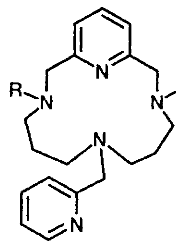
Studies of Pendant-arm Macrocyclic Ligands. Part 8.[1] Synthesis of Two Pentaazamacrocycles based upon Pyridine-containing Tetraazamacrocycles with a Single Pendant Co-ordinating 2-Pyridylmethyl Arm, and Characterisation of Their Nickel(II), Copper(II) and Zinc(II) Complexes. Crystal Structure of 7-(2′-pyridylmethyl)-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-trienezinc(II) Tetrafluoroborate†

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

Two new quinquedentate pentaazamacrocycles, 7-(2′-pyridylmethyl)-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene L^1 and its 3,11-dimethyl derivative L^2, have been characterised, together with their metal complexes of formulae $[ML(OH_2)][BF_4]_2$ (M = Ni or Cu) and $[ZnL][BF_4]_2$ (L = L^1 or L^2). The crystal structure of $[ZnL^1][BF_4]_2$ shows a distorted square-pyramidal geometry, with the Zn 0.59 Å above the plane of the macrocyclic ring in the direction of the pendant co-ordinated pyridyl group.

Recently there have been a number of studies in which co-ordinating 2-pyridylmethyl pendant arms have been attached to the N atom(s) of azamacrocycles.[1–11] This is usually achieved (but not always[6]) by direct alkylation of all of the available macrocyclic secondary amino groups with 2-chloromethylpyridine. In this way new macrocyclic ligands have been produced with one,[2] two,[1,3–6] three,[7,8] or four[9–11] 2-pyridylmethyl pendant arms. Whilst direct *N*-alkylation is an attractive synthetic approach because of the relative ease of the reactions, of necessity all of the ligands produced in this way have only tertiary N donors. The previously reported single pendant-arm macrocycle L^3 is of this type.[2] Single pyridylmethyl pendant-arm systems are relatively rare,[2,12] and so far only those that have the pendant arm attached to the carbon framework of the macrocycle[12] contain secondary amino groups accessible for further derivatisation.

We report here a synthetic route to a 14-membered ring tetraazamacrocycle with a single *N*-pendant 2-pyridylmethyl arm (L^1), which contains two secondary amino groups available for further reactions. Methylation of the two NH groups of L^1 gives the analogous macrocycle L^2. The co-ordination chemistry of L^1 and L^2 with cobalt(II), nickel(II), copper(II) has been investigated and compared, including an X-ray crystal structure determination of the geometry of the five-co-ordinate $[ZnL^1]^{2+}$ ion.



	R
L^1	H
L^2	Me
L^3	CH_2Ph

Experimental

Materials and Methods.—All chemicals were of the highest available purity and were not purified further. Dimethyl sulfoxide complexes of Co^{II}, Ni^{II}, Cu^{II} and Zn^{II} as fluoroborate salts were synthesised from the hydrates by a published method.[13] Proton-decoupled ^{13}C NMR spectra were recorded at either 45.28 or 100.25 MHz with Bruker WH180 or WH400 FT NMR spectrometers, and ^1H NMR spectra at either 220 or 400 MHz with Perkin Elmer R34 or Bruker WH400 spectrometers respectively [the latter was used for proton nuclear Overhauser effect (NOE) difference measurements]. Mass spectra were obtained with a Kratos MS80 spectrometer, UV/VIS spectra with a Shimadzu 365, and Fourier-transform infrared spectra with a Perkin Elmer 1720X spectrometer. Conductivity measurements were made with a Philips PW9527 digital conductivity meter, and magnetic susceptibilities were measured at room temperature with a Johnson Matthey (Evans') susceptibility balance.

Preparations.—The synthetic routes are outlined in Scheme 1.

1,5-*Dicyano*-3-(2′-*pyridylmethyl*)-3-*azapentane*. To 2-aminomethylpyridine (8 g, 80 mmol) dissolved in acrylonitrile (92 g, 1.71 mol) was added ethanoic acid (7.2 g, 160 mmol) and the mixture was refluxed under dinitrogen for 24 h, giving a deep yellow solution. Excess acrylonitrile and ethanoic acid were removed under reduced pressure and dichloromethane (150 cm^3) added. The solution was washed with 0.88 ammonia (125 cm^3), distilled water (3 × 100 cm^3) and then dried with anhydrous $MgSO_4$. After filtration, the solvent was removed under reduced pressure to give the product as a yellow oil (9.76 g, 57%). Electron impact mass spectrum: *m/z* 214 (calc.

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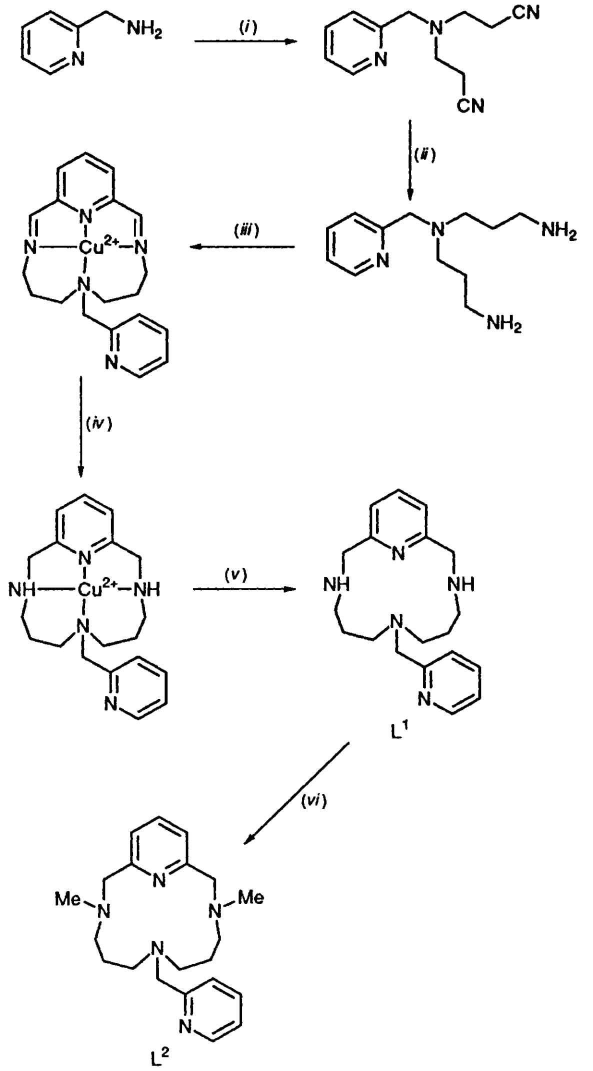
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.



Scheme 1 (*i*) CH_2=CHCN, $MeCO_2H$; (*ii*) $NaBH_4$, Raney Ni; (*iii*) pyridine-2,6-dicarbaldehyde, Cu^{2+}; (*iv*) $NaBH_4$; (*v*) Na_2S, $-CuS\downarrow$; (*vi*) HCHO–HCO_2H

for M^+, 214). Infrared (CN) at 2 248 cm^{-1}. NMR ($CDCl_3$): ^1H, δ 8.56 (d, 1 H), 7.75 (t, 1 H), 7.58 (d, 1 H), 7.24 (t, 1 H), 3.90 (s, 2 H), 2.95 (t, 4 H) and 2.60 (t, 4 H); ^{13}C, δ 158.07 (1 C), 149.03 (1 C), 136.83 (1 C), 123.09 (1 C), 122.53 (1 C), 118.75 (2 CN), 59.73 (1 C), 49.57 (2 C) and 16.70 (2 C).

4-(2′-Pyridylmethyl)-4-azaheptane-1,7-diamine. The procedure used was adapted from a literature method.[14] To a 50% suspension of active Raney nickel (7.1 g) in water was added a solution of 1,5-dicyano-3-(2′-pyridylmethyl)-3-azapentane (9.83 g, 46 mmol). The mixture was stirred vigorously and a solution of $NaBH_4$ (3.55 g, 93 mmol) in 8 mol dm^{-3} NaOH (50 cm^3) was added slowly at such a arate as to maintain a temperature of 60 °C. After complete addition, the mixture was stirred at room temperature overnight. Raney nickel was then removed by filtration through Celite, and the methanol removed under reduced pressure with a rotary evaporator. A further portion of 8 mol dm^{-3} NaOH (50 cm^3) was added to the residue, which was then extracted with dichloromethane (5 × 50 cm^3). The combined extracts were dried with anhydrous Na_2SO_4, and the solvent removed under reduced pressure with a rotary evaporator. The crude product was dissolved in dichloromethane, and the solution transferred to a column (2 cm × 20 cm) of neutral alumina. Elution with 20% methanol in dichloromethane gave the pure product (6.43 g, 63%). Electron impact mass spectrum: *m*/*z* 222 (calc. for M^+ 222). NMR ($CDCl_3$): ^1H, δ 8.55 (d, 1 H), 7.70 (t, 1 H), 7.45 (d, 1 H), 7.17 (t, 1 H), 3.72 (s, 2 H), 2.70 (t, 4 H), 2.55 (t, 4 H), 1.75 (br, 4 H) and 1.60 (p, 4 H); ^{13}C, δ 159.45 (1 C), 148.28 (1 C), 135.79 (1 C), 121.26 (1 C), 59.72 (1 C), 51.34 (2 C), 39.62 (2 C) and 29.60 (2 C).

7-(2′-Pyridylmethyl)-3,7,11,17-tetraazabicyclo[11.3.1]*heptadeca-*1(17),13,15-*triene* L^1. To a solution of $Cu(NO_3)_2\cdot 3H_2O$ (6.04 g, 25 mmol) in ethanol–water (1 : 1, 300 cm^3) in a 500 cm^3 round-bottom flask was added 4-(2′-pyridylmethyl)-4-azaheptane-1,7-diamine (5.57 g, 25 mmol) to give a royal blue solution. Pyridine-2,6-dicarbaldehyde (3.38 g, 25 mmol)[2] was then added, and the resulting solution heated on a steam bath for 3 h. During this time the solution changed to a deep blue/violet. The solution was transferred to a 2 dm^3 beaker, cooled to 0 °C with an ice bath, and $NaBH_4$ (4.18 g, 110 mmol) added slowly, with stirring, over a period of 1 h. The solution was then stirred at room temperature for 2 h, then heated on a steam bath for 2 h, cooled, and $Na_2S\cdot 9H_2O$ (32.4 g, 135 mmol) added. The mixture was heated on a steam bath for 1 h, and the precipitate of CuS removed by filtration through Celite. The filtrate was extracted with dichloromethane (6 × 50 cm^3), the combined extracts dried with anhydrous Na_2SO_4, and the solvent removed under reduced pressure with a rotary evaporator to leave a brown oil. The oil was dissolved in dichloromethane, transferred to a neutral alumina column (2 × 20 cm), and eluted with 2% methanol in dichloromethane. Pure L^1 is obtained by synthesis of the zinc(II) fluoroborate, and recrystallisation from nitromethane–diethyl ether (1 : 1) (see below); demetallation was achieved by treating the complex (7.90 g) with NaCN (1.75 g, 35 mmol) and extraction with dichloromethane, to give L^1 (4.63 g, 57% yield). Electron impact mass spectrum: *m*/*z* 326 [calc. for $(M + 1)^+$ 326]. NMR ($CDCl_3$): ^1H, δ 8.50 (d, 1 H), 7.65 (t, 1 H), 7.55 (t, 1 H), 7.28 (d, 1 H), 7.12 (t, 1 H), 7.08 (d, 2 H), 3.91 (s, 4 H), 3.65 (s, 2 H), 3.41 (br, 2 NH), 2.52 (t, 4 H), 2.48 (t, 4 H) and 1.75 (qnt, 4 H); ^{13}C, δ 157.78 (1 C), 156.09 (1 C), 147.21 (1 C), 135.53 (1 C), 134.87 (1 C), 121.73 (1 C), 120.52 (1 C), 119.40 (2 C), 57.56 (1 C), 51.99 (2 C), 50.54 (2 C), 44.63 (2 C) and 24.84 (2C).

3,11-Dimethyl-7-(2′-pyridylmethyl)-3,7,11,17-tetraazabicyclo[11.3.1]*heptadeca-*1(17),13,15-*triene* L^2. Ligand L^1 (0.43 g, 1.32 mmol) was dissolved in 98% formic acid (0.46 g, 10 mmol) and a solution of formaldehyde (37%, 0.1 g, 3.17 mmol) was added. The resulting solution was heated at 90 °C for 24 h, most of the solvent was removed by evaporation, and the product finally treated twice with concentrated HCl in small amounts with heating to remove any unreacted acid as the more volatile acid chloride. The residue was then made alkaline with NaOH to pH > 12, and L^2 extracted with dichloromethane (5 × 50 cm^3). The combined extracts were dried with anhydrous $MgSO_4$, filtered, and the solvent removed with a rotary evaporator to give the product as a pale yellow oil (0.42 g, 90% yield). Electron impact mass spectrum: *m*/*z* 354 [calc. for $(M + 1)^+$ 354].NMR ($CDCl_3$): ^1H, δ 8.42 (d, 1 H), 7.55 (t, 1 H), 7.40 (t, 1 H), 7.25 (d, 2 H), 7.06 (t, 1 H), 6.67 (d, 1 H), 3.70 (s, 4 H), 3.50 (s, 2 H), 2.40 (s, 6 H), 2.30 (t, 4 H), 2.22 (t, 4 H) and 1.49 (qnt, 4 H); ^{13}C, δ 160.20 (1 C), 157.52 (1 C), 147.63 (1 C), 135.92 (1 C), 135.27 (1 C), 122.30 (1 C), 122.07 (2 C), 120.95 (1 C), 64.01 (2 C), 61.11 (1 C), 52.55 (2 C), 51.66 (2 C), 43.47 (2 C) and 25.11 (2 C).

Preparation of Metal Complexes.—Solid complexes are obtained in good yields (> 70%) by mixing ethanolic solutions of L^1 or L^2 with equimolar solutions of $[M(Me_2SO)_n][BF_4]_2$ (M = Ni or Cu, *n* = 6; M = Zn, *n* = 4) in ethanol. The precipitated complexes were isolated by suction filtration under dry N_2. They may be recrystallised from nitromethane–ethanol–diethyl ether (1 : 2 : 2) (the Zn complex from nitromethane–diethyl ether, 1 : 1). Microanalytical data, UV/VIS spectra and conductivity data in nitromethane, and solid-state magnetic moments are collected in Table 1. Attempts were made to prepare the analogous cobalt(II) complexes under anaerobic conditions, using Schlenk tubes and nitrogen-

Table 1 Characterisation of the metal complexes of L^1 and L^2

Complex	Colour	UV/VIS[a] λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})	Microanalysis[b] (%) C	H	N	Conductivity[a]/ Ω^{-1} cm^2 mol^{-1}	μ_{eff}/μ_B[c]
$[NiL^1(OH_2)][BF_4]_2$	Blue–purple	804 (sh), 744 (16.6), 504 (11.0)	39.3 (39.6)	5.20 (5.10)	12.1 (12.2)	152.6	3.13
$[CuL^1(OH_2)][BF_4]_2$	Blue	600 (172)	38.8 (39.3)	4.75 (5.05)	11.7 (12.1)	149.5	1.95
$[ZnL^1][BF_4]_2$	White		40.2 (40.4)	4.70 (4.80)	12.3 (12.4)	160.2	0
$[NiL^2(OH_2)][BF_4]_2$	Green	804 (27), 600 (11), 540 (10)	41.3 (41.8)	5.40 (5.50)	11.3 (11.6)	161.6	3.21
$[CuL^2(OH_2)][BF_4]_2$	Blue	615 (196)	41.3 (41.4)	5.35 (5.45)	11.3 (11.5)	171.4	2.04
$[ZnL^2][BF_4]_2$	White		42.2 (42.6)	5.20 (5.25)	11.6 (11.8)	169.2	0

[a] In nitromethane. [b] Required values are given in parentheses. [c] For solid samples at room temperature, $\mu_B \approx 9.274 \times 10^{-24}$ J T^{-1}.

scrubbed solutions. However, the products were found to be very oxygen sensitive, and only brown μ-peroxo-bridged dicobalt(III) complexes of the type $[(CoL)_2O_2]^{4+}$ (L = L^1 or L^2) were isolated.

Crystallography.—A colourless crystal of {7-(2′-pyridylmethyl)-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene}zinc(II) tetrafluoroborate, $[ZnL^1][BF_4]_2$, $C_{19}H_{27}B_2F_8N_5Zn$, $M = 564.4$, orthorhombic, space group $P2_12_12_1$, $a = 11.017(9)$, $b = 14.515(13)$, $c = 14.902(13)$ Å, $U = 2\,383.8(3)$ Å^3, $Z = 4$, $T = 290$ K, Mo-Kα radiation, $\lambda = 0.710\,69$ Å, μ(Mo-Kα) = 11.3 cm^{-1} was grown from nitromethane–diethyl ether. Data were collected with a Nicolet $P2_1$ four-circle diffractometer in the ω–2θ mode. Maximum 2θ was 45°, with scan range 1.1(2θ), around Kα1-Kα2 angles, scan speed 4–29 min^{-1} depending on the intensity of a 2 s pre-scan; backgrounds were measured at the end of each scan for 0.25 of the scan time. *hkl* ranges were 0–13, 0–15, 0–15. Three standard reflections were monitored every 200 reflections, and showed no changes during data collection. Unit-cell dimensions were obtained by a least-squares fit to 15 reflections ($18 < 2\theta < 22°$). Reflections were processed using profile analysis to give 2672 unique reflections; 2051 were considered observed [$I/\sigma(I) > 2.0$] and used in refinement; they were corrected for Lorentz, polarisation and absorption effects, the last by the Gaussian method; maximum and minimum transmission factors were 0.86 and 0.79. Crystal dimensions were 0.13 × 0.36 × 0.60 mm. Systematic absences $h00$, $h = 2n$; $0k0$, $k = 2n$; $00l$, $l = 2n$ indicate the space group $P2_12_12_1$. The Zn atom was located by the Patterson interpretation section of SHELXTL,[15] and light atoms then found on successive Fourier syntheses. Anisotropic thermal parameters were used for all non-hydrogen atoms. Hydrogen atoms were given fixed isotropic thermal parameters, $U = 0.08$ Å^2. They were inserted at calculated positions and not refined; their initial orientation was taken from the strongest H-atom peaks on a Fourier difference synthesis. The absolute structure of the individual crystal chosen was checked by refinement of a $\delta f''$ multiplier. Final refinement was on F by least-squares methods, refining 316 parameters, including an isotropic extinction parameter. Largest positive and negative peaks on a final Fourier difference synthesis were of height 0.5 e Å^{-3}. A weighting scheme of the form $w = 1/[\sigma^2(F) + gF^2]$, where $g = 0.0027$, was used, and shown to be satisfactory by a weight analysis. Final $R = 0.050$ ($R' = 0.066$). Maximum shift/error in the final cycle was 0.10. Computing was with SHELXTL PLUS[15] on a DEC MicroVax II. Scattering factors in the analytical form and anomalous dispersion factors were taken from ref. 16. Final atomic coordinates are in Table 2, and selected bond lengths and angles are in Table 3. The molecular geometry of the cation is shown in Fig. 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Table 2 Atomic coordinates (× 10^4) for $[ZnL^1][BF_4]_2$

Atom	*x*	*y*	*z*
Zn	9 558.7(7)	−299.4(5)	2 065.9(5)
B(1)	10 559(9)	1 164(6)	5 020(6)
F(11)	10 315(5)	325(4)	5 405(4)
F(12)	11 403(8)	1 612(4)	5 507(6)
F(13)	9 560(6)	1 667(5)	4 889(5)
F(14)	11 050(9)	1 037(5)	4 205(5)
B(2)	8 631(9)	1 919(7)	9 417(6)
F(21)	9 382(8)	1 703(4)	10 108(5)
F(22)	8 431(7)	1 176(5)	8 908(5)
F(23)	7 542(7)	2 203(7)	9 693(6)
F(24)	9 106(9)	2 607(7)	8 958(7)
N(1)	11 245(5)	−453(5)	2 572(4)
N(2)	9 221(6)	−1 288(5)	3 142(4)
N(3)	8 241(5)	−871(4)	1 225(4)
N(4)	10 676(6)	107(4)	912(4)
N(5)	8 319(5)	696(4)	2 270(4)
C(1)	11 405(8)	−936(6)	3 326(5)
C(2)	10 241(9)	−1 246(7)	3 767(6)
C(3)	9 173(8)	−2 178(5)	2 633(6)
C(4)	7 968(9)	−2 305(6)	2 168(6)
C(5)	7 406(8)	−1 454(6)	1 761(6)
C(5)	8 662(9)	−1 404(7)	428(5)
C(6)	9 610(9)	−941(6)	−149(5)
C(7)	10 793(7)	−700(6)	324(6)
C(8)	11 886(7)	408(6)	1 275(6)
C(9)	12 181(6)	−119(5)	2 118(5)
C(11)	13 360(7)	−244(8)	2 432(6)
C(12)	13 520(9)	−728(8)	3 210(7)
C(13)	12 573(10)	−1 076(7)	3 651(6)
C(14)	7 575(8)	−37(6)	935(6)
C(15)	7 409(7)	643(6)	1 671(5)
C(16)	6 409(7)	1 228(6)	1 707(6)
C(17)	6 367(9)	1 877(6)	2 395(6)
C(18)	7 304(8)	1 919(6)	3 012(6)
C(19)	8 249(8)	1 322(5)	2 926(5)

Table 3 Selected bond lengths (Å) and angles (°) for the $[ZnL^1]^{2+}$ ion

Zn–N(1)	2.018(8)	Zn–N(2)	2.188(9)
Zn–N(3)	2.091(8)	Zn–N(4)	2.198(9)
Zn–N(5)	2.013(8)		
N(1)–Zn–N(2)	79.0(3)	N(1)–Zn–N(3)	145.1(3)
N(1)–Zn–N(4)	79.0(3)	N(1)–Zn–N(5)	130.3(3)
N(2)–Zn–N(3)	93.5(3)	N(2)–Zn–N(4)	147.9(3)
N(2)–Zn–N(5)	104.2(3)	N(3)–Zn–N(4)	91.4(3)
N(3)–Zn–N(5)	84.6(3)	N(4)–Zn–N(5)	107.8(3)

Results and Discussion

Syntheses of the Macrocycles L^2 *and* L^2.—The Michael addition of 2 moles of acrylonitrile to 2-aminomethylpyridine is facilitated by the use of ethanoic acid as catalyst, producing a product of higher purity and with reduced reaction times. Initial attempts to reduce 1,5-dicyano-3-(2′-pyridylmethyl)-3-azapentane (*e.g.* with sodium in ethanol) were unsuccessful, but reduction with a mixture of sodium tetrahydroborate and Raney nickel as suggested by Egli[14] gave good yields of the

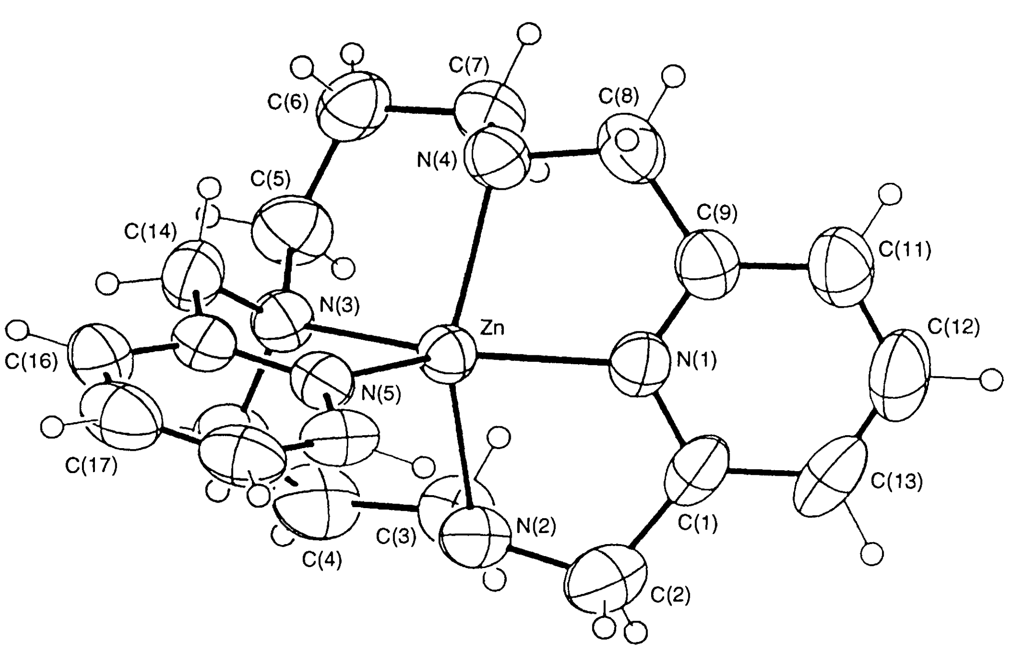


Fig. 1 Structure of the $[ZnL^1]^{2+}$ cation showing the atomic numbering

required amine. The method is recommended for the reduction of nitriles in the presence of aromatic groups. The product, 4-(2′-pyridylmethyl)-4-azaheptane-1,7-diamine, is a useful synthon for the production of a range of amine ligands, and azamacrocycles with 2-pyridylmethyl pendant arms. Ligand L^1 was obtained in good yield by a template reaction using copper(II) which gives better yields than nickel(II) in these template reactions.[1]

The three-step synthesis of L^1 (Scheme 1) is an improved method for the preparation of a single pyridylmethyl pendant-arm macrocycle. The method also allows subsequent derivatisation of the remaining secondary amine functionalities, as shown by the ready synthesis of L^2 from L^1 in high yield. Attachment of other alkyl groups is straightforward using the published procedure.[17]

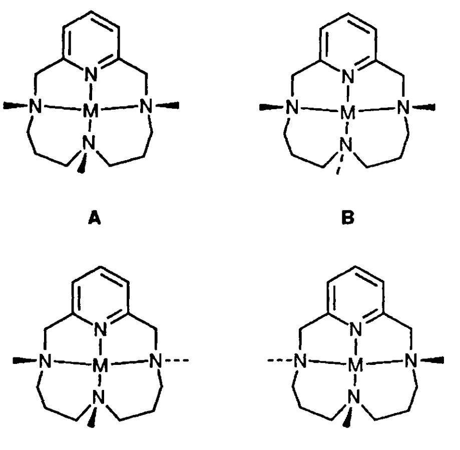


Fig. 2 Schematic representation of the four possible geometric isomers of the type $[ML]^{2+}$ (M = Ni, Cu or Zn, L = L^1 or L^2)

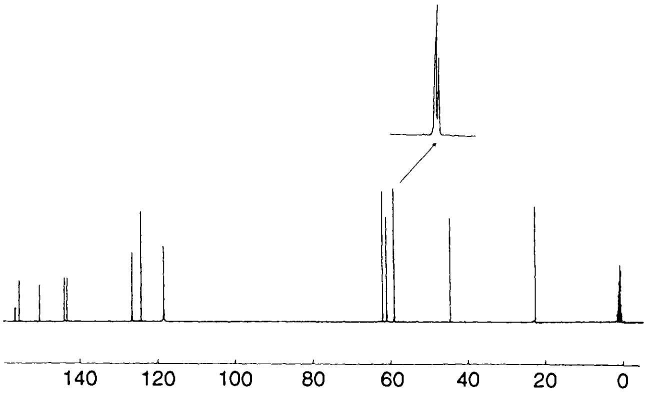


Fig. 3 Proton-decoupled ^{13}C NMR spectrum of $[ZnL^2][BF_4]_2$ in CD_3CN solution

Metal Complexes of L^1 *and* L^2.—The microanalytical data, UV/VIS spectra, and magnetic moments of the nickel(II) and copper(II) complexes are as expected for six-co-ordinate species of the type $[ML(OH_2)][BF_4]_2$ (M = Cu or Ni, L = L^1 or L^2). Six-co-ordinate structures are evident for the nickel(II) complexes, based on the position and number of UV/VIS bands, and their low molar absorption coefficients. Five-co-ordinate nickel(II) structures, in which the water molecule (evident in the infrared spectra) is un-co-ordinated lattice water, can be ruled out since the molar absorption coefficients of the visible bands would be much larger in this instance. By analogy with the nickel(II) complexes, and confirmed by the microanalytical data, a six-co-ordinate structure seems likely for the copper(II) complexes. However, five-co-ordinate structures of the type $[CuL][BF_4]_2 \cdot H_2O$ cannot be ruled out entirely. The zinc(II) complexes analyse as five-co-ordinate species of the type $[ZnL][BF_4]_2$. Conductivities of all six complexes in nitromethane solution are as expected for 2:1 electrolytes. Due to the three chiral N centres, there are four isomers (**A**–**D**) possible for five- or six-co-ordinate complexes of L^1 or L^2 as shown schematically in Fig. 2. Structures **C** and **D** are enatiomeric. The proton-decoupled ^{13}C NMR spectrum of $[ZnL^2][BF_4]_2$ in CD_3CN solution (Fig. 3) shows the presence of a single symmetric isomer (either **A** or **B**). Proton NOE difference spectra of $[ZnL^2][BF_4]_2$ were recorded at 400 MHz, and showed that the pendant arm lies on the same side of the macrocyclic plane as the two *N*-methyl groups. For example, irradiation of the *N*-methyl protons produced significant NOE enhancements of the *ortho* hydrogen of the pendant pyridyl group, as well as the methylene protons of the pendant arm; $[ZnL^2][BF_4]_2$ can, therefore, be assigned structure **A**.

Structure **A** was also established for $[ZnL^1]^{2+}$ in the solid state (Fig. 1). In the crystal structure the zinc(II) is seen to have a distorted square-pyramidal geometry, with the zinc 0.59 Å above the plane of the macrocyclic ring in the direction of the pendant pyridyl group. The two N–H groups also point in the direction of the pendant arm. The Zn–N distances to the two pyridyl groups (average 2.015 Å) are significantly shorter than those to the two secondary amino groups (average 2.193 Å) as is normal in pyridyl containing macrocycles; that to the tertiary N atom carrying the pendant arm [Zn–N(3) 2.091(8) Å] is somewhat shorter than that those to the secondary amino groups. Movement of the zinc out of the macrocyclic plane results in three N(5)–Zn–N bond angles greater than 90° [range 104–130°, except N(5)–Zn–N(3) which is only 84.6°], and by N(1)–Zn–N(3) and N(2)–Zn–N(4) bond angles of 145.1(3) and 147.9(3)° respectively. In the closely related structure $[\mathrm{ZnL^3}]^{2+}$ which contains much bulkier N-benzyl groups, further distortion is evident and the structure approaches that of a distorted trigonal bipyramid.[2] The cobalt(II) complexes of $\mathrm{L^1}$ and $\mathrm{L^2}$ are also significantly different to $[\mathrm{CoL^3}]^{2+}$ since the latter was found to be air stable, whereas the former are readily oxidised by dioxygen to give μ-peroxo-bridged dimers. The air stability of $[\mathrm{CoL^3}]^{2+}$ can be attributed to the presence of the bulky benzyl groups.

Rapid protonation of th pendant pyridyl group occurs upon acidifying a solution of $[\mathrm{NiL^1(OH_2)}]^{2+}$ in nitromethane with $\mathrm{CF_3SO_3H}$ [equation (1)], as indicated by the visible

$$[\mathrm{NiL^1(OH_2)}]^{2+} + \mathrm{H^+} \rightleftharpoons [\mathrm{Ni(HL^1)}]^{3+} \tag{1}$$

spectral changes (Fig. 4). The protonation involves a colour change from blue to yellow, and is directly analogous to that observed in previous studies.[2,18] Further decomposition to aquated nickel(II) occurs on standing, and so prevented isolation of the yellow, square-planar complex. The intense visible band expected for the square-planar species (at *ca.* 450 nm) is obscured by the strong absorbance of the nitromethane solvent.

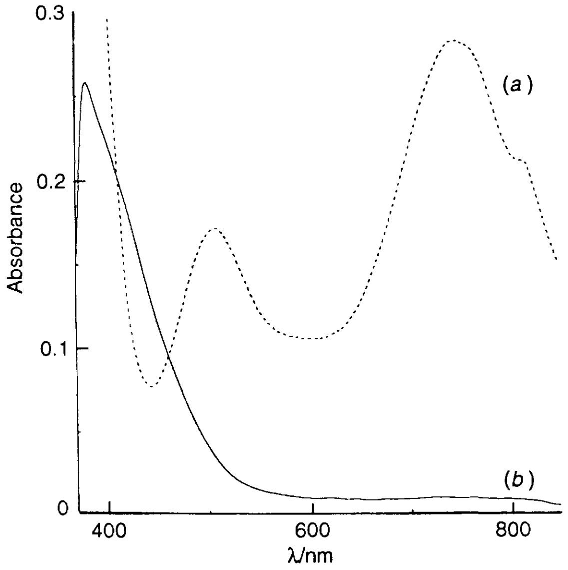


Fig. 4 UV/VIS spectrum of $[\mathrm{NiL^1}]^{2+}$ (1.7×10^{-2} mol dm^{-3}) prior to (*a*), and after addition of one drop of concentrated $\mathrm{CF_3SO_3H}$ (*b*)

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