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Quick and selective synthesis of $Li_6[\alpha\text{-}P_2W_{18}O_{62}]\cdot 28H_2O$ soluble in various organic solvents†

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Herein we report the synthesis of α-Dawson type POM, $Li_6[\alpha\text{-}P_2W_{18}O_{62}]\cdot 28H_2O$, directly from the use of Li_2WO_4 as the tungstate source. The salt obtained was soluble not only in water but also in a range of polar and non-polar organic solvents, such as benzene.

Polyoxometalates (POMs) are anionic molecular metal-oxides that consist of early transition metals such as molybdenum, tungsten and vanadium. Owing to their stability and high redox activity, POMs have been widely explored as oxidation catalysts. Among them, several types of POMs exhibit characteristics of water splitting under irradiation with visible light.[1] In addition, their structural diversity such as unique molecular shape at the nano scale and high nuclearities (capsule, ring, fullerene shape and lemon) and their physical properties[2] have allowed the development of functional molecular materials.[3–7] Examples are shown by single molecular magnets (SMMs) where POM clusters act as unique inorganic ligands,[8,9] and application in battery materials where POM clusters exhibit multiple-stage redox reactions, acting as a so-called 'electron-sponge'.[10]

In addition, POM cluster anions have been utilized in a wide range of advanced functional materials,[11,12] especially the Keggin- and Dawson-type clusters as well as lacunary-type clusters which are prepared by controlling the solution pH. As shown before, these types of lacunary clusters have been used as inorganic ligands that yield unique metal configurations, structures and solubility, when compared with organic ligands. Moreover, lacunary clusters provide a platform for the construction of a variety of organic/inorganic composites. Organic moieties can be grafted *via* an addenda organometallic compound on lacunary clusters. Self-assembled nano structures, surfaces and hybrid molecules have been reported *via* powerful covalent binding with POMs.

In these pioneering studies, Keggin- and Dawson-type clusters were widely utilized because of their well-investigated structure as well as their properties and easy synthesis in the case of Keggin-type clusters. In contrast to the Keggin-type POMs (some of which are commercially available), Dawson-type POMs need a lot of time and effort to prepare.[13,14] This in depth analysis of the $[P_2W_{18}O_{62}]^{6-}$ was highlighted and summarized by Finke in 2008[15] and a recipe and synthetic procedure reported by Nadjo in 2004 has been widely used[16] by which the yield was improved to over 90%. However, this method is still complex and time consuming, requiring 4–5 steps and 8–12 days for the purified sample, due to the difficulty in purification of the structural isomers of the α- and β-type clusters that take 72 h for the isomerization reaction, followed by separation *via* crystallization. In this work, we have successfully improved the time consuming reaction from 8–12 days to 1–2 days with high isometric purity of the $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$ cluster. This was achieved by employing a tungstate source of lithium tungstate changed from sodium tungstate used in the traditional synthesis, leading to $Li_6[\alpha\text{-}P_2W_{18}O_{62}]\cdot 28H_2O$ as single crystals.

From time-dependent characterization of the reaction process by ^{31}P-NMR, we revealed that our reaction leads to the α-isomer with high isomeric purity (>90%), even in the reaction process without formation of other hetero-POMs. In addition, our Dawson lithium salt has a higher solubility than the potassium salt, and is even able to be dissolved in low polarity organic solvents such as benzene and this opens up a vast number of additional applications.

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† Electronic supplementary information (ESI) available: ^{7}Li-NMR spectrum, ^{31}P-NMR spectrum, IR spectrum and TG curve for $Li_6[\alpha\text{-}P_2W_{18}O_{62}]$. CCDC 933195. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt51120k

Lithium tungstate (Li_2WO_4, 7.64 g, 0.029 mol) was dissolved in boiling water (12 mL in a 50 mL round-bottomed flask) and stirred for 10 min. Then, 16 g of 85% phosphoric acid (H_3PO_4) was added slowly. After refluxing for 2 h followed by cooling to 60 °C, lithium chloride (LiCl, 10 g) was added to the lukewarm solution, followed by refluxing for 1 h, yielding a precipitate. The precipitate was first recrystallized from methanol and then subsequently recrystallized from 30 mL LiCl solution (3.28 M). If a slight white precipitate persists, it is filtered off. Further recrystallization is required for single crystals, giving colorless block crystals (yield: 87% based on tungsten). The existence of lithium ions was validated by ^{7}Li-NMR of a 0.2 M deuterium oxide solution of the compound measured with a deoxidized 0.3 M lithium chloride–methanol solution as the reference.† A singlet peak was observed at 0.006 ppm which signifies the presence of solvated (in this case, hydrous) lithium ions. In addition, the elemental analysis found: P, 1.48; W, 66.2; Li, 0.76% (calcd: P, 1.26; W, 67.41; Li, 0.85%).

The single crystal X-ray structural analysis at 173 K showed that $Li_6[\alpha\text{-}P_2W_{18}O_{62}]\cdot 28H_2O$ crystallizes in a trigonal system, space group $R\bar{3}m$, a = 15.2104(16), c = 56.239(6) (Å), V = 11 268(2) (Å^3), Z = 6.‡ Crystal structure determination reveals that the crystals contain only the α-isomer of the Dawson cluster as shown in Fig. 1 and packing structures are shown in Fig. 2. We confirmed the isomeric purity by using ^{31}P-NMR where a single peak was observed at −12.89 ppm with weak peaks at −11.38 and −12.17 ppm. They corresponded to those for α (−12.5 ppm) and β (−11.0 and −11.7 ppm) isomers of the $[P_2W_{18}O_{62}]^{6-}$ anion, respectively.[17] The intensity ratios of α-type *vs.* β-type were estimated at 30 : 1,† showing a high isomeric purity of 97% for α-type, which is comparable with that for previous work at 97–99%.[15] The structural framework of the cluster anion is comparable with that previously reported with regard to bond length and angle. The crystals were colorless and bond valence sum calculations showed that all W atoms have an oxidation state of +6, showing that the Dawson cluster is fully oxidized. In addition, BVS values for oxygen atoms were in the range of 1.6–2.1 showing that there are no protonated oxygen ligands. The IR spectrum of this compound was characterized by its preparation as a KBr pellet.† Strong absorption bands were observed for the stretching mode for W–O–W (791 cm^{-1} and 951 cm^{-1}), W=O (980 cm^{-1}) and P–O (1090 cm^{-1}).[17] The bands are typical for the reported $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$ anion.

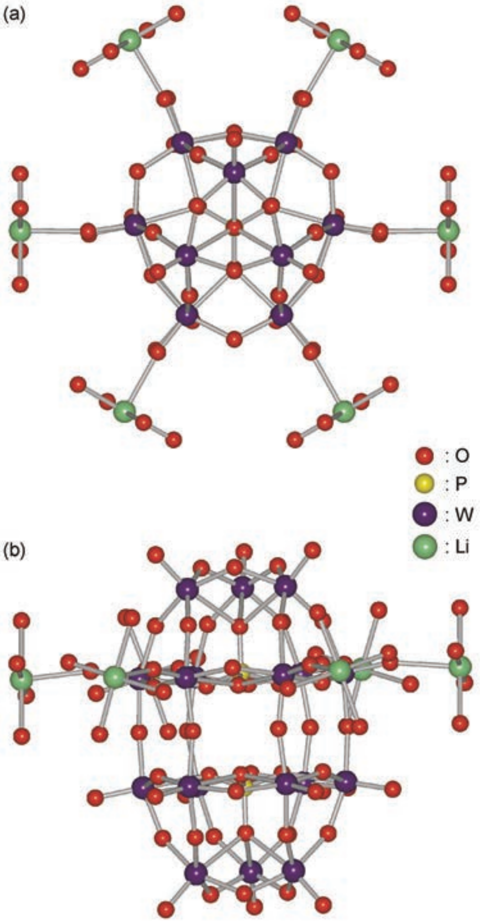

Fig. 1 (a) Top and (b) side views of the structure around $[\alpha\text{-}P_2W_{18}O_{62}]^{-6}$ in the crystal.

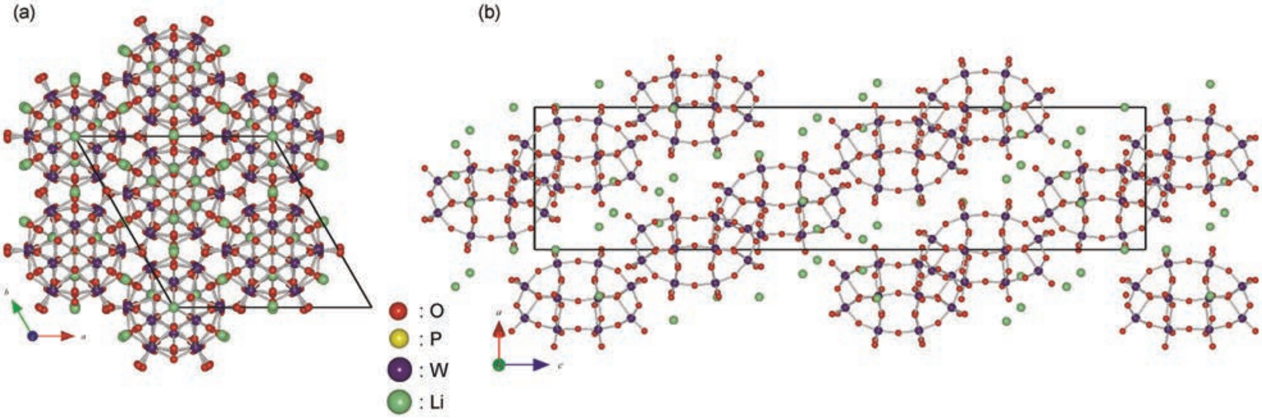

Fig. 2 Crystal packing of $Li_6[\alpha\text{-}P_2W_{18}O_{62}]\cdot 28H_2O$ salt viewed along (a) the c-axis and (b) the b-axis. Crystallization water molecules are omitted for clarity.

As described above, the synthetic procedure for the $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$ anion requires β → α isomerization by refluxing the solution for 72 h as well as purification of the α isomer by crystallization. Thus, even in the method reported by Nadjo, which are the best conditions reported thus far, the whole synthetic procedure takes, in total, 86 hours of reflux (12 h for reaction + 72 h for isomerization + others). However, our procedure decreases it to 3 h. Next, we characterized the reaction process using ^{31}P-NMR in order to reveal contaminations.

The isomeric purity of the resulting product was monitored during the course of the reaction from 20 minutes to 72 hours using ^{31}P-NMR. The purity was almost time-consistent at around 90% and the formation of other hetero POMs, such as Keggin-type and Preyssler-type, was not confirmed. It was suggested that the high isomeric purity in our procedure originates from the fact that the formation of the β-isomer is restricted under the reaction conditions.

In our work, we used Li_2WO_4 as a tungstate source and obtained the $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$ anion. However, a similar reaction starting with Na_2WO_4 gave Preyssler-type $\{P_5W_{30}\}$ as the main product.[18] This indicates that the Preyssler cluster requires the sodium ion as a template for its formation. Although it has similar building blocks to the $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$ anion, the Preyssler cluster $\{P_5W_{30}\}$ encapsulates the sodium ion at the center of the cluster, forming a metal crown ether-like complex. By excluding any sodium template from reaction, the $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$ anion was formed, instead of $\{P_5W_{30}\}$. Also pH is another important key in our recipe. It has been reported that pH < 2 is needed for the synthesis of pure $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$ in high yield.[14]

The research field of acid catalysis is an important subject, and the solubility and reaction selectivity were characterized for various POMs.[3,19,20] In addition to stable redox activity, the high solubility of POMs against a variety of organic solvents has put POMs in a unique position as a class of inorganic compounds. $H_3[PMo_{12}O_{40}]$ can dissolve not only in water, but also in low polarity organic solvents such as ether. These properties are considered to originate from the low charge density of the cluster anion compared with other anionic compounds. Our $Li_6[\alpha\text{-}P_2W_{18}O_{62}]\cdot 28H_2O$ salt also showed high solubility in organic solvents as shown in Table 1. It can be dissolved in acetone (dielectric constant $\varepsilon = 20.7$), ethanol ($\varepsilon = 24.3$), methanol ($\varepsilon = 32.6$), *N*,*N*-dimethylformamide ($\varepsilon = 36.7$), propylene carbonate ($\varepsilon = 64.4$), H_2O ($\varepsilon = 78.5$) and ethylene carbonate ($\varepsilon = 89.6$). In addition, despite the fact that the salt is a purely inorganic compound, it is fairly soluble in low polarity organic solvents, such as benzene ($\varepsilon = 2.3$), chloroform ($\varepsilon = 4.7$), tetrahydrofuran ($\varepsilon = 7.4$) and dichloromethane ($\varepsilon = 8.9$). The solubility is higher than that of potassium salt. The dissolution in low polarity organic solvents of well-defined $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$ anions widens the potential for material application to the POM/organic hybrid.

Table 1 Dielectric constants (ε) of solvents and $Li_6[\alpha\text{-}P_2W_{18}O_{62}]$ and $K_6[P_2W_{18}O_{62}]$ solubility in various solvents

Solvent	$\varepsilon^{21,22}$	$Li_6[P_2W_{18}O_{62}]$/ kg L^{-1}	$K_6[P_2W_{18}O_{62}]$/ kg L^{-1}
Hexane	1.9	Insoluble	Insoluble
Benzene	2.3	1.88×10^{-4}	Insoluble
Chloroform	4.7	1.28×10^{-4}	Insoluble
Tetrahydrofuran	7.4	3.36×10^{-4}	Insoluble
Dichloromethane	8.9	4.16×10^{-4}	Insoluble
Acetone	20.7	1.02	4.90×10^{-3}
Ethanol	24.3	1.61	4.01×10^{-3}
Methanol	32.6	1.39	1.66×10^{-2}
N,*N*-Dimethylformamide	36.7	7.79×10^{-1}	8.92×10^{-3}
Propylene carbonate	64.4[23]	0.205	0.106
Water	78.5	9.31	1.03
Ethylene carbonate	89.6[23]	1.77	0.412

In conclusion, we succeeded in synthesizing the $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$ anion as the lithium salt. The compound formula was assigned as a result of the single crystal X-ray structure analysis and elemental analysis, giving the formula $Li_6[\alpha\text{-}P_2W_{18}O_{62}]\cdot 28H_2O$. All the tungsten atoms are in the highest oxidation state so that the cluster is a hexavalent anion. ^{31}P-NMR characterization revealed that the crystal contains highly pure $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$. Our method requires only 1–2 days for the whole procedure, which is considerably shortened from the 8–12 days required as reported in the previously best method. Our lithium salt was well-defined in its structure and was soluble not only in water and highly polar solvents, but also in less polar solvents such as benzene. Our method using Li_2WO_4 as a tungstate source can promise remarkable improvement of the time-consuming synthesis of the $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$ anion with higher yield, which will accelerate the research, development and diffusion of POM based functional materials.

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Notes and references

‡Data were collected on an X-ray single crystal diffractometer equipped with a CCD detector (Bruker SMART APEX 2 Ultra) with Mo-Kα radiation (λ = 0.71075 Å), and a graphite monochromator by using the SMART software package. Crystal data: $H_{56}O_{90}Li_6P_2W_{18}$, M_w = 4820.66, T = 173 K, trigonal, space group $R\bar{3}m$ (no. 166), a = 15.1994(5), c = 56.421(3) Å, V = 11 288.1(7) Å^3, Z = 6, D_{calc} = 4.333 g cm^{-3}, final R, R_w = 0.0158, 0.0374. I_o = 2575 'observed' [$I > 2.0\sigma(I)$] reflections out of I = 2774 unique.

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