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Strong influence of structures around aluminum centers constructed in polyoxotungstates for catalytic oxidation of alcohols with dioxygen in water

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Abstract

Water-soluble aluminum-coordinated polyoxotungstates, $Cs_4[\alpha\text{-}PW_{11}\{Al(OH_2)\}O_{39}]\cdot 8H_2O$ (**Cs-1**), $[(CH_3)_4N]_4[\alpha\text{-}PW_{11}\{Al(OH_2)\}O_{39}]\cdot 8H_2O$ (**TMA-1**), $K_6Na[(A\text{-}PW_9O_{34})_2\{W(OH)(OH_2)\}\{Al(OH)(OH_2)\}\{Al(\mu\text{-}OH)(OH_2)_2\}_2]\cdot 19H_2O$ (**KNa-2**), and $K_7[\alpha_2\text{-}P_2W_{17}\{Al(OH_2)\}O_{61}]\cdot 14H_2O$ (**K-3**), were used as homogeneous catalysts or catalyst precursors for the oxidation of alcohols with 1 atm molecular oxygen in a water-alcohol biphasic medium. The catalytic activities and the stabilities of polyoxoanions were significantly affected by the structures around the aluminum sites constructed in the polyoxotungstates. In particular, polyoxoanion **1** exhibited high turnover numbers and high selectivities of the corresponding carbonyl products, and the molecular structure of **1** was remarkably stable for oxidations with long time intervals.

Keywords: Aluminum complex; Polyoxometalate; Alcohol oxidation; Molecular oxygen; Water

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1. Introduction

Oxidation of alcohols to carbonyl compounds has attracted considerable attention owing to their applicability in environmentally friendly industrial processes and organic synthesis [1–4]. Numerous efforts have been made to develop new catalytic protocols for the oxidation of alcohols particularly with molecular oxygen as oxidant, in contrast to the traditional methods based on the use of stoichiometric amounts of noxious (inorganic or organic) oxidants. Among these studies, the progress in the aerobic oxidation of alcohols in water is considerably notable. Over the past dozen years or so, various efficient catalysts containing noble metals, e.g., Pd [5–9], Pt [10–12], Ru [13,14], Rh [15], and Au [16,17], were reported for aerobic oxidation of aliphatic and alicyclic alcohols with molecular oxygen in aqueous media. While we appreciate the use of noble metals as efficient homogeneous and heterogeneous catalysts, the development of an oxidation catalyst devoid of noble metals, i.e., *a noble metal-free* oxidation catalyst, is still a significant and challenging objective. For this purpose, copper-containing catalysts were reported; however, they required 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) and a base as co-catalysts [18,19].

Polyoxometalates (POMs) are of particular interest in the field of catalysis, surface science, and materials science because their chemical properties, such as redox potentials, acidity, and solubility in various media, can be finely tuned by choosing appropriate constituent elements and countercations [20–22]. In particular, the coordination of various species, e.g., metal ions and organometallics, into the vacant site(s) of lacunary POMs is one of the most powerful techniques for construction and stabilization of efficient and well-defined metal centers. The POM-based catalysts, $Na_5PV_2Mo_{10}O_{40}$ [23] and $K_8[\{(p\text{-cymene})Ru^{II}(H_2O)\}(\alpha_2\text{-}P_2W_{17}O_{61})]\cdot 16H_2O$ [24] have been reported for the aerobic oxidation of alcohols using molecular oxygen in water; however, the former required quinones as co-catalysts, and the latter contained a noble metal atom.

In this paper, we report the catalytic performances of cesium and tetramethylammonium salts of monomeric, α-Keggin mono-aluminum-substituted POM, $Cs_4[\alpha\text{-}PW_{11}\{Al(OH_2)\}O_{39}]\cdot 8H_2O$ (**Cs-1**) and $[(CH_3)_4N]_4[\alpha\text{-}PW_{11}\{Al(OH_2)\}O_{39}]\cdot 8H_2O$ (**TMA-1**), a potassium/sodium mixed salt of dimeric aluminum complex having mono- and di-aluminum sites sandwiched by tri-lacunary α-Keggin polyoxometalate $K_6Na[(A\text{-}PW_9O_{34})_2\{W(OH)(OH_2)\}\{Al(OH)(OH_2)\}\{Al(\mu\text{-}OH)(OH_2)_2\}_2]\cdot 19H_2O$ (**KNa-2**) [25], and a potassium salt of monomeric, α_2-Dawson mono-aluminum-substituted POM $K_7[\alpha_2\text{-}P_2W_{17}\{Al(OH_2)\}O_{61}]\cdot 14H_2O$ (**K-3**) for the aerobic oxidation of alcohols with 1 atm dioxygen in aqueous-organic biphasic media without any additives. The molecular structures of polyoxoanions **1** – **3** are shown in Fig. 1.

(Insert here Fig. 1)

2. Experimental Section

2.1. Materials

Compound **KNa-2**, $Na_3[\alpha\text{-}PW_{12}O_{40}]\cdot 16H_2O$, $K_7[\alpha\text{-}PW_{11}O_{39}]\cdot 16H_2O$, and $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]\cdot 26H_2O$ were synthesized as described in the literatures [25–28]. The number of solvated water molecules was determined by TG/DTA analyses. All reagents and solvents were obtained and used as received from commercial sources.

2.2. Instrumentation/analytical procedures

Elemental analyses were performed using a Mikroanalytisches Labor Pascher (Remagen, Germany) instrument. The samples were dried overnight at room temperature under 10^{-3} – 10^{-4} Torr vacuum before analyses. Infrared spectra were recorded on a Perkin Elmer Spectrum100 FT-IR spectrometer, in KBr disks, at room temperature. Thermogravimetric (TG) and differential thermal analysis (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 ºC per min between 20 and 500 ºC. Solution $^{31}P\text{-}\{^1H\}$ (242.95 MHz) nuclear magnetic resonance (NMR) spectra were recorded in 5-mm outer diameter tubes on a JEOL ECA-600 NMR spectrometer (Shizuoka University). The ^{31}P NMR spectra were measured in D_2O with reference to an external standard of 85% H_3PO_4 in a sealed capillary. Chemical shifts were reported as negative on the δ scale for resonances upfield of H_3PO_4 (δ 0).

*2.3. Synthesis of $Cs_4[\alpha\text{-}PW_{11}\{Al(OH_2)\}O_{39}]\cdot 8H_2O$ (**Cs-1**)*

A solid $K_7[\alpha\text{-}PW_{11}O_{39}]\cdot 16H_2O$ (1.014 g; 0.31 mmol) was added to a solution of $Al(NO_3)_3\cdot 9H_2O$ (0.1163 g; 0.31 mmol) dissolved in 35 mL of water. After stirring for 30 min at 90 °C, a solid CsCl (0.3349 g; 2.0 mmol) was added to the solution. A white precipitate was collected using a membrane filter (JG 0.2 μm), and washed with ethanol (30 mL) and diethylether (30 mL). At this stage, a crude product was obtained in 0.6886 g yield. For purification, the crude product (0.6886 g) was dissolved in 50 mL of H_2O at 90 °C; the resulting solution was filtered through a folded filter paper (Whatman #5). After standing in a refrigerator overnight, a white precipitate was collected with a membrane filter (JG 0.2 μm) to yield 0.2634 g of product. The percent yield was calculated using [mol of **Cs-1**]/[mol of $K_7[PW_{11}O_{39}]\cdot 16H_2O$] × 100 and was 25%. Elemental analysis results showed H, 0.22; Cs, 16.6; Al, 0.83; P, 0.92; W, 61.8 %. Calculations for $Cs_4[\alpha\text{-}PW_{11}\{Al(OH_2)\}O_{39}]\cdot xH_2O$ ($x = 3$) = $H_8Al_1Cs_4O_{43}P_1W_{11}$: H, 0.24; Cs, 16.07; Al, 0.82; P, 0.94; W, 61.13%. A weight loss of 2.52% was observed during overnight drying at room temperature under 10^{-3}–10^{-4} Torr before analysis, suggesting the presence of 5 weakly solvated or adsorbed water molecules (2.65%). TG/DTA under atmospheric conditions showed a weight loss of 5.67% below 500 °C without a clear endothermic point; calculations showed 4.75% for 9 water molecules. IR (KBr disk) results in the 1300–400 cm^{-1} region (polyoxometalate region) showed: 1081s, 980s, 884s, 801m, 745m, and 694m cm^{-1}. ^{31}P NMR (D_2O, 24.5 °C): δ -13.02.

*2.4. Synthesis of $[(CH_3)_4N]_4[\alpha\text{-}PW_{11}\{Al(OH_2)\}O_{39}]\cdot 8H_2O$ (**TMA-1**)*

The compound **TMA-1** was also synthesized by a stoichiometric reaction of $K_7[\alpha\text{-}PW_{11}O_{39}]\cdot 16H_2O$ (1.000 g; 0.31 mmol) with $Al(NO_3)_3\cdot 9H_2O$ (0.1165 g; 0.31 mmol) in an aqueous solution (100 mL), as reported for the compound **Cs-1**. A solid tetramethylammonium bromide (1.0961 g; 6.94 mmol) was added to the reaction mixture. A crude product was obtained in 0.8338 g yield. For purification, the crude product (0.8338 g) was dissolved in 50 mL of H_2O at 90 °C; the resulting solution was filtered through a folded filter paper (Whatman #5). After standing in a refrigerator overnight, a white precipitate was collected with a membrane filter (JG 0.2 μm) to yield 0.4242 g of product. The percent yield was 43%. Elemental analysis results showed C, 6.42; H, 1.73; N 1.97, K 0.03%. Calculations for $[(CH_3)_4N]_4[\alpha\text{-}PW_{11}\{Al(OH_2)\}O_{39}]\cdot xH_2O$ ($x = 4$) = $C_{16}H_{58}Al_1N_4O_{44}P_1W_{11}$: C, 6.22; H, 1.89; N 1.81, K 0%. A weight loss of 2.3% was observed during overnight drying at room temperature under 10^{-3}–10^{-4} Torr before analysis, suggesting the presence of 4 weakly solvated or adsorbed water molecules (2.28%). TG/DTA under atmospheric conditions showed a weight loss of 4.12% without a clear endothermic point observed below 329 °C; calculations showed 5.12% for 9 water molecules. Further, a weight loss of 9.18% with an exothermic peak at 435.2 °C was observed in the temperature range from 329 to 500 °C; calculations showed four $[(CH_3)_4N]^+$ (calcd. 8.99%). IR (KBr disk) results in the 1300 – 400 cm^{-1} region (polyoxometalate region) showed: 1077s, 966s, 892s, 817s, 750m, and 702m cm^{-1}. ^{31}P NMR (D_2O, 24.5 °C): δ -13.07. The ^{31}P NMR spectrum in D_2O of a mixture of **Cs-1** and **TMA-1** showed a signal at -13.26 ppm, showing that the molecular structure of **Cs-1** was the same as that of **TMA-1**.

*2.5. Synthesis of $K_7[\alpha_2\text{-}P_2W_{17}\{Al(OH_2)\}O_{61}]\cdot 14H_2O$ (**K-3**)*

K-3 was prepared by a modified literature method [29]. A solution of $Al(NO_3)_3{\cdot}9H_2O$ (0.750 g; 2.0 mmol) dissolved in 15 mL of water was added to a solution of $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]{\cdot}26H_2O$ (9.83 g; 2.0 mmol) and dissolved in 100 mL of hot water at 70 ºC. After stirring for 3 h at 25 ºC, the solution was evaporated at 40 ºC until a small amount of white precipitate was formed; then, this white precipitate was dissolved by heating it in a water bath at 40 ºC. The clear, colorless solution was allowed to stand overnight in a refrigerator. White crystals were collected using a membrane filter (JG 0.2 μm). At this stage, a crude product was obtained in 7.36 g. For purification, the crude product (7.36 g) was dissolved in 4 mL of H_2O at 90 °C; the resulting solution was filtered through a folded filter paper (Whatman #2). After standing in a refrigerator overnight, a white precipitate was collected with a membrane filter (JG 0.2 μm) to yield 4.42 g of product. The percent yield was calculated using [mol of **K-3**]/[mol of $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]{\cdot}26H_2O$] × 100 and was 47%. Elemental analysis results showed H, 0.16; Al, 0.59; W, 68.6; P, 1.35; K, 5.98%. Calculations for $K_7[\alpha_2\text{-}P_2W_{17}\{Al(OH_2)\}O_{61}]{\cdot}xH_2O$ (x = 3) = $H_8Al_1K_7O_{65}P_2W_{17}$: H, 0.18; Al, 0.59; W, 68.9; P, 1.37; K, 6.03%. A weight loss of 4.19% was observed during overnight drying at room temperature under 10^{-3}–10^{-4} Torr before analysis, suggesting the presence of 11 weakly solvated or adsorbed water molecules (4.19%). TG/DTA under atmospheric conditions showed a weight loss of 4.5% below 500 °C with an endothermic point at 71.4 °C; calculations showed 5.7% for 15 water molecules. IR (KBr disk) results in the 1300–400 cm^{-1} region (polyoxometalate region) showed: 1090s, 1018s, 952s, 916s, 796s, and 526w cm^{-1}. ^{31}P NMR (D_2O, 21.8 °C): δ -10.19, -13.53.

2.6. Oxidation catalysis

The liquid-phase reaction system comprised the aqueous-organic biphasic medium, in which the aqueous medium was composed of a water-soluble catalyst dissolved in 4 mL water and the organic medium contained alcohols (4 mL, 24.9 – 38.3 mmol). A sample catalyst was placed in a 60 mL Schlenk tube. Alcohols and water were added using a micropipette. The reaction mixture was purged with 1 atm dioxygen for a few minutes and heated in an oil bath at 95 ± 2 – 120 ± 2 ºC. The reaction solution was analyzed by gas chromatography (flame ionization detector, capillary column DB-WAX, 0.53 mm × 15 m and Gaskuropack-55 60/80, 3.2 mm × 2.0 m) and liquid chromatography (Shim-pack VP-ODS column, 4.6 mm × 150 mm). Values of the products were assigned by comparing the obtained results with the analysis results obtained from analyzing the authentic samples under the same conditions.

3. Results and discussion

The catalytic activities of aluminum-coordinated polyoxoanions **1** – **3** were examined during the benzyl alcohol oxidation, with 1 atm dioxygen in a water-alcohol biphasic medium without additives. The oxidation reactions of benzyl alcohol at 95 ± 2 °C, catalyzed by **Cs-1**, **TMA-1**, **KNa-2**, and **K-3** were monitored by chromatography, as shown in Fig. 2. The catalytic activities are summarized in Table 1. During the oxidation reactions, all catalysts in Table 1 were soluble in water. No reaction was observed in the absence of catalyst under the present reaction conditions. For polyoxoanion **1**, the initial rates were increased linearly until around 100 h, and then gradually decreased with time. When polyoxoanion **2** was used as a catalyst, the rates were increased in an approximately linear fashion during 288 h. For polyoxoanion **3**, the slower initial rates were observed; however, the rates were gradually increased with time. Benzaldehyde was obtained with >99% selectivity and benzoic acid was not detected in organic and aqueous phases during a 288 h oxidation period. For compound **Cs-1** (2.94 μmol), the pH of the catalyst solution changed from 5.57 to 5.30 after

288 h, suggesting that OH^- was not generated during the reaction. The turnover number (TON = (mol of products)/(mol of catalyst)) after 96 h was 158.7 when 2.94 μmol of **Cs-1** was used as a catalyst, and it reached 319.5 after 288 h. When **TMA-1** was used as a catalyst, benzaldehyde was also observed with >99% selectivity during the course of reaction. The TONs after 24 h were in the range of 2.29 to 18.5 by using 1.58 – 31.6 μmol of **TMA-1**, which were similar in order to those (2.78 – 51.1) of **Cs-1** (1.47 – 29.4 μmol). For polyoxoanion **1**, the rates decreased with a decrease in oxygen partial pressure ($P(O_2)$) from 1.0 to 0.2 atm (air), and no reaction was observed under argon atmosphere. Thus, dioxygen was indispensable for the present oxidation reactions. In addition, the activities of polyoxoanion **1** were not improved by the addition of acid and base. When the compound **KNa-2** (3.02 μmol) was used as a catalyst, the TONs were 109.0 after 96 h and 384.5 after 288 h, which were similar to those of polyoxoanion **1**; whereas, the compound **K-3** (2.89 μmol) showed lower activities (TON was 36.3 after 96 h) than those of polyoxoanions **1** and **2**.

(Insert here Table 1 and Fig. 2)

Here, the stability of polyoxoanions **1** – **3** during the oxidation of benzyl alcohol with 1 atm oxygen was determined by ^{31}P NMR spectroscopy, as shown in Fig. 3. After 96 h, the ^{31}P NMR spectrum in D_2O of **Cs-1** showed a signal at -13.0 ppm, which was the same as that of **Cs-1** (δ -13.0). The ^{31}P NMR spectrum in D_2O of **TMA-1** also showed no change of the molecular structure of **1**, and no signal due to the decomposition species was observed even after 288 h (Fig. S1). Such a high stability of polyoxoanion **1** was confirmed by a recycle experiment as follows: the oxidation of benzyl alcohol was performed twice with the same aqueous solution dissolving **Cs-1** at 95 ± 2 ºC. The TON of the second run (194.7 after 96 h) was almost the same as that of the first run (158.7 after 96 h) with >99% selectivity for benzaldehyde. In contrast, the molecular structure of **KNa-2** was gradually changed during the oxidation reaction, as shown in Fig. S2. Because of the two central phosphorous atoms in the polyoxoanion **2**, the intensity of one signal at -12.0 ppm decreased and the intensities of two new signals at -11.7 ppm and -13.2 ppm increased with time. Although the signal at -11.7 ppm was the unknown species, the signal at -13.2 ppm was assignable to polyoxoanion **1**. After 24 h, ca. 94% of the molecular structure of **2** was retained; however, after 288 h, the molecular structure of **2** was mainly transformed to that of polyoxoanion **1**. With regard to polyoxoanion **3**, two signals at -10.2 ppm and -13.5 ppm were observed due to the two central phosphorus atoms in **3**; these were the same as those of **K-3** (δ -10.2 and -13.5). As shown in Table 1, the activities of polyoxoanion **2** showed the high turnover numbers; however, it contains polyoxoanion **1** that act as the actual active species. As compared with the catalytic activity of the POM-based ruthenium complex $K_8[\{(p\text{-cymene})Ru^{II}(H_2O)\}(\alpha_2\text{-}P_2W_{17}O_{61})]\cdot 16H_2O$ [24] for the oxidation of benzyl alcohol with 1 atm dioxygen in water, the selectivities of benzaldehyde and benzoic acid without additives, at 85 ºC, resulted in 89% and 11% selectivity along with 167 TON after 336 h. Therefore, the activities (selectivity of benzaldehyde and TON) of **Cs-1** were not so inferior to those of the ruthenium complex. Other noble metal catalysts exhibited excellent activities for the oxidation of benzyl alcohols with dioxygen in an aqueous medium; however, a simple comparison is difficult to obtain since these systems were reacted under various reaction conditions, e.g., in the presence of some additives, in a wide range of reaction temperatures, and a high pressure of dioxygen or air.

(Insert here Fig. 3)

α-Keggin- and α-Dawson-type mono-lacunary polyoxometalates, $K_7[\alpha\text{-}PW_{11}O_{39}]\cdot 16H_2O$ (2.94 μmol) and $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]\cdot 26H_2O$ (2.94 μmol), showed turnover numbers of 114.8 and 33.1 with >99% selectivity towards benzaldehyde after 96 h. The ^{31}P NMR spectra in D_2O of these compounds showed that the molecular structure of $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ was completely decomposed (Fig. S3), and that of $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ was partially decomposed after 96 h (Fig. S4). For the oxidation of benzyl alcohol catalyzed by $Na_3[\alpha\text{-}PW_{12}O_{40}]\cdot16H_2O$ (2.94 μmol), benzaldehyde was also observed with >99% selectively during the course of the reaction; however, the selectivity for benzaldehyde decreased to 29% owing to the formation of benzyl ether with 71% selectivity after 96 h by using 30.9 μmol of $Na_3[\alpha\text{-}PW_{12}O_{40}]\cdot16H_2O$. As a control experiment, using $AlCl_3\cdot6H_2O$ (2.94 μmol) resulted in faster formation of benzaldehyde with >99% selectively; however, the rates were significantly reduced with time. When 207 μmol of $AlCl_3\cdot6H_2O$ was used as a catalyst, benzaldehyde, benzoic acid, and benzyl ether were produced with 86%, 5%, and 9% selectivity after 96 h. For $Al(NO_3)_3\cdot9H_2O$ (2.94 μmol), benzaldehyde, benzyl ether, benzoic acid, and benzyl benzoate were formed with 93%, 2%, 4%, and 1% selectivity after 96 h (TON was 311). A mixture of $AlCl_3\cdot6H_2O$ (207 μmol) and $Na_3[PW_{12}O_{40}]\cdot16H_2O$ (30.9 μmol) showed 4.4% selectivity for benzaldehyde after 96 h. In contrast, >99% selectivity of benzaldehyde was maintained at the higher conversions for the oxidation of benzyl alcohol catalyzed by 18.2 – 31.6 μmol of polyoxoanions **1** – **3**; this suggested that the isolated aluminum sites constructed in the polyoxometalate frameworks caused the high selectivity of benzaldehyde.

Compound **Cs-1** was also observed to catalyze the oxidation of primary and secondary aliphatic alcohols to the corresponding carbonyl products with >99% selectivities at 95 ± 2 – 120 ± 2 ºC, as shown in Table 2. For noble metal-containing catalysts, oxidation reactions via the formation of a metal-alcoholate intermediate lead to selective oxidation of primary hydroxyl groups [30]. As shown in Table 2, 1-hexanol, 1-heptanol, and 1-octanol were oxidized by **Cs-1**; however, the rates were significantly reduced with time, and they were lower than those for the oxidation of 2-hexanol, 2-heptanol, and 2-octanol. Competitive oxidations of 1-octanol and 2-octanol catalyzed by **Cs-1** also showed that the rates for

2-octanol oxidation were 3.1 – 4.9 times faster than those that for 1-octanol oxidation. These results suggested that the reaction pathway might include both radical species and alcoholate species as intermediates.

To determine the reaction mechanism, the oxidation of 1-butanols, fully deuterated ($1\text{-}C_4D_9OD$), and deuterated only at the hydroxyl group ($1\text{-}C_4H_9OD$), were examined at 120 ± 2 °C [12]. The rates for oxidation of 1-butanols (1.0 mL; 11 mmol) were slow; thus, the rates were observed after 48 h. TONs for the oxidation of $1\text{-}C_4H_9OH$, $1\text{-}C_4H_9OD$, and $1\text{-}C_4D_9OD$ were 4.5, 2.7, and 0.65, and the kinetic isotope effects, $k_{1\text{-}C4H9OH}/k_{1\text{-}C4H9OD}$ and $k_{1\text{-}C4H9OH}/k_{1\text{-}C4D9OD}$, were 1.7 and 6.9, respectively. These results suggested that both dissociative chemisorption of alcohol molecules to form alcoholate intermediate and hydride abstraction from the alcoholate intermediate affected the kinetically relevant steps. Further, the effect of radical scavenger, hydroquinone, was observed for benzyl alcohol oxidation catalyzed by **Cs-1** under the same reaction conditions. When hydroquinone (3.85 mmol; the molar ratio of benzyl alcohol : hydroquinone was 10 : 1) was added to the reaction mixture, the TON decreased to 16.6 after 24 h; this suggested that the radical species were also generated during the reactions [12].

(Insert here Table 2)

3. Conclusion

A water-soluble mono-aluminum-substituted α-Keggin-type polyoxoanion, $[\alpha\text{-}PW_{11}\{Al(OH_2)\}O_{39}]^{4-}$, showed efficient activity for the selective oxidation of a wide range of alcohols with 1 atm molecular oxygen in an aqueous medium. The polyoxoanion **1** was significantly stable during the oxidation reactions, and the aqueous solution dissolving polyoxoanion **1** can be recycled. As reported in previous works, various noble metal-containing catalysts exhibited high activities (turnover numbers and selectivities to the corresponding products) for the oxidation of various primary and secondary aliphatic and benzylic alcohols with 1 atm dioxygen in an aqueous medium; however, polyoxoanion **1** can act as a *noble metal-free* catalyst for the selective oxidation of alcohols without any additives.

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Figure captions

Fig. 1. Polyhedral representations of polyoxoanions (a) **1**, (b) **2**, and (c) **3**. WO_6 and AlO_6 units are represented by the white and blue octahedra, respectively. The internal PO_4 units are represented by the red tetrahedra. The molecular structures of **1** and **3** were monomeric compounds, in which an aluminum ion was located in the A-site of α-Keggin structure and the B-site of α-Dawson structure, respectively. The polyoxoanion **2** was a dimeric aluminum complex, in which two 6-coordinate aluminum ions linked with two bridging hydroxyl groups and four water molecules, i.e., $[Al^{III}_2(\mu\text{-}OH)_2(OH_2)_4]^{4+}$. A unit of a 6-coordinate tungsten ion linked with a hydroxyl group and a water molecule, i.e., $[W(OH)(OH_2)]^{5+}$; a unit of a 6-coordinate aluminum ion linked with a hydroxyl group and a water molecule, i.e., $[Al(OH)(OH_2)]^{2+}$, were sandwiched between two tri-lacunary α-Keggin polyoxotungstates.

Fig. 2. Time course for the oxidation of benzyl alcohol catalyzed by (a) **Cs-1** (2.94 μmol), (b) **KNa-2** (3.02μmol), and (c) **K-3** (2.89 μmol). Reaction conditions are shown in Table 1.

Fig. 3. ^{31}P NMR spectra in D_2O of (a) **Cs-1**(2.94 μmol), (b) **KNa-2** (18.2 μmol), and (c) **K-3** (21.1 μmol) after 96 h for the oxidation of benzyl alcohol with 1 atm dioxygen. Reaction conditions are shown in Table 1.

Table 1. Oxidation of benzyl alcohol with 1 atm dioxygen in water[a]

Catalyst (μmol)	Reaction time (h)	Benzaldehyde (μmol)	Benzoic acid (μmol)	Benzyl ether (μmol)	Selectivity of benzaldehyde (%)[b]	TON[c]
Cs-1 (2.94)	24	145.7	n.d.[d]	n.d.[d]	>99	49.6
	96	466.6	n.d.[d]	n.d.[d]	>99	158.7
	288	939.4	n.d.[d]	n.d.[d]	>99	319.5
TMA-1 (6.32)	24	88.2	n.d.[d]	n.d.[d]	>99	14.0
	96	215.9	n.d.[d]	n.d.[d]	>99	34.2
	288	612.1	n.d.[d]	n.d.[d]	>99	96.9
TMA-1 (31.6)	24	74.0	n.d.[d]	n.d.[d]	>99	2.34
	96	234.3	n.d.[d]	n.d.[d]	>99	7.41
	288	584.3	n.d.[d]	n.d.[d]	>99	18.5
KNa-2 (3.02)	24	207.0	n.d.[d]	n.d.[d]	>99	68.5
	96	329.1	n.d.[d]	n.d.[d]	>99	109.0
	288	1161.2	n.d.[d]	n.d.[d]	>99	384.5
KNa-2 (18.2)	24	50.4	n.d.[d]	n.d.[d]	>99	2.77
	96	232.6	n.d.[d]	n.d.[d]	>99	12.8
	288	486.9	n.d.[d]	n.d.[d]	>99	26.8
K-3 (2.89)	24	32.1	n.d.[d]	n.d.[d]	>99	11.1
	96	104.8	n.d.[d]	n.d.[d]	>99	36.3
	288	436.6	n.d.[d]	n.d.[d]	>99	151.1
K-3 (21.1)	24	n.d.[d]	n.d.[d]	n.d.[d]	–	–
	96	33.6	n.d.[d]	n.d.[d]	>99	1.59
$Na_3[\alpha\text{-}PW_{12}O_{40}]\cdot 16H_2O$ (2.94)	24	n.d.[d]	n.d.[d]	n.d.[d]	–	–
	96	155.4	n.d.[d]	n.d.[d]	>99	52.9
$Na_3[\alpha\text{-}PW_{12}O_{40}]\cdot 16H_2O$ (30.9)	48	110.5	n.d.[d]	289.8	28	13.0
	96	185.7	n.d.[d]	449.3	29	20.6
$K_7[\alpha\text{-}PW_{11}O_{39}]\cdot 16H_2O$ (2.94)	24	137.0	n.d.[d]	n.d.[d]	>99	46.6
	96	337.6	n.d.[d]	n.d.[d]	>99	114.8
$K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]\cdot 26H_2O$ (2.94)	24	34.5	n.d.[d]	n.d.[d]	>99	11.7
	96	97.2	n.d.[d]	n.d.[d]	>99	33.1
$AlCl_3\cdot 6H_2O$ (2.94)	24	602.4	n.d.[d]	n.d.[d]	>99	204.9
	96	645.3	n.d.[d]	n.d.[d]	>99	219.5
$AlCl_3\cdot 6H_2O$ (207)	24	583.6	7.50	166.1	77	3.66
	96	1583.7	89.5	172.9	86	8.92
$Na_3[PW_{12}O_{40}]\cdot 16H_2O$ (30.9)/ $AlCl_3\cdot 6H_2O$ (207)	24	n.d.[d]	n.d.[d]	n.d.[d]	–	–
	96	30.9	1.36	664.4	4.4	22.5[e]

[a] Reaction conditions: catalyst 2.89 – 207 μmol; water 4 mL; benzyl alcohol 38.3 mmol; $P(O_2)$ = 1 atm; reaction temperature 95 ± 2 ºC.

[b] Selectivity of benzaldehyde = [mol of benzaldehyde]/[mol of products] × 100 (%).

[c] Turnover number (TON) = [mol of products]/[mol of catalyst].

[d] n.d. = Not detected.

[e] TON calculated on the basis of [mol of products]/[mol of $Na_3[PW_{12}O_{40}]\cdot 16H_2O$].

Table 2. Catalytic activities for oxidation of primary and secondary aliphatic alcohols with 1 atm molecular oxygen catalyzed by **Cs-1**[a]

alcohol (mmol)	reaction time (h)	product (μmol)	Selectivity/%	TON[b]
cyclohexanol (36.8)	24	cyclohexanone (509.6)	>99	173.3
	96	cyclohexanone (726.5)	>99	247.1
1-hexanol (31.3)[c]	24	hexanal (32.5)	>99	11.1
	96	hexanal (33.9)	>99	11.5
2-hexanol (31.1)[c]	24	2-hexanone (112.6)	>99	38.3
	96	2-hexanone (307.2)	>99	104.5
1-heptanol (27.7)	24	heptanal (55.8)	>99	19.0
	96	heptanal (74.2)	>99	25.2
2-heptanol (27.6)	24	2-heptanone (323.2)	>99	109.9
	96	2-haptanone (1360)	>99	462.6
1-octanol (24.9)	24	octylaldehyde (73.8)	>99	25.1
	96	octylaldehyde (73.9)	>99	25.1
2-octanol (25.2)	24	2-octanone (73.9)	>99	25.1
	96	2-octanone (371.7)	>99	126.4
1-octanol (12.4)/2-octanol (12.3)[d]	24	octylaldehyde (25.8)	24	36.1
		2-octanone (80.3)	76	
	96	octylaldehyde (34.1)	17	68.7
		2-octanone (167.8)	83	

[a] Reaction conditions: **Cs-1** (2.94 μmol), cyclohexanol, 1-hexanol, 2-hexanol, 1-heptanol, 2-heptanol, 1-octanol, and 2-octanol (24.9 – 36.8 mmol), $P(O_2)$ = 1 atm, reaction temperature 120 ± 2 ºC.

[b] Turnover number (TON) = [mol of products]/[mol of catalyst].

[c] Reaction temperature 95 ± 2 ºC.

[d] A mixture of 1-octanol and 2-octanol was used as a substrate.

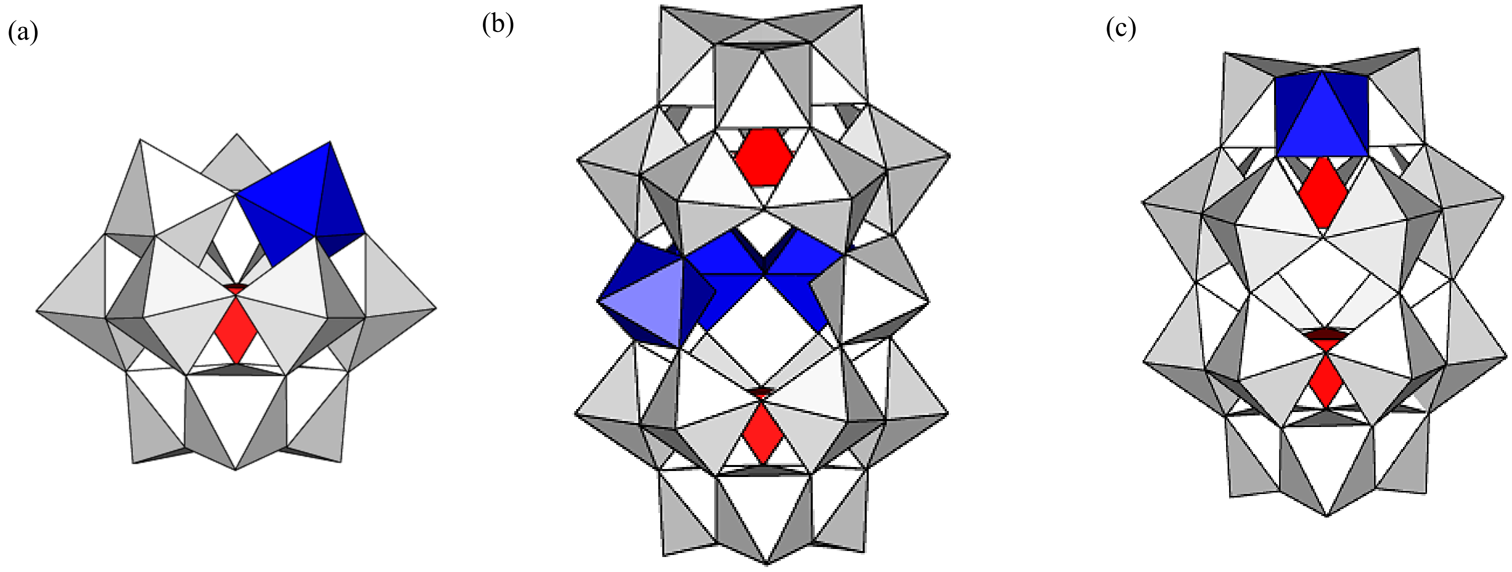
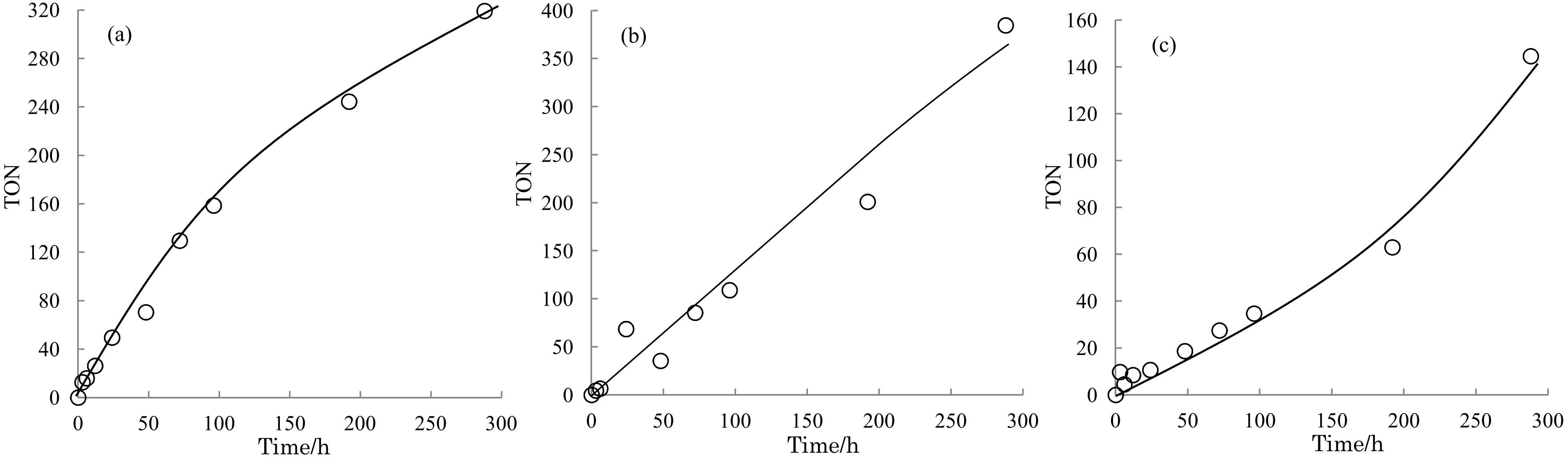


Fig. 1


(a)
(b)
(c)
TON
Time/h
0
40
80
120
160
200
240
280
320
0
50
100
150
200
250
300
350
400
0
20
40
60
80
100
120
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50
100
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200
250
300

Fig. 2

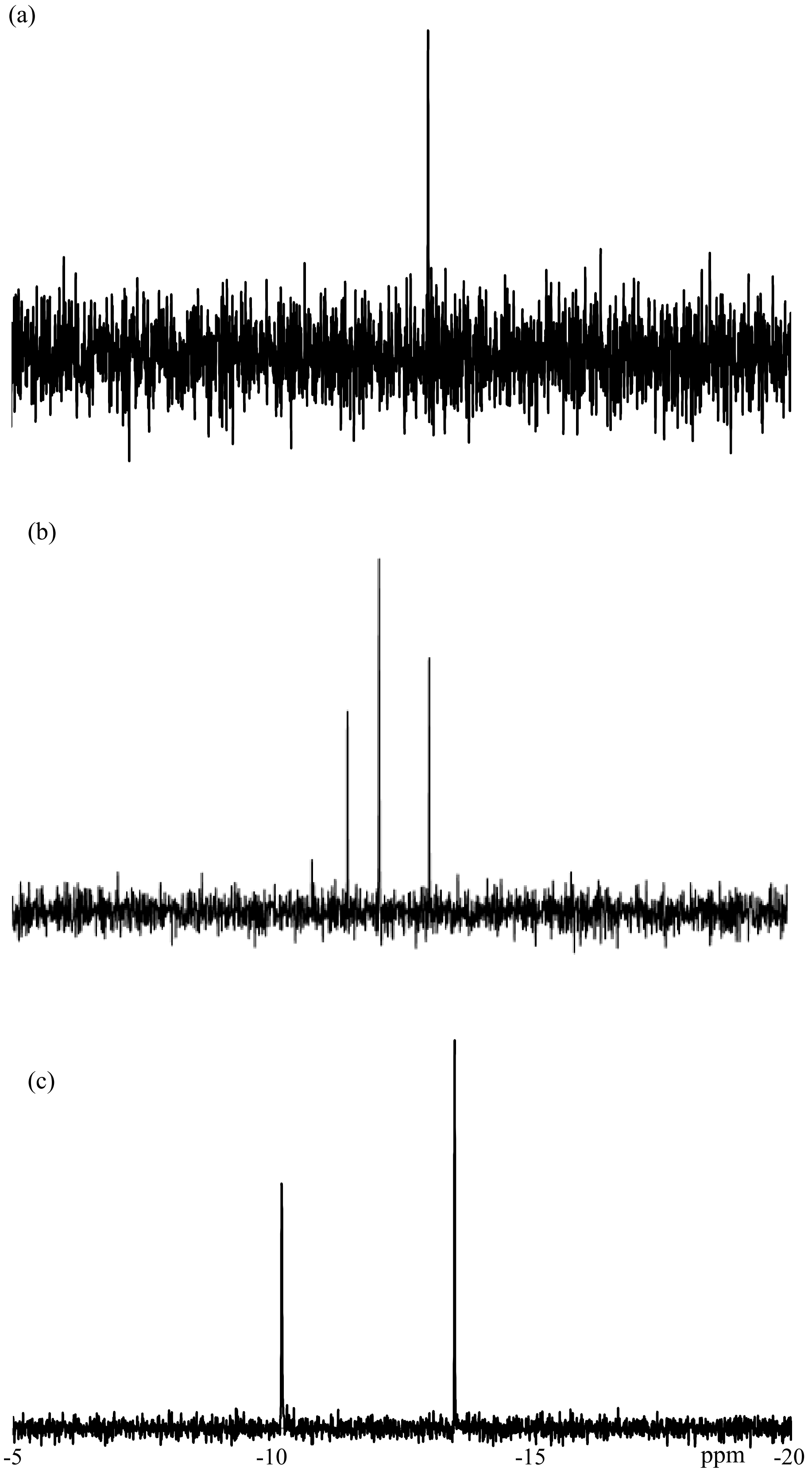

Fig. 3

Supporting information

Strong influence of structures around aluminum centers constructed in polyoxotungstates for catalytic oxidation of alcohols with dioxygen in water

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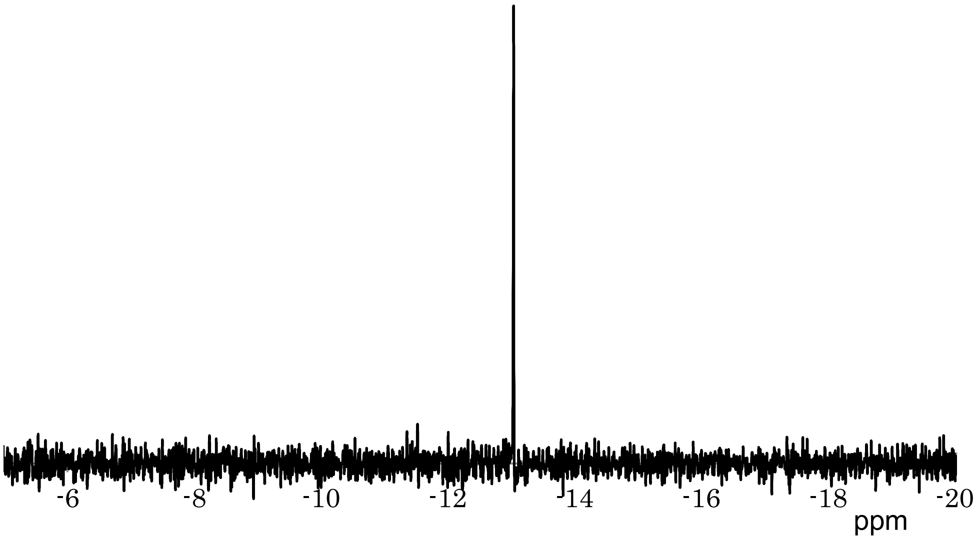
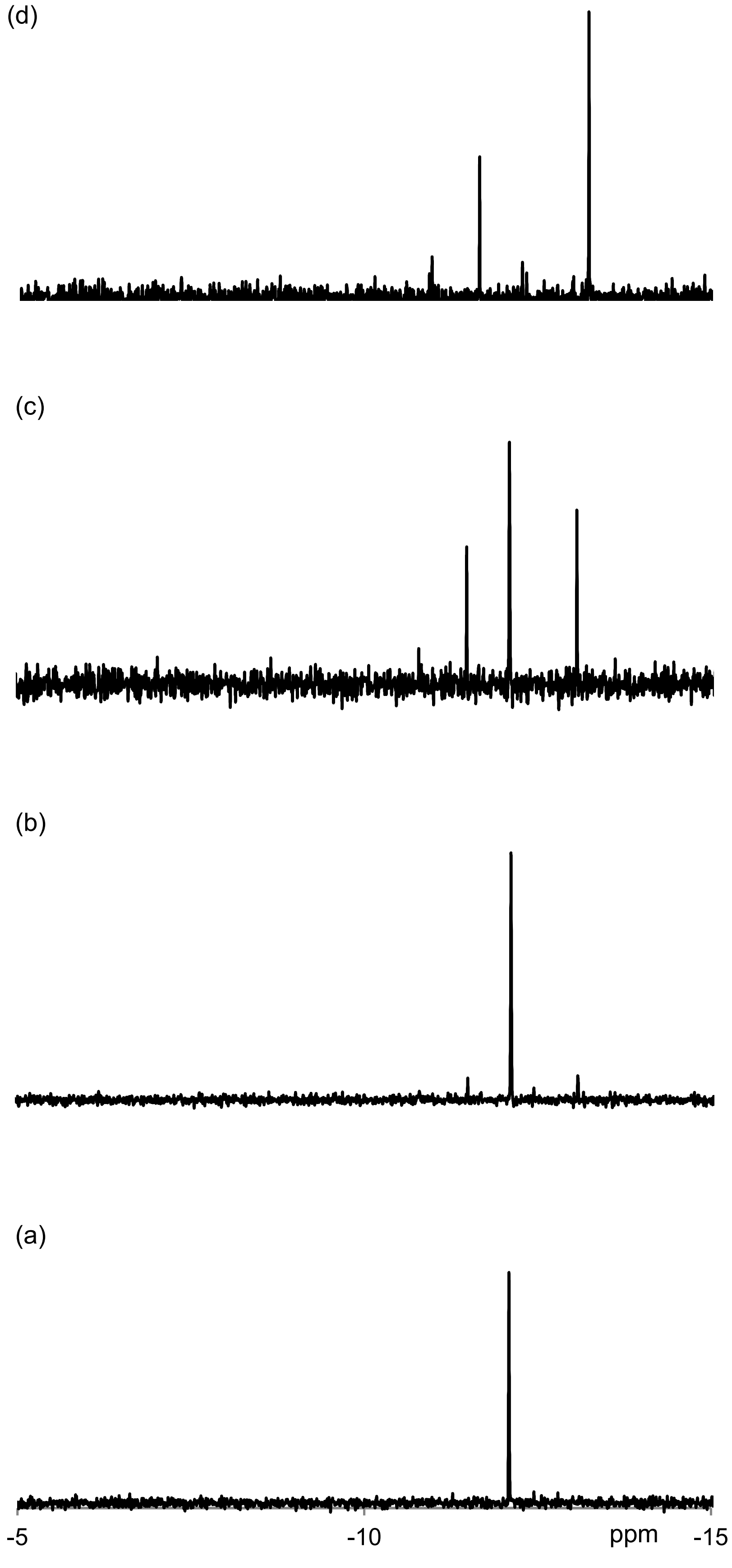


Fig. S1



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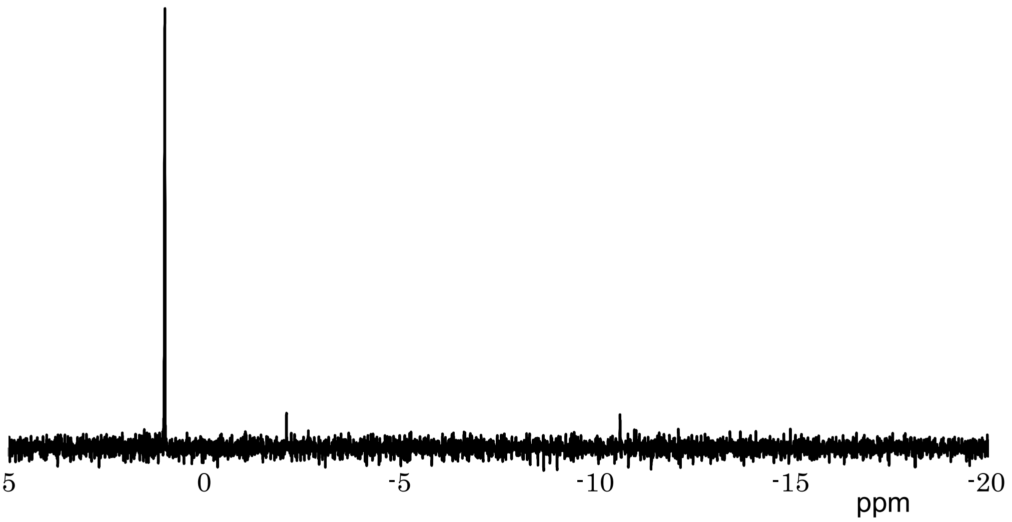

Fig. S3

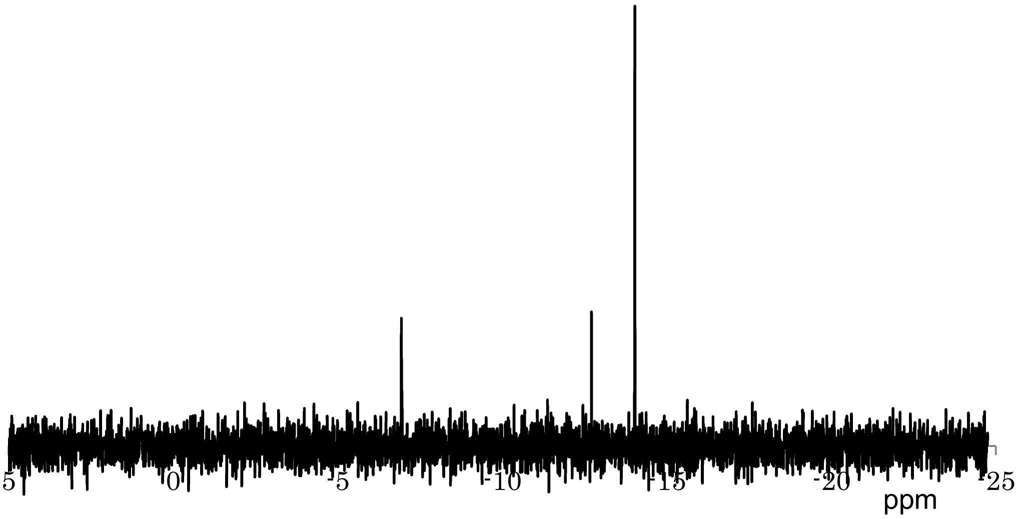

Fig. S4