Table I. Thermochemical Data Relating to α-Aminoalkyl Radicals (±2 kcal mol⁻¹)

| radical | $\Delta H_f(R_2\cdot)$, kcal mol⁻¹ | $D(R_2-H)$,[a] kcal mol⁻¹ | $E_s(R_2\cdot)$,[b] kcal mol⁻¹ | $IP(R_2\cdot)$, eV |
|---|---|---|---|---|
| $Me_2N\dot{C}H_2$ | 26 | 84 | 20 | 5.7[c] |
| $MeNH\dot{C}H_2$ | 30 | 87 | 17 | 5.9[c] |
| $H_2N\dot{C}H_2$ | 36, 37[d] | 94 | 10 | 6.2[c] |
| $C_6H_5\dot{C}H_2$ | 48[e] | 87 | 16 | 7.2[f] |
| $CH_2CH\dot{C}H_2$ | 39[e] | 86 | 18 | 8.1[f] |
| $CH_3O\dot{C}H_2$ | −3[g] | 93[g] | 11[g] | 6.9[i] |
| $HO\dot{C}H_2$ | −6[j] | 96[h] | 8 | 7.6[k] |

[a] $D(R_1-H) = \Delta H_f(R_2\cdot) + \Delta H_f(H) - \Delta H_f(R_2H)$. [b] See ref 2. [c] $IP(R_2\cdot) = \Delta H_f(R_2^+) - \Delta H_f(R_2\cdot)$. [d] From ref 7. [e] From ref 3 and 4. [f] From: Houle, R. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* 1978, *100*, 3290-3294. Lossing, F. P. *Can. J. Chem.* 1971, *49*, 357-362. [g] From ref 5. [h] From ref 6. [i] Lossing, F. P. *J. Am. Chem. Soc.* 1977, *99*, 7526-7530. [j] Golden, D. M.; Benson, S. W. *Chem. Rev.* 1969, *69*, 125-134. [k] From $\Delta H_f(HOCH_2^+) = 169$ kcal mol⁻¹ (ref i).

ergy-resolved electron beam from an electrostatic electron monochromator, combined with a quadrupole mass spectrometer.[10] The appearance energies for these reactions will, in the limit, correspond to the general relationship

$$AE(R_1^+) = \Delta H_f(R_1^+) + \Delta H_f(R_2\cdot) - \Delta H_f(R_1-R_2) \qquad (4)$$

The heat of formation of $(H_2NCH_2^+)$ is well established at 178 kcal mol⁻¹;[11] $\Delta H_f(Me_2NCH_2^+)$ and $\Delta H_f(MeNHCH_2^+)$ were found to be 158 ± 2 and 166 ± 2 kcal mol⁻¹, respectively,[12] from the AE of reactions analogous to the above in which the neutral fragments were H, $\dot{C}H_3$, and $\dot{C}H_2OH$, whose $\Delta H_f$ are known. The resulting thermochemical quantities for $R_2\cdot$ are given in Table I, along with comparable data for $C_6H_5\dot{C}H_2$, $CH_2CH\dot{C}H_2$, $CH_3O\dot{C}H_2$, and $HO\dot{C}H_2$. Heat of formation data for the parent R–H compounds were taken from Cox and Pilcher;[13] those for $R_1-R_2$, were calculated by group equivalents.[14]

It is immediately obvious that α-aminoalkyls have remarkably large stabilization energies which *increase* dramatically with N alkylation. This property must underlie many of the chemical and physical[15] properties of α-aminoalkyls. It is presumably the driving force for reactions such as the Stevens rearrangement[19] which proceeds by a radical-pair mechanism. Moreover, it explains why amines[20] are as reactive as highly conjugated hydrocarbons[21] in H abstractions with *tert*-butoxyl and *tert*-butylperoxyl. These reactions show a stereoelectronic effect[20] which must be a consequence of the conjugative delocalization. That is, H abstraction is most rapid when the C–H bond being broken is aligned with the principal axis of the nitrogen lone pair orbital. We note also that $k_5$ follows the order tertiary > secondary > primary amine as do the stabilization energies.

$$t\text{-BuO}\cdot + \;>CH-N< \;\rightarrow t\text{-BuOH} + \;>\dot{C}-N< \qquad (5)$$

α-Aminoalkyls have low ionization potentials which *decrease* with increasing N alkylation. The observed values are lower than those for the parent amines. In fact, the ionization potential for $Me_2N\dot{C}H_2$ is the lowest thus far reported for any organic species.[11,22] These results correlate with the observation that α-aminoalkyls are powerful one-electron reducing agents.[17,23]

The delocalization which forms the basis of these osbervations can be described in terms of the theory of the "three-electron bond".[24] This predicts that two of the three electrons formally designated by $>\ddot{N}-\dot{C}<$ will be in a bonding orbital, with the third in an energetically close antibonding orbital. Excitation between the levels should therefore occur at fairly low energies. This is indeed the case; α-aminoalkyls have absorption spectra which "tail" from the UV to the visible region (e.g., for $Me_2N\dot{C}H_2$, ϵ 510 ± 100 M⁻¹ cm⁻¹ cm⁻¹ at 340 nm.[25] These absorptions are considerably red shifted with respect to those of alkyls (e.g., for $Me_2\dot{C}H$, ϵ 1000 ± 50 *M*⁻¹ s⁻¹ at 220 nm).[26]

We conclude that the thermochemical parameters measured in this work form a basis for understanding the chemical and physical properties of α-aminoalkyls and that these can be modified in predictable ways by changing the extent of N (and C)[22] alkylation.

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[10] Holmes, J. L.; Lossing, F. P. *J. Am. Chem.* Soc. **1980**, *102*, 1591-1595.

[11] Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data, Suppl.* **1977**, *6*, 1-783.

[12] Lossing. F. P.; Maccoll, A., in preparation.

[13] Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: New York, 1970.

[14] Benson, S. W.; Cruickshank, F. R.; Golden, D. M.; Haugen, G. R.; O'Neal, H. E.; Rodgers, A. S.; Shaw, R.; Walsh, R. *Chem. Rev.* **1969**, *69*, 279-324.

[15] For example, it is reflected in the EPR parameters of α-aminoalkyls[16,17] which, by comparison with those of alkyls, benzyl, allyl, and α-alkoxyalkyls,[18] show that the unpaired electron is extensively delocalized.

[16] Wood, D. E.; Lloyd R. V. *J. Chem. Phys.* **1970**, *52*, 3840-3841; **1970**, **53**, 3932-3942. Neta, P.; Fessenden, R. W. *J. Phys. Chem.* **1971**, *75*, 738-748. Lyons, A. R.; Symons, M. C. R. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 502-508. See also: Kaba, R. A.; Griller, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1974**, *96*, 6202-6203.

[17] Norman, R. O. C.; Anderson, N. H. *J. Chem. Soc. B* **1971**, 993-1003.

[18] "Landolt-Börnstein, Group II"; Fischer, H., Hellwege, K.-H., Eds.; Springer-Verlag: New York, 1977; Vol. 9, Part b.

[19] See: Lepley, A. R. *J. Am. Chem. Soc.* **1969**, *91*, 1237-1239.

[20] Griller, D.; Howard, J. A.; Marriott, P.; Scaiano, J. C. *J. Am. Chem. Soc.*, in press.

[21] Effio, A.; Griller, D.; Ingold, K. U.; Scaiano, J. C.; Sheng, S. J. *J. Am. Chem. Soc.* **1980**, *102*, 6063-6068. See also: Small, R. D., Jr.; Scaiano, J. C.; Patterson, L. K. *Photochem. Photobiol.* **1979**, *29*, 49-56.

[22] Experiments are in progress to see if C alkylation increases the stabilization energies and reduces the ionization potentials of α-aminoalkyls.

[23] See for example: DeLaive, P. J.; Lee, J. T.; Sprintschnik, H. W.; Abruna, H.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* **1977**, *99*, 7094-7097. Chandrasekaran, K.; Whitten, D. G. *J. Am. Chem. Soc.* **1980**, *102*, 5119-5122.

[24] See, for example: Pauling, L. *J. Am. Chem. Soc.* **1931**, *53*, 3225-3237. Hudson, R. F. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 36-56. Baird, N. C. *J. Chem. Educ.* **1977**, *54*, 291-293. Harcourt, R. D. *Aust. J. Chem.* **1978**, *31*, 199-201. Gregory, A. R.; Malatesta, V. *J. Org. Chem.* **1980**, *45*, 122-125. Harcourt, R. D. *J. Am. Chem. Soc.* **1980**, *102*, 5195-5201.

[25] Griller, D.; Marriott, P. R., unpublished results. The spectra were recorded on a modulation spectrometer, the design for which was generously provided by Professor H. Fischer and Dr. C. Huggenberger.[26]

[26] Huggenberger, C.; Fischer, H. *Helv. Chim. Acta*, in press, and references cited therein. See also: Parkes, D. A. Quinn, C. P. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 1952-1971.

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# Trivacant Heteropolytungstate Derivatives: The Rational Synthesis, Characterization, and $^{183}W$ NMR Spectra of $P_2W_{18}M_4(H_2O)_2O_{68}^{10-}$ (M = Co, Cu, Zn)

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*Received August 18, 1980*

In addition to the fundamental interest in heteropolytungstates,[1] the preparation of hybrid organometallic–heteropolytungstate derivatives has attracted recent attention.[2] An interesting feature of heteropolytungstates and related iso- and heteropolymetalates is the triangular array of tungsten bridging oxygens present on their surfaces, oxygens which resemble discrete fragments of heterogeneous metal oxide surfaces.[3] We feel that these oxygens,

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[1] For reviews of heteropolytungstates, see: (a) Weakley, T. J. R. *Struct. Bonding* **1974**, *18*, 131. (b) Tsigdinos, G. *Top. Curr. Chem.* **1978**, *76*, 1. (c) Evans, H. T., Jr. *Perspect. Struct. Chem.* **1971**, *4*, 1.

[2] (a) Ho, R. K. C.; Klemperer, W. G. *J. Am. Chem. Soc.* **1978**, *100*, 6772. (b) Knoth, W. H. *Ibid.* **1979**, *101*, 759. (c) Zonnevijlle, F.; Pope, M. T. *Ibid.* **1979**, *101*, 2731.

0002-7863/81/1503-1587\$01.25/0

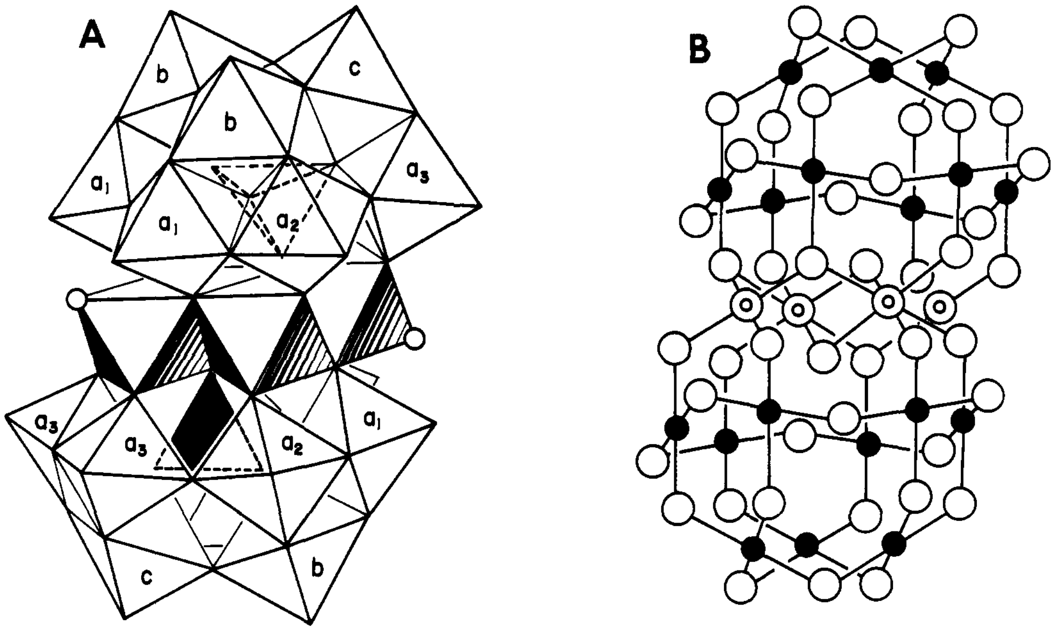

**Figure 1.** (a) Coordination polyhedra representation of the crystallographically determined[7a] $C_{2h}$ symmetry structure for $P_2W_{18}Co_4(H_2O)_2O_{68}^{10-}$. The cobalt atoms occupy the four central edge-linked polyhedra, and the circles show the positions of water molecules. The five types of W atoms are labeled $a_1$, $a_2$, $a_3$, b, and c. The two internal $PO_4^{3-}$ tetrahedra are shown with dashed lines. (b) Framework bond model of the $C_{2h}$ symmetry isomer of $P_2W_{18}Co_4(H_2O)_2O_{68}^{10-}$ also shown in (a). Open circles are bridging oxygens, filled circles are tungsten atoms, and the four central cobalt atoms are indicated by the circle within a circle. Terminal oxygens bound to tungsten and the two internal $PO_4^{3-}$ groups have been omitted for clarity. A triangular array of tungsten bridging oxygens can be clearly seen, for example, on the top and bottom of this figure.

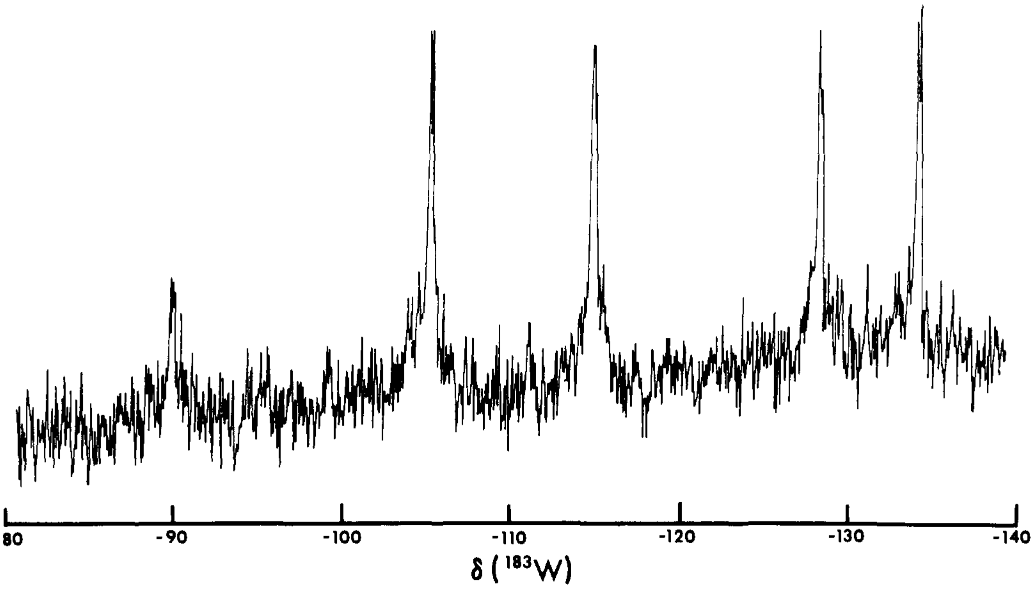

**Figure 2.** The 7.50-MHz $^{183}$W NMR spectrum of $[P_2W_{18}Zn_4(H_2O)_2O_{68}]^{10-}$ as a 0.08 M $D_2O$ solution observed by obtaining about 24000 scans over a period of 33 h. Chemical shift values are presented in the text.

as well as other features, make heteropolytungstates and their organometallic derivatives attractive as discrete models or mimics of metal oxide supported heterogeneous catalysts or, perhaps, as new types of hybrid homogeneous–heterogeneous,[4] metal oxide supported catalysts. Within this context, it is noteworthy that Besecker and Klemperer[5] have very recently succeeded in bonding a $M(CO)_3$ (M = Mn, Re) unit to a triangle of surface oxygens of $Nb_2W_4O_{19}^{4-}$.

With the goal of preparing $PW_9(ZnO)_3O_{34}^{9-}$, which should contain a $Zn_3O_3$ zinc oxide "mini surface" closely resembling a fragment of the "polar" (000$\bar{1}$) surface[6] of ZnO, we have examined the reaction of the trivacant heteropolytungstate $PW_9O_{34}^{9-}$ with $Zn^{2+}$ and other $M^{2+}$ ions. [$PW_9O_{34}^{9-}$ is $PW_{12}O_{40}^{3-}$ less a "$W_3O_6^{6+}$" unit, hence tri(tungsten)vacant].

Herein we report results demonstrating that the reaction of the *tri*vacant β-$PW_9O_{34}^{9-}$ with the inorganic $M^{2+}$ ions $Co^{2+}$, $Cu^{2+}$, $Zn^{2+}$ unexpectedly, yet exclusively, yields the *di*-substituted dimers $[K_5PW_9M_2(H_2O)O_{34}\cdot 10H_2O]_2$, as well as full characterization including $^{183}$W NMR of these complexes. There is only a single previous report[7a] of these "$P_2W_{18}M_4$" complexes in which they

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(3) Baker mentioned this feature in 1961: Baker, L. C. W., In "Advances in the Chemistry of the Coordination Compounds"; Kirschner, S., Ed.; MacMillan: New York, 1961; p 604. See also Pope, M. T.; Dale, B. W., *Q. Rev., Chem. Soc.* **1968**, *22*, 527.

(4) With $K^+$ and similar cations, heteropolytungstates are insoluble in organic solvents, while with $Bu_4N^+$ and related counterions, they are soluble in solvents like $CH_3CN$.

(5) Besecker, C. J.; Klemperer, W. G. *J. Am. Chem. Soc.* **1980**, *102*, 7598. We are grateful to Professor Klemperer for a preprint of this important work.

(6) 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.

were initially prepared in low yield either by the slow reaction of $PCo(H_2O)W_{11}O_{39}^{5-}$ with $Co^{2+}$ at pH 7–7.5 or by the prolonged, 100 °C reaction of a $H^+$–$HPO_4^{2-}$–$M^{2+}$–$WO_4^{2-}$ mixture of composition 11:2:4:18 to yield an unreported amount of $K_{10}P_2W_{18}M_4(H_2O)_2O_{68}$·$2OH_2O$ and byproducts.[7b] Routes toward the synthesis of $XW_9(ZnO)_3O_{34}^{n-}$ (X = P, *n* = 9; X = Si, *n* = 10) are being actively investigated and will be reported subsequently.[8]

The trivacant heteropolytungstate $\beta$-$PW_9O_{34}^{9-}$ has been previously described,[9a] although its structural characterization as the B-type $\beta$-$PW_9O_{34}^{9-}$ isomer[9b] relied solely upon indirect methods. This trivacant heteropolytungstate is known[9c] to exist in solution in fast, pH-dependent equilibria with $PW_{11}O_{39}^{7-}$ and other species. We discovered an unexpected $M^{2+}$ substitution pattern of $\beta$-$PW_9O_{34}^{9-}$ during its titration with $Co^{2+}$. The sequential addition of 0.5 equiv of solid $Co(NO_3)_2$·$6H_2O$ to 0.5 g (0.17 mmol) of $\beta$-$Na_8HPW_9O_{34}$·$24H_2O$ in 20 mL of unbuffered $H_2O$ showed a linear absorption increase at 570 nm, with a sharp break point and no further adsorbance change at 2.0 rather than the anticipated 3.0 equiv of $Co(NO_3)_2$ to each equiv of $\beta$-$PW_9O_{34}^{9-}$. A similar 2:1 titration is also obtained if the reverse order of addition, $PW_9O_{34}^{9-}$ to a solution of $Co(NO_3)_2$, is used, but a sharp 2:1 break point is not obtained in pH 4.5 OAc–/HOAc buffer. Solid samples of the compounds with $2M^{2+}$:$1PW_9O_{34}^{9-}$ stoichiometry were isolated in 71–79% yield as their $K^+$ salts for $M^{2+} = Co^{2+}$, $Cu^{2+}$, and $Zn^{2+}$ by the procedure detailed in the footnote.[10] Each of the Co, Cu, and Zn complexes analyzed, after recrystallization from hot $H_2O$ and 80 °C drying at <0.1 mmHg, to ±0.25% for K, P, W, and Co, Cu, or Zn for the formula $(K_5[P_1W_9M_2O_{34}$·$11H_2O])_n$.

It seemed likely that the $K_5PW_9M_2O_{34}$ had dimerized to become "saturated", yielding the crystallographically characterized, $C_{2h}$ symmetry, heteropolytungstate $K_{10}P_2W_{18}M_4(H_2O)_2O_{68}$·$20H_2O$ shown in Figure 1. X-ray powder patterns have been obtained of crystalline $P_2W_{18}Co_4$ prepared by the previously reported method[7a,b] and crystalline $P_2W_{18}Co_4$ ($\lambda_{max}$ 570 nm) and $P_2W_{18}Zn_4$ prepared by the method reported herein. The peak-for-peak similarity of the patterns strongly suggests that the $P_2W_{18}M_4$ samples from the two synthetic methods are isostructural in the solid state.

Using $^{183}W$ NMR,[11] we have established that the solid-state $C_{2h}$ symmetry structure persists[12] in solution in spite of the possibility of isomerization. The $^{183}W$ NMR of $P_2W_{18}Zn_4(H_2O)_2O_{68}^{10-}$ was obtained on a Bruker WH-180 spectrometer operating at a nominal 7.5 MHz and is the first $^{183}W$ NMR data on compounds of this structural type. When a mixture of 5.0 g of recrystallized $K_{10}P_2W_{18}Zn_4(H_2O)_2O_{68}$ in 11 mL of $D_2O$ (0.084 M) is used (solubilized by 10 equiv of $LiClO_4$ and filtered to remove the $KClO_4$ precipitate), five peaks with chemical shifts of −90.3, −105.4, −115.0, −128.4, and −134.2 ppm (relative[11c] to 2 M $Na_2WO_4$ in $D_2O$) and relative intensities of 1:2:2:2:2, respectively, were observed (Figure 2). Only the −105.4 and −134.2 peaks are resolved into well-defined doublets with $J$ ($^{31}P$–$^{183}W$) = 1.1 and 1.6 Hz, respectively. The five different resonances and their relative intensities are consistent only with[12] the $C_{2h}$ symmetry structure. In this structure each equivalent $PW_9O_{34}$ moiety above and below the plane of Zn atoms exhibits five nonequivalent W environments, $a_1$, $a_2$, $a_3$, b, and c (Figure 1a), with relative populations of 2:2:2:2:1. The −90.3-ppm tungsten resonance of relative intensity 1 can be assigned to the W atom labeled c. The $^{183}W$ NMR establishes that our $P_2W_{18}M_4(H_2O)_2O_{68}^{10-}$ contains the $PW_9$ isomer labeled[9b] B-type $\alpha$-$PW_9O_{34}^{9-}$. Our synthesis must include a W framework rearrangement of B-$\beta$-$PW_9$ to B-$\alpha$-$PW_9$, assuming, as is likely, that the literature assignment[9] of the structure of the $PW_9$ starting material as B-$\beta$-$PW_9$ is correct. Since an examination of models suggests that only B-type $PW_9M_2$ units can dimerize,[13] we conclude that the observed $2M^{2+}$:$1PW_9$ stoichiometry is primarily due to the B-type isomer structure of the $\beta$-$PW_9O_{34}^{9-}$ starting material. This conclusion is fortified by recent work[14] showing that A-type $\alpha$-$SiW_9O_{34}^{10-}$ can be trisubstituted to yield $\alpha$-$SiW_9M_3O_{40}^{n-}$ derivatives.

An important implication of these results is that $P_2W_{18}M_4(H_2O)_2O_{68}^{10-}$ is *not* unique but rather is just a single member of a previously unrecognized class of massive, disubstituted, trivacant heteropolytungstates. Possible members of this new class include $[(B\text{-}\alpha\text{-}PW_9O_{34}M_2)_2P_2W_{12}O_{50}]^{28-}$ or $-(M_2P_2W_{12}O_{50}M_2)_n{-}^{10n-}$ where $P_2W_{12}O_{50}^{18-}$ has two trivacant B-type structures at its opposite ends.[7b]

**Acknowledgment.** Financial support at Oregon was provided by National Science Foundation grant CHE78-11552 and a grant from Chevron Research. Support at Michigan State was provided by National Science Foundation Grant CHE28-10241. J.R.H. was on sabbatical leave for the 1979–1980 academic year from the Chemistry Department of Alma College, Alma, MI, and acknowledges the partial financial support of that institution.

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(7) (a) Weakley, T. J.; Evans, H. T., Junior; Showell, J. S.; Tourné, G. F.; Tourné, C. M. *J. Chem. Soc., Chem. Commun.* **1973**, 139. The formation of $P_2W_{18}Co_4$ from $PW_9O_{34}^{9-}$ and $Co^{2+}$ is mentioned, in a one line statement, in: Tourné, C.; Revel, A.; Tourné, G.; Vendrell, M. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1973**, *277*, 643. (b) In our hands, the 100 °C overnight reaction of a 11:2:4:18 mixture of HCl–$Na_2HPO_4$–$Co(NO_3)_2$–$Na_2WO_4$ on a 10-g scale of $Na_2WO_4$ in 50 mL of $H_2O$ gave, upon cooling, 1.3 g of a $H_2O$ insoluble, blue byproduct. KCl addition to the filtrate gave 3.1 g (29%) of $K_{10}P_2W_{18}Co_4(H_2O)_2O_{68}$·$20H_2O$, $\lambda_{max}$ ($H_2O$) 570, 510 (sh), 495 (sh) nm.

(8) Finke, R. G.; Droege, M.; Rapko, B., unpublished results.

(9) (a) $\beta$-$Na_8HPW_9O_{34}$·$24H_2O$ was prepared by the procedure of: Massart, R.; Contant, R.; Fruchart, J. M.; Ciabrini, J. P.; Fournier, M. *Inorg. Chem.* **1977**, *16*, 2916. (b) The four $PW_9O_{34}^{9-}$ isomers A-$\alpha$, A-$\beta$, B-$\alpha$, and B-$\beta$ are discussed in ref 9a. (c) Other references to $XM_9$ species and their pH-dependent solution equilibria and chemistry are: Contant, R.; Fruchart, J. M.; Hervé, G.; Tézé, A. *C. R. Hebd. Acad. Sci., Seances Ser. C.* **1974**, *278*, 199. Fournier, M.; Massart, R. *Ibid.* **1974**, *279*, 875. Tézé, A.; Hérve, G. *J. Inorg. Nucl. Chem.* **1977**, *39*, 999. Strandberg, R. *Acta Chem. Scand., Ser. A.* **1974**, *A28*, 217.

(10) (a) The following reactions were performed with $\beta$-$Na_8HPW_9O_{34}$·$24H_2O$ prepared on one-quarter the literature[9a] scale, washed with ca. 5 mL of unbuffered $H_2O$, and dried in a 140 °C oven for 1–2 h. In 15.0 mL of distilled, unbuffered $H_2O$, 2.0 g (0.70 mmol) of $\beta$-$Na_8HPW_9O_{34}$·$24H_2O$ and 0.236 g (1.40 mmol) of $CuCl_2$·$2H_2O$ were mixed and brought to a homogeneous lime green solution by a *minimum* of gentle steam bath warming, 10–20 min of stirring, and if necessary, warm filtration. The addition of excess KCl (4–6 g) gave an immediate green precipitate which, after 10 min of stirring and subsequent cooling, was washed with $H_2O$ and dried at 80 °C to yield 1.53 g (79%) of a green powder [$\lambda_{max}$ ($H_2O$) 800 nm]. Similar procedures using $ZnCl_2$ and $Co(NO_3)_2$ yielded, respectively, 1.47 g (77%) of a white powder and 1.37 g (71%) of a blue-purple powder [$\lambda_{max}$ ($H_2O$) 570, 510 (sh), 495 (sh) nm] from a reddish solution in the Co case. Analytically pure samples were obtained by recrystallization from hot, unbuffered $H_2O$. The recrystallized Zn derivative, $P_2W_{18}Zn_4$, showed a $^{31}P$ NMR signal at 4.8 ± 0.1 ppm upfield of a $H_3PO_4$ standard on a Varian XL-100 NMR. The reddish filtrate in the Co case has a visible spectrum identical with that of $PW_{11}CoO_{39}^{5-}$ [lit.[10b] $\lambda_{max}$ ($H_2O$) 541, 526, 505 (sh) nm], and deep red crystals characteristic of $PW_{11}CoO_{39}^{5-}$ have been obtained from slow crystallization of the filtrate. The use of a low heat (60 °C or air) dried $Na_8HPW_9O_{34}$ in the above procedure gives an initial Co(II) derivative with a visible spectrum different than that of the desired $P_2W_{18}Co_4$. (b) Komura, A.; Hayashi, M.; Imanaga, H. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 87.

(11) (a) Acerete, R.; Hammer, C. F.; Baker, L. C. W. *J. Am. Chem. Soc.* **1979**, *101*, 267. (b) Acerete, R.; Harmalker, S.; Hammer, C. F.; Pope, M. T.; Baker, L. C. W. *J. Chem. Soc., Chem. Commun.* **1979**, 777. (c) Gansow, O. A.; Ho, R. K. C.; Klemperer, W. G. *J. Organomet. Chem.* **1980**, *187*, C27.

(12) Rotation of a $PW_9$ group by $\pi/6$ gives a lower symmetry tungstate that should show a 2:2:2:2:1 set of W resonances for one $PW_9$ half and a different set of 2:2:2:2:1 resonances for the other $PW_9$ half. $\beta$-$PW_9$ in which a $W_3$ triad has been rotated $\pi/3$ removes either the $C_2$ axis or the horizontal plane of symmetry depending, respectively, upon whether the $W_3$ unit rotated is or is not bisected by the horizontal plane. The former case has, for example, 10 chemical shift inequivalent W atoms with relative intensities 1:2:2:2:2:2:2:2:2:1. If the $K_{10}P_2W_{18}M_4O_{68}$ dimer dissociated in solution, the resultant $K_5PW_9M_2O_{34}$ monomer could also explain the $^{183}W$ NMR. Solution molecular weight measurements are planned to unambiguously address this point.

(13) An examination of models suggests that each of the four $PW_9O_{34}^{9-}$ isomers A-$\alpha$, A-$\beta$, B-$\alpha$, B-$\beta$ could form trisubstituted $PW_9M_3$ derivatives except, possibly, for the high overall negative charge in, for example, unprotonated "[(B-type $\alpha$-$PW_9O_{34}$)($Co(H_2O)O)_3]^{9-}$". On the other hand, models suggest that only B-$\alpha$ and B-$\beta$ isomers of $PW_9M_2$ should be able to dimerize, thereby accounting for the 2:1 stoichiometry.

(14) Mossoba, M. M.; O'Connor, C. J.; Pope, M. T.; Sinn, E.; Hervé, G.; Tézé, A. *J. Am. Chem. Soc.* **1980**, *102*, 6864. The exact pH is probably another important parameter in controlling di- vs. trisubstitution of $XM_9$ species.