Axial Additions in Nickel(II) Complexes of (5*SR*,7*RS*,12*RS*,14*SR*)-Tetramethyl-1,4,8,11-tetra-azacyclotetradecane (L_α) and Crystal-structure Analysis of the Planar Orange and Octahedral Violet Perchlorate Salts $NiL_\alpha(ClO_4)_2$

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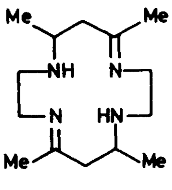
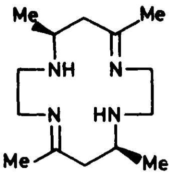
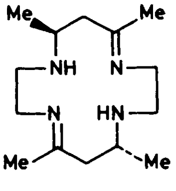
Reduction of the nickel(II) complex of *C-meso*-5,7,12,14-tetramethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene with $NaBH_4$ gives predominantly the nickel(II) complex of the title ligand, L_α. Both orange (1) and violet (2) isomers of $NiL_\alpha(ClO_4)_2$ have been characterised and structures established by *X*-ray crystallography. Crystals of (1) are monoclinic, space group $P2_1/c$ with two formula units in a unit cell of dimensions a = 8.244(1), b = 8.656(1), c = 16.701(1) Å, and β = 110.28(1)°. Crystals of (2) are triclinic, space group $P\bar{1}$ with two formula units in a cell of dimensions a = 10.645(1), b = 8.298(1), c = 14.198(2) Å, α = 121.36(1), β = 94.61(1), and γ = 82.77(1)°. Both structures were solved by the heavy-atom method and refined by full-matrix least-squares calculations. For (1), R = 0.036 for 2 434 observed reflections; for (2), R = 0.043 for 1 924 observed reflections. Orange complex (1) contains ionic perchlorate with the closest Ni···O contact 2.808(5) Å. In the centrosymmetric square-planar cation the Ni–N distances are 1.964(3) and 1.974(3) Å. The purple complex (2) contains two independent discrete half molecules (2a) and (2b) lying on inversion centres in the asymmetric unit, both with axially bound perchlorate. Principal distances are Ni–O 2.235(3) and 2.221(2) Å and Ni–N 2.063(2)—2.081(2) Å. The metal complexes have the *trans* III arrangement of the chiral nitrogen centres, with the four methyl groups equatorial. The complex $[NiL_\alpha]^{2+}$ undergoes axial additions with unidentate ligands (H_2O, Br^-, Cl^-, NCS^-, N_3^-, NO_2^-, O_2CMe^-) and *trans*-$[NiLX_2]^{n+}$ have been prepared and characterised. Infrared and *d–d* spectra are reported. The equilibrium $[NiL_\alpha]^{2+} + 2H_2O \rightleftharpoons [NiL_\alpha(OH_2)_2]^{2+}$ has been studied over a temperature range, yielding K = 5.06 at 25 °C with $\Delta H^\ominus$ = − 22.1 kJ mol^{-1} and $\Delta S^\ominus$ = −60.6 J K^{-1} mol^{-1}.

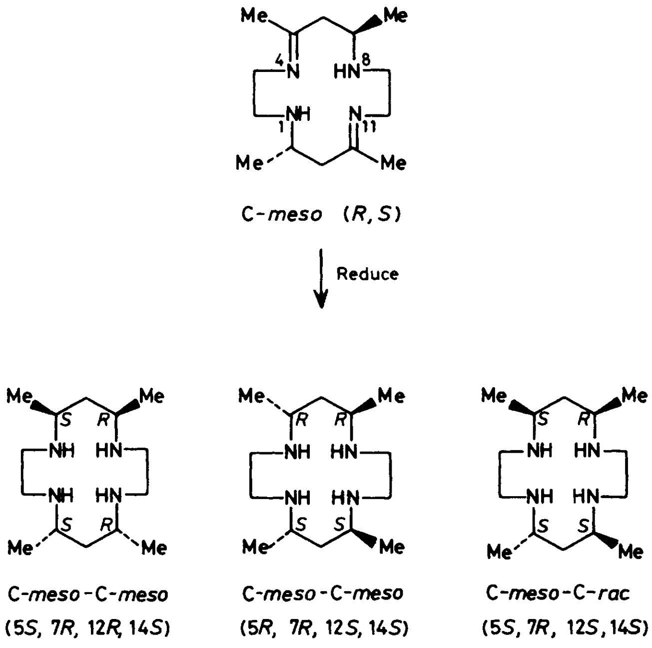
Kolinski and Korybut-Daszkiewicz[1] first described the nickel(II) complexes of the macrocyclic ligand 5,7,12,14-tetramethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene (I) (=L). The ligand contains two chiral carbon centres at C^7 and C^{14} so that *C-rac* (II) and *C-meso* (III) diastereoisomers can occur. Fractional crystallisation of [NiL][ClO_4]$_2$ from 90% methanol–10% water gives the *C-meso* diastereoisomer (orange crystals, major component) as the least-soluble fraction and the *C-rac* diastereoisomer as yellow needles. A chromatographic separation of the diastereoisomeric nickel(II) complexes on SP-Sephedex C-25 resin has recently been developed.[2] The structures of the two diastereoisomeric nickel(II) complexes have been established by *X*-ray crystallography.[3,4,†]


(I) = L


(II) *C-rac*


(III) *C-meso*

The present paper discusses the reduction of the *C-meso* diastereoisomer [as its nickel(II) complex]. Three diastereoisomeric tetra-amines can result (Scheme 1) and the nickel(II) complexes of one of these amines, (5*SR*,7*RS*,12*RS*,14*SR*)-tetramethyl-1,4,8,11-tetra-azacyclotetradecane, are discussed in detail in conjunction with a number of crystal-structure determinations.



Scheme 1 Reduction products of *C-meso*-5,7,12,14-tetramethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene

EXPERIMENTAL

5,7,12,14-Tetramethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene dihydroperchlorate was prepared essentially as

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† The *X*-ray data are rather ambiguous as the two isomers are not clearly defined. The crystal structure discussed in ref. 3 is that of the minor yellow diastereoisomer (*C-rac* ligand), *i.e.* compound VIIBα of ref. 1. The crystal structure described in ref. 4 is that of the main orange isomer (*C-meso* ligand) *i.e.* compound VIIAα of ref. 1. We thank Dr. R. A. Kolinski for clarifying this point.

previously described,[5] and the nickel (II) complex prepared as described by Kolinski and Korybut-Daszkiewicz [1] (perchlorate salt). The mixture of diastereoisomers was fractionally crystallised from hot water. The first fraction gave the orange isomer [Aα = N-*rac*-C-*meso*-(a-e)].* The ^{1}H n.m.r. spectrum of the Aα isomer was identical to that reported in the literature.[1] However, column chromatography on SP-Sephedex C-25 using 0.3 mol dm^{-3} sodium glycinate as eluant indicated 85% Aα isomer, 10% Bα isomer [Bα = N-*rac*-C-*rac* (a-a)], and 5% of the nickel(II) complex of 5,7,7,12,14-pentamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene.[2] Details of the chromatographic separations have been described.[2]

TABLE 1

Analytical data for *trans*-$[NiL_\alpha X_2]^{n+}$ complexes

Complex	Colour	Analysis (%) [a] C	H	N
$[NiL_\alpha Cl_2]$ [b]	Violet	43.3 (43.6)	8.3 (8.4)	13.8 (14.5)
$[NiL_\alpha Br_2]\cdot 2H_2O$	Violet	32.6 (32.9)	7.2 (7.1)	10.6 (10.95)
$[NiL_\alpha I_2]\cdot 2H_2O$	Violet	27.6 (27.8)	5.9 (6.0)	9.0 (9.3)
$[NiL_\alpha (NO_2)_2]\cdot 0.5H_2O$	Pale pink	40.7 (40.4)	7.9 (7.0)	20.5 (20.2)
$[NiL_\alpha (NCS)_2]$	Violet	44.8 (44.6)	7.4 (7.5)	19.0 (19.5)
$[NiL_\alpha (NH_3)_2][ClO_4]_2$	Violet	30.8 (30.7)	6.9 (7.0)	14.9 (15.3)
$[NiL_\alpha (dmso)_2][ClO_4]_2$	Violet	31.9 (32.2)	6.5 (6.6)	8.1 (8.4)
$[NiL_\alpha (CN)(ClO_4)]\cdot 0.5H_2O$	Violet	40.1 (40.1)	7.0 (7.4)	15.2 (15.6)
$[NiL_\alpha (O_2CMe)(OH_2)][ClO_4]$	Violet	39.3 (39.1)	7.4 (7.6)	11.3 (11.4)

[a] Calculated figures in parentheses. [b] Cl 18.1 (18.4)%.

Reduction of the Aα *Isomer*.—The crude Aα isomer (64.8 g, 0.127 mol) was dissolved in hot water (750 cm^3) and the solution cooled to room temperature. The pH of the solution was adjusted to *ca*. 9, and sodium tetrahydroborate (11.3 g, 0.3 mol) added in small portions to the warm solution (*ca*. 60 °C) with vigorous stirring. On completion of the addition, the solution was heated for a further 0.5 h, then filtered. The volume of the filtrate was reduced by half on a rotatory evaporator, and then allowed to stand overnight at room temperature. A crop of violet crystals (*ca*. 15 g) was collected (fraction 1). After a further 24 h a second crop of orange-red crystals (5 g) was obtained (fraction 2), and after a further 2 d a third crop (*ca*. 2 g) (fraction 3).

The violet crystals (fraction 1) were recrystallised from water to give a mixture of orange and violet prismatic crystals. This mixture was recrystallised from 6 mol dm^{-3} $NaClO_4$ to give a homogeneous red-orange complex. *X*-Ray crystallography establishes that the violet crystals contain unidentate perchlorate in the axial sites, while the red-orange crystals have only ionic perchlorate (see later).

Fractions 2 and 3 were also recrystallised from water, and reddish orange crystals were obtained from both fractions. It is convenient to label fractions 1, 2, and 3 as $[NiL_\alpha]^{2+}$, $[NiL_\beta]^{2+}$, and $[NiL_\gamma]^{2+}$ respectively [Found: C, 32.9; H, 6.1; N, 10.6. Calc. for $NiL_\alpha(ClO_4)_2$, $C_{14}H_{32}Cl_2N_4NiO_8$: C, 32.7; H, 6.3; N, 10.9. Found: C, 32.2; H, 6.1; N, 10.6. Calc. for $NiL_\beta(ClO_4)_2\cdot 0.5H_2O$: C, 32.15; H, 6.4; N, 10.7. Found: C, 32.9; H, 6.3; N, 10.8. Calc. for $NiL_\gamma(ClO_4)_2$: C, 32.7; H, 6.3; N, 10.9%.]. Some samples of $NiL_\alpha(ClO_4)_2$ appeared to contain some water (axial addition) and analysed as sesquihydrates.

Isolation of the Free Ligands.—The complex $NiL_\alpha(ClO_4)_2$ (1 g, 0.002 mol) was dissolved in hot water and solid sodium cyanide (0.6 g, 0.01 mol) added. The red-orange solution immediately became violet (axial addition of cyanide). The reaction mixture was heated under reflux for *ca*. 2 h, then taken to dryness on a rotatory evaporator. The solid residue was extracted with hot chloroform and the chloroform removed to give the solid macrocyclic amine which was recrystallised from xylene, m.p. 169—172 °C (Found: C, 65.3; H, 12.4; N, 22.0. Calc. for $C_{14}H_{32}N_4$: C, 65.6; H, 12.6; N, 21.9%).

The same procedure was employed to decompose the complexes $NiL_\beta(ClO_4)_2$ and $NiL_\gamma(ClO_4)_2$. The macrocyclic amines obtained, L_β and L_γ, had melting points 150—155 and 70—72 °C respectively. Amine L_α is the least soluble in xylene and L_γ is the most soluble. The three amines lack the band at 1 660 cm^{-1} due to ν(C=N) in the di-imine indicating complete reduction (Found: C, 59.0; H, 12.5; N, 19.4. Calc. for L_β, $C_{14}H_{32}N_4\cdot 1.5H_2O$: C, 59.3; H, 12.45; N, 19.8. Found: C, 57.3; H, 12.25; N, 19.1. Calc. for L_γ,$C_{14}H_{32}N_4\cdot 2H_2O$; C, 57.5; H, 12.4; N, 19.2%).

The subsequent preparations involved the reaction of orange $[NiL_\alpha][ClO_4]_2$ with the appropriate metal salt (NaCl, NaBr, NaI, $NaNO_3$, or KSCN) in water or water–methanol solution, to give the axial adducts. The following preparation is an illustrative example of the procedure employed.

trans-*Dichloro*(5,7,12,14-*tetramethyl*-1,4,8,11-*tetra-azacyclotetradecane*)*nickel*(II), *trans*-$[NiL_\alpha Cl_2]$.—To a hot solution of the complex $[NiL_\alpha][ClO_4]_2$ (0.5 g, 0.9 mmol) in methanol–water (25 cm^3, 1:1), was added sodium chloride (0.1 g, 1.9 mmol). On heating on a water-bath the solution became violet. Cooling in an ice-bath gave violet crystals which were filtered off, washed with ethanol then diethyl ether, and dried *in vacuo*. The analytical data for the various complexes are summarised in Table 1.

The diammine $[NiL_\alpha(NH_3)_2][ClO_4]_2$ was prepared by warming the orange complex (0.3 g) in water (25 cm^3) with ammonia solution (s.g. 0.88, 5 cm^3). The violet *product* was obtained on cooling in an ice-bath. On long standing in air the diammine loses the ammonia ligands and becomes red-orange.

The bis(dimethyl sulphoxide) complex $[NiL_\alpha(dmso)_2][ClO_4]_2$ was prepared by heating $[NiL_\alpha][ClO_4]_2$ in dimethyl sulphoxide. Long cooling in a refrigerator (2 d) gave the violet crystalline complex.

Crystallographic Measurements.—*Crystal data*. $C_{14}H_{32}Cl_2N_4NiO_8$, Orange isomer (1), M = 514.1, Monoclinic, a = 8.244(1), b = 8.656(1), c = 16.701(1) Å, β = 110.28(1)°, U = 1 124.6 Å^3, Z = 2, D_c = 1.52 g cm^{-3}, $F(000)$ = 540, Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 10.8 cm^{-1},

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* a = Axial and e = equatorial, referring to the ring methyl substituents.

space group $P2_1/c$ determined uniquely by systematic absences $0k0$, $k = 2n + 1$ and $h0l$, $l = 2n + 1$.

$C_{14}H_{32}Cl_2N_4NiO_8$, Violet isomer (2), $M = 514.1$, Triclinic, $a = 10.645(1)$, $b = 8.298(1)$, $c = 14.198(2)$ Å, $\alpha = 121.36(1)$, $\beta = 94.61(1)$, $\gamma = 82.77(1)°$, $U = 1\,059.0$ Å^3, $Z = 2$, $D_c = 1.61$ g cm^{-3}, $F(000) = 540$, λ(Mo-K_α) = 0.710 69 Å, μ(Mo-K_α) = 10.8 cm^{-1}, space group $P\bar{1}$ or $P1$, determined as the former from structure analysis.

For both orange (1) and violet (2) isomers, preliminary cell data were obtained from precession and Weissenberg photographs; accurate unit-cell data were obtained from a least-squares refinement of diffractometer setting angles of 12 strong general-order reflections. A Hilger and Watts Y290 computer-controlled diffractometer equipped with graphite-monochromatised Mo-K_α radiation was used for the data collections in a manner similar to that described previously.[6] A small (0.14 × 0.17 × 0.14 mm) crystal was chosen for data collection for (1). No small crystals of (2) gave suitable preliminary photographs and attempts to cut a large one to size resulted in cracked fragments; the crystal used for data collection measured 0.54 × 0.47 × 0.21 mm. For (1) data were collected to a maximum θ of 27° and 2 443 unique data were measured; for (2), the maximum θ was 22° and 2 781 unique reflections were measured. After corrections for Lorentz and polarisation effects [and absorption for (2)], the data with $I > 3\sigma(I)$ were labelled ' observed ' [1 924 for (2), 2 434 for (1)] and used in structure solution and refinement.

Structure solutions and refinement. For (1) the Ni atom is required to lie at an inversion centre from space-group considerations and a Patterson synthesis allowed the unique chlorine-atom position to be determined. The co-ordinates of the remaining non-hydrogen atoms were determined by the heavy-atom method. The Patterson distribution for (2) showed clearly that the two molecules in the unit cell lay on independent inversion centres (at *e.g.* 0,0,0 and $\frac{1}{2}$,0,$\frac{1}{2}$) and allowed positions for the Cl atoms to be determined. The remaining non-hydrogen atoms were then found from Fourier syntheses phased with Ni and Cl atom contributions.

Both structures were refined by full-matrix least-squares calculations [7] with anisotropic thermal parameters for the non-hydrogen atoms. Difference syntheses computed when R was 0.058 for (1) and 0.062 for (2) revealed maxima in the expected positions of all the hydrogen atoms. These were allowed for in geometrically expected positions (with C–H 1.08 Å and an overall isotropic thermal parameter) but not refined in subsequent calculations. In the refinements a weighting scheme of the form $w = 1/[\sigma^2(F) + pF^2]^{\frac{1}{2}}$ was used where the final p values were 0.0022 for (1) and 0.0034 for (2). Refinement converged with $R = 0.043$ and $R' = 0.071$ for (2), and $R = 0.036$ and $R' = 0.048$ for (1). Final difference syntheses were devoid of any chemically significant features. The scattering factors used for the non-hydrogen atoms were taken from ref. 8 and those for hydrogen from ref. 9.

Table 2 * contains the final fractional co-ordinates with estimated standard deviations for (1) and (2). Details of bond lengths, angles, and torsion angles are in Table 3.

TABLE 2

Final fractional co-ordinates with estimated standard deviations in parentheses

(*a*) Orange isomer (1)

Atom	*x*	*y*	*z*
Ni	0.0	0.0	0.0
N(1)	−0.125 5(3)	0.178 1(3)	0.022 6(2)
C(2)	−0.042 1(5)	0.218 9(4)	0.114 6(2)
C(3)	0.148 2(5)	0.205 5(4)	0.135 3(2)
N(4)	0.180 8(4)	0.048 1(3)	0.110 6(2)
C(5)	0.367 1(5)	0.024 7(5)	0.121 0(3)
C(51)	0.483 8(6)	0.060 9(9)	0.213 7(4)
C(6)	0.398 4(5)	−0.137 8(5)	0.096 8(3)
C(7)	0.318 0(4)	−0.173 5(4)	0.002 9(3)
C(71)	0.389 0(7)	−0.325 9(6)	−0.017 5(4)
Cl	0.067 6(1)	0.304 0(1)	−0.136 3(1)
O(1)	0.168 7(6)	0.189 6(7)	−0.083 0(4)
O(2)	0.160 5(6)	0.398 8(4)	−0.175 2(2)
O(3)	0.010 1(11)	0.398 8(5)	−0.081 2(4)
O(4)	−0.081 9(6)	0.238 6(7)	−0.196 0(3)

(*b*) Violet isomer (2a)

Atom	*x*	*y*	*z*
Ni(1)	0.0	0.0	0.0
N(11)	0.194 1(2)	−0.023 9(3)	−0.019 0(2)
C(12)	0.233 1(3)	0.168 3(4)	0.055 1(3)
C(13)	0.164 3(3)	0.258 5(4)	0.163 5(3)
N(14)	0.025 9(2)	0.257 6(3)	0.140 8(2)
C(15)	−0.048 5(3)	0.307 6(4)	0.238 9(2)
C(151)	−0.022 1(3)	0.500 6(5)	0.339 1(3)
C(16)	−0.190 7(3)	0.308 0(4)	0.208 5(2)
C(17)	−0.242 5(3)	0.116 8(4)	0.133 5(3)
C(171)	−0.387 1(3)	0.144 6(5)	0.134 2(3)
Cl(1)	0.121 9(1)	−0.276 3(1)	0.100 5(1)
O(1)	0.020 7(2)	−0.143 9(3)	0.097 5(2)
O(2)	0.088 7(2)	−0.332 4(3)	0.173 7(2)
O(3)	0.237 5(2)	−0.186 6(4)	0.134 9(3)
O(4)	0.139 3(2)	−0.436 2(3)	−0.007 9(2)

(*c*) Violet isomer (2b)

Atom	*x*	*y*	*z*
Ni(2)	0.5	0.0	0.5
N(21)	0.338 1(2)	−0.100 5(3)	0.512 4(2)
C(22)	0.277 5(3)	−0.191 2(4)	0.400 6(3)
C(23)	0.380 8(3)	−0.298 9(4)	0.316 3(2)
N(24)	0.470 7(2)	−0.164 8(3)	0.330 3(2)
C(25)	0.585 5(3)	−0.260 8(4)	0.260 8(2)
C(251)	0.551 9(3)	−0.360 1(5)	0.137 2(3)
C(26)	0.681 9(3)	−0.121 3(4)	0.287 0(2)
C(27)	0.751 5(3)	−0.038 9(4)	0.399 3(3)
C(271)	0.867 8(3)	0.051 9(5)	0.397 2(3)
Cl(2)	0.663 1(1)	−0.314 7(1)	0.560 0(1)
O(21)	0.608 0(2)	−0.261 0(3)	0.482 5(2)
O(22)	0.689 2(3)	−0.511 1(4)	0.506 1(3)
O(23)	0.584 2(3)	−0.240 5(5)	0.649 7(3)
O(24)	0.780 8(3)	−0.229 5(4)	0.596 4(3)

The tables of thermal parameters, calculated hydrogen-atom positions, and structure-factor listings have been deposited as Supplementary Publication No. SUP 23310 (34 pp.)† Figure 1(*a*), prepared with the aid of ORTEP,[10] shows the orange isomer (1), Figure 1(*b*) and 1(*c*) show the violet isomers (2a) and (2b), and Figures 2 and 3 are stereoviews of the molecular packing for (1) and (2) respectively.

RESULTS AND DISCUSSION

Reduction of the nickel(II) complex of *C-meso*-5,7,12,14-tetramethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene (I) with $NaBH_4$ can give the nickel(II) complexes of the three amines, Scheme 1. If the nickel(II) complexes are assumed to have the most thermodynamically stable ***trans*** III (R,S,S,R) arrangement of the chiral

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* In Table 2, the atoms of molecule (2) are numbered to correspond with those of molecule (1) as shown in Figure 1(*a*). In the crystallographic discussion for clarity, the two independent molecules of (2) we ' designate ' (2a) and (2b). For the crystallographic numbering scheme used in Table 1 and Figures 1(*b*) and 1(*c*), the numbers 1 and 2 have been added to the atom labels, *e.g.* C(1) in molecule (2a) is labelled C(11), C(1) in molecule (2b) is labelled C(21), *etc.*

† For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

TABLE 3

Bond lengths (Å), angles (°), torsion angles (°), and hydrogen-bond distances (Å)

(*a*) Bond lengths

	(1)	(2a)	(2b)
Ni–O(1)	2.808(5) [a]	2.235(3)	2.221(2)
Ni–N(1)	1.964(3)	2.077(2)	2.064(3)
Ni–N(4)	1.974(3)	2.063(2)	2.081(2)
N(1)–C(2)	1.497(4)	1.474(4)	1.489(4)
N(1)–C(7$^{\mathrm{I}}$) [b]	1.499(3)	1.495(4)	1.491(3)
C(2)–C(3)	1.490(5)	1.520(5)	1.513(4)
C(3)–N(4)	1.475(5)	1.483(4)	1.484(4)
N(4)–C(5)	1.497(5)	1.494(4)	1.494(4)
C(5)–C(51)	1.545(6)	1.532(4)	1.534(4)
C(5)–C(6)	1.510(5)	1.540(4)	1.523(5)
C(6)–C(7)	1.508(6)	1.524(4)	1.537(4)
C(7)–C(71)	1.529(5)	1.528(4)	1.538(5)
Cl–O(1)	1.398(4)	1.454(2)	1.447(3)
Cl–O(2)	1.423(3)	1.423(3)	1.393(3)
Cl–O(3)	1.431(4)	1.436(3)	1.391(3)
Cl–O(4)	1.409(4)	1.422(2)	1.440(3)

(*b*) Bond angles

	(1)	(2a)	(2b)
O(1)–Ni–N(1)		93.0(1)	87.9(1)
O(1)–Ni–N(4)		90.9(1)	84.9(1)
N(1)–Ni–N(4)	86.1(1)	85.5(1)	85.6(1)
Ni–N(1)–C(2)	107.3(2)	105.7(1)	106.3(2)
Ni–N(1)–C(7$^{\mathrm{I}}$)	120.2(2)	117.8(1)	116.5(2)
C(2)–N(1)–C(7$^{\mathrm{I}}$)	111.4(2)	113.6(2)	112.8(2)
N(1)–C(2)–C(3)	107.0(3)	108.9(3)	108.2(2)
C(2)–C(3)–C(4)	106.7(3)	109.0(2)	108.9(2)
Ni–N(4)–C(3)	107.7(2)	106.2(1)	104.6(2)
Ni–N(4)–C(5)	119.5(2)	116.4(2)	117.1(1)
C(3)–N(4)–C(5)	111.8(3)	112.8(2)	113.2(2)
N(4)–C(5)–C(6)	111.0(3)	109.1(3)	111.5(3)
N(4)–C(5)–C(51)	110.3(4)	112.3(3)	111.9(3)
C(51)–C(5)–C(6)	110.6(4)	109.8(2)	109.0(3)
C(5)–C(6)–C(7)	114.5(3)	117.6(2)	117.9(3)
N(1$^{\mathrm{I}}$)–C(7)–C(6)	110.0(3)	111.2(3)	109.1(2)
N(1$^{\mathrm{I}}$)–C(7)–C(71)	111.4(3)	111.2(3)	112.0(2)
C(6)–C(7)–C(71)	110.2(4)	109.3(2)	109.5(3)
O(1)–Cl–O(2)	113.8(3)	109.1(1)	109.7(2)
O(1)–Cl–O(3)	104.7(4)	108.9(2)	109.9(2)
O(1)–Cl–O(4)	110.4(4)	108.8(1)	105.3(2)
O(2)–Cl–O(3)	108.3(2)	111.6(2)	113.5(2)
O(2)–Cl–O(4)	112.7(2)	110.6(2)	108.8(2)
O(3)–Cl–O(4)	106.4(4)	107.7(2)	109.4(2)

(*c*) Torsion angles

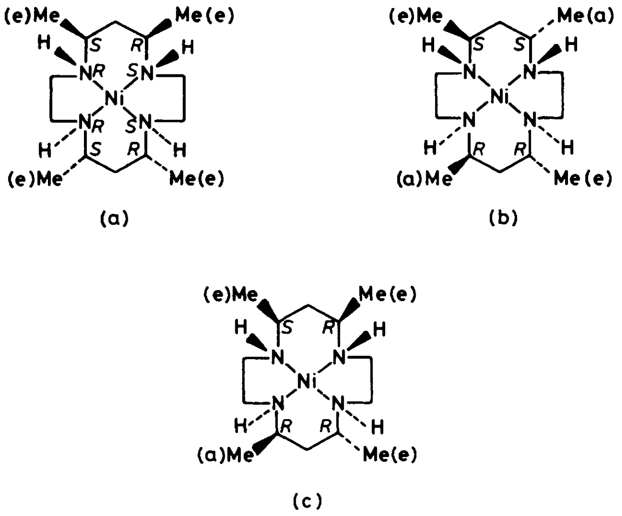
	(1)	(2a)	(2b)
C(7$^{\mathrm{I}}$)–N(1)–C(2)–C(3)	174.7	172.3	172.6
N(1)–C(2)–C(3)–C(4)	−54.9	−56.4	−58.3
C(2)–C(3)–N(4)–C(5)	174.9	168.6	169.1
C(3)–N(4)–C(5)–C(6)	179.1	178.6	178.6
N(4)–C(5)–C(6)–C(7)	68.9	73.4	72.7
C(5)–C(6)–C(7)–N(1$^{\mathrm{I}}$)	−69.1	−69.4	−69.5
C(6)–C(7)–N(1$^{\mathrm{I}}$)–C(2$^{\mathrm{I}}$)	177.9	175.5	173.6

(*d*) Hydrogen-bond distances and angles

	(1)	(2a)	(2b)
N(1) · · · O(2$^{\mathrm{II}}$)			3.143
H(1) · · · O(2$^{\mathrm{II}}$)			2.275
N(1) · · · O(3)	3.041	3.092	
H(1) · · · O(3)	2.020	2.185	
N(4) · · · O(3$^{\mathrm{I}}$)			3.204
H(4) · · · O(3$^{\mathrm{I}}$)			2.299
N(4) · · · O(4$^{\mathrm{I}}$)	3.109	3.252	
H(4) · · · O(4$^{\mathrm{I}}$)	2.070	2.312	
N(1)–H(1) · · · O(2$^{\mathrm{II}}$)			136.0
N(1)–H(1) · · · O(3)	157.4	140.0	
N(4)–H(4) · · · O(3$^{\mathrm{I}}$)			140.2
N(4)–H(4) · · · O(4$^{\mathrm{I}}$)	160.7	144.4	

[a] Not considered to be bonding but shown here for comparison. [b] The roman numeral superscripts refer to the following equivalent positions: I −*x*, −*y*, −*z* (for molecules 1 and 2a); 1 − *x*, −*y*, 1 − *z* (for molecule 2b); II 1 − *x*, −1 − *y*, 1 − *z*.

nitrogen centres, the configurations will be as shown in Scheme 2.



SCHEME 2 Configurations of the nickel complexes with the *R*,*S*,*S*,*R* arrangement of the chiral nitrogen centres (e = equatorial, a = axial)

The main fraction obtained on reduction (fraction 1) consisted of violet crystals, which could be recrystallised from water to give a mixture of orange and violet crystals. This mixture on recrystallisation from 6 mol dm^{-3} $NaClO_4$ solution gave a homogeneous orange complex. The orange isomer (1) contains discrete anions and centrosymmetric cations, Figure 1(*a*). The violet isomer contains two independent centrosymmetric molecules, (2a) and (2b), Figure 1(*b*) and 1(*c*). Details of bond lengths and angles are listed in Table 3. The analysis establishes that in the orange isomer (1) no perchlorate oxygen is directly bonded to nickel [shortest Ni · · · O 2.808(5) Å] although the two perchlorate ions are hydrogen bonded to the cation *via* N–H · · · O hydrogen bonds (N · · · O 3.041 and 3.109 Å, Table 3). In the centrosymmetric cation, the nickel atom has square-planar co-ordination with Ni–N distances of 1.964(3) and 1.974(3) Å, which are quite normal values for this bond.[11]

The crystals of the violet complex contain two independent centrosymmetric molecules of the octahedral complex in which the perchlorate groups are ‘ strongly ’ bonded to the nickel atom [Ni–O 2.235(3) and 2.221(2) Å]. In molecule (2a) the perchlorate groups are also hydrogen bonded to the ligand *via* intramolecular N–H · · · O hydrogen bonds (N · · · O 3.092 and 3.252 Å), whereas in the other molecule (2b) each perchlorate group is hydrogen bonded intra- and inter-molecularly (N · · · O 3.204 and 3.143 Å respectively). Each centrosymmetric molecule has octahedrally co-ordinated nickel with Ni–N distances of 2.063(2) to 2.081(2) Å, significantly longer than in the orange square-planar structure, but normal for octahedral complexes of this type.[12]

The intramolecular hydrogen bonding observed in (2a) is similar to that recently reported by Choinski *et* *al.*[13] for one isomer of the nickel(II) complex of 5,12-di-isopropyl-7,14-dimethyl-1,4,8,11-tetra-azacyclotetradecane, the structure of which is shown in (IV). In both complexes the ligand has identical stereochemistry and conformation, with the methyl groups equatorial and the ***trans*** III arrangement (*R,S,S,R* or *S,R,R,S* configuration) of the chiral nitrogen centres. The configuration is that shown in Scheme 2(a). In all three molecules (1a), (2a), and (2b), the torsion-angle data, Table 3, show that the conformation of the 14-membered ring is very similar. Small differences are presumably attributable to intermolecular packing effects and differences in hydrogen bonding. All six-membered rings adopt a chair conformation with equatorial methyl groups and the NH protons axial. The five-membered rings are *gauche*. The N–C distances [1.474(4)—1.499(3) Å] and the C–C distances [1.490(5)—1.545(6) Å] are in accord with previously reported values.[14] In the perchlorate groups the Cl–O distances are in the range 1.391(3)-1.454(2) Å, the longest bonds being associated with oxygen O(1), which is directly bonded to nickel in the violet complex.

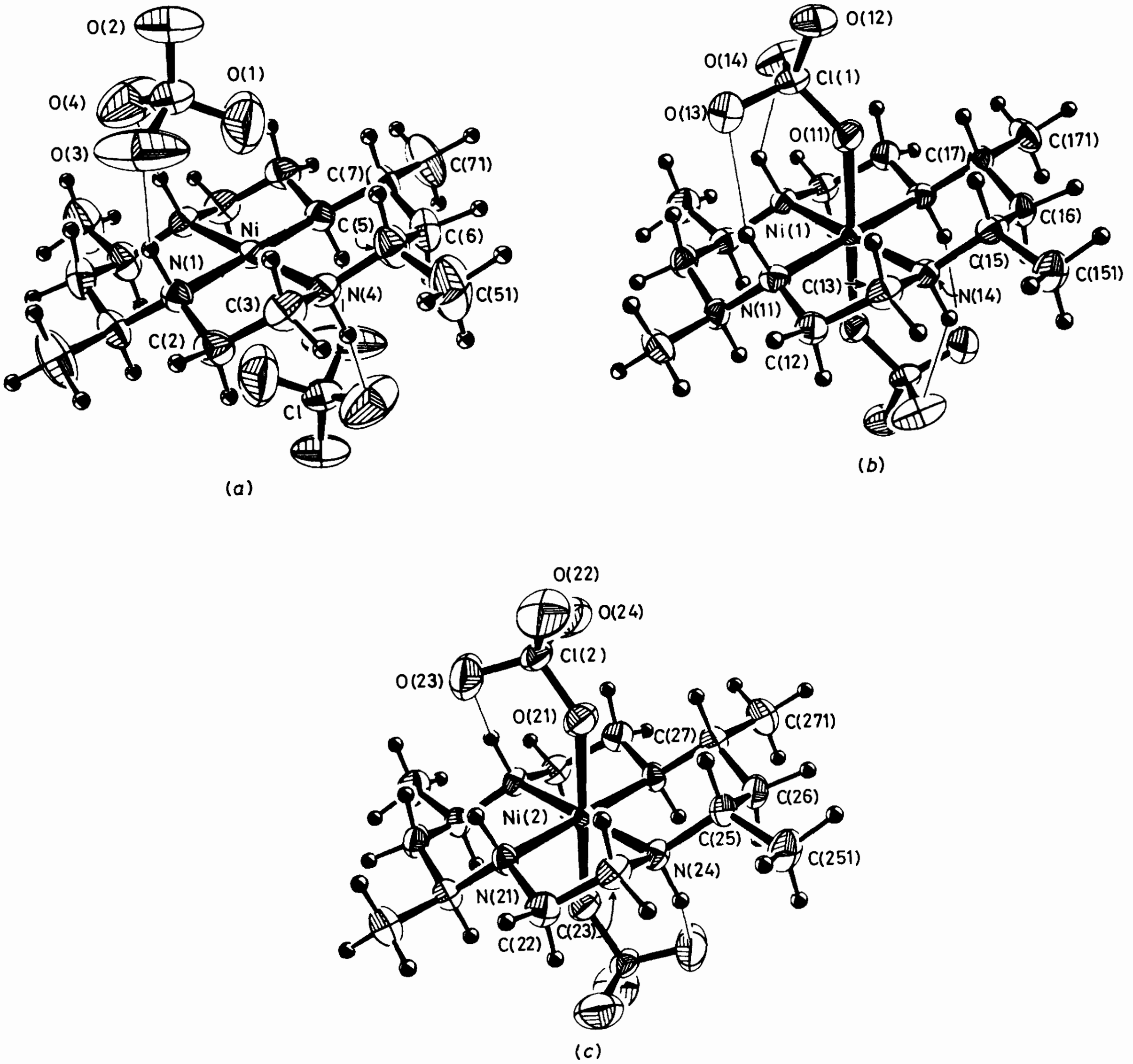
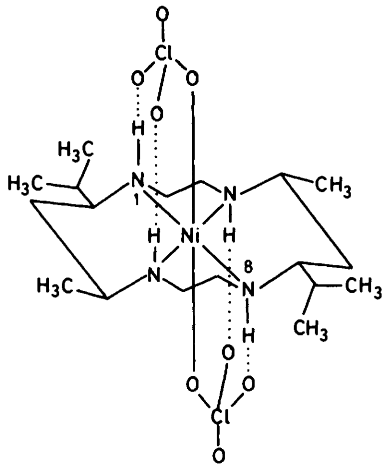


FIGURE 1 Structures of (*a*) the orange complex (1), (*b*) the violet complex (2a), and (*c*) the violet complex (2b), showing the crystallographic numbering scheme. Thermal ellipsoids are at the 50% probability level; for clarity the H atoms have been included with arbitrary isotropic thermal parameters

Axial Additions.—The visible spectrum of the violet perchlorate complex in water displays bands characteristic of both square-planar nickel(II) and octahedral nickel(II), Table 4. Recrystallisation of the violet perchlorate complex from 6 mol dm^{-3} NaClO$_4$ solution gave a homogeneous sample of the orange complex. The function of the NaClO$_4$ is to decrease the 'free' water concentration and so drive the equilibrium (i) to the left.



(IV)

The orange planar form has a single *d–d* band at 21 053

$$\text{square planar} + 2H_2O \rightleftharpoons \text{octahedral} \qquad \text{(i)}$$

cm^{-1} in the non-co-ordinating solvent nitromethane ($\varepsilon = 51$ dm^3 mol^{-1} cm^{-1}). A solution of the planar form in water gives the spectral data listed in Table 4.

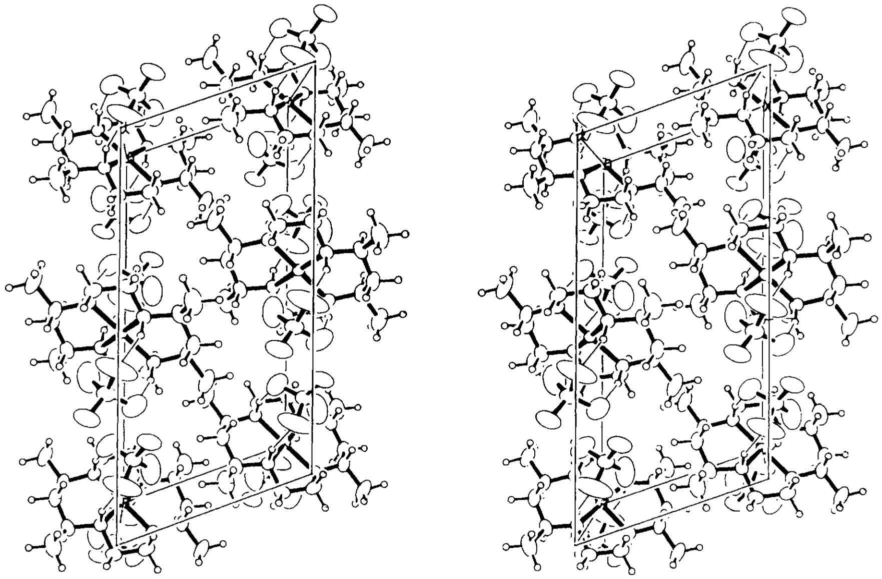


FIGURE 2 Stereoview of the packing of the orange complex (1)

Treatment of the orange isomer (1) with sodium cyanide [to remove the nickel(II)] gave initially the violet *trans*-dicyano-complex which decomposed on heating to give the free ligand (m.p. 169—172 °C) and $[Ni(CN)_4]^{2-}$. The tetra-amine (L_α) can be recrystallised from hot xylene. The same procedure applied to the planar complexes $[NiL_\beta]^{2+}$ and $[NiL_\gamma]^{2+}$ gave amines having m.p. 150—155 and 70—72 °C respectively, however these complexes were not studied in detail.

Since $[NiL_\alpha]^{2+}$ is the only nickel(II) complex to undergo axial additions it was assumed to be (a) of Scheme 2. Molecular models indicate that the two axial sites are quite open and accessible to unidentate ligands as the methyl groups are all equatorial. These views are fully confirmed by the *X*-ray data. Proton n.m.r. measurements using CD_3NO_2 solutions of $[NiL_\alpha]^{2+}$ indicate a single methyl doublet at δ 1.15 ($J = 6$ Hz) consistent with four equivalent equatorial methyl groups. [Equatorial methyl groups in such macrocyclic complexes of nickel(II) normally occur near δ 1.2 and axial methyl groups near δ 1.9.[1]]

TABLE 4

Electronic spectral data (cm^{-1}) for the violet nickel(II) complex in aqueous solution

		$\varepsilon_{obs.}$ *
Octahedral		
ν_3	29 200	10.4
ν_2	18 900	5.8
	14 300	2.9
ν_3	9 100	—
	8 700	—
Planar	21 053	8.8

* Observed absorption coefficient (dm^3 mol^{-1} cm^{-1}) based on the total complex concentration.

A number of complexes of $[NiL_\alpha]^{2+}$ with a variety of axial ligands (X) have been prepared and characterised [X = Cl, Br, I, NO_2, NH_3, SCN, dmso, and also (CN, ClO_4) and (O_2CMe, OH_2)]. The reactions are summarised in Scheme 3. The reaction of 2 equivalents of NaCN with $[NiL_\alpha][ClO_4]_2$ in aqueous solution gave $[NiL_\alpha(CN)(ClO_4)]$ containing unidentate perchlorate. The i.r. spectrum has bands at 1 100 (split), 940, and 625 cm^{-1}. The complex has $\Lambda = 73$ Ω^{-1} cm^2 mol^{-1} in water, a somewhat low value for a 1 : 1 electrolyte, but indicating that co-ordinated perchlorate is displaced by water to give a cyanoaquo-derivative.

The reaction of 2 equivalents of sodium acetate with $[NiL_\alpha][ClO_4]_2$ gives the aquoacetate complex $[NiL_\alpha(O_2CMe)(OH_2)][ClO_4]$, which has $\Lambda = 173$ Ω^{-1} cm^2

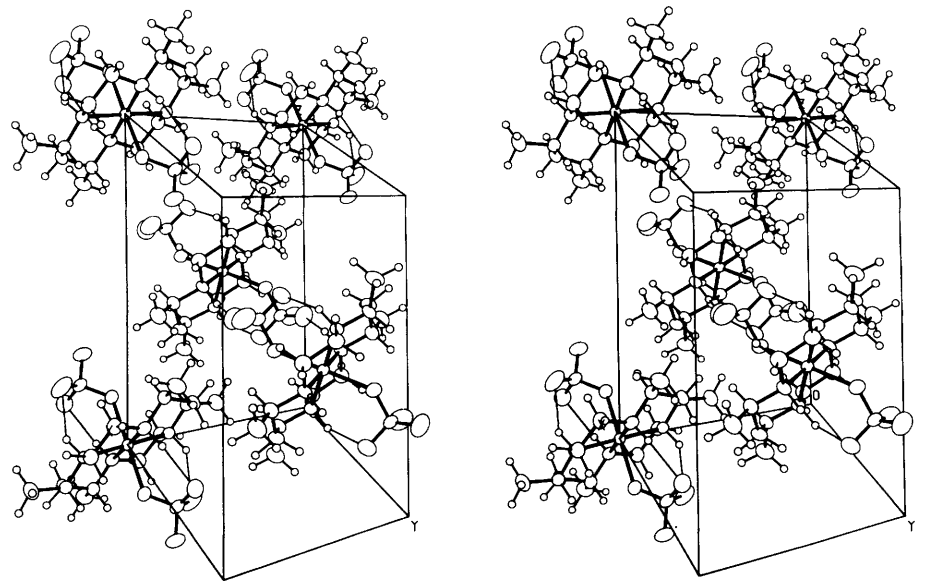
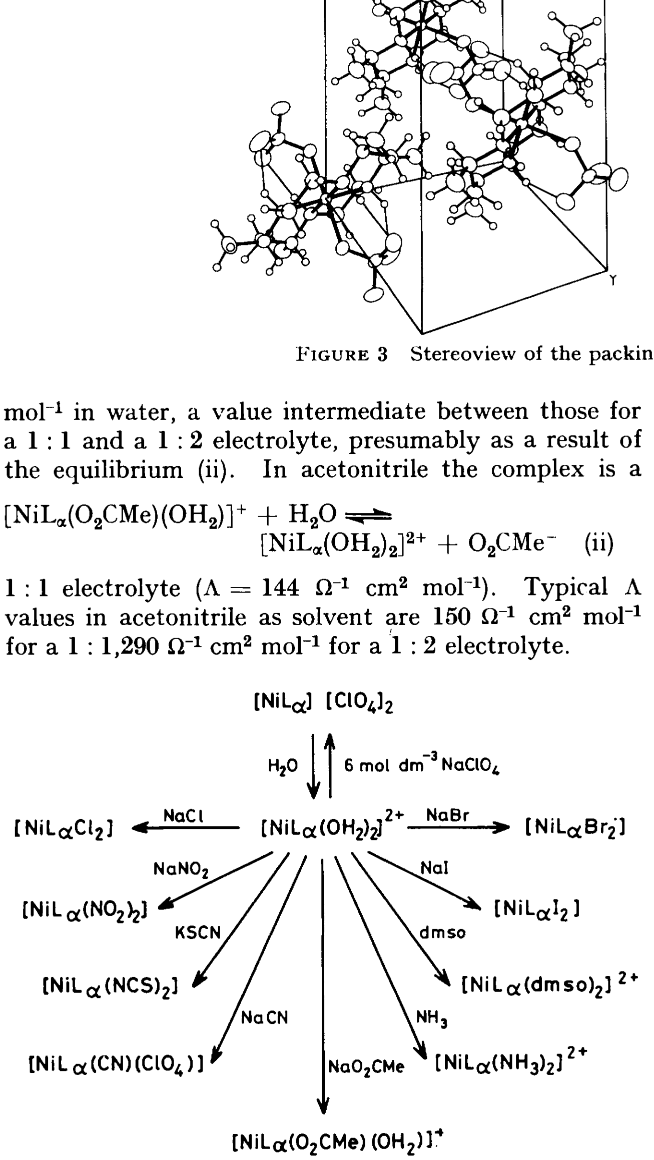


FIGURE 3 Stereoview of the packing of the violet complexes (2a) and (2b)

mol^{-1} in water, a value intermediate between those for a 1 : 1 and a 1 : 2 electrolyte, presumably as a result of the equilibrium (ii). In acetonitrile the complex is a

$$[NiL_\alpha(O_2CMe)(OH_2)]^+ + H_2O \rightleftharpoons [NiL_\alpha(OH_2)_2]^{2+} + O_2CMe^- \quad (ii)$$

1 : 1 electrolyte ($\Lambda = 144\ \Omega^{-1}\ cm^2\ mol^{-1}$). Typical Λ values in acetonitrile as solvent are 150 Ω^{-1} cm^2 mol^{-1} for a 1 : 1,290 Ω^{-1} cm^2 mol^{-1} for a 1 : 2 electrolyte.



SCHEME 3 Summary of the reactions of $[NiL_\alpha]^{2+}$

d–d *Spectra*.—The solid-state spectra of the various complexes display at least the three expected bands for nickel(II) in O_h symmetry. For nickel(II) in D_{4h} symmetry six bands are theoretically possible.[15] In cases where the ligand-field strength of the axial ligands differs markedly from that of the equatorial macrocycle as in $[NiL_\alpha I_2]$ five bands are observed. Thus, for $[NiL_\alpha I_2]$ the ${}^3A_{2g} \rightarrow {}^3T_{2g}$ (ν_1) occurs as two bands which can be assigned to ${}^3B_{1g} \rightarrow {}^3E_g{}^a$ (7 800 cm^{-1}) and ${}^3B_{1g} \rightarrow {}^3B_{2g}$ (9 000 cm^{-1}) in D_{4h} symmetry, while for the ${}^3A_{2g} \rightarrow {}^3T_{1g}$ (F) (ν_2) two bands are also observed ${}^3B_{1g} \rightarrow {}^3A_{2g}{}^a$ (14 700 cm^{-1}) and ${}^3B_{1g} \rightarrow {}^3E_g{}^b$ (18 900 cm^{-1}).

For the complex $[NiL_\alpha(NO_2)_2]$, which approximates more closely to O_h symmetry, only three bands are clearly seen: ν_3 at 29 000; ν_2 at 20 000 (some splitting can be detected); and ν_1 at 11 100 cm^{-1}. The solid-state spectra are very similar to those observed by Holtman and Cummings [16] for the six-co-ordinate nickel(II) complexes of the ligand 12,14-dimethyl-1,4,8,11-tetraazacyclotetradecane (Me$_2$cyclam). Thus, for [Ni(Me$_2$-cyclam)(NCS)$_2$], bands were observed at 10 929, 12 461, 19 608, and 30 769 cm^{-1} (solution spectra) while for $[NiL_\alpha(NCS)_2]$ bands were observed at 10 900 (ν_1), 13 500, 18 900 (ν_2), and 29 400 cm^{-1} (ν_3) in the solid state. The spectra are fully consistent with tetragonal nickel(II) (D_{4h}) stereochemistry. Table 5 summarises the electronic spectra of the various nickel(II) complexes studied.

TABLE 5

Electronic spectral data (cm^{-1}) of the various *trans* six-co-ordinate nickel(II) complexes

Complex (*a*) Solid state	ν_3	ν_2	ν_1
$[NiL_\alpha Cl_2]$	27 800	18 500, 14 300	8 900
$[NiL_\alpha Br_2]$	29 000	18 900, 14 700	9 000
$[NiL_\alpha I_2]$	29 000	18 900, 14 700	9 000, 7 800
$[NiL_\alpha(NO_2)_2]$	29 000	20 000 [a]	11 100
$[NiL_\alpha(NCS)_2]$	29 400	18 900, 13 500	10 900
$[NiL_\alpha(CN)(ClO_4)]$	30 300	19 400	12 350
$[NiL_\alpha(O_2CMe)(OH_2)][ClO_4]$	29 000	18 900, 14 100	9 500
(*b*) Solution spectra			
$[NiL_\alpha(dmso)_2][ClO_4]_2$ [b]	28 600	18 350, 14 100	—
$[NiL_\alpha(NH_3)_2][ClO_4]_2$ [c]	29 400	19 050	—

[a] Some splitting observable, band position is only approximate. [b] In dmso solution. [c] In ammonia solution.

Infrared Spectra.—The prominent i.r. bands in the complexes are listed in Table 6. For $[NiL_\alpha(NCS)_2]$ the

TABLE 6

Prominent i.r. bands (cm^{-1}) of the *trans* six-co-ordinate nickel(II) complexes as KBr discs

Compound	ν(NH)	$\nu(ClO_4^-)$	Other ligand bands
L_α	3 250vs	—	2 900br, s ν(CH)
$[NiL_\alpha Cl_2]$	3 200s	—	2 920vs ν(CH)
$[NiL_\alpha Br_2]\cdot 2H_2O$	3 170s	—	2 940 ν(CH), 1 650 $\delta(H_2O)$ 3 300 $\nu(H_2O)$
$[NiL_\alpha I_2]\cdot 2H_2O$	3 170s	—	3 300, 1 630 ν- and δ-(H_2O) 2 900 ν(CH)
$[NiL_\alpha(NO_2)_2]\cdot 0.5H_2O$	3 200vs	—	2 940 ν(CH) 815 $\delta(NO_2)$
$[NiL_\alpha(NCS)_2]$	3 230vs	—	2 950vs ν(CH) 2 080vs, br ν(co-ord. C=N)
$[NiL_\alpha(dmso)_2][ClO_4]_2$	3 210m	1 120br, vs 625s (δ)	2 950s ν(CH) 940 ν(SO)
$[NiL_\alpha(NH_3)_2][ClO_4]_2$	3 180s 3 260s 3 360m	1 100br, vs 620s (δ)	2 980 ν(CH)
$[NiL_\alpha(O_2CMe)(OH_2)][ClO_4]$	3 260m	1 165br, vs 625s (δ)	3 440 $\nu(H_2O)$ 2 980 ν(CH) 1 565 ν(COO)
$[NiL_\alpha(CN)(ClO_4)]\cdot 0.5H_2O$	3 270vs	1 100br, vs (split) br,vs 625(δ) 940	2 100 ν(CN)

i.r. data are consistent with the N-bonded isothiocyanato-structure as a strong broad band at 2 080 cm^{-1} is characteristic of M–N bonding.[17] The complex $[NiL_\alpha(O_2CMe)(OH_2)][ClO_4]$ has ν(OH) at 3 440 cm^{-1} and ClO_4^- bands at 1 165 cm^{-1} [ν(O–Cl)] and 625 cm^{-1} [$\delta(ClO_4)$] consistent with ionic perchlorate. However, in $[NiL_\alpha(CN)(ClO_4)]\cdot 0.5H_2O$ there is good evidence for unidentate perchlorate since the band at 1 100 cm^{-1} is split and in addition to the band at 625 cm^{-1} a band at 940 cm^{-1} is also present assigned to ν_4 in C_{3v}.[17]

$$[NiL_\alpha]^{2+} + 2H_2O \overset{K}{\rightleftharpoons} [NiL_\alpha(OH_2)_2]^{2+} \qquad \text{(iii)}$$

Equilibrium Studies.—The equilibrium (iii) was studied over a temperature range. The orange planar species has a single *d–d* band in nitromethane at 475 nm (21 053 cm^{-1}) ($\varepsilon = 51$ dm^3 mol^{-1} cm^{-1}). This value may be compared with bands at 22 470 and 22 420 cm^{-1} respectively for the corresponding complexes of 1,4,8,11-tetra-azacyclotetradecane and 1,9-diamino-3,7-diazanonane. The absorbance at 475 nm in aqueous solution is due exclusively to the planar species, and the proportion of the planar species was found to increase with increasing temperature (Table 7). Percentages of the planar species were obtained from the expression: % planar = $(\varepsilon_{obs.}/51) \times 100$, where 51 is the absorption coefficient obtained in nitromethane. The equilibrium constant K for equation (iii) is defined as K = [octahedral]/[planar]. The percentage of the planar species increases from 16.5 at 25 °C to 38.0 at 70 °C with $K = 5.06$ at 25 °C and 1.63 at 70 °C. A plot of log K *versus* $1/T$ is linear giving $\Delta H^\ominus = -22.2$ kJ mol^{-1} from the least-squares slope (correlation coefficient 0.9992). The value of $\Delta S^\ominus$ calculated at each temperature from the expression $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$ is -60.7 J K^{-1} mol^{-1}. These thermodynamic parameters are in good agreement with those previously obtained[18] for nickel(II) complexes of cyclam and open-chain tetra-amines (Table 8). Values of $\Delta S^\ominus$ are, as expected, negative due to constriction of two water molecules in the octahedral species.

The conversion of the planar into the octahedral species is an exothermic reaction. Formation of the octahedral species involves the creation of two axial Ni–OH_2 bonds and heat is released as a result. It has been suggested that stronger Ni–N bonds are involved in the square-planar species (Ni-N 1.90—1.91 Å)[19,20] compared with *ca.* 2.06 Å which occurs in $[Ni(cyclam)Cl_2]$.[21] This effect which is endothermic is overridden by the formation of the two axial Ni–OH_2 bonds which is exothermic. The present X-ray data are in accord with this view.

TABLE 7

The planar $\rightleftharpoons$ octahedral equilibrium in aqueous solution

θ/°C	A_{475} [a]	$\varepsilon_{obs.}$ [b]	% Planar [c]	% Octahedral	K
25	0.42	8.4	16.5	83.5	5.06
33	0.50	10.0	19.6	80.4	4.10
45	0.64	12.8	25.1	74.9	2.98
60	0.87	17.4	34.1	65.9	1.93
70	0.97	19.4	38.0	62.0	1.63

$\Delta H^\ominus = -22.1$ kJ mol^{-1}, $\Delta S^\ominus = -60.6$ J K^{-1} mol^{-1}

[a] Absorbance at 475 nm. [b] In dm^3 mol^{-1} cm^{-1}; calculated from the total concentration of the complex (4.99×10^{-2} mol dm^{-3}). [c] $(\varepsilon_{obs.}/51) \times 100$.

TABLE 8

Thermodynamic parameters for planar $\rightleftharpoons$ octahedral equilibria in aqueous solution for various nickel(II) complexes

Ligand	$\Delta H^\ominus$/ kJ mol^{-1}	$\Delta S^\ominus$/ J K^{-1} mol^{-1}	Ref.
cyclam	−22.6	−83.7	18
L_α	−22.2	−60.7	This work
1,9-Diamino-3,7-diazanonane	−14.2	−37.7	18
1,10-Diamino-4,7-diazadecane	−18.4	−62.8	18
1,4,7,10-Tetra-azacyclotridecane	−31.4	−125	18

For the planar orange species the Ni–N bond distances are 1.964 and 1.974 Å, while the violet octahedral complex has bond lengths of 2.063—2.081 Å.

Steric interactions are also of importance in determining the extent of axial addition. For the most thermodynamically stable chiral nitrogen arrangement the L_α isomer has four equatorial methyl groups, while the other isomers L_β and L_γ have one or two axial methyl groups (Scheme 2). Axial additions are not observed with nickel(II) complexes of L_β or L_γ since the axial methyl groups sterically conjest the axial sites. As a result ΔH becomes more positive (*i.e.* less negative) and since ΔS is negative the equilibrium lies on the side of the planar species. Similar effects have been noted in bis complexes of nickel(II) with ethylenediamine (en) and C-substituted ethylenediamines. Thus $[Ni(en)_2]^{2+}$ is blue (octahedral), bis(1,1-dimethylethylenediamine)nickel(II) is a 50% blue-yellow mixture at room temperature,[22] and bis(1,1,2,2-tetramethylethylenediamine)nickel(II) [21] exists only in the planar yellow form.[23]

[1/1436 *Received*, 14*th September*, 1981]

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