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Hydrothermal syntheses and crystal structures of five complexes with 3,5-dinitrosalicylate and N-donor ligand: Helical chains, 2D network and extended 3D structures

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Abstract

Five complexes with 3,5-dinitrosalicylate (3,5-$(NO_2)_2$sal) and N-donor ligand, $[Cd\{3,5\text{-}(NO_2)_2sal\}(phen)(H_2O)]_n$ (**1**), $Ni\{3,5\text{-}(NO_2)_2sal\}(phen)(H_2O)_2$ (**2**), $[Co\{3,5\text{-}(NO_2)_2sal\}(4,4'\text{-}bipy)(H_2O)\cdot(H_2O)]_n$ (**3**), $[Co\{3,5\text{-}(NO_2)_2sal\}(phen)]_n$ (**4**) and $[Zn\{3,5\text{-}(NO_2)_2sal\}(phen)]_n$ (**5**), have been synthesized by hydrothermal reactions and characterized by single crystal X-ray analysis, where phen = 1,10-phenanthroline and 4,4′-bipy = 4,4′-bipyridine. There are one-dimensional left- and right-handed helical chains in complexes **1**, **4** and **5**, an extended 3D structure in **2**, and a 2D rectangular grid-like network in **3**. The C–H···O hydrogen bonds lead to the formation of 3D supramolecular structures in the five title complexes. The fluorescent spectra study show that compounds **1** and **5** exhibit weak fluorescent emission in the solid state at room temperature.

Keywords: Coordination polymer; Helical chain; 3,5-Dinitrosalicylic acid; Hydrogen bond; Crystal structure

1. Introduction

Coordination polymers continue to be extensively studied because of not only for their intriguing structural features, but also for their potential applications such as magnetism, catalysis, chirality, luminescence, non-linear optics, molecular recognition and sorption [1–5]. Salicylic acid and its substituted derivatives continue to attract attention because of its versatile coordination modes [6–10] and biological applications [11–13]. Salicylate anion can also exist in solid state as phenolato anion or as carboxylato anion and/or as dianion. There has been continuous interest in the influence of deprotonation degree for salicylate on the structures of related complexes [14–18].

Hydrogen bond plays an important role in forming supramolecular architectures. A lot of hydrogen-bonded supramolecular architectures based on bipy-like and carboxylate ligands have been reported [19]. Some non-coordinated functional groups such as NO_2, NH_2, etc. are well known to form robust and strong hydrogen bond, the syntheses of metal–organic supramolecular assemblies employing organic ligands with NO_2 groups are limited [20,21]. As far as the reaction pathways, recent plentiful practice has prove that the hydrothermal synthesis is a promising technique in preparing metal complexes with novel structures and special properties, which are difficult to obtain by routine synthetic methods [22–25].

The self-assembly in metallacrowns based on 3d-series metals with *N*-acyl salicylhydrazides [7,26,27] has been reported in our group. In an extension of this research, 3,5-dinitrosalicylate (3,5-$(NO_2)_2$sal) is selected as a ligand to form coordination polymers. Because numerous coordination polymers with salicylic acid were found to display diverse structure types, but only a few complexes with 3,5-$(NO_2)_2$sal are reported [28–32]. Further,

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1,10-phenanthroline and 4,4′-bipyridine have also been chosen as a co-ligand, not only they can bind to metal ion to form coordination polymers, but also they can also act as hydrogen bond donors to form weak C–H···O hydrogen bonds with the NO_2 groups of 3,5-$(NO_2)_2$sal ligand [19,33]. Herein, we report hydrothermal syntheses and crystal structures of five complexes with mixed ligands (3,5-$(NO_2)_2$sal and N-donor ligand). These complexes are $[Cd\{3,5\text{-}(NO_2)_2sal\}(phen)(H_2O)]_n$ (**1**), $Ni\{3,5\text{-}(NO_2)_2sal\}(phen)(H_2O)_2$ (**2**), $[Co\{3,5\text{-}(NO_2)_2sal\}(4,4'\text{-}bipy)(H_2O)\cdot(H_2O)]_n$ (**3**), $[Co\{3,5\text{-}(NO_2)_2sal\}(phen)]_n$ (**4**) and $[Zn\{3,5\text{-}(NO_2)_2sal\}(phen)]_n$ (**5**) (phen = 1,10-phenanthroline, 4,4′-bipy = 4,4′-bipyridine).

2. Experimental

All of the chemicals were obtained from commercial sources and were used without further purification. Elemental analyses were conducted on a Perkin-Elmer 2400 CHN elemental analyzer. IR spectra were recorded on a Nicolet 360 FT-IR spectrometer with KBr pellets in the 4000–400 cm^{-1} region. Thermogravimetric analysis (TGA) of complex **1** was obtained on NETZSCH STA 449C thermogravimetric analyzer, carried out under N_2 with a heating rate of at 10 °C min^{-1}. Fluorescence spectroscopy was performed on a Perkin-Elmer LS 55 luminescence spectrometer.

*2.1. Synthesis of $[Cd\{3,5\text{-}(NO_2)_2sal\}(phen)(H_2O)]_n$ (**1**)*

A mixture of $Cd(NO_3)_2{\cdot}4H_2O$ (0.1 mmol), 1,10-phenanthroline (0.1 mmol), 3,5-dinitrosalicylic acid (0.2 mmol) and distilled water (10 ml) with pH value adjusted to 7 by addition of 1 M NaOH solution was put into a Teflon-lined autoclave (20 ml) and then heated at 180 °C for 72 h. Yellow block-like crystals of **1** were obtained with 25% yield based on Cd. Anal. Found: C, 42.58; H, 2.15; N, 10.35%. Calc. for $C_{19}H_{12}N_4O_8Cd$ (Mr = 536.73): C, 42.52; H, 2.25; N, 10.44%.

*2.2. Synthesis of $Ni\{3,5\text{-}(NO_2)_2sal\}(phen)(H_2O)_2$ (**2**)*

The same synthetic procedure as that for **1** was used except that $Cd(NO_3)_2{\cdot}4H_2O$ was replaced by $Ni(OAc)_2{\cdot}2H_2O$. Yellow chip-like crystals of **2** were synthesized with 30% yield based on Ni. Anal. Found: C, 45.60; H, 2.68; N, 11.12%. Calc. for $C_{19}H_{14}N_4O_9Ni$ (Mr = 501.05): C, 45.55; H, 2.82; N, 11.18%.

*2.3. Synthesis of $[Co\{3,5\text{-}(NO_2)_2sal\}(4,4'\text{-}bipy)(H_2O)\cdot(H_2O)]_n$ (**3**)*

A mixture of $Co(OAc)_2{\cdot}4H_2O$ (0.1 mmol), 4,4′-bipy (0.1 mmol), 3,5-dinitrosalicylic acid (0.2 mmol) and distilled water (10 ml) with the pH value adjusted to 7 by addition of 1 M NaOH solution was put into a Teflon-lined autoclave (20 ml) and then heated at 180 °C for 72 h, brown chunk-like crystals of **3** were obtained in 33% yield based on Co. Anal. Found: C, 42.80; H, 2.80; N, 11.64%. Calc. for $C_{17}H_{14}N_4O_9Co$ (Mr = 477.25): C, 42.78; H, 2.96; N, 11.74%.

*2.4. Synthesis of $[Co\{3,5\text{-}(NO_2)_2sal\}(phen)]_n$ (**4**)*

The same synthetic procedure as that for **1** was used except that $Cd(NO_3)_2{\cdot}4H_2O$ was replaced by $Co(OAc)_2{\cdot}4H_2O$. The green prism-like crystals of **4** were synthesized in 66% yield based on Co. Anal. Found: C, 49.08; H, 2.02; N, 11.91%. Calc. for $C_{19}H_{10}N_4O_7Co$ (Mr = 465.24): C, 49.05; H, 2.17; N, 12.04%.

*2.5. Synthesis of $[Zn\{3,5\text{-}(NO_2)_2sal\}(phen)]_n$ (**5**)*

The same synthetic procedure as that for **1** was used except that $Cd(NO_3)_2{\cdot}4H_2O$ was replaced by $Zn(NO_3)_2{\cdot}6H_2O$. The colorless chunk-like crystals of **5** were obtained in 80% yield based on Zinc. Anal. Found: C, 48.43; H, 2.03; N, 11.68%. Calc. for $C_{19}H_{10}N_4O_7Zn$ (Mr = 471.68): C, 48.38; H, 2.14; N, 11.88%.

2.6. X-ray crystallography

X-ray diffraction measurements of the five title complexes were carried out at 293 K on a Rigaku R-AXIS RAPID Weissengberg IP diffractometer with graphite monochrocmated Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods (SHELXTL-97) and refined on F^2 by full-matrix least-squares techniques. The crystallographic data of **1**–**5** are summarized in Table 1. The selected bond lengths and angles for **1**–**5** are listed in Table 2.

3. Result and discussion

*3.1. Structural description of $[Cd\{3,5\text{-}(NO_2)_2sal\}(phen)(H_2O)]_n$ (**1**)*

The X-ray diffraction analysis reveals that complex **1** exhibits a helical chain structure consisting of Cd{3,5-$(NO_2)_2$sal}(phen)(H_2O) entities. As shown in Fig. 1, each Cd(II) atom is coordinated by two N atoms from one chelating phen ligand, three O atoms (O2, O3 and O1A) from two 3,5-$(NO_2)_2$sal ligands and one coordinated water molecule O8 atom, forming a distorted octahedron. The Cd–N bond lengths are 2.338(3) and 2.350(3) Å. The Cd–O(3,5-$(NO_2)_2$sal) bond lengths are from 2.243(2) to 2.286(2) Å, while Cd–O8(water) bond length is 2.334(2) Å.

Every 3,5-$(NO_2)_2$sal ligand adopts a chelating–bridging mode. Each 3,5-$(NO_2)_2$sal bridging ligand is not only coordinated to one Cd(II) atom via its two oxygen atoms (phenolate oxygen O3 and carboxylate oxygen O2), but also coordinated to the other Cd(II) atom via carboxylate oxygen O1 atom (Fig. 2a). Therefore, the adjacent Cd atoms are bridged through the carboxylate CO_2 group to obtain a chain along the *a* axis (see Fig. 2a), the Cd···Cd distance

Table 1
Crystallographic data in complexes **1–5**

Compound	**1**	**2**	**3**	**4**	**5**
Formula	$C_{19}H_{12}N_4O_8Cd$	$C_{19}H_{14}N_4O_9Ni$	$C_{17}H_{14}N_4O_9Co$	$C_{19}H_{10}N_4O_7Co$	$C_{19}H_{10}N_4O_7Zn$
Formula weight	536.73	501.05	477.25	465.24	471.68
Crystal system	Orthorhombic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P bca	$P\bar{1}$	$P2_1/c$	$P2_1/n$	$P2_1/n$
a (Å)	7.926(2)	7.359(2)	11.415(4)	12.487 (6)	12.3182(4)
b (Å)	21.268(6)	11.041(2)	8.648(3)	7.944 (3)	8.0999(5)
c (Å)	21.887(6)	12.551(3)	19.142(9)	18.575(6)	18.4896(9)
α (°)	90	69.66(3)	90	90	90
β (°)	90	88.24(3)	94.76(1)	105.09(1)	104.434(2)
γ (°)	90	85.78(3)	90	90	90
V (Å^3)	3689(2)	953.6(3)	1883 (1)	1779(1)	1786.6(2)
Z	8	2	4	4	4
D_{calc} (g cm^{-3})	1.933	1.745	1.683	1.737	1.754
T (K)	293(2)	293(2)	293(2)	293(2)	293(2)
Color	Yellow	Yellow	Brown	Green	Colorless
Shape	Block	Chip	Chunk	Prism	Chunk
Dimension (mm)	0.15 × 0.25 × 0.28	0.05 × 0.20 × 0.35	0.10 × 0.10 × 0.25	0.10 × 0.15 × 0.59	0.10 × 0.15 × 0.10
μ (mm^{-1})	1.246	1.084	0.974	1.021	1. 431
F (000)	2128	512	972	940	952
θ_{min}, θ_{max} (°)	3.17, 27.48	3.04, 27.43	3.09, 25.00	3.07, 27.47	1.80, 27.48
$h_{min–max}$	$-10 \rightarrow 10$	$-9 \rightarrow 9$	$-12 \rightarrow 13$	$-16 \rightarrow 16$	$0 \rightarrow 15$
$k_{min–max}$	$-27 \rightarrow 27$	$-14 \rightarrow 14$	$-9 \rightarrow 10$	$-8 \rightarrow 10$	$0 \rightarrow 10$
$l_{min–max}$	$-27 \rightarrow 28$	$-16 \rightarrow 16$	$-22 \rightarrow 22$	$-23 \rightarrow 24$	$-24 \rightarrow 23$
R_{int}	0.0512	0.0545	0.0870	0.0435	0.0487
No. of unique	4214	4247	3314	4066	3979
No. of observed	3044	3250	2260	3153	2478
No. variables	289	354	277	278	278
R	0.0316	0.0498	0.0587	0.0506	0.0475
wR	0.0723	0.1062	0.1371	0.1231	0.1139
GOF	1.035	1.032	1.056	1.069	0.996
$(\Delta p)_{max,min}$ (e/Å^3)	0.468(−0.442)	0.521(−0.672)	0.786(−0.574)	0.796, −0.621	0.763(−0.424)

and Cd–Cd–Cd angle being 5.872(1) Å and 84.90(1)°, respectively.

There are a hydrogen bond O(8)–H(08A)···O(2A) between O(8)–H(08A) of coordinated water molecule and carboxylate O(2) atom and a hydrogen bond O(8)–H(08B)···O(6B) (O(6B) from a NO_2 group). These hydrogen bonds connect the neighboring chains into a 2D network structure along *ac* plane (Fig. 2a). There are two kinds of parallel helices correspondingly, one is right-handed helical chain (Fig. 2(b1)) and the other is left-handed helical chain (Fig. 2(b2)), they are parallel to each other along the *a*-axis. It is noteworthy that the major intermolecular force between the polymer chains in **1** is the C–H···O hydrogen bonds between the phenyl hydrogens of phen ligands and the NO_2 groups of 3,5-$(NO_2)_2$sal ligands (see Supplementary Fig. S1 and Table 3).

3.2. Structural description of Ni{3,5-$(NO_2)_2$sal}(phen)$(H_2O)_2$ (2)

Complex molecule **2** comprises of one Ni(II) atom, one 3,5-$(NO_2)_2$sal ligand, one phen ligand and two coordinated water molecules (Fig. 3).

The coordination geometry around the Ni(II) atom is an octahedron. Two oxygen atoms (O2 and O3) from 3,5-$(NO_2)_2$sal ligand (Ni–O lengths 1.980(2) and 1.989(2) Å), and two nitrogen atoms (N3 and N4) from chelating phen ligand (Ni–N lengths 2.061(3) and 2.084(3) Å) form the equatorial plane, while the two oxygen atoms (O8 and O9) from two coordination water molecules occupy the axial positions with Ni–O lengths of 2.125(3) and 2.151(3) Å. Each 3,5-$(NO_2)_2$sal ligand is coordinated to one Ni(II) atom only, coordinate mode of 3,5-$(NO_2)_2$sal ligand being O,O′-chelating fashion.

As illustrated in Fig. 4 and Table 3, there are rich hydrogen bonds among the coordinated water molecules, the carboxylate groups and the NO_2 groups of 3,5-$(NO_2)_2$sal ligands in **2**. These C–H···O hydrogen bonds with oxygen atoms (O4, O5, O6 and O7 from NO_2 group) and the O–H···O hydrogen bonds between the water O–H group and the carboxylate O1 atom connect the neighboring complex molecules, resulting in an extended 2D layer network down the *a* axis (see Figs. 4a and b).

All hydrogen bonds lead to the formation of three-dimensional framework structures (Fig. 4c). The hydrogen bonds based on NO_2 groups play an important role in the supramolecular formation of complex **2**.

3.3. Structural description of [Co{3,5-$(NO_2)_2$sal}(4,4′-bipy)$(H_2O)\cdot(H_2O)]_n$ (3)

Complex **3** exhibits a 2D rectangular grid-like network structure. As illustrated in Fig. 5, Co1 atom is coordinated

Table 2
Selected lengths (Å) and Angles (°) for complexes **1–5**

*Compound **1***					
Cd(1)–O(3)	2.243(2)	Cd(1)–O(2)	2.276(2)	Cd(1)–O(1)A	2.286(2)
Cd(1)–O(8)	2.334(2)	Cd(1)–N(4)	2.338(3)	Cd(1)–N(3)	2.350(3)
O(3)–Cd(1)–O(2)	77.49(7)	O(2)–Cd(1)–O(1)A	83.18(8)	O(3)–Cd(1)–O(1)A1	154.56(8)
O(2)–Cd(1)–O(8)	100.76(9)	O(1)A–Cd(1)–O(8)	81.27(8)	O(3)–Cd(1)–O(8)	86.22(9)
O(3)–Cd(1)–N(4)	78.67(8)	O(2)–Cd(1)–N(4)	147.84(8)	O(A)–Cd(1)–N(4)	98.89(9)
O(1)A–Cd(1)–N(4)	125.02(9)	O(1)A–Cd(1)–N(3)	80.49(8)	O(2)–Cd(1)–N(3)	102.83(8)
O(3)–Cd(1)–N(3)	119.72(9)	N(4)–Cd(1)–N(3)	71.19(9)	O(A)–Cd(1)–N(3)	148.07(9)
*Compound **2***					
Ni(1)–O(2)	1.980(2)	Ni(1)–O(3)	1.989(2)	Ni(1)–N(4)	2.084(3)
Ni(1)–N(3)	2.061(3)	Ni(1)–O(8)	2.126(3)	Ni(1)–O(9)	2.151(3)
O(2)–Ni(1)–O(3)	91.82(9)	O(3)–Ni(1)–O(9)	91.5(1)	O(2)–Ni(1)–N(3)	93.93(1)
O(3)–Ni(1)–N(3)	174.2(1)	O(2)–Ni(1)–O(9)	89.8(1)	O(2)–Ni(1)–N(4)	174.7(1)
O(3)–Ni(1)–N(4)	93.5(1)	N(3)–Ni(1)–O(9)	89.7(1)	N(3)–Ni(1)–N(4)	80.8(1)
O(2)–Ni(1)–O(8)	89.5(1)	N(4)–Ni(1)–O(8)	90.6(1)	O(3)–Ni(1)–O(8)	88.8(1)
N(3)–Ni(1)–O(8)	90.2(1)	N(4)–Ni(1)–O(9)	90.2(1)	O(8)–Ni(1)–O(9)	179.2(9)
*Compound **3***					
Co(1)–O(2)	2.037(3)	Co(1)–O(1)A	2.089(4)	Co(1)–O(3)	2.093(4)
Co(1)–N(4)B	2.177(4)	Co(1)–N(3)	2.184(4)	Co(1)–O(8)	2.117(4)
O(2)–Co(1)–O(1)A	81.5(1)	O(2)–Co(1)–N(3)	92.4(2)	O(2)–Co(1)–O(3)	84.8(1)
O(1)A1–Co(1)–O(3)	166.3(1)	O(3)–Co(1)–N(3)	87.4(1)	O(2)–Co(1)–O(8)	177.1(2)
O(1)A–Co(1)–O(8)	96.0(2)	N(4)B–Co(1)–N(3)	175.6(2)	O(3)–Co(1)–O(8)	97.7(2)
O(2)–Co(1)–N(4)B	91.4(1)	O(1)A–Co(1)–N(3)	94.3(2)	O(1)A–Co(1)–N(4)B	84.2(2)
O(3)–Co(1)–N(4)B	95.0(2)	O(8)–Co(1)–N(3)	86.2(2)	O(8)–Co(1)–N(4)B	89.8(1)
*Compound **4***					
Co(1)–O(3)	1.976(2)	Co(1)–O(2)	2.003(2)	Co(1)–O(1)A	2.010(2)
Co(1)–N(4)	2.109(3)	Co(1)–N(3)	2.144(3)	O(1)A–Co(1)–N(4)	111.2(1)
O(3)–Co(1)–O(2)	90.28(9)	O(3)–Co(1)–N(4)	92.7(1)	O(3)–Co(1)–N(3)	164.4(1)
O(3)–Co(1)–O(1)A	111.7(1)	O(2)–Co(1)–N(4)	135.3(1)	O(2)–Co(1)–N(3)	88.53(9)
O(2)–Co(1)–O(1)A	108.9(1)	O(1)A–Co(1)–N(3)	83.4(1)	N(4)–Co(1)–N(3)	77.4(1)
*Compound **5***					
Zn(1)–O(1)A	1.979(3)	Zn(1)–O(2)	2.009(3)	Zn(1)–O(3)	1.988(3)
Zn(1)–N(4)	2.139(3)	Zn(1)–N(3)	2.137(3)	O(3)–Zn(1)–N(3)	89.9 (1)
O(1)A–Zn(1)–O(3)	111.0(1)	O(1)A–Zn(1)–N(3)	111.4(1)	O(2)–Zn(1)–N(3)	136.5(1)
O(1)A–Zn(1)–O(2)	109.5(1)	N(3)–Zn(1)–N(4)	77. 5(1)	O(1)A–Zn(1)–N(4)	88.2(1)
O(3)–Zn(1)–O(2)	89.1 (1)	O(2)–Zn(1)–N(4)	89.6 (1)	O(3)–Zn(1)–N(4)	160.1(1)

Symmetry code: **1** (A) $x-1/2$, $-y+1/2$, $-z+1$. **3** (A) $-x+1$, $y-1/2$, $-z+3/2$; (B) $x-1$, y, z. **4** (A) $-x+3/2$, $y+1/2$, $-z+1/2$. **5** (A) $-x+1/2$, $y-1/2$, $-z+1/2$.

by three oxygen atoms from two 3,5-dinitrosalicylate ligands (Co–O lengths range 2.037(4)–2.094(7) Å), two nitrogen atoms from two 4,4′-bipyridine ligands (Co–N lengths 2.177(4), 2.184(5) Å) and one oxygen atom from coordination water (Co–O8 lengths 2.116(4) Å), forming a distorted octahedral geometry. The four oxygen atoms (O2, O3, O8 and O1A) consist the equatorial plane, two nitrogen atoms are in the axial positions, N3–Co1–N4B bond angle being 175.7 (1)°.

3,5-$(NO_2)_2$sal ligands adopt chelating–bridging mode. Every 3,5-$(NO_2)_2$sal ligand links two neighboring cobalt atoms into a 1D right-handed helix structure along the *b* axis. And then neighboring chains are connected through 4,4′-bipyridine ligands, forming a 2D rectangular grid-like network fragment (see Fig. 6). The Co···Co distance between the adjacent cobalt atoms through the carboxyl bridge is 5.183(2) Å, while the corresponding Co···Co distance through 4,4′-bipyridine is 11.415(4) Å. The vertex angles of lattice are 85.04(1)° and 94.96(1)°, respectively. The adjacent 2D fragments are further connected to each other by C–H···O hydrogen bonds between the phenyl hydrogens of 4,4′-bipy and the NO_2 groups of 3,5-$(NO_2)_2$sal ligands, resulting in a 3D framework structure (Supplementary Fig. S2).

*3.4. Structural description of [Co{3,5-$(NO_2)_2$sal}(phen)]$_n$ (**4**) and [Zn{3,5-$(NO_2)_2$sal}(phen)]$_n$ (**5**)*

The title complexes **4** and **5** crystallize in the $P2_1/n$ space group and adopt helical chain structure consisting of Co{3,5-$(NO_2)_2$sal}(phen) or Zn{3,5-$(NO_2)_2$sal}(phen) entities. The complexes **4** and **5** constitute a pair of isomorphous. Xu J.-N. et al. [30] reported that the hydrothermal synthesis of $Co(NH_3)_6Cl_3$, 1,10-phenanthroline, 3,5-dinitrosalicylic acid, and H_2O at 140 °C for 72 h yielded deep red platelet crystals of complex Co{3,5-$(NO_2)_2$sal}-(phen) with space group *C*c. The title complex [Co{3,5-$(NO_2)_2$sal}(phen)]$_n$ (**4**) and the complex in [30] are

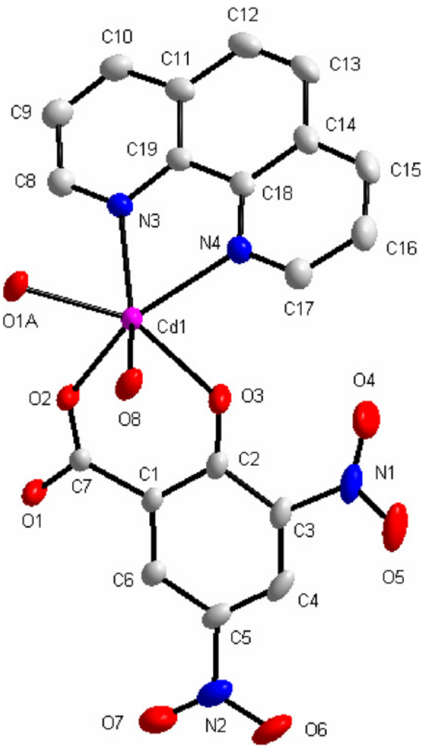

Fig. 1. Coordination arrangements of the Cd(II) atom in **1** with 30% probability ellipsoid. Hydrogen atoms are omitted for clarity. Symmetry code (A) $x - 1/2, -y + 1/2, -z + 1$.

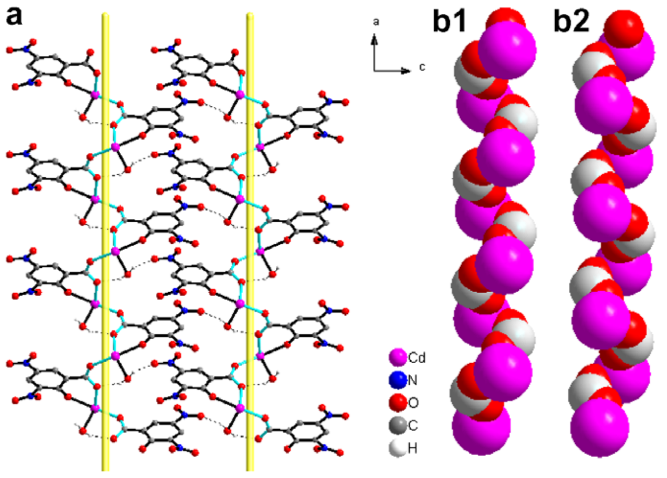

Fig. 2. (a) Extended 2D network structure along ac plane in **1**. 1,10-Phen are omitted for clarity. Dashed lines represent the hydrogen bonds. (b) Right-handed helix (b1) and left-handed helix (b2) in **1**. Unnecessary atoms are omitted for clarity.

Table 3
Hydrogen bond lengths (Å) and angles (°) for the complexes **1**–**5**

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	<(DHA)
Compound ***1***				
O(8)–H(08A)···O(2)^a	0.819(2)	1.937(2)	2.710(3)	157.0(2)
O(8)–H(08B)···O(6)^b	0.877(2)	2.436(3)	3.264(4)	157.8(2)
C(17)–H(17A)···O(5)^b	0.931(4)	2.535(3)	3.351(5)	146.6(2)
C(10)–H(10A)···O(4)^c	0.930(4)	2.619(4)	3.438(5)	147.1(2)
C(8)–H(8A)···O(6)^d	0.929(3)	2.642(3)	3.308(4)	129.1(2)
Compound ***2***				
O(9)–H(09A)···O(1)^a	0.87(1)	1.91(3)	2.77(4)	171.9(2)
O(9)–H(09B)···O(4)^b	0.81(1)	2.24(4)	3.04(5)	170.4(2)
O(8)–H(08B)···O(1)^c	0.86(2)	1.89(4)	2.74(6)	173.1(2)
O(8)–H(08A)···O(5)^d	0.79(9)	2.08(2)	2.85(3)	170.1(2)
C(10)–H(10A)···O(6)^e	0.95(1)	2.43(2)	3.11(3)	127.4(3)
C(13)–H(13A)···O(7)^f	0.99(2)	2.34(3)	3.26(5)	154.9(3)
Compound ***3***				
C(14)–H(14A)···O(4)^a	0.930(6)	2.40(1)	3.27(2)	155.3(5)
C(16)–H(16A)···O(6)^b	0.929(8)	2.54(1)	3.10(2)	119.41(4)
C(8)–H(8A)···O(5)^c	0.930(8)	2.56(2)	3.11(2)	117.51(6)
Compound ***4***				
C(10)–H(10A)···O(7)^a	0.930(5)	2.465(4)	3.038(6)	120.0(3)
C(16)–H(16A)···O(6)^b	0.930(4)	2.65(1)	3.42(1)	139.7(3)
C(12)–H(12A)···O(5)^c	0.929(5)	2.67(1)	3.47(2)	144.0(3)
Compound ***5***				
C(10)–H(10A)···O(7)^a	0.932(6)	2.482(4)	3.046(7)	119.1(4)
C(16)–H(16A)···O(6)^b	0.930(5)	2.645(5)	3.412(7)	140.2(3)
C(12)–H(12A)···O(5)^b	0.931(5)	2.63(1)	3.42(1)	142.7(4)

Symmetry code: **1** ^{a} $-0.5 + x,\ 0.5 - y,\ 1 - z$; ^{b} $-0.5 + x,\ y,\ 0.5 - z$; ^{c} $1 - x,\ -y,\ 1 - z$; ^{d} $x,\ 0.5 - y,\ 0.5 + z$. **2** ^{a} $-x,\ -y,\ 1 - z$; ^{b} $-x,\ 1 - y,\ 1 - z$; ^{c} $1 - x,\ -y,\ 1 - z$; ^{d} $1 - x,\ 1 - y,\ 1 - z$; ^{e} $-1 + x,\ y,\ -1 + z$; ^{f} $-1 + x,\ 1 + y,\ -1 + z$. **3** ^{a} $2 - x,\ -y,\ 2 - z$; ^{b} $2 - x,\ 1 - y,\ 2 - z$; ^{c} $x,\ 0.5 - y,\ -0.5 + z$. **4** ^{a} $0.5 + x,\ 0.5 - y,\ -0.5 + z$; ^{b} $0.5 - x,\ 0.5 + y,\ 0.5 - z$; ^{c} $0.5 + x,\ 1.5 - y,\ -0.5 + z$. **5** ^{a} $-0.5 + x,\ 1.5 - y,\ 0.5 + z$; ^{b} $1.5 - x,\ -0.5 + y,\ 0.5 - z$; ^{c} $-0.5 + x,\ 0.5 - y,\ 0.5 + z$.

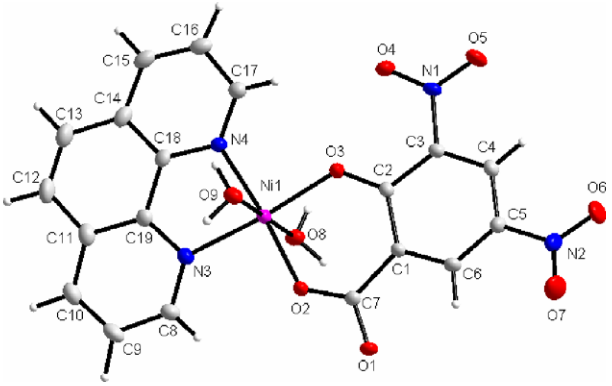

Fig. 3. Molecular structure of the complex **2** with 30% probability ellipsoid.

polymorphic. The Co···Co distance between the two neighboring cobalt atoms in the helical chain of complex **4** is 5.331 Å, while the corresponding Co···Co distance of the complex [30] is 4.085 Å.

The title complexes **4**, **5** and the complex $[Mn(phen)\{3,5\text{-}(NO_2)_2sal^{2-}\}]_n$ reported by [31] are isomorphous. They all exhibit the one-dimensional left- and right-handed helical chains (Supplementary Fig. S3). Because the van der Waals radius of cobalt and zinc are different from that of manganese, the corresponding distances of Co–O and Co–N, Zn–O and Zn–N are a little different from that of Mn–O and Mn–N.

As illustrated in Table 3 and the packing diagrams of complexes **4** and **5** (Supplementary Fig. S4), C–H···O hydrogen bonds between the phenyl hydrogens of phen

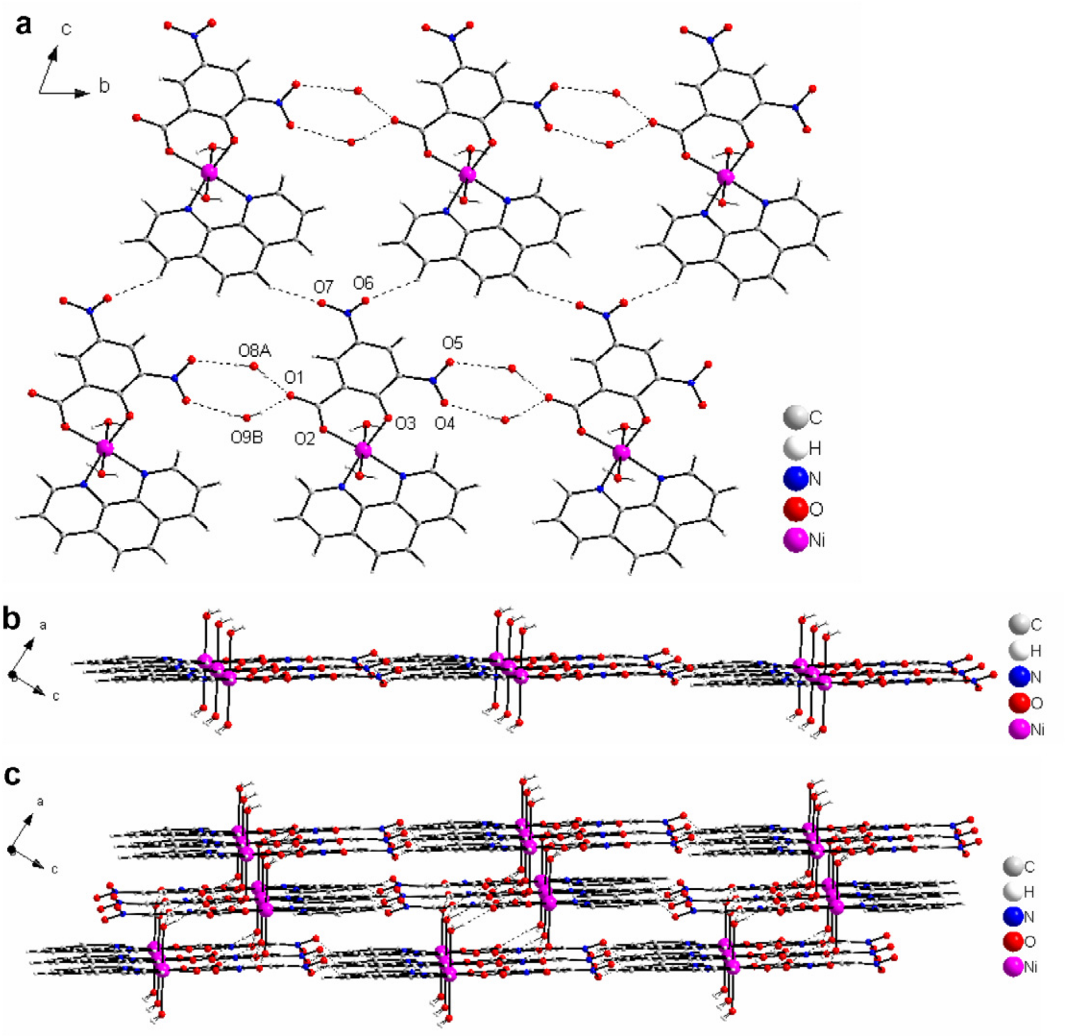

Fig. 4. (a) Extended 2D layer observed in **2** down the *a* axis, the discrete oxygen atoms represent the coordinated water molecules in order to clarity. Symmetry codes: (A) $1-x, -y, 1-z$; (B) $-x, -y, 1-z$. (b) Side view of the extended 2D layer in **2** down the *b* axis. (c) The 3D supramolecular structure in **2.** Dashed lines represent the hydrogen bonds.

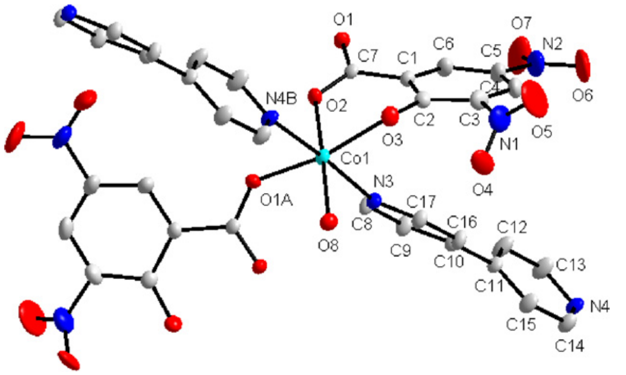

Fig. 5. Coordination environment of the Co(II) atom in **3** with 30% probability ellipsoid. Hydrogen atoms and solvent water molecules are omitted for clarity. Symmetry codes: (A) $-x+1, y-1/2, -z+3/2$; (B) $x-1, y, z$.

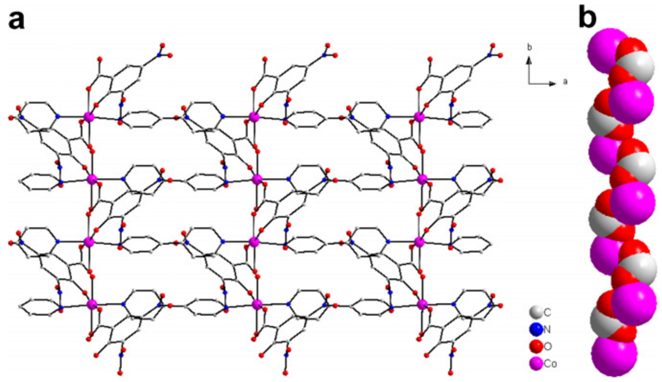

Fig. 6. (a) The 2D rectangular grid-like structure in **3**. Hydrogen atoms and solvent water molecules are omitted for clarity. (b) Right-handed helix in **3**. Unnecessary atoms are omitted for clarity.

ligands and the NO_2 groups of 3,5-$(NO_2)_2$sal ligands are the major intermolecular force between the neighboring chains and play an important role in stable the crystal structures Fig. 7.

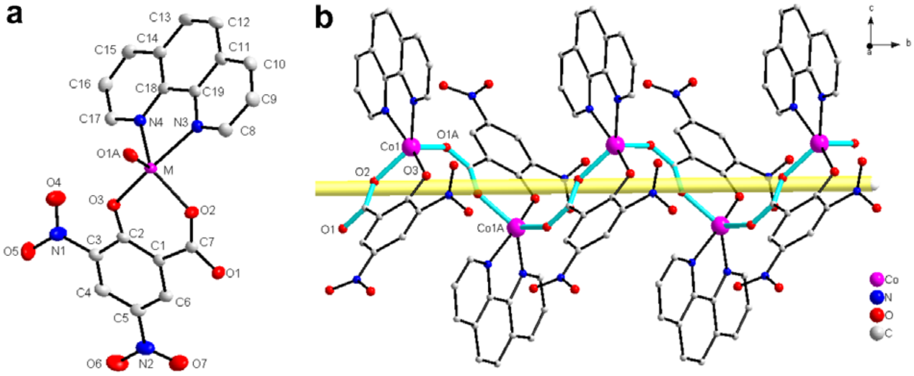

Fig. 7. (a) Coordination arrangements of the M(II) atoms (M = Co and Zn for complexes **4** and **5**, respectively) with 30% probability ellipsoid. Hydrogen atoms are omitted for clarity. (b) The 1D helical chain of complex **4** along *b* axis. Hydrogen atoms are omitted for clarity.

3.5. Thermogravimetric analysis

The thermogravimetric analysis of **1** (see Supplementary Fig. S5) shows the loss of one coordinated water molecule between 170 and 202 °C (found, 3.56%; calcd., 3.36%) and an explosive weight loss at 346 °C. The TG curve shows that complex **4** is stable up to 250 °C, an explosive weight loss at 402 °C. Complex **5** is stable up to 300 °C, an explosive weight loss at 422 °C. Metal complexes of 3,5-dinitrosalicylic acid are potentially explosive.

3.6. Photoluminescence

The emission spectra of complexes **1** and **5** and the free 3,5-$(NO_2)_2$sal ligand in the solid state at room temperature are investigated (Supplementary Figs. S6 and S7). Complex **1** exhibits stronger blue fluorescent emission at ca. 485 nm and weaker emission bands at 527 and 539 nm upon excitation at ca. 355 nm, while complex **5** exhibits stronger blue fluorescent emission at ca. 483 nm and weaker emission bands at 535 nm upon excitation at ca. 360 nm. The peaks at 485 and 483 nm in **1** and **5** would be assigned to the intraligand fluorescent emission because similar emissions are observed for the free 3,5-$(NO_2)_2$sal ligand. The weaker emission bands at 527, 539 and 535 nm would be assigned to the emission of LMCT [34,35].

3.7. IR spectra

Two absorption peaks at 1626 and 1426 cm^{-1} in the IR spectra for **2** and 1615 and 1428 cm^{-1} for **4** are attributed to the COO antisymmetric and symmetric stretching frequencies, respectively (Supplementary Figs. S8 and S9). The difference between the asymmetric and symmetric stretching vibrations ($\Delta v = v_{as}(COO^-) - v_s(COO^-)$) is 200 cm^{-1} for **2** and 187 cm^{-1} for **4,** suggesting that the 3,5-dinitrosalicylate anions are coordinated to metal atom as a unidentate group in **2** and a bridging bidentate group in **4** [36]. The peaks at 3551, 3481 cm^{-1} in **2** could be attributed to OH vibration of coordination water.

4. Conclusions

Three 1D helical coordination polymers (complexes **1**, **4** and **5**), one mononuclear complex (complex **2**) and one 2D rectangular grid-like coordination polymer (complex **3**) with mixed ligands (3,5-$(NO_2)_2$sal and N-donor ligand) have been hydrothermally synthesized and characterized. 3,5-$(NO_2)_2$sal ligands in **1**, **3**, **4** and **5** adopt chelating–bridging mode, while 3,5-$(NO_2)_2$sal in **2** has a mono-chelating mode. The C–H···O hydrogen bonds, formed between the NO_2 groups of 3,5-$(NO_2)_2$sal ligands and phenyl hydrogens of phen or 4,4′-bipy ligands, are the major binding force to lead to the formation of three-dimensional supramolecular framework structures. From the syntheses and structures among complexes **1**–**5**, we can conclude that the formation of these complexes is significantly dependent on many factors, such as the coordination geometry of the metal centers, the coordination modes of the 3,5-$(NO_2)_2$sal ligands, pH value of the solution, and temperature.

Acknowledgements

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Appendix A. Supplementary data

The crystallographic data of the structures described in this paper were deposited in the Cambridge Crystallographic Data Center with the CCDC deposition numbers 631506, 631507, 631508, 631509, 631510, respectively. The TG curves for complexes **1**, **4** and **5**, Emission spectra of compounds **1**, **5** and 3,5-$(NO_2)_2$sal ligand and the IR spectra of **2** and **4** were deposited in the online version. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2007.06.031.

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