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Organic–inorganic hybrids constructed by Anderson-type polyoxoanions and copper coordination complexes

Rui-Ge Cao, Shu-Xia Liu *, Ying Liu, Qun Tang, Liang Wang, Lin-Hua Xie, Zhong-Min Su

Key Laboratory of Polyoxometalates Science of the Ministry of Education, College of Chemistry, Northeast Normal University, Changchun City, JiLin 130024, PR China

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ABSTRACT

Four organic–inorganic hybrid compounds based on Anderson-type polyoxoanions, namely, $\{[Cu(2,2'\text{-bpy})(H_2O)_3]_2[Cr(OH)_6Mo_6O_{18}]\}\{[Cu(2,2'\text{-bpy})(H_2O)Cl][Cu(2,2'\text{-bpy})(H_2O)(NO_3)][Cr(OH)_6Mo_6O_{18}]\}\cdot 18H_2O$ (**1**), $[Cu(2,2'\text{-bpy})(H_2O)_2Cl]\{[Cu(2,2'\text{-bpy})(H_2O)_2][Cr(OH)_6Mo_6O_{18}]\}\cdot 4H_2O$ (**2**), $(H_3O)\{[Cu(2,2'\text{-bpy})(H_2O)_2]_2[Cu(2,2'\text{-bpy})(H_2O)]_2\}[Cr(OH)_6Mo_6O_{18}]_3\cdot 36H_2O$ (**3**), and $(H_3O)\{[Cu(2,2'\text{-bpy})(H_2O)_2]_2[Cu(2,2'\text{-bpy})(H_2O)]_2\}[Al(OH)_6Mo_6O_{18}]_3\cdot 33H_2O$ (**4**), were isolated by conventional solution method, and crystal structures have been determined by single-crystal X-ray diffraction. Among them, compound **1** displays a discrete supramolecular structure, compound **2** shows a chainlike structure with chloro-copper complexes as counteranions, and compounds **3** and **4** are isomorphic and exhibit unique 3D open frameworks with lattice water molecules residing in the channels. The compounds **3** and **4** represent the first example of 3D organic–inorganic hybrid compounds in the TMs/2,2′-bpy/POMs system. Investigation of the reaction conditions reveals that the geometry and size of the anions together with its coordinating abilities to the metal centers have a decisive influence on both the composition and the dimensionality of the final compounds.

1. Introduction

In the past decades, much attention has been paid toward the rational design and synthesis of novel organic–inorganic hybrids through the modification of metal oxides by organic molecules for the significance of discovering new materials [1]. Commonly, the structures and properties of these hybrids can be finely tuned by the choice of various inorganic building blocks. Polyoxometalates (POMs) as discrete anionic metal-oxygen clusters are ubiquitous inorganic building blocks possessing a wide range of the composition, highly alterable sizes, shapes, and charge densities [2]. Although the remarkable advance in the construction of POM-based organic–inorganic hybrids has been successfully achieved [3,4], the mechanisms of formation are still not yet well understood and are generally described as self-assembly. Thus, it is important to systematically analyze the influence of each individual factor in the construction of the structures to straightforward synthesis of multifunctional materials. In recent years, Mizuno and coworkers have systematically investigated the effect of the polyoxoanions with different charges on the structures and sorption properties of the compounds constructed by metal-organic macrocation and Dawson- or Keggin-type polyoxoanions [5]; Gutiérrez-Zorrilla and coworkers have reported that the different alkaline acetate buffer solution as the reaction medium has a decisive influence on the final structures of the Keggin-based hybrids [6]; moreover, Long and coworkers have studied the modulated effect of the pH of the solution [7], polyoxoanion of the inorganic building block [8], and the steric hindrance of the organic ligand [9] on the structures of Keggin-based hybrids. In contrast to several works that investigated the influence of different acidic anions on the structures of the metal-organic frameworks [10], the various acidic anions with different geometry and size together with their coordinating and hydrogen-bonding properties may also influence the final structures of POM-based compounds which encouraged our research interest.

It is noteworthy that: (i) the Anderson-type polyoxoanion exhibit attractive planar structure, and each Mo (or W) atom has two terminal O atoms which make them hold high reactivity, and then facilitate to integrate with the transition metal centers [11]; (ii) the d^9 Cu^{II} cation favors asymmetric coordination modes, and therefore alternative types of bonding might be expected [12], for example, apical and equatorial linkage with Anderson-type polyoxoanions; (iii) the chelating N-containing aromatic ligand 2,2′-bipyridine (2,2′-bpy), can not only affect the coordination geometry of metal centers but also bring about π–π stacking interactions [13], which are important for the construction of hybrids. Taking these into account, we chose the Anderson-type polyoxoanions as inorganic building blocks, the Cu^{II} cation as

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* Corresponding author. Fax: +86 431 8509 9328.
E-mail address: liusx@nenu.edu.cn (S.-X. Liu).

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linker, and the 2,2′-bpy as the organic component, isolated three kinds of compounds possessing different structures, and systematically researched the effect of the acidic anions ($Cl^-$and NO_3^-) of the reaction solution on the final structures of POM-based organic–inorganic hybrids. Herein, the syntheses and crystal structures of $\{[Cu(2,2'\text{-bpy})(H_2O)_3]_2[Cr(OH)_6Mo_6O_{18}]\}\{[Cu(2,2'\text{-bpy})(H_2O)Cl][Cu(2,2'\text{-bpy})(H_2O)(NO_3)][Cr(OH)_6Mo_6O_{18}]\}\cdot 18H_2O$ (**1**), $[Cu(2,2'\text{-bpy})(H_2O)_2Cl]\{[Cu(2,2'\text{-bpy})(H_2O)_2][Cr(OH)_6Mo_6O_{18}]\}\cdot 4H_2O$ (**2**), $(H_3O)\{[Cu(2,2'\text{-bpy})(H_2O)_2]_2[Cu(2,2'\text{-bpy})(H_2O)]_2\}[Cr(OH)_6Mo_6O_{18}]_3\cdot 36H_2O$ (**3**), and $(H_3O)\{[Cu(2,2'\text{-bpy})(H_2O)_2]_2[Cu(2,2'\text{-bpy})(H_2O)]_2\}[Al(OH)_6Mo_6O_{18}]_3\cdot 33H_2O$ (**4**) are reported.

2. Experimental

2.1. Materials

All chemicals were used as purchased without further purification. Elemental analyses were performed on a PLASMA-SPEC(I) ICP atomic emission spectrometer (Al, Cr, Cu, and Mo) and a Perkin-Elmer 2400 CHN elemental analyzer (C, H, and N). IR spectra were recorded in the range 400–4000 cm^{-1} on an Alpha Centaurt FT/IR spectrophotometer using KBr pellets. TG analyses were performed on a Perkin-Elmer TGA7 instrument in flowing N_2 with a heating rate of 10 °C/min. Powder X-ray diffraction measurements were performed on a Rigaku D/MAX-3 instrument with Cu$K\alpha$ radiation in the angular range $2\theta = 3$–90° at 293 K.

2.2. Synthesis

2.2.1. Synthesis of **1**

A sample of $Na_2MoO_4\cdot 2H_2O$ (0.90 g, 3.72 mmol) was dissolved in 30 mL of water and the pH of the solution was adjusted with the dilute HNO_3 solution (3 M) to approximately 4.5, then a solution of $CrCl_3\cdot 6H_2O$ (0.30 g, 1.12 mmol) in water (10 mL) was added. $CuCl_2\cdot 2H_2O$ (0.14 g, 0.80 mmol) and 2,2′-bipyridine (0.13 g, 0.80 mmol) were dissolved in a mixture 10 mL of water and 10 mL of methanol solution, and then it was added to the upper solution with stirring. The pH of the resulting cloudy solution was adjusted to 2.6 with the dilute HNO_3 solution (3 M), stirred for 30 min and filtered. The filtrate was kept for five days at ambient conditions, and blue block crystals of **1** were collected. Yield: 62% (based on Cu). Elemental *Anal. Calc.* for $C_{40}H_{96}ClCr_2Cu_4Mo_{12}N_9O_{77}$: C, 13.81; H, 2.78; N, 3.62; Cr, 2.99; Cu, 7.30; Mo, 33.08. Found: C, 14.12; H, 2.99; N, 3.36; Cr, 3.35; Cu, 7.66; Mo, 33.41. IR (KBr pellet): 3430(br), 1600(w), 1566(w), 1496(w), 1471(w), 1442(w), 1419(w), 1384(m), 1342(w), 1315(w), 1246(w), 1157(w), 1115(w), 1063(w), 1024(w), 943(s), 890(s), 777(m), 652(s), 575(m), 416(m) cm^{-1}.

2.2.2. Synthesis of **2**

Compound **2** was prepared following the procedure described for **1**, except that the HCl solution was used instead of HNO_3 solution. Yield: 68% (based on Cu). Elemental *Anal. Calc.* for $C_{20}H_{38}ClCrCu_2Mo_6N_4O_{32}$: C, 14.68; H, 2.34; N, 3.42; Cr, 3.18; Cu, 7.76; Mo, 35.17. Found: C, 14.29; H, 2.59; N, 3.06; Cr, 3.51; Cu, 7.99; Mo, 35.52. IR (KBr pellet): 3430(br), 1600(w), 1565(w), 1498(w), 1471(w), 1439(w), 1387(w), 1317(w), 1246(w), 1163(w), 1108(w), 1066(w), 945(m), 895(s), 766(m), 642(s), 567(m), 415(m) cm^{-1}.

2.2.3. Synthesis of **3**

Compound **3** was prepared similar to that of **1**, except that at the beginning $Cr(NO_3)_3\cdot 9H_2O$ and $Cu(NO_3)_2\cdot 3H_2O$ were used instead of $CrCl_3\cdot 6H_2O$ and $CuCl_2\cdot 2H_2O$, respectively. Yield: 56% (based on Cu). Elemental *Anal. Calc.* for $C_{40}H_{137}Cr_3Cu_4Mo_{18}N_8O_{115}$: C, 10.21; H, 2.93; N, 2.38; Cr, 3.31; Cu, 5.40; Mo, 36.68. Found: C, 9.86; H, 2.52; N, 2.56; Cr, 3.70; Cu, 5.77; Mo, 36.91. IR (KBr pellet): 3430(br), 1600(w), 1568(w), 1498(w), 1471(w), 1441(w), 1387(w), 1317(w), 1250(w), 1163(w), 1107(w), 947(m), 904(m), 771(m), 661(s), 538(m), 413(s) cm^{-1}.

2.2.4. Synthesis of **4**

A sample of $Na_2MoO_4\cdot 2H_2O$ (0.90 g, 3.72 mmol) was dissolved in 30 mL of water followed by addition of 5 mL of glacial acetic acid and 10 mL of aqueous solution of $Al(NO_3)_3\cdot 9H_2O$ (0.56 g, 1.50 mmol) with stirring. Then, the mixture of 10 mL aqueous solution of $Cu(NO_3)_2\cdot 3H_2O$ (0.19 g, 0.80 mmol) and 10 mL of methanol solution of 2,2′-bipyridine (0.13 g, 0.80 mmol) was added, light blue precipitate formed and the pH of the resulting mixture was adjusted to 2.6 with the dilute HNO_3 solution (3 M). The mixture was stirred for 30 min and then filtered. The filtrate was allowed to evaporate at room temperature. After 5 days blue block crystals of **4** were collected. Yield: 59% (based on Cu). Elemental *Anal. Calc.* for $C_{40}H_{131}Al_3Cu_4Mo_{18}N_8O_{112}$: C, 10.49; H, 2.88; N, 2.45; Al, 1.77; Cu, 5.55; Mo, 33.72. Found: C, 10.21; H, 2.52; N, 2.64; Al, 1.99; Cu, 5.93; Mo, 34.06. IR (KBr pellet): 3450(br), 1600(w), 1500(w), 1471(w), 1441(w), 1385(w), 1319(w), 1252(w), 1167(w), 943(m), 902(m), 771(m), 663(s), 573(m), 445(s) cm^{-1}.

2.3. X-ray crystallography

Diffraction intensities for compounds **1**–**4** were collected on a Siemens Smart CCD diffractometer equipped with graphite monochromatic Mo-$K\alpha$ radiation ($\lambda = 0.71073$ Å) at 293 K. The linear absorption coefficients, scattering factors for the atoms, and anomalous dispersion corrections were taken from International Tables for X-ray Crystallography. The structures were solved by the direct method and refined by the full-matrix least-squares method on F^2 using the SHELXTL crystallographic software package. Anisotropic thermal parameters were used to refine all non-hydrogen atoms. The hydrogen atoms for the 2,2′-bipyridine ligands were fixed in ideal positions and included in the refinement riding on their respective parent atoms. The hydrogen atoms of the central O atoms around the Cr^{3+} ions and partial water molecules were located in the difference Fourier maps for compounds **1** and **2**. In compound **1**, a Cl^- and NO_3^- were disordered, thus the $Cl^-$and NO_3^- were set to be half-occupied. Inside the frameworks of **3** and **4**, there are a number of disordered lattice waters, which show many peaks of low electronic density in the difference Fourier maps. So the SQUEEZE subroutine of PLATON software [14] was applied to create new reflection data where contribution from the disordered lattice waters were removed from the original data but were included in the structure factor calculations. The numbers of lattice waters for **3** and **4** were determined by elemental analyses, TG and calculations of electron count inside the frameworks with SQUEEZE. The crystal data and structure refinements of **1**–**4** are summarized in Table 1. The experimental and simulated X-ray powder diffraction patterns (XRPD) of these compounds are shown in the Supplementary material. The diffraction peaks on both experimental and simulated patterns match well in position, indicating their phase purity. Additionally, the XRPD of **3** and **4** are similar, which is in agreement with their isomorphic structures determined by single-crystal X-ray diffraction. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC reference number 682197–682200.

Table 1
Crystal data and structure refinements for **1–4**

	1	2	3	4
Empirical formula	$C_{40}H_{96}ClCr_2Cu_4Mo_{12}N_9O_{77}$	$C_{20}H_{38}ClCrCu_2Mo_6N_4O_{32}$	$C_{40}H_{137}Cr_3Cu_4Mo_{18}N_8O_{115}$	$C_{40}H_{131}Al_3Cu_4Mo_{18}N_8O_{112}$
M	3480.15	1636.71	4707.66	4578.55
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P{-1}$	$P{-1}$	$P{-1}$	$P{-1}$
a (Å)	13.252(3)	11.244(2)	14.1896(13)	14.1701(9)
b (Å)	13.791(3)	14.566(3)	15.6768(14)	15.6300(10)
c (Å)	14.277(3)	15.330(3)	16.2269(15)	16.2426(10)
α (deg)	90.71(3)	112.21(3)	65.4780(10)	65.3900(10)
β (deg)	108.34(3)	106.65(3)	70.5120(10)	70.0860(10)
γ (deg)	90.40(3)	93.90(3)	80.5860(10)	80.5460(10)
V (Å^3)	2476.3(9)	2182.6(8)	3094.6(5)	3074.0(3)
Z	1	2	1	1
Dc (mg m^{-3})	2.334	2.490	2.526	2.473
Abs coeff (mm^{-1})	2.655	3.023	2.808	2.594
Reflns collected	19,624	21,565	15,741	15,388
Independent reflns	8698	9894	10,735	10,723
θ range (deg)	3.11–25.00	3.01–27.47	1.85–25.00	1.43–25.00
GOF on F^2	1.042	1.056	1.126	1.050
R_1[a] ($I > 2\sigma(I)$)	0.0542	0.0424	0.0782	0.0499
wR_2[b] (all data)	0.1300	0.0825	0.2648	0.1555

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

3. Results and discussion

3.1. Synthesis

The compounds **1–4** were synthesized from the conventional solution method. Investigation of the reaction of polyoxoanions, Cu^{II} cation, and 2,2′-bipyridine in acidic aqueous solution reveals that the structure of final compound is influenced by the acidic anion. As shown in Scheme 1, in the presence of single Cl^-, it coordinated to the metal center; compound **2** with 1D chain-like structure was isolated, which is isomorphic with literature reported [11]. Interestingly, when the Cl^- and NO_3^- coexist in the solution, the result of competing reaction makes these anions coordinate to the metal centers together; for the geometry and size of NO_3^- is bigger, it may produce a big steric hindrance and force the compound to take a lower dimension, consequently, compound **1** with discrete supramolecular structure was achieved. Notably, in the presence of single NO_3^- with weaker coordination ability and bigger steric hindrance than Cl^-, the NO_3^- did not become a part of compounds **3** and **4**; due to the shortage of counterion, another polyoxoanion was captured to balance the charge and stable 3D structure was obtained.

Furthermore, we also make plenty of experiments with other acidic anions holding diverse charges, geometry and size (e.g. CH_3COO^-, SO_4^{2-}, and PO_4^{3-}) to obtain different structures under the similar conditions, but we could not obtain the expected compounds except amorphous precipitate.

3.2. Structure description

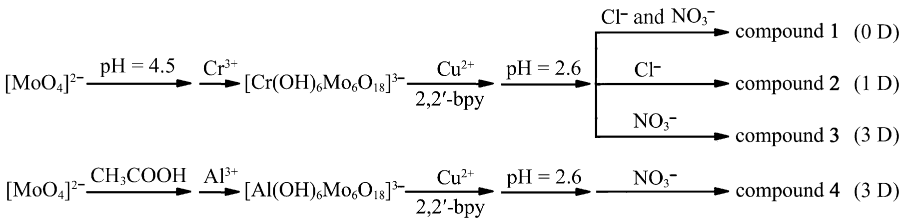
The structures of **1**, **2**, and **3** are all built up of polyoxoanion $[Cr(OH)_6Mo_6O_{18}]^{3-}$ ($CrMo_6$) and **4** is constructed by polyoxoanion $[Al(OH)_6Mo_6O_{18}]^{3-}$ ($AlMo_6$). The building blocks $CrMo_6$ and $AlMo_6$ belong to B-type Anderson structure, which consists of seven edge-sharing octahedral, six of which are $\{MoO_6\}$ octahedral, arranged hexagonally around the central $\{Cr(OH)_6\}$ and $\{Al(OH)_6\}$ octahedron. All bond lengths and angles of the polyoxoanions are within the normal ranges and conform to those literatures reported [3,11].

3.2.1. Structural analysis of *1*

Single crystal X-ray diffraction analysis reveals that the asymmetric unit of **1** contains two crystallographically independent half of $CrMo_6$ polyoxoanions, three kinds of copper coordination complexes, and 9 lattice water molecules (Fig. S1). Further studies show that **1** has a discrete structure, which is constructed from cation $\{[Cu(2,2'\text{-bpy})(H_2O)_3]_2[Cr(OH)_6Mo_6O_{18}]\}^+$ (**1a**) and anion $\{[Cu(2,2'\text{-bpy})(H_2O)Cl][Cu(2,2'\text{-bpy})(H_2O)(NO_3)][Cr(OH)_6Mo_6O_{18}]\}^-$ (**1b**). In both of the cation and anion, the $CrMo_6$ polyoxoanions act as bidentate ligands and are coordinated to two copper coordination complexes through two terminal O atoms of the polyoxoanions. In **1a**, the equatorial plane of the six-coordinated Cu atom is formed by two N atoms of 2,2′-bipyridine ligand (N_{bpy}) and two O atoms of coordinated water molecules (O_{aqua}), the axial positions are occupied by one terminal O atom of polyoxoanion (O_t) and one O_{aqua} in elongated octahedral coordination geometry. However, the Cu atom in **1b** is five-coordinated with distorted square-pyramidal coordination geometry, which is coordinated by two N_{bpy} atoms, one O_t atom, and one O_{aqua} atom at the equatorial sites, one Cl atom or one O atom of the NO_3^- at the apical position. Interestingly, the O…O hydrogen bonds between the neighboring **1a** cations form 1D cationic chains and, correspondingly, the O…Cl interactions between the neighboring **1b** anions form 1D anionic chains (Fig. 1). And then, the interchain hydrogen bonds between the protonated O atoms and terminal O atoms contribute to the formation of the 2D layer parallel to the *ac* plane (Fig. 2). Finally, extensive interlayer hydrogen bonds and π–π interactions of 2,2′-bipyridine ligands lead to the 3D supramolecular structure (Fig. S2). The typical hydrogen bond parameters are listed in Table 2.

3.2.2. Structural analysis of *2*

The asymmetric unit of **2** consists of two crystallographically independent half of $CrMo_6$ polyoxoanions, two kinds of copper coordination complexes, and 4 lattice water molecules (Fig. S3). The structure of **2** is assembled by discrete chloro-copper complexes $[Cu(2,2'\text{-bpy})(H_2O)_2Cl]^+$ (**2a**) as counterions and 1D anionic chains $\{[Cu(2,2'\text{-bpy})(H_2O)_2][Cr(OH)_6Mo_6O_{18}]\}_n^{n-}$ (**2b**) which are constructed from alternate copper coordination complexes $[Cu(2,2'\text{-bpy})(H_2O)_2]^{2+}$ and polyoxoanions $CrMo_6$ as bidentate ligands. In **2a**, the five-coordinated Cu atom coordinates to



Scheme 1. Schematic view of the syntheses of the compounds in this work.

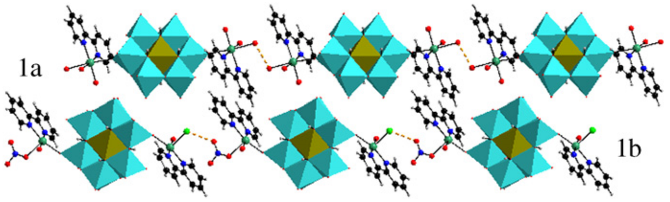


Fig. 1. Polyhedral representation of the 1D cationic (1a) and anionic (1b) chains of **1**.

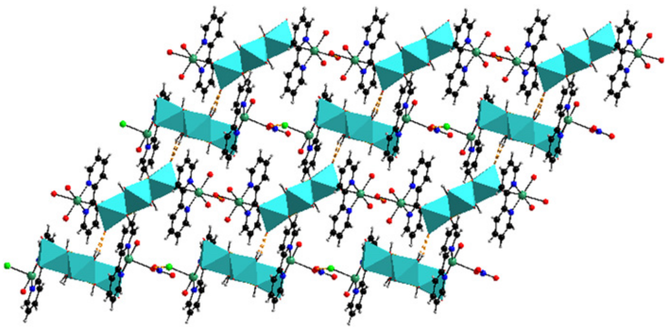


Fig. 2. Polyhedral representation of the 2D layer of **1**.

Table 2
Geometrical parameters of hydrogen bonds (Å, deg) in **1**[a]

D–H…A[b]	d(D–H)	d(H…A)	d(D…A)	□DHA
O(1)–H(21)…O(14)#1	0.850	1.936	2.712	151.30
O(2)–H(22)…O(23)#2	0.850	1.859	2.706	173.34
O(3)–H(23)…O(7W)#3	0.850	1.859	2.699	169.98
O(20)–H(24)…O(9W)	0.850	1.889	2.728	168.80
O(21)–H(25)…O(5W)#4	0.850	1.893	2.724	165.35
O(22)–H(26)…O(8W)#3	0.850	1.871	2.708	168.06
C(4)–H(4)…O(7)#5	0.930	2.519	3.222	132.56
C(7)–H(7)…O(7)#5	0.930	2.595	3.238	126.78
C(8)–H(8)…O(19)#6	0.930	2.319	3.223	163.74
C(10)–H(10)…O(18)#7	0.930	2.445	3.233	142.56
C(11)–H(11)…O(5)	0.930	2.569	3.457	159.86
C(14)–H(14)…O(17)#8	0.930	2.475	3.365	160.21
C(17)–H(17)…O(17)#8	0.930	2.544	3.420	157.41
C(20)–H(20)…O(7)#9	0.930	2.471	3.089	123.96

[a] D = donor, A = acceptor.

[b] Symmetry transformations used to generate equivalent atoms: #1 –*x*+1, –*y*+2, –*z*; #2 *x*–1, *y*, *z*; #3 *x*, *y*+1, *z*; #4 *x*+1, *y*+1, *z*; #5 –*x*+1, –*y*+1, –*z*+1; #6 –*x*+2, –*y*+1, –*z*+1; #7 *x*, *y*, *z*+1; #8 –*x*+2, –*y*+1, –*z*; #9 *x*+1, *y*, *z*.

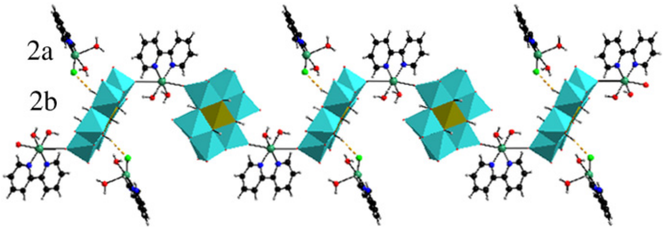


Fig. 3. Polyhedral representation of the 1D spiral-type chain of **2**.

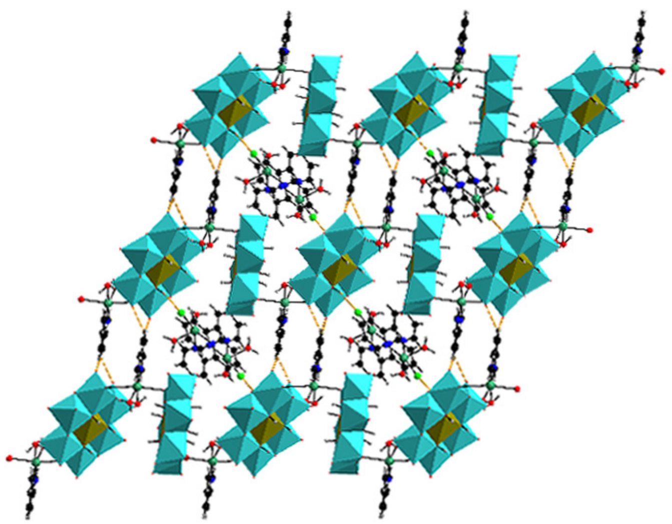


Fig. 4. Polyhedral representation of the 2D layer of **2**.

two N_{bpy} atoms, one Cl atom, and one O_{aqua} atom at the equatorial sites, one O_{aqua} atom at the apical position with distorted square-pyramidal coordination geometry. Whereas the Cu atom in **2b** is six-coordinated with elongated octahedral coordination geometry, the basal plane is composed of two N_{bpy} atoms and two O_{aqua} atoms, the apical sites are occupied by two O_t atoms. It is noteworthy that the O–H…Cl hydrogen bonds between the **2a** and **2b** lead to the 1D spiral-type chain (Fig. 3). Thereafter, the C–H…O hydrogen bonds between these chains contribute to the formation of the 2D layer parallel to the *bc* plane (Fig. 4). Finally, the interlayer O–H…O hydrogen bond interactions form the 3D structure (Fig. S4). It is believed that the extensive π–π interactions of 2,2′-bipyridine ligands play an important role in stabilizing the 3D structure of **2** (Fig. S5).

*3.2.3. Structural analysis of **3** and **4***

The asymmetric unit of **3** is made up of three crystallographically independent half of $CrMo_6$ polyoxoanions, two kinds of copper coordination complexes, and 18.5 lattice water molecules (Fig. S6). Further research shows that the structure of **3** is a unique 3D open framework constructed from $CrMo_6$ polyoxoanions and copper coordination complexes (Fig. S7). There are two crystallographically independent Cu atoms, both of which are six-coordinated in elongated octahedral coordination geometry. Cu1 atom is defined by two N_{bpy} atoms and two O_{aqua} atoms at the equatorial sites, two O_t atoms at the axial positions. However, Cu2 atom is coordinated by two N_{bpy} atoms, one O_t atom, and one O_{aqua} atom at the equatorial sites, two O_t atoms at the apical positions. In the structure, three crystallographically independent $CrMo_6$ polyoxoanions ($Cr1Mo_6$, $Cr2Mo_6$, and $Cr3Mo_6$) present, in which, $Cr1Mo_6$ and $Cr3Mo_6$ act as quadridentate ligands, but $Cr2Mo_6$ acts as bidentate ligand to coordinate with the copper coordination complexes through terminal O atoms of the polyoxoanions. As shown in Fig. 5, the $Cr1Mo_6$ and $Cr3Mo_6$ polyoxoanions are linked by Cu1 coordination complexes to form 2D layers, and then these 2D sheets are further pillared by the $Cr2Mo_6$ polyoxoanions which are linked by Cu2 coordination complexes to form the 3D open framework with lattice water molecules residing in the channels. It is noted that the extensive π–π interactions of 2,2′-bipyridine ligands and hydrogen bonds between the framework and lattice waters stabilize the 3D structure (Fig. S8).

Single crystal X-ray diffraction analysis reveals that **4** is isomorphic to **3** with differences just in bond lengths, bond angles, and the number of lattice waters. It is noteworthy that the rigid 2,2′-bipyridine ligand is a chelating ligand, which is inclined to chelate with transition metal centers and limits the possibility of propagating high dimensional structures. Consequently, compounds **3** and **4** represent the first example of 3D organic–inorganic hybrid compounds in the TMs/2,2′-bpy/POMs system.

The bond-valence calculations [15] suggest that all Cr and Al atoms are in the +3 oxidation state, all Cu atoms are in the +2 oxidation state and all Mo atoms are in the +6 oxidation state, and the bond-valence calculations for all the O atoms indicate that all of the μ_3-bridging O atoms around the Cr^{3+} and Al^{3+} are protonated in **1**–**4**. The overall charge of all atoms in the formula obtained form the single-crystal structure determination are balanced for **1** and **2**, but for **3** and **4**, the overall charge of all atoms is −1. The difference Fourier map reveals that no Na ion presents, which is further confirmed by elemental analyses. For the acidic synthetic condition of **3** and **4**, we presume that there is a protonated lattice water molecule to compensate for charge balance.

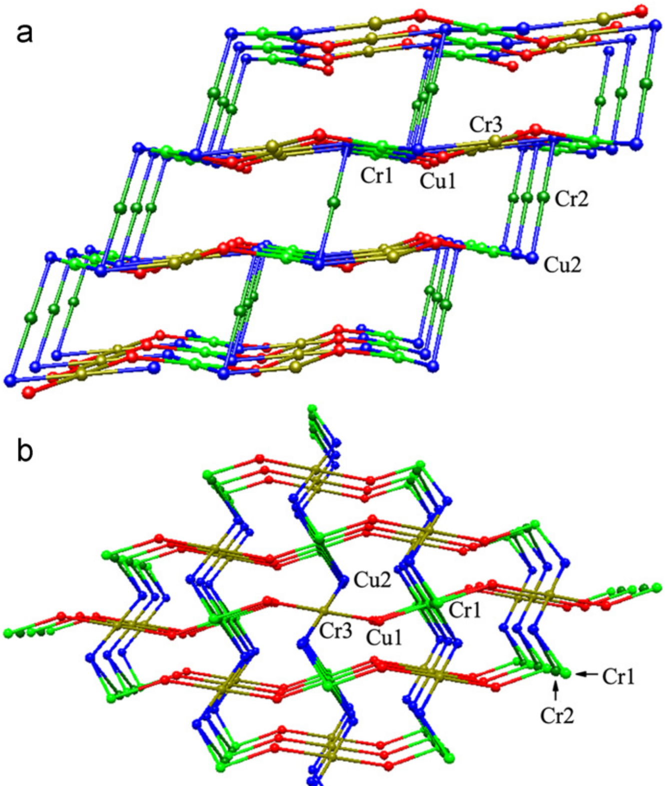


Fig. 5. Schematic representation of the 3D structure of **3** parallel to the *ab* (a) and *bc* (b) plane.

3.3. IR spectroscopy

The IR spectra of the compounds are alike (Fig. S9). In the low-wavenumber regions of the IR spectra, they display similar characteristic patterns of the B-type Anderson polyoxoanions [3,11], with bands between 400 and 600 cm^{-1} are attributed to the Mo–O_c stretching vibration, between 640 and 800 cm^{-1} belongs to the Mo–O_b stretching modes, and ranging from 890 to 950 cm^{-1} are assigned to the Mo–O_t characteristic vibration. The feature peaks ranging from 1000 to 1600 cm^{-1} are associated with the 2,2′-bipyridine ligands, which are of low intensity compared with those of the polyoxoanions. It is noted that the peak at 1384 cm^{-1} of compound **1** corresponds to the NO_3^- characteristic vibration.

3.4. Thermogravimetric analysis

The thermal gravimetric (TG) curve recorded at 20–600 °C reveals that there are four continuous weight loss stages for **1** (Fig. S10). The TG curve gives a total weight loss of 37.13% in the range of 20–500 °C, which agrees with the calculated value of 36.05%, corresponding to the loss of all water molecules, 2,2′-bipyridine ligands, and the decomposition of all OH groups and NO_3^- anion.

The compound **2** is stable up to 90 °C, because of the comparative strong hydrogen bond interactions among the water molecules, and then it exhibits two weight loss steps (Fig. S11). The overall weight loss (32.51%) is in agreement with the calculated value (31.19%) below 460 °C, considering the loss of all water molecules, 2,2′-bipyridine ligands, and the decomposition of all OH groups.

The TG curve of **3** exhibits two major weight loss steps (Fig. S12). The whole weight loss (33.45%) agrees well with the calculated value (33.36%). The first weight loss below 240 °C ascribes to the loss of all water molecules and the decomposition of all OH groups (weight loss: calc., 20.09%; found, 19.54%). The following weight loss in the range of 320–475 °C arises from the detachment of all 2,2′-bipyridine ligands (weight loss: calc., 13.27%; found, 13.91%). The TG curve of **4** is similar to that of **3** (Fig. S13).

4. Conclusions

In this paper, four organic–inorganic hybrid compounds based on Anderson-type polyoxoanions have been successfully synthesized by control of the acidic anions in the reaction solution. Compound **1** is a supramolecular structure which is constructed from cation $\{[Cu(2,2'\text{-}bpy)(H_2O)_3]_2[Cr(OH)_6Mo_6\text{-}O_{18}]\}^+$ and anion $\{[Cu(2,2'\text{-}bpy)(H_2O)Cl][Cu(2,2'\text{-}bpy)(H_2O)\text{-}(NO_3)][Cr(OH)_6Mo_6O_{18}]\}^-$. Compounds **2** is composed of 1D anionic chains $\{[Cu(2,2'\text{-}bpy)(H_2O)_2][Cr(OH)_6Mo_6O_{18}]\}_n^{n-}$ and discrete $[Cu(2,2'\text{-}bpy)(H_2O)_2Cl]^+$ as counterions. Compound **3** and **4** are isomorphic and show unique 3D open frameworks with lattice water molecules residing in the channels. From the three kinds of crystal structures obtained, it is clear that the intrinsic character of the acidic anions have a decisive influence on both of the composition and the dimensionality of the final compounds. It is hoped that more acid-anion-controlled assembly of hybrid compounds based on diverse polyoxoanions building blocks and more acidic anions will be prepared soon for further investigation.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2008.09.019.

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