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Synthesis and Crystal Structure of Tris(L-*iso*-leucinium(2*S*,3*S*))-dodecatungstophosphate 4.5 hydrate

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The asymmetric unit of the title salt contains two symmetrically independent $[PW_{12}O_{40}]^{3-}$ polyoxoanions, six L-*iso*-leucinium (2*S*,3*S*) cations and nine solvent water molecules. The anion shows a classical α-Keggin structure, which consists of a central PO_4 tetrahedron surrounded by four vertex-sharing W_3O_{13} trimers. The cation is mono-protonated L-*iso*-leucine amino acid. Most of the N–H units and all O–H units of six cations are involved in hydrogen-bonding interactions as H-donors, and some of the terminal and bridged oxygen atoms of the anions and the carbonyl oxygen atoms of three cations act as H-acceptors. The water molecules are also involved in hydrogen-bonding interactions. The extensive intermolecular N–H···O and O–H···O hydrogen bonds make a three-dimensional hydrogen-bonded network in the crystal structure.

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The programmed synthesis of salts containing polyoxoanions and organic cations is one of the interesting areas in chemistry, since it allows forming compounds with unique structures and properties.[1-3] In this domain, single-enantiomer compounds have attracted attention due to potential applications in nonlinear optics and chiral catalysts.[4] One approach for the synthesis of such compounds involves the use of single-enantiomer organic components such as single-enantiomer amino acids.[4]

Here, we report on the synthesis, spectroscopic characterization and single-crystal X-ray determination of the title salt, $(C_6H_{14}NO_2^+)_3[PW_{12}O_{40}^{3-}]\cdot 4.5(H_2O)$, Fig. 1. The title salt was prepared by the following method: A solution of $H_3PW_{12}O_{40}$ (5.76 g, 2 mmol) in water (40 ml) was added to a solution of L-*iso*-leucine (0.787 g, 6 mmol) in HCl (10 ml, 1 M) and stirred at room temperature for two hours; then, the resulting solution was filtered and kept until colorless crystals were obtained. ^{31}P-NMR (D_2O, 202.46 MHz, 85% H_3PO_4, δ_{ppm}): –15.61(s). ^{1}H-NMR (D_2O, 500.13 MHz, TMS, δ_{ppm}): 0.90 (t, CH_3), 0.91 (d, CH_3), 1.27 (m, CH), 1.44 (m, CH), 1.83 (m, CH), 3.81 (s, CH), 8.10 (s, NH_3^+). ^{13}C-NMR (D_2O, 125.77 MHz, TMS, δ_{ppm}): 11.61, 14.48, 25.15, 35.81, 56.27, 170.32. IR (KBr, cm^{-1}): 3530, 2931, 1723, 1601, 1481, 1245, 1083, 984, 900, 804, 511.

The crystallographic data are summarized in Table 1, and selected bond lengths and angles are given in Table 2. The asymmetric unit of the title salt contains two symmetrically independent $[PW_{12}O_{40}]^{3-}$ polyoxoanions, six L-*iso*-leucinium cations and nine solvent water molecules (Fig. 2). The $[PW_{12}O_{40}]^{3-}$ anion (Figs. 1S and 2S) shows a classical α-Keggin structure,[5] which consists of a central PO_4 tetrahedron surrounded by four vertex-sharing W_3O_{13} groups. Each W_3O_{13}

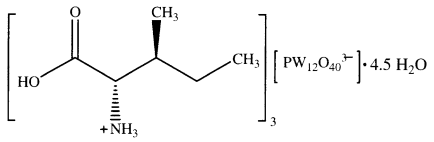

Fig. 1 Chemical diagram of the title compound.

Table 1 Crystal and experimental data

Chemical formula: $C_{18}H_{51}N_3O_{50.5}PW_{12}$	
Formula weight = 3354.79	
T = 100(2)K	
Crystal system: Triclinic	Space group: $P\bar{1}$
a = 13.6720(11)Å	α = 84.124(1)°
b = 13.7040(11)Å	β = 83.900(1)°
c = 16.9458(13)Å	γ = 62.994(1)°
V = 2807.5(4)Å^3	Z = 2
D_x = 3.968 g/cm^3	
Radiation: Mo K_α (λ = 0.71073 Å)	
μ(Mo K_α) = 24.616 mm^{-1}	F(0 0 0) = 2974
Crystal size = 0.17 × 0.17 × 0.15 mm^3	
No. of reflections collected = 72489	
No. of independent reflections = 26816	
θ range for data collection: 1.67 to 28.00°	
Data/restraints/parameters = 26816/243/1526	
Goodness-of-fit on F^2 = 1.022	
Flack parameter = 0.017(11)	
R indices [$I > 2\sigma(I)$]: R_1 = 0.0432, wR_2 = 0.0886	
R indices (all data): R_1 = 0.0513, wR_2 = 0.0923	
$(\Delta/\sigma)_{max}$ = 0.001	
$(\Delta\rho)_{max}$ = 2.797 e.Å^{-3}	$(\Delta\rho)_{min}$ = –3.047 e.Å^{-3}
Measurement: Bruker SMART APEX2 CCD area detector	
Program system: SHELXL-97[8]	
Structure determination: SHELXS-97	
Refinement: Full-matrix least-squares on F^2	
CCDC deposition number: 863164	

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Table 2 Selected bond lengths [Å] and bond angles [°] (e.s.d's are given in parentheses)

W(1)-O(7)	1.719(11)	W(24)-O(44)	2.392(11)
W(1)-O(8)	1.897(13)	P(1)-O(1)	1.548(12)
W(1)-O(5)	1.896(12)	P(2)-O(41)	1.554(12)
W(1)-O(6)	1.923(11)	O(1S)-C(1S)	1.20(2)
W(1)-O(9)	1.922(11)	N(1S)-C(2S)	1.50(2)
W(1)-O(1)	2.423(12)	N(6S)-C(32S)	1.53(2)
O(7)-W(1)-O(8)	101.6(5)	O(41)-P(2)-O(42)	108.8(7)
O(7)-W(1)-O(5)	102.1(6)	P(1)-O(1)-W(1)	125.1(7)
O(8)-W(1)-O(5)	156.3(5)	W(1)-O(1)-W(5)	89.3(4)
O(7)-W(1)-O(6)	102.6(5)	O(1S)-C(1S)-O(2S)	127.0(16)
O(8)-W(1)-O(6)	88.7(5)	N(1S)-C(2S)-C(1S)	108.0(13)
O(2)-P(1)-O(1)	108.8(7)	O(2S)-C(1S)-C(2S)	112.3(14)

trimer is composed of three WO_6 octahedra linked in a triangular arrangement by sharing edges. There are 4 different types of O atoms in each $[PW_{12}O_{40}]^{3-}$ anion, including 12 terminals ($O_{terminal}$), 4 oxygen atoms bonded to P and W ($O_{internal}$), $12WO_6$ octahedra corner-shared and $12WO_6$ octahedra edge-shared oxygen atoms (both two last classes of O atoms are so-called as $O_{bridged}$). The central PO_4 tetrahedron is slightly distorted: the P-O bond lengths range from 1.517(11)Å to 1.548(12)Å for P1-O, and 1.522(12)Å to 1.567(12)Å for P2-O bonds and the O-P-O angles are in the range of 108.7(7)° –110.2(7)° (at P1), and 108.8(7)° –110.4(7)° (at P2). The W-$O_{terminal}$, W-$O_{bridged}$ and W-$O_{internal}$ bond lengths (in the range of 1.668(12)Å to 1.724(12)Å, 1.855(12)Å to 1.955(12)Å and 2.390(11)Å to 2.468(12)Å, respectively) are within the expected values.[6] There are six symmetrically independent mono-protonated amino acid cations with major differences in the corresponding torsion angles. The C=O (with lengths in the range of 1.14(2)Å to 1.20(2)Å), C-O (1.27(2)Å to 1.33(2)Å) and C-N (1.46(2)Å to 1.54(2)Å) bond lengths are within the expected values.[7]

In the crystal structure, the carbonyl oxygen atoms of three cations (O1S, O7S and O11S) and some of the terminal oxygen atoms (O7, O21 and O38 in the polyoxoanion P1 and O56, O65, O70 and O79 in the polyoxoanion P2) and the bridged oxygen atoms O24 in P1 and O59 in P2 are involved in hydrogen-bonding interaction as H-acceptors. Most of the N-H units and all O-H units of six cations are involved in hydrogen-bonding interactions as H-donors. The water molecules are also involved in hydrogen-bonding. Then, the organic cations, inorganic anions and water molecules are assembled in a three-dimensional hydrogen-bonded network in the crystal structure through extensive intermolecular N-H···O and O-H···O hydrogen bonds (Table 1S and Fig. 3S). A view of the unit-cell packing of the title salt is given in Fig. 4S. The positions of hydrogen atoms attached to L-*iso*-leucinium cations were calculated, and then refined in an isotropic approximation within a riding model with the U_{iso}(H) parameters equal to $1.5U_{eq}$(Ci), $1.2U_{eq}$(Cj), $1.5U_{eq}$(N), $1.5U_{eq}$(O), where U(Ci) are the equivalent thermal parameters of the methyl carbon atoms, U(Cj) are the equivalent thermal parameters of the other carbon atoms, U(N) are the equivalent thermal parameters of the nitrogen atoms, and U(O) are the equivalent thermal parameters of the oxygen atoms, to which corresponding H atoms are bonded. The hydrogen atoms of water molecules could not be located because of the presence of very heavy atoms (12 W atoms) and high absorption. One of the water molecules (O9W) is disordered over two positions with 0.65/0.35 occupancies.

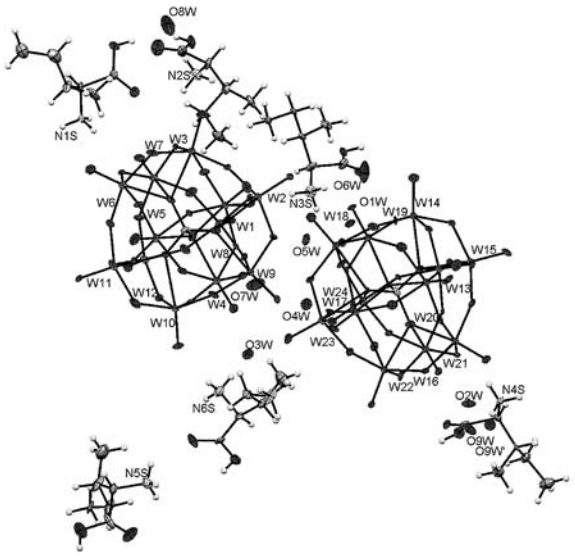

Fig. 2 ORTEP view of the title salt. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The hydrogen atoms of water molecules could not be located. The W atoms of anions and the O atoms of water molecules and the N atoms of cations are labeled.

Acknowledgements

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