

Structural and Spectral Studies on the Ni(II) Complexes of 1,5-Diazacyclooctane (DACO) Bearing Heterocyclic Pendants: Formation of a Two-dimensional Network via Hydrogen Bonds and π - π Stacking Interactions

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A penta-coordinated Ni(II) complex with a 1,5-diazacyclooctane (DACO) ligand functionalized by two imidazole donor pendants, $[\text{NiL}^1\text{Cl}](\text{ClO}_4) \cdot \text{H}_2\text{O}$ (**1**) (where $\text{L}^1 = 1,5$ -bis(imidazol-4-ylmethyl)-1,5-diazacyclooctane) has been synthesized and characterized by X-ray diffraction, infrared spectra, elemental analyses, conductance, thermal analyses and UV-Vis techniques. Complex **1** crystallizes in triclinic crystal system, *P*-1 space group with $a = 0.74782(7)$, $b = 1.15082(10)$, $c = 1.23781(11)$ nm, $\alpha = 82.090(2)$, $\beta = 73.011(2)$, $\gamma = 83.462(2)^\circ$, $V = 1.00603(16)$ nm³, $M_r = 486.00$, $Z = 2$, $D_c = 1.604$ g/cm³, final $R = 0.0435$, and $wR = 0.1244$. The structures of **1** and its related complexes show that in all the three mononuclear complexes, each Ni(II) center is penta-coordinated with a near regular square pyramid (RSP) to distorted square-pyramidal (DSP) coordination environment due to the boat/chair configuration of DACO ring in these complexes, and the degree of distortion increases with the augment of the size of the heterocyclic pendants. In addition, the most striking feature of complex **1** resides in the formation of a two-dimensional network structure through hydrogen bonds and stabilized by π - π stacking. The solution behaviors of the Ni(II) complexes are also discussed in detail.

Keywords Crystal structure, 1,5-diazacyclooctane, electronic spectra, Ni(II) complexes, two-dimensional network

Medium-sized cyclic ligands containing seven-

ten-membered rings occupy a very important position between acyclic and macrocyclic ligands for they can usually provide a steric effect along with a strong ligand field effect.¹ 1,5-Diazacyclooctane (DACO), the most typical example of the diazamesocyclic ligands, offers several attractive features as a framework for ligand development with exceptionally strong ligand fields, unique conformational requirements and the potential for further functionalization.²⁻⁴

Since DACO has only two nitrogen donors, two or more ligands are required for the formation of one metal center.^{2,4,5} However, appropriately substituted mesocycles can enhance the pre-organization of the ligand, thereby facilitating complexation.⁶ The first example of the DACO derivative, 1,5-diazacyclooctane-*N,N'*-diacetate (DACODA) and its Co(II), Ni(II), Cu(II) and Zn(II) complexes were reported by Legg and co-workers.⁷ The crystal structures show that DACO exhibits the interesting "boat/chair" configuration in its metal complexes. The hydrogen atoms of the trimethylene group on the backbone effectively block the sixth-coordination to the metal center to form complexes with penta-coordination mode⁸ and the flap-over ring could provide a sterically protected metal coordination site capable of sup-

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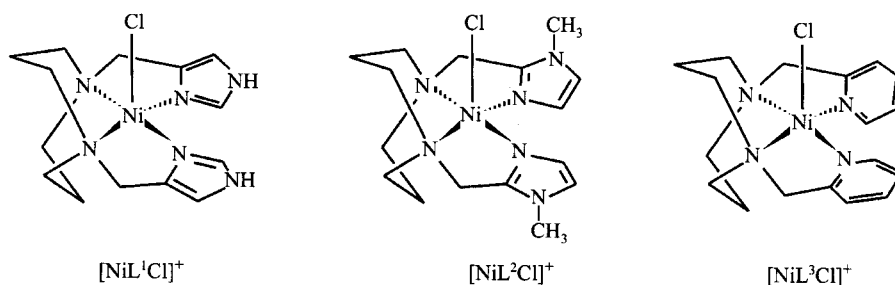
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porting interactions of small molecules or a highly reactive metal hydride functionality.⁹ Furthermore, the coordinating abilities of DACO ligands can be controlled through adjusting the donor pendants on it.¹⁰ This interesting chemistry promotes us to investigate the effects of the functional pendants of DACO on the coordination modes and properties of the metal complexes.

As a continuation of our efforts on this project,¹⁰ we report herein the synthesis and crystal structure of a new Ni(II) complex, $[\text{NiL}^1\text{Cl}](\text{ClO}_4) \cdot \text{H}_2\text{O}$ (**1**) ($\text{L}^1 = 1,5$ -bis(imidazole-4-ylmethyl)-1,5-DACO), which is assembled into a two-dimensional network via hydrogen

bonds and π - π stacking interactions. For comparison, two relevant complexes of **1**, $[\text{NiL}^2\text{Cl}](\text{ClO}_4)$ (**2**) and $[\text{NiL}^3\text{Cl}](\text{ClO}_4)$ (**3**) (where $\text{L}^2 = 1,5$ -bis(*N*-1-methylimidazol-2-ylmethyl)-1,5-diazacyclooctane and $\text{L}^3 = 1,5$ -bis(pyridyl-2-ylmethyl)-1,5-diazacyclooctane), have been investigated. These tetradentate ligands can form stable penta-coordinated mononuclear complexes (Scheme 1), which is still relatively unexplored for Ni(II).¹¹ The influences on the structural and spectral properties for all the Ni(II) complexes of various heterocyclic pendants are also investigated in detail.

Scheme 1



Experimental

Materials and general methods

All the reagents for syntheses and analyses were of analytical grade. FT-IR spectra (KBr pellets) were taken on a FT-IR 170SX (Nicolet) spectrometer and electronic absorption spectra on a Shimadzu UV-260 spectrophotometer. Elemental analyses were performed on a Perkin-Elmer 240C analyzer. Molar conductivities of the complexes were taken at room temperature using a DDS 11A conductometer. Thermal characterization (TG-DTA) studies were carried out on a Dupont thermal analyzer.

Syntheses

The ligand was prepared according to our previous work.^{10(c)} Complex **1** was synthesized as follows: the pH value of a solution containing equimolar amounts of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (36 mg, 0.1 mmol) in methanol (5 mL) and $\text{L}^1 \cdot 4\text{HCl} \cdot \text{H}_2\text{O}$ (44 mg, 0.1 mmol) in H_2O (5

mL) was adjusted to ca. 7 with dilute KOH aqueous solution. Green solution was filtered and left to stand at room temperature. Single crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent. Yield 29 mg (60%). IR (KBr pellet): 3387 (b), 2915 (w), 1589 (m), 1480 (m), 1458 (m), 1140 (w), 1106 (m), 1069 (vs), 1028 (m), 622 (s) cm^{-1} ; Anal. calcd for $\text{C}_{14}\text{H}_{24}\text{Cl}_2\text{NiN}_6\text{O}_5$: C 34.6, H 5.0, N 17.3; found C 34.2, H 5.1, N 17.2. Δ_{M} [water (acetonitrile)]: 126 (172) $\text{cm}^2 \cdot \Omega^{-1} \cdot \text{mol}^{-1}$.

The relevant Ni(II) complexes $[\text{NiL}^2\text{Cl}](\text{ClO}_4)$ (**2**) and $[\text{NiL}^3\text{Cl}](\text{ClO}_4)$ (**3**) were prepared according to our previous work.^{12,13} Δ_{M} [water (acetonitrile)]: 127 (174) $\text{cm}^2 \cdot \Omega^{-1} \cdot \text{mol}^{-1}$ for **2** and 192 (180) $\text{cm}^2 \cdot \Omega^{-1} \cdot \text{mol}^{-1}$ for **3**.

X-ray crystallography

Single-crystal X-ray diffraction measurement of **1** was carried out on a Bruker Smart 1000 CCD diffractometer equipped with a graphite crystal monochromator situated in the incident beam for data collection. The

determination of unit cell parameters and data collections were performed with Mo K α radiation ($\lambda = 0.071073$ nm). Unit cell dimensions were obtained with least-squares refinements and the structure was solved by direct methods. Ni(II) atoms were located from *E*-maps and the other non-hydrogen atoms and the hydrogen atoms of lattice water were located in successive difference Fourier syntheses. The final refinement was performed by full matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F^2 . The hydrogen atoms of the ligand were added theoretically, and riding on the concerned atoms and refined with fixed thermal factors. Crystallographic data and experimental details for structural analyses are summarized in Table 1.

Table 1 Crystallographic data and structure refinement summary for complex **1**

Formula	C ₁₄ H ₂₄ Cl ₂ N ₆ NiO ₅
M_r	486.00
Crystal system	Triclinic
Space group	<i>P</i> -1
<i>T</i> (K)	299 ± 2
<i>a</i> (nm)	0.74782(7)
<i>b</i> (nm)	1.15082(10)
<i>c</i> (nm)	1.23781(11)
α (°)	82.090(2)
β (°)	73.011(2)
γ (°)	83.462(2)
<i>V</i> (nm ³)	1.00603(16)
<i>D_c</i> (g/cm ³)	1.604
<i>Z</i>	2
w^{-1}	$\sigma^2(F_o^2) + (0.0807P)^2 + 0.6310P$
Absorption correction	Semi-empirical (SADABS)
<i>R</i>	0.0435
<i>wR</i>	0.1244
Max. Res. Peak (e/nm ³)	957

Results and discussion

Synthesis and general characterization

The syntheses of the complexes **1**–**3** were achieved by the reaction of the free ligand with Ni(ClO₄)₂·6H₂O. Since the corresponding ligands are the HCl salts, they must be neutralized with KOH aqueous solution prior to

complexation. The electrical conductance values of the complexes in water indicate that complexes **1** and **2** behave as 1:1 electrolytes, which is consistent with the results of X-ray analysis, implying that the coordination mode of Ni(II) is kept in water solution as in the solid state.¹⁴ However, complex **3** acts as an electrolyte between 1:1 and 2:1 indicating that the axial chloride anion maybe partly lost in the solution to form the square planar form. The electrical conductance results of the complexes in acetonitrile indicate that all the Ni(II) complexes behave as electrolytes between 1:1 and 2:1.¹⁴ The IR spectra of complex **1** show absorption bands resulting from the skeletal vibrations of imidazole rings in 1400–1600 cm⁻¹ region, and exhibit broad bands centered around 3400 cm⁻¹, which are assigned to the ν_{O-H} stretch of the lattice water. An interesting feature of the spectra is the occurrence of highly split ν_{Cl-O} stretches of the ClO₄⁻ ions (1140, 1106, 1069 and 1028 cm⁻¹), which provides good evidence of their involvement in the formation of hydrogen-bonding.

Complex **1** is air stable at room temperature and without melting point before decomposition. Thermal analyses (from room temperature to 800°C) showed that the decomposition starts when it is heated above 291°C and stops above 680°C. The TGA data indicate that the total weight loss (3.71% at 85–120°C) is consistent with the loss for one crystal water molecule (the theoretical weight loss is 3.56%).

Description of the crystal structure

The ORTEP structure of complex **1** with atom labeling is shown in Fig. 1, and the selected bond distances and angles are given in Table 2.

The structure of complex **1** consists of a discrete [NiL¹Cl]⁺ cation, a perchlorate anion and a water molecule. The coordination geometry around Ni(II) can be described as a near ideal square-pyramidal stereochemistry with $\tau = 0.01$ ($\tau = 0$ for an ideal square-pyramid, and $\tau = 1$ for an ideal trigonal bipyramid)¹⁵ generated by the basal least-square plane of N(1)–N(2)–N(3)–N(5) and apical Cl(1) anion. For L¹, the two nitrogen atoms of the imidazole pendants and other two nitrogen donors of the DACO ring are in *cis* positions in the coordination polyhedron, and the Ni(II) ion is deviated from the mean equatorial plane of the square-pyramid towards the apical Cl(1) by ca. 0.038 nm. The

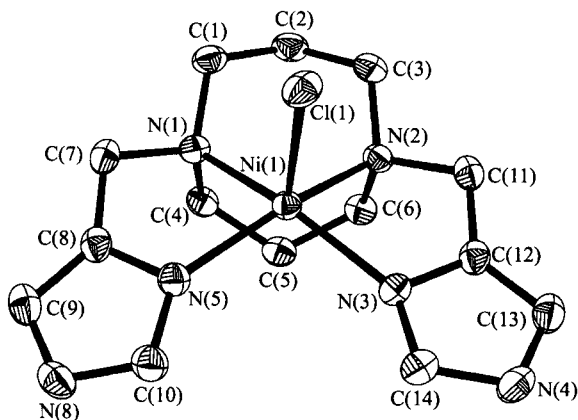


Fig. 1 ORTEP drawing of the complex cation $[\text{NiL}^1\text{Cl}]^+$ in **1** with 30% thermal ellipsoid probability.

dihedral angle of the two imidazole rings is 12.7° . In the complex, the ligand adopts a “boat/chair” configuration and gives rise with the metal ion to two five-membered

chelate rings $[\text{N}(2)\text{-C}(11)\text{-C}(12)\text{-N}(3)\text{-Ni}(1)]$ and $[\text{N}(1)\text{-C}(7)\text{-C}(8)\text{-N}(5)\text{-Ni}(1)]$, forming a $\text{N}(2)\text{-Ni}(1)\text{-N}(3)$ angle of $81.92(10)^\circ$ and a $\text{N}(1)\text{-Ni}(1)\text{-N}(5)$ angle of $81.82(10)^\circ$.

The Ni—N bond distances lie in the range of $0.2028(2)\text{--}0.2110(2)$ nm, all being normal Ni—N coordination bonds. However, the bond lengths of Ni— N_{DACO} ($0.2110(2)$ and $0.2101(2)$ nm) are longer than the Ni— $\text{N}_{\text{imidazole}}$ bond lengths ($0.2040(2)$ and $0.2028(2)$ nm), indicating weaker coordination of DACO ring compared with the imidazole pendants to Ni(II). The Ni—Cl bond distance is $0.23275(8)$ nm, indicating weak coordination of chloride ion. This makes it possible that other stronger donor atom, ion or small molecule can replace the chloride anion, which is important for further application of this complex as potential catalyst or as functional building block for the construction of bigger architectures.

Table 2 Selected bond lengths (10^{-1} nm) and angles ($^\circ$) for complex **1**

Bond lengths (10^{-1} nm)			
Ni(1)—N(1)	2.110(2)	Ni(1)—N(2)	2.101(2)
Ni(1)—N(3)	2.040(2)	Ni(1)—N(5)	2.028(2)
Ni(1)—Cl(1)	2.3275(8)		
Bond angles ($^\circ$)			
N(5)—Ni(1)—N(3)	102.33(10)	N(5)—Ni(1)—N(2)	157.18(10)
N(3)—Ni(1)—N(2)	81.92(10)	N(5)—Ni(1)—N(1)	81.82(10)
N(3)—Ni(1)—N(1)	157.68(10)	N(2)—Ni(1)—N(1)	86.25(10)
N(5)—Ni(1)—Cl(1)	102.19(8)	N(3)—Ni(1)—Cl(1)	98.66(7)
N(2)—Ni(1)—Cl(1)	99.26(7)	N(1)—Ni(1)—Cl(1)	101.88(7)

Comparing the structure of **1** with those of $[\text{NiL}^2\text{Cl}]$ **2** and $[\text{NiL}^3\text{Cl}]$ **3**,^{12,13} three notable features common to all complexes are found: (1) all these tetradentate DACO heterocyclic ligands can form stable five-coordinated mononuclear complexes with Ni(II). A pair of nitrogen atoms of DACO ring and two nitrogen donors of the heterocyclic pendants (in *cis*-positions) formed the basal plane and the chloride anion finishes the coordination polyhedron as the axis. (2) The ligand adopts a “boat/chair” configuration and gives rise with the metal ion to two five-membered chelate rings, which enhance the coordination ability to Ni(II) center. The central methylene C—H groups of the boat form shields the metal centers in the complexes with H—Ni distances of $0.2348(3)$, $0.2278(2)$ and $0.2273(3)$ nm, respectively, which effectively block the sixth coordination position to

give these penta-coordinated Ni(II) complexes. (3) The $\text{N}_{\text{DACO}}\cdots\text{N}_{\text{DACO}}$ nonbond distances are restricted within narrow limits ($0.2878(3)\text{--}0.2850(2)$ nm), which are much shorter than corresponding $\text{N}_{\text{pendant}}\cdots\text{N}_{\text{pendant}}$ ($0.3169(2)\text{--}0.3330(2)$ nm) separations, so that the angles of $\text{N}_{\text{DACO}}\text{-Ni-N}_{\text{DACO}}$ are limited in the range of $85.7(2)\text{--}86.25(10)^\circ$, being significant smaller than the angles of $\text{N}_{\text{pendant}}\text{-Ni-N}_{\text{pendant}}$ ($102.33(10)\text{--}104.2(1)^\circ$) due to the stereochemical requirements.

There are also some structural differences imposed by the additional heterocyclic pendants: (1) the stereochemistry of NiN_4Cl varies from distorted square-pyramidal coordination environment to near regular square pyramid with τ value from 0.01 to 0.13. The degree of distortion increasing with the augment of the size of the heterocyclic pendants (4-chloromethyl-imidazole \rightarrow 1-

methyl-2-chloromethyl-imidazole \rightarrow 2-chloromethyl-pyridine), which is consistent with the results of the Cu(II) complexes.¹⁰⁽²⁾ In complexes **1** and **2**, the Ni—N_{pendant} bond distances (0.2040 and 0.2028 nm for **1** vs. 0.2044 and 0.2025 nm for **2**) are so similar and obviously shorter than the Ni—N_{DACO} bond distances (0.2110 and 0.2101 nm for **1** vs. 0.2130 and 0.2099 nm for **2**), which indicates the stronger coordination. However, in complex **3**, the Ni—N_{pendant} bond distances (0.2108 and 0.2074 nm) are near to that of Ni—N_{DACO} (0.2088 and 0.2081 nm), which is due to steric hindrance resulting in the larger twisted angles of the pyridine rings (19.2°).

Another notable difference of complex **1** from **2** and **3** resides in the formation of a two-dimensional network in which H₂O molecules link complex cations and ClO₄⁻ counter anions through hydrogen bonds and further stabilized by strong π - π stacking interactions. The hydrogen atoms from the imidazole rings in the cation unit [NiLCl]⁺ have been activated by the positive charge due to the coordination of nitrogen atoms to the Ni(II) center. The axial chloride anion accepts the hydrogen atom of the uncoordinated nitrogen atom of the imidazole, forming a dimer through inter-molecule hydrogen bond. Each perchlorate anion forms acceptor of hydrogen bonds with one adjacent water molecule, and this water molecule also forms acceptors with the uncoordinated nitrogen donor of the imidazole ring. Each two neighboring imidazole rings in and between the dimer are parallel and separated by 0.33130(4) and 0.34898(5) nm, indicating the presence of significant face-to-face π - π stacking interactions^{16,17} to form a quasi-linear structure (along *b* axis). The Ni \cdots Ni nonbond distances are 0.7727 (intra-dimer) and 0.7251 nm (inter-dimer), respectively. In addition, the water molecule connects the axial chloride of another line through weak O—H \cdots Cl bond. Therefore, water molecules link uncoordinated perchlorate, the apical chloride anion and the imidazole ring, giving a 2-D network which is stabilized by close π - π stacking interactions between neighboring parallel imidazole rings as depicted in Fig. 2. The N(O) \cdots Cl(O) separations occur in the range of 0.2838—0.3213 nm with H \cdots Cl(O) separations in the 0.1996—0.2432 nm range, falling into the normal range of the hydrogen-bonding separations¹⁸ and the smallest bond angle is 150.15(4)°. In conclusion, it demonstrates a nice example that the hydrogen bonds together with π - π interac-

tions co-affect inorganic supramolecule formation. However, no interaction such as hydrogen bond has been found to exist in complexes **2** and **3**.

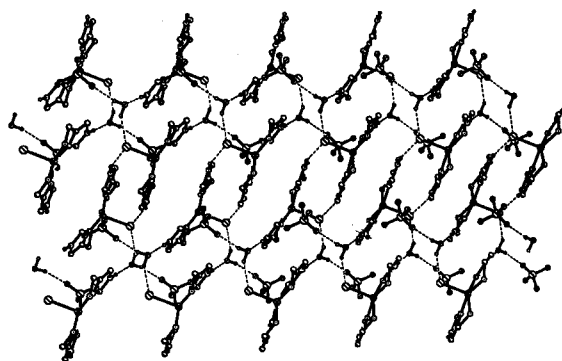


Fig. 2 View of the two-dimensional network for complex **1** (the methylene groups of DACO and irrelevant H atoms have been omitted for clarity). Important hydrogen bond distances (10⁻¹ nm) and angles (°): N(6) \cdots O(5) 2.838, N(4) \cdots Cl(1) 3.213, O(5) \cdots O(4) 2.843, O(5) \cdots Cl(1) 3.182; N(6)-H(6A) \cdots O(5) 165.81, N(4)-H(4A) \cdots Cl(1) 151.28, O(5)-H(52) \cdots O(4) 156.85, O(5)-H(51) \cdots Cl(1) 150.15.

Electronic spectra

The UV-Vis spectra of all the complexes in water and acetonitrile solution have been investigated at room temperature and the electronic spectral data were summarized in Table 3. It can be clearly seen that complexes **1** and **2** have very parallel absorption maxima in water solution, which is similar to the spectra of [Ni(DACO-DA)-H₂O], indicating that the square-pyramidal coordination environment is maintained in water solution.^{7(b),19} Combining the electrical conductance results of both complexes, it can be concluded that both complexes maintain the coordination geometry in water solution as in solid state. However, the absorption maximum (*d-d* band) for complex **3** shifts significantly lower with ϵ_{max} of 497 nm, which indicates that the coordination geometry changes into planar form.²⁰ Furthermore, electrical conductance value of **3** shows that it acts as between 1:1 and 2:1 electrolyte, indicating that the axial chloride anion may be lost to form four-coordinate planar geometry in water solution, which is consistent with the spectral data. This may result in the strong steric repulsion influence of the larger pyridine pendants comparing with imidazole. In addition, the solution spectra of all the complexes in 200—260 nm range also show $\pi \rightarrow \pi^*$ lig-

and transitions.

Table 3 Comparison of the UV-Vis spectra data for the five-coordinated mononuclear Ni(II) complexes

Complex	λ_{\max}/nm ($\epsilon_{\max}/\text{M}^{-1}\text{cm}^{-1}$)	Solvent
1	585 (42) 371 (123)	H ₂ O
2	590 (42) 370 (128)	H ₂ O
3	497 (137) 367 (54)	H ₂ O
1	649 (134) 404 (394) 372 (467) 359 (470)	CH ₃ CN
2	652 (55) 402 (159) 372 (198) 359 (200)	CH ₃ CN
3	645 (99) 406 (489) 376 (498) 359 (532)	CH ₃ CN

The electronic spectra of complexes 1—3 in acetonitrile solution are quite similar with [Ni(DACODA)-H₂O], indicating that they maintain the square-pyramidal geometry.^{7(b)} Otherwise, there are three strong absorption maxima in the range of 350—410 nm which may result in the ligand exchange at the axial position, that is the solvent molecules (CH₃CN) substitute the axial chloride anions. This can also be sustained by the electrical conductance measurement (all the complexes act as between 1:1 and 2:1 electrolyte in acetonitrile solution).

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