Synthesis and Co-ordination Chemistry of Two Penta-azamacrocycles containing a 1,4-Piperazine Backbone. Crystal Structure Determinations of 6,12-Dioxo-1,5,13,17,22-penta-azatricyclo[15.2.2.1^{7,11}]docosa-7(22),8,10-triene and 1,5,13,17,22-Penta-azatricyclo[15.2.2.1^{7,11}]docosa-7(22),8,10-trienenickel(II) Perchlorate†

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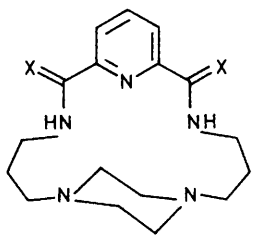
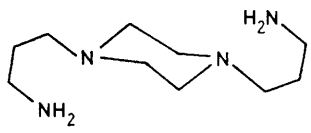
Two closely related pyridine-containing penta-azamacrocycles with a 1,4-piperazine backbone have been prepared, and the co-ordination chemistry of one of them {1,5,13,17,22-penta-azatricyclo[15.2.2.1^{7,11}]docosa-7(22),8,10-triene, L^2} with nickel(II), copper(II), and zinc(II) investigated. L^2 was obtained in low yield from the related diamide macrocycle 6,12-dioxo-1,5,13,17,22-penta-azatricyclo[15.2.2.1^{7,11}]docosa-7(22),8,10-triene, L^1, by reduction with BH_3·thf (thf = tetrahydrofuran). The crystal structure of L^1 shows that the 1,4-piperazine backbone adopts a chair conformation, with the lone pairs of the two 1,4-piperazine N atoms pointing in opposite directions, unfavourable for chelation. Complexes of L^1 could not be isolated. Complexes of L^2 with Ni^{2+}, Cu^{2+}, and Zn^{2+} were readily obtained, and the crystal structure of $[Ni(L^2)][ClO_4]_2$ shows the 1,4-piperazine is in the boat conformation required for chelation. The Ni^{2+} is co-ordinated to all five N atoms of the macrocycle in a symmetric, but distorted, trigonal-bipyramidal geometry, with the pyridine ring at right angles to the plane of the carbon framework of the 1,4-piperazine backbone. The pyridine and two 1,4-piperazine N atoms are equatorial, and the other two N atoms axial; the Ni–N bond lengths are in the ranges 2.16—2.18 Å (axial) and 2.02—2.08 Å (equatorial), with the Ni–pyridine–N bond length being the shortest. The ^{13}C n.m.r. spectrum of the Zn^{2+} complex is consistent with the same symmetric structure as the Ni^{2+} complex.

One of the features of large ring macrocyclic ligands is their ability to fold to give, for example, *cis*-octahedral complexes with tetradentate macrocycles. Recently, attempts to study the size match selectivity of azamacrocycles has involved the synthesis of ligands with rigid backbones to prevent the folding which can otherwise occur.[1–3] One way of achieving this is to build a 1,4-piperazine ring into the backbone of the macrocycle. However, the preferred chair conformation of 1,4-piperazine is unfavourable for chelation, and in open chain structures tends to give rise to oligomeric species with the 1,4-piperazine units bridging between metal ions.[4–9] With large metal ions, 1,4-piperazine has been observed to give metal chelates in which the 1,4-piperazine has a boat conformation.[10–12] Attempts to synthesise a macrocycle by cyclising the disodium salt of ditosylated L^3 with *p*-$MeC_6H_4O_2SO(CH_2)_3OSO_2C_6H_4Me$-*p* using the Richman–Atkins method gave (after detosylation) the large ring octa-azamacrocycle L^4 by a 'two plus two' addition,[13] almost certainly because of the preferred chair conformation of the 1,4-piperazine ring of L^3. Earlier thermodynamic studies of complex formation by 1,4-piperazine-*N*,*N*′-diethanoate indicate, from stability constant measurements, that the 1,4-piperazine ring does not form chelates with small metal cations.[14]

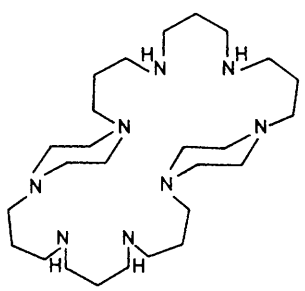
In this study two pyridine containing penta-azamacrocycles with a 1,4-piperazine backbone have been synthesised. The diamide macrocycle L^1 was obtained in reasonable yield by the reaction of L^3 with pyridine-2,6-dicarboxylic acid dichloride, in the presence of excess triethylamine, using high dilution conditions. Reduction of L^1 with BH_3·thf (thf = tetrahydrofuran) gave low yields of L^2, and the complexes of this new ligand with Ni^{2+}, Cu^{2+}, and Zn^{2+} have been isolated and characterised. The crystal structures of L^1 and $[Ni(L^2)][ClO_4]_2$ are also reported, the latter establishing a boat conformation for the 1,4-piperazine backbone, and the former a chair conformation. The ^{13}C n.m.r. spectra of the ligands, and of $[Zn(L^2)][ClO_4]_2$ were also obtained, the latter showing the presence of a single symmetric isomer.



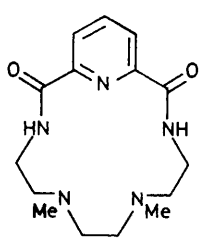
L^1 ; X = O
L^2 ; X = H_2



L^3



L^4



L^5

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

Table 1. ^{13}C N.m.r. chemical shifts (δ/p.p.m. reference $SiMe_4$) at 298 K in CD_3NO_2 solution unless specified otherwise (relative populations in parentheses)

Compound	Carbonyl	Pyridine (py) C					Piperazine		C–CH_2–C
		ortho	*para*	*meta*	py–CH_2–N	NH–CH_2–C		N–CH_2–C	
L^1*	166.06(2)	151.13(2)	140.22(1)	126.21(2)		59.34(2)	53.06(4)	41.65(2)	26.02(2)
L^2		159.12(2)	136.77(1)	129.02(2)	57.44(2)	55.69(2)	51.95(4)	50.70(2)	25.52(2)
$[Zn(L^2)][ClO_4]_2$		156.12(2)	143.31(1)	124.59(2)	55.41(2)	54.24(2)	53.14(2) 52.01(2)	47.96(2)	25.37(2)

* In CD_3OD; recorded at 100.62 MHz (other spectra at 45.28 MHz).

Experimental

Materials.—Toluene was dried, and pyridine-2,6-dicarboxylic acid dichloride synthesised as described previously.[15] The dimethyl sulphoxide solvates of metal perchlorates were obtained by a published method.[16] Other materials were obtained commercially and used without further purification. Their purity was established spectroscopically.

Spectra and Other Procedures.—Proton-decoupled ^{13}C n.m.r. spectra were obtained at 45.28 or 100.62 MHz with Bruker WH180 or WH400 Fourier-transform n.m.r. spectrometers, and proton n.m.r. spectra at 220 or 400 MHz with either Perkin-Elmer R34 continuous-wave or Bruker WH400 Fourier-transform instruments, respectively. Chemical shifts are reported on the δ scale relative to $SiMe_4$ at δ = 0 p.p.m. Infrared, u.v.–visible, and mass spectra were obtained with Perkin-Elmer 580B, Shimadzu 365, and Kratos MS80 spectrometers respectively. The magnetic moment of the copper(II) complex was measured at room temperature by the Evans n.m.r. method.[17] *X*-Ray data were collected with a Syntex $P2_1$ four-circle diffractometer. Computing was with SHELXTL[18] on a Data General DG30 computer.

Preparation of 6,12-*Dioxo*-1,5,13,17,22-*penta-azatricyclo*-[15.2.2.1^{7,11}]*docosa*-7(22),8,10-*triene*, L^1.—This ligand was prepared under high dilution conditions using a modification of a published method.[19] A 5-dm^3 three-neck flask was charged with dry toluene (2.5 dm^3), and the flask flushed with dry dinitrogen. The flask was fitted with a condenser, an efficient overhead stirrer, and a suba seal. Two oven dried 100-cm^3 all-glass syringes were charged separately with solutions of 1,4-bis(3′-aminopropyl)piperazine (Aldrich; 7.34 g, 36.7 mmol) and pyridine-2,6-dicarboxylic acid dichloride (7.50 g, 36.7 mmol), each dissolved in dry toluene (100 cm^3). The two syringes were connected to the flask *via* two long stainless steel needles (Aldrich) passing through the suba seal, and positioned above the vigorously stirred solvent in the flask. The syringes were mounted on a Sage Instruments model 355 syringe pump, to allow controlled slow addition of the two reagents over a period of 12 h. Triethylamine (7.42 g, 73.4 mmol) was added to the toluene in the flask, and the solution cooled in an ice-bath to below 5 °C before, and during, addition of the two reactants from the syringes. After addition was complete, the solution was stirred at room temperature for a further 36 h. The precipitated triethylammonium chloride was removed by filtration, and the solution evaporated with a rotary evaporator to leave a cream coloured solid. This was recrystallised from dichloromethane–light petroleum (b.p. 40—60 °C) (1:1), to give L^1 as a white powder (2.77 g, 8.4 mmol, 23%). Proton n.m.r. in CD_3OD: δ 8.73 (broad, 2 H, amide NH), 8.33 (d, 2 H, H^β of pyridine), 7.96 (t, 1 H, H^γ of pyridine), 3.61 (q, 4 H, piperazine), 3.00 (q, 4 H, CH_2–NH), 2.82 (t, 4 H, CH_2–piperazine), 2.47 (q, 4 H, piperazine), and 1.78 (p, 4 H, C–CH_2–C) p.p.m. The ^{13}C n.m.r. chemical shifts are in Table 1. The electron impact mass spectrum showed a parent ion peak at *m/z* 332 (calc. for $[HL^1]^+$, 332).

Table 2. Visible spectra [λ/nm (ε/dm^3 mol^{-1} cm^{-1})] of Ni^{2+} and Cu^{2+} complexes

Complex	Solvent	Colour	$\lambda_{max.}$(ε)
$[Ni(L^2)][ClO_4]_2$	CH_3NO_2	Violet	532 (32), 835 (78), 997 (sh), 1 065 (66)
$[Ni(L^2)][ClO_4]_2$	CH_3CN	Pale green	506 (36), 812 (24), 1 100 (55)
$[Cu(L^2)][ClO_4]_2$	CH_3NO_2	Blue	622 (131), 1 000 (135)

Table 3. Crystal data for L^1 and $[Ni(L^2)][ClO_4]_2$ (**1**)

Compound	L^1	(**1**)
Formula	$C_{17}H_{25}N_5O_2$*	$C_{17}H_{29}Cl_2N_5NiO_8$
M	331.4	561.1
System	Monoclinic	Monoclinic
Absences	*h*0*l*, *h* + *l* ≠ 2*n*	*h*0*l*, *l* ≠ 2*n*
	0*k*0, *k* ≠ 2*n*	0*k*0, *k* ≠ 2*n*
Space group	$P2_1/n$	$P2_1/c$
a/Å	9.944(2)	17.664(5)
b/Å	15.923(4)	16.871(5)
c/Å	12.246(3)	16.876(4)
β/°	100.45(2)	107.83(2)
U/Å^3	1 906.9(8)	4 768(2)
D_c/g cm^{-3}	1.15	1.56
Z	4	8
μ(Mo-K_α)/cm^{-1}	0.77	10.92
λ(Mo-K_α)/Å	0.710 69	0.710 69
F(000)	712	2 336
Total reflections	3 250	8 409
Reflections used in refinement	1 735	4 908
$2\theta_{max.}$/°	50	50
Range (2θ) about $K_{\alpha1}$–$K_{\alpha2}$	±1.15	±1.05
hkl ranges	0,0,−16 to 12,20,16	0,0,−21 to 20,20,21
Crystal dimensions/mm	0.60 × 0.40 × 0.46	0.53 × 0.43 × 0.30
Max. (min.) transmission factors	0.98 (0.97)	0.86 (0.83)
Parameters refined	229	595
Final *R* (*R*′)	0.072 (0.077)	0.044 (0.049)
Weighting factor, *g*	0.0021	0.000 81
Largest peak on *F* map/e Å^{-3}	+0.4 and −0.25	±0.5

* Unidentified part-occupied solvent omitted throughout.

Preparation of 1,5,13,17,22-*Penta-azatricyclo*[15.2.2.1^{7,11}]-*docosa*-7(22),8,10-*triene*, L^2.—L^1 (2.75 g, 8.3 mmol) was dissolved in dry tetrahydrofuran (thf, 50 cm^3) in a 250-cm^3 round-bottomed flask. The flask and contents were flushed with dry dinitrogen, and a solution of BH_3·thf (50 cm^3 of a 1 mol dm^{-3} solution in thf) added with the exclusion of air. The solution was refluxed under dry dinitrogen overnight, and excess borane was then destroyed by the dropwise addition of methanol. The solvents were removed by rotary evaporation, to

Table 4. Atomic co-ordinates ($\times 10^4$)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
(*a*) For L^1							
O(1)	4 308(3)	8 055(2)	2 011(3)	C(8)	4 422(5)	11 505(4)	431(4)
O(2)	−398(3)	9 891(2)	−2 250(3)	C(9)	2 486(6)	12 355(4)	−371(5)
N(1)	3 156(4)	9 224(2)	2 317(3)	C(10)	1 940(6)	12 030(4)	−1 490(5)
N(2)	4 845(4)	11 158(3)	2 386(3)	C(11)	755(5)	11 440(3)	−1 584(5)
N(3)	3 009(4)	11 722(3)	471(3)	C(12)	557(4)	9 925(3)	−1 445(4)
N(4)	1 130(4)	10 632(2)	−1 040(3)	C(13)	1 141(4)	9 134(3)	−888(4)
N(5)	1 926(3)	9 203(2)	123(3)	C(14)	900(5)	8 370(3)	−1 446(4)
C(1)	3 414(5)	8 578(3)	1 712(4)	C(15)	1 527(5)	7 664(3)	−964(4)
C(2)	3 982(5)	9 381(3)	3 414(4)	C(16)	2 359(5)	7 726(3)	58(4)
C(3)	5 409(5)	9 725(3)	3 360(4)	C(17)	2 518(4)	8 505(3)	583(4)
C(4)	5 571(6)	10 674(3)	3 307(5)	C(001)	3 624(13)	5 632(8)	559(10)
C(5)	3 448(5)	11 378(3)	2 434(4)	C(002)	4 493(21)	5 468(12)	−82(14)
C(6)	2 937(5)	12 039(3)	1 572(4)	C(003)	4 319(23)	4 811(17)	−96(18)
C(7)	4 951(5)	10 860(3)	1 288(4)				
(*b*) For $[Ni(L^2)][ClO_4]_2$ (**1**)							
Ni(1)	1 973.4(3)	6 774.5(3)	6 463.7(4)	C(12)	3 425(3)	7 528(3)	6 970(3)
Ni(2)	7 000.8(4)	6 799.1(4)	10 039.9(4)	C(13)	2 498(3)	7 375(3)	5 192(3)
Cl(1)	5 761.7(8)	8 085.2(7)	7 572.0(8)	C(14)	3 212(3)	6 869(3)	5 677(3)
Cl(2)	2 979.6(8)	9 269.9(8)	4 017.4(9)	C(15)	3676(3)	6 105(3)	6 984(4)
Cl(3)	9 515.3(8)	7 832.8(8)	9 128.3(9)	C(16)	3 382(4)	5 301(3)	6 599(4)
Cl(4)	2 263.9(9)	5 555.9(8)	3 571.0(9)	C(17)	2 517(3)	5 117(3)	6 494(3)
O(11)	6 545(3)	8 011(3)	8 130(3)	C(18)	1 125(3)	5 318(3)	5 693(3)
O(12)	5 523(3)	7 328(3)	7 272(4)	C(19)	796(3)	5 534(3)	6 381(3)
O(13)	5 247(2)	8 413(2)	7 991(2)	C(110)	217(4)	5 123(4)	6 605(4)
O(14)	5 789(4)	8 590(3)	6 927(3)	C(111)	−60(3)	5 425(4)	7 228(4)
O(21)	2 151(2)	9 319(3)	3 882(3)	C(112)	250(3)	6 111(3)	7 627(4)
O(22)	3 343(3)	9 289(3)	4 889(3)	C(113)	842(3)	6 493(3)	7 399(3)
O(23)	3 141(3)	8 550(3)	3 686(4)	C(114)	1 257(3)	7 226(3)	7 794(3)
O(24)	3 258(3)	9 926(3)	3 650(2)	C(115)	907(3)	8 102(3)	6 601(3)
O(31)	8 734(3)	8 104(3)	8 982(4)	C(116)	1 184(3)	8 670(3)	6 049(4)
O(32)	9 712(4)	7 970(4)	8 411(4)	C(117)	1 546(3)	8 304(3)	5 431(4)
O(33)	10 037(5)	8 238(3)	9 748(5)	C(21)	8 415(3)	7 608(3)	10 997(4)
O(34)	9 560(3)	7 015(3)	9 328(4)	C(22)	7 816(3)	8 210(3)	10 490(4)
O(41)	1 548(3)	5 912(3)	3 612(5)	C(23)	7 567(3)	7 106(4)	11 743(3)
O(42)	2 633(4)	5 259(3)	4 359(3)	C(24)	7 084(4)	7 850(4)	11 413(3)
O(43)	2 066(3)	4 960(4)	2 970(3)	C(25)	6 382(4)	8 477(3)	10 056(4)
O(44)	2 707(3)	6 161(3)	3 369(4)	C(26)	5 560(4)	8 183(3)	10 035(4)
N(11)	2 205(2)	7 755(2)	5 824(2)	C(27)	5 339(3)	7 374(3)	9 679(3)
N(12)	3 170(2)	6 770(2)	6 545(3)	C(28)	5 491(3)	5 948(3)	9 858(3)
N(13)	1 939(2)	5 630(2)	5 882(2)	C(29)	5 737(3)	5 740(3)	9 118(3)
N(14)	1 101(2)	6 204(2)	6 776(2)	C(210)	5 344(3)	5 215(3)	8 512(4)
N(15)	1 567(2)	7 652(2)	7 194(2)	C(211)	5 664(4)	5 032(3)	7 879(4)
N(21)	7 968(2)	6 893(2)	11 124(3)	C(212)	6 376(3)	5 372(3)	7 868(3)
N(22)	7 030(3)	7 930(2)	10 504(3)	C(213)	6 736(3)	5 898(3)	8 493(3)
N(23)	5 832(2)	6 729(2)	10 189(2)	C(214)	7 488(3)	6 337(3)	8 563(3)
N(24)	6 422(2)	6 069(2)	9 099(2)	C(215)	8 309(3)	5 782(3)	9 868(3)
N(25)	7 904(2)	6 500(2)	9 451(2)	C(216)	8 873(3)	5 924(4)	10 748(3)
C(11)	2 895(3)	8 171(3)	6 425(3)	C(217)	8 477(3)	6 195(4)	11 393(3)

give the borane salt of L^2 as an off-white solid. This solid was dissolved in a mixture of water (50 cm^3), methanol (50 cm^3), and concentrated HCl (30 cm^3), and the solution refluxed overnight. The pH was adjusted to *ca.* 12 with NaOH, and the solution extracted with dichloromethane (5 × 25 cm^3). The combined extracts were dried over anhydrous magnesium sulphate, filtered, and evaporated to give a colourless oil (b.p. 175 °C, 0.1 mmHg), which slowly crystallised to give a waxy white solid (82 mg, 0.27 mmol, 3.3%). Proton n.m.r. in CD_3OD: δ 7.79 (t, 1 H, H^γ of pyridine), 7.36 (d, 2 H, H^β of pyridine), 3.83 (s, 4 H, pyridine-CH_2), 3.31 (broad, 2 H, NH), 2.82 (t, 4 H, NH-CH_2-C), 2.71 (t, 4 H, CH_2-piperazine), 2.58 (broad, 8 H, piperazine), and 1.75 (4 H, C-CH_2-C) p.p.m. The ^{13}C n.m.r. chemical shifts are in Table 1. The electron impact mass spectrum showed a parent ion peak at *m/z* 303 (calc. for $[HL^2]^+$, 303).

Preparation of Complexes of L^2.—L^2 (100 mg, 0.3 mmol) was dissolved in ethanol (5 cm^3) and stirred during the addition of an equimolar solution of the dimethyl sulphoxide solvates of either Ni^{2+}, Cu^{2+}, or Zn^{2+} ions (5 cm^3). The solutions turned cloudy as the complexes precipitated, and stirring was continued for 5 min. The solids were collected by filtration and recrystallised from nitromethane–diethyl ether. Yields were 128 mg (69%), 93 mg (51%), and 99 mg (65%) for Cu^{2+}, Ni^{2+}, and Zn^{2+} respectively. The fast-atom bombardment (f.a.b.) mass spectra showed peaks at *m/z* 465 and 365 (Cu), 460 and 360 (Ni), and 466 and 366 (Zn) as expected for the ions $[M(L^2)ClO_4]^+$ and $[M(L^2 - H)]^+$ respectively (M = Cu, Ni, and Zn). In the f.a.b. mass spectrum of the Zn^{2+} complex, peaks were also evident at *m/z* 404 and 304 indicating decomposition to give $[H_2L^2(ClO_4)]^+$ and $[HL^2]^+$. The visible spectra of the complexes are collected in Table 2. The magnetic moment of the

Table 5. Principal bond lengths (Å) and angles (°) for L^1 and $[Ni(L^2)][ClO_4]_2$ (**1**)

(*a*) For L^1

O(1)–C(1)	1.225(6)	O(2)–C(12)	1.240(6)
N(1)–C(1)	1.319(6)	N(1)–C(2)	1.464(6)
N(2)–C(4)	1.447(7)	N(2)–C(5)	1.444(7)
N(2)–C(7)	1.447(7)	N(3)–C(6)	1.454(7)
N(3)–C(8)	1.457(6)	N(3)–C(9)	1.469(7)
N(4)–C(11)	1.467(6)	N(4)–C(12)	1.317(6)
N(5)–C(13)	1.343(5)	N(5)–C(17)	1.334(5)
C(1)–C(17)	1.507(6)	C(2)–C(3)	1.534(8)
C(3)–C(4)	1.522(8)	C(5)–C(6)	1.512(7)
C(7)–C(8)	1.495(8)	C(9)–C(10)	1.472(8)
C(10)–C(11)	1.495(7)	C(12)–C(13)	1.498(6)
C(13)–C(14)	1.393(7)	C(14)–C(15)	1.367(7)
C(15)–C(16)	1.373(7)	C(16)–C(17)	1.393(7)
C(1)–N(1)–C(2)	120.9(4)	C(4)–N(2)–C(5)	116.4(4)
C(4)–N(2)–C(7)	116.0(4)	C(5)–N(2)–C(7)	110.5(4)
C(6)–N(3)–C(8)	108.9(4)	C(6)–N(3)–C(9)	110.0(4)
C(8)–N(3)–C(9)	111.1(4)	C(11)–N(4)–C(12)	121.5(4)
C(13)–N(5)–C(17)	117.3(4)	O(1)–C(1)–N(1)	124.5(4)
O(1)–C(1)–C(17)	119.9(4)	N(1)–C(1)–C(17)	115.6(4)
N(1)–C(2)–C(3)	113.0(4)	C(2)–C(3)–C(4)	117.5(5)
C(2)–C(4)–C(3)	121.3(4)	N(2)–C(5)–C(6)	110.2(5)
N(3)–C(6)–C(5)	109.8(4)	N(2)–C(7)–C(8)	110.6(4)
N(3)–C(8)–C(7)	110.9(4)	N(3)–C(9)–C(10)	115.8(5)
C(9)–C(10)–C(11)	116.4(5)	N(4)–C(11)–C(10)	112.7(4)
O(2)–C(12)–N(4)	123.5(4)	O(2)–C(12)–C(13)	120.2(4)
N(4)–C(12)–C(13)	116.2(4)	N(5)–C(13)–C(12)	117.6(4)
N(5)–C(13)–C(14)	122.9(4)	C(12)–C(13)–C(14)	119.5(4)
C(13)–C(14)–C(15)	118.8(4)	C(14)–C(15)–C(16)	119.1(5)
C(15)–C(16)–C(17)	118.9(4)	N(5)–C(17)–C(1)	117.7(4)
N(5)–C(17)–C(16)	122.9(4)	C(1)–C(17)–C(16)	119.4(4)

(*b*) $[Ni(L^2)][ClO_4]_2$ (**1**)

	$n = 1$	$n = 2$
Ni(*n*)–N(*n*1)	2.081(4)	2.088(3)
Ni(*n*)–N(*n*3)	2.156(4)	2.157(4)
Ni(*n*)–N(*n*5)	2.180(4)	2.178(4)
Ni(*n*)–N(*n*2)	2.075(4)	2.056(4)
Ni(*n*)–N(*n*4)	2.018(4)	2.019(3)
N(*n*1)–Ni(*n*)–N(*n*2)	71.3(2)	71.3(2)
N(*n*1)–Ni(*n*)–N(*n*4)	143.2(1)	144.4(2)
N(*n*2)–Ni(*n*)–N(*n*3)	85.0(2)	85.4(2)
N(*n*2)–Ni(*n*)–N(*n*5)	118.0(1)	116.8(2)
N(*n*3)–Ni(*n*)–N(*n*5)	153.5(2)	154.1(1)
N(*n*1)–Ni(*n*)–N(*n*3)	117.4(2)	117.3(2)
N(*n*1)–Ni(*n*)–N(*n*5)	84.4(2)	84.1(2)
N(*n*2)–Ni(*n*)–N(*n*4)	145.5(2)	144.3(1)
N(*n*3)–Ni(*n*)–N(*n*4)	76.9(2)	77.6(2)
N(*n*4)–Ni(*n*)–N(*n*5)	76.6(2)	76.6(2)

Cu^{2+} complex was found to be 1.96 B.M. at room temperature. The ^{13}C n.m.r. chemical shifts of the Zn^{2+} complex are in Table 2.

Attempted Preparation of Complexes of L^1.—Attempts were made to react L^1 with the metal ethanoates of Cu^{2+}, Ni^{2+}, and Zn^{2+} using the procedure which is successful for the preparation of complexes of the type $[M(L^5 - 2H)]$ (M = Cu or Ni; $L^5 - 2H$ is L^5 with the two protons of the amide groups removed).[13] With L^1, all attempts failed to give corresponding products, the ligand being retrieved unchanged. The crystal structure of L^1 was determined to help to establish why complex formation fails with this macrocycle.

Crystal Structures.—Crystal data for L^1 and $[Ni(L^2)][ClO_4]_2$ (**1**) are collected in Table 3. Reflections were measured around the $K_{\alpha 1} - K_{\alpha 2}$ angles with scan speed 3—29° min^{-1} depending on the intensity of a 2 s pre-scan (*hkl* ranges in Table 3); backgrounds were measured at each end of the scan for 0.25 of the scan time. All data were taken at 290 K. Three standard reflections were monitored every 200 reflections and showed slight variations 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 ($20 < 2\theta < 22°$). Reflections were processed using profile analysis; those with $I/\sigma(I) > 2.0$ were used in the refinement of L^1, and with $I/\sigma(I) > 3.0$ in the refinement of (**1**). Corrections were made for Lorentz, polarisation and absorption affects, the latter by the Gaussian method; the maximum and minimum transmission factors are in Table 3. Hydrogen atoms were given fixed isotropic thermal parameters, $U = 0.07$ Å^2, and were inserted at calculated positions and not refined. Final refinement was by cascaded least-squares methods with anisotropic thermal parameters for all atoms other than hydrogen (and the solvent in L^1). A weighting scheme was used of the form $w = 1/[\sigma^2(F) + gF^2]$ (for g see Table 3), and shown to be satisfactory by a weight analysis. Final refinement was on F by cascaded least-squares methods. Scattering factors in the analytical form, and anomalous dispersion factors were taken from ref. 20. For L^1 the structure was solved by direct methods using SHELXTL.[18] Final Fourier syntheses located a disordered solvent position, approximated by three half-occupancy carbon atoms; these were adjacent to the centre of symmetry at ($\frac{1}{2}$, $\frac{1}{2}$, 0) and are attributed to a C_5, C_6, or mixed hydrocarbon molecule. For (**1**) the Ni atoms of the two independent cations were located by the Patterson interpretation section of SHELXTL,[18] and light atoms were then found on successive Fourier syntheses. Final atomic co-ordinates are in Table 4, and selected bond lengths and angles in Table 5.

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

The high dilution route to L^1 gives a moderately good yield (23%), but reduction of the amide groups with BH_3·thf proved to be much more difficult and the yield of L^2 was only 3.3%. The reduction of L^5 with BH_3·thf is much easier, and a yield of >80% was possible for the reduction stage.[15] This difficult reduction of L^1 is attributed to the presence of the rigid 1,4-piperazine backbone, and it may be that folding of the macrocycle is necessary for facile reduction of the amide bonds. The electron impact mass spectra, and ^{13}C n.m.r. spectra of the ligands (Table 1) are entirely consistent with their proposed structures.

The crystal structure of L^1 is shown in Figure 1. The macrocycle is planar and symmetric, with the 1,4-piperazine in a chair conformation [1,4-piperazine torsion angles N(2)–C(5)–C(6)–N(3), 59.5°; N(2)–C(7)–C(8)–N(3), −57.6°]. There are no unusual bond lengths or angle deviations in the molecule. The lone pairs of the piperazine N atoms are in *trans* positions and those of the amide N atoms are pointing away from the centre of the macrocyclic ring, both of which are unfavourable for chelation. This explains the reluctance of L^1 to form metal complexes, despite their ready formation[13] with the related ligand L^5 {with L^5, and related diamide macrocycles, complex formation is usually accompanied by loss of the two amide NH protons to give neutral complexes of the type $[M(L - 2H)]$ (M = divalent metal ion)}. Inversion of the 1,4-piperazine N atoms to give the required boat conformation is presumably

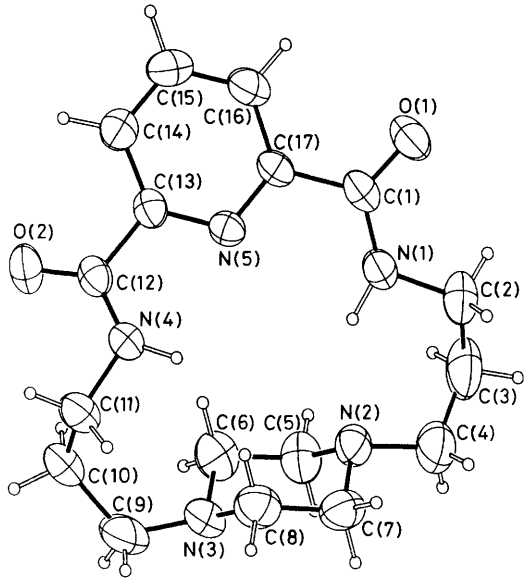


Figure 1. View of the molecule L^1 showing the atomic numbering

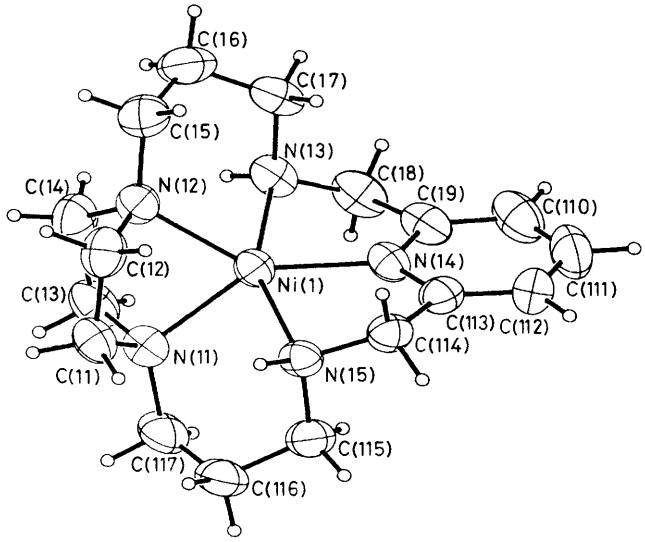


Figure 2. View of one cation of $[Ni(L^2)]^{2+}$ showing the atomic numbering

hindered by the amide linkages, with loss of the amide group protons made more difficult by the piperazine backbone.

Metal complex formation with L^2 is much easier, and in all cases the f.a.b. mass spectra are consistent with the formulation $[M(L^2)][ClO_4]_2$ (M = Cu, Ni, or Zn). The visible spectra of the Ni^{2+} and Cu^{2+} complexes are as expected for five-co-ordinate species (Table 2), and the room temperature paramagnetic moment of the Cu^{2+} complex (1.96 B.M.) is also as expected. The crystal structure of the Ni^{2+} complex shows the presence of two independent cations, but the differences between them are minor, with no significant structural differences. The structure of one of the two cations is shown in Figure 2; the geometry about the nickel atom is a distorted trigonal bipyramid. The 1,4-piperazine is in the boat conformation required for chelation [torsion angles N(11)–C(11)–C(12)–N(12), 15.1°; N(11)–C(13)–C(14)–N(12), 16.8°], with its two N atoms and the pyridine N atom equatorial. The plane of the carbon framework of the 1,4-piperazine ring is approximately at right angles to the pyridine ring, and the pyridine ring is, therefore, approximately perpendicular to the trigonal plane. The axial Ni–N bond lengths (2.16—2.18 Å) are significantly longer than the equatorial bond lengths (2.02—2.08 Å), with the Ni–pyridine bond distances being the shortest as in related complexes.[15] There is considerable distortion from a true trigonal-bipyramidal geometry; for example, the axial N–Ni–N bond angle is *ca.* 154°, and the equatorial N–Ni–N bond angles involving the pyridine N atom are *ca.* 145°, and only 71° between the two 1,4-piperazine N atoms. The small bond angle to the piperazine N atoms is as expected for a rigid chelating 1,4-piperazine boat.

The ^{13}C n.m.r. spectrum of $[Zn(L^2)][ClO_4]_2$ (Table 1) shows the presence of a single symmetric isomer, and the data are consistent with a structure directly analogous to that found for the Ni^{2+} complex. The Cu^{2+} complex is almost certainly identical.

We conclude that chelation by 1,4-piperazine incorporated into a macrocyclic ring is possible provided N inversion can occur to give the required boat conformation. In the diamide macrocycle, L^1, N inversion is hindered by the two amide linkages, and the unfavourable 1,4-piperazine chair conformation and difficult loss of the amide protons prevents complex formation, in contrast to the behaviour found for the less rigid diamide macrocycle, L^5.

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