

## Two Cr<sup>III</sup> containing metal-1-hydroxyethylidenediphosphonate compounds: Synthesis, structure, and morphology

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Two novel layered Cr<sup>III</sup> containing metal-hedp compounds, Na<sub>20</sub>AlCr<sup>III</sup>[CH<sub>3</sub>C(O)P<sub>2</sub>O<sub>6</sub>]<sub>6</sub>·O<sub>3</sub>·(H<sub>2</sub>O)<sub>26</sub>·(H<sub>3</sub>O)<sub>10</sub> (CH<sub>3</sub> CH<sub>2</sub> OH) and Na<sub>6</sub>Cr<sup>III</sup>[CH<sub>3</sub>C(OH)P<sub>2</sub>O<sub>6</sub>]<sub>3</sub>·(H<sub>2</sub>O)<sub>21</sub>(H<sub>3</sub>O)<sub>3</sub> (designated as DLES-AlCr and DLES-Cr<sup>III</sup> respectively), were hydrothermally synthesized. Their structures were determined by single-crystal X-ray diffraction. The two crystals are isostructural with propeller-like chiral motifs and hexagonal rings along [001]. DLES-AlCr crystal exhibits interesting hollow tubular hexagonal morphology, while DLES-Cr crystal possesses solid hexagonal morphology.

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### 1 Introduction

The recent interest in the crystal engineering of inorganic-organic hybrid open-framework materials continues to be very active because of their potentially important applications in catalysis, sorption and separation [1-3]. Our synthetic strategy for achieving inorganic-organic hybrid open-framework materials involves the use of 1-hydroxyethylidenediphosphonate (hedp) for introducing organic components into the structure, and employment of the hydrothermal method for realizing crystallization. The crystal structural roles of hedp ions and the structural characteristics of metal-hedp compounds have been reviewed previously [4-7]. In most cases, the metal-hedp compounds exhibit layered structures without open-framework. More recently, many efforts have been devoted to synthesizing open-framework metal-hedp compounds. The idea was highlighted by the studies on Sn<sub>2</sub>(hedp) [8]. In this compound, the linkage of the two fundamental structural motifs, {SnO<sub>3</sub>} pyramids and {O<sub>3</sub>PC} tetrahedrons, produces four- and eight-polyhedral rings, which fuse in turn to form the unusually complex framework aligned parallel to the a or c axis. Attempting to obtain open-framework by template-assisted method, Zheng et al. synthesized several metal-hedp compounds with different structures using different organic amines as the template [9-13]. The authors observed that the size of the template has great effects on the structures of the as-synthesized crystals.

In this work, we report on two novel Cr<sup>III</sup> containing metal-hedp single crystals of DLES-AlCr and DLES-Cr. DLES-AlCr exhibits interesting tubular morphology, while DLES-Cr displays hexagonal solid (herein solid means tubeless) morphology. The two crystals are isostructural and show orderly hexagonal rings containing propeller-like chiral motifs along [001]. The incorporation of a transition metal like chromium into the large hexagonal ring would generate different congeners of the hybrid inorganic-organic materials and be expected to endow the materials with some novel potential properties.

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## 2 Experimental

**SEM image and EDX point analysis** The SEM images were obtained by a JSM-5600LV at 12kV. The EDX point analysis was performed using an Oxford Instruments X-ray Microanalysis 1350 with an accelerating voltage of 20.00kV and a system resolution of 77eV. Na<sub>2</sub>O·Al<sub>2</sub>O<sub>3</sub>·6SiO<sub>2</sub> (albite), Al<sub>2</sub>O<sub>3</sub> (aluminum oxide), GaP (gallium phosphide) and Cr (stainless steel) were used as standards for Na, Al, P and Cr, respectively.

**<sup>1</sup>H NMR spectrum** <sup>1</sup>H NMR spectrum was recorded at room temperature on a Bruker DRX-400 spectrometer with a resonance frequency of 400.1MHz. The magnetic field was 9.4T, the number of scans was 200 and the chemical shift was referenced to the saturated aqueous solution of sodium 4, 4-dimethyl-4-silapentane sulfonate (DSS).

**Crystallographic data collection and structure determination** Unit cell parameters and intensity data were determined by using a Bruker Smart 1000 with graphite monochromated Mo-K $\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) radiation at 20(2) $^{\circ}$ C. The crystal structures were solved by the direct method and refined against  $F^2$  using the SHELXTL software package. Hydrogen atoms were geometrically placed.

**Synthesis** All chemicals were analytically pure and were used without further purification. Na<sub>20</sub>AlCr<sup>III</sup>[CH<sub>3</sub>C(O)P<sub>2</sub>O<sub>6</sub>]<sub>6</sub>·O<sub>3</sub>·(H<sub>2</sub>O)<sub>26</sub>·(H<sub>3</sub>O)<sub>10</sub>(CH<sub>3</sub>CH<sub>2</sub>OH) with hexagonal tubular morphology (designated as DLES-AlCr): Single crystal of DLES-AlCr was synthesized using a starting molar composition of 0.075Cr<sub>2</sub>O<sub>3</sub> (chromium (III) oxide): 0.075AlOOH (pseudo-boehmite), 0.75Na<sub>2</sub>C<sub>2</sub>H<sub>4</sub>O<sub>7</sub>P<sub>2</sub> (tetrasodium 1-hydroxyethylidenediphosphonate): 0.27C<sub>2</sub>H<sub>8</sub>N<sub>2</sub> (ethylenediamine): 0.020C<sub>2</sub>H<sub>5</sub>OH(ethanol): 3H<sub>2</sub>O (deionized water). The mixture was stirred at 30 $^{\circ}$ C until homogeneity, transferred into 200mL Teflon-lined stainless autoclave, and then heated at 160 $^{\circ}$ C for 15 days under autogenous pressure. The product was filtered, washed thoroughly with ethanol and dried at 40 $^{\circ}$ C. Yield is 78% based on Cr. EDX point analysis of DLES-AlCr gave the following molar ratio: Na: Al: Cr: P = 19.77: 1.16: 1.17: 14.96 (Calculated Na: Al: Cr: P = 20: 1:1: 12).

Na<sub>6</sub>Cr<sup>III</sup>[CH<sub>3</sub>C(OH)P<sub>2</sub>O<sub>6</sub>]<sub>3</sub>·(H<sub>2</sub>O)<sub>21</sub>(H<sub>3</sub>O)<sub>3</sub> (designated as DLES-Cr): DLES-Cr was synthesized by a starting reaction gel with a molar composition of 0.15Cr<sub>2</sub>O<sub>3</sub>: 0.75Na<sub>2</sub>C<sub>2</sub>H<sub>4</sub>O<sub>7</sub>P<sub>2</sub>: 0.27C<sub>2</sub>H<sub>8</sub>N<sub>2</sub>: 0.020C<sub>4</sub>H<sub>8</sub>O<sub>2</sub> (1,4-dioxane): 3H<sub>2</sub>O. Yield is 73% based on Cr. The rest was the same as that of DLES-AlCr. EDX point analysis of DLES-Cr gave the following molar ratio: Na: Cr: P = 5.94: 1.11: 6.95 (Calculated Na: Cr: P = 6: 1: 6).

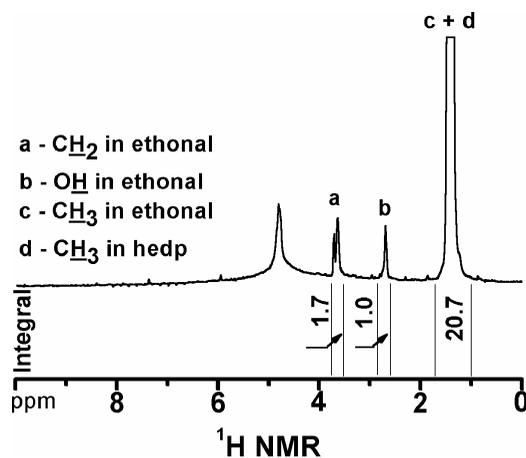
## 3 Results and discussion

**Tubular morphology of DLES-AlCr** DLES-Cr and DLES-AlCr are green, transparent, hexagonal crystals. DLES-Cr crystals show solid morphologies. However, DLES-AlCr crystals exhibit interestingly hollow tubular morphologies with conical ends, which are illustrated in figure 1. The tube could be clearly observed in the large crystals. Typically, DLES-AlCr is about 0.04mm thick and up to 2.7mm long. A diagonal length of the coaxial tube at an open end is ca. 0.08 mm. EDX point analyses were obtained from two different positions in one tubular crystal of DLES-AlCr. From these spectra, the same elemental ratios were derived (molar ratio Na: Al: Cr: P = 19.77: 1.16: 1.17: 14.96). The results suggest that the whole crystal has an identical composition. To our knowledge, DLES-AlCr is the first transition metal-diphosphonate with the hexagonal tubular morphology.



Fig. 1 SEM image of DLES-AlCr.

**$^1\text{H}$  NMR spectrum** Figure 2 shows the  $^1\text{H}$  NMR spectrum of DLES-AlCr. There are five well-resolved signals. The shoulder peaks at 4.80 and 4.77 ppm are ascribed to the solvent of  $\text{D}_2\text{O}$ . Ethanol incorporated in DLES-AlCr exhibits shoulder peaks ( $\delta = 3.70$  and 3.63 ppm) assigned to  $\text{CH}_2$  and a single peak at 2.68 ppm assigned to  $\text{OH}$ . The other peak in ethanol ( $\text{CH}_3$ ) is contained in the strong and broad peak at the right end of the spectrum. Moreover, the peak includes the signals produced by  $\text{CH}_3$  in ligand of hedp. All peaks are broadened considerably due to the effect of Cr in the structure [14-16]. The intensity ratio of a: b: c: d = 1.7: 1: (1 $\times$ 3): (20.7-1 $\times$ 3) = 1.7: 1: 3: 17.7 is in accordance with the ratio of the hydrogen atoms in the corresponding group of DLES-AlCr (calculated from molecular formula a: b: c: d = 2: 1: 3: 18). No other signal is observed in the spectrum, which supports the molecular formula deduced from single crystal X-ray diffraction.



**Fig. 2**  $^1\text{H}$  NMR spectrum of DLES-AlCr (data measured in  $\text{D}_2\text{O}$ ) with labeled peaks assigned to the corresponding protons in ethanol and hedp.

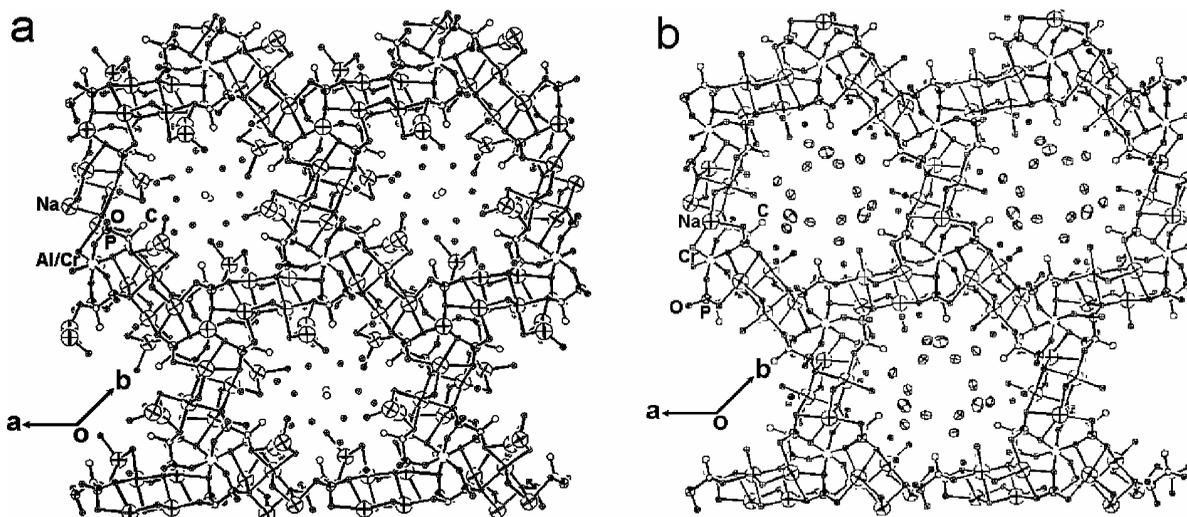
**Description of the crystal structures** The selected crystallographic data for DLES-AlCr and DLES-Cr are given in table 1.

**Table 1** Crystallographic Data for DLES-AlCr and DLES-Cr

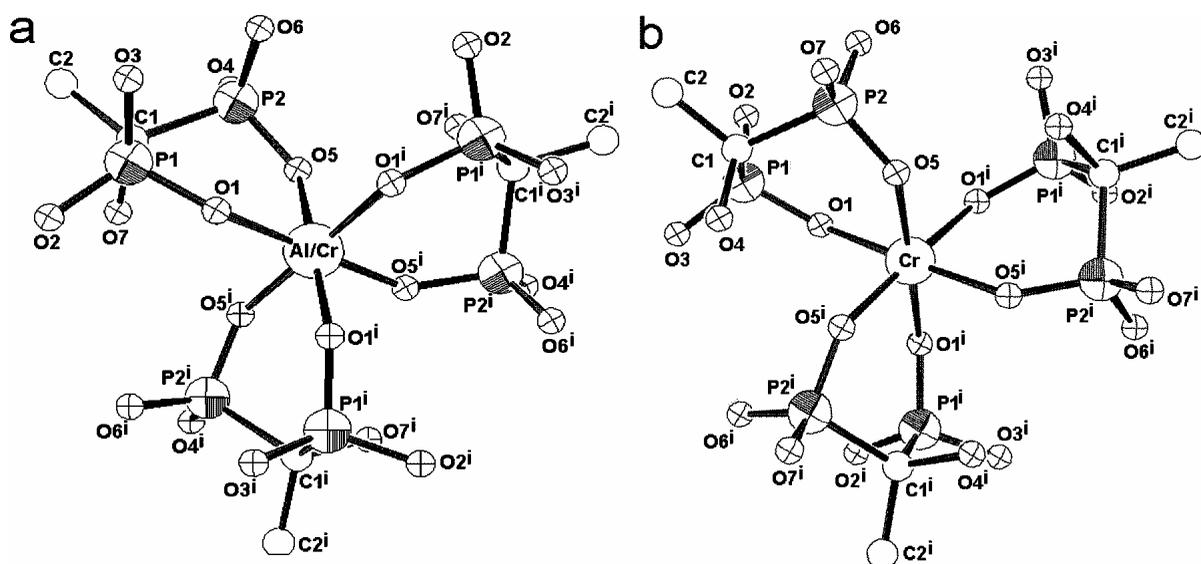
	DLES-AlCr	DLES-Cr
CCDC deposit no.	CCDC 205540	CCDC 198393
Empirical Formula	$\text{C}_{14}\text{H}_{106}\text{AlCrNa}_{20}\text{O}_{82}\text{P}_{12}$	$\text{C}_2\text{H}_{21.33}\text{Cr}_{0.33}\text{Na}_2\text{O}_{15.17}\text{P}_2$
Formula weight	2497.39	413.44
Crystal Size (mm)	0.08 $\times$ 0.08 $\times$ 0.06	0.15 $\times$ 0.10 $\times$ 0.05
Crystal system	Trigonal	Trigonal
Space group	P-3	P-3
T ( )	20 (2)	20 (2)
a (Å)	17.910 (3)	17.974 (4)
b (Å)	17.910 (3)	17.974 (4)
c (Å)	8.832 (3)	8.853 (4)
$\alpha$ (deg)	90	90
$\beta$ (deg)	90	90
$\gamma$ (deg)	120	120
V (Å <sup>3</sup> )	2453.4 (9)	2476.9 (14)
Z	1	6
Calculated density (g/cm <sup>3</sup> )	1.696	1.663
Reflections collected / unique	14256 / 3284 [R (int) = 0.0490]	9390 / 2684 [R (int) = 0.0635]
Completeness to theta =26.38°	98.3%	91.9%
Absorption correction	Semi-empirical from equivalent	Semi-empirical from equivalent
$\mu$ (mm <sup>-1</sup> )	0.527	0.591
R and w <sup>a</sup> R <sub>2</sub> [I > 2 $\sigma$ (I)]	0.0455 and 0.1161	0.0574 and 0.1436
R and w <sup>a</sup> R <sub>2</sub> (for all data)	0.0705 and 0.1299	0.0906 and 0.1619

<sup>a</sup> $W = 1/(\sigma^2(F_0^2) + (0.0813 \times P)^2 + 0.64 \times P)$ ,  $P = (\max(F_0^2, 0) + 2 \times F_c^2) / 3$ ; <sup>a2</sup> $W = 1/[\sigma^2(F_0^2) + (0.1039 \times P)^2 + 0.00 \times P]$ ,  $P = (\max(F_0^2, 0) + 2 \times F_c^2) / 3$

In order to clearly contrast the crystal structures of DLES-AlCr and DLES-Cr, their ORTEP drawings are exhibited side by side. The [001] projections of the two crystals are shown in figure 3. Commonly, they possess a layered structure parallel to the *ab* plane, in which six-coordinate aluminum and/or chromium centers are sharing the vertices with the {P(C)O<sub>3</sub>} tetrahedrons forming chiral propeller-like motifs, and the chiral motifs are linked together by –O-Na-O-Na-O- ionic chains forming hexagonal rings.



**Fig. 3** Comparison of DLES-AlCr (a) and DLES-Cr (b) structures viewed along [001] (Thermal ellipsoids are drawn at 30% probability and hydrogen atoms are omitted for clarity. i: equivalent atom. Legends for elements are labeled in figure).



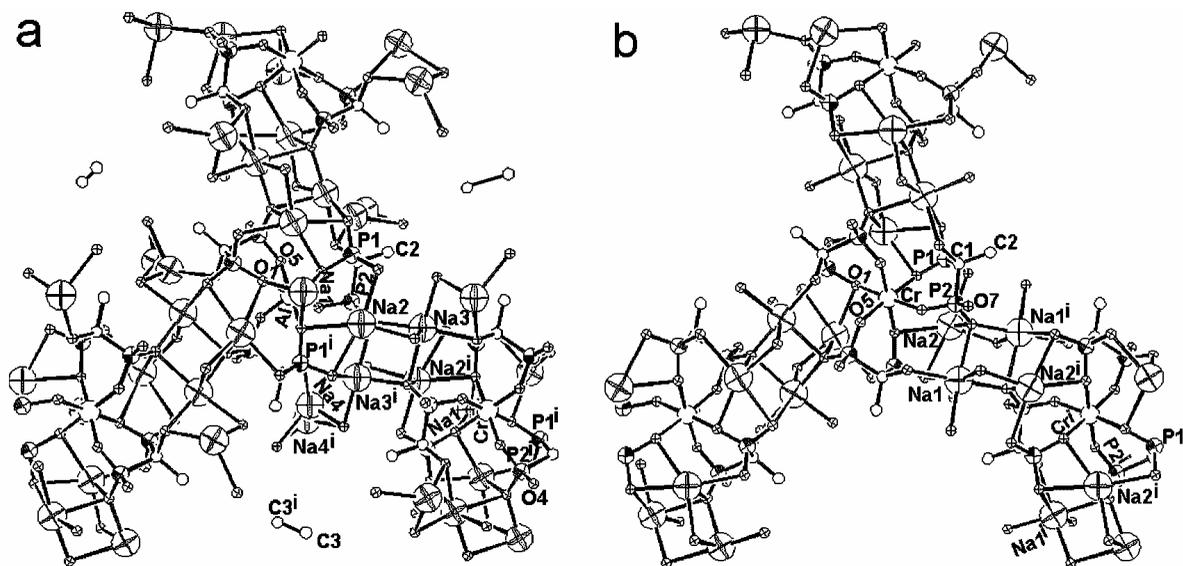
**Fig. 4** Propeller type environments around the aluminium and/or chromium center of DLES-AlCr (a) and DLES-Cr (b) along [001] (Thermal ellipsoids are drawn at 30% probability and hydrogen atoms are omitted for clarity. i: equivalent atom. Legends for elements are labeled in figure).

**DLES-AlCr** The atomic coordinates and the equivalent isotropic displacement parameters are listed in the crystallographic file, and identical site occupancies of Al<sup>3+</sup> and Cr<sup>3+</sup> are observed. The result confirms the uniform distribution of the two ions in the compounds.

The chiral propeller-like motif is shown in figure 4a, which is formed by an aluminum/chromium-centered octahedron with three six-member rings. The O-Al/Cr-O bond angles for the three blades of the propeller are all equal to 92.56 degrees. The sum of the inner angles of C(1)-P(1)-O(1)-Al(1)/Cr(1)-O(5)-P(2)-C(1) is 686.4

degree. The torsion angles for O(4)-P(2)-C(1)-P(1), O(4)-P(2)-O(5)-Cr(1), O(5)-P(2)-C(1)-C(2), and O(1)-P(1)-C(1)-C(2) are 179.57 (14), -153.50 (16), -171.2 (2), and -170.7 (2) degree, respectively. It indicates that the six-member ring, P=O and methyl group nearly lie in a plane. It is a very interesting result. The nearly planar unit is linked together by covalent bonds and it is very stable. The stable and planar unit possesses very few steric hindrances; therefore, it could act as secondary building units for assembling new structures.

A fragment of DLES-AlCr viewed along the *c*-axis is shown in figure 5a. Methyl groups and coordinated water molecules are protruding into the channels. Two phosphorus atoms are all tetrahedrally surrounded by three oxygen atoms and one carbon atom forming a {P(C)O<sub>3</sub>} tetrahedron with one terminal P(2) – O(4) double bond. The length of this terminal P=O bond is 1.527Å. The value is in the range of reported P=O bond length in metal-1-hydroxylidenediphosphonates, but it is longer than that of in H<sub>4</sub>hedp (1-hydroxyethylidenediphosphonic acid) [9-13, 17, 18]. The result is due to strong hydrogen bonds between the P=O and the water molecules trapped between layers. Na (2) and Na (3) are connected together through an oxygen atom to form an ionic chain lying in the middle of the hexagonal edge. The above mentioned chiral motifs are linked together by the ionic chains forming hexagonal rings. Additionally, Na (1) also links the above ionic chains together through Na(1)-O(1)-Na(2) and helps to form the stable hexagonal rings. Na(4) replaces part of the water molecules linking with the  $\alpha$ -O atoms [O(7)] and the water molecules [O(10), O(11), O(12), O(13), and O(14)]. Na(4) and the protonated water molecules supply positive charges to balance the negative charges of the structure.



**Fig. 5** Fragments of DLES-AlCr (a) and DLES-Cr (b) (Thermal ellipsoids are drawn at 30% probability and hydrogen atoms are omitted for clarity. i: equivalent atom. Legends for elements are labeled in figure).

**DLES-Cr** Despite the fact that the basic crystal structure of DLES-Cr is similar to that of DLES-AlCr, a detailed examination of the structure reveals the differences. Compared the corresponding ORTEP drawings of the two crystals illustrated in figure 5, two main differences from DLES-AlCr could be found for DLES-Cr: (1) except Na (1) and Na (2), there are no additional sodium atoms in the crystal structure; (2) there are no ethanol molecules and Na (4) lying in the channels.

A chiral propeller-like motif of DLES-Cr is shown in Figure 4 (b). The chiral motif is formed by Cr centered octahedron with three six-member rings. The O-Cr-O bond angles for the three blades of the propeller are 94.75 degree. The summation of the inner angles of C(1)-P(1)-O(1)-Cr(1)-O(5)-P(2)-C(1) is 684.6 degree. The torsion angles for O(7)-P(2)-C(1)-P(1), O(7)-P(2)-O(5)-Cr(1), O(5)-P(2)-C(1)-C(2), and O(1)-P(1)-C(1)-C(2) are 178.2, 155.9, 168.7, and 170.5 degree, respectively. It suggests that the six-member ring, P=O and methyl groups also nearly lie in a plane. The chiral propeller-like motifs are linked through Na(1)-O-Na(2) ion bonds forming hexagonal rings. Based on the above description, a conclusion could be drawn that water molecules play an important role in the structure. First, protonated water molecules lying in the channels can balance the

negative charges of the structure. The phenomenon was also observed in AlPO-CJ4 [19]. Second, water molecules trapped between layers interact with the terminal oxygen atoms attached to the P atoms through hydrogen bonds, thus forming a stable structure.

## 4 Conclusion

In summary, we have synthesized two novel layered Cr<sup>III</sup> containing metal-hedp compounds, namely DLES-AlCr and DLES-Cr. The common crystal characteristics are propeller-like chiral motifs and hexagonal channels along [001]. Interestingly, DLES-AlCr exhibits a millimetre-scale tubular morphology. It is the first example of transition metal containing metal-hedp compounds with such a structure. Our further work would concern the synthesis of novel inorganic-organic hybrid tubular materials and investigating their properties. Meanwhile, decreasing the sizes of the present millimetre-scale tubular materials and investigating the size-effects so obtained would be another interesting topic for exploration.

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