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Hydrothermal synthesis and characterization of a novel supramolecular hybrid based on Keggin and Cu(I) complex

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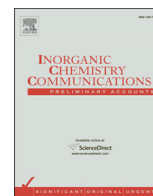
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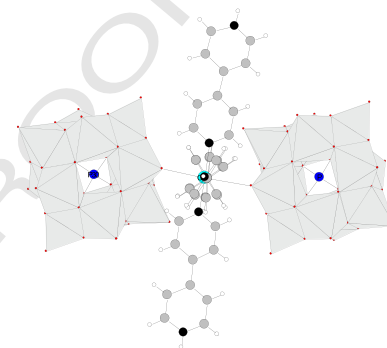
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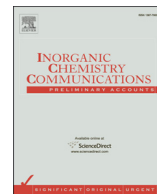
Mehtap Emirdag-Eanes*, Banu Önen*Inorganic Chemistry Communications*
xxx (2013) xxx–xxxHydrothermal synthesis and characterization
of a novel supramolecular hybrid based on
Keggin and Cu(I) complexStructure of $[\text{Cu}(4,4'\text{-bipyH})_3(4,4'\text{-bipy})][\text{HPW}_{12}\text{O}_{40}]_2 \cdot 12\text{-H}_2\text{O}$ consists of two Keggin polyoxoanion connected with Cu complex fragment forming a big molecule that extends in 3D via hydrogen bonding.



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Highlights

Hydrothermal synthesis and characterization of a novel supramolecular hybrid based on Keggin and Cu(I) complex*Inorganic Chemistry Communications xxx (2013) xxx – xxx*

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- $[\text{Cu}(\text{4,4'-bipyH})_3(\text{4,4bipy})][\text{HPW}_{12}\text{O}_{40}]_2 \cdot 12\text{H}_2\text{O}$ were synthesized using hydrothermal method.
- The effect of pH of reaction media is studied.
- Purple crystals were analysed using IR, UV and X-ray diffraction.
- Molecule extends in 3D through hydrogen bonding.

Q6 Supplementary material 1.

Q7 Supplementary material 2.

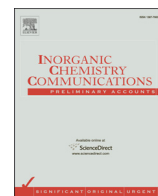
Q8 Supplementary material 3.

Table S2 Selected bond distances (Å) for [Cu(4,4'-bipyH)₃(4,4-bipy)][HPW₁₂O₄₀]₂·12H₂O.



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Hydrothermal synthesis and characterization of a novel supramolecular hybrid based on Keggin and Cu(I) complex

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ABSTRACT

A novel inorganic–organic hybrid molecule, $[\text{Cu}(4,4'\text{-bipyH})_3(4,4\text{bipy})][\text{HPW}_{12}\text{O}_{40}]_2 \cdot 12\text{H}_2\text{O}$ (**1**), has been hydrothermally synthesized and characterized by IR spectra, TG and single crystal X-ray diffraction analyses. Structural analysis reveals that the novel compound **1** composed of two Keggin polyoxoanion connected with Cu complex fragment forming a big molecule that extends in 3D via hydrogen bonding.

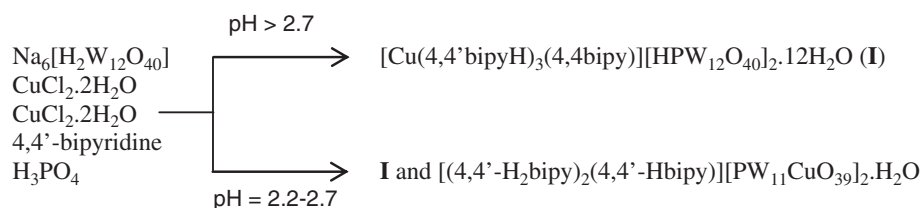
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Polyoxometallates (POMs) [1] have attracted great interest due to their structural diversity, electronic versatility, which enables them to have great potential applications in catalysis, magnetism, electrochemistry and photochemistry [2–6], and outstanding ability of constructing inorganic–organic hybrid materials. Recently the number of strategies designing inorganic–organic hybrid materials based on POMs has been developed [7]. One of the approaches to connect POM units with organic ligands is to use secondary transition metal acting as inorganic bridging groups under hydrothermal conditions. Inorganic–organic hybrid materials receive great attention because of the potential applications such as catalysis, ion exchange and medicine [8–10]. Design and synthesis of the novel inorganic–organic solid materials based on POMs and transition metal complexes of various organic groups provide combining the future and properties of both subunits (organic ligands or transition metal complexes) and POMs to increase the functionality of the hybrid materials. Some successful examples of Keggin polyoxometallates with copper complexes include $(\text{C}_{20}\text{H}_{16}\text{CuN}_4)_5(\text{PW}_{12}\text{O}_{40}) \cdot 2(\text{H}_2\text{O})$ [11], $(\text{C}_{20}\text{H}_{16}\text{CuN}_4)_3(\text{PW}_{12}\text{O}_{40})$ [12], $(\text{C}_{24}\text{H}_{16}\text{CuN}_4)_3(\text{PW}_{12}\text{O}_{40})$ [13], $(\text{PW}_{12}\text{O}_{40})\text{nn}(\text{C}_{20}\text{H}_{16}\text{CuN}_4)_3$ $4\text{n}(\text{C}_{20}\text{H}_{14}\text{Cu}_2\text{N}_4\text{O}_2)_3 \cdot 2\text{n}(\text{H}_2\text{O})$ [14], $(\text{C}_{24}\text{H}_{17}\text{CuN}_4)(\text{PW}_{12}\text{O}_{40})(\text{C}_{12}\text{H}_8\text{N}_2)$ [15]. Additionally, a number of the Keggin structures with Si atom in the middle have been reported [16–20]. However Keggin with P atom in the middle with copper complexes are fewer. As a part of the continuing efforts in the construction of inorganic–organic hybrid materials herein we report a novel copper tungstate with 4,4'-bipyridine ligand, $[\text{Cu}(4,4'\text{-bipyH})_3(4,4\text{bipy})][\text{HPW}_{12}\text{O}_{40}]_2 \cdot 12\text{H}_2\text{O}$.

All chemicals were obtained commercially and used without further purification. Crystals of $[\text{Cu}(4,4'\text{-bipyH})_3(4,4\text{bipy})][\text{HPW}_{12}\text{O}_{40}]_2 \cdot 12\text{H}_2\text{O}$ were synthesized with a mixture of $\text{Na}_6[\text{H}_2\text{W}_{12}\text{O}_{40}]$ (0.1 mmol, Alfa Easer 99%), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.5 mmol, Merck $\geq 99\%$), 4,4'-bipyridine (0.5 mmol, Alfa Aesar 98%) and H_3PO_4 (0.3 mmol, Sigma–Aldrich, 85%). The mixture was stirred for 1 h then transferred to a Teflon-lined autoclave (23 mL) and heated at 170 °C for 3 days. After cooling to room temperature, the mixture of greenish powder, clear and purple crystals was filtered off, washed with distilled water and acetone. Hydrothermal reaction for the title compound yielded a purple plate of $[\text{Cu}(4,4'\text{-Hbipy})_4][\text{HPW}_{12}\text{O}_{40}]_2 \cdot 12\text{H}_2\text{O}$ as a minor product. Other products were a mix of greenish unidentified powder and clear crystals of novel $[\text{Cu}(4,4'\text{-bpyH})_2(4,4'\text{-bpyH})][\text{PCuW}_{11}\text{O}_{39}] \cdot \text{H}_2\text{O}$ 1D Keggin chain that will be discussed with other similar structures in another paper. Synthesis of the title compound was done at pH 2.8. It is known that pH plays an important role to synthesize different type of POM compounds [21]. Synthesis was tried in different pH values and it is observed that even small changes of pH affect the type of the crystals obtained. The pH studies were at 20 °C, pH values between 2.2 and 2.7 only resulted in clear crystals however after pH 2.8 the purple crystals started to be formed. The formation of different crystals is shown in Scheme 1.

A purple plate single crystal with dimensions $0.15 \times 0.14 \times 0.05 \text{ mm}^3$ of the compound (**1**) was carefully selected and mounted on a glass fiber. The data was collected on Bruker APEK-II CCD diffractometer at 100 K using a graphite-monochromate Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). The structure of (**1**) was solved by direct method using SHELXL97 software [22,23] and refined by using least square methods. All of the heavy atoms were refined anisotropically. The positions of the hydrogen atoms attached to carbon atoms were fixed at their ideal positions with Ueq set at 1.2Ueq. Hydrogens attached to oxygen atoms of water were not located. Crystallographic data for the structure reported has been

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E-mail address: mehtapemirdag@iyte.edu.tr (M. Emirdag-Eanes).



Scheme 1. Schematic illustration of the synthesis route of title compound.

deposited with Cambridge Crystallographic Data Center, CCDC No 934771. During the structure solution, the program suggested the space group *Pbcn*, and the structure was solved based on this space group. However the R value was slightly high. When the systematic absences were checked, there was an ambiguity on the reflection *h0l*. Based on the systematic absences on *h0l*, *l* could be absent or not. The structure was analyzed for both cases. When *l* was absent, the suggested space group was *Pnca* (*Pbcn*) of which we initially tried to solve. When *l* was not absent there were two choices of the space group, *Pnma* and *Pn2₁a*. First *Pnma* was chosen and applied to structure but the result was not very successful. Prior to applying noncentrosymmetric *Pn2₁a*, space group was transformed to standard setting of *Pna2₁* using transformation matrix. Finally *Pna2₁* was applied as the space group. As a result the structure solution was done successfully with a low R value. Crystallographic information is given in Table 1.

The IR spectra were obtained on a Perkin-Elmer Spectrum 100 FT-IR spectrometer with KBr pellets in the 400–4000 cm^{-1} region. Keggin type of POMs can be identified with two regions in the IR spectrum (Fig. 1a). The first region over 1200 cm^{-1} is indicative of 4,4'-bipyridine ligand. Second region below 1200 cm^{-1} would have the characteristic bands for Keggin structure. The P–O vibrations are observed at 1081 cm^{-1} . The bands of 950–980 cm^{-1} are assigned to $\text{W}=\text{O}_t$ stretching vibrations. Bands between 750 and 800 cm^{-1} are attributed to $\text{W}-\text{O}_b-\text{W}$ stretching and bands between 500 and 700 cm^{-1} corresponds to $\text{W}-\text{O}_c-\text{W}$ vibrations.

To gain knowledge relating to the thermal stability of the synthesized organo-POM compound, the thermal gravimetric analyses (TGA) were

carried out on the 2962 SDT simultaneous DSC-TGA instruments in flowing N_2 with a heating rate of 20 $^\circ\text{C}/\text{min}$. TG curves (Fig. 1b) of the title compound undergo two step weight loss. First weight loss of 3245 % (calcd. 3.2%) between 100 and 340 $^\circ\text{C}$ was assigned to the removal of the lattice water molecules. The second continuous weight loss of approximately 13% (calcd. 13%), in the temperature range 340–550 $^\circ\text{C}$, corresponds to the release of four bipy molecules coordinated with Cu. The weight loss progress is well consistent with similar compounds in the literature [24].

The single crystal X-ray structural analysis shows that the crystals of the title compound contain two Keggin $[\text{HPW}_{12}\text{O}_{40}]^{2-}$ clusters, $[\text{Cu}(4,4'\text{-bipyH})_3(4,4\text{-bipy})]^{4+}$ complex and water molecules. Keggin polyoxotungstate structure composed of 12 tungsten atoms surrounded by three different types of oxygens, terminal, bridging and central. All

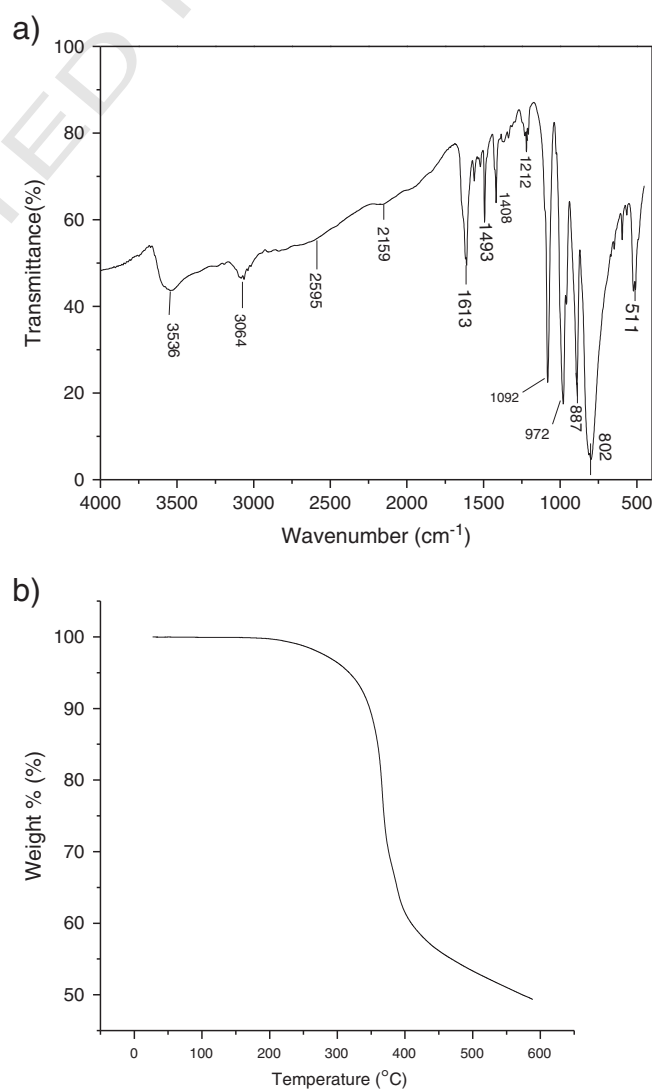


Fig. 1.

Table 1

Crystallographic data for $[\text{Cu}(4,4'\text{-bipyH})_3(4,4\text{-bipy})][\text{HPW}_{12}\text{O}_{40}]_2 \cdot 12\text{H}_2\text{O}$.

t1.3	Formula	$\text{PW}_{24}\text{O}_{92}\text{Cu}_4\text{N}_8\text{H}_{32}$
t1.4	Formula weight	6634.62
t1.5	Space group	<i>Pna2</i> (1)
t1.6	a, Å	20.185(5)
t1.7	b, Å	25.633(5)
t1.8	c, Å	20.199(5)
t1.9	α , $^\circ$	90
t1.10	β , $^\circ$	90
t1.11	γ , $^\circ$	90
t1.12	V, Å ³	10,451(4)
t1.13	Z	4
t1.14	D _{calc} , Mg/m ³	4.217
t1.15	Parameters	805
t1.16	μ , mm ⁻¹	26.64
t1.17	θ range, $^\circ$	2.39–29.2
t1.18	Reflections	
	Collected	93,382
	Independent	26,437
t1.21	Observed [$I \geq 2\sigma(I)$]	22,796
	R (int)	0.045
t1.23	Final R (obs. data) ^a	
	R ₁	0.0323
	wR ₂	0.0722
t1.26	Final R (all data)	
	R ₁	0.0437
	wR ₂	0.0764
t1.29	Goodness of fit on F ²	1.026
t1.30	Largest diff. peak, e/Å ³	3.074
t1.31	Largest diff. hole, e/Å ³	–2.846

^a $R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$; $wR_2 = \left\{ \frac{\sum w(F_o - F_c)^2}{\sum w F_o^2} \right\}^{1/2}$.

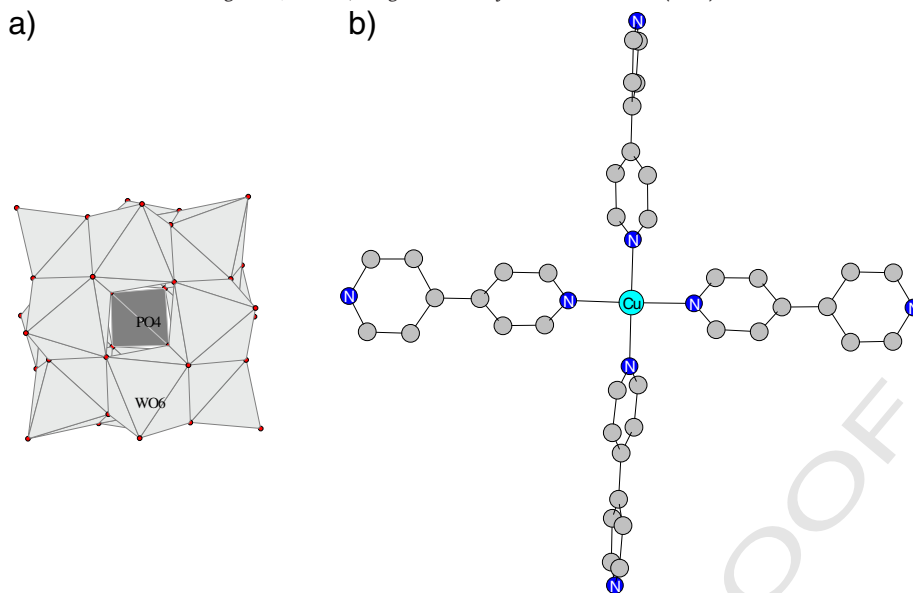


Fig. 2.

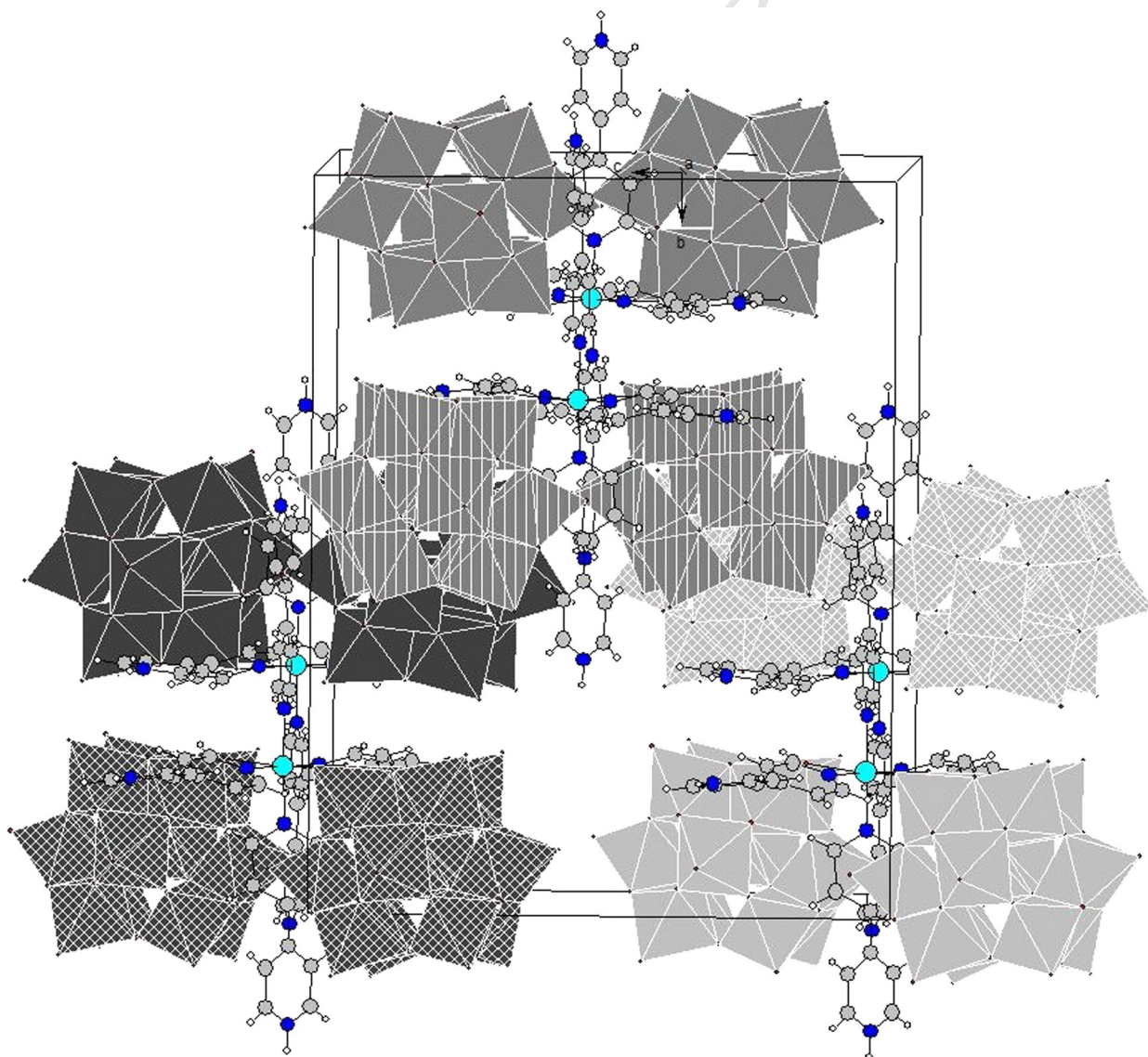


Fig. 3.

Q3

Q4

126 the tungsten atoms have one short bond to terminal oxygen with the
 127 average distance of 1.700(14) Å, four bonds to bridging oxygens ranging
 128 from 1.867(9) to 1.951(10) Å and one long bond to central oxygens with
 129 the average distance of 2.43(19) Å forming an octahedra. Keggin structure
 130 consists of WO_6 octahedra units linked by both corner and edge sharing
 131 interactions. Three WO_6 octahedras sharing edges form a W_3O_{13} units
 132 four of which encapsulating PO_4 tetrahedra shares corners to form Keggin
 133 structure (Fig. 2a). The central P atom in the compound is tetrahedrally
 134 coordinated to central oxygen atoms with the average bond distance of

135 1.528(9) Å. Connections between two Keggin cages are made through
 136 transition metal complex fragment, $[Cu(4,4'bipyH)_3(4,4bipy)]^{4+}$, to form
 137 a large molecule of two keggin cage and Cu complex. The Cu^{1+} ion
 138 forms a complex with four 4,4'bipyridine ligands connected through
 139 nitrogen atoms (Fig. 2). Three of the organic ligands, 4,4'bipyridine, in
 140 the complex fragment are monoprotonated, meaning they adopt the
 141 mono-dentate mode which terminates the extensibility of the structure.
 142 The Cu–N bond distances ranges from 2.002(8) to 2.033(9) Å. Each
 143 $[Cu(4,4'bipyH)_3(4,4bipy)]^{4+}$ fragments is located between two

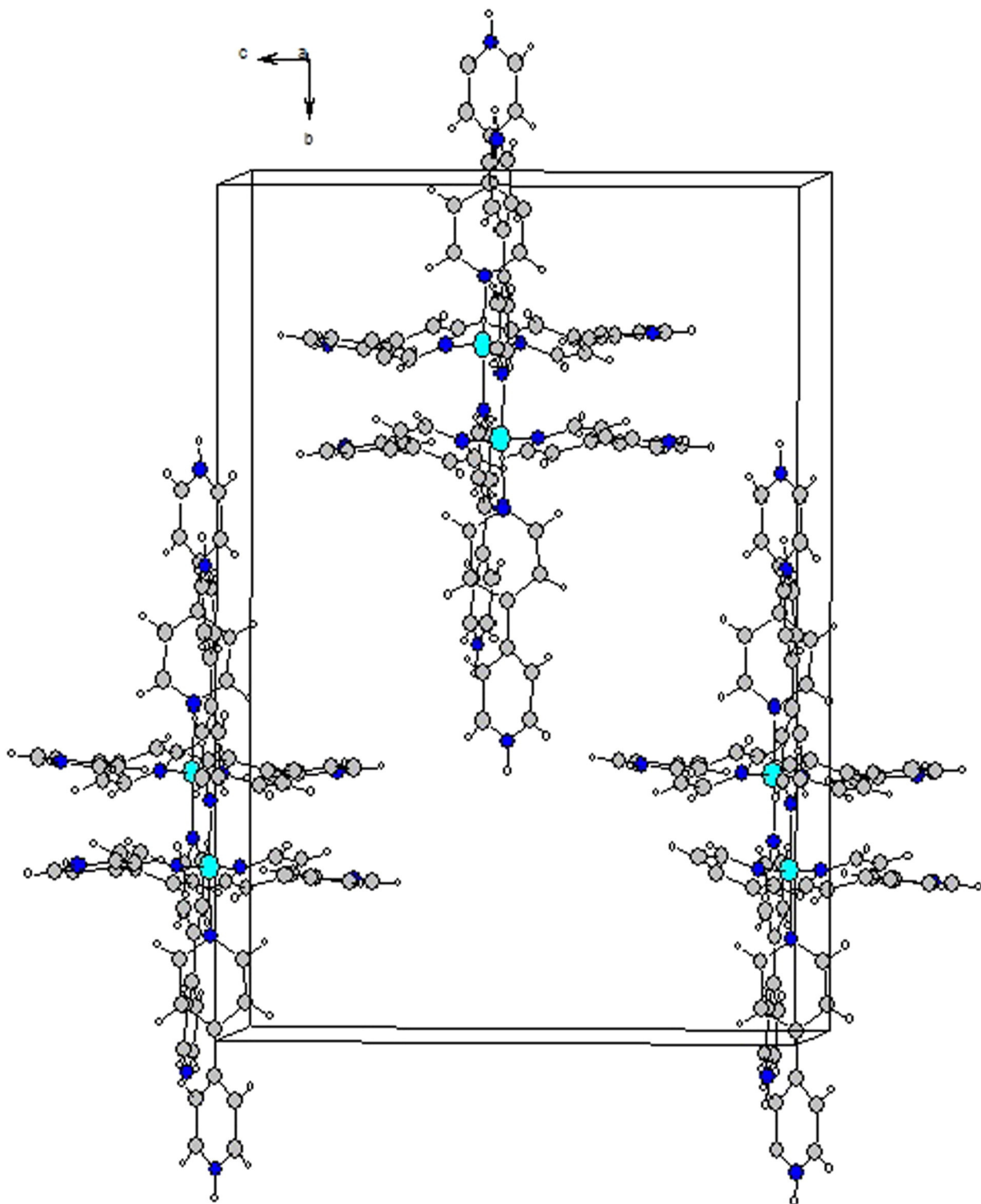


Fig. 4.

polyoxotungstate clusters and the connection is made through Cu–O bonds with the interactions ranging from 2.409(9) to 2.477(8) Å. Four of these large molecules form the unit cell of the title compound (Fig. 3). There is no connection between molecules except H bonding. Extension of the structure in 3D is constituted via hydrogen bonds. In Fig. 3, all the discrete molecules can be seen in different colors and styles. These molecules are located in the cell according to space group of Pna2₁. Fig. 4 is given to show the Cu complexes in the cell to have a better understanding of arrangement of the molecules and the structure. Selected bond distances are given in Table S1.

The valence bond sum calculations [25] confirm that all W and Cu bonds are +6 and +1 respectively. Reduction of the copper atom (Cu^{II} → Cu^I) may be due to the addition of 4,4'-bipyridine ligands [26,27]. For the charge balance and the coordination environments three of the uncoordinated nitrogen atoms (N10, N35 and N36) in the organic ligand are protonated, which is similar to the reported cases.[21,28].

There is an extensive hydrogen bonding among the lattice water molecules and oxygen atoms from the POMs, some of the representative hydrogen bonds are O750...O31 2.828 Å, O751...O35 2.921 Å, and O750...O17 2.841 Å. The water molecules of the title compound also have interactions with the hydrogen atoms on the 4,4'-bipyridine fragments via C–H...O or N–H...O hydrogen bonding. These hydrogen bonding interactions make the Keggin polyoxoanions and the complex cation, [Cu(4,4'-bipyH)₃(4,4'bipy)]⁴⁺, forming a 3D supramolecular network. The O–H...O hydrogen bonds also exist between two Keggin molecule in the title compound, as well. The O49 from one POM is connected to O22 from the other POM through hydrogen bonds with distance of 2.784 Å. The same type of interaction is also seen between O56 and O19 with distance of 2.773 Å. Based on these observations in the structure, position of the H atom in the [HPW₁₂O₄₀]⁴⁻ fragment can be assigned to O56 in one of the Keggin and O49 in the other Keggin cage.

In summary, a novel inorganic–organic hybrid material based on Keggin POMs, [Cu(4,4'-bipyH)₃(4,4'bipy)][HPW₁₂O₄₀]₂·12H₂O, has been synthesized and structurally characterized. The pH value of the reaction system plays an important role in the structure type and the yield of obtained product. While [(4,4'-H₂bipy)₂(4,4'-Hbipy)][PW₁₁CuO₃₉]₂·H₂O is the only product in lower pH, title compound was obtained at higher pH values.

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Appendix A. Supplementary material

CCDC 934771 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version. Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.inoche.2013.10.014>.

Appendix A. Supplementary material

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.inoche.2013.10.014>.

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