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Syntheses, Structures, Hirshfeld Surface Analyses and Magnetic Properties of a Series of Homopolynuclear Half-Salamo-Based Complexes

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Abstract. Two newly di- and tri-nuclear Cu(II) and Ni(II) complexes constructed from a half-salamo chelating ligand (HL: 2-[O-(1-ethyloxyamide)]oxime-6-methoxyphenol), $[Cu_2(L)_2(\mu - OAc)_2]$ (1) and $[{Ni_3(\mu - OAc)_2(L)_2(OAc)_2}] \cdot CHCl_3$ (2), and one tetranuclear Co(II) complex $[Co_4(L')_4(MeOH)_4]$ (3) based on an unexpected ligand H_2L' derived from the cleavage of HL have been synthesized and characterized by elemental analyses, IR, UV-vis spectra, and single crystal X-ray diffraction analyses. The single crystals of complexes 1, 2 and 3 in the process of synthesis are obtained through different routes. The complex 1 includes two Cu(II) atoms, two completely deprotonated (L)⁻ units and two μ -acetate ions, which displays a propeller-type motif. The complex 2 contains three Ni(II) atoms, two completely deprotonated (L)⁻ units, two μ -acetate ions, two chelating acetate ions and one crystallizing chloroform molecule, the crystal structure of complex 2 reveals a butterfly-type motif. The complex 3 is made up of four Co(II) atoms, four $(L')^{2-}$ completely deprotonated units (HL': 2-[O-(1-hydroxyethyl)]oxime-6-methoxyphenol) and four coordinated methanol molecules, which shows a windmill-type motif. Besides, magnetic properties and Hirshfeld surface analyses were discussed.

Keywords: Half-salamo ligand, Multinuclear complex, Synthesis, Crystal structure, Magnetic property

1. Introduction

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Salen-type ligands (R–CH=N–(CH₂)₂–N=CH–R) and their metal complexes have been extensively investigated in modern coordination chemistry for several decades [1–10]. Chemical modifications of substituents or functional groups in the salen ligands are effective in exchanging the structures or the main functions of complexes, such as salamo ligand, a salen analogue, (R–CH= N–O–(CH)_n–O–N=CH–R) is one of the most versatile ligand [11–18]. It is reported that salamo-type complexes are at least 10⁴ times more stable than salen-type complexes [19].

Fig. 1. Construction of complexes 1, 2 and 3 derived from the half-salamo ligand HL.

We have proceeded with the study of coordination behaviors of a series of multidentate flexible ligands. Half-salamo ligand (R-CH=N-O-(CH)_n-O-NH₂) as a first research has been reported in our recent study [20,21]. Flexible ligands may bring new changes to the structure, and simple synthesis methods will play a catalytic role in the development of such complexes [22–30]. The diverse coordination modes of acetate ions play an important role in the construction of complexes [31-38], for example, acetate ion can bridge two M(II) atoms in monodentate or bidentate mode [31-38]. However, systematic research on its structure and synthesis methods is still insufficient. In order to supplement and perfect the syntheses and structures of half-salamo complexes, in this study, we have synthesized three types of metal(II) complexes $[Cu_2(L)_2(\mu-OAc)_2]$ (1), $[{Ni_3(\mu-OAc)_2(L)_2(OAc)_2] \cdot CHCl_3}$ (2), and $[Co_4(L')_4(MeOH)_4]$ (3) with a new half-salamo bisoxime ligand (HL), and the unexpected ligand H_2L' is derived from the cleavage of HL in the process of complexation (Fig. 1). It is worth noting that the di-, tri- and tetra-nuclear complexes are obtained by different synthetic methods, and the crystal structures of these complexes show propeller-, butterfly- and windmill-type motifs, respectively.

2. Experimental

2.1. Materials and general methods

3-Methoxysalicylaldehyde (98%) was purchased from Alfa Aesar and used without further purification. Reagents and solvents were analytical grade reagents purchased from Tianjin Chemical Reagent Factory. C, H and N elemental analyses were performed on a GmbH VarioEL V3.00 automatic elemental analysis instrument. Elemental analyses for metals were detected with an IRIS ER/S-WP-1 ICP atomic emission spectrometer. Melting points were obtained by the use of a microscopic melting point apparatus made in Beijing Taike Instrument Limited Company and were uncorrected. IR spectra were recorded on a Vertex70 FT-IR spectrophotometer, with samples prepared as KBr (500-4000 cm⁻¹) and CsI (100–500 cm⁻¹) pellets. UV–vis absorption spectra were recorded on a Shimadzu UV-3900 spectrometer. ¹H NMR spectra were determined by a German Bruker AVANCE DRX-400 spectrometer. X-ray single crystal structure determinations were carried out on the Bruker APEX-II CCD and a SuperNova Dual (Cu at zero) diffractometer. Magnetic susceptibility data were collected on the powdered samples of complexes **1** and **2** at 1000 Oe in the 2–300 K temperature range using a Quantum Design model MPMS XL7 SQUID magnetometer.

2.2. Synthesis of HL

1,2-Bis(aminooxy)ethane was synthesized following the literature [7]. The major reaction steps involved in the synthesis of HL are in accordance with the previously reported procedure (Fig. 1) [4].

An ethanol solution (50 mL) of 3-methoxysalicylaldehyde (152.15 mg, 1.0 mmol) was added dropwise to 1,2-bis(aminooxy)ethane (138.15 mg, 1.5 mmol) in ethanol solution (50 mL). The resulting mixed solution was heated to 55 °C under stirring for 2 h. The solution was concentrated in *vacuo* and the residue was purified by column chromatography (SiO₂, chloroform / ethyl acetate, 15:1) to get a colorless crystalline solid (HL). Yield: 78.6 % (177.81 mg). m.p. 90~91 °C. Anal. Calc. for C₁₀H₁₄N₂O₄ (%): C 53.09; H 6.24; N 12.38. Found: C 53.19; H 6.17; N 12.33. ¹H NMR (400 MHz, CDCl₃), δ 9.87 (s, 1H), 8.22 (s, 1H), 6.91 (dd, J = 7.9, 1.5 Hz, 1H), 6.86 (s, 1H), 6.80 (dd, J = 7.7, 1.7 Hz, 1H), 5.52 (s, 2H), 4.40–4.33 (m, 2H), 4.00–3.94 (m, 2H), 3.91 (s, 3H).

2.3. Synthesis of Complex 1

The copper(II) acetate monohydrate (3.98 mg, 0.02 mmol) was dissolved in 2 mL ethanol solution, 2 mL n-hexane was slowly added, at this point in the liquid phase can be observed a clear dividing line, then HL (4.52 mg, 0.02 mmol) in ethanol (6 mL) was injected, with the gradual diffusion of solvent, several dark-green block-shaped single crystals suitable for X-ray crystallographic analysis were collected at the bottom after

three days at room temperature. Yield: 52.4 % (3.64 mg). Anal. Calcd for $C_{24}H_{32}Cu_2N_4O_{12}$ ([$Cu_2(L)_2(\mu$ -OAc)_2] (1)) (%): C, 41.44; H, 4.64; N, 8.05; Cu, 18.27. Found (%): C, 41.25; H, 4.76; N, 8.22; Cu, 18.16.

2.4. Synthesis of Complex 2

A solution of HL (4.52 mg, 0.02 mmol) in 1 mL of chloroform was added dropwise to a methanolic solution (1 mL) of nickel(II) acetate tetrahydrate (2.48 mg, 0.01 mmol). The color of the mixing solution turned to green immediately, and the mixture was kept stirring for 10 min. Then the mixture was filtered and the filtrate was obtained. The several green block-shaped single crystals suitable for X-ray crystallographic analysis were obtained by vapor diffusion of diethyl ether into the filtrate for three days at room temperature. Yield: 54.3 % (1.78 mg). Anal. Calcd for $C_{29}H_{39}Cl_3N_4Ni_3O_{16}$ [{Ni₃(μ -OAc)₂(L)₂(OAc)₂]·CHCl₃ (**2**)) (%): C, 35.47; H, 4.00; N, 5.70; Ni, 17.93. Found (%): C, 35.23; H, 4.16; N, 5.87; Ni, 17.71.

2.5. Synthesis of Complex 3

A solution of HL (4.52 mg, 0.02 mmol) in 2 mL of ethyl acetate was added dropwise to a methanolic solution (2 mL) of cobalt(II) nitrate hexahydrate (5.82 mg, 0.02 mmol). The color of the mixing solution turned to reddish brown immediately, the mixture solution was filtered and the filtrate was allowed to stand for about one week in the dark. The solvent was partially evaporated and several reddish brown block-shaped single crystals suitable for X-ray crystallographic analysis were collected by filtration and washed with n-hexane. Yield: 48.8 % (2.93 mg). Anal. Calcd for $C_{44}H_{60}Co_4N_4O_{20}$ ([$Co_4(L')_4(MeOH)_4$] (**3**)) (%): C, 44.01; H, 5.04; N, 4.67; Co, 19.63. Found (%): C, 43.82; H, 5.17; N, 4.77; Co, 19.41.

2.6. X-ray Structure Determinations of Complexes 1, 2 and 3

The crystal diffractometer provides a monochromatic beam of Mo $K\alpha$ radiation (0.71073 Å) produced using Graphite monochromator from a sealed Mo X-ray tube was used for obtaining crystal data of complexes **1**, **2** at 296(2) and **3** at 173.00(10) K, respectively. There are no special reasons for measuring the temperature of these complexes, mainly due to the different measurement methods used in different laboratories. The LP factor semi-empirical absorption corrections were applied using

the SADABS program [39]. The structures were solved by the direct methods (SHELXS-2014), and the H atoms were included at the calculated positions and constrained to ride on their parent atoms. All non-hydrogen atoms were refined anisotropically using a full-matrix least-squares procedure on F^2 with SHELXL-2014 [40]. The crystal data and experimental parameters relevant to the structure determinations are listed in Table 1. Supplementary crystallographic data for this paper have been deposited at Cambridge Crystallographic Data Centre (1579841, 1579840 and 1579842 for complexes 1, 2 and 3) and can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html.

Table 1 Crystallographic data and refinement parameters for complexes 1, 2 and 3.

3. Results and Discussion

3.1. IR Spectra

As shown in Fig. 2, the FT-IR spectra of HL and its complexes 1, 2 and 3 exhibit various bands in the 500–4000 cm⁻¹ region. Before the measurement of HL and its complexes 1, 2 and 3, the air scanning was carried out.

Fig. 2. The FT-IR spectra of the ligand HL and its complexes 1, 2 and 3 (cm⁻¹).

A typical C=N stretching band of the free ligand HL appears at 1575 cm⁻¹, while those of complexes **1**, **2** and **3** are observed at 1606, 1605 and 1601 cm⁻¹, respectively [41]. The C=N stretching frequencies are shifted to high frequencies, indicating that the metal(II) atoms are coordinated by oxime nitrogen atoms of the ligand units [42]. Meanwhile, the free ligand HL exhibits Ar–O stretching frequency at 1257 cm⁻¹, while the Ar–O stretching frequencies of complexes **1**, **2** and **3** appear at 1246, 1240 and 1221 cm⁻¹, respectively [43]. The Ar–O stretching frequencies of these complexes are shifted to low frequencies, which could be evidence of formation of the M–O bonds between metal(II) atoms and oxygen atoms of phenolic groups [44].

The far-infrared spectrum of the complex **1** shows v(Cu-O) and v(Cu-N) vibration absorption frequencies at 432 and 475 cm⁻¹, and the complex **2** for v(Ni-O) and v(Ni-N)at 456, 472 cm⁻¹; the complex **3** for v(Co-O), v(Co-N) at 416, 481 cm⁻¹, respectively. These assignments are consistent with the literature frequency values [14,18] and are not present in the spectra of the free ligands.

3.2. UV-vis Absorption Spectra

The UV–vis titration experiments of HL in methanol solution $(2.5 \times 10^{-5} \text{ M})$ were determined with Cu(OAc)₂·H₂O, Ni(OAc)₂·4H₂O and Co(NO₃)₂·6H₂O in methanol solution $(1 \times 10^{-3} \text{ M})$ are shown in Figs. S1–3, respectively.

Upon coordination of the ligand HL, the absorption intensities of complexes 1, 2 and 3 have undergone varying degrees of change, which indicates that the oxime nitrogen atoms are involved in coordination to the metal(II) atoms [45]. With the UV–vis titration experiments of complex 1, the absorbance of the solution hardly changed after Cu^{2+} was added up to 1 equiv. The spectroscopic titration has clearly indicated that the ratio of the replacement reaction is 1:1 (Fig. S1). Similar changes have also appeared in complexes 2 and 3 (Fig. S2 and Fig. S3), the results are corresponding to the crystal structures of complexes 1, 2 and 3, respectively [46].

The UV-vis spectra of HL and its complexes **1**, **2** and **3** (cm⁻¹) are shown in Fig. 3. Obviously, the absorption spectrum of the free ligand HL consists of two relatively intense absorption peaks centered at 268 and 317 nm, respectively, the first peak at 268 nm can be assigned to the π - π * transitions of the phenyl rings, the second peak at 317 nm can be assigned to the π - π * transitions of the oxime group [47]. Upon coordination of the ligand HL, the π - π * transitions of the phenyl rings in complexes **1**, **2** and **3** are bathochromically shifted to 276, 271 and 270 nm, respectively, which indicates the coordination of the ligand units with Cu(II), Ni(II) and Co(II) atoms, respectively [48]. Compared with the free ligand HL, the absorption peak at 317 nm disappears from the UV–vis spectra of complexes **1**, **2** and **3**, which indicates that the oxime nitrogen atoms are involved in coordination to the Cu(II), Ni(II) and Co(II) atoms [49]. Additionally, the new absorption peaks are observed at 378, 376 and 363 nm for complexes **1**, **2** and **3**, these new absorption peaks can be assigned to L→M charge-transfer (LMCT) transitions which are characteristic of the transition metal complexes with N₂O₂ coordination sphere [50].

Fig. 3. The UV-vis spectra of HL and its complexes 1, 2 and 3 in methanol (c = 2.5×10^{-5} M).

3.3. Crystal Structure Descriptions

3.3.1. Complex 1

As depicted in Fig. 4 and Table 2, complex **1** ($[Cu_2(L)_2(\mu-OAc)_2]$) crystallizes in the monoclinic system, space group P $2_1 / c$, and the crystal structure indicates that complex **1** is a symmetric homo-dinuclear complex, which consists of two Cu(II) atoms, two completely deprotonated (L)⁻ unit and two μ -acetate ions. The symmetry code is [#] -x+1, -y+1, -z+2.

Fig. 4. (a) Molecular structure and atom numberings of complex 1 with 30% probability displacement ellipsoids (hydrogen atoms are omitted for clarity). (b) Coordination polyhedra for Cu1 and Cu1[#] atoms of complex 1.

Table 2 Selected bond lengths (Å) and angles (°) for complex 1.

The Cu(II) atom (Cu1) is penta-coordinated by two oxime nitrogen (N1 and N2) and one phenoxo oxygen (O2) atom from the completely deprotonated $(L)^{-}$ units and two μ -acetate oxygen (O5 and O5[#]) atoms (Fig. 4a). The coordination environment around the Cu1 atom is best described as a slightly distorted tetragonal pyramidal geometry. The τ value is estimated to be $\tau = 0.1295$ (Fig. 4b) [51–54]. The oxime nitrogen (N1 and N2) atoms and phenolic oxygen (O2) atom of the (L)⁻ unit, and the μ -acetate oxygen (O5) atom constitute together the basal plane (Cu1-N1, 1.996(2) Å; Cu1-N2, 1.985(2) Å; Cu1-O2, 1.906(2) Å and Cu1-O5, 1.988(2) Å), and another μ -acetate oxygen (O5[#]) atom occupies the vertex position (Cu1-O5[#], 2.413(2) Å). The four coordination (N1, N2, O2 and O5) atoms on the base plane deviate from the mean plane, with N2 and O2 above average by 0.249(2) and 0.287(2) Å, and N1 and O5 below average by 0.246(2) and 0.289(2) Å, respectively. Meanwhile, the Cu1 atom is 0.276(2) Å displaced from the mean plane and the Cu...Cu distance is 3.359(2) Å. Additionally, the dihedral angle between the coordination planes of O2-Cu1-N1 and O5-Cu1-N2 is 23.59(2)°. The dihedral angle between the benzene ring and basal plane (metal N₂O plane) is $11.82(2)^{\circ}$, which defined as shown in Fig. S4a.

It is worth noting that the μ -acetate ions play an important role in the construction of propeller-type motif. As shown in Figs. 5 and 6, in the complex **1**, the two monodentate acetate ions bridge two Cu(II) atoms through the oxygen atoms, forming a binuclear symmetric structure. In the process of forming complex **1**, the oxygen (O5 and O5[#])

atoms of the two μ -acetate ions both occupy the vertex positions of the tetragonal pyramidal geometries and participate in the construction of the base plane of another tetragonal pyramidal geometry, which makes the structure of complex **1** exhibiting a highly distorted symmetry configuration.

Fig. 5. Acetic acid coordinated modes for complexes 1 and 2.

Fig. 6. Perspectives of the core in complexes 1, 2 and 3.

3.3.2. Complex 2

As shown in Fig. 7 and Table 3, X-ray crystallographic analysis of complex 2 $([{Ni_3(\mu-OAc)_2(L)_2(OAc)_2}]\cdot CHCl_3)$ reveals an asymmetric trinuclear structure. It crystallizes in the triclinic system, space group *P* -1, consists of three Ni(II) atoms, two completely deprotonated $(L)^-$ units, two μ -acetate ions, two chelating acetate ions and one crystallized chloroform molecule.

Fig. 7. (a) Molecular structure and atom numberings of complex 2 with 30% probability displacement ellipsoids (hydrogen atoms are omitted for clarity). (b) Coordination polyhedra for Ni1, Ni2 and Ni3 atoms of complex 2.

 Table 3 Selected bond lengths (Å) and angles (°) for complex 2.

As illustrated in Fig. 7a, the coordination model around the terminal Ni(II) (Ni2 and Ni3) atoms are very similar. Ni2 is hexa-coordinated by two oxime nitrogen (N3 and N4) atoms and one phenolic oxygen (O6) atom of the completely deprotonated (L)⁻ unit, two oxygen (O13 and O14) atoms from the chelating acetate ion and one oxygen (O9) atom from the μ -acetate ion. Ni3 is also hexa-coordinated by two oxime nitrogen (N1 and N2) atoms and one phenolic oxygen (O2) atom of the completely deprotonated (L)⁻ unit, two oxygen (O15 and O16) atoms from the chelating acetate ion and one oxygen (O12) atom from the μ -acetate ion. The coordination geometry around the terminal Ni(II) (Ni2 or Ni3) atom is found to be a slightly distorted octahedron [55–58]. The two Ni…Ni distances between the terminal (Ni2 or Ni3) and central Ni1 atoms are 3.496(2) and 3.507(2) Å, respectively. Meanwhile, the coordination sphere of the central Ni(II) (Ni1) atom is completed by two μ -phenoxo oxygen (O2 and O6) atoms and two methoxyl

oxygen (O1 and O5) atoms from two (L)⁻ units and two μ -acetate oxygen (O10 and O11) atoms, which indicates the central Ni1 atom finally has an O₂O₂O₂ coordination environment (Fig. 7b) [59–61]. The μ -acetate ions and two chelating acetate ions have two different coordination modes in the structure of complex 2 (Fig. 5). The two μ -acetate ions has been bridged with central Ni1 and terminal Ni2 or Ni3 atoms in both cases via familiar Ni–O–C–O–Ni bridges with the four μ -acetate oxygen (O9, O10, O11 and O12) atoms [62]. The dihedral angles between the benzene rings and basal planes (N₂O planes) are 16.71(2) and 10.74(2)°, respectively, which defined as shown in Fig. S4b. Besides, the four oxygen (O13, O14, O15 and O16) atoms of the chelating acetate ions coordinated with the terminal Ni2 or Ni3 atom, respectively, which satisfies the coordination number of Ni(II) atoms [63–66]. As shown in Figs. 5 and 6. Different from complex 1, in the complex 2, two bidentate acetate ions bridge the two terminals Ni(II) atoms by the two oxygen atoms, in addition, two acetate ions coordinate to the two terminal Ni(II) atoms in chelating bidentate, forming a trinuclear asymmetric structure. Different amounts of bridging metal centers of acetate ions may be due to different coordination numbers of different metal atoms, Cu(II) atoms tend to form a tetra-coordinated or penta-coordinated structures, and Ni(II) atoms are usually hexa-coordinated structures. In the asymmetric trinuclear structure, the framework of the butterfly-type motif is constructed by three Ni(II) atoms, and the deprotonated $(L)^{-1}$ units as the wings of the butterfly.

3.3.3. Complex 3

The crystallographic data reveal that complex **3** ($[Co_4(L')_4(MeOH)_4]$) crystallizes in the triclinic system, space group *P* -1, consists of four Co(II) atoms, four completely deprotonated $(L')^{2-}$ units and four coordinated methanol molecules.

As shown in Fig. 8a and Table 4, the crystal structure indicates that complex **3** is an asymmetric homo-tetranuclear complex, the coordination environment of Co1 atom is hexa-coordinated by one oxime nitrogen (N1) atom, one phenolic oxygen (O6) atom and one hydroxyl oxygen (O2) atom from the completely deprotonated $(L')^{2-}$ unit, one oxygen (O9) atom from the coordinated methanol molecule and the other two hydroxyl oxygen (O1 and O3) atoms from the adjacent half-salamo units. The coordination environment of other three Co(II) atoms in complex **3** are similar to Co1. All of the Co(II) atoms in complex **3** have slightly distorted octahedral geometries (Fig. 8b) [67].

The dihedral angles between the benzene rings and basal planes (NO₂ planes) are 14.80(2), 10.45(2), 5.26(2) and 1.52(2)° respectively, which defined as shown in Fig. S4c. The coordinated methanol molecules have satisfied the coordination number of Co(II) atoms. As shown in Fig. 5, the ligand H₂L' is derived from the cleavage of HL in the complexation of HL and Co(II) salt. The fragility of the ligand is similar to that reported previously [68–70]. This phenomenon is found in the salamo-type Co(II) complexes for the first time. The different directions of half-salamo units form the four sails of the windmill-type motif and the homo-tetranuclear of central position forms the basic framework. The cubic crystal skeleton is constructed by Co₄O₄, the four Co(II) atoms and four oxygen atoms occupy the vertex positions of the cube, respectively, and each surface is formed by two Co(II) atoms and two oxygen atoms lying on the diagonal, and the average lengths of the two Co…Co and O…O lengths are in the ranges of 3.132(3)-3.226(2) and 2.680(2)-2.796(3) Å, respectively (Fig. S4c).

Fig. 8. (a) Molecular structure and atom numberings of complex **3** with 30% probability displacement ellipsoids (hydrogen atoms are omitted for clarity). (b) Coordination polyhedra for Co1, Co2, Co3 and Co4 atoms of complex **3**.

Table 4 Selected bond lengths (Å) and angles (°) for complex 3.

3.4. Intermolecular Interactions

3.4.1. Complex 1

The main interactions in complex **1** are listed in Table S1, two pairs of the intramolecular N2–H2A···O1, N2–H2A···O2, N2–H2A···O5 and N2–H2B···O6 hydrogen bonds are formed. The protons (-N2H2A and -N2H2B) as donors from the $(L)^-$ units form hydrogen bonds with oxygen (O5) atom of the μ -acetate ion, phenolic oxygen (O2) and methoxyl oxygen (O1) atoms as acceptors of the $(L)^-$ units, respectively. The proton (-N2H2B) as donor from the $(L)^-$ unit forms hydrogen bond with oxygen (O6) atom as acceptor of the μ -acetate ion (Fig. 9a) [71]. Besides, two of the intermolecular C-H··· π stacking interactions in complex **1** are formed (Fig. 10). The Cg5 (C₂–C₇) of phenyl ring as acceptor from the $(L)^-$ unit forms two hydrogen bonds with the protons (-C1H1A and -C8H8) as donors of two adjacent complex **1** molecules, which adopts a 3D intermolecular structure [72]. The polyhedra of the Cu1 and Cu1[#]

atoms of complex **1** are shown in Fig. 10. The octahedra around the Cu atoms are depicted in green colour.

Fig. 9. Intramolecular hydrogen bonds of complexes **1**, **2** and **3** (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity).

Fig. 10. View of the 3D intermolecular structure of complex 1 showing the C-H $\cdots \pi$.

3.4.2. Complex 2

As illustrated in Fig. 9b and Table S2, four of the intramolecular N2–H2B···O10, N4-H4B···O11, C9-H9A···O15 and C19-H19A···O14 hydrogen bonds in complex 2 are formed. The protons (-N2H2B and -N4H4B) from imine groups of the (L)⁻ units form hydrogen bonds with oxygen (O10 and O11) atoms of the μ -acetate ions and the protons (-C9H9A and -C19H19A) of ethylenedioxime carbon atoms of the (L)⁻ units form hydrogen bonds with oxygen (O14 and O15) atoms of the chelating acetate ions [73]. As shown in Fig. 11, the 3D intermolecular structure of complex 2 is composed of two parts. The first part was linked by intermolecular N2-H2A...O15, N4-H4A···O14, C5-H5···O16 and C29-H29···O16 hydrogen bonds, the protons (-N2H2A, -N4H4A and -C5H5) of the (L)⁻ units form three hydrogen bonds with the oxygen (O15, O14 and O16) atoms of three adjacent complex 2 molecules. Meanwhile, the proton (-C29H29) of the crystallizing chloroform molecule as donor atom forms hydrogen bond with oxygen (O16) atom of adjacent complex 2 molecule [73]. Another part was made up of the C-H··· π and C-Cl··· π stacking interactions. The Cg6 (C₂–C₇) and Cg7 (C_{12} – C_{17}) of phenyl rings as acceptors form two stacking interactions with the protons (-C29Cl3 and -C11H11A) from the crystallizing chloroform molecules and the adjacent complex 2 molecules, respectively. The crystallizing chloroform molecules play an important role in intermolecular construction of complex 2 [74], which are similar to that in the previously reported complex, the strong intermolecular interactions were formed by solvent molecule. Finally, the complex formed a 1D intermolecular structure. The existence of the solvent molecules made the intermolecular force more abundant, and the structure more stable [75]. In addition,

complex 2 molecules form a 3D intermolecular structure by intermolecular hydrogen bonds, C-H··· π and C-Cl··· π stacking interactions. The polyhedra of the Ni1, Ni2 and Ni3 atoms of complex 2 are shown in Fig. 11. The octahedra around the Ni atoms are depicted in sky blue colour.

Fig. 11. View of the 3D intermolecular structure of complex 2 showing the C-H $\cdots\pi$.

3.4.3. Complex 3

As shown in Fig. 9c and Table S3, there are abundant intramolecular hydrogen bonds in complex **3**. The coordinated methanol hydrogen atoms as donors form hydrogen bonds with phenolic oxygen (O5, O6, O7 and O8) atoms and methoxyl oxygen (O11, O13, O14 and O15) atoms. The protons (–C9H9A, –C19H19A and –C29H29B) from ethylenedioxime carbon atoms form hydrogen bonds with oxime nitrogen (N1, N3 and N4) atoms [74]. Besides, the protons (–C10H10B, –C20H20B and –C40H40A) from ethylenedioxime carbon atoms form hydrogen bonds with the coordinated methanol oxygen (O12,O10 and O9) atoms. Furthermore, complex **3** molecules form a dimer by one pair of intermolecular hydrogen bonds (C29-H29A…O16) (Fig. 12) [74]. The polyhedra of Co1, Co2, Co3 and Co4 atoms of complex **3** are depicted in Fig. 12. The octahedra around the Co atoms are depicted in orange colour.

Fig. 12. View of a dimer formed by complex 3 molecules via the C-H \cdots O hydrogen bonding interactions.

3.5. Magnetic Properties

The magnetic analyses of the complexes 1 and 2 were tested under the applied magnetic field of 1000 Oe, and the magnetic susceptibility data of the complexes 1 and 2 in the temperature range of 2–300 K were measured, the measured sample with the single-crystals of the complexes 1 and 2. The temperature dependence of magnetic susceptibilities of complexes 1 and 2 are shown in Figs. 13 and 14, respectively. Because the ligand in the complex 3 is broken, it is not easy to get than the complexes 1

and **2**, and the magnetic measurement requires a large number of crystals, so there is no magnetic study of the complex **3**.

The $\chi_M T$ value at 300 K for complex **1** is 0.76 emu K mol⁻¹, which is larger than the the value of 0.7 emu K mol⁻¹ expected for two Cu(II) (S = 1/2) magnetically isolated ions. Upon lowering the temperature, the $\chi_M T$ value of complex **1** gradually decreases to reach a minimum value of 0.65 emu K mol⁻¹ at 50 K, which implies that a weak antiferromagnetic interaction exists in such a complex [76]. What is more, the magnetic susceptibilities ($1/\chi_M$) obey the Curie–Weiss law in the 2–300 K temperature range, giving a negative Weiss constant $\theta = -11.56$ K and C = 0.81 emu K mol⁻¹ (Fig. 13, inset), the best-fit for $\chi_M T$ vs. T with a Hamiltonian $H = -2J(S_{Cu1} \cdot S_{Cu2})$ leads to the parameters J = -21.86 cm⁻¹ for complex **1**, and confirming the antiferromagnetic interaction exhibited again [76]. It has similar property to the reported salen-type binuclear Cu(II) complex [77].

Fig. 13. Plots of $\chi_M T$ vs. T for complex **1** from 2 to 300 K. Inset: Temperature dependence of χ_M^{-1} . The red solid lines represent the best fitting results.

The $\chi_M T$ value at 300 K for complex **2** is 4.21 emu K mol⁻¹, which is larger than the the value of 3 emu K mol⁻¹ expected for three Ni(II) (S = 1) magnetically isolated ions. Upon lowering the temperature, the $\chi_M T$ value of complex **2** gradually decreases to reach a maximum value of 5.22 emu K mol⁻¹ at 14 K, the $\chi_M T$ value increased with decreasing temperature, indicating an intramolecular ferromagnetic interaction between the three Ni(II) atoms [76]. Then, the $\chi_M T$ value reduced to 1.81 emu K mol⁻¹ when the temperature reached 2 K. The magnetic susceptibilities $(1/\chi_M)$ obey the Curie–Weiss law giving a negative Weiss constant $\theta = 3.32$ K and C = 4.22 emu K mol⁻¹ (Fig. 14, inset), the best-fit for $\chi_M T$ vs. T with a Hamiltonian $H = -2J(S_{Ni1} \cdot S_{Ni2} + S_{Ni1} \cdot S_{Ni3})$ leads to the parameters J = 49.76 cm⁻¹ for complex **2**, exhibiting the ferromagnetically interaction in complex **2** [76]. Compared with the similar Ni(II) complex reported previously [63], it has different properties, probably due to the different coordination environment and bridging mode of the Ni(II) atoms.

Fig. 14. Plots of $\chi_M T$ *vs. T* for complex **2** from 80 to 300 K. Inset: Temperature dependence of χ_M^{-1} . The red solid lines represent the best fitting results.

3.6. Hirshfeld Surface Analyses

The Hirshfeld surfaces [78] provide a three-dimensional picture of close contacts in a crystal, and these contacts can be summarized in a fingerprint plot. The Hirshfeld surfaces of complexes **1**, **2** and **3** are depicted in Fig. S5, showing surfaces that have been mapped over *d*norm (a), *shape index* (b) and *curvedness* (c). Another important supplement for Hirshfeld surface is the 2D fingerprint plots [79], allowing quantitative analysis of the nature and type of intermolecular interactions between molecules. The $O \cdots H/H \cdots O$ intermolecular interactions are distinct spikes in the 2D fingerprint plot (Fig. 15). The $O \cdots H$ interactions are represented via a spike in the bottom left (donor) area of the fingerprint plot (Fig. 15), the $H \cdots O$ interactions are represented via a spike in the bottom right (acceptor) region of the fingerprint plot. The fingerprint plots can be decomposed to highlight particular atom pair close contacts. This decomposition enables separation of contributions from different interaction types, which overlap in the full fingerprint.

The relative contribution of the different interactions to the Hirshfeld surface was calculated for complexes **1**, **2** and **3** have been given in Fig. 16. The proportion of $O \cdots H/H \cdots O$, $C \cdots H/H \cdots C$ and $H \cdots H$ interactions comprises 25.1%, 16.8% and 51.3% of the total Hirshfeld surfaces for each molecule of the complex **1**, respectively. For the complex **2**, the proportion of $O \cdots H/H \cdots O$, $C \cdots H/H \cdots C$, $C I \cdots H/H \cdots CI$ and $H \cdots H$ interactions are 20.3%, 6.2%, 21.2%, and 47%, respectively, which can be seen that the interaction of $C I \cdots H$ by chloroform molecule is only less than $H \cdots H$, so the chloroform molecule makes the structure more stable. For the complex **3**, the proportion of $O \cdots H/H \cdots O$, $C \cdots H/H \cdots C$ and $H \cdots H$ interactions are 9.1%, 15.9% and 74.4%, respectively. The main contact in complexes **1**, **2** and **3** is $H \cdots H$ interactions. Because there are more hydrogen atoms in the crystal structures and most of them are short-range action, the interaction between H...H is the most, which is similar to the previously reported complexes [80].

Fig. 15. Fingerprint plot of the complexes 1 (a), 2 (b) and 3 (c): full and resolved into

full and resolved into $O \cdots H$, $C \cdots H$, $C \cdots H$ and $H \cdots H$ contacts showing the percentages of contacts contributed to the total Hirshfeld surface area of molecule.

Fig. 16. Relative contributions of various intermolecular contacts to the Hirshfeld surface area in complexes 1, 2 and 3.

4. Conclusions

The self-assembling of di-, tri- and tetra-nuclear Cu(II), Ni(II) and Co(II) complexes based on a half-salamo ligand HL were successfully synthesized and characterized structerally. The crystal structures of complexes 1, 2 and 3 show propeller-, butterfly- and windmill-type motifs, respectively. In complexes 1 and 2, the ideal size, shape as well as strong coordination ability of OAc⁻ as an anion significantly stabilize the aesthetic structure, while in complex 3, the hydroxyl radical of an unexpected ligand H₂L', which derived from the cleavage of HL are coordinated with three Co(II) atoms at the same time. Furthermore, magnetic properties of complexes 1 and 2 were also studied. The magnetic susceptibility measurement of the complex 1 shows that the Cu(II) centers are antiferromagnetically coupled. While, in the complex 2 the Ni(II) ions are ferromagnetically coupled. Quantification of the intermolecular interactions present in all complexes was realized by Hirshfeld surface analyses and 2D fingerprint plots. The close contacts of these complexes are dominated by H...H, C...H and O···H contacts. Meanwhile, the intermolecular interactions presented in the total crystal structures were discussed by Hirshfeld surface analyses in form of decomposed fingerprint plots.

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References

- [1] L. Gao, F. Wang, Q. Zhao, Y. Zhang, W.K. Dong, Polyhedron 139 (2018) 7.
- [2] J. Hao, L.L. Li, J.T. Zhang, S.F. Akogun, L. Wang, W.K. Dong, Polyhedron 134 (2017) 1.
- [3] F. Wang, L. Gao, Q. Zhao, Y. Zhang, W.K. Dong, Y.J. Ding, Spectrochim. Acta. A 190 (2018) 111.
- [4] H.L. Wu, G.L. Pan, Y.C. Bai, Y.H. Zhang, H. Wang, F.R. Shi, X.L. Wang, J. Kong, J. Photochem. Photobiol. B 135 (2014) 33.
- [5] X.Y. Li, Q.P. Kang, L.Z. Liu, J.C. Ma, W.K. Dong, Crystals 8 (2018) 43.
- [6] H.L. Wu, G.L. Pan, Y.C. Bai, H.Wang, J. Kong, F. Shi, Y.H. Zhang, X.L. Wang, J. Chem. Res. 38 (2014) 211.
- [7] H.L. Wu, Y.C. Bai, Y.H. Zhang, G.L. Pan, J. Kong, F.R. Shi, X.L. Wang, Z. Anorg. Allg. Chem. 640 (2014) 2062.
- [8] Y. Xu, D. Yuan, Y. Wang, Y. Yao, Dalton Trans. 46 (2017) 5848.
- [9] R. Irie, T. Katsuki, Chem. Rec. 4 (2004) 96.
- [10] T. Nabeshima, S. Akine, Chem. Rec. 8 (2008) 240.
- [11] H.L. Wu, GL. Pan, Y.C. Bai, H. Wang, J. Kong, Res. Chem. Intermed. 41 (2015) 3375.
- [12] S. Akine, T. Taniguchi, T. Nabeshima, Inorg. Chem. 43 (2004) 6142.
- [13] G. Li, J. Hao, L.Z. Liu, W.M. Zhou, W.K. Dong, Crystals 7 (2017) 217.
- [14] W.K. Dong, J.C. Ma, L.C. Zhu, Y. Zhang, X.L. Li, Inorg. Chim. Acta 445 (2016) 140.
- [15] Y.D. Peng, X.Y. Li, Q.P. Kang, G.X. An, Y. Zhang, W.K. Dong, Crystals 8 (2018) 107.
- [16] W.T. Guo, X.Y. Li, Q.P. Kang, J.C. Ma, W.K. Dong, Crystals 8 (2018) 154.
- [17] S. Akine, T. Taniguchi, T. Nabeshima, Angew. Chem. Int. Ed. 41 (2002) 4670.
- [18] W.K. Dong, Y.X. Sun, C.Y. Zhao, X.Y. Dong, L. Xu. Polyhedron 29 (2010) 2087.
- [19] S. Akine, T. Taniguchi, W.K. Dong, S. Masubuchi, T. Nabeshima, J. Org. Chem. 70 (2005) 1704.
- [20] X.Y. Dong, L. Gao, F. Wang, X.Y. Li, Y. Zhang, W.K. Dong, Crystals 7 (2017) 267.

- [21] Y.J. Dong, X.Y. Dong, W.K. Dong, Y. Zhang, L.S. Zhang, Polyhedron 123 (2017) 305.
- [22] C.Y. Chen, J.W. Zhang, Y.H. Zhang, Z.H. Yang, H.L. Wu, G.L. Pan, Y.C. Bai, J. Coord. Chem. 68 (2015) 1054.
- [23] X.Q. Song, P.P. Liu, Z.R. Xiao, X. Li, Y.A. Liu, Inorg. Chim. Acta 438 (2015) 232.
- [24] P.P. Liu, C.Y. Wang, M. Zhang, X.Q. Song, Polyhedron 129 (2017) 133.
- [25] P.P. Liu, L. Sheng, X.Q. Song, W.Y. Xu, Y.A. Liu, Inorg. Chim. Acta 434 (2015) 252.
- [26] L.Q. Chai, L.J. Tang, L.C. Chen, J.J. Huang, Polyhedron 122 (2017) 228.
- [27] X.Y. Dong, S.F. Akogun, W.M. Zhou, W.K. Dong, J. Chinese Chem. Soc. 64 (2017)412.
- [28] P. Wang, L. Zhao, Synth. React. Inorg. Met.-Org, Nano-Met. Chem. 46 (2016) 1095.
- [29] J.H. Hu, Y. Sun, J. Qi, Q. Li, T.B. Wei, Spectrochim. Acta Part A, 175 (2017) 125.
- [30] L.Q. Chai, K.Y. Zhang, L.J. Tang, J.Y. Zhang, H.S. Zhang, Polyhedron 130 (2017) 100.
- [31] C.H. Tao, J.C. Ma, L.C. Zhu, Y. Zhang, W. K. Dong, Polyhedron 128 (2017) 38.
- [32] X.Q. Song, Y.Q. Peng, G.Q. Cheng, X.R. Wang, P.P. Liu, W.Y. Xu, Inorg. Chim. Acta 427 (2015) 13.
- [33] X.Q. Song, G.Q. Cheng, Y.A. Liu, Inorg. Chim. Acta 450 (2016) 386.
- [34] S. Akine, Y. Morita, F. Utsuno, T. Nabeshima, Inorg. Chem. 48 (2009) 10670.
- [35] J. Hao, X.Y. Li, Y. Zhang, W.K. Dong, Materials 11 (2018) 523.
- [36] L. Wang, X.Y. Li, Q. Zhao, L.H. Li, W.K. Dong, RSC Adv. 7 (2017) 48730.
- [37] W.K. Dong, J.C. Ma, L.C. Zhu, Y.X. Sun, S.F. Akogun, Y. Zhang, Cryst. Growth Des. 16 (2016) 6903.
- [38] S. Akine, T. Matsumoto, T. Taniguchi, T. Nabeshima, Inorg. Chem. 44 (2005) 3270.
- [39] G.M. Sheldrick, SADABS: Program for Empirical Absorption Correction of Area Detector Data, University of Gottingen, Gottingen, Germany, (1996).
- [40] G.M. Sheldrick, SHELXL97: Program for the Refinement of Crystal Structures, University of Gottingen, Germany, (1997).
- [41] Y.J. Dong, X.L. Li, Y. Zhang, W.K. Dong, Supramol. Chem. 29 (2017) 518.

- [42] B.J. Wang, W.K. Dong, Y. Zhang, S.F. Akogun, Sensors and Actuators B 247 (2017) 254.
- [43] L.Gomes, E. Pereira, B. Castrode, J. Chem. Soc. Dalton. Trans. 8 (2000) 1373.
- [44] X.Q. Song, P.P. Liu, Y.A. Liu, J.J. Zhou, X.L. Wang, Dalton. Trans. 45 (2016) 8154.
- [45] L.Q. Chai, J.Y. Zhang, L.C. Chen, Y.X. Li, L.J. Tang, Res. Chem. Intermed. 42 (2016) 3473.
- [46] X.Y. Li, L. Chen, L. Gao, Y. Zhang, S.F. Akogun, W.K. Dong, RSC Adv. 7 (2017) 35905.
- [47] Y.X. Sun, L. Xu, T.H. Zhao, S.H. Liu, G.H. Liu, X.T. Dong, Synth. React. Inorg. Met.-Org. Nano-Met. Chem. 43 (2013) 509.
- [48] Y.X. Sun, X.H. Gao, Synth. React. Inorg. Met.-Org, Nano-Met. Chem. 41 (2011) 973.
- [49] L.Q. Chai, J.J. Huang, J.Y. Zhang, Y.X. Li, J. Coord. Chem. 68 (2015) 1224.
- [50] P. Wang, L. Zhao, Asian J. Chem. 4 (2015) 1424.
- [51] L. Xu, L.C. Zhu, J.C. Ma, Y. Zhang, J. Zhang, W.K. Dong, Z. Anorg. Allg. Chem. 641 (2015) 2520.
- [52] L. Wang, J.C. Ma, W.K. Dong, L.C. Zhu, Y. Zhang, Z. Anorg. Allg. Chem. 642 (2016) 834.
- [53] Y.J. Dong, J.C. Ma, L.C. Zhu, W.K. Dong, Y. Zhang, J. Coord. Chem. 70 (2017) 103.
- [54] L.Q. Chai, Y.X. Li, L.C. Chen, J.Y. Zhang, J.J. Huang, Inorg. Chim. Acta 444 (2016) 193.
- [55] X.Y. Dong, Q.P. Kang, X.Y. Li, J.C. Ma, W.K. Dong, Crystals 8 (2018) 139.
- [56] J.H. Hu, J.B. Li, J. Qi, Y. Sun, Silicon Relat. Elem. 191 (2016) 984.
- [57] Y.H. Yang, J. Hao, X.Y. Li, Y. Zhang, W.K. Dong, Crystals 8 (2018) 174.
- [58] Y.X. Sun, L. Wang, X.Y. Dong, Z.L. Ren, W.S. Meng, Synth. React. Inorg. Met.-Org, Nano-Met. Chem. 43 (2013) 599.
- [59] P. Wang, L. Zhao, Spectrochim. Acta Part A 135 (2015) 342.
- [60] A.W. Addison, T.N. Rao, J. Reedijk, J. Rijn, G.C. Verschoor, J. Chem. Soc., Dalton Trans. 7 (1984) 1349
- [61] H.L. Wu, Y. Bai, J.K. Yuan, H. Wang, G.L. Pan, X.Y. Fan, J. Kong, J. Coord. Chem.

65 (2012) 2839.

- [62] S. Akine, A. Akimoto, T. Shiga, H. Oshio, T. Nabeshima, Inorg. Chem. 47 (2008) 875.
- [63] L.W. Zhang, X.Y. Li, Q.P. Kang, J.C. Ma, W.K. Dong, Crystals 8 (2018) 173.
- [64] X.Y. Dong, X.Y. Li, L.Z. Liu, H. Zhang, Y.J. Ding, W.K. Dong, RSC Adv. 7 (2017) 48394.
- [65] Q.P. Kang, X.Y. Li, Q. Zhao, J.C. Ma, W.K. Dong, Appl Organometal Chem. (2018) e4379.
- [66] X.Y. Dong, Q.P. Kang, B.X. Jin, W.K. Dong, Z. Naturforsch. 72 (2017) 415.
- [67] L. Chen, W.K. Dong, H. Zhang, Y. Zhang, Y.X. Sun, Cryst. Growth Des. 17 (2017) 3636.
- [68] J.C. Ma, X.Y. Dong, W.K. Dong, Y. Zhang, L.C. Zhu, J.T. Zhang, J. Coord. Chem. 69 (2016) 149.
- [69] L.Q. Chai, G. Wang, Y.X. Sun, W.K. Dong, L. Zhao, X.H. Gao, J. Coord. Chem. 65 (2012) 1621.
- [70] F. Wang, L.Z. Liu, L. Gao, W.K. Dong, Spectrochim. Acta Part A 203 (2018) 56.
- [71] L. Gao, C. Liu, F. Wang, W.K. Dong, Crystals 8 (2018) 77.
- [72] S.S. Zheng, W.K. Dong, Y. Zhang, L. Chen, Y.J. Ding, New J. Chem. 41 (2017) 4966.
- [73] Z.F. Li, S.J. Wu, H. Ding, H. Lu, J.Y. Liu, Q.S. Huo, J.Q. Guan, Q.B. Kan, New J. Chem. 37 (2013) 4220.
- [74] X.Y. Dong, B.J. Wang, Q.P. Kang, W.K. Dong, Appl Organometal Chem. (2018) e4373.
- [75] X.Y. Li, Q.P. Kang, Q. Zhao, J.C. Ma, W.K. Dong, Phosphorus, Sulfur Silicon Relat. Elem. 193 (2018) 464.
- [76] H. Zhang, W.K. Dong, Y. Zhang, S.F. Akogun, Polyhedron 133 (2017) 279.
- [77] Q. Evrard, C. Leuvrey, P. Farger, E. Delahaye, P. Rabu, G. Taupier, K.D. Dorkenoo,J.M. Rueff, N. Barrier, O. Perez, G. Rogez, Cryst. Growth Des. 18 (2018) 1809.
- [78] A.D. Martin, K.J. Hartlieb, A.N. Sobolev, C.L. Raston, Cryst. Growth Des. 10 (2010) 5302.
- [79] A.L. Rohl, M. Moret, W. Kaminsky, K. Claborn, J.J. Mckinnon, B. Kahr, Cryst. Growth Des. 8 (2008) 4517.

[80] H.F. Clausen, M.S. Chevallier, M.A. Spackmanb, B.B. Iversen, New J. Chem. 34 (2010) 193.

Complex	1	2	3
Formula	$C_{24}H_{32}Cu_2N_4O_{12}$	C29H39Cl3N4Ni3O16	$C_{44}H_{60}Co_4N_4O_{20}$
Formula weight	695.61	982.12	1200.68
Temperature (K)	296 (2)	296(2)	173.00(10)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	<i>P</i> 2 ₁ /c	<i>P</i> -1	<i>P</i> -1
Unit cell dimensions			
<i>a</i> (Å)	10.729(5)	13.016(4)	14.0570(13)
<i>b</i> (Å)	15.964(8)	13.101(4)	14.8345(14)
<i>c</i> (Å)	9.351(5)	16.083(5)	16.9474(16)
α (°)	90°	113.500(7)	70.111(9)
β (°)	116.432(8)°	95.345(7)	74.191(8)
γ(°)	90°	112.054(7)	71.734(8)
$V(Å^3)$	1434.1(12)	2233.8(12)	3100.9(6)
Ζ	2	2	2
D_c (g cm ⁻³)	1.611	1.460	1.286
$\mu (\mathrm{mm}^{-1})$	1.551	1.495	1.117
F (000)	716	1008	1240
Crystal size (mm)	$0.26 \times 0.22 \times 0.19$	$0.28 \times 0.26 \times 0.22$	$0.26 \times 0.22 \times 0.18$
θ Range (°)	2.120-25.004	2.575-25.082	3.350-25.008
Index ranges	$-12 \le h \le 12$,	$-15 \le h \le 15$,	$-16 \le h \le 16$,
	$-18 \le k \le 14$,	$-15 \le k \le 14$,	$-17 \le k \le 17$,
	$-8 \le l \le 11$	$-18 \le l \le 19$	$-17 \le l \le 20$
Reflections collected	7875	7769	20058
Independent reflections	2522	7769	10908
R _{int}	0.0186	0.0626	0.0487
Completeness	99.8%	98.4%	99.7%
Data/restraints/parameters	2522/0/192	7769/0/503	10908/16/670
GOF	1.039	0.980	1.012
${}^{\mathrm{a}}R_{1} / {}^{b}wR_{2} \left[I > 2\sigma(I)\right]$	0.0244/ 0.0657	0.0663/0.1742	0.0495/0.1040
largest differences	0.338/-0.197	1.513/-1.083	0.645/-0.653
peak and hole (e $Å^{-3}$)			

 Table 1 Crystallographic data and refinement parameters for complexes 1, 2 and 3.

 ${}^{a}R_{1} = \Sigma ||F_{o}| - |F_{c}||\Sigma ||F_{o}|; \ {}^{b}wR_{2} = [\Sigma w(F_{o}^{2} - F_{c}^{2})^{2}/\Sigma w(F_{o}^{2})^{2}]^{1/2}.$

Bond			
Cu1-O2	1.906(2)	Cu1-N1	2.000(2)
Cu1-O5	1.988(2)	Cu1-N2	1.985(2)
Cu1-O5 [#]	2.413(2)	Cu1 [#] -O5	2.413(2)
Angles			
O2-Cu1-N2	166.19(7)	O2-Cu1-O5	86.20(8)
N2-Cu1-O5	86.99(8)	O2-Cu1-N1	90.02(8)
N2-Cu1-N1	100.62(8)	O5-Cu1-N1	158.42(7)
O2-Cu1-O5 [#]	85.45(6)	N2-Cu1-O5#	81.61(6)
O5-Cu1-O5 [#]	80.97(6)	N1-Cu1-O5 [#]	119.94(6)
Cu1-O5-Cu1#	99.03(6)		

Table 2 Selected bond lengths (Å) and angles (°) for complex 1.

Symmetry transformations used to generate equivalent atoms: # -x+1, -y+1, -z+2

Bond			
Ni1-O6	2.007(5)	Ni2-O6	2.021(5)
Ni1-O10	2.010(5)	Ni2-O9	2.071(4)
Ni1-O2	2.021(5)	Ni2-O13	2.117(5)
Ni1-O11	2.022(4)	Ni2-O14	2.160(5)
Ni1-O5	2.132(4)	Ni2-N3	2.109(5)
Ni1-O1	2.178(5)	Ni2-N4	2.053(5)
Ni3-O2	1.996(4)	Ni3-O15	2.139(4)
Ni3-O12	2.100(4)	Ni3-N1	2.107(6)
Ni3-O16	2.127(5)	Ni3-N2	2.048(6)
Angles			
O6-Ni1-O10	94.61(19)	O6-Ni2-N4	93.2(2)
O6-Ni1-O2	163.18(18)	O6-Ni2-O9	94.98(18)
O10-Ni1-O2	96.93(18)	N4-Ni2-O9	88.90(19)
O6-Ni1-O11	97.67(18)	O6-Ni2-N3	84.5(2)
O10-Ni1-O11	92.78(18)	N4-Ni2-N3	91.4(2)
O2-Ni1-O11	93.96(18)	O9-Ni2-N3	179.4(2)
O6-Ni1-O5	78.68(17)	O6-Ni2-O13	97.80(19)
O10-Ni1-O5	91.70(18)	N4-Ni2-O13	168.9(2)
O2-Ni1-O5	88.76(18)	O9-Ni2-O13	88.42(19)
011-Ni1-O5	174.44(17)	N3-Ni2-O13	91.4(2)
O6-Ni1-O1	90.41(19)	O6-Ni2-O14	159.62(17)
O10-Ni1-O1	174.02(19)	N4-Ni2-O14	107.2(2)
O2-Ni1-O1	77.49(19)	O9-Ni2-O14	86.72(19)
011-Ni1-O1	89.77(18)	N3-Ni2-O14	93.7(2)
O5-Ni1-O1	86.09(18)	O13-Ni2-O14	61.90(18)
O2-Ni3-N2	93.9(2)	O2-Ni3-O15	159.28(19)
O2-Ni3-O12	93.23(18)	N2-Ni3-O15	106.8(2)
O12-Ni3-O15	85.96(17)	O12-Ni3-N1	177.95(19)
N2-Ni3-O12	89.4(2)	N1-Ni3-O15	96.1(2)
O2-Ni3-N1	84.8(2)	O16-Ni3-O15	62.41(17)
N2-Ni3-N1	90.0(2)	O2-Ni3-O16	96.87(18)
N2-Ni3-O16	168.8(2)	O12-Ni3-O16	86.85(19)
N1-Ni3-O16	94.1(2)	Ni1-O6-Ni2	120.3(2)
Ni3-O2-Ni1	121.8(2)		

 Table 3 Selected bond lengths (Å) and angles (°) for complex 2.

Bond			
Co1-O1	2.192(2)	Co2-O2	2.108(3)
Co1-O2	2.020(2)	Co2-O3	2.198(2)
Co1-O3	2.114(3)	Co2-O4	2.010(2)
Co1-O6	1.991(2)	Co2-O5	1.981(2)
Co1-O9	2.159(3)	Co2-O10	2.199(3)
Co1-N1	2.105(3)	Co2-N2	2.102(3)
Co3-O1	2.010(2)	Co4-O1	2.118(3)
Co3-O2	2.174(2)	Co4-O3	2.020(2)
Co3-O4	2.103(3)	Co4-O4	2.184(2)
Co3-O7	1.987(2)	Co4-O8	2.001(2)
Co3-O18	2.171(3)	Co4-O12	2.146(2)
Co3-N3	2.110(3)	Co4-N4	2.114(4)
Angles			
O2-Co1-O1	79.24(9)	O2-Co2-O3	80.94(9)
O2-Co1-O3	85.06(9)	O2-Co2-O10	85.41(10)
O2-Co1-O9	93.63(9)	O3-Co2-O10	164.34(10)
O2-Co1-N1	92.25(11)	O4-Co2-O2	84.28(10)
O3-Co1-O1	80.72(9)	O4-Co2-O3	78.97(9)
O3-Co1-O9	85.69(10)	O4-Co2-O10	92.11(10)
O6-Co1-O1	87.83(9)	O4-Co2-N2	93.38(11)
O6-Co1-O2	166.56(10)	O5-Co2-O2	95.50(10)
O6-Co1-O3	96.55(10)	O5-Co2-O3	88.77(9)
O6-Co1-O9	99.79(10)	O5-Co2-O4	167.63(9)
O6-Co1-N1	88.10(11)	O5-Co2-O10	100.21(10)
O9-Co1-O1	165.11(10)	O5-Co2-N2	88.70(11)
N1-Co1-O1	107.40(11)	N2-Co2-O2	170.75(11)
N1-Co1-O3	170.86(10)	N2-Co2-O3	107.44(11)
N1-Co1-O9	85.77(11)	N2-Co2-O10	85.73(12)
O1-Co3-O2	79.90(9)	O1-Co4-O4	79.96(9)
O1-Co3-O4	84.45(10)	O1-Co4-O12	84.88(10)
O1-Co3-O18	90.44(10)	O3-Co4-O1	84.72(10)
O1-Co3-N3	93.02(11)	O3-Co4-O4	79.09(9)
O4-Co3-O2	80.50(9)	O3-Co4-O12	93.59(10)
O4-Co3-O18	86.24(11)	O3-Co4-N4	92.12(12)
O4-Co3-N3	170.01(10)	O8-Co4-O1	97.93(11)
O7-Co3-O1	170.16(10)	O8-Co4-O3	166.00(9)
O7-Co3-O2	90.45(9)	O8-Co4-O4	87.80(9)
O7-Co3-O4	95.97(10)	O8-Co4-O12	100.33(10)
O7-Co3-O18	99.41(11)	O8-Co4-N4	87.38(13)
O7-Co3-N3	88.18(11)	O12-Co4-O4	163.67(10)
O18-Co3-O2	164.24(11)	N4-Co4-O1	170.18(11)

 Table 4 Selected bond lengths (Å) and angles (°) for complex 3.

N3-Co3-O2	108.62(11)	N4-Co4-O4	108.62(11)
N3-Co3-O18	84.12(12)	N4-Co4-O12	86.04(12)
Co3-O1-Co1	100.18(9)	Co3-O1-Co4	99.24(10)
Co4-O1-Co1	93.64(10)	Co1-O2-Co2	98.77(11)
Co1-O2-Co3	100.50(9)	Co2-O2-Co3	94.02(9)
Co1-O3-Co2	93.22(10)	Co4-O3-Co1	99.01(11)
Co4-O3-Co2	100.48(10)	Co2-O4-Co3	99.17(10)
Co2-O4-Co4	101.25(10)	Co3-O4-Co4	94.40(9)



Fig. 1. Construction of complexes 1, 2 and 3 derived from the half-salamo ligand HL.



Fig. 2. The FT-IR spectra of the ligand HL and its complexes 1, 2 and 3 (cm⁻¹).



Fig. 3. The UV-vis spectra of HL and its complexes 1, 2 and 3 in methanol ($c = 2.5 \times 10^{-5}$ M).



Fig. 4. (a) Molecular structure and atom numberings of complex 1 with 30% probability displacement ellipsoids (hydrogen atoms are omitted for clarity). (b) Coordination polyhedra for Cu1 and Cu1[#] atoms of complex 1.



Fig. 5. Acetic acid coordinated modes for complexes 1 and 2.



Fig. 6. Perspectives of the core in complexes 1, 2 and 3.



Fig. 7. (a) Molecular structure and atom numberings of complex **2** with 30% probability displacement ellipsoids (hydrogen atoms are omitted for clarity). (**b**) Coordination polyhedra for Ni1, Ni2 and Ni3 atoms of complex **2**.



Fig. 8. (a) Molecular structure and atom numberings of complex **3** with 30% probability displacement ellipsoids (hydrogen atoms are omitted for clarity). (b) Coordination polyhedra for Co1, Co2, Co3 and Co4 atoms of complex **3**.





Fig. 9. Intramolecular hydrogen bonds of complexes **1**, **2** and **3** (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity).



Fig. 10. View of the 3D intermolecular structure of complex 1 showing the C-H $\cdots \pi$.



Fig. 11. View of the 3D intermolecular structure of complex 2 showing the C-H $\cdots \pi$.



Fig. 12. View of a dimer formed by complex 3 molecules via the C-H \cdots O hydrogen bonding interactions.



Fig. 13. Plots of $\chi_M T$ vs. T for complex **1** from 2 to 300 K. Inset: Temperature dependence of χ_M^{-1} . The red solid lines represent the best fitting results.



Fig. 14. Plots of $\chi_M T$ vs. T for complex **2** from 80 to 300 K. Inset: Temperature dependence of χ_M^{-1} . The red solid lines represent the best fitting results.



Fig. 15. Fingerprint plot of the complexes **1** (a), **2** (b) and **3** (c): full and resolved into full and resolved into $O \cdots H$, $C \cdots H$, $Cl \cdots H$ and $H \cdots H$ contacts showing the percentages of contacts contributed to the total Hirshfeld surface area of molecule.



Fig. 16. Relative contributions of various intermolecular contacts to the Hirshfeld surface area in complexes **1**, **2** and **3**.

Graphical Abstract



Graphical Abstract

The self-assembling of di-, tri- and tetra-nuclear metal(II) complexes shows propeller, butterfly and windmill type motifs, respectively. In complexes 1 and 2, the ideal size, shape as well as strong coordination ability of OAc⁻ as an anion significantly stabilize the aesthetic structure, while in complex 3, the hydroxyl radical of an unexpected ligand H₂L', which derived from the cleavage of HL are coordinated with three Co(II) atoms at the same time. Meanwhile, complexes 1, 2 and 3 possess a self-assembling 2D, 3D and 0D supramolecular structures by abundant noncovalent interactions. Besides, magnetic properties and Hirshfeld surface analyses were discussed.