Metal-ion Selectivity by Macrocyclic Ligands. Part 1. The Interaction of Ni^{II} and Cu^{II} with Pyridinyl-derived N_3O_2 Macrocycles; The X-Ray Structures of a Free Macrocycle, its Endomacrocyclic Complexes of Ni^{II} and Cu^{II} and an Exomacrocyclic Nickel(II) Complex†

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The interaction of Cu^{II} and Ni^{II} with two macrocycles L^1 and L^2, each containing an N_3O_2 donor set, has been investigated. Spectrophotometric studies in dimethyl sulphoxide reveal the formation of complexes with 1:1 and 1:2 metal:ligand ratios and conductometric studies in the same solvent indicated that all of the complexes were 1:2 electrolytes. Conductometric titration of the 1:1 copper(II) complexes with chloride in each case indicated the formation of a 1:1 electrolyte, presumably through co-ordination of a chloride ion to the central copper of each complex. Similar titration of the nickel(II) complexes gave evidence for the formation of dinuclear species; each of these was postulated to contain a bridging chloride anion. The stability constants of the complexes together with their enthalpies of co-ordination have been determined in 95% methanol. Extraction and related transport experiments were carried out and under the conditions employed Cu^{II} was favoured over Ni^{II}. The X-ray crystal structures of the free macrocycle L^1, the 1:1 complexes $[CuL^1(H_2O)][ClO_4]_2$ and $[NiL^1(I)]I\cdot MeOH$, and the 1:2 complex $[NiL^1_2(NO_3)]NO_3\cdot 2MeOH$ have been determined. The metal in $[CuL^1(H_2O)][ClO_4]_2$ is six-co-ordinate and lies within the folded macrocyclic cavity. The donor set comprises the five macrocyclic donor atoms and a water molecule. Overall, the co-ordination sphere corresponds to a restricted tetragonal rhombic arrangement. The complex $[NiL^1(I)]I\cdot MeOH$ also has all donors of the macrocycle co-ordinated with an iodide anion occupying the sixth site to yield a distorted-octahedral geometry. The structure of $[NiL^1_2(NO_3)]NO_3\cdot 2MeOH$ shows that the nickel is again six-co-ordinated, to the aliphatic nitrogen atoms from two macrocycles (each showing exo co-ordination) and a bidentate nitrate anion.

Aspects of macrocyclic ligand design which may lead to high selectivity in metal complex formation are pertinent to areas ranging from biochemistry to hydrometallurgy. The selective complexation and transport of metal ions may be facilitated by macrocyclic ligands of intermediate rigidity (that is, sufficient rigidity to present a donor set with a defined geometry to a metal ion but flexible enough to encourage favourable kinetics of metal-ion incorporation and release).[1] In some cases the stability constants of such complexes have been shown to correlate with the goodness of fit of the metal ion for the donor cavity, although other mechanisms for discrimination may also operate.[2] Nevertheless, when metal ions are discriminated against by a poor fit for the cavity the possibility exists that the favoured mode of interaction will involve exomacrocyclic complexation using only part of the macrocyclic donor set.[3]

In an earlier paper[2] we have discussed the reaction of Cu^{II} and Ni^{II} with the 15-membered macrocycle L^3 and have shown that the structures of the 1:1 complexes of Cu^{II} and Ni^{II} are markedly different. In the copper(II) complex all the donor atoms of L^3 bind to the central metal whereas, for Ni^{II}, only four (a N_3O set) of the five are bound.

Molecular models suggested that the 17-membered macrocycle L^1 provides a donor set which will bind fully with Ni^{II}. In the first part of this series we report the reaction of Cu^{II} and Ni^{II} with L^1 and L^2 together with the solution properties of the resulting complexes. The X-ray structures of L^1, $[CuL^1(H_2O)][ClO_4]_2$, $[NiL^1(I)]I\cdot MeOH$ and $[NiL^1_2(NO_3)]NO_3\cdot 2MeOH$ are also presented. A preliminary report of the X-ray structures of $[CuL^1(H_2O)][ClO_4]_2$ and $[NiL^1_2(NO_3)]NO_3\cdot 2MeOH$ has been published.[4]

Experimental

Microanalyses were determined by the University of Sheffield microanalytical service. Infra-red spectra were recorded on a Perkin-Elmer 297 spectrometer between 4000 and 600 cm^{-1} as KBr discs, liquid films or Nujol mulls. Mass spectra were obtained on Kratos MS 80 and MS 25 instruments using either electron impact (EI) or chemical ionisation (CI, reagent ammonia) on organic compounds and positive-ion fast-atom bombardment (FAB, 3-nitrobenzyl alcohol matrix, Xe^+ source) on compounds of high molecular mass. Ultraviolet–visible

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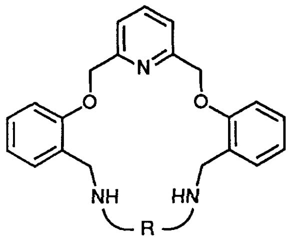
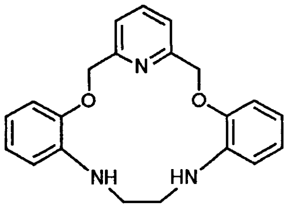
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.



L^1 R = CH_2CH_2
L^2 R = $CH_2CH_2CH_2$



L^3

spectra were recorded on a Perkin-Elmer 559 spectrophotometer, ^{1}H NMR spectra using either a Bruker WH 250 MHz or WH 400 MHz spectrometer or a continuous-wave Perkin-Elmer R34 220 MHz spectrometer, and proton-decoupled ^{13}C NMR spectra using a Bruker WH 250 MHz spectrometer. NMR spectra were referenced to tetramethylsilane for ^{1}H and ^{13}C.

Conductometric titrations were performed on the metal(II) perchlorate complexes in spectroscopic grade dimethyl sulphoxide (dmso) or methanol (*ca.* 1 mmol dm^{-3}), with ammonium chloride (*ca.* 30 mmol dm^{-3}) up to a mole ratio of 2.5:1 ([NH_4Cl]:[complex]) using a Pye Unicam conductivity bridge and cell. Metal(II) salt solutions in spectroscopic grade dmso or methanol were titrated spectrophotometrically by the addition of incremental amounts of solid macrocycle up to a mole ratio of 2.5:1 ([macrocycle]:[M^{2+}]); spectra were recorded on a Perkin-Elmer 559 UV/VIS spectrophotometer.

Thermodynamic Studies.—Thermodynamic stability constants (log *K*) were obtained by the potentiometric (pH) titration method in 95% methanol at 25 °C, the ionic strength being 0.1 mol dm^{-3} tetraethylammonium perchlorate; the equipment and data processing have been described elsewhere.[5] The enthalpy changes ($\Delta H^{\ominus}$) on complexation were determined under identical conditions to those described above using a modified LKB flow microcalorimeter. The modifications included the addition of extra heat exchangers, the incorporation of laboratory-constructed syringe pumps (both of these improved baseline stability), and interfacing of the calorimeter to a microcomputer. The experiments were performed by pumping solutions, of known concentrations, of the metal salt and the ligand under consideration, at predetermined flow rates (and hence stoichiometry). Baselines, before and after the mixing experiments, were obtained. The calorimeter temperature was 25.00 ± 0.01 °C.

Transfer and Extraction Studies.—The transfer and extraction studies involved aqueous chloroform phases. The aqueous source phase was buffered at pH 5.0 (2 mol dm^{-3} $MeCO_2H$–2 mol dm^{-3} $MeCO_2Na$) in each case. The chloroform phase for all experiments contained the macrocyclic ligand (1×10^{-3} mol dm^{-3}) as well as hexadecanoic acid (4×10^{-3} mol dm^{-3}). For the transport experiments involving aqueous source and receiving phases separated by a chloroform phase the receiving phase was maintained at pH 3.0 (1 mol dm^{-3} HCO_2H–1 mol dm^{-3} NaOH). The aqueous source phase for both sets of experiments also contained each metal to be transported/extracted at *ca.* 1.3×10^{-3} mol dm^{-3} as its nitrate salt. The extraction experiments were performed in glass phials (15 cm^{3}) which were shaken on an oscillating shaker for 1 h (at 22 ± 2 °C) at 150 cycles min^{-1}. The 'concentric' transport cell was based on a design previously reported.[6] In the present experiments both aqueous phases and the chloroform phase were stirred independently. Transport runs at 25 °C were terminated after 24 h. Atomic absorption spectroscopy was used to determine the degree of metal ion extraction/transport occurring in the respective experiments.

Synthetic Procedures.—Chemicals were generally used as supplied as were solvents unless stated in the text. Solvents for physical measurements were redistilled and dried prior to use.

2,6-*Bis*(*chloromethyl*)*pyridine*.[7] Thionyl chloride (100 cm^{3}) was added dropwise over 2 h to solid pyridine-2,6-dimethanol (20 g) with stirring and then warmed gently for 4 h. On cooling and addition of toluene (100 cm^{3}) the hydrochloride salt of the product precipitated, and was filtered off, washed with toluene, then diethyl ether and dried. The salt was slurried in water (100 cm^{3}) and neutralised with sodium hydroxide to yield the crude product. This was filtered off, washed with water, dried and recrystallised from light petroleum (b.p. 40–60 °C). Yield = 90–95%; IR (KBr disc)/cm^{-1} 1595 (C=N) and 680 (CCl) [Found (Calc.) for $C_7H_7Cl_2N$: C, 48.0 (47.8); H, 4.3 (4.0); Cl, 37.5 (40.0); N, 7.6 (8.0)%].

2,6-*Bis*(2-*formylphenoxymethyl*)*pyridine*.[8] Freshly prepared potassium 2-formylphenolate (0.5 mol) and 2,6-bis(chloromethyl)pyridine (0.25 mol) were refluxed for 2 h in dimethylformamide (dmf) (200 cm^{3}). The solution was then poured on to ice–water (800 cm^{3}) and the solid product filtered off and recrystallised from acetone with decolourising charcoal. Yield *ca.* 80%; IR (KBr disc)/cm^{-1} 1690 (C=O) and 1585 (C=N); MS (e.i.) *m/z* 347 [Found (Calc.) for $C_{21}H_{17}NO_4$: C, 72.6 (72.4); H, 4.9 (5.2) N, 4.0 (3.7)%]; ^{1}H NMR ($CDCl_3$) δ 10.53 (s, 2 H, CHO), 7.88 (dd, 2 H, aryl H), 7.80 (t, 1 H, pyridine H), 7.60–7.47 (m, 4 H, aryl and pyridine H), 7.13–7.00 (m, 4 H, aryl H) and 5.31 (s, 4 H, OCH_2).

Macrocycle L^1. This was prepared by a modification of the method recorded in ref. 2 in that the preparation was found to be more easily effected by a 'one-pot' synthesis without the isolation of the diimine intermediate.

1,2-Diaminoethane dihydrobromide (20 mmol) and potassium hydroxide (40 mmol) were stirred in warm methanol (400 cm^{3}), manganese(II) bromide (20 mmol) was added, and when the solution had cleared 2,6-bis(2-formylphenoxymethyl)pyridine (20 mmol) was added. The resulting solution was refluxed for 1.5 h and then allowed to cool. Excess of $NaBH_4$ (200 mmol) was added carefully in solid incremental amounts with stirring. When the reduction was completed (*ca.* 0.5 h) the solution was filtered and the filtrate volume reduced to 50 cm^{3} by rotary evaporation. Water (200 cm^{3}) was added and the macrocycle was extracted into chloroform (200 cm^{3}). A brown precipitate was removed by filtration through a well packed filter aid, which was washed with chloroform (100 cm^{3}); the combined chloroform solutions were separated and dried over magnesium sulphate. The chloroform was removed by rotary evaporation to leave a yellow oil. This was dissolved in hot ethyl acetate and refluxed for 0.5 h with some decolourising charcoal; filtration followed by rotary evaporation to low volume (*ca.* 25 cm^{3}) and cooling gave a white solid (*ca.* 50% yield). This was recrystallised from ethyl acetate. IR (KBr disc)/cm^{-1} 3320 (NH); δ_H($CDCl_3$) 2.61 (4 H, s, CH_2CH_2), 3.20 (br 2 H, NH), 3.82 (s, 4 H, CH_2NH), 5.15 (s, 4 H, CH_2O), 6.86, 7.04 (m, 4 H, phenyl), 7.12, 7.20 (m, 4 H, phenyl), 7.33 (d, 2 H, pyridine) and 7.74 (s, 1 H, pyridine); δ_C($CDCl_3$) 48.2, 51.0, 70.3, 111.8, 120.7, 122.2, 128.1, 128.8, 130.6, 137.1, 156.1 and 156.8; MS (FAB) *m/z* 376 [HL^1]$^+$ [Found (Calc.) for $C_{23}H_{25}N_3O_2 \cdot 0.5CH_3OH$: (recrystallised from MeOH–diethyl ether) C, 72.1 (72.4); H, 7.5 (7.3); N, 10.7 (10.8)%].

1:1 (*ligand*:*metal*) *Metal-ion complexes of* L^1. The appropriate metal(II) salt (0.5 mmol) was dissolved in a little methanol (*ca.* 5 cm^{3}) and added to a refluxing solution of L^1 (0.5 mmol) in methanol (*ca.* 10 cm^{3}). An immediate colour change was usually apparent. Products either precipitated directly, after filtration and cooling of the hot solution, or after the volume of the filtered cold solution had been reduced; addition of some diethyl ether (*ca.* 1 cm^{3}) in these cases aided precipitation. The products were filtered off, washed with a little cold ethanol and then diethyl ether. Recrystallisation media are noted in Table 6 for individual complexes. Crystalline products were filtered off,

Table 1 Atom coordinates (× 10^4) for $L^1\cdot0.5MeOH$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
O(1)	−50(7)	1385(3)	−2638(2)	N(4)	4536(7)	3713(4)	−3707(3)
O(2)	−3653(6)	415(3)	−927(3)	N(5)	5486(7)	5303(4)	−1777(3)
N(1)	−480(7)	1282(3)	−1287(3)	N(6)	1413(7)	4435(4)	−2597(3)
N(2)	−3031(8)	−289(4)	−3217(3)	C(24)	4048(9)	3857(4)	−4384(4)
N(3)	−5442(8)	561(4)	−2407(3)	C(25)	4188(10)	3319(5)	−5041(4)
C(1)	−446(9)	1125(4)	−623(4)	C(26)	4866(10)	2610(5)	−5000(4)
C(2)	905(10)	1682(5)	36(4)	C(27)	5348(10)	2426(4)	−4334(4)
C(3)	2288(10)	2411(5)	8(4)	C(28)	5144(9)	3003(4)	−3699(4)
C(4)	2259(10)	2570(5)	−667(4)	C(29)	5635(10)	2798(4)	−2957(4)
C(5)	823(9)	1993(4)	−1304(3)	C(30)	6675(9)	3579(4)	−1632(3)
C(6)	785(10)	2208(4)	−2040(4)	C(31)	6655(9)	2793(4)	−1442(3)
C(7)	−263(9)	1416(5)	−3371(4)	C(32)	7191(10)	2848(5)	−690(4)
C(8)	309(10)	2209(5)	−3556(4)	C(33)	7694(10)	3651(5)	−139(4)
C(9)	26(10)	2167(5)	−4314(4)	C(34)	7688(9)	4438(5)	−341(4)
C(10)	−820(10)	1345(5)	−4860(4)	C(35)	7200(9)	4421(4)	−1095(4)
C(11)	−1394(9)	567(5)	−4659(4)	C(36)	7241(9)	5280(4)	−1317(4)
C(12)	−1144(9)	573(4)	−3908(3)	C(37)	3958(10)	5118(5)	−1430(4)
C(13)	−1705(10)	−267(4)	−3689(4)	C(38)	2193(10)	5199(5)	−1899(4)
C(14)	−4743(9)	−116(5)	−3576(4)	C(39)	−247(9)	4504(5)	−3087(4)
C(15)	−6097(10)	−178(5)	−3094(4)	C(40)	87(10)	5294(5)	−3421(4)
C(16)	−6660(10)	503(5)	−1911(4)	C(41)	−629(11)	6008(6)	−3220(4)
C(17)	−6775(11)	−281(5)	−1588(4)	C(42)	−226(14)	6741(6)	−3496(5)
C(18)	−8408(11)	−1003(5)	−1773(4)	C(43)	863(14)	6760(6)	−3990(5)
C(19)	−8483(15)	−1745(7)	−1510(5)	C(44)	1569(11)	6047(5)	−4205(4)
C(20)	−6916(16)	−1758(6)	−1017(5)	C(45)	1220(10)	5332(5)	−3912(4)
C(21)	−5243(11)	−1049(5)	−799(4)	C(46)	3407(10)	4677(5)	−4383(4)
C(22)	−5206(10)	−330(5)	−1084(4)	C(47)	−4438(32)	−2687(16)	−2504(12)
C(23)	−1907(9)	314(5)	−623(4)	C(48)	−4240(34)	−2335(17)	−2488(12)
O(3)	6182(7)	3609(3)	−2365(2)	O(5)	−3318(18)	−2958(9)	−1962(8)
O(4)	1859(6)	4591(3)	−4076(3)	O(6)	−3397(21)	−2064(9)	−3034(9)

Atoms O(5), O(6), C(47) and C(48) constitute two disordered molecules of methanol, each with 50% occupancy.

washed with ethanol then diethyl ether, and finally air dried. Yields = 30–70%.

2:1 (*ligand:metal*) *Metal ion complexes of* L^1. A solution of the appropriate metal salt (0.5 mmol) in methanol (5 cm^3) was added to a stirred solution of the ligand (1 mmol) in methanol (10 cm^3), and a coloured precipitate developed immediately. The mixture was brought to reflux, the product filtered off, washed with hot methanol, then diethyl ether and air dried. Yields *ca.* 70%. Attempts at recrystallisation failed due either to insolubility or, because when soluble, isolation of the 1:1 (metal:ligand) complexes resulted. Crystals of the complex $NiL^1{}_2(NO_3)_2$ were obtained by dissolving $NiL^1(NO_3)_2$ (100 mg) in methanol (5 cm^3) and standing overnight.

Macrocycle L^2.[9,10] 1,3-Diaminopropane (10 mmol) in methanol (10 cm^3) was added to a solution of 2,6-bis(2-formylphenoxymethyl)pyridine (10 mmol) in hot methanol (400 cm^3). The reaction mixture was refluxed for 30 min, cooled, then solid $NaBH_4$ (30 mmol) was added carefully in incremental amounts. After the effervescence had stopped the solution was filtered, the solvent removed on a rotary evaporator, water (200 cm^3) added to the residues, and the macrocycle extracted into chloroform (2 × 50 cm^3). The chloroform solutions were combined and washed with water (50 cm^3), separated, and dried over anhydrous magnesium sulphate. The chloroform was removed *in vacuo* to leave a pale yellow viscous oil; this was dissolved in hot ethyl acetate with decolourising charcoal and refluxed for 30 min, filtered hot, the volume reduced by rotary evaporation (*ca.* 25 cm^3) and cooled to precipitate the product (yield = 20%). This was recrystallised from hot ethyl acetate. IR (KBr disc)/cm^{-1} 3250 (NH); $\delta_H(CDCl_3)$ 1.76 (q, 2 H, $CH_2CH_2CH_2$), 2.72 (t, 4 H, $CH_2CH_2CH_2$), 3.55 (br d, 2 H, NH), 3.80 (s, 4 H, CH_2NH), 5.04 (s, 4 H, CH_2O), 6.81, 6.98 (m, 4 H, phenyl), 7.27, 7.30 (m, 4, H, phenyl), 7.37 (d, 2 H, pyridine) and 7.63 (s, 1 H, pyridine); $\delta_C(CDCl_3)$ 29.2, 46.6, 48.9, 71.9, 112.4, 121.3, 123.0, 128.2, 129.0, 130.6, 137.4, 155.9 and 157.0; MS (FAB) *m/z* 390 $[HL^2]^+$ [Found (Calc.) for $C_{24}H_{27}N_3O_2$: C, 73.8 (74.0); H, 7.3 (7.0); N, 10.6 (10.8)%].

Metal complexes of L^2. The appropriate metal(II) salt 0.5 mmol) was dissolved in ethanol (5 cm^3) and added to a solution of L^2 (0.5 mmol) in ethanol (5 cm^3); a precipitate developed immediately. The mixture was heated to reflux then filtered hot. Precipitates which did not dissolve were recrystallised from a variety of solvents (see Table 1); other solutions on cooling developed crystalline precipitates. These were filtered off and washed with ethanol then diethyl ether. Yields = 30–60%.

Crystallography.—Three-dimensional, room-temperature X-ray data were collected in the ranges $3.5 < 2\theta < 45°$ ($L^1\cdot0.5MeOH$) and $3.5 < 2\theta < 50°$ {$[CuL^1(H_2O)][ClO_4]_2$, $[NiL^1{}_2(NO_3)]NO_3\cdot2MeOH$} on a Nicolet R3 four-circle diffractometer and in the range $6.5 < 2\theta < 50°$ {$[NiL^1(I)]I\cdot MeOH$} on a Stoe Stadi-2 two-circle diffractometer by the ω-scan method. Complex scattering factors were taken from the program package SHELXTL[11] as implemented on a Data General Nova 3 computer. Unit weights were used throughout the refinements. Tables 1–4 list atomic positional parameters with estimated standard deviations (e.s.d.s).

Crystal data for $L^1\cdot0.5MeOH$. $C_{23.5}H_{27}N_3O_{2.5}$, $M = 391.49$, crystallises from methanol–diethyl ether as colourless needles, crystal dimensions 0.85 × 0.20 × 0.18 mm, triclinic, space group $P\bar{1}$ (C_i^1, no. 2), $a = 7.594(12)$, $b = 15.895(37)$, $c = 18.985(34)$ Å, $\alpha = 103.55(16)$, $\beta = 101.48(14)$, $\gamma = 104.16(15)°$, $U = 2079(7)$ Å^3, $D_c = 1.251$ g cm^{-3}, $Z = 4$, Mo-Kα X-radiation ($\lambda = 0.710\,69$ Å) with graphite monochromator, μ(Mo-Kα) = 0.77 cm^{-1}, $F(000) = 835.85$.

The 3146 independent reflections (of 5437 measured) for which $|F|/\sigma(|F|) > 3.0$ were corrected for Lorentz and polarisation effects, but not for absorption. The structure was solved by multiple-solution direct methods and Fourier techniques and refined by blocked-cascade least squares. A

Table 2 Atom coordinates (× 10^4) for $[CuL^1(H_2O)][ClO_4]_2$

Atom	*x*	*y*	*z*
Cu	2340(1)	2269(1)	−284(1)
O(1)	3978(3)	1467(3)	172(3)
O(2)	1393(4)	3986(3)	−668(3)
O(3)	2151(4)	1949(4)	−1539(3)
N(1)	3503(4)	3236(4)	−454(3)
N(2)	1541(4)	1045(4)	−163(3)
N(3)	2003(4)	2597(4)	880(3)
C(1)	4085(5)	601(4)	612(4)
C(2)	5012(5)	368(5)	1222(4)
C(3)	5061(6)	−516(6)	1617(4)
C(4)	4199(7)	−1142(5)	1428(4)
C(5)	3278(6)	−889(5)	831(4)
C(6)	3199(5)	−21(5)	396(4)
C(7)	1236(5)	4236(5)	753(4)
C(8)	1451(5)	4634(5)	10(4)
C(9)	1675(5)	5589(5)	−49(5)
C(10)	1648(6)	6177(5)	637(5)
C(11)	1434(7)	5816(6)	1382(5)
C(12)	1220(6)	4843(6)	1438(5)
C(13)	4571(5)	3009(4)	−178(4)
C(14)	5418(6)	3525(5)	−408(5)
C(15)	5158(7)	4312(6)	−933(5)
C(16)	4058(7)	4556(5)	−1203(5)
C(17)	3250(5)	4012(5)	−959(4)
C(18)	4841(5)	2155(5)	392(4)
C(19)	2045(6)	4204(5)	−1292(4)
C(20)	2209(5)	185(5)	−299(4)
C(21)	1136(6)	1031(5)	655(4)
C(22)	1876(6)	1668(5)	1290(4)
C(23)	988(5)	3193(5)	821(4)
Cl(1)	1900(4)	7798(3)	−1686(2)
O(4)	2450(8)	8632(6)	−1822(5)
O(5)	1249(8)	7513(7)	−2456(5)
O(6)	1303(8)	7890(7)	−1048(6)
O(7)	2709(8)	786(8)	−1452(7)
Cl(2)	781(3)	−1412(3)	2174(2)
O(8)	534(6)	−1541(8)	1307(4)
O(9)	−161(9)	−1520(15)	2512(8)
O(10)	1586(12)	−2035(9)	2509(8)
O(11)	1201(13)	−505(7)	2402(8)
Cl(3)	1733(6)	7872(6)	−1679(5)
O(12)	2510(11)	8445(12)	−1949(11)
O(13)	697(10)	8271(17)	−1909(12)
O(14)	1989(15)	7774(11)	−808(5)
O(15)	1732(21)	6978(9)	−2064(12)
Cl(4)	630(4)	−1508(4)	2307(3)
O(16)	−76(15)	−787(9)	1960(11)
O(17)	1025(17)	−1250(13)	3140(7)
O(18)	1490(18)	−1608(17)	1891(19)
O(19)	83(13)	−2367(8)	2291(10)

Atoms Cl(1) and O(4)–O(7) comprise a perchlorate anion with occupancy 0.67, Cl(2) and O(8)–O(11) a perchlorate anion with occupancy 0.63, Cl(3) and O(12)–O(15) a perchlorate anion with occupancy 0.33 and Cl(4) and O(16)–O(19) a perchlorate anion with occupancy 0.37.

Table 3 Atom coordinates (× 10^4) for $[NiL^1(I)]I{\cdot}MeOH$

Atom	*x*	*y*	*z*
Ni	1837(1)	−991(1)	919(1)
I(1)	1106(1)	1766(1)	474(1)
I(2)	6993(1)	1301(1)	1887(1)
O(1)	368(5)	−1088(7)	1359(3)
O(2)	3530(5)	−526(8)	783(3)
O(3)	4326(9)	6790(15)	1880(4)
N(1)	2267(7)	138(10)	1589(3)
N(2)	2237(7)	−3160(10)	1205(3)
N(3)	1597(6)	−2013(9)	192(3)
C(1)	−1436(12)	−5003(16)	1353(5)
C(2)	−306(11)	−5054(14)	1459(5)
C(3)	297(9)	−3729(12)	1471(4)
C(4)	−252(8)	−2413(13)	1369(4)
C(5)	−1373(9)	−2341(15)	1239(4)
C(6)	−1966(10)	−3668(18)	1236(5)
C(7)	371(10)	−174(15)	1835(5)
C(8)	1482(9)	573(12)	1916(4)
C(9)	1680(11)	1644(14)	2320(4)
C(10)	2707(11)	2271(16)	2360(5)
C(11)	3521(10)	1810(14)	2022(4)
C(12)	3270(9)	730(12)	1630(4)
C(13)	4102(9)	125(14)	1266(4)
C(14)	4172(8)	−1328(12)	431(4)
C(15)	5295(8)	−1579(13)	528(4)
C(16)	5868(10)	−2416(16)	172(5)
C(17)	5332(11)	−3026(15)	−283(5)
C(18)	4219(9)	−2762(13)	−387(5)
C(19)	3618(8)	−1901(12)	−33(4)
C(20)	2428(8)	−1497(13)	−199(4)
C(21)	1523(9)	−3650(12)	261(4)
C(22)	2323(9)	−4155(11)	727(4)
C(23)	1510(9)	−3749(14)	1633(4)
C(24)	5022(27)	5415(30)	1764(10)

Atom I(2) is an iodide anion, O(3) and C(24) comprise a molecule of methanol of solvation.

molecule of methanol was found to be equally disordered between two interpenetrating sites in the lattice, and was refined with a fixed C–O of 1.417 Å. Hydrogen atoms were included in calculated positions, with isotropic thermal parameters related to those of the supporting atom, and refined in riding mode. Refinement converged at a final *R* 0.0770 (530 parameters; mean and maximum final Δ/σ 0.003 and 0.013 respectively), with allowance for the thermal anisotropy of all non-hydrogen atoms. A final difference electron-density synthesis showed minimum and maximum values of −0.23 and +0.42 e $Å^{-3}$.

Crystal data for $[CuL^1(H_2O)][ClO_4]_2$. $C_{23}H_{27}Cl_2CuN_3O_{11}$, *M* = 655.92, crystallises from methanol as deep blue prisms, crystal dimensions 0.50 × 0.30 × 0.30 mm, monoclinic, space group $P2_1/n$ (non-standard form of $P2_1/c$, C^5_{2h}, no 14), *a* = 12.350(27), *b* = 13.879(16), *c* = 15.954(30) Å, β = 101.16(8)°, *U* = 2683(8) $Å^3$, D_c = 1.624 g cm^{-3}, *Z* = 4, Mo-Kα X-radiation (λ = 0.710 69 Å) with graphite monochromator, μ(Mo-Kα) = 10.78 cm^{-1}, *F*(000) = 1347.78.

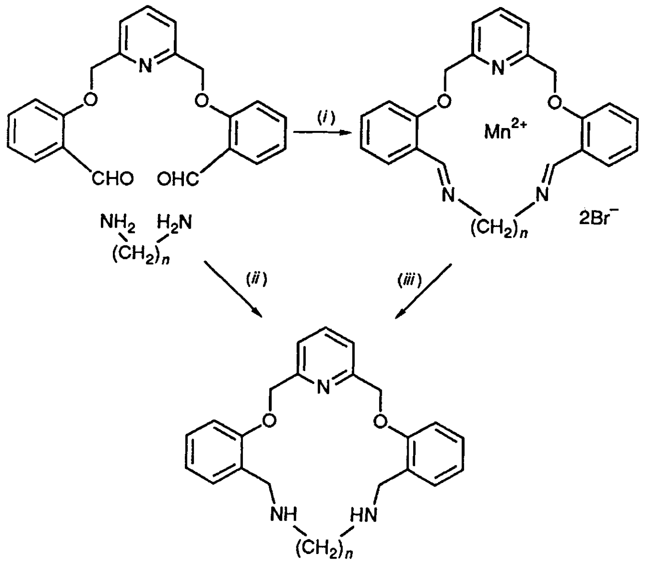
The 3266 independent reflections (of 5172 measured) for which $|F|/\sigma(|F|) > 3.0$ were corrected for Lorentz and polarisation effects, and for absorption by the analysis of 10 azimuthal scans. The structure was solved by Patterson and Fourier techniques and refined by blocked-cascade least-squares methods. The perchlorate anions were each found to be disordered in interpenetrating sites. The occupancies of the two components in each site were optimised with T_d geometry constrained for each component. Hydrogen atoms were included in calculated positions, with isotropic thermal parameters related to those of the supporting atom, and refined in riding mode. Refinement converged at a final *R* 0.0603 (452 parameters; mean and maximum final Δ/σ 0.030 and 0.287 respectively), with allowance for the thermal anisotropy of all non-hydrogen atoms. A final difference electron-density synthesis showed minimum and maximum values of −0.47 and +0.50 e $Å^{-3}$.

Crystal data for $[NiL^1(I)]I{\cdot}MeOH$. $C_{24}H_{29}I_2N_3NiO_3$, *M* =

Table 4 Atom coordinates (× 10^4) for $[NiL^1_2(NO_3)]NO_3 \cdot 2MeOH$

Atom	*x*	*y*	*z*
Ni	0	−1930(3)	2500
O(1)	440(12)	−3152(18)	5350(11)
O(2)	−2078(10)	−2360(16)	3553(10)
O(3)	0	−4532(24)	2500
O(4)	−501(11)	−3263(14)	2624(12)
O(5)	−137(37)	676(25)	2481(48)
O(6)	656(37)	1669(25)	2909(48)
O(6a)	−332(37)	2051(25)	2144(48)
O(7)	1158(14)	161(21)	3938(13)
N(1)	−1157(16)	−3155(23)	5015(15)
N(2)	434(10)	−1758(15)	3719(11)
N(3)	−846(12)	−1116(17)	2678(13)
N(4)	0	−3698(23)	2500
N(5)	67(37)	1463(25)	2501(48)
C(1)	−1814(16)	−3431(19)	4596(16)
C(2)	−1992(19)	−4350(18)	4574(19)
C(3)	−1491(15)	−4963(27)	5003(18)
C(4)	−830(17)	−4638(21)	5429(18)
C(5)	−618(20)	−3728(24)	5448(20)
C(6)	59(15)	−3338(21)	5887(16)
C(7)	1015(10)	−2593(14)	5569(13)
C(8)	1344(10)	−2316(14)	6328(13)
C(9)	1947(10)	−1745(14)	6510(13)
C(10)	2221(10)	−1452(14)	5934(13)
C(11)	1892(10)	−1730(14)	5175(13)
C(12)	1289(10)	−2300(14)	4992(13)
C(13)	915(17)	−2498(22)	4156(16)
C(14)	−185(13)	−1647(18)	3995(15)
C(15)	−621(17)	−871(23)	3502(17)
C(16)	−1522(14)	−1663(20)	2440(16)
C(17)	−2168(9)	−1237(14)	2611(12)
C(18)	−2491(9)	−463(14)	2187(12)
C(19)	−3108(9)	−87(14)	2288(12)
C(20)	−3402(9)	−483(14)	2814(12)
C(21)	−3079(9)	−1257(14)	3238(12)
C(22)	−2462(9)	−1634(14)	3137(12)
C(23)	−2285(19)	−2714(25)	4164(19)
C(24)	1140(20)	512(26)	4649(20)

Atoms O(5), O(6), O(6a) and N(5) comprise an unco-ordinated nitrate anion, which is disordered across the crystallographic C_2 axis, and each have 50% occupancy, O(7) and C(24) constitute a methanol molecule of solvation, and Ni(1), O(3) and N(4) lie on the C_2 axis and were assigned 50% occupancy during refinement.



Scheme 1 (*i*) $n = 2$, MeOH, $MnBr_2 \cdot 4H_2O$; (*ii*) $n = 3$, MeOH; (*a*) reflux, (*b*) $NaBH_4$; (*iii*) $NaBH_4$, MeOH

720.03, crystallises from methanol–ethanol as purple prisms, crystal dimensions 0.58 × 0.17 × 0.12 mm, monoclinic, space group $P2_1/c$ (C^5_{2h}, no 14) $a = 11.990(16)$, $b = 9.000(24)$, $c = 24.754(65)$ Å, $\beta = 92.42(9)°$, $U = 2669(11)$ Å^3, $D_c = 1.792$ g cm^{-3}, $Z = 4$, Mo-Kα X-radiation ($\lambda = 0.710\,69$ Å) with graphite monochromator, μ(Mo-Kα) = 30.47 cm^{-1}, $F(000) = 1407.80$.

The 3154 independent reflections (of 5247 measured) for which $I/\sigma(I) > 3.0$ were corrected for Lorentz and polarisation effects, and for absorption by the Gaussian integration method. The structure was solved by Patterson and Fourier techniques and refined by blocked-cascade least-squares methods. Hydrogen atoms were included in calculated positions, with isotropic thermal parameters related to those of the supporting atom, and refined in riding mode. Refinement converged at a final R 0.0509 (301 parameters; mean and maximum final Δ/σ 0.000 and 0.007 respectively), with allowance for the thermal anisotropy of all non-hydrogen atoms. A final difference electron-density synthesis showed minimum and maximum values of −1.10 and +0.96 e Å^{-3}.

Crystal data for $[NiL^1_2(NO_3)]NO_3 \cdot 2MeOH$. $C_{48}H_{58}N_8NiO_{12}$, $M = 997.74$, crystallises from methanol as pale blue needles, crystal dimensions 0.90 × 0.20 × 0.15 mm, monoclinic, space group $C2/c$ (C^6_{2h}, no. 15) $a = 19.665(29)$, $b = 14.449(28)$, $c = 18.335(19)$ Å, $\beta = 108.44(9)°$, $U = 4942(13)$ Å^3, $D_c = 1.341$ g cm^{-3}, $Z = 4$, Mo-Kα X-radiation ($\lambda = 0.710\,69$ Å) with graphite monochromator, μ(Mo-Kα) = 4.58 cm^{-1}, $F(000) = 2103.58$.

The 1388 independent reflections (of 4678 measured) for which $|F|/\sigma(|F|) > 3.0$ were corrected for Lorentz and polarisation effects, and for absorption by the analysis of eight azimuthal scans. Crystal decay of 30% magnitude was detected during the necessarily rapid data collection, and a correction was made, based on the monitoring of a standard reflection. The structure was solved by Patterson and Fourier techniques and refined by blocked-cascade least-squares methods. The phenyl rings were constrained to possess D_{6h} symmetry (C–C 1.395 Å), and the unco-ordinated nitrate anion, which was disordered near to the crystallographic C_2 axis, was refined with constrained D_{3h} geometry. Hydrogen atoms were included in calculated positions, with isotropic thermal parameters related to those of the supporting atom, and refined in riding mode. Refinement converged at a final R 0.1655 (154 parameters; mean and maximum final Δ/σ 0.017 and 0.303 respectively), with allowance for the thermal anisotropy of the nickel atom, the heteroatoms of the macrocycle, and the methanolic oxygen atom only. A final difference electron-density synthesis showed minimum and maximum values of −1.67 and +1.58 e Å^{-3}.

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

Results and Discussion

The N_3O_2 *Macrocycles.*—Ligand L[1] was synthesised in *ca.* 50% yield *via* Mn^{II}-templated cyclocondensation of the precursor dialdehyde and diamine followed by an *in situ* reductive demetallation of the manganese(II) Schiff-base intermediate by $NaBH_4$ (Scheme 1).[2] Attempts to synthesise L[2] by the same route failed and so a non-template approach [10] was used and gave yields *ca.* 20%. Careful recrystallisation from ethyl acetate was required to obtain the product which was often contaminated by higher oligomers. The precursor

Table 5 Bond lengths (Å) and angles (°) for $L^1 \cdot 0.5MeOH$

O(1)–C(6)	1.420(7)	O(1)–C(7)	1.381(9)	O(3)–C(30)	1.383(9)	O(4)–C(45)	1.373(10)
O(2)–C(22)	1.376(8)	O(2)–C(23)	1.401(9)	O(4)–C(46)	1.403(10)	N(4)–C(24)	1.353(10)
N(1)–C(1)	1.339(10)	N(1)–C(5)	1.319(9)	N(4)–C(28)	1.322(10)	N(5)–C(36)	1.454(9)
N(2)–C(13)	1.476(11)	N(2)–C(14)	1.463(10)	N(5)–C(37)	1.448(10)	N(6)–C(38)	1.471(8)
N(3)–C(15)	1.438(8)	N(3)–C(16)	1.448(11)	N(6)–C(39)	1.454(10)	C(24)–C(25)	1.377(10)
C(1)–C(2)	1.389(8)	C(1)–C(23)	1.480(10)	C(24)–C(46)	1.499(12)	C(25)–C(26)	1.361(12)
C(2)–C(3)	1.380(10)	C(3)–C(4)	1.361(11)	C(26)–C(27)	1.364(11)	C(27)–C(28)	1.395(10)
C(4)–C(5)	1.400(8)	C(5)–C(6)	1.510(11)	C(28)–C(29)	1.515(11)	C(30)–C(31)	1.377(11)
C(7)–C(8)	1.379(12)	C(7)–C(12)	1.391(9)	C(30)–C(35)	1.388(9)	C(31)–C(32)	1.381(10)
C(8)–C(9)	1.395(11)	C(9)–C(10)	1.373(9)	C(32)–C(33)	1.359(10)	C(33)–C(34)	1.392(13)
C(10)–C(11)	1.373(12)	C(11)–C(12)	1.399(10)	C(34)–C(35)	1.398(11)	C(35)–C(36)	1.516(11)
C(12)–C(13)	1.479(11)	C(14)–C(15)	1.507(12)	C(37)–C(38)	1.506(11)	C(39)–C(40)	1.526(12)
C(16)–C(17)	1.504(13)	C(17)–C(18)	1.385(11)	C(40)–C(41)	1.382(13)	C(40)–C(45)	1.391(12)
C(17)–C(22)	1.402(11)	C(18)–C(19)	1.379(15)	C(41)–C(42)	1.377(15)	C(42)–C(43)	1.368(16)
C(19)–C(20)	1.367(16)	C(20)–C(21)	1.388(12)	C(43)–C(44)	1.381(14)	C(44)–C(45)	1.371(12)
C(21)–C(22)	1.372(13)	O(3)–C(29)	1.403(8)	C(47)–O(5)	1.417	C(48)–O(6)	1.417
C(6)–O(1)–C(7)	118.9(5)	C(22)–O(2)–C(23)	116.0(6)	C(29)–O(3)–C(30)	118.9(6)	C(45)–O(4)–C(46)	117.5(6)
C(1)–N(1)–C(5)	118.0(5)	C(13)–N(2)–C(14)	111.0(6)	C(24)–N(4)–C(28)	116.5(6)	C(36)–N(5)–C(37)	111.9(6)
C(15)–N(3)–C(16)	114.2(5)	N(1)–C(1)–C(2)	122.1(6)	C(38)–N(6)–C(39)	112.4(6)	N(4)–C(24)–C(25)	123.6(7)
N(1)–C(1)–C(23)	116.8(5)	C(2)–C(1)–C(23)	121.1(7)	N(4)–C(24)–C(46)	116.0(6)	C(25)–C(24)–C(46)	120.4(7)
C(1)–C(2)–C(3)	119.3(7)	C(2)–C(3)–C(4)	118.6(6)	C(24)–C(25)–C(26)	117.6(7)	C(25)–C(26)–C(27)	121.1(7)
C(3)–C(4)–C(5)	118.8(6)	N(1)–C(5)–C(4)	123.1(7)	C(26)–C(27)–C(28)	117.2(7)	N(4)–C(28)–C(27)	123.9(7)
N(1)–C(5)–C(6)	119.3(5)	C(4)–C(5)–C(6)	117.6(6)	N(4)–C(28)–C(29)	118.2(6)	C(27)–C(28)–C(29)	117.9(7)
O(1)–C(6)–C(5)	108.5(6)	O(1)–C(7)–C(8)	123.4(5)	O(3)–C(29)–C(28)	109.0(6)	O(3)–C(30)–C(31)	123.8(5)
O(1)–C(7)–C(12)	113.7(7)	C(8)–C(7)–C(12)	122.9(7)	O(3)–C(30)–C(35)	113.8(6)	C(31)–C(30)–C(35)	122.5(6)
C(7)–C(8)–C(9)	118.8(6)	C(8)–C(9)–C(10)	119.9(7)	C(30)–C(31)–C(32)	118.6(6)	C(31)–C(32)–C(33)	121.6(8)
C(9)–C(10)–C(11)	119.9(7)	C(10)–C(11)–C(12)	122.5(6)	C(32)–C(33)–C(34)	119.0(7)	C(33)–C(34)–C(35)	121.6(6)
C(7)–C(12)–C(11)	115.9(7)	C(7)–C(12)–C(13)	121.4(6)	C(30)–C(35)–C(34)	116.8(7)	C(30)–C(35)–C(36)	121.6(6)
C(11)–C(12)–C(13)	122.6(5)	N(2)–C(13)–C(12)	116.1(6)	C(34)–C(35)–C(36)	121.7(6)	N(5)–C(36)–C(35)	116.9(5)
N(2)–C(14)–C(15)	109.8(6)	N(3)–C(15)–C(14)	112.5(5)	N(5)–C(37)–C(38)	110.4(6)	N(6)–C(38)–C(37)	110.2(7)
N(3)–C(16)–C(17)	114.6(7)	C(16)–C(17)–C(18)	122.7(7)	N(6)–C(39)–C(40)	115.8(6)	C(39)–C(40)–C(41)	121.8(7)
C(16)–C(17)–C(22)	121.5(6)	C(18)–C(17)–C(22)	115.8(8)	C(39)–C(40)–C(45)	119.8(7)	C(41)–C(40)–C(45)	118.3(8)
C(17)–C(18)–C(19)	122.7(8)	C(18)–C(19)–C(20)	119.2(8)	C(40)–C(41)–C(42)	121.0(9)	C(41)–C(42)–C(43)	120.0(10)
C(19)–C(20)–C(21)	120.9(10)	C(20)–C(21)–C(22)	118.3(8)	C(42)–C(43)–C(44)	119.8(9)	C(43)–C(44)–C(45)	120.2(9)
O(2)–C(22)–C(17)	112.0(7)	O(2)–C(22)–C(21)	125.0(7)	O(4)–C(45)–C(40)	113.7(7)	O(4)–C(45)–C(44)	125.6(8)
C(17)–C(22)–C(21)	123.0(7)	O(2)–C(23)–C(1)	106.5(7)	C(40)–C(45)–C(44)	120.6(8)	O(4)–C(46)–C(24)	107.5(6)

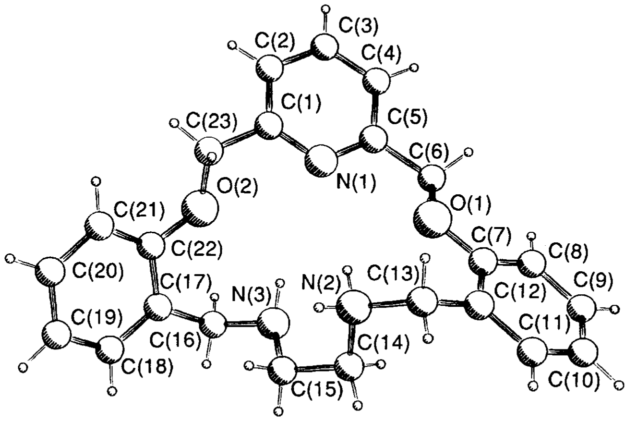


Fig. 1 The molecular structure with atom labelling of the macrocycle L^1

dialdehyde was prepared using a modified literature procedure.[7,8] The macrocycles were characterised by microanalysis, FAB, MS and NMR spectroscopy (^1H and ^{13}C). The protonation constants of the macrocycles were determined in 95% MeOH (0.1 mol dm^{-3} NEt_4ClO_4, 25 °C) using the potentiometric (pH) titration method previously described.[5] The respective first protonation constants (log β_1) have values (9.08, L^1; 10.40, L^2) which are typical of secondary amines; as expected the second protonations (log β_2) occur at lower basicities (15.25, L^1; 17.57, L^2) due to increasing electrostatic repulsions.[12] A third protonation constant (log β_3) was accessible for L^2 (19.86).

The macrocyclic integrity of L^1 was confirmed by an X-ray crystal structure (Fig. 1); bond lengths and angles with e.s.d.s are listed in Table 5. The structure is comprised of two non-symmetry-related molecules of the macrocycle together with a molecule of MeOH. The cyclic molecules are identical with the hydrogens on one of the amine nitrogens [N(2) in the first molecule N(5) in the second] disordered between two sites whereas the remaining amine hydrogens are ordered. These hydrogens [H(N3) and H(N6)] form weak intramolecular hydrogen bonds with their nearest ether oxygen atoms [N(3) ··· O(2) 2.955, H(N3) ··· O(2) 2.34; N(6) ··· O(4) 2.954, H(N6) ··· O(4) 2.34 Å]. The hydrogens on the other two nitrogen atoms can either form weak intramolecular hydrogen bonds with their own nearest ether oxygen atoms [N(2) ··· O(1) 2.847, H(N2a) ··· O(1) 2.24; N(5) ··· O(3) 2.881, H(N5a) ··· O(3) 2.28 Å], or can interact more strongly with an oxygen atom in one of the components of the methanol solvent molecule [N(2) ··· O(6) 2.876, H(N2b) ··· O(6) 1.94 Å] or with the oxygen atom of the other component in a translationally related methanol solvent (operation $1 + x$, $1 + y$, z) [N(5) ··· O(5) 2.818, H(N5b) ··· O(5) 1.88 Å]. This means that at any one time the molecule of macrocycle interacting with the methanol has its amine hydrogens pointing in roughly the opposite direction to each other while the other molecule of macrocycle present in the asymmetric unit has its amine hydrogens pointing in roughly the same direction to form its weak intramolecular hydrogen bonds. Alternatively both molecules could exist together with their disordered hydrogens occupying the same positions in each molecule. The conformation of the macrocycle is such that it does not show a large amount of buckling.

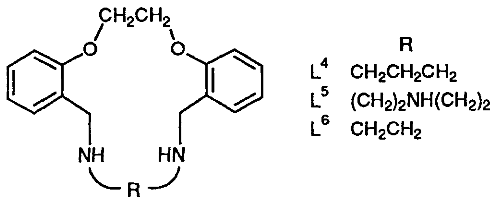
Table 6 Microanalytical and mass spectral data for the complexes of Cu^{II} and Ni^{II}

Complex[a]	Analysis (%)[b] C	H	N	Other	m/z for $[ML(X)]^+$
$NiL^1(NO_3)_2\cdot H_2O$[c]	47.9	4.8	12.0		495
	(47.9)	(4.7)	(12.2)		
$NiL^1(ClO_4)_2$	43.6	3.9	6.5	11.4 Cl	532
	(43.6)	(4.0)	(6.6)	(11.2)	
$NiL^1I_2\cdot 0.75EtOH$[d]	40.6	4.5	6.1	35.6 I	560
	(40.7)	(4.1)	(5.8)	(35.1)	
$CuL^1(NO_3)_2\cdot H_2O$	47.7	4.9	12.2		500
	(47.5)	(4.7)	(12.0)		
$CuL^1(ClO_4)_2\cdot H_2O$	41.9	4.1	6.4	10.9 Cl	537
	(42.1)	(4.2)	(6.4)	(10.9)	
$NiL^1_2(ClO_4)_2\cdot 4H_2O$	51.2	5.2	7.4	6.8 Cl	907
	(51.1)	(5.4)	(7.8)	(6.6)	
$NiL^1_2(NO_3)_2\cdot 2H_2O$	56.9	5.5	11.6		870
	(57.0)	(5.6)	(11.6)		
$CuL^1_2(ClO_4)_2\cdot H_2O\cdot MeOH$	52.8	5.3	7.3	6.7 Cl	913
	(53.1)	(5.3)	(7.9)	(6.7)	
$CuL^1_2(NO_3)_2\cdot 3H_2O$	55.6	5.7	11.0		875
	(55.7)	(5.7)	(11.3)		
$NiL^2(ClO_4)_2\cdot 3H_2O$[d]	40.5	4.1	6.2	10.2 Cl	546
	(41.1)	(4.7)	(6.0)	(10.1)	
$NiL^2(NO_3)_2\cdot 0.5H_2O\cdot EtOH$[d]	49.6	5.6	11.0		509
	(49.8)	(5.5)	(11.2)		
$CuL^2(ClO_4)_2\cdot H_2O$[d]	42.9	4.5	6.1	10.6 Cl	551
	(43.0)	(4.4)	(6.3)	(10.6)	
$CuL^2(NO_3)_2\cdot H_2O$[d]	48.8	4.8	11.6		514
	(48.4)	(4.9)	(11.8)		

[a] Recrystallised from MeOH unless otherwise stated. [b] Calculated values in parentheses. [c] Recrystallised from MeOH–EtOH. [d] Recrystallised from EtOH.

Table 7 Spectrophotometric data in dmso for the complexes of Cu^{II} and Ni^{II}

Metal salt	Isosbestic points/nm	λ/nm (ε/dm^3 mol^{-1} cm^{-1}) 1:1	Colour of complex	λ/nm (ε/dm^3 mol^{-1} cm^{-1}) 1:2	Colour of complex
For L^1					
$Cu(ClO_4)_2$	616	650 (150)	Royal blue	606 (133)	Purple
$Cu(NO_3)_2$	646	650 (160)	Royal blue	608 (182)	Purple
$Ni(ClO_4)_2$	666	660 (3.7)	Emerald green	622 (5.8)	Blue
	398	388 (17)		378 (22)	
$Ni(NO_3)_2$	672	656 (5.7)	Mauve	594 (9.1)	Blue
	416	388 (14.8)		366 (26.8)	
For L^2					
$Cu(ClO_4)_2$	622	664 (117)	Pale blue	658 (121)	
$Ni(ClO_4)_2$		670 (8.2)	Pale green		
		392 (22)			



Copper(II) *and Nickel*(II) *Complexes of* L^1 *and* L^2.—A series of metal complexes having 1:1 and 1:2 (metal:ligand) stoichiometries have been isolated from alcohol solutions and data concerning their characterisation are summarised in Table 6. The IR spectra of the complexes show secondary amine stretches in the region 3100–3300 cm^{-1} which are split and/or shifted relative to that of the corresponding free macrocycle (L^1, 3320; L^2 3250 cm^{-1}). Individual spectra are consistent with the presence of water, or other solvent when suggested to be present from the microanalytical data. Anion stretches were generally split or broadened due to co-ordination or hydrogen bonding. The FAB mass spectra contained peaks corresponding to $[ML(X)]^+$ ($L = L^1$ or L^2) for the 1:1 complexes and $[ML_2X]^+$ for the 1:2 complexes. A strong peak corresponding to $[HL]^+$ was also evident in the latter spectra.

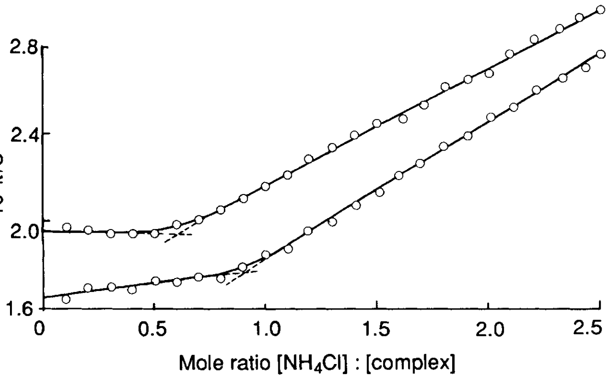


Fig. 2 Conductimetric titrations of L^2 with Ni^{II} (upper curve) and with Cu^{II} (lower curve)

Spectrophotometric titrations in dmso of nitrates or perchlorates of Cu^{II} or Ni^{II} with a solution of L^1 indicated the initial formation of a 1:1 species followed by formation of a 1:2 species in each case (Table 7). The shift of the bands to higher energy noted for the 1:2 complexes suggests a larger nitrogen-donor contribution to the donor set for these species. Similar solution behaviour has been reported for the related N_2O_2 macrocycle L^4 with Cu^{II}.[13] When parallel experiments were performed using L^2, Cu^{II} again yielded spectrophotometric behaviour which was in accordance with the formation of 1:1 and 1:2 species (with a clear isosbestic point being evident). In contrast, for Ni^{II}, the titration only gave evidence for the formation of a 1:1 species.

Conductometric titrations of the respective $ML(ClO_4)_2$ species with NH_4Cl in dmso[13] have also been carried out (Fig. 2); all of the complexes were initially shown to be 1:2 electrolytes. For each of the copper(II) systems an inflection was observed at a 1:1 ($[NH_4Cl]$:[complex]) mole ratio indicating the formation of a 1:1 adduct which is presumably of type $[ML(Cl)]^+$. In contrast, for both nickel(II) complexes inflections were detected at 1:2 ($[NH_4Cl]$:[complex]) mole ratios; it appears likely that such behaviour reflects the formation of dinuclear complexes (each containing a bridging chloride anion).

Thermodynamic stability constants (Table 8) were measured in 95% MeOH by the potentiometric (pH) titration method using the apparatus described previously.[5] The stability constants determined for the 1:1 complexes of Ni^{II} with both macrocycles were found to be closer to the log K value of 5.4 reported for the related N_2O_2 macrocycle L^4 than to the value of 10.0 (ref. 5) for the complex of N_3O_2 macrocycle L^5. This suggests that not all of the donor atoms (and possibly only the aliphatic nitrogen atoms) of L^1 and L^2 are bound to the Ni^{II} in solution. The drop of 1.51 log units on passing from the nickel(II) complex of L^1 to that of L^2 is probably a consequence of the substitution of a less stable six-membered chelate ring in L^2 for a five-membered chelate ring in L^1.[9] On passing from the copper(II) complex of L^1 to that of L^2 there is a marked drop in stability (Δ log K = 5.20). This difference seems too large to be accounted for purely on the basis of an increase in the size of a single chelate ring and hence a change in geometry and/or co-ordination number has probably occurred. Comparison with related systems shows that the 1:1 (metal:ligand) copper(II) complex of L^1 has a stability constant which is similar to those

Table 8 Thermodynamic stability constants and the enthalpies and entropies of co-ordination of the complexes of Cu^{II} and Ni^{II}

	Metal : ligand ratio	log *K*		ΔH*/kJ mol^{-1}		ΔS/ J K^{-1} mol^{-1}	
		L^1	L^2	L^1	L^2	L^1	L^2
Cu	1 : 1	13.92	8.72	−30.61	−26.80	160	74
	1 : 2			−8.94	3.46		
Ni	1 : 1	6.66	5.15	−5.04		110	
	1 : 2			−21.59			

* Estimated error *cq.* ±2%

Table 9 Extraction and transport data for systems incorporating macrocycles L^1 and L^2 [a]

	Extraction ratio, D_m [b]		Relative transport rates /mol h^{-1}	
Metal	L^1	L^2	L^1	L^2
Ni^{II}	0[c]	0.04	2.1×10^{-9}	1.1×10^{-9}
Cu^{II}	0.04	0.06	4.0×10^{-7}	2.2×10^{-8}
Ni^{II}/Cu^{II} [d]	0[c]/0.04	0.02/0.06	0[c]/4.9×10^{-7}	1.1×10^{-9}/ 2.6×10^{-8}

[a] The initial concentration of the respective metal nitrates in the aqueous source phase was $(1.3 \pm 0.1) \times 10^{-2}$ mol dm^{-3} in each case. All experiments were performed in duplicate or triplicate, the error for the metal extractions being ±20% while for metal transport it is estimated as ±15%. [b] $D_m = [M^{2+}]_{org}/[M^{2+}]_{total}$. [c] The nickel concentration was below the detection limit. [d] Competitive metal experiments; the concentration of each metal in the aqueous source phase was once again 1.3×10^{-2} mol dm^{-3}.

for the corresponding complexes of other N_3O_2 macrocycles (*e.g.* L^5, log $K = 14.4$), whereas the value for L^2 is similar to those for particular N_2O_2 macrocycles (*e.g.* L^6, log $K = 8.2$). A comparison of the stability constants for the complexes of Cu^{II} and Ni^{II} with both macrocycles shows that L^1 gives enhanced discrimination for Cu^{II}, although the stability trends observed for both ligand systems still follow the Irving–Williams series.[14]

In investigations of the thermodynamic properties of transition-metal complexes, systems involving acyclic[15] and cyclic[16,17] all-nitrogen ligands have been most studied and the measurements have been obtained in water.[18] In contrast, in the present study the enthalpy changes ($\Delta H°$) on co-ordination of the mixed-donor ligands were determined in 95% MeOH (using flow microcalorimetry) (Table 8). For polyamine ligands addition of a second ligand generally has a higher enthalpy of complexation than for the first[19] and this was observed to be the case for the interaction of L^1 and L^2 with Cu^{II}.

Favourable enthalpies and entropies occur for the 1:1 complexes of Cu^{II} with L^1 and L^2 and the enthalpies are nearly equivalent suggesting that similar donor environments are present. However, the entropies show a marked drop from L^1 to L^2 reflecting the observed drop in stability. This may be ascribed to a change in co-ordination geometry and/or number between the complexes. For example, in the complex of L^2, non-co-ordination of one or both ether oxygens may occur; the non-co-ordination of such donors to Cu^{II} has been previously documented.[14,20] In the X-ray structure of $[CuL^1(H_2O)][ClO_4]_2$ a long Cu–O bond (2.67 Å) is observed (see below) suggesting that in solution one ether oxygen of L^2 may be non-co-ordinating. In the case of Ni^{II} with L^1, the enthalpies for addition of the second ligand are lower than for addition of the first; while this is very likely associated with the change in co-ordination geometry around the metal ion on moving from endo- to exo-macrocyclic co-ordination, in the absence of further data it appears inappropriate to speculate on the reasons for the observed behaviour.

Extraction experiments (water–chloroform) and related transport experiments (water–chloroform–water) were successfully carried out using L^1 and L^2 in the respective chloroform phases which, in each case, also contained hexadecanoic acid. The use of hexadecanoate as a counter ion in the chloroform phase to inhibit bleeding into the aqueous phase of charged species such as the protonated macrocycle and/or the corresponding metal complexes has been discussed previously.[21] For the transport runs, the pH gradient across the cell served to 'drive' the transfer of metal from the source to the receiving phase in an analogous manner to that previously described.[22] The results of the present experiments are summarised in Table 9. Under the conditions employed, in all single-metal extraction and transport studies, Cu^{II} was favoured over Ni^{II}. Clearly the results from these transport and extraction studies parallel each other. In particular the transport results follow the respective log *K* values for the individual complexes although it is noted that this need not necessarily be the case.[23,24] The results from the competitive extraction and transport experiments also follow the above trends and confirm the potential of systems such as these for the discrimination of metals of the present type.

X-Ray Crystal Structures.—The X-ray structures of two 1:1 complexes and one 1:2 complex were undertaken.

$[CuL^1(H_2O)][ClO_4]_2$. The structure of the cation is illustrated in Fig. 3 with bond lengths and angles, with e.s.d.s, listed in Table 10. The structure shows the copper atom to be endomacrocyclically bound in a six-co-ordinated restricted-tetragonal rhombic environment provided by the five macrocyclic donor atoms and a water molecule. The Cu–O(ether) bond lengths show the longer copper–donor atom distances with that of Cu–O(2) particularly long (2.673 Å) but within the overall range reported for Cu–O distances (2.11–2.75 Å).[2,13,25] It is probable that the long Cu–O(ether) distances are in part due to Jahn–Teller distortion. Interestingly the macrocycle has been able to accommodate both of these elongated tetragonal bonds leaving the water molecule with a short Cu–O distance (2.02 Å). All of the other donor bond lengths were found to be normal.[2,13]

The conformation of the macrocycle is such that it is fairly twisted in order for one of the amine nitrogens [N(3)] to get above the plane defined by the four other macrocyclic donor atoms. To be able to achieve this a section of the macrocycle containing the phenyl rings must buckle significantly. The nitrogen configurations are *S,S* (or *R,R*), the protons being mutually *trans* to each other.

Each of the aromatic rings is essentially planar. The structure exhibits hydrogen bonding involving both amine hydrogen atoms which bind with the higher-occupancy component of one of the perchlorate anions related to the reference anion by inversion symmetry [operation $-x$, $-y$, $-z$; N(2)···O(8) 2.927, H(N2)···O(8) 2.03 Å] and by screw symmetry [operation $0.5 - x$, $0.5 + y$, $0.5 - z$; N(3)···O(10) 2.859, H(N3)···O(10) 2.11 Å] while one of the water hydrogens H(O3a) forms a hydrogen bond with the higher-occupancy component of the other perchlorate anion by another screw-axis symmetry operation [$0.5 - x$, $-0.5 + y$, $-0.5 - z$; O(3)··· O(5) 2.884, H(O3a)··· O(5) 2.20 Å].

$[NiL^1(I)]I{\cdot}MeOH$. The structure of the cation is illustrated in Fig. 4 with bond lengths and angles, with e.s.d.s, listed in Table 11. The structure comprises a six-co-ordinate nickel atom endomacrocyclically bound to the full donor set of the macrocycle and with an iodide anion occupying the remaining site. The metal geometry is found to be a distorted octahedron. The 'rigid' $N_{py}O_2$ donor set is meridional with the macrocycle twisting so that the aliphatic nitrogens can co-ordinate to the metal ion. The nickel–donor bond lengths all lie in the ranges expected[2,26] with Ni–N(2) lying *trans* to the iodine being slightly longer than the other two Ni–N bonds. This probably reflects the *trans* influence of the iodide anion.

Table 10 Bond lengths (Å) and angles (°) for $[CuL^1(H_2O)][ClO_4]_2$

Cu–O(1)	2.300(6)	Cu–O(2)	2.673(6)	C(10)–C(11)	1.362(13)	C(11)–C(12)	1.382(12)
Cu–O(3)	2.020(6)	Cu–N(1)	2.021(6)	C(13)–C(14)	1.375(10)	C(13)–C(18)	1.492(9)
Cu–N(2)	1.994(6)	Cu–N(3)	2.031(6)	C(14)–C(15)	1.375(11)	C(15)–C(16)	1.385(12)
O(1)–C(1)	1.384(8)	O(1)–C(18)	1.424(8)	C(16)–C(17)	1.367(11)	C(17)–C(19)	1.504(10)
O(2)–C(8)	1.397(8)	O(2)–C(19)	1.429(9)	C(21)–C(22)	1.512(9)	Cl(1)–O(4)	1.381(10)
N(1)–C(13)	1.345(8)	N(1)–C(17)	1.345(8)	Cl(1)–O(5)	1.388(9)	Cl(1)–O(6)	1.374(11)
N(2)–C(20)	1.490(9)	N(2)–C(21)	1.485(10)	Cl(1)–O(7)	1.403(11)	Cl(2)–O(8)	1.368(7)
N(3)–C(22)	1.468(9)	N(3)–C(23)	1.489(9)	Cl(2)–O(9)	1.381(13)	Cl(2)–O(10)	1.348(14)
C(1)–C(2)	1.391(8)	C(1)–C(6)	1.385(9)	Cl(2)–O(11)	1.383(12)	Cl(3)–O(12)	1.377(18)
C(2)–C(3)	1.374(11)	C(3)–C(4)	1.362(11)	Cl(3)–O(13)	1.377(16)	Cl(3)–O(14)	1.371(11)
C(4)–C(5)	1.380(10)	C(5)–C(6)	1.383(10)	Cl(3)–O(15)	1.386(16)	Cl(4)–O(16)	1.372(16)
C(6)–C(20)	1.510(9)	C(7)–C(8)	1.380(10)	Cl(4)–O(17)	1.371(13)	Cl(4)–O(18)	1.364(28)
C(7)–C(12)	1.383(11)	C(7)–C(23)	1.487(10)	Cl(4)–O(19)	1.367(14)		
C(8)–C(9)	1.361(10)	C(9)–C(10)	1.370(11)				
O(1)–Cu–O(2)	145.4(2)	O(1)–Cu–O(3)	97.6(2)	C(8)–C(9)–C(10)	119.2(7)	C(9)–C(10)–C(11)	121.1(7)
O(2)–Cu–O(3)	90.4(2)	O(1)–Cu–N(1)	76.1(2)	C(10)–C(11)–C(12)	119.1(8)	C(7)–C(12)–C(11)	120.9(7)
O(2)–Cu–N(1)	70.6(2)	O(3)–Cu–N(1)	87.8(2)	N(1)–C(13)–C(14)	122.7(6)	N(1)–C(13)–C(18)	118.4(6)
O(1)–Cu–N(2)	88.7(2)	O(2)–Cu–N(2)	125.4(2)	C(14)–C(13)–C(18)	119.0(6)	C(13)–C(14)–C(15)	118.4(7)
O(3)–Cu–N(2)	86.8(2)	N(1)–Cu–N(2)	163.1(2)	C(14)–C(15)–C(16)	118.9(8)	C(15)–C(16)–C(17)	120.1(7)
O(1)–Cu–N(3)	98.2(2)	O(2)–Cu–N(3)	81.5(2)	N(1)–C(17)–C(16)	121.1(6)	N(1)–C(17)–C(19)	116.9(6)
O(3)–Cu–N(3)	161.9(2)	N(1)–Cu–N(3)	104.5(2)	C(16)–C(17)–C(19)	121.9(6)	O(1)–C(18)–C(13)	108.3(4)
N(2)–Cu–N(3)	84.8(2)	Cu–O(1)–C(1)	124.9(4)	O(2)–C(19)–C(17)	111.7(5)	N(2)–C(20)–C(6)	115.9(5)
Cu–O(1)–C(18)	108.9(3)	C(1)–O(1)–C(18)	117.6(4)	N(2)–C(21)–C(22)	108.6(6)	N(3)–C(22)–C(21)	108.5(5)
Cu–O(2)–C(8)	116.2(3)	Cu–O(2)–C(19)	93.9(4)	N(3)–C(23)–C(7)	111.3(5)	O(4)–Cl(1)–O(5)	108.6(6)
C(8)–O(2)–C(19)	116.9(5)	Cu–N(1)–C(13)	118.6(4)	O(4)–Cl(1)–O(6)	112.9(6)	O(5)–Cl(1)–O(6)	112.3(6)
Cu–N(1)–C(17)	121.6(4)	C(13)–N(1)–C(17)	118.8(5)	O(4)–Cl(1)–O(7)	106.6(6)	O(5)–Cl(1)–O(7)	107.2(7)
Cu–N(2)–C(20)	111.7(4)	Cu–N(2)–C(21)	110.7(4)	O(6)–Cl(1)–O(7)	108.9(7)	O(8)–Cl(2)–O(9)	109.9(6)
C(20)–N(2)–C(21)	114.1(5)	Cu–N(3)–C(22)	105.6(4)	O(8)–Cl(2)–O(10)	108.7(7)	O(9)–Cl(2)–O(10)	112.8(10)
Cu–N(3)–C(23)	112.7(4)	C(22)–N(3)–C(23)	110.8(5)	O(8)–Cl(2)–O(11)	112.6(7)	O(9)–Cl(2)–O(11)	107.2(11)
O(1)–C(1)–C(2)	122.9(6)	O(1)–C(1)–C(6)	115.0(5)	O(10)–Cl(2)–O(11)	105.6(8)	O(12)–Cl(3)–O(13)	110.6(12)
C(2)–C(1)–C(6)	122.2(6)	C(1)–C(2)–C(3)	119.1(6)	O(12)–Cl(3)–O(14)	109.7(11)	O(13)–Cl(3)–O(14)	109.3(13)
C(2)–C(3)–C(4)	120.3(6)	C(3)–C(4)–C(5)	119.7(7)	O(12)–Cl(3)–O(15)	108.6(14)	O(13)–Cl(3)–O(15)	108.7(14)
C(4)–C(5)–C(6)	122.4(7)	C(1)–C(6)–C(5)	116.3(6)	O(14)–Cl(3)–O(15)	109.9(11)	O(16)–Cl(4)–O(17)	106.2(11)
C(1)–C(6)–C(20)	123.5(6)	C(5)–C(6)–C(20)	120.1(6)	O(16)–Cl(4)–O(18)	111.9(14)	O(17)–Cl(4)–O(18)	109.4(14)
C(8)–C(7)–C(12)	118.0(6)	C(8)–C(7)–C(23)	121.9(6)	O(16)–Cl(4)–O(19)	110.8(10)	O(17)–Cl(4)–O(19)	109.2(11)
C(12)–C(7)–C(23)	120.1(7)	O(2)–C(8)–C(7)	114.7(6)	O(18)–Cl(4)–O(19)	109.3(13)		
O(2)–C(8)–C(9)	123.7(6)	C(7)–C(8)–C(9)	121.6(6)				

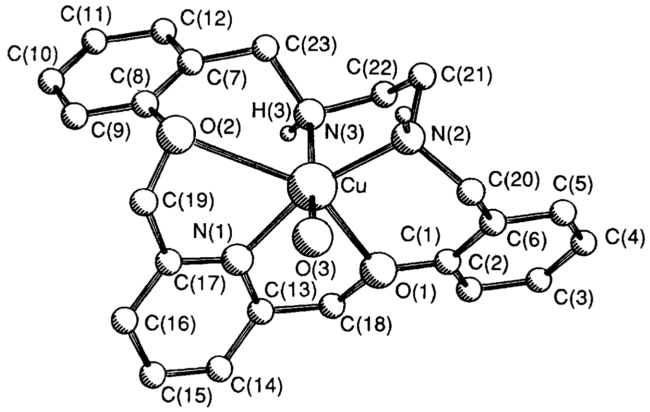


Fig. 3 The molecular structure with atom labelling of the complex cation $[CuL^1(H_2O)]^{2+}$

The conformation of the macrocycle is such that it is twisted in order for the amine nitrogen atom [N(2)] to take up the axial site opposite to the iodide. The nitrogen configurations were again found to be *S,S* (or *R,R*), the protons being mutually *trans* to each other. The conformation of the five-membered chelate ring is *gauche*, the thermodynamically most stable form.

Each of the aromatic rings is essentially planar. There are hydrogen-bonding interactions between an amine hydrogen and an oxygen of the methanol of solvation related by the translation operation [x, $-1 + y$, z; N(2) • • • O(3) 2.952, H(N2) • • • O(3) 2.00 Å] while the other amine hydrogen forms a weak link with one of the iodines in an inversion-related molecule (through $-x$, $-y$, $-z$) [N3 • • • I(1) 3.581, H(N3) • • • I(1) 2.65 Å]. There is a further weak interaction between the hydrogen on the methanol and the non-co-ordinating iodide related by a screw axis [operation $1 - x$, $0.5 + y$, $0.5 - z$; O(3) • • • I(2) 3.524, H(O3) • • • I(2) 2.59 Å].

$[NiL^1_2(NO_3)]NO_3{\cdot}2MeOH$. The structure of the cation is illustrated in Fig. 5 with bond lengths and angles, with e.s.d.s, listed in Table 12. The structure shows the nickel to be again six-co-ordinated the environment being provided by the aliphatic nitrogen atoms from the macrocycles, one pair from each ring, and a bidentate nitrate anion. The Ni^{II} is therefore complexed in an exomacrocyclic manner.

The nickel–donor atom distances are within the expected range[2,26] but the Ni–O(nitrate) distance (2.21 Å) is longer than expected. The distortion from an octahedron is caused by the different ligand bites provided by a bidentate nitrate and the diamino-bridge from the macrocycle. The non-co-ordination of ether oxygens to Ni^{II} has been observed previously for related macrocycles.[2,3]

The conformation of the macrocycle is such that the diamine fragment is 'inverted' in order to provide exomacrocyclic donor sets. This has the result of giving a much more open macrocycle than found for the endomacrocyclic complexes. The configurations of the aliphatic nitrogens are now *R,S* (or *S,R*), the protons being mutually *cis* to each other.

The aromatic rings are essentially planar and the two phenyl rings lie on the same side of the macrocyclic ring plane and are equally inclined to the pyridine ring. The phenyl and pyridine rings are almost mutually perpendicular. There are hydrogen-bonding interactions; one of the amine hydrogens forms a hydrogen bond with the oxygen of the methanol solvent

Table 11 Bond lengths (Å) and angles for [NiL^1(I)]I·MeOH

Ni–I(1)	2.838(19)	Ni–O(1)	2.111(15)	C(3)–C(4)	1.373(18)	C(3)–C(23)	1.492(18)
Ni–O(2)	2.114(15)	Ni–N(1)	1.994(15)	C(4)–C(5)	1.370(17)	C(5)–C(6)	1.390(22)
Ni–N(2)	2.124(17)	Ni–N(3)	2.032(16)	C(7)–C(8)	1.498(19)	C(8)–C(9)	1.402(19)
O(1)–C(4)	1.407(16)	O(1)–C(7)	1.436(17)	C(9)–C(10)	1.354(21)	C(10)–C(11)	1.377(20)
O(2)–C(13)	1.475(16)	O(2)–C(14)	1.389(15)	C(11)–C(12)	1.396(18)	C(12)–C(13)	1.477(18)
O(3)–C(24)	1.527(33)	N(1)–C(8)	1.325(16)	C(14)–C(15)	1.377(16)	C(14)–C(19)	1.402(16)
N(1)–C(12)	1.316(16)	N(2)–C(22)	1.491(17)	C(15)–C(16)	1.367(19)	C(16)–C(17)	1.387(20)
N(2)–C(23)	1.499(17)	N(3)–C(20)	1.491(16)	C(17)–C(18)	1.369(19)	C(18)–C(19)	1.392(18)
N(3)–C(21)	1.486(17)	C(1)–C(2)	1.370(22)	C(19)–C(20)	1.512(17)	C(21)–C(22)	1.537(18)
C(1)–C(6)	1.384(23)	C(2)–C(3)	1.395(19)				
I(1)–Ni–O(1)	89.2(4)	I(1)–Ni–O(2)	92.7(4)	C(4)–C(3)–C(23)	121.0(11)	O(1)–C(4)–C(3)	119.0(10)
O(1)–Ni–O(2)	156.7(5)	I(1)–Ni–N(1)	86.7(5)	O(1)–C(4)–C(5)	118.0(11)	C(3)–C(4)–C(5)	122.8(11)
O(1)–Ni–N(1)	77.5(5)	O(2)–Ni–N(1)	79.4(5)	C(4)–C(5)–C(6)	117.2(12)	C(1)–C(6)–C(5)	121.0(12)
I(1)–Ni–N(2)	173.8(4)	O(1)–Ni–N(2)	88.4(5)	O(1)–C(7)–C(8)	109.8(10)	N(1)–C(8)–C(7)	115.8(10)
O(2)–Ni–N(2)	91.7(5)	N(1)–Ni–N(2)	98.3(5)	N(1)–C(8)–C(9)	122.4(11)	C(7)–C(8)–C(9)	121.8(11)
I(1)–Ni–N(3)	91.3(4)	O(1)–Ni–N(3)	110.4(5)	C(8)–C(9)–C(10)	117.7(12)	C(9)–C(10)–C(11)	119.7(13)
O(2)–Ni–N(3)	92.8(5)	N(1)–Ni–N(3)	171.8(5)	C(10)–C(11)–C(12)	119.7(12)	N(1)–C(12)–C(11)	120.3(11)
N(2)–Ni–N(3)	84.3(5)	Ni–O(1)–C(4)	119.8(7)	N(1)–C(12)–C(13)	116.2(10)	C(11)–C(12)–C(13)	123.4(11)
Ni–O(1)–C(7)	115.2(7)	C(4)–O(1)–C(7)	117.1(9)	O(2)–C(13)–C(12)	109.8(9)	O(2)–C(14)–C(15)	122.7(9)
Ni–O(2)–C(13)	111.5(7)	Ni–O(2)–C(14)	124.0(7)	O(2)–C(14)–C(19)	116.7(9)	C(15)–C(14)–C(19)	120.6(10)
C(13)–O(2)–C(14)	117.6(8)	Ni–N(1)–C(8)	119.5(8)	C(14)–C(15)–C(16)	119.5(11)	C(15)–C(16)–C(17)	120.9(12)
Ni–N(1)–C(12)	118.3(8)	C(8)–N(1)–C(12)	120.2(10)	C(16)–C(17)–C(18)	119.9(12)	C(17)–C(18)–C(19)	120.4(11)
Ni–N(2)–C(22)	108.1(7)	Ni–N(2)–C(23)	115.5(8)	C(14)–C(19)–C(18)	118.6(10)	C(14)–C(19)–C(20)	122.9(10)
C(22)–N(2)–C(23)	114.3(9)	Ni–N(3)–C(20)	111.1(7)	C(18)–C(19)–C(20)	118.2(10)	N(3)–C(20)–C(19)	113.5(9)
Ni–N(3)–C(21)	110.7(7)	C(20)–N(3)–C(21)	115.4(9)	N(3)–C(21)–C(22)	109.9(9)	N(2)–C(22)–C(21)	110.8(9)
C(2)–C(1)–C(6)	120.7(14)	C(1)–C(2)–C(3)	118.9(12)	N(2)–C(23)–C(3)	113.2(9)		
C(2)–C(3)–C(4)	119.3(11)	C(2)–C(3)–C(23)	119.6(11)				

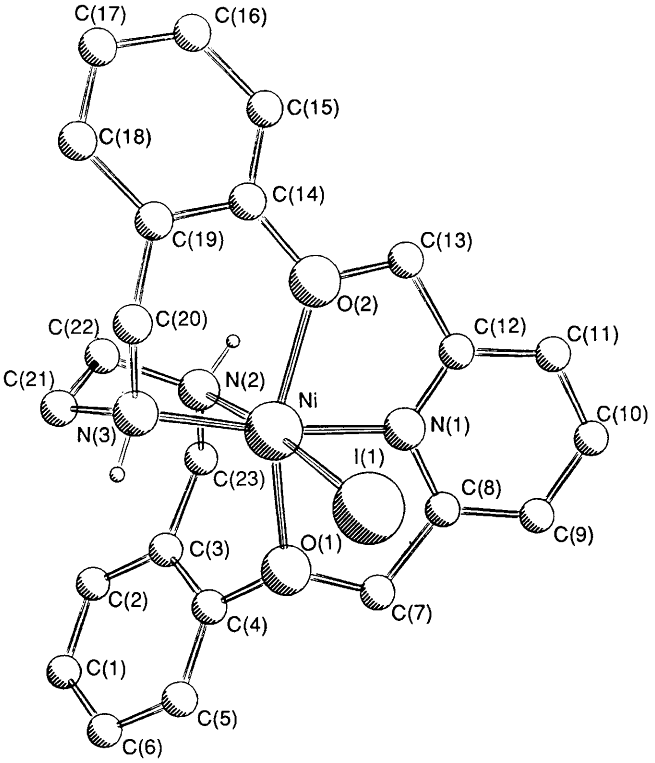


Fig. 4 The molecular structure with atom labelling of the complex cation [NiL^1(I)]$^+$

molecule [N(2) ··· O(7) 3.084, H(N2) ··· O(7) 2.15 Å] while the other amine hydrogen forms a hydrogen bond with one of the oxygens of the non-co-ordinating nitrate [N(3) ··· O(5) 3.016, H(N3) ··· O(5) 2.34 Å]. There is also an interaction between the hydrogen on the methanolic oxygen and an oxygen of the non-co-ordinating nitrate [O(7) ··· O(6) 2.846, H(O7) ··· O(6) 1.87 Å].

Table 12 Bond lengths (Å) and angles for [NiL$^1_2$(NO$_3$)]NO$_3$·2MeOH

Ni–N(2)	2.140(19)	Ni–N(3)	2.145(26)
Ni–O(4)	2.208(22)	O(1)–C(6)	1.439(42)
O(1)–C(7)	1.343(31)	O(2)–C(22)	1.375(28)
O(2)–C(23)	1.403(44)	O(3)–N(4)	1.205(48)
O(4)–N(4)	1.249(28)	O(5)–N(5)	1.202(2)
O(6)–N(5)	1.201(2)	O(6a)–N(5)	1.201(2)
O(7)–C(24)	1.410(47)	N(1)–C(1)	1.338(39)
N(1)–C(5)	1.381(44)	N(2)–C(13)	1.483(35)
N(2)–C(14)	1.468(37)	N(3)–C(15)	1.477(38)
N(3)–C(16)	1.489(36)	C(1)–C(2)	1.370(39)
C(1)–C(23)	1.446(43)	C(2)–C(3)	1.372(43)
C(3)–C(4)	1.370(41)	C(4)–C(5)	1.376(47)
C(5)–C(6)	1.434(43)	C(12)–C(13)	1.503(34)
C(14)–C(15)	1.523(39)	C(16)–C(17)	1.530(37)
C–C(phenyl)	1.395		
N(2)–Ni–N(3)	81.4(8)	N(2)–Ni–O(4)	92.2(8)
N(3)–Ni–O(4)	94.0(9)	N(2)–Ni–N(2a)	166.6(12)
N(2)–Ni–N(3a)	91.3(8)	N(3)–Ni–N(3a)	113.5(14)
N(2)–Ni–O(4a)	99.5(8)	N(3)–Ni–O(4a)	152.5(9)
O(4)–Ni–O(4a)	58.5(12)	C(6)–O(1)–C(7)	118.7(21)
C(22)–O(2)–C(23)	118.3(23)	Ni–O(4)–N(4)	91.0(18)
C(1)–N(1)–C(5)	125.3(31)	Ni–N(2)–C(13)	117.1(17)
Ni–N(2)–C(14)	105.8(13)	C(13)–N(2)–C(14)	110.4(22)
Ni–N(3)–C(15)	106.9(17)	Ni–N(3)–C(16)	109.2(18)
C(15)–N(3)–C(16)	112.2(25)	O(3)–N(4)–O(4)	120.2(16)
O(3)–N(4)–O(4a)	120.2(16)	O(4)–N(4)–O(4a)	119.6(33)
O–N(5)–O(nitrate)	120.0	N(1)–C(1)–C(2)	119.8(28)
N(1)–C(1)–C(23)	115.8(28)	C(2)–C(1)–C(23)	124.3(27)
C(1)–C(2)–C(3)	118.6(29)	C(2)–C(3)–C(4)	119.0(33)
C(3)–C(4)–C(5)	124.6(30)	N(1)–C(5)–C(4)	112.7(29)
N(1)–C(5)–C(6)	119.6(30)	C(4)–C(5)–C(6)	127.5(30)
O(1)–C(6)–C(5)	106.3(26)	O(1)–C(7)–C(8)	123.5(14)
O(1)–C(7)–C(12)	116.5(14)	C(7)–C(12)–C(13)	122.2(16)
C(11)–C(12)–C(13)	117.5(16)	N(2)–C(13)–C(12)	115.9(24)
N(2)–C(14)–C(15)	104.4(24)	N(3)–C(15)–C(14)	111.2(26)
N(3)–C(16)–C(17)	116.6(22)	C(16)–C(17)–C(18)	118.0(13)
C(16)–C(17)–C(22)	121.9(14)	O(2)–C(22)–C(17)	115.0(13)
O(2)–C(22)–C(21)	124.9(13)	C(17)–C(22)–C(21)	120.0(1)
O(2)–C(23)–C(1)	113.7(31)	C–C–C(phenyl)	120.0

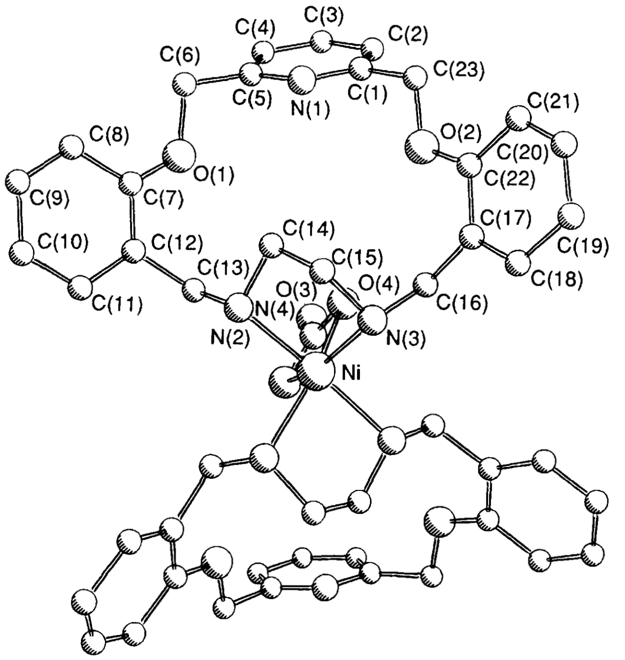


Fig. 5 The molecular structure with atom labelling of the complex cation $[NiL^1_2(NO_3)]^+$

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