

# (2,2'-bipy)[In<sub>2</sub>(OH)<sub>2</sub>(H<sub>2</sub>O)](SO<sub>4</sub>)<sub>2</sub>: The first indium sulfate with a layer structure

Zhenfen Tian, Li Wang, Tianyou Song, Ying Wang, Liangliang Huang, Lirong Zhang\*, Suhua Shi\*

Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Department of Chemistry, Jilin University, Changchun 130012, China

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## Abstract

The first indium sulfate coordination complex, (2,2'-bipy)[In<sub>2</sub>(OH)<sub>2</sub>(H<sub>2</sub>O)](SO<sub>4</sub>)<sub>2</sub> (2,2'-bipy = 2,2'-bipyridyl) was hydrothermally synthesized and characterized by single-crystal X-ray diffraction (XRD), the powder XRD, elemental analysis, inductively coupled plasma (ICP) analysis, thermogravimetric analysis (TGA), IR spectroscopy and fluorescent spectroscopy. It is noteworthy that this compound exhibits a novel two-dimensional layer structure, which is built up from two distinct motifs, a butlerite-type chain and a single 4-ring (S4R) unit. The adjacent layers are stably packed together and extended into three-dimensional supramolecular arrays via  $\pi$ - $\pi$  stacking interactions of the 2,2'-bipy ligands. Additionally, this compound shows strong fluorescent property at room temperature, which may be assigned to ligand-centered  $\pi^*$ - $\pi$  transitions.

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**Keywords:** Hydrothermal synthesis; Indium sulfate; Crystal structure; Fluorescent property

## 1. Introduction

Following the discovery of zeolites, considerable research has focused on the synthesis of microporous materials, due to their structural diversity as well as their potential applications in catalysis [1], gas storage [2], separation [3], ion exchange [4], etc. In these materials, metal phosphates constitute one of the largest families [5]. The phosphate anion has often been involved as a [TO<sub>4</sub>] unit ( $T$  = tetrahedrally coordinated element) in the formation of the inorganic framework. Besides the phosphates, considerable other types of hybrid materials based on other tetrahedral or pseudo-tetrahedral groups, such as germanates [6,7], phosphites [8,9] and arsenates [10,11] have also been reported in the literature. A recently employed research strategy for the design and synthesis new microporous materials is the use of the sulfate tetrahedron as a primary building unit in place of the phosphate tetrahedron. It is well known that though [SO<sub>4</sub>]<sup>2-</sup>

tetrahedron is approximately the same size and shape as [PO<sub>4</sub>]<sup>3-</sup>, there is a difference of the charge between them, so it could provide variety and novelty to the structures. After the first members of a family of organically templated open-framework cadmium sulfates were synthesized under hydrothermal conditions by Rao et al. [12,13], considerable interest has been focused on the synthesis of metal sulfates microporous materials. A challenge for synthetic work in metal sulfates is to use the organic component as ligand directly coordinated to the metal sulfate scaffolding to form the coordination complexes of the metal sulfates. Up to now, a very wide range of the elements in the periodic table have been incorporated into metal sulfate frameworks through hydrothermal routes, for example, lanthanide [14–16], uranium [17,18], iron [19], cobalt [20,21], vanadium [22] and nickel [23], etc. However, no exploratory work has been carried out on synthesizing indium-containing sulfates though other main group metal sulfates have been reported, such as aluminum [24] and tin [25]. With an aim toward searching for novel sulfates, we conducted our study on the hydrothermal synthesis in indium-sulfate-2,2'-bipy system and a new indium

\*Corresponding authors. Fax: +86 431 85671974.

E-mail address: [shish@mail.jlu.edu.cn](mailto:shish@mail.jlu.edu.cn) (S. Shi).

sulfate (2,2'-bipy)[In<sub>2</sub>(OH)<sub>2</sub>(H<sub>2</sub>O)](SO<sub>4</sub>)<sub>2</sub>, with novel two-dimensional (2D) layer structure, was successfully prepared. To our knowledge, it is the first coordination complex of indium sulfate. In this paper, we describe the synthesis, crystal structure and characterization of this compound, along with the fluorescent property.

## 2. Experimental

### 2.1. Materials and instrumentation

All chemicals were obtained from commercial sources and used without further purification. The elemental analysis was conducted on a Perkin-Elmer 2400 elemental analyzer. Inductively coupled plasma (ICP) analysis was performed on a Perkin-Elmer optima 3300DV ICP instrument. Powder X-ray diffraction (XRD) data were obtained using SHIMADAZU XRD-6000 diffractometer with CuK $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ), with the step size and the count time of  $0.02^\circ$  and 4 s, respectively. FT-IR spectra were recorded on a Nicolet Impact 410 spectrometer between 400 and  $4000 \text{ cm}^{-1}$  using the KBr pellet method. Thermogravimetric analysis (TGA) was conducted on a SHIMADAZU DTG 60 thermogravimetric analyzer with a heating rate of  $10^\circ \text{C min}^{-1}$ . Fluorescence spectrum was performed on a LS 55 fluorescence/phosphorescence spectrophotometer at room temperature.

### 2.2. Synthesis

The title compound was synthesized hydrothermally by a typical solution-mediated reaction: 0.05 g In<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, 0.05 ml H<sub>2</sub>SO<sub>4</sub> (2 M), 0.20 g 2,2'-bipy and 10 ml H<sub>2</sub>O were stirred for 1 h at room temperature, then transferred to a 23 ml Teflon-lined steel autoclave with a filling capacity of ~43% and heated at 433 K for 5 days. Then fine platelet-shaped single crystals were recovered by filtration and washed with deionized water and air dried. Yield: 70% (based on indium). The ICP and elemental analysis data were satisfactory: C obsd. (%), calcd. (%), 19.02, 19.07; H, 1.89, 1.92; N, 4.41, 4.45; In, 36.48, 36.45; S, 10.21, 10.18.

### 2.3. Crystal structure determination

Suitable single crystal with dimension of  $0.10 \times 0.10 \times 0.10 \text{ mm}^3$  was carefully selected for single-crystal XRD analysis. The intensity data were collected on a Siemens Smart CCD diffractometer equipped with graphite-monochromated MoK $\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) radiation in the  $\omega$  scanning mode at room temperature. No significant decay was observed during the data collection. Data were processed on a pentium PC using Bruker AXS windows NT SHELXTL software package (version 5.10) [26,27]. Neutral atom scattering factors were taken from Cromer and Waber [28]. The structures were solved by direct method. The In and S atoms were first located, and then the C, N and O atoms were found from difference Fourier maps. Hydrogen atoms

were placed geometrically and located in the difference Fourier map. The crystal data are listed in Table 1, selected bond distances and bond angles are summarized in Table 2.

CCDC 663154 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif) [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)].

## 3. Results and discussion

### 3.1. Characterizations

The XRD pattern of this compound is consistent with the simulated one on the basis of single-crystal structure, indicating the phase purity of the as-synthesized sample (Fig. 1).

The IR spectrum of the title compound showed a broad band centered at  $3459 \text{ cm}^{-1}$  which was due to the symmetric stretch of the bonded water molecule and hydroxyl groups. The bending mode of H<sub>2</sub>O was present at  $1630 \text{ cm}^{-1}$ . Band at  $3085 \text{ cm}^{-1}$  corresponded to the stretching vibration of C–H bands, and the bands at 1609, 1599, 1567, 1478, 1433, 1320 and  $1254 \text{ cm}^{-1}$  were assigned to the pyridine ring-stretching vibrations. The S–O stretches were present as a broad bands between 1029 and  $1145 \text{ cm}^{-1}$ . The bending modes of SO<sub>4</sub><sup>2-</sup> were found in the 400–500 and 600–700  $\text{cm}^{-1}$  regions. These results indicated the presence of 2,2'-bipy, H<sub>2</sub>O, OH and SO<sub>4</sub><sup>2-</sup>

Table 1  
Crystal data and structure refinement for the title compound

Empirical formula	C <sub>10</sub> H <sub>12</sub> In <sub>2</sub> N <sub>2</sub> O <sub>11</sub> S <sub>2</sub>
Formula weight	629.98
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	<i>P</i> –1
<i>a</i> (Å)	7.8570(16)
<i>b</i> (Å)	9.5323(19)
<i>c</i> (Å)	10.929(2)
$\alpha$ (deg)	91.16(3)
$\beta$ (deg)	98.11(3)
$\gamma$ (deg)	94.23(3)
<i>Z</i>	2
Calculated density (Mg m <sup>-3</sup> )	2.590
Absorption coefficient (mm <sup>-1</sup> )	3.180
<i>F</i> (000)	608
$2\theta$ range (deg)	3.01 to 27.44
Reflections collected/unique	7995/3651
Data/restraints/parameters	3651/13/263
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.120
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0326, <i>wR</i> <sub>2</sub> = 0.0653
<i>R</i> indices(all data)	<i>R</i> <sub>1</sub> = 0.0424 <i>wR</i> <sub>2</sub> = 0.0720
Largest diff. peak and hole(e <sup>-</sup> Å <sup>-3</sup> )	0.937 and –1.143

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, wR_2 = \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]}^{1/2}$$

Table 2  
Selected bond lengths (Å) and angles (deg) for the title compound

In(1)–O(1)	2.167(3)	In(1)–O(2)	2.089(3)
In(1)–O(3)	2.189(3)	In(1)–O(9) <sup>a</sup>	2.154(3)
In(1)–N(1)	2.243(4)	In(1)–N(2)	2.229(4)
In(2)–O(2)	2.156(3)	In(2)–O(2) <sup>b</sup>	2.156(3)
In(2)–O(4)	2.133(3)	In(2)–O(4) <sup>b</sup>	2.133(3)
In(2)–O(10)	2.176(3)	In(2)–O(10) <sup>b</sup>	2.176(3)
In(3)–O(4)	2.133(3)	In(3)–O(4) <sup>c</sup>	2.133(3)
In(3)–O(5)	2.166(3)	In(3)–O(5) <sup>c</sup>	2.166(3)
In(3)–O(6)	2.158(3)	In(3)–O(6) <sup>c</sup>	2.158(3)
O(2)–In(1)–O(1)	88.51(14)	O(2)–In(1)–O(3)	100.33(14)
O(2)–In(1)–O(9) <sup>a</sup>	97.28(14)	O(2)–In(1)–N(1)	97.45(14)
O(2)–In(1)–N(2)	171.77(15)	O(2) <sup>b</sup> –In(2)–O(2)	180.000(1)
O(2) <sup>b</sup> –In(2)–O(10) <sup>b</sup>	88.87(14)	O(2) <sup>b</sup> –In(2)–O(10)	91.13(14)
O(2)–In(2)–O(10)	88.87(14)	O(2)–In(2)–O(10) <sup>b</sup>	91.13(14)
O(4) <sup>c</sup> –In(3)–O(4)	180.000(1)	O(4)–In(3)–O(5)	91.93(14)
O(4) <sup>c</sup> –In(3)–O(5)	88.07(14)	O(4)–In(3)–O(6)	93.27(13)
O(4) <sup>c</sup> –In(3)–O(6)	86.73(13)	O(4) <sup>c</sup> –In(3)–O(6) <sup>c</sup>	93.27(13)

Symmetry transformations used to generate equivalent atoms:

<sup>a</sup>–*x*+2, –*y*+1, –*z*+2; <sup>b</sup>–*x*+2, –*y*+2, –*z*+2; and <sup>c</sup>–*x*+1, –*y*+2, –*z*+2.

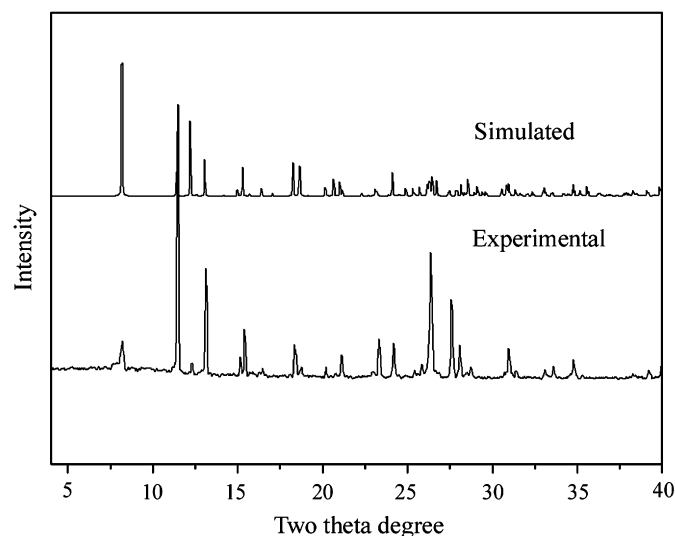


Fig. 1. Simulated and experimental powder X-ray diffraction patterns of the title compound.

groups, which were similar to those found in other related compounds [29–31].

TGA of the title compound was carried out in air with a heating rate of 10 °C min<sup>-1</sup>. As shown in Fig. 2, the TGA curve shows that it is stable up to about 200 °C and a gradual weight loss occurring in range of 200–700 °C corresponds to the loss of the bonded water, OH, SO<sub>3</sub> and the organic ligand. The total weight loss is 59.2% closed to the calculated value (58.5%).

The fluorescent spectrum of the title compound was measured in solid state at room temperature. On excitation at 334 nm, the compound displays a strong fluorescent emission band centered at 384 nm (Fig. 3). The free 2,2'-bipy ligand shows emission band at about 365 nm. The fluorescent emission band of the title compound is red-

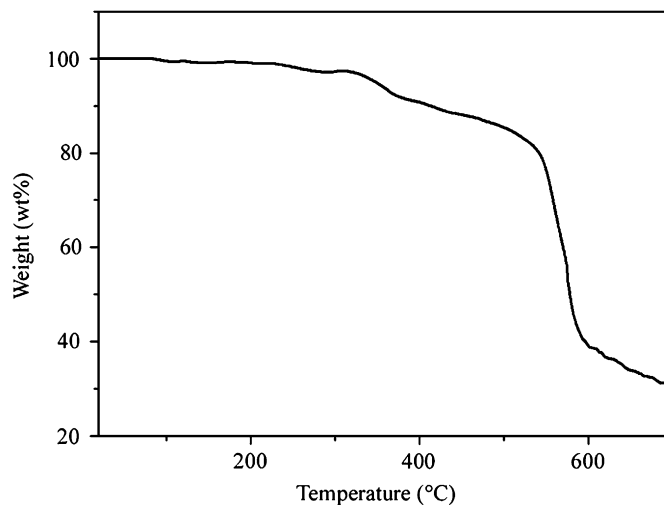


Fig. 2. TGA curve of the title compound measured under flowing air.

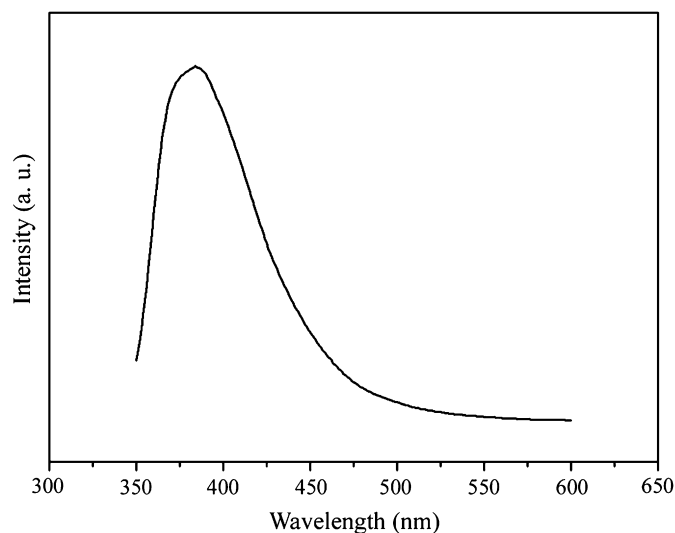


Fig. 3. Solid-state fluorescent emission spectrum of the title compound at room temperature.

shifted relative to the ligand, which may be due to perturbation of the  $\pi^*$ – $\pi$  transition of the 2,2'-bipy ligand by the metal atom. We may conclude that the fluorescent emission of the title compound originates from ligand-centered  $\pi^*$ – $\pi$  transitions [32,33].

### 3.2. Structural description

Single-crystal XRD analysis reveals that the asymmetric unit of (2,2'-bipy)[In<sub>2</sub>(OH)<sub>2</sub>(H<sub>2</sub>O)](SO<sub>4</sub>)<sub>2</sub> contains 28 non-hydrogen atoms, including three indium atoms, two sulfur atoms, 11 oxygen atoms, two nitrogen atoms and 10 carbon atoms (Fig. 4). The In(1) atom is in the general position, while In(2) and In(3) atoms are in special positions with an occupancy of 0.5. All In atoms adopt six-coordination geometry, but they present three different types of coordination environment. In(1) shares three vertex oxygen atoms with adjacent S atoms

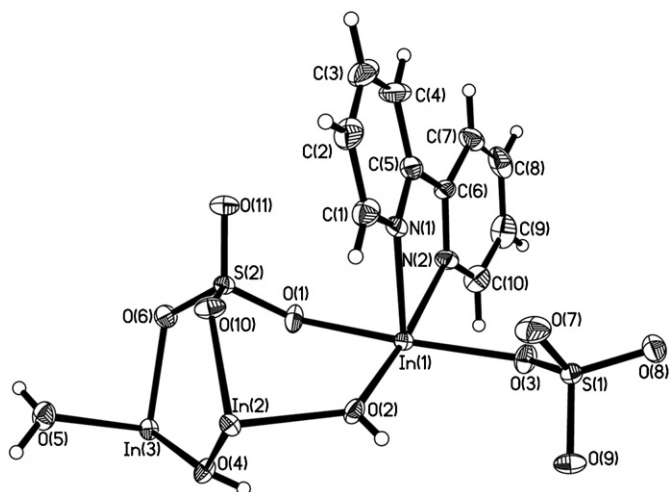


Fig. 4. ORTEP drawing of the asymmetric unit of the title compound (ellipsoids at 50%).

(av.  $\text{In}(1)\text{--O}_{\text{sulfate}} = 2.170 \text{ \AA}$ ), a bridging O atom with In(2) atom (av.  $\text{In}(1)\text{--O}_{\text{bridging}} = 2.089 \text{ \AA}$ ) and two nitrogen atoms from a 2,2'-bipy ligand (av.  $\text{In}(1)\text{--N}_{\text{ligand}} = 2.236 \text{ \AA}$ ). For In(1), one of oxygen atoms O(2) and one of nitrogen atoms N(2) occupy the two trans-apical positions with  $\text{O}(2)\text{--In--N}(2)$  angle being  $171.8^\circ$ , deflected from the ideal value  $180^\circ$ , indicating the octahedral geometry for In(1) is slightly distorted. Different from In(1) atom, In(2) bonds to two oxygen atoms from adjacent S atoms (av.  $\text{In}(1)\text{--O}_{\text{sulfate}} = 2.176 \text{ \AA}$ ) and four bridging oxygen atoms with In(1) and In(3) atoms (av.  $\text{In}(2)\text{--O}_{\text{bridging}} = 2.146 \text{ \AA}$ ). While In(3) atom is six-coordinated by two oxygen atoms from adjacent S atoms (av.  $\text{In}(3)\text{--O}_{\text{sulfate}} = 2.158 \text{ \AA}$ ), two bridging oxygen atoms with In(2) atom (av.  $\text{In}(3)\text{--O}_{\text{bridging}} = 2.133 \text{ \AA}$ ) and the remaining two are  $\text{H}_2\text{O}$  molecules (av.  $\text{In}(3)\text{--O}_{\text{water}} = 2.166 \text{ \AA}$ ). Interestingly, the trans-O–In–O bond angles for In(2) and In(3) atoms are all exactly  $180^\circ$ , indicating near-perfect octahedral geometry for In(2) and In(3) atoms, which is rarely documented in indium octahedron. Both S atoms form the centers of tetrahedral sulfate groups. S(1) atom shares two O vertices with In(1) atoms and the remaining two are terminal S=O groups. S(2) atom makes three S–O–In linkages to In(1), In(2) and In(3) atoms, respectively, and leaving a terminal S=O group. The S–O bond distances in the  $\text{SO}_4$  tetrahedra are in the range of  $1.435\text{--}1.502 \text{ \AA}$ , with the O–S–O bond angles in the range of  $106.2\text{--}112.7^\circ$ , thus the  $\text{SO}_4$  tetrahedra are appreciably distorted tetrahedra. The above bond lengths and bond angles (In–O, In–N, S–O, O/N–In–O/N, O–S–O) are all consistent with those reported in the literature [34,35].

The 2D layer structure of  $(2,2'\text{-bipy})[\text{In}_2(\text{OH})_2(\text{H}_2\text{O})](\text{SO}_4)_2$  is constructed from two distinct motifs, a one-dimensional (1D) butlerite-type chain and a single 4-ring (S4R) unit (Fig. 5). As shown in Fig. 5b,  $\text{In}(2)\text{O}_2(\text{OH})_4$  and  $\text{In}(3)\text{O}_2(\text{OH})_2(\text{H}_2\text{O})_2$  octahedra are linked through the bridging O(4)H group forming an infinite 1D linear chain which has a zigzag  $\{-\text{In}\text{--OH}\text{--In}\text{--OH}\text{--In}\}$  backbone. The

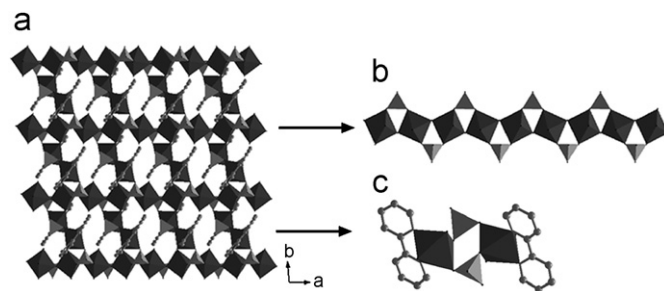


Fig. 5. (a) View of the two-dimensional layer structure of the title compound along [001], (b) polyhedral view of the one-dimensional chain, and (c) the S4R unit decorated by two 2,2'-bipy molecules.

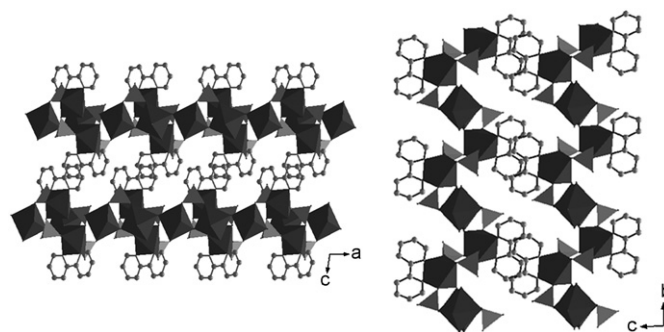


Fig. 6. View of the three-dimensional supramolecular framework of the title compound along [010] and [100].

$\text{S}(2)\text{O}_4$  tetrahedra grafted onto the trans vertexes of this central octahedral chain giving rise to a new 1D chain, which is an analog of the butlerite-type chain [36], that represents a common feature of many minerals and synthetic materials. The second building block is a S4R unit constructed by two  $\text{InO}_4\text{N}_2$  octahedra and two  $\text{SO}_4$  tetrahedra via vertex-sharing In–O–S bonds, to which two 2,2'-bipy rings are roughly perpendicular (Fig. 5c). The S4R units are linked to the 1D chains via the In–O–S and In–O–In linkages, giving rise to a unique layer structure as seen in Fig. 5a. Such layers are stacked in an AAAA sequence along  $c$ -axis. The 2,2'-bipy ligands reside alternately above and below the layers and project into the interlamellar regions. The distance between the planes of adjacent 2,2'-bipy is  $3.26 \text{ \AA}$ , indicating significant attractive intermolecular aromatic interaction [37]. Thus, the 2D layers are extended into three-dimensional (3D) supramolecular arrays via  $\pi\text{--}\pi$  stacking interactions of the 2,2'-bipy ligands (Fig. 6). In addition, the intralayer hydrogen-bond interactions of  $\text{O}\text{--H}\cdots\text{O}/\text{S}$  also perform a certain function on stabilizing the structure of the title compound (Table 3).

### 3.3. Discussion

Due to their sorption properties and quite large surface areas, layered compounds have attracted continuing interest in many different fields of research, such as selective separation, ion exchange chromatography, catalysis, and



Table 3  
Hydrogen bonds for the title compound

D–H...A	<i>d</i> (H...A)	<i>d</i> (D...A)	Angle (D–H...A)
O(2)–H(3)...O(3) <sup>a</sup>	2.55(6)	2.982(5)	125(6)
O(5)–H(1)...O(7) <sup>b</sup>	1.81(2)	2.647(5)	167(6)
O(5)–H(2)...O(8) <sup>c</sup>	1.92(2)	2.769(5)	176(8)
O(5)–H(1)...S(1) <sup>b</sup>	2.78(4)	3.464(4)	139(5)
O(5)–H(2)...S(1) <sup>c</sup>	2.86(4)	3.636(4)	152(7)

Symmetry transformations used to generate equivalent atoms:

<sup>a</sup>–*x*+2, –*y*+1, –*z*+2; <sup>b</sup>–*x*+2, –*y*+2, –*z*+2; and <sup>c</sup>*x*–1, *y*+1, *z*.

photopolymerization [38,39]. The title compound is the first indium sulfate coordination complex and it possesses a unique 2D layer structure, which is built up from two distinct motifs, a butlerite-type chain and a S4R unit. The 1D butlerite-type chain of the title compound forms the basic motif in many minerals, such as butlerite [Fe(OH)(H<sub>2</sub>O)<sub>2</sub>(SO<sub>4</sub>)], parabutlerite [Fe(OH)(H<sub>2</sub>O)(SO<sub>4</sub>)], and uklonskovite Na[MgF(H<sub>2</sub>O)<sub>2</sub>(SO<sub>4</sub>)] [40], and in synthetic materials, such as [H<sub>2</sub>N(CH<sub>2</sub>)<sub>4</sub>NH<sub>2</sub>][FeF<sub>3</sub>SO<sub>4</sub>] [41]. In butlerite and parabutlerite the chains are linked solely by hydrogen bonds, as there are no interstitial cations. In [H<sub>2</sub>N(CH<sub>2</sub>)<sub>4</sub>NH<sub>2</sub>][FeF<sub>3</sub>SO<sub>4</sub>] the chains are held together by the hydrogen-bonded assembly of the diprotonated piperazine molecules located in the interchain space to form the 3D supermolecular structure. However, in the title compound, the adjacent chains are further linked by the S4R units which constructed by two InO<sub>4</sub>N<sub>2</sub> octahedra and SO<sub>4</sub> tetrahedra to form the 2D layer structure.

Because of the similarity of [SO<sub>4</sub>]<sup>2–</sup> tetrahedron and [PO<sub>4</sub>]<sup>3–</sup> tetrahedron in size and shape, we compared the structure and property of the title compound to those of indium phosphates. The 1D butlerite-type chain in the title compound is similar to that in [enH<sub>2</sub>][CoIn(PO<sub>4</sub>)<sub>2</sub>H(OH)<sub>2</sub>F<sub>2</sub>] [42] with 2D sheet structure. But there are obvious differences between them. In the latter compound, the neighboring metal octahedra are linked together by fluoride bridges to form the 1D linear chain with a {–Co–F–In–F–Co–} backbone, and the adjacent chains are connected by sharing oxygen atoms of phosphate groups to form the 2D sheet structure. Whereas in the title compound, the neighboring metal octahedra of 1D butlerite-type chain are connected by the OH bridges, and the adjacent chains are linked together by the S4R units to giving rise to a unique 2D layer structure. One approach to designing and synthesizing novel microporous materials employs organic components as ligands, which can be directly coordinated to metal oxysalt scaffolding to form unique coordination complexes. Compared with inorganic ligands, organic multidentate ligands possess more rich coordination sites and a higher capacity of passivating metal sites by reducing the available metal ion binding sites, which may inhibit inorganic structure growth in certain directions. To date, using this approach, a rich structural chemistry has already been established in metal phosphates [43,44]. In these materials, using 2,2'-bipy as

the organic ligand, two indium phosphates, In<sub>3</sub>F<sub>2</sub>(2,2'-bipy)<sub>2</sub>(HPO<sub>4</sub>)<sub>2</sub>(H<sub>1.5</sub>PO<sub>4</sub>)<sub>2</sub> and In<sub>2</sub>F<sub>2</sub>(H<sub>2</sub>O)(2,2'-bipy)(HPO<sub>4</sub>)<sub>2</sub> have been reported and they exhibit novel framework structures [32]. In<sub>3</sub>F<sub>2</sub>(2,2'-bipy)<sub>2</sub>(HPO<sub>4</sub>)<sub>2</sub>(H<sub>1.5</sub>PO<sub>4</sub>)<sub>2</sub> has a 1D neutral chain structure which is built up by the heptamer units, In<sub>2</sub>F<sub>2</sub>(H<sub>2</sub>O)(2,2'-bipy)(HPO<sub>4</sub>)<sub>2</sub> possesses a 2D layer structure which consists of a corner-sharing-corner chain and an edge-sharing In<sub>2</sub>O<sub>6</sub>F<sub>4</sub> dimer. Though using the same metal center and organic ligand, these two indium phosphates exhibit very different framework structures from the title compound. We suppose that the difference of the structures may partly derive from the difference of charge between [SO<sub>4</sub>]<sup>2–</sup> tetrahedron and [PO<sub>4</sub>]<sup>3–</sup> tetrahedron.

The thermal stability between indium phosphates and indium sulfates are very different. Indium phosphates often exhibit better thermal stability and some compounds could display stable structures up to about 800 °C [45]. While compared to phosphates, the title compound is prone to decompose at elevated temperature. At higher temperature, the sulfate anions usually decompose to SO<sub>3</sub> groups, which could result in the collapse of the inorganic framework. This phenomenon may restrict the application of the metal sulfates in some fields.

#### 4. Conclusions

In summary, employing 2,2'-bipy as organic ligand, the first indium sulfate coordination complex has been prepared under hydrothermal conditions. Structural analysis indicates that the title compound has a novel 2D layer structure which is constructed from vertex-linking two distinct motifs, 1D butlerite-type chain and a S4R unit. Furthermore, the 2D layers can extended into a 3D supramolecular array via  $\pi$ – $\pi$  stacking interactions of the 2,2'-bipy ligands. It is noted that the title compound shows strong fluorescence in the solid state at room temperature. Our investigation indicates that it is possible to prepare more indium sulfates with novel structures by using hydrothermal technology and the influence of organic amine on inorganic frameworks. Further work on this theme is in progress.

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