Synthesis of a Pyridine-containing Tetra-aza Macrocycle, 7-Methyl-3,7,11,17-tetra-azabicyclo[11.3.1]heptadeca-1(17),13,15-triene (L^1), and Characterisation of Its Nickel(II), Copper(II), and Zinc(II) Complexes. Reduction of the Pyridine Ring of $[Ni(L^1)]^{2+}$ to give $[Ni(L^2)]^{2+}$ (L^2 = 7-Methyl-3,7,11,17-tetra-azabicyclo[11.3.1]heptadecane), and Characterisation of $[Ni(L^2)]^{2+}$ by *X*-Ray Crystallography†

Nathaniel W. Alcock, Peter Moore,* and Hadi A. A. Omar
Department of Chemistry, University of Warwick, Coventry CV4 7AL

The new ligand 7-methyl-3,7,11,17-tetra-azabicyclo[11.3.1]heptadeca-1(17),13,15-triene (L^1) has been prepared and isolated, together with its metal complexes of general formula $[M(L^1)]X_2$ ($M = Ni^{2+}, Cu^{2+}$, or Zn^{2+}; $X^- = ClO_4^-$ or NO_3^-). The diamagnetic perchlorate salts of Ni^{2+} and Zn^{2+} have been characterised by ^{13}C n.m.r. spectroscopy, and found to be single symmetric species in nitromethane solution, whereas the zinc nitrate complex is a mixture of symmetric and asymmetric species. Reaction of $[Ni(L^1)][ClO_4]_2$ with NCS^-, NO_2^-, or oxalate (ox) ions gives $[Ni(L^1)(NCS)_2]$, $[Ni(L^1)(NO_2)(ClO_4)]$, and $[L^1Ni(\mu\text{-ox})NiL^1][ClO_4]_2$ respectively, of which the thiocyanato- and nitro-complexes are *trans*-octahedral and in the μ-oxalato-complex the nickel(II) is *cis*-octahedral. Reduction of the pyridine ring of $[Ni(L^1)][ClO_4]_2$ with H_2 over Raney nickel gives a symmetric, diamagnetic, square-planar complex, $[Ni(L^2)][ClO_4]_2$, as shown by ^{13}C n.m.r., fast atom bombardment mass spectrometry, and the *X*-ray crystal structure. The crystals are orthorhombic, space group $P2_12_12_1$, with lattice constants $a = 12.798(4)$, $b = 9.939(3)$, $c = 16.604(7)$ Å, and $Z = 4$; the structure refined to an R value of 0.056 for 1 362 observed reflections. In nitromethane solution, ^{13}C n.m.r. spectroscopy shows that this square-planar complex is a mixture of two symmetric isomers.

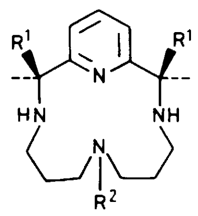
As part of our recent studies of tetra-aza macrocyclic ligands and their co-ordination chemistry, including macrocycles with pendant co-ordinating arms,[1-6] we recently synthesised the new macrocycle L^1. We report here the isolation and characterisation of this ligand, together with its complexes with nickel(II), copper(II), and zinc(II). Reduction of the pyridine ring in the nickel(II) perchlorate complex of L^1 afforded the new piperidine ligand L^2 in the square-planar complex $[Ni(L^2)][ClO_4]_2$.

The stereochemistry of L^2 in this nickel(II) complex has been established by *X*-ray crystallography, and all of the complexes have been investigated in solution by u.v.-visible, ^{13}C and ^1H n.m.r. spectroscopy. The fast atom bombardment (f.a.b.) mass spectra of $[Ni(L)][ClO_4]_2$ ($L = L^1$ or L^2) were also recorded.

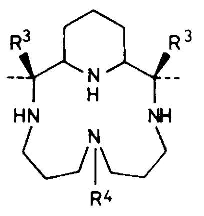
Experimental

Materials.—All chemicals were reagent grade commercial materials, except 2,6-pyridinedicarbaldehyde which was synthesised from 2,6-pyridinedimethanol by oxidation with selenium dioxide using the method reported previously.[1] The commercial materials were used without purification.

Spectra.—^{13}C N.m.r. spectra were recorded at 22.63 MHz and ^1H n.m.r. spectra at 220 MHz using Bruker WH90 Fourier-transform and Perkin-Elmer R34 continuous-wave spectrometers respectively. Chemical shifts were measured with reference to $SiMe_4$ at $\delta = 0$. U.v.-visible and i.r. spectra were recorded with Shimadzu (model 365) and Perkin-Elmer (model 580B) spectrometers respectively, and f.a.b. mass spectra with a Kratos (model MS80) instrument.



L^1 $R^1 = H$, $R^2 = Me$
L^3 $R^1 = Me$, $R^2 = H$
L^4 $R^1 = H$, $R^2 = CH_2CH_2NMe_2$



L^2 $R^3 = H$, $R^4 = Me$
L^5 $R^3 = Me$, $R^4 = H$

Analyses.—Combustion analyses were carried out commercially, and magnetic moments were measured by the method of Evans.[7]

Preparation of Ligand L^1.—The ligand was prepared following a published template method for the synthesis of the related macrocycle L^4.[1] A solution of 4-methyl-4-azaheptane-1,7-diamine (2.876 g, 19.8 mmol) in absolute ethanol (15 cm^3) was added to a solution of $NiCl_2 \cdot 6H_2O$ (4.7 g, 19.8 mmol) in water (15 cm^3). The resulting blue solution was stirred at room temperature during the addition of 2,6-pyridinedicarbaldehyde (2.675 g, 19.8 mmol), followed by glacial ethanoic acid (1.5 cm^3), to give a brown solution. This was stirred for 2 h, then heated at 65 °C overnight. The solution was then cooled in an ice-bath, and sodium tetrahydroborate (3.0 g, 79.4 mmol) was added in small portions over a period of 1 h. The reaction mixture was

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† *Supplementary data available* (No. SUP 56481, 3 pp.): complete bond length and angles, H-atom co-ordinates, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Non-S.I. units employed: mmHg ≈ 133 Pa, atm = 101 325 Pa, B.M. ≈ 9.27×10^{-24} A m^2, lbf in^{-2} ≈ 6 895 Pa.

Table 1. ^{1}H-Decoupled ^{13}C n.m.r. chemical shifts (δ/p.p.m. relative to $SiMe_4$). Figures in parentheses indicate relative numbers of carbon atoms (1 unless stated)

			$[Zn(L^1)][NO_3]_2$		$[Ni(L^2)][ClO_4]_2$		
L^1	$[Ni(L^1)][ClO_4]_2$	$[Zn(L^1)][ClO_4]_2$	Symmetric	Asymmetric	Major isomer	Minor isomer	Assignment
28.27 (2)	24.31 (2)	25.41(2)	25.15 (2)	25.54, 25.87	23.41	23.79	C–CH_2–C
					24.17	24.17	
					27.45	27.90	
41.34	44.20	44.00	43.55	45.24	44.23	44.56	CH_3–N
47.19 (2)	49.33 (2)	51.80 (2)	50.96 (2)	50.18, 51.41	50.26(2)	55.13(2)	C–CH_2–N
55.25 (2)	60.60 (2)	52.26 (2)	52.39 (2)	52.13, 52.84	58.98(2)	59.48(2)	
57.13 (2)	61.23 (2)	62.90 (2)	62.01 (2)	58.30, 62.66	60.05(2)	60.86(2)	
					62.51(2)	62.91(2)	
							pyridine
121.41(2)	121.93(2)	123.50(2)	123.30(2)	123.30(2)			β-*C*
137.53	142.80	143.45	142.73	142.86			γ-*C*
161.32(2)	158.52(2)	155.15(2)	155.08(2)	155.08(2)			α-*C*

Table 2. Elemental analyses (%)

		C		H		N	
Compound	Formula	Calc.	Found	Calc.	Found	Calc.	Found
L^1	$C_{14}H_{24}N_4$	67.70	67.05	9.75	10.25	22.55	22.30
$[Ni(L^1)][ClO_4]_2$	$C_{14}H_{24}Cl_2N_4NiO_8$	33.25	33.15	4.80	4.80	11.05	10.85
$[Ni(L^1)(NCS)_2]\cdot 0.5H_2O$	$C_{16}H_{25}N_6NiO_{0.5}S_2$	44.45	44.15	5.85	5.85	19.45	19.30
$[L^1Ni(\mu\text{-ox})NiL^1][ClO_4]_2\cdot H_2O$	$C_{30}H_{50}Cl_2N_8Ni_2O_{13}$	39.20	39.15	5.50	5.25	12.20	12.00
$[Ni(L^1)(NO_2)(ClO_4)]\cdot 0.5H_2O$	$C_{14}H_{25}ClN_5NiO_{6.5}$	36.45	36.20	5.45	5.15	15.15	14.70
$[Cu(L^1)][ClO_4]_2$	$C_{14}H_{24}Cl_2CuN_4O_8$	32.90	32.70	4.75	4.75	10.95	10.80
$[Zn(L^1)][NO_3]_2\cdot H_2O$	$C_{14}H_{26}N_6O_7Zn$	36.90	36.60	5.75	5.65	18.45	17.85
$[Ni(L^2)][ClO_4]_2\cdot H_2O$	$C_{14}H_{32}Cl_2N_4NiO_9$	31.70	31.40	6.10	5.85	10.55	10.20

stirred at room temperature for 2 h, then heated at 80 °C for a further 2 h. After cooling, the ethanol and ethanoic acid were removed under vacuum with a rotary evaporator, and an excess of sodium cyanide (8 g, 163 mmol) was added. After heating at 80 °C for 1 h, the reaction mixture was cooled to room temperature and basified with 15% aqueous NaOH to *ca.* pH 10. The solution was extracted with dichloromethane (3 × 100 cm^3), and the combined extracts dried with anhydrous $MgSO_4$. Filtration, evaporation, and distillation gave the product (2.06 g, 8.3 mmol) as a pale yellow oil, b.p. 100—115 °C (0.1 mmHg), in 42% yield. This oil crystallised when cooled to room temperature (m.p. 68—70 °C). Electron-impact mass spectrum: found, *m/z* 248.1; expected for L^1, *m/z* 248.2. ^1H N.m.r. ($CDCl_3$): δ 1.70 (6 H, p), 2.03 (3 H, s), 2.35 (4 H, t), 2.50 (4 H, t), 3.85 (4 H, s), 7.00 (2 H, d), and 7.52 (1 H, t). I.r.: 3 280 (N–H stretch), 3 060, 1 570, and 1 535 cm^{-1} (pyridine). The ^1H-decoupled ^{13}C n.m.r. chemical shifts are in Table 1, and a combustion analysis in Table 2.

Synthesis of Nickel(II) *Complexes of* L^1.—$[Ni(L^1)][ClO_4]_2$. To a solution of $[Ni(dmso)_6][ClO_4]_2$ (2.927 g, 4 mmol) (dmso = dimethyl sulphoxide) in ethanol (15 cm^3) was added a solution of L^1 (1 g, 4 mmol) in ethanol (10 cm^3). An orange precipitate immediately formed which was filtered off, washed with ethanol (5 cm^3), then diethyl ether (10 cm^3), and dried *in vacuo* to give the product (1.75 g, 7.0 mmol) in 86% yield. The ^{13}C n.m.r. data are in Table 1, a combustion analysis in Table 2, f.a.b. mass spectrum in Table 3, and visible spectrum in Table 4. I.r. (Nujol mull): 3 190 (N–H), 3 080, 1 530 (pyridine), and 1 110 cm^{-1} (ClO_4^-).

$[Ni(L^1)(NCS)_2]\cdot 0.5H_2O$. To a stirred solution of $[Ni(L^1)][ClO_4]_2$ (220 mg, 0.4 mmol) in ethanol (5 cm^3) was added a solution of sodium thiocyanate (65 mg, 0.8 mmol) in ethanol (50 cm^3). The mixture was stirred for 4 h at room temperature, and the resulting purple precipitate filtered off and recrystallised from nitromethane–diethyl ether (1:3). The product (114 mg, 0.27 mmol, 68%) analysed as $[Ni(L^1)(NCS)_2]\cdot 0.5H_2O$ (Table 2).

$[L^1Ni(\mu\text{-ox})NiL^1][ClO_4]_2\cdot H_2O$ [ox = *oxalate*(2−)]. To a stirred solution of $[Ni(L^1)][ClO_4]_2$ (230 mg, 0.46 mmol) in hot water (50 cm^3) was added a solution of $Na_2(ox)$ (184 mg, 1.37 mmol) in water (2.5 cm^3). The mixture was heated at 100 °C for 30 min, then allowed to cool slowly, whereupon violet crystals of the product separated. These were filtered off, washed with cold water, and air dried to give the product (285 mg, 0.31 mmol) in 68% yield. The combustion analysis is in Table 2.

$[Ni(L^1)(NO_2)(ClO_4)]\cdot 0.5H_2O$. The salt $[Ni(L^1)][ClO_4]_2$ (150 mg, 0.3 mmol) was dissolved in water (10 cm^3) at 100 °C and a solution of sodium nitrite (410 mg, 5.9 mmol) in water (5 cm^3) was added. The mixture was heated at 100 °C for 20 min, and on cooling violet crystals precipitated. These were filtered off, washed with cold water, and air dried. The product was recrystallised from nitromethane–diethyl ether (1:2), to give the product (87 mg, 0.19 mmol) in 65% yield. The combustion analysis is in Table 2. The i.r. spectrum showed two broad peaks in the region 1 100—1 250 cm^{-1} indicative of co-ordinated perchlorate ion.

Synthesis of Copper(II) *and Zinc*(II) *Complexes of* L^1.—$[Cu(L^1)][ClO_4]_2$. A solution of L^1 (50 mg, 0.2 mmol) in ethanol (2 cm^3) was added, with stirring, to a solution of $Cu(ClO_4)_2\cdot 6H_2O$ (75 mg, 0.2 mmol) in ethanol (5 cm^3). The resulting purple precipitate was filtered off, washed with ethanol, and dried *in vacuo* to give the product (70 mg, 0.13 mmol) in 73% yield.

$[Zn(L^1)][ClO_4]_2$. A solution of L^1 (208 mg, 0.83 mmol)

Table 3. Comparison of observed and calculated f.a.b. mass spectra for fragment ions of $[Ni(L)][ClO_4]_2$ ($L = L^1$ or L^2)

	$L = L^1$					$L = L^2$						
$[Ni(L)(ClO_4)]^+$												
Observed *m/z*	405	406	407	408	409	411	412	413	414	415	416	417
Height	100	34	78	20	24	100	41	71	30	32	14	13
Calc. *m/z*	405	406	407	408	409	411	412	413	414	415	416	417
Height	100	18	73	15	20	100	18	73	15	20	4	4
$[Ni(L - H)]^+$												
Observed *m/z*	305	306	307	308	309	311	312	313	314	315		
Height	100	75	54	29	12	100	56	66		9		
Calc. *m/z*	305	306	307	308	309	311	312	313	314	315		
Height	100	18	40	9	6	100	18	40	8	6		

Table 4. Visible spectra of nickel(II) and copper(II) complexes in nitromethane and water solvents ($\lambda_{max.}$/nm with ε/dm^3 mol^{-1} cm^{-1} in parentheses)

Complex	Colour	In CH_3NO_2	In water
$[Ni(L^1)][ClO_4]_2$	Orange	470(130)	469(59)
$[Ni(L^1)(NCS)_2]$	Purple	528(24), 764(23)	
$[Ni(HL^4)(NCS)_2]NCS$	Purple	530(27), 765(33)[a]	
$[L^1Ni(\mu\text{-ox})NiL^1][ClO_4]_2$	Violet	350(sh), 560(53.5), 920(40)[b]	
$[Ni(L^1)(NO_2)(ClO_4)]$	Violet	370(49), 560(36), 816(19), 856(21)	
$[Cu(L^1)][ClO_4]_2$	Purple	552(128)	560(176)
$[Ni(L^2)][ClO_4]_2$	Orange	472(136)	468(92), 808(16), 1 160(10)

[a] Data from ref. 2; included for comparison. [b] In CH_3CN solvent; in a Nujol mull, $\lambda_{max.}$ at 350(sh), 560, and 920 nm.

Table 5. Atomic co-ordinates (× 10^4) for $[Ni(L^2)][ClO_4]_2$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ni	9 070(1)	5 406(1)	4 483(1)	C(1)	7 852(9)	4 986(11)	3 020(6)
Cl(1)	7 009(2)	10 290(3)	6 381(2)	C(2)	8 315(12)	3 572(11)	2 912(7)
Cl(2)	3 508(2)	86(3)	9 446(2)	C(3)	8 457(9)	2 817(10)	3 658(6)
O(11)	6 260(7)	11 226(12)	6 653(7)	C(4)	9 279(9)	2 699(10)	4 980(6)
O(12)	6 616(12)	9 728(19)	5 733(8)	C(5)	9 967(8)	3 485(10)	5 524(6)
O(13)	7 157(12)	9 285(15)	6 944(11)	C(6)	10 114(9)	5 867(11)	5 923(6)
O(14)	8 014(9)	10 752(16)	6 327(10)	C(7)	9 574(10)	7 136(10)	5 779(6)
O(21)	4 399(7)	−201(13)	9 022(5)	C(8)	8 565(9)	8 291(9)	4 730(7)
O(22)	3 385(12)	−798(16)	10 070(7)	C(9)	8 349(8)	8 470(10)	3 853(7)
O(23)	2 618(7)	96(17)	8 938(5)	C(10)	7 865(8)	7 223(10)	3 486(7)
O(24)	3 582(11)	1 374(14)	9 718(12)	C(11)	9 477(9)	6 280(13)	2 891(6)
N(1)	8 524(6)	6 009(8)	3 435(4)	C(12)	10 063(10)	2 985(12)	6 404(7)
N(2)	9 175(7)	3 491(8)	4 227(4)	C(13)	10 701(10)	3 968(13)	6 886(7)
N(3)	9 509(5)	4 843(7)	5 508(4)	C(14)	10 256(9)	5 403(12)	6 813(6)
N(4)	9 328(7)	7 205(7)	4 902(5)				

in ethanol (2 cm^3) was added to a stirred solution of $Zn(ClO_4)_2{\cdot}6H_2O$ (312 mg, 0.83 mmol) in ethanol (5 cm^3). The complex was precipitated as an oil–solid by the addition of diethyl ether, and after removing the ethanol and ether the product was obtained as a white solid by stirring overnight with dry dichloromethane–diethyl ether (1:2; 9 cm^3) under dry nitrogen. The product (295 mg, 0.58 mmol) was filtered off and dried *in vacuo* (yield 70%). The ^{13}C n.m.r. shifts are in Table 1.

$[Zn(L^1)][NO_3]_2{\cdot}H_2O$. A solution of L^1 (175 mg, 0.7 mmol) in ethanol (5 cm^3) was added to $Zn(NO_3)_2{\cdot}6H_2O$ (210 mg, 0.7 mmol) in ethanol (5 cm^3). The complex was precipitated as an oil–solid by addition of diethyl ether, and a white solid obtained by removing the supernatant liquid and stirring under nitrogen in dry diethyl ether for 4 h. The solid was filtered off, washed with ether, and dried *in vacuo* to give the product (113.9 mg, 0.26 mmol) in 86% yield. The ^{13}C n.m.r. shifts are in Table 1, and the combustion analysis in Table 2.

Synthesis of $[Ni(L^2)][ClO_4]_2$.—The salt $[Ni(L^1)][ClO_4]_2$ (1.5 g, 3.0 mmol) was dissolved in water (100 cm^3) and W-2 Raney nickel (4 g) added. The mixture was transferred to a autoclave (200 cm^3), and hydrogenated at a hydrogen pressure of 80 atm. The temperature was gradually increased to 65 °C (24 h), then to 80 °C (2 h), before allowing the autoclave to cool overnight to room temperature. The catalyst was removed by filtration, the solution acidified with a few drops of 70% $HClO_4$, and then evaporated to a volume of *ca.* 5 cm^3. A mixture of yellow and orange crystals was collected by filtration and dried *in vacuo*. The orange crystals of the desired product (1.25 g, 2.4 mmol, 83%) were separated from a small amount of yellow material by extraction with nitromethane, and orange plates suitable for an *X*-ray diffraction study were obtained by slow evaporation of a saturated nitromethane solution. The combustion analysis is in Table 2, and the ^{13}C n.m.r. shifts in Table 1.

Crystal Structure Study of $[Ni(L^2)][ClO_4]_2$.—*Crystal data.* Orange plates of $C_{14}H_{30}Cl_2N_4NiO_8$, $M = 512.03$, orthorhombic, space group $P2_12_12_1$, $a = 12.798(4)$, $b = 9.939(3)$, $c = 16.604(7)$ Å, $U = 2\,112(1)$ Å^3, $Z = 4$, $D_c = 1.61$ g cm^{-3}, $F(000) = 1\,072$, $\mu(\text{Mo-}K_\alpha) = 12.2$ cm^{-1}.

Table 6. Selected bond lengths (in Å) and angles (in °) in $[Ni(L^2)][ClO_4]_2$. For atomic numbering refer to Figure 3

Ni-N(1)	1.969(8)	C(1)-C(2)	1.536(16)
Ni-N(4)	1.946(8)	C(5)-C(12)	1.547(15)
N(1)-C(11)	1.541(14)	C(8)-C(9)	1.492(16)
N(3)-C(5)	1.472(12)	C(13)-C(14)	1.540(17)
N(4)-C(8)	1.484(13)	Ni-N(3)	1.877(7)
C(4)-C(5)	1.484(15)	N(1)-C(10)	1.475(12)
C(6)-C(14)	1.558(14)	N(2)-C(4)	1.483(13)
C(12)-C(13)	1.504(17)	N(4)-C(7)	1.492(13)
Ni-N(2)	1.955(8)	C(2)-C(3)	1.460(15)
N(1)-C(1)	1.500(13)	C(6)-C(7)	1.458(15)
N(2)-C(3)	1.479(13)	C(9)-C(10)	1.514(14)
N(3)-C(6)	1.453(13)		
N(1)-Ni-N(2)	97.4(3)	N(1)-Ni-N(3)	176.5(3)
N(2)-Ni-N(3)	83.5(3)	N(1)-Ni-N(4)	95.5(3)
N(2)-Ni-N(4)	163.8(3)	N(3)-Ni-N(4)	84.2(3)

Data collection. A crystal of approximate dimensions 0.30 × 0.70 × 0.40 mm bounded by $\{101\}$, $1\bar{1}\bar{1}$, $\bar{1}\bar{1}1$, and $\bar{1}11$ was examined with a Syntex $P2_1$ four-circle diffractometer. The unit-cell dimensions were obtained by a least-squares fit to 15 high-angle reflections, using Mo-K_α graphite-monochromated radiation (λ = 0.710 69 Å). The systematic absences $h00$ $h \neq 2n$, $0k0$ $k \neq 2n$, and $00l$ $l \neq 2n$ indicated space group $P2_12_12_1$. Intensity data were collected from 3 to 50° in 2θ at a variable scan rate between 2 and 29° min^{-1} depending on the intensity of 20 pre-scans. The scan range was ± 1.0°(2θ) around the K_{α_1}-K_{α_2} angles, and the backgrounds were measured at the end of each scan for 0.25 of the scan time. Three standard reflections were monitored every 200 reflections, and showed no significant changes during data collections. 1 362 Observed reflections with $I/\sigma(I) > 3.0$ were used in refinement, and corrected for Lorentz, polarisation and absorption effects to give transmission factors in the range 0.70—0.80.[8]

Structure solution and refinement. The structure was solved by the heavy-atom method using a three-dimensional Patterson synthesis to locate the position of the nickel atom, and the light atoms were then found with successive Fourier syntheses. Hydrogen atoms were inserted at calculated positions with fixed isotropic thermal parameters, U = 0.07 Å^2, and were not refined; those of the methyl group were excluded. Final refinement was by least-squares methods in large blocks with anisotropic thermal parameters for all non-hydrogen atoms. The largest peak on a final Fourier difference synthesis was 0.5 e Å^{-3} near to the nickel atom. A weighting scheme of the form $w = 1/[\sigma^2(F) + gF^2]$ with g = 0.002 was used, and shown to be satisfactory by a weight analysis. The final R value was 0.056. Computing was performed with the SHELXTL system on a Data General Nova 3,[9] following initial processing on a Burroughs B6700. Scattering factors in the analytical form and anomalous dispersion factors were taken from ref. 10. Final atomic co-ordinates are in Table 5, and selected bond lengths and angles in Table 6.

Results and Discussion

Ligand L^1.—The synthesis of this ligand proceeds smoothly using the nickel(II) template method described for ligand L^4.[1] Its purity was established by an elemental analysis (Table 2), a mass spectrum, and the ^{1}H and ^{13}C n.m.r. (Table 1). The macrocycle has a plane of symmetry through the pyridine and methyl N atoms, and shows the expected eight ^{13}C resonances. No impurity ^{13}C n.m.r. peaks were evident.

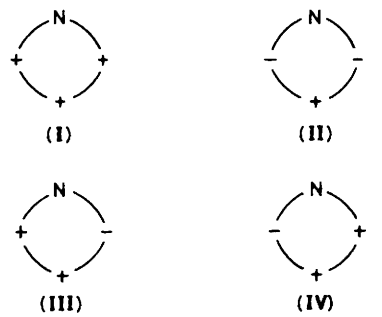

Figure 1. Schematic representation of the four isomers of $[Ni(L^1)]^{2+}$: N indicates the pyridine nitrogen atom, and the plus and minus signs represent the positions of either the secondary amine hydrogen atoms or the Me–N group either above (+) or below (−) the macrocyclic ligand plane

Metal Complexes of L^1.—The ^{13}C n.m.r. spectrum of diamagnetic square-planar $[Ni(L^1)][ClO_4]_2$ in $[^2H_3]$nitromethane solution (Table 1) shows eight resonances as expected for a single symmetric species. There are four isomers possible for $[Ni(L^1)]^{2+}$ (Figure 1), two of which, (**III**) and (**IV**), are an enantiomeric pair. This compares with the six possibilities for the related complexes of *meso*-L^3.[11] Based on our previous studies of $[Ni(L^4)]^{2+}$, and the cobalt(III) complexes of *meso*-L^3,[11] it is most probable that the single symmetric species observed in solutions of $[Ni(L^1)]^{2+}$ has structure (**I**) in which the two N–H groups and the Me–N group are all on the same side of the macrocyclic plane.[2] The f.a.b. mass spectrum of $[Ni(L^1)][ClO_4]_2$ (Table 3) shows clusters of peaks centred at m/z 405 and 305 as calculated for $[Ni(L^1)(ClO_4)]^+$ and $[Ni(L^1-H)]^+$, the latter species arising by loss of $HClO_4$ from the former. This behaviour is the same as that observed in our previous studies.[1] The visible spectrum in nitromethane solution, and in water (Table 4), is typical of that for a low-spin four-co-ordinate tetra-aminenickel(II) complex.

The complexes formed by adding the co-ordinating anions NCS^- and oxalate(2−) (ox) to $[Ni(L^1)]^{2+}$ are directly analogous to those reported for $[Ni(L^3)]^{2+}$.[12] The complex *trans*-$[Ni(L^1)(NCS)_2]$ has a paramagnetic moment of 3.17 B.M., and the visible spectrum is very similar to that obtained previously for *trans*-$[Ni(HL^4)(NCS)_2]^+$.[2] The i.r. spectrum of $[L^1Ni(\mu\text{-ox})NiL^1]^{2+}$ is identical to that reported for the analogous complex of L^3, and a similar *cis*-folded macrocycle structure can be assumed.[12] The complex obtained by reaction with nitrite ion is paramagnetic (μ = 3.25 B.M.), and analysed as $[Ni(L^1)(NO_2)(ClO_4)]$. A broad band in the i.r. spectrum in the region 1 075—1 095 cm^{-1} showed a splitting into two peaks as expected for co-ordinated perchlorate ion.[13] Overlapping bands from the macrocycle in the region 1 100—1 250 cm^{-1} made it impossible to establish whether the nitrite ion was *O*-or *N*-bonded, but by analogy with the complex $[Ni(L^3)(NO_2)(ONO)]$ which contains *N*- and *O*-bonded nitrite ion,[12] it is likely that $[Ni(L^1)(NO_2)(ClO_4)]$ contains *N*-bonded nitrite and *O*-bonded perchlorate.

The salt $[Cu(L^1)][ClO_4]_2$ has a visible spectrum (Table 4) which is typical of planar copper(II) amine complexes. The ^{13}C n.m.r. spectrum of the perchlorate salt of the analogous zinc(II) complex (Table 1) shows it to be a single symmetric species in nitromethane solution. However, the ^{13}C n.m.r. spectrum of $[Zn(L^1)][NO_3]_2$ (Figure 2) in the same solvent shows it to be a mixture of two species, one symmetric and the other asymmetric, in approximately equal amounts. The assignments, based on integrals and chemical shifts, are shown in Table 1. A distinction between the two symmetric possibilities, (**I**) and (**II**)

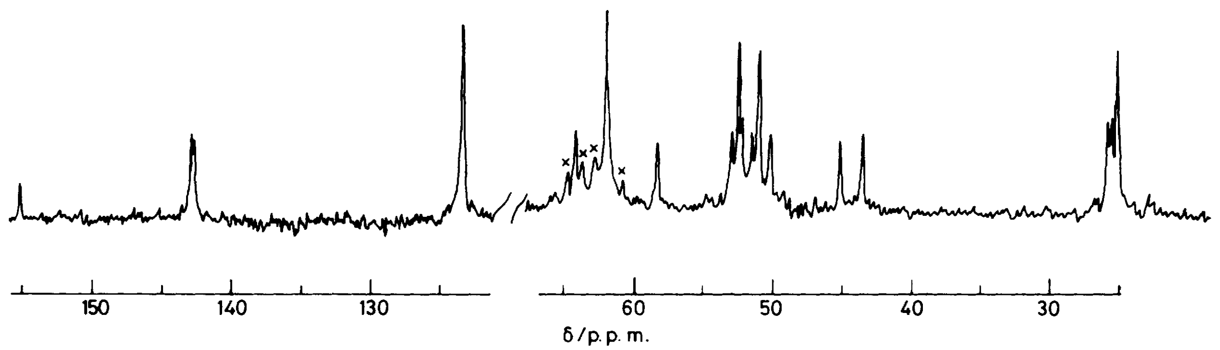

Figure 2. ${}^1H$-Decoupled ${}^{13}C$ n.m.r. spectrum of $[Zn(L^1)][NO_3]_2$ showing the presence of symmetric and asymmetric isomers. The positions of resonances from the solvent, $[{}^2H_3]$nitromethane, are indicated by x

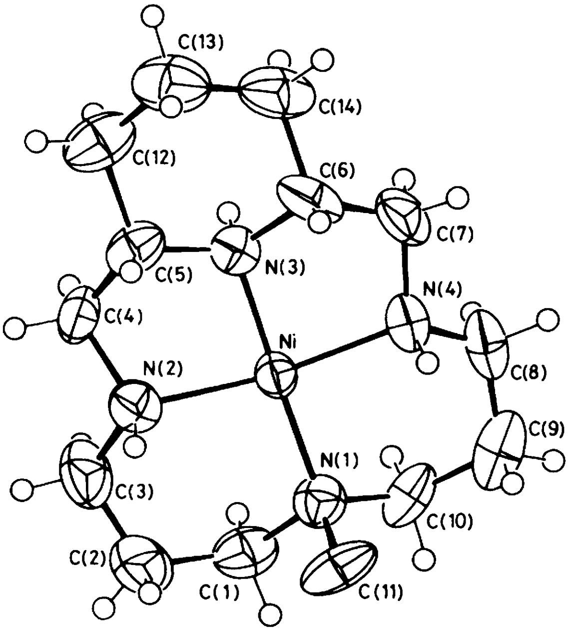

Figure 3. Molecular structure of the $[Ni(L^2)]^{2+}$ ion

(Figure 1), could not be made, although by comparison with previous studies[2,11] it seems likely that the symmetric species has structure (I). This conclusion is supported by the crystal structure of $[Ni(L^2)]^{2+}$.

Reduction of the Pyridine Ring of $[Ni(L^1)]^{2+}$ *to give* $[Ni(L^2)]^{2+}$.—Barefield[14] found it possible to reduce the pyridine ring of $[Ni(L^3)]^{2+}$ to co-ordinated piperidine using H_2 over Raney nickel at a pressure of only 50 lbf in^{-2}. Under these conditions we found only partial reduction of the pyridine ring of the nickel(II) complex of L^1 after 24 h, and so a higher temperature and pressure were used to obtain $[Ni(L^2)]^{2+}$ in good yield. The ${}^{13}C$ n.m.r. spectrum (Table 1) shows the presence of both symmetric isomers in a ratio of approximately 2:1. The f.a.b. mass spectrum (Table 3) shows clusters of peaks centred at m/z 411 and 311 as expected for $[Ni(L^2)(ClO_4)]^+$ and $[Ni(L^2 - H)]^+$ respectively. To establish the structure of the major isomer an *X*-ray analysis was carried out.

Crystal Structure of $[Ni(L^2)]^{2+}$.—The molecular structure is shown in Figure 3, and selected bond lengths and angles are in Table 6. The Me–N group and the two adjacent NH groups are on one side of the macrocyclic plane, and the piperidine NH group lies on the opposite side of this plane. This is the conformation predicted by Barefield[14] for $[Ni(L^5)]^{2+}$. The co-ordination about the nickel atom is only approximately square-planar as shown by the N–Ni–N angles across the molecule of 163.8(3) and 176.5(3)°. The molecule shows a tendency to fold about the N(1)–Ni–N(3) axis, whereas in $[Ni(L^4)]^{2+}$ folding occurs about the N(2)–Ni–N(4) axis.[2] This is presumably due to the presence of the piperidine ring which is more flexible than the rigid pyridine ring of L^4. The Ni–N(3) distance is 0.1 Å shorter than the other Ni–N distances. A similarly short Ni–N bond is consistently observed to the N atom of the pyridine ring of related pyridine-containing tetra-aza macrocycles,[15] and is presumably related to stronger bonding in the five-membered chelate rings of the macrocycle compared with the sterically more crowded six-membered chelate rings. The average C–C bond distance in the macrocyclic ring is 1.490 Å, whereas in the piperidine ring it is 1.533 Å. The C–C bonds are, therefore, stretched in the latter. The macrocyclic six-membered chelate rings have the expected chair–chair conformations minimising steric interactions between hydrogen atoms attached to carbon.

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