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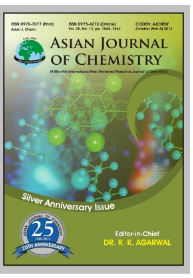

# A Supramolecular Trinuclear Nickel(II) Complex with Asymmetric Salamo-type Ligand: Synthesis and Crystal Structure

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A supramolecular trinuclear Ni(II) complex, namely $\{[NiL(EtOH)(\mu\text{-}OAc)]_2Ni\}\cdot EtOH$, has been synthesized through the complexation of nickel(II) acetate tetrahydrate with 5-methoxy-4'-bromo-2,2'-[ethylenedioxy*bis*(nitrilomethylidyne)]diphenol ($H_2L$). The Ni(II) complex comprises three Ni(II) atoms, two deprotonated $L^{2-}$ units, two acetate aions, two coordinated and one non-coordinated ethanol molecules. In the crystal structure, the terminal Ni(II) (Ni2 or Ni2$^{\#1}$) atom is located in the *cis*-$N_2O_2$ coordination cavity of the $L^{2-}$ units and coordinated to an oxygen (O7) atom from the μ-acetato anion and an oxygen (O8) atom from the coordinated ethanol molecule in the axial positions. Meanwhile, the central Ni(II) (Ni1) atom is completed by quadruple μ-phenoxo oxygen (O3, O4, O3$^{\#1}$ and O4$^{\#1}$) atoms from two $L^{2-}$ units and double μ-acetato oxygen (O6 and O6$^{\#1}$) atoms. All the Ni(II) atoms are hexa-coordinated, showing slightly distorted octahedral coordination arrangements. The Ni(II) complex is linked to form an infinite 2D layer supramolecular structure through intermolecular O-H···O, C-H···O and C-H···π hydrogen bond interactions.

**Key Words: Asymmetric Salamo-type ligand, Ni(II) complex, Synthesis, Crystal structure.**

## INTRODUCTION

The syntheses and researches of metal-organic complexes with supramolecular architectures are now ubiquitous[1-3]. The development of novel metal-organic complexes can provide new topologies for functional materials, in which pore size, coordination forms and functionality are all important variables[4-6]. These complexes can be used to obtain non-linear optical materials[7-9], models of biological systems[10,11], interesting magnetic properties[12-14] and building blocks for cyclic supramolecular structures[15]. Although some advances has been made in the studies of Salen-Ni(II) complexes[16-18], it still seems there could be new and specific applications for such a unique group of compounds. To change the structures or improve the functions of the resulted complexes, chemical modifications of the elemental Salen-type ligand are effective and inevitable. In particular, replacement of some atoms of the ligand with other elements often changes its properties drastically[19,20]. Herein, in continuation to our previous studies[21], we report the synthesis and crystal structure of a trinuclear Ni(II) complex with the new asymmetric ligand 5-methoxy-4'-bromo-2,2'-[ethylenedioxy*bis*(nitrilomethylidyne)]diphenol ($H_2L$).

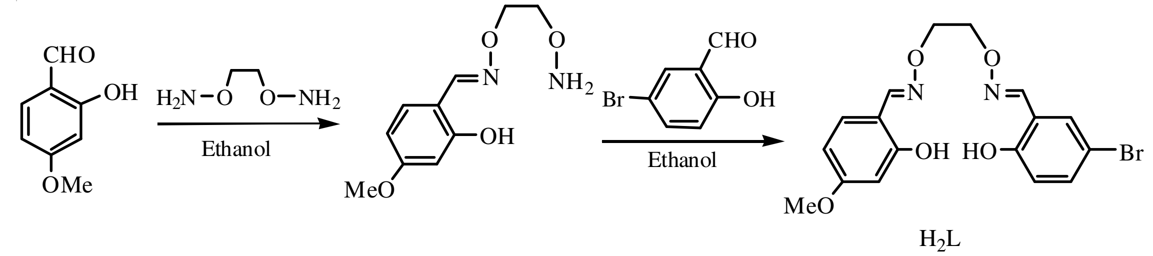
## EXPERIMENTAL

2-Hydroxy-4-methoxybenzaldehyde (≥ 99 %) and 2-hydroxy-5-bromobenzaldehyde (≥ 99 %) were purchased from Alfa Aesar and used without further purification. The other reagents and solvents were analytical grade from Tianjin Chemical Reagent Factory. Elemental analysis for Ni was detected by an IRIS ER/S·WP-1 ICP atomic emission spectrometer. C, H and N analyses were obtained using a GmbH VarioEL V3.00 automatic elemental analysis instrument. X-ray single crystal structure determination was carried out on a Bruker Smart 1000 CCD diffractometer. Melting points were measured by the use of a microscopic melting point apparatus made in Beijing Taike Instrument Limited Company and the thermometer was uncorrected.

**Synthesis of ligand $H_2L$:** The major reaction steps involved in the synthesis of $H_2L$ are given in **Scheme-I**.

$H_2L$ was synthesized according to an analogous method reported earlier[21d]. Yield 73.8 %. m.p. 385-387 K. Anal. calcd. for $C_{17}H_{17}N_2O_5Br$ (%): C, 49.89; H, 4.19; N, 6.85. Found: C, 49.75; H, 4.32; N, 6.99.

**Synthesis of Ni(II) complex:** A solution of $Ni(OAc)_2\cdot 4H_2O$ (3.73 mg, 0.015 mmol) in ethanol (2 mL) was added dropwise to a solution of $H_2L$ (4.09 mg, 0.01 mmol) in acetonitrile (2 mL) at room temperature. The colour of the mixing solution turned to green immediately, then stirred for 1 h at room temperature. The mixture was filtered off and the filtrate was allowed to stand at room temperature for about one week, the solvent was partially evaporated and obtained green block-like single



**Scheme-I:** Synthetic route to the asymmetrical salamo-type ligand $H_2L$

crystals suitable for X-ray crystallographic analysis. Anal. calcd. for $C_{46}H_{60}N_4O_{18}Br_2Ni_3$ (%): C, 42.73; H, 4.68; N, 4.33; Ni, 13.62. Found: C, 42.88; H, 4.85; N, 4.12; Ni, 13.58.

**X-Ray structure determination:** The crystal data and structure refinement for the Ni(II) complex are given in Table-1. The single crystal of the Ni(II) complex with the approximate dimensions of 0.14 × 0.09 × 0.08 mm was placed on a Bruker Smart 1000 CCD area detector. The reflections were collected using a graphite monochromated $MoK_{\alpha}$ radition ($\lambda$ = 0.71073 Å) at 298(2) K. The structure was solved by using the program SHELXL-97 and Fourier difference techniques and refined by the full-matrix least-squares method on $F^2$. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were added theoretically.

TABLE-1
CRYSTAL DATA AND STRUCTURE REFINEMENT
FOR THE Ni(II) COMPLEX

| | |
|---|---|
| Empirical formula | $C_{46}H_{60}N_4O_{18}Br_2Ni_3$ |
| Formula weight | 1292.93 |
| Temperature (K) | 298(2) |
| Wavelength (Å) | 0.71073 |
| Crystal system | Triclinic |
| Space group | P-1 |
| Cell dimensions, (Å, deg) | a = 9.2829(8), b = 11.0400(9), c = 14.220(1),<br>$\alpha$ = 69.940(1), $\beta$ = 84.361(2),<br>$\gamma$ = 77.960(1) |
| Volume (Å$^3$) | 1338.2(2) |
| Z | 1 |
| Density (calculated) (mg/m$^3$) | 1.604 |
| Absorption coefficient (mm$^{-1}$) | 2.611 |
| $F_{(000)}$ | 662 |
| Index ranges | $-11 \leq h \leq 10$, $-13 \leq k \leq 12$, $-14 \leq 1 \leq 16$ |
| Reflections collected | 6329/4537 [R(int) = 0.0520] |
| Independent reflections | 1313 |
| Data/restraints/parameters | 4537/0/364 |
| Goodness of fit indicator | 1.056 |
| R [I > 2σ(I)] | $R_1$ = 0.0525, $wR_2$ = 0.1191 |
| Largest diff. peak and hole (e Å$^{-3}$) | 1.201 and -0.947 |

## RESULTS AND DISCUSSION

**Crystal structure of the Ni(II) complex:** ORTEP representation of the Ni(II) complex is shown in Fig. 1. Selected bond lengths and angles are listed in Table-2.

X-ray crystallographic analysis reveals that the Ni(II) complex is a neutral homotrinuclear entity with crystallographic inversion symmetry and crystallizes in the triclinic system, space group P-1 with a linear trinuclear array of three Ni(II) ions coupled by both doubly μ-phenoxo oxygen atoms of $L^{2-}$ units and simultaneously two acetate anions in the syn-syn bridging mode, as well as one non-coordinated ethanol molecule. As shown in Fig. 1, all the hexa-coordinated Ni(II) ions of the Ni(II) complex have a slightly distorted octahedral coordinated polyhedron. The two terminal Ni(II) (Ni2 and Ni2$^{\#1}$) atoms are both located in the $N_2O_2$ coordination cavity of the $L^{2-}$ units and coordinated to oxygen (O7) atom from the μ-acetato anion and oxygen (O8) atom from the coordinated ethanol molecule in the axial positions. Meanwhile, the coordination sphere of the central Ni(II) atom (Ni1) is completed by quadruple μ-phenoxo oxygen (O3, O4, O3$^{\#1}$ and O4$^{\#1}$) atoms from two $L^{2-}$ units and double μ-acetato oxygen (O6 and O6$^{\#1}$) atoms, which adopt a familiar μ-O-C-O fashion. All the six oxygen atoms coordinated to Ni1 atom constitute an octahedral arrangement: one acetate anion serves as bridging group for Ni2 and Ni1 and the other coordinates to Ni2$^{\#1}$ and Ni1, in both cases via Ni-O-C-O-Ni bridges. In addition, the coordination equatorial plane of O3-O4-N2-N1 parallel to another equatorial plane of O3$^{\#1}$-O4$^{\#1}$-N2$^{\#1}$-N1$^{\#1}$.

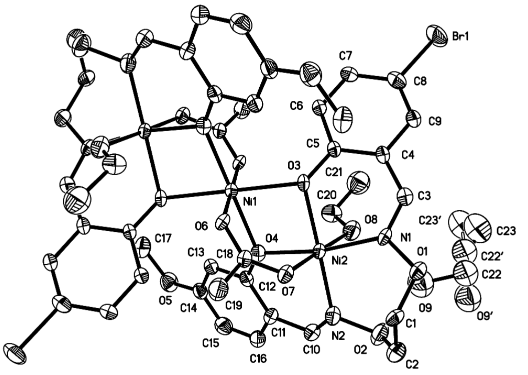


Fig. 1. ORTEP-style drawing of the Ni(II) complex

There is an inversion center through central Ni1 ion and the distance of Ni1-O3 [2.131(7) Å] is shorter than that of Ni1-O6 (2.047(8) Å), indicating a weaker steric effect. Furthermore, the terminal Ni(II) (Ni2 or Ni2$^{\#1}$) atom is 0.114(3) Å out of the $N_2O_2$ equatorial plane, but the central Ni(II) (Ni1) atom lies in the corresponding $O_2O_2$ equatorial plane. The Ni2-N1 bond [2.084(10) Å] is slightly longer than Ni2-N2 bond [2.049(11) Å], which is attributed to the ethanol molecule coordinating to the terminal Ni(II) (Ni2 and Ni2$^{\#1}$) ions, resulting in the larger steric hindrance. The Ni1-Ni2 distance [3.093(3) Å] is significantly longer than all the Ni-O and Ni-N bonds (2.016-2.220 Å), indicating weak inter-metal interaction, similar to that previously reported[22] for a Salen-type cluster, {[Ni(Salpr)$NC_5H_5$]$_2$(μOAc)$_2$Ni}.

TABLE-2
SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR THE COMPLEX

| Bond | Lengths | Bond | Lengths | Bond | Lengths |
|---|---|---|---|---|---|
| Ni1-O6$^{\#1}$ | 2.047(8) | Ni1-O4 | 2.139(8) | Ni2-N2 | 2.049(11) |
| Ni1-O6 | 2.047(8) | Ni1-O4$^{\#1}$ | 2.139(8) | Ni2-O7 | 2.076(8) |
| Ni1-O3$^{\#1}$ | 2.131(7) | Ni2-O4 | 2.016(8) | Ni2-N1 | 2.084(10) |
| Ni1-O3 | 2.131(7) | Ni2-O3 | 2.035(7) | Ni2-O8 | 2.220(10) |
| **Bond** | **Angles** | **Bond** | **Angles** | **Bond** | **Angles** |
| O6$^{\#1}$-Ni1-O6 | 180.0(4) | O4-Ni2-O3 | 83.8(3) | N1-Ni2-O8 | 85.4(4) |
| O6$^{\#1}$-Ni1-O3$^{\#1}$ | 88.2(3) | O4-Ni2-N2 | 90.1(4) | C3-N1-Ni2 | 122.3(8) |
| O6-Ni1-O3$^{\#1}$ | 91.8(3) | O3-Ni2-N2 | 168.8(4) | O1-N1-Ni2 | 126.3(7) |
| O6$^{\#1}$-Ni1-O3 | 91.8(3) | O4-Ni2-O7 | 87.9(3) | C10-N2-Ni2 | 123.6(8) |
| O6-Ni1-O3 | 88.2(3) | O3-Ni2-O7 | 94.3(3) | O2-N2-Ni2 | 120.4(8) |
| O3$^{\#1}$-Ni1-O3 | 180.0(1) | N2-Ni2-O7 | 94.8(4) | C5-O3-Ni2 | 122.4(6) |
| O6$^{\#1}$-Ni1-O4 | 90.9(3) | O4-Ni2-N1 | 170.3(3) | C5-O3-Ni1 | 133.1(7) |
| O6-Ni1-O4 | 89.1(3) | O3-Ni2-N1 | 86.8(3) | Ni2-O3-Ni1 | 95.9(3) |
| O3$^{\#1}$-Ni1-O4 | 101.4(3) | N2-Ni2-N1 | 98.8(4) | C12-O4-Ni2 | 128.2(7) |
| O3-Ni1-O4 | 78.6(3) | O7-Ni2-N1 | 95.2(4) | C12-O4-Ni1 | 134.2(7) |
| O6$^{\#1}$-Ni1-O4$^{\#1}$ | 89.1(3) | O4-Ni2-O8 | 91.6(3) | Ni2-O4-Ni1 | 96.2(3) |
| O6-Ni1-O4$^{\#1}$ | 90.9(3) | O3-Ni2-O8 | 86.9(3) | C18-O6-Ni1 | 129.5(8) |
| O3$^{\#1}$-Ni1-O4$^{\#1}$ | 78.6(3) | N2-Ni2-O8 | 83.9(4) | C18-O7-Ni2 | 126.2(8) |
| O3-Ni1-O4$^{\#1}$ | 101.4(3) | O7-Ni2-O8 | 178.6(3) | C20-O8-Ni2 | 128.5(8) |
| O4-Ni1-O4$^{\#1}$ | 180.0(1) | – | – | – | – |

Symmetry transformations used to generate equivalent atoms:$^{\#1}$ -x+1,-y+1,-z+1

TABLE-3
THE DATA FOR HYDROGEN-BONDING INTERACTIONS (Å, °)

| D-H···A | d(D-H) | d(H···A) | d(D···A) | ∠D-H···A | Symmetry code |
|---|---|---|---|---|---|
| O8-H8···O9 | 0.82 | 2.00 | 2.82(2) | 176 | x, y, z |
| O9-H9···O2 | 0.82 | 2.07 | 2.89(2) | 172 | x, y, z |
| C15-H15···O9 | 0.93 | 2.59 | 3.47(3) | 157 | -x,2-y,1-z |
| C1-H1A···O7 | 0.97 | 2.30 | 3.21(2) | 157 | x, y, z |
| C13-H13···O3 | 0.93 | 2.59 | 3.34(2) | 137 | 1-x,1-y,1-z |
| C20-H20A···O6 | 0.97 | 2.46 | 3.42(2) | 173 | 1-x,1-y,1-z |
| C2-H2B····$\pi_{centroid(C11–C16)}$ | 0.97 | 2.72 | 3.64(2) | 159 | 1-x,2-y,1-z |

**Intermolecular interactions of the Ni(II) complex:** The Ni(II) complex contains one non-coordinating ethanol molecule and complicated hydrogen bonding interactions, such as intramolecular, intermolecular and C-H···p hydrogen bonds and hydrogen bond data are summarized in Table-3.

The Ni(II) complex stabilized by three pairs of weak intramolecular C20-H20A···O6, C13-H13···O3 and C1-H1A···O7 hydrogen-bonding interactions (Fig. 2). Furthermore, each oxygen (O9) atom of the non-coordinating ethanol molecule is hydrogen-bonded to the -O8H8 group of the coordinating ethanol molecule and the -C15H15 group of the benzene ring, respectively, while its -O9H9 group is hydrogen- bonded

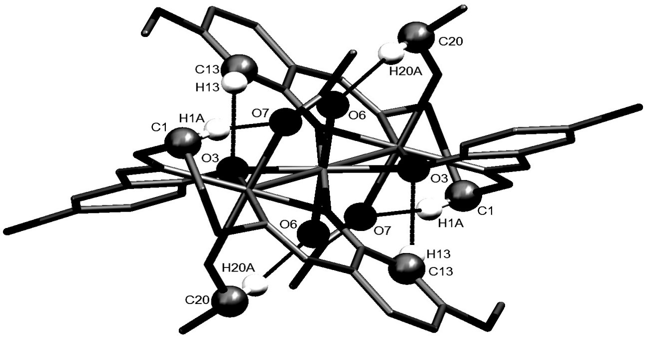


Fig. 2. View of the intramolecular hydrogen-bonding interactions of the complex

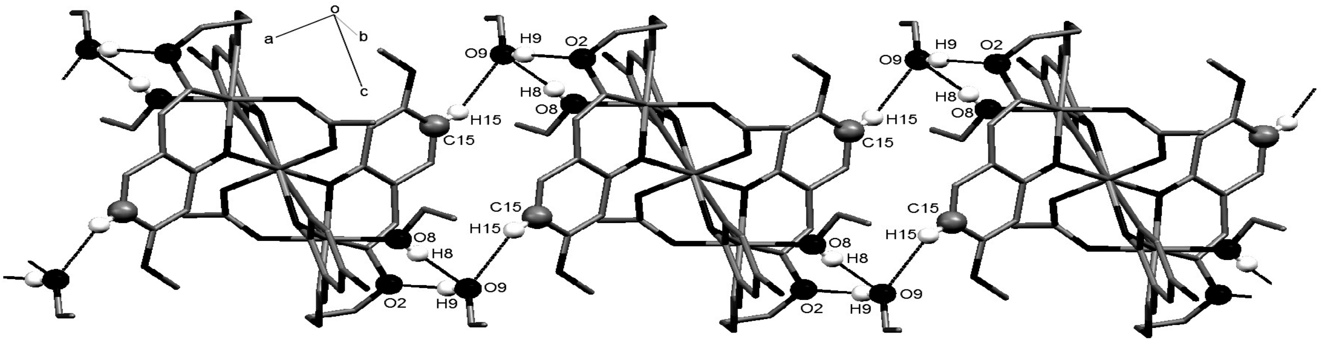


Fig. 3. View of the 1D chain motif of the complex units along the [110] crystallographic axis (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity)

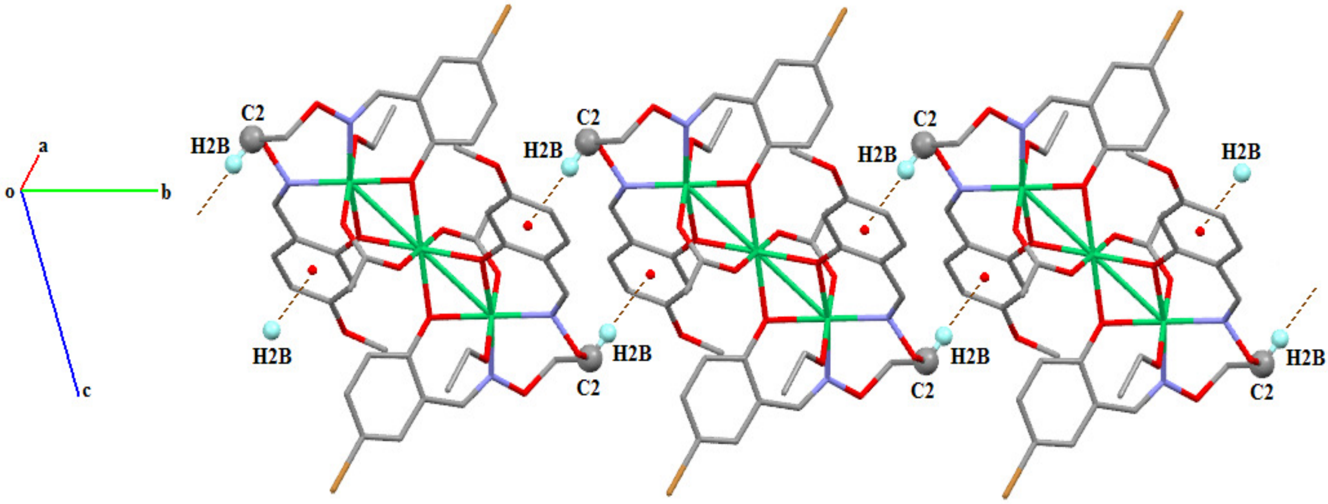


Fig. 4. (color online). View of the 1D chain motif of the complex units along the b axis (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity).

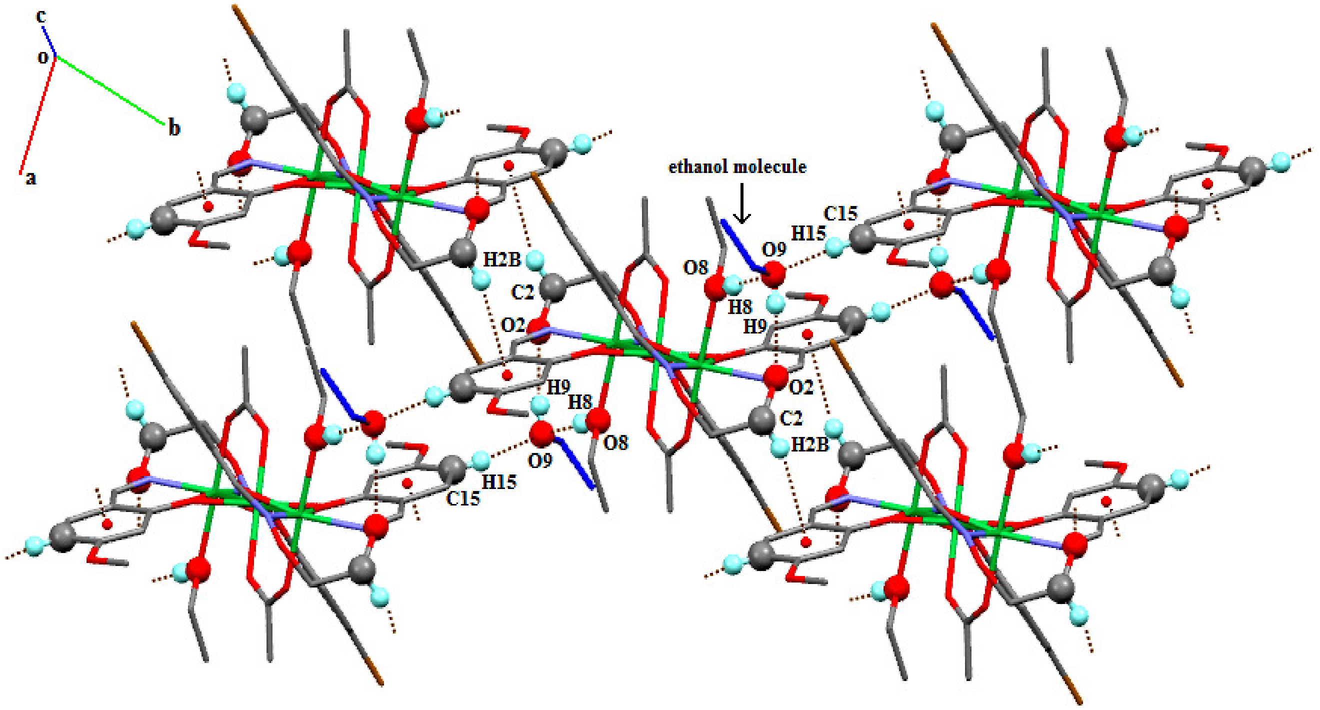


Fig. 5. (color online). View of the 2D layer motif (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity)

to the oxime oxygen (O2) atom of the L$^{2-}$ unit. Thus, the complex and the non-coordinating ethanol molecules are linked by intermolecular O8-H8···O9, O9-H9···O2 and C15-H15···O9 hydrogen bonds into an infinite 1D chain along the [110] crystallographic axis (Fig. 3). Synchronously, this linkage is further stabilized by two pairs of intermolecular C2-H2B···$\pi_{centroid(C11-C16)}$ hydrogen bonding interactions between the methylene (-C2H2B) unit of the O-alkyl chain and the benzene ring (C11-C16) of the coordinated L$^{2-}$ unit to form the other 1D infinite chain along the b-axis, as illustrated in Fig. 4.

Thus, the Ni(II) complex and crystallizing disordered ethanol molecule are linked to form an infinite 2D layer supramolecular structure (Fig. 5) through intermolecular O-H···O, C-H···O and C-H···π hydrogen bond interactions.

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