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ORIGINAL PAPER

Synthesis and characterization of two new macrobicyclic salts containing hexahydropyrimidine moieties: experimental and density functional theory studies

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Abstract Two macrocyclic Schiff base ligands (L^1, L^2) and their related reduced forms (L^3 and L^4) have been prepared. In the presence of nickel(II) perchlorate in methanol, the reinforced macrobicyclic salts containing hexahydropyrimidine cation moiety have been developed. Here, it seems that Ni(II) perchlorate acts as oxidizing agent converting methanol to the formaldehyde which in turn bridges two nitrogen atoms of reduced forms of macrocycle producing final products. All Schiff base ligands and their reduced forms together with related salts were characterized by elemental analysis, IR spectroscopy, ^{1}H and ^{13}C NMR, EI-Mass and in the case of $[L^{3'}](ClO_4)$ salt by X-ray crystallography. The proposed mechanism for the formation of macrobicyclic ligand $[L^{3'}]$ from the reaction of macrocyclic ligand L^3 and formaldehyde has also been studied via density functional theory (DFT).

Keywords Macrocyclic ligand · Hexahydropyrimidine moieties · X-ray crystal structure · Macrobicyclic ligand · Density functional theory

Introduction

Reinforced macrocycles are prepared by the inclusion of bridging alkyl groups between nitrogen atoms in the macrocyclic ring. Reinforced macrocycles showed much greater rigidity than those non-reinforced analogues [1]. The addition of an extra bridging group between nitrogen donors on macrocyclic ligands (to give a piperazine-like structure) leads to much more rigid ligands displaying selectivity for metal ions due to the match between the size of the metal ion and that of the macrocyclic cavity in comparison with conventional macrocyclic ligands [2].

Macrocyclic Schiff base ligands have gained favour due to both their relatively straightforward synthesis and their multidentate nature which results in very high binding constants for many d- and f-block metals [3]. Macrocyclic Schiff base ligands containing nitrogen donor groups have received particular attention because of their mixed hard–soft donor character, versatile coordination behaviour [4, 5] and biological activities, i.e. toxicity against bacterial growth [6], anticancerous [7] and other biochemical properties [8]. In some works, the presence of metal ion could change the structure of ligand and open the rings due to reversible nature of imines linkage [9], even in some cases not only open the rings but also rearrange the structure of ligands because of streak hindrance as a result of metal ion coordination [10]. In other work, the presence of various metal ion salts such as Ni(II) perchlorate has been oxidized methanol to formaldehyde [11] which in turn bridges two nitrogen atoms and a new ring has been formed in the structure of product [12].

We have also studied mono- and binuclear complexes of transition metal ions containing nitrogen and oxygen donors atoms in macrocyclic or macroacyclic ligands [13–16]. As an extension of this idea, we report in this work synthesis and characterization of four potentially tetradentate

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macrocyclic Schiff base ligands and their corresponding reduced forms, L[1], L[2], L[3] and L[4] (Fig. 1). After addition of the nickel(II) perchlorate to the reduced form of ligands (L[3] or L[4]) solutions, surprisingly two reinforced macrobicyclic ligands have been isolated (Scheme 1). We also reported the crystal structure of [$L^{3'}$](ClO_4) (Fig. 2).

Experimental

Chemical and starting materials

α,*α*′-Dibromo-*m*-xylene, 1,3-diaminopropane, 1,4-diaminobutane, ethanol, methanol, acetonitrile and metal salts were obtained from the Merck Company and were used without further purification.

Caution *α*,*α*′-Dibromo-*m*-xylene is a very caustic and it should be treated and handled with caution.

General synthesis of the 1, 3-bis(2-formyl phenoxy methyl)benzene

To a refluxing solution of salicylaldehyde (0.381 g, 3.125 mmol) in absolute ethanol (20 mL), a solution of sodium hydroxide in (10 mL) water was added (0.125 g, 3.125 mmol). The resulting mixture was magnetically stirred and heated for 30 min. Then, *α*,*α*′-dibromo-*m*-xylene (0.411 g, 1.56 mmol) and sufficient ethanol (20 mL) were added. Refluxing was continued for 48 h. The solution was then allowed to cool and the product formed as colourless crystals which were filtered off and recrystallized from acetonitrile.

Yield: 0.630 g (64.1%). Mp; 118 °C, IR (KBr, cm^{-1}) 1682 ν(C=O), ^1H NMR ($CDCl_3$, ppm) 5.24 (4H, 2-OCH_2), 7.09–7.84 (12H, Ar–H), 10.56 (2H, CHO), ^{13}C NMR ($CDCl_3$, ppm) 70.26, 113.114, 121.19, 126.09, 127.10, 130.87, 135.93, 141.39, 161.14 (Ar–C), 189.57 (2C, C=O).

General synthesis of the Schiff base ligands (2)

1, 3-Diaminopropane or 1, 4-diaminobutane (0.3 mmol) in dry methanol (10 mL) was added dropwise to a boiling solution of 1, 3-bis(2-formyl phenoxy methyl) benzene (0.104 g, 0.3 mmol) in methanol (15 mL). Refluxing continued for 24 h. We concentrated the solution to a volume 5 mL, which led to the deposition of a powdery precipitate washed with diethyl ether and dried in vacuum.

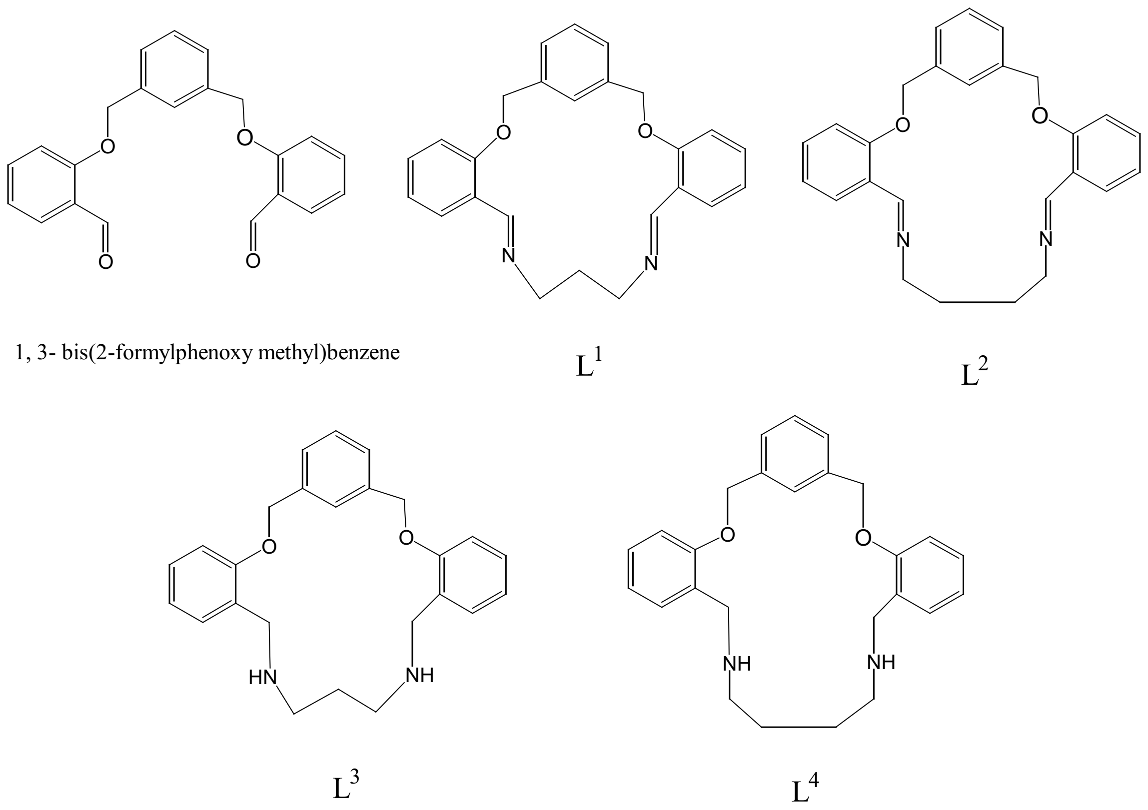
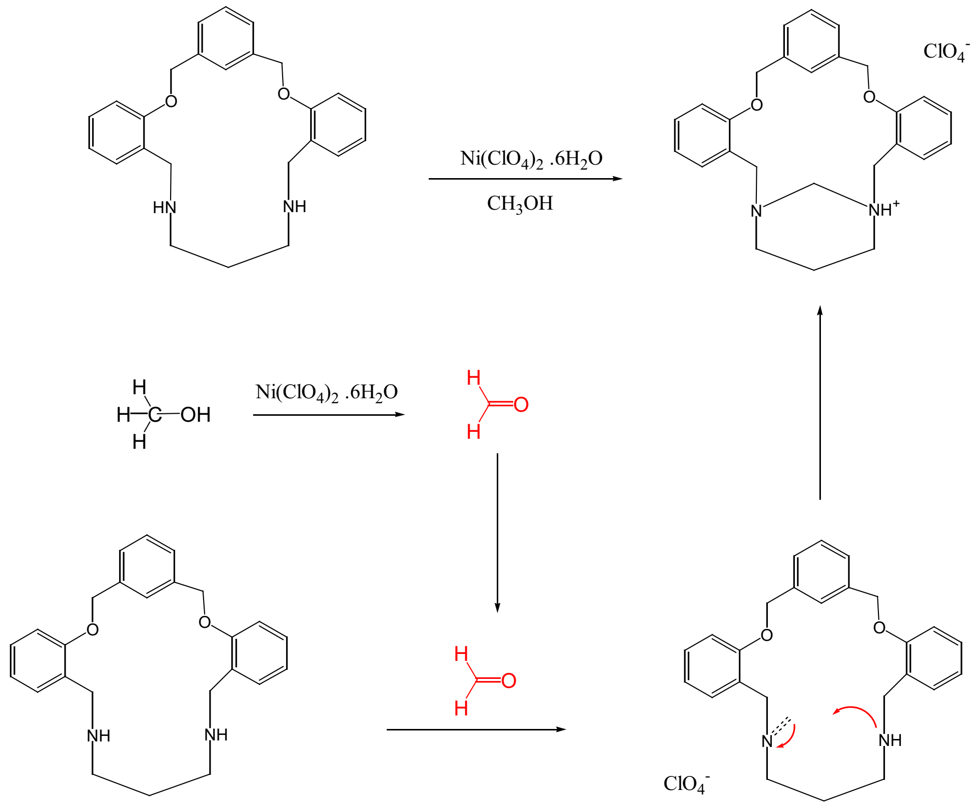


Fig. 1 The structure of aldehyde and synthesized ligands

Scheme 1 Schematic pattern for the formation of macrobicyclic ligand



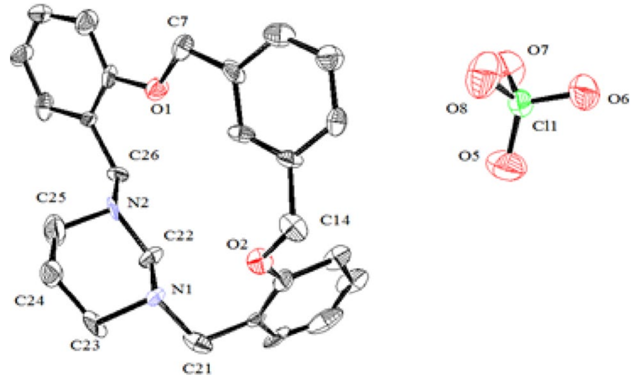


Fig. 2 View of $[L^{3'}](ClO_4)$ in the asymmetric unit showing the numbering scheme. Thermal ellipsoids are drawn at 30% probability level, while hydrogen size is arbitrary

L^1

Yield: 0.118 g (32%). Anal. Calc. for $C_{24}H_{22}N_2O_2$.: C, 78.1; H, 6.29; N, 7.28. Found: C, 79.0; H, 6.38; N, 7.34%. IR (KBr, cm^{-1}) 1641 ν(C=N), 1H NMR ($CDCl_3$, ppm) 3.51–3.63 (4H, CH_2–$CH_2^{(2,3)}$), 5.17–5.32 (4H, $2CH_2O$), 6.91–7.99(12H, Ar–H), 8.56, 8.58 (2H, 2CH=N), 13C NMR ($CDCl_3$, ppm) 29.17 (C^1), 58.23 (C^2, C^3) 70.05 (C^4, C^5) 117.04–158.99 (12C, Ar–C), 159.68 (C^6, C^7). EI-MS (m/z, %): 384 (Fig. 1).

L^2

Yield: 0.177 g (46%). IR (KBr, cm^{-1}) 1640 ν(C=N), Anal. Calc. for $C_{24}H_{22}N_2O_2$: C, 78.6; H, 6.8; N, 6.8. Found: C, 78.1; H, 6.41; N, 6.13%, ^{1}H NMR ($CDCl_3$, ppm) 1.23–1.47(4H, CH_2–$CH_2^{(2,3)}$), 3.72–3.84(4H, CH_2–$CH_2^{(1,4)}$), 5.09–5.26 (4H, $2CH_2O$), 6.83–7.98 (12H, Ar–H), 8.65, 8.72 (2H, 2CH=N), ^{13}C NMR ($CDCl_3$, ppm) 26.86 (C_2, C_3), 52.07 (C_1, C_4), 69.42 (C_5, C_6) 116.87–136.56 (12C, Ar–C), 161.75 (C_7, C_8). EI-MS (m/z, %): 398 (Fig. 1).

General synthesis of reduced forms of the ligands

$NaBH_4$ (2.4 g) was added slowly to the stirred solution of ligands (L^1, L^2), in dry methanol (10 mL). After the reaction had ceased, the solution was cooled and then filtered. On addition of ice to the filtrate, oily phase separated, which was extracted with chloroform (three times). The chloroform was removed by using a rotary evaporator. That eventually crystallized to form a white solid.

L^3

Yield: 0.19 g (40%). Anal. Calc. for $C_{25}H_{28}N_2O_2$: C, 77.30; H, 7.26; N, 7.21. Found: C, 77.96; H, 7.85; N, 7.67%. IR (KBr, cm^{-1}) 1600 ν(N–H), ^{1}H NMR ($CDCl_3$, ppm) 1.72 (2H, $CH_2^{(2)}$), 1.91 (2H, 2NH), 2.64 (4H, $2CH_2^{(1,3)}$), 3.80 (4H,

$2CH_2^{(6,7)}$), 5.17 (4H, $2CH_2^{(4,5)}$), 7.02–7.54 (12H, Ar–H), ^{13}C NMR ($CDCl_3$, ppm) 30.11 (C_2), 47.91 (C_1, C_3) 50.10 (C_6, C_7) 72.50 (C_4, C_5) 112.03–151.8 (12C, Ar–C). EI-MS (m/z, %): 388 (Fig. 1).

L^4

Yield: 0.19 g (42%). Anal. Calc. for $C_{26}H_{30}N_2O_2$.: C, 77.58; H, 7.51; N, 6.96. Found: C, 78.15; H, 8.27; N, 7.55%. IR (KBr, cm^{-1}) 1600 ν(N–H), ^1H NMR ($CDCl_3$, ppm) 1.35 (4H, $CH_2^{(2,3)}$), 2.15 (2H, 2NH), 2.50 (4H, $2CH_2^{(1,4)}$), 3.76 (4H, $2CH_2^{(7,8)}$), 5.05 (4H, $2CH_2^{(5,6)}$), 6.93–7.58 (12H, Ar–H). EI-MS (m/z, %): 402 (Fig. 1).

General method of synthesis of ligand salts

$Ni(ClO_4)_2$ (0.25 mmol) was dissolved in dry methanol (10 mL) and slowly added to a stirred boiling solution (20 mL) of L^3 or L^4 (0.3 mmol) in the same solvent with refluxing continuing for 6 h. The solution was reduced to ca. 5 mL, and the precipitate was filtered and washed with diethyl ether and dried in vacuum. Crystals suitable of $[L^{3'}]$ (ClO_4) for X-ray diffraction studies were obtained by slow diffusion of Et_2O vapour into the MeOH/MeCN solution of the above solid.

$[L^{3'}](ClO_4)$

Yield: 49%. Anal. Calc. for: C_{26} H_{29} Cl N_2 O_6: C, 62.33; H, 5.83; N, 5.59. Found: C, 62.40; H, 581; N, 5.78%. IR (KBr, cm^{-1}): 1601 υ(N–H), 1100 $\upsilon(ClO_4^-)$. EI-MS (m/z, %): 501.

$[L^{4'}](ClO_4)$

Yield: 42%. Anal. Calc. for: C_{27} H_{31} Cl N_2 O_6: C, 62.96; H, 6.06; N, 5.44. Found: C, 62.87; H, 6.22; N, 5.78%. IR (KBr, cm^{-1}): 1602 υ(N–H), 1100 $\upsilon(ClO_4^-)$. EI-MS (m/z, %): 515.

Physical measurements

IR spectra were measured on a PerkinElmer FT-IRGX spectrophotometer. Mass spectra were recorded using VARIAN 3400 GC-Mass spectrometer. NMR spectra were measured on Bruker DPX 400 spectrometers. Elemental analyses were performed in a Carlo-Erba EA microanalyser.

X-ray crystal structure determination

Single-crystal data for $[L^{3'}](ClO_4)$ were collected at room temperature with a Bruker APEX II CCD area detector diffractometer using Mo Ka radiation ($\lambda = 0.71073$ Å). Data collection, cell refinement, data reduction and absorption correction were performed using multiscan methods with Bruker software [17–19]. The structures were solved by direct methods using SIR2004 [20]. The non-hydrogen atoms were refined anisotropically by the full-matrix least squares method on F^2 using SHELXL [21]. The hydrogen atoms of NH_2 groups were found in difference Fourier map and refined isotropically. The other hydrogen (H) atoms were placed at the calculated positions and constrained to ride on their parent atoms. Details concerning collection and analysis are reported in Table 1.

Theoretical studies

The calculations were done with the Gaussian 03 suite of programs [22]. The reactants, intermediates, transition states and product were optimized at BP86/Def2-SVP level of theory. The frequencies were computed at BP86/Def2-SVP

Table 1 Crystal data and structure refinement for $[L^{3'}]$ (ClO_4)

Empirical formula	$C_{26}H_{29}ClN_2O_6$
Formula weight	500.96
Temperature (K)	293
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group unit cell dimensions	Pna2(1)
a (Å)	16.8734 (6)
b (Å)	9.2665 (3)
c (Å)	30.5482 (15)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	4776.4 (3)
Z	8
Dcalc (mg/m^3)	1.393
Absorption coefficient (mm^{-1})	0.206
F (000)	2112
Index ranges	$-20 \leq h \leq 20, -11 \leq k \leq 11, -33 \leq l \leq 36$
Reflections collected/unique [$R_{(int)}$]	0.206
29.16° (%) = Completeness to θ	99.60%
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	8227/73/602
Goodness-of-fit[a] on F^2	0.83
Final R^b indices [$I > 2\ s\ (I)$]	$R_1 = 0.0763$
	w$R_2 = 0.0905$
R^b indices (all data)	$R_1 = 0.1270$
	w$R_2 = 0.2201$
e.A^{-3} (largest diff. peak and hole)	0.263/– 0.193

[a] GOF is defined as $\{\sum[w(F_0^2 - F_c^2)]/(n - p)\}^{1/2}$ where n is the number of data and p is the number of parameters

[b] $R = \left\{ \sum ||F_0 - |F_c|||/\sum |F_0|, wR_2 = \left\{ \sum w\left(F_0^2 - F_c^2\right) \Big/ \sum w\left(F_0^2\right)^2 \right\}^{1/2} \right.$

level. All minima and transition structures were confirmed to have none and one imaginary frequency, respectively.

Results and discussion

The free Schiff base macrocyclic ligands, L^1 and L^2, were prepared from [1 + 1] cyclocondensation of 1, 3-diaminopropane or 1, 4-diaminobutane and 1, 3-bis (2-formyl phenoxy methyl)benzene. These ligands were precipitated as air-stable solid compounds. Then, these macrocyclic ligands reduced by sodium borohydride and diamine macrocyclic ligands L^3 or L^4 were obtained. All ligands were characterized by elemental analyses, EI-Mass, IR spectroscopy, ^{1}H NMR and ^{13}C NMR. In the presence of $Ni(ClO_4)_2$, in methanol solution, macrobicyclic ligand salts $[L^{3'}](ClO_4)$ and $[L^{4'}](ClO_4)$ were isolated from their reduced forms. These compounds were characterized by elemental analyses, EI-Mass and IR spectroscopy in two cases and X-Ray crystallography in the case of $[L^{3'}](ClO_4)$. In this compound, nickel(II) perchlorate acts vital role in converting methanol to formaldehyde and formaldehyde can form a new cycle in macrocyclic ligand and result in final compound instead of macrocyclic complex. In previous work, in similar structures, we have reported the closure of macrocyclic ring in the presence of Co(II) and Zn(II) metal ions [9] and in another work, because of the preferential structural requirement caused by exerting extra force due to steric hindrance imposed by the electronic nature of the copper(II) ion, polymeric open chain complexes were obtained instead of macrocyclic ones [10] and in this work we observed that Ni(II) perchlorate acts as oxidant, and the new macrobicyclic ligand salt was characterized.

The IR spectra of the compound show a sharp band in the range 1601 cm^{-1}, attributed to (N–H) and a wide band in the range 2600–2886 cm^{-1}, attributed to υ(N–H$^+$). This is indicative of the linking nitrogen atoms per carbon, and six- and seven-membered rings in the skeleton of macrocycle were obtained and separated as ligand salt's from metal ions.

Crystal structures

X-ray crystal structures of $[L^{3'}](ClO_4)$

Suitable crystals of $[L^{3'}](ClO_4)$ were obtained from an acetonitrile/methanol solution by slow diffusion of diethyl ether. The ORTEP view of the compound is shown in Fig. 2. Crystallographic data, structure refinement parameters and selected bond distances and angles are given in Table 1.

$[L^{3'}](ClO_4)$ crystallizes in the orthorhombic *Pna*2 space group. The asymmetric unit consists of two $L^{3'}$ unit and two crystallized perchlorates (ClO_4^-) anions. Interestingly, each macrobicyclic unit is stabilized by an intricate array of H-bonding interactions with crystallized lattice perchlorate anion. Supramolecular involves weak C–H···π interactions between the H atoms of the –CH$_2$ group of one macrobicyclic and the aromatic ring of another macrobicyclic, which is further reinforced by strong non-covalent H-bonding interactions involving lattice perchlorate anion, to form an overall 2D structure. The C–N(2)–C bond angle is smaller than C–N(1)–C in the six-membered ring and C–O(1)–C in another ring is smaller than C–O(2)–C. In the case of bond lengths C(1)–N(2) have taller, and C(2)–O(2) have shorter bond length in this compound (Tables 2 and 3).

Computational studies

The proposed mechanism for the formation of macrobicyclic ligand $[L^{3'}]$ from the reaction of macrocyclic ligand L^3 and formaldehyde has been investigated using density functional theory (DFT) (see Fig. 3). The geometries of all compounds investigated here were optimized at the BP86/Def2-SVP level as given in Fig. S1. The calculated structural data for $[L^{3'}]$ were compared with corresponding X-ray crystal structure (see Table S1). The result shows that there is good agreement between the calculated structural data with those derived with X-ray crystal structure for $[L^{3'}]$ (see Table S1). The relative Gibbs free energy (See Table S2) profile for the reaction pathway is shown in Fig. 3.

At first, according to experimental data derived in this study, oxidation of methanol to formaldehyde was observed. The

Table 2 A comparison between selected calculated bond lengths (Å) and bond angles for macrobicyclic ligand salt, and the corresponding experimental values

Bond lengths (Å)	Experimental	BP86/def2-SVP
C(1)–N(2)	1.430	1.430
In six-membered aliphatic ring		
C(1)–N(1)	1.520	1.520
In six-membered aliphatic ring		
C(1)–N(2)	1.522	1.522
C(1)–N(1)	1.484	1.484
C(1)–O(2)	1.431	1.431
C(2)–O(2)	1.369	1.369
C(1)–O(1)	1.377	1.377
C(2)–O(1)	1.449	1.449
Bond angle (°)		
C–O(2)–C	119.57	119.569
C–O(1)–C	118.25	118.249
C–N(1)–C	112.29	112.297
In six-membered aliphatic ring		
C–N(2)–C	109.50	109.496
In six-membered aliphatic ring		
C–N(1)–C	114.15	114.93
C–N(2)–C	113.83	112.96

Table 3 Calculated first vibrational frequency and zero point correction as well as thermal correction to Gibbs free energy and sum of electronic and thermal free energies (G) for the compounds investigated here at BP86/Def2-SVP

	L^3	TS-1	Int1	TS-2	Product
First vibrational frequency (cm^{-1})	25.26	−1141.22	21.70	−165.77	33.48
Zero point correction(ZPE) (Hartree)	0.470476	0.496946	0.501412	0.496336	0.476294
Thermal correction to Gibbs free energy (Hartree)	0.414818	0.438854	0.441817	0.440518	0.422383
Sum of electronic and thermal free energies (G) (Hartree)	−1228.136971	−1342.489687	−1342.541899	−1342.484583	−1266.204544

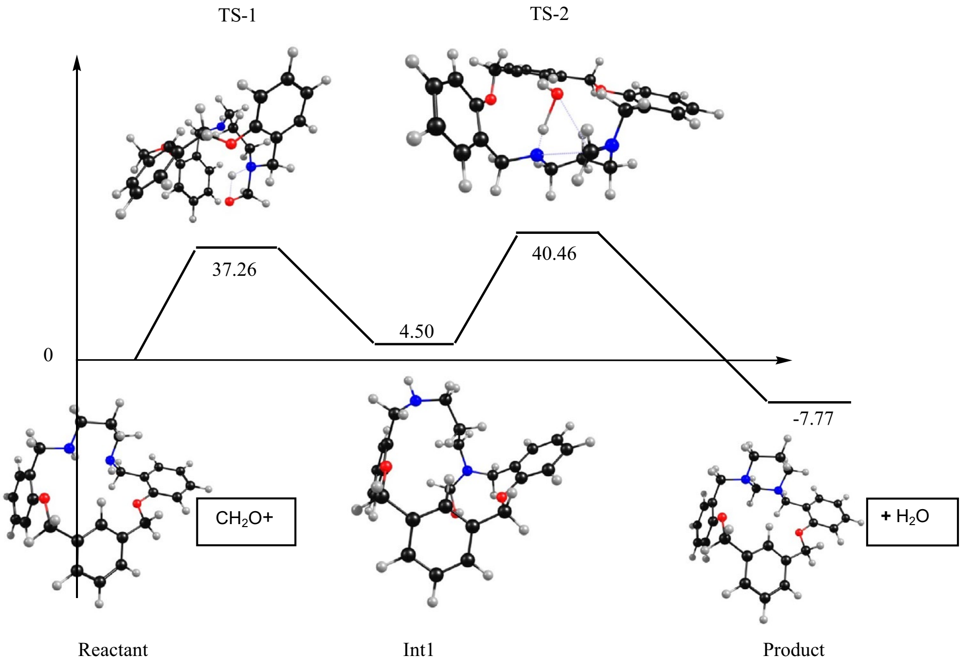


Fig. 3 Energy profile calculated for the synthesis of macrobicyclic ligand $[L^{3'}]$. The relative Gibbs free energy obtained at B3LYP/Def2-SVP

calculations show that the reaction starts with a nucleophilic attack of one of the amine groups of macrocyclic ligand L^3 to formaldehyde via transition structure TS1 which led to the formation of Int1.

The barrier energies for the calculated Int1 and corresponding TS1 are about 4.5 and 37.5 kcal mol^{-1} (see Fig. 3).

In continuation, the next nucleophilic attack in Int1 would give macrobicyclic ligand salt, $[L^{3'}](ClO_4)$ (see Fig. 3). The energy barrier for the calculated TS2 is about 40.50 kcal mol^{-1} (see Fig. 3), and these data are about +3.0 kcal mol^{-1} greater than that derived for TS1. The results show that the formation of macrobicyclic ligand salt $[L^{3'}]$ from the reaction of macrocyclic ligand L^1 and formaldehyde is exothermic and corresponding product $[L^{3'}]$ is about −7.8 kcal mol^{-1} more stable than reactant.

Conclusion

In summary, we report the successful synthesis of two macrocyclic Schiff base ligands (L^1, L^2) and their related reduced forms (L^3 and L^4). The synthesis of all ligands was carried out in dry methanol. The precipitated products which are air-stable solids and moderately insoluble in most common organic solvents were characterized by physical techniques.

After the addition of nickel(II) perchlorate to L^3 and L^4 ligands in methanol, surprisingly instead of forming corresponding complexes the macrocyclic salts containing hexahydropyrimidine moieties have been isolated. Here, Ni(II) perchlorate acts as oxidizing agent converting methanol to the formaldehyde which, in turn, bridges two nitrogen atoms of reduced forms of macrocycle producing hexahydropyrimidine cation. Similar work and also our computational study have confirmed our conclusion. The density functional theory (DFT) result confirms that the formation of $[L^{3'}]$ from the reaction of macrocyclic ligand L^3 and formaldehyde is exothermic.

Supplementary material

CCDC 1450551 contains the supplementary crystallographic data for complex $[L^{3'}](ClO_4)$ that had been deposited with the Cambridge Crystallographic Data Centre. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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