

## Helical structures in a lithium hexacyanocobaltate-based three-dimensional metal–cyanide framework



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### ABSTRACT

Inorganic–organic hybrid compound  $(C_3H_5N_2)_2(H_2O)\{[Li(H_2O)][Co(CN)_6]\}$  was synthesized by the reaction of  $Li_3[Co(CN)_6]$  with imidazolium chloride in aqueous solution. It crystallizes in the chiral orthorhombic space group  $P2_12_12_1$  at 293 K. The anionic chiral 3D structure is composed of helical chains based on the inorganic  $\{[Li(H_2O)][Co(CN)_6]\}$  building blocks. Imidazolium cations and crystallization water molecules reside in the voids of the anionic framework through rich hydrogen bonds.

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Chirality is one of the key issues in the fields of chemistry, biology, physics and materials science [1,2]. In coordination and supramolecular chemistry, one way to generate chiral materials from achiral building blocks is through spontaneous resolution of helical structures with both right- and left-handedness, designated as *P*- and *M*-helix, respectively. This strategy needs a deep understanding of various interactions among components, which, however, still lacks up to now [3,4]. Hence, exploration for new helical building blocks and structural motifs is of great importance for the generation of chiral solid-state structures.

Cyanometalates are very useful building blocks for the construction of inorganic–organic hybrid compounds with magnetic, electrical, optical, and porous properties [5–8]. They can show diverse structures varying from clusters, one- (1D) to three-dimensional (3D) structures. Hexacyanometalates  $[M(CN)_6]^{3-}$  ( $M = Cr, Mn, Fe, Co$ ), as octahedral building blocks, are among the mostly used structural units to build various architectures [9,10]. Although there are numerous compounds synthesized from the combination of the  $[M(CN)_6]^{3-}$  and transition metal ions, the number of alkali metal ion (e.g. lithium ion) involved in hexacyanometalates is still small [11–14]. Li ion usually shows tetrahedral coordination geometry [15]. When the tetrahedral Li is combined with the octahedral  $[M(CN)_6]^{3-}$ , the CN groups partly participate in the formation of coordination, acting as terminal and bridging ligands. This mismatch leaves much room for the generation of different topologies of frameworks, which can be tuned by different organic cations and solvent molecules.

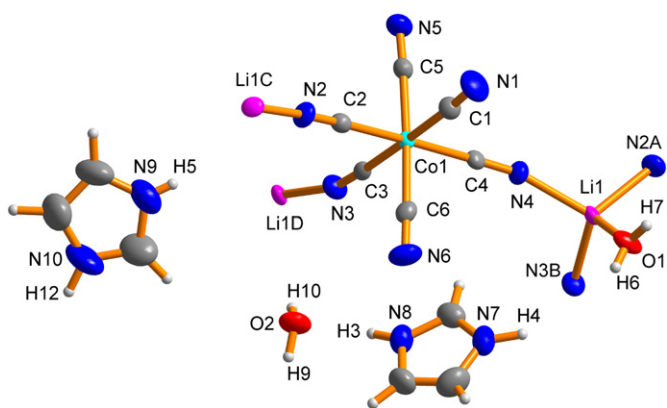
Herein we report a Li(I)-containing hexacyanocobaltate-based inorganic–organic hybrid compound,  $(HIm)_2(H_2O)\{[Li(H_2O)][Co(CN)_6]\}$  (**1**, HIm = imidazolium). In **1**, the Li(I) ions link the  $Co(CN)_6$  through three CN groups to result in 3D cationic framework. Notably, the framework is chiral, containing left- and right-handed helical chain substructures which are found in some reported cyanometalate compounds [16,17]. The imidazolium cation and the crystallization water molecules reside in the voids of the chiral framework through rich hydrogen bonds. They are indispensable for the occurrence of the chirality of **1**.

Compound **1** was synthesized from the combination of  $Li_3[Co(CN)_6]$  and  $(HIm)Cl$  in aqueous solution as block crystals [18]. Its IR spectrum shows typical broad bands of N–H and O–H at around  $3200\text{ cm}^{-1}$  and strong band of  $C \equiv N$  group at  $2118\text{ cm}^{-1}$ . Its structure was solved by X-ray diffraction at 293 K [19]. The asymmetric unit and selected bond lengths and angles of **1** are shown in Fig. 1. It contains one  $[Co(CN)_6]$  anion, one Li ion, two free HIm cations and two water molecules in which one is coordinated and the other is free. The octahedral  $[Co(CN)_6]^{3-}$  anion affords three CN groups to coordinate with three Li ions with a *mer* arrangement [20]. The Li ion is four-coordinated with three N atoms of CN groups from three  $[Co(CN)_6]$  anions and one O atom of water molecule, showing a distorted tetrahedral geometry [21]. The Li–N bond lengths are in the range of 2.021–2.074 Å, a little longer than the Li–O bond length of 1.931 Å. The values are comparable with those in reported compounds [11–13,22].

Li–N≡C is not strictly linear but a little bent with an averaged angle of about  $165^\circ$ , much larger than the values of about  $172^\circ$  in  $[N(CH_3)_4][Li(H_2O)_2[Co(CN)_6]]$  [11]. It composes the basic building block, that is,  $[NC-Co-CN-Li]$ , to assemble into a 3D anionic framework of **1**

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**Fig. 1.** Asymmetric structure unit of compound **1**. Displacement ellipsoids are drawn at the 50% probability level.

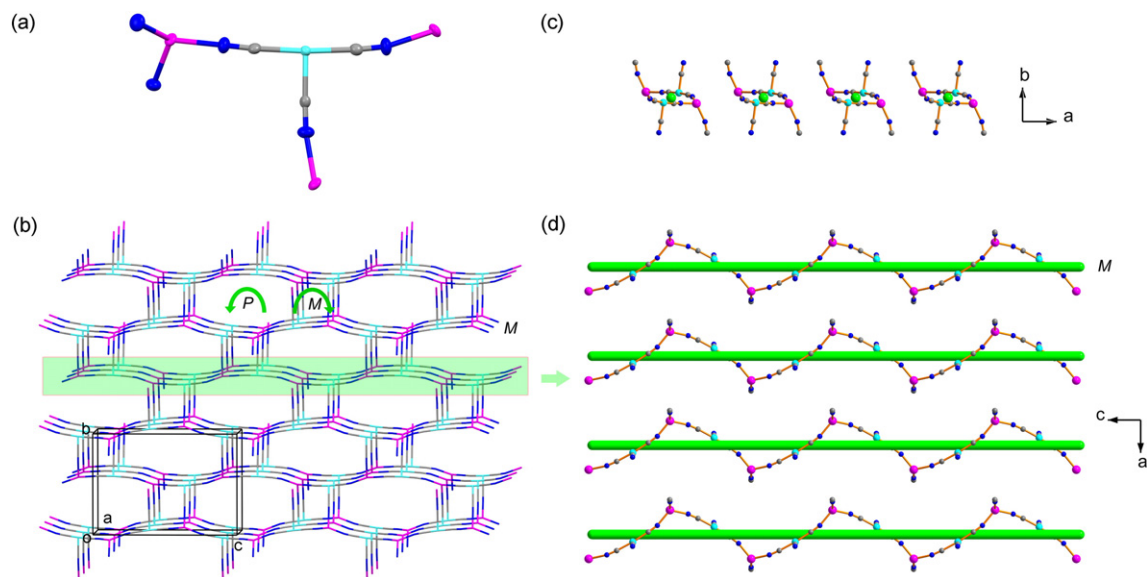
(Fig. 2a–b). In order to clearly show the topology of the framework, views of the slices through the crystal packing along the (001) and (010) planes are shown (Fig. 2c–d). [NC–Co–CN–Li] links one by one along the *c* axis with a seemingly wavy shape. The shortest inter-chain Li···Li distance is about 9.257 Å. Along the *b* axis, the neighboring chains are related by a  $2_1$  symmetry, that is, their directions are opposite. The chain is connected with four neighboring chains through Li–N bonds, two in the positive direction and the other two in the negative direction of the *b* axis. This leads to the final 3D topology of the compounds. One significant feature of the cationic framework of **1** is the helicity, noting that all the components appearing in the system are achiral but the compound crystallizes in the chiral space group  $P2_12_12_1$ . The helical chains extending along the *c* axis are left-handed (Fig. 2d). When viewed from the *a* axis, the helicity shows both left- and right-handedness (Fig. 2b). As a contrast, in a  $[N(CH_3)_4]$ -containing compound  $[N(CH_3)_4][Li(H_2O)_2[Co(CN)_6]]$ , there are only regular 1D zigzag chains.

Large voids exist in the anionic framework where the Hlm cations and crystallization water molecules reside. The guests interact with the host framework through N–H···N and N–H···O hydrogen bonds (Fig. 3). There are two types of Hlm cations in the structure, both of which have two hydrogen bonds with the uncoordinated water molecule and CN group with NH···O and NH···N distances of about 2.789(2)/2.768(6) and

2.978(5)/3.100(5) Å, respectively. The uncoordinated water is involved in four hydrogen bonds, acting as acceptors with two Hlm cations and donors with one coordinated water molecule and one terminal CN group. The O2···O/N bond distances are 2.713(4)–2.808(4) Å and O2–H···O/N angles 155(5)–169(4)°. Correspondingly, the coordinated water, besides the coordination bond Li1–O1, has three hydrogen bonds, that is, acting as donors with two CN groups (O1···N5 = 2.807(4) Å, O1–H6···N5 = 158(4)°; O1–H7···N1 = 2.760(4) Å, O1–H7···N1 = 172(4)°) and an acceptor with the uncoordinated water. As to the terminal CN groups, they interact with two coordinated water molecules and one uncoordinated water molecule, respectively. It is clear that these interactions tightly hold the anions, cations and water molecules together and contribute to the formation of the chiral 3D framework.

The water molecules in **1** have two states, i.e., one (O1) is coordinated to the Li ion and the other (O2) is only hydrogen-bonded with the neighboring CN group, water molecules and Hlm cations in the crystal lattice. This difference is witnessed by thermal analysis. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) of **1** were performed with a heating rate of 10 °C·min<sup>−1</sup> in the temperature range of 313–673 K (Fig. 4). The TGA curve of **1** displays three weight loss steps. The first two steps are caused by two one-water losses between 320 and 360 K (found 4.52%, calcd. 4.54%) and between 410 and 450 K (found 4.25%, calcd. 4.54%), respectively. The former loss corresponds to the coordinated water and the latter the uncoordinated water, which is verified by variable-temperature IR spectra (Fig. 5). At 298 K, the peaks at around 834, 746 and 678 cm<sup>−1</sup> could be ascribed to the coordination of the water molecule to the Li ions. They disappear at 393 K while the peaks at 3382 and 1679 cm<sup>−1</sup> become clear which are tentatively assigned to the uncoordinated water [23]. The third step of weight loss occurs between 530 and 610 K (found 44.79%, calcd. 47.95%), corresponding to a decomposition to a supposed LiCo(CN)<sub>4</sub> residue. The DSC curve is consistent with the TGA curve, showing four endothermic peaks at the water loss (340 K and 440 K) and decomposition regions (561 K and 588 K), respectively.

Release of the water molecules from **1** upon heating was also verified by dielectric measurement which is a sensitive indicator to reveal internal structural changes of compounds [24–26]. Fig. 6 shows the changes of the real part  $\epsilon'$  of the dielectric constant  $\epsilon = \epsilon' - i\epsilon''$  in a heating–cooling cycle. Upon heating, the  $\epsilon'$  value reaches two peaks at 350 K and 367 K, respectively, corresponding to the two steps of the



**Fig. 2.** View of the 3D structure of the anionic framework of **1**: (a) the basic unit of building block of the framework; (b) 3D packing diagram viewed along the *a* axis; (c) and (d) views of the slices through the crystal packing along the (001) and (010) planes, respectively. Green arrows and columns represent the  $2_1$  screw axis. Hlm cations, water molecules and terminal CN groups are omitted for clarity.

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