Preparation and Structure of Nickel(II) Complexes of N-Substituted Tetra-aza Macrocycles: Molecular Structure of [(1*RS*,4*SR*,5*RS*,8*SR*,11*RS*,12*SR*)-1,5,8,12-Tetramethyl-1,4,8,11-tetra-azacyclotetradecane]nickel(II) Diperchlorate†

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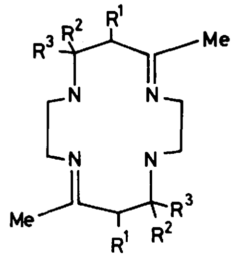
Reaction of *N*-methyl-1,2-diaminoethane monoperchlorate and but-3-en-2-one gives the N-substituted diaminodi-imine macrocycle 1,5,8,12-tetramethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene, L^6. The complexation of Ni^{II} to L^6 followed by reduction of the C=N double bonds with $NaBH_4$ leads to the exclusive formation of (*C-meso*-1,5,8,12-tetramethyl-1,4,8,11-tetra-azacyclotetradecane)nickel(II) ion (**3**). An *X*-ray crystal structure determination of the diperchlorate of (**3**) showed that it adopts an elongated octahedral geometry with C_i symmetry, where the perchlorates co-ordinate weakly to the apical sites. The N-methyl groups are located at the opposite side of the NiN_4 basal plane, and the complex has the N-*meso* configuration with both C-methyl groups being orientated equatorially. On the other hand, the free base of the C-*meso* macrocycle L^7 was obtained highly selectively by direct reduction of L^6 with $NaBH_4$ and the incorporation of Ni^{II} into L^7 gave a complex (**4**), instead of (**3**). Proton n.m.r. analysis revealed that complex (**4**) has a structure which differs from that of (**3**) with regard to the orientation of two C-methyl groups, which are equatorial in (**3**) but axial in (**4**).

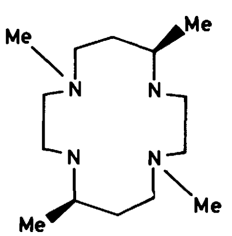
Curtis[1] first reported the formation of an amine–imine linkage upon condensation of two molecules of 1,2-diaminoethane with four molecules of acetone in the presence of Ni^{II} or Cu^{II} to give metal complexes of 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene (L^1). This reaction was extended by MacDermott and Busch,[2] who used α,β-unsaturated ketones and β-hydroxyketones in place of acetone to obtain metal complexes of macrocycles L^2 (R^1,R^2,R^3 = alkyl or benzyl). Further, such macrocycles were found to be produced by non-template reaction (Scheme 1).[3] Because of its simplicity for obtaining tetra-aza macrocycles, this type of reaction was used in subsequent studies.[4–8]

In previous papers,[9–13] we demonstrated that some N-substituted diaminodi-imine macrocyclic complexes can be obtained by template reactions of N-substituted heterocyclic diamines L^3—L^5 using Ni^{II} or Cu^{II} as the template (Scheme 2). The diamines used in those studies were, however, rather special ones, each having an asymmetric carbon centre and a heterocycle. The heterocyclic ring restricts the N-substituent in the axial orientation when the diamine is co-ordinated to a metal ion.[10] Therefore an investigation on the reaction of simple N-substituted diamines should be made to determine the more general effect of N-substituents on the formation and complexation of macrocycles.

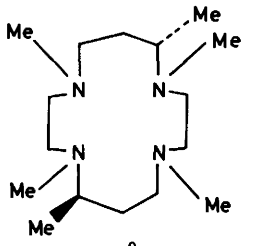
This paper describes the preparation of the diaminodi-imine macrocycle L^6 (Scheme 3) by a non-template reaction of the most simple N-substituted diamine, *N*-methyl-1,2-diaminoethane, with but-3-en-2-one, and the formation of its nickel(II) complex. The synthesis of macrocycle L^7 and the corresponding nickel(II) complex by reduction of L^6 and its nickel(II) complex are also described. The stereochemical aspects of these macrocyclic compounds are discussed in relation to the results of an *X*-ray diffraction study of the nickel(II) complex of L^7.



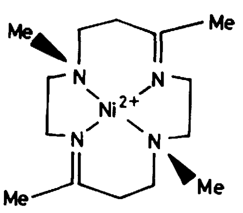
L^2



L^8



L^9



(**2**)

Experimental

All the reagents used were commercially available and of reagent grade. They were used as received.

1,5,8,12-*Tetramethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene Dihydroperchlorate*, $L^6\cdot 2HClO_4$.—Aqueous perchloric acid (60%, 23 cm³, 0.13 mol) was added dropwise with

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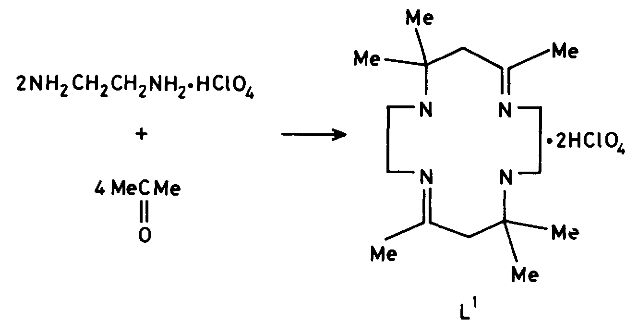
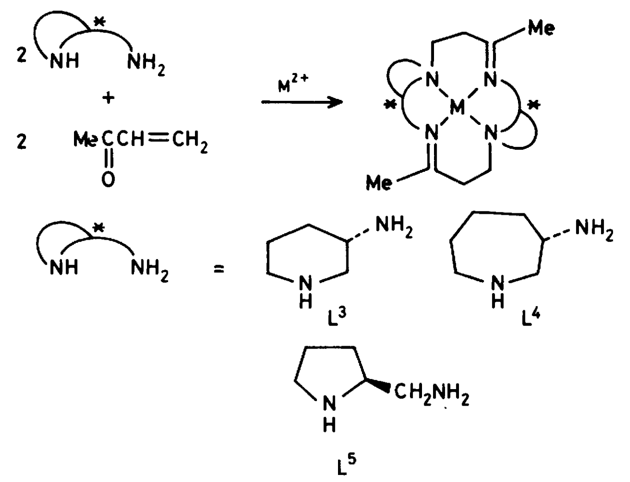
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.



Scheme 1. The formation of diaminodi-imine macrocycle[3] by non-template reaction



Scheme 2. The formation of tricyclic macrocycles from heterocyclic optically active diamines

continuous stirring to an ice-cooled solution of *N*-methyl-1,2-diaminoethane (10 g, 0.13 mol) in methanol (250 cm^3). After completion of the addition, but-3-en-2-one (9.7 g, 0.13 mol) was added slowly over a period of 30 min, with constant stirring and cooling in an ice–salt bath. The resulting mixture was then stirred for 2 h in the ice–salt bath. The white precipitate formed was collected, washed several times with diethyl ether, and dried *in vacuo* (12.2 g, 40%). The product was not stable, and was used immediately for the following reaction without further purification.

(N-meso-1,5,8,12-*Tetramethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene*)*nickel*(II) *Perchlorate*, (**1**).—Nickel(II) acetate tetrahydrate (2.74 g, 0.011 mol) and L^6·2HClO$_4$ (5.0 g, 0.011 mol) were dispersed in methanol (100 cm^3). The suspension was heated under reflux with stirring for *ca.* 3 h, and then cooled to room temperature. The yellow precipitate was filtered off, washed with ethanol and diethyl ether, and dried *in vacuo* (3.9 g, 69%) (Found: C, 32.55; H, 5.70; N, 10.8. Calc. for $C_{14}H_{28}Cl_2N_4NiO_8$: C, 32.95; H, 5.55; N, 11.0%).

(N-meso-1,5,8,12-*Tetramethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene*)*copper*(II) *Perchlorate*, [CuL^6][ClO$_4$]$_2$.—Copper(II) acetate monohydrate (1.57 g, 0.0079 mol) and L^6·2HClO$_4$ (3.37 g, 0.0075 mol) were dispersed in methanol (100 cm^3). The suspension was heated under reflux for *ca.* 3 h, and then cooled to room temperature. The purple precipitate was filtered off, washed with ethanol and diethyl ether, and dried *in vacuo* (2.1 g, 55%) (Found: C, 32.75; H, 5.55; N, 10.9. Calc. for $C_{14}H_{28}Cl_2CuN_4O_8$: C, 32.65; H, 5.50; N, 10.9%).

Table 1. Fractional atomic co-ordinates ($\times 10^4$) for complex (**3**)

Atom	*x*	*y*	*z*
Ni	0(0)	0(0)	0(0)
N(1)	1 581(2)	22(3)	695(2)
C(2)	2 137(2)	1 290(4)	−1(3)
C(3)	1 771(3)	1 198(4)	−1 376(3)
N(4)	508(2)	1 131(3)	−1 483(2)
C(5)	82(3)	641(4)	−2 807(3)
C(6)	−1 190(3)	722(4)	−2 936(3)
C(7)	−1 763(3)	−392(4)	−2 083(3)
C(1)1	2 121(3)	−1 492(4)	431(3)
C(5)1	595(4)	1 633(5)	−3 824(3)
Cl	361(1)	−4 292(1)	−1 924(1)
O(1)	52(3)	−3 068(3)	−1 107(3)
O(2)	1 415(2)	−4 947(4)	−1 471(3)
O(3)	421(4)	−3 706(5)	−3 161(3)
O(4)	−465(2)	−5 484(3)	−1 905(3)

C-meso-1,5,8,12-*Tetramethyl*-1,4,8,11-*tetra-azacyclotetradecane Dihydroperchlorate*, L^7·2HClO$_4$.—To a suspension of L^6·2HClO$_4$ (10 g, 0.022 mol) in methanol (200 cm^3) was added sodium tetrahydroborate (1.67 g, 0.044 mol) in small portions at room temperature. Upon completion of the addition the reaction mixture was refluxed for 1 h. Then water (200 cm^3) was added and methanol was removed on a rotary evaporator. The aqueous solution was allowed to stand in a refrigerator for 20 h. White crystals of the product were filtered off, washed with ethanol and diethyl ether, and dried *in vacuo* (7.6 g, 76%) (Found: C, 36.7; H, 7.50; Cl, 15.8; N, 12.35. Calc. for $C_{14}H_{34}Cl_2N_4O_8$: C, 36.75; H, 7.50; Cl, 15.5; N, 12.25%).

[(1RS,4SR,5RS,8SR,11RS,12SR)-1,5,8,12-*Tetramethyl*-1,4,8,11-*tetra-azacyclotetradecane*]*nickel*(II) *Diperchlorate*, (**3**).—To a suspension of complex (**1**) (2.0 g, 0.004 mol) in methanol (100 cm^3) was added NaBH$_4$ (0.59 g, 0.016 mol) in small portions with stirring. The reaction mixture was refluxed for 2 h with continuous stirring, and then cooled to room temperature. Orange crystals of the product were filtered off and recrystallized from methanol (0.61 g, 30%) (Found: C, 32.7; H, 6.40; N, 10.8. Calc. for $C_{14}H_{32}Cl_2N_4NiO_8$: C, 32.7; H, 6.25; N, 10.9%).

[(1RS,4SR,5SR,8SR,11RS,12RS)-1,5,8,12-*Tetramethyl*-1,4,8,11-*tetra-azacyclotetradecane*]*nickel*(II) *Diperchlorate*, (**4**).—Macrocycle L^7 (1.0 g, 0.002 mol) was dissolved in methanol (200 cm^3). To this solution were added an aqueous solution (200 cm^3) of nickel(II) acetate tetrahydrate (0.80 g, 0.002 mol) and a few drops of perchloric acid (60%). The mixture was then stirred and refluxed for 3 h. The solution gradually turned yellow indicating the formation of the complex. It was cooled, rotary-evaporated almost to dryness; and ethanol (20 cm^3) was added. The orange-yellow crystals of the product which formed upon cooling were filtered off, washed with ethanol and diethyl ether, and air-dried (0.20 g, 10%) (Found: C, 32.85; H, 6.35; N, 10.95. Calc. for $C_{14}H_{32}Cl_2N_4NiO_8$: C, 32.7: H, 6.25; N, 10.9%).

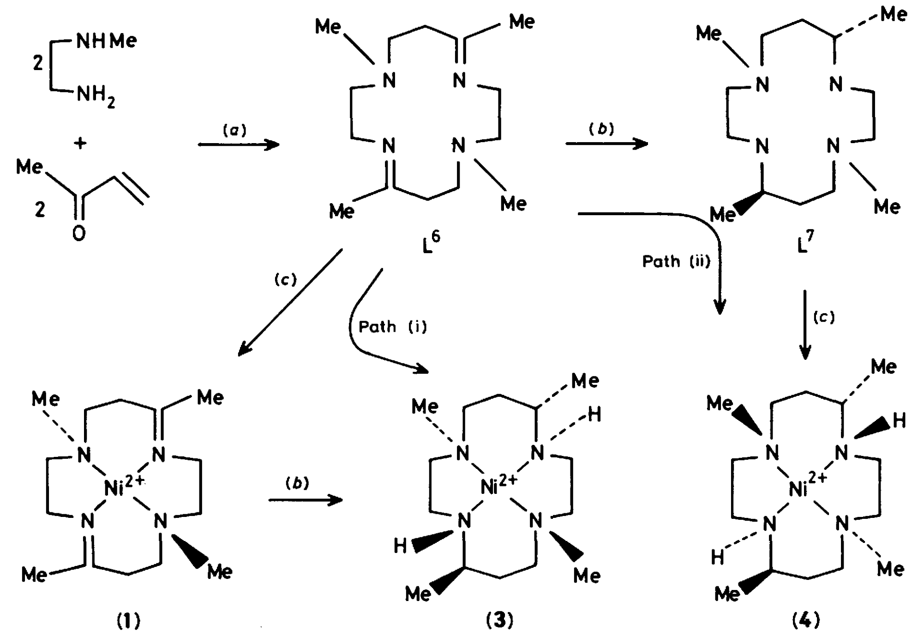
X-*Ray Structure Determination of Complex* (**3**).—Unit-cell parameters were derived from a least-squares fit of 18 values in the range $20 < 2\theta < 30°$. The nickel atom must lie on the origin since there are only two formula units in the unit cell. The complex is thus required to have a centre of symmetry. The positional parameters for non-hydrogen atoms are listed in Table 1.

Crystal data. $C_{14}H_{32}Cl_2N_4NiO_8$, $M = 514.03$, monoclinic, $a = 11.851(4)$, $b = 8.600(3)$, $c = 10.531(2)$ Å, $\beta = 94.30(2)°$, $U = 1\,070.2(5)$ Å^3, space group $P2_1/n$, $D_m = 1.590$ (at 293 K), $Z = 2$, $D_c = 1.595$ g cm^{-3}, $F(000) = 540$, orange prismatic

Table 2. Infrared, ^{1}H n.m.r., and visible absorption spectral data for the compounds obtained

	I.r. (cm^{-1})		^{1}H N.m.r.		Visible[a]	
Compound	ν(NH)	ν(C=N)	δ(C-Me)	δ(N-Me)	$\lambda_{max.}$/nm	$\varepsilon_{max.}$/dm^3 mol^{-1} cm^{-1}
L^6·2HClO$_4$	—	1 670	Unstable		—	—
L^7	3 230	—	1.01 (d),[b]	2.12 (s)[b]	—	—
(1)	—	1 650	2.13 (s),[c]	2.66 (s)[c]	448	111
(3)	3 180	—	Unobservable		463	83
(4)	3 200	—	1.83 (d),[c]	2.69 (s)[c]	456	83
[CuL^6][ClO$_4$]$_2$	—	1 650	Unobservable		526	179

[a] In aqueous solution. [b] In CDCl$_3$ solution. [c] In D$_2$O solution.



Scheme 3. The macrocycles and macrocyclic complexes obtained using *N*-methyl-1,2-diaminoethane and but-3-en-2-one as the starting materials. (*a*) 2 HClO$_4$; (*b*) NaBH$_4$; (*c*) Ni(O$_2$CMe)$_2$

crystal, dimensions 0.40 × 0.30 × 0.20 mm, μ(Mo-K_α) = 1.207 mm^{-1}.

Data collection and processing. Rigaku AFC-5 four-circle diffractometer, ω and ω–2θ (2θ > 30°) scan mode at a scan rate of 4.0° min^{-1}, graphite-monochromated Mo-K_α radiation. Four standard reflections monitored every 150 reflections which varied by <0.03. 2 077 Reflections measured (2θ < 55°), 1 887 independent with $|F_o| > 3\sigma(|F_o|)$, 698 unobserved. Intensity data were corrected for Lorentz and polarization factors, but not for absorption.

Structure analysis and refinement. Heavy-atom methods. Refined by block-diagonal least squares based on $|F_o|$. Unit weights used for all reflections. The positions of all hydrogen atoms were deduced from successive Fourier difference syntheses. All non-hydrogen atoms were assigned anisotropic thermal parameters, hydrogen atoms isotropic ones. The final indices *R* and *R'* were 0.035 and 0.034 respectively. The largest shift-to-error value in the final cycle was 0.34. Atomic scattering factors were taken from ref. 14. The crystallographic calculations were performed on a FACOM M-380 computer using the MULTAN 78[15] and UNICS III[16] programs.

Other Measurements.—Infrared spectra and visible absorption spectra were recorded with Shimadzu IR-400 and UV-210 spectrophotometers, respectively. 90-MHz Proton n.m.r. spectra were obtained with a Hitachi R-40 spectrometer.

Results and Discussion

The macrocycles and their complexes obtained in this work have two N-methyl groups at two non-adjacent nitrogen atoms. This is a natural consequence of the reaction involving *N*-methyl-1,2-diaminoethane, because the diamine has only one primary amino group to form a C=N double bond. The reactions examined and their products are summarized in Scheme 3. The i.r., ^{1}H n.m.r., and visible absorption spectral data are listed in Table 2.

Preparation of Macrocycles.—A white precipitate was obtained from the reaction of the monohydroperchlorate of *N*-methyl-1,2-diaminoethane and but-3-en-2-one. The i.r. spectrum (Table 2) showed a band at 1 670 cm^{-1} assignable to ν(C=N) but no ν(N–H) absorption around 3 200 cm^{-1}. These observations indicate the formation of a C=N double bond and the disappearance of N–H in the reaction. The existence of a perchlorate group is indicated by a band around 1 100 cm^{-1}. Although the compound was too unstable to perform an elemental analysis, the formation of the dihydroperchlorate of macrocycle L^6 is indicated on the basis of the preparation of its nickel(II) complex, as will be discussed later. It should be noted that the formation of the hydroperchlorate of L^6 is quite similar to that of the corresponding macrocycle with no N-methyl groups.[4]

It is highly probable that some side reactions compete with the above macrocycle-forming reaction. For example, C–N single-bond formation (Michael addition at the C=C of but-3-en-2-one) is also possible at the primary amino group of the diamine. This should result in the formation of an open-chain by-product. Even if such bond formation took place selectively at the secondary amino group, there still remains a possibility of by-products due to the condensation of more than three molecules each of ketone and diamine. Thus, the yield of *ca.* 40% for L^6 can be considered as reasonable and sufficient. This diaminodi-imine macrocycle can be characterized by the presence of two N-methyl groups alternating with two imines.

When two C=N bonds of L^6 are hydrogenated, two chiral carbon centres are newly formed, so that two diastereomeric macrocyclic tetramines, *meso*-L^7 and *rac*-L^8, are expected to occur. However, the reduction of L^6 with $NaBH_4$ gave selectively one of the two possible macrocyclic tetramines in the crystalline form (76%). The mother-liquor was examined carefully for the other tetramine, but the tetramine extracted from strongly basic solution with toluene was also the predominant species (total yield > 80%). The structure of this tetramine was determined through methylation of the remaining amino groups, as follows.

Authentic *C*-*meso*-1,4,5,8,11,12-hexamethyl-1,4,8,11-tetra-azacyclotetradecane, L^9, was obtained by the reported method.[4] The i.r. and ^{1}H n.m.r. spectra of this sample and those of the tetra-N-methyl compound synthesized from L^6 by the Leuckart reaction[17] were found to be indistinguishable, indicating that the predominant species obtained above is *meso*-L^7 and not *rac*-L^8.

It is quite interesting that the tetramines produced by the $NaBH_4$ reduction of L^6 and of the non-N-substituted macrocycle 5,12-dimethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene[4] are both exclusively *C*-*meso* isomers. The fact that L^6 and its non-N-substituted analogue give the *C*-*meso* isomers predominantly upon reduction is quite an unexpected result. The selection between the reaction path to form *C*-*meso* and *C*-*rac* isomers is made at the stage of reduction of the second C=N of the diaminodi-imine macrocycle, under the influence of the chiral carbon centre formed upon reduction of the first C=N. With regard to the structures of the macrocycles, the influence of the chiral carbon centre on the reduction of the second C=N seems to be very weak in these macrocycles, since it is located at the farthermost end of the macrocycle from C=N, where the selection between *C*-*meso* and *C*-*rac* isomers is made. Actually, both *rac* (major) and *meso* (minor) isomers are obtained upon reduction of macrocycle L^1.[5] Although the reason for this difference is still uncertain, such selectivity is useful from the viewpoint of synthesizing macrocycles.

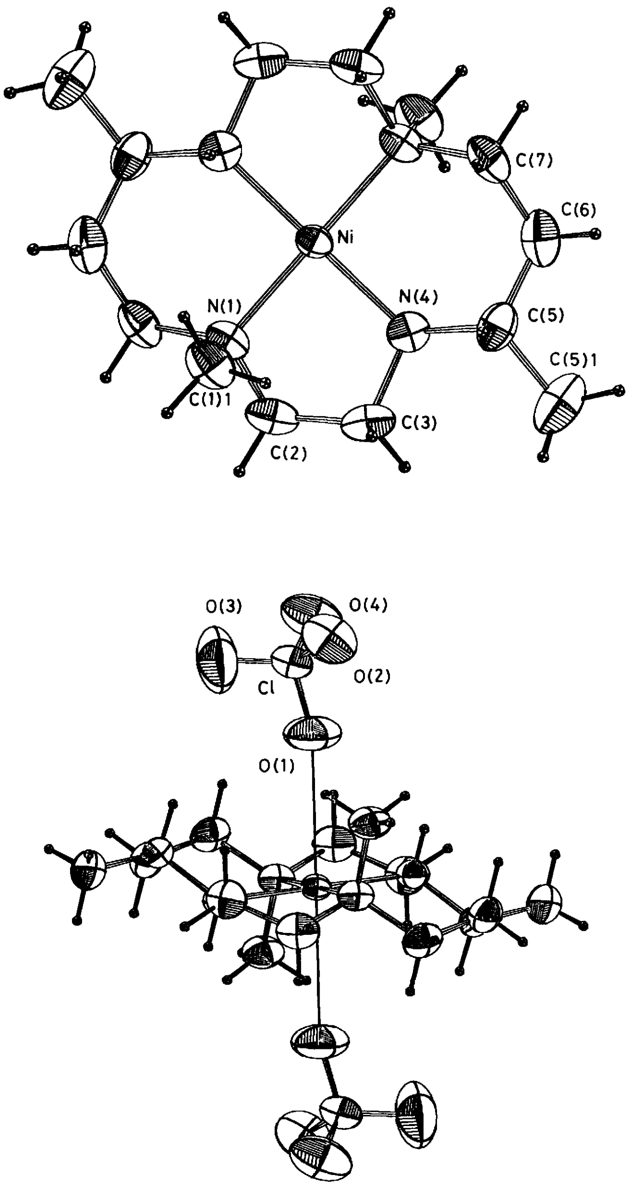


Figure 1. Perspective views of the macrocyclic complex (3)

Preparation and Structure of Macrocyclic Complexes.—The diaminodi-imine macrocycle L^6 captures metal ions such as Ni$^{\text{II}}$ and Cu$^{\text{II}}$ to give corresponding metal complexes. Their i.r. and visible absorption spectral data are given in Table 2. Both nickel(II) and copper(II) complexes have an absorption at around 1 670 cm^{-1} assignable to ν(C=N). The visible absorption data are similar to those of analogous macrocyclic diaminodi-imine complexes.[4]

The nickel(II) complex of L^6 has two newly formed chiral nitrogen centres, so that two isomeric complexes, *meso* [(**1**)] and *rac* [(**2**)], are possible. In the *meso* complex two N-methyl groups are orientated in the opposite direction with regard to the NiN_4 basal plane, while in the *rac* complex they are in the same direction. However, the ^{1}H n.m.r. spectrum of the crystalline product which precipitated from the reaction mixture revealed that it consisted of a single complex (**A**). The filtrate was examined by means of ion-exchange chromatography (SP-Sephadex C-25, 4 × 100 cm, sodium form; aqueous NaCl solution, 0.15 mol dm^{-3}), but only the complex (**A**) was obtained. Its structure can be determined from the structural analysis of the complex (**B**) obtained upon reduction of (**A**) with $NaBH_4$, as described later.

The reduction of (**A**), *i.e.* $[\mathrm{NiL^6}][\mathrm{ClO_4}]_2$, by $NaBH_4$ gave exclusively an orange complex (**B**). In the reduction process, two chiral carbon centres and two chiral nitrogen centres are newly formed. Together with two chiral nitrogen centres already present in the starting complex, these six chiral centres result in the possibility of 20 isomers (16 *rac* and 4 *meso*). These isomers can be classified into two groups with regard to the structure of the starting complex: 10 (6 *rac* and 4 *meso*) from (**1**) and 10 *rac* from (**2**). There are too many possible structures to determine the actual one for complex (**B**) by spectroscopic considerations. Further, its ^{1}H n.m.r. spectrum, which might give valuable information especially on the symmetry and orientations of the C-methyl groups, could not be observed due to its paramagnetism in aqueous solution. Thus, an *X*-ray diffraction study was performed on (**2**) which was obtained predominantly from the reduction and gave a suitable crystal.

Table 3. Selected bond lengths (Å) and angles (°) for complex (3)

Ni–N(1)	1.960(2)	C(5)–C(6)	1.505(5)
Ni–N(4)	1.973(2)	C(5)–C(5′)	1.531(5)
Ni–O(1)	2.887(3)	C(6)–C(7)	1.509(5)
N(1)–C(1′)	1.487(4)	C(7)–N(1′)	1.496(4)
N(1)–C(2)	1.494(4)	Cl–O(1)	1.425(3)
C(2)–C(3)	1.482(5)	Cl–O(2)	1.420(3)
C(3)–N(4)	1.493(4)	Cl–O(3)	1.403(4)
N(4)–C(5)	1.507(4)	Cl–O(4)	1.418(3)
N(1)–Ni–N(4)	87.18(9)	N(4)–Ni–O(1)	96.55(9)
N(1)–Ni–N(4)	92.82(9)	N(1)–Ni–O(1′)	83.61(10)
N(1)–Ni–O(1)	96.39(10)	N(4)–Ni–O(1′)	83.45(9)

Crystal Structure of Complex (**B**).—Figure 1 shows perspective drawings of the structure. Selected bond parameters are listed in Table 3. The complex is centrosymmetric as was deduced from the crystal data, and has a distorted octahedral structue with the perchlorates at two apical co-ordination sites. The macrocyclic tetramine co-ordinates to Ni^{II} as a quadridentate ligand, and its four nitrogen-donor atoms occupy planar co-ordination sites. The four Ni–N bond lengths are within the usual range (1.9—2.0 Å), indicating that the ligand is firmly co-ordinated to Ni^{II}.

The macrocyclic part of complex (**B**) can be drawn [Figure 2(*a*)] as illustrated for (**3**) with regard to the six chiral centres, and is *meso* as a whole. The macrocyclic ligand of complex (**3**) is *meso* with regard to the two newly formed chiral carbon centres. Thus (**3**) is a nickel(II) complex of *meso*-L^7 and not of *rac*-L^8. The macrocyclic complex is also *meso* with regard to the two chiral nitrogen centres having the N-methyl groups. These two methyl groups are orientated in the opposite directions of the NiN_4 plane. Thus complex (**3**) can be regarded as a reduced product of *meso* (**1**), whose N-methyl groups are also orientated in opposite directions. This fact strongly indicates that the starting diaminodi-imine complex (**A**) has the *meso* structure (**1**) rather than (**2**).

Nickel(II) *Complexation of Macrocycle* L^7.—The crystallographic analysis revealed that (**3**) is a nickel(II) complex of L^7, the *meso* macrocyclic tetramine, which is readily obtained by $NaBH_4$ reduction of L^6. Ten isomers are possible for the planar nickel(II) complex of L^7 [six *rac* and four *meso* isomers including (**3**)]. The nickel(II) complex of L^7 obtained from (**1**) by the reaction path (i) in Scheme 3 was *meso* (**3**). In principle, the nickel(II) complex produced *via* path (ii), where the reduction precedes the complexation, need not necessarily be identical to that from path (i). Thus, the complexation of L^7 with Ni^{II} was carried out and the reaction products were compared with complex (**3**).

The reaction of L^7 with nickel(II) acetate proceeded rather slowly, and gave complex (**C**) as the sole product in low yield. This complex was different from (**3**), giving clear ^1H n.m.r. signals: a singlet at 2.69 p.p.m. assignable to the N-methyl groups and a doublet at 1.84 p.p.m. assignable to the C-methyl groups, indicating C_i symmetry. Proton n.m.r. investigations of other nickel(II) complexes of tetra-aza macrocycles[11,18] have demonstrated that methyl groups orientated axially with respect to the NiN_4 plane appear at around 1.7—2.0 p.p.m. and those orientated equatorially at around 1.2 p.p.m. These observations suggest the orientation of the C-methyl groups of (**C**) to be axial. Therefore, complex (**C**) is assumed to take the structure (**4**) [Figure 2(*b*)].

The structure proposed for complex (**C**) has two five-membered chelates in *gauche* conformation, and two six-membered chelates in chair conformation similarly to (**3**). This chelate-ring combination for a fourteen-membered tetra-aza macrocycle is known as the most stable one. The significant difference between (**3**) and (**4**) is the orienations of two C-methyl groups; *i.e.* two methyl groups are axial in (**4**) but equatorial in (**3**). The structural characteristics of (**3**) and (**4**) can explain the difference in the magnetic properties of (**B**) and (**C**). It is highly probable that two C-methyl groups together with two N-methyl groups nearly perpendicular to the NiN_4 plane in (**4**) strongly interfere with the approach of solvents or other ligands to the apical co-ordination sites. This effect keeps the complex in the square-planar co-ordination, and thus in a diamagnetic state. On the other hand, the weak co-ordination of perchlorates to (**3**) observed in the crystalline form strongly suggests that (**B**) partially adopts an elongated tetragonal co-ordination in aqueous solution, which results in paramagnetism.

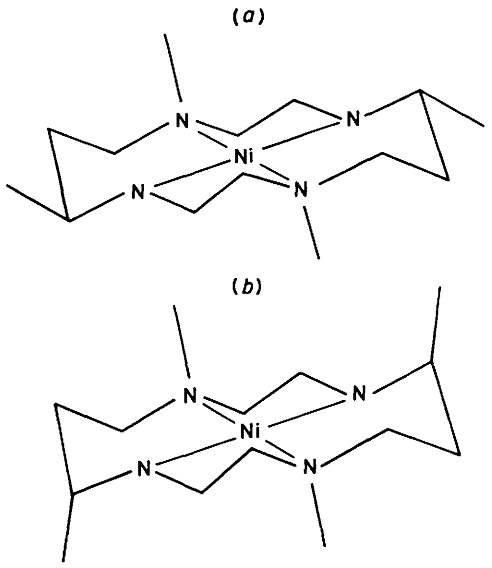


Figure 2. Schematic drawings of the structures of (*a*) complex (**3**) and (*b*) complex (**4**)

It is very interesting that diastereomeric complexes have been obtained just by changing the order of two processes, reduction and complexation. In the first reaction, either reduction or complexation, two chiral centres are newly formed to give a *meso* compound. In the second reaction, four chiral centres are formed selectively under the influence of two chiral centres already introduced. The structure of the tetramine complexes thus formed is fixed at this stage and does not transform into others, because the fully substituted chiral N centres are not interconvertible. This might be the reason why such isomerism is observed in this case and not in the case of non-N-substituted tetramines.

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Received 26*th January* 1987; *Paper* 7/128