# Trimetallo Derivatives of Lacunary 9-Tungstosilicate Heteropolyanions. Part 1. Synthesis and Characterization

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Salts of trimetallo derivatives of 9-tungstosilicate heteropolyanions have been prepared from the lacunary tungstates α- and β-$[SiW_9O_{34}]^{10-}$ and characterized by elemental analysis, spectroscopy and electrochemistry. Tungsten-183 NMR spectra of the (four) diamagnetic derivatives of Al and Ga consist of two lines (intensity ratio 1:2) as expected for the $C_{3v}$ structures of trisubstituted α- and β-Keggin anions. Molecular weight determinations by negative-ion fast atom bombardment mass spectrometry indicate the presence of small quantities of dimeric species ($Si_2W_{18}M_6$) in some of the products. Electronic spectra of the derivatives of Co, Cr, Ni and Cu are consistent with octahedral co-ordination and therefore the probable attachment of a water molecule to each cation. Magnetic measurements at 5–292 K demonstrate moderate to strong antiferromagnetic interactions in the derivatives of $Cr^{III}$, $Mn^{II}$ and $Cu^{II}$. The complexes are stable in aqueous solution between pH *ca.* 5 and 10. Below pH 5 they are slowly transformed into $[SiW_{11}O_{39}M(H_2O)]^{n-}$. In addition to the expected reducibility of all of the new complexes to heteropoly blue species at negative potentials, the complexes of Fe, Cu and Mn exhibit voltammetric redox features corresponding to reduction of $Fe^{III}$ to $Fe^{II}$, $Cu^{II}$ to $Cu^0$, and oxidation of $Mn^{II}$ to $Mn^{III}$ and $Mn^{IV}$.

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The chemistry of heteropolyanions of tungsten and molybdenum continues to attract much attention, particularly with respect to potential catalytic activity, but also with respect to biological and medical applications.[1] We are seeking ways to increase the reactivity of heteropolyanions, which normally have surfaces that are populated with weakly basic oxygen atoms.[2] The work of Klemperer[3] and Finke[4] and their co-workers has shown that the surface basicity of polyanions can be increased by partial substitution of $W^{VI}$ by $V^V$ or $Nb^V$, and these research groups have developed an extensive chemistry of derivatives of such substituted polyanions in which organometallic groups have been attached to the surface oxygen atoms. We have taken a different approach, namely to introduce lower-valent atoms into the tungsten sites of polyanion structures thereby forming sites of direct ligand binding. 'Substituted' heteropolyanions of this type, *e.g.* $[SiW_{11}O_{39}Co(H_2O)]^{6-}$, were first recognized by Baker[5] more than twenty years ago. Recently, it has been shown that such polyanions show considerable (metalloporphyrin-like) reactivity in non-aqueous solvents as a result of ligand substitution on the introduced metal cation.[6]

Several authors have noted that many polyanion structures have surfaces that are analogous to those of close-packed metal oxide lattices.[3,4,7] It is therefore of particular interest to synthesize polyanions in which several adjacent tungsten atoms have been replaced by lower-valent metals, thereby generating a soluble discrete model of an oxide surface. As a rational approach to such complexes, the lacunary anions such as *A*-† or *B*-$[PW_9O_{34}]^{9-}$ and $[P_2W_{15}O_{56}]^{12-}$ have been employed. Although successful synthesis of $[PW_9M_3O_{40}]^{n-}$ and $[P_2W_{15}M_3O_{62}]^{n-}$ could be achieved when M is penta- or hexavalent (V, Nb or Mo), the use of lower-valent cations has led to dimeric species, *e.g.* $[(B\text{-}PW_9O_{34})Co_4(OH_2)_2(B\text{-}PW_9O_{34})]^{10-}$ and $[(A\text{-}PW_9O_{34})Cu_3(A\text{-}PW_9O_{34})]^{14}$ in which the substituent heteroatoms are relatively inaccessible or are non-adjacent.[8]

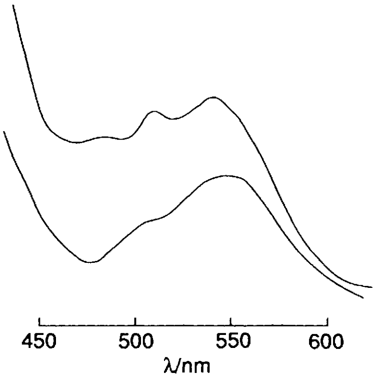

**Fig. 1** Comparative electronic absorption spectra, displaced for clarity, of (upper) β-$[SiW_9O_{34}\{Co(H_2O)\}_3]^{10-}$ and (lower) α-$[SiW_{11}O_{39}Co(H_2O)]^{6-}$ at pH 6.5. Both solutions contained 62 mg of the potassium salt in 5 $cm^3$ solution and have ε values at the *ca.* 550 nm maxima of 66 and 73 $dm^3\ mol^{-1}\ cm^{-1}$ respectively

Several years ago Hervé and Tézé[9] described the corresponding tungstosilicates α- and β-$[SiW_9O_{34}]^{10-}$. The structure of the sodium salt of the β anion revealed it to be A type, in which three adjacent corner-shared $WO_6$ octahedra of the β-Keggin structure had been removed.[10] Lèyrie and Tézé[11] and Ortéga[12] shortly thereafter demonstrated that these anions would react with $Cr^{III}$ and $Fe^{III}$ to produce $[SiW_9M_3O_{40}]^{n-}$ anions. We have since described the cobalt(II) derivative,[6a] and now report a more complete investigation of these and analogous complexes. The reactivity of these species in aqueous and non-aqueous solvents will be described in subsequent papers of this series.

## Results and Discussion

Analytical data for the new complexes are summarized in Table

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† Removal of three adjacent corner-sharing $MO_6$ octahedra from the Keggin structure yields the so-called *A* structure; removal of three adjacent edge-sharing octahedra yields the *B* structure.

**Table 1** Analytical data for salts of $[SiW_9O_{37}M_3(H_2O)_3]^{n-}$ anions, $n = 7$ or 10

| | Analysis (%)[a] | | | |
|---|---|---|---|---|
| Isomer, M, cation, hydrate | W | M | Na, K or Cs | $H_2O$[b] |
| β, Al, $K_4H_3$, 16 | 60.85 (59.45) | 2.90 (3.05) | 5.80 (5.60) | 10.45 (10.35) |
| β, Ga, $K_5H_2$, 15 | 54.95 (55.05) | 7.00 (6.95) | 7.00 (6.50) | 8.70 (9.00) |
| β, $Cr^{III}$, $Cs_4H_3$, 7 | 60.05 (59.10) | 5.25 (5.55) | 18.65 (19.00) | 4.65 (4.50)[c] |
| β, $Fe^{III}$, $K_7$, 7 | 57.60 (57.15) | 5.80 (5.80) | 9.40 (9.45)[d] | 4.10 (3.90)[c] |
| β, $Mn^{II}$, $K_6H_4$, 13 | 56.60 (55.95) | 5.35 (5.65) | 7.30 (7.95) | 9.85 (9.75) |
| β, $Co^{II}$, $[N(CH_3)_4]_{10}$, 10 | 48.30 (48.30) | 5.15 (5.15) | e | 5.45 (5.25) |
| β, $Co^{II}$, $[N(CH_3)_4]_4Na_2H_4$, 12 | 53.70 (53.95) | 5.30 (5.75) | 1.50 (1.50)[f] | 6.60 (6.25) |
| β, $Ni^{II}$, $K_6H_4$, 35 | 49.70 (49.80) | 4.90 (5.30) | 6.80 (7.05) | 15.00 (20.60)[g] |
| β, $Cu^{II}$, $K_6H_4$, 24 | 51.90 (51.85) | 6.00 (5.95) | 6.55 (7.35) | 10.85 (15.25)[g] |
| α, Al, $Cs_3H_4$, 9 | 55.35 (55.57) | 2.70 (2.70) | 12.85 (13.40) | 5.50 (5.45) |
| α, Ga, $K_5H_2$, 13 | 55.75 (55.75) | 7.00 (7.05) | 6.05 (6.60) | 7.80 (7.90) |
| α, $Cr^{III}$, $K_4H_3$, 7 | 58.85 (59.80) | 5.30 (5.65) | 5.25 (5.65) | 4.45 (4.55)[c] |
| α, $Fe^{III}$, $K_6H$, 8 | 57.50 (57.55) | 6.15 (5.85) | 7.80 (8.15) | 8.35 (6.90) |
| α, $Mn^{II}$, $K_6H_4$, 16 | 54.70 (54.80) | 5.30 (5.45) | 8.15 (7.75) | 11.80 (11.30) |
| α, $Co^{II}$, $K_6H_4$, 17 | 53.60 (54.25) | 5.90 (5.80) | 7.60 (7.70) | 9.10 (11.80)[g] |
| α, $Ni^{II}$, $K_5H_5$, 26 | 51.70 (52.10) | 5.30 (5.55) | 5.90 (6.15) | 13.05 (16.45)[g] |
| α, $Cu^{II}$, $K_6H_4$, 18 | 53.00 (53.70) | 6.05 (6.20) | 8.00 (7.60) | 12.60 (12.25) |

[a] Calculated values in parentheses. [b] Weight loss at 520 °C unless specified otherwise. [c] Weight loss at 150 °C. [d] Si 0.95 (0.95)%. [e] C 13.75 (14.00), H 4.35 (3.95), N 3.95 (4.20), Si 0.85 (0.80)%. [f] C 6.05 (6.25), H 2.45 (1.90), N 1.65 (1.85), Si 0.80 (0.90)%. [g] Very efflorescent salt.

**Table 2** Electronic absorption spectral data for $SiW_9M_3$ anions *

| M, isomer | Cation | Peak maximum/nm (ε/dm³ mol⁻¹ cm⁻¹) |
|---|---|---|
| $Cr^{III}$, β | Cs | 605 (85) |
| $Cr^{III}$, α | Cs | 605 (112) |
| $Fe^{III}$, β | K | 645 (7.3), 950 (4.2), 977 (sh) |
| $Fe^{III}$, α | K | 900 (170) |
| $Co^{II}$, β | $N(CH_3)_4$ | 485 (60), 505 (65), 535 (66) |
| $Co^{II}$, α | K | 490 (61), 512 (70), 535 (64) |
| $Ni^{II}$, β | K | 395 (sh), 690 (32), 760 (sh), 1050 (14) |
| $Ni^{II}$, α | K | 400 (18), 690 (15.5), 760 (14), 1160 (9.1) |
| $Cu^{II}$, β | K | 780 (57.5) |
| $Cu^{II}$, α | Cs | 790 (44) |

* Aqueous solution, pH 6.

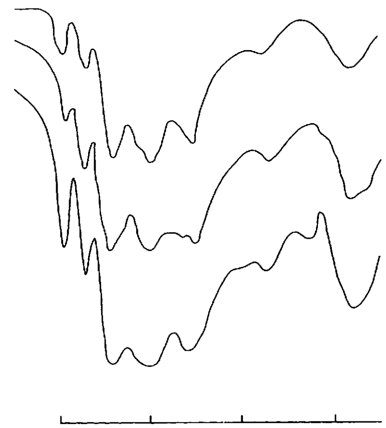

Fig. 2 Representative infrared spectra. From top to bottom: potassium salts of β-$SiW_9Ni_3$, β-$SiW_9Co_3$ and β-$SiW_9Mn_3$

**Table 3** Tungsten-183 NMR data[a]

| Anion | δ[b] | $^2J$(W–W)/Hz |
|---|---|---|
| β-$SiW_9Al_3$ | −109.6 (2), −122.8 (1) | 15.3 |
| β-$SiW_9Ga_3$ | −97.3 (2), −124.3 (1) | 15.2 |
| α-$SiW_9Al_3$ | −97.4 (2), −162.1 (1) | 15.4 |
| α-$SiW_9Ga_3$ | −80.4 (2), −159.7 (1) | 15.9 |

[a] In water–$D_2O$ solution, pH 6. [b] Relative intensity in parentheses.

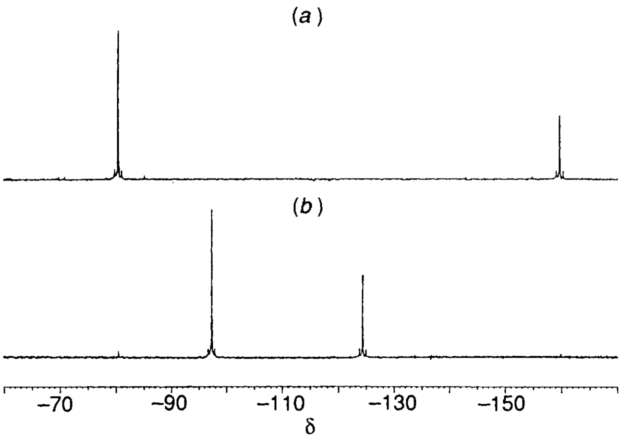

Fig. 3 12.505 MHz $^{183}W$ NMR spectra of α- (a) and β-$[SiW_9O_{37}\{Ga(H_2O)\}_3]^{7-}$ (b)

1, and electronic spectra in Table 2. Comparative spectra for $SiW_9Co_3$ and $SiW_{11}Co$ complexes are shown in Fig. 1. The electronic spectra are consistent with nominal octahedral co-ordination spheres for Co, Cr, Ni and Cu. Some representative infrared spectra are illustrated in Fig. 2.

The four diamagnetic derivatives of Al and Ga gave clean tungsten-183 NMR spectra with two lines in an intensity ratio of 1:2, see Fig. 3. Chemical shifts and W–W coupling constants are given in Table 3. Collectively these data support the 9:3 stoichiometry of the new heteropolyanions and the probable retention of the $SiW_9$ unit. Based on the known structure of β-$[SiW_9O_{34}]^{10-}$ and the presumed structure of the corresponding α isomer, we provisionally conclude that the new complexes contain the substituent heteroatoms in adjacent corner-shared octahedra of β- and α-Keggin structures respectively, Fig. 4. Water molecules are presumed to complete the co-ordination spheres of the introduced heteroatoms, as observed in the analogous $SiW_{11}M$ complexes.

An alternative structure that could account for the analytical and NMR data is a dimeric species with three M–O–M bridges. Dimerization of $[SiW_{11}O_{39}Fe(OH)]^{6-}$ to $[(SiW_{11}O_{39}Fe)_2O]^{12-}$ is governed by an equilibrium constant of 40 dm³ mol⁻¹ in 5 mol dm⁻³ LiCl.[13] Approximate formation constants for

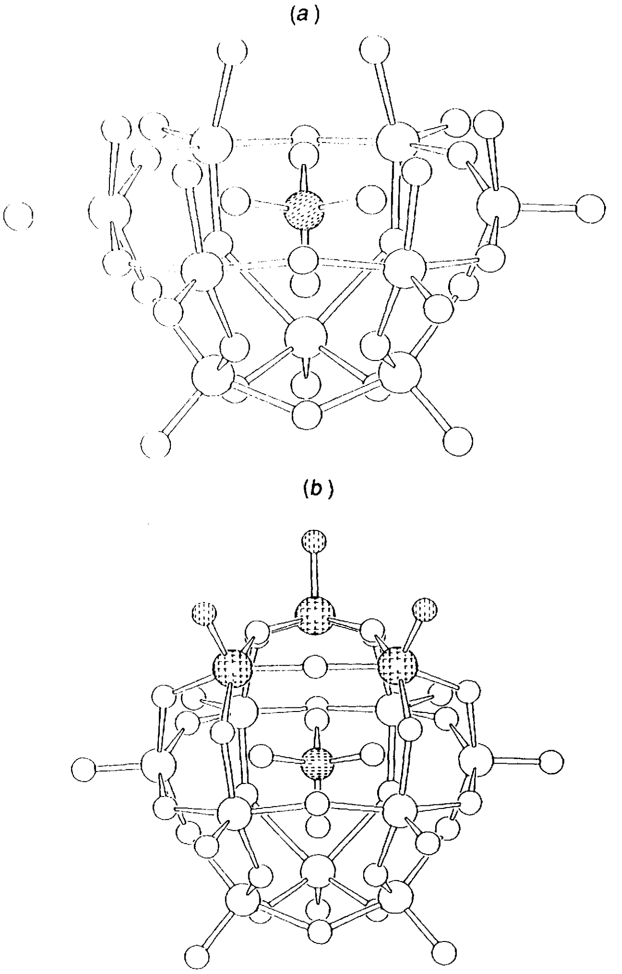

**Fig. 4** (*a*) Structure[10] of the lacunary anion β-$[SiW_9O_{34}]^{10-}$. (*b*) Presumed structure of β-$[SiW_9O_{37}\{M(H_2O)\}_3]^{n-}$. Large open circles, W; small open circles, O. Bonds between the oxygens attached to the central Si (shaded) and the surrounding metal atoms have been omitted for clarity. Aqua ligands attached to M atoms are indicated by small shaded circles

dimers of $[X^V{}_2W_{17}O_{61}Fe(OH)]^{8-}$ (*ca.* 20 dm$^3$ mol$^{-1}$) and $[X^VW_{11}O_{39}Fe(OH)]^{5-}$ (*ca.* 100 dm$^3$ mol$^{-1}$)[14] show that dimerization is less favourable for anions of higher charge. No evidence has been presented for the dimerization of other XW$_{11}$M species, including the cases where M is Cr$^{III}$.[14] It seemed unlikely therefore that the more highly charged SiW$_9$M$_3$ anions would be prone to analogous dimerization, except perhaps at high pH. In order to test this, molecular weight determinations were made using fast atom bombardment (FAB) mass spectrometry of aqueous glycerol solutions of the α-Co, α-Fe, β-Cr, α-Ni, β-Al and α-Ga derivatives, see Experimental section. Molecular weights corresponded in all cases to the W$_9$M$_3$ formulas, but peaks corresponding to 'dimers' were detected in each spectrum in small to modest amounts,* see Fig. 5 for example, except in the case of the cobalt derivative where only the monomer was detected. Since the NMR spectra of the derivatives of Al and Ga were exceptionally clean, we conclude that, in aqueous solution, dimeric species are hydrolysed to the monomers. To date, no crystals that are suitable for structural analysis have been discovered; those that are of suitable size have space groups that imply disorder, exhibit inappropriate habits (thin plates), or have very large cells. This situation is unfortunately only too common for this class of compounds, but the search continues for suitable crystals.

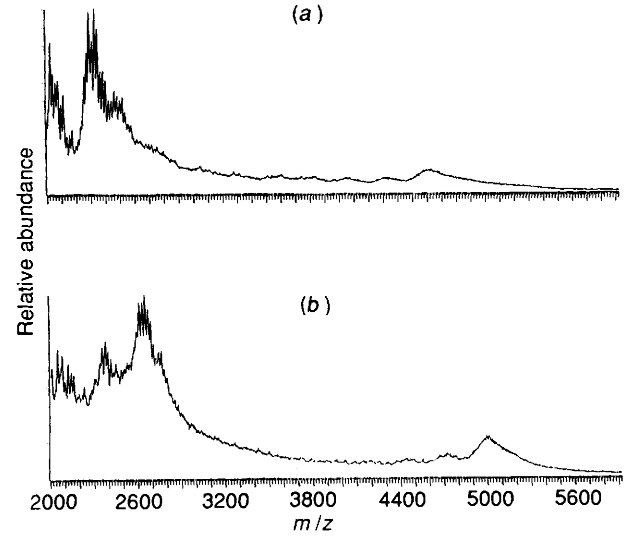

**Fig. 5** Liquid secondary ion mass spectra (LSIMS) in the negative mode recorded on aqueous glycerol solutions of (*a*) β-$K_4H_3[SiW_9O_{37}Al_3(H_2O)_3]$ and (*b*) α-$K_6H[SiW_9O_{37}Fe_3(H_2O)_3]$ (sums of three and four scans respectively). Structure results from loss of water and WO$_3$ from monomer and dimer clusters

With the exception of the derivatives of Al and Ga the complexes are strongly paramagnetic. The magnetic susceptibilities of β-$Cs_4H_3[SiW_9O_{37}\{Cr(H_2O)\}_3]\cdot 7H_2O$, β-$K_6H_4[SiW_9O_{37}\{Mn(H_2O)\}_3]\cdot 13H_2O$ and β-$K_6H_4[SiW_9O_{37}\{Cu(H_2O)\}_3]\cdot 13H_2O$ indicated strong antiferromagnetic interactions. For the chromium(III) complex, $\mu_{eff}$ per Cr fell from 3.37 at 293 K to 2.1 at 6 K, for the manganese(II) complex the corresponding values were 5.43 (291) and 4.22 (6 K), and for the copper(II) complex were 1.86 (292) and 0.90 (5 K). In each case the temperature variation of the susceptibility could not be well fitted by a simple trimer model, and further investigation is postponed until structural crystallographic information is available. Possible explanations for the magnetic behaviour are additional (intermolecular) antiferromagnetic coupling between adjacent anions, the presence of dimeric species, and a reduction in symmetry as a result of protonation at the bridging oxygen atoms. (The magnetic behaviour of the seemingly symmetric carboxylato $\mu_3$-oxo trimers of Fe$^{III}$, Cr$^{III}$, *etc.* is also not straightforward and is subject to controversy.[16]) The strong paramagnetism of most of the new complexes also rules out $^{183}$W NMR spectroscopy as a reliable structural probe in these cases. For example, a solution of the α-Co complex converted into the lithium salt *via* ion exchange gave a spectrum with two very broad lines at δ +708 ($\Delta\nu_{\frac{1}{2}}$ *ca.* 5 kHz) and −690 (*ca.* 10 kHz); the β-Cu complex similarly yielded a single broad line at δ +206 (*ca.* 3300 Hz). Considerable effort was devoted to trying to synthesize the zinc derivative, without success so far. The products of such attempts were pure samples of $\beta_n$-SiW$_{11}$M anions, as identified by $^{183}$W NMR spectroscopy. At pH 7.2 the $^{183}$W NMR chemical shifts of α-$[SiW_{11}O_{39}Zn(OH_2)]^{6-}$ are δ −62.8, −109.5, −133.7, −140.8, −159.7 and −175.1 (2:2:1:2:2:2)[17] whereas those of the new $\beta_n$ product were δ −82.6, −94.0, −115.3, −124.0, −160.7 and −185.4 (2:2:2:1:2:2). This pattern implies $C_s$ symmetry of either a $\beta_1$ or $\beta_3$ isomer.

The salts of the α-series anions were generally much less soluble than the corresponding β salts. This is true also for the lacunary SiW$_9$ anions themselves. It has therefore only been possible to obtain suitable crystals of β-SiW$_9$ for structural

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* Although ionic association is observed in LSIMS of *suspensions* of inorganic salts,[15] bombardment-induced association of solute species is an insignificant effect. The intensities of the 'dimer' peaks observed in the present investigation suggest the presence of small quantities of preformed species in the water–glycerol solutions. It is possible that more than one kind of dimer, *i.e.* with one, two or three M–O–M bridges, may be formed in these solutions.

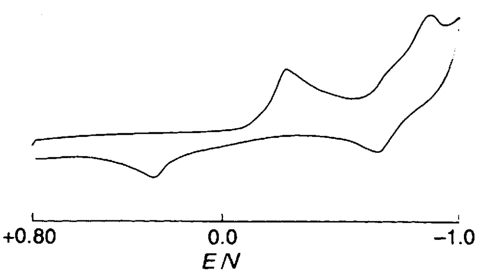

**Fig. 6** Cyclic voltammogram of β-$[SiW_9O_{37}\{Fe(H_2O)\}_3]^{7-}$ at pH 5 in acetate buffer

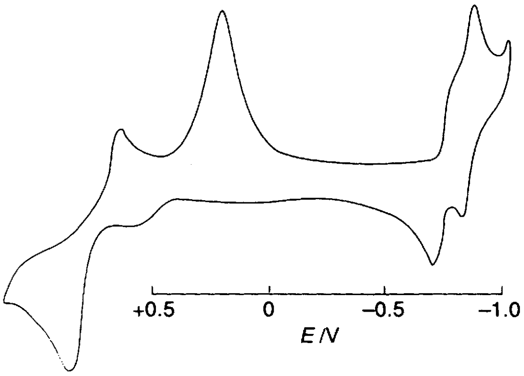

**Fig. 7** Cyclic voltammogram of β-$[SiW_9O_{37}\{Mn(H_2O)\}_3]^{10-}$ (1.0 mmol $dm^{-3}$) at pH 4.7 in 1.0 mol $dm^{-3}$ acetate. Sweep rate 2.0 V $min^{-1}$

analysis,[10] for example. Whereas the lacunary $SiW_9$ anions are unstable in solution, and are rapidly converted into $SiW_{11}$ species, the new complexes reported here may be repeatedly recrystallized from neutral aqueous solution. Based on spectrophotometric examination of 2–3 mmol $dm^{-3}$ solutions, each of the twelve anions appears to be stable (at least kinetically) between pH 5 and 10 (those of Co, Ni and Mn to pH 12, α-Fe to pH 9.5). This is an unprecedented range of alkaline stability for heteropolytungstates and opens up possibilities for further derivatization and for catalytic applications, which we are currently investigating. At pH < 5 the complexes are slowly converted into $SiW_{11}M$ species.

In most cases the anions were isolated as acid salts. When the substituent metal is divalent the anion charge is 10−, and with the exception of one tetramethylammonium salt prepared by slow evaporation the remaining compounds require four or five protons for charge balance. Potentiometric titration of these salts with either acid or base resulted in no clear inflection points however.

All of the complexes are distinguishable from $SiW_{11}$, $SiW_{11}M$ and $SiW_{12}$ species by their electrochemical behaviour. Polarograms of β-$SiW_9Fe_3$ at pH 4–6 showed three pH-dependent waves with heights in the ratio 3:2:2. Half-wave potentials at pH 4 are −0.12, −0.73 and −0.82 V with $\Delta E_{\frac{1}{2}}$/pH = 80–90 mV. The cyclic voltammogram at pH 5 (Fig. 6) shows the first reduction to be quite irreversible ($\Delta E \approx 500$ mV) and it is attributed to the simultaneous reduction of the three iron atoms to $Fe^{II}$. Controlled-potential electrolysis at −0.6 V (pH 6) resulted in the passage of 2.89 equivalents per mol. A cyclic voltammogram of the resulting yellow solution showed additional peaks at +0.04 and −0.65 V which indicated partial decomposition of the putative $SiW_9Fe^{II}_3$ species. The second and third reductions (at −0.73 and −0.82 V) correspond to heteropoly blue formation ($W^{VI}$ to $W^{V}$) as documented for other polytungstates.[18] Cyclic voltammograms were recorded for all of the new complexes. At pH 4.7 (1.0 mol $dm^{-3}$ acetate) tungsten reductions (in two- or four-electron steps) were observed at −0.88 ± 0.01 and −1.05 ± 0.05 V *vs.* saturated calomel electrode (SCE). The complexes of Fe (see above), Cu, and Mn showed additional features. Irreversible reduction of $Cu^{II}$ to $Cu^{0}$ was observed at −0.42 V. Voltammograms of β-$SiW_9Mn_3$ (see Fig. 7) showed quasireversible oxidation features at +0.55, +0.87 (pH 4.7) or at +0.09, +0.43 V (pH 7.5) that indicate oxidation to $Mn^{III}_3$ and $Mn^{IV}_3$ species respectively. This was confirmed by controlled-potential oxidation, pH 4.7, at +1.00 V (6 equivalents) and subsequent reduction at 0.46 V (3 equivalents). Further investigation of the manganese complexes is reported elsewhere.[19]

## Conclusion

The sixteen complexes reported here represent an unusual class of heteropolyanions in which a substantial fraction (25%) of the molecular surface can be regarded as a polycation, *e.g.* $[\{Fe^{III}(OH_2)\}_3O_3]^{3+}$ or as a neutral metal oxide, *e.g.* $[\{Co(OH_2)\}_3O_3]$. Such complexes can be expected not only to display reactivity similar to that demonstrated for the 'inorganic metalloporphyrins', $[XW_{11}O_{39}M(OH_2)]^{n-}$,[6] but also to model features of metal oxide surfaces such as multisite or co-operative binding and activation of ligand substrates. Subsequent papers of this series will describe the reactivity of these complexes in aqueous and non-aqueous solvents.

## Experimental

*Syntheses.*—The salts α-$Na_{10}[SiW_9O_{34}]\cdot 18H_2O$ ('α-$SiW_9$') and β-$Na_9H[SiW_9O_{34}]\cdot 23H_2O$ ('β-$SiW_9$') were prepared according to the method of Hervé and Tézé[9] and were identified by polarography.

β-$[SiW_9O_{37}\{Co(H_2O)\}_3]^{10-}$, *Tetramethylammonium salt.* To a solution of cobalt(II) acetate tetrahydrate (3.0 g, 0.012 mol) in water (100 $cm^3$) was added with vigorous stirring β-$SiW_9$ (11.2 g) in small amounts. After the addition was complete, the pH of the solution was 6.5–6.8. Stirring was continued for 15 min, after which traces of insoluble material were filtered off and the filtrate was passed through a cation-exchange column (Dowex 50, sodium form, 20 mesh, flow rate 0.5 $cm^3$ $min^{-1}$; the column had been conditioned by treatment with a solution of sodium acetate at pH 6.5). The eluate was then treated with a saturated solution of tetramethylammonium chloride (5 $cm^3$) and allowed to evaporate in a covered beaker at room temperature. After about 2 weeks a pink microcrystalline solid had formed. This was filtered off, washed several times with small amounts of water and ethanol, and recrystallized from hot water at pH 6.5. Yield: 6.5 g. Analytical data are given in Table 1.

*Other salts.* In order to speed up the above preparation, the eluate plus tetramethylammonium chloride may be treated with twice its volume of methanol, to yield an acid double salt (Table 1). Addition of KCl or CsCl to the eluate yields the more sparingly soluble potassium or caesium salts.

β-$[SiW_9O_{37}\{Fe(H_2O)\}_3]^{7-}$, *Potassium salt.* A solution of $[Fe_3(CH_3CO_2)_6(OH)_2Cl]$ (1.99 g, 3 mmol) in 0.5 mol $dm^{-3}$ sodium acetate (pH 6.5, 150 $cm^3$) was treated with β-$SiW_9$ (8.54 g, 3 mmol) as above, and the mixture heated to 50 °C for 15 min. After cooling to room temperature, KCl (*ca.* 0.5 g) was added, producing a red-brown turbidity that was filtered off. To the light green filtrate was added KCl (5 g) to yield an iridescent green precipitate. The solid was filtered off, washed with cold water and recrystallized from warm water to yield light green crystals (6.9 g). Because the potassium analysis was lower than expected, the compound (1.5 g) was dissolved in water (100 $cm^3$) and passed through a column (2 × 20 cm) of Dowex 50W-X2 in the potassium form. The crystals that formed almost immediately after elution were filtered off and washed with small amounts of cold water.

β-$[SiW_9O_{37}\{Cu(H_2O)\}_3]^{10-}$, *Potassium salt.* To a solution of copper(II) acetate (3.0 g, 15 mmol) in 0.5 mol $dm^{-3}$ sodium acetate (pH 6.5, 150 $cm^3$) was added β-$SiW_9$ (12.8 g, 4.5 mmol) as above. An initially formed blue precipitate redissolved to form a green solution. After cation-exchange treatment, a solution of KCl (4 g) in water (12 $cm^3$) was added. A green oil was formed that upon stirring changed to a green solid. The latter was recrystallized from water to yield green crystals (7.8 g).

β-$[SiW_9O_{37}\{Mn(H_2O)\}_3]^{10-}$, *Potassium salt.* To a solution of $Mn(CH_3CO_2)_2 \cdot 4H_2O$ (3.3 g, 13.5 mmol) in 0.5 mol $dm^{-3}$ sodium acetate (pH 6.5, 150 $cm^3$) was added β-$SiW_9$ (12.8 g, 4.5 mmol) as above. An initially formed yellow precipitate redissolved to give a yellow solution. After cation-exchange treatment, a solution of KCl (4 g) in water (12 $cm^3$) was added, producing a yellow precipitate which was filtered off and recrystallized from hot water (80 $cm^3$) to yield 7 g of product.

β-$[SiW_9O_{37}\{Ni(H_2O)\}_3]^{10-}$, *Potassium salt.* The previous preparation was repeated with $Ni(NO_3)_2 \cdot 6H_2O$ (3.0 g, 10.4 mmol) in 0.5 mol $dm^{-3}$ sodium acetate (pH 6.5, 120 $cm^3$) and β-$SiW_9$ (10.0 g, 3.5 mmol). After cation exchange, KCl was added as before to yield a green precipitate which was filtered off and recrystallized from hot water (30 $cm^3$).

β-$[SiW_9O_{37}\{Cr(H_2O)\}_3]^{7-}$, *Caesium salt.* To a solution of $[Cr_3O(CH_3CO_2)_6(H_2O)_3]Cl \cdot 5H_2O$[20] (6.5 g, 10 mmol) in 0.5 mol $dm^{-3}$ sodium acetate (pH 6.5, 250 $cm^3$) was added β-$SiW_9$ (28.5 g, 10 mmol) as above. Following cation exchange the green product was precipitated by the addition of CsCl (10 g), and was recrystallized from hot water (80 $cm^3$).

β-$[SiW_9O_{37}\{Al(H_2O)\}_3]^{7-}$, *Potassium salt.* The salt β-$SiW_9$ (11.2 g, 4 mmol) was added in small amounts with vigorous stirring to a solution of $Al(NO_3)_3 \cdot 9H_2O$ (4.3 g, 11.5 mmol) in water (80 $cm^3$). After the addition was complete, and a transient white precipitate had redissolved, the solution was adjusted to pH 5.5–6.0 with sodium carbonate, and KCl (5 g) was added, producing a white precipitate which was filtered off and recrystallized from hot water to yield 8.0 g product.

β-$[SiW_9O_{37}\{Ga(H_2O)\}_3]^{7-}$, *Potassium salt.* The salt β-$SiW_9$ (21.0 g, 7.6 mmol) was added in small amounts with vigorous stirring to a solution of $Ga(NO_3)_3$ (5.8 g, 22.7 mmol) in water (120 $cm^3$). After the addition was complete and a transient white precipitate had redissolved, the pH of the solution was 2.5–3.0. The pH was adjusted to 5.0–5.5 with sodium carbonate, the solution was stirred for 15 min, and KCl (6 g) was added. The resulting white precipitate was filtered off and recrystallized from hot water (20 $cm^3$) to yield 11.4 g product.

α-$[SiW_9O_{37}\{Co(H_2O)\}_3]^{10-}$, *Potassium salt.* To a solution of $Co(CH_3CO_2)_2 \cdot 4H_2O$ (12.00 g, 0.048 mol) in water (600 $cm^3$) was added α-$SiW_9$ (44.65 g, 0.016 mol) in small portions with vigorous stirring. Since the latter salt is insoluble the temperature was slowly raised during the addition. At about 80 °C the solution changed from red to brown and dissolution of $SiW_9$ became more apparent. Addition of water (400 $cm^3$) resulted in almost complete dissolution. After the solution had been stirred for 1 h at 80 °C it was allowed to cool and passed through a cation-exchange column to remove unreacted cobalt. Addition of a solution of KCl (13 g) in water (50 $cm^3$) to the eluate resulted in immediate precipitation of a microcrystalline brown solid (dark brown when dry). Yield *ca.* 40%. The product was recrystallized from hot water.

α-$[SiW_9O_{37}\{Fe(H_2O)\}_3]^{7-}$, *Potassium salt.* A solution of $Fe(NO_3)_3 \cdot 9H_2O$ (21.57 g, 0.053 mol) in water (200 $cm^3$) was slowly added to 0.5 mol $dm^{-3}$ sodium acetate (pH 6.5, 400 $cm^3$). To the resulting deep red solution (initial pH 4.2) was added α-$SiW_9$ (45.0 g, 0.016 mol) in small portions over 1 h at about 70 °C. The solution became dark brown and the pH increased to 5–6. After the addition was complete the solution was stirred for 1 h at 80 °C, allowed to cool and passed through a cation-exchange column. Addition of KCl (13 g in 50 $cm^3$ water) to the eluate caused the formation of a very fine rust-coloured precipitate. This was filtered off on a membrane filter and recrystallized from hot water. Yield: 50%.

α-$[SiW_9O_{37}\{Cu(H_2O)\}_3]^{10-}$, *Potassium salt.* To a solution of copper(II) acetate (3.0 g, 15 mmol) in 0.5 mol $dm^{-3}$ sodium acetate (pH 6.5, 150 $cm^3$) was added α-$SiW_9$ (13.9 g, 5 mmol) at 70 °C as above. After cation-exchange treatment a solution of KCl (4 g) in water (12 $cm^3$) was added. A green oil formed that upon stirring changed to a green solid which was recrystallized from hot water (30 $cm^3$) to yield green crystals (6 g).

α-$[SiW_9O_{37}\{Mn(H_2O)\}_3]^{10-}$, *Potassium salt.* To a solution of $Mn(CH_3CO_2)_2 \cdot 4H_2O$ (6.0 g, 25 mmol) in 0.5 mol $dm^{-3}$ sodium acetate (pH 6.5, 250 $cm^3$) was added α-$SiW_9$ (22.0 g, 7.9 mmol) as above at 70 °C. After the addition was complete the solution was stirred for 1 h at 70 °C, allowed to cool, and passed through a cation-exchange column. Addition of KCl (6 g) in water (20 $cm^3$) yielded a yellow precipitate which was filtered off and recrystallized from water (80 $cm^3$) to give 12 g product.

α-$[SiW_9O_{37}\{Ni(H_2O)\}_3]^{10-}$, *Potassium salt.* The preparation of the copper derivative was repeated exactly, using $NiSO_4 \cdot 7H_2O$ (3.4 g, 12 mmol) in 0.5 mol $dm^{-3}$ sodium acetate (150 $cm^3$) and α-$SiW_9$ (11.2 g, 4 mmol).

α-$[SiW_9O_{37}\{Cr(H_2O)\}_3]^{7-}$, *Potassium salt.* The preparation of the manganese derivative was repeated exactly, using a solution of $[Cr_3O(CH_3CO_2)_6(H_2O)_3]Cl \cdot 5H_2O$ (6.5 g, 10 mmol) in 0.5 mol $dm^{-3}$ sodium acetate (pH 6.5, 250 $cm^3$) and α-$SiW_9$ (27.6 g, 10 mmol). The green product was recrystallized from hot water (50 $cm^3$).

α-$[SiW_9O_{37}\{Al(H_2O)\}_3]^{7-}$, *Potassium salt.* To a solution of $Al(NO_3)_3 \cdot 9H_2O$ (4.3 g, 11.5 mmol) in water (80 $cm^3$) was added α-$SiW_9$ (11.2 g, 4 mmol) in small amounts with vigorous stirring. After the addition was complete and a transient white precipitate had redissolved the solution was adjusted to pH 4.5–5.0 with sodium carbonate. It was stirred for 15 min, KCl (5 g) was added, and the resulting white precipitate filtered off and recrystallized from warm (50 °C) water (20 $cm^3$). Yield: 7.1 g.

α-$[SiW_9O_{37}\{Ga(H_2O)\}_3]^{7-}$, *Potassium salt.* The preparation of the aluminium derivative was repeated using $Ga(NO_3)_3$ (5.8 g, 22.7 mmol) in water (120 $cm^3$) and α-$SiW_9$ (21.0 g, 7.6 mmol). The pH was adjusted to 5.0–5.5 after the addition was complete. Yield after recrystallization: 11.0 g.

*Analyses.*—Samples were heated with excess of KOH to ensure complete decomposition. Tungsten was determined gravimetrically as the quinolin-8-olate or as $WO_3$. Chromium was determined by precipitation as $PbCrO_4$, cobalt by hexacyanoferrate(III) titration, and other transition metals by titration with ethylenediaminetetraacetate. Potassium was determined gravimetrically as the tetraphenylborate. Water was determined by weight loss at 520 °C. Carbon, hydrogen and nitrogen analyses and some metal determinations were by E + R Microanalytical Laboratory, Corona, NY. All analytical data are given in Table 1.

*Physical Measurements.*—Electrochemical measurements were made on modular instruments constructed of Heath and McKee-Pedersen components, and a Brinkmann potentiostat, using dropping-mercury and glassy-carbon electrodes. Potentials are reported with reference to silver–silver chloride. Infrared spectra were recorded on KBr pellets using a Perkin-Elmer 225 spectrometer, electronic spectra on a Cary 14 instrument, and tungsten-183 NMR spectra (12.50 MHz) on a Bruker WP300 spectrometer using quadraphase detection. Magnetic susceptibility measurements were made on a SQUID susceptometer at the University of Virginia. Liquid secondary ion mass spectra (LSIMS) were acquired at the Massachusetts Institute of Technology (MIT) Mass Spectrometry Facility using the first two sectors of a JEOL HX110/HX110 tandem mass spectrometer, operated in the negative-ion mode at $-10$ kV accelerating voltage with $+18$ kV postacceleration at the detector. The primary beam was 22 keV (*ca.* $3.5 \times 10^{-15}$ J) $Cs^+$, produced by a JEOL gun at 2.4 A. A saturated aqueous solution of each sample was mixed 1:1 (v/v) with glycerol and 0.5 μl of the mixture was applied to the stainless-steel probe tip. Spectra were recorded as profiles at 1:1000 resolution during magnetic field scans under control of the JEOL

DA5000 data system. The spectra reported are the sum of one to three scans. The mass scale was calibrated with $(CsI)_nI^-$ clusters.

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