

# Syntheses, Characterization, and X-Ray Crystal Structure of a 1:1 Co-Crystal of bis{bis[[(2-(1*H*-imidazol-2-yl)methylidene)amino)phenolato- $\kappa^3N,N',O$ ]nickel(II)} and bis{bis[[(2-(1*H*-imidazol-2-yl)methylidene)amino)phenol- $\kappa^3N,N',O$ ]nickel(II)} tetra(chloride) pentahydrate

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## Abstract

The present investigation describes the synthesis and structural study of the ligand 2-((1*H*-imidazol-2-yl)methyleneamino)phenol, which was used to generate three dimensional supramolecular complex formulated as  $\{[\text{Ni}(\text{HL})_2]_2 \cdot [\text{Ni}(\text{H}_2\text{L})_2]_2 \cdot (\text{Cl})_4 \cdot (\text{H}_2\text{O})_5\}$ . The title compound crystallizes in the orthorhombic space group *Fddd* with the following unit cell parameters:  $a = 13.9269(4) \text{ \AA}$ ,  $b = 29.5295(16) \text{ \AA}$ ,  $c = 43.1739(15) \text{ \AA}$ ,  $V = 17755.5(12) \text{ \AA}^3$ ,  $Z = 8$ ,  $R_1 = 0.043$  and  $wR_2 = 0.129$ . For this compound, the structure reveals that one neutral mononuclear unit  $[\text{Ni}(\text{HL})_2]$  and one cationic mononuclear unit  $[\text{Ni}(\text{H}_2\text{L})_2]^{2+}$ . In the neutral unit, the organic molecule acts as a tridentate through one imino nitrogen atom, one nitrogen atom from the imidazole ring and one phenolate oxygen atom. In the cationic unit, it acts as tridentate through one imino nitrogen atom, one nitrogen atom from the imidazole ring and one oxygen atom of non-deprotonated phenol group. In both units the nickel(II) ion is hexacoordinated and the coordination environment can be described as distorted octahedral geometry. Numerous hydrogen bonds link the molecules into three dimensional network.

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## 1. Introduction

A large number of organic chelating ligands have been prepared and used to synthesize metal complexes of transition metals. These Schiff bases which constitute an important class of ligands are ubiquitous in coordination chemistry because of the many coordination possibilities they offer. Several studies have reported bi-, tri-, tetra-, penta- and hexadentate Schiff bases [1-5]. These Schiff bases usually have donor sites of the O, N, S type and form stable chelates with various configurations. The presence of nitrogen, oxygen and sulfur in these complexes strongly influences the physical, chemical, or biological properties of the transition metal complexes formed [6-9]. Due to the large number of carbonyl compounds and amines available which are the precursors of these Schiff bases, it is easy to prepare them. A wide variety of organic compounds with original structures and topologies are used as chelating ligands in the synthesis of a wide variety of metal complexes [10-12]. They are able to coordinate one or more metal atoms through the nitrogen of azomethine and other functional groups provided by the precursors of these Schiff bases [13,14]. The coordination geometries of such complexes depend on the nature of the ligand, the number and type of donor atoms, the configuration, and the chain length between the coordination sites [15-17]. The major challenge in coordination chemistry is the controlled preparation of new ligands to access metallic structures with specific properties [18-22]. Indeed, many and varied applications of transition metal complexes with Schiff bases have been developed in recent years. Complexes with catalytic [23-29], magnetic [30], optical [31], luminescent [32], antitumor [33], antibacterial [34], antifungal [35] properties are listed in the literature.

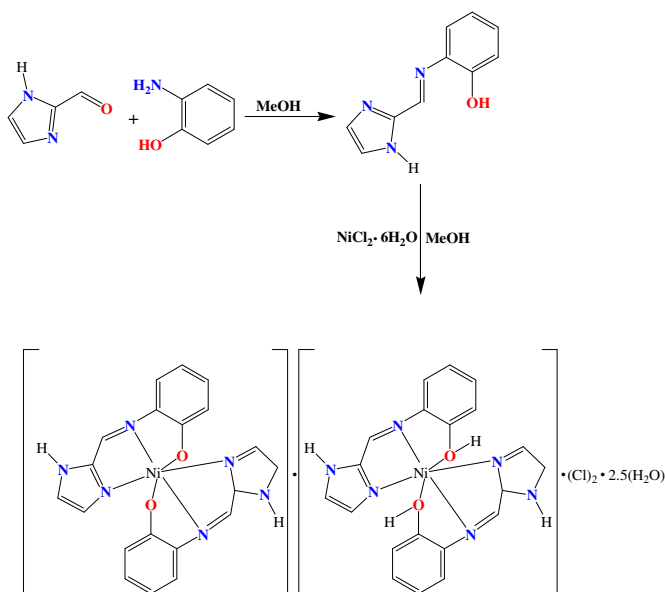
It is in this perspective that the work we report focused on the use of the H<sub>2</sub>L Schiff base (H<sub>2</sub>L = 2-((1*H*-imidazol-2-yl)methyleneamino)phenol) which possesses donors sites N, O capable to encapsulate metal ion. In this work, we report the synthesis and structure of a complex with one neutral unit {[Ni(HL)<sub>2</sub>] and one cationic unit [Ni(H<sub>2</sub>L)<sub>2</sub>]<sup>2+</sup>.

## 2. Materials and Methods

### 2.1. Starting materials and instrumentations

2-aminophenol, 1*H*-imidazole-4-carboxaldehyde, nickel chloride salt were commercial products (from Aldrich) and were used without further purifications. The solvents were reagent grade and were purified by usual methods. Elemental analyses were carried out using a VxRio EL Instrument. The IR spectra were recorded on a FTIR

Spectrum Two of Perkin Elmer (4000–400  $\text{cm}^{-1}$ ). The UV–Vis spectra were run on a Perkin-Elmer UV/Visible spectrophotometer Lambda 365(1000–200 nm). The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the Schiff bases were recorded in  $\text{DMSO-d}_6$  on a BRUKER 500 MHz spectrometer at room temperature using TMS as an internal reference. The molar conductance of  $10^{-3}$  M solutions of the metal complexes in DMF was measured at 25  $^\circ\text{C}$  using a WTW LF-330 conductivity meter with a WTW conductivity cell. Room temperature magnetic susceptibilities of the powdered samples were measured using a Johnson Matthey scientific magnetic susceptibility balance (Calibrant:  $\text{Hg}[\text{Co}(\text{SCN})_4]$ ).



**Scheme 1.** Synthetic procedure of the ligand and the complex.

## 2.2. Synthesis of the ligand 2-((1H-imidazol-2-yl)methyleneamino)phenol $\text{H}_2\text{L}$

In a 250 mL flask containing 30 mL of methanol, 1.028 g (9.42 mmol) of 2-aminophenol and 0.9052 g (9.42 mmol) of 1H-imidazole-4-carboxaldehyde were introduced. Two drops of glacial acetic acid were added to the mixture which was refluxed for two hours. After cooling in ice water bath, the yellow solution yield precipitate. The solid yellow compound recovered by filtration was washed with 2 x 10 mL of cold methanol and then with 20 mL of diethyl ether before being dried in a desiccator to yield 1.145 g of yellow compound (61.17 %). m.p. 216  $^\circ\text{C}$ . Anal. Calc for  $\text{C}_{10}\text{H}_9\text{N}_3\text{O}$ : C, 64.13, H, 4.81, N, 22.42. Found: C, 64.16, H, 4.85, N, 22.45. NMR  $^1\text{H}$  (300 MHz,  $\text{DMSO-d}_6$ ) (ppm): 6.35 – 8.32 (m, 4H, (Ph—H) + (2H Imidazole—H)), 8.69

(S, 1H, H—C=N), 9.59 (S, 1H, Imidazole—NH), 13.32 (S, 1H, PhO—H). NMR  $^{13}\text{C}$  (75 MHz, DMSO- $d_6$ ) (ppm): 156.24(C=N), 152.96 ( $\text{C}_{\text{Ph}}\text{—O}$ ), 146.95 ( $\text{C}_{\text{Ph}}\text{—N}$ ), 146.79 (C=N<sub>Imidazole</sub>), 141.30 ( $\text{C}_{\text{Ph}}$ ), 128.88 ( $\text{C}_{\text{Imidazole}}$ ), 126.62 ( $\text{C}_{\text{Ph}}$ ), 124.36( $\text{C}_{\text{Ph}}$ ), 122.1 (C—N<sub>Imidazole</sub>), 115.28 ( $\text{C}_{\text{Ph}}$ ). IR ( $\text{cm}^{-1}$ ): 3339, 3144, 1622, 1546, 1549, 1456, 1435, 1247, 1147, 830, 752.

### 2.3. Synthesis of the complex $\{[\text{Ni}(\text{HL})_2]_2.[\text{Ni}(\text{H}_2\text{L})_2]_2.(\text{Cl})_4.(\text{H}_2\text{O})_5\}$

To ethanolic solution (10 mL) of the ligand  $\text{H}_2\text{L}$  0.187 g (1 mmol) a solution of the  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  salt 0.2377 g (1 mmol) in methanol (10 mL) was added. The solution was stirred under reflux for one two hours. The reddish solution obtained was filtered and left to slow evaporation. After three days, brown crystals suitable for X-ray analysis were collected. Anal. Calc for  $\text{C}_{80}\text{H}_{78}\text{N}_{24}\text{O}_{13}\text{Cl}_4\text{Ni}_4$ : C, 49.05, H, 4.04, N, 17.11, Cl, 7.21. Found: C, 49.02, H, 4.01, N, 17.15, Cl, 7.23. IR ( $\text{cm}^{-1}$ ): 3400, 3147, 1605, 1551, 1431, 1303, 1108, 862, 834, 744.  $\mu_{\text{eff}}$  at room temperature is 3.51 BM.

### 2.4. Crystal structure determination

Crystals suitable for X-diffraction, of the reported compound, were grown by slow evaporation of MeOH solution of the complex. Details of the X-rays crystal structure solution and refinement are given in Table 1. Diffraction data were collected using a Rigaku XtaLAB PRO diffractometer with graphite monochromatized Mo  $\text{K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). All data were corrected for Lorentz and polarization effects. No absorption correction was applied. Using Olex2 [36] the structures were solved by intrinsic phasing methods with SHELXT [37] and SHELXL [38] was used for full matrix least squares refinement. The hydrogen atoms of water molecules and NH groups were located in the Fourier difference maps and refined. Others H atoms were geometrically optimized and refined as riding model by AFIX instructions. Molecular graphics were generated using ORTEP-3 [39].

**Table 1.** Crystal data and structure refinement for  $\{[\text{Ni}(\text{HL})_2]_2 \cdot [\text{Ni}(\text{H}_2\text{L})_2]_2 \cdot (\text{Cl})_4 \cdot (\text{H}_2\text{O})_5\}$ .

|  |   |
|--|---|
| Empirical formula                          | $\{[\text{Ni}(\text{HL})_2]_2 \cdot [\text{Ni}(\text{H}_2\text{L})_2]_2 \cdot (\text{Cl})_4 \cdot (\text{H}_2\text{O})_5\}$ |
| Formula weight                             | 1960.30   |
| T (K)                                      | 293   |
| $\lambda$ (Å)                              | 0.71073   |
| Crystal system                             | Orthorhombic  |
| Space group                                | <i>Fddd</i>   |
| Unit cell dimensions                       |   |
| a (Å)                                      | 13.9269 (4)   |
| b (Å)                                      | 25.5295 (16)  |
| c (Å)                                      | 43.1739 (15)  |
| $\alpha$ (°)                               | 90  |
| $\beta$ (°)                                | 90  |
| $\gamma$ (°)                               | 90  |
| V (Å <sup>3</sup> )                        | 17755.5 (2)   |
| Z  | 8   |
| $D_{\text{calc}}$ (Mg/m <sup>3</sup> )     | 1.467   |
| Absorption coefficient (mm <sup>-1</sup> ) | 1.03  |
| $F(000)$                                   | 8080  |
| Crystal size (mm)                          | 0.2 × 0.1 × 0.1   |
| $\theta$ range for data collection (°)     | 2.149–25.349  |
| Index ranges                               | $-16 \leq h \leq 16$ , $-35 \leq k \leq 30$ , $-52 \leq l \leq 48$  |
| Reflections collected                      | 27904   |

|  |                                 |
|--|---------------------------------|
| Independent reflections  | 4074                            |
| Completeness to theta (°)  | 99.9 %                          |
| Data/restrains/parameters  | 4074/1/299                      |
| Goodness-of-fit on $F^2$   | 1.11                            |
| Final $R$ indices [ $I > 2\sigma(I)$ ]                             | $R_1 = 0.043$ , $wR_2 = 0.1243$ |
| $R$ indices (all)  | $R_1 = 0.049$ , $wR_2 = 0.1286$ |
| Observed [ $I > 2\sigma(I)$ ] reflections                          | 3482                            |
| $\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ ( $e \text{ \AA}^{-3}$ ) | 0.47, -0.42                     |

### 3. Results and Discussion

#### 3.1. General study

The synthesis of the acyclic Schiff base  $H_2L$  is achieved in a one-step procedure using the direct condensation of the 2-aminophenol with 1*H*-imidazole-4-carboxaldehyde in 1/1 ratio. The coordination abilities of the  $H_2L$  with nickel (II) chloride salt was investigated in 1:1 ligand/metal ratio in methanol solutions (Scheme 1). The Ni(II) complex which was prepared under reflux gave precipitate on cooling its methanol solution. The solid is soluble in common organic solvents. The complex is characterized by elemental analysis, infrared and UV-visible spectroscopy and molar conductivity. The infrared spectrum of the ligand shows characteristic bands pointed at 3369, 3144, 1622 and 1686  $\text{cm}^{-1}$ , which are attributed, respectively to  $\nu_{\text{O-H}}$ ,  $\nu_{\text{N-H}}$ ,  $\nu_{\text{C=N}}$  and  $\nu_{\text{imidazole}}$ . Upon reaction of the ligand and nickel(II) chloride the spectrum of the resulting compound, shows a shift of *ca.* 15  $\text{cm}^{-1}$  frequencies of the imine and imidazole bands indicating a coordination of the ligand to the Ni(II) ion. The band at 1605  $\text{cm}^{-1}$  and 1551  $\text{cm}^{-1}$  attributed respectively to  $\nu_{\text{C=N}}$  and  $\nu_{\text{imidazole}}$  vibrations confirms the coordination of the ligand through the nitrogen azomethine atom and the azomethine nitrogen atom of the imidazole ring. The band at 3400  $\text{cm}^{-1}$  and 3147  $\text{cm}^{-1}$  due to  $\nu_{\text{O-H}}$  and  $\nu_{\text{N-H}}$  are indicative of the presence of non-deprotonated ligand molecules in the complex. Among the vibrations of the ligand, we are going to be interested in those of the functions likely to take part in the complexation of the metal ions. The broad band which appears at *ca.* 3300  $\text{cm}^{-1}$  on the spectrum of the complex is due to the presence of free water molecules.

Molar conductivity is measured for freshly prepared complexes  $10^{-3}$  M solution in DMF and after standing for two weeks. For complex the Ni(II) complex the conductance values increase very slightly with time. The conductance value of  $101.1 \text{ cm}^2\Omega^{-1} \text{ mol}^{-1}$  lies in the range observed for 2:1 electrolytes [40]. On standing for two weeks the conductance varies slightly indicating a stable complex in DMF solution.

The electronic spectrum of the complex shows a strong band in the range 250-300 nm at  $\lambda_{\text{max}} = 280 \text{ nm}$  attributed to an intraligand charge transfer (ILCT). The band at 445 nm is assigned to charge transfer, ligand metal charge transfer (LMCT). The band pointed at 508 nm attributed to  $d \rightarrow d$  transition is indicative of an octahedral geometry [41]. The room temperature magnetic moment value of  $3.51 \mu_{\text{B}}$  per ion in the nickel(II) complex is higher than the expected spin-only value of  $2.83 \mu_{\text{B}}$  expected for magnetically isolated Ni(II) system [41]. This observation is typical for a paramagnetic octahedral Ni(II) complex with  $d^8$  configuration. This value is consistent with those reported for a mononuclear nickel (II) MB complex [42,43]. The octahedral geometry of the complex is deduced from the UV-visible spectrum [41]. The elemental analyses agree the formulation proposed for the compound. Crystals of  $\{[\text{Ni}(\text{HL})_2]_2 \cdot [\text{Ni}(\text{H}_2\text{L})_2]_2 \cdot (\text{Cl})_4 \cdot (\text{H}_2\text{O})_5\}$  suitable for X-ray diffraction were obtained by slow evaporation of corresponding methanol solutions. The details of the crystals structures determination for all compounds are given in Table 1.

### 3.2. Structure description of the complex $\{[\text{Ni}(\text{HL})_2]_2 \cdot [\text{Ni}(\text{H}_2\text{L})_2]_2 \cdot (\text{Cl})_4 \cdot (\text{H}_2\text{O})_5\}$

Suitable single crystals for X-ray diffraction of The nickel(II) complex were obtained by slow solvent evaporation at room temperature. Crystal data, collection and refinement parameters are listed in Table 1. Selected bond lengths and angles are summarized in Table 2. Hydrogen bond data for the complex are gathered in Table 3. The Ni(II) complex crystallizes in the orthorhombic system with the space group  $Fddd$ . An ORTEP view of the structure is shown in Figure 1.

The crystal structure of the complex consists of a neutral mononuclear unit  $[\text{Ni}(\text{HL})_2]$ , a cationic mononuclear unit  $[\text{Ni}(\text{H}_2\text{L})_2]^{2+}$ , two water molecules and a half free water molecule that lies on a two-fold rotation axis and two chloride anions which act as counter anions. In the neutral  $[\text{Ni}(\text{HL})_2]$  unit, two tridentate Schiff base ligands in which the phenolic groups are deprotonated are bonded to the nickel(II) ion in a tridentate fashion resulting in a *mer* configuration. The Ni(II) cation is six-coordinated and is surrounded by two azomethine nitrogen atoms (N(1) and N(1i), two nitrogen atoms of

from imidazole rings (N(2) and N(2i)) and two phenolate oxygen atoms (O(1) and O(1i)) from two ligand molecules bearing a NiN<sub>4</sub>O<sub>2</sub> coordination sphere. The *transoid* angles around Ni(II) are in the range 158.97(8)-178.61(12)°, while the *cisoid* angles are in the range 79.26(8)-101.23(9)°. The geometry around the Ni(II) cation is best described as distorted octahedral. The largest deviations from octahedral geometry arise from the geometric constraints of this chelating ligand as shown by the *transoid* and *cisoid* angles values. The Ni—N bond distances are pretty close in the range 2.030(2)- 2.106(2) Å. The Ni—O bond distance value is 2.0962(18) Å (Table 2). These bond values are comparable to those reported for a similar complex [Ni(HL)(L)] where HL is *N*-2-pyridylmethylidene-2-hydroxyphenylamine [44]

**Table 2.** Selected bond distances (Å) and angles (°) for the nickel (II) complex.

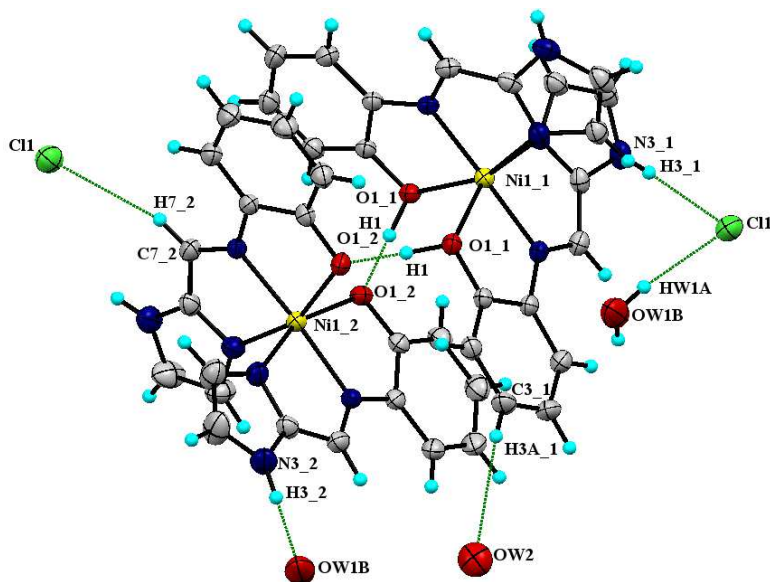
| Bond                    | Distance    | Bond                                       | Angle       |
|-------------------------|-------------|--|-------------|
| Ni1_1—N2_1 <sup>i</sup> | 2.106 (2)   | N1_1 <sup>i</sup> —Ni1_1—N1_1              | 178.61 (12) |
| Ni1_1—N2_1              | 2.106 (2)   | O1_1 <sup>i</sup> —Ni1_1—N2_1 <sup>i</sup> | 158.97 (8)  |
| Ni1_1—N1_1              | 2.030 (2)   | O1_1—Ni1_1—N2_1                            | 158.97 (8)  |
| Ni1_1—N1_1 <sup>i</sup> | 2.030 (2)   | N2_2i—Ni1_2—O1_2i                          | 158.20 (8)  |
| Ni1_1—O1_1              | 2.0962 (18) | N2_2—Ni1_2—O1_2                            | 158.20 (8)  |
| Ni1_1—O1_1 <sup>i</sup> | 2.0962 (18) | N1_2—Ni1_2—N1_2i                           | 175.91 (11) |
| Ni1_2—O1_2              | 2.1055 (19) | O1_1i—Ni1_1—N2_1                           | 92.37 (8)   |
| Ni1_2—O1_2 <sup>i</sup> | 2.1055 (19) | O1_1—Ni1_1—N2_1                            | 158.97 (8)  |
| Ni1_2—N2_2 <sup>i</sup> | 2.077 (2)   | O1_1—Ni1_1—N2_1i                           | 92.37 (8)   |
| Ni1_2—N2_2              | 2.077 (2)   | O1_1i—Ni1_1—O1_1                           | 92.61 (10)  |
| Ni1_2—N1_2              | 2.032 (2)   | N1_1i—Ni1_1—O1_1                           | 99.77 (7)   |
| Ni1_2—N1_2 <sup>i</sup> | 2.032 (2)   | N1_1—Ni1_1—O1_1                            | 79.25 (8)   |

Symmetry code: (i)  $-x+1/4, -y+5/4, z$ .



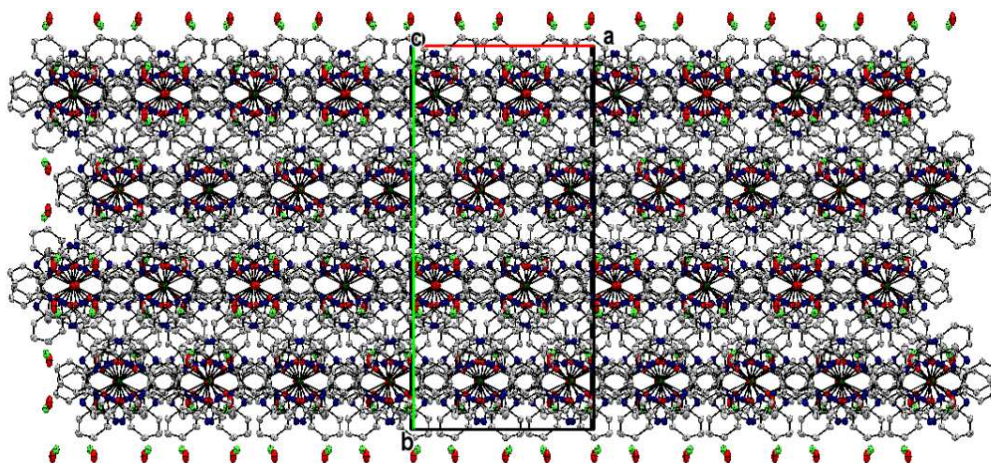
In each ligand molecule, the phenyl ring of the Schiff base lies in a plane including its phenolate oxygen (rms 0.0096 Å) and the imidazole ring lies in another plane (rms 0.0032 Å). The four atoms set comprising the azomethine C=C=N—C unit which bridges the phenyl ring and the imidazole ring, lies in a third plane with rms value of 0.0220 Å. The dihedral angles between these planes fall in the range 4–11°, so the entire ligand molecule is quite planar. The two means plane defined by the Ni(II) atom and the coordinated atoms of each ligand molecule are quite perpendicular with a dihedral angle of 88.78°.

In the cationic  $[\text{Ni}(\text{H}_2\text{L})_2]^{2+}$  unit, two non-deprotonated Schiff base ligands are bonded to the nickel(II) ion in a tridentate fashion resulting in a *mer* configuration. Each ligand acts in tridentate fashion through one azomethine, one nitrogen atom from imidazole ring and one phenolate oxygen atom. The nickel (II) atom is hexacoordinated, and the geometry around the manganese (II) center is best described as an octahedral polyhedron. The basal plane is occupied by O1\_2, N2\_2, N2\_2i and O1\_2i atoms, the apical positions being occupied by the two azomethine nitrogen atoms N1\_2 and N1\_2i. The sum of the angles subtended by the atoms in the basal plane is 368.09°, while the angle defined by the atoms in apical position (N1\_2—Ni1\_2—N2\_1<sup>i</sup> = 175.91(11)°) is different of the ideal value of 180°. These observations are indicative of a severely distorted octahedral polyhedron around the Ni(II) ion. Each ligand molecule forms together with nickel atom two five-membered metallocycles NCCNNi and NCCONi with bite angles values of 79.97(9)° [N—Ni—N] and 78.58(8)° [N—Ni—O], respectively]. The two means plane defined by the Ni(II) atom and the coordinated atoms of each ligand molecule are quite perpendicular with a dihedral angle of 89.48°. The Ni—N distances are in the range 2.032(2)—2.077(2) Å and are comparable to the values observed in the neutral unit. The Ni—O distance value is 2.1055(19)° and is close to values observed for other six-coordinated nickel (II) complexes [44,45].



**Figure 1.** Crystal structure of the co-crystal complex. Displacement ellipsoids are drawn at the 30% probability level.

The neutral unit and the cationic unit are connected by hydrogen bonds involving phenolic hydrogen atom and phenolate oxygen atom [O1<sub>1</sub>—H<sub>1</sub>···O1<sub>2</sub>], forming a dinuclear unit. Intramolecular hydrogen bonds are observed between a free water molecule oxygen atom which acts as donor and a free chloride cation which is the acceptor: OW2—HW2···Cl1. Thus, each dinuclear unit is connected with another dinuclear unit by hydrogen bonding interactions (N—H···Cl and N—H···O), leading to the formation of a supramolecular chain structure along *c* axis. In the N—H···Cl hydrogen bond, the free chloride ion of the second molecule complex is the acceptor while the donor is the secondary pyrazolyl nitrogen of the first molecule complex: N3<sub>1</sub>—H3<sub>1</sub>···Cl1<sup>ii</sup> (ii = -*x*+3/4, *y*, -*z*+3/4). The uncoordinated water molecules act via hydrogen bonds N—H···O as bridge between the chains leading to the formation of a 3D supramolecular structure. The oxygen atom of a free water molecule in one chain is the acceptor while the donor is the secondary pyrazolyl nitrogen: N3<sub>1</sub>—H3<sub>2</sub>···OW1B<sup>iii</sup> (*x*+1/4, *y*+1/4, -*z*+1, (iv) -*x*+1, -*y*+1, -*z*+1) (Figure 2, Table 3). The structure is consolidated by weak C—H···Cl (Table 3).



**Figure 2.** The packing of the compound in the crystal structure.

**Table 3.** Hydrogen-bond geometry (Å, °).

| <i>D</i> —H··· <i>A</i>         | <i>D</i> —H | H··· <i>A</i> | <i>D</i> ··· <i>A</i> | <i>D</i> —H··· <i>A</i> |
|---------------------------------|-------------|---------------|-----------------------|-------------------------|
| OW1B—HW1A···Cl1 <sup>i</sup>    | 0.85        | 2.32          | 3.098(3)              | 152.7                   |
| OW2—HW2···Cl1                   | 0.872(10)   | 2.41(6)       | 3.186(7)              | 148(10)                 |
| O1_1—H1···O1_2 <sup>ii</sup>    | 1.00(5)     | 1.43(5)       | 2.432(2)              | 174(4)                  |
| N3_1—H3_1···Cl1 <sup>i</sup>    | 0.79(4)     | 2.30(4)       | 3.092(3)              | 177(4)                  |
| N3_2—H3_2···OW1B <sup>iii</sup> | 0.86        | 1.83          | 2.681(4)              | 172.1                   |
| C5_2—H5_2···Cl1 <sup>iv</sup>   | 0.93        | 2.98          | 3.883(3)              | 164.8                   |
| C7_2—H7_2···Cl1 <sup>iv</sup>   | 0.93        | 2.75          | 3.638(3)              | 160.2                   |

Symmetry codes: (i)  $-x+3/4, y, -z+3/4$ ; (ii)  $-x+1/4, -y+5/4, z$ ; (iii)  $x+1/4, y+1/4, -z+1$ ; (iv)  $-x+1, -y+1, -z+1$ .

#### 4. Conclusion

The reported work is concerned with the synthesis and the structural study of a dinuclear-trinuclear co-crystal derived from the organic molecular ligand, 2-((1H-imidazol-2-yl)methyleneamino)phenol. In the neutral as well as in the cationic unit, the nickel ions are hexacoordinated. In both units the environments around the nickel ions are described as an octahedral polyhedron. In the neutral unit the ligand is monodeprotonated yielding a phenolate oxygen atom, while in the cationic unit the ligand remains undeprotonated. The mononuclear units interact each other through  $O_{(\text{Phenol})}—H \cdots O_{(\text{Phenolate})}$  hydrogen bonds yielding a dinuclear unit. The dinuclear unit are connected through intermolecular hydrogen bonds ( $N—H \cdots Cl$ ,  $N—H \cdots O$  and  $C—H \cdots Cl$ ) resulting in supramolecular network.

#### 5. Supporting Information

CCDC-2190508 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)-1223-336-033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk) (or <http://www.ccdc.cam.ac.uk>).

#### Conflicts of Interest

The authors declare that they have no conflict of interest.

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