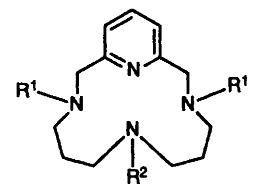
Studies of Pendant Arm Macrocyclic Ligands. Part 7.[1] Synthesis of Two Sexidentate Macrocycles based upon a Pyridine-containing Tetra-aza Macrocycle with either Two 2-Pyridylmethyl or Two 1-Pyrazolylmethyl Pendant Co-ordinating Arms, and Characterisation of Their Cobalt(II), Nickel(II), Copper(II), and Zinc(II) Complexes. Crystal Structure of {3,11-Di(2-pyridylmethyl)-3,7,11,17-tetra-azabicyclo[11.3.1]heptadeca-1(17),13,15-triene}nickel(II) Perchlorate†

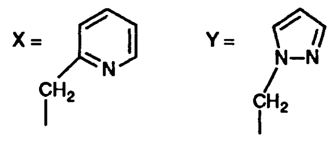
Karappulli P. Balakrishnan, Hadi A. A. Omar, Peter Moore,* Nathaniel W. Alcock, and Graham A. Pike
Department of Chemistry, University of Warwick, Coventry CV4 7AL

Two new sexidentate macrocycles, 3,11-di(2-pyridylmethyl)-3,7,11,17-tetra-azabicyclo[11.3.1]heptadeca-1(17),13,15-triene (L^1) and 7-methyl-3,11-di-(1-pyrazolylmethyl)-3,7,11,17-tetra-azabicyclo[11.3.1]heptadeca-1(17),13,15-triene (L^2), have been prepared and characterised, together with their metal complexes of formula $[M(L)][ClO_4]_2$ (M = Co, Ni, Cu, or Zn; L = L^1 or L^2). An *X*-ray crystal structure of $[Ni(L^1)][ClO_4]_2$ shows the nickel to be six-co-ordinate, with the macrocycle in a folded conformation, and with the two pendant 2-pyridylmethyl arms occupying *cis* co-ordination sites.

Previously we showed how, under mild conditions, alkylation of the parent pyridine-containing tetra-aza macrocycle, L^3, with benzyl chloride occurs preferentially at the two secondary amine groups flanking the pyridine ring, with little or no attack at the third secondary amine group.[1] The major product of the benzylation of L^3 is the dibenzyl derivative, L^5, and this is attributed to steric hindrance, the lone pairs of the NR^1 atoms (R^1 = H) being less hindered by the backbone carbon framework than that of the NR^2 atom (R^2 = H). In this study we demonstrate further the use of this selective alkylation of L^3, to give the new powerful sexidentate macrocycle L^1 containing two pendant co-ordinating 2-pyridylmethyl groups. The closely related sexidentate macrocycle, L^2, containing two pendant co-ordinating pyrazolyl groups has also been synthesised from the parent macrocycle L^4, for comparison with L^1. The ligands have been obtained in good yield, together with some of their metal complexes with the bivalent metal ions cobalt(II), nickel(II), copper(II), and zinc(II). As shown in Figure 1, *cis* and *trans* isomers are possible for octahedral complexes of L^1 and L^2, and an *X*-ray structure determination of the nickel(II) complexes of L^1 was carried out to establish the preferred co-ordination geometry.



L^1 R^2 = H, R^1 = X
L^2 R^2 = Me, R^1 = Y
L^3 R^2 = R^1 = H
L^4 R^2 = Me, R^1 = H
L^5 R^2 = H, R^1 = $PhCH_2$
L^6 R^2 = X, R^1 = $PhCH_2$
L^7 R^2 = Y, R^1 = $PhCH_2$
L^8 R^2 = R^1 = X
L^9 R^2 = R^1 = Me



Experimental

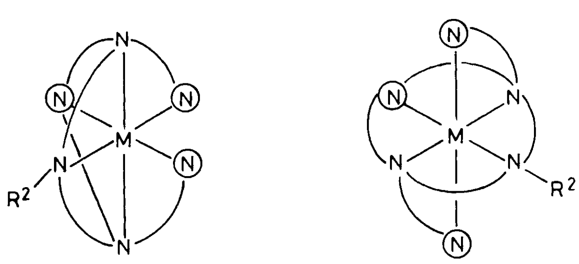
Materials and Methods.—Dimethyl sulphoxide solvates of the perchlorates of Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II} were prepared by a published method.[2] 1-(Hydroxymethyl)pyrazole and 2,6-pyridinecarbaldehyde were prepared from pyrazole and 2,6-pyridinedimethanol respectively (Aldrich) using published methods.[3,4] All other chemicals were of the highest available purity, and were not purified further. Hydrogen-1 decoupled ^{13}C n.m.r. spectra were recorded at either 45.28 or 100.58 MHz using a Bruker WH180 or WH400 n.m.r. spectrometer respectively, ^1H n.m.r. spectra with a 220-MHz Perkin-Elmer R34 instrument. Chemical shifts are reported on the δ scale relative to internal $SiMe_4$(δ 0). U.v.–visible spectra were recorded with a Philips PU 8700 spectrophotometer.

Preparations.—Previously we reported the syntheses of L^3 and L^4 using nickel(II) as a template metal ion.[5,6] However, we have since discovered that improved yields of these macrocycles may be obtained by using copper(II) rather than nickel(II), and this is illustrated by the following[7] preparation of L^3.

L^3. To a stirred solution of freshly prepared 2,6-pyridinedicarbaldehyde (9.81 g, 72.7 mmol) in ethanol (150 cm^3) was added a solution of $Cu(NO_3)_2 \cdot 4H_2O$ (17.56 g, 72.7 mmol) in water (150 cm^3). To the resulting pale green solution was added dropwise, with rapid stirring, a solution of 1,7-diamino-4-azaheptane (Aldrich; 9.54 g, 72.7 mmol) in ethanol (30 cm^3). The

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.



cis *trans*

Figure 1. Two geometric isomers possible for six-co-ordinate complexes of L^1 and L^2; M = metal ion, and the pyridine and pyrazolyl N atoms are circled

resulting deep blue solution was stirred whilst heating under reflux for 2 h, during which time an intense violet colour develops. The solution was transferred to a beaker (2 dm^3), cooled to 5 °C, and sodium tetrahydroborate (7 g, 184.2 mmol) added in small portions over a period of 30 min. The solution was stirred at room temperature for 30 min, and then heated on a hot water-bath for 30 min, before being left overnight at room temperature. The copper(II) was removed by treating the mixture with $Na_2S{\cdot}9H_2O$ (40 g, 167 mmol) followed by heating on a hot water-bath for 30 min. The solution was then cooled, and the copper(II) sulphide removed by filtration through a bed of Celite. The filtrate was extracted with dichloromethane (7 × 200 cm^3), the combined extracts dried with anhydrous $MgSO_4$, and the dichloromethane removed with a rotary evaporator to leave L^3 as an off-white solid (14.5 g, 62.0 mmol, 85.3%). This may be further purified by dissolving in dichloromethane, and passing through a neutral alumina column (2.5 × 20 cm) to give, after evaporation of the solvent, a white solid (14.0 g, 82.3%). The ^1H and ^{13}C n.m.r. spectra are identical to those previously reported.[5,6] Ligand L^4 was obtained in 73.1% yield by using the same procedure, replacing the 1,7-diamino-4-azaheptane with 1,7-diamino-4-methyl-4-azaheptane. In this case a mixture of dichloromethane (90%) and methanol (10%) was used to elute the final product from the alumina column.

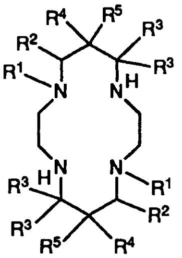
L^1. To L^3 (1.17 g, 5 mmol) in dichloromethane (50 cm^3) was added a solution of NaOH (0.8 g, 20 mmol) in water (30 cm^3). To this two-phase mixture was added dropwise, at room temperature and under nitrogen, a solution of 2-chloromethylpyridine hydrochloride (1.64 g, 10 mmol) in water (20 cm^3) over a period of 1—2 h. The mixture was stirred for 20 h, and the organic phase separated. The aqueous layer was extracted with dichloromethane (4 × 100 cm^3), the combined organic layers dried with anhydrous $MgSO_4$, and concentrated with a rotary evaporator. The product was obtained as a thick oil, which was purified by passing through a neutral alumina column (2.5 × 20 cm) and eluting with dichloromethane–methanol (95:5 v/v). The product is a yellow oil (1.5 g, 71%). ^1H N.m.r. in $CDCl_3$: δ 2.21 (q, 4 H), 2.80 (t, 4 H), 3.18 (t, 4 H), 3.73 (s, 4 H), 3.88 (s, 4 H), 7.03 (d, 2 H), 7.18 (m, 2 H), 7.30 (m, 2 H), 7.59 (m, 3 H), and 8.53 (d, 2 H). The ^{13}C n.m.r. data are in Table 1.

L^2. A solution of L^4 (0.84 g, 3.38 mmol) and 1-(hydroxymethyl)pyrazole (0.67 g, 6.8 mmol) in dry CCl_4 (20 cm^3) was stirred under nitrogen at room temperature for 24 h. Water produced during this reaction was removed by repeatedly drying with anhydrous $MgSO_4$. After 24 h the solution was concentrated to a small volume, and then passed through a neutral alumina column. The required product was eluted with dry dichloromethane, and the solvent removed with a rotary evaporator to leave the product, L^2 (1.40 g, 62%). During the preparation of this ligand, manipulations were carried out with a minimum exposure to heat and light. ^1H N.m.r. in CD_3NO_2: δ 1.53 (q, 4 H), 2.00 (s, 3 H), 2.25 (t, 4 H), 2.50 (t, 4 H), 3.92 (s, 4 H), 5.18 (s, 4 H), 6.32 (m, 2 H), 7.12 (d, 2 H), and 7.55 (m, 5 H). The ^{13}C n.m.r. chemical shifts are in Table 1.

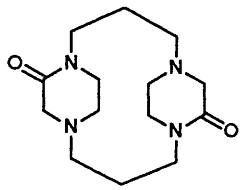
Metal complexes of L^1 *and* L^2. To a stirred solution of each ligand (0.5 mmol) in ethanol (10 cm^3) was added an equimolar solution of $[M(dmso)_n][ClO_4]_2$ (dmso = dimethyl sulphoxide; M = Co, Ni, or Cu, n = 6; M = Zn, n = 4) in ethanol (10 cm^3). The precipitated complexes of formula $[M(L)][ClO_4]_2$ (L = L^1 or L^2) were collected by filtration, washed with a little ice-cold ethanol then diethyl ether, and dried *in vacuo*. The yields are generally high (63—82%), and are recorded in Table 2 together with the colours of the complexes and their microanalytical data. The complexes may be recrystallised from nitromethane–ethanol or nitromethane–diethyl ether. A crystal of $[Ni(L^1)][ClO_4]_2$ suitable for crystallography was grown from nitromethane by slow diffusion of diethyl ether into the solvent.

Crystallography.—Crystal data. A purple crystal of {3,11-di-(2-pyridylmethyl)-3,7,11,17-tetra-azabicyclo[11.3.1]heptadeca-1(17),13,15-triene}nickel(II) perchlorate, $C_{25}H_{32}Cl_2N_6NiO_8$, M = 674.19, rhombohedral, transformed to hexagonal for structure refinement, space group $R3$, a = 16.901(4), c = 26.947(8) Å, U = 6 666(3) $Å^3$ [rhombohedral constants a = 13.263(4) Å, α = 79.17(2)°, U = 2 229.4(1.0) $Å^3$], Z = 9, D_c = 1.51 g, cm^{-3}, Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 8.93 cm^{-1}, T = 293 K, $F(000)$ = 3 149.

Data were collected with a Syntex $P2_1$ four-circle diffractometer in the ω—2θ mode. Maximum 2θ was 45°, with scan range $\pm 0.9(2\theta)$ around the $K_{\alpha1}$–$K_{\alpha2}$ angles, scan speed 5—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 a slight 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 reflections ($18 < 2\theta < 21°$). Reflections were processed using profile analysis to give 3 154 unique reflections (R_{int} = 0.048); 1 664 were considered observed [$I/\sigma(I) \geqslant 3.0$] 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 0.78. Crystal dimensions were 0.2 × 0.4 × 0.25 mm. There were no systematic absences, giving a choice of space groups $R3(1)$; $R\bar{3}(\bar{1})$; $R32(2)$; $R3m(m)$; $R\bar{3}m(2/m)$ with the symmetry constraints indicated in parentheses. Consideration of the likely symmetry of the cation suggested that only $R3$, $R32$, or $R3m$ were likely. Structure solution was attempted in each, but was only successful in space group $R3$, with three of the four independent $[ClO_4]^-$ groups being positioned on the three-fold axis. Apart from the symmetry of these groups, it is not clear to us what feature of the crystal packing leads to this unusual space group in the absence of any symmetry in the cation. Heavy atoms were located by the Patterson interpretation section of SHELXTL, and light atoms were then found on successive Fourier syntheses. Anisotropic thermal parameters were used for all non-H atoms. Hydrogen atoms were given fixed isotropic thermal parameters, U = 0.07 $Å^3$. Those defined by the molecular geometry were inserted at calculated positions and not refined. The z co-ordinate of Ni was fixed to define the origin. Refinement of a $\delta f''$ multiplier showed that the hand originally used was incorrect for the individual chiral crystal chosen [$\eta = -1.09(10)$], and the structure was therefore inverted. Final refinement was on F by cascaded least-squares methods refining 375 parameters. Largest positive and negative peaks on a final difference Fourier syntheses were of height +1.1 and −0.45 e $Å^{-3}$. A weighting scheme of the form $w = 1/[\sigma^2(F) + gF^2]$ with g = 0.0080 was used and shown to be



L^{10} $R^1 = CH_2CO_2H$, $R^2 = R^3 = Me$, $R^4 = R^5 = H$
L^{11} $R^1 = H$, $R^2 = R^3 = Me$, $R^4 = R^5 = H$
L^{12} $R^1 = CH_2CO_2H$, $R^2 = R^3 = R^4 = R^5 = H$
L^{14} $R^1 = R^2 = R^3 = H$, $R^4 = Me$, $R^5 = NH_2$



L^{13}

satisfactory by a weight analysis. Final $R = 0.0626$ ($R' = 0.0637$). Maximum shift/error in the final cycle was 0.216.

Computing was with SHELXTL[8] on a Data General DG30 computer. Scattering factors in the analytical form and anomalous dispersion factors were taken from ref. 9. Final atomic co-ordinates are in Table 3, and selected bond lengths and angles in Table 4. The molecular geometry of the cation is shown in Figure 2.

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

Results and Discussion

Syntheses of the Macrocycles.—The yields of L^3 and L^4 are substantially improved by using copper(II) rather than nickel(II) as a template metal ion. For example, the yield of L^3 increases from *ca.* 43% using nickel(II) ion[5] to *ca.* 82% using copper(II). The reason for this is uncertain, but may be related to the greater stability of the complexes formed by copper(II) compared with nickel(II). Conversion of L^3 and L^4 into L^1 and L^2 respectively is readily achieved in good yield using methods similar to those reported previously[1] for L^5—L^7. During the synthesis of L^1 small amounts of the trisubstituted macrocycle L^8 were also observed to form, but separation was readily achieved by chromatography on a neutral alumina column. The stereochemically preferred alkylation at the two secondary amine groups nearest to the macrocyclic pyridine N atom confirms the behaviour observed previously during the benzylation reactions.[1] The difficulty in preparing macrocycles with two pendant co-ordinating arms has been noted in a recent review,[10] and the present method offers a further route to such species. It is somewhat analogous to the stereochemically directed syntheses of L^{10} from tet-*a* (L^{11}), where the *gem*-dimethyl groups of L^{11} are found to hinder the alkylation of the adjacent secondary amine groups, leading directly to 1,8 substitution.[11] A less direct approach to tetra-azamacrocycles with two pendant co-ordinating arms is illustrated by the partial tosylation of 1,4,8,11-tetra-azacyclotetradecane (cyclam), followed by separation of the 1,8-ditosyl derivative, and alkylation of the two remaining secondary amine sites with $BrCH_2CO_2C_2H_5$.[12] In this way, after detosylation and hydrolysis, the macrocycle L^{12} containing two pendent co-ordinating carboxylate arms was obtained, along with L^{13}, a rather unreactive dilactam derived from L^{12}.

Complexes.—The microanalytical data (Table 2) are as expected for metal complexes of formula $[M(L)][ClO_4]_2$ (M = Co, Ni, Cu, or Zn; L = L^1 or L^2). The ^{13}C n.m.r. spectra of the diamagnetic zinc(II) complexes of L^1 and L^2 (Table 1) show that a single symmetric isomer is formed with each of these sexidentate ligands. The visible spectra of the paramagnetic metal complexes (Table 5) are as expected for six-co-ordinate species, except for that found for the $[Co(L^2)]^{2+}$ ion. Solutions of the cobalt(II) complex in nitromethane are pink, and the spectrum shows a broad peak centred around 540 nm with fine structure evident at 481.7, 510.6, 538.9, and 560.1 nm. The absorption coefficients of these peaks are typical of those expected for a six-co-ordinate complex. However, in water in the presence or absence of dioxygen, the solution is brown, and the visible spectrum changes completely showing only a shoulder at *ca.* 450 nm next to a much stronger u.v. band. Such marked changes with solvent are not evident for the nickel(II) and copper(II) complexes, indicating that either a solvation or geometric change occurs for the cobalt(II) complex in going from one solvent to another. One possibility is that in the presence of a co-ordinating solvent like water one of the pendant pyridyl arms becomes unco-ordinated, with solvent occupying the vacated co-ordination site. Without further evidence, such as a crystal structure, the nature of the cobalt(II) complexes remains uncertain.

Crystal Structure.—The crystal structure of the $[Ni(L^1)]^{2+}$ ion (Figure 2) shows the preference of this macrocycle to give complexes with a folded *cis* geometry (Figure 1). This is analogous to the six-co-ordinate complexes of L^{10}, and contrasts with the *trans* structures found for the sexidentate

Table 1. ^{13}C N.m.r. chemical shifts [δ/p.p.m. relative to $SiMe_4$ (δ 0)] for macrocycles L^1 and L^2 and their diamagnetic zinc(II) complexes in CD_3NO_2 solution (relative populations in parentheses)

Compound							
L^1	158.40(2)	157.87(2)	149.13(2)	137.00(1)	136.87(2)	123.45(2)	122.47(2)
$[Zn(L^1)][ClO_4]_2$	155.45(2)	149.52(2)	143.70(1)	143.24(2)	141.73(2)	127.72(2)	126.31(2)
L^2	159.75(2)	139.83(2)	137.85(1)	131.15(2)	123.78(2)	106.16(2)	71.38(2)
$[Zn(L^2)][ClO_4]_2$	154.09(2)	143.51(2)	142.40(2)	134.87(1)	124.60(2)	109.24(2)	72.67(2)

Compound						
L^1	121.94(2)	60.30(2)	58.02(2)	51.62(2)	49.22(2)	23.31(2)
$[Zn(L^1)][ClO_4]_2$	123.71(2)	59.44(2)	56.87(2)	53.68(4)		26.56(2)
L^2	60.56(2)	55.50(2)	48.59(2)	43.40(1)	26.10(2)	
$[Zn(L^2)][ClO_4]_2$	62.80(2)	55.43(2)	54.05(2)	41.77(1)	22.79(2)	

Table 2. Microanalytical data (calculated values in parentheses), colours and synthetic yields for the complexes $[M(L)][ClO_4]_2$ (M = Co, Ni, Cu, or Zn; L = L^1 or L^2)

Complex	Formula	Colour	Analysis/% C	H	N	Yield/%
$[Co(L^1)][ClO_4]_2\cdot H_2O$	$C_{25}H_{34}Cl_2CoN_6O_9$	Brown	43.4 (43.4)	4.85 (4.90)	11.9 (12.1)	82
$[Ni(L^1)][ClO_4]_2$	$C_{25}H_{32}Cl_2N_6NiO_8$	Purple	44.1 (44.5)	4.70 (4.80)	12.5 (12.5)	80
$[Cu(L^1)][ClO_4]_2$	$C_{25}H_{32}Cl_2CuN_6O_8$	Blue	44.4 (44.2)	5.10 (4.75)	11.9 (12.4)	81
$[Zn(L^1)][ClO_4]_2$	$C_{25}H_{32}Cl_2N_6O_8Zn$	White	44.0 (44.1)	4.85 (4.75)	12.2 (12.3)	76
$[Co(L^2)][ClO_4]_2$	$C_{22}H_{32}Cl_2CoN_8O_8$	Purple	39.4 (39.6)	4.95 (4.85)	16.2 (16.8)	63
$[Ni(L^2)][ClO_4]_2$	$C_{22}H_{32}Cl_2N_8NiO_8$	Blue	39.6 (39.7)	4.85 (4.85)	16.8 (16.8)	73
$[Cu(L^2)][ClO_4]_2$	$C_{22}H_{32}Cl_2CuN_8O_8$	Blue	39.2 (39.4)	4.85 (4.80)	16.7 (16.7)	64
$[Zn(L^2)][ClO_4]_2$	$C_{22}H_{32}Cl_2ZnN_8O_8$	White	39.1 (39.3)	4.80 (4.80)	16.6 (16.7)	70

Table 3. Atom co-ordinates (× 10^4) for $[Ni(L^1)][ClO_4]_2$

Atom	*x*	*y*	*z*
Ni	2 990.6(11)	9 654.3(11)	5 000.0
Cl(1)	6 667	3 333	9 131(2)
Cl(2)	10 000	10 000	8 499(3)
Cl(3)	3 333	6 667	9 041(3)
Cl(4)	3 583	3 983	7 092(2)
N(1)	3 038(7)	8 907(7)	4 465(4)
N(2)	1 663(8)	8 459(8)	5 110(5)
N(3)	3 516(9)	9 095(9)	5 538(5)
N(4)	2 109(8)	9 878(8)	4 388(6)
N(5)	3 198(8)	10 807(8)	5 373(5)
N(6)	4 332(7)	10 606(7)	4 704(5)
O(11)	6 667	3 333	8 625(8)
O(12)	6 956(7)	2 718(8)	9 316(4)
O(21)	10 000	10 000	9 070(15)
O(22)	10 468(9)	9 586(9)	8 389(8)
O(31)	3 333	6 667	8 505(8)
O(32)	2 837(8)	5 756(8)	9 211(4)
O(41)	4 218(15)	4 156(23)	6 755(9)
O(42)	3 328(20)	4 685(16)	7 065(12)
O(43)	3 868(16)	3 993(14)	7 589(7)
O(44)	2 793(13)	3 253(15)	6 952(11)
O(001)	3 333	6 667	7 131(40)
C(1)	2 341(10)	8 050(11)	4 415(6)
C(2)	1 631(11)	7 698(9)	4 833(7)
C(3)	1 396(14)	8 153(12)	5 642(8)
C(4)	2 044(16)	7 973(14)	5 930(7)
C(5)	2 972(16)	8 775(17)	6 024(8)
C(6)	4 556(14)	9 651(14)	5 645(8)
C(7)	5 075(12)	9 950(13)	5 171(8)
C(8)	5 149(11)	10 797(12)	4 966(8)
C(9)	4 338(11)	10 301(11)	4 188(6)
C(10)	3 724(11)	9 293(11)	4 126(6)
C(11)	3 720(11)	8 768(11)	3 741(6)
C(12)	3 014(12)	7 886(12)	3 690(7)
C(13)	2 304(12)	7 519(11)	4 027(7)
C(14)	4 329(10)	11 510(10)	4 705(7)
C(15)	978(10)	8 682(11)	4 943(7)
C(51)	2 765(14)	10 874(12)	5 771(7)
C(52)	3 021(12)	11 693(11)	6 006(7)
C(53)	3 761(11)	12 471(12)	5 826(8)
C(54)	4 222(10)	12 405(11)	5 413(7)
C(55)	3 917(9)	11 578(9)	5 184(6)
C(61)	2 370(16)	10 347(14)	3 962(7)
C(62)	1 745(18)	10 087(17)	3 591(8)
C(63)	892(18)	9 348(17)	3 654(9)
C(64)	654(13)	8 919(13)	4 071(7)
C(65)	1 247(10)	9 174(10)	4 446(6)

Table 4. Selected bond lengths (Å) and angles (°) in $[Ni(L^1)]^{2+}$ ion

Ni–N(1)	1.944(12)	Ni–N(2)	2.161(10)
Ni–N(3)	2.150(17)	Ni–N(4)	2.375(16)
Ni–N(5)	2.059(13)	Ni–N(6)	2.171(10)
N(1)–Ni–N(2)	81.7(5)	N(1)–Ni–N(3)	93.1(6)
N(1)–Ni–N(4)	79.7(6)	N(1)–Ni–N(5)	158.9(4)
N(1)–Ni–N(6)	80.9(4)	N(2)–Ni–N(3)	87.7(5)
N(2)–Ni–N(4)	78.6(5)	N(2)–Ni–N(5)	115.0(5)
N(2)–Ni–N(6)	162.6(5)	N(3)–Ni–N(4)	165.4(4)
N(3)–Ni–N(5)	100.1(6)	N(3)–Ni–N(6)	93.7(5)
N(4)–Ni–N(5)	90.7(5)	N(4)–Ni–N(6)	97.6(5)
N(5)–Ni–N(6)	81.8(5)		

Table 5. Visible spectra of metal complexes of L^1 and L^2

Complex	Solvent	λ/nm (ε/dm^3 mol^{-1} cm^{-1})
$[Ni(L^1)][ClO_4]_2$	$MeNO_2$	376.7 (95.6), 568.8 (40.01), 805.6 (19.1)
$[Ni(L^1)][ClO_4]_2$	Water	564.8 (39.7), 805.1 (24.0)
$[Cu(L^1)][ClO_4]_2$	$MeNO_2$	657.6 (200.2)
$[Cu(L^1)][ClO_4]_2$	Water	660.8 (197.4)
$[Co(L^2)][ClO_4]_2$	$MeNO_2$	481.7 (65.7), 510.6 (75.9), 538.9 (77.1), 560.1 (77.5)
$[Co(L^2)][ClO_4]_2$	Water	451.1 (sh) (258.6)
$[Ni(L^2)][ClO_4]_2$	$MeNO_2$	580.0 (62.5), 778.5 (23.3)
$[Ni(L^2)][ClO_4]_2$	Water	362.4 (90.0), 577.7 (53.6), 585.9 (24.1)
$[Cu(L^2)][ClO_4]_2$	$MeNO_2$	651.2 (225.4)
$[Cu(L^2)][ClO_4]_2$	Water	640.0 (193.5)

macrocycles L^{12} and L^{14}. The latter contain either two N-pendant carboxylato-groups or two C-pendant primary amino-groups which co-ordinate in axial positions.[12,13] In *trans* complexes of L^{12} and L^{14} the four macrocyclic ring N atoms have chiralities *RRSS*, with NR^1 and NH groups at positions 1 and 11 on one side of the macrocyclic ligand plane, and those at positions 4 and 8 on the other side of this plane. In the folded *cis* complexes of L^{10} the N-atom chiralities are *RSRS* with the NR^1 and NH groups alternating above (positions 1 and 8) and below (positions 4 and 11) the macrocyclic ligand plane. In *cis*-$[Ni(L^1)]^{2+}$ the situation is analogous to that found in *cis*-$[Ni(L^{10})]^{2+}$, with the two pendant co-ordinating arms of L^1 on the opposite side of the macrocyclic plane to the NR^2 group (R^2 = H). The set of N-chiralities in *cis*-$[Ni(L^1)]^{2+}$ is also the same as that found in the five-co-ordinate complexes $[Ni(L)X]^{n+}$ (L = L^5 or L^9; X = halide or solvent; *n* = 1 or 2), where the macrocycle is folded about the $R^1N\cdots NR^1$ axis, and the unidentate ligand, X, is in a *trans* position to the pyridine N atom of the macrocyclic ring.[5,14] In contrast, a recent crystal structure of *trans*-$[IrCl(Et)L^9]^+$ shows that an unfolded

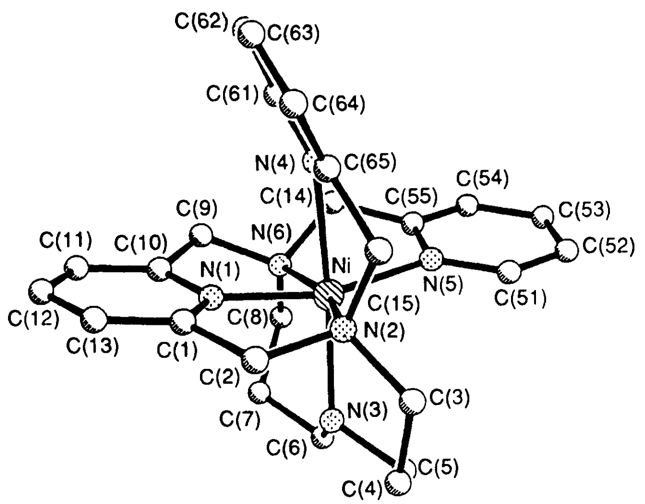


Figure 2. Structure of the $[Ni(L^1)]^{2+}$ cation showing the atomic numbering

macrocyclic ring is possible in which all three MeN groups of L^9 are on the same side of the macrocyclic plane.[15]

In *cis*-$[Ni(L^1)]^{2+}$ the overall geometry at the Ni is octahedral, though some distortions are introduced by the constraints imposed by the ligand. The relatively short N(1)···N(2), N(1)···N(6), N(5)···N(6), and N(2)···N(4) distances lead to N–Ni–N bond angles significantly less than 180°, N(1)–Ni–N(5) 158.9(4), N(2)–Ni–N(6) 162.6(5), and N(3)–Ni–N(4) 165.4°. Typically,[14] the Ni–N(1) distance to the macrocyclic pyridine ring is the shortest metal–ligand distance, with Ni–N(5), to the pendant pyridine *trans* to this, also very short. The distances to the aliphatic N atoms N(2), N(3), and N(6) are rather longer [2.161(5) Å, mean], with the final distance to the pyridine nitrogen, Ni–N(4), remarkably long [2.375(16) Å]. We attribute the difference between the distances to the two pendant pyridine N atoms to the influence of the different atoms in *trans* positions to them.

Acknowledgements

We thank the S.E.R.C. for financial support, and for provision of n.m.r. and *X*-ray facilities.

References

1 Part 6, N. W. Alcock, K. P. Balakrishnan, A. Berry, P. Moore, and C. J. Reader, *J. Chem. Soc., Dalton Trans.*, 1988, 1089.
2 J. Selbin, W. E. Bull, and L. H. Holmes, *J. Inorg. Nucl. Chem.*, 1961, **16**, 219.
3 W. L. Driessen, *Recl. Trav. Chim. Pays-Bas*, 1982, **101**, 441.
4 N. W. Alcock, R. G. Kingston, P. Moore, and C. Pierpoint, *J. Chem. Soc., Dalton Trans.*, 1984, 1937.
5 N. W. Alcock, K. P. Balakrishnan, P. Moore, and G. A. Pike, *J. Chem. Soc., Dalton Trans.*, 1987, 889.
6 N. W. Alcock, P. Moore, and H. A. A. Omar, *J. Chem. Soc., Dalton Trans.*, 1986, 985.
7 K. A. Foster, E. K. Barefield, and D. G. van Derveer, *J. Chem. Soc., Chem. Commun.*, 1986, 680.
8 G. M. Sheldrick, SHELXTL User Manual, Nicolet XRD Corporation, Madison, Wisconsin, 1983.
9 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.
10 R. W. Hay, 'Current Topics in Macrocyclic Chemistry in Japan,' ed. E. Kimura, Hiroshima University School of Medicine, 1987, p. 56.
11 Xu Jide, Ni Shi-sheng, and Lin Yu-juan, *Inorg. Chim. Acta*, 1986, **111**, 61.
12 I. M. Helps, D. Parker, J. Chapman, and G. Ferguson, *J. Chem. Soc., Chem. Commun.*, 1988, 1094.
13 P. V. Bernhardt, G. A. Lawrance, and T. W. Hambley, *J. Chem. Soc., Dalton Trans.*, 1989, 1059; N. F. Curtis, G. J. Gainsford, T. W. Hambley, G. A. Lawrance, K. R. Morgan, and A. Siriwardena, *J. Chem. Soc., Chem. Commun.*, 1987, 295.
14 N. W. Alcock, P. Moore, and H. A. A. Omar, *J. Chem. Soc., Dalton Trans.*, 1987, 1107.
15 H. A. A. Omar, P. Moore, N. W. Alcock, and G. A. Pike, *J. Chem. Soc., Chem. Commun.*, 1990, 280.

Received 23rd *March* 1990; *Paper* 0/01270J