

Synthesis, X-ray crystal structure and spectroscopic characterization of a hybrid material based on glycine and α -Keggin type polyoxotungstate

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DOI: 10.1016/j.mencom.2012.05.009

The solvated hybrid material $[C_2H_6NO_2]_3[(PO_4)W_{12}O_{36}] \cdot 5H_2O$ was synthesized from glycine and an α -Keggin polyoxo anion under normal conditions.

The chemistry of polyoxometalates (POMs) is of considerable current interest because of their applications in medicine, materials science and catalysis.^{1–4} Thus, many heteropoly anions have been reported and some of them, especially of the α -Keggin type, have been structurally and spectrally characterized.⁵ The incorporation of organic moieties into inorganic oxide clusters provides a powerful method for the structural modification and synthesis of novel inorganic-organic hybrid materials with hydrogen-bonded frameworks.⁶ In particular, the 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. As the coating of viral particles consists of proteins and the antiviral and anticancer properties of POMs have been shown,⁷ the synthesis of POM–protein compounds is of considerable interest. In this context, chemical reactions of amino acids as the building blocks of proteins with POMs have been the focus of attention.

We isolated a novel ionic hybrid **1**[†] based on the dodecatungstophosphate anion and glycine as a biologically active organic compound, which is the building block of proteins.^{8–11} The single crystal X-ray structure analysis of compound **1** showed that it consists of one discrete $[(PO_4)W_{12}O_{36}]^{3-}$ anion, three $[C_2H_6NO_2]^+$ monocationic moieties and five water molecules, which linked together *via* hydrogen-bonding interactions (Figure 1).[‡] The anion

[†] Commercial chemicals were used without further purification. A Buck-500 scientific spectrometer was employed to record the IR spectrum. The Raman spectrum was collected using a 180° back scattering geometry and a Bomem MB-154 Fourier transfer spectrometer equipped with a ZnSe beam splitter and a TE cooled GaAs detector. The ¹H NMR spectrum was recorded on a Bruker BRX-100 AVANCE spectrometer. Elemental analysis was performed on a Thermo Finnigan Flash-1112EA microanalyzer.

General procedure for the preparation of 1. Powdery α -Na₃[(PO₄)W₁₂O₃₆]·8H₂O (0.20 g, 0.06 mmol) was added to a solution of glycine (0.05 g, 0.67 mmol) in 3 ml of HCl (1 N) with vigorous stirring within 3 h. The colourless prism crystals of the title compound were formed after 7 days. The respective solid was filtered off and washed with EtOH/H₂O. The solution was filtered and the filtrate was allowed to evaporate slowly at ambient temperature in the dim light position. After a few days, colourless good quality crystals suitable for X-ray single-crystal diffraction were obtained in ~60% yield (based on W). IR (KBr, ν/cm^{-1}): 3400 (m), 2940 (m), 1615 (m), 1534 (m), 1470 (m), 1455 (m), 1077 (m), 978 (s), 885 (m), 800 (m). ¹H NMR (D₂O) δ : 3.70 (m, 2H, glycine). Found (%): C, 2.22; H, 0.88; N, 1.27. Calc. for **1** (%): C, 2.25; H, 0.87; N, 1.31. The total number of water molecules was deduced from the TGA data.

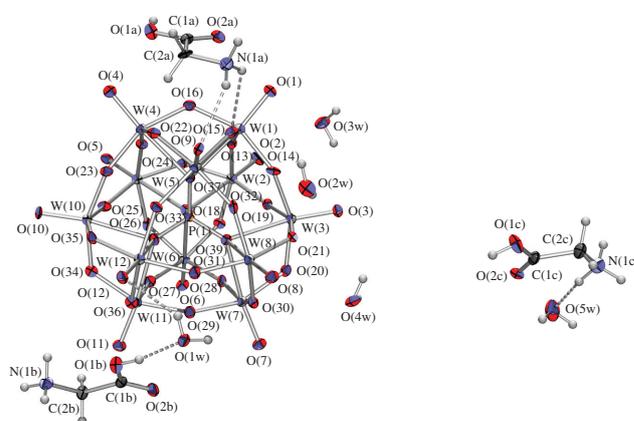


Figure 1 View of hybrid **1** showing the numbering scheme at a 30% probability level. Hydrogen bonding interactions are depicted as dashed lines.

in the title compound is the well-known α -Keggin cluster consisting of four groups of tri-metallic W₃O₁₀ units. Each (WO₆) octahedron in a tri-metallic unit shares edges with neighbours, and the W₃O₁₀ units link together *via* corner sharing (WO₆)

[‡] *Crystal data.* Crystals of **1** ($M = 3195.48$) are monoclinic, space group $P2_1/c$. At 110 K: $a = 12.4816(14)$, $b = 19.972(2)$ and $c = 17.933(2)$ Å, $\beta = 102.218(2)^\circ$, $V = 4369.2(8)$ Å³, $Z = 4$, $d_{\text{calc}} = 4.858$ g cm⁻³.

Data were collected on a colourless prismatic crystal mounted and centered on a Bruker SMART APEX II CCD area detector with graphite monochromated MoK α radiation ($\lambda = 0.71073$ Å). The final unit cell was determined from 5657 reflections in the range of $1.55^\circ < \theta < 30.00^\circ$. 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 and difference Fourier analysis using the SHELX-97 suite of software. The H(C) and H(N) atom positions were calculated. The H atoms of water molecules and OH groups were located in difference Fourier synthesis. All hydrogen atoms were refined in isotropic approximation in riding model with the $U_{\text{iso}}(\text{H})$ parameters of $1.2 U_{\text{eq}}(\text{C}_i)$ and $1.5 U_{\text{eq}}(\text{O}, \text{N})$, where $U(\text{C}_i)$ and $U(\text{O}, \text{N})$ are respectively the equivalent thermal parameters of the carbon, oxygen and nitrogen atoms to which corresponding H atoms are bonded.

CCDC 685644 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2012.

octahedral to form a cluster cage with a (PO_4) tetrahedron located in the centre. There are four kinds of oxygen atoms in the heteropoly anion $\alpha\text{-}[(\text{PO}_4)\text{W}_{12}\text{O}_{36}]^{3-}$, 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 . Crystal packing is stabilized by classical $\text{N}\cdots\text{H}\cdots\text{O}$ and $\text{O}\cdots\text{H}\cdots\text{O}$ hydrogen bonds. The P–O bonds in the respective polyoxo anion are single [1.528(7)–1.552(7) Å]. The P atom has a slightly distorted tetrahedral configuration and the O–P–O angles are in the range of 108.9(4)–110.2(4)°. Within the α -Keggin polyoxo anion, all the W centres exhibit a highly distorted octahedral coordination geometry, $\{\text{WO}_6\}$, with the W–O bond distances and internal *cis*-O–W–O and *trans*-O–W–O octahedral angles in the ranges of 1.688(7)–2.469(7) Å, 70.9(3)–105.0(3)° and 155.0(3)–172.8(3)°, respectively. The W– O_t , W– O_a and W– $\text{O}_{b/c}$ bond lengths in the WO_6 octahedral should fall in the ranges of 1.667(8)–1.718(8), 2.383(3)–2.473(9) and 1.883(0)–1.997(6) Å, respectively (see Online Supplementary Materials). The vibrational spectrum exhibits characteristic bands associated with the building constituents: the heteropoly anions and organic species. The IR spectrum of the hybrid has some characteristic bands for the organic moiety at 1455, 1470, 1534, 1615 and 3400 cm^{-1} . Absorption bands at 1455 and 1470 cm^{-1} are attributed to symmetric and asymmetric stretching vibrations of C–O and C–N groups. The band at 1615 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 1077, 978, 885 and 800 cm^{-1} attributed to $\nu_{\text{as}}(\text{P}-\text{O}_a)$, $\nu_{\text{as}}(\text{W}=\text{O}_t)$, $\nu_{\text{as}}(\text{W}-\text{O}_b-\text{W})$ and $\nu_{\text{as}}(\text{W}-\text{O}_c-\text{W})$, respectively. These results indicate that the 12-polyoxotungstates in the title hybrid still retain the basic α -Keggin structure, but they are distorted due to the effects of hydrogen bonding interaction. This is consistent with the results of the single crystal X-ray diffraction analysis. The Raman spectrum was recorded in the range of 1050–200 cm^{-1} . There are three prominent bands at 1007, 987 and 217 cm^{-1} for compound **1**, which can be attributed to $\nu_s(\text{W}=\text{O}_t)$, $\nu_{\text{as}}(\text{W}=\text{O}_t)$ and $\nu_s(\text{W}-\text{O}_a)$, respectively. These bands demonstrate that the $[(\text{PO}_4)\text{W}_{12}\text{O}_{36}]^{3-}$ anion retains its Keggin structure. Raman bands for glycine molecules have low intensities, and they cannot be assigned unambiguously. The TGA curve displays a three-step 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 five crystallization water molecules. The second set of peaks at about 250–350 °C was attributed to the decomposition of the $[\text{C}_2\text{H}_6\text{NO}_2]^+$ cations. The last peak at 750 °C can be assigned to the complete decomposition of the polyoxo anion. The distributions of cationic and anionic fragments within the crystal network of the hybrid are exactly comparable with our previous published data.^{12–14} Since the $[\text{C}_2\text{H}_6\text{NO}_2]^+$ cations lie around a cluster anion, a striking structural feature can be described as two-dimensional inorganic infinite plane-like ($2\text{D}/\infty[(\text{PO}_4)\text{W}_{12}\text{O}_{36}]^{3-}$), which is formed *via* the intermolecular interactions of $\text{O}\cdots\text{O}$ between $[(\text{PO}_4)\text{W}_{12}\text{O}_{36}]^{3-}$ fragments along the *x* axis. The inorganic infinite planes are well separated by the amino acid cations and water molecules. On the other hand, the organic moieties and water molecules linked

parallel polyoxo anion sheets *via* hydrogen bond interactions. Cationic organic units and water molecules, located between the inorganic planes, are bonded to each other by a complex network of hydrogen bonds. The IR spectrum of the residue material clearly suggests the presence of a WO_3 fragment. Furthermore, the observed total weight loss is also consistent with thermal decomposition, which usually leads to a mixture of metal oxides.

In summary, in this work, we have prepared and structurally characterized a new 2D-network inorganic-organic hybrid containing glycine and an α -Keggin polyoxo anion. It contains the infinite planes of inorganic moieties. The arrangement of these 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 a solid state. The fact that the compound is also stable in the solution phase makes it a viable candidate for applications in homogeneous catalysis. There may be potential pharmaceutical benefits that are yet to be explored.

This study was supported by the Ferdowsi University of Mashhad (grant no. P/604).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2012.05.009.

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Received: 31st October 2011; Com. 11/3826