

Synthesis & Characterisation of Isomers of Bis(thiosalicylohydrazidato)nickel(II) and Kinetics & Mechanisms of Their Interconversion Reactions in Solution

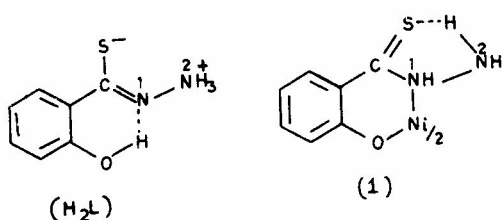
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Bis(thiosalicylohydrazidato)nickel(II), $[\text{Ni}(\text{HL})_2]$ has been found to exist in pale yellow *trans*-I, green *cis*-II and greenish yellow *trans*-III forms. In each isomer bonding sites are oxygen and secondary amine nitrogen. In alkaline medium *trans*-I as well as *cis*-II isomer get oxidised and are transformed to chocolate coloured (S, O) bonded disulphide, $[\text{Ni}_2\text{L}_4]$ with the liberation of hydrogen gas. Kinetics of *cis*-II \rightarrow *trans*-I isomerisation in DMF in the presence of acid and of *trans*-I \rightarrow *cis*-II isomerisation in DMSO have been reported. The former transformation takes place through the formation of conjugate-acid and the latter through an associative mechanism involving the formation of pentacoordinated species as an intermediate. The role of water in DMSO in *trans*-I \rightleftharpoons *cis*-II isomerisation is pH dependent. The plausible mechanism of *cis*-II \rightarrow *trans*-I isomerisation in DMF is suggested to involve the attack of polarized DMF on the basic and acidic centres of the coordinated ligand through hydrogen bonding. In *cis*-II \rightleftharpoons *trans*-I isomerisation, similar polarization phenomenon also occurs with the attack of polarized H_2O as required by the system. Isomerisation of *cis*-II \rightarrow *trans*-I in solid state has been found to take place through a twist mechanism involving formation of four-coordinated tetrahedral species as an intermediate. Kinetics of *cis*-II \rightarrow (S, O) bonded disulphide species in solution suggest the transformation to occur through free radical intermediate species resulting by the rearrangement of bonding sites of *cis*-II isomer.

In an earlier paper¹ we reported the interesting behaviour of thiosalicylohydrazide (H_2L) and its derivatives with metal ions. Interesting stereochemical and reactivity patterns of its complex, bis(thiosalicylohydrazidato)nickel(II), $[\text{Ni}(\text{HL})_2]$ (I) in the presence of different nucleophiles in acid and alkaline media were observed². It was further noted³ that I changed its colour from pale yellow to green on treatment with mild alkali and to red when treated with strong alkali. This red species transformed first to green and then to pale yellow on treatment with acid. We believe that these colour changes might be associated either with a change in geometry or in bonding or in formation of free radical species⁴. All these observations lead us in search of isomers of I or any other new product in solid state and to perform the kinetic experiments on the observed interconversion phenomena for venturing the mechanistic path of transformation. The present paper reports (i) the synthesis and characterisation of isomers of I, (ii) reaction kinetics and mechanisms of isomerisations in solution and (iii) the plausible mechanism of oxidation of $[\text{Ni}(\text{HL})_2]$ through the formation of base-promoted free radical species.



Materials and Methods

All chemicals and solvents used were of AR grade. The solvents were distilled before use and water was doubly distilled.

trans-Bis(thiosalicylohydrazidato)nickel(II), $[\text{Ni}(\text{HL})_2]$ (pale yellow) (I)

It was prepared following the method reported by us¹. This may be synthesised from isomer-II derived from I by reacting II with dil. mineral acid. Preparation of this compound was also possible by pyrolysis of II at 170°C in dynamic air instead of doing mild acid treatment (Found: C, 42.0; H, 3.7; N, 14.3; Ni, 15.0. Calc. for $\text{C}_{14}\text{H}_{14}\text{N}_4\text{S}_2\text{O}_2\text{Ni}$: C, 42.8; H, 3.6; N, 14.3; Ni, 15.0%).

cis- $[\text{Ni}(\text{HL})_2]$ (green) (II)

Ammonium hydroxide (10 ml, 3 mol dm⁻³) was added to I (1 g) and stirred for 2 hr. The pale yellow solid slowly transformed to green. The green compound was filtered, washed with water and dried in a desiccator over fused calcium chloride (Found: C, 42.4; H, 3.6; N, 14.1; Ni, 14.9. Calc. for $\text{C}_{14}\text{H}_{14}\text{N}_4\text{S}_2\text{O}_2\text{Ni}$: C, 42.8; H, 3.6; N, 14.3; Ni, 15.0%).

trans- $[\text{Ni}(\text{HL})_2]$ (greenish yellow) (III)

Isomer-I (1 g) was dissolved in DMSO (20 ml) and stirred for 10 min. Water was added dropwise to the filtered solution until a turbidity appeared. On keeping greenish yellow crystals separated out slowly. The crystals were filtered, washed with water and dried in a

desiccator over fused calcium chloride (Found: C, 42.9; H, 3.5; N, 14.2; Ni, 15.1. Calc. for $C_{14}H_{14}N_4S_2O_2Ni$: C, 42.8; H, 3.6; N, 14.3; Ni, 15.0%).

$[Ni_2L_4]$ (chocolate) (IV)

The mixture of I and alcoholic KOH solution (25 ml , 0.25 mol dm^{-3}) was stirred for 30 min and then filtered. A chocolate coloured precipitate was found to separate slowly while neutralising the chocolate coloured filtrate to pH 6-7 by adding 1 mol dm^{-3} hydrochloric acid dropwise to it. The precipitate was filtered, washed thoroughly with water, recrystallised from acetone and dried in a desiccator over fused calcium chloride. IV can also be prepared starting from II following the same route (Found: C, 42.9; H, 3.2; N, 14.2; Ni, 15.2. Calc. for $C_{28}H_{24}N_8S_4O_4Ni_2$: C, 43.0; H, 3.1; N, 14.3; Ni, 15.0%). The mol. wt of IV, determined using Knauer vapour pressure osmometer, came out to be 765 (calc. 781.4).

Physical measurements

The instruments used for recording IR, far-IR, electronic (solution and mull), diffuse reflectance and EPR spectra, and for measuring magnetic susceptibilities and conductances were the same as reported earlier^{1,2}. For kinetic experiments absorbance was recorded with the help of Pye-Unicam SP8-150 and Hilger spectrophotometers. Isomerisation in solid state was studied using a Hungarian MOM derivatograph. The pH values were measured with a Beckman 4500 pH meter. The X-ray powder diffraction patterns were recorded on a Philips powder diagram camera, using CuK_α radiation.

Kinetic experiments

$Cis-II \rightleftharpoons trans-I$ isomerisation was studied spectrophotometrically in DMF and DMF containing $HClO_4$ ($\sim 70\%$) following the change in absorbance at 780 nm. The acid concentration ($\sim 6.9 \times 10^{-3}\text{ mol dm}^{-3}$) was kept at least seven times higher than the $cis-II$ concentration ($\sim 1.0 \times 10^{-4}\text{ mol dm}^{-3}$) in order to ensure pseudo-first order conditions. Kinetic runs for $trans-I \rightarrow cis-II$ was followed in DMSO as well as in DMSO-water mixture. Pseudo-first order condition was also maintained during water addition to DMSO. Microsyringe was used to add water to DMSO solution. Ionic strength was adjusted in both the cases by the addition of tetramethylammonium perchlorate. The kinetics have been studied up to three half-lives in each case. The observed rate constants were evaluated from the linear first order plots of $\log_{10}(A_t - A_\infty)$ versus time for $cis-II \rightarrow trans-I$ and $\log_{10}(A_\infty - A_t)$ versus time for $trans-I \rightarrow cis-II$, where A_t is the absorbance at any time (t) and A_∞ is the absorbance evaluated from values of $trans-I$ ($\epsilon_{780}\text{ nm}$, $2100\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$ in DMF)

and $cis-II$ ($\epsilon_{775}\text{ nm}$, $3800\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$ in DMSO) respectively.

Kinetic runs for $cis-II$ to the oxidised (S, O) bonded species were carried out as follows: $2 \times 10^{-2}\text{ mol dm}^{-3}$ DMF solution of $cis-II$ was prepared accurately. An aqueous solution (total volume 50 ml) containing requisite amount of sodium hydroxide and sodium perchlorate (to maintain the ionic strength of 0.10 mol dm^{-3}) was thermostated for about 20-30 min. To this a solution (0.25 ml) of $cis-II$ was injected by a microsyringe. The whole solution was shaken vigorously and then placed in the thermostatic bath. An aliquot from this was immediately withdrawn with the help of jacketted pipette containing ice pieces to quench the reaction and its absorbance noted at 850 nm.

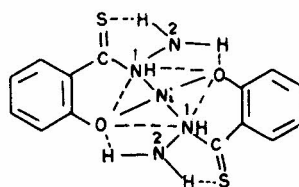
Kinetic runs for all the systems were carried out at three/four different temperatures, varying $[H^+]$ (6.9 to $41.4 \times 10^{-3}\text{ mol dm}^{-3}$), H_2O ($2.7 \times 10^{-1}\text{ mol dm}^{-3}$) and $[OH^-]$ (2.5 to $10.0 \times 10^{-2}\text{ mol dm}^{-3}$) in the respective systems. The activation parameters (ΔH^\ddagger and ΔS^\ddagger) were calculated from the Eyring plots of $-\log(k_2h/KT)$ versus $1/T$.

Activation energy (E_a) for $cis-II \rightarrow trans-I$ transformation in solid state was determined from the analysis of DTA curve using Borchardt and Daniels⁵ equation. ΔH^\ddagger value was evaluated from the area of DTA curve.

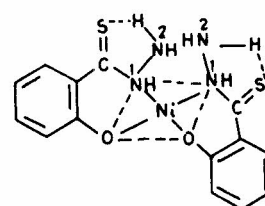
Results and Discussion

Isomerisation of $trans-I$ (pale yellow) to $cis-II$ (green)

Treatment of $[Ni(HL)_2]$ (pale yellow) (I) with ammonia (3 mol dm^{-3}) affords the isomeric green product II which is diamagnetic and nonelectrolyte. IR and PMR spectral data (Tables 1 and 2) of the green product suggest Ni-N¹ and Ni-O bonding as described earlier¹ for pale yellow form (I). However, $\nu(NH_2)$, $\rho_w(NH_2)$, $\nu(Ni-N)$ and $\nu(Ni-O)$ of II are found to be split (Table 1). But for high intensities, the electronic spectral band positions (Table 3) of II are not much different from those of I in the same solvent, indicating that II possesses a lower symmetry than the parent I. This loss in symmetry^{6,7} is probably due to cis -configuration (2) of II. This implies that the parent I has a $trans$ -configuration (3). The $cis-II$ does not involve both the hydrogens of $-N^2H_2$ in hydrogen bonding as is evident from the shift of the $-N^2H_2$ proton signal (Table 2) towards higher field. On the



(2)



(3)

Table 1—Infrared Spectral Data (cm^{-1}) of Isomers of $[\text{Ni}(\text{HL})_2]$ and $[\text{Ni}_2\text{L}_4]$ ($\text{H}_2\text{L} = \text{thiosalicylohydrazide}$)

Compound	$\nu(\text{NH}_2)$	$\beta(\text{NH}_2)/(\text{NH}) + \nu(\text{CN})$	$\rho_w(\text{NH}_2)^a$	$\rho_w(\text{NH}_2)^b$	$\nu(\text{CS}) + \nu(\text{NH}) + \nu(\text{CN})$	$\nu(\text{Ni}-\text{N})$	$\nu(\text{Ni}-\text{O})$
<i>trans</i> -I ^{c,d}	3200s	1482vs 1445m	1380m 1300vw	935w	750s	535w, 520w 412s, 392vw	310(sh) 292vs
<i>cis</i> -II ^d	3260(sh) 3210s	1480vs 1442s	1380m 1338m 1310w	935vw	750vs	535w, 520w 410vs, 390w	310w, 291vs
<i>trans</i> -III ^d	3205s 3080br	1495(sh) 1480vs 1440s	1380m 1340(sh) 1310w	930vw	750vs	535(sh), 520m 410s, 390(sh)	305(sh), 290s
$[\text{Ni}_2\text{L}_4]$	3030w	1470vs 1450(sh)	1365m		745s	405 ^e , 390m	310(sh), 303w, 285(sh)

(a) In-plane NH_2 wagging¹⁰; (b) NH_2 wagging; (c) sample synthesised from *cis*-II also shows identical spectrum; (d) I, II and III stand for $[\text{Ni}(\text{HL})_2]$; (e) $\nu(\text{Ni}-\text{S})$.

 Table 2—PMR Spectral Data (in δ -scale relative to TMS) of Isomers of $[\text{Ni}(\text{HL})_2]$ and $[\text{Ni}_2\text{L}_4]$

$[\text{H}_2\text{L} = \text{thiosalicylohydrazide}$; spectra of *trans*-I, *cis*-II and *trans*-III were recorded in pyridine- d_5 and that of Ni_2L_4 in acetone- d_6]

Compound	Ring protons	$-\text{N}^2\text{H}_2$	$-\text{N}^1\text{H}_2$
<i>trans</i> -I	7.00m } (6) 7.30m } 8.60d(2)	7.90-10.66bs(4)	11.16-13.16bs(2)
<i>cis</i> -II	6.97m } (6) 7.30m } 8.60d(2)	7.90-10.00bs(4)	11.33-12.66bs(2)
<i>trans</i> -III	7.34m(6) 8.60d(2)	8.00-10.10bs(4)	12.51-13.51bs(2)
$[\text{Ni}_2\text{L}_4]$	6.80-8.60br(16)	2.90bs(8)	

 Table 3—Electronic Spectral Data^a (cm^{-1}) of Isomers of $[\text{Ni}(\text{HL})_2]$ and $[\text{Ni}_2\text{L}_4]$

($\text{H}_2\text{L} = \text{thiosalicylohydrazide}$)

Compound	λ_{max}		λ_{max}^b (mull)	λ_{max}^b (diffuse reflectance)
	In DMSO ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)	In DMF ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)		
<i>trans</i> -I ^c	10638(200) 12820(400) 18132sh(110) 20080sh(150) 22727sh(260)	11467(1400) 12820(2100) 18248(780) 19685(980) 22222(1050) 23585(1100)	17857 22989sh	17544 22727sh
<i>cis</i> -II ^c	10753(3400) 12903(3800) 18182sh(1200) 19608(1500) 21978(1450)	11415(4800) 12820(6300) 18116(2400) 20000(3500) 21186(4400) 22222(4900) 23585(5700)	14085 22727sh	12987 17391 18349sh 21739
<i>trans</i> -III ^c	10638(300) 12821(350) 18518sh(160) 19608sh(200)		10204 12195 17544 23529sh	17241 22727
$[\text{Ni}_2\text{L}_4]$	20833(5100) 23529(7300) 24691(7400)		17094sh 22727sh 28169	16667sh 17094sh 21978br

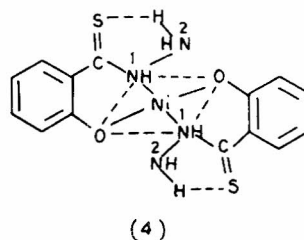
(a) Mull spectral range (28571-8333 cm^{-1}); reflectance spectral range (28571-12500 cm^{-1}); (b) arbitrary absorbance; (c) I, II and III stand for $[\text{Ni}(\text{HL})_2]$.

other hand, both the hydrogens of $-N^2H_2$ of *trans*-I are hydrogen bonded as is evident from the downfield shift of $-N^2H_2$ proton signal (Table 2) compared to that of II. The difference in the characteristic $\rho_w(NH_2)$ at $\sim 1350\text{ cm}^{-1}$ in the two isomers (I and II) seems to be due to different modes of hydrogen bonding of $-N^2H_2$ group⁸. The diffuse reflectance as well as electronic spectra in mull (Table 3) of II are different from the parent I, and according to Maki⁹ the bands are ascribed to the $^1A_{1g}(D) \rightarrow ^1A_{2g}(G)$, $^1A_{1g}(D) \rightarrow ^1B_{2g}(G)$, $^1A_{1g}(D) \rightarrow E_g(G)$ transitions. However, these two spectra cannot distinguish between *cis* and *trans*. The *d*-lines (Table 4) of *trans*-I and *cis*-II show that the crystal symmetries of the two compounds are not the same, possibly due to different modes of hydrogen bonding.

Isomerisation of trans-I (pale yellow) to trans-III (greenish yellow)

Addition of water to DMSO solution of *trans*-I affords an isomeric, diamagnetic and nonelectrolyte greenish yellow product (III). IR and electronic spectral data of III (Tables 1 and 3) in DMSO are almost similar to those of *trans*-I, suggesting III to be a *trans*-isomer possessing similar bonding sites. However, diffuse reflectance and mull spectra (Table 3) of III are different from those of I indicating structural differences in I and III. This is further supported by the fact that freshly prepared DMSO solutions of I and III

having almost similar colour, gave different coloured solutions when kept for equal span of time; I was converted into green and III into red. In the PMR spectrum $-N^2H_2$ protons in III appear at the same position as observed in the case of II, suggesting that one of the hydrogens of $-N^2H_2$ is involved in hydrogen bonding as shown in (4). Structurally two different isomeric species characterised by changes of *d*-lines (Table 4) and having *trans* planar configuration (D_{2h} symmetry) are not unlikely. The occurrence of two *trans* forms such as α -*trans* and β -*trans* of bis(N-methylsalicylaldiminato)nickel^{10,11} can be cited in support of this.



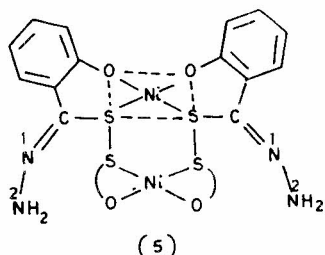
Transformation of trans-I (N¹, O bonded) (pale yellow) to (S, O) bonded oxidised (chocolate) product (IV)

Reaction of *trans*-I with alcoholic KOH affords chocolate coloured solution. On neutralising this solution with dil. hydrochloric acid, a diamagnetic, nonelectrolyte, chocolate precipitate IV separates out, which analyses for $C_{28}H_{24}N_8S_4O_4Ni_2$. Mol. wt determination supports this formulation. The PMR spectrum of IV displays $-N^2H_2$ signal at high field ($\delta 2.90$) suggesting the noninvolvement of N^1 in bonding with the metal ion, unlike the isomers I, II and III. Both IR and PMR spectra (Tables 1 and 2) exhibit the absence of OH group suggesting Ni—O bonding. On the other hand, the ν_{CS} appearing at $\sim 750\text{ cm}^{-1}$ in I is shifted to lower frequency in IV, suggesting Ni—S bonding. This is supported by surprisingly high intensity of the bands in solution. The three bands (Table 3) in the absorption spectrum at 20833, 23529 and 24691 cm^{-1} are closely spaced and arise due to overlap of CT and *d*→*d* transitions. These have been assigned to $(M \rightarrow L_{\pi^*}) + (^1A_{1g} \rightarrow ^1B_{1g})?$, $(M \rightarrow L_{\pi^*}) + (^1A_{1g} \rightarrow ^1E_g)?$ and $M \rightarrow L_{\pi^*}$ transitions respectively on the basis of work of Ballhausen¹² and Livingstone *et al.*¹³. The preparative procedure of IV, $[Ni_2L_4]$ is almost similar to that of binuclear oxidised glutathione Cu(II) complex¹⁴. Moreover, the H_2L possesses thiol group in alkaline medium. As a result, there is greater possibility of H_2L getting oxidised, thereby forming a bridge between two molecules of (S, O) bonded *cis*- $[Ni(HL)_2]$ in solution, as this configuration is the most feasible one to form disulphide via S—S sites (5). The oxidation is indirectly supported by the absence of

Table 4—X-Ray Powder Data (*d*-lines) for Isomers of Bis(thiosalicylohydrazidato)Nickel(II)

<i>trans</i> -I	<i>cis</i> -II	<i>trans</i> -III
9.38 (w)	6.42 (m)	9.21 (w)
7.40 (w)	5.78 (vs)	7.43 (w)
6.59 (w)	4.06 (m)	6.49 (w)
5.96 (vs)	3.72 (vs)	5.90 (vs)
4.99 (m)	3.35 (s)	5.08 (vw)
4.44 (w)	3.20 (s)	4.65 (vw)
4.19 (w)	3.08 (w)	4.22 (m)
3.79 (vs)	2.94 (m)	3.79 (vs)
3.52 (s)	2.54 (w)	3.48 (s)
3.41 (s)	2.39 (w)	3.28 (w)
3.26 (w)	2.24 (m)	3.09 (vw)
3.10 (w)	2.07 (m)	2.97 (vw)
2.65 (vw)	1.97 (w)	2.81 (vw)
2.53 (vw)	1.88 (w)	2.68 (w)
2.31 (w)	1.84 (w)	2.50 (vw)
2.16 (vw)	1.80 (vw)	2.34 (vw)
2.04 (vw)	1.76 (vw)	2.13 (vw)
1.95 (w)	1.57 (vw)	2.03 (w)
1.86 (w)	1.54 (vw)	1.96 (w)
1.70 (vw)	1.48 (vw)	1.82 (vw)
1.59 (w)	1.42 (vw)	
1.41 (w)		

vw = very weak, w = weak, m = medium, s = strong, vs = very strong.



(SH) group in its IR and PMR spectra (Tables 1 and 2). Lesser number of bands in the IR spectrum are probably due to delocalisation, since sulphur atoms have lone pairs. However, crystal structure determination is necessary for further proof.

Kinetics of cis-II → *trans-I* isomerisation †
in DMF solution

The isomerisation *cis-II* → *trans-I* in DMF is accelerated in the presence of acid. The rate of reaction

decreases sharply with increasing ionic strength (Table 5) at very low salt concentrations and $[H^+] = 6.9 \times 10^{-3} \text{ mol dm}^{-3}$, but the decrease in rate is almost negligible at ionic strength in the range, $I = 0.05\text{--}0.10 \text{ mol dm}^{-3}$; the ionic strength was 0.1 mol dm^{-3} in all kinetically evaluated experiments. On the other hand, in the absence of acid, the rate of reaction does not decrease sharply with the increase in ionic strength (Table 5) and it is practically independent of ionic strength in the range of $0.03\text{--}0.10 \text{ mol dm}^{-3}$.

In order to study of the effect of $[H^+]$ on the reaction, rate constants were evaluated by varying $[H^+]$ in the range of 6.9 to $41.4 \times 10^{-3} \text{ mol dm}^{-3}$. The reaction at higher $[H^+]$ could not be followed as the reaction became too fast to be followed. Good first order plots were obtained throughout the course of the reaction. The plots of pseudo-first order rate constants (Table 5) against $[H^+]$ are linear at three different

Table 5—Rate Constants and Activation Parameters for Isomerisation, *cis-II*^a → *trans-I* in DMF

Temp. (±0.1°C)	<i>I</i> (mol dm ⁻³)	10 ³ [H ⁺] (mol dm ⁻³)	10 ⁴ <i>k</i> _{obs} (s ⁻¹)	<i>k</i> ₂ (dm ³ mol ⁻¹ s ⁻¹)	Δ <i>H</i> [‡] (kJ mol ⁻¹)	Δ <i>S</i> [‡] (JK ⁻¹ mol ⁻¹)	
15.1	—	—	3.1	—	63	-94	
21.0	—	—	5.8	—			
28.8	—	—	10.0	—			
28.8	0.01	6.9	39.6				
	0.015	6.9	26.6				
	0.02	6.9	23.0				
	0.04	6.9	19.0				
	0.05	6.9	13.8				
	0.08	6.9	13.0				
	0.10	6.9	12.8				
	0.10	—	—	7.5			
28.8	0.02	—	6.4				
	0.04	—	5.5				
	0.05	—	5.6				
	0.10	—	2.4 (2.5) ^b		49	-146	
	0.10	—	4.1 (4.4) ^b				
31.8	0.10	—	7.0 (7.2) ^b				
17.1	0.10	6.9	4.6				
	0.10	13.8	5.8				
	0.10	27.6	9.0	0.232			
	0.10	34.5	10.5				
	0.10	41.4	12.1				
	23.0	0.10	6.9	7.5			
		0.10	13.8	10.2			
		0.10	27.6	15.6	0.401	62	-44
		0.10	34.5	18.5			
		0.10	41.4	21.2			
31.8	0.10	6.9	14.0				
	0.10	13.8	18.2				
	0.10	27.6	29.5	0.835			
	0.10	34.5	36.5				
	0.10	41.4	39.4				
	0.10	—	—	—			

(a) $[cis-II] = 1 \times 10^{-4} \text{ mol dm}^{-3}$; (b) values in the parentheses are evaluated from the intercepts of the linear plots of k_{obs} versus $[H^+]$ at the respective temperature.

†The ionization could not be studied in DMSO in view of the explosive character of DMSO IN 70% HClO₄ at ambient temperature.

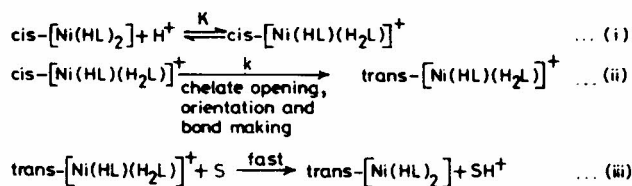
temperatures with positive slopes and intercepts. The intercept is consistent with the experimental k_{obs} value in the absence of acid. This observation suggests that the reaction follows two independent paths: i.e. acid-dependent (k_2) and acid-independent (k_1), respectively. Second order rate constants for the acid-dependent path and the rates for acid-independent path are given in Table 5, wherein the values of activation parameters derived from Eyring equation are also included. The rate expression may be represented by Eq. (1)

$$-d \ln [cis-II]/dt = k_{\text{obs}} = k_2 [H^+] + k_1 \quad \dots (1)$$

The role of $[H^+]$ in the isomerisation of *cis*-II does not suggest ion pair formation at the primary stage as *cis*-II species is a nonelectrolyte. As there is a basic centre ($-N^2H_2$) within the complex species, it may exist as the 'protonated species' (conjugated species) in acidic solution. It has been observed² that the acid salts exhibit an absorption band at 780 nm, almost similar to that observed in either *trans*-I or *cis*-II form. This would lead to an idea that conjugate-acid is being formed although there is no change in the spectrum of the complex at 'zero time' by the addition of acid. Since the conjugate-acid isomerises more rapidly than the parent compound, the experimental rate constant should increase with increase in concentration of conjugate-acid (or H^+). Moreover, it has been observed³ by us that *cis*-II also forms acid salts like *trans*-I but the exhaustive washing of the salt with water yields *trans*-I. This observation implies that conjugate-acid may be an intermediate in the generation of *trans*-I. The reaction sequence (Scheme 1) probably involves a rapid acid-base equilibrium of *cis*-II (Eq. 2), followed by the rate-determining isomerisation of the conjugate-acid (Eq. 3). The species formed in the step (3) deprotonates rapidly by reaction with a solvent molecule resulting in the formation of *trans*-I (see Eq. 4).

Although the mechanism represented by Scheme 1 is rather complex, it seems that rate step involves opening of the chelate ring¹⁵ followed by orientation and bond making while the rapid attack of solvent molecule regenerates the *trans*-I by isomerisation which is the preferable one rather than the substitution of solvent. The chelate opening at the Ni-N¹ site is the most feasible as in the conjugate-acid, $-N^2H_2$ becomes $-N^2H_3^+$ whereby electron clouds of N¹ shifts to N² resulting in weakening of the Ni-N¹ bonding, and ultimately opening of the chelate ring.

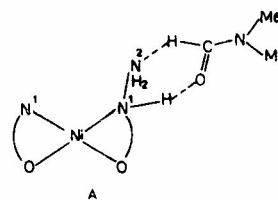
It is interesting to note that in different media the entropy of activation (ΔS^\ddagger) (Table 5) decreases in the order: $I+S+H^+ > S > I+S$; I, S and H^+ are ionic, solvent and acidic media respectively. In the case of $I+S+H^+$ medium the small negative entropy value ($-44 \text{ JK}^{-1} \text{ mol}^{-1}$) is compatible with the conjugate-



SCHEME 1

acid mechanism, and it seems that interaction of solvent molecule with the metal ion is probably negligible. On the other hand, solvation effect may be the predominant factor for the loss of entropy¹⁶ ($-94 \text{ JK}^{-1} \text{ mol}^{-1}$) in only solvent (S) medium, since the complex species possesses both acidic and basic centres which help the solvent molecule to be solvated through hydrogen bonding (vide supra). The large negative entropy value ($-146 \text{ JK}^{-1} \text{ mol}^{-1}$) in the I+S medium seems to be due to the fact that solvent molecules are strongly oriented around the ions of the system. Moreover, the high ΔH^\ddagger values (Table 5) in the media $I+S+H^+$ and S in comparison to that in $I+S$ medium are possibly due to the same reason as stated above.

In solvent (S) medium alone, the isomerisation is possibly occurring through hydrogen bond formation^{17,18} between solvent molecule and the acidic and basic centres of the *cis*-II species in the intermediate step as shown in A.



The significance of such hydrogen bonding is that the solvent molecule may probably be associated with N¹ hydrogen and N² nitrogen resulting in ring-opening and orientation as proposed in the case of acid medium ($S+H^+$). As a consequence, the isomerisation, *cis*-II \rightarrow *trans*-I also takes place in DMF ($pH 11.43$) though its pH is in the basic region. Such isomerisation may be suggested as 'solvent-assisted-isomerisation' similar to solvent-assisted-dissociation proposed by Jones *et al.*¹⁹.

Cis-II \rightarrow *trans*-I isomerisation in solid state

Cis-II species transforms to *trans*-I species on heating around 200°C . The isomerisation probably occurs through the formation of four-coordinated tetrahedral species as an intermediate similar to the transformation of square planar²⁰ *cis*-[PtI₂(py)₂] complex. Twist mechanism may be plausible here as low ΔH value (39 kJ mol^{-1}) and low activation energy (36 kJ mol^{-1}) do not favour ring-opening of the chelate ring.

Trans-I → *cis-II* isomerisation in DMSO
in alkaline pH range

Pale yellow colour of *trans-I* in DMSO slowly transforms to green colour at ~40°C. The spectrum of the green coloured solution matches that of *cis-II* in DMSO. *Trans-I* → *cis-II* isomerisation has been investigated kinetically at 780 nm in DMSO solution at elevated temperature (40–60°C) as the transformation is very slow at ambient temperature. The observed rates at 50.5°C remain practically constant in the ionic strength range of 0.01–0.10 mol dm⁻³. The effect of addition of water to DMSO provides interesting results. The observed rate of the isomerisation increases with the increase in ionic strength in the range of 0.01 to 0.10 mol dm⁻³ at constant water concentration (0.55 mol dm⁻³). This phenomenon may probably be due to increase in pH with the addition of salt. The effect of addition of water has been studied in detail at *I* = 0.10 mol dm⁻³. The dependence of pseudo-first order rate constant on water concentration at 41.4°C is illustrated in Fig. 1. The reaction rate increases initially with the increase in [H₂O] in the range 0.28 to 0.83 mol dm⁻³. Thereafter it decreases with further addition of water, reaching a plateau where the rate is practically independent of water concentration. Such an observation implies that initially *trans-I* → *cis-II* isomerisation is taking place followed by the *cis-II* → *trans-I* transformation. The variation of *k*_{obs} as well as pH with the increase in [H₂O] in DMSO are given in Table 6. The increase/decrease of observed rates with the increase in [H₂O] are consistent with increase/decrease of pH of the solution. As a consequence, it is obvious that pH of the solution would be the main factor affecting isomerisation. The dependence of pseudo-first order rate constant on [H₂O] for isomerisation has also been followed at two different temperatures at [H₂O] in the range of 0.27 to 0.77 mol dm⁻³. The plots of *k*_{obs} versus [H₂O] are linear with positive slopes and intercepts. The second order rate constants for the water-dependent path and the rates for water-independent path, i.e. the solvent path are given in Table 7. The *k*_{obs} for the solvent path in the absence of ionic strength is consistent with the rate constant (*k*_{solvent}) evaluated from the positive intercepts of the plots of *k*_{obs} versus [H₂O]. The rate expression for the isomerisation may then be given by Eq. (5)

$$-d\ln [\textit{trans-I}]/dt = k_{\text{obs}} = k_2 [\text{H}_2\text{O}] + k_1 \quad \dots (5)$$

where *k*₂ and *k*₁ are the rate constants for water-dependent and water-independent paths respectively. As the effect of pH is implied for isomerisation, it will be prudent to take recourse to the polarization of H₂O for attacking the acid centre of *trans-I*. As a consequence, water molecule possibly associates with

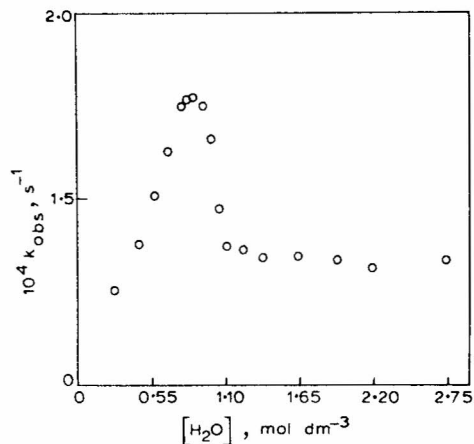
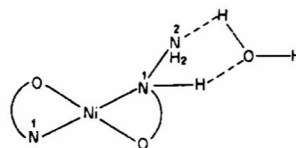


Fig. 1—Variation of *k*_{obs} with [H₂O] for the isomerisation, *trans-I* → *cis-II* in [H₂O] range of 0.28–2.75 mol dm⁻³ at 41.4°C maintaining [*trans-I*] = 5 × 10⁻⁴ mol dm⁻³ and *I* = 0.10 mol dm⁻³ constant.

Table 6—Rate Constants and pH for Isomerisation, *trans-I*^a → *cis-II* in DMSO at Different [H₂O] and 41.4 ± 0.1°C

<i>I</i> (mol dm ⁻³)	[H ₂ O] (mol dm ⁻³)	<i>k</i> _{obs} (s ⁻¹)	pH
0.1	0.275	1.26 ^b	8.77
0.1	0.44	1.38	9.30
0.1	0.55	1.51	9.59
0.1	0.66	1.61	9.75
0.1	0.77	1.75	9.81
0.1	0.82	1.76	9.85
0.1	0.88	1.76	9.77
0.1	0.93	1.74	9.69
0.1	0.99	1.65	9.65
0.1	1.04	1.47	9.53
0.1	1.10	1.37	9.48
0.1	1.21	1.36	9.49
0.1	1.37	1.34	9.54
0.1	1.65	1.40	9.51
0.1	1.92	1.33	9.57
0.1	2.20	1.31	9.50
0.1	2.75	1.34	9.45
0.1	—	1.42	9.48
—	—	1.05 (1.04) ^c	8.78

(a) *trans-I* = 5 × 10⁻⁴ mol dm⁻³; (b) second order rate constant (*k*₂) = 1.80 × 10⁻⁴ dm³ mol⁻¹ s⁻¹ considering [H₂O] in the range of 0.275–0.77 mol dm⁻³; (c) value in the parenthesis is evaluated from the intercept of the linear plot of *k*_{obs} versus [H₂O] in the range of 0.275–0.77 mol dm⁻³.



B

the acidic and basic centres of *trans-I* through hydrogen bonding^{17,18} as shown in (B).

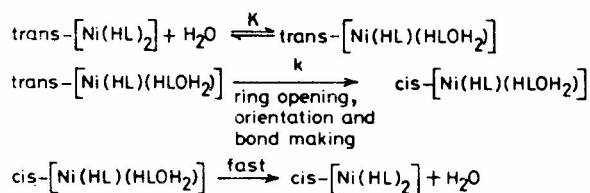
This situation probably weakens the Ni–N bond, resulting in ring-opening, orientation of the ligand and reformation of Ni–N bond similar to *cis-II* → *trans-I*

Table 7—Rate Constants and Activation Parameters for Isomerisation, *trans*-I^a→*cis*-II in DMSO

Temp. (±0.1°C)	<i>I</i> (mol dm ⁻³)	[H ₂ O] (mol dm ⁻³)	10 ⁴ <i>k</i> _{obs} (s ⁻¹)	10 ⁴ <i>k</i> ₂ (dm ³ mol ⁻¹ s ⁻¹)	Δ <i>H</i> [‡] (kJ mol ⁻¹)	Δ <i>S</i> [‡] (JK ⁻¹ mol ⁻¹)
50.5	0.01	—	3.14			
	0.03	—	3.13			
	0.07	—	3.10			
	0.10	—	3.14			
50.5	0.01	0.55	2.92			
	0.03	0.55	3.21			
	0.07	0.55	3.43			
	0.10	0.55	3.70			
41.4	—	—	1.05 (1.04) ^b			
50.5	—	—	2.21 (2.18) ^b		67	-111
59.2	—	—	4.31 (4.11) ^b			
41.4	0.10	—	1.42			
50.5	0.10	—	3.14		69	-101
59.2	0.10	—	6.17			
50.5	0.10	0.27	2.97	2.71 ^c		
		0.44	3.37			
		0.55	3.68			
		0.66	3.98			
		0.77	4.29			
59.2	0.10	0.27	5.41	4.68 ^c		45
		0.44	6.19			
		0.55	6.73			
		0.66	7.21			
		0.77	7.75			

(a) [*trans*-I] = 5 × 10⁻⁴ mol dm⁻³; (b) values in the parentheses are evaluated from the intercepts of the linear plots of *k*_{obs} versus [H₂O] (0.275-0.77 mol dm⁻³); (c) rate constants at 41.4°C are shown in Table 6.

isomerisation in DMF. The plausible mechanism is presented in Scheme 2:

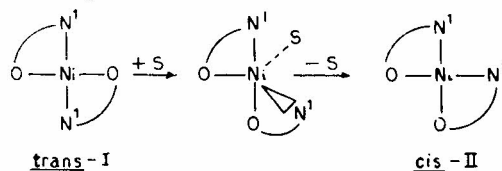


SCHEME 2

The reactivity of H₂O molecule towards *cis*-II for isomerisation at [H₂O] ≥ 9.4 × 10⁻¹ mol dm⁻³ is expected to follow a mechanism similar to that proposed for *trans*-I → *cis*-II isomerisation. However, here H₂O molecule is involved in hydrogen bonding with the *cis*-II species in a manner similar to that proposed for *trans*-I → *cis*-II isomerisation (vide infra) with H₂O in DMSO. Low Δ*H*[‡] (45 kJ mol⁻¹) and the large negative Δ*S*[‡] (-175 JK⁻¹ mol⁻¹) values are possibly due to the same reason as proposed in the case *cis*-II → *trans*-I isomerisation in I+S medium (vide infra). Interaction of solvent molecule with the metal ion in the transition state may also be responsible for the process. However, the dipole-dipole interaction of H₂O with the complex species would necessitate association of H₂O through hydrogen bonding. If the complex species is devoid of acidic and basic centres at

the coordinated ligand, metal-solvent interaction would be preferred for isomerisation.

In the presence of solvent DMSO the metal-solvent interaction would be preferred for its polarizability is less than that of H₂O. The isomerisation may then involve formation of an unstable pentacoordinated intermediate (Scheme 3) possessing a trigonal bipyramidal structure where DMSO molecule occupies the basal plane. By the removal of the coordinated solvent molecule from the intermediate, isomerisation occurs with new adjustment of bond angles. The negative Δ*S*[‡] values (-111 JK⁻¹ mol⁻¹, *I* = 0, H₂O = 0; -101 JK⁻¹ mol⁻¹, *I* = 0.10 mol dm⁻³, H₂O = 0) also support such associative process. In the absence of H₂O and *I* = 0, the Δ*H*[‡] value (67 kJ mol⁻¹) is almost equal to that (Δ*H*[‡] = 69 kJ mol⁻¹) at *I* = 0.1 mol dm⁻³. The high Δ*H*[‡] values for these two systems at *I* = 0 and 0.1 mol dm⁻³ as compared to that (Δ*H*[‡] = 45 kJ mol⁻¹) in the presence of water and *I* = 0.1 mol dm⁻³, favour an associative process rather than a dissociative process.



SCHEME 3

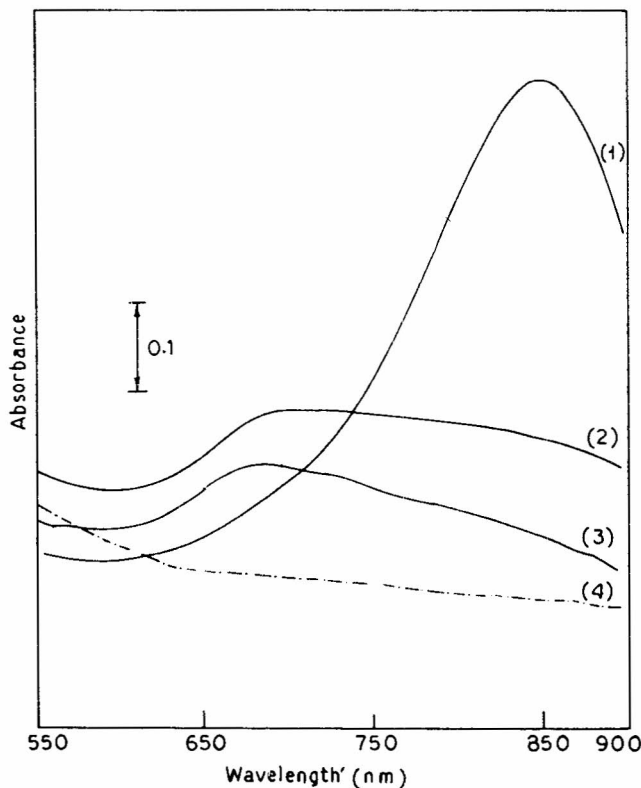
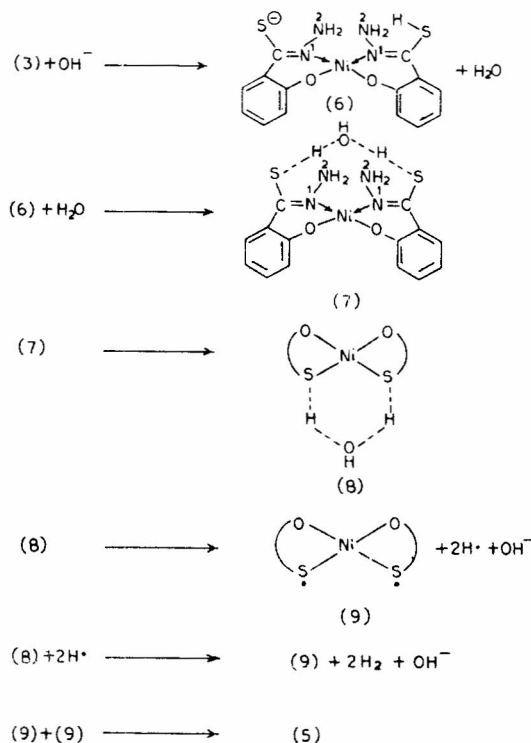


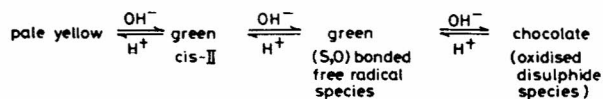
Fig. 2—Electronic spectra of *trans*-I at different $[\text{OH}^-]$ and 30°C ; $[\text{trans-I}] = 6 \times 10^{-5} \text{ mol dm}^{-3}$; $I = 0.1 \text{ mol dm}^{-3}$; (1) fresh solution, $[\text{OH}^-] = 0.05 \text{ mol dm}^{-3}$; (2) fresh solution, $[\text{OH}^-] = 0.02 \text{ mol dm}^{-3}$; (3) fresh solution, $[\text{OH}^-] = 0.01 \text{ mol dm}^{-3}$; (4) after 2 hr, $[\text{OH}^-] = 0.05 \text{ mol dm}^{-3}$



SCHEME 4

cis-II (N^1, O bonded) \rightarrow (S, O bonded) disulphide species in NaOH solution

With the addition of *trans*-I in DMF to NaOH solution, the pale yellow colour of *trans*-I changes partially to green at $[\text{OH}^-] = 0.01 \text{ mol dm}^{-3}$, exhibiting a broad peak at 680 nm (Fig. 2), a characteristic peak of *cis*-II, as is also evident from the similar absorption band position of *cis*-II in mull (Table 3). However, at $[\text{OH}^-] = 0.05 \text{ mol dm}^{-3}$ instantaneous transformation to an intense green colour occurs which exhibits a band at 850 nm ($\epsilon = 12000 \text{ mol}^{-1} \text{ cm}^{-1} \text{ dm}^3$) (Fig. 2). It is expected that the green transient corresponds to the $\text{Ni}(\text{II})$ with a free radical intermediate ($t_{1/2} = 3.8 \text{ min}$) as shown in Scheme 4 (It was not possible to record EPR spectrum of the intermediate in aqueous solvent because of strong microwave absorption). The band decays forming an intense chocolate coloured, oxidised, (S, O) bonded disulphide compound with the evolution of hydrogen gas. The liberation of H^\bullet radical in alkaline medium of the system was authenticated (experiment was followed at $0.10 \text{ mol dm}^{-3} \text{ OH}^-$ and $2.0 \times 10^{-3} \text{ mol dm}^{-3} \text{ cis-II}$ when solid $[\text{Ni}_2\text{L}_4]$ separated) by the iodometric titration of the unreacted H_2O_2 obtained after the completion of reaction of H_2O_2 with the liberated H^\bullet . That H^+ is not liberated in the system is supported by the fact that pH of the medium remains constant (11.5) after the completion of reaction. On the other hand, the chocolate coloured solution transforms first to green and then to pale yellow on acidification. The reaction sequence then follows the path shown in Scheme 5.



SCHEME 5

As the absorption spectra of chocolate coloured solution developed by the decay of 850 nm band and that of the solid $[\text{Ni}_2\text{L}_4]$ (IV) in the same medium are similar, apparently acid treatment of IV in the same medium should exhibit the reverse reaction as observed with the chocolate solution. The latter presumably contains free radical species capable of accelerating the backward reaction in the presence of acid, whilst the absence of such free radical species in the former precludes the cleavage of the disulphide bond and hence the reverse reaction is not observed. Interference from other species present in the system frustrated our attempts to determine molecular weights of the intermediate and the species forming the chocolate solution.

In the light of above arguments one can safely presume that IV and the species responsible for the

Table 8—Rate Constants for Transformation, *cis*-II
 \rightarrow $[\text{Ni}_2\text{L}_4]$ in NaOH-NaClO₄
 [Complex] = 6×10^{-5} mol dm⁻³; $I = 0.1$ mol dm⁻³

Temp. ($\pm 0.1^\circ\text{C}$)	$[\text{OH}^-]$ (mol dm ⁻³)	$10^4 k_{\text{obs}}$ (s ⁻¹)	$10^2 k_2$ (mol ⁻¹ dm ³ s ⁻¹)	$10^5 k_1$ (s ⁻¹)
15	0.025	3.28	1.19	2.77
	0.033	4.22		
	0.050	6.47		
	0.075	9.57		
	0.10	12.70		
20	0.025	4.33	1.59	4.21
	0.033	5.97		
	0.050	8.50		
	0.075	12.67		
	0.10	16.80		
25	0.025	5.92	2.16	5.12
	0.033	7.80		
	0.050	11.50		
	0.075	17.00		
	0.10	22.53		
30	0.025	10.00	3.03	25.90
	0.033	12.83		
	0.050	17.80		
	0.075	25.25		
	0.10	32.03		

$$\Delta H^\ddagger = 43 \text{ kJ mol}^{-1}$$

$$\Delta S^\ddagger = -153 \text{ JK}^{-1} \text{ mol}^{-1}$$

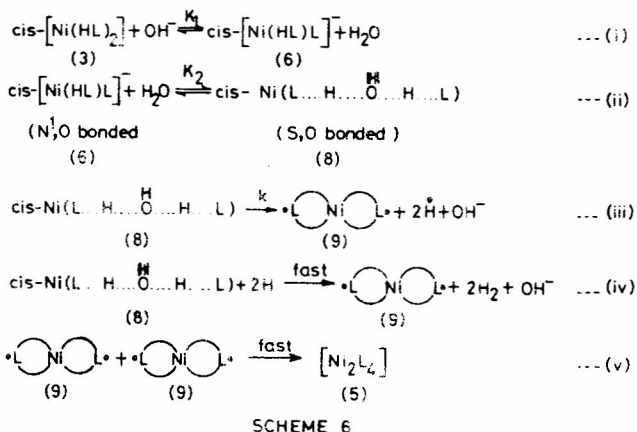
chocolate solution are both $[\text{Ni}_2\text{L}_4]$. The formation of disulphide species was followed kinetically at $[\text{OH}^-] = 0.025$ to 0.10 mol dm⁻³. For $[\text{OH}^-]$ activity determination, OH^- concentration was varied by a multiple of four. The concentration of OH^- higher than 0.01 mol dm⁻³ could not be used for the reaction was very fast, whilst the concentration of OH^- lower than 0.025 mol dm⁻³ could not be used at all to study the backward reaction of the free radical intermediate to green *cis*-II.

Table 8 records the rate of formation of disulphide species from *cis*-II in aqueous solution at different $[\text{NaOH}]$. For convenience *cis*-II was taken here as a starting material. k_{obs} values were evaluated employing conventional pseudo-first order plots which were linear upto 3 half-lives of the reaction. The plots of k_{obs} versus $[\text{OH}^-]$ are linear with positive slopes and intercepts. Second order rate constants for the alkali-dependent path and the rates for alkali-independent path are given in Table 8. The values of activation parameters derived from Eyring equation are also included in Table 8. The rate expression for the isomerisation may then be given by Eq. (6).

$$-d \ln [\text{cis-II}]/dt = k_{\text{obs}} = k_2 [\text{OH}^-] + k_1 \quad \dots (6)$$

where k_2 and k_1 are the rate constants for the base-dependent and base-independent paths respectively.

As *cis*-II contains acid N^1-H , the reactivity of OH^- towards *cis*-II for disulphide formation is believed to follow initially a conjugate-base (Scheme 6) dissociation of the type as discussed for the base hydrolysis of Co(III) amines²¹ and Pd(II) complex²²,



The reaction seems to follow a rapid acid-base equilibrium (step i). The acid and base centres of conjugate-base then attack a molecule for its amphoteric character while the cleavage of $\text{Ni}-\text{N}^1$ bond and formation of $\text{Ni}-\text{S}$ bond occur in a concerted manner in a fast equilibrium (step ii). The bonding of sulphur with metal ion is probably due to the fact that $\text{Ni}(\text{II})$ also possesses *B*-type character²³. The rate-determining step is expected to be the free radical formation (step iii). This is followed by the rapid formation of another free radical (9) (step iv). The step-v involves rapid association of two radicals forming disulphide. Since addition of base sometimes favours the formation of free radicals, the experimental rate constant, i.e. k_{obs} will increase with the increase in $[\text{OH}^-]$ (Table 8). The large negative ΔS^\ddagger value ($-153 \text{ JK}^{-1} \text{ mol}^{-1}$) is possibly due to the highly oriented transition state of the system in Scheme 6.

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