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Di- and Tri-Cobalt Silicotungstates: Synthesis, Characterization, and Stability Studies

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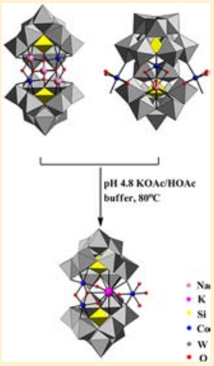
Supporting Information

ABSTRACT: Di- and tricobalt silicotungstate complexes, $K_5Na_4H_4[\{Na_3(\mu\text{-}OH_2)_2Co_2(\mu\text{-}OH)_4\}(Si_2W_{18}O_{66})]\cdot 37H_2O$ (**1**) and $K_6Na_3[Na(H_2O)\{Co(H_2O)_3\}_2\{Co(H_2O)_2\}(Si_2W_{18}O_{66})]\cdot 22H_2O$ (**2**), have been synthesized through reaction of cobalt chloride and $[A\text{-}\alpha\text{-}SiW_9O_{34}]^{10-}$ in acidic buffer solution. They have been characterized by X-ray crystallography, elemental analysis, cyclic voltammetry, infrared, and UV−vis spectroscopy. In **1**, two cobalt atoms as well as three sodium atoms are incorporated in the central pocket of the $[Si_2W_{18}O_{66}]^{16-}$ polyanion. In **2**, one cobalt atom and one sodium atom are incorporated in the pocket of $[Si_2W_{18}O_{66}]^{16-}$; two other cobalt atoms in this complex protrude outside the pocket and connect with WO_6 units of other $[Si_2W_{18}O_{66}]^{16-}$ polyanions to form a one-dimensional polymeric structure. The crucial parameters in the synthesis of these two compounds are discussed, and their stability in different buffer solutions is studied. The decomposition of **1** or **2** in heated potassium acetate buffer (pH 4.8, 1 M) yields $K_{11}[\{Co_2(H_2O)_8\}K(Si_2W_{18}O_{66})]\cdot 17H_2O$ (**3**) based on spectroscopic studies and an X-ray crystal structure.



INTRODUCTION

Catalysts for multielectron-transfer events, such as oxidation of organic substrates and water oxidation, usually need multiple proximal metal (or metal oxide) centers. Molecular materials containing these active centers have advantages over their heterogeneous counterparts because molecules are far more tunable and their properties can be probed more thoroughly by experimental and computational methods. Polyoxometalates (POMs) are attractive as all inorganic ligands for these catalysts because they are oxidatively and hydrolytically resistant over wide pH ranges depending on alterable properties of the particular POM family.[1−7] In addition, many synthetically accessible structural families of POMs can bind two or more redox-active 3d or 4d metals in close proximity and release protons to facilitate multielectron transfer events with redox leveling. Furthermore, additional features ranging from chirality to organic derivatization of metal-substituted POMs can be achieved by adjusting pH, ionic strength, buffer, other metals or organic groups and POM counterions.[7−18] The extensive tunability of multimetal-substituted POMs makes them attractive in applications ranging from chemotherapy[19−23] to catalysis.[24−29]

The higher number of missing metal-oxo groups that a lacunary POM structure has, the more metal atoms it can theoretically incorporate into its framework. The multidefect phosphotungstates, $[P_2W_{12}O_{48}]^{14-}$[30−32] and $[H_7P_8W_{48}O_{184}]^{33-}$[13,17,32−37] have been used to incorporate large clusters of transition metals, although their silicon analogues have never been made. The silicotungstate, $[Si_2W_{18}O_{66}]^{16-}$ can accommodate several d-electron metal centers in the lacunary cavity; however, tetra-iron,[38] penta-copper,[39] penta-nickel,[40] and dimerized hexa-zinc oxides clusters[41] are the only known derivatives to date that have more than two transition metals in such a cavity. Efforts have been made to incorporate three or more cobalt atoms in lacunary POMs, but even with partial decomposition of $[Si_2W_{18}O_{66}]^{16-}$, only four cobalt atoms were incorporated in the center.[42] Here we report the synthesis and structural characterization of dicobalt and tricobalt POMs based on the $[Si_2W_{18}O_{66}]^{16-}$ multidefect unit, as well as their decomposition product.

EXPERIMENTAL SECTION

General Methods and Materials. $K_{10}A\text{-}\alpha\text{-}[SiW_9O_{34}]\cdot 13H_2O$ was prepared by the literature procedure,[43] and its purity was checked by IR spectroscopy. Except for tris(2,2′-bipyridyl) dichlororuthenium(II) hexahydrate, which was recrystallized using the literature procedure,[44] all other reagents were the highest quality available from commercial sources and used as received. Elemental analyses for K, Na, Co, Si, and W were performed by Galbraith Laboratories (Knoxville, Tennessee). IR spectra (2% samples in KBr pellet) were collected on a Nicolet 6700 FT-IR spectrometer. The electronic absorption spectra were obtained on an Agilent 8453 UV−vis spectrometer. Electrochemical data were obtained using a BAS CV-50W electrochemical analyzer at room temperature equipped with a glassy-carbon working, a Pt-wire auxiliary, and a Ag/AgCl (3 M NaCl) BAS reference electrodes. All redox potentials are reported relative to this reference electrode. Dynamic light scattering (DLS) measurements were made on a Zetasizer Nano ZS 90 instrument (Malvern Instruments Ltd., U.K.), which can measure particle sizes from 0.3 to 5000 nm (diameter).

$K_5Na_4H_4[\{Na_3(\mu\text{-}OH_2)_2Co_2(\mu\text{-}OH)_4\}(Si_2W_{18}O_{66})]\cdot 37H_2O$ (1). $K_{10}[A\text{-}\alpha\text{-}SiW_9O_{34}]\cdot 13H_2O$ (1 g, 0.32 mmol) was dissolved in 40 mL of 1 M sodium acetate (NaOAc) buffer (pH 4.8). To this solution, 210 mg (0.88 mmol) of $CoCl_2\cdot 6H_2O$ was added. The solution was heated to 85 °C for 1 h, cooled to room temperature, and then filtered through a fine frit. The filtrate afforded red needle crystals after 1 week

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of evaporation in air. Yield: 22% (based on W). IR (2% in KBr, ν/cm^{-1}): 997 (m), 941 (m), 878 (s), 804 (m), 726 (s), 630 (m), 548 (w), 525 (w) cm^{-1}. Elemental analysis calcd (%) for **1**: K, 3.45; Na, 2.84; Co, 2.08; Si, 0.99; W, 58.4. Found (%): K, 3.44; Na, 2.94; Co, 1.64; Si, 1.16; W, 57.8.

$K_6Na_3[Na(H_2O)\{Co(H_2O)_3\}_2\{Co(H_2O)_2\}(Si_2W_{18}O_{66})]\cdot 22H_2O$ (2). $K_{10}[A\text{-}\alpha\text{-}SiW_9O_{34}]\cdot 13H_2O$ (0.5 g, 0.16 mmol) was dissolved in 10 mL of 1 M NaOAc buffer (pH 4.8). To this solution, 105 mg (0.44 mmol) of $CoCl_2\cdot 6H_2O$ was added. The solution was heated to 85 °C for 1 h, cooled to room temperature, and then filtered through a fine frit. Pink needle crystals appeared after several hours of evaporation in air, and were collected after 24 h. Yield: 20% (based on W). IR (2% in KBr, ν/cm^{-1}): 996 (m), 944 (m), 887 (s), 835 (w), 802 (w), 730 (s), 615 (m), 554 (w), and 533(w) cm^{-1}. Elemental analysis calcd (%) for **2**: K, 4.28; Na, 1.68; Co, 3.22; Si, 1.02; W, 60.4. Found (%): K, 3.84; Na, 1.61; Co, 3.29; Si, 0.97; W, 58.1.

$K_{11}[\{Co_2(H_2O)_8\}K(Si_2W_{18}O_{66})]\cdot 17H_2O$ (3). Complex **1** or **2** (300 mg) is dissolved in 12 mL of pH 4.8 KOAc/HOAc buffer (1 M) by heating. The solution was stirred for 1 h at 80 °C, cooled down to room temperature, and then filtered through a fine frit. Pink needle crystals can be obtained in a 20 mL beaker after one day or several days of slow evaporation, depending on the starting material used. Yield: 35% (based on W). IR (2% in KBr, ν/cm^{-1}): 996 (m), 943 (m), 884 (s), 862 (sh), 804 (m), 730 (s), 667 (m), 650 (m), 547 (w), and 525 (w) cm^{-1}. Elemental analysis calcd (%) for **3**: K, 8.60; Co, 2.16; Si, 1.03; W, 60.6. Found (%): K, 7.85; Co, 1.70; Si, 1.07; W, 58.0.

X-ray Crystallography. Single crystals of **1**, **2**, and **3** suitable for X-ray analysis were investigated using a Bruker D8 SMART APEX CCD sealed tube diffractometer. Diffraction intensities were measured using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 173(2) K. Data collection, indexing, and initial cell refinements were obtained by SMART.[45] Frame integration and final cell refinements were done using SAINT.[46] The molecular structure of each complex was determined using direct methods and refined by the standard full-matrix least-squares procedures. Face-indexing absorption correction was applied using the program SADABS.[47] Structure solution, refinement, graphic, and generation of publication materials were performed by using SHELXTL-97/Olex2.[48,49] Crystal data collection and refinement parameters are given in Table 1 (**1** and **2**) and Supporting Information, Table S1 (**3**). Complete details can be found in the accompanying .cif file.

The purity of each sample was checked using powder diffraction (PXRD). PXRD experiments were performed using a Bruker D8 DIFFRAC powder diffractometer (Co K-alpha radiation) with a VANTECH detector in $\theta-\theta$ mode. We found that grinding the samples resulted in poor diffraction, and that the microcrystalline material gave better diffraction. $\theta-\theta$ scans were performed in the 2θ ranges 8−90 degrees with a step width of 0.01 degrees and scan time of 1 s/step.

RESULTS AND DISCUSSION

Structures. The polyanion units in both **1** and **2** consist of a $[Si_2W_{18}O_{66}]^{16-}$ framework which can be viewed as a fusion of two A-α-$[SiW_9O_{34}]^{10-}$ units through two W−O−W corner-shared junctions. This structure type was first described by Hervé et al.[50,51] Complexes **1** and **2** have been characterized by their IR spectra (Supporting Information, Figure S1). The strong similarities between these compounds and $K_{16}\alpha$-$[Si_2W_{18}O_{66}]\cdot 25H_2O$ in the low-frequency IR region (ν < 1100 cm^{-1}) strongly suggest that all of them contain the $[Si_2W_{18}O_{66}]^{16-}$ structural unit. Each complex displays subtle differences in the absorption frequencies of these bands.

Table 1. Crystal Data and Structure Refinement for 1 and 2

	1	2
molecular formula	$Co_2H_{86}K_5Na_4O_{109}Si_2W_{18}$	$Co_3\ H_{62}K_6Na_4O_{97}Si_2W_{18}$
formula wt./g mol^{-1}	5670.37	5483.25
temperature/K	173(2)	173 (2)
radiation (λ)/Å	0.71073	0.71073
crystal system	triclinic	monoclinic
space group	$P\overline{1}$	$P2_1/m$
a/Å	12.846(5)	13.3935(12)
b/Å	18.671(7)	16.1715(15)
c/Å	20.889(7)	20.3596(18)
α/deg	69.166(5)	90.00
β/deg	87.147(6)	106.3640(10)
γ/deg	81.561(6)	90.00
V/Å^3	4632(3)	4231.1(7)
Z	2	2
ρ_{calcd}/g cm^{-3}	4.111	4.164
μ/mm^{-1}	22.988	25.390
$F(000)$	4576	4635
crystal size/mm^3	0.17 × 0.15× 0.12	0.10 × 0.02 × 0.02
reflections collected	94080	82692
independent reflections	28073	13265
absorption correction	numerical	numerical
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
goodness-of-fit on $|F|^2$	1.043	1.016
final R indices [R > $2\sigma(I)$]	$R_1{}^a$ = 0.0524, $wR_2{}^b$ = 0.1430	$R_1{}^a$ = 0.0487, $wR_2{}^b$ = 0.1025
R indices (all data)	$R_1{}^a$ = 0.0681, $wR_2{}^b$ = 0.1520	$R_1{}^a$ = 0.0952, $wR_2{}^b$ = 0.1212
largest diff. peak and hole/e Å^{-3}	12.199 and −7.053	4.860 and −3.256

$^aR_1 = \sum||F_o| - |F_c||/\sum|F_o|$. $^bwR_2 = \sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]^{1/2}$.

Compound **1** has C_2 symmetry (Figure 1a). The two Co^{2+} cations in **1** are localized in the central pocket. Each cobalt cation is coordinated to one-half of the polyanion through a central oxygen atom shared with the SiO_4 tetrahedron and two oxygen atoms that bridge to tungsten. Three Na^+ cations are also incorporated in the central pocket. Two of the Na^+ cations (Na1 and Na3) are coordinated to each half of the polyanion in the same manner as the cobalt atoms, while Na2 sits in the center of the polyanion, connecting other Na atoms, Co atoms, and $[Si_2W_{18}O_{66}]^{16-}$ unit through bridging oxygens. Bond valence sum (BVS) calculations indicate that O38 and O39 are diprotonated, whereas other bridging oxo groups between cobalt atoms are all monoprotonated. In contrast to **1**, the complex $[Cu_5(OH)_4(H_2O)_2(A\text{-}\alpha\text{-}SiW_9O_{33})_2]^{10-}$ (Figure 3a)[39] has a similar cluster fragment, with $\{Cu_5(OH)_4(H_2O)_2\}^{6+}$ moiety instead of $\{Na_3(\mu\text{-}OH_2)_2Co_2(\mu\text{-}OH)_4\}^{3+}$ in the open Wells−Dawson framework.

In compound **2**, three Co(II) centers reside in the cavity of $[Si_2W_{18}O_{66}]^{16-}$ (Figure 1b). The W−O−W corner junction angles between the two $\{SiW_9\}$ units in **2** (142.6°) is larger than that in **1** (139.2°) (smaller dihedral angle defined by the two $\{SiW_9\}$ subunits). Na3 is located inside the pocket, bound to only one-half of $[Si_2W_{18}O_{66}]^{16-}$ through five bridging oxygen atoms. It is also bound to the central cobalt through two oxygen atoms and to one terminal water ligand. All three cobalt atoms have at least two bonds to the $[Si_2W_{18}O_{66}]^{16-}$ framework. The central cobalt atom Co1 is bound to the two bridging oxygen atoms at the two $\{SiW_9\}$ junctions and two central oxygen atoms of the central SiO_4 tetrahedron. The other two cobalt atoms (two Co2 atoms) are located outside the central pocket of $[Si_2W_{18}O_{66}]^{16-}$; they are bonded to one

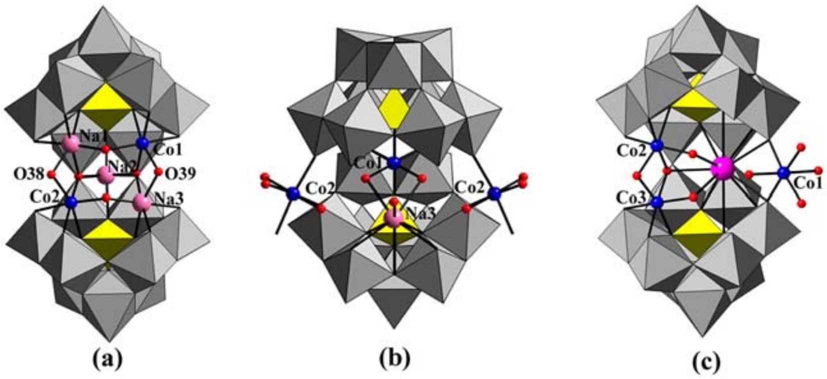
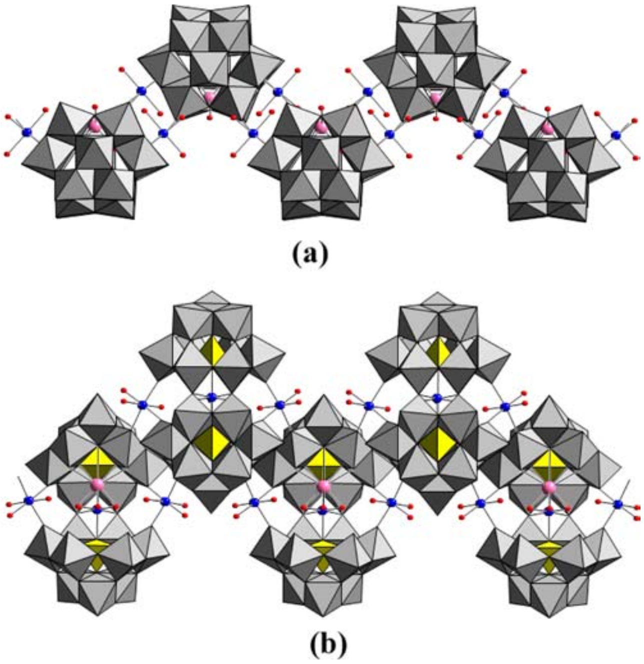


Figure 1. Combined polyhedral/ball-and-stick representations of the polyanion units in **1** (a), **2** (b), and **3** (c). WO_6 units, gray polyhedra; SiO_4 units, yellow tetrahedra; Na, pink spheres; K, magenta spheres; Co, blue spheres; O, red spheres.

oxygen atom on each $\{SiW_9\}$ subunit. A third Co—O—W′ bond connects with another $[Si_2W_{18}O_{66}]^{16-}$ unit of **2** forming a zigzag-shaped one-dimensional chain (Figure 2a and 2b). A tricobalt POM in the literature, $[\{Co(H_2O)_2\}_3(SiW_9O_{34})_2]^{14-}$ (Figure 3b),[43] has three Co(II) centers sandwiched between two separate $\{SiW_9\}$ subunits. The complex $[\{Mn(H_2O)\}K(\mu\text{-}H_2O)_2K\{Mn(H_2O)_4\}(Ge_2W_{18}O_{66})]^{10-}$ (Figure 3c)[52] also has a chain structure, but with germanotungstate as the framework, and the chains are linked by potassium and manganese cations.


(a)

(b)

Figure 2. Combined polyhedral/ball-and-stick representations of the one-dimensional chains of **2**; top view (a), side view (b). WO_6 units, gray polyhedra; SiO_4 units, yellow tetrahedra; Na, pink spheres; Co, blue spheres; O, red spheres.

Compound **3** has an almost identical structure to a literature compound $K_{11}[\{Co(H_2O)\}(\mu\text{-}H_2O)_2K\{M(H_2O)_4\}(Si_2W_{18}O_{66})]\cdot 36H_2O$ (abbreviated as "1Co2−K(B)" in the literature)[51] but with better refinement of the X-ray crystal parameters (Figure 1c). It contains one potassium ion and two Co(II) in the cavity. Co1 is fully occupied, linking the two $\{SiW_9\}$ units, while Co2 and Co3 are disordered (with a best refinement of 30% and 70% occupancies, respectively), leaning toward either $\{SiW_9\}$ unit. Interestingly, the disorder in **3** and in the literature compound are quite similar despite the completely different synthesis used to make these two complexes (the other study fixed the occupancies as 0.33 and 0.67).

Synthesis. The synthesis of these new multicobalt polytungstates, **1** and **2**, like other d-electron-metal-substituted POMs, depends on many factors, including pH, the counterions of the POMs, the temperature, and the nature of the substituted metal center. We now address the later three factors.

Factor 1: Counterions. Complexes **1** and **2** were obtained using the same molar ratio of $CoCl_2\cdot 6H_2O$ to $K_{10}A\text{-}\alpha\text{-}[SiW_9O_{34}]$, but the reactant solutions had different initial concentrations. Different K^+ concentrations (from the POM precursor) dictate the formation of different products. The higher concentration of K^+ in the synthesis of **2** leads to its rapid crystallization (several hours), while a lower concentration of K^+ in the synthesis of **1** leads to slow crystallization (several days). The proper K^+ concentration is needed to both keep the open-mouthed $[Si_2W_{18}O_{66}]^{16-}$ structure present and control the specific location of cobalt atoms in both **1** and **2**. The ratio of K^+ to Na^+ is also important to the formation of different structures. In the literature study, it was concluded that the central K^+ bridging the two $\{SiW_9\}$ units defined the angle of the cavity and the locations of the transition metal cations in compounds $K_{13}[\{Co(H_2O)\}(\mu\text{-}H_2O)_2K(Si_2W_{18}O_{66})]\cdot 40H_2O$ and $K_{11}[\{Co(H_2O)\}(\mu\text{-}H_2O)_2K\{Co(H_2O)_4\}(Si_2W_{18}O_{66})]\cdot 36H_2O$;[51] however, in **1** and **2**, the involvement of Na^+ leads to a different arrangement of cobalt cations.

Factor 2: Temperature. Lowering the temperature of the reaction medium from 85 to 80 °C leads to the formation of **2** under either set of synthetic conditions.

Factor 3: the Nature of the Transition Metal. The number of transition metal(s) incorporated into the framework is highly dependent on the nature of the transition metal. When replacing the Co(II) centers in **1** and **2** with Ni(II), only powders were obtained. When Cu(II) is used as the starting material, the C_{2v} symmetry penta-copper polytungstate, $[Cu_5(OH)_4(H_2O)_2(A\text{-}\alpha\text{-}SiW_9O_{33})_2]^{10-}$ (Figure 3a) is obtained. In this paper, slight variations in reaction conditions, and with Co(II) precursor in excess, lead to two or three cobalt atoms (**1** or **2**) being incorporated into the framework. Table 2 summarizes the synthetic conditions, related products, and transformations between different cobalt-substituted silicotung-

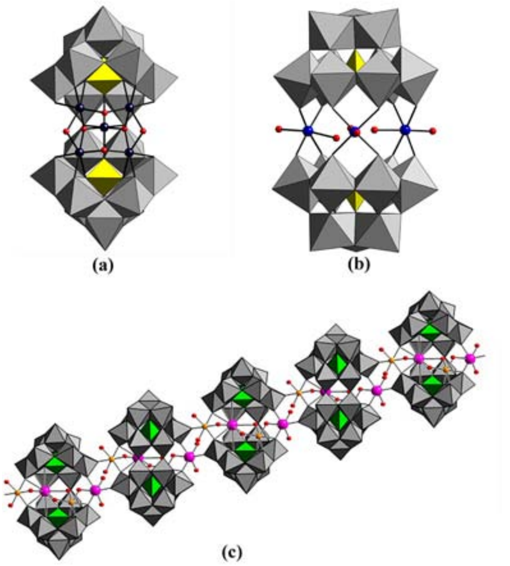


Figure 3. Combined polyhedral/ball-and-stick representations of $[Cu_5(OH)_4(H_2O)_2(A\text{-}\alpha\text{-}SiW_9O_{33})_2]^{10-}$ (a),[39] $[\{Co(H_2O)_2\}_3(SiW_9O_{34})_2]^{14-}$ (b),[43] and the one-dimensional chains of $[\{Mn(H_2O)\}K(\mu\text{-}H_2O)_2K\{Mn(H_2O)_4\}(Ge_2W_{18}O_{66})]^{10-}$ (c).[52] WO_6 units, gray polyhedra; SiO_4 units, yellow tetrahedra; GeO_4 units, green tetrahedra; K, magenta spheres; Co, blue spheres; Cu, dark blue spheres; Mn, orange spheres; O, red spheres.

states in literature studies as well as this work. As evident from the table, the fused dimeric lacunary $[Si_2W_{18}O_{66}]^{16-}$ structures are more easily maintained by using the potassium salt of $[SiW_9O_{34}]^{10-}$ or excess KCl added before the crystallization process under acidic conditions (entries 1−3),[51] while the reconstituted (substituted plenary) Keggin structures and sandwich structures are more often obtained by using the sodium salt of α-$[SiW_9O_{34}]^{10-}$ or β-$[SiW_9O_{34}]^{10-}$ (entries 4−10).[42,43,53−55] Using $K_8[\gamma\text{-}SiW_{10}O_{36}]$ as a precursor can produce a variety of cobalt-substituted lacunary silicotungstates, which are formed by losing one or two tungsten atoms from $K_8[\gamma\text{-}SiW_{10}O_{36}]$ in acidic or basic conditions(entries 11−18).[56−59] These structures are minimally predictable based on the synthetic protocol. Interestingly, $K_8[\gamma\text{-}SiW_{10}O_{36}]$ can also form a dimeric structure via two W−O−W bridges under acidic conditions (entries 19 and 20).[60,61] The presence of carboxylato, azido, carbonato, cyanato ligands,[53] and the buffer *N,N′*-bis(2-hydroxylethyl)piperazine (bhep)[58] can facilitate the isolation of some unusual POM structures (entries 5−6, 11−13). Monocobalt substituted silicotungstates are synthesized by using plenary (parent structure) 12-tungstosilicic acid (entry 21, 22).[62]

Electrochemistry. The cyclic voltammetry (CV) of **1** and **2** was recorded in sodium acetate buffer solutions (0.02 M NaOAc/HOAc with 0.38 M $NaNO_3$, or in 0.4 M NaOAc/HOAc, pH 4.8). No oxidation/reduction processes at the metal Co centers are observed at the glassy carbon electrode in either positive or negative potential domains, but the reduction of W centers is readily seen and is well-defined (Figure 4 and Supporting Information, Figure S2). In 0.02 M NaOAc/HOAc buffer solution, the cathodic peak potentials of **1** are at −0.73, − 0.93 V vs Ag/AgCl (3 M NaCl), and those of **2** are at −0.72 and −0.86 V (Figure 4). The CVs are more reversible in 0.02 M NaOAc/HOAc with 0.38 M $NaNO_3$ than in 0.4 M NaOAc/HOAc buffer (Supporting Information, Figure S2).

The CVs of 1 mM **1** and **2** were also recorded in pH 9 sodium borate buffer. When the applied potential is higher than 1.0 V, a film (with uncharacterized structure) is formed on the glassy carbon anode. This film is catalytically active in water oxidation at $E > 1.0$ V, in the same manner as the cobalt oxide film generated in situ from $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ studied by Stracke and Finke.[63]

Stability Studies. The natural pH of 3 mM **1** in water is 8.3, while that of 3 mM **2** is 6.3. These complexes have a very low absorbance in the range 450−700 nm. Acid/base titration shows reversible behavior (based on several successive titrations in both pH directions) involving 6 protons/(hydroxyl anions) in the pH region of 3.0−8.9 for both **1** and **2** (Supporting Information, Figure S3). As a consequence of having this many pK_a values in close proximity, the titration curves are nearly featureless (no marked inflection points). The UV−vis spectra of both **1** and **2** obtained during acid/base titration show significant but also reversible changes in accordance with the pH changes in the region of 3.0−8.9 (Figures 5, 6 and Supporting Information, Figure S4 and S5). The changes in spectral shape are significant at pH values around their natural pH, which very likely reflects protonation/deprotonation of oxygens in the cobalt cores.[64] Both compounds are also relatively stable in NaOAc/HOAc buffer (80 mM, pH 4.8) and in pH 9 sodium borate buffer. The overnight changes in absorbance are less than 9% for **1** (7 mM), less than 2% for **2** (7.5 mM) in sodium acetate buffer (Supporting Information, Figures S6 and S7), and less than 2% for both **1** and **2** in pH 9 borate buffer (Supporting Information, Figures S8 and S9). No particle formation is observed after aging μM level solutions of **1** and **2** in 80 mM borate buffer at pH 9 for one month by Dynamic Light Scattering (DLS).

The stability of **1**, **2**, and the literature related compounds $K_{13}[\{Co(H_2O)\}(\mu\text{-}H_2O)_2K(Si_2W_{18}O_{66})]\cdot 40H_2O$,[51] $K_{11}[\{Co(H_2O)\}(\mu\text{-}H_2O)_2K\{Co(H_2O)_4\}(Si_2W_{18}O_{66})]\cdot 36H_2O$[51] and $K_{10.2}Na_{0.8}[\{Co_4(\mu\text{-}OH)(H_2O)_3\}(Si_2W_{19}O_{70})]\cdot 31H_2O$,[42] were all investigated under the same high temperature (80 °C) conditions. Heating 5 mM solutions of each of these five compounds in deionized water, pH 4.8 HOAc/NaOAc buffer (1 M), NaCl (1 M) or KCl (1 M) lead, in all cases, to powders after slow evaporation of water. However, needle-like pink crystals were obtained from all five compounds when pH 4.8 HOAc/KOAc buffer (1 M) was used as the solvent. X-ray crystallography and IR spectra indicate that the resulting pink crystals from all 5 compounds have only one structure, that of compound **3**. These results indicate that in particular pH ranges and at high K^+ concentrations, compound **3** is the most stable POM. The natural pH of 3 mM of **3** is 7.5 in water, and the UV−vis spectra of complexes **1**, **2**, and **3** at neutral pH are compared in Supporting Information, Figure S10. Powder X-ray Reflection Diffraction patterns were studied to track the purity of all three complexes. The measured PXRD data perfectly match the simulated ones from single X-ray diffraction (Supporting Information, Figure S11), indicating the bulk materials are exactly the same complexes as the single X-ray crystallography describes, and the transformations between these complexes are complete.

■ CONCLUSIONS

Two new Co^{II}-silicotungstate complexes have been synthesized using $K_{10}A\text{-}\alpha\text{-}[SiW_9O_{34}]\cdot 13H_2O$ as the precursor. Both compounds comprise two or three cobalt atoms in a central multioxygen ligation pocket afforded by the polyanion

Table 2. Summary of Synthetic Conditions for Cobalt Substituted Silicotungstates

entry	molar ratio of the Co^{2+} cation to the precursor	*T* (°C)	reaction system	product	reference number
1	$Co^{2+}/K_{10}A\text{-}\alpha\text{-}[SiW_9O_{34}] = 2.8/1$	85	NaOAc/HOAc buffer	**1** or **2**	this work
2	$Co^{2+}/K_{10}A\text{-}\alpha\text{-}[SiW_9O_{34}] = 1/1$	R.T.	aqueous solution	$K_{11}[\{Co(H_2O)\}(\mu\text{-}H_2O)_2K\{Co(H_2O)_4\}(Si_2W_{18}O_{66})]\cdot 25H_2O$	50,51
3	$Co^{2+}/K_{10}A\text{-}\alpha\text{-}[SiW_9O_{34}] = 0.5/1$	R.T.	aqueous solution	$K_{13}[\{Co(H_2O)\}(\mu\text{-}H_2O)_2K(Si_2W_{18}O_{66})]\cdot 40H_2O$	51
4	$Co^{2+}/Na_{10}A\text{-}\ \alpha\text{-}[SiW_9O_{34}] = 4.1/1$	40	1 M KOAc aqueous solution	$K_5Na_3[(A\text{-}\alpha\text{-}SiW_9O_{34})Co_4(OH)_3(CH_3COO)_3]\cdot 18H_2O$	53
5	$Co^{2+}/Na_{10}A\text{-}\ \alpha\text{-}[SiW_9O_{34}] = 4.1/1$	40	1 M KOAc aqueous solution+sodium azide	$K_5Na_3[(A\text{-}\alpha\text{-}SiW_9O_{34})Co_4(OH)(N_3)_2(CH_3COO)_3]\cdot 18H_2O$	53
6	$Co^{2+}/Na_{10}A\text{-}\alpha\text{-}[SiW_9O_{34}] = 4.1/1$	R.T.	0.5 M NaOAc aqueous solution, CO_3^{2-}	$K_8Na_8[(A\text{-}\alpha\text{-}SiW_9O_{34})_2Co_8(OH)_6(H_2O)_2(CO_3)_3]\cdot 52H_2O$	53
7	$Co^{2+}/Na_{10}A\text{-}\alpha\text{-}[SiW_9O_{34}] = 4.1/1$	80	aqueous solution	$K_{10.2}Na_{0.8}[\{Co_4(\mu\text{-}OH)(H_2O)_3\}(Si_2W_{19}O_{70})]\cdot 31H_2O$	42
8	$Co^{2+}/K_{10}A\text{-}\alpha\text{-}[SiW_9O_{34}] = 1.5/1$	R.T.	aqueous solution	$K_{10.75}[Co(H_2O)_6]_{0.5}[Co(H_2O)_4Cl]_{0.25}A\text{-}\alpha\text{-}[K_2\{Co(H_2O)_2\}_3(SiW_9O_{34})_2]\cdot 32H_2O$	43
9	$Co^{2+}/Na_9[\beta\text{-}SiW_9O_{34}H] = 2.0/1$	80	KOAc/HOAc buffer	$K_{10}[Co_4(H_2O)_2\ (B\text{-}\alpha\text{-}SiW_9O_{34}H)_2]\cdot 21H_2O$	54
10	$Co^{2+}/\alpha\text{-}Na_{10}[SiW_9O_{34}]\cdot 15H_2O = 3.0/1$	70 to 80	aqueous solution	$K_{11}Na_1[Co_4(H_2O)_2(SiW_9O_{34})_2]\cdot nH_2O$	55
11	$Co^{2+}/K_8[\gamma\text{-}SiW_{10}O_{36}] = 0.9/1$	20	pH 8.0, 1 M NaCl,bhep	$K_9Na_3[Co_3(H_2O)(B\text{-}\beta\text{-}SiW_9O_{34})(B\text{-}\beta\text{-}SiW_8O_{29}(OH)_2)]\cdot 18H_2O$	58
12	$Co^{2+}/K_8[\gamma\text{-}SiW_{10}O_{36}] = 0.9/1$	20	pH 8.8, 1 M NaCl, bhep	$K_2Na_{12}\ [Co_3(H_2O)(B\text{-}\alpha\text{-}SiW_9O_{34})(B\text{-}\beta\text{-}SiW_8O_{31})]\cdot 26H_2O$	58
13	$Co^{2+}/K_8[\gamma\text{-}SiW_{10}O_{36}] = 0.9/1$	50	pH 8.0, 1 M NaCl, bhep	$K_{15}Na_2[Co_9Cl_2(OH)_3(H_2O)_9(B\text{-}\beta\text{-}SiW_8O_{31})_3]\cdot 29H_2O$	58
14	$Co^{2+}/K_8[\gamma\text{-}SiW_{10}O_{36}] = 13.2/1$	50	NaCl aqueous solution	$Na_5[Co_6(H_2O)_{30}\{Co_9Cl_2(OH)_3(H_2O)_9(\beta\text{-}SiW_8O_{31})\}]\cdot 37H_2O$	57
15	$Co^{2+}/K_8[\gamma\text{-}SiW_{10}O_{36}] = 2.2/1$	50	NaOAc/HOAc bufferr	$K_{10}Na_{12}[\{Co_3(B\text{-}\beta\text{-}SiW_9O_{33}(OH)(B\text{-}\beta\text{-}SiW_8O_{29}(OH)_2)\}_2]\cdot 49H_2O$	56
16	$Co^{2+}/K_8[\gamma\text{-}SiW_{10}O_{36}] = 2.1/1$	R.T.	AcO^-	$K_{20}[\{B\text{-}\beta\text{-}SiW_9O_{33}(OH))(\beta\text{-}SiW_8O_{29}(OH)_2)Co_3(H_2O)\}_2Co(H_2O)_2]\cdot 47H_2O$	53
17	$Co^{2+}/K_8[\gamma\text{-}SiW_{10}O_{36}] = 2.1/1$	R.T.	cyanate	$K_7[Co_{1.5}(H_2O)_7)][(\gamma\text{-}SiW_{10}O_{36})(\beta\text{-}SiW_8O_{30}(OH))Co_4(OH)(H_2O)_7]\cdot 36H_2O$	53
18	$Co^{2+}/(K_8[\beta\text{-}SiW_{11}O_{39}]+ K_8[\gamma\text{-}SiW_{10}O_{36}]) = 5.7/1$	boil	aqueous solution, NaN_3	$K_4Na_6Co_2(H_2O)_{12}\{Co(H_2O)_4[Co_2(H_2O)_{10}Co_4(H_2O)_2(B\text{-}\alpha\text{-}SiW_9O_{34})_2]_2\}\cdot 40H_2O$	59
19	$Co^{2+}/K_8[\gamma\text{-}SiW_{10}O_{36}] = 1.1/1$	50	aqueous solution	$K_{10}[Co(H_2O)_2(\gamma\text{-}SiW_{10}O_{35})_2]\cdot 8.25H_2O$	60
20	$Co^{2+}/K_8[\gamma\text{-}SiW_{10}O_{36}] = 2.7/1$	45	imidazole, pH 3.6	$(HIm)_8[\{K(H_2O)\}_2\{(\mu_3\text{-}H_2O)Co(H_2O)\}(Si_2W_{20}O_{70})]\cdot 9H_2O^a$	61
21	$Co^{2+}/H_3SiW_{12}O_{40}\cdot nH_2O = 1.1/1$	boil	aqueous solution	$K_6[Co^{II}(H_2O)SiW_{11}O_{39}]$	62
22	$Co^{2+}/H_3SiW_{12}O_{40}\cdot nH_2O = 1.1/1$	80 or R.T.	oxidizing $K_6[Co^{II}(H_2O)SiW_{11}O_{39}]$ by $Na_2S_2O_8$ at high temperature or electrolysis at R.T.	$Cs_5[Co^{III}(H_2O)SiW_{11}O_{39}]/(CN_8H_6)_5[Co^{III}(H_2O)SiW_{11}O_{39}]$	62

[a] Im: imidazole.

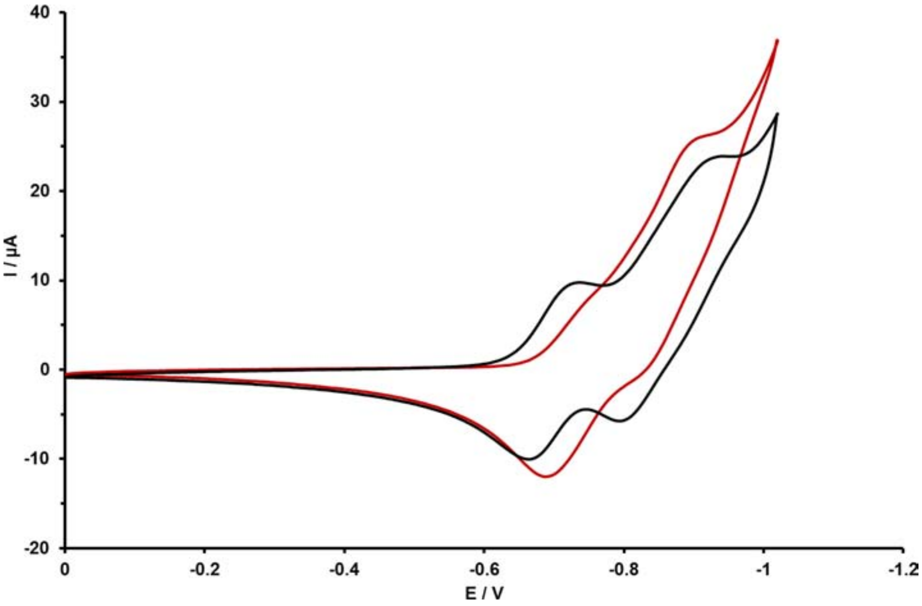


Figure 4. CV of 1 mM **1** (black line) and **2** (red line) obtained in the solution of 0.02 M pH 4.8 NaOAc/HOAc buffer with 0.38 M $NaNO_3$, scan rate 25 mV s^{-1}.

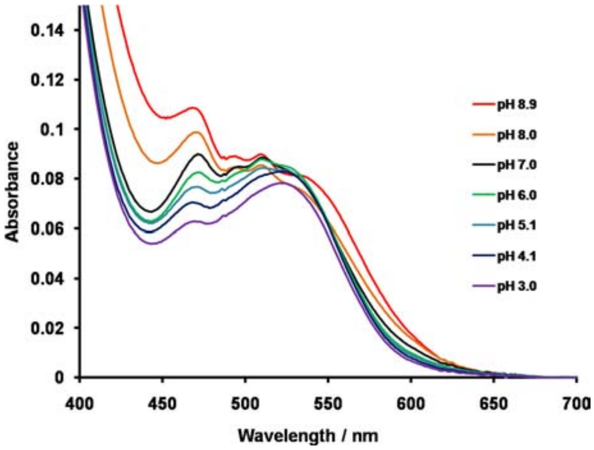


Figure 5. Electronic absorption spectra obtained during acid/base titration of 3 mM **1** (dilution-corrected). *l* = 1 cm.

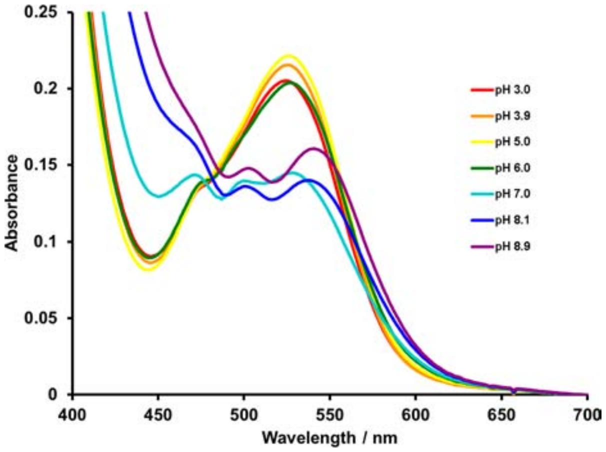


Figure 6. Electronic absorption spectra obtained during acid/base titration of 3 mM **2** (dilution-corrected). *l* = 1 cm.

framework. Both **1** and **2** have been characterized by X-ray crystallography and several spectroscopic methods. They are fairly stable over a range of pH values, but convert to **3** in pH 4.8 potassium acetate buffer at elevated temperature.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Infrared spectra, crystal data, and structure refinement for **3**, cyclic voltammograms, acid/base titration, UV−vis absorption spectra, PXRD patterns, and crystallographic data in CIF format for **1**, **2**, and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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