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Reassignment, Isolation, Spectral and X-ray Characterization of Diastereoisomers of the Macrocyclic Ligand 3,10-*meso*-3,5,7,7,10,12,14,14-Octamethyl-1,4,8,11-tetraazacyclotetradecane and their Ni^{II} and Cu^{II} Complexes

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Reduction of the macrocyclic ligand, 3,10-*meso*-3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradecane-4,11-diene dihydroperchlorate (L), with sodium borohydride yielded three [L_b (**1**), L_c (**2**), and L_d (**3**)] of four possible diastereoisomers. The diastereoisomeric macrocycles and their Ni^{II} and Cu^{II} complexes have been characterized and confirmed by IR, UV/Vis, and NMR spectroscopy as well as X-ray crystallography. The chiral carbon centers and methyl groups at the 5 and 12 positions of **1**, **2** and **3** have the 5*S*,12*R*-C-*meso*, 5*S*,12*S*-C-*racemic*, and 5*R*,12*R*-C-*racemic* configurations, respectively. In accordance with the X-ray structure determination, the geometry around the Ni^{II} ion in the complexes is approximately square-planar and the Cu^{II} ion has an octahedral geometry. The N–H configuration of $[NiL_c](ClO_4)_2(H_2O)_{0.5}$ (**5**) is *trans*-II, different from the most thermodynamically stable *trans*-III configuration that is found in $[NiL_b](ClO_4)_2$ (**4**), $[CuL_b(H_2O)_2](ClO_4)_2$ (**7**), and $[CuL_d(ClO_4)_2]$ (**8**). UV/Vis spectra reveal that Ni^{II} complexes exhibit almost 100 % planar species in aqueous solution resulting from steric effects produced by numerous methyl groups, especially axial orientations and distorted structures. In six coordinate Cu^{II} complexes, acetonitrile acts as a better axial donor than the water molecule; the weaker axial bonding is a result of steric interactions that lead to stronger in-plane coordinations.

Introduction

The 14-membered tetraazacyclotetradecane macrocyclic ligands have been exploited extensively in different fields of research such as catalysis, bioinorganic, biomimetic, building blocks in supramolecular, and coordination chemistry.[1] These ligands have provided the ideal coordination sites for many metal ions and have been used as metal ion binding sites in medical techniques such as MRI and radioimmunotherapy.[2] Many of these metal complexes can be used as catalysts in redox reactions.[3] For instance, nickel complexes are used to produce CO through the photochemical and electrochemical reduction of CO_2.[4]

The stereochemistry of the 14-membered tetraazacyclotetradecane macrocyclic ligands and their metal complexes is very rich because of the presence of several asymmetric carbons and four N–H groups on their skeleton.[5] One such macrocyclic ligand can have numerous diastereoisomeric forms.[5] The macrocyclic molecule 3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclo-tetradecane-4,11-diene, Me_8-[14]diene, which has two chiral centers at the 3 and 10 positions, exhibits three noninterconvertible diastereoisomers, 3*S*,10*R*-*meso*- Me_8[14]diene (L), 3*R*,10*R*-*racemic*-Me_8[14]-diene, and 3*S*,10*S*-*racemic*-Me_8[14]diene (Scheme 1). Nickel(II) complexes of these ligands were obtained from a template reaction of tris[(±)-1,2-propanediamine]nickel(II) perchlorate, tris[(+)-1,2-propanediamine]nickel(II) perchlorate, or tris[(–)-1,2-propanediamine]nickel(II) perchlorate with acetone and were characterized by proton NMR spectroscopy.[6] In addition, the Nickel(II) complex of 3,10-*meso*-Me_8[14]diene was confirmed by X-ray crystallography.[6a,7] In a different approach, the reaction of (±)-1,2-propanediamine hydroperchlorate with acetone yields stereospecifically only the crystalline 3,10-*meso*-Me_8[14]-diene·$2HClO_4$.[6a,8] Failure to isolate any C-*rac* isomer apparently results from a higher solubility of the C-*rac* salt. Treatment of (–)-1,2-propanediamine hydroperchlorate with

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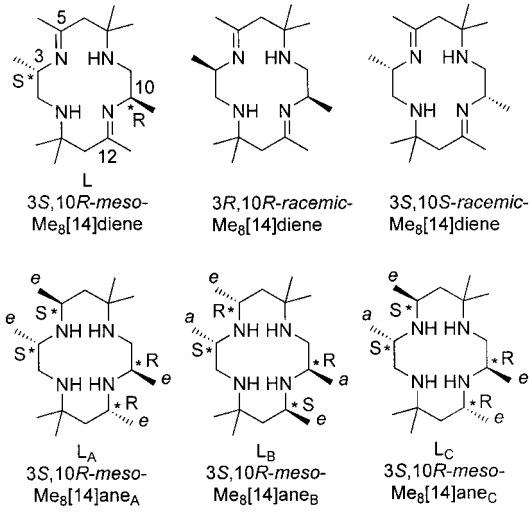
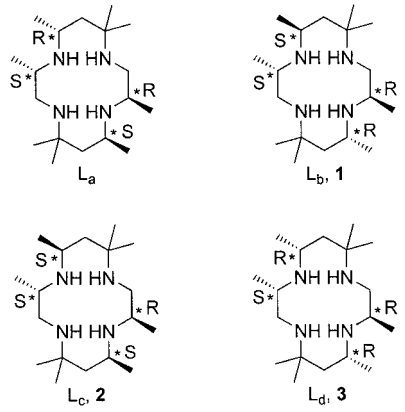
acetone yields no crystalline product under these conditions.[6a] The configuration of 3,10-*meso* is designated as 3*S**,10*R**-*meso*. Reduction of 3,10-*meso*-Me_8[14]diene with $NaBH_4$ generates another two chiral centers at the 5 and 12 positions and gives an isomeric mixture of the corresponding saturated macrocycles, 3,10-*meso*-Me_8[14]anes.[8] These molecules and their *N*-alkylated derivatives have been characterized and studied in the field of kinetics, coordination chemistry, and environmental monitoring.[9] The Cr^{III} complexes of these ligands have been used as sensor materials, artificial ionophores, and in membrane electrodes.[10] Antimicrobial activity of these ligands and their complexes have been investigated.[11] Despite their huge importance and usefulness in different fields of science, proper assignment of these diastereoisomeric ligands and their complexes has been lacking.



Scheme 1.

Although the assignment of diastereoisomeric forms of macrocyclic ligands and their complexes are an arduous problem, Bembi et al.[8] argued that the reduction of 3,10-*meso*-Me_8[14]diene would give three isomeric 3,10-*meso*-Me_8[14]anes. These were isolated and denoted as 3,10-*meso*-Me_8[14]ane_A (L_A), 3,10-*meso*-Me_8[14]ane_B (L_B) and 3,10-*meso*-Me_8[14]ane_C (L_C) (Scheme 1). Bembi and coworkers characterized these ligands and their complexes by either NMR spectroscopy on its own or by both NMR spectroscopy and X-ray crystallography. In this context we have found two main flaws with their assignment and characterization of these ligands and their complexes: (i) The basis on which they have assigned the ligands L_A–L_C is nebulous. The *RS*-configuration of the chiral methyls of L_A and L_C are the same. L_C differs from L_A in having one chiral methyl at the axial position. Thus, L_C is nothing but a conformer of L_A. The methyl orientations (axial or equatorial) of ligand L_A (or L_C) in its complexes with metals match those of L_b rather than those of L_A (or L_C), although they have the same *RS*-configuration, i.e., L_A and L_C are conformers of L_b. (ii) Ligand L_B and its Ni^{II} complex, $[NiL_{B\alpha}](ClO_4)_2$, were characterized by X-ray crystallography,[8,9h] but if one undertakes a critical investigation it can be seen that in both cases crystal structures of the ligand moiety appeared as the conformer of L_A and not L_B. Thus, proper assignment of the diastereoisomers obtained from the reduction reaction of 3,10-*meso*-Me_8[14]diene is very much needed and important. In this paper we describe the reassignment, isolation, spectral and X-ray characterization of diastereoisomers of 3,10-*meso*-3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradecane and their Ni^{II} and Cu^{II} complexes. The assignment of diastereoisomers has been performed on the basis of *RS*-configuration. Thus, reduction of 3,10-*meso*-Me_8[14]diene would give four diastereoisomeric macrocycles, L_a (*SRRS*), L_b (**1**, *SSRR*), L_c (**2**, *SSRS*) and L_d (**3**, *SRRR*) (Scheme 2). Over the course of reduction, the configurations of chiral methyls at position 3 (3*S*) and 10 (10*R*) remain intact. L_a and **1** have mesomeric configuration whereas **2** and **3** are enantiomers of one another. Isomers were separated by fraction crystallization from a methanol/water mixture. The solubility of the *meso* isomers is lower and hence they separated first. Isomer L_a cannot be isolated following the experimental methods described in the text, but we have still assigned it as 3*S*,10*R*-C-*meso*-5*R*,12*S*-C-*meso*-Me_8[14]ane. According to the results from NMR spectroscopy and X-ray crystallography studies, the structures of isomers **2** and **3** are indeed different from the literature reports. The square-planar Ni^{II} and elongated octahedral Cu^{II} complexes have also been characterized by UV/Vis spectroscopy in order to study the behavior of the d–d transitions and axial additions.



Scheme 2.

Results and Discussion

Synthesis

Reduction of L with $NaBH_4$ gave an isomeric mixture of the corresponding saturated macrocycles, 3*S*,10*R*-*meso*-Me_8[14]anes. 3*S*,10*R*-C-*meso*-Me_8[14]ane exists as four diastereoisomeric isomers, two 5,12-C-*meso* (L_a, **1**) and two 5,12-C-*racemic* (**2**, **3**) forms. By using the partial crystallization method, the *meso* and *racemic* isomers could easily be separated. Although the isomer L_a could not be isolated following the experimental methods described in the text, we have assigned it as 3*S*,10*R*-C-*meso*-5*R*,12*S*-C-*meso*-

Me_8[14]ane. The two *rac* forms are enantiomers of each other and are difficult to separate completely because of their similar chemical properties. To date no effective method has been found to separate isomeric C-*rac*-macrocycles, e.g. a (7*S*,14*S*)/(7*R*,14*R*)-C-*rac*-Me_6[14]ane (tet b) or (5*S*,12*S*)/(5*R*,12*R*)-C-*rac*-Me_2[14]ane mixture. Crystals of **1** and **2** were obtained from ether solutions. The reactions of isomeric ligands with nickel acetate tetrahydrate in a refluxing methanol solution produced green nickel(II) complexes. After adding lithium perchlorate trihydrate, the yellow square-planar nickel(II) complexes were obtained. The complexes were crystallized from acetonitrile or a water/methanol mixture. Reacting copper perchlorate hexahydrate with the isomeric ligands provided the octahedral Cu^{II} complexes. Crystals were obtained from the methanol/water mixture.

^{1}H NMR Spectroscopy

Although the one-dimensional ^{1}H NMR spectra of macrocycles and their Ni^{II} complexes are not well resolved, they present some key features that can be used to assign their configurations. From the ^{1}H NMR spectra the chiral and geminal methyl groups can easily be identified as well as the equatorial and axial methyls. The splitting pattern of the signals for the chiral methyls is a doublet whereas for the geminal methyls a singlet signal is seen. Thus geminal dimethyl groups give two singlet signals, one for the equatorial and the other for the axial methyl group. The number of chiral methyl signals varies depending on their axial and equatorial positions. The singlet at the higher field is assigned to the signal for the equatorial methyl protons and the remaining intense singlet to the axial group.[6b,8,9c,9h,12] In the case of **1** and **4**, ^{1}H NMR spectra (Table 1) show four signals; two for the geminal dimethyls and the remaining two for the chiral methyls. This reveals that the molecules **1** and **4** have centrosymmetric symmetry. In the case of **2** and **5** eight signals are observed, four for the geminal dimethyls and the remaining four for the chiral methyls. This reveals that the molecules **2** and **5** are asymmetric.

Table 1. Selected ^{1}H NMR spectroscopic data of ligands **1**–**2** and Ni^{II} complexes **4**–**5**.[a]

Ligands / Complexes	Geminal dimethyl	Methyl on chiral carbon atoms
1	1.05 s (*e*, 6 H)	0.96 d (*e*, 6 H)
	1.11 s (*a*, 6 H)	1.01 d (*a*, 6 H)
2	0.98 s (*e*, 3 H)	0.91 d (*e*, 3 H)
	0.99 s (*e*, 3 H)	0.97 d (*a*, 3 H)
	1.03 s (*a*, 3 H)	1.01 d (*a*, 3 H)
	1.06 s (*a*, 3 H)	1.02 d (*a*, 3 H)
4	1.20 s (*e*, 6 H)	1.15 d (*e*, 6 H)
	1.81 s (*a*, 6 H)	1.60 d (*a*, 6 H)
5	1.17 s (*e*, 3 H)	1.14 d (*e*, 3 H)
	1.27 s (*e*, 3 H)	1.19 d (*e*, 3 H)
	2.29 s (*a*, 3 H)	1.50 d (*a*, 3 H)
	2.49 s (*a*, 3 H)	1.93 d (*a*, 3 H)

[a] s = singlet, d = doublet, *a* = axial, *e* = equatorial.

Ligand 1 and Complex 4

In both cases, the methyl signals appear as two singlets and two doublets corresponding to six protons each. This requires the structure to have centrosymmetric symmetry, since the methyl groups are clearly pair-wise equivalent. In the case of **1**, two singlets at δ = 1.05 and 1.11 ppm can be assigned to the geminal dimethyl groups at the 7 and 14 positions. The upfield singlet at δ = 1.05 ppm can be assigned to equatorial methyl groups and the downfield singlet at δ = 1.11 ppm to axial methyl groups. The upfield doublet at δ = 0.96 ppm is due to two equatorially oriented methyl groups, whereas the downfield doublet at δ = 1.01 ppm is assigned to two axially oriented methyl groups. Similar observations have also been found in the case of **4**, two singlets at δ = 1.20 and 1.81 ppm can be assigned to geminal dimethyl groups at the 7 and 14 positions. The upfield singlet at δ = 1.20 ppm can be assigned to equatorial methyl groups and the downfield singlet at δ = 1.81 ppm to axial methyl groups. The 1.15 ppm (J_{HH} = 5.75 Hz) doublet is assigned to two equatorially oriented methyl groups, while the 1.60 ppm (J_{HH} = 6.71 Hz) doublet is assigned to two axially oriented methyl groups. A diequatorial-diaxial arrangement for the four chiral methyl groups is possible in **1** and **4**.

Ligand 2 and Complex 5

Differing greatly from **1**, the spectra of **2** and **5** show that the methyl signals give four singlets and four doublets, where each signal corresponds to three protons. In the case of **2**, the singlets at 0.98, 0.99, 1.03, and 1.06 ppm can be assigned to geminal dimethyl groups at the 7 and 14 positions and the doublets at 0.91, 0.97, 1.01, and 1.02 ppm can be assigned to four chiral methyl groups at the 3, 5, 10, and 12 positions. Two upfield singlets at δ = 0.98 and 0.99 ppm appear due to two equatorially oriented methyl groups, while the downfield doublet at δ = 1.03 and 1.06 ppm is assigned to two axially oriented methyl groups. The doublet at the highest field can be assigned to an equatorially oriented methyl group and another doublet at δ = 0.97 ppm to an axially oriented methyl group. The similar chemical shifts and coupling constants of the two remaining doublets at δ = 1.01 and 1.02 ppm indicate that the two chiral methyl groups have a similar chemical environment. Therefore, the two doublets at the lower field should be assigned to axial oriented methyl groups. Thus an equatorial-triaxial arrangement for the four chiral methyl groups is possible in the structure. In the case of **5**, the methyl signals also give four singlets and four doublets, where each signal corresponds to three protons. The singlets at 1.17, 1.27, 2.29, and 2.49 ppm can be assigned to the 7,7,14,14-tetramethyl groups. Two upfield singlets at δ = 1.17 and 1.27 ppm appear due to two equatorially oriented methyl groups and the downfield doublets at δ = 2.29 and 2.49 ppm are due to two axially oriented methyl groups. The doublets at 1.14 (J_{HH} = 6.46 Hz), 1.19 (J_{HH} = 5.75 Hz), 1.50 (J_{HH} = 7.21 Hz), and 1.93 (J_{HH} = 7.43 Hz) ppm can be assigned to four chiral methyl groups, where the two doublets at higher field can be assigned to equatorially oriented methyl groups

and the other two doublets to the axially oriented methyl group. A diequatorial-diaxial arrangement for the four chiral methyl groups is possible in the structure. The different results of the methyl orientations in **2** and **5** are because of the nitrogen inversions.

^{13}C NMR Spectroscopy

On the basis of ^{13}C NMR spectra, the symmetric and asymmetric macrocyclic ligands and their nickel(II) complexes can clearly be distinguished. Each stereochemically distinct carbon atom displays a separate resonance. However, most resonances cannot be assigned to corresponding carbons by using ^{13}C NMR spectra alone. Even so, there is enough evidence to define whether the structures are symmetric or asymmetric from the ^{1}H NMR, ^{13}C NMR and X-ray spectral studies. The ^{13}C NMR spectra of **1** and **4** show nine peaks as a result of pair-wise equivalence of the carbon atoms, while eighteen peaks are seen in the case of **2** and **5** because of the eighteen nonequivalent carbon atoms. On the basis of DEPT-135 experiments, the peaks in the range from 15 to 30 ppm can be assigned to eight carbon atoms of peripheral methyl groups and the remaining peaks in the range from 40 to 60 ppm correspond to ring carbon atoms. The results are supported by similar observations for C-*meso*-Me_8[14]diene and Me_4[14]denen. Both complexes, [Ni(*Aα*-Me_4[14]denen)]$^{2+}$ (symmetry) and [Ni(*Bβ*-Me_4[14]denen)]$^{2+}$ (asymmetry), containing fourteen carbon atoms show fourteen and seventeen peaks, respectively.[13] Similar observations have also been found in the case of two isomeric *trans*-[Co([15]ane)Cl_2]$^{+}$ complexes.[14] In the case of symmetric C-*meso* and C-*rac*-Me_6[22]ane, twelve peaks are seen owing to the pair-wise equivalence of the carbon atoms.[15]

Cu^{II} complexes (**7** and **8**) are NMR inactive. Hence, these were confirmed by X-ray crystallography.

Crystal Structures

The crystal structures of ligands and complexes are shown in Figures 1, 2, 3, 4, 5, and 6, which are drawn with ORTEP at the 30% probability level. Structural configurations and methyl orientations are shown in Scheme 3. Selected bond lengths and bond angles are listed in Tables 2, 3, and 4. The geometry around the nickel(II) ion in the complexes is approximately square-planar and around the copper(II) ion it is octahedral.

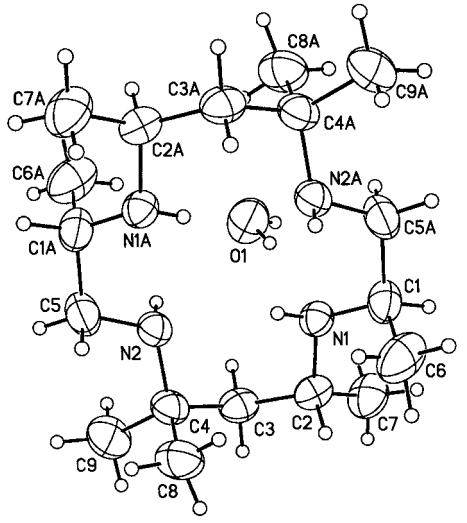


Figure 1. An ORTEP view of ligand **1**.

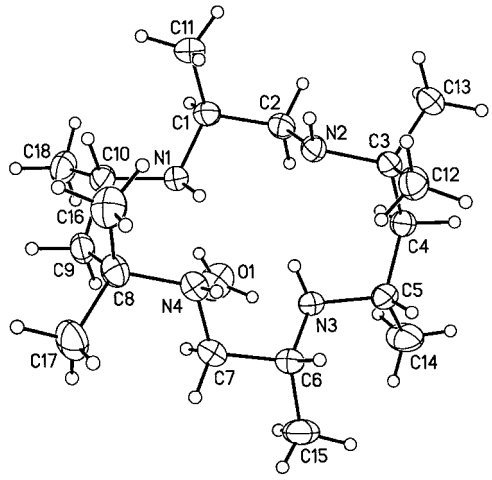


Figure 2. An ORTEP view of ligand **2**.

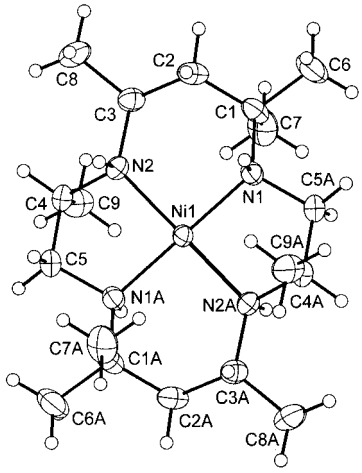


Figure 3. An ORTEP view of complex **4**.

Ligand 1

An inversion center is present in the molecule. The structure determination indicates that the ring lies in a zigzag shape with tetramine equatorial positions. The configurations of the four chiral carbon centers are 3*S*, 5*S*, 10*R*, and 12*R*. The 3,10-dimethyl groups occur on opposite sides of the ring in a *meso* configuration and have an axial orientation. Moreover, the 5,12-dimethyl groups also occur on opposite sides of the ring in a *meso* configuration but have an equatorial orientation. All distances and angles fall within the normal ranges. The H(1) atom of the water molecule forms an O–H···N hydrogen bond with a length of 2.129(1) Å with the N(1) atom of the secondary amine. The other distance, between the water H(1) atom and the amine

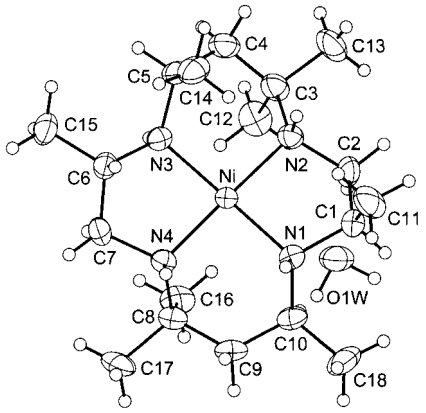


Figure 4. An ORTEP view of complex **5**.

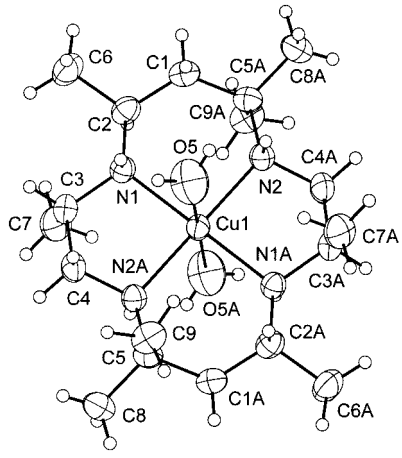


Figure 5. An ORTEP view of complex **7**.

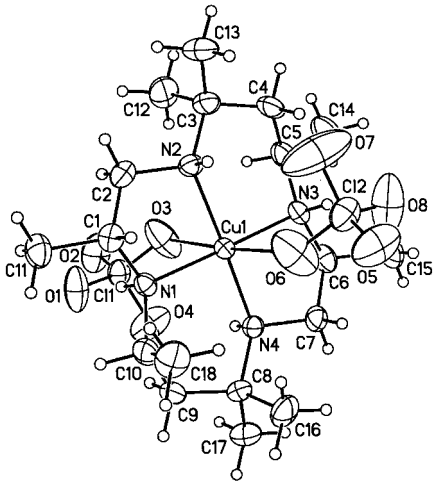
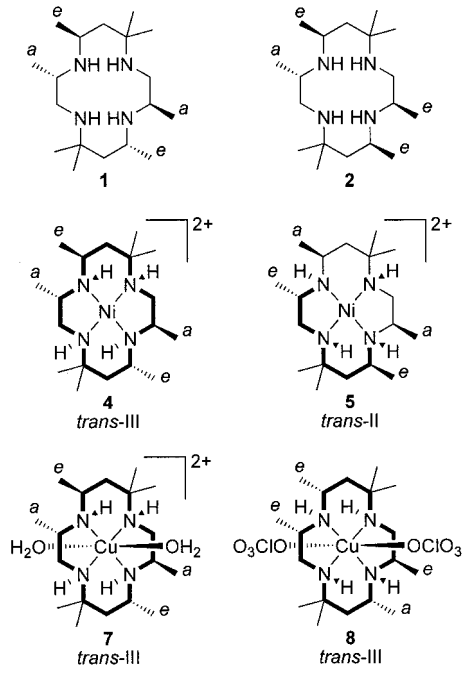


Figure 6. An ORTEP view of complex **8**.

N(2) atom, is 2.993(2) Å. The distance, 2.619(2) Å, between the O(1) atom and the H(2A) atom shows that the water O(1) atom is also slightly hydrogen bonded to the amine H(2A) atom. A diequatorial-diaxial arrangement for the four chiral methyl groups is observed in the structure, where the methyl groups at the 5 and 12 positions occupy a *meso* configuration.



Scheme 3. *gauche* conformations of the five-membered chelate rings and chair conformations of the six-membered chelate rings are indicated by heavier lines.

Ligand 2

The 14-membered ring has a noncentrosymmetric and folded structure where two diagonal nitrogen atoms point up and the other two down, and a water molecule is located on a crystallographic two-fold center. The configurations of the four chiral carbon centers are 3*S*, 5*S*, 10*R*, and 12*S*. All four NH groups and the 3-methyl group lie on the same side of the ring, while the water molecule and 5,10,12-trimethyl groups are on the other side. The 3-methyl group retains an axial orientation and the 5,10,12-trimethyl groups have an equatorial orientation with 3,10-dimethyl in a *meso* configuration and 5,12-dimethyl in a *racemic* configuration. The distances of the intermolecular O(1)–H(1A)···N(1) and O(1)–H(1B)···N(3) hydrogen bonds are 2.218(1) and 2.052(1) Å, respectively. An equatorial-triaxial arrangement for the four chiral methyl groups is possible in the structure, where the methyl groups at the 5 and 12 positions occupy a *racemic* configuration.

Complex 4

The X-ray analysis reveals that the Ni^{II} ion is located on a center of inversion and coordinated by four nitrogen atoms in equatorial positions to form a distorted square-planar geometry. The 14-membered ring consists of two six-membered chelate rings in chair conformations and two five-membered chelate rings in *gauche* conformations. The complex has a 1*R*,4*S*,8*S*,11*R* configuration of the four N chiral centers. The most thermodynamically stable nitrogen configuration is supposed to be the *trans*-III (–++–)[5a] configuration. The four chiral carbon centers are in the

Table 2. Selected bond lengths [Å] and angles [°] for ligands **1** and **2**.[a]

1			
N(1)–C(1)	1.464(2)	N(1)–C(2)	1.469(2)
N(2)–C(5)	1.460(1)	N(2)–C(4)	1.480(1)
C(1)–C(5^{i})	1.523(2)	C(1)–C(6)	1.527(2)
C(2)–C(7)	1.524(2)	C(2)–C(3)	1.527(2)
C(3)–C(4)	1.541(2)	C(4)–C(8)	1.528(2)
C(4)–C(9)	1.541(2)	C(5)–C(1^{i})	1.523(2)
C(1)–N(1)–C(2)	116.73(8)	C(5)–N(2)–C(4)	117.02(9)
N(1)–C(1)–C(5^{i})	108.60(9)	N(1)–C(1)–C(6)	114.57(10)
C(5^{i})–C(1)–C(6)	112.17(10)	N(1)–C(2)–C(7)	110.03(9)
N(1)–C(2)–C(3)	110.74(8)	C(7)–C(2)–C(3)	109.47(9)
C(2)–C(3)–C(4)	119.39(9)	N(2)–C(4)–C(8)	109.43(9)
N(2)–C(4)–C(3)	107.32(8)	C(8)–C(4)–C(3)	110.93(10)
N(2)–C(4)–C(9)	111.95(9)	C(8)–C(4)–C(9)	109.35(11)
C(3)–C(4)–C(9)	107.85(10)	N(2)–C(5)–C(1^{i})	111.46(9)
2			
N(1)–C(10)	1.461(2)	N(1)–C(1)	1.467(2)
N(2)–C(2)	1.458(2)	N(2)–C(3)	1.489(2)
N(3)–C(6)	1.464(2)	N(3)–C(5)	1.471(2)
N(4)–C(7)	1.457(2)	N(4)–C(8)	1.486(2)
C(1)–C(2)	1.526(2)	C(1)–C(11)	1.527(2)
C(3)–C(12)	1.515(2)	C(3)–C(4)	1.536(2)
C(3)–C(13)	1.536(2)	C(4)–C(5)	1.524(2)
C(5)–C(14)	1.536(3)	C(6)–C(15)	1.514(2)
C(6)–C(7)	1.518(2)	C(8)–C(16)	1.524(2)
C(8)–C(9)	1.540(2)	C(8)–C(17)	1.541(2)
C(9)–C(10)	1.526(2)	C(10)–C(18)	1.517(2)
C(10)–N(1)–C(1)	118.06(10)	C(2)–N(2)–C(3)	118.33(10)
C(6)–N(3)–C(5)	116.28(10)	C(7)–N(4)–C(8)	116.62(11)
N(1)–C(1)–C(2)	107.35(10)	N(1)–C(1)–C(11)	115.09(12)
C(2)–C(1)–C(11)	112.31(12)	N(2)–C(2)–C(1)	110.62(10)
N(2)–C(3)–C(12)	105.55(10)	N(2)–C(3)–C(4)	111.34(10)
C(12)–C(3)–C(4)	111.00(12)	N(2)–C(3)–C(13)	111.51(11)
C(12)–C(3)–C(13)	109.20(12)	C(4)–C(3)–C(13)	108.24(11)
C(5)–C(4)–C(3)	120.48(11)	N(3)–C(5)–C(4)	111.24(10)
N(3)–C(5)–C(14)	111.20(13)	C(4)–C(5)–C(14)	107.42(12)
N(3)–C(6)–C(15)	112.86(13)	N(3)–C(6)–C(7)	109.72(11)
C(15)–C(6)–C(7)	108.83(13)	N(4)–C(7)–C(6)	112.79(11)
N(4)–C(8)–C(16)	106.28(11)	N(4)–C(8)–C(9)	110.66(10)
C(16)–C(8)–C(9)	111.03(13)	N(4)–C(8)–C(17)	111.78(12)
C(16)–C(8)–C(17)	109.23(13)	C(9)–C(8)–C(17)	107.90(12)
C(10)–C(9)–C(8)	118.78(11)	N(1)–C(10)–C(18)	110.42(11)

[a] Symmetry transformations used to generate equivalent atoms: (i) $-x + 1, -y + 1, -z$.

Table 3. Selected bond lengths [Å] and angles [°] for complexes **4** and **5**.[a]

4			
Ni(1)–N(1)	1.955(2)	Ni(1)–N(2)	1.962(2)
N(1)–Ni(1)–N(1^{i})	180.0	N(1)–Ni(1)–N(2)	94.23(10)
N(1)–Ni(1)–N(2^{i})	85.77(10)		
5			
Ni–N(1)	1.949(4)	Ni–N(4)	1.925(4)
Ni–N(2)	1.932(4)	Ni–N(3)	1.933(4)
N(4)–Ni–N(2)	176.22(17)	N(4)–Ni–N(1)	91.97(15)
N(4)–Ni–N(3)	86.79(16)	N(2)–Ni–N(1)	87.46(16)
N(2)–Ni–N(3)	94.23(16)	N(3)–Ni–N(1)	172.93(16)

[a] Symmetry transformations used to generate equivalent atoms: (i) $-x + 1, -y + 1, -z + 2$.

3*S*,5*S*,10*R*,12*R* configuration. 3,10-Dimethyl groups on five-membered chelate rings have an axial orientation in a *meso* configuration *trans* to the H atom of the neighboring amine group. 5,12-Dimethyl groups on six-membered chelate rings also occur on opposite sides of the macrocyclic ring in a *meso* configuration but have stable equatorial orientations and lie away from the Ni^{II} ion center. A diequatorial-diaxial arrangement of the four chiral methyl groups is observed in the structure.

The Ni–N distances 1.955(2) and 1.962(2) Å are almost equivalent to the reported values in [Ni(3,10-C-*meso*-5,12-C-*meso*-Me_8[14]ane$_{Ba}$)]$(ClO_4)_2$ ([1.953(2) and 1.962(2) Å][9g] and [Ni(3,10-C-*meso*-5,12-C-*meso*-Me_8[14]ane$_{Ca}$)]$(ClO_4)_2$ [1.948(3) and 1.961(2) Å],[9a] but shorter than the values found in [Ni(1,8-bis(2-cyanoethyl)-3,10-C-*meso*-5,12-C-*meso*- Me_8[14]ane)]$(ClO_4)_2$ [1.972(2) and 2.008(2) Å][9j] and [Ni(1,8-diallyl-3,10-C-*meso*-5,12-C-*meso*-Me_8[14]ane$_{Ca}$)]-$(ClO_4)_2$ [1.984(2) and 2.000(2) Å].[16] The N–Ni–N bond angle [85.77(10)°] involved in the five-membered chelate ring is smaller than that [94.23(10)°] in the six-membered chelate ring, as usual. In the perchlorate group, the anion

Table 4. Selected bond lengths [Å] and angles [°] for complexes **7** and **8**.[a]

7			
Cu(1)–N(1)	2.035(3)	Cu(1)–O(5)	2.816(4)
Cu(1)–N(2)	2.038(3)		
N(1)–Cu(1)–N(2)	85.38(10)	N(1)–Cu(1)–N(1^{i})	180.00
N(2)–Cu(1)–N(1^{i})	94.62(10)	N(2)–Cu(1)–N(2^{i})	180.00
N(1)–Cu(1)–O(5)	77.84(10)	N(2)–Cu(1)–O(5)	82.61(11)
O(5)–Cu(1)–O(5^{i})	180.00		
8			
Cu(1)–N(1)	2.015(2)	Cu(1)–N(2)	2.047(2)
Cu(1)–N(4)	2.021(2)	Cu(1)–O(3)	2.731(3)
Cu(1)–N(3)	2.043(2)	Cu(1)–O(6)	2.570(4)
N(1)–Cu–N(2)	84.43(7)	N(1)–Cu–N(3)	176.89(8)
N(1)–Cu–N(4)	94.42(8)	N(2)–Cu–N(3)	95.73(7)
N(2)–Cu–N(4)	177.17(7)	N(3)–Cu–N(4)	85.28(7)
N(1)–Cu(1)–O(3)	85.01(8)	N(1)–Cu(1)–O(6)	98.61(9)
N(2)–Cu(1)–O(3)	92.94(9)	N(2)–Cu(1)–O(6)	85.91(9)
N(3)–Cu(1)–O(3)	91.88(8)	N(3)–Cu(1)–O(6)	84.50(9)
N(4)–Cu(1)–O(3)	84.38(9)	N(4)–Cu(1)–O(6)	96.82(9)
O(3)–Cu(1)–O(6)	176.07(10)		

[a] Symmetry transformations used to generate equivalent atoms: (i) $-x + 1, -y, -z + 2$.

is hydrogen bonded to pairs of adjacent N–H groups with normal N···O distances of 2.983 and 3.151 Å.

Complex 5

The Ni^{II} ion is four-coordinate in a distorted square-planar geometry with the four N-atoms of **2**. The complex cation is a noncentrosymmetric structure and has a 1*S*,4*R*,8*S*,11*S* configuration of the four chiral nitrogen centers in the *trans*-II (+–++) configuration, different from the most thermodynamically stable *trans*-III. The chiral carbon centers and 3,5,10,12-tetramethyl groups are in configurations of 3*S*,10*R*-C-*meso* and 5*S*,12*S*-C-*racemic*, where 3,12-dimethyl groups occupy an equatorial orientation and 5,10-dimethyl groups an axial orientation. The five-membered chelate ring, Ni, N(3), C(6), C(7), N(4), has a thermodynamically stable *gauche* conformation with the equatorial methyl group in the one structure and a distorted eclipsed conformation with the axial methyl group in the other. The six-membered chelate ring, Ni, N(4), C(8), C(9), C(10), N(1), has a chair conformation with the equatorial methyl group in the one structure and a twist-boat conformation with the axial methyl group in the other. The 3-methyl group and the neighboring amine group are found on the same side of the coordination plane *trans* to the other methyl and amine groups. A diequatorial-diaxial arrangement of the four chiral methyl groups is observed in the structure.

The Ni–N bond lengths in the range 1.925(4) to 1.949(4) Å are shorter than the values found in **4**, but similar to those found in [Ni(3,10-C-*rac*-5,12-C-*rac*-Me_8[14]ane)]$(ClO_4)_2$ [1.926(2) and 1.931(2) Å],[17] where the four N–H groups are on the same side and the 14-membered ring has a basket configuration. The N–Ni–N bond angles of the *gauche* and chair chelate rings are 86.79(16) and 91.97(15)°, respectively, smaller than those found in the eclipse [87.46(16)°] and twist-boat chelate rings [94.23(16)°]. In the second perchlorate ion [Cl(2)], three oxygen atoms are found to be disordered over two positions. The abnormal O–Cl(2)–O bond angles of the perchlorate ions, ranging from 52.2(8) to 135.9(9)°, suggest further complicated disorder. Hydrogen bonds between water molecules, perchlorate ions, and amine groups help to stabilize the crystal structure. The water molecule is placed between two perchlorate ions to form HO–H···O–ClO_3 hydrogen bonds in the range 2.094 to 2.628 Å. The distances of the hydrogen bonds between the perchlorate O atom and the amine H atom are in the range 2.063 to 2.508 Å.

Complex 7

The copper(II) ion is coordinated by four nitrogen atoms in equatorial positions and two oxygen atoms in *trans* axial positions from water to form a distorted octahedron. The complex cation has a 1*R*,4*S*,8*S*,11*R* configuration of the four chiral nitrogen centers in the *trans*-III (–++–) configuration with both six-membered chelate rings in chair conformations and both five-membered chelate rings in *gauche* conformations. Each of the two methyl groups on the five-membered chelate rings has an axial orientation *trans* to the H atom of the neighboring amine group. Four of the six methyl groups at the 5, 7, 12, and 14 positions on the six-membered chelate rings are in a stable equatorial plane and lie away from the metal ion center. A diequatorial-diaxial arrangement for the four chiral methyl groups is observed in the structure.

The Cu–O (axial) bond is considered to be very weakly coordinated, since the Cu–O(5) distance of 2.816(4) Å is longer than the typical values for Cu^{II} complexes and is significantly longer than the four Cu–N (equatorial) distances, 2.035(3) and 2.038(3) Å. In fact, the axial bonds of most six-coordinate Cu^{II} complexes are often elongated as a result of the Jahn–Teller effect. These facts support the complex belonging to a six-coordinate (4 + 2) geometry.[18] The axial Cu–O bond length is compared to those in [Cu(3,10-C-*meso*-5,12-C-*meso*-Me_8[14]ane)$(H_2O)_2$]$(NO_3)_2$,[9d] [Cu(C-*meso*-1,5,8,12-tetramethyl-1,4,8,11-tetraazacyclotetradecane)$(H_2O)_2$]$(NO_2)_2$,[19a] and [Cu(C-*meso*-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane)$(H_2O)_2$]Cl_2-$(H_2O)_2$.[19b] Each of the water molecules forms intramolecular hydrogen bonds with one H atom of an amine group and one O atom of the perchlorato group, as well as an intermolecular hydrogen bond with the perchlorate O atom of a neighboring molecule. The N(1)–H(1)···O(5) distance is 2.428 Å and the N(2)–H(2)···O(5) distance 2.713 Å. The distances between the coordinated water H(5B) atom and the perchlorate O atoms are in the range 2.097 to 2.973 Å.

Complex 8

The complex has a distorted octahedral coordination geometry with the macrocyclic tetradentate amine N atoms in equatorial positions and two O atoms of two perchlorato groups in *trans* axial positions with the angle O(6)–Cu–O(3) equal to 176.07(10)°. The four N atoms of the macrocyclic ligand form a square plane. The largest deviation from the

least-squares plane is 0.0044(10) Å. The deviation of the Cu atom from the relevant plane is 0.0507(10) Å. The tetradentate ligand adopts its most stable conformation with two six-membered chelate rings in chair conformations and two five-membered chelate rings in *gauche* conformations. The complex has a 1*S*,4*R*,8*R*,11*S* configuration of the four chiral N centers in the *trans*-III (+—+) configuration. The configurations of the four chiral carbon centers are 3*S*, 5*R*, 10*R*, and 12*R* with 3,5,10-trimethyl groups in equatorial positions and the 12-methyl group in an axial position. The axial methyl group on the six-membered chelate ring makes the chair conformation unstable while the methyl group on the other six-membered chelate ring is in the stable equatorial position. A triequatorial-axial arrangement for the four chiral methyl groups is observed in the structure.

The Cu–O(3) distance [2.731(3) Å] is longer than the other axial Cu–O(6) distance [2.570(4) Å] and the four Cu–N distances [2.015(2)–2.047(2) Å]. This result shows that $[CuL_d(ClO_4)_2]$ forms an unusual six-coordinate (4 + 1 + 1′) structure in which the complex has four strongly coordinated atoms, one weakly coordinated atom and one very weakly coordinated atom. The Cu–O bond lengths are compared to those in [Cu(1,4,7,11-tetraazacyclotetradecane)$(ClO_4)_2$][20a] and [Cu(C-*meso*-1,5,8,12-tetramethyl-1,4,8,11-tetraazacyclotetradecane)$(ClO_4)_2$].[20b] The N–Cu–N angles of five- and six-membered rings are in the expected range. Hydrogen bonds between amine hydrogen atoms and O atoms of perchlorato groups help to stabilize the crystal structure. The distances are N(1)–H(1B)···O(1) 2.146 Å, N(2)–H(2C)···O(7) 2.645 Å, N(3)–H(3A)···O(8) 2.211 Å, and N(4)–H(4C)···O(4) 2.491 Å.

Spectra and Properties

The infrared spectra of the Ni^{II} and Cu^{II} complexes show a sharp NH stretching vibration of secondary amines around 3200 cm^{-1} with a broad strong band at about 1100 cm^{-1} resulting from the perchlorate anions.

The UV/Vis spectra of the Ni^{II} complexes, **4** and **5**, show strong absorption bands of the planar chromophore at 469 and 455 nm, respectively. For low-spin nickel(II) tetramine complexes the energy of the d–d band is a measure of the energy of the equatorial Ni–N interactions. The single absorption band of **4** at 469 nm (21,322 cm^{-1}) is assigned to the $^1A_{1g} \rightarrow {}^1E_g$ transition of the square planar nickel(II) complex and is approximately 656 cm^{-1} lower in frequency than that of **5** at 455 nm (21,978 cm^{-1}), establishing that **4** exerts weaker metal-donor atom interactions than its diastereoisomeric complex **5**. Similar observations have been found with $[Ni(tet\ a)]^{2+}$ (*meso*) and $[Ni(tet\ b)]^{2+}$ (*racemate*).[21] In aqueous solution, Ni^{II} complexes of 14-membered tetrazamacrocyclic ligands exist as an equilibrium mixture of low-spin square planar (yellow, planar) and high-spin pseudooctahedral (blue, *cis*-diaqua and *trans*-diaqua) complex cations.[22] The *cis*-diaqua form is much more unstable than the low-spin square-planar and *trans*-diaqua high-spin pseudooctahedral complex cations. The equilibrium can be affected by various factors: addition of salts, temperature, solvent, ionic strength, pH value, and steric effect, etc.[23] In addition, the proportion of planar species also increases by an increase in the number of methyl groups on the macrocyclic ligand.[24] In nitromethane (a noncoordinating solvent), **4** and **5** have molar extinction coefficients of ε = 77.9 and 90.6 $dm^3 mol^{-1} cm^{-1}$ in 100% planar species, respectively.[25] The values are almost equal to those found in aqueous solution over a range of temperatures. This result shows that the intensities of the bands are temperature-independent and axial additions are not observed. In other words, **4** and **5** exhibit almost 100% planar species in aqueous solution, which may result from the steric effect produced by numerous methyl groups, especially axial orientations and the distorted structures.

Both Cu^{II} complexes, **7** and **8**, exhibit two bands, one falls in the visible region and the other falls in the ultraviolet region. Previous studies show that the most Cu^{II} complexes are six-coordinate tetragonal with long axial bonds. The higher energy band (≈270 nm) in the ultraviolet region is assigned to ligand-metal charge-transfer transitions associated with the nitrogen donors.[26] The lower d–d transition in the visible region of the spectrum is believed to be a combination of the three possible transitions d_{xy}, d_{xz}, $d_{yz} \rightarrow d_{x^2-y^2}$ and is characteristic of many Cu^{II} complexes.[26] The expected $d_{z^2} \rightarrow d_{x^2-y^2}$ transition appearing at the lowest energy (near-IR region), indicative of the splitting of the e_g (in O_h) caused by the tetragonal distortion (Jahn–Teller), was not observed in the visible region. Cheng and Chung reported that the rod-like acetonitrile is coordinated more strongly than H_2O in the axial position of $[Ni(tet\ b)]^{2+}$ because of steric interactions, even though the donor ability of H_2O is greater than acetonitrile,[26d] indicating that acetonitrile is a better axial donor. As the axial bond weakens, the copper atom becomes more positive, and attracts the in-plane ligands more strongly. Some interesting results are provided in the visible spectra where the visible band of **7** at 511 nm (19,569 cm^{-1}) in acetonitrile is some 391 cm^{-1} lower in frequency than that at 501 nm (19,960 cm^{-1}) in aqueous solution, while the bands of **8** are observed at 528 nm (18,939 cm^{-1}) in both acetonitrile and aqueous solution. These results indicate that the axial donor is more strongly bound in **8** than that found in **7**, as seen from the crystal structures, resulting in weaker in-plane coordinations.[26a] In this work, the axial coordination is largely affected by the steric interactions between the axial donor and the axial methyl groups. When **7** is dissolved in aqueous solution, the entire band envelope shifts to the blue region, indicating that water molecules are more weakly bound or unbound since the axial methyl groups almost sterically congest the axial sites.

Conclusions

In summary, four diastereoisomers of 3,10-*meso*-3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradecane were distinguished by the *RS*-configurations of the

chiral methyls at the 5 and 12 positions. Ligands **1**, **2**, and **3** were isolated and assigned as 5*S*,12*R*-C-*meso*, 5*S*,12*S*-C-*racemic* and 5*R*,12*R*-C-*racemic*, respectively. The isomer L_a could not be isolated following the experimental methods described in the text, and we assigned it as 5*R*,12*S*-C-*meso*-Me_8[14]ane. Spectral studies show that **1** is centrosymmetric whereas **2** and **3** are noncentrosymmetric. Nickel(II) and copper(II) complexes of these ligands were isolated. In accordance with the X-ray structure determination, the geometry around the Ni^{II} ion in the complexes is approximately square-planar and the Cu^{II} ion octahedral. The configuration of **5** is *trans*-II, different from the most thermodynamically stable *trans*-III complex as shown in **4**, **7**, and **8**. In complexes **7** and **8** unusual six-coordinate (4 + 2) and (4 + 1 + 1′) geometries, respectively, were formed because of the longer Cu–O distances compared with the equatorial Cu–N distances. UV/Vis spectra show that both Ni^{II} complexes exhibit almost 100% planar species in aqueous solution as a result of the steric effect produced by numerous methyl groups, especially axial orientations and the distorted structures. In six coordinate Cu^{II} complexes, acetonitrile turns out to be a better axial donor than the water molecule, and the weaker axial bonding is a result of the steric interactions producing stronger in-plane coordinations.

Experimental Section

Physical Measurements: A Bruker DMX-600 MHz or AC300 MHz spectrometer was used to obtain ^1H and ^{13}C NMR spectra that are referenced to the solvent. Infrared spectra were recorded with a Perkin–Elmer System 2000 FT-IR spectrophotometer as KBr pellets. UV/Vis spectra were recorded with a Hitachi Model U-3300 spectrophotometer. High-resolution mass spectra were obtained using a MAT-95XL mass spectrometer. Microanalysis (C, H, N) was performed using a Heraeus CHNOS Rapld F002 elemental analyzer.

Synthesis of Ligands and Complexes: All the chemicals used were of reagent grade and were not purified further. The reaction of (±)-1,2-propanediamine with acetone in perchloric acid yielded stereospecifically only the crystalline 3,10-*meso*-Me_8[14]diene·$2HClO_4$.[6a,8]

Caution! Although no problem was encountered in this work, the transition metal perchlorate is potentially explosive. It should be prepared in small quantities and handled with care.

L_b (1): Ligand L (73.0 g, 143 mmol) was suspended in methanol (300 mL) and stirred. An aqueous solution of sodium hydroxide (25.0 g of NaOH in 250 mL of H_2O) was then added until the ligand L completely dissolved. Thereafter sodium borohydride (43.0 g, 1.14 mol) was added pinchwise to the solution until no more bubbles appeared. The mixture was then refluxed for 3.0 h. After the mixture had cooled to room temperature, an aqueous solution of sodium hydroxide (16.0 g of NaOH in 400 mL of H_2O) was added and stirred for 30 min; a white precipitate subsequently appeared. This precipitate, a mixture of isomers 3*S*,10*R*-C-*meso*-Me_8[14]anes (34.5 g, 77%), was washed with cold water and dried. The isomer **1** was separated by the partial crystallization method: a mixture of isomers of 3*S*,10*R*-C-*meso*-Me_8[14]anes (30.0 g, 96.1 mmol) was dissolved in boiling methanol (400 mL) and filtered while hot. Deionized water (400 mL) was added to the hot filtrate and stirred until the solution had cooled to room temperature. A white precipitate of **1** was formed, which was filtered and recrystallized from hot ether. Yield 18.2 g (61%). M.p. 125 °C (from ether). $C_{18}H_{40}N_4$ (312.54): calcd. C 69.17, H 12.90, N 17.93; found C 69.02, H 12.82, N 17.85. FT-IR (KBr disk): $\tilde{\nu}$ = 3265, 2966, 2910, 2826, 1475, 1185 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ = 0.96 (d, J = 6.14 Hz, 6 H), 1.01 (d, J = 6.44 Hz, 6 H), 1.05 (s, 6 H), 1.11 (s, 6 H), 1.22 (d, J = 2.58 Hz, 1 H), 1.25 (d, J = 2.57 Hz, 1 H), 1.62 (m, 2 H), 2.57 (m, 2 H), 2.64 (m, 2 H), 2.99 (m, 2 H), 3.08 (m, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.6 (CH_3), 20.4 (CH_3), 25.7 (CH_3), 29.1 (CH_3), 45.4 (CH), 47.4 (CH), 47.6 (CH_2), 48.7 (CH_2), 52.9 (C) ppm. HRMS (EI^+, m/z): calcd. for $C_{18}H_{40}N_4$ 312.3253, found 312.3253. The filtrate (F_1) was kept for further treatment.

L_c (2): Deionized water (200 mL) was added to the above filtrate (F_1) and continuously stirred for 30 min. A small amount of white precipitate containing a mixture of the isomers was removed. The filtrate (F_2) was then evaporated on a rotary evaporator and gave a mixture of *rac* isomers, L_c and L_d. Yield 10.4 g (35%). This mixture was then dissolved in ether and partial crystals of **2** were obtained in the first fraction by slow evaporation at room temperature. M.p. 91 °C (from ether). $C_{18}H_{40}N_4{\cdot}H_2O$ (330.56): calcd. C 65.40, H 12.81, N 16.95; found C 65.29, H 12.73, N 16.88. FT-IR (KBr disk): $\tilde{\nu}$ = 3246, 2966, 2930, 2837, 1500, 1174 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ = 0.91 (d, J = 6.11 Hz, 3 H), 0.97 (d, J = 6.76 Hz, 3 H), 1.01 (d, J = 2.88 Hz, 3 H), 0.98 (s, 3 H), 0.99 (s, 3 H), 1.01 (d, J = 2.88 Hz, 3 H), 1.02 (d, J = 2.44 Hz, 3 H), 1.03 (s, 3 H), 1.04 (d, J = 2.83 Hz, 1 H), 1.06 (s, 3 H), 1.08 (d, J = 2.56 Hz, 1 H), 1.67 (m, 2 H), 2.44 (m, 3 H), 2.63 (m, 1 H), 2.76 (m, 2 H), 2.97 (m, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.2 (CH_3), 20.5 (CH_3), 21.5 (CH_3), 25.3 (CH_3), 27.1 (CH_3), 27.6 (CH_3), 29.1 (CH_3), 29.5 (CH_3), 43.5 (CH_2), 45.9 (CH), 46.0 (CH_2), 47.2 (CH), 47.4 (CH_2), 49.4 (CH_2), 50.8 (CH), 52.3 (C), 53.1 (C), 54.4 (CH) ppm. HRMS (EI^+, m/z): calcd. for $C_{18}H_{40}N_4$ 312.3253, found 312.3253. After removing all the crystals, the filtrate (F_3) was kept for further treatment.

L_d (3): The above filtrate (F_3) was air-dried and a white damp residue (R_1) was obtained with no crystals. We had hoped it contained a small amount of **2** but only the predominant form of 3 was present. Since these two *racemic* forms are enantiomers of each other and have identical chemical properties it was very difficult to separate them completely and characterize them separately by spectral studies. An X-ray study was the ideal tool for a unique characterization of **3** and was therefore obtained for $[CuL_d(ClO)_2]$ to provide the necessary evidence.

$[NiL_b](ClO_4)_2$ (4): A methanol solution (20 mL) of **1** (0.520 g, 1.66 mmol) was added to a boiling methanol solution (20 mL) of nickel acetate tetrahydrate (0.411 g, 1.65 mmol). The solution was heated over a steam bath for 2.0 h and the volume was reduced to 30 mL. After adding lithium perchlorate trihydrate (0.610 g, 3.80 mmol), the reaction mixture was again heated for 5 min and then cooled to room temperature. A bright orange-yellow precipitate was filtered off and washed with methanol followed by ether. The solid was then dissolved in a hot acetonitrile solution. Slow evaporation of the solvent at room temperature gave an orange-yellow crystalline complex **4** that was filtered off and air-dried. Yield 0.634 g (67%). $C_{18}H_{40}Cl_2N_4NiO_8$ (570.13): calcd. C 37.92, H 7.07, N 9.83; found C 37.75, H 7.03, N 9.78. UV/Vis (CH_3NO_2): λ (ε) = 469 nm (77.9 $dm^3\,mol^{-1}\,cm^{-1}$). FT-IR (KBr disk): $\tilde{\nu}$ = 3541, 3245, 3026, 2975, 1438, 1086 cm^{-1}. ^{13}C NMR (75 MHz, CD_3NO_2): δ = 13.1 (CH_3), 16.2 (CH_3), 21.2 (CH_3), 24.7 (CH_3), 45.5 (CH), 46.4 (CH_2), 49.1 (CH_2), 50.4 (CH), 53.5 (C) ppm.

$[NiL_c](ClO_4)_2(H_2O)_{0.5}$ (5): A methanol solution (20 mL) of **2** (1.49 g, 4.78 mmol) was added to a boiling methanol solution (20 mL) of nickel acetate tetrahydrate (1.19 g, 4.78 mmol). The pH of this solution was adjusted between 11 and 12 with sodium hydroxide. After stirring for 3.0 h, lithium perchlorate trihydrate (1.49 g, 9.29 mmol) was added and the solution was cooled to room temperature. The pH of the solution was adjusted to neutrality with perchlorate acid. Yellow crystals were obtained by slow evaporation of the water/methanol mixture. The bright yellow complex **5** was filtered off and washed with methanol and ether. Yield 1.66 g (61%). $C_{18}H_{41}Cl_2N_4NiO_{8.50}$ (579.14): calcd. C 37.33, H 7.14, N 9.67; found C 37.15 H 7.08, N 9.60. UV/Vis (CH_3NO_2): λ (ε) = 455 nm (90.6 $dm^3 mol^{-1} cm^{-1}$). FT-IR (KBr disk): $\tilde{\nu}$ = 3430, 3195, 2975, 2873, 1635, 1462, 1115 cm^{-1}. ^{13}C NMR (75 MHz, CD_3NO_2): δ = 9.84 (CH_3), 16.9 (CH_3), 17.1 (CH_3), 19.9 (CH_3), 21.5 (CH_3), 24.3 (CH_3), 26.6 (CH_3), 27.3 (CH_3), 43.7 (CH_2), 44.3 (CH), 47.5 (CH_2), 48.0 (CH_2), 48.4 (CH), 49.2 (CH_2), 51.5 (CH), 53.7 (C), 54.6 (CH), 56.1 (C) ppm.

$[NiL_d](ClO_4)_2\ x{\cdot}H_2O$ (6): This complex was synthesized by following the same method as used for **5**, except ligand **3** was used instead of **2**. Spectral data are not given because they are identical to those of **5**. Unfortunately we were unable to obtain single crystals of this compound.

$[CuL_b(OH_2)_2](ClO_4)_2$ (7): A methanol solution (20 mL) of copper perchlorate hexahydrate (2.73 g, 7.38 mmol) was added to a methanol solution (20 mL) of **1** (2.18 g, 6.98 mmol). The mixture was refluxed for 1.0 h and then cooled to room temperature. The pink solid that precipitated was separated by filtration and washed several times with methanol and ether. The solid was then dissolved in a hot methanol/water mixture. Slow evaporation of the solvent at room temperature gave the purplish red crystalline complex **7**, which was filtered off and air-dried. Yield 4.02 g (84%). $C_{18}H_{44}Cl_2CuN_4O_{10}$ (611.01): calcd. C 35.38, H 7.26, N 9.17; found C 35.18, H 7.21, N 9.11. UV/Vis (H_2O): λ (ε) = 279 (10464), 501 nm (131 $dm^3 mol^{-1} cm^{-1}$). FT-IR (KBr disk): $\tilde{\nu}$ = 3463, 3152, 2971, 2880, 1147, 1088 cm^{-1}.

$[CuL_d(ClO_4)_2]$ (8): Copper perchlorate hexahydrate (0.593 g, 1.60 mmol) was added to a methanol solution (20 mL) of R_1 (0.501 g, 1.60 mmol). The mixture was refluxed for 1.0 h and cooled to room temperature. The red precipitate was filtered off and washed with methanol and ether. Red crystals of **8** were obtained by slow evaporation of the methanol/water mixture. Yield 0.791 g (86%). $C_{18}H_{40}Cl_2CuN_4O_8{\cdot}H_2O$ (574.98): C 37.60, H 7.01, N 9.74; found C 37.41, H 6.96, N 9.69. UV/Vis (H_2O): λ (ε) = 275 (6956), 527 nm (151 $dm^3 mol^{-1} cm^{-1}$). FT-IR (KBr disk): $\tilde{\nu}$ = 3183, 2967, 2893, 1146, 1090 cm^{-1}.

$[CuL_c(ClO_4)_2]$ (9): The complex was synthesized by following the same method used for **8**, except ligand **2** was used instead of **3**. Spectral data are not given because these are identical to those of **8**. Unfortunately we were unable to obtain single crystals of this compound.

Crystallography: Single crystals of ligands were obtained by slow evaporation of either ether solutions, methanol/water mixtures, or acetonitrile solutions. Intensity data were collected with a Siemens Smart CCD diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Data reduction and empirical absorption corrections were performed with the XTAL package or NRCVAX programs.[27] Structures were solved by the heavy atom method with SHELXS 97 and refined by full-matrix least-squares analysis on F^2 with SHELXL.[28] All the non-hydrogen atoms were refined anisotropically and the hydrogen atoms fixed at calculated positions and refined using a riding model. A summary of the crys-

Table 5. Summery of crystallographic data for ligands **1**–**2**.

	1	**2**
Empirical formula	$C_{18}H_{42}N_4O$	$C_{18}H_{42}N_4O$
Formula mass	330.56	330.56
Temperature [K]	296(2)	294(2)
Crystal system	monoclinic	monoclinic
Space group	*C*2/*c*	$P2_1/n$
a [Å]	11.4892(8)	9.9814(6)
b [Å]	14.7100(8)	19.2850(10)
c [Å]	12.6084(8)	10.8842(6)
α [°]	90	90
β [°]	99.269(2)	93.405(1)
γ [°]	90	90
V [Å^3]	2103.1(2)	2091.4(2)
Z	4	4
$D_{calcd.}$ [Mg m^{-3}]	1.044	1.050
Absorption coefficient [mm^{-1}]	0.065	0.066
F(000)	744	744
Crystal size [mm]	0.50 × 0.30 × 0.20	0.40 × 0.30 × 0.15
θ range [°]	2.27 to 28.29	2.11 to 28.30
	$-15 \le h \le 15$	$-9 \le h \le 13$
	$-19 \le k \le 19$	$-25 \le k \le 25$
	$-16 \le l \le 16$	$-14 \le l \le 14$
Reflections collected	10646	15466
Independent reflections	2534 [*R*(int) = 0.0305]	5191 [*R*(int) = 0.0380]
Data/restraints/parameters	2534/0/105	5191/0/208
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0422	R_1 = 0.0511
	wR_2 = 0.1235	wR_2 = 0.1308
R indices (all data)	R_1 = 0.0649	R_1 = 0.0834
	wR_2 = 0.1311	wR_2 = 0.1450
GOF on F_2	0.989	0.897
Largest difference peak/hole [e Å^{-3}]	0.229/–0.113	0.208/–0.174

Table 6. Summery of crystallographic data for complexes **4**,**5** and **7**,**8**.

	4	**5**	**7**	**8**
Empirical formula	$C_{18}H_{40}Cl_2N_4NiO_8$	$C_{18}H_{41}Cl_2N_4NiO_{8.5}$	$C_{18}H_{44}Cl_2CuN_4O_{10}$	$C_{18}H_{40}Cl_2CuN_4O_8$
Formula mass	570.15	579.16	611.01	574.98
Temperature [K]	294(2)	294(2)	294(2)	294(2)
Crystal system	monoclinic	orthorhombic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_12_12_1$	$P2_1/c$	$P2_1/c$
a [Å]	8.6052(6)	9.0716(8)	8.2077(5)	9.4358(6)
b [Å]	17.3298(13)	13.4218(12)	16.0955(10)	31.5816(19)
c [Å]	8.9614(7)	21.526(2)	10.4400(6)	8.9911(6)
α [°]	90	90	90	90
β [°]	104.325(1)	90	103.295(1)	102.510(1)
γ [°]	90	90	90	90
V [Å^3]	1294.83(17)	2620.9(4)	1342.23(14)	2615.7(3)
Z	2	4	2	4
$D_{calcd.}$ [Mg m^{-3}]	1.462	1.468	1.512	1.460
Absorption coefficient [mm^{-1}]	1.003	0.994	1.069	1.087
$F(000)$	604	1228	646	1212
Crystal size [mm]	0.50 × 0.30 × 0.30	0.15 × 0.10 × 0.10	0.50 × 0.40 × 0.40	0.70 × 0.10 × 0.05
θ range [°]	2.35 to 28.26	1.79 to 28.36	2.37 to 25.70	1.29 to 25.69
	$-9 \le h \le 11$	$-12 \le h \le 11$	$-7 \le h \le 10$	$-10 \le h \le 11$
	$-20 \le k \le 23$	$-17 \le k \le 17$	$-19 \le k \le 14$	$-29 \le k \le 38$
	$-11 \le l \le 10$	$-20 \le l \le 28$	$-12 \le l \le 11$	$-10 \le l \le 10$
Reflections collected	8223	19612	7360	15869
Independent reflections	3067 [R(int) = 0.0330]	6525 [R(int) = 0.0710]	2551 [R(int) = 0.0249]	4958 [R(int) = 0.0449]
Data/restraints/parameters	3067/0/151	6525/4/328	2551/0/160	4958/0/298
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0478	R_1 = 0.0469	R_1 = 0.0498	R_1 = 0.0375
	wR_2 = 0.1467	wR_2 = 0.1197	wR_2 = 0.1431	wR_2 = 0.0949
R indices (all data)	R_1 = 0.0680	R_1 = 0.1180	R_1 = 0.0555	R_1 = 0.0554
	wR_2 = 0.1549	wR_2 = 0.0959	wR_2 = 0.1494	wR_2 = 0.1033
GOF on F_2	1.025	0.673	1.066	0.604
Largest difference peak/hole [e Å^{-3}]	0.603/–0.522	0.499/–0.242	1.001/–0.447	0.451/–0.284

tallographic data and structure refinement parameters is given in Tables 5 and 6.

CCDC-279963 (for **1**), -279964 (for **2**), -279803 (for **4**), -279802 (for **5**), -279961 (for **7**), and -279962 (for **8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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