原位产生的 SO₄²⁻配位的二维无机钴配合物 K₂[Co₃(OH)₂(SO₄)₃(H₂O)₂]的水热合成及晶体结构

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摘要: 相同的水热反应条件下 4-氨基-二(2-吡啶基)-1,2,4-三氮唑(abpt)、KSCN 与钴盐(CoCl₂·6H₂O)反应合成了 2 种新的钴配合物:零维的单核配合物[CoSCN(abpt)] (**1α**)和二维的无机层状配合物 K₂[Co₃(OH)₂(SO₄)₃(H₂O)₂] (**1β**),并通过元素分析和红外光谱对其进行了表征。配合物 **1α** 的晶体属于单斜晶系,$P2_1/c$ 空间群。配合物 **1β** 晶体属于正交晶系,$Cmc2_1$ 空间群。在配合物 **1α** 中,abpt 和 SCN⁻配体都参与配位与 Co(Ⅱ)离子形成了 2 个不同的单核单元,这些单核单元又通过 S 原子和 N 原子之间的氢键作用连成了三维超分子结构;在配合物 **1β** 中,abpt 配体没有参与配位,而 SCN⁻配体则被氧化成了 SO₄²⁻离子并与 Co(Ⅱ)离子配位形成了二维配位层状结构,相邻层之间进一步通过氢键作用形成了沿 c 轴方向有孔道的三维超分子网络,这些孔道里面填充着反离子 K⁺。

关键词: 配位聚合物;水热原位反应;4-氨基-二(2-吡啶基)-1,2,4-三氮唑
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Hydrothermal Synthesis and Crystal Structure of 2D K₂[Co₃(OH)₂(SO₄)₃(H₂O)₂] Coordination Polymer with the *In-Situ* Formation of SO₄²⁻

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Abstract: Reaction of CoCl₂·6H₂O, 4-amino-3,5-di(2-pyridyl)-4H-1,2,4-triazole (abpt), KSCN results in formation of two new complexes, 0D mononuclear complex named [CoSCN(abpt)] (**1α**) and 2D inorganic coordination framework K₂[Co₃(OH)₂(SO₄)₃(H₂O)₂] (**1β**), in the same hydrothermal reaction system and were characterized by elemental analysis and IR. X-ray diffraction crystal structure analysis shows that **1α** crystallizes in monoclinic system, space group $P2_1/c$ with a=1.073 91(11) nm, b=1.589 59(16) nm, c=1.740 41(18) nm, β=106.720(2)°, V=2.845 4(5) nm³, Z=4; and **1β** crystallizes in orthorhombic system, space group $Cmc2_1$ with a=1.794 24(17) nm, b=0.755 83(7) nm, c=0.976 05(10) nm, V=1.323 7(2) nm³, Z=4. In complex **1α**, both abpt and SCN⁻ ligands are coordinated to Co(Ⅱ) to form two different mononuclear units and further generate a 3D supramolecular architecture by the hydrogen bonds between the S atoms and uncoordinated N atoms of the abpt ligand. While in **1β**, the abpt ligand is uncoordinated and the SCN⁻ anion is changed to SO₄²⁻ anion coordinated to Co(Ⅱ) atoms to result in a 2D coordination layer. Adjacent layers are linked to each other by hydrogen bonds to generate a 3D porous supramolecular architecture with 1D channels running along the c-axis, which are occupied by the counter K⁺ ions. CCDC: 658233, **1α**; CSD: 418495, **1β**.

Key words: coordination polymer; *in-situ* hydrothermal reaction; 4-amino-3,5-bis(2-pyridyl)-1,2,4-triazole

As a very important research field in both coordination chemistry and organic chemistry, *in situ* metal/ligand reactions have been extensively investigated for many decades for the discovery of new organic reactions, the elucidation of reaction mechanisms, as well as the generation of novel coordination compounds, especially for those that are inaccessible in direct preparation from the ligands [1,2]. Hydro (solvo)thermal method has been widely adopted in the preparations of new metal-organic frameworks (MOFs)[3~5]. Many novel materials with different potential applications have been prepared from ligand reactions, including the hydrolysis of carboxylate esters, organic nitriles and aldehydes into the corresponding carboxylates [6], the cleavage of acetonitrile/ethylene carbon-carbon bonds and 1,3,4-oxadiazole carbon-nitrogen/carbon-oxygen bonds[7], the cleavage and formation of disulfide bonds[8], the substitution of aromatic groups[9], and the decarboxylation of aromatic carboxylates[10]. The 4-amino-3,5-bis (2-pyridyl)-1,2,4-triazole (abpt) ligand has been extensively adopted to prepare spin-crossover compounds[11]. Moreover, the amino group can be deviated from it to in situ form 3,5-bis (2-pyridyl)-1,2,4-triazole (bpt) ligand, which can be used to construct novel metal-organic frameworks[12]. Honestly, our intention of employing the abpt was to chelate the Co(II) ions that can be further bridged to construct 3D metal-organic frameworks by the bridged anion SCN^-. Unexpectedly, we obtained an unprecedented two dimensional inorganic coordination framework $K_2[Co_3(OH)_2(SO_4)_3(H_2O)_2]$ (**1β**) with 1D channel filled with the counter ions K^+, in which the SO_4^{2-} anions is in situ formed from the oxidation of SCN^- in the high temperature and press hydrothermal system with the presence of oxygen, as well as another mononuclear complex named [CoSCN (abpt)] (**1α**) as a different phase.

1　Experimental section

1.1　Materials and physical measurements

The $CoCl_2 \cdot 6H_2O$ and KSCN were commercially available and used as received without further purification. 4-amino-3,5-bis (2-pyridyl)-1,2,4-triazole (abpt) ligand could be obtained directly from the two reactants by employing the one-pot procedure described by Lagrenée and co-workers[13]. The C, H, N and S microanalyses were carried out with an Elementar Vario-EL CHNS elemental analyzer. The FTIR spectra were recorded from KBr tablets in the range 4 000~400 cm^{-1} on a Bio-Rad FTS-7 spectrometer.

1.2　Hydrothermal synthesis

A mixture of $CoCl_2 \cdot 6H_2O$ (119 mg, 0.5 mmol), 4-amino-3,5-di (2-pyridyl)-4H-1,2,4-triazole (abpt) (118 mg, 0.5 mmol), KSCN (50 mg, 0.5 mmol) and H_2O (10 mL) was sealed in a 23 mL Teflon-lined reactor and heated in an oven at 180 ℃ for 72 h and then at 90 ℃ for 12 h. After 15 h gradual cooling to room temperature, red block crystals of [CoSCN(abpt)] (**1α**) (yield *ca.* 11% based on Co) and violet sheet $K_2[Co_3(OH)_2(SO_4)_3(H_2O)_2]$ (**1β**) (yield *ca.* 5% based on Co) were obtained, and then filtered, washed, and dried in air. Elemental analysis calcd (%) $C_{26}H_{20}CoN_{14}S_2$ for **1α**: C 47.93, H 3.09, N 30.09, S 9.84; found (%): C 47.88, H 3.06, N 30.12, S 9.66; $H_6Co_3K_2O_{16}S_3$ for **1β**: H 0.99, S 15.69; found (%): H 1.01, S 15.61. IR (KBr, cm^{-1}) for **1α**: 3 432 (m), 2 084 (s), 2 056 (m), 1 604 (s), 1 589 (m), 1 571 (m), 1 490 (m), 1 428 (m), 1 052 (m), 1 027 (w), 794 (m), 746 (m), 698 (w), 607 (w); for **1β**: 3 428 (s), 1 572 (s), 1 409 (m), 1 343 (w), 1 119 (w), 1 019 (w), 648 (m).

1.3　Crystal structure determination

Data collection of **1α** and **1β** was performed on a Bruker Apex CCD diffractometer with Mo $K\alpha$ radiation (λ =0.071 073 nm) at 293 (2) K. The raw data frames were integrated with SAINT$^+$, and the corrections were applied for Lorentz and polarization effects. Absorption correction was applied by using the multiscan program SADABS [14]. The structures were solved by direct methods, and all non-hydrogen atoms were refined anisotropically by least-squares on F^2 using the SHELXTL program [15]. Hydrogen atoms on organic ligands were generated by the riding mode (C-H=0.093 nm). Crystal data as well as details of data collection and refinements for complexes **1α** and **1β** are summarized in Table 1. Selected bond distances and bond angles are listed in Table 2. Hydrogen bonds are listed in Table 3.

CCDC: 658233, **1α**; CSD: 418495, **1β**.

<div align="center">Table 1   Crystal data and structure refinement parameters for complexes 1α and 1β</div>

Identification code	1α	1β
Empirical formula	$C_{26}H_{20}CoN_{14}S_2$	$H_6Co_3K_2O_{16}S_3$
Formula weight	651.61	613.22
Temperature / K	293(2)	293(2)
Wavelength	0.710 73	0.710 73
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$Cmc2_1$
a / nm	1.073 91(11)	1.794 24(17)
b / nm	1.589 59(16)	0.755 83(7)
c / nm	1.740 41(18)	0.976 05(10)
β / (°)	106.720(2)	
Volume / nm³	2.845 4(5)	1.323 7(2)
Z	4	4
D_c / (g·cm⁻³)	1.521	3.077
Absorption coefficient / mm⁻¹	0.796	4.911
F(000)	1 332	1 204
Crystal size / mm	0.17 × 0.14 × 0.14	0.25 × 0.21 × 0.13
θ range for data collection / (°)	1.77~26.00	2.27~25.98
Limiting indices	$-13 \leqslant h \leqslant 12, -19 \leqslant k \leqslant 17, -21 \leqslant l \leqslant 21$	$-20 \leqslant h \leqslant 22, -9 \leqslant k \leqslant 9, -10 \leqslant l \leqslant 12$
Reflections collected	15 623	3 571
Independent reflections (R_{int})	5 524 (0.045 6)	1 204 (0.036 7)
Completeness / %	98.6	99.9
Max. and min. transmission	0.87 93 and 0.898 1	0.911 0 and 0.838 4
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	5 932 / 4 / 407	1 204 / 6 / 125
Goodness-of-fit on F^2	1.005	1.063
Final R indices [$I>2\sigma(I)$]	$R_1{}^a$=0.055 7, $wR_2{}^b$=0.116 2	$R_1{}^a$ =0.021 8, $wR_2{}^b$=0.051 7
R indices (all data)	$R_1{}^a$=0.094 3, $wR_2{}^b$=0.133 7	$R_1{}^a$=0.022 2, $wR_2{}^b$=0.051 5
Largest diff. peak and hole	0.498, −0.519	0.512, −0.414

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

<div align="center">Table 2   Bond lengths (nm) and angles (°) for 1α and 1β</div>

1α					
Co(1)-N(7a)	0.209 0(3)	Co(1)-N(1)	0.216 3(3)	Co(2)-N(9b)	0.211 1(3)
Co(1)-N(7)	0.209 0(3)	Co(1)-N(1a)	0.216 3(3)	Co(2)-N(9)	0.211 1(3)
Co(1)-N(2a)	0.210 0(3)	Co(2)-N(14)	0.210 0(4)	Co(2)-N(8)	0.213 3(3)
Co(1)-N(2)	0.210 0(3)	Co(2)-N(14b)	0.210 0(4)	Co(2)-N(8b)	0.213 3(3)
N(7a)-Co(1)-N(7)	180.0(2)	N(7a)-Co(1)-N(1a)	90.30(12)	N(9b)-Co(2)-N(9)	180.00
N(7a)-Co(1)-N(2a)	92.70(13)	N(7)-Co(1)-N(1a)	89.70(12)	N(14)-Co(2)-N(8)	89.80(12)
N(7)-Co(1)-N(2a)	87.30(13)	N(2a)-Co(1)-N(1a)	76.31(11)	N(14b)-Co(2)-N(8)	90.20(12)
N(7a)-Co(1)-N(2)	87.30(13)	N(2)-Co(1)-N(1a)	103.69(11)	N(9b)-Co(2)-N(8)	103.14(11)
N(7)-Co(1)-N(2)	92.70(13)	N(1)-Co(1)-N(1a)	180.00(18)	N(9)-Co(2)-N(8)	76.86(11)
N(2a)-Co(1)-N(2)	180.0(3)	N(14)-Co(2)-N(14b)	180.00(19)	N(14)-Co(2)-N(8b)	90.20(12)
N(7a)-Co(1)-N(1)	89.70(12)	N(14)-Co(2)-N(9b)	88.15(12)	N(14b)-Co(2)-N(8b)	89.80(12)
N(7)-Co(1)-N(1)	90.30(12)	N(14b)-Co(2)-N(9b)	91.85(12)	N(9b)-Co(2)-N(8b)	76.86(11)

Continued Table 2

N(2a)-Co(1)-N(1)	103.69(11)	N(14)-Co(2)-N(9)	91.85(12)	N(9)-Co(2)-N(8b)	103.14(11)
N(2)-Co(1)-N(1)	76.31(11)	N(14b)-Co(2)-N(9)	88.15(12)	N(8)-Co(2)-N(8b)	180.00(16)
1β					
Co(1)-O(2)	0.209 7(4)	Co(1)-O(7)	0.213 0(3)	Co(2)-O(2)	0.210 6(3)
Co(1)-O(3a)	0.209 8(2)	Co(1)-O(8b)	0.217 8(4)	Co(2)-O(9b)	0.211 2(3)
Co(1)-O(3)	0.209 8(2)	Co(2)-O(6c)	0.205 9(3)	Co(2)-O(4)	0.212 6(3)
Co(1)-O(1)	0.210 1(4)	Co(2)-O(1d)	0.209 9(3)	Co(2)-O(1W)	0.213 5(3)
O(2)-Co(1)-O(3a)	97.39(7)	O(2)-Co(1)-O(8b)	94.50(15)	O(2)-Co(2)-O(9b)	87.76(13)
O(2)-Co(1)-O(3)	97.39(7)	O(3a)-Co(1)-O(8b)	88.34(9)	O(6c)-Co(2)-O(4)	85.01(11)
O(3a)-Co(1)-O(3)	165.06(14)	O(3)-Co(1)-O(8b)	88.34(9)	O(1d)-Co(2)-O(4)	174.35(13)
O(2)-Co(1)-O(1)	88.63(15)	O(1)-Co(1)-O(8b)	176.87(15)	O(2)-Co(2)-O(4)	97.93(11)
O(3a)-Co(1)-O(1)	91.26(10)	O(7)-Co(1)-O(8b)	76.80(15)	O(9b)-Co(2)-O(4)	86.27(11)
O(3)-Co(1)-O(1)	91.26(10)	O(6c)-Co(2)-O(1d)	95.38(12)	O(6c)-Co(2)-O(1W)	91.57(11)
O(2)-Co(1)-O(7)	171.29(17)	O(6c)-Co(2)-O(2)	168.88(13)	O(1d)-Co(2)-O(1W)	88.17(12)
O(3a)-Co(1)-O(7)	82.53(7)	O(1d)-Co(2)-O(2)	82.75(12)	O(2)-Co(2)-O(1W)	99.31(13)
O(3)-Co(1)-O(7)	82.53(7)	O(6c)-Co(2)-O(9b)	81.71(12)	O(9b)-Co(2)-O(1W)	170.30(11)
O(1)-Co(1)-O(7)	100.07(15)	O(1d)-Co(2)-O(9b)	99.37(14)	O(4)-Co(2)-O(1W)	86.18(11)

Symmetry codes for **1α**: (a) $-x$, $-y$, $-z$; (b) $-x$,$-y+1$,$-z$; for **1β**: (a) $-x$, y, z; (b) $-x$, $-y+2$, $z-1/2$; (c) x, $-y+1$, $z-1/2$; (d) $-x$, $-y+1$, $z-1/2$.

Table 3　Hydrogen bonds for 1α and 1β

D−H⋯A	d(D-H) / nm	d(H⋯A) / nm	d(D⋯A) / nm	∠(DHA) / (°)
1α				
N(5)−H(5A)⋯N(6)	0.090 4(10)	0.207(2)	0.287 5(6)	147(4)
N(5)−H(5B)⋯S(2a)	0.090 2(10)	0.275(3)	0.360 3(5)	159(6)
N(12)−H(12A)⋯S(2b)	0.089 9(10)	0.274(2)	0.361 9(5)	166(6)
N(12)−H(12B)⋯N(7c)	0.089 8(10)	0.260(5)	0.333 6(6)	139(6)
1β				
O(1W)−H(1WA)⋯O(5a)	0.085	0.197	0.275 7(4)	154.0
O(1W)−H(1WB)⋯O(7b)	0.085	0.215	0.299 9(4)	174.4
O(1)−H(1O)⋯O(8)	0.084 6(10)	0.225 7(12)	0.305 8(5)	158.1(12)
O(2)−H(2O)⋯O(9b)	0.084 6(10)	0.259 4(16)	0.335 6(5)	150(2)
O(2)−H(2O)⋯O(9c)	0.084 6(10)	0.259 4(16)	0.335 6(5)	150(2)

Hydrogen atoms are omitted for clarity: A: $-x$, $-y$, $-z$; B: $-x$, $-y+1$, $-z$.

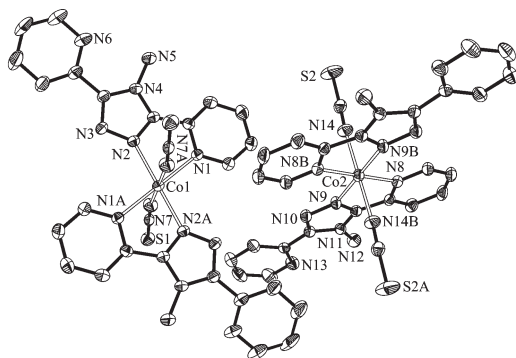## 2　Results and discussion

2.1　Synthesis

As is well known, there are a variety of hydrothermal parameters such as time, temperature, pH value, and molar ratio of reactants, and small changes in one or more of the parameters can have a profound influence on the final reaction outcome. The coordinated SO_4^{2-} ligand in complex **1β** is in situ formed from the starting material KSCN, of which the formation mechanism is not clear. We have attempted to use the sulfate salts to be the reactants or changed the reaction at lower temperature, as well as in the condition without the abpt ligand, to find no formation of **1β**. Schug and co-workers′ studies have revealed that sulfur atoms of SCN^- could be converted into sulfate anions by the SCN-H_2O_2 reaction[16,17]. In the formation of reported complex $[Cu_3(pzc)_2(CN)_2(H_2O)_2 \cdot 2H_2O]_n$ (pzc=2-pyrazinecarboxylate), the coordinated CN^- anion is produced by the oxidative desulfation of SCN^- anions with the SO_4^{2-} as

by-product[18]. Considering this, we assume that the SO_4^{2-} ligand is produced by the redox reaction of the SCN⁻ anions with the presence of oxygen as the oxidative reactant, in which the abpt ligand also plays a vital role.

2.2　Structure of [CoSCN(abpt)] (1α)

Single crystal structure of 1α reveals a neutral mononuclear Co(II) complex that crystallizes in monoclinic space group $P2_1/c$. There are two unique mononuclear units in the asymmetric unit (Fig.1). Both Co(II) atoms have the same coordination environment of a slightly distorted octahedral [CoN₆]. The equatorial coordination sphere is formed by the pyridyl N atoms and triazole N atoms of two abpt molecules, with the Co1-N1 and Co1-N2 distances 0.216 3(3) and 0.210 0(3) nm, Co2-N8 and Co2-N9 0.213 3(3) and 0.211 1(3) nm, respectively. And the axial positions are occupied by two monodentate coordinating SCN⁻ groups with the Co1-N7 and Co2-N14 coordination distances of 0.209 0(3) and 0.210 0(4) nm. The angular distortions of coordination octahedron are determined by the chelate formation and result in the expected substantial deviations of the chelate bite angle N1-Co1-N2 76.31(11)° and N8-Co1-N9 76.86(11)° from 90°. In the Co1 unit, the dihedral angle between the coordinated pyridyl group and the triazolato ring is 6.5°, while that between the noncoordinating pyridyl group and the triazolato ring is 21.2°, forming an intramolecular hydrogen bond with the amino group of the abpt ligand (N(5)N(6)=0.287 5(6) nm, N(5)−H(5A)···N(6)=147(4)°) (Table 3). Different from the Co1 unit, the dihedral angles of the Co2 unit

are 2.3° and 6.9°, avoiding the intramolecular hydrogen bonding with the amino group, but forming the intermolecular hydrogen bond with the N7 atom of SCN⁻ in the Co1 unit (N(12)···N(7)=0.333 6(6) nm, N(12)−H(12B)···N(7)=139(6)°). Moreover, the SCN⁻ group of the Co2 unit forms two N−H···S hydrogen bonds: an intramolecular N(12)−H(12A)···S(2) (0.361 9(5) nm, 166(6)°) and an intramolecular N(5)−H(5B)···S(2) (0.360 3(5) nm, 159(6)°) with the Co1 unit, extending the mononuclear species into a 3D molecular architecture.

2.3　Structure of K₂[Co₃(OH)₂(SO₄)₃(H₂O)₂] (1β)

The crystal structur reveals that 1β contains two unique Co(II) atoms, one of which lies on special position, one μ_3-SO_4^{2-} ligand on general position and one μ_4-SO_4^{2-} ligand on special position, two μ_3-OH⁻ on special positions, a coordinated water molecule and a K⁺ anion (Fig.2). Co1 adopts octahedral coordination geometry [CoO₆], coordinated by two O atom from two μ_3-OH⁻ ligand and four O atoms from one μ_3-SO_4^{2-} and one μ_4-SO_4^{2-} ligand (Co1-O=0.209 7(4)~0.217 8(4) nm, O-Co1-O=82.53(7)°~176.87(15)°). Co2 is surrounded by two O atoms from two μ_3-OH⁻ ligand, three O atoms from one μ_3-SO_4^{2-} and one μ_4-SO_4^{2-} ligand, as well as a water molecule in a distorted octahedral coordination environment (Co2-O=0.205 9(3)~0.213 5(3) nm, O-Co2-O=81.71(12)°~174.35(13)°).

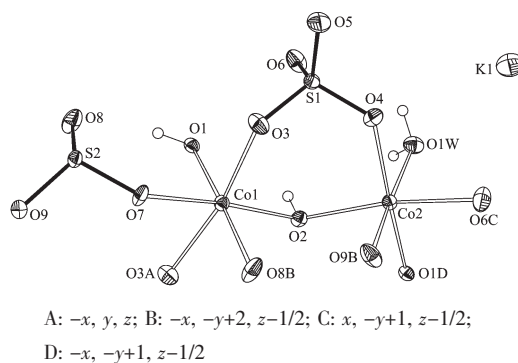A: −x, y, z; B: −x, −y+2, z−1/2; C: x, −y+1, z−1/2;
D: −x, −y+1, z−1/2

Fig.2　Coordination environment of cobalt atoms in the asymmetric unit of 1β

Interestingly, two Co2 atoms was bridged by two μ_3-O a four-member ring, which is further connected to the Co1 atoms alternately by the μ_3-O bridges resulting in a 1D Co-OH chain along the c-axis (Fig.3a). Adjacent chains are linked to generate a 2D layer by

Hydrogen atoms are omitted for clarity
A: −x, −y, −z; B: −x, −y+1, −z

Fig.1　Coordination environment of cobalt atoms the two different moieties in a asymmetric unit of 1α

the μ_3-SO$_4^{2-}$ and μ_3-SO$_4^{2-}$ bridges (Fig.3b). There are existing rich hydrogen bonds between the O atoms of OH$^-$ and SO$_4^{2-}$, as well as the coordinated water molecules (O···O=0.305 8(5) and 0.335 6(5) nm, O−H···O= 150 (2)° and 158.1 (12)° ; O1W ··· O =0.275 7 (4) and

0.299 9(4) nm, O1W−H···O=154.0° and 174.4°) (Table 3). The 2D layers are linked by the hydrogen bonds to a 3D porous supramolecular framework filled with the K$^+$ ions along the c-axis (Fig.3c).
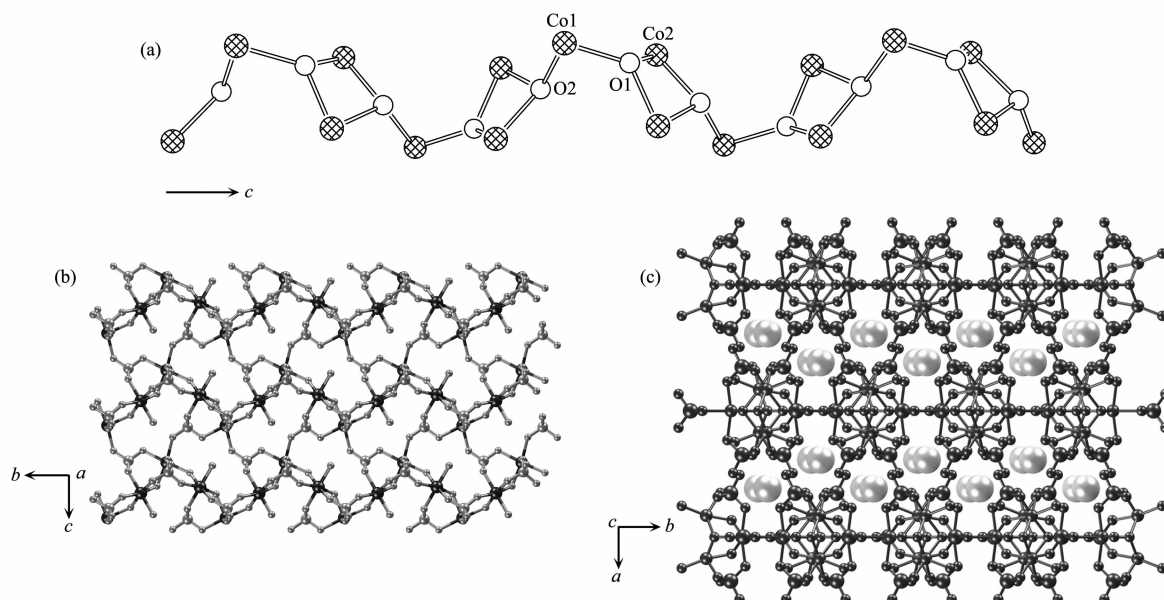

Fig.3　Perspective views of the 1D Co-OH chain along the c-axis (a), 2D layer viewed along the a-axis (b) and the 3D porous supramolecular framework with K$^+$ ions (c) of **1β**

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