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The isolation and X-ray characterization of a new sodium heptamolybdate compound, $\text{Na}_7[\text{Mo}_7\text{O}_{24}]\text{OH}\cdot 21\text{H}_2\text{O}$

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Abstract

The sodium heptamolybdate compound (**1**) was crystallized at $\text{pH} \sim 6.9$ from an acidified sodium molybdate solution. X-ray structural analysis shows a novel empirical formula of $\text{Na}_7[\text{Mo}_7\text{O}_{24}]\text{OH}\cdot 21\text{H}_2\text{O}$ for this compound in which a complex network of ion–dipole interactions and hydrogen bonds were found to stabilize the crystal structure.

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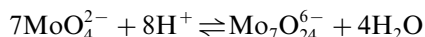
Keywords: Sodium heptamolybdate; Crystal structures; Polyoxometallates

1. Introduction

Polyoxometallate compounds are of interest due to applications in various fields such as catalysis, analytical and clinical chemistry, biochemistry and medicine [1]. The heptamolybdate polyanion in the compound $[\text{NH}_3\text{Pr}^+]\text{[Mo}_7\text{O}_{24}]\cdot 3\text{H}_2\text{O}$, for example, has been found to exhibit potent antitumor activity [2]. The structure of the $[\text{Mo}_7\text{O}_{24}]^{6-}$ polyanion is well-established [3–9]. The first compounds to be analyzed by X-ray crystallography were the ammonium [3–5] and potassium salts [6], $(\text{NH}_4)_6[\text{Mo}_7\text{O}_{24}]\cdot 4\text{H}_2\text{O}$ and $\text{K}_6[\text{Mo}_7\text{O}_{24}]\cdot 4\text{H}_2\text{O}$, but various other cations have been used to isolate the heptamolybdate ion in the solid state from an acidified molybdate solution, e.g. sodium [7], guanidinium [9], n-propylammonium [10], 4-aminopyridinium [11], n-pentylammonium [12], diethylenetriammonium [13] and tetramethylammonium [14].

The compounds are usually crystallized at $\text{pH} 5\text{--}6$ in the presence of the appropriate cation either from an acidified sodium molybdate solution or from a neutralized molybdenum trioxide solution. The degree of protonation of molybdate in these solutions corresponds to ~ 1.14 (8/7) as is required for the formation of the

heptamolybdate ion according to the reaction



Crystals of the new sodium heptamolybdate compound of which the structure is described herein were obtained from a solution at $\text{pH} \sim 6.9$ for which the calculated degree of protonation of molybdate was only 0.77. The conditions chosen for the crystallization of the compound were based on the results of computer treatment of potentiometric data [15] which indicated for the first time the presence of a polyoxoanion, possibly decameric, occurring at higher pH than the $[\text{Mo}_7\text{O}_{24}]^{6-}$ ion. The isolated compound, however, contained the typical $[\text{Mo}_7\text{O}_{24}]^{6-}$ unit, but since only seven protons are consumed in its formation, seven sodium ions are needed to balance the charges giving rise to its unique composition.

2. Experimental*2.1. Crystal preparation*

A mixture of 24.2 g (0.10 mol) $\text{Na}_2\text{MoO}_4\cdot 2\text{H}_2\text{O}$ (analytical grade) and 7.5 cm³ 10.32 M (0.774 mol) HCl were stirred in sufficient distilled water until all molybdenum trioxide that formed was dissolved and a clear solution was obtained. This solution was diluted to

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50.0 cm³ to obtain the required analytical concentrations of molybdate (2.0 M) and hydrochloric acid (1.55 M). After allowing the solution to stand for about 12 h in a covered beaker in a refrigerator a layer of colorless crystals of the compound was obtained.

2.2. X-ray crystallography

The crystal and refinement data for the sodium heptamolybdate compound (**1**) are summarized in Table 1. A suitable crystal was selected from the prepared crystalline mass of **1** and mounted on a glass fiber for diffraction data collection. Low temperature (173 K) data were collected on a Nonius KappaCCD diffractometer [16] using graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å) and scaled, reduced and corrected for Lorenz, polarization and absorption

Table 1
Crystallographic data for **1**

	1
Chemical formula	Mo ₇ O ₂₄ Na ₇ OH·21H ₂ O
Molecular weight (g mol ⁻¹)	1611.85
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	12.8407(1)
<i>b</i> (Å)	9.9279(1)
<i>c</i> (Å)	16.2632(2)
α (°)	90
β (°)	92.293(1)
γ (°)	90
Volume (Å ³)	2071.59(4)
<i>Z</i>	2
<i>D</i> _{calc} (g cm ⁻³)	2.584
Temperature (K)	173(2)
μ Mo K α (cm ⁻¹)	2.253
<i>T</i> _{min/max}	0.592/0.614
Absorption correction	empirical
Diffractometer	Nonius KappaCCD
Measurement method	φ and ω scans to fill Ewald sphere
2 θ _{min/max} (°)	2.51/52.00
Radiation	Mo K α , graphite monochromated
Crystal size (mm)	0.26 × 0.25 × 0.24
Index range	−15 ≤ <i>h</i> ≤ 15, −11 ≤ <i>k</i> ≤ 12, −18 ≤ <i>l</i> ≤ 20
Number of reflections collected	9627
Number of independent reflections	4053 (<i>R</i> _{int} = 0.0333)
Number of observed reflections	3903
Refinement	SHELXL on <i>F</i> ²
Parameters	275
Extinction correction (SHELXL)	0.0109(3)
Scattering factors	[21]
<i>S</i>	1.210
<i>R</i> ₁ (<i>F</i> _o > 2 σ <i>F</i> _o)	0.0454
<i>wR</i> ₂ (all data),	0.0867
<i>w</i> = 1/[σ^2 (<i>F</i> _o ²) + (0.0 <i>P</i>) ² + 29.706 <i>P</i>]	
where <i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)/3	

effects using DENZO-SMN [17]. The structure was solved by direct methods (SHELXS) [18] and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares calculations (SHELXL-97) [18] on *F*². Although the positions of most of the hydrogen atoms on the water molecules could be located on the difference Fourier map, bond lengths and angles showed these to be inaccurate, most likely due to slight disorder in these positions. Instead the refinement of the hydrogen atom positions in the structure of **1** was carried out as follows: a Cambridge Crystallographic Database [19] search yielded an average bond length of 0.830 Å for H–O bonds in Na⁺ coordinated water molecules at 173 K. It follows from this result that the H–H separation in each water molecule is approximately 1.288 Å. The inaccurate hydrogen atom positions found for the water molecules in **1** on the difference Fourier map were then restrained to the above-mentioned distances on each water molecule, thus allowing for refinement of the hydrogen atom positions within the intensely hydrogen bonded framework with retention of the geometry of each water molecule. Thermal parameters for all the hydrogen atoms in **1** were fixed at 1.5 times the thermal parameters of their parent atoms. ORTEP III for Windows [20] was used to generate Figs. 2–5.

3. Results and discussion

3.1. Compound in relation to solution equilibria

The distribution of species in a 2.0 M solution as a function of pH (in the range 8.0–3.5) based on a reaction model [15] pertaining to high molybdate concentration is shown in Fig. 1. It is seen that the [Mo₇O₂₄]^{6−} ion reaches its maximum concentration at pH ~ 5.6. The conditions chosen for crystallization

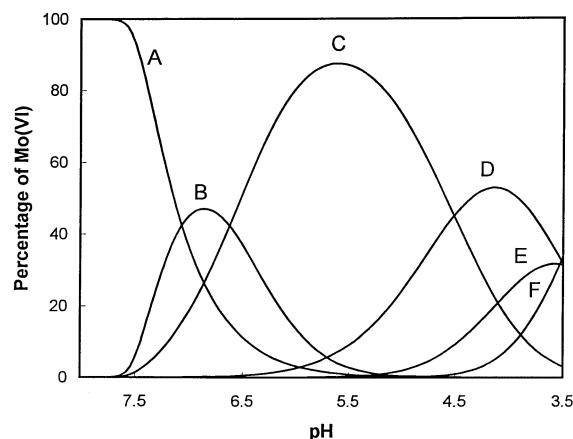


Fig. 1. Distribution of molybdenum(VI) species in a 2.0 M Na₂MoO₄ solution as a function of pH: A = [MoO₄]^{2−}; B = [Mo₁₀O₃₅]^{10−}; C = [Mo₇O₂₄]^{6−}; D = [HMo₇O₂₄]^{5−}; E = [H₃Mo₈O₂₈]^{5−}; F = [Mo₈O₂₆]^{4−}.

correspond to a solution of pH 6.9 consisting of 26.5% $[\text{MoO}_4]^{2-}$, 26.5% $[\text{Mo}_7\text{O}_{24}]^{6-}$ and 47.0% of the decameric polyanion of unknown structure, for convenience formulated as $[\text{Mo}_{10}\text{O}_{35}]^{10-}$ to comply with the reaction stoichiometry. These conditions are clearly not the most favorable for the isolation of the $[\text{Mo}_7\text{O}_{24}]^{6-}$ ion which is usually crystallized at pH 5–6 [3–14]. Therefore, depending on the solubility, one would reasonably expect the crystallization of a decameric or related polyanion with degree of protonation of ≤ 1.0 . Although the degree of protonation of the isolated compound is 1.0 the typical heptamolybdate unit is retained resulting in the unique structure described below. It may well be that the polyanion occurring in the solution converts to $[\text{Mo}_7\text{O}_{24}]^{6-}$ during crystallization because of the stability of the latter structure within the complex network of ion–dipole and hydrogen bonding interactions in the crystal. From a solution point of view the crystallization of this compound rather than the normal heptamolybdate is of importance as it can be regarded as indirect evidence for the existence of a polyanion at pH ~ 7 . Also, in view of the special role of the sodium cations in the stabilization of the structure it might be possible to isolate a different polyanion by using some other counterion.

3.2. Structural results

In the crystal, molecules of **1** pack in the centrosymmetric space group $P2_1/n$ with two formula units in the unit cell. The asymmetric unit thus contains half of the formula unit related to the other half through a twofold rotation axis. The rotation axis is located in the middle of the heptamolybdate anion and goes through one molybdenum atom (Mo4) as well as the oxygen atom of an uncoordinated water molecule (O24). Selected bond lengths and angles obtained for the well known heptamolybdate anion, $[\text{Mo}_7\text{O}_{24}]^{6-}$, found in the structure of **1** (Fig. 2) are listed in Table 2. Despite the fact that this is the first example of a low temperature (173 K) X-ray structural analysis of this moiety, these bond lengths and angles are in excellent agreement with those described in the literature [3–13].

Of greater interest in the structure of **1**, however, is the complex arrangement of the Na^+ -cations and the unusually large number of water molecules between each of the $[\text{Mo}_7\text{O}_{24}]^{6-}$ clusters. The structure of **1** exhibits a unique ratio of seven Na^+ -cations to every $[\text{Mo}_7\text{O}_{24}]^{6-}$ anion. In the absence of any other possible anions in the structure the additional negative charge required to balance the ionic charges must be provided by a hydroxide ion (OH^-), taking the place of one of the water molecules coordinated to a Na^+ -cation. However, due to the twofold symmetry observed in the structure, the position of the OH^- coordination site must be disordered over at least two possible positions.

Whether there are more than two possible sites for the OH^- anion is unclear from the structure of **1** as the hydrogen atom positions for the water molecules could not be assigned reliably from the difference Fourier map. It is, therefore, not possible to distinguish between a water molecule and an OH^- ion from the diffraction data. Regarding the twofold rotation axis in the structure as pseudo-symmetric and solving the structure in a lower symmetry space group ($P\bar{1}$) also did not yield a definite OH^- coordination position and, furthermore, gave a much poorer fit to the diffraction data. Although the position of the OH^- ion is thus not known, O19 was arbitrarily chosen as the site of the disordered OH^- coordination for the purposes of refinement of the final structure with the correct empirical formula.

Bond lengths and angles around the Na^+ -cations are listed in Table 3. The Na^+ -cations, each coordinated to six oxygen atoms in distorted octahedra, are packed in linear groups of five in zig-zag channels that are orientated obliquely with respect to the *a*- and *c*-axes (Fig. 3). Each linear group of five Na^+ -cations is formed as a result of a twofold rotation axis situated at Na1. Each group of five cations is then diagonally linked to the next by a crystallographic inversion center situated next to Na4, thus forming infinite chains of edge-shared Na^+ -cation octahedra (Fig. 4).

Due to the different types of oxygen atoms coordinated to Na^+ (μ^2 -bridged H_2O molecules, terminal coordinating H_2O molecules and Mo=O terminally bonded oxygen atoms) four different kinds of oxygen surroundings are identified for the four unique Na^+ -ions in the asymmetric unit. Na1 lies on a crystallographic twofold rotation axis and interacts with two terminal coordinating water molecules (O13 and O13') situated on the axial positions and four μ^2 -bridging H_2O molecules, coordinating through O14, O15, O14' and O15', filling the equatorial plane. Na2 is coordinated to the $[\text{Mo}_7\text{O}_{24}]^{6-}$ anion through O2. Coordinated *trans* to O2 on Na2 is a terminal coordinating water molecule (O16). The remaining oxygen coordination positions on Na2 are filled by four μ^2 -bridged H_2O molecules, coordinating through O14, O15, O17 and O18. Na3 is coordinated to the $[\text{Mo}_7\text{O}_{24}]^{6-}$ anion through O4. In a *cis* position to O4 lies a terminally coordinated water molecule (O19). The remaining three *cis* positions as well as the *trans* position, relative to O4 on Na3, are occupied by μ^2 -bridged H_2O molecules (O17, O18, O20 and O21). This oxygen conformation between Na3 and Na4 results in the kink observed in the Na^+ -ion channel at this point. Na4 is coordinated to two $[\text{Mo}_7\text{O}_{24}]^{6-}$ anions through O1 and O8 on its axial positions. Oxygen coordination positions in the equatorial plane are occupied by four μ^2 -bridged H_2O molecules coordinating to Na4 through O20, O21, O22 and O22'. Of the 12 unshared oxygen atoms in the $[\text{Mo}_7\text{O}_{24}]^{6-}$ anion, eight (O1, O2, O4 and O8 and their symmetry equiva-

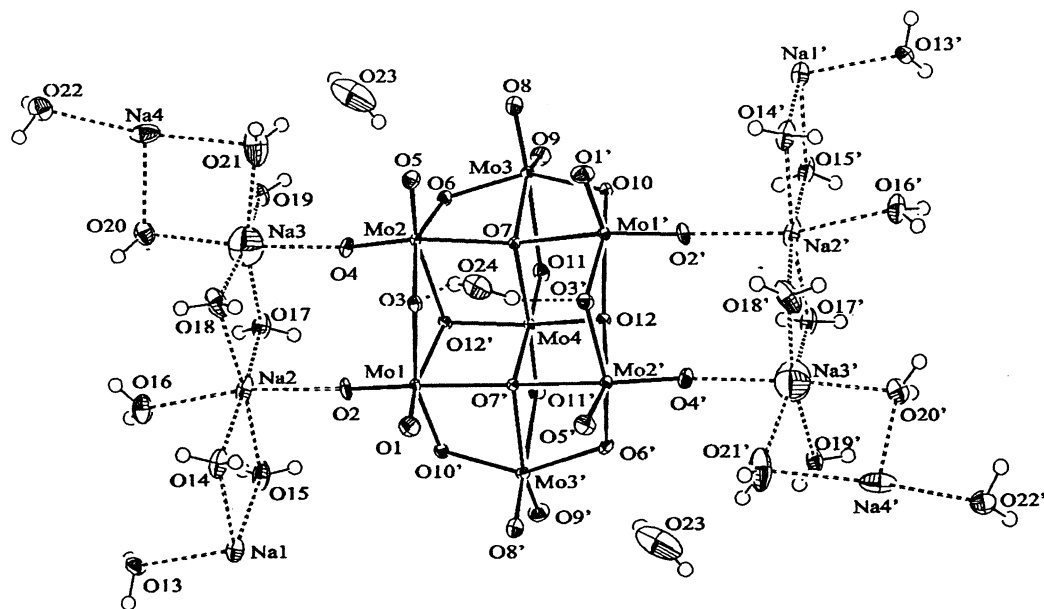


Fig. 2. ORTEP view of the formula unit of **1**, at the 50% probability level (Na1 and O23 at 1/2 site occupancy), showing numbering scheme and Na⁺ coordination positions.

Table 2
Selected bond lengths and angles for the [Mo₇O₂₄]⁶⁻ anion in **1**

Bond lengths (Å)		Bond angles (°)	
Mo1–O1	1.708(5)	O1–Mo1–O12	163.4(2)
Mo1–O2	1.715(5)	O2–Mo1–O7'	156.6(2)
Mo1–O3	1.949(4)	O3–Mo1–O10'	156.2(2)
Mo1–O7'	2.148(4)	O3–Mo2–O6	155.5(2)
Mo1–O10'	1.991(5)	O4–Mo2–O7	159.5(2)
Mo1–O12'	2.279(4)	O5–Mo2–O12'	162.2(2)
Mo2–O3	1.959(4)	O6–Mo3–O10	146.4(2)
Mo2–O4	1.715(5)	O7–Mo3–O9	148.1(2)
Mo2–O5	1.714(5)	O8–Mo3–O11	176.0(2)
Mo2–O6	1.945(5)	O7–Mo4–O11'	172.2(2)
Mo2–O7	2.185(4)	O12–Mo4–O12'	143.7(3)
Mo2–O12'	2.238(4)	O1–Mo1–O3	97.0(2)
Mo3–O6	1.952(4)	O1–Mo1–O10'	100.6(2)
Mo3–O7	2.175(4)	Mo1–O3–Mo2	114.7(2)
Mo3–O8	1.721(5)	Mo1–O12'–Mo2	93.5(2)
Mo3–O9	1.712(5)	O3–Mo2–O5	95.1(2)
Mo3–O10	1.896(4)	O5–Mo2–O6	101.4(2)
Mo3–O11	2.510(5)	Mo2–O6–Mo3	111.5(2)
Mo4–O7	2.258(4)	Mo2–O7–Mo3	95.3(2)
Mo4–O11	1.745(4)	O7–Mo3–O8	106.7(2)
Mo4–O12	1.890(4)	O8–Mo3–O9	105.1(2)
O1–Na4 ^a	2.370(6)	Mo3–O7–Mo4	101.2(2)
O2–Na2	2.366(5)	Mo3–O10–Mo1'	111.7(2)
O4–Na3	2.338(7)	Mo3–O11–Mo4	105.8(2)
O8–Na4 ^a	2.384(6)	O7–Mo4–O12'	77.6(2)
		O11–Mo4–O12'	101.7(2)
		Mo1–O1–Na4 ^a	168.4(3)
		Mo1–O2–Na2	172.6(3)
		Mo2–O4–Na3	170.3(3)
		Mo3–O8–Na4 ^a	162.4(3)

^a Interaction with Na4 in neighboring asymmetric unit.

lents) thus have Na⁺ ions coordinated to them whereas the remaining four (O5 and O9 and their symmetry equivalents) are available for hydrogen bonding interaction, as discussed below.

The heptamolybdate anions in **1** are stacked on top of each other along the *b*-axis of the unit cell (Fig. 5). The voids between the anions are filled with an uncoordinated water molecule (O24) that is hydrogen bonded to O3 and O3' of the anion. Furthermore, O16, O20, O16' and O20', coordinated to neighboring Na⁺-ion channels, form a network of four hydrogen bonds to O24 as well as two each to O11 and O11' in the adjacent heptamolybdate anion. The anions are further also linked by hydrogen bonds from the O22 (O22') and O13 (O13') water molecules that link the terminal Mo=O atoms, O5 and O9, with a series of three hydrogen bonds. A second free water molecule, represented by O23, is also incorporated in the crystal structure of **1**. O23 is situated on a special position between adjacent heptamolybdate anions (Fig. 1) and exhibits hydrogen bonding interactions with two μ^2 -bridged O21 water molecules.

Although the crystal structures of the sodium and potassium salts of the heptamolybdate anion, Na₆[Mo₇O₂₄]·14H₂O and K₆[Mo₇O₂₄]·4H₂O have been reported previously [7,6], these structures contain far fewer water molecules and do not exhibit the unique cation–anion ratio found in the structure of **1**. Also, the reported crystal structures of various ammonium salts of the heptamolybdate anion contain a maximum of seven water molecules in each formula unit and always exhibit a 6:1 or 12:2 cation to anion ratio [10–14,22,23]. The

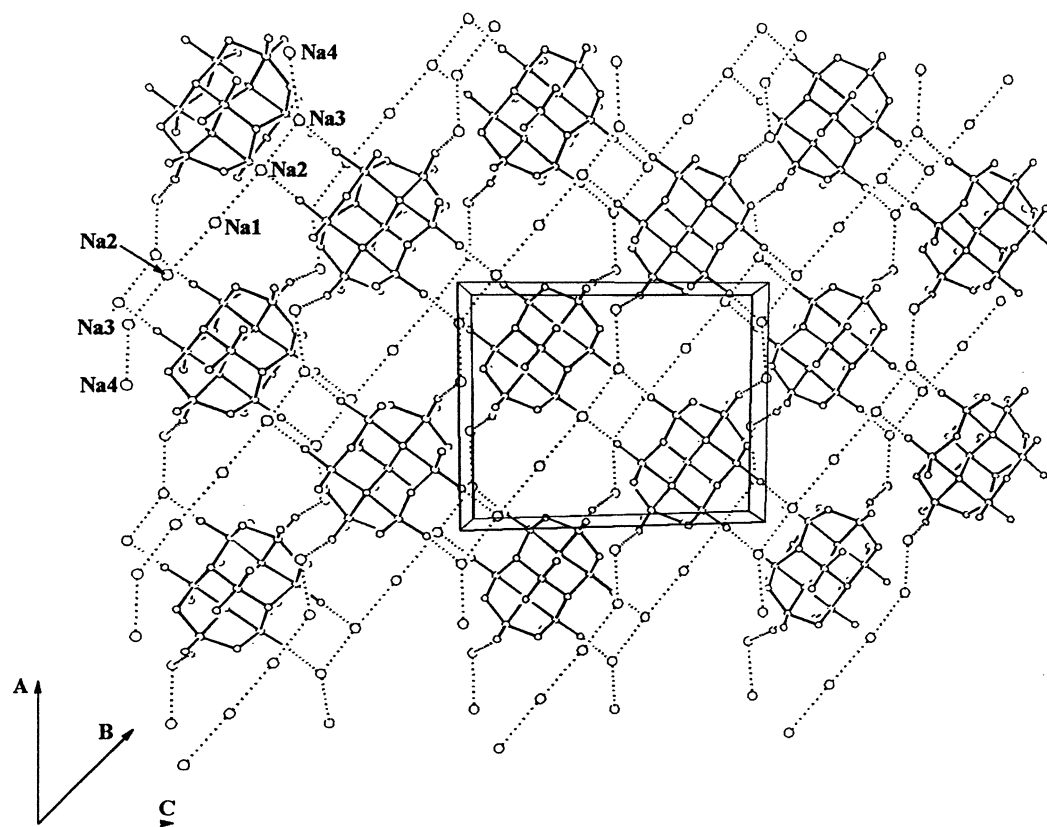


Fig. 3. Packing diagram of **1**, viewed along the *b*-axis, showing Na^+ channels (all H_2O molecules are omitted for clarity).

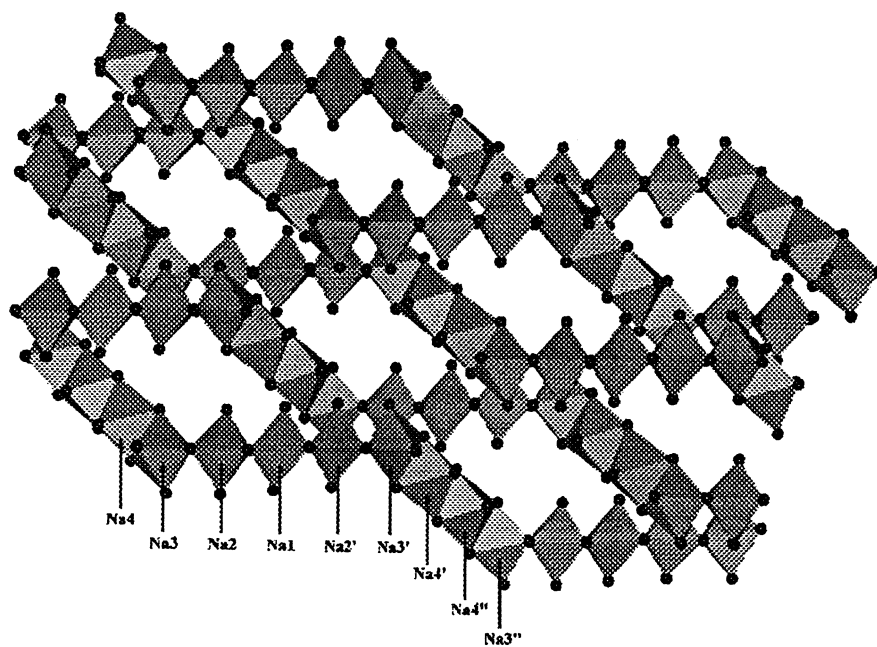


Fig. 4. Schematic illustration of the infinite chains of edge shared Na^+ -cation octahedra found in **1** (hydrogen atoms, $[\text{Mo}_7\text{O}_{24}]^{6-}$ anions and free water molecules are omitted for clarity).

Table 3
Selected bond lengths and angles for the Na⁺ ions in **1**

Bond lengths (Å)		Bond angles (°)	
Na1–O13 (terminal H ₂ O)	2.340(5)	O13–Na1–O13'	176.5(3)
Na1–O14 (μ ² -bridging H ₂ O)	2.429(6)	O15–Na1–O14'	176.4(2)
Na1–O15 (μ ² -bridging H ₂ O)	2.426(6)	O2–Na2–O16	166.6(2)
Na2–O2 (terminal Mo=O)	2.366(5)	O14–Na2–O17	173.3(2)
Na2–O14 (μ ² -bridging H ₂ O)	2.402(6)	O15–Na2–O18	174.3(2)
Na2–O15 (μ ² -bridging H ₂ O)	2.460(7)	O4–Na3–O20	170.3(3)
Na2–O16 (terminal H ₂ O)	2.367(6)	O17–Na3–O21	160.3(3)
Na2–O17 (μ ² -bridging H ₂ O)	2.370(6)	O18–Na3–O19	170.6(3)
Na2–O18 (μ ² -bridging H ₂ O)	2.424(7)	O1–Na4–O8	168.7(2)
Na3–O4 (terminal Mo=O)	2.338(7)	O20–Na4–O22'	164.3(2)
Na3–O17 (μ ² -bridging H ₂ O)	2.325(8)	O21–Na4–O22	168.0(3)
Na3–O18 (μ ² -bridging H ₂ O)	2.282(8)	O13–Na1–O13'	176.5(3)
Na3–O19 (terminal H ₂ O)	2.358(8)	O15–Na1–O14'	176.4(2)
Na3–O20 (μ ² -bridging H ₂ O)	2.355(8)	O2–Na2–O16	166.6(2)
Na3–O21 (μ ² -bridging H ₂ O)	2.427(10)	O14–Na2–O17	173.3(2)
Na4–O1 (terminal Mo=O)	2.370(6)	O15–Na2–O18	174.3(2)
Na4–O8 (terminal Mo=O)	2.384(6)	O4–Na3–O20	170.3(3)
Na4–O20 (μ ² -bridging H ₂ O)	2.350(6)	O17–Na3–O21	160.3(3)
Na4–O21 (μ ² -bridging H ₂ O)	2.564(7)	O18–Na3–O19	170.6(3)
Na4–O22 (μ ² -bridging H ₂ O)	2.382(7)	O1–Na4–O8	168.7(2)
Na1–O13 (terminal H ₂ O)	2.339(5)	O20–Na4–O22'	164.3(2)
Na1–O14 (μ ² -bridging H ₂ O)	2.429(6)	O21–Na4–O22	168.0(3)
Na1–O15 (μ ² -bridging H ₂ O)	2.426(6)		
Na2–O2 (terminal Mo=O)	2.366(5)		
Na2–O14 (μ ² -bridging H ₂ O)	2.402(6)		
Na2–O15 (μ ² -bridging H ₂ O)	2.460(7)		
Na2–O16 (terminal H ₂ O)	2.367(6)		
Na2–O17 (μ ² -bridging H ₂ O)	2.370(6)		
Na2–O18 (μ ² -bridging H ₂ O)	2.424(6)		
Na3–O4 (terminal Mo=O)	2.337(7)		
Na3–O17 (μ ² -bridging H ₂ O)	2.325(8)		
Na3–O18 (μ ² -bridging H ₂ O)	2.283(8)		
Na3–O19 (terminal H ₂ O)	2.356(7)		
Na3–O20 (μ ² -bridging H ₂ O)	2.356(7)		
Na3–O21 (μ ² -bridging H ₂ O)	2.429(9)		
Na4–O1 (terminal Mo=O)	2.370(6)		
Na4–O8 (terminal Mo=O)	2.385(6)		
Na4–O20 (μ ² -bridging H ₂ O)	2.351(6)		
Na4–O21 (μ ² -bridging H ₂ O)	2.563(7)		
Na4–O22 (μ ² -bridging H ₂ O)	2.383(6)		

unique 7:2 cation to anion ratio found in **1** enables the formation of the complex frameworks of ion–dipole and hydrogen bonding interactions that stabilize the crystal lattice. Also, the positions of hydrogen atoms, and therefore also the hydrogen bonds, were not described in the previous structural analyses of the sodium and potassium salts of the heptamolybdate anion. The analysis of the structure of **1** reported here thus represents the first description of the important role that hydrogen bonding can play in stabilizing the crystal lattice of inorganic heptamolybdate salts. This generates new insights into the importance of hydrogen bonding and ion–dipole interactions in the ‘capturing’ of inorganic polyoxometallate species.

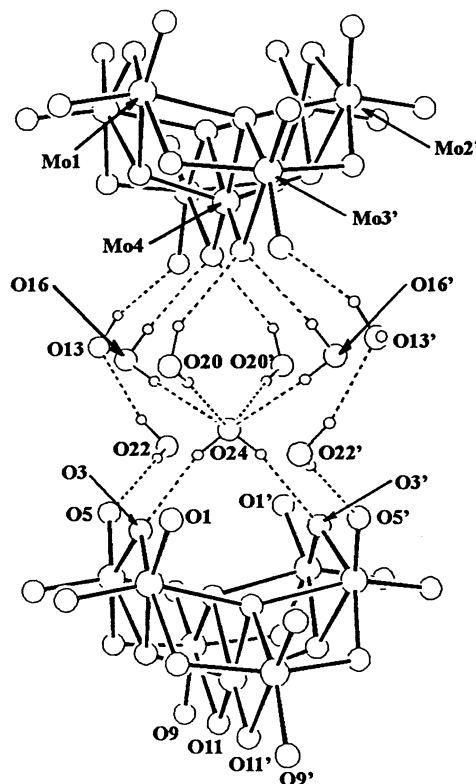


Fig. 5. Complex hydrogen bonding framework observed between neighboring [Mo₇O₂₄]⁶⁻ anions in **1** (sodium atoms are omitted for clarity).

4. Supplementary material

Structure factors as well as tables of atomic position parameters and anisotropic thermal parameters for **1** are available from the authors upon request. Complete crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Centre, CCDC No. 412788. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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