



# Designed synthesis of copper(II) and nickel(II) complexes with a tridentate N<sub>2</sub>O donor Schiff base: Modulation of crystalline architectures through C–H···π and anion···π interactions



Mithun Das, Shouvik Chattopadhyay\*

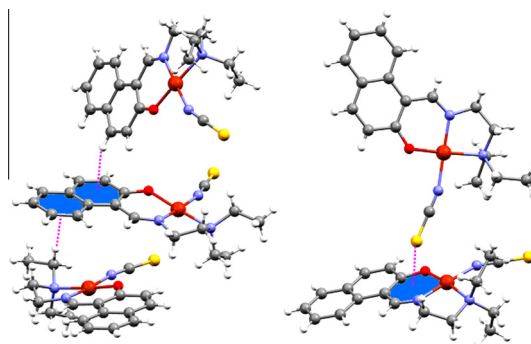
Department of Chemistry, Inorganic Section, Jadavpur University, Kolkata 700 032, India

## HIGHLIGHTS

- Synthesis and characterization of two copper(II) and two nickel(II) complexes with a tridentate N<sub>2</sub>O donor Schiff base.
- The molecular structures on the basis of X-ray crystallography.
- Modulation of crystalline architectures by C–H···π and anion···π interactions.

## GRAPHICAL ABSTRACT

Two copper(II) and two nickel(II) complexes have been prepared using a tridentate N<sub>2</sub>O donor Schiff base. All four complexes are mononuclear with the central metal ions assuming square planar geometries. The Schiff base is so designed that no H-bonding interactions are present in all the complexes. C–H···π and anion···π interactions modulate the crystalline architectures of the complexes.



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## ABSTRACT

Two copper(II) complexes, Cu(L<sup>1</sup>)Cl (**1**), Cu(L<sup>1</sup>)NCS (**3**) and two nickel(II) complexes Ni(L<sup>1</sup>)Cl (**2**), Ni(L<sup>1</sup>)NCS (**4**), where HL<sup>1</sup> = 1-[(2-diethylamino-ethylimino)-methyl]-naphthalen-2-ol act as tridentate N<sub>2</sub>O donor ligand, have been prepared and characterized by elemental analysis, IR and UV–Vis spectroscopy and single crystal X-ray diffraction studies. The geometry of the central metal ion in each of the four complexes is square planar. The existence of C–H···π interactions in **2** gives rise to one dimensional chain structure. Complex **3** shows two C–H···π interactions and one anion···π interactions which leads to a two dimensional layer structure. Each mononuclear unit of **4** has two C–H···π interactions along *b* axis to form a double strand one dimensional array of the molecules in crystal packing.

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## 1. Introduction

The chemistry of the metal Schiff base complexes has been paid significant attention for a long period of time and it is still a promising area of research [1,2]. The ease of synthesis, stability under a variety of oxidative and reductive conditions, and structural

\* Corresponding author. Tel.: +91 33 24572941.

E-mail address: [shouvik.chem@gmail.com](mailto:shouvik.chem@gmail.com) (S. Chattopadhyay).

versatility make Schiff bases very important chelating ligands in main group metal and transition metal coordination chemistry [3,4]. Schiff bases are frequently used in designing molecular ferromagnets, in biological modeling applications, in catalysis and in preparing liquid crystals [5–8]. The Salen type ligands, prepared from the condensation of a diamine with salicylaldehyde or its derivative, are probably receiving the most attention among all the Schiff bases as they can be used to prepare high-nuclearity complexes exploiting the ability of the phenoxo oxygen atoms to form  $\mu^2$ -bridges [9–12].  $N_2O$  donor tridentate Schiff bases can also easily be prepared on refluxing N-substituted diamine with salicylaldehyde or 2-hydroxy-1-naphthaldehyde [13,14]. The ligands can then be used to form complexes with several transition metals [15–17]. The molecular as well as crystalline architecture of the complexes can be manipulated by tactful exploitation of supra-molecular interactions [18].

Supramolecular systems based on coordination complexes have already received much interest because of their potential use as sensors, probes, photonic devices, catalysts etc. [19–24]. Synthesis and characterization of a large number of supramolecular metal complexes have been reported in the last several years [25–29]. To employ hydrogen bonds [30–34] is the most commonly used approach for engineering the crystal structures of such complexes. This has resulted in the construction of pre-designed 2D or 3D supramolecular architectures. The molecular as well as crystalline architecture of the complexes can also be managed by  $\pi \cdots \pi$ , C–H  $\cdots \pi$  and anion  $\cdots \pi$  interactions [35–38], which have attracted considerable interest due to their relative strength, directionality, and ability to act synergically, thus providing a directing force for the organization of individual molecules into well-defined supra-molecular assemblies. It seems interesting to execute a systematic investigation on a designed series of transition metal complexes with the aim to realize the way in which these interactions assist and direct the supra-molecular assembly of the molecular building blocks.

We have already controlled the molecular architectures of Schiff base complexes by H-bonding [13]. In the present work, we have used a tridentate  $N_2O$  donor Schiff base, 1-[(2-diethylamino-ethylimino)-methyl]-naphthalen-2-ol, to prepare two new copper(II) and two new nickel(II) complexes. The tridentate Schiff base is so designed that it cannot participate in H-bonding interaction. Thus the supra-molecular architecture is totally guided

by other interactions. Herein, we report the synthesis, spectroscopic characterization and X-ray crystal structures of four new complexes as well as their interesting crystalline architectures formed by supra-molecular interactions.

## 2. Experimental

All chemicals were of reagent grade and were used without further purification.

**Caution!!!** Although no problems were encountered in this work, perchlorate salts containing organic ligands are potentially explosive. Only a small amount of the material should be prepared and they should be handled with care.

### 2.1. Preparations

#### 2.1.1. Synthesis of the ligand [1-[(2-diethylamino-ethylimino)-methyl]-naphthalen-2-ol ( $HL^1$ )]

The tridentate Schiff base ligand  $HL^1$  was synthesized by refluxing N,N-diethyl-1,2-diaminoethane (1 mmol, 0.14 mL) with 2-hydroxynaphthyl-1-carboxaldehyde (1 mmol, 172 mg) in methanol solution (20 mL) for ca. 30 mins as per literature [39]. The ligands were not isolated. The methanolic solutions were used for the syntheses of the complexes.

#### 2.1.2. Synthesis of complex [Cu( $L^1$ )Cl] (**1**)

A methanol solution (20 mL) of copper(II) chloride dihydrate (1 mmol, 170 mg) was added with constant stirring to the methanol solution (1 mmol) of  $HL^1$  and stirred further for 1 h. Diffraction quality single crystals were obtained from the dark green mother liquor on slow evaporation. (Yield: 280 mg, 76%). Anal. Calc. for  $C_{17}H_{21}ClCuN_2O$  (368.36): C, 55.43; H, 5.75; N, 7.60. Found: C, 55.6; H, 5.6; N, 7.8%.  $\lambda_{max}$  (nm) [ $\epsilon_{max}$ (L mol<sup>-1</sup> cm<sup>-1</sup>)] (DMF) 644 (436), 395 (4631). Magnetic moment: 1.72 BM.

#### 2.1.3. Synthesis of complex [Ni( $L^1$ )Cl] (**2**)

It was prepared in a similar method to that of complex **1** except that nickel(II) chloride hexahydrate (1 mmol, 240 mg) was used instead of copper(II) chloride dihydrate. Diffraction quality red colored single crystals were obtained from the red mother liquor of the reaction on slow evaporation. (Yield: 290 mg, 79%). Anal. Calc.

**Table 1**  
Crystal data and refinement details of complexes **1**, **2**, **3** and **4**.

	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>
Formula	$C_{17}H_{21}ClCuN_2O$	$C_{17}H_{21}ClNiN_2O$	$C_{18}H_{21}CuN_3OS$	$C_{18}H_{21}Ni_3NiOS$
Formula weight	368.36	363.50	391.00	386.14
Temperature (K)	293	293	293	293
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1$	$P2_1/c$	$P2_1/c$
<i>a</i> (Å)	6.6692(2)	6.6862(2)	12.7729(5)	18.8382(5)
<i>b</i> (Å)	12.8246(5)	12.4152(5)	24.1748(8)	6.6690(2)
<i>c</i> (Å)	10.0572(4)	10.2808(4)	11.7506(4)	15.6663(4)
$\alpha$ (deg)	90	90	90	90
$\beta$ (deg)	103.968(2)	105.487(2)	98.668(2)	113.579(2)
$\gamma$ (deg)	90	90	90	90
<i>Z</i>	2	2	8	4
$d_{calc}$ (g cm <sup>-3</sup> )	1.465	1.468	1.448	1.422
$\mu$ (mm <sup>-1</sup> )	1.471	1.344	1.343	1.200
<i>F</i> (000)	382	380	1624	808
Total reflections	7743	13,898	20,060	13,067
Unique reflections	3519	4139	3883	3081
Observed data [ $I > 2\sigma(I)$ ]	3220	3896	3190	2610
No. of parameters	199	199	433	217
<i>R</i> (int)	0.027	0.028	0.045	0.023
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.0354, 0.0923	0.0293, 0.0645	0.0483, 0.0917	0.0592, 0.1570
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ $I > 2\sigma(I)$ ]	0.0309, 0.0850	0.0267, 0.0635	0.0362, 0.0859	0.0507, 0.1457
Largest diff. in peak and hole (e Å <sup>-3</sup> )	-0.45, 0.24	-0.30, 0.59	-0.26, 0.67	-0.87, 0.79

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