A novel organic–inorganic hybrid based on Anderson-type polyoxometalate: $\text{H}(\text{C}_5\text{N}_5\text{H}_5)_2(\text{C}_5\text{N}_5\text{H}_6)_2[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]\cdot 10\text{H}_2\text{O}$

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Abstract. A new organic–inorganic hybrid compound, $\text{H}(\text{C}_5\text{N}_5\text{H}_5)_2(\text{C}_5\text{N}_5\text{H}_6)_2[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]\cdot 10\text{H}_2\text{O}$, has been synthesized and structurally characterized by single crystal X-ray diffraction, elemental analyses, IR, UV–Vis spectra and thermogravimetric analyses. This compound crystallized in the triclinic system, space group $P\bar{1}$, with $a = 8.033(5)$ Å, $b = 9.960(4)$ Å, $c = 16.797(7)$ Å, $\alpha = 73.43(3)^\circ$, $\beta = 87.85(1)^\circ$, $\gamma = 81.47(1)^\circ$ and $Z = 1$. The crystal structure can be described by infinite polyanions $[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{3-}$ organized in layers parallel to the c -direction alternating with organic cations associated in ribbons spreading along the b -direction. Multiple hydrogen bonds originating from amine, hydroxyl groups and water molecules connect different components of the lattice.

Keywords. Polyoxometalate; organic–inorganic hybrid; Anderson anion; adenine; crystal structure.

1. Introduction

Polyoxometalates (POMs) have been employed as inorganic building blocks for the construction of nanostructured clusters or one-, two- and three-dimensional extended open frameworks owing to their discrete structures and notable photochemical properties, which lead to a vast range of potential applications in different areas such as catalysis, electrochemistry, medicine and magnetism (Pope 1983; Kozhenikov IV 1998; Clemente-Juan and Coronado 1999a; Keita *et al* 2006; Proust *et al* 2008). Especially, spherical surface of POM anions gives a better opportunity to form hydrogen bond interactions with the organic/inorganic moieties. So far, several successful strategies have been developed to design POM-based supramolecular compounds (Ren *et al* 2006; Wang *et al* 2010; Yan *et al* 2011). Supramolecular structures of POMs with organic molecules such as TTF type (Peng *et al* 1999; Ouahab *et al* 2003), organic amines (Zhang *et al* 2009) and others (An *et al* 2008; Liu *et al* 2009; Ma *et al* 2011) have been successfully constructed. These materials are particularly interested in some important aspects of chemistry such as catalysis, nonlinear optical properties and charge transfer salts based on their supramolecular assembly (Gomez-Garcia *et al* 1994; Hagraman *et al* 1999; Finn *et al* 2000).

In this paper, we chose heteropolymolybdate cluster as the building block and flexible adenine molecule as the

structure-directing agent to construct supramolecular compounds: $\text{H}(\text{C}_5\text{N}_5\text{H}_5)_2(\text{C}_5\text{N}_5\text{H}_6)_2[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]\cdot 10\text{H}_2\text{O}$.

2. Experimental

2.1 Materials and general methods

All reagents were purchased commercially and used without further purification. The infrared spectra were recorded as KBr pellets, in the 4000–400 cm^{-1} range on a Nicolet 470 FTIR spectrophotometer (resolution: 0.125 cm^{-1}). UV–Visible absorption spectrum was recorded on a Perkin-Elmer Lambda 19 spectrophotometer. A Setaram TG–DTA92 thermo analyser was used to perform thermal treatment on samples of the title compound. TG–DTA thermograms were obtained with 30–20 mg. Samples were placed in an open platinum crucible and heated in air with 10°C/min heating rate; an empty crucible was used as reference.

2.2 Chemical preparation

To a solution of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (0.307 g) and $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ (0.15 g) in 20 mL of distilled water was added, dropwise, 8 mL of glacial acetic acid containing 0.04 g of adenine that was stirred for 1 h at room temperature. The filtrate was kept for 4 days at room temperature and then colourless block crystals suitable for (1) were collected in about 40% yield (based on Mo). Elem. Anal. Found: Mo, 33.65; Al, 1.53; C, 14.87; H,

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2.96 and N, 16.23; (%). Calcd: Mo, 33.68; Al, 1.58; C, 14.05; H, 2.48 and N, 16.39(%).

2.3 X-ray crystallography

Compound (1) was stable under ambient conditions and colourless single crystal was carefully selected and glued on the end of a glass capillary. X-ray diffraction data were collected in the range of $2.2 < \theta < 27$ on a Enraf–Nonius CAD-4 diffractometer, operating at 293 K with MoK α ($\lambda = 0.71073$ Å) (CAD4, Software, version 5.0, Enraf Nonius, Delft, The Netherlands, 1989). A total of 7594 reflections were measured ($-10 < h < 3$, $-12 < k < 12$, $-21 < l < 21$). The structure of 1 was solved by the Patterson method and refined by full-matrix least-squares on F^2 using the SHELXL 97 software (Sheldrick 1997, SHELXS-97). All non-hydrogen atoms were refined anisotropically. Other hydrogen atoms were not located. The details of data collection and structure refinements for this compound are listed in table 1.

3. Results and discussion

3.1 Structure description

Single-crystal X-ray analysis reveals that this material consists of one Anderson-B polyoxoanions $[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{3-}$, four adenine molecules and ten free water molecules.

A projection of the structure showing displacement ellipsoids, is presented in figure 1. From a general point

of view (figure 2), this structure can be described as a succession of an alternating organic and inorganic sheets extending along the c -direction. A purely organic sheet presents a stack in zigzag of adenine. The second is characterized by alternating water molecules and $[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{3-}$ anionic clusters. To the best of our knowledge, no analogous 3D structure consisting of Anderson-type POM building blocks and adenine bases has been reported in literature.

The polyoxoanion $[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{3-}$ is formed by close packing of oxygen atoms with Al and Mo atoms in

Table 1. Crystal structure data for 1.

Chemical formula	$\text{C}_{20}\text{H}_{46}\text{N}_{20}\text{O}_{34}\text{AlMo}_6$
Formula weight	1709.3 g mol $^{-1}$
Crystal system	Triclinic
Space group/Z	P-1/1
a (Å)	8.033(5)
b (Å)	9.960(4)
c (Å)	16.797(7)
α (Å)	73.43(3)°
β (°)	87.85(1)
γ (°)	81.47
Volume (Å 3)	1274.03
Calculated density (g cm $^{-3}$)	2.23
Absorption coefficient (mm $^{-1}$)	1.56
No. of independent reflections	5508 [$R_{\text{int}} = 0.022$]
Unic reflections included	4705
No. of refined parameters	378
Goodness-of-fit on F^2	1.02
R (anisotropic)	0.067
R_w (anisotropic)	0.199

Figure 1. An ORTEP drawing of compound 1.

Figure 2. View of three-dimensional network of the compound along the *a*-axis.

the distorted octahedral voids. A perspective view of the $[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{3-}$ anion with its numbering scheme is shown in figure 1. In this anion, the octahedral unit, AlO_6 , is surrounded by six MoO_6 groups. The six Mo atoms, forming a hexagon around Al, give overall approximate D_{3d} symmetry to the anion. Three kinds of oxygen atoms exist in this polyoxoanion according to the manner of oxygen coordination: the terminal oxygen O_t , with the molybdenum–oxygen distances of Mo–O_t , 1.698(5)–1.737(5) Å; central oxygen (O_c) linked to two molybdenum atoms and the aluminum atom, with the molybdenum–oxygen distances of Mo–O_c , 2.280(4)–2.317(4) Å; the bridging oxygen (O_b) common to two molybdenum octahedra, with the molybdenum–oxygen distances of Mo–O_b , 1.909(4)–1.958(5) Å. These values are similar to those found in other compounds (An *et al* 2004, 2005; Xiao *et al* 2005). The Mo–Mo distances lie in the 3.310(2)–3.338(2) Å range. The Al–Mo distances are in the 3.312(2)–3.327(7) Å ranges. In the crystal structure, central Al–O distances vary from 1.904(5) to 1.910(5) Å. The bond angles of $\text{O–Al–O}_{\text{cis}}$ range from 83.8(2)° to 96.2(2)° and $\text{O–Al–O}_{\text{trans}}$ is 180°. The bridging oxygen atoms around the Al^{3+} ion are protonated, which makes the anion become both the acceptor and the donor of hydrogen bond. The bond lengths within the anion are listed in tables 2 and 3.

BVS calculations (Softbv web page by Prof. Stefan Adams, <http://kristall.uni.mki.gwdg.de/softbv>) revealed that all the molybdenum atoms have valence sums ranging from 5.970 to 6.045, with an average value of 6.001, close to the ideal value of 6 for Mo^{VI} . The calculated average value of aluminum (+III), oxygen (–II) atoms are, respectively 3.071 and 1.970.

Four amine molecules, corresponding to two crystallographically independent moieties are inserted between layers of water molecules. As listed in table 4, the adenine base associated into dimers by N–H...N hydrogen bonds (figure 3). These dimers are further hydrogen bonded to $\text{Ow}(3)$ and $\text{Ow}(5)$ in order to form an unprecedented 1D chain. The typical hydrogen bonds are $\text{Ow}(3)\dots\text{N}(11)$, 2.504 Å and $\text{N}(12)\dots\text{Ow}(5)$, 1.987 Å. In fact, 1D Anderson-type POM building blocks were previously reported such as the $[(\text{Na}(\text{H}_2\text{O})_2(\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}))_n]^{n-}$ (Thabet *et al* 2012), $[(\text{H}_2\text{O})_{14}\text{Cd}_3(\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18})_2]$ (An *et al* 2009), $[(\text{H}_2\text{O})_6\text{Dy}(\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18})]$ (Xiao *et al* 2005) chains in which the polyanions are linked by Na^+ , Cd^{2+} and Dy^{3+} ions, respectively. However, to the best of our knowledge, this is a rare example where polyanions coordinate with organic ligand without introduction of the metal cations to generate such polymeric 1D structure.

In the 1D chain, there exists striking π – π interactions between two adjacent adenine molecules with the average distance of aromatic units, 3.661 Å, which makes the chains more stable (figure S1). Finally, these chains are linked up together to form a 3D supramolecular network via strong hydrogen-bonding interactions among free water molecules and central and terminal oxygen atoms of polyoxoanion.

By comparison with the tautomeric forms of adenine (Taylor 1973; Hingerty *et al* 1981; Mohamed *et al* 2009), it can be assumed that both organic molecules adopt the N(5)H-amino configuration: the angles at N(4) of the present compound and all others in references agree well with the average value, 102.6°, for an unprotonated N(4), but the angles at N(5) are all between 106.4 and 108.1° for a protonated N(5). The protonation of

Table 2. The final atomic coordinates and equivalent temperature factors for 1.

Atom	X	Y	Z	Ueq
Mo1	0.107(5)	0.268(4)	0.182(1)	0.027(4)
Mo2	0.235(6)	0.495(7)	−0.166(6)	0.02(4)
Mo3	0.349(2)	0.269(3)	0.017(9)	0.023(4)
Al	0	0.5	0	0.019(2)
O1	0.064(4)	0.301(7)	0.042(7)	0.022(3)
O2	0.027(2)	0.503(3)	0.111(0)	0.022(0)
O3	−0.231(3)	0.496(3)	0.029(2)	0.021(8)
O4	0.318(7)	0.301(0)	0.125(0)	0.028(6)
O5	0.271(4)	0.303(5)	−0.095(0)	0.025(6)
O6	0.137(0)	0.690(0)	−0.186(0)	0.029(8)
O7	0.161(7)	0.299(0)	0.271(5)	0.050(8)
O8	0.124(5)	0.087(8)	0.204(3)	0.045(2)
O9	0.368(1)	0.090(0)	0.044(7)	0.040(3)
O10	0.550(1)	0.311(5)	0.001(6)	0.035(5)
O11	0.437(1)	0.528(5)	−0.183(3)	0.041(3)
O12	0.175(4)	0.457(0)	−0.253(9)	0.038(4)
N11	0.551(9)	0.169(6)	0.655(2)	0.040(6)
N21	0.692(3)	0.040(3)	0.564(1)	0.122(0)
N31	0.354(0)	0.373(3)	0.601(9)	0.097(5)
N41	0.415(7)	0.342(5)	0.432(1)	0.041(3)
N51	0.605(9)	0.156(6)	0.427(2)	0.049(1)
N12	0.014(3)	0.209(8)	0.698(0)	0.044(3)
N22	0.140(7)	0.085(2)	0.614(5)	0.085(6)
N32	−0.184(1)	0.422(0)	0.656(3)	0.086(8)
N42	−0.126(2)	0.382(3)	0.478(3)	0.039(3)
N52	0.056(8)	0.192(5)	0.471(9)	0.034(6)
C11	0.6506(2)	0.060(7)	0.636(1)	0.089(5)
C21	0.597(1)	0.150(3)	0.507(7)	0.065(4)
C31	0.478(9)	0.267(7)	0.510(0)	0.064(1)
C41	0.462(1)	0.266(3)	0.593(4)	0.094(2)
C51	0.500(4)	0.267(9)	0.385(3)	0.039(7)
C12	0.115(0)	0.097(6)	0.689(4)	0.069(5)
C22	0.048(4)	0.191(2)	0.553(5)	0.042(7)
C32	−0.066(5)	0.309(8)	0.557(7)	0.043(5)
C42	−0.080(4)	0.316(1)	0.641(6)	0.070(1)
C52	−0.046(2)	0.308(3)	0.429(6)	0.036(4)
OW1	0.250(4)	0.622(5)	0.165(7)	0.058(6)
OW2	0.390(4)	0.861(0)	−0.217(9)	0.068(6)
OW3	0.420(6)	−0.155(8)	0.173(6)	0.160(0)
OW4	−0.141(3)	0.130(0)	0.014(2)	0.059(3)
OW5	0.057(0)	0.137(9)	−0.129(3)	0.037(0)
OW6	0.204(7)	0.090(5)	−0.154(9)	0.055(7)

Table 3. Selected bond lengths (Å) of 1.

Mo1–O7	1.699(4)	Al–O3 ⁱ	1.907(3)
Mo1–O8	1.729(6)	N11–C41	1.341(8)
Mo1–O4	1.941(11)	N11–C11	1.363(3)
Mo1–O6i	1.949(9)	N21–C11	1.319(6)
Mo1–O1	2.301(7)	N21–C21	1.385(3)
Mo1–O2	2.308(7)	N31–C41	1.311(8)
Mo2–O12	1.721(5)	N41–C51	1.329(8)
Mo2–O11	1.696(3)	N41–C31	1.381(6)
Mo2–O5	1.934(2)	N51–C51	1.309(7)
Mo2–O6	1.919(1)	N51–C21	1.381(6)
Mo2–O3i	2.330(7)	N12–C42	1.318(4)
Mo2–O2i	2.276(7)	N12–C12	1.279(5)
Mo3–O9	1.697(2)	N22–C12	1.296(1)
Mo3–O10	1.722(3)	N22–C22	1.389(8)
Mo3–O4	1.913(5)	N32–C42	1.327(3)
Mo3–O5	1.940(9)	N42–C52	1.333(8)
Mo3–O1	2.311(2)	N42–C32	1.387(3)
Mo3–O3i	2.305(2)	N52–C52	1.352(5)
Al–O1	1.897(3)	N52–C22	1.363(9)
Al–O1 ⁱ	1.897(2)	C21–C31	1.402(6)
Al–O2	1.896(9)	C31–C41	1.399(5)
Al–O2 ⁱ	1.896(9)	C22–C32	1.405(7)
Al–O3	1.907(3)	C32–C42	1.419(9)

Figure 3. Geometry and environment of the amine molecules in $\text{H}(\text{C}_5\text{N}_5\text{H}_3)_2(\text{C}_5\text{N}_5\text{H}_6)_2[\text{Al}(\text{OH}_6)\text{Mo}_6\text{O}_{18}]\cdot 10\text{H}_2\text{O}$.

the adenine base on the N(1) sites are reflected in the change in bond angle. The angle C(21)–N(11)–C(41) at the unprotonated N(11) atom is $118.42(2)^\circ$, while in the case of the protonated N(12) atom, the angle, C(22)–N(12)–C(42), is $125.14(2)^\circ$. To our knowledge, this configuration is not very frequent in the solid state. These assumptions are also supported by the hydrogen bonding scheme: besides the interactions between A and B, N31...N42, N32...N41 and N51...N22, N52...N21, these organic bases exchange hydrogen bonds with two water molecules at N(1).

The abundant water molecules which are significant elements in our structure, act as good candidates of bonds. They form several hydrogen bonds with the nearest

lattice water molecules. $[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{3-}$ clusters and adenine molecules are used to obtain the 3D supramolecular structure. The typical hydrogen bonds between the polyoxoanions are shown in figure S2(a); neighbouring polyoxoanions are connected by the water bridge. In figure S2(b), the adenine bases are bridged by water molecules.

3.2 Infrared spectroscopy

IR spectrum of compound 1 is shown in figure S3. Both characteristic peaks for the Anderson polyoxoanions and the adenine molecules can be observed. The characteristic peaks at $946, 892, 800, 659, 579$ and 451 cm^{-1} for 1 could

Table 4. Selected hydrogen bonds.

D–H...A	D–H	H...A	D...A	⟨DHA⟩
O1–H1...OW4	0.80	1.89	2.69	170.8
O2–H2...OW1	0.81	1.82	2.61	161.1
O3–H3...O10	0.75	2.11	2.86	169.5
N31–H4...N42	0.806	1.893	2.692	170.83
N51–H6...N22	1.101	2.091	3.111	152.78
N12–H7...OW5	1.003	1.987	2.791	135.34
N32–H9...N41	1.061	2.000	2.869	136.96
N52–H11...N21	1.032	2.075	3.039	154.38
OW1–H1W1...OW5	0.801	2.516	3.102	131.19
OW1–H1W1...OW4	0.801	2.602	3.354	157.07
OW1–H2W1...OW3	0.982	1.870	2.800	156.84
OW1–H2W1...OW3	0.982	1.870	2.800	156.84
OW2–H1W2...O6	0.797	2.085	2.785	146.50
OW2–H1W2...O11	0.797	2.586	3.157	129.91
OW2–H2W2...O4	0.939	1.953	2.864	162.91
OW3–H1W3...OW1	0.884	2.163	2.800	128.54
OW3–H2W3...OW6	0.850	2.457	3.161	140.74
OW3–H2W3...N11	0.850	2.504	2.838	130.32
OW4–H1W4...OW5	0.901	1.959	2.819	159.10
OW4–H1W4...OW6	0.901	2.170	2.824	128.95
OW4–H2W4...OW5	1.052	1.997	2.821	132.93
OW5–H1W5...O5	0.648	2.121	2.731	157.33
OW5–H2W5...N12	0.710	2.316	2.791	125.74
OW6–H2W6...OW2	0.961	2.390	2.989	120.00

be ascribed to the Anderson polyoxoanions, which are similar to those reported in literature (Shivaiah *et al* 2002; Drewes *et al* 2004; An *et al* 2005b; Gao *et al* 2006). The bands in the range of 1100–1987 cm^{−1} could be ascribed to the stretching vibration modes of $\nu(\text{C–N})$ and $\nu(\text{C–C})$ groups. The presence of strong band at 1623 cm^{−1} corresponds to bending vibrations of the OH groups of the water molecules. A broad band extending from 3300 to 2390 cm^{−1} is observed in the IR spectrum. This broad band must be due to the symmetric and asymmetric stretching modes of NH, CH and OH.

3.3 UV–Visible spectra

UV–Vis spectrum is recorded in aqueous solution at a concentration of 10^{−3} mol L^{−1}. The resulting spectrum is shown in figure S4. UV spectra have two absorption bands, the strong absorption band at ca. 215 nm is attributed to the charge transfer of Mo–Ot and the absorption band at ca. 268 nm is attributed to that of Mo–Ob and Mo–Oc (An *et al* 2005, 2006, 2007).

3.4 Thermal behaviour

Figure S5 shows both TG and DTA thermograms of 1. TG curve of the title compound shows that three steps occur for the loss of water molecules. First step occurs in the range of 40–85 °C (weight loss, obs. 2.38%, cal. 2.09%) corresponding to the loss of two H₂O molecules; second step: 85–175 °C (weight loss, obs. 5.52%,

cal. 5.24%) corresponding to the loss of five H₂O molecules; and the third step: 175–275 °C (obs. 6.14%, cal. 6.29%) corresponding to the loss of six H₂O molecules. Ten water molecules are the lattice water molecules and the rest water molecules are the so-called constituting water molecules corresponding to the –OH groups in the anion. This dehydration is related to the first three endothermic peaks on the DTA curve at 64, 132 and 250 °C. Compound 1 can lose non-coordinated water molecules in part at room temperature. The error is due to the fact that crystal easily loses lattice H₂O at room temperature. The following stage representing a set of endotherms from 275 to 450 °C is assigned to the degradation of the organic cations. This progressive pyrolysis is indicated, in the TGA curve, by a continuous weight loss.

4. Conclusions

Recently, studies of polyoxometalates have been improved, which show that the POMs get more and more attention. We have successfully synthesized a new compound based on the Anderson-type [Al(OH)₆Mo₆O₁₈]^{3−} polyoxoanion building block by slow evaporation at room temperature. The studies of the title compounds not only afford a preparation route concerning the [Al(OH)₆Mo₆O₁₈]^{3−}, but also expand the family of hybrid materials from a structural point of view.

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Supplementary material

CCDC 886339 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif, by e-mailing 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.

Supplementary material pertaining to this article is available on the Bulletin of Materials Science website (www.ias.ac.in/maternal).

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