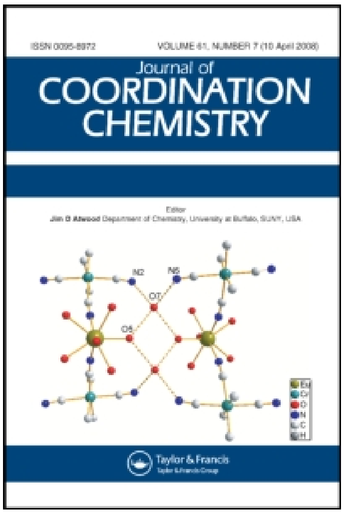

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Synthesis, crystal structure and properties of a novel 1D chain organic-inorganic rare earth coordination polymer: $Gd_{0.5}H_{0.5}\{[Gd(H_2O)_6][Gd(H_2O)_2(DMSO)][\alpha\text{-}SiW_{11}O_{39}]\}\cdot 7H_2O$

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Synthesis, crystal structure and properties of a novel 1D chain organic–inorganic rare earth coordination polymer: $Gd_{0.5}H_{0.5}\{[Gd(H_2O)_6]\ [Gd(H_2O)_2(DMSO)]\ [\alpha\text{-}SiW_{11}O_{39}]\}\cdot 7H_2O$

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A 1D chain organic–inorganic rare earth coordination polymer $Gd_{0.5}H_{0.5}\{[Gd(H_2O)_6][Gd(H_2O)_2(DMSO)][\alpha\text{-}SiW_{11}O_{39}]\}\cdot 7H_2O$ has been synthesized by reaction of $\alpha\text{-}K_8SiW_{11}O_{39}\cdot 13H_2O$, $HClO_4$, Gd_2O_3 with dimethyl sulfoxide (DMSO) and characterized by elemental analysis, IR, UV, ESR spectra and X-ray diffraction. The title compound crystallizes in a monoclinic lattice, $P2_1/c$ space group, with $a = 23.544(5)$, $b = 11.527(2)$, $c = 23.297(5)$ Å, $\beta = 109.05(3)°$, $V = 35976(2)$ Å^3, $Z = 4$, $R_1 = 0.0838$, $wR_2 = 0.1300$. The neighboring polyanion units $\{[Gd(H_2O)_6][Gd(H_2O)_2(DMSO)][\alpha\text{-}SiW_{11}O_{39}]\}^{2-}$ are bridged together forming a 1D chain structure by means of $[Gd(H_2O)_2(DMSO)]^{3+}$ ions. The ESR spectra of the title compound at room temperature are composed of eight lines, indicating the strong effect of the crystal field generated by the nearest surrounding ligands of the Gd^{III} cation.

Keywords: Silicotungstic acid; Polyoxometalates; Mono-vacant Keggin structure; Rare earth ions

1. Introduction

Polyoxometalates are versatile inorganic building blocks for the construction of molecular-based materials. By means of their multiple coordination requirements and oxophilicity, lanthanide cations are suitable to link polyoxometalate building blocks to form new classes of materials with potentially useful magnetic and luminescent properties [1–4]. It is also a very interesting problem to elucidate the role and nature of the 4*f*-elements in coordination chemistry. Peacock and Weakley studied the interactions between $[\alpha\text{-}SiW_{11}O_{39}]^{8-}$ and lanthanide cations [5], reporting that $[\alpha\text{-}SiW_{11}O_{39}]^{8-}$ forms both 1 : 1 and 1 : 2 compounds with rare earth metals. In 1998, Pope reported rhodium-carbon bond functionalized heteropolytungstates: $[XW_{11}O_{39}RhCH_2COOH]^{5,6-}$ (X = P, Si) [6]. In 2000, Bagno investigated one-step

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synthesis of $[PW_{11}O_{39}Ru(DMSO)]^{5-}$, which was characterized by NMR spectra [7]. In 2000, Pope *et al.* investigated the structural characterization of the one-dimensional 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 [8]. In 2003, Mialane *et al.* also reported the solid-state structures of the $Ln/[\alpha\text{-}SiW_{11}O_{39}]^{8-}$ ($Ln = Yb^{III}$, Nd^{III}, Eu^{III}, Gd^{III}) [9]. In 2004, Mialane *et al.* reported the dimeric $K_{12}[(SiW_{11}O_{39}Ln)_2$ $(\mu\text{-}CH_3COO)_2]$ ($Ln = Gd^{III}$, Yb^{III}) complexes [10]. All above studies indicate interest in the lanthanide cation and mono-vacant Keggin-type polyanion system; however, there is no report on an organic–inorganic rare earth coordination polymer with mono-vacant $[\alpha\text{-}SiW_{11}O_{39}]^{8-}$ building blocks. Herein, we report the synthesis, crystal structure and properties of an organic–inorganic rare earth derivative $Gd_{0.5}H_{0.5}\{[Gd(H_2O)_6][Gd(H_2O)_2(DMSO)]$ $[\alpha\text{-}SiW_{11}O_{39}]\} \cdot 7H_2O$ with the mono-vacant $[\alpha\text{-}SiW_{11}O_{39}]^{8-}$ building block.

2. Experimental

2.1. *Materials*

$\alpha\text{-}K_8SiW_{11}O_{39} \cdot 13H_2O$ was prepared according to the literature [11] and confirmed by IR spectra. All other chemicals used for synthesis and physical measurements were reagent grade and used without further purification.

2.2. *Physical techniques*

Elemental analyses (C, H and S) were conducted on a Perkin-Elmer 240 C analyzer. Inductively coupled plasma (ICP) analyses were carried out on a Jarrel-Ash J-A1100 spectrometer. IR spectra were obtained from a KBr pellet on a Nicolet AVATAR 360 FTIR spectrophotometer over the range 4000–400 cm^{-1}. UV spectra were obtained on a Unican UV-500 spectrometer (distilled water as solvent) in the range 400–190 nm. The thermogravimetric (TG/DTA) analysis was on a Exstar 6000 analyzer in the air with a heating rate of 10°C min. The ESR spectra of polycrystalline powder were recorded on a Bruker ER-200-D-SRC spectrometer at 9.4 GHz microwave frequency (X-band) at 110 K and room temperature.

2.3. *Preparation of the title compound*

Single crystals of the title compound suitable for X-ray diffraction were synthesized as follows: The oxide Gd_2O_3 (0.54 g, 1.5 mmol) was first suspended in distilled water (5 mL), to which a solution of $HClO_4$ (1.5 mL, 12.19 M) was added dropwise under stirring. The mixture was refluxed at 70°C under stirring for 1 h, and then the pH was adjusted to 5.30 by addition of a solution of NaOH (0.4 M). Then $\alpha\text{-}K_8SiW_{11}O_{39} \cdot 13H_2O$ (1.65 g, 0.5 mmol) and dimethyl sulfoxide (1.5 mL) were added. The mixture was refluxed continuously for 1 h, and then allowed to cool to ambient temperature. After filtration, distilled water (20 mL) was added to the filtrate, and the obtained solution was left to evaporate slowly at room temperature; colorless polyhedral crystals were obtained after several weeks. Anal. Calcd for

Table 1. Crystallographic data and structure refinement for the title compound.

Empirical formula	$C_2H_{36.5}Gd_{2.5}O_{55}SSiW_{11}$
Formula weight	3416.44
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 23.544(5)$ Å,
	$b = 11.527(2)$ Å, $\beta = 109.05(3)^\circ$
	$c = 23.297(5)$ Å,
Volume (Å^3), Z	5976 (2), 4
Density (calculated) ($Mg\,m^{-3}$)	3.797
Absorption coefficient (mm^{-1})	23.964
$F(000)$	5970
Crystal size (mm^3)	$0.16 \times 0.11 \times 0.09$
θ range for data collection (°)	1.99 to 25.00
Limiting indices	$-27 \leq h \leq 27$, $-13 \leq k \leq 0$, $-27 \leq l \leq 27$
Reflections collected	12234
Independent reflections	7347 ($R_{int} = 0.1885$)
Absorption correction	Empirical
Max. and min. transmission	0.2216 and 0.1142
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7347/930/677
Goodness-of-fit on F^2	0.960
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0838$, $wR_2 = 0.1300$
Largest diffraction peak and hole (eÅ^{-3})	3.242 and −2.537

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o||$, $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

$Gd_{0.5}H_{0.5}\{[Gd(H_2O)_6][Gd(H_2O)_2(DMSO)][\alpha\text{-}SiW_{11}O_{39}]\} \cdot 7H_2O$ (%): C, 0.70; H, 1.08; S, 0.94; Si, 0.82; Gd, 11.51; W, 59.19. Found: C, 0.72; H, 0.97; S, 0.89; Si, 0.75; Gd, 11.44; W, 59.23.

2.4. *X-ray structure determination of the title compound*

Crystals of the title compound with dimensions $0.16 \times 0.11 \times 0.09$ mm were carefully selected under an optical microscope and glued at the tip of a thin glass fiber with cyanoacrylate (super glue) adhesive. Intensity data were collected with a Rigaku RAXIS-IV image plate area detector using graphite monochromatized Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293(2) K. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXTL-97 [12]. Intensity data were corrected for Lorentz and polarization effects as well as for empirical absorption. All of the non-hydrogen atoms were refined anisotropically. Experimental data for the structure determination of the title compound are listed in table 1. Selected bond distances and angles are represented in table 2.

3. Results and discussion

3.1. *Synthesis*

The title compound can be formed in the pH range of 4.5–5.5. Moreover, in order to introduce more Gd^{III} cations into the one-dimensional framework of the title

Table 2. Selected bond lengths (Å) and angles (°).

Gd(1)–O(31)	2.256(18)	Gd(1)–O(24)	2.292(19)
Gd(1)–O(25)	2.29(2)	Gd(1)–O(1A)	2.321(18)
Gd(1)–O(29)	2.344(18)	Gd(1)–O(2W)	2.42(3)
Gd(1)–O(2)#1	2.425(19)	Gd(1)–O(1W)	2.48(2)
Gd(2)–O(7W)	2.27(3)	Gd(2)–O(5W)	2.32(2)
Gd(2)–O(6W)	2.36(2)	Gd(2)–O(4W)	2.369(18)
Gd(2)–O(10)	2.398(19)	Gd(2)–O(8W)	2.421(19)
Gd(2)–O(3W)	2.47(2)	Si(1)–O(37)	1.55(2)
Si(1)–O(38)	1.55(2)	Si(1)–O(39)	1.73(2)
Si(1)–O(36)	1.59(2)	S(1)–O(1A)	1.462(19)
S(1)–C(2)	1.79(3)	S(1)–C(1)	1.92(4)
O(31)–Gd(1)–O(24)	76.8(7)	O(31)–Gd(1)–O(25)	119.4(7)
O(24)–Gd(1)–O(25)	71.6(7)	O(31)–Gd(1)–O(1A)	145.6(7)
O(24)–Gd(1)–O(1)	83.9(7)	O(25)–Gd(1)–O(1A)	79.6(7)
O(31)–Gd(1)–O(29)	75.9(7)	O(24)–Gd(1)–O(29)	119.1(7)
O(25)–Gd(1)–O(29)	75.6(6)	O(1A)–Gd(1)–O(29)	137.4(7)
O(31)–Gd(1)–O(2W)	136.8(8)	O(24)–Gd(1)–O(2W)	145.3(8)
O(25)–Gd(1)–O(2W)	81.1(8)	O(1A)–Gd(1)–O(2W)	70.1(8)
O(29)–Gd(1)–O(2W)	72.2(8)	O(31)–Gd(1)–O(2)#1	76.3(7)
O(24)–Gd(1)–O(2)#1	141.6(7)	O(25)–Gd(1)–O(2)#1	146.5(7)
O(1A)–Gd(1)–O(2)#1	103.8(7)	O(29)–Gd(1)–O(2)#1	80.4(7)
O(2W)–Gd(1)–O(2)#1	69.4(8)	O(31)–Gd(1)–O(1W)	75.9(7)
O(24)–Gd(1)–O(1W)	76.9(7)	O(25)–Gd(1)–O(1W)	139.5(6)
O(1A)–Gd(1)–O(1W)	72.2(7)	O(29)–Gd(1)–O(1W)	143.7(7)
O(2W)–Gd(1)–O(1W)	114.4(8)	O(2)#1–Gd(1)–O(1W)	70.2(7)

compound in the synthetic process, we employed much more $HClO_4$ than the previous method [9] to get rid of all the K^+ cations, mainly because the resulting $KClO_4$ can be precipitated and filtered out. Therefore, according to our experiments, we believe that using much more ClO_4^- to eliminate all the K^+ may provide necessary conditions for the introduction of more Gd^{3+} cations into the framework of the title compound in the one-dimensional structural construction. In addition, the amount of DMSO was also investigated. When the usage amount of DMSO varies in the range of 1–4 mL under the conditions above, one DMSO is found in the asymmetric structural unit of the title compound. If the amount of DMSO is more than 4 mL, the reaction mixture does not produce crystals but amorphous powders.

3.2. *IR and UV spectra*

In the IR spectra, the title compound displays characteristic vibration peaks of the Keggin-type structure, namely, $\nu(W–O_d)$, $\nu(Si–O_a)$, $\nu(W–O_b)$ and $\nu(W–O_c)$, at 950, 897, 831 and 703 cm^{-1}. Compared to the IR spectra of α-$K_8SiW_{11}O_{39} \cdot 13H_2O$, the $\nu(W–O_d)$ has a red-shift of 6 cm^{-1}, the major reason for which may be that the charge compensation cations have stronger interactions to the terminal oxygen atoms of the polyanion, reducing the $W–O_d$ bond force constant and leading to decreasing of the $W–O_d$ vibration frequency. The $\nu(Si–O_a)$, $\nu(W–O_b)$ and $\nu(W–O_c)$ have blue-shifts of 9, 31 and 24 cm^{-1}, respectively, the possible reason for which is that the polyanion symmetry of the title compound increases compared to that of α-$K_8SiW_{11}O_{39} \cdot 13H_2O$. In addition, the resonance at 1008 cm^{-1} in the title compound is assigned to $\nu(S{=}O)$ asymmetric stretching vibration of DMSO molecules. Comparing with free DMSO,

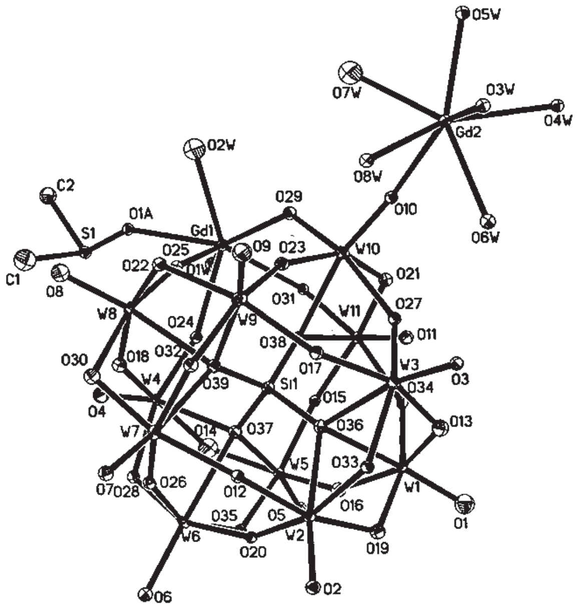

Figure 1. ORTEP drawing of the structural unit of the title compound. The hydrogen, discrete Gd^{3+} ions and crystal water molecules are omitted for clarity.

the ν(S=O) shifts from 1028 to 1008 cm^{-1}, confirming that the DMSO ligands have coordinated to the rare earth ion by oxygen. The UV spectra in aqueous solution for the title compound, α-$K_8SiW_{11}O_{39} \cdot 13H_2O$ and α-$H_4SiW_{12}O_{40} \cdot xH_2O$ reveal an absorption band at ca. 255 nm, which is assigned to the *pπ–dπ* charge transfer transitions of $O_{b(c)} \rightarrow W$ bond [13].

3.3. *X-ray crystal structure of the title compound*

To the best of our knowledge, a crystal structure of a 1D organic–inorganic rare earth derivative with mono-vacant $[\alpha\text{-}SiW_{11}O_{39}]^{8-}$ building blocks has not been reported; prior to investigation of the X-ray single-crystal structure of $Gd_{0.5}H_{0.5}\{[Gd(H_2O)_6][Gd(H_2O)_2(DMSO)][\alpha\text{-}SiW_{11}O_{39}]\} \cdot 7H_2O$ in the present paper. The polyanion structural unit $\{[Gd(2)(H_2O)_6][Gd(1)(H_2O)_2(DMSO)][\alpha\text{-}SiW_{11}O_{39}]\}^{2-}$ of the title compound is composed of one $[Gd(2)(H_2O)_6]^{3+}$, one $[Gd(1)(H_2O)_2(DMSO)]^{3+}$ and one $[\alpha\text{-}SiW_{11}O_{39}]^{8-}$ building blocks (figure 1). The neighboring polyanion structural units $\{[Gd(2)(H_2O)_6][Gd(1)(H_2O)_2(DMSO)]\ [\alpha\text{-}SiW_{11}O_{39}]\}^{2-}$ are bridged forming a novel 1D chain structure by means of $[Gd(1)(H_2O)_2(DMSO)]^{3+}$ ions (figure 2). The polyhedron/ball-and-stick packing of the title compound viewed down *b* and *c* axes are shown in figure 3.

$Gd^{3+}(1)$ located in the defect site of the $[\alpha\text{-}SiW_{11}O_{39}]^{8-}$ fragment, resides in a distorted square antiprismatic geometry with Gd(1)–O distances of 2.256(18)–2.48(2) Å. In the coordination geometry of $Gd^{3+}(1)$ (figure 4), O24, O25, O29, O31 group and O2, O1A, O1W, O2W group constitute two planes of the square antiprism, and their average deviations are 0.0125 and 0.0687 Å, respectively. The distances between

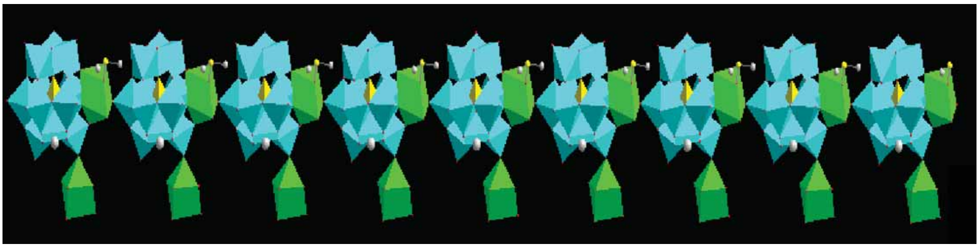

Figure 2. The 1D chain motif of the structural units in the title compound. The hydrogen atoms, discrete Gd^{3+} coordination ions and crystal water molecules are omitted for clarity.

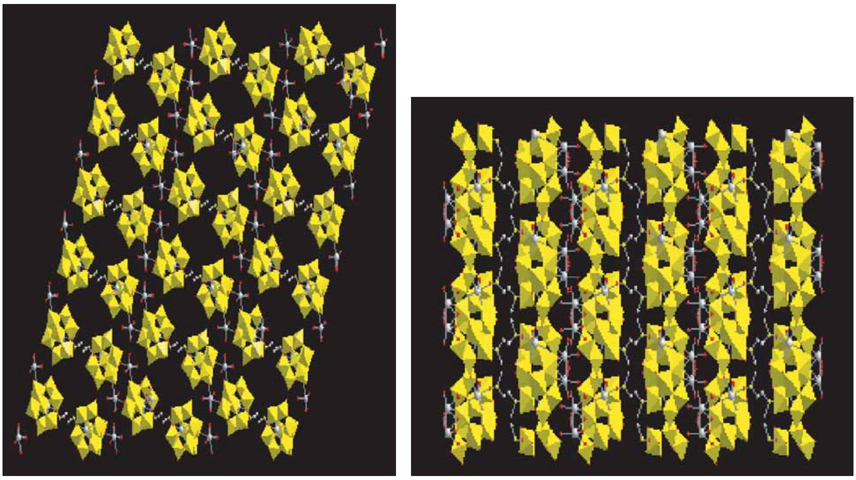

Figure 3. The polyhedron/ball-and-stick packing viewed down *b* (left) and *c* (right) axis. The hydrogen, discrete Gd^{3+} ions and crystal water molecules are omitted for clarity.

Gd^{3+}(1) and the two planes are 1.1587 and 1.3940 Å, respectively. But the seven-coordinate Gd^{3+}(2) coordination cation has a distorted monocapped trigonal prism with Gd(2)–O distances of 2.27(3)–2.47(2) Å, defined by six water molecules and one terminal oxygen atom from the $[\alpha\text{-SiW}_{11}O_{39}]^{8-}$. In the coordination polyhedron around Gd^{3+}(2) ion (figure 4), O10, O3W, O4W, O8W group, O3W, O5W, O7W, O8W group and O10, O4W, O5W, O7W group constitute the three side surfaces, respectively, the average deviations are 0.0606, 0.0516 and 0.1053 Å. The distances between Gd^{3+}(1) cation and the three side planes are 0.6115, 1.2602 and 0.6459 Å, respectively. O6W occupies the 'cap' position over the side plane defined by O10, O3W, O4W and O8W. The distance of the 'cap' oxygen atom and the side plane is 1.7429 Å. O3W, O4W, O5W and O7W, O8W, O10 constitute the two bottom planes; the separations of Gd^{3+}(2) and bottom planes are 1.6027 and 1.6393 Å, respectively. In addition, Gd^{3+}(3) and Gd^{3+}(4) ions are crystallographically disordered and have the site of occupation factor of 0.25 in the crystal lattice.

In the polyanion structural unit $\{Gd(2)(H_2O)_6][Gd(1)(H_2O)_2(DMSO)][\alpha\text{-SiW}_{11}O_{39}]\}^{2-}$, the Si atom resides in the center of SiO_4 tetrahedron, which has been somewhat deformed from removal of one $[W=O_d]^{4+}$ group and the incorporation

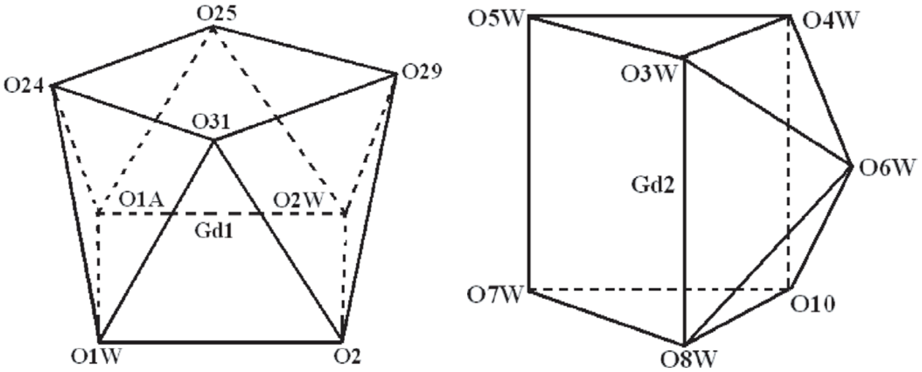

Figure 4. Coordination polyhedron of Gd^{3+}(1) coordination cation (left) and coordination polyhedron of Gd^{3+}(2) coordination cation (right).

of a Gd^{III} into the mono-vacant polyoxometalate framework as compared to saturated Keggin structure. The Si–O bond distances in the SiO_4 polyhedron vary between 1.55(2) and 1.73(2) Å and the O–Si–O bond angles are in the range of 105.4(11)–116.0(11)°. Moreover, the oxygen atoms in the polyanion structural unit of $\{Gd(2)(H_2O)_6]$ $[Gd(1)(H_2O)_2(DMSO)][\alpha\text{-}SiW_{11}O_{39}]\}^{2-}$, can be classified into six types, O_a, $O_{b(c)}$, O_d, O_e and O_f according to their coordination numbers and types of coordination atoms. O_a is bound to the central Si and three W atoms; $O_{b(c)}$ is shared by two W atoms (O_b is shared by two W atoms of different W_3O_{13} clusters; O_c is shared by two W atoms of the same W_3O_{13} unit); O_d is the terminal oxygen atom combined with only one W atom; O_e is shared by a W and a Gd; O_f is only coordinated to one Gd; O_g is connected with Gd and S atoms. The W–O_a, W–$O_{b(c)}$, W–O_d and W–O_e distances are in the range of 2.20(2)–2.392(19) Å, 1.801(18)–2.466(18) Å, 1.49(2)–1.829(19) Å and 1.786(19)–1.864(18) Å.

Extended experiments could be done employing other rare earth ions or transition metal ions taking the place of Gd(III) ions, or using other mono-vacant polyanions (such as $[GeW_{11}O_{39}]^{8-}$, $[TiW_{11}O_{39}]^{8-}$, $[P_2W_{17}O_{61}]^{6-}$, etc.) in place of $[\alpha\text{-}SiW_{11}O_{39}]^{8-}$. Many novel structures are likely to be obtained, paving the way for the further development of our synthetic work.

3.4. *Thermal analysis*

The TG curve of the title compound shows a slow weight loss of 11.24% between 22 and 700°C, which approximately agrees with the theoretical value of 10.33%. In the corresponding DTA curve, there is a strong endothermal peak at 85°C, resulting from the removal of water of crystallization, coordination water, structural water and DMSO. In addition, the exothermal peak observed at 574°C in the DTA curve indicates the collapse of the polyanion framework.

3.5. *ESR spectra*

Electron spin resonance (ESR) is a powerful method of studying the magnetic properties and crystal-field symmetry of lanthanide(III) complexes. The 4*f* electronic shell of Gd^{3+} is half-full with the $^8S_{7/2}$ electron configuration in the free ion ground state. Because its spin-lattice relaxation time is comparatively long, ESR spectra are easily observed at room temperature. ESR study of Gd^{III} with $[\alpha\text{-SiW}_{11}O_{39}]^{8-}$ ligand provides detailed information on the interaction between Gd^{III} and $[\alpha\text{-SiW}_{11}O_{39}]^{8-}$. The spin Hamiltonian of the Gd^{III} ion is known as [14]: $H = g_0\beta BS + D[S_Z^2 - 1/3S(S+1) + E(S_X^2 - S_Y^2)]$, where g_0 is the g-value of the S-state, D and E are the zero-field splitting parameters. There is eightfold spin degeneracy of the Gd^{3+} free ion with $S = 7/2$. The strong crystal field splits the free ion level into four doubly degenerate energy levels. The Zeeman field removes such remaining degeneracy. As a result of transitions of unpaired electrons between these eight split levels, additional spectral lines of $g \gg 2.0$ and $g < 2.0$ are observed. The presence of these additional lines indicates a strong crystal field [15].

The ESR spectra of Gd^{3+} ions doped into glasses and of Gd-sandwiched- and encapsulated-polyoxometalate complexes have been previously studied [15–17]. In the case of Gd^{III} doped into glasses, X-band ESR first-derivative spectra were characterized by three groups of lines with effective g-values of 6.0, 2.8, 2.0, and a wide absorption band for magnetic field corresponding to $g < 2$ was described [16]. This type of spectrum has been labeled as *U*-spectrum in view of its *ubiquity* in vitreous materials and polycrystalline materials, such as zeolites and ceramics [18]. In the case of Gd-sandwiched- and encapsulated-polyoxometalate complexes, the ESR spectra differ markedly from the *U*-spectrum characteristics for Gd^{III} doped into glasses [15, 17].

These types of spectra are relatively complicated. For example, the ESR spectra of $[Gd(P_2W_{17}O_{61})_2]^{17-}$consist of 10 lines with the effective g-values: 11.01, 8.05, 5.45, 3.78, 2.72, 2.49, 2.06, 1.95, 1.79 and 1.58; the ESR spectra of $Gd(SiW_{11}O_{39})_2^{13-}$ comprise 11 lines with the effective g-factors: 10.7, 5.74, 4.68, 3.78, 3.37, 2.59, 1.97, 1.79, 1.59, 1.39 and 1.22 [17]. The ESR spectra of the title compound at room temperature are composed of eight lines with the following g values: 13.67, 6.34, 4.07, 2.62, 2.18, 1.87, 1.68 and 1.38 (figure 5). These indicate the strong effect of the crystal field around Gd^{III}. Previous studies showed a relationship between the presence of particular g values and the number of inner-sphere water molecules as well as the type of Gd^{III} compound in the solid [17]. Therefore, we presume that the distinction in the resonance

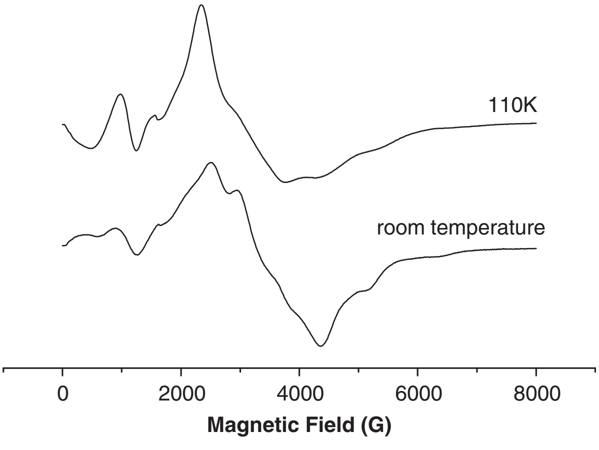

Figure 5. ESR spectra of the powders of the title compound at room temperature and 110 K.

absorption bands of the title compound, $[Gd(P_2W_{17}O_{61})_2]^{17-}$ and $Gd(SiW_{11}O_{39})_2^{13-}$ may be caused by changes of the crystal field generated by the nearest surrounding ligands of the Gd^{III} cation [19].

In comparison with those at room temperature, the intensity and number of the ESR spectral lines of the title compound at 110 K increases and decreases, respectively. The mainly reasons can be elucidated as follows: (1) the stronger spin-orbital coupling at room temperature than 110 K; (2) weaker spin-lattice relaxation at 110 K than at room temperature; (3) less thermal motion at 110 K than at room temperature; (4) the $^8S_{7/2}$ free ion ground state in the crystal field is split into four Kramers doublets, and at room temperature those doublets are equally populated; as the temperature decreases, the Kramers doublets of higher energy are successively depopulated.

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