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Article

Coordination Nature of 4-Mercaptoaniline to Sn(II) Ion: Formation of a One Dimensional Coordination Polymer and Its Decomposition to a Mono Nuclear Sn(IV) Complex

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Abstract: The coordination of the bifunctional ligand 4-mercaptoaniline with aqueous tin(II) metal ion was studied. A coordination polymer was synthesized when an aqueous solution of SnCl₂ was treated with 4-MA. The crystalline material is stable under atmospheric conditions retaining its oxidation state. However, when submerged in a solution saturated with oxygen, the compound oxidizes to a mononuclear tin(IV) complex. Both the compounds were characterized by single crystal X-ray diffraction studies. Although the structure of the tin(IV) complex was previously reported, crystal structure of this compound was redetermined.

Keywords: tin(II); tin(IV); coordination complex; polymer; metal sulfide; 4-Aminothiophenol; mercaptoaniline; aqueous; synthesize; redox

1. Introduction

Recently, we have investigated various separation techniques in order to isolate metal ions from aqueous waste streams. Methods that can yield recyclable treated material are of interest. One such technique involves the use of 4-mercaptoaniline (4-MA) as a precipitant. The precipitated material from this method can be recycled as metal sulfides.

4-MA is commonly used to conduct surface enhanced Raman spectroscopy (SERS) [1], as the metal-binding terminal end of conductive nanowires [2], and to synthesize gold nanoparticles [3]. Sulfur serves as a “soft” ligand (base) with affinity for “soft” metals (acids), according to hard soft acid base (HSAB) theory. Sulfur can coordinate both in terminal and bridging fashion to a metal center [4]. We are exploring the feasibility of using 4-MA as a precipitating agent to treat aqueous metal ion waste streams. 4-MA is known to exist as a zwitterion in both solid and pure liquid forms [5].

Tin is a group 14 metal with common oxidation states of +2 and +4. It finds many applications in fuel cells [6], batteries [7] and photovoltaics [8] to chemical sensors [9], semiconducting nanowires [10], and window coatings [11]. Many types of catalysis utilizing tin species have been reported [12], including hydrogenations [13], cross-coupling reactions [14], oxidation of carbon monoxide [15] and ethanol [16] and the reduction of carbon dioxide [17] and NO_x [18]. Tin oxides [19] and tin sulfides [20] are well known and characterized for their structures and activities.

Previously Eichhöfer and co-workers reported the synthesis of a one dimensional polymer compound (2) that was formed by one tin(II) and two thiophenol units per monomer [21]. One thiolate bridges the tin backbone while the other “sticks out” from the chain. This synthesis was carried out in dimethyl ether (DME) and PhSSiMe_3 was used as a source of thiophenol moiety. Our studies on separation techniques demand execution in water, hence we have studied the coordination of tin(II) in aqueous medium with ethanolic 4-MA under ambient conditions. We also examined the coordination of tin(II) in nonaqueous solution under ambient conditions. Studies with tin(IV) and thiophenols have also been carried out in nonaqueous medium at elevated temperature, using the disulfide form of MA [22,23]. Complexes of inorganic or organic mercury and 4-MA have been synthesized, yielding polymeric substances [24].

We studied the application of 4-MA as a mercury(II) precipitant using cold vapor atomic absorption spectroscopy (CVAAS). We suspected that there could be some chemical interference due to coordination of excess 4-MA (from mercury treatment) to tin(II) used in CVAAS. The method for mercury analysis using this technique requires the use of tin(II) ion to reduce mercury(II) to mercury(0) followed by atomic absorption spectroscopy. Since tin(II) is similarly “soft” as mercury(II) we anticipated that it was a good candidate for complexation with 4-MA. We were able to remove over 98% of tin(IV) from a 6000 ppm synthetic waste stream. In this article we report a study on the coordination nature of tin(II) chloride with 4-MA in ambient conditions.

2. Results and Discussion

The tin solution used in CVAAS is acidic and hence, we treated SnCl_2 in 10% v/v HCl with ethanolic 4-MA solution. This yielded no precipitation. However, when an acid-free solution of SnCl_2 was treated with ethanolic 4-MA, precipitation did occur. We were also interested in learning if tin(II) can be oxidized to tin(IV) when coordinating with 4-MA and thereby making tin(II) unavailable for the reduction of mercury(II).

When colorless aqueous solution of SnCl_2 is treated with ethanolic 4-MA, solution color changes to yellow. If this solution is shaken, microcrystalline material begins to form. Diffraction quality crystals can be formed by taking the un-disturbed solution and storing it overnight in the fridge. It must be noted that in every synthesis of tin(II) complex attempted, both tin(II) and tin(IV) complexes formed. Single

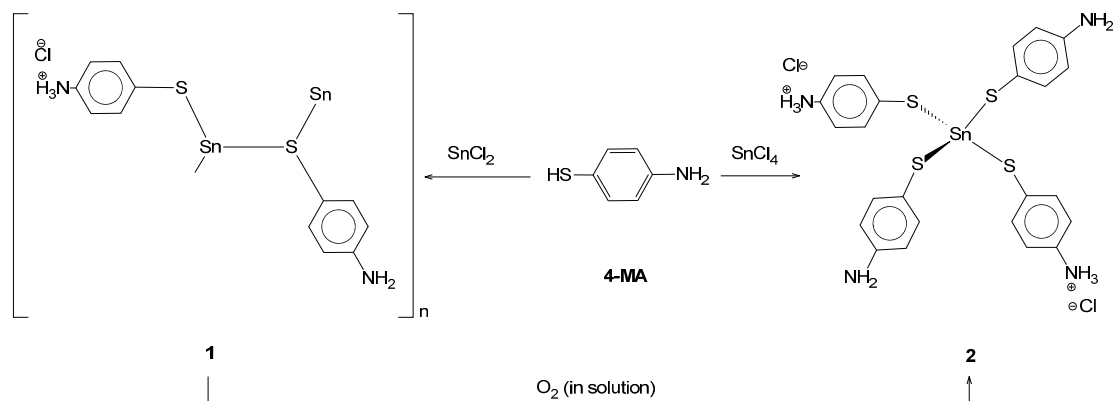
crystal X-ray diffraction analysis of such crystals revealed the polymeric structure of compound **1** and tetrahedral mononuclear compound **2**. Table 1 contains the crystallographic data of compounds **1** and **2**.

Table 1. Crystallographic data for compound **1** and **2**.

Compound	1	2
Empirical formula	C ₁₂ H ₁₅ ClN ₂ O ₂ Sn	C ₂₄ H ₂₆ Cl ₂ N ₄ S ₄ Sn
Formula weight	421.52 g mol ⁻¹	688.32 g mol ⁻¹
Temperature	273(2) K	273(2) K
Wavelength	0.71075 Å	0.71075 Å
Crystal system	Monoclinic	Monoclinic
Space group	P 2(1)/c	C 2/c
Unit cell dimensions	a = 17.328(14) Å; α = 90° b = 12.160(9) Å; β = 95.404(1)° c = 7.253(6) Å; γ = 90°	a = 31.03(2) Å; α = 90° b = 7.961(6) Å; β = 97.377(9)° c = 11.718(9) Å; γ = 90°
Volume	1521(2) Å ³	2871(4) Å ³
Z	4	4
Density (calculated)	1.840 Mg/m ³	1.593 Mg/m ³
Absorption coefficient	2.122 mm ⁻¹	1.388 mm ⁻¹
F(000)	832	1384
Crystal size	0.29 × 0.16 × 0.03 mm ³	0.23 × 0.15 × 0.14 mm ³
Theta range for data collection	2.049 to 27.418°	2.643 to 27.482°
Index ranges	-20 ≤ h ≤ 22, -15 ≤ k ≤ 15, -9 ≤ l ≤ 9	-40 ≤ h ≤ 38, -10 ≤ k ≤ 10, -15 ≤ l ≤ 15
Reflections collected	8800	11610
Independent reflections	3443 [R(int) = 0.0726]	3281 [R(int) = 0.0427]
Completeness to theta = 27.418°	98.9%	99.9%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	1.00 and 0.870	1.000 and 0.829
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data/restraints/parameters	3443/12/200	3281/0/211
Goodness-of-fit on F ²	1.064	1.074
Final R indices [I > 2σ(I)]	R1 = 0.0536, wR2 = 0.1091	R1 = 0.0321, wR2 = 0.0798
R indices (all data)	R1 = 0.0974, wR2 = 0.1091	R1 = 0.0373, wR2 = 0.0832
Extinction coefficient	n/a	n/a
Largest diff. peak and hole	0.806 and -1.030 e.Å ⁻³	0.465 and -0.838 e.Å ⁻³

The 1-D coordination polymer of tin and 4-MA can also be synthesized by layering ethanolic 4-MA on top of anhydrous SnCl₂. This yields better crystals than the aqueous route. Compound **1** can be converted to complex **2** by dissolving complex **1** in acetone and bubbling air through the solution overnight (Scheme 1). Whether simple stoichiometric variation could lead to the formation of **2** was also investigated. When anhydrous SnCl₂ is treated by layering ethanolic 4-MA in a 4:1 ligand to metal ratio and the material was allowed to crystallize overnight in the fridge, both compounds **1** and **2** form. Compound **2** can also be synthesized by treating SnCl₄·5H₂O in the same manner with 4-MA (Scheme 1).

Scheme 1. Synthesis of one dimensional coordination polymer (followed by its subsequent decomposition to the tin(IV) complex).



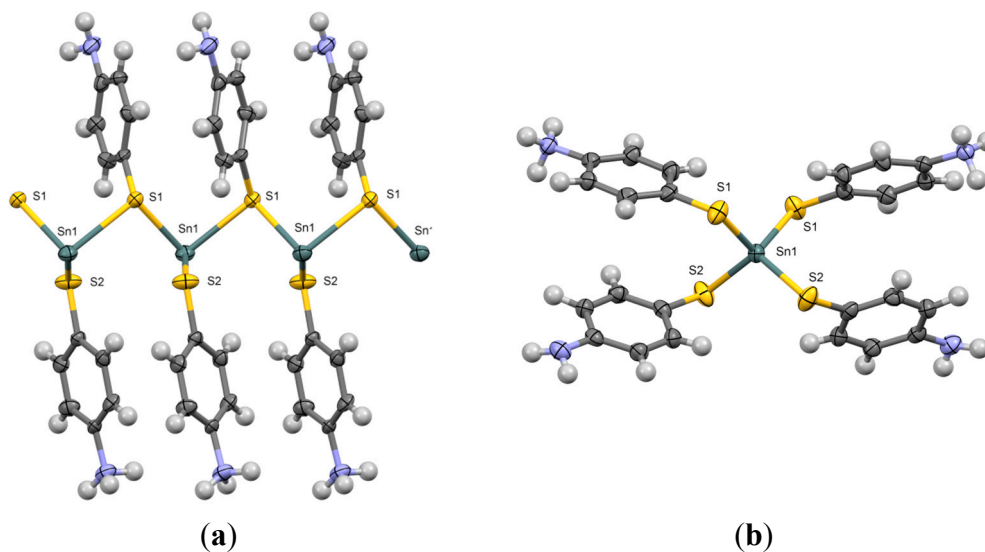
For the 1-D polymeric tin(II) complex we report trigonal pyramidal geometry around the tin(II) center. The polymer backbone of the tin(II) complex is composed of alternating tin-sulfur bonds in a “zipper” shape (when viewed along the *b* axis). The bonds between the tin center and bridging sulfur are two distinct lengths; the “primary” μ sulfur-tin bond length is 2.594(3) Å and the “secondary” μ sulfur-tin bond length is 2.702(2) Å (Table 2). These bridging ligands each have a terminal amine group. Each tin(II) center has an additional terminal 4-MA ligand. Unlike the bridging ligands, the terminal amine groups of the terminal ligands are protonated and paired with chloride counter anions. The distance between tin and sulfur of two neighboring strands is 3.778 Å. As mentioned, Eichhöfer’s group previously synthesized a tin-containing 1-D coordination polymer which utilized thiophenol as the bridge [21] between two neighboring tin. They also report distorted trigonal pyramidal geometry around tin. The S1–Sn1 bond length in this compound was 2.518(2) Å, the S2–Sn1 bond length was 2.577(2) Å and the S2’–Sn1 bond length was 2.731(2) Å. The reported S1–Sn1–S2 angle is 77.16(6)°, the S1–Sn1–S2’ angle is 92.68(6)°, and the S2–Sn1–S2’ angle is 87.58(5)°.

Table 2. Selected bond distance and bond angles for compounds **1** and **2**.

1		2	
Bond lengths, Å			
Sn(1)–S(1)	2.563(3)	Sn(1)–S(1)	2.399(1)
Sn(1)–S(2)	2.702(2)	Sn(1)–S(2)	2.395(1)
Bond angles, °			
S(1)–Sn(1)–S(2)	92.28(6)	S(2)–Sn(1)–S(1)	101.73(5)

Wang and co-workers have previously synthesized and characterized compound **2** [Sn(4-SC₆H₄NH₂)₂(4-SC₆H₄NH₃)₂Cl₂] [25]. Complex **2** is a mono-nuclear compound with tetrahedral coordination around tin. Two 4-MA moieties contain terminal amine groups and two of them contain terminal ammonium groups with associated chloride counter ions. The Sn–S2 bond length (for each amine-terminal ligand) is 2.3955(12) Å; the Sn–S1 length (for each ammonium-terminal ligand) is 2.3989(13) Å. The sulfur-tin-sulfur angle in the asymmetric unit is 101.73(5)°. Figure 1a,b are the ORTEP diagrams of compound **1** and compound **2**, respectively.

Figure 1. (a) ORTEP diagram of Sn (II) containing one dimensional polymer (1) and (b) ORTEP diagram of Sn(IV) containing mononuclear complex (2).



3. Experimental Section

3.1. General

Both complex **1** and complex **2** were synthesized under ambient conditions. Reagents were obtained commercially and used without further purification. XRD data were collected on a Rigaku (The Woodlands, TX, USA) XtaLAB mini. Infrared spectra were recorded on a Thermo Scientific Nicolet (Madison, WI, USA) iS10 with smart iTR accessory.

3.2. Synthesis of $[\{Sn(\mu\text{-}4\text{-}C_6H_4NH_3S)(4\text{-}C_6H_4NH_2S)\}Cl \cdot H_2O]_n$

The tin(II) complex (**1**) was prepared by two routes.

Route 1: 0.0759 g (0.4 mmol) $SnCl_2$ was dissolved in 1 mL of deionized water to which 0.1056 g (0.8 mmol) 4-MA dissolved in 1.5 mL of ethanol was added. The two components were mixed thoroughly and small yellow crystals quickly formed. The contents were dried *in vacuo* then washed with diethyl ether and washed with acetone until colorless wash was obtained (7×15 mL). Some of compound **1** will be converted to compound **2** during workup. However, in a separate experiment we have determined that compound **2** has very limited solubility in acetone, compared to compound **1**. In order to selectively isolate compound **3** from potential mixture of compound **1** and compound **2**, the mixture was washed with acetone. All of the acetone washes were combined and solvent was removed under reduced pressure. Dry solid yielded 33.9% complex **1**.

Route 2: 0.0844 g (0.4 mmol) of $SnCl_2$ was added to a round bottom flask along with 0.1203 g (1 mmol) 4-MA dissolved in 15 mL ethanol and mixed vigorously. The mixture was dried under vacuum then washed with diethyl ether to remove excess 4-MA. The remaining mixture was washed with acetone to isolate tin(II) complex. This acetone fraction was then dried under vacuum. Dry solid yielded 40.3% complex **1**; IR (cm^{-1}) 3333, 3247, 3158, 3047, 2921, 2851, 2745, 2585.

3.3. Synthesis of $[Sn(4-SC_6H_4NH_2)_2(4-SC_6H_4NH_3)_2Cl_2]$

The tin(IV) complex (**2**) was prepared by two routes as well.

Route 1: A solution was prepared by dissolving 0.1003 g (0.2 mmol) of compound **1** in 10 mL of acetone. A gentle stream of air was bubbled through the solution for 12 h. This method resulted in an impure product containing compounds **1** and **2**.

Route 2: 0.0509 g $SnCl_4 \cdot 5H_2O$ (0.1 mmol) was combined with 0.0736 g (0.6 mmol) ethanolic 4-MA in a vial. A yellow solution forms and, upon further disturbance, small yellow crystals precipitate from solution. This mixture was dried under vacuum then washed with water (3×1 mL), followed by further washing with acetone and diethyl ether. The dry solid yielded 64.2% of compound **2**. IR (cm^{-1}) 3332, 3245, 3158, 3047, 2825, 2744, 2585.

3.4. X-ray Crystallography

A greenish yellow platelet crystal of compound **1** having dimensions of $0.29 \times 0.16 \times 0.03$ mm and a yellow prism crystal of compound **2** having dimensions of $0.23 \times 0.15 \times 0.14$ mm were attached to a MiTeGen (Ithaca, NY, USA) loop by Apiezon (Manchester, UK) grease and mounted on a Rigaku Mercury (The Woodlands, TX, USA) 375R/M CCD (XtaLAB mini) diffractometer using graphite monochromated Mo- $K\alpha$ radiation (0.71075 \AA) at 273 K. The crystals were positioned at 49.50 mm from the CCD system. Data were collected and processed using Crystal Clear (Rigaku, The Woodlands, TX, USA). The data were corrected for Lorentz and polarization effects. The structures of both the complexes were solved using direct methods with SHELXS97 program [26]. The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in calculated positions (riding model) with U_{iso} set at 1.2 times the U_{eq} of the parent atom. The structures were refined on F^2 by full-matrix least-squares using SHELXL97 [26]. Crystallographic data for compounds **1** and **2** have been deposited with the Cambridge Crystallographic Data Centre (CCDC). The CCDC deposition number for compound **1** is 1009828. The CCDC deposition number for compound **2** is 1027160. This data can be obtained free of charge from www.ccdc.cam.ac.uk/data_request/cif.

4. Conclusions

A new one dimensional coordination polymer of tin(II) and 4-mercaptoaniline was synthesized by a simple procedure under ambient conditions. The compound was studied for structural insight. The tin center has a distorted trigonal pyramidal geometry, where one of the ligands coordinates in a terminal fashion, whereas, the other two ligands are bridging the tin centers in μ^2 fashion, giving rise to one dimensional polymeric structure. The terminal ligand had the amine group protonated with a chloride counter anion. Upon treatment with oxygen this polymer oxidized to a mononuclear tin(IV) complex. The tin center for this complex has a tetrahedral geometry with two of the four ligands having protonated amine groups with chloride counter anions.

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Author Contributions

Both authors contributed to all the sections of this article.

Conflicts of Interest

The authors declare no conflict of interest.

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