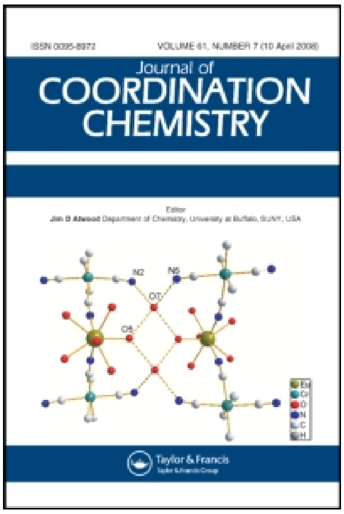

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Effect of ionic radii of lanthanide ions on reaction with A-$PW_9O_{34}^{9-}$. Synthesis and characterization of $[(A\text{-}PW_9O_{34})_2(H_2OM)_3CO_3]^{11-}$ (M = Eu^{3+}, Gd^{3+}) and $[(W_5O_{18})_2M]^{9-}$ (M = Pr^{3+}, Nd^{3+})

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The reaction of A-$PW_9O_{34}^{9-}$ with carbonate solution of lanthanide ions produces different products under the same conditions. The sandwich-type complexes of $[(A\text{-}PW_9O_{34})_2(H_2OM)_3CO_3]^{11-}$ are the main products of the reaction of A-$PW_9O_{34}^{9-}$ with Eu^{3+} and Gd^{3+} while, with Pr^{3+} and Nd^{3+} products are decatungstometalate complexes $[(W_5O_{18})_2M]^{9-}$. The products have been isolated and characterized by elemental analysis, infrared, ^{31}P NMR spectroscopy, thermogravimetric analysis (TGA), and single crystal structure analysis. The structures of the first complexes consist of two trivacant polyoxometalates A-$PW_9O_{34}^{9-}$ which are linked by a $(MOH_2)_3CO_3$ belt. The ν_3 vibrational band of CO_3^{2-} at 1471–1485 cm^{-1} and a break in the TGA curves at 425°C confirm the presence of coordinated CO_3^{2-} in the structures. The single crystal structure analysis was carried out on $K_6Na_2(H_3O)[(W_5O_{18})_2Pr] \cdot 18H_2O$ ($H_{38}K_6Na_2O_{55}PrW_{10}$). The anion consists of two $[W_5O_{18}]^{6-}$ linked *via* Pr^{3+}. The Pr^{3+} is eight coordinate with overall anion symmetry close to D_{4d}.

Keywords: Polyoxometalates; Lanthanide ions; Sandwich-type complexes; Decatungstometalate complexes; Single crystal structure analysis

1. Introduction

Lanthanide-polyoxometalates (POMs) have structural variety and interesting properties in catalysis, magnetism, luminescence, and materials science [1–6]. Monovacant lacunary POMs derived from Keggin- and Dawson-type POMs are the major precursors, as pentadentate ligands, but structures indicate that the lanthanide ions are too big to fully coordinate. They usually sit above the lacunary hole coordinated to the four equatorial oxygens of the polyoxoanion. The coordination sphere is completed in solution by water, but these monomeric species have a tendency to oligomerize in the presence of acetate, oxalate, or DMSO to form 1-D chain, 2-D layer, and 3-D network [7–15]. The trivacant polyoxotungstates, $[XW_9O_{34}]^{n-}$ ($X = P^{5+}, Si^{4+}, As^{5+}$) have

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potential to support lanthanide clusters. $[XW_9O_{34}]^{n-}$ is derived from the Keggin structure and has six oxygens available for bonding in the Aα form and seven in the Bα form [16–23]. The B-$[XW_9O_{34}]^{n-}$ derivatives with transition metal ions are thermally stable and are suitable precursor for the preparation of inorganic–organic composite polyoxoanions [24, 25]. The A-$[XW_9O_{34}]^{n-}$ usually reacts with di- and trivalent ions to form 2 : 3 mole ratio sandwich type polyoxoanions [17, 26]. The first complex of trilacunary Keggin POM with lanthanides was reported by Knoth in 1986. This complex has a sandwich-type structure consisting of two A-$[PW_9O_{34}]^{9-}$ units connected by a belt of three lanthanides [17]. The belt contains three oxygens, alternating with three lanthanides [17]. In 2003, lanthanide complexes of $[(XW_9O_{34})_2Ln_3O_3(OH_2)_2\}]^{15-}$, where Ln = Ce^{3+}, La^{3+} and X = P^{5+}, As^{5+}, were reported [27] with a structure similar to the Ce^{4+} complex reported by Knoth and co-workers [17]. The lanthanide derivatives revealed the presence of two types of lanthanides, one six-coordinate lanthanide and the other two seven-coordinate lanthanides. Hill [28] synthesized the first examples of sandwich-type POMs that encapsulate CO_3^{2-} in the center of $[(A\text{-}PW_9O_{34})_2(H_2OY)_3CO_3]^{11-}$. We have synthesized the first lanthanide derivatives of this category, $[(A\text{-}AsW_9O_{34})_2(H_2OM)_3CO_3]^{11-}$ ($M = Y^{3+}, Sm^{3+}, Yb^{3+}$) [29] and $[(A\text{-}SiW_9O_{34})_2(H_2OM)_3CO_3]^{13-}$ ($M = Y^{3+}, Yb^{3+}$) [30], formed by reaction of A-α-$XW_9O_{34}^{9-}$ with M^{3+} in an aqueous Na_2CO_3 solution in modest yield and in high purity. Francesconi showed a variety of reactions of $[PW_9O_{34}]^{9-}$ with aqueous solutions of Eu^{3+}. The aqueous speciation is a function of pH, countercation, and stoichiometry [31].

The objective of this work is to examine the reaction products of $PW_9O_{34}^{9-}$ with Eu^{3+}, Gd^{3+}, Pr^{3+}, and Nd^{3+} in aqueous Na_2CO_3. Sandwich-type POMs of $[(A\text{-}PW_9O_{34})_2(H_2OM)_3CO_3]^{11-}$ ($M = Eu^{3+}$ and Gd^{3+}) and decatungstometalate complexes of $[(W_5O_{18})_2M]^{9-}$ ($M = Pr^{3+}$ and Nd^{3+}) were isolated and characterized by elemental analysis, infrared (IR) and ^{31}P NMR spectroscopy, thermogravimetric analysis (TGA), and single crystal structure analysis. The complexes of $[(W_5O_{18})_2M]^{9-}$ are related to the well-known decatungstometalate complexes first structurally characterized by Weakley and coworkers. The heteroatom achieves eight-coordination by attachment to two W_5O_{18} groups which may be viewed as lacunary derivatives of $W_6O_{19}^{2-}$ [32]. Although a complete set of lanthanide derivatives of $[W_5O_{18}]^{6-}$ have been synthesized and characterized, single crystal structure determination for trivalent lanthanides has not been performed [33].

2. Experimental

2.1. *Chemical and apparatus*

All reagents were commercially obtained and used without purification. $PrCl_3 \cdot 6H_2O$ and $EuCl_3 \cdot 6H_2O$ were purchased from Acros Company and $NdCl_3 \cdot 6H_2O$ and $GdCl_3 \cdot H_2O$ from Alfa Aesar. $Na_9H[A\text{-}a\text{-}PW_9O_{34}] \cdot xH_2O$ was prepared according to the literature [16]. IR spectra were recorded in KBr plates on a Thermo Nicolet FT-IR model Nexus-670 and NMR spectra were recorded on a BRX-500 AVANCE spectrometer. Resonance frequency is 121.5 MHz for ^{31}P and chemical shift is given with respect to phosphoric acid. TGA was carried out using a PL-1500 TGA apparatus. Electronic spectra were recorded on a Varian, CARY 1 E UV-Vis spectrophotometer.

ICP was used for elemental analysis of praseodymium, neodymium, europium, gadolinium, and tungsten, and flame photometry was used for elemental analysis of sodium and potassium. TGA was used for analysis of carbon and crystallization water. Strongly acidic (Dowex HCR-W2 H^+ form) and basic (Amberjet 4200 Cl^- form) resins packed into a column (20 cm length; 1 cm diameter) were used for ion exchange chromatography. For acidification, solutions of the complexes were eluted through the acidic form of the cationic resin column. For cation exchange, first 1 mol L^{-1} KOH was eluted through the acidic form of the cationic resin followed by distilled water and then solutions of the complexes. In order to exchange anions, solutions of the complexes were eluted through the anion exchange column. The eluants were collected and studied by IR spectroscopy after solvent evaporation.

2.2. *Preparation of complexes*

2.2.1. $K_{10}Na[(A\text{-}PW_9O_{34})_2(EuOH_2)_3CO_3] \cdot 28H_2O$ (1). A 0.59 g (1.6 mmol) of $EuCl_3 \cdot 6H_2O$ was dissolved in 20 mL distilled water and 2 mL of 1 mol L^{-1} Na_2CO_3 was slowly added to the solution with stirring. The slurry was heated to 80°C and then solid $Na_9H[A\text{-}\alpha\text{-}PW_9O_{34}] \cdot xH_2O$ (2.00 g, 1.0 mmol) was quickly added with vigorous stirring. The solution was maintained at 80°C for 30 min and then cooled to room temperature. Insoluble materials were removed by centrifugation. Solid KCl (3.0 g) was added and the solution was cooled in an ice water bath and then filtered. The crude product was recrystallized at least twice in hot water. Colorless crystals were obtained by slow evaporation. Yield: 0.56 g (27%). Anal. Calcd for $K_{10}Na[(A\text{-}PW_9O_{34})_2(EuOH_2)_3CO_3] \cdot 31H_2O$ (%): C, 0.20; Na, 0.38; K, 6.52; W, 55.20; Eu, 7.60; H_2O, 9.20. Found (%): C, 0.22; Na, 0.30; K, 6.48; W, 56.30; Eu, 7.79; H_2O, 9.15.

2.2.2. $K_8Na_3[(A\text{-}PW_9O_{34})_2(GdOH_2)_3CO_3] \cdot 22H_2O$ (2). The procedure for **1** was repeated, but using $GdCl_3 \cdot 6H_2O$ (0.59 g). Yield: 0.72 g (35%). Anal. Calcd for $K_8Na_3[(A\text{-}PW_9O_{34})_2(GdOH_2)_3CO_3] \cdot 25H_2O$ (%): C, 0.21; Na, 1.20; K, 5.45; W, 57.70; Gd, 8.03; H_2O, 7.84. Found (%): C, 0.20; Na, 1.15; K, 5.82; W, 57.30; Gd, 7.85; H_2O, 7.70.

2.2.3. $K_6Na_2(H_3O)[(W_5O_{18})_2Pr] \cdot 19H_2O$ (3). A 0.57 g (1.6 mmol) of $PrCl_3 \cdot 6H_2O$ was dissolved in 20 mL distilled water and 2 mL of 1 mol L^{-1} Na_2CO_3 was slowly added to the solution with stirring. The slurry was heated to 80°C and then solid $Na_9H[A\text{-}\alpha\text{-}PW_9O_{34}] \cdot xH_2O$ (2.00 g, 1.0 mmol) was quickly added with vigorous stirring. The solution was maintained at 80°C for 30 min and then cooled to room temperature. Insoluble materials were removed by centrifugation. Solid KCl (3.0 g) was added and the solution was cooled in an ice water bath and then filtered. The slight precipitation ($[A\text{-}\alpha\text{-}PW_9O_{34})^{9-}]$ salt) was discarded and the filtrate cooled to 5°C. Light green crystals obtained after two days were recrystallized at least twice in hot water. Yield: 0.25 g. Anal. Calcd for $K_6Na_2(H_3O)[(W_5O_{18})_2Pr] \cdot 19H_2O$ (%): Na, 1.44; K, 7.38; W, 57.85; Pr, 4.43; H_2O, 10.76. Found (%): Na, 1.50; K, 7.49; W, 58.60; Pr, 4.47; H_2O, 10.82.

2.2.4. $K_6Na_2(H_3O)[(W_5O_{18})_2Nd] \cdot 19H_2O$ (4). The procedure for **3** was repeated using $NdCl_3 \cdot 6H_2O$ (0.57 g, 1.6 mmol). Yield: 0.28 g. Anal. Calcd for $K_6Na_2(H_3O)$

Table 1. Crystal data collection and refinement parameters for **3**.

Empirical formula	$H_{38}K_6Na_2O_{55}PrW_{10}$
Formula weight	3178.29
Temperature (K)	100(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	*Cc*
Unit cell dimensions (Å, °)	
a	9.5010(9)
b	19.9553(18)
c	26.530(2)
β	93.030(2)
Volume (Å^3), *Z*	5022.9(8), 4
Calculated density (Mg m^{-3})	4.203
Absorption coefficient (mm^{-1})	24.388
F(000)	5652
Crystal size (mm^3)	$0.12 \times 0.10 \times 0.10$
θ range for data collection	2.04–28.00°
Index ranges	$-12 \leq h \leq 12$; $-26 \leq k \leq 26$; $-35 \leq l \leq 35$
Reflections collected	36406
Independent reflections	11952 [$R(\text{int}) = 0.0335$]
Completeness to $\theta = 28.00$ (%)	98.9
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.094 and 0.068
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	11,952/2/421
Goodness-of-fit on F^2	1.044
Final *R* indices [for 11698 reflections with $I > 2\sigma(I)$]	$R_1 = 0.0670$, $wR_2 = 0.1677$
R indices (all data)	$R_1 = 0.0678$, $wR_2 = 0.1682$
Largest difference peak and hole (e Å^{-3})	5.808 and −2.626

$[(W_5O_{18})_2Nd] \cdot 19H_2O$ (%): Na, 1.45; K, 7.38; W, 57.79; Nd, 4.53; H_2O, 10.75. Found (%): Na, 1.43; K, 7.23; W, 57.24; Nd, 4.46; H_2O, 10.70.

2.3. *X-ray structure determination*

Crystal data collection and refinement parameters for **3** are given in table 1. The data were collected at 100 K on a Bruker APEX 1000 CCD area detector single crystal diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Data collection, indexing, and initial cell refinements were all handled using APEX2 software [34]. The final cell parameters were determined by least-squares refinement on 11,698 reflections. The multi-scan method was used to carry out absorption corrections. The structure was solved by using direct methods and difference maps (SHELXTL, v. 6.12) [35]. All metals were refined anisotropically. Scattering factors and anomalous dispersion corrections were taken from the International Tables for X-ray Crystallography [36]. Structure solution, refinement, and generation of publication materials were performed by using SHELXTL, V. 6.12 [35]. Selected bond lengths and angles of **3** are given in table 2.

Table 2. Dimensions of $[(W_5O_{18})_2Pr]^{9-}$ and $[(W_5O_{18})_2M]^{8-}$ ($M = Ce^{4+}$, U^{4+}) anions for comparison.

	Bond length (Å)		
Bond type	$M^a = Ce^{4+}$	$M^a = U^{4+}$	$M^b = Pr^{3+}$
$W–O_d$	1.70–1.80	1.63–1.78	1.72–1.76
W–O(W)	1.86–2.05	1.78–2.03	1.88–2.04
W–O(M)	1.76–1.80	1.80–1.87	1.76–1.80
$W–O(W_4)$	2.24–2.39	2.24–2.42	2.24–2.39
M–O	2.38–2.40	2.29–2.32	2.43–2.56

[a]Ref. [33]; [b]Ref. [this work].

3. Results and discussion

3.1. *Syntheses*

In an aqueous Na_2CO_3 solution, A-α-$[PW_9O_{34}]^{9-}$ reacts with MCl_3 (M = Pr, Nd, Eu, and Gd) to form two different products. The reaction of A-α-$[PW_9O_{34}]^{9-}$ with Eu^{3+} and Gd^{3+} produce sandwich-type POMs of $[(A\text{-}[PW_9O_{34}])_2(MOH_2)_3CO_3]^{11-}$ in modest yields and high purity [28–30]. But, the reaction of A-α-$[PW_9O_{34}]^{9-}$ with Pr^{3+} and Nd^{3+} produce the decatungstometalate complexes of $[(W_5O_{18})_2M]^{9-}$. The A-α-$[PW_9O_{34}]^{9-}$ anion in alkaline solution decomposes producing $[W_5O_{18}]^{6-}$. The $[(W_5O_{18})_2M]^{9-}$ complexes have been synthesized by self-assembly of WO_4^{2-} and the lanthanide ions in alkaline solution (pH 7–9) previously [33]. Pr^{3+} and Nd^{3+} do not form sandwich-type POMs containing carbonate, perhaps due to their size. This is confirmed by the observation that carbonate-containing, sandwich-type POMs with Eu^{3+} and Gd^{3+} [this work] and in our pervious work with $[A\text{-}XW_9O_{34}]^{n-}$ ($X = As^{5+}, Si^{4+}$), Yb^{3+} and Sm^{3+} have been isolated, but not with La^{3+}, Ce^{+3}, Pr^{3+}, and Nd^{3+} [29, 30]. Although ionic radii variation is small from La^{3+} to Gd^{+3}, it affects properties and reactivity [37]. Formation of sandwich-type POMs containing carbonate decrease as the lanthanide ion size increases. Complexes **1** and **2** are stable in unbuffered H_2O, and in the pH range 5–10 for a long time. When **1** and **2** are passed through a strongly acidic ion exchange column and then dried, the product is $[P_2W_{21}O_{71}]^{6-}$, confirming an A-type sandwich POM structure for **1** and **2** [17]. Unlike MCl_3, when solutions of **1** and **2** are eluted through the cation exchange resin column (K^+ form) no retention of the complexes is observed. The IR spectrum of each individual eluant is the same as that of the parent complex. On the other hand, unlike MCl_3 behavior, when solutions of the complexes are loaded onto an anion exchange column (Cl^- form) the anionic complexes are retained [27]. These observations provide good evidence for the inner-sphere bonding of the M^{3+} cations to $[PW_9O_{34}]^{9-}$ anion.

3.2. *IR and NMR spectroscopy*

IR spectra of **1** and **2** are similar to that of A-$[PW_9O_{34}]^{9-}$. A shift of the stretching vibrations in the 1200–700 cm^{-1} range to higher frequencies is observed on comparing the spectra of the complexes with that of A-$[PW_9O_{34}]^{9-}$ (Supplementary material). This is consistent with a decrease of negative charge per A-$[PW_9O_{34}]^{9-}$ in the complexes. Characteristic bands assigned to asymmetric stretching vibrations of

P–O_a (1063 and 1010 cm^{-1}), characteristic ν_3 vibrational modes of PO_4 with splitting due to the loss of local symmetry as expected for the A-type trivacant Keggin unit [38], terminal W–O_d (950–900 cm^{-1}), and bridging W–O_c–W (710–790 cm^{-1}) are observed from 1200 to 700 cm^{-1} [23, 27]. W–O_b–W overlap with the broad W–O_c–W band (O_d is a terminal oxygen and O_b is a bridging oxygen between corner-sharing octahedra, and O_c is a bridging oxygen between edge-sharing octahedra) [38]. IR spectra of **1** and **2** show bands at 1491–1465 cm^{-1}, assigned to the doubly degenerate ν_3 vibrational mode of CO_3^{2-} with a splitting of 10 cm^{-1} [39] attributed to distortion of CO_3^{2-} [28, 29]. The other two IR active modes, ν_2 and ν_4, overlap with W–O stretching bands. The characteristic bands in the IR spectra of **3** and **4** are compared well with literature data [33]. Strong bands at 940–970 cm^{-1} have been attributed to W–O_d stretch. The (W–O–W) stretching bands, however, are clearly recognized in the 820–850 and 760–800 cm^{-1} regions of the IR spectra (Supplementary material). Peak at 28.56 ppm in the ^{31}P NMR spectrum of **1** is attributed to the two symmetry-equivalent P's in A-$[PW_9O_{34}]^{9-}$. By comparing with the values observed for other 3 : 2 sandwich complexes of A-$[PW_9O_{34}]^{9-}$ (−7.5 to −12.0 ppm), this peak is shifted due to the coordination of the paramagnetic Eu^{3+} [27, 31].

3.3. *Electronic spectra*

UV spectra of **1** and **2** show two absorptions. The lower energy band at 195 nm is attributed to charge transfer O_d–W, and the higher energy band at ~250 nm to (Oc/Ob)–W [32]. In both POM complexes these bands shift to lower frequencies compared with A-$[PW_9O_{34}]^{9-}$ due to the coordination of the lanthanide cations. The UV spectra of **3** and **4** show the characteristic band of decatungstometalate complexes $[(W_5O_{18})_2Ln]^{9-}$ at *ca* 255 nm [33].

3.4. *Thermogravimetric analysis*

TGA curves of **1** and **2** show two mass-loss regions below 500°C. The first, 30–300°C, with 9.15% and 7.70% weight loss, are assigned to lattice and coordinated water (bonded to M^{3+}) loss, equal to 31 (28 + 3) and 25 (22 + 3) molecules for **1** and **2**, respectively. The second region, 400–500°C, with approximately 0.81% and 0.73% weight loss for **1** and **2**, respectively, are assigned to loss of one CO_2 from decomposition of CO_3^{2-} (S1 Supplementary material). On the basis of TGA studies it can be thus concluded that **1** and **2** are thermally stable to 400°C.

3.5. *Structures*

Results of ion-exchange experiments and UV spectra provide good evidence for the bonding of Eu^{3+} and Gd^{3+} to $[PW_9O_{34}]^{9-}$ in **1** and **2** [40]. Formation of $[P_2W_{21}O_{71}]^{6-}$ under treatment with strongly acidic ion exchange also confirms the A-type sandwich POM structures for **1** and **2**. IR spectra and TGA suggest an A-type sandwich POM, isostructural with $[(A\text{-}PW_9O_{34})_2(YOH_2)_3CO_3]^{11-}$ [28] and $[(A\text{-}AsW_9O_{34})_2(MOH_2)_3CO_3]^{11-}$ ($M = Y^{3+}, Sm^{3+}, Yb^{3+}$) [29] for **1** and **2** (figure 1). The complexes consist of two lacunary A-α-$[PW_9O_{34}]^{9-}$ Keggin moieties linked by a $(MOH_2)_3CO_3$ belt

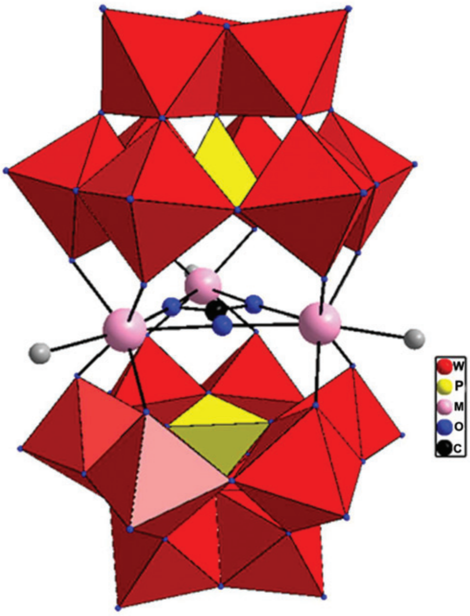

Figure 1. Proposed structures of **1** and **2**.

into an assembly of virtual D_{3h} symmetry. The CO_3^{2-} is encapsulated in the M^{3+} plane and ligated by its oxygens at the midpoints of the sides of the triangle formed by M^{3+} ions. The X-ray structure of **3** reveals that Pr^{3+} is sandwiched between two $W_5O_{18}^{6-}$ moieties into an assembly of virtual D_{4d} symmetry (figure 2). The W_5O_{18} group is derived from the hexatungstate, $W_6O_{19}^{2-}$, by removal of a W–O_d; this anion has four oxygens available for bonding. The Pr–O bond lengths vary from 2.43 to 2.56 Å, with average of 2.48 Å. Two types of Pr–O bonds can be distinguished by their lengths, as described previously [41]. There are four "long" Pr–O bonds and four "short" ones in **3**. The averages of long and short Pr–O bonds are 2.52 and 2.44 Å, respectively. As shown in figure 2, the trivalent lanthanide has a coordination number of eight and occupies a slightly distorted square anti-prismatic geometry. The four unsaturated oxygens from the same $[W_5O_{18}]^{6-}$ are in a plane (O (9), O (10), O (11), O (12) in plane I, and O (13), O (14), O (15), O (16) in plane II), but the two planes are not exactly parallel, forming an angle of 2.47°. The angle of the square faces is 48.59° instead of 45°. Dimensions of $[(W_5O_{18})_2Pr]^{9-}$ and $[(W_5O_{18})_2M]^{8-}$ ($M = Ce^{4+}$, U^{4+}) are given for comparison in table 2. As expected due to the metal charge, the Pr–O and W–O(Pr) bond lengths are longer and shorter than M^{4+}–O and W–O(M^{4+}), respectively.

4. Conclusion

Reactions of A-$[PW_9O_{34}]^{9-}$ with carbonate solution of Eu^{3+}, Gd^{3+}, Pr^{3+}, and Nd^{3+} produce different products. The sandwich-type complexes of [(A-$[PW_9O_{34})_2$

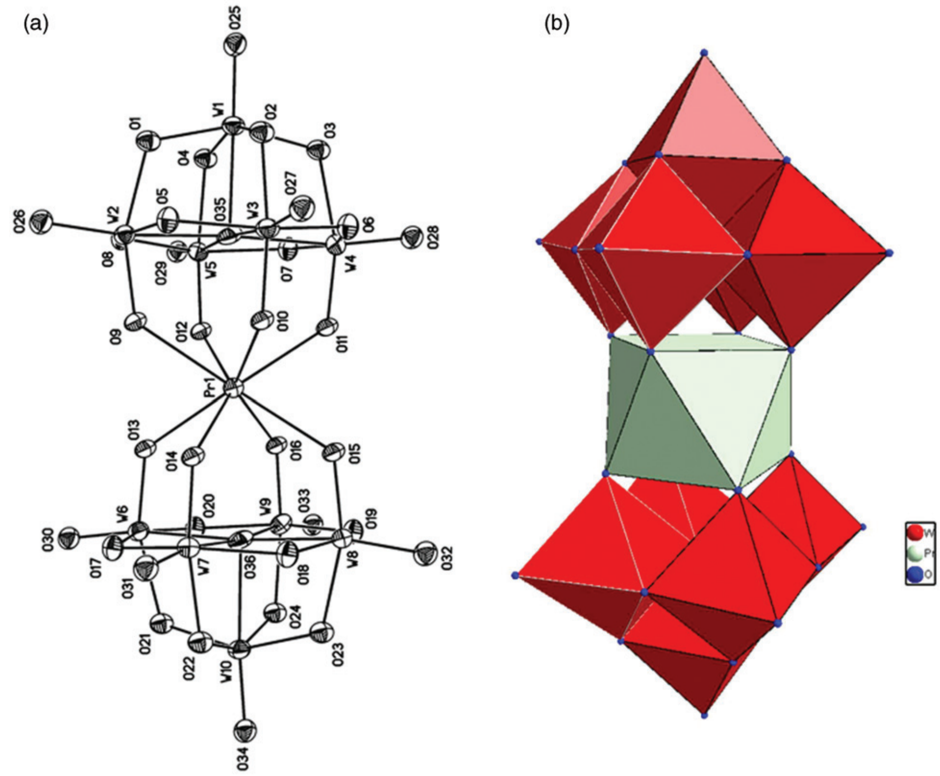

Figure 2. Structure of **3** (a) ORTEP representation (50% probability ellipsoids) and (b) polyhedral representation.

$(MOH_2)_3CO_3]^{11-}$ are from reaction of A-$PW_9O_{34}^{9-}$ with Eu^{3+} and Gd^{3+} while, with Pr^{3+} and Nd^{3+}, the products are $[(W_5O_{18})_2M]^{9-}$. The formed products in these studies have been isolated and characterized by elemental analysis, IR, ^{31}P NMR spectroscopy, TGA, and single crystal structure analysis. The single crystal structure analysis was carried out on $K_6Na_2(H_3O)[(W_5O_{18})_2Pr] \cdot 18H_2O$ which consists of two $W_5O_{18}^{6-}$ linked *via* Pr^{3+}. The Pr^{3+} ion is eight-coordinate with overall anion symmetry close to D_{4d}.

Supplementary material

TG curve of **1** and **2**; IR spectra of **1**–**4** and Crystallographic data (CIF file) for the structural analysis have been deposited with the Fachinformationszentium Karlsruhe (FIZ), CSD-number 421460 ($H_{38}K_6Na_2O_{55}PrW_{10}$). These data can be obtained free of charge *via* Email: crysdata@FIZ-Karsruhe.de; Tel.: 49 7247 808 310; Fax: 49 7247 808 136.

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