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THE CHEMISTRY OF NICKEL(II) COMPLEXES OF 1,4,7,11-TETRA-AZACYCLOTETRADECANE (ISOCYCLAM)

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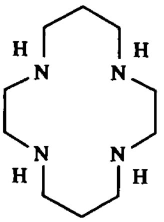
Abstract—The cyclic tetradentate ligand 1,4,7,11-tetra-azacyclotetradecane (isocyclam, = L) has been prepared by the Richman–Atkins procedure. The nickel(II) complexes of the ligand have been studied in detail. The complex $[NiL](ClO_4)_2$ undergoes a square planar$\rightleftharpoons$octahedral equilibrium in aqueous solution: $[NiL]^{2+} + 2H_2O \overset{K}{\rightleftharpoons} [NiL(OH_2)_2]^{2+}$; the equilibrium constant K has been determined as a function of temperature and $\Delta H^\circ = -22.6 \pm 1$ kJ mol^{-1} and $\Delta S^\circ = -74.9 \pm 2$ J K^{-1} mol^{-1}. Reaction of ethylenediamine with $[NiL](ClO_4)_2$ leads to folding of the macrocycle and formation of the blue octahedral *cis*-$[NiL(en)](ClO_4)_2$. The complex $[NiL]^{2+}$ displays a reversible one-electron reduction at -1.45 V versus SCE in aqueous solution and a reversible oxidation to the nickel(III) complex at $+0.85$ V versus SCE. $[Ni(isocyclam)]^{2+}$ was found to be a good electrocatalyst for the two-electron reduction of CO_2 to CO but is not as efficient as $[Ni(cyclam)]^{2+}$.

The ligand 1,4,8,11-tetra-azacyclotetradecane (cyclam, **1**) has a system of alternating five- and six-membered chelate rings, while its isomer isocyclam (**2** = L) gives a system of five- and six-membered rings which are separately grouped. Although the coordination chemistry of cyclam has been extensively studied, only limited work has been carried out with isocyclam. Fabbrizzi and co-workers[1–3] first reported that isocyclam reacts with nickel(II) to give both low-spin planar complexes and high-spin pseudo-octahedral complexes. Boeyens[4] determined the crystal structure of $[NiL](ClO_4)_2$ and established that nearly square planar coordination occurs. *Cis*-folded nickel(II) complexes have recently been described by Sataki and co-workers.[5] The present paper deals with further aspects of the chemistry of the nickel(II) complexes.



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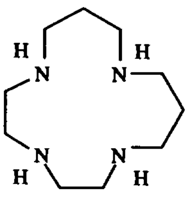

(2)

EXPERIMENTAL

Physical measurements

IR spectra (as KBr discs) were recorded on a Perkin–Elmer 1710 FT instrument. Visible spectra were recorded with a Perkin–Elmer Lambda 5 UV–vis spectrophotometer. Conductance measurements were made with an AGB 1000 conductivity meter and a dip-type cell with platinized electrodes. Measurements were made using 1×10^{-3} mol dm^{-3} aqueous solutions of the complexes. ^1H NMR spectra were determined at 300 MHz using TMS as reference in $CDCl_3$ solution.

In the cyclic voltammetry experiments, a 1×10^{-3} mol dm^{-3} solution of the complex in 0.1 mol dm^{-3} $NaClO_4$ was used. The working electrode was a hanging mercury drop electrode (HMDE) with a surface area of 0.0139 cm^2. The counter electrode was a coiled platinum wire and a standard calomel

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electrode (SCE) was used as the reference electrode. The solution was degassed with argon prior to carrying out the electrochemical measurements. Potentiometric titrations were carried out using a Radiometer Titralab system.

Reagents and synthesis

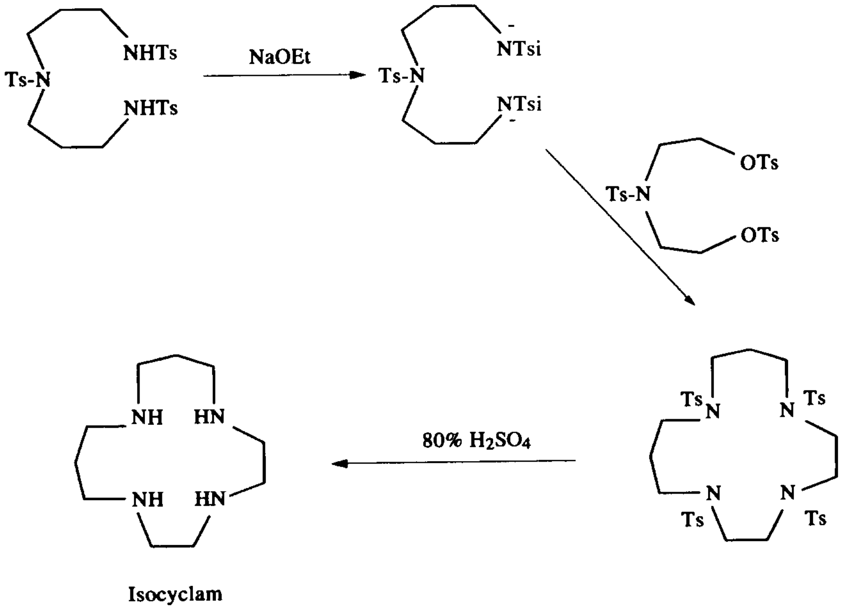
All chemicals used were of reagent grade. The ligand isocyclam was prepared as outlined in Scheme 1.

1,4,7 - *Tris*(p - *toluenesulphonyl*) - 1,7-*diamino* - 4 - *azaheptane*. 1,7-Diamino-4-azaheptane (dipropylenetriamine; 10.0 g, 0.076 mol) and sodium hydroxide (9 g, 0.230 mol) were dissolved in water (50 cm^3) and stirred vigorously at room temperature. *p*-Toluenesulphonyl chloride (43 g, 0.230 mol) in diethyl ether (150 cm^3) was added dropwise to the stirred solution. After completion of the addition, the solution was stirred for a further hour and allowed to stand overnight. The white solid was filtered off and recrystallized from ethanol, yield 35.5 g (79%). The disodium salt was prepared as follows. Sodium (0.32 g, 13.6 mmol) was dissolved in anhydrous ethanol (50 cm^3) and the solution stirred. The tosylated triamine (6.3 mmol) was added in small amounts and the solution stirred for a further hour. The white precipitate was filtered off and washed with anhydrous ethanol then dry ether, and dried *in vacuo*, yield 2.6 g (60%).

Tritosyldiethanolamine was prepared as described previously.[6]

1,4,7,11 - *Tetrakis*(p - *toluenesulphonyl*) - 1,4,7,11 - *tetra-azacyclotetradecane*. The disodium salt prepared above (2.6 g, 4.1 mmol) was dissolved in dry DMF (60 cm^3) and heated on an oil bath to 110°C. Tritosyldiethanolamine (2.3 g, 4.1 mmol) in DMF (30 cm^3) was added dropwise with stirring over a period of 2 h. The resulting mixture was stirred for a further hour and allowed to cool overnight. Most of the DMF was removed under reduced pressure and water added to the residue to precipitate the tetratosylate. The tetratosylate was dissolved in hot toluene and the solution filtered. The toluene was removed and the residue dissolved in hot ethanol. On cooling the product crystallized and was filtered off and dried *in vacuo*, yield 2.5 g (75%).

Hydrolysis of the tetratosylated isocyclam was carried out as follows. The tosylated isocyclam (2.2 g, 2.7 mmol) was suspended in sulphuric acid (80%, v/v) and the mixture heated slowly with manual stirring on an oil bath to 150°C. The temperature was maintained for 1 h, by which time the solid had completely dissolved. The reaction mixture was then cooled and added very slowly, with vigorous stirring, to methanol–ether (1 : 1, 50 cm^3) in an ice bath. The resulting solid was filtered off and washed with ether. The hydrosulphate salt was dissolved in water and a solution of sodium hydroxide added to liberate the free base. The solution was extracted with dichloromethane (six times) and the extracts dried over anhydrous sodium sulphate. After filtration the solvent was removed under reduced pressure to give a viscous oil, which gave the following ^1H NMR spectrum in $CDCl_3$: 1.50–2.10 (m, 4H); 2.50–3.13 (m, 16H); 3.75–4.05 (s, 4H, NH).



Scheme 1.

The oil was dissolved in the minimum volume of methanol and concentrated HBr added dropwise with stirring to precipitate the colourless tetrahydrobromide salt, which was filtered off and dried *in vacuo*, yield 0.45 g (32%).

[Ni(*isocyclam*)](ClO_4)$_2$. The ligand tetrahydrobromide (0.10 g) was dissolved in the minimum volume of water and the solution heated on a water bath. An excess of solid basic nickel(II) carbonate was added. On heating the solution became orange. The excess carbonate was filtered off and a few drops of a concentrated aqueous solution of sodium perchlorate added. On standing the orange complex crystallized and was recrystallized from the minimum volume of hot water.

RESULTS AND DISCUSSION

Isocyclam can be readily prepared in acceptable yield by the Richman–Atkin's procedure (Scheme 1) followed by detosylation with 85% sulphuric acid. Isocyclam is a relatively low melting solid, m.p. 75–76°C,[1] and was isolated as a very viscous oil. It was found most convenient to convert this oil to the tetrahydrobromide salt, which can be readily purified by recrystallization. The molecular weight of the tetrahydrobromide was checked by potentiometric titration found: 522.6; calc. for $C_{10}H_{28}N_4Br_4$: 524.0).

The orange nickel(II) complex [NiL](ClO_4)$_2$ was readily prepared by reaction of excess basic nickel (II) carbonate with L · 4HBr in an aqueous slurry, followed by addition of sodium perchlorate. The *d–d* spectrum of the complex in aqueous solution has a strong band at 466 nm typical of planar nickel(II); however, there are weak bands ν_2 and ν_3 present characteristic of octahedral nickel(II). The intensity of the 466 nm band is also strongly temperature-dependent, indicating the existence of a planar $\rightleftharpoons$ octahedral equilibrium in aqueous solution (Fig. 1). In the non-coordinating solvent nitromethane, the nickel complex has an absorption coefficient $\varepsilon = 116.3$ dm^3 mol^{-1} cm^{-1}, a value which is in almost exact agreement with the figure 116.4 dm^3 mol^{-1} cm^{-1} quoted by Sabatini and Fabbrizzi[1] in 7.2 mol dm^{-3} aqueous sodium perchlorate solution, where the complex is 100% planar. Values of the equilibrium constant K = [octahedral]/[planar] were obtained over the temperature range 14.6–59.8°C, as outlined in Table 1. Least squares analysis of the plot of ln K versus $1/T$ (Fig. 2) gives $\Delta H^\circ = -22.6 \pm 0.5$ kJ mol^{-1} and $\Delta S^\circ = -74 \pm 2$ J K^{-1} mol^{-1} for the equilibrium:

$$[NiL]^{2+} + 2H_2O \overset{K}{\rightleftharpoons} [NiL(OH_2)_2]^{2+}.$$

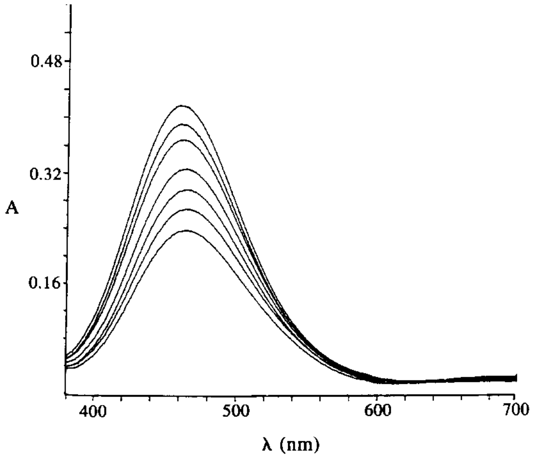


Fig. 1. Temperature dependence of the *d–d* band of [Ni (isocyclam)](ClO_4)$_2$. Complex concentration 5.11×10^{-3} mol dm^{-3}. The spectra were determined (in terms of increasing absorbance) at 14.6, 21.7, 29.1, 35.8, 44.4, 51.2 and 59.8°C.

These values compare well with the available literature data for such equilibria (Table 2). The reactions are exothermic due to the formation of two new Ni—O bonds in the octahedral complex. However, this effect is counterbalanced to a degree by the weaker Ni—N bonds in the octahedral complex, where the Ni—N bonds are somewhat longer (207–210 pm) than those observed in the planar species (188–191 pm). Constriction of two water molecules leads to a negative entropy change.

For low-spin nickel(II) tetramine complexes the energy of the *d–d* band is a measure of the energy of the equatorial Ni—N interactions. The band of the planar [Ni(isocyclam)]$^{2+}$ at 466 nm (21,460 cm^{-1}) is some 1000 cm^{-1} lower in frequency than

Table 1. Square planar $\rightleftharpoons$ octahedral equilibrium of [NiL]$^{2+}$ in aqueous solution

Temp. (°C)	Abs.	ε	% Planar	% Octahedral	K
14.6	0.239	46.8	40.2	59.8	1.49
21.7	0.270	52.8	45.4	54.6	1.20
29.1	0.298	58.3	50.1	49.9	1.00
35.8	0.325	64.2	55.2	44.3	0.81
44.4	0.370	72.4	62.3	37.7	0.61
51.2	0.392	76.7	66.0	34.0	0.52
59.8	0.419	82.0	70.5	29.5	0.42

Values of ε were calculated from the absorbance at 466 nm. The complex concentration was 5.11×10^{-3} mol dm^{-3}. The absorbance coefficient of the pure planar form is 116 dm^3 mol^{-1} cm^{-1}. The temperature dependence of K gives $\Delta H^\circ = -22.6 \pm 1$ kJ mol^{-1} and $\Delta S^\circ = 74 \pm 2$ J K^{-1} mol^{-1}.

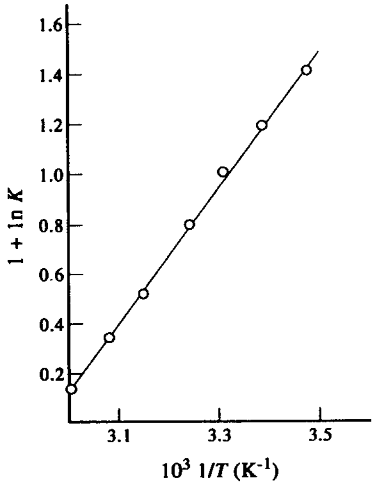


Fig. 2. Plot of ln K versus $1/T$ for the planar $\rightleftharpoons$ octahedral equilibrium of $[Ni(isocyclam)]^{2+}$.

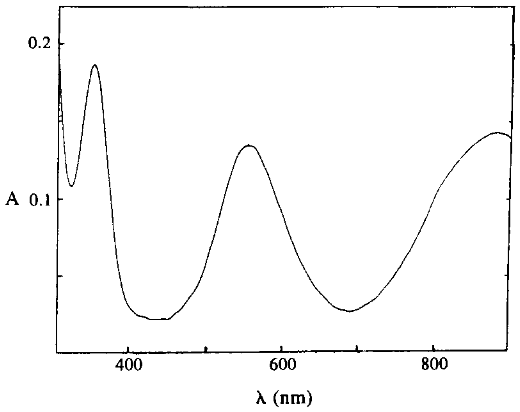


Fig. 3. Visible spectrum of the $[Ni(isocyclam)(en)]^{2+}$ cation.

that of $[Ni(cyclam)]^{2+}$ (22,470 cm^{-1}), establishing that the asymmetric macrocycle exerts weaker metal donor atom interactions than its more symmetrical isomer.

The complex $[Ni(cyclam)]^{2+}$ is known to fold readily to give *cis*-complexes in the presence of chelating ligands such as ethylenediamine.[11] Similar behaviour is also observed with $[Ni(isocyclam)]^{2+}$. Addition of ethylenediamine (en) to an aqueous solution of the planar complex gives the blue octahedral *cis*-$[Ni(isocyclam)(en)]^{2+}$, which gives the visible spectrum shown in Fig. 3. The complex $[Ni(isocyclam)Cl_2]$ has been isolated previously by addition of Cl^- to the planar perchlorate salt in methanol solution.[1] This complex presumably has a *trans* stereochemistry. The electronic spectrum recorded at liquid nitrogen temperature displays six bands in the 350–1200 nm region due to the weak ligand field exerted by the axial Cl^- ligands and the stronger in-plane field exerted by the nitrogen donors. A much simpler spectrum is observed with the *cis*-NiN_6 chromophore found in *cis*-$[Ni(isocyclam)(en)]^{2+}$.

Table 2. Thermodynamic parameters for square planar $\rightleftharpoons$ octahedral equilibria in nickel(II) complexes of cyclic and non-cyclic tetramines

Ligand	λ_{max} (nm)	ΔH° (kJ mol^{-1})	ΔS° (J K^{-1} mol^{-1})	Ref.
Cyclam	444	−22.6	−83.7	7
Isocyclam	466	−22.6	−74	this work[a]
[12]aneN_4	430	−7.1	−23	8
[13]aneN_4	466	−31.4	−30	9
3,2,3-tet		−18.4	−63	7
2,3,2-tet		−14.2	−37.7	7, 10
2,2,2-tet		−14.2	−12.6	10

[a] Sabatini and Fabbrizzi[1] quote for this equilibrium $\Delta H^\circ = -22.2 \pm 0.4$ kJ mol^{-1} and $\Delta S^\circ = -78.2 \pm 2$ J K^{-1} mol^{-1}.

Nickel(II) complexes of saturated tetra-aza macrocycles undergo chemical and electrochemical oxidation and reduction in solvents such as acetonitrile. Detailed studies on the electrochemistry of nickel(II) macrocyclic complexes has established that these redox processes involve the formation of authentic nickel(III) and nickel(I) species.[12] Recently, there has been considerable interest in the use of nickel(II) macrocyclic complexes as electrocatalysts for the reduction of CO_2 to CO. CO_2 undergoes a one-electron reduction at −2.21 V versus SCE, which is much lower than the thermodynamic potential of −0.52 V. Nickel(II) tetra-aza macrocyclic complexes are known to catalytically reduce CO_2 to CO at voltages as low as −1.4 V.[13,14] The most important catalyst to date is $[Ni(cyclam)]^{2+}$, which selectively reduces CO_2 to CO. Recently, we have reported another nickel(II) polyaza macrocyclic complex which is more effective in 9 : 1 acetonitrile–water solvent.[15]

$[Ni(isocyclam)]^{2+}$ shows a reversible one-electron redox couple at −1.45 V *versus* SCE whose peak current i_{pc} has a linear dependence on (scan rate)$^{1/2}$ (Table 3). This potential is close to that reported by Sabatini and Fabbrizzi[1] using acetonitrile as solvent (−1.628 V vs Ag/Ag^+). The more anodic potential observed here is due to the different solvent and reference electrode employed. In addition, in aqueous solution there is a different ratio of the planar and octahedral species. When CO_2 was bubbled through the solution for 20 min and the cyclic voltammogram recorded, an increase in the cathodic current i_{pc} from 2 to 26 μA was observed, accompanied by a shift of E_p^c from −1.52 to −1.32

Table 3. Electrochemical measurements with $[Ni(cyclam)]^{2+}$ and $[Ni(isocyclam)]^{2+}$

Complex	Ni^{III}/Ni^{III} (V)	Ni^{II}/Ni^{I} (V)	E_{pc} (V)
$[Ni(isocyclam)]^{2+}$	+0.85 (100)	−1.45 (140)	−1.32
$[Ni(cyclam)]^{2+}$	+0.81 (60)	−1.59 (180)	−1.48

Measurements were made in aqueous solution. The concentration of $[Ni(cyclam)]^{2+}$ was 1.043×10^{-3} mol dm^{-3} and of $[Ni(isocyclam)]^{2+}$ 1.104 mol dm^{-3}. Under CO_2 there was an increase in the cathodic current with the isocyclam complex to 26 μA, while with the cyclam complex the cathodic current increased to 122 μA. The values in parentheses are the peak height separations in mV.

V compared with the measurements made under argon. The cyclic voltammograms obtained under argon and CO_2 are shown in Fig. 4. Although the catalytic current produced by $[Ni(isocyclam)]^{2+}$ is less than that for $[Ni(cyclam)]^{2+}$, $E_p^c(CO_2)$ is reduced by 160 mV. If CO_2 is allowed to pass through the solution for a longer period of time, the current does not alter but E_p^c is further shifted to −1.26 V.

Rotating disc electrochemistry was also carried out using a copper electrode (area 0.071 cm^2) as the working electrode. The electrode was rotated from 400 to 6400 rpm and the current recorded. The scans obtained are shown in Fig. 5. The slope of the plot of the limiting current versus (rotation rate)$^{1/2}$ is 0.00363, which is in close agreement with the value obtained for $[Ni(cyclam)]^{2+}$ (0.00322) for the two-electron reduction of CO_2 to CO, indicating a similar two-electron reduction process.

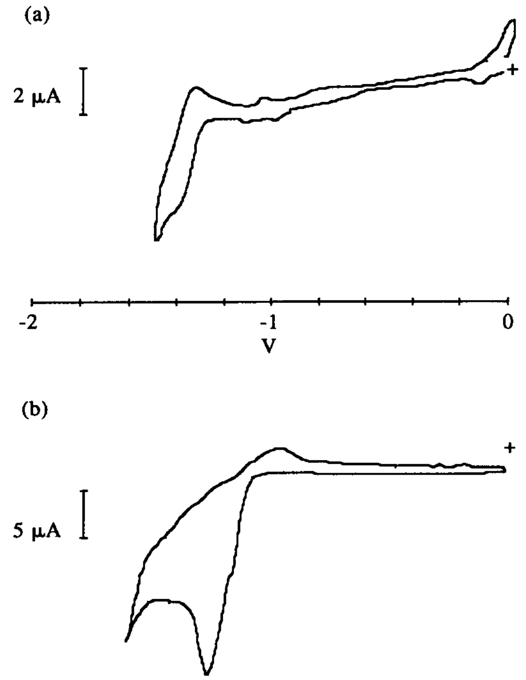


Fig. 4. Cyclic voltammograms for $[Ni(isocyclam)]^{2+}$ (1.043×10^{-3} mol dm^{-3}) in 0.1 mol dm^{-3} $NaClO_4$ with an HMDE working electrode, a platinum wire counter electrode and an SCE reference electrode: (a) under argon; (b) under CO_2.

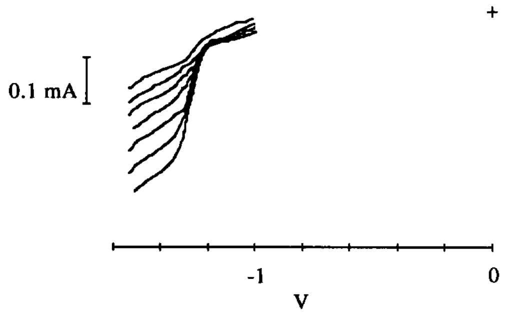


Fig. 5. Rotating disc electrochemistry of $[Ni(isocyclam)]^{2+}$ (1.043×10^{-3} mol dm^{-3}) in 0.1 mol dm^{-3} $NaClO_4$ with a copper working electrode, a platinum wire counter electrode and an SCE reference electrode under CO_2.

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