ANALYTICAL SCIENCES 2006, VOL. 22 x281

X-ray Structure Analysis Online

Crystal Structure of New POM-Based Organic-Inorganic Hybrid: Tris(glycinium) 12-phosphomolybdate·pentahydrate

Mehrdad POURAYOUBI, Ali REZA MAHJOUB,† and Elnaz LATIFI

Department of Chemistry, Tarbiat Modares University, P.O. Box 14115-175, Tehran, Iran

The title POM-based organic-inorganic hybrid compound consists of one $PMo_{12}O_{40}^{3-}$ polyoxoanion, three symmetrically independent glycinium cations and five solvated H_2O molecules; several N–H···O and O–H···O hydrogen bonds between organic cations, inorganic anions and solvated H_2O molecules in the crystal lattice lead to a 3-D supramolecular framework.

(Received July 15, 2006; Accepted September 25, 2006; Published on web December 1, 2006)

Crystal engineering has indicated much interest in developing organic-inorganic hybrid materials that have many different structures and an extended range of properties.[1] Work on composite materials based on nanosized discrete metal-oxygen cluster anions (polyoxometalate, henceforth POM for convenience) has been qualified.[2] The great roles of POM-based organic-inorganic hybrids have been developed to apply in catalysis and medicine.[3] As an organic donor to make $(glycine)_2H_4SiW_{12}O_{40}\cdot 5.5H_2O$ and $(Hglycine)_4[HPMo_{12}O_{40}]_2\cdot 22H_2O$, glycine has been used.[4,5] In this work, information about $[Hglycine]_3[PMo_{12}O_{40}]\cdot 5H_2O$ (Fig. 1) has been obtained. The crystal and experimental data are listed in Table 1, and selected bond lengths and angles are given in Table 2. Besides the inorganic $PMo_{12}O_{40}^{3-}$ anion and solvated H_2O molecules, there are three symmetrically independent glycinium cations in the structure with some differences in the bond lengths, angles and torsion angles. For example, the O(1S)–C(1S), O(3S)–C(3S) and O(5S)–C(5S) bond lengths are 1.210(5)Å, 1.226(5)Å and 1.213(5)Å, respectively. The inorganic anion in the title hybrid has a *Keggin* structure with 4 different kinds of O atoms: a) the 12 terminal, b) the 4 bonded to P and Mo, c) the 12 MoO_6 octahedra corner-shared and d) the 12 MoO_6 octahedra edge-shared. The P–O bond lengths in the polyoxoanion are single (1.532(3) – 1.540(3)Å), the P atom has a tetrahedral configuration and the O–P–O angles are in the range of 109.25(14)° – 109.65(14)°. Several N–H···O and O–H···O hydrogen bonds between organic cations, inorganic anions and solvated H_2O molecules in the crystal lattice (Table 3) have lead to a 3-D supramolecular framework. The hydrogen atoms of NH_3, H_2O and OH groups were found in difference Fourier synthesis. The H(C) atom positions were calculated. All of the hydrogen atoms were refined in an isotropic approximation within the riding model with the U_{iso}(H) parameters equal to 1.2Ueq(C_i), 1.5Ueq(O_j) and 1.5Ueq(N_k), where U(C_i), U(O_j) and U(N_k) are the equivalent thermal parameters of the carbon,

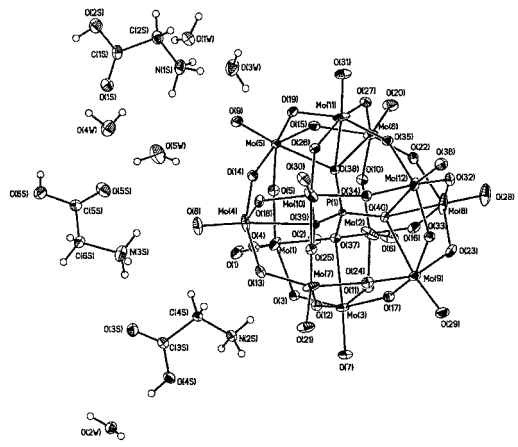

Fig. 1 View of the title POM-based organic-inorganic hybrid, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by circles of arbitrary size.

Table 1 Crystal data and structure refinement for $[C_2H_6NO_2]_3[PMo_{12}O_{40}]\cdot 5H_2O$

Formula: $C_6H_{28}Mo_{12}N_3O_{51}P$	
Formula weight = 2140.56	
Crystal system: monoclinic	
Space group: $P2_1/c$	$Z = 4$
a = 12.4919(6)Å	β = 102.1010(10)°
b = 19.9389(10)Å	
c = 17.9292(9)Å	
V = 4366.5(4)Å^3	
D_x = 3.256 Mg/m^3	
No. of reflections used = 12570	
$2\theta_{max}$ = 60.04 with Mo K_α	
R = 0.0370	
$(\Delta/\sigma)_{max}$ = 0.002	
$(\Delta\rho)_{max}$ = 2.620 e.Å^{-3}	
$(\Delta\rho)_{min}$ = –3.023 e.Å^{-3}	
Measurement: Bruker SMART 1000 CCD	
Program system: SHELXTL	
Structure determination: SHELXTL	
Refinement: full-matrix least-squares on F^2	

CCDC 604765 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

† To whom correspondence should be addressed.
E-mail: mahjouba@modares.ac.ir

Table 2 Selected bond lengths (Å) and angles (deg) for the title compound

Mo(1)-O(1)	1.681(3)	O(1S)-C(1S)	1.210(5)
Mo(12)-O(40)	2.425(3)	O(4S)-C(3S)	1.292(5)
P(1)-O(40)	1.532(3)	N(1S)-C(2S)	1.473(5)
P(1)-O(38)	1.537(3)	O(5S)-C(5S)	1.213(5)
P(1)-O(39)	1.540(3)	N(3S)-C(6S)	1.481(5)
O(1)-Mo(1)-O(5)	102.63(14)	O(40)-P(1)-O(38)	109.49(15)
O(5)-Mo(1)-O(2)	90.34(12)	O(40)-P(1)-O(37)	109.64(15)
O(36)-Mo(12)-O(40)	172.28(12)	P(1)-O(37)-Mo(2)	125.48(14)
O(33)-Mo(12)-O(40)	73.59(10)	P(1)-O(37)-Mo(1)	125.46(14)
N(1S)-C(2S)-C(1S)	110.0(3)	O(1S)-C(1S)-C(2S)	122.4(4)
O(1S)-C(1S)-O(2S)	126.3(4)	O(3S)-C(3S)-O(4S)	126.9(4)

Table 3 Hydrogen bond D-H...A for the title compound

D-H...A	D-H	H...A	D...A	∠(DHA)
O(2S)-H(2OS)...O(3S)#1	0.84	1.886	2.611(3)	144
N(1S)-H(1NB)...O(1W)#2	0.97	1.870	2.730(3)	146
N(1S)-H(1NA)...O(5W)#2	0.95	2.254	3.194(3)	171
N(1S)-H(1NC)...O(3W)#2	0.95	1.911	2.836(3)	163
O(4S)-H(4OS)...O(2W)#2	0.83	1.843	2.675(3)	178
N(2S)-H(2NA)...O(4W)#3	0.94	1.775	2.701(3)	167
N(2S)-H(2NB)...O(3)#2	0.93	2.078	2.988(3)	166
N(2S)-H(2NC)...O(5W)#3	0.92	1.976	2.808(3)	149
O(6S)-H(6OS)...O(2W)#1	0.82	1.951	2.719(3)	155
N(3S)-H(3NA)...O(3S)#2	0.97	2.061	2.996(3)	160
N(3S)-H(3NB)...O(31)#4	0.96	2.221	3.028(3)	141
N(3S)-H(3NB)...O(21)#5	0.96	2.270	2.932(3)	125
N(3S)-H(3NC)...O(8)#2	0.95	2.149	2.886(3)	134
N(3S)-H(3NC)...O(5S)#2	0.95	2.174	2.668(3)	111
O(1W)-H(1WA)...O(11)#6	0.86	2.014	2.869(3)	171
O(1W)-H(1WB)...O(32)#7	0.84	2.299	3.016(3)	144
O(1W)-H(1WB)...O(30)#8	0.84	2.327	2.973(3)	134
O(2W)-H(2WA)...O(1S)#9	0.85	1.868	2.719(3)	175
O(2W)-H(2WB)...O(30)#5	0.85	2.327	3.030(3)	135
O(3W)-H(3WA)...O(29)#10	0.86	2.148	2.930(3)	151
O(3W)-H(3WB)...O(19)#2	0.86	2.254	2.863(3)	128
O(4W)-H(4WA)...O(18)#8	0.84	2.147	2.904(3)	149
O(4W)-H(4WB)...O(35)#7	0.92	1.994	2.915(3)	179
O(5W)-H(5WA)...O(5S)#2	0.85	2.081	2.891(3)	158

Symmetry codes: #1 $-x-1, y-1/2, -z+1/2$; #2 x, y, z; #3 $-x-1, -y+2, -z$; #4 $x, -y+3/2, z+1/2$; #5 $-x-2, -y+2, -z$; #6 $-x-1, y-1/2, -z-1/2$; #7 $x+1, -y+3/2, z+1/2$; #8 $x+1, y, z$; #9 $-x-1, y+1/2, -z+1/2$; #10 $-x-2, y-1/2, -z-1/2$.

oxygen or nitrogen atoms to which corresponding H atoms are bonded. The rather large displacement factors of some Mo and terminal O atoms [O(1), O(6), O(8), O(9), O(20), O(21), O(28), O(29), O(36)] in the polyanion can be described as follows: a) high liberation of polyhedron as a rigid body; b) it can be a consequence of the considerable absorption effects that could not be completely corrected. The liberation is not so high as to allow split positions of Mo atoms, but is considerable enough to cause an increase of the ADP absolute values as well as to lead to high anisotropy of the atomic motion. Thus, the maximum positive residual density (2.62 e.Å^{-3}) is located near the Mo(8) center (distance 0.61 Å) and atoms of the Mo(8) – O(28) group are characterized by the maximum values of U(eq) [28(1) and 33(1)Å$^2 \times 10^3$ respectively].

Acknowledgements

Support of this investigation by Educational Council of Tarbiat Modares University is gratefully acknowledged. This work was done as a part of Dr. Mehrdad Pourayoubi's research for his postdoctoral degree at Tarbiat Modares University. We thank Institute of Organoelement Compounds of the Russian Academy of Science for determining the crystal structure by X-ray crystallography.

References

1. S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen, and I. D. Williams, *Science*, **1999**, *283*, 1148.
2. J. Kang, J. A. Nelson, M. Lu, B. Xie, Z. Peng, and D. R. Powell, *Inorg. Chem*., **2004**, *43*, 6408.
3. D. E. Katsoulis, *Chem. Rev*., **1998**, *98*, 359.
4. L. Bi, Q. He, Q. Jia, and E. Wang, *J. Molec. Struc*., **2001**, *597*, 83.
5. Z.-B. Han, Y.-P. Chang, H.-Y. An, and E. Wang, *Chem. Res. Chin. Univ*., **2003**, *15*, 19.