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Synthesis and Characterization of the Platinum-Substituted Keggin Anion α-$H_2SiPtW_{11}O_{40}{}^{4-}$

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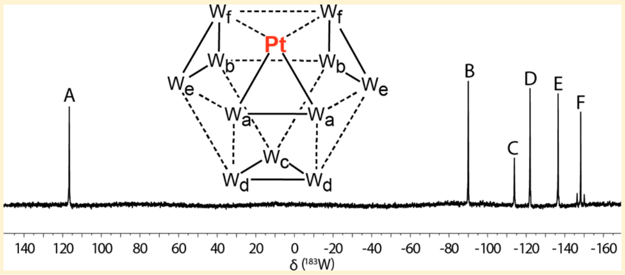
Ⓢ *Supporting Information*

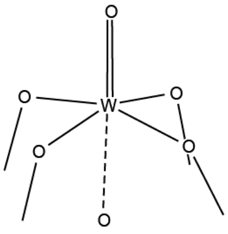
ABSTRACT: Acidification of an aqueous solution of $K_8SiW_{11}O_{39}$ and $K_2Pt(OH)_6$ to pH 4 followed by addition of excess tetramethylammonium (TMA) chloride yielded a solid mixture of TMA salts of $H_2SiPtW_{11}O_{40}{}^{4-}$ (**1**) and $SiW_{12}O_{40}{}^{4-}$ (**2**). The former was separated from the latter by extraction into an aqueous solution and converted into tetra-*n*-butylammonium (TBA) and potassium salts **TBA-1** and **K-1**. The α-$H_2SiPtW_{11}O_{40}{}^{4-}$ was identified as a monosubstituted Keggin anion using elemental analysis, IR spectroscopy, X-ray crystallography, electrospray ionization mass spectrometry, ^{195}Pt NMR spectroscopy, ^{183}W NMR spectroscopy, and ^{183}W−^{183}W 2D INADEQUATE NMR spectroscopy. Both **TBA-1** and **K-1** readily cocrystallized with their unsubstituted Keggin anion salts, **TBA-2** and **K-2**, respectively, providing an explanation for the historical difficulty of isolating certain platinum-substituted heteropolyanions in pure form.



INTRODUCTION

Platinum-containing polytungstates and -molybdates were first described by Gibbs and Rosenheim in the late 19th century,[1] but none of these reports have been independently repeated,[2] most likely due to formation of cocrystallizing mixtures and double salts.[3] More recently, well-defined platinum-containing polyborate,[4] polyphosphate,[5] polyvanadate,[6] polymolybdate,[7] polytungstate,[8] and phosphovanadotungstate[9] complexes have been isolated. Other complexes have proved to be less tractable, namely, silicotungstates[10] and phosphotungstates[11] (see below).

Although numerous polyoxometalates (POMs) and platinum compounds are proven catalysts for a variety of chemical reactions,[12] none of the platinum-containing POMs isolated to date have been demonstrated to act as catalysts as opposed to catalyst precursors.[8j,9,13] In some cases the platinum center is embedded in a metal oxide framework such that it has no terminal ligands and is apparently not catalytically active unless activated under conditions sufficiently vigorous to degrade the POM.[13] In other cases the platinum center is bonded to a POM ligand in only a bidentate fashion,[8j,9] presumably facilitating dissociation of platinum from the POM framework. The present study aims to rectify this situation through the synthesis of platinum-substituted polytungstate anions structurally derived from a parent Keggin anion by replacing a pentacoordinated W═O unit (see **a**) with a pentacoordinated Pt−L unit (see **b**).



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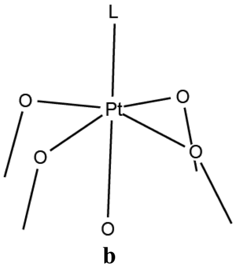

b

Embedding the platinum center in a Keggin anion framework in this fashion might serve to combine the structural stability associated with tungstate Keggin anions[14] with the potential reactivity associated with terminal ligands bonded to platinum centers.[15] Analogous noble metal polytungstate Keggin anion derivatives are known for Ru,[16,17] Os,[16] Rh,[16,18] and Ir.[16,18] Here we report the synthesis and characterization of the tetra-*n*-

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butylammonium salt $[(n\text{-}C_4H_9)_4N]_4H_2[\alpha\text{-SiPtW}_{11}O_{40}]$ (**TBA-1**) and the potassium salt $K_4H_2[\alpha\text{-SiPtW}_{11}O_{40}]\cdot 18H_2O$ (**K-1**) where the $SiPtW_{11}O_{40}$ framework has the structure shown in Figure 1.

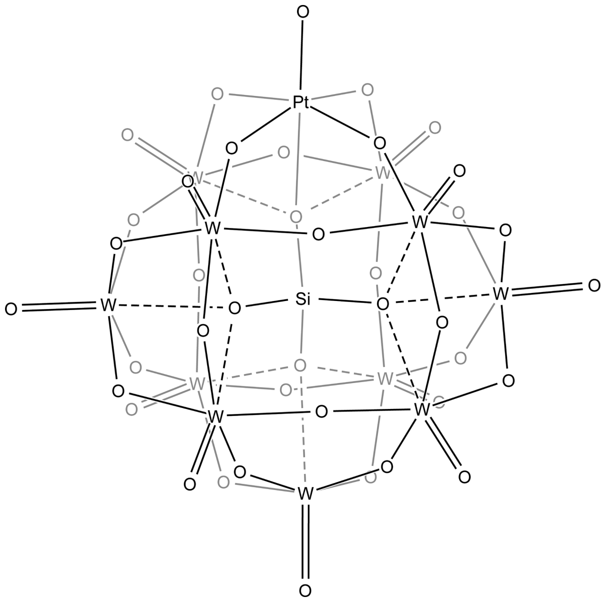

Figure 1. Structure of the $\alpha\text{-SiPtW}_{11}O_{40}$ framework in **TBA-1** and **K-1**.

Platinum(IV)-substituted polyoxometalates containing terminal oxo, hydroxy, and or aquo ligands have attracted attention because of their potential chemical reactivity. However, these species have proven extremely difficult to characterize in the absence of characteristic ^{183}W and ^{195}Pt NMR spectra.[19] The principal result of the present study is observation of fully resolved 1D and 2D ^{183}W NMR spectra, complete with $^{183}W-^{195}Pt$ couplings, indicating unambiguously that a platinum center has been incorporated into the $SiPtW_{11}$ framework of a Keggin anion derivative. Combined with X-ray crystal structure determinations of tetra-*n*-butylammonium and potassium salts, this result allows for the identification of the $SiPtW_{11}O_{40}{}^{6-}$ anion plus charge-compensating cations in the solid state. The solid state structure is not necessarily retained in solution since the anion could undergo condensation in solution while still maintaining the $SiPtW_{11}$ framework established using NMR spectroscopy. But this is an unlikely possibility given the kinetic inertness associated with d^6 octahedral centers like Pt(IV).

■ RESULTS

Preparation of TBA-1. Addition of $(n\text{-}C_4H_9)_4NBr$ (TBABr) to an aqueous solution of $K_8SiW_{11}O_{39}\cdot 13H_2O$ and $K_2Pt(OH)_6$ acidified to pH 4 as described in the Experimental Section yielded an orange precipitate whose IR spectrum is shown in Figure 2a. This spectrum was very similar to the spectrum of $[(n\text{-}C_4H_9)_4N]_4SiW_{12}O_{40}$ (**TBA-2**)[20] differing principally by the presence of a band at 956 cm^{-1} labeled "y" in Figure 2a. In the IR spectrum measured after crystallization of the precipitate from acetone/ethyl ether, the 956 cm^{-1} absorption had grown in intensity relative to the $[(n\text{-}C_4H_9)_4N]_4SiW_{12}O_{40}$ peak at 967 cm^{-1} labeled x in Figure 2a,b. Moreover, a new band appeared at 911 cm^{-1}, the band labeled "z" in Figure 2b. Since the crystallization yielded a visually homogeneous mass of cubic crystals, this result suggested cocrystallization of the $[(n\text{-}C_4H_9)_4N]_4SiW_{12}O_{40}$ with one or more structurally similar compounds. An attempt was therefore made to obtain a purer sample by adding excess $(CH_3)_4NCl$ to the original reaction solution and extracting the resulting precipitate with water, taking advantage of the relatively low solubility of $[(CH_3)_4N]_4SiW_{12}O_{40}$ in water. The aqueous solutions containing extracted material were then treated with TBABr, and the resulting precipitates were examined IR spectroscopically. As shown in Figure 2c, the $[(n\text{-}C_4H_9)_4N]_4SiW_{12}O_{40}$ band at 966 cm^{-1} labeled "x" was much less intense than the 956 cm^{-1} band labeled "y", and the 911 cm^{-1} band labeled "z" had a relative intensity greater than that observed in Figure 2b. Finally, crystallization of this material from acetonitrile/diethyl ether yielded a product where the $[(n\text{-}C_4H_9)_4N]_4SiW_{12}O_{40}$ absorption labeled "x" was no longer resolved in its IR spectrum (see Figure 2d). This material was formulated as the Keggin anion salt $[(n\text{-}C_4H_9)_4N]_4H_2[\alpha\text{-SiPtW}_{11}O_{40}]$ (**TBA-1**) using X-ray crystallography, electrospray-ionization mass spectrometry, NMR spectroscopy, and elemental analysis.

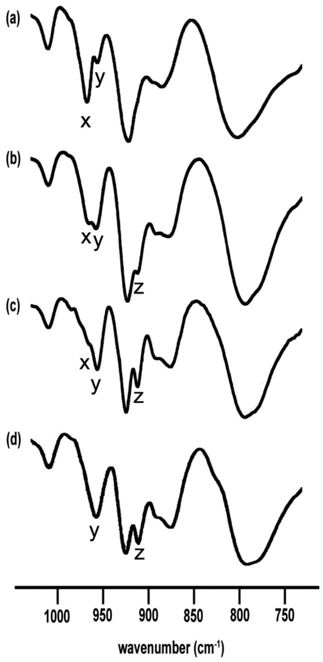

Figure 2. Infrared spectra monitoring the progress of the preparation of **TBA-1**. Spectra of the (a) tetra-*n*-butylammonium (TBA) salt precipitated from the reaction mixture, (b) TBA salt precipitated from the reaction mixture after crystallization from acetone, (c) TBA salt precipitated from a solution of tetramethylammonium (TMA) salt, and (d) TBA salt precipitated from a solution of TMA salt after crystallization from acetone. See text for details.

Crystal Structure of TBA-1. X-ray crystallographic examination of single-crystalline **TBA-1** and **TBA-2** (see Supporting Information) showed that the compounds were isostructural and had the same body-centered cubic structure typically observed for TBA_4 salts of Keggin anions.[21]

Electrospray Ionization Mass Spectra (ESI-MS) of TBA-1. Major peaks observed in the ESI-MS spectra of **TBA-1** may be assigned to $SiPtW_{11}O_{40}{}^{6-}$ ions plus charge-compensating H^+ and $[(n\text{-}C_4H_9)_4N]^+$ (TBA^+) cations for negative ion spectra in the 1100−3900 *m*/*z* region (Figure 3a) and positive ion spectra in the 2100−4400 *m*/*z* region (Figure 3b,c) according to the

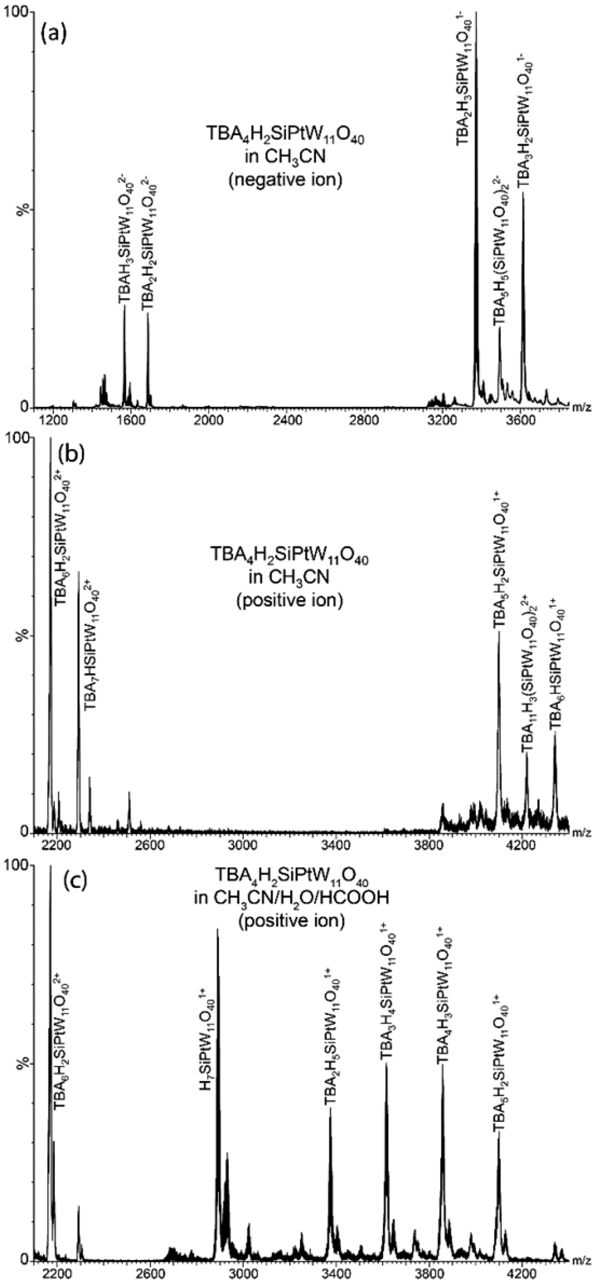

Figure 3. ESI mass spectra of **TBA-1**: (a) negative ion spectrum of a CH_3CN solution in the *m*/*z* 1100−3840 region, (b) positive ion spectrum of a CH_3CN solution in the *m*/*z* 2100−4400 region, and (c) positive ion spectrum of a CH_3CN/HCOOH solution in the *m*/*z* 2100−4400 region. For expansions and simulations of the individual peaks, see Supporting Information Figures S7−S9.

peak expansions and simulations shown in Supporting Information Figures S7−S9. Experimental and simulated spectra were in reasonable agreement for all of the peaks assigned, with the exception of the peak assigned to the $TBA_6H_2SiPtW_{11}O_{40}{}^{2+}$ cation in Figure 3c, which displayed excess intensity in the low *m*/*z* region (see Supporting Information Figure S9a). This shoulder could be assigned to $TBA_6SiW_{12}O_{40}{}^{2+}$ (see Supporting Information Figures S9 and S11a), an impurity presumably arising from **TBA-2**.

Note that the observation of peaks for $SiPtW_{11}O_{40}{}^{6-}$ plus countercations in the mass spectrometer detector by no means implies that such species are present in solutions of **TBA-1**. There are three reasons for this. First, ESI-MS is not in general a reliable technique for studying inorganic polyanion solutions due to the multiple transformations that can occur during the several stages involved in the transfer of ions from the solution phase to ions detected in the gas phase.[22] For example, oxoanion self-condensation in the course of ESI-MS experiments has been demonstrated, as in the case of the $WO_4{}^{2-}$ anion which self-condenses to the $W_2O_7{}^{2-}$ anion, a species unknown in condensed phases.[23] Second, ESI-MS results are extremely dependent upon experimental parameters,[23] and the spectra shown in Figure 3 and Supporting Information Figure S10 were observed only after optimizing solution concentrations, cone voltage, and collision energy as to maximize the intensities of peaks that could be assigned to $SiPtW_{11}O_{40}{}^{6-}$ plus countercations. Finally, the ESI-MS experiment only yields mass values and hence empirical formulations as opposed to structural formulas. For example, the peak assigned to $TBA_{11}H_3(SiPtW_{11}O_{40})_2{}^{2+}$ in Figure 3c could equally well be assigned to $TBA_{11}(H_2O)[(SiPtW_{11}O_{39})_2OH]$, a protonated, hydrated self-condensation product of the $SiPtW_{11}O_{40}H^{5-}$ ion. Self-condensation of this type is well-known in the solution chemistry of monosubstituted Keggin ion derivatives, yielding well-characterized species such as $(PTiW_{11}O_{39})_2OH^{7-}$,[24] $(PTiW_{11}O_{39})_2O^{8-}$,[25] $(SiRuW_{11}O_{39})_2O^{n-}$,[26] and $(PFeW_{11}O_{39})_2O^{10-}$.[27]

The ESI-MS spectral assignments given in Figure 3 are in themselves by no means definitive for the reasons just outlined. However, when considered in conjunction with the X-ray diffraction study implicating a platinum-containing Keggin anion derivative and an ^1H NMR study establishing the presence of TBA cations (see below), they are suggestive of $TBA_nH_{6-n}SiPtW_{11}O_{40}$ as a formulation of **TBA-1**.

^{195}Pt and ^1H NMR Spectra of TBA-1. A ^{195}Pt spectrum of TBA-1 was measured in acetonitrile solution (see Supporting Information Figure S12) with the hope that ^{195}Pt−^{183}W spin−spin coupling might be observed and serve to demonstrate incorporation of a platinum center into the Keggin framework. The chemical shift observed, 3666 ppm, is characteristic of platinum in the +4 but not the +2 oxidation state.[28] Unfortunately, no ^{195}Pt−^{183}W coupling could be observed in the ^{195}Pt NMR spectrum of TBA-1 (see Supporting Information Figure S12), most likely due to the 250 Hz line width of the resonance, which served to obscure any ^{183}W satellites (see below).

Proton NMR spectra of **TBA-1** in a variety of organic solvents consistently displayed resonances characteristic of the TBA cation. The chemical shifts and intensities of the remaining ^1H NMR resonances observed were dependent upon the solvent utilized, raising the possibility of proton dissociation in solution.

Elemental Analysis of TBA-1. Elemental analysis was used to determine the countercation composition in the formula $TBA_nH_{6-n}SiPtW_{11}O_{40}$ proposed above. When crude **TBA-1** was crystallized from diethyl ether/acetonitrile, CHN analysis consistently yielded results indicating n = ∼4.5.[29] However, crystallization from a diethyl ether/acetonitrile solutions containing a small amount of aqueous HCl yielded analytically pure $TBA_4H_2SiPtW_{11}O_{40}$ (see Experimental Section).

Preparation and Elemental Analysis of K-1. Preparation of **K-1** followed the same initial steps used to prepare **TBA-1**, but following extraction of the $(CH_3)_4N^+$ salt as described above, the solution was treated with KCl to form a precipitate. A solution of this material was then passed through a cation exchange resin in its K^+ form, and following removal of solvent, the crude product was crystallized from water. Elemental analysis yielded a W:Pt:Si:K mole ratio of 11.0:1.0:1.0:4.0 and weight percentages consistent with the Keggin salt hydrate formulation $K_4H_2SiPtW_{11}O_{40}\cdot 18H_2O$.

Crystal Structure of K-1. X-ray crystallographic analysis of **K-1** (see Supporting Information) revealed a quartz-like[30] structure observed previously for the hydrated Keggin anion salts $K_5CoW_{12}O_{40}\cdot 20H_2O$,[31] $K_4SiW_{12}O_{40}\cdot 17H_2O$,[32] $K_6CoW_{12}O_{40}\cdot nH_2O$,[31c,33] $K_5AlW_{12}O_{40}\cdot 17H_2O$,[34] $K_5BW_{12}O_{40}\cdot 16H_2O$,[35] $K_2H_2SiMo_{12}O_{40}\cdot 11H_2O$,[36] $K_2Na_2SiW_{12}O_{40}\cdot 8H_2O$,[36] $K_2NaHGeW_{12}O_{40}\cdot 7H_2O$,[37] $K_2NaH_2BW_{12}O_{40}\cdot 12H_2O$,[38] $K_6(H_2SiW_{12}O_{40})_3\cdot 35H_2O$,[39] and $K_6(H_2GeW_{12}O_{40})_3\cdot 41H_2O$.[39] When the structure of **K-1** is compared with the redetermined $K_4SiW_{12}O_{40}\cdot 17H_2O$ structure described in the Supporting Information, the two are seen to be insignificantly different, supporting the formulation of **K-1** as a platinum-substituted Keggin anion with an average of one platinum atom per Keggin ion.

^{195}Pt NMR Spectrum of K-1. The ^{195}Pt NMR spectrum (see Supporting Information Figure S13) of **K-1** in aqueous solution displayed a resonance at 3616 ppm with satellite peaks separated by 115 Hz assigned to ^{195}Pt−^{183}W spin−spin coupling. Since platinum atoms in a substituted platinum Keggin anion have two different sets of symmetry-equivalent nearest-neighbor tungsten atoms, two different couplings should be observed. Failure to observe a second coupling can be attributed to the 15 Hz line width of the ^{195}Pt resonance which obscured a second, weaker coupling (see below).

^{183}W NMR Spectra of K-1. As expected for a monosubstituted PtW_{11} Keggin anion, the ^{183}W NMR spectrum of **K-1** (see Figure 4b) displayed six resonances with relative intensities 2:2:1:2:2:2. On the basis of the integration values, one of these resonances could be assigned, namely, the low-intensity resonance C, which could be assigned to W_c using the labeling scheme given in Figure 4a. Resonance F displayed coupling to ^{195}Pt, with $^2J_{W-Pt}$ = 115.8 Hz, in good agreement with the value of $^2J_{Pt-W}$ = 116 ± 3 Hz (see above). Resonance F must therefore be assigned to W_a or W_f, since these are the only two types of tungsten atoms adjacent to platinum atoms in the PtW_{11} Keggin anion framework. A complete assignment of the ^{183}W NMR spectrum shown in Figure 4b could be achieved using the spin−spin coupling constants (see Experimental Section) and connectivities obtained from the ^{183}W−^{183}W 2D INADEQUATE NMR spectrum shown in Figure 4c. The values of the coupling constants fell into two ranges, 5−9 Hz and 18−25 Hz corresponding to edge-sharing and corner-sharing octahedral tungsten coordination polyhedra, respectively.[40] Resonance F could be uniquely assigned to W_f (see Figure 4a) since its $^2J_{W-W}$ value of 6.8 Hz indicated edge-sharing, consistent with W_f but not W_a. Resonance C, already assigned to W_c (see above), displayed two satellites with $^2J_{W-W}$ = 7.1 and 19.4 Hz with connectivities to resonances D and B in the 2D INADEQUATE spectrum, respectively, implying assignment of resonances D and B to W_d and W_b, respectively. Resonance E could then be assigned to W_e due to the connectivity observed between resonances E and F. By default, resonance A was then assigned to W_a. Three satellites were observed for resonance A in the 1D ^{183}W NMR spectrum (see Supporting Information Figure S14) with coupling constants of 7.8, 18.1, and 24.1 Hz. Since the two largest coupling constants arose from coupling to W_d and W_e, and since tungsten−tungsten coupling to W_a can be observed for only two of its three adjacent tungsten nuclei, the smallest coupling constant must be $^2J_{W_a\text{-Pt}}$. The observation of two distinct ^{183}W−^{195}Pt spin−spin coupling constants is important in that it shows that the C_s-symmetric $SiW_{11}O_{39}{}^{8-}$ ligand is bonded to platinum using oxygen atoms bonded to two different types of symmetry-equivalent tungsten atoms; that is, the platinum atom has become completely integrated into the Keggin framework.

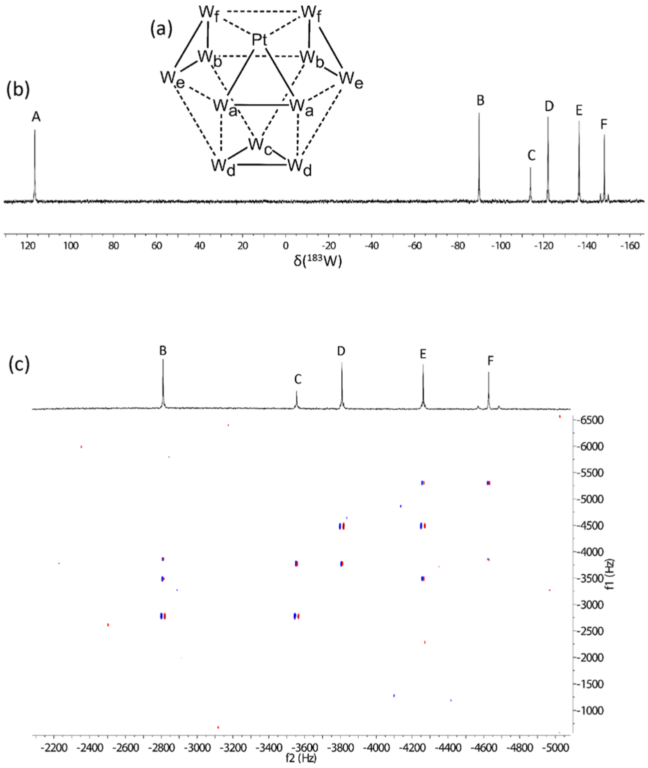

Figure 4. (a) Graph showing relationships between adjacent metal centers in the C_s-symmetric PtW_{11} Keggin structure: metal centers whose octahedral coordination polyhedra are linked by edge sharing are connected by solid lines; metal centers whose octahedral coordination polyhedra are linked by corner sharing are connected by broken lines. Symmetry-equivalent tungsten centers are labeled with the same lower case subscript. (b) 31.22 MHz ^{183}W NMR spectrum of **K-1** in D_2O solution. (c) 31.22 MHz ^{183}W−^{183}W 2D INADEQUATE NMR spectrum of **K-1** in D_2O solution. In parts b and c, resonances are labeled with upper case letters. In part c, the spectral bandwidth encompasses resonances B−F only. See Experimental Methods section for numerical data and Supporting Information Figures S14−S19 for expansions and deconvolutions of the individual peaks in the 1D spectrum.

The ^{183}W NMR spectra just described also gave evidence for the purity and stability of **K-1**. First, no resonance was observed in the −103 to −105 ppm region associated with $SiW_{12}O_{40}{}^{4-}$,[41] indicating a low level of $K_4SiW_{12}O_{40}$ contamination. Second, ^{183}W NMR spectra measured 1 day and 13 days after dissolving **K-1** in D_2O were indistinguishable, reflecting the stability of **K-1** in aqueous solution at ambient temperature.

DISCUSSION

Protonation State. Data presented in the Results section provide strong evidence for the synthesis of TBA and potassium salts of the $H_2SiPtW_{11}O_{40}{}^{4-}$ anion, but they fail to provide evidence regarding the location of the two protons, whose very existence is dictated only by charge balance arguments based on NMR data implicating W(VI) and Pt(IV) oxidation states. The pK_{a1} values for $PtCl_5(H_2O)^-$ have been reported as 3.48[42] and 3.851 and the pK_{a1} and pK_{a2} values for *trans*-$PtCl_4(H_2O)_2$ as 2.64 and 4.49, respectively.[43] Two tautomers are therefore plausible: one where an aqua ligand is bonded to the platinum center and another where a hydroxo ligand is bonded to the platinum center and the remaining proton is either dissociated or bonded to a different oxygen atom, most likely a Pt(IV)−O−W(VI) doubly bridging oxygen atom.[44] Since $H_2SiPtW_{11}O_{40}^{4-}$ salts are prepared from pH ~4 aqueous solution, it is hardly surprising that crude **TBA-1** contains both monoprotonated anion and diprotonated anion and requires recrystallization in the presence of acid to obtain analytically pure product.

Cocrystallization Phenomena. Cocrystallization of platinum-substituted polyoxometalates and their unsubstituted analogues is a potential problem that has been raised repeatedly for over a century. The possibility was first considered by Clarke[3] in 1909 in a critical discussion of Gibbs' research and was raised more recently by Cao et al.[10b] for the α-$SiPt_2W_{10}O_{40}^{8-}$ anion reported by Lee et al.[8e] and by Kortz et al.[10c] for the $P_2PtW_{18}O_{70}H_2^{16-}$ anion reported by Anderson et al.[11c] In the present study, infrared spectroscopy has been used to demonstrate unambiguously that TBA salts of the $SiW_{12}O_{40}^{4-}$ anion (**TBA-2**) and its monosubstituted platinum derivative $H_2SiPtW_{11}O_{40}^{4-}$ (**TBA-1**) do in fact cocrystallize, and the infrared technique proved to be useful in developing a protocol for separating the two species involved. Moreover, the crystal structures of **TBA-1** and **TBA-2** as well as **K-1** and **K-2** were isomorphous providing an explanation for their forming solid solutions. Recently, a platinum-substituted phosphotungstate has been reformulated as the corresponding unsubstituted polytungstate anion plus platinum counterion.[11f] The present study suggests an alternative interpretation, namely, cocrystallization of the platinum-substituted and unsubstituted anions.

Enantiomeric Preferences. The space groups of **K-1** and **K-2** were determined several times in the process of selecting suitable crystals for the single-crystal X-ray diffraction studies. Examination of eight different crystals of **K-1** from three different recrystallization batches and four different crystals of **K-2** from two different batches yielded the same result, namely, $P6_222$ as opposed to the enantiomorphic space group $P6_422$. Enantiomeric excess was first reported for crystals of **K-2** by Wyrouboff[46] and was later confirmed independently by Soret[47] and Copaux.[48] Crystals examined in the present study were dextrorotary, the same form that predominated in earlier studies.

Outlook. The hope expressed above in the Introduction that a Pt(IV)-substituted Keggin anion might combine the stability of a Keggin anion with the reactivity associated with platinum centers has proved to be justified. The terminal ligand bonded to Pt(IV) in **K-1** can be replaced by other ligands such as nitrate.[49] Moreover, chemical reduction of **K-1** yields a Pt(II)-substituted Keggin anion that can be oxidized back to **K-1**.[50] We will describe this chemistry in future publications.

EXPERIMENTAL METHODS

Reagents, Solvents, and General Procedures. Literature procedures were used to prepare $K_8[\alpha\text{-}SiW_{11}O_{39}]\cdot 13H_2O$,[51] $K_4SiW_{12}O_{40}\cdot 17H_2O$[32] (**K-2**), and $[(n\text{-}C_4H_9)_4N]_4SiW_{12}O_{40}$[52] (**TBA-2**). Sodium metasilicate, chloroplatinic acid hexahydrate, tetramethylammonium chloride, tetra-*n*-butylammonium bromide, potassium chloride, potassium hydroxide, tungstosilicic acid hydrate, hydrochloric acid, and Amberlite IR 120 ion-exchange resin (styrene-divinylbenzene-sulfonic acid, 8% cross-linked, 620−830 μm particle size, 1.8 mequiv/mL by wetted bed volume) were all purchased from Sigma-Aldrich and used without further purification. The Amberlite IR 120 was converted from acid form to potassium form by running through an excess (20 mL) of 1 M KOH until eluent was strongly basic by pH paper (pH = 14) and then washing with deionized water to remove excess KOH until the eluent was neutral (pH = 7). Anhydrous diethyl ether was freshly used and purchased from EMD Millipore and used only from freshly opened containers. Acetonitrile purchased from Alfa Aesar was dried over 3 Å molecular sieves prior to use. The sieves were activated by heating at 200 °C for 24 h and then cooling to room temperature while under vacuum. NMR solvents, D_2O (Cambridge Isotope Laboratories), and acetonitrile-d_3 (Acros Organics) were used as supplied. Nylon membrane filters (0.45 μm pore size) were used for all filtrations.

Analytical Instrumentation. Platinum-195 FT-NMR spectra were recorded at 25 °C on a Bruker Avance II 500 MHz spectrometer equipped with a 5 mm $^{15}N-^{31}P$ broadband probe; chemical shifts were referenced to a 1.2 M Na_2PtCl_6 solution in D_2O by the sample replacement method. Tungsten-183 FT-NMR spectra were recorded at 25 °C using a 10 mm Nalorac $^{73}Ge-^{15}N$ low frequency broadband probe on a Varian (Agilent) VNMRS 750 MHz spectrometer and VNMRJ 3.2 A software; chemical shifts were referenced to 1 M Na_2WO_4 in D_2O using the sample replacement method. Infrared spectra were recorded on a PerkinElmer 1600 Series FTIR spectrometer. The ICP-OES metal analysis was measured on an ICP Optima 7000 DV instrument at the University of California, Berkeley Microanalytical Laboratory. High purity water (EMD, OmniTrace Ultra) and nitric acid (Fluka, TraceSELECT) were used to prepare the samples, and standards were purchased from Inorganic Ventures (1000 ppm solutions in 5% v/v HNO_3 for platinum, potassium, silicon, and tungsten). CHN elemental analyses were performed by University of California, Berkeley Microanalytical Laboratory. Electrospray ionization mass spectra were recorded in the negative and positive ion modes on a Waters/Micromass Q-ToF Ultima hybrid quadrupole time-of-flight mass spectrometer in V-mode controlled by a PC using MassLynx software.

Preparation of $K_2Pt(OH)_6$.[53] A 250 mL round-bottom flask was charged with 2.00 g (3.86 mmol) of chloroplatinic acid hexahydrate ($H_2PtCl_6\cdot 6H_2O$), 30 mL deionized water, and a magnetic stir bar, and it then was placed in an oil bath and heated with stirring to 95 °C. To this orange solution was added 45 mL of 6 M aqueous KOH to form a yellow solution and yellow precipitate. The flask was equipped with a reflux condenser, and the mixture was heated at reflux for 18 h; the precipitate fully dissolved during this time. After cooling to room temperature, 200 mL of ethanol was added to the yellow solution with stirring to produce a light yellow precipitate which was collected by vacuum filtration and then washed with 20 mL ethanol. The light yellow solid was allowed to dry in air overnight to remove any residual ethanol, yielding 1.38 g (3.67 mmol) of crude product. This material was dissolved in 25 mL of 4 M aqueous KOH, and the resulting solution was allowed to evaporate slowly in a desiccator over KOH until about two-thirds of the water had evaporated, which required about 3 d. The yellow single crystals which had formed were collected by vacuum filtration, washed with 5 mL of ice cold water, and allowed to dry for about 10 min. Crystalline $K_2Pt(OH)_6$ (1.14 g, 3.04 mmol) was obtained with 79% yield.

Preparation of $[(n\text{-}C_4H_9)_4N]_4H_2[\alpha\text{-}SiPtW_{11}O_{40}]$ (TBA-1). A 250 mL round-bottom flask fitted with a reflux condenser was charged with a magnetic stir bar and 150 mL of water. After heating in an oil bath to 85 °C, 11.20 g (3.477 mmol) of α-$K_8SiW_{11}O_{39}\cdot 13H_2O$ was added and allowed to dissolve fully with stirring. Next, 1.31g (3.49 mmol) of $K_2Pt(OH)_6$ was added causing a light yellow precipitate to form in the pH 7 yellow solution. The reaction mixture was heated at reflux for 3 h resulting in a clear, deep amber colored solution. After allowing the solution to cool to room temperature, 1 M HCl was added dropwise with stirring until the solution reached pH 4. About 9.5 mL was required. If a slightly cloudy solution was obtained, the solution was filtered before adding 11.20 g (102.2 mmol) of tetramethylammonium chloride. The pale orange precipitate that formed was filtered off, washed twice with 20 mL diethyl ether, and dried in air overnight. The 3.45 g of pale orange powder obtained was then added to 20 mL of water, and the resulting suspension was stirred for 3 h and filtered. The yellow filtrate was kept, and the pale orange solid, now lighter in color, was placed in another 20 mL of water and stirred for 3 h. These extractions were repeated until the filtrate was no longer yellow. Typically, a total of 6 extractions were required, with extractions 2−5 having the deepest color. These solutions were used to prepare both the tetra-*n*-butylammonium (TBA) and potassium salts of **1**.

The TBA salt was prepared by adding 1.55 g (4.81 mmol) of TBA bromide to each of the solutions with stirring. Precipitates were formed immediately, and the suspensions obtained were then combined, filtered off, and washed twice with 10 mL diethyl ether. After drying in air for 12 h, 1.398 g of crude product was obtained as an orange powder. This crude product was recrystallized by dissolving 108 mg in 1 mL of acetonitrile with 2 drops of 0.5 M HCl added at room temperature in a 4 mL vial. This vial was placed in a 20 mL vial containing 5 mL diethyl ether which was allowed to diffuse into the solution at 0 °C over a 12 h time period. The orange, cubic crystals that formed were filtered under vacuum, washed with 5 mL of ice cold diethyl ether, and dried in air for 12 h, yielding 99 mg of analytically pure **TBA-1**. The overall yield for the preparation was 9.5% based on Pt. The sample was dried for 12 h in vacuo to remove any residual solvent prior to elemental analysis. Anal. Calcd for $C_{64}H_{146}N_4SiPtW_{11}O_{40}$: C, 19.93; H, 3.81; N, 1.45. Found C, 19.88; H, 3.80; N, 1.38. IR (700−1050 cm^{-1}): 791 (vs, br), 876 (m), 892 (m, sh), 911 (s), 924 (s), 957 (m), 1010 (m). ^{1}H NMR (500 MHz, DMSO-d_6): in addition to TBA resonances at δ 3.20−3.16, 1.60−1.54, 1.36−1.29, and 0.95−0.92, a weak and very broad peak was observed at δ 3.37. ^{195}Pt NMR (107.9 MHz, CD_3CN, see Supporting Information Figure S12): δ 3666, line width fwhm = 250 ± 25 Hz.

Preparation of $K_4H_2[\alpha\text{-}SiPtW_{11}O_{40}]\cdot 18\ H_2O$ (K-1). The potassium salt was prepared by adding 5 g KCl to each extraction solution (see above) with vigorous stirring. A light orange precipitate formed in each solution, and the resulting suspensions were combined. The precipitate was collected by filtration, washed with 20 mL of diethyl ether, and air-dried for 12 h to yield 820 mg of orange powder. This material was then dissolved in 20 mL of water and passed through a 9 cm ion exchange column containing 2 g of Amberlite IR 120 resin (K^+ form). The orange solution thus obtained was evaporated to dryness at 60 °C on a rotary evaporator. This crude product was dissolved in 5 mL of hot (90 °C) deionized water and held at this temperature until 2.5 mL of solution remained. The resulting clear solution was allowed to cool slowly to room temperature over a 3 h time period and then placed into a refrigerator at 0 °C for 12 h. The orange needle-shaped crystals that formed were isolated by vacuum filtration. A total of 807 mg (0.240 mmol) of product was obtained in 6.9% yield based on Pt. Single crystal samples suitable for X-ray diffraction studies required a second crystallization. These crystals were also used for elemental analysis. Anal. Calcd for $K_4H_2SiPtW_{11}O_{40}\cdot 18H_2O$: K, 4.64; Si, 0.83; Pt, 5.79; W, 60.04. Found: K, 4.61; Si, 0.82; Pt, 5.92; W, 60.16. IR (400−4000 cm^{-1}): 757 (vs, b), 873 (s), 914 (s, sh), 930 (s), 972 (m) 1020 (m). ^{195}Pt NMR (107.9 MHz, D_2O, see Supporting Information Figure S13): δ 3616 ($^2J_{\text{Pt-Wb}}$ = 117 ± 3 Hz), line width fwhm = 15 Hz. ^{183}W NMR (31.22 MHz, D_2O, see Figure 4a for labeling scheme): 1D spectrum (see Figure 4b) δ_a 116.6 ($^2J_{\text{Wa-Wd}} = 18.1$, $^2J_{\text{Wa-We}} = 24.1$, $^2J_{\text{Wa-Pt}} = 7.8$ Hz), δ_b −90.0 ($^2J_{\text{Wb-Wc}} = 7.6$, $^2J_{\text{Wb-We/f}} = 19.4$ Hz), δ_c −113.9 ($^2J_{\text{Wc-Wb}} = 19.4$, $^2J_{\text{Wc-Wd}} = 7.1$ Hz), δ_d −122.0 ($^2J_{\text{Wd-Wa/e}} = 19.6$, $^2J_{\text{Wd-Wc}} = 7.2$ Hz), δ_e −136.5 ($^2J_{\text{We-Wa}} = 23.8$, $^2J_{\text{We-Wb/f}} = 8.3$, $^2J_{\text{We-Wd}} = 20.5$ Hz), δ_f −148.2 ($^2J_{\text{Wf-Wb/e}} = 6.8$, $^2J_{\text{Wf-Pt}} = 115.8$ Hz). For ^{183}W−^{183}W 2D INADEQUATE spectrum (see Figure 4c), a total of 12 cross peaks were observed: $^2J_{\text{Wb-Wc}} = 19.9$, $^2J_{\text{Wb-We}} = 8.3$, $^2J_{\text{Wb-Wf}} = 5.8$, $^2J_{\text{Wc-Wb}} = 19.8$, $^2J_{\text{Wc-Wd}} = 7.1$, $^2J_{\text{Wd-Wc}} = 7.5$, $^2J_{\text{Wd-We}} = 20.5$, $^2J_{\text{We-Wb}} = 8.0$, $^2J_{\text{We-Wd}} = 20.3$, $^2J_{\text{We-Wf}} = 8.5$, $^2J_{\text{Wf-Wb}} = 6.4$, $^2J_{\text{Wf-We}} = 9.1$ Hz.

X-ray Crystallography. For **TBA-1** and **TBA-2**, data was collected at the Advance Light Source, Lawrence Berkeley National Lab on beamline 11.3.1, λ = 0.774 90 Å. Suitable cubic single crystals were selected and mounted on a cryoloop using Paratone oil (Hampton Research), and the data was collected at 100 K. For **K-1** and **K-2**, data was collected on a Bruker D8 Venture diffractometer equipped with a Photon-100 CMOS area detector using Mo Kα (λ = 0.710 73 Å) radiation from a conventional sealed tube source. Suitable prismatic single crystals were selected and mounted on a cryoloop using Paratone oil (Hampton Research) and collected at 293 K. For each of the four structure determinations, the unit cell was determined using least-squares fitting methods. The reflections collected were integrated and scaled using the APEX2[54] software package. All of the structures were solved using direct methods and then refined by the full-matrix least-squares methods using the SHELXL[55] software package. Further details are given in the Supporting Information.

Electrospray Ionization Mass Spectrometry. Negative and positive ion spectra of **TBA-1** and **TBA-2** in CH_3CN solution were both measured from 10^{-5} M solutions. Positive ion spectra of **TBA-1** in $CH_3CN/H_2O/HCOOH$ solution were measured from 10^{-4} M solutions in 55/45 v/v CH_3CN/H_2O containing 1 vol % formic acid. Positive ion spectra of **TBA-2** in $CH_3CN/H_2O/HCOOH$ solution were measured from 10^{-3} M solutions in 2/1 v/v CH_3CN/H_2O containing 2 vol % formic acid. Instrumental conditions: desolvation gas (nitrogen) flow rate, 300 L/h; cone gas (nitrogen) flow rate, 200 L/h; liquid flow rate, 10 μL/min; source temperature, 80 °C; desolvation temperature, 150 °C; capillary voltage, 3.25 kV for negative mode and 3.5 kV for positive mode; cone voltage, 35 V; collision energy, 5 eV for **TBA-1** in CH_3CN solution (negative ion) and **TBA-2** in $CH_3CN/H_2O/HCOOH$ solution (positive ion), 10 eV for **TBA-1** in CH_3CN solution (positive ion) and **TBA-1** in $CH_3CN/H_2O/HCOOH$ solution (positive ion).

^{183}W NMR Spectroscopy. All data was collected from a sample of 450 mg of **K-1** in 3 mL of D_2O. As a result of the large chemical shift separations involved, the spectral window of the 1D ^{183}W spectrum was set to 351 ppm (10 965 Hz). An acquisition time of 3 s (0.33 Hz digital resolution), a 1 s delay between pulses, and a 70° pulse angle were used; a total of 16 640 scans was collected. For the full spectrum shown in Figure 4b, a line broadening of 1 Hz and zero-filling up to 2 times of number of points (65 790) were applied during data processing using Mnova 8.1.1 (Mestrelab Research S.L.). In addition, back-linear prediction to 6 data points and baseline correction with 3 orders of Bernstein polynomial fit were utilized. In the 2D ^{183}W−^{183}W phase-sensitive INADEQUATE experiment[56] (see Figure 4c) a smaller spectral window was used (sw = 3004.8 Hz and sw1 = 6009.6 Hz) to enhance especially the digital resolution in the indirect dimension (t1) within a reasonable experimental time period. The ^{183}W frequency carrier was set to −114.5 ppm to cover five of the six ^{183}W resonances of **K-1** such that the resonance at 116.6 ppm was excluded. An acquisition time of 0.6 s (1.67 Hz digital resolution) and 0.5 s relaxation delay were used in the direct-detection dimension, and 80 points [75.1 Hz (2.4 ppm) digital resolution] were employed in the indirect-detection dimension (t1). The long-range ^{183}W−^{183}W J coupling value was set to 15 Hz (it ranges from 5 to 25 Hz), requiring a delay in the spin−echo portion of the INADEQUATE pulse sequence of 16.7 ms ($1/(4J)$). A total of 3072 scans per t1 time point was collected. For data processing, zero-filling to 4096 points was applied to both dimensions with a 90° shifted sine-bell square window function (Mnova 8.1.1). The baseline correction with 3 orders of Bernstein polynomial fit was also utilized.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data in CIF format. X-ray crystallographic details, ESI-MS peak expansions and simulations, ^{195}Pt NMR spectra, and ^{183}W NMR peak expansions. This material is available free of charge via the Internet at http://pubs.acs.org.

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(2) The fact that these nineteenth century preparations have not been repeated does not necessarily imply that they are irreproducible. Consider, for example, the case of molybdenum blues, first crystallized in 1866:[2a] crystallization of hydroxylamine-derived material, first reported in 1896,[2b] was not repeated until 1927[2c] and 1986;[2d] crystallization of hydrazine sulfate-derived material, first reported in 1933,[2e] was not repeated until 1998.[2f] (a) Rammelsberg, C. *Ann. Phys. Chemie.* **1866**, *203*, 281−292. (b) von der Heide, K.; Hofmann, K. A. *Z. Anorg. Chemie.* **1896**, *12*, 277−292. (c) Canneri, G. *Gazz. Chim. Ital.* **1927**, *57*, 872−880. (d) Zhang, S.; Daiqing, L.; Shao, M.; Tang, Y. *J. Chem. Soc., Chem. Commun.* **1986**, 835−836. (e) Jakob, W. F.; Reznar, M. R. *Collect. Czech. Chem. Commun.* **1933**, *5*, 93−102. (f) Müller, A.; Krickemeyer, E.; Bögge, H.; Schmidtmann, M.; Peters, F. *Angew. Chem., Int. Ed.* **1998**, *37*, 3360−3363.

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