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Pyrophosphate Complexation of Tin(II) in Aqueous Solutions as Applied in Electrolytes for the Deposition of Tin and Tin Alloys Such as White Bronze

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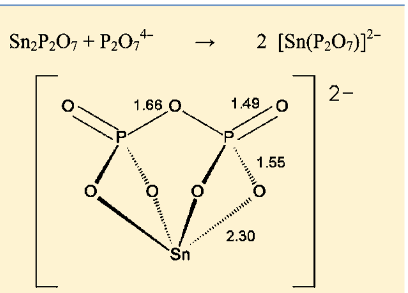

ABSTRACT: Electrodeposition of tin and tin alloys from electrolytes containing tin(II) and pyrophosphates is an important process in metal finishing, but the nature of the tin pyrophosphate complexes present in these solutions in various pH regions has remained unknown. Through solubility and pH studies, IR and ^{31}P and ^{119}Sn NMR spectroscopic investigations of solutions obtained by dissolving $Sn_2P_2O_7$ in equimolar quantities of either $Na_4P_2O_7 \cdot 10H_2O$ or $K_4P_2O_7$ the formation of anionic 1:1 complexes $\{[Sn(P_2O_7)]\}_n^{2n-}$ has now been verified and the molecular structures of the monomer ($n = 1$) and the dimer ($n = 2$) have been calculated by density functional theory (DFT) methods. Whereas the alkali pyrophosphates $Na/K_4P_2O_7$ give strongly alkaline aqueous solutions (pH ~13), because of partial protonation of the $[P_2O_7]^{4-}$ anion, the $[Sn(P_2O_7)]^{2-}$ anion is not protonated and the solutions of $Na/K_2[Sn(P_2O_7)]$ are almost neutral (pH ~8). The monomeric dianion appears to have a ground state with C_{2v} symmetry with the Sn atom in a square pyramidal coordination and the lone pair of electrons in the apical position, while the dimer approaches C_2 symmetry with the Sn atoms in a rhombic pyramidal coordination, also with a sterically active lone pair. A comparison of experimental and calculated IR details favors the monomer as the most abundant species in solution. With an excess of pyrophosphate, 3:2 and 2:1 complexes (P_2O_7):(Sn) are first formed, which, in the presence of more pyrophosphate, undergo rapid ligand exchange on the NMR time scale. The structure of the 2:1 complex $[Sn(P_2O_7)_2]^{6-}$ was calculated to have a pyramidal complexation by two 1,5-chelating pyrophosphate ligands. Neutralization of these alkaline solutions by sulfuric or sulfonic acids (H_2SO_4, $MeSO_3H$), as also practiced in electroplating, appears to afford the tin(II) hydrogen pyrophosphates $[Sn(P_2O_7H)]^-$ and $[Sn(H_2P_2O_7)]^0$. The molecular structures of the mononuclear model units have also been calculated and were shown to have an unsymmetrical complexation and to feature trigonal pyramidal (pseudotetrahedral) coordination. NMR observations have shown that, contrary to the results obtained for Sn^{II} compounds, Sn^{IV} as present in K_2SnO_3 or its hydrated form $(K_2Sn(OH)_6)$ does not form a pyrophosphate complex in aqueous solution near pH 7. There is also no interference of sulfite.

■ INTRODUCTION

Electroplating of metallic objects with a layer of tin or its alloys in particular with copper, such as bronze and "white bronze" for corrosion protection and for decorative finishing of metals, has been an established process for about two centuries. Typical electrolytes for copper−tin layers were initially based on cyanide complexes of these metals and kept at high pH values.[1] For the alkaline region, a technology using alkali stannates Na_2SnO_3 or K_2SnO_3, which dissolve as the hexahydroxystannates $Na/K_2[Sn(OH)_6]$, has later been introduced; this procedure is still widely practiced today.[2,3] This method goes back to very early experiments,[4] which have been reproduced many times with different additives in efforts to optimize the quality of the deposits.[5,6] The method suffers from the rapid absorption of CO_2 from the atmosphere into the electrolyte kept at high pH, leading to a load of carbonates in the baths.[2]

Early observations have also shown that tin plating could generally also be carried out with aqueous solutions of tin(II) salts containing *pyrophosphate*.[7−9] In secondary literature of the early 19th century, it has been mentioned that, already in 1850, the "Roseleur solutions" obtained from stannous chloride and sodium pyrophosphate were found to be a potential source for tin plating.[10,11] This method was tested again by Vaid and Rama Char, who used the solution obtained from stannous pyrophosphate and sodium pyrophosphate, and reported "a complex being formed".[8] Because both copper(II)[12] and zinc(II)[13] also form soluble complexes with pyrophosphate in an intermediate pH region, the same system was applied in the electrodeposition of bronzes.

This work was preceded by the isolation of a stannous pyrophosphate $Sn_2P_2O_7$ in 1936. This white solid was prepared via the pyrolysis of stannous hydrogen phosphate ($SnHPO_4$) and described as an amorphous, air-stable compound which is insoluble in water and only slowly soluble in diluted mineral acids.[14,15] A solution of $SnCl_2 \cdot 2H_2O$ in aqueous acetic acid was

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treated with an excess of $Na_2P_4O_7{\cdot}6H_2O$ to give a colorless precipitate.[16] In more recent work $Sn_2P_2O_7$ was prepared by heating a stoichiometric mixture of SnO and $NH_4H_2PO_4$ in a dynamic vacuum or in flowing argon at 820 K.[17] Surprisingly, there was no evidence provided that $Sn_2P_2O_7$ would form a soluble stannous pyrophosphate complex.

$Sn_2P_2O_7$ is now an inexpensive commercial product that is applied in several currently highly important technologies, including not only tin plating, but also negative electrode materials for lithium batteries. For this application, various doped materials have been developed.[15,17−19]

Several metals form complexes with pyrophosphate. Zinc was assigned both a 1:1 and a 1:2 complex with $[P_2O_7]^{4-}$, but it was noted (in 1949) that “no information appears to be available on tin”.[20,21] In fact, a large review on pyrophosphates of divalent metals that was published in 1936 did not contain any tin(II) examples. On the other hand, these authors provided clear evidence for complexes $[Cu^{II}(P_2O_7)]^{2-}$ and $[Cu^{II}(P_2O_7)_2]^{6-}$, which give rise to an intense blue color of their solutions.[22]

The results of a conductometric and potentiometric study suggested a 1:1 complex $[Sn(P_2O_7)]^{2-}$ for tin(II), but a 2:1 complex $[Zn(P_2O_7)_2]^{6-}$ for zinc in solution.[18] A review on “Metal Complexing by Phosphates” did not consider this work and still had no entries on tin(II) pyrophosphates.[23] Subsequently, Mesmer and Irani published experimental work on stannous polyphosphates and tripolyphosphates, which was based on solution studies of SnO in aqueous $Na_4P_2O_7$. It was concluded that at least two complexes were formed in solution, with the relative abundance being influenced by the overall concentration and the pH value. The stoichiometry remained unclear.[24] This work was followed by polarographic and potentiometric studies,[25−27] which yielded selected stability constants for the pH range from 7.1 to 8.2, including the 1:1 and 1:2 complexes $[SnP_2O_7]^{2-}$ and $[Sn(P_2O_7)_2]^{6-}$, but also a mixed hydroxo complex $[Sn(OH)(P_2O_7)]^{3-}$ has been considered. For higher pH (8.3−11.1), the anions $[Sn(OH)_2(P_2O_7)]^{4-}$ and $[Sn(OH)(P_2O_7)_2]^{7-}$ have been postulated.[26,27] A summary of these investigations is available.[2,3] It has been shown that the chemistry of tin(II) pyrophosphates in aqueous solution is still not completely understood. In addition, the complexation of tin(IV) with pyrophosphate in aqueous solution has not been studied, even though it may have an influence on the performance of oxidized baths.

In the present report the results of a study of tin pyrophosphate model solutions are described. The solutions were investigated by ^{119}Sn and ^{31}P NMR spectroscopy and the results compared with data obtained from reference chemicals. IR spectroscopy was also employed for discriminating $[P_2O_7]^{4-}$ species in various modes of complexation or as a free solvated anion. These tests were preceded by solubility studies which determined the lower limit of complexation. Theoretical calculations using DFT methods have provided molecular structures for the mononuclear anions $[Sn(P_2O_7)]^{2-}$, $[Sn_2(P_2O_7)_2]^{4-}$, $[Sn(P_2O_7)_2]^{6-}$, and $[Sn(P_2O_7H)]^{-}$, and the molecule $[Sn(P_2O_7H_2)]^0$ as the dominating species in weakly alkaline and neutralized solutions, respectively.

EXPERIMENTAL PART

Chemicals. $Sn_2P_2O_7$, $Na_4P_2O_7{\cdot}10H_2O$, $K_4P_2O_7$, $Na_5P_3O_{10}$, Na_2SO_3, $SnCl_2{\cdot}2H_2O$, and $K_2SnO_3{\cdot}3H_2O$ were commercial products and used as received.

Solutions. $Sn_2P_2O_7$ is insoluble in water, and solutions were only obtained with at least 1 mol equiv of a pyrophosphate. For all spectroscopic measurements, clear and colorless aqueous solutions were prepared of the reference compounds and of the complexes. The molar ratios (Sn^{II}): (P_2O_7) varied as shown in the captions to Figure 1−4 and as mentioned in the text. The concentration was 0.1 ML^{-1} at ambient temperature (23 °C) for $Na_4P_2O_7{\cdot}10H_2O$, $K_4P_2O_7$, $Na_5P_3O_{10}$, Na_2SO_3, and $K_2SnO_3{\cdot}3H_2O$. For the Sn^{II} pyrophosphate complexes the concentration of $[Sn^{II}]$ was also 0.1 ML^{-1}, but the concentration of $[P_2O_7]$ was increased as indicated by the molar ratios, i.e. from 0.1 to 0.15, 0.2, etc. $[ML^{-1}]$.

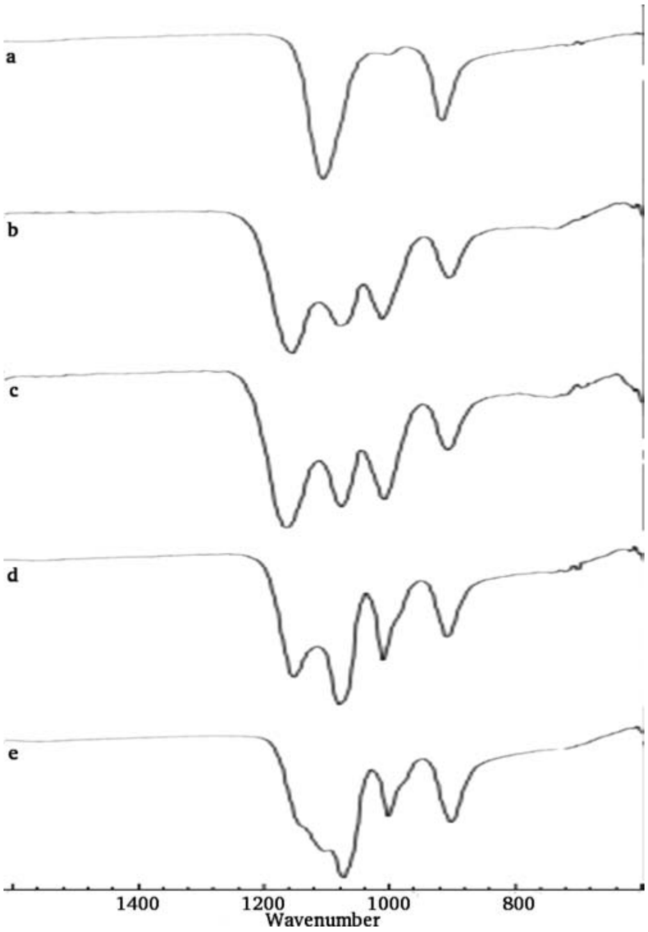


Figure 1. IR spectra of aqueous solutions of (a) $K_4P_2O_7$, (b) $K_2[Sn(P_2O_7)]$, (c) $Na_2[Sn(P_2O_7)]$, (d) $[Sn(P_2O_7)_2]^{6-}$, and (e) $[Sn(P_2O_7)_2]^{6-}$ + $4[P_2O_7]^{4-}$.

IR Spectroscopy. IR spectra of the solutions were recorded on a Varian 670 IR FT-IR spectrometer with a PikeGladi ATR.

NMR Spectroscopy. ^{31}P NMR spectra were recorded on a Bruker Avance III 400 NMR spectrometer, and ^{119}Sn NMR spectra were recorded on Bruker Avance 400 and Avance III 400 NMR spectrometers. ^{31}P NMR (162 MHz) used 85% H_3PO_4 and ^{119}Sn (149 MHz) used 90% $SnMe_4$ in C_6D_6 as an external standard.

Computational Details. The structures of the studied species were investigated with the ab initio hybrid density functional B3LYP method in Gaussian09.[28,29] The def2-TZVP basis sets, an additional ECP for Sn, and a PCM model with water as solvent were applied in the calculations.[30] All structures were fully optimized, molecular symmetry was utilized where possible, and the optimized structures were confirmed as true local minima by performing harmonic frequency calculations. Calculations on C_{2v}-symmetric $SnP_2O_7H_2$ and C_s-symmetric $SnP_2O_7H^-$ led to transition states.

■ RESULTS AND DISCUSSION

Solubility and pH Studies. Commercial stannous pyrophosphate $Sn_2P_2O_7$ is a fine white powder. We confirm that the material is insoluble in water.[15] A *slurry* in deionized water shows pH 6−7 at 23 °C. Upon addition of an aqueous solution of either anhydrous potassium pyrophosphate $K_4P_2O_7$ (pH 13) or sodium pyrophosphate decahydrate $Na_4P_2O_7 \cdot 10H_2O$ (pH 12) to this slurry of $Sn_2P_2O_7$ the solid was gradually dissolved, but a clear colorless solution (pH ca. 7−8) was obtained only when the stoichiometry reached a molar ratio of (Sn):(P_2O_7) of 1:1. This is evidence that $Sn_2P_2O_7$ can only be dissolved in water at pH 7 if at least one additional equivalent of $[P_2O_7]^{4-}$ is provided to reach the 1:1 ratio (eq 1), the dissolved compounds having then the formula $Na_2SnP_2O_7$ (aq) or $K_2SnP_2O_7$ (aq), respectively:

$$Sn_2P_2O_7 + K_4P_2O_7 \rightarrow 2K_2[Sn(P_2O_7)] \qquad (1)$$

As shown below, the nature of the $[SnP_4O_7]^{2-}$ part in solution is independent of the alkali counterion, since both IR and $^{31}P/^{119}Sn$ NMR spectroscopy show virtually identical characteristics. The maximum solubility was not determined, but solutions containing up to 150 g L^{-1} remained clear and stable for a long time in the laboratory atmosphere.

With an excess of alkali pyrophosphate, beyond the 1:1 ratio, the dissolution kinetics of $Sn_2P_2O_7$ is enhanced and the solutions obtained are also clear and stable, but their pH is gradually increased up to ca. 12, unless a substantial amount of acid is used for neutralization. This adjustment of pH was initially not executed systematically, in order to have data on the "native" solutions.

It is important to remember that the high pH of alkali pyrophosphate solutions (pH ca. 11−13) is due to an equilibrium as shown in eq 2. The $[P_2O_7]^{4-}$ tetraanion is partly converted to dihydrogen pyrophosphate, generating two OH^- responsible for the alkalinity observed. The fact that the 1:1 complex $[Sn(P_2O_7)]^{2-}$ gives almost neutral aqueous solutions (pH ca. 8) at comparable concentrations shows that, upon formation of the tin(II) complex, the diprotonation of the pyrophosphate is reversed, meaning that the pyrophosphate is *not* protonated in the complex as shown in eqs 1 and 3.

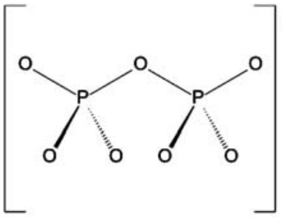
$$[P_2O_7]^{4-} + 2H_2O \rightarrow [H_2P_2O_7]^{2-} + 2OH^- \qquad (2)$$

$$[H_2P_2O_7]^{2-} + Sn^{2+} \rightarrow [Sn(P_2O_7)]^{2-} + 2H^+ \qquad (3)$$

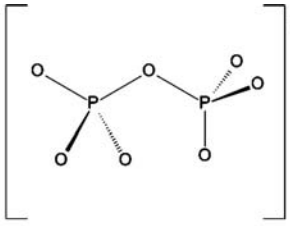
$$2OH^- + 2H^+ \rightarrow 2H_2O \qquad (4)$$

The 1:1 complex may be present as a mononuclear or a dinuclear anion (see below). Upon addition of acid, reprotonation is expected to take place to give tin(II) complexes of hydrogen pyrophosphates.

Infrared Spectroscopy. The IR and Raman spectra of aqueous solutions containing the pyrophosphate tetraanion $[P_2O_7]^{4-}$ were studied several times.[31−33] The investigation of solutions of $Na_4P_2O_7 \cdot 10\ H_2O$, $K_4P_2O_7$, and $(NH_4)_4P_2O_7$ in H_2O and D_2O has shown that the vibrational characteristics of the anion are not influenced by the nature of the cations. This observation is proof that the cations Na^+, K^+, and NH_4^+ are not complexed by the tetraanion, even in saturated solutions. The prominent bands of the vibrations of the P_2O_7 skeleton are found at 916 ± 6 and 1115 ± 5 cm^{-1}, along with weaker bands at ca. 425, 560, 726, and 1025 cm^{-1}. This set could be assigned to the normal vibrations of a bent and eclipsed anion with C_{2v} symmetry (Formula A). The bent staggered anion with C_s symmetry (Formula B) seems to be higher in energy in aqueous solutions. These results are valid only for the tetraanion $[P_2O_7]^{4-}$ in a fluctuating environment of water dipoles and alkali cations. In a crystal lattice of salts or their hydrates, the packing forces may induce different conformations.



A



B

The IR spectrum of an aqueous solution of $K_4P_2O_7$ (pH 13, 0.1 M) has been reproduced in this work, the two most significant bands being detected at 915 and 1104 cm^{-1} (see Figure 1a). By contrast, the aqueous solutions obtained by dissolving $Sn_2P_2O_7$ in exactly equimolar quantities of $Na_4P_2O_7 \cdot 10H_2O$ and $K_4P_2O_7$ (v.s.), having pH 8 at a 0.1 M concentration, show an entirely different, but mutually consistent, set of peaks in the corresponding frequency region: 1154, 1077, 1010, 904, and 742 cm^{-1} for $K_2SnP_2O_7$ (Figure 1b); 1162, 1075, 1007, 906, and 742 cm^{-1} for $Na_2SnP_2O_7$ (Figure 1c). This result suggests that the pyrophosphate anion is engaged in the complexation of Sn^{2+}, but not of Na^+ or K^+.

The IR spectra undergo further changes as the molar ratio of (P_2O_7):(Sn) is gradually increased to 2:1, indicating some modified complexation to occur between the 1:1 and 2:1 ratios (Figure 1d). For ratios >2: 1, the spectra show an overlap of the bands with those of free $[P_2O_7]^{4-}$ (Figure 1e). As the ratio is increased from 1:1 to 4:1, the pH of the solution also increases from ∼8 to ∼13 (depending also on concentration).

Therefore, from the IR investigations, it appears that Sn^{2+} undergoes complex formation with $[P_2O_7]^{4-}$ up to a molar ratio of 2:1 for (P_2O_7):(Sn). Excess $[P_2O_7]^{4-}$ is not involved in the complexation. This conclusion is valid for the "naturally" produced pH regime established by just dissolving the two chemicals $Sn_2P_2O_7$ and $K_4P_2O_7$ in water and with no acid or base used to make pH adjustments. Under these increasingly alkaline conditions, the $[P_2O_7]^{4-}$ anion is the predominant species, whereas, upon addition of acid, the hydrogen pyrophosphate anions $[H_nP_2O_7]^{(4-n)-}$ increase in concentration rendering the system more complex. This is in good agreement with the results of the electrochemical studies obtained by other groups.[31−34]

^{31}P NMR Spectroscopy. The aqueous solutions obtained by dissolving $Sn_2P_2O_7$ in increasing amounts of $K_4P_2O_7$ with molar ratios (P_2O_7):(Sn) from 1:1 to 5: 1 with their "natural" pH (from 8 to 13) were studied by ^{31}P NMR spectroscopy at ambient temperature. It was not expected to see separate resonance for different complexes, because a rapid exchange of free and complexed $[P_2O_7]^{4-}$ anions must lead to signal averaging at 25 °C and even at the freezing limit of the solvent (ca. −10 °C). For the same reason, no $^{31}P-^{119/117}Sn$ spin−spin coupling was expected, which is also eliminated by the exchange processes. However, with the chemical shift δP of the reference resonances of free $[P_2O_7]^{4-}$ anions in aqueous solutions of $K_4P_2O_7$ (Figures 2a, 2j) and of the complex present

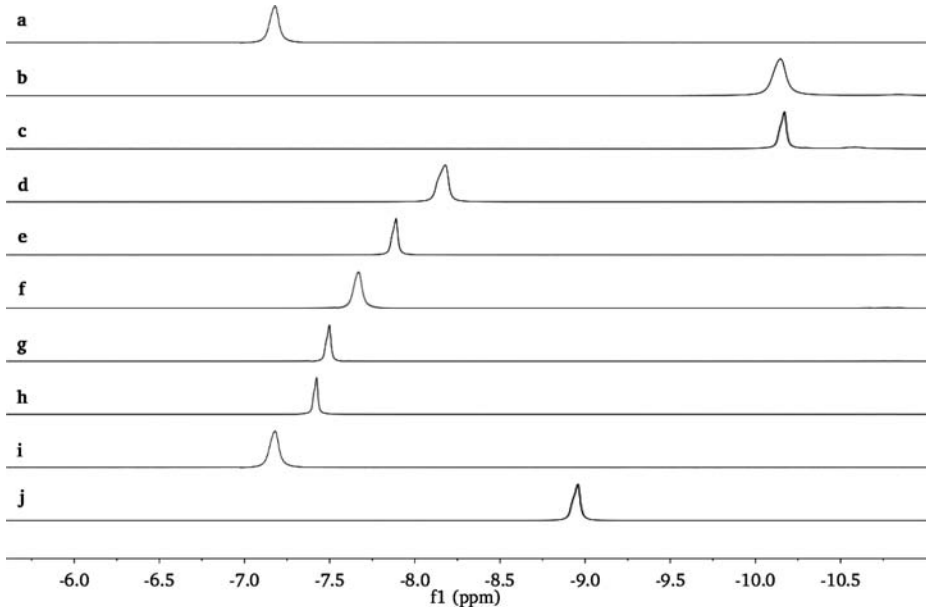


Figure 2. ^{31}P NMR spectra of aqueous solutions of (a and i) $K_4[P_2O_7]$, (b) $K_2[Sn(P_2O_7)]$, (c) $Na_2[Sn(P_2O_7)]$, and of solutions with the molar ratios $(P_2O_7{}^{4-})$:(Sn^{2+}) of (d) 3:2, (e) 3.5:2, (f) 4:2, (g) 5:2, (h) 6:2, prepared from the appropriate quantities of $K_4P_2O_7$ and $Sn_2P_2O_7$. (j) Sample from spectrum (h), neutralized to pH 8.

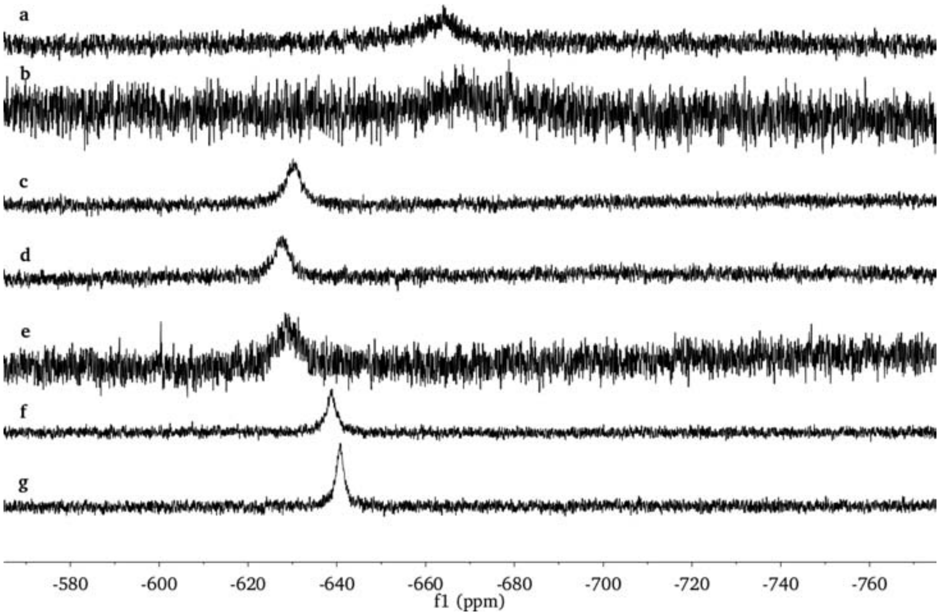


Figure 3. ^{119}Sn NMR spectra of aqueous solutions of (a) $K_2[Sn(P_2O_7)]$ and (b) $Na_2[Sn(P_2O_7)]$, and of solutions with the molar ratios (P_2O_7):(Sn) of (c) 3:2, (d) 3.5:2, (e) 4:2, (f) 5:2, (g) 6:2, prepared from the appropriate quantities of $K_4P_2O_7$ and $Sn_2P_2O_7$.

in solutions with the 1:1 molar ratio (Figure 2b), two benchmark values were obtained for δP values of other mixtures (Figures 2c−h).

As a control, the 1:1 complex produced with $Na_4P_2O_7{\cdot}10H_2O$ instead of $K_4P_2O_7$ was also investigated (Figure 2c). The anion $[SnP_2O_7]^{2-}$ has the same chemical shift, $\delta P = -10.2 \pm 0.1$ ppm, independent of the cation present (Na^+, K^+). This signal is first shifted very strongly (Figure 2d) and then in smaller steps toward the signal of the free $[P_2O_7]^{4-}$ at $\delta P = -7.2$ ppm (Figure 2i), as more $K_4P_2O_7$ is added (Figure 2c−h).

The shift difference $\Delta\delta$ between the free pyrophosphate anion (present in the aqueous solution of $K_4P_2O_7$ at pH 13) and the 1:1 complex (in aqueous solution at pH 7) is ca. 3 ppm. Whereas for the molar ratios 2:1 to 5:2, the corresponding $\Delta\delta$ values decrease continuously by a total of only 1 ppm, a large shift of $\Delta\delta = 2$ ppm is observed for the step from the 1:1 to the 3:2 and 2:1 ratios. This indicates that other species are formed after the 1:1 complex, which then simply undergo pyrophosphate exchange as more pyrophosphate is added. The nature of these species is as yet uncertain, since, upon going from 1:1 via 2:1 to 5:1 for (P_2O_7):(Sn), there are two drastic changes in pH, from 7 via 9 to 12. This may influence the protonation of the complexes, which must be lowest at the highest (P_2O_7):(Sn) ratio (5:1). Simple stoichiometric formulas like $[Sn_2(P_2O_7)_3]^{8-}$ or $[Sn(P_2O_7)_2]^{6-}$ show that these anions have an exceedingly

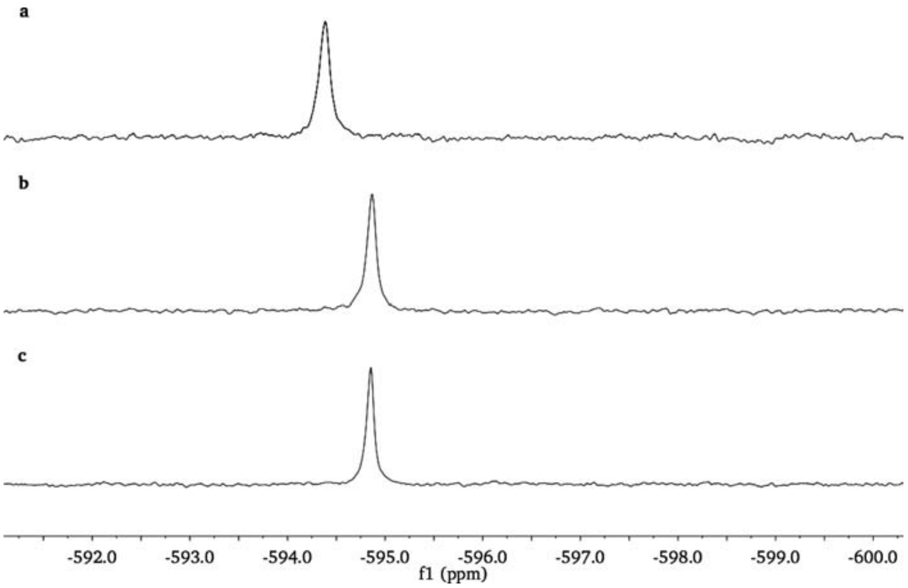


Figure 4. ^{119}Sn NMR spectra of aqueous solutions of (a) $K_2[Sn(OH)_6]$, (b) $K_2[Sn(OH)_6]$ with an excess of $K_4P_2O_7$, and (c) with an excess of $Na_5P_3O_{10}$.

high negative charge, which calls for partial assembly with the counterions and for hydrogen bonding or even protonation. The latter will further increase the pH, as indeed observed.

The influence of the acid, which provides the protons required for the compensation of the high negative charges of the tin complexes, becomes obvious from the ^{31}P resonance of a solution with the 5:1 ratio, which was neutralized to pH 8. The peak is now shifted in the opposite direction to $\delta P = -9$ ppm. This shift is the average of free and coordinated pyrophosphate groups, which are all protonated (Figure 2j).

^{119}Sn NMR Spectroscopy. The ^{119}Sn nuclei were observed in the same solutions as used for the ^{31}P measurements, and the results are complementary. The signals obtained were generally broad with no ^{31}P−^{119}Sn splitting resolved, as expected for a system with ligand exchange being rapid on the NMR time scale.

The solutions with the 1:1 ratio (P_2O_7):(Sn) gave the same value $\delta Sn = -665 \pm 3$ ppm, independent of the nature of the alkali cations present (Na^+, K^+), confirming that the alkali cations are not part of the $[SnP_2O_7]^{2-}$ complex (see Figures 3a and 3b). With increasing amounts of $[P_2O_7]^{4-}$, the signal δSn is shifted first downfield to ∼628 ppm (ratios (P_2O_7):(Sn) = 3:2, 4:2, and 5:2) suggesting that for these ratios at least one other pyrophosphate-rich complex is formed (see Figures 3c−e). For the ratios 5:2 and 6:2 (see Figures 3f and 3g), there is an unexpected upfield shift to $\delta Sn \approx -638$ ppm. A further upfield shift is observed if the pH of the 6:2 solution is adjusted to 8.5 with acid, resulting in $\delta Sn = -650$ ppm (Figure 3g). The linewidth of the signals becomes smaller with an increase of the relative $[P_2O_7]^{4-}$ ligand concentration and at lower pH.

The results suggest that the broad resonance near $\delta Sn = -665$ ppm must be assigned to the solvated complex anion $[SnP_2O_7]^{2-}$ for which the δP resonance was found at 10.2 ppm. The equally broad resonances near $\delta Sn = -630$ ppm can be ascribed accordingly to the highly charged complexes $[Sn(P_2O_7)_2]^{6-}$ or $[Sn_2(P_2O_7)_3]^{8-}$, which undergo ligand exchange and had averaged values of $\delta P \approx 7.7$ ppm. The large linewidth at these stoichiometries (2:2, 3:2, or 4:2) is probably due to the greater anisotropy tensors which shorten the relaxation time of the nuclei, and to a certain degree of fluxionality within the complex regarding the hapticity (see below). With an excess of $[P_2O_7]^{4-}$, the ligand exchange becomes rapid and leads to a time-averaged environment, giving rise to sharper signals. At lower pH, this exchange is even further enhanced, because of the reversible formation of an increasing amount of O−H bonds in the $[HP_2O_7]^{3-}$ and $[H_2P_2O_7]^{2-}$ anions involved in O−H···O hydrogen bonding.

For comparison, the ^{119}Sn NMR spectra of some tin(II) and tin(IV) reference solutions have also been investigated. For the former, $SnCl_2$ hydrate was dissolved in hydrochloric acid and in potassium hydroxide. The acid solution showed a broad signal at $\delta Sn = -589$, while the alkaline gave a sharp signal at $\delta Sn = -578$ ppm. These shifts for the hydrogen chlorostannites $[SnCl_3]^-$ and hydroxystannites $[Sn(OH)_3]^-$, respectively, differ by more than 50 ppm from those of the pyrophosphate complexes under consideration.[35]

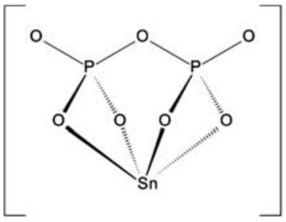
Potassium stannate $K_2SnO_3 \cdot 3H_2O$, which dissolves in water as the hexahydroxystannate(IV) $K_2[Sn(OH)_6]$, gives a signal at $\delta Sn = -595.3$ ppm, in agreement with some older literature data[36] and more recent results for $Rb_2[Sn(OH)_6]$ with $\delta Sn = 590.5$ ppm.[37]

It is important to note in the present context that $K_2[Sn(OH)_6]$ obviously does not form a pyrophosphate complex in aqueous solution: The signal at $\delta Sn = 594.8$ ppm obtained if $Na_4P_2O_7 \cdot 10H_2O$ is added to the solution of $K_2[Sn(OH)_6]$ shows no significant shift from the original position (pH 9 is established under these conditions). The same is true for the addition of $Na_5P_3O_{10}$, which yields a solution of pH 10 (Figures 4a−c). These results imply that formation of tin(IV) either by direct oxidation or by disproportionation of tin(II) is not influenced significantly by pyrophosphate or tripolyphosphate.

Finally, it was observed that sulfite $[SO_3]^{2-}$ is *not* a reductant for $[Sn(OH)_6]^{2-}$. The addition of sulfite to the solution has no effect on the δSn resonance of $[Sn(OH)_6]^{2-}$. Therefore, sulfite will not assist in the electrochemical reduction of tin(IV) baths.

No crystals could be grown from any of the tin(II) pyrophosphates investigated in this work. Upon evaporation of the solvent or upon addition of a cosolvent like methanol, only glassy or powdery precipitates were obtained, respectively. It should be noted that the structures of crystalline samples anyway may not necessarily reflect the structure in solution. Therefore, attempts were made to calculate meaningful structures of the dissolved species by quantum chemical methods.

Structural Considerations. *The Mononuclear Complexes of 1:1 Stoichiometry.* For a theoretical approach, several structures of mononuclear species are to be considered, which include arrangements of C_s or C_{2v} symmetry (C, D), together with those without an element of symmetry. The $[P_2O_7]^{2-}$ ligands can chelate metal atoms with up to four oxygen donor centers. For tin(II), there is a $5s^2$ lone pair of electrons that, in standard cases, may be sterically active. It is important to remember that the dianion $[Sn(P_2O_7)]^{2-}$ in aqueous solution is stabilized by an environment of water molecules through hydrogen bonding and through the electric field of the alkali cations embedded in the matrix of water dipoles.



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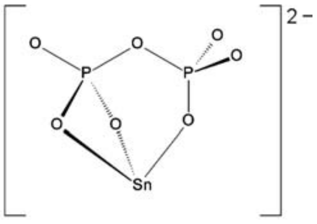

D

From crystal structure determinations of various tin(II) phosphates[38−40] including the pyrophosphate $Sn_2P_2O_7$,[17], it appears that there is a preference for three short Sn−O bonds (2.10−2.25 Å) for each tin(II) center, with all other Sn···O contacts much longer (>2.75 Å). In the two modifications of α- and β-$Sn_2P_2O_7$,[17] the $[P_2O_7]^{4-}$ anions have approximately C_s conformation (B) with P−O−P angles of 131.5° and 137.1°. The Sn^{2+} cations are chelated by one of the anions and further coordinated to a single oxygen atom of the next anion with Sn−O distances in the range of 2.108−2.234 Å. A fourth O atom is found 2.885 Å away. The crystal structures of α- and β-$Sn_2P_2O_7$ contain no water molecules and therefore no hydrogen bonds contribute to the packing forces.

Tin(IV) pyrophosphate SnP_2O_7 exists in modifications with ordered and randomly oriented pyrophosphate groups, but the vague structural details have only been deduced from powder X-ray diffraction (XRD) data complemented by IR, Raman, and ^{119}Sn Mössbauer measurements. The solids were prepared from a stoichiometric mixture of $SnCl_4 \cdot 5H_2O$ and phosphoric acid, which was calcined and finally fired at temperatures up to 900 °C. The products are insoluble in water.[41] No access to the compound from solution has been reported.

Calculations of the structure of the dianion $[Sn(P_2O_7)]^{2-}$ as a gas phase species (i.e., without a polar environment) are unrealistic, because of the high negative charge, which labilizes the electrons in the HOMOs. Therefore, the dianion was placed in a standard model environment representing the state in an aqueous solution with dipolar water molecules.

With this periphery, the dianion $[Sn(P_2O_7)]^{2-}$ was calculated, allowing a free refinement without symmetry restraints. The resulting model clearly approached a structure of C_{2v} symmetry with four of the six O atoms bonded to the Sn atom in the form of a rectangle capped by the Sn atom (Figure 5a). Another refinement, restrained to C_{2v} symmetry, gave the same result with only marginal differences in the bond lengths and angles. As expected, the terminal P═O bonds are significantly shorter than the P−O bonds contacting the Sn atom (1.49 vs 1.55 Å), with all O−P−O/O−P═O angles near the tetrahedral standard. The P−O−P bridge has the longest P−O bonds (1.66 Å) and an angle of 123.35°. The four equivalent Sn−O contacts are 2.30 Å long. Note that the pyrophosphate unit has the eclipsed conformation A.

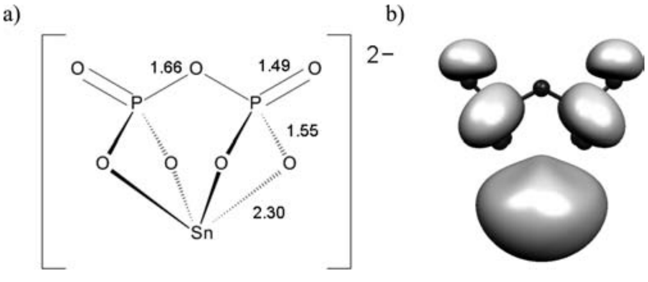

Figure 5. (a) Calculated structure of the $[SnP_2O_7]^{2-}$ dianion in C_{2v} symmetry (bond lengths given in Å). (b) HOMO-2 of $[SnP_2O_7]^{2-}$.

A comparison with the data compiled for the crystal structure of β-$Sn_2P_2O_7$[17] shows that therein all bonds are significantly shorter, because of the close packing of dications and tetraanions. Through this packing, each P_2O_7 unit is attached to several Sn centers, making coordinated P−O and "terminal" P═O bonds indistinguishable (1.504−1.527 Å). The difference is only obvious for the P−O−P bridges (P−O 1.594−1.608 Å, 131.5° and 137.1° for two independent anions). It should be noted that distances calculated for an isolated species by DFT methods can be taken as generally overestimated, while those determined by XRD are to be taken as underestimated.

In the dianion, the Sn atom is in a distorted square pyramidal SnO_4 coordination with the four O atoms at the rectangular base and the lone pair of electrons at the apex (Figure 5b). This is a rare coordination environment in tin(II) phosphate chemistry, where trigonal pyramidal SnO_3 coordination prevails,[17] but another, more strongly deformed pyramidal SnO_4 coordination with two shorter (2.209 Å) and two longer Sn−O distances (2.466 Å) has been observed in crystals of $Sn(H_2PO_4)_2$. This configuration is already approaching a trigonal bipyramidal array with the lone pair of electrons in an equatorial position.[39]

It is very likely that the symmetrical tetracoordination of the tin atom in the $[Sn(P_2O_7)]^{2-}$ dianion is enforced by the high negative charge of the $[P_2O_7]^{4-}$ tetraanion exerting strong Coulomb interaction with the Sn^{2+} dication.

Therefore, the neutral molecule $[Sn(P_2O_7H_2)]$ was chosen as a suitable model system with reduced Coulomb attraction, and also as a model for the species present in neutral or acidic aqueous solutions of tin(II) pyrophosphates. This molecule was also calculated in a model polar environment simulating the solution state. For this species, the protonated structural alternatives derived from C and D are valid, where each of the two phosphate units of the pyrophosphate ligand receives one proton for neutralization. Double protonation at only one of the two phosphate units was excluded.

The result presented in Figure 6a shows the dihydrogen pyrophosphate dianion in a staggered conformation (B) and the Sn atom in a trigonal pyramidal coordination mode. The coordinated oxygen atoms show P−O bond lengths of 1.52 (2×) and 1.53 Å and Sn−O bond lengths of 2.14 Å (single coordination) and 2.26/2.27 Å (chelating coordination). The

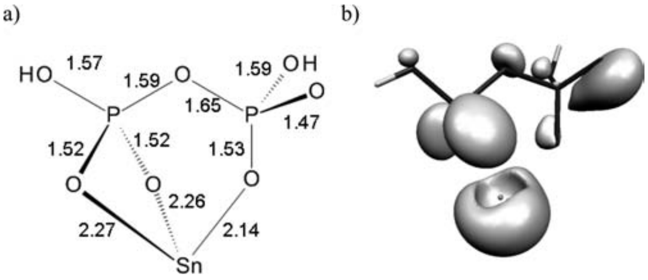

Figure 6. (a) Calculated structure of the $SnP_2O_7H_2$ molecule (bond lengths are given in Å). (b) HOMO-3 of $SnP_2O_7H_2$.

single P═O distance is 2.47 Å long, and the P−OH distances are 1.57 and 1.59 Å. The O−P−O bridge is unsymmetrical with P−O distances 1.59 and 1.65 Å long. The positioning of the lone pair of electrons at the Sn atom is illustrated in Figure 6b.

The calculations for $[Sn(P_2O_7H)]^-$ with the single proton attached to one or the other of the two phosphate units gave very similar results with the $[HP_2O_7]^{3-}$ unit in a staggered conformation and the Sn atom tricoordinated (see Figures 7a and 7b). The P−O and Sn−O distances differ very little from those in the diprotonated complex (Figure 6a) and are not discussed here any further. The position of the proton has only a minor influence on the details of the structure.

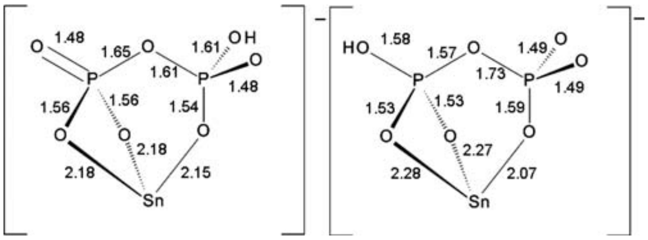

Figure 7. Calculated structure of two tautomeric forms of $[SnP_2O_7H]^-$ (bond lengths are given in Å). The two structures are very similar in energy.

The Dinuclear Complexes of 1:1 Stoichiometry. In all previous studies, the formation of polynuclear aggregates of the mononuclear unit $[Sn(P_2O_7)]^{2-}$ has not been considered. However, species such as the dinuclear anion $[Sn_2(P_2O_7)_2]^{4-}$ cannot be excluded in particular for concentrated solutions. Therefore, cyclic dimers were calculated with no symmetry restraints and with imposed C_2 symmetry. The results are very similar and afforded a common overall energy minimum. The structural details and bond lengths are shown in Figure 8.

The two Sn atoms are in a rhombic pyramidal coordination (η^4 SnO_4) with Sn−O bond lengths of 2.17 and 2.38 Å. The two Sn atoms are in transannular positions with a distance of 6.30 Å. As compared to the 6-membered ring in the mononuclear anion, the 12-membered ring of the dinuclear anion must have a high degree of conformational flexibility in solution at room temperature, which should also allow for a high interconversion rate between the two aggregates. It should be noted that the monomer has a high dipole moment, while in the dimer the centers of the positive and negative charges are coinciding, which favors the dimerization. However, experimental and calculated IR details clearly favor the monomer as the most abundant species in solution. Mass spectral and conductivity studies of the aqueous solutions may lead to unrealistic conclusions, because of the high negative charge of the complex anions and the presence of their partially protonated forms.[25−27]

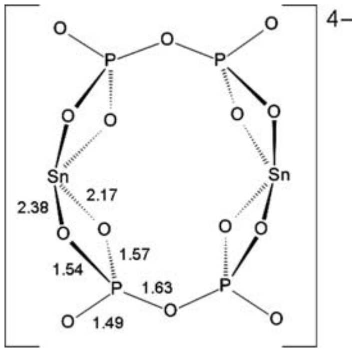

Figure 8. Calculated structure of the C_2-symmetric dinuclear complex anion $[Sn_2(P_2O_7)_2]^{4-}$ (bond lengths are given in Å). The C_2 axis runs through the two Sn atoms.

The Mononuclear Complex of 1:2 Stoichiometry. Calculations of the mononuclear complex $[Sn(P_2O_7)_2]^{6-}$ have shown that a bis-1,5-chelated anion with pyramidal (SnO_4) geometry of C_2 symmetry is lowest in energy (Figure 9a). The Sn−O distances differ significantly (2 × 2.17 Å and 2 × 2.34 Å) and show a marked deviation from an ideal square pyramidal geometry. By contrast, calculations for models with bis-1,3-chelation (Figure 9b), have shown that this configuration is higher in energy. For this, structures with C_2 symmetry as shown in Figure 9b have been considered, together with the corresponding anions with a center of inversion (one pyrophosphate unit rotated into the opposite direction).

In summary, the results of the calculations suggest that the complexation of the Sn^{2+} cation by one pyrophosphate anion depends strongly on the protonation of the latter and thus on the pH of the solution. At high pH (>7), the tetracoordination by oxygen atoms prevails, while monoprotonation and diprotonation lead to tricoordination. The energy differences between these ground states are rather small and certainly allow a high degree of structural fluxionality, in agreement with assumptions made on the basis of NMR investigations. Because of the uncertainties in the numerical data, with small differences between large contributions, a detailed discussion of the ground state energies may not lead to meaningful conclusions at this stage.

■ CONCLUSIONS

In the present work, an attempt was made to identify the components of the complex equilibria established by complexation of tin(II) by pyrophosphate in aqueous medium. These solutions are used extensively for electroplating of tin and tin alloys on a variety of metallic and other conductive substrates. The 1:1 complexes formed at various pH ranges at room temperature have been identified by solubility observations, IR and NMR spectroscopic investigations and DFT calculations. At pH 8 an unprotonated pyrophosphate anion is attached to the tin(II) center, with a structure predicted by theoretical calculations to be square pyramidal with C_{2v} symmetry. For higher molar ratios (P_2O_7):(Sn) > 1:1, IR and NMR spectral data suggest the formation of 2:3 and 2:1 complexes, which undergo rapid ligand exchange if excess pyrophosphate is present. Upon the addition of acid, partial protonation of the complex anions will occur, including complexes of lower or even no negative charge, such as $[Sn(HP_2O_7)]^-$ or [Sn-

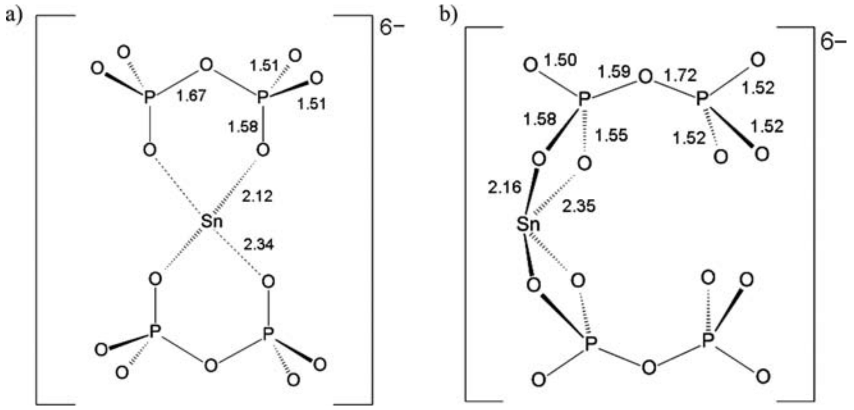

Figure 9. (a, b) Calculated structures of the complex anion $[Sn(P_2O_7)_2]^{6-}$ (bond lengths given in Å).

$(H_2P_2O_7)]^0$. In these complexes, the metal atom is expected to be only tricoordinated. From the NMR observations, it appears that $Sn^{(IV)}$ as present in K_2SnO_3 or its hydrated form $K_2Sn(OH)_6$ does not form a pyrophosphate complex in aqueous solution near pH 7 and at room temperature. There is also no interference of sulfite.

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Notes

The authors declare no competing financial interest.

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