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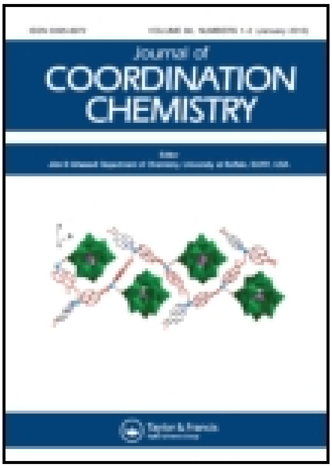

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Dimerization of cobalt-substituted Keggin phosphotungstate, $[PW_{11}O_{39}Co(X)]^{5-}$, in nonpolar solvents

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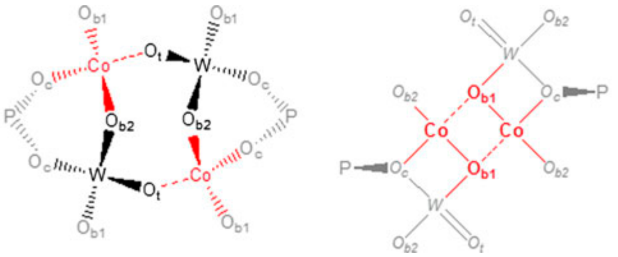

The tetraheptylammonium (THA) salt of cobalt-substituted polyoxotungstate with Keggin-like structure, $(THA)_5[PW_{11}O_{39}Co^{II}(X)]$, was investigated by ^{31}P NMR and UV/VIS spectroscopies in toluene. A solution obtained after transferring $PW_{11}Co$ from aqueous solution into toluene, using THABr as a transfer agent, and rigorous drying, gives multiple peaks in the ^{31}P NMR spectrum. The spectrum in dry toluene significantly simplifies, after extracting a hexane solution several times with water, which removes simple inorganic ions. However, even the dry toluene solution after purification has ^{31}P NMR and UV/VIS spectra which cannot be explained using the known equilibrium between $(THA)_5[PW_{11}O_{39}Co(H_2O)]$ and $(THA)_5[PW_{11}O_{39}Co(\_\_)]$. Both ^{31}P NMR and UV/VIS spectroscopies indicate the existence of dimers in dry toluene solutions, $(THA)_{10}[(PW_{11}O_{39}Co)_2]$. Pure $(THA)_5[PW_{11}O_{39}Co(\_)]$ with five-coordinate cobalt can, however, be obtained in dry toluene in the presence of excess inert salt (high ionic strength conditions). Quantum mechanical/molecular mechanical calculations also support dimer formation in toluene.

Keywords: Polyoxometalates; Dimerization; Nonpolar solvents

Introduction

Transition-metal-substituted polyoxotungstates, TMSPOTs, a subgroup of polyoxometalates [1], are applied as redox catalysts owing to their capacity for reversible multiple electron transfer, high stability in multiple redox states, and tunable redox potentials. The most

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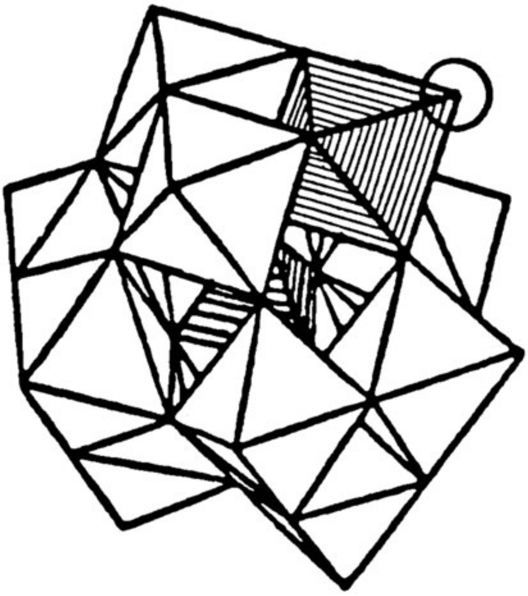

Figure 1. Polyhedral model of transition-metal-substituted polyoxotungstates (TMSPOTs) with a Keggin structure. Each vertex of a polyhedron locates an oxygen atom. A tungsten atom is within each white octahedron. The shaded tetrahedron contains the heteroatom X. The shaded octahedron contains the substituted transition metal atom M. The circled vertex locates the coordination site for the attached water molecule.

widely studied TMSPOTs are those that adopt a Keggin-like structure. The Keggin structure has a central XO_4 tetrahedron surrounded by 12 WO_6 octahedra arranged in four groups of three edge-shared octahedra (W_3O_{13}). TMSPOTs with Keggin-like structures are made by replacing 1 of the 12 tungsten atoms by another octahedrally coordinated metal atom, M. When M is a first-row transition metal, its sixth outer coordination site is occupied by a water molecule. These TMSPOT anions have the formula: $[XW_{11}O_{39}\ M(H_2O)]^{m-}$ (where typically X = Si, P, B and M = Cr, Mn, Fe, Co, Ni, Cu, Zn), expressed herein shorthand notation as $XW_{11}M$ (see figure 1).

In 1984, Katsoulis and Pope [2] demonstrated that TMSPOTs are easily transferred from water to a variety of nonpolar solvents by using tetraheptylammonium (THA) bromide as the phase-transfer agent. TMSPOTs exist in nonpolar solvents in ion pairs with THA cations. This architecture has been referred to as surfactant-encapsulated clusters (SECs) [3]. Katsoulis and Pope reported that such polyanions show metalloporphyrin-like reactivity in nonpolar solvents. A major feature of the new chemistry is the facile loss of the coordinated water molecule, which leads to a coordinatively unsaturated site on the surface of the polyanion, e.g.

$$[XW_{11}O_{39}M(H_2O)]^{n-} \rightarrow [XW_{11}O_{39}M(\_)]^{n-} + H_2O \qquad (1)$$

For metals like Co(II) the process is readily detected spectroscopically. The “hydrated” complex is red and the anhydrous complex (with square pyramid five-coordinate Co(II)) is green. However, a significant difference exists between the behavior in toluene of cobalt-substituted Keggin anion with silicon or boron in the center ($SiW_{11}Co$, $BW_{11}Co$) and cobalt-substituted Keggin anion with phosphorus in the center ($PW_{11}Co$). Pope and Katsoulis reported that it is relatively easy to remove coordinated water from Co in $SiW_{11}Co$ and $BW_{11}Co$ [2]. As the toluene solutions of $SiW_{11}Co$ and $BW_{11}Co$ are dried, the solution color changes from red (assigned to $[SiW_{11}O_{39}Co(H_2O)]^{6-}$ or $[BW_{11}O_{39}Co(H_2O)]^{7-}$) to green (assigned to $[SiW_{11}O_{39}Co(\_)]^{6-}$ or $[BW_{11}O_{39}Co(\_)]^{7-}$). On the other hand, the color of $PW_{11}Co$ solution in dry toluene remains red regardless of how rigorously the solution is dried. This behavior was attributed to the difficulty in removing the coordinated water molecule from the cobalt. While we confirmed this observation, we also observed that the dry solid $PW_{11}Co$ does have a green color. On the other hand, a toluene or hexane solution of $PW_{11}Co$ remains red even with a H_2O to Co ratio equal to 0.02 (2 mM H_2O and 100 mM $PW_{11}Co$).

In 1998 our group reported reactions of THA salts of TMSPOTs in toluene with CO_2, making them likely catalysts for CO_2 reduction [4]. Subsequently, in 2006 we reported a potential photocatalytic reduction of CO_2 by nickel-substituted silicotungstate with Keggin structure, $(THA)_6[SiW_{11}O_{39}Ni]$, in the presence of alcohols [5]. In 2010, Neumann *et al.* reported the coordination of CO_2 to ruthenium-substituted silicotungstate, $(C_6H_{13})_5[SiW_{11}O_{39}Ru^{III}]$, and its photochemical reduction in the presence of tertiary amines [6]. A mechanism for cycloaddition of CO_2 with epoxides catalyzed by tetraalkylammonium salts

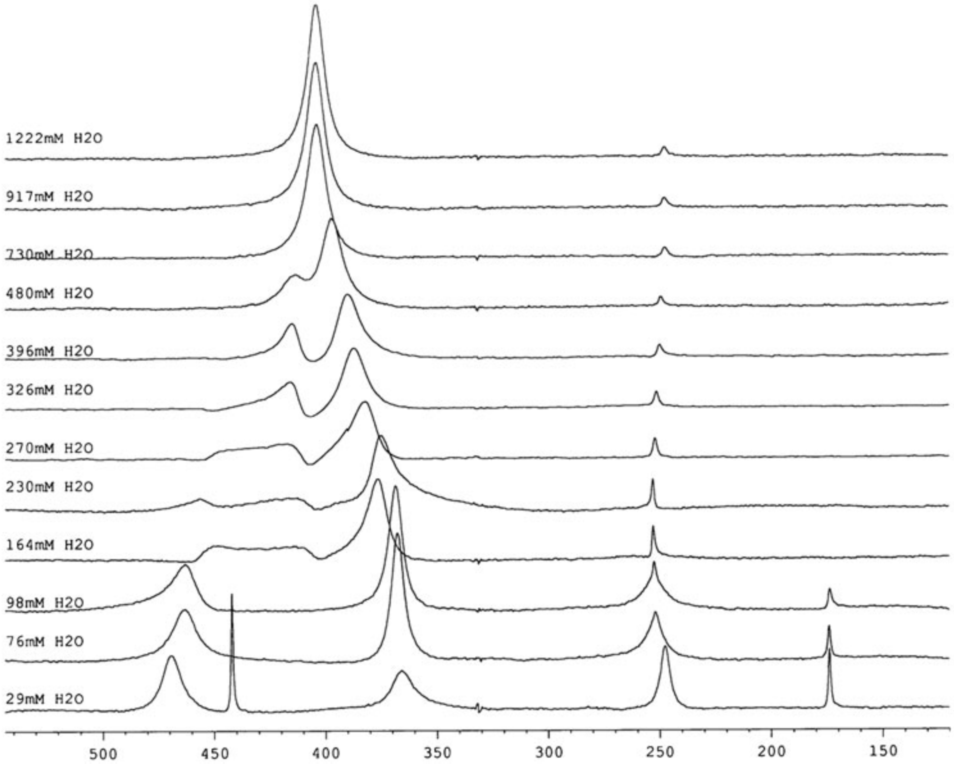

Figure 2. ^{31}P NMR spectra for 100 mM solutions of THA salt of $PW_{11}Co$ in toluene as the water content (listed above each spectrum) changes from 29 mM (lower spectrum) to 1222 mM (upper spectrum).

of TMSPOTs was investigated in detail [7]. Clearly, there is a growing interest in reactivity of TMSPOTs in nonpolar solvents.

In 2002, we reported observation of the unexpected multiple ^{31}P NMR signals for $(THA)_5[PW_{11}O_{39}Co(H_2O)]$ in dry toluene [8]. These signals were inconsistent with the literature interpretation that TMSPOTs under dry conditions simply lose coordinated water and the transition metal becomes five-coordinate. Instead of two ^{31}P peaks, expected for a mixture of complexes with five- and six-coordinate cobalt, $[PW_{11}O_{39}Co(\_)]^{5-}$ and $[PW_{11}O_{39}Co(H_2O)]^{5-}$, *five* major signals were observed. As water was added to the dry toluene solution, several peaks coalesced, eventually resulting in one major signal (see figure 2). We hypothesized then that during the transfer procedure some K^+ and Br^- ions were also transferred into toluene, where they became trapped with the THA-TMSPOT ion pairs. Thus, as water is removed from the solution, Br^- ions coordinate to Co^{2+} and K^+ ions form ion pairs with $PW_{11}Co$ anion. As a result, several species could be present in solution: $[PW_{11}O_{39}Co(\_)]^{5-}$, $[PW_{11}O_{39}Co(H_2O)]^{5-}$, and $[PW_{11}O_{39}Co(Br)]^{6-}$, and all three anions ion-paired with K^+, leading to multiple ^{31}P NMR signals.

Because the detailed structures of THA-TMSPOT ion pairs have important consequences for their catalytic behavior, we decided to investigate this phenomenon in more detail.

Results and discussion

^{31}P NMR spectroscopy

As seen in figure 2 five major peaks appear in ^{31}P NMR spectrum for 100 mM $PW_{11}Co$ solution in dry toluene ($[H_2O]$ = 29 mM, $H_2O : Co = 1 : 3.4$). As expected for paramagnetic species, all peaks are observed far away (between 100 and 500 ppm) from the typical region for diamagnetic polyoxotungstates (from 0 to −20 ppm). However, when the spectrum is recorded in the presence of excess (THA)Br, only one peak around 240 ppm appears. That peak is assigned to $[PW_{11}O_{39}CoBr]^{6-}$, with the bromide ion occupying the sixth coordination site around Co. A variable temperature study was performed for 35 mM $PW_{11}Co$ in toluene with 1.2 M (THA)Br (seven times stoichiometric excess) and 100 mM water (see figure 3). At these conditions two peaks whose line widths increase with temperature are observed at temperatures from −10 to 10 °C and one very broad peak at 25 °C, which narrows as temperature further increases. These spectra demonstrate a ligand exchange reaction.

$$[PW_{11}O_{39}Co(Br)]^{6-} + H_2O \rightleftharpoons [PW_{11}O_{39}Co(H_2O)]^{5-} + Br^- \qquad (2)$$

Refluxing the solution of $PW_{11}Co$ in hexane with water (10 mM solution, 1 : 1 volume solution to water, 60 °C) removed K^+ and Br^- ions. Hexane was chosen instead of toluene, owing to its lower dielectric constant, and total immiscibility with water. After six refluxes, the wet solution in hexane was evacuated, dried under vacuum, $PW_{11}Co$ was redissolved in dry toluene, and ^{31}P NMR spectrum was recorded. In between subsequent refluxes, we monitored the concentration of bromide ions in the aqueous layer by ion chromatography. This procedure removed 3.3 µM Br^- from a 100 µM $PW_{11}Co$ sample at approximately

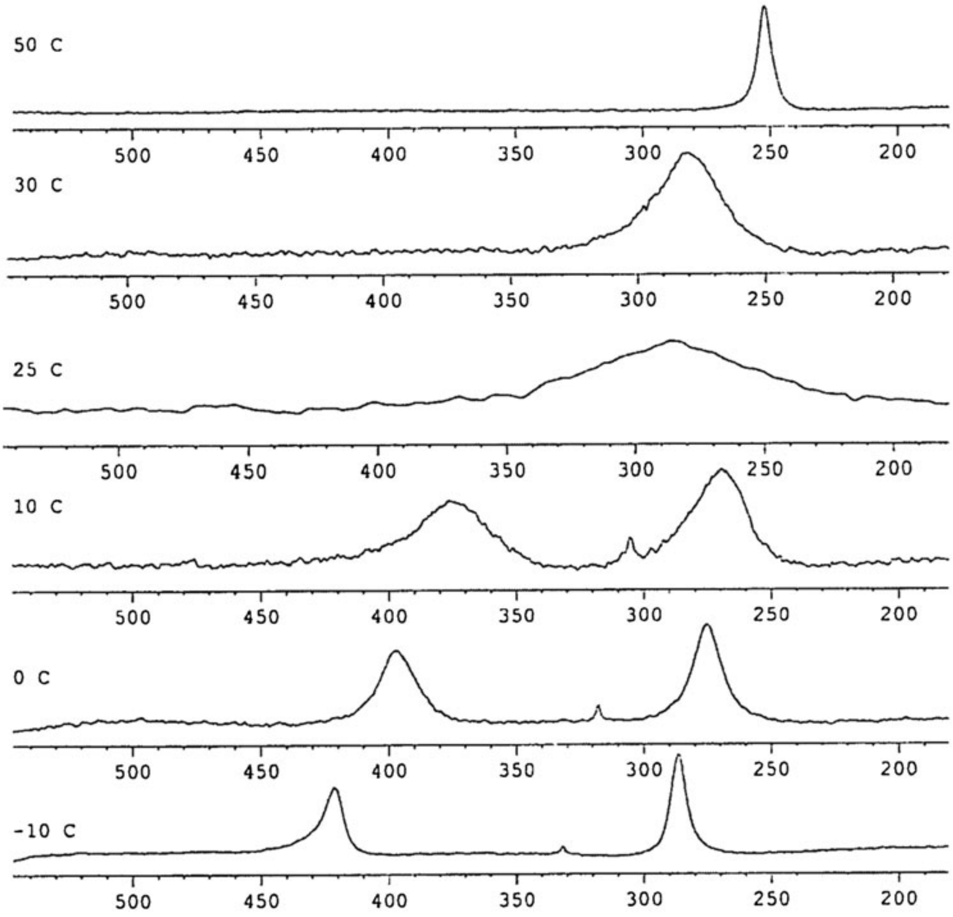

Figure 3. ^{31}P NMR spectra for the mixture of 35 mM $PW_{11}Co$ with 7× excess (1.2 M) of THABr and 100 mM water in toluene at the temperatures between −10 and 50 °C.

10 mM concentration in hexane. After six refluxes the bromide concentration was below the detection limit.

Figure 4 shows the ^{31}P NMR spectra of refluxed dry solutions as a function of temperature. The spectra are significantly simplified when compared to the spectra obtained before refluxing the solutions. However, even after refluxing $PW_{11}Co$ in hexane for six times with water there were still more than two signals present in ^{31}P NMR of $PW_{11}Co$ in dry toluene. At 25 °C the spectrum shows three peaks, a very intense and relatively narrow signal at 445 ppm (line width around 50 Hz), a very broad, 10 times less intense signal at 225 ppm (line width greater than 1000 Hz), and a second relatively narrow minor signal at 175 ppm (line width around 50 Hz). The three peaks integrate as 89 : 8 : 3. A fourth, very broad but minor signal appears at 370 ppm at temperatures below 15 °C. This broad signal at 370 ppm (in addition to the three signals at 440, 225, and 175 ppm) appears at room temperature when a water concentration is increased to 10 mM. The two very broad signals at 370 and 225 ppm narrow significantly as the temperature is lowered below 0 °C. As expected

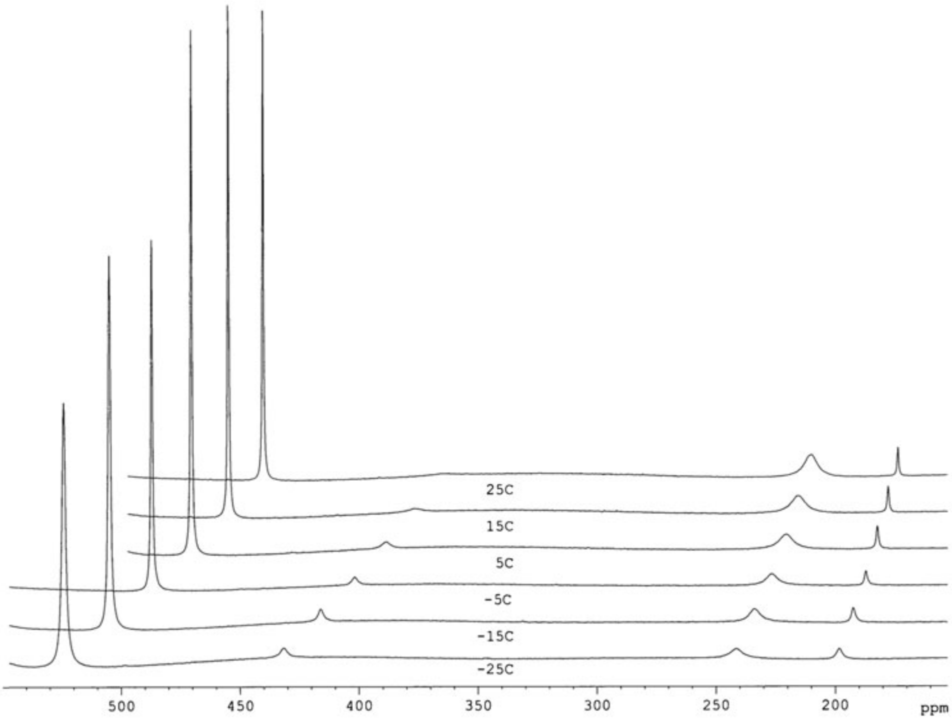

Figure 4. ^{31}P NMR spectra of 100 mM $PW_{11}Co$ in dry toluene (3 mM H_2O), after removing inorganic ions, at temperatures from −25 to 25 °C.

for paramagnetic signals the chemical shifts of all peaks change with temperature. They move towards the diamagnetic range as temperature increases. For example, the most paramagnetic signal shifts from 530 ppm at −25 °C to 440 ppm at 25 °C. On the other hand, the narrowing of the broad signals as the temperature decreases indicates a chemical exchange in the slow exchange regime.

Based on these observations, we assigned the two very broad signals at 370 and 225 ppm to $[PW_{11}O_{39}Co(H_2O)]^{5-}$ and $[PW_{11}O_{39}Co(\_)]^{5-}$, respectively. The two species are significantly broadened by the exchange of water molecule between the six- and five-coordinate cobalt. The chemical shift for the signal assigned to $[PW_{11}O_{39}Co(H_2O)]^{5-}$ is the same as the chemical shift observed for the signal in "very wet" toluene (over 300 mM H_2O in toluene). Note that the complex with five-coordinate cobalt represents only around 3% of total cobalt, which explains why the toluene solution is not green. On the other hand, the fact that the solution remains red indicates that the remaining species must contain six-coordinated cobalt. Because the ratio of water to cobalt is very small (around 0.03), the remaining species must not include water as the sixth ligand. The only logical explanation is that $PW_{11}Co$ in a very dry toluene solution forms dimers. The sixth coordination site on cobalt in the dimer is occupied by an oxygen from a neighboring monomer $PW_{11}Co$. There is no NMR evidence for any other oligomers.

Formation of dimers by TMSPOTs has been observed to date, but only in aqueous and acetonitrile solutions. Dimeric and trimeric structures of Ti, [9] Zr, [10] Mn, [11] Fe, [12]

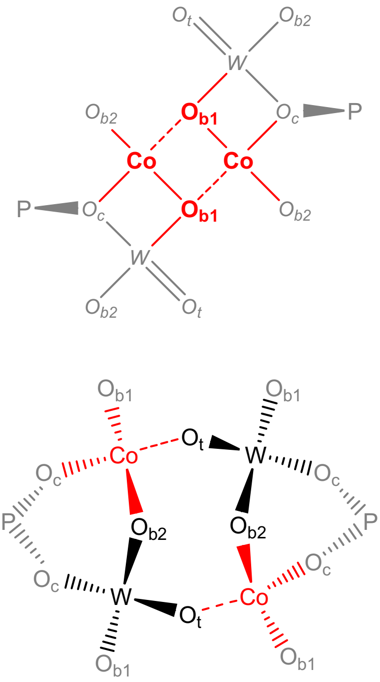

Figure 5. Fragments of structures near the Co atoms for two isomers of the dimer in toluene. Subscripts on O atoms indicate O_c – oxygens connected to central phosphorus, O_{b1} and O_{b2} – two kinds of bridging oxygens, b_1 – corner sharing, b_2 – edge sharing, O_t – terminal oxygens. In the first isomer (at the bottom), Co from one monomer is connected with the second monomer through one of the terminal oxygens of the W atom neighboring with the Co atom in the second monomer. The Co atom in the second monomer is connected in the same way with the first isomer, leading to two parallel W–O_t–Co bridges. In the second isomer (at the top) both Co atoms are connected to each other through the bridging oxygens.

Ru, [13] Co, [14] Ni, [15] and Cu [16] substituted Keggin anions have been determined by X-ray crystallography. However, our data represent the first evidence that TMSPOTs can also form dimers in very dry nonpolar solvents. This discovery also explains why $PW_{11}Co$ does not react with CO_2 gas in dry toluene solution [4].

The fact that there are two extra species in addition to $[PW_{11}O_{39}Co(H_2O)]^{5-}$ and $[PW_{11}O_{39}Co(\_)]^{5-}$ indicates isomerism. One obvious kind of isomerism is related to the type of oxygen atoms used for bridging the two monomers. The atoms could be terminal or bridging (from W–O–W bridges within the monomers) oxygens (see figure 5). Both kinds of bridges have been reported in the literature for dimers existing in aqueous solutions.

Two additional experiments were performed in order to confirm the existence of dimers in toluene solution of $PW_{11}Co$. In the first experiment we prepared a mixture of THA salts of $PW_{11}Co$ and $PW_{11}Zn$. A dry toluene solution of $PW_{11}Zn$ alone contains only one signal in the diamagnetic region of the spectrum (very narrow signal at −12 ppm) and no signals in the paramagnetic region. On the other hand, the mixture of 60 mM $PW_{11}Co$ and 40 mM $PW_{11}Zn$ in dry toluene (10 mM H_2O) contains, in addition to the signals observed in pure $PW_{11}Co$ and pure $PW_{11}Zn$, three new signals in the paramagnetic region and three new signals in the diamagnetic region. These signals can only be explained by the existence of

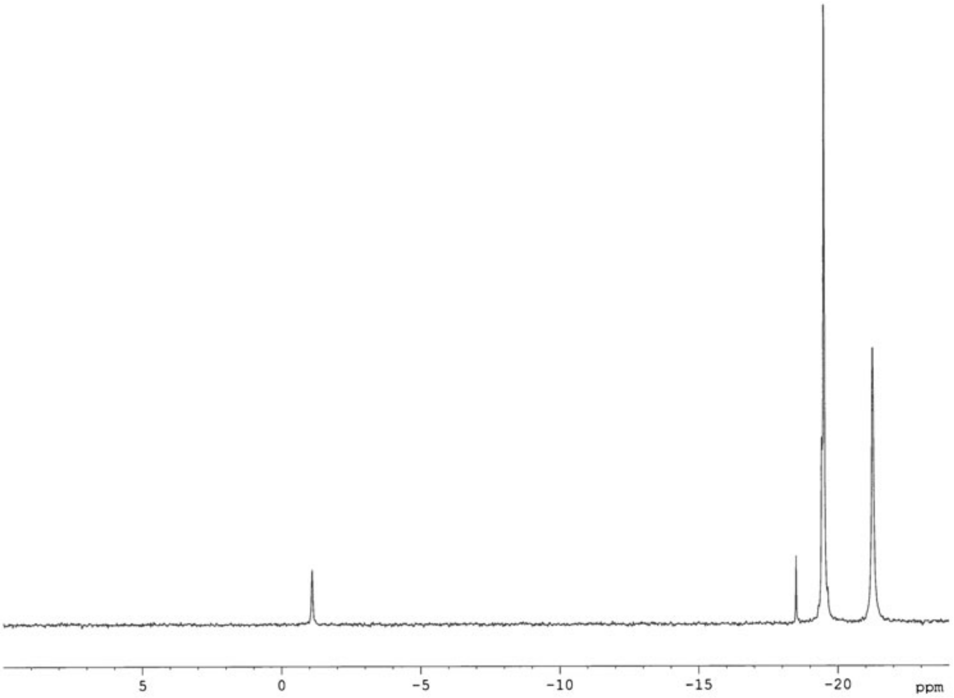

Figure 6. Diamagnetic region of ^{31}P NMR spectrum for 60 mM $PW_{11}Co$ and 40 mM $PW_{11}Zn$ in dry toluene (3 mM H_2O).

$PW_{11}Co$–$PW_{11}Zn$ dimers. Figure 6 shows the diamagnetic region of the NMR spectrum for the mixture.

The second experiment investigated the ionic strength effect on the appearance of the spectrum of $PW_{11}Co$. Four peaks are observed in a 10 mM solution of pure $PW_{11}Co$ in very dry toluene (two dimers, pentacoordinated, and hydrated monomer). In order to increase the ionic strength of the solution, increasing amounts of diamagnetic nonphosphorus containing THA salt of $SiW_{11}Zn$ was added. (Si containing TMS-HPTs do not extensively dimerize. ^{29}Si NMR spectra for $SiW_{11}Zn$ and for $SiW_{11}Co$ show only one peak each in dry toluene.) As the concentration of $SiW_{11}Zn$ (and the ionic strength of solution) was increased, the dimer to monomer ratio decreased to the point that only one signal (at 250 ppm) was observed in the solution of 10 mM $PW_{11}Co$ and 90 mM $SiW_{11}Zn$, and the solution turned green. We interpret this result as the influence of ionic strength (and activity coefficients) on the equilibrium between the $PW_{11}Co$ monomers and $PW_{11}Co$–$PW_{11}Co$ dimers.

For the reaction $2\ M \leftrightarrows D$, the thermodynamic equilibrium constant K is expressed in terms of activities $K = \frac{a_D}{a_M^2} = \frac{\gamma_D}{\gamma_M^2} \times \frac{c_D}{c_M^2}$ where a_D and a_M represent activities of the dimer and monomer, respectively, γ_D and γ_M their activity coefficients, and c_D and c_M their concentrations. As ionic strength increases and both activity coefficients decrease, the activity coefficient term $(\frac{\gamma_D}{\gamma_M^2})$ increases. In order to keep the thermodynamic equilibrium constant, a constant number, the concentration term $(\frac{c_D}{c_M^2})$ must decrease, by shifting the equilibrium to the left. Therefore, the monomer concentration should increase as the ionic strength increases, as is observed. Comparison of drying behavior for $PW_{11}Co$ to $SiW_{11}Co$ and $BW_{11}Co$ also supports our interpretation. Of the three anions, $[PW_{11}O_{39}Co]^{5-}$, $[SiW_{11}O_{39}Co]^{6-}$, and $[BW_{11}O_{39}Co]^{7-}$, only the anion with the least negative charge ($[PW_{11}O_{39}Co]^{5-}$) forms dimers in dry toluene solutions. For other two anions Coulombic repulsion appears too large to bring the two anions together.

UV/VIS spectroscopy

Figure 7(a) and (b) shows the UV/VIS spectra of (a) $SiW_{11}Co$ and (b) $PW_{11}Co$ in wet and dry toluene. The spectra in wet toluene are similar to each other. Both consist of a series of transitions between 480 and 550 nm. However, the spectra in dry toluene differ significantly. For $SiW_{11}Co$, the transitions between 480 and 550 disappear and a new very strong transition around 600 nm appears. For $PW_{11}Co$, the new 600 nm transition also appears but the original multiple transitions between 480 and 550 remain. This observation was interpreted in the past as indicating a mixture of hydrated and five-coordinate cobalt for the solution of PW_1Co in dry toluene. Figure 8 shows the spectra of $PW_{11}Co$ in toluene in the presence of 10× excess of $SiW_{11}Zn$ (high ionic strength). This spectrum is very different from the $PW_{11}Co$ in wet toluene. In fact, the difference is observable by eye. The sample in wet toluene is red and the sample in dry toluene is green, nearly the same as for $SiW_{11}Co$. This result confirms the NMR observation that $PW_{11}Co$ can be prepared with five-coordinate

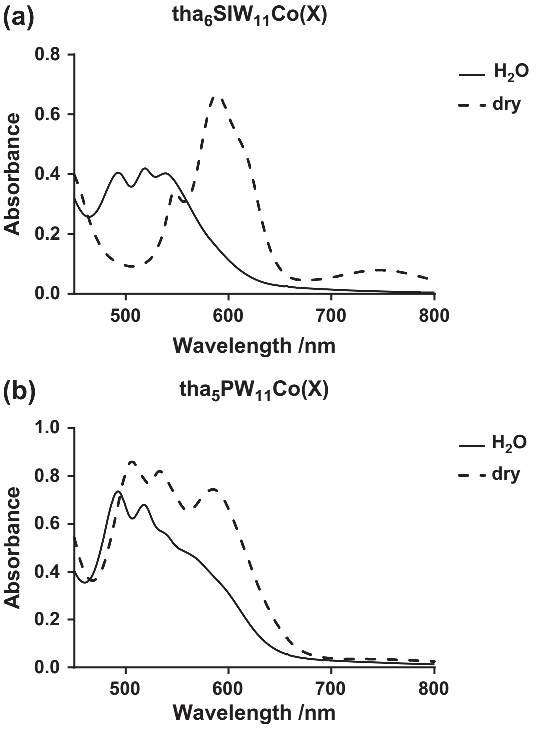

Figure 7. UV/VIS spectra for $THA_6[SiW_{11}CoO_{39}(X)]$ (a) and $THA_5[PW_{11}CoO_{39}(X)]$ (b) in wet and dry toluene.

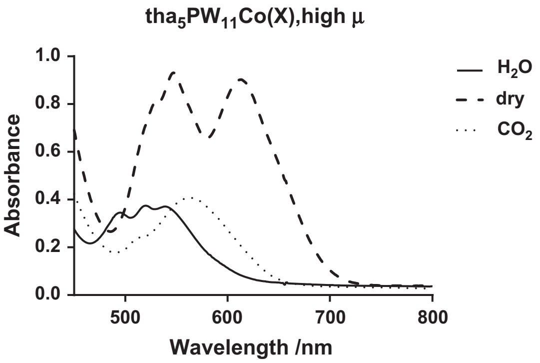

Figure 8. UV/VIS spectra for $THA_5[PW_{11}CoO_{39}(X)]$ in wet and dry toluene in the presence of 10× excess of $THA_6[SiW_{11}ZnO_{39}]$ (high ionic strength). The dotted curve is the spectrum of $THA_5[PW_{11}CoO_{39}(CO_2)]$ in dry toluene at high ionic strength.

cobalt in the presence of excess inert salt. Interestingly, the dry solid sample of $(THA)_5[PW_{11}O_{39}Co(\_\_)]$ is also green.

Reaction with CO_2

Both UV/VIS and ^{31}P NMR in high ionic strength environment support the existence of $[PW_{11}O_{39}Co(\_\_)]^{5-}$ anion with five-coordinate cobalt. Therefore, we decided to test reactivity of this species by bubbling dry CO_2 gas through that solution. In the past we reported that according to UV/VIS spectra $PW_{11}Co$ in dry toluene did not react with CO_2 [4]. On the other hand, the reaction does take place in dry toluene in the presence of excess inert salt. After bubbling with CO_2, a single ^{31}P NMR signal is observed at 430 ppm, which we assign to $[PW_{11}O_{39}Co(CO_2)]^{5-}$. At the same time the UV/VIS spectrum changes significantly as well, and becomes characteristic of six-coordinate cobalt(II) (see figure 8).

Quantum mechanical/molecular mechanical calculations

Geometry optimizations were carried out on the monomer and the dimer in vacuum and in toluene solution using a combined quantum mechanical (QM) and molecular mechanical (MM) model for the polyoxometalate anion and the THA shell, respectively. The dimer geometry was optimized with corner sharing of a terminal oxygen on W from one anion, and Co from the second anion. See the structure at the bottom of figure 5. Our preliminary results fully support the interpretation of the experimental data. Whereas in vacuum two molecules of $THA_5[PW_{11}CoO_{39}]$ were found to be more stable than one dimer molecule of $THA_{10}[PW_{11}CoO_{39}\text{-}PW_{11}O_{39}Co]$ by about 850 $kJ\,M^{-1}$, the opposite is true in toluene where the dimer is more stable by approximately 900 $kJ\,M^{-1}$. In a follow-up study, we will present a detailed density functional theory (DFT) study of these systems.

Conclusion

It is possible to remove coordinated water from cobalt in cobalt-substituted phosphotungstate with the Keggin structure in toluene solution. However, even though water is removed, the dry solution remains red as the result of dimer formation in a very dry solution. On the other hand, it is possible to prepare green monomers with five-coordinate cobalt in $PW_{11}Co$ at a high ionic strength in toluene solution or in the solid state. The $PW_{11}Co$ with five-coordinate cobalt reacts with carbon dioxide gas. Future work will include more detailed DFT calculations and data for tungsto-phospho-cobaltates with other structures.

Experimental

Computational details

The geometry optimizations were carried out using the ADF software package [17] and the Quantum-regions Interconnected by Local Descriptions program [18] within the QM/MM [19] scheme. The THA shell was treated via molecular mechanics using the TRIPOS force field constants [20] supplemented by parameters from UFF [21] (for interactions where TRIPOS parameters were not available). Since the QM and MM regions of our system are not bonded, it was not necessary to employ link atoms. The QM portion consisted of the polyoxometalate anion for which unrestricted calculations were performed assuming three unpaired electrons in the monomer, and six in the dimer. We used the VWN local density approximation [22] and the BP86 generalized gradient approximation [23] in the DFT calculations. Scalar relativistic effects were included via the ZORA Hamiltonian [24], and triple-zeta Slater type basis sets with polarization functions from the ADF basis-set library were employed for all atoms except for O where a double-zeta basis set was used instead. The geometries were optimized in the gas phase, as well as in solution using the conductor-like screening model as implemented in ADF [25] and parameters for toluene.

Materials

HPLC-grade nonpolar solvents, toluene and hexane were purchased from Aldrich. Toluene was distilled over sodium/benzophenone and stored under nitrogen, over molecular sieves. The water content in dried solvents was typically less than 1 mM. The phase transfer agent, THA bromide, was obtained from Aldrich. $K_5[PW_{11}O_{39}Co(H_2O)]$, $K_5[PW_{11}O_{39}Zn(H_2O)]$, $K_6[SiW_{11}O_{39}Co(H_2O)]$, and $K_6[SiW_{11}O_{39}Zn(H_2O)]$ were prepared according to the methods published previously [26–28]. The IR and UV/VIS spectra agreed with the data reported in the literature. (IR, all data in cm^{-1}: $PW_{11}Co$, observed-1085, 1064, 972, 895, 812, 760, 712, reported-1080, 1060, 970, 896, 811, 758, 710; $PW_{11}Zn$, observed-1096, 1058, 970, 892, 811, 760, 711, reported-1098, 1060, 972, 895, 810, 758, 718; $SiW_{11}Co$, observed-1000, 959, 902, 802, 755, 694, reported-1002, 962, 905, 803, 758, 698; $SiW_{11}Zn$, observed-1003, 958, 895, 796, 759, 699, reported-1008, 961, 902, 800, 758, 702; Vis, λ (nm), ε (M^{-1}, cm^{-1}): $PW_{11}Co$, observed-508(sh), 542 (71.5); reported-510(sh), 541(72); $SiW_{11}Co$, observed-520(sh), 557(72); reported-515(sh), 558(72)).

Phase transfer

A slight modification of the method introduced by Katsoulis and Pope [2] was used. Typically, an unbuffered 10 mM aqueous solution of the potassium salt of TMSPOT was shaken briefly with an equal volume of the stoichiometric amount of THABr in toluene. The concentration of THABr solution was 50 mM for $PW_{11}Co$ and $PW_{11}Zn$, and 60 mM for $SiW_{11}Co$ and $SiW_{11}Zn$. After the two phases had been allowed to settle for 10 min, they were separated. The organic layer at this stage was determined, via coulometric Karl Fisher titration, to contain between 20 and 25 water molecules per TMSPOT. Next, the wet toluene was removed by heating to 50 °C under vacuum. The solid was dissolved in hexane and the hexane solution was refluxed in the presence of an equal volume of water for 20 min at 60 °C. It took six refluxing extractions to remove all K^+ and Br^- ions. Next, the hexane was removed by heating at 50 °C under vacuum on a Schlenk line. Dry toluene was added using a gas tight syringe. Typically, the final water concentration was then around 5 mM. For the experiments with controlled amounts of water, wet solution containing the same ion concentration was added using gas tight syringes.

Spectroscopy

UV/VIS spectra were recorded using a HP 8452A diode array spectrophotometer. Vibrational spectra were acquired using a Nicolet 6700 FTIR spectrometer in compressed KBr pellets. NMR spectra were recorded using a Bruker Avance 250 or Agilent 400-MR DD2 spectrometer.

Water measurements

Water was determined by coulometric Karl Fisher titration using Metrohm 684 KF Coulometer filled with Aquastar coulomat single solution.

Ion chromatography

Bromide ion was determined by ion chromatography using a Dionex ICS 3000 Ion Chromatograph in anion mode with ion suppression and conductivity detection.

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