
| 2.5 | 5 | 2.18 |
| 3.7 | 5 | 1.7 |
| 3.7 | 5 | 1.9 |
| 6.2 | 5 | 2.28 |
| 6.2 | 5 | 2.12 |
| 7.5 | 5 | 2.06 |
| 7.5 | 5 | 1.80 |
| | | Average 2.01 $\pm$ 0.18 |
| 5.0 | 2.5 | 1.92 |
| 5.0 | 2.5 | 1.96 |
| 5.0 | 5.0 | 2.10 |
| 5.0 | 7.5 | 1.95 |
| | | Average 1.97 $\pm$ 0.07 |

**Table 3.** Observed rate constants for the dimerisation of $[Co(Hphto)]^+$ in methanol–water (70 : 30 v/v) solution at 25 °C and $I = 0.5$ mol dm$^{-3}$ NaClO$_4$

| $10^4[Co(Hphto)]^+$/ mol dm$^{-3}$ | $10^3[NaOH]$/ mol dm$^{-3}$ | $10^{-7} \times$ Second-order rate constant/dm$^3$ mol$^{-1}$ s$^{-1}$ |
|---|---|---|
| 2.5 | 5 | 3.26 |
| 2.5 | 5 | 3.16 |
| 3.7 | 5 | 3.10 |
| 3.7 | 5 | 2.96 |
| 5.0 | 5 | 3.42 |
| 5.1 | 5 | 3.22 |
| 6.2 | 5 | 2.92 |
| 6.2 | 5 | 2.48 |
| 7.5 | 5 | 3.5 |
| 7.5 | 5 | 3.36 |
| | | Average 3.13 $\pm$ 0.27 |
| 5.0 | 2.5 | 3.2 |
| 5.0 | 2.5 | 3.14 |
| 5.0 | 5.0 | 2.94 |
| 5.0 | 5.0 | 2.86 |
| 5.0 | 7.5 | 3.26 |
| 5.0 | 7.5 | 3.28 |
| | | Average 3.11 $\pm$ 0.15 |

mechanism shown in Scheme 1. Under pseudo-first-order conditions when pH $\ll$ p$K_a$, Scheme 1 predicts that for com-

$$M^{2+} + H_2L \underset{k_{-HL}}{\overset{k_{HL}}{\rightleftharpoons}} [M(HL)]^+ + H^+$$

$$\Big\Vert K_a$$
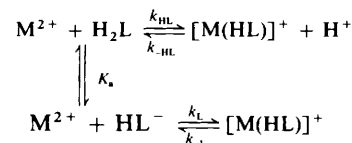
$$M^{2+} + HL^- \underset{k_{-L}}{\overset{k_L}{\rightleftharpoons}} [M(HL)]^+$$

**Scheme 1.**

plex-formation reactions with the metal in excess $k_{obs.}$ will have the form of equation (1) where $K_f = k_L/k_{-L} = [M(HL)^+ ]/[M^{2+}][HL^-]$ and $K_a$ is the first dissociation constant of $H_2$phto ($10^{-8.39}$). The use of this equation to fit the kinetic data gives $k_{HL} = 3.48 \pm 1.9$ and $0.60 \pm 0.03$ dm$^3$ mol$^{-1}$ s$^{-1}$ and values of $k_L = (5.14 \pm 0.02) \times 10^4$ and $(1.26 \pm 0.09) \times 10^6$ dm$^3$ mol$^{-1}$ s$^{-1}$ for $Ni^{2+}$ and $Co^{2+}$ respectively. Equation (1)

$$k_{obs.} = (k_{HL}[H^+] + k_L K_a)\{[M^{2+}]/ (K_a + [H^+]) + (K_a K_f)^{-1}\} \quad (1)$$

predicts that a plot of $k_{obs.}\{[M^{2+}](K_a + [H^+])^{-1} + (K_a K_f)^{-1}\}^{-1}$ against $[H^+]$ should be linear with a slope of $k_{HL}$ and intercept $k_L K_a$. The Figure clearly shows this to be the case.

The conversion of the 1:1 into the 2:2 complexes was monitored by treating solutions of $[M(HL)]^+$ with a large excess of standard sodium hydroxide. An absorbance increase which was the sum of two separable reactions was observed at around 430 nm. An initial investigation showed that the faster of the two reactions was second-order in complex concentration and first order in hydroxide-ion concentration. Consequently, the usual first-order methods could not be used to determine the rate constants for the first step. The rate constants were evaluated as described in the Experimental section. The data are given in Tables 2 and 3.

The rate law for conversion of the 1:1 complexes of $H_2$phto with $Ni^{II}$ and $Co^{II}$ into the 2:2 complexes is clearly different to that found for the corresponding reaction of heptane-2,4,6-trione.[1] In the case of heptane-2,4,6-trione, both steps of the conversion were first order in substrate and zero-order in hydroxide-ion concentration. A perusal of the chemical

## Results and Discussion

When solutions of $H_2$phto were treated with solutions of either $Ni^{II}$ or $Co^{II}$ in the range pH 5—7 an absorbance change corresponding to a single exponential was observed. The kinetic data are given in Table 1. These data are consistent with the

**Table 4.** Summary of rate constants for formation and dissociation of the complexes of 1-phenylhexane-1,3,5-trione in methanol–water (70:30 v/v) solution, at 25 °C and $I = 0.5$ mol dm⁻³ NaClO₄

| Rate constant[a]/dm³ mol⁻¹ s⁻¹ | Nickel(II) | Cobalt(II) |
|---|---|---|
| $k_{HL}$ (exptl.) | $3.48 \pm 1.9$ | $0.60 \pm 0.03$ |
| $k_{HL}$ (predicted) | $2.7 \times 10^4$ | $6.6 \times 10^5$ |
| $R$ | $1.71 \times 10^{-4}$ | $1.21 \times 10^{-6}$ |
| $k_L$ (exptl.) | $(5.14 \pm 0.02) \times 10^4$ | $(1.26 \pm 0.09) \times 10^6$ |
| $k_L$ (predicted) | $1.1 \times 10^5$ | $4.4 \times 10^6$ |
| $R$ | 0.62 | 0.38 |
| $k_{-HL}$ (exptl.) | $(1.74 \pm 0.08) \times 10^3$ | $(1.04 \pm 0.02) \times 10^3$ |
| $k_{-HL}$ (calculated)[b] | $1.32 \times 10^3$ | 791 |
| $k_{-L}$ (exptl.)/s⁻¹ | 0 | $42.2 \pm 0.2$ |
| $k_{-L}$ (calculated)[b]/s⁻¹ | 0.08 | 6.8 |
| $k_{1:1 \longrightarrow 2:2}$ (fast step) | $(1.99 \pm 0.18) \times 10^7$ | $(3.12 \pm 0.27) \times 10^7$ |
| $k_{1:1 \longrightarrow 2:2}$ (slow step)/s⁻¹ | 0.34 | 0.16 |

[a] $R = 4k_f/3K_ok_s$ where $k_f$ is the rate of complex formation, $K_o$ is the outer-sphere association constant, and $k_s$ is the rate of solvent exchange. [b] Calculated from $k_{HL}$ (exptl.), $k_L$ (exptl.), $K_f$, and $K_a$.
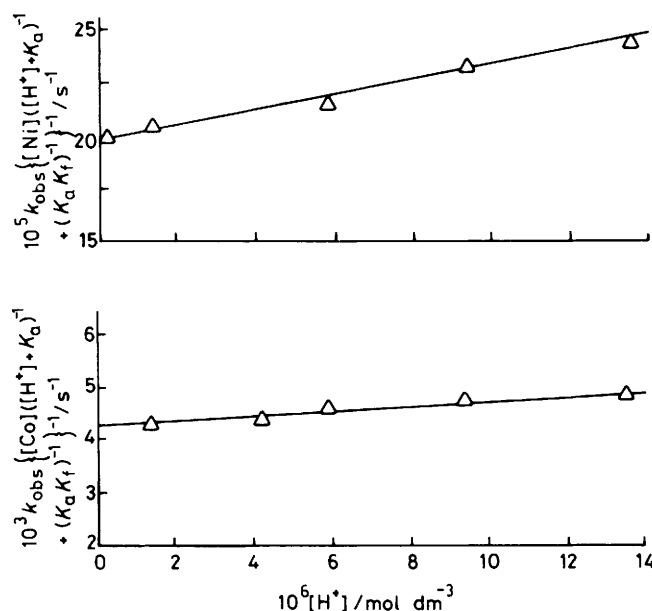


**Figure.** Plot suggested by equation (1) for the reactions of Ni^II and Co^II with 1-phenylhexane-1,3,5-trione in methanol–water (70:30 v/v) solution at 25 °C and $I = 0.5$ mol dm⁻³ NaClO₄

literature failed to reveal any complex-formation reactions similar to the ones under investigation.

The mechanism shown in Scheme 2 successfully accounts for

$$[M(HL)]^+ + OH^- \xrightleftharpoons{K(=\,k_1/k_{-1})} [ML] + H_2O$$

$$[ML] + [M(HL)]^+ \xrightarrow{k_2} [M_2L_2] + H^+$$
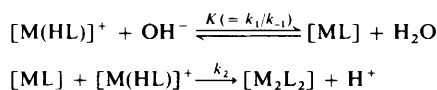
**Scheme 2.**

the kinetic data. In the first step of this mechanism a molecule of [M(HL)]⁺ reacts with OH⁻ in a rapid non-rate-determining step to give the fully deprotonated species [ML]. This then reacts with another molecule of [M(HL)]⁺ to give [M₂L₂]. The mechanism in Scheme 2 predicts the rate equation (2), in

$$d[M_2L_2]/dt = k_2K[OH^-][M(HL)^+]^2 \qquad (2)$$

agreement with the experimental data. Alternatively, [ML] may be assumed to be in a steady state $(K = k_1/k_{-1})$, resulting in expression (3). Two conditions can arise in this instance. Case 1

$$\frac{d[M_2L_2]}{dt} = \frac{k_1k_2[OH^-][M(HL)^+]^2}{k_{-1} + k_2[M(HL)^+]} \qquad (3)$$

where $k_{-1} \gg k_2[M(HL)^+]$ gives the equation (4) which is the

$$\frac{d[M_2L_2]}{dt} = \frac{k_1k_2}{k_{-1}}[OH^-][M(HL)^+]^2 \qquad (4)$$

same as equation (2), i.e. it assumes that proton transfer is rapid compared to dimerisation. Case 2 where $k_{-1} \ll k_2[M(HL)^+]$ gives equation (5), of which the first order dependences in both

$$d[M_2L_2]/dt = k_1[OH^-][M(HL)^+] \qquad (5)$$

[OH⁻] and [M(HL)⁺] are not in accordance with the experimental facts.

The kinetic data give values of $2 \times 10^7$ and $3 \times 10^7$ dm³ mol⁻¹ s⁻¹ for the dimerisation reactions of the 1:1 complexes of Ni²⁺ and Co²⁺ respectively. These values may be equated with $Kk_2$ in equation (2) or $k_1k_2/k_{-1}$ in equation (4).

For both Ni^II and Co^II the second-order reaction was followed by a slower first-order reaction having rate constants of 0.34 and 0.16 s⁻¹ respectively. In the case of the corresponding reaction with heptane-1,4,6-trione, this reaction was associated with some form of rearrangement of a dimeric precursor complex to give the final 2:2 product.[1] In the present instance, this is clearly the case, as the preceding second-order reaction provides unambiguous evidence for the prior formation of the 2:2 complex.

When solutions of [M(HL)]⁺ were treated with solutions containing various concentrations of perchloric acid, a single reaction step was observed. The kinetic data may be conveniently represented by equations (6) and (7) for Ni^II and

$$k_{Ni}^H = 0 + (1.74 \pm 0.08) \times 10^3[H^+] \qquad (6)$$

$$k_{Co}^H = (42.2 \pm 0.2) + (1.04 \pm 0.02) \times 10^3[H^+] \qquad (7)$$

Co^II respectively. The complex dissociation data can be analysed using equation (1) with $[M^{2+}] = 0$ [equation (8)].

$$k_{obs.} = k_{HL}[H^+]/K_aK_f + (k_L/K_f) \qquad (8)$$

Thus the intercepts in equations (6) and (7) should be equal to $k_L/K_f = k_{-L}$ while the slopes should be equal to $k_{HL}/K_aK_f$. For both Ni^II and Co^II the experimental values of $k_{-HL}$ are in good agreement with those calculated from $k_{HL}$ and $K_f$. The calculated and experimental values of $k_{-L}$ for the nickel(II) reactions are also in good agreement. However there is an apparent discrepancy in the experimental and calculated values of $k_{-L}$ in the case of Co^II. The reason for this is not immediately obvious. However, it may be associated with a two-step mechanism involving a monodentate intermediate, although this is not obvious from the kinetic data, cf. the Figure.

Hydrolysis of the 2:2 complexes results in a single reaction for both Ni^II and Co^II. The rate data are described by equations (9) and (10). In the case of both Ni^II and Co^II, hydrolysis of the

$$k_H^{Ni} = (0.17 \pm 0.02) + (3.76 \pm 0.08)[H^+] \qquad (9)$$

$$k_H^{Co} = (1.75 \pm 0.10) + (285 \pm 3)[H^+] \qquad (10)$$

2:2 complexes is slower than hydrolysis of the 1:1 complexes. This is consistent with the fact that only a single reaction step is observed in the hydrolysis of the 2:2 complexes.

Table 4 summarises the kinetic data. We have previously suggested[1] that the normal complex-formation reactions of $Ni^{II}$ and $Co^{II}$ should be approximately two and a half times faster in methanol–water (70:30 v/v) than in 100% water. The calculated values of $k_{HL}$ and $k_L$ in Table 4 have been obtained on that basis. As in the case of $H_2hpto$ the values of $k_L$ for $Ni^{2+}$ and $Co^{2+}$ are in relatively good agreement with those calculated on the basis of the Eigen–Wilkins mechanism.[10] Complexation with the fully protonated neutral forms of the ligand yields rate constants that are too slow by a factor of 5 848 in the case of $Ni^{2+}$ and $8.3 \times 10^5$ in the case of $Co^{2+}$ compared to those calculated using $K_o$ the outer-sphere association constant and the solvent-exchange rate.

When pH-jump experiments were carried out with $H_2phto$ the absorbance changes were so rapid on the stopped-flow time-scale that rate constants could not be measured. Consequently, at pH $\approx pK$, the rate constant for ionisation must be $\geqslant 300$ s$^{-1}$. The rate constant for non-base-catalysed proton loss from $H_2phto$ may be estimated to be greater than 82 s$^{-1}$ from the relationship $K_a = k_{-H}/k_H$ assuming that $k_H$ the rate constant for the recombination of the proton and its conjugate base is diffusion controlled. Initial rate measurements similar to those carried out for $H_2hpto$[1] show that the acid pseudo-equilibrium is maintained up to $[H^+] = 10^{-8}$ mol dm$^{-3}$ in the case of $Ni^{2+}$ and $10^{-7}$ mol dm$^{-3}$ in the case of $Co^{2+}$. Consequently, it is clear that ionisation is not the rate-determining step in the reactions of $Ni^{2+}$ and $Co^{2+}$ with the fully protonated form of the ligand. It is likely that disruption of the strong intramolecular hydrogen bonds is involved.

The second-order rate constants for the dimerisation reactions of $[Ni(Hphto)]^+$ and $[Co(Hphto)]^+$ are $2.0 \times 10^7$ and $3 \times 10^7$ dm$^3$ mol$^{-1}$ s$^{-1}$ respectively. If the proposed mechanism is correct, then these rate constants are equal to the product $Kk_2$ in Scheme 2. The effects of ligands co-ordinated to a metal on both the rate of exchange of the remaining solvent molecules and the rates of additional complex formation have been the subjects of a number of investigations.[11] Although in many instances, the rate of solvent exchange of the remaining water molecules is considerably enhanced, the rate of additional complex formation is frequently considerably less than the rates predicted on the basis of the outer-sphere association constant and the solvent-exchange rates. For example, $[Ni(trien)]^{2+}$ (trien = triethylenetetramine) reacts with 1,10-phenanthroline 34 times slower than predicted on the basis of $K_o$ and the solvent exchange rate,[12] while it reacts with glycine approximately 15 times slower than predicted on the same basis.[13] Consequently, it is unlikely that $k_2$ in Scheme 2 is greater than $1 \times 10^4$ dm$^3$

mol$^{-1}$ s$^{-1}$ in the case of $Ni^{2+}$; indeed in view of the bulk of the ligands involved it is probably less. This sets an upper limit of about 10.5 for the p$K$ of the dissociable proton in $[Ni(Hphto)]^+$. Similar arguments apply in the case of $Co^{2+}$.

A referee has pointed out that in view of the fact that the first step of the reaction in Scheme 2 is faster than the rate of solvent exchange on $Ni^{II}$, the reaction could be viewed as a co-ordinated ligand reaction in which the deprotonated species [ML] rather than co-ordinate to the metal in $[M(HL)]^+$ (or [ML]) acts as a nucleophile on a second [ML]. It was argued that had the metal centres been involved to a significant extent some differences in $k_2$ might have been anticipated. This is not inconsistent with the mechanism as proposed in Scheme 2 and it is difficult to decide which of the interpretations is correct. The problem could be resolved by carrying out these reactions using inert metal ions. However to date we have been unable to do this as in the case of the common inert metal ions the dimerisation reactions do not occur.[2,3]

In conclusion, it may be stated that, while previous investigations provided a broad outline of the processes involved,[1] the present investigations provide relatively detailed information regarding the mechanism involved in the conversion of 1:1 metal–triketone complexes into the 2:2 binuclear species. Very few similar reactions have been previously investigated.

## References

1 Part 2, M. J. Hynes and J. Walsh, *J. Chem. Soc., Dalton Trans.*, 1985, 2565.
2 M. D. Glick and R. L. Lintvedt, *Prog. Inorg. Chem.*, 1976, 21, 233.
3 U. Casellato and P. A. Vigato, *Coord. Chem. Rev.*, 1977, 23, 31.
4 M. J. Hynes and J. Walsh, *J. Chem. Soc., Dalton Trans.*, 1985, 1543.
5 C. R. Hauser and T. M. Harris, *J. Am. Chem. Soc.*, 1958, 80, 6360.
6 G. Gran and A. Johansson, *Analyst (London)*, 1981, 106, 231.
7 M. J. Hynes and B. D. O'Regan, *J. Chem. Soc., Dalton Trans.*, 1980, 7.
8 Y. K. Agrawal, *Talanta*, 1979, 26, 599.
9 J. H. Espenson, *J. Chem. Educ.*, 1980, 57, 160.
10 M. Eigen and R. G. Wilkins, *Adv. Chem. Ser.*, 1965, 49, 55.
11 D. W. Margerum, G. R. Cayley, D. C. Weatherburn, and G. G. Pagenkopf, in 'Coordination Chemistry,' ed. A. E. Martell, ACS Monograph 174, Washington D.C., 1978, vol. 2, ch. 1.
12 R. K. Steinhaus and J. A. Boersma, *Inorg. Chem.*, 1972, 11, 1505.
13 R. K. Steinhaus and B. I. Lee, *Inorg. Chem.*, 1982, 21, 1829.