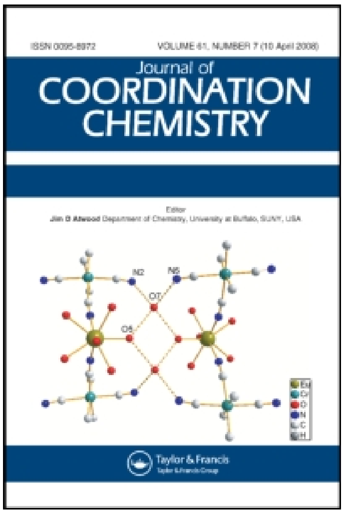

Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, structure and properties of rare earth substituted germanotungstates: Pr/[α-$GeW_{11}O_{39}$]

Jingping Wang[a]; Xiaodi Du[a]; Qingxia Yan[a]; Jingyang Niu[a]
[a] Institute of Molecular and Crystal Engineering, School of Chemistry and Chemical Engineering, Henan University, Kaifeng 475001, P.R. China

To cite this Article Wang, Jingping , Du, Xiaodi , Yan, Qingxia and Niu, Jingyang(2008) 'Synthesis, structure and properties of rare earth substituted germanotungstates: Pr/[α-$GeW_{11}O_{39}$]', Journal of Coordination Chemistry, 61: 21, 3467 — 3475

To link to this Article: DOI: 10.1080/00958970802068870

URL: http://dx.doi.org/10.1080/00958970802068870

Journal of Coordination Chemistry
Vol. 61, No. 21, 10 November 2008, 3467–3475

Synthesis, structure and properties of rare earth substituted germanotungstates: Pr/[α-$GeW_{11}O_{39}$]

JINGPING WANG, XIAODI DU, QINGXIA YAN and JINGYANG NIU*

Institute of Molecular and Crystal Engineering, School of Chemistry
and Chemical Engineering, Henan University, Kaifeng 475001, P.R. China

(*revised 15 January 2008; in final form 18 January 2008*)

Two new polyoxometalate compounds based on the lacunary Keggin anion [α-$GeW_{11}O_{39}]^{8-}$ and the rare earth cation Pr^{III}, $[(CH_3)_4N]_{2.25}H_{1.25}[Pr_{1.5}(GeW_{11}O_{39})(H_2O)_{5.75}] \cdot 1.25H_2O$ (**1**) and $[Pr_{0.5}(H_2O)_{2.25}]H_{0.5}[Pr_2(GeW_{11}O_{39})(DMSO)_2(H_2O)_8] \cdot 5.75H_2O$ (**2**), have been synthesized and characterized by elemental analysis, inductively coupled plasma (ICP) analysis, IR and UV spectroscopy, and single-crystal X-ray diffraction. The solid-state structure of **1** consists of one-dimensional zig-zag chains built of [α-$GeW_{11}O_{39}]^{8-}$ anions connected by Pr^{3+}. In **2**, DMSO (DMSO = dimethyl sulfoxide) leads to a double-parallel chainlike structure constructed by two linear wires $\{[Pr(GeW_{11}O_{39})(DMSO)(H_2O)_2]^{5-}\}_n$ linked by Pr^{3+} coordination cations.

Keywords: Polyoxometalate; Monovacant Keggin derivative; Rare earth; Germanotungstate

1. Introduction

Polyoxometalates (POMs) are well-defined, discrete transition metal oxide clusters with potential applications in fundamental and applied science [1–5]. Recently, chemistry of POMs produced fascinating topology and important electronic, optical, magnetic and catalytic properties [6, 7]. The multiple coordination and oxophilicity make trivalent rare earth ions of interest to link polyoxometalates in supramolecular chemistry with magnetic and luminescent properties [8–10]. The substitution of one or more atoms by rare earth metal cations led to increasing attention for class of compounds.

In 1971, Peacock and Weakley first reported that the monovacant Keggin anions $[XW_{11}O_{39}]^{n-}$ ($X = Si^{IV}$, P^{V}) form both 1 : 1 and 1 : 2 compounds with rare earth ions in solution [11]. For a period of time, only 1 : 2 complexes were isolated [11, 12]. Finally, in 2000, Pope *et al.* reported structural characterization of the one-dimensional (1D) 1 : 1 $[Ln(\alpha\text{-}SiW_{11}O_{39})(H_2O)_3]^{5-}$ ($Ln = La^{III}$, Ce^{III}) compounds, showing that these anions are polymeric in the solid state, creating interest in rare earth/monovacant POMs of the non-1 : 2 type [10b, 13–15]. Phosphotungstates and silicotungstates are the most intensively studied systems because they exhibit a large variety of lacunary precursor species. The number of germanium-containing polyoxoanions is very small and previous work is based on the Keggin-type germanododecamolybdate, $[GeMo_{12}O_{40}]^{4-}$,

---

*Corresponding author. Email: jyniu@henu.edu.cn

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2008 Taylor & Francis
DOI: 10.1080/00958970802068870

and the analogous germanotungstate, $[GeW_{12}O_{40}]^{4-}$ [16]. Although Hervé and Tézé reported different isomers of the first monolacunary germanotungstate $[GeW_{11}O_{39}]^{8-}$ in 1977 [17], derivatives based on the monovacant germanotungstates are rare. In 1980, Tourné *et al.* reported the first rare earth derivative of the monolacunary germanotungstate, $Cs_{12}[U(GeW_{11}O_{39})_2] \cdot 13\sim14H_2O$ [18]. In 1987, Liu *et al.* reported on a series of *bis*(undecatungstogermanate) lanthanides [19], in which all the anions have a structure similar to $Cs_{12}[U(GeW_{11}O_{39})_2] \cdot 13\sim14H_2O$; no other crystal structures of rare earth cations with $[\alpha\text{-}GeW_{11}O_{39}]^{8-}$ have been reported. $[\alpha\text{-}GeW_{11}O_{39}]^{8-}$ has a larger bite angle in the vacant site than $[\alpha\text{-}SiW_{11}O_{39}]^{8-}$ for binding rare earth ions. In this article, we report two compounds based on the monovacant Keggin polyanion $[\alpha\text{-}GeW_{11}O_{39}]^{8-}$ and rare earth ions, $[(CH_3)_4N]_{2.25}H_{1.25}[Pr_{1.5}(GeW_{11}O_{39})(H_2O)_{5.75}] \cdot 1.25H_2O$ (**1**) and $[Pr_{0.5}(H_2O)_{2.25}]H_{0.5}[Pr_2(GeW_{11}O_{39})(DMSO)_2(H_2O)_8] \cdot 5.75H_2O$ (**2**).

2. Experimental

2.1. *Physical measurements and materials*

$\alpha\text{-}K_8GeW_{11}O_{39} \cdot nH_2O$ was prepared according to the literature [20] and confirmed by IR spectroscopy. Other reagents were purchased commercially and used without further purification.

Infrared spectra were recorded on a Nicolet AVATAR 360 FTIR spectrophotometer (KBr pellets in 400–4000 cm^{-1} region). Ultraviolet spectra were obtained on a Unican UV-500 spectrometer (distilled water as solvent in 400–190 nm region). Elemental analyses (C, H, N and S) were conducted on a Perkin–Elmer 240C analyzer. Inductively coupled plasma (ICP) analyses (Ge, W, Pr) were carried out on a Jarrel–Ash J-A1100 spectrometer.

2.2. *Preparations of compounds*

2.2.1. $[(CH_3)_4N]_{2.25}H_{1.25}[Pr_{1.5}(GeW_{11}O_{39})(H_2O)_{5.75}] \cdot 1.25H_2O$ (1). A 2.32 g (0.71 mmol) sample of $\alpha\text{-}K_8[GeW_{11}O_{39}] \cdot nH_2O$ was dissolved in 20 mL of water at 80°C, followed by dropwise addition of 0.35 g (1.42 mmol) of $PrCl_3$ in 5 mL of water. After 1 h, the solution was cooled to room temperature and the precipitate removed by filtration. Then 0.4 g of tetramethylammonium bromide was added. The resulting clear solution was filtered and left to evaporate at room temperature. The next day, greenish pillar-like crystals of **1**, suitable for X-ray diffraction, were collected. Yield: 1.56 g (68%). IR (KBr pellets, ν/cm^{-1}): 949 (s), 877 (s), 808 (s), 704 (s), 526 (m). Anal. Calcd for $C_9H_{42.25}N_{2.25}O_{46}GePr_{1.5}W_{11}$(%): C, 3.35; H, 1.32; N, 0.98; Ge, 2.25; Pr, 6.56; W, 62.72. Found: C, 3.31; H, 1.30; N, 1.02; Ge, 2.29; Pr, 6.60; W, 62.66.

2.2.2. $[Pr_{0.5}(H_2O)_{2.25}]H_{0.5}[Pr_2(GeW_{11}O_{39})(DMSO)_2(H_2O)_8] \cdot 5.75H_2O$ (2). A 2 mL (21 mmol) sample of $HClO_4$ (10.37 M) was added dropwise into the powder of 1.9 g (2.87 mmol) of Pr_4O_6 under heating until the Pr_4O_6 dissolved entirely. The resulting solution was added to 30 mL water solution containing 6 g (2 mmol) of α-$K_8[GeW_{11}O_{39}] \cdot nH_2O$ at 80°C. After 1 h, the solution was cooled to room temperature and a precipitate containing potassium perchlorate was removed by filtration. Then, 1 mL of DMSO was added, and after 0.5 h the resulting clear solution was left to evaporate at room temperature. Several days later, yellow crystals were collected. Yield: 4.6 g (65%). IR (KBr pellets, ν/cm^{-1}): 946 (s), 881 (m), 812 (vs), 702 (m), 522 (m). Anal. Calcd for $C_4H_{44.50}O_{57}S_2GePr_{2.50}W_{11}$(%): C, 1.37; H, 1.28; S, 1.82; Ge, 2.07; Pr, 10.02; W, 57.51. Found: C, 1.33; H, 1.32; S, 1.78; Ge, 2.03; Pr, 10.06; W, 57.47.

2.3. *X-ray crystallography and structure solution*

Single-crystal X-ray diffraction measurements for the two compounds were carried out on a Rigaku RAXIS-IV image plate area detector using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) at 293(2) K. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL-97 package [21]. Intensity data were corrected for Lorentz and polarization effects as well as for empirical absorption. All non-hydrogen atoms were refined anisotropically and hydrogens, except in water, were located in calculated positions. Experimental details for the structural determination of **1** and **2** are listed in table 1. Selected bond distances and angles for **1** and **2** are listed in **S1** (supplementary materials).

3. Results and discussion

3.1. *Crystal structure of 1 and 2*

Single crystal X-ray diffraction reveals that the solid-state structures of **1** and **2** consist of infinite 1D arrangements built up of [α-$GeW_{11}O_{39}]^{8-}$ anions connected

Table 1. Crystal data and refinement parameters for **1** and **2**.

	1	**2**
Empirical formula	$C_9H_{42.25}N_{2.25}O_{46}GePr_{1.5}W_{11}$	$C_4H_{44.50}O_{57}S_2GePr_{2.50}W_{11}$
Formula weight	3224.38	3516.11
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	Pbca
Unit cell dimensions (Å, °)		
a	18.758(4)	11.5223(9)
b	13.487(3)	25.5547(19)
c	27.599(6)	44.365(3)
α	90	90
β	105.72(3)	90
γ	90	90
$V(\text{Å}^3)$	6721(2)	13063.3(17)
Z	4	8
D_{Calcd} g (cm^{-3})	3.187	3.575
Abs coeff (mm^{-1})	20.324	21.723
T (K)	293(2)	293(2)
Reflns collected	17939	89260
Independent reflns	10225	11459
Final *R* indices $[I > 2\sigma(I)]$	$R_1 = 0.0770$; $wR_2 = 0.1656$	$R_1 = 0.0517$; $wR_2 = 0.1139$
R indices (all data)	$R_1 = 0.1018$; $wR_2 = 0.1773$	$R_1 = 0.0587$; $wR_2 = 0.1162$

by Pr^{3+} cations. The $[\alpha\text{-}GeW_{11}O_{39}]^{8-}$ is obtained by removal of a $W{=}O_d$ group from $[\alpha\text{-}GeW_{12}O_{40}]^{4-}$ formed of $12\{WO_6\}$ octahedra forming four $\{W_3O_{13}\}$ fragments. Compared to the isostructural monovacant species $[\alpha\text{-}SiW_{11}O_{39}]^{8-}$, the $[\alpha\text{-}GeW_{11}O_{39}]^{8-}$ anion contains a larger "bite angle" which in the lacunary site is influenced by the effective radius of the central element (Ge^{4+}, 53 pm and Si^{4+}, 40 pm). The larger bite angle for $[\alpha\text{-}GeW_{11}O_{39}]^{8-}$ may allow the rare earth cation to bind deeper into the defect site [22], resulting in different arrangement. In addition, the H^+ ions in **1** and **2** are added to neutralize the excessive negative charge. (According to the valence sum calculations [23] for all the O atoms, O4 and O9 in **1** and O6 in **2** are 1.55, 1.53, 1.55, respectively.) All the water molecules, except O1W, O2W and O3W in **1** and O1W-O8W, O18W and O19W in **2**, are disordered.

The asymmetric structural unit of **1** consists of $2.25[(CH_3)_4N]^+$ cations, $1.25H^+$, $[Pr_{1.5}(GeW_{11}O_{39})(H_2O)_{5.75}]^{3.5-}$ and 1.25 waters of crystallization. The polyanion unit $[Pr_{1.5}(GeW_{11}O_{39})(H_2O)_{5.75}]^{3.5-}$ is composed of $[Pr(1)(H_2O)_3]^{3+}$, $0.5[Pr(2)(H_2O)_4(H_2O)_{1.5}]^{3+}$, and one $[\alpha\text{-}GeW_{11}O_{39}]^{8-}$ building block. The structure of **1** is represented in figure 1 and the coordination environments around $Pr^{3+}(1)$ and $Pr^{3+}(2)$ are shown in figure 2. The $Pr^{3+}(1)$ cation occupies the vacant site of an

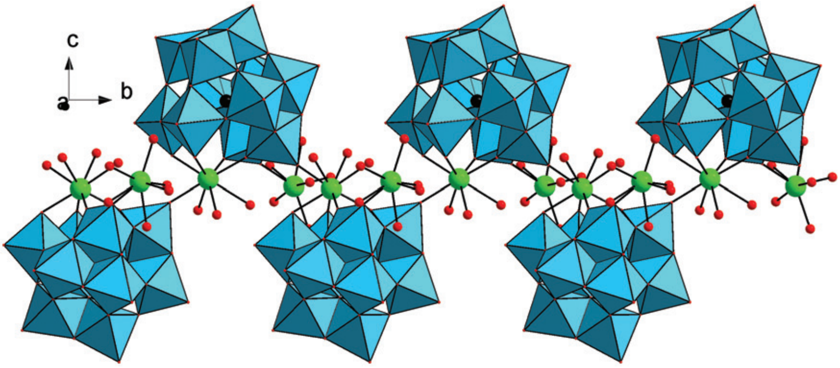

Figure 1. Polyhedralrepresentation of **1**. The water molecules are omitted for clarity. Key (online): Pr, green; $\{WO_6\}$, blue octahedra.

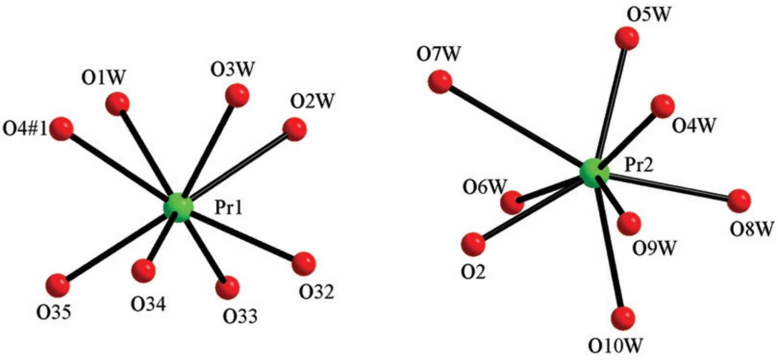

Figure 2. The coordination environment around $Pr^{3+}(1)$, $Pr^{3+}(2)$ in **1**.

$[\alpha\text{-GeW}_{11}O_{39}]^{8-}$ subunit and is coordinated to the four available oxygens of the lacunary site ($d_{\text{Pr(1)-Ob,c}} = 2.412$ Å); connection of the neighboring $[\alpha\text{-GeW}_{11}O_{39}]^{8-}$ subunits occurs via Pr(1)–O_d (O4#1) ($d_{\text{Pr(1)-Od}} = 2.505(17)$ Å) forming the 1D infinite zig-zag chainlike structure along the *a*-axis, with the shortest interchain Pr–Pr distance of 6.828 Å. The coordination sphere of $Pr^{3+}(1)$ is completed by three waters ($d_{\text{Pr(1)-O(H}_2\text{O)}} = 2.584$ Å). Thus, Pr(1) is eight-coordinate, adopting a distorted square antiprism geometry. The $Pr^{3+}(2)$ links to the $[\alpha\text{-GeW}_{11}O_{39}]^{8-}$ subunit via terminal oxygen (O_2) ($d_{\text{Pr(2)-O}_2} = 2.43(2)$ Å) and its occupancy is 0.5 due to crystallographic disorder. The $Pr^{3+}(2)$ center is also eight-coordinate, completed by seven waters (the occupancy of three waters is 0.25 and of the other four waters is 0.5) ($d_{\text{Pr(2)-O(H}_2\text{O)}} = 2.586$ Å). Along the *bc* plane, the $Pr^{3+}(2)$ ions are located on opposite sides of the chains from steric hindrance.

The asymmetric structural unit of **2** consists of $[Pr_{0.5}(H_2O)_{2.25}]^{1.5+}$, $0.5H^+$, $[Pr_2(GeW_{11}O_{39})(DMSO)_2(H_2O)_8]^{2-}$ and 5.75 waters of crystallization. The polyanion unit $[Pr_2(GeW_{11}O_{39})(DMSO)_2(H_2O)_8]^{2-}$ is composed of $[Pr(1)(DMSO)(H_2O)_2]^{3+}$, $[Pr(2)(DMSO)(H_2O)_6]^{3+}$, and $[\alpha\text{-GeW}_{11}O_{39}]^{8-}$. The structure of **2** is represented in figure 3 and the coordination environments around $Pr^{3+}(1)$ and $Pr^{3+}(2)$ are shown in figure 4. Compound **2** displays an interesting 1D double-parallel chain-like structure, in which two parallel chains $\{[Pr(1)(GeW_{11}O_{39})(DMSO)(H_2O)_2]^{5-}\}_n$ are joined through $[Pr(2)(DMSO)(H_2O)_6]^{3+}$ moieties (figure 5). In the $[Pr(1)(GeW_{11}O_{39})(DMSO)(H_2O)_2]^{5-}$ subunit, $Pr^{3+}(1)$, similar to **1**, is incorporated into the vacant site of the polyanion $[\alpha\text{-GeW}_{11}O_{39}]^{8-}$ and is eight-coordinate, antiprismatic coordination geometry, with four oxygens from the vacant site ($d_{\text{Pr(1)-Ob,c}} = 2.408$ Å), two from waters ($d_{\text{Pr(1)-OH2O}} = 2.595$ Å), one from DMSO ($d_{\text{Pr(1)-O(DMSO)}} = 2.410(15)$ Å), and another from the terminal oxygen O6#1 of the adjacent $[\alpha\text{-GeW}_{11}O_{39}]^{8-}$ subunit ($d_{\text{Pr(1)-Od}} = 2.432(12)$ Å). In such an arrangement, one linear chain $\{[Pr(1)(GeW_{11}O_{39})(DMSO)(H_2O)_2]^{5-}\}_n$ is formed with shortest interchain Pr(1)–Pr(1) distances of 11.522 Å. The $Pr^{3+}(2)$, which is unlike $Pr^{3+}(2)$ in **1**, is nine-coordinate with a monocapped antiprismatic geometry defined by nine oxygens, six from waters ($d_{\text{Pr(2)-OH}_2\text{O}} = 2.511$ Å), one from DMSO

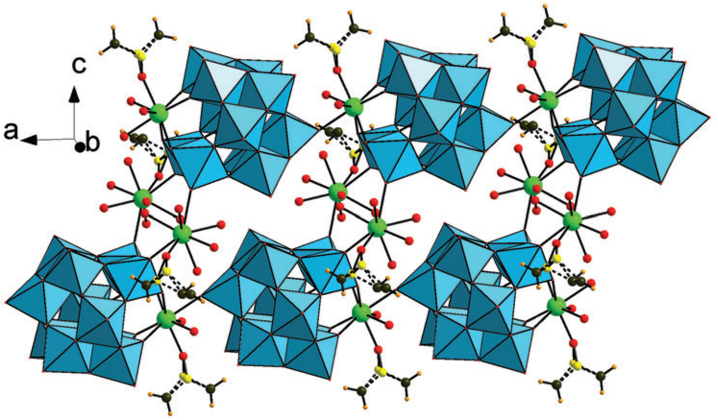

Figure 3. Polyhedral representation of **2**. The water molecules are omitted for clarity. Key (online): Pr, green; $\{WO_6\}$, blue octahedra.

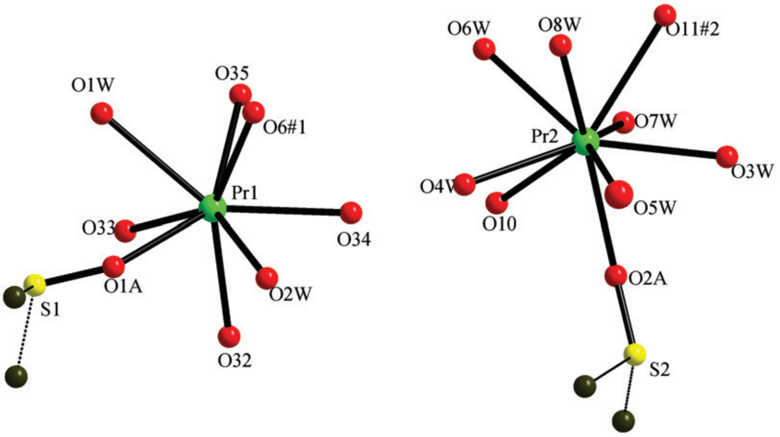

Figure 4. The coordination environment around Pr^{3+}(1), Pr^{3+}(2) in **2**.

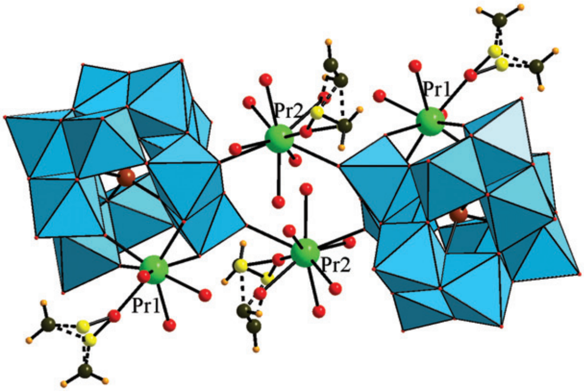

Figure 5. The connection between two parallel chains for **2**. Key (online): Pr, green.

($d_{\mathrm{Pr(2)-O(DMSO)}}$ = 2.424(13) Å) and two from terminal oxygen atoms of neighboring [α-$GeW_{11}O_{39}$]$^{8-}$ anions from a separate chain ($d_{\mathrm{Pr(2)-O10}}$ = 2.525(11) Å, $d_{\mathrm{Pr(2)-O11\#2}}$ = 2.623(11) Å). Thus, the two parallel chains are joined by two bridging [Pr(2)(DMSO)$(H_2O)_6$]$^{3+}$. In the coordination polyhedron around Pr^{3+}(2), the terminal oxygen atom O10 occupies the cap position. Because of steric hindrance, the bond angle of O10–Pr2–O11#2 is 131.0(4)°, "V" shaped and the coordinated DMSO is stretched outward. The separation distance between the two [Pr(2)(DMSO)$(H_2O)_6$]$^{3+}$ moieties ($d_{\mathrm{Pr2-Pr2\#2}}$) supported by the same two heteropolyanions [α-$GeW_{11}O_{39}$]$^{8-}$ is 7.181 Å. Additionally, the nearest Pr(1)–Pr(2) distance is 6.688 Å. Compared to **1**, instead of [$(CH_3)_4N$]$^+$ counterions, disordered lanthanide cations [Pr(3)$_{0.5}$$(H_2O)_{2.25}$]$^{1.5+}$ balance the charge. In **2**, the sulfur atoms S1 and S2 are crystallographically disordered. The average bond length of Pr-O_{DMSO} (2.417 Å) is shorter than that of Pr-O_w (2.511 Å) indicating the electron-donating of DMSO is stronger than water. Compared to free DMSO (1.513 Å) [24], shortened and elongated S=O bond distances are found in **2**. These distances do not differ in a statistically significant sense [24, 25] is partially caused by disordered S atoms and the large uncertainties.

Comparing **2** with **1**, there are three points: First, adjacent polyanions are polymerized to an infinite 1D arrangement by bridging Pr^{3+} ions, with **1** displaying 1D zig-zag chains and **2** a double-parallel chainlike structure. Second, in both compounds $Pr^{3+}(1)$ incorporated into the vacant site of $[\alpha\text{-}GeW_{11}O_{39}]^{8-}$ is eight-coordinate. Third, introduction of DMSO also effects the structural arrangement.

For **1** and **2**, in the $[\alpha\text{-}GeW_{11}O_{39}]^{8-}$ anion, the Ge–O_a bond distances and O-Ge-O bond angles range from 1.714(17)–1.741(16) Å, 106.6(7)–112.1(7)° and 1.721(10)–1.749(11) Å, 107.2(5)–112.8(5)°, W–$O_{b,c}$ are in the range 1.73(2)–2.110(15) Å and 1.769(11)–2.071(15) Å, W–O_d are in the range 1.690(19)–1.76(2) Å and 1.689(14)–1.755(12) Å, W–O_a distances range from 2.221(15) to 2.396(17) Å and 2.229(10) to 2.349(10) Å, respectively.[1] The Pr–O distances lie in the ranges of 2.36(2)–2.95(9) and 2.371(12)–2.623(9) Å in **1** and **2** and with mean distances of 2.527 and 2.488 Å, respectively.

3.2. *IR spectra*

In the low–wavenumber region of the IR spectrum ($\nu < 1000 cm^{-1}$), **1** and **2** display characteristic vibration patterns of the Keggin-type structure. Four characteristic asymmetric vibrations resulting from Keggin heteropolyanion, ν(W–O_d), ν(W–O_b), ν(W–O_c), and ν(Ge–O_a),[1] appear at 949, 877 and 808, 704 and 526 cm^{-1} for **1** and 946, 881 and 812, 702 and 522 cm^{-1} for **2**. Comparing the IR spectra of **1** and **2** with that of $\alpha\text{-}K_8[GeW_{11}O_{39}] \cdot nH_2O$, the vibration of W–$O_d$ shifts from 958 to 949 cm^{-1} for **1** and from 958 to 946 cm^{-1} for **2**; one vibration of the W–O_b bonds shifted from 882 to 877 cm^{-1} for **1** and from 882 to 881 cm^{-1} for **2**, and another shifted from 850 to 808 cm^{-1} for **1** and from 850 to 812 cm^{-1} for **2**; and the Ge–O_a bonds and the W–O_c bonds are nearly identical to that of $\alpha\text{-}K_8[GeW_{11}O_{39}] \cdot nH_2O$. Thus, the polyanion of **1** and **2** retain the basic Keggin structure, but are distorted due to coordination, in agreement with the results of the single-crystal X-ray diffraction analysis. In addition, a series of characteristic bands for $[(CH_3)_4N]^+$ are at 2962, 2874, 1465 and 1375 cm^{-1} in **1**. Comparing the IR spectra in **2** with that of free DMSO [24], ν_{as}(S=O) falls from 1055 to 1030 cm^{-1}, verifying that DMSO is coordinated to the metal by oxygen [26]. The ν_{as}(C–S) frequency increases from 698 to 720 cm^{-1}, perhaps from increase in the electron donating of methyl. The IR spectra indicate strong interaction exists between the polyanion and DMSO in the solid state for **2**.

3.3. *UV spectra*

The UV spectra of **1** and **2** in distilled water are similar to that of $\alpha\text{-}K_8[GeW_{11}O_{39}] \cdot nH_2O$ (201 and 270 nm), suggesting that the compounds are disrupted in dilute solution. The first absorption band in each group is strong and assigned to the $p\pi$–$d\pi$ charge-transfer absorption band of $O_d \rightarrow W$; the lower energy absorption are characteristic absorptions of Keggin-type polyanions and assigned to the $p\pi$–$d\pi$ charge-transfer absorption band of $O_{b,c} \rightarrow W$.

---

[1] O_a is the oxygen atom bond to the Ge atom, O_b is the bridging oxygen atom shared by two W atoms of different W_3O_{13} clusters, O_c is the bridging oxygen atom shared by two W atoms from the same W_3O_{13} cluster, O_d is the terminal oxygen atom combined with only one W atom.

4. Conclusions

By controlling the synthetic conditions, we prepared two new germanotungstates. The solid-state structure of **1** consists of 1D zig-zag chains built of $[\alpha\text{-GeW}_{11}\text{O}_{39}]^{8-}$ connected by $\text{Pr}^{3+}(1)$. In **2**, introduction of DMSO leads to a double-parallel chainlike structure constructed by two linear wires $\{[\text{Pr}(1)(\text{GeW}_{11}\text{O}_{39})(\text{DMSO})(\text{H}_2\text{O})_2]^{5-}\}_n$ linked by $\text{Pr}^{3+}(2)$ coordination cations.

Supplementary material

CCDC 657143 and 657144 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44) 1223-336-033; or Email: deposit@ccdc.cam.ac.uk).

Acknowledgements

This work was supported by the National Nature Science Foundation of China, Program for New Century Excellent Talents in University of Henan Province, and the Natural Science Foundation of Henan Province.

References

[1] M.T. Pope. *Heteropoly and Isopoly Oxometalate*, Springer-Verlag, Berlin (1983).

[2] (a) M.T. Pope, A. Müller. *Angew. Chem. Int. Ed. Engl.*, **30**, 34 (1991); (b) U. Kortz, M.G. Savelieff, B.S. Bassil, M.H. Dickman. *Angew. Chem. Int. Ed. Engl.*, **40**, 3384 (2001).

[3] V.W. Day, W.G. Klemperer. *Science*, **228**, 533 (1985).

[4] C.L. Hill, C.M. Prosser-McCartha. *Coord. Chem. Rev.*, **143**, 407 (1995).

[5] (a) M.T. Pope, A. Müller (Eds.), *Polyoxometalates Chemistry*: *From Topology via Self-Assembly to Applications*, Kluwer, Dordrecht (2001); (b) C. Hill, *Chem. Rev.*, **98**, 1 (1998).

[6] (a) M.T. Pope, A. Müller. *Polyoxometalates*: *From Platonic Solid to Anti-Retroviral Activity*, Kluwer, Academic Publishers, Dordrecht, The Netherlands (1994); (b) T. Yamase, M.T. Pope. *Polyoxometalate Chemistry for Nano-Composite Design*, Kluwer, Academic Publishers, Dordrecht, The Netherlands (2002); (c) J.J. Borrás–Almenar, E. Coronado, A. Müller, M.T. Pope (Eds.), *Polyoxometalate Molecular Science*, Kluwer, Academic Publishers, Dordrecht, The Netherlands (2004).

[7] D.L. Long, P. Kögerler, L.J. Farrugia, L. Cronin. *Angew. Chem. Int. Ed.*, **42**, 4180 (2003).

[8] (a) J.C. Bunzli, G. Choppin (Eds.), Luminescent Probes, In *Lanthanide Probes in Chemistry, Biology and Earth Sciences*, pp. 219–293, Elsevier, Amsterdam (1989); (b) J. Kido, Y. Okamoto. *Chem. Rev.*, **102**, 2357 (2002).

[9] R.C. Howell, F.G. Perez, S. Jain, W.D. Horrocks, Jr, A.L. Rheingold, L.C. Francesconi. *Angew. Chem.*, **113**, 4158 (2001); *Angew. Chem. Int. Ed.*, **40**, 4031 (2001).

[10] (a) D. Drewes, E.M. Limanski, B. Krebs. *Dalton Trans.*, 2087 (2004); (b) C. Zhang, R.C. Howell, K.B. Scotland, F. Perez, L. Todaro, L.C. Francesconi. *Inorg. Chem.*, **43**, 7691 (2004).

[11] R.D. Peacock, T.J.R. Weakley. *J. Chem. Soc. A*, 1836 (1971).

[12] (a) W.P. Griffith, R.G.H. Moreea, H.I.S Nogueira. *Polyhedron*, **15**, 3493 (1996); (b) L.Y. Qu, Z.Y. Niu, J.F. Liu. *Chem. J. Chin. U.*, **12**, 1434 (1991).

[13] M. Sadakane, M.H. Dickman, M.T. Pope. *Angew. Chem. Int. Ed.*, **39**, 2914 (2000).

[14] P. Mialane, L. Lisnard, A. Mallard, J. Marrot, E. Antic-Fidancev, P. Aschehoug, D. Vivien, F. Sécheresse. *Inorg. Chem.*, **42**, 2102 (2003).
[15] (a) P. Mialane, A. Dolbecq, E. Rivière, J. Marrot, F. Sécheresse. *Eur. J. Inorg. Chem.*, **33**, (2004); (b) J.Y. Niu, J.W. Zhao, J.P. Wang. *Inorg. Chem. Commun.*, **7**, 876 (2004); (c) J.Y. Niu, J.W. Zhao, J.P. Wang. *J. Mol. Struct.*, **701**, 19 (2004); (d) J.P. Wang, J.W. Zhao, J.Y. Niu. *Sci. China Ser.*, **B48**, 343 (2004).
[16] (a) H. Katano, T. Osakai, S. Himeno, A. Saito. *Electrochim. Acta*, **40**, 2935 (1995); (b) E.N. Dorokhova, L.P. Kazanskii, G.V.Zh. Prokhorova. *Neorg. Khim.*, **39**, 2795 (1985); (c) M. Biquard, P. Souchay. *Ann. Chim. Paris*, **10**, 163 (1975); (d) M.C.R. Biquard. *Acad. Sci. Ser.*, **C281**, 309 (1975); (e) M. Leyrie, G.C.R. Herve. *Acad. Sci. Ser.* **C276**, 911 (1973); (f) M. Biquard, M. Lamache. *Bull. Soc. Chim. France*, **1**, 32 (1971).
[17] G. Hervé, A. Tézé. *Inorg. Chem.*, **16**, 2115 (1977).
[18] C. Tourné, G. Tourné, M. Brianso. *Acta Crystallogr. Sect. B*, **36**, 2012 (1980).
[19] C.Y. Rong, J.F. Liu, X. Chen, E.B. Wang. *Inorg. Chim. Acta*, **130**, 265 (1987).
[20] A. Tézé, G.J. Hervé. *Inorg. Nucl. Chem.*, **39**, 999 (1977).
[21] G.M. Sheldrick. *SHELXTL-97*, *Programs for Crystal Structure Refinement*, University of Göttingen, Germany (1997).
[22] C.E. VanPelt, W.J. Crooks, G.R. Choppin. *Inorg. Chim. Acta*, **346**, 215 (2003).
[23] N.E. Brese, M. O'Keeffe. *Acta. Cryst. B*, **47**, 192 (1991).
[24] F.A. Cotton, E.V. Dikarev, M.A. Petrukhina, S.E. Stiriba. *Inorg. Chem.*, **39**, 1748 (2000).
[25] (a) J.Y. Niu, Q. Wu, J.P. Wang. *J. Chem. Soc., Dalton Trans.*, **12**, 2512 (2002); (b) J.P. Wang, X.Y. Duan, J.Y. Niu. *J. Mol. Struct.*, **692**, 17 (2004).
[26] R. Thomsa, C.B. Shoemaker, K. Erinks. *Acta. Cryst.*, **21**, 12 (1966).