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Macrocyclic Ligands and Their Metal Ion Complexes. Part VI.* Preparation, Stereochemistry and Conformational Analysis of Polyalkyl-1,4,8,11-tetra-azacyclotetradeca-4,11-dienenickel(II) Diperchlorates**

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α,β-Unsaturated ketones react with ethylenediamine monohydrogenperchlorate to form dihydrogenperchlorates of polyalkyl-1,4,8,11-tetra-azacyclotetradeca-4,11-dienes (L). These Schiff's base amines react with nickel(II) acetate to form square-planar complexes NiL(ClO_4)$_2$. The C- and N-diastereoisomeric complexes were separated and ligand configuration and conformation were assigned on the basis of chemical and spectroscopical, mainly p.m.r. evidence. Partial resolution of some complexes was achieved by chromatography on starch.

Introduction

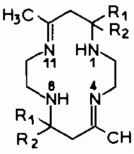
The chemistry of metal ion complexes of synthetic macrocyclic ligands has attracted recently a great interest, because of their fascinating stereochemistry and properties and because of their relation to the natural complexes of macrocyclic ligands. One of the most thoroughly investigated compound is 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-dienenickel(II) diperchlorate, first described by Curtis[1,2]. Curtis has succeeded in separating this compound into two interconvertible forms[3]. It was shown[4–7] that the isomerism is caused by the presence of two chiral centres on nitrogen atoms of the secondary amine groups, and that the isomers possess the N-meso- and N-racemic configurations.

This paper reports on synthetic and stereochemical investigations of more complicated systems, *viz.* 5,12-dimethyl-7,14-dialkyl-1,4,8,11-tetra-azacyclotetradeca-4,11-dienenickel(II) complexes. They contain two more chiral centres on ring carbon atoms 7 and 14 in addition to those present on the amine nitrogen atoms.

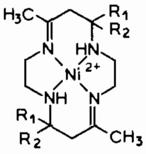
Results and Discussion

Synthesis

The macrocyclic ligand perchlorates (I–V) were prepared by condensation of α,β-unsaturated ketones with ethylenediamine monohydrogen perchlorate[8,9]. The complexes VI–X were obtained by the reactions of Schiff's base amines dihydrogen perchlorates I–V with nickel(II) acetate. Again, complexes VI–X were obtained in the reactions of free ligands with anhydrous nickel(II) perchlorate[10].


2HClO$_4$

-[14]-4,11-diene N$_4$


2ClO$_4^-$

-Ni[14]-4,11-diene N$_4$

I	$R_1=R_2=H$	5,12-Me$_2$-	VI
II	$R_1=H$; $R_2=CH_3$	5,7,12,14-Me$_4$-	VII
III	$R_1=H$; $R_2=C_2H_5$	5,12-Me$_2$-7,14-Et$_2$-	VIII
IV	$R_1=H$; $R_2=i\text{-}C_3H_7$	5,12-Me$_2$-7,14-i-Pr$_2$-	IX
V	$R_1=R_2=CH_3$	5,7,7,12,14,14-Me$_6$-	X

We were successful in separating several complexes in isomeric forms. With complex VII, two stable isomers, designated VIIA and VIIB, were isolated from neutral solutions. The isomers cannot be interconverted and two different amine ligands were obtained in the reactions of the complexes with potassium cyanide[10]. Hence, their isomerism is connected with the chiral carbon atoms in positions 7 and 14 of the ring, and the isomeric ligands and complexes are the C-meso and C-racemic modifications.

Complexes VI, VIIA, VIIB, and VIII were separated as labile interconvertible isomers (designated as the α-, β-, and γ-forms) by crystallisation from acidified methanolic solutions. We were unable to separate isomers of complex IX. The α-forms are the most stable

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* For Part V see ref. 19.

** Presented in part to the XIII[th] I.C.C.C., Cracow, Zakopane, Poland, 1970. Proceedings of the XIII[th] I.C.C.C., vol, I, p. 320.

and the only ones crystallising from neutral or alkaline solutions. Easy isomerisation of the α-, β-, and γ-forms indicates that the isomerism is connected with the chiral nitrogen atoms of complexed secondary amino groups of the ligands. Hence, these compounds are the N-meso and N-racemic modifications like Curtis' complexes Xα and Xβ[4–7].

The structures of the ligands I–IV and of the isomeric complexes VI–IX were established in terms of elemental analyses, reactions, and spectral evidence. Curtis' ligand V and complexes Xα and Xβ were also investigated as reference compounds.

Infrared Spectra

The characteristic infrared absorption bands are given in Table I.

TABLE I. Characteristic Infrared Absorption Bands of the Complexes (Nujol mulls, cm^{-1}).

Compound	ν_{N-H}	$\nu_{C=N}$	$\nu_{ClO_4^-}$
VIα	3210	1647	1093
VIβ	3213	1648	1103
VIIAα	3193	1668 1653	1101
VIIAβ	3203	1656	1093
VIIBα	3175	1653	1102
VIIBβ	3200	1655	1090
VIIIα	3206	1651	1104
VIIIβ	3194	1668 1654	1102
IX	3203	1658	1099
Xα	3170	1662	1090
Xβ	3177	1654	1100

The medium intensity absorption bands at *ca.* 3200 cm^{-1} and 1655 cm^{-1} are assigned to N–H and C=N stretching vibrations, respectively. The band at 3200 cm^{-1} is shifted to *ca.* 2350 cm^{-1} in the spectra of deuterated compounds, what strongly supports the assignement. A very strong band occurring at *ca.* 1100 cm^{-1} is characteristic of a noncoordinated perchlorate anion.

The fingerprint region of the spectra is of great value for identification of some isomers. The spectra of complexes VIα and VIβ are reproduced as examples in the Experimental.

Ultraviolet and Visible Spectra

The results of measurements of electronic spectra are given in Table II.

All complexes exhibit an absorption band of low intensity in the region 439–454 nm characteristic of nickel(II) square-planar complexes [nickel(II) $d \rightarrow d$ transition][4, 11]. The square-planar configuration of the complexes was confirmed by magnetic susceptibility measurements. All the complexes are diamagnetic in the solid state and in nitromethane solutions.

The ultraviolet absorption bands at 208–216 nm and 227–234 nm are assigned to the charge transfer transitions and the 280–290 nm band, in conflict with Curtis'[4] and our[9] assignments, is presumably attributable to the "metal to ligand" (d–π^*) charge transfer transition[11].

Proton Magnetic Resonance Spectra

P.m.r. spectra of the complexes were taken in nitromethane-d$_3$ solutions. Nitromethane has several advantages as solvent: first, it is a good or fairly good solvent for this class of compounds; secondly, there is

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

Sovent:	Methanol				Nitromethane
Assignment:	Charge transfer			$d \rightarrow d$	$d \rightarrow d$
Complex	$\lambda_{max}(\varepsilon)$	$\lambda_{max}(\varepsilon)$	$\lambda_{max}(\varepsilon)$	$\lambda_{max}(\varepsilon)$	$\lambda_{max}(\varepsilon)$
VIα	208 (18150)	227sh (12450)	290 (4650)	448 (82)	448 (87)
VIβ	209 (16180)	227sh (11840)	283 (4670)	448 (80)	447 (81)
VIIAα	215 (13340)	231sh (10850)	282 (4300)	442 (95)	446 (90)
VIIAβ	216 (12500)	231sh (11280)	282 (4300)	444 (85)	450 (87)
VIIBα	213 (13500)	230sh (10850)	282 (4040)	450 (81)	440 (85)
VIIBβ	208 (15100) 214sh[a] (14160)	232sh (11180)	281 (4235) 285 (4275)	452 (81)	454 (96)
VIIIα	213 (14600)	234sh (11770)	283 (4850)	444 (90)	452 (95)
VIIIβ	213 (14700)	234sh (11360)	283 (4600)	444 (90)	446 (94)
IX	214 (13800)	232sh (10900)	280 (4440)	446 (92)	451 (97)
Xα	215 (16000)	230sh (12000)	282 (5000)	442 (101)	
Xβ	216 (17000)	232sh (13000)	282 (5000)	439 (93)	

[a] sh = shoulder.

practically no coordination of the solvent to the complex cations, all the complexes remaining diamagnetic in the solution; thirdly, the labile forms practically do not isomerise in nitromethane solutions (no other isomers were detected after 24 hr at room temperature, except for complex VIIBβ which isomerised to some extent).

The signals of ring protons of complexes VI–X are complicated and will not be interpreted. No olefinic proton signals were observed, which rules out the enamine structure of the ligands as a possibility. The most prominent features in the spectra of compounds VI–X are the intense resonances of protons of alkyl substituents of the ligands, which appear in the high-field portion of the spectra. The chemical shifts of these protons are collected in Table III.

The singlet signals at 2.2 p.p.m. are assigned to the "imine" methyl groups in positions 5 and 12 of the ring because of their low-field position caused by deshielding of the methyls by double bond, and because of their singlet structure. There are no protons on adjacent carbon atom, which could split this signal as a result of spin–spin coupling. The allylic position of protons of these methyl groups in relation to the imine double bond and the electron-withdrawing effect of the metal ion causes them to be acidic and to exchange for deuterium in basic D_2O[7]. The deuteration experiments on complexes VI–IX fully corroborated this assignment; the signals at 2.2 p.p.m. disappeared in deuterated compounds.

The overlapping of the signals of both "imine" methyls of the molecule and a relative intensity of this signal reminiscent of six protons indicate that both methyls have the same chemical shift, *i.e.* both possess the same chemical environment. This indicates that both six-membered rings of the complex possess the same conformation.

The doublet resonances in the spectra of complexes VII (Fig. 1, Table III) at 1.73–1.80 p.p.m. and at 1.15–1.37 p.p.m. are assigned to 7- and 14-methyl groups, since their signals ought to be split by coupling to a proton on adjacent 7- and 14-ring carbon atoms. Since the resonances occur at two distinct fields and the conformation of both six-membered rings is identical, the different chemical shifts of these groups have to result from their different chemical environments. It seems most reasonable to explain this by the known fact that one chemical shift is characteristic to a (pseudo-) axial (perpendicular to the plain of the molecule) conformation of the methyl group and the other to a (pseudo-) equatorial (parallel to the plain of the molecule) conformation of the methyl group. Buckingham and Stevens[12] have predicted a large deshielding effect for protons situated above the plane of square-planar platinum(II) complexes. In so far as d^8 systems resemble each other, a similar situation should be expected for analogous nickel(II) complexes. The extent of deshielding observed should be a function of the radial and angular orientation of the axial methyl groups with respect to the NiN_4 plane and the per-

TABLE III. Proton Magnetic Resonance Data for the Complexes (CD_3NO_2 solutions, δ, p.p.m. downfields from internal TMS, 100 MHz).

Complex	R	"Imine" CH_3[a]	R-axial[a]	C-7-H, C-14-H equatorial	R-equatorial[a]	C-7-H, C-14-H axial
VIα	H	2.22s (6)	–	–	–	–
VIβ	H	2.22s (6)	–	–	–	–
VIIAα	CH_3	2.20s (6)	1.73d J=6.5 (3)[c]	2.63[c]	1.25d J=6 (3)[d]	3.29[d]
VIIAβ	CH_3	2.20s (6)	–	–	1.21d J=6 (6)[c]	3.29[c]
VIIBα	CH_3	2.18s (6)	1.87d J=6.5 (6)[c]	2.67[c]	–	–
VIIBβ	CH_3	2.21s (6)	–	–	1.15d J=6 (6)[c]	3.30[c]
VIIBγ[b]	CH_3	2.27s (6)	1.80d J=6.5 (3)	–	1.37d J=7 (3)	
VIIIα	C_2H_5	2.19s (6)	–	–	1.63m (4)[c,d] 0.86t J=7 (6)[c]	3.3[d]
VIIIβ	C_2H_5	2.21s (6)	2.37m (2)[c,d] 1.00t J=7 (3)[c]	2.6[d]	1.66m (2)[e,f] 0.89t J=7 (3)[e] 2.26m (2)[c,d,e]	3.3[f]
IX	i-C_3H_7	2.22s (6)	–	–	1.05d J=7 (6)[c] 0.81d J=7 (6)[d]	3.32[e]
Xα	$\left\{\begin{matrix} CH_3 \\ CH_3 \end{matrix}\right.$	2.17s (6)	2.08s (6)	–	1.30s (6)	–
Xβ	$\left\{\begin{matrix} CH_3 \\ CH_3 \end{matrix}\right.$	2.22s (6)	1.73s (6)	–	1.28s (6)	–

[a] Relative signal intensities in parentheses; J in Hz; s singlet, d doublet, t triplet, m multiplet.

[b] Not isolated as a pure substance. Present in a mixture with compound VIIBβ.

[c, d, e] Coupling of nuclei denoted by the same superscript was demonstrated by double resonance experiments.

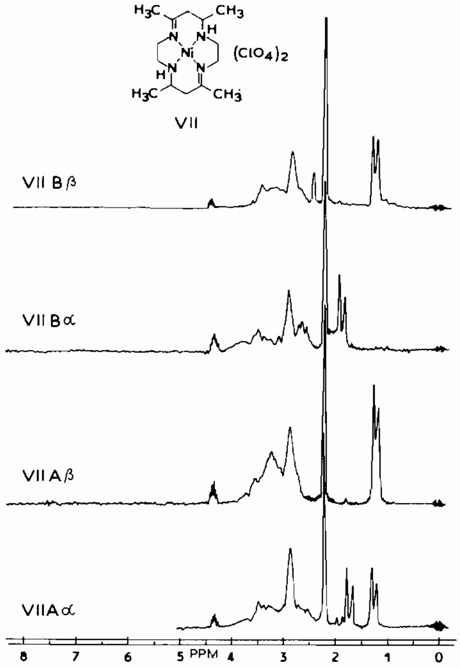


Figure 1. P.m.r. spectra of isomeric complexes VII in nitromethane-d_3 solutions.

pendicular axis through the metal ion centre. The obvious alternative explanation that protons of axial methyl groups are deshielded due to the anisotropy of the imine double bonds is excluded by the observation that axial methyl groups in saturated tetra-azacyclotetradecane complexes give signals at lower fields than do equatorial groups[13,14]. Based on this theoretical prediction and on Busch assignments on complex X[7] the low-field signals are ascribed to the axial and the high-field signals to the equatorial 7- and 14-methyl groups.

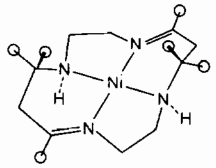
To confirm these assignments the chemical shifts of protons situated on ring carbon atoms 7- and 14- were determined by double resonance experiments on complexes deuterated in the allylic positions, *i.e.* on the "imine" methyls and on the 6- and 13- ring carbon atoms. The results are also collected in Table III. For protons coupled to the methyl groups assigned as axial, resonances were observed at higher field (2.6 p.p.m.) than those for protons adjacent to the equatorial methyl groups, in full agreement with the theoretical prediction that axial proton resonances will occur at lower field than do equatorial ones. The very narrow range of chemical shifts of these protons make them a valuable tool for the determination of conformation of substituents in the 7- and 14- positions of the ring.

Methyl groups of ethyl and isopropyl substituents in complexes VIII and IX are situated far away from the central nickel(II) ion. Therefore, the anisotropy of nickel(II) ion does not affect much their chemical shifts and assignments are difficult to make. Interpretation of spectra of complexes VIIIα and VIIIβ is based on the chemical shifts of the diastereotopic methylene groups of the ethyl substituents and on the chemical shifts of the protons coupled with them on ring carbon atoms 7 and 14. The signal at 2.37 p.p.m. is ascribed to the methylene group of an axial ethyl and the signals at 1.63 and 1.67 p.p.m. are ascribed to the equatorial ethyls.

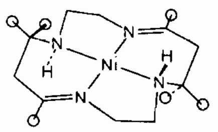
With complex IX only one chemical shift was found for protons on C-7 and C-14 (3.32 p.p.m.) indicative of the axial conformations of these protons and equatorial conformations of both isopropyl groups. Appearance of two doublet signals for methyls of two equivalent isopropyl groups should be explained by their anisochronism resulting from the neighbourhood of the asymmetric carbon atoms C-7 and C-14.

Stereochemical Considerations

An important stereochemical feature of 1,4,8,11-tetra-azacyclotetradeca-4,11-diene metal ion complexes of the square-planar configuration is the chirality of the nitrogen atoms (1-N and 8-N) of the complexed secondary amino groups, which renders N-meso and N-racemic modifications possible. The relative configuration of these nitrogen atoms determines the ring conformation of the macrocyclic ligands in their complexes. In a complex of N-racemic configuration the ligand exists in two enantiomeric ring conformations (Xα, one enantiomer shown). In the N-meso complex the idealised conformation of the macrocyclic ring is centrosymmetric, with the centre of inversion on the metal ion (Xβ). As mentioned above, the first example of such an isomerism was discovered by Curtis[3] and by Busch[6,7], who also have established the structures shown.



Xα N-rac



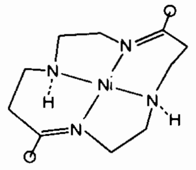
Xβ N-meso

Hereinafter the prefixes N-rac and N-meso will be regarded as synonymous with the enantiomeric and centrosymmetric ring conformations. In both conformations of the macrocycle the six-and the five-membered chelate rings are pairwise identical.

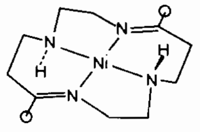
The inversion of configuration of one asymmetric nitrogen atom causes partial conversion of the macrocyclic ring conformation, for instance, from the enantiomeric to the centrosymmetric or *vice versa*. Obviously, the consecutive inversion of both asymmetric nitrogen atoms results in a total ring conversion, *i.e.* from one ring conformation to its mirror image. Conversion of the ring conformation is accompanied by inversion of the 7 and 14 substituents conformation (axial–equatorial), but it does not affect the configuration of these chiral carbon atoms. In consequence, it is possible to correlate the substituent conformations with the relative configuration of the nitrogen chiral centres. This correlation has a key meaning for the following structural assignements of complexes VI–IX.

Complexes VI

Isomeric complexes VIα and VIβ contain only the "imine" methyls. Their p.m.r. signal occurs as a singlet at 2.22 p.p.m., and brings no information about the ligand conformation. The structures of the isomers were proposed based on the known exception to the Laporte selection rule which expects a higher extinction coefficient of the *d–d* transition for a less symmetric compound[15]. The N-rac configuration was assigned to the VIα compound and the N-meso configuration to the VIβ compound (ε = 87 and 81, respectively).



VIα



VIβ

The assignement was recently unequivocally confirmed by Śledziewska[16], who has partially resolved complex VIα into optically active forms.

Complexes VII

Complexes VII–IX contain two chiral nitrogen atoms (1-N and 8-N), and two chiral carbon atoms (7-C and 14-C) in the molecule. This affords a possibility of ten diastereoisomers: two all-meso forms and four racemic mixtures. The idealised structures of the isomers are shown in Figure 2; only one enantiomer for each racemate is shown.

The isomers belong to two sets, one derived from a C-meso ligand (a,b,c) and another from a C-racemic ligand (d,e,f). As mentioned above, the complexes of one C-configuration (say, VIIA) are not convertible into the complexes of another configuration (say, VIIB), whereas the N-configurations are easily isomerised within each set.

The structures in Figure 2 represent also the correlation of the conformations of substituents in positions 7 and 14 with the relative configurations of the chiral nitrogen atoms, and simultaneously with the macrocyclic ring conformation.

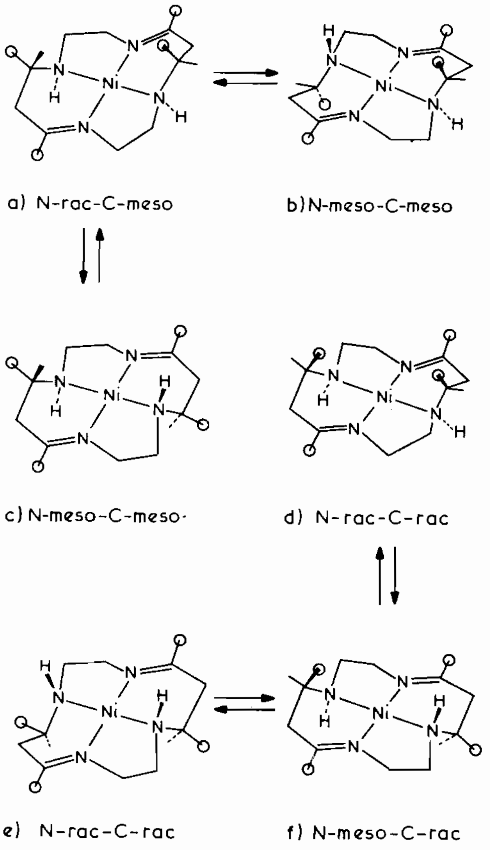


Figure 2. Substituent conformations – N-configuration (ring conformation) correlation diagram.

The assignment of C-configurations to the isomers VIIA and VIIB can be achieved by the resolution of the C-racemic one. The situation is complicated by the fact that the N-rac–C-meso isomer is also resolvable. A partial resolution of complexes VIIAα, VIIBα and VIIBβ was achieved by the method of Śledziewska[16] (Table IV). The solutions of resolved complexes show a strong Cotton effect in the 450-nm band (Figure 3).

The optically active solution of complex VIIAα completely lost its rotation in neutral medium (during purification on an ion-exchange column), as a result of N-isomerisation – a fact indicative of its N-rac–C-meso structure. Complex VIIBα was also isomerised under these conditions, and rotation in the opposite direction was observed. Its CD curve after isomerisation is also shown in Figure 3. The retention of optical activity of complex VIIBα after isomerisation unequivocally determines its structure as C-racemic.

By taking into account the methyl groups conformations in complexes VII known from the p.m.r. spectra (Table III), the C-configurations known from resolution experiments, and correlating them with the N-

TABLE IV. Partial Resolution of Complexes VIIAα, VIIBα and VIIBβ into Optical Isomers.

Fraction	VIIAα[a]			VIIBα[b]			VIIBβ[c]		
	α_{546}[d]	c[e]	$[\alpha_{546}]_M$[f]	α_{546}[d]	c[e]	$[\alpha_{546}]_M$[f]	α_{546}[d]	c[e]	$[\alpha_{546}]_M$[f]
1	+0.775	0.0056	+704	+0.807	0.0120	+343	+0.045	0.0006	+382
2	+0.522	0.0124	+214	+0.850	0.0122	+356	+0.493	0.0034	+738
3	+0.348	0.0135	+131	+0.353	0.0145	+124	+0.504	0.0045	+570
4	+0.228	0.0130	+ 89	+0.031	0.0127	+ 12	+0.284	0.0043	+336
5	+0.026	0.0118	+ 11	−0.112	0.0110	− 52	+0.129	0.0038	+173
6	−0.070	0.0095	− 37	−0.173	0.0092	− 96	−0.007	0.0031	− 11
7	−0.105	0.0076	− 70	−0.193	0.0076	−129	−0.050	0.0019	−134
8	−0.113	0.0056	−102	−0.188	0.0062	−154	−0.064	0.0018	−181
9	−0.106	0.0047	−115	−0.171	0.0051	−178	−0.060	0.0013	−235
11	−0.083	0.0029	−145	−0.128	0.0035	−186	−0.042	0.0008	−267
13	−0.034	0.0018	−144	−0.081	0.0022	−187	−0.027	0.0004	−344
15	−0.021	0.0010	−163	−0.051	0.0016	−162	−0.019	0.0003	−321

[a] 2 g in 75 cm^3 of 0.02*N* hydrochloric acid, one fraction = 12 cm^3.
[b] 2 g in 50 cm^3 of 0.02*N* hydrochloric acid, one fraction = 10 cm^3.
[c] 1 g in 20 cm^3 of 0.02*N* hydrochloric acid, one fraction = 12 cm^3.
[d] Sample path length, 1 dcm. [e] Concentration, g/cm^3, determined spectrophotometrically.
[f] $[\alpha_{546}]_M = \frac{\alpha_{546}}{l \times c} \times \frac{M}{100}$ (l in dcm).

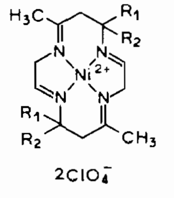
configurations in Figure 2, the structures of all isomers are assigned as follows:

	7-14-CH_3		Formula of Figure 2
VIIAα	ax,eq	N-rac–C-meso	a
VIIAβ	eq,eq	N-meso–C-meso	c
VIIBα	ax,ax	N-rac–C-rac	d
VIIBβ	eq, eq	N-rac–C-rac	e
VIIBγ	ax,eq	N-meso–C-rac	f

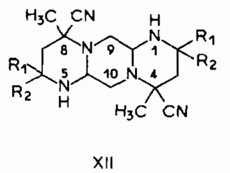
The structures of isomers VIIAα and VIIBα established in this work are in full agreement with those found for these compounds by Krajewski *et al.*[17, 18] by an X-ray crystallographic analysis.

Complexes VIII and IX

An attempted resolution of complexes VIIIα, VIIIβ, and IX was unsuccessful. Nevertheless, the C-configurations of these compounds can be proposed, based on an indirect evidence. Complexes VIIAα, VIIIα, and IX are oxidatively dehydrogenated by nitric acid[19] to the respective complexes XI, which react with potassium cyanide to form 2,6-dialkyl-4,8-dicyano-4,8-dimethyl-1,4a,5,8a-tetra-azaperhydroanthracenes (XII)[10].



XI

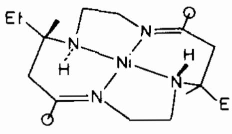


XII

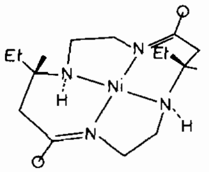
-[14]-1,4,8,11-tetraene N_4

Since complex VIIAα has the C-meso configuration, and all compounds XII have the centrosymmetric configuration, then if the same reaction mechanism is postulated for all, an identical configuration ought to be assigned to all substrates, *i.e.* C-meso configuration to complexes VIII and IX.

Complex VIIIα contains both ethyl groups in the equatorial conformation (Table III) and, since its configuration is C-meso, its overall configuration (from Figure 2) ought to be N-meso–C-meso. Complex VIIIβ has one axial and one equatorial ethyl (Table III), hence, its configuration is N-rac–C-meso.

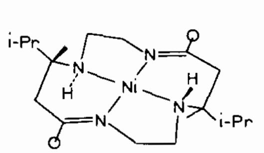


VIIIα



VIIIβ

Analogously, complex IX contains both isopropyl groups in the equatorial conformation which, in connection with its C-meso configuration, allows to ascribe the N-meso–C-meso configuration to it.



IX

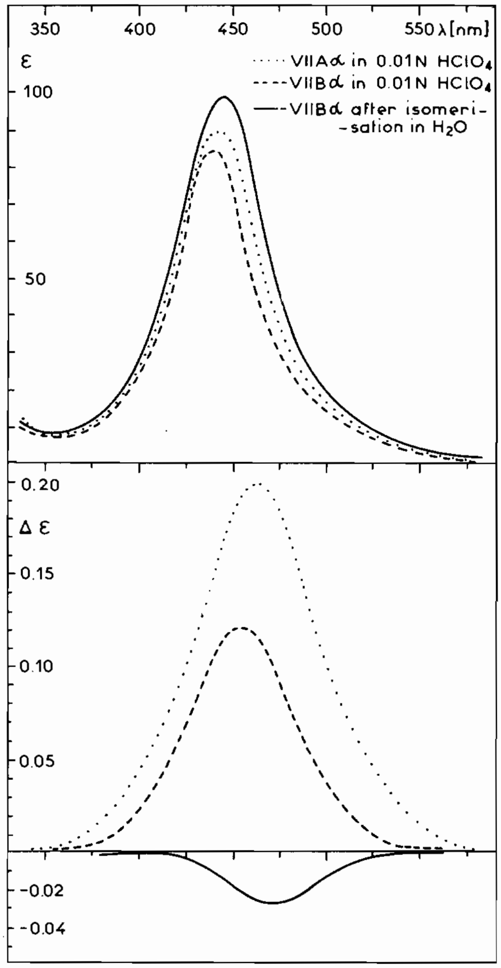


Figure 3. Visible absorption bands and CD curves for isomeric complexes VII.

Conclusion

The ratio of N-diastereoisomers in the series of C-meso complexes VI, VIIA, VIII, IX, and X at equilibrium in neutral methanolic solutions was found as follows:

	N-rac	N-meso
VI	99	*ca.* 1
VIIA	95	5
X[7]	93	7
VIII	50	50
IX	–	100

This suggests that the enantiomeric (N-rac) conformation of the 5,12-dimethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene ring in the square-planar nickel (II) complexes is strongly energetically preferred. The axial 7- and/or 14 methyl groups in complexes VIIA and X do not crowd considerably the molecule and influence the equilibrium position only slightly. An axial ethyl group is energetically less convenient for the enantiomeric ring conformation, and the equilibrium is shifted towards the centrosymmetric configuration of the ring with both ethyls equatorial. The complex IX with an axial isopropyl group practically does not exist. The energy of the enantiomeric ring conformation with an axial isopropyl group is clearly much higher than the energy of the centrosymmetric ring conformation with both isopropyls equatorial. In consequence, the isopropyl group can be considered the conformation-holding group for the centrosymmetric conformation of the discussed macrocycle in its nickel(II) square-planar complexes.

Experimental

Starting Materials

Methyl vinyl ketone, mesityl oxide, anhydrous ethylenediamine, perchloric acid, nickel(II) acetate, nickel (II) perchlorate, and solvents were commercial reagent materials and were used without further purification.

Other α,β-unsaturated ketones: 3-penten-2-one, 3-hexen-2-one, and 5-methyl-3-hexen-2-one (*trans* isomers) were prepared according to known procedures, *i.e.* by condensation of acetone with acetaldehyde, propionaldehyde, and isobutyraldehyde, respectively, in the presence of NaOH solution, followed by dehydration of the resulting ketoles by distillation over phosphoric acid. The products were purified by fractional distillation, and fractions containing more than 95% of the desired ketone (g.l.c.) were used for further reactions.

Polyalkyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene Dihydrogen Perchlorates (I–V)

Perchloric acid (72%, 1 mol) was added dropwise to cooled (0° C) 10% methanolic solution of anhydrous ethylenediamine (1 mol). α,β-Unsaturated ketone (1 mol) was added to the above solution at 0° C with stirring continued until precipitation of the product has started. Stirring was continued for 4 hours and then the reaction mixture was allowed to warm up to ambient temperature. The reactions with 5-methyl-3-hexen-2-one and with mesityl oxide are slower than those with other ketones. Therefore, in these cases the reaction mixture was heated slowly up to 40° C, kept at this temperature for 3 hr, and left overnight to complete crystallisation. The solid white product was filtered off, washed with methanol and ether, and dried over P_4O_{10} *in vacuo* at room temperature.

Melting points, yields, and elemental analyses are collected in Table V.

Characteristic infrared absorption bands in the spectra of compounds I–V are: $\nu_{N^+H_2}$ 3150–3180 cm^{-1},

TABLE V. Characterisation Data of Polyalkyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene Dihydrogen Perchlorates.

Starting Ketone	Ligand	M.p.[a], °C	Yield %	Required , %			Found, %[b]		
				C	H	N	C	H	N
$CH_3COCH=CH_2$	I[c]	109–110	33	33.9	6.2	13.0	33.9	6.2	12.8
$CH_3COCH=CHCH_3$	II[d]	119–123	65	37.1	6.7	12.4	37.5	6.7	12.5
$CH_3COCH=CHC_2H_5$	III	126–127	75	39.9	7.1	11.6	40.5	6.8	11.8
$CH_3COCH=CHCH(CH_3)_2$	IV	121–123	66	42.4	7.5	11.0	43.0	7.6	11.1
$CH_3COCH=C(CH_3)_2$	V[e]	152–153	40	39.9	7.1	11.6	40.3	6.8	11.4

[a] Melting points are uncorrected. All compounds melt with decomposition. [b] Microdetermination by classical methods. Small explosions on combustion werc a nuisance in analysis. [c] *Cf.* ref. 9. [d] Mixture of C-7, C-14-diastereoisomers. [e] *Cf.* ref. 8.

$\delta_{N^+H_2}$ 1545–1550 cm^{-1}, $\nu_{C=N}$ 1660–1670 cm^{-1} and $\nu_{ClO_4^-}$ 1100 cm^{-1}.

Polyalkyl-1,4,8,11-tetra-azacyclotetradeca-4,11-dienenickel(II) Diperchlorates (VI–X)

From ligand dihydrogenperchlorates

An appropriate polyalkyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene dihydrogenperchlorate (0.1 mol) was stirred in a 10% methanolic solution of nickel(II) acetate tetrahydrate (0.1 mol) and refluxed for 2 hr. The reaction mixture was cooled and a solid complex was filtered off. The filtrate was evaporated to a small volume and an additional crop of crystals was collected. The product was recrystallised from 90% methanol and dried over P_4O_{10} *in vacuo.* Yield *ca.* 90%.

From free ligands

Anhydrous nickel(II) perchlorate solution, prepared by shaking nickel(II) perchlorate hexahydrate (0.005 mol) with 5 cm^3 of 2,2-dimethoxypropane for 2 hr at ambient temperature, was added to a stirred 20% methanolic solution of an appropriate polyalkyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene[10] (0.005 mol). A complex precipitated immediately; it was isolated by filtration, washed with methanol and recrystallised from 90% methanol. The yield was 90% (based on the ligand).

Separation of Complex VII into Stable Forms (C-diastereoisomers) VIIAα and VIIBα

Fractional crystallisation of the crude complex VII from the 90% methanol gave two isomeric forms VIIAα (orange crystals, less soluble) and VIIBα (yellow needles) in the ratio 5 : 1.

Separation of Labile Forms (N-diastereoisomers) of Complexes VI–VIII

Complex VIIAβ

A solution of complex VIIAα (20 g) in 90% methanol (200 cm^3) was refluxed for 1 hour. Perchloric acid (72%, 1 cm^3) was added and the solution was left for crystallisation. A first crop of crystals consists of unchanged VIIAα; it was filtered off and rejected. The filtrate was reduced to *ca.* 20 cm^3 and, upon cooling, a mixture of orange (VIIAα) and red (VIIAβ) crystals was obtained. After several recrystallisations from 0.02*N* perchloric acid pure VIIAβ isomer was obtained. Yield, 1 g (*ca.* 5%).

Complex VIβ was obtained in 1% yield by the above method. As complexes VIα and VIβ differ slightly in colour and in p.m.r. spectrum, their i.r. spectra are reproduced in Figure 4 for identification.

Complex VIIIβ was obtained by the above method in 50% yield.

Complexes VIIBβ and VIIBγ

Following the same procedure with complex VIIBα only a very small second crop of orange crystals was obtained (*ca.* 2%) and about 40% of the substance remained as on oily residue.

The p.m.r. spectrum of the crystalline fraction showed that this was a mixture of VIIβ and another complex marked VIIBγ. Separation of complex VIIBγ was unsuccessful, because of its great lability in solution.

The oily residue which includes mainly complex VIIBβ was dissolved in nitrobenzene, and benzene was added to induce crystallisation. Orange crystals of VIIBβ·

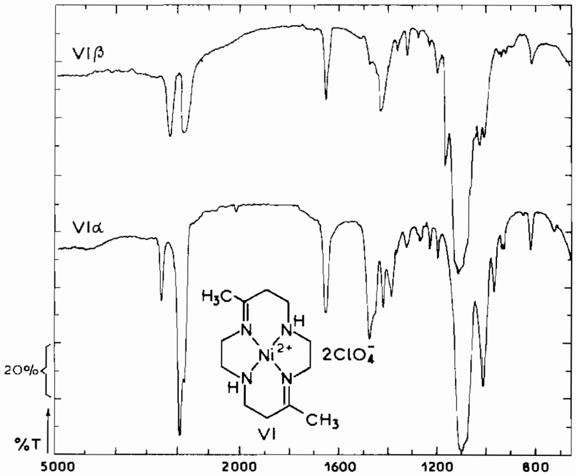


Figure 4. Infrared spectra of isomeric complexes VI (solid samples as Nujol mulls).

TABLE VI. Characterisation Data of Polyalkyl-1,4,8,11-tetra-azacyclotetradeca-4,11-dienenickel(II) Diperchlorates.

Complex	Colour	Required, %				Found, %			
		C	H	N	Ni	C	H	N	Ni
VIα[b]	orange	29.9	5.0	11.6	12.2	30.1	5.0	11.5	12.2
VIβ	orange					30.2	5.0	11.4	12.1
VIIAα	orange	33.0	5.5	10.98	11.57	32.9	5.5	11.1	11.3
VIIAβ	red					32.8	5.5	11.2	11.3
VIIBα	yellow					33.4	5.5	11.2	11.5
VIIBβ	orange					33.1	5.6	10.6	11.5
VIIIα	orange	35.7	6.0	10.4	10.9	36.1	5.9	10.5	10.9
VIIIβ	yellow					36.0	5.8	10.4	10.8
IX[c]	orange	38.2	6.4	9.9	19.4	38.2	6.3	10.0	10.4

[a] Small explosions on combustion were a nuisance in analysis. [b] *Cf.* ref. 9. [c] Anhydrous compound. Complex IX forms an unstable violet hydrate, which releases water under reduced pressure at 80° C.

$2C_6H_6$ were obtained. To obtain VIIBβ free of solvent, VIIB$\beta \cdot 2C_6H_6$ was dried under reduced pressure at 80° C.

Characterisation data and elemental analyses for all the complexes are collected in Table VI.

C-Deuteration

C-deuteration of the complexes was carried out by the method of Busch *et al.*[7].

Partial Resolution

Partial resolution of the complexes into optical isomers was achieved after Śledziewska[16] by chromatography on potato starchpacked columns with 0.02*N* hydrochloric acid as eluent.

Optically active fractions of solutions of complexes VIIAα and VIIBα were purified from small quantities of the starch hydrolysate washed out from the starch column, by absorption in an Amberlite CG-50 column, washing with water and elution with 2% perchloric acid.

Physical Measurements

I.r. spectra were recorded as paraffin oil mulls on Unicam SP-200 and Hilgar H-800 spectrometers. Electronic spectra were obtained on a Unicam SP-500 spectrometer. C.D. and O.R.D. spectra were recorded on a JASCO UV/ORD-5 spectrometer. P.m.r. spectra were obtained on Varian HA-60-IL and JEOL INM 4H-100 spectrometers with T.M.S. as internal standard. Magnetic susceptibilities were measured by Gouy's method. Optical rotations were determined on a Perkin–Elmer 141 polarimeter in a 10 cm cell.

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