956 *Inorg. Chem.* **2011**, *50*, 956–960
DOI: 10.1021/ic102149c

Inorganic Chemistry
Article

Yttrium(III)-Containing Tungstoantimonate(III) Stabilized by Tetrahedral WO_4^{2-} Capping Unit, $[\{Y(\alpha\text{-}SbW_9O_{31}(OH)_2)(CH_3COO)(H_2O)\}_3(WO_4)]^{17-}$

Masooma Ibrahim,[†] Sib Sankar Mal,[†,‡] Bassem S. Bassil,[†] Abhishek Banerjee,[†] and Ulrich Kortz*[,†]

[†] *Jacobs University, School of Engineering and Science, P.O. Box 750 561, 28725 Bremen, Germany.*
[‡] *Current address: Center For Catalysis Research and Innovation, Department of Chemistry, University of Ottawa, 10 Marie Curie, K1N 6N5, ON, Canada.*

Received August 4, 2010

The yttrium(III)-containing tungstoantimonate(III) $[\{Y(\alpha\text{-}SbW_9O_{31}(OH)_2)(CH_3COO)(H_2O)\}_3(WO_4)]^{17-}$ (**1**) has been synthesized in a simple one-pot reaction of Y^{3+} ions with $[\alpha\text{-}SbW_9O_{33}]^{9-}$ and WO_4^{2-} in a 3:3:1 molar ratio in 1 M LiOAc/AcOH buffer at pH 5.3. Polyanion **1** is composed of three (α-SbW_9O_{33}) units linked by three Y^{3+} ions and a capping, tetrahedral WO_4^{2-} capping unit, resulting in an assembly with C_{3v} symmetry. The hydrated ammonium-sodium salt of **1** was investigated in the solid state by single-crystal XRD, FT-IR spectroscopy, thermogravimetric and elemental analyses, and in solution by multinuclear NMR spectroscopy.

Introduction

Polyoxometalates (POMs) are a large class of discrete, anionic metal-oxide fragments comprising early transition metals in high oxidation states such as W^{VI}, Mo^{VI}, or V^{V}.[1] There has been increasing interest in the synthesis of POMs because of potential applications in various fields including catalysis, magnetism, medicine, materials science, and chemical analysis.[2] Heteropolyanions, in contrast to isopolyanions, contain a heterogroup X, which is often tetrahedrally coordinated (e.g., PO_4, SiO_4) or exhibits a trigonal pyramid (e.g., $As^{III}O_3$, $Sb^{III}O_3$), due to the presence of a lone pair of electrons. Lacunary derivatives of the latter type include species such as $[XW_9O_{33}]^{9-}$ (X = As^{III}, Sb^{III}, Bi^{III}). Because of the presence of the lone pair, the closed Keggin unit cannot be formed, and hence "unconventional" structures may be obtained, such as $[NH_4As_4W_{40}O_{140}Co_2(H_2O)_2]^{23-}$, $[As_4W_{20}O_{72}(H_2O)_2]^{12-}$, $[H_2AsW_{18}O_{60}]^{7-}$, or $[AsW_8O_{30}AsOH]^{7-}$.[3−5] Lone pair-containing, trilacunary polyanions are also known to act as multidentate ligands for lanthanide[6−10] and transition metal ions.[11]

Lanthanide (Ln) and yttrium(III) ions are of special interest because of their oxophilicity and large coordination numbers (CN = 8−12).[12] They can link two or more polyanion units to form very large structures, such as Pope's $[As_{12}Ce_{16}(H_2O)_{36}W_{148}O_{524}]^{76-}$.[6] Furthermore, POMs achieve certain functionalities, specially photoluminescence, in the presence of lanthanide ions.[13] The reactivity of lanthanide

---

*To whom correspondence should be addressed. E-mail: u.kortz@jacobs-university.de; Fax: +49 421 200 3229; Tel: +49 421 200 3235.

(1) (a) Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer-Verlag: Berlin, 1983. (b) Pope, M. T.; Müller, A. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 34.

(2) (a) Hill, C. L.; Prosser-McCartha, C. M. *Coord. Chem. Rev.* **1995**, *143*, 407. (b) Hill, C. L., Ed. Special Issue on Polyoxometalates. *Chem. Rev.* **1998**, *98*. (c) Müller, A.; Roy, S. *Coord. Chem. Rev.* **2003**, *245*, 153. (d) Cronin, L. In *Comprehensive Coordination Chemistry II*, Vol. *7*; McCleverty, J. A, Meyer, T. J., Eds.; Elsevier: Amsterdam, 2004; p 1. (d) Hasenknopf, B.; Micoine, K.; Lacôte, E.; Thorimbert, S.; Malacria, M.; Thouvenot, R. *Eur. J. Inorg. Chem.* **2008**, 5001. (h) Kortz, U.; Müller, A.; van Slageren, J.; Schnack, J.; Dalal, N. S.; Dressel, M. *Coord. Chem. Rev.* **2009**, *253*, 2315. (i) Kortz. U., Guest Ed. Issue dedicated to Polyoxometalates. *Eur. J. Inorg. Chem.* **2009**, *34*. (j) Long, D. L.; Tsunashima, R.; Cronin, L. *Angew. Chem., Int. Ed.* **2010**, *49*, 1736.

(3) Mialane, P.; Marrot, J.; Riviére, E.; Nebout, J.; Hervé, G. *Inorg. Chem.* **2001**, *40*, 44.

(4) Yamase, T.; Botar, B.; Ishikawa, E.; Fukaya, K. *Chem. Lett.* **2001**, 56.

(5) (a) Jeannin, Y.; Martin-Frère, J. *Inorg. Chem.* **1979**, *18*, 3010. (b) Robert, F.; Leyrie, M.; Hervé, G.; Tézé, A.; Jeannin, Y. *Inorg. Chem.* **1980**, *19*, 1746. (c) Leyrie, M.; Tézé, A.; Hervé, G. *Inorg. Chem.* **1985**, *24*, 1275.

(6) Wassermann, K; Dickman, M. H.; Pope, M. T. *Angew. Chem., Int. Ed.* **1997**, *36*, 1445.

(7) (a) Yamase, T.; Naruke, H.; Sasaki, Y. *J. Chem. Soc. Dalton Ttrans.* **1990**, 1687. (b) Naruke, H.; Yamase, T. *J. Alloys Compd.* **1998**, *68*, 100. (c) Naruke, H.; Yamase., T. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 1289. (d) Naruke, H.; Yamase, T. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 1275. (e) Fukaya, K.; Yamase, T. *Angew. Chem., Int. Ed.* **2003**, *42*, 654.

(8) Howell, R. C.; Perez, F. G.; Horrocks, W. D.; Jain, S.; Rheingold, A. L.; Francesconi, L. C. *Angew. Chem., Int. Ed.* **2001**, *40*, 4031.

(9) Drewes, D.; Piepenbrink, M.; Krebs, B. *Z. Anorg. Allg. Chem.* **2006**, *632*, 534.

(10) Ozeki, T.; Yamase, T.; Naruke, H.; Sasaki, Y. *Inorg. Chem.* **1994**, *33*, 409.

(11) (a) Bösing, M.; Nöh, A.; Loose, I.; Krebs, B. *J. Am. Chem. Soc.* **1998**, *120*, 7252. (b) Kortz, U.; Al-Kassem, N. K.; Savelieff, M. G.; Al Kadi, N. A.; Sadakane, M. *Inorg. Chem.* **2001**, *40*, 4742. (c) Kortz, U.; Savelieff, M. G.; Bassil, B. S.; Keita, B.; Nadjo, L. *Inorg. Chem.* **2002**, *41*, 783. (d) Bi, L.-H.; Reicke, M.; Kortz, U.; Keita, B.; Nadjo, L.; Clark, R. J. *Inorg. Chem.* **2004**, *43*, 3915. (e) Bi, L.-H.; Li, B.; Wu, L. X; Bao, Y. Y. *Inorg. Chim. Acta* **2009**, *362*, 3309.

(12) (a) Kepert, D. *Inorganic Stereochemistry*; Springer: Berlin, 1982. (b) Bünzli, J. C. G. *Basic and Applied Aspects of Rare Earths*; Editional Complutense: Madrid, 1997.

ions with lacunary polytungstate precursors has been investigated predominantly by the groups of Pope, Yamase, Francesconi, Krebs, and Ozeki.[6-10] The groups of Gouzerh, Boskovic, and Patzke have also synthesized high-nuclearity lanthanide-containing polyoxotungstates.[14-16] Our group has also reported several examples of such species.[17]

In 1971, Peacock and Weakley were the first to describe the yttrium(III)- and lanthanide(III)-containing sandwich-type decatungstate.[18] In 2000, these salts were used as catalysts with H_2O_2 for alcohol oxidations and alkene epoxidations by H_2O_2.[19] In 2008, our group reported on the synthesis and solid-state structure of the yttrium-derivative $[YW_{10}O_{36}]^{9-}$, as well as its solution properties by ^{183}W and ^{89}Y NMR.[20] This polyanion consists of two monolacunary Lindqvist-based $[W_5O_{18}]^{6-}$ fragments encapsulating a central Y^{3+} ion with a square-antiprismatic coordination. In 2009, we reported another class of yttrium(III)- and lanthanide(III)-containing isopolytungstates, $[M_2(H_2O)_{10}W_{22}O_{72}(OH)_2]^{8-}$ (M^{3+} = Y, La, Ce, Tb, Dy, Ho, Er, Tm, Yb, Lu).[17e] These isostructural polyanions are composed of a 22-tungsten isopolyanion unit $\{W_{22}\}$, which is coordinated to two Y(III)/Ln(III) ions. Very recently the Y-containing, acetate-bridged, dimeric undecatungstate $[Y(CH_3COO)XW_{11}O_{39}(H_2O)]^{6-}$ (X = Si^{IV} and Ge^{IV}) was reported.[21] Our group prepared a family of yttrium(III)- and lanthanide(III)-encapsulated heteropolypalladates, $[X^{III}Pd^{II}_{12}(AsPh)_8O_{32}]^{5-}$ (X = Y, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu). These cuboid-shaped polyanions consist of a cage of twelve Pd^{2+} ions with eight capping phenylarsonate heterogroups and a central guest ion X.[22] Francesconi's group reported on the Y-containing tungstophosphate $[(PY_2W_{10}O_{38})_4(W_3O_{14})]^{30-}$, which is composed of four $[PW_9O_{34}]^{9-}$ units connected via a central $[Y_8W_7O_{30}]^{6+}$ assembly.[8] Solution studies demonstrated that this polyanion self-assembles to single-layer, vesicle-like structures in dilute aqueous solution.[23] Hill and co-workers reported two sandwich-type PM structures, whose formation requires the presence of the carbonate ions in the reaction mixture.[24] In the polyanion $[(YOH_2)_3(CO_3)(A\text{-}\alpha\text{-}PW_9O_{34})_2]^{11-}$ three Y^{3+} ions are sandwiched between two $[A\text{-}\alpha\text{-}PW_9O_{34}]^{9-}$ moieties encapsulating a central carbonate ion. However, the Wells–Dawson-based Y-containing polyanion $[\{Y_4(\mu_3\text{-}OH)_4(H_2O)_8\}(\alpha\text{-}P_2W_{15}O_{56})_2]^{16-}$ does not contain a carbonate ion.[25] One-dimensional solid state structures constructed by Y^{3+} and $[GeW_{11}O_{39}]^{8-}$ have also been reported.[26] The Y^{3+} containing 40-tungsto-4-arsenate(III) $[Y(H_2O)_5\{Ni(H_2O)\}_2As_4W_{40}O_{140}]^{21-}$ is composed of the known polyanion $[As_4W_{40}O_{140}]^{28-}$ with Y^{3+} in the central S1 site and Ni^{2+} in the S2 sites.[27]

We decided to further investigate the reactivity of yttrium(III) ions with lone-pair containing, trilacunary heteropolytungstates. Herein, we report the synthesis and structural characterization of a novel yttrium(III)-containing, trimeric tungstoantimonate(III).

Experimental Section

Reagents and Materials. $Na_9[\alpha\text{-}SbW_9O_{33}]\cdot 19.5H_2O$ was prepared according to the published procedure and characterized by IR spectroscopy.[28] All other reagents were used as purchased without further purification.

Instrumentation. All reagents were used as purchased without further purification. Infrared spectra were recorded on KBr pellets using a Nicolet AVATAR 370 FT-IR spectrometer. All NMR spectra were recorded on a 400 MHz JEOL ECX instrument at room temperature. The ^{1}H and ^{13}C NMR spectra were recorded using 5 mm tubes, whereas the ^{183}W and ^{89}Y NMR spectra were recorded in 10 mm tubes, after dissolution of 3 g of solid **1a**. The respective resonance frequencies were 16.69 (^{183}W), 19.63 (^{89}Y), 399.78, (^{1}H), and 100.53 MHz (^{13}C). The chemical shifts are reported with respect to the references Na_2WO_4 (^{183}W), $Y(NO_3)_3$ (^{89}Y), and TMS (^{1}H and ^{13}C). Elemental analyses for Na, W, Sb, and Y were performed by Kanti Laboratories, Tirupathi, India, and CHN analyses were performed by Service Central d'Analyse, Solaize, France.

Synthesis of $Na_{16}(NH_4)[\{Y(\alpha\text{-}SbW_9O_{31}(OH)_2)(CH_3COO)(H_2O)\}_3(WO_4)]\cdot 48H_2O$ (1a). $Na_9[\alpha\text{-}SbW_9O_{33}]\cdot 19.5H_2O$ (2.153 g, 0.750 mmol) and YCl_3 (0.228 g, 0.750 mmol) were added to 20 mL of 1 M LiOAc/AcOH buffer at pH 5.3. To the reaction mixture 0.083 g (0.250 mmol) of Na_2WO_4 were added. The solution was heated to 80 °C for 60 min and filtered when it was still hot. Then 0.5 mL of 1.0 M NH_4Cl solution was added to the yellow filtrate, which was then allowed to evaporate in an open beaker at room temperature. After two weeks, a yellow crystalline product appeared, which was collected by filtration and air-dried. Yield: 1.56 g (23%). IR (2% KBr pellet, ν/cm^{-1}): 1629(s), 1541(s), 1460(w), 1348(sh), 934(m), 896(sh), 836(m), 784(m), 683(sh), (505)w, 437(m). Elemental analysis (%) calcd for $Na_{16}(NH_4)[\{Y(\alpha\text{-}SbW_9O_{31}(OH)_2)(CH_3COO)(H_2O)\}_3(WO_4)]\cdot 48H_2O$ (**1a**): Na 4.13, W 57.74, Sb 4.12, Y 2.99, C 0.81, H 1.32, N 0.16. Found: Na 4.39, W 57.60, Sb 4.21, Y 3.12, C 1.08, H 1.21, N 0.20. Product recrystallized from NMR tube, $Na_{14}(NH_4)[\{Y(\alpha\text{-}SbW_9O_{31}(OH)_2)\}_3(CH_3COO)(H_2O)_7(WO_4)]\cdot 48H_2O$ (**1b**): C 0.27, H 1.41, N 0.16. Found: C 0.32, H 1.20, N 0.23.

Thermogravimetric Analysis. Thermogravimetric analysis of **1a** was performed between 25 and 900 °C under a nitrogen atmosphere to determine the amount of crystal water present in the polyanion salt (see Figure S3, Supporting Information). We observed a weight loss of approximately 10.5% between 25 and

---

(13) (a) Yamase, T.; Naruke, H. *J. Chem. Soc., Dalton Trans.* **1991**, 285. (b) Yamase, T.; Kobayashi, T.; Sugeta, M.; Naruke, H. *J. Phys. Chem. A.* **1997**, *101*, 5046. (c) Yamase, T.; Naruke, H. *J. Phys. Chem. B.* **1999**, *103*, 8850. (d) Granadeiro, C. M.; Ferreira, R. A. S.; Soares-Santos, P. C. R.; Carlos, L. D.; Nogueira, H. I. S. *Eur. J. Inorg. Chem.* **2009**, 5088.

(14) Xue, G. L.; Vaissermann, J.; Gouzerh, P. *J. Cluster Sci.* **2002**, *13*, 409.

(15) Hussain, F.; Gable, R. W.; Speldrich, M.; Kögerler, P.; Boskovic, C. *Chem. Commun.* **2009**, 328.

(16) (a) Hussain, F.; Spingler, B.; Conrad, F.; Speldrich, M.; Kögerler, P.; Boskovic, C.; Patzke, G. R. *Dalton Trans.* **2009**, 4423. (b) Hussain, F.; Conrad, F.; Patzke, G. R. *Angew. Chem., Int. Ed.* **2009**, *48*, 9088.

(17) (a) Kortz, U.; Holzapfel, C.; Reicke, M. *J. Mol. Struct.* **2003**, *656*, 93. (b) Kortz, U. *J. Cluster Sci.* **2003**, *14*, 205. (c) Bassil, B. S.; Dickman, M. H.; von der Kammer, B.; Kortz, U. *Inorg. Chem.* **2007**, *46*, 2452. (d) Bassil, B. S.; Dickman, M. H.; Römer, I.; von der Kammer, B.; Kortz, U. *Angew. Chem., Int. Ed.* **2007**, *46*, 6192. (e) Ismail, A. H.; Dickman, M. H.; Kortz, U. *Inorg. Chem.* **2009**, *48*, 1559.

(18) Peacock, R. D.; Weakley, T. J. R. *J. Chem. Soc. A* **1971**, 1836.

(19) Griffith, W. P.; Morley-Smith, N.; Nogueira, H. I. S.; Shoair, A. G. F.; Suriaatmaja, M.; White, A. J. P.; Williams, D. J. *J. Organomet. Chem.* **2000**, *607*, 46.

(20) Barsukova, M.; Dickman, M. H.; Visser, E.; Mal, S. S.; Kortz, U. *Z. Anorg. Allg. Chem.* **2008**, *634*, 2423.

(21) Hussain, F.; Degonda, A.; Sandriesser, S.; Fox, T.; Mal, S. S.; Kortz, U.; Patzke, G. R. *Inorg. Chim. Acta* **2010**, *363*, 4324.

(22) Barsukova, M.; Izarova, N. V.; Ngo Biboum, R.; Keita, B.; Nadjo, L.; Ramachandran, V.; Dalal, N. S.; Antonova, N. S.; Carbó, J. J.; Poblet, J. M.; Kortz, U. *Chem.—Eur. J.* **2010**, *16*, 9076.

(23) Mishra, P. P.; Jing, J.; Francesconi, L. C.; Liu, T. *Langmuir* **2008**, *24*, 9308.

(24) Fang, X.; Anderson, M. T.; Neiwert, W. A.; Hill, C. L. *Inorg. Chem.* **2003**, *42*, 8600.

(25) Fang, X.; Anderson, T. M.; Benelli, C.; Hill, C. L. *Chem.—Eur. J.* **2005**, *11*, 712.

(26) Wang, J. P.; Duan, X. Y.; Du, X. D.; Niu, J. Y. *Cryst. Growth Des.* **2006**, *6*, 2266.

(27) Xue, G.; Liu, B.; Hua, H.; Yang, J.; Wang, J.; Fu, F. *J. Mol. Str.* **2004**, *690*, 95.

(28) Bösing, M.; Loose, I.; Pohlmann, H.; Krebs, B. *Chem.—Eur. J.* **1997**, *3*, 1232.

270 °C, which can be assigned to the loss of 48 crystal waters and the 3 coordinated aqua ligands per formula unit (calcd 11.4%). In addition, there is a weight loss of approximately 2.2% from 271 to 490 °C corresponding to the decomposition of the three acetate ligands and the ammonium countercation in **1a.** This hypothesis was confirmed by heating a solid sample of **1a** to 500 °C, and a subsequent FT-IR measurement did not show anymore the characteristic stretching frequencies of acetate (see Figure S2, Supporting Information). Thermogravimetric analysis was also carried out on **1b**, which was recrystallized from an NMR tube (see Figure S1, Supporting Information). An obvious change in the thermogram can be observed in the region where acetate decomposes. This observation is consistent with FT-IR and elemental analysis of **1b**, indicating that two of the originally three coordinated acetate ligands have been replaced by a total of 4 water ligands.

X-ray Crystallography. A yellow, plate-shaped crystal of **1a** with dimensions 0.27 × 0.23 × 0.08 mm^3 was isolated in oil to prevent water loss and mounted in a Hampton cryoloop under constant nitrogen flow for indexing and intensity data collection at 173 K on a Bruker D8 APEX II CCD single-crystal diffractometer using Mo Kα radiation (λ = 0.71073 Å). The SHELX software package (Bruker) was used to solve and refine the structure.[29] Of the 255904 reflections collected ($2\theta_{\max}$ = 45.98°, 99.3% complete), 10856 were unique (R_{int} = 0.1402) and 7682 reflections were considered observed ($I > 2\sigma(I)$). Routine Lorentz and polarization corrections were applied and an absorption correction was performed using the *SADABS* program.[30] Direct methods were used to locate the tungsten and yttrium atoms. Then the remaining atoms were found from successive Fourier maps.[31] The final cycle of refinement, including the atomic coordinates, anisotropic thermal parameters (all W, Y, and Sb atoms and Na1 and Na2) and isotropic thermal parameters (all O atoms and Na3−Na6) converged at R = 0.0762 ($I > 2\sigma(I)$) and R_w = 0.2358 (all data). In the final difference map, the deepest hole was −1.937 e Å^{-3}, and the highest peak 3.393 eÅ^{-3}. Crystallographic data are summarized in Table 1.

Table 1. Crystal Data for $Na_{16}(NH_4)[\{Y(\alpha\text{-}SbW_9O_{31}(OH)_2)(CH_3COO)(H_2O)\}_3(WO_4)].48H_2O$ (**1a**)

empirical formula	$C_6H_{121}NNa_{16}O_{160}Sb_3W_{28}Y_3$
formula weight, g/mol	8915.66
crystal system	orthorhombic
space group	*Pnma*
a, Å	26.11(3)
b, Å	32.049(14)
c, Å	18.408(11)
volume, Å^3	15406(20)
Z	4
D_{calcd}, g/cm^3	3.844
absorption coefficient	22.610
F(000)	15 752
crystal size, mm	0.27 × 0.23 × 0.08
θ range for data collection, deg	3.31−22.99
reflections collected	255 904
independent reflections	10 856
R(int)	0.1402
observed ($I > 2\sigma(I)$)	7682
$T_{\min}/T_{\max}$	0.2268
goodness-of-fit on F^2	1.094
R_1 [$I > 2\sigma(I)$][a]	0.0762
R_w (all data)[b]	0.2358

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

Results and Discussion

Synthesis and Structure. We have synthesized the yttrium(III)-containing tungstoantimonate(III) $[\{Y(\alpha\text{-}SbW_9O_{31}(OH)_2)(CH_3COO)(H_2O)\}_3(WO_4)]^{17-}$ (**1**) in a simple one-pot reaction of Y^{3+} ions with $[\alpha\text{-}SbW_9O_{33}]^{9-}$ and WO_4^{2-} in a 3:3:1 molar ratio in 1 M LiOAc/AcOH buffer at pH 5.3. The hydrated sodium-ammonium salt $Na_{16}(NH_4)[\{Y(\alpha\text{-}SbW_9O_{31}(OH)_2)(CH_3COO)(H_2O)\}_3(WO_4)]\cdot 48H_2O$ (**1a**) was characterized in the solid state by IR spectroscopy, thermogravimetric (TGA), and elemental analyses. Single-crystal XRD on **1a** revealed that the triangular title polyanion **1** is composed of three (α-SbW_9O_{33}) units linked by three 8-coordinated yttrium(III) ions and a capping, tetrahedral tungstate group leading to a structure with idealized C_{3v} point group symmetry (see Figures 1 and 2). Each Y^{3+} ion bridges two Keggin units via four Y−O(W) bonds, two from each (SbW_9O_{33}) subunit involving corner-shared WO_6 octahedra. Such type of assembly is also found in our previously reported tin-containing, trimeric assembly $[\{Sn(CH_3)_2(H_2O)\}_2\{Sn(CH_3)_2\}As_3(\alpha\text{-}AsW_9O_{33})_4]^{21-}$, which is capped by a formally neutral $\{As_3(\alpha\text{-}AsW_9O_{33})\}$ fragment.[32] However, the three tin centers have a different coordination number (six and seven) than the yttrium ions (eight) in **1**. Furthermore, the capping tungstate unit in polyanion **1** appears to be more strongly bound than the tungstoarsenate cap in our organotin species.

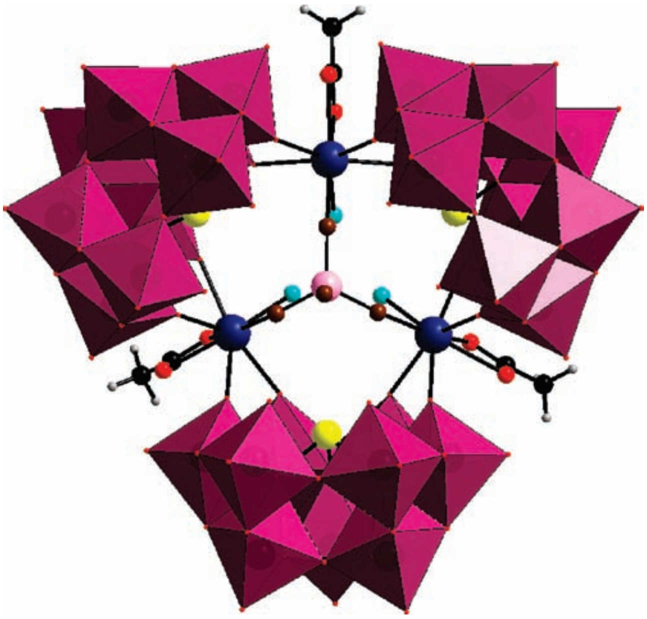

Figure 1. Top view of **1** along the 3-fold axis. Color code: WO_6 octahedra (plum), Sb (yellow), Y (dark blue), unique , tetrahedrally coordinated W (rose), O of unique W (brown), O of acetate (red), O_{aq} (light blue), C (black), and H (gray).

Each of the three Y^{3+} ions in **1** is also coordinated by an external, terminal acetate group, bound in a bidentate fashion via the carboxylate function (see Figure 2). The two remaining coordination sites of the yttrium(III) ions are filled by an aqua ligand from one side and a Y−O(W) bridge to the capping, tetrahedral WO_4^{2-} unit from the other side. The coordination geometry of each Y^{3+} ion can be considered as distorted square-antiprismatic with Y−O bond distances in the range 2.24(5)−2.45(4) Å.

---

(29) Sheldrick, G. M. *SHELXS-97*; University of Göttingen: Göttingen, Germany, 1997.

(30) Sheldrick, G. M. *SADABS*; University of Göttingen: Göttingen, Germany, 1996.

(31) Sheldrick, G. M. *Acta Crystallogr.* **2007**, *A64*, 112.

(32) Hussain, F.; Kortz, U. *Chem. Commun.* **2005**, 1191.

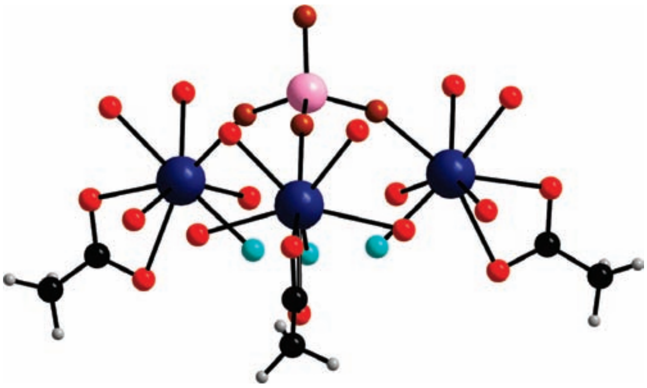

Figure 2. View of the capping tungstate group in **1** and the coordination spheres of the three yttrium ions. The color code is the same as in Figure 1.

The presence of the tetrahedral, capping tungstate group in **1** is interesting and surprising, as tungsten is usually 6-coordinated in POMs and no extra tungstate was added when we isolated **1** for the first time. A possible source might have been minor tungstate impurities in the lacunary polyanion precursor salt or in-situ generation of WO_4^{2-} because of partial decomposition of [α-SbW_9O_{33}]$^{9-}$ during the reaction. We discovered that the yield of **1** increased upon addition of one equivalent of tungstate during the reaction. Hence, the tetrahedral WO_4^{2-} group appears to play an important templating role during the formation of **1**. Three oxygen atoms of the {WO_4} moiety coordinate each to an Y^{3+} ion, whereas the fourth oxygen is terminal, being situated on the 3-fold axis of the title polyanion. The capping tungstate group has idealized tetrahedral symmetry with W−O bond lengths in the range 1.68(5)−1.80(5) Å and O−W−O angles in the range of 106.9(12)−112.6(17)°. The template effect of small anions in POM chemistry is well-known and several examples have been reported.[33] Very recently, Wang's group reported a nickel-containing tungstophosphate with an encapsulated, tetrahedral tungstate group and W−O bond lengths in the range of 1.716(17)−1.821(17) Å and O−W−O angles in the range of 106.8(9)−111.6(8)°.[34]

We also performed bond valence sum (BVS) calculations on **1** to identify possible protonation sites on the oxygens of the polyanion.[35] The BVS values for the terminal oxygens of the yttrium ions (0.43−0.48) suggest that these oxygen atoms are diprotonated, corresponding to aqua ligands. Also, the two terminal oxygens at the lacunary site of each (α-SbW_9O_{33}) unit have a BVS range of 1.19−1.38, indicating monoprotonation. The total charge of **1** is therefore 17−, which is balanced by one ammonium and 16 sodium counter cations in the solid state.

The number of counter cations was determined by elemental analysis (see Experimental Section), whereas the number of water molecules was determined by TGA. Only 6 Na counter cations and 14 crystal waters could be determined by single-crystal XRD due to disorder, which is a common feature in POM (in particular polyoxotungstate) crystallography. As expected, the ammonium countercation could also not be located by single-crystal XRD, but its presence was identified by elemental analysis.

IR Spectroscopy. Figure S1, Supporting Information, shows the IR spectra of **1a** and **1b**, the latter being obtained in the NMR tube when a solution of redissolved **1a** for NMR measurements was left open for slow evaporation of the solvent. Both FT-IR spectra display a fingerprint region that is characteristic for POMs,[36] and an additional band appearing at around 836 cm^{-1} belongs to vibrations of Y−O(W) bonds. The very intense peaks related to acetate carboxylate groups are observed only in **1a**. The bands at 1541, 1460, and 1409 cm^{-1} are attributed to stretching bands of the acetate carboxylate groups. The bands belonging to rocking vibrations of these carboxylate groups are observed at 620 and 505 cm^{-1}. The peaks at 1348 and 1230 cm^{-1} are attributed to bending and rocking vibrations of the acetate methyl groups in **1a**.[37] While the IR spectrum of **1b** shows actetate bands with much reduced intensity, the structure of polyanion **1** remains essentially unchanged, suggesting loss of some acetate groups. This indicates that the title polyanion **1** hast lost some acetate groups. These observations are consistent with elemental and thermogravimetric analyses of **1b** (see Figure S3, Supporting Information). Figure S2, Supporting Information, is a comparison of the IR spectra of **1a** and after this salt had been heated to 500 °C. In the latter, no characteristic stretching bands associated with the acetate groups are observed, indicating that they have decomposed at this temperature. The broad peak at 3432 cm^{-1} and a strong peak at 1629 cm^{-1} correspond to stretching and bending vibrations of crystal waters, respectively. The characteristic IR bands of the precursor salt Na_9[α-SbW_9O_{33}]·19.5H_2O and **1a** are summarized in Table 2.

NMR Spectroscopy. We have also performed multinuclear NMR studies on **1a** redissolved in H_2O/D_2O to study the solution stability of the title polyanion. The ^{183}W NMR spectrum consists of six singlets at −20.0, −74.6, −93.7, −143.7, −166.0, and −209.5 ppm with relative intensities 6:6:6:6:3:1 (see Figure 3). These results are fully consistent with the C_{3v} symmetry of **1** observed in the solid-state. The four downfield signals of largest intensity (−20.0, −74.6, −93.7, and −143.7 ppm) can be assigned to the three pairs of belt and one pair of cap tungstens in each of the three Keggin units. The signal of medium intensity (−166.0 ppm) can be assigned to the unique cap tungstens in each of the three Keggin units. Finally, the most upfield signal (−209.5 ppm) of lowest intensity can be assigned to the unique, tetrahedrally coordinated tungesten atom. The ^{89}Y NMR spectrum showed the expected singlet at 47.2 ppm (see Figure 4). The ^{13}C spectrum showed singlets at 23.5 and 181.6 ppm,

---

(33) (a) Müller, A.; Döring, J. *Z. Anorg. Allg. Chem.* **1991**, *595*, 251. (b) Clemente-Juan, J.; Coronado, E.; Galán-Mascarós, J.; Gómez-García, C. *Inorg. Chem.* **1999**, *38*, 55. (c) Zhao, J.; Zhang, J.; Zheng, S.; Yang, G. *Inorg. Chem.* **2007**, *46*, 10944. (d) Fang, X.; Kögerler, P. *Angew. Chem., Int. Ed.* **2008**, *47*, 8123. (e) Al-Kadamany, G.; Hussain, F.; Mal, S. S.; Dickman, M. H.; Leclerc-Laronze, N.; Marrot, J.; Cadot, E.; Kortz, U. *Inorg. Chem.* **2008**, *47*, 8574.

(34) Zhang, H.; Li, Y.; Lu, Y.; Clérac, R.; Zhang, Z.; Wu, Q.; Feng, X.; Wang, E. *Inorg. Chem.* **2009**, *48*, 10889.

(35) Brown, I. D.; Altermatt, D. *Acta Crystallogr.* **1985**, *B41*, 244.

(36) (a) Rocchiccioli-Deltcheff, C.; Fournier, M.; Franck, R.; Thouvenot, R. *Inorg. Chem.* **1983**, *22*, 207. (b) Thouvenot, R.; Fournier, M.; Franck, R.; Rocchiccioli-Deltcheff, C. *Inorg. Chem.* **1984**, *23*, 598. (c) Crâciun, C.; David, L.; Rusu, M.; Cozar, O.; Marcu, G. *J. Radioanal. Nucl. Chem.* **2001**, *247*, 307. (d) Hossu, M.; Rusu, D.; Rusu, M.; Cozma, D.; David, L.; Cozar, O. *J. Optoelectron. Adv. Mater.* **2008**, *10*, 2346.

(37) Nickolov, Z.; Georgieva, G.; Stoilova, D.; Ivanova, I. *J. Mol. Struct.* **1995**, *354*, 119.

Table 2. Characteristic FT-IR Bands (cm^{-1}) of the Precursor Salt $Na_9[\alpha\text{-}SbW_9O_{33}]\cdot 19.5H_2O$ and the Title Polyanion Salt **1a**[a]

band	$Na_9[\alpha\text{-}SbW_9O_{33}]\cdot 19.5H_2O$	**1a**
$\nu_{as}(W{=}O_t)$	925 s	934 s
$\nu_{as}(Sb-O_i)$	890 s	896 m
$\nu_{as}(Y-O)$		836 m
$\nu_{as}(W-O_c)$	767 w	785 s
	702 b	720 sh
$\nu_{as}(W-O_b)$	618 w	683 m

[a] Abbreviations: s strong, m medium, w weak, b broad, sh shoulder, O_t terminal oxygen, O_i oxygen linking Sb and W, O_c oxygen linking corner-shared WO_6 octahedra, O_b oxygen linking edge-shared WO_6 octahedra.

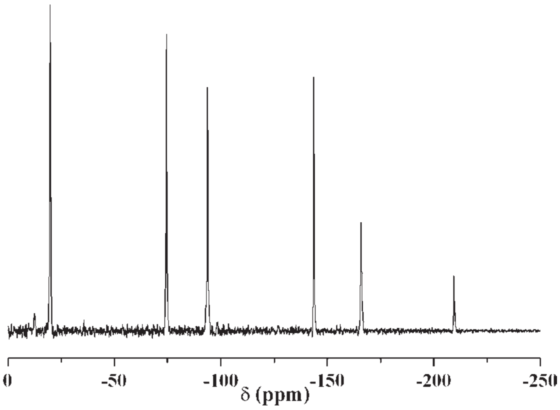

Figure 3. Solution ^{183}W NMR spectrum (at RT) of a freshly prepared solution of **1a** redissolved in H_2O/D_2O.

which also corresponds to the chemical shifts of free acetate. Addition of solid sodium acetate to the solution did not result in the appearance of any new signals, indicating that the three acetate groups bound to **1** in the solid state are labile in solution and are most likely replaced by aqua ligands. This hypothesis is reinforced by IR spectroscopy, thermogravimetric analysis and elemental analysis of the crystalline solid $Na_{16}(NH_{14})[\{Y(\alpha\text{-}SbW_9O_{31}(OH)_2)\}_3(CH_3COO)(H_2O)_7(WO_4)]\cdot 48H_2O$ (**1b**). This material could be crystallized in the NMR tube when the solution of **1a** was kept (after the NMR measurements) in an open vial allowing for slow evaporation of the solvent. The IR spectrum of **1b** showed actetate bands with reduced intensity, but the core structure of polyanion **1** remained unchanged (see Figure S1, Supporting Information). Elemental analysis for **1b** is consistent with the loss of two (of the three) acetate ligands, which were replaced by 4 water molecules from the solvent. Efforts to perform single-crystal XRD measurements on **1b** were unsuccessful because of insufficient quality of the crystals.

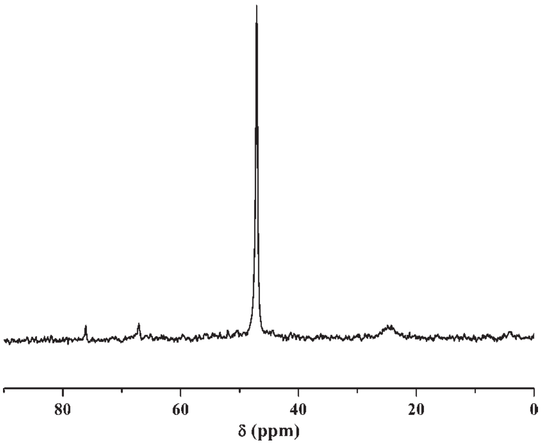

Figure 4. Solution ^{89}Y NMR spectrum (at RT) of a freshly prepared solution of **1a** redissolved in H_2O/D_2O.

Conclusions

In summary, we have synthesized the yttrium(III)-containing tungstoantimonate(III) $[\{Y(\alpha\text{-}SbW_9O_{31}(OH)_2)(CH_3COO)(H_2O)\}_3(WO_4)]^{17-}$ (**1**) using a simple, one-pot procedure by reacting the trilacunary POM precursor $[\alpha\text{-}SbW_9O_{33}]^{9-}$ with $Y^{3+}$and free WO_4^{2-} ions. Polyanion **1** has an open, trimeric structure and is capped by a tetrahedral tungstate group. It is likely that derivatives of **1** may be formed with the acetate ligands replaced by other carboxylic acids or carboxylate containing functionalities. We have discovered that the presence of WO_4^{2-} ions in the reaction mixture is the key factor for the formation of **1**. Multinuclear NMR studies are consistent with the solution stability of the title polyanion. Currently we are also investigating if the arsenic(III) analogue of **1** can be formed. A study of the homogeneous oxidation catalysis properties of **1** is also planned.

Acknowledgment. U.K. thanks the German Science Foundation (DFG-KO-2288/3-2), the Fonds der Chemischen Industrie, and Jacobs University for research support. M.I. thanks DAAD and Higher Education Commission of Pakistan for a doctoral fellowship. She also thanks the University of Balochistan, Quetta, Pakistan, for allowing her to pursue her Ph.D. studies at Jacobs University, Germany. Figures 1 and 2 were generated by *Diamond*, version 3.2 (copyright Crystal Impact GbR).

Supporting Information Available: Infrared spectra and thermograms for **1a**, as well as crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.