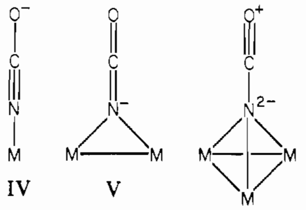
Shown below is a scheme that illustrates why the decomposition of NCO may be promoted by polynuclear species via the successive weakening of the N–C bond.



IV V VI

Structures IV and V are documented,[32] but examples of NCO bridging more than two metals either as a mono, di, or trihapto ligand are unknown. The reverse reaction of a nitrido cluster to form an isocyanate would not occur under mild conditions but was clearly demonstrated at high CO pressure. $[Ru_6N(CO)_{16}]^-$ was dissolved in THF and the solution pressurized to 3000 psig CO at 70 °C for 3 h. The infrared spectrum of the solution observed after the pressure was released revealed absorbances characteristic of a mixture of $[Ru_5N(CO)_{14}]^-$ and $[Ru_4(NCO)(CO)_{13}]^-$. In particular, the sharp peak at 2189 cm^{-1} confirms the re-formation of a coordinated isocyanate. The details of this unique method of forming carbon–nitrogen bonds and the reactivity of $[Ru_6N(CO)_{16}]^-$ are being studied.

Acknowledgment. We gratefully acknowledge the National Science Foundation for support of this work (Grant No. CHE8106096). We also thank Professor John Shapley for early communication of this results on the nitrosylation of $[Ru_6(CO)_{18}]^{2-}$.

Supplementary Material Available: Lists of atomic coordinates, thermal parameters, observed and calculated structure factors, and distances and angles (12 pages). Ordering information is given on any current masthead page.

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Trivacant Heteropolytungstate Derivatives. 2. Synthesis, Characterization, and ^{183}W NMR of $P_4W_{30}M_4(H_2O)_2O_{112}^{16-}$ (M = Co, Cu, Zn)

Sir:

Recently[1a] we described the high-yield, rational synthesis and full characterization of the M = Co, Cu, Zn disubstituted, tri(tungsten)vacant[2a] heteropolytungstates B-$P_2W_{18}M_4(H_2O)_2O_{68}^{10-}$. As a result of these studies, we concluded that an important implication is that B-$P_2W_{18}M_4(H_2O)_2O_{68}^{10-}$ is not unique but rather is just the first member[1b] of a previously unrecognized class of massive, disubstituted, trivacant heteropolytungstate dimers.

Herein we report the synthesis, characterization, and ^{31}P and ^{183}W NMR of B-$P_4W_{30}M_4(H_2O)_2O_{112}^{16-}$ (M = Co, Cu, Zn), thereby providing the second member of this class of heteropolytungstates. The results described below fortify our earlier preliminary conclusion[1a] that a B-type[2b] trivacant heteropolytungstate is a key structural requirement for the formation of this class of heteropolytungstates. The results also support a single structural assignment from among the 16 possible structural isomers and correct the previous misformulation of these complexes[3] as "$P_2W_{16}M_2(H_2O)_2O_{60}^{10-}$"

The trivacant heteropolytungstate starting material, α-$Na_{12}P_2W_{15}O_{56}\cdot xH_2O$ (previously thought to be α-$Na_{12}P_2W_{16}O_{59}$),[3a] was prepared as described in the literature[3b] by base degradation of α-$K_6P_2W_{18}O_{62}$. The Co, Cu, and Zn derivatives of α-$P_2W_{15}O_{56}^{12-}$ were prepared in 77–88% yields from $Co(NO_3)_2\cdot 6H_2O$, $CuCl_2\cdot 2H_2O$, and $ZnBr_2$ in 1 M NaCl or in an acetate buffer.[3d] In the case of the Zn complex, 0.56 g (2.0 equiv) of $ZnBr_2$ was dissolved in 50 mL of 1 M NaCl followed by 5.0 g of $Na_{12}P_2W_{15}O_{56}$ and gentle heating and stirring to obtain a homogeneous solution. Cooling overnight at 5 °C yielded 4.44 g (88%) of white crystalline solid, which was dried at 80 °C under vacuum for ≤0.5 h *but not for longer times or at higher temperatures* as it was discovered, after considerable experimentation, that more vigorous drying produces a product with different ^{31}P and ^{183}W NMR data[4] (vide infra) via an apparent solid-state isomerization reaction.[5] The white crystalline solid was formulated as the disubstituted dimer $Na_{16}[P_2W_{15}Zn_2(H_2O)O_{56}]_2 = Na_{16}P_4W_{30}Zn_4(H_2O)_2O_{112}$ on the basis of a ±0.4% Na, P, W, Zn elemental analysis, molecular weight measurements (M_r(calcd) for $P_4W_{30}Zn_4(H_2O)_2O_{112}^{16-} = 7728$; M_r(obsd) = 7652) obtained by using an ultracentrifuge and the sedimentation equilibrium method,[6] and the ^{31}P and ^{183}W NMR data presented below.

In the case of the Co and Cu derivatives, 4.20 g (83%) of a dark green powder ($\lambda_{max}(H_2O)$ = 570 nm) and 3.92 g (77%) of light green-yellow crystals ($\lambda_{max}(H_2O)$ = end absorption beginning at 600 nm) were formed, respectively. Significantly, the distinctive[7] λ_{max} = 570 nm of the cobalt derivative of $P_2W_{15}O_{56}^{12-}$ is identical with the λ_{max} = 570 nm of the $PW_9O_{34}^{9-}$-derived dimer, $[PW_9Co_2(H_2O)O_{34}]_2^{10-}$, indicating a very similar ligand field and thus primary coordination

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(1) (a) Finke, R. G.; Droege, M.; Hutchinson, J. R.; Gansow, O. *J. Am. Chem. Soc.* **1981**, *103*, 1587. (b) The B-$P_2W_{18}M_4(H_2O)_2O_{68}^{10-}$ heteropolytungstates were first reported in 1973: Weakley, T. J. R.; Evans, H. T., Jr.; Showell, J. S.; Tourné, G. F.; Tourné, C. M. *J. Chem. Soc. Chem. Commun.* **1973**, 139.

(2) (a) $P_2W_{15}O_{56}^{12-}$ and $PW_9O_{34}^{9-}$ are derived by formally removing a "$W_3O_6^{6+}$" unit from the saturated tungstates $P_2W_{18}O_{62}^{6-}$ and $PW_{12}O_{40}^{3-}$, respectively, and hence are referred to as tri(tungsten)vacant, or just trivacant, heteropolytungstates. (b) For a discussion of A, B, α, and β isomerism see: Massart, R.; Contant, R.; Fruchart, J. M.; Ciabrini, J. P.; Fournier, M. *Inorg. Chem.* **1977**, *16*, 2916.

(3) (a) The $Na_{12}P_2W_{15}O_{56}\cdot xH_2O$ preparation used was that listed under[3b] "α-$Na_{12}P_2W_{16}O_{59}$". In a subsequent paper,[3c] it is noted that "new samples (of "$Na_{12}P_2W_{16}O_{59}$") agree with $Na_{12}P_2W_{15}O_{56}\cdot xH_2O$". The data presented in the text strongly suggest that this material is primarily, but maybe not completely, $Na_{12}P_2W_{15}O_{56}\cdot xH_2O$. (b) Contant, R.; Ciabrini, J. P. *J. Chem. Res., Miniprint* **1977**, 2601; *J. Chem. Res., Synop.* **1977**, 222. (c) Contant, R.; Ciabrini, J. P. *J. Inorg. Nucl. Chem.* **1981**, *43*, 1525. (d) Use of an acetate buffer produced identical $P_4W_{30}M_4(H_2O)_2O_{112}^{16-}$ by ^{31}P and ^{183}W NMR and elemental analysis (M = Zn^{2+}).

(4) Major NMR peaks: ^{31}P in D_2O $\delta = -3.43, -3.90, -4.01, -12.27$; ^{183}W in D_2O $\delta = -122.1, -132.3, -152.6, -157.8, -180.1, -183.4, -186.7, -237.3, -267.4, -272.4, -272.8$.

(5) Finke, R. G.; Droege, M. W., unpublished results.

(6) Chervenka, C. H. "A Manual of Methods for the Analytical Ultracentrifuge"; Spinco Division of Beckman Instruments: Palo Alto, CA, 1969.

(7) (a) The following monosubstituted heteropolytungstates appear at shorter wavelengths: $P_2W_{17}Co(H_2O)O_{61}^{10-}$ ($\lambda_{max}(H_2O)$ = 540–550 nm);[3b] $PW_{11}Co(H_2O)O_{39}^{5-}$ ($\lambda_{max}(H_2O)$ = 540, 526, 505 (sh) nm).[7b] (b) Komura, A.; Hayashi, M.; Imanaga, H. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 87.

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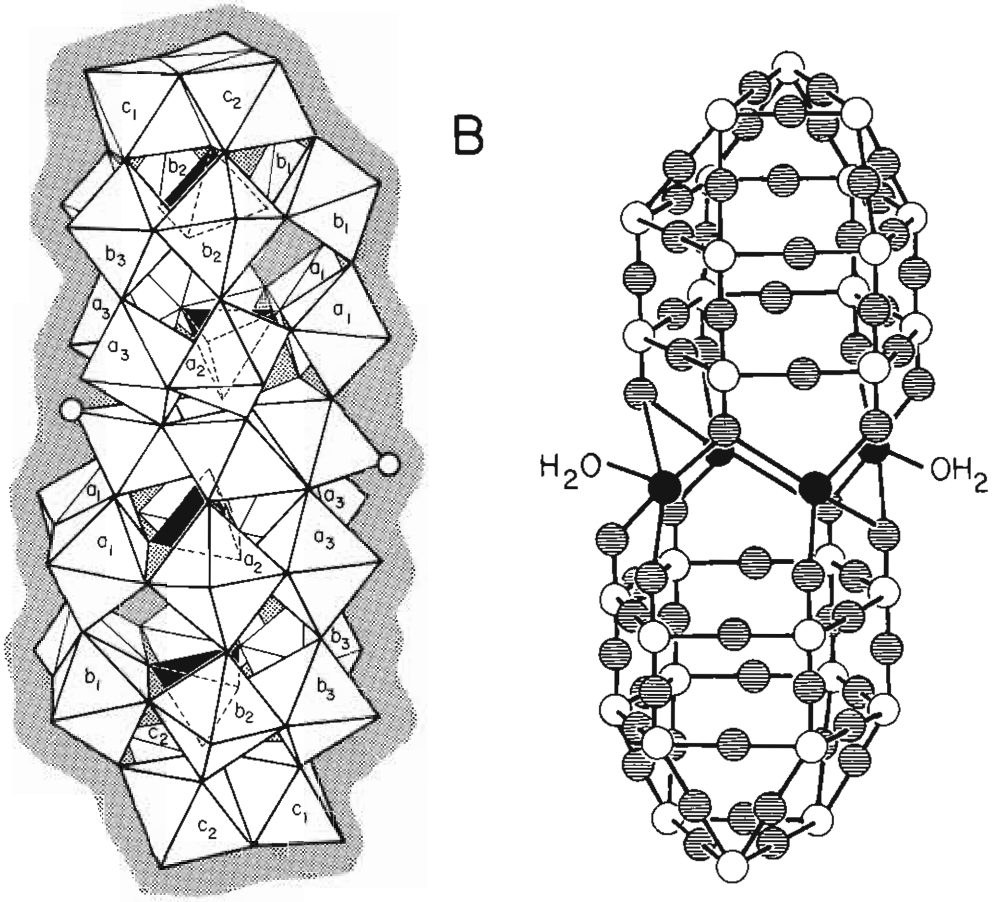

Figure 1. (A) Coordination polyhedra representation of $P_4W_{30}M_4(H_2O)_2O_{112}^{16-}$ (M = Co, Cu, Zn). The four central octahedra (only three are easily visible) are the MO_6 (M = Co, Cu, Zn) octahedra, and the circles represent the two M^{2+}-bound waters. The two $P_2W_{15}O_{56}^{12-}$ units, with their internal (dark) PO_4^{3-} tetrahedra, lie above and below the four central octahedra and have eight chemical shift inequivalent tungstens labeled a_1, a_2, a_3, b_1, b_2, b_3, c_1, and c_2. The C_{2h} symmetry isomer shown is labeled[11] $\alpha\beta\beta\alpha$. (B) idealized ball-and-stick representation of $P_4W_{30}M_4(H_2O)_2O_{112}^{16-}$, where the central, filled circles represent M (Co, Cu, Zn), the shaded circles represent oxygen, and the open circles represent W. This figure shows only the molecule's connectivity where, for simplicity's sake, no attempt was made to accurately portray the W–O–W, O–W–O and other angles, for example.

environment for the Co in the two complexes. The filtrate from the cobalt derivative showed a broad λ_{max} = 540–550 nm characteristic of[3b] $P_2W_{17}Co(H_2O)O_{61}^{10-}$.

From the ^{183}W NMR[8] and ^{31}P NMR[9] spectra of the diamagnetic zinc derivative, the structure of $P_4W_{30}Zn_4(H_2O)_2O_{112}^{16-}$ was shown to be a C_{2h} symmetry dimer, $[P_2W_{15}Zn_2(H_2O)O_{56}]_2^{16-}$, analogous to the C_{2h} symmetry dimer, $[PW_9Zn_2(H_2O)O_{34}]_2^{10-}$, we previously described.[1a] The ^{183}W and ^{31}P NMR spectra were both recorded on a Nicolet Technology NT-360 system with use of the instrumental parameters detailed in footnote 10. Eight ^{183}W NMR resonances were observed for 0.10 M $Na_{16}[P_4W_{30}Zn_4(H_2O)_2O_{112}]$ in D_2O at 40 °C: δ(upfield of saturated $Na_2WO_4\cdot2H_2O$ in D_2O) = −150.4, −160.5, −162.0, −180.0, −185.0, −238.2, −243.4, −244.7 (Figure 2), with relative intensities 1:2:2:2:2:2:2:2 within experimental error for a total of 15 tungstens. The ^{183}W NMR data and $P_4W_{30}Zn_4(H_2O)_2O_{112}^{16-}$ molecular formula require a C_{2h} symmetry, dimer formulation, $[P_2W_{15}Zn_2(H_2O)O_{56}]_2^{16-}$, such as the structure shown in Figure 1A with its 8 types of tungstens, a_1, a_2, a_3, b_1, b_2, b_3,

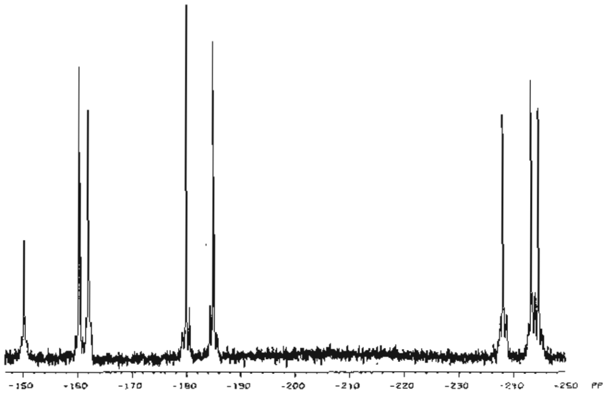

Figure 2. The 15.04-MHz ^{183}W NMR spectrum of 0.1 M $P_4W_{30}Zn_4(H_2O)_2O_{112}^{16-}$ in D_2O acquired through ca. 7 × 10^4 scans over ca. 40 h. Chemical shift values and discussion are provided in the text. $^2J_{W-W}$ coupling[8f,i,j] is clearly visible at the base of the major peaks and has been used to assign most of the observed resonances.[5]

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(9) A summary of ^{31}P NMR data for heteropolytungstates has appeared.[2b]

(10) ^{183}W NMR spectra were recorded in 10-mm tubes at a spectral frequency of 15.042 MHz and a pulse width of 40.0 μs, with a repetition rate of 2 s and a D_2O lock. ^{31}P NMR spectra were recorded in 12-mm tubes at a spectral frequency of 146.161 MHz and a pulse width of 16.0 μs, with a pulse delay of 5.0 s and a D_2O lock. ^{31}P chemical shifts in δ are reported relative to a sealed capillary of 85% H_3PO_4 supported in the center of the 12-mm NMR tube.

c_1, and c_2. Of the 16 possible isomeric $[P_2W_{15}Zn_2(H_2O)O_{56}]_2^{16-}$ dimers, only 3 other C_{2h} symmetry isomers are possible although they are less consistent with the observed ^{31}P and other data.[11]

The ^{31}P NMR data provide further confirmation of the structure shown in Figure 1 and especially for the B-type structure,[2b] where the phosphate connected to the a_1, a_2, and a_3 tungstens has a P–O bond (phosphate apex) pointing toward the four central Co, Cu, or Zn MO_6 octahedra. For 0.01 M $[P_2W_{15}Zn_2(H_2O)O_{56}]_2^{16-}$ in D_2O, the ^{31}P NMR showed only two peaks, δ(upfield of 85% H_3PO_4) = −4.31 and −14.30, similar to the $\delta = -4.5 \pm 0.1$ resonance for $[PW_9M_2(H_2O)O_{34}]_2^{10-}$ (M = Zn) with its crystallographically determined[1b] (M = Co) C_{2h} symmetry, B-type structure and to the $\delta = -12.7$ peak observed[9] for α-$P_2W_{18}O_{62}^{6-}$. The data allow assignment of the $\delta = -4.31$ resonance to the phosphorus atom surrounded by tungstens a_1, a_2, and a_3 and connected to the central ZnO_6 octahedra and the −14.30 resonance to the other phosphorus surrounded by tungstens b_1, b_2, b_3, c_1, and c_2.

All of the above results as well as the literature data and additional ^{31}P and ^{183}W NMR studies cited below require that the complexes previously thought[3b] to be "$P_2W_{16}M_2(H_2O)_2O_{60}^{10-}$" on the basis of elemental analysis, a $M = Co^{2+}$ titration, and ^{31}P NMR data are incorrect and should be reformulated as $[P_2W_{15}M_2(H_2O)O_{56}]_2^{16-}$ described herein. First and foremost our molecular weight measurements (M_r(obsd) = 7652) rule out a "$P_2W_{16}M_2(H_2O)_2O_{60}^{10-}$" ($M_r$(calcd) = 4445) formulation although it is noteworthy that a publishable ±0.4% P, W, M analysis cannot easily distinguish between the two formulations.[12] Second, the literature λ_{max} = 570 nm[3b] for $M = Co^{2+}$ and the ^{31}P $\delta = -4.4$ and −14.05 ($M = Zn^{2+}$)[9] reported for "$P_2W_{16}M_2(H_2O)_2O_{60}^{10-}$" are identical within experimental error with the λ_{max} = 570 nm ($M = Co^{2+}$) and $\delta = -4.3$, −14.3 ($M = Zn^{2+}$) values for $P_4W_{30}M_4(H_2O)_2O_{112}^{16-}$. Finally, a sample of "$P_2W_{16}Zn_2(H_2O)_2O_{60}^{10-}$" was prepared in acetate buffer[3d] exactly as described in the literature and examined both in the "crude" solution and after the crystallization step by ^{31}P and ^{183}W NMR, respectively. Exactly *and only* the resonances described above for $P_4W_{30}Zn_4(H_2O)_2O_{112}^{16-}$ were observed, ruling out rapid solution degradations such as $2P_2W_{16}Zn_2(H_2O)_2O_{60}^{10-} \rightarrow P_4W_{30}Zn_4(H_2O)_2O_{112}^{16-} + 2WO_4^{2-}$ (not observed) + $2H_2O$. Clearly there is no evidence for "$P_2W_{16}M_2(H_2O)_2O_{60}^{10-}$" complexes where M = divalent cations although we note that with higher valent M = V(V),[13a] Mo(VI),[3c] or PhSn(IV)[13b] $P_2W_{16}M_2O_{62}^{n-}$ and $(PhSn)_2[P_2W_{16}O_{60}]^{8-}$, respectively, have been described.

In summary, the second member of a class of massive, disubstituted, B-type trivacant heteropolytungstates has been described, $P_4W_{30}M_4(H_2O)_2O_{112}^{16-}$, correcting the earlier report of these complexes as "$P_2W_{16}M_2(H_2O)_2O_{60}^{10-}$" and emphasizing the importance of the direct structural techniques, ^{31}P and ^{183}W NMR, in heteropolytungstate chemistry. Pope's preparation[13a] of B-$P_2W_{15}O_{56}^{12-}$ *trisubstituted* with the higher valent V^{5+}, B-$P_2W_{15}V_3O_{62}^{n-}$ (n = 9, 10), suggests that both the lower valent cations, M^{2+} = Co, Cu, Zn, and the B-type $P_2W_{15}O_{56}^{12-}$ are required to form the B-$P_4W_{30}M_4(H_2O)_2O_{112}^{16-}$ derivatives reported herein. Another significant conclusion is that the "P_2W_{18}" series and "PW_{12}" series ($P_2W_{18}O_{62}^{6-}$, $P_2W_{17}O_{61}^{10-}$, $P_2W_{16}O_{59}^{12-}$, $P_2W_{15}O_{56}^{12-}$ and $PW_{12}O_{40}^{3-}$, $PW_{11}O_{39}^{7-}$, $PW_{10}O_{37}^{9-}$, $PW_9O_{34}^{9-}$) now show a more common chemistry in that only $P_2W_{16}O_{59}^{12-}$ and[14] $PW_{10}O_{37}^{9-}$ are not well-known and do not readily form isolable, M^{2+}-substituted derivatives. It is likely that additional members of this new class of heteropolytungstates will be discovered.[15]

Acknowledgment. Financial support was provided by NSF Grant CHE-8018199. The NT-360 NMR was purchased with funds provided by grants from the NSF Instrumentation Division and the M. J. Murdock Charitable Trust. R.G.F. is a Dreyfus Teacher-Scholar (1982–1987) and an Alfred P. Sloan Foundation Fellow (1982–1984).

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(11) (a) There are four possible α or β type[2b] structural isomers in $P_4W_{30}M_4(H_2O)_2O_{112}^{16-}$ for a total of $2^4 = 16$ possible isomers. Only four of these, $\alpha\beta\beta\alpha$, $\beta\beta\beta\beta$, $\alpha\alpha\alpha\alpha$, and $\beta\alpha\alpha\beta$, have the C_{2h} symmetry required by the ^{183}W NMR data, however. This α,β type of isomerism and why only the $\alpha\beta\beta\alpha$ isomer (Figure 1) is fully consistent with the ^{31}P and ^{183}W NMR data are discussed next. The isomer shown in Figure 1a can be labeled $\alpha\beta\beta\alpha$. Rotation by $\pi/3$ of both the top and bottom W_3 triads composed of WO_6 octahedra c_1, c_1, and c_2 gives the $\beta\beta\beta\beta$ C_{2h} symmetry isomer. In this isomer, the top point in Figure 1A of the WO_6 octahedra labeled c_2 is shifted from the α form, where it is between two corner-sharing WO_6 groups, b_2 and b_1 (Figure 1A), to between the edge-sharing WO_6 groups, b_2 and b_3, i.e. the β form. Another previously unrecognized type of rotational and therefore $\alpha \rightleftharpoons \beta$ type of isomerism occurs if both the P_2W_{15} units shown in Figure 1A are rotated by $\pi/6$ about their individual axes (composed of a line drawn through each of the two PO_4 tetrahedra) to give a possible, but as yet unprecedented,[11c] C_{2h} symmetry isomer $\alpha\alpha\alpha\alpha$. The fourth possible C_{2h} symmetry isomer is $\beta\alpha\alpha\beta$, and the other 12, lower symmetry isomers, that would be expected to show 16 ^{183}W NMR resonances, are $\alpha\beta\alpha\beta$, $\beta\alpha\beta\alpha$, $\beta\alpha\alpha\alpha$, $\alpha\beta\alpha\alpha$, $\alpha\alpha\beta\alpha$, $\alpha\alpha\alpha\beta$, $\alpha\alpha\beta\beta$, $\beta\beta\alpha\alpha$, $\alpha\beta\beta\beta$, $\beta\alpha\beta\beta$, $\beta\beta\alpha\beta$ and $\beta\beta\beta\alpha$. The probable α form[3] of the $P_2W_{15}O_{56}^{12-}$ starting material and the fact that the one ^{31}P NMR signal of $P_4W_{30}Zn_4(H_2O)_2O_{112}^{16-}$ ($\delta = -14.3$) is closer to that for α-$P_2W_{18}O_{62}^{6-}$ ($\delta = -12.7$)[9] than to that for β-$P_2W_{18}O_{62}^{6-}$ ($\delta = -11$ to -11.6)[9] suggests, but does not prove, that our product is either the $\alpha\beta\beta\alpha$ or $\alpha\alpha\alpha\alpha$ isomer (given that the ^{183}W NMR spectrum requires a C_{2h} symmetry isomer). The fact that the other, $\delta = -4.31$, ^{31}P NMR signal is very close to that for $[PW_9Zn_2(H_2O)O_{34}]_2^{10-}$ ($\delta = -4.23$), with its crystallographically determined[1b] β form[11b] of attachment of the trivacant $PW_9O_{34}^{9-}$ to the four central M = Co, Cu, or Zn MO_6, is most consistent with a $\alpha\beta\beta\alpha$ formulation for $P_4W_{30}M_4(H_2O)_2O_{112}^{16-}$ as shown in Figure 1A. (b) To avoid confusion, it should be noted β form of *attachment* of the P_2W_{15} or PW_9 to the four central MO_6 octahedra is different from the W_3 triad *rotational* α,β isomerization known for $PW_9O_{34}^{9-}$ that leads to the β-$PW_9O_{34}^{9-}$ label and the α,β isomerization referred to[1a] in the synthesis of $[B\text{-}\alpha\text{-}PW_9Zn_2(H_2O)O_{34}]_2^{10-}$ from B-β-$PW_9O_{34}^{9-}$. A different type of nomenclature to better distinguish these two α,β types of rotational isomerism may be required in the future. (c) The α form of attachment of the P_2W_{15} to the four central MO_6 octahedra is also less likely to the extent that there are severe steric interactions with the bound H_2O and the bridging oxygen between tungstens a_3 and a_2 (although Figure 1A overemphasizes this steric interaction). We thank Professor Walter Klemperer for bringing this point to our attention.

(12) Anal. Calcd for $Na_{10}P_2W_{16}Zn_2(H_2O)_2O_{60}$: P, 1.42; W, 67.47; Zn, 3.00. Calcd for $Na_{16}[P_2W_{15}Zn_2(H_2O)O_{56}]_2$: P, 1.53; W, 68.12; Zn, 3.23. The more sensitive Na analysis (5.27% vs. 4.54%, respectively (found 4.13%)) apparently[3b] was not previously done.

(13) (a) Harmalker, S. P.; Pope, M. T. *J. Am. Chem. Soc.* **1981**, *103*, 7381. (b) Knoth, W. H. *Ibid.* **1979**, *101*, 759.

(14) Knoth, W. H.; Harlow, R. L. *J. Am. Chem. Soc.* **1981**, *103*, 1865.

(15) Possibilities include $[H_x(PW_9O_{34}M_4)_2P_2W_{12}O_{50}]^{x-20}$, $[H_x(P_2W_{15}O_{56}M_4)_2P_2W_{12}O_{50}]^{x-26}$, or a highly charged, probably insoluble oligomer $[-M_2P_2W_{12}O_{50}M_2-]_n^{10-}$.

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