Square-Planar and Octahedral Nickel(II) Complexes of Isomeric *cis*-2,9-Bis(aminomethyl)-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecanes

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Isomeric *cis*-2,9-bis(aminomethyl)-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecanes (**6a** and **6b**) and their octahedral (**4**) and square-planar nickel(II) complexes (**5**) have been prepared and characterized. X-ray crystallographic investigations of the octahedral complexes have confirmed a folded conformation of the macrocyclic ring. Protonation of the pendant amino groups results in a change in the Ni configuration, which is accompanied by a concomitant change of the macrocycle conformation from a folded to a planar one. The structures of the protonated, square-planar complexes and of the free ligands have been established mainly on the basis of their ^{1}H- and ^{13}C-NMR spectra.

Introduction

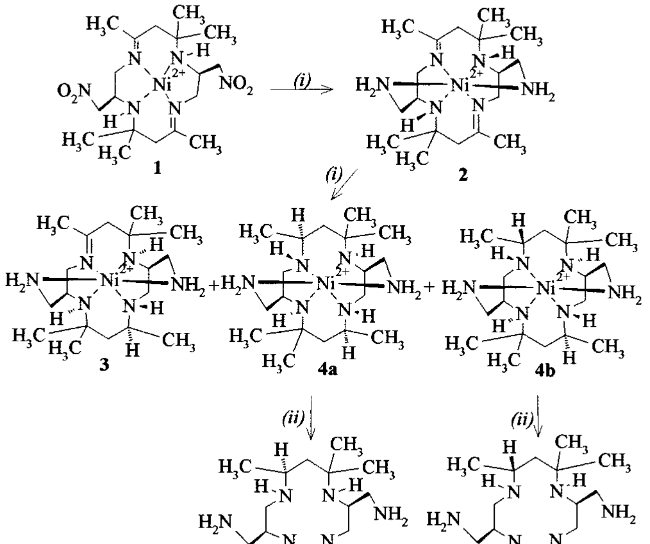
Tetraaza macrocyclic ligands functionalized with pendant donor groups form diamagnetic square-planar nickel(II) complexes when the donor groups are protonated and cannot coordinate, whereas at higher pH coordination of the pendant donors leads to paramagnetic, octahedral complexes.[1,2] In the case of monosubstituted ligands, coordination of the pendant donor occurs at one of the axial sites, and the second axial site is occupied by an anion or solvent molecule.[3,4] Pendant methylnitronato[5] or carboxylate[6] groups, by virtue of their ability to offer two possible donor oxygen atoms, may also fill this coordination site and act as a bridge between nickel(II) ions forming one-dimensional polymers.

Nickel(II) complexes of cyclam derivatives substituted with two pendant amino groups are subject to similar pH-dependent equilibria. *trans*-Substituted ligands form octahedral complexes, with the nitrogen atoms of the macrocycle occupying an equatorial plane and the pendant groups in axial positions.[7−9] However, coordination of both pendant groups in the case of *cis*-substituted cyclam derivatives requires folding of the macrocycle conformation. Such folding occurs upon coordination of the pendant amino groups in *cis*-2,9-bis(aminomethyl)-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene nickel(II) diperchlorate (**2**).[8] Hydrogenation of complex **2** gave two violet nickel(II) complexes of isomeric *cis*-2,9-bis(aminomethyl)-substituted cyclam derivatives, **4a** and **4b**. Crystallographic data for these two octahedral nickel(II) complexes, as well as the spectroscopic characterization of their diamagnetic square-planar protonation products and free ligands, are described in the present paper.

Results and Discussion

Synthesis

The synthesis of the isomeric complexes **4a**, **4b** and the free ligands **6a**, **6b** is outlined in Scheme 1.



Scheme 1. Reagents: (*i*) zinc amalgam and HCl; (*ii*) NaCN in water under reflux

Reduction of the nitro groups in the *cis*-2,9-bis(nitromethyl)-substituted complex **1**, followed by hydrogenation of the C=N double bonds with zinc amalgam and hydrochloric acid led to the isomeric 2,9-bis(aminomethyl)-substituted Ni complexes **4a**, **4b** and the intermediate product **3**. Work-up of the mixture after a shorter reaction time allowed isolation of the previously described, unsaturated complex **2**. The use of zinc amalgam in place of the zinc dust used in published procedures[9,10] proved advantageous

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since the degree of decomposition accompanying reduction of the nitro groups was lower. The two isomeric, fully saturated, octahedral Ni^{II} complexes were separated by chromatography on an SP Sephadex C-25 column and were isolated in the form of their diperchlorate salts **4a** and **4b**.

Upon acidification with 72% perchloric acid, violet nitromethane solutions of complexes **4a** and **4b** gave deep-red and orange solutions of the square-planar tetraperchlorates **5aα** and **5b**, respectively, with protonated pendant arms. Complexes **5aα** and **5b** were found to readily undergo isomerization in protic solvents and thus they were characterized only in nitromethane solution. *N*-Isomeric **β** and **γ** forms of complex **5a** were isolated in solid form, but only an oily mixture of isomers was precipitated upon addition of diethyl ether to an ethanolic solution of complex **5b**.

Demetallation of **4a** and **4b** in aqueous solution using an excess of sodium cyanide gave the free ligands **6a** and **6b**.

Crystal Structures of 4a and 4b

Selected bond lengths and valence angles in cations **4a** and **4b**, as shown in Figures 1 and 2, are listed in Table 1.

Table 1. Selected bond lengths [Å] and angles [°] for cations **4a** and **4b**

Bond	**4a**	**4b**	Angle	**4a**	**4b**
N1−Ni	2.135(6)	2.130(6)	N1−Ni−N4	79.8(3)	80.7(3)
N4−Ni	2.104(7)	2.082(7)	N1−Ni−N8	105.9(3)	101.1(3)
N8−Ni	2.141(7)	2.102(8)	N1−Ni−N11	97.5(3)	95.7(3)
N11−Ni	2.115(7)	2.123(8)	N1−Ni−N16	82.8(3)	82.9(3)
N16−Ni	2.122(9)	2.113(8)	N1−Ni−N18	170.7(3)	176.5(3)
N18−Ni	2.126(8)	2.120(8)	N4−Ni−N8	97.7(3)	95.4(3)
C2−N1	1.49(1)	1.484(9)	N4−Ni−N11	175.3(3)	173.7(3)
C14−N1	1.50(1)	1.52(1)	N4−Ni−N16	87.1(4)	85.5(4)
C3−C2	1.53(1)	1.53(1)	N4−Ni−N18	96.0(3)	99.4(4)
C15−C2	1.53(1)	1.51(1)	N8−Ni−N11	79.2(3)	80.2(3)
N4−C3	1.50(1)	1.48(1)	N8−Ni−N16	170.7(3)	176.0(3)
C5−N4	1.47(1)	1.51(1)	N8−Ni−N18	82.9(3)	82.4(4)
C6−C5	1.53(1)	1.51(1)	N11−Ni−N16	96.5(4)	99.2(4)
C19−C5	1.51(1)	1.52(1)	N11−Ni−N18	87.1(3)	84.6(4)
C7−C6	1.53(1)	1.54(1)	N16−Ni−N18	88.7(4)	93.6(4)
N8−C7	1.51(1)	1.52(1)	Ni−N1−C2	96.7(5)	97.0(5)
C20−C7	1.52(1)	1.53(1)	Ni−N1−C14	121.4(5)	121.5(5)
C21−C7	1.54(1)	1.53(2)	Ni−N4−C3	107.2(6)	107.9(6)
C9−N8	1.50(1)	1.51(1)	Ni−N4−C5	119.5(5)	117.6(6)
C10−C9	1.51(1)	1.51(1)	Ni−N8−C7	121.1(5)	127.2(6)
C17−C9	1.52(1)	1.52(1)	Ni−N8−C9	96.1(5)	98.2(6)
N11−C10	1.50(1)	1.49(1)	Ni−N11−C10	107.4(6)	108.0(6)
C12−N11	1.49(1)	1.51(1)	Ni−N11−C12	118.4(5)	122.2(6)
C13−C12	1.50(1)	1.49(1)	Ni−N16−C15	109.0(7)	107.8(6)
C22−C12	1.53(1)	1.50(2)	Ni−N18−C17	108.5(6)	108.8(7)
C23−C14	1.53(1)	1.52(1)	N1−C2−C3	106.0(8)	104.3(7)
C24−C14	1.54(1)	1.57(1)	N1−C2−C15	110.4(7)	110.9(8)
N16−C15	1.47(1)	1.48(1)	N1−C14−C13	111.2(6)	112.3(8)
N18−C17	1.46(1)	1.45(1)	N1−C14−C23	105.6(7)	111.3(9)
			N1−C14−C24	112.3(7)	103.3(8)

Both cations have an irregular octahedral Ni^{II} coordination sphere with the macrocycle coordinated in a folded conformation, with fold angles (N1−Ni−N8) of 106° and 101° in **4a** and **4b**, respectively. All N−Ni−N angles in the five-membered chelate rings are rather small (79−83°). The angles in the six-membered chelate rings incorporating the macrocyclic nitrogen atoms are large (95−98°), while those incorporating the aminomethyl pendant arms are small (84−87°). The Ni−N distances fall in the range typical for octahedral coordination (2.10−2.14 Å for **4a**; 2.08−2.13 Å for **4b**).

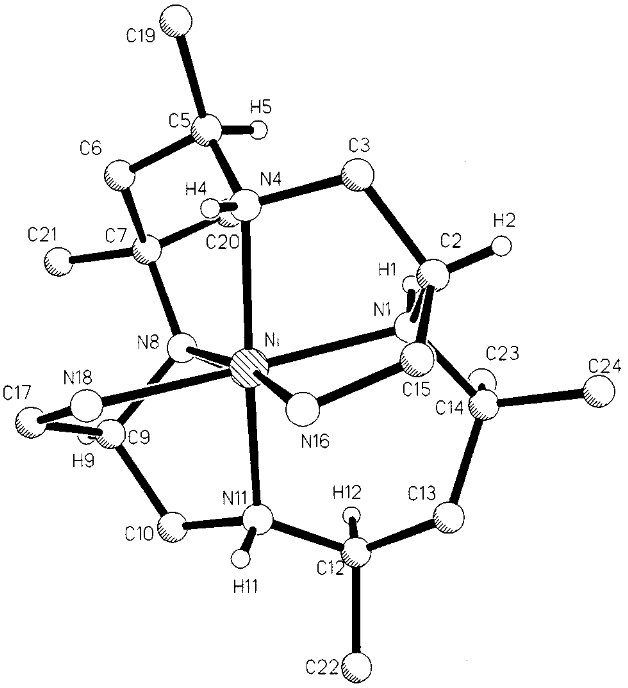


Figure 1. Molecular structure together with atomic labelling for cation **4a**

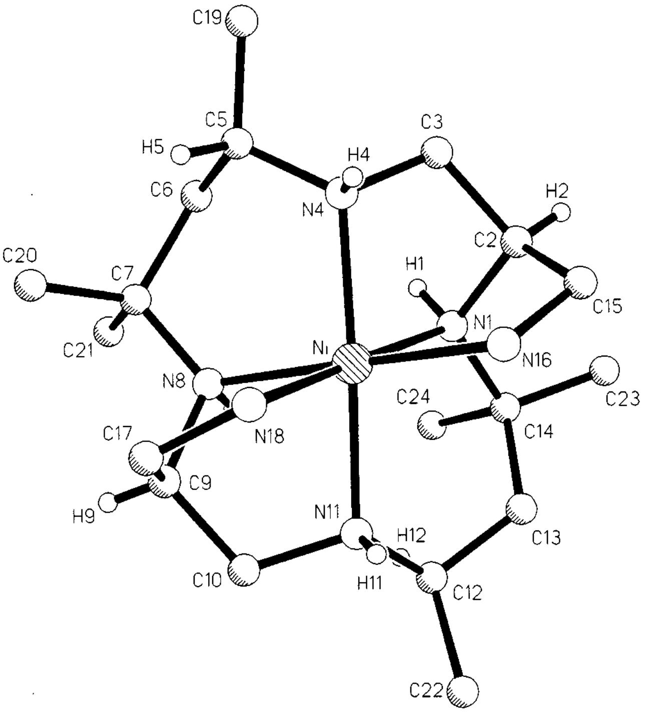


Figure 2. Molecular structure together with atomic labelling for cation **4b**

The shape and symmetry of any given ring is precisely described by its set of endocyclic torsion angles (ETAs) and the sequence of their signs.[11] The ETAs of complexes **4a** and **4b** are collected in Table 2, together with the appropriate *n*-butane conformational codes.

Table 2. Endocyclic torsion angles [°] and sequences of their configurational codes[a] for **4a** and **4b**

Torsion angles	**4a**		**4b**	
C3−C2−N1−C14	164.8	*a*	163.9	*a*
N4−C3−C2−N1	45.6	*g*	53.1	*g*
C5−N4−C3−C2	−134.5	−*ac*	−145.1	−*ac**
C6−C5−N4−C3	162.5	*a*	81.7	*g**
C7−C6−C5−N4	−77.0	−*g*	81.8	*g**
N8−C7−C6−C5	68.1	*g*	−63.5	−*g*
C9−N8−C7−C6	96.8	*ac**	152.0	*a**
C10−C9−N8−C7	164.4	*a*	154.1	*a**
N11−C10−C9−C8	45.3	*g*	49.5	*g*
C12−N11−C10−C9	−133.7	−*ac*	−145.6	−*ac**
C13−C12−N11−C10	164.6	*a*	150.8	*a**
C14−C13−C12−N11	−79.3	−*g*	−68.8	−*g*
N1−C14−C13−C12	69.7	*g*	69.7	*g*
C13−C14−N1−C2	97.0	*ac**	97.8	*ac**

[a] Codes for torsion angles: *a:* antiperiplanar (180 ± 30°), *ac:* anticlinical (120 ± 30°), *g:* gauche (60 ± 30°), *sp:* synperiplanar (0 ± 30°). − * Deformation > 20°.

The folded macrocycle of cation **4a** has C_2 symmetry and its conformation according to Boeyens notation[12] can be assigned as type V [3434]. The macrocycle forms two five-membered chelate rings in E_2 (*envelope*) and two six-membered rings in ^4E (*sofa*) conformation. In the isomeric cation **4b**, both of the endomacrocyclic five-membered rings and one of the six-membered chelate rings adopt similar E_2 (*envelope*) and ^4E (*sofa*) conformations, respectively. The second six-membered ring [N(4)−N(8)] adopts a $^3H_4$ (*half-chair*) conformation and the folded cyclam macrocycle assumes a type V [21434] form.

The 5,12-dimethyl and 2,9-bis(aminomethyl) substituents in isomer **4a** are located on the same side of the macrocyclic ring and the relative configuration of the chiral N and C atoms, according to Cahn−Ingold−Prelog rules,[13] is assigned as (1*R*2*S*4*R*5*S*8*R*9*S*11*R*). The methyl group attached to C-5 in cation **4b** is located on the opposite side of the macrocycle and the configuration of this isomer is assigned as (1*R*2*S*4*R*5*R*8*R*9*S*11*R*). The 5,12-dimethyl groups assume *equatorial* positions and the coordinated pendant arms are *axially* arranged in both isomeric complexes.

Structures of Square-Planar Complexes 5

The structures of the free ligands and of the diamagnetic complexes were established mainly on the basis of their ^{13}C- and ^{1}H-NMR spectra (Tables 3 and 4).

Under acidic conditions in nitromethane solution, the amino groups on the side-chains of complexes **3**, **4a** and **4b** are protonated, leaving the Ni^{II} ions in a square-planar configuration. This change in the Ni^{II} configuration is accompanied by a concomitant change in the conformation of the macrocycle from a folded to a planar one. However, the secondary nitrogen atoms in the ring retain their configurations in the course of this process. This can clearly be seen in the ^{1}H-NMR spectra of protonated complex **5aα** and its *N*-isomeric forms (**5aβ** and **5aγ**), most notably in the chemical shifts of the 7- and 14-geminal methyl substituent signals (Table 4).

The conformations of the methyl groups and of the six-membered chelate rings can be assigned on the basis of the known deshielding effects observed for axially oriented substituents in the ^{1}H-NMR spectra of square-planar macrocyclic Ni^{II} complexes.[14−17] The 5,12-dimethyl groups retain an *equatorial* arrangement in all the isomeric **5aα**, **5aβ** and **5aγ** complexes (Scheme 2).

The geminal 7,14-dimethyl groups in complex **5aα**, due to the non-chair conformation of the six-membered chelate

Table 3. 125.8-MHz ^{13}C-NMR spectra of complexes **5** and free ligands **6** (δ in ppm relative to TMS)

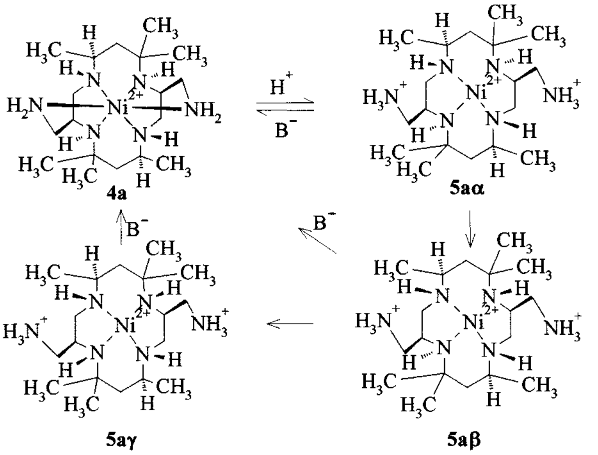
	Compound/Solvent						
Carbon atom	**5aα**[a] CD_3NO_2 + $HClO_4$	**5aβ** CD_3NO_2	**5aγ(ClO_4)$_4$**[a] CD_3CN	**5aγCl_4**[a] D_2O + DCl	**5b** CD_3NO_2 + $HClO_4$	**6a**[a] $CDCl_3$	**6b**[a] $CDCl_3$
7,14-CH_3	29.3 *ax*	24.8	26.2 *ax*	25.8 *ax*	25.6	25.4	24.5
	29.8 *eq*	26.9	28.2 *eq*	26.3 *eq*	27.3	28.9	28.3
		29.3			28.4		29.5
		29.9			29.5		31.1
5,12-CH_3	21.7	18.9	20.0	18.4	19.7	21.7	21.6
		18.9			19.7		22.0
2,9-CH_2NH_3	40.9	41.0	41.5	40.9	40.0	46.1	46.3
		41.9			41.7		47.2
C-2,9	51.8	54.4	54.5	55.4	55.7	52.9	51.8
		57.0			56.0		54.0
C-3,10	47.6	49.5	52.8	53.5	47.3	51.3	51.4
		52.7			50.2		52.5
C-5,12	55.0	53.8	53.6	53.9	52.1	51.7	50.8
		55.4			52.6		52.2
C-6,13	50.0	50.0	49.3	49.0	49.5	51.8	51.1
		50.0			49.9		52.2
C-7,14	56.5	56.5	59.3	58.7	57.5	54.0	52.6
		61.2			57.8		53.6

[a] Assignments were confirmed by 2D heteronuclear (^{1}H−^{13}C) experiments.

Table 4. 500.13-MHz ^{1}H-NMR spectra of complexes **5** and free ligands **6** (δ in ppm relative to TMS, *J* in Hz)[a]

Assignment	Compound/Solvent **5aα**[b] CD_3NO_2 + $HClO_4$	**5aβ** CD_3NO_2	**5aγ(ClO$_4$)$_4$**[b] CD_3CN	**5aγCl$_4$**[b] D_2O + DCl	**5b** CD_3NO_2 + $HClO_4$	**6a**[b] $CDCl_3$	**6b**[b] $CDCl_3$
7,14-CH_3	1.70 s 1.73 s	1.37 s, 1.47 s 1.74 s, 2.44 s	1.31 s 2.12 s	1.28 s 2.16 s	1.48 s, 1.57 s 1.58 s, 1.63 s	1.07 s 1.09 s	1.06 s, 1.07 s 1.10 s, 1.13 s
5,12-CH_3	1.27 d (5.2)	1.19 d (6.2) 1.26 d (7.0)	1.16 bd (2.6)	1.13 d (6.7)	1.31 d (6.0) 1.42 d (6.2)	0.98 d (6.1)	0.98 d (6.1) 1.04 d (6.4)
5,12-CH	3.87 b	3.65 m 3.58 m	3.76 bm	3.78 m		2.75 m	2.74 m 2.76 m
2,9-CH_2NH_3	3.88 b		3.61 dd (13.3, 4.0)	3.71 dd (13.6, 8.0)		2.66 dd (12.0, 6.9)	2.66 m 2.66 m
	4.55 b	2.6−4.1	3.75 dd (13.3, 10.0)	3.84 dd (13.6, 6.8)		2.76 m	2.58 dd (12.3, 6.9) 2.77 dd (12.3, 3.3)
2,9-CH	3.43 b		3.46 b	3.42 m		2.80 m	2.66 m 2.80 m
6,13-CH_2	1.59 dd (15.3, 9.4) 1.90 d (15.3)	1.52 dd (16.2, 12.2) 1.95 dd (16.2, 2.0) 1.67 dd (15.7, 10.2) 2.02 dd (15.7, 5.3)	1.48 dd (15.6, 11.5) 1.80 d (15.6)	1.53 dd (15.4,11.6) 1.84 d (15.4)	1.5−5.2	1.36 dd (14.7, 1.8) 1.53 dd (14.7, 11.1)	1.34 dd (14.5, 1.7) 1.49 dd (14.5, 9.5) 1.39 dd (14.8, 2.7) 1.46 dd (14.8, 10.9)
3,10-CH_2	2.54 b, 3.81 b	2.6−4.1	2.72 b 3.13 bd (11.1)	2.74 m 2.90 dd (13.3, 4.3)		2.44 dd (11.3, 3.3) 2.75 m	2.14 dd (10.6, 9.2) 2.82 dd (10.6, 2.9) 2.36 dd (11.1, 3.6) 2.92 dd (11.1, 2.3)
NH	3.20 b 4.19 b		2.47 b 3.08 b	3.75 bm 4.75 bs			
NH_3	7.35 b	7.22 b 7.36 b	6.90 b		7.10 b 7.25 b		

[a] s: singlet, d: doublet, m: multiplet, b: broad; coupling constants in parentheses. – [b] Assignments were confirmed by 2D heteronuclear (^{1}H–^{13}C) experiments.



Scheme 2. Isomerization pathway and configurations of square-planar complexes **5a**

rings, resonate at almost the same frequency. This indicates that the macrocycle in **5aα** retains a type-V conformation. The inversion at N(1) causes a switch in the N(1)–N(11) six-membered chelate-ring conformation to the chair form. This is reflected in the large separation of *axial* and *equatorial* 14-methyl group signals in the spectrum of **5aβ** and indicates a type-II conformation of the macrocycle. The second isomerization, caused by inversion at N(8), followed by conformational change in the second six-membered ring, results in formation of the cation **5aγ**. The macrocycle in **5aγ** adopts a type-I conformation, with all secondary amino protons and substituents in 2,5,9,12-positions on the same side of the ring.

Addition of perchloric acid to a nitromethane solution of the octahedral complex **4b** results in the formation of an orange square-planar complex, **5b**. The chemical shifts of the geminal methyl groups indicate a non-chair conformation of both six-membered chelate rings and a type-V conformation of the macrocycle. This complex also undergoes isomerization upon addition of protic solvents, but attempts to isolate and characterize the individual species as solids were not successful.

Electronic spectra in nitromethane solution, acidified with perchloric acid, show d–d transition bands at 506 nm ($\varepsilon = 188$) and 476 nm ($\varepsilon = 122$) for **5aα** and **5b**, respectively. The wavelengths of the bands are substantially longer and the molar absorption coefficients are higher than typically observed for Ni^{II} complexes of cyclam derivatives ($\lambda_{max} \approx 450$ nm, $\varepsilon \approx 80$).[18] This indicates strong distortion of the square-planar Ni^{II}N$_4$ geometry,[19] especially in the case of isomer **5aα**, which has six substituents on the same side of the macrocyclic ring. After isomerization, the less strained complex **5aβ** absorbs at 462 nm and the most stable cation **5aγ** at 454 nm, close to the usual wavelength for Ni^{II} square-planar complexes.

Conclusion

In Ni^{II} complexes of *cis*-2,9-bis(aminomethyl)-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecanes, coordination of the two pendant amino groups located on the same side of the tetraaza macrocyclic ring forces the ring to adopt a folded conformation. Protonation of the pendant donor groups by perchloric acid in nitromethane solution is accompanied by a concomitant return of the macrocycle to a preferred planar arrangement around the central Ni^{II} ion. Steric crowding in **5aα** and **5b**, as well as the unusual type-V conformation of the cyclam ring, leads to severe distortion of the square-planar geometry and to weakening of the ligand field. In the presence of protic solvents, consecutive inversions at chiral nitrogen atoms, accompanied by conversion of the macrocyclic ring conformation, lead to the more stable isomers **5aβ** and **5aγ**.

Experimental Section

General Remarks: IR spectra (paraffin oil mulls) were recorded with a Perkin-Elmer 1600 FT-IR spectrometer. NMR spectra were obtained with a Bruker AM 500 spectrometer using TMS as internal standard. Electronic spectra were recorded using a Cary 1E UV/Vis spectrophotometer and mass spectra with an AMD 604 spectrometer.

Synthesis: ***Caution! Perchlorate salts are potentially explosive!*** Preparation of complex **1** and its reduction with zinc dust and hydrochloric acid has been described previously.[8−10] Zinc amalgam was prepared according to the standard procedure.[20] Hydrochloric acid, perchloric acid, and solvents were commercial materials and were used without further purification.

Reduction of [5,7,7,12,14,14-Hexamethyl-2,9-*cis*-bis(nitromethyl)-1,4,8,11-tetraazacyclotetradeca-4,11-diene]nickel(II) Diperchlorate (1): Concentrated hydrochloric acid (75 mL) was added dropwise to a vigorously stirred mixture of zinc amalgam (25 g) and complex **1** (35 g) in a 1:1 water/methanol solution (400 mL), while the temperature was maintained below 20°C. After 24 h, the mixture was filtered, the filtrate was diluted with water (400 mL) and applied to a Dowex 50WX2 cation-exchange column (H^+ form). The column was washed with 1 M HCl (1 L) and then eluted with 3 M HCl. An orange eluate was obtained, which was concentrated to dryness. The residue was dissolved in 1 M perchloric acid and the solution was made alkaline by the addition of 50% sodium hydroxide solution. The violet precipitate thus obtained was filtered off, redissolved in 0.02 M perchloric acid, and the resulting orange solution was filtered and applied to an SP Sephadex C-25 column (12 × 60 cm). The column was washed with water and eluted with 0.2 M sodium sulfate solution. Four orange bands were collected, which were each absorbed onto Dowex 50WX2 columns and, after washing with 1 M HCl, were eluted with 3 M HCl. Orange eluates were obtained, which were concentrated to dryness. The respective residues were dissolved in 1 M perchloric acid and neutralized with NaOH (50%). On cooling, violet crystals formed, which were filtered off and recrystallized from water. Minor fractions 1 and 2 were found to contain two isomeric products **4a** (0.5 g, 1.7%) and **4b** (0.3 g, 1%), respectively, in which besides the nitro groups both of the C=N double bonds were reduced. The third fraction contained product **3** (3.2 g, 10%) with two aminomethyl groups and one C=N double bond. The major fourth fraction contained complex **2** (12.5 g, 39%).

[2,9-Bis(aminomethyl)-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane]nickel(II) Diperchlorates 4a and 4b: Concentrated hydrochloric acid (30 mL) was added dropwise over a period of 30 min to a vigorously stirred mixture of zinc amalgam (10 g) and complex **2** (4 g) in water (200 mL), while the temperature was maintained below 20°C. Stirring was continued for 72 h and then the mixture was applied to a Dowex 50WX2 cation-exchange column (H^+ form). The column was washed with 1 M HCl and eluted with 3 M HCl. An orange eluate was collected, which was concentrated to dryness. The residue was dissolved in water and the resulting solution was applied to an SP Sephadex C-25 column (5 × 50 cm). Four fractions were eluted with 0.2 M sodium sulfate solution and were worked up according to the same procedure as described above. 2.3 g (58%) of **4a**, 0.9 g (22%) of **4b**, 0.5 g (12%) of **3**, and 0.2 g (5%) of **2** were isolated and crystallized from water. − **3**: $C_{18}H_{40}Cl_2N_6NiO_8$ (598.2): calcd. C 36.0, H 6.7, Cl 11.8, N 14.0; found C 35.9, H 7.3, Cl 11.3, N 14.0. − ^1H NMR (500.13 MHz, CD_3NO_2 + $HClO_4$): δ = 1.32 (d, *J* = 6.8 Hz, 12-CH_3), 2.29 (s, 5-CH_3), 1.51, 1.54, 1.59, 1.71 (s, 7,14-CH_3). − ^{13}C NMR (125.8 MHz, CD_3NO_2 + $HClO_4$): δ = 19.2, 24.5, 25.9, 26.5, 28.3, 29.2 (CH_3), 39.4 and 43.1 (CH_2NH_3), 50.0, 50.0, 52.8, 55.3, 55.3, 55.8, 56.0, 56.4, 56.9, 191.9 (macrocyclic ring C atoms). − IR (Nujol): $\tilde{\nu}$ = 3354, 3308, 3280, 3201 cm^{-1} (ν N−H); 1652 (ν C=N), 1622 (δ N−H), 1099 and 624 (ClO_4^-). − UV/Vis (methanol): λ_{max} (ε_{max}) = 331 nm (67 $dm^3cm^{-1}mol^{-1}$), 510 (11.8), 813 (9.5). − **4a**: $C_{18}H_{42}Cl_2N_6NiO_8\cdot H_2O$ (618.2): calcd. C 35.0, H 7.2, Cl 11.5, N 13.6; found C 34.6, H 7.3, Cl 11.5, N 14.4. − IR (Nujol): $\tilde{\nu}$ = 3612, 3542 cm^{-1} (ν H_2O); 3346, 3306, 3283, 3204 (ν N−H); 1617 (δ N−H), 1110 and 623 (ClO_4^-). − UV/Vis (methanol): λ_{max} (ε_{max}) = 332 nm (13.2 $dm^3cm^{-1}mol^{-1}$), 516 (10.3), 812 (9.8). − **4b**: $C_{18}H_{42}Cl_2N_6NiO_8$ (600.2): calcd. C 36.0, H 7.1, Cl 11.8, N 14.0; found C 36.0, H 7.6, Cl 11.1, N 14.5. − IR (Nujol): $\tilde{\nu}$ = 3348, 3301, 3287 sh, 3276 sh, 3209 cm^{-1} (ν N−H); 1607 (δ N−H), 1099 and 625 (ClO_4^-). − UV/Vis (methanol): λ_{max} (ε_{max}) = 331 nm (14.8 $dm^3cm^{-1}mol^{-1}$), 514 (10.6), 814 (9.8).

[2,9-Bis(ammoniomethyl)-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane]nickel(II) Tetrachloride (5aγ): The fraction containing **4a** in hydrochloric acid, eluted from the Dowex column as described above, was concentrated to dryness. The remaining oily residue was crystallized from methanol. Orange crystals were filtered off and dried in vacuo. − $C_{18}H_{44}Cl_4N_6Ni \cdot H_2O$ (563.1): calcd. C 38.4, H 8.2, Cl 25.2, N 14.9; found C 38.2, H 8.1, Cl 25.2, N 14.9. − IR (Nujol): $\tilde{\nu}$ = 3401 cm^{-1} (ν O−H), 3106, 3070 (ν N−H); 1607 and 1541 (δ N−H and δ O−H). − UV/Vis (methanol): λ_{max} (ε_{max}) = 452 nm (117 $dm^3cm^{-1}mol^{-1}$).

[2,9-Bis(ammoniomethyl)-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane]nickel(II) Tetraperchlorate (5aβ): Complex **4a** (0.124 g, 0.2 mmol) was dissolved in 1 mL of nitromethane, acidified with perchloric acid (70%, 0.2 mL). The solution was then diluted with absolute ethanol (10 mL), whereupon the color changed from deep-red to orange. The solvents were removed under reduced pressure to leave an orange solid (ca. 0.10 g), which was washed with ethanol and dried in vacuo. The complex **5aβ** isomerized into **5aγ** (tetraperchlorate tetrahydrate) during recrystallization from ethanol. − **5aβ**: $C_{18}H_{44}Cl_4N_6NiO_{16} \cdot 4\ H_2O$ (873.2): calcd. C 24.8, H 6.0, Cl 16.2, N 9.6; found C 24.3, H 6.2, Cl 17.0, N 9.4. − IR (Nujol): $\tilde{\nu}$ = 3598, 3543 cm^{-1} (ν O−H); 3191 (ν N−H), 1620 and 1531 (δ N−H and δ O−H); 1095, 625 (ClO_4^-). − UV/Vis (nitromethane): λ_{max} (ε_{max}) = 462 nm (115 $dm^3cm^{-1}mol^{-1}$). − **5aγ**: $C_{18}H_{44}Cl_4N_6NiO_{16} \cdot 4\ H_2O$ (873.2): calcd. C 24.8, H 6.0, Cl 16.2, N 9.6; found C 24.9, H 5.9, Cl 16.0, N 9.7. − IR (Nujol): $\tilde{\nu}$ = 3610 sh, 3536 cm^{-1} (ν O−H); 3189 (ν N−H), 1619 sh, 1598, 1521 (δ N−H and δ O−H); 1107, 624 (ClO_4^-). − UV/Vis (nitromethane): λ_{max} (ε_{max}) = 454 nm (120 $dm^3cm^{-1}mol^{-1}$).

2*SR*,9*SR*-Bis(aminomethyl)-5*SR*,7,7,12*SR*,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (6a): A mixture of sodium cyanide (0.75 g, 0.015 mol) and complex **4a** (1.5 g, 2.5 mmol) in 50 mL of water was refluxed for 2 h. After cooling, sodium hydroxide (2 g) was added and the solution was extracted with chloroform. The combined chloroform extracts were dried with magnesium sulfate, filtered, and concentrated to dryness. The oily residue was dissolved in acetonitrile (5 ml) and the resulting solution was stored

Table 5. Crystal data and measurement conditions for **4a** and **4b**

	4a	**4b**
Formula	$C_{18}H_{42}Cl_2N_6NiO_8 \cdot H_2O$	$C_{18}H_{42}Cl_2N_6NiO_8$
Molecular weight	618.19	600.17
Crystal system	monoclinic	orthorhombic
a [Å]	10.692(1)	16.417(2)
b [Å]	20.985(2)	16.039(2)
c [Å]	12.614(1)	20.384(3)
β [°]	99.74(1)	90
V [Å^3]	2789.4(5)	5367.4(12)
Z	4	8
Calculated density [g · cm^{-3}]	1.47	1.49
Space group	$P2_1/n$	$Pbca$
Radiation (graphite-monochromated)	Mo-K_α	Mo-K_α
Wavelength [Å]	0.71069	0.71069
Linear absorption coeff. μ [mm^{-1}]	0.94	0.97
Number of electrons F(000)	1312	2544
Crystal size [mm]	0.25 × 0.22 × 0.18	0.27×0.23×0.21
Temperature [°C]	22 ± 1	22 ± 1
Diffractometer	Syntex P2$_1$	Syntex P2$_1$
Scan mode	Θ/2Θ	Θ/2Θ
Scan range (2Θ) [°]	0−54	0−54
Number of collected data:		
totally measured	2666	2739
unique [with $I > 2\ \sigma(I)$]	2138	2081
$R1$	0.0595	0.0666
$wR2$	0.1140	0.1262
GooF	1.092	1.089

in a refrigerator until crystals formed. After ca. one week, 0.7 g (81%) of colorless crystals were filtered off and dried in vacuo; m.p. 89−90°C. − $C_{18}H_{42}N_6 \cdot 2\ H_2O$ (378.4): calcd. C 57.1, H 12.2, N 22.2; found C 57.7, H 12.1, N 21.8. − HR MS: calcd. for $C_{18}H_{42}N_6$ 342.3471; found 342.3467.

2*SR*,9*SR*-Bis(aminomethyl)-5*RS*,7,7,12*SR*,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (6b): The free ligand was prepared from complex **4b** according to the same procedure as above; m.p. 92−96°C. − Yield 80%. − $C_{18}H_{42}N_6 \cdot H_2O$ (360.4): calcd. C 60.0, H 12.3, N 23.3; found C 60.2, H 12.0, N 23.1. − HR MS: calcd. for $C_{18}H_{42}N_6$ 342.3471; found 342.3457.

X-ray Crystallography: Well-shaped crystals of compounds **4a** and **4b** were selected for X-ray-diffractometric measurements. In both cases, the cell constants were obtained from least-squares refinement based on 25 setting angles. The stabilities of the crystals were checked by monitoring 2 control reflections at 50 reflection intervals; no appreciable decay was observed. Lorentz and polarization corrections were applied to all collected data. No absorption corrections were performed at the measurement stage. Table 5 shows the crystal data and measurement conditions for **4a** and **4b**. Models of the two structures were obtained by direct methods using the program SHELXS-86[21] and a series of subsequent Fourier difference syntheses (program SHELX-93[22]) revealed the positional parameters for all non-hydrogen atoms. The same refinement procedure was applied in both cases: Initially, the positional and isotropic temperature factors for non-hydrogen atoms were refined by full-matrix, least-squares procedures (program SHELX-93). Further refinement steps were performed in anisotropic mode for the non-hydrogen atoms. The positional parameters for *C*-attached hydrogen atoms were calculated from assumed geometries. They were added to parameter sets and refined in isotropic mode in separate blocks. The highest residual electron density peaks observed in each case on final difference maps were below 0.4 eÅ^{-3}.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101460. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44-1223/336033; E-mail: deposit@ccdc.cam.ac.uk].

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