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Macrocyclic Ligands and their Metal Ion Complexes.
Part VIII*. Preparation and structure of Isomeric Tetramethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene-iron(II) Diperchlorates and their Dehydrogenation by Elemental Oxygen for Elucidation of the Ligands' Constitutional Isomerism

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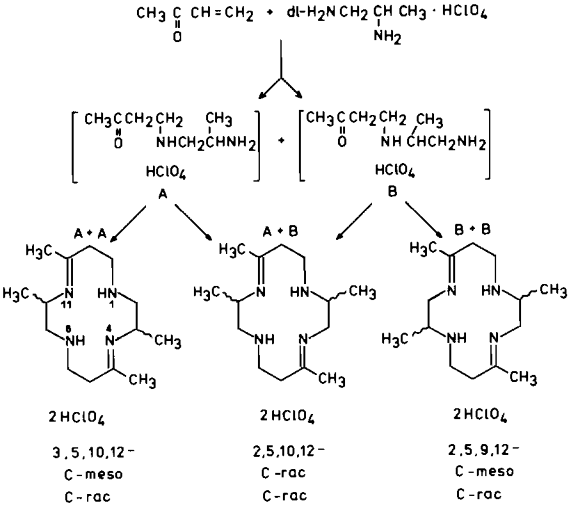
Isomeric 2,5,9,12-, 2,5,10,12-, and 3,5,10,12-tetramethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-dienenickel(II) diperchlorates were obtained from methyl vinyl ketone, R,S- *and* R-(–)-*1,2-propylene diamines monohydrogenperchlorates, and nickel(II) acetate. The C- and N-diastereoisomeric forms of complexes were isolated and the ligand configuration and conformation were assigned to them on the basis of the resolution, the racemisation and the mutarotation of complexes, the dehydrogenation of ligand in complexes, and the spectroscopic evidence. All complexes are diamagnetic square-planar nickel(II) compounds except of* $IINi(ClO_4)_2 \cdot 2/3H_2O$ *complex which is paramagnetic in the solid state (1.78 B.M.). We formulate this complex as a solid equilibrium mixture of N-*racemic *(α) and N-*meso *(β) diastereoisomers:* $2[IINi(ClO_4)_2\alpha] \cdot [IINi(ClO_4)_2\beta \cdot 2H_2O]$ *with two molecules of water coordinated apically to an octahedral nickel(II) ion.*

Introduction

In Part VI [1] we reported the synthesis and structure of several substituted 1,4,8,11-tetra-azacyclotetradeca-4,11-dienes and their nickel(II) complexes which were obtained from α,β-unsaturated ketones and ethylenediamine. Since we were also interested in the synthesis and stereochemistry of tetra-azacyclotetradeca-4,11-dienes with substituents in the diamine residue we undertook a study of the condensation of methyl vinyl ketone with 1,2-propylenediamine.

The first synthesis of tetra-azacyclotetradeca-4,11-diene complexes derived from 1,2-propylenediamine was carried out by Curtis using a template condensation of racemic tris-(1,2-propylenediamine)nickel(II) diperchlorate with acetone [2]. Only 3,10-substituted ligands were obtained with *meso* and *racemic* C-configurations. The optically active amine gives the optically active macrocycle [3]. The *meso*-3,10-substituted product was also obtained in the condensation of *racemic*-1,2-propylenediamine monohydrogen perchlorate with mesityl oxide or acetone [3].

We used methyl vinyl ketone for the condensation in the hope that the reaction of less substituted ketone in comparison to mesityl oxide would lead to compounds with various substituent locations as shown in Scheme 1.



Scheme 1.

The expected first step of the reaction is the addition of the diamine to the double bond of the α,β-

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*Part VI: see ref. 1.

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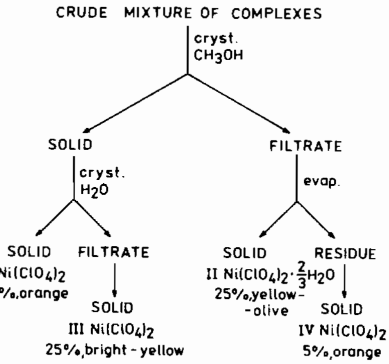
unsaturated ketone. The addition of the less hindered amino-group will predominate, and the aminoketone **A** should be produced in excess. The situation is reversed in the cyclisation step, when the more hindered amino-group has to react with keto-group of another aminoketone molecule. Therefore, it is impossible to predict which cyclic amine will be produced in excess. The combination of the aminoketones **A** and **B** leads to six cyclic amines, differing in substituents location 3,10-, 2,10-, and 2,9-, and in the relative configuration of the asymmetric carbon atoms. When optically active 1,2-propylenediamine is used the number of possible macrocyclic products is reduced to three.

1,4,8,11-Tetra-azacyclotetradeca-4,11-dienes react with nickel(II) ions to form complexes which contain two chiral centres at nitrogen for the secondary amino-groups. These complexes may exist in interconvertible forms possessing N-*meso* and N-*racemic* configurations [1]. This gives rise to ten possible isomers for each symmetric 2,9- and 3,10-substituent location, and twelve isomers for the 2,10-substituted ligands.

Results and Discussion

Synthesis

The mixture of macrocyclic Schiff's base Ni(II) complexes I–IV $Ni(ClO_4)_2$ was prepared by condensation of methyl vinyl ketone with *R,S*-1,2-propylenediamine monohydrogen perchlorate followed by reaction of ligand perchlorate mixture with nickel(II) acetate. The product was separated (scheme 2) into four compounds by crystallisation from methanol or water.



Scheme 2.

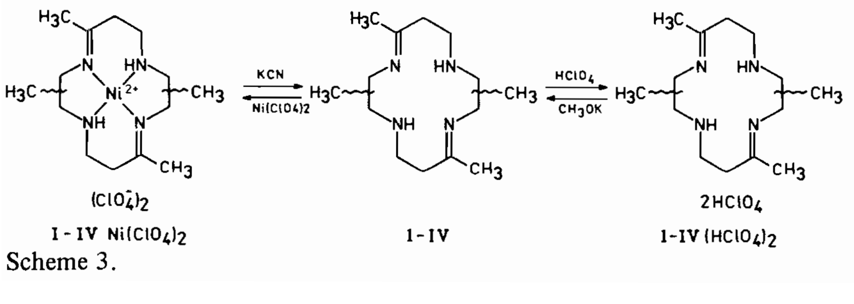
Complex $INi(ClO_4)_2$ is sparingly soluble in all solvents and crystallises first from solution together with complex $IIINi(ClO_4)_2$. They were separated by crystallisation from water. Complexes $INi(ClO_4)_2$, $IINi(ClO_4)_2 \cdot 2/3H_2O$ and $IIINi(ClO_4)_2$ were obtained in nearly equal yields, but complex $IVNi(ClO_4)_2$ is a minor isomer which was isolated from tarry crystallisation residues.

In order to find the number of isomeric ligands we liberated them from the complexes by reaction with potassium cyanide (scheme 3). We obtained four different compounds I–IV, which react with anhydrous nickel(II) perchlorate to re-form the individual starting complexes. Individual dihydrogen perchlorates I–IV$(HClO_4)_2$ were obtained from the free bases I–IV by reaction with perchloric acid.

Nitrogen isomers

Complexes $INi(ClO_4)_2$ and $IVNi(ClO_4)_2$ exist in stable nitrogen configurations and we were unable to isomerise them in basic medium to observe any further isomers.

Complex $IINi(ClO_4)_2 \cdot 2/3H_3O$ was separated into $IINi(ClO_4)_2\alpha$ and $IINi(ClO_4)_2\beta$ isomers by fractional precipitation with benzene from nitromethane solution. They were obtained in a solvated form $IINi(ClO_4)_2\alpha \cdot 2C_6H_6$ and $IINi(ClO_4)_2\beta \cdot 2C_6H_6$ from which the benzene of solvation was subsequently removed by heating under vacuum. Both isomers are stable as solids but they isomerise in aqueous solution to give an equilibrium mixture of the isomers α and β in the ratio 2:1 as evidenced by PMR spectra. Isomer β has a marked tendency to coordinate polar solvents H_2O, CH_3CN, $(CH_3)_2SO$ to form paramagnetic species in solution. The solid complexes $IINi(ClO_4)_2\alpha$ and $IINi(ClO_4)_2\beta$ are diamagnetic, whereas the $IINi(ClO_4)_2 \cdot 2/3H_2O$ complex has a magnetic moment of 1.78 B.M. The investigation of magnetic properties of this complex will be published elsewhere [4]. The PMR spectrum of $IINi(ClO_4)_2 \cdot 2/3H_2O$ in nitromethane is a superposition of spectra of $IINi(ClO_4)_2\alpha$ and $IINi(ClO_4)_2\beta$ in a ratio 2:1. The UV-VIS spectrum of solid complex $IINi(ClO_4)_2 \cdot 2/3H_2O$ contains bands at 11600, 16900, and 29900 cm^{-1}, which are characteristic for octahedral Ni(II) coordination. Taking into account the



Scheme 3.

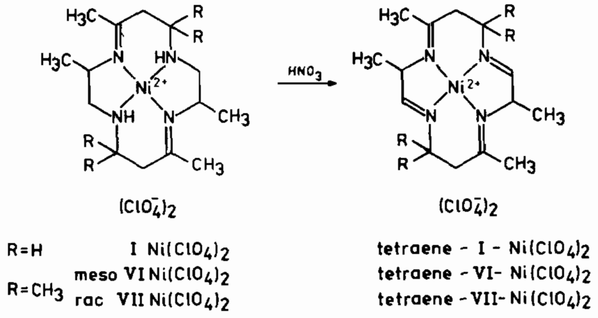
well-known tendency of nonhindered square-planar nickel(II) complexes of macrocyclic ligands to coordinate two solvent molecules, or two anions in apical positions, we propose the structure 2[IINi$(ClO_4)_2\alpha$]·[IINi$(ClO_4)_2\beta\cdot 2H_2O$] for complex IINi$(ClO_4)_2\cdot$ 2/3H_2O.

Complex IIINi$(ClO_4)_2$ was isolated as the stable nitrogen isomer α, which could be isomerised in basic solution into the IIINi$(ClO_4)_2\beta$ form. The resulting mixture was separated into the individual IIINi$(ClO_4)_2\beta$ and IIINi$(ClO_4)_2\alpha$ isomers by fractional crystallisation from nitromethane–benzene solution. Both complexes crystallised with ½ molecule of benzene and in case of isomer IIINi$(ClO_4)_2\alpha\cdot$½C_6H_6 the solvent could not be removed under vacuum at temperatures up to 140 °C.

Location of Substituents

In order to establish the location of the substituents in the macrocylic ring we decided to use the ligand dehydrogenation reaction. It has been shown that the dehydrogenation occurs in the 1,8-positions in five-membered chelate rings, even if positions in six-membered rings are accessible for the reaction [5].

We first performed the dehydrogenation of the *meso* VINi$(ClO_4)_2$ and *racemic* VIINi$(ClO_4)_2$ isomers of 3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-dienenickel(II) perchlorate [2] using nitric acid. Both isomeric -1,4,8,11-tetraenes [tetraene-VINi$(ClO_4)_2$ and tetraene-VIINi$(ClO_4)_2$] were obtained in a good yield. The infrared spectra (Table I) of both isomers are nearly identical and contain two C=N stretching absorption bands, at 1650 and 1670 cm^{-1}. The electronic spectra (Table II) of the meso and racemic isomers differ substantially in the region of the *d–d* absorption band. This appears at 431 nm with a molar extinction coefficient of 64 for the meso isomer [tetraene-VINi$(ClO_4)_2$] and at 434 nm with the expected higher extinction coefficient of 71 for the less symmetric racemic isomer [tetraene-VIINi$(ClO_4)_2$]. Also the PMR spectra of both tetraenes (Table III) are very similar, consisting of three singlets at 1.21 ppm and 1.39 ppm for the pseudoaxial and pseudoequatorial geminal methyl groups and at 2.32 ppm for the 'imine' methyl groups. The doublet signal of the pseudoaxial 3 and 10 methyl groups at 1.54 ppm is coupled to the multiplet at 4.98 ppm assigned to protons in positions 3 and 10 which, in turn, are coupled to 'vinylic' protons in positions 2 and 9 (7.91 ppm) with a small coupling constant (1.7 Hz). The geminal protons in positions 6 and 13 form an AB type spectrum at 2.80 and 3.04 ppm with a coupling constant of 18 Hz.



Scheme 4.

We were successful in dehydrogenating complex INi$(ClO_4)_2$ with nitric acid. Characteristic PMR signals of 1,4,8,11-tetraene (Table III) are the broad singlet of the 'vinylic' protons at 8.21 ppm, and the preserved doublet of the methyl groups at 1.48 ppm indicated that the methyl groups occupy positions 3 and 10.

Dehydrogenation of the other isomeric nickel(II) complexes leads to complete decomposition of these materials. Therefore, we employed another dehydrogenation method described by Busch [6]; namely the dehydrogenation of the ligands in an iron(II) complex by elemental oxygen. The synthesis and structures of the iron(II) complexes of ligands I–IV and their dehydrogenation products are described elsewhere [7]. It was possible to establish the location of the methyl substituents in the ligands II, III and IV. Ligands II and IV are diastereoisomeric, substituted in positions 2 and 9, and ligand III is substituted in positions 2 and 10 of the macrocyclic ring [7].

C-Configurations (Optically Active Ligands)

The reaction of optically active *R*-(–)-1,2-propylenediamine monohydrogen perchlorate with methyl vinyl ketone was investigated in order to confirm the structures of the ligands having the same configuration at both asymmetric carbon atoms. We also expected that when only one enantiomer of diamine was present in the reaction mixture, further isomers of macrocyclic Schiff's base could be formed in recoverable amounts.

Optically active isomers IIINi$(ClO_4)_2\alpha$, IVNi$(ClO_4)_2$ and an additional complex of a fifth isomeric ligand VNi$(ClO_4)_2$ were isolated in this experiment. Complexes of ligands I and II were not formed which implies that they possess C-*meso* configurations.

Infrared Spectra

The characteristic infrared absorption bands for all of the compounds discussed are given in Table I. In the spectra of the free bases, their perchlorates and Ni(II) complexes, we observed N–H stretching absorption bands in the 3200–3300 cm^{-1} region and intense imine C=N stretching absorption near 1660 cm^{-1}. The N–H absorption band disappeared and a second C=N stretching absorption band was observed in the spectra of 1,4,8,11-tetraene Ni(II) complexes.

TABLE I. Characteristic Infrared Absorption Bands of Free Ligands, their Perchlorates, and Nickel(II) Complexes (Nujol, cm^{-1}).

Compound	$\nu_{NH,N^+H_2,OH}$	$\nu_{C=N}$	$\nu_{ClO_4^-,PF_6^-}$	$\delta_{N^+H_2,H_2O}$
I	3320	1650		
II	3290	1660		
III[a]	3320	1665		
IV[a]	3280	1665		
$I(HClO_4)_2$	3200	1660	1100	1550
$II(HClO_4)_2$	3200 3130	1670	1090	1545
$III(HClO_4)_2$	3200	1665	1100	1555
$IV(HClO_4)_2$	3200	1670	1100	1550
$INi(ClO_4)_2$	3290	1640	1095	
$INi(PF_6)_2$	3300	1650	850	
$IINi(ClO_4)_2 \cdot 2/3H_2O$	3540 3375 3260 3185	1675 1650	1095	1625
$IINi(ClO_4)_2\alpha$	3210	1650	1095	
$IINi(ClO_4)_2\beta$	3260	1675	1100	
$IIINi(ClO_4)_2$	3220	1650	1090	
$IIINi(ClO_4)_2\alpha \cdot \frac{1}{2}C_6H_6$	3220	1650	1095	
$IIINi(ClO_4)_2\beta$	3230	1650	1100	
$IVNi(ClO_4)_2$	3200	1660	1100	
$VNi(ClO_4)_2$	3250	1650	1095	
tetraene-$INi(ClO_4)_2$		1680 1650	1090	
tetraene-$VINi(ClO_4)_2$		1670 1650	1095	
tetraene-$VIINi(ClO_4)_2$		1670 1650	1095	

[a] Spectra of liquid samples.

An O–H absorption band is present in the spectrum of the complex $IINi(ClO_4)_2 \cdot 2/3H_2O$ indicating the presence of water. The very strong band occurring at *ca.* 1100 cm^{-1} is characteristic of a non-coordinated perchlorate anion.

Ultraviolet and Visible Spectra

The results of electronic spectra measurements for Ni(II) complexes are given in Table II. All of the complexes exhibit the characteristic absorption band of low intensity in the region 423–450 nm for square-planar nickel(II) *d–d* transitions. The square-planar configuration of the complexes was confirmed by magnetic susceptibility measurements. All of the complexes except the solid complex $IINi(ClO_4)_2 \cdot 2/3H_2O$ are diamagnetic in the solid state and in nitromethane solution. The solid complex $IINi(ClO_4)_2 \cdot 2/3H_2O$ has a magnetic moment of 1.78 B.M. and a full investigation of its magnetic properties will be published elsewhere [4].

The ultraviolet absorption band at 204–218 nm with a shoulder at 219–231 nm is assigned to charge transfer transitions and the 278–291 nm band is interpreted as the metal to ligand d–π charge transfer transition [8].

Proton Magnetic Resonances Spectra

The results of PMR measurements are given in Table III. The signals of the ring protons in the spectra of the free ligands, as well as their complexes, are very complicated and difficult to interpret. No olefinic proton signals were observed, which rules out the possibility of the ligands having an enamine structure.

The PMR spectra of the free ligands indicated that amines I, II, and IV are symmetrically substituted:

TABLE II. Electronic Spectra of the Nickel(II) Complexes (λ_{max}, nm).

Solvent Assignment Complex	0.01 *N* Perchloric Acid				Nitro-methane
	Charge Transfer		*d–π*	*d–d*	*d–d*
	$\lambda_{max}(\epsilon)$	$\lambda_{max}(\epsilon)$	$\lambda_{max}(\epsilon)$	$\lambda_{max}(\epsilon)$	$\lambda_{max}(\epsilon)$
$INi(ClO_4)_2$	218(16100)	–	281(4800)	444(66)	444(70)
$INi(PF_6)_2$	218(15850)	–	282(4300)	450(61)	446(73)
$IINi(ClO_4)_2\alpha$	210(17000)	229sh(12800)	279(5100)	444(93)	446(92)
$IINi(ClO_4)_2\beta$	211(16750)	230sh(11750)	280(4600)	442(83)	446(89)
$IIINi(ClO_4)_2$	213(16500)	231sh(11900)	280(4550)	440(73)	
$IIINi(ClO_4)_2\alpha \cdot \frac{1}{2}C_6H_6$	211(17800)	231sh(12250)	280(4750)	442(68)	444(76)
$IIINi(ClO_4)_2\beta$	216(15600)	226sh(13700)	278(4800)	438(93)	442(72)
$IVNi(ClO_4)_2$	209(16900)	228sh(12600)	278(4950)	448(91)	450(97)
$VNi(ClO_4)_2$	213(19200)	–	278(5850)	431(76)	434(71)
tetraene-$INi(ClO_4)_2$	204(18900)	219sh(14750)	287(6750)	431(74)	423(69)
tetraene-$VINi(ClO_4)_2$	210(16900)	226sh(14800)	290(6400)	431(64)	
tetraene-$VIINi(ClO_4)_2$	211(16650)	226sh(14100)	291(6150)	434(71)	

TABLE III. Proton Magnetic Resonance Data of Free Ligands and Diene- and Tetraene-Nickel(II) Complexes (δ, ppm downfield from internal TMS, 100 MHz).

Compound	Solvent	'Imine' CH_3[a]	$\rangle C\langle^{CH_3}_{H}$[a]	$\rangle C\langle^{CH_3}_{H}$[a,b]	$\rangle N{=}C\langle^{H}$
I	C_6D_6	1.50s(6)	1.08d J = 6.5(6)	3.7	–
II	C_6D_6	1.40s(6)	1.18d J = 6.5(6)	2.9	–
III	C_6D_6	1.55s(3)	1.05d J = 5.7(3)	3.7	–
		1.43s(3)	0.98d J = 7.2(3)		
IV	C_6D_6	1.40s(6)	1.07d J = 6.5(6)	3.1	–
$INi(PF_6)_2$	CD_3NO_2	2.33s(6)	1.22d J = 6.5(6)	4.0(2)	–
$IINi(ClO_4)_2\alpha$	CD_3NO_2	2.30s(6)	1.73d J = 6.0(3)	2.8	–
			1.28d J = 7.0(3)	3.4	
$IINi(ClO_4)_2\beta$	CD_3NO_2	2.21s(6)	1.22d J = 5.5(6)	3.3	–
$IIINi(ClO_4)_2$	CD_3NO_2	2.36s(3)	1.38d J = 7.0(3)	4.0(1)	
		2.23s(3)	1.22d J = 6.0(3)	3.6	
$IIINi(ClO_4)_2\alpha \cdot \frac{1}{2}C_6H_6$	CD_3NO_2	2.32s(3)	1.36d J = 6.0(3)	4.0(1)	
		2.19s(3)	1.25d J = 6.7(3)	3.6	–
$IIINi(ClO_4)_2\beta$	CD_3NO_2	2.25s(3)	1.44d J = 7.0(3)	3.3	–
		2.19s(3)	1.36d J = 7.0(3)	3.9(1)	
$IVNi(ClO_4)_2$	CD_3NO_2	2.19s(6)	1.22d J = 5.5(6)	3.1	–
$VNi(ClO_4)_2$	CD_3NO_2	2.24s(6)	1.47d J = 6.5(6)	3.9(2)	–
tetraene-$INi(ClO_4)_2$[c]	$(CD_3)_2SO$	2.33s(6)	1.48d J = 7.0(6)	5.01(2)	8.21(2)
tetraene-$VINi(ClO_4)_2$	$(CD_3)_2SO$	2.32s(6)	1.54d J = 7.0(6)	4.98(2)	7.91(2)
tetraene-$VIINi(ClO_4)_2$	$(CD_3)_2SO$	2.32s(6)	1.53d J = 7.0(6)	4.96(2)	7.91(2)

[a] Relative intensities in parentheses, J in Hz, s-singlet, d-doublet. [b] Chemical shifts of these protons were established by double resonance experiments. [c] Spectrum taken at elevated temperature +85 °C.

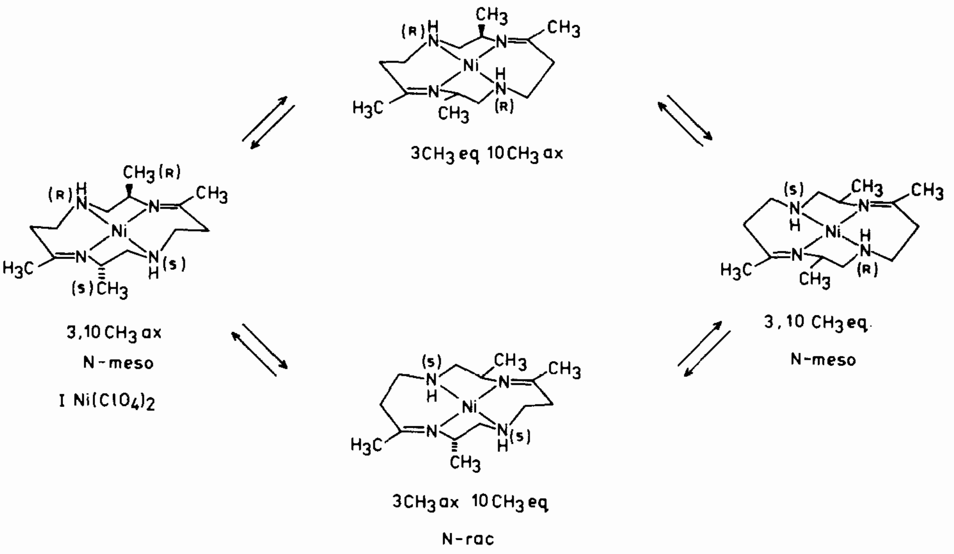


Fig. 1. $INi(ClO_4)_2$.

one singlet signal was observed for both imine methyl groups and one doublet for propylenediamine residue methyl groups. The spectrum of amine III exhibited two methyl singlets and two methyl doublets, indicative of an asymmetric substitution of this amine in agreement with the 2,10-dimethyl structure.

The most prominent PMR signals are those of the methyl substituents. The chemical shifts of the ring protons in the propylene diamine residues coupled to the methyl groups, were determined by double resonance experiments.

Buckingham and Stevens predicted a deshielding effect for the protons located above the plane of low-spin d^8 metal ion system [9]. This deshielding effect has been observed for axially oriented methyl groups and for axial protons in various nickel(II) complexes [1, 10]. We used this effect, symmetry properties, and N-configuration-substituent-conformation diagrams to determine the ligand conformation in the complexes.

$INi(ClO_4)_2$ and $INi(PF_6)_2$

We found that the complex $INi(PF_6)_2$ is substituted in positions 3, 10 and is optically inactive. The PMR spectrum contains one singlet for the two imine methyl groups and one doublet for the 3,10-methyl groups, which indicates the presence of a centre or a two fold axis of symmetry in the molecule. Inspection of Dreiding models shows that the complex derived from the C-*meso* ligand (which has a symmetric PMR spectrum) has to possess a conformation with the *meso* configuration of nitrogen atoms. The remaining structural feature to be established was whether 3,10-methyl substituents were in axial or equatorial positions (Fig. 1).

Equatorial 3,10-methyl groups in $INi(PF_6)_2$ would be sterically very crowded by the 5,12-imine methyl groups. We have therefore assigned the axial conformation to the 3,10-methyl groups and the equatorial conformation to the 3,10-protons. The high field position of the methyl signals could be explained by the fact that these groups exist in the shielding cone of the anisotropic C=N double bond, and that this shielding cancels the deshielding effect of anisotropic nickel(II) ion. The low field position of the signal of the 3,10-equatorial protons is then conveniently explained by their location in the deshielding zone of the C=N double bond. This last assignment is corroborated by the occurrence of 3,10-equatorial protons signal at 4.1 ppm in the PMR spectra of complexes $VINi(ClO_4)_2$ and $VIINi(ClO_4)_2$ of known configurations [3, 11].

The proposed C-*meso*-N-*meso*-3,10-diaxial structure of the complex $INi(ClO_4)_2$ was fully confirmed by an X-ray structure determination [12].

We have found that complexes $INi(ClO_4)_2$ or $(PF_6)_2$ do not isomerise in nitrogen under any conditions – confirming that the equatorial conformation of the 3,10-methyl groups is energetically unlikely and that in consequence the axial methyl groups are nitrogen configuration holding groups in this case.

$IINi(ClO_4)_2\alpha$ and $IINi(ClO_4)_2\beta$

Ligand II is substituted in positions 2 and 9, and possesses the C-*meso* configuration. Four possible structures for its nickel(II) α and β isomeric complexes are shown in the Fig. 2. The chemical environment of substituents on the C-2 and C-9 carbon atoms is very similar to that of substituents on carbon atoms C-7 and C-14. Therefore, it is very likely

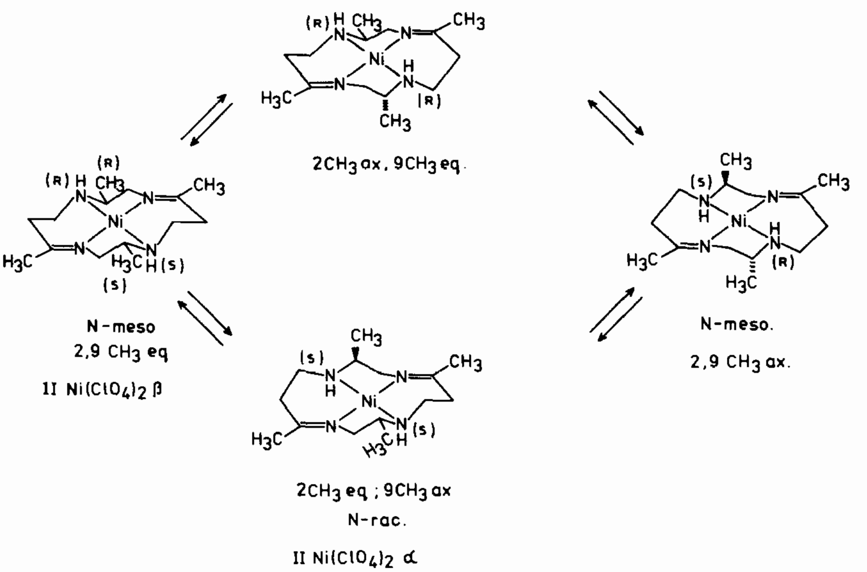


Fig. 2. IINi$(ClO_4)_2\alpha$ and IINi$(ClO_4)_2\beta$.

that the nickel(II) deshielding effect will be predominant and that the chemical shifts of substituents will be in the same range for axial and equatorial groups as for positions 7 and 14 of the nickel(II) coordinated fourteen-membered macrocyclic ring [1]. We found a symmetric spectrum for the IINi$(ClO_4)_2\beta$ complex. One singlet for the imine methyls at 2.21 ppm and one doublet for the 2,9-methyl groups at 1.22 ppm, with coupled protons at 3.3 ppm, were observed. These chemical shifts indicate an equatorial conformation for the 2 and 9-methyl groups and an axial conformation for the protons in these positions. Therefore, we assigned the C-*meso*-N-*meso*-2,9-diequatorial structure to the IINi$(ClO_4)_2\beta$ complex.

The PMR spectrum indicates that the IINi$(ClO_4)_2\alpha$ isomer is an asymmetric one. The 1.73 ppm and 2.8 ppm signals are characteristic for an axial methyl group and an equatorial proton. The second doublet signal at 1.28 ppm coupled with multiplet at 3.4 ppm is characteristic for an equatorial methyl group and an axial proton. Thus, this isomer has C-*meso*-N-*rac*-2-axial-9-equatorial structure.

IVNi$(ClO_4)_2$

Ligand IV has the 2,9-racemic configuration and was obtained also from optically active *R*-(−)-1,2-propylenediamine. The complex IVNi$(ClO_4)_2$ has a symmetric PMR spectrum with a doublet from the equatorial 2- and 9-methyl groups at 1.22 ppm, coupled with the multiplet from the axial protons at 3.1 ppm. The C-*rac*-N-*rac*-2,9-diequatorial structure proposed for the complex IVNi$(ClO_4)_2$ is shown in Fig. 3.

IIINi$(ClO_4)_2\alpha$ and IIINi$(ClO_4)_2\beta$

We have isolated only one 2,10-substituted ligand III, spectroscopically identical with the enantiomer obtained from optically active *R*-(−)-1,2-propylenediamine. This allows us to limit our considerations to the structures with the same configuration at C-2 and C-10 carbon atoms (Fig. 4), and to exclude the 2 *R*, 10 *S*- and 2 *S*, 10 *R*-structures.

The PMR spectrum of isomer IIINi$(ClO_4)_2\alpha$ contains two doublets at 1.25 ppm and 1.36 ppm. The latter is coupled to the proton at 4.0 ppm. These chemical shifts indicate an axial 10-methyl group.

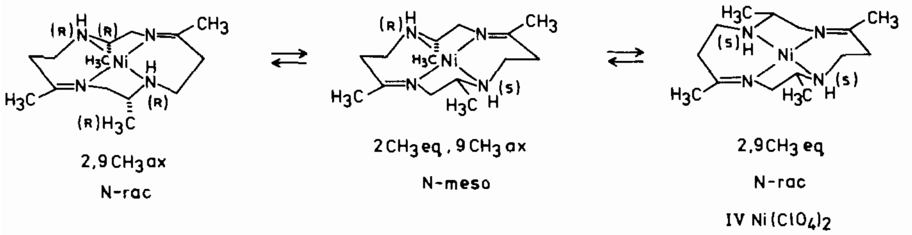


Fig. 3. IVNi$(ClO_4)_2$.

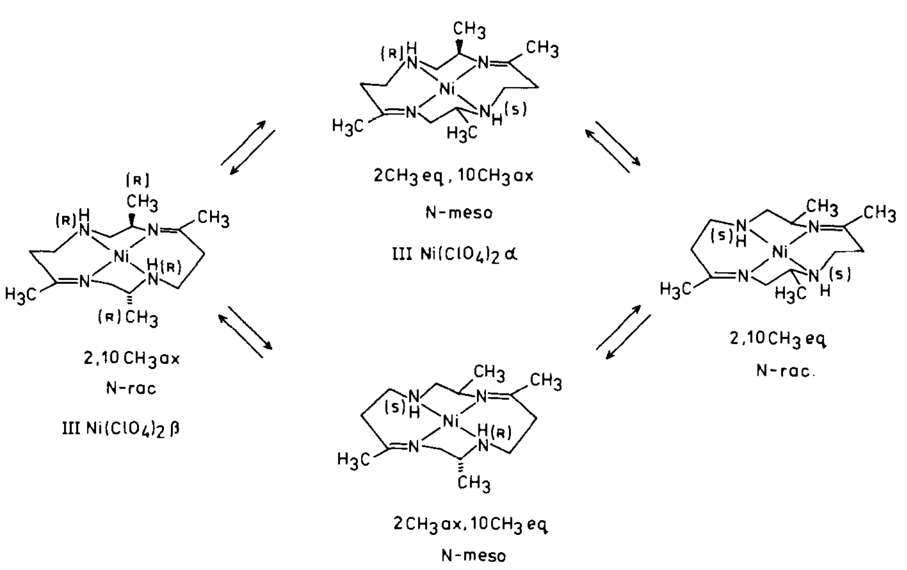


Fig. 4. IIINi(ClO$_4$)$_2$α and IIINi(ClO$_4$)$_2$β.

The doublet at 1.25 ppm, coupled to the proton at 3.6 ppm, indicates an equatorial methyl group in position 2. Isomerisation of IIINi(ClO$_4$)$_2$α into IIINi(ClO$_4$)$_2$β occurs on nitrogen atom 1 and inverts an equatorial methyl group into an axial one. The nitrogen atom in position 8 does not invert, as this is prevented by the configuration holding methyl group in position 10. This inversion is clearly seen from chemical shifts: the 2-methyl group is deshielded (1.44 ppm) and the proton in position 2 is shielded (3.3 ppm) after isomerisation. Thus, complex IIINi(ClO$_4$)$_2$α has C-*rac*-N-*meso*-2-equatorial-10-axial structure and IIINi(ClO$_4$)$_2$β C-*rac*-N-*rac*-2,10-diaxial structure.

VNi(ClO$_4$)$_2$

Ligand V has a racemic configuration and its nickel(II) complex has a symmetric PMR spectrum, very similar to that of INi(ClO$_4$)$_2$. The chemical shifts of methyl groups (1.47 ppm) and coupled protons (3.9 ppm) indicate an axial position for the 3 and 10-methyl substituents. The symmetric spectrum of the optically active complex indicates the presence of a two-fold axis of symmetry in the molecule, and this can only be achieved if the ligand possesses the racemic configuration at the chiral nitrogen atoms as in Fig. 5.

The C-*rac*-N-*rac*-3,10-diaxial conformation proposed for the complex VNi(ClO$_4$)$_2$ is identical with the conformation established for 'yellow' 1 *S*, 3 *R*, 8 *S*, 10 *R*-3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-dienenickel(II) perchlorate [VIINi(ClO$_4$)$_2$ obtained from *R*-(−)-1,2-propylenediamine]. Its circular dichroism spectrum [13] and that of 1 *R*, 3 *R*, 8 *R*, 10 *R*-VNi(ClO$_4$)$_2$ (Fig. 6) are nearly identical, which again proves the structure.

The configurations and conformations of all isomeric diene-complexes are given in Table IV.

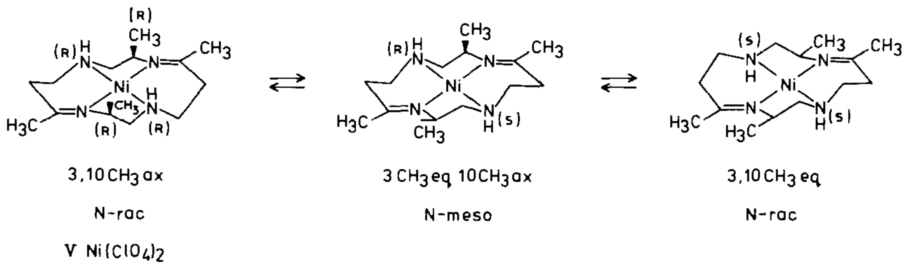


Fig. 5. VNi(ClO$_4$)$_2$.

TABLE IV. Relative and Absolute C- and N-Configurations and Conformations of Methyl Groups in Complexes I–VNi(ClO_4)$_2$.

Complex	Configurations						Conformations of Methyl Groups			
	2C	3C	9C	10C	1N	8N	2C	3C	9C	10C
INi(ClO_4)$_2$^{a}	–	S,R	–	R,S	S,R	R,S	–	ax	–	ax
INi(PF_6)$_2$										
IINi(ClO_4)$_2$α^a	S,R	–	R,S	–	S,R	S,R	eq	–	ax	–
IINi(ClO_4)$_2$β^a	S,R	–	R,S	–	S,R	R,S	eq	–	eq	–
IIINi(ClO_4)$_2$α^a	R,S	–	–	R,S	S,R	R,S	eq	–	–	ax
IIINi(ClO_4)$_2$α^b	R	–	–	R	S	R	eq	–	–	ax
IIINi(ClO_4)$_2$β^a	R,S	–	–	R,S	R,S	R,S	ax	–	–	ax
IVNi(ClO_4)$_2$^{a}	R,S	–	R,S	–	S,R	S,R	eq	–	eq	–
IVNi(ClO_4)$_2$^{b}	R	–	R	–	S	S	eq	–	eq	–
VNi(ClO_4)$_2$^{b}	–	R	–	R	R	R	–	ax	–	ax

^{a}Relative configuration. ^{b}Absolute configuration.

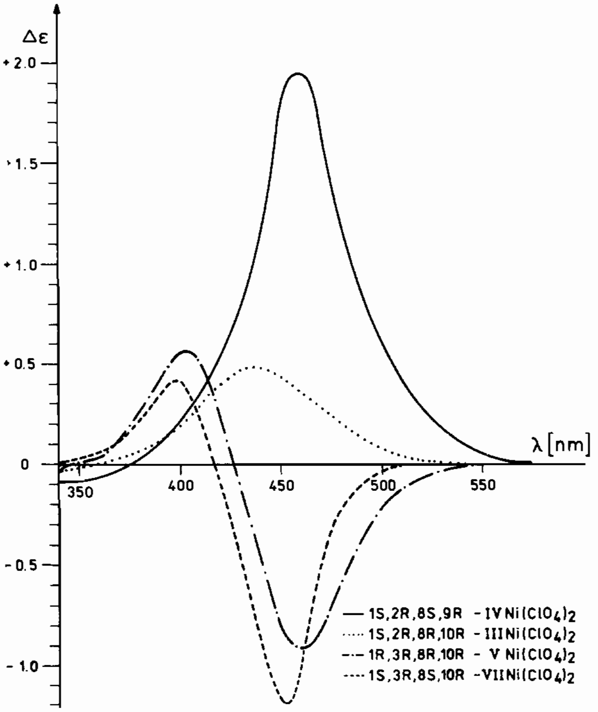


Fig. 6. C.D. curves for complexes in 0.01 *N* $HClO_4$.

Experimental*

Starting Materials

R,S-1,2-propylenediamine, 72% perchloric acid, nickel(II) perchlorate, nickel(II) acetate, potassium cyanide, ammonium hexafluorophosphate, 2,2-dimethoxypropane and solvents were commercial grade materials and were used without further purification. Commercial methyl vinyl ketone was distilled before use. *R*-(–)-1,2-propylenediamine ($[\alpha]_D^{20}$ = –34.5°) was obtained by resolving the commercial racemate according to known procedure [14].

meso- and *racemic*-3,5,7,7,10,12,14,14-Octamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene-nickel(II) perchlorates [VINi(ClO_4)$_2$ and VIINi(ClO_4)$_2$] were obtained according to known procedure [2, 3, 11].

Tetramethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene dihydrogen perchlorates

A. Mixture of Isomers I–IV($HClO_4$)$_2$

Perchloric acid (72%, 1 mol) was added dropwise to a cooled (0 °C) 10% ethanolic solution of anhydrous *R,S*-1,2-propylenediamine (1 mol). The solution was evaporated to dryness under reduced pressure, the residue was dissolved in 500 ml of anhydrous ethanol, and after addition of 300 ml of dry benzene was again evaporated to dryness.

The anhydrous 1,2-propylenediamine monohydrogen perchlorate was then dissolved in 600 ml of dry ethanol and methyl vinyl ketone (1 mol) was added at 15–20 °C with stirring until precipitation of product had started. After 4 hours the reaction mixture was cooled and left overnight in a refrigerator to complete crystallisation. The solid product was filtered, washed with ethanol and ether, and dried over P_4O_{10} *in vacuo* at room temperature. Yield 50–52%.

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*CAUTION! Amine perchlorates and complex perchlorates described in this paper are explosive.

TABLE V. Elemental Analyses of Tetramethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene Dihydrogen Perchlorates [I–IV-$(HClO_4)_2$].

Compound	M.p.[a] °C	Required, %			Found, %		
		C	H	N	C	H	N
$I(HClO_4)_2$	163	37.1	6.7	12.3	36.9	6.6	12.2
$II(HClO_4)_2$	153				36.9	6.7	12.1
$III(HClO_4)_2$	149				36.9	6.7	12.1
$IV(HClO_4)_2$	137				36.6	7.0	12.4

[a] Melting points are uncorrected. All compounds decomposed on melting.

B. Optically Active III–V$(HClO_4)_2$

Anhydrous R-(–)-1,2-propylenediamine monohydrogen perchlorate (1 mol), prepared by the same method as the racemate in A, was dissolved in dry ethanol (400 ml). Freshly distilled methyl vinyl ketone (1 mol) was added dropwise to the stirred solution at –10 °C. The temperature of the reaction mixture was kept at about –10 °C for 24 hours. The colourless crystalline product was collected by filtration and washed with ethanol and ether. A second crop of product was collected from the mother liquors 24 hours later. Yield 9%.

C. Individual Salts I–IV$(HClO_4)_2$ from Free Bases I–IV

Perchloric acid (72%, 0.04 mol) was added dropwise to a cooled (0 °C) solution of free macrocyclic amine (I–IV, 0.02 mol) in anhydrous methanol (30 ml). Precipitating salt was filtered off, washed with methanol and dried over P_4O_{10} *in vacuo* at room temperature. Yield 95%.

Elemental analyses for all perchlorates are given in Table V.

Tetramethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-dienenickel(II) diperchlorates [I–IVNi$(ClO_4)_2$]

A mixture of ligand dihydrogen perchlorates [I–IV$(HClO_4)_2$, 0.5 mol] was added slowly (1.5 hr) to a boiling solution of nickel(II) acetate tetrahydrate (0.5 mol) in anhydrous methanol (1000 ml) and refluxed for 3 hours. The reaction mixture was cooled and the solid complex was filtered off. The first crop of crystalline product contained mainly isomers $INi(ClO_4)_2$ and $IIINi(ClO_4)_2$ which were separated by fractional crystallisation from water (70 ml of water for 1 g of complex). Orange needles of complex $INi(ClO_4)_2$ crystallised first from the solution and the bright yellow isomer $IIINi(ClO_4)_2$ was obtained from the concentrated aqueous filtrates.

Yellow-olive needles of complex $IINi(ClO_4)_2 \cdot 2/3H_2O$ were collected from the methanol filtrate after slow evaporation of the solvent. After separation of isomer $IINi(ClO_4)_2 \cdot 2/3H_2O$ and evaporation of the remaining solvent, the tarry residues were dissolved in nitromethane, filtered, and the fourth isomeric complex $IVNi(ClO_4)_2$ was precipitated with benzene.

The isolated crude complexes $INi(ClO_4)_2$, $IINi(ClO_4)_2 \cdot 2/3H_2O$ and $IIINi(ClO_4)_2$ were recrystallised from water, and isomer $IVNi(ClO_4)_2$ was crystallised from ethanol. The complexes were dried over P_4O_{10} *in vacuo* at room temperature.

The overall yield was 80–90% and complexes $INi(ClO_4)_2$, $IINi(ClO_4)_2 \cdot 2/3H_2O$, $IIINi(ClO_4)_2$ and $IVNi(ClO_4)_2$ were isolated in ratios of 7:5:5:1 respectively.

INi$(PF_6)_2$

Complex $INi(ClO_4)_2$ (1 g) dissolved in water (80 ml) was absorbed on a column filled with Amberlite CG-50 ion exchange resin (Na^+ form) and washed out with 5% aqueous ammonium hexafluorophosphate solution. The solution was concentrated to give orange crystals of $INi(PF_6)_2$ complex which were recrystallised from water and dried *in vacuo* over P_4O_{10}. Yield 60%.

Separation of the labile forms of complexes

A. IINi$(ClO_4)_2\alpha$ and IINi$(ClO_4)_2\beta$

Anhydrous benzene was slowly added to a boiling solution of $IINi(ClO_4)_2 \cdot 2/3H_2O$ (10 g) in nitromethane (50 ml). When precipitation had started a few drops of nitromethane were added to dissolve the precipitate, and the solution was left to crystallise at room temperature. The first crop of crystals contained mainly the $IINi(ClO_4)_2\alpha \cdot 2C_6H_6$ isomer (*ca.* 7 g) which was purified by the crystallisation from nitromethane–benzene. The second isomer ($IINi(ClO_4)_2\beta \cdot 2C_6H_6$) was obtained from the concentrated filtrate (*ca.* 1 g) and was recrystallised from nitromethane–benzene. To obtain $IINi(ClO_4)_2\alpha$ and $IINi(ClO_4)_2\beta$ free of solvent, the isolated crystals were dried under reduced pressure at 140 °C for 24 hours.

TABLE VI. Elemental Analyses of Nickel(II) Complexes.

Compound	Required, %				Found, %				$[\alpha]_D^{20}$ [a]
	C	H	N	Ni	C	H	N	Ni	
$INi(ClO_4)_2$	32.9	5.5	11.0	11.5	32.8	5.4	11.0	11.2	
$INi(PF_6)_2$	28.0	4.7	9.3	9.8	27.7	4.6	9.3	10.4	
$IINi(ClO_4)_2 \cdot 2/3H_2O$	32.2	5.7	10.7	11.2	32.0	5.8	10.4	10.9	
$IINi(ClO_4)_2\alpha$	32.9	5.5	11.0	11.5	32.7	5.6	10.7	11.5	
$IINi(ClO_4)_2\beta$	32.9	5.5	11.0	11.5	32.7	5.5	10.8	11.4	
$IIINi(ClO_4)_2$	32.9	5.5	11.0	11.5	32.6	5.6	10.9	11.7	
$IIINi(ClO_4)_2\alpha \cdot ½C_6H_6$	37.2	5.7	10.2	10.7	36.4	5.7	10.2	10.8	
1*S*, 2*R*, 8*R*, 10*R*-$IIINi(ClO_4)_2\alpha$	32.9	5.5	11.0	11.5	32.6	5.5	10.9	–	+35.4
$IIINi(ClO_4)_2\beta$	32.9	5.5	11.0	11.5	32.8	5.4	10.9	11.5	
$IVNi(ClO_4)_2$	32.9	5.5	11.0	11.5	32.8	5.6	10.8	11.5	
1*S*, 2*R*, 8*S*, 9*R*-$IVNi(ClO_4)_2$	32.9	5.5	11.0	11.5	32.9	5.5	10.7	–	+125.8
1*R*, 3*R*, 8*R*, 10*R*-$VNi(ClO_4)_2$	32.9	5.5	11.0	11.5	33.0	5.6	10.7	–	–72.4
tetraene-$INi(ClO_4)_2$	33.2	4.8	11.1	11.6	33.0	4.9	11.0	11.8	
tetraene-$VINi(ClO_4)_2$	38.5	5.7	10.0	10.4	38.7	6.0	10.0	–	
tetraene-$VIINi(ClO_4)_2$	38.5	5.7	10.0	10.4	38.2	5.9	10.0	10.6	

[a] $[\alpha]_D^{20} = \alpha_{589} \times l^{-1} \times c^{-1} \times M \times 100^{-2}$ (1 in dcm), measured in 0.01 *N* $HClO_4$.

B. $IIINi(ClO_4)_2\alpha \cdot ½C_6H_6$ *and* $IIINi(ClO_4)_2\beta$

A solution of complex $IIINi(ClO_4)_2$ (20 g) in basic water (pH = 9, 500 ml) was refluxed for 1 hour. The solution was acidified with perchloric acid and evaporated to dryness. The residue was fractionally crystallised from nitromethane–benzene. The less soluble isomer $IIINi(ClO_4)_2\alpha \cdot ½C_6H_6$ (*ca.* 10 g) crystallised first. Isomer $IIINi(ClO_4)_2\beta \cdot ½C_6H_6$ (*ca.* 5 g) was isolated from the filtrates. After 24 hours drying under reduced pressure at 140 °C the solvent was removed and the pure isomer $IIINi(ClO_4)_2\beta$ was obtained. Benzene could not be removed from the crystals of isomer $IIINi(ClO_4)_2\alpha \cdot ½C_6H_6$ under these conditions.

Optically active tetramethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-dienenickel(II) diperchlorates III-VNi-(ClO₄)₂

A mixture of optically active perchlorates (III–V $(HClO_4)_2$, 0.1 mol) was slowly added to a boiling solution of nickel(II) acetate tetrahydrate (0.1 mol) in methanol (500 ml) containing 2,2-dimethoxypropane (15 ml). The mixture was refluxed for 1 hour and left at room temperature for crystallisation. After 24 hours the red crystalline precipitate, containing mainly the optically active isomer III-$Ni(ClO_4)_2\alpha$, was filtered off. The filtrate was evaporated to dryness, dissolved in nitromethane and after filtration, the next crop of product was precipitated with benzene. This material was fractionally crystallised from water [to separate isomer 1 *S*, 2 *R*, 8 *R*, 10 *R*-$IIINi(ClO_4)_2\alpha$], methanol [isomer 1 *S*, 2 *R*, 8 *S*, 9 *R*-$IVNi(ClO_4)_2$] and from nitromethane-benzene solution [isomer 1 *R*, 3 *R*, 8 *R*, 10 *R*-$VNi(ClO_4)_2$]. The optically active products were isolated in the ratio 94:5:1 respectively.

Elemental analyses for all complexes are given in Table VI.

Tetramethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-dienes I–IV

Tetramethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene-nickel(II) diperchlorate [I–$IVNi(ClO_4)_2$, 0.02 mol] was slurried in anhydrous methanol (200 ml) containing potassium cyanide (0.08 mol). For ligand II, 2,2-dimethoxypropane (5 ml) was added in order to remove water from the complex IINi-$(ClO_4)_2 \cdot 2/3H_2O$.

After 4 hours the reaction mixture was filtered, methanol was evaporated under reduced pressure, and the residue was extracted with dry benzene. The benzene solution was filtered through a 10 cm layer of neutral alumina and evaporated to dryness under reduced pressure. Solid amines I and II were recrystallised from hexane and liquid products III and IV were analysed and used without further purification. The yields, melting points and elemental anlyses are given in Table VII.

3,5,10,12-Tetramethyl-1,4,8,11-tetra-azacyclotetradeca-1,4,8,11-tetraenenickel(II) diperchlorate [tetraene-INi(ClO₄)₂]

The starting complex $INi(ClO_4)_2$ (0.005 mol) was dissolved in 60 ml of boiling 10% nitric acid. The

TABLE VII. Elemental Analysis of Tetramethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-dienes (I–IV).

Compound	Yield	M.p.[a]	Required, %			Found, %		
	%	°C	C	H	N	C	H	N
I	80	116.5	66.5	11.2	22.2	66.2	11.1	22.1
II	80	78				66.1	11.1	22.3
III	80	–				66.4	11.3	22.1
IV	60	–				67.0	11.1	22.3

[a] Melting points are uncorrected.

reaction mixture was refluxed for 10 minutes and cooled to room temperature. The solution was diluted with 100 ml of ethanol and allowed to crystallise. The resulting solid was filtered, washed with ethanol, recrystallised from water and dried *in vacuo* over P_4O_{10}. Yield 10%. Elemental analyses of the product are given in Table VI.

meso- *and* racemic-*3,5,7,7,10,12,14,14-Octamethyl-1,4,8,11-tetraazacyclotetradeca-1,4,8,11-tetraenenickel(II) diperchlorates [tetraene-VINi(ClO_4)$_2$ and tetraene-VIINi(ClO_4)$_2$]* were obtained by the method described above, by refluxing the reaction mixture for 2 hours. Yield 90%. Elemental analyses of the products are also included in Table VI.

Physical Measurements

Infrared spectra were recorded on a Unicam SP-200 spectrometer. Electronic spectra were obtained on a Unicam SP-500 spectrometer. CD spectra were recorded on a JASCO UV/ORD-5 spectrometer. PMR spectra were obtained on JEOL INM 4H-100 spectrometer with TMS as internal standard. Optical rotations were determined on a Perkin-Elmer 141 polarimeter in a 10 cm cell.

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