Special Issue in Memory of Professor M.T. Pope

The Anion $[PO_4W_8O_{26}]^{7-}$ - A New Keggin Fragment[1]

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ABSTRACT

Studies on the behavior of [*A*-*α*/*β*-$PO_4W_9O_{30}$]$^{9-}$ in aqueous solution in the presence of the alkaline ions Li^+, Na^+, K^+ and Cs^+ led to the new anion $[PO_4W_8O_{26}]^{7-}$, a fragment of the Keggin structure. It can be prepared in a one-pot synthesis of sodium tungstate and phosphoric acid and careful addition of acetic acid and cesium chloride at pH 8 in water. The isolated salt $Cs_{4.5}Na_{2.5}[PO_4W_8O_{26}]\cdot 23H_2O$ was characterized by single-crystal X-ray diffraction, FT-IR, ^{31}P solid-state NMR spectroscopy, elemental and thermogravimetric analyses as well as solution-state ^{31}P NMR. The single-crystal structural analysis revealed six {WO_6} octahedra linked to the central {PO_4} tetrahedron arranged in two double-edge linked {W_3O_{15}} moieties of corner-sharing {WO_6} octahedra. This "half" of the *α*-Keggin anion is capped by two distorted {WO_5} square pyramids carrying two terminal oxygen atoms each.

KEYWORDS: polyoxometalates, tungstophosphates, iso-and heteropolyanions, Keggin-anion-fragment

1. Introduction

Polyoxometalates (POMs) are an exciting class of compounds that are of both theoretical and commercial interests [1-29]. Strategies for the synthesis of new compounds include the use of lacunary Keggin anions to obtain metal-substituted heteropoly anions [30-58]. In 1933 James Fargher Keggin (student of W.L. Bragg) had described the structure of $H_3[\alpha$-$PO_4W_{12}O_{36}]\cdot 5H_2O$ (***α*-PW$_{12}$**) by solving its X-ray diffraction pattern and it has been named after him ever since [59]. Figure 1A shows the polyhedral representation of its *α*-isomer. The structure has overall T_d symmetry and is based on a central {PO_4} tetrahedron surrounded by twelve {WO_6} octahedra arranged in four groups of three edge-shared octahedra {W_3O_{13}}. These groups are linked by shared corners to each other and the central {PO_4} tetrahedron [1, p.23]. The successful introduction of a low-valent metallic ion $M^{II/III}$ as heteroelement to the well-studied anion depends both on the stability of the

[1]The original experiments and structural description of the title anion date back to 1995 [64]. In September of 2026 K.W. went back to the laboratory of Prof. Ulrich Kortz at Constructor University to generate crucial experimental data to report the results in the Journal's Special Issue in memory of Prof. M.T. Pope. While working in his laboratory and visiting him in the hospital discussing science and other topics, our friend and colleague Uli Kortz passed away. All authors are forever in debt to Uli's generosity and treasure the privilege to have met him, to share his passion for POMs, science and life.

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precursor anion as well as the reactivity of the heteroelement.

We were interested in the synthesis and characterization of multiple chromium(III)-substituted Keggin anions and have reported on the following compounds:

- $K_{5.25}H_{0.75}[A\text{-}\alpha\text{-}SiO_4W_9MoO_{33}(OH)Cr_2(OH)(OH_2)]\cdot 11H_2O$ [64,65],
- $K_3H[A\text{-}\alpha\text{-}SiO_4W_9O_{30}(OH)_3Cr_3(OH_2)_3]\cdot 11H_2O$ [66],
- $(Bu_4N)_3H_2[\gamma\text{-}SiO_4W_{10}O_{32}(OH)Cr_2(OOCCH_3)_2(OH_2)_2]\cdot 3H_2O$ [67],
- $(NH_4)_{11}[\{A\text{-}\alpha\text{-}SiO_4W_9O_{30}(OH)_3Cr_3\}_2(OH)_3]\cdot 6H_2O\cdot 2.5NH_4Cl$ [65].[2]

A common feature of these compounds is the linkage of $\{CrO_6\}$ octahedra via common-corner oxygen atoms. In order to expand the range of multiple chromium(III)-substituted Keggin anions, we also explored the use of lacunary tungstophosphates aiming to realize structures with $\{CrO_6\}$ octahedra linked via common-edge oxygen atoms.
Reported preparations for lacunary tungstophosphates include an instruction to convert $[A\text{-}\alpha/\beta\text{-}PO_4W_9O_{30}]^{9-}$ (***A*-PW$_9$**) by thermal treatment to $[B\text{-}\alpha\text{-}PO_4W_9O_{30}]^{9-}$ (***B*-PW$_9$**) - a lacunary Keggin anion in which a complete $\{W_3O_{13}\}$ triade is "missing" [47,68,69]. This anion could accept multiple heteroelements and therefore facilitates an arrangement of edge-shared $\{CrO_6\}$ octahedra.

In the following we report our findings on the behavior of both ***A*-PW$_9$** and ***B*-PW$_9$** in the presence of the alkaline ions Li^+, Na^+, K^+ and Cs^+ and the formation of a new fragment of the Keggin anion, $[PO_4W_8O_{26}]^{7-}$ (**PW$_8$**) in which "half" of the Keggin structure is capped by two distorted $\{WO_5\}$ square pyramids.

2. Experimental

Instrumentation and Analytical Procedures. Freeze drying was conducted using an LDC-1 apparatus (Christ, Osterode, Germany). Fourier Transform infrared (FT-IR) spectra were recorded on a Perkin-Elmer IR 580 B, and for 2026 samples **X-XVI** on a SHIMADZU IR Spirit spectrometer, all KBr discs. The relative peak intensities are denoted as w = weak, m = medium, ms = medium-strong, s = strong, vs = very strong, sh = shoulder and br = broad. Solid-state ^{31}P nuclear magnetic resonance (NMR) data were obtained on a Bruker NMR-spectrometer MSL 400, (rotational frequency of 4 mm ZrO_2-rotors 15 to 18 kHz, room temperature). External standard 85% H_3PO_4, frequency 162 MHz; accumulation rate ~100; pulsing 0.3 to 1.0 s. Room-temperature ^{31}P NMR solution spectra were recorded on a JEOL ECX 400 MHz spectrometer, using D_2O as locking solvent. The ^{31}P resonance frequency was 162.14 MHz, and all chemical shifts were referenced to a 1 M H_3PO_4 solution. The elemental content was determined with an inductively coupled plasma (ICP) Spectro Flame (Li, Na, K) and Flame AAA PE3100 (Cs). The tungsten content was obtained by calculating the difference between the sum of all non-tungsten oxides and 100%. Phosphorus was analyzed gravimetrically as dodecamolybdophosphate after Dahlgren [70]. The thermogravimetric analysis (TGA) of sample **XVI** was carried out on a TA Instruments SDT Q600 thermobalance under a nitrogen atmosphere by heating the sample from room temperature to 600 °C at a rate of 5 °C min^{-1}. Elemental analysis of Na, P, Cs and W was conducted by Technische Universität Hamburg, Zentrallabor Chemische Analytik, Eißendorfer Straße 38, Gebäude O, 21073 Hamburg, Germany. The water content of other samples was determined as loss on ignition (L.O.I.) at 600 °C in a muffle furnace. In some cases the determination of all elements and/or loss of ignition L.O.I. could not be performed due to the lack of material. A pH 96 meter (WTW, Weilheim Germany) was used for pH measurements. For experiments conducted in 2026 (synthetic methods 2-5) a FiveEasy™ F20 pH meter (Mettler Toledo) was used.

Single-crystal X-ray diffraction data were collected at 100 K on a Rigaku XtaLAB Synergy single-crystal diffractometer equipped with a Dualflex source and HyPix detector system, using kappa geometry. The instrument, configured with a graphite monochromator, possessing a MoKα radiation source (λ = 0.71073 Å) and CuKα radiation (λ = 1.54184 Å). Suitable crystals were mounted on Hampton cryoloops with Paratone-N oil prior to data collection. Data collection, reduction, and initial processing were

[2]Professor Joachim Fuchs at the Free University (FU) in Berlin conducted the X-ray structural analyses of the listed compounds. We were very fortunate to work with him and the colleagues of Prof. Hans Hartl's group as a result of the historic events in 1989, bringing together POM researchers in a reunited Berlin. In 1979, while working on the manuscript of [1], Prof. Michael Pope visited the FU. His host Prof. Joachim Fuchs (1924-2002) [60] was a student of Karl-Friedrich Jahr (1904-1973) [61], who himself was a student of Gerhart Jander (1892-1961) [62], who on his part was a student of Arthur Rosenheim (1865-1942) [63]. Arthur Rosenheim, professor from 1906 to 1933 at the Friedrich-Wilhelms-University of Berlin (since 1949 Humboldt-University), was a very productive chemist establishing POM research at the beginning of the 20th century.

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carried out using CrysAlisPro software package [71]. Absorption effects were corrected empirically using the ABSPACK program [72]. The structure was solved using Olex2 [73] and refined against F^2 by full-matrix least-squares methods with the SHELX program package [74,75]. The SQUEEZE method embedded in PLATON was applied to standardize the disorder arising from the lattice atoms [76,77]. The crystallographic and refinement parameters are summarized in Table 1. CIF files are available free of charge from the Cambridge Crystallographic Data Centre, 2596036 for **XII**, 2596037 for **XVI**.

Materials: All compounds were of reagent grade and used as supplied.

Preparation of $Na_9[A\text{-}\alpha/\beta\text{-}PO_4W_9O_{30}]\cdot 22H_2O$ (I). The compound was synthesized according to [69] and verified by elemental analysis and IR spectroscopy. Elemental analysis and L.O.I. (%) found (calculated): Na 8.60 (7.30), P 1.25 (1.09), W 57.78 (58.41), H_2O 14.53 (13.99); IR (cm^{-1}, polyoxoanion area): 1053 (s), 1014 (m), 937 (vs), 881 (s), 838 (vs), 824 (sh), 748 (vs), 650 (m), 622 (w) 596 (w), 514 (m), 461 (sh), 352 (s), 317 (m).

Preparation of $Li_9[A\text{-}\alpha/\beta\text{-}PO_4W_9O_{30}]\cdot 14H_2O$ (II). A glass column (Ø 4 cm) was filled with 150 mL of the strong acid cation exchanger LEWATIT® S100 and loaded with Li^+ using a 2 M aqueous solution of LiCl and then washed with bidistilled water free of chloride. 50 mL of the resin was removed and in a beaker combined with 400 mL water. Next, 28.0 g (10 mmol) of **I** were added in small portions. The colorless solution was separated and passed through the column (Ø 2.5 cm) containing the remaining ion exchanger (drop rate: 2-4 $mL\cdot min^{-1}$). The eluate was distributed to four to six 250 mL flasks, frozen and then freeze-dried. The hygroscopic material was kept in a P_4O_{10}-containing desiccator and characterized. Elemental analysis and L.O.I. (%) found (calculated): Li 2.69 (2.46), P 1.26 (1.22), W 66.30 (65.03), H_2O 10.39 (9.91); IR (cm^{-1}, polyoxoanion area): 1069 (s), 1015 (m), 938 (vs), 880 (sh, br), 822 (vs), 717 (vs), 623 (w), 512 (m), 360 (m), 310 (sh).

Preparation of $Na_{9-x}Li_x[A\text{-}\alpha/\beta\text{-}PO_4W_9O_{30}]\cdot nH_2O$ (III). 1.5 g (0.6 mmol) of **II** were dissolved in 25 mL bidistilled water (pH 7.8) and stirred for 2 hours. The pH value dropped to 7.5 during the first five minutes and then remained stable. Addition of 8.5 g (145 mmol) NaCl led to a milky solution after 20 minutes and finally to a precipitate. The precipitate was collected after 45 minutes, dried on air and characterized. IR and ^{31}P magic-angle spinning (MAS) NMR data matched that of **I**. The same result was obtained at an extended stirring time of 8 hours. The experiment was also repeated at elevated temperatures of 50 °C and 75 °C (stirred for 2 and 8 hours each) and the pH dropped to 7.1 and 7.0, respectively. The characterization by IR matched the spectra obtained for **I**.

Preparation of $K_9[A\text{-}\alpha/\beta\text{-}PO_4W_9O_{30}]\cdot nH_2O$ (IV). 5.4 g (2.2 mmol) of **II** were dissolved in 25 mL bidistilled water, pH 8.2. The solution was passed through a hard filter to remove any cloudiness and mechanical impurities, pH 8.0. Then 6.0 g (80.5 mmol) KCl dissolved in 25 mL bidistilled water (3.2 M) were added to the stirred solution. After a few minutes the solution turned cloudy and a precipitate (2.3 g) was collected after 12 minutes. Elemental analysis (%) found (calculated): K 11.86 (12.04), W 55.39 (56.59). IR (cm^{-1}, polyoxoanion area): 1060 (s), 1011 (m), 937 (s), 921 (s), 883 (sh), 830 (vs), 760 (vs), 637 (sh), 596 (w), 512 (m), 455 (sh), 363 (s), 320 (sh).

Preparation of $Cs_6Li[\alpha\text{-}PO_4W_{11}O_{35}]\cdot nH_2O$ (V), **$Cs_8Li[A\text{-}\alpha/\beta\text{-}PO_4W_9O_{30}]\cdot nH_2O$ (VI)** and **$Cs_6Na[PO_4W_8O_{26}]\cdot 4H_2O$ (VII)**, **synthetic method 1**. At first 8.1 g (3.2 mmol) of **II** were dissolved in 110 mL bidistilled water (pH 8.1). The solution was passed through a hard filter to remove any cloudiness and mechanical impurities (pH 8.0). Addition of 12.0 g (71.3 mmol) CsCl dissolved in 10 mL bidestilled water (7 M) to the stirred solution immediately produced a precipitate. The precipitate was collected after 4 minutes (9 g) and characterized as **$Cs_6Li[\alpha\text{-}PO_4W_{11}O_{35}]\cdot nH_2O$ (V)**. The filtrate at pH 8.3 turned again cloudy and the precipitate was collected (<0.5 g) after 35 minutes. IR data indicated a mixture of the cesium salts of $[\alpha\text{-}PO_4W_{11}O_{35}]^{7-}$ and $[A\text{-}\alpha/\beta\text{-}PO_4W_9O_{30}]^{9-}$. Next, the filtrate was cooled to 5 °C. After 3 hours a white precipitate (<0.5 g) was collected on a hard filter and characterized as **$Cs_8Li[A\text{-}\alpha/\beta\text{-}PO_4W_9O_{30}]\cdot nH_2O$ (VI)**. The filtrate was kept at room temperature and reoccurring fine microcrystalline precipitates were removed. After a few days, well-shaped crystals were formed including fine needles growing in bundles. The latter were isolated and analyzed by IR and ^{31}P MAS NMR spectroscopy as well as single-crystal X-ray analysis (see supporting information) which revealed the composition **$Cs_6Na[PO_4W_8O_{26}]\cdot 4H_2O$ (VII)**. In a modification of the above mentioned experiment CsCl was added as a solid or the reaction solution was kept at 2 °C. In all cases the same types of precipitates were obtained. Elemental analysis (%) found (calculated) of **V**: Cs 26.33 (21.25), Li 0.18 (0.19), P 0.87 (0.82), W 50.93 (53.90); IR (cm^{-1}, polyoxoanion area): 1091 (s), 1043 (s), 949 (vs), 894 (s), 851 (vs), 793 (vs), 748 (m), 591 (w), 512(m), 477 (sh), 435 (w), 408 (sh), 385 (sh), 372 (s), 335 (sh). Elemental analysis (%) found

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(calculated) of **VI**: Cs 31.96 (29.05), Li 0.18 (0.19), W 43.42 (45.21). IR (cm^{-1}, polyoxoanion area): 1060 (s), 1006 (m), 932 (vs), 919 (vs), 890 (sh), 880 (vs), 824 (vs), 748 (vs), 687 (sh), 623 (w), 592 (w), 576 (sh), 509 (m), 453 (sh), 362 (s). IR of **VII**: IR (cm^{-1}, polyoxoanion area): 1128 (s), 1062 (s), 1000 (s), 966 (sh), 947 (s), 929 (vs), 918 (vs), 893 (vs), 880 (sh), 848 (vs), 822 (vs), 745 (vs), 712 (s), 687 (s), 624 (m), 596 (m) 573 (sh), 524 (sh), 503 (m), 447 (sh), 404 (sh), 385 (m), 368 (m), 344 (sh), 332 (sh), 311 (sh).

Preparation of $Cs_3[\alpha\text{-}PO_4W_{12}O_{36}]\cdot nH_2O$ (VIII). 5.8 g (3.0 mmol) of commercial $H_3[\alpha\text{-}PO_4W_{12}O_{36}]\cdot nH_2O$ (Merck) were dissolved in 40 mL bidistilled water, pH 1.7. Addition of 3.0 g (17.8 mmol) CsCl dissolved in 5 mL water (3.6 M) to the stirred solution led to a precipitate which was collected after a few minutes. It was rinsed with water, separated by vacuum filtration and dried on air. IR (cm^{-1}, polyoxoanion area): 1080 (vs), 995 (sh), 984 (vs), 890 (vs), 830 (sh), 798 (vs), 595 (m), 524 (s), 482 (sh), 429 (sh), 381 (s), 335 (m).

Thermal Treatment to obtain the *B*-PW_9 Isomer. Amounts of 0.5-1.0 g of salts **I**-**IV** and **VI** were heated in a drying oven at 140 °C for 6 hours [47,69 p. 100].

Preparation of $Na_9[B\text{-}\alpha\text{-}PO_4W_9O_{30}]\cdot nH_2O$ (IX): 1.0 g of **I** was added to a glass dish or ceramic tray and heat-treated in a drying oven at 140 °C for 6 hours. The product is a mixture of isomers ***A*-PW_9** and ***B*-PW_9**. IR (cm^{-1}, polyoxoanion area): 1176 (m), 1061 (s), 1015 (sh), 996 (m), 975 (sh), 950 (sh), 899 (vs), 824 (s), 746 (vs), 588 (w), 575 (sh), 510 (m), 471 (sh), 418 (w), 368 (s), 342 (m).[3]

Preparation of $Cs_7[PO_4W_8O_{26}]\cdot 10H_2O$ (XII), synthetic method 2 via ion exchange, based on the original instruction but without a freeze-drying step. A narrow 100 mL shaking funnel was filled with 70 mL of the strong acid cation exchanger DOWEX® 50WX8 100-200 and loaded with Li^+ using 200 mL of a 2 M aqueous solution of LiCl and then rinsed with 350 mL deionized water. Next, 40 mL of the resin was removed, added to a beaker and mixed with 40 mL water using a magnetic stirring bar. Next, 15.0 g (5.3 mmol) of **I** were added in small portions to the stirred resin and aqueous mixture. Within 5 minutes the substance was fully dissolved, pH 8.2. Both, resin and clear colorless solution were added back to the shaking funnel on top of the unused Li-loaded resin and the ion exchange was completed (drop rate 2-4 mL min^{-1}). Final volume 80 mL, pH 7.9. Addition of 20 g (119.0 mmol) CsCl dissolved in 15 mL water to the stirred eluate immediately produced a white precipitate. It was collected after 4 minutes (11 g) and characterized by IR spectroscopy as the cesium salt of $[\alpha\text{-}PO_4W_{11}O_{35}]^{7-}$ **(X)** IR (cm^{-1}, polyoxoanion area): 1092 (s), 1046 (s), 951 (vs), 893 (s), 852 (vs), 796 (vs), 738 (m), 595 (w), 513 (m). The filtrate, pH 8.1, turned cloudy again and was placed in a refrigerator at 6 °C. The next day a white precipitate (1 g) was collected on a hard filter and later characterized by IR as the cesium salt of $[\alpha\text{-}PO_4W_9O_{30}]^{9-}$ (**XI**) IR (cm^{-1}, polyoxoanion area): 1058 (s), 1006 (m), 918 (vs), 878 (vs), 824 (vs), 754 (vs), 580 (sh), 505 (m). The mother liquor was kept at room temperature and a fine microcrystalline precipitate was removed after 7 hours, <0.5 g. The next day fine needles were found at the bottom of the beaker, collected and identified by IR spectroscopy as the cesium salt of $[PO_4W_8O_{26}]^{7-}$, <0.1 g. New needles formed a few days later were isolated for IR spectroscopy and X-ray structural analyses **XII** CCDC 2596036. IR (cm^{-1}, polyoxoanion area): 1129 (s), 1064 (ms), 1002 (ms), 950 (sh), 929 (vs), 890 (vs), 848 (vs), 821 (vs), 747 (vs), 709 (sh), 689 (s), 623 (m), 595 (m) 570 (sh), 525 (sh), 505 (m).

Preparation of $Cs_{7-x}Na_x[PO_4W_8O_{26}]\cdot xH_2O$[4] (XIII), synthetic method 3. 6.6 g (20.0 mmol) of $Na_2WO_4\cdot 2H_2O$ were dissolved in 50 mL deionized water, pH 9.5. Then 2.5 mL of H_3PO_4 (1 M) were slowly added to the stirred solution, pH 8.0. Next 3.5 mL of diluted glacial acetic acid (5.9 M) were added over a period of 16 minutes. The first 2 mL were added in two 1 mL portions over a period of 4 minutes, pH 8.0. The remaining 1.5 mL were added in 0.1-0.3 mL increments, final pH 7.6. The clear solution was stirred for another 10 minutes, pH 7.7, before 5.2 g (30.0 mmol) CsCl dissolved in 10 mL water were slowly added. A white precipitate formed halfway through the addition. The mixture was stirred for an additional 10 minutes before the precipitate was removed by vacuum filtration, pH 7.7, ~10 g (moist). The IR spectrum indicated a mixture of compounds. Characteristic were the medium-strong bands at 1005, 1060 and 1128 cm^{-1}, rough intensity ratio 1:2:1, Figure S6. This precipitate was recrystallized in 75 mL water at 75 °C. A fine white powder was removed after 1 hour (<1 g). The IR spectrum matched that of **PW_8** and the beaker was placed on a shelf, pH 7.4. The next day very fine needles filled the beaker. The solid material was separated by vacuum filtration ~ 4 g (moist), IR spectrum matched that of **PW_8**, pH 7.2. It was recrystallized in 40 mL water at 75 °C, pH 7.1. The next day a crystalline precipitate was separated by vacuum filtration ~1 g, IR spectrum matched that of **PW_8**, pH 7.2. (**XIII**): IR (cm^{-1}, polyoxoanion area):

[3] Spectroscopic data in [69] of the thermally heated product: IR mineral oil, $Na_{9-x}H_x[A\text{-}PO_4W_9O_{30}]\cdot nH_2O$ 1052 (s), 1017 (m), 941 (s), 886 (m), 836 (s), 740-760 (s, br) and $Na_{9-x}H_x[B\text{-}PO_4W_9O_{30}]\cdot nH_2O$ 1174 (m), 1062 (m), 1018 (w), 995 (m), 897 (s), 823 (s), 739 (s).

[4] Elemental analysis was not performed.

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1130 (s), 1064 (ms), 1002 (ms), 950 (sh), 930 (vs), 891 (vs), 847 (vs), 821 (vs), 746 (vs), 710 (sh), 689 (s), 623 (m), 596 (m) 570 (sh), 525 (sh), 503 (m).

The recrystallization did not lead to larger crystals. A second precipitate was collected from the mother liquor 24 hours after the first vacuum filtration. It was separated by vacuum filtration ~1.5 g (moist), IR spectrum matched that of **PW_8**, pH 7.9. It was recrystallized in 25 mL water at 75 °C, pH 7.2. Beside fine needles rectangular well-shaped crystals formed a few days later. IR and single X-ray diffraction identified the anion as ***γ*-PW_{10}**. The liquids used for recrystallization were kept and observed. In all cases well-shaped rectangular crystals appeared and the anion was identified by IR spectroscopy as ***γ*-PW_{10}**, $Cs_{7-x}Na_x[\gamma\text{-}PO_4W_{10}O_{32}]\cdot nH_2O$ (**XIV**) IR (cm^{-1}, polyoxoanion area): 1085 (ms), 1052 (m), 1025 (m), 960 (sh), 937 (s), 892 (s), 850 (sh), 826 (vs), 751 (vs), 659 (m), 583 (m), 519 (m).[5]

Preparation of $Cs_{7-x}Na_x[PO_4W_8O_{26}]\cdot xH_2O$ [6] (XV), synthetic method 4. 26.4 g (80 mmol) of $Na_2WO_4\cdot 2H_2O$ were dissolved in 200 mL deionized water, pH 9.5. Then 6.7 g (40 mmol) CsCl were added to the stirred solution, pH 9.5. Next 10 mL H_3PO_4 (1 M) and 12 mL of diluted glacial acetic acid (5.9 M) were combined together before added slowly over a period of 10 minutes in 1 mL increments. Upon the addition of 8 mL (4 minutes) a white precipitate occurred, pH 8.3. The addition of acid continued, resulting pH 7.7. The mixture was stirred for another 3 minutes, before the precipitate was removed by vacuum filtration, pH 7.8, ~29 g (moist), IR spectrum as observed for **PW_8**.

The precipitate was then suspended in 80 mL water at room temperature for 3 minutes and separated by vacuum filtration, ~20 g (moist), pH 7.1. (The filtrate remained free of any precipitate over the next two weeks, pH 7.4.)

Next, 100 mL of water were heated to 45 °C before the above mentioned precipitate (20.0 g) was added and stirred for 3 minutes. Liquid and remaining solid were separated by vacuum filtration, ~13 g (moist), pH 7.1. In the filtrate a precipitate of fine needles formed on the beaker walls after a week, <1 g, not further characterized (crystal habit like **PW_8** crystals), pH 7.5.

Next, 145 mL of water were heated to 60 °C before the above mentioned filter cake (~13 g) was added and stirred for 2.5 minutes. Liquid and remaining solid were separated by vacuum filtration, ~7 g (moist), IR spectrum as observed for PW_8, pH 7.2. (In the filtrate small needles and well-shaped rectangular crystals formed, <2.0 g, pH 7.4 which were isolated after 2 days.)

Next, 120 mL of water were heated to 60 °C before the above mentioned filter cake (7.0 g) was added which dissolved completely, pH 7.2. Well-shaped rectangular crystals formed after 2 days characterized as γ-PW_{10} by IR spectroscopy, <1 g, pH 7.4.

In the original mother liquor, a precipitate started to form a few hours after the removal of the first precipitate. The voluminous needle-like precipitate (consistent habitus under the microscope) was collected after 12 days and identified as **PW_8** (**XV**) 5.0 g yield ~20%, pH 7.7. IR (cm^{-1}, polyoxoanion area): 1128 (s), 1064 (ms), 1004 (ms), 950 (sh), 929 (vs), 891 (vs), 847 (vs), 823 (vs), 746 (vs), 712 (sh), 689 (s), 624 (m), 595 (m) 570 (sh), 525 (sh), 504 (m).

Preparation of $Cs_{4.5}Na_{2.5}[PO_4W_8O_{26}]\cdot 23H_2O$ (XVI), synthetic method 5. 3.3 g (10.0 mmol) of $Na_2WO_4\cdot 2H_2O$ were dissolved in 50 mL deionized water, pH 9.5. Then 1.25 mL (1 M) H_3PO_4 were slowly added to the stirred solution, pH 8.0. Next 0.4 mL of diluted glacial acetic acid (5.9 M) were added. The pH dropped initially to 7.8 and went back to 8.0 after 10 minutes. Then 1.75 mL of a 3 M CsCl solution were slowly added, pH 8.0. The solution remained clear and was placed on a shelf. Fine needles formed overnight, among them crystals used for structural analysis, CCDC 2596037. The white precipitate was filtered off (0.8 g, yield ~20%) and used for IR, elemental and TGA analyses as well as for ^{31}P solution NMR studies. Elemental analysis (%) found (calculated): Cs 20.0 (19.6), Na 1.9 (1.9), P 1.1 (1.0), W 48.0 (48.2). IR (cm^{-1}, polyoxoanion area): 1129 (s), 1064 (ms), 1002 (ms), 950 (sh), 929 (vs), 890 (vs), 847 (vs), 822 (vs), 746 (vs), 711 (sh), 689 (s), 623 (m), 596 (m) 570 (sh), 525 (sh), 503 (m).

[5] Spectroscopic data of $Cs_7[\gamma\text{-}PO_4W_{10}O_{32}]\cdot xH_2O$ in [69]: IR mineral oil, IR (cm^{-1}, polyoxoanion area): 1086 (ms), 1053 (m), 1023 (m), 965 and 952 (sh), 937 (s), 892 (s), 850 (m), 830 (m), 735 (vs, br).

[6] Elemental analysis was not performed.

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Table 1. Crystallographic data for **XII** and **XVI**

Compound	**XII** CCDC 2596036	**XVI** CCDC 2596037
Empirical Formula	$Cs_4O_{30}PW_8$[a]	$Cs_{17}O_{120}P_4W_{32}$[b]
M_r	2513.33	10186.23
color and habit	colorless needle	colorless needle
crystal system	Orthorhombic	Monoclinic
space group	*Pbcn*	$P2_1/c$
a (Å)	17.2046 (2)	10.3823 (1)
b (Å)	23.5703 (3)	17.4355 (2)
c (Å)	10.25442 (13)	23.4835 (2)
α (deg)	90	90.0
β (deg)	90	90.016(1)
γ (deg)	90	90.0
V Å^3	4158.33 (9)	4251.00 (7)
Z	4	1
Radiation type	MoKα (λ=0.71073Å)	CuKα (λ=1.54185Å)
$D_{calc.}$ g·cm^{-3}	4.015	3.979
T (K)	100	100
Absorption coefficient, mm^{-1}	25.597	67.833
F(000)	4268	4323
Θ (deg)	4.936 – 48.998	3.157 – 64.486
Index ranges	$-20 \le h \le 20$	$-12 \le h \le 12$
	$-27 \le k \le 27$	$-20 \le k \le 20$
	$-11 \le l \le 11$	$-27 \le l \le 27$
measured reflections	100492	91738
independent reflections	3447	7113
observed reflections [I>2σ(I)]	3390	7042
Data/restraints/parameters	3447/211/156	7113/335/252
Goodness-of-fit on F^2	1.040	1.079
R_{int}	0.0595	0.106
R_1,[c] wR_2[c] ($I > 2\sigma(I)$)	$R_1 = 0.0554$, $wR_2 = 0.1414$	$R_1 = 0.1620$, $wR_2 = 0.3442$
R_1,[c] wR_2[c] (all data)	$R_1 = 0.0559$, $wR_2 = 0.1416$	$R_1 = 0.1625$, $wR_2 = 0.3444$
Largest diff peak & hole, e Å^{-3}	10.11 and -4.66	10.63 and -8.10

[a]Elemental analysis was not performed for **XII**. The formula $Cs_7[PO_4W_8O_{26}]\cdot 10H_2O$ was based on single-crystal X-ray analysis.
[b]Chemical formula of **XVI** based on elemental analysis and TGA: $Cs_{4.5}Na_{2.5}[PO_4W_8O_{26}]\cdot 23H_2O$.
[c]$R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c]$wR_2 = [\sum w (F_o^2 - F_c^2)^2 / \sum w (F_o^2)^2]^{1/2}$

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X-ray Structural Analysis. Colorless needle-shaped crystals were mounted on a Hampton cryoloop using Paraton-N oil on a Rigaku XtaLAB Synergy single-crystal diffractometer. The data collection for **XII** was acquired using MoKα radiation at a temperature of 100 K. The determination of the lattice parameters revealed an orthorhombic space group, *Pbcn* within standard deviation three angles at 90°. The final refinements were performed using OLEX2, and refined against F^2 by full-matrix least-squares method with the SHELX program package, which included atomic positions of W, O, P and Cs atoms and their anisotropic thermal parameters. The lattice atoms were found to be disordered. Therefore the SQUEEZE method embedded in PLATON was applied. For **XVI** data collection was accomplished using CuKα radiation at a temperature of 100 K. However, extinction pattern suggested the monoclinic space group $P2_1/c$. Solving the structure in that space group by employing the above mentioned strategy resulted in the structural solution of the polyoxoanion. Attempts of solving the structure of **XVI** using the orthorhombic space groups, such as *Pbcn*, *Pmcm*, $Pmc2_1$ or *P2cm* did not result in any reasonable solution. In case of $P2_1/c$ additional maxima were detected supporting the presence of twinned crystals. Refinement with SHELX in OLEX2 using eight tungsten and one phosphorus positions gave a R_{int}-value of 10.6% (Table 1). The structures in Figures 1, 4, 5 and 6 were generated with Diamond, version 3.2 [78].

3. Results and Discussion

Synthesis. Figure 1 shows the polyhedral representations of the α-isomer of the Keggin structure and the lacunary forms $[A\text{-}\alpha\text{-}PO_4W_9O_{30}]^{9-}$, $[A\text{-}\beta\text{-}PO_4W_9O_{30}]^{9-}$, and $[B\text{-}\alpha\text{-}PO_4W_9O_{30}]^{9-}$. The *A*-isomer is obtained by „removing“ three corner-shared $\{WO_6\}$octahedra. Here, the central $\{PO_4\}$ tetrahedron is still linked to all tungsten atoms. On the other hand, the *B*-isomer displays one terminal oxygen at the central tetrahedron. The *β*-isomer is obtained by rotating a $\{W_3O_{13}\}$ triplet by 60° [79]. The compound $Na_9[A\text{-}\alpha/\beta\text{-}PO_4W_9O_{30}]\cdot nH_2O$ was used to convert the *A*- to the *B*-isomer by thermal treatment at 140 °C for 6 hours. The thermally treated product (called **Δ-PW$_9$**) is a mixture of the *A*- and *B*-isomers [30,47,68,69].

The spectroscopic data confirmed such a mixture indicating a conversion yield of 30-50%. The observed IR band at 1175 cm^{-1} is characteristic for the terminal oxygen's P–O–stretch vibration of ***B*-PW$_9$**. The band at 995 cm^{-1} is typical for a P–O stretch vibration linked to the three $\{W_3O_{13}\}$ groups [47].

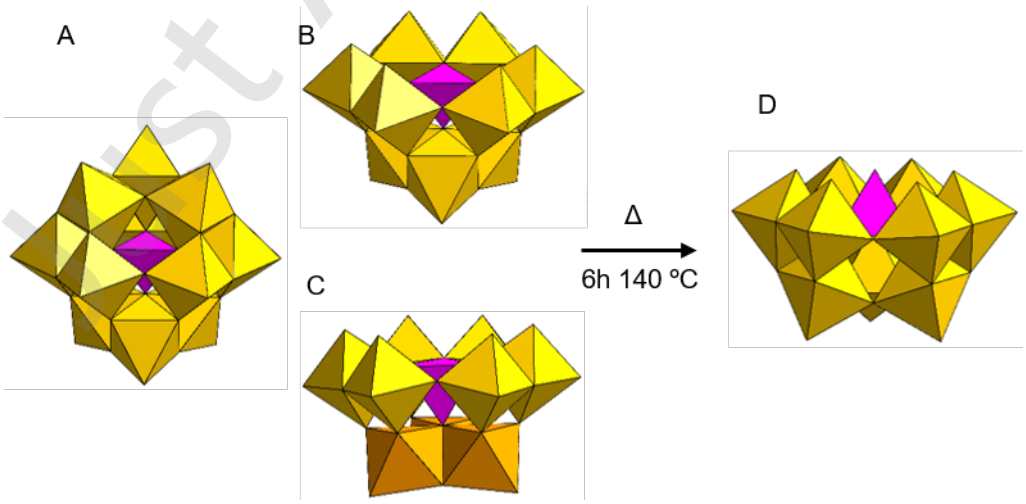

Figure 1. Polyhedral representations of the polyoxoanions ***α*-PW$_{12}$** (A), ***A*-*α*-PW$_9$** (B), ***A*-*β*-PW$_9$** (C), and ***B*-*α*-PW$_9$** (D). Color code: $\{PO_4\}$ (pink),$\{WO_6\}$ (yellow) and rotated $\{W_3O_{13}\}$ triplet (orange).

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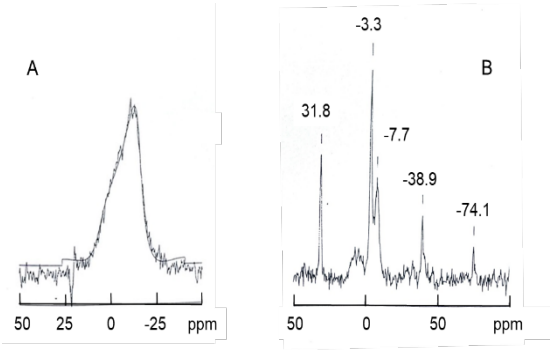

Figure 2. ^{31}P-MAS-NMR spectra of $Na_9[A\text{-}\alpha/\beta\text{-}PO_4W_9O_{30}]\cdot 22H_2O$ (**I**): static (A) and the thermally treated material **Δ-PW₉** (**IX**) ω_{rot} = 5.7 KHz (B).

The ^{31}P-MAS-NMR results also support the presence of the *A*- and *B*-isomers, Figure 2.

***A*-PW₉**: δ_{iso} = -7.7 ppm, Δδ = < 20 ppm,
([69]: δ_{iso} = -8 ppm, Δδ = + 27.5 ppm
***B*-PW₉**: δ_{iso} = -3.3 ppm, Δδ = + 117 ppm,
([69]: δ_{iso} = -3 ppm, Δδ = + 116 ppm)

The thermally treated product **Δ-PW₉** (**IX**) was used without further purification. Its reaction in aqueous solutions with chromium(III) did not produce the desired product of a multiple chromium(III)-substituted Keggin anion. Instead, only the potassium salt of the anion $[\alpha\text{-}PO_4W_{11}O_{35}Cr(OH_2)]^{4-}$ (**PW₁₁Cr**) was isolated and characterized.[7]
The thermally treated material **IX** (**Δ-PW₉** sodium salt) showed a limited solubility in water. Conversion to the lithium salt should enhance the solubility and then favor a multiple substitution with Cr^{3+}. The compound $Li_9[A\text{-}\alpha/\beta\text{-}PO_4W_9O_{30}]\cdot 14H_2O$ (**II**) was prepared via ion exchange and freeze drying and was used as is or in its thermally treated form to react with an aqueous solution of chromium nitrate. Only mono-chromium substituted **PW₁₁Cr** was collected as its potassium salt. Notably, the thermal treatment of **II** did not lead to the *B*-isomer. Consequently, we also prepared the potassium and cesium salts of ***A*-PW₉**. Table 2 lists chemical shift values δ_{iso} for the Li, K, and Cs salts of ***A*-PW₉** which differ slightly compared to the corresponding sodium salt. This is attributed to the nature of the alkali ions [80-82]. A sodium salt of ***A*-PW₉** (**III**) obtained from **II** could still be partially converted to the *B*-isomer. However, the formation of the *B*-isomer was not detected for the thermally treated potassium and cesium salts. The finding is unexpected, significantly more experimental work is needed to assess whether the A → B isomerization of **PW₉** is limited to the sodium salt [83, p.79].

Next, we will discuss the title anion $[PO_4W_8O_{26}]^{7-}$ (**PW₈**). The anion was initially isolated upon adding $Li_9[A\text{-}\alpha/\beta\text{-}PO_4W_9O_{30}]\cdot 14H_2O$ (**II**) and CsCl to water to obtain the cesium salt of ***A*-PW₉**, **synthetic method 1**, see scheme 1. Any occurring precipitates were separated and characterized. The bulk product (>90%) was identified as $Cs_6Li[\alpha\text{-}PO_4W_{11}O_{35}]\cdot nH_2O$ (**V**) plus small quantities of $Cs_8Li[A\text{-}\alpha/\beta\text{-}PO_4W_9O_{30}]\cdot nH_2O$ (**VI**). The compound $Cs_6Na_6[PO_4W_8O_{26}]\cdot 4H_2O$ (**VII**) was isolated after a few days in the mother liquor (composition based on a single-crystal X-ray analysis, see supplementary material) and IR and ^{31}P MAS NMR spectroscopy.

Surprising was the isolation of mainly **PW₁₁**. However, the result confirmed that **PW₉** is not stable in aqueous solution [1, p.67]. In fact the ^{31}P NMR analysis of the eluate of the ion exchange, described by **synthetic method 2**, detected two nearly equally intense signals at –11.53 and 2.3 ppm, corresponding **PW₁₁** and free phosphate, see Figure S12 [1, pp.66,84,85]. Noteworthy is our observation that the sodium **III** and potassium **IV** salts of **PW₉** were obtained following scheme 1 when substituting CsCl. Upon addition of either NaCl or KCl initially no precipitation occurred. It took a few minutes before the precipitation started. Clearly the interaction of Na^+ and K^+ with **PW₁₁** are different compared to Cs^+. The large cesium cation electrostatically bonds to **PW₁₁** leading to the immediate formation of a precipitate. For sodium and potassium only a hydrogen bonded ion-pairing is observed [86] and hence no **PW₁₁** precipitate. However, we did obtain precipitates of **PW₉** after a certain induction period. Here, the interaction of hydrated Na^+ and K^+ "reversed" **PW₁₁** back to **PW₉**. Helpful to understand this phenomenon is the comparison of charge density (charge/number of atoms) and charge-to-metal ratio (q/M) of **PW₁₁**: -7/51 = **-0.137** and 7/11 = **0.636**, compared to **PW₉**: -9/46 = **-0.196** and 9/9 = **1**. The larger values for both terms support a stronger interaction of Na^+ and K^+ with **PW₉** rather than with **PW₁₁** [87]. Also, the solution in scheme 1 or the ion exchange eluate in **synthetic method 2** still contained free phosphate available to react with any "released" tungstate from **PW₁₁**.

[7] IR data for $K_4[\alpha\text{-}PO_4W_{11}O_{35}Cr(OH_2)]\cdot nH_2O$, KBr disc: 1088 (m), 1059 (m), 974 (s), 890 (s), 800 (vs), 675 (sh), 593 (sh), 510 (s), 386 (sh), 369 (s) [64].

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Table 2. Tensor data δ_{iso} and $\Delta\delta$ (^{31}P MAS NMR) of salts of nona-, undeca- and dodecatungstophosphates, η ~0

Compound	**δ_{iso} / ppm ($\Delta\delta$ / ppm) No thermal treatment**	**δ_{iso} / ppm ($\Delta\delta$ / ppm) Treated at 140 °C for 6 h**
$Na_9[A\text{-}\alpha/\beta\text{-}PO_4W_9O_{30}]\cdot 22H_2O$	-7.3 (-20)	-7.7 (< -20) ***A*-PW$_9$** -3.3 (+117) ***B*-PW$_9$**
$Na_9[A\text{-}\alpha/\beta\text{-}PO_4W_9O_{30}]\cdot 22H_2O$ obtained from Li-salt	-7.1 (-20)	-8.5 (< -20) ***A*-PW$_9$** -3.3 (+120) ***B*-PW$_9$**
$Li_9[A\text{-}\alpha/\beta\text{-}PO_4W_9O_{30}]\cdot 14H_2O$	-9.7 (< -30)	-11.7 (< -20)
$K_9[A\text{-}\alpha/\beta\text{-}PO_4W_9O_{30}]\cdot nH_2O$	-7.1 (-19)[8]	-9.2 (< -20)
$Cs_8Li[A\text{-}\alpha/\beta\text{-}PO_4W_9O_{30}]\cdot nH_2O$	-8.9 (-19)	-8.6 (< -20) ***A*-PW$_9$**
$Cs_6Li[\alpha\text{-}PO_4W_{11}O_{35}]\cdot nH_2O$	-12.8 (+25)	
$Cs_3[\alpha\text{-}PO_4W_{12}O_{36}]\cdot nH_2O$	-15.7 (0)	
$H_3[\alpha\text{-}PO_4W_{12}O_{36}]\cdot nH_2O$	-15.7 (0)	

Start	$Li_9[A\text{-}\alpha/\beta\text{-}PO_4W_9O_{30}]\cdot 14H_2O$
↓	+ H_2O, pH 8.1, 25 °C,
↓	+ CsCl sol., pH 8.1
4min	$Cs_6Li[\alpha\text{-}PO_4W_{11}O_{35}]\cdot nH_2O$
↓	pH 8.0, 25 °C
35min	$Cs_6Li[\alpha\text{-}PO_4W_{11}O_{35}]\cdot nH_2O$ and $Cs_8Li[A\text{-}\alpha/\beta\text{-}PO_4W_9O_{30}]\cdot nH_2O$
↓	pH 8.3, 5 °C
3hours	$Cs_8Li[A\text{-}\alpha/\beta\text{-}PO_4W_9O_{30}]\cdot nH_2O$
↓	pH 8.3, 25 °C
> 2 days	$Cs_{7-x}Na_x[PO_4W_8O_{26}]\cdot nH_2O$

Scheme 1. Reaction sequence after addition of $Li_9[A\text{-}\alpha/\beta\text{-}PO_4W_9O_{30}]\cdot 14H_2O$ and CsCl to water.

Based on the 1995 results we continued our studies in 2026. As mentioned in the experimental section we simplified the original method and eliminated the freeze-drying step, see **synthetic method 2**. The system still behaved as outlined in scheme 1 and produced as a minor product colorless fine needles. These were isolated and analyzed by IR and single-crystal X-ray structural analysis, and confirmed to be the cesium salt of $[PO_4W_8O_{26}]^{7-}$ (**XII**).

Next, we approached the direct synthesis of **PW$_8$**, see **synthetic methods 3-5**. The cesium salt of **PW$_8$** can be produced in good yields. However, a number of critical steps need to be considered.

Following the original synthesis a pH value around 8 seemed favorable. However, when conducting the synthesis according to the formal stoichiometric equation the final pH was 7.3. **PW$_8$** was identified by IR spectroscopy, but for process optimization other conditions were chosen.

$$16Na^+ + 8WO_4^{2-} + PO_4^{3-} + 12H^+ + 9OAc^- \rightarrow [PO_4W_8O_{26}]^{7-} + 16Na^+ + 9OAc^- + 6H_2O \quad (1)$$

Further experiments were conducted using a lesser quantity of acetic acid to obtain a pH around 8. **Synthetic method 3** uses 12.5% less acetic acid providing a pH of 7.7. **PW$_8$** was formed in good quantities but attempts to purify the material and obtain larger crystals through recrystallization were unsuccessful. Of concern was also that the addition of CsCl could precipitate any other formed polyoxoanion. For instance, the observed initial precipitate by **synthetic method 3** showed three strong IR bands above 1000 cm^{-1} at a ratio 1:2:1 indicating a mixture of compounds, potentially a combination of the salts of **PW$_8$** and **PW$_9$**, see Figure S7.

[8] Chemical shift of -7.0 ppm ^{31}P MAS NMR reported in [83]

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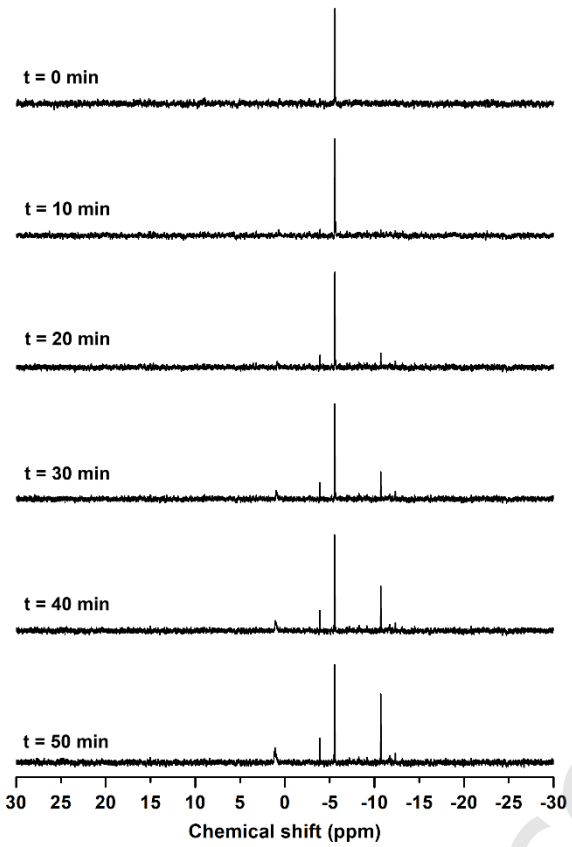

Figure 3. Time-dependent ^{31}P NMR spectra of **XVI** recorded immediately after dissolution in water/D_2O. Over a period of 50 min (top to bottom), the decomposition of the **PW_8** polyoxoanion is shown. After 50 min, four major resonances are observed at δ = 1.10, -3.91, -5.55, and -10.71 ppm.

Synthetic method 4 used only 75% of the stoichiometric acetic acid amount and a lower cesium chloride quantity which was added at the start. Now the initial precipitate appeared already as a relatively pure form of PW_8. However, attempts to grow larger crystals through recrystallization failed again. Most notably was the formation of well-shaped rectangular crystals, which were identified as ***γ*-PW_{10}** by IR and X-ray analysis (fragmented data set of phosphorus and tungsten positions).

Finally, the acetic acid amount was reduced to 20% and only a small amount of cesium chloride was added at pH 8, **synthetic method 5**. The quantity of CsCl was determined in side experiments to ensure the solution would stay clear upon all cesium chloride had been added to foster slow crystal growth. The yield of this procedure for $Cs_{4.5}Na_{2.5}[PO_4W_8O_{26}]\cdot 23H_2O$ (**XVI**) was at least 20%.

All methods showed that PW_8 formed rather easily around pH 8 but would partially decompose during recrystallization. In fact, when dissolving PW_8 one can already observe its instability. Figure 3 shows the ^{31}P NMR solution spectra of **PW_8** recorded in water over a period of 50 minutes. The observed chemical shift of - 5.55 ppm is in good agreement with our solid state ^{31}P NMR data [δ_{iso} = (-5.5 ± 0.5) ppm] which will be discussed later on. The instability is not surprising considering the structure of the anion and the presence of two fivefold-coordinated tungsten atoms.

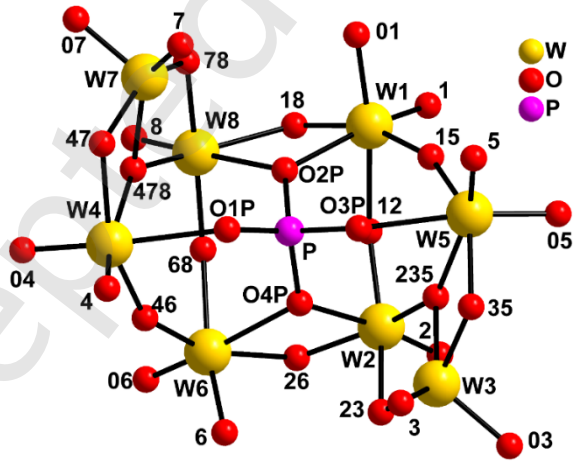

Figure 4. Ball-and-stick representation of $[PO_4W_8O_{26}]^{7-}$. Color code: P (pink), W (yellow), and O (red).

The ball-and-stick representation of the anion $[PO_4W_8O_{26}]^{7-}$ is given in Figure 4. The single-crystal X-ray analysis of **XII** and **XVI** revealed a Keggin fragment. It is built up by six $\{WO_6\}$ octahedra linked to the central $\{PO_4\}$ tetrahedron arranged as two $\{W_3O_{15}\}$ moieties of three corner-sharing $\{WO_6\}$ octahedra each (W1–W2–W5 and W4–W6–W8), which are edge-linked to another. This "half" of the *α*-Keggin structure is capped by two distorted square pyramids (W3 and W7) displaying two terminal oxygen atoms each (O3, O03 and O7, O07). Using the ball-and-stick drawing one can recognize the $\{WO_5\}$ pyramids located at the 4:30 and 10:30 o'clock positions. Alternatively, the 1:30 and 7:30 o'clock locations are occupied. Both chiral isomers are connected in the lattice by cesium cations, Figures 5 and 6. The requirement of a perfect alternating placement of the isomers in the solid state likely also contributed to the difficulties to obtain crystals without disorder.

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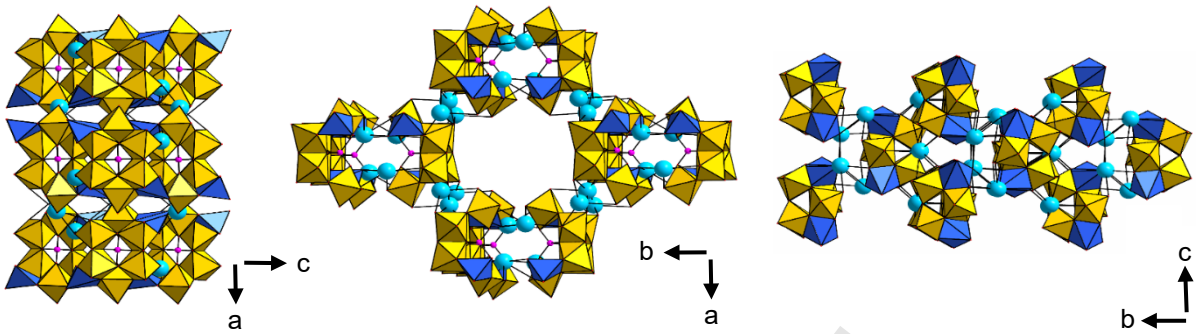

Figure 5. Packing view of **PW_8** and cesium cations in the crystal lattice. The water molecules were omitted for clarity. Color code: Phosphorus pink, cesium light blue, {WO_5} (blue) and {WO_6} (yellow).

The single crystal X-ray analysis showed that the **PW_8** polyoxoanion displays a concave molecular surface. Cesium cations occupy positions between neighboring **PW_8** units and link them through multiples Cs-O bonds. Cs-O distances range from 3.0-3.8 Å. These interactions stabilize the structural packing and the relative orientations of the neighboring **PW_8** polyoxoanions. Figure 5 demonstrates how discrete and geometrically anisotropic **PW_8** units were organized into ordered supramolecular framework through the Cs^+ and **PW_8** polyoxoanion interactions.

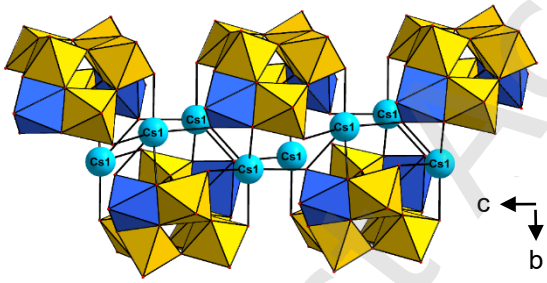

Figure 6. Linkage between cesium cations and PW_8 polyoxoanions. Color code: {WO_5} (blue) and {WO_6} (yellow).

A number of stable Keggin fragments are known with 9, 10, or 11 tungsten atoms [1, pp.58-68,88]. However, little is known of stand-alone fragments with fewer than nine tungsten atoms. The reported anion $[PO_4W_8O_{26}]^{7-}$ provides insight into the early formation stage of a Keggin anion. The addition of two five-fold coordinated tungsten atoms led to a stable arrangement of high symmetry. It follows Lipscomb's rule that no hetero- or isopolyoxoanion should contain addenda {MO_6} octahedra with more than two unshared oxygen atoms [1, pp.19,89]. A fivefold {WO_5} coordination is rare among POMs. A first example was reported for $[As_2W_{21}O_{69}(H_2O)]^{6-}$ [90]. In this structure only one terminal oxygen atom was identified for each of the two quadratic square pyramids.

The herein reported structure of $[PO_4W_8O_{26}]^{7-}$ completes a "puzzle" published by Domaille et al. in 1990 [69]. The authors had reported the formula $(Cs_{13-x}H_x[PW_8O_{33}])_n$ based on chemical analysis as well as spectroscopic IR and solid-state ^{31}P NMR data, but could not provide a structural solution. Figure 7 shows the IR spectra of the cesium and sodium salts of the newly reported anion $[PO_4W_8O_{26}]^{7-}$, as well as $[A\text{-}\alpha/\beta\text{-}PO_4W_9O_{30}]^{9-}$, $[\gamma\text{-}PO_4W_{10}O_{32}]^{7-}$, and $[\alpha\text{-}PO_4W_{11}O_{35}]^{7-}$, all displaying characteristic fingerprints. The three strong P-O stretching vibrations of **PW_8** at 1129, 1064 and 1002 cm^{-1} and multiple O-P-O deformation vibrations at 600-400 cm^{-1} as well as W-O stretching vibrations match very well with the reported results by Domaille et al. [69, p.102]. Both, PW_8 and γ-PW_{10} exhibit three very characteristic P−O stretching vibrations. Noteworthy is the significant shift to higher frequency for two of these vibrations in **PW_8** demonstrating stronger P-O bonds due to fewer tungsten atoms compared to **γ-PW_{10}** [93]. The review of W-O and P-O bond lengths and O-P-O angles (°) of **XII** and **XVI** shows commonly observed values, Table 4.[9,10,11] [1, pp.24,66,94].

[9] O_i: belonging to the central tetrahedron, O_c: corner-sharing oxygen, O_e: edge-sharing oxygen, O_t: terminal oxygen atom.

[10] Average distances [Å] in $H_3[\alpha\text{-}PO_4W_{12}O_{36}]\cdot 3H_2O$ [94]: P-O_i 1.53(1), W−O_i 2.43(1), W−O_c 1.90(1), W−O_e 1.91(1), W−O_t 1.70(1), W−W_c: 3.75(1)-3.98(1), W−W_e: 3.35(1).

[11] Spectroscopic data of $(Cs_{13x}H_x[PW_8O_{33}])_n$ in [69]: IR mineral oil, 1127 (s), 1060 (s), 1000 (m), 950 (m), 934 (s, +sh), 893 (s), 846 (m), 816 (m), 684 (s). Solid state ^{31}P NMR MAS single line at -5.1 ppm.

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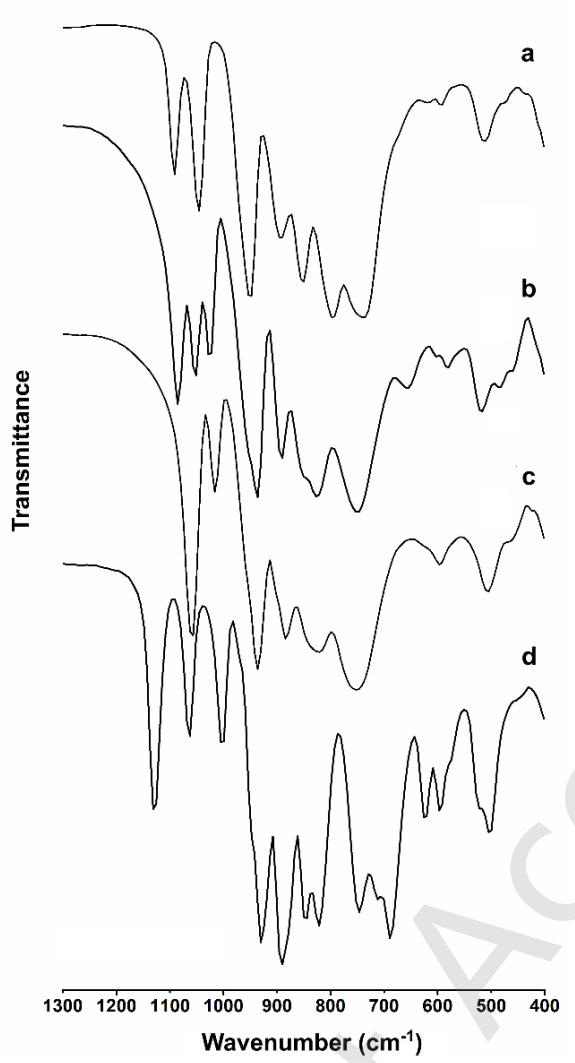

Figure 7. IR spectra of ***α*-PW$_{11}$ (XI)** a, ***γ*-PW$_{10}$ (XII)** b, ***A*-PW$_9$ (I)** c and **PW$_8$ (XVI)** d. Ranges of stretching vibrations P-O 1150-1000 cm^{-1}, W-O$_t$ 1000-960 cm^{-1}, W-O$_c$-W 890-850 cm^{-1}, W-O$_e$-W 800-760 cm^{-1} [91,92].

The bond valence sum (BVS) calculations [95] for **XII** were observed to be in the range of 5.6 – 6.3, confirming the oxidation state of the five- and six-fold coordinated tungsten atoms to be +6, see Table S1. The BVS calculations for **XVI** were found to be in the range of 5.5 – 6.5, also indicating an oxidation state of +6 for the five- and six-fold coordinated tungsten atoms, see Table S2. The disorder present in **XVI** led to a subtle deviation of the BVS calculations for the tungsten atoms in **XVI**.

Table 4. Selected bond lengths, distances (Å) and O-P-O angles (°) of **XII** and **XVI**. Values for five-fold coordinated tungsten in bold.

W1O1	1.733(15)	W1O001	1.747(14)	W1O12	1.854(13)
W1O14	2.125(13)	W1O4^{i}	1.971(12)	W1O1P	2.208(13)
W2O2	1.769(14)	W2O02	1.762(15)	W2O12	1.970(13)
W2O23	1.931(14)	W2O234	2.184(12)	W2O2P^{i}	2.195(13)
W3O3	**1.753(3)**	**W3O03**	**1.786(15)**	**W3O23**	**1.942(14)**
W3O234	**2.050(12)**	**W3O34**	**1.919(13)**	W4O4	1.854(12)
W4O04	1.731(14)	W4O14	1.809(13)	W4O234	1.960(12)
W4O34	1.987(13)	W4O1P^{i}	2.368(13)		
P1O1P	1.558(14)	P1O2P	1.549(13)	P1O2P^{i}	1.549(13)

O1P-P1-O2P	109.2(7)	O1P-P1-O1Pi	107.1(11)
O1P-P1-O2Pi	110.4(7)	O1Pi-P1-O2P	110.4(7)
O1Pi-P1-O2Pi	109.2(7)	O2P-P1-O2Pi	110.6(10)

W1O1	1.737(17)	W1O001	1.838(19)	W1O12	2.04(5)
W1O15	1.88(4)	W1O18	1.77(5)	W1O2P	2.20(3)
W2O2	1.737(18)	W2O12	1.86(5)	W2O23	1.90(4)
W2O235	1.89(4)	W2O26	1.86(3)	W2O4P	2.22(3)
W3O3	**1.68(3)**	**W3O003**	**1.81(4)**	**W3O23**	**2.10(3)**
W3O003	**1.8112(4)**	**W3O35**	**1.9059(5)**	W4O4	1.63(4)
W4O04	1.695(18)	W4O46	1.98(4)	W4O47	2.04(4)
W4O478	2.16(5)	W4O1P	2.26(3)	W5O5	1.71(5)
W5O05	1.76(4)	W5O15	1.92(4)	W5O235	2.17(4)
W5O35	1.99(4)	W5O3P	2.17(4)	W6O6	1.80(3)
W6O06	1.796(14)	W6O26	2.03(3)	W6O46	1.89(4)
W6O68	2.13(3)	W6O4P	2.29(3)	**W7O7**	**1.81(3)**
W7O07	**1.701(19)**	**W7O47**	**1.96(5)**	**W7O478**	**2.03(5)**
W7O78	**1.93(3)**	W8O8	1.73(6)	W8O18	2.09(5)
W8O478	1.99(5)	W8O68	1.86(3)	W8O78	1.93(3)
W8O2P	2.30(3)	P1O1P	1.45(3)	P1O2P	1.60(3)
P1O3P	1.57(4)	P1O4P	1.64(3)		

O1P-P1-O2P	110.4(18)	O1P-P1-O3P	110.2(19)
O1P-P1-O4P	115.9(19)	O2P-P1-O3P	114.1(19)
O2P-P1-O4P	102.8(17)	O3P-P1-O4P	103.4(19)

XII W−O$_i$: 2.20(4)-2.37(2) Å; W−O$_c$: 1.81(2)-2.13(2) Å; W−O$_e$: 1.91(2)-2.19(1) Å; W−O$_t$: 1.73(2)-1.97(2) Å, P−O$_i$: 1.55(2)-1.56(2) Å; O-P-O: 107(1)-111(1) ° and **XVI** W−O$_i$: 2.17(4)-2.30(3) Å; W−O$_c$: 1.86(5)-2.13(3) Å; W−O$_e$: 1.77(5)-2.17(4) Å; W−O$_t$: 1.63(4)-1.83(2) Å, P−O$_i$: 1.45(3)-1.64(3) Å; O-P-O: 103(2)-116(2) °.

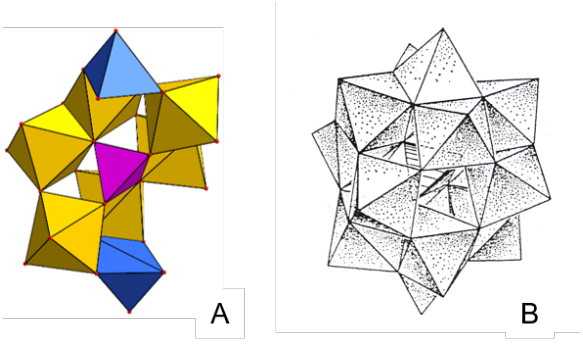

Figure 8. Polyhedral representations of [PO$_4$W$_8$O$_{26}$]^7 (A) and [PO$_4$V$_{14}$O$_{38}$]$^{9-}$ (B) [1, p.77, with permission from the estate of Michael T. Pope]. Color code: {PO$_4$} (pink), {WO$_5$} (blue), and {WO$_6$} (yellow).

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Lastly, “capping” a Keggin anion with two five-fold coordinated atoms was also observed for the anions $[PO_4V_{14}O_{38}]^{9-}$ and $[VO_4V_{14}O_{38}]^{9-}$. Here, $\{VO_5\}$ pyramids occupy the same positions as the $\{WO_5\}$ pyramids in **PW₈**, Figure 8 [96,97].

Figure 9 shows the ^{31}P-MAS-NMR spectra of polycrystalline powders of **VII** as well its simulated graph and calculated parameters. The spectra confirm the C_2 symmetry of PW_8. The high value of the asymmetric parameter η confirms the large distortion from the axial symmetry of phosphorus atoms. The determined isotropic value of the chemical shift δ_{iso} fits well the series of evaluated complete and lacunary phosphorus-containing Keggin anions (data in ppm):

***B*-PW₉** -3.2; **PW₈** -5.5; ***A*-PW₉** -7.7;
***α*-PW₁₁** -12.8; ***α*-PW₁₂** -15.7.

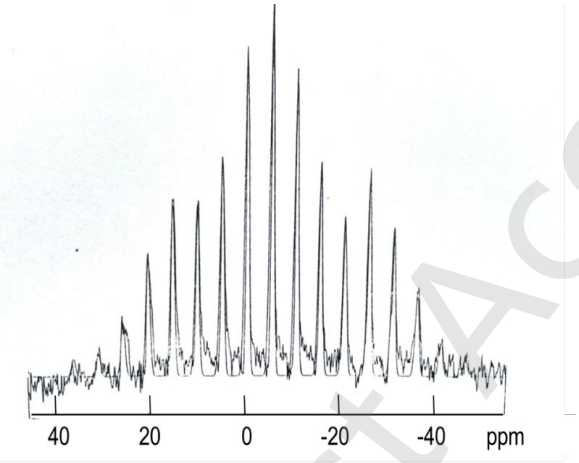

Figure 9. Measured (ω_{rot} = 840 Hz) and simulated ^{31}P-MAS-NMR spectra of **VII**, δ_{iso} = (-5.5 ± 0.5) ppm, Δδ = (50.0 ± 2.0) ppm, and η = 0.95 ± 0.05.

The high-field shift follows the trend of an increasing number of $\{WO_6\}$ octahedra surrounding the central $\{PO_4\}$ tetrahedron. The anion ***B*-PW₉** with one terminal oxygen atom at the $\{PO_4\}$ tetrahedron shows the smallest shift relative to 85% phosphoric acid.

4. Conclusions

In the presented study we reported our findings on the system of alkali cations and ***A*-PW₉**. Our experiments showed that the partial conversion of the *A*- to the *B*-isomer only occurs for the sodium salt. Attempts to isolate a cesium salt of ***A*-PW₉** surprisingly led to the formation of the new anion $[PO_4W_8O_{26}]^{7-}$ as a minor product.
We developed a synthetic method to prepare $[PO_4W_8O_{26}]^{7-}$ in good yields in a one-pot synthesis in which acetic acid and cesium chloride were added to an aqueous solution of sodium tungstate and phosphoric acid. The comprehensive characterization of $Cs_{4.5}Na_{2.5}[PO_4W_8O_{26}]\cdot 23H_2O$ included also its single-crystal X-ray diffraction. The analysis revealed six $\{WO_6\}$ octahedra linked to the central $\{PO_4\}$ tetrahedron arranged in two double-edge linked $\{W_3O_{13}\}$ moieties of corner-sharing $\{WO_6\}$ octahedra. This "half" of the *α*-Keggin anion is capped by two distorted $\{WO_5\}$ square pyramids carrying two terminal oxygen atoms each. This analysis finally provides the detailed structure of the **PW₈** polyoxoanion which had been detected by other researchers before. Furthermore, the newly characterized Keggin fragment provides insight into the early formation stage of the Keggin anion.

Data availability

The original single crystal data (CCDC 2596036 and 2596037). 2026 Bond valence calculations, TGA, IR spectra, ^{31}P NMR solution spectra and original 1995 information are provided in the supporting material.

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Declaration of Competing Interest

The authors have no competing interests to declare. The author Ulrich Kortz was a guest editor of a special issue and an advisory board member of this journal, but he was not involved in the peer review of this article.

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Author contribution statement

K.W.: Synthesis, data analysis, manuscript writing. H.-J.L: Technical discussion, editing. R.P.: Original X-ray analysis - single crystal selection, film data and analysis. J.F.: Original single crystal data collection and analysis, solving of twin structure. A.-R.G.: Collection of ^{31}P-MAS NMR data and analysis, technical discussion, editing. A.S.: Single crystal selection, analysis and validation, editing, technical discussion. S.K.: ^{31}P solution NMR and IR studies; elemental and TGA analysis, editing, literature search, technical discussion. U.K.: Technical discussion and laboratory support.

K.W., H.-J.L., A.-R.G., A.S. and S.K. have approved the final manuscript.

Use of AI statement: None

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Knut Wassermann received his doctoral degree in Chemistry from Humboldt University of Berlin, Germany (mentor Hans-Joachim Lunk) in 1995: *Synthesis and characterization of chromium(III)-containing polyoxoxometalates.* He spent four years in Michael Pope's laboratory at Georgetown University in Washington, DC before joining industrial research at Engelhard Corporation, later BASF Corporation. There he developed catalysts for automotive applications and led international teams supporting the development of emission control systems meeting stringent global emission standards, until retiring in 2024.



Hans-Joachim Lunk earned his M.S. degree at Humboldt University of Berlin in 1964 and his doctoral thesis from the Department of Chemistry, Moscow Lomonosov State University/Soviet Union in 1968: *Study of several aquo- and heteropolytungstates*. From 1968-1995 he worked at Humboldt University, first as an assistant professor and from 1985 onward as an associate professor. In 1982 Dr. Lunk defended his habilitation thesis: *On the role of dope elements and heteropoly compounds during tungsten powder production*. In May 1995, he moved to the United States joining OSRAM Sylvania's Chemical and Metallurgical Division (since 2008 Global Tungsten & Powders Corp.) in Towanda, PA working in research until his retirement in 2013.



Rosemarie Palm worked for over 30 years at the Institute for Inorganic and Analytical Chemistry at the Free University in Berlin. In the mid-sixties she became the technical assistant to Professor Joachim Fuchs. She was instrumental in carrying out new preparations and characterizations, including spectroscopic and initial diffraction measurements. Back then, this involved determining cell parameter with X-ray film methods. In her career she had developed a broad tool box how to grow and handle crystals which made her become the go-to-person in the department.



Joachim Fuchs (1924-2002) was a student of Karl-Friedrich Jahr. In 1967 he defended his habilitation thesis: *On the formation of polynuclear compounds by solvolysis of metal alkoxides in the presence of bases, salts, or acids* and became full professor for Inorganic Chemistry at the Free University Berlin two years later. He advanced the knowledge and understanding in the area of isopoly- and heteropolyoxometalates with major contributions to syntheses in aqueous solutions and organic solvents as well as structural characterization by single-crystal X-ray analysis and spectroscopic methods. He retired from official duties in 1989 but continued to support multiple research groups with his crystallographic work until 2002.



Arnd-Rüdiger Grimmer received his doctorate in Chemistry at Humboldt University of Berlin (HUB) in 1968 and obtained his habilitation in 1988 for *Contributions to the development of high-resolution solid-state NMR and their application to inorganic Chemistry*. In 1962 he set up the Department for solid-state NMR at the Academy of Sciences of the GDR in Berlin (since 1992 part of HUB) and remained its head until his retirement in 2004. He was a visiting professor at ESPCI in Paris, France and on behalf of IAEA in Havanna, Cuba as well as an extensive collaborator with groups in the Soviet Union, Estonia, United Kingdom and France. His primary scientific interest lies in the measurement and interpretation of chemical shift anisotropy in solids.

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Sahar Khandan received her Ph.D. in Chemistry from Constructor University, Bremen, Germany, in 2026, under the supervision of Prof. Ulrich Kortz in the POM Lab. Her doctoral thesis was entitled *Peroxo-Polyoxometalates of d- and f-block elements: Synthesis, structures and properties.* She is currently a postdoctoral researcher at Constructor University. Her research interests focus on the synthesis and characterization of polyoxometalates, with particular emphasis on their structural diversity, solution behavior, and catalytic applications.



Anupam Sarkar received his Ph.D. in Chemistry from Indian Institute of Science Bangalore, India in 2023, under the supervision of Prof. Srinivasan Natarajan. His doctoral thesis was entitled *Metal-Organic Framework (MOF) compounds: Synthesis, structure and catalytic studies*. He joined Prof. Kortz' laboratory in January 2024 as a postdoctoral fellow. His primary research interests focus on the synthesis, structural characterization, X-ray crystallography and catalytic studies of polyoxometalates and polyoxo-noble-metalates as well as polyoxo-noble-metalate-based metal-organic frameworks.



Ulrich Kortz (1963-2026) was a Chemistry professor at Constructor University (formerly Jacobs University) in Bremen, Germany since 2002. He obtained a Ph.D. at Georgetown University in Washington, DC under the supervision of M. T. Pope (1995), followed by postdoctoral research stays at the University of Florence, Italy (D. Gatteschi) and the University of Versailles, France (G. Hervé, A. Tézé). In 1997 he started his independent academic career at the American University of Beirut (AUB) in Lebanon. His research interests included synthetic inorganic and organometallic chemistry, structural chemistry, polyoxometalates, polyoxo-noble-metalates, MOFs, catalysis, magnetism, and electrochemistry.

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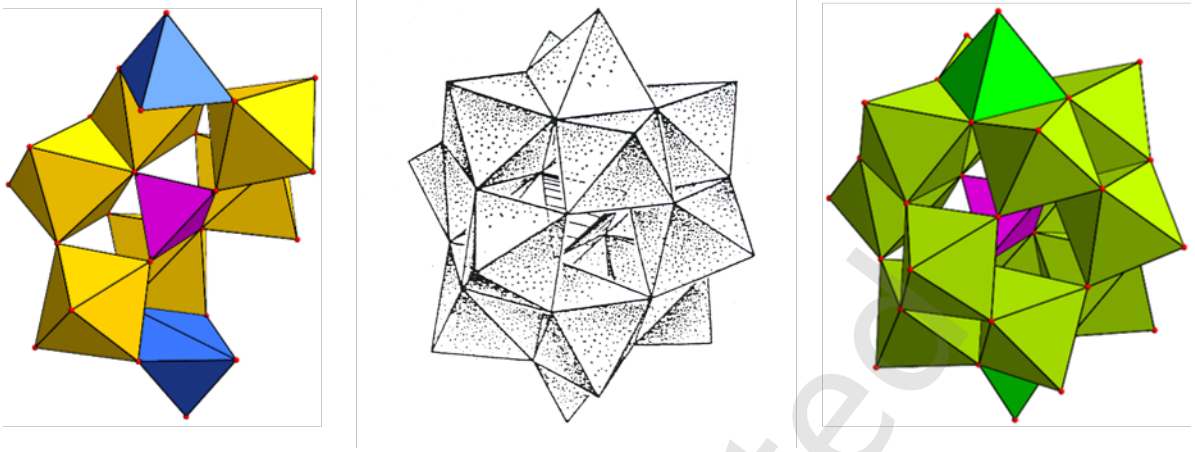

The new Keggin fragment $[PO_4W_8O_{26}]^{7-}$ with two five-fold coordinated $\{WO_5\}$ units (blue) - a structural motif also seen in the double-capped anions $[PO_4V_{14}O_{38}]^{9-}$ and $[VO_4V_{14}O_{38}]^{9-}$, $\{VO_5\}$ units (light green).

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