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Synthesis, Crystal Structure, Fluorescence, and Surface Photo-Electric Properties of a New Co(II) Complex Based on Organosulfonate Ligand[1]

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Abstract—A new Co(II) coordination complex with the formula $[Co(IS)_2(H_2O)_4]$ (**I**), where HIS = isoquinoline-5-sulfonic acid, has been synthesized and characterized by single crystal X-ray diffraction, IR spectroscopy, elemental analysis, fluorescence and surface photovoltage spectroscopy (SPS). X-ray diffraction analyses indicated that center Co^{2+} ion adopts six-coordinated with a N_2O_4 donors set of the two IS^- and four aqua ligands, resulting in an ideal octahedral. Topological analysis on complex **I** considering $\{Co(IS)_2(H_2O)_4\}$ as nodes and hydrogen bonds as linkers gives a uninodal ten-connected net bct with point symbol $(3^{12} \times 4^{28} \times 5^5)$. In the crystal packing, the components interact with pairs of intermolecular O–H···O hydrogen bonds and π–π stacks forming a 3D supramolecular network. The SPS of **I** indicates that there are positive response bands in the range of 300–600 nm showing photo-electric conversion properties. The solid-state photoluminescence property of **I** has also been investigated.

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INTRODUCTION

Self-assembly of metal-organic coordination compounds through the choice of metals and ligands has been attracting considerable research attention from chemists and material scientists since 1990s [1–6] due to the intriguing topologies and potential applications showing by the as-synthesized crystalline materials [7, 8]. In comparison with other organic acidato anion ligands, such as carbonates and phosphonates, the coordination chemistry of sulfonate has been less well investigated due to the perception that sulfonate is a poor ligand [9]. Recently, many porous MOFs have been designed and constructed with polycarboxylate [10] and phosphonate ligands [11], however, sulfonate ligands are rare in designing and constructing microporous MOFs [12–14]. Sulfonate RSO_3^- anions are structurally analogous to phosphonate RPO_3^{2-} anions, both having trioxy anionic units with an organic pendant having local C_{3v} symmetry. The obvious difference is the greater anionic charge associated with the phosphonate [15]. However, sulfonate ligands have been much less studied owing to the preoccupation that they are weakly coordinating ligands [16–19]. Significant progress has been made in understanding the supramolecular chemistry in extended solids with sulfonate groups built up by cooperative coordination and other weak intermolecular interactions [20, 21]. In particular, hydrogen bonded interactions play a key role in the guanidinium sulfonate and disulfonate compounds systematically studied by Ward and coworkers [15–18]. Cai [12] and Côté and Shimizu [9, 13] have explored the coordination chemistry of the sulfonate group and the structural properties of metal arenesulfonates. In fact, the sulfonate group, as a tetrahedral oxygen-donating building block, may bridge sites of a coordination polymer chains to dictate the interchain geometry. Based on this background, many transition metal sulfonate complexes with novel 0–3D porous structures [20–30] were obtained showing that the sulfonate group can directly coordination to the metal ion, competing successfully with water molecules [31–34]. It is somewhat surprising that many crystal structures of model pyridine sulfonamides and sulfonic acids have been analyzed in the literature, but there are no crystal structures of isoquinoline sulfonic acid and its related derivatives in the CSD.

In this paper, a new organosulfonate ligand, isoquinoline-3-sulfonic acid, was chosen to build coordination complexes based on the following two considerations. One is that the coordination chemistry of organosulfonate ligands was not well investigated in comparison with the chemistry of organonitrogen, organocarboxylate and organophosphate ligands. The

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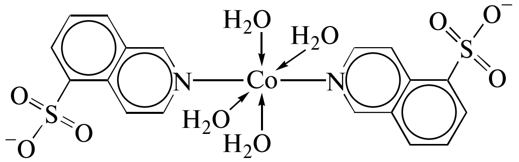
[1] The article is published in the original.

Table 1. Crystal data and structure refinements for complexes **I**

Parameter	Value
Formula weight	547.43
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions:	
a, Å	7.3830(15)
b, Å	8.0564(16)
c, Å	10.276(2)
α, deg	109.43(3)
β, deg	90.23(3)
γ, deg	111.96(3)
V, Å^3	528.8(3)
Z	1
F(000)	281
ρ_{calcd}, g/cm^3	1.725
Crystal size, mm	0.30 × 0.20 × 0.12
μ, mm^{-1}	1.07
Scan mode	ω–2θ
$\theta_{max}/\theta_{min}$, deg	3.01/27.5
Limiting indices h, k, l	$-9 \le h \le 9$, $-10 \le k \le 10$, $-13 \le l \le 13$
Reflections collected	5560
Independent reflections (R_{int})	2423 (0.0409)
Max and min transmission	0.880 and 0.774
Data/restraints/parameters	2423/0/151
Goodness-of-fit on F^2	1.072
R indices ($I > 2\sigma(I)$)	$R_1 = 0.0708$, $wR_2 = 0.1075$
R indices (all data)	$R_1 = 0.0483$, $wR_2 = 0.0999$
Largest diff. peak and hole, eÅ^{-3}	0.386 and –0.491

other is that organosulfonate ligands are known to form interesting supramolecular networks due to their ability to form hydrogen bonds and the weak coordination properties. Herein, we reported the syntheses, crystal structure and surface photovoltage spectroscopy (SPS) [35, 36] properties of a new organosulfonate cobalt(II) coordination complex $[Co(IS)_2(H_2O)_4]$ (**I**). A view of the coordination mode of the IS$^-$ ligand in I is the following:



EXPERIMENTAL

Materials and methods. All starting chemicals were commercially available and used as received without further purification. Elemental analyses (C, H, and N) were performed on a PerkinElmer 2400II elemental analyzer. FT-IR spectra were recorded from KBr pellets in the range of 4000–450 cm^{-1} on a Bio-Rad FTS-7 spectrometer. The SPS was recorded with a home-built surface photovoltage spectrophotometer. Fluorescence spectra were obtained from a 970CRT spectrofluorophotometer.

Synthesis of I. A mixture of $Co(CH_3COO)_2 \cdot 4H_2O$ (0.249 g, 1 mmol) and isoquinoline-5-sulfonic acid (0.420 g, 2 mmol) were added to 10 mL water, and the solution was heated to 70°C with stirring. The pH of the solution was adjusted to about 5.0 using dilute aqueous NaOH. The resulting clear purple solution was allowed to stand in air for 4 weeks. Red block crystals of **I** suited for single crystal X-ray diffraction analyses formed with a yield of approximate 40% (based on Co).

For $C_{18}H_{20}N_2O_{10}S_2Co$

anal. calcd., %:	C, 39.46;	H, 3.65;	N, 5.11;	S, 11.69.
Found, %:	C, 39.39;	H, 3.69;	N, 5.19;	S, 11.71.

IR characteristics for complex **I** (KBr; ν, cm^{-1}): 1625 s, 1538 m, 1425 s, 1327 m, 1224 s, 1187 s, 1143 s, 1039 s, 1015 s, 807 m, 735 m, 706 m, 635 s, 579 w, 513 w.

X-ray crystallography. A prism-shaped single crystal of **I** with size of 0.30 × 0.20 × 0.12 mm was used for structure determination. Data were collected at 296(2) K on a Bruker SMART APEX CCD area-detector diffractometer equipped with a graphite-monochromatic MoK_α (λ = 0.71073 Å) radiation by using a multi-scan mode. The raw frame data were integrated with the SAINT program [37] and absorption corrections were applied by using the SADABS program [37]. The unit cell data were obtained with the least-squares refinements and the structure was

Table 2. Selected bond lengths (Å) and angles (deg) for structure **I***

Bond	*d*, Å	Bond	*d*, Å
Co(1)–O(1*w*)	2.089(3)	S(1)–O(5)	1.460(3)
Co(1)–O(2*w*)	2.112(3)	S(1)–C(4)	1.782(4)
Co(1)–N(1)	2.182(3)	N(1)–C(9)	1.319(5)
S(1)–O(7)	1.456(3)	N(1)–C(1)	1.372(5)
S(1)–O(6)	1.459(3)	C(8)–C(9)	1.416(5)
Angle	**ω, deg**	**Angle**	**ω, deg**
O(1*w*)Co(1)O(2*w*)	91.20(11)	O(2*w*)Co(1)N(1)	91.74(12)
O(7)S(1)O(5)	113.25(17)	O(7)S(1)O(6)	112.66(18)
O(7)S(1)C(4)	108.13(17)	O(6)S(1)O(5)	111.46(17)
O(5)S(1)C(4)	105.05(17)	O(6)S(1)C(4)	105.63(17)
C(9)N(1)C(1)	116.9(3)	C(9)N(1)Co(1)	120.8(2)
O(1*w*)Co(1)N(1)	92.21(11)	C(1)N(1)Co(1)	122.2(2)

Table 3. Geometric parameters of hydrogen bonds for **I***

Contact D–H···A	Distance, Å			Angle D–H···A, deg
	D–H	H···A	D···A	
O(1*w*)–H(1*w*)···O(5)$^{\text{i}}$	0.85	1.93	2.763(4)	167
O(1*w*)–H(2*w*)···O(6)$^{\text{ii}}$	0.85	1.89	2.734(4)	170
O(2*w*)–H(3*w*)···O(5)$^{\text{iii}}$	0.85	1.89	2.728(4)	166
O(2*w*)–H(4*w*)···O(7)$^{\text{iii}}$	0.85	2.06	2.817(4)	148

* Symmetry codes: $^{\text{i}}$ $1 - x, 1 - y, -z$; $^{\text{ii}}$ $x, y, 1 + z$; $^{\text{iii}}$ $-x, 1 - y, -z$.

solved by direct methods with SHELXTL-97 program [38, 39]. The final refinement was performed by full-matrix least-squares techniques with anisotropic thermal parameters for the non-hydrogen atoms on F^2. All H atoms were placed geometrically and were subsequently refined in a riding-model approximation with distances of d(C–H) = 0.93 and d(O–H) = 0.85 Å, and U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(O). The crystal data

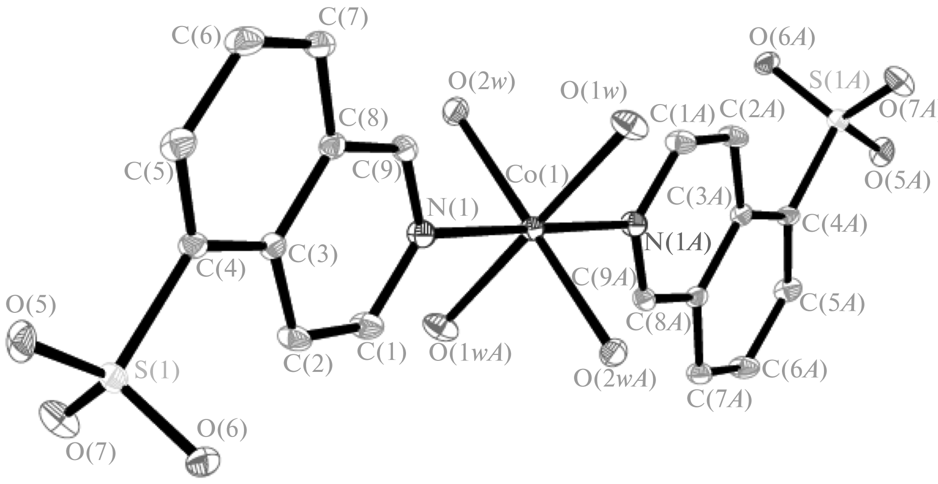


Fig. 1. The molecular structure of **I** showing displacement ellipsoids at the 30% probability level. Hydrogen atoms have been omitted for clarity. Atoms labeled with the suffix *A* are at the symmetry position $1 - x, 2 - y, 1 - z$.

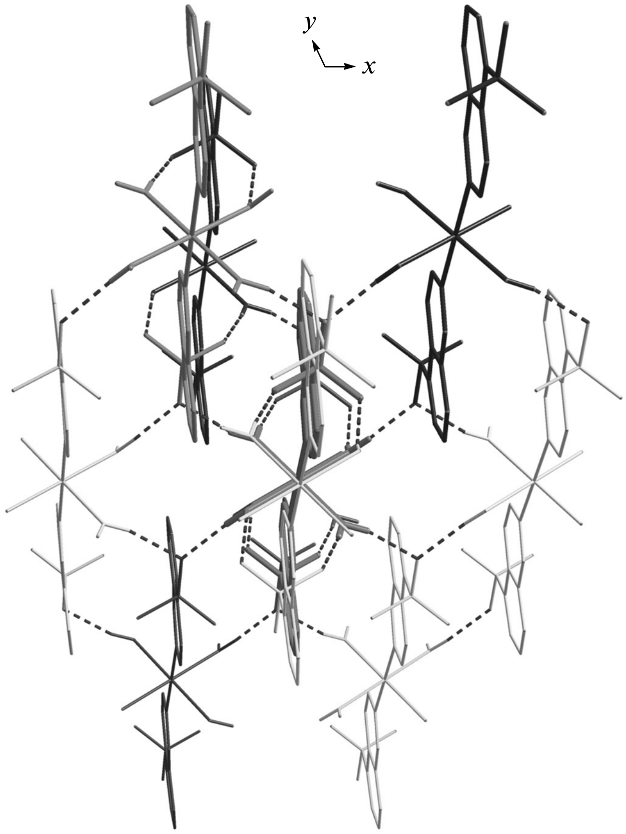


Fig. 2. A view of the ten-connected molecular unit. Central and linking units are shown in different shades.

are summarized in Table 1. Selected bond lengths and angles are given in Table 2. Hydrogen bonds are listed in Table 3. The atomic coordinates and other parameters of structure **I** have been deposited with the Cambridge Crystallographic Data Centre (no. 968694; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The single crystal X-ray structure analysis reveals that compound **I** consists of a crystallographically unique cobalt atom, two deprotonated HIS ligands and two coordinated water molecules, and the asymmetric unit contains one half of the formula components. The Co(1) is coordinated by two nitrogen donors of two IS^- ligands and four aqua ligands with Co–N bond length of 2.182(3) Å and Co–O(*w*) distances of 2.089(3) and 2.112(3) Å to form an octahedral coordination environment around the metal center (Fig. 1). It is worth noticing that the sulfonate groups of IS^- ligands in complex **I** do not coordinate to metal centers and are involved in the formation of hydrogen bonding with the aqua ligands on the metal centers. A 3D supramolecular network is given birth by the extension of the coordinative moieties via hydrogen bonds (Fig. 2a). Classical hydrogen bond length is $O(w)-H\cdots O_{sulfonate}$ (2.728–2.817 Å). Topological analysis on complex **I** considering $\{Co(IS)_2(H_2O)_4\}$ as nodes and hydrogen bonds as linkers gives a uninodal ten-connected net bct (Figs. 2b and 3) with point symbol $(3^{12} \times 4^{28} \times 5^5)$. Supramolecular complexes can fulfill a molecular nodes extended by flexible and complex supramolecular bonding to realize a comparable achievement.

Intermolecular hydrogen bonding and π-stacking interactions are important supramolecular forces to govern the process of recognition and self-assembly [14]. In the crystal structure, a notable feature of **I** lies in the 3D network built through hydrogen bonds. There are several hydrogen bonds in the structure because of the three uncoordinated sulfonate O and four coordinated water molecules. The neighboring coordination complexes are connected by hydrogen bonds O–H···O with the O···O distances of 2.728(4)–2.817(4) Å (Table 3). The neighboring layers are also connected by intermolecular no-classical C–H···O hydrogen bonds of sulfonate oxygen atoms (O(6)) with the C···O distance 3.432(5) Å (Fig. 4). In addition, π···π stacking interactions can also be observed between the isoquinoline rings of adjacent chains with the shortest interplanar perpendicular and ring-centroid distances of 3.5939(17) and 3.740(3) Å, respectively. The chains interact with each other into reverse alternate arrangements shown in Fig. 5. The neighboring coordination complexes are connected by pairs of intermolecular π···π, resulting in a 2D layers. Molecules from neighboring stacks are further interacted in the *z* direction, thus leading to an interwoven three-dimensional network held together by O–H···O, C–H···O interactions and π···π stacking stabilizing the coordination complex.

In this paper, energy-band theory of semiconductor and crystal field theory were combined to analyze and assign the SPS, we consider that the 2*s*2*p* orbits of coordinated oxygen atom are the valence band of semiconductor and the 4*s*4*p* orbits of metal ions are the conduction band of semiconductor, otherwise the *d* orbits of metal ions are impurities level of semiconductor. Then proceed to discuss the surface electron behaviors under light-induced and photo-electric conversion properties of complex according to the results of the SPS.

In Fig. 6, there is a wide photovoltage response band in the range of 300–600 nm which reveals that the complex has a certain photoelectric conversion properties, and four photovoltage response bands were obtained by treated with Origin 7.0: $\lambda_{max} = 337$, 381, 454, 505 nm. The response bands at $\lambda_{max} = 337$ and 381 nm can be attributed to charge transition between ligand and metal, O → Co (LMCT) and N → Co (LMCT). The overlapped response band at $\lambda_{max} = 454$ and 505 nm is assigned to $d \rightarrow d^*$ transitions of Co^{2+} (d^7) ion ($^4T_{1g} \rightarrow {}^4A_{2g}$, $^4T_{1g} \rightarrow {}^4T_{1g}$).

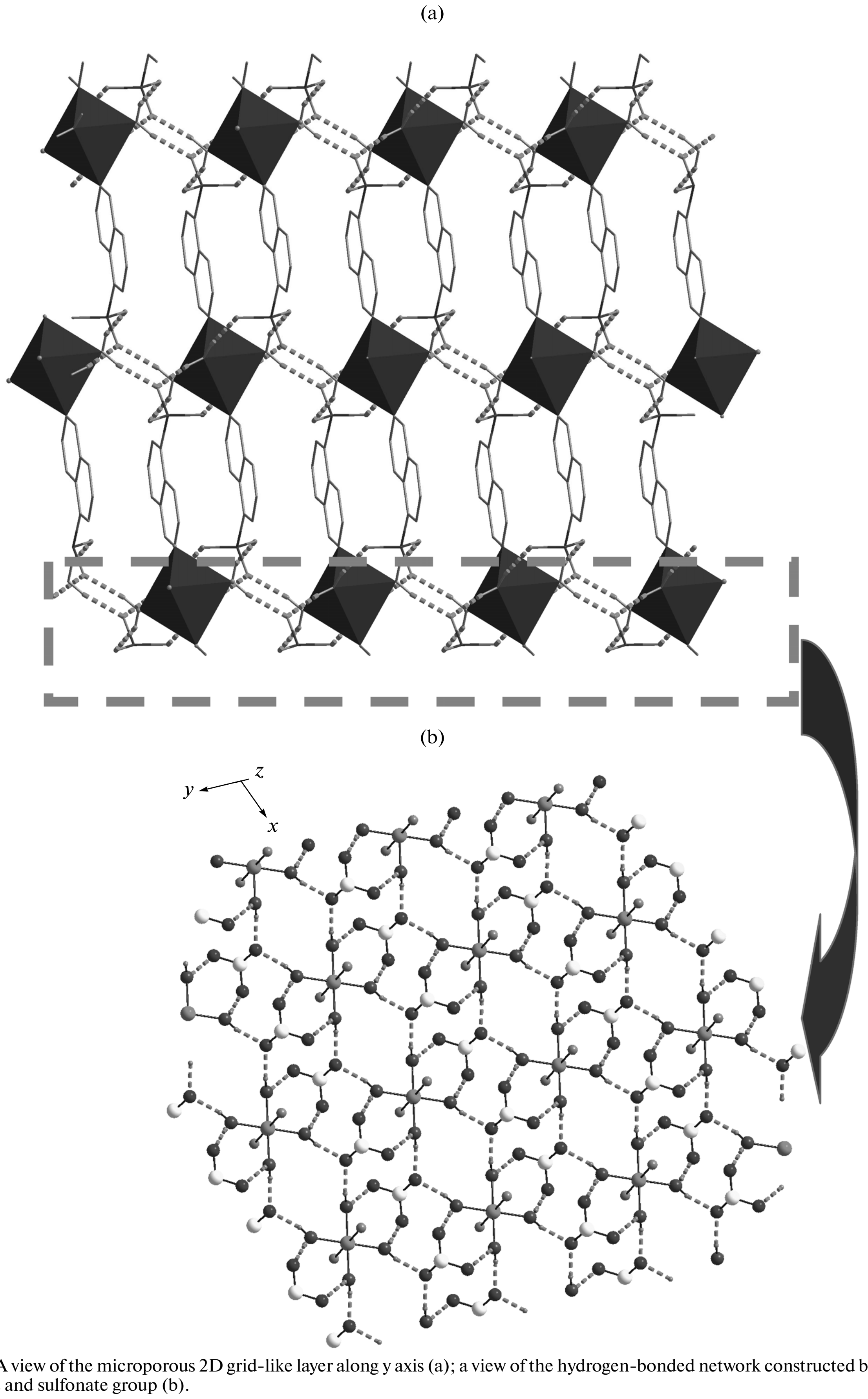


Fig. 3. A view of the microporous 2D grid-like layer along y axis (a); a view of the hydrogen-bonded network constructed by water clusters and sulfonate group (b).

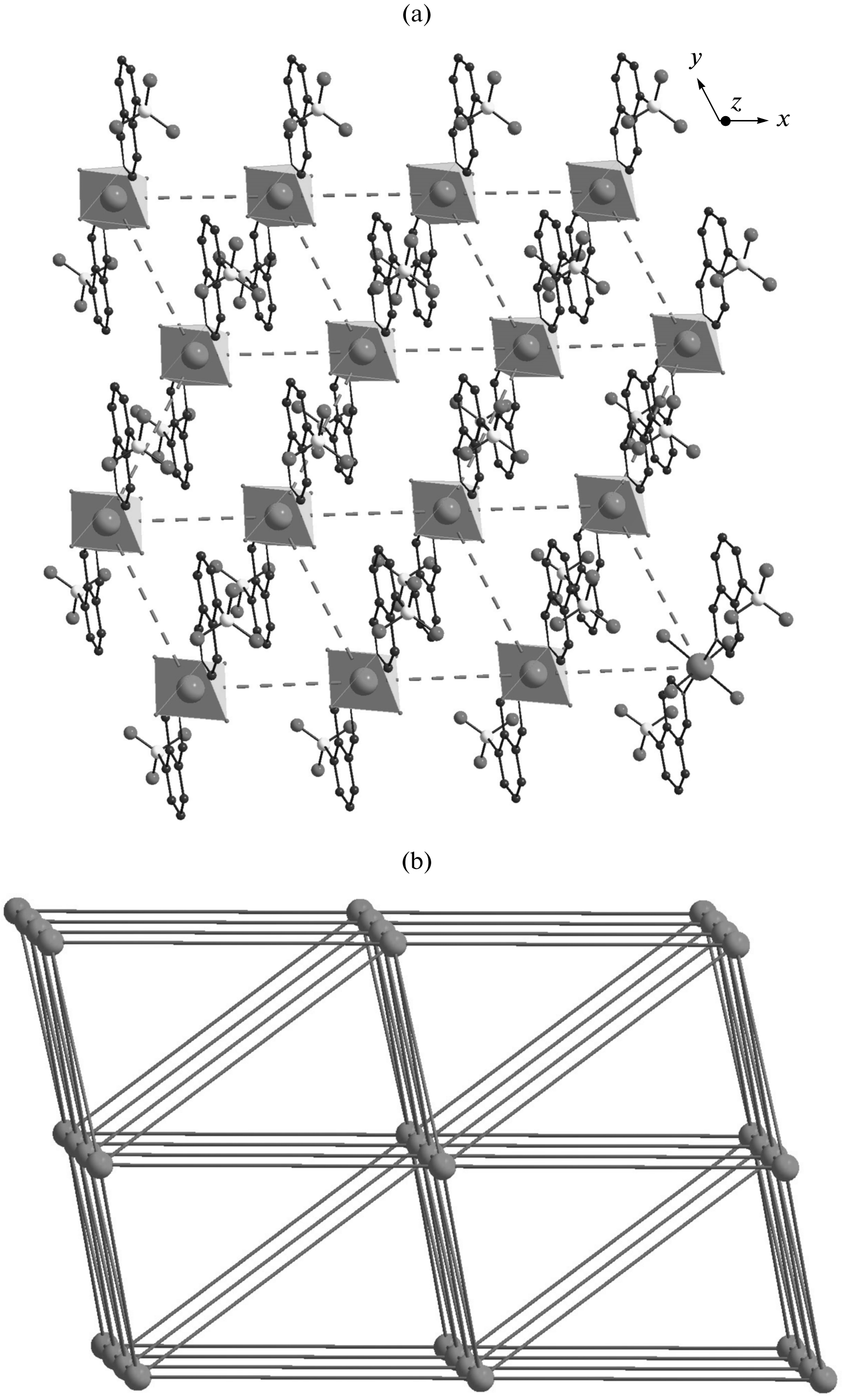


Fig. 4. The 2D quasi layer unit of complex **I** (a); a view of the simplified bct network of **I** (b).

The photoluminescence spectra of compounds **I** and free ligand in the solid-state at room temperature are shown in Fig. 7. Compared with free HIS, **I** has similar band shape and position with it and is greatly intensified. We suppose the emission of I arises from intraligand π–π^* transitions of HIS–ligand. The enhanced emission intensity of I comes from two parts. One is coordination effect, the other is hydrogen bonding interactions [40] in its 3D structures.

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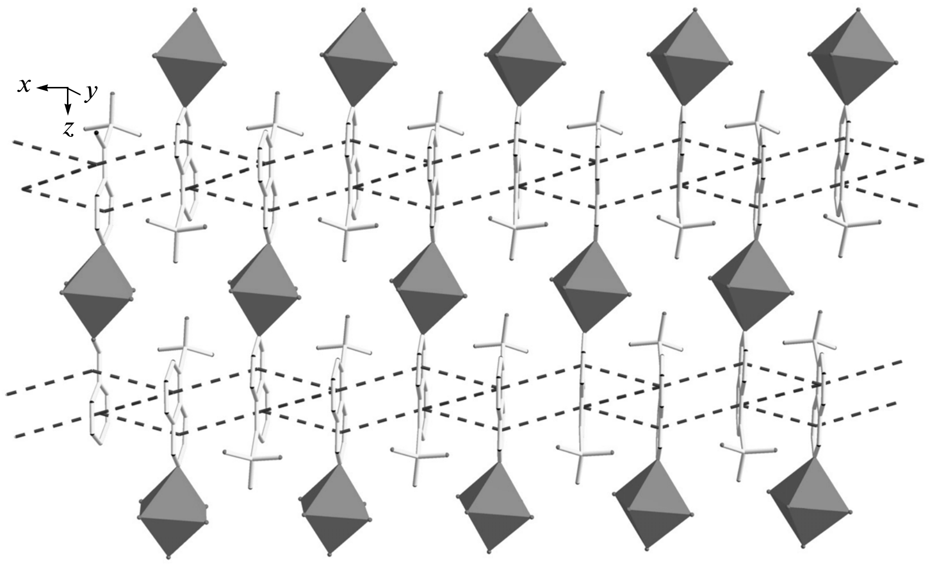

Fig. 5. View of 2D network for **I**, showing π···π stacks as dashed lines (H atoms have been omitted for clarity).

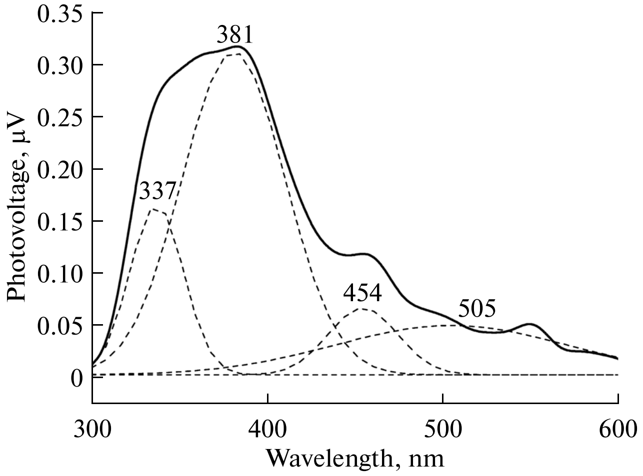

Fig. 6. The SPS of **I**.

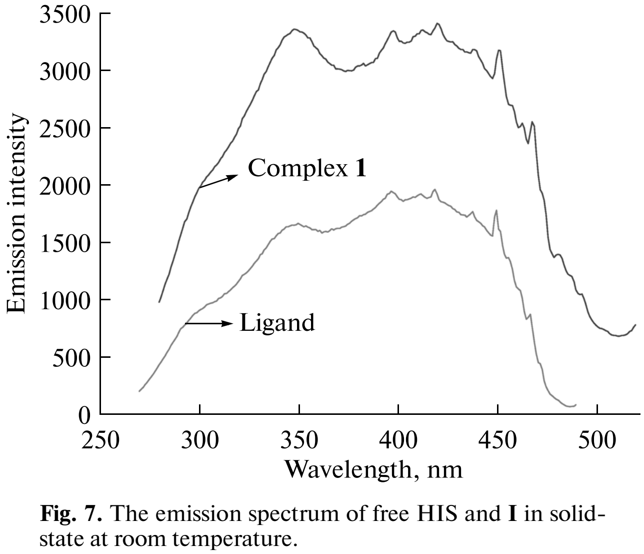

Fig. 7. The emission spectrum of free HIS and **I** in solid-state at room temperature.

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