by a combination of mechanisms including a $Pt_2(\mu-P_2O_5H_2)_4^{4-}$-catalyzed pathway, a slower bimolecular substitution mechanism, and a very slow dissociative pathway. By contrast the μ-hydrogen phosphato complexes $Pt_2(\mu-PO_4H)_4X_2^{4-}$ have labile axial halides that undergo rapid hydration.

2. The kinetic data indicate association between $Pt_2(\mu-P_2O_5H_2)_4^{4-}$ and either I^- or $Pt_2(\mu-P_2O_5H_2)_4Cl_2^{4-}$.

3. The replacement of X^- in $Pt_2(\mu-P_2O_5H_2)_4X_2^{4-}$ by Y^- is photoaccelerated. Dissociation from the triplet $d\sigma^1 d\sigma^{*1}$ state is selectively axial.

4. The substitution reactions of $Pt_2(\mu-P_2O_5H_2)_4X_2^{4-}$ show qualitative similarity to those of monomeric platinum(IV) complexes, there being no abnormal kinetic effects induced by the diplatinum(III) bonds.

Acknowledgment. We thank A. J. Poë for his critical reading of our manuscript and R. H. Schmehl for helpful discussions. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

Supplementary Material Available: Appendices detailing the rate law derivations, a spectral overlay, and several plots of k_{obsd} against complex or halide ion concentrations (10 pages). Ordering information is given on any current masthead page.

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Trivacant Heteropolytungstate Derivatives. 3.[1] Rational Syntheses, Characterization, Two-Dimensional ^{183}W NMR, and Properties of $P_2W_{18}M_4(H_2O)_2O_{68}^{10-}$ and $P_4W_{30}M_4(H_2O)_2O_{112}^{16-}$ (M = Co, Cu, Zn)

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The full details are reported on the rational, high-yield, and isomerically pure syntheses of $P_2W_{18}M_4(H_2O)_2O_{68}^{10-}$ and $P_4W_{30}M_4(H_2O)_2O_{112}^{16-}$ ($M = Co^{2+}, Cu^{2+}, Zn^{2+}$). The products are well-characterized, including 2-D ^{183}W NMR in the case of $M = Zn^{2+}$, which allows the unambiguous assignment of the ^{183}W NMR spectra. The results allow a number of conclusions to be drawn: (i) the B-type tri(tungsten)vacant form of B-$PW_9O_{34}^{9-}$ and B-$P_2W_{15}O_{56}^{12-}$ is a key structural requirement for formation of the dimetal(2+)-substituted dimers $P_2W_{18}M_4(H_2O)_2O_{68}^{10-}$ and $P_4W_{30}M_4(H_2O)_2O_{112}^{16-}$; (ii) these disubstituted dimers are not unique but rather are just the first two members of a conceptually more general, previously unrecognized class of heteropolyanions; (iii) the Cu^{2+} product $P_2W_{18}Cu_4(H_2O)_2O_{68}^{10-}$ is different from the M^{2+} = Zn, Co members as well as different from $P_4W_{30}Cu_4(H_2O)_2O_{112}^{16-}$ in that it is thermally unstable in solution; (iv) both $PW_9O_{34}^{9-}$ and $P_4W_{30}Zn_4(H_2O)_2O_{112}^{16-}$ undergo previously unknown solid-state isomerizations; (v) the complex previously reported as "$P_2W_{16}M_2(H_2O)_2O_{60}^{10-n}$" was misformulated and is in fact $P_4W_{30}M_4(H_2O)_2O_{112}^{16-}$. Additional results and conclusions are detailed in the text and in the Summary and Conclusions.

Introduction

In 1973 Weakley, Evans, Showell, Tourné, and Tourné isolated[3] $K_{10}P_2W_{18}Co_4(H_2O)_2O_{68}$ from the prolonged reaction of a 11:2:4:18 mixture of $HCl/Na_2HPO_4/Co(NO_3)_2/Na_2WO_4$ at 90–100 °C and determined its structure by X-ray diffraction (Figure 1A). Beginning in 1979, as part of our initial efforts[1a,b] aimed at preparing the series of trimetal (M)-substituted heteropolyanions $SiW_9M_3O_{40}^{x-}$ and $P_2W_{15}M_3O_{62}^{y-}$ (Figure 2) for use as organic-solvent-soluble metal oxide analogues in catalysis,[1c] we attempted the synthesis of "$PW_9(ZnO)_3O_{34}^{9-n}$", a potential ZnO analogue.[4] Despite the fact that the trisubstituted Co^{2+} derivative $(Me_4N)_{10}SiW_9Co_3(H_2O)_3O_{34}\cdot 10H_2O$ apparently exists,[4d,5] a spectral titration using Co^{2+} in place of Zn^{2+} with $PW_9O_{34}^{9-}$ in

(1) (a) Part 1: Finke, R. G.; Droege, M.; Hutchinson, J. R.; Gansow, O. *J. Am. Chem. Soc.* **1981**, *103*, 1587–1589. (b) Part 2: Finke, R. G.; Droege, M. W. *Inorg. Chem.* **1983**, *22*, 1006–1008. (c) For part 1 of our work on "Trisubstituted Heteropolyanions as Soluble Metal Oxide Analogues", see: Finke, R. G.; Droege, M. W. *J. Am. Chem. Soc.* **1984**, *106*, 7274–7277. For part 2 see: Finke, R. G.; Rapko, B. M.; Domaille, P. J. *Organometallics* **1986**, *5*, 175. For part 3 see: Finke, R. G.; Rapko, B. M.; Saxton, R. J.; Domaille, P. J. *J. Am. Chem. Soc.* **1986**, *108*, 2947. For part 4 see: Edlund, D. J.; Finke, R. G., submitted for publication in *Organometallics*.

(2) (a) University of Oregon. (b) E. I. du Pont de Nemours and Company; Contribution No. 3965.

(3) (a) Weakley, T. J. R.; Evans, H. T., Jr.; Showell, J. S.; Tourné, G. F.; Tourné, C. M. *J. Chem. Soc., Chem. Commun.* **1973**, 139–140. Although a yield was not reported, repeating their synthesis provided 3.1 g (29%) of this product along with 1.3 g of a blue insoluble byproduct.[1a] A deep rose-pink crystalline byproduct from this synthesis has been identified by a single-crystal X-ray diffraction analysis[26] as $P_5Co_9W_{27}O_{119}H_{17}^{16-}$. (b) Professor Weakley has kindly provided us with a preprint of a follow-up full paper concerning this work: Evans, H. T., Jr.; Tourné, C. M.; Tourné, G. F.; Weakley, T. J. R. *J. Chem. Soc., Dalton Trans.* **1986**, 2699. Described therein are the full details of their syntheses and of the original[3a] $P_2W_{18}Cu_4(OH_2)_2O_{68}^{10-}$ and now $As_2W_{18}Zn_4(OH_2)_2O_{68}^{10-}$ X-ray diffraction structural analyses and the ^{183}W NMR spectrum of $P_2W_{18}Zn_4(OH_2)_2O_{68}^{10-}$ (see also Table I *herein*).

(4) (a) We chose to try to mimic ZnO initially because ZnO is one of the best characterized examples among oxides as far as surface intermediates and reaction mechanisms are concerned[4b] (in large part due to the good IR properties of ZnO) and because the $(ZnO)_3$ zinc oxide "minisurface" in "$PW_9(ZnO)_3O_{34}^{9-n}$" closely resembles the 000$\bar{1}$ or polar plane of ZnO.[4c] Our focus on trisubstituted heteropolyanions like $SiW_9M_3O_{40}^{x-}$ is derived in part from the fact that such a trisubstituted heteropolyanion offers the largest possible planar M_xO_y (e.g. Zn_3O_3) minisurface on the Keggin, $XW_{12}O_{40}^{n-}$, anion. Other design features include a high surface charge density, the possibility of A- vs B-type $XW_9M_3O_{40}^{n-}$ comparisons, high (C_{3v}) symmetry simplifying spectroscopic properties, the ^{183}W, X = ^{31}P, ^{29}Si, and M = ^{51}V NMR handles, and the possibility of the comparative series of $SiW_9M_3O_{40}^{x-}$ and $P_2W_{15}M_3O_{40}^{y-}$ for M = V^{5+}, Nb^{5+}, Ta^{5+} and Ti^{4+}, Zr^{4+}, Hf^{4+}. For further details see ref 1c. (b) John, C. S. In *Catalysis*; Kemball, G., Dowden, D. A., Eds.; The Chemical Society: London, 1980; Vol. 3, pp 169, 187. (c) Gay, R. R.; Nodine, M. H.; Henrich, V. E.; Zeiger, H. J.; Solomon, E. I. *J. Am. Chem. Soc.* **1980**, *102*, 6752. See Figure 1 therein. (d) The high anionic charge, the large size of Zn^{2+} vs the size of the lacunary hole in $PW_9O_{34}^{9-}$, and the apparent high stability of $P_2W_{18}Zn_4(H_2O)_2O_{68}^{10-}$ are factors that appear to mitigate against the, as yet unknown, $PW_9(ZnO)_3O_{34}^{9-}$ (or $PW_9(ZnOH_2)_3O_{37}^{9-}$), although $SiW_9(CoOH_2)_3O_{37}^{10-}$ has been reported in a preliminary communication.[5]

(5) Katsoulis, D. E.; Pope, M. T. *J. Am. Chem. Soc.* **1984**, *106*, 2737.

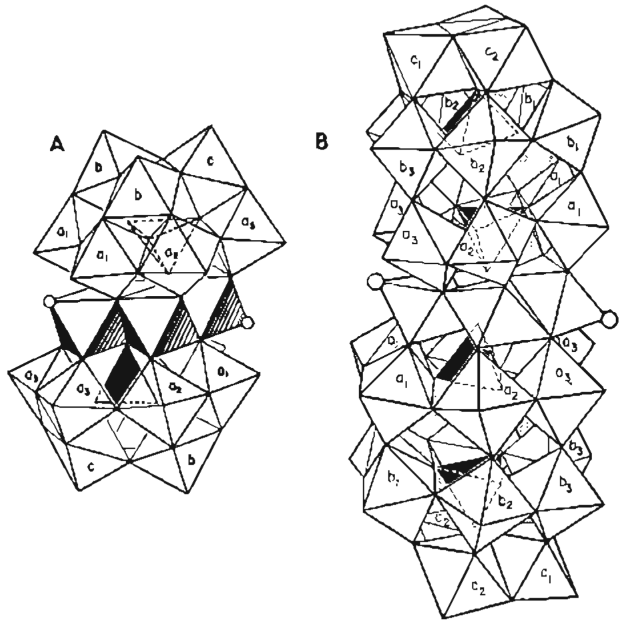

Figure 1. (A) Coordination polyhedra representation of the C_{2h} symmetry structure for $P_2W_{18}Co_4(H_2O)_2O_{68}^{10-}$. The cobalt atoms occupy the four central edge-linked polyhedra; the circles show the positions of the two constitutional water molecules. The five symmetry-distinct types of W atoms are labeled a_1, a_2, a_3, b, and c. (B) Coordination polyhedra representation of $P_4W_{30}M_4(H_2O)_2O_{112}^{16-}$ ($M = Co^{2+}, Cu^{2+}, Zn^{2+}$). The four unlabeled central octahedra are the MO_6 edge-shared planar array; the open circles represent the two constitutional waters. The four shaded tetrahedra represent the PO_4 heterogroups. The two $P_2W_{15}O_{56}^{12-}$ units lie above and below the four central edge-shared octahedra and have eight symmetry-inequivalent (C_{2h}) W atoms labeled a_1, a_2, a_3, b_1, b_2, b_3, c_1, and c_2.

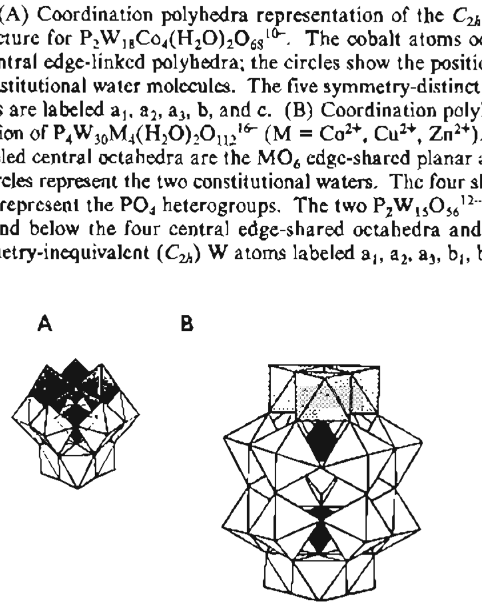

Figure 2. Coordination polyhedra representation of the trimetal (M)-substituted heteropolyanions $SiW_9M_3O_{40}^{x-}$ (A) and $P_2W_{15}M_3O_{62}^{y-}$ (B). The shaded octahedra indicate the three adjacent sites where, formally, WO_6 octahedra have been replaced by MO_6 octahedra.

unbuffered H_2O showed a break point at 2.0 equiv rather than 3.0 equiv of Co^{2+}. The rational, high-yield synthesis of the disubstituted dimers $[PW_9M_2(H_2O)O_{34}]_2^{10-} = P_2W_{18}M_4(H_2O)_2O_{68}^{10-}$ ($M = Co^{2+}, Cu^{2+}, Zn^{2+}$) (Figure 1A) quickly followed and was reported in a preliminary communication.[1a] These findings allowed the important prediction that $P_2W_{18}M_4(H_2O)_2O_{68}^{10-}$ is not unique but rather is just one member of a previously unrecognized class of massive, disubstituted heteropolytungstates derived from trivacant polyoxoanion precursors.

This prediction was followed 2 years later by our preliminary report[1b] that $Na_{12}P_2W_{15}O_{56}$ formed the previously unknown, massive, disubstituted dimers $[P_2W_{15}M_2(H_2O)O_{56}]_2^{16-} = P_4W_{30}M_4(H_2O)_2O_{112}^{16-}$ ($M = Co^{2+}, Cu^{2+}, Zn^{2+}$) in 77–88% yields (Figure 1B). This work also confirmed the suggestion of Contant and Ciabrini[6a] that what was previously thought[6b] to be "$Na_{12}P_2W_{16}O_{59}$" is largely $Na_{12}P_2W_{15}O_{56}$, a conclusion now shared by others.[6c] This work also corrected the previous misformulation[6b] of $[P_2W_{15}M_2(H_2O)O_{56}]_2^{16-}$ as "$P_2W_{16}M_2(H_2O)_2O_{60}^{10-}$".

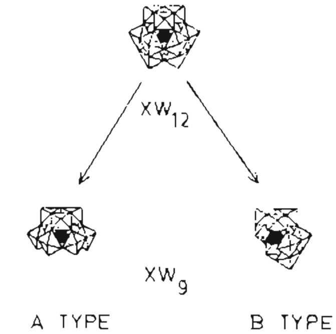

Figure 3. A-type (base of central tetrahedron exposed) and B-type (apex of central tetrahedron exposed) trivacant heteropolyanion structures.

However, a number of questions or problems remained unanswered by the two preliminary reports. These include the following: (a) An unequivocal assignment of the ^{183}W NMR resonances, possible by $^{183}W\{^{31}P\}$ and 2-D ^{183}W NMR, remained to be done. In the case of $P_4W_{30}Zn_4(H_2O)_2O_{112}^{16-}$, some of the assignments obtained by these techniques and reported here turn out to be counterintuitive and emphasize once again that the only unambiguous method for making ^{183}W NMR assignments is via $^2J_{W-O-W}$ coupling constants.[7] (b) An explanation for the empirically determined need to predry/heat $Na_8HPW_9O_{34}$ at 140 °C in the formation of $P_2W_{18}M_4(H_2O)_2O_{68}^{10-}$ complexes was lacking. It seemed likely at the time[1a] that this was probably due to a solid-state isomerization of the $PW_9O_{34}^{9-}$ starting material, then thought[8a] to be the "B-β-$PW_9O_{34}^{9-}$" isomer,[8b] to the B-α-$PW_9O_{34}^{9-}$ form present in the crystallographically characterized product, $P_2W_{18}Co_4(H_2O)_2O_{68}^{10-}$. We noted in our preliminary publication[1a] that the formulation by others of the starting materials as the B-β isomer[8b] was based solely upon indirect methods of characterization. Knoth, Domaille, and Farlee have since studied the effect of heating or not heating $Na_8HPW_9O_{34}$ upon its substitution chemistry and have shown[9] that unheated $Na_8HPW_9O_{34}$ reacts with Co^{2+} to form $P_2W_{18}Co_3(H_2O)_3O_{68}^{12-}$ instead of $P_2W_{18}Co_4(H_2O)_2O_{68}^{10-}$. Through a variety of studies, including solid-state ^{31}P NMR, they provided the first strong evidence that the $Na_8HPW_9O_{34}$ starting material is predominantly A-$PW_9O_{34}^{9-}$, which then rearranges to B-$PW_9O_{34}^{9-}$ on heating (Figure 3). This is consistent with the changes in the infrared spectrum of $Na_8HPW_9O_{34}$ that we had observed to occur on heating (see Figure 4). However, the observed solid-state ^{31}P NMR spectrum contained additional, unexplained resonances of significant (ca. 50%) intensity and it was found, as we also find, that the exact drying conditions (temperature, pressure, time) give rise to spectroscopically distinct forms of "$PW_9O_{34}^{9-}$". Several details of the solid-state composition and structure of what is nominally "$Na_8HPW_9O_{34}$" remain to be determined. (c) Additional studies were warranted to establish the details of what was apparently a solid-state isomerization of $Na_{16}P_4W_{30}Zn_4(H_2O)_2O_{112}$ that, upon heating, leads to a material with new ^{31}P and ^{183}W NMR spectra. Combined with the effect of heating $Na_8HPW_9O_{34}$, these two

(6) (a) Contant, R.; Ciabrini, J. P. *J. Inorg. Nucl. Chem.* **1981**, *43*, 1525. (b) Contant, R.; Ciabrini, J. P. *J. Chem. Res., Miniprint* 1977, 2601; *J. Chem. Res., Synop.* 1977, 222. (c) Acerete, R.; Hammer, C. F.; Baker, L. C. W. *Inorg. Chem.* **1984**, *23*, 1478.

(7) (a) Lefebvre, J.; Chauveau, F.; Doppelt, P.; Brevard, C. *J. Am. Chem. Soc.* **1981**, *103*, 4589. (b) Brevard, C.; Schimpf, R.; Tourné, G.; Tourné, C. M. *J. Am. Chem. Soc.* **1983**, *105*, 7059. (c) Domaille, P. J.; Knoth, W. H. *Inorg. Chem.* **1983**, *22*, 818.

(8) (a) Massart, R.; Contant, R.; Fruchart, J. M.; Ciabrini, J. P.; Fournier, M. *Inorg. Chem.* **1977**, *16*, 2916–2921. (b) A vs B isomers (see Figure 3) refer to the removal of three MO_6 octahedra, one from each of three separate W_3 triads of edge-sharing MO_6 octahedra in the case of the A isomer (so that the face of the central PO_4 tetrahedron faces the vacancy) or one whole W_3 triad of three edge-sharing octahedra in the case of the B isomer (so that the apex of the central PO_4 tetrahedron faces the vacancy). The α,β-type of isomerism refers to a $\pi/3$ rotation of a W_3 triad of edge-sharing octahedra, such as a $\pi/3$ rotation of a W_3 triad "cap" of $P_2W_{15}M_3$ (see Figure 2B). For additional discussion see ref 1b, footnote 11.

(9) Knoth, W. H.; Domaille, P. J.; Farlee, R. D. *Organometallics* **1985**, *4*, 62–68.

examples appear to be the first observations of solid-state polyoxoanion fluxionality.[10] (d) There was a need to better understand the reaction of $PW_9O_{34}^{9-}$ with Cu^{2+} since Knoth et al.,[11] while able to reproduce our syntheses for the Co^{2+} and Zn^{2+} derivatives, found an additional product besides $P_2W_{18}Cu_4(H_2O)_2O_{68}^{10-}$. It seemed likely that the exact reaction conditions, including pretreatment of $PW_9O_{34}^{9-}$, were important in determining the outcome of these substitution reactions. Finally, the recent observation by Pope[5] that polyoxoanions such as $P_2W_{18}Co_4(H_2O)_2O_{68}^{10-}$, $SiW_{11}Co(H_2O)O_{39}^{6-}$, and $SiW_9(Co(H_2O))_3O_{37}^{10-}$ can be dehydrated in organic solvents to yield coordinatively unsaturated, reactive Co(II) derivatives suggests, as Pope first noted,[5] an extensive but unexplored chemistry for these and other substituted polyoxoanions. Due to the potential interest in such compounds, it is appropriate that full details of the syntheses, characterizations, and properties of $P_2W_{18}M_4(H_2O)_2O_{68}^{10-}$ and $P_4W_{30}M_4(H_2O)_2O_{112}^{16-}$ be reported. In separate publications[1c] we have summarized our studies toward the syntheses, characterizations, and applications of trisubstituted and other heteropolytungstates in catalysis. That work continues to be our major focus.[1c]

Experimental Section

All chemicals were commercially available reagent grade quality and were used as received. Distilled water was used for all syntheses. Visible spectra were recorded with a Cary 15 spectrophotometer. Infrared spectra were recorded on a Sargent-Welch SP3-200 IR spectrophotometer with samples prepared as KBr disks and calibrated to the 1601-cm^{-1} band of polystyrene. Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, TN, Schwartzkopf Laboratories, New York, NY, or Mikroanalytisches Labor Pascher, Bonn, West Germany. The analytical results obtained have been inconsistent from laboratory to laboratory even for identical samples. However, the most consistent and reliable results were obtained from the West German laboratory. Solution molecular weights were obtained by the equilibrium sedimentation ultracentrifugation method.[1b,c] X-ray diffraction powder patterns were recorded with either a GE XRO-7 X-ray generator or a Norelco type 12045 X-ray generator/diffractometer using Cu Kα radiation and a nickel filter. Diffractions were detected by a photomultiplier tube and were recorded as counts per second vs. $2\theta°$. Samples were prepared by thoroughly grinding the crystalline products in a mortar containing a few milliliters of acetone. The sample was then fixed to the sample holder by applying the acetone/sample suspension and allowing complete evaporation of the acetone. Reproducibility seemed to be affected by crystallinity of the sample before grinding. The water of hydration was determined by thermal gravimetric analysis (TGA) with a Du Pont 1090 thermal gravimetric analyzer. TGA results were obtained courtesy of Catalytica Associates Inc., Mountain View, CA.

^{31}P NMR. ^{31}P NMR spectra were recorded at a nominal frequency of 146 MHz on a Nicolet Technology NT-360 FT-NMR system. All spectra were digitized by using 8192 data points at a spectral resolution of 2.4 Hz/data point. The spectrometer was locked on the ^{2}H resonance of the internal deuteriated solvent. Spectra were recorded referenced to external 85% H_3PO_4 in a sealed capillary centered in a 12-mm sample tube. Chemical shifts upfield of H_3PO_4 are reported as negative values. Experimental parameters were as follows: pulse width, 30 μs (60° pulse); delay time, 5.00 s; spectral width, ±5000 Hz. Samples were prepared at typical concentrations of 0.01 M by dissolving in distilled water with 25–50% added D_2O.

^{183}W NMR. ^{183}W NMR spectra were recorded at a nominal frequency of 15 MHz on a Nicolet Technology NT-360 FT-NMR system. All spectra were digitized by using either 8192 or 16 384 data points with a spectral resolution of 1.2 or 0.6 Hz/datum point, respectively. The spectrometer was locked on the ^{2}H resonance of the internal deuteriated solvent. Spectra were obtained with 10-mm sample tubes and are reported referenced to external Na_2WO_4 saturated in D_2O at the operating temperature. The operating temperature was 21 °C unless otherwise noted. Chemical shifts upfield of Na_2WO_4 are reported as negative values. The broad-band power amplifier was attenuated by 6 dB to prevent probe arcing. Transmitter pulse breakthrough always contaminated the first six data points of the FID, causing severe base line problems. This was eliminated by a 100-μs delay before acquisition.

The spectral parameters used for Na_2WO_4 were obtained by optimizing the pulse width and delay between pulses for maximum signal to noise. The maximum signal was found with a pulse width of 40 μs, a delay of 1.2 s, a sweep width of ±2500 Hz, and an acquisition time of 819.4 ms.

The optimum spectral parameters for $K_{10}P_2W_{18}Zn_4(H_2O)_2O_{68}$ were obtained by determining both the $\pi/2$ pulse and T_1 for all lines in the spectrum. With use of standard Nicolet software, the $\pi/2$ pulse width was found to be 70 μs. T_1, obtained by inversion recovery, ranged from 0.4 to 0.7 s. Optimum spectral parameters were as follows: pulse width, 70 μs; delay, 1 ms; typical sweep width, ±2500 Hz; typical acquisition time, 819.4 ms. The delay was set to a small value since the acquisition time provided a sufficient delay between pulses. These parameters have been found to be reasonably optimum for all heteropolyanions, in any solvent, examined to date. Typical sample concentrations were about 0.1 M in D_2O.

^{183}W NMR spectra with ^{31}P decoupling were obtained with a Nicolet NT-360WB spectrometer using a 20 mm diameter sideways-spinning solenoidal probe. A concentric tunable (50–150 MHz) decoupler coil was used to introduce resonant CW ^{31}P irradiation at power levels of 50–300 mW. The ^{31}P decoupling frequency was obtained by intercepting a software-controlled PTS-160 synthesizer (at 146 MHz) and directing it to an Amplifier Research 10LA amplifier. The amplifier output was passed through a 146-MHz band-pass filter to the probe. The broadband (5–150 MHz) preamplifier of the receiver channel was protected from the decoupler power by insertion of a 15-MHz band-pass filter (Cir-Q-Tel) between the probe and receiver input. Double ^{31}P irradiation in $P_4W_{30}Zn_4(H_2O)_2O_{112}^{16-}$ was achieved by sinusoidal modulation of the carrier with an Anzac MD-140 mixer. The carrier was positioned midway between the ^{31}P NMR resonances and the modulation increased until both lines were irradiated.

2-D ^{183}W–^{183}W connectivity experiments[18] were done by using the 2-D INADEQUATE pulse sequence with the Mareci–Freeman[19] modification of a $3\pi/4$ conversion pulse. Other details of phase cycling, processing, etc. are contained in ref 18.

Preparations. Δ-$Na_8HPW_9O_{34}\cdot 19H_2O$ ("Δ-PW_9"). This high-temperature dried form of $Na_8HPW_9O_{34}$ is known to provide predominantly B-$Na_8HPW_9O_{34}$ and is labeled with the Δ symbol as suggested by Knoth.[9] This product was prepared on a scale one-fourth of that reported by Massart et al.[12] for $Na_8HPW_9O_{34}\cdot 24H_2O$. First 30.0 g of $Na_2WO_4\cdot 2H_2O$ was dissolved in 37 mL of distilled water with stirring. Then 0.75 mL of 85% H_3PO_4, followed by 5.5 mL of glacial acetic acid, was added to the stirring solution. After a few seconds the solution became cloudy and after about 1 min a heavy white precipitate had formed. The solid was collected on a sintered-glass frit and dried under aspiration until easily manipulated. This product is suggested[9] to be predominantly A-$Na_8HPW_9O_{34}$. Figure 4a is the infrared spectrum of this product.

Δ-PW_9 resulted when the aspirated solid was first dried at room temperature for 24 h or longer and then dried at 140 °C for about 6 h. This transformation is most easily followed by changes in the infrared spectrum, and the final product gave the spectrum shown in Figure 4c. This spectrum compares closely with the infrared spectrum reported by Knoth for Δ-$PW_9O_{34}^{9-}$. Drying the aspirated solid for only 1–2 h at 140 °C gave a product with an intermediate spectrum as shown in Figure 4b. This partially thermolyzed $PW_9O_{34}^{9-}$ was successfully used in a number of preparations which gave good yields of $P_2W_{18}M_4(H_2O)_2O_{68}^{10-}$ (M = Co, Zn) presumably due to the 100 °C recrystallization step (see Results and Discussion). Each procedure that follows lists the exact conditions used for drying $Na_8HPW_9O_{34}$ (pressure, temperature, time) unless Δ-PW_9 is used.

Yields of $Na_8HPW_9O_{34}$ in all cases were about 23 g (80%) after drying. The dried solid is very hygroscopic, and after equilibration at ambient atmospheric humidity for 2–3 days, TGA finds 19 H_2O (12.54% H_2O found; 12.42% H_2O calculated for $Na_8HPW_9O_{34}\cdot 19H_2O$).

We caution that the precise conditions used for drying $Na_8HPW_9O_{34}$ are important. Knoth notes[9] that "the conversion of PW_9 to Δ-PW_9 is somewhat erratic" and uses 140–150 °C at 230 Torr for 2 h followed by 1 Torr for 1 h to obtain Δ-PW_9 with an IR spectrum very similar to that in Figure 4c. Knoth also notes that "if the entire thermolysis is conducted

(10) (a) Fluxionality of polyoxoanions in solution[10b–d] and the solid state is probably more general but remains little studied. (b) Klemperer, W. G.; Shum, W. *J. Am. Chem. Soc.* **1976**, *98*, 8291. (c) Masters, A. F.; Gheller, S. F.; Brownlee, R. T. C.; O'Connor, M. J.; Wedd, A. G. *Inorg. Chem.* **1980**, *19*, 3866. (d) Sethuraman, P. R.; Leparulo, M. A.; Pope, M. T.; Zonnevijlle, F.; Brevard, C.; Lemerle, J. *J. Am. Chem. Soc.* **1981**, *103*, 7665. (e) Wasfi, S. H.; Kwak, W.; Pope, M. T.; Barkigia, K. M.; Butcher, R. J.; Quicksall, C. O. *J. Am. Chem. Soc.* **1978**, *100*, 7786. (f) Klemperer, W. G.; Schwartz, C.; Wright, D. A. *J. Am. Chem. Soc.* **1985**, *107*, 6941. This work provides evidence for intramolecular reorientations of T_d MO_4^{2-} groups and discusses a 90° reorientation about a T_d PO_4^{3-} C_2 axis as one component of the A-$PW_9O_{34}^{9-}$ to B-$PW_9O_{34}^{9-}$ conversion (see p 6950).

(11) Knoth, W. H., private communication.

(12) Massart, R.; Contant, R.; Fruchart, J. M.; Ciabrini, J. P.; Fournier, M. *Inorg. Chem.* **1977**, *16*, 2916–2921.

at 1 Torr, a product with a distinctly different infrared and solid state ^{31}P MAS NMR spectrum was obtained." This product has not yet been identified.

Co^{2+} Titration of $Na_8HPW_9O_{34}$. Four separate Co^{2+} solutions were prepared by dissolving 0.0526 g (0.181 mmol), 0.1051 g (0.362 mmol), 0.1577 g (0.543 mmol), and 0.2102 g (0.724 mmol) of $Co(NO_3)_2 \cdot 6H_2O$ each in 20.0 mL of water. To each solution was added 0.5000 g of $PW_9O_{34}^{9-}$ (0.181 mmol; dried at 140 °C for 1–2 h at 1 atm), which was dissolved with heating, if necessary. An aliquot from each solution was used to obtain the visible spectrum monitoring the absorbance at 570 nm. Background absorbance due to excess Co^{2+} past the 2.0-equiv point was accounted for by directly subtracting the absorbance observed for the excess amounts of Co^{2+} (1 and 2 equiv) in the 20.0-mL volume of water alone. This experiment was reproducible with a given sample of $PW_9O_{34}^{9-}$ but gave variable results depending upon the exact sample of $PW_9O_{34}^{9-}$ used and how it was dried.

$K_{10}P_2W_{18}Zn_4(H_2O)_2O_{68} \cdot 20H_2O$. Solid $ZnCl_2$ (0.19 g, 1.4 mmol) was dissolved in 15 mL of water. To this solution was added with stirring 2.0 g of solid $Na_8HPW_9O_{34}$ (1 atm, 140 °C, 1–2 h). The solution was heated until nearly homogeneous and then filtered hot by gravity filtration through paper (Whatman #1). Excess solid KCl (4–6 g) was added to the clear filtrate, resulting in the immediate precipitation of a white solid. After the mixture was cooled to room temperature, this solid was collected on a sintered-glass frit and dried under aspiration. The slightly damp solid was redissolved in about 5–10 mL of hot water and allowed to recrystallize overnight at 5 °C. A crystalline white solid was collected and dried at 80 °C under vacuum for 2 h. The yield was 1.47 g (77%) of a white solid. Slow crystallization at room temperature will result in large well-formed white to clear crystals. Anal. Calcd for $K_5PW_9Zn_2O_{34} \cdot 11H_2O$: K, 7.10; P, 1.12; W, 60.08; Zn, 4.75. Found: K, 6.77; P, 1.13; W, 60.01; Zn, 4.94.

The ^{183}W NMR sample was prepared by dissolving 2.9 g of $K_{10}P_2W_{18}Zn_4(H_2O)_2O_{68}$ in 3 mL of D_2O containing 0.8 g of $LiClO_4$. The insoluble $KClO_4$ that formed was removed by centrifugation.

$K_{10}P_2W_{18}Co_4(H_2O)_2O_{68} \cdot 20H_2O$. Solid $Co(NO_3)_2 \cdot 6H_2O$ (0.41 g, 1.4 mmol) was dissolved in 15 mL of water. To this light pink solution was added with stirring 2.0 g of solid $Na_8HPW_9O_{34}$ (1 atm, 140 °C, 1–2 h). The solution was heated until a homogeneous purple to burgundy solution resulted. Excess solid KCl (4–6 g) was added, and a blue–purple precipitate formed. After the mixture was cooled to room temperature, this solid was collected on a sintered-glass frit and dried under aspiration. The slightly damp solid was redissolved in about 5–10 mL of hot water and allowed to recrystallize overnight at 5 °C. A crystalline blue-purple solid was collected and dried at 80 °C under vacuum for 2 h. The yield was 1.37 g (71%) of a blue-purple solid. Slow crystallization at room temperature will result in large well-formed crystals. Anal. Calcd for $K_5PW_9Co_2O_{34} \cdot 11H_2O$: K, 7.13; P, 1.12; W, 60.08; Co, 4.29. Found: K, 7.02; P, 1.15; W, 60.13; Co, 4.05.

$K_7Na_3P_2W_{18}Cu_4(H_2O)_2O_{68} \cdot 20H_2O$. Solid $CuCl_2 \cdot 2H_2O$ (0.62 g, 3.6 mmol) was dissolved in 12 mL of water. To this light blue solution was added 5.0 g (1.8 mmol) of solid Δ-PW_9 with stirring at room temperature until all the Δ-PW_9 was dissolved. Solid KCl (0.66 g, 8.8 mmol) was added to the light green solution, resulting in the precipitation of a pale green solid. This mixture was stirred for 10 min. The mixture was warmed under hot (60 °C) water or on a steam bath for brief periods (1–5 min) until the bulk of the precipitated solid had redissolved. The slightly cloudy solution was centrifuged for about 5 min to remove the fine blue suspension. The clear light green supernatant was removed and allowed to crystallize at room temperature. Pale green crystalline cubes began to form immediately and continued to crystallize for 6–12 h. After this time the product was collected on a sintered-glass frit and air-dried under aspiration for several hours. The yield was 1.3 g (27%) of light green cubes. Anal. Calcd for $K_{3.5}Na_{1.5}PW_9Cu_2O_{34} \cdot 11H_2O$: K, 5.02; Na, 1.26; P, 1.14; W, 60.69; Cu, 4.66; H_2O, 6.61. Found: K, 5.13; Na, 1.26; P, 1.15; W, 61.00; Cu, 4.69; H_2O, 6.23 (TGA).

A light yellow thermolysis product (see Results and Discussion) may be crystallized (ca. 60%) from the filtrate or will deposit on the pale green cubes in the original solution after about 12 h at room temperature.

$K_{10}P_2W_{18}Co_4(H_2O)_2O_{68} \cdot 20H_2O$ Prepared after the Method Suggested by Weakley.[3a] Mixed in 50 mL of water were 10 g (30.3 mmol) of $Na_2WO_4 \cdot 2H_2O$, 1.95 g (6.7 mmol) of $Co(NO_3)_2 \cdot 6H_2O$, 0.48 g (3.4 mmol) of Na_2HPO_4, and 3.1 mL (18.5 mmol) of 6 M HCl. Immediate precipitation of an insoluble blue material and a pink to burgundy solution resulted. The mixture was refluxed overnight. After this mixture was cooled, the insoluble blue solid was removed by filtration and excess solid KCl (10–20 g) was added to the filtrate. The solution was allowed to cool at 5 °C overnight. The deep blue-purple crystals that formed on cooling were collected and air-dried. The yield was 3.1 g (29%).

α-$K_6P_2W_{18}O_{62} \cdot 14H_2O$. This synthesis of pure α-P_2W_{18} is based on Wu's observation[13a] that $P_2W_{17}O_{61}^{10-}$ formed from β-$P_2W_{18}O_{62}^{6-}$ regenerates only α-$P_2W_{18}O_{62}^{6-}$ in the presence of WO_4^{2-} and acid.

(1) Preparation of α,β-$K_6P_2W_{18}O_{62}$. $Na_2WO_4 \cdot 2H_2O$ (100 g) was added to 350 mL of water, and the solution was heated to boiling. Then 150 mL of 85% H_3PO_4 was slowly added to the boiling solution, and the resulting yellow-green solution was refluxed for 5–13 h. The solution was cooled, and the product was precipitated by addition of 100 g of solid KCl. The light green precipitate was collected, redissolved in a minimum amount of hot water, and allowed to crystallize at 5 °C overnight. The typical yield was 70 g after drying at 80 °C under vacuum for several hours. The $K_6P_2W_{18}O_{62}$ prepared this way is always a mixture of α and β isomers (ca. 90–95% α form) identified by ^{31}P NMR (α, −12.7 ppm; β, −11 and −11.6 ppm) and ^{183}W NMR (α, −125 and −170 ppm; β, −112, −131, −171, and −191 ppm).[13b]

(2) Preparation of α-$K_6P_2W_{18}O_{62}$. About 70 g of the α,β-$K_6P_2W_{18}O_{62}$ mixture was dissolved in 250 mL of water, contained in a 1500-mL flask, by heating. A drop of bromine was added to the warm solution, causing the green solution to turn bright yellow by oxidizing any reduced polyoxoanion. The solution was then cooled to room temperature. A 10% $KHCO_3$ solution was slowly poured into the stirring P_2W_{18} solution. After addition of ca. 250 mL of $KHCO_3$, the solution became cloudy and the white salt $K_{10}P_2W_{17}O_{61}$ precipitated. The $KHCO_3$ addition was continued until the solution was colorless and no more salt formed. Approximately 400 mL more $KHCO_3$ was needed to reach this point. About 110 mL of 6 M HCl was carefully added to the P_2W_{17} mixture, regenerating a clear yellow solution of α-P_2W_{18}. This solution was then boiled for 1 h, reducing the volume to ca. 1000 mL. Any insoluble material was removed by hot filtration. Solid KCl (100 g) was added to the hot solution, and the mixture was cooled at 5 °C overnight. A typical yield was 50–60 g (70–85% recovery) of the yellow crystalline salt, α-$K_6P_2W_{18}O_{62}$. Isomeric purity was confirmed by ^{31}P NMR (−12.7 ppm) and ^{183}W NMR (−125 and −170 ppm).

β-$K_6P_2W_{18}O_{62}$. This complex was prepared by metathesis of β-$(NH_4)_6P_2W_{18}O_{62}$ (prepared as described by Wu[13]) with $KClO_4$. β-$K_6P_2W_{18}O_{62}$ NMR: −11, −11.6 ppm (^{31}P); −112, −131, −171, −191 ppm (^{183}W).

$Na_{12}P_2W_{15}O_{56} \cdot 18H_2O$. The salt $K_6P_2W_{18}O_{62} \cdot 14H_2O$ (20.0 g; the pure α salt unless indicated otherwise) was dissolved in 50 mL of H_2O with mild heating. After the solution had cooled to room temperature, 15 g of $NaClO_4$ was added. A white precipitate of $KClO_4$ formed immediately, but the mixture was stirred for 1 h. $KClO_4$ was removed by filtration. Na_2CO_3 (1 M) was added dropwise to the filtrate. At pH 8.5, a white precipitate began to form. More base was added until pH 9, and this pH was maintained by intermittent base addition for 1 h. The solid $Na_{12}P_2W_{15}O_{56}$ was collected and washed with 75 mL of a saturated NaCl solution, 75 mL of 95% ethanol, and 75 mL of diethyl ether. The solid was dried in a desiccator over concentrated H_2SO_4 for 2 days. The yield was 15.2 g of a white solid (85%). TGA results indicate 18 H_2O (7.53% H_2O found; 7.51% calculated for $Na_{12}P_2W_{15}O_{56} \cdot 18H_2O$). Drying for longer times resulted in a hygroscopic product.

$Na_{12}P_2W_{15}O_{56}$ derived from β-$P_2W_{18}O_{62}^{6-}$ was obtained by using the same procedure but substituting β-$K_6P_2W_{18}O_{62}$ for α-$K_6P_2W_{18}O_{62}$.

$Na_{16}P_4W_{30}Zn_4(H_2O)_2O_{112}$. $ZnBr_2$ (0.56 g, 2.5 mmol) was dissolved in 50 mL of a 1 M NaCl solution with stirring. $Na_{12}P_2W_{15}O_{56}$ (5.0 g, 1.25 mmol) was then added and dissolved by heating and stirring. Any insoluble material was removed by hot gravity filtration through paper (Whatman #1). The clear solution was cooled overnight at 5 °C. The white crystalline solid that formed was collected and dried at 80 °C under vacuum for ≤0.5 h. The yield was 4.44 g of a white crystalline solid (88%). Anal. Calcd for $Na_8P_2W_{15}Zn_2(H_2O)O_{66}$: Na, 4.54; P, 1.53; W, 68.12; Zn, 3.23. Found: Na, 4.24; P, 1.49; W, 67.99; Zn, 3.02; H_2O, <0.01 (dried to constant weight at 200 °C).

The ^{183}W NMR sample was prepared by dissolving 2.0 g of $P_4W_{30}Zn_4$ in 3.0 mL of D_2O at 40 °C. The temperature was maintained at 40 °C during acquisition to prevent crystallization of the sample (the Na_2WO_4 reference was also measured at 40 °C).

$Na_{16}P_4W_{30}Co_4(H_2O)_2O_{112}$. $Co(NO_3)_2 \cdot 6H_2O$ (0.73 g, 2.5 mmol) was dissolved in 50 mL of a 1 M NaCl solution. Solid $Na_{12}P_2W_{15}O_{56}$ (5.0 g, 1.25 mmol) was then added and dissolved by heating and stirring. The original light pink solution became a homogeneous red-brown solution that reflected green. The solution was cooled at 5 °C overnight. Patches of a crystalline green-brown product formed on cooling. When collected, the product lost its crystalline form and immediately became an amorphous green-brown solid. The product was dried at 80 °C under vacuum for ≤0.5 h. The yield was 4.20 g of a green-brown powder (83%). Anal. Calcd for $Na_8P_2W_{15}Co_2(H_2O)O_{66}$: Na, 4.56; P, 1.54; W, 68.34; Co, 2.92. Found: Na, 4.32; P, 1.46; W, 67.67; Co, 2.74; H_2O not specifically determined.

(13) (a) Wu, H. *J. Biol. Chem.* **1920**, *43*, 189–220. (b) Acerete, R.; Hammer, C. F.; Baker, L. C. W. *J. Am. Chem. Soc.* **1979**, *101*, 267.

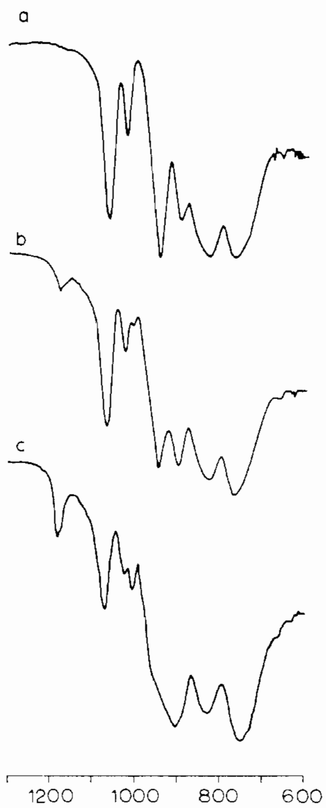

Figure 4. Infrared study of the effect of heat treatments on $PW_9O_{34}^{9-}$. If freshly prepared PW_9 is simply allowed to air-dry at room temperature, the IR spectrum shown in (a) is observed. If, however, the fresh solid is completely dried at 140 °C for 1–2 h, then the spectrum shown in (b) is observed. The changes associated with this drying process are characterized by the appearance of new bands at 1170 and 1000 cm^{-1} while the terminal and bridging W—O bands (950–700 cm^{-1}) only change in intensity. Prolonged heating (>15 h) at 140 °C causes no further change in the IR spectrum shown in (b). However, if fresh PW_9 is first air-dried (24–48 h) and then dried at 140 °C for about 6 h, the IR bands at 1170 and 1000 cm^{-1} increase in intensity at the expense of both the 1060- and 1030-cm^{-1} bands as shown in (c). The W—O bands also exhibit further changes. Spectrum b seems to be an intermediate case between spectrum a and spectrum c while spectrum c appears to be approaching a spectrum characterized by three prominent P—O bands at 1170, 1060, and 1000 cm^{-1}. The three P—O bands are consistent with a C_{3v} symmetry anion, and the unusual higher energy band at 1170 cm^{-1} is indicative of a P=O stretch.[32] A higher energy P=O band is observed at 1130 cm^{-1} for the known B-type anion $P_2W_{15}O_{56}^{12-}$ (see Figure 10).

$Na_{16}P_4W_{30}Cu_4(H_2O)_2O_{112}$. $CuCl_2{\cdot}2H_2O$ (0.43 g, 2.5 mmol) was dissolved in 50 mL of a 1 M NaCl solution. Solid $Na_{12}P_2W_{15}O_{56}$ (5.0 g, 1.25 mmol) was then added and dissolved with heating and stirring. The pale blue solution turned light green. The green suspension that remained was removed by hot filtration through a fine sintered-glass frit. The clear green filtrate was cooled at 5 °C overnight. The product was dried at 80 °C under vacuum for ≤0.5 h. The yield was 3.92 g of pale green crystals (77%). Anal. Calcd for $Na_8P_2W_{15}Cu_2(H_2O)O_{66}$: Na, 4.55; P, 1.53; W, 68.18; Cu, 3.14. Found: Na, 4.36; P, 1.49; W, 67.92; Cu, 3.17; H_2O not specifically determined.

$Na_{16}P_4W_{30}Zn_4(H_2O)_2O_{112}$ (Prepared by Using $Na_{12}P_2W_{15}O_{56}$ Derived from β-$K_6P_2W_{18}O_{62}$). $ZnBr_2$ (0.56 g, 2.5 mmol) was dissolved in 50 mL of a 1 M NaCl solution with stirring. Solid $Na_{12}P_2W_{15}O_{56}$ derived from β-$P_2W_{18}O_{62}^{12-}$ (5.0 g, 1.25 mmol; see above for $Na_{12}P_2W_{15}O_{56}{\cdot}18H_2O$) was then added and dissolved by heating and stirring. Any insoluble material was removed by hot gravity filtration through paper (Whatman #1). The clear solution was cooled overnight at 5 °C. The white crystalline solid that formed was only air-dried at room temperature to prevent possible β to α isomerization and therefore contains additional waters of crystallization.[23] The product produced by this procedure appears to be a mixture of α,α-, α,β-, and possibly β,β-$P_4W_{30}Zn_4(H_2O)_2O_{112}^{16-}$ as determined by ^{183}W NMR (see Results and Discussion and Table II).

Solid-State Thermolysis Reaction of $Na_{16}P_4W_{30}Zn_4(H_2O)_2O_{112}$. The filtered, but still damp, crystalline product of $P_4W_{30}Zn_4(H_2O)_2O_{112}^{12-}$

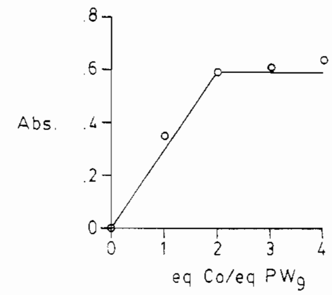

Figure 5. Co^{2+} titration in water of $PW_9O_{34}^{9-}$ (heated at 140 °C, 1–2 h) monitored by visible spectroscopy at 570 nm. The solid line indicates the idealized curve of this $PW_9O_{34}^{9-}$ sample-dependent experiment (see the Experimental Section). The curve suggests that most, but not all, of the Δ-$PW_9O_{34}^{9-}$ is B-type $PW_9O_{34}^{9-}$; hence, this less than optimum titration curve is presented here.

(prepared as described above) was dried in a drying pistol under vacuum at 80 °C for 1–4 h. The resulting white powder appears to be a mixture of α,α-, α,β-, and possibly β,β-$P_4W_{30}Zn_4(H_2O)_2O_{112}^{16-}$ as determined by an elemental analysis and ^{183}W NMR spectrum (see Results and Discussion and Table II) identical[23] with those for authentic material synthesized from β-$P_2W_{18}O_{62}^{6-}$-derived $P_2W_{15}O_{56}^{12-}$. The infrared spectrum is identical with that obtained for the starting (i.e. before thermolysis) $P_4W_{30}Zn_4(H_2O)_2O_{112}^{16-}$ (see Figure 11).[24c]

Results and Discussion

Δ-$Na_8HPW_9O_{34}{\cdot}19H_2O$ (Δ-PW_9). One of the most crucial observations from this work is the finding that only thermolyzed $Na_8HPW_9O_{34}$ (labeled Δ-$Na_8HPW_9O_{34}$)[9] gives high yields of $P_2W_{18}M_4(H_2O)_2O_{68}^{10-}$ products. The exact conditions of temperature, pressure, and time are important (as discussed in greater detail in the Experimental Section); assurance that the initially precipitated $Na_8HPW_9O_{34}$ is fully converted to Δ-$Na_8HPW_9O_{34}$ is most easily monitored by IR spectroscopy (Figure 4). No experiments were done to more fully probe the exact composition and structure of Δ-PW_9; we simply note that we agree with Knoth, Domaille, and Farlee[9] that the available data argue for unheated $Na_8HPW_9O_{34}$ as being predominantly, but not exclusively,[14] A-PW_9, and Δ-$Na_8HPW_9O_{34}$ as being predominantly, but not exclusively,[14] B-PW_9. The form of the PW_9 is important as illustrated in Figure 5, which is a titration showing that heated PW_9 (but not unheated PW_9) shows a sharp break point at 2.0 equiv of Co^{2+}/equiv of Δ-PW_9 due to the formation of $(PW_9O_{34})_2Co_4(OH_2)_2^{10-}$ (or $P_2W_{18}Co_4(OH_2)_2O_{68}^{10-}$). The spectral titration is, of course, a valuable way to find optimum conditions leading to a given product. As noted earlier, Knoth et al. have shown[9] that the $P_2W_{18}(WO)_3O_{68}^{6-}$ ("P_2W_{21}") analogue $P_2W_{18}(CoOH_2)_3O_{68}^{12-}$ results if unheated PW_9 is allowed to react with Co^{2+}. This $P_2W_{18}(CoOH_2)_3O_{68}^{12-}$ is converted to the thermodynamically more stable $P_2W_{18}Co_4(H_2O)_2O_{68}^{10-}$ (and other unknown products) in hot aqueous solution even in the absence of the stoichiometrically required 1 equiv of Co^{2+}.

$P_2W_{18}M_4(H_2O)_2O_{68}^{12-}$ (M = Co, Zn). The reaction of PW_9 (1 atm, 140 °C, 1–2 h) with 2 equiv of Co^{2+} or Zn^{2+} in water according to eq 1, followed by isolation as the potassium salt and recrystallization from hot water, results in good yields of the crystalline blue-purple Co (71%) and white Zn (77%) complexes.

$$2\Delta\text{-}PW_9O_{34}^{9-} + 4M^{2+} + 2H_2O \rightarrow [PW_9M_2(H_2O)O_{34}]_2^{10-} \quad (1)$$

Elemental analysis is consistent with the titration results, indicating disubstitution of PW_9, and determines an empirical formula of $(K_5PW_9M_2O_{34}{\cdot}11H_2O)_x$, where M = Zn, Co. Molecular weight determinations, IR spectra, X-ray diffraction powder patterns, and ^{31}P and ^{183}W NMR spectra (M = Zn^{2+}) were used to establish that the reactions are indeed rational syntheses of the products first described by Weakley et al.,[3a] $P_2W_{18}M_4(H_2O)_2O_{68}^{10-}$ (Figure 1a).

The molecular formula is determined to be a dimer in the case of the Zn derivative by solution molecular weight measurements.

(14) The interested reader is referred to the work of Knoth, Domaille, and Farlee[9] for solid-state NMR data and further discussion on this point.

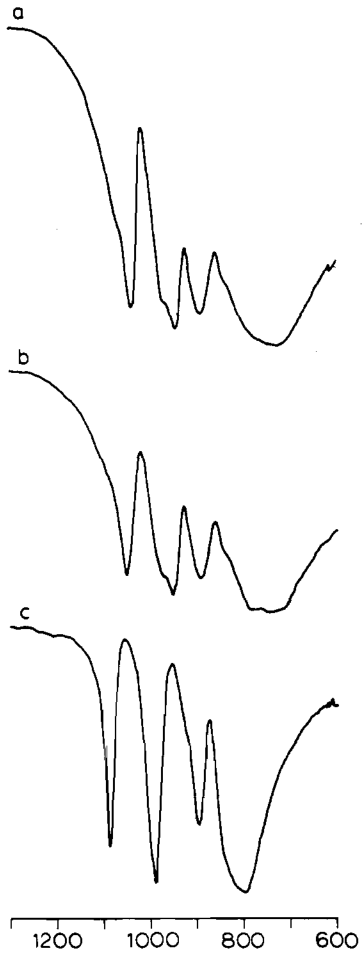

Figure 6. Infrared spectra of (a) $P_2W_{18}Zn_4(H_2O)_2O_{68}^{10-}$, (b) $P_2W_{18}Co_4(H_2O)_2O_{68}^{10-}$, and (c) $H_3PW_{12}O_{40}{\cdot}xH_2O$.

Sedimentation equilibrium ultracentrifugation (Figure A, supplementary material) in H_2O/KCl yields an observed molecular weight of 4414. This value is within 7% of the calculated weight of 4757 for the unsolvated dimeric anion $P_2W_{18}Zn_4(H_2O)_2O_{68}^{10-}$ ($P_2W_{18}Zn_4$).

The infrared spectra of both the Zn^{2+} and Co^{2+} derivatives are very similar to each other and to the IR spectrum of $PW_{12}O_{40}^{3-}$ (PW_{12}) as shown in Figure 6c. The IR spectrum of PW_{12} is characterized by four prominent bands: P–O, W–O (terminal), W–O–W (corner-sharing WO_6 octahedra), and W–O–W (edge-sharing octahedra) at 1080, 985, 887, and 807 (br) cm^{-1}, respectively.[15] The asymmetric phosphate stretch in PW_{12} is triply degenerate so that lowering the symmetry from tetrahedral removes the degeneracy and results in band splitting.[16] However, both the Zn and Co derivatives appear to show a single band at about 1030 cm^{-1}, near the P–O band position of PW_{12}, suggesting that significant restoration of (pseudo) tetrahedral symmetry to the phosphate group has occurred on metal substitution to PW_9. The IR spectra also indicate that the Co and Zn derivatives are structurally similar.[3b]

X-ray powder diffraction pattern data further confirm that $P_2W_{18}Zn_4$ and $P_2W_{18}Co_4$ prepared from heated PW_9 are isostructural. Both $P_2W_{18}Zn_4$ and $P_2W_{18}Co_4$ were compared to $P_2W_{18}Co_4(H_2O)_2O_{68}^{10-}$ prepared by Weakley's method (see the Experimental Section). The X-ray powder diffraction patterns

(15) Rocchiccioli-Deltcheff, C.; Thouvenot, R.; Franck, R. *Spectrochim. Acta, Part A* **1976**, *32A*, 587–597.
(16) Knoth, W. H.; Domaille, P. J.; Harlow, R. L. *Inorg. Chem.* **1986**, *25*, 1577. This work reports novel complexes from A-type PW_9 such as $P_2W_{18}Cu_3(NO_3)O_{68}^{13-}$, where the NO_3^- group is internally coordinated in a "P_2W_{21}" structure. We thank Dr. Knoth for providing us with a preprint.

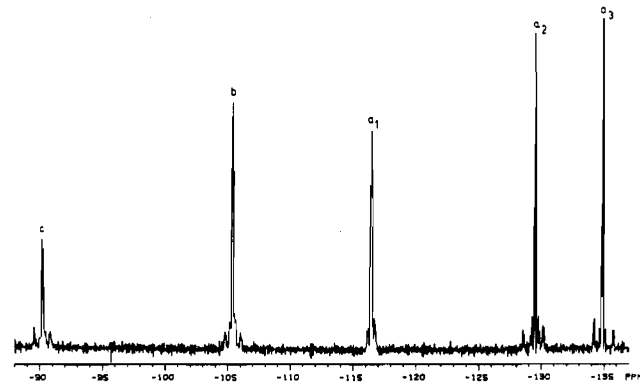

Figure 7. ^{183}W NMR spectrum of $Li_{10}P_2W_{18}Zn_4(H_2O)_2O_{68}$ (0.17 M in D_2O at 21 °C, with 100 000 transients).

Table I. ^{183}W NMR Chemical Shifts (±0.1 ppm), Relative Intensities, and Coupling Constant Data (±0.6 Hz) for $P_2W_{18}Zn_4(H_2O)_2O_{68}^{10-}$

chem shift[a]	rel intens	$^2J_{W-O-W}$ intertriad	$^2J_{P-O-W}$	assignt
−90.3 (−90.7)	1	18.6	1.2	c
−105.4 (−105.8)	2	19.2	1.2	b
−116.5 (−117.8)	2	none	not resolved[b]	a_1
−129.6 (−130.5)	2	23.8	1.6	a_2
−134.9 (−135.6)	2	23.5	1.5	a_3

[a] Chemical shifts in parentheses were recently reported by Evans, Tourné, Tourné, and Weakley[3b] in 60% D_2O at 30 °C. [b] An apparent triplet fine structure in this peak has been reported, and possible explanations for it, other than $^2J_{P-O-W}$ coupling, have been offered.[3b]

(Figure B, supplementary material) exhibited a peak-for-peak similarity, strongly suggesting that samples from the two synthetic methods are isostructural in the solid state.

^{31}P and ^{183}W NMR were used to confirm that the C_{2h} symmetry solid-state structure of $P_2W_{18}Zn_4(H_2O)_2O_{68}^{10-}$ persists in solution. A single resonance is observed in the ^{31}P NMR spectrum, −4.5 ± 0.1 ppm upfield of external 85% H_3PO_4, which confirms that the dimeric complex contains only one type of phosphorus. Figure 7 shows the 1-D ^{183}W NMR spectrum for the C_{2h} symmetry dimer with the expected five lines of intensity 1:2:2:2:2. The large narrow doublets are the result of $^2J_{P-O-W}$ coupling[17,18] (^{31}P: $I = {}^1/_2$, 100% natural abundance), and the low-intensity doublets are due to $^2J_{W-O-W}$ coupling[7] (^{183}W: $I = {}^1/_2$, 14.27% natural abundance). Chemical shift, relative intensity, and coupling constant data are summarized in Table I.[3b]

Assignment of the ^{183}W NMR spectrum is possible and was originally made by using the $^2J_{W-O-W}$ coupling constants available from the one-dimensional spectrum. The W atom connectivities implied from the $^2J_{W-O-W}$ values are based on the following empirical correlations.[7] Pairs of tungsten atoms connected by edge-shared (intratriad) oxygen have $^2J_{W-O-W}$ values of ca. 5–12 Hz, while those that are connected by corner-sharing (intertriad) oxygens have $^2J_{W-O-W}$ values of 15–30 Hz. The W atom labeled c can be unambiguously assigned from its relative intensity to the resonance at −90.3 ppm. From Figure 1A, atom b is coupled only to atom c by corner-shared oxygens, and Table I shows that the lines at −90.3 and −105.4 ppm have a reciprocal $^2J_{W-O-W}$ coupling of ca. 19 Hz. Therefore, b must be the resonance at −105.4 ppm. The tungsten labeled a_1 is not coupled to any magnetically inequivalent W atom by corner-shared oxygens and should not have a large-magnitude coupling (>15 Hz). The resonance at −116.6 ppm has no large-magnitude coupling and is therefore assigned to a_1. The remaining two resonances at −129.6 and −134.9 ppm (a_2 and a_3, respectively) are coupled to each other by corner-sharing oxygens and show identical large-magnitude $^2J_{W-O-W}$

(17) Acerete, R.; Hammer, C. F.; Baker, L. C. W. *J. Am. Chem. Soc.* **1979**, *101*, 267–269.
(18) Domaille, P. J. *J. Am. Chem. Soc.* **1984**, *106*, 7677–7687.

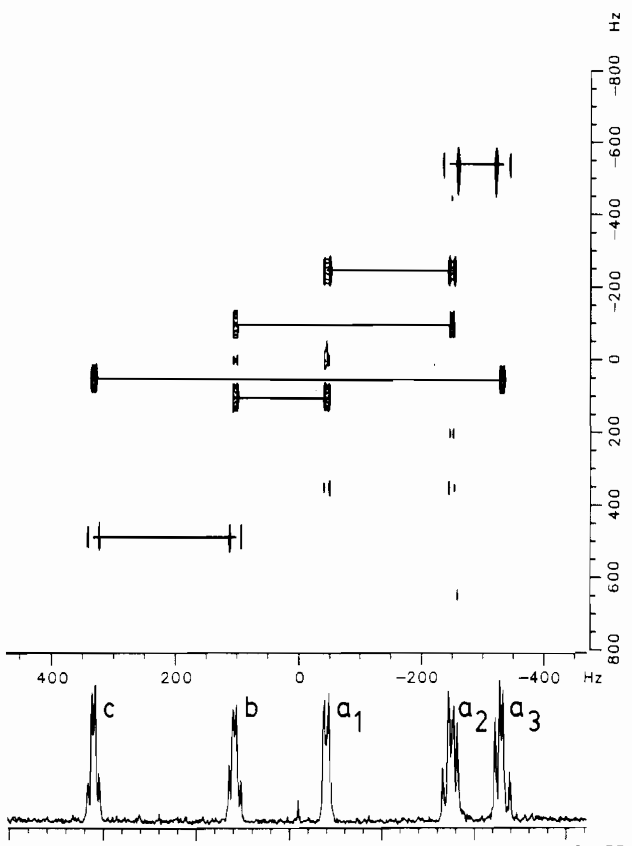

Figure 8. 2-D INADEQUATE $^{183}W\{^{31}P\}$ NMR spectrum of $Li_{10}P_2W_{18}Zn_4(H_2O)_2O_{68}$ (ca. 0.14 M in D_2O at 30 °C). Horizontal lines on the contour map connect coupled tungsten sites. See text for assignments.

values of ca. 24 Hz. This coupling is also apparent from the slight second-order effects exhibited as the beginning of an AB pattern consistent with the observed $\Delta\nu/J = 3.4$. The large-magnitude coupling does not allow an unambiguous assignment of which resonance is a_2 and which is a_3. However, complete assignment of the tungsten resonances was obtained from the tungsten connectivity pattern determined from the two-dimensional INADEQUATE ^{183}W NMR spectrum[7b,c,19] of $P_2W_{18}Zn_4$. Figure 8 shows both the INADEQUATE spectrum and the corresponding two-dimensional contour map. Horizontal lines on the contour map connect coupled tungsten resonances, and the $^2J_{W-O-W}$ magnitudes appear as either closely spaced vertical bars for edge-shared W–O–W octahedra or as well-separated vertical bars for corner-shared W–O–W octahedra.

Assignment of the spectrum is straightforward and follows that described for the one-dimensional spectrum. From Figure 1A, unique resonance c (−90.27 ppm) is only corner coupled to b and only edge coupled to a_3. Figure 8 shows that c has a large-magnitude coupling with the resonance at −105.42 ppm, which must be the tungsten atom labeled b, and a small-magnitude coupling with the −134.87 ppm resonance, which must be a_3. The tungsten atom labeled a_3 has only a large-magnitude corner coupling with a_2. From the 2-D spectrum, a_3 is observed to have a large-magnitude coupling with the −129.59 ppm resonance, which can be assigned to a_2. The tungsten atom labeled a_1 (−116.49 ppm) can be assigned by difference, and this assignment is confirmed by the observed two small-magnitude corner couplings to atoms b and a_2.

$K_{10}P_2W_{18}Cu_4(H_2O)_2O_{68}$. Our preliminary communication reported that $K_{10}P_2W_{18}Cu_4(H_2O)_2O_{68}$ could also be obtained from mixing $CuCl_2·2H_2O$ and $Na_8HPW_9O_{34}$ (dried at 140 °C, 1 atm, 1–2 h) and bringing the mixture "to a homogeneous lime green solution by a minimum of gentle steam bath warming".[1a] We were aware at that time of the need to avoid thermolysis in solution

(19) Mareci, T. H.; Freeman, R. *J. Magn. Reson.* **1982**, *48*, 158–163.

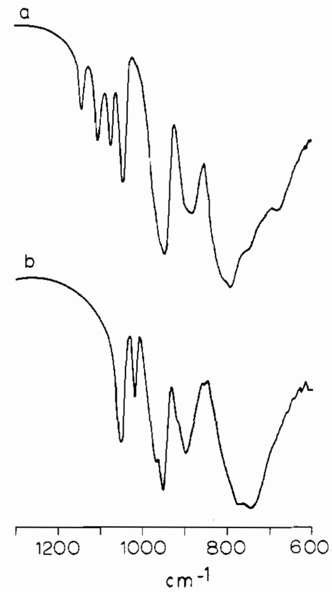

Figure 9. Infrared spectra of isolated products from the reaction of α-PW_9 and Cu^{2+}: (a) major product, not yet identified; (b) minor product, $K_7Na_3P_2W_{18}Cu_4(H_2O)_2O_{68}$.

of the less stable Cu^{2+} product and had noted some differences in the X-ray diffraction powder pattern as compared to those of the more thoroughly characterized Co^{2+} and Zn^{2+} derivatives. Knoth's finding[11,16] that differences in the IR spectra could also be detected (the extent of which are undoubtedly dependent upon the exact PW_9 drying procedure and the treatment of the resultant $P_2W_{18}Cu_4$) caused us to repeat our experiments. Attempts to reproducibly prepare $P_2W_{18}Cu_4(H_2O)_2O_{68}^{10-}$ by using partially heated $PW_9O_{34}^{9-}$ (104 °C, 1 atm, 1–2 h) and the recrystallization conditions (100 °C, H_2O) used for the Co^{2+} and Zn^{2+} derivatives met with failure. Generally, the major product was the same product by IR analysis (Figure 9a) as obtained by thermolysis of authentic $P_2W_{18}Cu_4(H_2O)_2O_{68}^{10-}$ at 100 °C in solution plus small amounts of the desired $P_2W_{18}Cu_4(H_2O)_2O_{68}^{10-}$. Clearly the observed results are highly dependent upon the reaction solution temperature and times, so that a lower temperature (<60 °C), shorter time synthesis was required. Additional experimentation yielded the procedure reported in the Experimental Section, where the product is formed from $CuCl_2·2H_2O$ and fully thermolyzed Δ-$PW_9O_{34}^{9-}$ (dried at 25 °C, 1 atm, 24 h and then 140 °C, 1 atm, 6 h) at 25 °C, followed by precipitating with KCl, gently redissolving at 60 °C for 1–5 min, and crystallizing at room temperature. A moderate yield (27%) of light green cubes found to be clean by IR (Figure 9b) and giving an analysis as the mixed K^+, Na^+ salt $K_7Na_3P_2W_{18}Cu_4(H_2O)_2O_{68}·20H_2O$ is obtained. Light yellow microneedles of the thermolysis product can also be obtained and are actually still the major product (ca. 60% yield). This product has not been characterized further, except to show that its X-ray diffraction powder pattern is, like its IR spectrum, different from that of $K_7Na_3P_2W_{18}Cu_4(H_2O)_2O_{68}$. The powder pattern of the latter, desired $P_2W_{18}Cu_4$ complex (provided as supplementary material, Figure C) shows a pattern of peaks similar to that observed for $P_2W_{18}M_4$ (M = Co, Zn), especially around 2θ = 18 and 30°.

The IR spectrum provides some hints as to the possible reasons for the lower thermal stability of the Cu^{2+} complex compared to that for the Zn^{2+} and Co^{2+} derivatives. The IR spectrum of the Cu^{2+} derivative is similar in the W–O regions but different for the P–O region in that two bands (1053 and 1020 cm^{-1}) are observed as compared to one P–O band (1030 cm^{-1}) observed for the Co^{2+} and Zn^{2+} complexes. We suggest that this indicates that CuO_6 octahedra have only a weak interaction with the B-type phosphorus oxygen such that a lower symmetry still exists (similar to the case for Δ-PW_9). Weak Cu^{2+} interaction with phosphate oxygen has also been observed in other Cu^{2+}-substituted heteropolyanions.[20]

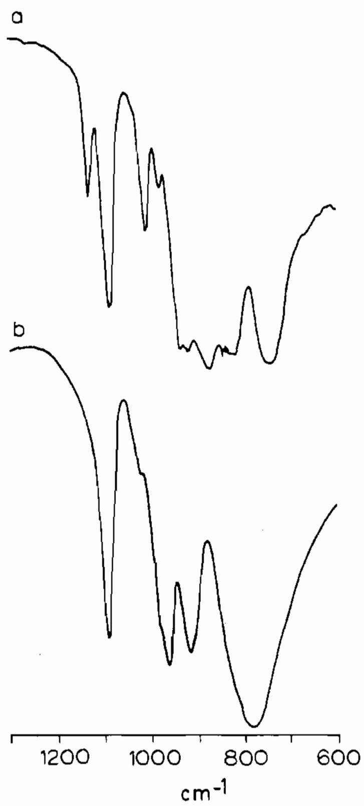

Figure 10. Infrared spectra of (a) $Na_{12}P_2W_{15}O_{56}$ and (b) $K_6P_2W_{18}O_{62}$.

The origin of this weak interaction is possibly due to the well-known tendency of Cu^{2+} to undergo axial Jahn–Teller distortions.[21] This suggests that the $P_2W_{18}Cu_4$ thermal instability might result in part from these distortions causing a lower anion cohesion than is observed for the Co^{2+} and Zn^{2+} derivatives. Neither Co^{2+} nor Zn^{2+} exhibit this distortion, and therefore, they have a stronger interaction with the B-type phosphorus oxygen (restoring near-T_d symmetry to the central phosphate group) as is demonstrated by their IR spectra. X-ray crystallographic characterization of $P_2W_{18}Cu_4$, its comparison to the $P_2W_{18}Co_4$ structure,[3a] and structural characterization of the yellow thermolysis product are needed to help settle this point. Interestingly, the $P_4W_{30}Cu_4(H_2O)_2O_{116}^{12-}$ polyoxoanion described in one of the sections that follows is unaffected by prolonged boiling in aqueous solution, requiring that some aspect of the heteropolyanion structure (i.e. $PW_9O_{34}^{9-}$ vs $P_2W_{15}O_{56}^{12-}$) be another important factor in establishing thermal instability/stability of these complexes.

$Na_{12}P_2W_{15}O_{56}\cdot 18H_2O$ ("α-P_2W_{15}"). The synthesis of α-P_2W_{15} used is similar to that in the literature[22] listed under "$Na_{12}P_2W_{16}O_{59}$" but more recently reformulated[1a,6a,i] as $Na_{12}P_2W_{15}O_{56}$; however, it is still not clear that P_2W_{15} is the exclusive product. It is worth noting that elemental analyses are too insensitive to distinguish between these two formulations and, since the complex is unstable in solution, spectroscopic techniques such as ^{31}P and ^{183}W NMR are not applicable for solution studies.

The synthesis reported in this work provides isomerically pure[8b] α-P_2W_{15}. It takes advantage of Wu's observation[13] that β-$P_2W_{18}O_{62}^{6-}$ degraded by 6 OH^- to $P_2W_{17}O_{61}^{10-}$ re-forms only α-$P_2W_{18}O_{62}^{6-}$ when reacidified in the presence of WO_4^{2-}. Drying over H_2SO_4 for 2 days at 25 °C without heating was used to preserve isomeric purity following our experience with Δ-$PW_9O_{34}^{9-}$. The IR spectrum of α-P_2W_{15} is shown in Figure 10 and is compared to that of the parent anion P_2W_{18}. The most notable feature is the appearance of a higher energy band at 1130 cm^{-1}. This band is probably analogous to the 1170 cm^{-1} band observed for B-type PW_9 and is consistent with assignment as a P=O stretch. This stretch would be expected for a P_2W_{15} complex that is formed by removal of one capping triad from P_2W_{18}, resulting in B-type $P_2W_{15}O_{56}^{12-}$. The P—O region in the IR spectrum of P_2W_{15} is necessarily more complex since this compound contains two phosphate heterogroups, only one of which is perturbed.

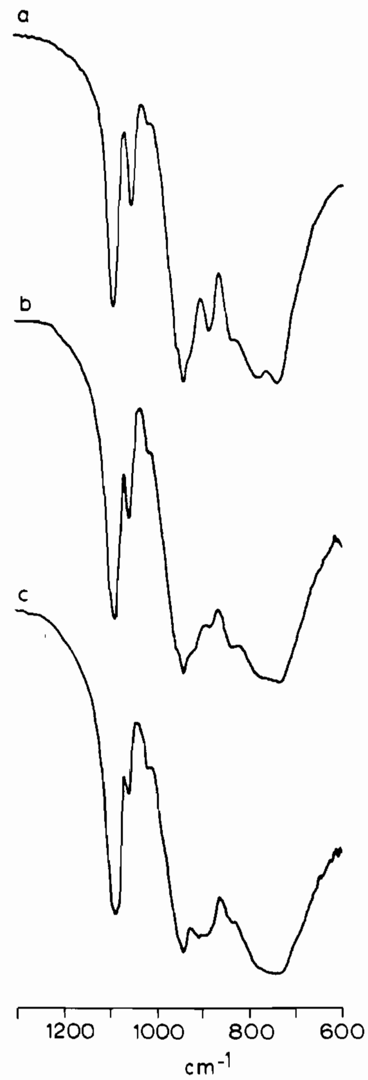

Figure 11. Infrared spectra of (a) $P_4W_{30}Zn_4(H_2O)_2O_{112}^{16-}$, (b) $P_4W_{30}Co_4(H_2O)_2O_{112}^{16-}$, and (c) $P_4W_{30}Cu_4(H_2O)_2O_{112}^{16-}$.

$Na_{16}P_4W_{30}M_4(H_2O)_2O_{112}$ ($M = Zn^{2+}, Co^{2+}, Cu^{2+}$). The reaction of $Na_{12}P_2W_{15}O_{56}$ with 2 equiv of Zn^{2+}, Co^{2+}, or Cu^{2+} in 1 M $NaCl/H_2O$ leads to good yields (77–88%) of the crystalline white Zn, dark green Co, and pale green Cu substituted derivatives isolated as sodium salts. Elemental analyses for all three complexes are consistent with the empirical formula $[Na_8P_2W_{15}M_2O_{56}]_x$, where M = Zn, Co, Cu. The molecular formula in the case of the Zn derivative is found to be dimeric by solution molecular weight measurements. Sedimentation equilibrium ultracentrifugation (Figure D, supplementary material) in $H_2O/NaCl$ yields an observed molecular weight of 7652, which is within 1% of the calculated weight of 7728 for the unsolvated dimeric anion $P_4W_{30}Zn_4(H_2O)_2O_{112}^{16-}$ ($P_4W_{30}Zn_4$).

The IR spectra of the Zn, Co, and Cu derivatives reveal two features (Figure 11). First, the higher energy P=O band at 1130

(20) Rocchiccioli-Deltcheff, C.; Thouvenot, R. *J. Chem. Res., Synop.* **1977**, 46–47; *J. Chem. Res., Miniprint* 544–571.
(21) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley-Interscience: New York, 1980; pp 678–682.
(22) Harmalker, S. P.; Leparulo, M. A.; Pope, M. T. *J. Am. Chem. Soc.* **1983**, *105*, 4286–4292.
(23) Anal. Calcd for $[Na_8P_2W_{15}Zn_2(H_2O)O_{56}\cdot 13H_2O]_2$ synthesized from β-P_2W_{15}: Na, 4.30; P, 1.45; W, 64.4; Zn, 3.05. Found: Na, 4.39; P, 1.47; W, 64.4; Zn, 3.14. Note that the emprical formula (Found: P, 1.0; W, 7.4; Zn, 1.0; Na, 4.0. Calcd: P, 1.0; W, 7.5; Zn, 1.0; Na, 4.0), when combined with the ^{183}W NMR results, requires an isomeric mixture.

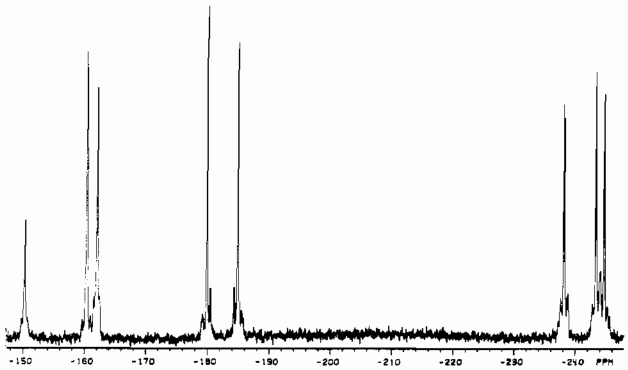

Figure 12. ^{183}W NMR spectrum of $Na_{16}P_4W_{30}M_4(H_2O)_2O_{112}$ (0.1 M in D_2O at 40 °C, with 70 000 transients).

cm^{-1} is now absent and the remaining P—O bands are nearly identical with those of the parent P_2W_{18}. This suggests that metal substitution has filled all the vacancies of P_2W_{15}, restoring symmetry and a degree of bonding interaction with the phosphate oxygen similar to that observed for P_2W_{18}. Second, the IR spectra of the three derivatives are very similar to each other, indicating a corresponding structural similarity, even for the Cu^{2+} complex, in the $P_4W_{30}M_4$ series.

The Co derivative is characterized by its distinctive 570 nm absorption maximum. This absorption is identical with that observed for $P_2W_{18}Co_4$, indicating a very similar ligand field and primary coordination environment for Co in the two complexes.

The ^{31}P NMR spectrum of $P_4W_{30}Zn_4$ shows only two peaks at −4.31 and −14.30 (±0.1) ppm upfield of 85% H_3PO_4. The −14.30 ppm peak is in the same region as observed for P_2W_{18} (−12.7 ppm)[12] and is assigned to the phosphate farthest removed from the Zn^{2+} atoms. The other signal at −4.31 ppm is nearly identical with the −4.5 ppm resonance observed for $P_2W_{18}Zn_4$ and is assigned to the phosphate directly bonded to the Zn^{2+} atoms. This chemical shift behavior is consistent with that of other Zn^{2+}-substituted heteropolytungstates such as α_2-$P_2W_{17}Zn(H_2O)O_{61}^{8-}$ (α_2 = cap-substituted Zn^{2+} atom), where the phosphate bonded to Zn^{2+} moves downfield (−8.6 ppm) and the other phosphate moves upfield (−13.8 ppm) as compared to P_2W_{18} (−12.7 ppm).[12] The similar chemical shift values of the phosphate bonded to the Zn^{2+} atoms for $P_4W_{30}Zn_4$ and $P_2W_{18}Zn_4$ suggests a similar electronic environment around phosphorus in these two complexes.

All these results and the close analogy of P_2W_{15} with B-type PW_9 indicate that the Zn, Co, and Cu derivatives should be formulated as C_{2h} symmetry dimers (Figure 1B), $P_4W_{30}M_4(H_2O)_2O_{112}^{16-}$, strictly analogous to the $P_2W_{18}M_4$ dimer.

This proposed structure is confirmed, in the case of the Zn derivative, by its ^{183}W NMR spectrum (Figure 12). Eight ^{183}W NMR resonances at −150.4, −160.5, −162.0, −180.0, −185.0, −238.4, −243.4, and −244.7 (±0.1) ppm with relative intensities of 1:2:2:2:2:2:2:2, respectively, are observed at 40 °C (referenced to Na_2WO_4 at 40 °C). In addition to the splitting of the main peaks into narrow doublets due to $^2J_{P-O-W}$ coupling,[17] the $^2J_{W-O-W}$ coupling satellites are also clearly observed at the base of all the peaks. Unfortunately, due to the complexity of the expected coupling patterns and the overlapping of peaks, connectivity patterns cannot be deduced by simple inspection. However, the eight ^{183}W resonances, their relative intensities, and the dimeric molecular formula require a C_{2h} symmetry dimer structure as shown in Figure 1B with the eight types of tungsten atoms labeled a_1, a_2, a_3, b_1, b_2, b_3, c_1, and c_2.

Some insight concerning assignment of the tungsten resonances is available from the ^{31}P-decoupled ^{183}W NMR spectrum of $P_4W_{30}Zn_4$. Figure 13 shows the changes that occur on phosphorus decoupling. In comparison to the fully coupled spectrum in Figure 13A, decoupling the −4.31 ppm phosphate generates three sharp singlets at −160.5, −180.0, and −185.0 ppm as shown in Figure 13B. Since this phosphorus resonance has been assigned to the phosphorus directly bonded to the Zn^{2+} atoms, these tungsten resonances must correspond to atoms a_1, a_2, and a_3. Similar decoupling of the −14.3 ppm phosphate shows that the tungsten resonances at −150.5, −162.0, −238.4, −243.4, and −244.7 ppm now become sharp singlets as shown in Figure 13C. These resonances correspond to atoms b_1, b_2, b_3, c_1, and c_2. Although the tungsten resonances can now be generally divided as being bonded to one phosphate group or the other, except for c_1, it is still not possible to assign individual tungsten resonances to the structurally distinct tungsten atoms.

Unambiguous assignment of the tungsten resonances was obtained by the tungsten connectivity pattern determined from the two-dimensional INADEQUATE ^{183}W NMR spectrum of $P_4W_{30}Zn_4$. Figure 14 shows both the INADEQUATE spectrum and the corresponding two-dimensional contour map. Horizontal lines on the contour map connect coupled tungsten resonances, and the $^2J_{W-O-W}$ magnitudes appear as either small circles for edge-shared W–O–W octahedra or as closely spaced double circles for corner-shared W–O–W octahedra.

Assignment of the spectrum starts with the resonance c_1 (−150.4 ppm, previously assigned by its relative intensity) and uses the labeling scheme shown in Figure 1B. From Figure 1B, c_1 is only edge-coupled to c_2 and only corner-coupled to b_3. Figure 14 shows that c_1 is edge-coupled to the −162.0 ppm resonance, which can now be assigned to c_2, and corner-coupled to the −243.4 ppm resonance, which must be b_3. An additional corner-coupling is observed for b_3 with the −160.5 ppm resonance indicating that this peak is a_3. Edge-coupling is also observed for b_3 with the −238.4 ppm resonance, assigning that resonance to b_2. Of the two corner-shared peaks (b_1, b_2) that are coupled to c_2, the resonance at −244.7 ppm is b_1 since b_2 has already been assigned. Besides corner-coupling to c_2 and b_2, b_1 has another corner-coupling to the −180.0 ppm resonance, which must be a_1. The final resonance, a_2, is assigned by the edge-shared coupling between a_3 and the −185.0 ppm resonance, indicating that this resonance is a_2. Only a_1 and a_2 did not show coupling on the contour map. The appearance of a strong AB pattern in the one-dimensional spectrum (Figure 12) shows that these two lines are coupled to each other. It is probably this strong AB coupling that prevents detection of the coupled pair in the two-dimensional experiment since observation of such coupling is optimum for an AX system. The

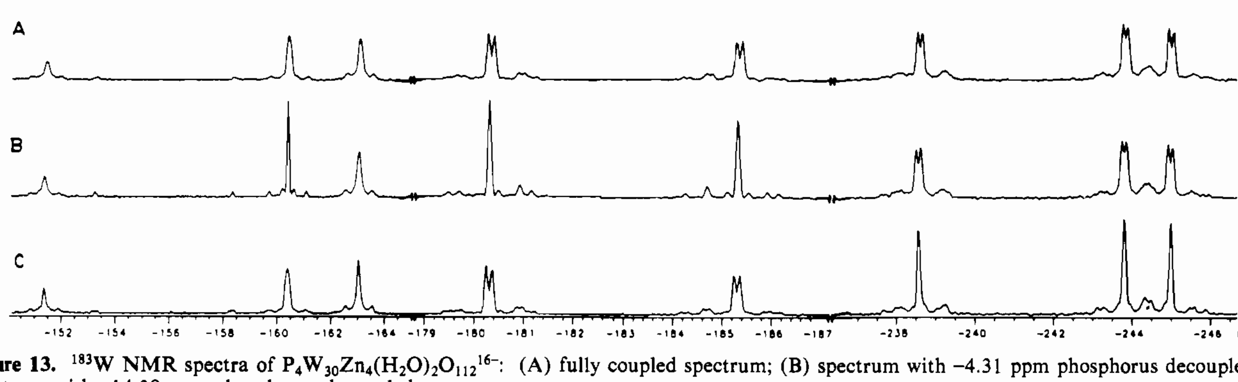

Figure 13. ^{183}W NMR spectra of $P_4W_{30}Zn_4(H_2O)_2O_{112}^{16-}$: (A) fully coupled spectrum; (B) spectrum with −4.31 ppm phosphorus decoupled; (C) spectrum with −14.30 ppm phosphorus decoupled.

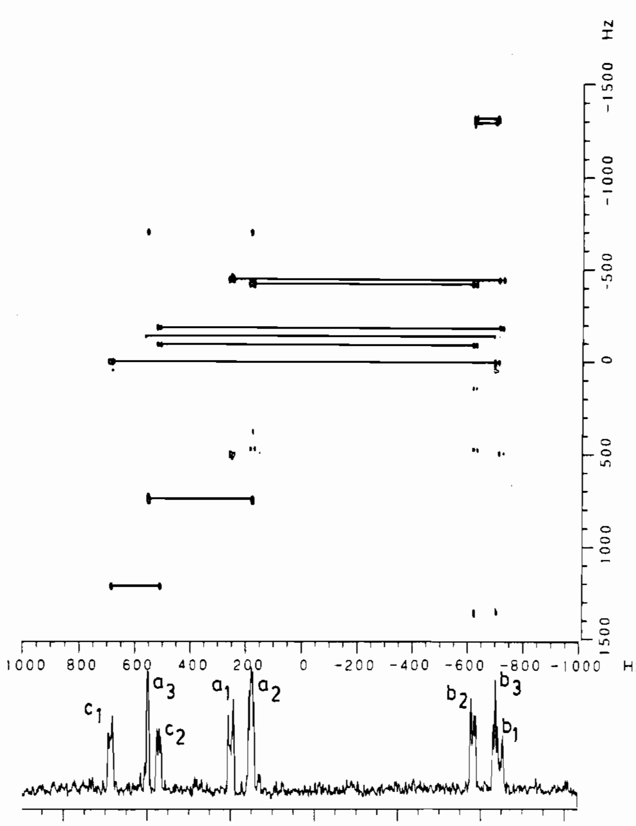

Figure 14. 2-D INADEQUATE $^{183}W\{^{31}P\}$ NMR spectrum of $Li_{16}P_4W_{30}Zn_4(H_2O)_2O_{112}$ (ca. 0.17 M in D_2O at 30 °C).

tungsten connectivities observed are consistent with the $^{183}W\{^{31}P\}$ results and fully support the proposed structure of $P_4W_{30}Zn_4(H_2O)_2O_{112}^{16-}$ as shown in Figure 1B.

It is of interest, in light of the instability of $P_2W_{18}Cu_4(H_2O)_2O_{68}^{10-}$, that these $P_4W_{30}M_4$ complexes appear very stable in solution and are resistant to thermolysis. Prolonged boiling of aqueous solutions of these complexes has no effect, even for the Cu^{2+} complex. This behavior departs dramatically from that observed for $P_2W_{18}Cu_4$, suggesting that there is a structural factor which stabilizes $P_4W_{30}Cu_4$. Molecular models, *based on idealized octahedra*, show that $P_4W_{30}M_4$ complexes can be easily constructed while significant distortions of the planar M^{2+} array are required for construction of $P_2W_{18}M_4$ complexes. Clearly, a crystallographic structure determination of both $P_2W_{18}Cu_4$ and $P_4W_{30}Cu_4$ is desirable and should prove most informative.

In the solid state, $P_4W_{30}Zn_4$ (and presumably the others of this series) undergoes what appears to be a thermal isomerization. Heating $P_4W_{30}Zn_4$ at temperatures of 80 °C or higher for longer than 30 min results in the appearance of 3 additional ^{31}P and 11 additional ^{183}W NMR resonances listed in Table II in variable yields (up to 50–60% as estimated by ^{183}W NMR). The thermal product that possesses these new spectral features is not removed by recrystallization. Moreover, elemental analysis of the mixture gave a good Na, P, W, and Zn analysis and requires that the new product does in fact have the same composition; thus, the new product is an isomer. It is unlikely that the thermal product is formed by the precedented loss[5] of one of the constitutional Zn-bound water molecules, yielding a C_s symmetry anion, because the ^{183}W NMR spectrum is recorded in water, where water binding should be kinetically rapid and thermodynamically favorable.

There is little definitive literature on polyoxoanion fluxionality and isomerizations.[10] What does exist indicates that the longest (often >2.2 Å) and presumably the weakest M- - -O bonds are often the ones cleaved and re-formed during known isomerizations. Isomerizations involving a $\pi/3$ rotation of a triad or cap of edge-sharing octahedra (α–β isomerization) are also well-known.[8b,24a]

Table II. ^{31}P and ^{183}W NMR Resonances (ppm) for $P_4W_{30}Zn_4(H_2O)_2O_{112}^{16-}$ and Its Thermal Rearrangement Product

$P_4W_{30}Zn_4$		thermal product^a			$P_4W_{30}Zn_4^b$	
^{31}P	^{183}W	^{31}P	^{183}W		^{183}W	
−4.31	−150.4	−3.73	−122.1	−183.4	−121.8	−182.7
−14.30	−160.5	−4.31	−132.3	−184.4	−131.7	−184.5
	−162.0	−4.41	−150.6	−186.7	−150.4	−186.8
	−180.0	−12.67	−152.6	−236.9	−152.6	−236.9
	−185.0	−14.30	−157.8	−237.3	−157.4	−237.3
	−238.2		−159.8	−242.8	−159.8	−242.7
	−243.4		−162.0	−243.7	−162.3	−243.6
	−244.7		−179.5	−267.4	−178.9	−266.8
			−180.1	−269.4	−179.8	−269.0
				−272.8		−272.6

^{a} Note that the ^{183}W NMR spectrum of the mixture contains 11 new lines for the thermal product in addition to those observed for $P_4W_{30}Zn_4$ for a total of 19 ^{183}W resonances. ^{b} This compound was synthesized from β-P_2W_{18}-derived P_2W_{15}; these 19 lines are, as indicated in the data, identical within experimental error with those of the thermolysis product.

In the case of $P_4W_{30}M_4$, $\pi/3$ rotation of one of the polar caps in, for example, the "top" half of P_2W_{15} in Figure 1B would lower the symmetry from C_{2h} to C_s via an $\alpha \rightarrow \beta$ isomerization; 4 ^{31}P and 16 ^{183}W NMR resonances corresponding to the number of symmetry-inequivalent nuclei might be resolved under optimum circumstances. In practice, we have observed only 3 new ^{31}P and 11 new ^{183}W peaks for the $P_4W_{30}Zn_4$ thermolysis product (Table

(24) (a) Pope, M. T. In *Heteropoly and Isopoly Oxometallates*; Springer-Verlag: New York, 1983. (b) The study by Contant and Ciabrini[6b] of the alkaline degradation of α- plus β-$P_2W_{18}O_{62}^{6-}$ is relevant. They note both that significant β- to α-P_2W_{18} isomerization is observed at pH >2 and that β to α isomerization is "much faster" for defect compounds such as $P_2W_{17}O_{61}^{10-}$. (This latter effect may possibly be due to a cation ion-pairing effect similar to what might occur in the solid state.) Both of the conditions are met during the preparation of P_2W_{15} from β-P_2W_{18} as P_2W_{17} is an intermediate and the final solution pH is 9. As a result, significant β to α isomerization is possible during the degradative synthesis of P_2W_{15} from β-P_2W_{18} resulting in the mixture α-P_2W_{15} plus β-P_2W_{15}. (c) A second explanation that was considered involves a reorientation of one of the two PO_4^{3-} cores in $P_4W_{30}Zn_4$. This possibility follows from the recent work by Klemperer's group[10f] on the rearrangements of a T_d MO_4^{2-} subunit as a key to α-$Mo_8O_{26}^{4-}$ and related isomerizations. Klemperer notes that the A-α-$PW_9O_{34}^{9-}$ to B-α-$PW_9O_{34}^{9-}$ rearrangement can be accomplished by a 90° rotation of the central T_d PO_4^{3-} group (with its long ca. 2.4 Å M- - -OPO_3 bonds) about one of its C_2 axes. (As shown in Figure 3, the A to B isomerization also requires an interconversion between edge- and corner-sharing octahedra.) In the case of the thermolyzed $P_4W_{30}Zn_4$, it is at least conceivable that one of the two PO_4^{3-} units in a P_2W_{15} half (Figure 1B) could undergo such an isomerization. However, the resultant PO_4^{3-} group would have lower symmetry and additional infrared P–O band splitting (as in $PW_9O_{34}^{9-}$ or $P_2W_{15}O_{56}^{12-}$, Figures 4 and 10, respectively) should be observed. This, however, is not the case for the thermolyzed $P_4W_{30}Zn_4$; only the P–O bands at ca. 1080 and 1050 cm^{-1} are observed, identical with those observed in the infrared spectrum of nonthermolyzed $P_4W_{30}Zn_4$ (Figure 11). Furthermore, the independent synthesis of such an isomer from "α,β-P_2W_{15}" (derived from β-P_2W_{18}) that possesses a reorientated PO_4^{3-} would be difficult to explain. (d) A third possible isomer involving an α or β *attachment* (to be distinguished from α,β triad rotational isomerism[1b,8b]) of a P_2W_{15} half-unit to the planar M^{2+} array is judged less likely for two reasons: (I) precedent is established for the β form of attachment by the crystallographically determined structure of $P_2W_{18}Co_4$ and (II) the α form of attachment is less likely due to possible steric interactions between the bound waters of the M^{2+} array and the bridging oxygens between the tungstens labeled a_3 and a_2. (e) One experiment of interest is to see whether or not α-$P_2W_{18}O_{62}^{6-}$ will undergo isomerization to the β form in the solid state.[24g] Another is to monitor both this possible isomerization and the $P_4W_{30}Zn_4$ thermolysis by solid-state ^{31}P NMR, including CSA (chemical shift anisotropy) experiments, which should show a smaller CSA for A-type vs B-type[24d] PO_4^{3-}. A 2-D ^{183}W NMR study of a pure sample[24f] of the $P_4W_{30}Zn_4$ thermolysis product or even a mixture would be very useful. It is also possible that reliable integrated intensities for the 1-D ^{183}W and ^{31}P NMR experiments would prove of value. (f) Attempts to isolate the pure thermal product by either the direct synthesis route or by prolonged heating for complete characterization have been unsuccessful. (g) Two ^{31}P signals in the solid-state NMR spectrum of $P_2Mo_{18}O_{62}^{6-}$ have been assigned, but without other evidence, to α and β isomers: Black, J. B.; Clayden, N. J.; Griffiths, L.; Scott, J. D. *J. Chem. Soc., Dalton Trans.* **1984**, 2765.

II). This in turn suggests that only one P_2W_{15} half of $P_4W_{30}Zn_4$ contains the perturbing isomerization and that this perturbation is relayed only as far as the a_1, a_2, a_3 tungsten belt and the PO_4^{3-} attached to these tungstens in the "bottom" P_2W_{15} half in Figure 1B. This provides a consistent, although unproven, explanation for the deficit number of observed ^{31}P and ^{183}W lines.

To provide further evidence for an $\alpha \rightarrow \beta$ isomerization, $P_4W_{30}Zn_4$ was prepared from β-$P_2W_{18}O_{62}^{6-}$-derived $P_2W_{15}O_{56}^{12-}$. The mixture α,α-$P_4W_{30}Zn_4$, α,β-$P_4W_{30}Zn_4$, and possibly β,β-$P_4W_{30}Zn_4$ is expected from this synthesis since, in principle, either an α or β cap can be removed by base degradation of β-P_2W_{18}, resulting presumably in both[24b] α-P_2W_{15} and β-P_2W_{15}. In the absence of some special directing effect, α,β-P_2W_{15} should then react with Zn^{2+}, forming the above isomeric $P_4W_{30}Zn_4$ mixture. In fact, the isomeric $P_4W_{30}Zn_4$ mixture formed via this synthesis *showed exactly only those ^{31}P and ^{183}W NMR resonances exhibited by the thermolyzed $P_4W_{30}Zn_4$* (Table II). The results strongly indicate a solid $\alpha \rightarrow \beta$ thermal isomerization of $P_4W_{30}Zn_4$; no other explanation consistent with all the data has been found.[24c,d] The energetics of this process and the specific solid-state effects that are presumably important remain obscure. In solution, the opposite energetics are the rule with α isomers being more stable than β isomers.[24a] The same is apparently true for $P_4W_{30}Zn_4$, since in solution no α to β isomerization is observed (the reverse reaction to demonstrate that this process is under thermodynamic control has not been attempted). Clearly, additional studies are required,[24e,f] including X-ray crystallography and 2-D ^{183}W NMR studies, to provide unequivocal structural information.

Summary and Conclusions

The major findings and conclusions of this work can be summarized as follows:

(1) The rational syntheses of the $P_2W_{18}M_4(H_2O)_2O_{68}^{10-}$ and the $P_4W_{30}M_4(H_2O)_2O_{112}^{16-}$ ($M = Co^{2+}, Zn^{2+}, Cu^{2+}$) complexes are described as is their full characterization, including one- and two-dimensional ^{183}W NMR and unambiguous assignment of their ^{183}W NMR spectra.[3b]

(2) The B-type trivacant heteropolyanions such as B-$PW_9O_{34}^{9-}$ and B-$P_2W_{15}O_{56}^{12-}$ are shown to be key structural requirements for formation of these disubstituted, dimeric heteropolyanions.

(3) One implication, following (1) and (2), is that the $P_2W_{18}M_4$ and $P_4W_{30}M_4$ complexes are not unique but rather are just the first two examples of a conceptually more general, previously unrecognized class of massive, disubstituted dimers. Possible new members include $[PW_9O_{34}{\cdot}M_4(P_2W_{12}O_{50})M_4{\cdot}PW_9O_{34}]^{20-}$, $[P_2W_{15}O_{56}{\cdot}M_4(P_2W_{12}O_{50})M_4{\cdot}P_2W_{15}O_{56}]^{26-}$ (for M^{2+}), or the highly charged, probably insoluble oligomer $-[M_2P_2W_{12}O_{50}M_2]-_n$. However, the required B-type isomer of $P_2W_{12}O_{50}^{18-}$ which has both "$W_3O_6^{6+}$" caps removed from the $P_2W_{18}O_{62}^{6-}$ structure (see Figure 1B) is different from the presently known[25] isomer of $P_2W_{12}O_{50}^{18-}$.

Interestingly, the above implication has already had impact upon the work of others. Weakley has recently published the X-ray structure of $[(PW_9O_{34})_3Co_9(\mu\text{-}OH)_3(H_2O)_6(HPO_4)_2]^{16-}$ and has predicted that a related series of $P_2W_{15}O_{56}^{12-}$- and $P_2W_{12}O_{50}^{18-}$-derived complexes should exist.[26]

(4) The solution thermal stability of $P_2W_{18}Cu_4$ is documented in contrast to the stability of $P_4W_{30}M_4$ ($M = Co^{2+}, Zn^{2+}, Cu^{2+}$), leading to the suggestion that additional studies including X-ray diffraction structures of $P_2W_{18}Cu_4$, of its crystalline yellow thermolysis product, and of $P_4W_{30}M_4$ ($M = Co^{2+}, Cu^{2+}$) should prove of interest.

(5) The first and then the second observations of apparent solid-state thermal isomerizations are reported. The first is now known to be $PW_9O_{34}^{9-}$ (predominantly A-type) $\rightarrow$ Δ-$PW_9O_{34}^{9-}$ (predominantly B-type) on the basis of the work of Knoth, Domaille, and Farlee,[9] and the second is suggested to be α,α-$P_4W_{30}Zn_4 \rightarrow \alpha,\beta$-$P_4W_{30}Zn_4$. The facile solid-state isomerization of $P_4W_{30}Zn_4$ at 80 °C for >0.5 h is an especially interesting observation in light of the nonisomerization of $P_4W_{30}Zn_4$ that is more rapidly dried at 80 °C under vacuum for less than 0.5 h or that undergoes prolonged boiling in aqueous solution. These preliminary observations warrant verification and further study; the energetics of A $\rightleftharpoons$ B type rearrangements are obviously poorly understood. The implication is that solid-state as well as solution rearrangements of polyoxoanions are more general if not widespread.[10] These results also document the need to minimize and carefully record thermal drying procedures in the manipulation of polyoxoanions.

(6) The previous misformulation[11] of $P_4W_{30}M_4(H_2O)_2O_{112}^{16-}$ = $[P_2W_{15}M_2(H_2O)O_{56}]_2^{16-}$ as "$P_2W_{16}M_2(H_2O)_2O_{60}^{10-}$" has been corrected,[16] and additional evidence is provided that "$Na_{12}P_2W_{16}O_{59}$" is best reformulated as predominantly $Na_{12}P_2W_{15}O_{59}{\cdot}xH_2O$ (x = 18 under our conditions), complementing and confirming the findings of Contant and Ciabrini[6a] and Baker and co-workers.[6c]

(7) The finding that "P_2W_{16}" is largely P_2W_{15} makes apparent a more common, rather than a distinctly different, chemistry in the P_2W_{18} and PW_{12} series of complexes: $P_2W_{18}O_{62}^{6-}$, $P_2W_{17}O_{61}^{10-}$, ($P_2W_{16}O_{59}^{12-}$), $P_2W_{15}O_{56}^{12-}$ and $PW_{12}O_{40}^{3-}$, $PW_{11}O_{39}^{7-}$, ($PW_{10}O_{37}^{9-}$), and $PW_9O_{34}^{9-}$. Only $P_2W_{16}O_{59}^{12-}$ and[27] $PW_{10}O_{37}^{9-}$ are less well-known and do not readily form isolable, M^{2+}-substituted derivatives.

(8) Finally, we believe that the characterization of a massive,[28] M_r = 7728 polyoxoanion like $P_4W_{30}Zn_4(H_2O)_2O_{112}^{16-}$ in solution is significant. Polyoxoanion chemistry is poised for a rapid growth with applications in a wide range of areas,[29] but these applications, such as in catalysis, require rapid characterization in solution as well as in the solid state, where diffraction methods are available.[30] Other techniques for the rapid characterization of polyoxoanions, such as FAB mass spectroscopy,[29,31] also deserve mention in this context.

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Supplementary Material Available: Plots of ultracentrifugation molecular weight data for $P_2W_{18}Zn_4(H_2O)_2O_{68}^{10-}$ and $P_4W_{30}Zn_4(H_2O)_2O_{112}^{16-}$, and X-ray powder diffraction data for $P_2W_{18}Zn_4(H_2O)_2O_{68}^{10-}$, for $P_2W_{18}Co_4(H_2O)_2O_{68}^{10-}$ prepared by the method reported here and by Weakley's method, and for $P_2W_{18}Cu_4(H_2O)_2O_{68}^{10-}$ (4 pages). Ordering information is given on any current masthead page.

(25) Acerete, R. Ph.D. Dissertation, Georgetown University, 1981.
(26) Weakley, T. J. R. *J. Chem. Soc., Chem. Commun.* **1984**, 1406.
(27) (a) Knoth, W. H.; Harlow, R. L. *J. Am. Chem. Soc.* **1981**, *103*, 1865. (b) 1,4-$PV_2W_{10}O_{40}^{5-}$ has been described: Domaille, P. J.; Watunya, G. *Inorg. Chem.* **1986**, *25*, 1239. (c) Domaille, P. J.; Harlow, R. L. *J. Am. Chem. Soc.* **1986**, *108*, 2108.
(28) (a) One of the most massive, discrete heteropolyanions reported to date[28b,c] is $M^{n+}As_4W_{40}O_{140}^{n-28}$. (b) Leyrie, M.; Herve, G. *Nouv. J. Chim.* **1978**, *2*, 233. (c) Robert, F.; Leyrie, M.; Herve, G.; Teze, A.; Jeannin, Y. *Inorg. Chem.* **1980**, *19*, 1746.
(29) See ref 3-7 in: Finke, R. G.; Droege, M. W.; Cook, J. C.; Suslick, K. S. *J. Am. Chem. Soc.* **1984**, *106*, 5750-5751.
(30) See, however: Evans, H. T., Jr.; Pope, M. T. *Inorg. Chem.* **1984**, *23*, 501.
(31) Suslick, K. S.; Cook, J. C.; Rapko, B. M.; Droege, M. W.; Finke, R. G. *Inorg. Chem.* **1986**, *25*, 241.
(32) Corbridge, D. E. C. *The Structural Chemistry of Phosphorus*; Elsevier: Amsterdam, 1974; p 467.