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Synthesis, molecular structure, and characterization of a new 3D-layered inorganic–organic hybrid material: $[\text{D/L-}C_6H_{13}O_2N\text{–}H]_3[(PO_4)W_{12}O_{36}]\cdot 4.5H_2O$

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ABSTRACT

A new 3D-layered inorganic–organic hybrid $[\text{D/L-}C_6H_{13}O_2N\text{–}H]_3[(PO_4)W_{12}O_{36}]\cdot 4.5H_2O$ (**1**), as racemic material in the solid phase, has been synthesized and fully characterized by elemental microanalysis, single crystal X-ray diffraction, and infrared, Raman, and proton nuclear magnetic resonance spectroscopes. The most unique structural feature of **1** is its three-dimensional inorganic infinite tunnel-like framework that results in weak van der Waals interactions along the *a*-axis. A weak interlayer interaction between the titled layers provides a desirable condition to explore its potential as a host in a host–guest complex. The racemization has been observed in the crystal structure with the centric space group ($P2_1/c$). The latter consists of $\alpha\text{-}[(PO_4)W_{12}O_{36}]^{3-}$ and $[\text{D/L-}C_6H_{13}O_2N\text{–}H]^+$ moieties with water molecules linked together by a complex network of hydrogen bond interactions.

1. Introduction

Polyoxometallates (POMs) can be viewed as globular or spherical polyanionic structures that their anionic charges being borne by the peripherally located oxygen atoms. In POMs chemistry, a large variety of compounds, clusters and solid-state structures can be formed by linking of the well-defined metal-oxygen building blocks. The molecular and structural versatility, and their diverse characteristics, exhibit unusual topological and electronic properties that can find applications in variety of fields such as medicine, catalysis, magnetic materials, photo- and electro-chromism, and industrial processes [1–10]. The heteropolyacids (hereafter HPAs) as representative of this class of inorganic clusters have attracted considerable interest, as they are less toxic while having higher acidity [11–13]. HPAs are widely used in variety of homogenous and heterogeneous acid-catalyzed reactions [14–16].

To date, the antiviral and antitumoral activities of POMs, have dominated in the medicinal chemistry of these compounds. A third area of POMs activity has been demonstrated recently. When used in combination with β-lactam antibiotics, polyoxotungstates enhance the antibiotic effectiveness against otherwise resistant strains of bacteria [17]. There has been a growing interest in the synthesis of POMs–protein compounds since the coating of the viral and bacterial particles are made up of proteins and POMs have demonstrated their effective antiviral and anticancer activities. Amino acids play a central role as building blocks of proteins and as intermediates in metabolism. The biological activity of the proteins is determined by the chemical properties of the amino acids. Hence, it is desired to investigate the behavior of amino acids when they are hydrogen bonded to POMs. As a pertinent example, a new 3D structure has been synthesized by Chinese chemists [18]. The synthesis of this chiral 3D open framework could open the door for analogous structures based on POM anions with potential applications in medicine. The experimental results indicate that the polyoxoanion acts as a molecular acceptor that interacts with the nitrogen and oxygen atoms of the organic donor in this new molecular assembly.

In light of these findings, our research group is primarily concerned with analyzing van der Waals interactions between amino acids, bioorganic compounds, and POMs [19–22].

In this study, we report the synthesis, molecular structure, and characterization of a new 3D-layered inorganic–organic hybrid material $[\text{D/L-}C_6H_{13}O_2N\text{–}H]_3[(PO_4)W_{12}O_{36}]\cdot 4.5H_2O$, as a racemic material in the solid phase.

2. Experimental

2.1. Synthesis of $[\text{D/L-}C_6H_{13}O_2N\text{–}H]_3[(PO_4)W_{12}O_{36}]\cdot 4.5H_2O$

The reactant $\alpha\text{-}H_3[(PO_4)W_{12}O_{36}]\cdot 19H_2O$ was prepared by a well-known procedure [23]. Other chemicals were commercially

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purchased from Merck and used without further purification. The crystals of compound **1** were prepared as follows: a solution of L-leucine (0.1 g, 0.763 mmol) in 3 ml of 2N HCl was dropwisely added to a 5 ml solution of α-$H_3[(PO_4)W_{12}O_{36}]\cdot 19H_2O$ (0.5 g, 0.155 mmol) in water.

The obtained solution was kept at room temperature and stirred for several hours. After adjusting the pH to 1.5 with 3N perchloric acid, the resulting clear solution was left for several days. The white microcrystals of compound **1** were filtered and redissolved in DMF. The filtrate was kept for 3 weeks at ambient conditions and white block crystals of material **1** were isolated with a yield of ~30% based on W. It is interesting to know that our efforts to resynthesize the title compound using a reverse configuration of leucine amino acid (D-leucine as a starting material) than 1, however, failed. Anal. Calc. C, 6.49; H, 1.45; N, 1.26. Found: C, 6.54; H, 1.45; N, 1.23. IR (KBr pellet ν, cm^{-1}) 786 (s) $\nu_{as}(W–O_c–W)$; 875 (m) $\nu_{as}(W–O_b–W)$; 960 (s) $\nu_{as}(W = O_d)$; 1061 (m) $\nu_{as}(P–O_a)$; 1453 (w) $\nu_s(C–O)$; 1465 (sh) $\nu_{as}(C–N)$; 1642 (w) $\nu_s(N–H)$; 1737 (m) $\nu_{as}(C{=}O)$; 3520(b) $\nu_{as}(O–H)$.

Table 1
Crystal data: unit cell characteristics and refinement parameters for **1**.

Compound **1**	$[D/L\text{-}C_6H_{13}O_2N–H]_3[(PO_4)W_{12}O_{36}]\cdot 4.5H_2O$
Formula	$C_{18}H_{48}N_3O_{50.5}PW_{12}$
Formula wt.	3351.76
Crystal size	0.48 × 0.40 × 0.30
Crystal system	Monoclinic
Space group	$P2_1/c$
T (K)	173(2)
a (Å)	14.2876(12)
b (Å)	24.340(2)
c (Å)	16.5171(14)
β (°)	94.9020(10)
V (Å^3)	5723.1(8)
Z	4
ρ_{calcd} (g cm^{-3})	3.890
μ (Mo Kα, mm^{-1})	24.15
$2\theta_{max}$ (°)	56
# ref. meas., unique	54324, 13557
# ref. $[I > 2\sigma(I)]$	9765
# of parameters	775
R_{int}	0.0659
R_1, wR_2 $[I > 2\sigma(I)]$	0.0466, 0.1161
R_1, wR_2 (all data)	0.0732, 0.1250

2.2. Investigation techniques

The title compound has been characterized by various physicochemical methods: X-ray diffraction, ^1H NMR spectroscopy, IR and Raman spectroscopy, optical measurement, and elemental analysis.

2.2.1. X-ray diffraction

Experimental parameters pertaining to single crystal X-ray analysis of compound **1** are given in Table 1. Data were collected on a Siemens SMART 1000 CCD platform diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The final unit cell was determined from 9765 reflections in the range of $2.20° < \theta < 28.33°$. The data were integrated using the SAINT suite of software and corrected for the effects of absorption using SADABS. The structure was solved by direct methods and refined iteratively via full-matrix least squares on Fo^2 and difference

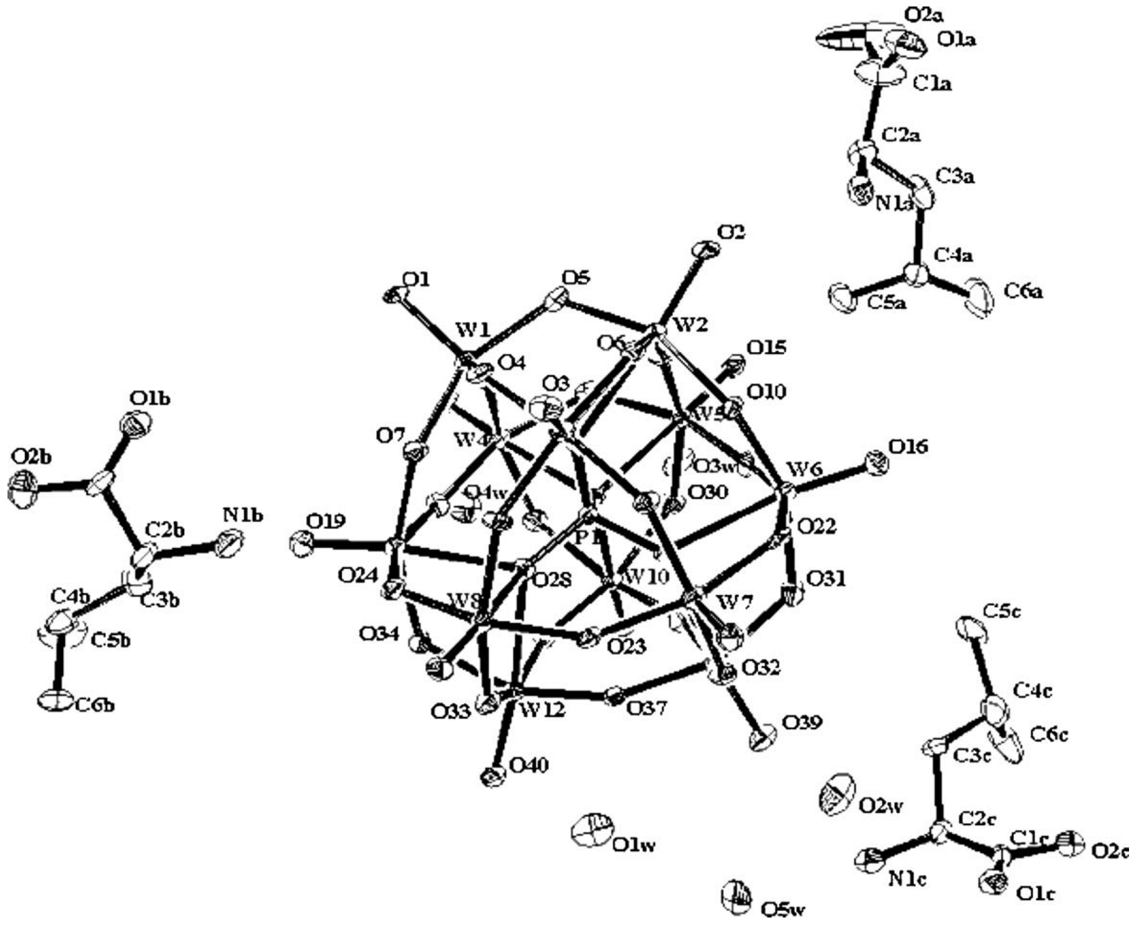

Fig. 1. The title material with ellipsoids at 30% probability. Hydrogen atoms are omitted for clarity.