

Polyoxometalates with pendant surface ligands. Synthesis and characterization of $[\text{SiW}_{11}\text{O}_{39}\text{M}(\text{H}_3\text{P}_2\text{O}_7)]^{7-}$ †

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Novel Keggin anions with covalently bonding pendant surface ligands, formulated as $[\text{SiW}_{11}\text{O}_{39}\text{M}(\text{H}_3\text{P}_2\text{O}_7)]^{7-}$, ($\text{M} = \text{Mn}^{\text{II}}$, Co^{II} , Ni^{II} and Zn^{II}), were synthesized, and characterized by elemental analyses and IR, CV and NMR physical measurements. The novel complexes are expected to have the ability to anchor the clusters on supports *via* terminal phosphato group–support linkages.

Introduction

Polyoxometalates (POMs) have attracted much interest in materials science, since they possess special properties such as photo- and electrochromism, catalysis and magnetism.^{1–2} Several strategies to design materials based on POMs have recently been reported, including hybrid networks based on organic polymers covalently cross-linked by heteropolyanions,³ supramolecular compounds based on POMs,⁴ *n*-dimensional hybrid materials based on organic-polyoxometalate,^{5–14} functional films and gels doped with POMs,^{15–18} mesoporous materials utilizing polyoxometalate cluster–surfactant salts as precursors.^{19–22} A large field of application for polyoxometalates is based on their catalytic activities as either acidic or redox catalysts. However, immobilization of POMs has been the key problem that has limited their commercial uses. Many efforts have recently been made to find better supports and more feasible methods for immobilization of POMs. Supports based on immobilized POMs, such as active carbon or carbon fiber,^{3,23–24} silicate,²⁵ layered double hydroxides,²⁶ titania²⁷ and platinum,²⁸ have been extensively studied. However, structural collapse often occurs during the immobilization of POMs or in the preparation of porous materials utilizing organic templates. For example, Keggin ions show very little tendency to condense in the surfactant salt structures and attempts to remove the template cations and polymerize the inorganic clusters invariably lead to dense $\text{WO}_3 - x$ phases.²⁰ We are exploring an approach, shown in Scheme 1, to the synthesis of heteropoly

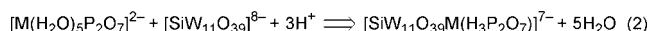
avoiding structural collapse and to anchor the clusters *via* terminal ligand–support linkages.

Preliminary investigations on substitutions of the terminal oxygen atoms of POMs were carried out in aqueous solution.^{29,30} Extensive studies then were continued in nonpolar organic solvents.^{31–34} We report here the first terminally ligated PP polyoxometalate complexes, which are isolated from the reaction of the monolacunary tungstosilicate with transition metal complexes of the form $\text{MP}_2\text{O}_7^{2-}$. We unambiguously prove the stoichiometry of the pyrophosphato derivatives of $[\text{SiW}_{11}\text{O}_{39}\text{M}(\text{L})]^{7-}$, ($\text{M} = \text{Mn}^{\text{II}}$, Co^{II} , Ni^{II} and Zn^{II} , and $\text{L} = \text{H}_3\text{P}_2\text{O}_7^-$), using elemental analysis and spectroscopic techniques.³⁵

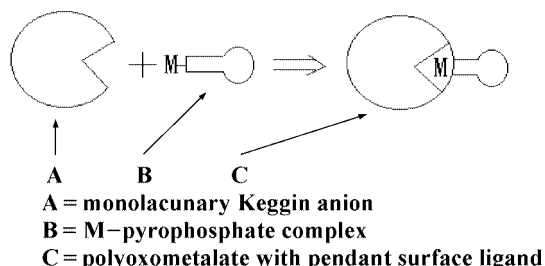
Results and discussion

Syntheses

The key conditions for preparing terminally ligated pyrophosphato complexes are the pH of the aqueous solution, the molecular ratio and the temperature. The preparative route designed is in two steps (see Scheme 2). In the first step, a transi-



Scheme 2



Scheme 1

compounds with covalently bonding pendant surface ligands. The strategy is to cross-link the inorganic clusters while

tion metal complex of pyrophosphate is formed with an $\text{M} : \text{P}_2\text{O}_7$ ratio of 1 : 1. This requires acidic aqueous conditions ($\text{pH} = 3\text{--}4$) to avoid the hydrolysis of M^{2+} and a stoichiometric amount of $\text{P}_2\text{O}_7^{4-}$ to avoid the formation of complexes with other metal to ligand ratios. In the second step, an active unsaturated 11-tungstosilic anion coordinates to the transition metal pyrophosphate complex formed in the first step, resulting in a new complex in which an $\text{M-P}_2\text{O}_7$ group binds to the monovacant 11-tungstosilic anion. In fact, formation of the intermediate metal complex in step 1 is observable *via* changes in color of the solutions, except for the Zn derivative.

Formulation

The results of the elemental analyses suggest that the poly-anions, either the tungstate or the pyrophosphate, are protonated. Empirical bond strength–bond length parameters have been used in the calculation of bond strength sums and the

† Electronic supplementary information (ESI) available: IR spectra of $\alpha\text{-SiW}_{11}\text{Co-P}_2\text{O}_7$, $\alpha\text{-SiW}_{11}$ and $\text{Na}_4\text{P}_2\text{O}_7$ (Fig. 1) and tables of ^{31}P NMR data (Tables 1 and 2). See <http://www.rsc.org/suppdata/dt/b1/b104132k/>

prediction of hydrogen atom positions.^{36,37} Since there is no crystal structural data available for these complexes, universal bond length data for Keggin anions,^{38,39} and $[\text{Cr}(\text{H}_2\text{O})_4\text{P}_2\text{O}_7]^{-40}$ are used in the calculation of the bond strength sums. Possible protonation sites in the tungstate are corner- and edge-sharing oxygen atoms ($\text{O}_{\text{b/c}}$), the bond strengths of which are in the range 0.76–1.45. Possible protonation sites in the pyrophosphate are unshared oxygen atoms (O_t), the bond strengths of which are in the range 1.09–1.34. The calculated bond strength sums indicate that basicity decreases in the sequence $\text{O}_\text{t} > \text{O}_{\text{b/c}}$. We therefore deduce that the pyrophosphate is protonated and the complexes can be formulated as $[\text{SiW}_{11}\text{O}_{39}\text{M}(\text{L})]^{7-}$, where $\text{L} = \text{H}_3\text{P}_2\text{O}_7^-$ (for brevity, compounds will be written as $\text{SiW}_{11}\text{M-P}_2\text{O}_7$ hereafter). This should be verified by means of ^{17}O NMR spectroscopy and neutron diffraction.

To verify that M^{2+} is incorporated into the parent anion, an electrophoresis test was done for $\text{SiW}_{11}\text{Co-P}_2\text{O}_7$. An observable purple band moved toward the anode, suggesting that the Co^{2+} ion is incorporated into the lacunary tungstosilic anion, rather than being simply a counter-ion.

IR spectra

The $\text{SiW}_{11}\text{M-P}_2\text{O}_7$ series have similar IR spectra, although they are markedly different from those for the precursors $\text{K}_8\text{SiW}_{11}\text{O}_{39}$ (SiW_{11} hereafter) and $\text{Na}_4\text{P}_2\text{O}_7$ (see ESI Fig. 1). The bands at ~ 960 , ~ 900 and $\sim 800\text{ cm}^{-1}$ are assigned to the asymmetric stretching vibrations of the W-O_a , the Si-O_a and the $\text{W-O}_{\text{b/c}}-\text{W}$ bonds, respectively.⁴¹ The (W-O-W) vibrations at $\sim 800\text{ cm}^{-1}$ for the pyrophosphate derivatives are quite similar to those for transition metal-substituted Keggin salts.⁴² This indicates that the oxygen atoms located in the vacant positions of the anion $[\text{SiW}_{11}\text{O}_{39}]^{8-}$ are coordinated to an M^{2+} ion bonded with a P_2O_7 group.

Cyclic voltammetry

The cyclic voltammetric and polarographic behaviors of the phosphoric derivatives show no remarkable change compared with their parent SiW_{11} , showing two clearly resolved reversible two-electron reductions of the polytungstate “ligand”, see Fig. 1

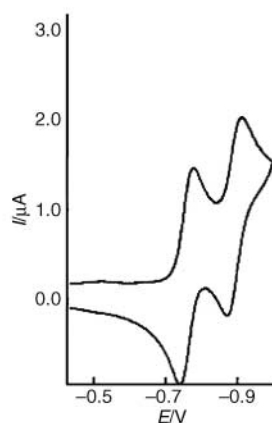


Fig. 1 Cyclic voltammetry of $\alpha\text{-SiW}_{11}\text{Co-P}_2\text{O}_7$.

and Table 1. Therefore, they are expected to generate a new series of heteropoly blues.⁴³

^{183}W NMR

^{183}W NMR data is summarized in Table 2 with a comparison of related compounds. The ^{183}W NMR spectrum for $\text{SiW}_{11}\text{ZnP}_2\text{O}_7$ shows six-line resonances (2 : 2 : 1 : 2 : 2 : 2), confirming that this series has the anticipated C_s structure of $\alpha\text{-}[\text{SiW}_{11}\text{O}_{39}\text{M}(\text{H}_3\text{P}_2\text{O}_7)]^{7-}$. The pattern of lines is similar to that for $\alpha\text{-}[\text{SiW}_{11}\text{O}_{39}\text{Zn}(\text{H}_2\text{O})]^{6-}$ and, hence, suggests analogous assignments based on the literature,⁴⁴ shown in Fig. 2(a). Although six

Table 1 Polarogrammetric data (V)^a

Complex	$E_{1/2}$	$E_{1/2}$	$\Delta E_{1/2}$
$\alpha\text{-SiW}_{11}\text{Mn-P}_2\text{O}_7$	−0.704	−0.812	0.108
$\alpha\text{-SiW}_{11}\text{Co-P}_2\text{O}_7$	−0.680	−0.816	0.136
$\alpha\text{-SiW}_{11}\text{Ni-P}_2\text{O}_7$	−0.696	−0.832	0.136
$\alpha\text{-SiW}_{11}\text{Zn-P}_2\text{O}_7$	−0.740	−0.876	0.136
$\alpha\text{-SiW}_{11}$	−0.740	−0.900	0.160

^a HAc–NaAc buffer solution, pH 4.7; scan rate 50 mV s^{-1} .

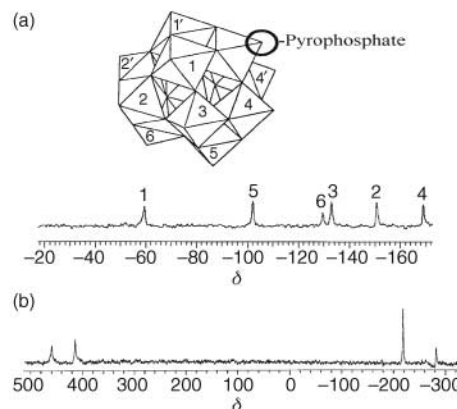


Fig. 2 ^{183}W NMR spectra of $\alpha\text{-SiW}_{11}\text{Zn-P}_2\text{O}_7$ (a) and $\alpha\text{-SiW}_{11}\text{Co-P}_2\text{O}_7$ (b).

lines would also be expected in the W NMR spectrum of $\text{SiW}_{11}\text{Co-P}_2\text{O}_7$, only four are observed, see Fig. 2(b). The tungsten atoms adjacent to the paramagnetic Co^{II} center presumably undergo rapid relaxation and are undetectable.^{44,45}

^{31}P NMR

^{31}P NMR spectroscopy is a critical method for the verification of phosphato complexes.⁴⁶ As expected, a two-line pattern in the ^{31}P NMR spectra is observed for $\text{SiW}_{11}\text{M-P}_2\text{O}_7$, see Fig. 3. Compared with the monosubstituted Keggin and Wells–Dawson series, the $\text{SiW}_{11}\text{M-P}_2\text{O}_7$ series exhibits marked differences in their ^{31}P NMR spectra (see ESI Table 1). The chemical shifts of the peaks due to both P atoms change by less than 2 ppm for the paramagnetic $\text{SiW}_{11}\text{M-P}_2\text{O}_7$ ($\text{M} = \text{Co}^{2+}$ and Ni^{2+}) compounds relative to the responding diamagnetic Zn isomorph. We assign the upfield line to the P atom nearest M [denoted P(1)] and the downfield one to the P atom farthest from M [denoted P(2)], based on the literature,⁴⁷ in which coordination chemical shifts of around -10 ppm for phosphato species were reported. In contrast, the resonances due to P(1) (close to M) move downfield by ca. 250 ppm for the paramagnetic $\text{P}_2\text{W}_{17}\text{M}$ ($\text{M} = \text{Co}^{2+}$ and Ni^{2+}), relative to the responding diamagnetic Zn isomorphs. For comparison, the ^{31}P NMR spectra are shown in Fig. 4. It can be deduced that the influence of the d electrons on the terminally ligated P atoms, as in the $\text{SiW}_{11}\text{M-P}_2\text{O}_7$ case, is much less than that on the P atoms located inside the cluster, as in the $\text{P}_2\text{W}_{17}\text{M}$ case. The chemical shift mechanism for the P atoms in the phosphato species might be quite different from that in the monosubstituted Keggin and Wells–Dawson species. If magnetic anisotropy factors are taken to be equal for the paramagnetic atoms, in the $\text{SiW}_{11}\text{M-P}_2\text{O}_7$ and $\text{PW}_{11}\text{M-D}_2\text{O}$ cases, a pure dipolar shift mechanism for localized spins would keep both the broadenings and the changes in chemical shifts constant for a given paramagnetic metal ion. On the other hand, a pure contact shift mechanism would cause the ratios of the changes in line widths to equal the square of the ratios of the corresponding changes in chemical shifts.^{44,48} Compared with the $\alpha\text{-P}_2\text{W}_{17}\text{M-H}_2\text{O}/\alpha\text{-PW}_{11}\text{M-D}_2\text{O}$ couple, the $\alpha\text{-SiW}_{11}\text{M-P}_2\text{O}_7/\alpha\text{-PW}_{11}\text{M-D}_2\text{O}$ pair deviates from the criteria to a greater extent (see ESI Table 2). This leads to

Table 2 ^{183}W NMR chemical shifts (in ppm from 1 M Na_2WO_4) for $\text{SiW}_{11}\text{M-P}_2\text{O}_7$, (M = Co and Zn) at 297 K, saturated solution of K salts in 20% D_2O

Complex	δ					
$\alpha\text{-SiW}_{11}\text{Co-P}_2\text{O}_7$	461.0	413.9	−206.6	−266.7		
$\alpha\text{-SiW}_{11}\text{Co-H}_2\text{O}$	437.6	390.2	−222.2	−280.2		
$\alpha\text{-SiW}_{11}\text{Zn-P}_2\text{O}_7$	−59.6	−102.0	−129.6	−133.0	−150.9	−169.1
$\alpha\text{-SiW}_{11}\text{Zn-H}_2\text{O}$	−71.6	−115.1	−139.9	−146.4	−166.3	−182.9

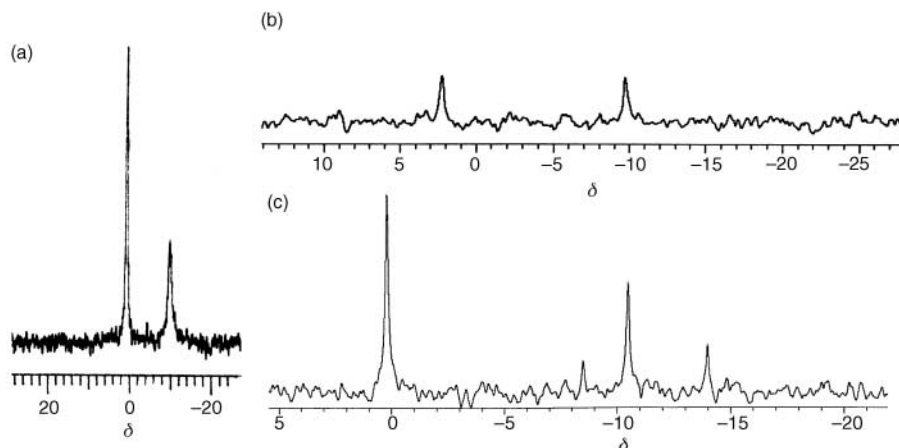


Fig. 3 ^{31}P NMR spectra in 20% D_2O of $\alpha\text{-SiW}_{11}\text{Co-P}_2\text{O}_7$ (a), $\alpha\text{-SiW}_{11}\text{Ni-P}_2\text{O}_7$ (b) and $\alpha\text{-SiW}_{11}\text{Zn-P}_2\text{O}_7$ (c); 10% impurity present at -8.5 and -13.9 ppm, presumably $\alpha_2\text{-P}_2\text{W}_{17}\text{Zn-H}_2\text{O}$.

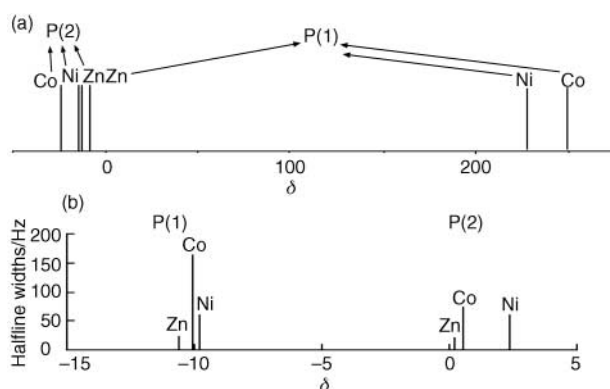


Fig. 4 ^{31}P NMR spectra of $\alpha_2\text{-P}_2\text{W}_{17}\text{M-D}_2\text{O}$ (a) and $\alpha\text{-SiW}_{11}\text{M-P}_2\text{O}_7$ (b). P(1) closest to M, P(2) farthest from M.

the conclusion that while the chemical shift mechanism is primarily contact in character for Ps in the Keggin $\text{PW}_{11}\text{M-D}_2\text{O}$ series,⁴⁴ both contact and dipolar interactions probably make significant contributions to the ^{31}P chemical shifts for the $\text{SiW}_{11}\text{M-P}_2\text{O}_7$ series.

Experimental

Synthesis

$\text{K}_8\text{SiW}_{11}\text{O}_{39}\cdot 13\text{H}_2\text{O}$ (SiW_{11}). Prepared by the literature method⁴⁹ and identified by IR spectroscopy and cyclic voltammetry. All common laboratory chemicals were reagent grade.

$\text{K}_7[\text{SiW}_{11}\text{O}_{39}\text{Co}(\text{H}_3\text{P}_2\text{O}_7)]$ ($\text{SiW}_{11}\text{Co-P}_2\text{O}_7$). $\text{Na}_4\text{P}_2\text{O}_7$ (0.3 g, 1 mmol) was dissolved in 30 ml of water with the addition of H^+ -form resin to adjust the pH to 3.0. To the pyrophosphate solution, 0.2 g of $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (*ca.* 1 mmol) was added under stirring and heating for 8 min in a water bath at 85°C , the color of the solution changed from pink to purple. To the resulting solution, 3.2 g of $\text{K}_8\text{SiW}_{11}\text{O}_{39}\cdot 13\text{H}_2\text{O}$ (*ca.* 1 mmol)

was added. After heating for 10 min, the solution then was filtered and *ca.* 0.5 g of KCl was added to the filtrate. The resulting solution was treated with a 1 : 1 (v/v) water–acetone mixture, to provide a red precipitate. Yield: 3 g (0.88 mmol). The product was recrystallised by dissolution in water containing a small amount of acetonitrile (30%, v/v). Rhombic purple crystals were harvested after leaving the solution to stand for three weeks. Elemental analysis calc. (found) for $\text{K}_7[\text{SiW}_{11}\text{O}_{39}\text{Co}(\text{H}_3\text{P}_2\text{O}_7)]\cdot 13\text{H}_2\text{O}$: K, 7.90 (8.2); Co, 1.71 (1.6); P, 1.79 (1.6); Si, 0.81 (0.8); W, 58.58 (60.0); H_2O , 7.81 (7.9)%. IR (cm^{-1}): 1000.0sh, 963.5s, 901.1s, 801.0s, 760.0sh, 695.6s, 531.9s.

$\text{K}_7[\text{SiW}_{11}\text{O}_{39}\text{Mn}(\text{H}_3\text{P}_2\text{O}_7)]$ ($\text{SiW}_{11}\text{Mn-P}_2\text{O}_7$). The preparation procedure was similar to that for $\text{SiW}_{11}\text{Co-P}_2\text{O}_7$, except that MnSO_4 (0.16 g, *ca.* 1 mmol) was used. The product was obtained in the form of brown crystals. Yield: 0.64 mmol. Elemental analysis calc. (found) for $\text{K}_7[\text{SiW}_{11}\text{O}_{39}\text{Mn}(\text{H}_3\text{P}_2\text{O}_7)]\cdot 15\text{H}_2\text{O}$: K, 7.91 (8.0); Mn, 1.59 (1.6); P, 1.80 (2.0); Si, 0.81 (0.8); W, 58.65 (62.3); H_2O , 7.80 (8.2)%. IR (cm^{-1}): 993.1sh, 959.8s, 898.2s, 801.3s, 760.7sh, 704.0s, 533.7s.

$\text{K}_7[\text{SiW}_{11}\text{O}_{39}\text{Ni}(\text{H}_3\text{P}_2\text{O}_7)]$ ($\text{SiW}_{11}\text{Ni-P}_2\text{O}_7$). The preparation procedure was similar to that for $\text{SiW}_{11}\text{Co-P}_2\text{O}_7$, except that $\text{Ni}(\text{NO}_3)_2$ (0.14 g, *ca.* 1 mmol) was used. The product was obtained in the form of green crystals. Yield: 0.81 mmol. Elemental analysis calc. (found) for $\text{K}_7[\text{SiW}_{11}\text{O}_{39}\text{Ni}(\text{H}_3\text{P}_2\text{O}_7)]\cdot 15\text{H}_2\text{O}$: K, 7.90 (8.0); Ni, 1.68 (1.7); P, 1.79 (1.5); Si, 0.81 (0.8); W, 58.60 (60.0); H_2O , 7.80 (8.3)%. IR (cm^{-1}): 1006.8sh, 961.7s, 903.2s, 792.2, 760sh, 699.7s, 532.1s.

$\text{K}_5\text{H}_2[\text{SiW}_{11}\text{O}_{39}\text{Zn}(\text{H}_3\text{P}_2\text{O}_7)]$ ($\text{SiW}_{11}\text{Zn-P}_2\text{O}_7$). The preparation procedure was similar to that for $\text{SiW}_{11}\text{Co-P}_2\text{O}_7$, except that ZnCl_2 (0.13 g, *ca.* 1 mmol) was used. The product was obtained in the form of colourless crystals. Yield: 0.44 mmol. Elemental analysis calc. (found) for $\text{K}_5\text{H}_2[\text{SiW}_{11}\text{O}_{39}\text{Zn}(\text{H}_3\text{P}_2\text{O}_7)]\cdot 28\text{H}_2\text{O}$: K, 5.41 (5.7); Zn, 1.81 (1.5); P, 1.71 (1.4); Si, 0.78 (0.6); W, 55.89 (59.3)%; H_2O , 13.93 (13.0). IR (cm^{-1}): 1000.0sh, 958.5s, 912.3s, 792.7s, 760sh, 672.4s, 520.6s.

Physical measurements

Elemental analyses were carried out on a Plasme-Spec(I) ICP emission spectrometer. IR spectra were recorded on a FTS-7 spectrophotometer from KBr pellets. Cyclic voltammograms were recorded on a 384B polarographic analyzer with 303A electrodes. Thermal gravimetric analyses were carried out on a TGA7 derivatograph. NMR spectra were recorded on a Buker AMX 400MHz NMR spectrophotometer.

Electrophoresis

Solutions of $\text{SiW}_{11}\text{Co-P}_2\text{O}_7$ and $\text{Co}(\text{NO}_3)_2$ were respectively loaded onto the holes located in the middle of an agarose gel (1%) plate. The gel was just submerged in a solution of NaAc (pH 5.0). Electrophoresis was carried out under 80 V for about 10 min until red bands for the two samples could be observed running separately in opposite directions.

Conclusion

A novel kind of Keggin anion with covalently bonded pendant surface ligands, formulated as $[\text{SiW}_{11}\text{O}_{39}\text{M}(\text{L})]^{7-}$ ($\text{M} = \text{Mn}^{\text{II}}$, Co^{II} , Ni^{II} and Zn^{II} , $\text{L} = \text{H}_3\text{P}_2\text{O}_7^-$) were synthesized from unsaturated 11-tungstosilicate, M^{2+} and pyrophosphate. Studies are underway to determine the applicability of utilizing the terminal ligand group, which in this case is pyrophosphato, to condense the inorganic portion of the structure and to anchor the clusters *via* covalent bonding pendant surface ligand-support linkages.

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