Inorg. Chem. **1986**, *25*, 1577–1584

comments. Also, we thank the Fonds der Chemischen Industrie for financial support.

Registry No. $KV(SO_4)_2$, 14520-79-7; $KHSO_4$, 7646-93-7; V_2O_5, 1314-62-1; V_2O_4, 12036-21-4; SO_2, 7446-09-5.

Supplementary Material Available: A table of observed and calculated structure factors and a table (Table IX) of coordinates of the atoms in the unit cell and temperature factor coefficients for $KV(SO_4)_2$ at −130 °C (3 pages). Ordering information is given on any current masthead page.

Contribution No. 3795 from the Central Research & Development Department,
Experimental Station, E. I. du Pont de Nemours & Company, Wilmington, Delaware 19898

Heteropolyanions of the Types $M_3(W_9PO_{34})_2^{12-}$ and $MM'M''(W_9PO_{34})_2^{12-}$: Novel Coordination of Nitrate and Nitrite

W. H. Knoth,*† P. J. Domaille, and R. L. Harlow

Received August 21, 1985

Reaction of $A\text{-}W_9PO_{34}^{9-}$ with divalent Mn, Fe, Ni, Cu, Zn, and Pd gives anions of the formula $M_3(W_9PO_{34})_2^{12-}$, similar to $Co_3(W_9PO_{34})_2^{12-}$ we previously reported; reaction with Ce(IV) gives $(OCe)_3(W_9PO_{34})_2{\cdot}2H_2O^{12-}$. A crystal structure of the latter clearly shows the geometry of the anion although most of the K^+, H_3O^+, and H_2O species that surround the anion are disordered: $K_9(H_3O)_3[(Ce_3O_3{\cdot}2H_2O)(W_9PO_{34})_2]{\cdot}26(?)H_2O$; $W_{18}Ce_3K_9P_2O_{102}H_{65}$; monoclinic, $C2/m$; at −100 °C, $a = 33.219$ (4) Å, $b = 15.903$ (1) Å, $c = 17.385$ (2) Å, $\beta = 98.41°$, $Z = 4$. Several nitrate and nitrite complexes are also described; the crystal structure of $Cu_3(W_9PO_{34})_2{\cdot}NO_3^{13-}$, which has a nitrate group reversibly coordinated within the central skeletal cavity, is reported: $K_{11}\{[Cu_3(NO_3)](W_9PO_{34})_2\}(H_3O)_2{\cdot}28(?)H_2O$; $W_{18}Cu_3K_{11}P_2O_{101}NH_{62}$; monoclinic, $P2_1/m$; at −100 °C, $a = 12.224$ (3) Å, $b = 33.502$ (8) Å, $c = 12.346$ (4) Å, $\beta = 118.29$ (1)°, $Z = 2$. Other nitrate and nitrite complexes are also described. Further reactions of the $M_3(W_9PO_{34})_2^{12-}$ anions lead to related species with dissimilar belt metals. Examples include $Zn_2(O_2W)(W_9PO_{34})_2^{12-}$, $Cu_2Co(W_9PO_{34})_2{\cdot}NO_3^{13-}$, $NiCu(O_2W)(W_9PO_{34})_2^{12-}$, and $CoFe(O_2W)(W_9PO_{34})_2^{12-}$.

Introduction

We have pursued our earlier discovery[1] that unthermolyzed $Na_8HW_9PO_{34}$[2] has an A-type structure and reacts with cobalt(II) to form $(H_2OCo)_3(A\text{-}W_9PO_{34})_2^{12-}$, whereas thermolyzed (150 °C) $Na_8HW_9PO_{34}$ has a B-type structure and is known[3-5] to react with cobalt(II) to form $(H_2O)_2Co_4(B,\alpha\text{-}W_9PO_{34})_2^{10-}$. This paper reports a number of analogues of $(H_2OCo)_3(A\text{-}W_9PO_{34})_2^{12-}$, including some with two or three dissimilar metals between the W_9P moieties, and some chemistry of these anions, including novel coordination of nitrate and nitrite ions. Crystal structures of two anions are included.

Results and Discussion

A. $(OCe)_3(A,\alpha\text{-}W_9PO_{34})_2^{12-}$. Reaction of ceric ammonium sulfate with $W_9PO_{34}^{9-}$ gives a yellow anion that can be precipitated as a potassium salt. This initial product displays four ^{31}P NMR lines (−6.32, −6.97, −7.64, and −8.33 ppm at pH 4.7) of variable intensities, establishing that it is a mixture. After the mixture is refluxed in water for 1 h, the spectrum changes to that of a single species (^{31}P NMR: one line, −7.57 ppm at pH 5.2). The ^{183}W NMR spectrum of this single species consists of two lines, at −151.9 and −161.1 ppm in a 1:2 ratio. The latter line is very broad but sharpens considerably on lowering the pH to 3.1 (HCl). The sharper line displays tungsten–tungsten coupling ($^2J_{W-O-W} = 14.3$ Hz). These data, together with analysis of several salts, suggest a structure consisting of two A-type $W_9PO_{34}^{9-}$ units connected by a belt of three cerium atoms.

A crystal structure determination on $Ce_3(W_9P)_2$ reveals that it is really $(OCe)_3(W_9PO_{34})_2{\cdot}2H_2O^{12-}$ (Figure 1) in the solid state. The belt contains three oxygen atoms alternating with the three cerium atoms; two of the latter also have external water ligands. The presence of the bridging oxygen atoms in the final product offers an explanation for the ^{31}P NMR observations. The initial product may be a mixture of $[(HO)_2Ce]_3(W_9P)_2$ and its successive condensation products $(HO)_2Ce(HOCe)_2O(W_9P)_2$, $(HOCe)_2O_2Ce(W_9P)_2$, and $(OCe)_3(W_9P)_2$ with complete condensation to the last occurring during the subsequent reflux period.

The crystal structure of $(OCe)_3(W_9P)_2$ confirms not only that it contains $A\text{-}W_9P$ groups but that these are A,α, not A,β. The same is true of a copper complex discussed later. These structures make it quite likely that the starting material, unthermolyzed $Na_8HW_9PO_{34}$, also has an $A,\alpha\text{-}W_9P$ group, not an $A,\beta\text{-}W_9P$ group.

B. Other $M_3(A,\alpha\text{-}W_9PO_{34})_2^{12-}$ Anions. The reactions of $A,\alpha\text{-}W_9PO_{34}^{9-}$ with divalent manganese, iron, cobalt, nickel, copper, zinc, and palladium in water proceed rapidly to give anions of the type $L_nM_3(A,\alpha\text{-}W_9PO_{34})_2^{x-}$. The ligands L may be nitrate or nitrite as discussed later or water as in the case of $(H_2OCo)_3(W_9PO_{34})_2^{12-}$, which we reported previously.[1] We have not established the presence or absence of aquo ligands in the other species described here. Potassium salts of all these anions have quite similar infrared spectra (see Figure 9 in ref 1 for the spectrum of the cobalt complex) from 1200 to 600 cm^{-1} and are presumably isostructural. The skeletal structure postulated earlier[1] for the cobalt complex $Co_3(A\text{-}W_9PO_{34})_2$ is consistent with a crystal structure done on $Cu_3(W_9PO_{34})_2{\cdot}NO_3^{13-}$ (see Figure 2 and discussion later), which provides the additional information that the W_9P groups are α.

Potassium salts of the $Co_3(W_9P)_2$ and $Zn_3(W_9P)_2$ anions are converted to the corresponding $(H_2O)_2M_4(B,\alpha\text{-}W_9P)_2$ salts in boiling water, as shown by elemental and infrared analyses and by the ^{183}W NMR spectrum[5] of the zinc complex. $Cu_3(W_9P)_2$ is changed in boiling water to an anion whose potassium salt analyses for $K_{10}(H_2O)_2Cu_4(W_9PO_{34})_2$. However, the infrared spectrum of this product is grossly different from that of the other $M_4(W_9P)_2$ salts and it cannot have an identical structure. The P–O region exhibits four bands (1137, 1100, 1072, 1043 cm^{-1}) in the P–O region compared to the maximum of three for a nondegenerate PO_4 spectrum and the degenerate or nearly degenerate (20-cm^{-1} splitting at most) P–O bands we observe for the other $M_4(W_9P)_2$ salts. The established $M_4(W_9P)_2$ structure[4] calls for the metal M to assume octahedral coordination; this is difficult for copper(II) because of the Jahn–Teller effect.

The manganese, iron, and nickel $M_3(W_9P)_2$ complexes are also unstable in boiling water; infrared analysis suggests the major

---

† Present address: Box 6, Mendenhall, PA 19357.

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

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

(3) Tourné, C.; Revel, A.; Tourné, G.; Vendrell, M. *C. R. Seances Acad. Sci., Ser. C* **1973**, *277*, 643–645.

(4) Weakley, T. J.; Evans, H. T., Jr.; Showell, J. S.; Tourné, G. F.; Tourné, C. M. *J. Chem. Soc., Chem. Commun.* **1973**, 139.

(5) Finke, R. G.; Droege, M.; Hutchinson, J. R.; Gansow, O. *J. Am. Chem. Soc.* **1981**, *103*, 1587–1589.

0020-1669/86/1325-1577$01.50/0

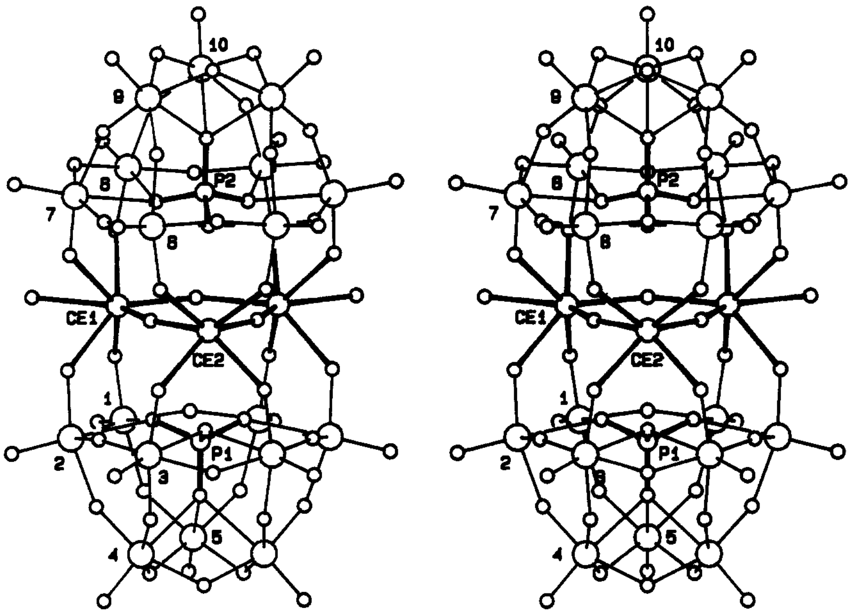

Figure 1. Structure of $(OCe)_3(W_9PO_{34})_2^{12-}$. The radii of the atoms have been arbitrarily assigned according to atom type. The tungsten atoms have been labeled with numbers only. A crystallographic mirror plane passes through Ce(2), P(1), P(2), W(5), and W(10). Ce(1) is seven-coordinate; Ce(2) is six-coordinate.

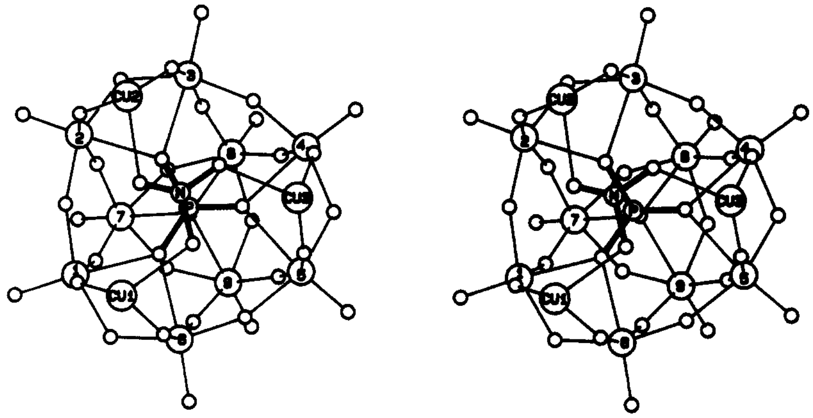

Figure 2. Structure of the asymmetric unit of $Cu_3(W_9PO_{34})_2{\cdot}NO_3^{13-}$. A crystallographic mirror plane passes through the nitrate ion and the three copper atoms. The copper atoms are five-coordinate.

products are the corresponding $M_4(B,\alpha\text{-}W_9P)_2$ anions, but analytically pure salts of these have not been obtained by this method.

Potassium salts of all the $M_3(W_9P)_2$ anions can be recrystallized unchanged at sufficiently low temperature, generally below 60 °C, although the manganese complex is best recrystallized below room temperature.

C. Coordination of Nitrate and Nitrite. Cupric nitrate reacts with $A,\alpha\text{-}W_9PO_{34}^{9-}$ to form a bluish green anion. A potassium salt recrystallized at pH 3 exhibits an infrared band at 1391 cm^{-1}, indicative of nitrate retention. A crystal structure determination (Figure 2) shows that a nitrate anion is complexed *inside* the central cavity of the $Cu_3(A,\alpha\text{-}W_9P)_2$ structure. The nitrate is coplanar with the three copper atoms, which are each in a distorted square-pyramidal environment. The pyramidal apices face inward and are occupied by the nitrate oxygen atoms. The $A,\alpha\text{-}W_9P$ groups are directly over each other; there is no "side-slip" such as that observed in $Cu_3(B\text{-}W_9As)_2$.[6] This "side-slip" was attributed to the repulsive effect of the arsenic(III) lone pairs, which have no counterpart in the present structure.

This coordination of nitrate is readily reversible; the nitrate is lost upon recrystallization of $K_{13}Cu_3(W_9P)_2{\cdot}NO_3$ from neutral water and is regained at lower pH in the presence of nitrate. This complexation of an anion by an anion can be rationalized by postulating that there is little negative charge density in the region of the belt. The negative charge probably remains largely localized on the phosphate groups whereas the belt, consisting of three dipositive metals, probably has localized positive charge.

The crude reaction products of cobalt nitrate and of manganous nitrate with W_9P exhibit nitrate bands in the infrared region, suggesting they are also nitrate complexes. Upon recrystallization, nitrate is completely lost from the cobalt complex but retained by the manganese complex. The nickel complex $Ni_3(W_9P)_2$ shows no tendency to complex with nitrate; the zinc, iron, and palladium complexes given ambiguous results.

Nitrite also forms complexes with $Cu_3(W_9P)_2$ and $Co_3(W_9P)_2$, as shown by elemental analysis and by the inclusion of a sharp nitrite band at 1255 cm^{-1} (Cu) or 1265 cm^{-1} (Co). In the absence of a crystal structure it is reasonable to postulate these nitrite groups are also coordinated inside the central cavity like the nitrate group. The infrared spectra of the potassium salts of $Cu_3(W_9P)_2{\cdot}NO_3$, $Cu_3(W_9P)_2{\cdot}NO_2$, and $Cu_3(W_9P)_2$ are quite similar except for the nitrate and nitrite absorptions.

D. Acidification of $M_3(A,\alpha\text{-}W_9P)_2$ Anions. Unlike $A\text{-}Na_8HW_9PO_{34}$ and $K_4(H_2O)_2Co_4(B,\alpha\text{-}W_9PO_{34})_2$, salts of the $M_3(A\text{-}W_9P)_2$ anions do not form $W_{12}PO_{40}^{3-}$ as the main product when passed through a strongly acidic ion-exchange column. Instead, all except the iron and cerium complexes are converted to a $W_2(W_9P)_2$ anion, which can be precipitated as a potassium salt or converted to the known $W_3(W_9P)_2$ anion[7-9] by taking its

---

(6) Robert, F.; Leyrie, M.; Hervé, G. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1982**, *B38*, 358–362.

(7) Souchay, P. *Ann. Chim. (Paris)* **1947**, *2*, 203.

Table I. ^{31}P and ^{183}W NMR Chemical Shifts (ppm)

anion	^{31}P	^{183}W
$Zn_2(O_2W)(W_9PO_{34})_2^{12-}$	−12.27	−103.8 (4) −166.3 (8), −173.3 (4), −194.1 (1), −208.8 (2)
$(O_2W)_2(W_9PO_{34})_2^{14-}$	−12.30	−74.6 (2), −103.6 (4), −142.4 (4), −159.2 (4) −159.6 (4), −195.9 (2)
$PZnW_{11}O_{40}^{7-}$	−11.52	−73.0 (2), −106.5 (2), −130.1 (1), −130.6 (2), −140.4 (2), −157.1 (2)
$(O_5W)_3(W_9PO_{34})_2H_6^{4-}$	−13.20	−108.4 (4 + 2), −123.9 (4), −129.2 (4), −130.3 (4), −153.6 (1), −225.6 (2)

acidic solution to dryness. This behavior suggested a stepwise loss of M from $M_3(W_9P)_2$ on acidification; acidification studies with hydrochloric acid confirmed this. The general reaction course is

$$M_3(W_9P)_2 \xrightarrow{\text{pH 3}} M_2W(W_9P)_2 \xrightarrow{\text{pH 1-2}} W_2(W_9P)_2 \xrightarrow[-H_2O]{\Delta} W_3(W_9P)_2$$

However, this sequence is not followed in all cases. Exceptions include the iron complex, which does not proceed past the $Fe_2W(W_9P)_2$ stage even when passed through a strongly acidic ion-exchange column, the palladium complex, in which case we were unable to isolate an intermediate $Pd_2W(W_9P)_2$ species, and the cerium complex, which retains cerium even when strongly acidified to give a mixture of uncharacterized products. Another exception is $Cu_3(W_9P)_2{\cdot}NO_3$, which can be recrystallized unchanged at pH 3 although nitrate-free $Cu_3(W_9P)_2$ converts to $Cu_2W(W_9P)_2$ at this pH.

Finally, although $Ni_3(W_9P)_2$ is converted to $Ni_2W(W_9P)_2$ at pH 4–5, this loses another nickel atom at pH 2–3 to form $NiW(W_9P)_2$. A crystal structure determination on this has given generally unsatisfactory results. The W_9P groups, however, are definitely A,α, and the belt tungsten is octahedral, bridged to each W_9P group by two oxygen atoms. One nonbridging oxygen atom on this tungsten is directed toward the center of the belt (W–O bond distance 1.7 Å), and the other is trans to this (W–O bond distance 2.4 Å). There appears to be an octahedrally coordinated nickel in the belt that is bonded to four water ligands and only one, rather than two, terminal oxygen atom from each W_9P group. These W_9P terminal oxygen atoms are nonadjacent to those that bond to the belt tungsten. The observed nickel–oxygen distances are acceptable, but the occupancy factor for nickel is unaccountably low.

The course of the acidification reaction was also studied by monitoring the ^{183}W NMR spectrum of the zinc complex during acidification:

$$Zn_3(W_9PO_{34})_2^{12-} \xrightarrow[H_2O]{\text{pH 3–4}} Zn_2(O_2W)(W_9PO_{34})_2^{12-} \xrightarrow[H_2O]{\text{pH 1–2}} (O_2W)_2(W_9PO_{34})_2^{14-}$$

The ^{183}W NMR spectrum of $Zn_3(W_9PO_{34})_2^{12-}$ was not determined because of instability in solution, but the spectra of $Zn_2(O_2W)(W_9PO_{34})_2^{12-}$ and $(O_2W)_2(W_9PO_{34})_2^{14-}$ (Figure 3) have the correct intensity distributions and satellite couplings for the proposed structures. The absence of zinc in the latter anion is confirmed by analysis.

The solution of $Zn_2(O_2W)(W_9PO_{34})_2^{12-}$ is moderately unstable at pH 4.5 and 30 °C and converts to $PZnW_{11}O_{40}^{7-}$ in several hours, thus limiting data acquisition. Nevertheless, the ^{183}W NMR spectrum has relative integrals of 4:4:4:4:1:2 with the unique tungsten (−194.1 ppm) corner sharing ($^2J_{W-O-W}$ = 16.1 Hz) with two equivalent pairs of tungstens (−166.3 ppm) as required. Additional connectivity information is dubious because of the limited sensitivity. The ^{183}W spectrum of $(O_2W)_2(W_9PO_{34})_2^{14-}$ at pH 3.4 has the correct integrated intensity distribution of 2:4:4:4:4:2 and more complete satellite information. The pair of bridging tungstens shows two very similar corner couplings (^2J = 19.4 and 18.6 Hz) with the correct satellite intensity for sharing with two different pairs of tungstens in the two PW_9 moieties. Other satellite information can be measured to give a plausible assignment of −195.9 (W_6), −74.6 (W_1), −142.4 (W_2), −103.6 (W_5), −159.6 (W_4), and −159.2 (W_3) with the numbering scheme of Figure 4. ^{183}W and ^{31}P NMR data for all species are collected in Table I.

Analyses of the potassium salts of $M_2W(W_9P)_2$ (M = Mn, Ni, Co, Cu, Zn) are consistent with 11 or 12 potassium atoms; i.e., the belt tungstens are octahedral, as depicted for the zinc series above, and may be protonated in some cases. The iron complex $Fe_2W(W_9P)_2$ has been isolated only as $K_9H_3Fe_2(O_2W)(W_9PO_{34})_2$. Attempted deprotonation at pH 6 caused loss of one iron to give

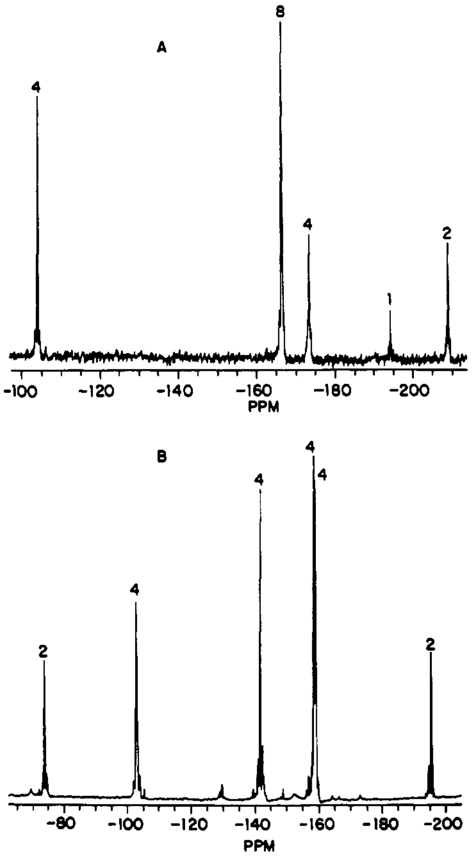

Figure 3. ^{183}W NMR spectra of (a) $Zn_2(O_2W)(W_9PO_{34})_2^{12-}$ and (b) $(O_2W)_2(W_9PO_{34})_2^{14-}$.

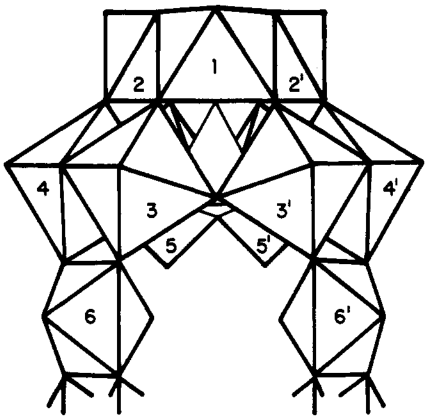

Figure 4. Numbering scheme for $(O_2W)_2(W_9PO_{34})_2^{14-}$.

---

(8) Tourné, C.; Tourné, G.; Revel, A. *Abstracts*, Polyoxometalate Workshop, St. Lambert des Bois, France, July 1983.

(9) Weakley, T. J. R. *Abstracts*, Polyoxometalate Workshop, St. Lambert des Bois, France, July 1983.

Table II. Infrared Absorptions (cm^{-1})

$Co_2W(W_9P)_2$		$W_3(W_9P)$	
Tourné	present work	(Tourné)	assignt
1095	1092	1095	P–O
1080	1080	1085	
1020	1023	1030	
960 sh	990 sh, 960 sh	972	W–O and W–O–W
940	946	940	
890	935 sh, 910 sh	890	
825	804	790	
740	723	750	
715		700	
700		670	

an $Fe(O_2W)(W_9PO_{34})_2^{14-}$ anion, which may be analogous to $Ni(O_2W)(W_9PO_{34})_2^{14-}$.

Tourné has reported[8,10] a series of anions of the type $M_2W(W_9P)_2$ as the product of $W_{19}P_2O_{69}^{14-}$ with divalent transition-metal cations. The W_9P units in these anions are believed to be B-type, and the belt tungsten is assigned a square-pyramidal rather than an octahedral configuration. Tourné's series would therefore appear to differ from our $M_2(O_2W)(A\text{-}W_9P)_2$ series. However, the evidence that Tourné's anions contain B-type units is not conclusive, nor is the evidence for square-pyramidal belt tungstens.

Substantial differences have been noted between the P–O stretching vibrations of A-W_9P and B-W_9P,[1] and we would expect similar differences between the P–O stretching vibrations of $M_3(W_9P)_2$ anions with A-type W_9P groups and those with B-type groups. The infrared data reported by Tourné[10] for $Co_2W(W_9P)_2$ and $W_3(W_9P)_2$ are compared with our $Co_2W(W_9P)_2$ data in Table II. The striking similarities between the P–O stretching vibrations of these three anions strongly suggest they all have the same type of W_9P group. Crystal structures[8,9] have established that $W_3(W_9P)_2$ has A-type W_9P groups, and the structure studies we are reporting establish that our $M_3(W_9P)_2$ anions also have A-type W_9P groups; we believe therefore that Tourné's $Co_2W(W_9P)_2$ has A-type W_9P groups. However, the differences between the W–O and W–O–W absorptions of Tourné's $Co_2W(W_9P)_2$ and those of ours suggest they may in fact be different anions. There is also a difference in the visible spectra in the 500-nm region. (Reported by Tourné: λ_{max} (ϵ) 480 nm (69), 540 nm (55), 620 nm (99). Found for our $Co_2W(W_9P)_2$: λ_{max} (ϵ) 504 nm, (49.5), 539 nm (47), 624 nm (82).) Whether this difference can be ascribed simply to a square-pyramidal belt tungsten vs. an octahedral one cannot be decided at this time.

There are recent reports[12] that the octahedral belt tungsten atoms in $W_3(W_9As)_2$ are strongly shielded and that the square-pyramidal belt tungsten is strongly deshielded. We find that the two belt tungsten atoms in $W_2(W_9P)_2$ are equivalent by tungsten NMR and are strongly shielded (Figure 3b). Analysis of a potassium salt suggests 14 potassium atoms are present. We therefore favor a structure with two octahedral belt tungsten atoms. This is consistent with our hypothesis above that the $M_2W(W_9P)_2$ ions, which are precursors of $W_2(W_9P)_2$, have octahedral belt tungsten atoms, and with the poorly refined crystal structure of $NiW(W_9P)_2$, which shows an octahedral belt tungsten.

Fuchs[13] also recently reported an anion with two A,α-W_9P groups connected by two octahedral tungsten atoms; a crystal structure showed the unshared terminal oxygens on these tungsten atoms to be cis, whereas we would expect them to be trans in our $W_2(W_9P)_2$. The infrared spectrum published by Fuchs is very similar to the spectrum of our $W_2(W_9P)_2$, but there are enough differences (most notably the complete absence in our spectrum of a 643-cm^{-1} band that is quite noticeable in his) to suggest these two $W_2(W_9P)_2$ anions are isomeric and not identical.

There is also some question about the exact structure of the final product in our acidification series, $W_3(W_9P)_2$. The ^{183}W NMR spectrum we find for $W_3(W_9P)_2$ is identical with that reported by Tourné et al.[8] for $(O_4W_3)(W_9PO_{34})_2H_2^{6-}$, which they characterize as having two square-pyramidal tungsten atoms and one octahedral tungsten atom (with nonbridging oxygens trans) in the belt. Weakley, however, characterizes[9] what is apparently the same anion as $(O_5W_3)(W_9PO_{34})_2H_6^{4-}$ with one square-pyramidal tungsten and two octahedral tungstens (both with trans nonbridging oxygen atoms) in the belt. We lean slightly in favor of the Weakley structure because of our assignment of two octahedral belt tungsten atoms to the $W_2(W_9P)_2$ precursor of $W_3(W_9P)_2$.

E. Anions Containing Dissimilar Belt Metals. The complexation of nitrate and nitrite within $M_3(W_9P)_2$ or $M_2W(W_9P)_2$ anions raises the question of whether the chemistry of these or other groups might be affected by such complexation. The possibility of affecting their chemistry in significant fashion is probably greater if the belt metals are dissimilar. The $M_2W(W_9P)_2$ anions already discussed constitute one class of such anions. We have prepared others as shown in eq 1–5.

$$Co_3(W_9P)_2 + Cu(NO_3)_2 \xrightarrow{\text{pH } 3} \underset{\text{major prod.}}{CuCo(O_2W)(W_9P)_2} + \underset{\text{minor prod.}}{Cu_2Co(W_9P)_2{\cdot}NO_3} \qquad (1)$$

$$Co_3(W_9P)_2 + Cu(NO_3)_2 \xrightarrow{\text{pH } 7} Co_2Cu(W_9P)_2 \qquad (2)$$

$$Co_2(O_2W)(W_9P)_2 + Cu(NO_3)_2 \xrightarrow{\text{pH } 4} CuCo(O_2W)(W_9P)_2 \qquad (3)$$

$$Co_3(W_9P)_2 + FeSO_4 \xrightarrow{\text{pH } 3} CoFe(O_2W)(W_9P)_2 \qquad (4)$$

$$Ni_3(W_9P)_2 + Cu(NO_3)_2 \xrightarrow{\text{pH } 3} NiCu(O_2W)(W_9P)_2 \qquad (5)$$

$Cu_2Co(W_9P)_2{\cdot}NO_3$, the minor product in eq 1, is the most stable nitrate complex of those we have discovered. It survives recrystallization at 100 °C without loss of nitrate or other change. In fact, we have not yet prepared nitrate-free $Cu_2Co(W_9P)_2$. Attempts to do so by using cupric acetate in reaction 1 gave only $CuCo(O_2W)(W_9P)_2$. Conversely, using excess nitrate (as potassium nitrate) in attempts to increase the yield of $Cu_2Co(W_9P)_2{\cdot}NO_3$ gave $Cu_3(W_9P)_2{\cdot}NO_3$ as the major product.

The area of $M_3(W_9P)_2$ anions containing homogeneous or heterogeneous belts and their complexation and possible activation of various groups, exemplified so far only by nitrate and nitrite, are a new aspect of heteropolyanion chemistry that we find particularly intriguing.

Experimental Section

NMR Spectra. ^{31}P NMR spectra were obtained with either a Nicolet NT-360WB (12-mm tubes) a Nicolet or NT-300WB (10-mm tubes) spectrometer. Chemical shifts are externally referenced to 85% H_3PO_4 at 30 °C by using the sample replacement method. Samples have a concentric capillary of D_2O for constant field/frequency lock. Spectra recorded in this manner are not sensitive to solvent shifts but do depend on susceptibility differences. As a result, there is a constant shift difference of 0.70 ppm between vertical B_0 fields of superconducting magnets (with vertical samples) and horizontal fields of iron-core magnets ($\delta_{Fe} = \delta_{SC} = -0.70$). These differences are often not appreciated when chemical shift values from different laboratories are compared.

^{183}W NMR spectra (15 MHz) were all determined on a Nicolet NT-360WB spectrometer with a 20-mm-diameter sideways-spinning solenoidal probe using D_2O as solvent/lock and are referenced to 2 M Na_2WO_4 in D_2O at 30 °C.

Crystal Structure Analyses. The crystals used in this investigation were sealed in glass capillaries to prevent dehydration and mounted on a Syntex P3 diffractometer equipped with a low-temperature apparatus and Mo radiation (graphite monochromator, $\lambda = 0.71069$ Å).

Crystal data for the potassium salt of the $Cu_3(W_9P)_2{\cdot}NO_3$ anion (at −100 °C): space group $P2_1/m$; $a = 12.224$ (3) Å, $b = 33.502$ (8) Å, $c = 12.346$ (4) Å, $\beta = 118.29$ (1)°, $V = 4452$ Å^3; $\mu = 250\ cm^{-1}$; $D_c = 4.24\ g\ cm^{-3}$. The refinement of 396 variables using 5601 reflections [$F^2 > 3.0\sigma(F^2)$; 4° < 2θ < 55°; 10 361 independent reflections; ψ-scan trans-

---

(10) Tourné, C.; Revel, A.; Tourné, G. *Rev. Chim. Miner.* **1977**, *14*, 537–552.

(11) Lefebvre, F.; Leyrie, M.; Hervé, M.; Hervé, G.; Sanchez, G.; Livage, J. *Inorg. Chim. Acta* **1983**, *73*, 173–178.

(12) (a) Contant, R.; Hervé, G.; Thouvenot, R. *Abstracts*, Polyoxometalate Workshop, St. Lambert des Bois, France, July 1983. (b) Jeannin, Y.; Martin-Freré, J. *J. Am. Chem. Soc.* **1981**, *103*, 1664–1667.

(13) Fuchs, J.; Palm, R. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1984**, *39B*, 757–762.

Table III. Positional Parameters and Their Estimated Standard Deviations for the Potassium Salt of the $Cu_3(W_9P)_2 \cdot NO_3$ Anion[a]

atom	*x*	*y*	*z*	*B*, Å²	atom	*x*	*y*	*z*	*B*, Å²
W(1)	0.1668 (1)	0.15656 (4)	−0.1617 (1)	1.30 (2)	OT(6)	−0.129 (2)	0.1513 (5)	−0.034 (1)	0.2 (3)*
W(2)	0.5141 (1)	0.15602 (4)	−0.0111 (1)	1.28 (2)	OT(7)	0.339 (2)	0.0285 (6)	−0.101 (2)	2.1 (4)*
W(3)	0.6755 (1)	0.15776 (4)	0.2936 (1)	1.31 (2)	OT(8)	0.612 (2)	0.0278 (6)	0.402 (2)	1.7 (4)*
W(4)	0.5171 (1)	0.15653 (4)	0.4876 (1)	1.24 (2)	OT(9)	0.098 (2)	0.0295 (6)	0.182 (2)	1.6 (4)*
W(5)	0.2084 (1)	0.15728 (4)	0.3507 (1)	1.32 (2)	O(12)	0.339 (2)	0.1648 (6)	−0.112 (2)	1.3 (4)*
W(6)	0.0226 (1)	0.15718 (4)	0.0072 (1)	1.33 (2)	O(16)	0.022 (2)	0.1440 (7)	−0.146 (2)	2.3 (5)*
W(7)	0.3422 (1)	0.06469 (4)	−0.0015 (1)	1.24 (2)	O(17)	0.220 (2)	0.1006 (6)	−0.102 (2)	1.3 (4)*
W(8)	0.5141 (1)	0.06513 (4)	0.3122 (1)	1.24 (2)	O(23)	0.658 (2)	0.1435 (6)	0.137 (2)	1.2 (4)*
W(9)	0.1946 (1)	0.06513 (4)	0.1741 (1)	1.28 (2)	O(27)	0.459 (2)	0.0993 (5)	−0.001 (2)	0.9 (3)*
Cu(1)	0.0977 (6)	0.250	−0.0778 (5)	1.6 (1)	O(34)	0.621 (2)	0.1643 (6)	0.415 (2)	2.0 (4)*
Cu(2)	0.5906 (6)	0.250	0.1358 (5)	1.5 (1)	O(38)	0.616 (2)	0.1003 (5)	0.293 (2)	1.1 (3)*
Cu(3)	0.3660 (6)	0.250	0.4177 (5)	1.5 (1)	O(45)	0.364 (2)	0.1451 (6)	0.484 (2)	1.6 (4)*
K(1)	0.681 (1)	0.250	0.474 (1)	2.9 (3)	O(48)	0.508 (2)	0.0999 (6)	0.422 (2)	1.6 (4)*
K(2)	0.037 (1)	0.250	0.180 (1)	2.3 (3)	O(56)	0.085 (2)	0.1649 (7)	0.177 (2)	2.1 (4)*
K(3)	0.341 (1)	0.250	−0.1725 (9)	2.0 (2)	O(59)	0.208 (2)	0.1001 (6)	0.294 (2)	1.8 (4)*
K(4)	0.6888 (7)	0.0557 (2)	0.1228 (7)	2.0 (2)	O(69)	0.083 (2)	0.1003 (7)	0.056 (2)	2.1 (4)*
K(5)	0.3760 (8)	0.0567 (2)	0.5338 (7)	2.5 (2)	O(78)	0.471 (2)	0.0415 (6)	0.151 (2)	1.9 (4)*
K(6)	−0.0059 (9)	0.0903 (2)	−0.5228 (7)	2.8 (2)	O(79)	0.228 (2)	0.0417 (6)	0.050 (2)	1.3 (4)*
K(7)	−0.2897 (8)	0.0910 (2)	−0.1754 (7)	2.4 (2)	O(89)	0.357 (2)	0.0435 (7)	0.290 (2)	2.3 (5)*
P	0.3521 (9)	0.1506 (2)	0.1619 (7)	1.5 (1)*	OWH	−0.058 (2)	0.0571 (6)	−0.186 (2)	1.9 (4)*
OC(1)	0.134 (2)	0.2094 (5)	−0.164 (2)	1.2 (3)*	OW(1)	0.872 (6)	0.193 (2)	0.625 (5)	13 (2)*
OC(2)	0.552 (2)	0.2086 (6)	0.011 (2)	1.3 (4)*	OW(2)	−0.059 (6)	0.228 (2)	0.334 (5)	4 (1)*
OC(3)	0.677 (2)	0.2105 (6)	0.264 (2)	1.7 (4)*	OW(3)	−0.220 (5)	0.225 (1)	0.017 (4)	2 (1)*
OC(4)	0.489 (2)	0.2094 (5)	0.499 (2)	1.2 (3)*	OW(4)	0.185 (5)	0.221 (1)	−0.412 (4)	3 (1)*
OC(5)	0.240 (2)	0.2098 (6)	0.376 (2)	1.2 (4)*	OW(5)	0.504 (5)	0.222 (1)	−0.274 (4)	3 (1)*
OC(6)	0.018 (2)	0.2092 (6)	−0.023 (2)	2.1 (4)*	OW(6)	0.832 (2)	0.0372 (7)	0.011 (2)	2.5 (5)*
ON(1)	0.237 (4)	0.250	0.135 (3)	3.5 (8)*	OW(7)	0.903 (3)	0.1013 (7)	0.205 (2)	3.1 (5)*
ON(2)	0.379 (4)	0.250	0.077 (3)	2.8 (7)*	OW(8)	0.831 (3)	0.0282 (7)	0.369 (2)	2.9 (5)*
ON(3)	0.435 (4)	0.250	0.274 (3)	3.8 (9)*	OW(9)	0.126 (3)	0.0286 (7)	0.425 (2)	2.9 (5)*
OP(1)	0.229 (2)	0.1652 (6)	0.048 (2)	1.5 (4)*	OW(10)	0.635 (3)	0.0366 (8)	0.648 (2)	3.3 (6)*
OP(2)	0.464 (2)	0.1634 (5)	0.150 (2)	1.2 (4)*	OW(11)	0.318 (3)	0.0988 (9)	0.684 (3)	4.6 (7)*
OP(3)	0.359 (2)	0.1638 (5)	0.284 (1)	0.7 (3)*	OW(12)	0.084 (3)	0.0423 (8)	−0.314 (2)	3.3 (6)*
OP(4)	0.352 (2)	0.1041 (6)	0.160 (2)	1.6 (4)*	OW(13)	−0.163 (4)	0.100 (1)	−0.407 (3)	7 (1)*
OT(1)	0.112 (3)	0.1455 (7)	−0.318 (2)	2.7 (5)*	OW(14)	−0.463 (3)	0.0432 (8)	−0.152 (2)	3.1 (5)*
OT(2)	0.558 (2)	0.1445 (6)	−0.117 (2)	1.6 (4)*	OW(15)	0.022 (2)	0.2100 (5)	−0.480 (1)	0.4 (3)*
OT(3)	0.834 (2)	0.1502 (7)	0.387 (2)	2.8 (5)*	OW(16)	−0.324 (2)	0.2116 (6)	−0.174 (2)	1.3 (4)*
OT(4)	0.619 (2)	0.1468 (6)	0.637 (2)	2.0 (4)*	N	0.361 (5)	0.250	0.159 (4)	4 (1)*
OT(5)	0.117 (2)	0.1490 (6)	0.415 (2)	1.8 (4)*					

[a] Starred values indicate that the atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

mission coefficients from 0.32 to 1.00] converged at $R = 0.065$ and $R_w = 0.065$.

Crystal data for the potassium salt of the $Ce_3(W_9P)_2$ anion (at −100 °C): space group $C2/m$, $a = 33.219$ (4) Å, $b = 15.903$ (1) Å, $c = 17.385$ (2) Å, $\beta = 98.41$ (1)°, $V = 9085$ Å^3; $\mu = 253$ cm^{-1}; $D_c = 4.27$ g cm^{-3}. The refinement of 389 variables using 5119 reflections [$F^2 > 3.0\sigma(F^2)$; $4° < 2\theta < 55°$; 10821 independent reflections; ψ-scan transmission coefficients from 0.20 to 1.00] converged at $R = 0.060$ and $R_w = 0.055$.

Crystal data for the potassium salt of the $NiW(W_9P)_2$ anion (at −70 °C): space group $C2/m$, $a = 33.101$ (6) Å, $b = 16.868$ (4) Å, $c = 17.645$ (5) Å, $\beta = 108.74$ (2)°, $V = 9329$ Å^3. The present model includes 314 variables and has refined to $R = 0.068$ and $R_w = 0.077$ by using 4193 reflections [$F^2 > 3.0\sigma(F^2)$; $4° < 2\theta < 50°$; 8481 independent reflections].

All three crystal structures suffer from disorder problems. The $Cu_3(W_9P)_2 \cdot NO_3$ anion appears to be ordered across a crystallographic mirror plane that passes through the three Cu atoms and the nitrate ion of the belt, but a second $(W_9P)_2$ structure (translated from the original structure by $x = 0.1$) appears in the final difference Fourier with peaks as high as 5.2 e Å^{-3}. Although most of the potassium ions and water molecules have been identified, some water molecules are disordered and some sites may be occupied in part by potassium and in part by oxygen.

The $Ce_3(W_9P)_2$ anion also resides across a crystallographic mirror, but in this case, it is perpendicular to the Ce_3 belt and contains only one of the Ce atoms. Although the difference map contains numerous large peaks (up to 4 e Å^{-3}), no "shadow" $(W_9P)_2$ structure is found. In this case, the potassium ions and water molecules surrounding the anion are badly disordered. Some of these have been identified and have been included in the refinement; the remaining peaks have been ignored because they do not make chemical sense, even within the context of a disordered model.

Although the $W(W_9P)_2$ moiety of the $NiW(W_9P)_2$ anion was found and refined, the belt contains confusing electron densities. Additional complications arise from the presence of a crystallographic mirror plane that is perpendicular to the belt and passes through the lone tungsten atom. Disordered water molecules only add to the problems. At this point, efforts to model the disorder are continuing although we have little hope of success.

Alternative models, second data sets, alternative space groups, and use of programs such as DIFABS to model the absorption effects failed to help with the disorder problems of these three crystal structures. We believe that we have extracted as much structural information from the data as is reasonably possible.

The solution and refinement of the structure were carried out on a PDP-11 computer using local modifications of the program supplied by the Enraf-Nonius Corp.[14] The atomic scattering factors were taken from the tabulations of Cromer and Waber;[15a] anomalous dispersion corrections were by Cromer. In the least-squares refinement, the function minimized was $\sum w(|F_o| - |F_c|)^2$ with the weights, w, assigned as $1/\sigma^2(F_o)$. The standard deviations of the observed structure factors, $\sigma(F_o)$, were based on counting statistics and an "ignorance factor", p, of 0.02.[16]

Analyses. Elemental analyses were performed by E&R Microanalytical Laboratory Inc., Corona, NY. Water was determined by thermogravimetric analysis; the rate of heating was 10 °C min^{-1}.

Preparations. $\mathbf{(OCe)_3(W_9PO_{34})_2^{12-}}$. Ceric ammonium sulfate (24 g, 28 mmol) was added to a fresh slurry of hydrated $Na_8HW_9PO_{34}$[2] (60 g, ca. 22 mmol) in water (400 mL). The mixture was stirred for 3 min and filtered. Potassium chloride (40 g) was added to the filtrate to precipitate a yellow solid. This was recrystallized from water (100 mL) at 75 °C to obtain 26.6 g of a yellow crystalline solid. The ^{31}P NMR spectrum in water (pH 4.7) exhibited four lines, at −6.3, −7.0, −7.6, and −8.3 ppm in 50:1:8:63 ratios. The exact positions of these lines vary with pH; the relative intensities vary with sample history. Twenty-five grams of this

---

(14) Frenz, B. A. *Computing in Crystallography*; Schenk, H., Olthof-Hazehamp, R., van Koningsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978; pp 64–71.

(15) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV: (a) Table 2.2b; (b) Table 2.3.1.

(16) Corfield, B. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 197.

Table IV. Positional Parameters and Their Estimated Standard Deviations for the Potassium Salt of the $Ce_3(W_9P)_2$ Anion[a]

atom	*x*	*y*	*z*	*B*, Å²	atom	*x*	*y*	*z*	*B*, Å²
W(1)	0.16335 (4)	0.38273 (8)	0.43332 (6)	0.92 (2)	OT(8)	0.3219 (7)	0.327 (1)	−0.026 (1)	1.3 (4)*
W(2)	0.14867 (5)	0.27499 (7)	0.26308 (7)	0.95 (2)	OT(9)	0.4610 (9)	0.325 (2)	0.111 (1)	2.6 (5)*
W(3)	0.13419 (4)	0.39269 (8)	0.07592 (6)	0.97 (2)	OT(10)	0.498 (1)	0.500	0.387 (2)	3.3 (8)*
W(4)	0.05263 (4)	0.39324 (8)	0.20206 (6)	1.13 (2)	O(1)	0.264 (1)	0.500	0.371 (2)	1.6 (6)*
W(5)	0.06652 (6)	0.500	0.3752 (1)	1.04 (3)	O(2)	0.2447 (7)	0.408 (1)	0.217 (1)	1.1 (4)*
W(6)	0.37163 (5)	0.38272 (9)	0.40761 (7)	1.56 (3)	O(3)	0.2641 (9)	0.219 (1)	0.403 (1)	2.4 (5)*
W(7)	0.34837 (5)	0.27579 (8)	0.23945 (7)	1.24 (2)	O(11)	0.171 (1)	0.500	0.452 (2)	1.2 (5)*
W(8)	0.32231 (4)	0.39243 (8)	0.05210 (6)	1.08 (2)	O(12)	0.1466 (7)	0.282 (1)	0.375 (1)	1.2 (4)*
W(9)	0.42866 (4)	0.39255 (8)	0.15504 (7)	1.37 (2)	O(15)	0.1053 (8)	0.416 (1)	0.407 (1)	1.8 (4)*
W(10)	0.45279 (7)	0.500	0.3261 (1)	1.69 (4)	O(23)	0.1465 (7)	0.314 (1)	0.160 (1)	1.3 (4)*
Ce(1)	0.25720 (6)	0.3607 (1)	0.32934 (9)	1.01 (3)	O(24)	0.0919 (7)	0.319 (1)	0.250 (1)	0.9 (3)*
Ce(2)	0.23603 (9)	0.500	0.1313 (1)	1.01 (5)	O(33)	0.119 (1)	0.500	0.029 (1)	0.9 (5)*
K(1)	0.2349 (3)	0.2574 (5)	0.1297 (4)	2.0 (1)*	O(34)	0.0812 (7)	0.402 (1)	0.120 (1)	1.3 (4)*
K(2)	0.4291 (3)	0.1563 (4)	0.1471 (4)	1.7 (1)*	O(44)	0.026 (1)	0.500	0.171 (2)	1.2 (5)*
KO(3)	0.0606 (6)	0.254 (1)	0.3925 (9)	5.5 (4)*	O(45)	0.0373 (8)	0.418 (1)	0.306 (1)	1.5 (4)*
KO(4)	0.3043 (6)	0.088 (1)	0.3184 (8)	5.0 (3)*	O(66)	0.366 (1)	0.500	0.429 (1)	1.0 (5)*
KO(5)	−0.0310 (7)	0.230 (1)	0.364 (1)	6.6 (4)*	O(67)	0.3745 (8)	0.283 (1)	0.343 (1)	1.7 (4)*
KO(6)	0.3063 (8)	0.354 (1)	0.565 (1)	8.1 (5)*	O(78)	0.3265 (7)	0.317 (1)	0.137 (1)	0.7 (3)*
KO(7)	0.0421 (8)	0.155 (1)	0.214 (1)	7.9 (5)*	O(79)	0.4007 (8)	0.320 (1)	0.211 (1)	1.5 (4)*
KO(8)	0.409 (1)	0.500	−0.049 (1)	6.6 (6)*	O(88)	0.326 (1)	0.500	0.002 (2)	1.4 (6)*
P(1)	0.1459 (5)	0.500	0.2581 (7)	1.3 (2)*	O(89)	0.3822 (7)	0.402 (1)	0.082 (1)	1.3 (4)*
P(2)	0.3505 (4)	0.500	0.2322 (6)	1.0 (2)*	O(99)	0.450 (1)	0.500	0.118 (2)	2.0 (6)*
OC(1)	0.2161 (7)	0.366 (1)	0.427 (1)	1.3 (4)*	O(610)	0.4227 (9)	0.417 (2)	0.366 (1)	2.7 (5)*
OC(2)	0.2039 (7)	0.270 (1)	0.279 (1)	1.2 (4)*	O(910)	0.4645 (8)	0.417 (1)	0.251 (1)	2.2 (5)*
OC(3)	0.1870 (7)	0.408 (1)	0.066 (1)	1.0 (4)*	OW(1)	0.2877 (9)	0.147 (2)	0.077 (1)	2.5 (5)*
OC(6)	0.3191 (7)	0.364 (1)	0.414 (1)	1.4 (4)*	OW(2)	0.233 (1)	0.111 (2)	0.235 (2)	5.4 (7)*
OC(7)	0.2994 (7)	0.271 (1)	0.268 (1)	1.6 (4)*	OW(3)	0.4567 (9)	0.111 (2)	0.297 (1)	3.4 (5)*
OC(8)	0.2696 (7)	0.409 (1)	0.055 (1)	1.3 (4)*	OW(4)	0.389 (1)	0.000	0.138 (2)	2.3 (7)*
OP(1)	0.1632 (8)	0.421 (1)	0.299 (1)	1.7 (4)*	OW(5)	0.471 (2)	0.071 (4)	0.036 (3)	14 (2)*
OP(2)	0.155 (1)	0.500	0.174 (1)	1.0 (5)*	OW(6)	0.013 (2)	0.344 (3)	0.489 (4)	16 (2)*
OP(3)	0.100 (1)	0.500	0.260 (2)	1.3 (5)*	OW(7)	0.256 (2)	0.000	0.423 (2)	5 (1)*
OP(4)	0.3430 (7)	0.420 (1)	0.278 (1)	0.9 (3)*	OW(8)	0.306 (1)	0.000	0.170 (2)	3.0 (8)*
OP(5)	0.323 (1)	0.500	0.154 (1)	0.6 (5)*	OW(9)	0.114 (2)	0.000	0.228 (2)	5 (1)*
OP(6)	0.395 (1)	0.500	0.220 (2)	1.7 (6)*	OW(10)	0.076 (1)	0.175 (2)	0.073 (2)	5.3 (8)*
OT(1)	0.1617 (8)	0.347 (1)	0.526 (1)	1.5 (4)*	OW(11)	0.080 (2)	0.500	0.611 (3)	8 (2)*
OT(2)	0.1364 (7)	0.171 (1)	0.247 (1)	1.0 (4)*	OW(12)	0.500	0.276 (2)	0.000	2.8 (7)*
OT(3)	0.1175 (8)	0.327 (1)	−0.001 (1)	1.5 (4)*	OW(13)	0.500	0.347 (3)	0.500	6 (1)*
OT(4)	0.0140 (8)	0.326 (1)	0.167 (1)	1.8 (4)*	OW(14)	0.333 (2)	0.500	−0.167 (3)	9 (2)*
OT(5)	0.038 (1)	0.500	0.449 (2)	2.3 (7)*	OW(15)	0.540 (3)	0.500	0.152 (4)	10 (2)*
OT(6)	0.3941 (8)	0.346 (1)	0.496 (1)	2.3 (5)*	OW(16)	0.171 (2)	0.000	0.338 (3)	9 (2)*
OT(7)	0.3581 (9)	0.168 (1)	0.223 (1)	2.5 (5)*	OW(17)	0.075 (2)	0.323 (3)	0.548 (2)	9 (1)*

[a] Starred values indicate that the atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

product was refluxed for 1 h in water (35 mL); the solution was allowed to cool to obtain 15.7 g of a yellow crystalline solid that exhibited one ^{31}P line (−7.57 ppm) in aqueous solution at pH 5.2. The analytical sample was recrystallized two more times from water. Anal. Calcd for $K_9(NH_4)H_2(OCe)_3(W_9PO_{34})_2 \cdot 20H_2O$: K, 6.21; Ce, 7.42; N, 0.25; W, 58.45; H_2O, 6.4. Found: K, 5.98; Ce, 7.90; N, 0.31; W, 58.40; H_2O, 6.7.

In a similar preparation, the once-recrystallized product that exhibited four ^{31}P lines was analyzed. Anal. Calcd for $K_9(NH_4)H_2(OCe)_3(W_9PO_{34})_2 \cdot 14H_2O$: K, 6.30; Ce, 7.59; W, 59.8; H_2O, 4.6. Found: K, 6.55; Ce, 7.67; W, 60.8; H_2O, 5.0.

Three grams of $K_9(NH_4)H_2(OCe)_3(W_9PO_{34})_2$, which exhibited only one ^{31}P NMR line, was dissolved in water (50 mL). The pH was raised to 8.1 from 4.6 with dilute aqueous potassium hydroxide. The yellow color of the solution faded considerably; the addition of potassium chloride (3 g) precipitated a cream-colored solid, which was recrystallized from water to obtain $K_{12}(OCe)_3(W_9PO_{34})_2 \cdot 18H_2O$. Anal. Calcd for $K_{12}(OCe)_3(W_9PO_{34})_2 \cdot 18H_2O$: K, 8.20; Ce, 7.35; W, 57.84; H_2O, 5.7. Found: K, 7.75; Ce, 8.17; W, 58.21; H_2O, 5.6.

Twenty grams of $K_9(NH_4)H_2(OCe)_3(W_9PO_{34})_2 \cdot 20H_2O$ was dissolved in water (100 mL) at 90 °C and passed through 30 mL of the potassium salt of a strongly acidic ion-exchange resin. Ten grams of potassium chloride was added to the effluent; the precipitated solid was refluxed in water for 1 h and then allowed to cool to separate 7.1 g of yellow crystalline $K_{10}H_2(OCe)_3(W_9PO_{34})_2 \cdot 14H_2O$. Anal. Calcd for $K_{10}H_2(OCe)_3(W_9PO_{34})_2 \cdot 14H_2O$: K, 7.02; Ce, 7.54; W, 59.38; N, 0.00; H_2O, 4.5. Found: K, 7.16; Ce, 7.21; W, 59.50; N, <0.07; H_2O, 4.5. This salt was recrystallized from water (pH 2.6) to obtain the crystal used for the structure determination described above.

Other $M_3(W_9PO_{34})_2^{12-}$ Anions. $Na_8HW_9PO_{34} \cdot xH_2O$ (30 g, ca. 11 mmol) and nickel nitrate hexahydrate (6.0 g, 21 mmol) were added simultaneously to 240 mL of water. The mixture was stirred for 2 min to obtain a clear greenish yellow solution. This was filtered; potassium chloride (34 g) was added to the filtrate, and the mixture was then stirred for another 2 min and filtered to obtain 24 g (80%) of $K_{12}Ni_3(W_9PO_{34})_2 \cdot 20H_2O$. Three grams of this was recrystallized from 30 mL of water with heating to 50 °C only and filtration through Celite. Recovery was 1.2 g (40%). Anal. Calcd for $K_{12}Ni_3(W_9PO_{34})_2 \cdot 20H_2O$: K, 8.50; Ni, 3.19; W, 59.96; H_2O, 6.5. Found: K, 8.03; Ni, 3.51; W, 59.13; H_2O, 7.0.

Analogous complexes of manganese, iron, copper, zinc, and palladium were prepared similarly, as summarized in Table V.

Aqueous Thermolysis of $K_{12}M_3(W_9PO_{34})_2$. Potassium salts of various $M_3(W_9PO_{34})_2^{12-}$ anions (M = Co, Zn, Cu) were heated in refluxing water for 10–30 min to obtain the products shown in Table VI.

Acidification of $M_3(W_9PO_{34})_2^{12-}$ Salts. $K_{12}Zn_2(O_2W)(W_9PO_{34})_2$. A solution of $K_{12}Zn_3(W_9PO_{34})_2$ (6.0 g) in water (30 mL) was adjusted to pH 2.6 with 12 M hydrochloric acid and then filtered. Potassium chloride (5 g) was added to the filtrate; the mixture was stirred for 5 min and then refiltered to obtain 3.2 g of $K_{12}Zn_2(O_2W)(W_9PO_{34})_2 \cdot 25H_2O$. The analytical sample was recrystallized from water at 60 °C. Anal. Calcd for $K_{12}Zn_2(O_2W)(W_9PO_{34})_2 \cdot 25H_2O$: K, 8.14; Zn, 2.27; W, 60.63; H_2O, 7.8. Found: K, 7.79; Zn, 2.23; W, 60.16; H_2O, 7.6.

Similar reactions of the corresponding cobalt, nickel, copper, and manganese complexes are summarized in Table VII.

$K_9H_3Fe_2(O_2W)(W_9PO_{34})_2$. A solution of $K_{12}(H_2OFe)_3(W_9PO_{34})_2$ (5.0 g) in water (100 mL) was passed through an ion-exchange column containing 50 mL of strongly acidic ion-exchange resin. The yellow effluent had a pH of 1.6. Ten grams of potassium chloride was added; the solution was concentrated to 100 mL and chilled in ice to precipitate 3.3 g of a cream-colored solid. Part of this (2.9 g) was dissolved in water (10 mL) at ambient temperature; the solution was chilled overnight at 4 °C to separate 1.7 g of a light yellow crystalline solid. Anal. Calcd for $K_9H_3Fe_2(O_2W)(W_9PO_{34})_2 \cdot 12H_2O$: K, 6.57; Fe, 2.08; W, 65.20; H_2O, 4.1. Found: K, 6.37; Fe, 2.24; W, 65.50; H_2O, 4.3.

Table V. Preparations of $K_{12}M_3(W_9P)_2 \cdot xH_2O$ from W_9P

			anal. calcd (found), %			
coreactant	yield[a]	x, mol	K	M	W	H_2O
$MnSO_4$	89	15	8.04 (7.85)[c]	3.08 (3.86)	61.89 (61.46)	5.0 (5.6)
$FeSO_4$	89	25	8.38 (8.91)	2.99 (2.97)	59.09 (59.13)	8.0 (8.6)
$Cu(NO_3)_2$	95[b]	18	8.62 (8.27)	3.50 (3.08)	60.80 (60.26)	6.0 (5.3)
$Zn(NO_3)_2$	60	15	8.61 (8.60)	3.60 (4.19)	60.73 (60.37)	5.0 (5.1)
$Pd(NO_3)_2$	80	20	8.37 (8.11)	5.69 (5.86)	59.01 (59.47)	6.4 (6.2)

[a] Yield = percent yield of crude salt. In general, the infrared spectra of the crude salt and the recrystallized analytical samples were identical except for sulfate impurities when metal sulfates were used as starting materials. The recrystallizations were done at 60 °C or lower. The manganese and zinc salts are particularly heat-sensitive in solution. The manganese complex was recrystallized by extraction with water at ambient temperature and chilling the filtered extracts at 0 °C. [b] The crude product is a nitrate complex as discussed elsewhere. The analytical values are for the nitrate-free salt, which is obtained easily by recrystallization of the crude product from water at 50 °C. (Found: N, <0.04). [c] This is a K_{11} Na salt. (Calcd: Na, 0.43. Found: Na, 0.42.)

Table VI. Aqueous Thermolysis of $K_{12}M_3(W_9PO_{34})_2$

				anal. calcd for $K_{10}(H_2O)_2M_4(W_9PO_{34})_2 \cdot xH_2O$ (found), %			
M	amt of $K_{12}M_3(W_9P)_2$, g	amt of prod., g	x, mol in prod.	K	M	W	H_2O
Zn	5.6	1.6	20	7.10 (7.95)	4.83 (5.04)	60.08 (59.78)	6.5 (6.4)
Co	1.5	0.74	14	7.28 (7.01)	4.39 (5.04)	61.58 (62.18)	5.4 (6.2)
Cu[a]	7.3	5.0	20	7.12 (7.29)	4.63 (4.22)	60.27 (60.71)	6.6 (6.7)

[a] Although analysis of the copper salt suggests a $Cu_4(W_9PO_{34})_2^{10-}$ anion, the infrared spectrum shows it is not isostructural with the cobalt and zinc complexes in this table; see text.

Table VII. Acidification of $M_3(W_9PO_{34})_2^{12-}$ To Form $M_2(O_2W)(W_9PO_{34})_2^{12-}$

					anal. calcd for $K_{12}M_2(O_2W)(W_9PO_{34})_2 \cdot xH_2O$ (found), %			
M	amt of $K_{12}M_3(W_9P)_2$, g	amt. of prod., g	reacn pH	x	K	M	W	H_2O
Co	10.0	5.2	4.0	18	8.35 (8.59)	2.10 (2.49)	62.13 (61.60)	5.8 (5.7)
Ni	15.0	9.5	4.0	25	8.16 (8.37)	2.04 (1.91)	60.77 (61.33)	7.8 (7.4)
Mn[a]	16.8	8.9	4.0	25	7.52 (7.24)	1.92 (2.32)	61.06 (60.80)	8.8 (7.9)
Cu	6.0	1.7	3.0	20	8.33 (8.29)	2.26 (2.98)	62.03 (62.14)	6.4 (5.9)

[a] Analytical values calculated for the $K_{11}H$ salt; see text.

$Ni(O_2W)(W_9PO_{34})_2^{14-}$ and $Fe(O_2W)(W_9PO_{34})_2^{14-}$. A solution of $K_{12}Ni_3(W_9PO_{34})_2$ (20.4 g) in water (150 mL) was adjusted to pH 2.5 with 12 M hydrochloric acid. A clear light green solution formed. This was filtered; potassium chloride (15 g) was added to the filtrate to precipitate 10.0 g of a yellow solid. Four grams of this was recrystallized from water (10 mL) at boil to obtain 1.1 g of highly crystalline $K_{13}HNi(O_2W)(W_9PO_{34})_2 \cdot 15H_2O$. Anal. Calcd for $K_{13}HNi(O_2W)(W_9PO_{34})_2 \cdot 15H_2O$: K, 9.22; Ni, 1.07; W, 63.37; H_2O, 4.9. Found: K, 9.31; Ni, 1.01; W, 62.85; H_2O, 4.4.

A solution of $K_{12}Fe_3(W_9PO_{34})_2$ (30.0 g) in water (500 mL) was passed through 150 mL of a strongly acidic ion-exchange resin. Potassium hydroxide solution (5%) was added to the yellow effluent to raise the pH from 1.3 to 6.0; the solution darkened as the pH increased. The solution was then concentrated to 80 mL, and potassium chloride was added. The solution was stirred for 15 min and filtered to obtain a mixture of solids (9.6 g) that was not satisfactorily purified. The filtrate slowly separated 2.2 g of crystalline $K_{13}HFe(O_2W)(W_9PO_{34})_2 \cdot 10H_2O$. Anal. Calcd for $K_{13}HFe(O_2W)(W_9PO_{34})_2 \cdot 10H_2O$: K, 9.38; Fe, 1.03; W, 64.44; H_2O, 3.3. Found: K, 9.39; Fe, 1.04; W, 64.36; H_2O, 4.0.

$(O_2W)_2(W_9PO_{34})_2^{12-}$ and $(O_5W_3)(W_9PO_{34})_2^{10-}$. A mixture of $K_{12}Zn_3(W_9PO_{34})_2$ (40 g) and water (150 mL) was treated with 12 M hydrochloric acid until the pH was lowered to 1.7 and then stirred 15 min. Fifteen grams of potassium chloride was added to the resulting clear solution. After 10 min of stirring, the mixture was filtered. The filter cake (20 g) was dissolved in water (15 mL) at 58 °C. The pH was 2.9 and was lowered to 1.9 by the addition of more hydrochloric acid. The solution was then allowed to cool overnight and filtered to obtain 5.6 g of $K_{12}Zn_2(O_2W)(W_9PO34)_2$, identical by infrared and ^{183}W NMR analysis with that described above. The filtrate was chilled in ice to separate 5.6 g of another white crystalline solid, shown to contain the $(O_2W)_2(W_9PO_{34})_2^{14-}$ anion by NMR as discussed above. The salt was solubilized for NMR purposes by stirring it with the lithium salt of a strongly acidic ion-exchange resin. The recovered NMR solution was passed through 30 mL of the potassium salt of a strongly acidic ion-exchange resin. The effluent was slightly acid and was treated with 10% potassium hydroxide solution to raise the pH to 7. The solution was then concentrated until a crystalline solid (3.8 g) separated. This was analyzed. Anal. Calcd for $K_{14}(O_2W)_2(W_9PO_{34})_2 \cdot 15H_2O$: K, 9.59; W, 64.41; Zn, 0.0; H_2O, 4.7. Found: K, 9.64; W, 64.71; Zn, 0.06; H_2O, 4.6.

The same product was obtained by a similar acidification of $K_{12}(H_2OCo)_3(W_9PO_{34})_2$ to pH 2.5 with hydrochloric acid. In another experiment, $K_{12}(H_2OCo)_3(W_9PO_{34})_2$ was dissolved in water (100 mL) and passed through a column containing 50 mL of a strongly acidic ion-exchange resin. Ten grams of potassium chloride was added to the effluent, which was then concentrated until 3.5 g of a white solid precipitated. This was identical by infrared analysis with the $(O_2W)_2(W_9PO_{34})_2^{14-}$ salt prepared above. The same result was obtained in similar reactions with other $M_3(W_9P)_2^{12-}$ salts (M = Ni, Mn, Cu, Zn, Pd; not Fe or Ce). Very minor amounts of $W_{12}PO_{40}^{3-}$ were also detected in all cases by ^{31}P NMR analysis of the crude products.

A solution of $K_{12}(H_2OCo)_3(W_9PO_{34})_2$ (5.0 g) in water (100 mL) was passed through a column containing 40 mL of a strongly acidic ion-exchange resin. The effluent was stripped to dryness on a rotary evaporator maintaining the temperature below 40 °C. The residue was redissolved in water and shown by ^{18}W NMR, as discussed above, to contain $W_3(W_9P)_2$. The same result was obtained with other $M_3(W_9P)_2$ salts (M = Ni, Mn, Cu, Zn, Pd; not Fe or Ce).

Nitrate and Nitrite Complexes. $Cu_3(W_9PO_{34})_2 \cdot NO_3^{13-}$. Crude $K_{13}Cu_3(W_9PO_{34})_2 \cdot NO_3$ (20.7 g; see Table I) was stirred in water (100 mL). Hydrochloric acid was added dropwise to lower the pH to 2.6. The color changed from light green to clear blue. Potassium chloride (10 g) was added to the clear solution, and the mixture was then stirred for 10 min and filtered to obtain 13.5 g of a light green solid. This was recrystallized from water (200 mL) with heating to 52 °C to obtain 4.4 g of a highly crystalline bright blue solid. A crystal structure determination, discussed above, showed this contained the $Cu_3(W_9PO_{34})_2 \cdot NO_3^{13-}$ anion. The infrared spectrum exhibited a strong sharp band at 1391 cm^{-1} for the nitrate group. Anal. Calcd for $K_{13}Cu_3(W_9P_{34})_2 \cdot NO_3 \cdot 13H_2O$: K, 9.32; Cu, 3.50; W, 60.67; H_2O, 4.3. Found: K, 9.31; Cu, 3.30; W, 61.58; H_2O, 5.0.

In a separate experiment, crude $K_{13}Cu_3(W_9PO_{34})_2 \cdot NO_3$ was recrystallized from water at 55 °C without prior acidification. The nitrate-free complex was obtained as shown by infrared and elemental analysis (see Table I). A portion of the nitrate-free $K_{12}Cu_3(W_9PO_{34})_2$ complex was dissolved in water; the pH was lowered to 3 with dilute nitric acid. The addition of potassium chloride precipitated $K_{13}Cu_3(W_9PO_{34})_2 \cdot NO_3$ as shown by infrared analysis.

$Cu_3(W_9PO_{34})_2 \cdot NO_2^{13-}$. Dilute (3%) hydrochloric acid was added to a solution of $K_{12}Cu_3(W_9PO_{34})_2$ (5.0 g) in water (40 mL) to lower the pH from 5.9 to 4.0. Potassium nitrite (2.0 g) was added; the solution was warmed to 60 °C and filtered. The green filter cake (3.7 g) exhibited an infrared band at 1255 cm^{-1}, assigned to the coordinated nitrite group.

Anal. Calcd for $K_{13}Cu_3(W_9PO_{34})_2\cdot NO_2\cdot 20H_2O$: K, 9.14; Cu, 3.43; N, 0.25; W, 59.47; H_2O, 6.5. Found: K, 9.17; Cu, 3.17; N, 0.19; W, 59.27; H_2O, 5.8.

$Co_3(W_9PO_{34})_2\cdot NO_2{}^{13-}$. Two grams of sodium nitrite was added to 5 g of $K_{12}(H_2OCo)_3(W_9PO_{34})_2$ in water (40 mL). The mixture was warmed to 55 °C and filtered. Purple crystals (0.9 g) of $K_9Na_4Co_3(W_9PO_{34})_2\cdot NO_2\cdot 20H_2O$ separated from the solution on cooling. Anal. Calcd for $K_9Na_4Co_3(W_9PO_{34})_2\cdot NO_2\cdot 20H_2O$: K, 6.41; Na, 1.68; Co, 3.22; Ni, 0.26; W, 60.32; H_2O, 6.6. Found: K, 6.21; Na, 1.49; Co, 3.12; N, 0.14; W, 59.52; H_2O, 8.0. The infrared spectrum included a band at 1265 cm^{-1} for the nitrite group.

$Mn_3(W_9PO_{34})_2\cdot NO_3{}^{13-}$. Twelve milliliters of 50% aqueous manganous nitrate was added to water (228 mL). Hydrated $Na_8HW_9PO_{34}$ (30 g, 11 mmol) was added, and the mixture was stirred for 2 min. The mixture was filtered; potassium chloride (34 g) was added to precipitate a yellow solid (19.2 g). The infrared spectrum was the same as that of $K_{12}Mn_3(W_9PO_{34})_2$ (Table I) except for a doublet at 1395, 1384 cm^{-1} assigned to nitrate. Part of this product was recrystallized from water at 55 °C; infrared analysis indicated partial conversion to an $Mn_4(W_9P)_2$ salt. Accordingly, 3 g of the crude product was extracted with 75 mL of water at ambient temperature. The filtered extracts were chilled in an ice–water bath for 2 h and then refiltered to get 0.89 g of crystalline yellow $K_{13}Mn_3(W_9PO_{34})_2\cdot NO_3\cdot 20H_2O$. Anal. Calcd for $K_{13}Mn_3(W_9PO_{34})_2\cdot NO_3\cdot 20H_2O$: K, 9.15; N, 0.25; Mn, 2.97; W, 59.58; H_2O, 6.5. Found: K, 8.87; N, 0.12; Mn, 3.30; W, 59.50; H_2O, 6.7.

The nitrate absorptions were retained in the infrared spectrum of the recrystallized salt.

$MM'M''(W_9PO_{34})_2$ Anions. $CuCo(O_2W)(W_9PO_{34})_2{}^{12-}$ and $Cu_2Co(W_9PO_{34})_2\cdot NO_3{}^{13-}$. $K_{12}(H_2OCo)_3(W_9PO_{34})_2\cdot 10H_2O$ (16.5 g, 3.0 mmol) was added to a solution of cupric nitrate hydrate (0.7 g, 3.0 mmol) in water (100 mL). Hydrochloric acid (12 M) was added dropwise with stirring to the blue solution to lower the pH from 6.0 to 3.2. The resulting dark red solution was filtered; potassium chloride (20 g) was added to the filtrate to precipitate a purple solid. This was recrystallized from boiling water (60 mL). A green crystalline solid separated initially from the solution as it cooled; this was removed by filtration after the solution had cooled for 13 min. Refiltration after another 5 min gave a trace of red solid, which was discarded. The filtrate was then allowed to stand overnight; a red oil separated and slowly crystallized. The green and red solids were recrystallized separately from boiling water to obtain 1.0 g of $K_{13}Cu_2Co(W_9PO_{34})_2\cdot NO_3\cdot 20H_2O$ (blue-green after drying) and 5.0 g of $K_{11}HCoCu(O_2W)(W_9PO_{34})_2\cdot 15H_2O$ (purple after drying). The infrared spectrum of the former includes an asymmetric nitrate absorption at 1389 cm^{-1}. Anal. Calcd for $K_{13}Cu_2Co(W_9PO_{34})_2\cdot NO_3\cdot 20H_2O$: K, 9.12; Co, 1.06; Cu, 2.28; N, 0.25; W, 59.35; H_2O, 6.5. Found: K, 9.14; Co, 0.74; Cu, 2.47; N, 0.25; W, 60.03; H_2O, 5.6. Calcd for $K_{11}HCoCu(O_2W)(W_9PO_{34})_2\cdot 15H_2O$: K, 7.82; Co, 1.07; Cu, 1.16; W, 63.52; H_2O, 4.9. Found: K, 7.57; Co, 1.05; Cu, 1.17; W, 63.47; H_2O, 4.1.

$K_{12}Co_2(O_2W)(W_9PO_{34})_2$ (2.7 g, 0.5 mmol) was added to a solution of cupric nitrate hydrate (0.11 g, 0.5 mmol) in water (25 mL), forming a red solution. Potassium chloride (4.0 g) was added; the mixture was stirred for 2 min and filtered. The red filter cake was recrystallized from boiling water (1 mL) to obtain 2.1 g of red $K_{11}HCoCu(O_2W)(W_9PO_{34})_2$, identical by infrared and analysis with that prepared above. Anal. Found: K, 7.62; Co, 1.02; Cu, 1.21; W, 63.37.

$Co_2Cu(W_9PO_{34})_2{}^{12-}$. $K_{12}(H_2OCo)_3(W_9PO_{34})_2\cdot 10H_2O$ (2.0 g, 0.36 mmol) was added to a solution of cupric nitrate hydrate (0.10 g, 0.43 mmol) in water (50 mL). The solution was warmed to 50 °C and then filtered. The filtrate was red with a pH of 7.0. A purple solid (1.5 g) was precipitated by the addition of potassium chloride and was recrystallized from water (5 mL at 50 °C) to obtain 0.74 g of crystalline purple $K_{12}Co_2Cu(W_9PO_{34})_2\cdot 20H_2O$. Anal. Calcd for $K_{12}Co_2Cu(W_9PO_{34})_2\cdot 20H_2O$: K, 8.56; Co, 2.15; Cu, 1.16; W, 60.39; H_2O, 6.6. Found: K, 8.75; Co, 2.24; Cu, 0.82; W, 59.42; H_2O, 6.3.

$FeCo(O_2W)(W_9PO_{34})_2{}^{12-}$. $K_{12}(H_2OCo)_3(W_9PO_{34})_2$ (8.0 g, 1.4 mmol) was added to a solution of ferrous sulfate (0.35 g, 1.3 mmol) in 50 mL of water. Hydrochloric acid was added dropwise with stirring to lower the pH from 6.8 to 3.0. The mixture was filtered; potassium chloride (10 g) was added to the filtrate, and the mixture was then stirred for 15 min. Filtration gave 3.2 g of a light brown solid. Part of this (2.8 g) was recrystallized from boiling water (10 mL) to obtain 1.0 g of a dark green crystalline solid. The infrared spectra of the crude and recrystallized products were essentially the same. Anal. Calcd for $K_{11}HFeCo(O_2W)(W_9PO_{34})_2\cdot 12H_2O$: K, 7.91; Co, 1.08; Fe, 1.03; W, 64.26; H_2O, 4.0. Found: K, 7.65; Co, 1.19; Fe, 1.00; W, 64.55; H_2O, 4.0.

$NiCu(O_2W)(W_9PO_{34})_2{}^{12-}$. $K_{12}Ni_3(W_9PO_{34})_2\cdot 20H_2O$ (8.0 g, 1.4 mmol) was added to a solution of cupric nitrate hydrate (0.35 g, 1.5 mmol) in water (5.0 mL). Hydrochloric acid was added to lower the pH to 3.0. The mixture was stirred for 5 min and filtered, and potassium chloride (10 g) was added to the filtrate. The solution was stirred for 15 min and filtered to obtain 7.1 g of a light green solid. Part of this (5.2 g) was recrystallized from boiling water (12 mL) to obtain 2.6 g of $K_{11}HNiCu(O_2W)(W_9PO_{34})_2\cdot 15H_2O$. Anal. Calcd for $K_{11}HNiCu(O_2W)(W_9PO_{34})_2\cdot 15H_2O$: K, 7.82; Cu, 1.16; Ni, 1.07; W, 63.53; H_2O, 4.9. Found: K, 8.00; Cu, 1.43; Ni, 1.11; W, 62.80; H_2O, 3.8.

Acknowledgment. We are grateful to J. H. McCartney, L. F. Lardear, and G. Watunya for fine technical assistance.

Registry No. $K_9(NH_4)H_2(OCe)_3(W_9PO_{34})_2$, 101346-84-3; $K_{12}(OCe)_3(W_9PO_{34})_2$, 101346-86-5; $K_{10}H_2(OCe)_3(W_9PO_{34})_2$, 101346-85-4; $K_{12}Ni_3(W_9PO_{34})_2$, 101347-11-9; $Na_8HW_9PO_{34}$, 63950-57-2; $K_{12}Mn_3(W_9PO_{34})_2$, 101347-09-5; $K_{12}Fe_3(W_9PO_{34})_2$, 101347-04-0; $K_{12}Cu_3(W_9PO_{34})_2$, 101346-99-0; $K_{12}Zn_3(W_9PO_{34})_2$, 101347-13-1; $K_{12}Pd_3(W_9PO_{34})_2$, 101347-12-0; $K_{12}Co_3(W_9PO_{34})_2$, 101346-93-4; $K_{10}(H_2O)_2Zn_4(W_9PO_{34})_2$, 101347-05-1; $K_{10}(H_2O)_2Co_4(W_9PO_{34})_2$, 93455-39-1; $K_{10}(H_2O)_2Cu_4(W_9PO_{34})_2$, 101347-00-6; $K_{12}Co_2(O_2W)(W_9PO_{34})_2$, 101346-91-2; $K_{12}Ni_2(O_2W)(W_9PO_{34})_2$, 101347-10-8; $K_{12}Mn_2(O_2W)(W_9PO_{34})_2$, 101347-07-3; $K_{12}Cu_2(O_2W)(W_9PO_{34})_2$, 101346-95-6; $K_9H_3Fe_2(O_2W)(W_9PO_{34})_2$, 101347-02-8; $K_{12}(H_2OFe)_3(W_9PO_{34})_2$, 101347-03-9; $K_{13}HNi(O_2W)(W_9PO_{34})_2\cdot 15H_2O$, 101347-06-2; $K_{13}HFe(O_2W)(W_9PO_{34})_2\cdot 4H_2O$, 101347-01-7; $K_{14}(O_2W)_2(W_9PO_{34})_2$, 101347-15-3; $K_{12}(H_2OCo)_3(W_9PO_{34})_2$, 93425-27-5; $[(O_5N_3)(W_9PO_{34})_2H_6]^{4-}$, 101347-16-4; $K_{13}Cu_3(W_9PO_{34})_2\cdot NO_3$, 101346-98-9; $K_{13}Cu_3(W_9PO_{34})_2\cdot NO_2$, 101346-96-7; $K_9Na_4Co_3(W_9PO_{34})_2\cdot NO_2$, 101346-92-3; $K_{13}Mn_3(W_9PO_{34})_2\cdot NO_3$, 101347-08-4; $K_{13}Cu_2Co(W_9PO_{34})_2\cdot NO_3$, 101346-88-7; $K_{11}HCoCu(O_2W)(W_9PO_{34})_2$, 101346-87-6; $K_{12}Co_2Cu(W_9PO_{34})_2$, 101346-90-1; $K_{11}HFeCo(O_2W)(W_9PO_{34})_2$, 101346-89-8; $K_{11}HNiCu(O_2W)(W_9PO_{34})_2$, 101346-94-5; $K_{12}Zn_2(O_2W)(W_9PO_{34})_2$, 101347-14-2; $K_9(H_3O)_3[(Ce_3O_3\cdot 2H_2O)(W_9PO_{34})_2]\cdot xH_2O$, 101346-83-2; $K_{11}\{[Cu_3(NO_3)](W_9PO_{34})_2\}(H_3O)_2\cdot xH_2O$, 101346-97-8.

Supplementary Material Available: Listings of the details of the crystal structure analyses, refined temperature factor expressions, and selected bond distances and angles for the copper and cerium complexes (87 pages). Ordering information is given on any current masthead page.