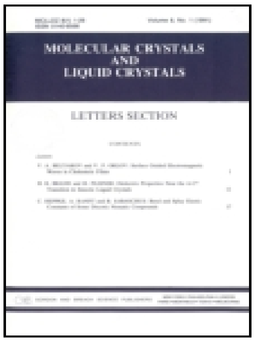
MOLECULAR CRYSTALS AND LIQUID CRYSTALS

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Synthesis, characterization, and crystal structure of macrocyclic nickel(II) complexes bearing *a,e-cis*-1,4-chdc and *e,e-trans*-1,4-chdc (chdc = cyclohexanedicarboxylate) ligands

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ABSTRACT
Two macrocyclic nickel(II) complexes, [Ni(**L**)(*a,e-cis*-1,4-chdc)]·4H_2O (**1**) and [{Ni(**L**)(H_2O)}$_2$(*e,e-trans*-1,4-chdc)](ClO_4)$_2$ (**2**) (**L** = 1,4,8,11-tetraazacyclotetradecane, cyclam), were prepared by the reaction of [Ni(**L**)](ClO_4)$_2$ and *a,e-cis-/e,e-trans*-1,4-chdcH_2 in basic solvents. Both complexes were characterized by EA, IR, and TGA techniques. In addition, molecular structures were determined by single crystal X-ray diffraction methods. In **1**, the *a,e-cis*-1,4-chdc ligand bridges nickel(II) macrocycles to form an undulated 1D coordination polymer, whereas the complex **2** shows a dimer in which the *e,e-trans*-1,4-chdc ligand bridges two nickel(II) cyclams.

KEYWORDS
Coordination polymer; macrocycle; nickel complex; 1,4-chdc

Introduction

Rigid aromatic polycarboxylates have widely been employed and achieved great success in the construction of coordination polymers and supramolecular coordination complexes [1–5]. In contrast to aromatic carboxylate ligands, flexible aliphatic polycarboxylates with metal ions often produce coordination polymers that exhibit more unpredictable metal-ligand connection and arrangement. Nonetheless, the coordination polymers with flexible polycarboxylates have been growing rapidly and attract attention due to their wide applications [6–13]. The dicarboxylic acid, 1,4-chdcH_2, is one of the best known flexible ligands, which can adopt three different conformations, i.e. *a,e-cis*-1,4-chdcH_2, *e,e-trans*-1,4-chdcH_2 and *a,a-trans*-1,4-chdcH_2 [11–13] (Scheme 1). Since the energies of intermolecular interactions in supramolecules could be higher enough than those of barrier energies between the conformers, attempts have been carried out on the isolation of specific conformation in appropriately designed systems [14–21]. The pHs are known to affect the conformation of 1,4-chdc in the isolated complexes although several reports show that those are not always true [15–20,22,23]. Other conditions such as the nature of metal ions, ancillary ligands, and solvents used are also ascribed to influence the conformation of the isolated 1,4-chdc ligand in the complexes [24–26]. However, the complexity of concerning factors in most systems makes

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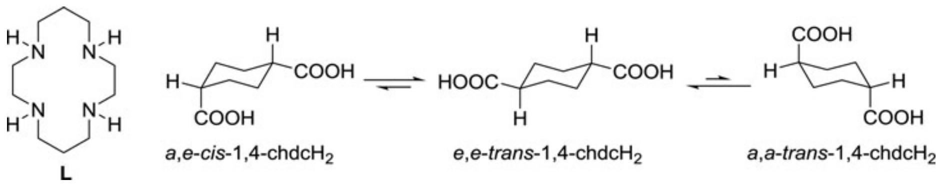
CCDC Nos. 992885 (**1**) and 1006623 (**2**) contain the supplementary crystallographic data. Supplemental data for this article can be accessed at http://www.ccdc.cam.ac.uk/data_request/cif and on the publisher's website.



Scheme 1. Ligand **L** and three different conformations of $chdcH_2$.

it difficult to understand what factors are involved in and how to affect for the formation of specific conformation of chdc ligand in the complexes. On this account, we attempted to synthesize macrocyclic nickel(II) complexes bearing 1,4-chdc ligands to secure more examples and understand their coordination tendencies and intermolecular interactions. From the reaction between $[Ni(\mathbf{L})](ClO_4)_2$ and *cis,trans*-1,4-$chdcH_2$ mixture in basic conditions, we successfully obtained nickel(II) macrocycles bearing *a,e-cis*-1,4- or *e,e-trans*-1,4-chdc ligands. Herein, we report the details of syntheses, structures, and properties of $[Ni(\mathbf{L})($*a,e-cis*-1,4-chdc$)]\cdot 4H_2O$ (**1**) and $[\{Ni(\mathbf{L})(H_2O)\}_2($*e,e-trans*-1,4-chdc$)](ClO_4)_2$ (**2**).

Experimental

Materials and measurements

All chemicals were commercially available and were used as received. Water was distilled before use for all procedures. Nujol mull (KBr discs) infrared spectra were recorded on a Perkin-Elmer Spectrum X spectrophotometer. The thermal and elemental analyses were performed at the analytical laboratory of KRICT, Korea. The starting material $[Ni(\mathbf{L})](ClO_4)_2$ was prepared by the equimolar reaction between cyclam and $Ni(ClO_4)_2\cdot 6H_2O$ in refluxing methanol. Caution! The perchlorate salts are potentially explosive and should be handled in small quantities.

Synthesis of 1 and 2

The complex $[Ni(\mathbf{L})($*a,e-cis*-1,4-chdc$)]\cdot 4H_2O$ (**1**) was prepared by dissolving *cis,trans*-mixture of 1,4-$chdcH_2$ (86 mg, 0.5 mmole) in a minimum amount of H_2O with an excess amount of triethylamine, then adding to a DMF solution of $[Ni(\mathbf{L})](ClO_4)_2$ (230 mg, 0.5 mmole). The mixture was left until pink needles of **1** formed. The crystals were filtered and dried in air. Yield: 35.2% based on $[Ni(\mathbf{L})](ClO_4)_2$. Anal. Calc. for $C_{18}H_{42}N_4O_8Ni$: C, 43.09; H, 8.38; N, 11.17. Found C, 42.86; H, 8.38; N, 10.87%. IR (Nujol, cm^{-1}): 3404 (νH_2O), 3233, 3181 (νNH), 1651 (δH_2O), 1553 ($\nu_{as}CO_2$), 1401 ($\nu_s CO_2$). The complex $[\{Ni(\mathbf{L})(H_2O)\}_2($*e,e-trans*-1,4-chdc$)](ClO_4)_2$ (**2**) was prepared by using the same method as described for the synthesis of **1** except the exclusion of DMF from solvents. The pink plates of **2** formed from the aqueous solution of reactant mixture. The crystals were filtered and dried in air. Yield: 23.8% based on $[Ni(\mathbf{L})](ClO_4)_2$. Anal. Calc. for $C_{28}H_{62}N_8Cl_2O_{14}Ni_2$: C, 36.39; H, 6.71; N, 12.13. Found C, 36.47; H, 6.77; N, 12.20%. IR (Nujol, cm^{-1}): 3481, 3278 (νH_2O), 3232, 3156 (νNH), 1666 (δH_2O), 1542 ($\nu_{as}CO_2$), 1399 ($\nu_s CO_2$), 1101 (νClO_4), and 626 (δClO_4).

X-ray crystallography

Crystallographic data for **1** and **2** are summarized in Table 1. Bruker APEX2 or Nonius Kappa APEX-DUO CCD X-ray diffractometers with Mo-K_α radiation ($\lambda = 0.71073$ Å) were used for

Table 1. Crystal data and structure refinement for **1** and **2**.

	1	2
Empirical formula	$C_{18}H_{42}N_4O_8Ni$	$C_{28}H_{62}Cl_2N_8O_{14}Ni_2$
Formula weight	501.27	923.17
Temperature(K)	150(1)	147(2)
Wavelength(Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1$
a(Å)	16.5728(8)	10.3128(8)
b(Å)	15.1586(8)	15.0857(10)
c(Å)	9.4987(5)	13.0610(9)
β(°)	98.058(2)	102.1450(19)
V(Å^3)	2362.7(2)	1986.5(2)
Z	4	2
D_{calcd}(Mg/m^3)	1.409	1.543
Absorption coefficient(mm^{-1})	0.870	1.155
F(000)	1080	976
Crystal size(mm^3)	0.30 × 0.22 × 0.10	0.450 × 0.280 × 0.014
Theta range for data collection	1.83–27.00°	1.595–27.505°
Index range	$-14 \le h \le 21$, $-19 \le k \le 19$, $-12 \le l \le 11$	$-11 \le h \le 13$, $-18 \le k \le 19$, $-14 \le l \le 16$
Reflections collected	19755	12675
Independent reflections	5089 [R(int) = 0.0307]	8322 [R(int) = 0.0231]
Completeness to theta	98.8%(theta = 27.00°)	99.9%(theta = 25.242°)
Absorption correction	*Semi-empirical from equivalents*	*Semi-empirical from equivalents*
Max. and min. transmission	0.9180 and 0.7802	0.7456 and 0.6387
Refinement method	*Full-matrix least-squares on* F^2	*Full-matrix least-squares on* F^2
Data/restraints/parameters	5089/0/320	8322/1/499
Goodness-of-fit on F^2	1.022	1.022
Final R indices[$I > 2\sigma(I)$]	$R_1 = 0.0273$, $wR_2 = 0.0644$	$R_1 = 0.0344$, $wR_2 = 0.0703$
R indices (all data)	$R_1 = 0.0397$, $wR_2 = 0.0696$	$R_1 = 0.0508$, $wR_2 = 0.0768$
Largest diff. peak and hole(e. Å^{-3})	0.301 and −0.377	0.480 and −0.431

data collection. To collect sufficient data, a combination of ϕ and ω scans with κ offsets were used. The data frames were integrated and scaled using the Denzo-SMN package [27]. The structures were solved and refined, using the SHELXTL/PC V6.1 package [28]. Refinement was performed by full-matrix least squares on F^2, using all data (negative intensities included). Hydrogen atoms were included in calculated positions.

Results and discussion

Synthesis and structural description

The complex **1** (needles) was crystallized from the equimolar reaction of [Ni(**L**)]$(ClO_4)_2$ and *a,e-cis-*/*e,e-trans*-1,4-chdcH_2 mixture in basic DMF/H_2O. Meanwhile, the complex **2** (thin plates) was crystallized first from the same reactants in basic H_2O. The *a,e-cis*-1,4-chdc ligand in **1** affords more hydrogen-bonded water molecule aggregations than the *e,e-trans*-1,4-chdc ligand in **2**. Similar trend has been observed in a recent report by Qiblawi and LaDuca [9].

As illustrated in Fig. 1, the structure **1** exhibits a 1D coordination polymer which consists of [Ni(**L**)]$^{2+}$ units and *a,e-cis*-1,4-chdc bridging ligands. The coordination environment of nickel(II) ion shows a distorted octahedron with four Ni-N and two Ni-O bonds. The Ni-N distances of 2.0685(13) Å, 2.0716(13) Å, 2.0816 Å, 2.0528(11) Å, and Ni-O distances of Ni-$O_{ax\ COO}$ = 2.1182(10) Å, Ni-$O_{eq\ COO}$ = 2.1720 Å are normal for such a geometry in macrocyclic nickel(II) complexes [29,30]. Two discrete coordination geometries around

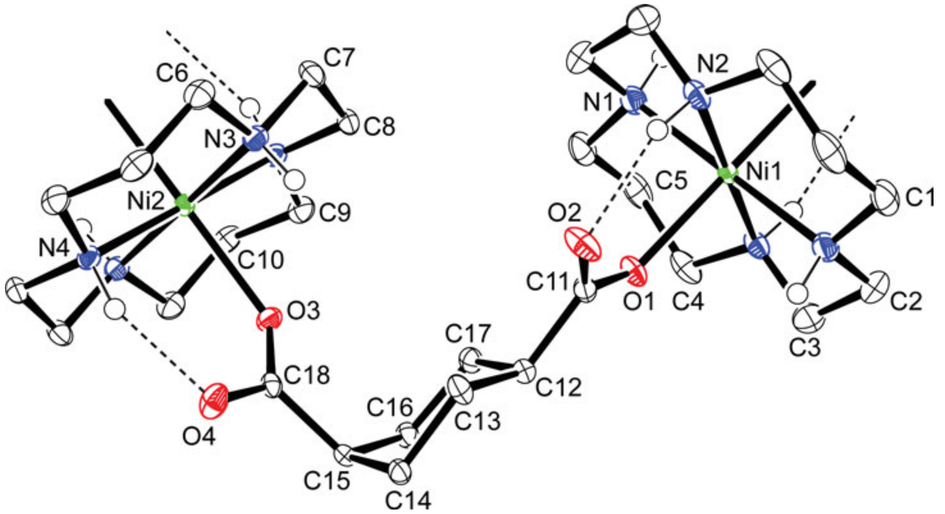


Figure 1. Molecular structure of **1** with atom-labeling scheme. Hydrogen atoms other than those participating in hydrogen bonding are omitted for clarity.

nickel(II) ions are found in **1**. The both axial sites of nickel(II) cyclam are occupied by oxygen atoms of COO_{ax} of *a,e-cis*-1,4-chdc ligands in one type, whereas both axial sites of nickel(II) cyclam are occupied by oxygen atoms of COO_{eq} of *a,e-cis*-1,4-chdc ligands in other type. These two types of macrocyclic nickel(II) units repeat alternately to form the undulated coordination polymer **1**. Selected bond distances and angles are summarized in Table 2. The Ni-O bonds are reinforced by intramolecular hydrogen bonds between the pre-organized N-H groups of the macrocycle and the non-coordinating oxygen atoms of the carboxylates of bridging *a,e-cis*-1,4-chdc ligands (N2-H2···O2: d(D···A) = 2.8759(16) Å, ∠(DHA) = 152.9°; N4-H4···O4#2: d(D···A) = 2.8786(16) Å, ∠(DHA) = 155.2°, symmetry code: #2 $-x+1,-y+1,-z+1$, Fig. 2, Table 3). Since the inherent "L" shape of an *a,e-cis*-1,4-chdc ligand, each 1D coordination polymer in **1** is undulated. Each 1D coordination polymer in **1** is further connected by hydrogen bonds with 1D H_2O chain, resulting in the formation of a 2D supramolecule (Fig. 2, Table 3). In detail, the four lattice water molecules form a 1D hydrogen-bonded H_2O chain in which each 1D H_2O chain crosses over 1D coordination polymer chains. The interactions between 1D coordination polymer chain and 1D H_2O chain at the intersection are achieved by the hydrogen bonds between the carboxylate groups of *a,e-cis*-1,4-chdc and water molecules (Fig. 2, Table 3). It is well known that the carboxylate groups

Table 2. Selected bond distances (Å) and angles (°) for **1**.

Ni1-N1	2.0685(13)	Ni1-N2	2.0716(13)
Ni2-N3	2.0816(12)	Ni2-N4	2.0528(11)
Ni1-O1	2.1182(10)	Ni2-O3	2.1720(10)
C11-O1	1.2577(17)	C11-O2	1.2617(19)
C18-O3	1.2585(17)	C18-O4	1.2645(17)
N1-Ni1-N2	85.25(5)	N1-Ni1-N2#1	94.75(5)
N1-Ni1-O1	90.77(5)	N2-Ni1-O1	93.39(4)
N1-Ni1-O1#1	89.23(5)	N2-Ni1-O1#1	86.61(4)
N3-Ni2-N4	85.17(5)	N3-Ni2-N4#2	94.83(5)
N3-Ni2-O3	90.25(4)	N4-Ni2-O3	87.91(4)
N3-Ni2-O3#2	89.75(4)	N4-Ni2-O3#2	92.09(4)

Symmetry transformations used to generate equivalent atoms: #1 $-x,-y+1,-z+1$
#2 $-x+1,-y+1,-z+1$

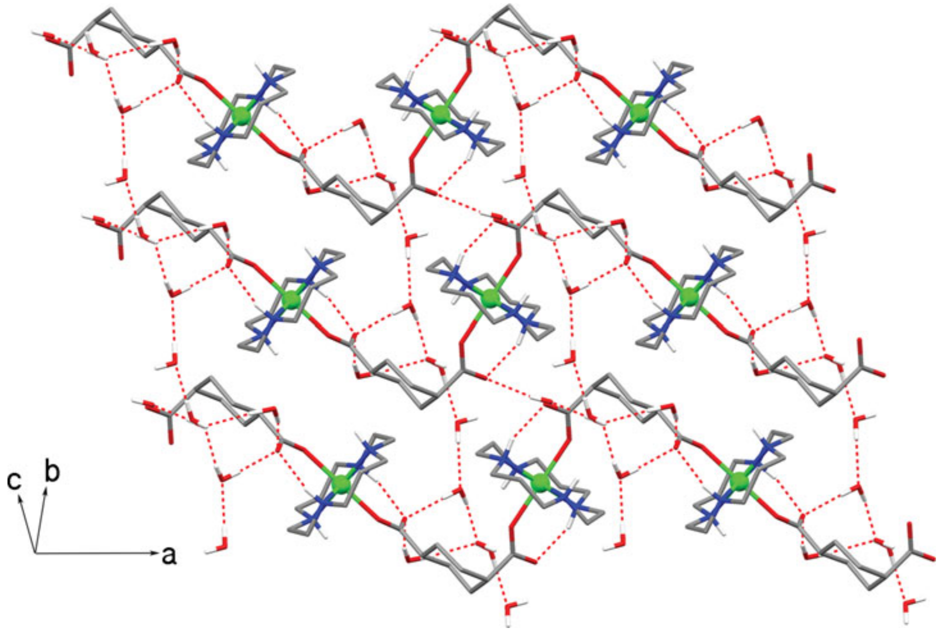


Figure 2. View of 1D coordination polymer and hydrogen bonding interactions between 1D chains in **1**.

of organic ligands can stabilize water molecules through the formation of strong hydrogen bonds [6]. The macrocyclic nickel(II) dimer **2** with bridging *e,e-trans*-1,4-chdc was crystallized from the equimolar reaction of [Ni(**L**)](ClO_4)$_2$ and *a,e-cis-/e,e-trans*-1,4-chdcH_2 mixture in basic aqueous solution. The solid state structure of **2** reveals that an *e,e-trans*-1,4-chdc ligand bridges two [Ni(**L**)(H_2O)]$^{2+}$ units (Fig. 3). The bond distances of Ni-N (avg. 2.068 Å) are normal for octahedral d^8 nickel(II) ions. The Ni-O distances of Ni1-O1 = 2.115(4), Ni2-O4 = 2.104(4) Å for Ni-O$_{\text{carboxylato}}$ bonds and Ni1-O3 = 2.203(4), Ni2-O6 = 2.206(4) Å for Ni-O$_{\text{aqua}}$ bonds exhibit that the Ni1-O$_{\text{aqua}}$ bond is weaker than that of Ni1-O$_{\text{carboxylato}}$ [21,29,30]. The important bond distances and angles are listed in Table 4. As found in **1**, the

Table 3. Hydrogen bonds for **1** (Å and °).

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
N1-H1···O4W#4	0.93	2.31	3.086(2)	140.7
N1-H1···O4WA#4	0.93	2.36	3.276(7)	170.7
N2-H2···O2	0.93	2.02	2.8759(16)	152.9
N3-H3···O1W	0.93	2.61	3.2759(18)	128.6
N4-H4···O4#2	0.93	2.01	2.8786(16)	155.2
O1W-H1WA···O2	0.82(2)	2.00(2)	2.8228(18)	177(2)
O1W-H1WB···O2W	0.82(2)	2.07(3)	2.8731(19)	168(2)
O2W-H2WA···O1W#5	0.80(2)	2.03(2)	2.832(2)	179(2)
O2W-H2WB···O3W	0.83(2)	2.00(2)	2.820(2)	172(2)
O3W-H3WA···O4	0.82(3)	1.96(3)	2.7777(18)	171(2)
O3W-H3WB···O4#6	0.79(2)	2.07(2)	2.8463(17)	168(2)
O4W-H4WA···O2	0.88(3)	2.02(3)	2.884(2)	168(2)
O4W-H4WB···O2W	1.00(4)	1.99(4)	2.992(2)	176(3)
O4WA-H4WC···O2	0.84	2.06	2.898(7)	179.8
O4WA-H4WD···O2#3	0.84	2.51	3.350(7)	179.9

Symmetry transformations used to generate equivalent atoms:
#1 -x, -y + 1, -z + 1 #2 -x + 1, -y + 1, -z + 1 #3 -x, -y + 1, -z #4 x,y,z + 1
#5 x, -y + 3/2, z-1/2 #6 -x + 1, -y + 1, -z

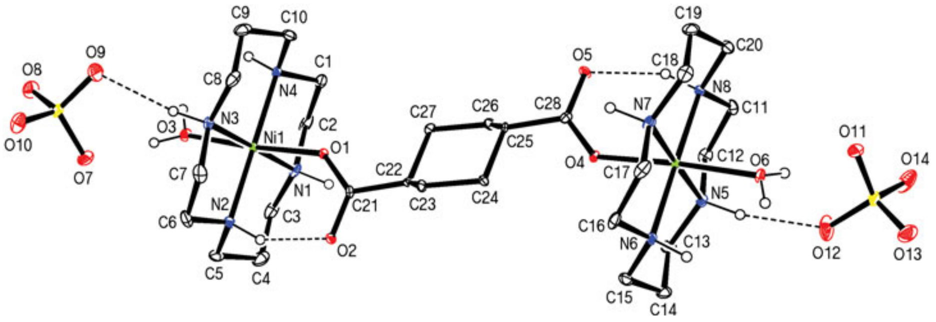


Figure 3. Molecular structure of **2** with atom-labeling scheme. Hydrogen atoms other than those participating in hydrogen bonding are omitted for clarity.

intramolecular hydrogen bonds between N-H and O atoms of COO of *e,e-trans*-1,4-chdc ligand and support the Ni-O bond (N2-H2C···O2: d(D···A) = 2.919(6) Å, ∠(DHA) = 153.1°; N8-H8C···O5: d(D···A) = 2.913(6) Å, ∠(DHA) = 152.5°, Fig. 3, Table 5). The dimer cations are connected to perchlorate anions through N-H···O hydrogen bonds (N3-H3C···O9: d(D···A) = 3.194(6) Å, ∠(DHA) = 167.9°; N5-H5C···O12: d(D···A) = 3.121(6) Å, ∠(DHA) = 159.6°, Fig. 3, Table 5). The nickel(II) dimer **2** extends its structure by O-H···O hydrogen bonds to form a 2D supramolecule containing cavities (O3-H3OB···O5#2: d(D···A) = 2.738(5) Å, ∠(DHA) = 166(6)°; O6-H6OB···O2#3: d(D···A) = 2.733(5) Å, ∠(DHA) = 173(7)°, symmetry code: #2 –*x*+1,*y*-1/2,-*z*+1, #3 –*x*,*y* + 1/2,-*z*, Fig. 4, Table 5). It is noteworthy that the crystallization of complexes **1** and **2** bearing *a,e-cis*-1,4-chdc and *e,e-trans*-1,4-chdc, respectively, from the *a,e-cis-/e,e-trans*-1,4-chdcH$_2$ mixture is highly dependent on the solvents employed. The influence for the crystallization of **1** and **2** by solvents may be different since the shape of *a,e-cis*-1,4-chdc in **1** is “L” that is expected to be more polar than the linear form of *e,e-trans*-1,4-chdc in **2**. Thus, the addition of aprotic polar solvent DMF to an aqueous solution induces the crystallization of coordination polymer **1**. Generally, the effects of solvents are explained by their difference of size, shape, and coordination ability [31–33]. As those above

Table 4. Selected bond distances (Å) and angles (°) for **2**.

Ni1-N1	2.060(5)	Ni1-N2	2.059(4)
Ni1-N3	2.060(4)	Ni1-N4	2.084(4)
Ni1-O1	2.115(4)	Ni1-O3	2.203 (4)
Ni2-N5	2.068(5)	Ni2-N6	2.089(4)
Ni2-N7	2.063(5)	Ni2-N8	2.058(4)
Ni2-O4	2.104(4)	Ni2-O6	2.206 (4)
C21-O1	1.260(6)	C21-O2	1.274(6)
C28-O4	1.267(6)	C28-O5	1.258(6)
N1-Ni1-N2	94.02(18)	N2-Ni1-N3	85.19(18)
N1-Ni1-N4	85.27(19)	N3-Ni1-N4	95.52(18)
N1-Ni1-O1	88.20(18)	N2-Ni1-O1	92.44(16)
N3-Ni1-O1	92.05(16)	N4-Ni1-O1	88.08(16)
N1-Ni1-O3	89.94(17)	N2-Ni1-O3	92.18(17)
N3-Ni1-O3	89.87(17)	N4-Ni1-O3	87.28(17)
N5-Ni2-N6	94.88(17)	N6-Ni2-N7	85.72(18)
N5-Ni2-N8	85.30(17)	N7-Ni2-N8	94.09(17)
N5-Ni2-O4	91.70(16)	N6-Ni2-O4	88.16(16)
N7-Ni2-O4	88.90(18)	N8-Ni2-O4	92.60(15)
N5-Ni2-O6	90.69(17)	N6-Ni2-O6	86.78(17)
N7-Ni2-O6	88.76(17)	N8-Ni2-O6	92.46(16)
O1-Ni1-O3	175.13(15)	O4-Ni2-O6	174.57(15)

Symmetry transformations used to generate equivalent atoms:

Table 5. Hydrogen bonds for **2** (Å and °).

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
N1-H1C···Cl1#1	1.00	2.94	3.795(5)	143.8
N1-H1C···O10#1	1.00	2.20	3.163(7)	161.7
N2-H2C···O2	1.00	1.99	2.919(6)	153.1
N3-H3C···O9	1.00	2.21	3.194(6)	167.9
N4-H4B···O5#2	1.00	2.29	3.265(6)	165.4
N5-H5C···O12	1.00	2.16	3.121(7)	159.6
N6-H6C···O2#3	1.00	2.18	3.169(6)	170.0
N7-H7C···O14#4	1.00	2.14	3.117(7)	165.1
N8-H8C···O5	1.00	1.99	2.913(6)	152.5
O3-H3OA···O7	0.86(6)	2.09(5)	2.912(6)	159(5)
O3-H3OB···O5#2	0.83(6)	1.93(6)	2.738(5)	166(6)
O6-H6OA···O11	0.80(5)	2.09(5)	2.866(5)	164(5)
O6-H6OB···O2#3	0.74(5)	1.99(6)	2.733(5)	173(7)

Symmetry transformations used to generate equivalent atoms:
#1 x-1,y,z #2 -x+1,y-1/2,-z+1 #3 -x,y+1/2,-z #4 x+1,y,z

are different in DMF and H_2O molecules, the isolated product could be different. The separation of *a,e-cis*-1,4-chdc (in DMA = N,N-dimethylacetamide) and *e,e-trans*-1,4-chdc (in H_2O) conformations from *a,e-cis-*/*e,e-trans*-1,4-chdcH_2 mixture by means of different solvents has been reported in the coordinated p-block metals [34]. However, there is no such report in the transition metals. The crystallization of **1** and **2** provides the rare example of the separation of *a,e-cis*-1,4-chdc and *e,e-trans*-1,4-chdc conformations from *a,e-cis-*/*e,e-trans*-1,4-chdcH_2 mixture by changing solvent in the transition metal complexes. Commercially available *a,e-cis-*/*e,e-trans*-1,4-chdcH_2 mixture is known to contain *a,e-cis*-1,4-chdcH_2 and *e,e-trans*-1,4-chdcH_2 in the ratio of ca. 3:2 (mixture of *cis* and *trans*, 99%). Rational syntheses of **1** (the ratio of [Ni(**L**)]$(ClO_4)_2$:*a,e-cis*-1,4-chdc = 1:1) and **2** (the ratio of [Ni(**L**)]$(ClO_4)_2$:*e,e-trans*-1,

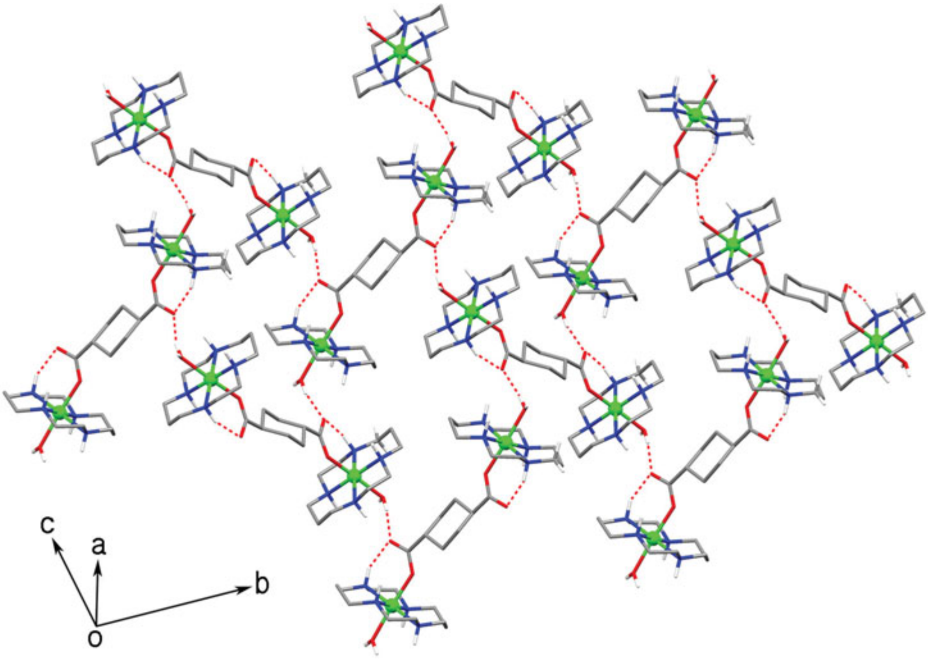


Figure 4. View of the dimer and extended structure by hydrogen bonding interactions in **2**.

4-chdc = 2:1) were carried out by using [Ni(**L**)](ClO_4)$_2$ and pure *a,e-cis*-1,4-chdcH_2 or *e,e-trans*-1,4-chdcH_2, showing that there was no indication of conformational interconversion during the crystallization of **1** and **2**.

IR Spectra and TGA

In agreement with the structures determined by X-ray diffraction methods, broad bands at 3404 cm^{-1} (**1**) and 3481 cm^{-1} (νH_2O) (**2**) in the IR spectra prove the presence of water molecules (Fig. S1). Weak bands at 3233, 3181 cm^{-1} (**1**) and 3232, 3156 cm^{-1} (νNH) (**2**) indicate that the macrocycles are present in the complexes. The bands at 1553 cm^{-1} ($\nu_{as}CO_2$), 1401 cm^{-1} ($\nu_{s}CO_2$) (**1**) and 1542 cm^{-1} ($\nu_{as}CO_2$), 1399 cm^{-1} ($\nu_{s}CO_2$) (**2**) were observable due to coordinated carboxylate ligands [25,35]. In addition, perchlorate ions were identified from the bands at 1101 cm^{-1} (νClO_4), 626 cm^{-1} (δClO_4) in **2**. The TGA curve for **1** showed a first weight loss of 16.0% (calc. 14.3%) between 40°C and 105°C, corresponding to the loss of four lattice water molecules (Fig. S2). Further weight loss due to the loss of chdc and macrocyclic ligands was observed over 235°C–736°C range. The metallic Ni composition (obs. 11.7%, calc. 11.7%) was observed at ~930°C as a final residue. The TGA curve for **2** showed a first weight loss of 4.2% (calc. 3.9%) over the range 91°C–135°C, corresponding to the loss of two coordinated aqua ligands (Fig. S2). On further heating, weight losses were observed in the range 260°C–700°C with the loss of perchlorate ions, chdc, and macrocycles. The final NiO residue (obs. 8.1%, calc. 8.1%) was remained above ~850°C.

Conclusions

We successfully synthesized and structurally characterized two new complexes **1** and **2** in which bridging chdc ligands take *a,e-cis*-1,4-chdc (in **1**) and *e,e-trans*-1,4-chdc (in **2**) form, respectively. The crystallization of **1** and **2** from the reaction of [Ni(**L**)](ClO_4)$_2$ and *a,e-cis-/e,e-trans*-1,4-chdc mixture was highly dependent on the solvents employed during the synthesis. The coordination polymer **1** bearing the *a,e-cis*-1,4-chdc ligand was crystallized from basic DMF/H_2O solvent mixtures. Meanwhile, the dimer **2** containing the *e,e-trans*-1,4-chdc ligand was crystallized from basic H_2O solvent. The structure **1** exhibits an undulated 1D coordination polymer, where each 1D coordination polymer chain is hydrogen bonded to 1D hydrogen-bonded H_2O chain to form a 2D grid. The solid state structure of **2** reveals that an *e,e-trans*-1,4-chdc ligand bridges two nickel(II) macrocycles to form a dimer in which each sixth site of nickel(II) ion is occupied by aqua ligand. The dimer **2** further extends by hydrogen bonds, resulting in the formation of cavity containing a 2D supramolecule.

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