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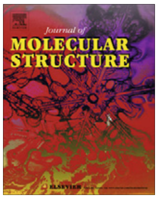

Crystal structures of transition metal complexes with an asymmetrical tridentate Schiff-base ligand

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ABSTRACT

The asymmetrical tridentate Schiff base (**H_2L** = (E)-N′-(2-hydroxybenzylidene)-4-hydroxybenzohydrazide) has been designed and synthesized. The four transition metal complexes with this ligand [Cu(HL)(NO_3)](H_2O) (**1**), [$Zn_2$$(HL)_2$(bipy)$(H_2O)_2$]$(NO_3)_2$ (**2**), [Cu(HL)(H_2O)]$_2$$(NO_3)_2$ (**3**) and [Cu(HL)(Me_2NCO)]$_2$ (**4**) have been studied. The unsaturated coordination site of metal ion in complexes **1** and **2** is occupied by secondary ligand of nitrate and 4,4′-bipyridine. The crystal structure of complex **1** exhibits supramolecular framework with homochirality. Complexes **3** and **4** are dinuclear complexes bridged by the phenol oxygen atoms and the fifth coordination is occupied by H_2O molecular and DMF anion respectively. Hydrogen bonding and π–π stacking exist in all four complexes to construct supramolecular architecture.

1. Introduction

In recent years, transition metal complexes of asymmetrical Schiff-base ligands have attracted enormous attentions due to their diversity of molecular structures [1–9] and important properties, such as catalytic, magnetic, fluorescent and electrochemical properties [8–18]. Tridentate Schiff bases with N, O donors set atoms provide fixed coordination mode for a wide variety of metal ions [3,11–13,19], and the unsaturated coordination site of metal ion in complexes can be occupied by secondary ligand (e.g. anionic or neutral ligands) or solvents [6,8,20,21]. It offers an effective way to control the structural diversities through the shapes and charges of secondary ligands.

To the best of our knowledge, the tridentate Schiff bases are normally with O, N, O donors set [12,22]. Herein, a novel asymmetrical tridentate Schiff bases ligand, (E)-N′-(2-hydroxybenzylidene)-4-hydroxybenzohydrazide (H_2L), was designed and synthesized (Scheme 1).

As part of our continuing research into carboxamido- containing ligand, we study coordination chemistry of H_2L. Four new complexes of [Cu(HL)(NO_3)](H_2O) (**1**), [$Zn_2$$(HL)_2$(bipy)$(H_2O)_2$]$(NO_3)_2$ (**2**), [Cu(HL)(H_2O)]$_2$$(NO_3)_2$ (**3**), [Cu(HL) (Me_2NCO)]$_2$ (**4**) and have been studied. Structural diversity of complexes **1**, **2**, **3** and **4** is tunable by hydrogen bonding and aromatic stacking to construct 2D and 3D architectures.

2. Experimental

2.1. Materials and measurements

All starting materials and solvents used in this work were of analytical grade and used as purchased from Alfa Aesar Chemical Company without further purification. Elemental analyses (C, H, N) were performed using a Vario EL elemental analyzer. FT-IR spectrum is measured as KBr pellets on a Nicolet Nexus FT-IR spectrometer in the 4000–400 cm^{-1} region.

2.2. Preparation of the ligand H_2L

The ethanol (15 mL) solution salicylaldehyde (1.700 g, 0.015 mmol) was added dropwise to the ethanol (40 mL) solution of p-hydroxybenzoylhydrazone (2.000 g, 0.015 mmol) with stirring. Then, the mixture was refluxed for 48 h with vigorous stirring and subsequently cooled to room temperature. The resulting white precipitate was collected by vacuum filtration. A white powder was obtained after being washed with ethanol and dried in air. Yield: 76%. The schematic diagram showing the synthesis of **H_2L** is shown in Scheme 1. Slow concentration of the methanol solution of **H_2L** afforded crystals suitable for X-ray analysis. Anal. Calcd. for $C_{14}H_{13}N_2O_3$: C, 65.40; H, 5.06; N, 10.89. Found: C, 65.35; H, 4.98; N, 10.93. Selected IR (KBr pellet, cm^{-1}): ν(O–H) 3316; ν(C═O) 1653; ν(C═N) 1619; ν(C–N) 1168.

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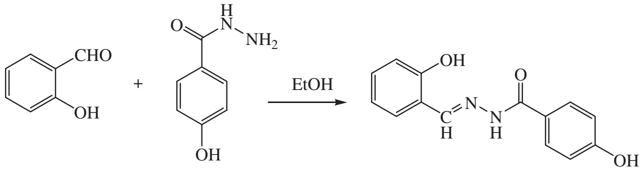

Scheme 1. Synthetic route of the ligand H_2L.

2.3. Preparation of complex [Cu(HL)(NO_3)](H_2O) (**1**)

The solution of $Cu(NO_3)_2{\cdot}2H_2O$ (12 mg, 0.05 mmol) in 3 mL methanol was added by solution of $\mathbf{H_2L}$ (13 mg, 0.05 mmol) in 3 mL methanol. The reaction solution was filtrated after stirring with 20 min. Green single crystals suitable for X-ray diffraction analysis were obtained from diethyl ether vapour diffusion into the filtrate for several days. Yield: 78%. Anal. Calcd. for $C_{14}H_{12}CuN_3O_7$: C, 44.22; H, 3.04; N, 10.55; O, 28.12. Found: C, 44.28; H, 3.08; N, 10.53. Selected IR (KBr pellet, cm^{-1}): ν(C=N) 1607 and ν(C–N) 1169.

2.4. Preparation of complex [$Zn_2(HL)_2$(bipy)($H_2O)_2$]($NO_3)_2$ (**2**)

The solution of $Zn(NO_3)_2{\cdot}6H_2O$ (15 mg, 0.05 mmol) in 1 mL MeOH was added by MeOH/MeCN (V:V = 2:3) solution (5 mL) of $\mathbf{H_2L}$ (0.1 mmol), followed by 0.05 mmol triethylamine at room temperature with constant stirring. After ca. 15 min, a MeOH/MeCN (V:V = 1:1) solution (2 mL) of 4,4′-bipyridine (0.05 mmol) was added, and stirring was continued for ca. 15 min. Suitable pale-yellow parallelogram single crystals for X-ray diffraction were obtained by slow evaporation of the mother liquor for five days. Yield: 82%. Anal. Calcd. for $C_{38}H_{34}N_8O_{14}Zn_2$: C, 47.67; H, 3.58; N, 11.71. Found: C, 47.71; H, 3.59; N, 11.68. Selected IR (KBr pellet, cm^{-1}): ν(C=N) 1607; ν(C–N) 1174; ν(C=N) (aromatic) 133,31,307.

2.5. Preparation of complex [Cu(HL)(H_2O)]$_2$(NO_3)$_2$ (**3**)

The ethanol (10 mL) solution of H_2L (26 mg, 0.10 mmol) was mixed with an ethanol solution (5 mL) of $Cu(NO_3)_2{\cdot}2H_2O$ (24 mg, 0.10 mmol) with continuous stirring ca. 30 min. The result solution was then filtered and left at room temperature to give a deep green solution. Green single crystal suitable for X-ray analysis was produced by slow evaporation of the mother liquor for several days. Yield: 65% Anal. Calcd. for $Cu_2C_{28}H_{26}N_6O_{14}$: C, 42.11; H, 3.26; N, 10.53. Found: C, 42.08; H, 3.28; N, 10.51. Selected IR (KBr pellet, cm^{-1}): ν(C=O) 1652; ν(C=N) 1600; ν(C–N) 1169.

2.6. Preparation of complex [Cu(HL)(Me_2NCO)]$_2$ (**4**)

When the ethanol solution of $\mathbf{H_2L}$ (26 mg, 0.10 mmol) was mixed with the ethanol solution of $CuCl_2{\cdot}2H_2O$ (17 mg, 0.10 mmol) with stirring, the precipitate appeared. Then DMF was added dropwise to the mixture solution until the precipitate dissolved. The mixture was stirred with ca. 30 min. at room temperature to give a deep green solution. Suitable green single crystals for the structure determination were obtained by slow evaporation of the mother liquor for a week. Yield: 72%. Anal. Calcd. for $Cu_2C_{34}H_{34}N_6O_8$: C, 52.24; H, 4.35; N, 10.76. Found: C, 52.20; H, 4.39; N, 10.77. Selected IR (KBr pellet, cm^{-1}): ν(C=O) 1648; ν(C=N) 1609; ν(C–N) 1173.

2.7. X-ray crystal structure determinations

Diffraction intensities for the ligand and four complexes were collected on a Rigaku RAXIS–RAPID CCD diffractometer equipped with a graphite-monochromatic Mo Kα radiation (λ = 0.71073 Å) using an ω scan mode at 296 ± 2 K ($\mathbf{H_2L}$), 93 ± 2 K (complex **2**) and 293 ± 2 K (complexes **1**, **3**, and **4**). Diffraction intensity data were collected in the θ range of 1.59–28.44° for $\mathbf{H_2L}$, 1.68–27.77° for complex **1**, 3.12–25.25° for complex **2** and 2.09–27.67° for complex **3**, 1.86–27.56° for complex **4**. The collected data were reduced using the SAINT program [23], and empirical absorption corrections were performed using the SADABS program [23]. Five structures were solved by direct methods [24] and refined using full-matrix least square techniques on F^2 [25] with the program SHELXL-97 [23]. All nonhydrogen atomic positions were located in difference Fourier maps and refined anisotropically. Some of hydrogen atoms were placed in their geometrically generated positions and other hydrogen atoms were located from the different Fourier map and refined isotropically. Crystallographic data are given in Table 1. Selected bond distances and angles are given in Table 2.

Table 1
Crystal data and structure refinement for free ligand ($\mathbf{H_2L}$) and complexes **1–4**.

	H_2L	1	2	3	4
Formula	$C_{14}H_{13}N_2O_3$	$CuC_{16}H_{13}N_3O_7$	$Zn_2C_{38}H_{34}N_8O_{14}$	$Cu_2C_{28}H_{26}N_6O_{14}$	$Cu_2C_{34}H_{34}N_6O_8$
fw	257.26	422.83	957.47	797.65	419.88
T (K)	296(2)	293(2)	93(2)	293(2)	293(2)
Cryst. syst.	Monoclinic	Orthorhombic	Triclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P2_12_12_1$	P-1	P-1	$P2_1/c$
a (Å)	13.6062(14)	5.1268(15)	9.816(2)	7.5439(15)	11.9635(13)
b (Å)	8.2437(8)	16.798(5)	10.112(2)	10.352(2)	14.6749(16)
c (Å)	11.5135(11)	17.607(5)	10.197(2)	10.410(2)	10.7734(12)
α (°)	90	90	104.408(2)	70.537(2)	90
β (°)	109.487(2)	90	99.046(3)	82.524(2)	114.090(2)
γ (°)	90	90	93.263(2)	89.464(2)	90
V ($Å^3$)	1217.4(2)	1516.3(8)	963.2(4)	759.5(3)	1726.7(3)
Z	4	4	1	3	4
ρ calcd. ($mg\ m^{-3}$)	1.404	1.852	1.651	1.744	1.504
F(0 0 0)	540	860	490	406	804
θ rang. (°)	1.59–28.44	1.68–27.77	3.12–25.25	2.09–27.67	1.86–27.56
μ (mm^{-1})	0.100	1.493	1.328	1.484	1.291
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
R (int)	0.0290	0.0522	0.0236	0.0267	0.0800
Final *R*1, w*R*2 [$I > 2\sigma(I)$]	0.0579, 0.1730	0.0543, 0.1327	0.0386, 0.0928	0.0328, 0.0798	0.0538, 0.1065
R1, wR2 (all data)	0.0834, 0.1964	0.0814, 0.1480	0.0432, 0.0960	0.0425, 0.0854	0.1219, 0.1300
Peak and hole (e $Å^{-3}$)	0.442, −0.615	0.368, −0.369	1.404, −0.503	0.371, −0.375	0.531, −0.644

3. Results and discussion

3.1. Crystal structure of $\mathbf{H_2L}$

The molecular structure of $\mathbf{H_2L}$ is shown in Fig. 1. The imine-N, carbonyl-O and phenolate-O atom in $\mathbf{H_2L}$ provides a fixed coordination mode with ONO tridentates in a plane. The C(13)–O(1), C(7)–O(3) and C(15)–N(2) bond distances of 1.368(2) Å, 1.227(2) Å and 1.272(2) Å, respectively, is consistent with C–O single bond, C═O double bond and C═N double bond. The conjugated system of the ligand makes its planar molecular structure. Hydroxy and amide groups exist in $\mathbf{H_2L}$ and will offer the donors and acceptors of H-bonding. A strong intramolecular interaction occurs between the phenolic oxygen atom O1 which acts as donor and the imine nitrogen atom N2 [N(2)···H(1B) = 1.791 Å, O(1)···N(2) = 2.618 Å, O(1)–H(1B)···N(2) = 150.5°]. This type of intramolecular hydrogen bonds which we talked above is typical of Schiff bases derived from salicylaldehydes [26].

Intermolecular hydrogen bonds exist between the amido nitrogen atom N1 and the phenolic oxygen atom O1 [O(1)···H(1AA) = 2.384 Å, O(1)···N(1A) = 3.164 Å, N(1A)–H(1AA)···O(1) = 151.1°], which links $\mathbf{H_2L}$ molecules to exhibit hydrogen-bonded 1D chain (Fig. S1). Additional H-bondings occur between the carbonyl oxygen atom O3 and phenolic oxygen atom O2 [O(3A)···H(2B) = 1.888 Å, O(3A)···O(2) = 2.706 Å, O(2)–H(2B)···O(3A) = 174.2°]. The strong π–π stacking interaction is found in solid state of the ligands with the distance between two benzene planes of 3.420 Å. The 3D packing picture exhibits two types of channels (diamond and parallelogram) by hydrogen bondings and π–π stacking interactions. So, crystal structure of $\mathbf{H_2L}$ shows supramolecular architecture constructed by hydrogen bondings and π–π stacking interactions.

3.2. Structure descriptions of the complexes **1** and **2**

Complex **1** is mononuclear four-coordinated copper complex. The molecular structure is given in Fig. 2. The copper (II) centre in **1** adopts a slightly distorted square-planar geometry [N(4)–Cu–O(4): 173.5(2)° and O(2)–Cu–O(8): 175.62(17)°]. The tridentate ligand coordinated with Cu (II) through the imine-N, carbonyl-O and phenoxo-O atom which make one five-membered and one six-membered chelate rings. The remaining fourth coordination is occupied by one O atom from nitrate as secondary ligand.

Compared with the bond lengths of the free ligand, the C(6)–O(8) bond lengthens and C(5)–O(2) shortens significantly (by ca. 0.031 and 0.054 Å respectively). While, the bond lengths of C(6)–N(1), N(1)–N(4) and C(18)–N(4) are unaffected by complexation. The Cu–O (phenoxo) bond length observed here are within the range reported for other similar complexes of Cu [27–32]. The Cu–O (carbonyl) and Cu–N (imine) bond lengths are shorter than the related Cu complexes [27–32].

The achievements in supramolecular chemistry tell us that chirality can be described not only on the molecular level and coordination frameworks but also on the supramolecular level [27,33–35]. Complex **1** exhibits hydrogen-bonded chiral helical chain structure crystallizes in the orthorhombic chiral space group $P2_12_12_1$. It is noteworthy that the oxygen atom of phenol group uncoordinated to Cu(II) ions in HL^- has intermolecular H-bonding with uncoordinated O atom from nitrate [O(5)···H(3) = 2.07Å, O(5)···O(3) = 2.8072 Å and O(3)–H(3)···O(5) = 150°]. Additionally, each molecule of **1** interacts with two neighbors to form two types of H-bond through the NO_3^- group. One is a conventional H-bonding [O(5)···H(3) = 2.07 Å, O(5)···O(3) = 2.8072 Å, O(3)–H(3)···O(5) = 150°] in 2D layer. The other is a weak non-conventional H-bonding [O(5)···H(20A) = 2.50 Å, O(5)···C(20) = 3.3796 Å and C(20)–H(20A)···O(5) = 158°] along 3D direction. The hydrogen bond lengths and angles are collected in Table 3. These interactions constructed the helices which are all right-handed helical chains (Fig. 3). Therefore, the overall structure can be viewed as a homochiral supramolecular framework.

The unsaturated coordination sites of metal ions in $M(HL)^{+1}$ allow to use different secondary ligands to produce structural diversity. The linear bridge ligand 4,4′-bipyridine is chosen to construct binuclear complex **2**. The molecular structure of complex **2** consists of $[Zn_2L_2(bipy)]^{2+}$ and two uncoordinated nitrate counterions (Fig. 4). Each Zn atom is bonded to three atoms of the ligand, with one oxygen atom O(1) at 1.994(2) Å and O(2) at 2.147 Å and one nitrogen atom N(1) at 2.077(2) Å. Furthermore, the remaining coordination site is occupied by oxygen atom of water molecular. The coordination polyhedron around the Zn(II) can be described as a distorted square pyramid. The two metal-centred moieties were bridged by heterocyclic nitrogen atom of bipy [Zn(1)–N(3) = 2.040(2) Å], with metal–metal separation of Zn(1), Zn(1A) 11.1827 Å. Interestingly, the two water molecules are linked to two Zn (II) atoms in opposite direction, respectively. Therefore, the tridentate ligand can not act as bridge ligand because of the small steric hindrance and rigidity of 4,4′-bipyridine.

In complex **2**, the uncoordinated nitrate anions, –OH and –NH group play a key role in hydrogen-bonded networks. Building block units $[Zn_2L_2(bipy)]^{2+}$ and NO_3^- are connected into a 2D grid network (Fig. S2a) via two types of hydrogen bondings, O–H···O and N–H···O. The hydroxy O(3) acts as a single hydrogen bonding donor to O(6B) of one neighbor and a single hydrogen bonding acceptor from N(2C) atom of the another neighbor [O(6B)···H(3O) = 1.899 Å, O(3)···O(6B) = 2.692 Å, O(3)–H(3O)···O(6B) = 164°, O(3)···H(2ND) = 2.220 Å, N(2C)···O(3) = 3.180 Å, N(2C)–H(2ND)···O(3) = 160.5°]. These 2D H-bonded layers are further linked to each other through hydrogen bonding interactions O–H···O [O(4A)···H(4BA) = 1.833 Å, O(1)···O(4A) = 2.756 Å, O(1)–H(4BA)···O(4A) = 165.6°] to form the supramolecular metal–organic framework (Fig. S2b). The hydrogen bond lengths and angles are collected in Table 3.

3.3. Structure description of the complexes **3** and **4**

Ligand containing phenolate oxygen atom can connect two neighbor metal units by two μ-O bridges to form a dimmer. By changing the metal salts and solvent, complexes **3** and **4** which are both binuclear are obtained (Fig. 5). The Cu (II) ions in both complexes are five coordinated with approximately square pyramidal. In complex **3,** the coordinating water molecule occupied the apical sites of square pyramidal. The bond length of Cu–O(w) of axial position of 2.273(2) Å and Cu–O–Cu bridging angle of 99.99(7)° are very close to the complex with identical coordination spheres which has been reported [12]. While in complex **4**, the apical axis of square pyramidal is occupied by a DMF anion. The DMF anion is unusual. To our best knowledge, this is the first example that DMF acts as anion to coordinate in schiff base complex. We concluded the DMF anion based on the crystallography data. The bond length of N(3)–C(2) is 1.307(5) Å, a double bond. It can be explained by the fact that the C(2) atom lost a hydrogen atom and form a conjugate N═C═O of DMF anion. Both of these two complexes comprised two equivalent Cu(II) in crystallography and two parts are linked by phenolate oxygen atom with μ_2-O bridge mode. However, their molecular structures are different. In complex **3**, the μ_2-O bridge mode is symmetrical because the Cu–O (phenoxo) bond lengths are same [Cu(1)–O(1) = 1.9350(15) Å)]. But, the μ_2-O bridge mode is asymmetrical in complex **4** based on the two bond lengths of Cu(1)–O(2) (1.897(3) Å) and Cu(1)–O(2A) (2.478 Å). Therefore, the Cu···Cu distance in complexes **3** and **4** are 2.9890(6) Å and 3.200 Å respectively. The Cu···Cu

Table 2
Selected bond distances (Å) and bond angles (°) for ligand H_2L complexes **1–4**.

H_2L			
C(7)–O(3)	1.227(2)	O(3)–C(7)–N(1)	120.09(16)
C(7)–N(1)	1.363(2)	O(3)–C(7)–C(6)	122.88(16)
N(1)–N(2)	1.379(2)	N(1)–C(7)–C(6)	117.01(16)
N(2)–C(15)	1.272(2)	C(15)–N(2)–N(1))	118.30(15)
C(13)–O(1)	1.368(2)	N(2)–C(15)–C(14)	120.17(17)
1			
Cu–O(2)	1.883(4)	O(2)–Cu–O(8)	175.62(17)
Cu–O(8)	1.951(4)	N(4)–Cu–O(4)	173.5(2)
Cu–N(4)	1.914(4)	O(2)–Cu–N(4)	93.98(18)
Cu–O(4)	1.979(4)	N(4)–Cu–O(8)	81.72(18)
C(6)–O(8)	1.258(7)	O(2)–Cu–O(4)	91.89(17)
N(1)–N(4)	1.378(6)	O(8)–Cu–O(4)	92.36(17)
N(4)–C(18)	1.284(7)		
N(1)–C(6)	1.355(7)		
C(5)–O(2)	1.314(7)		
2			
Zn(1)–O(1)	1.994(2)	O(1)–Zn(1)–O(2)	162.95(8)
Zn(1)–N(1)	2.077(2)	N(3)–Zn(1)–N(1)	138.15(10)
Zn(1)–O(2)	2.147(2)	O(4)–Zn(1)–O(1)	100.89(9)
Zn(1)–N(3)	2.040(2)	O(4)–Zn(1)–N(3)	109.09(9)
Zn(1)–O(4)	1.973(2)	O(4)–Zn(1)–O(2)	89.10(9)
O(2)–C(8)	1.241(3)	O(4)–Zn(1)–N(1)	110.29(9)
N(1)–C(7)	1.288(4)		
N(1)–N(2)	1.386(3)		
N(2)–C(8)	1.350(4)		
3			
Cu(1)–O(1)	1.9350(15)	O(1)–Cu(1)–O(2)	165.83(7)
Cu(1)–N(1)	1.9339(19)	N(1)–Cu(1)–O(1)#1	167.49(7)
Cu(1)–O(2)	1.9593(16)	O(1)–Cu(1)–O(4)	97.95(7)
Cu(1)–O(1)#1	1.9672(16)	N(1)–Cu(1)–O(4)	94.85(8)
Cu(1)–O(4)	2.273(2)	O(2)–Cu(1)–O(4)	95.05(8)
Cu(1)–Cu(1)#1	2.9890(6)	O(1)#1–Cu(1)–O(4)	95.97(8)
O(2)–C(8)	1.262(3)	O(1)–Cu(1)–O(1)#1	80.01(7)
N(1)–C(7)	1.283(3)	Cu(1)–O(1)–Cu(1)#	99.99(7)
N(1)–N(2)	1.381(2)		
N(2)–C(8)	1.336(3)		
4			
Cu(1)–O(2)	1.899(3)	O(2)–Cu(1)–O(3)	175.37(12)
Cu(1)–O(2A)	2.478	N(2)–Cu(1)–O(4)	165.57(12)
Cu(1)–N(2)	1.915(3)	O(2)–Cu(1)–N(2)	93.95(13)
Cu(1)–O(3)	1.927(3)	N(2)–Cu(1)–O(3)	81.43(13)
Cu(1)–O(4)	1.974(3)	O(2)–Cu(1)–O(4)	90.95(12)
O(3)–C(3)	1.280(5)	O(3)–Cu(1)–O(4)	93.46(12)
N(2)–C(6)	1.280(5)		
N(2)–N(1)	1.386(4)		
N(1)–C(3)	1.386(4)		
Cu1–Cu1A	3.200		
N(3)–C(2)	1.306(5)		
O(4)–C(2)	1.265(5)		

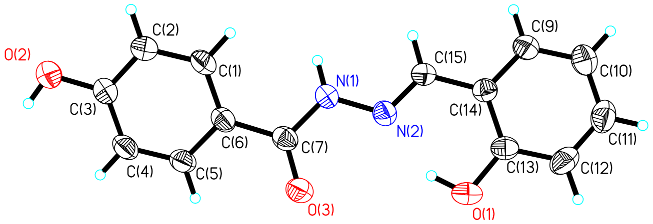

Fig. 1. ORTEP picture of the ligand $\mathbf{H_2L}$ (30% probability ellipsoids).

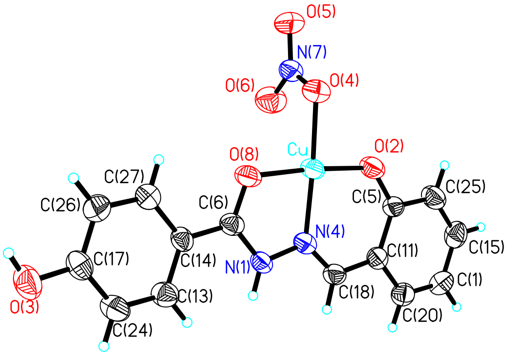

Fig. 2. ORTEP diagram of complex **1** (30% probability ellipsoids).

Table 3
Distances (Å) and angles (°) of hydrogen bonds for $\mathbf{H_2L}$ and **1–4**.

D–H···A	*d*(H···A)	*d*(D···A)	∠D–H···A
H_2L			
O(2)–H(2B)···O(3A)	1.888	2.706	174.2
N(1A)–H(1AA)···O(1)	2.384	3.164	151.1
O(1)–H(1B)···N(2)	1.791	2.618	150.5
1			
N(1)–H(1A)···O(1)	1.94	2.7812	164
O(3)–H(3)···O(5)	2.07	2.8072	150
C(13)–H(13A)···O(1)	2.53	3.4292	163
C(20)–H(20A)···O(5)	2. 50	3.3796	158
C(26)–H(20A)···O(6)	2.52	3.3825	155
2			
O(3)–H(3O)···O(6B)	1.899	2.692	164
N(2C)–H(2ND)···O(3)	2.220	3.180	160.5
O(1)–H(4BA)···O(4A)	1.833	2.756	165.6
3			
O(3A)–H(3A)···O(7)	1.893	2.705	170.2
C(7)–H(7)···O(5)	2.416	3.180	139.4
N(2)–H(2N)···O(5)	1.988	2.773	162.3
O(4B)–H(4AB)···O(3)	2.064	2.845	167.3
O(4C)–H(4F)···O(6B)	2.262	2.900	169.4
4			
O(1)–H(1B)···N(1B)	1.855	2.686	165.2
C(17)–H(17C)···O(1B)	2.559	3.409	147.6

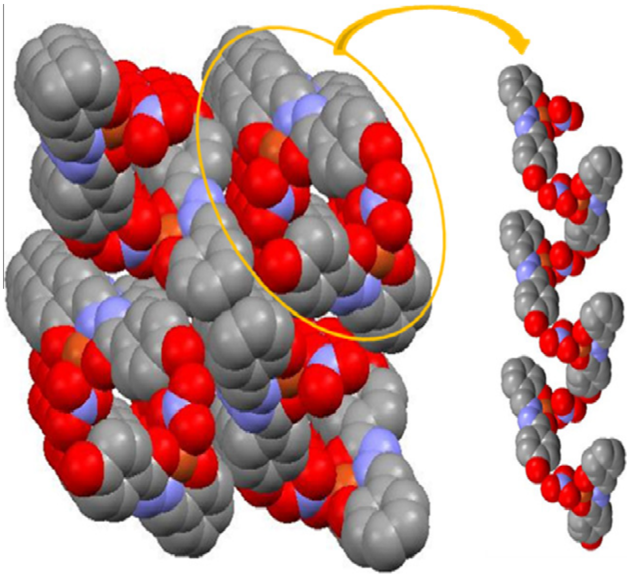

Fig. 3. The 3D space-filling packing picture of complex **1** view down from *a* axis.

distance in complex **3** is slightly shorter than that reported in $[Cu_2(Hfsadmpn)_2(H_2O)_2](ClO_4)_2$ and $[Cu(HL)H_2O]_2\cdot 2NO_3$ [12,36]. The molecular shape of the complex **3** is almost planar with the coordinated water molecules located the both side of the plane. The core part of this plane is formed by Cu(1), Cu(1A), N(1), N(1A), O(1), O(1A), O(2), O(2A) with a mean deviation of 0.0731 Å. In complex **4**, two coordinated tridentate ligands are

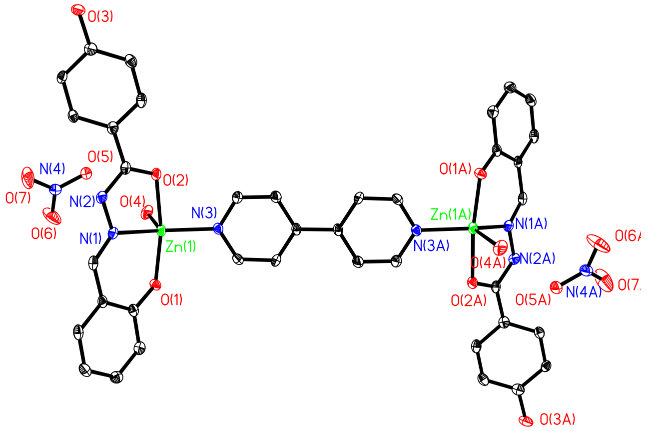

Fig. 4. ORTEP diagram of complex **2** (50% probability ellipsoids, hydrogen atoms are omitted for clarity).

not on a plane. The two deprotonated phenoxo oxygen coordinated to Cu(II) ion to form the bridging CuO_2Cu core which is planar. The dihedral angle between the mean planes through CuO_2Cu core and O(2), C(5), C(13), C(6), N(2) and Cu(1) is 76.6°.

Although the nitrate anions are not coordinated to the Cu(II) centres in complex **3**, they are involved in a hydrogen bonding. Nitrate anions regard as bridges connecting neighboring Cu(II) dimeric units to form the 1D belt structure (Fig. 6). The nitrate O(5) acts as a double hydrogen bonding acceptor from N2 and C7 atoms of the same molecular [O(5)···H(2N) = 1.988 Å, O(5)···N(2) = 2.773 Å, N(2)–H(2N)···O(5) = 162.3°, O(5)···H(7) = 2.416 Å, O(5)···C(6) = 3.180 Å, C(7)–H(7)O(5) = 139.4°] and nitrate O(7) acts as a single hydrogen bonding acceptor from O(3A) atoms of the another neighbor-[O(7)···O(3A) = 1.893 Å, O(7)···H(3A) = 2.705 Å, O(3A)–H(3A)···O(7) = 170.2°]. These 1D H-bonded belts are linked by strong hydrogen bonds formed between the coordinated water molecules and the phenolic groups from adjacent binuclear entities [O(3)···H(4AB) = 2.064 Å, O(4B)···O(3) = 2.845 Å, O(4B)–H(4AB)···O(3) = 167.3°], resulting in 2D ladder structure (Fig. 6). The water

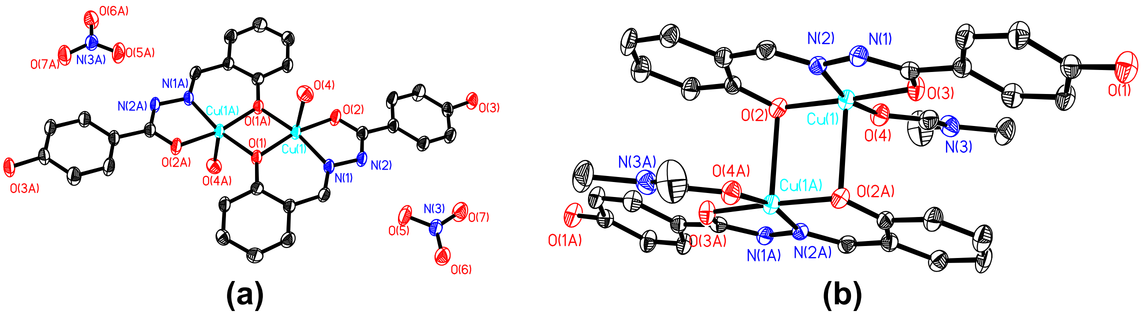

Fig. 5. ORTEP diagrams of complex **3** (a) and complex **4** (b). Displacement ellipsoids are drawn at the 50% probability level for **3** and at the 30% probability level for **4**. H atoms have been omitted for clarity.

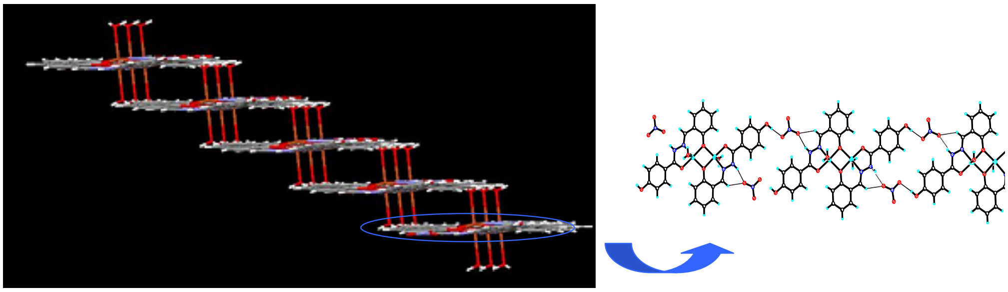

Fig. 6. The 1D belt structure and the 2D ladder structure of complex **3** by H-bonding.

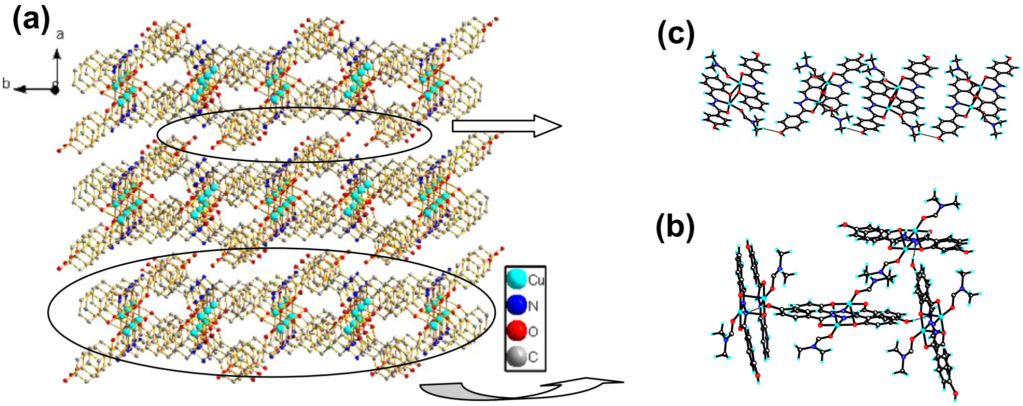

Fig. 7. (a) The 3D picture of the complex **4** view down from *c* axis (b) The hydrogen bondings O–H···N in complex **4** from *a* axis (c) The weak intermolecular C–H···O hydrogen interactions in complex **4** from *b* axis.

molecules act as pillars to connect and stabilize the overall structure. Further, these 2D structures extended to 3D network by hydrogen bonding from O–H⋯O [O(6B)⋯H(4F) = 2.262 Å, O(4C)⋯O(6B) = 2.900 Å, O(4C)–H(4F)⋯O(6B) = 169.4°]. The hydrogen bond lengths and angles are collected in Table 3.

In complex **4**, the uncoordinated phenolic oxygen atom O(1) acts as a H-bonding donor to N(1) and a H-bonding acceptor to C(17) atom in construction of supramolecular architecture. A strong intermolecular H-bonding exists between the phenolic oxygen atom O(1) and the amido nitrogen atom N(1B) with O–H⋯N type [N(1B)⋯H(1B) = 1.855 Å, N(1B)⋯O(1) = 2.686 Å, O(1)–H(1B)⋯N(1B) = 165.2°], which link the molecules to exhibit 2D supramolecular structure. The resulting 2D supramolecular structure is held together via weak non-conventional H-bonding C–H⋯O [O(1B)⋯H(17C) = 2.559 Å, C(17)⋯O(1B) = 3.409 Å, C(17)–H(17C)⋯O(1B) = 147.6°] (Fig. 7). The π–π stacking interaction that plays a key role to stabilize the structure is found between conjugate $N\overset{\cdots}{-}C\overset{\cdots}{-}O$ from DMF anion and aromatic ring of salicylaldehyde with the distance of 3.568 Å.

4. Conclusions

An asymmetrical tridentate ligand with NOO donor schiff base has been designed and synthesized in this work. Its transition metal complexes are obtained successfully. The studies of their crystal structures and supramolecular interactions indicated that the diverse structural motifs using. The unsaturated coordination site of metal ion in mononuclear complex **1** is occupied by secondary ligand of nitrate and the overall structure exhibits supramolecular framework with homochirality. In complex **2**, 4,4′-bipyridine as a linear bridge ligand in conjugation with **H$_2$L** to form a dimmer. Two phenol oxygen atoms of the two tridentate ligands acting as bridge connects the two Cu atoms to form binuclear complexes **3** and **4** with the secondary ligand of H_2O and DMF anion respectively. The negative secondary ligand (NO_3^-) made complex **1** adopt mononuclear form, and the secondary ligand (4,4′-bipy, H_2O and DMF anion) made complexes **2–4** adopt binuclear form. It offers an effective way to control the structural diversities through the shapes of secondary ligands. **H$_2$L** exists multiple hydrogen bonding sites which play an important role in constructing supramolecular architecture. Hydrogen bonds exist in complexes **2** and **3** through NO_3^- to control in the assembly of molecular complexes, so the counter ion in the system is another factor to tune the molecular packing in solid state.

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Appendix A. Supplementary material

Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers: CCDC_757897 (1), CCDC_757900 (2), CCDC_757899 (3), CCDC_757898 (4), CCDC_757896 (H_2L). Copies of the data can be obtained free of charge on application to CCDC, 12, Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; E-mail: deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2010.09.014.

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