Studies in Nickel(IV) Chemistry. Part 3.† Kinetics of Metal(II) Ion-mediated Acid Decomposition of Tris(dimethylglyoximato)-nickelate(IV) in Aqueous Medium

Gautam Neogi, Sridhara Acharya, and Rama Krushna Panda *
Department of Chemistry, Berhampur University, Berhampur 760 007, India
Dorai Ramaswamy
Chemical Laboratories, Central Leather Research Institute, Madras 600 020, India

The kinetics of metal(II) ion-mediated acid decomposition of tris(dimethylglyoximato)nickelate(IV), [Ni(dmg)$_3$]$^{2-}$, with concomitant intramolecular electron transfer to produce [M(Hdmg)$_2$] and Ni^{2+}(aq) have been studied at 35 °C and ionic strength 0.57 mol dm^{-3} in aqueous medium in the range 3.6 $\lesssim$ pH $\lesssim$ 6.8. The reactions proceed via equilibrium formation of 1 : 1 adducts involving the protonated Ni^{IV} complex and M^{II}(aq) (M = Cu, Zn, or Ni) present in the medium. While the rate-determining steps in the reactions with Cu^{II} are envisaged to involve acid decomposition of the adduct formed in addition to proton-assisted decomposition of the Ni^{IV} complex, those in the reactions with Zn^{II} and Ni^{II} proceed essentially by routes parallel to the proton-assisted decomposition. U.v.–visible spectral changes in the Ni^{IV}–Cu^{II} reaction indicate the formation of the 1 : 1 adduct.

It has been recognised that if ligand dissociation of a metal chelate occurs via a dissociative interchange mechanism involving a metal–ligand bond scission, then as a result of the bond rupture a released end of the ligand would be available for attack by electrophiles (M^{n+} or H$^+$).[1] Added metal ions (M^{n+}), in capturing the released site to form an adduct, may compete with H$^+$ of the medium.[2] Concerted attempts [3–5] have been made to prepare adducts of a variety of metal ions with bis(salicylideneimine) complexes of bivalent transition metals and with the organometallic [Co(CH$_3$)(salen)(OH$_2$)] [salen = NN'-ethylenebis(salicylideneiminate)]. Such adduct formation, arising from involvement of the oxygen atoms of the ligand, has been found to result in shifts in the ^{1}H n.m.r. and visible spectra of the original metal chelate. Iron(III) adduct formation in aqueous medium has been described as taking place by planar replacement of the intramolecularly bonded hydrogen in the pseudomacrocycles [Co(CH$_3$)(Hdmg)$_2$(OH$_2$)] and [Co(OH$_2$)$_2$(Hdmg)$_2$]$^+$ (Hdmg$^-$ = dimethylglyoximate monoanion).[6] Similarly, tris(dimethylglyoximato)cobaltate(III), [Co(dmg)$_3$]$^{3-}$, a low-spin d^6 pseudo-octahedral complex in which the dmg^{2-} units are bonded to the central Co^{III} through nitrogen donors only, forms a clathrochelate [7] and metallomers [8] by bonding BF$_3$ and ML$_3^{n+}$ groups, respectively through the triangular arrays of oxygen atoms on the opposite faces of the [Co(dmg)$_3$]$^{3-}$ octahedron. One general aspect of these adducts is that upon formation from metal ions and metal chelates, the intensities of the visible absorptions of the latter are greatly increased without significant alteration in the positions of the maxima.

We have been interested in the chemistry of tris(dimethylglyoximato)nickelate(IV), [Ni(dmg)$_3$]$^{2-}$, which is isoelectronic with [Co(dmg)$_3$]$^{3-}$, and have reported its preparation and characterisation,[9] stability in aqueous solutions,[10] and reaction with L-ascorbic acid.[11] The proton-assisted decomposition rates [10,11] of this complex are significantly influenced by the presence of added M^{2+}(aq). This report presents a study of M^{II}-mediated acid decomposition of the nickel(IV) complex (M = Cu, Zn, or Ni) in aqueous medium and at ionic strength 0.57 mol dm^{-3}.

Experimental

Materials.—All solutions were prepared using freshly prepared doubly distilled water. The aqueous solutions of [Ni(dmg)$_3$]$^{2-}$ were obtained by dissolving freshly prepared crystals of K$_2$[Ni(dmg)$_3$]·6H$_2$O in water as described elsewhere.[9–11] Solutions of metal(II) ions were prepared using B.D.H. (AnalaR) grade reagents of chlorides of Cu^{II}, Zn^{II}, and Ni^{II}; the concentrations of M^{II} were estimated by the standard edta method.[12] Stock solutions of M^{II} were freshly prepared before use; they were appropriately diluted and their pH was adjusted, as required. The other reagents were of analytical reagent grade. Standard buffer solutions in water were prepared using potassium acetate and acetic acid.

Kinetics.—The kinetics of the reactions were followed by monitoring the disappearance of the Ni^{IV} absorption at 460 nm (ε_{460} = 9.6 × 10^3 dm^3 mol^{-1} cm^{-1}) continuously as a function of time, with a Pye Unicam SP 1800 or a Zeiss VSU 2-P spectrophotometer, or with an Aminco stopped-flow assembly as described elsewhere.[9–11] The pH values of the solutions were measured before and after the reactions, and the average (which did not differ by more than ±0.01 units from the measured values) was taken after correction for the ionic strength effect.[13] The supporting electrolyte for maintaining ionic strength (I) was potassium chloride. In a typical experiment, an aqueous solution of Ni^{IV} was rapidly mixed with an equal volume of M^{II} solution at the desired pH, ionic strength, and temperature (±0.1 °C), and the progress of the reaction was monitored. Since the pH values of the reaction in a single run showed virtually no change (±0.01 units), the pH–temperature jump effect on mixing was considered negligible. Pseudo-first-order disappearance of the Ni^{IV} was observed for more than three half-lives and in the range 1 × 10^{-5} $\leqslant$ [Ni^{IV}]$_0$ $\leqslant$ 2 × 10^{-4} mol dm^{-3}. The pseudo-first-order rate constants ($k_{obs.}$) were calculated from the log (absorbance) and time data. Change in the monitoring wavelength (440—480 nm) or use of a nitrogen atmosphere did not essentially alter the rate constants. The added M^{II} and the products of the reactions had negligible absorbance in the wavelength range used. The hydroxides of M^{II} did not precipitate under the employed conditions and the reaction mixtures were perfectly homogeneous. The rate constants in two to four replicates were reproducible to within ±5%.

† Parts 1 and 2 are refs. 9 and 10.

Products.—The main products of the Ni^{IV}-M^{II} reactions were Ni^{II}(aq) and [M(Hdmg)$_2$]. In a set of experiments at pH 4.8, 5.4, and 6.0, an aqueous solution of Ni^{IV} (0.02 mol, 25 cm^3) was treated with a solution of M^{II} (0.02 mol, 25 cm^3). After the reaction was complete, the mixture was brought to pH *ca.* 8 and extracted with diethyl ether. The solvent was evaporated from the ether layer, and the residue was vacuum dried and identified as [M(Hdmg)$_2$] by elemental analysis and i.r. spectra. The aqueous layer containing Ni^{II} (aq), on treatment with aqueous alkaline dimethylglyoxime, furnished [Ni(Hdmg)$_2$] [identical (i.r.) with an authentic sample]. The formation of [Ni(Hdmg)$_2$], a product of acid decomposition of [Ni(dmg)$_3$]$^{2-}$ at pH $\gtrsim 4.5$ in the absence of M^{II}, was negligible under the present conditions employed. The (dmg)$_{ox}$, represen-

$$[Ni(dmg)_3]^{2-} + M^{II} (aq) + 2 H^+ \longrightarrow$$
$$Ni^{II} (aq) + [M(Hdmg)_2] + (dmg)_{ox} \quad (i)$$
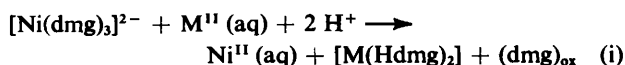
ting the oxidised product of dimethylglyoxime, was identified earlier [10] as 3,4-dimethylfurazan 5-oxide.

Spectrophotometric Titrations.—Spectrophotometric titrations were performed by mixing known volumes of aqueous solutions of Ni^{IV} and M^{II} at the desired pH, temperature, and *I*, and rapidly recording the spectra in the 210—380 and 380—600 nm regions (by point-by-point scanning). Low concentrations of Ni^{IV} and M^{II} were employed to minimise precipitation and decomposition.

Results and Discussion

(A) *Reaction with* Cu^{II}.—The values of $k_{obs(Cu)}$ at varying [Cu^{II}] for different pH values are listed in Table 1. Since the Ni^{IV} complex was found to undergo proton-assisted decomposition,[10] the pseudo-first-order rate constants for the

Table 1. First-order rate constants for the Cu^{II}-mediated acid decomposition of Ni^{IV}; 35 °C, $I = 0.57$ mol dm^{-3}, [Ni^{IV}]$_0$ = (1—3) × 10^{-5} mol dm^{-3} *

pH	10^5[Cu^{II}]/mol dm^{-3}	$10^3 k_{obs(Cu)}$/s^{-1}	$10^3 k_{dec(Cu)}$/s^{-1}	a/s^{-1}	b/dm^3 mol^{-1}
3.6	0	34.7 ± 0.7	0		
	4	36.9 ± 0.7	2.2		
	8	39.0 ± 0.7	4.3	3.1	17
	10	40.1 ± 0.8	5.4		
	12	41.1 ± 0.8	6.4		
	16	43.3 ± 0.8	8.6		
	20	45.4 ± 1	10.7		
4.4	0	5.5 ± 0.2	0		
	4	6.25 ± 0.1	0.75		
	8	6.99 ± 0.1	1.49	0.14	135
	10	7.36 ± 0.2	1.86		
	12	7.72 ± 0.2	2.22		
	16	8.45 ± 0.2	2.95		
	20	9.17 ± 0.3	3.67		
4.85	0	1.95 ± 0.07	0		
	4	3.23 ± 0.07	1.28		
	6	3.88 ± 0.08	1.93		
	8	4.33 ± 0.08	2.38		
	12	5.84 ± 0.1	3.89	6×10^{-2}	5.3×10^2
	16	6.81 ± 0.1	4.86		
	20	7.62 ± 0.1	5.67		
	24	8.43 ± 0.1	6.48		
	28	9.16 ± 0.2	7.21		
	32	10.4 ± 0.2	8.48		
	36	11.6 ± 0.2	9.66		
	40	12.0 ± 0.2	10.1		
5.6	0	0.35 ± 0.01	0		
	4	2.61 ± 0.03	2.26		
	8	3.95 ± 0.08	3.6	8.8×10^{-3}	8.7×10^3
	10	4.45 ± 0.1	4.1		
	12	4.85 ± 0.1	4.5		
	16	5.45 ± 0.1	5.1		
	20	5.95 ± 0.1	5.6		
6.15	0	0.1 ± 0.004	0		
	4	2.23 ± 0.04	2.13		
	8	2.52 ± 0.05	2.42	2.7×10^{-3}	8.4×10^4
	10	2.63 ± 0.05	2.53		
	16	2.67 ± 0.05	2.57		
	28	2.70 ± 0.05	2.60		
	40	2.77 ± 0.06	2.67		
6.55	0	0.04 ± 0.001	0		
	4	1.36 ± 0.02	1.32		
	8	1.40 ± 0.02	1.36	1.4×10^{-3}	4×10^5
	10	1.41 ± 0.02	1.37		
	12	1.41 ± 0.03	1.37		
	16	1.42 ± 0.02	1.38		
	20	1.43 ± 0.02	1.39		

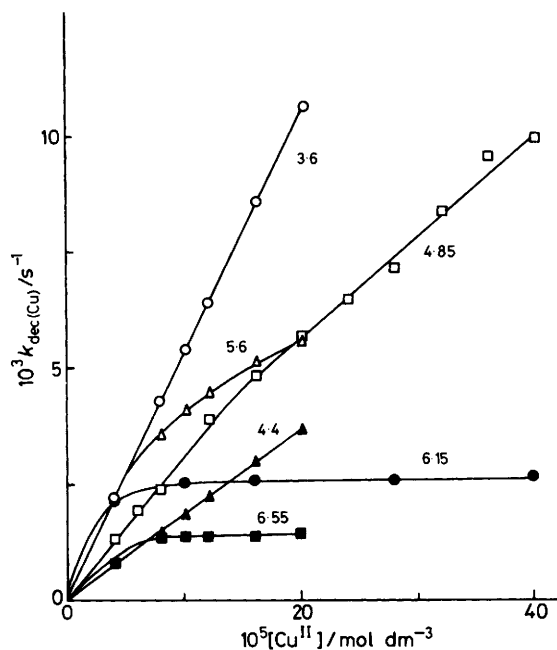* The constants a and b are defined by equation (iii).

Figure 1. Plots of $k_{dec(Cu)}$ vs. $[Cu^{II}]_0$; $I = 0.57$ mol dm^{-3}, 35 °C; pH values are indicated
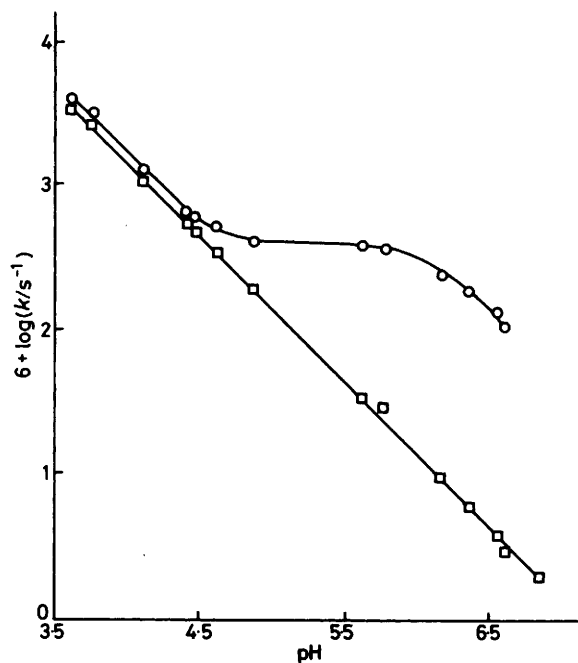

Figure 2. Plots of log $k_{obs(Cu)}$ (O) and log k_{ad} ($\square$) vs. pH; $I = 0.57$ mol dm^{-3}, 35 ° C

process (k_{ad}) were collected independently (in the absence of Cu^{II} ions) in the pH range of the study. The observed first-order rate constants, $k_{obs(Cu)}$, would then conform to equation (ii), where $k_{dec(Cu)}$ refers to the pseudo-first-order rate constant

$$k_{obs(Cu)} = k_{ad} + k_{dec(Cu)} \qquad (ii)$$

for the Cu^{II}-mediated acid decomposition of the Ni^{IV} complex and is a function of $[Cu^{II}]_0$ and $[H^+]$.

Equation (iii) was found to express the relationship between $k_{dec(Cu)}$ and $[Cu^{II}]_0$ at a given pH. The average values of

$$k_{dec(Cu)} = a\,b[Cu^{II}]_0/(1 + b[Cu^{II}]_0) \qquad (iii)$$

the pH-dependent constants a and b, obtained as (1/intercept) and (intercept/slope) of least-squares plots of $k_{dec(Cu)}^{-1}$ vs. $[Cu^{II}]^{-1}$, are presented in Table 1 for different pH values. Figure 1 presents the dependence of $k_{dec(Cu)}$ on $[Cu^{II}]_0$ at various pH values.

The effect of changing pH, at constant and low $[Cu^{II}]_0$, on $k_{obs(Cu)}$ and $k_{dec(Cu)}$ was complex (Table 2). The $k_{dec(Cu)}$ value registered a decrease with increasing pH in the pH range 3.6—4.4, progressively increased in the range 4.46—5.76, and then again decreased in the range 5.76—6.6. The log $k_{obs(Cu)}$-pH plot (Figure 2) and the $k_{dec(Cu)}$-pH plot at constant $[Cu^{II}]$ (Figure 3) indicated that more than one $[H^+]$ term might be involved in the reaction sequence.

The observed kinetic data can be rationalised in terms of Scheme 1, which envisages equilibrium interactions, with H^+ loss, of various species of Ni^{IV} with those of Cu^{II}, which may exist in solution under the employed conditions, to form adducts; the decomposition of the latter, in the presence of H^+, to yield products may constitute the rate-controlling step(s). The K_{Cu} value of $10^{-6.8}$ mol dm^{-3} (at 25 °C) [14] was employed with the assumption that the enthalpy change for the equilibrium (iv) was negligibly small in the temperature range used.

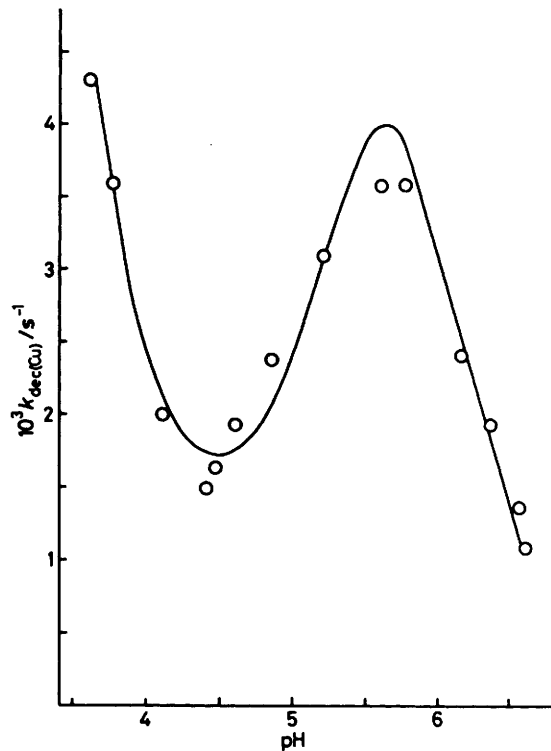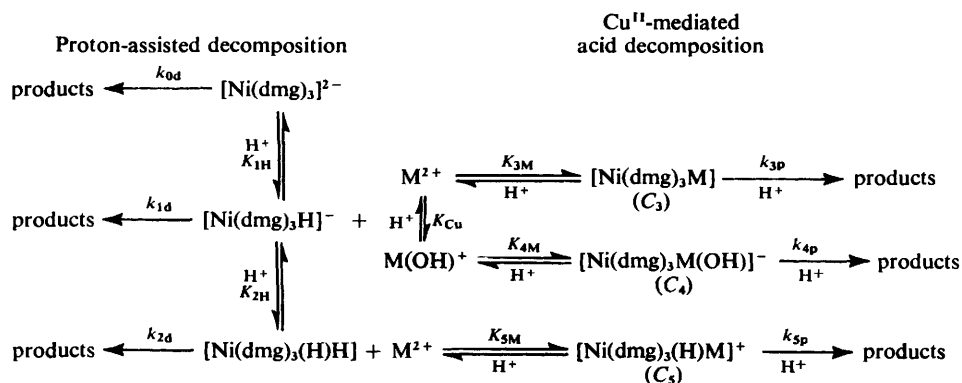In the pH range of the study, the k_{ad} values conform to

$$Cu^{2+} + H_2O \xrightleftharpoons[\quad]{K_{Cu}} Cu(OH)^+ + H^+ \qquad (iv)$$

Figure 3. Plot of $k_{dec(Cu)}$ vs. pH; $I = 0.57$ mol dm^{-3}, 35 °C; the solid line refers to calculated values

equation (v) since the solvent-assisted decomposition rate constant (k_{0d}) of the complex is negligible.[10]

$$k_{ad} \approx \frac{k_{1d}K_{1H}[H^+] + k_{2d}K_{1H}K_{2H}[H^+]^2}{1 + K_{1H}[H^+] + K_{1H}K_{2H}[H^+]^2} \qquad (v)$$

Proton-assisted decomposition

Cu^{II}-mediated
acid decomposition

$$\text{products} \xleftarrow{\ k_{0d}\ } [\text{Ni(dmg)}_3]^{2-}$$

Scheme 1. M = Cu; aqua ligands have been omitted for convenience

A rate expression which can be derived from Scheme 1 is shown as equation (vi) where k_{np} and K_{nM} are pH- and [Cu^{II}]-dependent quantities.

While the two-protonated nickel(iv) complex apparently reacts about 10^4 times faster than the one-protonated species, the aquacopper(ii) does so about 100 times slower than the hydr-

$$k_{\text{obs(Cu)}} - k_{\text{ad}} = k_{\text{dec(Cu)}} = \frac{(k_{3p}K_{3M}[\text{H}^+]^2 + k_{4p}K_{4M}K_{\text{Cu}}[\text{H}^+] + k_{5p}K_{5M}K_{2H}[\text{H}^+]^3)[\text{Cu}^{II}]_0}{[\text{H}^+](K_{\text{Cu}} + [\text{H}^+])(1 + K_{2H}[\text{H}^+]) + (K_{3M}[\text{H}^+] + K_{4M}K_{\text{Cu}} + K_{5M}K_{2H}[\text{H}^+]^2)[\text{Cu}^{II}]_0} \quad \text{(vi)}$$

In deriving (vi) it has been assumed that the reactions of [Ni(dmg)$_3$]$^{2-}$ and the [Ni(dmg)$_3$(H)H]-M(OH)$^+$ reaction have negligible contribution to the overall reaction in the pH range employed.

From (vi) it follows that the value of (intercept/slope) of the plot of $1/k_{\text{dec(Cu)}}$ vs. $1/[\text{Cu}^{II}]$ at different pH values, identified by the parameter b of equation (iii) (Table 1), can be expressed in terms of equation (via). A plot of Y vs. [H$^+$] was

oxocopper(ii). Evidently, factors other than the simple electrostatic one may be responsible in deciding the relative reactivity.

That the reaction of the Ni^{IV} complex with Cu^{II} does not follow a different mechanistic pathway, Ni^{IV} + Cu^{II} $\longrightarrow$ Ni^{III} + Cu^{III}, is revealed from the following facts. (a) In the Cu^{II}-catalysed oxidation of hydroxylamine by the Ni^{IV} complex, the disappearance of the Ni^{IV} was pseudo-zero-order, suggesting that a Cu^{III}-Cu^{II} redox cycle was most probably

$$b[\text{H}^+](K_{\text{Cu}} + [\text{H}^+])(1 + K_{2H}[\text{H}^+]) = Y = K_{3M}[\text{H}^+] + K_{4M}K_{\text{Cu}} + K_{5M}K_{2H}[\text{H}^+]^2 \quad \text{(via)}$$

linear, giving the values of K_{3M} and K_{4M} as $(4.18 \pm 0.2) \times 10^{-3}$ and 0.3 ± 0.02, respectively. The K_{5M} value was assumed to be negligible since in the lower pH range (pH ca. 3.6), where the step represented by K_{5M} is more prevalent, the $k_{\text{dec(Cu)}}$ values were linearly dependent on [Cu^{II}]$_0$.

Rearrangement of (vi), in this event, leads to (vii). A least-

not involved.[15] (b) The redox potential of the couple Ni^{IV}-Ni^{III} (ca. 0.4 V)[16] is not sufficient to oxidise Cu^{II}(aq) to Cu^{III}(aq) [Cu^{II}(aq)-Cu^{III}(aq) $\gtrsim$ −1.8 V].[17]

(B) *Reactions with Zn^{II} and Ni^{II}.*—The pseudo-first-order rate constant for the disappearance of the Ni^{IV} in the presence

$$\frac{k_{\text{dec(Cu)}}\{[\text{H}^+](K_{\text{Cu}} + [\text{H}^+])(1 + K_{2H}[\text{H}^+]) + (K_{3M}[\text{H}^+] + K_{4M}K_{\text{Cu}})[\text{Cu}^{II}]\}}{[\text{Cu}^{II}][\text{H}^+]} = Z$$

$$= k_{4p}K_{4M}K_{\text{Cu}} + k_{3p}K_{3M}[\text{H}^+] + k_{5p}K_{5M}K_{2H}[\text{H}^+]^2 \quad \text{(vii)}$$

squares analysis of the data in Table 2, in accordance with (vii), resulted in values of $k_{3p}K_{3M}$, $k_{4p}K_{4M}$, and $k_{5p}K_{5M}$ as 10 ± 0.5, $(1.26 \pm 0.05) \times 10^3$, and $(8.2 \pm 0.4) \times 10^4$ dm^3 mol^{-1} s^{-1}, respectively. The $k_{\text{dec(Cu)}}$ values calculated from these values agree reasonably with the observed $k_{\text{dec(Cu)}}$ values (Table 2). Table 3 presents the various resolved constants for the proton-assisted and the Cu^{II}-mediated acid decomposition of the Ni^{IV} complex.

In spite of the apparent complexity of the rate law (vi), and of the fact that the values of the statistically resolved (pH- and [Cu^{II}]-dependent) constants can only approximately indicate the relative importance of various species in the reaction, a reasonably simple picture emerges. The relative magnitudes of the product of the apparent equilibrium constant for the formation of the adduct and the acid-decomposition rate constant of the adduct ($k_{np}K_{nM}$) are given below.

of Zn^{II} or Ni^{II}, $k_{\text{obs(M)}}$, was found to be lower than the corresponding k_{ad} value at a particular pH. An increase in [M^{II}]$_0$ (M = Zn or Ni) was accompanied by a decrease in $k_{\text{obs(M)}}$ (Table 4). In the case of reactions with Zn^{II}, the decrease in rate was initially marginal, the $k_{\text{obs(Zn)}}$ changing by about 15% for an almost sixteen-fold increase in [Zn^{II}]$_0$; but at higher [Zn^{II}]$_0$, the retardation was more pronounced [Figure 4(a)]. In comparison, the fall in $k_{\text{obs(Ni)}}$ with increasing [Ni^{II}]$_0$ at lower [Ni^{II}]$_0$ was much more pronounced, the decrease becoming gradually smaller with increasing [Ni^{II}]$_0$ and tending to level off at [Ni^{II}]$_0$ $\gtrsim$ 3.6 × 10^{-4} mol dm^{-3} [Figure 4(b)]. Equation (viii) appears to satisfy the observed kinetic results, and on rearrangement becomes equation (ix); d is a

$$k_{4p}K_{4M}/k_{3p}K_{3M} \approx 10^2, \quad k_{5p}K_{5M}/k_{3p}K_{3M} \approx 10^4$$

$$k_{\text{obs(M)}} = k_{\text{ad}}/(1 + d[\text{M}^{II}]_0) \quad \text{(viii)}$$

$$[k_{\text{ad}} - k_{\text{obs(M)}}]/k_{\text{obs(M)}} = d[\text{M}^{II}]_0 \quad \text{(ix)}$$

Table 2. First-order rate constants for the Cu^{II}-mediated acid decomposition of Ni^{IV}: 35 °C, $I = 0.57$ mol dm^{-3}; $[Ni^{IV}]_0 = (2—3) \times 10^{-5}$, $[Cu^{II}]_0 = (7—9) \times 10^{-5}$ mol dm^{-3}

pH	$10^3 k_{obs(Cu)}/$ s^{-1}	$10^3 k_{ad}/$ s^{-1}	$10^3 k_{dec(Cu)}/$ s^{-1} [a]	$10^3 k_{dec(Cu)}/$ (calc.)/ s^{-1} [b]
3.60	39.0 ± 1.3	34.7 ± 0.7	4.30	4.5
3.76	30.7 ± 0.8	27.1 ± 0.5	3.60	3.5
4.10	13.0 ± 0.5	11.0 ± 0.4	2.0	2.2
4.40	7.00 ± 0.16	5.51 ± 0.2	1.49	1.7
4.46	6.24 ± 0.17	4.60 ± 0.1	1.64	1.7
4.60	5.40 ± 0.17	3.47 ± 0.1	1.93	1.8
4.85	4.33 ± 0.15	1.95 ± 0.07	2.38	2.0
5.20	4.00 ± 0.15	0.90 ± 0.02	3.10	3.1
5.60	3.95 ± 0.11	0.35 ± 0.01	3.60	4.0
5.76	3.90 ± 0.11	0.30 ± 0.01	3.60	3.9
6.15	2.52 ± 0.07	0.10 ± 0.004	2.42	2.5
6.35	2.00 ± 0.08	0.06 ± 0.002	1.94	1.7
6.55	1.40 ± 0.05	0.04 ± 0.001	1.36	1.2
6.60	1.12 ± 0.02	0.03 ± 0.001	1.09	1.0
6.85	—	0.02 ± 0.001	—	—

[a] $k_{dec(Cu)} = k_{obs(Cu)} - k_{ad}$. [b] Calculated from equation (vii).

Table 3. Average values of various constants for the proton-assisted and the Cu^{II}-mediated acid decomposition of Ni^{IV}: 35 °C, $I = 0.57$ mol dm^{-3}

Constant	Average value	Ref.
k_{0d}/s^{-1} [a]	2.6×10^{-7}	10
$K_{1H}/dm^3\ mol^{-1}$ [b]	8.07×10^{10} (8.33×10^{10}) [c]	10
k_{1d}/s^{-1}	2.2×10^{-6}	This work
$K_{2H}/dm^3\ mol^{-1}$ [b]	2.24	
k_{2d}/s^{-1}	22.7	This work
$k_{3p}K_{3M}/dm^3\ mol^{-1}\ s^{-1}$	10	This work
$k_{4p}K_{4M}/dm^3\ mol^{-1}\ s^{-1}$	1.26×10^3	
$k_{5p}K_{5M}/dm^3\ mol^{-1}\ s^{-1}$	8.21×10^4	

[a] Solvent-assisted decomposition rate constant in the pH range 11.6—12.3 (monitored for disappearance of initial Ni^{IV} in nine runs over 20 days). [b] Value obtained from potentiometric pH titrations. [c] Value obtained from spectrophotometric pH titrations.
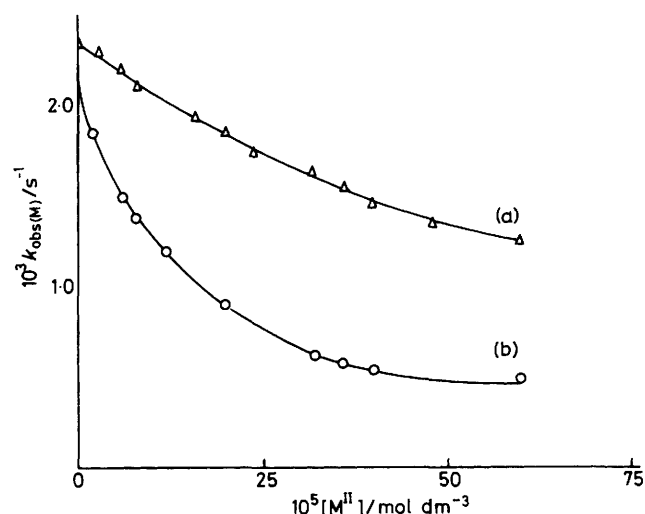
Table 4. First-order rate constants for the M^{II}-mediated acid decomposition of Ni^{IV} (M = Zn or Ni): 35 °C, $I = 0.57$ mol dm^{-3}, pH 4.75—4.79; $[Ni^{IV}]_0 = (2—3) \times 10^{-5}$ mol dm^{-3}

$10^5[M^{II}]/mol\ dm^{-3}$	$10^3 k_{obs(Zn)}/s^{-1}$	$10^3 k_{obs(Ni)}/s^{-1}$
0	2.35 ± 0.07	2.35 ± 0.07
2	—	1.85 ± 0.04
3	2.30 ± 0.06	—
6	2.20 ± 0.07	1.49 ± 0.05
8	2.11 ± 0.05	1.38 ± 0.03
12	—	1.18 ± 0.03
16	1.94 ± 0.04	—
20	1.86 ± 0.06	0.91 ± 0.03
24	1.74 ± 0.05	—
32	1.63 ± 0.04	0.62 ± 0.02
36	1.55 ± 0.05	0.57 ± 0.02
40	1.45 ± 0.05	0.53 ± 0.02
48	1.35 ± 0.03	—
60	1.24 ± 0.02	0.49 ± 0.01

Figure 4. Plots of $k_{obs(M)}$ vs. $[M^{II}]$; (a) Zn^{II}, (b) Ni^{II}; $I = 0.57$ mol dm^{-3}, 35 °C

composite function of $[M^{II}]_0$ and $[H^+]$. Least-squares fits of data to equation (ix) resulted in values of $d(Zn)$ and $d(Ni)$ (neglecting the small values of the intercepts), respectively, as $(1.56 \pm 0.05) \times 10^3$ dm^3 mol^{-1} and $(8.6 \pm 0.4) \times 10^3$ dm^3 mol^{-1} at pH 4.75—4.79, $I = 0.57$ mol dm^{-3}, and 35 °C.

The influence of pH on $k_{obs(M)}$ at constant $[M^{II}]_0$ was studied (Table 5). In the pH ranges employed, the log $k_{obs(M)}$ vs. pH profiles (Figure 5) run almost parallel to that of log k_{ad} vs. pH. The $k_{obs(Zn)}$ values were only marginally smaller than the k_{ad} values, while the $k_{obs(Ni)}$ values were substantially smaller.

One reaction scheme (Scheme 2), which envisages pre-equilibrium between M^{II} (aq) and protonated Ni^{IV} species to

give 1 : 1 adducts and subsequent rate-determining decomposition to form the products, can explain the kinetic observations.

If the reasonable assumptions are made that (a) in the pH range explored, the $[Ni(dmg)_3]^{2-}$ species does not make a significant contribution to the overall reaction, (b) M^{II} is present predominantly as $M^{2+}(aq)$ (cf. $K_{Zn} = 10^{-8.8}$ and $K_{Ni} = 10^{-10.6}$,[14] and (c) $k_{-7M} \gg k_{7x}$, $k_{-8M} \gg k_{8x}$ (where $K_{nM} = k_{nM}/k_{-nM}$), equations (x)—(xii) are derivable from Scheme 2; the pH-dependent term $(1 + d[M^{II}])$ has been assumed to be the

$$M^{2+} + H_2O \xrightleftharpoons{K_M} M(OH)^+ + H^+$$

$$[Ni(dmg)_3(H)]^- + M^{2+} \xrightleftharpoons{K_{7M}} [Ni(dmg)_3(H)M]^+ \xrightarrow{k_{7x}} products$$

$$[Ni(dmg)_3(H)]^- \xrightarrow{k_{1d}'} products$$

$$[Ni(dmg)_3(H)H] + M^{2+} \xrightleftharpoons{K_{8M}} [Ni(dmg)_3(H)HM]^{2+} \xrightarrow{k_{8x}} products$$

$$[Ni(dmg)_3(H)H] \xrightarrow{k_{2d}'} products$$
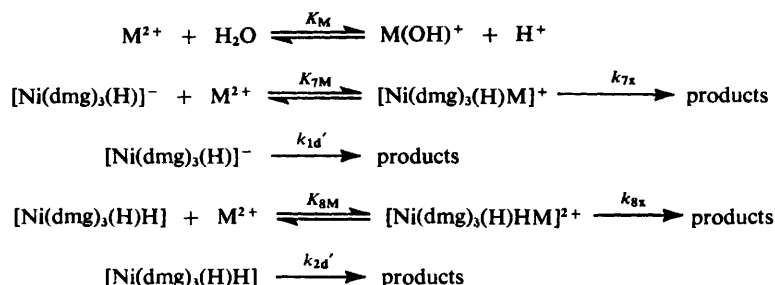
Scheme 2. Aqua ligands have been omitted for convenience

Table 5. First-order rate constants for the M^{II}-mediated acid decomposition of Ni^{IV} (M = Zn or Ni); 35 °C, I = 0.57 mol dm⁻³; $[Ni^{IV}]_0$ = (2—3) × 10⁻⁵ mol dm⁻³

pH	$10^3 k_{obs(Zn)}/s^{-1}$ ᵃ	$10^3 k_{calc(Zn)}/s^{-1}$ ᵃ,ᵇ	pH	$10^3 k_{obs(Ni)}/s^{-1}$ ᶜ	$10^3 k_{calc(Ni)}/s^{-1}$ ᵇ,ᶜ
3.60	32.3 ± 0.7	32.4	3.71	16.5 ± 0.6	16.6
3.79	20.9 ± 0.7	21.0	3.83	12.5 ± 0.3	12.6
3.95	14.5 ± 0.5	14.6	3.87	11.6 ± 0.3	11.5
4.08	11.2 ± 0.3	10.8	4.11	6.65 ± 0.2	6.60
4.30	6.73 ± 0.2	6.57	4.41	3.32 ± 0.1	3.31
4.77	1.86 ± 0.07	1.90	4.77	1.18 ± 0.04	1.25
5.04	1.20 ± 0.04	1.29	5.14	0.66 ± 0.02	0.62
5.34	0.60 ± 0.02	0.70	5.56	0.26 ± 0.01	0.24
5.64	0.37 ± 0.01	0.41	5.94	0.10 ± 0.003	0.11
			6.85	0.02 ± 0.0004	0.02

ᵃ $[Zn^{II}]$ = (19—21) × 10⁻⁵ mol dm⁻³. ᵇ Average values calculated by using equation (xi). ᶜ $[Ni^{II}]$ = (11—13) × 10⁻⁵ mol dm⁻³.

$$k_{obs(M)} = \frac{\left(\dfrac{k_{1d}' K_{1H}[H^+]}{1 + K_{7M}[M^{II}]}\right) + \left(\dfrac{k_{2d}' K_{1H} K_{2H}[H^+]^2}{1 + K_{8M}[M^{II}]}\right)}{1 + K_{1H}[H^+] + K_{1H} K_{2H}[H^+]^2} \qquad (x)$$

$$k_{obs(M)} \approx \frac{k_{1d}' K_{1H}[H^+] + k_{2d}' K_{1H} K_{2H}[H^+]^2}{(1 + K_{1H}[H^+] + K_{1H} K_{2H}[H^+]^2)(1 + d[M^{II}])} \qquad (xi)$$

$$\frac{k_{obs(M)}(1 + K_{1H}[H^+] + K_{1H} K_{2H}[H^+]^2)(1 + d[M^{II}])}{K_{1H}[H^+]} = k_{1d}' + k_{2d}' K_{2H}[H^+] \qquad (xii)$$

net variation in rate with varying $[M^{II}]_0$. Equation (xi) is similar in nature to that for k_{ad} [equation (v)]. Using the values of $d(Zn)$ and $d(Ni)$ obtained earlier, the values $k_{1d(Zn)}'$, $k_{2d(Zn)}'$, $k_{1d(Ni)}'$, and $k_{2d(Ni)}'$ were evaluated from (xi) as (1.5 ± 0.1) × 10⁻⁴, 27.8 ± 2, (1.9 ± 0.1) × 10⁻⁵, and 28.4 ± 2 s⁻¹, respectively. The $k_{calc(M)}$ values estimated from these values agree well with those experimentally obtained. Table 6 lists various

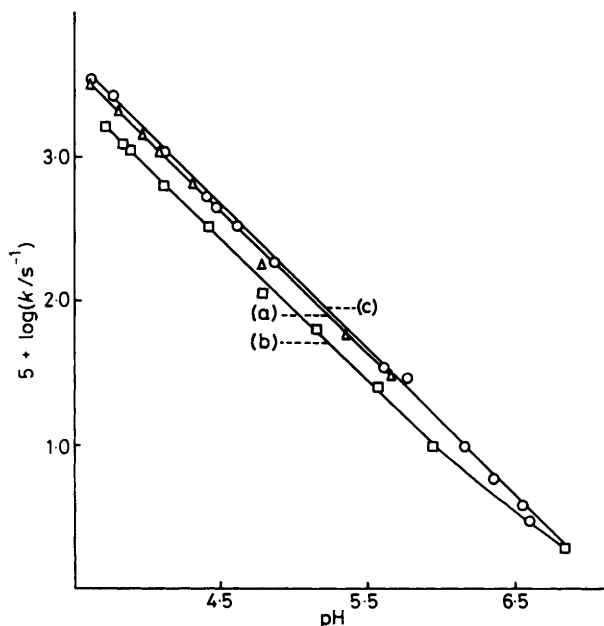**Figure 5.** Plots of log k vs. pH; (a) $k_{obs(Zn)}$, (b) $k_{obs(Ni)}$, (c) k_{ad}; I = 0.57 mol dm⁻³, 35 °C; solid lines refer to calculated values

constants pertaining to the proton-assisted, and the Zn^{II}- and Ni^{II}-mediated acid decompositions of the Ni^{IV} complex.
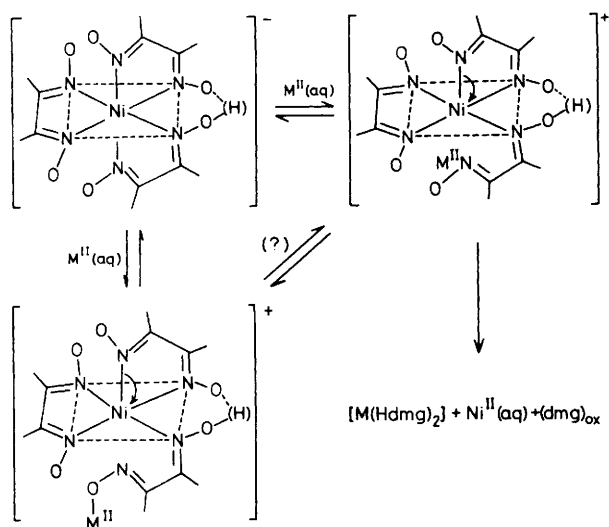
In writing the mechanism of the metal(II)-mediated acid decomposition of the Ni^{IV} complex it has been assumed that a 1 : 1 adduct is formed involving the Ni^{IV} and M^{II} species (M = Cu, Zn, or Ni) present in the medium. There was an abrupt increase in absorbance at 460 nm as soon as the Ni^{IV} and Cu^{II} were rapidly mixed at pH ca. 4, but monitoring of the absorbance increase was not possible on the stopped-flow time-scale. It has been shown [9,10] that the original Ni^{IV} complex, $[Ni(dmg)_3]^{2-}$, has a pseudo-octahedral (D_3) structure, with the dmg^{2-} units bonded through nitrogen donors only. The first (outside) protonation results in the formation of an intramolecular hydrogen bond (O−H···O) involving dioximate oxygens of two ligands; subsequent rupture of an axial Ni−N-(ligand) bond results in decomposition (with concomitant intramolecular electron transfer) of the Ni^{IV} complex. The second protonation most probably occurs via a direct proton transfer to a ring-opened nitrogen site. Thus the acid decomposition is a consequence of a ruptured Ni−N(ligand) bond in the specified pH region. The added M^{II} would, therefore, be expected to have a released (or weakened) end of a ligand nitrogen of the Ni^{IV} available. The metal(II) may be ligated to the ring-opened end or the dioximate oxygen end of the ligand to form the proposed adduct, the nature of which will largely depend on the nature of the metal(II) ion and the pH of the reaction medium; this will, in turn, be reflected in the subsequent decomposition of the adduct to give $[M(Hdmg)_2]$ and $Ni^{II}(aq)$. Apparently M^{II} has to compete with H^+ for the ligand ring-opened (nitrogen) site. This kind of ligand dissociation mechanism has been encountered frequently in reactions of complexes involving bidentate chelates. The overall picture is shown in Scheme 3.

A comparison of the apparent equilibrium quotients of the adducts, K_{add} [as defined by parameters $b(Cu)$, $d(Zn)$, and

Table 6. Comparison of various constants * for the proton-assisted and M^{II}-mediated acid decomposition of $[Ni(dmg)_3]^{2-}$

Proton-assisted		Zn^{II}-mediated		Ni^{II}-mediated	
k_{1d}/s^{-1}	2.2×10^{-6}	k_{1d}'/s^{-1}	1.5×10^{-4}	k_{1d}'/s^{-1}	1.9×10^{-5}
k_{2d}/s^{-1}	22.7	k_{2d}'/s^{-1}	27.8	k_{2d}'/s^{-1}	28.4
$k_{1d}K_{1H}/dm^3\ mol^{-1}\ s^{-1}$	1.8×10^5	$dk_{1d}'/dm^3\ mol^{-1}\ s^{-1}$	2.3×10^{-1}	$dk_{1d}'/dm^3\ mol^{-1}\ s^{-1}$	1.6×10^{-1}
$k_{2d}K_{2H}/dm^3\ mol^{-1}\ s^{-1}$	50.8	$dk_{2d}'/dm^3\ mol^{-1}\ s^{-1}$	4.3×10^4	$dk_{2d}'/dm^3\ mol^{-1}\ s^{-1}$	2.4×10^5

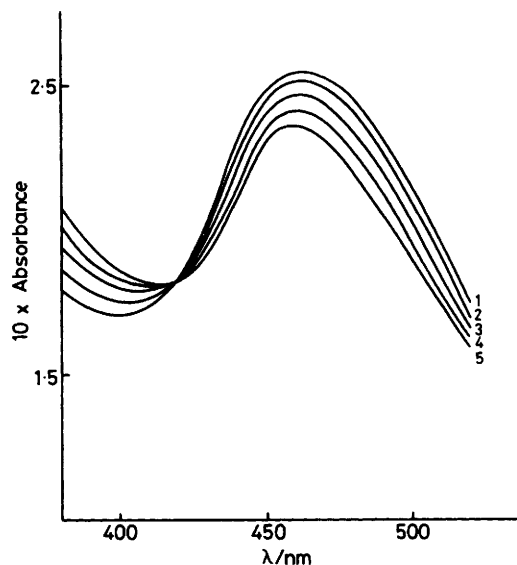* Average values; $I = 0.57$ mol dm^{-3}, 35 °C.

Scheme 3.

Figure 6. Spectral scans of solutions containing Ni^{IV} and Cu^{II} in the visible region; $[Ni^{IV}] = 2.7 \times 10^{-5}$ mol dm^{-3}, pH 5, $I = 0.57$ mol dm^{-3}, 35 °C; $10^5[Cu^{II}] = 0$ (1), 4 (2), 8 (3), 12 (4), and 16 mol dm^{-3} (5)

d(Ni)] at constant pH (ca. 4.8), formed by interaction of the Ni^{IV} complex and M^{II} (M = Cu, Zn, or Ni), shows that $K_{add(Cu)} < K_{add(Zn)} < K_{add(Ni)}$; the log k_{add} values at pH ca. 4.8 for different M^{II} show an approximately linear relationship with pK_M of M^{II}. Since the K_{add} values are strongly pH dependent, no meaningful inference can be drawn from these observations. It is, nevertheless, gratifying to note (from Tables 3 and 6) that the second-order rate constants, $k_{np}K_{nM}$ for Cu^{II} and dk_{nd} for Zn^{II} and Ni^{II}, are much lower than the rate constants for exchange of water from the first co-ordination sphere of the corresponding M^{II}(aq) (ca. 10^{10} s^{-1} for Cu^{II}, 10^8 s^{-1} for Zn^{II}, and 10^5 s^{-1} for Ni^{II}),[18] suggesting that the reactions proceed through the substitution of an aqua ligand in M^{II}(aq) by the ring-opened species of the nickel complex.

(C) *Spectrophotometric Titrations.*—The results of spectrophotometric titrations support the mechanistic picture presented. When solution mixtures of Ni^{IV} and Cu^{II} at pH 5 were rapidly scanned in the 380—500 nm range, the 460 nm band was found to decrease and gradually acquire an asymmetric shape with a slight shift towards the higher energy region. The absorbance at 390 nm, on the other hand, appeared to increase in intensity as $[Cu^{II}]$ was increased. Figure 6 shows that the original 460 nm band, *i.e.* with $[Cu^{II}]_0 = 0$, is shifted by about 15 nm when $[Cu^{II}]_0 = 16 \times 10^{-5}$ mol dm^{-3}. A clear isosbestic point was observed at 420 nm. The spectra beyond 500 nm did not show any meaningful difference when increasing amounts of Cu^{II} were added, except a gradual decrease in intensity. If it is assumed that the Ni^{IV} species and Cu^{II} undergo a 1 : 1 interaction, and since Cu^{II} and the products of the reaction have negligible absorbance in the 380—500 nm region, a Benesi-Hildebrand type equation [19] (xiii) can

$[Ni^{IV}](\Delta A)^{-1} = (K\varepsilon[Cu^{II}])^{-1} + \varepsilon^{-1}$ at $[Ni^{IV}] < [Cu^{II}]$ (xiii)

be applied to the absorbance increase at 390 nm, where K and ε respectively refer to the equilibrium quotient and the molar absorptivity of the 1 : 1 adduct. The average values of K and ε at 390 nm, as obtained from the absorbance and $[Cu^{II}]$ data in accord with equation (xiii), are found to be 662 dm^3 mol^{-1} and 8 640 dm^3 mol^{-1} cm^{-1}, respectively, at pH 5, 35 °C, and $I = 0.57$ mol dm^{-3}. In view of the fact that there may be some decomposition under the conditions employed, this value agrees fairly with the value of b (5.3 $\times$ 10^2 dm^3 mol^{-1}) obtained from the treatment of the kinetic data at pH ca. 4.85. The K value at pH 6 also agrees with that of b at pH ca. 6.15.

The 265 nm band in the u.v. spectrum of an aqueous alkaline solution (pH $\gtrsim$ 11.5) of the Ni^{IV} complex disappeared at pH ca. 6, giving rise to two new bands at 225 and 278 nm.[10] The 225 nm band was assigned to π-π^* transitions of protonated dimethylglyoxime ligand [20,21] in the complex, while the 278 nm band was thought to be caused probably by π-π^* transitions of the oxidised ligand and/or the N-protonated species [22] (produced after ring opening). When solutions of Ni^{IV} and Cu^{II} were mixed at pH 6, the spectrum of Ni^{IV} at this pH was significantly altered. While the 278 nm band was found to increase in intensity with a small but distinct shift towards higher energy, the band at 225 nm went on decreasing with increasing $[Cu^{II}]$. A clear isosbestic point was noticeable at 245 nm (Figure 7). Even though these results are in no way conclusive, they may be taken to indicate that the addition of Cu^{II} to a solution of Ni^{IV} alters the pattern of
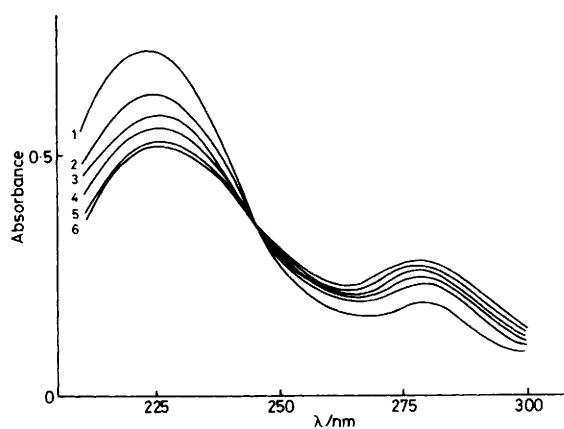
Figure 7. Spectral scans of solutions containing Ni^{IV} and Cu^{II} in the u.v. region; $[Ni^{IV}] = 5 \times 10^{-6}$ mol dm^{-3}, pH 6, $I = 0.57$ mol dm^{-3}, 35 °C; $10^{5}[Cu^{II}] = 0$ (1), 1 (2), 2 (3), 4 (4), 6 (5), and 10 mol dm^{-3} (6)

the Ni^{IV} spectrum at pH 6, and that a new species is in equilibrium with the Ni^{IV} species at this pH. Since the predominant Ni^{IV} species at pH 6 is the one-protonated species, the spectra may be considered, to a first approximation, to belong to the adduct. From the change in absorbance at 278 nm with varying $[Cu^{II}]$, and applying equation (xiii), the average values of K and ε were found to be 84.5×10^3 dm^3 mol^{-1} and 20 900 dm^3 mol^{-1} cm^{-1} at pH 6, 35 °C, and $I = 0.57$ mol dm^{-3}. The K value agrees with the b value at pH ca. 6.15 ($b = 84 \times 10^3$ dm^3 mol^{-1}). The spectrophotometric titration results with Zn^{II} and Ni^{II} were not meaningful.

Our conclusions need further confirmation; the changes occurring have inherent complexities. The unambiguous assignment of the second-protonation site in the Ni^{IV} complex is difficult as is often the case when questions of protonation of such systems are considered, and the problem is not easily resolved. The initial M^{II} co-ordination site in the adduct is also not without doubt and may or may not be related to the second-protonation site preference in the Ni^{IV} complex. Repeated attempts to record the ^{13}C n.m.r. spectra of the Ni^{IV} complex at various pH values were not successful. Experiments at higher pH (e.g. 9.5) were accompanied by copious precipitation of $[Ni(Hdmg)_2]$. Similarly, recording the ^{13}C n.m.r. spectra at pH 4.5 was not possible owing to rapid decomposition. Nevertheless, we tentatively suggest that the added M^{II} ions interact with the protonated species of the Ni^{IV} complex forming an intermediate adduct before the final products are obtained.

Acknowledgements

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