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Complexation of tin with amide ligands: two cases of mixed oxidation state tin complexes

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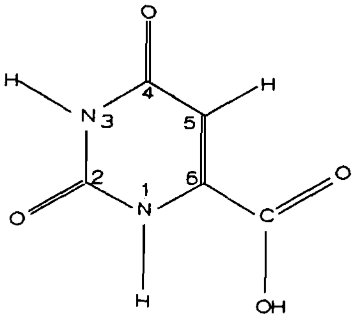
Abstract

The reaction of $SnCl_2$ with the sodium salts of orotic and 2-thioorotic acids under aerobic conditions leads to the formation of compounds with empirical formulae $Sn(H_2or)\cdot 0.5H_2O$ and $Sn(H_2thor)_3$, where H_3or = orotic acid and H_3thor = 2-thioorotic acid. Variable temperature ^{119m}Sn Mössbauer spectroscopy shows that these compounds contain tin in both the II and IV oxidation states. The Mössbauer data taken together with the vibrational and ^1H NMR data lead to the conclusion that the two complexes are best formulated as $[Sn_2^{II}Sn_2^{IV}L_{12}]_n$, where $L^- = H_2or^-$ or H_2thor^-. The central cluster of two Sn(II) and two Sn(IV) atoms is proposed to be held together by eight bidentate bridging carboxylate groups, each of which bridges one Sn(II) and one Sn(IV) atom, while the remaining four ligands appear to form links among the clusters via bridging carboxylate groups.

Introduction

It is becoming increasingly apparent that the coordination chemistry of tin has a great importance in a wide variety of chemical [1], technological [2], environmental [3] and biological [4] problems. A survey of the literature on tin complexes reveals that ligands involving amide groups as potential donor sites have received little attention [5] so far. We are currently seeking to develop the area of tin(II)–, tin(IV)–, and organotin(IV)–amide interactions, as part of our research programme [6, 7] that is directed towards the study of the complexation of tin species with biological ligands as well as the elucidation of the pharmacological properties and structure–activity relationships of the most relevant products. This investigation has been stimulated by the anti-tumor activity of a few inorganic tin(IV) and of many organotin(IV) complexes [4]; a biological activity is also considered possible for tin(II) complexes with two ligands in *cis* equatorial positions [8]. We herein report on the reaction of $SnCl_2$ with two amide-/thioamide- and carboxylate-containing ligands, *i.e.* orotic acid (I, H_3or) and 2-thioorotic acid (II, H_3thor), which leads to the remarkable mixed-valence complexes with empirical formulae $Sn(H_2or)_3\cdot 0.5H_2O$ and $Sn(H_2thor)_3$.



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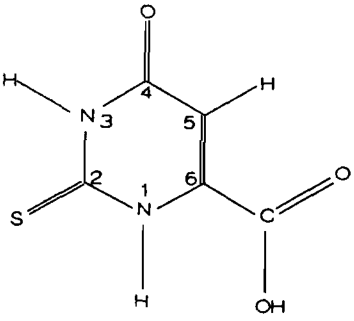

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Experimental

All manipulations were carried out under aerobic conditions using materials as received.

For the preparation of $Sn(H_2or)_3 \cdot 0.5H_2O$ (**1**), a solution of $SnCl_2 \cdot 2H_2O$ (0.63 g, 2.8 mmol) in ethanol (2 ml) was added to a stirred solution of NaH_2or (1.0 g, 5.6 mmol) in hot water (75 ml). Precipitation of a microcrystalline pale yellow solid began almost immediately. Stirring was continued for a further 15 min at 60–70 °C, the precipitate was collected by filtration, washed with small amounts of H_2O, EtOH and Et_2O, and dried *in vacuo* over silica gel; yield 1.02 g (92% based on the ligand). *Anal.* Calc. for $C_{15}H_{10}N_6O_{12.5}Sn$: C, 30.38; H, 1.70; N, 14.18; Sn, 20.02. Found: C, 30.47; H, 1.81; N, 14.04; Sn, 19.47%. IR (KBr, cm^{-1}): $\nu(O\text{–}H)_{H_2O}$ at 3420(mb), ν(N–H) at 3155(sb) and 3101(s), ν(C=O) at 1720(sb) and 1665(s), ν_{as}(COO) at 1616(s), ν_s(COO) at 1435(m), δ(NH) at 1494(m) and 1382(s). Raman (solid state): ν(N–H) at 3160(vw) and 3108(w), ν(C=O) at 1717(m) and 1655(m), ν_{as}(COO) at 1614(m), ν_s(COO) at 1433(s) cm^{-1}.

^1H NMR (d_6-DMSO): δ 11.72 (sb, N_1H), 11.23 (sb, N_3H), 6.25 (s, C_5H), and 3.41 (sb, H_2O) ppm (s = singlet, b = broad).

Λ_M (DMSO, 10^{-3} M, 25 °C) = 4 S cm^2 mol^{-1}.

For the preparation of $Sn(H_2thor)_3$ (**2**), 2.9 ml of an aqueous 1 M NaOH solution were slowly added to a stirred slurry of H_3thor (0.5 g, 2.9 mmol) in EtOH (5 ml) and H_2O (25 ml). To the clear solution so obtained 0.33 g (1.45 mmol) of $SnCl_2 \cdot 2H_2O$ dissolved in 2 ml of EtOH was added and a yellow powder was obtained. The reaction mixture was stirred for a few more minutes; the precipitate was finally collected by filtration, washed with EtOH and Et_2O, and dried *in vacuo*; yield 0.60 g (98% based on the ligand). *Anal.* Calc. for $C_{15}H_9N_6O_9S_3Sn$: C, 28.50; H, 1.44; N, 13.30; Sn, 18.78. Found: C, 28.73; H, 1.51; N, 13.46; Sn, 18.24 %.

IR (KBr, cm^{-1}): ν(N–H) at 3151(s) and 3099(s), ν(C=O) at 1730(m), ν_{as}(COO) at 1648(vsb), ν_s(COO) at 1408(m), ν(C=S) at 904(m). Raman (solid state): ν(C=O) at 1725(s), ν_{as}(COO) at 1640(mb), ν_s(COO) at 1410(vs), ν(C=S) at 899(m) cm^{-1}.

^1H NMR (d_6-DMSO): δ 12.56 (sb, N_1H), 11.71 (sb, N_3H), and 6.29 (s, C_5H), ppm (s = singlet, b = broad).

Λ_M (DMSO, 10^{-3} M, 25 °C) = 6 S cm^2 mol^{-1}.

Mössbauer effect spectra were obtained on a conventional constant-acceleration spectrometer that utilized a room temperature $Ca^{119m}SnO_3$ source by using a liquid nitrogen cryostat equipped with a variable temperature insert; spectra were recorded at several temperatures between 80 K and room temperature.

Results and discussion

Our studies on the Sn/orotate system chemistry were initiated with the investigation of the reaction between $SnCl_2$ and NaH_2or in water in a 1:2 ratio. The formula of the product and Mössbauer spectroscopy established it as being a mixed-valence compound (*vide infra*). The access to a $Sn^{II}Sn^{IV}$ species from H_2or^- suggested that the reaction system might be capable of extension to other orotate ligands. The same procedure, but with H_2thor^-, was found to successfully yield a completely analogous complex in quantitative yield. The preparation of Sn/thioorotate complexes was particularly desirable over Sn/orotate complexes because H_2thor contains the easily coordinated thioamide unit, allowing the possibility of generating species with a Sn–S bond.

Complexes **1** and **2** are stable in atmospheric conditions, insoluble in chloroform, alcohols, acetone and nitromethane, soluble only in DMF and DMSO. This insolubility is a strong evidence of their polymeric form. Attempts to grow single crystal from DMF or DMSO for X-ray structural studies were unsuccessful. The complexes are non-electrolytes in DMSO. The X-ray powder diffraction patterns are simple and indicate that **1** and **2** represent definite compounds, which are not contaminated with starting materials. The TG/DTG curve of **1** shows a first mass loss between 70 and 105 °C, corresponding to the release of the water content; the low temperature of the water loss shows that it is lattice held. Both complexes decompose without formation of stable intermediates.

The absence of large systematic shifts of ν(N–H), ν(C=O) and ν(C=S) in the vibrational spectra of the complexes, in comparison with the frequencies of these modes in the spectra of NaH_2or and NaH_2thor, implies that there is no interaction between the neutral amide or thioamide groups and tin. In the spectra of both the complexes only one band is attributed to ν_{as}(COO) and to ν_s(COO), in agreement with the existence of one type of carboxylato coordination [9]. For both the complexes $\Delta_{complex} < \Delta_{sodium\ salt\ of\ the\ ligand}$ ($\Delta = \nu_{as}(COO) - \nu_s(COO)$); this suggests that the carboxylate group of H_2or^- and of H_2thor^- is coordinated as a bidentate, bridging or chelate, ligand [9].

The occurrence of the N_1H and N_3H signals at almost the same δ values in the ^1H NMR spectra of **1** and **2** and of the corresponding sodium salts of the ligands indicates the non-involvement of the nitrogen atoms in the coordination. No NMR evidence for keto-enolic tautomeric structures was found.

^{119m}Sn Mössbauer effect data (Table 1 and Fig. 1) clearly establish that compounds **1** and **2** contain tin atoms in both II and IV oxidation states and

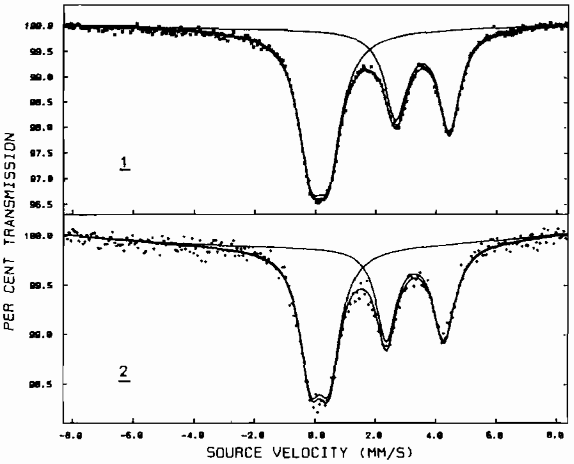

Fig. 1. ^{119m}Sn Mössbauer effect spectra of $Sn(H_2or)_3 \cdot 0.5H_2O$ (1) and $Sn(H_2thor)_3$ (2).

TABLE 1. ^{119}Sn Mössbauer effect spectral parameters[a] for complexes 1 and 2

Compound	δ[b] (mm/s)	ΔE_Q (mm/s)	Γ (mm/s)	A (%)	$\frac{\partial \ln(A_T/A_{80})}{\partial T}$
1 Sn(IV)	0.02	0.65	1.00[c]	58	-2.0×10^{-3}
Sn(II)	3.43	1.77	0.90[d] 0.83[e]	42	-9.5×10^{-3}
2 Sn(IV)	0.04	0.62	0.87[c]	56	-5.6×10^{-3}
Sn(II)	3.20	1.91	0.80[d] 0.87[e]	44	-1.3×10^{-2}

[a]Measured at 80 K. [b]Relative to room temperature $CaSnO_3$. [c]Doublet constrained to be symmetric. [d]Low velocity component. [e]High velocity component.

should be formulated as mixed oxidation state complexes. The spectra present three absorptions that cannot be realistically attributed to three different tin species, all with a nearly cubic structure. A comparison of the spectra with the data reported in the literature allowed an easy attribution of the spectral components to a single tin species. Mössbauer effect data are available only for tin(II) carboxylato complexes that present isomer shift values of ≃3mm/s and quadrupole splittings of ≃1.7 mm/s [10], for $Sn(SbF_6)_2$ [11], $Sn_2(O_3SCF_3)_6$ [10], and Sn(II) / 15-crown-5 derivatives [12] that present an isomer shift of about 4.5 mm/s and a zero quadrupole splitting. The relative areas of the individual absorptions rule out the possibility that these spectra are composed of two quadrupole split doublets with their low velocity components nearly coincident [13]. So the only realistic assignment is that the broad absorption at about 0 mm/s is due to a Sn(IV) species in an O_h or T_d environment, with the other two absorptions being a quadrupole doublet from a Sn(II) species in a much more distorted environment [13, 14].

From an examination of the results in Table 1, it is clear that, while the tin(IV) coordination is virtually identical for the two samples, small differences exist for the tin(II) centers. In fact, sample **1** presents higher isomer shifts and lower quadrupole splittings at all the investigated temperatures. As the other spectroscopic results point out that only carboxylic oxygen atoms are involved in the bonds of the two ligands with the tin(II) ions, the small differences can be explained with slightly different bond angles and distances in the two compounds. Clearly, sample **2** presents the shortest bonds as this causes a higher d electron density on the tin center; this, in turn, increases the shielding of the s electrons from the nucleus and consequently the isomer shift decreases. The very low quadrupole splitting values for the tin(IV) centers are indicative of highly symmetric structures, while the large values for the tin(II) centers points to severely distorted coordination geometries with a probable involvement of the lone pair electrons.

Variable temperature data can offer information on the lattice dynamics and, particularly, on the eventual presence of significant intermolecular association [10, 15]. By plotting the natural logarithm of the resonance area normalized to 80 K against the temperature, straight lines are obtained for the data from about 80 to 170 K for the tin(IV) atoms and to room temperature for the tin(II) atoms. The slope of these lines are reported in Table 1 and are indicative of extensive intermolecular interactions, especially for **1**. This gives a strong support to the polymeric structure proposed in Fig. 2. In both compounds, tin(IV) seems to be much more tightly bonded than tin(II). The slight asymmetry that is apparent for the tin(II) components in the spectra (Fig. 1) may be due to an anisotropy in the recoil-

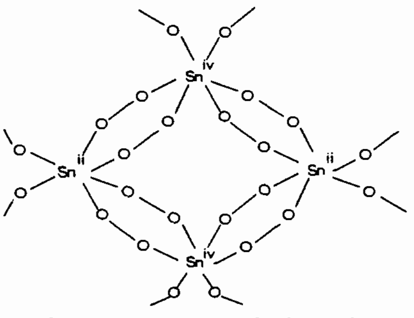

Fig. 2. Proposed structural scheme for **1** and **2**. The symbol O——O represents the carboxylate group of H_2or^- or H_2thor^-.

free fraction [13], but it is also characteristic of asymmetrically bonded tin atoms [14].

Complexes **1** and **2** join only a handful of well characterized mixed-valence tin compounds [11, 14–23], most of which [14–18] contain a carboxylate ligand. The X-ray structures of three mixed-valence tin carboxylate complexes $[Sn_2^{II}Sn_2^{IV}O_2(O_2CC_6H_4NO_2\text{-}o)_8(THF)_2]$ (**3**) [17], $[Sn_2^{II}Sn_2^{IV}O_2(O_2CCF_3)_8]\cdot C_6H_6$ (**4**) [18] and $[Sn_4^{II}Sn^{IV}O_2(O_2CCF_3)_8]$ (**5**) [14] are known. The Mössbauer hyperfine parameters for complexes **3** [14, 17], **4** and related compounds [14] are similar to those of **1** and **2**, indicating that the structures of all these complexes are closely related. Complexes **3** and **4** have very similar structures, being centrosymmetric tetramers of tin atoms, two tin(II) and two tin(IV), held together by two μ_3-oxo bridges and bidentate bridging carboxylate groups. The coordination geometry around Sn(II) in **3** and **4** is pentagonal bipyramidal with the stereochemically active, non-bonding electron pair of the metal ion occupying one of the axial positions, but with one of the equatorial positions vacant in **4**; in both complexes Sn(IV) has a nearly regular octahedral environment.

From the overall study presented above, it is concluded that **1** and **2** have the same polymeric structure, that is most probably based on tetranuclear units (Fig. 2); thus, the complexes are better formulated as $[Sn_2^{II}Sn_2^{IV}L_{12}]_x$, where $L^- = H_2or^-$ or H_2thor^-. The central cluster of two Sn(II) and two Sn(IV) atoms is proposed to be held together by eight bidentate bridging carboxylate groups, each of which bridges a Sn(IV) and a Sn(II). The remaining four ligands appear to form links among the clusters via bridging carboxylate groups. In this way, the Sn(IV) atoms could achieve a nearly regular octahedral coordination, while around the tin(II) atoms a pentagonal bipyramidal arrangement is proposed with the non-bonding electron pair in the seventh coordination site. Molecular models show that such a structure is quite feasible. However, more complicated structures cannot be ruled out. Why partial rather than complete oxidation of tin by atmospheric oxygen has occurred in **1** and **2** is difficult to rationalize.

It is worth noting that on complexation with tin in water–ethanol medium, the sulfur atom of H_2thor^- remains uncoordinated. The exact reason for this is not obvious. However, several suggestions are possible as, for instance, the fact that this interaction cannot be stabilized by the closure of a stable chelate ring, or the 'hard acid' character of Sn(IV) and the 'borderline' character of Sn(II) [24], or the high thermodynamic stability of the mixed-valence compounds with exclusively carboxylate coordination. In conclusion, the use of orotate ligands under aerobic conditions enforces a partial oxidation of tin(II) and yields two members of what promises to be a new family of Sn/carboxylate complexes. Work in progress is providing additional members of this family with different structures and the results will be described in a subsequent report.

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