# Studies in Nickel(IV) Chemistry. Part 1. Preparation, Characterization, and Kinetics of Formation of Tris(dimethylglyoximato)nickelate(IV) in Aqueous Alkaline Media †

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

Potassium tris(dimethylglyoximato)nickelate(IV), $K_2[Ni(dmg)_3]$, has been prepared in aqueous alkaline medium from nickel(II) and dimethylglyoximate ($dmg^{2-}$) in the presence of an excess of two-electron oxidant. Electronic, i.r., and $^1H$ n.m.r. spectra are in conformity with an octahedral ($D_3$) geometry for this compound, with $dmg^{2-}$ units bonded through nitrogen donors. The lack of any significant e.s.r. signal establishes that the central nickel is in the oxidation state IV. The formation of $[Ni(dmg)_3]^{2-}$, from $Ni^{II}$ and $dmg^{2-}$ in the presence of hypoiodite generated *in situ* from tri-iodide and hydroxide, exhibits pseudo-first-order kinetics. The rate constants of formation, $k_{obs.}$, show linear dependence on $[oxidant]_0$ in the concentration range employed. At $[OH^-] = 4.8 \times 10^{-2}$ mol dm$^{-3}$, the $k_{obs.}$ values show a linear increase with increasing $[dmg^{2-}]_0$, tending to limiting values at higher relative $[dmg^{2-}]_0$. The $k_{obs.}$ values remain almost constant with decreasing $[OH^-]$ in the range $0.105 \geqslant [OH^-] \geqslant 1.1 \times 10^{-2}$ mol dm$^{-3}$, but exhibit a significant decrease with decrease in $[OH^-]$ in the range $1.1 \times 10^{-2} \geqslant [OH^-] \geqslant 6 \times 10^{-4}$ mol dm$^{-3}$. The kinetic results are interpreted in mechanistic terms.

Dioximes are good ligands for stabilization of higher oxidation states of transition metals, *e.g.* nickel(IV),[1-5] because of their π-donor character. Simek[5] reported that a solution of nickel(II) dimethylglyoximate in 1–2 mol dm$^{-3}$ KOH was easily oxidized by oxidants like hypoiodite, hypobromite, and peroxodisulphate, resulting in a red solution of a diamagnetic $Ni^{IV}$ complex. Use of lead dioxide in oxidizing a mixture of nickel(II) sulphate and dimethylglyoximate in 1.5 mol dm$^{-3}$ NaOH also yielded a red solution, which was shown from reversible polarographic studies to be a $Ni^{IV}$ complex.[6] On the other hand, the product of pulse-radiolytic treatment of an $N_2O$-saturated solution of nickel(II) sulphate and dimethylglyoximate, in 0.5 mol dm$^{-3}$ NaOH or 4 mol dm$^{-3}$ $NH_4OH$, displayed an intense band at *ca.* 450 nm; the reaction showed pseudo-first-order kinetics, and the product was assumed to be a $Ni^{III}$ species since the oxidation was brought about by one-electron oxidants such as OH or $NH_2$ radicals.[7] The reaction of $[Ni(Hdmg)_2]$ with bromine or iodine in pyridine was reported to give a compound originally believed[8] to contain nickel(IV), but later shown to be a nickel(III) species.[9] On the basis of e.s.r. studies of the red solution, Marov *et al.*[10] suggested that whereas peroxodisulphate exclusively oxidized a mixture of $Ni^{II}$ and $dmg^{2-}$ to a $Ni^{IV}$ complex, some $Ni^{III}$ species was obtained in solution on oxidation of a mixture of $Ni^{II}$ and $dmg^{2-}$ by $OX^-$ (X = Cl, Br, or I) or $H_2O_2$ in 3 mol dm$^{-3}$ $OH^-$; when the oxidizing agent was hypoiodite, the maximum accumulation of the $Ni^{III}$ species (20—30%) in solution was observed with a reactant ratio ($Ni^{II}$ : $dmg^{2-}$ : $OI^-$) of 1 : 6 : 1.8. The stoicheiometry, structure, and metal oxidation state of the red solution were the subjects of many investigations, the distribution of $Ni^{III}$ and/or $Ni^{IV}$ being strongly dependent on the experimental conditions.[3,11] In view of these conflicting reports, we were interested in the preparation, characterization, and unambiguous establishment of the oxidation state of the central metal of this complex of higher-valent nickel.

Simek[5] reported a qualitative mechanism for the formation of tris(dimethylglyoximato)nickelate(IV), envisaging an initial inner-sphere substitution of a dimethylglyoximato ligand by a hydroxo ligand in the covalent bis(dimethylglyoximato)-nickel(II), $[Ni(Hdmg)_2]$, which was followed by attachment of two other ligands and subsequent two-electron transfer. In view of the known reluctance of $[Ni(Hdmg)_2]$ to undergo exchange with a hydroxo ligand, we thought it worthwhile to investigate the kinetics of formation of the $Ni^{IV}$ species, in order to elucidate the mechanism.

## Experimental

*Materials.*—The reagents used were of analytical grade. All the solutions were freshly prepared before use by dilution exclusively with doubly distilled water. Solutions of nickel(II) sulphate or chloride (B.D.H.) were standardized by the standard edta method.[12] Fresh stock solutions of dimethylglyoximate ($dmg^{2-}$) were prepared by dissolving dimethylglyoxime (Poole, England; m.p. 241 °C) in carbonate-free potassium hydroxide solution; requisite amounts of these were used within 3 h of preparation. The estimations of $OH^-$ and oxidants were performed by standard procedures.[12] The concentrations of hydroxide in kinetic runs were determined both before and after the reactions and the results were found to be reproducible. In experiments with lower concentrations of hydroxide, the concentrations were calculated from the average pH values (±0.01 units) after correction for the ionic strength effect.[13]

*Preparation of Potassium Tris(dimethylglyoximato)nickelate(IV), $K_2[Ni(dmg)_3]$.*—Simek's method[5] was modified, yielding better results.

(a) *With chlorine gas as oxidant.* To a cold solution of nickel(II) chloride (0.1 mol) in water (10 cm$^3$), KOH (2 mol dm$^3$, 10 cm$^3$) was added. The resulting suspension of $Ni(OH)_2$ was stirred well and a stream of pure chlorine gas was passed slowly (1 cm$^3$ min$^{-1}$) until a permanent shining greyish black mass was obtained. Pure nitrogen was then bubbled through the suspension for about half an hour, after which a calculated amount of a cold alkaline (*ca.* 0.1 mol dm$^{-3}$ $OH^-$) dimethylglyoximate solution (such as to obtain a concentration of $dmg^{2-}$ slightly greater than 0.3 mol dm$^{-3}$ in the final solution) was added with vigorous stirring. The mixture was kept stirred for about 1 h, after which the resulting deep reddish brown solution was

---

† Presented in part at the All India Symposium on Recent Developments in Chemical Kinetics, Waltair, India, 1981.

*Non-S.I. Unit employed:* 1 G = $10^{-4}$ T.

filtered. The filtrate was repeatedly washed with diethyl ether and the final aqueous solution was run through a column (1.5 × 12.5 cm) of anion-exchange resin (Dowex 1 − X 8; 200—400 mesh) in $Cl^-/OH^-$ form and eluted (0.5 $cm^3$ $min^{-1}$; 0—5 °C) with 0.02 mol $dm^{-3}$ KCl adjusted to pH *ca.* 11.6. Only one coloured band appeared, the middle portion of which was collected. The solution was vacuum-dried to yield red needle-like crystals (decomp. 82 °C; 70% yield) (Found: C, 24.3; H, 4.9; N, 14.2; Ni, 10.0. Calc. for $C_8H_{12}K_2N_4NiO_4{\cdot}6H_2O$: C, 24.5; H, 5.1; N, 14.3; Ni, 10.0%).

Prolonged drying of these crystals *in vacuo* furnished a red powdery mass (Found: C, 29.4; H, 4.0; N, 17.0; Ni, 11.9. Calc. for $C_8H_{12}K_2N_4NiO_4$: C, 30.0; H, 3.8; N, 17.5; Ni, 12.2%).

(b) *With other oxidants.* Alternative methods involved use of standard hypohalogenite ($OX^-$; X = Cl, Br, or I) or peroxodisulphate solutions as oxidant. The suspension of nickel(II) hydroxide was treated with a known excess of the oxidant solution, and dimethylglyoximate solution was then added, producing the characteristic red solution. Purification and subsequent isolation of the crystals were performed as described in (a).

(c) *Using higher-valent oxides of nickel.* In a slightly modified procedure, the black higher-valent oxide [14] of nickel was employed to yield red solutions of the complex. Treatment of an alkaline solution of $Ni^{II}$ sulphate with an excess of standard peroxodisulphate solution produced a black mass which was filtered and air-dried over several days. A suspension of the black solid in water was treated with a calculated excess of an alkaline solution of dimethylglyoximate with constant stirring. The deep red colour was found to develop slowly. The best results were obtained when a slight excess of $dmg^{2-}$ (over the $[dmg^{2-}]:[Ni^{II}]$ ratio of 3 : 1) was used. The crystals were obtained after purification by anion exchange and vacuum drying.

The crystals obtained in (b) and (c) analysed satisfactorily for the formulation $K_2[Ni(dmg)_3]{\cdot}6H_2O$, showed identical electronic spectra (in aqueous solution), i.r. spectra, and $^1H$ n.m.r. spectra, and did not display any significant e.s.r. signal.

(d) *Preparation of aqueous solutions of the complex.* The aqueous solutions of the complex were made by dissolving freshly prepared crystals in water. The crystals and their aqueous solutions were stable at lower temperatures (0—5 °C), but on being warmed to *ca.* 80 °C they decomposed slowly to give nickel(II) dimethylglyoximate. The aqueous solutions in the presence of alkali (pH $\gtrsim$ 11.5) when stored at 0 °C were stable for months. However, aqueous solutions were freshly prepared before use.

*Elemental Analyses.*—Total nickel was estimated by the edta method [12] after decomposing the $Ni^{IV}$ complex in *ca.* 1 mol $dm^{-3}$ $H^+$ and adjusting the pH to *ca.* 7. Analyses for C, H, and N were performed at the Organic Chemistry Laboratory, Madras University. Elemental analyses were carried out on the crystals and on the powdery solid.

*Magnetic Susceptibility and Conductance Data.*—Room temperature (27 °C) magnetic susceptibility data of the crystalline samples were obtained by the Faraday method using an electronic vacuum microbalance (Cahn R. G.) in conjunction with an electromagnet (Brucker, Stuttgart) with $Hg[Co(SCN)_4]$ as calibration standard. The molar conductance data of an aqueous solution of the complex (5 × $10^{-4}$ mol $dm^{-3}$) were measured on a Mullard Conductivity Bridge.

*Spectra.*—Electronic spectra (in the 210—750 nm region) were recorded on a Pye Unicam SP 1 800 spectrophotometer. I.r. spectra of $H_2dmg$, $[Ni(Hdmg)_2]$, and $K_2[Ni(dmg)_3]$ were obtained for KBr discs using a Perkin-Elmer IR-337 grating instrument. $^1H$ N.m.r. spectra of $H_2dmg$ and $[Ni(Hdmg)_2]$ in $CDCl_3$ solution and $K_2[Ni(dmg)_3]$ in $(CD_3)_2SO$ were run on a Varian T 60 spectrometer with $SiMe_4$ as internal reference. E.s.r. spectra of the (powdered) crystalline complex at 300 and 123 K and of a solution of the complex (1 × $10^{-2}$ mol $dm^{-3}$) in aqueous glass at 123 K were taken on a Varian E4 *X*-band instrument (using quartz e.s.r. tubes and flat cells). The e.s.r. spectra of solution mixtures of $[Ni(dmg)_3]^{2-}$ (1 × $10^{-4}$ mol $dm^{-3}$) and L-ascorbic acid (1 × $10^{-4}$ to 3 × $10^{-4}$ mol $dm^{-3}$) were recorded by mixing equal volumes of the solutions at 0—2 °C (pH 9.2 or 3) and immediately quenching in liquid nitrogen.

*Potentiometric Measurements.*—The first and second proton-dissociation constants ($K_{a1}$ and $K_{a2}$) of $H_2dmg$ were determined by potentiometric pH titrations in an atmosphere of nitrogen, using a Systronics 335 digital pH meter equipped with glass and saturated calomel electrodes. The pH meter was standardised before use. The concentrations of $H^+$ were calculated from measured pH (±0.01 units), with due correction for the ionic strength effect.[13] The average values of $K_{a1}$ and $K_{a2}$ were, respectively, 7 × $10^{-7}$ and 4.4 × $10^{-10}$ mol $dm^{-3}$ at 30 °C [$I$ = 0.14 mol $dm^{-3}$ (KCl)].

*Oxidation Equivalence.*—Measured samples of aqueous solutions of the $Ni^{IV}$ complex (2 × $10^{-4}$ mol $dm^{-3}$) were mixed with equal portions of standard $VO^{2+}$ solutions of various concentrations (2 × $10^{-5}$ to 5 × $10^{-5}$ mol $dm^{-3}$) at pH 4—5 in citrate buffer. The complex remaining was estimated by recording the absorbance at 460 nm in an Aminco stopped-flow spectrophotometer. It was found that 2.05 ± 0.03 mol of $VO^{2+}$ reacted with 1 mol equiv. of the complex.

Potentiometric redox titrations (using platinum foil and saturated calomel electrodes) were also utilised to show that the $Ni^{IV}$ complex behaved as an effective two-electron oxidant. A known volume of the complex solution of known strength was titrated potentiometrically with a standard $As^{III}$ solution at pH 4—5. One mol of the former was found to react quantitatively with 1.03 ± 0.03 mol equiv. of $As^{III}$.

*Spectrophotometric Titrations.*—Measured samples of nickel(II) chloride and $dmg^{2-}$ solutions were mixed in the presence of a known fixed excess of the oxidant solution ($OX^-$) at pH 12.4 ($I$ = 0.14 mol $dm^{-3}$) and 30 °C. The spectra were recorded in the 210—380 and 380—650 nm regions.

From the absorbance noted at 460 nm, it was observed that 1 mol of $Ni^{II}$, in the presence of the oxidant, reacted with 3.01 ± 0.03 mol of $dmg^{2-}$ for the formation of $[Ni(dmg)_3]^{2-}$ [equation (i)]. The formation constant of $[Ni(dmg)_3]^{2-}$ was

$$Ni^{2+} + 3\,dmg^{2-} - 2\,e \longrightarrow [Ni(dmg)_3]^{2-} \qquad (i)$$

determined using earlier reported procedures.[15] {Nickel(II) was transparent at 460 nm; $[Ni(dmg)_3]^{2-}$ was the only detectable species formed under these conditions.} The log $\beta_3$ value was 10.6 ± 0.3 (pH range 11.7—12.4, aqueous medium, 30 °C, $I$ = 0.14 mol $dm^{-3}$).

*Kinetics.*—Kinetics were followed for the formation of $[Ni(dmg)_3]^{2-}$ at 460 nm ($\Delta A/\Delta t > 0$) in an Aminco stopped-flow spectrophotometer assembly with quartz windows and 10-mm light path, comprising a Beckman DU monochromator, an R-136 Hamamatsu photomultiplier, an Aminco linear log photometer, and a Tektronix 564 B storage oscilloscope. The nominal mixing time for this instrument is 2 ms. The temperature of the mixing cell was maintained (±0.1 °C) by water circulation through the cell holder. In a typical experiment, an aqueous solution of $Ni^{II}$ chloride, iodine, and potassium iodide was mixed with an aqueous alkaline solution of $dmg^{2-}$ at the appropriate temperature and ionic strength ($I$, adjusted by the supporting electrolyte, KCl). The change in absorbance at 460 nm {the absorbance maximum of $[Ni(dmg)_3]^{2-}$ in the visible region} was traced as a function of time. The rate constants calculated were reproducible to ±5%. For every entry, at least seven to ten replicates were performed. Under the conditions employed, the direct oxidation of $dmg^{2-}$ by the oxidant was negligibly small. Computations were performed with a DCM Data Products minicomputer, Microsystem 1121.

## Results and Discussion

Under the experimental conditions employed ([oxidant] $\gg$ $[Ni^{II}]$) and in the presence of an appreciable concentration of $OH^-$, the ion-exchange chromatographic and spectral data showed that $[Ni(dmg)_3]^{2-}$ was the only product. The elemental analytical data for the crystalline and powder samples satisfactorily agreed with the formulations $K_2[Ni(dmg)_3]\cdot 6H_2O$ and $K_2[Ni(dmg)_3]$, respectively. The molar conductance data of an aqueous solution ($5 \times 10^{-4}$ mol $dm^{-3}$) at 27 °C showed the complex to be a 1 : 2 electrolyte. The room temperature magnetic susceptibility data after diamagnetic corrections[5] yielded a zero effective magnetic moment showing the complex to be diamagnetic. That the complex was an effective two-electron oxidant was seen from the oxidation equivalence data.

The u.v.-visible spectrum (in the 210—380 and 380—650 nm ranges) of an aqueous solution of the complex in alkaline medium (pH 11.6—12.4) exhibited absorption maxima at 265 ($\varepsilon_{265} = 15.1 \times 10^4$ $dm^3$ $mol^{-1}$ $cm^{-1}$) and 460 nm ($\varepsilon_{460} = 9.6 \times 10^3$ $dm^3$ $mol^{-1}$ $cm^{-1}$). The former was assigned to $\pi$–$\pi^*$ transitions due to the co-ordinated $dmg^{2-}$ ligand;[16,17] the latter might be due to ligand-to-metal charge transfer (l.m.c.t.) contributions (see later). The $\pi$–$\pi^*$ band at 265 nm was obscured by a band at 278 nm produced when the aqueous solution was warmed or the pH was lowered (<9). The new band might be due to $\pi$–$\pi^*$ transitions of the oxidised form of the ligand or to an *N*-protonated species.[18]

The results of the spectrophotometric titrations (210—380 nm range) suggested that at a 3 : 1 molar ratio of $dmg^{2-}$ to $Ni^{II}$, in the presence of an excess of oxidant and an appreciable concentration of $OH^-$ ($[Ni^{II}]_0 \ll [\text{oxidant}]_0 \lesssim [dmg^{2-}]_0$), $[Ni(dmg)_3]^{2-}$ was the only detectable product formed with $dmg^{2-}$ as the ligand. The 265 nm band, characteristic of $\pi$–$\pi^*$ transitions due to co-ordinated $dmg^{2-}$, did not undergo much change even when $[dmg^{2-}]/[Ni^{II}] > 3$. However, at $[\text{ligand}]/[Ni^{II}] < 3$, the original band at 265 nm was reduced in intensity, with a shift towards the lower energy region, while a concomitant appearance of a new band at 225 nm was observed. Clear isosbestic points were noticed at 244 and 276 nm (Figure 1). Since the 225 nm band is assignable to $\pi$–$\pi^*$ transitions of the protonated forms of dimethylglyoxime,[16,17] these results (in conjunction with other spectral evidence) might be taken to indicate that under conditions where $[\text{oxidant}]_0 \gg [Ni^{II}]_0$, $[Ni(dmg)_3]^{2-}$ was the only species formed when $[dmg^{2-}]/[Ni^{II}] \geqslant 3$, and that this species underwent a change when $[dmg^{2-}]/[Ni^{II}] < 3$, leading to a new species which displayed the characteristics of the 225 nm band.

The i.r. spectrum of the powdery sample of $K_2[Ni(dmg)_3]$ exhibited, in addition to the metal–nitrogen (ligand) absorptions around 500 $cm^{-1}$, significant absorptions at 1 560 ($\nu_{C=N}$),[19] and 1 240 and 1 093 $cm^{-1}$ ($\nu_{N-O}$),[16] but no bands around 2 300, 1 750, and 3 500 $cm^{-1}$, indicating the absence of intramolecular hydrogen bonding {as in $[Ni(Hdmg)_2]$}[16] and oxime hydroxy group {as in $[Cu(H_2dmg)_2]$}[16] respectively. It is pertinent to compare here the i.r. spectra of $K_2[Ni(dmg)_3]$ with those of the isoelectronic $[Fe(Hdmg)_2]$ and $[Co(Hdmg)_3]$. While the $Ni^{IV}$ complex did not show any absorptions due to hydrogen bonding, $[Co(Hdmg)_3]$ showed a significant and broad absorption due to OH stretching at *ca.* 3 500—3 000 $cm^{-1}$, assigned[16] to a much weaker hydrogen bridge, fundamentally different from the strong intramolecular hydrogen-bonding between dioximato oxygens of two ligands co-ordinated to the metal {as in $Pd^{II}$, $Ni^{II}$, $Co^{II}$, $Cu^{II}$, $Fe^{II}$, $Fe^{III}$, and $[Co^{III}(Hdmg)_2L^1L^2]$}. The lower frequency corresponding to $\nu_{C=N}$ of $[Fe(Hdmg)_2]$ and many such complexes of $Fe^{II}$ has been assigned to metal $\longrightarrow$ ligand (antibonding) charge-transfer contributions.[16,20] We believe that the low value of $\nu_{C=N}$ in the $Ni^{IV}$ complex might be due to strong ligand (bonding) $\longrightarrow$ metal charge transfer.[3,21] The 460 nm (broad) visible absorption may, by analogy, be assigned to l.m.c.t. in the $Ni^{IV}$ complex; when a c.t. state is close to the ground state, appreciable c.t. contributions may be expected. The conclusions drawn from i.r. data and those from electronic spectral data appear to be in harmony.

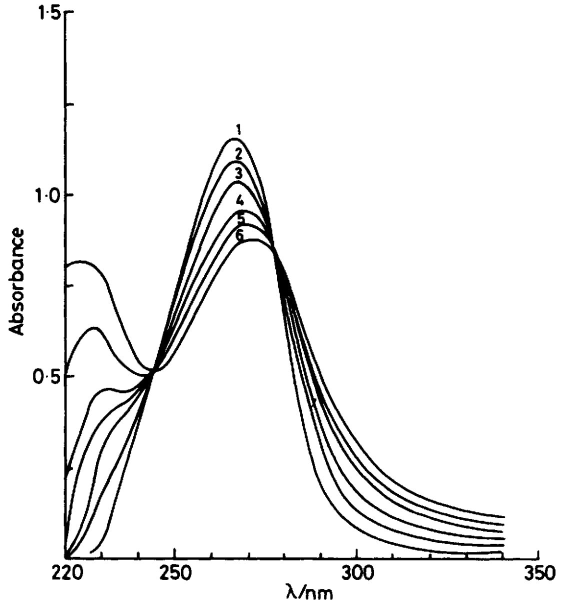


**Figure 1.** Spectrophotometric titrations; mixtures containing $[dmg^{2-}]_0 = 6 \times 10^{-5}$, $[OI^-]_0 = 10 \times 10^{-5}$, and $10^6[Ni^{II}]_0$ = 0 (1), 7 (2), 14 (3), 20 (4), 25 (5), and 30 mol $dm^{-3}$ (6); pH = 12.4, $I$ = 0.14 mol $dm^{-3}$, 30 °C

The $^1H$ n.m.r. spectrum of the anhydrous sample of $K_2[Ni(dmg)_3]$ in $(CD_3)_2SO$ solution showed only a singlet at 151.5 Hz (2.0 Hz half-width) downfield of $SiMe_4$, due to equivalent methyl protons; this is consistent with that expected from a complex with dimethylglyoximate units bonded symmetrically (*cf.* i.r. data) through nitrogen-donors only.[16,22] Thus $[Ni(dmg)_3]^{2-}$ has a pseudo-octahedral ($D_3$) structure with three $dmg^{2-}$ units co-ordinated through nitrogens to the central metal.

It has been stated that the stoicheiometry, structure, and true metal oxidation state ($Ni^{III}$, $Ni^{III}$–ligand radical ion, $Ni^{IV}$, or a mixture of $Ni^{III}$ and $Ni^{IV}$) are strongly dependent on the nature of the oxidant and the experimental conditions.[4-11] We have observed from the e.s.r. studies (see later) that $[Ni(dmg)_3]^{2-}$ (with the central nickel in oxidation state IV) is the only product when $[\text{oxidant}]_0/[Ni^{II}]_0 > 2$ (oxidant = $S_2O_8^{2-}$, $OCl^-$, $OBr^-$, or $OI^-$); but some $Ni^{III}$ species was formed in the bulk of the $Ni^{IV}$ solution with $[\text{oxidant}]_0/[Ni^{II}]_0 \lesssim 1$ (oxidant = hypohalogenite). With peroxodisulphate as the

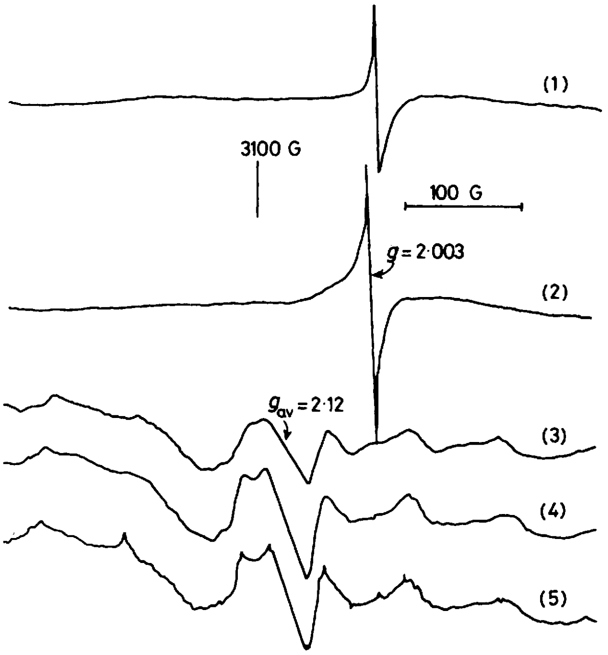


**Figure 2.** E.s.r. spectra at 123 K of (1) pure powdered $K_2[Ni(dmg)_3]\cdot 6H_2O$ (signal due to marker); (2) pure aqueous $[Ni(dmg)_3]^{2-}$ ($1.2 \times 10^{-2}$ mol dm$^{-3}$) (signal due to marker); (3) Ni$^{IV}$ solution with Ni$^{III}$ impurity ($[OI^-]_0/[Ni^{II}]_0 < 1$); (4) Ni$^{IV}$ solid with Ni$^{III}$ impurity ($[OI^-]_0/[Ni^{II}]_0 < 1$); and (5) pure $[Ni(dmg)_3]^{2-}$ ($1 \times 10^{-4}$ mol dm$^{-3}$) + L-ascorbic acid ($1 \times 10^{-4}$ mol dm$^{-3}$) (*ca.* 0 °C, pH 9.2)

oxidant, Ni$^{III}$ was not formed, as was reported earlier.[10] For example, at $[OX^-]_0 = 0.5 \times 10^{-3}$ to $0.8 \times 10^{-3}$ mol dm$^{-3}$, $[Ni^{II}]_0 = 1 \times 10^{-3}$ to $1.5 \times 10^{-3}$ mol dm$^{-3}$, and $[dmg^{2-}]_0 = 6.0 \times 10^{-3}$ to $10 \times 10^{-3}$ mol dm$^{-3}$ in 0.1 mol dm$^{-3}$ KOH, the formation of the Ni$^{III}$ species in the Ni$^{IV}$ solution was indicated by a weak e.s.r. signal for the former, but with $[OX^-]_0 = 1 \times 10^{-3}$ to $2 \times 10^{-3}$ mol dm$^{-3}$, under the same conditions, the signal for the Ni$^{III}$ was much weaker. Use of higher values of $[OX^-]_0/[Ni^{II}]_0 \gtrsim 2$ was found to render the formation of the Ni$^{III}$ impurity almost insignificant (*ca.* <1%). It is, therefore, inferred that the primary factor responsible for the formation of some Ni$^{III}$ impurity in the Ni$^{IV}$ solution is the use of small values of $[OX^-]_0/[Ni^{II}]_0$ in the preparation, and that when $[OX^-]_0/[Ni^{II}]_0 > 2$, the exclusive product is Ni$^{IV}$, with an Ni$^{III}$ impurity of less than 1%. The Ni$^{IV}$ solution or solid, prepared by employing a large excess of [oxidant] over [Ni$^{II}$], did not show any indication of the Ni$^{III}$ impurity.

Nickel(III) is a $d^7$ system, and a genuine low-spin Ni$^{III}$ in a tetragonal field will have the ground state configuration $(d_{z^2})^1$ ($s = \frac{1}{2}$).[2,23] The $g$ tensors are given by equation (ii),

$$g_\perp = 2 - 6(\lambda/\Delta), \qquad g_\parallel = 2 \qquad \text{(ii)}$$

where $\Delta$ = energy gap $E[(e_g)^3(b_{2g})^2(a_{1g})^2] - [E(e_g)^4(b_{2g})^2(a_{1g})^1]$, and $\lambda$ = spin-orbit coupling constant (*ca.* $-715$ cm$^{-1}$ in the free ion),[24] whence $g_\perp > g_\parallel$.

The e.s.r. spectra in aqueous glass of the red solution prepared using $[OX^-]_0/[Ni^{II}]_0 \lesssim 1$, or of the solid (after vacuum drying of the solution) at 123 K showed a signal at $g_{av}$ *ca.* 2.12 (Figure 2). The spectrum was, to a first approximation, axial, with $g_\perp = 2.17$, $g_\parallel = 2.03$, $A_\parallel = 23.6$ G, as might be expected for an Ni$^{III}$ species.[23,24] On the other hand, the e.s.r. spectra of a solid sample of $K_2[Ni(dmg)_3]\cdot 6H_2O$ at 123 K and of a solution of $[Ni(dmg)_3]^{2-}$ ($1 \times 10^{-2}$ mol dm$^{-3}$) in aqueous glass were devoid of any significant signal showing that the Ni$^{III}$ impurity was not in detectable quantity under the conditions. Furthermore, the e.s.r. data enabled us to distinguish between the diamagnetic Ni$^{IV}$ species and paramagnetic Ni$^{III}$ species (with the unpaired electron belonging to the metal ion) or the Ni$^{III}$ radical ion. It is, therefore, concluded that the $[Ni(dmg)_3]^{2-}$ complex prepared in this study is a genuine Ni$^{IV}$ complex.

The intermediacy of the Ni$^{III}$ species in the overall two-electron reduction of $[Ni(dmg)_3]^{2-}$ to $[Ni(Hdmg)_2]$ and/or $Ni^{2+}$ (aq) by L-ascorbic acid has been established[25] from e.s.r. spectra of a solution mixture of $[Ni(dmg)_3]^{2-}$ and ascorbic acid. The formation of a paramagnetic Ni$^{III}$ intermediate is indicated by a signal at $g_{av}$ *ca.* 2.12 (Figure 2), when solutions of Ni$^{IV}$ and ascorbic acid are mixed at pH 9.2 (or pH 3).

*Kinetics.*—In order to examine possible pathways for the formation of $[Ni(dmg)_3]^{2-}$ from Ni$^{II}$ and $dmg^{2-}$, in the presence of an excess of hypoiodite as oxidant (generated *in situ* from $I_3^-$ and $OH^-$), a series of experiments was designed. Under the conditions employed in kinetic runs (containing an excess of other reagents over Ni$^{II}$ in most cases), $[Ni(dmg)_3]^{2-}$ was the only species formed and there was virtually no formation of $[Ni(Hdmg)_2]$ or higher-valent oxides of nickel, as indicated by the perfect homogeneity of the reaction medium. In some experiments, however, instead of maintaining pseudo-first-order conditions, only a stoicheiometric excess of the reactants was used, to enable a study of the effect of variation of concentration on the reaction, Ni$^{II}$ being the limiting reactant in all cases.

As soon as the solution of Ni$^{II}$ containing $I_2$ (or $I_3^-$) was mixed with an equal volume of alkaline $dmg^{2-}$ solution, the absorbance at 460 nm underwent a very rapid decrease due to the formation of $OI^-$ or HOI from $I_2$ (or $I_3^-$) and $OH^-$ [$\lambda_{max.}$ of $I_3^-$ = 460 nm, $\varepsilon_{460}(I_3^-) = 746$ dm$^3$ mol$^{-1}$ cm$^{-1}$],[26] followed by an increase in absorbance because of the formation of $[Ni(dmg)_3]^{2-}$. The initial decrease was, however, discernible on the stopped-flow time-scale only in the case of a few 'slow' kinetic runs performed at low [$OH^-$]. This portion of the curve when extrapolated met the time-axis at zero for all replicates in such cases. The pseudo-first-order rate constants of formation of $[Ni(dmg)_3]^{2-}$, $k_{obs.}$, were computed by a least-squares analysis of log absorbance *vs.* time data in accordance with equation (iii), where $A_\infty$, $A_0$, and $A_t$, respectively,

$$\ln(A_\infty - A_t) = \ln(A_\infty - A_0) - k_{obs.}t \qquad \text{(iii)}$$

represent the absorbance at effective infinite time, the absorbance at time zero (an unknown), and the absorbance at time $t$. Equation (iii) was valid for more than three half-lives of the formation of Ni$^{IV}$ for most of the reactions. However, for a few experiments with higher $[\text{oxidant}]_0/[dmg^{2-}]_0$ (>0.7), the equation was satisfied up to only about 60% formation; the $k_{obs.}$ values were calculated accordingly. Since the deviations from first-order behaviour were small under the conditions employed, there was no difficulty in calculating $k_{obs.}$ values. (With $[\text{oxidant}]_0 \gg [dmg^{2-}]_0$, there was a slow decomposition of the complex, probably due to oxidation of the ligand environment.)

The reaction conditions were maintained such that one reactant ($OH^-$) and one product ($I^-$) were normally present at relatively high concentrations. In that event the rate constant for the formation of HOI may be thought of as being higher than the reported equilibrium constant [equation (v)], *i.e.* >46 s$^{-1}$, and as the dissociation constant[27] of HOI ≈ $10^{-10.64}$ mol dm$^{-3}$, the rate constant for formation of $OI^-$ [equation (vi)] would be $>46 \times 10^{3.36}$ s$^{-1}$ at 30 °C. Thus the assumption that the abrupt decrease in absorbance at 460 nm (in some runs) of $I_2$ (or $I_3^-$) due to its reaction with $OH^-$ to form $OI^-$ (or HOI) was too rapid to affect the main part of the reaction under study was not unjustified.

The $k_{obs.}$ values were found to exhibit pesudo-first-order dependence on $[Ni^{2+}]_0$ in the range $0.5 \times 10^{-4}$ to $4 \times 10^{-4}$ mol dm$^{-3}$. The kinetics also showed first-order dependence on $[I_2]_0$ over a 12-fold range ($5.0 \times 10^{-4}$ to $6.3 \times 10^{-3}$ mol dm$^{-3}$) (Table 1, footnote *a*). (Throughout, $[Ni^{II}]_0$ and $[I_2]_0$ represent the analytical initial concentrations.) The dependence of $k_{obs.}$ on $[dmg^{2-}]_0$ was found to be linear over a limited range ($1.0 \times 10^{-3}$ to $7.5 \times 10^{-3}$ mol dm$^{-3}$ at $[OH^-] = 6 \times 10^{-4}$ mol dm$^{-3}$, and $1.0 \times 10^{-3}$ to $8.0 \times 10^{-3}$ mol dm$^{-3}$ at $[OH^-] = 4.8 \times 10^{-2}$ mol dm$^{-3}$), beyond which it tended to non-linearity, indicating a complex dependence on $[dmg^{2-}]_0$ (Table 1). The $[OH^-]$ dependence of $k_{obs.}$ was complex (Table 2, Figure 3). The rate was almost constant when there was a ten-fold decrease in $[OH^-]$ in the range $0.105 \geqslant [OH^-] \geqslant 1.1 \times 10^{-2}$ mol dm$^{-3}$, but below $1.1 \times 10^{-2}$ mol dm$^{-3}$ $OH^-$, it showed a significant decrease with decreasing $[OH^-]$. Kinetic data could not be

**Table 1.** Observed first-order rate constants for the formation of $[Ni(dmg)_3]^{2-}$: aqueous medium, 30 °C, $I = 0.14$ mol dm$^{-3}$; $[I^-] = 2.3 \times 10^{-2}$, $[Ni^{II}]_0 = (1.0—1.4) \times 10^{-4}$, $[I_2]_0 = (2.5—2.9) \times 10^{-3}$ mol dm$^{-3}$

| $10^3[OH^-]$/ mol dm$^{-3}$ | $10^3[dmg^{2-}]$/ mol dm$^{-3}$ | $k_{obs.}$/s$^{-1}$ |
|---|---|---|
| 48 | 1.0 | 0.58 ± 0.02 |
| | 2.0 | 1.17 ± 0.06 |
| | 4.0 | 2.28 ± 0.10 [a] |
| | 4.2 | 2.38 ± 0.09 |
| | 8.0 | 4.40 ± 0.11 |
| | 10 | 5.43 ± 0.21 |
| | 20 | 10.1 ± 0.26 |
| | 25 | 12.2 ± 0.5 |
| 0.6 | 1.0 | 0.20 ± 0.006 |
| | 2.5 | 0.49 ± 0.02 |
| | 3.4 | 0.66 ± 0.03 |
| | 4.2 | 0.80 ± 0.03<br>(0.78 ± 0.03) [b] |
| | 5.6 | 1.06 ± 0.04<br>(1.10 ± 0.05) [b] |
| | 6.4 | 1.19 ± 0.04<br>(1.18 ± 0.05) [b] |
| | 7.5 | 1.40 ± 0.05<br>(1.52 ± 0.07) [b] |

[a] Linear dependence on $[I_2]_0$ is observed; $k_{obs.}$ values range from 0.42 ± 0.02 to 5.3 ± 0.2 s$^{-1}$ in the range $5 \times 10^{-4}$ to $6.3 \times 10^{-3}$ mol dm$^{-3}$ of $[I_2]_0$ (seven entries). [b] In the presence of $1 \times 10^{-4}$ mol dm$^{-3}$ added D-mannitol.

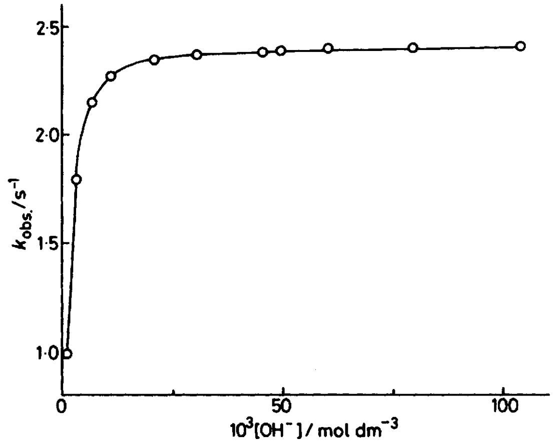


**Figure 3.** Plot of $k_{obs.}$ *vs.* $[OH^-]$; $I = 0.14$ mol dm$^{-3}$, 30 °C

$$I_2 + I^- \rightleftharpoons I_3^- \qquad K_T = 7.82 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \qquad \text{(iv)}^{a}$$

$$I_2 + OH^- \rightleftharpoons HOI + I^- \qquad K_1 = 46 \qquad \text{(v)}^{b}$$

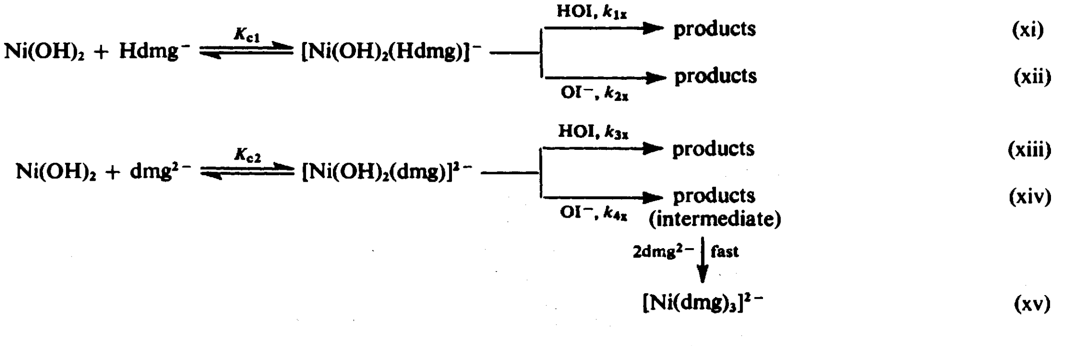
$$HOI + OH^- \rightleftharpoons OI^- + H_2O \qquad K_2 = 10^{3.36} \qquad \text{(vi)}^{c}$$

$$Ni^{2+} + OH^- \rightleftharpoons Ni(OH)^+ \qquad K_{2a} = 2.51 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \qquad \text{(vii)}^{d}$$

$$Ni(OH)^+ + OH^- \rightleftharpoons Ni(OH)_2 \qquad K_{2b} = 2.49 \times 10^{12} \text{ dm}^3 \text{ mol}^{-1} \qquad \text{(viii)}^{e}$$

$$Hdmg^- + H_2O \rightleftharpoons H_2dmg + OH^- \qquad K_{1h} = 1.4 \times 10^{-8} \qquad \text{(ix)}^{f}$$

$$dmg^{2-} + H_2O \rightleftharpoons Hdmg^- + OH^- \qquad K_{2h} = 2.3 \times 10^{-5} \qquad \text{(x)}^{f}$$



$$Ni(OH)_2 + Hdmg^- \xrightleftharpoons{K_{c1}} [Ni(OH)_2(Hdmg)]^- \begin{cases} \xrightarrow{HOI,\ k_{1x}} \text{products} & \text{(xi)} \\ \xrightarrow[OI^-,\ k_{2x}]{} \text{products} & \text{(xii)} \end{cases}$$

$$Ni(OH)_2 + dmg^{2-} \xrightleftharpoons{K_{c2}} [Ni(OH)_2(dmg)]^{2-} \begin{cases} \xrightarrow{HOI,\ k_{3x}} \text{products} & \text{(xiii)} \\ \xrightarrow[OI^-,\ k_{4x}]{} \text{products (intermediate)} \xrightarrow[\text{fast}]{2dmg^{2-}} [Ni(dmg)_3]^{2-} & \text{(xiv), (xv)} \end{cases}$$

**Scheme 1.** Aqua ligands have been omitted for convenience. [a] L. I. Katzin and E. Geburt, *J. Am. Chem. Soc.*, 1955, **77**, 5814. [b] Using $I_2 + H_2O \xrightleftharpoons{4.6 \times 10^{-13}\ \text{mol dm}^{-3}} HIO + H^+ + I^-$ and $K_w$; G. Horiguchi and H. Hagisawa, *Bull. Inst. Phys. Chem. Res. Jpn.*, 1943, **22**, 661. [c] Ref. 27. [d] Using $Ni^{2+} + H_2O \xrightleftharpoons{10^{-10.6}} Ni(OH)^+ + H^+$ and $K_w$; J. Bjerrum, G. S. Schwarzenbach, and L. G. Sillen, 'Stability Constants,' Chem. Soc. Special Publ., 1957; L. G. Sillen and A. E. Martell, *ibid.*, 1964. [e] $K_{2a}K_{2b} = (1.5 \times 10^{-16})^{-1}$; W. M. Latimer, 'Oxidation Potentials,' 2nd edn., Englewood Cliffs, New Jersey, 1962, p. 200. [f] Present work; calculated from the potentiometrically determined values of the first and second proton-dissociation constants of $H_2dmg$ (at 30 °C and $I = 0.14$ mol dm$^{-3}$).

obtained when $[OH^-] < 6 \times 10^{-4}$ mol dm$^{-3}$, owing to slow precipitation of $[Ni(Hdmg)_2]$.

*Rate Law and Mechanism.*—Interpretation of the reaction pathways must take into account the above kinetic behaviour and the fact that the formation of $[Ni(dmg)_3]^{2-}$ from $Ni^{II}$ involves two basically different but important processes of ligation of the $dmg^{2-}$ units to the central nickel and the oxidation of $Ni^{II}$ to $Ni^{IV}$. A scheme which can rationalise the observed kinetic data is presented in equations (iv)—(xv).

The literature values of the constants, as defined by equations (iv)—(viii), were used for calculations of rate data at 30 °C and $I = 0.14$ mol dm$^{-3}$, assuming the enthalpy variation with temperature to be negligible in the temperature range employed. The primary points concerning hydrolysis are that $I_2$–HOI (or $OI^-$) equilibria are rapid and that the formation of $IO_3^-$ is very slow compared with the time-scale of the experiments in the present study.

**Table 2.** Observed first-order rate constants for the formation of $[Ni(dmg)_3]^{2-}$: aqueous medium, 30 °C, $I = 0.14$ mol dm$^{-3}$; $[I^-] = 2.3 \times 10^{-2}$, $[Ni^{II}]_0 = (1.0—1.4) \times 10^{-4}$, $[I_2]_0 = (2.5—2.9) \times 10^{-3}$, $[dmg^{2-}] = (4.1—4.3) \times 10^{-3}$ mol dm$^{-3}$

| $10^3[OH^-]$/ mol dm$^{-3}$ | $k_{obs.}$/s$^{-1}$ | $k_{calc.}$/s$^{-1}$ * |
|---|---|---|
| 0.6 | 0.80 ± 0.03 | 0.82 |
| 1.0 | 0.99 ± 0.04 | 0.98 |
| 3.3 | 1.80 ± 0.06 | 1.80 |
| 6.7 | 2.15 ± 0.08 | 2.14 |
| 11 | 2.27 ± 0.09 | 2.27 |
| 21 | 2.34 ± 0.08 | 2.34 |
| 31 | 2.37 ± 0.08 | 2.36 |
| 46 | 2.38 ± 0.09 | 2.38 |
| 48 | 2.38 ± 0.09 | 2.38 |
| 50 | 2.38 ± 0.08 | 2.38 |
| 62 | 2.39 ± 0.07 | 2.38 |
| 80 | 2.39 ± 0.08 | 2.39 |
| 105 | 2.40 ± 0.1 | 2.39 |

* Calculated (average) values from a least-squares fit of data to equation (xvi).

Assuming that in the concentration ranges employed (*a*) almost all the $[I_2]_0$ is present as $OI^-$ and HOI, (*b*) no other oxidising species makes any significant contribution to the formation rate, and (*c*) $[Ni(OH)_2] = (K_{2a}K_{2b}[OH^-]^2[Ni^{2+}])/(1 + K_{2a}[OH^-] + K_{2a}K_{2b}[OH^-]^2) \approx [Ni^{2+}]_0$, the rate of

$$\frac{d[Ni^{IV}]}{dt} = \frac{\{k_{1x}K_1K_{2h}K_{c1} + (k_{2x}K_1K_2K_{2h}K_{c1} + k_{3x}K_1K_{c2})[OH^-] + k_{4x}K_1K_2K_{c2}[OH^-]^2\}[OH^-]^2[I_2]_0[dmg^{2-}]_0[Ni^{2+}]_0}{\{[I^-] + K_T[I^-]^2 + K_1[OH^-] + K_1K_2[OH^-]^2\}\{K_{1h}K_{2h} + K_{2h}[OH^-](1 + K_{c1}[dmg^{2-}]_0) + [OH^-]^2(1 + K_{c2}[dmg^{2-}]_0)\}} \quad \text{(xvi)}$$

$$k_{obs.} = \frac{(a + b[OH^-] + c[OH^-]^2)[OH^-]^2[I_2][dmg^{2-}]}{Y_1Y_2} = \frac{(a + b[OH^-] + c[OH^-]^2)[OH^-]^2[I_2][dmg^{2-}]}{Y_1[OH^-]\{K_{2h} + [OH^-] + (K_{2h}K_{c1} + [OH^-]K_{c2})[dmg^{2-}]\}} \quad \text{(xvia)}$$

where

$$a = k_{1x}K_1K_{2h}K_{c1}$$

$$b = (k_{2x}K_1K_2K_{2h}K_{c1} + k_{3x}K_1K_{c2})$$

$$c = k_{4x}K_1K_2K_{c2}$$

$$Y_1 = [I^-] + K_T[I^-]^2 + K_1[OH^-] + K_1K_2[OH^-]^2$$

$$Y_2 = [OH^-]\{K_{2h} + [OH^-] + (K_{2h}K_{c1} + [OH^-]K_{c2})[dmg^{2-}]\}$$

formation can be derived [from equations (iv)—(xv)] as in equation (xvi), which can be expressed in the form (xvia) by neglecting the $K_{1h}K_{2h}$ term in the denominator.

The intercept and slope of the plot of $1/k_{obs.}$ *vs.* $1/[dmg^{2-}]$ at constant $OH^-$, $I^-$, and $I_2$ concentrations are related as in (xvib). From the values of (intercept/slope) (7.25 and 13.15 at

$$\text{(intercept/slope)} = \frac{K_{c1}K_{2h} + K_{c2}[OH^-]}{K_{2h} + [OH^-]} \quad \text{(xvib)}$$

$[OH^-] = 6 \times 10^{-4}$ and $4.8 \times 10^{-2}$ mol dm$^{-3}$, respectively), the values of $K_{c1}$ and $K_{c2}$ were calculated as 169 ± 7 and 7.2 ± 0.4 dm$^3$ mol$^{-1}$.

Rearrangement of equation (xvia) gives (xvic) or (xvid) since

$$\frac{k_{obs.}Y_1Y_2}{[OH^-]^2[I_2][dmg^{2-}]} = a + b[OH^-] + c[OH^-]^2 \quad \text{(xvic)}$$

$$\frac{k_{obs.}Y_1(1 + K_{c2}[dmg^{2-}])}{[I_2][dmg^{2-}]} = a + b[OH^-] + c[OH^-]^2 \quad \text{(xvid)}$$

in the concentration ranges employed $Y_2 \approx [OH^-]^2(1 + K_{c2}[dmg^{2-}])$.

At constant $[I^-]$ and limiting $[Ni^{II}]$, a least-squares fit of the data of Table 2 in accord with (xvid) [or (xvic)] furnished the values of *a*, *b*, and *c* as (2.9 ± 0.2) × 10$^4$ dm$^3$ mol$^{-1}$ s$^{-1}$, (5 ± 0.3) × 10$^5$ dm$^6$ mol$^{-2}$ s$^{-1}$, and (2.3 ± 0.1) × 10$^{10}$ dm$^9$ mol$^{-3}$ s$^{-1}$, respectively. The $k_{calc.}$ values, as calculated using these values, agree well with the experimental $k_{obs.}$ values (Table 2). The unambiguous values of $k_{1x}$ and $k_{4x}$ calculated were (1.62 ± 0.08) × 10$^5$ and (3.04 ± 0.2) × 10$^4$ dm$^3$ mol$^{-1}$ s$^{-1}$, respectively, at 30 °C and $I = 0.14$ mol dm$^{-3}$

Simek's postulated mechanism [5] appears untenable, as no $[Ni(Hdmg)_2]$ is formed. However, an alternative mechanism (Scheme 2) with some modifications to Simek's scheme can also explain the present data. Since almost no $[Ni(Hdmg)_2]$ is formed under the conditions employed, it can be assumed that $K_{20}[Ni(dmg)_2{}^{2-}][Hdmg^-] \ll k_{-19}[Ni(Hdmg)_2][OH^-]^2 \gg k_{19}$-$[Ni(dmg)_2{}^{2-}]$. If the magnitude of the values reported for $K_{17}$, $K_{18}$, and $K_{19}$ ($K_{17}K_{18}K_{19} \gtrsim 10^{22.5}$, $K_{18} > K_{17}$, at 25 °C and in 50% aqueous dioxan) [28] is any indication, under the conditions $[Ni^{2+}]_0 \ll [dmg^{2-}]_0$, the oscilloscopic response for tracing the absorbance increase (at 460 nm for $[Ni(dmg)_3]^{2-}$ formation) would miss the steps represented by equations (xvii) and (xviii). Then equation (xxii) applies. In this event, from equations (xvii)—(xx), a rate expression essentially similar to equation (xvi) is derivable.

Schemes 1 and 2 basically differ only in the pattern of

$$[Ni(dmg)_2]^{2-} = \frac{K_{17}K_{18}[Ni^{2+}]_0[dmg^{2-}]_0^2}{1 + K_{17}[dmg^{2-}]_0 + K_{17}K_{18}[dmg^{2-}]_0^2} \approx [Ni^{2+}]_0 \quad \text{(xxii)}$$

$$\mathrm{Ni^{II}} + \mathrm{dmg^{2-}} \rightleftharpoons [\mathrm{Ni(dmg)}] \qquad K_{17} \qquad \text{(xvii)}$$

$$[\mathrm{Ni(dmg)}] + \mathrm{dmg^{2-}} \rightleftharpoons [\mathrm{Ni(dmg)_2}]^{2-} \qquad K_{18} \qquad \text{(xviii)}$$

$$[\mathrm{Ni(dmg)_2}]^{2-} + 2\,\mathrm{H_2O} \rightleftharpoons [\mathrm{Ni(Hdmg)_2}] + 2\,\mathrm{OH^-} \quad K_{19} = k_{19}/k_{-19} \qquad \text{(xix)}$$

$$[\mathrm{Ni(dmg)_2}]^{2-} + \mathrm{Hdmg^-} \overset{K_{20}}{\rightleftharpoons} [\mathrm{Ni(dmg)_2(Hdmg)}]^{3-} - \left\{ \begin{array}{ll} \xrightarrow{\mathrm{HOI},\ k_{1f}} \text{products} & \text{(xx)} \\ \xrightarrow[\mathrm{OI^-},\ k_{2f}]{} \text{products} & \text{(xxa)} \end{array} \right.$$

$$[\mathrm{Ni(dmg)_2}]^{2-} + \mathrm{dmg^{2-}} \overset{K_{21}}{\rightleftharpoons} [\mathrm{Ni(dmg)_3}]^{4-} - \left\{ \begin{array}{ll} \xrightarrow{\mathrm{HOI},\ k_{3f}} \text{products} & \text{(xxi)} \\ \xrightarrow[\mathrm{OI^-},\ k_{4f}]{} \text{products} & \text{(xxia)} \end{array} \right.$$

**Scheme 2.** Products include $[\mathrm{Ni(dmg)_3}]^{2-}$

ligation of two out of the three $\mathrm{dmg^{2-}}$ units. In the former case, they are assumed to be ligated in very rapid steps after the rate-determining electron transfer has taken place with the one $\mathrm{dmg^{2-}}$ ligated $\mathrm{Ni^{II}}$ species; however, in the latter, the ligation of the third $\mathrm{dmg^{2-}}$ and the subsequent electron transfer are envisaged as important events. The present kinetic data are insufficient to differentiate between the two schemes, but as a means of distinguishing between possibilities, Scheme 2 appears more likely since $\mathrm{Ni^{IV}}$ complexes are relatively substitution inert (we thank a referee for this suggestion). However, further evidence appears necessary for an unequivocal choice.

## Acknowledgements

Thanks are due to the U.G.C. and C.S.I.R., New Delhi for grants (under National Associate and S.R. schemes), and research fellowships (to S. A. and G. N.). We thank the Director, C.L.R.I. for some of the facilities, and Professor P. S. Radhakrishna Murti and Dr. T. Ramasami for discussions.

## References

1 E. I. Baucom and R. S. Drago, *J. Am. Chem. Soc.*, 1971, **93**, 6469.
2 R. S. Drago and E. I. Baucom, *Inorg. Chem.*, 1972, **11**, 2064.
3 A. Chakravorty, *Coord. Chem. Rev.*, 1974, **13**, 1; A. N. Singh, R. P. Singh, J. G. Mohanty, and A. Chakravorty, *Inorg. Chem.*, 1977, **16**, 2597; K. Nag and A. Chakravorty, *Coord. Chem. Rev.*, 1980, **31**, 87 and refs. therein.
4 M. A. Bambenek and R. T. Pflaum, *Inorg. Chem.*, 1963, **2**, 289; M. K. Boreiko, B. I. Kazantsev, and I. I. Kalinichenko, *Russ. J. Inorg. Chem.*, 1967, **12**, 137; I. I. Kalinichenko and M. K. Boreiko, *ibid.*, 1969, **14**, 401; M. Bartusek and A. Okac, *Collect. Czech. Chem. Commun.*, 1961, **26**, 883.
5 M. Simek, *Collect. Czech. Chem. Commun.*, 1962, **27**, 220, 461 and refs. therein.
6 D. J. Davis and E. A. Boudreaux, *J. Electroanal. Chem.*, 1964, **8**, 434.
7 J. Lati and D. Meyerstein, *Isr. J. Chem.*, 1972, **10**, 735.
8 L. E. Edelman, *J. Am. Chem. Soc.*, 1950, **72**, 5765; M. Simek, *Collect. Czech. Chem. Commun.*, 1962, **27**, 337.
9 A. S. Foust and R. H. Soderberg, *J. Am. Chem. Soc.*, 1967, **89**, 5507; H. J. Keller and K. Seibold, *ibid.*, 1971, **93**, 1309.
10 I. N. Marov, E. K. Invanova, A. T. Paniflov, and N. P. Luneva, *Russ. J. Inorg. Chem.*, 1975, **20**, 67.
11 D. G. Batyr and L. Ya. Kistruga, *Russ. J. Inorg. Chem.*, 1975, **20**, 69.
12 A. I. Vogel, ' A Text Book of Quantitative Inorganic Analysis,' 4th edn., ELBS and Longman, London, 1978.
13 L. Meites, ' Handbook of Analytical Chemistry,' McGraw-Hill, London, 1963, sect. 1, p. 8.
14 W. Levason and C. A. McAuliffe, *Coord. Chem. Rev.*, 1974, **12**, 172 and refs. therein.
15 H. M. Irving and H. S. Rossotti, *J. Chem. Soc.*, 1953, 3397; 1954, 2904.
16 K. Burger, I. Ruff, and F. Ruff, *J. Inorg. Nucl. Chem.*, 1965, **27**, 179; K. Burger, ' Coordination Chemistry: Experimental Methods,' Butterworths, London, 1973, pp. 122—295, 389.
17 M. Bossa and G. O. Morpurgo, *Ricerca Sci.*, 1967, **37**, 1131; G. O. Morpurgo and A. A. G. Tomlinson, *J. Chem. Soc., Dalton Trans.*, 1977, 744.
18 R. M. Silverstein and G. C. Bassler, ' Spectroscopic Identification of Organic Compounds,' 2nd edn., Wiley, New York, 1967, ch. 5.
19 M. S. Ma and R. J. Angelici, *Inorg. Chem.*, 1980, **19**, 363; A. Nakamura, A. Konishi, and S. Otsuka, *J. Chem. Soc., Dalton Trans.*, 1979, 488.
20 N. Sanders, *J. Chem. Soc. A*, 1971, 1563; K. Nakamoto, *Adv. Chem. Coord. Comp.*, 1961, 437.
21 J. G. Mohanty, R. P. Singh, and A. Chakravorty, *Inorg. Chem.*, 1975, **14**, 2179.
22 D. R. Boston and N. J. Rose, *J. Am. Chem. Soc.*, 1968, **90**, 6859; R. S. Drago and J. H. Eliss, *J. Am. Chem. Soc.*, 1977, **99**, 6570.
23 A. G. Lappin, C. K. Murray, and D. W. Margerum, *Inorg. Chem.*, 1978, **17**, 1630.
24 L. F. Mehne and B. B. Wayland, *Inorg. Chem.*, 1975, **14**, 881; A. Desideri and J. B. Raynor, *J. Chem. Soc., Dalton Trans.*, 1977, 2051.
25 S. Acharya, G. Neogi, R. K. Panda, and D. Ramaswamy, *J. Chem. Soc., Dalton Trans.*, submitted for publication.
26 A. D. Awtry and R. E. Connick, *J. Am. Chem. Soc.*, 1951, **73**, 4546.
27 Y.-T. Chia, U.S. Energy Commission Report UCRL-8311, 1958 (*Chem. Abstr.*, 1959, **53**, 2914e).
28 K. Burger and D. Dyrssen, *Acta Chem. Scand.*, 1963, **17**, 1489; K. Burger, L. Korecz, I. B. A. Manuaba, and P. Mag, *J. Inorg. Nucl. Chem.*, 1966, **28**, 1673; K. Burger and E. Papp-Molnar, *Acta Chim. Acad. Sci. Hung.*, 1967, **53**, 111.

*Received* 18*th May* 1982; *Paper* 2/828