

# Facile Incorporation of Platinum(IV) into Polyoxometalate Frameworks: Preparation of $[\text{H}_2\text{Pt}^{\text{IV}}\text{V}_9\text{O}_{28}]^{5-}$ and Characterization by $^{195}\text{Pt}$ NMR Spectroscopy\*\*

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The class of polyoxometalates (POMs) is composed of edge- and corner-shared  $[\text{MO}_6]$  octahedra with early-transition-metal ions in high oxidation states (e.g.  $\text{W}^{\text{VI}}$ ,  $\text{V}^{\text{V}}$ ).<sup>[1]</sup> POMs are discrete molecular species which have gained increasing attention over the last 30 years, largely owing to a unique combination of their properties. In addition to the enormous structural and compositional variety, which is unmatched in inorganic chemistry, POMs can be tuned in solubility, redox activity, color, thermal stability, charge density, and so on. As a result, POMs exhibit potential applications in many different and diverse areas such as catalysis, magnetism, bio- and nanotechnology, and medical and materials sciences.<sup>[2]</sup>

Polyoxovanadates (POVs) are a subclass of POMs, and they also exhibit a rich structural variety,<sup>[1,2]</sup> largely because the vanadium center can adopt variable coordination geometries, including octahedral, square-pyramidal, and tetrahedral. Furthermore, the reduction of vanadium from the +V to the +IV oxidation state is facile, and as a result, mixed-valence POVs can be formed.<sup>[3]</sup> For this reason, POVs are very interesting for redox applications in catalysis and materials science.<sup>[4]</sup>

Although POVs cover a large range of size, shape, and composition, they have not been investigated as much as polyoxotungstates and -molybdates.<sup>[2]</sup> In particular, Müller's group has been quite active in this area, reporting several reduced and mixed-valence heteropolyoxovanadates.<sup>[5]</sup> These authors isolated some interesting clathrate-type POVs containing a variety of heteroatomic groups such as  $\text{Cl}^-$ ,  $\text{N}_3^-$ ,  $\text{HCOO}^-$ , and  $\text{NO}_2^-$ , thus demonstrating that the shape of the anionic guest predetermines the overall shape and size of the resulting POV.

The area of isopolyvanadates is dominated by the famous decavanadate ion  $[\text{H}_x\text{V}_{10}\text{O}_{28}]^{(6-x)-}$  ( $\text{V}_{10}$ ).<sup>[6]</sup> It is well established that this POM can also be isolated in mono-, di-, tri-, and tetraprotonated forms.<sup>[7]</sup> However, incorporation of other transition metals besides vanadium into this structural type has not been reported yet. In particular, substitution of one or more vanadium atoms by late 4d or 5d transition metals in high oxidation states (e.g.  $\text{Pt}^{\text{IV}}$ ,  $\text{Pd}^{\text{IV}}$ ) would result in mixed-metal derivatives with highly promising catalytic properties.

To date, only a few Pt-containing POMs are known, and interestingly all of them are polyoxotungstates and -molybdates with the Anderson–Evans or Keggin structure. In 1983 Lee et al. reported on  $[\text{H}_3\text{Pt}^{\text{IV}}\text{W}_6\text{O}_{24}]^{5-}$ ,<sup>[8]</sup> and in 1984 Lee and Sasaki described the  $\alpha$  and  $\beta$  isomers of the molybdenum analogue  $[\text{Pt}^{\text{IV}}\text{Mo}_6\text{O}_{24}]^{8-}$ .<sup>[9]</sup> During the last two decades the Lee group has investigated both polyoxomolybdate and -tungstate  $[\text{H}_x\text{Pt}^{\text{IV}}\text{M}_6\text{O}_{24}]^{n-}$  ( $\text{M} = \text{Mo}, \text{W}$ ) systems in much detail, reporting numerous derivatives with different degrees of protonation.<sup>[10,11]</sup>

In 2003 the Lee group also reported on the  $\text{Pt}^{\text{IV}}$ -containing Keggin ion  $[\alpha\text{-SiPt}^{\text{IV}}_2\text{W}_{10}\text{O}_{40}]^{8-}$ , which represents the first late-transition-metal oxo complex.<sup>[12]</sup> In 2004 Hill and co-workers reported the  $\text{Pt}^{\text{IV}}$ -containing Knoch-type tungstophosphate dimer  $[\text{O}=\text{Pt}^{\text{IV}}(\text{H}_2\text{O})(\text{PW}_9\text{O}_{34})_2]^{16-}$ , but no  $^{183}\text{W}$  or  $^{195}\text{Pt}$  NMR spectra were shown.<sup>[13]</sup> Already in 1997 Liu et al. reported on a  $\text{Pt}^{\text{IV}}$ -containing Wells–Dawson ion with the formula  $[\alpha_2\text{-P}_2\text{W}_{17}\text{Pt}(\text{OH}_2)\text{O}_{61}]^{6-}$ , but this formulation is not supported by the shown  $^{31}\text{P}$  and  $^{183}\text{W}$  NMR spectra.<sup>[14]</sup>

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Supporting information for this article is available on the WWW under <http://www.angewandte.org> or from the author.

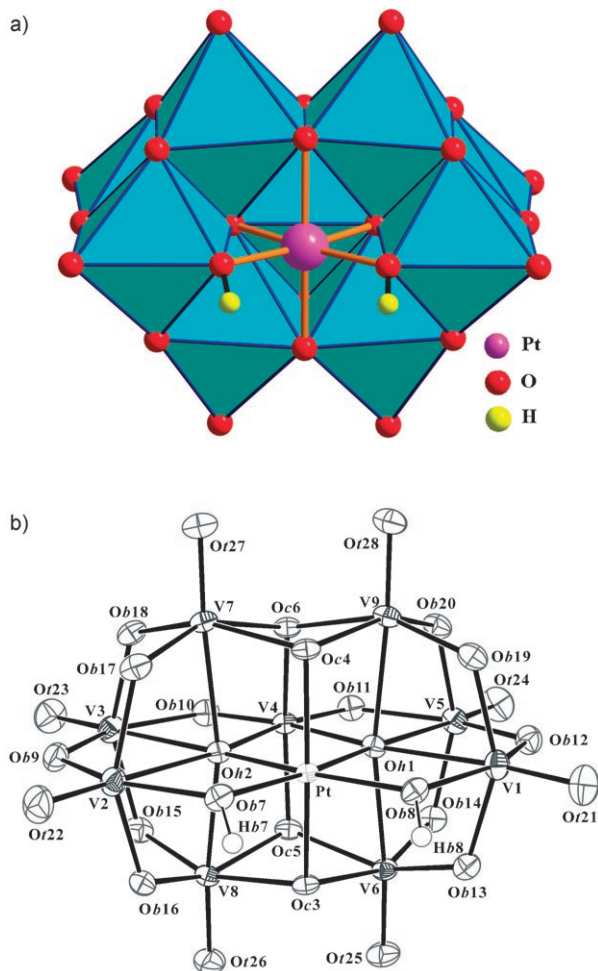
Herein we report on the successful incorporation of  $\text{Pt}^{\text{IV}}$  into the decavanadate structure. The polyanion  $[\text{H}_2\text{Pt}^{\text{IV}}\text{V}_9\text{O}_{28}]^{5-}$  (**1**) was prepared by a simple, one-pot stoichiometric reaction of  $\text{Na}_2[\text{Pt}(\text{OH})_6]$ <sup>[15]</sup> with  $\text{NaVO}_3$  in aqueous solution (pH 4.3), and then isolated as the hydrated sodium salt  $\text{Na}_5[\text{H}_2\text{Pt}^{\text{IV}}\text{V}_9\text{O}_{28}] \cdot 21\text{H}_2\text{O}$  (**1a**).<sup>[16]</sup> Polyanion **1** has the well-known decavanadate structure, but one of the two central addenda sites is now occupied by platinum(IV) in a regioselective fashion (Figure 1). Therefore, **1** represents the first transition-metal-substituted decavanadate derivative and the first platinum(IV)-containing polyoxovanadate. Interestingly, **1** exhibits no disorder of the platinum(IV) ion over any of the remaining eight decavanadate sites (which all have a terminal oxo ligand). This observation indicates that the  $\text{Pt}^{\text{IV}}$  ion in **1** favors a coordination environment consisting exclusively of bridging oxo ligands. The bond lengths around the octahedral Pt center are very regular, ranging from 1.980(3) to 2.027(3) Å (see Figure 1).

The polyanion **1** has idealized  $C_{2v}$  symmetry. Both H atoms attached to **1** (see Figure 1) were not only identified

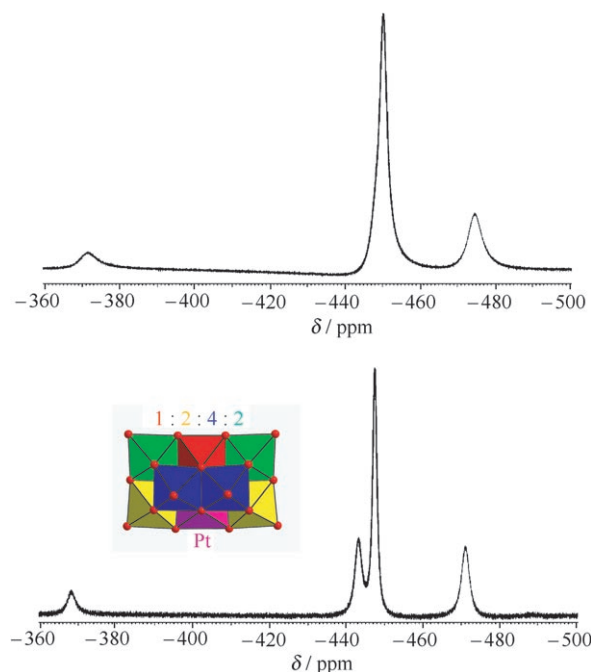
by bond valence sum (BVS) calculations,<sup>[17]</sup> but were actually located in the difference Fourier map and refined with the  $\text{O}\cdots\text{H}$  separations restrained to 0.85(10) Å. These protons are particularly important in the solid state as they enforce formation of a dimer assembly,  $[\text{H}_4(\text{Pt}^{\text{IV}}\text{V}_9\text{O}_{28})_2]^{10-}$ , through four interanion  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds (see the Supporting Information). We also prepared derivatives of **1** with different degrees of protonation, such as  $[\text{H}_x\text{Pt}^{\text{IV}}\text{V}_9\text{O}_{28}]^{(7-x)-}$  ( $x = 2.5, 3, 4, 5$ ), as shown by single-crystal X-ray analysis. Considering that the  $\{\text{PtO}_6\}$  octahedron is significantly larger than the other nine  $\{\text{VO}_6\}$  octahedra, we believe that **1** must tolerate some strain. However, our solid-state and solution (see below) results indicate that **1** is rather stable.

To complement our solid-state XRD results on **1** with solution studies, we performed  $^{51}\text{V}$  and  $^{195}\text{Pt}$  NMR measurements on **1a** redissolved in  $\text{H}_2\text{O}/\text{D}_2\text{O}$ . All NMR spectra were recorded on a 400 MHz JEOL ECX instrument at room temperature using 5-mm tubes. The resonance frequencies used for  $^{51}\text{V}$  and  $^{195}\text{Pt}$  NMR were 105.155 and 85.941 MHz, respectively, and the chemical shifts are reported with respect to neat  $\text{VOCl}_3$  and aqueous 2M  $\text{K}_2[\text{Pt}(\text{CN})_6]$ . All chemical shifts downfield of the references are reported as positive values. The  $^{51}\text{V}$  NMR spectrum exhibits only 3 broad peaks ( $\delta = -371.4, -450.3$ , and  $-475.1$  ppm) with approximate relative intensities 1:2:6 rather than the expected four peaks with relative intensities 1:2:2:4. However, upon heating the solution to 60 °C we observed a splitting of the central, most intense peak (with intensity 6) into two peaks (with intensities 2:4), resulting in exactly the expected spectrum ( $\delta = -368.3, -443.0, -446.9$ , and  $-471.5$  ppm; see Figure 2).

Based on their relative intensities, the largest signal at  $\delta = -446.9$  ppm can be assigned to the four equivalent vanadium centers (blue, Figure 2), and the smallest signal at  $\delta =$



**Figure 1.** a) Polyhedral representation of **1** ( $\{\text{VO}_6\}$  octahedra: light blue). b) Ball-and-stick representation of **1** showing 30% thermal ellipsoids and complete atom labeling. Bond lengths [Å] and angles [°]: Pt–Oh1 1.985(3), Pt–Oh2 1.980(3), Pt–Oc3 2.020(3), Pt–Oc4 2.026(3), Pt–Ob7 2.027(3), Pt–Ob8 2.021(3); Oh1–Pt–Ob7 173.1(1), Oh2–Pt–Ob8 173.3(1), Oc3–Pt–Oc4 168.4(1), Oh1–Pt–Oh2 85.3(1), Oh2–Pt–Ob7 88.0(1), Oh1–Pt–Ob8 88.1(1), Ob7–Pt–Ob8 98.7(1).



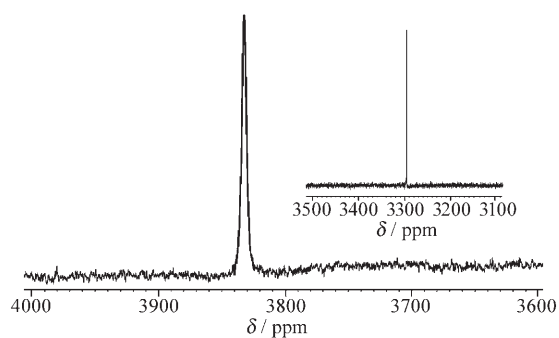
**Figure 2.**  $^{51}\text{V}$  NMR spectrum of **1a** redissolved in  $\text{H}_2\text{O}/\text{D}_2\text{O}$  at 293 K (top) and 333 K (bottom).

−368.3 ppm corresponds to the unique vanadium atom (red). The situation is somewhat more complicated for the two vanadium centers shown in yellow and green, but we suggest the following assignment (based exclusively on structural considerations) for the two peaks of equal intensity:  $\delta = -443.0$  (yellow) and  $-471.5$  ppm (green).

Interestingly, the temperature-induced change of the  $^{51}\text{V}$  NMR spectrum is fully reversible. In other words, after allowing the solution of **1** to cool down to room temperature, we observe again the three-line spectrum (Figure 2, top). Possible reasons for this phenomenon are a decreasing half-width of the NMR signals with increasing temperature and/or downfield shift of the NMR signals with increasing temperature (by about 3 ppm). In addition, the fact that two molecules of **1** form hydrogen-bonded dimers in the solid state (see above) could also be important. It is possible that the NMR spectrum at 293 K actually corresponds to the weakly bound dimer assembly, whereas heating to 333 K breaks them apart, resulting in monomeric **1**. It must be remembered that the  $^{51}\text{V}$  NMR experiments take several hours. We plan to investigate the thermodynamic stability of the dimer assembly in the future by using appropriate techniques (e.g. size exclusion chromatography, ultracentrifugation, cryo-mass spectrometry).

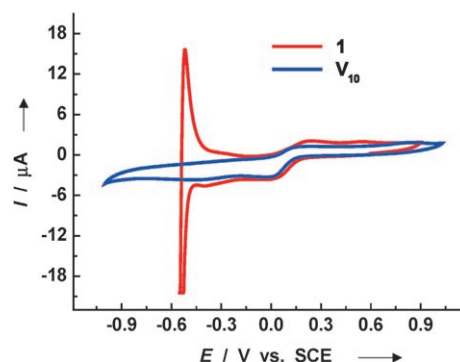
Already more than 30 years ago Pope and O'Donnell investigated the decavanadate ion  $\text{V}_{10}$  by  $^{51}\text{V}$  NMR spectroscopy in solution, and they discovered that the chemical shifts are pH dependent.<sup>[18]</sup> Since then also other groups have engaged in  $^{51}\text{V}$  and  $^{17}\text{O}$  NMR studies of  $\text{V}_{10}$ ,<sup>[7a,19]</sup> but to our knowledge no study on the temperature dependence of the chemical shifts has been reported for  $\text{V}_{10}$ . Our results above show that such a study could be interesting, in particular for derivatives of  $\text{V}_{10}$  with different degrees of protonation.

Next, we performed  $^{195}\text{Pt}$  NMR measurements on **1a** redissolved in  $\text{H}_2\text{O}/\text{D}_2\text{O}$ . This technique had only been applied once before in POM chemistry for  $[\alpha\text{-SiPtW}_{11}\text{O}_{40}]^{6-}$ , but no signal was observed.<sup>[20]</sup> We located the expected singlet for **1** at  $\delta = 3832$  ppm (Figure 3). The corresponding  $^{195}\text{Pt}$  NMR signal for the precursor  $\text{Na}_2[\text{Pt}(\text{OH})_6]$  appeared significantly more upfield (3294 ppm). The combination of  $^{51}\text{V}$  and  $^{195}\text{Pt}$  NMR is fully consistent with the solid-state structure of **1** and hence provides unequivocal evidence for the presence of this polyanion also in solution. Importantly, this is the first report ever on the successful use of  $^{195}\text{Pt}$  NMR in POM chemistry.



**Figure 3.**  $^{195}\text{Pt}$  NMR spectrum of **1a** and of the precursor  $\text{H}_2[\text{Pt}(\text{OH})_6]$  (inset) in  $\text{H}_2\text{O}/\text{D}_2\text{O}$  at 293 K.

We also performed electrochemistry studies of **1** in solution. Detailed cyclic voltammetric and electrocatalytic data are included in the Supporting Information and are summarized here. Both cyclic voltammograms (CVs) of **1** and  $\text{V}_{10}$ , respectively, exhibit a first redox couple with closely spaced reduction potentials (Figure 4). A controlled potential



**Figure 4.** Superposition of the cyclic voltammograms of **1** and  $\text{V}_{10}$  ( $2 \times 10^{-4}$  M solutions in 0.4 M  $\text{CH}_3\text{COONa}/\text{H}^+$  at pH 5). Working electrode: glassy carbon; reference electrode: SCE; scan rate:  $10 \text{ mV s}^{-1}$ .

electrolysis performed with the glassy carbon potential set at +0.03 V shows a consumption of 8 electrons per molecule for both compounds. This couple is attributed to the reduction of  $\text{V}^{\text{V}}$  centers. The other waves of **1** that do not exist in the CV of  $\text{V}_{10}$  are associated with the reduction of the  $\text{Pt}^{\text{IV}}$  center, including the nucleation process, and subsequent reduction of protons on the deposited  $\text{Pt}^0$  film. Upon potential reversal, oxidation of the resulting dihydrogen is observed. This hydrogen evolution reaction occurs with a very small overpotential, and the corresponding Tafel parameters compare favorably with the best parameters for Pt electrodes. The deposited Pt film also exhibits high performance in the electro-oxidation of  $\text{CH}_3\text{OH}$ . Polyanion **1** constitutes a good candidate for elaborating very active carbon-supported Pt nanoparticles, because it has a perfectly defined molecular stoichiometry, and without chloride present it is not prone to easy hydrolysis.

In summary, we have synthesized and structurally characterized a monoplatinum(IV) derivative of the decavanadate ion. Polyanion **1** represents the first  $\text{Pt}^{\text{IV}}$ -containing polyoxovanadate, and its solution characterization by  $^{195}\text{Pt}$  NMR spectroscopy is unprecedented in POM chemistry. The simple and straightforward synthetic methodology of **1**, combined with the analytical power of  $^{195}\text{Pt}$  NMR spectroscopy in solution, appears also applicable to lacunary polyoxotungstates and hence may allow us to prepare  $\text{Pt}^{\text{IV}}$ -containing heteropolytungstates. We have already completed solution and solid-state studies for diplatinum(IV)-substituted tungstosilicates of the Keggin type (such as  $[\text{SiPt}_2\text{W}_{10}\text{O}_{40}]^{8-}$ ) or the Anderson–Evans type ( $[\text{H}_x\text{Pt}^{\text{IV}}\text{M}_6\text{O}_{24}]^{(8-x)-}$ ;  $\text{M} = \text{W}^{\text{VI}}, \text{Mo}^{\text{VI}}$ ). We are currently in the process of preparing the first examples of lone-pair-containing Krebs-type heteropolytungstates with incorporated  $\text{Pt}^{\text{IV}}$  centers. Also, we are interested in synthesizing

examples of Pt<sup>IV</sup>-containing tungstophosphates. For such projects we consider <sup>195</sup>Pt NMR spectroscopy (and also <sup>183</sup>W NMR) in solution as an indispensable analytical tool. All the Pt<sup>IV</sup>-containing polyanions described above are highly interesting catalyst precursors with low Pt content. Therefore, we are planning electrochemistry/-catalysis as well as homogeneous and heterogeneous catalysis studies.

### Experimental Section

**1a:** H<sub>2</sub>[Pt(OH)<sub>6</sub>] (0.20 g, 0.67 mmol; synthesized according to reference [21]) was dissolved in aqueous NaOH solution at pH 11 (10 mL), followed by addition of a solution prepared by dissolving NaVO<sub>3</sub> (0.73 g, 6.0 mmol) in H<sub>2</sub>O (20 mL). This combined solution was heated in a water bath for 30 minutes, allowed to cool to room temperature, and then the pH was adjusted to 4.3 with 3 M nitric acid. The volume of the solution was reduced to about 15 mL in a water bath. After a day, very stable, red-brown, hexagonal-prismatic crystals of **1a** formed, which were isolated by filtration and then dried in air. Yield: 0.65 g (61 %). IR for **1a**:  $\tilde{\nu}$  = 988 (s), 976 (s), 846 (s), 750 (s), 648 (w), 591 (sh), 527 (m), 431 (w), 419 cm<sup>-1</sup> (w). Elemental analysis (%) calcd for **1a**: Na 7.2, V 28.7, Pt 12.2; found: Na 6.9, V 28.9, Pt 12.0.

The thermogram (20–900 °C) and IR spectrum of **1a** are shown in the Supporting Information.

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- [15] We were also able to crystallize the Pt<sup>IV</sup> precursor ion [Pt(OH)<sub>6</sub>]<sup>2-</sup> as the guanidinium salt [C(NH<sub>2</sub>)<sub>3</sub>]<sub>2</sub>[Pt(OH)<sub>6</sub>]: cubic, *F*<sub>43m</sub>, *a* = 10.5763(2) Å. The <sup>195</sup>Pt NMR spectrum of [Pt(OH)<sub>6</sub>]<sup>2-</sup> is shown in Figure 3 as an insert.
- [16] Crystal data for **1a**: A dark brown block of **1a** with dimensions 0.42 × 0.35 × 0.21 mm<sup>3</sup> was mounted on a glass fiber for indexing and intensity data collection at 298 K on a Stoe STADI4 single-crystal diffractometer using MoK<sub>α</sub> radiation ( $\lambda$  = 0.71069 Å). Of the 9856 unique reflections ( $2\theta_{\text{max}}$  = 54.94°), 8957 reflections (*R*<sub>int</sub> = 0.000) were considered observed (*I* > 2σ(*I*)). Direct methods were used to solve the structure and to locate the platinum and vanadium atoms (SHELXS-97). Then the remaining atoms were found from successive difference maps (SHELXL-97). The final cycle of refinement, including determination of the atomic coordinates and anisotropic thermal parameters of the Pt, V, Na, and O atoms, converged at *R* = 0.034 and *R*<sub>w</sub> = 0.086 (*I* > 2σ(*I*)). The two hydrogen atoms Hb7 and Hb8 covalently bonded to **1** (to Ob7 and Ob8, respectively) were identified in the Fourier difference map, and their displacement parameters were refined freely. However, the H atoms of the water molecules were placed in calculated positions and were included in the refinement using the riding-motion approximation, with *U*<sub>iso</sub>(H) = 1.5 *U*<sub>eq</sub>(O). In the final difference map the deepest hole was −2.05 e Å<sup>-3</sup> (0.78 Å from H18A) and the highest peak 2.19 e Å<sup>-3</sup> (1.21 Å from H18A). Routine Lorentz and polarization corrections were applied, and a numerical absorption correction was performed using the program X-SHAPE (Stoe, 1996). Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-418364.
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