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Copper(II), Copper(III) and Nickel(II) Complexes of the Macrocyclic Diamide Ligands 1,4,7,10-tetra-azacyclododecane-2,3-dione, 1,4,7,11-tetra-azacyclotridecane-2,3-dione, 1,4,8,11-tetra-azacyclotetradecane-2,3-dione and Electrochemical Studies on the Copper and Nickel Complexes of 1,4,8,11-tetra-azacyclotetradecane-5,7-dione

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The syntheses of three new macrocyclic diamide ligands, 1,4,7,10-tetra-azacyclododecane-2,3-dione (L_A), 1,4,7,11-tetra-azacyclotridecane-2,3-dione (L_B) and 1,4,8,11-tetra-azacyclotetradecane-2,3-dione (L_C) are described. A number of copper(II) and nickel(II) complexes of these ligands have been characterised in the solid state. The complexes are non-electrolytes in aqueous solution due to ionisation of two amide protons to give neutral complexes [M(L–2H)]. The yellow planar nickel(II) complex of L_B, [Ni(L_B–2H)] exists in equilibrium with the blue octahedral species [Ni(L_B–2H)(H_2O)$_2$]. For the octahedral $\rightleftharpoons$ planar equilibrium, $K = 0.51$ at 25 °C, and the corresponding thermodynamic parameters are $\Delta H^\circ = 4.23$ kcal mol^{-1} and $\Delta S^\circ_{298} = +12.8$ cal K^{-1} mol^{-1}. The copper(II) complexes of L_A, L_B and L_C are oxidised in aqueous solution by hydrogen peroxide to give the corresponding copper(III) complexes. The copper(III) complexes are brownish–yellow in colour with d–d bands at ca. *350 nm.*

Cyclic voltammetry on the copper(II)/copper(III) and nickel(II)/nickel(III) redox systems with 1,4,8,11-tetraazacyclotetradecane-5,7-dione (L_D) indicate complete reversibility of the copper(II)/copper(III) couple in N,N-dimethylsulphoxide solution ($E_{1/2} = +0.43$ V versus *Ag/AgCl at 25 °C). The nickel(II)/nickel(III) couple is irreversible in aqueous solution.*

Introduction

A number of recent papers have dealt with the coordination chemistry of macrocyclic diamide ligands. Thus a variety of 12–15 membered dione ligands have been prepared and their metal complexes studied in some detail [1–5]. These potentially quadridentate macrocycles have been shown to form four coordinate N_4 donor complexes (by deprotonation of two amide groups), with divalent metal ions such as Cu(II), Ni(II) and Co(II). Their molecular structure mimics that of analogous complexes of tripeptides such as triglycine. Rybka and Margerum [6] have recently prepared the 14-membered macrocyclic ligand *cyclo*-(β-alanylglycyl-β-alanylglycyl) (I) which reacts with copper(II) and releases four protons in base to form [Cu(L–4H)]$^{2-}$. In addition, copper(III) and nickel(III) complexes of some macrocyclic diamide ligands can be generated in aqueous solution by chemical or anodic oxidation of the corresponding Cu(II) and Ni(II) species [4, 9]. Similar observations have been made with tripeptide ligands [10]. The present paper discusses the preparation and coordination chemistry of the macrocycles 1,4,7,10-tetra-azacyclododecane-2,3-dione (II = L_A); 1,4,7,11-tetra-azacyclotridecane-2,3-dione (III = L_B); 1,4,8,11-tetra-azacyclotetradecane-2,3-dione (IV = L_C) and electrochemical studies on the copper(II)/copper(III) and nickel(II)/nickel(III) redox systems with the dianion of the macrocycle 1,4,8,11-tetra-azacyclotetradecane-5,7-dione (V = L_D).

The ligands L_A, L_B and L_C appear to be the first examples of macrocycles in which the dione groups occupy adjacent positions in the five-membered chelate rings. Open chain ligands of this general type have been previously characterised [7], and interesting tetranuclear complexes of the type shown in (VI) have been prepared [8].

Experimental

The ligand 1,4,8,11-tetra-azacyclotetradecane-2,3-dione (L_C) was prepared as follows. 1,10-Diamino-4,7-diazadecane (3,2,3-tet) (7.0 g, 0.04 mol) was dissolved in dry methanol (250 cm^3), and cooled to 0 °C in an ice-bath. Then with stirring, diethyl oxalate

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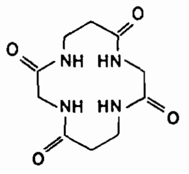
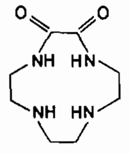
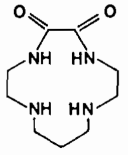


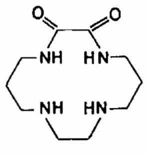
(I)



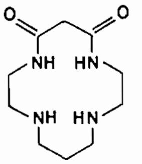
(II) = L_A



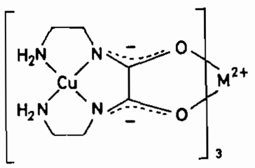
(III) = L_B



(IV) = L_C



(V) = L_D



(VI) M = Co^{II}, Ni^{II}

(5.85 g, 0.04 mol) was added. After stirring for *ca.* 2 hours, the solvent was removed on a rotatory evaporator to give a colourless solid (4 g) which could be recrystallised from hot ethanol or hot water, m.p. 156–158 °C. *Anal.* Calc. for $C_{10}H_{20}N_4O_2\cdot H_2O$: C, 48.8; H, 9.0, N, 22.7. Found: C, 49.1; H, 8.8; N, 22.8%. The water content is dependent on the degree of drying and some samples analysed as hemihydrates or sesquihydrates rather than as monohydrates. The IR spectrum shows the characteristic νOH bands due to water, with νNH bands at 3050, 3160 and 3280 cm^{-1} with amide bands at 1650 and 1510 cm^{-1}.

The ligand 1,4,7,10-tetra-azacyclododecane-2,3-dione (L_A) was prepared as follows. 1,8-Diamino-3,6-diazaoctane (2,2,2-tet) (4 g, 0.027 mol) was dissolved in dry methanol (250 cm^3) and diethyl oxalate (4 g, 0.027 mol) in methanol (50 cm^3) was added dropwise with stirring at room temperature. After stirring (4 h) the solvent was removed to give an oily solid. Cold ethanol was then added and a colourless solid was obtained by slow evaporation (yield 0.75 g). *Anal.* Calc. for $C_8H_{16}N_4O_2\cdot H_2O$: C, 44.0; H, 8.3; N, 25.7. Found: C, 43.9; H, 8.0; N, 25.9%.

An exactly analogous procedure was employed to prepare 1,4,7,11-tetra-azacyclotridecane-2,3-dione (L_B) using 1,9-diamino-3,7-diazanonane (2,3,2-tet) (10 g, 0.06 mol) and diethyl oxalate (9.12 g, 0.06 mol). The yield in this case was 1.6 g. *Anal.* Calc. for $C_9H_{18}N_4O_2\cdot 1.5H_2O$: C, 44.8; H, 8.8; N, 23.2. Found: C, 44.5; N, 8.7; N, 22.6%.

The ligand 1,4,8,11-tetra-azacyclotetradecane-5,7-dione and its copper(II) and nickel(II) complexes were prepared as previously described [5].

The copper(II) and nickel(II) complexes of 1,4,7,11-tetra-azacyclotridecane-2,3-dione (L_B) were prepared as follows.

(a) Copper(II) Complex

The ligand L_B (0.21 g, 0.01 mol) was dissolved in methanol (50 cm^3) and added slowly to copper(II) sulphate pentahydrate (0.25 g, 0.01 mol) dissolved in the minimum volume of methanol–water (1:1 v/v). The solution was heated on a water bath (10 min) and the pH adjusted to *ca.* 8.0 with sodium hydroxide (1 mol dm^{-3}). The solution was then taken to dryness on a steam bath and the residue extracted with hot methanol. The methanol extract was filtered and concentrated to small volume, and water (5 cm^3) added. On standing overnight blue crystals deposited, which were filtered, washed with ethanol then ether and dried *in vacuo*. *Anal.* Calc. for $C_9H_{16}N_4O_2Cu\cdot 3H_2O$: C, 32.74; H, 6.72; N, 16.97. Found: C, 32.86; H, 6.95; N, 16.69%.

(b) Nickel(II) Complex

The ligand L_B (0.21 g) was dissolved in the minimum volume of water–methanol (1:1 v/v) and a few drops of dilute sulphuric acid added. To this solution was added nickel(II) sulphate·$7H_2O$ (0.28 g) and the mixture was then heated on a steam bath for *ca.* 15 min. The hot solution was then treated with dilute $Ba(OH)_2$ solution to precipitate the SO_4^{2-} ions present. The pH rose to *ca.* 8 during the addition and the solution was then digested on a steam bath for *ca.* 1 h and allowed to stand overnight. The yellow solution was filtered and the filtrate evaporated to small volume. The complex crystallised on addition of ethanol, and was further purified by dissolving in the minimum volume of hot water and reprecipitating with ethanol. *Anal.* Calc. for $C_9H_{16}N_4O_2Ni\cdot 2.5H_2O$: C, 34.21; H, 6.69; N, 17.73. Found: C, 34.61; H, 6.58; N, 17.94%.

The copper(II) complex of 1,4,7,10-tetra-azacyclododecane-2,3-dione (L_A) was prepared essentially as described for the ligand L_B. The complex is greenish–blue in colour and was purified by dissolving in the minimum volume of water and reprecipitating with excess ethanol. *Anal.* Calc. for $C_8H_{14}N_4O_2Cu\cdot 2.5H_2O$: C, 31.31; H, 6.24; N, 18.26. Found: C, 31.35; H, 6.61; N, 18.47%.

The copper(II) complex of L_C was prepared as follows. A solution of copper(II) sulphate pentahydrate (0.25 g, 0.001 mol) in water (5 cm^3) was added slowly to a hot solution of the ligand L_C (0.23 g, 0.001 mol) in methanol (15 cm^3). The solution was heated on a steam bath for *ca.* 15 min and treated with 1 mol dm^{-3} sodium hydroxide (2 cm^3). The deep blue solution was evaporated to dryness

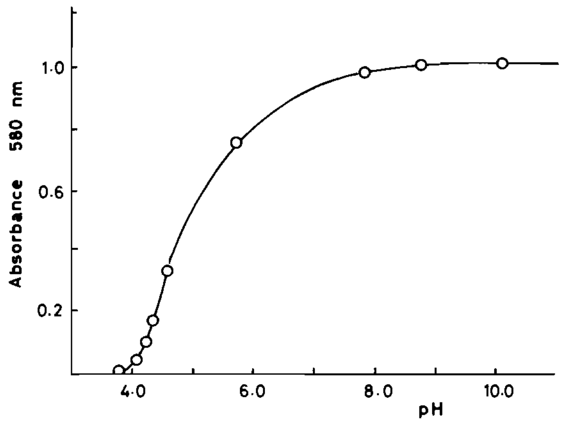


Fig. 1. Spectrophotometric titration of a 1:1 ratio of copper(II) and L_B at 580 nm.

and the residue extracted with hot methanol. The solution was filtered and evaporated to dryness *in vacuo* to give a glass. *Anal.* Calc. for $C_{10}H_{18}N_4O_2Cu \cdot 3.5H_2O$: C, 34.03; H, 7.11; N, 15.67. Found: C, 34.80; H, 6.93; N, 15.17%.

Infrared spectra were determined as KBr discs using a Perkin-Elmer 457 instrument. Visible spectra were determined using a Perkin-Elmer 402 spectrophotometer. Conductivity measurements were made with a Portland Electronics Model P310 conductivity meter using 10^{-3} mol dm^{-3} solutions at 25 °C. All pH measurements were made with a Radiometer PHM64 pH meter, which was standardised using 0.05 mol dm^{-3} potassium hydrogen phthalate (pH 4.008) and phosphate buffer (0.025 mol dm^{-3}), pH 6.86 at 25 °C.

Electrochemistry was carried out using a PAR170 electrochemistry system. Measurements were made using 1×10^{-3} mol dm^{-3} solutions. The working electrode was a platinum or carbon paste electrode.

Results and Discussion

The macrocyclic diamides prepared have 12-(L_A), 13-(L_B), 14-(L_C) and 14-(L_D) membered rings with variable cavity sizes. The disposition of the dione groupings is varied between L_C and L_D. Significantly more strain is expected in metal complexes of L_C compared with L_D since deprotonation of L_C should lead to an essentially planar five-membered chelate ring. The macrocycles are readily prepared by the reaction of the appropriate tetramine with diethyl oxalate (or malonate in the case of L_D). All the ligands are hydrated, presumably due to hydrogen bonding of water molecules to the amide groups.

Addition of concentrated hydrochloric acid to L_B in methanol gives a solid dihydrochloride $L_B \cdot 2HCl$. Potentiometric titration of the dihydrochloride in aqueous solution with sodium hydroxide gives inflexion points after the addition of one and two equivalents of base and the expected molecular weight (Calc. 287.2; Found 286). The approximate pK_a values for the equilibria (1) and (2) are 7.35 and 9.25 respectively at 25 °C.

TABLE I. Properties of the Copper(II) Complexes.[a]

Ligand	Λ_M at 25 °C (S cm^2 mol^{-1})	Ring size	λ_{max} (nm)	($M^{-1\epsilon}$ cm^{-1})
L_A	21.5	12	595	153
L_B	23	13	575	131
L_C	21	14	575	107
L_D	18	14	506	86

[a] In aqueous solution. For $[Cu[12]aneN_4](NO_3)_2$ which is five coordinate, λ_{max} is 590 nm with $\epsilon = 257\ M^{-1}$ cm^{-1} in aqueous solution, values which are comparable to those of the copper complex of L_A.

$$L_BH_2^{2+} \rightleftharpoons L_BH^+ + H^+ \quad (1)$$

$$L_BH^+ \rightleftharpoons L_B + H^+ \quad (2)$$

Copper(II) Complexes

Spectrophotometric titration of a 1:1 ratio of $L_B \cdot 2HCl$ and copper(II) at 580 nm shows that formation of the copper(II) complex is essentially complete in the pH range 9–10, Fig. 1, and requires four equivalents of base corresponding to the equilibrium (3)

$$L_BH_2^{2+} + Cu^{II} \rightleftharpoons [Cu(L_B{-}2H)] + 4H^+ \quad (3)$$

The copper complex is quite labile in acidic solution and rapidly dissociates unlike the copper(II) complex of 1,4,7,10-tetra-azacyclotridecane ([13]aneN_4). Acid lability is a general feature of all the copper(II) complexes here described.

Macrocyclic diamide complexes of copper(II) normally display a single d–d band in the region 520–620 nm with absorption coefficients in the range 80–150 dm^3 mol^{-1} cm^2 [4]. Strain in the ring system is indicated by high values of the absorption coefficient and shifts of the d–d band to longer wavelengths. The copper(II) complex of L_A with λ_{max} 595 nm (ϵ = 153) exhibits the greatest strain as expected, and the least strain is observed in the complex of L_D (λ_{max} 506 nm, ϵ = 86), Table I. Considerably more strain occurs with L_C compared with L_D, since the former ligand has a *geminal* dione grouping in the five-membered chelate ring.

In the complex $[Cu([12]aneN_4)NO_3]NO_3$ the copper has a square pyramidal stereochemistry with a nitrato ligand in the fifth coordination site [11]. The copper(II) lies 0.5 Å above the plane of the

TABLE II. Cyclic Voltammetry of the Copper Complex of L_D at 25 °C.[a]

Cyclic Voltammetry on Pt versus *s.c.e.*[a]

Ep(c) (V)	Ep(a) (V)	ν (mV/s)	$\nu^{1/2}$ $(mV/s)^{1/2}$	Ip(c) (μA)	Ip(a) (μA)	Ip(c)/Ip(a)	ΔEp (mV)	½Ep (V)
0.73	0.64	50	7.07	32.5	31.5	1.03	90	+0.69
0.75	0.62	100	10.0	45.0	41.0	1.09	130	+0.69
0.74	0.62	200	14.4	65.0	54.0	1.20	120	+0.68
0.76	0.60	500	22.3	87.5	85.0	1.02	160	+0.68

Cyclic Voltammetry on Pt versus *Ag/AgCl.*[b]

Ep(c) (V)	Ep(a) (V)	ν (mV/s)	$\nu^{1/2}$ $(mV/s)^{1/2}$	Ip(c) (μA)	Ip(a) (μA)	Ip(c)/Ip(a)	ΔEp (mV)	½Ep (V)
0.47	0.40	50	7.07	6.0	5.0	1.20	70	+0.43
0.47	0.40	100	10.0	8.5	7.0	1.21	70	+0.43
0.47	0.40	200	14.14	12.0	10.25	1.17	70	+0.43
0.46	0.39	500	22.3	18.5	16.5	1.12	70	+0.43

[a] Aqueous solution, 0.1 *M* $NaClO_4$ supporting electrolyte, 25 °C. [b] Dimethylsulphoxide solution, 0.3 *M* tetra n-butyl ammonium perchlorate supporting electrolyte, 25 °C.

nitrogen donors. Such a 'sitting atop' structure seems probable for $[Cu(L_A-2H)]\cdot 2.5H_2O$ since the cavity size will be reduced by the two amide anions. A very flattened tetrahedral geometry (*i.e.* distorted planar) seems most probable for the copper complexes of L_B and L_C. All the complexes have low molar conductivities in aqueous solution (18–23S cm^{-2} mol^{-1}), Table I, consistent with their formulation as non-electrolytes and ionisation of the two amide protons. Unfortunately the conductivity data in these complexes does not give any information regarding the coordination number of the metal ion.

The M–N distances in the saturated macrocyclic N_4 complexes lie in the range 2.03–2.10 Å for copper(II) which is longer than 1.86–1.92 Å for low spin nickel(II). A significant increase in the thermodynamic stability of the complexes is expected on oxidation from d^9 copper(II) to d^8 copper(III), as a result of the size contraction (to fit the cavity) and the stronger preference for square-planar coordination by the d^8 system (similar to low spin nickel(II), but somewhat smaller due to the higher charge).

Addition of hydrogen peroxide to aqueous solutions of the copper(II) complexes of L_A, L_B and L_C leads to relatively slow oxidation to the yellow–brown colour of the copper(III) complex. All the copper(III) derivatives show the characteristic absorption band at *ca.* 350 nm and the complete absence of any d–d band in the 500–600 nm due to copper(II), Fig. 2. Similar absorption bands have been reported for the copper(III) complexes of peptides where $E_{1/2}$ is *ca.* 0.4 V *versus* s.c.e. [10]. The copper(II) complex of L_D is readily oxidised to the copper(III) derivative in aqueous solution using peroxydisulphate as the oxidant [9].

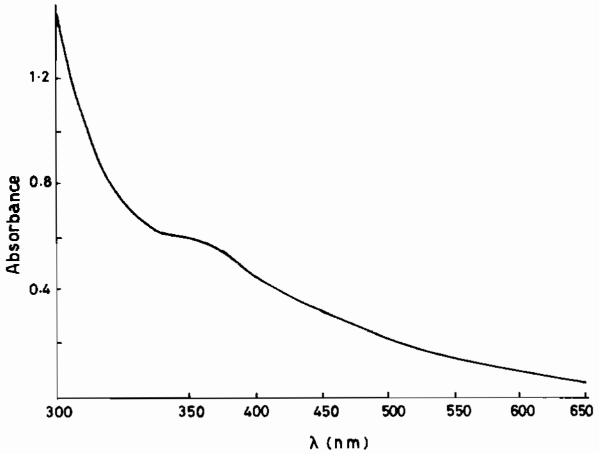


Fig. 2. Absorption spectrum of the copper(III) complex of L_B prepared by H_2O_2 oxidation, showing the copper(III) band at *ca.* 350 nm. The band due to copper(II) at 575 nm is absent.

Cyclic voltammetry of *ca.* 1 × 10^{-3} *M* solutions of the copper(II) complex of L_D were carried out using a platinum working electrode and a saturated calomel reference electrode (s.c.e.) or Ag/AgCl electrode. Typical results are summarised in Table II.

In N,N-dimethylsulphoxide solution, cyclic voltammetry on platinum shows a fully reversible one-electron oxidation at +0.43 V *versus* Ag/AgCl. A plot of peak height ($I_p(c)$) *versus* the square root of the scan rate ($\nu^{1/2}$) is linear passing through the origin indicating diffusion control. The separation

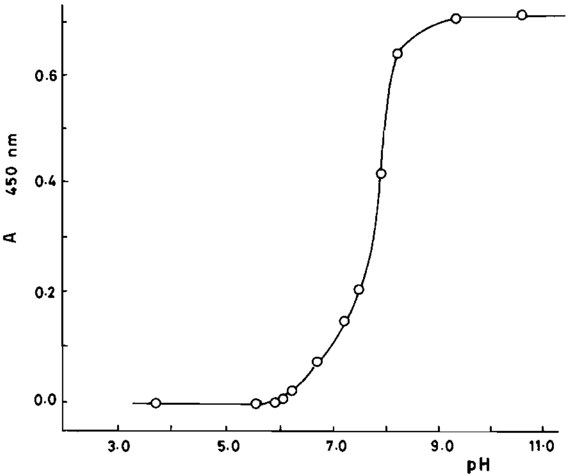


Fig. 3. Spectrophotometric titration of a 1:1 ratio of nickel(II) and L_C at 450 nm.

of the anodic and cathodic peaks, ΔE, is 70 mV and peak height ratios are close to unity. In addition $E_p(c)$, and $E_p(a)$ and $\frac{1}{2}E_p$ are independent of the scan rate.

In aqueous solution cyclic voltammetry on platinum shows a quasi-reversible one electron oxidation at +0.69 V *versus* s.c.e. A plot of peak height *versus* the square root of the scan rate is linear indicating diffusion control. However, ΔE ranges from 90 mV at 50 mV s^{-1} to 165 mV at 500 mV s^{-1} implying that electron transfer is slightly sluggish. The peak height ratio is close to unity, establishing that the copper(III) complex is stable on the time scale of the experiment and is available for reduction.

Similar experiments using a carbon paste working electrode and an s.c.e. as reference electrode (1×10^{-3} *M* complex in water, 0.1 *M* $NaClO_4$ supporting electrolyte) showed a one-electron oxidation at $\frac{1}{2}E_p$ = +0.68 V *versus* s.c.e. A plot of $I_p(c)$ *versus* $\nu^{1/2}$ is curved suggesting an absorption process. Values of ΔE depend on the scan rate (50 mV at ν = 20 mV s^{-1} to 210 mV at ν = 200 mV s^{-1}). The proximity of the wave to the anodic limit prevented the determination of $I_p(a)$ so that peak height ratios could not be determined. The E value in aqueous solution +0.69 V *versus* s.c.e. is in reasonable agreement with a recently determined value of +0.64 V by Kodama and Kimura [4], but somewhat different from the +0.7 V quoted by Fabbrizzi and Poggi [9].

Nickel(II) Complexes

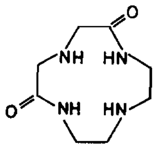
Nickel(II) reacts with L_C in basic solution to give a yellow solution of the planar complex. Spectrophotometric titration at 450 nm, Fig. 3, indicates that the complex is essentially fully formed at pH > 8. Attempts to isolate an analytically pure sample of the complex were unsuccessful. Unlike the copper(II) derivative, the nickel(II) complex shows little solubility in methanol.

TABLE III. Temperature Dependence of the Octahedral ⇌ Planar Equilibrium of the Nickel(II) Complex of L_B.

Temp. (°C)	ϵ^a	% Planar	% Octahedral	K^b
25	17.5	33.9	66.1	0.51
32	18.5	35.9	64.1	0.56
42	21.2	41.1	58.9	0.70
45	22.8	44.2	55.8	0.79
50	24.3	47.1	52.9	0.89

[a] Value of the absorption coefficient at 445 nm based on the stoichiometric concentration of the complex. In 6 *M* $NaClO_4$, the value of ϵ = 50.6 and this is assumed to be 100% of the planar form. [b] From the temperature dependence of K, ΔH° = 4.23 kcal mol^{-1} and ΔS° = +12.8 cal K^{-1} mol^{-1}.

Complex formation between nickel(II) and the ligand L_A could not be detected, and it is presumed that the small hole size, and the strain induced on deprotonation precluded the formation of such a complex (see later). Nickel(II) reacts with L_B in basic solution to give $[Ni(L_B-2H)]\cdot 2.5H_2O$. The complex shows an absorption band at 445 nm typical of a planar complex but the extinction coefficient (ϵ = 25 M^{-1} cm^{-1}) is quite low. Square planar macrocyclic diamide complexes of nickel(II) normally show a single absorption band in the range 410–460 nm with absorption coefficients in the range 80–100 [4]. Kodama and Kimura [4] have recently observed an octahedral ⇌ planar equilibrium in the nickel(II) complex derived from the ligand (VII). At 25 °C there is *ca.* 85% planar and 15% of the octahedral species (K = planar/octahedral = 5.67) with ΔH° = 8.7 kcal mol^{-1} and ΔS° = 33 cal K^{-1} mol^{-1}. Such octahedral ⇌ planar equilibria are well established for a variety of nickel(II) complexes of macrocyclic tetra-aza ligands [12–16], and a similar situation occurs with the nickel(II) complex of L_B.



(VII)

Potentiometric and spectrophotometric titrations indicate that the nickel(II) complex of L_B is essentially completely formed at pH 9, giving a weak absorption band at 445 nm typical of the planar complex. The band intensity is markedly increased

TABLE IV. Thermodynamic Parameters for Octahedral ⇌ Planar Equilibria in Nickel(II) Complexes of Macrocycles.

Ligand	ΔH° (kcal mol^{-1})	ΔS° (cal K^{-1} mol^{-1})	Ref.
[12]aneN_4	1.7	5.5	16
[13]aneN_4	7.5	30	12
[14]aneN_4	5.4	20	12
(VII)	8.7	33	4
L_B	4.2	12.8	This work

TABLE V. Spectral Parameters for Planar Nickel(II) Complexes of Tetra-aza Macrocycles and their Dioxo-derivatives including Polyamine Complexes.

Ligand	Ring size	λ_{max}[a]	Ref.
L_A	12	not formed	This work
L_B	13	445	This work
L_C	14	450	This work
L_D	14	464(77)	5
(VII)	12	465(100)	4
(VIII)	13	412(110)	4
[12]aneN_4	12	430	15
[13]aneN_4	13	466	15
[14]aneN_4	14	444	15
iso[14]aneN_4	14	463	17
[15]aneN_4	15	464	15
2,2,2-tet		444	15
2,3,2-tet		446	15
3,2,3-tet		459	15
3,3,3-tet		475	15

[a] Absorption coefficients in parenthesis.

by the addition of sodium perchlorate (6 *M*) or by raising the temperature. This behaviour is consistent with the equilibrium (4) [13].

$$[Ni(L_B-2H)(OH_2)_2] \rightleftharpoons [Ni(L_B-2H)] + 2H_2O \qquad (4)$$

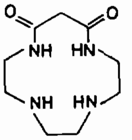
blue, high spin   yellow, low spin

At 25 °C there is *ca.* 34% of the planar species and 66% of the octahedral (K = 0.51). The temperature dependence of K gives $\Delta H^\circ = 4.23$ kcal mol^{-1} and $\Delta S^\circ_{298} = +12.8$ cal K^{-1} mol^{-1} over the temperature range 25–50 °C, Table III.

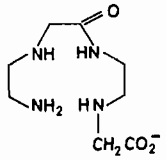
As expected the equilibrium (4) is endothermic and is displaced to the right by either an increase in the temperature or by an increase in the concentration of an inert salt which reduces the 'free' water concentration. Equilibria of type (4) display ΔH values in the range +1.7 to +8.7 kcal mol^{-1} and ΔS values of +5.5 to +3.3 cal K^{-1} mol^{-1} for a variety of macrocycles, Table IV.

It has been suggested that a possible explanation for the relatively low entropy term for the equilibrium involving Ni[12]aneN_4 arises due to the formation of a five-coordinate complex rather than a four coordinate complex, leading to the loss of fewer water molecules [16], and a similar explanation may also apply to the nickel(II) complex of L_B.

The nickel(II) complexes of 12-, 13- and 14-membered tetra-aza macrocycles exist in solution as an equilibrium mixture of the blue high-spin form and the yellow low-spin species [12–16]. The position of the equilibrium varies with ring size, and ratios of high-spin to low-spin forms at 25 °C are 99:1 ([12]aneN_4), 13:87 ([13]aneN_4), 29:71 ([14]aneN_4) and 99:1 ([15]aneN_4). Complexes of the 12- and 15-membered rings are more than 99% in the blue form while the 13- and 14-membered rings exist predominantly as the yellow form. Spin pairing in the yellow species involves a reduction in the Ni–N bond length (Ni–N for high spin 2.10 Å; low spin 1.90 Å) [12]. The energy of the d–d band has been used as a measure of the Ni–N interactions in the planar complexes [12]. Amongst nickel(II) complexes of dioxo-ligands, the longest wavelength band (465 nm, ε = 100 M^{-1} cm^{-1}) is observed with the 12-membered ligand (VII) and the 14-membered ligand L_D. The strongest field is exerted by the 13-membered ligand (VIII) with λ_{max} 412 nm which compares closely with the complex of tetraglycine (IX) with λ_{max} 412 nm [4]. The two amide anions decrease the cavity size of the 12-membered ring which is optimum for low spin nickel(II), Table V, thus making the 13-membered ring the size of best fit. It is relevant that we were unable to prepare a nickel(II) complex of the 12-membered L_A, although it was possible to isolate a copper(II) complex. Copper(II) is known to 'sit atop' the ligand in its complexes with 12aneN_4 with the copper being 0.51 Å out of the plane of the ring [11]. The nickel(II) complex of the 12-membered dioxo ligand (VII) can be prepared since this ligand does not involve a geminal dione grouping and less strain is thus engendered in the ring system.



(VIII)



(IX)

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