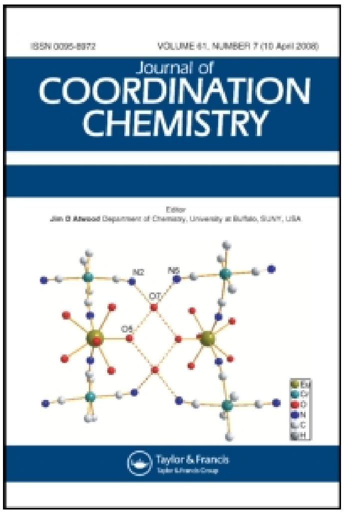

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Hydrothermal synthesis and characterization of La^{III} and Cu^{II} coordination polymers with 5-nitroisophthalic acid (H$_2$Nip), [La$_2$(μ-Nip)(μ-SO$_4$)$_2$(H$_2$O)$_5$]<i>_n and {[Cu$_3$(μ-OH)$_2$(μ-Nip)$_2$(μ-H$_2$O)$_2$] · 2H$_2$O}<i>_n

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Hydrothermal synthesis and characterization of La^{III} and Cu^{II} coordination polymers with 5-nitroisophthalic acid (H_2Nip), $[La_2(\mu\text{-Nip})(\mu\text{-}SO_4)_2(H_2O)_5]_n$ and $\{[Cu_3(\mu\text{-}OH)_2(\mu\text{-Nip})_2(\mu\text{-}H_2O)_2]\cdot 2H_2O\}_n$

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3D La^{III} and 2D Cu^{II} coordination polymers with 5-nitroisophthalate anions, $[La_2(\mu\text{-Nip})(\mu\text{-}SO_4)_2(H_2O)_5]_n$ (**1**) and $\{[Cu_3(\mu\text{-}OH)_2(\mu\text{-Nip})_2(\mu\text{-}H_2O)_2]\cdot 2H_2O\}_n$ (**2**), have been synthesized, characterized and studied by X-ray crystallography. The La atoms have eight–coordinate geometries in distorted square antiprism environments and the Cu atoms have five- and six–coordinate geometries with distorted square pyramidal and octahedral environments. Self-assembly of these compounds in the solid state occurs through coordination and hydrogen bonding.

Keywords: Lanthanide(III); Copper(II); 5-nitroisophthalate; Coordination polymer

1. Introduction

Transition metal ions and organic spacers to form new extended framework structures with desirable physical and chemical properties are of interest for applications such as catalysis, nonlinear optics, gas separation, magnetic devices and molecular recognition [1–4]. In the design and construction of these frameworks organic ligands play crucial roles as even small changes in flexibility, length, or symmetry of the ligands can result in a remarkable diversity of architectures and functions [1–4]. Thus, tuning the properties of metal-organic frameworks through systematic change of organic ligands provides an impetus for further research on metal-organic supramolecular architectures. A large number of benzenedicarboxylate (bdc) coordination polymers with metal-organic frameworks have been synthesized [5–15]. The bdc ditopic ligand has two potentially

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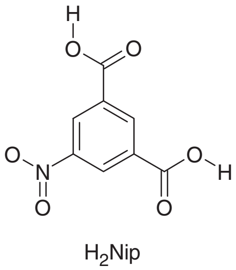


Scheme 1. The organic ligand H_2Nip.

equivalent coordinating carboxylate groups, thus the variable topologies in assembled networks constructed by this ligand are limited. The 5-nitroisophthalic acid (H_2Nip) ligand attracted our attention because of the potential structural chemistry of its multifunctional coordination modes via the carboxylate groups and nitro oxygen atoms, allowing for formation of polymeric structures.

Metal carboxylate polymers from isophthalic acid and its derivative, 5-nitroisophthalic acid, have been reported [16–17]. The nitro group (–NO_2) as an electron-withdrawing group in isophthalic acid is a hydrogen bond acceptor and also takes on spatial effects in the formation of polymeric networks [18]. Some coordination polymers of 5-nitroisophthalic acid (Scheme 1) have been prepared [19–20] that show some interesting structures. In this work, we describe the syntheses, characterization and also X-ray crystal structures of $[La_2(\mu\text{-Nip})(\mu\text{-}SO_4)_2(H_2O)_5]_n$ (**1**) and $\{[Cu_3(\mu\text{-}OH)_2(\mu\text{-Nip})_2(\mu\text{-}H_2O)_2]\cdot 2H_2O\}_n$ (**2**).

2. Experimental

2.1. *Physical property measurements*

All reagents and solvents for the synthesis and analysis were commercially available and used as received. IR spectra were recorded using Perkin-Elmer 597 and Nicolet 510P spectrophotometers. Microanalyses were carried out using a Heraeus CHN–O– Rapid analyzer. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected.

2.2. *Synthesis of $[La_2(\mu\text{-Nip})(\mu\text{-}SO_4)_2(H_2O)_5]_n$ (1)*

$La_2(SO_4)_3$ (0.5 mmol), 5-nitroisophthalic acid (0.5 mmol) and 2,2-bipyridine (0.5 mmol) were placed in a 30 mL Teflon-lined, stainless-steel Parr bomb with water (18 mL). The bomb was heated at 423 K for five days and cooled slowly to room temperature to furnish colorless crystals. Anal. Calcd. for $C_8H_{13}NO_{19}S_2La_2$: C 12.49, H 1.70, N 1.82%; found: C 12.36, H 1.59, N 1.71%.

IR (selected signals, cm^{-1}): 3419s, 3083w, 1607vs, 1586s, 1546s, 1421s, 1378s, 1175s, 1093m, 1027m, 923m, 849s, 774m, 718m, and 618m.

Table 1. Crystal data and structure refinement data for $[\mathrm{La_2(\mu\text{-}Nip)(\mu\text{-}SO_4)_2(H_2O)_5}]_n$ (**1**) and $\{[\mathrm{Cu_3(\mu\text{-}OH)_2(\mu\text{-}Nip)_2(\mu\text{-}H_2O)_2}]\cdot \mathrm{2H_2O}\}_n$ (**2**).

Identification code	**1**	**2**
Empirical formula	$\mathrm{C_8\,H_{13}\,La_2\,N\,O_{19}\,S_2}$	$\mathrm{C_{16}H_{16}Cu_3N_2O_{18}}$
Formula weight	769.13	714.93
Temperature (K)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073
Crystal system, space group	Monoclinic, $P2_1/c$	Triclinic, $P\bar{1}$
Unit cell dimensions (Å, °)		
a	6.7478(4)	5.6317(9)
b	10.9966(7)	10.6231(18)
c	25.8104(16)	11.1386(19)
α		118.087(3)
β	96.6330(10)	99.187(3)
γ		94.385(3)
Volume (Å^3)	1902.4(2)	571.50(16)
Z, Calculated density (Mg m^{-3})	4, 2.685	1, 2.077
Absorption coefficient (mm^{-1})	4.752	2.862
F(000)	1464	357
Crystal size (mm^3)	$0.41 \times 0.30 \times 0.26$	$0.21 \times 0.16 \times 0.05$
θ range for data collection (°)	2.39 to 28.29	2.13 to 25.29
Limiting indices	$-8 \le h \le 7$, $-12 \le k \le 13$, $-28 \le l \le 31$	$-6 \le h \le 6$, $-12 \le k \le 12$, $-13 \le l \le 13$
Reflections collected/unique	9691/3450 [$R_{(\mathrm{int})} = 0.0208$]	4257/2061 [$R_{(\mathrm{int})} = 0.0258$]
Completeness to θ	99.7%	99.2%
Absorption correction	Multi-scan	Multi-scan
Max. and min. transmission	0.290 and 0.193	0.8701 and 0.5847
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3429/0/178	2061/0/178
Goodness-of-fit on F^2	1.151	1.227
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0249$, $wR_2 = 0.0794$	$R_1 = 0.0664$, $wR_2 = 0.1426$
R indices (all data)	$R_1 = 0.0253$, $wR_2 = 0.0798$	$R_1 = 0.0691$, $wR_2 = 0.1441$
Largest diff. peak and hole (e A^{-3})	1.082 and −0.725	0.934 and −1.642

2.3. *Synthesis of* $\{[\mathrm{Cu_3(\mu\text{-}OH)_2(\mu\text{-}Nip)_2(\mu\text{-}H_2O)_2}]\cdot \mathrm{2H_2O}\}_n$ *(2)*

$\mathrm{Cu(CH_3COO)_2 \cdot H_2O}$ (0.5 mmol), 5-nitroisophthalic acid (0.5 mmol) and 1,2-di (4-pyridine)ethylene (0.5 mmol) were placed in a 30 mL Teflon-lined, stainless-steel Parr bomb together with water (18 mL). The bomb was heated at 403 K for five days and cooled slowly to room temperature to furnish blue crystals. Anal. calcd. for $\mathrm{C_{16}H_{16}Cu_3N_2O_{18}}$: C 26.88, H 2.26, N 3.92%; found: C 26.52, H 2.11, N 3.76%.

IR (selected signals, cm^{-1}): 3549s, 3098w, 1607vs, 1560s, 1521s, 1457s, 1378s, 1348s, 1201w, 1083m, 924m, 785m, 730m, and 590m.

2.4. *Crystallography*

X-ray measurements were made at 298(2) using a Siemens R3m V^{-1} diffractometer. The intensity data were collected within the range 1.59 to 25.30° for **1** and 2.13 to 25.29° for **2** using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Accurate unit cell parameters and an orientation matrix for data collection were obtained from least–squares refinement. The structures were solved by direct methods and refined by full–matrix least–squares on F^2. Crystal data and refinement parameters are given in table 1. Selected bond lengths and angles are given in tables 2–3.

Table 2. Bond lengths (Å) and angles (°) for [La$_2$(μ-Nip)(μ-SO$_4$)$_2$(H$_2$O)$_5$]$_n$ (**1**).

La1–O1	2.48(1)
La1–O11	2.49(1)
La1–O7	2.54(1)
La1–O16	2.57(1)
La1–O15	2.64(1)
La1–O18	2.68(1)
La1–O17	2.71(1)
La2–O2^{i}	2.35(1)
La2–O8^{i}	2.42(1)
La2–O3^{ii}	2.54(1)
La2–O14	2.54(1)
La2–O19	2.57(1)
La2–O13	2.57(1)
La2–O12	2.60(1)
La2–O4	2.61(1)
La2–O4^{ii}	2.81(1)
O1–La1–O7	84.31(1)
O11–La1–O7	133.51(1)
O1–La1–O16	145.30(1)
O11–La1–O16	76.47(1)
O7–La1–O16	77.37(1)
O1–La1–O15	75.94(1)
O11–La1–O15	130.76(1)
O7–La1–O15	72.80(1)
O16–La1–O15	70.61(1)
O1–La1– O18	68.63(1)
O11–La1–O18	68.38(1)
O7–La1–O18	150.93(1)
O16–La1–O18	131.30(1)
O15–La1–O18	108.91(1)
O1–La1–O17	132.45(1)
O11–La1–O17	69.27(1)
O7–La1–O17	64.83(1)
O16–La1–O17	63.91(1)
O15–La1–O17	122.59(1)
O18–La1–O17	127.05(1)
O2^{i} –La2–O8^{i}	87.98(1)
O2^{i} –La2–O3^{i}	148.02(1)
O8^{i} –La2–O3^{i}	70.57(1)
O2^{i} –La2–O14	78.90(1)
O8^{i} –La2–O14	79.61(1)
O3^{i}–La2–O14	74.20(1)
O2^{i} –La2–O19	80.61(1)
O8^{i} –La2–O19	141.48(1)
O3^{i} –La2–O19	101.29(1)
O14–La2–O19	62.15(1)
O2^{i} –La2–O13	73.31(1)
O8^{i} –La2–O13	78.97(1)
O3–La2–O13	122.73(1)
O14–La2–O13	145.25(1)
O19–La2–O13	130.82(1)
O2^{i} –La2–O12	127.01(1)
O8^{i} –La2–O12	76.24(1)
O3^{i} –La2–O12	71.74(1)
O14–La2–O12	143.16(1)
O19–La2–O12	138.63(1)
O13–La2–O12	54.23(1)
O2^{i} –La2–O4^{ii}	97.55(1)
O8^{i} –La2–O4^{ii}	149.28(1)

(*Continued*)

Table 2. Continued.

O3^{i} –La2–O4^{ii}	113.08(1)
O14–La2–O4^{ii}	131.10(1)
O19–La2–O4^{ii}	69.12(1)
O13–La2–O4^{ii}	73.85(1)
O12–La2–O4^{ii}	76.38(1)
O2^{i} –La2–O4^{ii}	152.23(1)
O8^{i} –La2–O4^{ii}	117.51(1)
O3^{i} –La2–O4^{ii}	48.49(1)
O14–La2–O4^{ii}	94.24(1)
O19–La2–O4^{ii}	72.51(1)
O13–La2–O4^{ii}	119.93(1)
O12–La2–O4^{ii}	73.32(1)
O4–La2–O4^{ii}	66.66(1)

Symmetry transformations used to generate equivalent atoms: i: $-x,\ y+1/2,\ -z+1/2$; ii: $x, -y+1/2,\ z+1/2$.

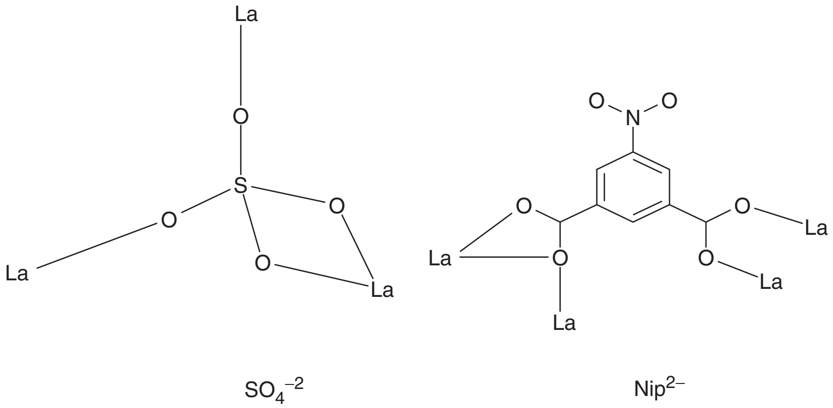
Table 3. Bond lengths (Å) and angles (°) for $\{[Cu_3(\mu\text{-}OH)_2(\mu\text{-}Nip)_2(\mu\text{-}H_2O)_2]\cdot 2H_2O\}_n$ (**2**).

Cu(1)–O(7)	1.94(1)
Cu(1)–O(1)	1.95(1)
Cu(1)–Cu(2)#1	3.02(1)
Cu(1)–Cu(2)	3.02(1)
Cu(2)–O(3)#2	1.90(1)
Cu(2)–O(2)	1.96(2)
Cu(2)–O(7)#1	1.98(1)
Cu(2)–O(8)	2.29(1)
O(7)–Cu(1)–O(7)#1	180.0(1)
O(7)–Cu(1)–O(1)	87.97(2)
O(7)#1–Cu(1)–O(1)	92.03(2)
O(7)–Cu(1)–O(1)#1	92.03(2)
O(7)#1–Cu(1)–O(1)#1	87.97(2)
O(1)–Cu(1)–O(1)#1	180.0(1)
O(3)#2–Cu(2)–O(2)	85.5(2)
O(3)#2–Cu(2)–O(7)#1	174.9(2)
O(2)–Cu(2)–O(7)#1	91.26(2)
O(3)#2–Cu(2)–O(7)#3	103.5(2)
O(2)–Cu(2)–O(7)#3	166.0(2)
O(7)#1–Cu(2)–O(7)#3	78.97(2)
O(3)#2–Cu(2)–O(8)	97.4(2)
O(2)–Cu(2)–O(8)	99.2(2)
O(7)#1–Cu(2)–O(8)	86.99(2)
O(7)#3–Cu(2)–O(8)	90.34(2)

Symmetry transformations used to generate equivalent atoms: #1 $-x+2,\ -y,\ -z+2$; #2 $-x+3,\ -y+1,\ -z+2$; #3 $x+1,\ y,\ z$.

3. Results and discussion

Reaction between 2,2′-bipyridine, lanthanum(III) sulfate and 5-nitroisophthalic acid as well as 1,2-di(4-pyridine)ethylene, copper(II) acetate monohydrate and 5-nitroisophthalic acid in water solution provided crystalline materials analyzing as $[La_2(\mu\text{-}Nip)(\mu\text{-}SO_4)_2(H_2O)_5]_n$ (**1**) and $\{[Cu_3(\mu\text{-}OH)_2(\mu\text{-}Nip)_2(\mu\text{-}H_2O)_2]\cdot 2H_2O\}_n$ (**2**). The IR spectra and CHN analyses showed that 2,2′-bipyridine and 1,2-di(4-pyridine)ethylene, do not



Scheme 2. The coordination of SO_4^{2-} and Nip^{2-} in $[La_2(\mu\text{-Nip})(\mu\text{-}SO_4)_2(H_2O)_5]_n$.

coordinate in **1** and **2**, respectively. IR spectra display characteristic absorption bands for "Nip^{2-}", water and SO_4^{2-} in the **1** and for "Nip^{-2}", H_2O and OH^- in **2.** The relatively weak absorption bands at 3086 and 3098 cm^{-1} are due to aromatic ring hydrogen atoms in **1** and **2**, respectively. Absorption bands with variable intensity in the frequency range 1400–1600 cm^{-1} correspond to ring vibrations of the "Nip^{2-}". The characteristic bands of carboxylate appear at 1586 $\upsilon_{as(C–O)}$ and 1378 $\upsilon_{sym(C–O)}$ cm^{-1} for **1** and 1607 $\upsilon_{as(C–O)}$ and 1378 $\upsilon_{sym(C–O)}$ cm^{-1} for **2**. The strong and broad peak at 3419 and 3549 cm^{-1} suggest the existence of water molecules in **1** and **2**, respectively, and the broadness suggests hydrogen bonding interactions.

Single X-ray crystal analysis reveals that $[La_2(\mu\text{-Nip})(\mu\text{-}SO_4)_2(H_2O)_5]_n$ crystallizes in monoclinic with space group $P2_1/c$. The structure may be considered as a three-dimensional coordination polymer of lanthanum(III) coordinated by "Nip^{2-}", "SO_4^{2-}" and H_2O. There are two different La atoms, La1 and La2. The La1 atoms are coordinated by one oxygen atom from "Nip^{2-}", three oxygen atoms from "SO_4^{2-}" and four water ligands whereas La2 atoms are coordinated by three oxygen atoms from "Nip^{2-}", one H_2O and four oxygen atoms from "SO_4^{2-}". The coordination number of La1 and La2 in this complex is eight and the environment of lanthanum is LaO_8. The coordination around the La1 and La2 atoms are distorted square antiprism. Each "NIP" anion is a five-donor ligand, connecting four La^{3+} ions. One carboxylate from "NIP" is bidentate and another is tridentate. The oxygen atoms of the nitro group are not coordinated to La atoms (Scheme 2). Each SO_4^{2-} is a four-donor ligand, connecting three La^{3+} ions (Scheme 2).

The coordinated water molecules in $[La_2(\mu\text{-Nip})(\mu\text{-}SO_4)_2(H_2O)_5]_n$ are involved in hydrogen bonding acting as hydrogen-bond acceptors towards O of the $–COO^-$ and $–NOO^-$ groups from "NIP" as potential hydrogen-bond donors (figure 3).

Single X–ray crystal analysis reveals that $\{[Cu_3(\mu\text{-OH})_2(\mu\text{-Nip})_2(\mu\text{-}H_2O)_2]\cdot 2H_2O\}_n$ (**2**) crystallizes in triclinic space group of $P\bar{1}$. The structure may be considered as a two-dimensional coordination polymer of copper(II) coordinated by ligands Nip^{2-}, H_2O and OH^- (figures 4 and 5). There are two different Cu atoms, Cu1 and Cu2. Cu1 is coordinated by two oxygen atoms from Nip^{2-}, two oxygen atoms of H_2O and two oxygen atoms of OH^- whereas Cu2 is coordinated by two oxygen atoms from Nip^{2-} ligands, one oxygen atom of H_2O and two oxygen atoms of OH^-. The Cu1 $\cdots$ Cu2

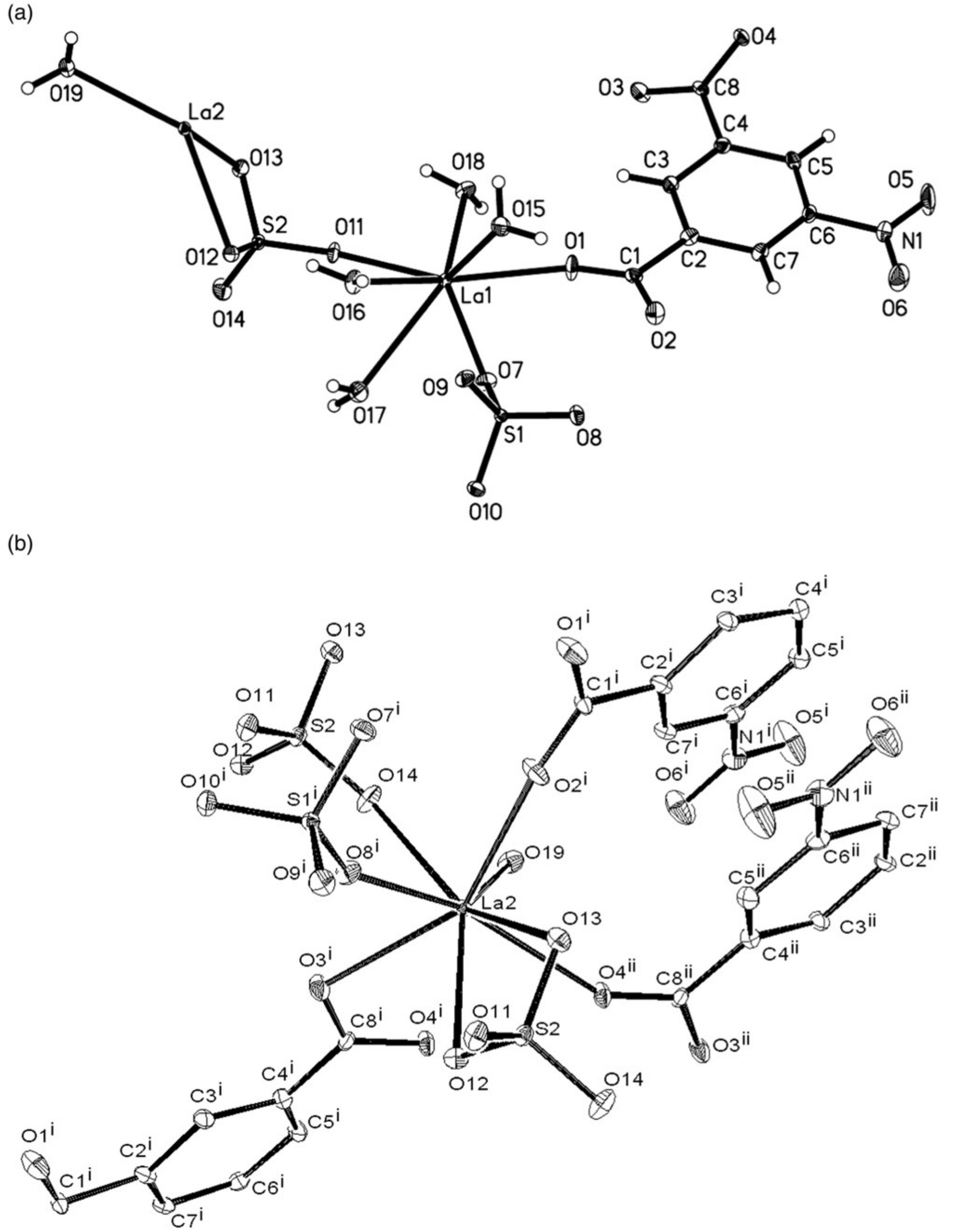


Figure 1. Molecular structure of the $[La_2(\mu\text{-Nip})(\mu\text{-SO}_4)_2(H_2O)_5]_n$ (**1**). (a) for La11 and (b) for La2, Ellipsoids 30% probability. i:$-x$, $y+1/2$, $-z+1/2$; ii: x, $-y+1/2$, $z+1/2$.

distance is 3.023 Å, more than twice the van der Waals radius of Cu (2.8 Å) [21], indicating no significant copper–copper interactions. Coordination number of Cu1 and Cu2 in this complex is six and five with $Cu1O_6$ and $Cu2O_5$. Coordination around Cu1 and Cu2 are distorted octahedral and distorted square pyramidal. Each Nip^{2-} is

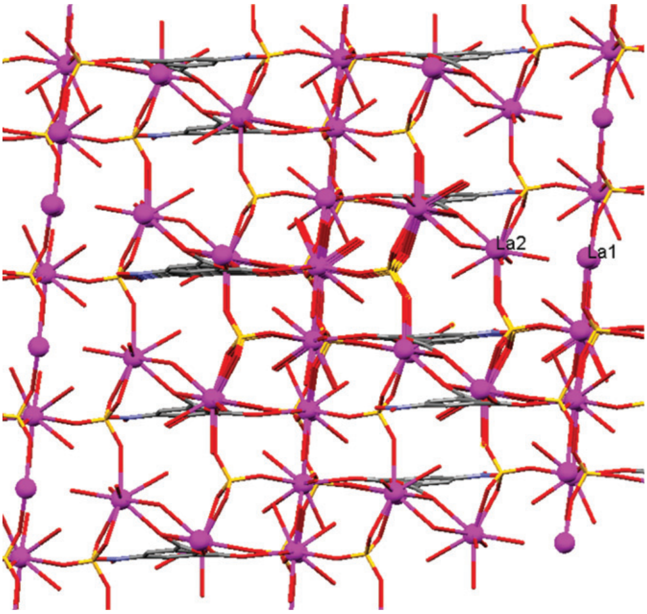


Figure 2. A perspective view of the packing down the *a* axis and three-dimensional network in $[La_2(\mu\text{-Nip})(\mu\text{-SO}_4)_2(H_2O)_5]_n$ (**1**).

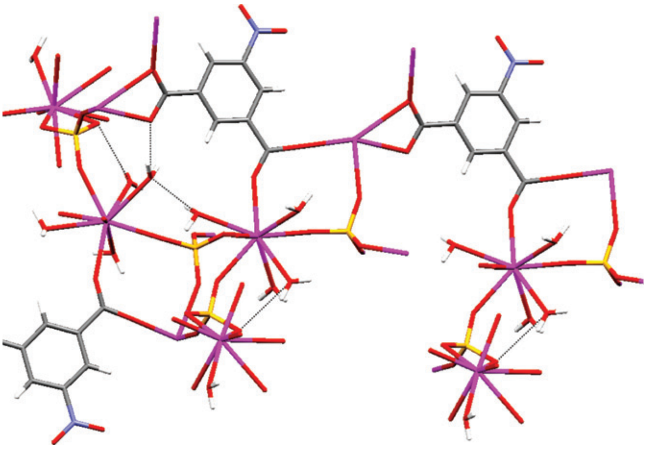


Figure 3. Hydrogen bonds of the coordinated water molecules in $[La_2(\mu\text{-Nip})(\mu\text{-SO}_4)_2(H_2O)_5]_n$ (**1**).

a three-donor ligand, connecting three Cu^{2+} ions. One carboxylate from Nip^{2-} is bidentate and the other is monodentate. The nitro group is not coordinated to Cu. The $\{[Cu_3(\mu\text{-OH})_2(\mu\text{-Nip})_2(\mu\text{-H}_2O)_2]\cdot 2H_2O\}_n$ is involved in hydrogen bonding. Two water molecules in the lattice of $\{[Cu_3(\mu\text{-OH})_2(\mu\text{-Nip})_2(\mu\text{-H}_2O)_2]\cdot 2H_2O\}_n$ are involved in a hydrogen bonding network (figure 6). Coordinated and uncoordinated waters are hydrogen-bond acceptors towards the O atoms of the $–COO^-$ groups Nip^{2-} as potential hydrogen-bond donors (figure 6). Consequently, the 2D structure is grown by hydrogen bonds into a hybrid three-dimensional network. As the guest water molecules

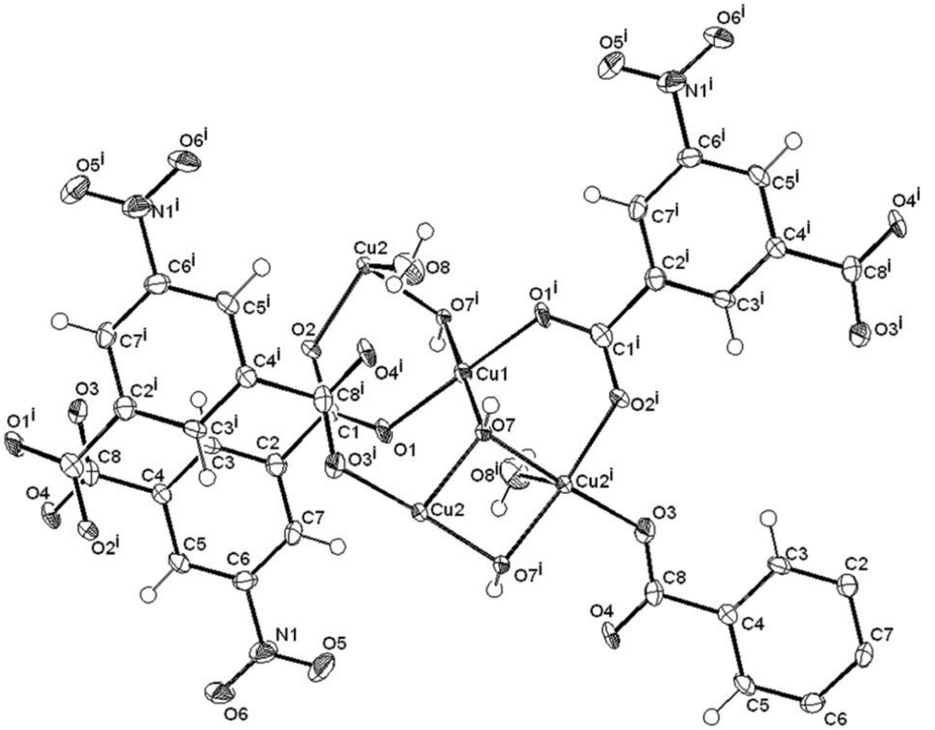


Figure 4. Molecular structure showing two different Cu(II) coordination spheres in $\{[Cu_3(\mu\text{-}OH)_2(\mu\text{-Nip})_2(\mu\text{-}H_2O)_2]\cdot 2H_2O\}_n$ (**2**). $i: -x, -y, -z$.

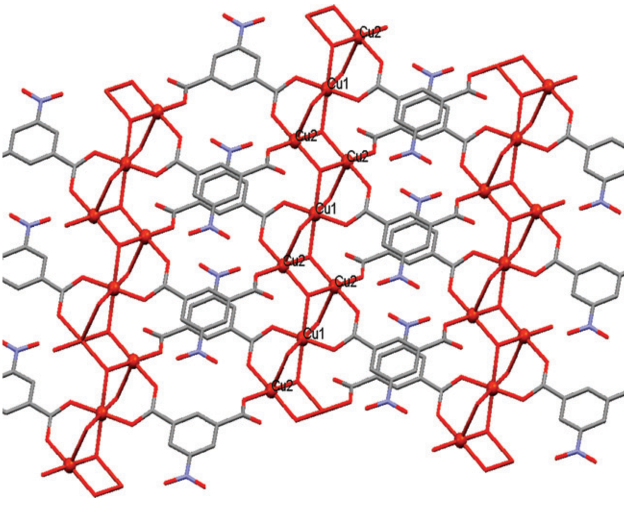


Figure 5. A perspective view of the two-dimensional layers in $\{[Cu_3(\mu\text{-}OH)_2(\mu\text{-Nip})_2(\mu\text{-}H_2O)_2]\cdot 2H_2O\}_n$(**2**).

are tightly hydrogen bonded their removal does not create any significant solvent accessible voids within the structure [22].

In summary, we synthesized two 3-D lanthanum(III) and 2-D copper(II) metal-organic frameworks, $[La_2(\mu\text{-Nip})(\mu\text{-}SO_4)_2(H_2O)_5]_n$ (**1**) and $\{[Cu_3(\mu\text{-}OH)_2(\mu\text{-Nip})_2$

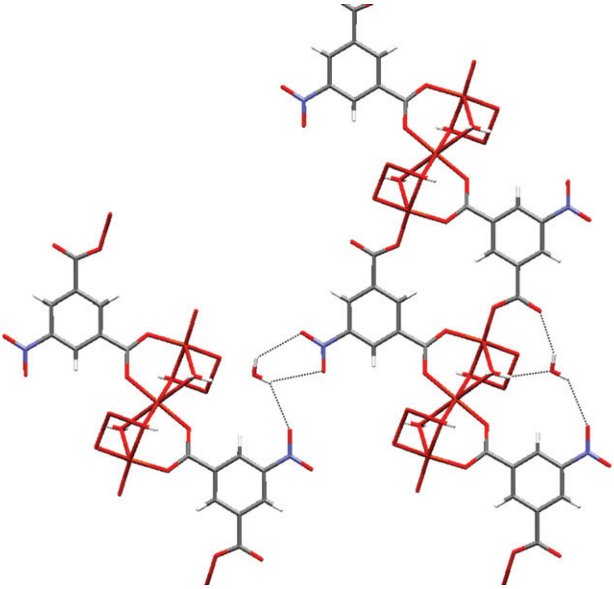


Figure 6. Hydrogen bonds of free water molecules in $\{[Cu_3(\mu\text{-}OH)_2(\mu\text{-}Nip)_2(\mu\text{-}H_2O)_2]\cdot 2H_2O\}_n$(**2**).

$(\mu\text{-}H_2O)_2]\cdot 2H_2O\}_n$ (**2**), under hydrothermal conditions. In $[La_2(\mu\text{-}Nip)(\mu\text{-}SO_4)_2(H_2O)_5]_n$, the lanthanums are linked with carboxylate groups and $\mu_4\text{-}SO_4^{2-}$ to form polynuclear chains. Adjacent chains are connected through Nip^{2-} to form a 3-D network. In $\{[Cu_3(\mu\text{-}OH)_2(\mu\text{-}Nip)_2(\mu\text{-}H_2O)_2]\cdot 2H_2O\}_n$, the coppers are linked with carboxylate groups and μ_2-OH, μ_3-OH and $\mu_2\text{-}OH_2$ to form polymer chains. Adjacent chains are connected through Nip^{-2} to form 2-D layer structure. Three dimensional supramolecular framework is further formed via inter-layer hydrogen bonding interaction.

Supplementary material

Crystallographic data for the structures reported in the article has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no, CCDC-659592 for $[La_2(\mu\text{-}Nip)(\mu\text{-}SO_4)_2(H_2O)_5]_n$ and CCDC-658249 for $\{[Cu_3(\mu\text{-}OH)_2(\mu\text{-}Nip)_2(\mu\text{-}H_2O)_2]\cdot 2H_2O\}_n$. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44–1223/336033; Email: deposit@ccdc.cam.ac.uk].

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