taining 0.1 g (0.18 mmol) of *ttt*-$RuCl_2(tap)_2$ and 0.07 g (0.18 mmol) of $Ph_2P(CH_2)_2PPh_2$ was boiled for 12 h. The solution color changed from green to orange. The compound was isolated as the perchlorate salt with a procedure similar to that given above. The purification was done by chromatography. An orange band was eluted out by using a 1:4 benzene–acetonitrile mixture. Crystals were obtained by complete evaporation of the solvent. The yield was 40%. Anal. Calcd for $RuC_{50}H_{48}N_6O_9Cl_2P_2$: C, 54.74; H, 4.41; N, 7.66; Cl, 6.48. Found: C, 54.68; H, 4.72; N, 7.23; Cl, 6.20.

(1,3-Bis(diphenylphosphino)propane)bis[2-(phenylazo)pyridine]ruthenium(II) Perchlorate Hydrate, $[Ru(Ph_2P(CH_2)_3PPh_2)(pap)_2](ClO_4)_2 \cdot H_2O$. This was prepared by following the method given in the cases of $[Ru(Ph_2P(CH_2)_2PPh_2)(tap)_2](ClO_4)_2 \cdot H_2O$ but with *ttt*-$RuCl_2(pap)_2$ and $Ph_2P(CH_2)_3PPh_2$ used instead of *ttt*-$RuCl_2(tap)_2$ and $Ph_2P(CH_2)_2PPh_2$, respectively. The yield was 40%. Anal. Calcd for $RuC_{49}H_{46}N_6O_9Cl_2P_2$: C, 53.64; H, 4.23; N, 7.66; Cl, 6.49. Found: C, 53.95; H, 4.19; N, 7.58; Cl, 6.60.

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Registry No. $[RuCl(PPh_3)(pap)_2]ClO_4$, 81554-91-8; $[RuCl(PPh_3)(tap)_2]ClO_4$, 81554-93-0; $[RuCl(P(p\text{-tol})_3)(pap)_2]ClO_4$, 81554-95-2; $[RuCl(PPh_2Me)(pap)_2]ClO_4$, 81554-64-5; $[RuCl(PPh_2Me)(tap)_2]ClO_4$, 81554-66-7; $[RuBr(PPh_2Me)(pap)_2]ClO_4$, 81554-68-9; $[RuI(PPh_2Me)(pap)_2]ClO_4$, 81554-70-3; $[RuCl(PPhMe_2)(pap)_2]ClO_4$, 81554-72-5; $[Ru(PPhMe_2)_2(tap)_2](ClO_4)_2$, 81554-74-7; $[Ru(Ph_2P(CH_2)_2PPh_2)(tap)_2](ClO_4)_2$, 81554-76-9; $[Ru(Ph_2P(CH_2)_3PPh_2)(pap)_2](ClO_4)_2$, 81554-78-1; C_2-$RuCl_2(tap)_2$, 81600-80-8; *ttt*-$RuCl_2(pap)_2$, 77321-07-4; *ttt*-$RuBr_2(pap)_2$, 77321-08-5; *ttt*-$RuI_2(pap)_2$, 77341-75-4; *ttt*-$RuCl_2(tap)_2$, 77321-09-6.

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Preparation and Characterization of Heteropolytungstates Containing Group 3A Elements

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The polytungstate ions α-$XM^{III}(OH_2)W_{11}O_{39}{}^{n-}$ (X = B, Si, Ge, P, As; M^{III} = Al, Ga, In, Tl) and $X_2M^{III}(OH_2)W_{17}O_{61}{}^{7-}$ (X = P, As; M^{III} = as above) are reported. Their stability in acidic to slightly basic aqueous solution, both with and without supporting electrolyte, is classified in terms of X and M(III). The sensitivity to changes in M(III) of the P–O asymmetric stretch vibration splitting in the tungstophosphates is described. All anions are reducible to W(V)-containing species; their redox behavior resembles that of the parent lacunary anions. A series of two-electron reduced gallatotungstates has been isolated. The crystal symmetries found for the alkali metal and ammonium salts can be classified according to the number of cations and, to a lesser degree, the number of molecules of hydration water. Differences in behavior of the group 3A element substituted polyanions are generally small for a given central atom.

Introduction

Among the extensive class of heteropolyoxoanions of the group 5 and 6 transition metals, the best studied series of compounds are those having, or derived from, the so-called Keggin structure[2] and the related Dawson structure[3] of general formula $XM_{12}O_{40}{}^{n-}$ (X = B, Si, Ge, P, As, various transition metals; M = W, Mo) and $X_2M_{18}O_{62}{}^{p-}$ (X = P, As; M = W, Mo).

The basic unit in both structural types is a M_3O_{13} group consisting of three edge-sharing octahedra that are slightly (in the case of W) or more severely (in the case of Mo) distorted, the metal atoms being displaced outwardly. Several isomers of both structures are known,[4-11] e.g., through rotation of one M_3O_{13} unit, the most symmetric ones, generally labeled α,[9] are usually thermodynamically the most stable.

Increasing the basicity of a solution of such a polyanion may result in the formation of so-called lacunary polyanions, which have lost one or more M–O groups while maintaining the same basic structure.[4] The more easily prepared series have the general formula $XM_{11}O_{39}{}^{q-}$ (X and M as above) and $X_2M_{17}O_{61}{}^{r-}$ (X and M as above) (see Figure 1).

It is possible to refill the lacuna with one of numerous transition- and main-group-metal ions[12-14,18] or to complex two lacunary units around a sufficiently large central metal ion capable of high coordination numbers (e.g., some lanthanides and actinides).[15,16] The lacunary compound may be considered as a pentadentate or tetradentate ligand, respectively. Most 1:1 complexes that have so far been prepared contain bivalent transition-metal ions,[12-14] probably because they are comparatively easy to synthesize and isolate as solids. Several compounds have been studied however that contain tri-, tetra-, or pentavalent transition-metal ions: Co(III),[12,17,18] Mn(III),[19]

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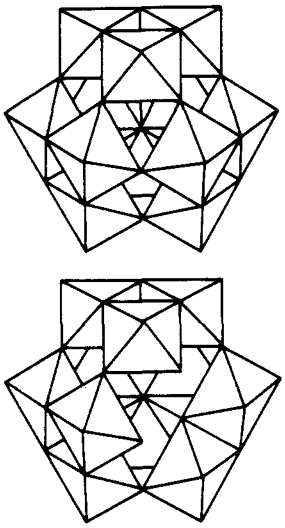

Figure 1. Idealized structures (metal coordination octahedron representation) of α-XM_{12} (Keggin structure) (top) and α-XM_{11} (lacunary Keggin structure) (bottom). The central XO_4 tetrahedron is omitted for clarity.

Fe(III),[20] V(IV), and V(V),[20-26] but also Al[20,27-29] and Ga.[14]

However, a complete series of alkali-metal salts of anions of general formula $XM^{III}(OH_2)M_{11}O_{39}{}^{s-}$ or $X_2M^{III}(OH_2)M_{17}O_{61}{}^{7-}$ has not been reported, except for Cr(III).[30]

It seemed interesting to prepare several series containing the group 3A elements Al, Ga, In, and Tl, all as trivalent ions, in order to be able to make a comparative study along a column of the periodic table.

This paper reports the preparation, isolation, and some of the properties of the anions $XM^{III}(OH_2)W_{11}O_{39}{}^{s-}$ (X = B, Si, Ge, P, As; M(III) = Al, Ga, In, Tl) and $X_2M^{III}(OH_2)W_{17}O_{61}{}^{7-}$ (X = P, As; M(III) = as above). Analogous ions containing central metal ions will be reported separately.[42] As far as we are aware, among these are the first reported well-characterized heteropolyanions that contain indium or thallium(III).[55]

All compounds reported here are the stable, more symmetrical α-isomers; this in order to obtain a homogeneous, comparable series.

Although the group 3A metal ions hydrolyze rapidly to form rather insoluble basic salts or hydrated oxides in the pH range imposed by the stability limits of the starting materials, the most straight-forward reaction, direct addition to the lacunary compound, proceeds sufficiently rapidly to prevent significant precipitation of such insoluble products, especially in hot aqueous solution. Furthermore, in most cases the addition reaction goes to completion even when there is considerable precipitation, as the basic salt slowly redissolves to react.

Experimental Section

Starting Materials. The α isomers of the XW_{11} and X_2W_{17}[31] series are all stable compounds, both as solids and in aqueous solution, except AsW_{11}; their preparation is straightforward.[14,32] AsW_{11} was prepared directly, in situ,[14,30] just prior to the addition of the trivalent metal ion (see next section). Ca. 1 M solutions of $InCl_3$, $In(NO_3)_3$, $GaCl_3$, and $Ga(NO_3)_3$ were prepared by slowly dissolving indium shot (99.995%) or gallium chunks (99.99%) in the stoichiometric amount of 1:2 HCl or HNO_3, at room temperature. Thallium(III) was added in the form of analytical grade $Tl(NO_3)_3$.

Preparations. Detailed descriptions are given for the preparation and isolation (usually as the potassium salt) of all reported aluminum-containing heteropolytungstates and of a few salts of every other group 3A element containing heteropolytungstate series, the modifications necessitated by these elements being relatively small.

Aluminatoheteropolytungstates. $K_5SiAl(OH_2)W_{11}O_{39}\cdot{\sim}13H_2O$. To a stirred solution of 64.0 g (0.0200 mol) of $K_8SiW_{11}O_{39}\cdot{\sim}13H_2O$ in 125 mL of hot water (90 °C) is added in small portions 7.58 g (0.0202 mol) of solid $Al(NO_3)_3\cdot 9H_2O$. After completion of the addition, the solution is heated for 10 min and then cooled and filtered. To the cold (5 °C) filtrate is added twice its volume of cold methanol. The precipitated white salt is filtered off, washed with a 2:1 (v/v) methanol/water mixture, and recrystallized three times from warm water (50–60 °C), to which methanol is added until the salt begins to precipitate. After filtering, the salt is air-dried.

$K_5GeAl(OH_2)W_{11}O_{39}\cdot{\sim}11H_2O$. This preparation is similar to that of the preceding salt, with the same amounts of $Al(NO_3)_3\cdot 9H_2O$ and $K_8GeW_{11}O_{39}\cdot{\sim}12H_2O$.

$[C(NH_2)_3]_4AsAl(OH_2)W_{11}O_{39}\cdot{\sim}8H_2O$. A 3.12-g (0.0100-mol) sample of Na_2HAsO_4 and 36.3 g (0.110 mol) of $Na_2WO_4\cdot 2H_2O$ are dissolved separately in 80 mL of hot (80 °C) water each. The hot solutions are mixed, stirred, heated to 90 °C, and acidified with 12.32 mL of 13.8 M HNO_3. The pH of this solution should be between 3.0 and 4.0. A 3.79-g (0.0101-mol) sample of solid $Al(NO_3)_3\cdot 9H_2O$ is added in small portions. The solution is heated for 5 min and filtered while still hot. The addition of a small excess of a concentrated solution of guanidinium nitrate provokes the immediate precipitation of a white salt, that is filtered, washed with cold water, and recrystallized twice from hot (90 °C) water.

$[C(NH_2)_3]_4PAl(OH_2)W_{11}O_{39}\cdot{\sim}11H_2O$. This procedure is similar to that of $SiAlW_{11}$, with the same amount of $Al(NO_3)_3\cdot 9H_2O$ and 64.5 g (0.0200 mol) of $K_7PW_{11}O_{39}\cdot{\sim}15H_2O$. The guanidinium salt is precipitated and recrystallized as described above.

$K_6BAl(OH_2)W_{11}O_{39}\cdot{\sim}14H_2O$. Because of the relative instability of the $BW_{11}O_{39}{}^{9-}$ anion, the order of addition is inversed: to a hot (90 °C) solution of 3.79 g (0.0101 mol) of $Al(NO_3)_3\cdot 9H_2O$ in 50 mL of water is added in one time 32.0 g (0.0100 mol) of $K_9BW_{11}O_{39}\cdot{\sim}10H_2O$, with vigorous stirring. After 5 to 10 min, all $K_9BW_{11}O_{39}\cdot{\sim}10H_2O$ is dissolved and reacted; the remaining white insoluble solid (paradodecatungstate, unavoidable impurity contained in the $K_9BW_{11}O_{39}$ salt) is filtered off after the solution is rapidly cooled to room temperature. To the filtrate is added twice its volume of cold methanol (5 °C). The precipitated white solid is filtered, washed with a cold 1:1 (v/v) water/methanol mixture, and rapidly recrystallized from warm (70 °C) water.

$K_7P_2Al(OH_2)W_{17}O_{61}\cdot{\sim}22H_2O$. To a stirred suspension of 29.5 g (0.006 00 mol) of $K_{10}P_2W_{17}O_{61}\cdot{\sim}20H_2O$ in 100 mL of hot (85 °C) water is gradually added 2.27 g (0.006 06 mol) of solid $Al(NO_3)_3\cdot 9H_2O$. The suspended fraction of $K_{10}P_2W_{17}O_{61}$ dissolves slowly, while the solution is heated to 95 °C and slowly evaporated to ca. 50 mL. When the solution is cooled to 2 °C, the sought-after white salt crystallizes. It is filtered, washed with a 1:1 (v/v) methanol/water mixture, and recrystallized thrice from hot (90 °C) water. The yield may be increased considerably by applying the methanol precipitation procedure described above.

$K_7As_2Al(OH_2)W_{17}O_{61}\cdot{\sim}20H_2O$. This preparation is analogous to that of the preceding salt, with the same amount of $Al(NO_3)_3\cdot 9H_2O$ and 29.6 g of $K_{10}As_2W_{17}O_{61}\cdot{\sim}21H_2O$. The reaction takes place more

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slowly (ca. 30 min instead of ca. 15 min).

Gallatoheteropolytungstates. The preparations are analogous to those of the aluminum-containing ions, apart from the use of an aqueous solution of the Ga(III) ion. A detailed example is given below.

$K_5SiGa(OH_2)W_{11}O_{39}\cdot\sim 15H_2O$. To a hot (90 °C) stirred solution of 32.0 g (0.0100 mol) of $K_8SiW_{11}O_{39}\cdot 13H_2O$ in 60 mL of water is added dropwise a solution of 1.78 g (0.0101 mol) of $GaCl_3$ in 20 mL of water. After each addition a transient precipitate appears that redissolves before the next drop is added. After completion of the addition the solution is heated for 5 to 10 min. The excess gallium precipitates, presumably as $Ga(OH)_3$, and is filtered off, after cooling of the solution, on a PVC membrane filter. The filtrate is treated with twice its volume of cold (5 °C) methanol. The resulting precipitate is filtered, washed with a 1:1 (v/v) methanol/water mixture, and redissolved in warm (50 °C) water; after dissolution, methanol is added until a white precipitate appears. After the mixture is cooled to 2 °C, the precipitate is filtered and recrystallized twice in the same way. It is then air-dried.

Indatoheteropolytungstates. The preparation of indium-containing heteropolytungstates resembles closely that of the gallato anions; it is somewhat more complicated because of the tendency of In(III) ions to function as countercations. A detailed example is given below.

$K_5SiIn(OH_2)W_{11}O_{39}\cdot\sim 10H_2O$. To a stirred solution of 32.0 g (0.0100 mol) of $K_8SiW_{11}O_{39}\cdot\sim 13H_2O$ in 60 mL of hot water (90 °C) is added dropwise a solution of 2.23 g (0.0101 mol) of $InCl_3$ in 20 mL of water. After each addition a transient precipitate appears that redissolves before the next drop is added. After completion of the addition, the solution is heated for 10 min. Most of the excess indium precipitates, presumably as a basic chloride, and is filtered off, after cooling, on a PVC membrane filter. To the filtrate is added twice its volume of cold (5 °C) methanol. The precipitated white salt, that often first separates as a viscous oil before solidifying after cooling to 2 °C, is filtered and washed with a 1:1 (v/v) methanol/water mixture. It is redissolved in water at room temperature and passed on an Amberlite IR-120 cation-exchange column in K^+ form to remove the remaining excess indium that partly replaces potassium as countercation. The resulting dilute solution is evaporated until the indatotungstosilicate anion concentration is ca. 0.15 M. Twice the volume of methanol is then added (at 5 °C), and the precipitated salt is filtered and recrystallized twice as described for the gallatoheteropolytungstates.

Thallatoheteropolytungstates. As hydrolysis of the thallium(III) ion successfully competes with the addition reaction at pH values above 3.5, the heteropolytungstate solutions have to be buffered with acetic acid just before the addition reaction is carried out. Examples of preparations that otherwise are similar to those of the indatoheteropolyanions are given below. Most syntheses are carried out at pH 3.2.

$K_5SiTl(OH_2)W_{11}O_{39}\cdot\sim 10H_2O$. To an almost boiling (100 °C) solution of 32.0 g (0.0100 mol) of $K_8SiW_{11}O_{39}\cdot\sim 13H_2O$ in 100 mL of water, brought to pH 3.2 with glacial acetic acid, is added dropwise a solution of 3.98 g (0.0102 mol) of $Tl(NO_3)_3$ in 15 mL of water. A transient precipitate appears after each drop that redissolves slowly before the next drop is added. Toward the end of the addition some thallium(III) hydrolyzes and does not redissolve. The pH of the solution after completion of the addition should be between 2.5 and 3.0. The solution is alkalinized carefully with 1 M NaOH to pH 4.5 and cooled rapidly. The excess thallium is filtered off on a PVC membrane filter. To the filtrate is added twice its volume of cold (5 °C) methanol. The precipitated yellowish white salt is subjected to the ion-exchange treatment described above and recrystallized twice.

$K_6BTl(OH_2)W_{11}O_{39}\cdot\sim 12H_2O$. To 3.98 g (0.0102 mol) of $Tl(NO_3)_3$ dissolved in 100 mL of warm water (50 °C) is added 32.0 g (0.0100 mol) of solid $K_9BW_{11}O_{39}\cdot\sim 10H_2O$. The latter slowly dissolves and partly reacts with thallium(III) and partly decomposes in the acidic solution. After dissolution is complete, the pH is rapidly raised to 5.0 by adding 1 M NaOH, and the solution is cooled to 2 °C. A considerable amount of insoluble material is filtered off, and the filtrate is evaporated slowly to yield off-white crystals of the sought salt. These are filtered, washed, and purified by the ion-exchange method described above and then recrystallized twice.

Hydroxo Ligand Complexes. Hydroxo ligand heteropolytungstates of formula $XM(OH)W_{11}O_{39}{}^{6-}$ (X = Si, Ge; M = Al, Ga, In, Tl) and $X_2M(OH)W_{17}O_{61}{}^{8-}$ (X = P(V), As(V); M = as before) may be isolated as the potassium salt by the following general method: To an aqueous ca. 1 M solution of the chosen "regular" potassium salt is slowly added the stoichiometric amount of KOH, dissolved in some water (i.e., 1 mol/mol of aquo ligand anion). The resulting solution is slowly evaporated, and the separated solid is filtered, washed with some ice-cold water, and air-dried. Alternatively, the salt may be precipitated by adding an equal volume of ethanol to the solution.

Reduced Gallatoheteropolytungstates. **$K_7SiGa(OH_2)W^V{}_2W^{VI}{}_9O_{39}\cdot\sim 15H_2O$.** A ca. 0.01 M aqueous solution of the "regular" (fully oxidized) salt, buffered at pH 4.0 with acetic acid, is reduced electrolytically under a nitrogen atmosphere at a controlled potential of −0.85 V vs. SCE with a mercury pool cathode. After the degree of reduction is checked (see next section), one precipitates a dark blue crystalline salt by adding finely divided solid KCl to the solution. It is filtered off, washed with some ice-cold water, and dried in a nitrogen stream.

$K_7GeGa(OH_2)W^V{}_2W^{VI}{}_9O_{39}\cdot\sim 16H_2O$. This preparation is similar to that of the preceding salt. The electrolysis is carried out at −0.75 V vs. SCE and at a pH of 3.0.

$K_9P_2Ga(OH_2)W^V{}_2W^{VI}{}_{15}O_{61}\cdot\sim 28H_2O$. This preparation is similar to those of the preceding salts. When a 0.01 M solution is used, the reduced form crystallizes during the electrolysis. Electrolysis conditions: −0.60 V vs. SCE at pH 3.0.

$K_9As_2Ga(OH_2)W^V{}_2W^{VI}{}_{15}O_{61}\cdot\sim 29H_2O$. This preparation is similar to those of the preceding salts. The reduced form is again insoluble. Electrolysis conditions: −0.55 V vs. SCE at pH 3.0.

Acids of Lacunary and Substituted Heteropolytungstate Anions. Solutions of these acids were prepared by an ion-exchange method: A salt solution, the concentration of which varies from 0.02 M (guanidinium salt) to 0.05 M (potassium salt), is passed on an Amberlite IR-120 cation-exchange column in H^+ form; the column is cooled to 2.0 ± 0.5 °C by surrounding it with a water and ice-containing jacket. The operation is repeated on the eluate. The concentration of the final solution is determined by calcination at 600 °C of 1 aliquot evaporated to dryness; the residue only consists of oxides according to its X-ray powder diffractogram.

Analytical data for all isolated salts and for the acid solutions are presented in Table I.

Analyses. Tungsten, aluminum, gallium, and indium were determined gravimetrically as their 8-hydroxyquinoline complexes.[33,34] Indium was also weighed as the diethyldithiocarbamate[35] or determined volumetrically (back-titration of an excess of EDTA with $ZnCl_2$[36]). Thallium was determined gravimetrically as the complex with diantipyrylpropylmethane[37] after tungsten was precipitated and removal as WO_3 in strongly acidic solution.

Analysis of the central atoms consisted of determining silicon as SiO_2, of phosphorus as $MgNH_4PO_4$, of germanium as GeO_2, of arsenic by the silver dithiocarbamate method after As was transformed to AsH_3,[39] and of boron by atomic emission spectroscopy, by using a Perkin-Elmer 5000 ICP instrument. The degree of reduction of reduced polyanions was determined by back-titrating an excess of iron(III) added to 1 aliquot of the solution, with bichromate.

Potassium, guanidinium, and tetraalkylammonium ions were precipitated as the tetraphenylborate complex at an appropriate pH.[33,38] Except for the last-mentioned method, every analysis was preceded by alkaline destruction of the polyanion. The water contents was determined by thermogravimetry.

Physical Measurements. UV-visible spectra were recorded on a Jobin & Yvon "Maroc" and a Cary 14 spectrophotometer. IR spectra (mainly with KBr pellets) were obtained with a Perkin-Elmer 356 instrument. Conductivity and potentiometry measurements were carried out with a Tacussel CD 6, Heath EU-302A, or Philips PW 9408 instrument. Polarographic experiments were conducted on a Radiometer PO4 DME polarometer; cyclic voltammograms were obtained with an MPI system and a polished graphite electrode (Princeton Instruments).

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Table I. Analytical Results

		found (calcd)					
	yield,[a] %	% cation	% central atom[b]	% group 3A element	% W	% H_2O[c]	deg of redn[e]
Salts							
$K_5SiAl(OH_2)W_{11}O_{39}\cdot 13.4H_2O$	80	5.95 (6.19)	0.868 (0.881)	0.884 (0.855)	64.11 (64.07)	7.65	
$K_5GeAl(OH_2)W_{11}O_{39}\cdot 12.6H_2O$	75	6.04 (6.14)	2.310 (2.278)	0.853 (0.847)	63.51 (63.46)	7.13	
$[C(NH_2)_3]_4PAl(OH_2)W_{11}O_{39}\cdot 9.3H_2O$	70	7.65 (7.68)	1.012 (0.989)	0.892 (0.862)	64.03 (64.60)	5.36	
$[C(NH_2)_3]_4AsAl(OH_2)W_{11}O_{39}\cdot 8.3H_2O$	65	7.57 (7.62)	2.328 (2.374)	0.876 (0.855)	63.86 (64.07)	4.75	
$K_6BAl(OH_2)W_{11}O_{39}\cdot 14.4H_2O$	70	7.18 (7.34)	0.327 (0.338)	0.843 (0.846)	63.37 (63.27)	8.12	
$K_7P_2Al(OH_2)W_{17}O_{61}\cdot 22.4H_2O$	80	5.79 (5.60)	1.262 (1.268)	0.549 (0.552)	64.77 (63.97)	8.26	
$K_7As_2Al(OH_2)W_{17}O_{61}\cdot 20.1H_2O$	70	5.62 (5.55)	3.021 (3.039)	0.545 (0.547)	64.36 (63.38)	7.33	
$K_5SiGa(OH_2)W_{11}O_{39}\cdot 14.9H_2O$	80	6.15 (6.06)	0.848 (0.871)	2.178 (2.162)	62.95 (62.70)	8.30	
$K_5GeGa(OH_2)W_{11}O_{39}\cdot 14.9H_2O$	80	6.05 (5.98)	2.178 (2.219)	2.110 (2.132)	62.09 (61.85)	8.18	
$K_4PGa(OH_2)W_{11}O_{39}\cdot 13.9H_2O$	40	4.86 (4.93)	0.968 (0.977)	2.201 (2.198)	63.26 (63.76)	7.89	
$[C(NH_2)_3]_4AsGa(OH_2)W_{11}O_{39}\cdot 11.0H_2O$	60	7.32 (7.40)	2.348 (2.307)	2.155 (2.147)	62.46 (62.27)	6.11	
$K_6BGa(OH_2)W_{11}O_{39}\cdot 17.3H_2O$	80	6.81 (7.13)	0.341 (0.328)	2.177 (2.118)	61.68 (61.45)	9.47	
$K_7P_2Ga(OH_2)W_{17}O_{61}\cdot 20.0H_2O$	90	5.72 (5.60)	1.287 (1.268)	1.424 (1.427)	64.01 (63.98)	7.39	
$K_7As_2Ga(OH_2)W_{17}O_{61}\cdot 22.0H_2O$	90	5.65 (5.45)	2.969 (2.991)	1.422 (1.392)	61.73 (62.39)	7.92	
$K_5SiIn(OH_2)W_{11}O_{39}\cdot 10.4H_2O$	75	6.45 (6.13)	0.863 (0.880)	3.96 (3.60)	63.20 (63.40)	5.86	
$K_5GeIn(OH_2)W_{11}O_{39}\cdot 12.4H_2O$	70	6.03 (5.98)	2.207 (2.220)	3.88 (3.51)	62.10 (61.85)	6.80	
$K_4PIn(OH_2)W_{11}O_{39}\cdot 11.9H_2O$	50	5.33 (4.92)	1.003 (0.973)	3.50 (3.61)	63.40 (63.56)	6.76	
$[N(CH_3)_4]_4AsIn(OH_2)W_{11}O_{39}\cdot 11.6H_2O$	50	9.39 (8.89)	2.261 (2.230)	3.10 (3.42)	60.70 (60.20)	6.21	
$K_6BIn(OH_2)W_{11}O_{39}\cdot 12.2H_2O$	60	6.95 (7.23)	0.325 (0.333)	3.63 (3.54)	62.48 (62.34)	6.77	
$K_7P_2In(OH_2)W_{17}O_{61}\cdot 17.2H_2O$	80	6.09 (5.61)	1.254 (1.270)	2.38 (2.35)	63.80 (64.05)	6.35	
$K_7As_2In(OH_2)W_{17}O_{61}\cdot 18.7H_2O$	75	5.64 (5.48)	3.028 (3.000)	2.39 (2.30)	62.41 (62.58)	6.74	
$K_5SiTl(OH_2)W_{11}O_{39}\cdot 9.7H_2O$	70	5.90 (5.98)	0.851 (0.860)	6.31 (6.26)	61.95 (61.91)	5.34	
$K_5GeTl(OH_2)W_{11}O_{39}\cdot 11.0H_2O$	60	5.88 (5.86)	2.198 (2.176)	6.19 (6.13)	60.24 (60.63)	5.95	
$K_4PTl(OH_2)W_{11}O_{39}\cdot 12.0H_2O$	40	4.59 (4.78)	1.003 (0.947)	6.44 (6.25)	62.09 (61.81)	6.59	
$[C(NH_2)_3]_4AsTl(OH_2)W_{11}O_{39}\cdot 10.9H_2O$	75	7.42 (7.11)	2.231 (2.217)	5.89 (6.05)	60.23 (59.84)	5.79	
$K_6BTl(OH_2)W_{11}O_{39}\cdot 12.1H_2O$	15	7.21 (7.04)	0.316 (0.324)	6.01 (6.13)	61.14 (60.69)	6.56	
$K_7P_2Tl(OH_2)W_{17}O_{61}\cdot 17.0H_2O$	60	5.57 (5.51)	1.258 (1.248)	4.16 (4.12)	62.73 (62.94)	6.17	
$K_7As_2Tl(OH_2)W_{17}O_{61}\cdot 18.9H_2O$	50	5.48 (5.38)	3.002 (2.945)	4.18 (4.02)	61.68 (61.43)	6.69	
$K_6SiAl(OH)W_{11}O_{39}\cdot 8.5H_2O$	90[d]	7.58 (7.55)	0.884 (0.904)	0.864 (0.869)	64.82 (65.11)	4.92	
$K_6GeAl(OH)W_{11}O_{39}\cdot 10.4H_2O$	90[d]	7.42 (7.37)	2.237 (2.279)	0.854 (0.847)	63.56 (63.50)	5.89	
$K_8P_2Al(OH)W_{17}O_{61}\cdot 21.4H_2O$	95[d]	6.43 (6.38)	1.248 (1.263)	0.552 (0.550)	63.98 (63.71)	7.86	
$K_8As_2Al(OH)W_{17}O_{61}\cdot 23.1H_2O$	95[d]	6.19 (6.23)	2.960 (2.982)	0.544 (0.537)	62.01 (62.20)	8.28	
$K_6SiGa(OH)W_{11}O_{39}\cdot 11.5H_2O$	95[d]	7.29 (7.33)	0.886 (0.877)	2.189 (2.177)	63.02 (63.14)	6.48	
$K_6GeGa(OH)W_{11}O_{39}\cdot 15.0H_2O$	90[d]	6.97 (7.09)	2.228 (2.192)	2.112 (2.106)	60.97 (61.08)	8.16	
$K_8P_2Ga(OH)W_{17}O_{61}\cdot 20.4H_2O$	90[d]	6.44 (6.34)	1.261 (1.256)	1.404 (1.414)	63.78 (63.39)	7.46	
$K_8As_2Ga(OH)W_{17}O_{61}\cdot 21.2H_2O$	90[d]	6.29 (6.22)	3.011 (2.977)	1.379 (1.385)	62.04 (62.10)	7.58	
$K_6SiIn(OH)W_{11}O_{39}\cdot 9.5H_2O$	85[d]	7.35 (7.30)	0.856 (0.874)	3.56 (3.58)	62.58 (62.96)	5.33	
$K_6GeIn(OH)W_{11}O_{39}\cdot 12.2H_2O$	85[d]	7.24 (7.10)	2.218 (2.197)	3.42 (3.48)	61.42 (61.20)	6.63	
$K_8P_2In(OH)W_{17}O_{61}\cdot 19.8H_2O$	90[d]	6.34 (6.30)	1.239 (1.248)	2.29 (2.31)	62.48 (62.95)	7.18	
$K_8As_2In(OH)W_{17}O_{61}\cdot 20.2H_2O$	90[d]	6.23 (6.18)	3.01 (2.96)	2.26 (2.27)	61.45 (61.77)	7.19	
$K_7SiGa(OH_2)W^{V}_{2}W^{VI}_{9}O_{39}\cdot 15.1H_2O$	70[d]	8.30 (8.27)	0.855 (0.849)	2.12 (2.11)	60.92 (61.14)	8.23	2.00
$K_7GeGa(OH_2)W^{V}_{2}W^{VI}_{9}O_{39}\cdot 16.2H_2O$	60[d]	8.16 (8.12)	2.147 (2.153)	2.09 (2.07)	59.58 (59.97)	8.66	1.99
$K_9P_2Ga(OH_2)W^{V}_{2}W^{VI}_{15}O_{61}\cdot 28.1H_2O$	90[d]	6.88 (6.89)	1.197 (1.212)	1.35 (1.33)	61.22 (61.17)	9.91	1.99
$K_9As_2Ga(OH_2)W^{V}_{2}W^{VI}_{15}O_{61}\cdot 29.7H_2O$	80[d]	6.68 (6.73)	2.844 (2.867)	1.33 (1.33)	60.14 (59.80)	10.24	2.00
Acid Solutions							
$H_5SiAl(OH_2)W_{11}O_{39}$	i	5.00 (5.00)[f]	g	1.003 (1.014)[h]	76.10 (75.99)[h]		
$H_5GeAl(OH_2)W_{11}O_{39}$	i	5.00 (5.00)[f]	g	0.997 (0.997)[h]	75.26 (74.74)[h]		
$H_6BAl(OH_2)W_{11}O_{39}$	i	5.70 (6.00)[f]	g	1.003 (1.024)[h]	75.24 (76.72)[h]		
$H_4PAl(OH_2)W_{11}O_{39}$	i	3.80 (4.00)[f]	g	0.745 (1.010)[h]	75.82 (75.68)[h]		
$H_4AsAl(OH_2)W_{11}O_{39}$	i	4.00 (4.00)[f]	g	0.984 (0.993)[h]	74.68 (74.46)[h]		
$H_7P_2Al(OH_2)W_{17}O_{61}$	i	6.84 (7.00)[f]	g	0.662 (0.653)[h]	75.31 (75.60)[h]		
$H_7As_2Al(OH_2)W_{17}O_{61}$	i	6.98 (7.00)[f]	g	0.653 (0.646)[h]	74.48 (74.80)[h]		
$H_5SiGa(OH_2)W_{11}O_{39}$	i	5.02 (5.00)[f]	g	2.572 (2.578)[h]	74.50 (74.79)[h]		
$H_5GeGa(OH_2)W_{11}O_{39}$	i	5.00 (5.00)[f]	g	2.528 (2.536)[h]	73.78 (73.57)[h]		
$H_6BGa(OH_2)W_{11}O_{39}$	i	5.90 (6.00)[f]	g	2.625 (2.603)[h]	75.72 (75.49)[h]		
$H_4PGa(OH_2)W_{11}O_{39}$	i	3.85 (4.00)[f]	g	2.562 (2.568)[h]	73.89 (74.49)[h]		
$H_4AsGa(OH_2)W_{11}O_{39}$	i	4.18 (4.00)[f]	g	2.533 (2.527)[h]	73.11 (73.30)[h]		
$H_7P_2Ga(OH_2)W_{17}O_{61}$	i	7.00 (7.00)[f]	g	1.662 (1.669)[h]	74.96 (74.82)[h]		
$H_7As_2Ga(OH_2)W_{17}O_{61}$	i	7.00 (7.00)[f]	g	1.647 (1.635)[h]	72.91 (73.28)[h]		
$H_5SiIn(OH_2)W_{11}O_{39}$	i	5.10 (5.00)[f]	g	4.15 (4.18)[h]	73.28 (73.56)[h]		
$H_5GeIn(OH_2)W_{11}O_{39}$	i	5.25 (5.00)[f]	g	4.14 (4.11)[h]	72.12 (72.39)[h]		
$H_6BIn(OH_2)W_{11}O_{39}$	i	6.00 (6.00)[f]	g	4.21 (4.22)[h]	74.47 (74.24)[h]		
$H_4PIn(OH_2)W_{11}O_{39}$	i	4.00 (4.00)[f]	g	4.08 (4.16)[h]	73.18 (73.27)[h]		
$H_4AsIn(OH_2)W_{11}O_{39}$	i	3.80 (4.00)[f]	g	3.98 (4.09)[h]	72.49 (72.12)[h]		
$H_7P_2In(OH_2)W_{17}O_{61}$	i	7.00 (7.00)[f]	g	2.74 (2.72)[h]	73.86 (74.02)[h]		
$H_7As_2In(OH_2)W_{17}O_{61}$	i	7.00 (7.00)[f]	g	2.69 (2.66)[h]	72.39 (72.51)[h]		
$H_5SiTl(OH_2)W_{11}O_{39}$	i	5.05 (5.00)[f]	g	7.22 (7.20)[h]	71.38 (71.24)[h]		
$H_5GeTl(OH_2)W_{11}O_{39}$	i	5.10 (5.00)[f]	g	7.14 (7.09)[h]	70.02 (70.14)[h]		
$H_6BTl(OH_2)W_{11}O_{39}$	i	6.00 (6.00)[f]	g	7.20 (7.26)[h]	72.30 (71.88)[h]		
$H_4PTl(OH_2)W_{11}O_{39}$	i	3.90 (4.00)[f]	g	7.09 (7.17)[h]	71.34 (70.97)[h]		
$H_4AsTl(OH_2)W_{11}O_{39}$	i	4.00 (4.00)[f]	g	7.03 (7.06)[h]	70.12 (69.89)[h]		
$H_7P_2Tl(OH_2)W_{17}O_{61}$	i	7.05 (7.00)[f]	g	4.77 (4.74)[h]	72.38 (72.49)[h]		
$H_7As_2Tl(OH_2)W_{17}O_{61}$	i	7.05 (7.00)[f]	g	4.70 (4.65)[h]	71.19 (71.04)[h]		

[a] After recrystallization. [b] Defined as the atom or atoms in tetrahedral site or sites (Si, Ge, B, P, or As). [c] Excluding the aquo (or hydroxo) ligand of the group 3A element. [d] With respect to the initial aquo ligand salt or, respectively, the fully oxidized salt. [e] Expressed in number of electrons per anion. [f] Expressed as number of mol of free protons/mol of polyanion. [g] Not determined. [h] With respect to the mass of the calcined residue. [i] Not applicable.

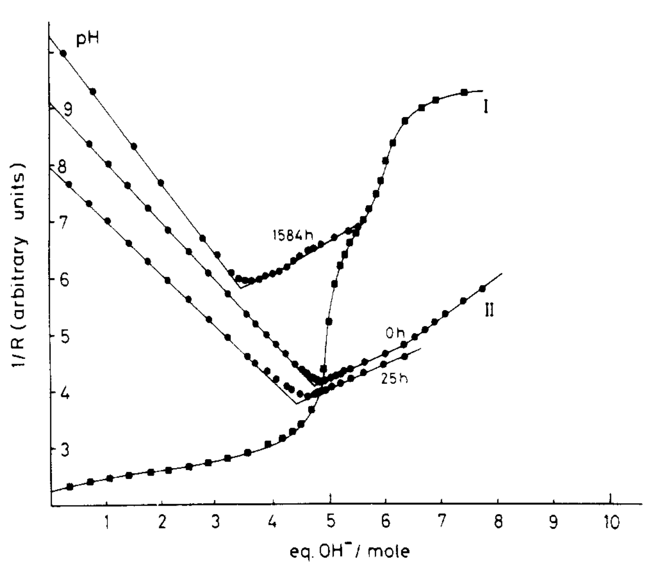

Figure 2. Neutralization of a 1.30 × 10^{-3} M solution of $H_5GeAl(OH_2)W_{11}O_{39}$: I, direct potentiometric titration, immediately after preparation; II, direct conductometric titration, immediately after preparation, and at various moments afterwards (solution kept at 5 °C).

Crystallographic measurements were performed with a Siemens Kristalloflex 700 equipped with a Stoe reciprocal lattice explorer.

Results and Discussion

Stability. The heteropolyanion's tungsten–oxygen framework, although compact, is relatively flexible; comparable W–O distances vary appreciably, depending on their spatial relation to the lacuna (cf. the broad absorption peaks in the infrared spectra of the lacunary compounds[40]). Conversely, the lacuna accommodates cations of widely varying size, ranging from 53 pm (Al^{3+}) to at least 88 pm (Tl^{3+})[41] ionic radius; the corresponding radius of the W^{6+} ion is 58 pm. The insertion reaction proceeds markedly slower for both indium and thallium, however; their ionic radii are probably near the upper limit; likewise their electronegativity is lower. The formation constants are also smaller than for the lighter group 3A elements, although still quite high. The molar variation method was used to verify the formation of 1:1 complexes for every reaction and to estimate the formation constants of the resulting complexes. The results clearly show the formation of 1:1 complexes only; the method fails to give quantitative information on the formation constants, except that they are all larger than 10^4; qualitatively, however, differences between the reactions involving indium and, especially, thallium, and those with aluminum and gallium could be observed.

Once formed, these substituted polyanions are remarkably resistant toward decomposition or rearrangement, especially in acidic solution. This behavior is in marked contrast with that of their homologues that contain bivalent metal ions.[14,34]. In order to quantitatively study their behavior as a function of pH, it is preferable to start with the corresponding acids.

The stability of the acids and their behavior upon neutralization is studied by conductometric and potentiometric methods. Both techniques are complementary, especially when used in different ways: first, by rapid direct and complete titration; second, by measuring separate samples that have been alkalinized stepwise. The first method yields information on the proton neutralization mainly, the second one on the stability of the anion itself. Figures 2 and 3 show some examples of the results obtained.

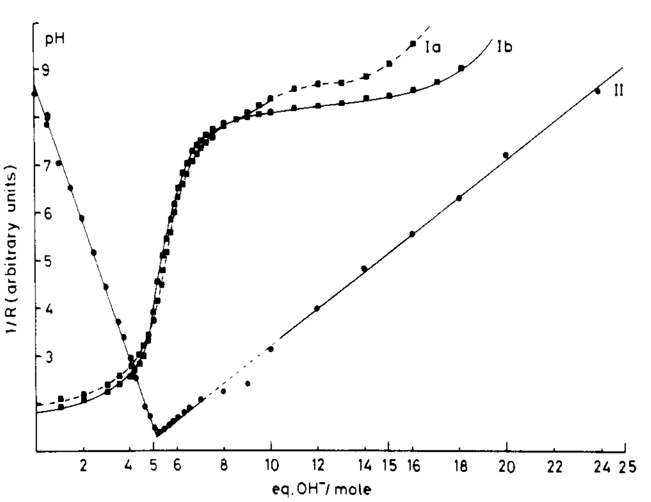

Figure 3. Neutralization and alkaline decomposition of a 1.25 × 10^{-3} M solution of $H_5SiGa(OH_2)W_{11}O_{39}$: Ia, potentiometric titration of separate, successively more alkalized samples, immediately after preparation; Ib, as Ia but measured after ten days (solutions kept at 5 °C); II, immediate direct conductometric titration.

Typically the acids are stable in dilute aqueous solution for at least 1 week at 5 °C. Decomposition is accelerated by concentrating the solution (it is not possible to isolate the solid acids in this manner) or by raising the temperature. As a group, only the aluminum derivatives are fairly unstable, as are most metallotungstoborates. The destabilization of the aluminum polytungstates may be rationalized in terms of a preferential protonation of the comparatively more negative oxygen octahedron around the aluminum atom. This would cause a decrease of the distortion of this octahedron and thus a decrease in the stabilization energy of the aluminum ion with respect to the "simple" hexahydrated ion in solution; this decrease should be more important for aluminum than for the heavier group 3A elements. The relative instability of the tungstoborates may be attributed to the fact that the probable primary decomposition product, the $BW_{11}O_{39}^{9-}$ ion, is not very stable itself and does not exclusively transform to $BW_{12}O_{40}^{5-}$; it is then not possible to arrive at an equilibrium state for these anions, in contrast to the others, which form stable XW_{12} ions. Also, the higher negative charge of the BMW_{11} ions promotes the protonation of the outer oxygens of the octahedron surrounding the group 3A element, thus facilitating its ejection (see above). Conductometric titrations show that the tungstoborate acids contain three or four protons that are more strongly bound than the others; all other acids possess protons that are all equally, and strongly, acidic (see below).

The nature of the decomposition products can often be determined by polarography. Usually the XW_{11} and X_2W_{17} ions, initially formed, evolve to the XW_{12} and X_2W_{18} species. For $GeAlW_{11}$, e.g., the overall decomposition reaction may be written as eq 1. This scheme is supported by polarographic

$$12GeAl(OH_2)W_{11}O_{39}^{5-} + 52H^+ + 34H_2O \rightarrow 11GeW_{12}O_{40}^{4-} + 12Al(H_2O)_6^{3+} + GeO_2 \quad (1)$$

estimation of the amount of GeW_{12} formed, and by the fact that, e.g., after 68 days at 5 °C, a 5 × 10^{-3} M solution of the $GeAlW_{11}$ acid was found to contain 34.6% of the total amount of aluminum in the free hexahydrated form. Neglecting the acidity of the "free" aluminum, this would correspond to a consumption of 0.346 × 52/12 = 1.50 mol of H^+/mol of anion. The experimental value is 1.62 mol of H^+/mol of $GeAlW_{11}$.

The titrations also show the frequent presence of one or two additional weakly acidic protons. These protons are part of

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(39) Kolthoff, I. M.; Elving, P. J. "Treatise on Analytical Chemistry"; Interscience: New York, 1978; Part II, Vol. 10.

(40) Rocchiccioli-Deltcheff, C.; Thouvenot, R. *J. Chem. Res., Synop.* **1977**, 46.

(41) Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr., Sect. B* **1970**, *B26*, 1076.

the H_2O ligand that completes the hexacoordination around the group 3A element.[18] Their acidity depends to some degree on the group 3A element but more strongly on the central atom, particularly on its charge. From the potentiometric titration curves of the undecatungstates one can estimate the pKa_1's: $AsMW_{11}$, 3–4; PMW_{11}, ~4; $GeMW_{11}$, 5–6; $SiMW_{11}$, 6–7; BMW_{11}, 7–8. A higher charge on the central atom seems to cause a higher acidity of the H_2O ligand protons. For the PMW_{11} and $AsMW_{11}$ anions it is even impossible to distinguish potentiometrically the "free" protons from the H_2O ligand protons. The increase in acidity of these protons may be produced by a shift in the position of the group 3A element toward the center of the anion when the charge on the central atom increases; this would result in a lengthening of the $M-O(H_2)$ bond. Shifts in the frequency of the maxima of the Fe ← O charge-transfer bands with charge changes of the central atom, observed for comparable ferratotungstates, support this hypothesis.[42] The pKa_1 values for the P_2MW_{17} and As_2MW_{17} anions are also fairly low on average, but they vary much more, from about 3 (M = In, Tl) to about 7 (M = Al). This order, although more difficult to rationalize, corresponds to the hydrolysis pK_1 value order of the hexahydrated metal ions.

As the P_2MW_{17} and As_2MW_{17} anions are stable up to pH 8, it is sometimes possible to obtain partial deprotonation of the OH_2 ligand, e.g., for P_2InW_{17}, As_2InW_{17}, P_2TlW_{17}, and As_2TlW_{17}. In these and several other cases,[42] "basic" hydroxo ligand salts can be isolated. The deprotonation reaction is slow and probably complex;[19] the presence of acidic H_2O ligand protons is much more evident when a potentiometric titration curve is obtained after equilibrium is reached, by using the multiple-sample technique.

Resistance to alkaline decomposition strongly depends on the central atom and on the relative stability of the parent lacunary polyanion (see above); the influence of the particular group 3A element is much smaller. The stability order is $AsMW_{11} \sim PMW_{11} < GeMW_{11} < SiMW_{11} \sim BMW_{11} < As_2MW_{17} < P_2MW_{17}$ and follows, grosso modo, the order of the charge on the central atom.[43] Complete decomposition of a 0.01 M solution of pH ~10 takes, at room temperature and in the absence of a background electrolyte, from 1 week to several months. The final decomposition products are WO_4^{2-}, $M(OH)_3$ (mainly), $HSiO_3^-$, $HGeO_3^-$, BO_2^-, HPO_4^-, and $HAsO_4^-$.

Electronic Spectra. As might be expected, all solid salts are white, except for a slight yellow tinge for the indium and thallium compounds. Evidently, no d–d transitions can take place; the UV–visible spectra are characterized mainly by an intense slowly rising broad absorption band at (34–39) × 10^3 cm^{-1} ($\epsilon_{max} \sim 10^5$). This complex W ← O charge-transfer (CT) band[19] is almost identical with that of the parent lacunary compound. For the gallium and, especially, indium and thallium compounds there is also a diffuse extension of the W ← O CT band to longer wavelengths; this "tail", which is responsible for the yellow tinge, may be interpreted as a M(III) → O CT band[19] that in the case of thallium(III) just reaches the visible region. Because of the broadness of this band and its featureless character, a more quantitative treatment is not feasible.

Infrared Spectra. The infrared (IR) spectra of the group 3A element-substituted heteropolytungstates closely resemble those reported of some first-row transition element substituted homologues.[40,44] The conclusions of Rocchiccioli-Deltcheff et al.[40] regarding the tungsten–oxygen framework distortion in these anions and the partial restoration of the symmetry on filling the lacuna are also valid for this series of substituted polyanions. As they have shown, the splitting of the distinctive ν_3 asymmetric stretch vibration frequency of the P–O bonds of the distorted central PO_4 tetrahedron in the PMW_{11} and P_2MW_{17} series is a useful indirect measure of the strength of the $M-O(PO_4)$ bond. A comparison of the splittings observed for the first-row transition element substituted tungstophosphates with those measured for the group 3A element substituted homologues is instructive (see Table II) (for the P_2MW_{17} compounds the variations are much smaller (5–10 cm^{-1})).

Table II. Observed Splittings (cm^{-1}) of the ν_3(P–O) Asymmetric Stretch Frequency in Tungstophosphates

anion[a]	ν_{as}(P–O)	ν_{av}	$\Delta\nu$	anion[a,b]	ν_{as}(P–O)	ν_{av}	$\Delta\nu$
PW_{12}	1080	1080	0	$PMnW_{11}$	1085, 1058	1071	27
PW_{11}	1085, 1040	1062	45	$PFeW_{11}$	1084, 1060	1072	24
$PAlW_{11}$	1090, 1067	1078	23	$PCoW_{11}$	1080, 1060	1070	20
$PGaW_{11}$	1083, 1055	1069	28	$PNiW_{11}$	1068	1068	0
$PInW_{11}$	1086, 1048	1067	35	$PCuW_{11}$	1105, 1065	1085	40
$PTlW_{11}$	1087, 1042	1064	45	$PZnW_{11}$	1098, 1060	1079	38

[a] All measurements were made on KBr pellets of potassium salts of the anions. [b] All data in this column are taken from ref 39.

For first-row transition elements the splitting increases with decreasing ligand field stabilization energy as calculated for octahedral coordination by weak-field ligands (the lacunary anions may be considered as such[45]).[40] Thus, the splitting is large for, say, zinc and copper; in the absence of such a stabilization energy, the splitting is expected to be large for group 3A elements also. The observed splitting is large for indium and thallium but considerably smaller for aluminum and gallium, however; there must be a strong electrostatic interaction between the phosphorus-bound oxygen and these two small and relatively highly charged ions.

Redox Properties. The redox properties of many heteropolyanions, especially the "saturated" ones, have been studied extensively.[4] Many heteropolytungstates and -molybdates can be reduced and reoxidized with complete structure retention. The redox properties of both lacunary and group 3A element substituted heteropolytungstates were investigated by standard dc polarographic and cyclic voltammographic methods in the pH range 1–8, with fresh and aged solutions of ca. 10^{-3} M in polytungstate and 1 M in buffer and supporting electrolyte ($NaClO_4$) concentration.

In Figure 4 a number of half-wave potential ($E_{1/2}$) vs. pH diagrams are assembled. Assigning numbers of electrons to each wave is not always straightforward, mainly because of viscosity changes of the buffer solutions, but this problem can be overcome by continuous comparison with the polarograms of the well-studied metatungstate (H_2W_{12}) anion obtained under identical conditions. From these and similar plots, and the way they change with time, one can draw the following conclusions.

The diagrams of the lacunary complexes are generally similar to those of their "saturated" homologues,[46] except for BW_{11}, the stability range of which is very limited; however, the $E_{1/2}$ values of corresponding waves are on average 0.20 V more negative for the lacunary complexes. The negative charge of these ions is four units higher than that of their "saturated" homologues, and this shift may be rationalized in terms of a simple electrostatic model,[47] in which the anions are considered as negatively charged spheres. The model furnishes a value of –0.04 V per unit of charge change for the

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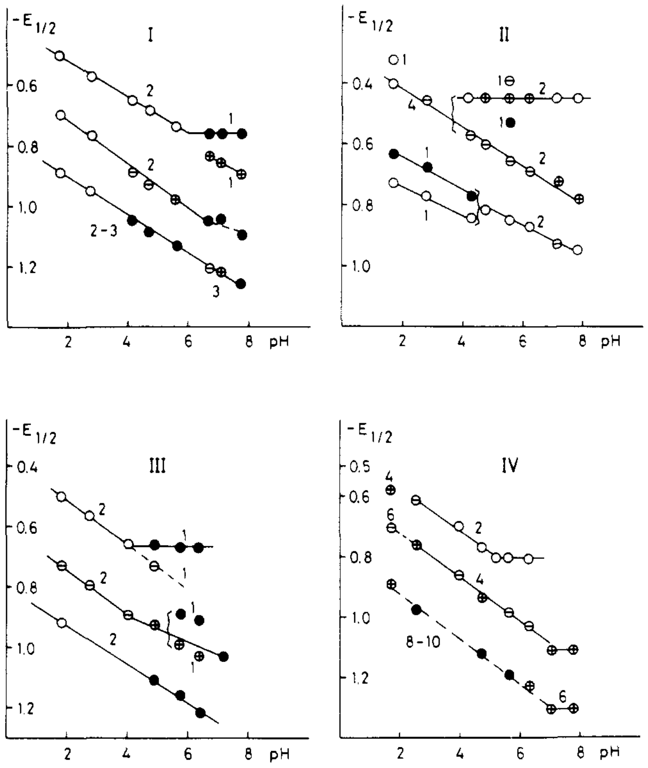

Figure 4. Polarographic half-wave potential (in V vs. SCE) vs. pH diagrams, measured immediately after preparation of solutions of (I) $K_5GeAl(OH_2)W_{11}O_{39}$, (II) $K_7As_2Al(OH_2)W_{17}O_{61}$, (III) $K_4PGa(OH_2)W_{11}O_{39}$, and (IV) $K_5SiIn(OH_2)W_{11}O_{39}$. The fullness of the circles indicates qualitatively the degree of polarographic reversibility of the reduction wave: ○, (approximately) reversible; ⊖, fairly reversible; ⊕, hardly reversible; ●, (almost) irreversible.

change in $E_{1/2}$ value, in good agreement with the measured value of 0.20/4 = 0.05 V per charge unit change. The presence of a "hole" in the structure seems to have but little influence in itself. The application of the Ilkovic and Stokes–Einstein equations for example yields values of 560 pm for the hydrodynamic radii of XW_{12},[47] XW_{11}, and XMW_{11} anions and of 1000 pm for the X_2W_{18}, X_2W_{17}, and X_2MW_{17} species.[47,55]

The slope of the $E_{1/2}$ vs. pH plots is approximately −0.090 V/pH for the first two-electron wave of the XW_{11} anions and −0.060 V/pH for most other waves. This implies that the reduction is accompanied by protonation (one to two protons per electron). This prevents a charge build-up of the anion, that would otherwise be destabilized.[47] Splitting of two-electron waves in two pH-independent one-electron waves, common for most saturated heteropolyanions,[48-50] is infrequent, not being favored by the increased ion charge. There are usually two (XMW_{11}) or three (X_2MW_{17}) two-electron waves for each substituted anion. This is in contrast to the saturated anions that show at least three (XW_{12}) and sometimes four (X_2W_{18}) two-electron waves. There is evidence[50] that for each two-electron wave both electrons are taken up by two tungsten atoms of the same W_3O_{13} group. It is then reasonable to suppose that in the lacunary and group 3A element substituted polyanions (see below) the first two electrons are taken up by the W_3O_{13} group trans to the lacuna, the next pair(s) by the adjacent W_3O_{13} groups, and none by the lacunary or substituted group. The multielectron wave often found at more negative potentials probably involves a destructive reduction of the polyanion.

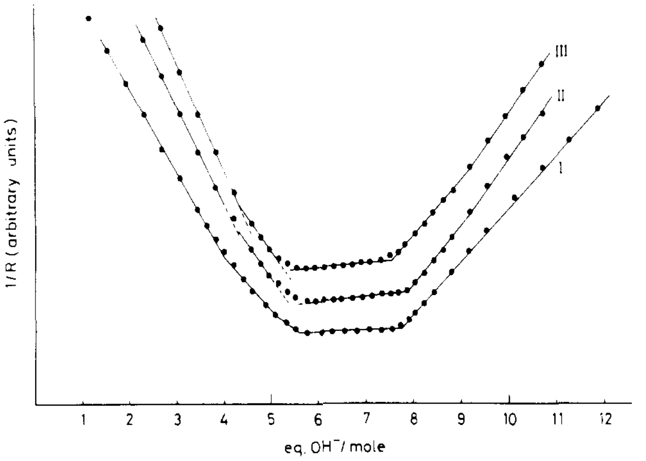

Figure 5. Conductometric neutralization curves for a 1.20×10^{-3} M solution of $H_8SiW_{11}O_{39}$: I, immediately after preparation of the acid; II, after 1 day at 5 °C; III, after 10 days at 5 °C.

The diagrams of the substituted polyanions are generally very similar to those of the lacunary homologues. The effect of the presence of the group 3A element is surprisingly small. In terms of the above-mentioned electrostatic model this would mean that the effective charge of the tungsten–oxygen "cluster" changes little. This is also noted for bi- or trivalent transition element substituted polytungstates,[20,34] and it may be related to the retention of the tungsten–oxygen framework distortion, as noted above. On the other hand, a third two-electron wave is much more frequent; it links the substituted polyanions to the saturated complexes. It is missing in most transition-metal homologues (e.g. iron(III) and rhodium(III)[42]). The influence of the particular group 3A element is limited to variations in the shift to less negative potentials, in the frequency of appearance of a third two-electron wave, and in the frequency of coalescence of two waves to a four-electron wave. Both frequencies increase with the atomic number of the group 3A element.

By repeating the polarographic measurements on solutions kept at room temperature (27–29 °C) over a period of about 50 days, the resistance to acid and alkaline decomposition can be estimated and checked against the conductometric and potentiometric results. The high ionic strength of the polarography solutions accelerates decomposition: reduction waves of the parent saturated anions are found for solutions of pH <4.5 of the aluminatopolytungstates after 2 days already and an appreciable decrease in wave heights for solutions of pH >6.4 of the indium- and thallium-containing anions.

Solutions of lacunary anions are unexpectedly stable at high ionic strength, both at pH 1–2 and at pH 8. A beginning of decomposition is in both cases noticeable after several days only, except for the unstable BW_{11}. At pH >7.0, PW_{11} and BW_{11} decompose completely to non-reducible species, as do P_2W_{17} and As_2W_{17}, but after a much longer lapse of time. At pH <2.1, SiW_{11} and GeW_{11} slowly transform to the dodecatungstate, characterized by one-electron waves. A solution of PW_{11} at pH 2.0 shows after several days a reduction wave with $E_{1/2}$ = −0.55 V vs. SCE; simultaneously a crystalline precipitate is formed, and the total height of the waves decreases: PW_{11} dismutating to PW_{12} and $P_2W_{21}O_{71}{}^{6-}$,[51] P_2W_{21} causing the wave at −0.55 V, and $K_3PW_{12}O_{40}$ being sparingly soluble. BW_{11} transforms partially to BW_{12}, which rapidly decomposes to nonreducible species. P_2W_{17} and As_2W_{17} slowly form P_2W_{18} and As_2W_{18}, respectively, at pH 2.0.

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Table III. Structural Classification of the Cesium, Potassium, Rubidium, and Ammonium Salts of Lacunary and Substituted Heteropolytungstates

no. and kind of cations for given polytungstate series[a]	crystal system	space group, *Z*[b]	parameters	remarks
XW_{11}, XMW_{11}: 4, 5, 6 Cs^+ (4: Rb^+ also)	cubic, face centered	*Pn*3*m*, 2	$a \approx 1190$ pm	Rb salts of $AsM^{III}W_{11}$ and $PM^{III}W_{11}$ only, most Cs salts
XW_{11}, XMW_{11}: 4 K^+, Rb^+, NH_4^+	hexagonal	$P6_222$ or $P6_422$, 3	$a = 1900–1910$ pm $c = 1240–1250$ pm $c/a \approx 0.655$	almost exclusive system for this no. of cations
XW_{11}, XMW_{11}: 5 K^+, Rb^+, NH_4^+	tetragonal, type Q_β, appr centered	$P\bar{4}2m$ or $P\bar{4}m2$, 2	$a \approx 1420$ pm $c \approx 1245$ pm $c/a \approx 0.875$	by far most common form for this no. of cations
XW_{11}, XMW_{11}: 6 K^+, Rb^+, NH_4^+	tetragonal, type Q_β	as above	as above	as above
XW_{11}, XMW_{11}: 6 K^+, Rb^+, NH_4^+	tetragonal, type Q_α, pseudocubic	as above	$a \approx 1260$ pm $c \approx 1800$ pm $c/a \approx 1.429 \approx 2^{1/2}$	not found for salts discussed here but common for water-rich derivatives[14,41]
XW_{11}, XM_{11}: 7, 8, 9 K^+, Rb^+, NH_4^+	cubic, face centered	*Pn*3*m*, 2	$a \approx 1190$ pm	not found for substituted salts discussed here, common for lacunary compounds[14]
X_2MW_{17}: 7, 8 K^+, Rb^+, NH_4^+	rhombohedral	for the equiv hexagonal unit cell: 1	$a = 1980–1990$ pm $c = 1510–1540$ pm $c/a = 0.76–0.77$	almost exclusive system for these series, unit cell dimensions vary with water contents

[a] Notation of ref 14. [b] Number of molecules per unit cell.

These results incited us to prepare ca. 10^{-3} M solutions of lacunary anion acids by the described ion-exchange method and to follow their evolution, mainly by conductometry. Figure 5 shows various conductometric titrations of $H_8SiW_{11}O_{39}$ solutions. Only $H_9BW_{11}O_{39}$ decomposes very rapidly under these conditions (see above). Immediately after preparation one finds almost exactly the "expected" number of free protons. The acidity of these protons varies considerably. Apart from a number of essentially free protons, there are about four bound protons, two much more strongly than the remaining two. The difference may be caused by selective protonation of the four "equatorial" oxygens surrounding the lacuna. The absence of any metal ion in the center of the lacunary oxygen octahedron increases the charge on those four oxygen atoms appreciably: two belong to the amputated W_2O_{12} group and the other two to two different complete W_3O_{13} groups. The latter two would have less tendency to bind protons than the former. Protonation would "relax" the lacunary octahedron and increase its stability with respect to addition.

Considering the reversible character of at least the first two polarographic waves (corroborated by cyclic voltammetry), it should be possible to obtain quantitatively the two- or four-electron-reduced forms of numerous substituted polyanions by controlled-potential electrolysis. A restricted series of experiments was carried out with the gallatopolytungstates. Electrolyses were carried out in ca. 10^{-2} M aqueous solutions at an optimum pH as determined by polarography and cyclic voltammetry. In this manner, all two-electron-reduced members of this series may be isolated, except for $BGaW^V{}_2W^{VI}{}_9{}^{8-}$, which during electrolysis dismutates to nonreduced $BGaW_{11}$ and to an unstable reddish brown tungsten(IV)-containing derivative, reduced by ca. 8 electrons.

The stability of the isolated two-electron-reduced compounds varies, although not in a systematic fashion: $GeGaW^V{}_2W^{VI}{}_9$ is reoxidized rapidly, $As_2GaW^V{}_2W^{VI}{}_{15}$ more slowly; the others are stable, when stored under nitrogen and protected against sunlight. The latter markedly accelerates the reoxidation process. The UV–visible solution spectra, very similar to those reported of the reduced saturated homologues,[50] show that they contain only tungsten(V) as reduced species.[50] The same substance is in fact obtained when the group 3A element is added to the reduced lacunary anion, and there is no evidence for charge transfer to the group 3A element. The isolated solids are not expected to be protonated;[50] this is confirmed by the analytical data. The position of the various absorption maxima depends only slightly on the central atom and the group 3A element, in correspondence with the hypothesis that only tungsten atoms are reduced.

Structural Classification. The molecular structure of the lacunary, and derived substituted undeca- and heptadecatungstates is by now well-established.[52,53,56] Although the molecular symmetry of the substituted lacunary anions is only *m*, the crystal symmetry often is much higher, sometimes approaching the $\bar{4}3m$ symmetry of the idealized Keggin anion. This is due to a disorder effect: the lacunae are distributed randomly over the 12 possible positions. This disorder can sometimes be eliminated by the introduction of bulky cations or by the exchange of the sixth, usually aquo, ligand of the substituted element against a more voluminous ligand;[42] the structure may then be solved by X-ray methods.[52]

Debye–Scherrer powder diffractograms show that all potassium salts of the polyanions discussed here are isostructural with the corresponding rubidium and ammonium salts. These three salt series can be classified in structural families. This is possible only for these medium-sized cations; neither lithium, sodium nor, say, tetraalkylammonium salts show extended isomorphism. Some guanidinium salts are isostructural, but not with other salts, whereas almost all cesium salts tend to

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crystallize in compact, body-centered-cubic structures that are hardly hydrated (cf. the cubic symmetry of many dodecatungstates,[3] usually more compact than the related undecatungstate, possibly because of their lower ionic charge).

For the medium-sized cations it is primarily the number of cations that determines the overall symmetry, the number of molecules of hydration playing a secondary role,[14] although it is sometimes responsible for a change in structure (see Table III). Another classification is based on the compactness of the various structures;[3] the two criteria are of course related, but the former is easier to use. The classification is summarized in Table III.

It is clear, that there are only one or two possible crystal symmetries for a given number of cations. It is therefore often possible to predict accurately the crystal symmetry knowing the number of cations (especially when the number of hydration water molecules is also known) and vice versa. It should be pointed out that the corresponding salts of the lacunary polyanions also obey these "rules".

Conclusions

α-Type heteropolytungstates containing a group 3A atom can be prepared fairly easily in aqueous solution, despite a strong tendency to hydrolyze the heavier group members. As far as the properties investigated in this paper are concerned, these substituted polyanions all closely resemble their lacunary homologues. Their properties vary little with the group 3A element. The principal differences that have been found are, first, their stability toward both acids and bases is higher than that of both lacunary and saturated homologues and, second, the variation in the splitting of the P–O asymmetric stretching vibration frequency with the group 3A element is important.

Striking similarities include the virtually identical redox behavior and the predictability of the crystal symmetry of the potassium, rubidium, and ammonium salts.

It is clear that refilling the lacuna with an element very different from tungsten or molybdenum, as all group 3A elements are, does not shift the properties of the obtained polyanions toward those of the saturated homologues to an appreciable extent.

Acknowledgment. Generous material support by and helpful discussions with Dr. Michael T. Pope, Georgetown University, are gratefully acknowledged by F.Z.

Registry No. $K_5SiAl(OH_2)W_{11}O_{39}$, 81552-57-0; $K_5GeAl(OH_2)W_{11}O_{39}$, 81552-54-7; $[C(NH_2)_3]_4AsAl(OH_2)W_{11}O_{39}$, 81571-88-2; $[C(NH_2)_3]_4PAl(OH_2)W_{11}O_{39}$, 81571-89-3; $K_6BAl(OH_2)W_{11}O_{39}$, 81552-52-5; $K_7P_2Al(OH_2)W_{17}O_{61}$, 81552-61-6; $K_7As_2Al(OH_2)W_{17}O_{61}$, 81552-49-0; $K_5SiGa(OH_2)W_{11}O_{39}$, 81553-38-0; $K_5SiIn(OH_2)W_{11}O_{39}$, 81553-61-9; $K_5SiTl(OH_2)W_{11}O_{39}$, 81553-70-0; $K_6BTl(OH_2)W_{11}O_{39}$, 81553-04-0; $K_7SiGa(OH_2)W^{V}{}_2W^{VI}{}_9O_{39}$, 81553-39-1; $K_7GeGa(OH_2)W^{V}{}_2W^{VI}{}_9O_{39}$, 81553-32-4; $K_9P_2Ga(OH_2)W^{V}{}_2W^{VI}{}_{15}O_{61}$, 81553-42-6; $K_9As_2Ga(OH_2)W^{V}{}_2W^{VI}{}_{15}O_{61}$, 81552-79-6; $K_5GeGa(OH_2)W_{11}O_{39}$, 81553-31-3; $K_4PGa(OH_2)W_{11}O_{39}$, 81553-36-8; $[C(NH_2)_3]_4AsGa(OH_2)W_{11}O_{39}$, 81571-90-6; $K_6BGa(OH_2)W_{11}O_{39}$, 81552-97-8; $K_7P_2Ga(OH_2)W_{17}O_{61}$, 81553-41-5; $K_7As_2Ga(OH_2)W_{17}O_{61}$, 81552-78-5; $K_5GeIn(OH_2)W_{11}O_{39}$, 81553-46-0; $K_4PIn(OH_2)W_{11}O_{39}$, 81553-59-5; $[N(CH_3)_4]_4AsIn(OH_2)W_{11}O_{39}$, 81552-68-3; $K_6BIn(OH_2)W_{11}O_{39}$, 81553-00-6; $K_7P_2In(OH_2)W_{17}O_{61}$, 81553-63-1; $K_7As_2In(OH_2)W_{17}O_{61}$, 81552-83-2; $K_5GeTl(OH_2)W_{11}O_{39}$, 81553-50-6; $K_4PTl(OH_2)W_{11}O_{39}$, 81553-66-4; $[C(NH_2)_3]_4AsTl(OH_2)W_{11}O_{39}$, 81571-92-8; $K_7P_2Tl(OH_2)W_{17}O_{61}$, 81553-74-4; $K_7As_2Tl(OH_2)W_{17}O_{61}$, 81552-87-6; $K_6SiAl(OH)W_{11}O_{39}$, 81552-59-2; $K_6GeAl(OH)W_{11}O_{39}$, 81552-55-8; $K_8P_2Al(OH)W_{17}O_{61}$, 81552-62-7; $K_8As_2Al(OH)W_{17}O_{61}$, 81552-50-3; $K_6SiGa(OH)W_{11}O_{39}$, 81553-33-5; $K_6GeGa(OH)W_{11}O_{39}$, 81553-29-9; $K_8P_2Ga(OH)W_{17}O_{61}$, 81553-34-6; $K_8As_2Ga(OH)W_{17}O_{61}$, 81552-76-3; $K_6SiIn(OH)W_{11}O_{39}$, 81553-53-9; $K_6GeIn(OH)W_{11}O_{39}$, 81553-43-7; $K_8P_2In(OH)W_{17}O_{61}$, 81553-54-0; $K_8As_2In(OH)W_{17}O_{61}$, 81552-80-9; $H_5SiAl(OH_2)W_{11}O_{39}$, 81552-58-1; $H_5GeAl(OH_2)W_{11}O_{39}$, 81552-53-6; $H_6BAl(OH_2)W_{11}O_{39}$, 81552-51-4; $H_4PAl(OH_2)W_{11}O_{39}$, 81552-56-9; $H_4AsAl(OH_2)W_{11}O_{39}$, 81552-47-8; $H_7P_2Al(OH_2)W_{17}O_{61}$, 81552-60-5; $H_7As_2Al(OH_2)W_{17}O_{61}$, 81552-48-9; $H_5SiGa(OH_2)W_{11}O_{39}$, 81553-37-9; $H_5GeGa(OH_2)W_{11}O_{39}$, 81553-30-2; $H_6BGa(OH_2)W_{11}O_{39}$, 81552-96-7; $H_4PGa(OH_2)W_{11}O_{39}$, 81553-35-7; $H_4AsGa(OH_2)W_{11}O_{39}$, 81552-66-1; $H_7P_2Ga(OH_2)W_{17}O_{61}$, 81553-40-4; $H_7As_2Ga(OH_2)W_{17}O_{61}$, 81552-77-4; $H_5SiIn(OH_2)W_{11}O_{39}$, 81553-60-8; $H_5GeIn(OH_2)W_{11}O_{39}$, 81553-45-9; $H_6BIn(OH_2)W_{11}O_{39}$, 81552-99-0; $H_4PIn(OH_2)W_{11}O_{39}$, 81553-58-4; $H_4AsIn(OH_2)W_{11}O_{39}$, 81552-69-4; $H_7P_2In(OH_2)W_{17}O_{61}$, 81553-62-0; $H_7As_2In(OH_2)W_{17}O_{61}$, 81552-82-1; $H_5SiTl(OH_2)W_{11}O_{39}$, 81553-69-7; $H_5GeTl(OH_2)W_{11}O_{39}$, 81553-49-3; $H_6BTl(OH_2)W_{11}O_{39}$, 81553-03-9; $H_4PTl(OH_2)W_{11}O_{39}$, 81553-65-3; $H_4AsTl(OH_2)W_{11}O_{39}$, 81552-70-7; $H_7P_2Tl(OH_2)W_{17}O_{61}$, 81553-73-3; $H_7As_2Tl(OH_2)W_{17}O_{61}$, 81552-86-5; $K_8SiW_{11}O_{39}$, 37300-95-1; $K_8GeW_{11}O_{39}$, 81553-51-7; $K_7PW_{11}O_{39}$, 37300-94-0; $K_9BW_{11}O_{39}$, 81553-05-1; $K_{10}P_2W_{17}O_{61}$, 5911-46-5; $K_{10}As_2W_{17}O_{61}$, 81552-88-7; Na_2HAsO_4, 7778-43-0; Na_2WO_4, 13472-45-2; $Hg_8SiW_{11}O_{39}$, 81553-75-5.