Dedicated to the memory of Yurii A. Simonov

SYNTHESIS AND CRYSTAL STRUCTURE OF NOVEL MIXED-VALENCE HEXATUNGSTATE SALT

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Novel mixed-valence hexatungstate salt of composition $[Na(H_2O)_8]_x[Na(H_2O)_6]_{2x}[N(CH_3)_4]_{3-3x}[W^{V}W_5{}^{VI}O_{19}]$, x = 0.69091 has been synthesized and characterized by X-ray single crystal structural analysis. The crystal structure is built-up from a Lindquist type hexatungstate $[W^{V}W_5{}^{VI}O_{19}]^{3-}$ polyoxoanions and three types of disordered cations: $[Na(H_2O)_8]^{1+}$, $[Na(H_2O)_6]^{1+}$ and $[N(CH_3)_4]^{1+}$, which statistically occupy two different Wyckoff positions in the crystal.

1. Introduction

Polyoxometalates exhibit fascinating electron acceptor properties whereby these systems can take, often in steps, a multiple number of electrons to form reduced and mixed valence compounds without any significant change in their molecular structures [1-3]. Partially reduced and mixed valence metal oxide clusters are of current interest due to their unusual electronic and magnetic properties [2-8] and their direct relevance to several geochemical and biochemical processes, catalysis, and materials science [2, 7-10]. Hexatungstate, $[W_6O_{19}]^{2-}$ [11] is a prominent member of the hexametalate series $[M_6O_{19}]^{n-}$ (M = Mo, W; n = 2; M = Nb, Ta; n = 8) [1] of polyoxoanions with a Lindquist type structure [12-14] that has attracted considerable attention [13-15] in recent years. Herein we report synthesis and crystal structure of the novel hexatungstate salt.

2. Experimental

2.1. Synthesis

In 100 mL of water, 16.5 g (20 mmol) of $Na_2WO_4 \cdot H_2O$ and 3.2g (0.2 mmol) $NaVO_3$ $2H_2O$ were dissolved and heated to 60°C. Then 1.2 g (0.9 mmol) of H_2SeO_3 was added to the solution under continuous stirring. The pH of the solution was adjusted to 4.5 by addition of 4*N*·HCl. Then the reaction mixture was heated up to 90°C and after 1.5 h was cooled down to room temperature and filtered. The light brown single crystals having the rectangular prisms habitus were precipitated from this solution. The transparent, well-defined sample of the suitable size has been selected for X-ray single crystal investigation.

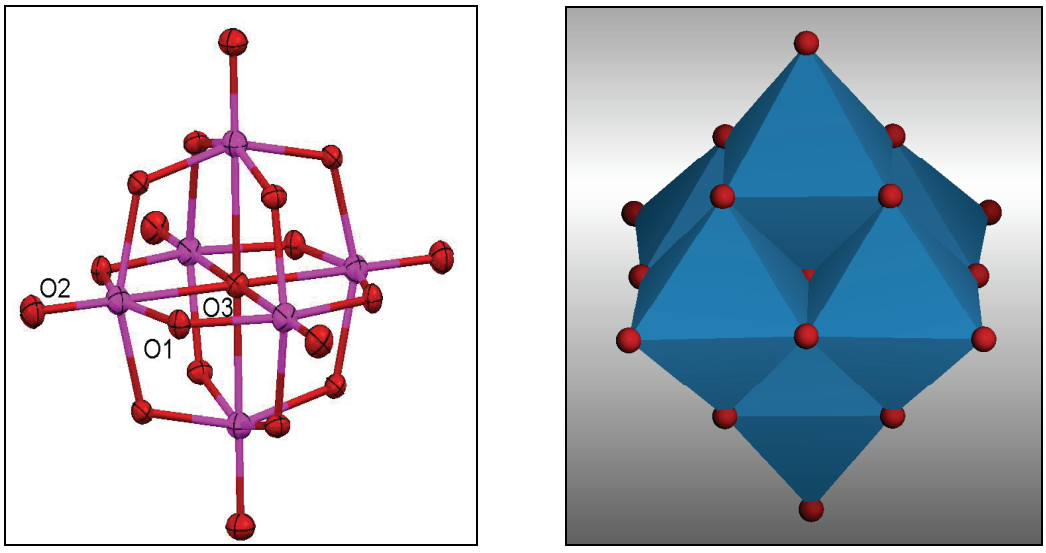
2.2. X-ray investigation

Crystal data: $C_{3.71}H_{11.14}N_{0.93}Na_{2.07}O_{32.81}W_6$, M = 1761.55, crystal size 0.15 x 0.10 x 0.10 mm, space group *Fm3m*, a = 14.1700(16) Å, V = 2845.2(6) Å^3, Z = 4, D_c = 4.073 g/cm^3, μ(Mo-K$_\alpha$) = 24.318 mm^{-1}, T = 293(2) K. The θ-range for data collection is 4.07-29.94°, the number of all collected reflections is 4620, the number of unique reflections is 238, the number of parameters is 30, and the goodness of fit on F^2 1.002, R_1 = 0.0346, wR_2 = 0.1059 (I>2σ(I)), R_1 = 0.0353, wR_2 = 0.1067 (all data).

Experimental X-ray data were collected using a Nonius Kappa CCD diffractometer with graphite monochromated Mo $K\alpha$ radiation using ω scan with the sample to detector distance of 50 mm. Preliminary orientation matrices and unit cell parameters were obtained from the peaks found in the first 10 frames, and refined using the whole data set. The frames were integrated and corrected for Lorentz and polarization effects using DENZO [16]. The scaling, as well as the global refinement of crystal parameters, was performed by SCALEPACK [16]. The reflections that were partly measured on previous and following frames were used to scale these frames on each other. The absorption correction was introduced by a semi-empirical method [17]. The structures were solved by a direct method and refined by full-matrix least squares based on F^2 using SHELXL-97 [18]. Hydrogen atoms of methyl groups were placed in calculated positions and refined isotropicaly in riding mode.

3. Results and discussion

The X-ray crystal structure investigation determined the composition of the compound as $[Na(H_2O)_8]_x[Na(H_2O)_6]_{2x}[N(CH_3)_4]_{3-3x}[W^{V}W_5{}^{VI}O_{19}]$, x = 0.69091. The hexatungstate polyoxoanion $[W^{V}W_5{}^{VI}O_{19}]^{3-}$ (Fig. 1) resides on Wyckoff positions *b* (4 positions per unit cell) with point symmetry m3m thus having an O_h molecular symmetry. Cations occupy two different Wyckoff positions *a* and *c* with number of points 4 and 8 per unit cell, respectively.



a) *b)*

Fig. 1. ORTEP drawing with numbering scheme *(a)* and polyhedron representation *(b)* of hexatungstate polyoxoanion $[W^{V}W_5{}^{VI}O_{19}]^{3-}$. Ellipsoids are shown for 30% probability level.

Table 1. Bond lengths (Å) and angles (deg) for **1**.

W(1)-O(2)	1.658(13)	Na(2)-O(2W)	2.46(2)
W(1)-O(1)	1.924(4)	N(1)-C(1)	1.47(2)
W(1)-O(3)	2.3071(7)	N(2)-C(2)	1.44(3)
Na(1)-O(1W)	2.47(2)		

O(1)-W(1)-O(2)	103.0(2)	O(1W)-Na(1)-O(1W)#3	109.5
O(1)-W(1)-O(1)#1	154.1(4)	O(1W)-Na(1)-O(1W)#4	70.529(2)
O(1)#1-W(1)-O(1)#2	87.11(9)	O(1W)-Na(1)-O(1W)#5	180.0(11)
O(2)-W(1)-O(3)	180.0	O(2W)-Na(2)-O(2W)#6	106.6(7)
O(1)-W(1)-O(3)	77.0(2)	O(2W)-Na(2)-O(2W)#7	91.45(15)

Symmetry transformations used to generate equivalent atoms:
#1 -z+1/2,-x+1/2,-y; **#2** -z+1/2,-x+1/2,y; **#3** -x+1,y,-z; **#4** -x+1,y,z; **#5** -x+1,-y+1,-z; **#6** -x+1, -y+1,z; **#7** -y+1/2,-z+1/2,x.

This set of positions determines the anion to cations ratio in the crystal as 1:3. The Wyckoff positions *a* (point symmetry m3m) are occupied statistically by octa-aqua sodium (Na1) and tetramethylammonium (N1) cations with probability ~69% and ~31%, respectively. The methyl groups (C1) of tetramethylammonium cations are statistically disordered over two locations possible for tetrahedral species in this point. The Wyckoff positions *c* (point symmetry -43m, T_d) are occupied statistically by hexa-aqua sodium (Na2) and tetramethylammonium (N2) cations with the same probability ~69% and ~31%, respectively. Although the Wyckoff positions *a* and *c* are independent, a strong correlation exists for occupancy of these positions by octa-aqua sodium cations and tetramethylammonium cations due to the steric effect, and the probability of occupancy for both these positions by aqua sodium and tetramethylammonium cations should be the same. This correlation determines the formula of the compound, which assumes the existence of isomorphs with different composition of cations. It is interesting to note that hydrophilic aqua sodium cations and hydrophobic tetramethylammonium cations may occupy the place in the crystal structure.

The mixed-valence species $[W^{V}W_5{}^{VI}O_{19}]^{3-}$ adopts the Lindquist type structure composed of six $\{WO_6\}$, octahedrons sharing common edges similar to those observed in the fully oxidized species $[W_6O_{19}]^{2-}$. Each of the six $\{WO_6\}$ octahedrons shares four edges with four adjacent $\{WO_6\}$ octahedrons. The six terminal, twelve doubly-bridging, and one central μ_6-O (six-coordinated) oxogroups determine three types of W-O bonds with

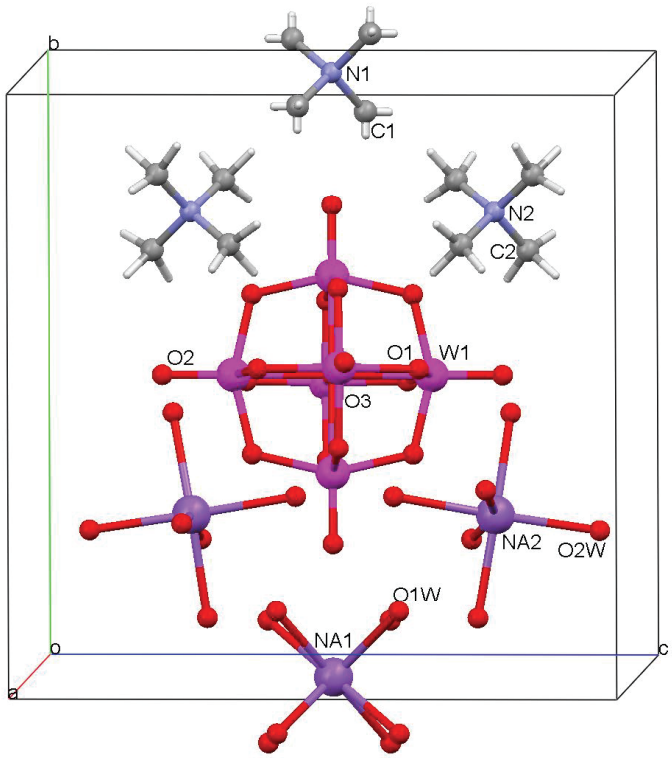


Fig. 2. Fragment of the crystal structure $[Na(H_2O)_8]_x[Na(H_2O)_6]_{2x}[N(CH_3)_4]_{3-3x}[W^{V}W_5{}^{VI}O_{19}]$.

bond lengths of 1.658(13), 1.924(4) and 2.307(1) Å, respectively (Table 1). In comparison with the fully-oxidized hexatungstate core, $[W_6^{VI}O_{19}]^{2-}$ [19, 20], the bond lengths and angles in the one-electron reduced species do not change significantly. The Na(1) atom is surrounded by eight water molecules and its coordination polyhedron is a cube (Fig. 2). The six atoms O(2W) of the water molecules in the surrounding of Na(2) atom form the distorted octahedron which is statistically disordered over two cites with the position of the sodium metal atom common to both sites. A fragment of packing that illustrates possible ordered distribution of cations is shown in Fig. 2.

4. Conclusions

The composition and structure of novel hexatungstate salt $[Na(H_2O)_8]_x[Na(H_2O)_6]_{2x}[N(CH_3)_4]_{3-3x}[W^VW_5^{VI}O_{19}]$ X = 0.69091 has been determined by single crystal X-ray method. The mixed-valence anions $[W^VW_5^{VI}O_{19}]^{3-}$ adopts the Lindquist type structure and has an O_h molecular symmetry.

Three types of disordered cations: $[Na(H_2O)_8]^{1+}$, $[Na(H_2O)_6]^{1+}$, and $[N(CH_3)_4]^1$ statistically occupy two different Wyckoff positions in crystal. The molecular formula assumes the existence of different isomorphs, which differ by composition of cations. The hydrophilic and hydrophobic cations may occupy the same position in the crystal.

5. Supplementary material

Crystallographic data for **1** have been deposited with the Cambridge Crystallographic Data Center, CCDC 753310. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

6. Acknowledgements

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