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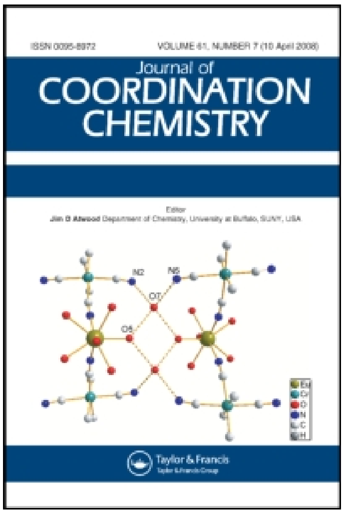

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NICKEL(II) COMPLEXES OF NOVEL MACROCYCLIC LIGANDS CONTAINING PENDANT NITRO GROUPS

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NICKEL(II) COMPLEXES OF NOVEL MACROCYCLIC LIGANDS CONTAINING PENDANT NITRO GROUPS

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The addition of nitromethane anion to the C=N group of polyalkyl-1,4,8,11-tetraazacyclotetradeca-4,11-dienenickel(II) diperchlorate gave Ni(II) complexes of new macrocyclic ligands containing a pendant 5-nitromethyl group. Variable temperature (80–290 K) magnetic susceptibilities were determined for the paramagnetic monoperchlorates and the diamagnetic square-planar diperchlorates. Conformations of the nitromethyl groups in the macrocyclic ligands were established on the basis of ^1H NMR evidence.

Key words: Nickel, macrocycles, synthesis, conformation, complexes

INTRODUCTION

Combination of rigid cyclic together with flexible open-chain structural elements in the one ligand molecule enables the synthesis of a new class of metal complexes having interesting properties with respect to their structure and stability.[1] Pendant arm macrocyclic ligands are usually obtained either by alkylation of secondary nitrogen atoms present in the macrocyclic ring[2] or by synthesis of macrocycles from synthons where the functional side chain is built in at early stage of the synthesis.[3]

Recently, we have communicated the synthesis of pendant arm 1,4,8,11-tetraazacyclotetradecane derivatives where the functional side chain was located on the carbon atom of the macrocyclic ring.[4] In this paper we describe in more detail the synthesis and properties of 5-nitromethylpolyalkyl-1,4,8,11-tetraazacyclotetradeca-11-enenickel(II) mono- (**2**) and diperchlorates (**3**).

EXPERIMENTAL

Synthesis

5-Nitromethylpolyalkyl-1,4,8,11-tetraazacyclotetradeca-11-enenickel(II) monoperchlorates, **2**

Polyalkyl-1,4,8,11-tetraazacyclotetradeca-4,11-dienenickel(II) diperchlorate **1** (0.02 mol) was dissolved in nitromethane (50 cm^3), then triethylamine (4.2 cm^3, 0.03 mol) was added, the reaction mixture left overnight at room temperature, then cooled in a refrigerator in order to complete crystallization. Precipitated product was filtered off, washed with nitromethane, methanol, then ether and dried *in vacuo* over P_2O_5. Analytical samples were dissolved in 25% ammonia (1g in 5 cm^3) diluted with methanol to 100 cm^3 and crystallized during evaporation of these solutions at temperatures below 20°C. Complex **2b** crystallized with one molecule of NH_3 in the crystal lattice instead of H_2O in the crude product.

Analysis: Calcd. for **2a**: C, 35.28; H, 5.92; N, 15.82%. Found: C, 35.31; H, 5.97; N, 15.77% (yield 60%). Calcd. for **2bα**·H_2O : C, 36.87; H, 6.60; N, 14.33%. Found: C, 36.78; H, 6.48; N, 14.49% (yield 48%). Calcd. for **2bα**·NH_3 : C, 36.95; H, 6.82; N, 17.23%. Found: C, 36.88; H, 6.82; N, 17.23% (yield 50%). Calcd. for **2c**: C, 38.28; H, 6.43; N, 14.88%. Found: C, 38.19; H, 6.13; N, 15.13% (yield 56%). Calcd. for **2d**: C, 38.28; H, 6.43; N, 14.88%. Found: C, 38.58; H, 6.33; N, 14.69% (yield 86%).

5-Nitromethylpolyalkyl-1,4,8,11-tetraazacyclotetradeca-11-enenickel(II) diperchlorates, 3

Monoperchlorate **2** (10g) was stirred in 50 cm^3 water (**2a** and **2c**) or methanol-nitromethane 10:1 (**2b** and **2d**), then 4.5 cm^3 of 70% perchloric acid was added and stirring was continued for the next 4 hours at room temperature. Precipitated orange product was recrystallized from methanol and dried *in vacuo* over P_2O_5.

Diperchlorate 3bβ

Diperchlorate **1b** (20.4g, 0.04 mol) was dissolved in 100 cm^3 of nitromethane, then trimethylamine (*ca* 4g, 0.06 mol) was added to the solution and the reaction mixture was left overnight at room temperature. Precipitated solid was filtered off (*ca* 8g) dried, then dissolved in 250 cm^3 of boiling methanol acidified with 4 cm^3 of 70% perchloric acid. On cooling, red crystals of diperchlorate **3bβ** crystallized as a first fraction and were filtered off and dried *in vacuo* (*ca* 1g, 5%). Remaining fractions contained mainly starting diperchlorate **1b**.

Analysis: Calcd. for **3a**: C, 28.75; H, 5.01; N, 12.90%. Found: C, 28.89; H, 4.99; N, 12.99% (yield 82%). Calcd. for **3bα**: C, 31.55; H, 5.47; N, 12.26%. Found: C, 28.89; H, 4.99; N, 12.99% (yield 70%). Calcd. for **3bβ**: C, 31.55; H, 5.47; N, 12.26%. Found: C, 31.53; H, 4.99; N, 12.99% (yield 70%). Calcd. for **3bβ**;: C, 31.55; H, 5.47; N, 12.26. Found: C, 31.53; H, 5.47; N, 12.21% (yield 5%). Calcd. for **3c**: C, 31.55; H, 5.47; N, 12.26%. Found: C, 31.60; H, 5.53; N, 12.46% (yield 86%). Calcd. for **3d**: C, 31.55; H, 5.47; N, 12.26%. Found: C, 31.33; H, 5.25; N, 12.21% (yield 85%).

Materials

Nitromethane, triethylamine, trimethylamine and solvents were commercial reagents used without further purification. Preparation of nickel(II) complexes **1** was described elsewhere.[5,6]

Physical measurements

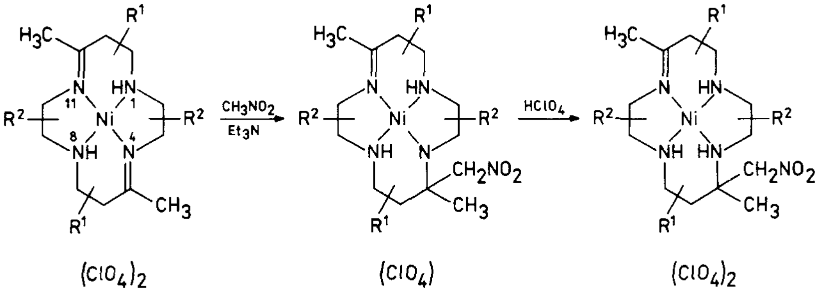
The electronic spectra of the complexes in solution were recorded in the range 200–1000 nm on a Cary 14 spectrophotometer. The reflectance spectra of undiluted compounds were measured in the 350–1500 nm region on a Beckman UV spectrophotometer and those of Li_2CO_3 diluted compounds in the 200–800 nm region on a Hitachi 356 spectrophometer. The infrared spectra were measured in nujol mulls and in KBr pellets on a Perkin Elmer 180 spectrophotometer. The ^{13}C and ^1H NMR spectra of the compounds were obtained in JEOL JNM 4H-100 spectrometer with TMS as internal standard.

Magnetic susceptibilities were measured using the Faraday method with a Cahn RG-HV electrobalance. Magnetic measurements were carried out on polycrystalline samples weighing about 60 mg in the temperature range 290–80 K, in a magnetic field of *ca* 0.505 T. Magnetic susceptibilities of all samples were found to be field independent.

The susceptibilities were corrected for the diamagnetism of all constituents[7] and the t.i.p. of the nickel(II) ion. The calibrant employed was $HgCo(SCN)_4$, for which $\chi_g = 16.44$ cm^3 g^{-1} at 293 K.[8] Temperature was determined with an accuracy of about ± 0.1 K.

RESULTS AND DISCUSSION

Polyalkyl-1,4,8,11-tetraazacyclotetradeca-4,11-dienenickel(II) diperchlorates **1** in nitromethane solution in the presence of base add nitromethane anion to the carbon atom of one of the C=N bonds giving sparingly soluble violet monoperchlorates of the 5-nitromethyl derivatives **2**.



1 2 3

1a	R^1 = H; R^2 = H	**2a**	**3a***
1b	R^1 = *meso*-7,14-CH_3; R^2 = H	**2bα (2bβ)***	**3bα**,
1c	R^1 = H; R^2 = *meso*-2,9-CH_3	**2c**	**3c**
1d	R^1 = H; R^2 = *rac*-2,10-CH_3	**2d**	**3d**
1e	R^1 = H; R^2 = *meso*-3,10-CH_3		
1f	R^1 = *meso*-6,13-CH_3; R^2 = H	**(2f)***	**(3f)***
1g	R^1 = *rac*-7,14-CH_3; R^2 = H	**(2g)***	**(3g)***

*Compounds in parentheses not isolated in a pure state.

The paramagnetic complexes **2** protonated with perchloric acid form the more stable yellow or orange diamagnetic diperchlorates **3**. Yields of the addition reaction depend on substitution of the macrocycle and on the nature of base. 3,5,10,12-Methyl substituted ligand **1e** does not react with nitromethane, whereas 2,5,10,12-methyl substituted complex **1d** reacts with high yield in the presence of triethylamine. 5,12-, 5,7,12,14-, and 2,5,9,12-Methyl substituted complexes (**1a**, **1b**, **1c**) react in the presence of triethylamine forming 5-nitromethyl derivatives **2** with good yields. 5,6,12,13-Methyl substituted complex **1f**, where the unsaturated carbon atoms are sterically hindered by the neighbouring methyl groups, forms in this reaction a di-μ-fulminato dimer[9] as the main product, and only a trace of the expected 5-nitromethyl derivative **2f** can be detected in the reaction products.

When the unsaturated carbon atoms are sterically hindered the nitromethane anion reacts with the nickel(II) ion and after dehydration forms coordinated fulminate anion. Also, when the reaction was carried out in the presence of trimethylamine in all cases, except for **1e** where the nickel(II) ion was also hindered by two axial 3,10-methyl groups, we observed the formation of di-μ-fulminato dimers as well as compounds **2**.[9]

5-Nitromethyl monoperchlorates **2** are soluble in 25% ammonia and can be easily separated from the insoluble di-μ-fulminato dimers. Evaporation of the ammonia at temperatures below 25°C and crystallization of the residue from methanol gave pure complexes **2**. Complex **2bα**, isolated initially as a monohydrate, crystallized from ammonia with one molecule of NH_3 instead of H_2O in the crystal lattice.

Only one of the possible isomers was isolated from the reaction mixture in most cases. From the reaction of the C-*meso* complex **1b** with nitromethane in the presence of trimethylamine, besides a di-μ-fulminato dimer, was isolated with low yield (*ca* 5%) the second isomer of the 5-nitromethyl complex **3bβ**. The C-*rac* isomer of the 5,7,12,14-tetramethyl complex **1g** also gave a mixture of isomeric 5-nitromethyl derivatives which, due to low stability in solution, were not resolved into pure isomers.

The characteristic infrared absorption bands for compounds **2** and **3** are given in Table I. The bands in the region 3100–3300 cm^{-1} and 1650–1670 cm^{-1} are assigned to N–H and C=N stretching vibrations respectively, and a very strong absorption band at *ca* 1100 cm^{-1} to stretching vibrations of the anion.

TABLE I

Characteristic infrared absorption bands for monoperchlorates **2** and diperchlorates **3** (cm^{-1}, KBr).

Complex	ν_{N-H} and ν_{C-H}	ν_{C-N}	$\nu as NO_2$	$\nu s NO_2$	νClO_4
2a	3260 3180	1655	1560	1384	1095
3a	3180	1650	1545	1376	1100
2bα·H_2O	3420 3242 3200	1663	1555	1382	1090
2bα·NH_3	3540 3345 3245 3180 3102	1670	1555	1384	1100
3bα	3170	1656	1550 1545	1380	1100
3bβ	3210	1658	1558	1380	1100
2c	3255 3200	1668	1568	1390	1100
3c	3250 3180	1658	1565	1390	1100
2d	3278 3250 3180	1661	1563 1543	1384	1095
3d	3220 3150	1658	1550	1377	1100

Strong absorption bands at 1545–1565 cm^{-1} in the spectra of the square planar diperchlorates **3** are typical for asymmetric vibrations of the free NO_2 group. These bands become broader and are shifted toward higher frequencies (3–15 cm^{-1}) in the spectra of the paramagnetic monoperchlorates **2** where the NO_2 group is bonded to the central Ni(II) ion. Symmetric stretching vibrations bands of the NO_2 group are observed at *ca* 1380 cm^{-1}.

Results of electronic spectral measurements for the diperchlorates **3** are collected in Table II. All diperchlorates **3** exhibit an absorption band of low intensity at *ca* 22200 cm^{-1} characteristic of nickel(II) square-planar complexes.[5,6,10] Intensive charge-transfer absorption bands occur in the UV at *ca* 47000 cm^{-1}.

TABLE II
Ultraviolet and visible spectra for diperchlorates **3** in 0.01 N $HClO_4$ (λ_{max} in cm^{-1}).

Complex	$\lambda_{max}(\varepsilon)$	$\lambda_{max}(\varepsilon)$
3a	46950 (16140)	22470 (82)
3bα	48780 (12490) 45870 (14930)	22120 (53)
3bβ	29940 (sh 70)*	22030 (72)
3c	46950 (14780)	22320 (84)
3d	45870 (16430)	22620 (76)

*sh = shoulder.

The **2c** type compounds show ligand field bands in the region 9000-30000 cm^{-1} and also strong charge-transfer bands beyond 25000 cm^{-1} (Table III).

TABLE III
Reflectance spectra of the monoperchlorates **2a**.

Compound	Band position (cm^{-1})							
2a	45500sh*	41200	37300sh	28900	19700	15400b	12400	9200
2bα·H_2O	44500sh	38200		29700	19700	15500b	12400	9100
2bα·NH_3	47100sh	38900		29400	19400	14000b	12500	10300
2c	46300sh	39700		29600	19600	15500b	12500	9700
2d	45500sh	40400		29400	19500	15400b	12500	9100

*b = broad, sh = shoulder.

The electronic spectra of these compounds can be interpreted by assuming a tetragonal distortion of the crystal field. The bands at *ca* 9500 and *ca* 12500 cm^{-1} correspond to the transitions $^3B_{1g} \rightarrow {}^3B_{2g}$ and $^3B_{1g} \rightarrow {}^3E_g$, split components of the $^3T_{2g}$ term. The band connected with the $^3B_{1g} \rightarrow {}^3E_g$ transition is of much lower intensity. The bands at *ca* 15000 cm^{-1} and *ca* 19500 cm^{-1} are assigned to the components of the $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ octahedral ligand field transition $^3B_{1g} \rightarrow {}^3E_g^b, {}^3A_{2g}$. The latter band corresponding to the transition of the octahedral ligand field $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ appears at *ca* 29000 cm^{-1} and does not suggest the presence of tetragonal components.

Magnetic susceptibilities of mono- and diperchlorates were measured employing the Faraday method in the temperature range 80-290 K. Diperchlorates exhibited diamagnetism and suggest square-planar coordination at the nickel(II) ion.

The magnetic data for the monoperchlorates are collected in Table IV. In the 80-290 K range susceptibilities conform approximately to the Curie-Weiss law $\chi = C(T - \theta)$. For the calculation of the Curie and Weiss constants the minimization of the sum $\sum_{i=1}^{n} (\chi_i^{calcd} - \chi_i^{exptl})^2$ was the criterion used to determine the best fit. The effective magnetic moments of the monoperchlorates calculated from the formula $\mu_{eff} = 2.83\,(\chi_{Ni}^{corr} \cdot T)^{1/2}$ are typical for a tetragonal symmetry of the nickel (II) compound.

^{13}C NMR data for the diperchlorates **3** are given in Table V. The spectra are typical for compounds of this class.[1] The most characteristic ^{13}C NMR signals are those belonging to the carbon atom of the 5-nitromethyl group observed at *ca* 80 ppm.

TABLE IV

Magnetic parameters[a] of the monoperchlorates **2**.

Compound	Weiss constant (K)	Curie constant ($cm^3\ mol^{-1}\ K$)	Spectroscopic splitting factor[b] <g>	Diamagnetic corrections $\times 10^6$ ($cm^3\ mol^{-1}$)	t.i.p.[c] $\times 10^6$ ($cm^3\ mol^{-1}$)	μ_{eff}[d] (B.M.)
2d	9.4	1.13	2.13	−237	+229	3.10
2a	5.7	1.07	2.07	−222	+227	2.96
2bα·H_2O	2.8	1.16	2.15	−245	+229	3.07
2bα·NH_3	1.4	1.16	2.15	−270	+202	3.06
2c	6.5	1.12	2.12	−243	+215	3.03

[a] temperature range 80–290 K. [b] calculated from $C=N\beta^2g^2\,[S(S+1)]/3k$ where $S=1$. [c] calculated from $\text{t.i.p.} = 8\,N\beta^2/10Dq$. [d] at 290 K.

TABLE V
^{13}C NMR data for complexes **3** (CF_3COOD).

Complex	CH_3	CH_2NO_2	$C{=}N$	other carbon atoms								
3a	21.8 24.3	79.3	186.9	36.8	40.3	45.5	46.1	46.5	52.4	53.3	56.1	59.6
3bα	18.0 18.8 22.6 24.6	79.4	187.4	45.9	47.1	48.7	50.0	50.6	52.2	52.8	55.8	59.7
3bβ	19.5 20.9 25.6 26.0	80.4	187.4	45.6	47.3	49.0	49.0	49.7	51.7	52.1	55.0	58.9
3c	14.4 16.4 24.9 25.1	80.4	187.7	39.0	40.1	43.2	45.4	53.5	59.5	59.7	60.7	62.8
3d	14.4 19.9 25.0 25.0	80.5	188.1	39.0	41.2	44.0	48.2	53.6	59.3	59.5	59.9	62.5

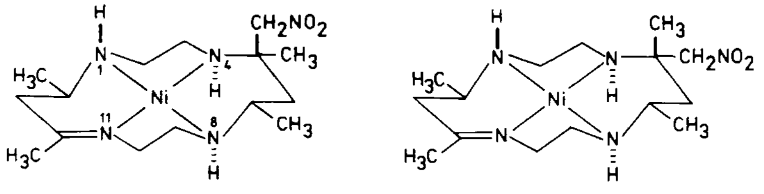
^1H NMR data for the diperchlorates **3** are collected in Table VI. The signals of the ring protons are very complicated and difficult to interpret. The most prominent signals are those of the 5-nitromethyl group. The chemical shifts of the ring protons coupled to the protons of the methyl groups were determined by double resonance experiments. Those chemical shifts allowed us to establish conformations of the substituents.[5,6] Knowing the relative configurations the methyl-substituted carbon atoms in substrates **1b** – **d**[5,6] we could then assign the relative configurations of the asymmetric carbon atoms in complexes **3b** and **3d**.

TABLE VI
^1H NMR data for the complexes **3** (CD_3NO_2, TMS, 100 MHz)*.

Complex	$\mathit{CH}_3\diagdown\overset{}{C}\diagup$ ‖ N	$\mathit{CH}_3\diagdown C\diagup$ H	$CH_3\diagdown C\diagup$ H	CH_3-C-CH_2NO_2
3a	2.21s(3)			1.44s(3) 5.08d(1), 6.31d(1) J=12
3bα	2.20s(3)	1.30d(6)	3.55	1.50s(3) 5.22d(1), 6.50d(1) J=11.5
3bβ	2.35s(3)	1.30d(6)	3.22	2.45s(3) 4.55d(1), 4.95d(1) J=12.5
3c	2.22s(3)	1.20d(3) 1.25d(3)	3.39 2.96	1.44s(3) 5.17d(1), 6.43d(1) J=12
3d	2.28s(3)	1.21d(3) 1.41d(3)	3.36 4.01	1.45s(3) 5.39d(1), 6.11d(1) J=11
3f**	2.32s(3)	1.23d(3) 1.42d(3)		1.55s(3) 5.23d(1), 6.08d(1) J=12.5

*Relative signal intensities in parentheses; J in Hz; s = singlet, d = doublet. **Signals from the spectrum of a mixture of **1f** and **3f** in CF_3COOH.

Two isomeric compounds **3bα** and **3bβ** were obtained from the *C-meso* complex **1b**.[5] The chemical shifts of the 7,14-methyl groups and coupled protons in both isomers are typical for an equatorial conformation of substituents in these positions. Equatorial conformation is possible only when the protons on the 1,8-nitrogen atoms are located on opposite sides of the macrocyclic ring ("*N-meso*" conformation) and are in a *cis*



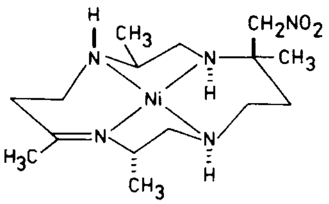
3bα 3bβ

FIGURE 1

configuration relative to neighbouring methyl groups. Assumption that six-membered chelate rings exist in chair conformations leads to the conclusion that protons on the *N*-4 and *N*-8 nitrogen atoms have to be located on the same side of the chelate ring as is shown on Figure 1.

The chemical shifts of the C-5 methyl groups are 1.50 and 2.45 ppm in the spectra of isomers **3bα** and **3bβ**, respectively. According to known deshilding effects[5,6,12] for protons situated above the plane of square-planar nickel(II) complexes the low-field 2.45 ppm signal is ascribed to an axial methyl group in isomer **3bβ**, and the high-field signal (1.50 ppm) signal to an equatorial methyl group in isomer **3bα**. This conclusion is confirmed by the opposite order of chemical shifts of the 5-nitromethyl methylene protons which occupy axial (5.22 and 6.50 ppm) and equatorial (4.55 and 4.95 ppm) positions in isomers **3bα** and **3bβ**, respectively, as shown in Figure 1.

Complex **3d** has an axial 5-nitromethyl group, a pseudoequatorial 2-methyl group, and a pseudoaxial 10-methyl group. Hypothetical structures with a 12-nitromethyl group can be excluded on the basis of the much lower reactivity of the 12-carbon atom. The 3,10-diaxial substituted complex **1e** does not react with nitromethane under the same conditions. Conformations of the 2- and 10-methyl groups remain the same as in the *N-meso* isomer of the starting complex **1c**.[6] Thus, complex **3d** also possesses the *N-meso* conformation as shown in Figure 2.

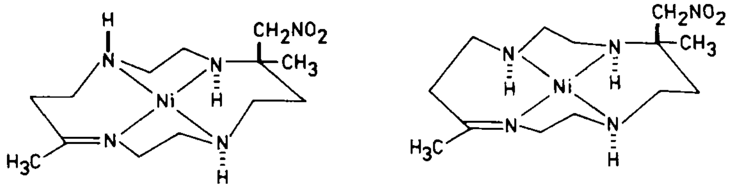


3d

FIGURE 2

Complex **3a** has only one asymmetric carbon atom, C-5. The 5-nitromethyl group occupies an axial conformation. Two *N*-isomeric structures with *N-meso* and *N-rac* conformations of the macrocyclic ring (Figure 3) are possible for this complex.

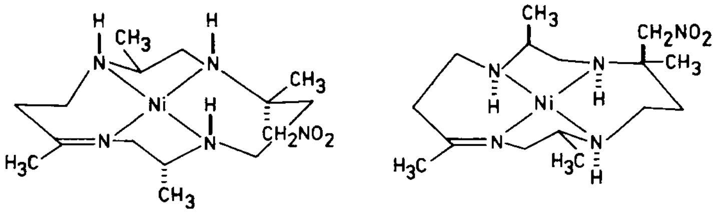
Chemical shifts of C-5 methyl group protons (1.44 ppm) and of 5-nitromethyl group methylene protons (5.17 and 6.43 ppm) are typical for an equatorial conformation of the methyl group and an axial conformation of the nitromethyl group. The relative configurations of C-2 and C-9 carbon atoms in the substrate complex **1c** was *C-meso*[6] and could not be changed during the nitromethane addition to the C=N double bond. The 2- and 9-methyl groups in complex **3c** occupy pseudo-axial (1.25 ppm doublet coupled to the signal of the ring proton at 2.96 ppm) and psuedo-equatorial (1.20 ppm doublet coupled to the signal at 3.39 ppm) conformations. This is possible only if the



3a

FIGURE 3

macrocyclic ring possesses an *N-rac* conformation (N-1 and N-8 protons located on the same side of the ring). In Figure 4 are shown two alternative structures of complex **3c** with an axial 5-nitromethyl group resulting from the addition of nitromethane anion to C-5 or C-12 carbon atoms in the substrate **1c**. The structure having the equatorial conformation of the 2-methyl group and the axial conformation of the 9-methyl group seems to be more reasonable as its being the less strained one. The large axial nitromethyl substituent has a *trans* configuration with respect to the nearest 2-equatorial methyl group in this structure, whereas in the second structure the 2-axial methyl and 5-axial nitromethyl groups possess a *cis* configuration and would give rise to non-bonded repulsive interactions.



3c

FIGURE 4

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