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Preparation and Characterization of Iron(III)- and Rhodium(III)-Containing Heteropolytungstates. Identification of Novel Oxo-Bridged Iron(III) Dimers

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Polytungstate ions $\alpha\text{-XM}^{\text{III}}(\text{OH}_2)\text{W}_{11}\text{O}_{39}{}^{\text{r}-}$ ($\text{X} = \text{B, Si, Ge, P, As; M(III)} = \text{Fe, Rh}$) and $\alpha\text{-X}_2\text{M}^{\text{III}}(\text{OH}_2)\text{W}_{17}\text{O}_{61}{}^{7-}$ ($\text{X} = \text{P, As; M(III)} = \text{as above}$) are reported. The rhodium derivatives are the first well-characterized series of heteropolytungstates that contain this element. Electronic and infrared spectra and redox properties are reported. Most polyanions are stable in acid to weakly basic solution. The aquo ligand of the M(III) element can be completely or partially deprotonated. In about neutral aqueous solution the iron(III)-containing anions form dimers of formula $\text{XW}_{11}\text{O}_{39}\text{FeOFeO}_{39}\text{W}_{11}\text{X}{}^{\text{r}-}$, which have been isolated as solid salts. No evidence is found for the existence of 1:2 complexes that have been reported recently. These may in fact be inert ion associates.

Introduction

In a preceding paper² we reported the preparation and properties of group 3A element substituted lacunary heteropolytungstates of the Keggin and Dawson structure type. In this paper we give data for the analogous iron(III)- and rhodium(III)-containing polyanions. Similarities and differences between the various series will be discussed.

So far, no comprehensive studies have been published concerning these series of complexes. The $\text{XFeW}_{11}\text{O}_{39}{}^{\text{r}-}$ series has been described in broad terms,^{3,4} with detailed results on SiFeW_{11} ⁵ only being reported.^{6,7} Brief reports have appeared on some related organorhodium derivatives⁸ and on the anions $\text{Rh}(\text{PW}_{11})_2$ and $\text{Rh}(\text{P}_2\text{W}_{17})_2$ that we failed to detect (see below).⁹

Experimental Section

Starting Materials. As for the group 3A element derivatives, only the potassium salts of the more stable α isomers of the XW_{11} ($\text{X} = \text{B, Si, Ge, P(V), As(V)}$) and X_2W_{17} ($\text{X} = \text{P(V), As(V)}$) polyanions were used.³ With modifications, the preparative procedures outlined below can be adapted to other isomers. Analytical grade $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Rh}(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$, and so-called $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ from commercial sources were used without further purification. $\text{Na}_3\text{RhCl}_6 \cdot 2\text{H}_2\text{O}$ was prepared according to Barbieri's method,^{10a} as modified by Tsigdinos.^{10b} All substituted heteropolyanions are also α isomers.

Preparations. Ferratoheteropolytungstates. $\text{K}_5\text{SiFe}(\text{OH}_2)\text{W}_{11}\text{O}_{39}{}^{\text{r}-} \sim 14\text{H}_2\text{O}$. To a stirred solution of 64.0 g (0.0200 mol) of $\text{K}_8\text{SiW}_{11}\text{O}_{39}{}^{\text{r}-} \sim 13\text{H}_2\text{O}$ in 125 mL of hot (95 °C) water is added in small portions 8.15 g (0.0202 mol) of solid $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. After ca. 10 min of heating the solution after completion of the addition, the excess iron precipitates as hydrated iron(III) hydroxide and is filtered off, after coagulation, on a PVC membrane filter. To the cooled filtrate is added twice its volume of a 1:1 (v/v) methanol-ethanol mixture. The precipitated light yellow salt is filtered off and recrystallized thrice from warm (45 °C) water, to which methanol is added until precipitation begins, followed by cooling to 2 °C. The purified salt is air-dried as are all salts described in this section.

$\text{K}_5\text{GeFe}(\text{OH}_2)\text{W}_{11}\text{O}_{39}{}^{\text{r}-} \sim 14\text{H}_2\text{O}$. This procedure is similar to that

of the preceding salt. The yield is lower because of the considerably higher solubility of the salt. The starting material is $\text{K}_8\text{GeW}_{11}\text{O}_{39}{}^{\text{r}-} \sim 13\text{H}_2\text{O}$.

$\text{K}_3\text{PFe}(\text{OH}_2)\text{W}_{11}\text{O}_{39}{}^{\text{r}-} \sim 14\text{H}_2\text{O}$. This preparation is similar to that of the preceding salts. The potassium salt being very soluble in water, the yield is low (see Table I), and the polyanion may be more efficiently isolated as the guanidinium, tetramethylammonium, rubidium, or cesium salt (see below).

$\text{K}_3\text{BFe}(\text{OH}_2)\text{W}_{11}\text{O}_{39}{}^{\text{r}-} \sim 14\text{H}_2\text{O}$. Addition of an acidic iron(III) solution to a warm aqueous solution of the BW_{11} anion leads to partial decomposition of the latter. Thus the order of addition must be inverted.

To a solution of 8.15 g (0.0202 mol) of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 100 mL of hot (80–90 °C) water is added at one time 64.0 g (0.0200 mol) of solid $\text{K}_9\text{BW}_{11}\text{O}_{39}{}^{\text{r}-} \sim 10\text{H}_2\text{O}$, with vigorous stirring. After 5–10 min, all $\text{K}_9\text{BW}_{11}\text{O}_{39}$ is dissolved and reacted. The remaining insoluble solids (hydrolyzed excess iron(III) and potassium paradodecatungstate, common impurity of $\text{K}_9\text{BW}_{11}\text{O}_{39}$) are filtered off after rapidly cooling the solution. To the filtrate is added twice its volume of methanol to precipitate a yellow-green salt, which is recrystallized rapidly from warm (60 °C) water.

$\text{K}_3\text{P}_2\text{Fe}(\text{OH}_2)\text{W}_{17}\text{O}_{61}{}^{7-} \sim 21\text{H}_2\text{O}$. To a stirred suspension of 0.00600 mol of $\text{K}_{10}\text{P}_2\text{W}_{17}\text{O}_{61}{}^{7-} \sim 20\text{H}_2\text{O}$ (29.5 g) in 100 mL of hot (90 °C) water is slowly added (over ca. 15 min.) 2.45 g (0.00606 mol) of solid $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in small portions. The suspended fraction of $\text{K}_{10}\text{P}_2\text{W}_{17}\text{O}_{61}$ slowly dissolves; the coagulated hydrolyzed excess of iron(III) is filtered off after the resulting solution is heated for another 10 min. The filtrate is reheated to 80–90 °C and slowly evaporated down to ca. 50 mL. On cooling a yellow salt crystallizes; an additional amount of salt precipitates on adding an equal volume of methanol to the almost cooled off solution. The salt is recrystallized twice from hot water (90 °C).

$\text{K}_7\text{As}_2\text{Fe}(\text{OH}_2)\text{W}_{17}\text{O}_{61}{}^{7-} \sim 21\text{H}_2\text{O}$. This preparation is similar to that of the preceding salt. The addition reaction takes place more slowly and lasts ca. 30 min for the same amount of starting material (which is $\text{K}_{10}\text{As}_2\text{W}_{17}\text{O}_{61}{}^{7-} \sim 21\text{H}_2\text{O}$). The precipitated yellow-brown solid is recrystallized three times with the water-methanol method described above.

$[\text{C}(\text{NH}_2)_3]_4\text{AsFe}(\text{OH}_2)\text{W}_{11}\text{O}_{39}{}^{\text{r}-} \sim 10\text{H}_2\text{O}$. As the $\text{AsW}_{11}\text{O}_{39}{}^{7-}$ anion is unstable, and the potassium salt of $\text{AsFe}(\text{OH}_2)\text{W}_{11}\text{O}_{39}{}^{4-}$ is very soluble in water, only the much less soluble guanidinium, rubidium, and cesium salts have been isolated from AsW_{11} solutions prepared in situ. A 3.12-g (0.0100-mol) sample of Na_2HAsO_4 and 36.3 g (0.110 mol) of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ are dissolved, separately, in 80 mL of hot (80 °C) water each. The hot solutions are mixed, heated to 90 °C, and acidified with 12.32 mL of 13.8 M HNO_3 . To this solution, the pH of which should be between 3.0 and 4.0, is added 4.03 g (0.0100 mol) of solid $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in small portions. As the formation of AsW_{11} is not complete, a considerable amount of excess Fe(III) hydrolyzes and is removed by filtering. Addition of a small excess of a concentrated solution of guanidinium nitrate provokes the almost immediate precipitation of a yellow salt. The latter is recrystallized thrice from hot (90 °C) water.

Other Guanidinium and Tetraalkylammonium Salts. Adding guanidinium nitrate or a tetraalkylammonium chloride to a solution of any of the potassium salts of the above-mentioned ferratoheteropolytungstates leads

- (1) Abstracted in part from the Thèse d'Etat of Frans Zonnevillje, USTL, 34060 Montpellier Cedex, France; CNRS No. AO 13.026. (b) Institut de Chimie Minérale et Analytique, Université de Lausanne, CH-1005 Lausanne, Switzerland.
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- (4) Tézé, A.; Souchay, P. *Rev. Chim. Miner.* **1970**, 7, 539.
- (5) The formulas $\text{XW}_{11}\text{O}_{39}{}^{\text{r}-}$, etc. will be abbreviated to XW_{11} , etc., whenever feasible.
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- (7) Tézé, A. Thèse d'Etat, Université Paris VI, 1973, CNRS No. AO 8568.
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to almost immediate precipitation of the corresponding organic cation salt, which no longer contains any potassium, especially after recrystallization from hot water. The tetraalkylammonium salts are however very insoluble.

Rubidium and Cesium Salts. Pure rubidium and cesium salts, exempt from potassium, can be obtained with a cation-exchange method. The potassium or guanidinium salt of the polyanion is dissolved in water, cooled to 2 °C, and passed twice on an Amberlite IR-120 cation exchanger in H⁺ form, maintained at 2.0 ± 0.5 °C with an ice- and water-containing jacket. The concentration of the acidic solution is adjusted to ca. 0.05 M and the stoichiometric amount of Rb₂CO₃ or Cs₂CO₃, dissolved in some ice-cold water, is slowly added. Large crystals appear on further cooling and slow evaporation. Larger yields are obtained by adding an equal volume of a cold 1:3 (v/v) methanol-ethanol mixture. The salts are recrystallized from hot (80 °C) water.

Hydroxo Ligand Containing Ferratopolytungstates. The following method furnishes monomeric salts of all above-mentioned iron(III) containing heteropolytungstates of general formula K_mXFe(OH)W₁₁O₃₉·nH₂O or K₈X₂Fe(OH)W₁₇O₆₁·pH₂O.

To a suspension of 2 mmol of the chosen aquo ligand potassium salt in 50 mL of wet methanol, containing up to 1% (v/v) water, is added slowly 2 mmol of KOH dissolved in some methanol. The suspension is stirred for 2–4 days at room temperature. The color of the suspended solid changes from yellow to yellow-brown. When the color does not deepen any more, the crystalline salt is filtered off and air-dried.

In a similar fashion, suspensions of guanidinium salts in methanol are treated with the stoichiometric amount of guanidinium carbonate.

Dimeric Ferratopolytungstates. The following method may be used for all cited iron(III)-containing heteropolytungstates, except for the guanidinium salts which yield impure products.

To an aqueous ca. 0.1 M solution of the chosen aquo ligand salt is added the stoichiometric amount of KOH dissolved in water (1 mol/mol of polyanion). The solution turns slowly maroon. On slow evaporation it yields a green-yellow salt of the dimeric anion. Alternatively an equal volume of ethanol is added. The filtered solid is washed with some ice-cold water and air-dried.

Acids of Ferrato- and Rhodatoheteropolytungstate Anions. The acids are prepared according to the ion-exchange procedure described in the preceding paper.²

Rhodatoheteropolytungstates. K₃Rh(OH₂)W₁₁O₃₉·~14H₂O. To a hot (90 °C) stirred solution of 3.20 g (0.00100 mol) of K₈SiW₁₁O₃₉·~13H₂O is added dropwise a solution of 0.266 g (0.00101 mol) of so-called "RhCl₃·3H₂O" in 10 mL of water. The solution is heated for ca. 30 min, or until the color of the solution, which slowly becomes red-brown, does not deepen any more. It is then cooled to ca. 50 °C and filtered. Adding an equal volume of ethanol or methanol to the lukewarm filtrate provokes the precipitation of the sought potassium salt, contaminated by cationic rhodium(III). The latter is removed by passing a solution of the salt on an Amberlite IR-120 cation exchanger in K⁺ form. The red-brown potassium salt is reprecipitated twice by adding methanol or ethanol to the solution. It is washed with some ice-cold water and air-dried.

K₅GeRh(OH₂)W₁₁O₃₉·~14H₂O. This preparation is similar to that of the preceding salt. The starting materials are "RhCl₃·3H₂O" and K₈GeW₁₁O₃₉·~13H₂O.

K₆BRh(OH₂)W₁₁O₃₉·~15H₂O. To a hot (90 °C) vigorously stirred solution of 0.425 g (0.00101 mol) of Na₃RhCl₆·2H₂O in 10 mL of water is added in one time 3.20 g (0.00100 mol) of solid K₉BW₁₁O₃₉·~10H₂O. After dissolution of the polyanion salt, the solution is stirred and heated for about 20 min, cooled to 50 °C, and filtered. The sought brown-red salt precipitates on addition of an equal volume of methanol to the lukewarm filtrate. After a cation-exchange treatment, it is redissolved in warm (50 °C) water and reprecipitated with methanol. The solid salt is washed with ice-cold water and air-dried.

K₇P₂Rh(OH₂)W₁₇O₆₁·~22H₂O. This was prepared in a manner analogous to that of K₅SiRh(OH₂)W₁₁O₃₉·~14H₂O. One starts with a hot (95 °C) suspension of K₁₀P₂W₁₇O₆₁ in water. The reaction time is about 40 min.

K₇As₂Rh(OH₂)W₁₇O₆₁·~20H₂O. This preparation is similar to that of the preceding salt. One starts with a hot (90 °C) suspension of K₁₀As₂W₁₇O₆₁ in water. The reaction time is about 60 min.

K₅PRh(OH)W₁₁O₃₉·~11H₂O. To a hot (90 °C) stirred solution of 3.23 g (0.00100 mol) of K₇PW₁₁O₃₉·~15H₂O in 10 mL of water,

adjusted to pH 2.0–2.5 with 1 M HNO₃, is added dropwise a solution of 0.328 g (0.00101 mol) of Rh(NO₃)₃·2H₂O dissolved in 10 mL of water. After about 30 min of heating at 90 °C, the brownish red color of the solution reaches its maximum intensity; the solution is then cooled and filtered. Slow evaporation yields a brown-red salt. It is recrystallized from hot (80 °C) water. Addition of organic solvents leads to partial decomposition. The aquo ligand salt has not been isolated (see below). The analogous AsRh(OH₂)W₁₁O₃₉⁽⁴⁻⁵⁾⁻ anion is unstable and has not been isolated either.

Other Hydroxo Ligand Containing Rhodatoheteropolytungstates. Slow evaporation of aqueous solutions of the potassium salt of all rhodatoheteropolytungstates mentioned above yields solid salts the composition of which corresponds to K_{m+x}Rh(OH_{1-x})W₁₁O₃₉·nH₂O or to K_{8+x}X₂Rh(OH_{1-x})W₁₇O₆₁·pH₂O, with x ranging from 0.00 to 0.49 (see Table II). It is possible to reduce the value of x by adding acid to the solution; aquo ligand salts are not thus obtained, however, as acid salts will precipitate instead. The presence of hydroxo ligands in these salts is confirmed by their electronic and infrared spectra (see below).

Oxo Ligand Containing Rhodatoheteropolytungstates. Slow evaporation of aqueous solutions of the potassium salt of all hydroxo ligand rhodatoheteropolytungstates, to which the stoichiometric amount of base is added in the form of KHCO₃ or K₂CO₃ (i.e., 1 - x mol of base/mol of polyanion, K_{m+x}XRh(OH_{1-x})W₁₁O₃₉·nH₂O) yields the corresponding oxo ligand complex, except for BRh(O)W₁₁O₃₉⁸⁻, which is unstable.

Analytical results for all isolated salts and for solutions of the acids are given in Tables I and II.

Analysis. The central atoms, tungsten, potassium, and water of crystallization were determined as before;² rubidium and cesium were also weighed as the tetraphenylborate complex. Iron was transformed to the hydroxide, filtered off, redissolved in 6 M HCl, reduced to iron(II) by SnCl₂, and reoxidized with standard bichromate to a diphenylaminesulfonate end point.¹¹ Rhodium was precipitated with NaOH as a basic tungstate, filtered off, and redissolved in 9 M HCl; after adjustment of pH to 4.5, rhodium was reprecipitated with 1,2,3-benzotriazole and weighed as Rh(C₆HNN₂)₃·3H₂O.¹²

Stoichiometry. The molar variation method¹⁵ was used to detect the possible formation of any other stable complex besides the expected¹⁶ 1:1 compounds. No such complexes were found at M(III) to polytungstate ratios of up to 4:1. Specifically, no evidence was found for the existence of 1:2 metal-polytungstate complexes, which has recently been claimed for rhodium(III)⁹ and indium(III)¹³ (see discussion in ref 2). This claim elicits the following remarks. First, the analytical data are somewhat unsatisfactory for the proposed formulas K₁₁Rh(OH₂)(PW₁₁)₂ and K₁₇Rh(OH₂)(P₂W₁₇)₂, although to a lesser extent than would appear from the published calculated values that seem to be based on the formulas K₁₀Rh(PW₁₁)₂ and K₁₆Rh(P₂W₁₇)₂. Second, the published IR spectra are identical with those of the parent lacunary heteropolytungstate anions. This implies that the rhodium atom is not or weakly coordinated to an oxygen of the central PO₄ tetrahedron; the most probable coordination number is then eight,² rather uncommon for rhodium(III). Third, the positions and, to a lesser extent, the intensities of the maxima in the ligand field spectra are very similar to those of RhCl₅(OH₂)²⁻ and RhCl₄(OH₂)⁻ and clearly indicate that the rhodium is octahedrally coordinated. Finally, a product prepared according to the authors' method,⁹ redissolved in water, and passed on a cation-exchange column in K⁺ form loses its rhodium contents almost quantitatively. These observations strongly suggest that these "1:2 complexes" are in fact kinetically inert ion associates as are presumably their indium(III) homologues.^{2,13} The inertness would also account for the reported electrophoresis data.

Physical Measurements. The instrumentation used has been described.² In addition, standard Sephadex G-10 and G-50 gel filtration columns (with gravity-controlled flow rate) and a standard CAMAG high-voltage paper-electrophoresis setup were used (typical conditions:

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- (15) Zonnevijlle, F. Thèse d'Etat, Université des Sciences et Techniques du Languedoc, Montpellier, France, 1976; CNRS No. AO 13.026.
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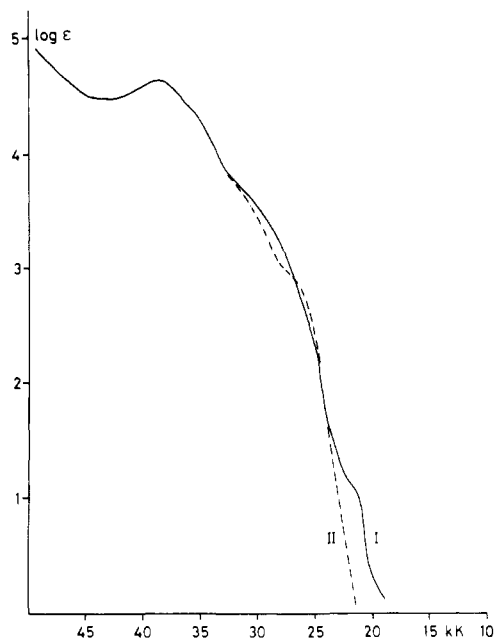


Figure 1. UV-visible absorption spectrum of 10^{-3} M solutions of (I) $K_4PFe(OH_2)W_{11}O_{39}$ and (II) $H_4PFe(OH_2)W_{11}O_{39}$.

40-min electrolysis at 1000V/100 mA, 40×1.0 cm Whatman No. 1 strips).

Characterization and Discussion

Electronic Spectra. The UV-visible spectra of both series of compounds are characterized by an intense, slowly rising absorption band at $(30\text{--}50) \times 10^3 \text{ cm}^{-1}$ that peaks at ca. $39 \times 10^3 \text{ cm}^{-1}$ ($\epsilon \sim 10^4\text{--}10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$) and contains broad shoulders at about $28 \times 10^3 \text{ cm}^{-1}$ ($\epsilon \sim 10^3$), ca. 26 ($\epsilon \sim 500\text{--}1000$) (rhodium series only), and at ca. $22 \times 10^3 \text{ cm}^{-1}$ ($\epsilon \sim 400$) (rhodium series only). The shape of the spectrum is, for energies over about $30 \times 10^3 \text{ cm}^{-1}$, almost identical with that of the parent lacunary compound;¹⁷ the maximum at ca. $39 \times 10^3 \text{ cm}^{-1}$ is attributed to a $W \leftarrow O$ charge-transfer (CT) band¹⁷ and that at ca. $28 \times 10^3 \text{ cm}^{-1}$ to a Fe (or Rh) $\leftarrow O$ CT band. Possible weak spin-forbidden d-d transition bands for the iron series are completely masked by the low-energy $Fe \leftarrow O$ CT band. d-d transitions do appear in the visible spectrum of the rhodium(III)-containing polyanions; they indicate, as expected,¹⁷ an approximately octahedral weak-field coordination of the rhodium(III) ion. The lower energy band at about $22 \times 10^3 \text{ cm}^{-1}$ is assigned to the $^1A_g \rightarrow ^1T_{1g}$ transition, whereas the broad shoulder at about $26 \times 10^3 \text{ cm}^{-1}$ probably corresponds to the $^1A_g \rightarrow ^1T_{2g}$ transition, superimposed on the tail of the combined tungsten and rhodium CT bands. Both $M(III) \leftarrow O$ CT bands decrease in intensity and shift to higher energies in the corresponding acids; this is probably caused by a partial protonation of the four equatorial oxygens that form part of the $M(III)$ coordination octahedron; this diminishes its distortion and increases the crystal field strength around the $M(III)$ ion. The position ($\times 10^3 \text{ cm}^{-1}$) of the maxima of the $Fe \leftarrow O$ CT bands depends on the charge and size of the central atom: $BFeW_{11}$, 29.0; $SiFeW_{11}$, 27.6; $GeFeW_{11}$, 27.2; $PFeW_{11}$, 26.8; $AsFeW_{11}$, 26.5. A similar progression is found for the rhodium(III) complexes. It may be rationalized in terms of a shift in the position of the iron or rhodium atom toward the central atom with increasing charge and size of the latter. This would imply a longer $M^{III}\text{--}O(H_2)$ bond, and thus an increase in the acidity of the aquo ligand

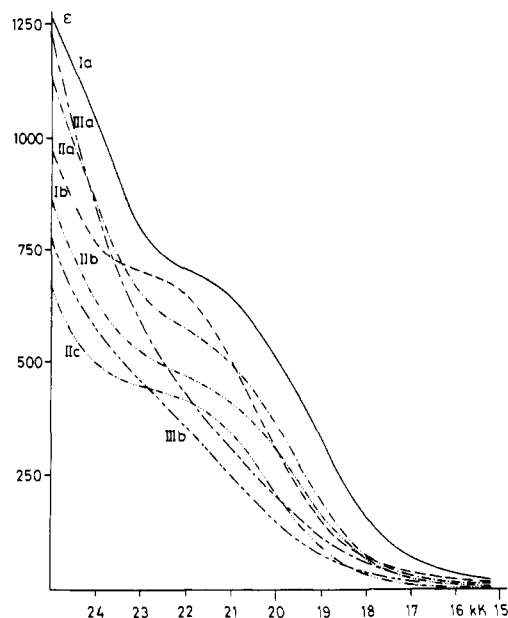


Figure 2. Near-UV-visible absorption spectrum of 10^{-3} M solutions of (Ia) $K_6SiRh(OH)W_{11}O_{39}$, (Ib) $H_5SiRh(OH_2)W_{11}O_{39}$, (IIa) $K_7B-Rh(OH)W_{11}O_{39}$, (IIb) $H_6BRh(OH_2)W_{11}O_{39}$, (IIc) $H_6BRh(OH_2)W_{11}O_{39}$ after 7 days, (IIIa) $K_8P_2Rh(OH)W_{17}O_{61}$, and (IIIb) $H_7P_2-Rh(OH_2)W_{17}O_{61}$.

protons. This is in fact the case (see below). Detailed X-ray crystallographic data are needed to confirm this rationalization but are difficult to obtain because of disorder problems.^{16,17}

Infrared Spectra. The infrared spectra of all Fe(III)- and Rh(III)-containing heteropolytungstates are virtually identical with those of their group 3A² and first-row transition-metal¹⁸ substituted homologues. These have been analyzed in detail.^{2,18} Again, the only vibration sensitive to the nature of the substituted element is the, usually split, ν_3 asymmetric stretch of the P-O bonds of the central tetrahedron in phosphotungstate. The relation between the splitting and the nature of the sixth ligand of the $M(III)$ ion will be discussed later. For the aquo ligand polyanions the frequency values (cm^{-1}) are as follows: $PFeW_{11}$, 1084 and 1060; P_2FeW_{17} , 1090; $PRhW_{11}$, 1085 and 1063; P_2RhW_{17} , 1090 (all measured on the potassium salts). One would indeed expect a splitting of about 25 cm^{-1} for the undecatungstates.¹⁸ The virtual disappearance of the splitting is characteristic of most P_2MW_{17} polyanions; they contain two oxo-bridged PO_4 tetrahedra and allow for a larger degree of relaxation of the tungsten-oxygen framework.¹⁸

Redox Properties. Like those of the group 3A element substituted heteropolytungstates,² the redox properties of the iron(III) and rhodium(III) series were investigated systematically as a function of pH and time by dc polarography and cyclic voltammetry. Under suitable conditions all polyanions can be reduced reversibly to mixed-valence $W(V)\text{--}W(VI)$ species; the results closely parallel those obtained previously;² i.e., the half-wave potential ($E_{1/2}$) vs. pH diagrams feature two- or three two-electron waves that are usually pH dependent and are shifted to more negative potentials compared to the "saturated" homologues. There are however some characteristic differences:

(1) For the $XFeW_{11}$ and X_2FeW_{17} anions one finds a reversible, often pH-independent one-electron wave at less negative potential than the tungsten reduction waves ($E_{1/2} \approx -0.22 \text{ V vs. SCE}$), indicative of the reduction of iron(III) to iron(II);^{2,3,7} accordingly, $XFe^{II}W_{11}$ and $X_2Fe^{II}W_{17}$ can be isolated either by reduction of the iron(III) compound or by

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Table I. Analytical Results for the Iron-Containing Compounds

	yield, ^a %	found (calcd)				
		% cation	% central atom ^b	% Fe	% W	% H ₂ O ^{c,h}
Salts						
K ₅ SiFe(OH ₂)W ₁₁ O ₃₉ ·13.7H ₂ O	80	5.90 (6.13)	0.872 (0.881)	1.735 (1.750)	62.74 (63.41)	7.70
K ₅ GeFe(OH ₂)W ₁₁ O ₃₉ ·13.6H ₂ O	75	5.92 (6.04)	2.242 (2.246)	1.739 (1.728)	63.04 (62.57)	7.54
K ₆ BFe(OH ₂)W ₁₁ O ₃₉ ·14.5H ₂ O	70	6.86 (7.23)	0.344 (0.333)	1.810 (1.721)	62.89 (62.34)	8.04
K ₄ PFe(OH ₂)W ₁₁ O ₃₉ ·14.1H ₂ O	20	5.10 (4.95)	0.973 (0.980)	1.758 (1.766)	63.68 (63.96)	8.04
[C(NH ₂) ₃] ₄ PFe(OH ₂)W ₁₁ O ₃₉ ·9.7H ₂ O	80	7.50 (7.58)	0.984 (0.978)	1.756 (1.765)	64.45 (63.88)	5.52
[C(NH ₂) ₃] ₄ AsFe(OH ₂)W ₁₁ O ₃₉ ·10.1H ₂ O	50	7.42 (7.46)	2.338 (2.329)	1.742 (1.736)	63.12 (62.87)	5.67
K ₇ P ₂ Fe(OH ₂)W ₁₇ O ₆₁ ·21.3H ₂ O	80	5.58 (5.59)	1.270 (1.266)	1.142 (1.145)	63.81 (63.89)	7.83
K ₇ As ₂ Fe(OH ₂)W ₁₇ O ₆₁ ·21.2H ₂ O	70	5.52 (5.50)	2.974 (3.009)	1.098 (1.122)	62.67 (62.77)	7.61
Rb ₅ SiFe(OH ₂)W ₁₁ O ₃₉ ·12.7H ₂ O	90 ^d	12.67 (12.56)	<i>e</i>	1.638 (1.641)	59.23 (59.42)	6.70
Rb ₅ GeFe(OH ₂)W ₁₁ O ₃₉ ·7.9H ₂ O	90 ^d	12.69 (12.71)	<i>e</i>	1.670 (1.661)	60.43 (60.13)	4.25
Rb ₆ BFe(OH ₂)W ₁₁ O ₃₉ ·11.7H ₂ O	65 ^d	15.13 (14.85)	<i>e</i>	1.632 (1.617)	58.70 (58.55)	6.08
Rb ₄ PFe(OH ₂)W ₁₁ O ₃₉ ·8.5H ₂ O	80 ^d	10.22 (10.53)	<i>e</i>	1.708 (1.720)	62.05 (62.30)	4.72
Rb ₄ AsFe(OH ₂)W ₁₁ O ₃₉ ·7.9H ₂ O	85 ^d	10.54 (10.43)	<i>e</i>	1.710 (1.703)	61.34 (61.67)	4.34
Rb ₇ P ₂ Fe(OH ₂)W ₁₇ O ₆₁ ·16.2H ₂ O	90 ^d	11.95 (11.67)	<i>e</i>	1.081 (1.089)	60.82 (60.96)	5.68
Rb ₇ As ₂ Fe(OH ₂)W ₁₇ O ₆₁ ·14.9H ₂ O	85 ^d	11.37 (11.52)	<i>e</i>	1.075 (1.076)	60.10 (60.20)	5.17
Cs ₅ SiFe(OH ₂)W ₁₁ O ₃₉ ·8.6H ₂ O	95 ^d	18.72 (18.62)	<i>e</i>	1.562 (1.565)	56.43 (56.67)	4.36
Cs ₅ GeFe(OH ₂)W ₁₁ O ₃₉ ·8.4H ₂ O	95 ^d	18.48 (18.42)	<i>e</i>	1.537 (1.548)	56.08 (56.05)	4.18
Cs ₂ BFe(OH ₂)W ₁₁ O ₃₉ ·6.7H ₂ O	70 ^d	21.54 (21.86)	<i>e</i>	1.536 (1.531)	55.13 (55.43)	3.28
Cs ₄ PFe(OH ₂)W ₁₁ O ₃₉ ·7.2H ₂ O	80 ^d	15.62 (15.58)	<i>e</i>	1.632 (1.637)	59.17 (59.28)	3.78
Cs ₄ AsFe(OH ₂)W ₁₁ O ₃₉ ·6.6H ₂ O	80 ^d	15.52 (15.43)	<i>e</i>	1.640 (1.621)	58.62 (58.69)	3.45
Cs ₇ P ₂ Fe(OH ₂)W ₁₇ O ₆₁ ·14.1H ₂ O	95 ^d	16.97 (17.16)	<i>e</i>	1.032 (1.030)	57.89 (57.66)	4.69
Cs ₇ As ₂ Fe(OH ₂)W ₁₇ O ₆₁ ·14.7H ₂ O	90 ^d	17.03 (16.85)	<i>e</i>	1.021 (1.012)	56.80 (56.62)	4.80
K ₆ SiFe(OH)W ₁₁ O ₃₉ ·5.9H ₂ O	95 ^f	7.65 (7.60)	<i>e</i>	1.799 (1.808)	65.54 (65.49)	3.44
K ₆ GeFe(OH)W ₁₁ O ₃₉ ·10.3H ₂ O	95 ^f	7.38 (7.31)	<i>e</i>	1.745 (1.739)	62.71 (62.97)	5.78
K ₇ BFe(OH)W ₁₁ O ₃₉ ·8.1H ₂ O	95 ^f	8.66 (8.69)	<i>e</i>	1.767 (1.773)	64.13 (64.21)	4.86
[C(NH ₂) ₃] ₅ PFe(OH)W ₁₁ O ₃₉ ·7.3H ₂ O	95 ^f	9.58 (9.44)	<i>e</i>	1.725 (1.755)	63.21 (63.56)	4.12
[C(NH ₂) ₃] ₅ AsFe(OH)W ₁₁ O ₃₉ ·6.3H ₂ O	95 ^f	9.43 (9.37)	<i>e</i>	1.712 (1.741)	62.79 (63.05)	3.52
K ₈ P ₂ Fe(OH)W ₁₇ O ₆₁ ·14.0H ₂ O	95 ^f	6.60 (6.52)	<i>e</i>	1.154 (1.163)	64.74 (65.10)	5.25
K ₈ As ₂ Fe(OH)W ₁₇ O ₆₁ ·17.0H ₂ O	95 ^f	6.25 (6.33)	<i>e</i>	1.124 (1.130)	63.37 (63.23)	6.19
K ₁₂ O[SiFeW ₁₁ O ₃₉] ₂ ·29.0H ₂ O	80 ^f	7.29 (7.25)	<i>e</i>	1.730 (1.727)	62.28 (62.53)	8.08
K ₁₂ O[GeFeW ₁₁ O ₃₉] ₂ ·28.8H ₂ O	80 ^f	7.31 (7.23)	<i>e</i>	1.728 (1.721)	62.18 (62.32)	8.00
K ₁₄ O[BFeW ₁₁ O ₃₉] ₂ ·17.9H ₂ O	85 ^f	8.65 (8.67)	<i>e</i>	1.762 (1.769)	63.91 (64.08)	5.11
K ₁₆ O[P ₂ FeW ₁₇ O ₆₁] ₂ ·31.8H ₂ O	90 ^f	6.54 (6.48)	<i>e</i>	1.162 (1.157)	64.89 (64.76)	5.94
K ₁₆ O[As ₂ FeW ₁₇ O ₆₁] ₂ ·30.1H ₂ O	90 ^f	6.28 (6.39)	<i>e</i>	1.147 (1.140)	63.62 (63.80)	5.53
Acid Solutions						
H ₅ SiFe(OH ₂)W ₁₁ O ₃₉	<i>g</i>	5.00 (5.00) ^h	<i>e</i>	2.064 (2.076) ⁱ	74.83 (75.17) ⁱ	
H ₅ GeFe(OH ₂)W ₁₁ O ₃₉	<i>g</i>	5.00 (5.00)	<i>e</i>	2.012 (2.042) ⁱ	74.08 (73.94) ⁱ	
H ₆ BFe(OH ₂)W ₁₁ O ₃₉	<i>g</i>	5.80 (6.00)	<i>e</i>	2.114 (2.096) ⁱ	76.14 (75.89) ⁱ	
H ₄ PFe(OH ₂)W ₁₁ O ₃₉	<i>g</i>	4.00 (4.00)	<i>e</i>	2.061 (2.067) ⁱ	74.56 (74.87) ⁱ	
H ₄ AsFe(OH ₂)W ₁₁ O ₃₉	<i>g</i>	4.00 (4.00)	<i>e</i>	2.018 (2.034) ⁱ	74.02 (73.67) ⁱ	
H ₇ P ₂ Fe(OH ₂)W ₁₇ O ₆₁	<i>g</i>	7.00 (7.00)	<i>e</i>	1.293 (1.341) ⁱ	74.82 (73.52) ⁱ	
H ₇ As ₂ Fe(OH ₂)W ₁₇ O ₆₁	<i>g</i>	6.95 (7.00)	<i>e</i>	1.301 (1.314) ⁱ	73.42 (73.52) ⁱ	

^a After recrystallization. ^b Defined as the atom or the atoms in tetrahedral site or sites (Si, Ge, B, P, or As). ^c Excluding the aquo ligand of the trivalent metal ion. ^d With respect to the initial potassium salt. ^e Not determined. ^f With respect to the initial aquo or hydroxo ligand salt. ^g Not applicable. ^h Expressed as number of moles of free protons per mole of polyanion. ⁱ With respect to the mass of the calcined residue. ^j Prepared directly. ^k No calculated figures are given, as most water molecules are only loosely bound; the water contents may vary considerably from one preparation to another.

direct addition of iron(II) to the lacunary anion.^{3,7} This is in contrast to the analogous iron polymolybdates: XFe^{II}Mo^{VI}₁₁ does not exist, as Mo(VI) is more easily reduced than Fe(III).^{3,19} It is not clear why only in some cases this wave is pH dependent in acidic solution.

(2) A similar wave is not found for the rhodium(III) series, but, on the other hand, the rhodium ion seems to promote to some degree the delocalization of the added electrons. At low pH values all three two-electron waves of the X₂RhW₁₇ anions merge to a single six-electron wave. The half-wave potential of this and other waves is considerably less negative than for the iron(III) homologues and comes close to that found for similar waves in the "complete" polyanions. The total number of two-electron waves is nevertheless the same as for the lacunary polytungstates (i.e., one less than for the "complete" anion²). Thus the redox behavior of the rhodium(III) complexes is intermediate between that of the lacunary and "complete" polyanions.

A full comparison with the redox properties of analogous rhodium(III) polymolybdates should be instructive.

The polarograms and cyclic voltammograms were recorded several times over at least a 50-day period (average temperature 28 °C). The E_{1/2} vs. pH plots did not change with time. Both series of complexes are stable over a remarkably wide pH range of at least 2–8 (vide infra).

Stability. Heteropolytungstates that contain a trivalent or higher valent substituted ion are often markedly more stable than bivalent metal substituted anions in acid media.^{2,20} Solutions of the acids can be obtained by ion exchange,^{2,17} but it is usually not possible to isolate pure solid acids. Most iron(III)- and rhodium(III)-containing heteropolytungstate acids are stable in fairly dilute (0.01–0.05 M) solution, in the absence of supporting electrolyte, up to 40 °C, except for the BW₁₁ derivatives; a possible reason for this instability has been given.² H₆BFeW₁₁ may be obtained pure immediately after preparation at 2 °C, but H₆BRhW₁₁ already starts to de-

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Table II. Analytical Results for Rhodium-Containing Compounds

	yield, ^a %	found (calcd)					x
		% cation	% central atom ^b	% Rh	% W	% H ₂ O ^{c,k}	
Salts							
K ₅ SiRh(OH ₂)W ₁₁ O ₃₉ ·14.1H ₂ O	70	6.04 (6.02)	0.894 (0.865)	3.23 (3.17)	62.16 (62.32)	7.83	
K ₅ GeRh(OH ₂)W ₁₁ O ₃₉ ·14.1H ₂ O	60	5.97 (5.94)	2.224 (2.206)	3.17 (3.13)	61.68 (61.47)	7.72	
K ₆ BRh(OH ₂)W ₁₁ O ₃₉ ·15.0H ₂ O	50	7.28 (7.19)	0.325 (0.336)	3.21 (3.15)	61.72 (62.94)	8.23	
K ₇ P ₂ Rh(OH ₂)W ₁₇ O ₆₁ ·22.2H ₂ O	70	5.71 (5.66)	1.287 (1.281)	2.15 (2.13)	64.38 (64.61)	8.07	
K ₇ As ₂ Rh(OH ₂)W ₁₇ O ₆₁ ·20.4H ₂ O	50	5.54 (5.48)	3.115 (3.098)	2.05 (2.06)	62.68 (62.57)	7.33	
K _{6+x} SiRh(OH _{1-x})W ₁₁ O ₃₉ ·12.3H ₂ O	80 ^f	7.23 (7.22)	<i>e</i>	3.27 (3.17)	62.14 (62.20)	6.84	0.00
K _{6+x} GeRh(OH _{1-x})W ₁₁ O ₃₉ ·14.0H ₂ O	75 ^f	7.34 (7.06)	<i>e</i>	3.16 (3.09)	60.64 (60.81)	7.58	0.40
K _{7+x} BRh(OH _{1-x})W ₁₁ O ₃₉ ·18.6H ₂ O	80 ^f	8.03 (8.08)	<i>e</i>	3.07 (3.04)	60.07 (59.72)	9.90	0.00
K _{8+x} PRh(OH _{1-x})W ₁₁ O ₃₉ ·11.0H ₂ O	30 ^j	6.10 (6.14)	<i>e</i>	3.28 (3.23)	63.23 (63.56)	6.23	0.00
K _{8+x} P ₂ Rh(OH _{1-x})W ₁₇ O ₆₁ ·24.1H ₂ O	90 ^f	6.56 (6.21)	<i>e</i>	2.03 (2.04)	61.84 (62.10)	8.64	0.45
K _{8+x} As ₂ Rh(OH _{1-x})W ₁₇ O ₆₁ ·28.5H ₂ O	70 ^f	6.41 (6.04)	<i>e</i>	2.02 (1.99)	60.57 (60.34)	9.90	0.49
K ₇ SiRh(O)W ₁₁ O ₃₉ ·15.0H ₂ O	70 ^f	8.14 (8.20)	<i>e</i>	3.07 (3.08)	60.28 (60.60)	8.10	
K ₇ GeRh(O)W ₁₁ O ₃₉ ·15.1H ₂ O	55 ^f	8.00 (8.09)	<i>e</i>	3.06 (3.04)	59.62 (59.76)	8.05	
K ₆ PRh(O)W ₁₁ O ₃₉ ·14.4H ₂ O	55 ^f	7.11 (7.13)	<i>e</i>	3.10 (3.13)	61.67 (61.45)	7.91	
K ₉ P ₂ Rh(O)W ₁₇ O ₆₁ ·26.9H ₂ O	80 ^f	6.79 (6.87)	<i>e</i>	2.03 (2.01)	60.91 (61.05)	9.48	
K ₉ As ₂ Rh(O)W ₁₇ O ₆₁ ·30.0H ₂ O	65 ^f	6.73 (6.69)	<i>e</i>	1.99 (1.96)	59.48 (59.39)	10.27	
Acid Solutions							
H ₅ SiRh(OH ₂)W ₁₁ O ₃₉	<i>g</i>	5.25 (5.00) ^h	<i>e</i>	3.77 (3.76) ⁱ	73.56 (73.88)		
H ₅ GeRh(OH ₂)W ₁₁ O ₃₉	<i>g</i>	5.25 (5.00)	<i>e</i>	3.68 (3.70) ⁱ	72.41 (72.70)		
H ₆ BRh(OH ₂)W ₁₁ O ₃₉	<i>g</i>	~5.0 (6.00)	<i>e</i>	3.54 (3.79) ⁱ	74.85 (74.57)		
H ₄ PRh(OH ₂)W ₁₁ O ₃₉	<i>g</i>	~4.2 (4.00)	<i>e</i>	3.77 (3.74) ⁱ	73.12 (73.59)		
H ₇ P ₂ Rh(OH ₂)W ₁₇ O ₆₁	<i>g</i>	7.10 (7.00)	<i>e</i>	2.43 (2.44) ⁱ	74.06 (74.23)		
H ₇ As ₂ Rh(OH ₂)W ₁₇ O ₆₁	<i>g</i>	7.05 (7.00)	<i>e</i>	2.42 (2.39) ⁱ	72.57 (72.72)		

^a Footnotes a-k are the same as those in Table I.

compose on the ion-exchange column (see Table II).

The neutralization of solutions of the acids has been studied by conductometry and potentiometry, as described previously.² A conductometric titration curve enables one to discriminate between more or less acidic "free" protons and to distinguish these from the usually much less acidic M(III)-aquo ligand protons. Although a potentiometric titration curve sometimes does not show a pH jump between these two types of protons, it often shows one between the two aquo ligand protons. Figure 3 presents some typical curves which exemplify the difference between the iron(III) and rhodium(III) series. The acid protons are all essentially free, except for an occasional last one. The difference in acidity of the aquo ligand protons is clearly visible. Generally, one finds for the iron(III) compounds a single titratable ligand proton. Occasionally both protons are titrated almost simultaneously (SiFeW₁₁). Of the rhodium(III) derivatives, usually both protons are of about equal acidity. The pK_a value for the first aquo ligand proton ranges from 3.5 (PRhW₁₁) to 4.3 (SiRhW₁₁) for the rhodium series and from 4.3 (PFeW₁₁) to 5.2 (SiFeW₁₁) for the iron(III) complexes. The acidity increases with increasing charge of the central atom (vide supra).

As the aquo ligand may be, at least partially, deprotonated within the pH stability range of the polyanion, it should be possible to obtain pure hydroxo or even oxo ligand containing species. In fact, for the rhodium(III) complexes it turns out to be more difficult to isolate the pure aquo ligand form. These can be obtained pure only by adding alcohol to the aqueous solution. Pure oxo ligand forms are isolated from carefully alkalinized aqueous solutions. The formulas of these polyanions are fully analogous to those of the parent saturated (or "complete") heteropolytungstates. Rhodium(III) resembles in this respect vanadium(IV) and -(V) (cf. redox properties).

The deepening of the color to dark red-brown is due to the change in outer ligand and the concomitant shift in the position of the rhodium ion (confirmed by the measured increase in the splitting of the ν₃(P-O) asymmetric stretch frequency in the IR spectrum), in a direction opposite to that found for the acids (see above). Analogous oxo ligand iron(III) derivatives are not stable; the polyanion starts to decompose before deprotonation is complete.

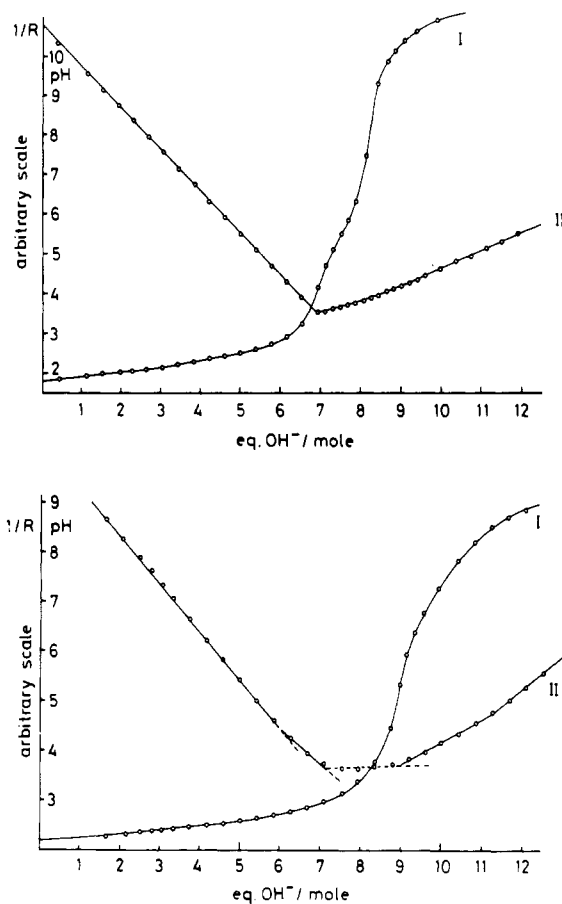


Figure 3. (Top) neutralization of a 0.95×10^{-3} M solution of $H_7As_2Fe(OH_2)W_{17}O_{61}$ and (bottom) neutralization of a 0.90×10^{-3} M solution of $H_7As_2Rh(OH_2)W_{17}O_{61}$: (I) immediate direct potentiometric titration; (II) immediate direct conductometric titration.

Dimerization. On the other hand, the iron(III) hydroxo ligand homologues can, apparently, be prepared pure almost effortlessly. The situation is more complicated, though. If one adds 1 mol of KOH to an aqueous solution containing 1

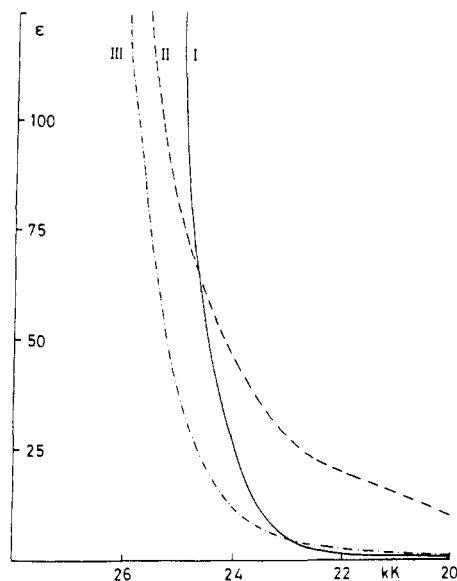


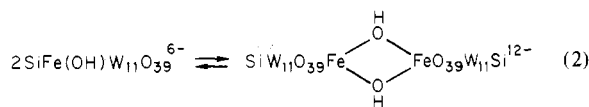
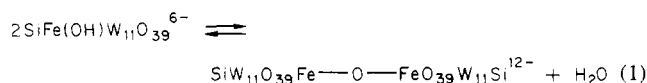
Figure 4. Visible absorption spectrum of 10^{-3} M solutions of (I) $K_3SiFe(OH_2)W_{11}O_{39}$, (II) $K_6SiFe(OH)W_{11}O_{39}$, and (III) $K_{12}[SiFe(O)_{1/2}W_{11}O_{39}]_2$.

mol of the aquo ligand polyanion, the solution turns maroon and yields on evaporation two distinctly different salts, one yellowish ocher to yellow-brown, the other greenish yellow and efflorescent.

Although analysis of both series of salts gives identical results, the X-ray powder diffractograms are quite different: those of the former series fit the scheme described previously,² taking into account the increased number of potassium ions; no isomorphism is found for the latter series.

If one tries to quantitatively isolate the hydroxo ligand complex by evaporation or by precipitation through addition of alcohol to a concentrated aqueous solution (>0.05 M), one obtains solely the second, nonisomorphous type, which will be shown to be a dimeric species.

Tézé has investigated the solution behavior of "SiFe(OH) $W_{11}O_{39}$ "⁶⁻⁷ and found certain anomalies (e.g., deviations from Beer's law) that may be explained by assuming the formation of a dimer according to the equilibrium reaction (1) or (2). The monomer and dimer have different UV-visible



spectra (Figure 4), in agreement with Tézé's results. For this particular case, Tézé calculated an apparent formation constant of approximately 40 for reaction 1. The dimerization reaction is general for all iron(III) heteropolytungstates, with similar values for the apparent formation constant (ca. 20 for the X_2FeW_{17} anions to ca. 100 for the X^VFeW_{11} anions); the variations are clearly related to size and charge of the polyanion.

The method described above affords the pure, moderately crystalline potassium salt of the dimer, except for the AsW_{11} and PW_{11} derivatives that are obtained somewhat impure because of partial decomposition. Salts of other cations are also impure and cannot be recrystallized successfully.

Pure monomers can be isolated from an almost water-free medium as described above. Apparently, deprotonation takes place between dissolved species only; the reaction is slowed down when the water content is decreased. The monomeric

character is confirmed by the isomorphism found for the X-ray powder diffractograms.

The monomer-dimer equilibrium is probably reversible but slow to establish at low ionic strength: the monomer, dissolved in water, yields the dimer on concentrating the solution, whereas the dimer slowly dissociates when suspended in methanol. The assumption of dimer formation in aqueous solution is confirmed by cryoscopy in $Na_2SO_4 \cdot 10H_2O$, paper electrophoresis, and gel filtration experiments. The second technique qualitatively confirms the presence of different charge/size ratios for the monomer and dimer. Gel filtration elution profiles were obtained, at appropriate pH values, for mixtures of (1) $XFe(OH_2)W_{11}$, $X_2Fe(OH_2)W_{17}$, $U(PW_{11})_2$ and $U(P_2W_{17})_2$ (2) monomeric $XFe(OH)W_{11}$ and $X_2Fe(OH)W_{17}$, $U(PW_{11})_2$ and $U(P_2W_{17})_2$, and (3) the dimeric homologues and the same uranium complexes. A comparison of these profiles confirms the monomeric and dimeric character of the respective anions. Dimeric species and uranium dipolyanion homologues show an almost identical behavior, suggesting a structure for the dimer that is similar to the known "dumbbell" shape of the uranium complexes.²¹

The dimers can be considered as bulky and extremely heavy derivatives of the aquoiron(III) dimer found in partially hydrolyzed iron(III) salt solutions. Convincing evidence has been given for the presence of a single oxo bridge between the iron atoms.²² The formula of the aquo dimer is decaquo- μ -diron(III), exactly the same coordination type one would expect for the iron(III) heteropolytungstate dimers, in which the polyanion functions as a pentadentate ligand. One can imagine single- or double-hydroxo-bridged species, but analytical data rule out the single-hydroxo-bridged species, whereas a double hydroxo bridge would result in either a sterically improbable seven-coordination around the iron ion or in an outward shift of this ion. Such a shift would lead to an increase of the ν_3 asymmetric stretch frequency in the IR spectrum of the $PFeW_{11}$ derivative to 45–50 cm^{-1} .^{2,18} One finds a much smaller value of 32 cm^{-1} , compared to 24 and 27 cm^{-1} for the aquo and hydroxo ligand forms. These are reasonable values, as the Fe–O distance becomes shorter in Fe–OH₂, Fe–OH, and Fe–O–Fe bonds.²³

No such dimers have been found for the rhodium(III) polytungstates, nor for those containing a group 3A element (with the exception of thallium).²⁴ Pure hydroxo ligand forms of the last group can be obtained by the methanol–KOH method. If dimers are formed at all, the formation constants must be quite small. Attempts to shift a possible equilibrium to the dimer side by concentrating aqueous solutions lead to gradual decomposition. The IR spectra of anhydrous tetraalkylammonium salts of the hydroxo ligand forms show that after repeated suspension of the solid in absolute methanol, no bands attributable to the aquo or oxo ligand are present. The hydroxo ligand form is thus a well-defined species.

Some evidence is found²⁴ for the existence, at low concentrations, of μ -oxo chromium(III) heteropolytungstate dimers under similar conditions (careful alkalization of the aquo ligand form, prepared according to Colom,²⁵ in aqueous solution). The visible-near-UV spectrum of the brownish blue solids contains peaks in the $(22-28) \times 10^3$ cm^{-1} region that strongly resemble the intense bands found in the recently characterized decaquo- μ -oxo-dichromium(III) complex.²⁶ Likewise, one

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finds dimer-attributable peaks in the X-ray powder diffractograms. For the thallium(III) derivatives there is some spectroscopic and X-ray powder diffraction evidence for a different type of dimerization. Here the thallium atom seems to shift so far outward that it is no longer bonded to the inner oxygen. There may well be two hydroxo bridging groups, as is found for most partially hydrolyzed aquo ligand group 3A dimers.^{27,28}

It is maybe not surprising that only iron(III) forms oxo-bridged dimers to an appreciable extent. For similar simpler μ -oxo dimers there is abundant evidence for strong interactions via the bridging oxygen, due to strong antiferromagnetic superexchange coupling and/or to strong π bonding ($2p\pi-3d\pi$ for Al^{23,29} and Cr,^{26,30,31} perhaps $2p\pi-4p\pi$ or $2p\pi-4d\pi$ for Fe).²³ These interaction energies have to offset unfavorable entropy and electrostatic repulsion³² effects. Relatively small variations in the electronic and magnetic interaction energies may lead to large differences in stability of the dimer.

One may also compare these μ -oxo dimers to another type of "dumbbell" heteropolyanion of formula $XW_{11}CoN(pz)NCoW_{11}X^{33}$ (pz = pyrazine), for which the cobalt-ligand interactions are probably weaker, but the electrostatic repulsion is also.

Structural Data. Debye-Scherrer powder diffractograms show that, with the logical exception of the dimers, the crystal symmetry of the potassium salts of all heteropolyanions discussed here can be correctly deduced from the structure classification rules assembled in ref 2. For example, the crystal symmetry of the compound $K_{4+x}PRh(OH_{2-x})W_{11}O_{39}$ ($x = 0-2$) changes with increasing deprotonation of the aquo ligand from hexagonal ($x = 0$) to tetragonal ($x \geq 1$). The potassium salts of $XRh(OH)W_{11}O_{39}^{6-}$ ($X = Si, Ge$) represent the rather uncommon Q_{α} ³⁴ tetragonal symmetry type ($c/a \approx 2^{1/2}$); they are not transformed into the more common Q_{β} type (approximately centered tetragonal symmetry)³⁴ as has been found for several other examples of the Q_{α} form.³⁵ The high overall symmetry implies that the anions are disordered in the solid state, as has been verified for numerous homologues.³⁶

Conclusion

The preparation of all iron(III) and rhodium(III) 1:1 heteropolytungstate complexes is fairly straightforward, although one has to take into account the inertness and/or tendency to

hydrolyze of most rhodium(III) starting materials. It is not necessary to start with rhodium in a different oxidation state, as is recommended for chromium(III).²⁵ The properties of these substituted heteropolytungstates are very similar to those reported for the group 3A element derivatives,² except for some readily explicable differences in redox behavior and the presence of a ligand-field absorption spectrum.

Unexpected members of these series are the oxo-bridged dimers that are formed in approximately neutral aqueous solution by the iron(III)-containing polyanions. These should possess interesting electronic and magnetic properties, which deserve a detailed study, if possible in combination with an X-ray structure determination.

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Registry No. K₅SiFe(OH₂)W₁₁O₃₉, 81553-20-0; K₅GeFe(OH₂)W₁₁O₃₉, 81553-10-8; K₄PFe(OH₂)W₁₁O₃₉, 81553-16-4; K₆BFe(OH₂)W₁₁O₃₉, 81552-94-5; K₇P₂Fe(OH₂)W₁₇O₆₁, 81553-24-4; K₇As₂Fe(OH₂)W₁₇O₆₁, 81552-73-0; [C(NH₂)₃]₄AsFe(OH₂)W₁₁O₃₉, 81571-91-7; Rb₅SiFe(OH₂)W₁₁O₃₉, 81553-21-1; Rb₅GeFe(OH₂)W₁₁O₃₉, 81553-11-9; Rb₆BFe(OH₂)W₁₁O₃₉, 81552-95-6; Rb₄PFe(OH₂)W₁₁O₃₉, 81553-17-5; Rb₄AsFe(OH₂)W₁₁O₃₉, 81552-65-0; Rb₇P₂Fe(OH₂)W₁₇O₆₁, 81553-25-5; Rb₇As₂Fe(OH₂)W₁₇O₆₁, 81552-75-2; Cs₅SiFe(OH₂)W₁₁O₃₉, 81553-18-6; Cs₅GeFe(OH₂)W₁₁O₃₉, 81553-08-4; Cs₆BFe(OH₂)W₁₁O₃₉, 81552-92-3; Cs₄PFe(OH₂)W₁₇O₆₁, 81553-14-2; Cs₄AsFe(OH₂)W₁₁O₃₉, 81552-63-8; Cs₇P₂Fe(OH₂)W₁₇O₆₁, 81553-22-2; Cs₇As₂Fe(OH₂)W₁₇O₆₁, 81552-71-8; K₆SiFe(OH)W₁₁O₃₉, 37300-77-9; K₆GeFe(OH)W₁₁O₃₉, 81553-07-3; K₇BFe(OH)W₁₁O₃₉, 81552-91-2; [C(NH₂)₃]₃PFe(OH)W₁₁O₃₉, 81553-12-0; [C(NH₂)₃]₅AsFe(OH)W₁₁O₃₉, 81552-67-2; K₈P₂Fe(OH)W₁₇O₆₁, 81553-13-1; K₈As₂Fe(OH)W₁₇O₆₁, 81552-74-1; K₁₂O[SiFeW₁₁O₃₉]₂, 81553-27-7; K₁₂O[GeFeW₁₁O₃₉]₂, 81553-26-6; K₁₄O[BFeW₁₁O₃₉]₂, 81553-06-2; K₁₆O[P₂FeW₁₇O₆₁]₂, 81553-28-8; K₁₆O[As₂FeW₁₇O₆₁]₂, 81552-90-1; H₅SiFe(OH₂)W₁₁O₃₉, 81553-19-7; H₅GeFe(OH₂)W₁₁O₃₉, 81553-09-5; H₆BFe(OH₂)W₁₁O₃₉, 81552-93-4; H₄PFe(OH₂)W₁₁O₃₉, 81553-15-3; H₄AsFe(OH₂)W₁₁O₃₉, 81552-64-9; H₇P₂Fe(OH₂)W₁₇O₆₁, 81553-23-3; H₇As₂Fe(OH₂)W₁₇O₆₁, 81552-72-9; K₆SiRh(OH)W₁₁O₃₉, 81553-56-2; K₆GeRh(OH)W₁₁O₃₉, 81553-44-8; K₇BRh(OH)W₁₁O₃₉, 81552-98-9; K₈P₂Rh(OH)W₁₇O₆₁, 81553-57-3; K₈As₂Rh(OH)W₁₇O₆₁, 81552-81-0; K₇SiRh(O)W₁₁O₃₉, 81553-77-7; K₇GeRh(O)W₁₁O₃₉, 81553-52-8; K₆PRh(O)W₁₁O₃₉, 81553-76-6; K₉P₂Rh(O)W₁₇O₆₁, 81553-78-8; K₉As₂Rh(O)W₁₇O₆₁, 81552-89-8; H₅SiRh(OH₂)W₁₁O₃₉, 81553-67-5; H₅GeRh(OH₂)W₁₁O₃₉, 81553-47-1; H₆BRh(OH₂)W₁₁O₃₉, 81553-01-7; H₄PRh(OH₂)W₁₁O₃₉, 81553-64-2; H₇P₂Rh(OH₂)W₁₇O₆₁, 81553-71-1; H₇As₂Rh(OH₂)W₁₇O₆₁, 81552-84-3; K₈SiW₁₁O₃₉, 37300-95-1; K₈GeW₁₁O₃₉, 81553-51-7; K₉BW₁₁O₃₉, 81553-05-1; K₁₀P₂W₁₇O₆₁, 59111-46-5; K₁₀As₂W₁₇O₆₁, 81552-88-7; K₅SiRh(OH₂)W₁₁O₃₉, 81553-68-6; K₅GeRh(OH₂)W₁₁O₃₉, 81553-48-2; K₆BRh(OH₂)W₁₁O₃₉, 81553-02-8; K₇P₂Rh(OH₂)W₁₇O₆₁, 81553-72-2; K₇As₂Rh(OH₂)W₁₇O₆₁, 81552-85-4; K₅PRh(OH)W₁₁O₃₉, 81553-55-1; K₇PW₁₁O₃₉, 37300-94-0; Na₂HAsO₄, 7778-43-0; Na₂WO₄, 13472-45-2; Na₃RhCl₆, 14972-70-4.

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