The Preparation of 5,7,7,12,14-Pentamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene and its Complexes with Copper(II), Nickel(II), Zinc(II), and Cobalt(III)

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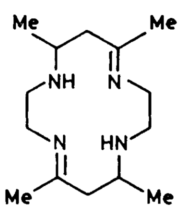
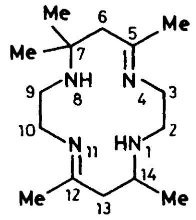
The reaction of 1,2-diaminoethane monohydroperchlorate with an equimolar mixture of mesityl oxide and pent-3-en-2-one in methanol solution gives a number of macrocyclic tetra-azacyclotetradecadienes, however, the main product (*ca.* 70%) is the new macrocyclic ligand 5,7,7,12,14-pentamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene (L) as its dihydroperchlorate salt. The characterisation of the ligand and some copper(II), nickel(II), and zinc(II) complexes is described. In addition, a series of cobalt(III) complexes of the type *trans*-$[CoLX_2]^+$ [$X_2 = Cl_2, (NO_2)_2, Br_2, (N_3)_2, Cl(NO_2)$, or $(NCS)_2$] and the μ-peroxo complex $[(H_2O)LCo(\mu\text{-}O_2)CoL(H_2O)][ClO_4]_4$ have been prepared. Infrared and electronic spectra are reported.

The reaction of 1,2-diaminoethane monohydroperchlorate with pent-3-en-2-one in methanol solution gives the *C-meso* (*ca.* 80%) and C-racemic (*ca.* 20%) diastereoisomers of the dihydroperchlorate salt of the macrocycle 5,7,12,14-tetramethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene (L′).[1,2]



L′



L

Chromatography of the diastereoisomeric nickel(II) complexes on ion-exchange Sephadex C-25 using sodium glycinate as eluant led to the isolation of small quantities (*ca.* 5%) of a further complex which was identified by ^1H n.m.r. as the nickel(II) complex of the, as yet unreported, macrocyclic ligand 5,7,7,12,14-pentamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene (L).[3] This ligand could arise due to the presence of small amounts of mesityl oxide (4-methylpent-3-en-2-one) [or diacetone alcohol (4-hydroxy-4-methylpentan-2-one)] in the pent-3-en-2-one sample employed in the synthesis. Pent-3-en-2-one is prepared by the base-catalysed condensation of acetaldehyde with acetone, and some self condensation of acetone is likely to occur to give mesityl oxide. Mesityl oxide has a b.p. 130—131 °C and pent-3-en-2-one b.p. 122 °C, so that the two α,β-unsaturated ketones may not be cleanly separated by distillation.

These observations suggested that 1,2-diaminoethane monohydroperchlorate could be treated with an equimolar mixture of pent-3-en-2-one and mesityl oxide to give L in acceptable yields. Such 'mixed' reactions involving two different α,β-unsaturated ketones have not been previously reported, but could provide a useful route to new substituted tetra-aza macrocycles, and so extend the scope of the original macrocycle synthesis.[4]

Experimental

The α,β-unsaturated ketones mesityl oxide (B.D.H.) and pent-3-en-2-one (Aldrich) were used as received.

5,7,7,12,14-*Pentamethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene Dihydroperchlorate.*—Perchloric acid (41.5 cm^3, 72%, 0.5 mol) was added dropwise with continuous stirring to a cooled (−5—0 °C, ice-salt bath) solution of 1,2-diaminoethane (33.5 cm^3, 0.5 mol) in methanol (350 cm^3). A mixture of pent-3-en-2-one (21.0 g, 0.25 mol) and mesityl oxide (24.5 g, 0.25 mol) in methanol (60 cm^3) was then added dropwise to the above solution with continuous stirring during which time the temperature was maintained between 0 and 4 °C. Stirring was continued for a further 4 h and the temperature of the solution was allowed to rise to ambient. The white product slowly precipitated as the temperature increased. The ligand salt was filtered off, washed thoroughly with methanol, and then with diethyl ether and recrystallised from methanol to give shining white crystals. (**CAUTION**: amine perchlorate salts can detonate with great violence, a water-bath should be used for the recrystallisation step.) Yield: 40 g, m.p. 124—125 °C (Found: C, 38.45; H, 6.80; N, 12.05. Calc. for $C_{15}H_{32}Cl_2N_4O_8$: C, 38.55; H, 6.90; N, 12.00%). The filtrate on standing in a refrigerator for *ca.* 24 h gave a further crop of the product as shining white crystals, which were filtered off, washed thoroughly with methanol followed by diethyl ether, and dried *in vacuo* over silica gel (Found: C, 38.90; H, 7.00; N, 11.90%).

$[CuL][ClO_4]_2$.—A mixture of copper(II) carbonate (0.25 g) and the ligand dihydroperchlorate (0.93 g) in methanol–water (20 cm^3, 1:1 v/v) was heated in a water-bath for *ca.* 30 min. The resulting red-purple solution was filtered hot. On standing overnight the reddish purple complex crystallised. The complex was recrystallised from methanol (Found: C, 33.80; H, 5.65; N, 10.65. Calc. for $C_{15}H_{30}Cl_2CuN_4O_8$: C, 34.05; H, 5.70; N, 10.60%).

$[NiL][ClO_4]_2$.—A mixture of nickel(II) acetate tetrahydrate (0.5 g) and the ligand dihydroperchlorate (0.94 g) in 20% methanol–water (50 cm^3) was refluxed for *ca.* 1 h. The mixture was filtered hot and evaporated to *ca.* 15 cm^3. A few drops of concentrated $HClO_4$ were added and the solution allowed to stand overnight giving yellow crystals of the complex which were filtered off, washed with propan-2-ol, and recrystallised from methanol (Found: C, 33.80; H, 5.25; N, 10.60. Calc. for $C_{15}H_{30}Cl_2N_4NiO_8$: C, 34.40; H, 5.80; N, 10.70%).

An alternative preparation for this complex is as follows. A mixture of basic nickel(II) carbonate (6.0 g, excess) and the ligand dihydroperchlorate (5.0 g) in water (100 cm^3) was heated, with stirring for *ca.* 1 h on a water-bath and filtered hot. The volume of the filtrate was reduced to *ca.* 5 cm^3 on a rotary evaporator. The resulting complex was dissolved in the minimum volume of hot methanol. Cooling in ice gave orange-yellow crystals which were collected by filtration, washed with ice-cold methanol, then diethyl ether and dried *in vacuo* over silica gel (Found: C, 33.10; H, 5.50; N, 10.50. Calc. for $C_{15}H_{30}Cl_2N_4NiO_8$: C, 34.40; H, 5.80; N, 10.70%).

$[ZnL][ClO_4]_2$.—The ligand dihydroperchlorate (1.0 g) and basic zinc(II) carbonate (excess, 1.5 g) in methanol–water (*ca.* 50 cm^3) were heated on a water-bath for *ca.* 30 min and then filtered to remove the unreacted zinc(II) carbonate. A solution of lithium perchlorate (1.0 g) in water (10 cm^3) was added to the filtrate. Cooling in a refrigerator for 48 h gave white crystals of the product (Found: C, 34.30; H, 6.00; N, 10.30. Calc. for $C_{15}H_{30}Cl_2N_4O_8Zn$: C, 33.95; H, 5.70; N, 10.55%).

trans-$[CoLCl_2]ClO_4$.—To a hot solution of cobalt(II) acetate tetrahydrate (2.7 g, 0.01 mol) in methanol–water (100 cm^3, 1:1 v/v) was added the ligand dihydroperchlorate (5.0 g, 0.01 mol). The reaction mixture was heated on a water-bath for *ca.* 1 h and filtered hot to remove any unreacted cobalt(II) acetate. The filtrate was diluted with methanol–water (100 cm^3, 1:1 v/v) and air passed through the dull red solution for *ca.* 30 h. The methanol was removed on a rotary evaporator and concentrated HCl (40 cm^3) added to the dull red solution. The green complex slowly crystallised as the solution was slowly evaporated on a water-bath (cooling may be necessary). The complex was recrystallised from methanol giving pale green crystals (Found: C, 36.35; H, 6.15; N, 11.05. Calc. for $C_{15}H_{30}Cl_3CoN_4O_4$: C, 36.35; H, 6.10; N, 11.30%).

trans-$[CoLBr_2]ClO_4$.—A filtered solution of cobalt(II) bromide hexahydrate (3.25 g) in methanol (50 cm^3) was added with stirring to the ligand dihydroperchlorate (4.6 g) in methanol (100 cm^3). The mixture was gently heated on a water-bath for several minutes and filtered hot. The filtrate was then heated on a water-bath for a further 1.5 h, during which time the solution changed from brown to green. After standing for several hours the apple green crystals which formed were filtered off, washed thoroughly with methanol, and dried *in vacuo* over silica gel (yield 2.0 g). A second crop of crystals (0.5 g) could be isolated from the filtrate on evaporation to *ca.* 25 cm^3 (Found: C, 30.65; H, 5.05; N, 9.85. Calc. for $C_{15}H_{30}Br_2ClCoN_4O_4$: C, 30.80; H, 5.15; N, 9.60%).

trans-$[CoL(NO_2)_2]ClO_4$.—To a suspension of *trans*-$[CoLCl_2]ClO_4$ (0.40 g) in methanol–water (40 cm^3, 1:1 v/v) was added a solution of sodium nitrite (0.09 g) in water (5 cm^3) and the mixture was heated on a water-bath for *ca.* 15 min and filtered hot. The filtrate was allowed to cool slowly to room temperature giving dark orange crystals. The crystals were filtered off and washed with the minimum volume of cold water, followed by methanol and ethanol and then dried in a desiccator over silica gel (Found: C, 34.50; H, 5.70; N, 16.25. Calc. for $C_{15}H_{30}ClCoN_6O_8$: C, 34.85; H, 5.85; N, 16.25%).

trans-$[CoL(NCS)_2]ClO_4$.—A solution of potassium thiocyanate (0.10 g) in water (10 cm^3) was added with stirring to a suspension of *trans*-$[CoLCl_2]ClO_4$ (0.50 g) in methanol–water (20 cm^3, 1:1 v/v). The mixture was heated on a water-bath for *ca.* 10 min and the resulting red solution filtered hot. On standing overnight a white precipitate appeared and this was filtered off and discarded. The filtrate was concentrated to *ca.* 10 cm^3 and the pale red crystals obtained were recrystallised from ethanol (Found: C, 37.30; H, 5.55; N, 16.25. Calc. for $C_{17}H_{30}ClCoN_6O_4S_2$: C, 37.75; H, 5.60; N, 16.55%).

trans-$[CoLCl(NO_2)]ClO_4{\cdot}0.5H_2O$.—A suspension of *trans*-$[CoLCl_2]ClO_4$ (0.20 g) in methanol–water (10 cm^3, 1:1 v/v) was heated to boiling on a water-bath. Sodium nitrite (0.03 g) in water (5 cm^3) was added and the resulting mixture heated on a water-bath for *ca.* 30 min, during which time the solution changed from green to reddish pink. The chloro-nitro complex was obtained as a reddish pink powder on cooling. The complex was filtered off, washed with aqueous methanol, and dried in a vacuum desiccator over silica gel (Found: C, 34.60; H, 5.80; N, 13.45. Calc. for $C_{15}H_{31}Cl_2CoN_5O_{6.5}$: C, 34.95; H, 6.05; N, 13.60%).

trans-$[CoL(N_3)_2]ClO_4{\cdot}0.5H_2O$.—Sodium azide (0.07 g) in water (5 cm^3) was added with stirring to a suspension of *trans*-$[CoLCl_2]ClO_4$ (0.30 g) in methanol–water (10 cm^3, 1:1 v/v) and the resulting mixture heated on a water-bath for *ca.* 1 h. Cooling in an ice-bath gave brown crystals which were filtered off and recrystallised from methanol (Found: C, 34.90; H, 5.55; N, 27.40. Calc. for $C_{15}H_{31}ClCoN_{10}O_{4.5}$: C, 34.80; H, 6.05; N, 27.80%).

trans-$[\{CoL(H_2O)\}_2(O_2)][ClO_4]_4$.—A concentrated aqueous solution of cobalt(II) perchlorate hexahydrate (3.6 g) was added with stirring to a solution of the ligand dihydroperchlorate (4.7 g) in the minimum volume of water. The solution rapidly became deep brown, and a concentrated

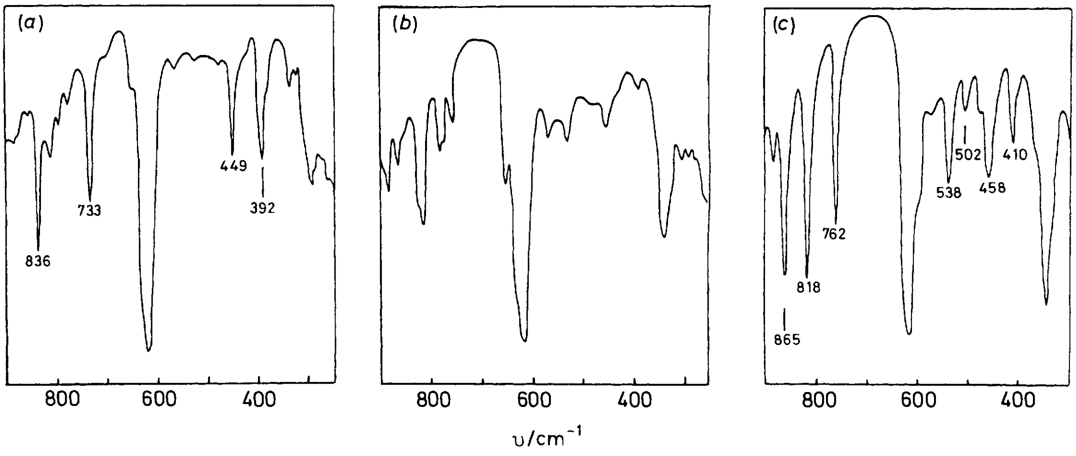


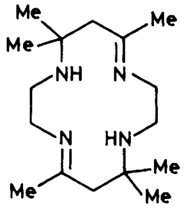
Figure 1. Comparison of the i.r. spectra of the three ligand dihydroperchlorate salts in the region 900—300 cm^{-1}: (*a*) $L'{\cdot}2HClO_4$, (*b*) $L{\cdot}2HClO_4$, and (*c*) $L''{\cdot}2HClO_4$

aqueous solution of sodium perchlorate (5 cm^3) was added. Cooling in an ice-bath gave the brown complex which was filtered off, washed with ethanol, then diethyl ether and dried *in vacuo* over silica gel (Found: C, 33.15; H, 5.90; N, 10.70. Calc. for $C_{30}H_{60}Cl_4Co_2N_8O_{18}$: C, 33.35; H, 5.60; N, 10.35%).

General.—I.r. spectra were determined as KBr discs using a Perkin-Elmer 457 instrument. U.v.–visible spectra were determined using aqueous solutions or where appropriate solutions in acetonitrile. Solid-state spectra were recorded as Nujol mulls on filter paper. Measurements were made with a Perkin-Elmer Lambda 3 instrument.

Results and Discussion

The reaction of 1,2-diaminoethane dihydroperchlorate with an equimolar mixture of mesityl oxide and pent-3-en-2-one in methanol solution is expected to give a mixture of three tetra-azacyclotetradecadienes, L, L′, and L″ as their dihydroperchlorate salts. However, the major product is L·2HClO$_4$ which can be freed from traces of the other macrocyclic dihydroperchlorates by recrystallisation from methanol. Authentic samples of the dihydroperchlorate salts of L′[1] and L″[4] were prepared by standard literature routes. Comparison of the i.r. spectra of the three ligand dihydroperchlorate salts in the region 900—300 cm^{-1} provided a useful criterion of purity, Figure 1. The tetramethyl ligand L′ has strong characteristic bands at 836, 733, 449, and 392 cm^{-1}, while the hexamethyl derivative L″ has bands at 818, 762, 538, 502, 458, and 410 cm^{-1}, Table 1. The band at 733 cm^{-1} which is characteristic of L′·2HClO$_4$ and the 410 cm^{-1} band characteristic of L″·2HClO$_4$ are completely lacking in the i.r. spectrum of a sample of L·2HClO$_4$ recrystallised from methanol, Figure 1. The i.r. spectra thus provide a rapid method for establishing ligand homogeneity.



L″

The approximate composition of the crude ligand dihydroperchlorate mixture was established by chromatographic techniques. The mixed dihydroperchlorate salts were treated with an aqueous slurry of basic nickel(II) carbonate to generate the nickel(II) macrocyclic complexes. After filtration the mixed nickel(II) complexes were then chromatographed on Sephadex-C25 using sodium glycinate as eluant.[3] This technique allowed the ready separation of the nickel complexes. On this basis the initial ligand composition was established to be L (70%), *C-rac*-L′ (15%), and *C-meso*-L′ (15%). Only traces of L″ are produced in the reaction. A chromatographically pure sample of [NiL][ClO$_4$]$_2$ was prepared by this technique.

Table 1. Differences in the i.r. spectra of the ligand dihydroperchlorate salts*

L′	L	L″
836s		
733s	812s	818s
	755w	762s
449s		538s
		502m
		458s
392s		410s

* Spectra determined as KBr discs.

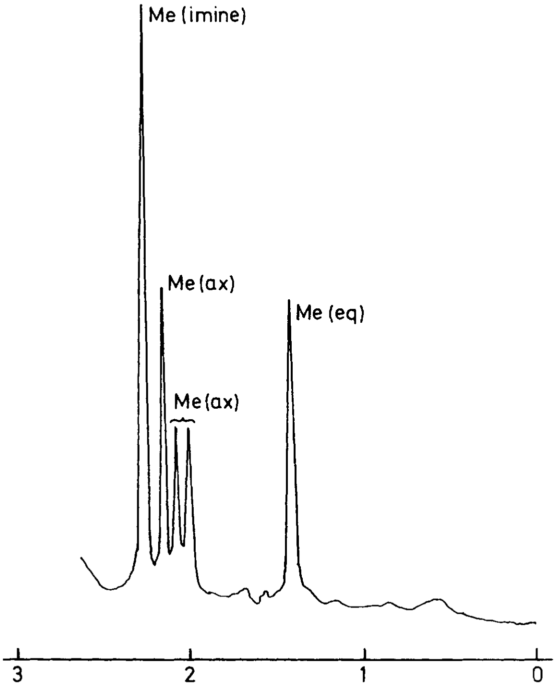


Figure 2. ^1H N.m.r. spectrum of [NiL][ClO$_4$]$_2$ in trifluoroacetic acid solvent with SiMe$_4$ reference

Table 2. Methyl signals in the ^1H n.m.r. spectra of nickel(II) complexes*

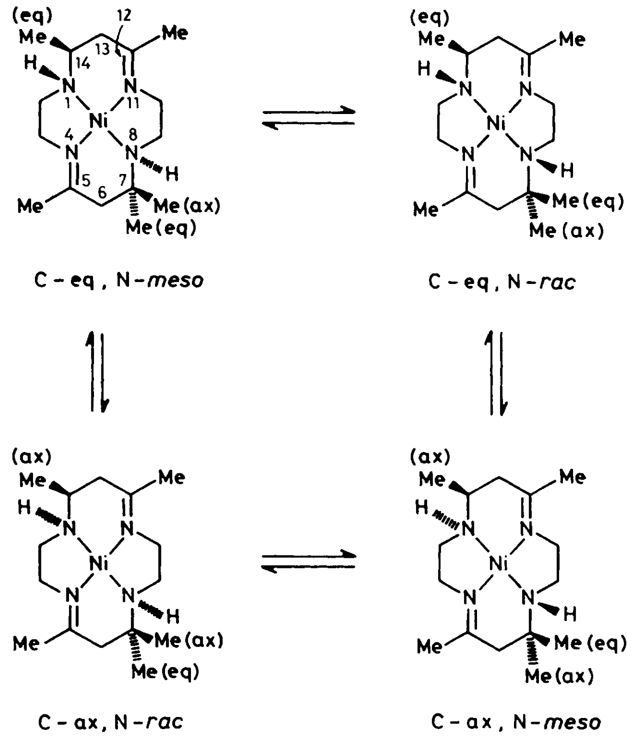
		Methyl resonances		
Complex (isomer)	Solvent	Imine	Axial	Equatorial
[NiL′][ClO$_4$]$_2$	CD$_3$NO$_2$	2.20(6)	1.74 (d) (3), *J* 7	1.26 (d) (3), *J* 6
(*C-meso-N-rac*)	CF$_3$CO$_2$H	2.26(6)	1.83 (d) (3), *J* 7	1.34 (d) (3), *J* 6
[NiL′][ClO$_4$]$_2$	CD$_3$NO$_2$	2.22(6)	1.90 (d) (6), *J* 6	
(*C-rac-N-rac*)	CF$_3$CO$_2$H	2.27(6)	1.96 (d) (6), *J* 6	
[NiL″][ClO$_4$]$_2$	CD$_3$NO$_2$	2.19(6)	2.10(6)	
(*N-rac*)	CF$_3$CO$_2$H	2.23(6)	2.16(6)	
[NiL][ClO$_4$]$_2$	CD$_3$NO$_2$	2.21(6)	2.08(3); 1.97 (d), (3), *J* 6	1.33(3)
	CF$_3$CO$_2$H	2.24(6)	2.13(3); 2.03 (d) (3), *J* 7	1.40(3)

* δ In p.p.m. downfield from internal SiMe$_4$ at 90 MHz, d = represents a doublet; numbers of protons are given in parentheses; *J* in Hz.

Table 3. Electronic spectral details of complexes of L[a]

Complex	$\lambda_{max.}$/nm	ε/dm^3 mol^{-1} cm^{-1}
$[CuL][ClO_4]_2$	505	98
$[NiL][ClO_4]_2$	433	82
trans-$[CoLCl_2]ClO_4$	618[b]	44
	430 (sh)[b]	
trans-$[CoLBr_2]ClO_4$	658[b]	59
	388[b]	2.4×10^3
trans-$[CoLCl(NO_2)]ClO_4 \cdot 0.5H_2O$	510[b]	86
	350 (sh)[b]	2.1×10^3
trans-$[CoL(NO_2)_2]ClO_4$	442	177
	350	3.6×10^3
trans-$[CoL(N_3)_2]ClO_4 \cdot 0.5H_2O$	558	522
	344	1.1×10^4
trans-$[CoL(NCS)_2]ClO_4$	519	276
	330	2.3×10^3
trans-$[\{CoL(H_2O)\}_2(O_2)][ClO_4]_4$	550 (sh)[c]	
	445[c]	
	315[c]	

[a] Spectra recorded in aqueous solution unless otherwise stated. [b] Spectra recorded in acetonitrile. [c] Solid-state spectrum. The aqueous solution spectrum of the μ-peroxo complex has $\lambda_{max.}$ 450 (ε 154) and 310 (sh) nm (ε 2×10^3 dm^3 mol cm^{-1}).



Scheme. Diastereoisomers of $[NiL]^{2+}$. Point groups are all C_1. The C-axial, N-*meso* diastereoisomer with the axial methyl substituents on opposite sides of the ring is probably favoured

Nickel(II) *Complex.*—The ^{1}H n.m.r. spectrum of the orange diamagnetic complex $[NiL][ClO_4]_2$ in CF_3CO_2H displays four sets of methyl resonances, Table 2 and Figure 2. A single sharp resonance at δ 2.24 is due to the imine methyls at ring positions 5 and 12. Methyl singlets at δ 1.40 and 2.13 can be assigned to the equatorial and axial *gem*-dimethyl substituents respectively, while the methyl doublet (J = 7 Hz) at δ 2.03 indicates that the single methyl group at C^{14} occupies an axial site.[1,5]

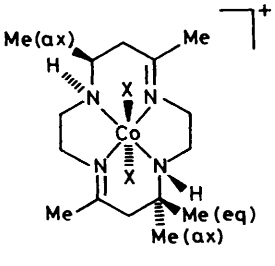
The ligand L has a single chiral carbon centre at C^{14} and thus exists as a pair of enantiomers. Co-ordination in a planar ligand stereochemistry generates two chiral nitrogen centres and thus four diastereoisomers are possible, Scheme. Each diastereoisomer (C_1 symmetry) is enantiomeric so that a total of eight stereoisomers is possible for this system.

The *X*-ray data on macrocyclic tetra-azadiene complexes[6] indicate that the five-membered chelate rings have close to envelope conformations (four atoms in plane and one out of plane), and the six-membered rings are in approximate sofa conformations (five atoms in plane and one out of plane). If the rings in $[NiL]^{2+}$ have these conformations and the single methyl group at C^{14} is axial as indicated by the ^{1}H n.m.r. spectrum, the complex must be either the C-axial, N-racemic diastereoisomer or the C-axial, N-*meso* diastereoisomer (Scheme) or a mixture of both. In the N-*meso* diastereoisomer the two axial methyl groups *trans* to the adjacent NH groups lie on opposite sides of the molecule. The N-*meso* diastereoisomer is less sterically crowded and might thus be favoured.

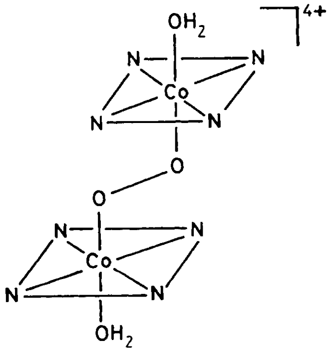
The complex $[NiL][ClO_4]_2$ has a strong band in aqueous solution at 433 nm (ε 82 dm^3 mol^{-1} cm^{-1}) typical of singlet ground-state nickel(II). There is little tendency to add axial water ligands to give blue octahedral species as is frequently observed with macrocyclic tetra-aza nickel(II) complexes. Folding of the complex to give the blue *cis*-$[NiL(en)]^{2+}$ species does not occur on adding neat 1,2-diaminoethane (en) to an aqueous solution of $[NiL][ClO_4]_2$.

Cobalt(III) *Complexes.*—The green *trans*-$[CoLCl_2]ClO_4$ is readily prepared by aeration of a mixture of cobalt(II) acetate and the ligand dihydroperchlorate in methanol–water solvent, followed by treatment with concentrated hydrochloric acid. The electronic spectrum, Table 3, is fully consistent with a *trans* stereochemistry. The ^{1}H n.m.r. spectrum of the complex in $(CD_3)_2SO$ has a singlet at δ 2.51 (6 H) due to the imine methyls at ring positions 5 and 12. Methyl singlets at δ 1.5 (3 H) and 2.46 (3 H) can be assigned to the axial and equatorial *gem*-dimethyl substituents respectively [in cobalt(III) complexes the axial methyl resonances occur at higher field [7]]. A methyl doublet at δ 1.45 (3 H, J = 7.2 Hz) indicates that the single methyl substituent at C^{14} occupies an axial site as in the nickel(II) complex.

Using *trans*-$[CoLCl_2]ClO_4$ it is possible to prepare a large number of derivatives *trans*-$[CoLX_2]^+$ [X_2 = $(NO_2)_2$, Br_2, $(N_3)_2$, $Cl(NO_2)$, or $(NCS)_2$] by anion metathesis reactions in methanol–water. The spectral properties of these complexes, Table 3, are consistent with a *trans* stereochemistry. The i.r. data, Table 4, confirm that *trans*-$[CoL(NCS)_2]^+$ has the expected isothiocyanato structure. It is probable that all of these complexes have the C-axial, N-*meso* structure (**I**).



(**I**)



(**II**)

Table 4. Prominent i.r. absorption bands in L and its metal complexes*

Compound	ν(C=N)	ν(N-H)	$\nu(ClO_4^-)$	Other ligand bands
$L \cdot 2HClO_4$	1 660s	3 150s,br	1 110vs,br 620s	
$[NiL][ClO_4]_2$	1 650s	3 180s,br	1 085vs,br 620s	
$[CuL][ClO_4]_2$	1 668s	3 220s	1 110vs,br 618s	
trans-$[CoLCl_2]ClO_4$	1 658s	3 182s	1 075vs,br 616s	
trans-$[CoLBr_2]ClO_4$	1 655s	3 182s	1 080vs,br 618s	
trans-$[CoL(NO_2)_2]ClO_4$	1 658s	3 130s	1 080vs,br 618s	1 395s [$\nu_{asym}(NO_2)$] 1 308s [$\nu_{sym}(NO_2)$] 818s [$\delta(NO_2)$]
trans-$[CoLCl(NO_2)]ClO_4 \cdot 0.5H_2O$	1 658s	3 200(sh) 3 185s	1 095vs,br 620s	1 375m [$\nu_{asym}(NO_2)$] 1 316s [$\nu_{sym}(NO_2)$] 823s [$\delta(NO_2)$]
trans-$[CoL(N_3)_2]ClO_4 \cdot 0.5H_2O$	1 657s	3 280m 3 200s	1 090vs,br 620s	3 500br [ν(OH)] 3 480br [ν(OH)] 2 010vs,br [$\nu_{asym}(N_3)$] 1 288s [$\nu_{asym}(N_3)$]
trans-$[CoL(NCS)_2]ClO_4$	1 655s	3 128s,br	1 070vs,br 618s	2 068vs,br [ν(C≡N)] 830s [ν(C–S)]
trans-$[\{CoL(H_2O)\}_2(O_2)][ClO_2]_4$	1 652s	3 155m,br 3 098m,br	1 080vs,br 620s	

* vs = Very strong, s = strong, m = medium, sh = shoulder, and br = broad.

Aeration of aqueous solutions of $L \cdot 2HClO_4$ and cobalt(II) gives the brown μ-peroxo-dicobalt(III) species (**II**) which can readily be characterised as a perchlorate salt. The axial water ligands in (**II**) can readily be substituted by anions such as NO_2^-.

Copper(II) *Complex.*—The complex $[CuL][ClO_4]_2$ was readily characterised as reddish purple crystals. The complex has $\lambda_{max.}$ 505 nm (ε 98 dm^3 mol^{-1} cm^{-1}) and is a 2:1 electrolyte in aqueous solution. In the solid state it is likely that the complex is tetragonal with perchlorate anions in the axial sites.

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