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Controlled assembly of polyoxometalate-based composite materials containing zero- and one-dimensional structures

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Three polyoxometalate-based composite compounds containing zero-dimensional cross-like and one-dimensional chain-like structures, $[Gd(DMF)_6(H_2O)_2]_2\cdot[P_2W_{18}O_{62}]\cdot4DMF\cdot2H_2O$ (**1**), $[Ce(NMP)_3(H_2O)_5][Ce(NMP)_3(H_2O)_4][(P_2W_{18}O_{62})]\cdot4H_2O$ (**2**) and $[\{Gd(DMF)_6\}\{Gd(DMF)_7\}(P_2W_{18}O_{62})]\cdot0.5DMF$ (**3**), were constructed from octadecatungstodiphosphorate clusters interacting with $[RE(donor)]^{3+}$ [RE = Gd(III), Ce(III); donor = DMF (*N*,*N*-dimethylformamide), NMP (*N*-methyl-2-pyrrolidone)] groups. Single crystal X-ray structural analyses reveal that, for compound **1**, the interactions between the polyanions and the charge compensating cations are mainly hydrogen bonds, van der Waals forces and electrostatic forces; for compound **2**, two terminal oxygen (O_t) atoms located in "belt" sites of the polyanion are coordinated by RE cations, which generates an unprecedented zero-dimensional isolated structure; for compound **3**, the adjacent polyanions are polymerized to form a one-dimensional infinite linear chain by the bridging RE coordination cations and exhibit the type –ACACAC–. The apparent difference in the ESR spectra of the two compounds containing Gd(III) ions seems to be related to different coordination environments of the Gd(III) ions. Thermal analyses show that the frameworks of the polyanions decompose at 611, 615 and 602 °C in compounds **1**–**3**, respectively, and the stability of polyanions in compounds **1**–**3** is much stronger than that in the parent acid.

Introduction

The design and assembly of organic-inorganic solid-state materials with active physical properties, such as electrical, magnetic and optical properties, have become a focus of a great deal of interest in recent years.[1–13] Many studies have shown that such properties are associated with the structures constructed by so-called anion/cation salts or host/guest solids. Polyoxometalates with the general formula $[X_xM_mO_y]^{-q}$ (M = W, Mo, Nb, V, *etc.*; X = Si, P, B, Co, Fe, Cu, *etc.*) constitute a large fundamental class of inorganic compounds.[1,2] As inorganic building blocks, they can be assembled to form supramolecular composite materials through charge compensating cations[14,15] or organic π-electron donors, such as tetrathiofulvalene (TTF)[16–18] and bi(ethylenedithio)tetrathiofulvalene (ET).[19–23] An effective strategy in the realization of this assembly relies on linking polyanions through metal complex cations acting as inorganic bridging ligands.[24] In some cases, this strategy results in successful syntheses of composite materials containing lower dimensional structures.[14,15,24–28] However, systematic structural design of composite materials possessing unique structures and properties remains extremely challenging. In addition, most known structures are derived from Keggin,[25,26,29,30] Anderson[31–33] and Silverton type anions.[34] The polyoxometalates derived from the well-known Wells–Dawson type anions with lower dimensions are much less common; the only two notable examples include $[Cu(en)_2(OH_2)]_2[H_2en][\{Cu(en)_2\}P_2CuW_{17}O_{61}]\cdot5H_2O$ and $[Cu(en)_2(OH_2)]_2[Cu(en)_2]_{0.5}[H_2en]_{0.5}[\{Cu(en)_2\}P_2CuW_{17}O_{61}]\cdot5H_2O$,[35] which are based on substituted polyoxometalate anions and synthesized by hydrothermal methods.

Lanthanide complexes have attracted increasing interest due to the fascinating coordination geometry and interesting structures, in addition to their special properties.[36–40] In view of the high affinity of lanthanide ions for hard donor atoms and ligands containing only oxygen atoms or both oxygen and nitrogen atoms,[41] we attempted to make use of polyoxoanions as inorganic bridging ligands linking RE(III) coordination ions[42] in order to realize the molecular assemblies. Herein, we report the syntheses and single crystal structures of compounds **1**–**3**: $[Gd(DMF)_6(H_2O)_2]_2\cdot[P_2W_{18}O_{62}]\cdot4DMF\cdot2H_2O$ (**1**), $[Ce(NMP)_3(H_2O)_5][Ce(NMP)_3(H_2O)_4][(P_2W_{18}O_{62})]\cdot4H_2O$ (**2**) and $[\{Gd(DMF)_6\}\{Gd(DMF)_7\}(P_2W_{18}O_{62})]\cdot0.5DMF$ (**3**).

All three compounds belong to the general type (anion)M (donor) in different stoichiometries. The novelty of these materials lies in the fact that we have demonstrated, for the first time, an example in which the Wells–Dawson type polyoxometalates with 0-D or 1-D structures are formed by the use of rare earth metal cations. The main aims of this investigation were to study the structures of polyoxometalate-based composite materials and to report a new synthetic strategy, by which 0-D or 1-D infinite stacking assemblies between the polyanions and cationic units are achieved in aqueous solution.

Results and discussion

Syntheses

As for the charge-transfer polyoxometalates, the interactions between the polyanions and organic groups are mainly hydrogen bonds, van der Waals forces and electrostatic forces. In the present paper, the aim of introducing the RE(III) metal ions into charge-transfer polyoxometalates is to obtain more stable crystals. Based on this concept, compounds **1**–**3** were prepared by diverse methods. Compounds **1** and **3** were obtained from the same starting materials, employing different reaction temperatures: compound **1** was synthesized at 80 °C, while compound **3** was prepared at room temperature. For compound

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1, continuous heating results in the appearance of the insoluble product. For compounds **2** and **3**, the difference of synthetic methods lies in that compound **2** was fully isolated by offering excess organic donor to produce the amorphous product.

Crystals of compounds **1**–**3** are extremely sensitive to sunlight, which makes them promising as potential photosensitive materials. When exposed to sunlight, light yellow powders of compounds **1**–**3** turn deep blue instantly. We attribute this phenomenon to electron transfer between electron-rich organic molecules and electron-accepting polyoxometalate anions. The final result is that some heavy atoms with high oxidation states in the polyoxometalate anions are reduced and form mixed-valence compounds, leading to the observed photochromism.[43] Thus, exposure of the solution to sunlight should be avoided when growing crystals.

Structural description

Polyhedral crystals of compounds **1**–**3** were used for X-ray diffraction. For details of the X-ray single-crystal structural analyses, see the Experimental. Selected bond lengths and bond angles are listed in Tables 1–3.

Compound **1** contains one $[P_2W_{18}O_{62}]^{6-}$ and two $[Gd(DMF)_6(H_2O)_2]^{3+}$ subunits (Fig. 1). Like other polyoxometalate compounds derived from Wells–Dawson anions,[1,44] the charge compensation cations detach from the polyanions and interact with the anions by electrostatic forces of the general type {(anion)···M(donor)} (M = Gd; anion = $P_2W_{18}O_{62}{}^{6-}$; donor = DMF). The Gd^{3+} cation has an eight-coordinate distorted bicapped trigonal prismatic coordination. Three side planes are constituted by the O2A, O4A, O6A, O2W group, O3A, O4A, O6A, O1W group and O2A, O3A, O1W, O2W group. O5A and O1A occupy the two cap positions over two of the former side planes. The Gd^{3+} ion is nearly located in the center of the trigonal prism and its distance from the two bottom surfaces is 1.7081 and 1.5998 Å.

Compound **2** consists of one $[P_2W_{18}O_{62}]^{6-}$ and two $[Ce(1)(NMP)_3(H_2O)_5]^{3+}$, $[Ce(2)(NMP)_3(H_2O)_4]^{3+}$ subunits (Fig. 2). In comparison with compound **1**, the unusual feature lies in that the two RE(III) coordination ions covalently bond to two "belt" O_t atoms located on the opposite sides of the polyanion, thus forming two "arms" on the anion, and exhibiting a {(anion)M–donor} (M = Ce; anion = $P_2W_{18}O_{62}{}^{6-}$; donor = NMP) interaction. The shortest contact of the Ce^{3+} ion and the O_t atom from the adjacent polyanion is 4.261 Å and the interactions among them are mainly facilitated by hydrogen bonds, van der Waals forces and electrostatic forces. Two "belt"[45] terminal oxygen atoms of the anion, O5 and O13, as bridging atoms link the polyanion and Ce^{3+} coordination cations. The distances W(5)–O(5), 1.716(16) Å, and W(13)–O(13), 1.738(16) Å, are 0.021(16) and 0.043(16) Å longer than the mean value of W–O_t, 1.695(16) Å, respectively. The coordination polyhedron around Ce^{3+}(1) ion can be described as a bicapped square antiprism, in which the two groups of atoms O1W, O2W, O3W, O5W and O5, O4W, O2A, O3A, act as the top and bottom surfaces, respectively; their mean deviations are 0.0826 and 0.1737 Å, respectively. O1A occupies the cap position over the surface containing the O5, O4W, O2A, O3A group and the distance between them is 1.7197 Å. The coordination polyhedron around the Ce^{3+}(2) ion can be described as a square antiprism, in which the O13, O9W, O4A, O6A and O6W, O7W, O8W, O5 groups act as the two bottom planes; their mean deviations are 0.0707 and 0.0100 Å, respectively.

Table 1 Selected bond lengths (Å) and bond angles (°) for compound **1**

W(1)–O(1)	1.695(19)	W(2)–O(2)	1.68(2)
W(1)–O(23)	1.829(19)	W(2)–O(24)	1.87(2)
W(1)–O(27)	1.860(19)	W(2)–O(19)	1.888(18)
W(1)–O(14)	1.95(2)	W(2)–O(26)	1.91(2)
W(1)–O(21)	1.967(17)	W(2)–O(23)	1.940(18)
W(1)–O(28)	2.378(16)	W(2)–O(30)	2.345(15)
Gd(1)–O(3A)	2.38(3)	Gd(1)–O(6A)	2.30(3)
Gd(1)–O(4A’)	2.44(10)	Gd(1)–O(4A)	2.31(4)
Gd(1)–O(2W)	2.47(2)	Gd(1)–O(5A)	2.32(3)
Gd(1)–O(1A)	2.34(2)	Gd(1)–O(2A)	2.38(2)
Gd(1)–O(1W)	2.50(3)	O(6A)–Gd(1)–O(4A)	118.5(12)
O(6A)–Gd(1)–O(5A)	81.0(10)	O(4A)–Gd(1)–O(5A)	78.3(11)
O(6A)–Gd(1)–O(1A)	79.8(10)	O(4A)–Gd(1)–O(1A)	76.6(10)
O(5A)–Gd(1)–O(1A)	135.8(10)	O(6A)–Gd(1)–O(2A)	88.9(10)
O(4A)–Gd(1)–O(2A)	136.8(11)	O(5A)–Gd(1)–O(2A)	73.65(10)
O(1A)–Gd(1)–O(2A)	144.8(9)	O(6A)–Gd(1)–O(3A)	73.2(10)
O(4A)–Gd(1)–O(3A)	145.4(10)	O(5A)–Gd(1)–O(3A)	136.0(9)
O(1A)–Gd(1)–O(3A)	73.8(8)	O(2A)–Gd(1)–O(3A)	71.0(8)

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

W(5)–O(5)	1.716(16)	W(13)–O(13)	1.738(16)
W(5)–O(35)	1.853(15)	W(13)–O(45)	1.873(13)
W(5)–O(31)	1.877(13)	W(13)–O(48)	1.890(14)
W(5)–O(32)	1.908(15)	W(13)–O(44)	1.901(14)
W(5)–O(22)	1.962(15)	W(13)–O(38)	1.907(15)
W(5)–O(55)	2.330(14)	W(13)–O(61)	2.310(12)
Ce(1)–O(1W)	2.309(18)	Ce(1)–O(2W)	2.560(17)
Ce(1)–O(1A)	2.400(16)	Ce(1)–O(3W)	2.715(19)
Ce(1)–O(3A)	2.415(19)	Ce(2)–O(6A)	2.362(15)
Ce(1)–O(2A)	2.48(2)	Ce(2)–O(5A)	2.378(16)
Ce(1)–O(4W)	2.486(18)	Ce(2)–O(4A)	2.44(2)
Ce(1)–O(5W)	2.522(18)	Ce(2)–O(13)	2.467(16)
Ce(1)–O(5)	2.546(16)	Ce(2)–O(6W)	2.480(14)
Ce(2)–O(8W)	2.518(16)	Ce(2)–O(9W)	2.60(2)
Ce(2)–O(7W)	2.535(14)	W(5)–O(5)–Ce(1)	164.8(8)
W(13)–O(13)–Ce(2)	163.9(9)		

Table 3 Selected bond lengths (Å) and angles (°) for compound **3**[a]

W(6)–O(6)	1.721(7)	W(18)–O(18)	1.721(8)
W(6)–O(28)	1.887(8)	W(18)–O(50)	1.896(9)
W(6)–O(34)	1.890(9)	W(18)–O(51)	1.896(8)
W(6)–O(33)	1.922(7)	W(18)–O(53)	1.909(8)
W(6)–O(24)	1.923(9)	W(18)–O(54)	1.928(9)
W(6)–O(55)	2.347(7)	W(18)–O(62)	2.366(8)
Gd(1)–O(2A)	2.316(10)	Gd(1)–O(6A)	2.378(10)
Gd(1)–O(1A)	2.325(10)	Gd(1)–O(5A)	2.383(10)
Gd(1)–O(4A)	2.335(11)	Gd(1)–O(6)	2.500(7)
Gd(1)–O(3A)	2.353(10)	Gd(1)–O(4)#1	2.516(8)
Gd(2)–O(10A)	2.365(12)	Gd(2)–O(8A)	2.399(11)
Gd(2)–O(12A)	2.377(11)	Gd(2)–O(9A)	2.402(9)
Gd(2)–O(13A)	2.378(11)	Gd(2)–O(11A)	2.405(9)
Gd(2)–O(7A)	2.396(12)	Gd(2)–O(18)	2.456(9)
O(6)–Gd(1)–O(4)#1	129.4(3)	W(6)–O(6)–Gd(1)	171.6(4)
W(4)–O(4)–Gd(1)#2	161.8(5)	W(18)–O(18)–Gd(2)	154.9(5)

[a] Symmetry transformations used to generate equivalent atoms: #1 x, $-y+1/2$, $z+1/2$; #2 x, $-y+1/2$, $z-1/2$

Compound **3** consists of a novel 1-D infinite chain built from alternating polyanions and $[Gd(1)(DMF)_6]^{3+}$ subunits (Fig. 3) and it exhibits a $\{(anion)M\text{–}donor\}_n$ (M = Gd; anion = $P_2W_{18}O_{62}{}^{6-}$; donor = DMF) structure. This compound contains a third subunit, $[\{Gd(2)(DMF)_7\}]^{3+}$, in addition to the above-mentioned two subunits. It is interesting that the third subunit does not participate in the connection of the chain and only coordinates to a "cap"[45] O_t atom. The former two subunits alternately connect with each other in the 1-D chain, forming a linear –ACACAC– motif through M–μ-O_t–W linkages. The linking mode of –ACACAC– is distinct from that of the above-cited

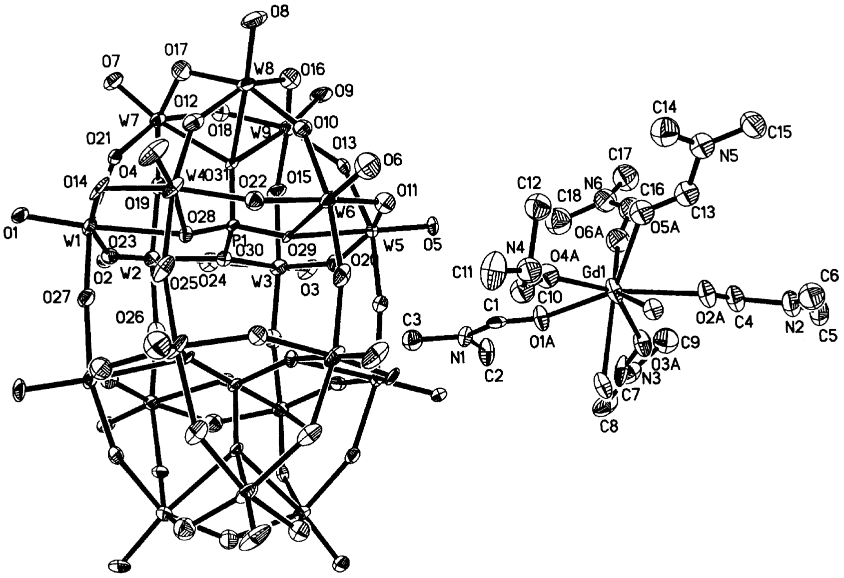


Fig. 1 Molecular structure of compound **1**. Solvent molecules and hydrogen atoms are omitted for clarity.

compound, $[\{Ba(DMSO)_5(H_2O)_2\}_2(SiMo_{12}O_{40})]$,[26] in which both Ba^{2+} ions are bonded to the polyanion through bridging O_t and participate in connection of the 1-D chain, and adjacent Ba^{2+} ions are bridged by the O atoms from DMSO and H_2O, thus forming a –ACCACC– type chain.

In compound **3**, the two coordination cations are located on the two hemispheres of one anion. Two terminal oxygen atoms, O6 and O18, form the bridges that link the polyanion and Gd^{3+} coordination cations. The distances W(6)–O(6), 1.721(7) Å, and W(18)–O(18), 1.721(8) Å, are 0.019(7) and 0.019(8) Å longer than the mean value of W–O_t, 1.701(8) Å, respectively. Both Gd^{3+} ions are eight-coordinate and their coordination environments are similar to those described in compound **1**. For Gd(1), the coordination polyhedron can be described as a bicapped trigonal prism, three side planes are made up of the O4, O2A, O5A, O6A, O1A, O2A, O4A, O6A and O4, O1A, O4A, O5A groups; O3A and O6 occupy the two cap positions over two of the former side planes. The separation of Gd^{3+} ion and the two bottom surfaces is 1.6822 and 1.4865 Å. For Gd(2), the coordination polyhedron can also be described as a bicapped trigonal prism; three side planes are constituted by the O7A, O10A, O12A, O13A, O18, O7A, O11A, O12A and O18, O10A, O11A, O13A groups; O8A and O9A occupy the two cap positions over the former two side planes. The separation of Gd^{3+} ion and the two bottom surfaces is 1.5826 and 1.5715 Å.

Comparing compound **3** with compound **2**, the major differences lie in two points: firstly, the isolated structural units exhibited in compound **3**, linked as {(anion)M–donor}, can be polymerized through the bridging O_t atoms to form a 1-D chain of the type $\{(anion)M\text{–}donor\}_n$; secondly, the O_t atoms coordinated by RE ions are both located in "belt" sites of the anion in compound **2** but in compound **3**, they are located in "cap" and "belt" sites.

Compounds **1**–**3** are derived from the $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$ anion. The $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$ anion is composed of two $[\alpha\text{-}PW_9O_{34}]^{3-}$

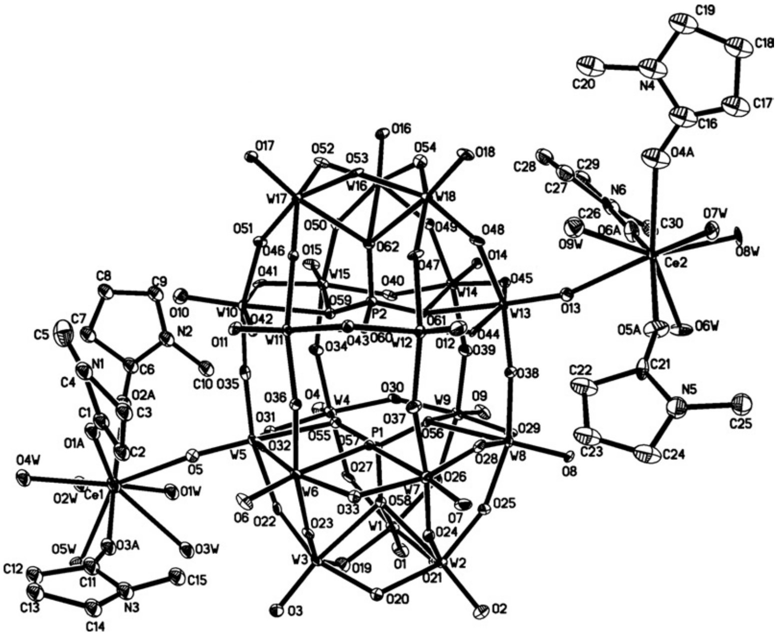


Fig. 2 Molecular structure of compound **2**. The solvent molecules (N7, C31, C32, C33, C34, C35 and O7A are all crystallographically disordered, their occupancies are one-half) and hydrogen atoms are omitted for clarity.

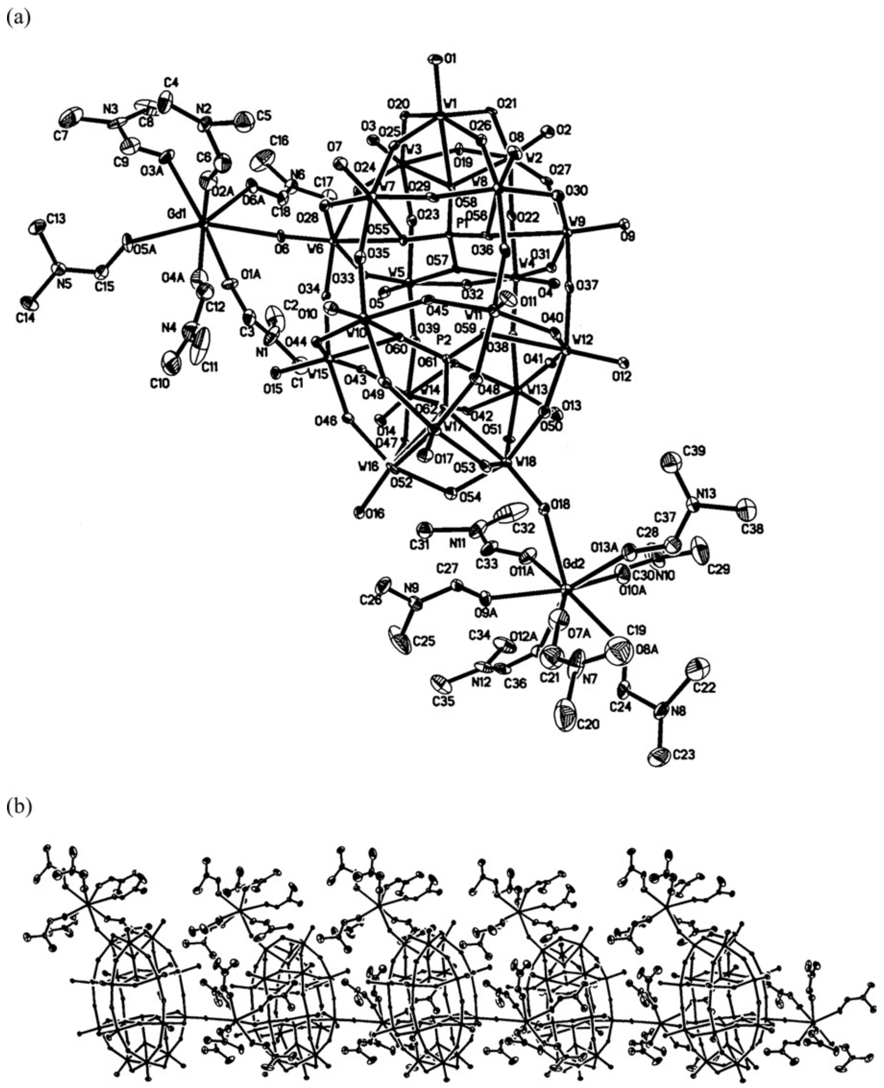


Fig. 3 (a) Molecular structural unit of compound **3**. The solvent molecules (N14, C40, C41, C42 and O14A are all crystallographically disordered, their occupancies are one-half) and hydrogen atoms are omitted for clarity. (b) View of the 1-D chain in compound **3**. The solvent molecules and hydrogen atoms are omitted for clarity.

units (each derived from the well-known $[\alpha\text{-PW}_{12}\text{O}_{40}]^{3-}$ anion by the removal of a set of three corner-sharing WO_6 octahedra), which are linked through corner-sharing with the elimination of six oxygen atoms.[46,47] The anion $[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ has D_{3h} point group symmetry and contains only two structurally distinct types of W atoms: six "cap" atoms on a vertical mirror plane, grouped into two sets of three, and twelve "belt" atoms that do not lie on a mirror plane, grouped into two sets of six.[45] For compounds **1**–**3**, W–O distances were 1.670(17)–1.71(3), 1.670(15)–1.738(16) and 1.683(8)–1.721(7) Å for terminal oxygen atoms, 1.83(2)–1.989(19), 1.843(16)–1.962(15) and 1.873(9)–1.966(9) Å for μ-bridging oxygen atoms, 2.345(15)–2.394(15), 2.310(12)–2.404(11) and 2.329(7)–2.406(7) Å for μ_3-bridging oxygen atoms, respectively. The structure determinations are in good agreement both with the Dawson[46] and d'Amour[47] structures of Wells–Dawson type anions. The RE–O bond distances lie in the ranges of 2.30(3)–2.50(3), 2.309(18)–2.715(19), and 2.316(10)–2.516(8) Å in compounds **1**–**3** and their mean distances are 2.38(4), 2.478(17) and 2.393(10) Å, respectively.

IR and UV spectra

In the IR spectra of compounds **1**–**3** (Table 4), there are four characteristic asymmetric vibrations resulting from heteropolyanions with the Wells–Dawson structure, namely, $\nu_{as}(\text{P–}\mu_3\text{-O}_a)$, $\nu_{as}(\text{W–O}_t)$ and $\nu_{as}(\text{W–}\mu\text{-O}_b)$[48] (the vibration band W–μ-O_b is split into two peaks); these peaks appear at 1090,

Table 4 IR spectra (cm^{-1}) of compounds **1**–**3** and related compounds

Compound	$\nu_{as}(\text{P–}\mu_3\text{-O}_a)$	$\nu_{as}(\text{W–O}_t)$	$\nu_{as}(\text{W–}\mu\text{-O}_b)$	$\nu(\text{C=O})$	$\nu(\text{C–H})$
1	1090	953	907, 779	1644	1378, 1491, 1244
2	1091	959	910, 786	1633	1508, 1114
3	1090	959	912, 785	1653	1406, 1507, 1260
$\alpha\text{-H}_6\text{P}_2\text{W}_{18}\text{O}_{62}\cdot n\text{H}_2\text{O}$	1090	961	913, 780		
DMF				1678	1386, 1255
NMP				1666	1506

953, 907 and 779 cm^{-1}, respectively, for compound **1**, at 1091, 959, 910 and 786 cm^{-1}, respectively, for compound **2**, and at 1090, 959, 912 and 785 cm^{-1}, respectively, for compound **3**. A series of characteristic bands of the DMF group appear at 1644, 1378, 1491, 1244 cm^{-1} in compound **1** and 1653, 1406, 1507, 1260 cm^{-1} in compound **3**, attributed to the vibrations of ν_{as}(C=O) and ν_{as}(C–N), and a series of characteristic bands for the NMP group appear at 1633, 1508 and 1114 cm^{-1} in compound **2**. Comparing the IR spectra of compounds **1** and **3** with that of free DMF,[49] the vibrational frequency of ν_{as}(C=O) decreases approximately 34 and 25 cm^{-1}, respectively. Comparing the IR spectra of compound **2** with that of free NMP,[50] the vibrational frequency of ν_{as}(C=O) decreases approximately 33 cm^{-1}. The characteristic bands of Gd–O were detected at 426 and 409 cm^{-1} in compounds **1** and **3**, respectively, which suggests that, due to the coordination of one or two polyanions, the vibration band of the Gd–O bond is red-shift 17 cm^{-1} (this is in agreement with the results of the single-crystal X-ray diffraction analyses). All the above results verify that the DMF or NMP molecules have been coordinated as ligands to metal ions through their oxygen atoms.

The UV spectra of compounds **1**–**3** measured in water are similar to that of α-$H_6P_2W_{18}O_{62}\cdot nH_2O$ (194, 250 and 310 nm), which suggests that the compounds are entirely disrupted in dilute solution. The first absorption band in each group is strong ($\varepsilon > 10^4$ L mol^{-1} cm^{-1}) and is assigned to the pπ–dπ charge-transfer absorption band of $O_t \rightarrow W$; the other two lower energy absorption bands can be regarded as characteristic absorption peaks of Wells–Dawson type polyanions;[51] they are assigned to the pπ–dπ charge-transfer absorption band of $O_b \rightarrow W$.

ESR spectra

The ESR spectra of Gd^{3+} ions doped into glasses and of Gd-sandwiched- and encapsulated-polyoxometalate complexes have been previously studied.[52–54] In the case of Gd^{3+} doped into glasses, the X-band ESR first-derivative spectra is characterized by three groups of lines with effective g values of ~6.0, 2.8, 2.0 and a wide absorption band for the magnetic field corresponding to $g < 2$ was described.[52] This type of spectrum has been labelled as a U-spectrum in view of its *ubiquity* in vitreous materials and polycrystalline materials, such as zeolites and ceramics.[55] In the case of Gd-sandwiched- and encapsulated-polyoxometalate complexes, the ESR spectra markedly differ from the U-spectrum characteristics for Gd(III) doped into glasses.[53,54]

These types of spectra are relatively complicated. For example, the ESR spectrum of $[Gd(P_2W_{17}O_{61})_2]^{17-}$ consists of 10 lines (with the following g values: 11.01, 8.05, 5.45, 3.78, 2.72, 2.49, 2.06, 1.95, 1.79 and 1.58).[54] In this paper, we selected two compounds containing Gd^{3+} ions to be examined in an ESR study, one was coordinated by water molecules and DMF molecules as exhibited by compound **1** [with a Gd(III) content of 5.28%], the other was coordinated by polyoxometalate and DMF molecules as exhibited by compound **3** [with a Gd(III) content of 5.55%]. Their spectra are shown in Fig. 4.

The spectrum of a polycrystalline sample of **1** (line a in Fig. 4) consists of five resonance absorption bands, with effective g values of 15.2, 5.79, 3.39, 2.35 and 1.97. A broad, featureless high-field tail with magnetic field corresponding to $g < 2$ was also discovered. An irradiated sample of **1** (line b) also consists of five resonance absorption bands with g values of 15.6, 5.79, 3.32, 2.44 and 1.97 and a broad, featureless high-field tail. A comparison of these ESR spectra shows that their effective g values and the numbers of resonance absorption bands are very similar. However, the intensity of the resonance absorption band with $g = 1.97$ the irradiated (ΔH_{pp} = 460 G) is much higher than that in the nonirradiated sample (ΔH_{pp} = 530 G). We attribute this signal to molybdenum(V) atoms, which come from the raw materials, behaving as selective "electron traps" under reducing conditions.[56,57] The resonance for this appears at $g \sim 1.94$ and overlaps the original signal of Gd^{3+} (g = 1.97, ΔH_{pp} = 530 G). This indicates that electron transfer phenomenon occurs between the organic substrates and the polyoxometalate anions under irradiation conditions. Unexpectedly, the signal of W^V did not appear, probably because the temperature is not low enough.

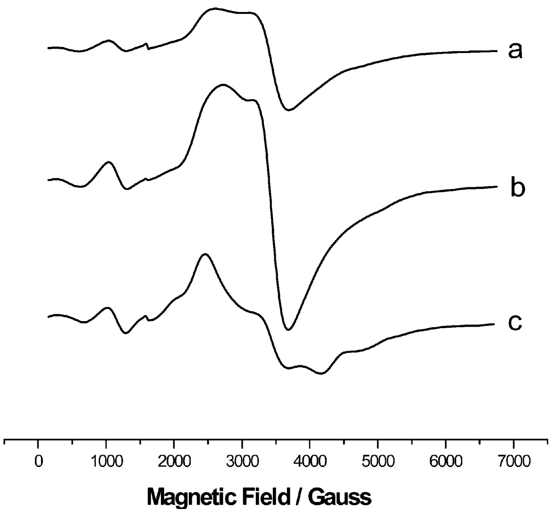


Fig. 4 The ESR spectra of compounds **1** and **3** at low temperature (110 K): (a) polycrystalline powder of compound **1**, (b) polycrystalline powder of compound **1**, which was irradiated for 15 min by a 300 W ac lamp, (c) polycrystalline powder of compound **3**. (All the signals with a g value ~4.2 in the three ESR spectra were assigned to the absorption band of the capillary glass tube.)

For compound **3** (line c in Fig. 4), the ESR spectrum consists of eight lines (with the following g values: 15.7, 5.86, 3.27, 2.41, 1.98, 1.69, 1.46 and 1.28). Compared with the ESR spectra of compound **1**, the striking difference lies in that there are three additional resonance bands that appear at high-field, corresponding to $g < 2$ for compound **3**. Previous studies show a relationship between the presence of particular g values of the spectral lines and the number of inner-sphere water molecules as well as the type of Gd(III) compound in the solid.[54] Single crystal X-ray structural analyses have revealed that, in compound **1**, the Gd^{3+} cation is coordinated by two water molecules and six DMF molecules, while in compound **3** the Gd(1) and Gd(2) coordination spheres have one or two polyanions in place of the water molecules. We therefore think that the changes in the resonance absorption bands for compounds **1** and **3** are caused by changes of the crystal field generated by the nearest surrounding ligands of the Gd^{3+} cation.

Furthermore, the ESR spectrum of compound **2**, which was irradiated for 15 min by a 300 W ac lamp, shows a intense and broad signal, which is assigned to $[P_2W_{18}O_{62}]^{6-}$ on the basis of its g value (g = 1.86, ΔH_{pp} = 187 G). A weak, broad signal with g = 1.95 (*ca.* ΔH_{pp} = 250 G) was assigned to the Ce^{3+} cation. The signal at g = 2.01 is assigned to the absorption band of the free radical ion.[57]

In addition, when left in the dark, the allochromatic compounds gradually came back to their starting color. This phenomenon reveals that the photochromic process is reversible. The photochromic mechanism in compounds **1**–**3** may be similar to that for the solvated polyoxometalate complex $H_3PMo_{12}O_{40}\cdot 6DMA\cdot CH_3CN\cdot 0.5H_2O$.[43] Weak intermolecular interactions between the DMA molecules and the polyoxoanions result in the photosensitive behavior of the compound. In compounds **1**–**3**, electron transfer between organic groups and polyoxometalate anions may be driven by both secondary Coulombic and induced-dipole effects.[43]

Thermal analyses

The results of the thermal analyses of compounds **1**–**3** are in good agreement with the structural determination and the variable temperature IR results. In compound **1**, the TG curve shows three weight loss steps , which suggests a multiple-stage decomposition process. Heating from about 25 to 110 °C leads to the loss (weight loss of *ca.* 5.5%) of 2 free water molecules and 4 free DMF molecules and an endothermal peak at 75 °C is observed in the DTA curve. This weak endothermal peak is caused by loss of the coordinated water molecules. From about 310 to 510 °C, the weight loss corresponds to the loss of 12 coordinated DMF molecules (weight loss of *ca.* 14.5%), a stronger exothermal peak appears at 423 °C in the DTA curve. An exothermal peak at 611 °C in the DTA curve corresponds to the decomposition of the polyanion backbone; this result is also verified by the variable-temperature IR analyses. The effect of temperature on the IR spectrum of compound **1** is shown in Fig. 5(a). The polyanion backbone breaks down in the range of 590 to 620 °C, which is determined by the disappearance of the M–O_b–M (M = Mo, W, V, *etc.*) bands.[58] In compound **2**, the TG/DTA curves show two stages with weight losses of 1.1% (4 hydration water molecules) at 65–154 °C and 14.1% (6 NMP and 9 coordination water molecules) at 154–520 °C. The DTA curve shows the polyanion backbone decomposes at 616 °C. In compound **3**, the TG/DTA curves show that the DMF molecules are lost in three stages with weight losses of 3.8% (3 DMF molecules) at 140–230 °C, 9.0% (7 DMF molecules) at 320–420 °C and 3.9% (3 DMF molecules) at 440–490 °C. An exothermal peak in the DTA curve shows that the polyanion decomposes at 602 °C. Comparing the decomposition temperature of α-$H_6P_2W_{18}O_{62}\cdot nH_2O$, whose decomposition temperature is 380 °C under the same conditions [the result was verified by the variable-temperature IR spectra in Fig. 5(b)]; apparently, the stability of the α-$P_2W_{18}O_{62}^{6-}$ anion in compounds **1**–**3** is much higher than that in the parent acid.

Conclusion

The successful isolation of solid materials **1**–**3** provides novel examples of the assembly of polyoxometalate clusters through $[RE(donor)]^{3+}$ groups for the design of composite materials. Relying on controlled reaction temperatures, compounds **1** and **3** were constructed with different linking models. These results verify the conclusion[14] that the dimensionality of solid architectures is, to some degree, controllable, while the key leading to success lies in the kinetic aspects of the assembly process. We plan to extend these concepts in several directions by replacing the RE(III) with alkali earth ions or transition metal ions.

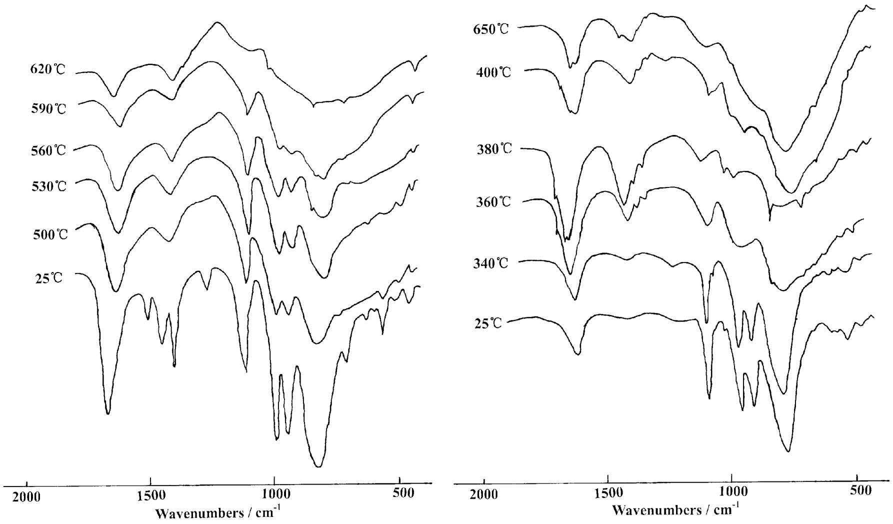
Experimental

General remarks

All organic solvents and materials used for the syntheses and recrystallization were of reagent grade and were used without further purification. α-$H_6P_2W_{18}O_{62}\cdot nH_2O$ was prepared according to the literature method and identified by IR and UV spectra.[59–60] C, H, N elemental analyses were performed on a Perkin–Elmer 240C elemental analyzer. IR spectra were recorded on a Nicolet 170 SXFT-IR spectrometer using KBr pellets in the 4000–400 cm^{-1} range. Electronic spectra were obtained on a Shimazu UV-250 spectrometer in the 500–200 nm range (in aqueous solution). Thermogravimetric analyses (TG/DTA) were performed under nitrogen gas on a Perkin–Elmer 7 thermogravimetric analyzer with a heating rate of 10 °C per min from room temperature to 700 °C. ESR spectra were recorded on a Bruker ER200-D-SRC spectrometer operating at the X-band (9.4 GHz).

Syntheses of the compounds 1–3

Crystals of compounds **1**–**3** were isolated as follows: for compound **1**, $Gd_2P_2W_{18}O_{62}$ (4.9 g, 1 mmol) was dissolved in 20 mL of the mixed solvent of acetonitrile and water in a ratio of 5:2 (V/V) and then DMF (1.5 mL) was added. The mixture was heated to continuous boiling until some colloidal precipitate appeared. After cooling to room temperature, the precipitate was collected and dissolved in the mixed solvent of acetonitrile and water. The resulting solution was filtered, left in a dark place and slowly evaporated at room temperature; light yellow crystals were obtained after several days. The yield based on W: 75%. Calcd for $C_{48}H_{124}O_{84}N_{16}Gd_2P_2W_{18}$: C, 9.68; H, 2.10; N, 3.76. Found: C, 9.61; H, 2.02; N, 3.54. For compound **2**, to 20 mL of a stirred solution of water and acetonitrile containing $Ce_2P_2W_{18}O_{62}$ (4.9 g, 1 mmol), NMP was added until no more amorphous precipitate formed; it was filtered, the amorphous precipitate was collected, redissolved in the mixed solvent, the mixture was set in a dark place and slowly evaporated at room temperature. Several days later, light yellow crystals were obtained. The yield based on W: 65%. Calcd



(a) (b)

Fig. 5 Temperature variation of the IR spectra of (a) compound **1** and (b) α-$H_6P_2W_{18}O_{62}\cdot nH_2O$.

for $C_{32}H_{80}O_{81}N_6Ce_2P_2W_{18}$: C, 6.58; H, 1.47; N, 1.54. Found: C, 6.82; H, 1.52; N, 1.60. For compound **3**, to 20 mL of a stirred solution of water and acetonitrile containing $Gd_2P_2W_{18}O_{62}$ (4.9 g, 1 mmol), DMF (1.2 mL) was added dropwise at room temperature; the mixture was stirred for 10 min, filtered, slowly evaporated at room temperature. Several days later, light yellow crystals were obtained. The yield based on W: 70%. Calcd for $C_{40.5}H_{94.5}O_{75.5}N_{13.5}Gd_2P_2W_{18}$: C, 8.59; H, 1.68; N, 3.34. Found: C, 8.81; H, 1.62; N, 3.44.

X-Ray crystallographic study

The intensity data of compounds **1**–**3** were collected on a Rigaku RAXIS-IV image plate area detector using graphite-monochromated Mo Kα ($\lambda = 0.7103$ Å) radiation at 293(2) K. The structures were solved by direct methods and refined by the full-matrix least-squares method on F^2. The intensity data were corrected for Lorentz and polarization effects as well as for absorption by an empirical method.[61] The non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed in calculated positions. All calculations were performed using the SHELX 97 programs.[62]†

$C_{48}H_{124}O_{84}N_{16}Gd_2P_2W_{18}$(**1**), $M_r = 5955.37$, monoclinic, $C2/c$, $a = 19.114(4)$, $b = 21.214(4)$, $c = 31.878(6)$ Å, $\beta = 94.56(3)°$, $D_c = 3.070$ g cm^{-3}, $U = 12\,885(4)$ Å^3, $Z = 4$, $T = 293(2)$ K, μ(Mo Kα) $= 17.133$ mm^{-1}, $R_{int} = 0.0591$, $R_1 = 0.0793$, $wR_2 = 0.1803$ for 8891 independent reflections with $[I > 2(\sigma)I]$.

$C_{30}H_{80}O_{81}N_6Ce_2P_2W_{18}$ (**2**), $M_r = 5472.48$, triclinic, $P\bar{1}$, $a = 14.137(3)$, $b = 14.661(3)$, $c = 26.806(5)$ Å, $\alpha = 80.63(3)°$, $\beta = 81.65(3)°$, $\gamma = 68.01(3)°$, $D_c = 3.590$ g cm^{-3}, $U = 5061.9(17)$ Å^3, $Z = 2$, $T = 293(2)$ K, $\mu = 21.374$ mm^{-1}, $R_{int} = 0.0000$, $R_1 = 0.0616$, $wR_2 = 0.1345$ for 13 955 independent reflections with $[I > 2(\sigma)I]$.

$C_{40.5}H_{94.5}O_{75.5}N_{13.5}Gd_2P_2W_{18}$ (**3**), $M_r = 5664.54$, monoclinic, $P2(1)/c$, $a = 19.229(4)$, $b = 23.776(5)$, $c = 24.237(5)$ Å, $\beta = 98.09(3)°$, $D_c = 3.430$ g cm^{-3}, $U = 10\,971(4)$ Å^3, $Z = 4$, $T = 293(2)$ K, $\mu = 20.107$ mm^{-1}, $R_{int} = 0.0000$, $R_1 = 0.0391$, $wR_2 = 0.0591$ for 15 824 independent reflections with $[I > 2(\sigma)I]$.

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† CCDC reference numbers 201223 (**1**), 201225 (**2**) and 201224 (**3**). See http://www.rsc.org/suppdata/nj/b4/b401769b/ for crystallographic data in .cif or other electronic format.

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