Kinetic and Spectroscopic Studies with a Rapid-scanning Spectrometer. Part 1. Transient Intermediates in the Dissociation of Nickel(II) Polyamine Complexes

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Successive stages in the acid-catalysed aquation of several polyamine chelates of Ni^{II} have been characterised both optically and kinetically by means of a rapid-scanning spectrometer. Complete spectra of several new transient intermediates are reported and assigned. When two terdentate ligands, *viz.* diethylenetriamine (dien), are involved it is established that one is completely removed in two stages before the second starts to disengage. The stepwise acid dissociation of the $[Ni(trien)(OH_2)_2]^{2+}$ ion (trien = triethylenetetramine) is shown to be much more complex than had previously been indicated.†

STOPPED-FLOW kinetic spectrophotometry based on single-beam detection, while now well established, is less effective in the study of transient intermediates: spectra are constructed on a point-to-point basis which introduces a degree of experimental scatter becoming unacceptable when overlapping of spectra of successive intermediates or of the product occurs. Various approaches have been made to the goal of complete instantaneous displays of successive spectra of transient intermediates in a stopped-flow system. In this department we have successfully applied a stopped-flow spectrograph [1] to the determination of time-resolved spectra of the unstable peroxonitrous acid in solution. Other previous designs [2] have utilised rapidly oscillating mirrors, prisms, and monochromators as well as the static silicon-target vidicon tube. These, with the aid of on-line computing, have produced some interesting continuous and point-to-point spectra of various transient intermediates. Two of the shortcomings of these designs have been the limit of spectral range (*e.g.* early versions of the vidicon tube to $\lambda > 400$ nm) and the lack of immediacy of some of the spectra due to off-line computer processing.

In the present investigation, we have studied transient spectra of intermediates in the decomposition of $[Ni(en)_3]^{2+}$ (en = ethylenediamine), $[Ni(dien)_2]^{2+}$ (dien = diethylenetriamine), $[Ni(dien)(OH_2)_3]^{2+}$, and $[Ni(trien)(OH_2)_2]^{2+}$ (trien = triethylenetetramine) by means of a rapid-scanning stopped-flow spectrophotometer featuring no moving parts and covering a spectral range of 250—750 nm. This has enabled us to obtain complete spectra of certain of the intermediates and also the kinetics and rates of the various stages. In those cases where rates had been determined by single-wavelength methods [3] the data are in fair agreement. In some examples the process of acid-catalysed dechelation is more complex than had previously been supposed.

EXPERIMENTAL

Rapid-scanning Spectrophotometer.—This was a model 610A Multiplex spectrometer supplied by Applied Photophysics Ltd., London. Radiation from a power-stabilised 150-W xenon-arc lamp is channelled through the reaction cell of a stopped-flow spectrophotometer featuring an all-glass inlet system, from which it is focused on the entrance slit of a modified F/4 Czerny–Turner grating monochromator. The monochromator produces a spectrum in the plane of a row of quartz optical fibres which are split into 30 groups, each of which is taken to a separate model IP28 photomultiplier in the detector unit. The signal outputs are coupled to precision amplifiers and, following controlled analogue signal 'multiplexing,' the outputs are 'multiplexed' on a single output line. Individual gain controls are available for each channel to correct for the wavelength dependences both of the photomultiplier gain and the lamp output. Up to 900 scans can be recorded, with delays of between 0.5 ms and 5 s between scans. The spectra may be observed over a range of 150 or 300 nm, depending on the diffraction grating used. The signal is displayed on a Tektronix model 5115 storage oscilloscope as a stepped function with 30 horizontal lines corresponding to a 5- or 10-nm band of the spectrum. In addition to the observation of time-resolved spectra, curves of transmittance against time can be obtained at one or more wavelength bands simultaneously (as in Figure 2), enabling comparison of reaction rates at different monitoring wavelengths.

Materials.—Nickel(II) chloride and HCl were of AnalaR grade and the en and dien ligands were purified by redistillation. Triethylenetetramine was purified *via* conversion into the nitrate salt which was then recrystallised. Purity was confirmed by ^{13}C n.m.r. spectroscopy which distinguishes trien from the isomer tren (2,2′,2″-triaminotriethylamine). The chloride salt (trien·4HCl) was then prepared, using a Dowex-1 ion-exchange resin in the Cl^- form, and recrystallised.

RESULTS AND DISCUSSION

$[Ni(en)_3]^{2+}$.—Ahmed and Wilkins [3c] investigated the rates of the stepwise dechelation of $[Ni(en)_3][NO_3]_2$ in $HClO_4$, forming the view that rupture of the first Ni–N chelate bond was rate-determining at each stage. The three stages seemed to be acid-independent in the range pH 1—4. They attributed their findings that each successive stage is slower than the previous one to a *trans* nitrogen–nitrogen effect which decreases with less chelation. The dissociation rates are related inversely to the known stability constants ($K_1 > K_2 > K_3$). The rates were measured spectrophotometrically directly and

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† Diethylenetriamine = 3-azapentane-1,5-diamine; triethylenetetramine = 3,6-diazaoctane-1,8-diamine.

also by an indicator method which monitored the uptake of hydrogen ions at each stage.

We found that absorption by $[NO_3]^-$ masks the nickel–ligand band in the 350—400 nm region and so Cl^- was used as counter ion in place of $[NO_3]^-$ and the hydrolysis was effected by hydrochloric acid. Single-wavelength curves of transmittance against time at 520 nm were analysed for three stages (*cf.* ref. 3*c*). Although the reaction rates are separated by at least one order of magnitude, some difficulty was experienced in the processing of the results and accordingly the rates were calculated from computer fits to the various stages of the reaction (Table 1, first row of data).

From multiplex runs at 293 K, the expected three stages were observed and separated by monitoring the shift in isosbestic points. Figure 1 shows the u.v.–visible spectra compiled from oscilloscope photographs of the multiplex traces in the range 300—750 nm. The largest transmittance change occurs in the region 300—400 nm and isosbestic points in this region were used as guides for single-wavelength studies (Table 1, final row of data).

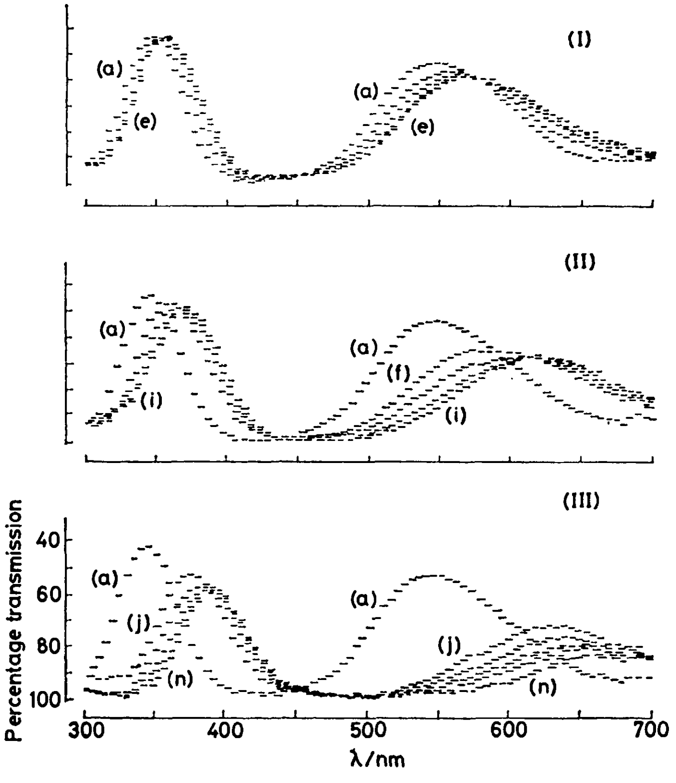


FIGURE 1 Successive u.v.–visible spectra recorded during the aquation of $[Ni(en)_3]^{2+}$ by HCl (0.5 mol dm^{-3}) at 293.5 K. Trace (a) of digrams (I)—(III) is the spectrum recorded immediately after mixing and (b)—(n) were recorded at subsequent timed intervals: (Ib)—(Ie) at 15-ms intervals, (IIf)—(IIi) at 200 ms intervals, and (IIIj)—(IIIn) at 3-s intervals after (a). $[Ni(en)_3{}^{2+}] = 0.025$ mol dm^{-3}

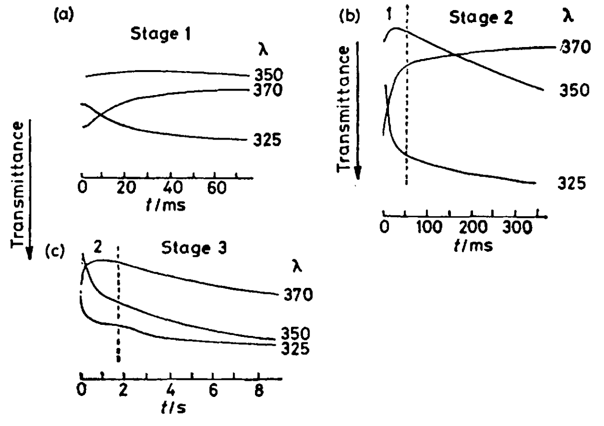


FIGURE 2 Simultaneous traces of transmittance against time for aquation of $[Ni(en)_3]^{2+}$ by 0.5 mol dm^{-3} HCl at different wavelengths (in nm). Trace (b) is expanded ×2

Simultaneous curves of transmittance against time at 325, 350, and 370 nm are shown in Figure 2 from which it is possible to see the three stages of dechelation. For a reaction (1) the time after the start for production of $[B]_{max.}$ is given by (2) (if at $t = 0$, $[B] = [C] = 0$).

$$A \xrightarrow{k} B \xrightarrow{k'} C \qquad (1)$$

$$t([B]_{max.}) = \frac{\ln(k/k')}{(k - k')} \qquad (2)$$

Using the observed values of the rate constants (Table 1), we obtain $t_{max.} = 45$ and 825 ms respectively for the first two stages of the reaction. The u.v.–visible spectra were constructed from Figure 1 at these times after the start and the values of $\lambda_{max.}$ and $\varepsilon_{max.}$ are given in Table 2.

The intermediate $[Ni(en)_2(OH_2)_2]^{2+}$ species could possibly exist in *cis* or *trans* forms. Tomlinson *et al.*[4] have investigated the existence of *cis–trans* isomerism

TABLE 1

Aquation rates of ethylenediamine complexes of Ni^{II} in dilute aqueous acid

$$[Ni(en)_3]^{2+} \xrightarrow{k_1} [Ni(en)_2]^{2+} \xrightarrow{k_2} [Ni(en)]^{2+} \xrightarrow{k_3} Ni^{2+}$$

Medium	T/K	k_1/s^{-1}	k_2/s^{-1}	k_3/s^{-1}
HCl [a] 0.5 mol dm^{-3}	299.7	70	3.7	0.18
$HClO_4$ [b] 0.2 mol dm^{-3}	298.0	87	5.2	0.15
HCl [c] 0.5 mol dm^{-3}	297.7	77 ±3 [d]	4.0 ±0.05 [e]	0.17 ±0.015

[a] All data at λ = 520 nm; $[Ni]_T = 0.05$ mol dm^{-3}, $[en]_T = 0.18$ mol dm^{-3}. [b] Data from ref. 3*c*. [c] $[Ni(en)_3{}^{2+}] = 0.025$ mol dm^{-3}. [d] λ = 375 nm. [e] λ = 395 nm. [f] λ = 370 nm.

TABLE 2

Values of $\lambda_{max.}$ and $\varepsilon_{max.}$ * for nickel(II) species formed in the dissociation of $[Ni(en)_3]^{2+}$

	$\lambda_{max.}$(300—750 nm)	
Species	$^3T_1(P) \leftarrow {}^3A_2$	$^3T_1(F) \leftarrow {}^3A_2$
$[Ni(en)_3]^{2+}$	345 ± 5 (7.8)	550 ± 5 (6.0)
$[Ni(en)_2]^{2+}$ (after 45 ms)	360 ± 5 (7.8)	570 ± 5 (5.0)
$[Ni(en)]^{2+}$ (after 800 ms)	373 ± 5 (6.7)	625 ± 5 (3.8)
Ni^{2+} (aq) (after 15 s)	390 ± 5 (5.1)	650 ± 5 (1.6)

* Given in parentheses, units dm^3 mol^{-1} cm^{-1}, with ±5% accuracy.

TABLE 3

Spectroscopic data for $[Ni(en)_2(OH_2)_2]^{2+}$ ions in solution

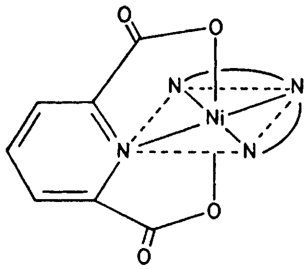
Complex	$\lambda_{max.}$/nm				Ref.
	$^3T_1(P) \leftarrow {}^3A_2$	$^3T_1(F) \leftarrow {}^3A_2$		$^3T_2 \leftarrow {}^3A_2$	
$[Ni(en)_2(OH_2)_2]^{2+}$	360 ± 5 (7.8 ± 0.4) [a]	570 ± 5 (5.0 ± 0.25)			Table 2
$[Ni(en)_2(OH_2)_2][ClO_4]_2$	356 (9.1)	564 (5.7)		943 (7.1)	5
$[Ni(en)_2(OH_2)_2][BF_4]_2$	356 (8.9)	562 (5.7)		926 (6.8)	5
$[Ni(tren)]^{2+}$	365 (10.5)	565 (7.8)	775 [b] (5.0)	940 (14.1)	3*a*
	360	562	781	952	6

[a] Figures in parentheses refer to molar absorption coefficients in $dm^3\ mol^{-1}\ cm^{-1}$. [b] Assigned to spin-forbidden triplet-to-singlet transition.[5]

of diaquabis(ethylenediamine)nickel(II) ion. The perchlorate and tetrafluoroborate salts have been assigned *trans* structures in the solid state, whereas the tetraphenylborate salt has been assigned a *cis* structure by Farago *et al.*[5] This is substantiated by the relative ease of removal of the water molecules from the *trans* forms to yield a square-planar structure. In solution, however, both the perchlorate and tetrafluoroborate seem to have the *cis* configuration from investigation of the electronic spectra (Table 3).

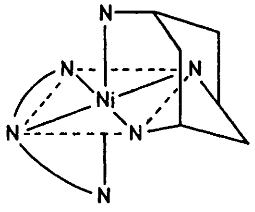
The observed spectrum of the intermediate $[Ni(en)_2]^{2+}$ species corresponds well with that of the known *cis* octahedral species (Table 3), and we incline to this assignment.

$[Ni(dien)(OH_2)_3]^{2+}$.—Nickel(II) can form both mono and bis complexes with diethylenetriamine. To suppress formation of the bis complex, excess of nickel(II) was used in the mol ratio Ni^{II} : dien = 2 : 1. Nelson [7] states that dien usually co-ordinates meridionally (*mer*) in octahedral complexes, *i.e.* with the two primary nitrogens *trans* to each other, but cases of facial (*fac*) co-ordination (with two primary nitrogens *cis* to each other) are also known {*e.g.* in $[Mo(dien)(CO)_3]$ [8]}. Reilley and co-workers [9] have investigated the possible conformations of dien in nickel(II) complexes. An *X*-ray study of $[Ni(dien)_2Cl_2]\cdot H_2O$ showed that the two dien groups are meridional. The stereochemistry of $[Ni(dien)(OH_2)_3]^{2+}$ was also investigated by ^1H n.m.r.[9] The spectrum of dien in this species was compared with that of dien in other complexes where the conformation of dien is constrained (either *fac* or *mer*). Reilley and co-workers [9] showed that for $[Ni(dien)(OH_2)_3]^{2+}$ the *fac* isomer is more stable in solution, but interconversion is taking place.



mer - $[Ni(H_2pydca)(dien)]^{2+}$

H_2pydca = pyridine-2,6-dicarboxylic acid



fac - $[Ni(cta)(dien)]^{2+}$

cta = *cis,cis*-cyclohexane-1,3,5-triamine

Melson and Wilkins [3b] previously investigated the dechelation of $[Ni(dien)(OH_2)_3]^{2+}$ in 0.5 mol dm^{-3} HNO_3. They reported that the reaction was complicated, and that there was some difficulty in separating the two stages at 550 nm. Rate determinations, made by monitoring the change in acidity using an indicator, show that there are two stages of comparable rate, *viz.* (3) with $k_1 = 14.2\ s^{-1}$ and $k_2 = 3.0\ s^{-1}$ at 298 K.

$$[Ni(dien)]^{2+} \xrightarrow{k_1} [Ni(Hdien)]^{3+} \xrightarrow{k_2} Ni^{2+} \quad (3)$$

The dechelation of $[Ni(dien)]^{2+}$ in 0.5 mol dm^{-3} HCl was studied in the range 300—750 nm and two stages were indeed apparent. Isosbestic points in the regions 375—380 and 395—400 nm were observed for the two stages respectively, and these were used as the bases for single-wavelength studies, which revealed that, at 298 K with a $[Ni(dien)]^{2+}$ concentration of 0.025 mol dm^{-3} in 0.5 mol dm^{-3} HCl, $k_1(402\ nm) = 4.7\ s^{-1}$ and $k_2(375\ nm) = 0.83\ s^{-1}$. These rates do not agree particularly well with the earlier work in HNO_3, but the quotients k_1/k_2 are in good agreement.

The theoretical time for maximum concentration of $[Ni(Hdien)]^{3+}$ after the first stage is 450 ms. The multiplex spectra were therefore recorded at 0, 500 ms, and 7 s. Because of the presence of excess of Ni^{2+} in solution, the spectra of the $[Ni(dien)]^{2+}$, the intermediate $[Ni(Hdien)]^{3+}$, and the final Ni^{2+} were calculated by subtracting out the spectrum of the excess of Ni^{2+}. The computed spectra for the various stages are shown in Figure 3, and the wavelengths of the peaks are given in Table 4.

Melson and Wilkins [3b] propose that a terminal primary NH_2–Ni bond is broken first, rather than the central secondary N–Ni bond. The spectrum of the intermediate $[Ni(Hdien)]^{3+}$ resembles that of $[Ni(en)]^{2+}$

TABLE 4

Values for $\lambda_{max.}$ and $\varepsilon_{max.}$ [a] for nickel(II) species formed in the dissociation of $[Ni(dien)]^{2+}$

			$\lambda_{max.}$/nm	
			$^3T_1(P) \leftarrow {}^3A_2$	$^3T_1(F) \leftarrow {}^3A_2$
$[Ni(dien)]^{2+}$ ($t = 0$)			360 ± 5 (8)	590 ± 5 (6)
$[Ni(Hdien)]^{3+}$ (t = 500 ms)			375 ± 5 (6)	615 ± 5 (4)
Ni^{2+} (aq) (t = 7s)			395 ± 5 (5)	665—720 ±5 (2)
$[Ni(dien)]^{2+}$	360 (8.0)	595 (5.0)	740 (2.7)	950 (9.0) [b]

[a] Given in parentheses, units $dm^3\ mol^{-1}\ cm^{-1}$, with ±5% accuracy. [b] Ref. 3*a*.

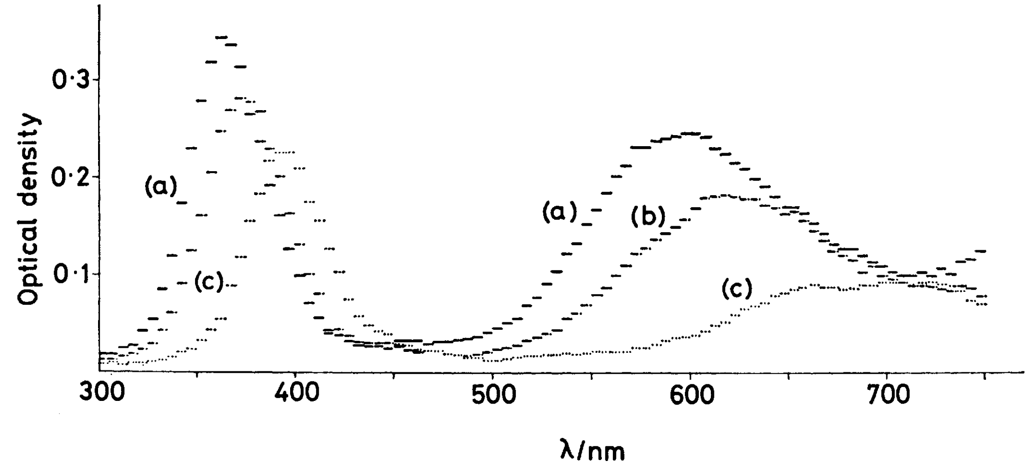


FIGURE 3 Computed spectra from the aquation of $[Ni(dien)(OH_2)_3]^{2+}$ by HCl (0.5 mol dm^{-3}): (a) $[Ni(dien)(OH_2)_3]^{2+}$ on mixing, *i.e.* $t = 0$; (*b*) $[Ni(Hdien)(OH_2)_2]^{3+}$ at $t = 500$ ms; (*c*) $[Ni(OH_2)_6]^{2+}$ at $t = 7$ s. $[Ni(dien)^{2+}] = 0.025$ mol dm^{-3}, cell length = 1.78 ± 0.08 cm

(Table 2), a similarly co-ordinated species, and thus tends to support their postulate.

$[Ni(dien)_2]^{2+}$.—The bis(dien) species was prepared using excess of dien in the mol ratio dien : $Ni^{II} = 2 : 1$. The electronic spectrum, $\lambda_{max.}$ 347 (8.6) and 530 nm (7.5 dm^3 mol^{-1} cm^{-1}) compares favourably with that reported by Margerum and Rosen[10] ($\lambda_{max.}$ 340 and 540 nm). From preliminary multiplex runs at room temperature (293.5 K), four separate stages could be seen in the dechelation by HCl. However, the initial spectrum obtained on mixing did not correspond to the observed spectrum of $[Ni(dien)_2]^{2+}$, which implies that the first stage is partially over within the dead time of the stopped-flow apparatus. From the observation of isosbestic points, the times for the four stages were *ca.* 0—5 ms, 10—60 ms, 100—500 ms, and 1—10 s. To observe the rapid first stage of the reaction, the apparatus was cooled to 280 K where the initial spectrum obtained on mixing corresponded to that expected of $[Ni(dien)_2]^{2+}$. The spectral changes for the stages are shown in Figure 4 and the spectra of the intermediates after each stage of the reaction have been calculated (Table 5). Isosbestic points for each stage were used as bases for single-wave-

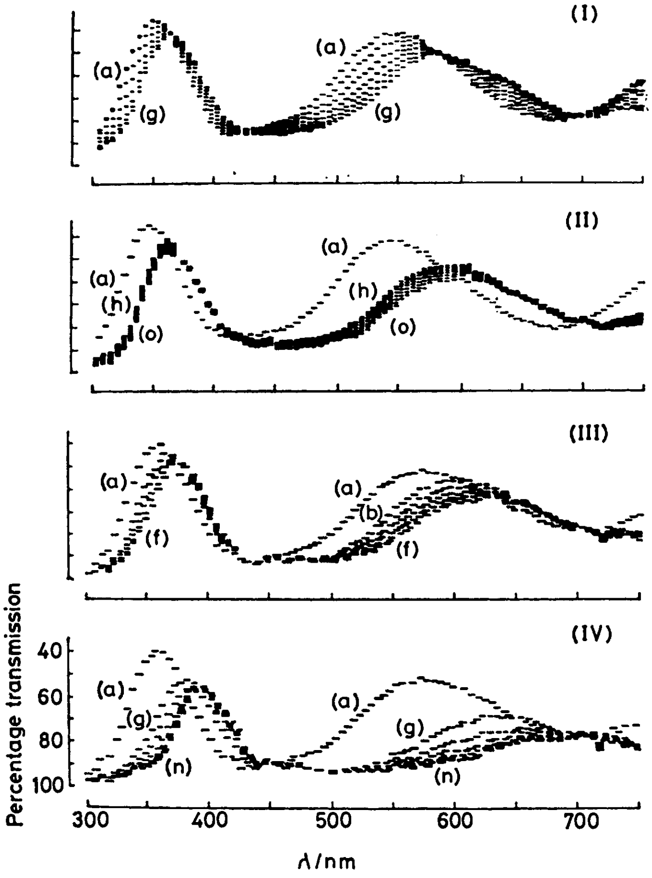


FIGURE 4 U.v.–visible spectra recorded during the aquation of $[Ni(dien)_2]^{2+}$ by HCl (0.5 mol dm^{-3}) at 280 and 293.5 K. (I) and (II) show transient spectra at 280 K; (a) on mixing, (b)—(g) at 4-ms intervals, and (h)—(o) at 50-ms intervals after (a). (III) and (IV) show spectra recorded at 293.5 K; (a) on mixing, (b)—(f) at 100-ms intervals and (g)—(n) at 1-s intervals after (a). $[Ni(dien)_2{}^{2+}] = 0.025$ mol dm^{-3}

TABLE 5

Summary of the spectral profile of the aquation of $[Ni(dien)_2]^{2+}$ in 0.5 mol dm^{-3} HCl at 280 K

	Time, *t*	$\lambda_{max.}$/nm	
$[Ni(dien)_2]^{2+}$	0	345 ± 5 (9) *	540 ± 5 (7.8)
↓ stage 1			
$[Ni(dien)(Hdien)]^{3+}$	20 ms	360 ± 5 (8)	575 ± 5 (6)
↓ stage 2			
$[Ni(dien)]^{2+}$	350 ms	367 ± 5 (8)	595 ± 5 (5)
↓ stage 3			
$[Ni(Hdien)]^{3+}$	3 s	375 ± 5 (7)	620 ± 5 (4)
↓ stage 4			
Ni^{2+} (aq)	32 s	393 ± 5 (6)	660—720 ± 5 (2)

* Figures in parentheses refer to molar absorption coefficients, units dm^3 mol^{-1} cm^{-1}, with ±10% accuracy except for $[Ni(dien)_2]^{2+}$ where accuracy is ±5%.

length studies, the results for which are compiled in Table 6.

TABLE 6

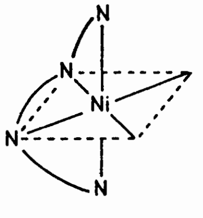
Summary of rate coefficients for the aquation of $[Ni(dien)_2]^{2+}$ in 0.5 mol dm^{-3} HCl; $[Ni(dien)_2{}^{2+}]$ = 0.025 mol dm^{-3}

T = 298 K:	k_3 at 402 nm = 5.1 s^{-1}
	k_4 at 375 nm = 0.86 s^{-1}
T = 280.8 K:	k_1 at 380 nm = 105 s^{-1}
	k_3 at 395 nm = 0.90 s^{-1}
	k_4 at 360 nm = 0.21 s^{-1}

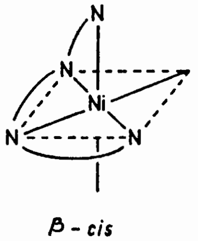
Comparing the data of Tables 4 and 5, it is clear that stages 3 and 4 of Table 5 refer to $[Ni(dien)]^{2+}$ and related species summarised in Table 4. The relatively small spectral change in stage 2 of Table 5 made it impossible to extract a value for its rate (k_2). Our view that one dien ligand is completely lost before the second begins to unwind is supported by a comparison of the rates of the various stages; thus k_3 (Table 6) is closely similar to k_1 for $[Ni(dien)]^{2+}$ (see above) whilst k_4 (Table 6) is similar to k_2 for $[Ni(dien)]^{2+}$ (see above).

A similar reaction pathway has been proposed for the replacement of dien in $[Ni(dien)_2]^{2+}$ by ethylenediamine-tetra-acetate (edta) in solution.[10,11]

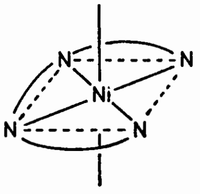
$[Ni(trien)]^{2+}$.—The facultative nature of trien allows the formation of three different octahedral species with nickel(II), α-*cis*, β-*cis*, and *trans*. The *cis* structures are believed to be the more stable in solution at room temperature, but on heating or addition of salt the solution turns brown-yellow and a peak in the visible spectrum at *ca.* 440 nm appears, suggesting that isomerisation to a tetragonal structure is taking place.[12]



α - *cis*



β - *cis*



trans

Jørgensen [13] considers that the similarity between the electronic spectra of $[Ni(trien)]^{2+}$ and $[Ni(tren)]^{2+}$ is strong evidence for a *cis* configuration since $[Ni(tren)]^{2+}$ can only exist in the *cis* form.

Melson and Wilkins [3b] investigated the dechelation of

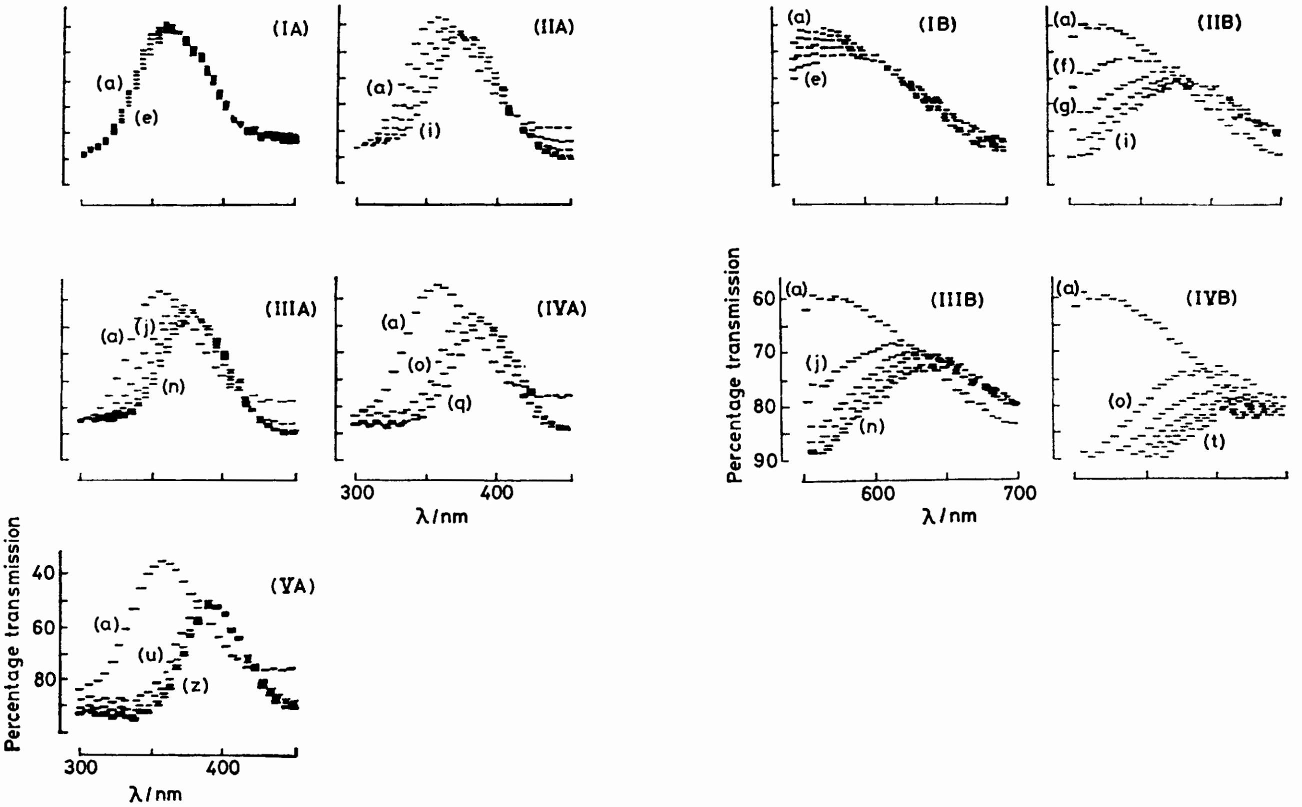


FIGURE 5 Transient spectra observed in the aquation of $[Ni(trien)(OH_2)_3]^{2+}$ by HCl (0.5 mol dm^{-3}) at 293 K. (IA)—(VA) show five stages in the wavelength range 300—450 nm and (IB)—(IVB) show corresponding absorbance changes (expanded scale) in the range 550—700 nm: (a) at t = 0, (b)—(e) at 20-ms intervals, (f)—(i) at 100-ms intervals, (j)—(n) at 200-ms intervals, (o)—(t) at 1-s intervals, and (u)—(z) at 3-s intervals after trace (a). $[Ni(trien)^{2+}]$ = 0.025 mol dm^{-3}

$[Ni(trien)(OH_2)_2]^{2+}$ in HNO_3, producing some evidence for a three-stage process, where $k_1 = 15$ s^{-1}, $k_2 = 4$ s^{-1}, and $k_3 = 2$ s^{-1} (rate determinations from single-wavelength and pH studies).

$$\begin{tikzcd}[Ni(trien)]^{2+} \arrow[r, "k_1"] & [Ni(Htrien)]^{3+} \arrow[r, "k_2"] & [Ni(H_2trien)]^{4+} \arrow[d, "k_3"] \\ & & Ni^{2+}(aq)\end{tikzcd} \qquad (4)$$

In this work $[Ni(trien)]^{2+}$ was prepared from trien·4HCl and nickel(II) chloride (1 : 1) and neutralised to pH 8.0 with sodium hydroxide solution. Its spectrum ($\lambda_{max.}$/nm) may be summarised (with absorption coefficients in parentheses):

Present data	357 (9)	562 (6)		
Ref. 3*a*	360 (10.9)	565 (6.1)	775 (5.0)	920 (12.4)
Ref. 6	360	562	781	952

The decomposition of $[Ni(trien)]^{2+}$ in 0.5 mol dm^{-3} HCl was explored in the range 300—450 nm for isosbestic points and their duration. The photographs (Figure 5) demonstrate the complexity of the reaction, and it is difficult to separate the stages. Five stages were however examined in the regions 300—450 and 550—700 nm. An analysis of these traces is shown in Tables 7 and 8. Table 7 shows the wavelengths at which isosbestic points were occurring and the time of their duration, and Table 8 sets out the $\lambda_{max.}$ and $\varepsilon_{max.}$ values corresponding to the ends of these intermediate stages. The spectrum after 100 ms corresponds to some extent with that calculated by Melson and Wilkins [3a] for $[Ni(Htrien)]^{3+}$, *i.e.* $\lambda_{max.}$ = 370 (8.3), 590 (5.3), 740 (3.3),

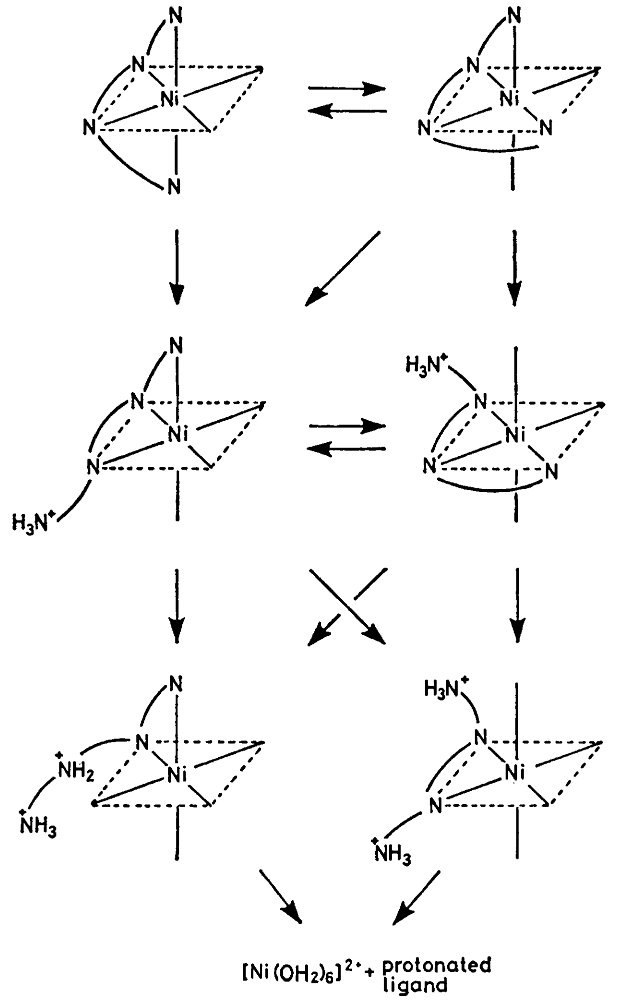


FIGURE 6 Mechanistic scheme for aquation of α-*cis*- and β-*cis*-$[Ni(trien)(OH_2)_2]^{2+}$

TABLE 7

Isosbestic points in the aquation of $[Ni(trien)]^{2+}$ in HCl solution

Time, *t*	λ/nm
0—100 ms	365—370, 410—415, 615—620
200—400 ms	375—380, 410—415, 640—645
400 ms—1 s	385—390, 660—670
1—3 s	390—395
3 s	410—420

TABLE 8

Values of $\lambda_{max.}$ and $\varepsilon_{max.}$ corresponding to the end of each isosbestic point in the aquation of $[Ni(trien)]^{2+}$

Time, *t*	λ/nm (all ±5)	
0	357 (9.1) *	560 (6.0)
100 ms	365 (8.2)	585
400 ms	377 (7.6)	620
1 s	383 (6.9)	640
3 s	390 (6.5)	650—700
20 s	395 (5.8)	650—700

* Figures in parentheses refer to molar absorption coefficients, units dm^3 mol^{-1} cm^{-1}, with ±10% accuracy.

TABLE 9

Peak positions of octahedral Ni^{II} co-ordinated to polyamines

Co-ordination	λ/nm		Ref.
NiN_6			
$[Ni(en)_3]^{2+}$	345 ± 5	540 ± 5	This work
$[Ni(dien)_2]^{2+}$	347 ± 5	530 ± 5	This work, 6
$[Ni(trien)(en)]^{2+}$	344	535	6
$[Ni(penten)]^{2+}$	362	546	3*a*
$NiN_5(H_2O)$			
$[Ni(dien)(Hdien)]^{3+}$	360 ± 5	575 ± 5	This work
$[Ni(Hpenten)]^{3+}$	365	562	3*a*
$NiN_4(H_2O)_2$			
$[Ni(en)_2]^{2+}$	360 ± 5	570 ± 5	This work
$[Ni(tren)]^{2+}$	365	565	3*a*
$[Ni(trien)]^{2+}$	360 ± 5	565 ± 5	This work
$[Ni(H_2penten)]^{4+}$	366	565	3*a*
$NiN_3(H_2O)_3$			
fac-$[Ni(ptn)]^{2+}$	365	595	3*a*
$[Ni(dien)]^{2+}$	360 ± 5	595 ± 5	This work
$[Ni(dapa)]^{2+}$	375	625	3*a*
$[Ni(Htrien)]^{3+}$	370 ± 5	590 ± 5	This work
$NiN_2(H_2O)_4$			
$[Ni(en)]^{2+}$	373 ± 5	625 ± 5	This work, 3*a*
$[Ni(Hptn)]^{3+}$	375	625	3*a*
$[Ni(Hdien)]^{3+}$	375 ± 5	615 ± 5	This work

penten = *NNN'N'*-Tetra(2-aminoethyl)ethylenediamine, dapa = 2,2'-diaminodipropylamine, and ptn = propane-1,2,3-triamine.

and 920 nm (10.2 dm^3 mol^{-1} cm^{-1}), and the final spectrum (after 20 s) with Ni^{2+}(aq).

A complete analysis of the reaction does not seem possible due to the complexity of the spectra. The consecutive stages of dechelation are not significantly separable and also concurrent reactions may be occurring *via* isomeric pathways. Figure 6 shows schematically the possible pathways of dechelation of α-*cis*- and β-*cis*-[Ni(trien)]$^{2+}$ assuming that a primary NH_2–N bond is broken first in the ring-opening process.

In Table 9 the spectra of the various assigned intermediates are compared with known species of similar geometries and in most cases the agreement is seen to be good.

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