Mechanistic Implications of Kinetic Data for the Acid-catalysed Dissociation of a Tetraazamacrocyclic Ligand Complex of Nickel(II)†

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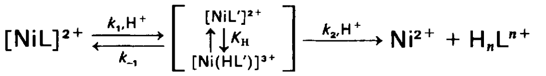
The dissociation kinetics of $[NiL]^{2+}$ (L = 2,4,4,10,12,12-hexamethyl-1,5,9,13-tetraazacyclohexadeca-1,9-diene) has been studied spectrophotometrically in 0.10–2.25 mol dm^{-3} $HClO_4$ at 25 °C. The reaction scheme (i) is followed with $k_1 = 1.4 \times 10^{-4}[H^+] + 1.1 \times 10^{-5}$ s^{-1}, $k_{-1} = (9.2 \times 10^{-5} + 8.8 \times 10^{-4}[H^+]/(1 + 24[H^+])$ s^{-1}, $K_H = 24$ dm^3 mol^{-1} and $k_2 = (1.9 \times 10^{-5} + 6.7 \times 10^{-4}[H^+] + 3.8 \times 10^{-5}[H^+]^2)/(1 + 24[H^+])$. Possible pathways for the cleavage and reformation of the Ni–N bonds, the factors influencing the dissociation rates, and the factors affecting the relative importance of each of the pathways are discussed.



$$[NiL]^{2+} \underset{k_{-1}}{\overset{k_1,H^+}{\rightleftarrows}} \left[\begin{array}{c} {[NiL']^{2+}} \\ \uparrow\downarrow K_H \\ {[Ni(HL')]^{3+}} \end{array}\right] \xrightarrow{k_2,H^+} Ni^{2+} + H_nL^{n+} \qquad (i)$$

Acid-assisted dissociation kinetics of open-chain polyamine nickel(II) complexes has been extensively studied,[1–12] and many of these works have been reviewed.[11] The corresponding kinetics of acid-catalysed dissociation of tetraazamacrocyclic nickel(II) complexes has received very little attention. The dissociation kinetics of the nickel(II) complex of a macrocyclic ligand 2,4,4,10,12,12-hexamethyl-1,5,9,13-tetraazacyclohexadeca-1,9-diene, $[NiL]^{2+}$, in 0.1–1.0 mol dm^{-3} $HClO_4$ at 50, 55, 60, 65 and 70 °C has recently been studied by Banerjea and co-workers.[13] They reported that the complex dissociated quite slowly with the observed pseudo-first-order rate constants showing an acid dependence. In this work we studied the kinetics of the same reaction in 0.10–2.25 mol dm^{-3} $HClO_4$ at 25.0 °C. The dissociation process of this complex at 25.0 °C was found to occur not in a single stage but in consecutive reversible steps similar to the acid-catalysed dissociation reactions of the tetraazamacrocyclic ligand complexes of copper(II).[14–17] The aim of this investigation is to study this reaction in detail, thus enabling a firm mechanistic assignment to be made.

Experimental

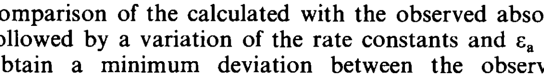
Reagents.—The complex $[NiL][ClO_4]_2$ was prepared as described in the literature.[18] All the chemicals used were of reagent grade from Merck or Fluka.

Kinetic Measurements.—Kinetic runs for the dissociation reactions of $[NiL]^{2+}$ were initiated by mixing a freshly prepared $[NiL][ClO_4]_2$ solution with a solution containing the desired quantities of $HClO_4$ and $NaClO_4$. All samples were then well mixed and transferred to a thermostatted quartz cell. These reactions were followed spectrophotometrically by repetitive scanning through the range 400–800 nm, with particular focus on 431 nm (a maximum for $[NiL]^{2+}$, $\varepsilon_{max} = 121$ dm^3 mol^{-1} cm^{-1}). A Hitachi U-3200 spectrophotometer was used and the temperature maintained at 25.0 ± 0.1 °C for all the solutions studied. The rate constants were obtained by using a CDC Cyber 180/840 computer.

Results and Discussion

Electronic Absorption Spectrum.—The macrocyclic complex $[NiL][ClO_4]_2$ dissolves in water to give a yellow-orange solution, the electronic absorption spectrum of which is typical of singlet-state, four-co-ordinate square-planar nickel(II).[19] The characteristic band at 431 nm is assigned to the ${}^1A_{1g} \longrightarrow {}^1E_g$ transition.[20]

Kinetic Results for the Reaction in Strongly Acidic Media.—The dissociation reaction of this complex was found to occur not in a single stage but in consecutive reversible steps. This feature is illustrated by the typical set of scans in 1.50 mol dm^{-3} $HClO_4$ shown in Fig. 1 and the molar absorption coefficient *vs.* time profile in Fig. 2. The simplest kinetic scheme that can accommodate these observations involves consecutive first- or pseudo-first-order processes with a reversible step as shown in equation (1). Here $[NiL']^{2+}$ and $[Ni(HL')]^{3+}$ are intermediates in which one of the four Ni–N bonds has been broken. The equilibrium reaction between these two intermediates is very rapid, and the approximate apparent molar absorption coefficient of these intermediates, ε_a, was estimated from the scan spectra, and approximate values of the rate constants were estimated from kinetic results. Rodiguin and Rodiguina integration[21] gave values of the concentrations $[NiL^{2+}]$, of the sum of the intermediates, and $[Ni^{2+}]$, as a function of time. A comparison of the calculated with the observed absorbances, followed by a variation of the rate constants and ε_a so as to obtain a minimum deviation between the observed and calculated values, led to the correct rate constants. The resulting values are given in Table 1. The experimental curve and the best-fit curve in 1.50 mol dm^{-3} $HClO_4$, calculated with the rate constants listed in Table 1, are shown in Fig. 2. The experimental curves in different $[HClO_4]$ are very similar.



$$[NiL]^{2+} \underset{k_{-1}}{\overset{k_1,H^+}{\rightleftarrows}} \left[\begin{array}{c} {[NiL']^{2+}} \\ \uparrow\downarrow K_H \\ {[Ni(HL')]^{3+}} \end{array}\right] \xrightarrow{k_2,H^+} Ni^{2+} + H_nL^{n+} \qquad (1)$$

The results given in Table 1 indicate that k_1, k_{-1} and k_2 are $[H^+]$ dependent. The value of k_1 increases as $[H^+]$ increases. A plot of k_1 *vs.* $[H^+]$ is linear (SUP 56828); least-squares analysis

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† *Supplementary data available* (No. SUP 56828, 4 pp.): kinetic plots. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

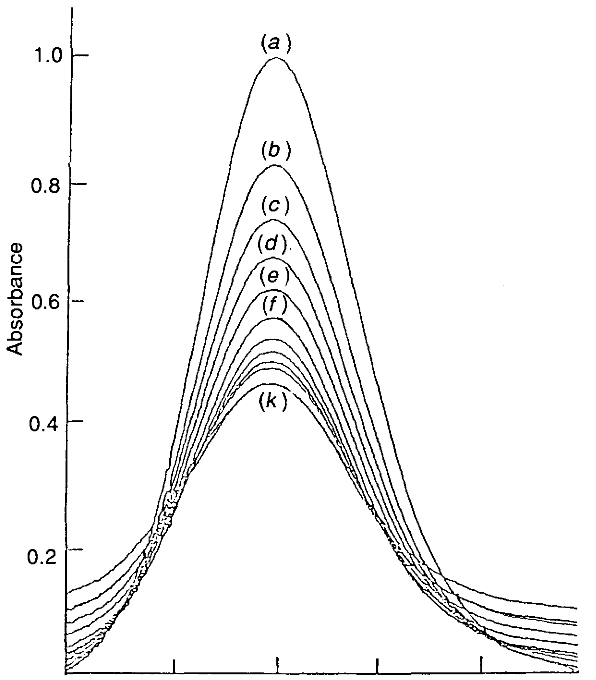


Fig. 1 Change in absorption spectra during the consecutive concurrent dissociation of $[NiL]^{2+}$ in 1.50 mol dm^{-3} $HClO_4$ (I = 5.0 mol dm^{-3}) at 25.0 °C. Downward from curve (*a*) to (*k*) at 431 nm, reaction times are 2, 42, 82, 122, 162, 202, 242, 282, 322, 362 and 402 min, respectively

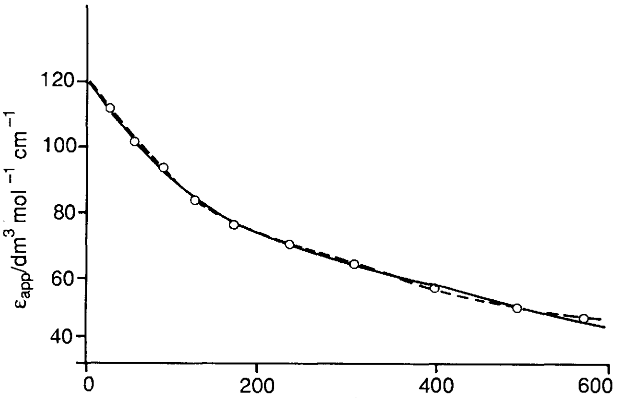


Fig. 2 Apparent molar absorption coefficient *vs.* time for the reaction of $[NiL]^{2+}$ in 1.50 mol dm^{-3} $HClO_4$ (I = 5.0 mol dm^{-3}) at 431 nm and 25.0 °C. The solid line is the experimental curve, and the dashed line is the best fit calculated with the constants listed in Table 1; $\varepsilon_{app} = A_{obs}/bC_T$ where b is the cell path-length in cm and C_T is the total concentration of the nickel(II) complexes

of the data gives equation (2). The value of k_{-1} decreases as

$$k_1 = 1.4 \times 10^{-4}[H^+] + 1.1 \times 10^{-5} \quad (2)$$

$[H^+]$ increases at low acid concentrations; a limiting rate was observed at high acid concentrations. This situation is accommodated by an equation of the form (3). A plot of $k_{-1}(1 +$

$$k_{-1} = \frac{9.2 \times 10^{-5} + 8.8 \times 10^{-4}[H^+]}{1 + 24[H^+]} \quad (3)$$

$24[H^+])$ against $[H^+]$ gives a straight line (SUP 56828). The value of k_2 increases as $[H^+]$ increases. A plot of k_2 *vs.* $[H^+]$ (Fig. 3) indicates that the kinetic situation is very complicated. Careful analysis shows expression (4) is applicable.

Table 1 Rate constants for the dissociation of the complex $[NiL]^{2+}$ in aqueous $HClO_4$ at 25.0 °C and I = 5.0 mol dm^{-3} ($HClO_4$ + $NaClO_4$)[a]

$[HClO_4]$/mol dm^{-3}	$10^5k_1{}^b/s^{-1}$	$10^5k_{-1}{}^b/s^{-1}$	$10^5k_2{}^b/s^{-1}$
0.10	1.75	5.29	2.55
0.15	3.19	4.88	2.60
0.25	4.13	4.46	2.67
0.35	5.03	4.27	2.74
0.40	6.81	4.23	2.80
0.75	12.40	4.09	2.86
1.00	15.10	4.04	2.89
1.25	20.00	3.85	2.94
1.50	21.3	3.81	3.01
1.75	25.2	3.79	3.03
2.00	29.2	3.78	3.08
2.25	30.3	3.77	3.18

[a] Conditions: $[NiL^{2+}] = 6.55 \times 10^{-4}$ mol dm^{-3}; λ = 431 nm. [b] Mean value of at least four kinetic runs.

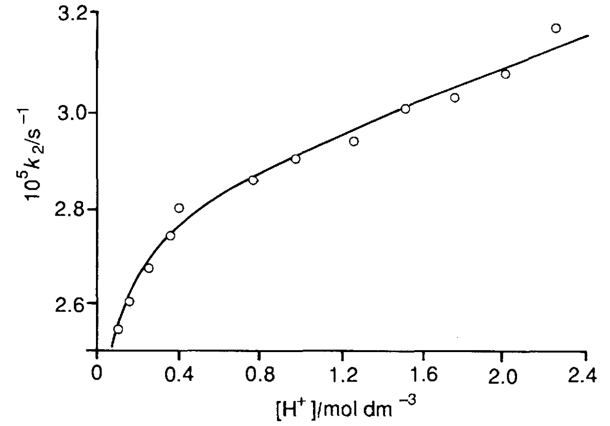


Fig. 3 Dependence of k_2 on $[H^+]$ at 25.0 °C and I = 5.0 mol dm^{-3} ($HClO_4$ + $NaClO_4$). The open circles are the experimental results; the line is calculated from $k_2 = (1.9 \times 10^{-5} + 6.7 \times 10^{-4}[H^+] + 3.8 \times 10^{-5}[H^+]^2)/(1 + 24[H^+])$

$$k_2 = \frac{1.9 \times 10^{-5} + 6.7 \times 10^{-4}[H^+] + 3.8 \times 10^{-5}[H^+]^2}{1 + 24[H^+]} \quad (4)$$

This reaction has been studied at high temperature (50–70 °C) by Banerjea and co-workers.[13] At 50 °C they found that the complex dissociated in acid media with the experimental pseudo-first-order rate constant, k_{obs},[13] showing acid dependence as follows: $k_{obs} = 2.20 \times 10^{-4}[H^+] + 1.6 \times 10^{-5}$. This value is slightly larger than the value of k_1 at 25 °C found in this work [equation (2)].

Proposesd Mechanism.—A modification of the mechanism proposed by Margerum and co-workers[11,12] to explain the kinetic results is shown in Scheme 1. For the cleavage of each of the Ni–N bonds there are two possible pathways, the solvent dissociation pathway (k_{nS}) and the protonation pathway (k_{nH}); $[NiL']^{2+}$ and $[Ni(HL')]^{2+}$ are the intermediates in which one of the four Ni–N bonds is broken, $[Ni(L'')]^{2+}$ is a reaction intermediate where two Ni–N bonds are broken, $[Ni(HL'')]^{3+}$ and $[Ni(H_2L'')]^{4+}$ are the mono- and di-protonated species of $[Ni(L'')]^{2+}$, respectively.

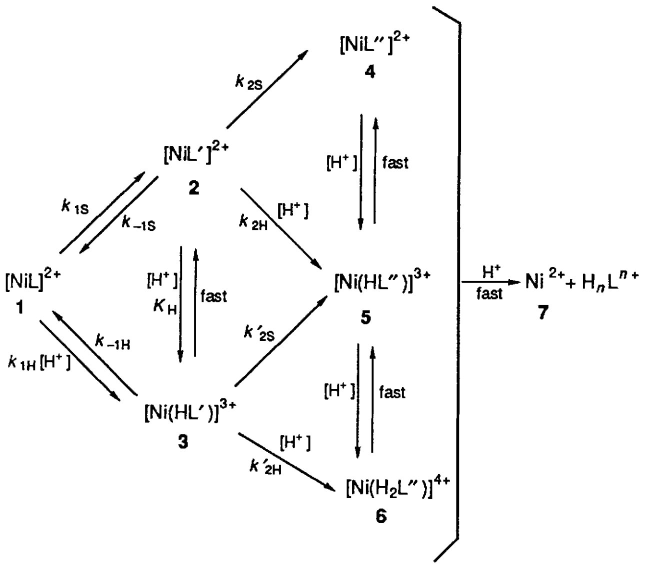
Cleavage of the first nickel–nitrogen bond. For the cleavage of the first Ni–N bond both the protonation (step **1** ⟶ **3**) and the solvent-dissociation pathways (step **1** ⟶ **2**) make contributions to the rate [equation (5)]. Here k_{1H} and k_{1S} are the

$$k_1 = k_{1H}[H^+] + k_{1S} \quad (5)$$

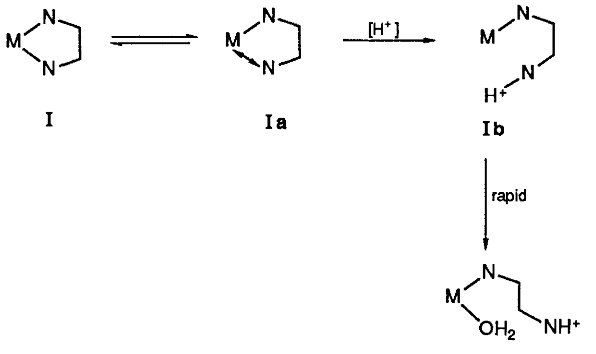
Table 2 Dissociation rate constants for nickel(II) complexes and ratios representing the relative importance of the two pathways (25.0 °C, *cf.* Scheme 1)

Complex	k_{1H}/dm^3 mol^{-1} s^{-1}	k_{1S}/s^{-1}	$k_{1H}k_{1S}^{-1}$/dm^3 mol^{-1}
$[NiL]^{2+}$	1.4×10^{-4}	1.1×10^{-5}	14
$[Ni(en)]^{2+}$ *	0.056	0.108	0.52
$[Ni(NH_3)]^{2+}$ *	0.54	5.76	0.09

* Data from ref. 12.



Scheme 1 Proposed mechanism for the acid-catalysed dissociation of $[NiL]^{2+}$



Scheme 2 Possible intermediate steps in the protonation reaction of nickel(II) polyamine complexes in concentrated acid as proposed by Read and Margerum[12]

rate constants for the protonation pathway and the solvent-dissociation pathway, respectively. Comparing this equation with (2) we obtained the values of these rate constants.

The values of k_{1H}, k_{1S} and the ratio k_{1H}/k_{1S} for this reaction and the analogous reactions of $[Ni(en)]^{2+}$ (en = ethane-1,2-diamine) and $[Ni(NH_3)]^{2+}$ are in Table 2. As preliminary observations on these results, the following are particularly noteworthy: (1) both k_{1H} and k_{1S} decrease in the order $[Ni(NH_3)]^{2+} > [Ni(en)]^{2+} > [NiL]^{2+}$; (2) k_{1H}/k_{1S} increases in the order $[Ni(NH_3)]^{2+} < [Ni(en)]^{2+} < [NiL]^{2+}$.

The results can readily be explained by the detailed mechanism proposed by Read and Margerum (Scheme 2).[12] In the first step ($\mathbf{I} \longrightarrow \mathbf{I_a}$) one nitrogen donor is dissociated from nickel(II) without its replacement by a solvent molecule. In this step the chelate ring has not been opened sufficiently to move the nitrogen donor out of the first co-ordination sphere of the metal ion.[12] Thus the nitrogen atom is weakly basic and susceptible to protonation to form species **Ib** which undergoes rapid metal-ion solvation. The breaking of the first Ni–N bond in $[Ni(en)]^{2+}$ involves some expansion of the bond angles in one chelate ring.[12] However, the breaking of the first Ni–N bond in $[NiL]^{2+}$ involves some expansion of the bond angles in two chelate rings, resulting in much larger activation energy for $[NiL]^{2+}$ than that for $[Ni(en)]^{2+}$. There is no angular expansion in the reaction of $[Ni(NH_3)]^{2+}$. Therefore the values of k_{1H} and k_{1S} decrease in the order $[Ni(NH_3)]^{2+} > [Ni(en)]^{2+} > [NiL]^{2+}$.

The ratio k_{1H}/k_{1S} represents the relative rate of dissociation by the protonation and the solvation pathways.[12] As shown in Scheme 2, species **Ia** is a reaction intermediate in which one nitrogen donor is dissociated from nickel(II). If this nitrogen donor is unrestricted and able to move easily out of the first co-ordination sphere, as in the reaction of $[Ni(NH_3)]^{2+}$, the presence of acid has little effect. However, for nickel(II) complexes of tetraazamacrocyclic ligands, the restrictions imposed by the macrocyclic ligand hold the donor atom strongly in the first co-ordination sphere. Consequently, the direct protonation pathway becomes very important for the dissociation reactions of this type of complex; therefore, the ratio of the rate constant for dissociation by the direct protonation pathway to the rate constant by the solvation pathway for the macrocyclic ligand complex in planar co-ordination is extremely large. Therefore, the ratio k_{1H}/k_{1S} increases in the order $[Ni(NH_3)]^{2+} < [Ni(en)]^{2+} < [NiL]^{2+}$.

Reformation of the nickel–nitrogen bond. The rate law for the recombination of the Ni–N bond obtained from kinetic results [equation (3)] can readily be explained by the mechanism shown in Scheme 1. According to this mechanism, the rate for the reformation of the Ni–N bond is given by equation (6).

$$k_{-1}\{[NiL'^{2+}] + [Ni(HL')^{3+}]\} = k_{-1S}[NiL'^{2+}] + k_{-1H}[Ni(HL')^{3+}] \quad (6)$$

Assuming rapid equilibration of $[NiL']^{2+}$ and $[Ni(HL')]^{3+}$ and defining $K_H = [Ni(HL')^{3+}]/[NiL'^{2+}][H^+]$ leads to expression (7). Comparing this equation with (3) we obtained the

$$k_{-1} = \frac{k_{-1S} + k_{-1H}K_H[H^+]}{1 + K_H[H^+]} \quad (7)$$

values of the rate and equilibrium constant (Table 3). The small value of K_H is mainly due to the electrostatic and inductive effects of nickel(II) ion. The constraints of a cyclic structure decrease the distance between nickel(II) and the unco-ordinated nitrogen atom in $[NiL']^{2+}$, resulting in a very large electrostatic effect. The small values of k_{-1S} and k_{-1H} are mainly due to the multidesolvation of the metal ion. As mentioned above, $[NiL]^{2+}$ is a four-co-ordinate, square-planar complex. Thus, multidesolvation of the metal ion is expected in these steps (steps $\mathbf{2} \longrightarrow \mathbf{1}$ and $\mathbf{3} \longrightarrow \mathbf{1}$ in Scheme 1). The similarity between the values of k_{-1S} and k_{-1H} indicates that these steps are very insensitive to the nature of the entering group. As discussed above, the cleavage of the first Ni–N bond is very sensitive to the nature of the leaving group. These results indicate that the extent of bond breaking in the transition state is large and that of bond making is small. Clearly, the dissociation of this complex is a dissociatively activated reaction as shown in Scheme 2.

Cleavage of the second nickel–nitrogen bond. According to Scheme 1 the rate for the cleavage of the second Ni–N bond is as given in equation (8). Substituting $[Ni(HL')^{3+}] = K_H[H^+][NiL'^{2+}]$ gives equation (9). Comparing this equation

$$k_2\{[NiL'^{2+}] + [Ni(HL')^{3+}]\} = k_{2S}[NiL'^{2+}] + k_{2H}[H^+][NiL'^{2+}] + k'_{2S}[Ni(HL')^{3+}] + k'_{2H}[H^+][Ni(HL')^{3+}] \quad (8)$$

Table 3 Summary of rate and equilibrium constants shown in Scheme 1 for individual steps in the dissociation of $[NiL]^{2+}$ at 25.0 °C and $I = 5.0$ mol dm^{-3} ($HClO_4$ + $NaClO_4$)

$k_{1H} = 1.4 \times 10^{-4}$	$dm^3\ mol^{-1}\ s^{-1}$	$k_{-1H} = 3.7 \times 10^{-5}$	$dm^3\ mol^{-1}\ s^{-1}$
$k_{1S} = 1.1 \times 10^{-5}$	s^{-1}	$k_{2S} = 1.9 \times 10^{-5}$	s^{-1}
$K_H = 24$	$dm^3\ mol^{-1}$	$k_{2H} + k'_{2S}K_H = 6.7 \times 10^{-4}$	$dm^3\ mol^{-1}\ s^{-1}$
$k_{-1S} = 9.2 \times 10^{-5}$	s^{-1}	$k'_{2H} = 1.6 \times 10^{-6}$	$dm^3\ mol^{-1}\ s^{-1}$

$$k_2 = \frac{k_{2S} + (k_{2H} + k'_{2S}K_H)[H^+] + k'_{2H}K_H[H^+]^2}{1 + K_H[H^+]} \qquad (9)$$

with (4), we obtained the values of the rate constants (Table 3). The extremely small k'_{2H} is mainly due to the very large electrostatic and inductive effects.

Acknowledgements

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References

1 D. W. Margerum, D. B. Rorabacher and J. F. G. Clarke, *Inorg. Chem.*, 1963, **2**, 667.
2 S. K. S. Ahmed and R. G. Wilkins, *J. Chem. Soc.*, 1960, 2901.
3 G. A. Melson and R. G. Wilkins, *J. Chem. Soc.*, 1962, 2662.
4 R. G. Wilkins, *J. Chem. Soc.*, 1962, 4475.
5 A. K. S. Ahmed and R. G. Wilkins, *Proc. Chem. Soc.*, 1959, 399.
6 A. K. S. Ahmed and R. G. Wilkins, *J. Chem. Soc.*, 1959, 3700.
7 A. K. S. Ahmed and R. G. Wilkins, *J. Chem. Soc.*, 1960, 2895.
8 R. F. Childers and R. A. D. Wentworth, *Inorg. Chem.*, 1969, **8**, 2218.
9 D. C. Weatherburn, E. J. Billo, J. P. Jones and D. W. Margerum, *Inorg. Chem.*, 1970, **9**, 1557.
10 G. B. Kolski and D. W. Margerum, *Inorg. Chem.*, 1969, **8**, 1129.
11 D. W. Margerum, G. R. Cayley, D. C. Weatherburn and G. K. Pagenkopf, *ACS Monogr.*, 1978, **174**, 1.
12 R. A. Read and D. W. Margerum, *Inorg. Chem.*, 1981, **20**, 3143.
13 A. K. Pondit, A. K. Das and D. Banerjea, *Transition Met. Chem.*, 1988, 437.
14 B.-F. Liang and C.-S. Chung, *Inorg. Chem.*, 1981, **20**, 2152.
15 J.-W. Chen, D.-S. Wu and C.-S. Chung, *Inorg. Chem.*, 1986, **25**, 1940.
16 B.-F. Liang and C.-S. Chung, *Inorg. Chem.*, 1983, **22**, 1017.
17 L.-H. Chen and C.-S. Chung, *Inorg. Chem.*, 1988, **27**, 1980.
18 D. A. House and N. F. J. Curtis, *J. Am. Chem. Soc.*, 1964, **86**, 223.
19 C.-S. Lee, S.-Y. Wu and C.-S. Chung, *Inorg. Chem.*, 1984, **23**, 1298.
20 J.-W. Chen and C.-S. Chung, *Inorg. Chem.*, 1986, **25**, 2841.
21 N. M. Rodiguin and E. N. Rodiguina, *Consecutive Chemical Reactions*, Van Nostrand, Princeton, NJ, 1964.

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