

Available online at www.sciencedirect.com



POLYHEDRON

Polyhedron 26 (2007) 5365-5369

# Crystal structure and chemical bonding in tin(II) acetate

Varvara S. Stafeeva, Alexander S. Mitiaev, Artem M. Abakumov \*, Alexander A. Tsirlin, Artem M. Makarevich, Evgeny V. Antipov

Department of Chemistry, Moscow State University, 119991 Moscow, Russia

Received 5 July 2007; accepted 3 August 2007 Available online 24 September 2007

#### Abstract

Tin(II) acetate was prepared and its crystal structure was solved from X-ray powder diffraction data. Tin(II) acetate adopts a polymeric structure consisting of infinite  $Sn(CH_3COO)_2$  chains running along the *c*-axis which are packed into groups of four. The acetate groups bridge the Sn atoms along the chains. The Sn atoms are asymmetrically surrounded by four oxygen atoms with two short Sn–O distances (2.170(6), 2.207(6) Å) and two longer ones (2.293(7), 2.372(8) Å). The coordination environment of the Sn atoms is completed up to a strongly distorted trigonal bipyramid SnO<sub>4</sub>E by the sterically active lone electron pair E. The coordination environment of the Sn atoms is virtually identical for Sn(CH<sub>3</sub>COO)<sub>2</sub> in the gaseous and solid phase: the two short Sn–O bonds and the lone electron pair are located in the equatorial plane of the trigonal bipyramid and the two longer Sn–O bonds are directed towards the apical vertexes. Localization of the lone electron pair on Sn(II) was confirmed by electron localization function (ELF) analysis. The polymeric nature of the tin(II) acetate crystal structure was confirmed by a MALDI-TOF experiment. © 2007 Elsevier Ltd. All rights reserved.

Keywords: Tin(II) complex; Acetate; Crystal structure; X-ray powder diffraction; Chemical bonding

## 1. Introduction

Tin(II) acetate  $Sn(CH_3COO)_2$  has been known from 1882 [1]. Since that time the preparation and properties of this compound have been comprehensively characterized [2]. The physical constants, chemical stability, decomposition at various experimental conditions, powder X-ray diffraction pattern and unit cell parameters have been described [2], and infrared spectra have been measured [3]. Due to a low sublimation temperature in dynamic vacuum, the molecular structure of tin(II) acetate was studied in the gas phase using electron diffraction [4]. The structure of the  $Sn(CH_3COO)_2$  molecule is based on a strongly distorted  $SnO_4E$  trigonal bipyramid (Fig. 1), where four vertexes are occupied by oxygen atoms of the acetate groups and the fifth one is formed by the sterically active lone elec-

tron pair. The acetate groups behave as bidentate chelate ligands. The oxygen atoms of each acetate group form one short (2.19 Å) and one long (2.34 Å) bond to the Sn atoms; the apical oxygens of the SnO<sub>4</sub>E trigonal bipyramid correspond to the long Sn–O separations, whereas the short Sn–O bonds are located in the equatorial plane together with the lone electron pair.

Up until now there has been no information on the crystal structure of tin(II) acetate. The structural study of this material using single crystal X-ray diffraction is hampered by experimental difficulties in growing single crystals of suitable quality for the diffraction experiment. An assumption was made based on the low solubility of Sn(CH<sub>3</sub>COO)<sub>2</sub> in non-polar solvents that the structure in the solid phase should be polymeric [2], but there are no conclusive evidences supporting this assumption. Taking into account the importance of tin(II) acetate as a precursor for other tin(II)-based compounds, we have undertaken the determination and refinement of the Sn(CH<sub>3</sub>COO)<sub>2</sub> crystal structure from X-ray powder diffraction data.

<sup>\*</sup> Corresponding author. Tel.: +7 495 939 52 44; fax: +7 495 939 47 88. *E-mail address:* abakumov@icr.chem.msu.ru (A.M. Abakumov).

<sup>0277-5387/\$ -</sup> see front matter @ 2007 Elsevier Ltd. All rights reserved. doi:10.1016/j.poly.2007.08.010



Fig. 1. Structure of the  $Sn(CH_3COO)_2$  molecule in the gas phase (after Smart et al. [4]). The overall symmetry is  $C_2$  and the molecule is viewed perpendicular to the twofold axis. The bond angles of 90° (solid line) and 121° (dashed line) are marked. The tentative  $SnO_4E$  (E – lone electron pair) trigonal bipyramid is outlined.

## 2. Experimental

The commercially available starting reagents SnO ("Spektrkhim", Russia) and glacial acetic acid (Aldrich) were of analytical grade and were used as received. Elemental analysis (C, H) was performed by the Microanalytical Service of the Centre for Drug Chemistry (Moscow, Russia). IR spectra were recorded on a Perkin–Elmer 1600 FTIR spectrophotometer as Nujol and hexachlorobutadiene mulls between KBr plates in the region 4000–400 cm<sup>-1</sup>. Isothermal dynamic sublimation experiments were run with samples in glass test tubes at a pressure of  $10^{-2}$  Torr.

For the synthesis of Sn(CH<sub>3</sub>COO)<sub>2</sub> · 2CH<sub>3</sub>COOH the procedure described in Ref. [3] was used: a mixture of SnO (3 g, 22,2 mmol) and glacial acetic acid (11 ml, 192.3 mmol) was refluxed under stirring until the SnO was completely dissolved, and after cooling the yellowish product was collected. Sn(CH<sub>3</sub>COO)<sub>2</sub> was formed as a white crystalline sublimate by removal of the acetic acid and sublimation at 150–160 °C and at  $10^{-2}$  Torr. Yield ~90%. Mp 183 °C. *Anal.* Calc. for C<sub>4</sub>H<sub>6</sub>O<sub>4</sub>Sn: C, 20.25; H, 2.53. Found: C, 19.96; H, 2.52%. IR, cm<sup>-1</sup>: 661 v (COO sym. deformation), 930 v (C–C stretch), 1015 v (CH<sub>3</sub> rock), 1334 v (CH<sub>3</sub> deformation), 1395 v (COO sym. stretch), 1530 v (COO asymm. stretch). The melting temperature and IR spectra are in good agreement with the data of Donaldson et al. [3].

In spite of the good visual quality of the obtained transparent colorless needle-like crystals, it was found that every needle is composed of numerous finer needles, so that no single crystal suitable for an X-ray diffraction experiment could be selected. The structure solution was performed from X-ray powder diffraction (XRPD) data. The preliminary investigation and unit cell parameter determination were performed with a Huber G670 Guinier diffractometer (Cu K<sub> $\alpha$ 1</sub>-radiation, curved Ge monochromator, transmission mode, image plate). The TREOR90 program was used for indexing the XRPD pattern [5]. The data for the structure determination and Rietveld refinement were collected with a STADI-P diffractometer (Cu K<sub> $\alpha$ 1</sub>-radiation, curved Ge monochromator, transmission mode, linear PSD). FOX software was used for the structure solution [6]. The JANA2000 program package was used for Rietveld refinement of the crystal structure [7].

The initial experiments with matrix-assisted laser desorption/ionization mass spectroscopy (MALDI-TOF-MS) were performed with an Autoflex II (Bruker Daltonics, Germany) instrument. The spectra were recorded in a positive mode (accelerating voltage 19 kV) with a nitrogen laser (337 nm, impulse duration 1 ns). The typical procedure of sample preparation for MALDI was applied [8]. Absolutely dry THF was used as a solvent and anthracene was used as a matrix.

The chemical bonding in tin(II) acetate was analyzed using the electron localization function (ELF) [9]. The ELF distribution was determined from the results of density functional theory (DFT) calculations. A self-consistent DFT calculation was performed with the TB-LMTO-ASA program [10], and the Barth-Hedin exchange-correlation potential was applied. The ELF distribution was obtained using the intrinsic procedure of the LMTO program. The k mesh contained 64 points within the first Brillouin zone. The geometrical parameters for the calculation were taken from the XRPD structure refinement. The hydrogen atoms of the methyl groups were attached according to the constraints  $d(C-H) = 0.98 \text{ Å}, \ \angle H-C-H = \angle C-C-H = 109.4^{\circ}$ typical for acetates [11]. A random mutual orientation of the  $C(2)H_3$  and  $C(4)H_3$  methyl groups was chosen. We assume that this choice does not influence the basic features of the ELF distribution on the Sn, C and O atoms.

## 3. Results and discussion

## 3.1. Crystal structure determination

The XRPD pattern of tin(II) acetate was indexed on a body-centered orthorhombic unit cell with the cell parameters listed in Table 1. The reflection conditions hkl: h+k+l=2n, 0kl, k,l=2n and h0l, h,l=2n correspond to the space group *Ibam* and its acentric subgroup *Iba2*. The observed unit cell parameters are similar to those reported by Donaldson et al. [2] (a = 14.11(3), b =21.35(4), c = 4.96(1) Å, given in the *bca* setting), although

Table 1

Crystallographic information and selected parameters from Rietveld refinement for  $Sn(CH_3COO)_2$ 

Formula	Sn(CH <sub>3</sub> COO) <sub>2</sub>
Space group	Iba2
a (Å)	13.9859(4)
$b(\mathbf{A})$	21.1870(6)
c (Å)	4.5400(1)
$V(\text{\AA}^3)$	1345.28(6)
Ζ	8
$D_{\rm calc} ({\rm g}{\rm cm}^{-3})$	2.338
Radiation	$\operatorname{Cu} \mathbf{K}_{\alpha 1},  \lambda = 1.5406  \mathrm{\AA}$
$2\theta$ Range, step (°)	5-80, 0.01
Number of reflections	243
Number of refined crystallographic parameters	12
Preferred orientation parameter and axis	0.790(2), [001]
$R_{\rm I}, R_{\rm P}, R_{\rm wP}$	0.045, 0.037, 0.050

the latter are substantially larger (see Table 1 for comparison). Moreover, weak reflections violating the body-centering were observed on the XRPD pattern of tin(II) acetate by Donaldson et al. Careful inspection of the XRPD pattern of the tin(II) acetate prepared in the present work revealed that such forbidden reflections are definitely absent. The reason for this discrepancy is not completely clear.

Because structure solution from XRPD data is not a trivial matter, the applied procedure is explained in detail. The search for the initial structure model was performed using a Monte-Carlo based global optimization [6]. It provided the exact positions of the Sn atoms, whereas the positions of the acetate groups could not be unambiguously determined. The acetate groups were localized using a Rietveld refinement of the crystal structure. One can expect that the reliable determination of the atomic coordinates of such light scatterers as C and O will be hampered by the significant impact of the heavy scattering Sn atoms. In order to overcome this difficulty, the rigid body approximation was used to define the acetate group as a scattering unit. The geometry of the acetate group was assumed to be identical to the one determined for the structure of the  $Sn(CH_3COO)_2$  molecule in the gas phase (d(C-C) = 1.51 Å, d(C-O) = 1.26 Å,  $\angle O-C-O = 122^{\circ})$  [4]. The hydrogen atoms were not taken into account. The positions of the acetate groups in the unit cell were defined by the coordinates of the C atom of the carboxyl groups and the three rotation angles. Thus six positional parameters were used for each acetate group instead of the 12 parameters in the atomic approximation.

Taking into account the assumption about a possible polymeric structure of the tin(II) acetate, the acetate groups were initially located at positions bridging the Sn atoms by the oxygen atoms of their carboxyl groups into infinite chains running along the *c*-axis. In such an initial model, the  $m_c$  plane of the *Ibam* space group becomes a mirror plane of the acetate groups. However, the refinement in the centrosymmetric Ibam space group resulted in unacceptably high reliability factors ( $R_{\rm I} = 0.128$ ,  $R_{\rm P} = 0.128$ ,  $R_{\rm wP} = 0.219$ ) and large atomic displacement parameters (ADPs) for the atoms of the acetate groups. A significant improvement was achieved by a transformation of the initial model into the *Iba2* space group. In this group the positions and rotations of the acetate groups are not fixed by symmetry elements. The final refinement was performed with overall ADPs for the carbon and oxygen atoms, whereas the ADP for the Sn atom was refined independently. The preferred orientation along the [001] axis was taken into account using the March-Dollase formula. Reasonably low values of the reliability factors were achieved:  $R9_{\rm I} = 0.045$ ,  $R_{\rm P} = 0.037$ ,  $R_{\rm wP} = 0.050$ . The crystallographic and atomic parameters (as calculated from the rigid body approximation) and the most relevant interatomic distances are given in Tables 1-3. Fig. 2 represents the experimental, calculated and difference XRD profiles.

Table 2			
Atomic coordinates and atomic dis	placement	parameters for S	n(CH <sub>3</sub> COO) <sub>2</sub>

Atom	Position	x/a	y/b	z/c	$U_{\rm iso}({\rm \AA}^2)$
Sn	8 <i>c</i>	0.3749(1)	0.41691(7)	0	0.0375(6)
C(1)	8 <i>c</i>	0.3839(4)	0.3185(3)	0.557(2)	0.027(2)
C(2)	8 <i>c</i>	0.3928(4)	0.2522(3)	0.439(2)	0.027(2)
C(3)	8 <i>c</i>	0.2116(4)	0.4215(2)	0.410(2)	0.027(2)
C(4)	8 <i>c</i>	0.1117(4)	0.4176(2)	0.534(2)	0.027(2)
O(1)	8 <i>c</i>	0.3396(4)	0.3274(3)	0.795(2)	0.027(2)
O(2)	8 <i>c</i>	0.4210(4)	0.3632(3)	0.415(2)	0.027(2)
O(3)	8c	0.2795(4)	0.4364(2)	0.578(2)	0.027(2)
O(4)	8 <i>c</i>	0.2243(4)	0.4096(2)	0.141(2)	0.027(2)

Table 3

Main interatomic distances (Å) and bond angles (°) for Sn(CH<sub>3</sub>COO)<sub>2</sub>

$Sn-O(1)^2$	$2.170(6) \times 1$	$Sn-O(3)^2$	$2.372(8) \times 1$
	[0.563]		[0.326]
$Sn-O(2)^1$	$2.293(7) \times 1$	$Sn-O(3)^1$	$2.972(8) \times 1$
	[0.404]		[0.064]
$Sn-O(2)^2$	$2.961(7) \times 1$	$Sn-O(4)^1$	$2.207(6) \times 1$
	[0.066]		[0.507]
$O(1)^2 - Sn - O(2)^1$	89.0(3)	$O(2)^{1}$ -Sn- $O(3)^{2}$	155.3(2)
$O(1)^2 - Sn - O(3)^2$	71.2(2)	$O(2)^{1}$ -Sn- $O(4)^{1}$	89.7(3)
$O(1)^2 - Sn - O(4)^1$	81.1(2)	$O(3)^2 - Sn - O(4)^1$	73.1(3)

The impact of each Sn–O bond into BVS for the Sn atom is given in square brackets.

Symmetry codes:  $^{1}-x, y, z; ^{2}-x, y, z-1$ .



Fig. 2. Experimental, calculated and difference powder X-ray diffraction profiles for Sn(CH<sub>3</sub>COO)<sub>2</sub>.

#### 3.2. Crystal structure discussion

The crystal structure of tin(II) acetate is shown in Fig. 3. The Sn atoms are arranged in columns oriented along the c-axis and combined in groups of four. The Sn atoms are bridged by two acetate groups along the column, coordinating the Sn atoms by the oxygen atoms of their carboxyl groups. The chains do not directly interact with each other and their packing in groups of four is caused by minimized repulsion between the methyl groups of the acetate anions and the sterical activity of the lone electron pairs (not

Fig. 3. The arrangement of the  $Sn(CH_3COO)_2$  columns in the crystal structure of tin(II) acetate. Hydrogen atoms are not shown.

shown in Fig. 3) on the Sn atoms. The structure of the single Sn(CH<sub>3</sub>COO)<sub>2</sub> chain is shown in Fig. 4. The experimentally observed positions of the acetate groups demonstrate a large deviation from those dictated by the *Ibam* symmetry. This causes the Sn atoms to be asymmetrically surrounded by four oxygen atoms with two short Sn–O distances (d(Sn–O(1)) = 2.170(6) Å, d(Sn–O(4)) = 2.207(6) Å) and two longer ones (d(Sn–O(2)) = 2.293(7) Å, d(Sn– O(3)) = 2.372(8) Å). The bond valence sum (BVS) for the Sn atoms, calculated using the impacts of the four Sn–O distances given above was found to be equal to 1.8, that is noticeably lower than the nominal value. Much closer agreement (BVS = 1.93) with the formal valence of +2 is achieved if two long Sn-O(2) and Sn-O(3) bonds of 2.961(7) and 2.972(8) Å are taken into account (marked by dashed lines in Fig. 4). Thus the acetate groups can be regarded as tridentate bridging ligands with some chelate character.

The ELF isosurface (Fig. 5) for tin(II) acetate reveals two types of attractors. The first one is presented by large lobes near the tin atoms. Such lobes are usually associated with sterically active (or, in other words, localized) lone pairs, although the nature of these pairs (mixed Sn 5s–5p character or mixed Sn 5s–O 2p antibonding state with empty Sn 5p orbitals) is still being discussed [12]. Attractors of the second type are located between the C atoms of the acetate groups and correspond to covalent non-polar C–C bonds. Thus, the ELF distribution confirms the basic features of the chemical bonding in tin(II) acetate: localized lone pairs on the tin atoms and covalent non-polar C–C bonds. The C–O and Sn–O bonds are polar, therefore the corresponding attractors are shifted to the oxygen atoms and are not visible in Fig. 5 due to the lower ELF values.

The first coordination sphere of the Sn atoms should be discussed considering the localization of the lone electron pair. Along with the four oxygen atoms of the acetate groups, the lone electron pair forms a strongly distorted trigonal bipyramid, SnO<sub>4</sub>E (E is the lone electron pair), around the Sn atoms. The lone electron pair and the O(1) and O(4) atoms with the shortest d(Sn-O) = 2.17-2.21 Å distances define the equatorial plane of the trigonal bipyramid. The O(2) and O(3) atoms with longer d(Sn-O = 2.29 - 2.37 Å distances are at the apical vertexes of the trigonal bipyramid. The O-Sn-O bond angles deviate significantly from their nominal values for an ideal trigonal bipyramid. The in-plane O(1)-Sn-O(4) angle is only  $81.1(2)^{\circ}$ , much smaller than its nominal value of  $120^{\circ}$ . The O(2)-Sn-O(3) angle should be straight in a perfect trigonal bipyramid, whereas its has a value of  $155.3(2)^{\circ}$  in the



Fig. 4. Structure of the single  $Sn(CH_3COO)_2$  chain. The bonding of the Sn atoms to the oxygen atoms of the second coordination sphere with d(Sn-O) = 2.96-2.97 Å is shown with dashed lines.



Fig. 5. ELF isosurface ( $\eta = 0.85$ ) for Sn(CH<sub>3</sub>COO)<sub>2</sub>. The [001] projection of the four Sn(CH<sub>3</sub>COO)<sub>2</sub> chains is shown along with the lobes of the lone electron pairs. Hydrogen atoms are not shown.





Fig. 6. MALDI-TOF mass spectrum of  $Sn(CH_3COO)_2$  with anthracene as a matrix.

tin(II) acetate structure. It should be noted that in spite of the significantly different arrangement of the acetate groups around the Sn atoms in the gaseous and the solid phase, the coordination environment of Sn remains virtually the same. For the Sn(CH<sub>3</sub>COO)<sub>2</sub> molecule in the gaseous phase (Fig. 1) the in-plane O–Sn–O bond angle (90°) and the O–Sn–O angle (121°) along the threefold axis of the SnO<sub>4</sub>E trigonal bipyramid are also significantly smaller than their ideal values of 120° and 180° [4]. Such distortion can be accounted for by a strong repulsion between the oxygen atoms and the lone electron pair that causes the oxygen atoms to move away from the position of the lone electron pair with a decrease of the corresponding bond angles.

# 3.3. MALDI-TOF spectroscopy

The polymeric nature of the tin(II) acetate crystal structure was indirectly confirmed by a MALDI experiment. The MALDI-TOF spectrum of [Sn(CH<sub>3</sub>COO)<sub>2</sub>] (Fig. 6) displays polynuclear fragments  $[Sn_2O]^+$  (m/z 254.2),  $[Sn_2O(CH_3COO)_2]^+$  (m/z 313.0),  $[Sn_3O_2(OH)]^+$  (m/z 404.9),  $[Sn_3O_2(CH_3COO)]^+$  (m/z 446.8),  $[Sn_4O_3(OH)]^+$ (m/z 540.7),  $[Sn_5O_4(OH)]^+$  (m/z 674.5),  $[Sn_5O_4(CH_3-$ (M/z 716.5). The characteristic isotopic abundance of tin was useful in identifying these species. Presumably, polymeric [Sn(CH<sub>3</sub>COO)<sub>2</sub>] undergoes a deep cleavage of the acetate groups by desorption/ionization by laser irradiation but the Sn-O-Sn fragments are not destroyed so much. A similar behavior of metal-organic coordination compounds during MALDI-TOF experiments was noted in [8]. The extremely low stability of [Sn(CH<sub>3</sub>COO)<sub>2</sub>] with respect to the UV laser (337 nm) action are in good agreement with the results by Maruyama and Morishita [13], where the deep cleavage of [Sn(CH<sub>3</sub>COO)<sub>2</sub>] under UV irradiation was described.

## 4. Conclusion

The crystal structure of tin(II) acetate was solved and refined from X-ray powder diffraction data. Tin(II) acetate

adopts a polymeric structure consisting of infinite  $Sn(CH_3COO)_2$  chains running along the *c*-axis and packed into groups of four. The acetate groups bridge the Sn atoms along the chains and can be considered as tridentate bridging ligands with some chelate character. The first coordination sphere of the Sn atoms is described as a strongly distorted trigonal bipyramid,  $SnO_4E$  (E is a lone electron pair). This coordination environment is virtually identical to that in the  $Sn(CH_3COO)_2$  molecule in the gaseous phase [4]. In both cases the two short Sn–O bonds and the lone electron pair are located in the equatorial plane and the two longer Sn–O bonds are directed towards the apical vertexes. The distortion of the SnO<sub>4</sub>E trigonal bipyramid clearly demonstrates the sterical activity of the lone electron pair.

### Acknowledgements

The authors thank Prof. Natalya P. Kuz'mina and Prof. Joke Hadermann for fruitful discussions.

## Appendix A. Supplementary material

CCDC 653018 contains the supplementary crystallographic data for  $Sn(CH_3COO)_2$ . These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/ conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2007.08.010.

#### References

- [1] A. Ditte, Ann. Chim. Phys. 27 (1882) 115.
- [2] J.D. Donaldson, W. Moser, W.B. Simpson, J. Chem. Soc. (1964) 5942.
- [3] J.D. Donaldson, J. F Knifton, S.D. Ross, Spectrochim. Acta 21 (1965) 275.
- [4] B.A. Smart, L.E. Griffiths, C.R. Pulham, H.E. Robertson, N.W. Mitzel, D.W.H. Rankin, J. Chem. Soc., Dalton Trans. 9 (1997) 1565.
- [5] P.-E. Werner, L. Eriksson, M. Westdahl, J. Appl. Crystallogr. 18 (1985) 367.
- [6] V. Favre-Nicolin, R. Černy, J. Appl. Crystallogr. 35 (2002) 734.
- [7] V. Petricek, M. Dusek, JANA2000: Programs for Modulated and Composite Crystals, Institute of Physics, Praha, Czech Republic, 2000.
- [8] S.W. Hunsucker, R.C. Watson, B.M. Tissue, Rapid Commun. Mass Spectrom. 15 (2001) 1334.
- [9] A. Savin, O. Jepsen, J. Flad, O.K. Andersen, H. Preuss, H.G. von Schnering, Angew. Chem., Int. Ed. 31 (1992) 187.
- [10] G. Krier, O. Jepsen, A. Burkhart, O.K. Andersen, The TB-LMTO-ASA Program, Stuttgart, 1995.
- [11] M. Schurmann, F. Huber, Acta Cryst. C 50 (1994) 1710.
- [12] M.W. Stoltzfus, P.M. Woodward, R. Seshadri, J.-H. Klepeis, B. Bursten, Inorg. Chem. 46 (2007) 3839.
- [13] T. Maruyama, T. Morishita, Thin Solid Films 251 (1994) 19.