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Synthesis, structure and properties of supramolecular Mn^{II}, Co^{II}, Ni^{II} and Zn^{II} complexes containing Salen-type bisoxime ligands

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ABSTRACT

Four supramolecular complexes $[MnL^1(H_2O)_2]$ (1), $\{[CoL^2(OAc)(H_2O)]_2Co\}$ -5CH₃CH₂OH (2), $\{[NiL^3(OAc)-(CH_3OH)]_2Ni\}$ -2CH₃COCH₃·2CH₃OH (3) and $\{[ZnL^2(OAc)]_2Zn\}$ -CHCl₃ (4), have been synthesized and characterized by elemental analyses, IR, UV–Vis spectra and X-ray diffraction techniques. All the complexes have the trinuclear configuration except for Mn^{II} complex being mononuclear configuration. Every trinuclear complex contains two acetate ions coordinate to the three metal ions via a familiar M–O–C–O–M (M = Co, Ni, Zn) coordinated mode. Although complexes 1 and 3 display 1D supramolecular chains, the different coordination environments (mononuclear in 1, trinuclear in 3) provoke divergence in the structures and aggregations of the chain subunits. Complex 2 forms a 3D hydrogen-bonding supramolecular networks possessing a channel composing of six O–H…O hydrogen bonds, while complex 4 exhibits a 2D hydrogen-bonding supramolecular networks with the formation of "grottos" occupied by chloroform molecules through intermolecular hydrogen-bond interactions. The spectral properties of the title complexes have been further discussed in detail.

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1. Introduction

The self-assembly and investigating synthetic routes have been developed maturely in the field of metal–organic complexes or supramolecular architectures [1]. And the development of metal–organic complex would be allowed to design new topologies of functional materials, in which pore size, coordination forms and functionality could be varied in large scale [2]. Recently a significant increase in the research of coordination supramolecules in which metal ion centers are bridged through organic molecules has been observed because of their enormous variety of intriguing structural topologies and their fascinating properties as well as great potential applications in optoelectronics, magnetism, and catalysis [3–10]. This subject is currently being pursued in our research, including functional oxime groups and metal atoms with magnetism, photoelectricity and catalysis.

To generate target complexes by design, a judicious choice of ligands provides a way of controlling supramolecular interactions. In general, ligands with certain features, such as rigidity and symmetry, are suitable for obtaining coordination supramolecules. In order to optimize the properties and explore the varied possibilities of transition metal coordination supramolecules, we have explored Salen-type bisoxime ligands (Scheme 1) with the interesting characteristics: they can provide N and O donor sites to coordinate with metal atoms, and the presence of O and N atoms and aromatic rings may form hydrogen bonds and π – π stacking interactions to extend and stabilize the whole framework series. Hence, diverse supramolecular structures may result from these interesting ligands.

Here, we selected three Salen-type bisoxime ligands for the design of the new coordinated supramolecule with oxime resulting in four new complexes: $[MnL^1(H_2O)_2]$ (1), $\{[CoL^2(OAc)(H_2O)]_2Co\}$ -5CH₃CH₂OH (2), $\{[NiL^3(OAc)(CH_3OH)]_2Ni\}$ -2CH₃COCH₃·2CH₃OH (3) and $\{[ZnL^2(OAc)]_2Zn\}$ -CHCl₃ (4). The structures 1 and 3 consist of a chain with hydrogen bonding or π - π stacking interactions, while 2 is self-assembled to a three-dimensional networks with channels composing of hydrogen bonds, and 4 exhibits a two-dimensional networks with "grottos" occupied by chloroform molecules. To our knowledge, the two- or three-dimensional transition metal networks assembled motifs with "grottos" or channels are uncommon.

2. Experimental

2.1. Materials and instruments

C, H, N elemental analyses were performed with a GmbH VarioEL V3.00 automatic elemental analysis instrument. Elemental analyses for Mn, Zn, Co and Ni were detected by an IRIS ER/ S·WP-1 ICP atomic emission spectrometer. Molar conductance





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Scheme 1. The synthesis route of the ligands: H_2L^1 , H_2L^2 and H_2L^3 .

value measurements were carried out on a model DDS-11D type conductivity bridge using 1.0×10^{-3} mol dm⁻³ solution in DMF at 18 °C. 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. ¹H NMR spectra were determined by German Bruker AVANCE DRX-400 spectroscopy. The electronic spectra were recorded with a RF-540 spectrophotometer in diluted DMF solution. Fluorescence measurements were made with a Hitachi F-4500 spectrophotometer and a shimadzu RF-540 spectrofluorophotometer equipped with quartz cuvettes of 1 cm path length. An excitation slit of 2.5 nm and an emission slit of 2.5 nm were used for the measurements.

2.2. Synthesis of ligands H_2L^1 , H_2L^2 and H_2L^3

5-Bromosalicylaldehyde and 3,5-dibromosalicylaldehyde from Alfa Aesar were used without further purification. 1,2-Dibromoethane and 1,3-dibromopropane were dried and redistilled before use. 1,2-Bis(aminooxy)ethane and 1,3-bis(aminooxy)propane were synthesized according to an analogous method reported earlier [11]. The other reagents and solvents were of analytical reagent grade and were used without further purification. The ligands H₂L¹, H₂L² and H₂L³ have been prepared according to a literature procedure [12,13]. H₂L¹: yield 479.1 mg (78.6%); m.p. 189– 190 °C. ¹H NMR (400 MHz, DMSO-*d*₆, δ , ppm) 4.49 (s, 4H, CH₂), 7.68 (d, *J* = 2.4 Hz, 2H, Ar–H), 7.82 (d, *J* = 2.4 Hz, 2H, Ar–H), 8.47 (s, 2H, =C–H), 10.43 (s, 2H, OH). IR (KBr, cm⁻¹): 3078(w) ν (C–H arom); 2936(w), 2872(w) ν (C–H); 1603(m) ν (C=N oxime);

Table 1

Crystallographic data, data collection and structure refinement for the obtained crystals.

Complex	1	2	3	4
CCDC	696151	696146	696133	696150
Empirical formula	$C_{16}H_{14}Br_4MnN_2O_6$	C46H64Br4C03N4O19	C48H62Br4N4Ni3O18	C37H31Br4Cl3N4O12Zn3
Formula weight	704.87	1473.44	1478.79	1345.76
Crystal system	monoclinic	triclinic	triclinic	monoclinic
Space group	C2/c	ΡĪ	ΡĪ	Pn
Unit cell dimensions				
a (Å)	17.574(3)	10.8568(9)	9.7769(10)	10.6045(14)
b (Å)	15.181(2)	12.3018(13)	11.9802(12)	9.1876(12)
c (Å)	7.9451(16)	12.3023(13)	12.9019(14)	24.997(3)
α (°)	90.00	87.379(2)	92.3930(10)	90
β (°)	96.520(2)	74.8090(10)	94.486(2)	92.755(2)
γ (°)	90.00	65.8710(10)	94.048(2)	90
V (Å ³)	2106.0(6)	1443.6(2)	1501.1(3)	2432.6(5)
Ζ	4	1	1	2
$D_{\rm c} ({\rm Mg}{\rm m}^{-3})$	2.223	1.695	1.636	1.837
μ (Mo K α) (mm ⁻¹)	8.252	3.692	3.662	4.976
F(000)	1348	741	746	1316
Crystal size (mm)	$0.42\times0.18\times0.17$	$0.19 \times 0.18 \times 0.17$	$0.40\times0.35\times0.29$	$0.40\times0.39\times0.37$
θ for data collection (°)	1.78-25.00	1.72-25.01	1.58-25.00	1.63-25.01
Index ranges	$-17\leqslant h\leqslant 20$,	$-12 \leqslant h \leqslant 11$,	$-11\leqslant h\leqslant 11$,	$-12\leqslant h\leqslant 12$,
	$-18\leqslant k\leqslant 17$,	$-14\leqslant k\leqslant 12$,	$-14\leqslant k\leqslant 14$,	$-10\leqslant k\leqslant 10$,
	$-9 \leqslant l \leqslant 9$	$-14 \leqslant l \leqslant 14$	$-15 \leqslant l \leqslant 12$	$-14 \leqslant l \leqslant 29$
Reflections collected	5096	7489	7405	11 672
Independent reflections	1805	4992	5087	5643
R _{int}	0.0520	0.0232	0.0316	0.0772
Completeness to θ = 25.00 (%)	97.1	98.2	95.9	99.6
Data/restraints/parameters	1805/0/132	4992/0/361	5087/1/354	5643/2/569
Goodness-of-fit (GOF) on F^2	1.029	1.020	1.012	1.054
R_1	0.0453	0.0459	0.0447	0.0826
$wR_2 [I > 2\sigma(I)]$	0.1084	0.1180	0.1183	0.1956
$\Delta ho_{ m max,min}$ (e Å ⁻³)	1.773 and -0.484	1.355 and -0.613	0.649 and -1.049	1.388 and -1.523

1271(m) ν (C–O). Anal. Calc. for C₁₆H₁₂N₂O₄Br₄ (%): C, 31.20; H, 1.96; N, 4.55. Found: C, 31.18; H, 1.98; N, 4.54%. The data of H₂L² and H₂L³ have been reported previously [12,13].

2.3. Synthesis of complexes 1-4

2.3.1. Complex 1

A solution of Mn^{II} acetate tetrahydrate (0.05 mmol) in methanol (15 ml) was added dropwise to a solution of H_2L^1 (0.05 mmol) in THF (45 ml) at room temperature. After continuing stirring for 2 days at room temperature, the mixture was filtered and the filtrate was allowed to stand at room temperature for several weeks. Then the yellow needle-like single crystals suitable for X-ray crystallographic analysis were obtained. The elemental analyses showed that the metal complexes obtained are composed of a 1:1 ratio of M^{II} to ligand. This ratio was later unequivocally confirmed by X-ray crystallographic analyses. Data for $[MnL^1(H_2O)_2]$ (1), $C_{16}H_{14}Br_4MnN_2O_6$ (704.87): Yield: 41.6%. Anal. Calc. for





Scheme 2. The general structures of the mono- or trinuclear complexes 1, 2, 3 and 4.

 $[MnL^{1}(H_{2}O)_{2}]$: C, 27.35; H, 2.03; N, 3.97; Mn, 7.83. Found: C, 27.26; H, 2.00; N, 3.95; Mn, 7.81%. IR (KBr, cm⁻¹): 3073(w) ν (C–H arom); 2951(w), 2889(w) ν (C–H); 1601(m) ν (C=N oxime); 1308(m) ν (C–O).

2.3.2. Complexes 2 and 4

A solution of cobalt acetate tetrahydrate (or zinc acetate dihydrate) (0.10 mmol) in ethanol (20 ml) was added dropwise to a solution of H_2L^2 (0.10 mmol) in acetone (or chloroform) (20 ml) at room temperature. The mixture was stirred at room temperature for 4 h, and the solution was filtered. Upon standing the filtrate at room temperature for several weeks, single crystals suitable for X-ray crystallographic analysis were obtained, respectively. The elemental analyses showed that the metal complexes obtained were composed of a 3:2 ratio of M^{II} to ligand. This ratio was later unequivocally confirmed by X-ray crystallographic analyses. Data for { $[CoL^{2}(OAc)(H_{2}O)]_{2}Co\} \cdot 5CH_{3}CH_{2}OH$ (2), $C_{46}H_{64}Br_{4}Co_{3}N_{4}O_{19}$ (1473.44): yield, 35.7%. Anal. Calc. for {[CoL²(OAc)(H₂O)]₂Co}-5CH₃CH₂OH: C, 37.48; H, 4.35; N, 3.82; Co, 12.02. Found: C, 37.50; H, 4.38; N, 3.80; Co, 12.00%. IR (KBr, cm⁻¹): 3364(vw) v(O-H); 3074(w) v(C-H arom); 2918(w), 2872(w) v(C-H); 1610(m) v(C=N oxime); 1250(m) v(C-O). Data for { $[ZnL^2(OAc)]_2Zn$ } CHCl₃ (4), C₃₇H₃₁Br₄Cl₃N₄O₁₂Zn₃ (1345.76): Yield, 42.6%, Anal. Calc. for {[ZnL²(OAc)]₂Zn}·CHCl₃: C, 33.01; H, 2.34; N, 4.13; Zn, 14.58. Found: C, 33.02; H, 2.32; N, 4.16; Zn, 14.55%. IR (KBr,cm⁻¹): 3090(w) v(C-H arom); 2928(w), 2854(w) v(C–H); 1607(m) v(C=N oxime); 1294(m) v(C-O).

2.3.3. Complex **3**

Table 2

A solution of nickel acetate tetrahydrate (0.10 mmol) in methanol (20 ml) was added dropwise to a solution of H_2L^3 (0.10 mmol)

Selected bond lengths and bond angles for complex 1 [Å, $^\circ$].			
Bond	Distance	Bond	Distance
Mn-O2 ⁱ Mn-O2 Mn-O3	2.123(3) 2.123(3) 2.157(3)	Mn-O3 ⁱ Mn-N1 Mn-N1 ⁱ	2.157(3) 2.306(4) 2.306(4)
Bond	Angle	Bond	Angle
02 ⁱ -Mn-O2 02-Mn-O3 02-Mn-O3 ⁱ 03-Mn-O3 ⁱ 02 ⁱ -Mn-N1	93.4(2) 94.5(1) 93.7(1) 168.0(2) 172.9(1)	02-Mn-N1 03-Mn-N1 03 ⁱ -Mn-N1 02-Mn-N1 ⁱ 03-Mn-N1 ⁱ	79.9(1) 84.6(1) 88.3(1) 172.9(1) 88.3(1)

Symmetry transformations used to generate equivalent atoms: (i) -x + 1, y, -z + 1/2.



Fig. 1. ORTEP drawing of the Mn^{II} complex showing the local coordination environment of the crystallographically independent Mn^{II} center (thermal ellipsoids at 30% probability).

in acetone (20 ml) at room temperature. The mixture was stirred at room temperature for 2 h, and the solution was filtered. Upon

standing the filtrate at room temperature for several weeks, single crystals suitable for X-ray crystallographic analysis were obtained.



Fig. 2. View of the 1D chain of the Mn^{II} complex along the c-axis (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity).



Fig. 3. ORTEP drawing of complex 2 showing the local coordination environment of the crystallographically independent Coll center (thermal ellipsoids at 30% probability).

The elemental analyses showed that the metal complexes obtained were composed of a 3:2 ratio of Ni^{II} to ligand. This ratio was later unequivocally confirmed by X-ray crystallographic analyses. Data for {[NiL³(OAc)(CH₃OH)]₂Ni}·2CH₃COCH₃·2CH₃OH (**3**), C₄₈H₆₂Br₄-N₄Ni₃O₁₈(1478.79): Yield, 37.24%. *Anal.* Calc. for {[NiL³(OAc)-(CH₃OH)]₂Ni}·2CH₃COCH₃·2CH₃OH: C, 38.97; H, 4.26; N, 3.79; Ni, 11.95. Found: C, 38.99; H, 4.25; N, 3.76; Co, 11.91%. IR (KBr, cm⁻¹): 3412(vw) ν (O–H); 2937(w), 2882(w) ν (C–H); 1605(m) ν (C=N oxime); 1304(m) ν (C–O).

2.4. X-ray diffraction crystallography

A single crystal suitable for detection was selected and subsequently glued to the tip of a glass fiber. The determination of the crystal structure at 25 °C was carried out with an X-ray diffractometer (Bruker Smart-1000 CCD) using graphite-monochromated Mo K α radiation (λ = 0.71073 Å). All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in calculated positions and included in the final cycles of refinement using a riding model. The programs used for structure solution and refinement were SHELXS-97 and SHELXL-97, respectively. A summary of the key crystallographic information for complexes is given in Table 1.

3. Results and discussion

The synthetic route of the ligands is shown in Scheme 1.

Complexes **1**, **2**, **3** and **4** have been obtained in yields of 35-43% by reaction of the tetradentate N₂O₂ Salen-type ligands with different metalline acetate M(OAc)₂·*n*H₂O (M = Mn, Co, Ni, Zn; *n* = 4, 4, 4, 2) in a refluxing solvent of anhydrous ethanol. The general structures of these new mono- or trinuclear complexes are shown in Scheme 2.

3.1. IR spectra analyses

The salient feature of the IR spectrum is the free ligands H_2L^1 . H_2L^2 and H_2L^3 exhibit characteristic C=N stretching bands at 1603, 1612 and 1612 cm⁻¹, which appeared at 1601, 1607, 1610 and 1605 cm⁻¹ in the Mn^{II}, Zn^{II}, Co^{II} and Ni^{II} complexes, and the lower shifting of C=N stretching frequencies verified the coordination of the oxime nitrogen to M^{II} ions. The typical absorptions for the C-H vibrations in complexes 1, 2, 3 and 4 were detected in the range 2854–2937 cm⁻¹, which is generally not significantly different from that of the ligands. Infrared spectrum of complex 1 shows the expected absorptions due to the stretching, bending and wagging modes of water molecules at 3418, 1631 and 546 cm⁻¹ (3364, 1635 and 542 cm⁻¹ in complex **2**), respectively, which indicate the presence of coordinated water molecules. The O-H stretching frequency band of complex 3 appears at 3412 cm⁻¹, indicating the presence of coordinated methanol molecules. The absorption characteristic for the phenolic hydroxyl groups in complex 4 is missing, thus confirming the Zn–O bonds were formed between the Zn^{II} ion and oxygen atoms of phenolic groups.

The far-infrared spectra of complexes **1**, **2**, **3** and **4** were also obtained in the region 500–100 cm⁻¹ in order to identify frequencies due to the M–O and M–N bonds. The far-infrared spectra of the complex **1** shows v(Mn–O) and v(Mn–N) vibration absorption frequencies at 472 and 440 cm⁻¹, and complex **2** for v(Co–O) and v(Co–N) at 415, 480 cm⁻¹; complex **3** for v(Ni–O), v(Ni–N) at 455, 473 cm⁻¹; complex **4** for v(Zn–O), v(Zn–N) at 420 and 473 cm⁻¹, respectively. These assignments are consistent with the literature frequency values [14–16] and are not present in the spectrum of the free ligands. As pointed out by Percy and

Thornton [17], the metal–oxygen and metal–nitrogen frequency assignments are at times very difficult.

3.2. Structure analyses

In order to determine the correct configuration of the complexes, X-ray crystallographic studies have been realized for complexes **1**, **2**, **3** and **4**.

3.2.1. Crystal structure of 1

Single crystal determination shows that complex 1 forms a selfassembling continual supramolecular structure by hydrogenbonding interactions and π - π stacking. Complex **1** is crystallized in the monoclinic system, space group C2/c. The coordination geometry around the Mn^{II} ion can be best described as slightly distorted octahedral geometry with a hexa-coordination. In complex 1 (Fig. 1), the two phenolic oxygen atoms and the two oxime nitrogen atoms of $(L^1)^{2-}$ unit constitute the basal plane, and two oxygen atoms of the coordinated water molecules are occupying the axial positions. The bond distances of Mn-N(2.306(4) Å) and Mn-O(2.123(3) Å) (Table 2) of phenolic oxygen are in the range observed for similar systems [14]. The four N₂O₂ donor atoms of $(L^{1})^{2-}$ unit are approximately coplanar, and the dihedral angle of O2–Mn–N1° and O2ⁱ–Mn1–N1ⁱ is 3.38°. The oxygen atoms in the axial sites of Mn^{II} ion forms a considerably large angle of O3-Mn-O3ⁱ (167.99(16)°). It is noticeably that the bond distance Mn–O3 (2.157(3)Å) is the same with Mn–O3ⁱ, which indicates the same coordination abilities of the two μ -oxo bridges.

The introduction of the coordinated water molecule in complex **1** successfully lead to the 1D chains assembly of $[MnL^{1}(H_{2}O)_{2}]$ units by hydrogen-bonding interactions (Fig. 2). Four hydrogen bonds (O3–H3B···O2, O3–H3B···Br1, O3–H3C···O2 and O3–H3C···Br1) are also formed, each oxygen atom of the coordinated water molecules in complex **1** is bound to both phenolic oxygen atoms (O2 and O2ⁱ) and bromine atoms (Br1 and Br1ⁱ) of $(L^{1})^{2-}$ unit from the adjacent monomer. The angle of the two neighboring benzene rings is 3.31° and the mean distance between the two neighboring benzene rings is 3.698 Å, indicating weak π - π stacking interaction.

Table 3 Selected bond lengths and bond angles for complex 2 [Å, °].

Bond	Distance	Bond	Distance
Co1-O4 Co1-O4 ⁱⁱ Co1-O3 Co1-O3 ⁱⁱ Co1-O5 ⁱⁱ Co1-O5 Bond	2.094(3) 2.094(3) 2.103(3) 2.103(3) 2.142(4) 2.142(4) Apgle	Co2-O4 Co2-O3 Co2-O6 Co2-O7 Co2-N2 Co2-N1 Bond	2.037(3) 2.054(3) 2.059(4) 2.099(4) 2.119(5) 2.132(5)
	Aligie		Aligie
$\begin{array}{c} O(4)^{ii}-Co(1)-O(3)^{ii}\\ O(4)-Co(1)-O(3)^{ii}\\ O(4)-Co(1)-O(3)\\ O(4)-Co(1)-O(3)\\ O(4)^{ii}-Co(1)-O(3)\\ O(4)^{ii}-Co(1)-O(5)^{ii}\\ O(4)-Co(1)-O(5)^{ii}\\ O(3)^{ii}-Co(1)-O(5)^{ii}\\ O(3)^{ii}-Co(1)-O(5)^{ii}\\ O(4)^{ii}-Co(1)-O(5)\\ O(4)^{ii}-Co(1)-O(5)\\ O(4)-Co(1)-O(5)\\ O(4)-Co(1)-O(5)\\ O(3)^{ii}-Co(1)-O(5)\\ O(3)^{ii}-Co(1)$	78.4(1) 101.6(1) 101.6(1) 78.4(1) 180.0(1) 88.9(1) 91.2(1) 88.9(1) 91.1(1) 91.2(1) 88.9(1) 91.1(1) 91.1(1)	O(4)-Co(2)-O(6) O(3)-Co(2)-O(6) O(4)-Co(2)-O(7) O(3)-Co(2)-O(7) O(6)-Co(2)-O(7) O(4)-Co(2)-N(2) O(3)-Co(2)-N(2) O(6)-Co(2)-N(2) O(7)-Co(2)-N(2) O(4)-Co(2)-N(1) O(3)-Co(2)-N(1) O(6)-Co(2)-N(1) O(7)-Co(2)-N(1) O(6)-Co(2)-N(1) O(7)-Co(2)-	92.7(2) 90.2(2) 89.2(1) 93.4(2) 176.2(2) 86.5(2) 167.3(2) 89.4(2) 87.4(2) 166.3(2) 86.5(2) 92.6(2) 92.6(2)

Symmetry transformations used to generate equivalent atoms: (ii) -x + 1, -y + 1, -z + 1.

3.2.2. Crystal structure of 2

The complex **2** crystallizes in the *P*-1 space group with a linear trinuclear array of three Co^{II} atoms coupled by both doubly μ -phenoxo oxygens of $(L^2)^{2-}$ and simultaneously two acetate anions in the *syn–syn* bridging mode. The coordination geometry around the terminal Co^{II} centers may be regarded as distorted octahedral geometry with a hexa-coordination (Fig. 3). The equatorial plane of each of the two equivalent terminal Co^{II} atoms (Co2 and Co2^{II}) are formed by the two *O*-alkyl oxime nitrogen atoms (N1, N2) and two μ -phenoxo oxygen atoms (O3, O4) coming from the (L²)²⁻ moiety. The apical positions are occupied by one oxygen atom (O7) from the coordinated water molecules and another oxy-

gen atom (O8) from the bridging acetate group. The dihedral angle between the two coordination planes, N1–Co2–O3 and N2–Co2– O4, is $5.28(2)^\circ$, which indicates significant distortion toward tetrahedral geometry from the square planar structure. It is noticeably that the bond distance Co2–O6 (2.060(3) Å) is different from Co2– O7 (2.100(2) Å) (Table 3) in complex **2**, the oxygen atoms in the axial sites of Co^{II} forms a considerably large angle of O6–Co2–O7 (176.21(2)°), which indicates the different coordination abilities of the two oxygen atoms.

However, the coordination geometry of the central Co1 atom deviates slightly from an ideal octahedron. The central Co1 atom has an O_2O_2 donor set from four μ -phenoxo oxygen atoms (O3,



Fig. 4. (a) View of a 1D single chain motif within Co^{II} complex along the *a*-axis (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity). (b) View of the 1D single chain motif within Co^{II} complex along the *c*-axis (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity). (c) View of the 1D single chain motifs within Co^{II} complex along the *c*-axis (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity). (c) View of the 1D single chain motifs within Co^{II} complex along the *b*-axis, showing the channels formed from the linking of the 12-membered rings (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity).

O4, O3ⁱⁱ and O4ⁱⁱ) of the two $(L^2)^{2-}$ moieties. Meanwhile, each of the two acetate anions bridges the terminal Co2 and central Co1 atoms in a *syn-syn* fashion. Hence the central Co1 atom finally has an O₂O₂O₂ donor set (four equatorial oxygen atoms coming from four deprotonated μ -phenoxo oxygens of the two $(L^2)^{2-}$ moieties and two axial oxygen atoms from the bridging acetates). It is interesting that the coordinated angle (O5–Co–O5ⁱⁱ) is 180°, which is along the octahedral central axis of two μ -acetato ligands with Co1. The trinuclear structure is probably stabilized by the two μ acetato ligands bridging Co1–Co2 and Co1–Co2ⁱⁱ, which neutralize the whole charge of complex **2**. Similar trinuclear structures supported by two acetato ligands are also found in salicylideneimine complexes containing Zn^{II} [18], Cd^{II} [19], and Cu^{II} [11].

The complex **2** contains five non-coordinating ethanol molecules and there are complicated hydrogen-bonding interactions in the structure of **2** (Fig. 4). The complex **2** is stabilized by a pair of C7–H7…O2 hydrogen bonds linking both molecules into an 1D infinite chain parallel to the *a*-axis (Fig. 4a). Furthermore, Each oxygen atom O10 of the two non-coordinating ethanol molecule is hydrogen-bonded to the –C18H18B group of the bridged acetic ions, while its –O10H10 group and –C23H23A group is hydrogen-bonded to the oxime oxygen atom O1 of the ligands and the oxygen atom O6 of the bridged acetic ions. Thus, complex **2** and



Fig. 5. ORTEP drawing of Ni^{II} complex showing the local coordination environment of the crystallographically independent Ni^{II} center (thermal ellipsoids at 30% probability).

the non-coordinating ethanol molecule are linked by intermolecular hydrogen bonds to form the other 1D infinite chain along the *c*-axis (Fig. 4b).

In addition, there exist intermolecular hydrogen bonds, O8– H8…O5, which is formed between the oxygen atoms (O5) of the bridged acetate ions and the –OH group of a non-coordinating ethanol molecule (–O8H8); C1–H1B…O9, which is formed between the oxygen atoms (O9) of the non-coordinating ethanol molecule and the –C1H1B group of the O-alkyl chain of $(L^2)^{2-}$ unit. This linkage is further stabilized by another hydrogen-bond interactions, C21–H21B… $\pi_{centroid(C11-C16)}$ and C19–H19A… $\pi_{centroid(C4-C9)}$, from between each of –CH group of the two non-coordinating ethanol molecules and each of two aromatic rings of $(L^2)^{2-}$ unit, respectively. Consequently, **2** is stabilized by different hydrogen-bond interactions in an infinite chain along the *b*-axis (Fig. 4c).

It is interesting that two coordinating water molecules and four non-coordinating ethanol molecules are linked through hydrogen bonds, O9–H9…O8, O7–H7B…O8 and O7–H7A…O9, to form a slightly disordered 12-membered hexagon, which shows a nearly ideal chair conformation cavities. The crystal packing of complex **2** shows that a notable feature of this structure resides in the formation of a new 3D hydrogen-bonding supramolecular networks through intermolecular C–H…O, O–H…O and C–H… π interactions. It is noteworthy that the channels composing of six O–H…O hydrogen bonds run along the *a*-axis (Fig. 4c), having dimensions of approximately 5.975 × 4.684 Å as defined by the oxygen–oxygen distances.

3.2.3. Crystal structure of 3

The complex **3** crystallizes in the triclinic space group $P\bar{1}$, which consists of three nickel atoms, two $(L^2)^{2-}$ moieties, two acetate ions, two coordinated methanol molecules, two crystallizing methanol and two crystallizing acetone molecules (Fig. 5). All the nickel atoms of **3** have an octahedral geometry. The structural features of **3** are very similar to those of **2** except that the apical positions of the distorted octahedral coordination geometry around the terminal Ni^{II} centers (Ni2) are not occupied by an oxygen atom from the coordinated water but one oxygen atom (O7) from the coordinated methanol molecule.

The complex **3** contains uncoordinated methanol molecule and there are hydrogen-bond interactions between the methanol molecule and $\{[NiL^3(OAc)(CH_3OH)]_2Ni\}$ unit as shown in Fig. 6. Selected bond lengths and bond angles data are given in Table 4. Each of the hydroxyls (-O8H8) in two crystallizing methanol molecules bonded to the oxygen atom (O5) of the bridging acetate group, respectively. Simultaneously, each of the hydroxyls



Fig. 6. View of the 1D chain of Ni^{II} complex along the *a*-axis (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity).

Table 4
Selected bond lengths and bond angles for complex 3 [Å, °].

Bond	Distance	Bond	Distance
Ni1-03 Ni1-03 ⁱⁱⁱ Ni1-04 ⁱⁱⁱ Ni1-04 Ni1-05	2.055(3) 2.055(3) 2.084(4) 2.084(4) 2.108(4)	Ni2-06 Ni2-04 Ni2-03 Ni2-07 Ni2-N1	2.006(4) 2.029(4) 2.042(4) 2.090(5) 2.094(5)
Ni1-O5 ⁱⁱⁱ	2.108(4)	Ni2-N2	2.106(5)
Bond	Angle	Bond	Angle
03-Ni1-03 ⁱⁱⁱ 03-Ni1-04 ⁱⁱⁱ 03 ⁱⁱⁱ -Ni1-04 ⁱⁱⁱ 03-Ni1-04 03 ⁱⁱⁱ -Ni1-04 04 ⁱⁱⁱ -Ni1-04 03-Ni1-05 03 ⁱⁱⁱ -Ni1-05 04 ⁱⁱⁱ -Ni1-05 03-Ni1-05 03-Ni1-05 ⁱⁱⁱ 03 ⁱⁱⁱ -Ni1-05 ⁱⁱⁱ	$180.0(2) \\103.3(2) \\76.7(2) \\76.7(2) \\103.3(2) \\180.00(1) \\90.6(2) \\89.4(2) \\90.5(2) \\89.5(2) \\89.5(2) \\89.4(2) \\90.6(2)$	06-Ni2-04 06-Ni2-03 04-Ni2-07 04-Ni2-07 03-Ni2-07 06-Ni2-N1 04-Ni2-N1 03-Ni2-N1 07-Ni2-N1 06-Ni2-N2 04-Ni2-N2	93.2(2) 93.7(2) 78.2(2) 174.1(2) 92.1(2) 90.0(2) 87.3(2) 164.3(2) 86.1(2) 88.3(2) 88.8(2) 88.8(2) 86.2(2)
04 ¹¹¹ -Ni1-05 ¹¹¹ 04-Ni1-05 ¹¹¹¹ 05-Ni1-05 ¹¹¹¹	89.5(2) 90.5(2) 180.00(1)	03-Ni2-N2 07-Ni2-N2 N1-Ni2-N2	164.3(2) 88.8(2) 109.5(2)

Symmetry transformations used to generate equivalent atoms: (iii) -x + 1, -y + 1, -z + 1.

(-O7H7) of two coordinated methanol molecules bonded to the oxygen atom (O8) of the crystallizing methanol molecules, respectively. The {[NiL³(OAc)(CH₃OH)]₂Ni} units self-assemble via a pair of intermolecular C19H19C…O1 hydrogen-bonding interactions

Bond	Distance	Bond	Distance
Zn1-011	2.05(1)	Zn2-N2	2.07(2)
Zn1-09	2.07(1)	Zn2-04	2.07(1)
Zn1-08	2.11(1)	Zn2-N1	2.11(2)
Zn1-03	2.12(1)	Zn3-07	1.98(1)
Zn1-07	2.12(1)	Zn3-012	1.99(1)
Zn1-04	2.15(1)	Zn3-N4	2.06(2)
Zn2-010	1.96(1)	Zn3-08	2.07(1)
Zn2-03	1.98(1)	Zn3–N3	2.12(2)
Bond	Angle	Bond	Angle
011-Zn1-09	175.4(5)	010-Zn2-04	96.2(5)
011-Zn1-08	88.0(5)	03-Zn2-04	84.3(5)
09-Zn1-08	91.5(5)	N2-Zn2-O4	88.5(6)
011-Zn1-03	91.3(5)	010-Zn2-N1	100.2(6)
09-Zn1-03	89.4(5)	03-Zn2-N1	86.6(6)
08-Zn1-03	176.8(5)	N2-Zn2-N1	87.7(6)
011-Zn1-07	89.5(5)	04-Zn2-N1	162.6(6)
09-Zn1-07	94.9(5)	07-Zn3-012	109.3(5)
08-Zn1-07	76.9(5)	07-Zn3-N4	139.5(6)
03-Zn1-07	99.9(5)	012-Zn3-N4	110.4(6)
011-Zn1-04	87.4(5)	07-Zn3-08	81.1(5)
09-Zn1-04	88.2(5)	012-Zn3-08	95.2(5)
08-Zn1-04	104.2(5)	N4-Zn3-08	87.6(6)
03-Zn1-04	78.9(5)	07-Zn3-N3	86.0(6)
07-Zn1-04	176.6(5)	012-Zn3-N3	104.3(6)
010-Zn2-03	102.5(6)	N4-Zn3-N3	91.8(6)
010-Zn2-N2	121.9(7)	08-Zn3-N3	159.3(5)
03-Zn2-N2	135.6(6)		

where the -CH group of the bridging acetate group acts as the hydrogen-bond donor to the oxime O atoms forming 1D infinite chain. A comparison of the structures of the similar complexes



Fig. 7. ORTEP drawing of the Zn^{II} complex showing the local coordination environment of the crystallographically independent Zn^{II} center (thermal ellipsoids at 30% probability).

Table 5

Selected bond lengths and bond angles for complex 4 [Å, °].

reveals an interesting feature: when trinuclear Ni^{II} complexes are formed by both phenoxo- and anion bridges, the resulting complexes are linear, in which the four μ -phenoxo groups occupy a square plane (four meridional positions) of the central Ni^{II} leaving its axial positions to be occupied by the bridging anions [18,20].



Fig. 8. (a) View of the 1D single chain motif within Zn^{II} complex along the *a*-axis (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity). (b) View of the 1D single chain motif within Zn^{II} complex along the *b*-axis (chloroform molecules and hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity). (c) Extended structure of the Zn^{II} complex, showing the chloroform molecules occupied "grottos" running along *c*-axis.

3.2.4. Crystal structure of 4

The asymmetric units of complex **4** contains three Zn^{II} atoms, two $(\mu-L^2)^{2-}$ units, two acetate ions and one chloroform molecule (Fig. 7). The central Zn^{II} (Zn1) is hexa-coordinated, the coordination sphere is completed by μ -phenoxo oxygen atoms (O3, O4, O7, O8) from two $[Zn(L^2)]$ chelates, and both of oxygen atoms O9 and O11 from the ligating acetate ions which adopt a familiar μ O–C–O fashion, and constitute a slightly distorted octahedral geometry. It is noteworthy that the terminal Zn^{II} ions (Zn2 and Zn3) are both penta-coordinated, and located in the N₂O₂ moieties of the ligand. The oxygen atoms O10 and O12 from the bridging acetate ions are also coordinated to Zn2 and Zn3, respectively. This is different from 2 and 3, and the only possible explanation for this change might be the templating effect resulting from the different transitional metal ions due to all the complexes crystallized under nearly the same conditions. Consequently, the coordination geometry around Zn2 and Zn3 approaches to a distorted square pyramid. The trinuclear structure is stabilized by the two μ -acetato ligands bridging Zn1–Zn2 and Zn1–Zn3, which neutralize the whole charge of the complex (Table 5).

Analysis of the crystal packing of **4** shows that a notable feature of this structure resides in the formation of a new 2D hydrogenbonding supramolecular networks through intermolecular C–H···Br, C–H···Cl, C–H···O and C–H··· π (Ph) interactions. As shown in Fig. 8, complex **4** monomers are linked by the intermolecular C17–H17A···Br1, C9–H9···O12 and C1–H1A··· $\pi_{centroid}$ (C27–C32) interactions into 1D infinite chains along the *a*-axis (Fig. 8a). Moreover, the molecules are further linked by intermolecular C23–H23···Br1 hydrogen-bonds interactions to form the others 1D infinite chain along *b*-axis are further held together by the intermolecular C26–H26···Br1 hydrogen bonds (Fig. 8b). Obviously, the bromine atoms could be considered as the 3-connected nodes, and assemble the chains into 2D supramolecular network structure parallel to the *ab* planes.

The most significant feature is the formation of "grottos" running through the inter-chains region (Fig. 8c). The dimensions of the "grottos" are approximately 10.6×9.2 Å as defined by the shortest channel metal–metal distances. It is noteworthy that the uncoordinated guest chloroform molecules are situated in the "grottos" through intermolecular C36–H36B…Cl2 hydrogen-bond interactions.

3.3. Photophysical properties of ligand H_2L^1 , H_2L^2 , H_2L^3 and of the complexes

The UV-Vis absorption spectra of the three ligands and their corresponding complexes in diluted DMF solution. We can see the absorption peaks of the complexes are obviously different from those of the ligands upon complexation. The electronic absorption spectrum of Salen-type ligands H_2L^1 , H_2L^2 and H_2L^3 consist of two relatively intense bands centered at 266 and 325 nm (324 nm for H_2L^3), assigned to the $\pi - \pi^{T}$ transitions of the benzene ring of salicylaldehyde and the oxime group, respectively. Upon coordination of the ligand, the absorption bands at about 325 nm disappears from the UV–Vis spectra of the transition metal complexes, which indicates that the oxime nitrogen atom is involved in coordination to the metal ion. The intraligand $\pi - \pi^*$ transition of the oxime group is slightly shifted in the corresponding complexes and appears at 266, 265, 266 and 269 nm for complex 1, 2, 3 and 4. Moreover, the new bands observed at 376, 361, 371 and 367 nm for complex 1.2.3 and 4 are assigned to that of $L \rightarrow M$ charge-transfer transition which are characteristic of the transition metal complexes with N₂O₂ coordination spheres [21].

3.4. Luminescence properties of the complex

The excitation and emission spectra of complex **4** in dilute DMSO solution (concentration: 5×10^{-4} mol/L) at room tempera-

ture was determined. The blue-green emission for the Zn^{II} complex can be observed, where the maximum emission wavelength at 464 nm. The excitation peak of the complex was located at around 378 nm. It can be also seen that the intensity of the excitation is stronger than the emission for the complex. The Stokes shift between the maximum wavelength of fluorescence emission spectrum and the fluorescence excitation spectrum was 86 nm. This red-shift might be related to the coordination of zinc atom with the ligand, which makes the conjugated system larger.

4. Conclusions

Four divalent transition metal combinations with three Salentype bisoxime ligands have been has resulted in the crystallization of four supramolecular complexes with 1D chain, 2D and 3D networks structural motifs. Complex 1 adopts a slightly distorted octahedral geometry with a hexa-coordination. And the introduction of the coordinated water molecule successfully lead to the assembly of the 1D chains by hydrogen-bonding interactions. Complexes 2 and 3 are rigorously centrosymmetric, the central metal ion Ni^{II} or Co^{II} sits on a crystallographic inversion center in the crystal. The structure of 2 and 3 adopts a slightly distorted octahedral geometry for every hexa-coordinated M^{II} center. In 4, the asymmetric unit contains three Zn^{II} ions, the central Zn^{II} is sixcoordinated adopting a slightly distorted octahedral geometry, the two terminal Zn^{II} ions are five-coordinated, and the coordination geometry approaches to a distorted square pyramid. Although 1 and 3 display 1D supramolecular chains, the different coordination environments (mononuclear in 1, trinuclear in 2) provoke divergence in the structures and aggregations of the chain subunits. Complex 2 forms the 3D hydrogen-bonding supramolecular networks possessing a channel, while 4 exhibits the 2D hydrogenbonding supramolecular networks with the formation of "grottos" occupied by chloroform molecules through intermolecular hydrogen-bond interactions.

5. Supplementary data

Supplementary data CCDC 696151, 696146, 696133 and 696150 contain the supplementary crystallographic data for **1**, **2**, **3** and **4**. 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; or e-mail: deposit@ccdc.cam.ac.uk.

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