Synthesis of Pyridine-containing Tetra-aza Macrocycles: 3,7,11,17-Tetra-azabicyclo[11.3.1]heptadeca-1(17),13,15-triene (L^1), Its 3,11-Dibenzyl (L^2) and 3,7,11-Tribenzyl (L^3) Derivatives, and Their Nickel(II), Copper(II), and Zinc(II) Complexes: Crystal Structures of L^2·HCl and $[Ni(L^2)Cl]ClO_4·H_2O$†

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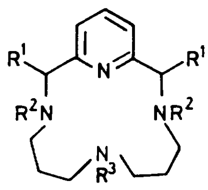
Three pyridine-containing 14-membered-ring tetra-aza macrocycles, 3,7,11,17-tetra-azabicyclo-[11.3.1]heptadeca-1(17),13,15-triene (L^1), its 3,11-dibenzyl (L^2) and 3,7,11-tribenzyl (L^3) derivatives, and their metal complexes with Ni^{2+}, Cu^{2+}, and Zn^{2+} have been prepared and characterised. The structure of $[Ni(L^2)Cl]ClO_4·H_2O$ has been established by *X*-ray crystallography. The Ni^{2+} ion co-ordination is approximately square pyramidal, with the macrocycle folded about an axis defined by the two $N-CH_2Ph$ groups, the secondary amine group co-ordinated at the apex of the square pyramid, and the chloride ion in the basal plane along with the other three N-donor atoms (Cl^- in a *trans* position to the pyridine N atom). The crystal structure of L^2·HCl is also reported.

In 'picket-fence' porphyrins and similar ligands, bulky groups are added to the ligands to allow reversible uptake of dioxygen by suitable centrally placed metal ions, without irreversible oxidation of the metal to μ-peroxo- (*e.g.* Co) or μ-oxo- (*e.g.* Fe) bridged species.[1–4] In the absence of these bulky groups, kinetics studies of synthetic macrocyclic cobalt(II) complexes reveal the formation of superoxo-complexes which are rapidly converted to μ-peroxo-bridged species.[5,6] The synthesis of macrocyclic ligands with attached bulky groups is, therefore, of interest in the development of synthetic oxygen carriers, and in this study we report the synthesis of three new pyridine-containing 14-membered-ring tetra-aza macrocyclic ligands, L^1—L^3, two of which have bulky benzyl groups attached to the secondary amine groups. The ligands are somewhat analogous to the 12-membered-ring macrocycle 1,4,7,10-tetrabenzyl-1,4,7,10-tetra-azadodecane (tetrabenzylcyclen) studied previously,[7,8] although in L^2 and L^3 the larger macrocyclic ring and the more rigid pyridine ring gives rise to square-pyramidal rather than the trigonal-bipyramidal complexes postulated for tetrabenzylcyclen. We report the crystal structures of $[Ni(L^2)Cl]ClO_4·H_2O$ and L^2·HCl, and the synthesis and characterisation of the Ni^{2+}, Cu^{2+}, and Zn^{2+} complexes of L^1—L^3.

Experimental

Materials and Methods.—All chemicals were of the highest available purity and were not purified further. 1,7-Diamino-4-azaheptane was obtained from Fluka. 2,6-Pyridinedicarbaldehyde was prepared from 2,6-pyridinedimethanol as described previously.[9] Dimethyl sulphoxide (dmso) solvates of formula $[M(dmso)_n][ClO_4]_2$ (n = 6, M = Ni or Cu; n = 4, M = Zn) were prepared as described.[10] These salts were used in the synthesis of metal complexes. Proton-decoupled natural-abundance ^{13}C n.m.r. spectra were obtained at either 45.28 or 100.6 MHz with Bruker WH180 and WH400 spectrometers respectively. Proton n.m.r. spectra were recorded at 220 MHz with a Perkin-Elmer R34 spectrometer. Chemical shifts are reported on the δ scale relative to $SiMe_4$ at $\delta = 0$. Infrared, u.v.–visible and mass spectra were obtained with Perkin-Elmer 580B, Shimadzu 365 and Kratos MS80 spectrometers respectively. Microanalyses for the metal complexes were obtained commercially (Table 1). The ^{13}C n.m.r. data are in Table 2, and the visible spectra in Table 3.



L^1 ; $R^1 = R^2 = R^3 = H$
L^2 ; $R^1 = R^3 = H$, $R^2 = CH_2Ph$
L^3 ; $R^1 = H$, $R^2 = R^3 = CH_2Ph$
L^4 ; $R^1 = Me$, $R^2 = R^3 = H$
L^5 ; $R^1 = H$, $R^2 = R^3 = Me$

Preparation of L^1.—A template reaction with Ni^{2+} was used. $NiCl_2·6H_2O$ (8.75 g, 36.9 mmol) was dissolved in ethanol–water (1:1, 100 cm^3) and 1,7-diamino-4-azaheptane (4.85 g, 36.9 mmol) was added dropwise giving a blue solution. 2,6-Pyridinedicarbaldehyde (4.98 g, 36.9 mmol) was added followed by ethanoic acid (1.5 cm^3) as a catalyst. The resulting reddish brown solution was stirred at room temperature for 2 h, and then heated at 60 °C for 6 h. The solution was cooled with an ice-bath, and sodium tetrahydroborate (6 g, 158 mmol) added in small portions over a period of 30 min. The mixture was warmed to room temperature, stirred until effervescence ceased, and then heated at 80 °C for 2 h using an oil-bath. The ethanol was removed with a rotary evaporator and potassium cyanide (10 g, 154 mmol) was added. Heating was continued at 80 °C for 1 h, and the mixture was then cooled and basified with aqueous sodium hydroxide solution (15%) to *ca.* pH 12. L^1 was extracted with dichloromethane (5 × 200 cm^3), and the combined

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† 3,11-Dibenzyl-3,7,11,17-tetra-azabicyclo[11.3.1]heptadeca-1(17),13,15-triene–hydrochloride and -chloronickel(II) perchlorate monohydrate respectively.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: mmHg ≈ 133 Pa.

Table 1. Microanalytical data (%) for the metal complexes*

Complex	Formula	Colour	C	H	N
$[Ni(L^1)][ClO_4]_2$	$C_{13}H_{22}Cl_2N_4NiO_8$	Yellow	31.9 (31.5)	4.2 (4.5)	11.0 (11.4)
$[Cu(L^1)][ClO_4]_2$	$C_{13}H_{22}Cl_2CuN_4O_8$	Blue-purple	31.5 (31.4)	4.5 (4.5)	11.0 (11.3)
$[Zn(L^1)][NO_3]_2{\cdot}H_2O$	$C_{13}H_{24}N_6O_7Zn$	Colourless	35.2 (35.3)	5.1 (5.5)	19.2 (19.0)
$[Ni(L^2)Cl]ClO_4{\cdot}H_2O$	$C_{27}H_{36}Cl_2N_4NiO_5$	Green	51.6 (51.8)	5.8 (5.8)	8.9 (8.9)
$[Ni(L^2)][ClO_4]_2{\cdot}H_2O$	$C_{27}H_{36}Cl_2N_4NiO_9$	Yellow	46.9 (47.0)	5.0 (5.3)	8.4 (8.1)
$[Cu(L^2)][ClO_4]_2{\cdot}H_2O$	$C_{27}H_{36}Cl_2CuN_4O_9$	Blue	46.7 (46.6)	5.1 (5.2)	8.0 (8.1)
$[Zn(L^2)][NO_3]_2$	$C_{27}H_{34}N_6O_6Zn$	Colourless	53.2 (53.7)	5.6 (5.7)	13.9 (13.9)
$[Ni(L^3)(dmso)][ClO_4]_2$	$C_{36}H_{46}Cl_2N_4NiO_9S$	Blue-green	50.9 (51.5)	5.3 (5.5)	7.1 (6.7)
$[Cu(L^3)][ClO_4]_2$	$C_{34}H_{40}Cl_2CuN_4O_8$	Blue	53.1 (53.2)	5.6 (5.3)	7.4 (7.3)
$[Zn(L^3)(dmso)][ClO_4]_2$	$C_{36}H_{46}Cl_2N_4O_9SZn$	Colourless	50.6 (51.0)	5.5 (5.5)	6.9 (6.6)

* Calculated values are given in parentheses.

Table 2. Natural-abundance ^{13}C n.m.r. chemical shifts (δ/p.p.m.) of L^1—L^3 and their diamagnetic Ni^{2+} and Zn^{2+} complexes in $[^2H_3]$nitromethane solution at 298 K (relative populations in parentheses)

	Pyridine C			Phenyl C		$PhCH_2N$	$N{=}\overset{\vert}{C}CH_2N$	NCH_2C		CCH_2C
Compound	*ortho*	*para*	*meta*							
L^1	161.29 (2)	137.56 (1)	121.41 (2)				55.23 (2)	48.66 (2)	47.54 (2)	30.35 (2)
$[Ni(L^1)][ClO_4]_2$[a]	158.96 (2)	142.65 (1)	121.12 (2)				61.02 (2)	51.19 (2)	49.97 (2)	27.16 (2)
$[Ni(L^1)][ClO_4]_2$[b]	156.16 (2)	142.84 (1)	124.08 (2)				58.78 (2)	49.68 (2)	47.21 (2)	27.16 (2)
$[Ni(L^1)][ClO_4]_2$[c]	160.44 (1)	142.62 (1)	120.66 (1)				62.17 (1)	52.54 (1)	50.79 (1)	27.65 (1)
	159.45 (1)		120.56 (1)				61.41 (1)	48.99 (1)	48.39 (1)	24.85 (1)
$[Zn(L^1)][NO_3]_2$[a]	155.74 (2)	142.85 (1)	123.26 (2)				53.16 (2)	51.78 (2)	50.93 (2)	29.29 (2)
$[Zn(L^1)][NO_3]_2$[b]	156.20 (2)	143.01 (1)	123.12 (2)				52.17 (2)	51.91 (2)	50.63 (2)	25.29 (2)
L^2	160.36 (2)	141.59 (1)	123.71 (2)	137.72 (2)	130.40 (4)	59.73 (2)	60.43 (2)	51.80 (2)	49.09 (2)	27.18 (2)
				129.57 (4)	128.19 (2)					
$[Ni(L^2)][ClO_4]_2$[a]	159.49 (2)	144.10 (1)	122.56 (2)	133.25 (2)	131.80 (4)	64.18 (2)	69.37 (2)	56.78 (2)	50.14 (2)	25.14 (2)
				131.47 (4)	131.38 (2)					
$[Ni(L^2)][ClO_4]_2$[b]	157.45 (2)	144.10 (1)	122.07 (2)	133.94 (2)	133.09 (4)	64.18 (2)	68.34 (2)	58.98 (2)	49.32 (2)	25.61 (2)
				130.98 (4)	130.49 (2)					
$[Zn(L^2)][NO_3]_2$[a]	155.74 (2)	143.87 (1)	124.54 (2)	133.78 (2)	132.99 (4)	55.36 (2)	58.65 (2)	51.98 (2)	50.93 (2)	24.95 (2)
				129.96 (4)	129.83 (2)					
$[Zn(L^2)][NO_3]_2$[b]	156.10 (2)	144.26 (1)	125.03 (2)	133.78 (2)	132.63 (4)	55.26 (2)	57.37 (2)	54.44 (2)	53.77 (2)	24.33 (2)
				130.29 (4)	129.96 (2)					
L^3	160.40 (2)	141.82 (1)	123.77 (2)	137.71 (2)	130.45 (4)	61.18 (2)	61.52 (2)	53.58 (2)	52.92 (2)	26.34 (2)
				129.59 (4)	129.34 (2)					
				142.30 (1)[d]	130.22 (2)	60.94 (1)				
				128.22 (2)	127.88 (1)					
$[Zn(L^3)(dmso)][ClO_4]_2$[a,e]	155.08 (2)	144.20 (1)	124.70 (2)	132.43 (2)	133.25 (4)	57.93 (2)	63.25 (2)	52.96 (2)	55.95 (2)	22.78 (2)
				130.23 (4)	129.93 (2)					
				130.52 (2)	132.10 (1)[d]	51.39 (1)				
				130.59 (2)	128.91 (1)					

[a] One symmetric isomer. [b] Second symmetric isomer. [c] Unsymmetric isomer. [d] Tertiary C atom. [e] δ(dmso) = 40.34 p.p.m.

extracts were dried with anhydrous $MgSO_4$ and then evaporated with a rotary evaporator to leave a thick brown oil. This oil was fractionated using a Kügelröhr apparatus to give L^1 (4 g, 17 mmol, 46%) as a colourless liquid (b.p. 110 °C, 0.1 mmHg) which solidified on cooling. ^{13}C N.m.r. ($CDCl_3$; relative numbers of C atoms given in parentheses): δ 159.37 (2), 136.36 (1), 120.44 (2), 54.47 (2), 47.77 (2), 46.73 (2), 29.31 (2) p.p.m. ^1H N.m.r. ($CDCl_3$): δ 7.57 (1 H, t), 7.04 (2 H, d), 3.92 (4 H, s), 2.93 (3 H, br), 2.81 (4 H, t), 2.67 (4 H, t), 1.80 (4 H, quintet).

Preparation of $L^2{\cdot}HCl$.—The macrocycle L^1 (1 g, 4 mmol) was dissolved in dichloromethane (50 cm^3) and mixed with a solution of sodium hydroxide (0.43 g, 10 mmol) in water (50 cm^3). The mixture was stirred vigorously during the dropwise addition of benzyl chloride (1.36 g, 10 mmol) over a period of 10 min. The mixture was stirred under nitrogen for 24 h, and then the organic phase was carefully separated. The aqueous layer was extracted with dichloromethane (3 × 50 cm^3), the combined organic layers were dried with anhydrous $MgSO_4$ and the volume was reduced with a rotary evaporator to leave a thick oil. Trituration of this oil with light petroleum (b.p. 40—60 °C) gave a white powder which was filtered off, washed with diethyl ether, and recrystallised from dichloromethane–ether. Surprisingly the solid analysed as $L^2{\cdot}HCl$ (1 g, 2.2 mmol, 55%), and the presence of the hydrochloride was confirmed by *X*-ray crystallography. Combustion analysis (Found: C, 69.65;

Table 3. U.v.–visible spectra [λ/nm (ε/dm^3 mol^{-1} cm^{-1})] of Ni^{2+} and Cu^{2+} complexes in nitromethane solution

Complex	$\lambda_{max.}(\varepsilon)$
$[Ni(L^1)][ClO_4]_2$	460 (166)
$[Cu(L^1)][ClO_4]_2$	544 (175)*
$[Ni(L^2)Cl]ClO_4$	406 (141), 656 (54), 952 (32)
$[Ni(L^2)][ClO_4]_2$	466 (167)
$[Cu(L^2)][ClO_4]_2$	580 (289)*
$[Ni(L^3)(dmso)][ClO_4]_2$	374 (150), 580 (61), 756 (39)
$[Cu(L^3)][ClO_4]_2$	610 (409)*

* Broad peak with an ill-defined shoulder to shorter wavelengths.

Table 4. Atomic co-ordinates (× 10^4) for L^2·HCl

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cl	2 096(2)	4 125(2)	3 856(1)	C(12)	4 115(6)	−284(6)	6 643(4)
N(1)	1 675(4)	3 393(4)	6 361(3)	C(13)	5 262(7)	−1 060(7)	6 464(5)
N(2)	4 368(5)	3 350(5)	7 247(4)	C(14)	6 366(8)	−512(8)	6 252(5)
N(3)	4 054(4)	1 019(4)	6 599(3)	C(15)	6 348(6)	806(7)	6 209(5)
N(4)	1 679(4)	−90(4)	7 007(4)	C(16)	5 157(6)	1 567(6)	6 369(4)
C(1)	479(5)	2 751(5)	6 676(5)	C(17)	5 061(7)	3 044(7)	6 300(5)
C(2)	177(6)	1 894(6)	5 937(5)	C(18)	5 145(6)	2 723(7)	8 273(5)
C(3)	1 264(6)	768(6)	5 919(5)	C(19)	4 326(7)	2 656(7)	9 273(5)
C(4)	658(6)	−916(6)	7 477(5)	C(20)	3 236(7)	2 008(7)	9 409(5)
C(5)	975(6)	−1 736(6)	8 634(5)	C(21)	2 449(7)	1 963(7)	10 294(5)
C(6)	1 230(6)	−1 161(6)	9 458(5)	C(22)	2 750(7)	2 579(6)	11 096(5)
C(7)	1 480(6)	−1 901(7)	10 536(5)	C(23)	3 856(8)	3 210(7)	10 976(6)
C(8)	1 467(6)	−3 272(7)	10 801(6)	C(24)	4 629(8)	3 241(7)	10 090(6)
C(9)	1 211(8)	−3 884(7)	9 990(7)	C(25)	4 000(7)	4 823(6)	7 078(6)
C(10)	964(7)	−3 111(6)	8 936(6)	C(26)	2 795(8)	5 370(6)	6 327(6)
C(11)	2 919(6)	−949(5)	6 946(5)	C(27)	1 639(7)	4 650(5)	6 725(5)

Table 5. Bond lengths (Å) and angles (°) in L^2·HCl

N(1)–H(011)	1.079(42)	N(1)–H(012)	0.992(39)	C(7)–C(8)	1.373(10)	C(8)–C(9)	1.380(12)
N(1)–C(1)	1.477(7)	N(1)–C(27)	1.489(8)	C(9)–C(10)	1.355(10)	C(11)–C(12)	1.488(9)
N(2)–C(17)	1.466(9)	N(2)–C(18)	1.460(7)	C(12)–C(13)	1.380(9)	C(13)–C(14)	1.329(11)
N(2)–C(25)	1.478(8)	N(3)–C(12)	1.330(7)	C(14)–C(15)	1.352(12)	C(15)–C(16)	1.400(9)
N(3)–C(16)	1.331(7)	N(4)–C(3)	1.445(7)	C(16)–C(17)	1.501(10)	C(18)–C(19)	1.499(9)
N(4)–C(4)	1.466(8)	N(4)–C(11)	1.458(7)	C(19)–C(20)	1.368(10)	C(19)–C(24)	1.381(11)
C(1)–C(2)	1.507(10)	C(2)–C(3)	1.499(8)	C(20)–C(21)	1.364(10)	C(21)–C(22)	1.387(10)
C(4)–C(5)	1.485(8)	C(5)–C(6)	1.368(10)	C(22)–C(23)	1.373(11)	C(23)–C(24)	1.358(11)
C(5)–C(10)	1.377(8)	C(6)–C(7)	1.371(8)	C(25)–C(26)	1.502(10)	C(26)–C(27)	1.500(10)
H(011)–N(1)–H(012)	105.4(33)	H(011)–N(1)–C(1)	112.0(25)	C(5)–C(10)–C(9)	122.7(7)	N(4)–C(11)–C(12)	117.7(5)
H(012)–N(1)–C(1)	112.3(25)	H(011)–N(1)–C(27)	107.2(24)	N(3)–C(12)–C(11)	118.9(5)	N(3)–C(12)–C(13)	122.6(6)
H(012)–N(1)–C(27)	108.1(28)	C(1)–N(1)–C(27)	111.6(5)	C(11)–C(12)–C(13)	118.4(6)	C(12)–C(13)–C(14)	119.9(7)
C(17)–N(2)–C(18)	111.0(5)	C(17)–N(2)–C(25)	111.6(5)	C(13)–C(14)–C(15)	119.4(7)	C(14)–C(15)–C(16)	119.0(7)
C(18)–N(2)–C(25)	111.8(5)	C(12)–N(3)–C(16)	117.3(5)	N(3)–C(16)–C(15)	121.9(6)	N(3)–C(16)–C(17)	116.5(5)
C(3)–N(4)–C(4)	110.7(5)	C(3)–N(4)–C(11)	109.8(5)	C(15)–C(16)–C(17)	121.6(6)	N(2)–C(17)–C(16)	110.6(5)
C(4)–N(4)–C(11)	110.4(4)	N(1)–C(1)–C(2)	112.8(5)	N(2)–C(18)–C(19)	112.1(5)	C(18)–C(19)–C(20)	120.8(7)
C(1)–C(2)–C(3)	114.0(5)	N(4)–C(3)–C(2)	113.3(5)	C(18)–C(19)–C(24)	121.9(7)	C(20)–C(19)–C(24)	117.2(6)
N(4)–C(4)–C(5)	113.3(5)	C(4)–C(5)–C(6)	122.0(5)	C(19)–C(20)–C(21)	122.3(7)	C(20)–C(21)–C(22)	119.9(7)
C(4)–C(5)–C(10)	121.2(7)	C(6)–C(5)–C(10)	116.8(6)	C(21)–C(22)–C(23)	118.2(6)	C(22)–C(23)–C(24)	121.0(8)
C(5)–C(6)–C(7)	122.6(6)	C(6)–C(7)–C(8)	118.7(7)	C(19)–C(24)–C(23)	121.4(7)	N(2)–C(25)–C(26)	111.7(6)
C(7)–C(8)–C(9)	120.2(6)	C(8)–C(9)–C(10)	119.0(6)	C(25)–C(26)–C(27)	112.5(5)	N(1)–C(27)–C(26)	111.9(5)

H, 7.90; Cl, 7.50; N, 12.20. Calc. for $C_{27}H_{35}ClN_4$: C, 70.75; H, 7.80; Cl, 7.80; N, 12.40%). ^{13}C N.m.r. ($CDCl_3$): δ 158.10 (2), 138.41 (2), 136.87 (1), 128.94 (4), 128.45 (4), 127.36 (2), 122.04 (2), 58.49 (2), 57.99 (2), 50.60 (2), 49.22 (2), 22.85 (2). ^1H N.m.r. ($CDCl_3$): δ 7.60 (1 H, t,), 7.36 (10 H, m), 7.06 (2 H, d), 3.89 (4 H, s), 3.59 (4 H, s), 3.06 (4 H, t), 2.78 (4 H, t), 2.32 (4 H, quintet).

Preparation of L^2.—The macrocycle L^2·HCl (1 g, 2.2 mmol) was dissolved in methanol (50 cm^3), and solid sodium hydroxide (0.27 g, 6.7 mmol) was added. The mixture was stirred for 5 min and the solution was then evaporated under reduced pressure to give a solid residue. This residue was extracted with dry dichloromethane (3 × 50 cm^3), and the combined extracts were concentrated using a rotary evaporator to give a thick oil. The oil was passed over a neutral alumina column (15 × 2 cm) and eluted with dry dichloromethane. On concentrating L^2 was obtained as a pale yellow oil (0.9 g, 2.16 mmol, 98%). Electron impact mass spectrum: M^+ at *m*/*z* 415 (calc. 415). ^{13}C N.m.r. ($CDCl_3$): δ 158.66 (2), 139.53 (2), 136.11 (1), 128.88 (4), 128.22 (4), 126.84 (2), 122.30 (2), 58.98 (2), 58.72 (2), 50.56 (2), 48.13 (2), 25.97 (2). ^1H N.m.r. ($CDCl_3$): δ 7.40 (11 H, m), 6.98 (2 H, d), 3.67 (4 H, s), 3.64 (4 H, s), 2.68 (4 H, t), 2.60 (4 H, t), 1.82 (4 H, quintet).

Preparation of L^3.—The macrocycle L^2 (1 g, 2.4 mmol) was dissolved in methanol (50 cm^3) and stirred with sodium hydroxide (0.3 g, 7.5 mmol). Benzyl chloride (0.9 g, 7 mmol) was added dropwise, and the solution heated under nitrogen at 50 °C for 72 h. Afterwards the solution was evaporated using a rotary evaporator, and excess benzyl chloride removed by pumping at 50 °C at a pressure of 0.1 mmHg. The resulting oil was passed through a neutral alumina column and eluted with dichloromethane. Work-up as described for L^2 gave L^3 as a white solid. Electron impact mass spectrum: M^+ at *m*/*z* 505 (calc. 505). The ^{13}C n.m.r. of L^3 is compared with that of its Zn^{2+} complex in Table 4. ^1H N.m.r. ($CDCl_3$): δ 7.61 (1 H, t), 7.33 (15 H, m), 7.11 (2 H, d), 3.74 (4 H, s), 3.67 (4 H, s), 3.34 (2 H, s), 2.57 (4 H, t), 2.29 (4 H, t), 1.53 (4 H, quintet).

Preparation of Metal Complexes.—The complexes of L^1—L^3 were obtained in 80% yields by mixing ethanolic solutions of the appropriate ligand and the salts $[M(dmso)_6][ClO_4]_2$ (M = Ni or Cu), $[Zn(dmso)_4][ClO_4]_2$, or $Zn(NO_3)_2·6H_2O$ in a 1:1 molar ratio. In most cases the complexes precipitated immediately; otherwise dry diethyl ether was added dropwise to precipitate the complexes. The solids were recrystallised from nitromethane–ethanol mixtures.

Crystal Structures.—Crystal data for L^2·HCl. Crystals (colourless blocks) of the ligand monohydrochloride, $C_{27}H_{35}ClN_4$, M = 440.5, are triclinic, space group $P\bar{1}$, with a = 10.228(5), b = 10.376(6), c = 12.651(8) Å, α = 74.48(5), β = 89.76(4), γ = 81.88(4)°, U = 1 270 Å^3, Z = 2, D_c = 1.15 g cm^{-3}, T = 293 K, Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 1.68 cm^{-1}, F(000) = 4 841; $2\theta_{max.}$ = 50°, scan ranges ±1.1°. 3 322 Unique reflections [1 328 with $I/\sigma(I) \geqslant 3.0$]; no systematic absences. Weighting parameter, g = 0.002; R = 0.053, R' = 0.056.

Crystal data for [Ni(L^2)Cl]ClO_4·H_2O. The crystals (green plates) of formula $C_{27}H_{36}Cl_2NiO_5$, M = 570.2, are orthorhombic, space group $P2_1ca$, with a = 19.068(4), b = 7.508(1), c = 19.643(4) Å, U = 2 812(1) Å^3, Z = 4, D_c = 1.35 g cm^{-3}, Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 9.22 cm^{-1}, T = 293 K, F(000) = 1 447; $2\theta_{max.}$ = 50°, scan ranges −0.85, +1.05°. 3 687 Unique reflections [1 680 with $I/\sigma(I) \geqslant 3.0$]. Weighting parameter, g = 0.002; R = 0.049, R' 0.053.

For both compounds data were collected with a Syntex $P2_1$ four-circle diffractometer, with maximum 2θ and scan range (2θ) around $K_{\alpha1}$–$K_{\alpha2}$ angles as specified, scan speed 2—29 ° min^{-1} depending on the intensity of a 2 s pre-scan; backgrounds were measured at each end of the scan for 0.25 of the scan time. Three standard reflections were monitored every 200 reflections, and showed slight changes during data collection. The data were rescaled to correct for this. Unit-cell dimensions and standard deviations were obtained by a least-squares fit to 15 high-angle reflections. Reflections were processed using profile analysis and those with $I/\sigma(I) \geqslant 3.0$ were used in the refinement; these were corrected for Lorentz and polarisation, but not absorption effects. Anisotropic thermal parameters were used for all non-hydrogen atoms, and H atoms were given fixed isotropic thermal parameters, U = 0.07 Å^2, inserted at calculated positions and not refined, except as noted below. Final refinement on F was by cascaded least-squares methods. Weighting schemes were used of the form $w = 1/[\sigma^2(F) + gF^2]$, and found to be satisfactory by a weight analysis. Computing was with SHELXTL[11] on a Data General DG30 computer. Scattering factors in the analytical form and anomalous dispersion factors were taken from ref. 12.

For L^2·HCl, the data showed no systematic absences, and the structure was solved by direct methods using SHELXTL. The protons on N(1) were located and refined.

For [Ni(L^2)Cl]ClO_4·H_2O, the data showed systematic absences $h0l$, $l \neq 2n$, $hk0$, $h \neq 2n$ which indicate either space group $Pmca$ (non-standard setting of $Pbcm$) or $P2_1ca$ (non-standard setting of $Pca2_1$); the former requires the cation to show m symmetry. As this was considered unlikely, the latter was chosen, and shown to be correct by the success of the refinement. The Ni and both the Cl atoms were located by the Patterson interpretation section of SHELXTL, and the light atoms then found on successive Fourier syntheses. One residual peak was treated as the oxygen atom of a lattice water molecule, probably partly disordered as it has very high thermal parameters. The hand of the individual crystal chosen was checked by refinement of a f'' multiplier; the refined value of 0.08(7) indicates that the material is a twin of left- and right-handed crystals. The x co-ordinate of the Ni atom was fixed to define the origin.

Final atomic co-ordinates are given in Tables 4 and 6, and the selected bond lengths and angles in Tables 5 and 7.

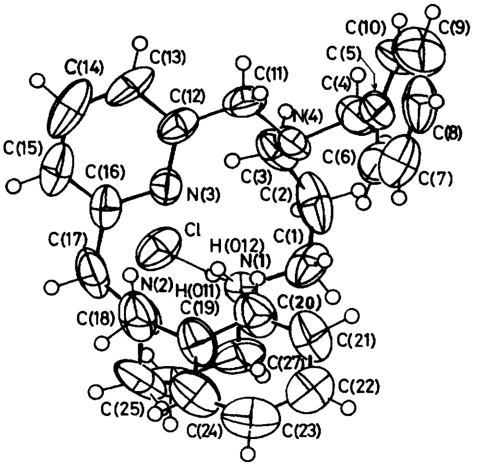

Figure 1. Molecular structure of L^2·HCl showing atomic numbering

Results and Discussion

The template synthesis of L^1 follows closely that reported for the analogous macrocycle L^4.[13] The benzylation of L^1 proceeds smoothly to give L^2 and L^3 as described. The product obtained depends on the medium used in the syntheses; for example, the major product of the reaction of L^1 with a five-fold molar excess of benzyl chloride containing five molar equivalents of sodium hydroxide, when carried out in a two-phase dichloromethane–water mixture, is L^2·HCl. However, using a single-phase medium (methanol) the product obtained is L^3. Addition of MCl (M = alkali metal or NH_4^+) to chloroform solutions of L^2·HCl caused small (up to 0.1 p.p.m.) chemical shifts in the ^1H n.m.r. spectrum, attributed at first to alkali-metal ion complexation. However, precipitation gave only the monohydrochloride salt, and we attribute the small chemical shifts to changes in the medium. There were no significant chemical shifts observed when alkali-metal salts were added to unprotonated L^2 which we isolated later. The nature of L^2·HCl was established by X-ray crystallography, and by ^{13}C n.m.r. spectroscopy. Both showed that the symmetrically dibenzylated derivative is produced in the two-phase reaction. These medium-dependent syntheses are puzzling, although a recent crystal structure[14] of the related macrocycle L^4 gives a clue to the preferred formation of the symmetrically dibenzylated derivative. In this crystal structure the N lone pairs on atoms 3 and 11 (those which are most readily benzylated) point outwards and can readily attack the benzyl chloride, whereas the lone pair on N-7 is sterically hindered by the propyl backbones of the macrocyclic ring. In L^2, protonation of N-7 (the most basic N atom) is not, of course, sterically hindered; the resulting monohydrochloride is surprisingly lipophilic and is readily extracted into the organic phase, where it is accessible to benzylation in the two-phase reaction.

The isolation of L^2 from its hydrochloride is readily achieved, and we have found L^2 to be a very useful starting material for the synthesis of macrocycles with single co-ordinating pendant arms, by further attack at the remaining secondary amine group. For example, a macrocycle with a pendant co-ordinating 2-pyridylmethyl group can be made readily in this way.[15] The macrocycle L^2 can also be converted to L^3 by further reaction with benzyl chloride as described.

A view of the molecular structure of L^2·HCl is shown in Figure 1. The direct location of the hydrogen atoms on N(1) confirms the expected position of protonation. The four nitrogen atoms show a reasonably planar arrangement, though N(1) is folded towards N(3), as compared with the conformation when co-ordinated; this apparently results from a weak hydrogen bond [N(1)–H(012)···N(3) with bond angle 149(3)° and H(012)···N(3) distance 2.27(4) Å]. The two benzyl groups project to the same side of the macrocyclic ring, a conformation which persists in the metal complexes. The second hydrogen attached to N(1) projects almost perpendicular to the ring

Table 6. Atomic co-ordinates (× 10^4) for $[Ni(L^2)Cl]ClO_4 \cdot H_2O$

Atom	*x*	*y*	*z*
Ni	0	5 432(1)	6 719(1)
Cl(1)	3 869(2)	9 443(4)	722(2)
Cl(2)	−394(1)	8 194(3)	6 432(1)
O(001)	4 157(20)	9 106(15)	2 511(7)
O(11)	4 519(8)	9 530(38)	663(11)
O(12)	3 617(8)	10 411(22)	1 218(10)
O(13)	3 422(12)	9 864(41)	207(13)
O(14)	3 698(14)	7 796(18)	763(13)
N(1)	−879(4)	4 397(11)	7 097(4)
N(2)	−26(5)	4 316(9)	5 699(3)
N(3)	739(4)	3 511(10)	6 817(3)
N(4)	501(4)	6 191(9)	7 696(3)
C(1)	−1 455(5)	4 317(16)	6 581(6)
C(2)	−1 252(5)	3 250(15)	5 962(5)
C(3)	−771(5)	4 124(15)	5 445(5)
C(4)	332(5)	2 581(13)	5 729(5)
C(5)	892(5)	2 549(11)	6 267(4)
C(6)	1 501(5)	1 517(12)	6 237(5)
C(7)	1 950(5)	1 574(14)	6 775(5)
C(8)	1 781(5)	2 561(13)	7 355(5)
C(9)	1 168(5)	3 546(11)	7 343(5)
C(10)	906(6)	4 587(12)	7 926(5)
C(11)	−35(6)	6 714(11)	8 199(4)
C(12)	−634(6)	5 416(15)	8 295(5)
C(13)	−1 156(6)	5 397(15)	7 695(6)
C(14)	321(5)	5 488(15)	5 177(4)
C(15)	1 119(5)	5 632(13)	5 295(4)
C(16)	1 584(5)	4 552(13)	4 928(5)
C(17)	2 292(6)	4 629(14)	5 047(5)
C(18)	2 548(6)	5 752(15)	5 535(6)
C(19)	2 101(5)	6 883(14)	5 883(5)
C(20)	1 380(5)	6 822(12)	5 766(4)
C(21)	993(4)	7 708(11)	7 539(4)
C(22)	1 382(4)	8 515(11)	8 131(4)
C(23)	2 091(5)	8 125(13)	8 215(5)
C(24)	2 460(6)	8 922(17)	8 751(6)
C(25)	2 151(8)	10 075(16)	9 188(6)
C(26)	1 451(7)	10 500(15)	9 092(6)
C(27)	1 070(6)	9 699(14)	8 577(5)

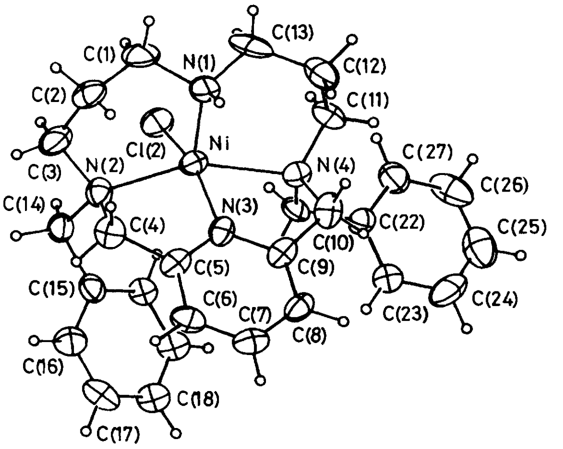

Figure 2. Molecular structure of $[Ni(L^2)Cl]ClO_4 \cdot H_2O$ showing atomic numbering

plane, and is hydrogen-bonded to the Cl atom [H(011) ··· Cl 2.00(4) Å, N(1)–H(011) ··· Cl 177(3)°].

Metal Complexes of L^1.—Ethanolic solutions of the dimethyl sulphoxide solvates of $M(ClO_4)_2$ (M = Ni, Cu, or Zn) react rapidly with L^1 (1:1 molar ratio) to give excellent yields of the complexes shown in Table 1. The Zn^{2+} complex prepared in this manner is extremely hygroscopic and difficult to handle, so a more tractable product was obtained by using $Zn(NO_3)_2 \cdot 6H_2O$ as the starting material. The ^{13}C n.m.r. spectrum of the yellow diamagnetic $[Ni(L^1)][ClO_4]_2$ in $[^2H_3]$nitromethane solution (Table 2) recorded immediately after dissolution showed it to be a mixture of one symmetric and one unsymmetric isomer. However, when the spectrum of the same solution was recorded 24 h later, we observed that the symmetric isomer had isomerised to the other symmetric isomer, whilst the unsymmetric isomer remained apparently unaffected. No further change was observed after 3—4 d. These three isomers arise from the possible positions of the H atoms attached to the secondary amine groups pointing either above or below the macrocyclic ligand plane as explained previously.[16]

Table 7. Selected bond lengths (Å) and angles (°) for $[Ni(L^2)Cl]ClO_4 \cdot H_2O$

Ni–Cl	2.277(3)	Ni–N(3)	2.025(7)
Ni–N(1)	1.991(8)	Ni–N(4)	2.217(7)
Ni–N(2)	2.174(6)		
Cl–Ni–N(1)	99.8(2)	N(1)–Ni–N(3)	105.8(3)
Cl–Ni–N(2)	96.6(2)	N(2)–Ni–N(3)	80.1(3)
Cl–Ni–N(3)	154.4(2)	N(1)–Ni–N(4)	98.1(3)
Cl–Ni–N(4)	97.1(2)	N(2)–Ni–N(4)	155.1(3)
N(1)–Ni–N(2)	100.0(3)	N(3)–Ni–N(4)	78.6(3)

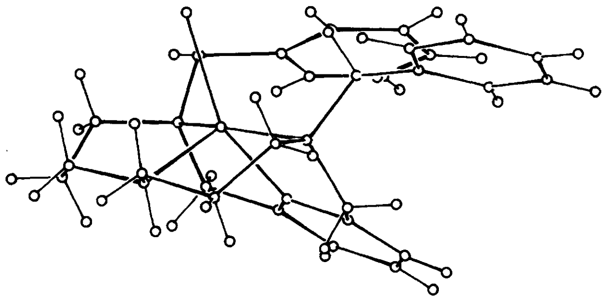

Figure 3. View of $[Ni(L^2)Cl]ClO_4 \cdot H_2O$ showing how the macrocycle is folded, and how the benzyl groups block the base of the square pyramid around Ni

The ^{13}C n.m.r. spectrum of $[Zn(L^1)][NO_3]_2$ in $[^2H_3]$-nitromethane (Table 2) shows the presence of both symmetric isomers, but there was no evidence for isomerisation reactions. The visible spectra of the Ni^{2+} and Cu^{2+} complexes (Table 3) are as expected for planar NiN_4^{2+} and CuN_4^{2+} chromophores.[17]

Metal Complexes of L^2.—These were prepared in the same way as those of L^1. Starting from $L^2 \cdot HCl$, reaction with $[Ni(dmso)_6][ClO_4]_2$ in a 1:1 molar ratio in ethanolic solution gave green crystals which analysed as $[Ni(L^2)Cl]ClO_4 \cdot H_2O$, whereas reaction with the unprotonated ligand in the same way gave the yellow diamagnetic $[Ni(L^2)][ClO_4]_2$. Reaction of the latter complex with one molar equivalent of NaCl gave the former product as expected. The ^{13}C n.m.r. spectra of the diamagnetic Ni^{2+} and Zn^{2+} complexes in $[^2H_3]$nitromethane solution (Table 2) show the presence of two symmetric isomers in each case, and there is no evidence for an isomerisation reaction as found for the $[Ni(L^1)]^{2+}$ ion. The bulky benzyl groups undoubedly prevent N inversions from occurring in the complexes of L^2.

The molecular structure of $[Ni(L^2)Cl]ClO_4 \cdot H_2O$ was established by *X*-ray crystallography (Figures 2 and 3). The Ni^{2+} ion is approximately square pyramidal, with the secondary amine group [N(1) in Figure 2] at the apex and the chloride ion co-ordinated in the basal plane along with the three tertiary amine groups (chloride in a *trans* position to pyridine N). As is usual with this geometry, the Ni atom is above the basal plane (by 0.40 Å; *trans* angles 154.4—155.1°). The macrocycle is folded about the N–C(benzyl)–N–C(benzyl) axis. Similar structures have been found in the closely related complexes of the trimethylated macrocycle, $[Ni(L^5)X]^{n+}$ (X = Cl or dmso;[18] X = H_2O or N_3[19]). The bulk of the Cl^- ligand produces some distortion of the basal plane, with the Cl–Ni–N angles (96.6, 97.1°) rather larger than the N–Ni–N angles (78.6, 80.1°), but otherwise the structure is very regular. The shortest Ni–N bond lengths are to the apical N and pyridine N atoms, with the Ni–N–C(benzyl) bond lengths *ca.* 0.2 Å longer.

The visible spectra of $[M(L^2)][ClO_4]_2$ (M = Ni or Cu) and $[Ni(L^2)Cl]ClO_4$ in nitromethane solution (Table 3) are typical of those for four- and five-co-ordinate complexes respectively.[17]

Complexes of L^3.—Reaction of the dimethyl sulphoxide solvates of Ni^{2+}, Cu^{2+}, and Zn^{2+} with L^3 in ethanol gives the five-co-ordinate monosolvated complexes $[M(L^3)(dmso)][ClO_4]_2$ (M = Ni or Zn) and the four-co-ordinate $[Cu(L^3)][ClO_4]_2$. Attempts to make a four-co-ordinate Ni^{2+} complex failed, the product always containing a co-ordinated solvent molecule (dmso or H_2O), indicating a stronger affinity for a fifth ligand in this case. The ^{13}C n.m.r. spectrum of $[Zn(L^3)(dmso)][ClO_4]_2$ shows the presence of a single symmetric isomer (Table 2).

A comparison of the visible absorption band observed for the Cu^{2+} complexes (Table 3) shows a gradual shift to longer wavelengths, and an increase in the absorption coefficients as more benzyl groups are added to the parent macrocycle. This could arise from either a gradual weakening of the macrocyclic ligand field strength, or a movement of the Cu^{2+} ion from the centre of a square-planar geometry due to increasing steric crowding by the benzyl groups.

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