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A novel sandwich polyoxometalate linked by mixed RE/TM interlayer: $[Fe(phen)_3]_2[As_2W_{18}Fe_2\{Y(OH_2)_2\}_2O_{68}]\cdot 6.5H_2O$

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Abstract

A novel sandwich polyoxometalate, $[Fe(phen)_3]_2[As_2W_{18}Fe_2\{Y(H_2O)_2\}_2O_{68}]\cdot 6.\ 5H_2O$ **1**, (phen = 1,10-phenanthroline), has been hydrothermally synthesized and characterized by elemental analyses, IR(25 ~ 650 °C), single-crystal X-ray diffraction, ESR spectroscopy and thermal analyses (TG-DTA). The crystallographic analysis reveals that the dimeric polyanion, $[As_2W_{18}Fe_2\{Y(OH_2)_2\}_2O_{68}]^{6-}$, are constructed from two $[B\text{-}AsW_9O_{34}]^{9-}$ fragments linked by two Y^{3+} ions and two Fe^{3+} ions. The ESR spectra exhibit that the high spin state and the low spin state of Fe(III) coexist in the title compound.

Keywords: Polyoxometalates; Sandwich-type; Mixed interlayer; Hydrothermal synthesis

1. Introduction

Polyoxometalates (POMs) are a well-known class of metal–oxygen clusters with an unmatched structural variety combined with a multitude of properties [1–3]. In recent years, the sandwich-type POMs encapsulating clusters of early transition metals have received much attention both from applied and fundamental research perspectives [4–7]. The great advantage of these complexes is the possibility of varying either the type of the metallic cluster (its topology and the nature of the transition metals) or the hetero-atom [8]. Synthesis of such compounds is usually accomplished by the reaction of divalent or trivalent transition-metal ions (ab. TM; e.g. Cu^{2+}, Mn^{2+}, Fe^{3+}, Co^{2+}) and the trivacant Keggin or Dawson ligands (e.g. $XW_9O_{34}^{9-}$, $X'_2W_{15}O_{56}^{12-}$ X = P, As, Ge, Si, Co, Zn et al.; X′ = P, As) [9]. The study of this family has led to the discovery of numerous compounds that have been investigated for their synthesis and properties [9–20]. On the other hand, the RE^{3+} ions generally display large and variable coordination numbers (CN = 8–12) and show minimal stereochemical preferences due to the small energy differences associated with the various coordination geometries [21], this makes it difficult to control the coordination environment of the RE^{3+} centers and therefore impedes fine-tuning of the electronic, spectronic, and magnetic properties of such clusters [22]. As a result, in contrast with the TM_xO_y (x = 2–6) interlayer containing sandwich-type POMs that have been intensively explored, a few works have been carried out on the RE_xO_y analogues [22–25] as in the cases of $[\{Y_4(H_2O)_8(\mu_3\text{-}OH)_4\}\ (\alpha\text{-}P_2W_{15}O_{62})_2]^{16-}$ [22] and $[\{Ce_3O_3(OH_2)_2\}_2(PW_9O_{34})_2]^{12-}$ [24]. Attentively, to date all of the structurally characterized sandwich-type POMs is built up from the trivacant moieties linked by either TM_xO_y or RE_xO_y interlayer, while no sandwich-type POMs with mixed TM/RE linkage has been observed. We thus describe in this paper the hydrothermal synthesis, characterization and crystal structure of a novel sandwich polyoxometalate, $[Fe(phen)_3]_2[As_2W_{18}Fe_2\{Y(OH_2)_2\}_2O_{68}]\cdot\ 6.5H_2O$ (**1**), in which two Y^{3+} ions and two Fe^{3+} ions are sandwiched by two $AsW_9O_{34}^{9-}$ units.

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2. Experimental

2.1. General information

$YCl_3 \cdot nH_2O$ was prepared through adding Y_2O_3 to concentrated HCl, then the solution was evaporated to dry at water bath (90 °C). The other chemicals were commercially purchased and used without further purification. C, H and N elemental analyses were performed on a Perkin-Elmer 2400 II elemental analyzer. IR spectra were recorded on a Nicolet 170 FT-IR spectrometer using KBr pellets in the range of 4000–400 cm^{-1}. TG-DTA curves were obtained with EXSTAR 6000 instrument under air atmosphere at a heating rate of 10 °C/min. The ESR spectra of powder were recorded on a Bruker ER-200-D-SRC spectrometer at X-band at room temperature and 110 K.

2.2. Synthesis of the title compound

The title compound was prepared from hydrothermal system in pretreated solution. A solution of $Na_2HAsO_4 \cdot 7H_2O$ (0.52 g), $Na_2WO_4 \cdot 2H_2O$ (6.1 g), $FeSO_4 \cdot 7H_2O$(0.18 g), $YCl_3 \cdot nH_2O$ (0.3 g) in water (15 ml) was acidified with 65% nitric acid (pH = 4.2) and stirred for 0.5 h at 90 °C, thereafter added to a solution of 1,10-phenanthroline (0.08 g) in dehydrated alcohol (1 ml). The resulting solution was stirred for 4 h and adjusted to pH = 4.7 by 6 M NaOH, then the mixture was sealed in a 30 ml Teflon-lined autoclave and heated at 165 °C for 12 days. After cooling to room temperature slowly (65 h), the red-black block crystals of **1** were collected by filtration, washed by distilled water and dried in air (21% yields based on Fe). Anal. Calcd. for $C_{72}H_{48}As_2Fe_4N_{12}O_{78.5}W_{18}Y_2$(%): C, 13.90; H, 1.15; N, 2.70. Found (%): C, 13.84; H, 1.21; N, 2.76.

2.3. X-ray diffraction

The structure of compound **1** was determined by single-crystal X-ray diffraction. Intensity data were collected with a Rigaku-RAXIS-IV image plate area detector using graphite monochromatized Mo-Kα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct method and refined by the Full-matrix least-squares method on F^2 using SHELXL-97 [26] to $R = 0.0599$ for compound **1** for 9658 independent reflections [$I > 2\sigma(I)$] of 33509 reflections collected with $-15 \leqslant h \leqslant 15$, $-16 \leqslant k \leqslant 16$, $-21 \leqslant l \leqslant 21$ in the $1.82 \leqslant \theta \leqslant 25.00°$ range. Intensity data were corrected for Lorentz and polarization effects as well as for empirical absorption. All of the non- hydrogen atoms were refined anisotropically. Hydrogen atoms were added according to the theoretical models. Crystal data collection parameters along with the values for the residuals after final refinement are summarized in Table 1. Selected bond lengths relevant to the structural discussion of the title compound are listed in Table 2.

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

Empirical formula	$C_{72}H_{48}As_2Fe_4N_{12}O_{78.5}W_{18}Y_2$
Formula weight	6220.52
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	12.8882(2)
b (Å)	13.4613(2)
c (Å)	17.7548(3)
α (°)	95.0130(10)
β (°)	104.1520(10)
γ (°)	97.8220(10)
Volume (Å^3)	2935.60(8)
Z	1
Crystal size (mm^3)	0.18 × 0.16 × 0.14
D_{cal} (g/cm$_3$)	3.555
Absorption coefficient (mm^{-1})	19.676
Reflections collected	33509
Independent reflections	9658 ($R_{int} = 0.0599$)
Data/restraints/parameters	9658/12/875
Goodness-of-fit on F^2	1.032
Final R indices [$I > 2\sigma$(I)]	$R_1 = 0.0473$, $wR2 = 0.1044$
R indices (all data)	$R_1 = 0.0574$, $wR_2 = 0.1089$

$w^{-1} = [\sigma^2(F_0^2) + (0.0000P)^2 + 760.0160P]$, $P = (F_o^2 + 2F_c^2)/3$, $R_1 = \sum||F_o| - |F_c||/\sum|F_o||$, $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table 2
Selected bond lengths (Å) and angles (°) for the title compound

Y(1)–O(26)	2.166(13)	W(4)–O(4)	1.686(10)
Y(1)–O(2w)	2.458(14)	W(5)–O(27)#1	1.758(15)
Y(1)–O(2w)	2.428(14)	W(8)–O(33)	2.363(9)
Y(1)–O(34)#1	2.615(9)	W(9)–O(9)	1.724(9)
O(34)–Y(1)#1	2.615(9)	W(9)–O(23)	2.207(11)
Fe(1)–O(28)#1	1.874(9)	W(9)–O(24)	1.840(9)
Fe(1)–O(34)#1	2.296(9)	O(29)#1–Fe(1)–O(30)	162.7(4)
Fe(2)–N(1)	1.978(11)	O(25)–Fe(1)–O(34)#1	164.4(4)
Fe(2)–N(5)	2.009(13)	O(28)#1–Fe(1)–O(34)	166.1(4)
As(1)–O(33)	1.688(9)	N(1)–Fe(2)–N(4)	174.0(5)
As(1)–O(34)	1.662(9)	N(6)–Fe(2)–N(3)	172.2(5)
W(1)–O(14)	1.852(11)	N(2)–Fe(2)–N(5)	176.4(5)
W(1)–O(31)	2.496(9)	O(32)–As(1)–O(33)	106.7(4)
W(2)–O(24)	1.724(9)	O(34)–As(1)–O(31)	112.9(5)

3. Results and discussion

3.1. Synthesis and the oxide state of Fe

The crystal of the title compound was prepared from the hydrothermal system without precursors (S1 in SI), this situation is different from the most cases of the known sandwich analogues that involve trivacant precursors, $XW_9O_{34}^{9-}$ or $X_2'W_{15}O_{56}^{12-}$(S2 in SI). Other else, the title compound was isolated as the composite complex, while the most of known sandwich-type POMs exist as the salts of K^+ or Na^+. The synthesis of **1** seemly indicates an interesting approach to the synthesis of sandwich-type polyoxometalates.

Even though the title compound was prepared from ferrous starting materials, three lines of evidence are consistent with the Fe^{III} oxidation state in **1**: first, bond-length-based valence sum calculations [27] from the crystal structure yield an average oxidation state for Fe of 3.28 ± 0.27; second, the lack of significant Jahn–Teller distortion is more consistent with Fe(III) centers than with Fe(II) centers [12]; third, the ESR spectra exhibit obviously that there are two kinds of Fe^{3+}: high spin state and low spin state in the title compound. The analogous case of Fe(II) → Fe(III) has been reported by Hill et al. [12].

3.2. Structural description

As shown in Fig. 1, the structure unit of the title compound consists of one sandwich polyanion $[As_2W_{18}Fe_2\{Y(OH_2)_2\}_2O_{68}]^{6-}$, two discrete cations $[Fe(phen)_3]^{3+}$, and 6.5 crystal water molecules. Although the structure of the title polyanion shows the general modes proposed earlier for sandwich analogues with 4 cores by Hill *et al* and Wang et al. [12,16], interestingly, the two equivalent moieties, $[AsW_9O_{34}]^{9-}$, are held together by two RE ions (Y^{3+}) and two TM ions (Fe^{3+}), this situation has never been observed in sandwich POM chemistry. The unprecedented interlayer, $Fe_2Y_2(H_2O)_4O_{16}$(Fig. 2), consists of two FeO_6 octahedra and two YO_8 bicapped trigonal prisms via edge sharing, exhibiting the regular rhombic arrangement (S3 in SI). For the FeO_6 groups (S4 in SI), each iron atom is defined by three oxygen atoms on each $[AsW_9O_{34}]^{9-}$ polyanion (O34, O28, O29 and O30, O25, O34), the Fe–O bond lengths very from 1.874(3) to 2.296(11) Å while the opposed O–Fe–O angles are in the range of 162.69(40) ~ 166.12(39)°. For the yttrium groups (S5 in SI), each Y atom is bonded to two aqua ligands (O1W and O2W) and three oxygen atoms on each $[AsW_9O_{34}]^{9-}$ polyanion (O27, O26, O24 and O23, O30, O29) with distorted bicapped trigonal prismatic configuration, the range of Y–O bond distances are in the range of 2.166(13) ~ 2.615(9) Å, while the distance between Y atom and two triangular bases α(O27, O30, O1w) and β(O26, O29, O2w), are 1.4766 and 1.4159 Å, respectively. The above data exhibit that the four polyhedra have been distorted, which may be attributed to the effect of various coordination atoms.

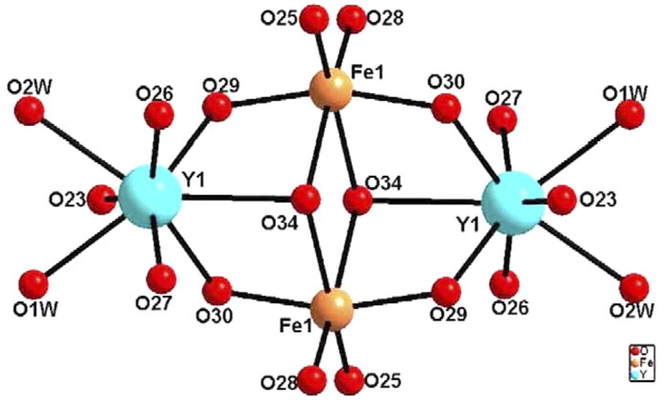

Fig. 2. Ball-and-stick illustration of the structure of central $Y_2Fe_2O_{16}(H_2O)_4$ unit.

The trivacant Keggin unit, $[B\text{-}AsW_9O_{34}]^{9-}$, linked by the mixed Fe_2Y_2 unit is in a centrosymmetric arrangement (C_{2h} symmetry). The $[B\text{-}AsW_9O_{34}]^{9-}$ moiety derives from the removal of one edge-sharing W_3O_{13} triad from the parent Keggin structure $[AsW_{12}O_{40}]^{3-}$. Each $[B\text{-}AsW_9O_{34}]^{9-}$ polyanion provides seven oxygen atoms (one from the AsO_4 group and one each from the six WO_6 group) that are capable of bonding to the central tetrameric metal unit. The nine WO_6 octahedra in $[B\text{-}AsW_9O_{34}]^{9-}$ moiety have essentially similar distorted octahedral environments defined by one terminal oxo-group with short W–O bond length (1.686–1.724 Å), four doubly bridging oxo-groups with intermediate W–μ–O bond lengths (1.852–2.008 Å), and one μ_4-oxygen, also bonded to As, with long W–μ_4–O distances (2.363–2.496 Å). The As–O bond distances in the AsO_4 polyhedra vary from 1.662(9) to 1.688(9) Å, and the O–As–O bond angles vary from 106.7(4)° to 112.9(5)°. The above data indicate that the AsO_4 tetrahedra have been distorted to some extent, which could be attributed to the effect of rhombic interlayer, the analogous

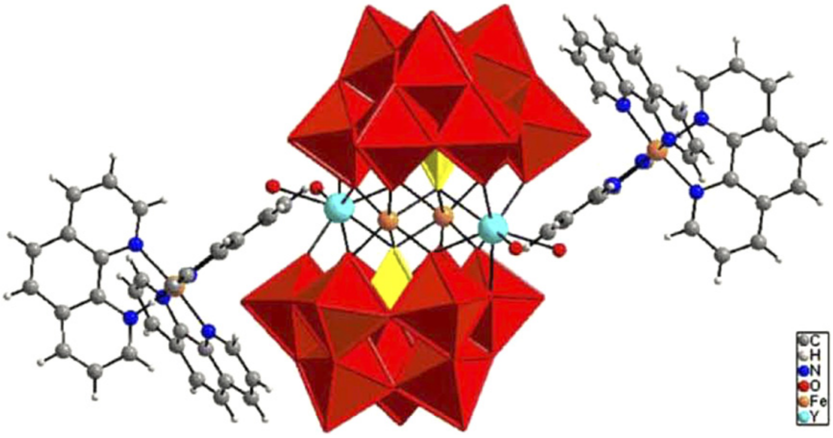

Fig. 1. Structure unit of the title compound, the free water molecules have been omitted for clarity, polyhedra represent the WO_6 (red) and AsO_4(yellow). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

situation were reported in the $[As_2W_{18}M_4(H_2O)_2O_{68}]^{10-}$ examples [16].

Each Fe site in $[Fe(phen)_3]^{3+}$ discrete cations is defined by six nitrogen atoms from three phen molecules with distorted octahedral configuration. For Fe(2) group, the Fe–N bond lengths are in the range of 1.978(13)–2.009(13) Å (av. 1.994 Å), the opposed N–Fe–N angles vary from 172.19(56)° to 176.43(49)°, the small maximum difference in Fe–N bond distance (0.03 Å) and the almost linear N–Fe–N angles indicate the slightly distortion of FeN_6 octahedra. While the dihedral angles among three ideal phen planes are 91.4°, 87.4° and 90.3°, which indicates that the three ideal phen planes in each $[Fe(phen)_3]^{3+}$ fragment are nearly vertical to each other. Besides, in Fe(2) group, the mean deviations of three phen ideal planes, γ(N1, N1, C1 to C12), δ(N3, N4, C13–C24) and ε(N5, N6, C25, C36) are 0.0249, 0.0373 and 0.5048 Å, and the Fe(2) atom deviates 0.0376, 0.0579, and 0.8484 Å from the ideal planes γ, δ and ε, respectively. It is the evidence that the Fe(2) atom is nearly in the plane γ.

In addition, it is worth to note the distortion of FeO_6 and FeN_6 groups. On one hand, both FeO_6 groups and FeN_6 groups exhibit the slight Jahn–Teller effect, indicated by the small difference values between axial bonds and the equatorial bonds, 0.067 Å for FeO_6 groups and 0.018 Å for FeN_6 groups (Fig. 3). On the other hand, the various coordination environments may play an important role in the distortion of $FeL_6(L = N, O)$. For Fe(1) group, Fe(1) atom is bonded to one μ_4-O atom (bonded to As atom), one μ_3-O atom (shared by a W atom and two metal atoms) and one μ_2-O atom (shared by a W atom and a metal atom) from each $AsW_9O_{34}^{9-}$ moiety. For Fe(2) group, the Fe atom is coordinated to six N atoms from three phen molecules. It is visible that the coordination environment in FeO_6 group are more complicated than those in FeN_6 group, so it is expectable that the FeO_6 octahedra exhibit the stronger distortion.

3.3. IR spectroscopy

In the IR spectrum of **1** at room temperature (S6 in SI), the peaks at 960, 771, and 888 cm^{-1} can be assigned to the characteristic vibrations of $v(W\text{–}O_d)$, $v(W\text{–}O_c)$ and $v(As\text{–}O_a)$, respectively [28]. Compared with those of $\alpha-AsW_{12}O_{40}^{3-}$, these peaks are shifted towards low frequency region apparently and the last vibration overlaps that of $v(W\text{–}O_b)$, resulting from the increase of the negative charges of the anion, this situation has been reported by Wang et al. [16]. The bonds in the region of 1350–1050 cm^{-1} can be attributed to the characteristic peaks of 1,10-phenanthroline cyclobackbone. The coordination between metal atoms and N donors are safely indicated by the red-shifts of flexural oscillations δ(C–H) outside the 1,10-phenanthroline plane from 865, 742 cm^{-1} to 839, 719 cm^{-1} [29,30]. In addition, the strong peaks at 3445 cm^{-1} can be assigned to the telescopic oscillations of water molecules, then outside plane rocking vibrations of water appear 583 cm^{-1}, which exhibit the presence of crystal water and coordination water molecules, respectively [30]. As shown in S6b, the temperature variation of the IR spectra exhibits the disappearances of characteristic peaks for phen groups and polyanion framework in the regions of 400 ~ 450 °C and 550 ~ 600 °C, respectively.

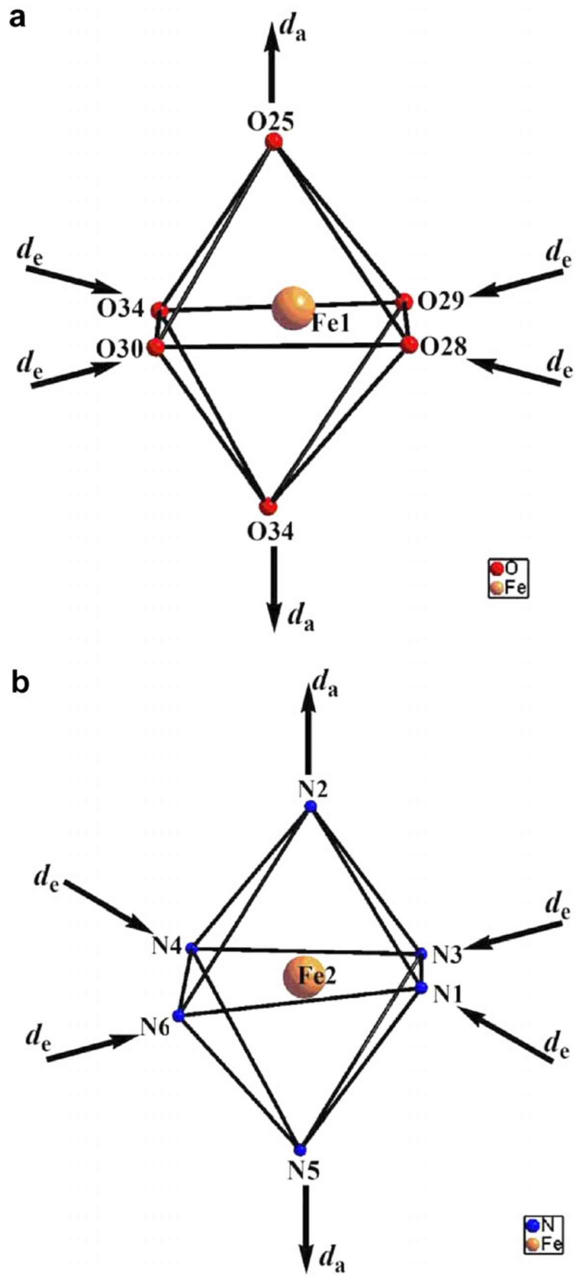

Fig. 3. View of the Jahn–Teller distortion of the FeO_6(a) and FeN_6(b), d_a = mean axial distance, d_e = mean equatorial distance. (a) FeO_6 case, $d_a - d_e = 0.067$Å; (b) FeN_6 group, $d_a - d_e = 0.018$Å.

3.4. ESR spectrum

The ESR spectra of $[Fe(phen)_3]_2[As_2W_{18}Fe_2\{Y(H_2O)_2\}_2O_{68}]\cdot 6\ 5H_2O$ reveal obviously that there are two kinds of Fe(III): high spin state and low spin state in compound

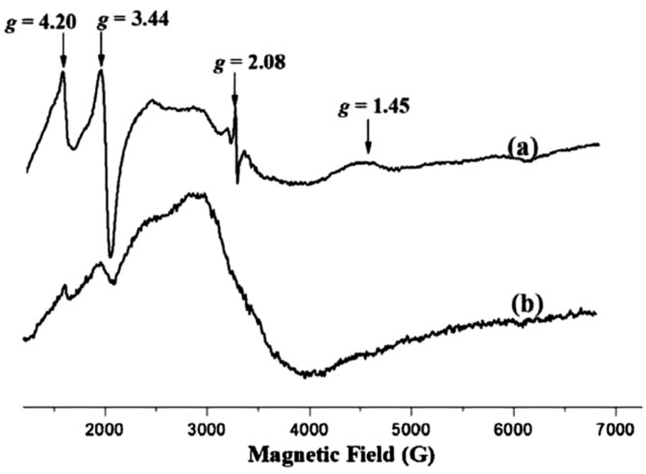

Fig. 4. ESR spectra of the title compound: (a) 110 K, 9.4867 GHz; (b) room temperature, 9.7763 GHz.

1 (Fig. 4). At 110 K, the ESR spectrum display a broad signal centered at $g = 1.44$ and three narrow symmetric bands $g = 4.20, 3.44, 2.08$. It has been reported that the Fe^{3+} with high spin ($S = 5/2$) incorporated in silicotungstate and phosphatomolydbate structures with the distorted octahedral coordination give the isotropic ESR signal at $g = 4.12$ [31] and 4.1–4.2, respectively [32,33]. Therefore, the signal at $g = 4.20$ is assigned to the Fe sites in central layer with FeO_6 coordination. On the other hand, the parameters $g = 3.44$ and 1.45 are consistent with the presence of low spin Fe^{3+} ($S = 1/2$) [34–37], which could be attributed to the Fe sites in discrete cations $[Fe(phen)_3]^{3+}$. When the temperature increases to room temperature, The ESR signal $g = 1.45$ disappears, which may be caused by the zero-field splitting, and at the same time other signals $g = 4.20, 3.44, 2.08$ decrease. In addition, the noise signals become stronger owing to the increasing spin-lattice relaxation time. The analogous situations have been observed in our previous work for Co^{2+} with high spin state and low spin state in same complex [38].

3.5. Thermal analysis

Thermal stability of the title compound has been studied by the means of thermogravimetric and differential thermal measurements (Fig. 5). TG curve of **1** exhibits two stages for loss of weight. The first slow weight loss of 3.10% occurs between room temperature and 300 °C, corresponding to the loss of crystal water molecules (cacl. 3.04%); the second sharp weight loss of 17.39% occurs from 300 to 700 °C, resulting from the loss of phen groups (cacl. 17.36%). A strong and wide endothermal peak is observed at 251.5 °C in DTA curve, this heating-absorbing process should be related to the release of water molecules. Meanwhile, the two strong exothermal peaks appeared at 446.8 and 580.8 °C show the combustion of phen groups and the decomposition of the polyanion framework, respectively, which are accord with the results of the temperature variation of the IR spectra.

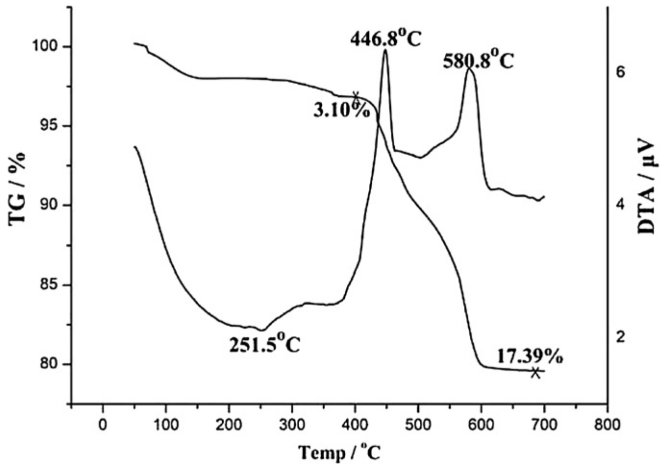

Fig. 5. TG-DTA curves of $[Fe(phen)_3]_2[As_2W_{18}Fe_2\{Y(H_2O)_2\}_2O_{68}]\cdot 6.5H_2O$.

4. Conclusions

In summary, we have successfully synthesized a novel sandwich type polyoxometalate $[Fe(phen)_3]_2[As_2W_{18}Fe_2\{Y(H_2O)\ _2\}_2O_{68}]\cdot 6\ 5H_2O$, exhibited by the incorporation of the mixed RE/TM interlayer. The presence of the title compound enriches the field of sandwich POMs and may promote the further development of this subclass. Moreover, the synthesis of the title compound validates the two-step hydrothermal synthetic protocol and the feasibility of sandwich-type polyoxometalates.

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Appendix A. Supplementary data

Crystallographic data for structural analysis reported in this paper have been deposited with the Cambridge crystallographic Data center with the deposited numbers 604523 for the title compound. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2007.03.003.

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