



## Synthesis and Crystal Structure of Novel Macrocyclic Molecule: $\{[\text{Ni}(\text{C}_{26}\text{H}_{20}\text{N}_6\text{S}_2)\text{Cl}_2]_2\}(\text{H}_2\text{O})_2$

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A novel Ni(II) complex with the formula ( $\{[\text{Ni}(\text{C}_{26}\text{H}_{20}\text{N}_6\text{S}_2)\text{Cl}_2]_2\}(\text{H}_2\text{O})_2$ ) was synthesized by pyridyl-pyrimidinyl dithioethers and  $\text{NiCl}_2$ , as the dinuclear [2+2] macrocyclic motif. The present compound shows six-coordinate core ( $\text{Ni}_4\text{Cl}_2$ ), which is distorted octahedral geometry and led to a novel 3D supramolecular complex by the intermolecular hydrogen bonds interactions among the adjacent dinuclear units. The crystal is monoclinic crystal system, space group  $\text{P}2_1/c$  with unit cell parameters:  $a = 11.9071(11) \text{ \AA}$ ,  $b = 11.7096(11) \text{ \AA}$ ,  $c = 19.2484(18) \text{ \AA}$ ,  $\alpha = 90.00^\circ$ ,  $\beta = 101.886(2)^\circ$ ,  $\gamma = 90.00^\circ$ ,  $V = 2626.2(4) \text{ \AA}^3$ ,  $Z = 2$ ,  $M_r = 1256.45$ ,  $D_c = 1.589 \text{ g/cm}^3$ ,  $\mu = 1.135 \text{ m m}^{-1}$ ,  $F_{(000)} = 1288.0$ ,  $R = 0.0633$ ,  $wR = 0.1718$  for 2869 reflections with  $I > 2\sigma(I)$ .

**Key Words:** Pyridyl-pyrimidinyl dithioether, Macrocyclic molecule.

### INTRODUCTION

Over the past decade, metal-organic frameworks (MOFs), formed by coordination bonds between metal ions or clusters and organic linkers, have attracted great interest for their fascinating properties as potential functional materials or their intriguing variety of topologies<sup>1-4</sup>. In this respect, organic sulfur-containing heterocycles, have emerged as a versatile class of organic building blocks in recent years, which often reacted with  $d^{10}$  electron configuration metal ions (e.g.  $\text{Cu}^+$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ag}^+$ ), giving rise to a range of coordination polymers and hydrogen-bonded supramolecular architectures. In our research group, several complexes formed by  $d^{10}$  electron configuration metal with sulfur-containing heterocycles have also been previously reported<sup>5,6</sup>.

As our continuing study, herein reported is dinuclear metallosupramolecular nickel complex derived from pyridyl-pyrimidinyl dithioether.

### EXPERIMENTAL

Solvents and reagents were commercially sourced and used without further purification. Infrared spectra were performed on a Bruker Vector 22 FI-IR spectrophotometer on KBr pellets.  $^1\text{H}$  NMR spectra were recorded on a Bruker AM-500 NMR spectrometer. Mass spectra were measured with a Finnigan MAT SSQ 710 mass spectrometer in a scan range 100-1200 amu. Elemental analysis was measured on a Perkin-Elmer 1400C analyzer.

**Synthesis of ligand:** Ligand(L) was synthesized by a similar way as following<sup>6a</sup>: To the solution of 4-(2-pyridinyl)-pyrimidine-2-thiol (3.78 g, 20 mmol) and sodium hydroxide (0.80 g, 20 mmol) in dry ethanol (300 mL), 1,2-bis(bromomethyl)-benzene (2.64 g, 10 mmol) in  $\text{CCl}_4$  (30 mL) was added. The mixture was stirred and refluxed for 8 h. After cooled, precipitates were filtered, washed by water and ethanol and dried in vacuum. For L: yield 91.2 %, m.p. 153-155 °C. Anal. calcd. (%) for  $\text{C}_{26}\text{H}_{20}\text{N}_6\text{S}_2$ : C, 64.98; H, 4.19; N, 17.49. Found (%): C, 64.93; H, 4.29; N, 17.45 %. IR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 1560 (vs), 1532 (s), 1474 (w), 1420 (m), 1352 (m), 1335 (m), 1212 (m), 1201 (m), 1085 (w), 829 (w), 795 (w), 766 (m). ESI-MS: 503.0 (100 %)  $[\text{L} + \text{Na}]^+$ .  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ): 8.69 (d, 2H, pyridyl-H), 8.56 (d, 2H, pyrimidyl-H), 8.41 (d, 2H, pyrimidyl-H), 7.97 (d, 2H, pyridyl-H), 7.83 (t, 2H, pyridyl-H), 7.53 (t, 2H, pyridyl-H), 7.40 (t, 2H, aryl-H), 7.28 (d, 2H, aryl-H), 4.77 (s, 4H, methylene-H).

**Synthesis of macrocyclic molecule:** L was treated with  $\text{NiCl}_2 \cdot 4\text{H}_2\text{O}$  in DMF in ratio 2:1 in room temperature. The solution was introduced into crystallization tubes and diffused with ether. Blue crystals formed after few days. Anal. calcd. for  $\text{C}_{52}\text{H}_{44}\text{N}_{12}\text{O}_2\text{S}_4\text{Ni}_2\text{Cl}_4$ : C, 55.36; H, 3.90; N, 14.90 found: C, 55.38; H, 3.91; N, 14.84 %. Main IR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3432 (bm), 1654 (w), 1567 (s), 1547(s), 1478(w), 1412(s), 1337(s), 1216(m), 1205(m), 1171(w), 1022(w), 801(w), 726(m).

**Crystal structure determination:** A single crystal of compound with dimensions of 0.20 mm  $\times$  0.20 mm  $\times$  0.30 mm was selected for the crystallographic data collection at

291(2)K and structure determination on a Bruker SMART CCD-4K diffractometer employing graphite-monochromated  $\text{MoK}_\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). A total of 12706 reflections were collected in the range of  $1.80^\circ \leq \theta \leq 25.0^\circ$ , of which 4609 reflections were unique with  $R_{\text{int}} = 0.045$ . The data were collected using SMART and reduced by the program SAINT. All the structures were solved by direct methods and refined by full-matrix least squares method on  $F^2_{\text{obs}}$  by using SHELXTL-PC software package. Non-hydrogen atoms were placed in geometrically calculated positions. Hydrogen atoms were added according to theoretical model. The final full-matrix least-squares refinement including 351 variable parameters for 4609 reflections with  $I > 2\sigma(I)$  and converged with unweighted and weighted agreement factors of

$$R_1 = \frac{\sum(|F_0| - |F_c|)}{\sum |F_0|} = 0.0633 \quad (1)$$

and

$$wR_2 = \left\{ \frac{\sum [w(F_0^2 - F_c^2)^2]}{\sum w(f_0^2)^2} \right\}^{1/2} = 0.1718 \quad (2)$$

where  $w = 1/[\sigma^2(F_0^2) + (0.0970P)^2]$  and  $P = (F_0^2 + 2F_c^2)/3$ . The maximum and minimum peaks on the final difference Fourier map are corresponding to 1.20 and  $-0.42 \text{ e/\AA}^3$ , respectively.

## RESULTS AND DISCUSSION

The selected bonds and hydrogen bonds are shown in Tables 1 and 2 and a perspective view of the present complex with the atom-numbering scheme is shown in Fig. 1. The packing diagram of the present complex is shown in Fig. 2. The title complex crystallizes in monoclinic crystal system and  $P2_1/c$  space group. Each symmetric unit consists of two ligands, two  $\text{Ni}^{2+}$  ions, four coordinated  $\text{Cl}^-$  anions and one free water molecule to form a dinuclear  $[2 + 2]$  macrocycle motif. As shown in Fig. 1, each  $\text{Ni}^{2+}$  is in a distorted octahedral geometry, surrounded by four nitrogen atoms from two ligands, two coordinated  $\text{Cl}^-$  anions. The equatorial positions are occupied by  $\text{N}_4$ ,  $\text{N}_1$ ,  $\text{Cl}_1$ ,  $\text{Cl}_2$ , while the axial positions are occupied by  $\text{N}_3$  and  $\text{N}_6$ . Due to Jahn-Teller distortion, both

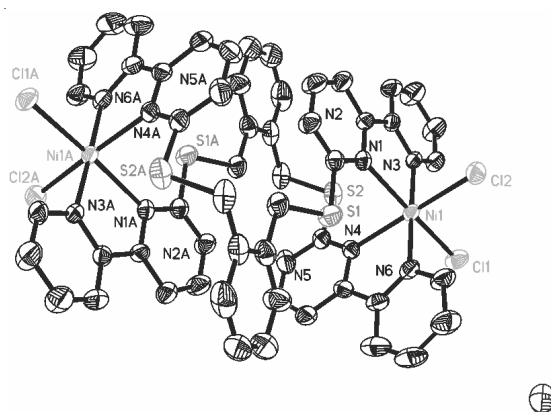


Fig. 1. Molecular structure of the present Ni(II) complex

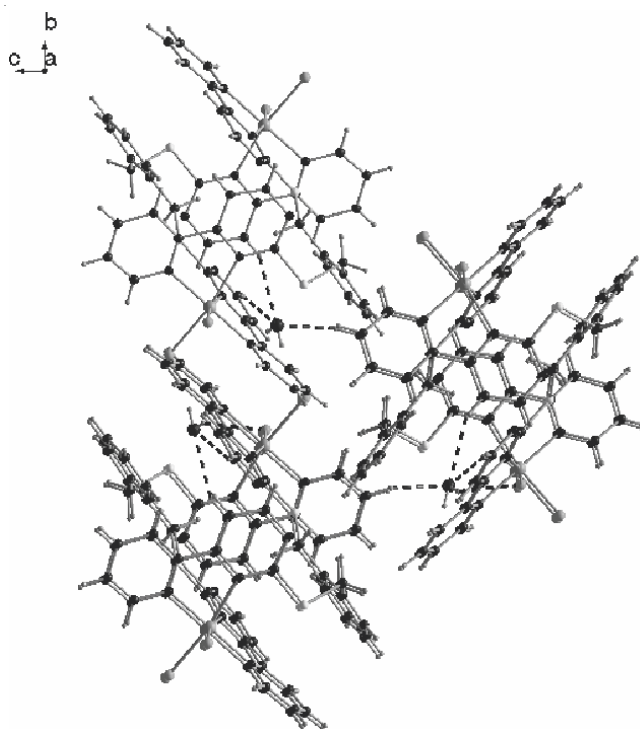


Fig. 2. Perspective view of the helices held by hydrogen bonds

TABLE-1  
SELECTED BOND DISTANCES ( $\text{\AA}$ ) AND ANGLES ( $^\circ$ )

Ni(1)-N(3)	2.068(4)	Ni(1)-N(6)	2.074(5)	Ni(1)-N(4)	2.197(5)
Ni(1)-N(1)	2.213(4)	Ni(1)-Cl(1)	2.3808(16)	Ni(1)-Cl(2)	2.418(17)
N(3)-Ni(1)-N(6)	178.70(18)	N(3)-Ni(1)-N(4)	103.12(17)	N(6)-Ni(1)-N(4)	77.2(2)
N(3)-Ni(1)-N(1)	76.86(17)	N(6)-Ni(1)-N(1)	104.42(17)	N(4)-Ni(1)-N(1)	87.62(16)
N(3)-Ni(1)-Cl(1)	93.74(13)	N(6)-Ni(1)-Cl(1)	85.00(13)	N(4)-Ni(1)-Cl(1)	89.77(12)
N(1)-Ni(1)-Cl(1)	169.38(12)	N(3)-Ni(1)-Cl(2)	85.57(13)	N(6)-Ni(1)-Cl(2)	94.24(16)
N(4)-Ni(1)-Cl(2)	168.94(13)	N(1)-Ni(1)-Cl(2)	87.73(12)	Cl(1)-Ni(1)-Cl(2)	96.55(7)

TABLE-2  
HYDROGEN BOND DISTANCES AND ANGLES

D-H...A	H...A	D...A	$\angle\text{DHA}$	A
O1-H1B...Cl1	2.64(12)	3.322(8)	137(10)	$x, 3/2-y, 1/2+z$
C2-H2...O1	2.5700	3.398(11)	148.00	$-1+x, 3/2-y, -1/2+z$
C8-H8...Cl1	2.8200	3.433(7)	124.00	$1-x, 2-y, -z$
C17-H17A...N5	2.4500	2.975(9)	114.00	$-x, 1-y, -z$
C9-H9...Cl1	2.6000	3.246(6)	127.00	—
C16-H16...S1	2.5500	2.974(7)	108.00	—
C25-H25...O1	2.6000	3.389(11)	143.00	—
C26-H26...Cl2	2.6200	3.278(7)	129.00	—

equatorial Ni-N [2.197(5) Å, 2.213(4) Å] and Ni-Cl [2.3808(16) Å, 2.4180(17) Å] bond lengths are longer than their counterparts in axial positions. In the motif, the distance of two metal ions is about 9.547 Å.

It should be noted that in crystal packing, the free water molecule works as adhesion agent, the O-H...Cl and C-H...O hydrogen bond are formed between adjacent motifs resulting in a 3D supramolecular framework.

### Conclusion

Different from the reported structures<sup>6a</sup>, the title compound is the dinuclear [2+2] macrocyclic motif with the distance of 9.547 Å between two metal ions and the free water molecules play an important role in crystal packing acting as the adhesion agent.

### Supplementary material

Crystallographic data for the structure reported in this communication have been deposited with the Cambridge Crystallographic Data Center as supplementary publication No. CCDC 935343.

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