Synthesis, Characterization, and Oxidation Catalysis of a Novel Dawson Polyoxometalate-supported Platinum(II) Complex, $[\{Pt(cod)\}(P_2W_{15}V_3O_{62})]^{7-}$ (cod = 1,5-cyclooctadiene)

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A novel Dawson polyoxotungstate-based organometallic platinum(II) complex, $[\{Pt(cod)\}(P_2W_{15}V_3O_{62})]^{7-}$ (cod = 1,5-cyclooctadiene), which showed effective catalytic activity for oxidation of cyclohexanol with 30% aqueous hydrogen peroxide, was synthesized and spectroscopically characterized.

Polyoxometalate-based catalysts have attracted much attention because their acidic and redox properties can be controlled at molecular levels.[1] One significant technology for the modification of polyoxometalate-based catalysts is the direct supporting of metal ions onto the surface oxygens of polyoxometalates at molecular levels.[2]

Molecular design based on a combination of platinum[3] and vanadium[4] atoms is quite interesting to develop new oxidation catalysts because each of them is effective for the functionalization of hydrocarbons. Various kinds of vanadium-substituted polyoxometalate-supported organometallics have been reported,[5] but there is no precedent of a vanadium-substituted polyoxometalate-supported platinum (II) complex.

Herein we report the synthesis and characterization of a novel trivanadium(V)-substituted Dawson polyoxotungstate-supported organometallic platinum(II) complex, $(NBu_4)_7[\{Pt(cod)\}(P_2W_{15}V_3O_{62})]\cdot 2NBu_4BF_4$ **1** (Figure 1), which shows effective catalytic activity for oxidation of cyclohexanol with 30% aqueous hydrogen peroxide. Complex **1** was not obtained by the previously reported synthetic conditions.[2,5]

Formation of **1** is shown in Eqs 1 and 2. The 1:1-molar ratio reaction of $(NBu_4)_9[P_2W_{15}V_3O_{62}]$ with the in situ-generated $[Pt(cod)]^{2+}$ species in CH_2Cl_2 gave **1** as an adduct with two NBu_4BF_4 molecules. The synthetic stoichiometry of **1** was based on the UV-vis absorption titration experiment[2a] at 316 nm: The changes in absorbance were measured by changing the molar ratios of $[Pt(cod)]^{2+}/[P_2W_{15}V_3O_{62}]^{9-}$ in CH_2Cl_2. The titration experiment showed a formation of the 1:1-type complex because a clear break point of absorbance was found at the point of 1:1 molar ratio of $[Pt(cod)]^{2+}/[P_2W_{15}V_3O_{62}]^{9-}$.

$$[PtCl_2(cod)] + 2AgBF_4 + xCH_2Cl_2 \rightarrow [Pt(CH_2Cl_2)_x(cod)](BF_4)_2 + 2AgCl \quad (1)$$

$$[Pt(CH_2Cl_2)_x(cod)](BF_4)_2 + (NBu_4)_9[P_2W_{15}V_3O_{62}] \rightarrow (NBu_4)_7[\{Pt(cod)\}(P_2W_{15}V_3O_{62})] + xCH_2Cl_2 + 2NBu_4BF_4 \quad (2)$$

The precursors, $[PtCl_2(cod)]$[6] and $(NBu_4)_9[\alpha\text{-}1,2,3\text{-}P_2W_{15}V_3O_{62}]$,[5a,d] were prepared according to the literature. Complex **1** was obtained as analytically pure, pink-orange powder in 71.3% (0.79 g scale) yield,[7] and the composition and formula were consistent with complete elemental analysis, TG/DTA, FTIR, and (^{31}P, ^{51}V, ^{183}W, ^{1}H, and ^{13}C) NMR spectroscopy.[8]

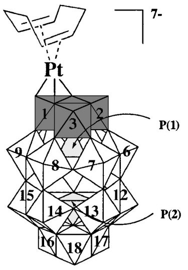

Figure 1. Polyhedral representation of $[\{Pt(cod)\}(P_2W_{15}V_3O_{62})]^{7-}$ **1** with C_s symmetry. The three vanadium atoms are represented as hatched octahedra in the 1,2,3-positions (B-site) of the α-Dawson vanadotungstate-support $[\alpha\text{-}1,2,3\text{-}P_2W_{15}V_3O_{62}]^{9-}$. The WO_6 octahedra occupy the white octahedra, and PO_4 groups are shown as the internal, pale gray tetrahedra.

In FTIR of **1** in the 1300–400 cm^{-1} region, a major change relative to $(NBu_4)_9[P_2W_{15}V_3O_{62}]$ was seen; the 936 and 877 cm^{-1} bands changed to explicit split bands at (938, 954) and (910, 884) cm^{-1}, respectively, and the 776 cm^{-1} band shifted to higher energy band at 787 cm^{-1}. Such a phenomenon might be due to decreasing of symmetry in the polyoxometalates from C_{3v} to C_s.[9]

The ^{31}P NMR spectrum in CD_2Cl_2 of **1** showed a clean, two-line spectrum at −7.77 ppm [assigned to the P(1) atom] and −13.90 ppm [assigned to the P(2) atom] with 1:1 intensity ratio, the chemical shifts of which were substantially different from the ^{31}P resonances at −6.74 and −14.48 ppm of $(NBu_4)_9[P_2W_{15}V_3O_{62}]$. The P(1) signal was shifted to higher field, whereas the P(2) signal to lower field, upon bonding of the $[Pt(cod)]^{2+}$ group to the V_3 surface oxygens.

The ^{51}V NMR spectrum in CD_2Cl_2 of **1** showed a clean, two-line spectrum at −486.4 ppm ($\Delta\nu_{1/2}$ 809.5 Hz) and −523.7 ppm ($\Delta\nu_{1/2}$ 285.7 Hz) with 2:1 intensity ratio, the spectrum of which was substantially different from the single-line spectrum in CD_2Cl_2 at −484.8 ppm of $(NBu_4)_9[P_2W_{15}V_3O_{62}]$ with C_{3v} symmetry. Thus, the $[Pt(cod)]^{2+}$ group is attached to the polyoxoanion-support, $[P_2W_{15}V_3O_{62}]^{9-}$, in a way that yields an overall C_s symmetry. The line at −523.7 ppm was assigned to the one vanadium(V) site on which the $[Pt(cod)]^{2+}$ group was bonded, while the line at −486.4 ppm was assigned to the two vacant vanadium(V) sites (Figure 1).

The ^{183}W NMR in CD_2Cl_2 of **1** (Figure 2) showed an eight-line spectrum at −124.7 (2W), −129.9 (1W), −141.9 (2W), −187.6 (2W), −191.9 (2W), −194.0 (4W), −201.1 (2W) with relative intensities of 2:1:2:2:2:[2 + 2]:2. The line at −194.0 ppm included a broadened signal and the line at −201.1 ppm was considerably broadened. The ^{183}W NMR spec-

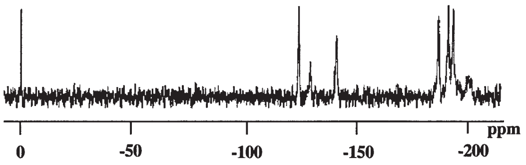

Figure 2. ^{183}W NMR spectrum of **1** in CD_2Cl_2 at 22.8 °C. The spectrum was measured with references to an external saturated Na_2WO_4-D_2O solution.

trum of **1**, being quite different from that of the previously reported complexes with C_{3v} symmetry showing a three-line spectrum,[2d,e] also suggested that **1** took C_s symmetry. The eight-line ^{183}W NMR spectrum has been reported in the 1:1-type complex $(NBu_4)_6[(TiCp)(P_2W_{15}V_3O_{62})]$ with C_s symmetry.[5f]

^{1}H and ^{13}C NMR spectra in CD_2Cl_2 at room temperature for the coordinating cod ligand in **1** showed at 2.11, 2.12, 2.66, 2.73, 3.21, 6.26 ppm and at 30.8, 49.2, 49.2, 93.2 ppm, respectively. The six ^{1}H peaks and four ^{13}C peaks are characteristic of the square-pyramidal geometry around the Pt^{II} atom (five-coordinate by two olefinic C=C bonds of the cod ligand plus three oxygens of the polyoxoanion-support).[5b,c]

Oxidation of cyclohexanol with 30% aqueous hydrogen peroxide catalyzed by **1**, $(NBu_4)_9[P_2W_{15}V_3O_{62}]$ **2**, and the 1:1-molar ratio mixture of $[PtCl_2(cod)]/(NBu_4)_9[P_2W_{15}V_3O_{62}]$ **3** was examined in a Schlenk tube containing a magnetic stir bar. The reaction solution was periodically sampled and analyzed by gas chromatography on TC-WAX capillary column. The activity of $[(cod)PtCl_2]$ was low and the reaction stopped after 1 h. No reaction was observed without the catalyst.

Table 1 shows the results of catalytic activities by **1**, **2**, and **3** at 20 °C under Ar in acetonitrile. The main product was cyclohexanone with 100% selectivity and an induction period was not observed. The turnover frequency (TOF) of **1** was $8.5 \times 10^{-4}\,s^{-1}$ after 1 h, which was higher than $4.4 \times 10^{-4}\,s^{-1}$ and $6.9 \times 10^{-4}\,s^{-1}$ for **2** and **3**, respectively. The activities of **1** and **3** increased with time but the reaction catalyzed by **2** stopped after 1 h. The turnover number (TON) of **1** reached 18 after 72 h. This value was also higher than 1.6 after 1 h for **2** and 11 after 72 h for **3**. During the course of the reaction, the color of reaction solutions of **1** and **3** stayed orange, while that of **2** changed from orange to dark-green after adding H_2O_2. These facts suggest that V^{4+}–V^{5+} redox processes prevail to a major extent in the mechanism and the main role of the Pt^{II} atom might be reoxidation of V^{4+} to V^{5+}. The activity of **1** was higher than that of **3**, suggesting that the direct bonding of the Pt^{II} atom onto the V_3 site would be more effective to reoxidize V^{4+} to V^{5+} under the tested conditions.

In conclusion, the polyoxometalate-based organometallic platinum(II) complex **1** was first synthesized and its effective catalytic activity for cyclohexanol oxidation with 30% hydrogen peroxide was found.

Table 1. Oxidation of cyclohexanol with H_2O_2 at 20 °C[a]

Catalyst	TOFs^{-1} [b]	TON
1	8.5×10^{-4}	18[c]
2	4.4×10^{-4}	1.6[d]
3	6.9×10^{-4}	11[c]

[a]Reaction conditions: catalyst 50 μmol, cyclohexanol 9.5 mmol, 30% aq. H_2O_2 9.7 mmol, CH_3CN 10 mL under Ar. [b]TOF = (turnover number (= mol of products/mol of polyoxometalate)/s) after 1 h. [c]After 72 h. [d]After 1 h.

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7 Synthesis of **1**: In an ice-cooled bath, 1.00 g (0.16 mmol) of $(NBu_4)_9[P_2W_{15}V_3O_{62}]$[5a,d] was dissolved in 50 mL of CH_2Cl_2 (infinitely-pure grade; Wako). Dry N_2 was passed through the solution for 20 min. Separately in a glove box, to 0.0695 g (0.36 mmol) of solid $AgBF_4$ placed in 20 mL beaker was added 0.060 g (0.16 mmol) of $[PtCl_2(cod)]$ dissolved in 8 mL of CH_2Cl_2 in 20 mL beaker. The washings with 2 mL of CH_2Cl_2 were also introduced to the mother solution. The mixture was *vigorously stirred* for 20 min in an ice-cooled bath [*Note*: the key point is to complete a formation of AgCl]. Outside of glove box, a white precipitate of AgCl formed was filtered off and the colorless filtrate was dropwise introduced to the clear orange solution of the polyoxotungstate. The AgCl precipitate was washed with ca. 5 mL of CH_2Cl_2 and the washings were introduced to the polyoxotungstate solution. Upon the introduction of the in situ-generated $[(cod)Pt(CH_2Cl_2)_x](BF_4)_2$ solution, the color of the polyoxotungstate solution changed from orange to red. The resulting solution was stirred under a stream of N_2 for 15 min under ice-cooled conditions. The solution was filtered and the filtrate was added to the 500 mL of stirred diethyl ether in an ice-cooled bath to form a pink-orange powder. The powder was washed (10 mL × 2) with diethyl ether, and dried in vacuo for 2 h. Yield: 71.3% (0.79 g).

8 **1**: Anal. Found (parentheses and brackets are from repeat trials for CHN analysis): C, 29.01 (27.97) [28.89]; H, 5.47 (5.13) [5.20]; N, 2.08 (1.83) [1.87]; B, 0.32; F, 1.83; O, 15.7; P, 0.89; V, 2.18; Pt, 2.79; W, 39.9; total 100.17%. Calcd for $C_{152}H_{336}N_9B_2F_8O_{62}P_2V_3PtW_{15}$ or $(NBu_4)_7[\{Pt(cod)\}(P_2W_{15}V_3O_{62})]\cdot 2NBu_4BF_4$: C, 27.56; H, 5.11; N, 1.90; B, 0.33; F, 2.29; O, 15.0; P, 0.94; V, 2.31; Pt, 2.95; W, 41.6%. TG/DTA data: no weight loss observed below 150 °C, suggesting no solvation. Decomposition gradually began around 166 °C with exothermic peaks at 166, 176, 239, 329 and 404 °C. FTIR bands (KBr disk) in 1300–400 cm^{-1} region (polyoxometalate region): 1151w, 1084vs [P–O], 1055s [BF_4^-], (938vs, 954s sh) [M–$O_{terminal}$], (910s, 884s) [M–O_{corner}–M], 787vs (br) [M–O_{edge}–M], 599w, 527m, 472w, 420w cm^{-1}. ^{1}H NMR (500.16 MHz; CD_2Cl_2, 22.4 °C): δ (cod) 2.11, 2.12, 2.66, 2.73, 3.21, 6.26. ^{13}C NMR (125.78 MHz; CD_2Cl_2, 25.8 °C): δ (cod) 30.8, 49.2, 49.2, 93.2. ^{31}P NMR (CD_2Cl_2, 26.2 °C): δ −7.77, −13.90. ^{51}V NMR (CD_2Cl_2, 26.5 °C): δ −486.4 ($\Delta\nu_{1/2}$ 809.5 Hz), −523.7 ($\Delta\nu_{1/2}$ 285.7 Hz). ^{183}W NMR (CD_2Cl_2, 22.8 °C): δ −124.7 (2W), −129.9 (1W), −141.9 (2W), −187.6 (2W), −191.9 (2W), −194.0 (4W), −201.1 (2W).

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