

Synthesis and Characterization of Pd-supported Fluoro-dodecavanadates

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Abstract of Dissertation

Synthesis and Characterization of Pd-supported fluoro-dodecavanadates

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Introduction

Polyoxometalates are inorganic metal oxide which their properties can be controlled by the constituent elements, structures, and counter cations. The area of POMs application are on the catalysis, medicine, bioanalysis and materials science¹.

Polyoxovanadates represent an important subclass of POMs. Vanadium has many oxidation states and exhibit various coordination geometries so that it can provide more structural flexibility and have general tendency to form cluster with shell and cages like topologies. POV clusters can contain mixed valence species ($V^{IV/V}$) that arise from the full or partial delocalization of the single 3d electrons of the vanadium ions over both valence types or the complete localization over the paramagnetic ions²³.

Pd(II) compounds are frequently four-coordinated square planar which can be the building blocks in the construction of extended self-assembled structures.⁴ Palladium (II) is a class b or a soft metallic center. Therefore, it forms various stable complexes with soft ligands.⁵

The design of coordination frameworks based on polyoxometalates (POMOFs), e.g. how to introduce a linker unit on the polyoxometalate frameworks, is essential. Even if the coordination ability of polyoxometalates are commonly small due to the relatively small surface electron density, the introduction of the metal binding sites with available coordination sites are suitable for inorganic functional nanoscale structures.⁶ The motive of this research is how to construct a Palladium supported Polyoxovanadate that can provide free binding metal site Palladium useful as linker for the construction of POMOFs material.

Synthesis of $\{n\text{-Bu}_4\text{N}\}_4[\text{V}_{12}\text{O}_{30}(\text{F})_2] \cdot \text{CH}_3\text{CN}$

In the objective of synthesizing metal inorganic polyoxovanadate (POV) linkers, a core structure for the linker is firstly synthesized. Because POM itself is generally weak coordinator, we started from special kind of POV where Fluoride is incorporated at the center of the POV cluster so that it can enhance the coordination ability of POV. It is a fluoride-incorporated polyoxovanadates $\{n\text{-Bu}_4\text{N}\}_4[\text{V}_{12}\text{O}_{30}(\text{F})_2] \cdot \text{CH}_3\text{CN}$ (**1**) that play important role as core structure for the linker target.

Anion of (**1**) $[\text{V}_{12}\text{O}_{30}(\text{F})_2]^{4-}$ a structural modification of its precursor $[\text{HV}_{11}\text{O}_{29}\text{F}_2]^{4-}$. $[\text{V}_{12}\text{O}_{30}(\text{F})_2]^{4-}$ is a mixed valence V^{IV}/V^V state polyoxovanadate which has square pyramidal vanadium units. Crystallographic study of this complex shows that the polyoxoanion has two

fluoride anions incorporated and four $\{n\text{-Bu}_4\text{N}\}^+$ counter cations. No hydrogen bond interactions were observed.

In this study, we investigated reduction of $[\text{HV}_{11}\text{O}_{29}\text{F}_2]^{4-}$ in nitromethane solvent which leads to a discovery of simple syntheses of $[\text{V}_{12}\text{O}_{30}(\text{F})_2]^{4-}$. The reduction of $[\text{HV}_{11}\text{O}_{29}\text{F}_2]^{4-}$ has a significant effect which not only reduced the vanadium atoms, but also modified the structure unit giving rise to mixed valence $[\text{V}^{\text{IV}}_2\text{V}^{\text{V}}_{10}\text{O}_{30}(\text{F})_2]^{4-}$.

The successful isolation of the product allows the full characterization by X-ray crystallography, IR, UV/visible (UV/Vis), and cyclic voltammetry. Compound **(1)** crystallize in orthorhombic crystal system with space Group Pccn (#56). The molecular structure was determined by X-ray crystallographic analysis (figure 1).

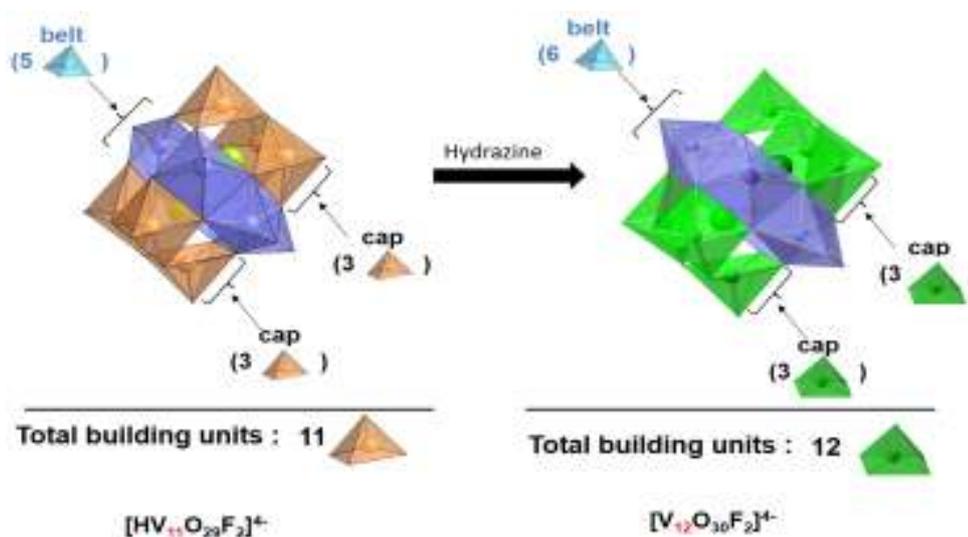


Figure 1 Structural comparison between precursor $[\text{HV}_{11}\text{O}_{29}\text{F}_2]^{4-}$ and product $[\text{V}_{12}\text{O}_{30}(\text{F})_2]^{4-}$. The anion $[\text{V}_{12}\text{O}_{30}(\text{F})_2]^{4-}$ is constructed of six belt VO_5 square pyramids (blue) and six capping VO_5 square pyramids (green). Four counter cations $\{n\text{-Bu}_4\text{N}\}^+$ and the solvated CH_3CN molecule are omitted for clarity.

The anionic $[\text{V}_{12}\text{O}_{30}(\text{F})_2]^{4-}$ cluster anion consists of twelve VO_5 square pyramids with V–O bond lengths range from 1.8010(2) - 2.022(2), while the V–F range from 1.593(3) - 2.217(2). The V–O bond lengths decrease with the decreasing coordination number of the oxygen atom, with values for coordination: $\mu_1\text{-O} = 1.593(3) - 1.603(2)$, $\mu_2\text{-O} = 1.810(2) - 1.836(2)$ and $\mu_3\text{-O} = 1.867 - 2.011$.

BVS calculation shows delocalization of charge of mixed valence complex $[\text{V}^{\text{V}}_{10}\text{V}^{\text{IV}}_2\text{O}_{30}\text{F}_2]^{4-}$ due to spherical shape. The $\mu_3\text{-F}$ bridge is an interesting feature of all of these anions. Bond

distance of V-F 2.18 Å can be said that F in the sphere just sit and floating in the sphere by having ionic interaction with spherical POV in the surrounding. Even if F⁻ ion is too small to be a guest in the cavity without covalent interaction with V, but it creates a strong V-F interaction. Mixed valence state shown also by formula charge is also proven by Cyclic Voltammetry (CV) analysis.

The reversible reductive peaks in CV coupled with oxidative peaks appeared in the range. There are four reductive peaks at 0.39, 0.08, -0.67, and -1.27 V, and four oxidative peaks at -1.00, -0.50, 0.12, 0.53 V. The reductive peaks (V^V - V^{IV}) and oxidative peaks (V^{IV} - V^V) are redox pairs and reversible. The voltage at 0.08 V is the initial state of V^V₁₀V^{IV}₂O₃₀F₂]⁴⁻

Electrochemical behavior of **(1)** show that complex **(1)** can accept reversibly up to four electrons. This makes complex **(1)** is not only for precursor need, but also as a promising material for electron sponge for energy storage application capable of storing 4 electrons reversibly. The UV-vis spectrum of the compound **1** showed absorption bands above 600 nm, suggesting that the vanadium species are mixed valence of reduced V^{IV} and the oxidized to V^V.

The complex **(1)** exhibits characteristic FTIR absorption peaks of POV located in the range of 400 – 1000 cm⁻¹. The IR spectrum of **(1)** shows strong bands around 989 cm⁻¹, which correspond to the ν(V=O_{terminal}) stretching frequencies. Stretching of the V–O_{bridge} bond appears in the range 500–900 cm⁻¹. Complex **(1)** also has μ₂-O bridges and exhibits distinct peaks in the 750–900 cm⁻¹ region. The relatively weak spectrum in the range of 750 – 900 cm⁻¹ is due to the lack of μ₂-O bridges compared with μ₃-O bridges.⁷ So, by characterization of complex **(1)**, beside the use for precursor for synthesis of polyoxometalates framework linkers, compound **(1)** open up potential application in the field of catalysis due to presence catalyst active Pd and V atoms and also for energy storage material with high capacity.

Synthesis of Reduced Palladium Supported Fluoride Incorporated Dodecavanadate [VO(DMSO)₅]₂{[PD(DMSO)₂]₂V₁₂O₃₂(F)₂].2CH₃CN (compound 2).

This compound **2** is the first time of new POM based inorganic linker unit successfully synthesized. The linker is in a reduced form synthesized from the reduced POV precursor (compound **1**). To provide a bidentate coordination site of the linker unit, Pd²⁺ was chosen to react with anion **1** while the remaining two coordination sites of Palladium ion are occupied by leaving group ligands.

The synthesis by using reaction of Pd²⁺ ion with precursor synthesized before {*n*-Bu₄N}₄[V₁₂O₃₀(F)₂]·CH₃CN was performed by solution-based synthetic method and crystallization process was in ambient pressure and temperature. The POM starting materials are dissolved in the DMSO solvent by which the reaction with Pd²⁺ solution results in the reformation of metal oxide fragments to form a discrete mixed valence Pd-V₁₂ anionic clusters.

The title compound (**2**) crystallizes in the monoclinic space group, P21/c (#14). Compound (**2**) consists of Pd supported [$\{\text{Pd}(\text{DMSO})_2\}_2\text{V}_{12}\text{O}_{32}(\text{F})_2\}^{4-}$] anion. The [$\{\text{Pd}(\text{DMSO})_2\}_2\text{V}_{12}\text{O}_{32}(\text{F})_2\}^{4-}$] anion is composed of two tetrahedral VO₄ units and ten square pyramid VO₅ units, and two F⁻ reside inside the cage (polyhedra view in Figure 2). Each tetrahedral VO₄ is connected to Pd. Two DMSO ligands are connected to each Pd atom to form Pd square planar coordination geometry.

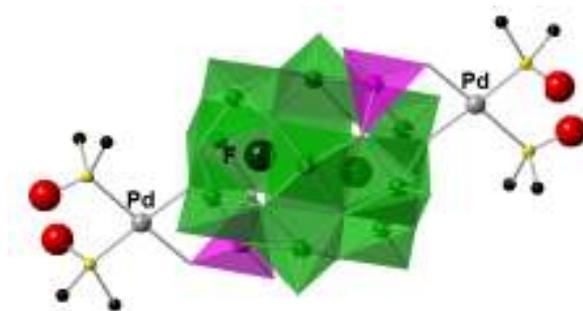


Figure 2 the anionic [$\{\text{Pd}(\text{DMSO})_2\}_2\text{V}_{12}\text{O}_{32}\text{F}_2\}^{4-}$], the VO₄ unit in purple tetrahedral and the VO₅ unit in green square pyramid. The dark green, gray, red, black spheres represent fluorine, palladium, oxygen, nitrogen, sulfur, and carbon atoms, respectively. Hydrogen atoms are omitted for clarity.

Single crystal X-ray analysis revealed that the asymmetric unit of the title compound consists of one half of the [$\{\text{Pd}(\text{DMSO})_2\}_2\text{V}_{12}\text{O}_{32}(\text{F})_2\}^{4-}$] anion and two molecules [VO(DMSO)₅]²⁺; the symmetrically dependent parts generated through the crystallographic center of symmetry. The acetonitrile molecules present in the crystal structure is confirmed by TG Analysis.

Like the precedented difluoride-incorporated polyoxovanadates that possess the structure of [V₁₂O₃₂(F₂)]ⁿ⁻ or its lacunary type structure, complex (**2**) has three layers of one belt layer sandwiched by two cap layers. As halide incorporated POVs, F⁻ ion is too small to be a single guest in the cavity, so two F ions are present in the cage. V-F, however creates a strong V-F

interaction although there is no bonding between them.⁸ The repulsion between F⁻ ions in the center also determine the structure (F...F = 2.946 Å).

From the structure, Pd atoms support the structure at both ends. The square planar Pd ion are accomplished with two DMSO molecules with S coordination to form coordination number four of Palladium ion. DMSO which have basic character is an excellent ligand. Two types of oxido bridges are present in the structure, with V- μ -O bridges with bond lengths in the range 1.712–1.930(1) Å and V- μ_3 -O bridges with bond lengths in the range 1.917–2.114 Å. The charges of V atoms as mixed valences of 4+ and 5+ as indicated by the bond valence sum calculations. In addition, UV/Vis spectrum of (**2**) clearly shows peak above 600 nm which is attributed with Intervalence Charge Transfer (IVCT) of POVs.

The anionic mixed valent [$\{\text{Pd}(\text{DMSO})_2\}_2\text{V}_{12}\text{O}_{32}(\text{F})_2$]⁴⁻ is a potential linker in Polyoxometalate based Metal Organic Framework Chemistry. Ligand DMSO can be considered a leaving ligand which can be replaced by other bidentate ligand to grow a framework structure. Besides that, making use catalytic active Pd site in addition to catalytic active V atoms is also interesting to explore.

Synthesis of fully oxidized $\{n\text{-Bu}_4\text{N}\}_4[\{\text{Pd}(\text{NO}_3)(\text{DMSO})\}_2\text{V}_{12}\text{O}_{32}(\text{F})_2]\cdot 2\text{DMSO}$

In the objective of obtaining stable Pd-Polyoxovanadate linker unit against oxidation, complex $\{n\text{-Bu}_4\text{N}\}_4[\{\text{Pd}(\text{NO}_3)(\text{DMSO})\}_2\text{V}_{12}\text{O}_{32}(\text{F})_2]\cdot 2\text{DMSO}$ (**3**) was synthesized. The air stable complex **3** can be obtained by oxidation of both complex **2** as precursor and some other POVs.

In this work, we demonstrated the formation of a fully oxidized Pd supported fluoro decavanadate by deliberately choosing F⁻ as the incorporated anions and Nitrate as the other ligand beside DMSO for the complex. This give rise to the spherical fluoride-incorporated polyoxovanadate which also have Pd²⁺ units on the polyoxovanadate framework ready to use as linker sites (figure 3).

The synthesis of complex (**3**) was by addition of $\{n\text{-Bu}_4\text{N}\}_4[\text{V}_{10}\text{O}_{26}]$ and $\{n\text{-Bu}_4\text{N}\}\text{F}$ into the solution of Pd(NO₃)₂. The addition of excess amount of hydrogen peroxide was needed to assure the full oxidation of all vanadium atoms. To control the speciation of polyoxovanadate nitric acid was added⁷. Red crystal suitable for single X-ray crystallographic analysis (**3**) were obtained from the solution in ca 50% yield based on Pd²⁺ (Figure 3). Four tetra-*n*-butyl ammonium cations per one polyoxovanadate were determined. The anion structure of **3**

exhibited the basal fluoride-incorporated polyoxovanadates with three layers of one belt layer of four VO₅ units and two cap layers of [V₃O₁₃] fragments.

This is a new fully oxidized Pd supported polyoxometalate compound synthesized in mixed CH₃NO₂/DMSO media., crystallized in Orthorhombic space group Pbca.

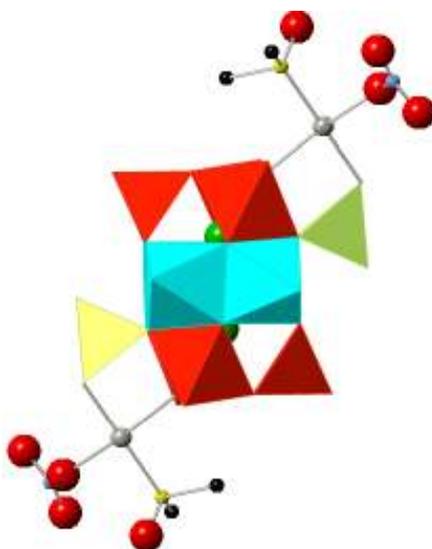


Figure 3 Polyhedral and ball-and-stick representation of the anion part of complex **(3)**. Polyhedra represent vanadium-oxygen units, green, gray, red, light blue, yellow and black spheres represent fluorine, palladium, oxygen, nitrogen, sulfur, and carbon atoms, respectively. Hydrogen atoms are omitted for clarity. Polyhedra in blue, red and yellow represent belt, capping, and addenda VO₄ units.

The shortest V...F distance (2.17 Å) is longer than that of the usual V–F bonds (ca. 1.8 Å). This suggests that the vanadium atoms and a fluoride anion are not directly bonded like other fluoride-incorporated polyoxovanadates. In addition to the parent structure, two VO₄ units existed between the belt and cap layers. The two Pd²⁺ atoms have square planar geometry bridged by an oxygen atom from a VO₄ unit and a bridging oxygen atom between edge-shared VO₅ units on the cap layer.

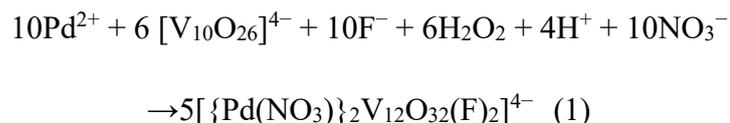
The peripheral sites of the anion are occupied by an oxygen atom from NO₃[−] and a sulfur atom of DMSO. The N–O distances of NO₃[−] are 1.22, 1.24, and 1.43 Å. The N–O distance with O coordinated to Pd is longer than the others.

While free DMSO has S–O distance 1.531 Å, the S–O and S–C distances of Pd-coordinated DMSO are 1.47, 1.77, and 1.78 Å, respectively. These values are comparable to those of free DMSO, indicating the weak interaction between Pd and DMSO. The anion is

discrete because the Pd-coordinated NO_3^- and DMSO were not connected to the other moieties. In the other report, $\text{Pd}(\text{DMSO})_2(\text{NO}_3)_2$ exhibit dimer configuration bridged by nitrate.⁹

From X-ray crystallographic, elemental, and thermogravimetric analyses show that the formula of **(3)** is $\{n\text{-Bu}_4\text{N}\}_4[\{\text{Pd}(\text{NO}_3)(\text{DMSO})\}_2\text{V}_{12}\text{O}_{32}(\text{F})_2]\cdot 2\text{DMSO}$.

The reaction equation for the formation of **(3)** can be expressed by the following equation (1):



Compound **(3)** is the first example of fully oxidized polyoxovanadates with available metal coordination sites as a linker unit, to best of our knowledge.

The charges of V atoms are all pentavalent by the bond valence sums. The IR spectra of **(3)** shows characteristic POV peak, in the region of $1000\text{--}400\text{ cm}^{-1}$. Interestingly these peaks are similar in shape to that of $[\text{HV}_{11}\text{O}_{29}\text{F}_2]^{4-}$,¹⁰ which possess the similar fully oxidized structure.

Two peaks of S–O stretching vibration at 1050 and 1110 cm^{-1} , are due to free and coordinated DMSO, respectively. The higher wavenumber of coordinated DMSO suggested the coordination to palladium center via sulfur atom, as shown in crystallographic analysis¹¹. Peaks due to symmetric and asymmetric vibration of NO_3^- were observed at 1356 and 1511 cm^{-1} , respectively¹¹.

The solution state of **(3)** was studied by NMR spectra measurement in CD_3CN . The assignments based the factor that the ^{51}V NMR signal of a vanadium-supported noble metal complex tends to resonate downfield with integration ratio of 2:1:2:1 were in accordance with the symmetry of the crystal structure of **3**. These result of ^{19}F NMR spectrum that shows single signal ascertains both the presence of F in the sphere and the structural integrity of the dodecavanadate framework of **3** in the solution state. For the ^1H NMR spectrum, the four peaks for to tetra-*n*-butylammonium as counter cations are observed, also the peak for free DMSO, Furthermore, by ^1H NMR test the exchangeable Pd-coordinated DMSO is observed¹².

Compared with the previous works, the peak at 3.37 ppm is due to Pd-coordinated DMSO via oxygen, and the other is due to that via sulfur, indicating that in the solution state DMSO coordination via oxygen atom to the Pd center is preferable.¹²

From the measurement of UV/Vis spectrum of **3** in CH₃CN, shows similar adsorption band in the similar region with the fully oxidized fluoride-incorporated polyoxovanadate, [HV₁₁O₂₉F₂]⁴⁻, which also has similar structural units with **3**.⁷

Here, a new Pd supported F⁻ inclusion dodecavanadate clusters. Anionic (**3**) is a new building block of polyoxometalates designed by utilizing the unique structural features of fluoride-incorporated polyoxometalates. By the combination of both tetrahedrally and square-pyramidally coordinated vanadium atoms, both cations and anions are stabilized by one polyoxovanadate framework. Measurement of ¹H NMR shows the ligand exchange property of Pd-coordinated DMSO with at the same time maintaining the polyoxovanadate framework.

Different from complex (**2**) which is insoluble in most solvents, complex (**3**) is soluble in most organic solvents. This enable the exploration of the chemistry of the complex better than previously prepared complex (**2**). Like anionic [$\{\text{Pd}(\text{DMSO})_2\}_2\text{V}_{12}\text{O}_{32}(\text{F})_2$]⁴⁻ in complex (**2**), anion $\{\text{Pd}(\text{NO}_3)(\text{DMSO})\}_2\text{V}_{12}\text{O}_{32}(\text{F})_2$ ⁴⁻ is also potential linker in Polyoxometalate based Metal Organic Framework Chemistry. Ligand DMSO and Nitrate are weakly bonded and considered as the leaving groups which can be replaced by other organic multidentate ligands to develop a framework structure. Apart from coordination polymer / POMOF linker, catalytic activity of complex (**3**) is also very interesting subject to study.

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学位論文審査報告書（甲）

1. 学位論文題目（外国語の場合は和訳を付けること。）

Synthesis and Characterization of Pd-supported Fluoro-dodecavanadates

(パラジウム担持型フルオロドデカバナデートの合成と性質)

2. 論文提出者 (1) 所属
- 物質化学専攻

(2) 氏名 Miftahul Khair

3. 審査結果の要旨（600～650字）

提出された学位論文について、審査員による予備審査を実施するとともに平成29年8月1日に開催された口頭発表および質疑応答の結果を踏まえ、その後開催した審査委員会で協議を行った。その結果、以下のように判定した。

ポリオキシメタレートと呼ばれる酸化物分子は、電子材料、磁性体、電池、触媒などに利用される酸化物を分子として切り出した物質であり構造と組成を完全に制御できる特徴がある。そこで、構造制御が困難である固体酸化物を酸化物分子から再構成することで構造と組成をより詳細に制御可能とする合成経路の開発が必要である。その第一歩として本論文ではポリオキシメタレートの弱い配位力を克服するために金属イオンをポリオキシメタレートに担持し、金属イオンの外側の配位座を置換可能な脱離基で保護した化合物の合成法を探索した。その結果、フッ化物イオンを導入したポリオキシバナデートを利用してパラジウム錯体を担持した酸化型および還元型化合物の合成に成功した。このフルオロポリオキシバナデートの両端に担持されたパラジウムには利用可能な配位座があることから無機構造体の連結部位と見なすことができる。ガス吸着や分離での利用が期待される金属有機構造体(MOF)や超分子における構造体の十字連結部位として応用可能な研究として意義深いことから、博士(理学)の学位に値するものと判断した。

4. 審査結果 (1) 判定 (いずれかに○印)
- 合格
- ・不合格

(2) 授与学位 博士(理学)