

Transition of Classic Decatungstate to Paratungstate: Synthesis, Structure and Luminescence Properties of Two Paratungstate-based 3-D Compounds

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Two new paratungstate-based compounds were isolated from the acetate buffer solution containing decatungstate $[W_{10}O_{32}]^{4-}$ at different reaction temperatures. The two compounds have been characterized by elemental analysis, IR spectroscopy, thermogravimetric analysis (TGA), and single crystal X-ray diffraction, and formulated as $(H_3O)_3[\{K(H_2O)\}_2\{Na_2(H_2O)_8\}_2(Na_{0.5}H_2O)_2(H_2W_{12}O_{42})] \cdot 6H_2O$ (**1**) and $(H_3O)_2[\{K(H_2O)_4\}_2\{Na_3(H_2O)_9\}_2(H_2W_{12}O_{42})] \cdot 2H_2O$ (**2**). Compounds **1** and **2** exhibit different three-dimensional architectures with bridging sodium and potassium as counteranions for the paratungstate anion. Compound **1** displays an intense blue luminescence in the solid state. The structural transformation from $[W_{10}O_{32}]^{4-}$ to $[H_2W_{12}O_{42}]^{10-}$ in an acetate buffer provides a route for the synthesis of new paratungstate-based compounds.

Key words: Paratungstate-B, Decatungstate, Structural Transformation, Luminescence

Introduction

Polyoxometalate (POM) chemistry has expanded to a very large field in recent years [1–3]. In the POM family, the decatungstate $[W_{10}O_{32}]^{4-}$ is a prominent case which is usually stable in nonaqueous solution but metastable in aqueous solution [4]. In the past century, much work has been done on exploring $[W_{10}O_{32}]^{4-}$ -based new compounds and studying their photoluminescent properties, especially on the lanthanide-containing derivatives [5–11]. Nevertheless, no report has been published on the decomposition and reassembly of $[W_{10}O_{32}]^{4-}$ into $[H_2W_{12}O_{42}]^{10-}$ in aqueous solution.

Usually, the paradodecatungstate derivatives can be prepared *via* two routes: one is starting from the matrix paradodecatungstate, the other is an *in situ* synthesis from tungstates $[WO_4]^{2-}$. Based on these two methods, a series of new $[H_2W_{12}O_{42}]^{10-}$ -based compounds have been synthesized [12]. In the course of our investigation of the reaction between $[W_{10}O_{32}]^{4-}$ and metal ions [13], we accidentally found that $[W_{10}O_{32}]^{4-}$ can be transformed into $[H_2W_{12}O_{42}]^{10-}$ in an acetate buffer medium. Herein, we report two

new compounds $(H_3O)_3[\{K(H_2O)\}_2\{Na_2(H_2O)_8\}_2(Na_{0.5}H_2O)_2(H_2W_{12}O_{42})] \cdot 6H_2O$ (**1**) and $(H_3O)_2[\{K(H_2O)_4\}_2\{Na_3(H_2O)_9\}_2(H_2W_{12}O_{42})] \cdot 2H_2O$ (**2**), which have been isolated from a sodium acetate buffer solution containing decatungstate $Na_4[W_{10}O_{32}]$ at different reaction temperatures. Compounds **1** and **2** exhibit three-dimensional (3-D) frameworks with the POM anions bridging sodium and potassium counteranions.

Results and Discussion

Synthesis

The two new paratungstates isolated as mixed sodium and potassium salts were prepared from a mixture of freshly prepared $Na_4[W_{10}O_{32}]$ and $CoCl_2$ in a molar ratio of 1 : 4 in a CH_3OONa/CH_3COOH buffer solution (pH = 5.5) at different reaction temperatures. Notably, the Co^{2+} ions are not included in the final compounds, however, the title compounds can not be obtained if Co^{2+} ions are absent in the reaction system. It is well known that many factors can influence the outcome of reactions, such as the solution

concentration, the pH value, the temperature, and the reaction time. In this preparation, the pH value and the reaction temperature are crucial for the formation of the title compounds. Compound **1** is obtained in a pH = 5 acetate buffer at a temperature of 80 °C, while the temperature needs to be 100 °C for isolating compound **2**. Further, if the pH was adjusted to 5.5, and the reaction temperature kept at 80 °C, another compound $(\text{H}_3\text{O})_3[\{\text{Na}(\text{H}_2\text{O})_4\}\{\text{Co}(\text{H}_2\text{O})_4\}_3(\text{H}_2\text{W}_{12}\text{O}_{42})]\cdot 24.5\text{H}_2\text{O}$ [14] was obtained. For pH > 6 or pH < 4, no crystalline phases could be obtained of this $[\text{W}_{10}\text{O}_{32}]^{4-}$ -containing reaction system.

Normally, $[\text{W}_{10}\text{O}_{32}]^{4-}$ is metastable in aqueous solution and can be transformed into the ψ -metatungstate β - $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$ or into $[\text{W}_7\text{O}_{24}]^{6-}$, which have already been investigated [15]. Nevertheless, no proof of the structural transformation of $[\text{W}_{10}\text{O}_{32}]^{4-}$ to $[\text{H}_2\text{W}_{12}\text{O}_{42}]^{10-}$ has been presented to date. In this work, two $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{10-}$ -based compounds were successfully isolated from the $[\text{W}_{10}\text{O}_{32}]^{4-}$ -containing acetate buffer and represent the first examples of the structural transformation $[\text{W}_{10}\text{O}_{32}]^{4-} \rightarrow [\text{H}_2\text{W}_{12}\text{O}_{42}]^{10-}$, thereby confirming the previous prediction of Pope [15].

Structure description

Single crystal X-ray diffraction analyses reveal that compounds **1** and **2** consist of paradodecatungstate $[\text{H}_2\text{W}_{12}\text{O}_{42}]^{10-}$ polyanions, sodium and potassium cations, and additional water molecules. The poly-

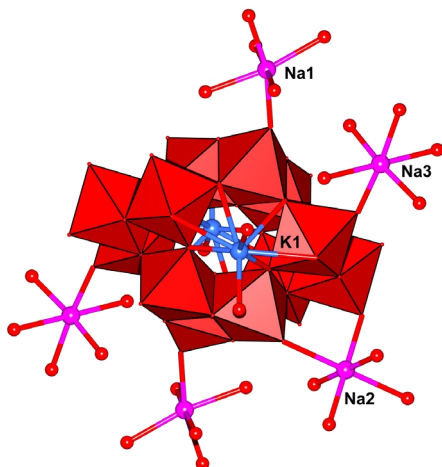


Fig. 1. Polyhedral and ball-and-stick representation of $[\{\text{K}(\text{H}_2\text{O})\}_2\{\text{Na}_2(\text{H}_2\text{O})_8\}_2(\text{Na}_{0.5}\text{H}_2\text{O})_2(\text{H}_2\text{W}_{12}\text{O}_{42})]^{3-}$ in compound **1**. Tungsten octahedra (red), sodium (pink), potassium (blue) and oxygen (red) (color online).

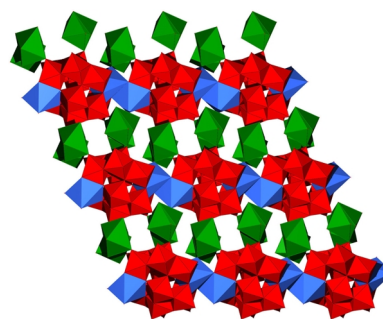


Fig. 2. Polyhedral representation of the layer parallel to the *ab* plane in the structure of compound **1**. Tungsten octahedra (red), potassium polyhedra (blue) and sodium octahedra (green) (color online).

oxoanion exhibits the well-known paratungstate-B structural feature which has been reported previously [16,17]. All the W centers possess the +VI oxidation state based on bond valence sum calculations [18], which give average values of 5.95 and 6.13 for compounds **1** and **2**, respectively.

Compound **1** exhibits a 3-D framework constructed from $[\text{H}_2\text{W}_{12}\text{O}_{42}]^{10-}$ anions and Na^+ , K^+ cation linkers. In the unit cell, five hexa-coordinated Na cations exhibit three different coordination environments (Fig. 1). The Na1 ion is coordinated to four aqua ligands and two oxygen atoms derived from two different $[\text{H}_2\text{W}_{12}\text{O}_{42}]^{10-}$ anions with Na–O distances in the range 2.32(2)–2.46(2) Å. The Na2 ion is coordinated to two aqua ligands and four oxygen atoms from two adjacent $[\text{H}_2\text{W}_{12}\text{O}_{42}]^{10-}$ anions with Na–O distances in the range 2.24(3)–2.78(14) Å. The Na3 ion is coordinated to five aqua ligands and one oxygen atom from a $[\text{H}_2\text{W}_{12}\text{O}_{42}]^{10-}$ anion with Na–O distances in the range 2.34(2)–2.63(2) Å. The K1 ion is coordinated to four oxygen atoms (O3, O6, O12 and O14) from one $[\text{H}_2\text{W}_{12}\text{O}_{42}]^{10-}$ anion and two oxygen atoms (O8 and O21) from another $[\text{H}_2\text{W}_{12}\text{O}_{42}]^{10-}$ anion. The oxygen atom (O8A) and an aqua ligand (O9W which bridges to Na3) are also coordinated to the K1 cation, thus leading to the eight-coordinated geometry with K–O distances in the range 2.36(2)–2.923(15) Å. In **1**, each $[\text{H}_2\text{W}_{12}\text{O}_{42}]^{10-}$ cluster acts as a heptadentate ligand linked to five Na and two K centers. Thus, the final 3-D framework can be described as follows: firstly, $[\text{H}_2\text{W}_{12}\text{O}_{42}]^{10-}$ units are joined by edge-sharing K linkers to form a chain along the *a* axis; secondly, adjacent chains are linked by Na1 atoms to construct a layer parallel to the crystallographic *ab* plane (see Fig. 2). The Na3 centers do not take part in extending the structure

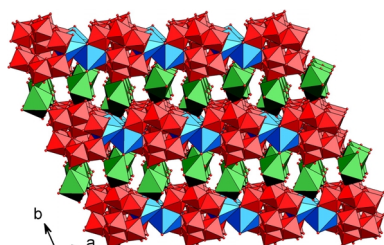


Fig. 3. Polyhedral representation of the 3-D network of **1**. Tungsten octahedra (red), potassium polyhedra (blue) and sodium octahedra (green) (color online).

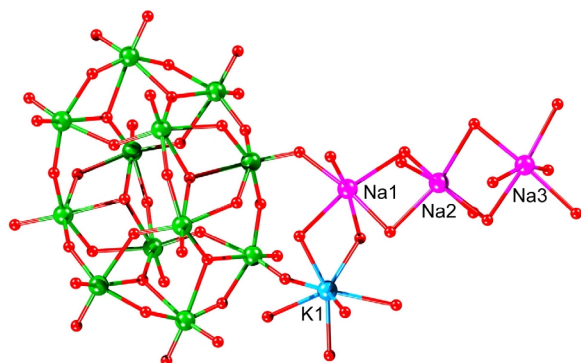


Fig. 4. Ball-and-stick representation of the $[\{K(H_2O)_4\}_2\{Na_3(H_2O)_9\}_2(H_2W_{12}O_{42})]^{2-}$ unit in compound **2**. Tungsten (green), sodium (pink), potassium (blue) and oxygen (red) (color online).

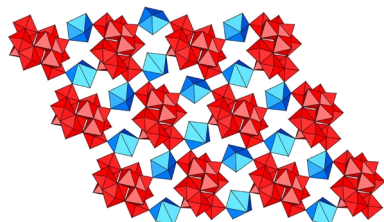


Fig. 5. Polyhedral representation of a layer in the structure of compound **2**. Tungsten octahedra (red), potassium polyhedra (blue) (color online).

but hang on the two sides of the layers; finally, neighboring layers are further held together by Na2 linkers to build up a 3-D architecture (see Fig. 3). The water molecules reside in the interstices of this 3-D framework.

Compound **2** exhibits a different 3-D architecture also built up from $[H_2W_{12}O_{42}]^{10-}$ polyoxoanions and a mixture of sodium and potassium cation linkers. As shown in Fig. 4, each $[H_2W_{12}O_{42}]^{10-}$ unit coordinates to K1 and Na1 *via* terminal oxygen atoms, and each potassium cation is in turn coordinated to three $[H_2W_{12}O_{42}]^{10-}$ clusters to yield a layer struc-

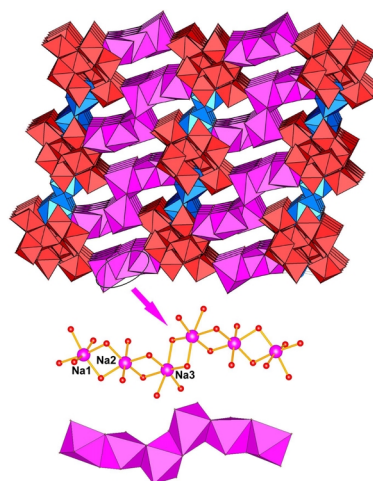
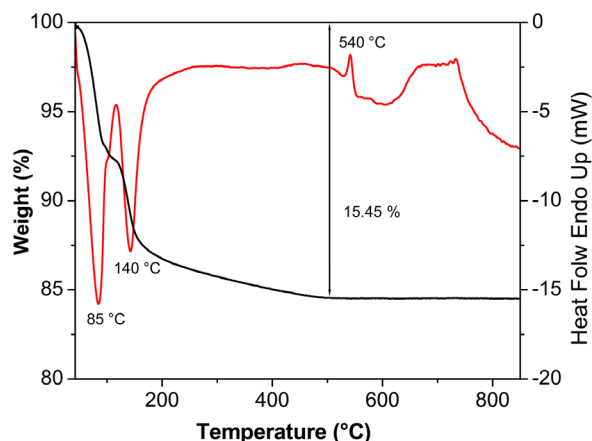
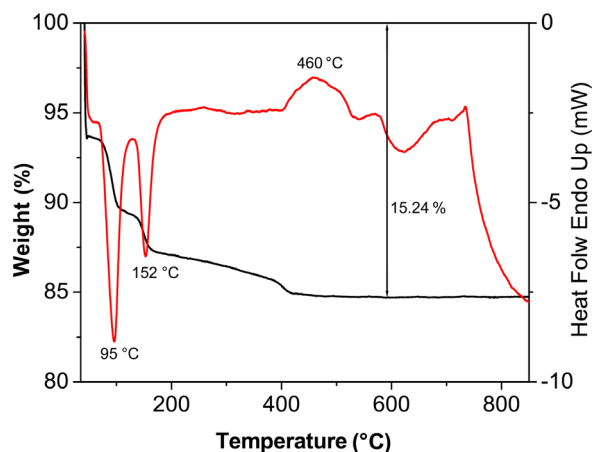


Fig. 6. Polyhedral representation of the 3-D network of **2**. Tungsten octahedra (red), potassium polyhedra (blue) and sodium polyhedra (pink) (color online).

ture (Fig. 5). The coordination environment of the K center shows an anomalous geometry formed by three oxygen atoms (O8, O9 and O21) derived from three paratungstate units and four water molecules (O1W, O2W, O3W, and O4W) to complete a seven-coordinated environment with K–O distances in the range 2.372(11)–3.422(13) Å. It is notable that six Na^+ ions exhibit three different coordination environments and form a hexanuclear Na cluster of polyhedra in an edge-sharing mode. These $[Na_6O_6(H_2O)_{20}]^{6-}$ clusters sew together the neighboring layers (as shown in Fig. 5) to form a 3-D framework (Fig. 6).

Thermal analysis

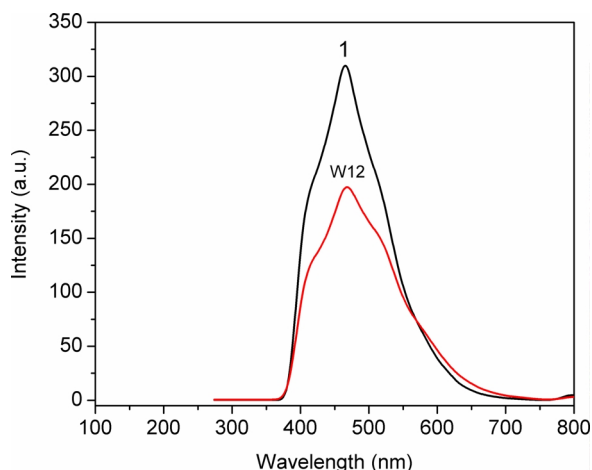
Thermogravimetric analyses of **1** and **2** were carried out in a nitrogen atmosphere with a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ in the temperature range of 42–850 $^\circ\text{C}$. The TG/DTA curves are shown in Figs. 7 and 8. The TG curve of compound **1** shows two steps of weight loss in the temperature range 42–500 $^\circ\text{C}$. The whole weight loss (15.5 %) is in good agreement with the calculated value for loss of water (14.7 %). The TG curve of compound **2** exhibits three steps of weight loss in the range 42–450 $^\circ\text{C}$, and the whole loss (15.2 %) is consistent with the calculated value (14.9 %). No weight loss occurs above 500 $^\circ\text{C}$. All the weight losses of compounds **1** and **2** between 85 to 152 $^\circ\text{C}$ are followed by two strong endothermic peaks in DTA curves, corresponding to the loss of water molecules. Additional exothermic peaks at 540 $^\circ\text{C}$ (for **1**) and 460 $^\circ\text{C}$ (for **2**)

Fig. 7. TG-DTA curves of compound **1**.Fig. 8. TG-DTA curves of compound **2**.

correspond to the phase transformations of the inorganic components. These results further confirm the formula of compounds **1–2**.

Luminescent properties

The emission spectrum of compound **1** in the solid state at r. t. is depicted in Fig. 9. It can be observed that an intense emission occurs at 466 nm ($\lambda_{\text{ex}} = 254$ nm). According to the previous literature [12], the core $[\text{H}_2\text{W}_{12}\text{O}_{42}]^{10-}$ possesses photoluminescence properties. The peak position and profile are in agreement with previous data, indicating that the photoluminescence of compound **1** also originates from the polyoxoanion core $[\text{H}_2\text{W}_{12}\text{O}_{42}]^{10-}$, and that the alkali ions do not affect the emission spectrum of the core. The emission spectrum exhibits a Gaussian distribution, so it belongs to the group of self-activated phosphors.

Fig. 9. Solid state emission spectra of compound **1** and $\text{Na}_{10}[\text{H}_2\text{W}_{12}\text{O}_{42}] \cdot 20\text{H}_2\text{O}$ (W12) at room temperature.

It is well known that luminescence originating from transitions between $4f$ levels is predominantly due to electric dipole or magnetic dipole interactions [19–23]. The luminescence properties of many tungstates $\{\text{MWO}_4\}$ ($\text{M} = \text{Ca}, \text{Ba}, \text{Pd}, \text{Sr}$) have been reported [24, 25] and their emitting blue luminescence related to the tetrahedral WO_4 groups of the Scheelite host lattice [26, 27]. We presume that the photoluminescence of $[\text{H}_2\text{W}_{12}\text{O}_{42}]^{10-}$ and compound **1** are related to the octahedral WO_6 groups of the polyoxoanion.

Conclusions

In summary, two new $[\text{H}_2\text{W}_{12}\text{O}_{42}]^{10-}$ -based 3-D compounds were successfully synthesized from a $[\text{W}_{10}\text{O}_{32}]^{4-}$ -containing acetate buffer solution at different temperatures, offering a route for the preparation of paratungstate-based compounds. Furthermore, this synthesis provides a proof for the structural transformation $[\text{W}_{10}\text{O}_{32}]^{4-} \rightarrow [\text{H}_2\text{W}_{12}\text{O}_{42}]^{10-}$, confirming previous predictions by Pope. Further research on $[\text{H}_2\text{W}_{12}\text{O}_{42}]^{10-}$ -based high-dimensional frameworks is underway in our research group.

Experimental Section

General procedure

All reagents were purchased commercially and used without further purification. $\text{Na}_4[\text{W}_{10}\text{O}_{32}]$ was prepared according to the literature method [28]. Elemental analyses of K, Na and W were determined by a Leaman inductively coupled plasma (ICP) spectrometer. The IR spectra were obtained on an Alpha Centauri FTIR spectrometer in the 400–

Table 1. Crystal and structure refinement data for compounds **1** and **2**.

	1	2
Empirical formula	H ₅₈ K ₂ Na ₅ O _{71.5} W ₁₂	H ₆₄ K ₂ Na ₆ O ₇₂ W ₁₂
Formula weight	3593.81	3638.85
Crystal system	triclinic	monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> , Å	10.597(2)	15.434(5)
<i>b</i> , Å	12.114(2)	11.790(5)
<i>c</i> , Å	13.134(3)	18.238(5)
α , deg	102.75(3)	90.0
β , deg	107.53(3)	109.390(5)
γ , deg	108.25(3)	90.0
Volume, Å ³	1431.5(5)	3130.5(19)
<i>Z</i>	1	2
<i>d</i> _{calc} , g cm ^{−3}	4.17	3.86
μ (MoK α), mm ^{−1}	24.3	22.3
<i>F</i> (000), e	1607	3264
Data/parameters	4964/328	5504/381
Goodness-of-fit on <i>F</i> ²	1.027	1.075
<i>R</i> 1 ^a	0.039	0.043
<i>wR</i> 2 ^b	0.083	0.081
$\Delta\rho_{\text{fin}}$ (max/min), e Å ^{−3}	2.1/−2.5	2.6/−1.8

^a $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$; ^b $wR_2 = \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.0385P)^2 + 87.0434P]$, where $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Selected bond lengths (Å) for compound **1**^a.

W(1)–O(17)	1.731(12)	W(4)–O(9)	1.736(12)
W(1)–O(16)	1.848(12)	W(4)–O(8)	1.744(12)
W(1)–O(7)	1.850(10)	W(4)–O(14)	1.871(10)
W(1)–O(12)	1.951(13)	W(4)–O(13)	1.923(10)
W(1)–O(14)	1.965(10)	W(4)–O(3)	2.233(12)
W(1)–O(2)	2.258(11)	W(4)–O(4)	2.277(10)
W(2)–O(18)	1.738(14)	W(5)–O(20)	1.736(12)
W(2)–O(19)	1.745(12)	W(5)–O(21)	1.737(13)
W(2)–O(13) ^{#2}	1.913(10)	W(5)–O(12)	1.900(12)
W(2)–O(1)	1.918(12)	W(5)–O(1)	1.937(11)
W(2)–O(10) ^{#2}	2.277(12)	W(5)–O(6) ^{#2}	2.204(11)
W(2)–O(4) ^{#2}	2.279(10)	W(5)–O(10) ^{#2}	2.210(11)
W(3)–O(5)	1.697(14)	W(6)–O(11)	1.714(11)
W(3)–O(6)	1.821(11)	W(6)–O(3)	1.796(12)
W(3)–O(4)	1.879(10)	W(6)–O(10)	1.892(12)
W(3)–O(15) ^{#2}	1.974(10)	W(6)–O(15)	1.942(11)
W(3)–O(16)	2.042(11)	W(6)–O(7) ^{#2}	2.094(11)
W(3)–O(2)	2.263(11)	W(6)–O(2) ^{#2}	2.245(10)
O(1W)–Na(1)	2.30(4)	O(7W)–Na(3)	2.414(19)
O(1'W)–Na(1)	2.31(3)	O(8W)–Na(3)	2.336(18)
O(2W)–Na(1)	2.338(18)	O(9)–Na(3)	2.389(15)
O(3W)–Na(1)	2.347(18)	O(9W)–Na(3)	2.633(18)
O(5)–Na(1) ^{#4}	2.464(16)	O(3)–K(1) ^{#1}	2.533(11)
O(17)–Na(1)	2.407(14)	O(6)–K(1) ^{#3}	2.500(11)
Na(1)–O(4W)	2.410(16)	O(8)–K(1)	2.398(12)
O(10W)–Na(2)	2.26(2)	O(8)–K(1) ^{#1}	2.858(12)
O(19)–Na(2)	2.411(15)	O(9W)–K(1)	2.34(2)
Na(2)–O(11) ^{#2}	2.779(11)	O(14)–K(1) ^{#1}	2.848(13)
O(5W)–Na(3)	2.56(2)	O(21)–K(1) ^{#1}	2.917(12)
O(6W)–Na(3)	2.337(19)	K(1)–O(12) ^{#1}	2.745(13)

^a Symmetry transformations used to generate equivalent atoms: ^{#1} $-x, -y, -z+2$; ^{#2} $-x+1, -y, -z+2$; ^{#3} $x+1, y, z$; ^{#4} $-x+1, -y+1, -z+2$.

Table 3. Selected bond lengths (Å) for compound **2**^a.

O(1)–W(1)	1.926(9)	O(2)–W(1)	1.710(11)
O(3)–W(1)	2.098(9)	O(4)–W(1)	2.268(9)
O(10)–W(1) ^{#6}	1.807(10)	O(16)–W(1) ^{#6}	1.928(9)
O(3)–W(2)	1.843(10)	O(4)–W(2)	2.240(10)
O(5)–W(2)	1.755(10)	O(6)–W(2)	1.973(12)
O(7)–W(2)	1.893(9)	O(19)–W(2) ^{#6}	1.948(8)
O(6)–W(3)	1.862(12)	O(8)–W(3)	1.754(8)
O(9)–W(3)	1.748(9)	O(10)–W(3)	2.198(8)
O(11)–W(3)	2.198(8)	O(12)–W(3)	1.975(11)
O(11)–W(4)	2.328(11)	O(12)–W(4)	1.901(8)
O(13)–W(4)	1.743(9)	O(14)–W(4)	1.738(13)
O(15)–W(4)	1.908(8)	O(16)–W(4)	2.227(9)
O(15)–W(5)	1.976(8)	O(16)–W(5)	2.194(8)
O(17)–W(5)	1.732(13)	O(18)–W(5)	1.763(9)
O(19)–W(5)	1.883(8)	O(20)–W(5)	2.242(11)
O(1)–W(6)	1.976(11)	O(4)–W(6)	2.256(9)
O(7)–W(6)	2.039(10)	O(11)–W(6)	1.902(9)
O(20)–W(6)	1.787(9)	O(21)–W(6)	1.749(8)
K(1)–O(4W)	2.372(11)	K(1)–O(9)	2.379(10)
K(1)–O(2W)	2.381(14)	K(1)–O(3W)	2.416(10)
K(1)–O(1W)	2.423(11)	K(1)–O(21) ^{#1}	2.447(8)
K(1)–O(8) ^{#2}	2.451(10)	K(1)–O(6W)	3.422(13)

^a Symmetry transformations used to generate equivalent atoms: ^{#1} $-x+1/2, y+1/2, -z+1/2$; ^{#2} $-x, -y+1, -z$; ^{#6} $-x, -y, -z$.

4000 cm^{−1} region with KBr pellets. The TG analyses were performed on a Perkin-Elmer TGA7 instrument under flowing N₂ with a heating rate of 10 °C/min. Excitation and emission spectra were obtained on a SPEX FL-2T2 spectrofluorometer equipped with a 450 W xenon lamp as the excitation source.

Synthesis of compound **1**

Freshly prepared Na₄[W₁₀O₃₂] (0.24 g, 0.1 mmol) was dissolved in 15 mL of an aqueous solution of a CH₃OONa/CH₃COOH buffer (pH = 5.5) with stirring. Then CoCl₂ · 6H₂O (0.095 g, 0.4 mmol) was added. The pH value of the mixture was carefully adjusted to 5 by using 1 M CH₃OONa/CH₃COOH. The final solution was heated at 80 °C for 1 h, and then a solution of 4 M KCl (10 mL) was added to the reaction mixture at the same temperature. After cooling to r.t., the final pink suspension was filtered. The filtrate was kept for slow evaporation at r.t. Colorless columnar crystals of **1** were isolated after one week (yield 71 % based on W). Elemental analysis for H₆₄K₂Na₅O_{71.5}W₁₂: calcd. K 2.17, Na 3.20, W 61.35; found K 1.87, Na 3.5, W 61.65. – IR (KBr pellet): ν = 3421(vs), 1616(s), 947(s), 894(m), 726(m), 608(s), 471(w).

Synthesis of compound **2**

An identical procedure as described for **1** was followed to prepare **2** except that the reaction temperature was promoted to 100 °C. Colorless hexagonal crystals of **2** were isolated after one week (yield 78 % based on W). Elemental analysis for H₆₄K₂Na₆O₇₂W₁₂: calcd. K 2.14, Na 3.8, W 60.68;

found K 1.92, Na 4.01, W 60.9. – IR (KBr pellet): $\nu = 3371(\text{vs})$, $1629(\text{s})$, $936(\text{m})$, $874(\text{m})$, $782(\text{m})$, $708(\text{m})$, $616(\text{w})$, $497(\text{s})$.

X-Ray crystallography

Single crystals of compounds **1** and **2** with dimensions $0.380 \times 0.286 \times 0.163 \text{ mm}^3$ and $0.37 \times 0.31 \times 0.26 \text{ mm}^3$, respectively, were glued on a glass fiber. Crystal data were collected on a Rigaku RAXIS RAPID IP instrument with graphite-monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 293 K. The structures were solved by Direct Methods and refined by full-matrix least-squares on F^2 by using the SHELXS/L crystallographic software package [29]. In compound **1**, several oxygen atoms of the polyoxoanion and several water molecules were not refined anisotropically because of their non-positive-definite displacement parameters. In compound **2**, all non-hydrogen atoms were refined anisotropically. All hydrogen atoms of water molecules were not located and directly included in the final structural molecules. Crystallographic data are given in Ta-

ble 1, and selected bond lengths and angles are listed in Tables 2 and 3.

Further details of the crystal structure investigations may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition number CSD-418939 (**1**) and 418940 (**2**).

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- [1] M. T. Pope, A. Müller, *Angew. Chem.* **1991**, *103*, 56–70; *Angew. Chem. Int. Ed.* **1991**, *30*, 34–48.
- [2] J. T. Rhule, C. L. Hill, D. A. Judd, R. F. Schinazi, *Chem. Rev.* **1998**, *98*, 327–357.
- [3] D. L. Long, E. Burkholder, L. Cronin, *Chem. Soc. Rev.* **2007**, *36*, 105–121.
- [4] P. Souchay, M. Boyer, F. Chauveau, *Contributions to Coordination Chemistry in Solution*, **1972**, 259, 159–187.
- [5] Y. H. Wang, X. L. Wang, C. W. Hu, C. S. Shi, *J. Mater. Chem.* **2002**, *12*, 703–707.
- [6] T. R. Zhang, R. Lu, H. Y. Zhang, P. C. Xue, W. Feng, X. L. Liu, B. Zhao, Y. Y. Zhao, T. J. Li, J. N. Yao, *J. Mater. Chem.* **2003**, *13*, 580–584.
- [7] H. S. Kim, D. T. M. Hoa, B. J. Lee, D. H. Park, Y. S. Kwon, *Curr. Appl. Phys.* **2006**, *6*, 601–603.
- [8] T. Ozeki, T. Yamase, *Acta Crystallogr.* **1994**, *B50*, 128–134.
- [9] M. J. Stillman, J. Thomson, *J. Chem. Soc., Dalton Trans.* **1976**, 1138–1144.
- [10] T. Ozeki, T. Yamase, *Acta Crystallogr.* **1993**, *C49*, 1574–1577.
- [11] T. Ozeki, M. Takahashi, T. Yamase, *Acta Crystallogr.* **1992**, *C48*, 1370–1374.
- [12] L. Yuan, C. Qin, X. L. Wang, E. B. Wang, Y. G. Li, *Solid State Sci.*, in press, DOI: 10.1016/j.solidstatesciences.2007.12.011.
- [13] L. Yuan, C. Qin, X. L. Wang, E. B. Wang, *Z. Naturforsch.* **2007**, *62b*, 1471–1475.
- [14] C. Y. Sun, S. X. Liu, L. H. Xie, C. L. Wang, B. Gao, C. D. Zhang, Z. M. Su, *J. Solid State Chem.* **2006**, *179*, 2093–2100.
- [15] M. T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer, Berlin, **1983**.
- [16] H. T. Evans, Jr., E. Prince, *J. Am. Chem. Soc.* **1983**, *105*, 4838–4839.
- [17] V. R. Allmann, *Acta Crystallogr.* **1971**, *B27*, 1393–1404.
- [18] D. Brown, D. Altermatt, *Acta Crystallogr.* **1985**, *B41*, 244–247.
- [19] G. Blasse, B. C. Grabmeyer, *Luminescent Materials*, Springer, Berlin, **1994**.
- [20] S. Shionoya, W. M. Yen, *Phosphor Handbook*, CRC Press, Boca Raton, **1999**, 190.
- [21] S.-I. Mho, J. C. Wright, *J. Chem. Phys.* **1982**, *77*, 1183–1187.
- [22] B. R. Judd, *Phys. Rev.* **1962**, *127*, 750–761.
- [23] G. S. Ofelt, *J. Chem. Phys.* **1962**, *37*, 511–520.
- [24] D. Chen, G. Shen, K. Tang, H. Zheng, Y. Qian, *Mater. Res. Bull.* **2003**, *38*, 1783–1789.
- [25] M. V. Nazarova, D. Y. Jeona, J. H. Kanga, E.-J. Muresan, M. V. Zamoryanskaya, B. S. Tsukerblat, *Solid State Commun.* **2004**, *131*, 307–312.
- [26] F. Forgaciu, E. J. Popovici, C. Ciocan, L. Ungur, M. Vadan, *Spie Proc. Ser.* **1999**, *4068*, 124–129.
- [27] R. Grasser, A. Scharmann, *Phys. Stat. Sol.* **1990**, *A130*, 99–105.
- [28] D. C. Duncan, T. L. Netzel, C. L. Hill, *Inorg. Chem.* **1995**, *34*, 4640–4646.
- [29] G. M. Sheldrick, SHELXS/L-97, Programs for Crystal Structure Determination, University of Göttingen, Göttingen (Germany) **1997**.