Studies of Pendant Arm Macrocyclic Ligands. Part 6.† Synthesis of Two Penta-aza Macrocyclic Ligands containing Single Pendant Co-ordinating 2-Pyridylmethyl and 1-Pyrazolylmethyl Arms, and Characterisation of Their Nickel(II), Copper(II), Cobalt(II), and Zinc(II) Complexes. Crystal Structure of {3,11-Dibenzyl-7-(2′-pyridylmethyl)-3,7,11,17-tetra-azabicyclo[11.3.1]-heptadeca-1(17),13,15-triene}zinc(II) Perchlorate‡

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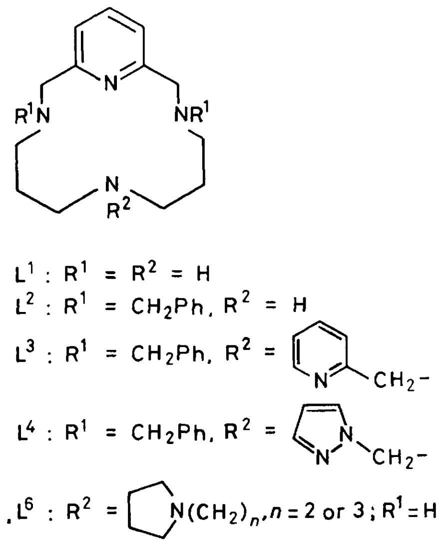
Reaction of the secondary amine group of 3,11-dibenzyl-3,7,11,17-tetra-azabicyclo[11.3.1]heptadeca-1(17),13,15-triene (L^2) with 2-chloromethylpyridine in the presence of base, or with 1-(hydroxymethyl)pyrazole, gives two new pendant-arm macrocycles, L^3 and L^4, having 7-(2′-pyridylmethyl) and 7-(1′-pyrazolylmethyl) groups, respectively. Complexes of Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} with L^3 and L^4 have been isolated and characterised. The structure of $[Zn(L^3)][ClO_4]_2$ has been established by *X*-ray crystallography, and confirms solution ^1H n.m.r. studies; the two benzyl groups and the pendant arm lie on the same side of the macrocycle. Proton-decoupled ^{13}C n.m.r. spectra of the Zn^{2+} complexes of L^3 and L^4 show the presence of only a single symmetric isomer in each case. In the $[Zn(L^4)(dmso)]^{2+}$ ion, the presence of a strongly co-ordinated dimethyl sulphoxide (dmso) molecule is confirmed both in the solid state and in solution, and solid complexes of formula $[M(L)(dmso)][ClO_4]_2$ ($L = L^3$ or L^4; M = Co, Ni, or Cu) have been prepared in all cases.

In many of the metal complexes which are known to bind dioxygen reversibly, an axial base (B) such as pyridine or imidazole has been found to be essential for activity.[1] These complexes are frequently of the type *trans*-$[M(L)B(O_2)]^{n+}$ in which a metal ion (M) is surrounded in-plane by the four N-donor atoms of a cyclic ligand L [*e.g.* *NN′*-ethylenebis(salicylideneiminate), a porphyrin, or a tetra-azamacrocycle], with the O_2 molecule co-ordinated (as superoxide ion) in a *trans* position to the base (B). The presence of sterically hindering groups on L is also helpful to avoid irreversible oxidation to μ-peroxy-bridged dimer species of the type $[B(L)M(\mu\text{-}O_2)M(L)B]^{n+}$ (*e.g.* the 'picket-fence' porphyrins).

In previous publications we have reported the ready synthesis of the symmetrically disubstituted macrocycle L^2 from the two-phase reaction of the parent macrocycle L^1 (prepared as described[2]) and benzyl chloride in the presence of base.[3,4] In these previous studies we attempted to add a 'picket-fence' to the secondary amine groups of L^1, and having isolated L^2 in good yield, we were in a position to explore the addition of a tail-base N-donor group of the type often used in O_2 activation. For example, reactions of the remaining secondary amine group of L^2 with 2-(chloromethyl)pyridine in the presence of base, and with 1-(hydroxymethyl)pyrazole have been carried out in this work to obtain the new functionalised macrocycles L^3 and L^4 respectively. We report here the preparation of these ligands together with their Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} complexes which have been isolated and characterised. The ligand L^3 is the simplest of the tail-base pyridyl macrocycles reported so far;[5,6] L^4 is the first pendant-pyrazolyl macrocycle, and is closely related to the pendant-pyrrolidyl macrocycles we reported recently.[2]



The structure of the $[Zn(L^3)]^{2+}$ ion, which was established previously in solution using two-dimensional ^1H n.m.r., nuclear Overhauser enhancement (n.O.e.) difference ^1H n.m.r. spectroscopy, and ^1H-decoupled ^{13}C n.m.r.,[3] has been confirmed in the solid state by *X*-ray crystallography. The paramagnetic metal complexes have been investigated by elemental analyses and by u.v.–visible spectroscopy.

Experimental

Materials and Methods.—All chemicals were of the highest available purity and were not purified further. Pyridine-2,6-dicarbaldehyde was prepared from pyridine-2,6-dimethanol as described previously.[7] Pyrazole (Aldrich) was converted to 1-(hydroxymethyl)pyrazole using a reported method.[8] The preparations of L^1 and L^2 have been reported previously.[2–4] Dimethyl sulphoxide (dmso) solvates of formula $[M(dmso)_n]$-

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† Part 5 is ref. 2.

‡ *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

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

Table 1. Analytical data for the metal complexes of L^3 and L^4

			Analysis (%)[a]		
Complex	Molecular formula	Colour	C	H	N
$[Ni(L^3)(dmso)][ClO_4]_2$	$C_{35}H_{45}Cl_2N_5NiO_9S$	Blue	49.7 (50.0)	5.0 (5.4)	8.6 (8.3)
$[Cu(L^3)(dmso)][ClO_4]_2$	$C_{35}H_{45}Cl_2CuN_5O_9S$	Deep blue	49.7 (49.7)	5.0 (5.4)	8.7 (8.3)
$[Co(L^3)(dmso)][ClO_4]_2$	$C_{35}H_{45}Cl_2CoN_5O_9S$	Purple	49.8 (49.9)	5.0 (5.4)	8.7 (8.3)
$[Zn(L^3)][ClO_4]_2$	$C_{33}H_{39}Cl_2N_5O_8Zn$	White	51.1 (51.5)	5.1 (5.1)	8.8 (9.1)
$[Ni(L^4)(dmso)][ClO_4]_2$[b]	$C_{33}H_{44}Cl_2N_6NiO_9S$	Green-blue	48.7 (47.7)	5.5 (5.3)	9.3 (10.1)
$[Cu(L^4)(dmso)][ClO_4]_2 \cdot H_2O$	$C_{33}H_{46}Cl_2CuN_6O_{10}S$	Blue	46.3 (46.5)	5.1 (5.4)	9.3 (9.8)
$[Co(L^4)(dmso)][ClO_4]_2$	$C_{33}H_{44}Cl_2CoN_6O_9S$	Purple	47.4 (47.7)	5.2 (5.3)	10.2 (10.1)
$[Zn(L^4)(dmso)][ClO_4]_2$	$C_{33}H_{44}Cl_2N_6O_9SZn$	White	47.7 (47.4)	4.8 (5.3)	9.6 (10.0)

[a] Required values are given in parentheses. [b] Calculated values for $0.5Et_2O$ solvate: C, 48.5; H, 5.7; N, 9.7% (possible contamination with wash solvent).

Table 2. Comparison of the ^{13}C n.m.r. chemical shifts (δ/p.p.m.) of L^3 and L^4 with those of their Zn^{2+} complexes in CD_3NO_2 solution. Values in parentheses are the relative populations

L^3	$[Zn(L^3)][ClO_4]_2$	Assignment	L^4	$[Zn(L^4)(dmso)][ClO_4]_2$	Assignment
162.08 (1)	156.63 (1)	*o*-C of pendant pyridine ring	160.09 (2)	155.73 (2)	*o*-C of pyridine ring
159.98 (2)	156.03 (2)	*o*-C of macrocyclic pyridine ring	141.59 (1)	144.58 (1)	
149.49 (1)	151.00 (1)		139.62 (2)	144.49 (2)	tertiary C of phenyl ring
141.30 (1)	144.95 (1)		137.76 (1)	136.07 (1)	*p*-C of pyridine ring
137.39 (2)	144.00 (1)		130.98 (1)	133.04 (1)	
137.10 (1)	132.89 (5)		130.37 (4)	131.95 (4)	*o*-C of phenyl ring
130.13 (4)	131.51 (1)		129.60 (4)	130.21 (4)	*m*-C of phenyl ring
129.27 (4)	130.23 (4)		129.54 (2)	129.94 (2)	*p*-C of phenyl ring
127.92 (2)	129.93 (2)		123.78 (2)	125.04 (2)	*m*-C of pyridine ring
123.88 (1)	127.50 (2)		106.15 (1)	110.72 (1)	
123.49 (2)	127.04 (2)	*m*-C of macrocyclic pyridine ring	70.25 (1)	70.81 (1)	N-CH_2-N
122.66 (1)			61.18 (2)	60.55 (2)	N-CH_2 of pyridine ring
61.55 (1)	60.07 (1)	N-*C* of pendant pyridine	61.11 (2)	58.73 (2)	N-CH_2 of phenyl ring
61.09 (2)	61.91 (2)	N-*C* of macrocyclic ring pyridine	52.06 (2)	56.95 (2)	N-CH_2-C
60.76 (2)	58.36 (2)	N-*C* of phenyl ring	50.63 (2)	55.37 (2)	N-CH_2-C
53.65 (2)	57.07 (2)	N-CH_2-C		40.47 (2)	dmso
52.41 (2)	54.97 (2)	N-CH_2-C	25.95 (2)	23.15 (2)	C-CH_2-C
25.97 (2)	23.38 (2)	C-CH_2-C			

$[ClO_4]_2$ (*n* = 6, M = Co, Ni, or Cu; *n* = 4, M = Zn) were prepared as described previously.[9] These salts were used in the syntheses of metal complexes. Proton-decoupled natural abundance ^{13}C n.m.r. spectra were obtained at either 45.26 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, and two-dimensional n.m.r. and n.O.e. difference spectra at 400 MHz with a Bruker WH400 instrument. 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 were obtained commercially; analytical data for the complexes are collected in Table 1.

Preparation of L^3.—The ligand L^2 (1 g, 2.4 mmol) was dissolved in methanol (50 cm^3) and stirred with solid sodium hydroxide (0.6 g, 15 mmol). 2-(Chloromethyl)pyridine (1.23 g, 7.5 mmol) was added and the resulting mixture stirred at room temperature under N_2 for 72 h. The mixture was then evaporated with a rotary evaporator, and unreacted 2-(chloromethyl)pyridine removed by pumping at 0.1 mmHg and 50—60 °C. The pale brown residue was dissolved in dichloromethane (10 cm^3) and passed down a neutral alumina column (20 cm long × 2 cm diameter). The column was eluted with dichloromethane (100 cm^3), and the extracts evaporated to give pure L^3 (0.95 g, 1.9 mmol, 78%). Electron impact mass spectrum: M^+ at *m/z* 505 (calc. 505). ^{13}C N.m.r. ($CDCl_3$ solution; relative populations in parentheses): δ 160.83 (1), 158.63 (2), 148.50 (1), 139.53 (1), 136.27 (1), 136.11 (1), 129.04 (4), 128.19 (4), 126.90 (2), 122.83 (2), 122.56 (2), 121.51 (1), 61.68 (1), 60.03 (2), 59.97 (2), 52.50 (2), 51.35 (2), and 24.72 (2). ^1H N.m.r. ($CDCl_3$): δ 8.45 (1 H, d), 7.60 (1 H, t), 7.33 (13 H, m), 7.11 (2 H, d), 3.73 (4 H, s), 3.67 (4 H, s), 3.53 (2 H, s), 2.59 (4 H, t), 2.36 (4 H, t), and 1.53 p.p.m. (4 H, quintet).

Preparation of L^4.—The ligand L^2 (1 g, 2.4 mmol) and 1-(hydroxymethyl)pyrazole (0.24 g, 2.4 mmol) were dissolved in CCl_4 (100 cm^3) and stirred at room temperature under nitrogen for 48 h. The solution was dried with anhydrous magnesium sulphate, filtered, and concentrated under reduced pressure. The residue was dissolved in dichloromethane (10 cm^3) and the solution passed through an alumina column as described for L^3. The product was eluted with dichloromethane containing 5%

Table 3. Atomic co-ordinates (× 10^4)

Atom	x	y	z
Zn(1)	1 958.0(8)	5 278.0(4)	7 000.7(4)
Zn(2)	5 762.2(9)	3 195.1(4)	9 548.8(4)
Cl(1)	9 302.8(22)	3 617.6(10)	4 326.6(10)
Cl(2)	128.7(22)	6 827.4(9)	2 155.9(11)
Cl(3)	4 369.0(21)	3 104.2(9)	6 764.2(10)
Cl(4)	1 345.4(22)	738.2(11)	6 127.6(10)
O(11)	9 423(6)	3 197(3)	4 689(3)
O(12)	8 515(6)	3 982(3)	4 550(3)
O(13)	10 411(6)	3 835(3)	4 263(3)
O(14)	8 881(7)	3 433(4)	3 821(3)
O(21)	−374(10)	6 788(4)	2 646(4)
O(22)	792(7)	7 264(3)	2 105(4)
O(23)	633(7)	6 389(3)	1 993(5)
O(24)	−875(10)	6 878(5)	1 829(5)
O(31)	4 736(8)	3 532(3)	6 511(5)
O(32)	3 495(9)	2 953(5)	6 459(5)
O(33)	3 909(12)	3 233(4)	7 244(3)
O(34)	5 225(7)	2 735(3)	6 798(4)
O(41)	1 345(6)	766(3)	6 707(3)
O(42)	1 162(14)	251(4)	5 962(4)
O(43)	566(9)	1 056(4)	5 876(4)
O(44)	2 410(8)	880(6)	5 949(4)
N(1)	449(5)	5 486(2)	7 537(2)
N(2)	2 294(5)	6 020(2)	7 185(2)
N(3)	3 722(6)	5 409(3)	6 598(3)
N(4)	2 456(6)	4 583(3)	7 352(3)
N(5)	1 188(5)	4 814(2)	6 413(3)
N(6)	7 484(5)	2 794(3)	9 828(3)
N(7)	5 300(5)	2 852(2)	10 245(2)
N(8)	3 810(5)	3 375(3)	9 572(2)
N(9)	5 944(6)	3 001(3)	8 738(3)
N(10)	6 424(6)	3 883(2)	9 323(2)
C(1)	855(7)	5 922(3)	7 872(3)
C(2)	1 681(7)	6 258(3)	7 574(3)
C(3)	1 884(8)	6 777(4)	7 700(3)
C(4)	2 775(8)	7 030(3)	7 435(4)
C(5)	3 404(8)	6 771(3)	7 055(3)
C(6)	3 138(7)	6 272(3)	6 924(3)
C(7)	3 709(7)	5 978(3)	6 481(3)
C(8)	3 970(7)	5 120(3)	6 081(3)
C(9)	4 976(8)	5 314(4)	5 764(4)
C(10)	4 819(11)	5 648(5)	5 337(5)
C(11)	5 726(13)	5 842(5)	5 052(6)
C(12)	6 780(14)	5 740(6)	5 189(6)
C(13)	7 018(11)	5 392(6)	5 595(7)
C(14)	6 099(9)	5 196(5)	5 889(5)
C(15)	4 591(7)	5 315(3)	7 053(4)
C(16)	4 633(7)	4 768(4)	7 275(4)
C(17)	3 615(7)	4 598(3)	7 631(4)
C(18)	1 565(8)	4 377(3)	7 743(4)
C(19)	1 057(8)	4 757(3)	8 143(3)
C(20)	63(7)	5 069(3)	7 915(3)
C(21)	−534(7)	5 657(3)	7 165(3)
C(22)	−1 550(8)	5 911(3)	7 425(3)
C(23)	−2 439(7)	5 626(4)	7 647(3)
C(24)	−3 337(8)	5 867(4)	7 900(4)
C(25)	−3 411(9)	6 383(5)	7 925(4)
C(26)	−2 536(11)	6 672(5)	7 710(5)
C(27)	−1 616(10)	6 435(4)	7 465(4)
C(28)	2 454(8)	4 206(3)	6 889(4)
C(29)	1 540(7)	4 324(3)	6 468(3)
C(30)	1 137(8)	3 940(3)	6 127(4)
C(31)	368(9)	4 053(4)	5 714(4)
C(32)	22(8)	4 560(4)	5 652(3)
C(33)	442(7)	4 926(4)	6 006(3)
C(51)	7 361(7)	2 753(3)	10 424(3)
C(52)	6 123(7)	2 696(3)	10 601(3)
C(53)	5 831(8)	2 523(3)	11 117(4)
C(54)	4 687(8)	2 513(3)	11 254(4)
C(55)	3 864(8)	2 669(3)	10 878(4)
C(56)	4 176(7)	2 826(3)	10 377(4)
C(57)	3 367(7)	2 949(3)	9 911(3)
C(58)	3 647(7)	3 883(3)	9 845(3)
C(59)	2 435(8)	4 000(3)	10 022(3)
C(60)	2 139(10)	3 889(4)	10 547(4)
C(61)	1 016(14)	3 986(4)	10 709(5)
C(62)	181(11)	4 202(5)	10 369(5)
C(63)	513(9)	4 321(4)	9 860(5)
C(64)	1 631(9)	4 221(4)	9 668(4)
C(65)	3 210(8)	3 360(4)	9 023(3)
C(66)	3 724(8)	2 970(4)	8 632(4)
C(67)	4 883(8)	3 128(4)	8 403(4)
C(68)	6 264(8)	2 448(3)	8 654(4)
C(69)	7 318(8)	2 248(3)	8 956(4)
C(70)	7 314(8)	2 268(3)	9 581(3)
C(71)	8 645(7)	3 020(4)	9 711(4)
C(72)	9 680(7)	2 681(3)	9 828(3)
C(73)	10 259(8)	2 442(4)	9 405(4)
C(74)	11 146(10)	2 095(4)	9 504(5)
C(75)	11 435(10)	1 979(5)	10 015(5)
C(76)	10 949(9)	2 208(4)	10 451(5)
C(77)	10 066(9)	2 577(4)	10 358(4)
C(78)	6 881(8)	3 353(4)	8 531(4)
C(79)	6 871(8)	3 862(4)	8 815(4)
C(80)	7 354(9)	4 297(4)	8 591(4)
C(81)	7 410(10)	4 737(5)	8 878(5)
C(82)	6 957(10)	4 764(5)	9 387(5)
C(83)	6 461(8)	4 330(4)	9 598(4)
N(100)	2 705(12)	823(5)	1 852(5)
O(100)	2 194(10)	828(4)	2 259(4)
O(101)	3 469(15)	614(6)	1 760(6)
C(100)	2 656(14)	1 358(5)	1 618(6)

methanol. ^{1}H N.m.r. ($CDCl_3$): δ 7.60 (1 H, t), 7.40 (12 H, m), 7.10 (2 H, d), 6.22 (1 H, m), 4.67 (2 H, s), 3.76 (4 H, s), 3.63 (4 H, s), 2.65 (4 H, t), 2.44 (4 H, t), and 1.59 p.p.m. (4 H, quintet). The ^{13}C n.m.r. chemical shifts in nitromethane solution are given in Table 2.

Preparation of Metal Complexes.—Solid complexes of L^3 and L^4 were obtained in high yields (> 80%) by mixing ethanolic solutions of the ligands and the dimethyl sulphoxide (dmso) solvates of the metal perchlorates in a 1:1 molar ratio. The solids were collected by suction filtration and washed with a small volume of cold ethanol followed by dry diethyl ether. Interestingly, products of formula $[M(L)(dmso)][ClO_4]_2$ (M = metal ion, L = L^3 or L^4) were obtained, except for the Zn^{2+} complex of L^3 which analysed as $[Zn(L^3)][ClO_4]_2$. The formulae were confirmed by the elemental analyses (Table 1), by the i.r. spectra which showed the presence of co-ordinated dmso around 1 025 cm^{-1} as expected,[10] and by the ^{1}H and ^{13}C n.m.r. spectra in the case of the diamagnetic zinc complexes.

Crystal Data for $[Zn(L^3)][ClO_4]_2$.—The crystals (colourless pyramids) of formula $C_{33}H_{39}Cl_2N_5O_8Zn{\cdot}0.5CH_3NO_2$, M = 816, are monoclinic, space group $P2_1/n$, with a = 11.517(2), b = 25.920(5), c = 24.445(5) Å, β = 91.00(1)°, U = 7 296.7 (2.7) Å^3, Z = 8, D_c = 1.486 g cm^{-3}, Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 8.88 cm^{-1}, F(000) = 3 200, T = 298 K.

Data were collected with a Syntex $P2_1$ four-circle diffractometer. Maximum 2θ was 45°, with scan range ±0.95 (2θ) around $K_{\alpha1} - K_{\alpha2}$ angles, 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 (5%) decrease 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. 4 667 Observed reflections with $I/\sigma(I) \geqslant 3.0$ were used in refinement, and corrected for Lorentz, polarisation and absorption effects, the last by Gaussian integration; maximum and minimum transmission factors were 0.86 and 0.79. The crystal dimensions were 0.36 × 0.30 × 0.51 mm. Systematic absences $h0l$ ($h + l \neq 2n$) and $0k0$ ($k \neq 2n$) indicated space group $P2_1/n$. The heavy atom was located by Patterson techniques, and light atoms were then found on successive Fourier syntheses, including one molecule of CH_3NO_2 of solvation. Hydrogen atoms were given fixed isotropic thermal parameters, $U = 0.07$ Å^2, as defined by the molecular geometry, and not refined. Final refinement was by cascaded least-squares methods, with anisotropic thermal parameters for all atoms other than hydrogen. The largest positive and negative peaks on a final difference-Fourier synthesis were of height 0.8 and −0.5 e Å^{-3}. A weighting scheme of the form $w = 1/[\sigma^2(F) + gF^2]$ with $g = 0.0013$ was used. This was shown to be satisfactory by a weight analysis. The final R value was 0.058 ($R' = 0.062$). Computing was with the SHELXTL system[11] on a Data General DG30 computer. Scattering factors in the analytical form and anomalous dispersion factors were taken from ref. 12. Final atomic co-ordinates are in Table 3, and selected bond lengths and angles in Table 4. Additional material available from the Cambridge Crystallographic Data Centre comprises the anisotropic thermal parameters, H-atom co-ordinates, and remaining bond lengths and angles.

Table 4. Selected bond lengths (Å) and angles (°) in the $[Zn(L^3)]^{2+}$ ion

Cation (1)		Cation (2)	
Zn(1)–N(1)	2.261(6)	Zn(2)–N(6)	2.330(6)
Zn(1)–N(2)	2.012(6)	Zn(2)–N(7)	2.001(6)
Zn(1)–N(3)	2.299(7)	Zn(2)–N(8)	2.298(6)
Zn(1)–N(4)	2.073(7)	Zn(2)–N(9)	2.060(6)
Zn(1)–N(5)	2.062(6)	Zn(2)–N(10)	2.020(6)
N(1)–Zn(1)–N(2)	77.8(2)	N(6)–Zn(2)–N(7)	77.9(2)
N(1)–Zn(1)–N(3)	155.2(2)	N(6)–Zn(2)–N(8)	155.7(2)
N(1)–Zn(1)–N(4)	100.2(2)	N(6)–Zn(2)–N(9)	94.2(2)
N(1)–Zn(1)–N(5)	102.6(2)	N(6)–Zn(2)–N(10)	98.6(3)
N(2)–Zn(1)–N(3)	77.7(2)	N(7)–Zn(2)–N(8)	78.1(2)
N(2)–Zn(1)–N(4)	133.5(2)	N(7)–Zn(2)–N(9)	138.0(3)
N(2)–Zn(1)–N(5)	142.4(2)	N(7)–Zn(2)–N(10)	137.1(2)
N(3)–Zn(1)–N(4)	93.8(2)	N(8)–Zn(2)–N(9)	100.9(2)
N(3)–Zn(1)–N(5)	99.3(2)	N(8)–Zn(2)–N(10)	101.6(3)
N(4)–Zn(1)–N(5)	84.0(2)	N(9)–Zn(2)–N(10)	84.7(3)

Results and Discussion

In this work we have taken advantage of the unique secondary amine site of L^2 to produce two new pendant-arm macrocycles L^3 and L^4 in good yield. Since the previously reported preparation of L^2 is also high-yielding,[3,4] this is an attractive route to macrocycles with co-ordinating tail-base 2-pyridylmethyl- and 1-pyrazolylmethyl-groups, and gives much better yields than the template method used to obtain the related pendant-pyrrolidyl macrocycles (L^5 and L^6).[2] Although previously we found a two-phase reaction in aqueous dichloromethane (1 : 1) a convenient way to prepare L^2 from the reaction of L^1 with benzyl chloride in the presence of sodium hydroxide, in this work we found it more convenient to prepare L^3 from the reaction of 2-(chloromethyl)pyridine with L^2 in methanol containing NaOH. Using a single-phase reaction, L^3 was the major reaction product, and was purified by column chromatography on neutral alumina; it was characterised by its mass spectrum, by ^{1}H and ^{13}C n.m.r., and by analysis of its metal complexes. The ligand L^4 was prepared in a similar way by reaction of L^2 with 1-(hydroxymethyl)pyrazole in CCl_4 solution, which was found to be the most effective of the various solvents tried. The reaction in 1,2-dichloroethane solution gave undesirable products, possibly due to addition of an ethylene bridge across adjacent N atoms of the macrocycle, and separation of L^4 from the contaminated product was unsuccessful. The ligand L^4 is heat- and light-sensitive, and was stored under nitrogen in a refrigerator; because of its thermal instability we could not obtain a satisfactory mass spectrum, but the ^{13}C n.m.r. spectrum and the analytical data for the complexes helped to establish its purity.

^{13}C *N.M.R. Spectra.*—A comparison of the ^{13}C n.m.r. spectra of L^3 and L^4 with those of their Zn^{2+} complexes in nitromethane solution is given in Table 2. The possibility that the N substituents can protrude either above or below the macrocyclic ligand plane leads to four possible isomers for the metal complexes (three geometric isomers, one of which is enantiomeric) as shown previously for analogous systems.[2,13] The ^{13}C n.m.r. data show conclusively that in each case only a single symmetric species is present in solution, and the ^{1}H n.m.r. data and *X*-ray structure establish that the two benzyl groups and the pendant arm lie on the same side of the macrocyclic ligand plane. The bulky pendant groups no doubt hinder inversion at N and the observed geometry is probably a 'locked-in' kinetically preferred product.

Two-dimensional ^{1}H *N.M.R. and N.O.E. Difference Spectra of* $[Zn(L^3)(dmso)][ClO_4]_2$.—The complete assignment of the proton n.m.r. spectra based on a 400-MHz two-dimensional (COSY) spectrum, integrals, spin–spin coupling patterns, and

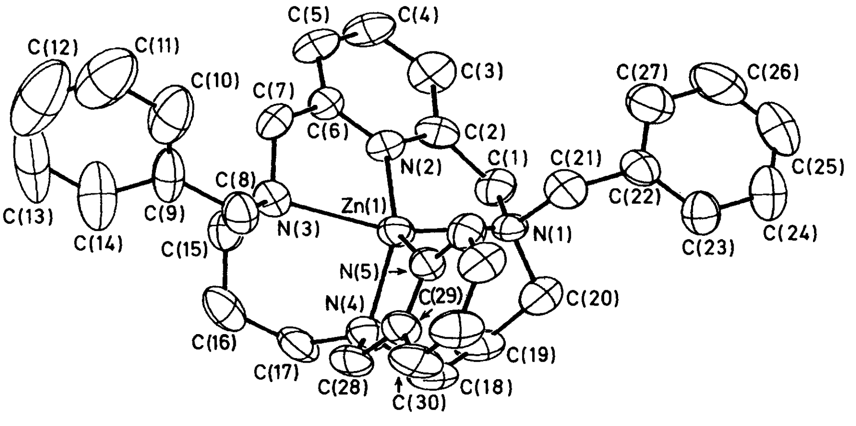

Figure 1. View of cation 1 of the $[Zn(L^3)]^{2+}$ ion showing the atomic numbering; atoms C(31)—C(33) follow in sequence from C(30)

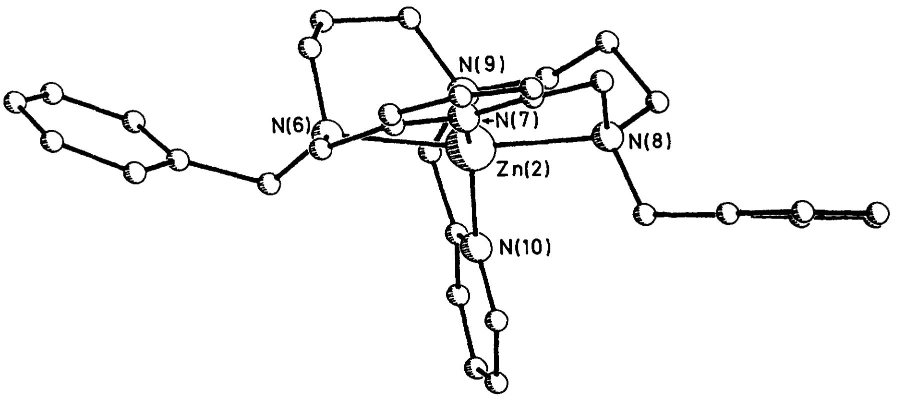

Figure 2. Side view of cation 2 of the $[Zn(L^3)]^{2+}$ ion showing the ring orientation and metal co-ordination geometry

Table 5. U.v.–visible spectroscopic data [λ/nm (ε/dm^3 mol^{-1} cm^{-1})] in nitromethane solution of complexes $[M(L)(dmso)][ClO_4]_2$ and $[M(HL)][ClO_4]_3$

M	L	Unprotonated complex λ$_{max.}$ (ε)	Protonated complex[a] λ$_{max.}$
Ni	L^3	536 (17), 850 (47)[b]	[c]
Cu	L^3	660 (363)[d]	594
Co	L^3[e]	508 (93), 578 (106), 714 (18), 1 150 (17)	528[f]
Ni	L^4	582 (33), 836 (35)[g]	472[c]
Cu	L^4	592 (597)[h]	594
Co	L^4	530 (150),[i] *ca.* 1 230 (12)	512[f]

[a] Protonated complexes were too unstable for accurate absorption coefficients to be obtained. [b] Signs of a weak peak at *ca.* 1 200 nm (ε *ca.* 5 dm^3 mol^{-1} cm^{-1}). [c] Very unstable. [d] Shoulders at *ca.* 820 and 570 nm. [e] Dissociation of the co-ordinated dmso occurs in nitromethane; addition of a few drops of dmso caused a shift in the spectrum to give broad peaks at 538 and 730 nm, and in dmso as solvent peaks appeared at 472 (26), 504 (25), 532 (24), 584 (22), and 1 260 nm (ε *ca.* 6 dm^3 mol^{-1} cm^{-1}). [f] Shoulder at *ca.* 650 nm. [g] A weak peak at *ca.* 1 260 nm (ε *ca.* 11 dm^3 mol^{-1} cm^{-1}). [h] Shoulder at *ca.* 530 nm. [i] Shoulder (overlaps charge-transfer band).

coupling constants was given in a preliminary communication.[3] The n.O.e. difference spectra showed unequivocally that the pendant arm and the two benzyl groups are on the same side of the macrocyclic ligand plane. For example, irradiation of the protons of the pendant-arm CH_2 group produced n.O.e. enhancements of the benzyl CH_2 resonances, and irradiation of the benzyl CH_2 protons gave an enhancement of the proton resonance from the *o*-H of the pendant pyridine ring.[3]

Crystal Structure.—Conclusive evidence for the structure postulated in solution came from the crystal structure (Figures 1 and 2). The two independent cations are essentially identical, apart from slight differences in the positioning of the benzyl groups. These groups are bent away from the zinc atoms, with their phenyl rings perpendicular to the pendant pyridine ring (Figure 2). The geometry around Zn is somewhat irregular, but can best be described as distorted trigonal bipyramidal, with angles between the axial substituents of 155.2(2) (cation 1) and 155.7(2)° (cation 2); most of the other angles around Zn also depart somewhat from idealised values. The Zn–N distances correlate with this geometry, with all the equatorial distances (mean 2.0388 Å) being shorter than the axial ones (mean 2.297 Å). This contrasts with previous results for various five-co-ordinate Ni^{2+} complexes of pendant-arm macrocycles,[2] in which the geometry is square pyramidal, and in which Ni–N(pyridine) is significantly shorter than the other Ni–N distances.

U.v.–Visible Spectra.—The spectral data for the Co^{2+}, Ni^{2+}, and Cu^{2+} complexes are collected in Table 5. As found in our previous studies[2,7] it was possible to protonate the pendant arms to give reduced co-ordination number species in nitromethane solution. However, the protonated complexes were found to be rather unstable, and we were unable to obtain accurate absorption coefficients for them. The visible spectra of the unprotonated Ni^{2+} and Co^{2+} complexes in nitromethane solution are as expected for six-co-ordinate species, but dissociation of the co-ordinated dmso occurs with $[Co(L^3)(dmso)]^{2+}$; addition of a few drops of dmso causes a change in the spectrum to give broad peaks at 538 and 730 nm with reduced absorption coefficients, and in dmso as solvent new peaks appeared as shown in Table 5. The Co^{2+} complexes were found to be surprisingly air-stable, presumably due to the dmso molecule blocking the site for O_2 attack, or possibly due to an unfavourable macrocyclic conformation in solution.

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