

Supramolecular assembly based on a heteropolyanion: Synthesis and crystal structure of $\text{Na}_3(\text{H}_2\text{O})_6[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 2\text{H}_2\text{O}$

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Abstract. Synthesis and structural characterization of a polyoxometalate compound $\text{Na}_3(\text{H}_2\text{O})_6[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 2\text{H}_2\text{O}$ (**1**) have been described. Compound **1** exhibits three-dimensional network structure in the solid state, which is assembled by Anderson-type heteropolyanions, $[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]_n^{3n-}$, as building blocks sharing sodium cations. **1** possesses “sinuous” channels occupied by supramolecular water dimers as guests. Anderson anions, sodium-coordinated water and crystal water are additionally involved in an intricate hydrogen-bonding network in the crystal of **1**.

Keywords. Anderson-type heteropolyanions; sodium cation as linkers; three-dimensional network structure; guest supramolecular water dimers; hydrogen-bonding interactions.

1. Introduction

Synthesis of new materials, formed via supramolecular assemblies based on metal oxide-based well-defined building units and with new physical properties in the solid state, is a challenging task in modern inorganic chemistry.¹ Polyoxometalates are interesting in this respect, as they can form metal oxide-based building blocks which can be linked to network structures with cavities and pores.² In recent years, polyoxometalates are intensely being explored because of their applications as new materials, structural aesthetics,² catalysts³ and biologically active compounds.⁴ Heteropolyanions of general formulae $[\text{X}^{n+}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{(6-n)-}$ (protonated form; X = heteroatom, e.g. Al^{3+} , Cr^{3+} , Co^{3+} , Cu^{2+}) and $[\text{X}^{n+}\text{Mo}_6\text{O}_{24}]^{(12-n)-}$ (non-protonated form; X = heteroatom, e.g. Te^{5+} , I^{7+}), known as Anderson-type anions,⁵ constitute a special class of polyoxometalate compounds have been of increasing interest.⁶ A number of Anderson anions have been reported and some of them were structurally characterized.^{7,8} They are mostly discrete cluster-like structures; but reports of compounds, where Anderson-type heteropolyanions are linked to extended structures, are very few.⁹ We report here the synthesis and characterization of a three-dimensional coordination

polymer, $\text{Na}_3(\text{H}_2\text{O})_6[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 2\text{H}_2\text{O}$ (**1**), which includes guest water dimers in its ‘S’-shaped channels. A preliminary report of this result has already appeared.¹⁰ We describe here the detailed structural description of **1**, including the complicated hydrogen-bonding network that involves the –OH groups of Anderson anions, sodium-coordinated and the guest water molecules.

2. Experimental section

Double-distilled water was used throughout. All other chemical reagents were of analytical grade purity. TGA analyses were performed on a Shimadzu DTG-50 thermal analyser under nitrogen atmosphere at a scan rate of 1°C min^{-1} . Powder X-ray diffraction spectra were recorded using Cu-K α ($\lambda = 1.54 \text{ \AA}$) radiation on a Phillips PW 3710 diffractometer at a scanning speed of 2.4°min^{-1} . The number of Al and Na sites, revealed by single-crystal X-ray structure analysis, is consistent with the result of EDAX analysis (Philips XL 30). The differential scanning calorimetry (DSC) experiments were conducted using a Perkin–Elmer DSC-4 calorimeter at a heating rate of $10^\circ\text{C min}^{-1}$. Hydrogen was analysed using a Perkin–Elmer model 240C elemental analyser. Infrared spectra were recorded by using KBr pellets and a Jasco-5300 FT-IR spectrophotometer.

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2.1 Synthesis of $\text{Na}_3(\text{H}_2\text{O})_6[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \times 2\text{H}_2\text{O}$ (**1**)

To a solution of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (1.5 g, 6.21 mmol) in 25 ml of water which was acidified with 10 ml of acetic acid (100%), $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (3.5 g, 14.46 mmol) was added and dissolved by stirring; the pH of the resulting clear solution was adjusted to 1.8 by the dropwise addition of 35% hydrochloric acid. The reaction mixture was kept at 20–22°C in an open 100 ml conical flask. After one week the precipitated white crystals of **1** were filtered, washed with water and dried at room temperature in air. Yield: 2.0 g (68% based on Mo).

Selected data for 1: IR (KBr pellet) ($\bar{\nu}$, cm^{-1}): 1620 m { $\mathbf{d}(\text{H}_2\text{O})$ }, 947s/920s { $\mathbf{n}(\text{Mo}=\text{O})$ }, 845w, 650s, 574m, 530w, 447w, 390w. Raman (KBr matrix) ($\bar{\nu}$, cm^{-1}): 958s, 890m, 568w, 362m, 224s. Anal. Calc. for $\text{AlH}_{22}\text{Mo}_6\text{Na}_3\text{O}_{32}$ (1205.77): Na, 5.72; H, 1.84%. Found: Na, 5.69; H, 1.79%. The number of Al and Na sites revealed by X-ray analysis is consistent with the result of EDAX analysis, which gives an average value of Mo : Al \approx 6.0 and Mo : Na \approx 2.0.

2.2 Removal of guest and coordinated water molecules

A freshly prepared sample of **1** (0.25 g) was heated at 125°C in a conventional oven for 2 h. The measured weight loss (0.021 g) was equivalent to the loss of 6 water molecules per formula unit (calcd 0.0224 g). This supports the formulation of the desolvated compound as $\text{Na}_3(\text{H}_2\text{O})_2[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]$. This is in agreement with the elemental analysis. Anal. Found (calcd): Na, 6.35 (6.28); H, 1.05 (0.92)%. This result is consistent with the first weight loss in the TGA curve (*vide infra*). The X-ray powder diffraction pattern of $\text{Na}_3(\text{H}_2\text{O})_2[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]$ reveals a new phase compared to that of **1**. This is not surprising because once sodium-coordinated monodentate water molecules are gone, some rearrangement of sodium coordination takes place with the formation of a new phase. This is consistent with the fact that compound **1** on heating shows an endothermic phase transition (80–125°C; peak 94°C) in the DSC curve. The enthalpy change of this transformation was estimated to be 208 kJ mol^{-1} by differential scanning calorimetry. Although it is a new phase, its IR spectrum is quite similar to that of **1**, suggesting a similar type of framework in $\text{Na}_3(\text{H}_2\text{O})_2[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]$. Compound **1** could not be regenerated from this new phase (as indicated by X-ray

powder diffraction studies) on resolution at room temperature. The resolution experiment was performed in a vacuum desiccator containing the dehydrated sample $\text{Na}_3(\text{H}_2\text{O})_2[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]$ and water separately.

2.3 Thermogravimetric analysis (TGA)

TGA performed on **1** showed a sharp weight loss (8.5%) at $\sim 50^\circ\text{C}$ and this corresponded to the loss of 5.7 water molecules per formula unit. Then the lower hydrate remained stable up to 180°C. Another weight loss (7.6%) was observed between 180 and 300°C, suggesting the loss of five water molecules (calcd 7.46%). The second weight loss occurred with the decomposition of the Anderson anion because five water molecules, associated with the second loss, include 6 OH^- groups attached to the central aluminum. No attempt was made to identify the products of decomposition. TGA curve confirmed the loss of a total of 11 water molecules (total weight loss: 16.55%; calcd 16.42%) per formula unit.

2.4 X-ray crystallographic analysis for compound **1**

Crystals of **1** were removed from the mother liquor and immediately cooled to 183(2) K on a Bruker AXS SMART diffractometer (three circle goniometer with 1 K CCD detector, Mo-K α radiation, graphite monochromator). Hemisphere data were collected in ω at 0.3° scan width at a detector distance of 5 cm. An empirical absorption correction using equivalent reflections was performed with the program SADABS. The structure was solved using SHELXS-97¹¹ and refined using SHELXL-97¹² to $R1 = 0.0215$, $wR2 = 0.0536$ for 9885 reflections with $I > 2s(I)$. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located from difference Fourier maps and refined isotropically. However, the hydrogen atoms on O(46), O(47) and O(48) became unstable during refinement, and therefore the corresponding O–H distances were constrained at 0.96 Å. This original cell was transformed to a smaller cell ($a = 6.4776(2)$ Å, $b = 10.8548(3)$ Å, $c = 10.8549(3)$ Å; $\mathbf{a} = 109.3800(10)^\circ$, $\mathbf{b} = 95.43^\circ$, $\mathbf{g} = 106.79^\circ$; $V = 673.80(3)$ Å³) based on the unit cell dimension of the known similar compound $\text{Na}_3[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 8\text{H}_2\text{O}$ (ref. 9a: $a = 10.9080(4)$ Å, $b = 0.9807(4)$ Å, $c = 6.4679(2)$ Å; $\mathbf{a} = 107.594(2)^\circ$, $\mathbf{b} = 84.438(2)^\circ$, $\mathbf{g} = 112.465(3)^\circ$) but the structure, obtained using a smaller cell, manifested disorder of

sodium and one oxygen atom. The sodium atoms are situated a little apart from the “ideal” positions and that is why the larger cell describes the situation more precisely. The crystallographic data are summarized in table 1. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum, Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-415139.

3. Results and discussion

The synthesis of **1** was performed at relatively low pH value in contrast to the preparations of other Anderson type compounds reported earlier.^{7,8} Compound **1** was prepared by treating an acidified aqueous solution of AlCl₃ with sodium molybdate. White crystals of **1** were characterized by elemental analysis, IR spectroscopy, thermogravimetry and unambiguously by single crystal X-ray structure analysis.

Table 1. Crystal data and structure refinement for **1**.

Formula	H ₂₂ AlMo ₆ Na ₃ O ₃₂
Formula weight	1205.77
Crystal class	Triclinic
Space group	<i>P</i> 1
<i>Z</i>	3
Cell constants	
<i>a</i>	12.0618(3) Å
<i>b</i>	13.1570(4) Å
<i>c</i>	14.1563(4) Å
<i>a</i>	80.7850(10)°
<i>b</i>	75.2660(10)°
<i>g</i>	68.9210(10)°
<i>V</i>	2021.43(10) Å ³
<i>m</i>	2.913 mm ⁻¹
Crystal size (mm)	0.20 × 0.18 × 0.08
<i>D</i> _{calc}	2.971 g/cm ³
<i>F</i> (000)	1728
Theta range	
for data collection	1.66 to 29.99°
Limiting indices	-16 ≤ <i>h</i> ≤ 16, -18 ≤ <i>k</i> ≤ 18, -19 ≤ <i>l</i> ≤ 19
Reflections collected	28895
Unique reflections	11686 (<i>R</i> _{int} = 0.0187)
Refinement method	Full-matrix least-squares on <i>F</i> ²
Number of parameters	679
Goodness-of-fit on <i>F</i> ²	1.058
Final <i>R</i> indices (<i>I</i> > 2 <i>s</i> (<i>I</i>))	<i>R</i> 1 = 0.0215, <i>wR</i> 2 = 0.0536
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0279, <i>wR</i> 2 = 0.0562
Largest diff. peak and hole (eÅ ⁻³)	1.453 and -1.013

The crystallographic unit cell contains 1.5 molecules as an asymmetric unit (figure 1). This shows the coordination environment of the Anderson anion, [Al(OH)₆Mo₆O₁₈]³⁻ which coordinates sodium cation via Mo=O terminal oxygen atoms. The Anderson heteropoly anion consists of seven edge-shared octahedra, six of which are Mo-octahedra arranged hexagonally around the central octahedron containing heterometal ion (for example Al³⁺ in the present case) at the centre (figure 1). Bond lengths and bond angles within the Anderson anion of **1** (table 2) are consistent with values found for other Anderson anions. The crystal structure of **1** shows three-dimensional framework having “sinuous” channels (figure 2), which is constructed by Anderson-type anions as building blocks sharing sodium cations (figure 1). The three-dimensional framework is formed by stacking of two-dimensional layers (figure 3a) that are linked laterally by sodium-water chains running in between these layers (figure 3b) through the coordination of Mo=O terminal oxygen atoms of Anderson anions. In the layer (figure 3a), each polyanion acts as a hexadentate ligand co-ordinating four Na⁺ ions around it through six terminal oxygen atoms of four MoO₄(OH)₂ octahedra. In other words, the co-ordination site of each Na⁺ ion in the layer is a distorted octahedron formed by two terminal oxygen atoms in

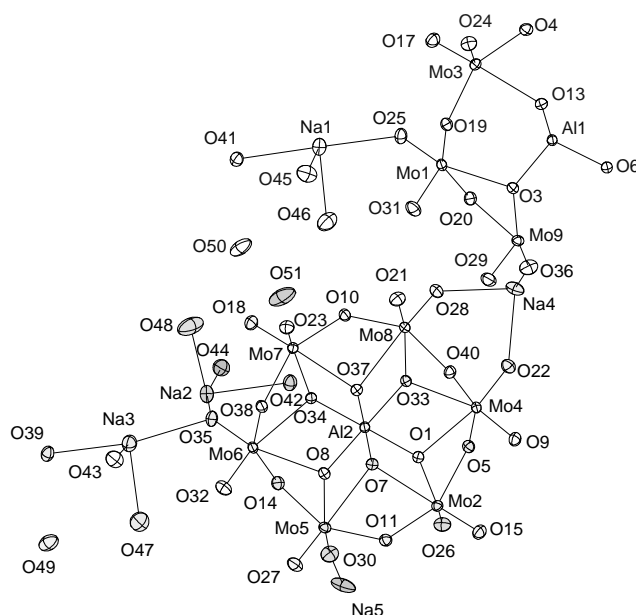


Figure 1. Asymmetric unit (as 1.5 molecules) in **1**. Sodium coordination of the Anderson anion via terminal oxygen atoms on molybdenum is shown. Thermal ellipsoids at 50% probability.

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

<i>Bond lengths (Å)</i>			
Mo(1)–O(31)	1.7020(14)	Mo(1)–O(25)	1.7209(14)
Mo(1)–O(3)	2.2929(13)	Mo(2)–O(15)	1.6987(14)
Mo(2)–O(26)	1.7208(14)	Mo(2)–O(11)	1.9152(13)
Mo(3)–O(24)	1.7239(14)	Mo(3)–O(4)	1.9064(13)
Mo(4)–O(22)	1.7053(14)	Mo(4)–O(9)	1.7194(14)
Mo(5)–O(30)	1.6981(14)	Mo(5)–O(27)	1.7072(14)
Mo(6)–O(14)	1.9192(13)	Mo(6)–O(38)	1.9401(13)
Mo(7)–O(18)	1.7042(14)	Mo(7)–O(23)	1.7197(13)
Mo(8)–O(21)	1.7082(14)	Mo(8)–O(28)	1.7116(14)
Mo(9)–O(29)	1.7044(14)	Mo(9)–O(36)	1.7126(14)
Al(1)–O(3)	1.8904(13)	Al(1)–O(6)	1.8947(13)
Al(2)–O(1)	1.8930(14)	Al(2)–O(8)	1.8938(14)
O(25)–Na(1)	2.4339(16)	O(28)–Na(4)	2.4707(14)
O(35)–Na(3)	2.5167(16)	O(36)–Na(4)	2.3008(14)
Na(1)–O(46)	2.3620(18)	Na(1)–O(45)	2.430(2)
Na(2)–O(44)	2.417(2)	Na(2)–O(42)	2.4506(17)
<i>Bond angles (°)</i>			
O(31)–Mo(1)–O(25)	105.64(7)	O(31)–Mo(1)–O(19)	98.00(7)
O(25)–Mo(1)–O(19)	99.88(6)	O(31)–Mo(1)–O(20)	99.48(6)
O(15)–Mo(2)–O(11)	98.89(6)	O(26)–Mo(2)–O(11)	102.51(6)
O(17)–Mo(3)–O(24)	106.24(7)	O(17)–Mo(3)–O(4)	99.08(6)
O(24)–Mo(3)–O(4)	101.71(6)	O(17)–Mo(3)–O(19)	99.55(6)
O(30)–Mo(5)–O(14)	98.93(6)	O(27)–Mo(5)–O(14)	101.78(6)
O(32)–Mo(6)–O(35)	104.92(7)	O(32)–Mo(6)–O(14)	101.53(6)
O(18)–Mo(7)–O(10)	98.82(6)	O(23)–Mo(7)–O(10)	101.89(6)
O(21)–Mo(8)–O(28)	105.34(7)	O(21)–Mo(8)–O(40)	101.90(6)
O(29)–Mo(9)–O(20)	101.79(6)	O(36)–Mo(9)–O(20)	101.68(6)
O(29)–Mo(9)–O(3)	90.56(6)	O(36)–Mo(9)–O(3)	163.72(6)
Al(2)–O(1)–Mo(4)	104.40(6)	Mo(2)–O(1)–Mo(4)	93.72(5)
O(48)–Na(2)–Na(3)	81.95(7)	O(44)–Na(2)–Na(3)	151.50(6)
Mo(6)–O(38)–Mo(7)	115.39(7)	Mo(8)–O(40)–Mo(4)	117.16(7)

Table 3. Geometrical parameters of hydrogen bonds (Å, deg) for the near-linear water dimer and its association with host (see figure 4) in **1**.

D–H...A	<i>d</i> (D–H)	<i>d</i> (H...A)	<i>d</i> (D...A)	<(DHA)
O(49)–H(49A)O...(50)#2	0.87(4)	1.99(4)	2.843(3)	170(3)
O(49)–H(49B)...O(4)#3	0.74(4)	2.15(4)	2.815(2)	149(4)
O(39)–H(39B)...O(49)	0.86(3)	1.82(3)	2.650(2)	163(3)
O(47)–H(47A)...O(49)	1.00 ^a	1.87	2.817(3)	157.2
O(50)–H(50A)··O(46)	0.91(4)	2.18(4)	2.938(3)	141(3)
O(50)–H(50B)··O(11)#1	0.74(4)	2.08(4)	2.754(2)	150(4)
O(41)–H(41B)··O(50)	0.81(3)	1.87(3)	2.664(2)	165(3)

^aRestrained; D = donor; A = acceptor.

Atoms with additional labels #1, #2 and #3 are related by symmetry operations: #1 $x - 1, y, z$; #2 $-x, -y, -z + 1$; #3 $x - 1, y - 1, z + 1$.

Table 4. Geometrical parameters of hydrogen bonds (Å, deg) among the Anderson anions (see figure 5).

D–H...A	<i>d</i> (D–H)	<i>d</i> (H...A)	<i>d</i> (D...A)	<(DHA)
O(1)–H...O(39)#1	0.82(3)	1.81(3)	2.625(2)	174(3)
O(37)–H(37)...O(38)#3	0.80(3)	2.18(3)	2.9706(19)	168(3)
O(8)–H(8)...O(23)#3	0.76(3)	2.00(3)	2.734(2)	163(3)
O(34)–H(34)...O(42)	0.81(4)	1.84(4)	2.634(2)	170(4)
O(7)–H(7)...O(19)#2	0.82(3)	2.17(3)	2.974(2)	166(3)
O(33)–H(33)...O(24)#2	0.76(3)	1.99(3)	2.753(2)	173(3)

D = donor; A = acceptor.

Atoms with additional labels #1, #2 and #3 are related by symmetry operations: #1 $x + 1, y, z$; #2 $x, y - 1, z$; #3 $-x + 1, -y, -z + 1$.

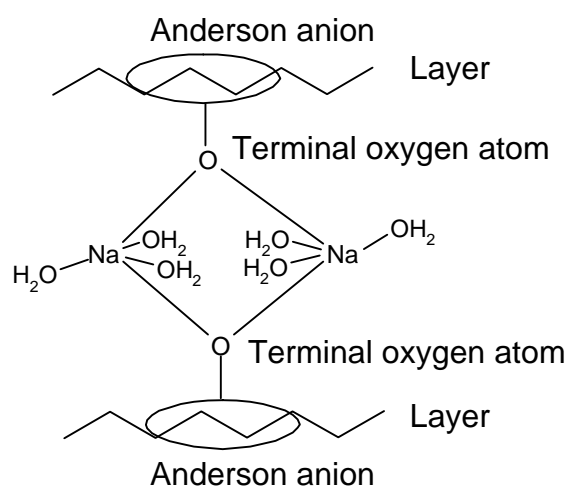


Figure 2. Illustration of the “sinuous” channels occupied by guest water molecules, including supramolecular water dimers in the polymer framework of **1**.

trans (axial) positions from two Anderson anion-units and the equatorial positions of the octahedron are co-ordinated by four terminal oxygen atoms from the two different Anderson anions. The sodium-water chain (figure 3b) can be thought to be formed as follows. Two terminal oxygen atoms of two different Anderson anions from the respective layers bridge two sodium ions, each of which is additionally coordinated to three water molecules making them co-ordinatively unsaturated (i.e. penta-coordinated sodium ions) as shown in scheme 1. The coordination saturation of each sodium ion is then achieved by inter-linking of these dimers via m_2 -type aqua bridge leading thereby to one dimensional sodium chain, which runs in between these layers (scheme 2).

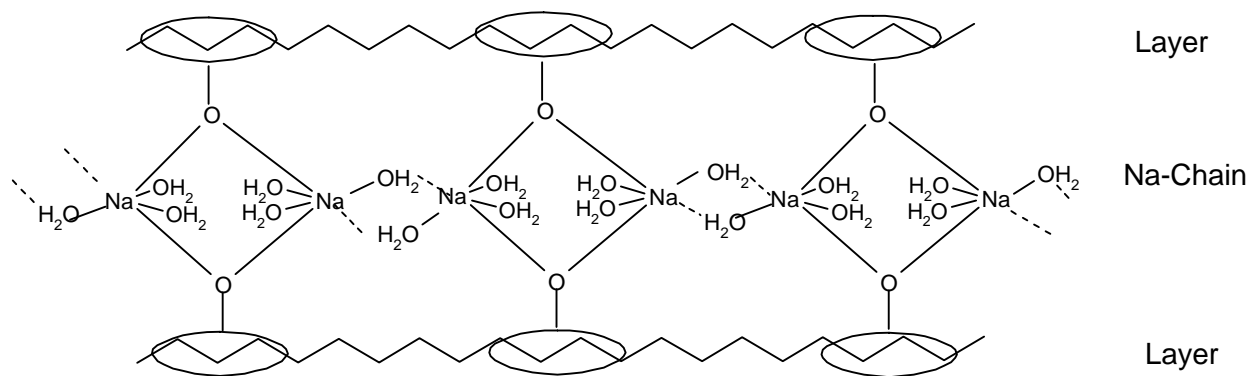
In the chain, each sodium is octahedrally coordinated and shares two edges from two opposite sides (2 O and 2 H₂O respectively, figure 3b).

The resulting three-dimensional network accommodates guest water molecules in its “S”-shaped channels (figure 2). There are total 8 water mole-



Scheme 1.

cules per formula unit of **1** (12 water molecules in the asymmetric unit consisting of 1.5 molecules). Among them, two water molecules (as guests) do not show any covalent interactions, but they are hydrogen-bonded to host channels (they are O(49), O(50) and O(51) waters in the asymmetric unit of 1.5 molecules). Whereas O(49) and O(50) water molecules arrange themselves to form a water dimer, the O(51) water molecule is hydrogen-bonded to one of the sodium-coordinated waters. The rest of the six water molecules of **1** are coordinated to sodium cations, two of which (they are O(43), O(44) and O(45) waters in the asymmetric unit) are coordinated in a m_2 -type bidentate fashion (forming sodium-water chain) and the remaining four (namely O(39), O(41), O(42), O(46), O(47) and O(48) waters in the asymmetric unit) are coordinated to sodium cations in the chain as monodentate ligands. The hydrogen-bonded water



Scheme 2.

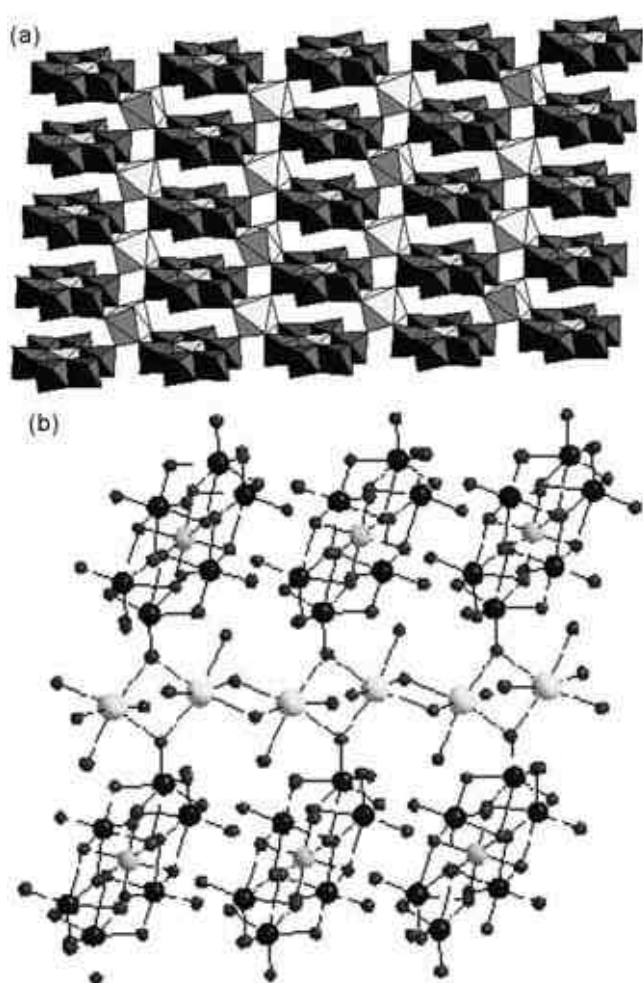


Figure 3. (a) Layer type of network formed by sodium octahedra and Anderson anions. (b) Sodium-water chain supported by the Anderson anions.

dimer (guest) and its association with host in the “S”-shaped channels (figure 2) are separately shown in figure 4. The relevant hydrogen-bonding parameters are presented in table 3.

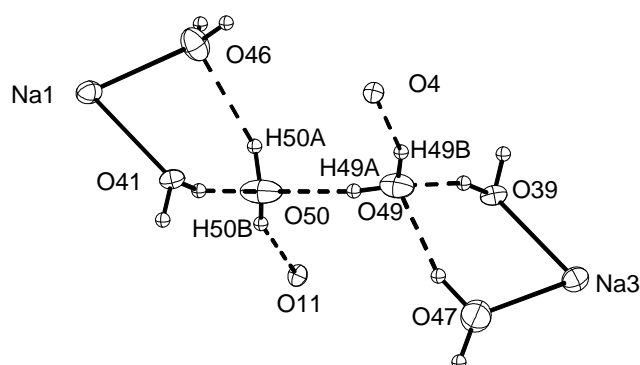


Figure 4. Representation of the supramolecular water dimer (guest) and its immediate environment (host) as found in **1** (50% thermal ellipsoids). Covalent chemical bonds are shown as solid lines and H-bonds as dashed lines. O(4) is bridging oxygen atom between two molybdenum atoms in an Anderson anion and O(11) is bridging oxygen atom of another Anderson anion (see figure 1). O(39), O(41), O(46) and O(47) are sodium-coordinated water ligands (part of the host), which show additional hydrogen bonding interactions with the guest water dimer.

In addition to these hydrogen bonding interactions between water dimer and the sodium-coordinated water molecules (figure 4), there exist O–H...O hydrogen bonds in between Anderson-anions (figure 5a) involving the coordinated hydroxide ions of the central Al(OH)₆ moiety and the peripheral terminal and bridging oxygen atoms of the Anderson heteropolyanion. More specifically, three-coordinated hydroxides on each face of the heteropolyanion (e.g. H1, H37, H8 at one face and H33, H7, H34 at the other face as shown in figure 5b) are involved in hydrogen-bonded interactions, both above and below the face of the anion, which extend into a chain. One of the hydroxyl hydrogens on both faces are hydrogen bonded to water molecule coordinated to sodium chain.

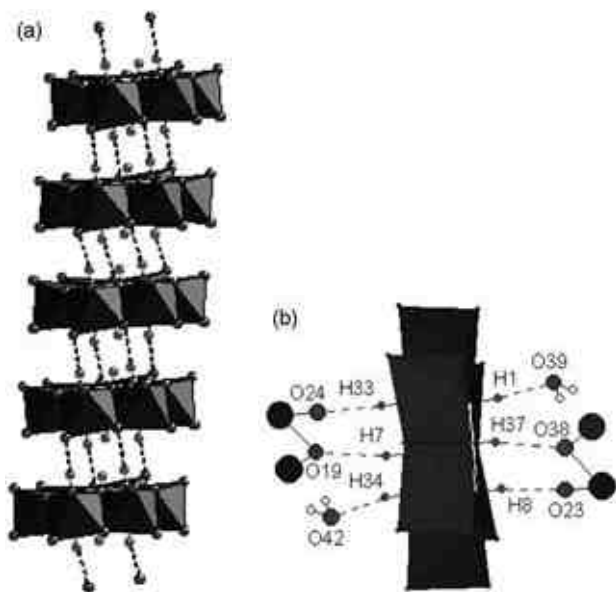


Figure 5. (a) Hydrogen bonding interactions among Anderson anions through O–H...O bonds. (b) Side view of an Anderson anion showing its hydrogen-bonding interactions that involve coordinated –OH groups of central $\{\text{Al}(\text{OH})_6\}$ moiety, bridging and terminal oxygen atoms of (adjacent) Anderson anions and sodium-coordinated waters.

4. Conclusion

In conclusion, a new type of supramolecular assembly has been described, which is formed from a heteropolyanion (as a building unit) sharing sodium cation as linker. This metal-oxide based material encapsulates supramolecular water dimers in its “sinuous” channels. An extensive hydrogen-bonding network is constructed by the interaction of the water molecules coordinated to sodium ions, the coordinated hydroxide ions of the central $\text{Al}(\text{OH})_6$ moiety of the Anderson anion, and the guest water molecules.

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