

# Synthesis and Structure of Hexatungstochromate(III), $[\text{H}_3\text{Cr}^{\text{III}}\text{W}_6\text{O}_{24}]^{6-}$

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Dedicated to Prof. Hans J. Breunig on the occasion of his 70th birthday

**Abstract:** The hexatungstochromate(III)  $[\text{H}_3\text{Cr}^{\text{III}}\text{W}_6\text{O}_{24}]^{6-}$  (**1**) was synthesized in aqueous, basic medium by simple reaction of chromium(III) nitrate nonahydrate and sodium tungstate dihydrate in a 1:6 ratio. Polyanion **1** represents the first Anderson-Evans type heteropolytungstate with a trivalent hetero element. The sodium salt of **1** with the formula  $\text{Na}_6[\text{H}_3\text{Cr}^{\text{III}}\text{W}_6\text{O}_{24}] \cdot 22\text{H}_2\text{O}$  (**1a**) was fully characterized in the solid state by single crystal XRD, FT-IR spectroscopy, and thermogravimetric analysis.

**Keywords:** Anderson-Evans structure · Chromium · Polyoxometalates · XRD

## Introduction

Polyoxometalates (POMs) are discrete, anionic metal-oxygen clusters of early *d* block metal ions in high oxidation states (e.g.  $\text{W}^{\text{VI}}$ ,  $\text{Mo}^{\text{VI}}$ ,  $\text{V}^{\text{IV}}$ )<sup>[1]</sup> with a very large structural and compositional variety, leading to interest in many different areas including materials science, catalysis, analytical chemistry, magnetism, and biomedical science.<sup>[2]</sup> The number of *3d* metal-containing POMs is very large, but only a few structurally characterized chromium-containing POMs are known.<sup>[3]</sup> The main obstacle for the development of Cr-POM chemistry is probably the kinetic inertness of  $[\text{Cr}(\text{OH}_2)_6]^{3+}$  towards ligand exchange in aqueous solution.<sup>[4]</sup>

Chromium-containing POMs possess interesting physicochemical properties, and the paramagnetic  $\text{Cr}^{\text{III}}$  is EPR active, which can find applications in integrated information storage, quantum computing, molecule-based magnets and spintronics.<sup>[5]</sup> In 1970, Perloff determined the crystal structure of hexamolybdochromate(III)  $[\text{CrMo}_6\text{O}_{24}\text{H}_6]^{3-}$ ,<sup>[3a]</sup> which was later described by Tsigdinos as  $[\text{CrO}_6\text{Mo}_6\text{O}_{15+n}\text{H}_{2n}]^{3-}$ .<sup>[6]</sup> Lunk's<sup>[3c-e]</sup> and

Mialane's<sup>[3j]</sup> groups reported the first structural examples of Cr-containing heteropolytungstates. In 2008, Xue's group reported two Cr<sup>III</sup>-substituted, sandwich-type heteropolymolybdates,  $[\text{Cr}_2(\text{AsMo}_7\text{O}_{27})_2]^{12-}$  and  $[\text{CrFe}(\text{AsMo}_7\text{O}_{27})_2]^{12-}$ .<sup>[3h,i]</sup> Recently, our group prepared two mono-Cr<sup>III</sup>-substituted heteropolytungstates  $[\text{Cr}^{\text{III}}(\text{HX}^{\text{V}}\text{W}_6\text{O}_{28})_2]^{13-}$  (X = P, As) by simple, one pot reactions, and these polyanions exhibit exceptionally large magnetic anisotropy.<sup>[3l]</sup>

An important subclass of POMs is the  $\{\text{XM}_6\text{O}_{24}\}$  structure type (also known as the Anderson-Evans structure), in which an octahedral  $\text{XO}_6$  hetero group is surrounded by six edge-shared  $\text{MO}_6$  octahedra. In 1948, Evans<sup>[7]</sup> reported the first example by determining the structure of  $[\text{TeMo}_6\text{O}_{24}]^{6-}$ , which had originally been proposed by Anderson in 1937.<sup>[8]</sup> To date, a large number of Anderson-Evans type polyanion derivatives  $[\text{H}_n\text{XM}_6\text{O}_{24}]^{m-}$  (M = W, Mo) is known, with many different *p*- and *d*- block elements acting as octahedrally coordinated hetero groups  $\text{XO}_6$ , with the oxidation states for X ranging from +2 to +6. The structural characterized tungsten-based derivatives  $[\text{H}_n\text{XW}_6\text{O}_{24}]^{m-}$  include the following hetero elements:  $\text{Te}^{\text{VI}}$ ,<sup>[9]</sup>  $\text{Sb}^{\text{V}}$ ,<sup>[10]</sup>  $\text{V}^{\text{V}}$ ,<sup>[11]</sup>  $\text{Pt}^{\text{IV}}$ ,<sup>[12]</sup>  $\text{Mn}^{\text{IV}}$ ,<sup>[13]</sup>  $\text{Ni}^{\text{IV}}$ ,<sup>[14]</sup>  $\text{Ni}^{\text{II}}$ ,<sup>[15a,b]</sup> and  $\text{Mn}^{\text{II}}$ .<sup>[15c]</sup> On the other hand, the molybdate family  $[\text{H}_n\text{XMo}_6\text{O}_{24}]^{m-}$  is known for the following hetero elements:  $\text{I}^{\text{VII}}$ ,<sup>[16]</sup>  $\text{Te}^{\text{VI}}$ ,<sup>[7,8]</sup>  $\text{Sb}^{\text{V}}$ ,<sup>[17]</sup>  $\text{V}^{\text{V}}$ ,<sup>[18]</sup>  $\text{Pt}^{\text{IV}}$ ,<sup>[19]</sup>  $\text{Pd}^{\text{IV}}$ ,<sup>[20]</sup>  $\text{Al}^{\text{III}}$ ,<sup>[21]</sup>  $\text{Cr}^{\text{III}}$ ,<sup>[3a,g,6,22]</sup>  $\text{Fe}^{\text{III}}$ ,<sup>[21b]</sup>  $\text{Co}^{\text{III}}$ ,<sup>[21b,23]</sup>  $\text{Ga}^{\text{III}}$ ,<sup>[24]</sup>  $\text{Rh}^{\text{III}}$ ,<sup>[25]</sup>  $\text{Mn}^{\text{II}}$ ,<sup>[21b]</sup>  $\text{Co}^{\text{II}}$ ,<sup>[21a,26]</sup>  $\text{Ni}^{\text{II}}$ ,<sup>[21b,27]</sup>  $\text{Cu}^{\text{II}}$ ,<sup>[28]</sup> and  $\text{Zn}^{\text{II}}$ .<sup>[21b,29]</sup> There are some reports on mixed addenda Anderson-Evans ions, such as  $[\text{Ni}^{\text{II}}(\text{OH})_6\text{Mo}_x\text{W}_{6-x}\text{O}_{18}]^{4-}$ ,<sup>[30]</sup> which was reinvestigated by Miwa's group.<sup>[21b]</sup>

It has also been demonstrated that organic functionalities can be attached to one or both sides of the Anderson-Evans

framework, in particular by the groups of Hasenknopf,<sup>[31]</sup> Cronin,<sup>[32]</sup> Wang,<sup>[33]</sup> Wei,<sup>[34]</sup> Wu,<sup>[35]</sup> and Song.<sup>[36]</sup>

Here, we report on the synthesis and structure of the chromium-centered Anderson-Evans type polytungstate derivative.

## Experimental Section

### Synthesis

All chemicals were commercially available and used without further purification.

### Synthesis of

### $\text{Na}_6[\text{H}_3\text{Cr}^{\text{III}}\text{W}_6\text{O}_{24}] \cdot 22\text{H}_2\text{O}$

#### Method 1

A sample of  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (0.20 g, 0.50 mmol) was dissolved in 20 mL of 1 M sodium acetate solution at pH 6.9, followed by addition of  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  (0.99 g, 3.00 mmol). The mixture was stirred for 1 h at 80 °C, allowed to cool to room temperature, and then filtered (final pH 8). Slow evaporation at room temperature led to the formation of green crystals of **1a** within three days (yield 0.15 g, 14%). IR ( $\text{cm}^{-1}$ ): 947 (m), 880 (s), 656 (s), 559 (w), 511 (m), 440 (m). Anal. calcd (found): Na 6.71 (7.15), W 53.65 (53.76), Cr 2.53 (2.69). Mw 2076.4 g/mol.

#### Method 2

A sample of  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (0.40 g, 1.00 mmol) was dissolved in 20 mL of 0.5 M sodium acetate solution at pH 6, followed by addition of  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  (2.64 g, 8.00 mmol). The mixture was stirred for 1 h at 80 °C, allowed to cool to room temperature, and then filtered (final

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pH 8). Slow evaporation at room temperature led to the formation of green crystals of **1a** within two days (yield 0.4 g, 19% based on Cr). The identity of **1a** was established by single crystal XRD and IR.

### Instrumentation

Infrared spectra were recorded on a Nicolet Avatar 370 FT-IR spectrophotometer using KBr pellets. The following abbreviations were used to assign the peak intensities: w = weak; m = medium; s = strong; br = broad. Thermogravimetric analysis was carried out on a TA Instruments SDT Q600 thermobalance with a 100 mL/min flow of nitrogen; the temperature was ramped from 20 to 800 °C at a rate of 5 °C/min. Elemental analysis was performed by CNRS, Service Central d'Analyse, Solaize, France.

### X-ray Crystallography

A single crystal of **1a** was mounted on a Hampton cryoloop in light oil for data collection at 100 K. Data collection and indexing were performed on a Bruker D8 SMART APEX II CCD diffractometer with kappa geometry (graphite monochromator,  $\lambda$  (Mo K $\alpha$ ) = 0.71073 Å). Data integration was performed using *SAINT*.<sup>[37]</sup> Routine Lorentz and polarization corrections were applied. Multiscan absorption corrections were performed using *SADABS*.<sup>[38]</sup> Direct methods (*SHELXS*) successfully located the tungsten atoms, and successive Fourier syntheses (*SHELXL*) revealed the remaining atoms.<sup>[38]</sup> Refinements were full-matrix least squares against  $|F|^2$  using all data. In the final refinement, the heavy atoms (Cr, W, Na) of the polyanion were refined anisotropically; the O atoms were refined isotropically. Crystallographic data are summarized in Table 1. The complete X-ray crystallographic data (CIF format) is available free of charge *via* the internet at the Fachinformationszentrum (FIZ) Karlsruhe (<http://www.fiz-karlsruhe.de/icsd.html>) under the CSD number 429800.

## Results and Discussion

### Synthesis and Structure

The novel polyanion  $[\text{H}_3\text{Cr}^{\text{III}}\text{W}_6\text{O}_{24}]^{6-}$  (**1**) was synthesized in a one-pot procedure under conventional 'open beaker' conditions, by reaction of  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  with  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  in aqueous  $\text{NaOAc}$  solution at 80 °C. The results show that the optimal ratio of  $\text{Cr}^{3+}/\text{WO}_4^{2-}$  is 1:6 for method 1 and 1:8 for method 2 (see Exp. Section). The ratio of  $\text{Cr}^{3+}/\text{WO}_4^{2-}$  represents the stoichiometric ratio in method 1, but not in 2. The reason is that the final pH is crucial for the successful isolation of **1a**, which should be carefully adjusted to 7.5–8.5. The starting pH in method 1 is 6.9, but 6 in method 2,

Table 1. Crystal data for **1a**.

Compound	$\text{Na}_6[\text{H}_3\text{Cr}^{\text{III}}\text{W}_6\text{O}_{24}] \cdot 22\text{H}_2\text{O}$
Formula weight [g/mol]	2076.4
Crystal system	Triclinic
Space group	$P\bar{1}$
$a$ [Å]	11.6313(10)
$b$ [Å]	12.3305(11)
$c$ [Å]	16.5066(13)
$\alpha$ [°]	68.336(2)
$\beta$ [°]	85.209(2)
$\gamma$ [°]	71.109(3)
Volume [Å <sup>3</sup> ]	2079.9(3)
Z	2
$D_{\text{calc}}$ [g/cm <sup>3</sup> ]	3.316
Absorption coefficient	16.962
F(000)	1898
Crystal size [mm]	0.24 × 0.19 × 0.18
Theta range for data collection [°]	3.491 – 27.877
Reflections collected	64511
Independent reflections	9767
R(int)	0.0435
Goodness-of-fit on F <sup>2</sup>	1.064
$R_1$ [I > 2 $\sigma$ (I)] <sup>a</sup>	0.0387
$wR_2$ (all data) <sup>b</sup>	0.1041

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b R_w = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}.$$

and therefore, an excess of  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  is needed in method 2 to keep the final pH in the range 7.5–8.5.

Single crystal X-ray analysis revealed that  $[\text{H}_3\text{Cr}^{\text{III}}\text{W}_6\text{O}_{24}]^{6-}$  has the so-called Anderson-Evans structure, consisting of a ring of six edge-shared  $\text{WO}_6$  octahedra surrounding the central  $\text{CrO}_6$  unit (Fig. 1). Hence, polyanion **1** represents the first Anderson-Evans type heteropolytungstate with a trivalent hetero element. The title

polyanion is isostructural with the molybdenum derivative  $[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{3-}$ , first reported in 1970.<sup>[3a]</sup> The central  $\text{Cr}^{\text{III}}$  ion in **1** has an almost ideal octahedral coordination environment, with Cr–O distances in the range of 1.962(5)–2.006(5) Å. These distances are very similar to those observed in the molybdenum derivative  $[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{3-}$  (Cr–O 1.968(3)–1.986(3) Å). The W–O distances in **1** can be grouped in three sets, terminal (W=O,

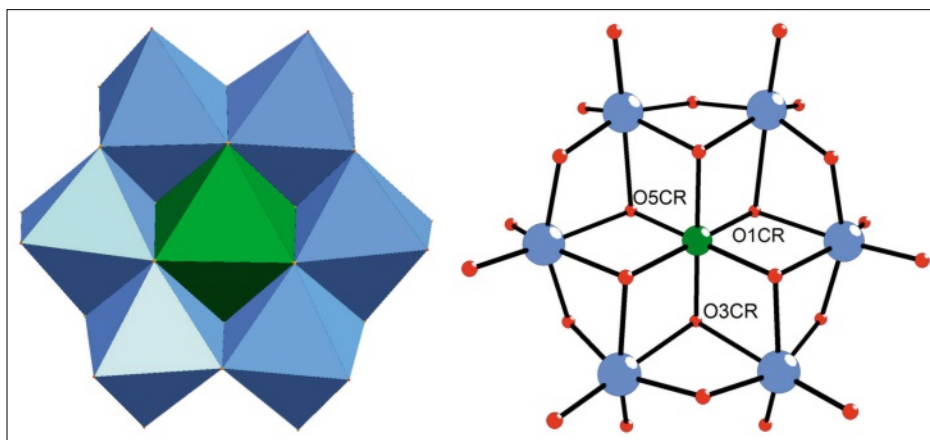


Fig. 1. Polyhedral (left) and ball-and-stick (right) representations of polyanion **1**. The positions of the three oxygens carrying non-disordered protons are indicated. Color code: W atoms and  $\text{WO}_6$  octahedra (blue), Cr atom and  $\text{CrO}_6$  octahedron (green), O atoms (red).

1.722(6)–1.763(6) Å), doubly-bridging ( $W-O_b$  1.916(6)–1.965(5) Å), and triply-bridging ( $W-O_c$ : 2.094(5)–2.413(5) Å). The same trend can be observed for the molybdenum analogue  $[Cr(OH)_6Mo_6O_{18}]^{3-}$  (see Table 2). Bond valence sum (BVS) calculations for **1** suggest that the triply bridging  $\mu_3$ -oxo groups O1CR, O3CR, and O5CR are monoprotonated (1.09, 1.18, and 1.22 respectively). Hence, polyanion **1** is tri-protonated, whereas Perloff's  $[Cr(OH)_6Mo_6O_{18}]^{3-}$  is hexa-protonated, which is probably due to the pH differences during synthesis (8 versus 4.5).

In the solid-state lattice of **1a**, each polyanion is surrounded by five  $Na^+$  counter cations, which are bound to a total of six terminal  $W=O$  oxygens of each polyanion (see Fig. 2). Two nearest neighbor polyanions are linked by the two  $Na(1)$  ions, and the distance between the central Cr atoms is about 6.771(4) Å. Moreover, the two neighboring polyanions are further linked with other  $Na^+$  ions to give an extended 3D network.

#### Fourier-transform Infrared Spectrum (FTIR)

The Fourier transform infrared (FTIR) spectrum of **1a** shows a fingerprint region characteristic for the tungsten-oxo framework (Fig. 3). The bands at about 947  $cm^{-1}$  and 880  $cm^{-1}$  arise from antisymmetric stretching vibrations of the terminal  $W=O$  bonds and  $Cr-O-W$  bridges, respectively. The strong band at approximately 656  $cm^{-1}$  is associated with the antisymmetric stretching of  $W-O-W$  bridges, whereas the medium band at 511  $cm^{-1}$  and a weak band at 559  $cm^{-1}$  correspond to bending vibrations of  $W-O-W$  bridges. The medium to strong bands at around 440  $cm^{-1}$  originate from the bending vibrations of the  $Cr-O-W$  bridges.

#### Thermogravimetric Analysis

The thermogram of **1a** (Fig. 4) shows a weight loss which starts at room temperature with a dehydration step ending at ca. 400 °C, corresponding to the loss of ~23 crystal water molecules and further loss of 1.5 compositional waters, involving the protons attached covalently to the polyanion [% calc. (found): 21.7 (20.5)].

#### Conclusions

The  $Cr^{III}$ -containing hexatungstate  $[H_3Cr^{III}W_6O_{24}]^{6-}$  (**1**) was prepared by a simple, one-pot reaction of  $Cr(NO_3)_3 \cdot 9H_2O$  and  $Na_2WO_4 \cdot 2H_2O$  in sodium acetate medium. Polyanion **1** represents the first chromium-derivative of the Anderson-Evans type heteropolytungstate family. The title compound was characterized in the solid state by IR spectroscopy, single-crystal

Table 2. Comparison of bond lengths between  $[H_3Cr^{III}W_6O_{24}]^{6-}$  (**1**) and  $[Cr(OH)_6Mo_6O_{18}]^{3-}$ .

	<b>1</b>		$[Cr(OH)_6Mo_6O_{18}]^{3-}$	
	Bond length [Å]	Average bond length [Å]	Bond length [Å]	Average bond length [Å]
Cr–O	1.962(5)–2.006(5)	1.982	1.968(3)–1.986(3)	1.647
M···M M = W, Mo	~ 3.150–3.192	3.175	~ 3.309–3.351	3.329
$M=O_t$	1.722(6)–1.763(6)	1.746	1.695(3)–1.720(4)	1.701
$M-O_b$	1.916(6)–1.965(5)	1.943	1.907(3)–1.985(5)	1.941
$M-O_c$	2.094(5)–2.413(5)	2.209	2.270(3)–2.347(3)	2.291

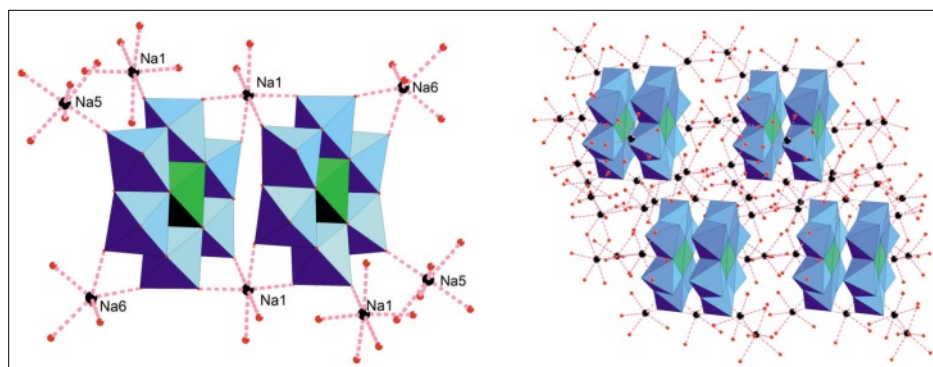


Fig. 2. Solid-state lattice of **1a** showing the polyanions being surrounded by  $Na^+$  counter cations (large pink balls). Water molecules are shown as small red balls, and the  $Na^+ \cdots OH_2$  interactions as dashed lines. Notice that not all  $Na^+$  ions could be found by single crystal XRD (see text for details).

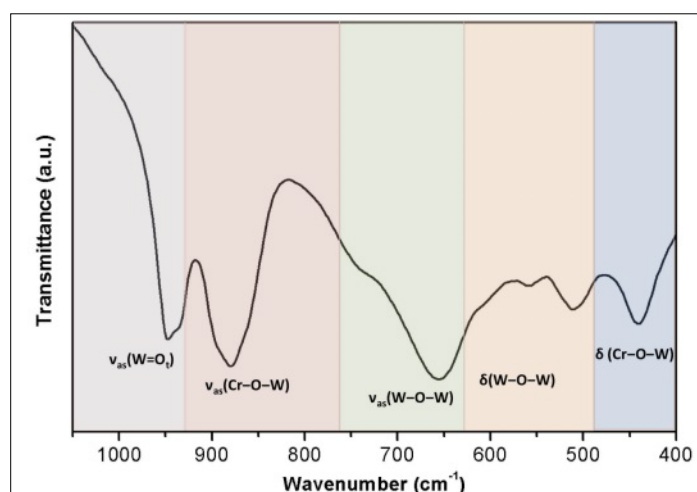


Fig. 3. FTIR spectrum of **1a**.

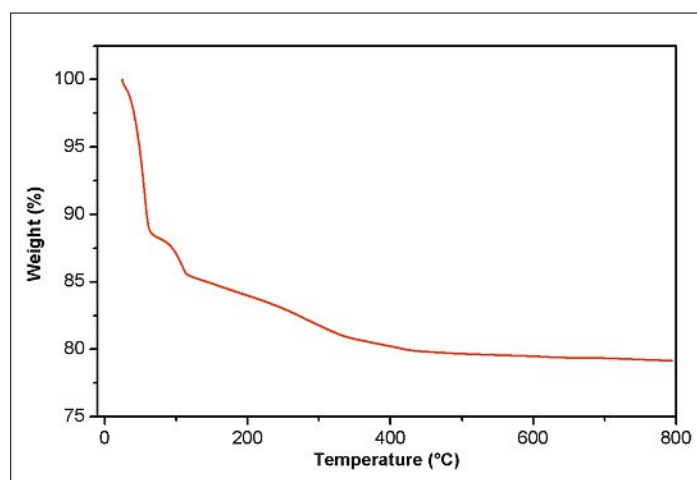


Fig. 4. Thermogram of **1a** from room temperature to 800 °C.

XRD, elemental and thermal analysis. We have already isolated several other, novel chromium-containing POMs, which will be reported elsewhere.

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