# Kinetics of the Reactions of 5,7,7,12,12,14-Hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,14-dienenickel(II) and 5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-dienenickel(II) with Cyanide

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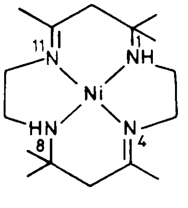
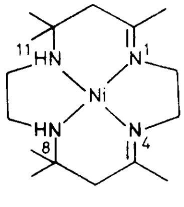
The reactions of the title compounds with cyanide to form $[Ni(CN)_4]^{2-}$ take place by way of different parallel paths. The effect on the reaction rate of varying the concentration of $CN^-$, $HCN^-$, and $OH^-$ was studied at 25 °C and $I$ = 0.1 mol dm$^{-3}$. Some differences between the two isomers are observed. A mechanism for the two reactions is proposed.

Macrocyclic square planar complexes of $Ni^{II}$ react with cyanide to give the $[Ni(CN)_4]^{2-}$ ion and the free ligands, with rapid formation of intermediate adducts with one or two $CN^-$.[1-3] In order to contribute to the understanding of the mechanisms of these reactions, we have studied the kinetics of the reactions of cyanide with the $Ni^{II}$ complexes of the *cis* and *trans* macrocyclic diene, shown opposite, in aqueous solution. In a preceding study,[4] differences between the rates of oxidation by peroxodisulphate of the two isomers were observed.



*trans* diene



*cis* diene

## Experimental

5,7,7,12,12,14-Hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,14-dienenickel(II) diperchlorate and the N-*meso* and N-*rac* diastereoisomers of 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-dienenickel(II) diperchlorate were prepared as described in the literature.[5,6] U.v.–visible and i.r. spectra were in agreement with those reported in the literature.[5,6] Solutions of KCN were protected from air by means of $N_2$, used in a few days, and titrated argentometrically. Acidimetric titrations gave the same results. The HCN was produced by adding $HClO_4$. Some runs were performed with an excess of $OH^-$ (NaOH). A p$K_a$ value of 9.0 was used for HCN.[7] The rates of formations of $[Ni(CN)_4]^{2-}$ were measured spectrophotometrically at 268 nm[8] {$[Ni(CN)_4]^{2-}$, $\varepsilon = 1.2 \times 10^4$ dm$^3$ mol$^{-1}$ cm$^{-1}$}. All runs were performed at 25 °C in the presence of excess of $CN^-$ and, except those intended to measure the ionic strength effect, at $I$ = 0.1 mol dm$^{-3}$ ($NaClO_4$). Pseudo-first-order rate constants, $k_{obs.}$, were calculated from the slopes of $\ln(A_\infty - A)$ against time, linear at least for 70—80% of the reaction. When the value of $A_\infty$ was not accessible in a relatively short time, rate constants were calculated by the Guggenheim method.[9] Both the N-*meso* and N-*rac* diastereoisomers of the *trans* diene produced the same results. It is known that these interconvert in an alkaline solution;[10] the results reported in this paper are obtained with the racemic form.

## Results

The *trans* diene isomer, after mixing with cyanide, immediately displayed a small decrease in absorbance of the bands at 282 and 435 nm ($\varepsilon = 5.6 \times 10^3$ and 97 dm$^3$ mol$^{-1}$ cm$^{-1}$ respectively), in agreement with the formation of an equilibrium between one complex molecule and one $CN^-$ ion [equation (1); L = diene]. By means of equation (2), obtained assuming $[NiL(CN)^+] = \Delta A/\Delta\varepsilon$, values of $K_1 = 7 \pm 3$ dm$^3$ mol$^{-1}$ and $\Delta\varepsilon = (5.9 \pm 2.4) \times 10^2$ dm$^3$ mol$^{-1}$ cm$^{-1}$ were obtained ($\Delta A$ is the immediate absorbance decrease at 282 nm, $\Delta\varepsilon$ the difference between the absorption coefficients, and $c$ the total complex concentration). No significant differences were observed, when varying the concentration of HCN or $OH^-$.

$$[NiL]^{2+} + CN^- \overset{K_1}{\rightleftharpoons} [NiL(CN)]^+ \quad (1)$$

$$[CN^-]^{-1} = K_1\Delta\varepsilon c/\Delta A - K_1 \quad (2)$$

Subsequently, the reaction continued to give $[Ni(CN)_4]^{2-}$ with the appearance of many isosbestic points in the u.v. spectrum (250, 277, and 289 nm). Table 1 reports the pseudo-first-order rate constants, $k_{obs.}$, at different complex, $CN^-$, HCN, and $OH^-$ concentrations. The reaction is first-order with respect to the complex, second-order with respect to the $CN^-$ ion, and between zero and first-order with respect to HCN.

Maintaining a constant $CN^-$ concentration, the third-order rate constant, $k_{obs.}/[CN^-]^2$, increases linearly with increasing [HCN], the slope of which diminishes with increasing $[CN^-]$. In the presence of large quantities of $OH^-$, and of course negligible quantities of HCN, the third-order rate constant also increases linearly with $OH^-$ concentration. The extrapolation to zero [HCN] or $[OH^-]$ is always the same. The empirical equation which is in accord with the experimental results is equation (3), with $a = 0.241 \pm 0.004$ dm$^6$ mol$^{-2}$ s$^{-1}$,

$$k_{obs.} = a[CN^-]^2 + \frac{b[CN^-]^2[HCN]}{1 + c[CN^-]} + \frac{d[CN^-]^2[OH^-]}{1 + e[CN^-]} \quad (3)$$

$b = 16.0 \pm 0.5$ dm$^9$ mol$^{-3}$ s$^{-1}$, $c = 15.1 \pm 0.9$ dm$^3$ mol$^{-1}$, $d = 2.19 \pm 0.14$ dm$^9$ mol$^{-3}$ s$^{-1}$, and $e = 14.1 \pm 2.5$ dm$^3$ mol$^{-1}$.

The *cis* diene isomer reacts with cyanide faster than the *trans* isomer with the appearance of many isosbestic points (277, 281, and 283 nm), without any appreciable immediate variation in the u.v. or visible spectrum. Table 2 reports the results obtained. The reaction order with respect to the $CN^-$ is greater than two. The third-order rate constant, $k_{obs.}/[CN^-]^2$, increases, but not linearly, with increasing $[CN^-]$ or [HCN]. Maintaining a constant $CN^-$ concentration without excess of $OH^-$, the experimental results are in agreement with the

**Table 1.** First-order rate constants for the reaction of *trans* diene with cyanide: [*trans* diene] = 1 × $10^{-4}$ mol $dm^{-3}$ in all runs except where stated otherwise

| $10^2[CN^-]$/ mol $dm^{-3}$ | $10^2[HCN]$/ mol $dm^{-3}$ | $10^4k_{obs.}/s^{-1}$ | $10^4k_{calc.}/s^{-1}$ |
|---|---|---|---|
| 1 | 0.0316 | 0.249 | 0.246 |
| 1 | 0.25 | 0.283 | 0.276 |
| 1 | 0.5 | 0.321 | 0.311 |
| 1 | 1 | 0.379 | 0.381 |
| 1 | 1.5 | 0.453 | 0.450 |
| 1 | 2 | 0.524 | 0.520 |
| 2 | 0.0447 | 0.977 | 0.989 |
| 2 | 0.25 | 1.07 | 1.09 |
| 2 | 0.5 | 1.17 | 1.21 |
| 2 | 1 | 1.43 | 1.46 |
| 2 | 2 | 1.97 | 1.95 |
| 2 | 2 | 1.93 [a] | 1.95 |
| 2 | 2 | 2.01 [b] | 1.95 |
| 2 | 4 | 2.88 | 2.94 |
| 4 | 0.5 | 4.78 | 4.67 |
| 4 | 1 | 5.46 | 5.47 |
| 4 | 2 | 6.96 | 7.09 |
| 4 | 4 | 10.5 | 10.3 |
| 6 | 1 | 11.6 | 11.7 |
| 6 | 2 | 14.8 | 14.8 |
| 6 | 4 | 20.7 | 20.9 |
| 8 | 1 | 20.1 | 20.2 |
| 8 | 2 | 24.7 | 24.9 |
| 2 |  | 1.09 [c] | 1.10 |
| 2 |  | 1.22 [d] | 1.24 |
| 2 |  | 1.36 [e] | 1.37 |
| 1 |  | 0.342 [e] | 0.356 |
| 4 |  | 5.21 [e] | 5.18 |

[a] [*trans* diene] = 0.5 × $10^{-4}$ mol $dm^{-3}$. [b] [*trans* diene] = 2 × $10^{-4}$ mol $dm^{-3}$. [c] $[OH^-]$ = 2 × $10^{-2}$ mol $dm^{-3}$. [d] $[OH^-]$ = 4 × $10^{-2}$ mol $dm^{-3}$. [e] $[OH^-]$ = 6 × $10^{-2}$ mol $dm^{-3}$.

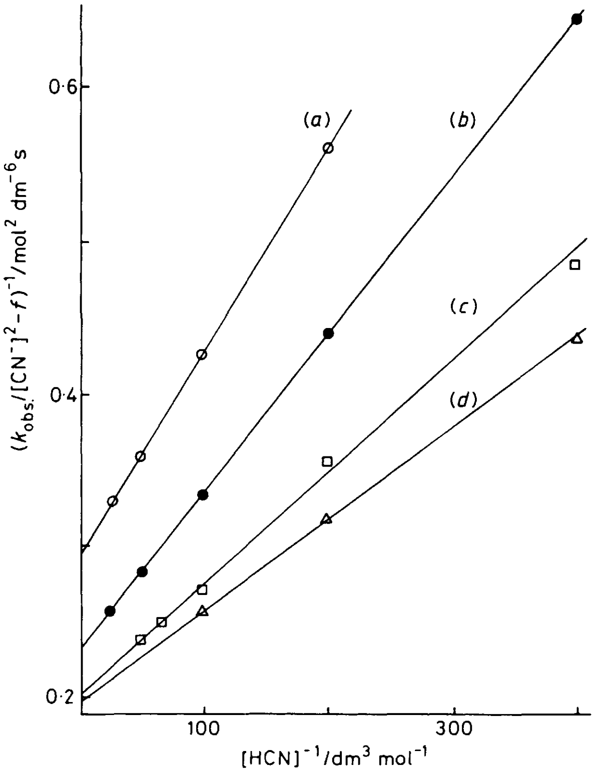


**Figure 1.** Test of equation (4) at $[CN^-]$ = (*a*) 0.04, (*b*) 0.02, (*c*) 0.01, and (*d*) 0.005 mol $dm^{-3}$: [*cis* diene] = 1 × $10^{-4}$ mol $dm^{-3}$

**Table 2.** First-order rate constants for the reaction of *cis* diene with cyanide: [*cis* diene] = 1 × $10^{-4}$ mol $dm^{-3}$ in all runs except where stated otherwise

| $10^2[CN^-]$/ mol $dm^{-3}$ | $10^2[HCN]$/ mol $dm^{-3}$ | $10^4k_{obs.}{}^a/s^{-1}$ |
|---|---|---|
| 0.5 | 0.1 | 0.85 |
| 0.5 | 0.25 | 1.11 |
| 0.5 | 0.5 | 1.32 |
| 0.5 | 1 | 1.51 |
| 1 | 0.0316 | 3.48 |
| 1 | 0.0316 | 3.41 [b] |
| 1 | 0.25 | 5.10 |
| 1 | 0.5 | 5.84 |
| 1 | 1 | 6.72 |
| 1 | 1.5 | 7.03 |
| 1 | 2 | 7.22 |
| 2 | 0.0447 | 18.4 |
| 2 | 0.25 | 23.0 |
| 2 | 0.5 | 25.9 |
| 2 | 1 | 28.8 |
| 2 | 2 | 30.9 |
| 2 | 4 | 32.3 |
| 4 | 0.5 | 113 |
| 4 | 1 | 122 |
| 4 | 2 | 129 |
| 4 | 4 | 133 |
| 0.5 |  | 0.58 [c] (0.57) |
| 0.5 |  | 0.74 [d] (0.74) |
| 1 |  | 3.30 [c] (3.27) |
| 1 |  | 3.73 [e] (3.83) |
| 1 |  | 4.41 [d] (4.41) |
| 2 |  | 19.4 [c] (18.7) |
| 2 |  | 23.0 [a] (22.6) |
| 2 |  | 26.9 [d] (26.4) |
| 4 |  | 108 [c] (103) |
| 4 |  | 130 [e] (126) |
| 4 |  | 152 [d] (149) |

[a] Values for $10^4k_{calc.}/s^{-1}$ are given in parentheses. [b] [*cis* diene] = 2.5 × $10^{-4}$ mol $dm^{-3}$. [c] $[OH^-]$ = 2 × $10^{-2}$ mol $dm^{-3}$. [d] $[OH^-]$ = 6 × $10^{-2}$ mol $dm^{-3}$. [e] $[OH^-]$ = 4 × $10^{-2}$ mol $dm^{-3}$.

**Table 3.** Coefficients of equations (4) and (8)

| $[CN^-]$/ mol $dm^{-3}$ | $f/dm^6$ $mol^{-2}\ s^{-1}$ | $g/mol^2$ $dm^{-6}$ s | $10^4\ h/mol^3$ $dm^{-9}$ s | $m/dm^6$ $mol^{-2}\ s^{-1}$ | $n/dm^9$ $mol^{-3}\ s^{-1}$ |
|---|---|---|---|---|---|
| 0.005 | 2.14 | 0.197 | 6.03 | 2.00 | 16 |
| 0.01 | 3.03 | 0.204 | 7.06 | 2.74 | 27 |
| 0.02 | 4.20 | 0.232 | 10.34 | 3.90 | 47 |
| 0.04 | 5.28 | 0.295 | 13.33 | 5.37 | 69 |

empirical equation (4), as shown in Figure 1. Table 3 reports

$$(k_{obs.}/[CN^-]^2 - f)^{-1} = g + h/[HCN] \qquad (4)$$

the coefficients of equation (4) for the different $CN^-$ concentrations examined. The values of $f$ were chosen tentatively so as to have the maximum correlation coefficients. The three coefficients of equation (4) are dependent on $[CN^-]$ according to equations (5)—(7), with $f'$ = 0.81 $dm^6$ $mol^{-2}$ $s^{-1}$, $f''$ =

$$f = f' + f''[CN^-]/(1 + f'''[CN^-]) \qquad (5)$$

$$g = g' + g''[CN^-] \qquad (6)$$

$$h = h' + h''[CN^-] \qquad (7)$$

330 ± 2 $dm^9$ $mol^{-3}$ $s^{-1}$, $f'''$ = 48.3 ± 1.0 $dm^3$ $mol^{-1}$, $g'$ = 0.178 ± 0.004 $mol^2$ $dm^{-6}$ s, $g''$ = 2.87 ± 0.18 mol $dm^{-3}$ s,

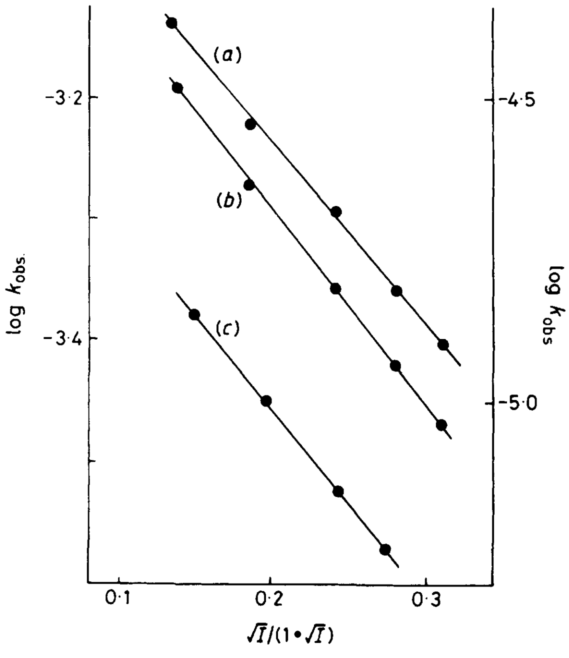


**Figure 2.** Ionic strength effect ($NaClO_4$). (*a*) [*trans* diene] = $1 \times 10^{-4}$ mol dm$^{-3}$, [KCN] = 0.01 mol dm$^{-3}$ (ordinate on the right); (*b*) [*cis* diene] = $1 \times 10^{-4}$ mol dm$^{-3}$, [KCN] = 0.01 mol dm$^{-3}$; (*c*) [*trans* diene] = $1 \times 10^{-4}$ mol dm$^{-3}$, [CN$^-$] = 0.02 mol dm$^{-3}$, [HCN] = 0.01 mol dm$^{-3}$

$h' = (5.24 \pm 0.62) \times 10^{-4}$ mol$^3$ dm$^{-9}$ s, and $h'' = (2.11 \pm 0.27) \times 10^{-2}$ mol$^2$ dm$^{-6}$ s.

Maintaining a constant $CN^-$ concentration in the presence of excess $OH^-$ ions, and therefore negligible HCN concentrations, the experimental results are in agreement with equation (8). Values of $m$ and $n$ calculated for the different

$$k_{obs.}/[CN^-]^2 = m + n[OH^-] \qquad (8)$$

$CN^-$ concentrations used are reported in Table 3. The values of $m$ are similar to those of $f$ and are in agreement with an equation equivalent to equation (5) {*i.e.*: $m = f' + f''[CN^-]/(1 + f'''[CN^-])$} with $f'' = 1.09$ dm$^6$ mol$^{-2}$ s$^{-1}$, $f'' = 204 \pm 3$ dm$^9$ mol$^{-3}$ s$^{-1}$, and $f''' = 22.4 \pm 1.8$ dm$^3$ mol$^{-1}$. Values of $n$ depend on $CN^-$ concentration as given by equation (9), with $n' = (3.64 \pm 0.12) \times 10^3$ dm$^{12}$ mol$^{-4}$ s$^{-1}$ and $n'' = 29.5 \pm 4.4$ dm$^3$ mol$^{-1}$. By combining equations (5)—(7) with equation (4) and adding (9), equation (10) is obtained.

$$n = n'[CN^-]/(1 + n''[CN^-]) \qquad (9)$$

$$k_{obs.} = f'[CN^-]^2 + \frac{f''[CN^-]^3}{1 + f'''[CN^-]} + \frac{[HCN][CN^-]^2}{h' + h''[CN^-] + g'[HCN] + g''[CN^-][HCN]} + \frac{n'[CN^-]^3[OH^-]}{1 + n''[CN^-]} \qquad (10)$$

Figure 2 shows the ionic strength effect on the two reactions studied. In each case the slopes of the straight lines obtained by plotting log $k_{obs.}$ against $\sqrt{I}/(1 + \sqrt{I})$ are nearly equal to three, as expected for a reaction with an activated complex formed by one +2 ion and two or three −1 ions in the presence or absence of neutral molecules.[11]

## Discussion

The reactions of the two isomers with cyanide take place by way of different parallel paths.

In the case of the *trans* diene isomer, the values of $c$ and $e$ in equation (3) are almost equal and are not very different from the value of $K_1$ calculated from the absorbance decrease at 282 nm. This suggests that the reacting species is $[NiL(CN)]^+$. The proposed mechanism is therefore shown by equations (11)—(16). Assuming the concentrations of $[NiL(CN)_2]$ and $[Ni(LH_{-1})(CN)]$ are very small with respect to those of $[NiL]^{2+}$ and $[NiL(CN)]^+$, this mechanism gives equation (17) for $k_{obs.}$: this is equivalent to equation (3) if

$$[NiL(CN)]^+ + CN^- \xrightarrow{k_1} \text{products} \qquad (11)$$

$$[NiL(CN)]^+ + CN^- \xrightleftharpoons{K_2} [NiL(CN)_2] \qquad (12)$$

$$[NiL(CN)_2] + CN^- \xrightarrow{k_2} \text{products} \qquad (13)$$

$$[NiL(CN)_2] + HCN \xrightarrow{k_3} \text{products} \qquad (14)$$

$$[NiL(CN)]^+ + OH^- \xrightleftharpoons{K_3} [Ni(LH_{-1})(CN)] + H_2O \qquad (15)$$

$$[Ni(LH_{-1})(CN)] + CN^- \xrightarrow{k_4} \text{products} \qquad (16)$$

$$k_{obs.} = \frac{k_1K_1[CN^-]^2}{1 + K_1[CN^-]} + \frac{k_2K_1K_2[CN^-]^3}{1 + K_1[CN^-]} + \frac{k_3K_1K_2[CN^-]^2[HCN]}{1 + K_1[CN^-]} + \frac{k_4K_1K_3[CN^-]^2[OH^-]}{1 + K_1[CN^-]} \qquad (17)$$

$k_1K_1 \simeq k_2K_2 = a$ (dm$^6$ mol$^{-1}$ s$^{-1}$), with $k_3K_1K_2 = b$ (dm$^9$ mol$^{-3}$ s$^{-1}$) and $k_4K_1K_3 = d$ (dm$^9$ mol$^{-3}$ s$^{-1}$). The values of $k_{calc.}$ of Table 1 are calculated using equation (17), and taking $K_1$ as the arithmetic mean of $c$ and $e$ of equation (3).

In the case of the *cis* diene isomer, the proposed mechanism contains the equations (1), (11), (12), (13), (15), and (18)—(21).

$$[NiL(CN)_2] \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} [NiL(CN)_2]^* \qquad (18)$$

$$[NiL(CN)_2]^* + HCN \xrightarrow{k_5} \text{products} \qquad (19)$$

$$[Ni(LH_{-1})(CN)] + CN^- \xrightleftharpoons{K_4} [Ni(LH_{-1})(CN)_2]^- \qquad (20)$$

$$[Ni(LH_{-1})(CN)_2]^- + CN^- \xrightarrow{k_6} \text{products} \qquad (21)$$

Assuming the steady-state approximation for $[NiL(CN)_2]^*$, the rate expression (22) is obtained, which is equivalent to the empirical equation (10) with $k_1K_1 = f'$ (dm$^6$ mol$^{-2}$ s$^{-1}$), $k_2K_1K_2 = (f'f''' + f'')$ (dm$^9$ mol$^{-3}$ s$^{-1}$), $k_5k_aK_1K_2/k_{-a} = 1/h'$ (dm$^9$ mol$^{-3}$ s$^{-1}$), $k_ak_5K_2/k_{-a} = 1/h''$ (dm$^6$ mol$^{-2}$ s$^{-1}$), $k_aK_1K_2 = 1/g'$ (dm$^6$ mol$^{-2}$ s$^{-1}$), $k_aK_2 = 1/g''$ (dm$^3$ mol$^{-1}$ s$^{-1}$),

$$k_{obs.} = \frac{k_1K_1[CN^-]^2}{1 + K_1[CN^-]} + \frac{k_2K_1K_2[CN^-]^3}{1 + K_1[CN^-]} + \frac{k_ak_5K_1K_2[CN^-]^2[HCN]}{(1 + K_1[CN^-])(k_{-a} + k_5[HCN])} + \frac{k_6K_1K_3K_4[CN^-]^3[OH^-]}{1 + K_1[CN^-]} \qquad (22)$$

and $k_6K_1K_3K_4 = n'$ ($dm^{12}$ $mol^{-4}$ $s^{-1}$). The quantitative agreement of equation (22) with the experimental results is very good in the presence of excess $OH^-$, when the term containing HCN is near zero and the values of $f'''$ and $n''$, that ought to be equal to $K_1$ (arithmetic media used for $k_{calc.}$ of Table 3), are very similar. The agreement is not as good for the results obtained without excess $OH^-$, when the last term of the equation (22) is almost zero, as may be expected from the fact that the $K_1$ values are different depending on whether they are calculated as $f'''$, $h''/h'$, or $g''/g'$ (48, 40, or 16 $dm^3$ $mol^{-1}$, respectively), even if within the same order of magnitude; values of $k_{calc.}$ in these conditions are not reported in Table 3 because they depend on what value of $K_1$ is used. We think that probably other reaction mechanisms could be operating.

The $[NiL(CN)]^+$ intermediate, in the case of the *trans* diene isomer, should be the five-co-ordinate complex with one $CN^-$ ion in an apical position over the $N_4$ plane. In $[NiL(CN)_2]$ the second $CN^-$ should be bonded to an amine nitrogen. It is known that in these compounds there is a strong tendency of the secondary amine protons to hydrogen bond to the anions.[10] In the case of the *cis* diene isomer, although the value of $K_1$ does not seem very small, no immediate variation in the u.v. or visible spectrum, after mixing with cyanide, is observed. This may be accounted for by assuming that the first $CN^-$ is linked to an amine nitrogen, and the second to the other amine nitrogen or in an apical position. Steps (11), (13), (16), and (21) should involve attack by $CN^-$ on the Ni atom. Steps containing HCN seem different for the two isomers. In a subsequent paper it will be shown that the rate of the reaction of $CN^-$ with hexamethyl-1,4,8,11-tetraazatetradecanenickel is retarded by the presence of HCN and that the reaction of $CN^-$ with hexamethyl-1,4,8,11-tetraazacyclotetradecatetraenenickel does not proceed in the absence of HCN.[12] We think that the HCN attack takes place through an imine nitrogen, and that this attack can be more effective if an adjacent nitrogen is destabilized by the presence of a $CN^-$ ion. If a $CN^-$ ion is linked at position 8, then, in the case of the *trans* diene isomer, the attack by HCN may take place in position 11. In the case of *cis* diene isomer, the attack must take place in position 4 and, due to a different steric hindrance, the $[NiL(CN)_2]$ probably needs some rearranging to form a more reactive $[NiL(CN)_2]^*$. Step (15) ought to be a deprotonation process [2] of an amine group which reduces the stability of the amine N–Ni bond. It is possible that the two amine groups are destabilized at the same time, one by $OH^-$, and the other by $CN^-$. If the two destabilized groups are adjacent, as in the case of the *cis* isomer, the Ni atom might be withdrawn further from the $N_4$ plane, and the intermediate become reactive (see Figure 3).

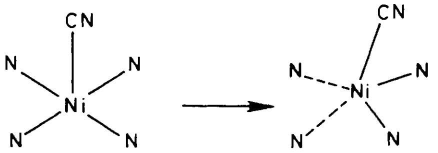


**Figure 3.** Effect of the destabilization of two adjacent N

## Acknowledgements

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