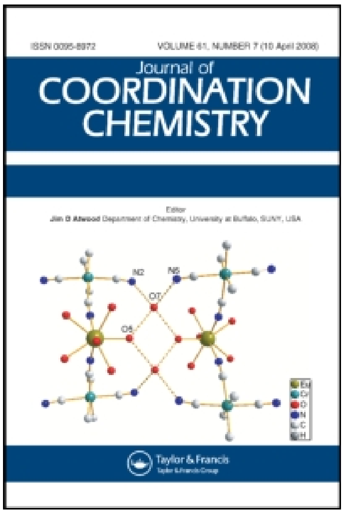


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Characterization of Diastereoisomeric [Ni(Me_8[14]ane)]$^{2+}$ Cations

Tapashi G. Roy[a]; Ramesh Bembi[b]; Saroj Hazari[a]; Benu K. Dey[a]; Tapan Acharjee[a]; Ernst Horn[cd]; Edward Tiekink[e]

[a] Department of Chemistry, University of Chittagong, Chittagong, Bangladesh [b] Department of Chemistry, University of Roorkee, Roorkee, Bangladesh [c] Department of Chemistry, Rikkyo University, Nishi-Ikebukuro, Tokyo, Japan [d] Tsukuba Advanced Research Alliance, University of Tsukuba, Tsukuba, Ibaraki, Japan [e] Department of Chemistry, The University of Adelaide, Australia

To cite this Article Roy, Tapashi G. , Bembi, Ramesh , Hazari, Saroj , Dey, Benu K. , Acharjee, Tapan , Horn, Ernst and Tiekink, Edward(2002) 'Characterization of Diastereoisomeric [Ni(Me_8[14]ane)]$^{2+}$ Cations', Journal of Coordination Chemistry, 55: 8, 853 — 862

To link to this Article: DOI: 10.1080/0095897022000002187

URL: http://dx.doi.org/10.1080/0095897022000002187

J. Coord. Chem., 2002, Vol. 55(8), pp. 853–862

Taylor & Francis
Taylor & Francis Group

CHARACTERIZATION OF DIASTEREOISOMERIC $[Ni(Me_8[14]ANE)]^{2+}$ CATIONS

TAPASHI G. ROY[a], RAMESH BEMBI[b], SAROJ K.S. HAZARI[a],
BENU K. DEY[a], TAPAN K. ACHARJEE[a], ERNST HORN[c]
and EDWARD R.T. TIEKINK[d,]*

[a]*Department of Chemistry, University of Chittagong, Chittagong-4331, Bangladesh;*
[b]*Department of Chemistry, University of Roorkee, Roorkee-247667, Bangladesh;*
[c]*Department of Chemistry, Rikkyo University, Nishi-Ikebukuro, Tokyo 171-8501,*
Japan and Tsukuba Advanced Research Alliance, University of Tsukuba, Tsukuba,
Ibaraki 305-8577, Japan; [d]*Department of Chemistry,*
The University of Adelaide, Australia 5005

(Received 11 September 2000; Revised 9 April 2001; In final form 25 September 2001)

The isomeric $Me_8[14]$anes, designated by L_A, L_B and L_C, on reaction with nickel(II) acetate tetrahydrate and subsequent addition of $LiClO_4 \cdot 3HO$ yield yellow or orange-yellow square planar $[NiL](ClO_4)_2$ diastereoisomers. It has been possible to isolate two N-chiral diastereoisomers for each ligand and these give distinct infrared and ^1H NMR spectra. The structures of these isomers have been assigned mainly on the basis of their ^1H NMR spectra. One structure, namely $[NiL_{B\alpha}](ClO_4)_2$, has been confirmed by x-ray crystallography.

Keywords: Nickel(II) complexes; Macrocyclic ligands; X-ray crystallography

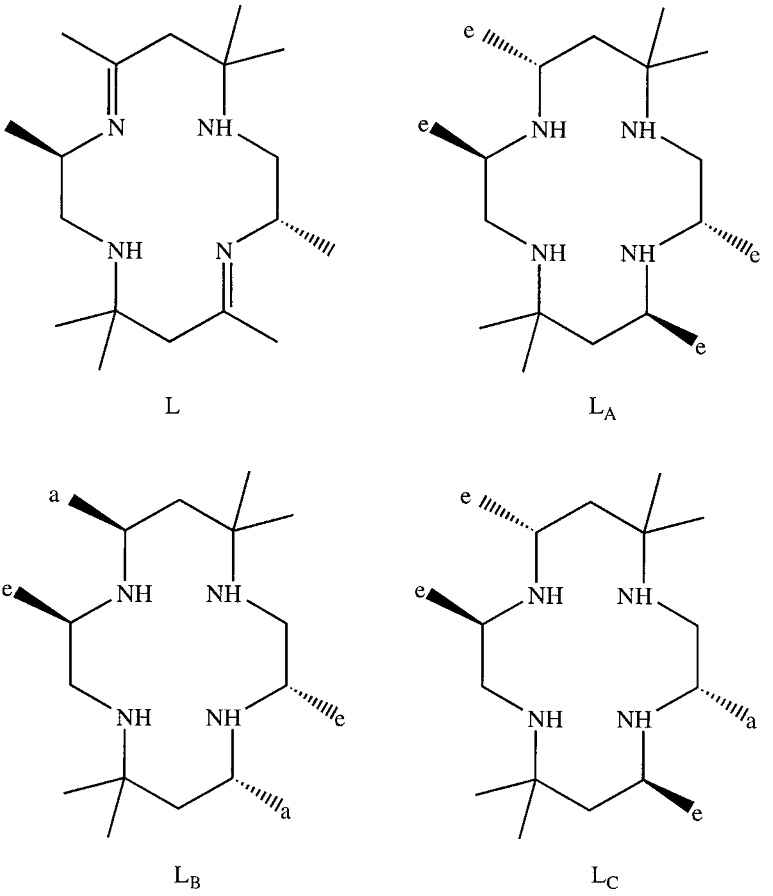
INTRODUCTION

The importance of synthetic macrocyclic ligands, especially tetradentate donors, and their metal complexes is now well established owing to their structural resemblance to naturally occurring macrocyclic complexes. This contribution focuses on the synthesis and characterization of diastereoisomeric square planar nickel(II) complexes of isomeric octamethyl tetraazacyclotetradecanes. It is known that condensation of 1,2-diaminopropane with acetone yields the stereospecific 3,10-C-meso isomer of the macrocycle 3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene, $Me_8[14]$diene, L (Scheme 1). The 3,10-C-meso assignment is based on ^1H NMR [1,2] and has been confirmed in the solid state by x-ray crystallography [3]. Nickel(II) complexes of L are known, including several crystal structures [1–3]. The focus of the present study is upon macrocyclic complexes of nickel(II) with the reduced form of L.

---

*Corresponding author. Present address: Department of Chemistry, National University of Singapore, Singapore 117543.
E-mail: etiekink@chemistry.adelaide.edu.au

ISSN 0095-8972 print: ISSN 1029-0389 online © 2002 Taylor & Francis Ltd
DOI: 10.1080/0095897022000002187



SCHEME 1

The reduction of the macrocycle, L, with $NaBH_4$ yields three isomeric Me_8[14]anes, i.e. Me_8[14]aneA (L_A), Me_8[14]aneB (L_B) and Me_8[14]aneC (L_C); see Scheme 1. The structures of these isomers have been established on the basis of ^1H NMR and in the case of L_B by an x-ray crystallographic study [4]. The interactions of these ligands with some metal centers have been investigated previously.

In one study, Bembi and coworkers [5] reported the preparation of a series of six-coordinate cobalt(III) complexes with these isomeric ligands, i.e. *trans*-$[CoLCl_2](ClO_4)$, in each case two N-chiral isomers were separated. Hence, it seemed likely that similar types of nickel(II) complexes and their N-chiral isomers could also be prepared. In principle [6,7], owing to the presence of four chiral nitrogen centers on these macrocycles, each of the above isomeric ligands can yield 16 diastereoisomeric $[NiL]^{2+}$ complexes. However, out of the 16 theoretically possible diastereoisomeric structures, only a few will be stable and sufficiently abundant to permit their isolation in the solid state. In the present study, where the characterization of these diastereoisomers and x-ray crystal structure of one example $[NiL_{B\alpha}](ClO_4)_2$ are reported, two diastereoisomers for each isomeric ligand have been separated.

EXPERIMENTAL

Instrumentation

The infrared spectra were recorded on a Perkin-Elmer Model-883 infrared spectrophotometer as KBr disks. Electronic spectra were recorded on a Shimadzu UV-visible spectrophotometer. The ^1H NMR spectra were obtained in $(CD_3)_2SO$ solution on a Bruker Wp80 90 MHz spectrometer using TMS as the internal reference. C, H and N analyses were carried out at the Chemistry Department, University of Stirling, Stirling, U.K. Conductance measurements were carried out on HANNA instruments with HI 8820 N conductivity cells at $25 \pm 0.1°C$.

Synthesis

3,10-C-meso-Me_8[14]diene · $2HClO_4$ was prepared as described previously and reduction of this ligand with $NaBH_4$ was carried out in a 1 : 1 water/methanol mixture [1]. The isomeric ligands L_A, L_B and L_C were separated by fractional crystallization from xylene [4].

Nickel(II) Complexes of L_A

A 0.5 g (1.6 mmol) sample of the ligand and 0.45 g (1.85 mmol) of nickel(II) acetate tetrahydrate were dissolved separately in 40 mL of hot methanol and mixed while hot. The reaction mixture was heated on a steam bath until the volume reduced to about 40 mL and an orange color developed. Then 0.5 g of lithium perchlorate trihydrate was added to the hot solution which was allowed to cool. After 1 h, orange-yellow crystals of $[NiL_{A\alpha}](ClO_4)_2$ were filtered off, washed with methanol followed by ether and dried *in vacuo*.

The yellow filtrate was concentrated until crystallization commenced. After cooling, the yellow product, $[NiL_{A\beta}](ClO_4)_2$, was obtained. This was recrystallized from acetonitrile, washed with ethanol, then with ether and dried *in vacuo*. Caution: Perchlorates are potentially explosive materials and should be handled with care, especially in the solid state.

Nickel(II) Complexes of L_B

A 1.0 g (3.25 mmol) sample of the ligand and 0.90 g (3.7 mmol) of nickel(II) acetate tetrahydrate were dissolved separately in 70 mL of cold dry distilled methanol. The ligand solution was added dropwise to the boiling solution of nickel(II) acetate with continuous stirring. The solution was heated on a steam bath for 1.5 h and the volume was reduced to 50 mL. A bright orange color developed. After adding 1.0 g of $LiClO_4 \cdot 3H_2O$, the solution was again heated for 5 min. and allowed to stand for about 2 h. The bright orange-yellow product, $[NiL_{B\alpha}](ClO_4)_2$, was filtered off, washed with methanol followed by ether. The product was finally recrystallized from an acetonitrile solution of the complex.

The filtrate was concentrated to about 3 mL and allowed to cool. The bright yellow product, $[NiL_{B\beta}](CLO_4)_2$, was filtered off, washed with isopropanol followed by ether and recrystallized from a 1 : 1 acetronitrile–isopropanol mixture.

Nickel(II) Complexes of L_C

A 1.0 g (3.25 mmol) sample of the ligand and 0.90 g (3.7 mmol) of the nickel(II) acetate tetrahydrate solution was added dropwise to the boiling nickel(II) acetate solution. A yellow color developed upon further heating of the solution. During this period the volume was reduced to about 40 mL. 1.0 g of $LiClO_4 \cdot 3H_2O$ was added and the solution was further heated for 15 min. On cooling, a sticky product separated out and the yellow solution was decanted off. On tituration with ethanol, the sticky product gave a yellow powder which was recrystallized from acetonitrile as $[NIL_{C\alpha}](ClO_4)_2$. This was washed with ethanol, then with ether and dried *in vacuo*.

The yellow solution that was decanted off gave a red sticky product upon further concentration. At this stage, the mother liquor was green, which was decanted off and rejected. On tituration with ethanol, the red sticky material gave a bright yellow product, $[NiL_{C\beta}](ClO_4)_2$, which was washed with ether and finally recrystallized from acetonitrile.

Analytical, spectral and conductance data for the complexes are given in Table I.

X-ray Structure Determination of $[NiL_{B\alpha}](ClO_4)_2$

Crystals of this isomer were obtained by the slow evaporation of an acetonitrile/ethanol (80/20 v/v) solution of the complex. Intensity data for an orange crystal (0.30 × 0.50 × 0.80 mm) were measured at room temperature on a Rigaku AFC7R diffractometer fitted with MoKα radiation using the $\omega:2\theta$ scan technique such that 2θ was 60.0°. The data was corrected for Lorentz and polarization effects [8] and an empirical absorption correction was applied [9]. Crystallographic data are summarized in Table II.

The structure was solved by heavy-atom methods [10] and refined by a full-matrix least-squares method based on F [8]. Non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were included in the model at their calculated positions. The asymmetric unit comprises half a complex cation (the Ni^{2+} ion is located on a center of inversion) and a perchlorate anion. Three of the perchlorate-oxygen atoms were found to be disordered over two positions. Refinement revealed relative occupancies of 0.85 : 0.15; the minor components were refined isotropically. The refinement was continued until convergence with a weighting scheme of the form $w = 1/[\sigma^2(F_0) + 0.00002|F_0|^2]$. Final crystallographic

TABLE I Analytical, spectral and conductance data

Complex	*Found*[a] (%)			*d-d band*[b] *ν*, cm^{-1}*(ε)*	*Molar conductivity* Ω^{-1} cm^2 mol^{-1}
	C	*H*	*N*		
$[NiL_{A\alpha}](ClO_4)_2$	38.92	7.08	9.82	21,000 (73)	220
$[NiL_{A\beta}](ClO_4)_2$	38.90	7.09	9.82	21,040 (67)	189
$[NiL_{B\alpha}](ClO_4)_2$	38.92	7.07	9.83	21,000 (79)	195
$[NiL_{B\beta}](ClO_4)_2$	38.91	7.10	9.82	21,100 (90)	170
$[NiL_{C\alpha}](ClO_4)_2$	38.90	7.09	9.81	21,460 (91)	172
$[NiL_{C\beta}](ClO_4)_2$	38.89	7.09	9.80	21,420 (112)	170

[a] Calculated for $C_{18}H_{40}ClN_4NiO_8$: C, 38.92; H, 7.07; N, 9.83%.

[b] Spectra recorded in 1% acetonitrile.

TABLE II Crystallographic data for $[NiL_{B\alpha}](ClO_4)_2$

Formula	$C_{18}H_{40}Cl_2N_4NiO_8$
Formula weight	570.1
Crystal system	monoclinic
Space group	$P2_1/n$
a, Å	10.270(4)
b, Å	8.778(3)
c, Å	14.475(3)
β, °	99.67(2)
V, Å^3	1286.3(6)
Z	2
μ(Mo–Kα), cm^{-1}	10.10
F(000)	604
D_x, g cm^{-3}	1.472
No. reflns meas.	4183
No. unique reflns	4026
No. reflns with $I \geq 3.0\sigma(I)$	2857
R	0.041
R_w	0.042
ρ, e Å^{-3}	0.39

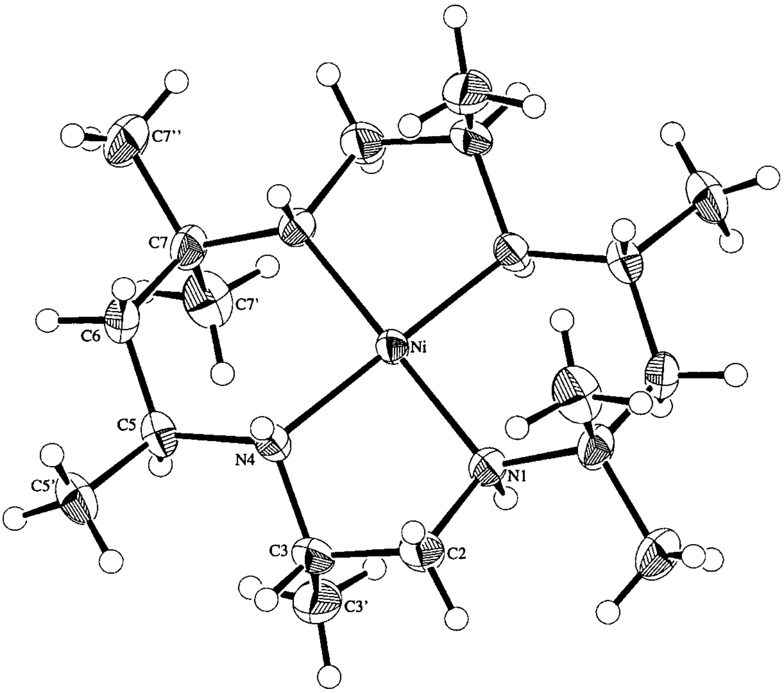


FIGURE 1 Molecular structure and crystallographic numbering scheme for the cation in $[NiL_{B\alpha}](ClO_4)_2$.

data are given in Table II and the numbering scheme employed is shown in Fig. 1 which was drawn with ORTEP [11] at the 50% probability level. The data have been deposited at the Cambridge Crystallographic Data Center with deposition number 145869.

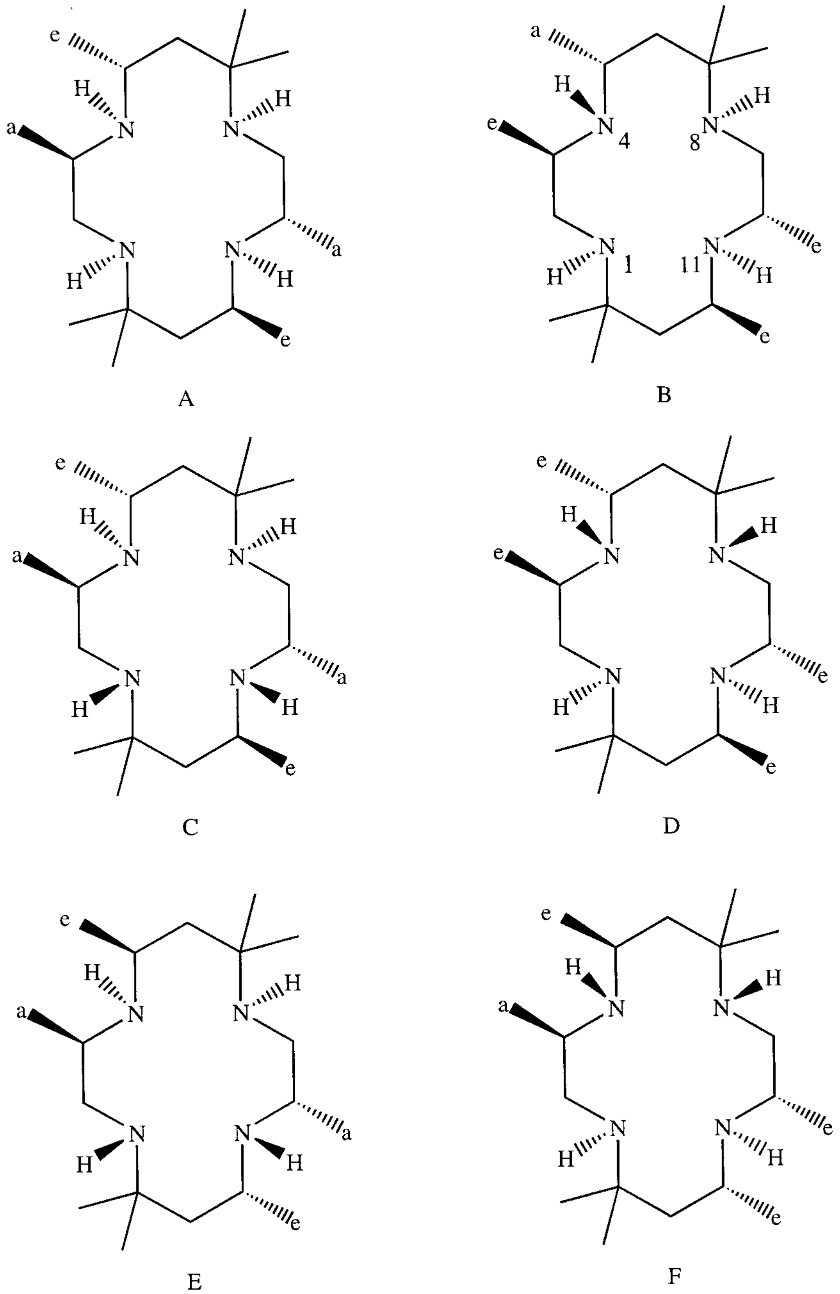
RESULTS AND DISCUSSION

On the basis of their ^1H and ^{13}C NMR spectra [4], each of L_A, L_B and L_C has been assigned a structure shown in Scheme 1. The reactions of these macrocyclic ligands with nickel(II) acetate tetrahydrate and subsequent addition of lithium perchlorate trihydrate yield yellow or orange-yellow complexes during the course of the synthesis. The separated diastereoisomers for L_A have been designated as $[NiL_{A\alpha}](ClO_4)_2$ and $[NiL_{A\beta}](ClO_4)_2$. A similar nomenclature was employed for the complexes containing the L_B and L_C macrocycles. The N-chiral diastereoisomers, as their perchlorate salts, have different solubilities and could be separated readily by sequential precipitation during synthesis. The electronic spectra (Table I) for these complexes show *d–d* bands in the region 21,000–21,460 cm^{-1} that can be assigned to the characteristic $^1A_{1g} \rightarrow {}^1B_{1g}$ transition for square planar Ni^{2+} [12–14]. The diastereoisomers show subtle differences in the fingerprint region of their IR spectra. Further, the IR spectra exhibit all the expected characteristic bands for such complexes with prominent νNH bands (around 3200 cm^{-1}) and perchlorate bands around 1000 and 620 cm^{-1}. The IR spectrum of each diastereoisomer is completely reproducible during their repeated syntheses. The molar conductivities were measured in 5% acetonitrile solution and have values in the range 170–220 $\Omega^{-1}cm^2mol^{-1}$, indicative of 1 : 2 electrolytes (Table I).

The ^1H NMR spectra of these complexes present some key features that can be used to assign their configurations. The most prominent feature of the spectra relates to the geminal methyl groups that appear as two singlets with each integrating to six protons. Each of methyl groups bound to a chiral carbon appears as a doublet. If the doublet is upfield, it is assigned to an equatorial position and conversely, a downfield doublet is due to an axially oriented methyl group [15,16]. A comparison of the expected pattern for a particular configuration with the previously observed data enables assignment of the configurations in the diastereoisomers reported herein [4–7].

In the case of $[NiL](ClO_4)_2$ ($L = L_A$ & L_C), where the isomers L_A, and L_C are conformers [i.e. they differ only in the axial and equatorial positions of the methyl groups bound to the chiral carbons, C(3,5,10 and 12)] out of the sixteen possible isomeric forms, molecular models show that only structures A, B, C and D (Scheme 2) are virtually strain free. The ^1H NMR spectrum of $[NiL_{A\alpha}](ClO_4)_2$ shows the appearance of two singlets at 1.18 and 1.70 ppm corresponding to six protons each. These singlets are assigned to the C(7) and C(14) *gem*-dimethyl groups having equatorial and axial orientations, respectively. Two doublets at 1.05 and 1.42 ppm, six protons each, can be assigned to a pair of equatorial and axial methyls. respectively. From symmetry, this pattern requires the two methyls at C(3), C(10) and C(5), C(12) to be pair-wise equivalent as found in structures A and C (Scheme 2) which places the C(5), C(12) pair in an equatorial orientation and the C(3), C(10) pair in an axial orientation. The downfield spectrum of this isomer is not well-resolved but it is possible to identify two broad signals at 2.55 and 2.75 ppm, assignable to the four β- and four α-protons, respectively.

Structure A has all the four NH hydrogens lying on one side of the NiN_4 plane and is the most stable form. Structure C has a '*trans*-III structure' similar to the thermodynamically most stable *trans*-III structure of cyclam, in that there is no steric crowding on the ring [6]. In terms of the steric crowding associated with the peripheral methyl groups, this structure appears to be less stable compared to structure A. In the case of the related nickel(II) complex of $(CH_2NH_2)Me_4[14]$ane, the isomer with all four



A B C D E F

SCHEME 2

NH hydrogens lying on one side of the NiN$_4$ plane crystallizes first and the one having an NH orientation similar to the *trans*-III form of cyclam crystallizes later [17]. By analogy to the behavior of this macrocycle, which has five peripheral substituents and is subject to steric crowding, the first fraction in the preparation of [NiL$_A$](ClO$_4$)$_2$

complexes should have all four NH hydrogens lying on one side of the NiN_4 plane and hence, the complex $[NiL_{A\alpha}](ClO_4)_2$ is assigned as the A conformer. The ^1H NMR spectrum of $[NiL_{A\beta}](ClO_4)_2$ shows two singlets at 1.10 and 1.71 ppm corresponding to the C(7) and C(14) *gem*-dimethyl pairs. Two doublets at 1.00 (equatorial) and 1.37 (axial) ppm are assigned to the remaining four methyl groups bound to the chiral carbon atoms. The integration of these signals corresponds to a 1 : 3 axial : equatorial ratio. This configuration is in the logical sequence of interconversion between diastereoisomeric configurations in the sense that conversion of the most stable structure to the next should involve epimerization of only one chiral NH group. The spectrum further shows two broad multiplets at 2.22 and 2.87 ppm corresponding to four protons each at the α- and β-positions. The complex $[NiL_{A\beta}](ClO_4)_2$ is therefore assigned to contain ligand B.

For the $[NiL_B](ClO_4)_2$ complexes, out of 16 possible diastereoisomers, there are two strain-free structures, E & F, as shown in Scheme 2.

The ^1H NMR spectrum of $[NiL_{B\alpha}](ClO_4)_2$ shows two signals at 1.10 (6H) and 1.62 (6H) ppm which are assigned to the two *gem*-dimethyl pairs. Two doublets at 1.02 ppm (6H) and 1.35 ppm (6H) are assigned to two equatorial and two axial methyl groups which are pairwise equivalent. Both structures E and F (Scheme 2) have a '*trans*-III' type structure and are reported to be thermodynamically equivalent [18]. However, structure F has three equatorially oriented methyls contrary to the observed ^1H NMR spectrum and hence, is ruled out for this diastereoisomer. Structure E is therefore assigned to $[NiL_{B\alpha}](ClO_4)_2$ and this has been confirmed by an x-ray crystallographic study (see later). The downfield spectrum of this isomer is not well resolved but two broad signals for β- and α-methylene protons at 2.45 and 2.80 ppm, respectively, can be identified. The ^1H NMR spectrum of $[NiL_{B\beta}](ClO_4)_2$ shows two singlets at 1.06 ppm (6H, equatorial) and 1.68 (6H, axial) ppm and are assigned to *gem*-dimethyl pairs. The observation of two doublets at 1.00 and 1.40 ppm with integration 9 : 3 allows the assignment of F as the conformation of the ligand in $[NiL_{B\beta}](ClO_4)_2$. The downfield spectrum shows a broad multiplet at 2.17 ppm (four β-methylene protons) and a broad multiplet at 2.72 ppm (four α-methylene protons). The remaining four chiral protons appear as two broad multiplets corresponding to two protons each at 3.55 and 4.15 ppm.

For the assignment of the structures of $[NiL_{C\alpha}](ClO_4)_2$ and $[Nil_{C\beta}](ClO_4)_2$ it should be noted that both L_A and L_C have the same relative disposition of four chiral methyl groups with respect to the NiN_4 plane and that in the free state, they differ only in their ring conformations [5]. Thus, the diastereoisomers that can be assigned for L_C will be identical with the ones for L_A. As conformations A and B have already been assigned to $[NiL_{A\alpha}](ClO_4)_2$ and $[NiL_{A\beta}](ClO_4)_2$, respectively, the remaining two structures C and D should be found in the structures of $[NiL_{C\alpha}](ClO_4)_2$ and $[NiL_{C\beta}](ClO_4)_2$. It should be emphasized that although $[NiL_{A\alpha}](ClO_4)_2$ and $[NiL_{C\alpha}](ClO_4)_2$ display similar ^1H NMR patterns, the two diastereisomers show very distinct infrared spectra in their fingerprint regions.

The ^1H NMR spectrum of $[NiL_{C\alpha}](ClO_4)_2$ features a broad signal at 1.02 ppm, a doublet at 1.40 ppm and a singlet at 1.70 ppm. The 1.70 ppm singlet (6H) is assigned to the axial components of the *gem*-dimethyl pair while the 1.40 ppm doublet (6H) is assigned to a pair of axial chiral methyl groups. The broad signal at 1.02 ppm corresponding to 12H is due to the overlap of the equatorial component of the *gem*-dimethyl pair with the doublet of the equatorial pair of chiral methyl groups. It is concluded that

$[NiL_{C\alpha}](ClO_4)_2$ should have a pair of axially and a pair of equatorially oriented methyl groups and hence, is assigned to contain structure C. This assignment has already been confirmed by an independent x-ray crystallographic study [19]. The downfield spectrum of this complex shows the β-methylene protons at 2.17 ppm (4H), the α-methylene protons at 2.62 ppm (4H) and the methine protons at 3.62 ppm (2H) and 4.07 ppm (2H).

The ^1H NMR spectrum of $[NiL_{C\beta}](ClO_4)_2$ shows very broad signals which indicate the presence of some paramagnetic character in the complex. However, the spectrum shows two broad signals at 1.08 and 1.70 ppm with an integration ratio of 1 : 3. The downfield 1.70 signal is assigned to the two axial methyls associated with the pair of *gem*-dimethyl groups. The signal at 1.08 ppm therefore corresponds to 18H : 6H due to the equatorial component of the pair of *gem*-dimethyl groups and 12H due to the four chiral methyl groups. The chemical shift of this resonance shows that all the chiral methyl groups should be equatorial. This orientation is present in ligand structure D.

X-ray Structure of $[NiL_{B\alpha}](ClO_4)_2$

The molecular structure of the cation in $[NiL_{B\alpha}](ClO_4)_2$ is represented in Fig. 1 and selected interatomic parameters are collected in Table III. The monoclinic unit cell comprises two complex cations and four perchlorate anions so that the Ni atom is located on a crystallographic center of symmetry. The geometry about the Ni atom is square planar defined by an N_4 donor set with a C-meso and N-meso configuration and the greatest deviation from the ideal geometry seen in the N(l)–Ni–N(4) angle of 86.47(9)°; from symmetry, the Ni atom is coplanar with the N_4 donor set. The macrocycle forms alternating five- and six-membered rings, the latter adopting chair conformations. The Ni–N distances are indistinguishable and are very similar to those found in the closely related complex $[NiL_{C\alpha}](ClO_4)_2$ [19]. Other parameters are as expected. The perchlorate anions form relatively short contacts with the Ni center, above and below the NiN_4 plane, such that Ni...O(3) is 3.257(2) Å. The structure determination confirms the presence of ligand E (Scheme 2). The *trans*-III structure [20] has been

TABLE III Selected interatomic parameters (Å, deg.) for $[NiL_{B\propto}](ClO_4)_2$[a]

Ni–N(1)	1.953(2)	Ni–N(4)	1.962(2)
N(1)–C(2)	1.491(4)	N(1)–C(7)	1.513(4)
N(4)–C(3)	1.496(4)	N(4)–C(5)	1.500(3)
C(2)–C(3)	1.501(4)	C(3)–C(3′)	1.514(5)
C(5)–C(5′)	1.527(4)	C(5)–C(6)	1.508(4)
C(6)–C(7)	1.522(4)	C(7)–C(7′)	1.527(5)
C(7)–C(7″)	1.534(4)		
N(1)–Ni–N(4)	86.47(9)	N(1)–Ni–N(4)′	93.53(9)
Ni–N(1)–C(2)	107.9(2)	Ni–N(1)–C(7)′	120.5(2)
C(2)–N(l)–C(7)′	112.7(2)	Ni–N(4)–C(3)	108.1(2)
Ni–N(4)–C(5)	124.0(2)	C(3)–N(4)–C(5)	111.7(2)
N(1)–C(2)–C(3)	108.3(2)	N(4)–C(3)–(2)	104.8(2)
N(4)–C(3)–C(3′)	112.1(3)	C(2)–C(3)–C(3′)	113.3(3)
N(4)–C(5)–C(5′)	111.0(2)	N(4)–C(5)–C(6)	112.0(2)
C(5′)–C(5)–C(6)	109.5(2)	C(5)–C(6)–C(7)	116.3(2)
N(1)–C(7)′–C(6)′	107.1(2)	N(1)–C(7)′–C(7′)′	109.8(2)
N(1)–C(7)′–C(7″)	109.8(3)	C(6)–C(7)–C(7′)	111.5(3)
C(6)–C(7)–C(7″)′	107.5(3)	C(7′)–C(7)–C(7″)	111.0(3)

[a] primed atoms are related by the symmetry operation.

shown to be the most stable configuration for [Co(R, S, R, S-cyclam)Cl$_2$]$^+$ and other related complexes [6–8,21].

Acknowledgements

The authors are thankful to the Ministry of Education, India for the award of a research fellowship to TGR and to the Ministry of Science and Technology, Government of Peoples Republic of Bangladesh for a grant to SKSH.

References

[1] N.F. Curtis, D.A. Swann, T.N. Waters and I.F. Maxwell (1969). *J. Am. Chem. Soc.*, **91**, 4588.
[2] T. Ito and D.H. Busch (1974). *Inorg. Chem.*, **13**, 1770.
[3] D.A. Swann, T.N. Waters and N.F. Curtis (1972). *J. Chem. Soc.*, *Dalton Trans.*, 1115.
[4] R. Bembi, S.M. Sondhi, A.K. Singh, A. K. Jhanji, T.G. Roy, J.W. Lown and R.G. Ball (1989). *Bull. Chem. Soc. Jpn.*, **15**, 3701.
[5] R. Bembi, M.G.B. Drew, R. Singh and T.G. Roy (1991). *Inorg. Chem.*, **30**, 1403.
[6] R.W. Hay, R. Bembi and D.A. House (1984). *J. Chem. Soc., Dalton Trans.*, 1921.
[7] R.W. Hay, D.A. House and R. Bembi (1984). *J. Chem. Soc.*, *Dalton Trans.*, 1927.
[8] *TEXSAN*. Structure Analysis Package (1997). Molecular Structure Corporation, TX.
[9] N. Walker and D. Stuart (1983). *Acta Crystallogr.*, **A39**, 158.
[10] P.T. Beurskens, G. Admiraal, G. Beurskens, W P. Bosman, S. García-Granda, J.M.M. Smits and C. Smykalla (1992). The DIRDIF program system, Technical Report of the Crystallography Laboratory. University of Nijmegen, The Netherlands.
[11] C.K. Johnson (1976). *ORTEP-II*, Report ORNL-5138. Oak Ridge National Laboratory, Oak Ridge, TN.
[12] R.A. Kolinski and B. Korybut-Daszkieurcz (1969). *Bull. Acad. Pol. Sc.*, **42**, 13.
[13] A.M. Tait and D.H. Busch (1977). *Inorg. Chem.*, **16**, 966.
[14] R.W. Hay, D.P. Piplani and B. Jerag (1977). *J. Chem. Soc.*, *Dalton Trans.*, 1951.
[15] R.A. Kolinski and B. Korybut-Daszkieuicz (1974). *Inorg. Chem. Acta.*, **14**, 237.
[16] N.F. Curtis (1974). *Aust. J. Chem.*, **27**, 71.
[17] B. Korybut-Daszkiewicz (1985). *J. Chem. Soc., Chem. Commun.*, 192.
[18] L.J. Dehays and D.H. Busch (1973). *Inorg. Chem.*, **12**, 2010.
[19] G. Ferguson, A.J. Lough and R. Bembi (1990). *Acta Crystallogr.*, **C46**, 213.
[20] B. Bosnich, C.K. Poon and M.L. Tobe (1963). *Inorg. Chem.*, **4**, 1102.
[21] T.W. Hambley (1986). *J. Chem. Soc.*, *Dalton Trans*, 565.