Studies of the Pyridine-containing Tetra-azamacrocycle 3,7,11-Trimethyl-3,7,11,17-tetra-azabicyclo[11.3.1]heptadeca-1(17),13,15-triene (L^1) and its Complexes with Ni^{2+}, Cu^{2+}, and Zn^{2+}. Crystal Structures of the Unsymmetric Isomer of $[Ni(L^1)][ClO_4]_2$, and the Five-co-ordinate Complexes $[Ni(L^1)(dmso)][ClO_4]_2$ (dmso = dimethyl sulphoxide) and $[Ni(L^1)Cl]ClO_4$†

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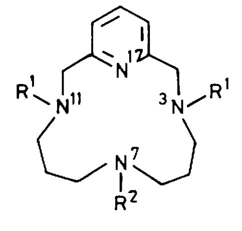
The pyridine-containing tetra-azamacrocycle 3,7,11-trimethyl-3,7,11,17-tetra-azabicyclo[11.3.1]-heptadeca-1(17),13,15-triene (L^1) has been prepared and isolated, together with its metal complexes of general formula $[M(L^1)]X_2$ (M = Ni, Cu, or Zn; X = ClO_4^- or NO_3^-). Three geometric isomers arise for these complexes due to the possible positions of the three Me–N groups above and below the macrocyclic ligand plane. All three isomers of the diamagnetic four-co-ordinate nickel(II) complex have been characterised by ^{13}C n.m.r. spectroscopy, and the structure of the unsymmetric isomer has been established by *X*-ray crystallography. One of the two symmetric isomers, with Me–N groups at positions 3 and 11 on one side of the macrocyclic plane and with that at position 7 on the opposite side, readily forms five-co-ordinate complexes $[Ni(L^1)X][ClO_4]_n$ [X = Cl^-, NCS^-, or NO_2^-, *n* = 1; X = co-ordinating solvent, dimethyl sulphoxide (dmso) or H_2O, *n* = 2]. An analogous zinc(II) complex, $[Zn(L^1)(dmso)][ClO_4]_2$, has also been isolated. Crystal structures of the nickel(II) complexes, with X = Cl and dmso, show that they are square pyramidal, with the macrocycle folded, with X co-ordinated in the basal plane in a *trans* position to the pyridine N atom, and with the N^7 position at the apex. A six-co-ordinate binuclear complex, $[(L^1)Ni(\mu\text{-ox})Ni(L^1)][ClO_4]_2$, containing a bridging oxalate (ox) ion, has also been isolated. Carbon-13 n.m.r. spectra show that the unsolvated complex of L^1 with zinc(II) nitrate is a mixture of symmetric and unsymmetric isomers, whereas the zinc(II) perchlorate complex is a mixture of both symmetric species.

Previously we reported the synthesis of the 14-membered-ring pyridine-containing macrocycles L^2—L^5, and the characterisation of their metal complexes with Ni^{2+}, Cu^{2+}, and Zn^{2+} ions.[1-3] A recent communication[4] describing the nickel(II) complexes of the related macrocycle L^1 prompts us to report our findings for this ligand, and its complexes with Ni^{2+}, Cu^{2+}, and Zn^{2+}. The structures of the diamagnetic complexes have been investigated in nitromethane solution by ^{13}C n.m.r. spectroscopy, and the complexes of Ni^{2+} and Cu^{2+} by u.v.–visible spectroscopy. As explained in our previous study,[1] there are four isomers possible for each of the planar metal complexes of L^1 due to the possible positions of the Me–N groups above and below the macrocyclic ligand plane (three geometric isomers, one of which is enantiomeric; Figure 1). We report the crystal structure of an asymmetric isomer formed by Ni^{2+} [isomer (**III**) or (**IV**) of Figure 1], and the crystal structures of five-co-ordinate complexes of the type $[Ni(L^1)X][ClO_4]_n$ [Me–N configurations as in isomer (**II**) of Figure 1; X = Cl, *n* = 1; X = dimethyl sulphoxide (dmso), *n* = 2]. The latter are closely related to $[Ni(L^4)Cl]ClO_4$ whose crystal structure we reported recently.[2]

Experimental

Materials and Methods.—All materials were the purest available commercially, and were used without further purification. Dimethyl sulphoxide solvates of metal perchlorates, used in the synthesis of metal complexes, were prepared by a published method.[5] Proton-decoupled, natural-abundance ^{13}C n.m.r. spectra were obtained at either 45.28 or 100.6 MHz with Bruker WH180 and WH400 spectrometers respectively. Proton n.m.r. spectra were recorded at 220 MHz with a Perkin-Elmer R34 spectrometer. Chemical shifts are reported on the δ scale relative to $SiMe_4$ at δ = 0. Infrared, u.v.–visible, and mass spectra were obtained with Perkin-Elmer 580B, Shimadzu 365, and Kratos MS80 spectrometers respectively. Microanalyses were obtained commercially; the analytical data for the complexes are collected in Table 1. Magnetic moments were measured by the method of Evans.[6]



L^1 $R^1 = R^2 =$ Me
L^2 $R^1 =$ H , $R^2 =$ Me
L^3 $R^1 = R^2 =$ H
L^4 $R^1 = CH_2Ph, R^2 =$ H
L^5 $R^1 = R^2 = CH_2Ph$

Preparation of Ligand L^1.—The ligand L^2 (6.0 g, 24.9 mmol; prepared as previously described[1]) was dissolved in 98% formic

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

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

Table 1. Combustion analyses (%); observed values in parentheses

Compound	Formula	C	H	N
L^1	$C_{16}H_{28}N_4$	69.5 (69.2)	10.2 (10.1)	20.3 (20.1)
$[Ni(L^1)][ClO_4]_2$	$C_{16}H_{28}Cl_2N_4NiO_8$	36.0 (35.7)	5.3 (5.0)	10.5 (10.3)
$[Ni(L^1)(dmso)][ClO_4]_2$	$C_{18}H_{34}Cl_2N_4NiO_9S$	35.3 (35.4)	5.6 (5.6)	9.2 (9.1)
$[Ni(L^1)Cl]ClO_4$	$C_{16}H_{28}Cl_2N_4NiO_4$	40.9 (40.8)	6.0 (5.9)	11.9 (11.8)
$[Ni(L^1)(NCS)]ClO_4$	$C_{17}H_{28}ClN_5NiO_4S$	41.5 (41.7)	5.7 (5.7)	14.2 (14.4)
$[Ni(L^1)(NO_2)]ClO_4$	$C_{16}H_{28}ClN_5NiO_6$	40.0 (40.0)	5.9 (5.9)	14.6 (14.5)
$[(L^1)Ni(\mu\text{-ox})Ni(L^1)][ClO_4]_2$	$C_{34}H_{56}Cl_2N_8Ni_2O_{12}$	42.7 (42.4)	5.9 (5.9)	11.7 (11.6)
$[Cu(L^1)][ClO_4]_2\cdot H_2O$	$C_{16}H_{30}Cl_2CuN_4O_9$	34.5 (34.5)	5.4 (5.4)	10.1 (9.9)
$[Zn(L^1)][NO_3]_2\cdot H_2O$	$C_{16}H_{30}N_6O_7Zn$	39.7 (40.1)	6.3 (5.9)	17.4 (17.1)
$[Zn(L^1)][ClO_4]_2$	$C_{16}H_{28}Cl_2N_4O_8Zn$	35.5 (35.7)	5.2 (5.8)	10.4 (10.8)

Table 2. ^{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)

		Pyridine C				N-CH_2-C		N-CH_3		
Compound	Isomer[a]	*ortho*	*para*	*meta*	py-CH_2-N					C-CH_2-C
L^1 [b]		159.19(2)	137.13(1)	123.26(2)	64.67(2)	55.82(2)	53.82(2)	44.05(2)	43.13(1)	25.64(2)
L^1 [c]		157.91(2)	136.34(1)	122.56(2)	64.08(2)	54.87(2)	53.33(2)	44.05(2)	43.46(1)	25.09(2)
$[Ni(L^1)][ClO_4]_2$	**(II)**	157.66(2)	143.68(1)	122.49(2)	72.07(2)	61.90(2)	59.83(2)	49.24(2)	45.46(1)	21.68(2)
	(I)	158.70(2)	143.77(1)	121.87(2)	73.02(2)	62.70(2)	60.95(2)	49.32(2)	45.17(1)	21.96(2)
	(III) or **(IV)**	158.67(2)	144.14(1)	122.56(2)	72.89(1)	62.62(1)	60.49(1)	48.35(1)	48.19(1)	22.07(1)
					72.17(1)	55.16(1)	52.83(1)	43.91(1)		20.59(1)
$[Zn(L^1)][NO_3]_2$	**(I)** or **(II)**	155.18(2)	143.80(1)	124.93(2)	64.60(2)	60.69(2)	60.50(2)	46.82(2)	41.13(1)	23.61(2)
	(III) or **(IV)**	155.77(2)	143.09(1)	124.57(2)	64.60(2)	61.32(1)	60.69(1)	45.86(1)	45.24(2)	23.61(1)
						59.05(1)	56.94(1)			22.69(1)
$[Zn(L^1)(dmso)][ClO_4]_2$ [d]	**(I)** or **(II)**	154.98(2)	144.26(1)	124.90(2)	62.83(2)	60.39(2)	59.01(2)	46.26(2)	41.26(1)	22.92(2)
	(I) or **(II)**	155.61(2)	144.33(1)	124.96(2)	64.31(2)	61.25(2)	59.15(2)	47.57(2)	46.88(2)	23.41(2)

[a] For assignment of isomer see Figure 1. [b] In CD_3NO_2. [c] In $CDCl_3$. [d] Co-ordinated dimethyl sulphoxide (dmso) at δ = 39.95 p.p.m.

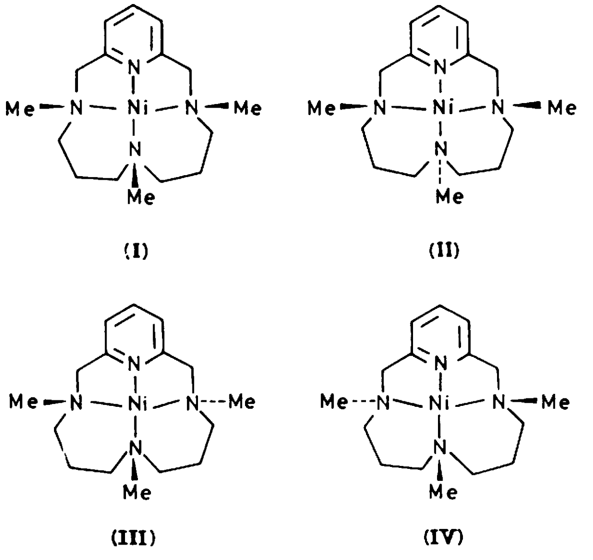


Figure 1. Possible isomers of the $[Ni(L^1)]^{2+}$ ion. Isomers **(III)** and **(IV)** are enantiomers

acid (20 cm³) and formaldehyde (20 cm³ of a 40% aqueous solution) was added. After heating at 90 °C for 24 h, the solution was cooled to room temperature and then basified to pH 12 with 15% aqueous NaOH. The product was extracted with dichloromethane (5 × 100 cm³), the combined extracts dried with anhydrous $MgSO_4$, filtered, and evaporated to leave a yellow oil. The oil was distilled with a Kügelröhr apparatus to give a colourless liquid (5.07 g, 18.36 mmol, 75% yield; b.p. 95—98 °C at 0.01 mmHg). ^1H N.m.r. ($CDCl_3$): δ 1.50 (4 H, qnt), 2.00 (3 H, s), 2.24 (4 H, t), 2.34 (4 H, t), 2.42 (6 H, s), 3.69 (4 H, s), 7.13 (2 H, d), and 7.58 (1 H, t). The elemental analysis is in Table 1, and the ^{13}C n.m.r. chemical shifts are in Table 2. I.r. (thin film): no N-H stretch. Electron-impact mass spectrum: m/z 276 (calc.: 276 for M^+).

Preparation of Metal Complexes of L^1.—In general these were prepared by adding a solution of L^1 (1 g, 3.62 mmol) in ethanol (10 cm³) to an equimolar amount of the dmso solvates of the metal perchlorates, or to $Zn(NO_3)_2\cdot 6H_2O$, in ethanol (5—25 cm³ depending on solubility). The perchlorate salts of the 1 : 1 complexes precipitate soon after mixing, but in the case of $Zn(NO_3)_2$ dry diethyl ether was added dropwise to cause precipitation. Yields of the perchlorate salts were 80—90%, and starting from $Zn(NO_3)_2$ the yield was 65%. The products analysed as $[M(L^1)][ClO_4]_2\cdot nH_2O$ (M = Ni or Zn, n = 0; M = Cu, n = 1), $[Zn(L^1)][NO_3]_2\cdot H_2O$, and $[Zn(L^1)(dmso)][ClO_4]_2$.

The nickel(II) complex, when prepared in this way and recrystallised twice from nitromethane–ethanol (1 : 3), gave red crystals which were found by ^{13}C n.m.r. to be the symmetric isomer **(II)** (Figure 1). However, when we repeated the preparation, the product was found to be a mixture of the symmetric isomer **(I)** and the asymmetric isomers [**(III)** and **(IV)**]. The ^{13}C n.m.r. spectra are characteristically different as shown in Table 2. It is reported that isomer **(I)** readily isomerises to **(III)** and **(IV)**, and **(III)** and **(IV)** equilibrate with largely **(II)** and some **(I)** in aqueous solution;[4] we found that when hydrated nickel(II) perchlorate was used in the preparation instead of the dimethyl sulphoxide solvate the product obtained after allowing the ethanolic solution to stand overnight was the symmetric isomer **(I)**. We conclude that **(II)** is the preferred isomer in solutions of co-ordinating solvents (and other unidentate anionic ligands), and that **(I)** is a kinetically formed first product. To obtain the asymmetric isomers [**(III)** and **(IV)**], a sample of the symmetric

Table 3. U.v. visible spectra [λ/nm (ε/dm^3 mol^{-1} cm^{-1})] and magnetic moments of the complexes of Ni^{2+} and Cu^{2+} (in nitromethane solution unless specified otherwise)

Complex	Colour	$\lambda_{max.}$ (ε)	$\mu_{eff.}$
$[Ni(L^1)][ClO_4]_2$	Orange	^{a}478 (215)	
	Red	^{b,c}498 (215)	
	Green-blue	^{d}372 (sh), 606 (61), 768 (43), 898 (35)	
	Blue	^{e}372 (sh), 592 (37), 769 (25), 888 (19)	
$[Ni(L^1)Cl]ClO_4$	Green	397 (170), 632 (61), 828 (36), 916 (24)	3.0
$[Ni(L^1)(NCS)]ClO_4$	Blue	372 (351), 586 (78), 780 (55), 908 (33)	3.1
$[Ni(L^1)(NO_2)]ClO_4$	Blue	375 (70), 598 (36), 824 (25), 916 (33)	3.0
$[(L^1)Ni(\mu\text{-ox})Ni(L^1)][ClO_4]_2$	Blue	378 (83), 606 (45), 808 (sh), 980 (67)	3.1
$[Cu(L^1)][ClO_4]_2$	Purple	^{f}584 (331)	1.7

^{a} Diamagnetic unsymmetric isomer (**III**) or (**IV**); $\lambda_{max.}$ 473 nm (ε 233 dm^3 mol^{-1} cm^{-1}).[4] ^{b} $\lambda_{max.}$ at 498 nm in the solid phase. ^{c} Diamagnetic symmetric isomer (**I**); $\lambda_{max.}$ 502 nm (ε 239 dm^3 mol^{-1} cm^{-1}).[4] ^{d} In dmso; paramagnetic five-co-ordinate dmso complex of isomer (**II**) (see crystal structure). ^{e} In water; paramagnetic five-co-ordinate aqua complex of isomer (**II**). ^{f} In water, $\lambda_{max.}$ = 602 nm (ε = 228 dm^3 mol^{-1} cm^{-1}).

Table 4. Crystal data for $[Ni(L^1)][ClO_4]_2$, (**A**), $[Ni(L^1)(dmso)][ClO_4]_2$, (**B**), and $[Ni(L^1)Cl][ClO_4]$, (**C**)

Compound	(**A**)	(**B**)	(**C**)
Formula	$C_{16}H_{28}Cl_2N_4NiO_8$	$C_{18}H_{34}Cl_2N_4NiO_9S$	$C_{16}H_{28}Cl_2N_4NiO_4$
M	534.0	556.1	470.0
System	Monoclinic	Orthorhombic	Triclinic
Space group	Cc	$Pn2_1a$	$P\bar{1}$
Absences	hkl, $h + k \neq 2n$; $h0l$, $l \neq 2n$	$hk0$, $h \neq 2n$; $0kl$, $k + l \neq 2n$	None
a/Å	10.043(3)	17.361(6)	7.425(2)
b/Å	13.842(3)	12.169(3)	10.322(3)
c/Å	15.473(9)	12.626(2)	13.933(4)
α/°	90	90	83.53(2)
β/°	91.65(4)	90	75.52(2)
γ/°	90	90	84.19(2)
U/Å^3	2 150.2(1)	2 667(1)	1 024.3(5)
D_c/g cm^{-3}	1.65	1.38	1.52
Z	4	4	2
μ(Mo-K_α)/cm^{-1}	12.1	10.2	12.4
F(000)	1 112	1 168	492
Reflections: total	1 977	1 855	3 626
[$I/\sigma(I) \geq 3.0$] observed	975	711	2 039
$2\theta_{max.}$/°	50	45	50
Range (2θ) about $\alpha_1 - \alpha_2$/°	$\pm$1.2	+1.0 to −0.9	$\pm$0.9
Speed (2θ)/° min^{-1}	1.5—29	1.5—29	1.2—29
Crystal dimensions/mm	0.19 × 0.24 × 0.13	0.04 × 0.25 × 0.15	0.07 × 0.13 × 0.12
Final R (R')	0.090 (0.094)	0.084 (0.088)	0.043 (0.042)
Weighting factor, g	0.007	0.003	0.0006
Largest peak on ΔF map/e Å^{-3}	0.9 (near Ni)	0.8	0.4

complex (**I**) (1.0 g, 0.187 mmol) was dissolved in water (25 cm^3) at 85 °C for 20 h, and the solution was then slowly concentrated to *ca.* 5 cm^3 when orange crystals of $[Ni(L^1)][ClO_4]_2$, (**A**), precipitated. These were collected by filtration and washed with ethanol (3 × 10 cm^3) and diethyl ether (yield 250 mg, 25%).

Preparation of the Complexes $[Ni(L^1)X][ClO_4]_n$.—Five-co-ordinate complexes of this formulation were prepared by adding excess of the unidentate ligand, X (X = dmso, n = 2; X = NCS^-, NO_2^-, or Cl^-, n = 1) to $[Ni(L^1)][ClO_4]_2$ in aqueous, ethanol, or nitromethane solution. They are all assumed to have the square-pyramidal structures established for the dmso and chloro-complexes by crystallography (see later).

$[Ni(L^1)(dmso)][ClO_4]_2$, (**B**). The complex $[Ni(L^1)][ClO_4]_2$ (200 mg, 0.37 mmol) was added to a solution of dmso (0.117 g, 1.5 mmol) in nitromethane (3 cm^3). The product was precipitated as a blue solid with ethanol (5 cm^3), filtered off, and washed with diethyl ether (3 × 5 cm^3) to give $[Ni(L^1)(dmso)][ClO_4]_2$ (210 mg, 0.34 mmol, 92% yield).

$[Ni(L^1)(NCS)]ClO_4$. To a stirred solution of $[Ni(L^1)][ClO_4]_2$ (250 mg, 0.47 mmol) in ethanol (5 cm^3) was added a solution of NaSCN (76 mg, 0.937 mmol) in ethanol (5 cm^3), and the mixture was stirred overnight at room temperature. The resulting blue solid was filtered off and recrystallised from nitromethane–diethyl ether (1:3; 8 cm^3) to give $[Ni(L^1)(NCS)][ClO_4]$ (200 mg, 0.41 mmol, 87% yield).

$[Ni(L^1)(NO_2)]ClO_4$. The complex $[Ni(L^1)][ClO_4]_2$ (200 mg, 0.37 mmol) was dissolved in water (10 cm^3) at 100 °C and a solution of sodium nitrite (509 mg, 7.4 mmol) in water (5 cm^3) was added. The mixture was heated at 100 °C for 30 min, and on cooling blue crystals precipitated. These were collected, washed with cold water (3 cm^3), ethanol (3 × 5 cm^3), and dried under vacuum to give $[Ni(L^1)(NO_2)]ClO_4$ (100 mg, 0.21 mmol, 56% yield).

$[Ni(L^1)Cl]ClO_4$ (**C**). A solution of $[Ni(L^1)][ClO_4]_2$ (500 mg; mixture of symmetric and unsymmetric isomers) in water (25 cm^3) was carefully transferred to a column (300 × 25 mm) packed with Sephadex C-25 resin (10 g) which had been swelled in distilled water. Elution with 0.4 mol dm^{-3} aqueous NaCl gave a green band (chloro-complex of symmetric isomer) followed by

Table 5. Atomic co-ordinates (× 10^4) for complexes (**A**), (**B**), and (**C**)

(A)	*x*	*y*	*z*		*x*	*y*	*z*
Ni	5 000	1 493(2)	7 500	C(1)	3 813(32)	3 270(21)	7 934(19)
Cl(1)	1 818(11)	1 000(6)	9 102(6)	C(2)	5 241(34)	3 341(25)	6 574(21)
O(11)	2 553	1 700	8 672	C(3)	4 095(30)	3 065(22)	5 910(18)
O(12)	2 280	82	8 880	C(4)	4 300(30)	1 842(21)	5 708(18)
O(13)	1 969	1 132	9 995	C(5)	2 509(29)	1 069(23)	6 627(19)
O(14)	471	1 084	8 860	C(6)	4 441(36)	375(23)	6 042(20)
Cl(2)	8 448(8)	1 057(5)	5 896(5)	C(7)	4 754(32)	−321(23)	6 797(19)
O(21)	7 815	384	5 350	C(8)	4 682(33)	−1 415(23)	6 956(23)
O(22)	8 971	1 802	5 398	C(9)	5 105(38)	−1 818(19)	7 645(19)
O(23)	7 529	1 438	6 466	C(10)	5 464(29)	−1 236(22)	8 363(19)
O(24)	9 478	605	6 369	C(11)	5 575(46)	−273(33)	8 189(28)
N(1)	5 072(35)	2 928(11)	7 550(23)	C(12)	5 698(37)	331(24)	8 934(20)
N(2)	3 992(24)	1 359(17)	6 477(14)	C(13)	7 479(57)	1 413(32)	8 462(31)
N(3)	5 050(32)	179(12)	7 520(22)	C(14)	5 807(30)	2 247(19)	9 247(18)
N(4)	6 057(37)	1 240(23)	8 663(21)	C(15)	6 496(32)	3 091(22)	8 861(18)
				C(16)	6 352(32)	3 291(23)	7 928(20)
(B)							
Ni	7 066(3)	5 000	4 353(3)	C(2)	9 020(21)	7 157(33)	3 422(26)
Cl(1)	3 517(7)	4 700(9)	4 247(10)	C(3)	5 904(25)	4 518(31)	6 065(29)
O(11)	3 281	4 051	3 392	C(4)	7 172(22)	5 287(28)	6 657(26)
O(12)	4 202	4 276	4 662	C(5)	7 615(21)	4 191(27)	6 748(27)
O(13)	2 947	4 692	5 029	C(6)	8 217(19)	4 042(33)	5 872(26)
O(14)	3 637	5 778	3 904	C(7)	8 523(25)	3 783(36)	4 082(32)
Cl(2)	9 543(7)	509(8)	4 380(9)	C(8)	7 448(22)	2 757(29)	4 807(27)
O(21)	9 912	−118	3 602	C(9)	6 887(17)	2 670(24)	3 969(22)
O(22)	9 814	1 589	4 335	C(10)	6 459(22)	1 722(28)	3 491(26)
O(23)	9 697	65	5 379	C(11)	5 886(22)	1 916(34)	2 845(28)
O(24)	8 748	498	4 203	C(12)	5 582(22)	2 937(27)	2 657(29)
O(101)	7 851(13)	6 206(20)	4 443(18)	C(13)	5 932(19)	3 816(25)	3 172(23)
S	8 108(8)	7 293(11)	4 159(10)	C(14)	5 638(18)	4 986(32)	3 089(26)
N(1)	6 550(16)	5 288(20)	5 778(21)	C(15)	6 673(23)	6 072(30)	2 283(29)
N(2)	7 920(18)	3 806(22)	4 873(21)	C(16)	5 972(22)	6 813(31)	3 853(26)
N(3)	6 552(16)	3 695(22)	3 771(20)	C(17)	5 689(22)	6 696(35)	4 901(28)
N(4)	6 289(19)	5 766(22)	3 342(21)	C(18)	6 195(19)	6 364(27)	5 790(26)
C(1)	8 455(23)	7 871(32)	5 308(28)				
(C)							
Ni	2 770.2(8)	2 048.8(7)	2 179.9(5)	C(4)	4(7)	116(5)	2 347(4)
Cl(1)	7 415(2)	6 761(1)	3 250(1)	C(5)	−512(7)	778(5)	3 288(4)
O(11)	7 812(10)	6 795(7)	2 239(4)	C(6)	−1 944(7)	455(6)	4 084(4)
O(12)	8 954(8)	7 104(5)	3 549(5)	C(7)	−2 352(8)	1 226(7)	4 861(4)
O(13)	7 188(8)	5 479(6)	3 665(5)	C(8)	−1 359(7)	2 278(6)	4 841(4)
O(14)	5 919(8)	7 566(7)	3 581(5)	C(9)	91(7)	2 552(5)	4 026(4)
Cl(2)	5 869(2)	1 755(2)	1 375(1)	C(10)	1 244(7)	3 698(5)	3 850(4)
N(1)	1 861(5)	3 289(4)	1 136(3)	C(11)	3 820(8)	4 654(6)	2 567(5)
N(2)	3 080(5)	3 437(4)	3 127(3)	C(12)	2 795(9)	5 263(6)	1 809(5)
N(3)	503(5)	1 789(4)	3 261(3)	C(13)	2 954(8)	4 469(6)	926(4)
N(4)	1 988(5)	276(4)	1 827(3)	C(14)	−161(7)	3 689(6)	1 420(4)
C(1)	2 291(8)	2 662(6)	172(4)	C(15)	3 155(9)	−798(6)	2 210(5)
C(2)	1 453(8)	1 372(7)	200(4)	C(16)	4 409(8)	2 797(7)	3 709(5)
C(3)	2 284(8)	208(7)	736(4)				

an orange-red band (unsymmetric isomer) which were collected separately. Slow evaporation of the water at room temperature over a long period (1 week) afforded green crystals from both bands. These were recrystallised from chloroform, and found to have identical analyses and visible spectra. We conclude that the unsymmetric isomer slowly isomerises to the chloro-complex of the symmetric isomer in aqueous chloride media.

Preparation of $[(L^1)Ni(\mu\text{-ox})Ni(L^1)][ClO_4]_2$ (ox = *oxalate ion*).—To a stirred solution of $[Ni(L^1)][ClO_4]_2$ (250 mg, 0.47 mmol) in hot water (50 cm^3) was added a solution of $Na_2(ox)$ (188 mg, 1.4 mmol) in water (2.5 cm^3). The mixture was heated to 100 °C for 30 min, then allowed to cool slowly, whereupon blue crystals of the product crystallised. These were filtered off, washed with a little cold water, and air dried to give the product (185 mg, 0.19 mmol, 83% yield).

Preparation of Copper(II) *and Zinc*(II) *Complexes.*—$[Cu(L^1)][ClO_4]_2{\cdot}H_2O$. The ligand L^1 (100 mg, 0.36 mmol) was dissolved in ethanol (5 cm^3) and added to $Cu(ClO_4)_2{\cdot}6H_2O$ (133 mg, 0.36 mmol) in ethanol (8 cm^3). The purple product precipitated, and was filtered off, washed with diethyl ether (3 × 5 cm^3), and dried under vacuum (yield 180 mg, 0.32 mmol, 90%).

$[Zn(L^1)][NO_3]_2{\cdot}H_2O$. The ligand L^1 (100 mg, 0.36 mmol) was dissolved in ethanol (5 cm^3) and $Zn(NO_3)_2{\cdot}6H_2O$ (107 mg, 0.36 mmol) in ethanol (5 cm^3) was added. The mixture was stirred for 30 min under dry N_2 and then dry diethyl ether (20

Table 6. Principal bond lengths (Å) and angles (°) for (**A**), (**B**), and (**C**)

(**A**) $[Ni(L^1)][ClO_4]_2$					
Ni–N(1)	1.99(2)	Ni–N(2)	1.86(2)	Ni–N(3)	1.82(2)
Ni–N(4)	2.09(3)				
N(1)–Ni–N(2)	98.7(1.2)	N(2)–Ni–N(4)	164.5(1.2)	N(2)–Ni–N(3)	86.0(1.3)
N(1)–Ni–N(4)	96.7(1.3)	N(1)–Ni–N(3)	175.2(1.3)	N(3)–Ni–N(4)	78.8(1.4)
(**B**) $[Ni(L^1)(dmso)][ClO_4]_2$					
Ni–N(1)	2.04(3)	Ni–N(2)	2.18(3)	Ni–N(3)	1.97(3)
Ni–N(4)	2.08(3)	Ni–O(101)	2.01(2)	O(101)–S	1.44(3)
S–C(1)	1.72(4)	S–C(2)	1.84(4)		
N(1)–Ni–N(2)	98.5(1.0)	Ni–O(101)–S	150.1(1.6)	N(3)–Ni–N(4)	80.7(1.1)
N(1)–Ni–N(4)	100.4(1.1)	O(101)–S–C(2)	108.0(1.7)	N(4)–Ni–O(101)	98.5(1.0)
N(2)–Ni–N(3)	83.3(1.1)	N(1)–Ni–N(3)	105.7(1.0)	O(101)–S–C(1)	105.9(1.7)
N(2)–Ni–O(101)	90.5(1.0)	N(1)–Ni–O(101)	97.0(1.0)	C(1)–S–C(2)	99.3(1.8)
N(3)–Ni–O(101)	157.1(1.0)	N(2)–Ni–N(4)	157.9(1.0)		
(**C**) $[Ni(L^1)Cl]ClO_4$					
Ni–N(1)	2.027(4)	Ni–N(2)	2.119(5)	Ni–N(3)	1.976(3)
Ni–N(4)	2.119(5)	Ni–Cl(2)	2.300(1)		
N(1)–Ni–N(2)	98.8(2)	N(3)–Ni–Cl(2)	156.6(1)	N(2)–Ni–N(4)	156.0(2)
N(1)–Ni–N(4)	98.9(2)	N(1)–Ni–N(3)	104.2(2)	N(3)–Ni–N(4)	79.7(2)
N(2)–Ni–N(3)	80.4(2)	N(1)–Ni–Cl(2)	99.3(1)	N(4)–Ni–Cl(2)	96.0(1)
N(2)–Ni–Cl(2)	96.9(1)				

cm^3) was added to precipitate the product as an oily solid; this was stirred in dry dichloromethane–diethyl ether (1:2) under dry N_2 overnight to give a white solid. The solid was filtered off in a dry-box and vacuum dried to give the product (113 mg, 0.23 mmol, 65% yield). The ^{13}C n.m.r. data are given in Table 2.

$[Zn(L^1)(dmso)][ClO_4]_2$. This was prepared in 75% yield as described for the nitrate salt using $[Zn(dmso)_4][ClO_4]_2$. Diethyl ether was again required to precipitate the product which analysed as $[Zn(L^1)(dmso)][ClO_4]_2$. The presence of co-ordinated dmso was confirmed by the ^{13}C n.m.r. spectrum (Table 2). Recrystallisation of the product from nitromethane–diethyl ether gave the unsolvated complex as shown by the combustion analysis (Table 1).

Visible Spectra.—The visible spectral data for the complexes of Ni^{2+} and Cu^{2+} in nitromethane solution are collected in Table 3. The spectrum of the nickel(II) complex was also recorded in dmso and aqueous solutions where it isomerises slowly to the five-co-ordinate solvated symmetric isomer whose structure was established by *X*-ray crystallography.

Crystal Structures.—Crystal data for $[Ni(L^1)][ClO_4]_2$ (**A**) [the unsymmetric isomer (**III**) or (**IV**)], $[Ni(L^1)(dmso)][ClO_4]_2$ (**B**), and $[Ni(L^1)Cl]ClO_4$ (**C**) are collected in Table 4; (**B**) and (**C**) were found to be five-co-ordinate complexes of the symmetric isomer (**II**) (Figure 1).

For all compounds data were collected with a Syntex $P2_1$ four-circle diffractometer; reflections were scanned around the $K_{\alpha 1} - K_{\alpha 2}$ angles, with variable scan speed 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. All data were taken at 290 K. Three standard reflections were monitored every 200 reflections; in each case they 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 high-angle reflections. Reflections with $I/\sigma(I) \geqslant 3.0$ were used in refinement, and corrected for Lorentz, polarisation but not absorption effects. For each structure (except as noted below) the heavy atom was located by Patterson techniques and the light atoms were then found on successive Fourier syntheses. Hydrogen atoms were given fixed isotropic thermal parameters, $U = 0.07$ Å^2. Those defined by the molecular geometry were inserted at calculated positions and not refined; methyl groups [included only for (**C**)] were treated as rigid CH_3 units, with their initial orientation taken from the strongest peak on a difference Fourier synthesis. Final refinement was by cascaded least-squares methods, with anisotropic thermal parameters for all atoms other than hydrogen in (**C**), but in (**A**) and (**B**) carbon atoms, and in (**B**) also nitrogen atoms, were kept isotropic, in view of the limited number of strong reflections. A weighting scheme of the form $w = 1/[\sigma^2(F) + gF^2]$ (for g see Table 4) was used, and in all cases was shown to be satisfactory by a weight analysis. Computing was with the SHELXTL system[7] on a Data General DG30. Scattering factors in the analytical form and anomalous dispersion factors were taken from ref. 8. Specific points were as follows.

For (**A**). The crystals were small pink blocks bounded by {110} and {001}, which diffracted only weakly. The systematic absences indicate either space group *C*2/*c* or *Cc*. The former would require two-fold molecular symmetry, unlikely on chemical grounds, and therefore the latter was chosen initially and shown to be correct by the successful refinement. Structure solution was somewhat difficult because of the false symmetry of the Ni atom; the ClO_4^- ions were described as rigid tetrahedra (Cl–O 1.40 Å), but the high thermal parameters strongly suggest partial disorder. In view of this, and the weak diffraction, the relatively high *R* value was considered satisfactory; it is possible that some further disorder affects the $(CH_2)_3$ chains, as the bond lengths were rather far from standard values. No attempt was made to define the absolute configuration of the chosen crystal.

For (**B**). The crystals were small blue flakes. Systematic absences indicated either space group *Pnma* or $Pn2_1a$ (non-standard setting of $Pna2_1$). The automatic Patterson solution routine of SHELXTL applied in both space groups gave successful results for $Pn2_1a$ but not for *Pnma*. Starting from one Ni and one Cl position the full structure was built up by successive Fourier syntheses; the pseudo-symmetry caused some problems that were resolved by the removal and insertion of suspect atoms when necessary. The ClO_4^- ions were treated as rigid bodies (Cl–O 1.40 Å), allowing for shrinkage due to high thermal motion. The largest peak on the final difference synthesis (0.8 e Å^{-3}) lay near to the S atom and suggested possible disorder of the CH_3 groups in the dmso ligand. Other peaks are concentrated around Cl(1), and in view of the high thermal parameters for O(11)—O(14) they may also have a second partially occupied position. The small number of reflections made it impossible to investigate this further.

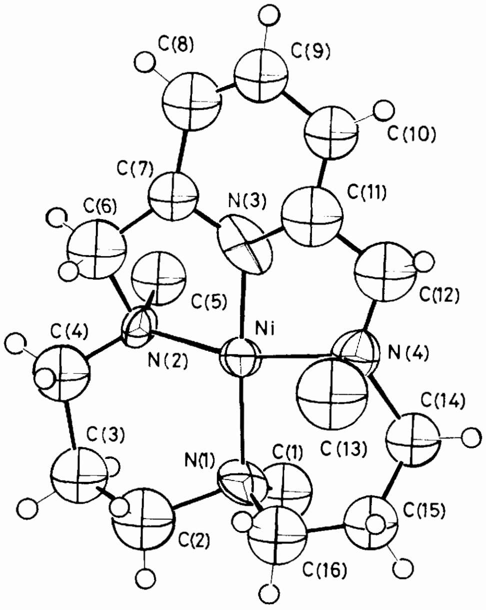


Figure 2. View of molecule (**A**) showing the atomic numbering

For (**C**). The crystals are small green prisms, and were excellently behaved in data collection, structure solution, and refinement.

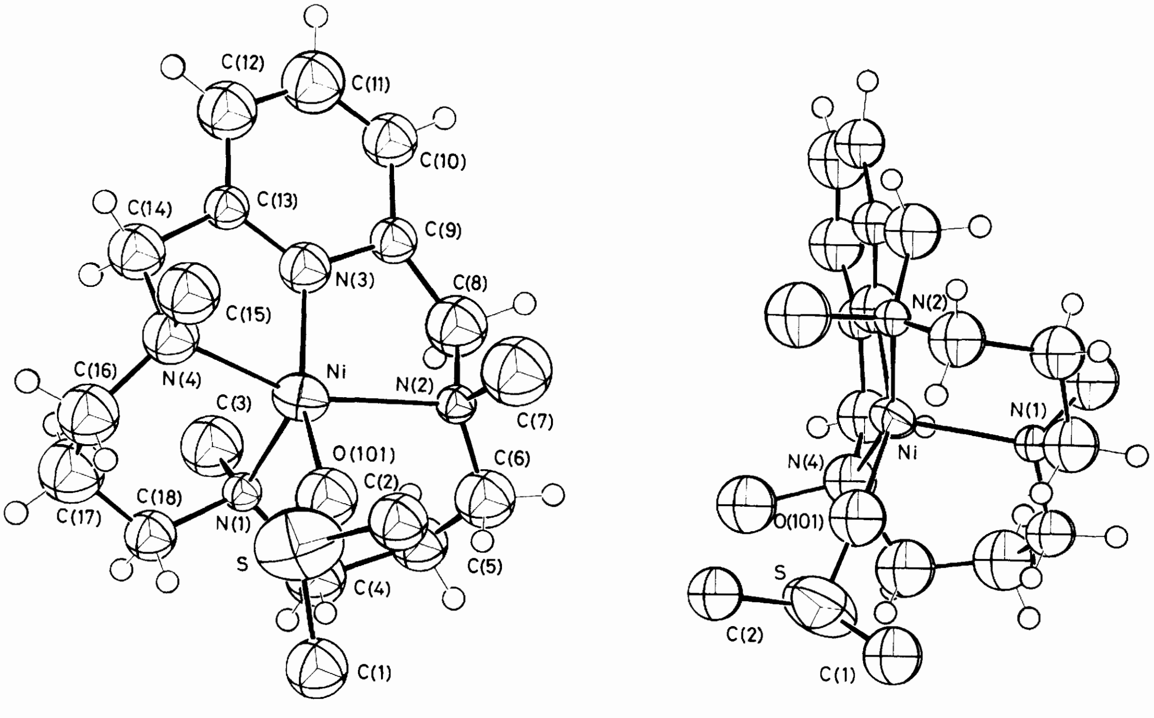
Atomic co-ordinates for (**A**)—(**C**) are given in Table 5, and principal bond lengths and angles in Table 6; bonds between ligand atoms had standard dimensions in all the structures (except as noted above).

Results and Discussion

Four-co-ordinate Nickel(II) *Complexes*.—We shall refer to the four isomers as shown in Figure 1. The two symmetric isomers [(**I**) and (**II**)] and the asymmetric isomer [(**III**) or (**IV**)] have characteristically different ^{13}C n.m.r. spectra as shown in Table 2. In earlier studies[9] it has been shown how the rate of Me–N inversions can be accelerated in the $[Ni(tmc)]^{2+}$ ion (tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane) by the addition of co-ordinating solvents such as dmso, and it is not surprising, therefore, to find a similar behaviour for the $[Ni(L^1)]^{2+}$ ion. Foster *et al.*[4] reported the rate and equilibrium constants for the equilibration of (I) and (II) in aqueous sodium perchlorate solutions, and our synthetic observations confirm that this isomerisation occurs. In addition we have observed

Table 7. Variation of the relative amounts (%) of isomers (**I**), and (**III**) + (**IV**), with time, in nitromethane solutions of $[Ni(L^1)][ClO_4]_2$ at 358 K (based on integrals of the Me–N ^{13}C n.m.r. resonances at δ 45.21 and 43.69 p.p.m.)

	t/d		
	1	8	20
(**I**)	52	34	25
(**III**) + (**IV**)	38	66	75



(*i*) (*ii*)

Figure 3. Two views of molecule (**B**); (*i*) showing the atomic numbering and general conformation, (*ii*) showing the folded geometry

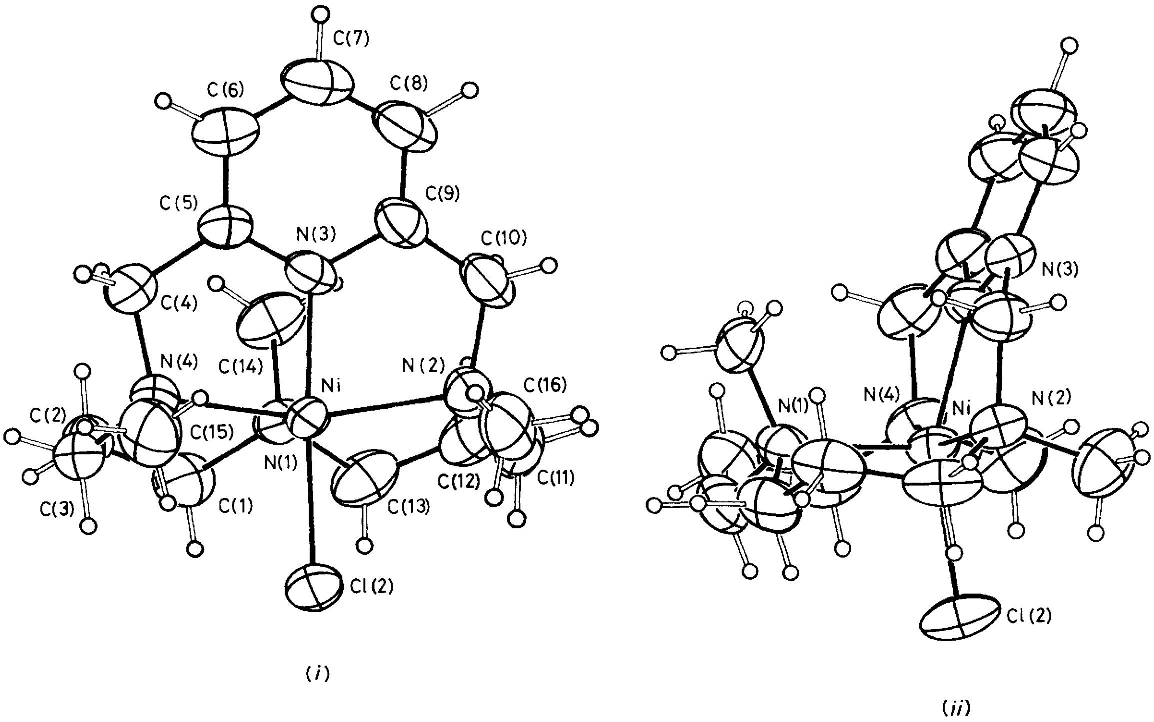


Figure 4. Two views of molecule (**C**); (*i*) showing the atomic numbering and general conformation, (*ii*) showing the folded geometry

that when solutions of isomer (**I**) are held at 358 K in the non-co-ordinating solvent nitromethane there is a slow equilibration with (**III**) and (**IV**). Approximate data for the isomerisation, based on integrations of ^{13}C n.m.r. resonances, are shown in Table 7. The approximate rate constant for the equilibration (sum of the forward and reverse rate constants) is 1.6×10^{-7} s^{-1} at 358 K, and the approximate equilibrium constant, [(**III** + **IV**)/**I**] = 3.0. The crystal structure of $[Ni(L^1)][ClO_4]_2$, (**A**) [isomer (**III**) or (**IV**), Figure 2], is discussed in the next section.

Five-co-ordinate Complexes.—In the presence of either co-ordinating solvents or anions such as Cl^- or NCS^- the favoured isomer has the N configurations of (**II**); this is shown by crystal structures of the aqua-,[4] dmso, (**B**), and chloro-complexes, (**C**) (Figures 3 and 4). In these crystal structures the Ni^{2+} ion adopts a square-pyramidal geometry, sitting above the basal plane (by *ca.* 0.37 Å), and with the unidentate ligand in the basal plane in a *trans* position to the pyridine N atom; the macrocycle is folded about the N(2) to N(4) axis, and the apex is occupied by N(1). This conformation allows easier N inversion at N(1), as observed. The Ni–N bond lengths are very similar in (**B**) and (**C**), with those to the pyridine N atom the shortest (1.97—1.98 Å). The bond angles are close to those of a regular square pyramid, with X–Ni–X angles across the basal plane of *ca.* 157°. As well as the aqua-complex,[4] this geometry has also been found in $[Ni(L^4)Cl]ClO_4$.[2]

In contrast to these, in isomer (**A**) the Ni atom adopts a square-planar geometry, with no additional co-ordinated ligand. The methyl groups on N(2) and N(4) are on opposite sides of the macrocyclic ring [isomer (**III**) or (**IV**)]; this arrangement reduces the ability of the macrocycle to fold and hinders the entry of a fifth ligand into the inner co-ordination sphere. As expected for a low-spin d^8 system in comparison to high-spin systems, the Ni–N distances are significantly shorter than in (**B**) or (**C**), though they have a relatively large spread of values. The Ni–N(pyridine) bond is again shorter than the other Ni–N distances.

Zinc(II) *Complexes.*—The ^{13}C n.m.r. spectra show that, in nitromethane solution, $[Zn(L^1)][NO_3]_2$ is a mixture of symmetric and unsymmetric isomers, whereas $[Zn(L^1)][ClO_4]_2$ is a mixture of both symmetric species. This behaviour is similar to that found in our earlier study of $[Zn(L^2)]X_2$ (X = ClO_4 or NO_3).[1]

Visible Spectra and Magnetic Moments.—The data are shown in Table 3. The visible spectra of the isomers of $[Ni(L^1)][ClO_4]_2$ in nitromethane solution are as expected for diamagnetic square-planar complexes, and in co-ordinating solvents the formation of five-co-ordinate monosolvento species is evident. Co-ordinating anions (Cl^-, NCS^-, or NO_2^-) give analogous five-co-ordinate complexes, and with oxalate ion the visible spectrum and analytical data are consistent with a bridged *cis* octahedral structure of the type found previously for the analogous complex of L^2.[1] The visible spectrum of the copper(II) complex in nitromethane solution is comparable to that found previously for analogous four-co-ordinate systems.[2] The magnetic moments are in the range expected for high-spin nickel(II) and copper(II) complexes.

Acknowledgements

We thank the S.E.R.C. for financial support, and for provision of the Bruker WH180 n.m.r. spectrometer, and the University of Al-Fateh, Tripoli, Libya for financial support (to H. A. A. O.).

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Received 13*th June* 1986; *Paper* 6/1198