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STRUCTURE, SPECTROSCOPIC AND THERMAL CHARACTERIZATION OF BIS(ACETYLACETONATO)DICHLOROTIN(IV) SYNTHESIZED IN AQUEOUS SOLUTION

Bis(acetylacetonato)dichlorotin(IV) is synthesized from the aqueous solutions of tin(IV) chloride and acetylacetonone followed by vacuum drying at room temperature. DTA/TGA, FTIR, UV-VIS, X-ray powder and single crystal, mass spectra and elemental analysis are performed to characterize the product. X-ray powder diffraction suggests that the sample may contain some impurities such as SnO, SnO₂ and Sn₂O₃ while the mass spectra indicates the existence of Sn(acac)₄, which is arguable due to the steric effect. Single crystal investigation reveals that the product synthesized in aqueous solution is Sn(acac)₂Cl₂, crystallized in monoclinic system in space group C2/c with unit cell constants $a=13.983(2)$, $b=7.8928(8)$, $c=13.7889(19)$ Å and $\beta=107.601(11)^\circ$, whose volume is 1.43 % smaller than the one synthesized in dry toluene.

INTRODUCTION. High optical transmittance together with high conductivity makes tin oxide a material useful for many promising technological applications such as gas sensors [1—6], photo-conducting devices [7], spectrally selective reflectors and dye-based solar cells [8—10], ultrafiltration membrane [11], transparent conductive glasses [12] and molecular shape recognition [13]. Due to its unique properties, tin oxide has been gaining even increasing attention both on methods of preparation [14—24] and its electrical and optical properties [15, 25].

Several methods for the preparation of tin oxide films and nanoparticles have been previously reported such as sonochemical [15], modified successive ionic layer adsorption and reaction [16], chemical vapor deposition [17], magnetron sputtering [18], pyrolysis of thin organometallic compounds [19, 20], evaporation of tin in oxygen atmosphere [19, 20], spray pyrolysis [21], sol-gel [14, 22], solution phase synthesis [23], molecular-beam deposition [24]. The synthesis of tin oxide nanoparticles with high crystallinity, homogeneous composition, and well-defined particle morphologies with narrow size distributions is of particular technological interest since grain size and morphology are extremely important on the electrical and optical properties as well as the gas sensitivity of tin oxides [6, 26—28]. Some of the methods used in producing tin oxide films are too expensive to employ in mass production while some suffer from broad particle size distribution which is extremely difficult to control. In these respect sol-gel methods gain importance since the particle size as well as the structure of tin oxide can be controlled in many ways such as changing the concentration of

precursor solution, heat treatment conditions.

Sol-gel methods are usually based on the decomposition of a complex of Sn(IV) and acetylacetonone, H(acac), namely Sn(acac)₂Cl₂, produced by different methods [29—32], which involve some tedious and time consuming processes since Sn(acac)₂Cl₂ is prepared in solvents such as chloroform [31] and dry toluene [32]. We report here a new simple method for the synthesis of Sn(acac)₂Cl₂ in aqueous solution and fully characterize the reaction product and its crystal structure using differential thermal analysis/thermo gravimetric analysis (DTA/TGA), elemental analysis, ion chromatography, Fourier transform infrared (FTIR), Ultraviolet-Visible (UVVIS), ¹H and ¹³C Nuclear Magnetic Resonance (NMR), XRay Diffraction (XRD) and Mass Spectrum (MS).

EXPERIMENTAL PART. Synthesis. 5 mL of 25 % water solution of NH₄OH is added into a freshly prepared solution of 0.12 mol (14 mL) Tin(IV) chloride dissolved in 50 mL icecold double distilled water. The solution is then poured into a solution of 0.5 mol (50 mL) acetylacetonone dissolved in 250 mL double distilled water held at 40 °C. Although thick and white sediment immediately appears, mixture is kept mixing for two hours. 600 mL distilled water is added in before it is allowed to settle down for 15 minutes. Sediment is then filtered and washed by double-distilled water subsequent to drying at 10⁻² mbar. Washing and drying processes are repeated once more with benzene to remove some possible organic residues. The product is crystallized by slow evaporation of acetone in which it is dissolved in at room temperature. All reagents are of AR grade.

Characterization. FTIR absorbance spectrum of

the samples is measured by Bruker–Tensor 27 spectrometer with 1.0 cm^{-1} interval with a resolution of 2 cm^{-1} . 20 scans are performed in the range $400\text{--}4000\text{ cm}^{-1}$. Solid samples are pelletized with dried KBr. UV-VIS absorbance spectra of the samples dissolved in acetone are recorded at room temperature in the wavelength range $300\text{--}1000\text{ nm}$ using Varian-Cary 100 Bio UV-VIS spectrophotometer.

Simultaneous thermogravimetry and differential thermal analysis are carried out with a Perkin–Elmer Exstar 6000 analyzer in air and nitrogen atmospheres with a heating rate of $10\text{ }^\circ\text{C}/\text{min}$. Carbon and hydrogen content are determined using Euro EA 2300 elemental analyzer whereas Cl and Sn analysis are performed after dissolving the product in HNO_3 using Waters 432 ion chromatography and Perkin Elmer ICP-OES Optima 2100 DV, respectively. ^1H and ^{13}C NMR spectra are recorded on a Varian AS 400 spectrometer operating at 400 MHz.

Powder XRD data is collected on Rigaku–Rad B-DMAXII diffractometer with graphite-monochromated $\text{CuK}\alpha$ radiation ($\lambda=1.54056\text{ \AA}$) from 2 to 80° (2θ) in steps of 0.01° whereas single crystal data are collected on a graphite-monochromated Stoe IPDS-II diffractometer using $\text{MoK}\alpha$ -radiation ($\lambda=0.71073\text{ \AA}$). Powder and crystal data are collected at room temperature. Single crystal data collection and cell refinement are performed using X-AREA [33] while data reduction is accomplished using X-RED32 [33]. SHELXL-97 [34] program system is used for solving and refining the crystal structure.

Mass spectrum is recorded using Agilent 6300 Series LC/MS system.

RESULTS AND DISCUSSION.

Thermal decomposition of the product (fig. 1) consists of several stages. Weight loss observed between the room temperature and $192.0\text{ }^\circ\text{C}$ which is about 4.0% is likely due to the evaporation of adsorbed and hydrated water. A well defined endothermic peak appearing at $204.0\text{ }^\circ\text{C}$ is associated with the melting point. TGA and DTA data (fig. 1), reveals an oxygen-related structuring in temperature range $192.0\text{--}308.5\text{ }^\circ\text{C}$, one at $277.4\text{ }^\circ\text{C}$ and the other at $286.6\text{ }^\circ\text{C}$. Slight increase in the slope of TGA data in air at $277.4\text{ }^\circ\text{C}$ suggests that this might be related to

the reaction of thermally decomposed fragments either with oxygen and/or hydrogen before they leave the structure. This is supported by the lack of steepness in DTA curve obtained in nitrogen atmosphere at the same temperature range. The strong exothermic peak appeared between 620 and $650\text{ }^\circ\text{C}$ in the DTA curve taken in air is not observed in the curve taken in nitrogen. Exothermic peak observed in air at around $650\text{ }^\circ\text{C}$ corresponds to weight loss of 1.5% and may due to combustion of organic residues be formed by the decomposition of acetylacetonate. Further increase in temperature does not result in any more weight loss. Residual weight at $308.5\text{ }^\circ\text{C}$ in fig. 1 is about 28% and can be associated with SnO_2 content of the product.

C, H, Sn and Cl contents of the product, which are 29.28 , 3.41 , $30.90 \pm 1.1\%$ and $16.50 \pm 0.60\%$, respectively, are comparable with the elemental ratios calculated for $\text{Sn}(\text{acac})_2\text{Cl}_2$ (30.97 , 3.64 , 30.61 and 18.28% , respectively) and for $\text{Sn}(\text{acac})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (28.34 , 4.28 , 28.00 and 16.73% , respectively). Although C, H and Sn content of the product are quite in agreement with $\text{Sn}(\text{acac})_2\text{Cl}_2$, measured Cl content addresses $\text{Sn}(\text{acac})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$. TGA result given in fig. 1 from which a residual weight of 28% is calculated seems to support it too. However, considering the sublimation of Sn that may take place during the heating, thermal analysis can be expected to present lower Sn content than what it should be. It can thus be argued that the results of thermal and elemental analysis are consistent and suggest the formula $\text{Sn}(\text{acac})_2\text{Cl}_2$.

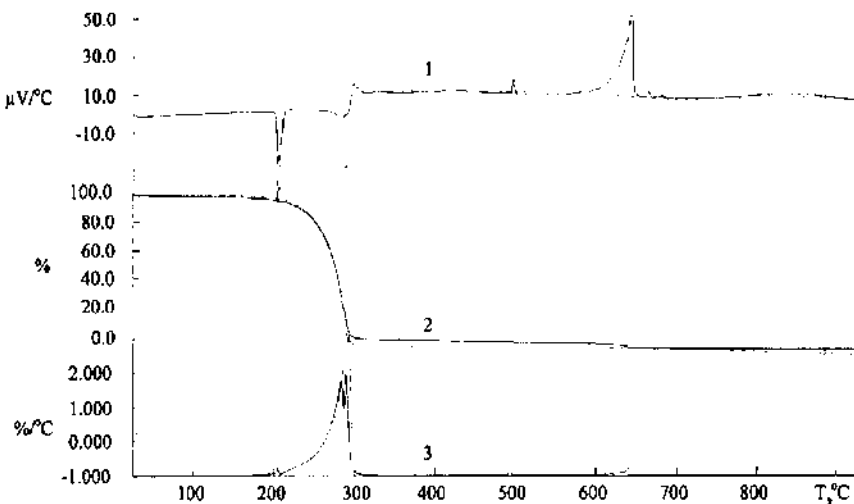


Fig. 1. DTA (1), TGA (2) and DTG (3) results of the product. Solid and broken lines represent the data taken in nitrogen and air, respectively.

Methyl group of acetylacetonato (acac) exhibits equal intensity singlet at 2.122 and 2.214 ppm due to CH₃ groups while CH protons gives singlet at 5.709 ppm in the ¹H NMR spectrum of the sample. ¹³C NMR resonances located at 27.973 and 102.655 ppm correspond to CH₃ and CH groups of acac, respectively, whereas the signals due to C=O and C—O groups appear at 195.856 and 196.421 ppm, respectively. As one may expect the amplitude ratio of the signals arising from CH and CH₃ groups is about 1/3 in ¹H NMR and signals from CH, C—O, C=O and CH₃ groups are about 1/2 in ¹³C NMR.

FTIR absorbance spectra of the product exhibits strong bands in the range 400—1600 cm⁻¹ and some weak bands placed on a small broad band located between 2400 and 3600 cm⁻¹ (fig. 2). None of the characteristic bands of benzene are observed on FTIR spectra of the sample indicates the effective removal of benzene. Vibrations extending from 2500 to 3600 cm⁻¹ have related to the presence of hydrogen bond involved in O—H oscillators arising from SnOH groups and/or adsorbed water molecules [35]. Based on Density Functional Theory (DFT) some bands appearing between 3031 and 3108 cm⁻¹ are however assigned to ν(CH)_{methyl} and (CH)CH₃ [36]. All but the vibration at 810 cm⁻¹ match quite well with the IR active bands of Sn(acac)₂Cl₂ [36]. Vibrations between 415 and 590 cm⁻¹ are assigned to the coupled modes of (SnO), (OSnCl), (OSnO) and (OSnCl/ OSnO)

[30, 35, 36] while the strong vibrations appearing at 1540 and 1570 cm⁻¹ were related to the enol form of acetylacetonate group bonded to tin [35, 36]. It can therefore be argued with confident that all (acac) groups are bonded to tin to form a complex and no free acetylacetonate exists in the product.

UV-VIS spectrum of the sample reveals strong absorbance at 331.6 nm due to (acac) group and confirms the FTIR results that acetylacetonate is bonded to tin. X-ray powder diffraction result (fig. 3), indicates that all peaks are due to Sn(acac)₂Cl₂ though some impurities which can be attributed to SnO, SnO₂ and Sn₂O₃ are also present.

Signals in the mass spectra of the product (fig. 4), are grouped at around 515.3, 417.0, 353.0, 314.3, 289.0 and 101.1 *m/z* in which the highest occurrence is at 353.0 *m/z*. 515.3 *m/z* at which the signal has the lowest occurrence (1/33th of the highest peak at 353.0 *m/z*) is consistent with Sn(acac)₄. Signal at 416.1 *m/z* can be related to Sn(acac)₃ e.g., one of four (acac) groups in Sn(acac)₄ is fragmented. Signals at 353.0 *m/z* and 317.95 *m/z* correspond to the fragments of

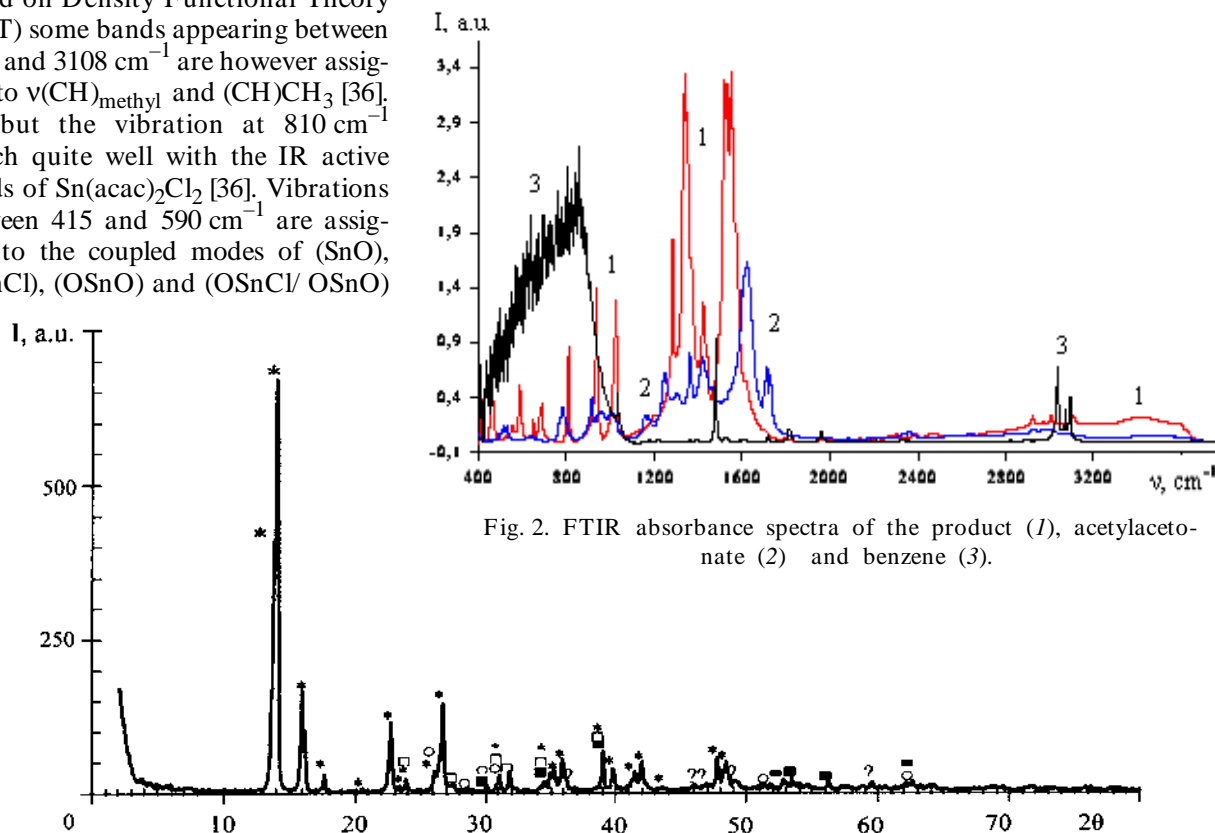


Fig. 2. FTIR absorbance spectra of the product (1), acetylacetonate (2) and benzene (3).

Fig. 3. Powder XRD pattern of the product. * — Sn(acac)₂Cl₂, • — SnO, o — SnO₂, ◦ — Sn₂O₃, ? — unknown.

$\text{Sn}(\text{acac})_2\text{Cl}_2$, namely $\text{Sn}(\text{acac})_2\text{Cl}$ and $\text{Sn}(\text{acac})_2$ in which one and two chlorine atoms are removed, respectively. The signal at 289.0 m/z is consistent with $\text{Sn}(\text{acac})$ while the one at 101.1 m/z is related to $\text{H}(\text{acac})$. Mass spectra of the product is in line with powder XRD data that the product is essentially $\text{Sn}(\text{acac})_2\text{Cl}_2$ but contains some traces of $\text{Sn}(\text{acac})_4$.

Single crystal investigation confirms that the product is $\text{Sn}(\text{acac})_2\text{Cl}_2$, crystallized in monoclinic system in space group $C2/c$ with unit cell constants $a=3.983(2)$, $b=7.8929$, $c=13.7889(19)\text{ \AA}$ and $\beta=107.601(11)^\circ$. Molecular structure of $\text{Sn}(\text{acac})_2\text{Cl}_2$ is depicted in fig. 5 while the crystal data and the measured bond lengths and angles are summarized in table 1 and table 2, respectively*. Unit cell parameters a , b and c given in table 1 differ 0.67%, -0.34% and -1.82% , respectively, from that of the samples produced in dry toluene [32]. Consequence of this, the unit cell volume of our product is smaller by 1.43% while the density is higher by 1.41% compared to the one produced in dry toluene [32]. Although $(\text{acac})^-$ in some cases binds to metals through the central carbon atom, C3 in fig. 5, molecular structure acqui-

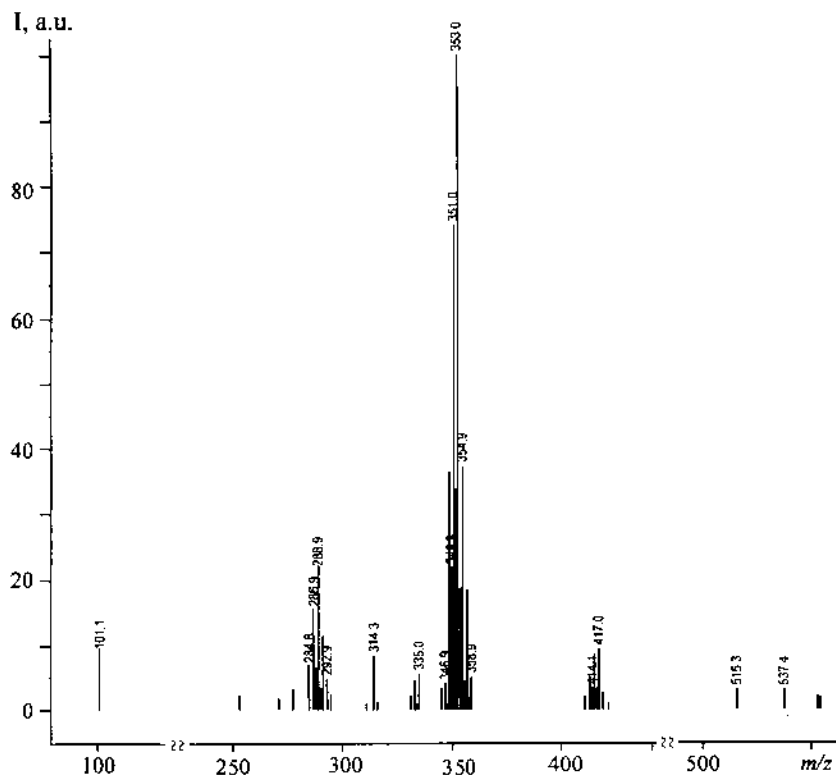


Fig. 4. Mass spectrum of the product.

red indicates that it is bonded to tin atom through oxygen.

Signals at 515.3 m/z and 416.1 m/z , which correspond to $\text{Sn}(\text{acac})_4$ and to $\text{Sn}(\text{acac})_3$, respectively, in fig. 4 suggest the presence of $\text{Sn}(\text{acac})_4$ and $\text{Sn}(\text{acac})_3\text{Cl}$ in the product. Signal at 416.1 m/z could only be due to the fragments of $\text{Sn}(\text{acac})_4$ and/or $\text{Sn}(\text{acac})_3\text{Cl}$ since $\text{Sn}(\text{acac})_3$ can not exist as a free standing compound. Such a possibility is not supported by thermal analysis since DTA reveals very sharp melting point at 204.0°C (fig. 1). Although DTA obtained in air indicates some complexities around 300°C , which could be related to the impurities such as those $\text{Sn}(\text{acac})_4$ and $\text{Sn}(\text{acac})_3\text{Cl}$, its wane in DTA taken in nitrogen atmosphere excludes such possibility. In this respect, FTIR and UV-VIS spectra are not so diagnostic though powder XRD should be more indicative. Library search of powder XRD indicates the existence of SnO , SnO_2 and Sn_2O_3 impurities (fig. 3), despite the fact that the

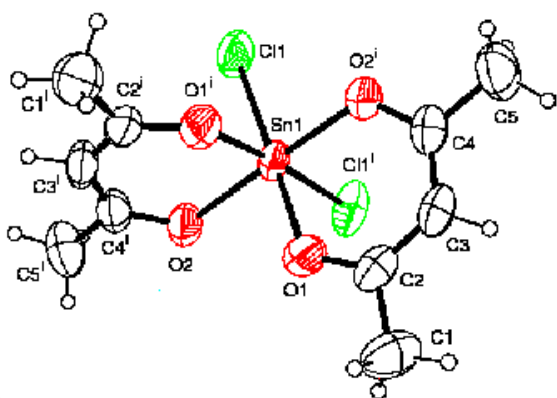


Fig. 5. Molecular structure of $\text{Sn}(\text{acac})_2\text{Cl}_2$.

* CCDC 735456 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Table 1

Crystal data and structure refinement parameters of bis-(acetylacetonato)dichlorotin (IV)

| Parameters | Crystal data |
|---|--|
| Empirical formula | Sn(C ₅ H ₇ O ₂) ₂ Cl ₂ |
| Formula weight | 387.80 |
| Temperature, K | 296 |
| X-ray, Å | MoK _α , 0.71073 |
| Crystal system | Monoclinic |
| Space group | C2/c |
| Unit cell parameters: | |
| <i>a</i> , <i>b</i> , <i>c</i> , Å | 13.983(2), 7.8928(8), 13.7889(19) |
| α, β, γ, ° | 90.00, 107.601(11), 90.00 |
| <i>Z</i> | 4 |
| <i>V</i> , Å ³ | 1450.5(3) |
| <i>D</i> , g/cm ³ | 1.776 |
| Absorption coefficient, mm ⁻¹ | 2.16 |
| № of reflection collected | 3440 |
| Theta range for data collection | 3.00–26.50 |
| Independent reflections | 1474 |
| Measurement | Stoe IPDS-II |
| Monochromator | Plane graphite |
| Structure determination | SHELXL-97 |
| Absorption correction | Integration Stoe X-RED |
| Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] | 0.0213 |
| <i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] | 0.0231 |
| w <i>R</i> (<i>F</i> ²) | 0.0583 |
| Goodness-of-fit on <i>F</i> ² | 1.145 |
| Peak and hole, Å ³ | 0.297, –0.674 |

sample is prepared at room temperature. Since XRD data of such compounds are not known no further comment is possible.

It should also be noted that yield of Sn(acac)₄ must be very low for the conditions deployed since it does not appear in significant amount despite the fact that the molar ratio of the constituents, namely M[SnCl₄] to M[H(acac)], is kept 1/4 or lower. Molecular structure depicted in fig. 5 and the data given in table 2 suggest that attaching the third and fourth (acac) units to Sn atom can not be so straightforward due to the steric effect.

CONCLUSION. Bis(acetylacetonato)dichlorotin (IV) is synthesized from the aqueous solutions of tin (IV) chloride and acetylacetone followed by vacuum drying at room temperature. All the analysis performed are consistent and suggest that the pro-

Table 2

Some selected bond lengths (Å) and angles (°) of bis(acetylacetonato)dichlorotin (IV)

| Bond | Bond length, Å | Bond | Angle, ° |
|-------------|----------------|--------------------------------|------------|
| Sn(1)–O(1) | 2.0733(17) | O(1)–Sn(1)–O(1) ^{i*} | 84.08(7) |
| Sn(1)–O(2) | 2.058(2) | O(1)–Sn(1)–O(2) ⁱ | 86.69(8) |
| Sn(1)–Cl(1) | 2.3543(9) | O(2)–Sn(1)–O(2) ⁱ | 172.22(6) |
| O(1)–C(2) | 1.280(3) | O(1)–Sn(1)–Cl(1) | 173.36(5) |
| O(2)–C(4) | 1.296(3) | O(2)–Sn(1)–Cl(1) | 93.74(6) |
| C(1)–C(2) | 1.491(4) | Cl(1)–Sn(1)–Cl(1) ⁱ | 97.00(3) |
| C(2)–C(3) | 1.381(4) | C(2)–O(1)–Sn(1) | 125.33(17) |
| C(3)–C(4) | 1.390(4) | C(4)–O(2)–Sn(1) | 124.70(17) |
| C(4)–C(5) | 1.490(5) | | |

* Symmetry code *i*: 1–*x*, *y*, ½–*z*.

duct is essentially Sn(acac)₂Cl₂. Single crystal data reveals that Sn(C₅H₇O₂)₂Cl₂ crystallized in monoclinic system in space group C2/c with unit cell dimensions *a* = 13.983(2), *b* = 7.8929, *c* = 13.7889(19) Å and β = 107.601(11)°. The unit cell is found to be about 1.43 % smaller than the one synthesized in dry toluene. Mass spectra indicates the existence of Sn(acac)₄ in the product whereas the molecular structure obtained makes it disputable due to the steric effect.

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РЕЗЮМЕ. Дихлордиацетилацетонат олова (IV) синтезирован в водном растворе хлорида олова (IV) и ацетилацетона с последующей сушкой в вакууме при комнатной температуре. Свойства синтезированного продукта исследованы методами ДТА/TGA, FTIR, UV-VIS, рентгеновской дифракции, масс-спектроскопии и элементного анализа. Согласно результатам рентгеновской дифракции порошков, образец может содержать немно-

го примесей, таких как SnO, SnO₂ и Sn₂O₃, в то же время массовые спектры указывают на существование Sn(асас)₄, что является спорным из-за стерического эффекта. Рентгенографические исследования отдельных кристаллов показывают, что продуктом, синтезированным в водном растворе, является Sn(асас)₂Cl₂, кристаллизованный в моноклинной системе в пространственной группе C2/c с постоянными решетки $a=13.983(2)$, $b=7.8928(8)$, $c=13.7889(19)$ Å, $\beta=107.601(11)^\circ$ и объемом на 1.43 % меньшим, чем объем вещества, синтезированного в сухом толуоле.

РЕЗЮМЕ. Діхлордіацетилацетонат олова (IV) синтезований у водному розчині хлориду олова (IV) і ацетилацетона з наступним сушінням у вакуумі при кімнатній температурі. Властивості синтезованого продукту досліджені методами ДТА/TGA, FTI, UV-VIS, рентгєнівської дифракції, мас-спектроскопії та елементного аналізу. Згідно з результатами рентгєнівської дифракції порошків зразок може містити небагато домішок, таких як SnO, SnO₂ і Sn₂O₃, у той же час масові спектри вказують на існування Sn(асас)₄, що є суперечним внаслідок стеричного ефекту. Рентгєнографічні дослідження окремих кристалів показують, що продуктом, синтезованим у водному розчині, є Sn(асас)₂Cl₂, кристалізований у моноклінній системі в просторовій групі C2/c із сталими ґратки $a=13.983(2)$, $b=7.8928(8)$, $c=13.7889(19)$ Å і $\beta=107.601(11)^\circ$ та об'ємом, на 1.43 % меншим за об'єм речовини, синтезованої в сухому толуолі.

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