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An ionic 2D inorganic–organic hybrid of tris[((1H-tetrazol-5-yl)methyl) morpholine] dodecatungstophosphate(V) pentahydrate: Synthesis X-ray crystal structure and spectroscopic characterizations

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Abstract

A unique ionic hybrid material $[C_6H_{12}N_5O]_3[(PO_4)W_{12}O_{36}]\cdot 5H_2O$ has been synthesized from the reaction of ((1*H*-tetrazole-5-yl)methyl)morpholine and α-$H_3[(PO_4)W_{12}O_{36}]\cdot 21H_2O$. It has successfully been characterized by elemental analysis, IR and ^1H NMR spectroscopies, TGA and single-crystal X-ray diffraction method. The title compound is constructed from the three $[C_6H_{12}N_5O]^+$ cations and α-Keggin $[(PO_4)W_{12}O_{36}]^{3-}$ polyoxoanion. The most remarkable structural feature of this hybrid can be described as two-dimensional inorganic infinite plane-like ($2D/\infty[(PO_4)W_{12}O_{36}]^{3-}$) which forming *via* van der Waals interactions along the *x* axis.
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The contemporary interest in the chemistry of polyoxometalates (POMs) [1] not only stems from their applications in fields such as medicine [2], material science [3], and catalysis (homogeneous and heterogeneous) [4] but also stems from their intriguing variety of architectures and topologies. Thus, many numbers of heteropoly anions have been reported and some of them, especially Keggin type, were structurally and spectrally characterized [5]. The incorporation of organic moieties into inorganic oxide clusters provides a powerful method for structural modification and synthesis of novel inorganic–organic hybrid materials. Effective strategies have been well developed through the choice and design of inorganic and organic building blocks, which possess hydrogen bonding donors and receptors, to give birth to a great variety of hydrogen-bonded frameworks with fascinating structures [6]. In particular, integration of organic ligands and POMs into hybrid compounds represents a fascinating subclass of hybrid solids owing to their distinctive natures and synergetic interactions between organic and inorganic compositions.

However, although much work on the hybrid compounds built by organoamine [7], organocarboxylate [8], and organophosphate [9] ligands and POMs has been reported, no hybrid compounds based on morpholine or tetrazole

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derivations and POMs have been found. Herein, as part of our longstanding efforts in the syntheses of inorganic–organic hybrid materials based upon POMs [5,10], we isolated a novel ionic hybrid based on dodecatungstophosphate anion and ((1*H*-tetrazole-5-yl)methyl)morpholine (**1**) as biologically active organic compound for the presence of tetrazole ring in molecular structure [11].

1. Experimental

Chemicals were commercially obtained and used without further purification. A Buck-500 scientific spectrometer was employed to record IR spectrum of **1**. ^{1}H NMR spectrum was recorded on a Bruker BRX-100 AVANCE spectrometer. The Elemental analysis was performed on a Thermo Finnigan Flash-1112EA microanalyzer. ((1*H*-tetrazole-5-yl)methyl)morpholine was recently prepared by our research group [12]. The W and P contents were measured by ICP method.

1.1. X-ray crystallography

Experimental parameters pertaining to single crystal X-ray analysis are given in Table 1. Data were collected on a colorless block crystal mounted on a Smart-Apex CCD (Bruker-AXS) diffractometer equipped with graphite monochromated Mo Kα radiation (λ = 0.71069 Å). The final unit cell was determined from 31381 reflections in the range of $1.50^\circ < \theta < 25.64^\circ$. The diffraction data were collected at 293 K with the ω-scan technique. The structure was solved by direct methods and refined by full-matrix least squares based on F^2 with weight $w = 1/[\sigma^2(F_o^2) + (0.0506P)^2 + 0.0000P]$ where $P = (F_o^2 + 2F_c^2)/3$ using the SHELXTL-97 software [13]. The nonhydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrical calculated positions and thereafter allowed to ride on their parent atoms.

X-ray crystallographic files in CIF format for the structure determination of title compound has been deposited with the Cambridge Crystallographic Data Center. The CCDC reference number is 691679. Copy of this information may be obtained, free of charge, from The Director, CCDC, 12 Union Road, Cambridge, CB2 IEZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

1.2. Synthesis of $C_{18}H_{45}N_{15}O_{49}PW_{12}$

A solution of the ((1*H*-tetrazole-5-yl)methyl)morpholine (0.14 g, 0.82 mmol) in 30 mL of water was added with vigorous stirring, to a solution of α-$H_3[(PO_4)W_{12}O_{36}]\cdot 21H_2O$ (0.50 g, 0.27 mmol) in 25 mL of water for synthesis of title compound. The colorless precipitate was formed after five hours. The solid was filtered, washed with DMF and dried at RT. The precipitate was redissolved in acetonitrile and the solution was cooled to ambient temperature, colorless block crystals were obtained, filtered, washed several times with distilled water, and dried in air (yield 30% based on W) and characterized by spectroscopy and X-ray crystallography [13]. ^{1}H NMR in D_2O: δ 2.65 (t, 4H, $(CH_2)_2N$), 3.80 (t, 4H, $(CH_2)_2O$), 4.15 (s, 2H, CH_2-$(N(CH_2)_2)$). Anal. calcd. for $C_{18}H_{45}N_{15}O_{49}PW_{12}$: C, 6.19; H, 1.30; N, 6.02; P, 0.90; W, 63.20. Found: C, 6.41; H, 1.41; N, 5.88; P, 0.85; W, 63.00.

2. Results and discussion

The compounds crystallize in the monoclinic crystal system space group $P2_1/n$. To the best of our knowledge, this material is the first crystalline hybrid structures with such polyoxoanion and organic moieties. The single crystal X-ray structure analysis reveals that title compound consists of one discrete anion $[(P)W_{12}O_{40}]^{3-}$, three $[C_6H_{12}N_5O]^+$ monocationic moieties and five water molecules which linked together *via* hydrogen bonding interactions (see Fig. 1). The anion in title compound is the well-known α-Keggin cluster consisting of four groups of tri-metallic W_3O_{10} units. Each (WO_6) octahedron in a tri-metallic unit shares edges with neighbours, and the W_3O_{10} units link together via corner sharing (WO_6) octahedral to form a cluster cage with a (PO_4) tetrahedron located in the center. There are four kinds of oxygen atoms in the heteropolyanion, α-$[PW_{12}O_{40}]^{3-}$, four O_a atoms which connect with a heteroatom (e.g. P) and three W atoms, twelve oxygen-bridge atoms O_b (corner-sharing oxygen-bridge between different W_3O_{13} sets), twelve oxygen-bridge atoms O_c (edge-sharing oxygen-bridge within W_3O_{13} sets) and twelve terminal oxygen atoms O_t [1]. The P–O bond lengths in the polyoxoanion are single (1.514(9)–1.547(1) Å).

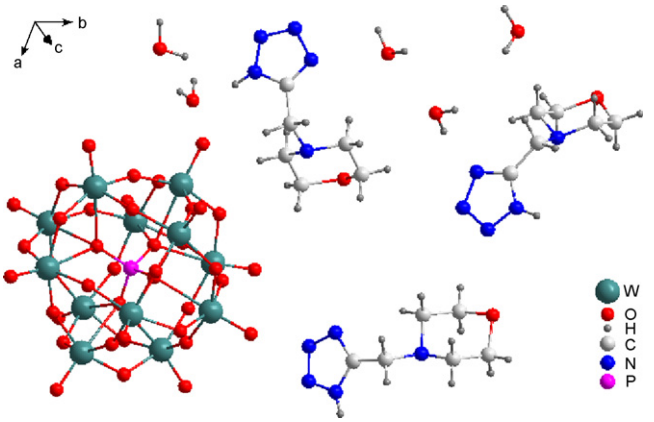

Fig. 1. Ball-and-stick molecular structure representation of $[C_6H_{12}N_5O]_3[(PO_4)W_{12}O_{36}]\cdot 5H_2O$.

The P atom has a slightly distorted tetrahedral configuration and the O–P–O angles are in the range of 108.76(6)–111.06(2)°. In the α-Keggin $[PW_{12}O_{40}]^{3-}$ polyoxoanion all the W centers exhibit a highly distorted octahedral coordination geometry $\{WO_6\}$, with the W–O bond distances, internal cis-O–W–O and trans-O–W–O octahedral angles being found in the 1.667(8)–2.473(9) Å, 71.7(1)–105.2(4)° and 152.8(9)–173.0(7)° ranges, respectively. The W-O_t, W-O_a, W-$O_{b/c}$ bond lengths in the WO_6 octahedral fall in the ranges 1.667(8)–1.718(8), 2.383(3)–2.473(9) and 1.883(0)–1.997(6) Å, respectively, and all the values are well within the normal ranges [14]. In the organic moieties, 1*H*-tetrazole ring and the methyl carbon atom lie in a same plane and the morpholine ring is in a chair-type configuration. Organic moieties are symmetrically independent with some differences in the bond lengths and angles. For example, the N(1)–C(2), N(6)–C(8) and N(11)–C(14) bond lengths are 1.495(5) Å, 1.505(5) Å and 1.445(5) Å, respectively and C(1)–C(2)–N(1), C(7)–C(8)–N(6) and C(13)–C(14)–N(11) bond angles are 114.94°, 114.16° and 110.63°, respectively.

$[C_6H_{12}N_5O]^+$ as charge-compensating cations and space-filling structural subunits, are connected to the one-side of $[PW_{12}O_{40}]^{3-}$ clusters by a multiple hydrogen interactions. Some distances of the hydrogen bonding and van der Waals interactions between organic moieties cations, water molecules and oxygen sites of $[PW_{12}O_{40}]^{3-}$ anions are: C(8)–H(8B)···O(19) 2.345 Å, C(18)–H(18A)···O(20) 2.470 Å, C(2)–H(2B)···O(14) 2.511 Å, C(2)–H(2B)···O(9) 2.598 Å, C(9)–H(9A)···O(13) 2.636 Å, C(17)–H(21B)···O(11) 2.596 Å, C(14)–H(14B)···O(37) 2.538 Å, C(3)–H(3B)···O(10) 2.580 Å, C(18)–H(18B)···O(5) 2.2.403 Å, O(3W)–H(23B)···O(5) 2.107 Å, O(1W)–H(21C)···O(5) 1.907 Å, O(5W)–H(25A)···O(6) 2.536 Å, O(5W)–H(25A)···O(31) 1.919 Å, O(3W)···O(36) 2.905 Å and N(11)···O(35) 2.786 Å. Since $[C_6H_{12}N_5O]^+$ cations lie at one-side of the anion, a striking structural feature can be described as two-dimensional inorganic infinite plane-like ($2D/\infty[PW_{12}O_{40}]^{3-}$) which form *via* intermolecular interactions: O(15)···O(15) 2.943 Å, O(13)···O(27) 2.930 Å and O(11)···O(30) 3.068 Å along the *x* axis (Fig. S1). The inorganic infinite planes are well separated by $[C_6H_{12}N_5O]^+$ cations and water molecules (Fig. S2). On the other hand, the organic moieties and water molecules link parallel polyoxoanion sheets via hydrogen bond interactions that mentioned previous. Cationic organic units and water molecules, located between the inorganic planes, are bonded to each other by a complex network of hydrogen interactions such as: O(1W)–H(21D)···N(3) 2.188 Å, N(2)–H(2C)···O(3W) 2.498 Å, O(3W)–H(23A)···N(12) 2.408 Å, N(15)–H(15C)···N(6) 2.289 Å, O(2W)–H(22A)···N(1) 2.536 Å, N(7)–H(7A)···O(4W) 1.890 Å, O(4W)–H(24B)···O(5W) 2.594 Å, O(4W)–H(24A)···O(5W) 1.708 Å.

The ^{1}H NMR showed 3 peaks on δ 2.65, 3.80 and 4.15 ppm due to morpholine N- adjacent methylens, morpholine *O*-adjacent methylens and (N and tetrazole ring) methylen respectively. The peaks for NH protons are masked by the solvent resonance absorptions. These peaks and patterns are consistent with the ten hydrogen atoms that are covalently bonded to the carbon atoms of ((1*H*-tetrazole-5-yl)methyl) morpholine.

The vibrational spectrum exhibits the characteristic bands associated with the building constituents from whom title hybrid was synthesized: the heteropolyanions and organic species. The IR spectrum of the title hybrid has some characteristic bands for the organic moiety at 1455, 1467, 1640 and 3550 cm^{-1}. Absorptions at 1455 and 1466 wave numbers are attributed to symmetric and asymmetric stretching vibrations of C–O and C–N group. The band at 1640 cm^{-1} is ascribed to the N–H bond. In addition, the IR spectrum of the title compound exhibits prominent bands

for the polyoxotungstate at 1063, 961, 877, 789 cm^{-1}, attributed to $\nu_{as}(P–O_a)$, $\nu_{as}(W = O_t)$, $\nu_{as}(W–O_b–W)$, $\nu_{as}(W–O_c–W)$, respectively. These results indicate that the polyoxotungstate in the title compound still retain the basic Keggin structure, but are distorted due to the effects of hydrogen bonding interaction. This is consistent with the results of the single crystal X-ray diffraction analysis. TGA curve displays a three-steps weight loss in the range of 20–800 °C. The first endothermic peak in the range of 20–170 °C corresponds to the removal of crystallization waters. The second set of peaks start at ca. 300–450 °C attributed to the decomposition of the $[C_6H_{12}N_5O]^+$ cations. The last peak, at 650 °C, can be attributed to the complete decomposition of the $[PW_{12}O_{40}]^{3-}$ polyoxoanion. The IR spectrum of the residue material clearly suggesting the presence of WO_3. Furthermore, the observed total weight loss is also consistent with a thermal decomposition, which usually leads to a mixture of metal oxides.

3. Conclusion

In summary, in this work we have prepared and characterized structurally a novel 2D-network inorganic–organic hybrid containing ((1*H*-tetrazol-5-yl)methyl)morpholine and Keggin-type polyoxoanion: $[C_6H_{12}N_5O]_3[PW_{12}O_{40}]\cdot 5H_2O$. According to the molecular structural analysis, this material contains infinite planes of inorganic moiety. The arrangement of these mentioned planes to each other make the specific space for the entering of organic molecules. The synthesis and characterization of this new organic–inorganic hybrid, is an important continuous step to incorporate organic molecules of biological significance into the network of inorganic cluster-compounds. A combination of electrostatic forces and hydrogen bonding keeps this ''adduct'' stable in the solid state. The fact that in the solution phase the compound is also stable makes it a viable candidate for applications as homogeneous catalysis [10,14]. There may be potential pharmaceutical benefits that are yet to be explored.

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