1D and 2D polyoxometalate-based composite compounds. Synthesis and crystal structure of  $[{Ba(DMSO)_5(H_2O)}_2-(SiMo_{12}O_{40})]$  and  $[{Ba(DMSO)_3(H_2O)}_3-{Ba(DMSO)_5(H_2O)}]$ 

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The composites  $[\{Ba(DMSO)_5(H_2O)\}_2(SiMo_{12}O_{40})]$  (1) and  $[\{Ba(DMSO)_3(H_2O)_3\}\{Ba(DMSO)_5(H_2O)\}(GeMo_{12}O_{40})]$  (2) have been synthesized and characterized by IR and UV spectroscopy, and single-crystal X-ray structural analysis. Compound 1 forms an unprecedented one-dimensional linear chain built from alternating polyanions and cationic units in the crystal, whereas crystalline 2 contains a novel two-dimensional network made up of polyanions, metal ions, H<sub>2</sub>O, and DMSO. The chain and net are both connected through Mo–O<sub>t</sub>-Ba-O-Ba links.

The design and assembly of organic-inorganic solid-state materials with active physical properties, such as materials with electrical, magnetic, and optical properties, has become a focus of a great deal of interest in recent years.<sup>1</sup> Many studies have shown that such properties are associated with structures constructed by so-called anion-cation salts or host-guest solids. In these fields, polyoxometalates have been found to be extremely versatile inorganic building blocks due to their ability to accept electrons. They can be combined with organic  $\pi$ -electron donors, such as tetrathiafulvalene (TTF)<sup>2-4</sup> and bis(ethylenedithio)tetrathiafulvalene (ET),<sup>5-8</sup> to form polyoxometalatebased hybrid materials with 1D or 2D structures. Besides organic donors, other donor molecules, such as decamethylferrocene, can be combined with polyoxometalate acceptors.9 Furthermore, a type of intermolecular complex which can enhance SHG nonlinear optical response through electron transfer between organic and inorganic units has also been reported.<sup>10</sup> The interactions existing in organic-inorganic or in organic-organic complexes are mainly facilitated by hydrogen bonds, van der Waals forces, and electrostatic forces in their structures. However, infinitely extended chains based on Keggin or Dawson-type anions, and joined together by W-O<sub>t</sub>-M<sup>11</sup> links are relatively rare; a few notable examples include  $[ET]_{8}[PMnW_{11}O_{39}] \cdot 2H_{2}O^{12} [NEt_{3}H]_{5}[XCoW_{11}O_{39}] \cdot 3H_{2}O (X =$ P or As),<sup>13</sup>  $[Co(dpa)_2(OH)_2]_2[Hdpa][PCoW_{11}O_{39}], [Cu(en)_2 (OH_2)_2[H_2en][{Cu(en)_2}P_2CuW_{17}O_{61}]\cdot 5H_2O$  (en = ethylenediamine), and  $[Cu(en)_2(OH_2)]_2[Cu(en)_2]_{0.5}[H_2en]_{0.5}[{Cu(en)_2} P_2CuW_{17}O_{61}$ ]·5H<sub>2</sub>O (M = Mn, Co or Cu),<sup>14</sup> which are based on substituted polyoxometalate anions or synthesized by hydrothermal methods.

From the standpoint of molecular design, we have attempted to make use of simple syntheses to realize such molecular assemblies. One aim of introducing metal ions into the framework formed by polyanions and organic units is to combine polyanions with organic groups through metal ions and gain stable crystals. Another aim is to acquire information on the optical properties of these compounds, since polyoxometalate anions are good electron acceptors, while DMSO molecules are electron-rich donors, thus, they can interact, leading to electron transfer. Finally, the combination of heavy atoms with high oxidation states and reduced polyoxometalate anions to form mixed-valence compounds can lead to crystals which exhibit photochromism. Here, we report the syntheses and X-ray single-crystal structure analyses of two infinitely extended polyoxometalate-based composites:  $[{Ba(DMSO)_5(H_2O)}_2(Si-Mo_{12}O_{40})]$  (1) and  $[{Ba(DMSO)_3(H_2O)_3} {Ba(DMSO)_5(H_2O)}_2(GeMo_{12}O_{40})]$  (2). In their structures, the metal ions are firstly coordinated by DMSO, H<sub>2</sub>O, and polyanion ligands to form a structure unit, then these structure units are connected through Ba–O–Ba–O<sub>t</sub>–Mo links to construct one-dimensional chain-like or two-dimensional net-like structures. To our knowledge, the types of structures exhibited by 1 and 2 have never been reported previously. This paper focuses primarily on solid-state structural aspects of organic–inorganic complexes and reveals novel structures in which infinite stacking assemblies between polyanions and cationic units are achieved. The structures of the title compounds may serve as useful models for the design of functional molecular assemblies.

# Experimental

# Synthesis

All organic solvents and materials used for the synthesis were of reagent grade and were used without further purification.  $\alpha$ -H<sub>4</sub>SiMo<sub>12</sub>O<sub>40</sub>•*n*H<sub>2</sub>O and  $\alpha$ -H<sub>4</sub>GeMo<sub>12</sub>O<sub>40</sub>•*n*H<sub>2</sub>O were prepared according to the literature method.<sup>15</sup>

[{Ba(DMSO)<sub>5</sub>(H<sub>2</sub>O)}<sub>2</sub>(SiMo<sub>12</sub>O<sub>40</sub>)] (1). The formation of the heteropolyacid barium salts was carried out by neutralization of the acids. H<sub>4</sub>SiMo<sub>12</sub>O<sub>40</sub>·nH<sub>2</sub>O (5 g, 2.5 mmol) was dissolved in 20 mL water, and BaCl<sub>2</sub>·2H<sub>2</sub>O (1.1 g, 4.5 mmol) was added at 90 °C with stirring until the solution was nearly dry. The solids were isolated and dried on a fritted-glass funnel for next stage. Dried powder (2 g) from the first stage was dissolved in 10 mL acetonitrile–water mixture (5 : 2 v/v), and 1 mL DMSO was added at 70 °C with stirring, the mixture was allowed to react for 15 min. After cooling to room temperature, the solution was filtered and left to evaporate at room temperature. Three days later, yellow crystals were obtained; yield based on  $\alpha$ -H<sub>4</sub>SiMo<sub>12</sub>O<sub>40</sub>·nH<sub>2</sub>O: 60%. Elemental analysis: C obs. 8.62 (calc. 8.24), H 1.92 (2.1)%.

[{Ba(DMSO)<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>}{Ba(DMSO)<sub>5</sub>(H<sub>2</sub>O)}(GeMo<sub>12</sub>O<sub>40</sub>)] (2). Compound 2 was prepared using a similar method to that employed for the synthesis of 1, with H<sub>4</sub>GeMo<sub>12</sub>O<sub>40</sub>·nH<sub>2</sub>O (5 g, 2.6 mmol) in place of H<sub>4</sub>SiMo<sub>12</sub>O<sub>40</sub>·nH<sub>2</sub>O. Yellow crystals were obtained; yield based on  $\alpha$ -H<sub>4</sub>GeMo<sub>12</sub>O<sub>40</sub>·nH<sub>2</sub>O: 40%. Elemental analysis: C obs. 6.68 (calc. 6.78), H 1.45 (1.96)%.

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	1	2
Molecular formula Crystal system Space group a/Å b/Å c/Å $\beta/°$ $V/Å^3$ Z $\mu/mm^{-1}$ Total no.of reflections Independent reflections R1 wR2	$\begin{array}{c} C_{20}H_{68}Ba_2SiMo_{12}O_{54}S_{10}\\ Monoclinic\\ P2_1/n\\ 14.279(3)\\ 14.805(3)\\ 18.778(4)\\ 92.12(3)\\ 3967.2(14)\\ 2\\ 3.174\\ 11818\\ 6580\\ 0.0481\\ 0.1056 \end{array}$	$\begin{array}{c} C_{16}H_{56}Ba_2GeMo_{12}O_{52}S_8 \\ Monoclinic \\ P2_1/c \\ 14.469(3) \\ 17.817(4) \\ 27.737(6) \\ 90.70(3) \\ 7150(2) \\ 4 \\ 3.852 \\ 21526 \\ 12020 \\ 0.0302 \\ 0.0723 \end{array}$

#### Characterization

C, H elemental analysis was performed on a Perkin-Elmer 240C elemental analyzer. IR spectra were recorded from KBr pellets on a Nicolet 170 SXFT-IR instrument. Electronic spectra ( $\lambda = 200-500$  nm) in MeCN-H<sub>2</sub>O (5 : 2 v/v) solutions were obtained on a Shimazu UV-250 spectrometer.

The crystal structures of 1 and 2 were determined from single-crystal X-ray diffraction data. The intensity data were collected by  $\theta$ -2 $\theta$  scans on a Rigaku RAXIS-IV image plate area detector using graphite monochromated Mo-Ka radiation  $(\lambda = 0.7103 \text{ Å})$  at 20 °C. The crystal parameters and details of the structure solution and refinement are listed in Table 1. The structures were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the SHELXTL-97 program.<sup>16</sup> In addition, all sulfur atoms and the C10 atom in 1, and the S2, S6, S7, and S8 atoms in 2, are disordered over two locations. The occupancies for S1, S4, S5, and C10 in 1 over two sites are 0.4, 0.6; for S2 and S3 in 1 they are 0.2 and 0.8; for S2 and S6 in 2 the occupanies are 0.1 and 0.9; and for the S7 and S8 in 2 they are 0.5 and 0.5 in 2. Selected bond lengths and angles are listed in Tables 2 and 3.

CCDC reference numbers 172566 and 172567.

See http://www.rsc.org/suppdata/dt/b2/b201287c/ for crystallographic data in CIF or other electronic format.

#### **Results and discussion**

Stable crystals of compounds 1 and 2 were obtained from acetonitrile-water mixtures at room temperature. Experiments proved that selection of a suitable solvent mixture was crucial for growing crystals of the title compounds. Compounds 1 and 2 are both soluble in DMSO, CH<sub>3</sub>CN, and their mixtures with water. When they were dissolved in DMSO and the solvent left to evaporate slowly, only powders were obtained; when dissolved in CH<sub>3</sub>CN, irregular crystals were obtained because the solvent is lost too quickly. Therefore, it is necessary to control the evaporation rate of the solution. Adding some water to the acetonitrile solved this problem. Adjusting the amount of water used controlled the speed at which the crystals grew. Using this technique, suitable crystals were eventually obtained. It should be noted that the crystals are sensitive to the sunlight, the reasons for which have been discussed above, so exposure of the crystallization solutions to sunlight should be avoided. In addition, it should be mentioned that, although the reaction conditions were identical when the experiments were repeated, it proved difficult to control the actual number of DMSO molecules incorporated in the cationic lattice and to identify which factors determine whether the one-dimensional or the two-dimensional lattice is formed. Much more data will need to be accumulated in order to clarify these problems.

1 consists of one-dimensional infinite chains built from alternate polyanions and  $[Ba(DMSO)_5(H_2O)]_2^{2+}$  units. As shown in Fig. 1, two crystallographically identical  $Ba^{2+}$  ions,



Fig. 1 Molecular structure unit of compound 1. The hydrogen atoms are omitted for clarity.

Ba1 and Ba1A, are located symmetrically at opposite sites of the polyanion, and both connect with the terminal oxygen atoms of the polyanion. The coordination polyhedra around the  $Ba^{2+}$  ions can be described as a distorted singly capped square antiprism [Fig. 2(a)], in which an oxygen atom from the



Fig. 2 (a) Coordination polyhedron around  $Ba^{2+}$  in 1. (b) Coordination environment of  $Ba^{2+}$  in 1.

polyanion occupies the cap position, and six oxygen atoms from DMSO molecules and two from water ligands occupy the other sites. It is notable that there are four bridging oxygen atoms between adjacent Ba<sup>2+</sup> ions, as shown in Fig. 2(b), from two DMSO and two water ligands. Therefore, [{Ba(DMSO)<sub>5</sub>-(H<sub>2</sub>O)}<sub>2</sub>(SiMo<sub>12</sub>O<sub>40</sub>)] units interconnect *via* Ba–O–Ba–O<sub>t</sub>–Mo bridges to give a one-dimensional chain-like structure (Fig. 3). The Ba–O distances range from 2.639 to 3.042 Å, the longest being the Ba–O<sub>t</sub> bond. The non-bonding Ba ··· Ba distance is 4.1930 Å.

The unit cell of  $[{Ba(DMSO)_5(H_2O)}_2(SiMo_{12}O_{40})]$  contains two independent anions located at inversion centers, as shown

in Fig. 1. The site symmetry  $\overline{1}$  is incompatible with the apparent tetrahedral symmetry of the Keggin structure.<sup>17,18</sup> The Si atom is located at an inversion center (0.5, 0.5, 0.5). Therefore, the structure of 1 has the central Si atom surrounded by a cube of eight oxygen atoms and the Mo atoms situated at the corners of a regular cubooctahedron. The Si–O distances (1.565–1.697 Å) are consistent with the results of previous studies.<sup>19,20</sup> The Mo–O distances vary over the very wide range 1.650–2.485 Å. The shortest Mo–O distances for the unshared oxygen atoms are in the range 1.650–1.662 Å, the mean value of 1.656 Å is 0.012 Å longer than that of the literature;<sup>19</sup> the longest Mo–O

**Table 2** Selected bond lengths (Å) and angles (°) for  $1^{a}$ 

Mo(1)-O(4)	1.803(5)	Mo(1)–O(14)	1.797(5)
Mo(1)–O(19)	2.024(5)	Mo(1)–O(17)	2.016(5)
Mo(2)–O(7)	1.801(6)	Mo(2)–O(17)	1.808(5)
Mo(2)-O(5)#1	2.004(6)	Mo(2)–O(18)	2.007(5)
Mo(3)–O(10)	1.806(5)	Mo(3)–O(18)	1.803(5)
Mo(3)-O(9)#1	2.017(5)	Mo(3)–O(14)	2.011(5)
Mo(4)–O(5)	1.795(6)	Mo(4)–O(6)	1.816(5)
Mo(4)–O(4)	1.989(6)	Mo(4)–O(13)#1	2.003(5)
Mo(5)–O(21)	1.800(5)	Mo(5)–O(19)	1.800(6)
Mo(5)-O(10)#1	2.011(6)	Mo(5)–O(6)	2.000(5)
Mo(6)–O(9)	1.799(6)	Mo(6)–O(13)	1.803(6)
Mo(6)–O(7)	1.998(6)	Mo(6)–O(21)	2.020(5)
Ba(1)–O(24)	2.639(6)	Ba(1)–O(27)	2.683(7)
Ba(1)–O(26)	2.700(6)	Ba(1)–O(25)	2.766(6)
Ba(1)–O(23)	2.831(5)	Ba(1)–O(23)#2	2.889(5)
Ba(1)-O(1W)	2.911(5)	Ba(1)–O(1W)#2	2.929(5)
Ba(1)–Ba(1)#2	4.1930(10)	O(8)–Ba(1)–Ba(1)#2	176.60(8)
Mo(6)-O(9) Mo(6)-O(7) Ba(1)-O(24) Ba(1)-O(26) Ba(1)-O(23) Ba(1)-O(1W) Ba(1)-Ba(1)#2	1.799(6) 1.998(6) 2.639(6) 2.700(6) 2.831(5) 2.911(5) 4.1930(10)	Mo(6)-O(13) Mo(6)-O(21) Ba(1)-O(27) Ba(1)-O(25) Ba(1)-O(23)#2 Ba(1)-O(1W)#2 O(8)-Ba(1)-Ba(1)#2	1.803(6 2.020(5 2.683(7 2.766(6 2.889(5 2.929(5 176.60(8)

<sup>*a*</sup> Symmetry transformations used to generate equivalent atoms: #1 -x + 1, -y + 1, -z + 1; #2 -x + 2, -y + 2, -z + 1. Mo–O bond lengths are selected from Mo–O<sub>b/e</sub>.

**Table 3** Selected bond lengths (Å) and angles (°) for  $2^a$ 



**Fig. 3** View of the one-dimensional chain in **1**. The H atoms and the lattice water are omitted for clarity.

distances involving O atoms of the central tetrahedron are in the range of 2.334–2.485Å, the mean value 2.4Å is 0.05Å longer than that of the literature;<sup>19</sup> the Mo–O distances for the bridging oxygen atoms vary from 1.795 to 2.024Å, the mean value 1.905Å is 0.02Å shorter than that reported in the literature.<sup>19</sup> These results show that the SiO<sub>4</sub> tetrahedron and MoO<sub>6</sub> octahedra of the anion are severely distorted, and further attest to the strong interaction between the polyanions and  $[Ba(DMSO)_5(H_2O)]^{2+}$  units. The structure of **2** can be described as follows: two

The structure of **2** can be described as follows: two  $[{Ba(DMSO)_3(H_2O)_3} {Ba(DMSO)_5(H_2O)} (GeMo_{12}O_{40})]$  molecules interconnected *via* Ba–O–Ba–O<sub>t</sub>–Mo bridges, forming a  $[{Ba(DMSO)_3(H_2O)_3} {Ba(DMSO)_5(H_2O)} (GeMo_{12}O_{40})]_2$  unit, as shown in Fig. 4(a). This unit then connects with other adjacent units *via* Mo–O<sub>t</sub>–Ba bridges constructing a two-dimensional network [Fig. 4(b)]. In this structure, two crystallographically different Ba<sup>2+</sup> ions are located at the same side of each polyanion (Fig. 5), which is different from the situation in **1**. Each Ba<sup>2+</sup> is surrounded by nine oxygen atoms at distances of 2.669–2.927 Å and 2.684–2.934 Å for Ba1 and Ba2, respectively, forming a singly capped square antiprism. Fig. 6 shows the coordination environments of the two independent barium ions. The ligands bonded to Ba1 include five DMSO molecules, two water, and two polyanions, but in the case of Ba2, there are

-y, -z + 1.

Mo(1)–O(32)	1.843(4)	Mo(1)–O(26)	1.831(4)
Mo(1)-O(2)	2.049(4)	Mo(1)–O(28)	2.047(4)
Mo(2)–O(4)	1.856(4)	Mo(2)–O(10)	1.838(4)
Mo(2)–O(13)	2.038(4)	Mo(2)–O(5)	2.018(4)
Mo(3)–O(17)	1.863(4)	Mo(3)–O(2)	1.824(4)
Mo(3)–O(4)	2.054(4)	Mo(3)-O(33)	2.019(4)
Mo(4)–O(19)	1.846(4)	Mo(4)–O(5)	1.829(4)
Mo(4)–O(14)	2.056(4)	Mo(4)–O(34)	2.053(4)
Mo(5)–O(28)	1.857(4)	Mo(5)–O(22)	1.837(4)
Mo(5)–O(23)	2.024(4)	Mo(5)-O(21)	2.009(4)
Mo(6)–O(29)	1.869(4)	Mo(6)–O(14)	1.825(4)
Mo(6)–O(20)	2.035(4)	Mo(6)–O(10)	2.023(4)
Mo(7)–O(13)	1.858(4)	Mo(7)–O(15)	1.822(4)
Mo(7)–O(17)	2.046(4)	Mo(7)–O(22)	2.039(4)
Mo(8)–O(21)	1.855(4)	Mo(8)–O(25)	1.839(4)
Mo(8)–O(15)	2.050(4)	Mo(8)–O(19)	2.035(4)
Mo(9)–O(20)	1.851(4)	Mo(9)–O(33)	1.837(4)
Mo(9)–O(26)	2.037(4)	Mo(9)–O(35)	2.031(4)
Mo(10)–O(23)	1.861(4)	Mo(10)–O(7)	1.823(4)
Mo(10)–O(32)	2.049(4)	Mo(10)–O(24)	2.032(4)
Mo(11)–O(34)	1.840(4)	Mo(11)–O(8)	1.830(4)
Mo(11)–O(7)	2.053(4)	Mo(11)–O(25)	2.039(4)
Mo(12)–O(35)	1.849(4)	Mo(12)–O(24)	1.847(4)
Mo(12)–O(29)	2.055(4)	Mo(12)–O(8)	2.025(4)
O(6)–Ba(1)	2.782(4)	O(12)–Ba(2)	2.934(4)
O(31)–Ba(1)#1	2.903(4)	Ba(1)–O(48)	2.669(5)
Ba(1)–O(45)	2.676(5)	Ba(1)–O(42)	2.722(4)
Ba(1)–O(43)	2.822(4)	Ba(1)-O(41)	2.876(4)
Ba(1)–O(31)#2	2.903(4)	Ba(1)-O(1W)	2.925(5)
Ba(1)–O(4W)#3	2.927(5)	Ba(1)–Ba(2)#3	4.4043(14)
Ba(2)–O(46)	2.684(6)	Ba(2)–O(44)	2.756(5)
Ba(2)–O(43)#3	2.780(4)	Ba(2)–O(47)	2.825(5)
Ba(2)–O(3W)	2.829(5)	Ba(2)–O(41)#3	2.847(4)
Ba(2)–O(2W)	2.866(5)	Ba(2)-O(4W)	2.924(5)
Ba(2)–Ba(1)#3	4.4043(14)	O(6)-Ba(1)-Ba(2)#3	77.34(8)
O(31)#2–Ba(1)–Ba(2)#3	169.64(8)	O(12)-Ba(2)-Ba(1)#3	146.64(8)
<sup>a</sup> Symmetry transformations used to generate equival Mo–O bond lengths are selected from Mo–O <sub>ble</sub> .	lent atoms: #1 $-x$ , $y -$	1/2, -z + 3/2; #2 - x, y + 1/2	2, -z + 3/2; #3 - x - 1,



Fig. 4 (a) The connections between  $[{Ba(DMSO)_3(H_2O)_3}{Ba-(DMSO)_5(H_2O)_5(GeMo_{12}O_{40})]}$  units in 2. (b) View of the two-dimensional network along the *a* axis in 2. The H atoms and the lattice water are omitted for clarity.



Fig. 5 Molecular structure unit of compound 2. The hydrogen atoms are omitted for clarity.

different numbers of each ligand. Ba2 is linked to five DMSO molecules, three water, and a polyanion. In the [{Ba(DMSO)<sub>3</sub>-(H<sub>2</sub>O)<sub>3</sub>}{Ba(DMSO)<sub>5</sub>(H<sub>2</sub>O)}(GeMo<sub>12</sub>O<sub>40</sub>)]<sub>2</sub> unit, four metal ions all bind with O<sub>t</sub> atoms of polyanions; two [{Ba(DMSO)<sub>3</sub>-(H<sub>2</sub>O)<sub>3</sub>}{Ba(DMSO)<sub>5</sub>(H<sub>2</sub>O)}(GeMo<sub>12</sub>O<sub>40</sub>)] molecular units are in inverse sites, and four polyanions are bridged by a pair of Ba–O–Ba–O<sub>t</sub>–Mo links, producing a square-like structure [Fig. 4(a)]. It should be noted that the connection between barium ions in **2** relies on three bridging O atoms, one from water, and two from DMSO molecules (Fig. 6). The non-bonding Ba ··· Ba distance is 4.4043 Å. Finally, the [{Ba(DMSO)<sub>3</sub>-(H<sub>2</sub>O)<sub>3</sub>}{Ba(DMSO)<sub>5</sub>(H<sub>2</sub>O)}(GeMo<sub>12</sub>O<sub>40</sub>)]<sub>2</sub> units are connected through a common oxygen atom from a polyanion, completing the construction of an infinite network. Here, it should be emphasized that, in **2**, three terminal oxygen atoms of each



**Fig. 6** Coordination environment of  $Ba^{2+}$  in **2**.

polyanion participate in coordination with  $Ba^{2+}$  ions, and their roles are all different.

In structure **2** (Fig. 5), the GeO<sub>4</sub> tetrahedron is almost regular. The Ge–O distances (1.731–1.739 Å) and O–Ge–O angles (109.29–109.74°) are in good agreement with values found in earlier investigations.<sup>21–23</sup> In the MoO<sub>6</sub> octahedra, the Mo–O<sub>4</sub>, Mo–O<sub>a</sub>, Mo–O<sub>b</sub>, Mo–O<sub>c</sub> bond distances fall in the ranges 1.682–1.699, 2.275–2.314, 1.822–1.869, and 2.009– 2.056 Å, and the mean values are 1.69, 2.3, 1.842, and 2.038 Å, respectively. All these values, except those for the Mo–O<sub>c</sub> bonds, are also in accord with the results of other investigations.<sup>21–23</sup> The mean value of the Mo–O<sub>c</sub> distances is 0.022 Å shorter than that reported in the literature,<sup>21</sup> corresponding to the decrease of the Mo–O<sub>c</sub> band in the IR spectrum of **2**. In conclusion, the MoO<sub>6</sub> octahedra become thinner and longer because of the influence of the outer coordination environment of the polyanion.

Comparing 2 with 1, the striking differences lie in that three terminal oxygen atoms of each polyanion participate in coordination with barium ions in 2, whereas only two terminal oxygen atoms do so in 1; two Ba<sup>2+</sup> ions are situated separately on the same side of each polyanion in 2, while they are located on opposite sides of the polyanion in 1. Obviously, these differences result in the formation of different structures, a twodimensional network for 2 and a one-dimensional chain for 1. It is these kinds of differences, as well as the interaction between the cationic groups and polyanions, that cause the subtle changes to the structure of the polyanions. First, the SiO<sub>4</sub> tetrahedron in 1 is distorted, while the GeO<sub>4</sub> tetrahedron in 2 is regular. Second, the Mo-O distance (1.654 Å) for the oxygen atom coordinated with a barium ion in 1 is shorter than the the other M-Ot distances, except for Mo1-O16, while the same bonds in 2, Mo6-O31C (1.699 Å) and Mo5-O12A (1.695 Å), are longer than the other M-Ot distances, except for Mo3-O6 (1.686 Å). The third difference is that the connection between the Ba<sup>2+</sup> ions relies on three bridging oxygen atoms in 2, but four in 1. The main analogies between 1 and 2 are that the Mo-O<sub>c</sub> distances are shortened in both to some extent; the chain and net structures of compounds 1 and 2 both have Mo-Ot-Ba links, which are also exhibited in [ET]8[PMnW11O39]·2H2O,  $[NEt_{3}H]_{5}[XCoW_{11}O_{39}]\cdot 3H_{2}O,$ [Co(dpa)<sub>2</sub>(OH)<sub>2</sub>]<sub>2</sub>[Hdpa][PCo- $W_{11}O_{39}$ ], [Cu(en)<sub>2</sub>(OH<sub>2</sub>)]<sub>2</sub>[H<sub>2</sub>en][{Cu(en)<sub>2</sub>}P<sub>2</sub>CuW<sub>17</sub>O<sub>61</sub>]·5H<sub>2</sub>O,  $[Cu(en)_2(OH_2)]_2[Cu(en)_2]_{0.5}[H_2en]_{0.5}[{Cu(en)_2}P_2CuW_{17}$ and O<sub>61</sub>)·5H<sub>2</sub>O, whose polyanions units are bridged by W-O<sub>t</sub>-M (M = Mn, Co, and Cu) sequences, forming chain-like structures.<sup>12-14</sup> However, it is noteworthy that, unlike these compounds in which the chains are solely linked through  $W-O_t-M$  (M = Mn, Co, and Cu) bonds, the links in compounds 1 and 2 include Mo-Ot-Ba and Ba-O-Ba sequences. The  $M'-O_t-M-O-M$  (M = Ba, M' = Mo) links in compounds 1 and

2 are very interesting: firstly because polyoxometalates as ligands are electron acceptors which, in some cases, can be reduced by one or more electrons, giving rise to mixed valency clusters. This enables the formation of hybrid materials in which delocalized electrons coexist in both the organic network and the inorganic clusters. Secondly, if magnetic atoms are introduced into the structures of compounds 1 and 2, it should be possible to produce novel solid-state materials in which delocalized electrons coexist with localized magnetic moments, thus affording the opportunity for the investigation of molecular systems combining magnetic and conducting properties. We are currently exploring these avenues. In this survey, the Ba–O distances found in both 1 and 2 are well within the ranges reported for comparable barium complexes, except for Ba1-O8 (3.042 Å) in 1, which is longer than observed previously.<sup>24,25</sup>

In addition, all the sulfur atoms in 1 and S6, S7, and S8 in 2 are all crystallgraphically disordered. The S-O distances for 1 and 2 lie in the ranges 1.335–1.584 and 1.408–1.606 Å, respectively. In the case of the bridging  $\mu$ -O coordination of DMSO, the S–O distances are within the range 1.50–1.56 Å.  $^{26\text{--}28}$  We observed in the crystal structures of 1 and 2 that there are not only some shortened, but also some elongated S-O distances relative to that in the free DMSO molecules (1.513 Å).<sup>29</sup> However, there is only one band at  $1024 \text{ cm}^{-1}$  in the IR spectra of 1 and 2. The differences in the bond lengths may be partially caused by the disorded S atoms, and other reasons, as pointed out by the literature: 30 because of the large uncertainties, these distances do not differ in a statistically significant sense. We observed that there is no direct contact between the polyanions and DMSO ligands, but they can interact through the barium ions.

In the IR spectra of 1 and 2, there are four characteristic asymmetric vibrations reslting from heteropolyanions with the Keggin structure, namely, v<sub>as</sub>(Mo=O<sub>t</sub>), v<sub>as</sub>(Mo-O<sub>b</sub>), v<sub>as</sub>(Mo-O<sub>c</sub>), and  $v_{as}(X-O_a)$  (X = Si, Ge). The peaks appear at 943, 865, 794, and 896 cm<sup>-1</sup>, respectively, for 1 and 946, 855, 777, and 900 cm<sup>-1</sup>, respectively, for 2. Comparing the IR spectra of compounds 1 and 2 with those of  $\alpha$ -H<sub>4</sub>SiMo<sub>12</sub>O<sub>40</sub> and  $\alpha$ -H<sub>4</sub>GeMo<sub>12</sub>O<sub>40</sub><sup>15</sup> the peak due to the Mo=O<sub>t</sub> bonds shifted from 957 to 943 cm<sup>-1</sup> for **1** and from 951 to 946 cm<sup>-1</sup> for **2**; the Mo–O<sub>c</sub> bond vibrations are shifted from 770 to 794  $\text{cm}^{-1}$  for 1 and from 760 to 777 cm<sup>-1</sup> for 2; the X–O<sub>a</sub> and Mo–O<sub>b</sub> bands appear at nearly identical frequencies to those found for  $\alpha$ -H<sub>4</sub>SiMo<sub>12</sub>O<sub>40</sub> and  $\alpha$ -H<sub>4</sub>GeMo<sub>12</sub>O<sub>40</sub>. These results indicate that the polyanions in the title compounds still retain the basic Keggin structure, but are distorted due to the effects of coordination. This is in agreement with the results of the singlecrystal X-ray diffraction analyses. In addition, the resonances at 1024 and 706cm<sup>-1</sup> in compounds **1** and **2** were assigned to the  $v_{as}$ (S=O) and  $v_{as}$ (C-S) asymmetric stretching vibrations of DMSO molecules. Comparing the IR spectra of 1 and 2 with that of free DMSO,<sup>29</sup>  $v_{as}$ (S=O) decreases by approximately 30 cm<sup>-1</sup>, from 1055 to 1024 cm<sup>-1</sup>, in both **1** and **2**. This result confirms that the DMSO as ligands are coordinated to the metal ions by means of their oxygen atoms.<sup>30</sup> The  $v_{as}(C-S)$ frequencies in both compounds rise slightly by approximately 8cm<sup>-1</sup>, from 698 to 706cm<sup>-1</sup>. This can be explained by the fact that the charge density over the oxygen and sulfur atoms is decreased due to the O atoms of the S=O bonds being coordinated to barium ions, leading to an increase in the electrondonating effect of the methyl groups. The IR spectra studies indicate that there is strong interaction between the polyanions and organic groups in solid state.

The UV spectra of compounds 1 and 2 measured in aqueous acetonitrile solution are both similar to those of a-H<sub>4</sub>Si- $Mo_{12}O_{40}$  and  $\alpha$ -H<sub>4</sub>GeMo<sub>12</sub>O<sub>40</sub> in the same solution. Only one absorption peak, appearing at 235 nm in the UV region was observed in the UV spectra of these compounds, which is assigned to the charge-transfer absorption band of the polyanion. This suggests that the compounds are entirely disruptive in dilute solution. This was observed in a previous paper too.<sup>10</sup>

## Conclusion

Two novel 1D and 2D polyoxometalate-based composite compounds have been synthesized and their structures elucidated by single-crystal X-ray diffraction. In their structures, the heteropolyanions are connected through Ba-O-Ba-O<sub>t</sub>-Mo links, resulting in the one-dimensional chain-like and twodimensional net-like arrangements.

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