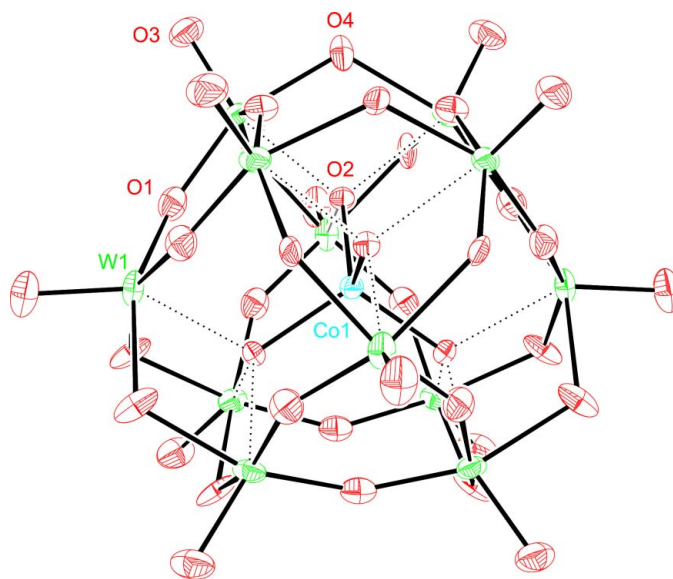


**K<sub>6</sub>H<sub>2</sub>[TiW<sub>11</sub>CoO<sub>40</sub>]·13H<sub>2</sub>O, with a mono-titanoundecatungstocobaltate(II) anion****Werner Kraus,<sup>a</sup> Holger Stephan,<sup>b</sup>  
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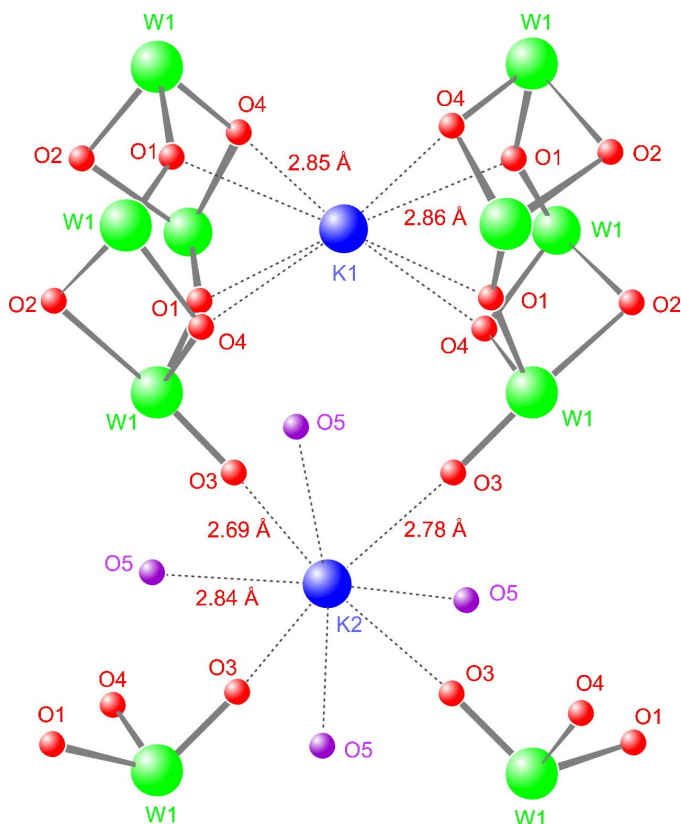
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**Key indicators**Single-crystal X-ray study  
*T* = 273 K  
Mean  $\sigma(\text{o}-\text{O}) = 0.010 \text{ \AA}$   
H-atom completeness 0%  
Disorder in main residue  
*R* factor = 0.039  
*wR* factor = 0.097  
Data-to-parameter ratio = 16.2For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.Hexapotassium dihydrogen monotitanoundecatungstocobaltate(II) tridecahydrate, K<sub>6</sub>H<sub>2</sub>[TiW<sub>11</sub>CoO<sub>40</sub>]·13H<sub>2</sub>O, crystallizes from aqueous solution in the cubic space group *P* $\bar{4}3m$ . The structure was refined as an inversion twin. The [TiW<sub>11</sub>CoO<sub>40</sub>]<sup>8-</sup> anion has a Keggin structure with one W-atom site occupied by titanium and a central tetrahedral CoO<sub>4</sub> group.**Comment**In recent years, interest in the chemistry of metal–oxygen clusters has grown due to their applications in areas including catalysis, materials chemistry and biochemistry (Pope, 1983; Pope & Müller, 2001). In the latter context, polyoxometalates (POMs) show unique transport behavior in living cells, and may act as antiviral and antitumoral agents (Rhule *et al.*, 1998). Specifically, the title compound, K<sub>6</sub>H<sub>2</sub>[TiW<sub>11</sub>CoO<sub>40</sub>], reveals promising antitumor activity when applied as starch and liposome hybrid materials (Wang *et al.*, 2003; Yang *et al.*, 2004). The structural characterization of K<sub>6</sub>H<sub>2</sub>[TiW<sub>11</sub>CoO<sub>40</sub>]-13H<sub>2</sub>O is reported here.The cluster ion has a Keggin (1933) structure. It can be viewed as a shell of {W<sub>11</sub>TiO<sub>36</sub>} encapsulating a central tetrahedral {CoO<sub>4</sub>} group (Fig. 1). Alternatively, the cluster anion may be described as constructed from 12{W<sub>0.92</sub>Ti<sub>0.08</sub>O<sub>6</sub>} octahedra. According to the coordination environment of oxygen in the anion cluster, the O atoms can be divided into**Figure 1**  
The cluster anion [TiW<sub>11</sub>CoO<sub>40</sub>]<sup>8-</sup>, showing 30% probability displacement ellipsoids. The labels of symmetry-equivalent atoms have been omitted for clarity.

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**Figure 2**  
The coordination spheres of the two K atoms.

four groups. Two kinds of O atoms in the shell are connected to the tungsten sites. One bridging O atom (O1) has a distance of only 1.819 (4) Å to tungsten and the  $W1^{IV}-O1-W1$  angle is 148.1 (9)°. The second bridging O atom (O4) has a distance of 2.034 (8) Å to tungsten and a smaller angle of 118.6 (7)° ( $W1^V-O4-W1$ ; symmetry codes are given in Table 1). Atom O4 forms hydrogen bonds to atom O5 of water molecules outside the shell [ $O4 \cdots O5 = 2.70$  (2) Å]. The terminal O3 atoms are connected to only one tungsten atom [ $O3-W1 = 1.711$  (11) Å]. The O2 atoms from the {CoO4} group connected to W1 have a distance of 2.231 (7) Å.

In the crystal packing, two symmetry-independent potassium atoms, K1 and K2, have been found, K2 being positionally disordered. K1 is coordinated by eight cluster O atoms, and K2 by four cluster O atoms and four water molecules (Fig. 2). The compound contains 13 water molecules per cluster. The coordination polyhedron formed by K atoms and water molecules stabilizes the cluster anions in a three-dimensional network.

$K_6H_2[TiW_{11}CoO_{40}] \cdot 13H_2O$  is soluble in water (~0.06 M) and practically insoluble in organic solvents. The visible absorption spectrum shows a broad peak with three shoulders in the range 520–680 nm, characteristic of tetrahedral  $Co^{II}$  complexes in polyoxotungstates (Nomiya *et al.*, 1981).  $K_6H_2[TiW_{11}CoO_{40}] \cdot 13H_2O$  exhibits the typical charge transfer band at 257 nm (bridging oxygen in  $W1-O1-W1$ ). This peak has been selected to study the hydrolytic stability of the title compound. A remarkable decrease of this charge transfer

band has been observed at a pH of 7.4, indicating the degradation of the cluster structure.

## Experimental

$K_6H_2[TiW_{11}CoO_{40}] \cdot 13H_2O$  was prepared according to the method described by Chen *et al.* (1997).  $TiOSO_4$  was used instead of  $Ti(SO_4)_2$  dissolved in  $H_2SO_4$ . X-ray quality crystals were grown by slow evaporation of an aqueous solution at room temperature. Analysis calculated for  $CoH_{28}K_6O_{53}TiW_{11}$ : H 0.87, K 7.24, Ti 1.48, Co 1.82, W 62.42%; found: H 0.88, K 7.2, Ti 1.5, Co 1.8, W 62.5%. UV/vis ( $H_2O$ , nm): 257 ( $\epsilon = 37000 M^{-1} cm^{-1}$ ), 570 ( $\epsilon = 120 M^{-1} cm^{-1}$ ), 590 ( $\epsilon = 200 M^{-1} cm^{-1}$ ), 625 ( $\epsilon = 300 M^{-1} cm^{-1}$ ); IR (KBr,  $cm^{-1}$ ):  $\nu_{as}$  443 (Co–O2), 759 (W–O1–W), 865 (W–O4–W), 933 (W=O3).

### Crystal data

$K_6H_2[TiW_{11}CoO_{40}] \cdot 13H_2O$   
 $M_r = 3240.00$   
 Cubic,  $P4_3m$   
 $a = 10.6850$  (16) Å  
 $V = 1219.9$  (3) Å<sup>3</sup>  
 $Z = 1$   
 $D_x = 4.410$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation

Cell parameters from 942 reflections  
 $\theta = 2.7$ – $28.1^\circ$   
 $\mu = 26.93$  mm<sup>-1</sup>  
 $T = 273$  (2) K  
 Block, blue  
 $0.09 \times 0.05 \times 0.04$  mm

### Data collection

Bruker SMART CCD area-detector diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)  
 $T_{min} = 0.217$ ,  $T_{max} = 0.390$   
 8248 measured reflections

730 independent reflections  
 516 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.091$   
 $\theta_{max} = 30.4^\circ$   
 $h = -14 \rightarrow 13$   
 $k = -10 \rightarrow 14$   
 $l = -14 \rightarrow 11$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.039$   
 $wR(F^2) = 0.097$   
 $S = 0.98$   
 730 reflections  
 45 parameters  
 H atoms not located  
 $w = 1/[\sigma^2(F_o^2) + (0.0494P)^2 + 8.0204P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$   
 $\Delta\rho_{max} = 1.64 e \text{ \AA}^{-3}$   
 $\Delta\rho_{min} = -1.66 e \text{ \AA}^{-3}$   
 Extinction correction: SHELXL97  
 Extinction coefficient: 0.0093 (8)  
 Absolute structure: Flack (1983), 315 Friedel pairs  
 Flack parameter: 0.43 (6)

**Table 1**

Selected geometric parameters (Å, °).

W1–O3	1.711 (11)	K1–O4	2.851 (12)
W1–O1 <sup>i</sup>	1.819 (4)	K1–O1	2.861 (15)
W1–O4 <sup>ii</sup>	2.034 (8)	K2–O3	2.70 (2)
W1–O2	2.231 (7)	K2–O3 <sup>iii</sup>	2.78 (2)
Co1–O2	1.906 (17)		
$W1^{IV}-O1-W1$	148.1 (9)	$W1^V-O4-W1$	118.6 (7)

Symmetry codes: (i)  $-z + 1, x, -y + 1$ ; (ii)  $z, x, y$ ; (iii)  $x, -y, -z + 1$ ; (iv)  $y, -z + 1, -x + 1$ ; (v)  $y, z, x$ .

Ti atoms are found to be statistically distributed over the tungsten positions. After location of the K atoms, the atoms of the Keggin anion and atom O5 of the water molecule, the strongest peak of the difference Fourier map was found in a large cavity and interpreted as an additional O atom (O6) of a rotationally disordered water molecule. This water molecule occupies a centre of symmetry and is linked in the crystal structure only by van der Waals interactions. The H atoms could not be located by difference Fourier synthesis. The highest peak and the deepest hole in the final difference Fourier map

are located 0.54 Å from W1 and 1.72 Å from O1, respectively. The refinement of the Flack (1983) parameter (0.43) clearly indicates the occurrence of an inversion twin.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINTE* (Bruker, 2001); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2001); software used to prepare material for publication: *SHELXTL*.

## References

- Bruker (1997). *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (2001). *SHELXTL* and *SAINTE*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Chen, Y. & Liu, J. (1997). *Synth. React. Inorg. Met.-Org. Chem.* **27**, 239–250.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Keggin, J. F. (1933). *Nature (London)*, **131**, 908.
- Nomiya, K., Miwa, M., Kobayashi, R. & Aiso, M. (1981). *Bull. Chem. Soc. Jpn.*, **54**, 2983–2987.
- Pope, M. T. (1983). *Heteropoly and Isopoly Oxometalates*. Berlin; Springer-Verlag.
- Pope, M. T. & Müller A. (2001). Editors. *Polyoxometalate Chemistry: From Topology via Self-Assembly to Applications*. Dordrecht/Boston/London: Kluwer Academic Publishers.
- Rhule, J. T., Hill, C. L., Judd, D. A. & Schinazi, R. F. (1998). *Chem. Rev.* **98**, 327–357.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Wang, X., Liu, J. & Pope, M. T. (2003). *Dalton Trans.* pp. 957–960.
- Yang, Y., He, J., Wang, X., Li, B. & Liu, J. (2004). *Trans. Metal Chem.* **29**, 96–99.