Chemistry of Structurally Developed Macrocycles. Part 2.[1] Synthesis and Complexing Properties of *N,N',N'',N'''*-Tetra(3-aminopropyl)-1,4,8,11-tetra-azacyclotetradecane with Nickel(II)

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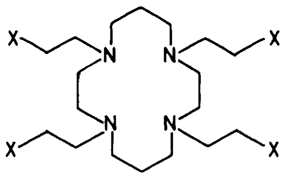
Reduction of *N,N',N'',N'''*-tetra(2-cyanoethyl)-1,4,8,11-tetra-azacyclotetradecane with sodium and ethanol in toluene generates the octa-amine *N,N',N'',N'''*-tetra(3-aminopropyl)-1,4,8,11-tetra-azacyclotetradecane in high yield. Complexation of this ligand with nickel(II) under neutral conditions leads to high-spin five-co-ordinate species in which the co-ordination occurs *via* the four tertiary amine nitrogen atoms and one of the pendant primary amine nitrogen atoms, irrespective of the nature of the anion. Further nickel may also be co-ordinated by the other three primary amine nitrogen atoms, leading to polymeric products. Selective protonation of the four pendant amine groups may be accomplished reversibly in ethanol without destroying the complex. The protonated primary amine groups serve to stabilise the co-ordination of weak donor anions such as ClO_4^-, BF_4^-, and HSO_4^- at the axial co-ordination site, leading to a variety of five-co-ordinate complexes. The spin state of the nickel is dependent on the ligand field strength of the axial group, with the crossover from low spin to high spin observed on changing from bromide to chloride. The direction of the crossover, in terms of axial ligand field strength, indicates a square-pyramidal, rather than a trigonal-bipyramidal structure for these compounds.

In Part 1 [1] I described the high yield synthesis of *N,N',N''*,-*N'''*-tetra(2-cyanoethyl)-1,4,8,11-tetra-azacyclotetradecane (tetracyanoethylcyclam), L^1, and suggested this compound as a possible precursor to macrocyclic systems in which the behaviour of a metal ion locked within a cyclic array of donor atoms and at the same time perturbed axially by donor groups pendant from the macrocycle, could be observed. Tetracyanoethylcyclam itself is unsuitable, because the linear nature of the nitrile groups prevents them from co-ordinating intramolecularly to their parent metal ion, and thus it is necessary to convert the nitriles into non-linear, co-ordinating functional groups. Potentially one of the most interesting conversions is their reduction to primary amines, producing the ligand *N,N',N'',N'''*-tetra(3-aminopropyl)-1,4,8,11-tetra-azacyclotetradecane (tetra-aminopropylcyclam), L^2, since attenuation of the co-ordinating ability of the pendant amines, by selective protonation in the manner already demonstrated by Lotz and Kaden,[2,3] would become possible.

Our first attempts to prepare L^2 by reduction with either lithium aluminium hydride or diborane were unsuccessful; however, treatment of L^1 with sodium and ethanol in toluene accomplishes the reduction effectively and in high yield, thus providing a means of studying L^2 as a co-ordinating species. We report here upon the co-ordination of this ligand, in both its protonated and neutral forms, to nickel(II).

Experimental

Carbon-13 n.m.r. spectra were recorded using a Brucker WH90 Fourier-transform spectrometer at 22.63 MHz, with proton noise decoupling. Infrared spectra were determined for Nujol mulls using a Perkin-Elmer 598 spectrometer. Magnetic moments were measured with a Newport Gouy balance and are corrected for ligand and inner-core diamagnetism using Pascal's constants. Electronic spectra were obtained with a Unicam SP 700A or SP 8000 spectrometer. Mass spectra were recorded with an A.E.I. MS902 spectrometer. Microanalyses were performed by the Analytical Department of the Queen's University of Belfast.



L^1; X = CN
L^2; X = CH_2NH_2

Tetracyanoethylcyclam was prepared as previously described.[1] All other reagents were obtained commercially and used without special purification.

N,N',N'',N'''*-Tetra*(3*-aminopropyl*)-1,4,8,11*-tetra-azacyclotetradecane*, L^2.—Tetracyanoethylcyclam (2 g) was dissolved in boiling sodium-dried toluene (120 cm^3) to which had been added sodium metal (6.4 g). Dry ethanol (32 cm^3) was added dropwise to the refluxing mixture over 2 h, and refluxing was continued for a further 1.5 h, after which all the sodium had dissolved. The mixture was cooled overnight in a refrigerator, then the sodium ethoxide was separated by filtration and washed thoroughly with toluene. The washings and filtrate were combined and evaporated to leave a sticky residue. This residue was extracted with boiling benzene (3 × 25 cm^3). Evaporation of the benzene left a pale yellow oil, which slowly crystallised (1.9 g, 92%).

The ligand L^2 was purified by first preparing the complex $[Ni(H_4L^2)(ClO_4)][ClO_4]_5$ (1), as described below, and then removing the pure L^2 from it according to the following procedure.

$[Ni(H_4L^2)(ClO_4)][ClO_4]_5$ (1 g) was dissolved in water (40 cm^3). The solution was basified to pH 7 with 10 mol dm^{-3} sodium hydroxide, and then sodium cyanide (0.22 g) was added. The solution was warmed on a steam-bath for 10 min, then the pH was raised to 13 with more 10 mol dm^{-3} sodium hydroxide. The solution was then evaporated to dryness and the residue extracted with benzene (3 × 20 cm^3). The benzene solution was dried (NaOH), filtered, and evaporated, yielding the pure product as a colourless oil which slowly crystallised

(0.3 g, 76%). ^{13}C N.m.r. (C_6D_6; p.p.m. downfield from $SiMe_4$): δ 25.5, 32.0, 41.1, 52.7, 52.8, and 53.5; *m/z* 428 (M^+; calc. 428). For analysis L^2 was converted into its crystalline octahydrochloride by dissolution in ethanol followed by addition of the stoicheiometric amount of concentrated aqueous hydrochloric acid. The crude product crystallised from concentrated hydrochloric acid on addition of ethanol as the *octahydrochloride dihydrate*, with the retention of two molecules of hydrogen chloride, m.p. 254 °C (decomp.) (Found: C, 31.8; H, 8.0; Cl, 42.5; N, 13.8. $C_{22}H_{66}Cl_{10}N_8O_2$ requires C, 31.9; H, 8.0; Cl, 42.7; N, 13.5%).

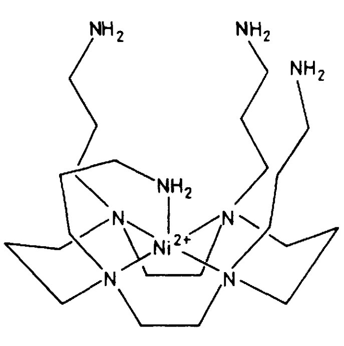
Perchlorato[N,N′,N″,N‴-*tetra*(3-*ammoniopropyl*)-1,4,8,11-*tetra-azacyclotetradecane*]*nickel*(II) *Pentaperchlorate* (1).—Crude tetra-aminopropylcyclam (1.9 g, *ca.* 4.4 mmol) was dissolved in boiling ethanol (75 cm^3) and a solution of hexa-aquanickel(II) diperchlorate (1.62 g, *ca.* 4.4 mmol) in ethanol (5 cm^3) was added dropwise over 5 min. Concentrated (62%) aqueous perchloric acid (1.9 cm^3, *ca.* 17.6 mmol) was then added and the resulting slurry was quickly filtered hot. The filtrate deposited fine purple crystals of the analytically pure product upon cooling (3.2 g, 66%). The compound, which is hygroscopic, was collected by filtration under dry nitrogen, washed with ethanol (2 × 10 cm^3), and dried *in vacuo*.

Compounds (2)—(4).—These compounds were prepared by the same general procedure as that for (1), but from, respectively, hexa-aquanickel(II) bis(tetrafluoroborate) and fluoroboric acid, hepta-aquanickel(II) sulphate and sulphuric acid, and tri-aquanickel(II) dibromide and hydrobromic acid in conjunction with L^2. The ligand L^2 must be pure in the case of (3) and (4), which precipitate immediately upon adding the acid, and thus cannot be separated from insoluble contaminants.

Chloro[N,N′,N″,N‴-*tetra*(3-*ammoniopropyl*)-1,4,8,11-*tetra-azacyclotetradecane*]*nickel*(II) *Chloride Tetraperchlorate* (5).—Tetra-aminopropylcyclam (176 mg, 0.4 mmol), hexa-aquanickel(II) dichloride (98 mg, 0.4 mmol), and sodium perchlorate (577 mg, 4 mmol) were dissolved in boiling ethanol (50 cm^3). The addition of concentrated (35%) aqueous hydrochloric acid (0.15 cm^3, 1.6 mmol) produced a copious yellow precipitate. This was collected by filtration and washed thoroughly with boiling, dry ethanol (3 × 15 cm^3), in order to remove occluded sodium perchlorate, thereby producing the pure compound after drying *in vacuo* (335 mg, 85%).

Isothiocyanato[N,N′,N″,N‴-*tetra*(3-*ammoniopropyl*)-1,4,8,11-*tetra-azacyclotetradecane*]*nickel*(II) *Chloride Tetraperchlorate* (6).—Compound (5) (150 mg, 0.16 mmol) was suspended in boiling dry ethanol (20 cm^3) under dry nitrogen. Sodium thiocyanate (13 mg, 0.16 mmol) was added and the mixture refluxed for 1 h. The pale green solid was collected by filtration, washed with hot, dry ethanol (2 × 10 cm^3), and dried *in vacuo*; i.r. (Nujol) ν(C≡N) 2 100, ν(C–S) 790 cm^{-1}.

The Polymeric N,N′,N″,N‴-*Tetra*(3-*aminopropyl*)-1,4,8,11-*tetra-azacyclotetradecanenickel*(II) *Perchlorate* (7).—The ligand L^2 (129 mg, 0.3 mmol) was dissolved in boiling acetonitrile (50 cm^3) and to the solution hexa-aquanickel(II) diperchlorate (110 mg, 0.3 mmol) was added. The resulting suspension was refluxed overnight, by which time a green solution had formed. This was cooled and to it was added diethyl ether until precipitation. The product was collected by filtration, washed with diethyl ether (2 × 10 cm^3), and dried *in vacuo* (135 mg, 55%).



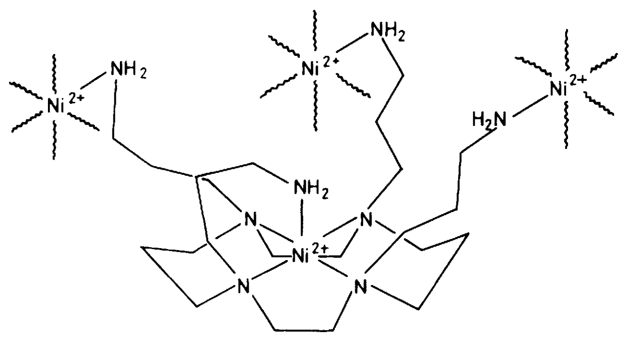
(I)

Results and Discussion

Reaction of tetra-aminopropylcyclam with an equimolar quantity of nickel(II), in various solvents, at neutral pH, leads to a dark green high-spin five-co-ordinate complex cation irrespective of the counter ion present. This is evident from the visible spectrum exhibited by the species in solution in which the low intensity, low energy absorptions characteristic of five-co-ordinate nickel(II)[4] occur. In the presence of ClO_4^-, BF_4^-, NO_3^-, Cl^-, Br^-, NCS^-, or N_3^- there are four spectral transitions, which occur, in aqueous solution, at 25 200 (160), 15 400 (49), 7 400 (16), and 5 800 (8) cm^{-1} (ε/dm^3 mol^{-1} cm^{-1} in parentheses). In view of the fact that both *N,N′,N″,N‴*-tetramethyl-1,4,8,11-tetra-azatetradecane (tetramethylcyclam, tmc)[5] and tetracyanoethylcyclam[1] show similar behaviour, under corresponding conditions, this is not unexpected, and suggests that here also the initial product is a kinetic one in which the macrocycle is bound with all four arms projecting from the same face [the *trans*-(I) configuration[6]] and in a partially folded conformation, such as is necessary to allow the four arms to diverge from one another, but which at the same time obstructs ligation at the axial co-ordination site on the concave face of the macrocycle. The complex derived from L^2, however, differs from those with tmc and L^1 in that its visible spectrum is independent of both the solvent and the anion present, indicating that the axial fifth-co-ordination site, occupied by solvent or counter ion in those cases, is here occupied exclusively by one of the four pendant amine nitrogen atoms; the other four co-ordination sites are occupied by the four tertiary amine nitrogen atoms of the macrocycle, giving rise to an approximately square-pyramidal structure (see later) as indicated in structure (I). Even the addition of strongly co-ordinating anions such as NCS^- and N_3^- to a solution of the perchlorate salt of $[NiL^2]^{2+}$ fails to alter the visible spectrum in any way, showing the reluctance of the bidentate assembly to undergo partial detachment, in a manner reminiscent of the behaviour of simple bidentate ligands.

Attempts to isolate $[NiL^2][ClO_4]_2$ from solution met with no success. Instead the material isolated (7), for example by precipitation from acetonitrile with diethyl ether, always gave analytical figures consistent with $[NiL^2][ClO_4]_2 \cdot \frac{1}{2}Ni[ClO_4]_2$, in agreement with the fact that approximately one-third of the original quantity of L^2 could be found retained in solution. The implication is that the metal ion located within the macrocycle is reasonably labile [and this is to be expected if L^2 is in fact in the *trans*-(I) configuration[5]] such that upon precipitation, migration of metal ions away from macrocyclic positions is possible and continues until such time as the co-ordinating power of the three pendant amino-groups, hitherto present on each metallated macrocycle, is fulfilled. Thus the resulting complex may be either dimeric or polymeric, depending upon how ordered is the distribution of the pendant amino-groups amongst the bridging nickel(II) centres, and contains both five-co-ordinate and six-co-ordinate nickel(II) centres in the ratio 2 : 1. Molecular models strongly suggest that simple dimers, with a bridging octahedral nickel(II), are unlikely, owing to the extreme steric interactions that occur between the macrocycle's arms when three of them converge towards the same point. It is more likely that (7) is polymeric, with each arm on a given macrocycle bonding to a different octahedral centre, as indicated in structure (II). This is supported by the low solubility of (7), in comparison with the unprecipitated species, which is well illustrated by the fact that addition of 0.5 mol equiv. of $Ni[ClO_4]_2 \cdot 6H_2O$ to a solution containing 1 mol equiv. each of L^2 and of $Ni[ClO_4]_2 \cdot 6H_2O$, in water, brings about instantaneous precipitation of (7).

Clarification of the nature of the two nickel sites in (7) was provided by its spectral and magnetic characteristics. The solid-state visible spectrum of (7) (Table 1) is typical of high-spin five-co-ordinate nickel(II) and is virtually identical with that of the unprecipitated species, except for the superposition of a relatively weak band at 9 800 cm^{-1}, attributable to the $^3A_{2g} \longrightarrow {}^3T_{2g}$ transition of the octahedral nickel(II). The frequency of this band, which is a measure of 10*Dq*, is close to the value (9 823 cm^{-1}) observed for the related compound hexakis(n-propylamine)nickel(II) diperchlorate.[7] The $^3A_{2g} \longrightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \longrightarrow {}^3T_{1g}(P)$ bands from the octahedral nickel(II) would be expected to occur [7] in regions of the spectrum that are already dominated by the considerably more intense bands due to the five-co-ordinate nickel(II), and are thus unobservable. Magnetic susceptibility measurements indicate a temperature-independent (293—80 K) magnetic moment of 3.25 B.M. per nickel ion, intermediate between the value expected for high-spin five-co-ordinate nickel(II) (*ca.* 3.30 B.M.) [8] and octahedral nickel(II) (*ca.* 3.15 B.M.) [8] under these circumstances. Whilst not diagnostic, this is consistent with a 2 : 1 distribution of these sites.



(II)

In order to avoid the polymeric linkage that develops whenever attempts are made to isolate the nickel(II) complex of neutral L^2, the possibility of blocking the co-ordinating ability of the pendant amino-groups responsible for it, by selective protonation, and so isolating monomeric complexes, was investigated. In water this did not prove to be possible: addition of 4 mol equiv. of acid to a solution containing $[NiL^2]^{2+}$ rapidly led to the displacement of the ligand, as its acid salt, accompanied by the formation of the hexa-aqua-nickel(II) ion. In ethanol, however, which is both a poorer ligand and a poorer solvent for these species, application of the same treatment resulted in the precipitation of compounds (1)—(6), in which the four pendant amino-groups are protonated, to the exclusion of the tertiary amino-groups which remain bound to the metal. This process can be readily reversed by the addition of the appropriate amount of aqueous sodium hydroxide to a suspension of the complex in ethanol.

As with the neutral ligand, it is evident on the basis of spectral and magnetic data (Table 1) that complexes (1)—(6) are five-co-ordinate, being either of the high-spin type already referred to, or low-spin, depending upon the counter ions present. The low-spin complexes are characterised by diamagnetism and the presence of two spectral bands at around 25 000 and 18 000 cm^{-1}, such as are generally observed for species of this type.[8] It is also possible that this combination of spectral and magnetic properties could indicate a square-planar structure, as there are some instances in which

Table 1. Electronic spectral and magnetic data

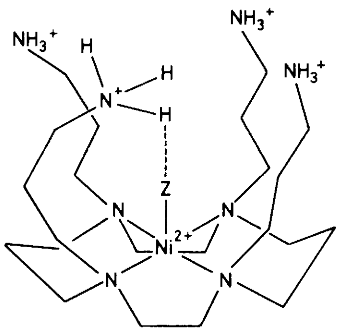
Compound	Colour	μ_{eff} [a]	Electronic spectral data (cm^{-1}) [b]
(1) $[Ni(H_4L^2)(ClO_4)][ClO_4]_5$	Purple	Diamagnetic	25 300, 18 300
(2) $[Ni(H_4L^2)(BF_4)][BF_4]_5$	Purple	Diamagnetic	25 200, 18 300
(3) $[Ni(H_4L^2)(HSO_4)][HSO_4]_5$	Pink	Diamagnetic	24 900, 18 400
(4) $[Ni(H_4L^2)Br]Br_5$	Pink	Diamagnetic	24 600, 18 500
(5) $[Ni(H_4L^2)Cl][ClO_4]_4Cl$	Yellow	3.25	23 200, 13 500, 8 600, 7 200
(6) $[Ni(H_4L^2)(NCS)][ClO_4]_4Cl$	Pale green	3.31	23 700, 14 300, 6 600, 5 700
(7) $[Ni_{1.5}L^2]_n[ClO_4]_{3n}$	Green	3.25 [c]	25 200, 15 400, 9 800, 7 400, 5 800

[a] B.M. at 20 °C; 1 B.M. = 9.27×10^{-24} A m^2. [b] Recorded by diffuse transmittance through Nujol mulls owing to low solubility of compounds. [c] Per nickel(II) ion.

Table 2. Analyses (%)

	Found			Calc.		
	C	H	N	C	H	N
(1) $[Ni(H_4L^2)(ClO_4)][ClO_4]_5$	24.4	5.2	10.1	24.3	5.2	10.3
(2) $[Ni(H_4L^2)(BF_4)][BF_4]_5$	25.9	5.85	11.4	26.1	5.6	11.1
(3) $[Ni(H_4L^2)(HSO_4)][HSO_4]_5$	24.6	5.9	10.4	24.6	5.8	10.4
(4) $[Ni(H_4L^2)Br]Br_5$	27.0	6.25	11.6	27.1	6.2	11.5
(5) $[Ni(H_4L^2)Cl][ClO_4]_4Cl$ [a]	27.3	5.9	11.4	27.5	5.9	11.7
(6) $[Ni(H_4L^2)(NCS)][ClO_4]_4Cl$	28.4	6.0	12.8	28.1	5.75	12.8
(7) $[Ni_{1.5}L^2]_n[ClO_4]_{3n}$ [b]	32.7	6.4	13.8	32.4	6.45	13.8

[a] Cl: Found 22.0; calc. 22.1%. [b] Cl: Found 12.7; calc. 13.0%. Ni: Found 10.3; calc. 10.8%.



(III) Z = co-ordinated anion

square-planar nickel(II) complexes, which are diamagnetic, exhibit two spectral absorptions at frequencies similar to those quoted here, rather than the more usual one.[9] However, the work of Nishida and Kida[9] shows that this occurs only with a quadridentate ligand which is both dianionic and of high π-basicity. As tetra-aminopropylcyclam satisfies neither of these criteria the possibility of the diamagnetic complexes being four-co-ordinate and square-planar has been discounted.

The fact that the complexes are five-co-ordinate suggests that the *trans*-(I) configuration is preserved during protonation, and the variation of the spectral and magnetic properties with counter ion strongly implicates one of the anions as the species present at the axial co-ordination site. In the cases where the counter ion was either perchlorate or tetrafluoroborate this conclusion was supported by the observation of moderately intense ν_1 (symmetric stretching) bands, which only become infrared-active when the symmetry of the anion is lowered from T_d to C_{3v}, at 930 and 764 cm^{-1}, respectively.[10] Indeed these complexes are remarkable for their ability to promote the co-ordination of normally weakly co-ordinating anions such as ClO_4^-, BF_4^-, and HSO_4^-. There are probably at least two reasons for this. First, there may be favourable hydrogen-bonding interactions between one or more of the protonated amino-groups and the co-ordinated anion, as shown in structure (III). Secondly, the co-ordination of weak field ligands at the axial site results in the formation of the complex in its relatively more stable low-spin state. This latter observation is clearly shown by the data in Table 1, and was predicted to be the case for square-pyramidal complexes by Ciampolini,[11] in contrast to the situation with trigonal-bipyramidal complexes, where axial ligands of high field strength give low-spin complexes. It is on the basis of this finding that the structures of complexes (1)—(7) are proposed as being basically square-pyramidal rather than having the alternative trigonal-bipyramidal structure.

The crossover point from low- to high-spin nickel(II) occurs in these complexes at an axial ligand-field strength intermediate between those produced by bromide and by chloride. Complex (4) was checked for the presence of a spin equilibrium, but none was apparent in the temperature range 293—80 K. In contrast to the low-spin species, which are readily isolated from acidified ethanol, the high-spin complexes are considerably more labile with respect to ligand displacement, thus severely limiting the number of species that could be isolated in a pure state.

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Received 11*th October* 1982; *Paper* 2/1749