Inorg. Chem. **2006**, *45*, 2055–2060

Inorganic Chemistry
Article

New Polyoxometalate Compounds Built up of Lacunary Wells–Dawson Anions and Trivalent Lanthanide Cations

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Received September 15, 2005

Five new polyoxometalate compounds built on lacunary Wells–Dawson anions and trivalent lanthanide cations, $KNa_3[Nd_2(H_2O)_{10}(\alpha_2\text{-}P_2W_{17}O_{61})]\cdot 11H_2O$ (**1**), $(H_3O)[Nd_3(H_2O)_{17}(\alpha_2\text{-}P_2W_{17}O_{61})]\cdot 6.75H_2O$ (**2**), $(H_2bpy)_2[Nd_2(H_2O)_9(\alpha_2\text{-}P_2W_{17}O_{61})]\cdot 4.5H_2O$ (**3**), $(H_2bpy)_2[La_2(H_2O)_9(\alpha_2\text{-}P_2W_{17}O_{61})]\cdot 4.5H_2O$ (**4**), and $(H_2bpy)_2[Eu_2(H_2O)_9(\alpha_2\text{-}P_2W_{17}O_{61})]\cdot 5H_2O$ (**5**), have been synthesized and characterized by elemental analysis, IR, TG, and single-crystal X-ray diffraction. Compound **1** shows a bisupporting polyoxometalate cluster structure where two $\{Nd(H_2O)_7\}^{3+}$ fragments are supported on the polyoxometalate dimer $[\{Nd(H_2O)_3(\alpha_2\text{-}P_2W_{17}O_{61})\}_2]^{14-}$; this represents the first bisupporting polyoxometalate compound based on a polyoxometalate dimer. Compound **2** displays a 1D chain structure built up of bisupporting polyoxoanions $[\{Nd(H_2O)_7\}_2\{Nd(H_2O)_3(\alpha_2\text{-}P_2W_{17}O_{61})\}_2]^{8-}$ and Nd^{3+} ions. Compounds **3**–**5** are isostructural and show a 2D structure constructed of 1D polyoxometalate chains of $[Ln(H_2O)_2(\alpha_2\text{-}P_2W_{17}O_{61})]_n^{7n-}$ linked by Ln^{3+} ions. Compounds **2**–**5** represent the first extended structures formed by lacunary Wells–Dawson anions and trivalent lanthanide ions. The influence of the $Ln^{3+}/[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ ratio on the syntheses of these five compounds has been studied. Furthermore, the fluorescent activity of compound **5** is reported.

Introduction

Over the past decades, polyoxometalates have been attracting extensive interest in the field of solid-state materials chemistry because of the wide range of their topological properties and their great potential for application in catalysis, photochemistry, electrochromism, and magnetism.[1−3] The evolution of polyoxometalate chemistry is dependent upon the synthesis of new solids possessing unique structures and properties, although synthesis of the materials remains a challenge. One of the important advances in the design of new polyoxometalate compounds is the use of the coordination abilities of the polyoxometalates to produce polyoxoanion-supported metal complexes[4] and metal complexes bridged polyoxoanion extended structures.[5] To date, the two most studied polyoxometalate types have been the famous Keggin[6]

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10.1021/ic0515857 CCC: $33.50

and Wells−Dawson[7] families, which can be represented by $[XM_{12}O_{40}]^{n-}$ and $[X_2M_{18}O_{62}]^{n-}$ ($X = P^{V}$, Si^{IV}; $M = W^{V,VI}$, $Mo^{V,VI}$, $V^{IV,V}$), respectively. The mono- and trivacant Keggin and Wells−Dawson polyoxoanions are easily obtained by the removal of one and three metal centers, respectively.[8] Recently, much attention has been focused on developing lanthanide (Ln) cations incorporating the lacunary Keggin polyoxoanion for structural reasons, as well as for their properties, in which the Ln^{3+} ions are used as linkers in the self-assembled structure. Extended polymeric structures were obtained from Ln complexes and the lacunary $SiW_{11}O_{39}{}^{4-}$ ions in 2000 by Pope and co-workers,[9] and three years later, several $\{Ln_n(SiW_{11}O_{39})\}$ polyoxoanions with one-dimensional chain or two-dimensional layer structures were also reported by Vivien et al.[10] In addition, trivacant Keggin anions have been linked by Ln^{3+} ions to form a series of interesting large clusters,[11] such as $[K\{Eu(H_2O)_2(\alpha\text{-}AsW_9O_{33})\}_6]^{35-}$,[11a] and $[Ln_{16}As_{12}W_{148}O_{524}(H_2O)_{36}]^{76-}$.[11b] In contrast, the lacunary Wells−Dawson polyoxometalates linked by Ln^{3+} ions have been rarely explored. So far, the only examples for Ln^{3+} ion-bridged monovacant Wells−Dawson polyoxometalates are the 1:1-type dimers, $[\{Ce(\alpha_1\text{-}P_2W_{17}O_{61})(H_2O)_4\}_2]^{14-}$ [12] and $[\{Eu(H_2O)_3(\alpha_2\text{-}P_2W_{17}O_{61})\}_2]^{14-}$,[13] as well as 1:2-type dimers, $[Lu(\alpha_2\text{-}P_2W_{17}O_{61})_2]^{17-}$.[14] In the case of trivacant Wells−Dawson polyoxometalates, the first example of a lanthanide ion-linked trivacant Wells−Dawson cluster, $[\{Yb_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_6(H_2O)_6\}(\alpha\text{-}P_2W_{15}O_{56})_2]^{14-}$, was reported very recently by Hill's group.[15] As a continuation of the synthesis of various new polyoxometalate compounds,[16] we are trying to construct new lacunary Wells−Dawson polyoxometalates linked by Ln^{3+} ions. Herein, we report five novel polyoxometalate compounds formed by lacunary Wells−Dawson anions $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ and Ln^{3+} ions: $KNa_3[Nd_2(H_2O)_{10}(\alpha_2\text{-}P_2W_{17}O_{61})]\cdot 11H_2O$ (**1**), $(H_3O)[Nd_3(H_2O)_{17}(\alpha_2\text{-}P_2W_{17}O_{61})]\cdot 6.75H_2O$ (**2**), $(H_2bpy)_2[Nd_2(H_2O)_9(\alpha_2\text{-}P_2W_{17}O_{61})]\cdot 4.5H_2O$ (**3**), $(H_2bpy)_2[La_2(H_2O)_9(\alpha_2\text{-}P_2W_{17}O_{61})]\cdot 4.5H_2O$ (**4**), and $(H_2bpy)_2[Eu_2(H_2O)_9(\alpha_2\text{-}P_2W_{17}O_{61})]\cdot 5H_2O$ (**5**). Compound **1** shows a bisupporting polyoxometalate cluster structure where two $\{Nd(H_2O)_7\}^{3+}$ fragments are supported on the polyoxometalate dimer, $[\{Nd(H_2O)_3(\alpha_2\text{-}P_2W_{17}O_{61})\}_2]^{14-}$; this represents the first bisupporting polyoxometalate compound based on a polyoxometalate dimer. Compound **2** displays a 1D chain structure built up of bisupporting $[\{Nd(H_2O)_7\}_2\{Nd(H_2O)_3(\alpha_2\text{-}P_2W_{17}O_{61})\}_2]^{8-}$ polyoxoanions and Nd^{3+} ions. Compounds **3**−**5** are isostructural and show a 2D structure constructed of 1D polyoxometalate $[Ln(H_2O)_2(\alpha_2\text{-}P_2W_{17}O_{61})]_n{}^{7n-}$ chains linked by Ln^{3+} ions. Compounds **2**−**5** represent the first extended structures formed by lacunary Wells−Dawson anions and trivalent lanthanide ions.

Experimental Section

General Considerations. Reagents were purchased commercially and used without further purification. $K_6[\alpha\text{-}P_2W_{18}O_{62}]\cdot 19H_2O$ was synthesized according to the literature[8] and characterized by IR spectrum and TG analysis. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer. W, P, Nd, La, Eu, K, and Na were determined by a Leeman inductively coupled plasma (ICP) spectrometer. The infrared spectra were obtained on an Alpha Centaurt FT/IR spectrometer with a pressed KBr pellet in the 4000−400 cm^{-1} regions. TG analyses were performed on a Perkin-Elmer TGA7 instrument in flowing N_2 with a heating rate of 10 °C min^{-1}. The photoluminescence spectrum was measured using a FL-2T2 instrument (SPEX) with a 150 W xenon lamp monochromatized by a double grating (1200).

Synthesis of $KNa_3[Nd_2(H_2O)_{10}(\alpha_2\text{-}P_2W_{17}O_{61})]\cdot 11H_2O$ (1). A solution of $K_6[\alpha\text{-}P_2W_{18}O_{62}]\cdot 19H_2O$ (0.592 g, 0.12 mmol) and $LiClO_4\cdot 3H_2O$ (0.96 g, 6 mmol) in water (20 mL) was heated at approximately 80 °C, and the solution pH was adjusted to 6.2 by the addition of Na_2CO_3 (0.005 g, 0.05 mmol) in water (1 mL). Then 10 mL of a water solution of $NdCl_3\cdot 6H_2O$ (0.258 g, 0.72 mmol) was added. The resulting cloudy solution was warmed to approximately 80 °C and stirred for 30 min, then filtered. The filtrate was kept for 2 days at ambient conditions, after which time pale-pink block crystals of **1** were isolated in about a 50% yield (based on W). The ICP analysis showed that compound **1** contained 64.5% W, 6.3% Nd, 1.5% P, 1.1% K, and 1.5% Na (calcd W, 63.3; Nd, 5.8; P, 1.3; K, 0.8; Na, 1.4). IR (KBr pellet, cm^{-1}): 3392(m), 1086(s), 943(s), 781(s), 709(s), 525(m).

Synthesis of $(H_3O)[Nd_3(H_2O)_{17}(\alpha_2\text{-}P_2W_{17}O_{61})]\cdot 6.75H_2O$ (2). A solution of $K_6[\alpha\text{-}P_2W_{18}O_{62}]\cdot 19H_2O$ (0.592 g, 0.12 mmol) and $LiClO_4\cdot 3H_2O$ (0.96 g, 6 mmol) in water (20 mL) was heated at approximately 80 °C, and the solution pH was adjusted to 6.2 by the addition of Na_2CO_3 (0.005 g, 0.05 mmol) in water (1 mL). Then 10 mL of a water solution of $NdCl_3\cdot 6H_2O$ (0.387 g, 1.08 mmol) was added. The resulting cloudy solution was warmed to approximately 80 °C and stirred for 30 min; then it was filtered. The filtrate was kept for 2 days under ambient conditions, after which time pale-pink block crystals of **2** were isolated in about a 60% yield (based on W). The ICP analysis showed that compound **2** contained 62.7% W, 9.1% Nd, and 1.4% P (calcd W, 62.0; Nd,

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Table 1. Crystal Data and Structure Refinements for **1**−**5**

	1	**2**	**3**	**4**	**5**
	$H_{42}KNa_3Nd_2O_{82}P_2W_{17}$	$H_{50.50}Nd_3O_{85.75}P_2W_{17}$	$C_{20}H_{47}N_4Nd_2O_{74.50}P_2W_{17}$	$C_{20}H_{47}La_2N_4O_{74.50}P_2W_{17}$	$C_{20}H_{48}Eu_2N_4O_{75}P_2W_{17}$
fw	4938.28	5043.01	5011.49	5000.83	5035.93
T (K)	293(2)	293(2)	293(2)	293(2)	293(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
cryst syst	monoclinic	triclinic	triclinic	triclinic	triclinic
space group	$P2(1)/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	17.3456(15)	14.297(3)	12.904(3)	12.970(3)	12.875(3)
b (Å)	23.918(2)	17.167(3)	12.951(3)	13.015(3)	12.914(3)
c (Å)	19.3417(17)	19.490(4)	25.514(5)	25.484(5)	25.503(5)
α (deg)	90	82.95(3)	88.24(3)	88.25(3)	88.24(3)
β (deg)	100.419(2)	74.68(3)	76.11(3)	76.11(3)	76.29(3)
γ (deg)	90	78.40(3)	64.66(3)	64.29(3)	64.97(3)
V (Å^3)	7892.0(12)	4507.3(16)	3728.4(13)	3749.1(13)	3721.1(13)
Z	4	2	2	2	2
D_c (g/cm^3)	4.156	3.716	4.464	4.430	4.495
μ (mm^{-1})	26.179	23.426	27.636	27.238	27.981
F(000)	8632	4409	4398	4386	4420
θ range (deg)	1.37−26.00	3.03−25.00	3.01−25.00	3.13−25.00	3.00−25.00
GOF on F^2	1.043	1.041	1.039	1.033	1.028
R1[a] [$I > 2\sigma(I)$]	0.0514	0.0735	0.0457	0.0500	0.0452
wR2[a] [$I > 2\sigma(I)$]	0.1466	0.1848	0.0892	0.1103	0.0862
R1[a] (all data)	0.0916	0.0917	0.0611	0.0656	0.0621
wR2[a] (all data)	0.1615	0.1988	0.0950	0.1173	0.0921

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$.

8.6; P, 1.2). IR (KBr pellet, cm^{-1}): 3369(m), 1087(m), 945(s), 787(s), 708(s), 523(m).

Synthesis of $(H_2bpy)_2[Nd_2(H_2O)_9(\alpha_2\text{-}P_2W_{17}O_{61})]\cdot 4.5H_2O$ (3). $K_6[\alpha\text{-}P_2W_{18}O_{62}]\cdot 19H_2O$ (0.592 g, 0.12 mmol) was dissolved in 20 mL of water. The solution pH was adjusted to 6.2 by the addition of Na_2CO_3 (0.005 g, 0.05 mmol) in water (1 mL). Then $NdCl_3\cdot 6H_2O$ (0.129 g, 0.24 mmol) and 4, 4′-bpy (0.05 g, 0.32 mmol) were added. The resulting cloudy solution was stirred for 20 min in air; then it was transferred to a Teflon-lined autoclave and held at 130 °C for 5 days. After the mixture was slowly cooled to room temperature, pale-pink crystals were filtered off, washed with distilled water, and dried in a desiccator at room temperature to give a yield of 40% based on W. The ICP analysis showed that compound **3** contained 63.0% W, 6.2% Nd, and 1.4% P (calcd W, 62.4; Nd, 5.8; P, 1.2). The elemental analysis found C, 5.1; H, 1.1; and N, 1.3 (calcd C, 4.8; H, 1.0; N, 1.1). IR (KBr pellet, cm^{-1}): 3406(m), 1489(m), 1365(w), 1236(w), 1209(w), 1086(m), 957(m), 918(m), 772(s), 692(m), 527(m).

Synthesis of $(H_2bpy)_2[La_2(H_2O)_9(\alpha_2\text{-}P_2W_{17}O_{61})]\cdot 4.5H_2O$ (4). Compound **4** was prepared following the procedure described for compound **3**, but $LaCl_3\cdot 7H_2O$ was used instead of $NdCl_3\cdot 6H_2O$. Yield: 45% (based on W). The ICP analysis showed that compound **4** contained 63.1% W, 6.0% La, and 1.4% P (calcd W, 62.5; La, 5.6; P, 1.2). The elemental analysis found C, 5.2; H, 1.1; and N, 1.3 (calcd C, 4.8; H, 1.0; N, 1.1). IR (KBr pellet, cm^{-1}): 3400(m), 1490(m), 1366(w), 1236(w), 1209(w), 1086(m), 947(m), 920(m), 771(s), 692(m), 527(m).

Synthesis of $(H_2bpy)_2[Eu_2(H_2O)_9(\alpha_2\text{-}P_2W_{17}O_{61})] \cdot 5H_2O$ (5). Compound **5** was prepared following the procedure described for compound **3**, but $EuCl_3\cdot 6H_2O$ was used instead of $NdCl_3\cdot 6H_2O$. Yield: 40% (based on W). The ICP analysis showed that compound **5** contained 62.7% W, 6.5% Eu, and 1.4% P (calcd W, 62.1; Eu, 6.0; P, 1.2). The elemental analysis found C, 5.2; H, 1.1; and N, 1.2 (calcd C, 4.8; H, 1.0; N, 1.1). IR (KBr pellet, cm^{-1}): 3400(m), 1490(m), 1366(w), 1238(w), 1209(w), 1086(m), 957(m), 918(m), 791(s), 692(m), 527(m).

X-ray Crystallography. Crystal structure determination by X-ray diffraction for compound **1** was performed on a Siemens SMART-CCD diffractometer with graphite-monochromated Mo Kα (λ = 0.71073Å) radiation at room temperature. Crystal structure determinations by X-ray diffraction for compounds **2**−**4** were performed on a R-axis RAPID IP diffractometer equipped with a normal focus, 18 kW sealed-tube X-ray source (Mo Kα radiation, λ = 0.71073 Å) at room temperature. The structures were solved by direct methods and refined using full-matrix least squares on F^2. All calculations were performed using the SHELX97 program package. Empirical absorption corrections were applied. In compound **1**, the hydrogen atoms attached to the water molecules were not located. In compound **2**, except for those attached to O4W, O1W, OW1, OW2, OW3, OW4, OW5, and OW6, the positions of the hydrogen atoms attached to the water molecules were not located. The O17W and O18W were refined with occupancy factors of 50%. In compounds **3** and **4**, the hydrogen atoms attached to nitrogen and carbon atoms were fixed in ideal positions, and the other hydrogen atoms were not located. In compound **5**, the hydrogen atoms attached to nitrogen and carbon atoms were fixed in ideal positions, while the hydrogen atoms attached to the water molecules were not located except for those attached to OW1 and OW2. A summary of the crystallographic data and structural determination for compounds **1**−**5** is provided in Table 1.

Results and Discussion

Preparation of Compounds. Compounds **1**−**5** were obtained by the reactions between the $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ anions and the Ln^{3+} cations. The $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ used in the syntheses of compounds **1**−**5** were all freshly prepared by adjustment of the pH of the solution of $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$ to 6.2 through the addition of Na_2CO_3. Compounds **1** and **2** were both synthesized from the solution reaction of $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$, $LiClO_4$, and $NdCl_3$ at 80 °C. The $Nd^{3+}/[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ ratio is a phase-determining factor in these syntheses. When the $Nd^{3+}/[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ ratio was lower than 6:1, no crystals were obtained. At a higher $Nd^{3+}/[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ ratio (6:1), compound **1** was obtained. When the $Nd^{3+}/[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ ratio was higher than 9:1, com-

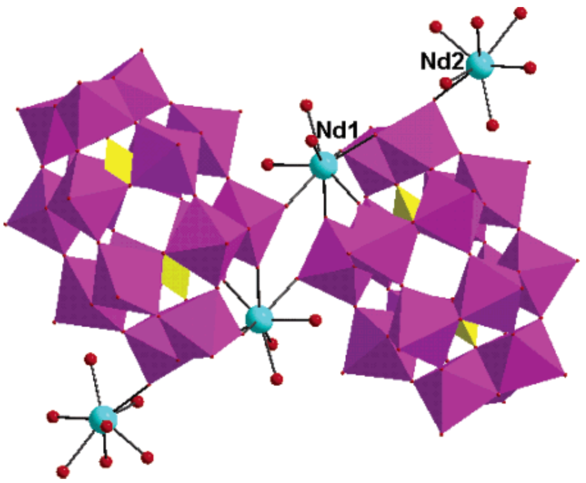

Figure 1. Polyhedral representation of the bisupporting $[\{Nd(H_2O)_8\}_2\text{-}\{Nd(H_2O)_3\ (\alpha_2\text{-}P_2W_{17}O_{61})\}_2]^{8-}$ anion in **1**. The PO_4 and WO_6 polyhedra are shown in yellow and purple, respectively. The Nd atoms are shown as a blue ball, and its terminal water molecule is shown as a red ball.

pound **2** was obtained as a single phase. In addition, $LiClO_4$ is necessary for the syntheses of compounds **1** and **2**, even though it is not incorporated in the final structure. Compounds **3**−**5** were separated from the hydrothermal reaction of $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$, $LnCl_3$, 4, 4′-bpy, and water at 130 °C for 5 days. The $Ln^{3+}/[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ ratio is also important for the syntheses of compounds **3**−**5**. Only when the $Ln^{3+}/[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ ratio is higher than 2:1 can compounds **3**−**5** be obtained.

Crystal Structures of Compounds. The structures of **1**−**5** are all built on monovacant Wells−Dawson polyoxoanions $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ and trivalent lanthanide ions. The polyoxoanion $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ derives from the parent anion $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$ by removal of a polar $W{=}O_d$ group. The parent anion $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$ may be described as two $[\alpha\text{-}PW_9O_{31}]^{3-}$ units, generated from the well-known $[\alpha\text{-}PW_{12}O_{40}]^{3-}$ by removal of a set of three corner-sharing WO_6 octahedra and fused into a cluster of virtual D_{3h} symmetry. The parent anion contains only two structurally distinct types of W atoms: six polar W atoms on vertical mirror planes grouped in two sets of three and twelve equatorial W atoms that do not lie on mirror planes grouped in two sets of six. In compounds **1**−**5**, the W−O bond distances are in the range of 1.666(12)−2.410(9) Å (av 1.949(10) Å for **1**, 1.949(15) Å for **2**, 1.950(10) Å for **3**, 1.951(11) Å for **4**, and 1.948(10) Å for **5**), and the O−W−O bond angles are within 70.6(4)−175.8(4)° (av 104.29(4)° for **1**, 104.31(7)° for **2**, 104.32(4)° for **3**, 104.29(5)° for **4**, and 104.23(4)° for **5**). The P−O distances vary between 1.501(11) and 1.597(11) Å (av 1.548(10) Å for **1**, 1.545(14) Å for **2**, 1.534(11) Å for **3**, 1.534(10) Å for **4**, and 1.541(10) Å for **5**).

Single-crystal X-ray structural analysis reveals that the crystal of **1** contains a bisupporting $[\{Nd(H_2O)_7\}_2\{Nd(H_2O)_3(\alpha_2\text{-}P_2W_{17}O_{61})\}_2]^{8-}$ polyoxoanion, one potassium cation, three sodium cations, and eleven lattice water molecules. As shown in Figure 1, the novel polyoxoanion $[\{Nd(H_2O)_7\}_2\{Nd(H_2O)_3(\alpha_2\text{-}P_2W_{17}O_{61})\}_2]^{8-}$ consists of a dimeric $[\{Nd(H_2O)_3(\alpha_2\text{-}P_2W_{17}O_{61})\}_2]^{14-}$ cluster and two $\{Nd(H_2O)_7\}^{3+}$ fragments. The centrosymmetric $[\{Nd(H_2O)_3(\alpha_2\text{-}P_2W_{17}O_{61})\}_2]^{14-}$ dimer is made of two $[P_2W_{17}Nd(1)O_{62}]^{9-}$ subunits connected through two common terminal oxygen atoms, which is similar to the $[\{Eu(H_2O)_3(\alpha_2\text{-}P_2W_{17}O_{61})\}_2]^{14-}$ dimer.[13] Each Nd1 cation has a coordination number of eight and is in the center of a distorted Archimedean antiprism formed by the four oxygen atoms that surround the vacant site of the lacunary anion, three water oxygen atoms, and a terminal oxygen of the second polyoxoanion with Nd−O distances in the range of 2.365(9)−2.526(14) Å. The dimeric $[\{Nd(H_2O)_3(\alpha_2\text{-}P_2W_{17}O_{61})\}_2]^{14-}$ cluster acts as a bidentate ligand and is coordinated to two $\{Nd(2)(H_2O)_7\}^{3+}$ fragments through two terminal oxygen atoms of two polar tungsten atoms adjacent to the two Nd1 cations in the two $[P_2W_{17}Nd(1)O_{62}]^{9-}$ subunits. Each Nd2 cation is coordinated by seven oxygen atoms from seven water molecules with Nd−O distances of 2.35(2)−2.730(11) Å and one oxygen atom from the dimeric $[\{Nd(H_2O)_3(\alpha_2\text{-}P_2W_{17}O_{61})\}_2]^{14-}$ cluster with an Nd−O distance of 2.434(10) Å to finish its distorted square-antiprismatic coordination environment. In addition, there are one K^+ and three Na^+ ions distributed around the bisupporting $[\{Nd(H_2O)_7\}_2\{Nd(H_2O)_3(\alpha_2\text{-}P_2W_{17}O_{61})\}_2]^{8-}$ cluster in **1**, which are coordinated to the bridging and terminal oxygen atoms of the $[\{Nd(H_2O)_7\}_2\{Nd(H_2O)_3(\alpha_2\text{-}P_2W_{17}O_{61})\}_2]^{8-}$ cluster, as well as to the lattice water molecules.

In the field of modified polyoxometalates, some interesting polyoxometalate-supported rare earth or transition metal compounds have been reported in the past decade, such as the monosupporting compound $[Ni(2,2'\text{-bipy})_3]_{1.5}[PW_{12}O_{40}\text{-}Ni(2,2'\text{-bipy})_2(H_2O)]\cdot 0.5H_2O$,[4a] the bisupporting compound $[NH_4]_2[\{Gd(DMF)_7\}_2(\beta\text{-}Mo_8O_{26})][\beta\text{-}Mo_8O_{26}]$,[4b] and the tetrasupporting compound $\{PW_9V_3O_{40}[Ag(2,2'\text{-bipy})]_2[Ag_2\text{-}(2,2'\text{-bpy})_3]_2\}$.[4c] However, the polyoxometalates in these compounds are only restricted to discrete polyoxoanion clusters. To our knowledge, compound **1** represents the first polyoxometalate-supported metal compound based on a polyoxometalate dimer.

The structure of **2** is formed by a bisupporting $[\{Nd(H_2O)_7\}_2\{Nd(H_2O)_3(\alpha_2\text{-}P_2W_{17}O_{61})\}_2]^{8-}$ anion linked by Nd^{3+} ions to yield a polymer chain running parallel to the *c* axis (Figure 2). The structure of the bisupporting $[\{Nd(H_2O)_7\}_2\{Nd(H_2O)_3(\alpha_2\text{-}P_2W_{17}O_{61})\}_2]^{8-}$ anion in **2** is similar to that in **1**. In this bisupporting polyoxoanion, each Nd1 atom resides in the center of a distorted Archimedean antiprism which is defined by eight oxygen atoms with an average Nd1−O bond length of 2.453(10) Å, and each Nd2 atom is in the center of a distorted square antiprism which is defined by eight oxygen atoms with an average Nd2−O bond length of 2.494(4) Å. In the polymer chain, each bisupporting $[\{Nd(H_2O)_7\}_2\{Nd(H_2O)_3(\alpha_2\text{-}P_2W_{17}O_{61})\}_2]^{8-}$ anion acts as a tetradentate ligand coordinating four Nd3 cations via four terminal oxygen atoms of tungsten. The Nd3 atom has a coordination number of nine and resides in the center of a distorted tricapped trigonal prism. The coordination oxygen atoms around the Nd3 atom can be divided into two classes according to different sources: the first one contains two terminal oxygen atoms of tungsten with an average Nd3−O bond length of 2.469(15) Å, and the other contains seven

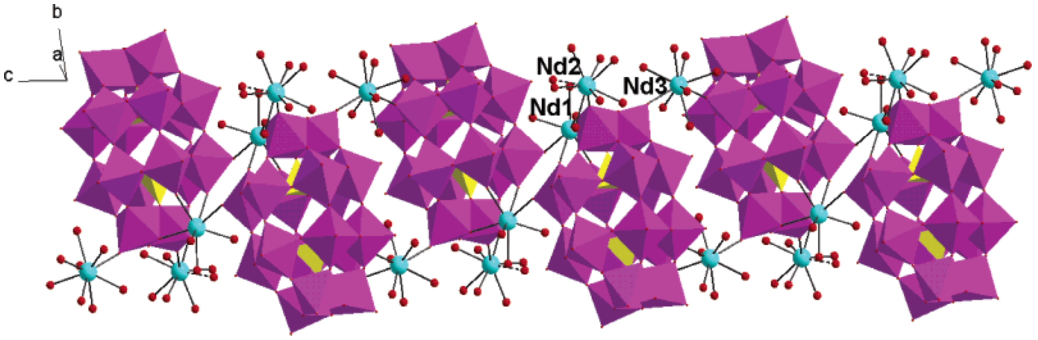

Figure 2. Polyhedral view of the 1D chain in **2**. The color code is the same as in Figure 1.

water oxygen atoms with a Nd3−O bond length in the range of 2.46(2)−2.54(2) Å. The connecting pattern in the polymer chain of **2** is different from that in the previously reported polymer chains formed by monovacant Keggin polyoxoanions and Ln^{3+} ions.[9,10] In all of the reported polymer chains formed by lacunary Keggin anions and Ln^{3+} ions, the lacunary Keggin anions are linked together only by the Ln^{3+} ions coordinated to the vacant sites. However, in the polymer chain of **2**, the lacunary Wells−Dawson anions are linked alternately by the Nd^{3+} ions coordinated to the vacant sites and discrete Nd^{3+} ion linkers. The negative charge retained in the structure of **2** is compensated by the protonation of a lattice water molecule.

The structure of **3** shows a 2D layer constructed of lacunary Wells−Dawson anions $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ linked by Nd^{3+} ions. In **3**, there are two crystallographically distinct Nd atoms: Nd1 and Nd2. The Nd1 atoms locate in the vacancies of the $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ anions and connect the adjacent $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ anions into a 1D chain (Figure 3a). The 1D $[Nd(H_2O)_2(\alpha_2\text{-}P_2W_{17}O_{61})]_n^{7n-}$ chain formed is similar to the 1D chain in the $Na_{0.5}Cs_{4.5}[Eu(\alpha\text{-}SiW_{11}O_{39})(H_2O)_2]\cdot 23H_2O$ compound.[10] Each Nd1 atom has a distorted Archimedean antiprism coordination environment, which is defined by the four oxygen atoms that surround the vacant site of the lacunary anion, two water oxygen atoms, and two terminal oxygen atoms from the adjacent two polyoxoanions with Nd−O distances in the range of 2.388(11)−2.569(12) Å. The Nd2 atoms are located between the 1D $[Nd(H_2O)_2(\alpha_2\text{-}P_2W_{17}O_{61})]_n^{7n-}$ chains and further link the adjacent chains into a 2D layer (Figure 3b). Each Nd2 atom displays a tricapped trigonal prism coordination geometry, which is defined by seven water oxygen atoms and two terminal oxygen atoms from the adjacent two polyoxoanions with Nd−O distances in the range of 2.403(11)−2.764(12) Å. The interlayer separation is approximately 6.284 Å, which is occupied by the free 4,4′-H_2bpy^{2+} cations and lattice water molecules. To date, $K_{0.5}Nd_{0.5}[Nd_2(\alpha\text{-}SiW_{11}O_{39})_2(H_2O)_{11}]\cdot 17H_2O$[10] is the only compound among the reported compounds formed by lacunary Keggin anions and Ln^{3+} ions that shows a 2D layer structure.[10] The 2D layer in $K_{0.5}Nd_{0.5}[Nd_2(\alpha\text{-}SiW_{11}O_{39})_2(H_2O)_{11}]\cdot 17H_2O$ is built on $[Nd_2(\alpha\text{-}SiW_{11}O_{39})_2(H_2O)_8]^{10-}$ dimers linked by Nd^{3+} ions, which is different from that in **3**.

FT-IR Spectroscopy. The IR spectrum of compound **1** shows a broad band at 3392 cm^{-1} associated with the aqua ligands; the compound also possesses a band at 1086 cm^{-1} attributed to ν(P−O) and characteristic bands at 943, 781, 709, and 525 cm^{-1} attributed to ν(W═O) and ν(W−O−W). The IR spectrum of compound **2** exhibits a broad band at 3369 cm^{-1} associated with the aqua ligands; the compound also possesses a band at 1087 cm^{-1} assigned to ν(P−O) and characteristic bands at 945, 787, 709, and 523 cm^{-1} assigned to ν(W═O) and ν(W−O−W). The IR spectra of compounds **3**−**5** show broad bands at 3406 (**3**), 3400 (**4**), and 3400 cm^{-1} (**5**) associated with the aqua ligands and a series of bands in the 1209−1490 cm^{-1} region associated with the 4,4′-bipyridine. The compounds also possess bands at 1086 cm^{-1} attributed to ν(P−O) and characteristic bands at 957, 918, 772, 692, and 527 (**3**); 947, 920, 771, 692, and 527 (**4**); and 957, 918, 791, 692, and 527 (**5**) attributed to ν(W═O) and ν(W−O−W) (Figures S1−S5).

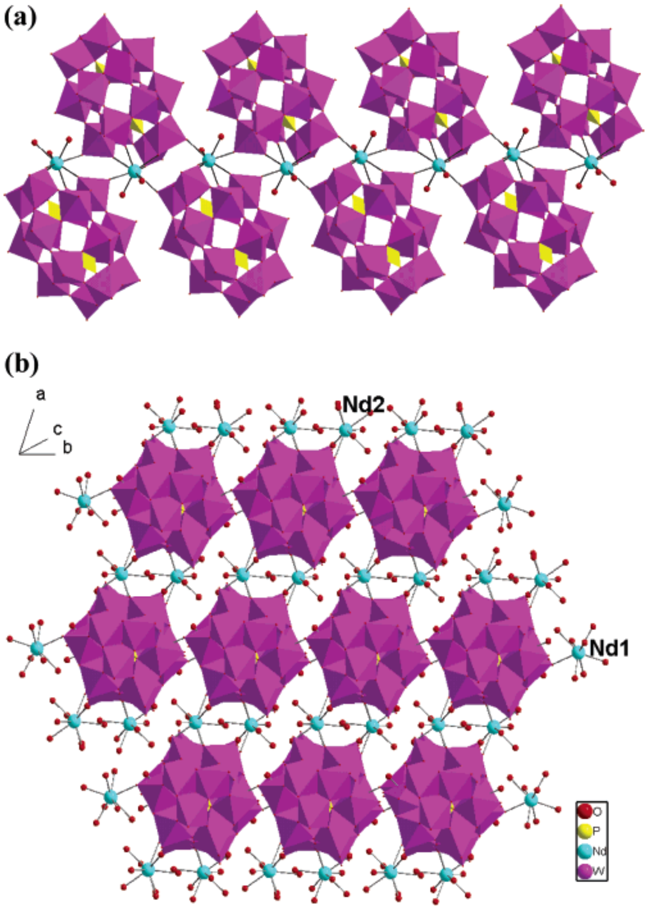

Figure 3. (a) Polyhedral view of the 1D chain in **3**. (b) View of the 2D layer in **3**. The color code is the same as in Figure 1.

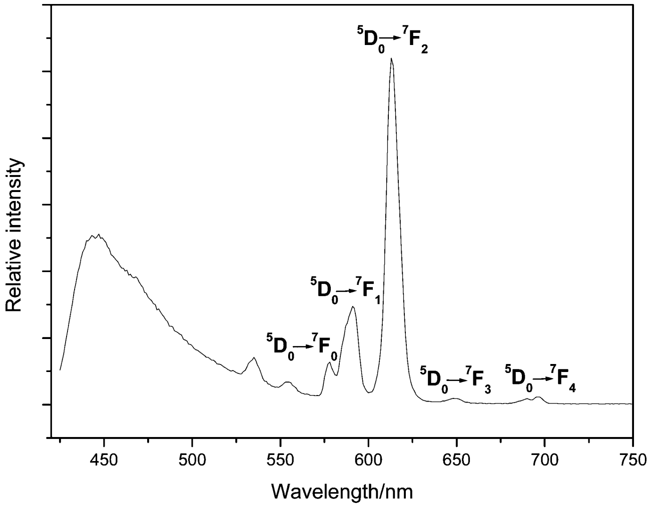

Figure 4. Luminescence spectrum of solid **5**.

TG Analyses. The thermal gravimetric (TG) curve of compound **1** exhibits two continuous weight loss stages in the range of 35−350 °C (Figure S6), corresponding to the release of all lattice and coordinated water molecules. The whole weight loss (8.1%) is in agreement with the calculated value (7.7%).

The TG curve of **2** is shown in Figure S7. It shows three continuous weight loss stages in the range of 35−390 °C, corresponding to the release of all water molecules. The total weight loss of 9.1% agrees with the calculated value of 8.9%.

The TG curve of **3** shows a total weight loss of 11.3% in the range of 50−310 °C, which agrees with the calculated value of 11.0% (Figure S8). The weight loss of 1.7% at 50−115 °C corresponds to the loss of lattice water molecules (calcd 1.6%). The weight loss of 9.6% at 120−310 °C comes from the loss of coordinated water and 4,4′-bpy molecules (calcd 9.4%).

The TG curve of **4** exhibits two continuous weight loss stages in the range of 50−315 °C (Figure S9), corresponding to the release of all water and 4,4′-bpy molecules. The whole weight loss (11.5%) is in agreement with the calculated value (11.0%).

The TG curve of **5** is shown in Figure S10. It shows four continuous weight loss stages in the range of 55−360 °C, corresponding to the release of all water and 4,4′-bpy molecules. The total weight loss of 11.7% agrees with the calculated value of 11.2%.

Photoluminescence Properties. We have measured the photoluminescence spectrum of powder samples of compound **5** at room temperature. As shown in Figure 4, the photoluminescence spectrum of compound **5** possesses two emission groups in the range of 425−560 and 572−700 nm ($\lambda_{ex} = 398$ nm), which are attributed to the H_2bpy^{2+} cation and Eu^{3+} ion, respectively. The photoluminescence spectrum of **5** exhibits the characteristic transition of the Eu^{3+} ion. The peaks at 578, 591, 613, 648, and 696 nm are attributed to the $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$, and $^5D_0 \rightarrow {}^7F_4$ transitions, respectively. It is well-known that the $^5D_0 \rightarrow {}^7F_0$ transition is strictly forbidden by symmetry. As the $^5D_0 \rightarrow {}^7F_0$ transition is observed, the spectrum reveals that Eu^{3+} in **5** occupy sites with low symmetry and without an inversion center. The $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions, magnetic and electric dipole transitions, respectively, are clearly observed in the photoluminescence spectrum of **5**. The intensity of the $^5D_0 \rightarrow {}^7F_2$ transition is extremely sensitive to chemical bonds in the vicinity of Eu^{3+}; it increases as the site symmetry of Eu^{3+} center decreases. On the other hand, the intensity of the $^5D_0 \rightarrow {}^7F_1$ transition depends only slightly on the nature of the environment of the Eu^{3+} center. Therefore, the $I(^5D_0 \rightarrow {}^7F_2)/I(^5D_0 \rightarrow {}^7F_1)$ ratio is widely used as a measure of the coordination state and site symmetry of the rare earth.[18] For compound **5**, the intensity ratio $I(^5D_0 \rightarrow {}^7F_2)/I(^5D_0 \rightarrow {}^7F_1)$ is equal to ca. 3.5, which also indicates the low site symmetry of the Eu^{3+} ion in **5**.

Conclusions

In this paper, we reported five new polyoxometalate compounds constructed of lacunary Wells−Dawson anions and trivalent lanthanide ions. Compound **1** possesses a bisupporting polyoxometalate cluster structure, which represents the first bisupporting polyoxometalate compound based on a polyoxometalate dimer. Compounds **2**−**5** show interesting 1D chain and 2D layer structures, which represent the first extended structures formed by lacunary Wells−Dawson anions and Ln^{3+} ions. The extended polymeric structures in compounds **2**−**5** display some different structural features compared with those formed by lacunary Keggin anion and Ln^{3+} ions. This phenomenon shows that the differences in the size and the number of inequivalent W atoms between the lacunary Keggin and Wells−Dawson anions may influence their Ln^{3+} ion-linked structure. In addition, compounds **3**−**5** were obtained from a hydrothermal reaction, which is different from that for all compounds formed by lacunary Keggin anions and Ln^{3+} ions (obtained from solution reactions). The syntheses of compounds **3**−**5** show that hydrothermal techniques offer a complementary method for the synthesis of new polyoxometalate compounds formed by lacuanry polyoxoanions and trivalent lanthanide ions.

Acknowledgment. The authors thank the National Natural Science Foundation of China (20171011) for financial support.

Supporting Information Available: X-ray crystallographic files in CIF format for compounds **1**−**5** and additional figures and tables. This material is available free of charge via the Internet at http://pubs.acs.org. Structures are available from the Cambridge Crystallographic Data Centre (CSD reference numbers 391340 for **1** and 391341 for **2** and CCDC reference numbers 282972 for **3**, 282973 for **4**, and 282974 for **5**).

IC0515857