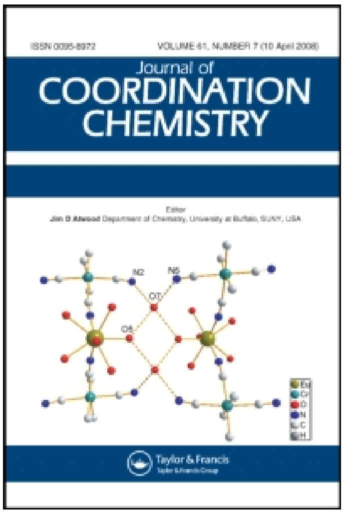

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Hydrogen bonded networks based on Ni(II)-tetraazamacrocycle (tet-b) complexes: synthesis, isolation and structural characterization of α-[Ni(tet-b)(Cl)](ClO_4) and α-[Ni(tet-b)(en)](ClO_4)$_2$

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Five- and six-coordinate, α-[Ni(tet-b)(Cl)](ClO_4) (**1**) and α-[Ni(tet-b)(en)](ClO_4)$_2$ (**2**) (tet-b = C-*racemic*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) complexes have been synthesized and isolated from the reactions of α-[Ni(tet-b)](ClO_4)$_2$, which has *trans*-V (1R,4R,8R,11R,7S,14S or 1S,4S,8S,11S,7R,14R) conformation, with t-Bu_4NCl and ethylenediamine (en), respectively. The complexes have been characterized by X-ray crystallography. The crystal structure of **1** shows a distorted trigonal bipyramidal (TBP) coordination geometry composed of four nitrogen atoms from tet-b and a chloro group with an N_4Cl chromophore about the nickel(II) ion. The complex cations of **1** are assembled by the perchlorate ions *via* N–H $\cdots$ O hydrogen bonding to form 1-D zigzag chains along the [001] direction. The chains are linked through intermolecular hydrogen bonding where the coordinated chloro group of the complex cation forms two-center double hydrogen bonds with the adjacent N–H groups of the macrocyclic ligand along the [100] direction, resulting in a two-dimensional α-network. The crystal structure of **2** shows a distorted octahedral coordination environment consisting of four nitrogen atoms from tet-b and two from en with an N_6 chromophore about nickel(II) ion. The crystal packing analysis shows that the complex cations, α-[Ni(tet-b)(en)]$^{2+}$ are interconnected by perchlorate ions through conventional two-center (N)H $\cdots$ O, and bifurcated (N)H $\cdots$ O $\cdots$ H(N) hydrogen bonding.

Keywords: Tetraaza macrocycle; Nickel complexes; Crystal structures; Hydrogen bonding

1. Introduction

The design and self-assembly of molecules with specific topologies as well as interesting properties that may be simple organic, inorganic or metal complexes are intriguing topics in supramolecular chemistry. The self-assembly can be the result of spontaneous aggregation of molecules through covalently or non-covalently joined ensembles, displaying multidimensional networks. Molecular recognition and self-assembly

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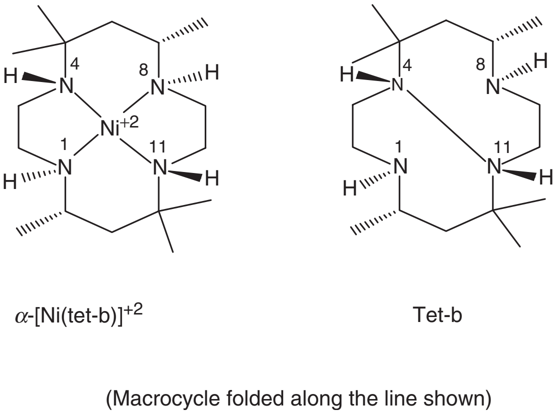
processes play an essential role in the formation and function of biological systems. There have been numerous reports demonstrating that assemblies are constructed by metal-ligand coordination [1–6], hydrogen bonding [7–15] and π–π stacking interactions [16, 17]. Among these, the last two play significant roles in highly specific biological reactions and are essential for molecular recognition and self-organization of molecules in supramolecular chemistry. The intermolecular assembly of metal complexes *via* hydrogen bonding has recently gained attention, where, rather than forming the more common coordination polymers using coordination bonds [1–6], neighboring metal complexes are connected and oriented through ligand–ligand or ligand-counter ion hydrogen bonds [7–15]. Such hydrogen-bonded systems containing transition metal ions are widely used in crystal engineering of non-linear optical, conducting and ferromagnetic materials [18–20].

In this context, different macrocyclic ligands and their metal complexes have been shown to be good building blocks for the formation of multidimensional hydrogen bonded networks, especially, tetraazamacrocyclic ligands and their metal complexes [21–31]. The tetraazamacrocycle, 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, exhibits two diastereoisomers: the *meso*(tet-a) and the *racemic*(tet-b) (Scheme 1). These two diastereoisomers have also been shown to be versatile building blocks in supramolecular chemistry [26–28] where organic acid derivatives have been employed as mediators to make the supramolecular arrays through hydrogen bonding. To the best of our knowledge, there is no report on the metal complexes of these macrocyclic ligands tet-a and tet-b which have been used as building blocks in supramolecular chemistry.

The nickel(II) complex cation of the *racemic* isomer, -[Ni(tet-b)]$^{+2}$ has been known to exist as five isomeric α-, β-, γ-, δ- and ε- forms among the ten possible isomers [32]. The isomerization arises due to the presence of two asymmetric carbons and the four stereogenic nitrogens on the macrocyclic backbone. The structures of these isomers have been characterized by X-ray analysis and ^{1}H NMR spectroscopy [32, 33]. Of the five isomers, only the α-isomer, which is folded and adopts *cis*-V conformation to make available space for *cis*-coordination while the complex reacts with chelating, bridging and even monodentate ligands to form *cis*-octahedral complexes [34–45], has been studied extensively because of its unique *trans*-V (RRRRSS or SSSSRR) (scheme 1)



Scheme 1. Chemical structure of α-[Nictet-b]$^{2+}$ and tet-b.

conformation. In this report, We describe the synthesis, isolation, and crystal structures of the products, α-[Ni(tet-b)(Cl)](ClO_4) (**1**) and α-[Ni(tet-b)(en)](ClO_4)$_2$ (**2**) obtained from reactions of α-[Ni(tet-b)](ClO_4)$_2$ with t-Bu_4NCl and ethylenediamine, respectively. The hydrogen bonding alignments of complexes in their unit cells are to be described as well.

2. Experimental

2.1. *Materials*

All reagents and solvents are commercially available and were used as received without further purification. The square planar complex, α-[Ni(tet-b)](ClO_4)$_2$, was prepared by following the reported procedure [45].

Caution! Perchlorate salts of metal complexes are often explosive and should be handled with a great degree of care.

2.2. *Synthesis of α-[Ni(tet-b)(Cl)]ClO$_4$ (1)*

To the solution, α-[Ni(tet-b)](ClO_4)$_2$ (1.0 g, 1.85 mmol) in 100 mL ethanol was added solid t-Bu_4NCl (1.0 g, 3.6 mmol). The reaction mixture was stirred at room temperature for 2 h and was then kept undisturbed for several days. Slow evaporation led to deep blue crystalline product. The crystals were isolated and used for crystallographic analysis. The yield was 70% ($C_{16}H_{36}Cl_2N_4NiO_4$, 477.70).

2.3. *Synthesis of α-[Ni(tet-b)(en)](ClO$_4$)$_2$ (2)*

Ethylenediamine (0.1 g, 1.67 mmol) in 20 mL EtOH was added slowly into a solution of α-[Ni(tet-b)](ClO_4)$_2$ (0.8 g, 1.48 mmol) in 100 mL ethanol with continuous stirring at room temperature. The mixture was then stirred for an additional 2 h. The color of the solution became blue. The reaction mixture was kept undisturbed at room temperature for several days for crystallization. The blue crystals were isolated and used for crystallographic analysis. The yield was 82% ($C_{18}H_{44}Cl_2N_6NiO_8$, 601.70).

2.4. *X-ray crystal structure analysis*

The determination of the crystal class, orientation matrix and accurate unit cell parameters of α-[Ni(tet-b)(Cl)]ClO_4 (**1**) and α-[Ni(tet-b)(en)](ClO_4)$_2$ (**2**) were performed using a Siemens SMART CCD diffractometer with graphite monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation. The planar macrocyclic structure reduces the observed number of collected reflections. The data were corrected for Lorentz-polarization and absorption effects by a multi-scan method [46]. The structures were solved by direct methods, checked by Patterson synthesis and refined by the full-matrix least-squares method. The absolute structures were determined following the reported methods [47]. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were located by geometrical calculation and rode on the parent atom with isotropic thermal parameters ($U_{iso}(H) = 1.2\, U_{eq}$(C or N)). All calculations

Table 1. Crystallographic data of α-[Ni(tet-b)(Cl)]ClO_4 (**1**) and α-[Ni(tet-b)(en)]$(ClO_4)_2$ (**2**).

	1	**2**
Emperical formula	$C_{16}H_{36}Cl_2N_4NiO_4$	$C_{18}H_{44}Cl_2N_6NiO_8$
Formula weight	478.10	602.20
Color	Blue	Blue
Temperature (K)	295(2)	295(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Tetragonal
Space group	$P2_12_12_1$	$P4_3$
Unit cell dimension (Å)		
a	6.6024(7)	10.4917(1)
b	17.1085(2)	10.4917(1)
c	19.929	24.241(4)
V (Å^3)	2251.1(4)	2668.4(7)
Z	4	4
D_{calcd} (Mg m^{-}3)	1.411	1.499
Absorption coefficient (mm^{-1})	1.127	0.980
F(000)	1016	1280
Crystal size (mm^3)	$0.26 \times 0.20 \times 0.15$	$0.25 \times 0.20 \times 0.15$
θ range (°)	1.60–28.30	1.94–28.28
Index ranges	$-8 \le h \le 8$, $-22 \le k \le 14$, $-24 \le l \le 26$	$-13 \le h \le 13$, $-9 \le k \le 13$, $-31 \le l \le 31$
Reflection collected	13612	15448
Independent reflections	5151 [R(int) = 0.045]	5753 [R(int) = 0.0967]
Completeness to $\theta = 28.30$	95.3%	91.2%
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3894/0/251	5121/2/374
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0429$, $wR_2 = 0.0988$	$R_1 = 0.0687$, $wR_2 = 0.1743$
R indices (all data)	$R_1 = 0.0643$, $wR_2 = 0.1067$	$R_1 = 0.0749$, $wR_2 = 0.1789$
Goodness-of-fit on F^2	0.990	1.048
Largest difference peak and hole (e Å^{-3})	0.40 and −0.33	1.049 and −0.530
Flack parameter	0.013 (17) with 1961 Friedel pairs	0.00(1)
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
Weighting scheme	$W = 1/[\sigma^2(F_0^2) + (0.0594P)^2]$, where $P = (F_0^2 + 2F_c^2)/3$	$W = 1/[\sigma^2\ (F_0^2) + (0.1199P)^2 + 2.0698P]$ where $P = (F_0^2 + 2F_c^2)/3$

were carried out using the SHELXL-97 program [48]. The crystallographic data and the parameters for structure refinement are summarized in table 1.

3. Results and discussion

3.1. *Synthesis and isolation*

The square planar complex, α-[Ni(tet-b)]$(ClO_4)_2$, which has *trans*-V (1R,4R,8R,11R,7S,14S or 1S,4S,8S,11S,7R,14R) conformation, is easily folded and makes available space at the *cis*-positions for the incoming ligands while reacting with either monodentate or bidentate ligands [34, 45]. Reactions with t-Bu_4NCl and ethylenediamine in ethanol, α-[Ni(tet-b)](ClO_4) forms five- and six-coordinate, α-[Ni(tet-b)(Cl)](ClO_4) (**1**) and α-[Ni(tet-b)(en)]$(ClO_4)_2$ (**2**) complexes, respectively. Good quality crystals of these complexes were isolated from reaction mixtures, which were kept undisturbed for several days.

3.2. *Crystal structure of α-[Ni(tet-b)(Cl)]ClO_4 (1)*

An ORTEP diagram of the complex cation in the complex, α-[Ni(tet-b)(Cl)](ClO_4) and its hydrogen bonded α-network with the atom numbering scheme are depicted in figures 1 and 2, respectively. The perchlorate ion, which is not shown in figure 1, shows large thermal ellipsoids. The relatively large thermal parameters probably account for the individual deviations from the average. The bond angles are regular tetrahedral. No appreciable orientational disorder of the O atoms is observed; positional disorder of perchlorate is revealed in its large temperature factors. The complex is best described as a distorted trigonal bipyramid (TBP) about Ni(II) with four secondary amines of the macrocycle, tet-b and one chloro group. The equatorial plane of the TBP is defined by two secondary amine nitrogens, N(1) and N(8) and a chloro group. The axial sites of the TBP are occupied by the remaining two secondary amine nitogens, N(4) and N(11) of the tet-b. Selected bond lengths and bond angles are given in table 2. We have previously reported [45] that reaction between the complex cation, α-[Ni(tet-b)]$^{2+}$ and NSC^- groups led to an octahedral complex with a formula, *cis*-α-[Ni(tet-b)$(NCS)_2$]. The Ni-N(tet-b) distances in (**1**) fall in the range 2.060–2.108 Å which are higher than the parent square-planar complex and less than the octahedral complex, *cis*-α-[Ni(tet-b)$(NCS)_2$] [45]. This is definitely related to the spin state of the Ni(II) ion, as it changes with the change of geometry from square planar, low spin to trigonal bipyramidal, high spin. The axial bonds, Ni(1)–N(4) (2.108 (3) Å) and Ni(1)–N(11) (2.105 (3) Å) are longer than those of equatorial bonds, Ni(1)–N(1) (2.076 (3) Å) and Ni(1)–N(8) (2.060 (3) Å). The *trans* bond angle, N(4)–Ni(1)–N(11), 176.7 (1)° and the

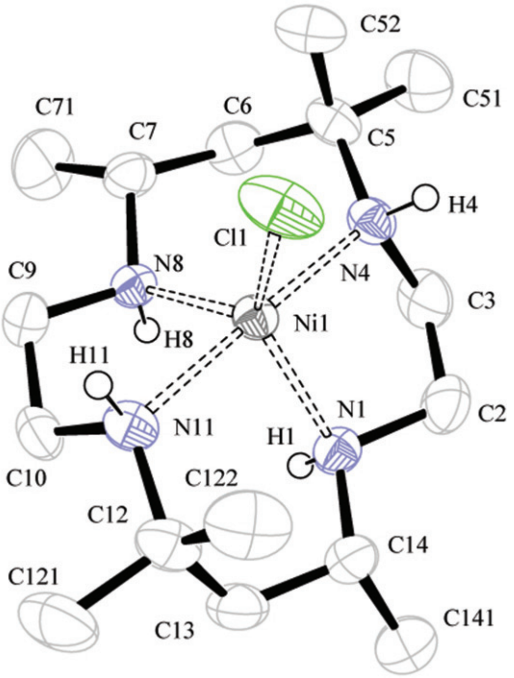


Figure 1. An ORTEP drawing of α-[Ni(tet-b)(Cl)](ClO_4) (**1**) with the atomic numbering scheme (30% probability ellipsoids shown), excluding perchlorate ion and H atoms attached to the C atoms.

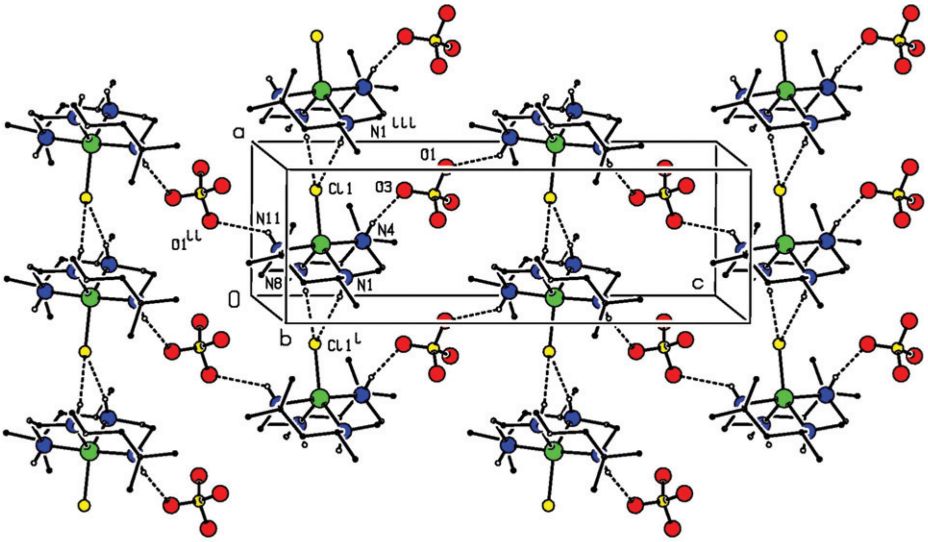


Figure 2. 2D hydrogen-bonded α-networks based on α-[Ni(tet-b)(Cl)](ClO$_4$) (**1**). Zigzag chains are along the *c*-axis; 1-D connections are along the *a*-axis.

Table 2. Selected bond lengths (Å) and bond angles (°) for **1**, along with estimated standard deviations.

Bond lengths			
Ni(1)–N(1)	2.076(3)	Ni(1)–N(11)	2.105(3)
Ni(1)–N(8)	2.060(3)	Ni(1)–Cl(1)	2.340(1)
Ni(1)–N(4)	2.108(3)		
Bond angles			
N(1)–Ni(1)–N(8)	103.2(1)	Ni(1)–N(1)–H(1N)	107.6(2)
N(1)–Ni(1)–N(4)	85.3(1)	Ni(1)–N(4)–C(5)–C(6)	−49.3(4)
N(8)–Ni(1)–N(4)	93.3(1)	N(4)–C(5)–C(6)–C(7)	66.1(4)
N(1)–Ni(1)–N(11)	92.3(1)	C(5)–C(6)–C(7)–N(8)	−72.9(4)
N(8)–Ni(1)–N(11)	85.1(1)	Ni(1)–N(8)–C(7)–C(6)	59.4(3)
N(4)–Ni(1)–N(11)	176.7(1)	Ni(1)–N(11)–C(12)–C(13)	−53.3(4)
N(1)–Ni(1)–Cl(1)	133.6(1)	N(11)–C(12)–C(13)–C(14)	67.5(4)
N(8)–Ni(1)–Cl(1)	123.2(1)	C(12)–C(13)–C(14)–N(1)	−69.4(4)
N(4)–Ni(1)–Cl(1)	92.3(1)	Ni(1)–N(1)–C(14)–C(13)	55.5(4)
N(11)–Ni(1)–Cl(1)	91.0(1)	Ni(1)–N(1)–C(2)–C(3)	−46.6(4)
C(5)–C(6)–C(7)	118.0(3)	N(1)–C(2)–C(3)–N(4)	59.6(4)
N(8)–C(7)–C(6)	110.9(3)	Ni(1)–N(4)–C(3)–C(2)	−38.7(3)
N(4)–C(5)–C(6)	110.3(3)	Ni(1)–N(8)–C(9)–C(10)	−43.9(4)
C(12)–C(13)–C(14)	118.9(3)	N(8)–C(9)–C(10)–N(11)	56.9(4)
N(1)–C(14)–C(13)	11.7(3)	Ni(1)–N(11)–C(10)–C(9)	−38.6(3)
N(11)–C(12)–C(13)	109.5(3)		

cis-bond angle, N(1)–Ni(1)–N(8), 103.2 (1)° are larger than that of the octahedral complex, *cis*-α-[Ni(tet-b)(NCS)$_2$] [45], indicating that the macrocycle is less folded in TBP geometry than octahedral geometry. The macrocycle is folded about N(4)–Ni(1)–N(11) where nitrogens are adjacent to the geminal dimethyl carbon atoms. A similar structural feature has been observed in the crystal structure of octahedral complexes such as *cis*-α-[Ni(tet-b)(NCS)$_2$] [45], α-[Ni(tet-b)(AcO$^-$)](ClO$_4$) [34], etc. When the macrocycle is folded from its coplanar nitrogen geometry, the nitrogen atom adjacent to

Table 3. Intermolecular hydrogen contact distances (Å) and angles (°) of **1**.

D	H	A	d(H···A)	d(D···A)	<(D–H···A)
N(4)	H(4)	O(3)	2.22	3.100(7)	163
N(1)	H(1)	Cl(1)^{i}	2.55	3.442(3)	166
N(11)	H(11)	O(1)^{ii}	2.65	3.141(7)	153
N(8)	H(8)	Cl(1)^{i}	2.51	3.384(3)	161

Symmetry codes: (i) $x-1$, y, z; (ii) $x+1$, y, z.

the single methyl carbon is more easily lifted than that adjacent to the geminal dimethyl carbon atom [35]. The magnitude of lifting of nitrogen atoms adjacent to the single methyl carbons may be dependent on the ligand field strength; Cl^- is a weaker ligand and exerted less force on the macrocycle than NCS^- ligands. It is now clear that why the complex cation, α-[Ni(tet-b)]$^{2+}$ forms TBP complex with Cl^- and *cis*-octahedral complex with NCS^-. The Ni(1)–Cl(1) bond distance is 2.340(1) Å which is essentially equivalent to that found (2.302 Å) in penta-coordinated (NiN_4Cl) Ni(II) complex [49]. The bond angles around nickel atom of the trigonal plane are 133.6(1)° for N(1)–Ni(1)–Cl(1), 123.2(1)° for N(8)–Ni(1)–Cl(1), and 103.2(1)° for N(1)–Ni(1)–N(8). The deviation of Ni atom (0.6726 Å) from the N(1)–N(4)–N(8)–N(11) plane is slightly higher than those of octahedral complexes, α-[Ni(tet-b)(AcO)]$^+$ (0.61 Å) [34].

The macrocycle forms alternative five- and six-membered chelate rings with Ni. It is generally observed that for a folded macrocycle, the six-membered and five-membered chelate rings adopt chair and symmetrical gauche conformation, respectively. In **1**, the mean chelate bite angles, the mean internal angle at the central methylene groups and the mean internal ring angle at the tetrahedral atoms in the six-member chelate rings are 92.8, 118.5 and 113.4°, respectively, indicating that the six-membered chelate rings in **1** are in chair conformations. The torsional angles (table 2) also support chair conformations. The torsional angles among the atoms in the six-membered chelate rings reveal that C(13) and C(6) are bent down whereas the Ni atom is up from the N–C bonds. The mean N–Ni–N bond angles in the five-member chelate ring is 85.16° and the C–C bonds are in gauche conformation (synclinal) (torsion angles: Ni(1)–N(1)–C(2)–C(3) = −46.6° and Ni(1)–N(4)–C(3)–C(2) = −38.7°) with the Ni–N bonds.

Complex **1** displays a two-dimensional hydrogen bonded α-network with a basic α-[Ni(tet-b)(Cl)](ClO_4) (figure 2). Hydrogen bond parameters are given in table 3. All nitrogen atoms at the periphery of the tet-b act as single two-center hydrogen bond donors whereas the coordinated chloro is a double two-center hydrogen bond acceptor. The complex units are linked by hydrogen bond formation between the coordinated chloro group and two secondary N–H groups (N(1) and N(8); equatorial N-atoms of TBP), giving a one-dimensional hydrogen-bonded infinite chain along (100) direction. This linear arrangement of complex cations, α-[Ni(tet-b)(Cl)]$^+$ in the crystal is analogous to the α-network in symmetrical di-substituted ureas [50–54]. Guy Orpen *et al.* [55] have reviewed the hydrogen bonding pattern of transition metal chloride complexes based on the Cambridge Structural Database (CSD) [56] and have argued that M–Cl moieties are much better hydrogen bond acceptors than are their organic analogues (organochlorine species, C–Cl). It had also been noted that metal assisted hydrogen bonds typically have short MCl···HN (or HO) distances in the range 2.2–2.6 Å and M–Cl···H angles in the range 90–120° with normal angles at hydrogen (e.g. N–H $\cdots$ Cl $\geq$ ca 140°) [57]. This is observed in **1**. The Cl $\cdots$ HN distances of 2.55 (Cl $\cdots$ H(1)) and 2.51 (Cl $\cdots$ HN(8)) (table 3) indicate that the coordinated chloro group is equidistant from each NH proton. The N–H $\cdots$ Cl angles, 166° for N(1)–H $\cdots$ Cl and 161° for N(8)–H $\cdots$ Cl, suggest that the N(1)–H bond dipole is more aligned toward Cl than N(8)–H. These parameters are in agreement with reported results [58] and indicate that the hydrogen bonding interactions between the Ni–Cl bond and N–H groups are short-range type. Interestingly, the extension of these networks occurs two-dimensionally when the remaining two secondary nitrogens N(4) and N(11) (axial atoms of TBP) of the macrocyclic ligand are engaged in formation of hydrogen bonds to adjacent noncoordinated perchlorate oxygens O(1) and O(3) separately.

3.3. *Crystal structure of α-[Ni(tet-b)(en)](ClO_4)$_2$ (2)*

The crystal structure and atom labeling scheme for the Ni(II)-complex cation in α-[Ni(tet-b)(en)](ClO_4)$_2$ (**2**), is depicted in figure 3. The complex cation, α-[Ni(tet-b)(en)]$^{2+}$ and its counter anions, ClO_4^-, are held together by electrostatic forces and hydrogen bonding interactions. The perchlorate ions are disordered and not shown in figure 3. Selected bond lengths and bond angles are given in table 4. The Ni^{2+} is six-coordinate with the four secondary amines (sec-N: N(1), N(3), N(5), and N(6)) from the macrocycle tet-b and two primary amines (pri-N: N(2) and N(4)) from en framing a distorted octahedral geometry. The ligand tet-b is folded along the N(1)–Ni–N(3) axis. The average bond lengths of Ni–N(tet-b), 2.176 Å, is essentially equivalent to that found (2.23 Å) in α-[Ni(tet-b)(AcO^-)](ClO_4) [34] and (2.145 Å) in *cis*-α-[Ni(tet-b)(NCS)] [45] and is greater than 2.09 Å, the minimum required length for folding of a [14] ane-N_4 to give *cis*-V conformation [58], supporting the octahedral geometry and triplet ground state of nickel(II). The equatorial bonds, Ni(1)–N(5) (2.138(4) Å) and Ni(1)–N(6) (2.137(4) Å) are shorter than the axial bonds, Ni(1)–N(1) (2.220(5) Å) and Ni(1)–N(3) (2.216(5) Å) and the angle N(1)–Ni(1)–N(3) (168.1(1)°) is smaller than the ideal 180°, indicating that the donor atoms are not able to get the axial positions of a

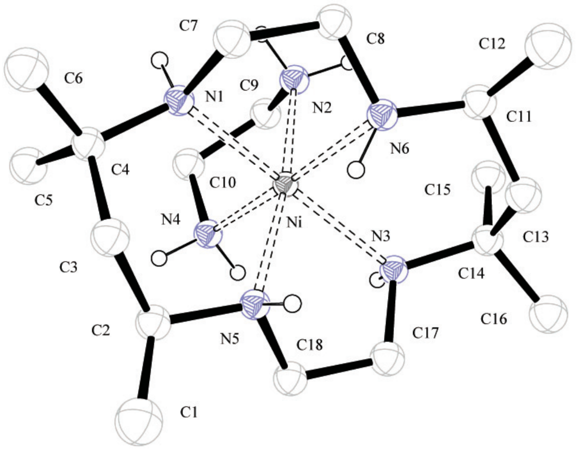


Figure 3. An ORTEP drawing of α-[Ni(tet-b)(en)](ClO_4)$_2$ (**2**) with the atomic numbering scheme (30% probability ellipsoids shown), excluding perchlorate ions and H atoms attached the C atoms.

Table 4. Selected bond lengths (Å) and bond angles (°) for **2**, along with estimated standard deviations.

Bond lengths			
Ni(1)–N(6)	2.137(4)	Ni(1)–N(2)	2.175(4)
Ni(1)–N(5)	2.138(4)	Ni(1)–N(3)	2.216(5)
Ni(1)–N(4)	2.171(4)	Ni(1)–N(1)	2.220(5)
Bond angles			
N(6)–Ni(1)–N(5)	97.6(2)	N(3)–C(14)–C(13)	109.9(5)
N(6)–Ni(1)–N(4)	170.0(2)	Ni(1)–N(1)–H(1N)	105.6
N(5)–Ni(1)–N(4)	91.8(2)	Ni(1)–N(6)–C(11)–C(13)	−58.4(6)
N(6)–Ni(1)–N(2)	91.5(2)	N(6)–C(11)–C(13)–C(14)	74.8(7)
N(5)–Ni(1)–N(2)	170.4(2)	C(11)–C(13)–C(14)–N(3)	−67.06
N(4)–Ni(1)–N(2)	79.3(2)	Ni(1)–N(5)–C(2)–C(3)	−57.7(7)
N(6)–Ni(1)–N(3)	89.3(2)	N(5)–C(2)–C(3)–C(4)	74.4(7)
N(5)–Ni(1)–N(3)	82.4(2)	C(2)–C(3)–C(4)–N(1)	−66.3(8)
N(4)–Ni(1)–N(3)	88.5(2)	Ni(1)–N(1)–C(7)–C(8)	28.4(6)
N(2)–Ni(1)–N(3)	100.6(2)	N(1)–C(7)–C(8)–N(6)	−57.7(7)
N(6)–Ni(1)–N(1)	82.9(2)	Ni(1)–N(3)–C(17)–C(18)	27.6(6)
N(5)–Ni(1)–N(1)	89.7(2)	N(3)–C(17)–C(18)–N(5)	−56.7(7)
N(4)–Ni(1)–N(1)	100.7(2)	Ni(1)–N(2)–C(9)–C(10)	42.7(6)
N(2)–Ni(1)–N(1)	88.6(2)	N(2)–C(9)–C(10)–N(4)	−57.4(6)
N(3)–Ni(1)–N(1)	168.1(1)	Ni(1)–N(6)–C(11)–C(12)	180.0(5)
C(4)–C(3)–C(2)	118.8(5)	Ni(1)–N(5)–C(2)–C(1)	180.0(5)
N(1)–C(4)–C(3)	110.6(5)	Ni(1)–N(1)–C(4)–C(5)	−76.4(6)
N(5)–C(2)–C(3)	111.5(5)	Ni(1)–N(1)–C(4)–C(6)	162.2(5)
C(11)–C(13)–C(14)	117.8(5)	Ni(1)–N(3)–C(14)–C(15)	−74.6(6)
N(6)–C(11)–C(13)	111.4(5)	Ni(1)–N(3)–C(14)–C(16)	166.7(4)

perfect octahedron. The bond angle between two en-N atoms about Ni(II) is 79.3(2)° which is somewhat less than reported values, 82.02° of $Ni(tren)(en)^{2+}$ [59] and 81.90° of the $Ni(en)_3{}^{2+}$ [60]. Ni–N(en) bond distances, Ni(1)–N(2) (2.175(4) Å) and Ni(1)–N(4) (2.171(4) Å) are almost equivalent and slightly longer than reported values [59, 60], perhaps due to steric strain exerted by the macrocyclic ligand. The nickel atom is somewhat below the defined square plane by 0.0108 Å from N(1)–N(3)–N(4)–N(6); the N(2) (en-N) and N(5) (tet-b-N) are almost equally disposed below and above this square plane.

As in **1**, it is expected that in **2** the macrocycle, tet-b, in folding would form chair and gauche conformation for six- and five-membered chelate rings, respectively. Unlike complex **1**, the mean N–Ni–N bond in the six-membered chelate rings in the complex of **2** is 89.5°, which is somewhat less than expected for a strain-free chair ring. Moreover, the mean internal angle at the central methylene groups, 118.3° and the mean internal ring angle at the tetrahedral atoms, 112° are concurrent with the chair. The torsion angles in different atoms in the six-membered chelate rings indicate that the C(3) and C(13) groups are above the N–C bonds whereas Ni-atom is down. Therefore, we conclude that the six-membered chelate rings are in chair forms but feel more angle strain than in **1**. The mean N–Ni–N bond angles in five-membered chelate rings in tet-b are equal, 82.7° and in en it is 79.3(2)°. The torsion angles in the atoms, Ni(1)–N(1)–C(7)–C(8) and Ni(1)–N(3)–C(17)–C(18) are 28.4° and 27.6°, respectively, less than for **1**, indicating that the C–C bonds are cynperiplanar to the Ni–N bonds. It is therefore, suggested that the five-member chelated rings formed by tet-b are gauche but feel more angle strain than in **1**.

Analysis of the crystal packing of α-[Ni(tet-b)(en)]$(ClO_4)_2$, in the unit cell shows the presence of multiple hydrogen-bonding interactions (figure 4). Selected hydrogen-bond lengths are given in table 5. Perchlorate ions are disordered.

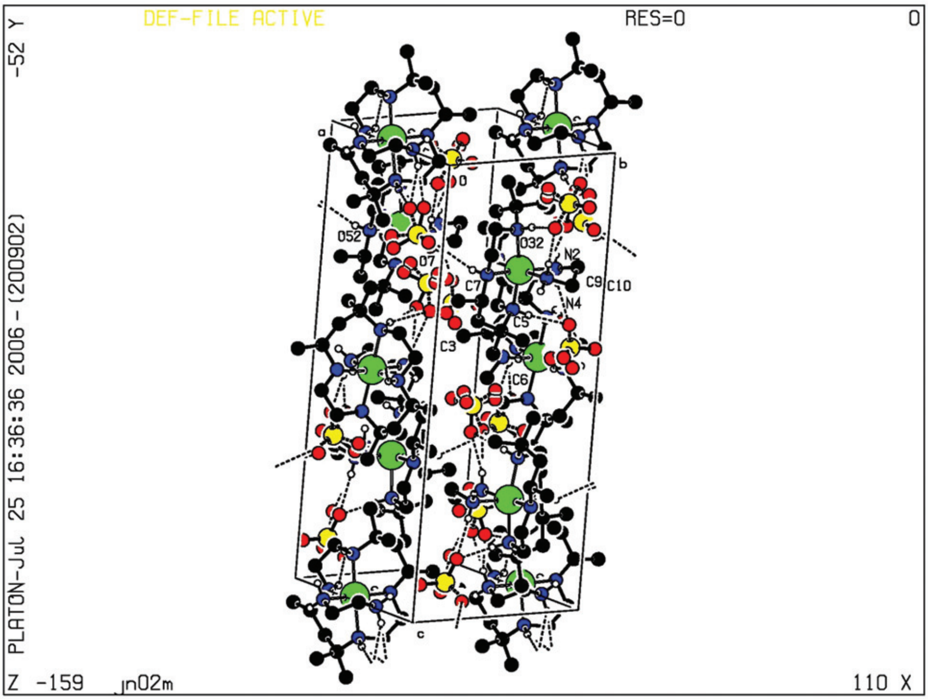


Figure 4. Hydrogen-bond networks based on α-[Ni(tet-b)(en)]$(ClO_4)_2$ (**2**). The hydrogen bond network screws along the *c*-axis through 4_3.

Table 5. Intermolecular hydrogen contact distances (Å) and angles (°) of **2**.

D	H	A	D(H ··· A)	d(D ··· A)	<(D–H ··· A)
N(1)	H(1)	O(61)^{i}	2.30	3.15(3)	156
N(2)	H(2A)	O(61)^{i}	2.19	3.08(3)	171
N(3)	H(3)	O(31)	2.26	3.16(2)	173
N(4)	H(4A)	O(31)	2.23	3.064(19)	153
N(5)	H(5)	O(81)	2.51	3.31(3)	148

Symmetry code: (i) $y, x-1, y, z+1/4$.

The perfect disordering scheme involves splitting of three oxygen atoms of each perchlorate ion over two sites. These were refined as shown in figure 4, with site occupancy factors of 0.54/0.46 for Ox1/Ox2 ($x = 1, 2, 3, 5, 6, 8$), respectively. Constraints in hydrogen geometry were applied, resulting in reasonable bond distances and bond angles. The three of four sec-N–H groups at the periphery of tet-b and two pri-N–H groups of ethylenediamine are involved in hydrogen bonding with perchlorate ions, resulting in a supramolecular hydrogen-bonded network. The hydrogen pairs: {N(2)–H(2A) (en-N), N(1)–H(1) (tet-b–N)} and {N(4)–H(4A) (en-N), N(3)–H(3) (tet-b–N)} form bifurcated hydrogen bonds with O61/O62 and O31/O32, respectively, with N–H ··· O bond distances in the range 3.064–3.211 Å. The sec-N–H, N(5)–H(5) from tet-b forms conventional two-center hydrogen bonds with perchlorate with N–H ··· O distance of 3.31 Å. In this complex the hydrogen-bonded network screws along the *c*-axis through 4_3.

4. Conclusion

We have demonstrated that a five-coordinate Ni(II) complex, α-[Ni(tet-b)(Cl)](ClO_4) (**1**) and six-coordinate α-[Ni(tet-b)(en)]$(ClO_4)_2$ (**2**) form hydrogen bonded networks. In **1**, the sec-N–H groups at the periphery of tet-b are involved in hydrogen bonding with the coordinated chloride group and also with the perchlorate ions. In **2**, we have found two kinds of hydrogen bonds: conventional two-center (N)H $\cdots$ O, and bifurcated (N)H $\cdots$ O $\cdots$ H(N), between the complex cations and the perchlorate ions.

Supplementary material

Deposition numbers with the Cambridge Crystallographic data Centre is 221376 (**1**) and 221377 (**2**). Copies of the information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; Email: deposit@ccdc.com.ac.uk or www.ccdc.cam.ac.uk).

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