ORIGINAL PAPER

Synthesis and Crystal Structure of an Organic-Polyoxometalate (POM) Hybrid Compound Containing a Keggin Type Mo–Si Polyanion

Shae Anne Vaughn · Mark D. Smith · Hans-Conrad zur Loye

Abstract Complex (**1**), which is comprised of a typical Keggin type anion, four protonated 3-amino-1,2,4-triazole (AmTAZ) ligands, one nitrate anion and an area of disordered unidentifiable species was synthesized via hydrothermal methods followed by slow evaporation. The structure is held together through a web of hydrogen bonding and crystallizes in the monoclinic space group P2$_1$/c with unit cell dimensions of $a = 13.789(3)$ $b = 15.551(3)$ $c = 24.401(7)$ Å, $\beta = 93.898(8)°$, $V = 5220(2)$ Å^3 $Z = 4$, $D = 2.896$ Mg/m^3.

Introduction

Polyoxometalates (POMs) are one of the most studied inorganic clusters due to their extensive applications in catalysis [1, 2], material science and medicine [3, 4]. Many complexes and coordination polymers have been made using POMs as secondary building units to form complexes and extended networks [5–7]. In this paper, we report the hydrothermal synthesis and structure characterization of a Keggin heteropolyanion $(SiMo_{12}O_{40})^{4-}$ with four protonated AmTAZ molecules as counterions $(C_2N_4H_5)^+$, the structure of which is held together through an intricate array of intermolecular hydrogen bonding [8].

Experimental Details

Materials

AmTAZ was purchased from Avocado (96%). MnCO$_3$ was purchased from Aldrich (99.9%). NaMoO$_4$·2H$_2$O was purchased from Alfa Aesar (99.5%).

Synthesis

Sodium molybdenum oxide dihydrate (0.12 mmol, 29 mg), manganese carbonate (0.28 mmol, 32 mg), AmTAZ (0.68 mmol, 46.9 mg) and approximately 10 mL of water, with a pH of 3, adjusted with nitric acid, were added to a Teflon-capped glass hydrothermal tube. The tube was heated to 160 °C at a rate of 1 °C per minute and held at that temperature for 3 days and cooled at a rate of 0.1 °C per minute to room temperature. The majority of the starting material went into solution upon heating. The solution was filtered and allowed to slowly evaporate over the course of approximately 5 days. Crystals of complex (**1**) were obtained as yellow irregular block crystals through the slow evaporation of a hydrothermal reaction in which silicon was etched from the high pressure tube and subsequently incorporated into complex (**1**).

Crystallographic Determination

X-ray intensity data from a yellow block crystal were measured at 295(2) K using a Bruker SMART APEX diffractometer (Mo Kα radiation, $\lambda = 0.71073$ Å). Raw area detector data frame processing was performed with the SAINT+ and SADABS programs [9]. Final unit cell

S. A. Vaughn · M. D. Smith · H.-C. zur Loye (✉)
Department of Chemistry and Biochemistry, University of South Carolina, 631 Sumter Street, Columbia, SC 29208, USA
e-mail: zurloye@mail.chem.sc.edu

Table 1 Crystal data and structure refinements for complex **1**

Empirical formula	$C_8H_{26}Mo_{12}N_{17}O_{46}Si$
Formula weight	2275.83
Temperature (K)	295(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	
a (Å)	13.789(3)
b (Å)	15.551(3)
c (Å)	24.401(7)
β (°)	93.898(8)
Volume (Å^3)	5220(2)
Z	4
Density (calculated) (Mg/m^3)	2.896
Absorption coefficient (mm^{-1})	2.931
$F(000)$	4,316
Crystal size (mm^3)	$0.19 \times 0.10 \times 0.05$
Theta range for data collection (°)	1.48 to 28.28
Index ranges	$-18 \leq h \leq 18$
	$-20 \leq k \leq 20$
	$-32 \leq l \leq 32$
Reflections collected	71,802
Independent reflections	12,967 [R(int) = 0.0216]
Completeness to theta = 28.31°	100.0%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.8018
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	12967/0/757
Goodness-of-fit on F^2	1.221
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0323$, $wR2 = 0.0765$
R indices (all data)	$R1 = 0.0369$, $wR2 = 0.0786$
Largest diff. peak and hole (e Å^{-3})	1.132 and 1.022

parameters were determined by least-squares refinement of 7501 reflections from the data set. Direct methods structure solution, difference Fourier calculations and full-matrix least-squares refinement against F^2 were performed with SHELXTL [10].

The compound crystallizes in the space group P2$_1$/c as determined by the pattern of systematic absences in the intensity data. The asymmetric unit consists of four protonated triazole cations, three water molecules, one nitrate anion, and a Keggin anion, which is composed of one silicon atom, twelve molybdenum atoms, and forty oxygen atoms. The compound also contains an unidentified disordered species located at (0.50, 0.50, and 0.00) in the unit cell along with symmetry related coordinates, near the

Keggin anion. It occupies a volume of 335.4 Å^3 (6.4% of the total unit cell volume). Extensive trial disorder modeling attempts did not give a clear indication of the contents of the region, but the species may be a protonated AmTAZ ligand, necessary for charge balance. The largest peak in this region refined to less than full occupancy if assigned as a carbon atom. It was necessary to remove their contribution to the diffraction data using the Squeeze feature of Platon [11]. If instead the disordered region is water or nitrate molecules then the Keggin ion may be protonated, in which case it is likely that some of the terminal Mo–O bonds of the Keggin ion bear some fractional amounts of a proton as seen for numerous related species [12]. Due to this region of disorder the empirical formula would be better represented by $C_8H_{26}Mo_{12}N_{17}O_{46}Si$ (unidentified species). Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in geometrically idealized positions and included as riding atoms. The hydrogen atoms of the water molecules could not be located in the difference map and were therefore omitted. Crystallographic data are given in Table 1.

Discussion

Single crystal X-ray diffraction analysis shows that complex (**1**) consists of a Keggin type anion (SiMo$_{12}$O$_{40}$)$^{4-}$, four discrete AmTAZ [(C$_2$N$_4$H$_5$)$_4$]$^{4+}$ cations, three water molecules, and a nitrate anion (NO$_3$)$^-$ (Fig. 1). The Keggin ion is formed from twelve MoO$_6$ octahedra and one SiO$_4$ tetrahedron. Each octahedron is edge shared with two neighboring octahedra and is corner shared with two neighboring octahedra to form the anionic cluster. The bond distances between Si–O range between 1.626(2) and 1.630(3) Å (average 1.629 Å), while the O–Si–O angles fall into the range of 109.06(13)–110.10(13)° (average 109.47°). The terminal Mo–O bond distances vary from 1.676(3) to 1.696(3) Å (average 1.683 Å). The Mo–O–Si bridging Mo–O bond distances vary from 2.318(2) to 2.352(2) Å (average 2.341 Å). The remaining bond distances between Mo–O fall into the range of 1.848(3)–1.988(3) Å (average 1.922 Å). The O–Mo–O bond angles vary from 73.28(10) to 174.19(13) Å, respectively, selected bond distances and angles can be found in Table 2.

The anionic cluster has an overall charge of 4– and is balanced by four AmTAZ ligands that were protonated in the reaction vessel, thereby creating four 1+ charged cations. One nitrate anion is also located in the structure and would therefore contribute a 1– charge; one proton is needed for charge neutrality, but was not crystallographically located.
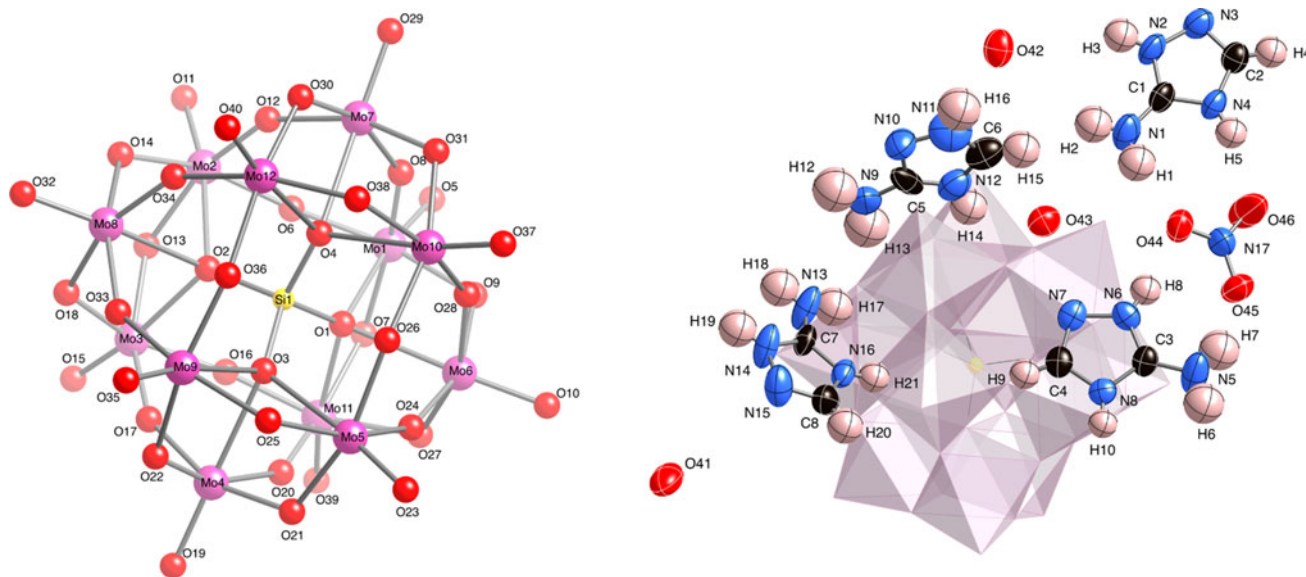
Fig. 1 Displacement ellipsoid plot (50% probability ellipsoids) of complex (**1**), POM cluster shown to the *left* and ligands shown to the *right*

Table 2 Selected bond distances (Å) and angles (°) for complex **1**

Selected bond distances			
Si1–O1	1.626(3)	N17–O44	1.249(6)
Si1–O2	1.630(2)	N17–O45	1.244(6)
Si1–O3	1.628(2)	N17–O46	1.191(7)
Si1–O4	1.630(2)	N1–C1	1.309(7)
Mo1–O1	2.349(2)	N2–N3	1.390(7)
Mo1–O5	1.677(3)	N3–C2	1.282(7)
Mo1–O6	1.888(3)	N4–C2	1.375(7)
Mo1–O7	1.896(3)	C1–N2	1.326(7)
Mo1–O8	1.971(3)	C1–N4	1.382(7)
Mo1–O9	1.941(3)		
Selected angles (°)			
O5–Mo1–O6	102.42(14)	O1–Si1–O4	109.41(13)
O5–Mo1–O7	99.92(14)	O1–Si1–O3	109.43(13)
O6–Mo1–O7	92.06(12)	O4–Si1–O3	110.07(13)
O5–Mo1–O9	99.20(14)	O1–Si1–O2	109.74(13)
O6–Mo1–O9	157.72(11)	O4–Si1–O2	109.01(13)
O7–Mo1–O9	89.52(12)	O3–Si1–O2	109.16(13)
O5–Mo1–O8	100.19(14)	C1–N2–N3	111.4(4)
O6–Mo1–O8	85.06(11)	C1–N4–C2	107.2(4)
O7–Mo1–O8	159.84(11)	C2–N3–N2	104.3(5)
O9–Mo1–O8	85.86(12)	N1–C1–N2	127.0(5)
O5–Mo1–O1	171.25(13)	N1–C1–N4	127.2(5)
O6–Mo1–O1	85.05(10)	N2–C1–N4	105.8(5)
O7–Mo1–O1	75.03(10)	N3–C2–N4	111.3(5)
O9–Mo1–O1	73.88(10)	O46–N17–O44	118.5(6)
O8–Mo1–O1	84.84(10)	O46–N17–O45	120.5(6)
		O44–N17–O45	120.9(5)

Fig. 2 Hydrogen bonding motif of one POM cluster, hydrogen bonding shown with *dashed lines*, four distinct ligands shown in *black*, all other symmetry equivalent ligands shown as *line drawings*

Complex (**1**) is linked through an intricate net of hydrogen bonding between the clusters, ligands, and nitrates. Each Keggin ion is bound to seven AmTAZ molecules through the terminal oxygen atoms of each cluster. There are two AmTAZ molecules that hydrogen bond the clusters directly together along the z-axis. Four clusters are intricately connected through hydrogen bonding via an AmTAZ molecule. AmTAZ is directly hydrogen bonded to three distinct clusters and further hydrogen bonded through a water molecule to a neighboring AmTAZ that in turn is bonded to a nitrate and another AmTAZ molecule that is connected to the terminal oxygens of a fourth cluster along the (100) plane. Figure 2 shows the hydrogen bonding around one Keggin ion, where each cluster is hydrogen bonded to eight neighboring clusters (Fig. 3). Hydrogen bonding distances and angles can be found in Table 3.

Conclusions

Inorganic–organic hybrid materials can be made via the in situ formation of a Keggin ion using sodium molybdenum oxide, manganese carbonate and AmTAZ under acidic conditions in a hydrothermal reaction followed by slow evaporation yielding $SiMo_{12}O_{40}(C_2N_4H_5)_4(H_2O)_3(NO_3)$ (unidentified species) yellow block crystals.
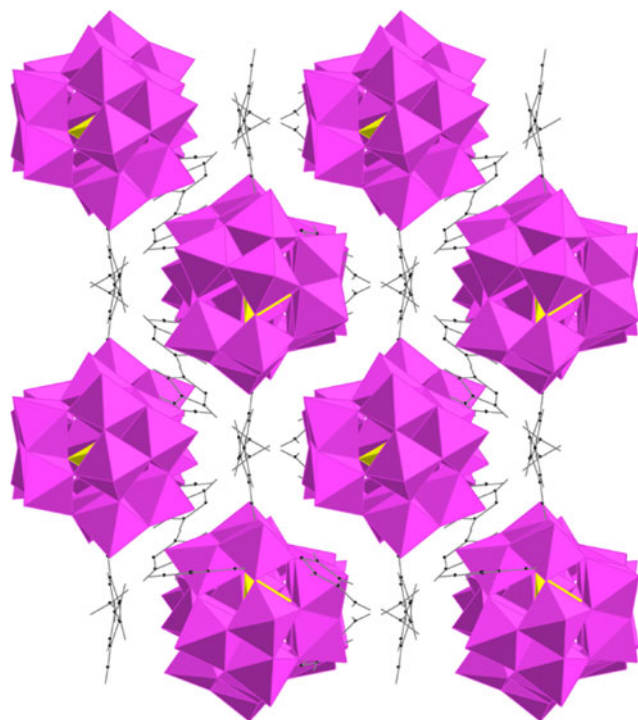
Fig. 3 Complex (**1**), extended structure shown along the 001 plane, AmTAZ shown as *stick bonds* for clarity

Table 3 Hydrogen bonding distances (Å) and angles (°) for complex **1**

D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
N(1)–H(2)···O(22)	0.86	2.13	2.972(5)	165.0
N(1)–H(1)···O(44)	0.86	2.09	2.926(6)	164.5
N(2)–H(3)···O(33)	0.86	2.13	2.984(5)	174.8
N(4)–H(5)···O(46)	0.86	2.04	2.859(7)	159.2
N(6)–H(8)···O(44)	0.86	1.94	2.790(6)	171.8
N(8)–H(10)···O(42)#2	0.86	1.95	2.803(6)	172.7
N(9)–H(11)···O(10)#4	0.86	2.21	2.929(7)	141.5
N(11)–H(15)···O(42)	0.86	1.92	2.694(9)	148.2
N(12)–H(13)···O(43)	0.86	2.07	2.752(7)	135.7
N(13)–H(17)···O(28)	0.86	2.13	2.927(5)	153.5
N(13)–H(16)···O(18)#5	0.86	2.16	2.888(5)	142.4
N(16)–H(20)···O(14)#5	0.86	2.17	3.021(5)	172.4

Symmetry transformations used to generate equivalent atoms: #1 x, $-y + 1/2$, $z - 1/2$; #2 $-x + 2$, $y + 1/2$, $-z + 1/2$; #3 $-x + 1$, $y + 1/2$, $-z + 1/2$; #4 $-x + 1$, $-y + 1$, $-z + 1$; #5 x, $-y + 1/2$, $z + 1/2$

Supporting Information

CCDC 820546 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

References

1. Mizuno N, Nozaki C, Hirose T, Tateishi M, Iwamoto M (1997) J Mol Catal A 117:159–168
2. Hill CL (2007) J Mol Catal A 262:2–6
3. Rhule JT, Hill CL, Judd DA, Schinazi RF (1998) Chem Rev 98:327–357
4. Menon D, Thomas RT, Narayanan S, Maya S, Jayakumar R, Hussain F, Lakshmanan V-K, Nair SV (2011) Carbohydr Polym 84:887–893
5. Pope MT, Mueller A (1991) Angew Chem 103:56–70
6. Dolbecq A, Dumas E, Mayer CR, Mialane P (2010) Chem Rev 110:6009–6048
7. Wang J-P, Shen Y, Bi D-Q, Niu J-Y (2009) J Chem Crystallogr 39:251–255
8. Keggin JF (1933) Nature 131:908–909
9. SMART Version 5630 (2003) SAINT+ Version 645 and SAD-ABS Version 210 Bruker Analytical X-ray Systems, Inc., Madison
10. SHELXTL Version 614 (2000) Bruker Analytical X-ray Systems, Inc., Madison
11. Spek AL (2009) Acta Cryst D65:148–155
12. Schulz-Dobrick M, Jansen M (2008) Z Anorg Allg Chem 634:2880–2884