

## Tetra-cobalt-substituted Dimeric Tungstoantimonate: Na<sub>10</sub>[Co<sub>4</sub>(H<sub>2</sub>O)<sub>10</sub>(B-β-SbW<sub>9</sub>O<sub>33</sub>)<sub>2</sub>]·36H<sub>2</sub>O

Rongxin Tan <sup>\*,1, a</sup>, Tongxin xiao <sup>1, b</sup>, Jin Wang <sup>1, c</sup> and Pingping Zhao <sup>1, d</sup>

<sup>1</sup> College of chemistry and chemical engineering, Mudanjiang Normal University, Mudanjiang 157012, P. R. China

<sup>a</sup> tanrx271@163.cn    <sup>b</sup> xiaotongxin0716@163.com

<sup>c</sup> wangjin5769@163.com    <sup>d</sup> zpp.0225@163.com

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**Abstract** A new tetra-cobalt-substituted dimeric tungstoantimonate Na<sub>10</sub>[Co<sub>4</sub>(H<sub>2</sub>O)<sub>10</sub>(B-β-SbW<sub>9</sub>O<sub>33</sub>)<sub>2</sub>]·36H<sub>2</sub>O **1** was synthesized in a weakly alkaline solution. The compound was characterized by elemental analysis and IR spectroscopy. A single-crystal X-ray analysis was carried out on the crystal **1** which crystallizes in monoclinic system, space group *P 21/n*, with *a* = 12.529 Å, *b* = 12.778 Å, *c* = 29.434 Å, *α* = 90.000°, *β* = 101.158°, *γ* = 90.000° and *Z* = 2. Polyanion **1** consists of two B-β-SbW<sub>9</sub> units which are linked by four cobalt ions leading to a Keggin-type tetra-cobalt-substituted dimeric structure.

### Introduction

Polyoxometalates (POMs), a unique class of inorganic compounds, has been known for about 200 years since Berzelius reported the first POM, (NH<sub>4</sub>)<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>·*n*H<sub>2</sub>O [1]. Until today, the unprecedented development of POMs due to their almost unmatched range of physical properties and the abilities in catalysis, materials science, and bioinorganic, analytical, and medicinal chemistry, and this explains the constantly increasing interest in this research area [2-8].

In recent years transition metals substituted POMs (TMSPs) have attracted increasing attention and constituted the largest subclass of POMs because of their highly tunable nature, coupled with their fascinating properties including catalytic, medicine, redox electrochemical and magnetic properties [9-11]. This should be attributed to the synergism and enhancement effect of transition metals on the properties of POMs, especially the POMs of containing cobalts [12, 13]. Therefore, substituting of multiple transition metals may be an effective way to tune properties of POMs for developing functional materials. So the synthesis of the POMs containing multiple cobalts has become a particularly meaningful work and has become one of the goal of our efforts.

However, the formation of POMs is considered via self-assembly, the discovery of novel TMSPs with new structures and properties continues to be a focus of considerable ongoing research. The synthetic attempt is often accompanied by the coordination of the transition metal ions onto the lacunary polyanions [14]. Therefore, a multiple lacunary precursor obtained easily with a high stability in a relatively large pH range is crucial. The tricacant tungstoantimonate precursor [α-B-SbW<sub>9</sub>O<sub>33</sub>]<sup>9-</sup> [15] completely with the previous conditions, is undoubtedly one of the best candidates. Therefore, we decided to investigate the Co<sup>2+</sup>/[SbW<sub>9</sub>O<sub>33</sub>]<sup>9-</sup> system in some detail and obtained successfully a tetra-cobalt-substituted dimeric Tungstoantimonate, Na<sub>10</sub>[Co<sub>4</sub>(H<sub>2</sub>O)<sub>10</sub>(B-β-SbW<sub>9</sub>O<sub>33</sub>)<sub>2</sub>]·36H<sub>2</sub>O.

As reported, the reacting products of [α-B-SbW<sub>9</sub>O<sub>33</sub>]<sup>9-</sup> and transition metals are usually two forms, one is α-B-type trisubstituted sandwich structure, such as [(VO)<sub>3</sub>(SbW<sub>9</sub>O<sub>33</sub>)<sub>2</sub>]<sup>12-</sup>, [(MnII(H<sub>2</sub>O))<sub>3</sub>(SbW<sub>9</sub>O<sub>33</sub>)<sub>2</sub>]<sup>12-</sup>, [{MnIII(H<sub>2</sub>O)}<sub>3</sub>(SbW<sub>9</sub>O<sub>33</sub>)<sub>2</sub>]<sup>9-</sup>, [(C<sub>6</sub>H<sub>5</sub>Sn)<sub>3</sub>Na<sub>3</sub>(α-SbW<sub>9</sub>O<sub>33</sub>)<sub>2</sub>]<sup>6-</sup>, [Sb<sub>2</sub>W<sub>18</sub>{Cu(H<sub>2</sub>O)}<sub>3</sub>O<sub>66</sub>]<sup>12-</sup>, [Sb<sub>2</sub>W<sub>18</sub>Zn<sub>3</sub>O<sub>66</sub>(H<sub>2</sub>O)<sub>3</sub>]<sup>10-</sup>, [Cs<sub>2</sub>Na(H<sub>2</sub>O)<sub>10</sub>Pd<sub>3</sub>(α-SbW<sub>9</sub>O<sub>33</sub>)<sub>2</sub>]<sup>9-</sup>, [(UO<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>(SbW<sub>9</sub>O<sub>33</sub>)<sub>2</sub>]<sup>14-</sup> and [{Na(H<sub>2</sub>O)<sub>2</sub>}]<sub>3</sub>{Co(H<sub>2</sub>O)}<sub>3</sub>(α-B-SbW<sub>9</sub>O<sub>33</sub>)<sub>2</sub> **2** [13, 16-23], the other is disubstituted Krebs type which comprises two [β-B-SbW<sub>9</sub>O<sub>33</sub>]<sup>9-</sup> units linked via a belt of two internal {WO<sub>2</sub>}<sup>2+</sup> and two external {M(H<sub>2</sub>O)}<sub>3</sub> groups, for instance, [(WO<sub>2</sub>)<sub>2</sub>M<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>(β-SbW<sub>9</sub>O<sub>33</sub>)<sub>2</sub>]<sup>*n-*</sup> **3** (M<sup>*n+*</sup> = Mn<sup>2+</sup>, Fe<sup>3+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, VO<sup>2+</sup>) [15, 17, 24-27]. However, tetra-substituted dimeric β-B-type tungstoantimonates are very rare, to date, only a handful of

structurally characterized have been reported, for example,  $[\text{Fe}_4(\text{H}_2\text{O})_{10}(\beta\text{-SbW}_9\text{O}_{33})_2]^{6-}$  **4** [28] synthesized by Kortz et. al. Thus, the synthesis of compound **1** not only enriches the POMs family, but also possesses certain potential value for the synerism and enhancement effect of multiple cobalts on the properties of POMs, particularly, the enhancement of antitumor activities [13].

## Experimental

**Materials and Methods** The precursor  $\text{Na}_9[\text{SbW}_9\text{O}_{33}] \cdot 19.5\text{H}_2\text{O}$  was prepared according to the literature [15] and its purity was confirmed by infrared spectroscopy. All other reagents were used as purchased without further purification. Water was purified by distillation. Infrared spectrum was obtained on Nicolet 205 FT/IR spectrometer with KBr pellets in the 400-4000  $\text{cm}^{-1}$  region. Elemental analyses were determined by a Leaman inductively coupled plasma (ICP) spectrometer. Suitable crystals for X-ray diffraction measurements were obtained by slow evaporation and mounted on a glass fiber for indexing and intensity data collection on a SMART-CCD single-crystal diffractometer, with graphite-monochromated Mo- $\kappa\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The structure was solved by directed methods and refined by full-matrix least squares on  $F^2$  using the SHELXTL crystallographic software package. No attempt was made to locate the hydrogen atoms of water. Crystal data and structure refinement parameters for **1** are listed in Table 1. The CCDC number is 1415277.

Table 1. Crystal data and structure refinement for compound **1**.

	Compound	(1)	
Empirical formula	$\text{Na}_{10}\text{Co}_4\text{Sb}_2\text{W}_{18}\text{O}_{112}\text{H}_{92}$	$\alpha$ (°)	90.000(5)
Formula weight( $\text{g/mol}^{-1}$ )	5902.26.	$\beta$ (°)	101.158(5)
Temperature (K)	293	$\gamma$ (°)	90.000(5)
Crystal system	monoclinic	Z	2
Space group	$P 21/n$	Volume ( $\text{\AA}^3$ )	4623(3)
a ( $\text{\AA}$ )	12.529(5)	$D_{\text{calcd}}/\text{mg m}^{-3}$	4.174
b ( $\text{\AA}$ )	12.778(5)	$\mu/\text{mm}^{-1}$	23.746
c ( $\text{\AA}$ )	29.434(5)	Goodness-of-fit on $F^2$	0.9900
Final R indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0801$ $wR_2 = 0.1868$	Indices (all data)	$R_1 = 0.1393$ $wR_2 = 0.2163$

**Synthesis of compound 1**  $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  (600 mg, 2.4 mmol) was dissolved in 60 mL of distilled water, solid  $\text{Na}_9[\text{SbW}_9\text{O}_{33}] \cdot 19.5\text{H}_2\text{O}$  (3 g, 1.2 mmol) was quickly added in small portions with magnetic stirring, at this point, the pH value of the blue solution was 7.6. Then,  $\text{NaN}_3$  (56mg, 2.4 mmol) was added in above solution resulting in the pH value increased to 7.7. After the solution was stirred for 1 hour in room temperature, five drops  $\text{CsCl}$  ( $6 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ ) were added in, and traces of a precipitate were removed by filtration. After slow evaporation in air, pink crystals of **1** suitable for X-ray analysis were obtained about one week (31.40% yield, based on cobalt). Elemental analysis: Anal. Calcd. for  $\text{Na}_{10}\text{Co}_4\text{Sb}_2\text{W}_{18}\text{O}_{112}\text{H}_{92}$ : Na, 3.90%; Co, 3.99%; Sb, 4.13%; W, 56.07%. Found Na, 3.01%; Co, 3.42%; Sb, 3.35%; W, 54.18%.

## Results and Discussion

**Synthesis** Crystals of compound **1** suitable for X-ray diffraction measurement were obtained from a weakly alkaline solution system in room temperature. When the pH value was decreased below 6.5, crystal **3** would be obtained and no crystal **1**, interestingly, the absence of  $\text{NaN}_3$  would result in a mixture of **1** and **3**. Therefore, the pH value of the reaction played a crucial role in the formation of compound **1** and the effect of  $\text{NaN}_3$  maybe a slightly conditioning agent of pH value. In addition, when the reaction temperature was increased to  $95^\circ\text{C}$  at the molar ratio of 3:2 (Co:Sb), the product would be crystal **2**. So, temperature and molar ratio of reactant were two other conditions that affect the products.

**Structure** A single-crystal X-ray structural analysis shows that polyoxoanion **1** consists of two B- $\beta$ - type  $[\text{SbW}_9\text{O}_{33}]^{9-}$  moieties linked by four  $\text{Co}^{2+}$  ions resulting in a structure with idealized  $C2h$  symmetry (see Figure 1). This structure is analogous to that of compound **4**.

In polyanion **1** the four  $\text{Co}^{2+}$  ions consist of two equivalent pairs, the inner two  $\text{Co}^{2+}$  ions and the outer two  $\text{Co}^{2+}$  ions. Each cobalt atom is an octahedron structure with six coordination numbers. The inner  $\text{Co}^{2+}$  ion has four Co-O bonds and two terminal  $\text{H}_2\text{O}$  ligands. Of the four Co-O bonds, two oxygen atoms are the “terminal” oxygen atoms coming from two different  $\text{W}_3\text{O}_{10}$  cluster of one  $[\text{SbW}_9\text{O}_{33}]^{9-}$  moiety, and the other two are the equivalent “terminal” oxygen atoms coming from the other  $[\text{SbW}_9\text{O}_{33}]^{9-}$  moiety. The outer  $\text{Co}^{2+}$  ion has three Co-O bonds and three terminal  $\text{H}_2\text{O}$  ligands. Of the three Co-O bonds, two oxygen atoms are the “terminal” oxygen atoms coming from two different  $\text{W}_3\text{O}_{10}$  cluster of one  $[\text{SbW}_9\text{O}_{33}]^{9-}$  moiety, and the other is the “terminal” oxygen atoms coming from the rotated  $\text{W}_3\text{O}_{10}$  cluster of the other  $[\text{SbW}_9\text{O}_{33}]^{9-}$  moiety. The average distance of Co-O(w) bonds is 2.053 Å and of Co-O( $\text{H}_2\text{O}$ ) is 2.148 Å.

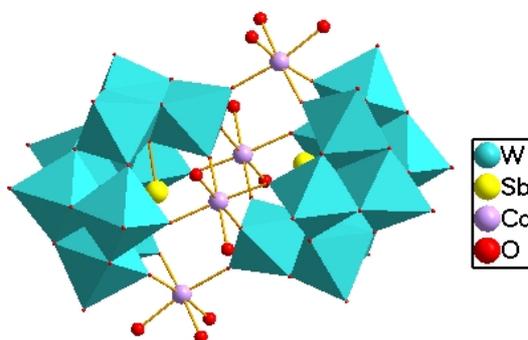


Figure1. Polyhedral representation of compound **1** with  $\text{Co}^{2+}$  in ball-and-stick representation.

**Infrared spectroscopy** The IR spectrum of compound **1** indicates characteristic bands, in agreement with the structure determined by X-ray crystallography. In the IR spectrum of compound **1**, the features at 943, 883, 821, 723, 684, 673 and 652  $\text{cm}^{-1}$  are characteristic stretching vibrational peaks for heteropolyanions with Keggin structure corresponding to *vas* (W-Od), *vas* (W-Ob) and *vas* (W-Oc).

## Conclusions

In the summary, a multiple cobalts substituted tungstoantimonates **1** has been synthesized. Compound **1** consists of two B- $\beta$ - $\text{SbW}_9$  units which are linked by four cobalts resulting in a tetra-cobalt-substituted dimeric polyanion. The tungstoantimonate **1** possible has a outstanding performance for the the synergism and enhancement effect of transition metals on the properties of POMs.

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## References

- [1] J. Berzelius: Ann. Phys. Vol.6 (1826), p. 369
- [2] M.T. Pope, A. Müller; Angew. Chem., Int. Ed. Engl. Vol. 30 (1991), p. 34
- [3] M.T. Pope, A. Müller; Polyoxometalates: From Platonic Solids to Retrovital Activity, ( The Netherlands, Dordrecht, 1994)
- [4] C.L. Hill (ed.): Special issue on polyoxometalates. Chem. Rev. Vol. 98 (1998), p. 1

- [5] M.T. Pope, A. Müller; *Polyoxometalate Chemistry: from Topology via Self-Assembly to Applications* (The Netherlands, Dordrecht, 2001)
- [6] M. Misono: *Chem. Commun.* (2001), p. 1141
- [7] A. Müller, S. Roy: *Coord. Chem. Rev.* Vol. 245 (2003) p. 153
- [8] U. Kortz, A. Müller, J. Van Slageren, et. al.: *Coord. Chem. Rev.* Vol. 253 (2009), p. 2315
- [9] C.L. Hil: *J. Mol. Catal. A-Chem.* Vol. 262 (2007) p.1
- [10] S.S. Mal, M.H. Dickman, U. Kortz, et.al.: *Chem. A Eur. J.* Vol. 14 (2008) p. 1186
- [11] N. Zamstein, A. Tarantul, B. Tsukerblat: *Inorg. Chem.* Vol. 46 (2007), p. 8851
- [12] R.X. Tan, X.H. Pang, H. Wang, et. al.: *Inorganic Chemistry Communications.* Vol. 25 (2012), p. 70
- [13] R.X. Tan, C. Wang, S.X Cui, et. al.: *Journal of Macromolecular Science, Part A:Pure and Applied Chemistry,* Vol. 51 (2014), p. 33
- [14] L.H. Bi, B. Li, L.X. Wu, Y.Y. Bao: *Inorganica Chimica Acta.* Vol. 362 (2009), p. 3309
- [15] M. Bösing, I. Loose, H. Pohlmann, B. Krebs: *Chem. Eur.* Vol. 3 (1997), p. 1232
- [16] T. Yamase, B. Botar, E. Ishikawa, K. Fukaya: *Chem. Lett.* Vol. 1 (2001), p. 56
- [17] M. Bösing, A. Nöh, I. Loose, B. Krebs: *J. Am. Chem. Soc.* Vol. 120 (1998), p.7252
- [18] D. Drewes, M. Piepenbrink, B. Krebs: *Journal of Cluster Science,* Vol. 17 (2006), p. 361
- [19] G. Sazani, M.H. Dickman, M.T. Pope: *Inorg. Chem.* Vol. 39 (2000), p. 939
- [20] P. Mialane, J. Marrot, E. Rivière, J. Nebout, G. Hervé, *Inorg. Chem.* Vol. 40 (2001), p. 44
- [21] U. Kortz, N.K. Al-Kassem, M.G. Savelieff, N.A. Al Kadi, M. Sadakane, *Inorg. Chem.* Vol. 40 (2001), p.4742
- [22] L.H. Bi, M. Reiche, U. Kortz, et. al.: *Inorg. Chem.* Vol. 43 (2004), p. 3915
- [23] A.J. Gaunt, I. May, R. Copping, et. al.: *Dalton Trans.* (2003), p. 3009
- [24] I. Loose, E. Droste, M. Bösing, et. al.: *Inorg. Chem.* Vol. 38 (1999), p. 2688
- [25] B. Krebs, E. Droste, M. Piepenbrink, G.C.R. Vollmer: *Acad. Sci., Ser. 11c: Chim.* Vol. 3 (2000), p. 205
- [26] M. Piepenbrink, E.M. Limanski, B. Krebs, *Z. Anorg. Allg. Chem.* Vol. 628 (2002), p. 1187
- [27] D. Drewes, E.M. Limanski, M. Piepenbrink, B. Krebs, *Z. Anorg. Allg. Chem.* Vol. 630 (2004), p. 58
- [28] U. Kortz, M.G. Savelieff, B.S. Bassil, B. Keita, L. Nadjo: *Inorg. Chem.* Vol. 41 (2002), p. 783