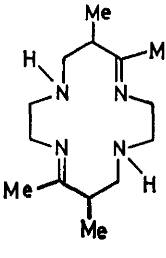
Transition-metal Complexes of the Macrocyclic Ligand 5,6,12,13-Tetramethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene

By **Robert W. Hay,* Dharam P. Piplani, and** (in part) **Bakir Jeragh,** Chemistry Department, University of Stirling, Stirling FK9 4LA

The title macrocyclic ligand (L) has been prepared as its dihydroperchlorate salt by the reaction of 3-methylbut-3-en-2-one with ethylenediamine monohydroperchlorate in methanol solution. The reaction gives the *trans*-di-imine and a *ca.* 7 : 3 mixture of the C-*meso* and C-*rac* diastereoisomers. Fractional crystallisation of $[NiL][ClO_4]_2$ from aqueous solution gives three isomers [(*a*)—(*c*)] identified by ^{1}H n.m.r. spectroscopy. *X*-Ray crystallography confirms that isomer (*b*) is the centrosymmetric N-*meso*-C-*meso* diastereoisomer and isomer (*c*) is the N-*rac*-C-*rac* diastereoisomer. Equilibration of (*a*) and (*b*) in Me_2SO–K[OH] gives isomer (*d*) which is the other member of the C-*meso* series. N.m.r. studies confirm that the reaction proceeds *via* the steps (*b*) → (*a*) → (*d*). Isomer (*b*) has a diequatorial arrangement of the ring methyls. A number of other metal(II) complexes (M = Cu, Zn, or Hg) have been characterised as their perchlorate salts. In addition a series of octahedral cobalt(III) complexes of the general type *trans*-$[CoX_2L]^{n+}$ [X_2 = Cl_2, Br_2, $(NO_2)_2$, $(NCS)_2$, $(N_3)_2$, $(NH_3)_2$, $(O_2CMe)_2$, or $Cl(NO_2)$] and *trans*-$[RhCl_2][ClO_4]_2$ have been synthesised, as has *cis*-$[Co(CO_3)L][ClO_4]\cdot 2H_2O$. Infrared and *d–d* spectra are reported.

THE reaction of ethylenediamine monohydroperchlorate, en·$HClO_4$, with α,β-unsaturated carbonyl compounds gives 14-membered tetra-azacyclotetradecadienes.[1–3] The reaction is normally stereospecific, giving the *transoid*- rather than the *cisoid*-di-imine. The reaction of 3-methylbut-3-en-2-one with en·$HClO_4$ in methanol solution gives the new macrocyclic ligand 5,6,12,13-tetramethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene (L) as its dihydroperchlorate salt. The present paper discusses some aspects of the co-ordination chemistry of this macrocyclic ligand.



L

EXPERIMENTAL

5,6,12,13-*Tetramethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene Dihydroperchlorate*, L·$2HClO_4$.—Aqueous perchloric acid [165 cm^3 (72%), 2 mol] was added dropwise with continuous stirring to a cooled (ice–salt bath) solution of ethylenediamine (134 cm^3, 2 mol) in methanol (1 200 cm^3). After completion of the addition, 3-methylbut-3-en-2-one (196 cm^3, 2 mol, Fluka) diluted with an equal volume of methanol was added slowly over a period of 2 h with the temperature being maintained between 0 and 5 °C. The resulting mixture was then stirred for 4 h, the temperature being allowed to slowly rise to ambient. The resulting suspension was stored overnight in a refrigerator. The white *product* was filtered off, washed several times with methanol then diethyl ether, and dried *in vacuo*, yield *ca.* 310 g, m.p. 132—134 °C, ν(C=N) at 1 669, ν(NH) at 3 170 cm^{-1} (Found: C, 36.9; H, 6.5; N, 12.35. $C_{14}H_{30}Cl_2N_4O_8$ requires C, 37.1; H, 6.7; N, 12.35%).

(5,6,12,13-*Tetramethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene)nickel*(II) *Perchlorate*, $[NiL][ClO_4]_2$.—An excess of ' basic ' nickel(II) carbonate and L·$2HClO_4$ were slurried in water and heated on a water-bath until evolution of carbon dioxide ceased (*ca.* 0.5 h). The solution was filtered while hot and the filtrate was reduced in volume. Cooling in an ice-bath gave orange needles [isomers (*a*) and (*b*)]. Isomer (*c*) is very soluble in both cold water and cold methanol and was recovered from the filtrates. The mixture of isomers (*a*) and (*b*) was recrystallised from hot water. Various fractions were monitored by ^{1}H n.m.r. using $(CD_3)_2SO$ as solvent. The complexes were dried *in vacuo* [Found for isomer (*b*): C, 32.85; H, 5.6; N, 10.85. Found for isomer (*c*): C, 32.7; H, 5.55; N, 10.8. $C_{14}H_{28}Cl_2N_4NiO_8$ requires C, 32.95; H, 5.5; N, 11.0%]. Isomer (*b*) is partially paramagnetic in $(CD_3)_2SO$ solution with broad signals at δ 1.2 and 1.6 p.p.m. Isomer (*c*) has a doublet at δ 1.26 p.p.m. (*J* 7.2 Hz) due to the ring methyls, and the imine methyls occur as a singlet at 2.02 p.p.m. Isomer (*a*) which occurs with isomer (*b*) is readily identified by *two* imine methyl singlets at δ 2.03 and 2.20 p.p.m.

(5,6,12,13-*Tetramethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene)zinc*(II) *Perchlorate*, $[ZnL][ClO_4]_2$.—Zinc(II) perchlorate hexahydrate (0.5 g) in water (10 cm^3) was added to L·$2HClO_4$ (0.55 g) dissolved in methanol. The mixture was heated on a water-bath for 30 min and the solution was filtered whilst hot. The filtrate was reduced to small volume (rotary evaporator) and methanol was added. Subsequent cooling in ice gave the white crystalline *product*, which was filtered off, washed with ethanol then diethyl ether, and dried *in vacuo* (Found: C, 32.8; H, 5.3; N, 10.7. $C_{14}H_{28}ClN_4O_8Zn$ requires C, 32.5; H, 5.45; N, 10.8%).

(5,6,12,13-*Tetramethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene)copper*(II) *Perchlorate*, $[CuL][ClO_4]_2$.—Copper(II) carbonate (0.5 g) was suspended in water (20 cm^3) and L·$2HClO_4$ (0.6 g) dissolved in aqueous methanol was added. The mixture was heated on a water-bath for 30 min and the resulting red-purple solution was filtered whilst hot. The crude *product* was obtained by concentration of the red filtrate, and recrystallised from methanol (Found: C, 32.35; H, 5.3; N, 10.9. $C_{14}H_{28}Cl_2CuN_4O_8$ requires C, 32.65; H, 5.5; N, 10.9%).

(5,6,12,13-*Tetramethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene)mercury*(II) *Perchlorate Pentahydrate* $[HgL][ClO_4]_2\cdot 5H_2O$.—Mercury(II) chloride (0.3 g) was dissolved in water (10 cm^3) and a slight excess of L·$2HClO_4$ (0.45 g)

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[1] N. F. Curtis and R. W. Hay, *Chem. Comm.*, 1966, 524.

[2] R. A. Kolinski and B. Korybut-Daskiewicz, *Bull. Acad. polon. Sci.*, 1969, **17**, 13.

[3] R. A. Kolinski and B. Korybut-Daskiewicz, *Inorg. Chim. Acta*, 1975, **14**, 237.

dissolved in aqueous methanol was added. The mixture was warmed on a water-bath (20 min) then filtered whilst hot. The volume of the solution was reduced to *ca.* 5 cm^3 on a rotary evaporator. Addition of methanol, then diethyl ether, and subsequent cooling gave pale white hygroscopic crystals which were filtered off and dried *in vacuo* for several hours (Found: C, 22.65; H, 5.1; N, 7.55. $C_{14}H_{28}Cl_2HgN_4O_8\cdot 5H_2O$ requires C, 22.5; H, 4.8; N, 7.7%).

trans-*Dichloro*(5,6,12,13-*tetramethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene*)*cobalt*(III) *Perchlorate*, $[CoCl_2L][ClO_4]$.—Trisodium tris(carbonato)cobaltate(III) trihydrate (0.8 g) and $L\cdot 2HClO_4$ (0.8 g) were mixed in methanol–water (30 cm^3, 1 : 1 v/v) and heated on a water-bath until effervescence ceased (20 min). The resulting red solution was filtered whilst hot. Concentrated hydrochloric acid (15 cm^3) was added to the filtrate and the volume was reduced on a water-bath. The shining green plates obtained on cooling in ice were filtered off, dried at 110 °C, and recrystallised from hot methanol. The *product* was washed with ethanol, then diethyl ether, and dried *in vacuo* (Found: C, 34.6; H, 6.1; N, 11.4. $C_{14}H_{28}Cl_3CoN_4O_4$ requires C, 34.9; H, 5.9; N, 11.6%).

trans-*Dibromo*(5,6,12,13-*tetramethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene*)*cobalt*(III) *Perchlorate Dihydrate*, $[CoBr_2L][ClO_4]\cdot 2H_2O$.—A solution of *trans*-$[CoCl_2L][ClO_4]$ (0.25 g) in methanol (*ca.* 25 cm^3) was treated with concentrated HBr (3 cm^3) and the solution was heated on a water-bath for 10 min. The solution was taken to dryness on a rotary evaporator and the bright green *product* so obtained was recrystallised from a small volume of hot ethanol, washed with ethanol, then diethyl ether, and dried *in vacuo* (Found C, 27.4; H, 5.1; N, 9.0. $C_{14}H_{32}Br_2ClCoN_4O_6$ requires C, 27.7; H, 5.3; N, 9.2%).

trans-*Dinitro*(5,6,12,13-*tetramethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene*)*cobalt*(III) *Perchlorate Monohydrate*, $[Co(NO_2)_2L][ClO_4]\cdot H_2O$.—A solution of *trans*-$[CoCl_2L][ClO_4]$ (0.25 g) in methanol (40 cm^3) was heated with a slight excess of sodium nitrite (0.075 g) on a water-bath for 30 min. The pale brown solution was filtered hot and the filtrate was cooled in an ice-bath. The orange-yellow crystals so obtained were washed with methanol, then diethyl ether, and dried *in vacuo* (Found: C, 32.6; H, 5.65; N, 16.0. $C_{14}H_{30}ClCoN_6O_9$ requires C, 32.4; H, 5.8; N, 16.1%).

trans-*Diazido*(5,6,12,13-*tetramethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene*)*cobalt*(III) *Perchlorate*, $[Co(N_3)_2L][ClO_4]$.—A solution of *trans*-$[CoCl_2L][ClO_4]$ (0.4 g) in water (20 cm^3) was treated with sodium azide (0.7 g). On heating on a water-bath for 30 min the solution rapidly changed from green to blue-violet. On standing, blue-violet crystals of the *product* separated; these were filtered off, washed with ethanol then diethyl ether, and dried *in vacuo* (Found: C, 33.6; H, 5.75; N, 28.7. $C_{14}H_{28}ClCoN_{10}O_4$ requires C, 34.0; H, 5.7; N, 28.3%).

trans-*Di-isothiocyanato*(5,6,12,13-*tetramethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene*)*cobalt*(III) *Thiocyanate Tetrahydrate*, $[Co(NCS)_2L][SCN]\cdot 4H_2O$.—To a solution of *trans*-$[CoCl_2L][ClO_4]$ (0.3 g) in hot aqueous methanol (25 cm^3) was added an excess of solid potassium thiocyanate. The mixture was heated on a water-bath for 15 min during which time the colour changed from green to red. The solution was filtered and the green filtrate was stored in a refrigerator for *ca.* 2 d, when shining red crystals of the *product* formed; these were filtered off, washed with cold methanol, then diethyl ether, and dried *in vacuo*. The i.r. spectrum of the complex did not exhibit perchlorate absorption, but bands due to ionic thiocyanate (Found: C, 36.8; H, 6.3; N, 18.0. $C_{14}H_{36}CoN_7O_4S_3$ requires C, 36.6; H, 6.5; N, 17.6%).

trans-*Diammine*(5,6,12,13-*tetramethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene*)*cobalt*(III) *Chloride Diperchlorate*, $[Co(NH_3)_2L]Cl[ClO_4]_2$.—To a solution of *trans*-$[CoCl_2L][ClO_4]$ (0.4 g) in the minimum volume of hot acetonitrile were added several drops of concentrated ammonia (s.g. 0.88). The colour of the solution gradually changed from green to orange-red on stirring for *ca.* 20 min. Addition of an ethanolic solution of lithium perchlorate (2 cm^3) followed by cooling in ice gave the orange-yellow *product*, which was recrystallised from hot water and dried *in vacuo* (Found: C, 28.2; H, 5.7; N, 14.8. $C_{14}H_{34}Cl_3CoN_4O_8$ requires C, 29.0; H, 5.9; N, 14.5%).

trans-*Diacetato*(5,6,12,13-*tetramethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene*)*cobalt*(III) *Perchlorate*, $[Co(O_2CMe)_2L][ClO_4]$.—A solution of *trans*-$[CoCl_2L][ClO_4]$ (1.0 g) in hot methanol was prepared and to this sodium acetate (0.75 g) followed by a few drops of glacial acetic acid were added. The solution was warmed on a water-bath for *ca.* 0.5 h. On standing, the purple-pink solution thus obtained deposited pink crystals of the *product*. The complex was recrystallised from hot aqueous methanol and dried *in vacuo* (Found: C, 41.2; H, 6.7; N, 10.8. $C_{18}H_{34}ClCoN_4O_8$ requires C, 40.9; H, 6.5; N, 10.6%).

trans-*Chloronitro*(5,6,12,13-*tetramethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene*)*cobalt*(III) *Perchlorate*, $[CoCl(NO_2)L][ClO_4]$.—The complex was prepared by stirring *trans*-$[CoCl_2L][ClO_4]$ (0.48 g) in hot 95% methanol (50 cm^3) with 1 mol equiv. (0.062 g) of sodium nitrite. After heating for *ca.* 0.5 h, the red-brown solution was filtered hot and the filtrate cooled in an ice-bath. The resulting orange-red *product* was filtered off, washed with ice-cold ethanol, then diethyl ether, and dried *in vacuo*. A second fraction could be obtained by the addition of diethyl ether to the filtrate, followed by cooling in an ice-bath (Found: C, 33.9; H, 5.5; N, 14.5. $C_{14}H_{28}Cl_2CoN_5O_6$ requires C, 34.15; H, 5.7; N, 14.2%).

cis-*Carbonato*(5,6,12,13-*tetramethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene*)*cobalt*(III) *Perchlorate Dihydrate*, $[Co(CO_3)L][ClO_4]\cdot 2H_2O$.—Trisodium tris(carbonato)cobaltate(III) trihydrate (0.9 g) and $L\cdot 2HClO_4$ (0.9 g) were mixed in methanol–water (50 cm^3, 1 : 1 v/v) and warmed on a water-bath for *ca.* 20 min, until CO_2 evolution ceased. The red solution was filtered while hot and concentrated to *ca.* 10 cm^3 on a rotary evaporator. Addition of a little methanol followed by cooling in a refrigerator overnight gave dark red crystals of the *product*, which were recrystallised from the minimum of hot water and dried *in vacuo* for several hours (Found: C, 35.2; H, 6.5; N, 11.4. $C_{15}H_{32}ClCoN_4O_7$ requires C, 35.5; H, 6.4; N, 11.05%).

trans-*Dichloro*(5,6,12,13-*tetramethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene*)*rhodium*(III) *Perchlorate Monohydrate*, $[RhCl_2L][ClO_4]\cdot H_2O$.—A solution of $L\cdot 2HClO_4$ (1.72 g) and rhodium trichloride trihydrate (0.75 g) was prepared in methanol–water. The resulting red solution was heated under reflux for *ca.* 5 h during which time the colour gradually changed to yellow. Perchloric acid (5 cm^3, 70%) was added to precipitate the yellow *product* which was recrystallised from methanol–water and dried *in vacuo* (Found: C, 30.7; H, 5.5; N, 9.9. $C_{14}H_{30}Cl_3N_4O_5Rh$ requires C, 30.9; H, 5.6; N, 10.3%).

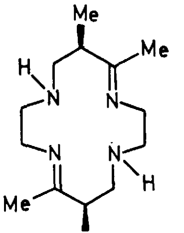
Infrared spectra were determined as KBr discs using a

Perkin-Elmer 457 spectrophotometer. Visible-spectral measurements were carried out with a Perkin-Elmer 402 instrument. Hydrogen-1 n.m.r. spectra were determined at 90 MHz using a Perkin-Elmer R-32 instrument with $(CD_3)_2SO$ or CD_3NO_2 as solvent and tetramethylsilane as internal standard.

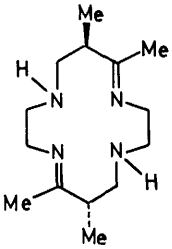
RESULTS AND DISCUSSION

The dihydroperchlorate salt of the ligand ($L{\cdot}2HClO_4$) has bands in the i.r. (KBr disc) at 1 669 [ν(C=N)] and 3 170 cm^{-1} [ν(N–H)] and the characteristic bands due to ionic perchlorate at 1 095br and 625 cm^{-1}.

The ligand L contains two chiral centres at C^6 and C^{13} so that C-*rac* (I) and C-*meso* (II) diastereoisomers of the ligand can occur. The ^1H n.m.r. spectrum of $L{\cdot}2HClO_4$ at 90 MHz [$(CD_3)_2SO$ solvent] has a methyl doublet at δ 1.16 p.p.m. (*J* 7 Hz) which can be assigned to the ring methyls coupled to the ring proton. The imine methyls occur as a sharp singlet at δ 1.93 p.p.m. Measurements at 220 MHz, however, show that the ring methyls are in fact two overlapping doublets and, in addition, splitting of the imine-methyl signal also occurs. The n.m.r. observations are consistent with a *ca.* 7 : 3 mixture of the two diastereoisomers. Further studies (see later) indicate that the C-*meso* diastereoisomer predominates.



C-*rac* (*RR*,*SS*)
(I)



C-*meso* (*RS*)
(II)

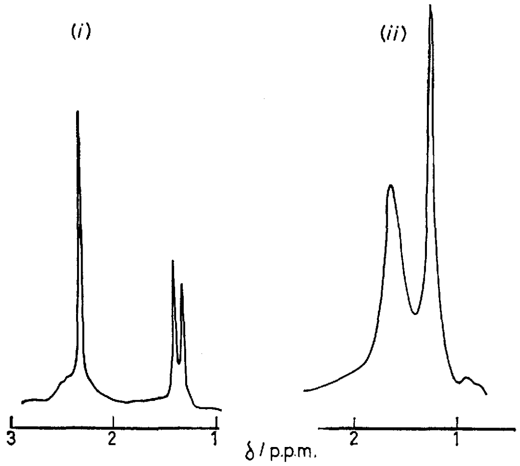


FIGURE 1 Hydrogen-1 n.m.r. spectra of $[NiL][ClO_4]_2$: (*i*) isomer (*b*) in CD_3NO_2; (*ii*) isomer (*b*) in $(CD_3)_2SO$

Fractional crystallisation of $[NiL][ClO_4]_2$ from water led to the characterisation of three isomers [(*a*), (*b*), and (*c*)]. Isomer (*b*) is partially paramagnetic in Me_2SO solution and diamagnetic in the non-co-ordinating solvent nitromethane. Isomer (*a*) is diamagnetic in Me_2SO, as is isomer (*c*). The three isomers are readily characterised by their n.m.r. spectra (Figures 1 and 2).

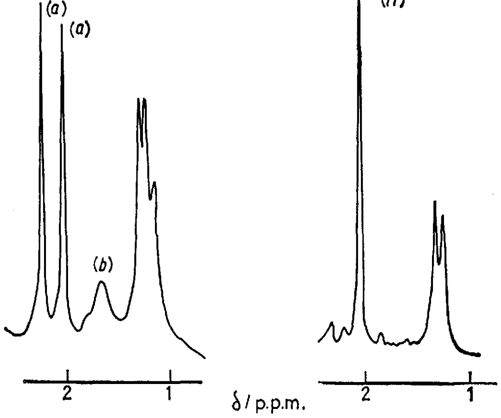
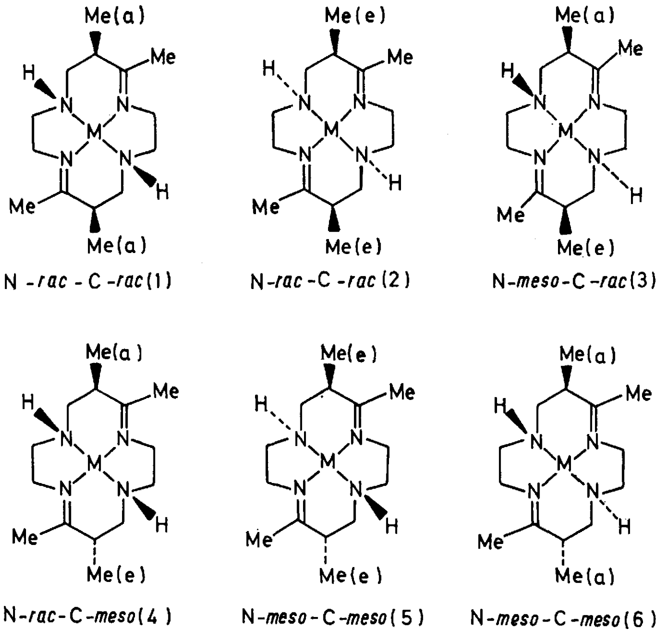


FIGURE 2 Hydrogen-1 n.m.r. spectra of $[NiL][ClO_4]_2$ in $(CD_3)_2SO$: (*i*) a mixture of isomers (*a*) and (*b*); (*ii*) isomer (*c*)

Metal complexes of the ligand L contain two chiral carbon centres and two chiral nitrogen centres. There is therefore the possibility of 10 stereoisomers: two all-*meso* forms and four *rac* mixtures. The various stereoisomers belong to two sets, one derived from the C-*rac* ligand and the other from the C-*meso* ligand. The possible stereoisomers are shown in Scheme 1. Stereoisomers (1) and (2) have a C_2 axis, while (3) and (4) have no elements of symmetry. Stereoisomers (5) and (6) have centres of symmetry. The complexes of one



SCHEME 1 Stereoisomers of metal complexes of 5,6,12,13-tetramethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene. The symbols (a) and (e) refer to the substituents being axial or equatorial respectively

C-configuration are not readily convertible into complexes of the other C-configuration, whereas base should isomerise the N-configurations within each set. In the C-*meso* series only the N-*rac*-C-*meso* diastereoisomer (4) can be resolved, since the other two diastereoisomers are all-*meso* forms.

X-Ray crystallography has been carried out on isomers (*b*)[4] and (*c*).[5] Isomer (*b*) is the N-*meso*-C-*meso* diastereoisomer (6) with both methyl groups axial, while (*c*) is the N-*rac*-C-*rac* diastereoisomer (1) which also has both methyl groups axial. The ^1H n.m.r. spectrum of isomer (*a*) (which has not been obtained isomerically pure) has two singlets at δ 2.03 and 2.20 p.p.m. (Table 1)

TABLE 1

Hydrogen-1 n.m.r. data [a] for the various isomers of $[NiL][ClO_4]_2$ in $(CD_3)_2SO$ solution

Isomer	Assignment	δ/p.p.m.
(*a*)	Ring methyls	1.16 (d) (*J* 7.2 Hz)
	Imine methyls	2.03 (s) 2.20 (s)
(*b*) [b]	Ring methyls	1.2 (s, br)
	Imine methyls	1.6 (s, br)
(*c*)	Ring methyls	1.26 (d) (*J* 7.2 Hz)
	Imine methyls	2.02 (s)
(*d*) (at 60 MHz)	Ring methyls	1.25 (d) (*J* 6 Hz)
	Imine methyls	1.98 (s)

[a] At 90 MHz with $SiMe_4$ as internal reference. [b] Partially paramagnetic in $(CD_3)_2SO$. In CD_3NO_2 the complex is diamagnetic: ring methyls, δ 1.32 (d), *J* 7.2 Hz; imine methyls, δ 2.28 (s) p.p.m.

which can be assigned to imine-methyl groups in different environments. Isomer (*a*) must therefore be (3) or (4) since only in these two isomers are the imine methyls non-equivalent. Isomer (*a*) is always found in association with (*b*). Treatment of a mixture of isomers (*a*) and (*b*) dissolved in $(CD_3)_2SO$ with a trace of solid potassium hydroxide leads to significant changes in the ^1H n.m.r. spectrum (Figure 3). The signals due to isomer (*b*) decrease, while, initially, the signals of isomer (*a*) increase with time; in addition, new signals due to a further isomer (*d*) appear. Subsequently (*a*) and (*b*) are completely converted into isomer (*d*), which must therefore be the other member of the C-*meso* series, *i.e.* isomer (5). Thus (*b*) isomerises *via* (*a*) to give (*d*) (Scheme 2).* The n.m.r. results confirm that the diequatorial N-*meso* derivative is the most thermodynamically stable diastereoisomer in the C-*meso* series of complexes.

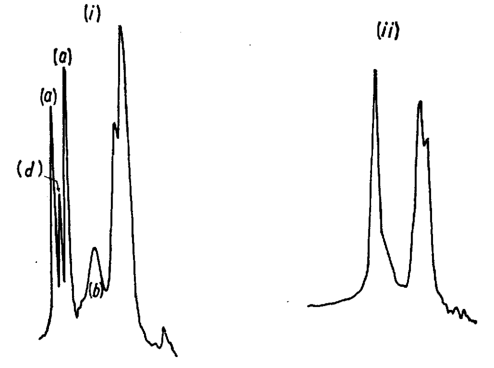
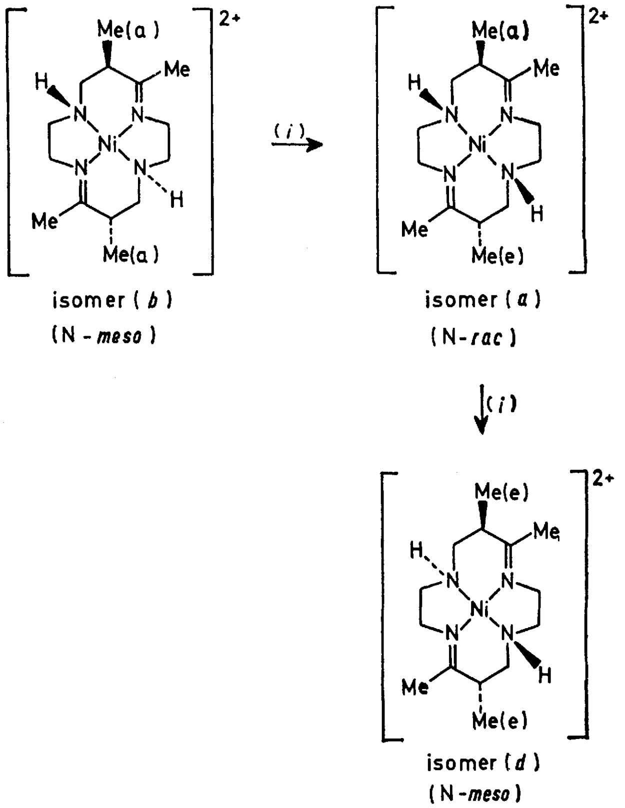


FIGURE 3 Hydrogen-1 n.m.r. spectra (60 MHz) of $[NiL][ClO_4]_2$: (*i*) a mixture of isomers (*a*) and (*b*) isomerising to (*d*) in $(CD_3)_2SO$–K[OH]; (*ii*) isomer (*d*) in $(CD_3)_2SO$



SCHEME 2 Interconversions in the C-*meso* series of $[NiL][ClO_4]_2$.(*i*) K[OH]–Me_2SO

Attempts to isomerise isomer (*c*) of the C-*rac* series by the same technique were unsuccessful. We therefore conclude that isomer (*c*) is the most thermodynamically stable member of this series of complexes. There is little difference between the *d*–*d* spectra of the various isomers. Isomer (*b*) has $\lambda_{max.}$ 446 nm (ε 90 dm^3 mol^{-1} cm^{-1}) and (*c*) has $\lambda_{max.}$ 446 nm (ε 86 dm^3 mol^{-1} cm^{-1}). Such a band is characteristic of square-planar nickel(II) complexes with four nitrogen donors and can be assigned to the ${}^1B_{1g} \leftarrow {}^1A_{1g}$ transition of square-planar Ni^{II}.[6] Isomer (*b*) has a tendency to accept axial ligands, and paramagnetic line broadening in the ^1H n.m.r. spectrum [$(CD_3)_2SO$ solution] can be attributed to the equilibrium

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* The n.m.r. data for (*c*) and (*d*) are quite similar, so that treatment of a mixture of (*a*) and (*b*) with base could possibly lead to isomerisation to isomer (*c*). The hydrogens at C^6 and C^{13} are quite acidic as they lie α to the imine bond. However, equilibration at carbon centres would probably give the C-*meso* rather than the C-*rac* diastereoisomer as the former is expected to be the most thermodynamically stable. We therefore feel that the discussion given in the text provides the best explanation for the experimental observations.

[4] G. Ferguson and R. J. Restivo, to be published.

[5] P. Murray-Rust and J. Murray-Rust, to be published.

[6] G. Maki, *J. Phys. Chem.*, 1958, **28**, 615; **29**, 62.

$[NiL_b]^{2+} + 2Me_2SO \rightleftharpoons [NiL_b(OSMe_2)_2]^{2+}$. Paramagnetic line broadening is not observed in Me_2SO solution with isomers (*a*), (*c*), or (*d*), or with (*b*) in nitromethane (Figures 1—3).

Other Metal(II) *Complexes.*—A number of other metal(II) complexes, $[CuL][ClO_4]_2$, $[ZnL][ClO_4]_2$, and $[HgL][ClO_4]_2 \cdot 5H_2O$, were readily prepared by the reaction of an aqueous methanolic solution of $L \cdot 2HClO_4$ with aqueous solutions of copper(II) and zinc(II) perchlorates and mercury(II) chloride. All the complexes (including the nickel derivatives) behave as 2 : 1 electrolytes in aqueous solution (Table 2) with conductivities in the range 209—234 S cm^2 mol^{-1} consistent with four-co-ordinate structures and ionic perchlorate. The i.r. spectra (Table 3) have bands assignable to ν(N–H) at *ca.* 3 200 cm^{-1} and ν(C=N) at 1 660 cm^{-1} and bands at 1 100br and 625 cm^{-1} due to ionic perchlorate. The mercury(II) derivative has typical ν(OH) and δ(HOH) bands. We did not attempt to prepare pure isomers of these derivatives. Mercury(II) is somewhat larger (102 pm) than Zn^{II} (74 pm),[7] but is complexed quite readily by the macrocycle. The *d–d* spectrum of the copper(II) complex has a single nearly symmetric band at 513 nm (ε 82 dm^3 mol^{-1} cm^{-1}). The wavelength and intensity of this band is comparable to values reported for copper(II) complexes of related tetra-aza-macrocycles.[8]

TABLE 2

Electronic spectra and conductivity data [a]

	$\lambda_{max.}$/nm (ε/dm^3 mol^{-1} cm^{-1})	Λ / S cm^2 mol^{-1}
$[NiL][ClO_4]_2$ [isomer (*b*)]	445 (90)	234
$[NiL][ClO_4]_2$ [isomer (*c*)]	445 (86)	201
$[CuL][ClO_4]_2$	513 (82)	214
$[ZnL][ClO_4]_2$		209
trans-$[RhCl_2L][ClO_4] \cdot H_2O$	395 (51)	
trans-$[CoCl_2L][ClO_4]$ [b]	624 (25), 430 (sh) (35), 320 (sh)	
trans-$[CoBr_2L][ClO_4] \cdot 2H_2O$ [c]	642 (46), 378 (114), masked	
trans-$[Co(NO_2)_2L][ClO_4]$	440 (166)	
trans-$[Co(NCS)_2L][SCN] \cdot 4H_2O$	518 (195)	
trans-$[Co(NH_3)_2L]Cl[ClO_4]_2$	446 (75), 333 (118)	
cis-$[Co(CO_3)L][ClO_4] \cdot H_2O$	506 (126), 364 (176)	
trans-$[CoCl(NO_2)L][ClO_4]$ [c]	506 (sh) (110), 355 (2 100)	

[a] Electronic spectra were determined in aqueous solution unless otherwise stated. Conductivities were determined for 10^{-3} mol dm^{-3} aqueous solutions. [b] Spectrum determined using 1 mol dm^{-3} HCl as solvent. [c] Dry acetonitrile as solvent.

TABLE 3

Prominent i.r. absorption bands (cm^{-1})

Compound	ν(C=N)	ν(N–H)	$\nu(ClO_4^-)$	Other ligand bands
$L \cdot 2HClO_4$	1 669s	3 170s	1 095vs, br, 625vs	
$[NiL][ClO_4]_2$ (orange)	1 643	3 212, 170	1 100br, 623vs	
$[NiL][ClO_4]_2$ (yellow)	1 638	3 205	1 100br, 622	
$[CuL][ClO_4]_2$	1 665vs	3 240vs	1 105s,br, 625vs	
$[ZnL][ClO_4]_2$	1 668vs	3 250vs	1 115s,br, 630vs	
$[HgL][ClO_4]_2 \cdot 5H_2O$	1 664br	3 190br	1 090br, 628vs	
trans-$[CoCl_2L][ClO_4]$	1 647s	3 205s	1 096vs, 624s	
trans-$[CoBr_2L][ClO_4]$	1 648s	3 214s	1 100vs, 623vs	
trans-$[Co(NO_2)_2L][ClO_4]$	1 646s	3 185m	1 098s, 625s	ν_{asym}(NO) 1 392 δ(O–N–O) 825
trans-$[Co(NCS)_2L][SCN] \cdot 4H_2O$	1 646	3 110br		ν(CN) 2 080s (co-ord. + ionic) ν(CS) 840m (co-ord.), δ(NCS) 470w
trans-$[Co(N_3)_2L][ClO_4]$	1 644	3 220s	1 090vs, 622s	$\nu(N_3)$ 2 020vs
trans-$[RhCl_2L][ClO_4] \cdot H_2O$	1 650	3 140s	1 098vs, 629s	ν(OH) 3 450, ν(Rh–N) 500w, CH_2 rock 881s

Cobalt(III) *Complexes.*—Green *trans*-$[CoCl_2L][ClO_4]$ was readily prepared by the reaction of $L \cdot 2HClO_4$ with $Na_3[Co(CO_3)_3] \cdot 3H_2O$ in methanol–water solution. Anion-metathesis reactions gave a series of *trans* complexes of the type $[CoX_2L]^{n+}$ [$X_2 = Br_2$, $(NO_2)_2$, $(NCS)_2$, $(N_3)_2$, $(O_2CMe)_2$, or $Cl(NO_2)$]. The diammine was also prepared. A *cis*-carbonato-complex $[Co(CO_3)L][ClO_4] \cdot 2H_2O$ was readily synthesised but attempts to isolate the analogous pentane-2,4-dionate derivative were unsuccessful. The red complex formed in solution but attempts to isolate it as the perchlorate salt gave only oily products. Complexes *trans*-$[CoX_2N_4]^{n+}$ have a basic D_{4h} symmetry with the $^1A_{1g} \rightarrow {}^1T_{1g}(O_h)$ splitting into two components, $^1A_{1g} \rightarrow {}^1E_{1g}(D_{4h})$ and $^1A_{1g} \rightarrow {}^1A_{2g}(D_{4h})$.[9,10] Where the tetragonal splitting is not very large (where X and N do not greatly differ in position in the spectrochemical series) only a single absorption band is observed under the $^1A_{1g} \rightarrow {}^1T_{1g}(O_h)$ envelope. No splitting is normally observed for *cis* complexes in which the lowest-energy transition can be assigned to $^1A_1 \rightarrow (^1E + {}^1B_2)$ in C_{2v}. In addition, *cis* complexes with no centre of symmetry often have larger absorption coefficients than the centrosymmetric *trans* complexes. The energies and intensities observed (Table 2) support the assignment of *trans* structures to the dianiono-complexes and the diammine, and a *cis* structure to the carbonato-derivative. The skeletal vibrations of the macrocyclic ligand in the 750—1 500 cm^{-1} region reflect changes in its geometry on co-ordination. A comparison of the i.r. spectra of $[CoCl_2L][ClO_4]$ and $[Co(CO_3)L][ClO_4] \cdot 2H_2O$ reflects the differences between the planar geometry in the former complex and the folded geometry in the latter, when due allowances are made for anion absorption. Bands in the carbonato-complex at 675,

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755, 830, and 1 630 cm^{-1} are consistent with chelated carbonate.[11,12] Bands observed for the chloro-complex in the 750—1 500 cm^{-1} region are either not observed in the folded carbonato-derivative or are shifted somewhat in position.

The i.r. spectra are consistent with an isothiocyanato-structure (*N*-bonded) for the thiocyanate derivative with ν(CN) at 2 080s, ν(CS) at 840 m, and δ(NCS) at 470w cm^{-1}. The dinitro-derivative has ν_{asym}(NO) at 1 392 and δ(ONO) at 825 cm^{-1}.

A *trans* configuration can be assigned to the rhodium(III) complex, $[RhCl_2L][ClO_4]\cdot H_2O$, on the basis of its *d–d* spectrum. Thus *cis*-$[RhCl_2L']^+$ has $\lambda_{max.}$ 354 nm (ε 223 dm^3 mol^{-1} cm^{-1}) while *trans*-$[RhCl_2L']^+$ has $\lambda_{max.}$ 406 nm (ε 78 dm^3 mol^{-1} cm^{-1}) (L′ = 1,4,8,11-tetraazacyclotetradecane).[13] The centrosymmetric *trans* complexes have lower absorption coefficients and the lowest-energy ligand-field band near 400 nm, while the non-centrosymmetric *cis* complexes have much higher absorption coefficients and the first ligand-field band near 350 nm. The *d–d* spectrum of $[RhCl_2L]^+$ with $\lambda_{max.}$ 395 nm (ε 51 dm^3 mol^{-1} cm^{-1}) (Table 1) is therefore fully consistent with the *trans* configuration. The i.r. spectrum also confirms this view. The ν(N–H), ν(Rh–N), and CH_2 rocking modes occur as single bands in the centrosymmetric *trans* complexes while two bands occur for the *cis* complexes.[13] Single bands occur at 3 140s [ν(N–H)], 881s [CH_2 rock], and 500w cm^{-1} [ν(Rh–N)] (Table 2) in *trans*-$[RhCl_2L][ClO_4]\cdot H_2O$ with a strong ν(O–H) band at 3 450 cm^{-1} due to the water of hydration.

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