A sandwich-type aluminium complex composed of tri-lacunary Keggin-type polyoxotungstate: synthesis and X-ray crystal structure of $[(A-PW_9O_{34})_2\{W(OH)(OH_2)\}\{Al(OH)(OH_2)\}\{Al(\mu-OH)(OH_2)_2\}_2]^{7-}$

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Sandwich-type aluminum complex composed of tri-lacunary Keggin-type polyoxotungstate: synthesis and X-ray crystal structure of

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†Electronic supplementary information (ESI) available: Bond lengths (Å) and angles (°) for **1** (Table S1); bond valence sum calculations for **1** (Table S2); and CCDC reference number 779365.

For ESI and crystallographic data in CIF or other electronic format, see DOI: xxxxxxxxxxxx.

The synthesis and molecular structure of a dimeric aluminum complex composed of tri-lacunary α -Keggin polyoxometalate is described. The polyoxometalate, $\text{K}_6\text{Na}[(\text{A-PW}_9\text{O}_{34})_2\{\text{W}(\text{OH})(\text{OH}_2)\}\{\text{Al}(\text{OH})(\text{OH}_2)\}\{\text{Al}(\mu\text{-OH})(\text{OH}_2)_2\}_2]\cdot 19\text{H}_2\text{O}$ (**KNa-1**), afforded by the reaction in water of tri-lacunary Keggin polyoxotungstate with excess aluminum nitrate, followed by the crystallization from water, was obtained as analytically pure, homogeneous, colorless crystals. The compound **KNa-1** was characterized by an elemental analysis, TG/DTA, FT-IR, solution NMR (^{31}P , ^{27}Al , and ^{183}W), and X-ray crystallography. The single-crystal X-ray structure analysis revealed that two 6-coordinate aluminum ions linked with two bridging hydroxyl groups and four water molecules, *i.e.*, $[\text{Al}^{\text{III}}_2(\mu\text{-OH})_2(\text{OH}_2)_4]^{4+}$; a unit of a 6-coordinate tungsten ion linked with a hydroxyl group and a water molecule, *i.e.*, $[\text{W}(\text{OH})(\text{OH}_2)]^{5+}$; a unit of a 6-coordinate aluminum ion linked with a hydroxyl group and a water molecule, *i.e.*, $[\text{Al}(\text{OH})(\text{OH}_2)]^{2+}$, were sandwiched between two tri-lacunary α -Keggin polyoxotungstates, resulting in an overall *Cs* symmetry.

Introduction

Aluminum and its derivatives, e.g., alloys, oxides, organometallics, and inorganic compounds, have attracted considerable attention because of their extreme versatility and unique range of properties, including acidities, hardness, and electroconductivities.¹ Since the properties and activities of an aluminum species are strongly dependent on the structures of the aluminum sites, the syntheses of aluminum compounds with structurally well-defined aluminum sites are considerably significant for the development of novel and efficient aluminum-based materials. However, the use of these well-defined aluminum sites is slightly limited by the conditions due to the hydrolysis of the aluminum species by water.²

Polyoxometalates (POMs) have been of particular interest in the fields of catalysis, surface science, and materials science because their chemical properties such as redox potentials, acidities, and solubilities in various media can be finely tuned by choosing appropriate constituent elements and counteranions.³ In particular, the coordination of metal ions into the vacant site(s) of lacunary polyoxometalates is one of the most powerful techniques used for constructing efficient and well-defined active metal centers. Knöth and co-workers have first synthesized the Keggin derivative $(\text{Bu}_4\text{N})_4(\text{H})\text{ClAlW}_{11}\text{PO}_{39}$.⁴ However, only a few aluminum-coordinated POMs determined by the X-ray crystallographic analysis have been reported, e.g., $\text{TBA}_3\text{H}[\gamma\text{-SiW}_{10}\text{O}_{36}\{\text{Al}(\text{OH}_2)\}_2(\mu\text{-OH})_2]\cdot 4\text{H}_2\text{O}$ (TBA = tetra-*n*-butylammonium)⁵ and $\text{K}_6\text{H}_3[\text{ZnW}_{11}\text{O}_{40}\text{Al}]\cdot 9.5\text{H}_2\text{O}$,⁶ and the well-characterized (by X-ray crystallographic analysis) aluminum-containing POMs are still one of the least reported compounds.

In this study, we successfully obtained a dimeric, aluminum complex composed of tri-lacunary α -Keggin POM in the form of crystals suitable for the X-ray structure analysis of $\text{K}_6\text{Na}[(\text{A-PW}_9\text{O}_{34})_2\{\text{W}(\text{OH})(\text{OH}_2)\}\{\text{Al}(\text{OH})(\text{OH}_2)\}\{\text{Al}(\mu\text{-OH})(\text{OH}_2)_2\}_2]\cdot 19\text{H}_2\text{O}$ (**KNa-1**).

In this paper, we report the synthesis, characterization, and molecular structure of compound **KNa-1** in complete detail.

Results and discussion

The polyoxoanion, $[(A-PW_9O_{34})_2\{W(OH)(OH_2)\}\{Al(OH)(OH_2)\}\{Al(\mu-OH)(OH_2)_2\}_2]^{7-}$ (**1**), was formed by the direct reaction of an excess aluminum nitrate with the tri-lacunary Keggin POM, $[A-PW_9O_{34}]^{9-}$ in an aqueous solution at 25 °C under air, followed by the crystallization from water. The polyoxoanion **1** was easily formed when the molar ratios of $Al(NO_3)_3 \cdot 9H_2O$: $[A-PW_9O_{34}]^{9-}$ ranged from 3:1 to 10:1. During the formation of **1**, the decomposition of a tri-lacunary α -Keggin polyoxotungstate occurred in order to provide the additional tungsten atom for the construction of the bridging mono-tungsten site. The addition of a solid $[A-PW_9O_{34}]^{9-}$ ion to the aluminum nitrate aqueous solution caused the change in pH from 2.83 to 3.35. It was noted that the polyoxoanion **1** was mainly obtained by a stoichiometric reaction, *i.e.*, 3.0:2.1 molar ratio (3Al:19W), of $Al(NO_3)_3 \cdot 9H_2O$ with $[A-PW_9O_{34}]^{9-}$ under acidic conditions (pH = 2.7–3.0), and could be easily purified by the crystallization from the aluminum nitrate aqueous solution but not from water. Therefore, the aluminum nitrate contaminated in the crude sample was required for crystallizing the polyoxoanion **1** that was synthesized by the reaction of $[A-PW_9O_{34}]^{9-}$ with excess aluminum nitrate. The compound **KNa-1** was finally isolated as analytically pure, colorless crystals in a 17.5% (0.088g scale) yield.

The sample for the elemental analysis was dried overnight at room temperature under a vacuum of 10^{-3} – 10^{-4} torr. The elemental results of H, Al, K, P, W, and Na were in good agreement with the calculated values for the formula with three hydrated water molecules for **KNa-1** (see Experimental). It should be noted that the N analysis revealed no contamination

of nitrate ions from the precursor.

The weight loss observed during the course of drying before the analysis was 4.22% for **KNa-1**; this corresponded to 16 weakly solvated or adsorbed water molecules. On the other hand, in the TG/DTA measurement performed under atmospheric conditions, a weight loss of 7.7% observed at below 172.4 °C corresponded to 25 water molecules. Therefore, the number of water molecules (25) observed by the TG/DTA measurement under atmospheric conditions was consistent with the sum of the water molecules (6) coordinated with the bridging aluminum and the tungsten sites, the hydrated water molecules (3) found in the elemental analysis, and the water molecules (16) corresponding to the weight loss observed during the course of drying before the analysis.

The molecular structure of **1** in **KNa-1** and the partial structures around the dialuminum site and around the aluminum/tungsten bridging sites are illustrated in Figs. 1a, 1b, and 1c, respectively. Selected bond lengths and angles around the dialuminum center and the bridging tungsten/aluminum sites are summarized in Tables 1 and 2, while other bond lengths (Å) and angles (°) (Table S1) and the bond valence sum (BVS) calculations of the W, P, Al, and O atoms (Table S2) are given in the ESI†.

The composition and the formula of **KNa-1** containing six potassium and a sodium counteranion, and 19 hydrated water molecules were determined by the elemental analysis and the TG/DTA analysis. The X-ray crystallography of **KNa-1** identified six potassium ions and a sodium ion per formula unit in the crystal structure, but the hydrated water molecules per formula unit were not completely determined because of the disorder.⁷

The X-ray crystallography of **1** revealed that a dialuminum diamond core structure was sandwiched between two tri-lacunary α -Keggin polyoxotungstates. Two 6-coordinate monometal sites bridged between two tri-lacunary α -Keggin polyoxotungstate units were aluminum and tungsten atoms with a 41.7%:58.3% probability (W(19) 41.7%, Al(3): 58.3%,

W(20): 58.3%, Al(4): 41.7%) due to the disorder. The anion part of **KNa-1** was a dimeric structure with *Cs* symmetry.

The bond valence sums (BVSs),⁸ that were calculated on the basis of the observed bond lengths for **KNa-1** were in the range of 5.740 – 6.086 (average 5.878) for the 18 W atoms in two Keggin units, 4.752 – 4.772 (average 4.762) for the two P atoms in two Keggin units, 1.491 – 2.047 (average 1.810) for the 60 oxygen atoms excluding O(3), O(4), O(5), O(6), O(37), O(38), O(39), and O(40) in two Keggin units, and 2.798 – 2.874 (average 2.836) for the two Al atoms in the central dialuminum diamond core. These values reasonably corresponded to the formal valences of W⁶⁺, P⁵⁺, O²⁻, and Al³⁺, respectively (Tables S2). The calculated BVS values of the oxygen atoms around the dialuminum center were as follows: O(69) 0.887, O(70) 1.010, O(71) 0.404, O(72) 0.457, O(73) 0.438, and O(74) 0.434. These BVS values of the oxygen atoms suggested that a proton was bound to each of the two bridging oxygen atoms between two aluminum atoms, and two water molecules were coordinated with each of the two aluminum atoms. Therefore, the central dialuminum diamond core was composed of the two 6-coordinate aluminum ions linked with the two bridging hydroxyl groups and the four water molecules, *i.e.*, [Al^{III}₂(μ-OH)₂(OH₂)₄]⁴⁺. The Al–Al length was 2.892(5) Å, which was similar to the bond length of TBA₃H[γ-SiW₁₀O₃₆{Al(OH₂)₃(μ-OH)₂}]·4H₂O (2.863(1) Å).⁵

For the bridging monometal sites between two Keggin units, the BVS calculations could not be carried out because of the disorder of the aluminum/tungsten atoms. However, the bond lengths of the W(19)/Al(3)-O(75) and W(20)/Al(4)-O(77) were 2.254(11) Å and 2.274(10) Å (average 2.264 Å), which were clearly longer than those of W(19)/Al(3)-O(76) (1.635(11) Å) and W(20)/Al(4)-O(78) (1.669(11) Å) (average 1.652 Å), suggesting that the O(75) and O(77) atoms were present as water molecules and the O(76) and O(78) atoms were present as the hydroxyl groups. The lengths of W(19)/Al(3)-O(5), W(19)/Al(3)-O(6), W(19)/Al(3)-O(39), and W(19)/Al(3)-O(40) were 1.914(13), 1.887(9), 1.970(8), and 1.905(13)

Å (average 1.919 Å), and those of W(20)/Al(4)-O(3), W(20)/Al(4)-O(4), W(20)/Al(4)-O(37), and W(20)/Al(4)-O(38) were 1.885(9), 1.960(12), 1.900(12), and 1.963(8) (average 1.927 Å).

These values were similar to those of the tungsten-oxygen bond lengths of Keggin units.

Therefore, the two bridging monometal sites were a 6-coordinate tungsten ion linked with a hydroxyl group and a water molecule, *i.e.*, [W(OH)(OH₂)]⁵⁺, and a 6-coordinate aluminum ion linked with a hydroxyl group and a water molecule, *i.e.*, [Al(OH)(OH₂)]²⁺.

(Insert here Fig. 1 and Tables 1 and 2)

The FTIR spectrum measured as a KBr disk of the compound **KNa-1** is shown in Fig. 2. The spectral pattern of **KNa-1** (1085, 1024, 957, 934, 865, 823, and 752 cm⁻¹) was different from that of [A-PW₉O₃₄]⁹⁻ (1057, 1015, 935, 881, 831, and 756 cm⁻¹) and that of [α-PW₁₂O₄₀]³⁻ (1080, 984, 893, and 808 cm⁻¹), suggesting that the aluminum atoms were coordinated to the vacant site of [A-PW₉O₃₄]⁹⁻. The band at 1385 cm⁻¹ due to the NO₃⁻ ion was observed for the crude product; however, this band completely disappeared after the crystallization from water. This was consistent with the elemental analysis result of the N atom (<0.1%).

(Insert here Fig. 2)

The ³¹P NMR spectrum of compound **KNa-1** in D₂O at ~25 °C showed a clear single line spectrum at -12.01 ppm due to the internal phosphorus atom, thereby confirming the purity and homogeneity, as shown in Fig. 3. The signal exhibited a shift from the signals of [A-PW₉O₃₄]⁹⁻ (δ -10.49) and [α-PW₁₂O₄₀]³⁻ (δ -14.51). The ²⁷Al NMR spectrum (Fig. 4) of compound **KNa-1** in D₂O at ~25 °C showed two signals at 7.78 and 12.6 ppm with ca. 2:1 intensities due to the dialuminum diamond core and the bridging mono-aluminum site, respectively. The ¹⁸³W NMR spectrum (Fig. 5) of **KNa-1** in D₂O at ~25 °C showed a ten-line spectrum of (δ -107.96, -116.39, -159.27, -162.57, -207.41, -208.02, -210.46, -214.98, -306.85, and -313.08 ppm). The ten-line spectrum of **KNa-1** showed that the nine tungsten

atoms in each oxoanion half corresponds to the other by a twofold rotation and a bridging tungsten atom sandwiched by two polyoxoanion units. Therefore, three Al ions are coordinated to the Keggin polyoxoanion with *Cs* symmetry. These spectral data were completely consistent with the X-ray structure, suggesting that the solid structure was maintained in the solution.

(Insert here Figs. 3 – 5)

Conclusion

A dimeric aluminum complex composed of tri-lacunary Keggin polyoxometalate was presented. We successfully obtained the single crystals of a water-soluble potassium/sodium mixed salt $\text{K}_6\text{Na}[(\text{A-PW}_9\text{O}_{34})_2\{\text{W}(\text{OH})(\text{OH}_2)\}\{\text{Al}(\text{OH})(\text{OH}_2)\}\{\text{Al}(\mu\text{-OH})(\text{OH}_2)_2\}_2]\cdot 19\text{H}_2\text{O}$ (**KNa-1**) by reacting aluminum nitrate with a tri-lacunary Keggin polyoxoanion. The characterization of compound **KNa-1** was accomplished by an X-ray structure analysis, elemental analysis, TG/DTA, FTIR, and solution (^{31}P , ^{27}Al , and ^{183}W) NMR spectroscopy. The single-crystal X-ray structure analysis of the **KNa-1** crystal revealed that two 6-coordinate aluminum ions linked with the two bridging hydroxyl groups and the four water molecules, *i.e.*, $[\text{Al}^{\text{III}}_2(\mu\text{-OH})_2(\text{OH}_2)_4]^{4+}$; a unit of a 6-coordinate tungsten ion linked with a hydroxyl group and a water molecule, *i.e.*, $[\text{W}(\text{OH})(\text{OH}_2)]^{5+}$; and a unit of a 6-coordinate aluminum ion linked with a hydroxyl group and a water molecule, *i.e.*, $[\text{Al}(\text{OH})(\text{OH}_2)]^{2+}$, were sandwiched between two tri-lacunary α -Keggin polyoxotungstates, resulting in an overall *Cs* symmetry.

Experimental section

Materials

$\text{Na}_9[\text{A-PW}_9\text{O}_{34}]\cdot 18\text{H}_2\text{O}$ was prepared as described in the literature.⁹ The number of solvated water molecules was determined by TG/DTA analyses. All the reagents and solvents (ethanol and diethyl ether) were obtained and used as received from commercial sources. $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ (Aldrich, 99.997% purity) was used.

Instrumentation/analytical procedures

The elemental analysis was carried out by using Mikroanalytisches Labor Pascher (Remagen, Germany). The samples were dried overnight at room temperature under $10^{-3} - 10^{-4}$ torr before analysis. Infrared spectra were recorded on a Parkin Elmer Spectrum100 FT-IR spectrometer in KBr disks at room temperature. Thermogravimetric (TG) and differential thermal analyses (DTA) data were obtained using a Rigaku Thermo Plus 2 series TG/DTA TG 8120. TG/DTA measurements were performed in air with a temperature increase of 4 °C per min between 20 and 500 °C. The ^{31}P NMR (161.70 MHz) spectra in the D_2O solution were recorded in tubes (outer diameter: 5 mm) on a JEOL ECA-600 NMR spectrometer (Shizuoka University). The ^{31}P NMR spectra were referenced to an external standard of 85% H_3PO_4 in a sealed capillary. Chemical shifts were reported as negative on the δ scale for resonance upfields of H_3PO_4 (δ 0). The ^{27}Al NMR (156.36 MHz) spectrum in D_2O was recorded in tubes (outer diameter: 5 mm) on a JEOL ECA-600 NMR spectrometer (Kyushu University). The ^{27}Al NMR spectrum was referenced to an external standard of the saturated $\text{AlCl}_3\text{-D}_2\text{O}$ solution (substitution method). Chemical shifts were reported as positive on the δ scale for resonance downfields of AlCl_3 (δ 0). The ^{183}W NMR (25.00 MHz) spectra were recorded in tubes (outer diameter: 10 mm) on a JEOL ECA-600 NMR spectrometer (Kyushu University). ^{183}W NMR spectra measured in D_2O were referenced to an external standard of the saturated $\text{Na}_2\text{WO}_4\text{-D}_2\text{O}$ solution (substitution method). Chemical shifts were reported as

negative for the resonance upfields of Na_2WO_4 (δ 0).

Preparation

$\text{K}_6\text{Na}[(\text{A-PW}_9\text{O}_{34})_2\{\text{W}(\text{OH})(\text{OH}_2)\}\{\text{Al}(\text{OH})(\text{OH}_2)\}\{\text{Al}(\mu\text{-OH})(\text{OH}_2)_2\}_2]\cdot 19\text{H}_2\text{O}$ (KNa-1).

Solid $\text{Na}_9[\text{A-PW}_9\text{O}_{34}]\cdot 18\text{H}_2\text{O}$ was finely ground in a mortar and dried under vacuum at $\sim 25^\circ\text{C}$ for 2 h. To a colorless clear solution of $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ (8.525 g, 22.7 mmol) dissolved in water (200 mL), 20.297 g (7.50 mmol) of a solid $\text{Na}_9[\text{A-PW}_9\text{O}_{34}]\cdot 18\text{H}_2\text{O}$ was added in a single step, followed by stirring in a water bath at 90°C for 30 min. After cooling to room temperature, the white suspension was filtered through a folded filter paper (Whatman #5). To the colorless clear solution, a solid KCl (5.666 g, 76 mmol) was added, followed by stirring at 25°C for 1 h. The solution was evaporated at around 40°C until a white precipitate was formed. The white precipitate was collected on a glass frit (G4) and washed with ethanol ($5\text{ mL} \times 3$) and ether ($5\text{ mL} \times 3$). At this stage, a crude product was obtained in a 5.559 g yield. The crude product (0.502 g) containing with unreacted aluminum nitrate was dissolved in 2.2 mL of water, followed by stirring in a water bath at $80\text{--}90^\circ\text{C}$. After 15 min, the solution was filtered through a folded filter paper (Whatman #5). The clear colorless solution was slowly evaporated at 25°C . After a week, colorless prism crystals were formed. The crystals were obtained in a 17.5% (0.088 g scale) yield based on $\text{K}_6\text{Na}[(\text{A-PW}_9\text{O}_{34})_2\{\text{W}(\text{OH})(\text{OH}_2)\}\{\text{Al}(\text{OH})(\text{OH}_2)\}\{\text{Al}(\mu\text{-OH})(\text{OH}_2)_2\}_2]\cdot 19\text{H}_2\text{O}$. The obtained product was soluble in water and dimethyl sulfoxide, and insoluble in methanol, ethanol, acetone, and diethyl ether. Elemental anal. Found: H, 0.50; K, 4.69; P, 1.25; Al, 1.58; W, 67.2; Na, 0.39; N, $<0.1\%$. Calc. for $\text{K}_6\text{Na}[(\text{A-PW}_9\text{O}_{34})_2\{\text{W}(\text{OH})(\text{OH}_2)\}\{\text{Al}(\text{OH})(\text{OH}_2)\}\{\text{Al}(\mu\text{-OH})(\text{OH}_2)_2\}_2]\cdot x\text{H}_2\text{O}$ ($x = 3$) = $\text{H}_{22}\text{Al}_3\text{K}_6\text{NaO}_{81}\text{P}_2\text{W}_{19}$: H, 0.43; K, 4.50; P, 1.19; Al, 1.55; W, 67.02; Na, 0.44; N, 0%. A

weight loss of 4.22% was observed during the overnight drying at room temperature under 10^{-3} – 10^{-4} torr before the analyses, suggesting the presence of 16 weakly solvated or adsorbed water molecules (5.24%). TG/DTA under atmospheric conditions: a weight loss of 7.7% with an endothermic point at 63.3, 69.9, 77.6, and 172.4 °C was observed below 500 °C; calc. 8.1% for 25 water molecules in

$\text{K}_6\text{Na}[(\text{A-PW}_9\text{O}_{34})_2\{\text{W}(\text{OH})(\text{OH}_2)\}\{\text{Al}(\text{OH})(\text{OH}_2)\}\{\text{Al}(\mu\text{-OH})(\text{OH}_2)_2\}_2]\cdot 19\text{H}_2\text{O}$. IR (KBr disk): 1085s, 1024m, 957s, 934s, 865sh, 823s, 752s cm^{-1} . ^{31}P NMR (25 °C, D_2O): δ -12.0. ^{27}Al NMR (25 °C, D_2O): δ 7.78, 12.58. ^{183}W NMR (25 °C, D_2O): δ -107.96, -116.39, -159.27, -162.57, -207.45, -208.02, -210.46, -214.98, -306.85, -313.08.

X-Ray crystallography. A colorless prism crystal of **KNa-1** ($0.07 \times 0.05 \times 0.01 \text{ mm}^3$) was surrounded by liquid paraffin (Patatone-N) to prevent its degradation. Data were collected by a Rigaku VariMax with Saturn connected to multi-layer mirror monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71075 \text{ \AA}$) at 93 K. Data were collected and processed using the CrystalClear for Windows software. The structural analysis was performed using the CrystalStructure for Windows software. All structures were solved by SHELXS-97 (direct methods) and refined by SHELXL-97.¹⁰

Crystal data for KNa-1. $\text{H}_{53.50}\text{Al}_3\text{K}_6\text{O}_{96.75}\text{P}_2\text{W}_{19}\text{Na}$; $M = 5495.49$, *triclinic*, space group *P-1*(#2), $a = 13.300(5)$, $b = 19.135(7)$, $c = 20.684(8) \text{ \AA}$, $\alpha = 65.975(10)$, $\beta = 81.948(19)$, $\gamma = 73.966(16)^\circ$, $V = 4618(3) \text{ \AA}^3$, $Z = 2$, $D_c = 3.951 \text{ g/cm}^3$, $\mu(\text{Mo-K}\alpha) 240.406 \text{ cm}^{-1}$. $R1 = 0.0508$, $wR2 = 0.1337$ (for all data). $\text{GOF} = 1.031$ (55017 total reflections, 20298 unique reflections where $I > 2\sigma(I)$). The polyoxoanion **1** consisting of 19 tungsten atoms, three aluminum atoms, two phosphorous atoms, 78 oxygen atoms, six potassium atoms, and a sodium atom per formula unit was identified, but the location of the hydrated water molecules

per unit was not determined because of the disorder. CCDC number 779365.

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Figure captions

Fig. 1. (a) Molecular structure of the polyoxoanion

$[(A-PW_9O_{34})_2\{W(OH)(OH_2)\}\{Al(OH)(OH_2)\}\{Al(\mu-OH)(OH_2)_2\}_2]^{7-}$ (**1**) in **KNa-1**, the partial structure around (b) the dialuminum diamond core site, and (c) the aluminum/tungsten bridging sites. In (c), the aluminum or tungsten atoms were presented with a 41.7%:58.3% probability (W(19) 41.7%, Al(3): 58.3%, W(20): 58.3%, Al(4): 41.7%) at the monometal bridging sites.

Fig. 2. FTIR spectra in the polyoxoanion region ($1800 - 400\text{ cm}^{-1}$), measured as KBr disks, of **KNa-1**.

Fig. 3. ^{31}P NMR spectrum in D_2O of **KNa-1**. The spectrum was referenced to an external standard of 85% H_3PO_4 in a sealed capillary.

Fig. 4. ^{27}Al NMR spectrum in D_2O of **KNa-1**. The spectrum was referenced to an external standard of a saturated $\text{AlCl}_3\text{-D}_2\text{O}$ solution (substitution method).

Fig. 5. ^{183}W NMR spectrum in D_2O of **KNa-1**. The spectrum was referenced to an external standard of a saturated $\text{Na}_2\text{WO}_4\text{-D}_2\text{O}$ solution (substitution method).

Table 1. Selected bond lengths (Å) and angles (°) around the dialuminum center in **1**

Lengths			
Al(1)-O(1)	1.873(13)	Al(1)-O(71)	1.955(11)
Al(1)-O(35)	1.876(14)	Al(1)-O(72)	1.910(10)
Al(2)-O(2)	1.874(13)	Al(2)-O(73)	1.925(10)
Al(2)-O(36)	1.852(13)	Al(2)-O(74)	1.929(12)
Average	1.869	Average	1.930
Al(1)-O(70)	1.878(10)		
Al(1)-O(69)	1.929(10)	Al(1)...Al(2)	2.892(5)
Al(2)-O(70)	1.867(9)		
Al(2)-O(69)	1.913(11)		
Average	1.897		
Angles			
Al(1)-O(69)-Al(2)	97.7(4)	O(69)-Al(1)-O(70)	80.3(4)
Al(1)-O(70)-Al(2)	101.1(4)	O(69)-Al(2)-O(70)	81.0(4)
Average	99.4	Average	80.7
O(1)-Al(1)-O(35)	172.4(5)	O(2)-Al(2)-O(36)	173.1(5)
O(1)-Al(1)-O(69)	91.3(4)	O(2)-Al(2)-O(69)	90.8(4)
O(1)-Al(1)-O(70)	92.8(5)	O(2)-Al(2)-O(70)	92.4(5)
O(1)-Al(1)-O(71)	86.1(5)	O(2)-Al(2)-O(73)	88.0(5)
O(1)-Al(1)-O(72)	89.3(5)	O(2)-Al(2)-O(74)	87.4(5)
O(35)-Al(1)-O(69)	90.9(5)	O(36)-Al(2)-O(69)	93.4(5)
O(35)-Al(1)-O(70)	94.8(5)	O(36)-Al(2)-O(70)	93.7(5)
O(35)-Al(1)-O(71)	86.4(5)	O(36)-Al(2)-O(73)	86.2(5)
O(35)-Al(1)-O(72)	89.0(5)	O(36)-Al(2)-O(74)	88.8(5)
O(69)-Al(1)-O(71)	93.9(4)	O(69)-Al(2)-O(73)	93.2(4)
O(69)-Al(1)-O(72)	176.3(4)	O(69)-Al(2)-O(74)	175.9(5)
O(70)-Al(1)-O(71)	174.1(4)	O(70)-Al(2)-O(73)	174.1(5)
O(70)-Al(1)-O(72)	96.1(4)	O(70)-Al(2)-O(74)	95.5(4)
O(71)-Al(1)-O(72)	89.7(4)	O(73)-Al(2)-O(74)	90.4(4)

Table 2. Selected bond lengths (Å) and angles (°) around the bridging tungsten/aluminum sites in **1**

Lengths			
W(19)/Al(3)-O(75)	2.254(11)	W(19)/Al(3)-O(76)	1.635(11)
W(20)/Al(4)-O(77)	2.274(10)	W(20)/Al(4)-O(78)	1.669(11)
Average	2.264	Average	1.652
W(19)/Al(3)-O(5)	1.914(13)	W(20)/Al(4)-O(3)	1.885(9)
W(19)/Al(3)-O(6)	1.887(9)	W(20)/Al(4)-O(4)	1.960(12)
W(19)/Al(3)-O(39)	1.970(8)	W(20)/Al(4)-O(37)	1.900(12)
W(19)/Al(3)-O(40)	1.905(13)	W(20)/Al(4)-O(38)	1.963(8)
Average	1.919	Average	1.927
Angles			
O(5)-W(19)/Al(3)-O(75)	80.0(4)	O(3)-W(20)/Al(4)-O(77)	81.2(3)
O(6)-W(19)/Al(3)-O(75)	82.7(3)	O(4)-W(20)/Al(4)-O(77)	80.7(4)
O(39)-W(19)/Al(3)-O(75)	81.3(3)	O(37)-W(20)/Al(4)-O(77)	82.2(4)
O(40)-W(19)/Al(3)-O(75)	82.1(4)	O(38)-W(20)/Al(4)-O(77)	79.6(3)
Average	81.6	Average	81.0
O(5)-W(19)/Al(3)-O(76)	100.1(6)	O(3)-W(20)/Al(4)-O(78)	98.6(4)
O(6)-W(19)/Al(3)-O(76)	96.4(4)	O(4)-W(20)/Al(4)-O(78)	99.3(5)
O(39)-W(19)/Al(3)-O(76)	99.7(4)	O(37)-W(20)/Al(4)-O(78)	97.8(5)
O(40)-W(19)/Al(3)-O(76)	97.9(6)	O(38)-W(20)/Al(4)-O(78)	100.6(4)
Average	98.6	Average	99.1
O(5)-W(19)/Al(3)-O(6)	88.9(4)	O(3)-W(20)/Al(4)-O(4)	88.5(4)
O(39)-W(19)/Al(3)-O(40)	86.5(4)	O(37)-W(20)/Al(4)-O(38)	86.7(4)
O(5)-W(19)/Al(3)-O(39)	82.7(4)	O(3)-W(20)/Al(4)-O(37)	97.9(4)
O(6)-W(19)/Al(3)-O(40)	96.9(4)	O(4)-W(20)/Al(4)-O(38)	81.2(4)
O(5)-W(19)/Al(3)-O(40)	160.4(4)	O(3)-W(20)/Al(4)-O(38)	159.4(4)
O(6)-W(19)/Al(3)-O(39)	162.9(4)	O(4)-W(20)/Al(4)-O(37)	160.6(3)
O(75)-W(19)/Al(3)-O(76)	179.0(4)	O(77)-W(20)/Al(4)-O(78)	179.8(3)

(a)

Fig. 1

Fig. 1-continued

Fig. 2

Fig. 3

Fig. 4

Fig. 5