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Reactions of Metal Ions with Triketones in Solution.
Part IV. Kinetics and Mechanisms of the Reactions of Nickel(II) and Cobalt(II) with 2-Aceto-1,8-dihydroxynaphthalene, 2,2′-Dihydroxybenzophenone and 1,5-Diphenylpentane-1,3,5-trione in Methanol–Water (70:30 *v/v*) Solution

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Abstract

The kinetics and mechanisms of the reactions of nickel(II) and cobalt(II) with 2-aceto-1,8-dihydroxynaphthalene (H_2adhna), 2,2′-dihydroxybenzophenone (H_2dhbpo) and 1,5-diphenylpentane-1,3,5-trione (H_2dppto) have been investigated in methanol–water solutions (70:30 *v/v*) at 25 °C and ionic strength 0.5 mol dm^{-3} $NaClO_4$. The formation reactions of the 1:1 complexes of both metal ions with H_2adhna and H_2dppto were investigated while in the case of H_2dhbpo only the reaction with nickel(II) could be investigated. The dimerization reactions of $[M(Hadhna)]^+$ ($M^{2+} = Ni^{2+}, Co^{2+}$) and $[Ni(Hdhbpo)]^+$ to form the 2:2 complexes were also investigated. Detailed mechanisms are proposed which account satisfactorily for the kinetic data.

Introduction

In general, fully protonated ligands can be considered to be relatively unreactive towards metal ions. However, the reactivity of partially protonated compared to unprotonated multidentate ligands can vary considerably depending on the nature of the metal ion and the ligand [1]. Some of these effects may be demonstrated using the reactions of Ni^{II} and Co^{II} with triketones and related ligands. To date, most of the investigations of metal triketone 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 solutions (70:30 *v/v*) both mononuclear (1:1) and binuclear (2:2) complexes are formed and the formation constants of a number of these complexes have been determined [4]. Additionally, the kinetics and mechanisms of the reactions of Ni^{II} and Co^{II} with heptane-2,4,6-trione (H_2hpto) [5] and 1-phenylhexane-1,3,5-trione (H_2phto) [6] have been reported. The mechanisms of the conversion of the 1:1 to the 2:2 complexes have been investigated [5, 6].

Resulting from our continued interest in the interactions of metal ions with triketones, we now report the results of our investigations into the kinetics and mechanisms of the reactions of Ni^{II} and Co^{II} with 2-aceto-1,8-dihydroxynaphthalene (H_2adhna), 2,2′-dihydroxybenzophenone (H_2dhbpo) and 1,5-diphenylpentane-1,3,5-trione (H_2dppto).

Experimental

Stock solutions of Ni^{II} and Co^{II} were prepared from their nitrates (BDH). These solutions were standardized by titration with ethylenediaminetetraacetate (edta). 1,5-Diphenylpentane-1,3,5-trione (H_2dppto) was prepared according to the method of Hauser and Harris [7]. 2,2′-Dihydroxybenzophenone (H_2dhbpo) was prepared as described by Richter [8] while 2-aceto-1,8-dihydroxynaphthalene (H_2adhna) was prepared by acetylation of 1,8-dihydroxynaphthalene using zinc chloride as described by Overeen [9]. Stock solutions of the ligands were standardized by titration with standard sodium hydroxide. End points were determined using an iterative computer program based on the method of Gran [10].

Methanol was purified by distillation from magnesium and iodine. All solutions were prepared using distilled water which had been boiled out for fifteen minutes. Methanol–water solutions (70:30 *v/v*) were prepared by adding water (300 cm^3) to a 1000 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 [11], was used to adjust the ionic strength of all solutions to 0.5 mol dm^{-3}.

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pH readings were measured using a Pye Model 290 pH meter equipped with a Pye Ingold E_0[7] combined electrode. The potassium chloride in the electrode compartment was replaced by 3 mol dm^{-3} sodium chloride. pH readings were converted to hydrogen ion concentrations as described by Agrawal [12]. Solutions of perchloric acid and sodium hydroxide were used to adjust the pH values of solutions. Cacodylic acid ($CH_3As(O)OH$), Hepes (*N*-(2-hydroxyethyl)piperazine-*N*'-ethane-2-sulphonic acid), 2,6-lutedine-3-sulphonic acid [13] and HCl–$HN(CH_2CH_2OH)_2$ were used to control pH. Blank experiments showed that these buffers did not interfere with the reactions at the concentrations used.

Rate constants were measured using an Applied Photophysics stopped-flow device interfaced to a BBC microcomputer via a Datalab DL901 transient recorder. Pseudo-first-order rate constants were calculated as previously described [5].

The kinetics of ionization of the ligands were investigated using a pH jump technique. A slightly acidic solution of the ligand at a concentration of 5×10^{-4} mol dm^{-3} was mixed in the stopped-flow apparatus with a series of HCl–$HN(CH_2CH_2OH)_2$ buffers at the same ionic strength and having pH values one to two units above the p*K* of the ligand. Blank experiments showed no contribution from external effects.

The kinetics of formation of the 1:1 complexes of Ni^{II} and Co^{II} were measured under pseudo-first-order conditions with the metal in excess. The reactions involving H_2dppto and H_2dhbo were monitored by observing an absorbance increase at 410 nm while the reaction involving I [illegible]na was monitored at 440 nm. Conversion of the 1:1 complexes of both Ni^{II} and Co^{II} with H_2dhbpo and H_2adhna to the 2:2 complexes was investigated by reacting solutions containing only the 1:1 complexes with standard sodium hydroxide solutions and observing an absorbance increase at 450 and 440 nm respectively. Due to the onset of precipitation when only about 10% of the 2:2 complexes of both Ni^{II} and Co^{II} with H_2dppto had formed, it was not possible to measure the rate constants for conversion of the 1:1 to the 2:2 complexes in this instance. Hydrolysis reactions were carried out by reacting solutions containing both metal and ligand at an appropriate pH with solutions containing perchloric acid and observing the absorbance changes at a suitable wavelength.

The p*K* values of H_2adhna and the stability constants of the complexes formed with Ni^{II} and Co^{II} were determined as previously described [4].

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

TABLE I. log β_{pqr} Values for the Species $L_pM_qH_r$ Relevant to the Present Investigation at 25 °C and $I = 0.5$ mol dm^{-3} $NaClO_4$ in Methanol–water (70:30 *v*/*v*).

H_2L	M	*p*	*q*	*r*	log β	Reference
Hdhbpo		1	0	1	10.38	4
		1	0	2	19.95	4
	Ni^{II}	1	1	1	14.97	4
	Ni^{II}	2	2	0	16.32	4
	Co^{II}	1	1	1	14.41	4
	Co^{II}	2	2	0	15.88	4
H_2adhna		1	0	1	10.94(±0.03)	this work
		1	0	2	18.07(±0.03)	this work
	Ni^{II}	1	1	1	16.14(±0.04)	this work
	Ni^{II}	2	2	0	17.87(±0.03)	this work
	Co^{II}	1	1	1	15.77(±0.02)	this work
	Co^{II}	2	2	0	16.13(±0.03)	this work
H_2dppto		1	0	1	10.74	4
		1	0	2	19.01	4
	Ni^{II}	1	1	1	16.97	4
	Co^{II}	1	1	1	16.29	4

Results and Discussion

Reaction of Ni^{II} and Co^{II} with H_2adhna and H_2dhbpo

Table I lists the equilibrium constants relevant to the present investigation. The absorbance changes associated with ionization of both ligands were so rapid that rate constants could not be measured using the stopped-flow device. However, the non-base catalysed rate constants for proton loss from uncomplexed H_2adhna and H_2dhbpo were estimated to be 1482 and 5.38 s^{-1} respectively. In spite of the large difference in the deprotonation rate constants, an initial rates analysis shows that during the formation of the 1:1 complexes of Ni^{II} and Co^{II} the pseudo-equilibrium is maintained up to pH 10 in the case of H_2adhna and 9.0 in the case of H_2dhbpo. All the kinetic data in Tables I and II were collected below these pH values.

When solutions of H_2adhna and H_2dhbpo were reacted with Ni^{II} and solutions of H_2adhna were reacted with Co^{II} an absorbance change corresponding to a single exponential was observed. The reaction of Co^{II} with H_2dhbpo could not be investigated due to the small degree of complex formation and the considerable overlap between the 1:1 and the 2:2 complexes. The kinetic data are presented in Tables II and III.

$$\begin{tikzcd}
M^{2+} + H_2L \arrow[r, shift left, "k_{HL}"] \arrow[d, shift left, "K_a"] & MHL^+ + H^+ \arrow[l, shift left, "k_{-HL}"] \\
M^{2+} + HL^{-1} \arrow[u, shift left] \arrow[r, shift left, "k_L"] & MHL^+ \arrow[l, shift left, "k_{-L}"]
\end{tikzcd}$$

Scheme 1.

TABLE II. Observed Rate Constants for the Reaction of Ni^{II} and Co^{II} with 2-Aceto-1,8-dihydroxynaphthalene (H_2adhna) in Methanol–Water (70:30 *v*/*v*) Solution at 25 °C, I = 0.5 $NaClO_4$, λ = 440 nm

Metal	Experiment	10^3 [M] (mol dm^{-3})	[H^+] (mol dm^{-3})	k_{obs} (s^{-1})	k_{calc} (s^{-1})
Ni^{II}	1	1.28	1.36×10^{-6}	0.39	0.41
	2	2.56	1.36×10^{-6}	0.75	0.79
	3	3.84	1.36×10^{-6}	1.01	1.17
	4	5.12	1.36×10^{-6}	1.55	1.55
	5	6.40	1.36×10^{-6}	1.93	1.93
	6	1.28	4.28×10^{-7}	0.83	0.82
	7	2.56	4.28×10^{-7}	1.75	1.61
	8	3.84	4.28×10^{-7}	2.50	2.41
	9	5.12	4.28×10^{-7}	3.30	3.21
	10	6.40	4.28×10^{-7}	4.11	4.01
	11	1.28	1.36×10^{-7}	1.79	1.71
	12	2.56	1.36×10^{-7}	3.60	3.41
	13	3.84	1.36×10^{-7}	5.10	5.08
	14	5.12	1.36×10^{-7}	6.73	6.77
	15	6.40	1.36×10^{-7}	8.30	8.45
Co^{II}	16	0.49	1.36×10^{-5}	12.2	11.8
	17	0.99	1.36×10^{-5}	14.0	13.6
	18	1.48	1.36×10^{-5}	15.1	15.4
	19	1.98	1.36×10^{-5}	16.8	17.2
	20	2.47	1.36×10^{-5}	18.6	19.0
	21	0.49	4.28×10^{-6}	14.1	12.8
	22	0.99	4.28×10^{-6}	18.2	17.4
	23	1.48	4.28×10^{-6}	22.1	21.1
	24	1.98	4.28×10^{-6}	26.0	25.3
	25	2.47	4.28×10^{-6}	30.1	29.6
	26	0.49	1.36×10^{-6}	21.5	19.6
	27	0.99	1.36×10^{-6}	32.1	31.0
	28	1.48	1.36×10^{-6}	44.0	43.1
	29	1.98	1.36×10^{-6}	54.6	55.2
	30	2.47	1.36×10^{-6}	66.7	67.2

TABLE III. Observed Rate Constants for the Reaction of Ni^{II} with 1,8-Dihydroxybenzophenone (H_2dhbpo) in Methanol–Water (70:30 *v*/*v*) solution at 25 °C, I = 0.5 $NaClO_4$, λ = 410 nm

Metal	Experiment	10^3 [M] (mol dm^{-3})	[H^+] (mol dm^{-3})	k_{obs} (s^{-1})	k_{calc} (s^{-1})
Ni^{II}	1	1.19	4.28×10^{-7}	1.87	1.87
	2	2.38	4.28×10^{-7}	1.90	1.93
	3	3.57	4.28×10^{-7}	1.92	1.99
	4	4.76	4.28×10^{-7}	1.94	2.04
	5	5.95	4.28×10^{-7}	1.95	2.06
	6	1.19	1.36×10^{-7}	1.78	1.60
	7	2.38	1.36×10^{-7}	1.90	1.81
	8	3.57	1.36×10^{-7}	2.03	2.01
	9	4.76	1.36×10^{-7}	2.15	2.10
	10	5.95	1.36×10^{-7}	2.30	2.27
	11	1.19	4.28×10^{-8}	1.84	1.85
	12	2.38	4.28×10^{-8}	2.05	1.95
	13	3.57	4.28×10^{-8}	2.23	2.31
	14	4.76	4.28×10^{-8}	2.40	2.56
	15	5.95	4.28×10^{-8}	2.60	2.81

The kinetic data are consistent with the mechanism outlined in Scheme 1. Under pseudo-first-order conditions with the metal in excess, Scheme 1 predicts that when pH $\ll$ pK_a k_{obs} will have the form of eqn. (1) where $K_f = [M(HL)^+]/[M^{2+}][HL^-] = k_L/k_{-L}$ and K_a is the first dissociation constant of the ligand.

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

Equation (1) suggests that plots of $k_{obs}\{[M^{2+}]/(K_a + [H^+]) + (K_a K_f)^{-1}\}^{-1}$ against $[H^+]$ should yield straight lines with slopes equal to k_{HL} and intercepts equal to k_L. Figures 1 and 2 show this to be the case. Fitting the kinetic data to eqn. (1) gives values of $k_{HL} = 121(\pm 11)$ and $1.24(\pm 0.17) \times 10^3$ and values of $k_L = 3.15(\pm 0.04) \times 10^3$ and $4.38(\pm 0.06) \times 10^5$ dm^3 mol^{-1} s^{-1} for the reaction of H_2adhna with nickel(II) and cobalt(II) respectively. Reaction of Ni^{II} with H_2dhbpo gives $k_{HL} = 16.0(\pm 0.3)$ and $k_L = 4.56(\pm 0.03) \times 10^4$ dm^3 mol^{-1} s^{-1}. R values [14] have been calculated and Tables IV and V give summaries of the results.

It is evident that the reaction of Ni^{II} with H_2dhbpo is similar to its reaction with heptane-2,4,6-trione [5]. The reaction of Ni^{2+} with the mono anion of H_2dhbpo is normal in terms of the Eigen–Wilkins mechanism [15] while the reaction with the protonated form of the ligand is retarded by a factor of 1600. This retardation is due to the fact that the protonated ligand is a poor entering group.

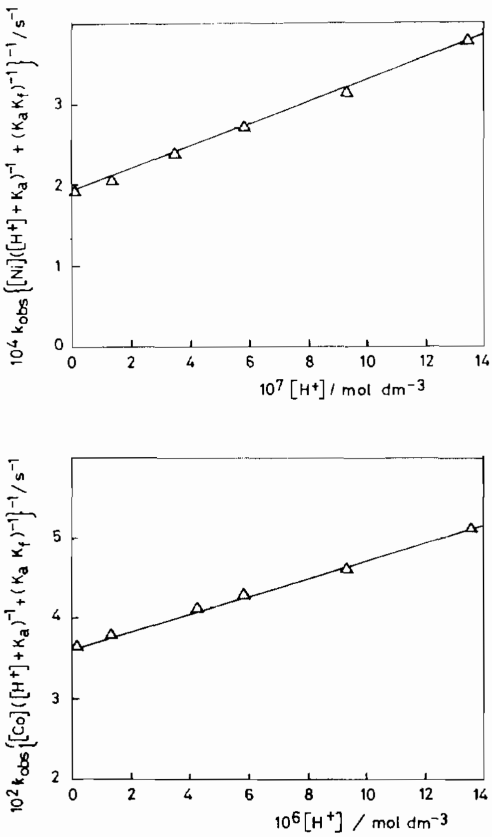


Fig. 1. Plot suggested by eqn. (1) for reaction of Ni^{2+} and Co^{2+} with 2-aceto-1,8-dihydroxynaphthalene (H_2adhna) in methanol–water (70:30 v/v) at 25 °C and ionic strength 0.5 mol dm^{-3} $NaClO_4$.

The reactions of Ni^{II} and Co^{II} with H_2adhna deviate from the above pattern however. The reaction of the fully protonated form of the ligand with both Ni^{2+} and Co^{2+} is still retarded and may be explained in terms of a poor entering group effect. The reactions of the mono-anionic form of H_2adhna with both metal ions are also retarded by factors of from 10–30. As already pointed out the rate of ionization of this ligand was investigated and was found to be rapid with $k_{obs} \geqslant 400$ s^{-1}, the upper limit of our stopped-flow device. Therefore this retardation cannot be explained in terms of an ionization process. The answer however is evident

TABLE IV. Summary of Rate Constants for Formation and Dissociation of the Monocomplexes of 2-Aceto-1, 8-dihydroxynaphthalene (H_2adhna) in Methanol–Water (70:30 v/v) Solution at 25 °C, I = 0.5 $NaClO_4$

Rate constant (dm^3 mol^{-1} s^{-1})	Nickel(II)	Cobalt(II)
k_{HL} (exp)	121 ± 11	1.24(±0.17) x 10^3
k_{HL} (predicted)	2.7 x 10^4	6.6 x 10^5
R^a	5.9 x 10^{-3}	1.8 x 10^{-3}
k_L (exp)	3.51(±0.04) x 10^3	4.38(±0.06) x 10^5
k_L (predicted)	1.1 x 10^5	4.4 x 10^6
R^a	3.5 x 10^{-2}	9.9 x 10^{-2}
k_{-HL} (exp)	32.20 ± 0.03	1.4(±0.06) x 10^4
k_{-HL} (predicted)	1.15 x 10^4	2.58 x 10^5
k_{-L} (s^{-1})(exp)	$\simeq$0	5.89 ± 0.04
k_{-L} (s^{-1})(predicted)	$\simeq$0	6.62

$^a R = 4k_f/3K_{os}k_s$.

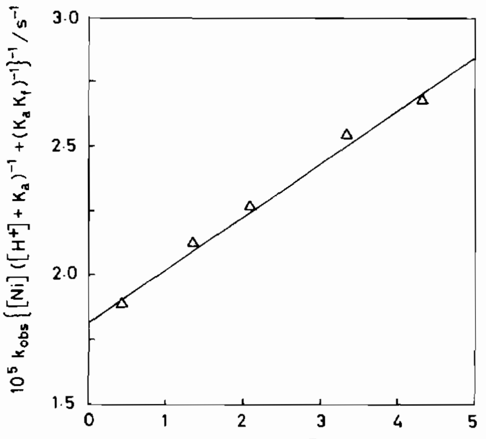


Fig. 2. Plot suggested by eqn. (1) for reaction of Ni^{2+} with 1,8-dihydroxybenzophenone (H_2dhbpo) in methanol–water (70:30 *v/v*) at 25 °C and ionic strength 0.5 mol dm^{-3} $NaClO_4$.

TABLE V. Summary of Rate Constants for Formation and Dissociation of the Monocomplexes of 1,8-Dihydroxybenzophenone (H_2dhbpo) in Methanol–water (70:30 *v/v* solution at 25 °C, $I = 0.5$ $NaClO_4$

Rate constant (dm^3 mol^{-1} s^{-1})	Nickel(II)
k_{HL} (exp)	16 ± 0.31
k_{HL} (predicted)	2.7×10^4
R	5.9×10^{-4}
k_L (exp)	$4.56(\pm 0.03) \times 10^4$
k_L (predicted)	1.1×10^5
R	0.55
k_{-HL} (exp)	796 ± 30
k_{-HL} (predicted)	1.56×10^6
k_{-L} (s^{-1}) (exp)	1.20 (±0.2)
k_{-L} (s^{-1}) (predicted)	1.19

$R = 4k_f/3K_{os}k_s$.

from a study of the structures of the mono anions (Fig. 3). It is evident that the reaction of a metal ion with the mono-anionic form of H_2dhbpo will take place via attack of the metal on the O^- atom. The metal is now in close proximity to the $\rangle C=O$ group and can therefore readily break the intramolecular hydrogen bond to form the chelated metal complex. The reaction therefore proceeds quite normally and this is reflected in the R value of 0.55. On the other hand the mono-anion of H_2adhna has no 'free' negatively charged oxygen atom at which initial attack by the metal ion can take place. Instead, the second proton is located at the coordination site and both potential oxygen donors are involved in a strong intramolecularly bonded six-membered ring. In order for the initial bond to be formed, this hydrogen bond must be broken. This is similar to the situation pertaining in the protonated enol tautomer of pentane-2,4-dione, which is known to react slowly with metal ions [16–18]. Thus the reaction of H_2adhna with Ni^{2+} is retarded by a factor of 30 while reaction with Co^{2+} is retarded by a factor of 10. In view of the higher stability of the complexes formed by Ni^{2+} compared to Co^{2+} it is perhaps surprising that the retardation is greater for the former. However, the result may be rationalized in terms of an equilibrium between the 'open' and 'closed' forms of the intramolecularly hydrogen bonded species similar to the situation pertaining in the ionization mechanism of intramolecularly hydrogen bonded acids [19]. The equilibrium between the open and closed forms would be independent of the metal species, but the rate of reaction of the open species with Co^{2+} would be greater than with Ni^{2+}.

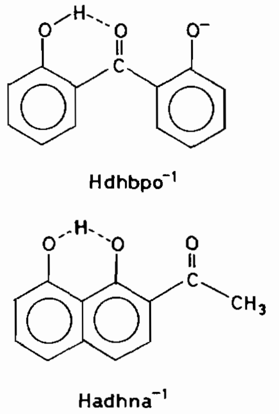


Fig. 3. Structures of the mono-anions of 1,8-dihydroxybenzophenone (H_2dhbpo) and 2-aceto-1,8-dihydroxynaphthalene (H_2adhna).

When solutions of $[M(HL)]^+$ were reacted with solutions containing varying concentrations of $[H^+]$ a single reaction was observed on the stopped-flow apparatus. The kinetic data may be represented by eqns. (2), (3) and (4).

$$H_2adhna:\ k_H{}^{Ni} = 0 + 32.2[H^+] \tag{2}$$

$$H_2adhna:\ k_H{}^{Co} = 5.89 + 1.4 \times 10^4\ [H^+] \tag{3}$$

$$H_2dhbpo:\ k_H{}^{Ni} = 120 + 796[H^+] \tag{4}$$

The rate law for the reverse reactions may be obtained by setting $[M^{2+}]$ in eqn. (1) to zero. Carrying out this substitution gives eqn. (5) where $k_L/K_f = k_{-L}$ and $k_{HL}/K_aK_f = k_{-HL}$.

$$k_{obs} = k_L/K_f + k_{HL}[H^+]/K_aK_f \tag{5}$$

In all cases the values of k_{-L} are in good agreement with the values of k_{-L} calculated from k_L and K_f.

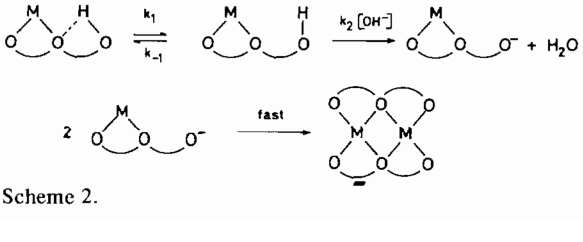
However, the experimental values of k_{-HL} are much less than predicted. Retarded values of k_{-HL} have been shown by Cox *et al.* to be quite normal [20, 21]. They have shown that in the case of the dissociation reactions of metal cryptates, the measured values of k_{-HL} may be retarded due to a slow rate-determining step in the dissociation. They have demonstrated that the extent of this retardation may be calculated from a knowledge of the formation and dissociation microscopic rate constants. However, in the present work, where only the macroscopic rate constants are known, such a calculation is not possible.

The kinetics of the conversion of the 1:1 to the 2:2 complexes were monitored by reacting solutions of $[M(HL)]^+$ with standard sodium hydroxide solutions. An absorbance increase which was the sum of two exponentials was observed at 450 nm for the H_2adhna reactions and 430 nm for the H_2dhbpo reactions. The rate constants are given in Table VI.

TABLE VI. Summary of Rate Constants for Formation and Dissociation of the Dinuclear 2:2 Complexes of 1,8-dihydroxybenzophenone (H_2dhbpo) and 2-Aceto-1,8-dihydroxynaphthalene (H_2adhna) in Methanol–Water (70;30 *v/v*) Solution at 25 °C, $I = 0.5$ $NaClO_4$

k	Nickel(II)	Cobalt(II)
H_2dhbpo		
1:1 → 2:2 (fast step) (s^{-1})	39.5 (±1.1)	
1:1 → 2:2 (slow step) (s^{-1})	0.60(±0.08)	
2:2 → 1:1 ($dm^3\ mol^{-1}\ s^{-1}$)	2.63(±0.92)	
2:2 → 1:1 (s^{-1})	$9.26(\pm 0.07) \times 10^{-2}$	
H_2adhna		
k_1 ($dm^3\ mol^{-1}\ s^{-1}$)	5.8×10^3	5.0×10^3
$k(OH^-)/k(H_2O)$ (s^{-1})	0.47	1.27
2:2 → 1:1 ($dm^3\ mol^{-1}\ s^{-1}$)	5.92 ± 0.13	497 ± 1.3
2:2 → 1:1 (s^{-1})	0.04 ± 0.001	12.2 ± 1.1

The dimerization reactions of $[Ni(Hdhbpo)]^+$ were found to be independent of both base and complex concentration. The values obtained for the two rate constants are 39.5 and 0.6 s^{-1}. The mechanism proposed is outlined in Scheme 2. This is a two-step process, the faster of the two stepts involving ionization of the $[M(HL)]^+$ species while the slower of the two steps involves the formation of the 2:2 complex. The k_1/k_{-1} step of the reaction represents the equilibrium between the 'closed' and 'open' forms of the hydrogen-bonded species, while the k_2 step involves removal of the proton by the base. In the present case where hydroxide ion is the base, the overall reaction is thermodynamically favoured and k_{obs} has the form of eqn. (6).



Scheme 2.

$$k_{obs} = k_1 k_2 [OH^-]/(k_{-1} + k_2 [OH^-]) \qquad (6)$$

If the step involving k_2 behaves as a normal diffusion controlled reaction, k_2 will have a value of *ca.* 2×10^{10} $dm^3\ mol^{-1}\ s^{-1}$. In most ionizations of hydrogen-bonded species investigated to date, k_{obs} is directly proportional to $[OH^-]$, and consequently the rate at which the open form reverts to the closed form (k_{-1}) must be greater that the rate of proton removal from the open form by base. However, in the present instance as in case of the same reaction when heptane-2,4,6-trione was the ligand [5] $k_2[OH^-] \gg k_{-1}$ so that $k_{obs} = k_1 = 39.5\ s^{-1}$.

The dimerization reactions of $[M(Hadna)]^+$ ($M = Ni^{2+}$, Co^{2+}) display the more usual behaviour and k_{obs} for the first step is directly proportional to $[OH^-]$. In this instance $k_{obs} = k_1 k_2 [OH^{-1}]/k_{-1}$. In the case of substituted salicylic acids k_{-1} has been estimated to be $\geqslant 6 \times 10^7\ s^{-1}$ and therefore with a value of K, ($= k_1/k_{-1}$) the equilibrium constant between open and closed forms of the intramolecularly bonded species, of $1 \times 10^{-3}\ mol^{-1}$, k_1 is estimated to be $\geqslant 6 \times 10^4\ s^{-1}$. In the reactions of Ni^{2+} and Co^{2+} with H_2adhna, $k_1 k_2/k_{-1}$ is found to be 5.8×10^3 and $5 \times 10^3\ s^{-1}$ respectively. These reactions also give small intercepts of 0.47 and 1.27 s^{-1} for Ni^{2+} and Co^{2+} respectively in the plots of k_{obs} against $[OH^-]$. These values are a measure of the competition between OH^- and H_2O as the base in the reactions. K may be estimated for the present reactions to be 2.9×10^{-7} and 2.5×10^{-7} for Ni^{2+} and Co^{2+} respectively. These values appear rather small when compared to the values found for substituted salicyclic acids [19]. This may be due to the following reasons. Firstly, the internal hydrogen bonding in $[M(Hadhna)]^+$ may be quite strong thus reducing the equilibrium between the open and closed forms of the hydrogen bonded complex. Secondly, the rate of proton transfer with OH^- as base may not necessarily be diffusion controlled, *i.e.* it may be less than $2 \times 10^{10}\ dm^3\ mol^{-1}\ s^{-1}$. The first step of the dimerization reaction is independent of complex concentration thus supporting the mechanism proposed, and eliminating direct dimerization as a rate-determining step. Such a step was found in the dimerization reaction of the Ni^{2+} and Co^{2+} complexes of 1-phenylhexane-1,3,5-trione [6]. The slow second reaction steps of 0.15 and 0.10 s^{-1} are again associated with a rate determining reorganization of some form of a dimeric precursor complex to form the final dinuclear 2:2 complex [5, 6].

Hydrolysis of the 2:2 complexes results in a single reaction in all cases. The rate data are described by eqns. (7) (8) and (9). In all cases the rate constants for hydrolysis of the 2:2 complexes are smaller than those for hydrolysis of the 1:1 complexes.

$$H_2adhna\ k_H{}^{Ni} = 4.12(\pm 0.02) \times 10^{-2} + 5.92(\pm 0.60)[H^+] \qquad (7)$$

$$H_2adhna\ k_H{}^{Co} = 12.2(\pm 1.1) + 497(\pm 6)[H^+] \qquad (8)$$

$$H_2dhbpo\ k_H{}^{Ni} = 9.26(\pm 0.04) \times 10^{-2} + 2.6(\pm 0.2)[H^+] \qquad (9)$$

Reaction of Ni^{II} and Co^{II} with H$_2$dppto

The kinetics of formation of the 1:1 complexes of both Ni^{II} and Co^{II} were meaured at 410 nm under pseudo-first-order conditions with the metal in excess. The reactions of Ni^{II} were investigated in the pH range 4–6 while the Co^{II} reactions were investigated in the pH range 5–6

The absorbance increase associated with the ionization of H_2dhpto was so rapid that rate constants could not be measured using the stopped-flow apparatus. The non-base catalysed rate constant for proton loss from uncomplexed H_2dppto is estimated to be ≃105 s^{-1}. An initial rates analysis of these observations shows that for complex formation reactions of Ni^{II} under the present experimental conditions, the pseudo equilibrium hold up to a pH of 7.5 while in the case of Co^{II} the crossover occurs at pH 6.5. The kinetic data for complex formation and dissociation of both the Ni^{II} and Co^{II} 1:1 complexes of H_2dppto were obtained at lower pH values, thus the measurement of 'erroneous rate constants' as described by Ando *et al.* [22] does not apply in this case.

When solutions of H_2dppto were reacted with solutions of either Ni^{II} or Co^{II}, an absorbance change corresponding to a single exponential was observed,

TABLE VII. Observed Rate Constants for the Reaction of Ni^{II} and Co^{II} with 1,5-Diphenylpentane-1,3,5-trione (H_2dppto) in Methanol–Water (70:30 *v/v*) Solution at 25 °C, I = 0.5 NaClO$_4$, λ = 410 nm

Metal	Experiment	10^3 [M] (mol dm^{-3})	[H$^+$] (mol dm^{-3})	k_{obs} (s^{-1})	k_{calc} (s^{-1})
Ni^{II}	1	1.19	1.36×10^{-4}	0.03	0.03
	2	2.38	1.36×10^{-4}	0.06	0.05
	3	3.57	1.36×10^{-4}	0.08	0.07
	4	4.76	1.36×10^{-4}	0.10	0.10
	5	5.95	1.36×10^{-4}	0.13	0.12
	6	1.19	1.36×10^{-5}	0.09	0.08
	7	2.38	1.36×10^{-5}	0.14	0.15
	8	3.57	1.36×10^{-5}	0.22	0.23
	9	4.76	1.36×10^{-5}	0.30	0.32
	10	5.95	1.36×10^{-5}	0.40	0.40
	11	1.19	1.36×10^{-6}	0.61	0.64
	12	2.38	1.36×10^{-6}	1.30	1.30
	13	3.57	1.36×10^{-6}	1.90	1.92
	14	4.76	1.36×10^{-6}	2.60	2.56
	15	5.95	1.36×10^{-6}	3.20	3.20
Co^{II}	16	1.25	1.36×10^{-5}	3.67	4.01
	17	2.50	1.36×10^{-5}	5.11	5.27
	18	3.75	1.36×10^{-5}	6.75	6.72
	19	5.00	1.36×10^{-5}	8.41	7.98
	20	6.25	1.36×10^{-5}	9.97	9.86
	21	1.25	4.28×10^{-6}	7.19	8.12
	22	2.50	4.28×10^{-6}	10.1	10.0
	23	3.75	4.28×10^{-6}	13.0	13.0
	24	5.00	4.28×10^{-6}	17.1	16.8
	25	6.25	4.28×10^{-6}	21.1	19.7
	26	1.25	1.36×10^{-5}	14.0	15.0
	27	2.50	1.36×10^{-5}	23.4	23.5
	28	3.75	1.36×10^{-5}	32.0	34.0
	29	5.00	1.36×10^{-5}	43.8	43.6
	30	6.25	1.36×10^{-5}	55.2	54.1

TABLE VIII. Summary of Rate Constants for Formation and Dissociation of the Monocomplexes of 1,5-Diphenylpentane-1,3,5-trione (H_2dppto) in Methanol–Water (70:30 *v/v*) Solution at 25 °C, $I = 0.5$ $NaClO_4$

Rate constant (dm^3 mol^{-1} s^{-1})	Nickel(II)	Cobalt(II)
k_{HL} (exp)	13.2 ± 1.0	7.13 ± 0.03
k_{HL} (predicted)	2.7×10^4	6.6×10^5
R^a	6.5×10^{-4}	1.4×10^{-5}
k_L (exp)	$1.32(\pm 0.07) \times 10^5$	$1.98(\pm 0.03) \times 10^6$
k_L (predicted)	1.1×10^5	4.4×10^6
R^a	1.60	0.33
k_{-HL} (exp)	$1.38(\pm 0.16) \times 10^3$	$3.08(\pm 0.05) \times 10^3$
k_{-HL} (predicted)	1.45×10^3	3.74×10^3
k_{-L} (s^{-1}) (exp)	0.21 ± 0.13	3.28 ± 1.1
k_{-L} (s^{-1}) (predicted)	0.077	5.58

$^a R = 4k_f/3K_{os}k_s$.

the kinetic data are given in Table VII. The data are consistent with the mechanism in Scheme 1 and the plots suggested by eqn. (1) yield straight lines. Fitting the kinetic data to eqn. (1) yields values of $k_{HL} = 13.25(\pm 1.00)$ and $7.13(\pm 0.30)$ dm^3 mol^{-1} s^{-1} for Ni^{2+} and Co^{2+} respectively and values of k_L = $1.32(\pm 0.07) \times 10^5$ and $1.98(\pm 0.03) \times 10^6$ dm^3 mol^{-1} s^{-1} for Ni^{2+} and Co^{2+} respectively. Table VIII summarizes the theoretical and experimental rate constants. Again, it is evident that the reaction of Ni^{2+} and Co^{2+} with the mono-anion of H_2dppto is normal and that complex formation takes place via an Eigen–Wilkins type mechanism. However, complexation with the protonated neutral form of the ligand yields rate constants that are 2000 and 10^5 times too slow. It is suggested that this rate retardation is due to the ligand acting as a poor entering group. This conclusion is reached because the rate of dissociation of a proton from H_2dppto is estimated to be 105 s^{-1}. Therefore, as the rate of complex formation by Ni^{2+} and Co^{2+} is in all cases much less that the rate of proton loss, it may reasonably be concluded that initial bond formation in which the ligand acts as a poor entering group is the rate determining step in the overall reaction.

When solutions of $[M(HL)]^+$ were reacted with solutions containing varying concentrations of hydrogen ion, a single reaction was observed. The kinetic data can be represented by eqns. (10) and (11).

$$k_H{}^{Ni} = 0.21 + 1.38 \times 10^3 [H^+] \tag{10}$$

$$k_H{}^{Co} = 3.28 + 3.08 \times 10^3 [H^+] \tag{11}$$

These values are consistent with eqn. (5) and as evident from Table VIII the experimental values of k_{-L} and k_{-HL} are in good agreement with those calculated from k_L and K_f.

These reactions illustrate the great difference in reactivity between fully protonated and partially protonated ligands in metal complex formation reactions. The dimerisation reactions are particularly interesting and they show how intramolecular hydrogen bonding can affect metal complex formation reactions. None of the reactions reported here exhibit the second-order kinetics observed when 1-phenylhexane-1,3,5-trione was the ligand [6]. The rate constant for the dimerization of the 1:1 nickel(II) complex of this ligand is greater than the estimated rate constant for solvent exchange at the metal centre. It was suggested that the reactions might best be viewed as coordinated ligand reactions rather than metal centre reactions. The rate laws obtained in the present investigation preclude a direct comparison with the 1-phenylhexane-1,3,5-trione reactions. The ambiguity as to whether the reactions are metal or ligand centered could be resolved by studying the reaction of these ligands with inert metals. Our current efforts are directed in this direction.

References

1 D. W. Margerum, G. R. Cawley, D. C. Weatherburn and G. G. Pagenkopf, in A. E. Martell (ed.), 'Coordination Chemistry', Vol. 2, ACS Monograph 174, Washington D.C., 1978, Chap. 1.

2 M. D. Glick and R. L. Lintvedt, *Inorg. Chem., 21,* 233 (1976).

3 U. Casellato, P. A. Vigato and M. Vidali, *Coord. Chem. Rev., 23,* 93 (1977).

4 M. J. Hynes and J. Walsh, *J. Chem. Soc., Dalton Trans.,* 1543 (1985).

5 M. J. Hynes and J. Walsh, *J. Chem. Soc., Dalton Trans.,* 2565 (1985).

6 J. Walsh and M. J. Hynes, *J. Chem. Soc., Dalton Trans.,* 2243 (1986).

7 C. R. Hauser and T. M. Harris, *J. Am. Chem. Soc., 80,* 6360 (1958).

8 R. Richter, *J. Prakt. Chem., 28,* 285 (1883).

9 J. C. Overeen, *Recl. Trav. Chim. Pays-Bas, 83,* 1017 (1964).

10 G. Gran and A. Johansson, *Analyst (London), 106,* 231 (1981).

11 M. J. Hynes and B. D. O'Regan, *J. Chem. Soc., Dalton Trans.,* 7 (1980).

12 Y. K. Agrawal, *Talanta, 26,* 599 (1979).

13 U. Bipa, H. Elias, M. Hauröder, G. Kleinhans, S. Pfeifer and K. J. Wannowius, *Inorg. Chem., 22,* 3862 (1983).

14 P. K. Chattopadhyay and J. F. Coetzee, *Inorg. Chem., 12,* 113 (1960).

15 M. Eigen and R. G. Wilkins, 'Advances in Chemistry Series', Vol. 49, *ACS,* Washington D.C., 1965, p. 55.

16 R. G. Pearson and O. P. Anderson, *Inorg. Chem., 9,* 39 (1970).

17 D. P. Fay, A. R. Nichols, Jr., and N. Sutin, *J. Am. Chem. Soc., 10,* 2096 (1971).

18 M. J. Hynes and B. D. O'Regan, *J. Chem. Soc., Dalton Trans.,* 162 (1979).

19 F. Hibbert, *Acc. Chem. Res., 17,* 115 (1984).

20 B. G. Cox and H. Schneider, *J. Am. Chem. Soc., 102,* 3628 (1980).

21 B. G. Cox, J. Garcia-Rosa and H. Schneider, *J. Am. Chem. Soc., 103,* 1054 (1981).

22 I. Ando, S. Nishijima, K. Ujimoto and H. Kurihara, *Bull. Chem. Soc. Jpn., 55,* 2881 (1982).