Inorganica Chimica Acta, 30 (1978) 23–27

Reactions of Tin Tetracarboxylates with β-Diketones

E. N. VASANTA, G. SRIVASTAVA and R. C. MEHROTRA*
Department of Chemistry, University of Rajasthan, Jaipur-302004, India

Received November 19, 1977

Reactions of tin tetraacetate and tetraproprionate with β-diketones (acetylacetone, benzoyl acetone and dibenzoylmethane) have been carried out in different stoichiometric ratios in refluxing toluene or chloroform. Mono-β-diketonate tricarboxylate and di-β-diketonate dicarboxylate derivatives of tin have been isolated as stable monomeric compounds. The latter derivatives are the final products, even when β-diketone is in excess. The acetate and propionate groups in these mixed β-diketonate carboxylate derivatives are easily replaced by thiobenzoate and thioacetate groups.

Introduction

A large number of β-diketonates of tin(IV) and organotin(IV) have been isolated during the last two decades and their structural studies have been carried out with the help of IR and PMR spectroscopy, dipole moment measurements and X-ray diffraction [1]. It is believed that trialkyltin acetylacetonates [2], dialkyltin diacetylacetonates [3, 4] and butyltin triacetylacetonate [5] contain 5,6 and 7 coordinate tin atoms respectively as suggested on the basis of IR data.

Reactions of tin tetrachloride with acetylacetone at room temperature, either alone or in the presence of benzene or chloroform have been shown by Mehrotra and Gupta [6] to yield an ionic complex, $[Cl_2Sn(CH_3COCH_2COCH_3)_2]^{++}[SnCl_6]^{=}$. Allred and Thompson [7] have isolated a neutral addition compound, $SnCl_4\cdot CH_3COCH_2COCH_3$, by mixing the reactants in methylene dichloride at 0 °C. The above reaction in refluxing benzene or chloroform, however, yields tin diacetylacetonate dichloride, $Cl_2Sn(acac)_2$ [6].

In this communication, we report for the first time the reactions of tin tetraacetate and tetrapropionate with β-diketones like acetylacetone, benzoylacetone and dibenzoylmethane. It may be pointed out here that except for reactions with dimethylamine [8], hydrogen chloride [8] and higher carboxylic acids [9], substitution reactions of tin tetracarboxylates have not been reported so far.

Experimental

Analysis of tin metal, acetate and propionate groups have been carried out as described before [9].

$Sn(OOCCH_3)_4$ and $Sn(OOCCH_2CH_3)_4$ were prepared as mentioned before [9].

Molecular weights in boiling chloroform were determined with a semimicro Gallenkamp ebulliometer, employing a thermistor sensing.

The IR spectra have been recorded as nujol mulls on a Perkin-Elmer 337 instrument in the range 4000–400 cm^{-1}. PMR spectra were recorded on a Perkin-Elmer R 12B spectrometer, in $CDCl_3$ solutions, using TMS as standard.

Synthesis of Tin Triacetate Monoacetylacetonate

A mixture of $Sn(OOCCH_3)_4$ (2.91 g; 8.2 mmol) and acetylacetone (0.82 g; 8.2 mmol) was refluxed in chloroform (35 ml) for about 4 hr. After cooling the clear solution to room temperature and removing the solvent at 30 °C/10 mm, a white powder (3.2 g; 100% yield) was obtained.

Alternatively, a mixture of $Sn(OOCCH_3)_4$ (2.02 g; 5.7 mmol) and acetylacetone (0.57 g; 5.7 mmol) was refluxed in toluene (~40 ml) for 4 hr. Acetic acid liberated in the reaction was collected in the form of azeotrope (b.p. 106 °C) with toluene (acetic acid in the azeotrope, 0.34 g; 5.7 mmol). After removing the solvent at 60–70 °C/1 mm, a white powder (2.2 g; 5.5 mmol) was obtained.

Use of toluene as a solvent thus had the advantage that the progress and completion of the reaction could be followed by estimating the acetic acid in the azeotrope. Propionic acid does not appear to form an azeotrope with toluene but can be distilled along with the solvent at 110 °C.

For sake of brevity, the results of the reactions of tin tetraacetate and tetrapropionate in 1:1 and 1:2 molar ratios with different β-diketonates are summarised in Table I.

---

*Present address: Delhi University, Delhi-110007.

0020-1693/78/0030-0023$2.25 Printed in Switzerland

TABLE I. Reactions between $Sn(OOCCH_3)_4$, $Sn(OOCCH_2CH_3)_4$ and β-Diketones in Toluene.

S. No.	$Sn(OOCR)_4$ (g)	β-diketone (g)	Molar Ratio	Nature and Formulae of Products Formed	Carboxylic Acid in the Azeotrope Found (Calcd)	Sn% Found (Calcd)	% Acetate Found (Calcd)	M.P. °C
1	2	3	4	5	6	7	8	9
	$Sn(OOCCH_3)_4$				Acetic acid			
1.	2.02	Acetylacetone 0.57	1:1[a]	$(CH_3COO)_3Sn(CH_3COCHCOCH_3)$[a] white solid	0.34 (0.34)	29.95 (30.07)	44.79 (44.85)	95
2.	1.94	Acetylacetone 1.09	1:2[a]	$(CH_3COO)_2Sn(CH_3COCHCOCH_3)_2$[a] white solid	0.65 (0.66)	27.24 (27.32)	27.09 (27.17)	125
3.	1.99	Benzoylacetone 0.91	1:1[a]	$(CH_3COO)_3Sn(C_6H_5COCHCOCH_3)$[a] light brown solid	0.35 (0.34)	26.19 (25.99)	38.69 (38.76)	122
4.	2.1	Benzoylacetone 1.94	1:2[a]	$(CH_3COO)_2Sn(C_6H_5COCHCOCH_3)_2$[a] reddish brown solid	0.72 (0.72)	21.38 (21.25)	21.26 (21.14)	115
5.	2.06	Dibenzoylmethane 1.3	1:1	$(CH_3COO)_3Sn(C_6H_5COCHCOC_6H_5)$ light brown solid	0.34 (0.35)	22.50 (22.69)	34.29 (34.16)	154
6.	1.77	Dibenzoylmethane 2.23	1:2	$(CH_3COO)_2Sn(C_6H_5COCHCOC_6H_5)_2$ light brown solid	0.59 (0.60)	17.14 (17.39)	17.21 (17.30)	168
	$Sn(OOCCH_2CH_3)_4$				Propionic acid			
7.	1.47	Acetylacetone 0.36	1:1	$(CH_3CH_2COO)_3Sn(CH_3COCHCOCH_3)$ viscous red solid	0.24 (0.26)	27.01 (27.18)	–	–
8.	2.23	Acetylacetone 1.09	1:2	$(CH_3CH_2COO)_2Sn(CH_3COCHCOCH_3)_2$ reddish viscous solid	0.84 (0.80)	25.95 (25.65)	–	–

[a] The reaction was carried out in dry chloroform also, giving identical product.

TABLE II. Reactions between Mixed Tin Carboxylate Acetylacetonate and Thiocarboxylic Acids in Toluene.

S. No.	$(RCOO)_nSn(acac)_{4-n}$ (g)	Thiocarboxylic Acid (g)	Molar Ratio	Nature and Formulae of the Products Formed	Carboxylic Acid in the Azeotrope (g) Found (Calcd)	Sn% Found (Calcd)	Sulphur% Found (Calcd)	M.P. °C
1.	$(CH_3COO)_3Sn(acac)$ 0.76	PhCOSH 0.80	1:3	$(C_6H_5COS)_3Sn(CH_3COCHCOCH_3)$ light brown solid	Acetic acid 0.33 (0.34)	18.98 (18.88)	15.38 (15.26)	160
2.	$(CH_3COO)_2Sn(acac)_2$ 1.26	PhCOSH 0.86	1:2	$(C_6H_5COS)_2Sn(CH_3COCHCOCH_3)_2$ light brown solid	0.37 (0.38)	20.33 (20.10)	10.69 (10.83)	176
3.	$(CH_3CH_2COO)_3Sn(acac)$ 0.96	PhCOSH 0.72	1:3	$(C_6H_5COS)_3Sn(CH_3COCHCOCH_3)$ light brown solid	Propionic acid 0.37 (0.38)	18.93 (18.88)	15.06 (15.26)	160
4.	$(CH_3CH_2COO)_2Sn(acac)_2$ 0.86	PhCOSH 0.51	1:2	$(C_6H_5COS)_2Sn(CH_3COCHCOCH_3)_2$ light brown solid	Propionic acid 0.27 (0.28)	20.15 (20.10)	10.42 (10.83)	176
5.	$(CH_3COO)_2Sn(acac)_2$ 1.30	CH_3COSH 0.45	1:2[a]	$(CH_3COS)_2Sn(CH_3COCHCOCH_3)_2$[a]	Acetic acid 0.34 (0.36)	25.30 (25.43)	–	290

[a] This reaction was done in dry chloroform also, giving identical product.

Synthesis of Tin Di(thiobenzoate)di(acetylacetonate)

Tin diacetate diacetylacetonate (1.26 g; 2.9 mmol) was mixed with thiobenzoic acid (0.86 g; 6.2 mmol) in toluene (35 ml) for 6 hr. Acetic acid–toluene azeotrope was removed at 106 °C and estimated for acetic acid (Found 0.37 g; 5.8 mmol). After cooling the clear solution to room temperature, the excess solvent was removed at 60 °C/10 mm. The final product was a brown solid (1.7 g; 100% yield).

Results of similar reactions of other carboxylate β-diketonates of tin with thioacetic and thiobenzoic acids have been summarised in Table II.

Results and Discussion

Reactions of tin tetracarboxylates with β-diketones in 1:1 and 1:2 molar ratios can be represented as:

$$Sn(OOCR)_4 + R'COCH_2COR'' \longrightarrow$$

$$(RCOO)_3Sn(R'COCHCOR'') + RCOOH\uparrow$$

I: $R = R' = R'' = CH_3$
II: $R = C_2H_5, R' = R'' = CH_3$
III: $R = R' = CH_3; R'' = C_6H_5$
IV: $R = CH_3, R' = R'' = C_6H_5$

$$Sn(OOCR)_4 + 2R'COCH_2COR'' \longrightarrow$$

$$(RCOO)_2Sn(R'COCHCOR'')_2 + 2RCOOH\uparrow$$

V: $R = R' = R'' = CH_3$
VI: $R = C_2H_5; R' = R'' = CH_3$
VII: $R = R' = CH_3; R'' = C_6H_5$
VIII: $R = CH_3; R' = R'' = C_6H_5$

All the mixed carboxylate β-diketonate derivatives are solids, with sharp melting points. These are soluble in chloroform and tend to hydrolyse readily in presence of moisture. These compounds are monomeric in refluxing chloroform, as shown by the ebullioscopic molecular weight determination. In reactions of tin tetracarboxylates with β-diketones in 1:>2 molar ratios, only 2 mol of the corresponding carboxylic acid are liberated, thereby showing that tin dicarboxylate di(β-diketonate) is the final product. It appears reasonable to conclude that the tin atom in tin dicarboxylate di(β-diketonate) is coordinatively saturated and therefore further replacement of carboxylate group is hindered.

All the carboxylate groups in tin monoacetylacetonate tricarboxylate and tin diacetylacetonate dicarboxylate are easily replaced by thiobenzoate and thioacetate groups in refluxing toluene:

TABLE III. PMR Spectra of Tin Mono- and Diacetate-β-diketonates.

S. No.	Compound	$>$C–H τ	$>$C–CH$_3$ τ	O–C(=O)CH$_3$ τ	$>$CC$_6$H$_5$ τ
1.	$Sn(OOCCH_3)_4$	–	–	7.85	–
2.	$(acac)Sn(OOCCH_3)_3$	4.25	7.74	7.80	–
3.	$(acac)_2Sn(OOCCH_3)_2$	4.25	7.35	7.85	–
4.	$(C_6H_5COCHCOCH_3)Sn(OOCCH_3)_3$	3.82	7.65	7.85	2.20
5.	$(C_6H_5COCHCOCH_3)_2Sn(OOCCH_3)_2$	3.45	7.70	7.88	2.25
6.	$(C_6H_5COCHCOC_6H_5)Sn(OOCCH_3)_3$	3.25	–	7.85	2.20
7.	$(C_6H_5COCHCOC_6H_5)_2Sn(OOCCH_3)_2$	3.28	–	7.85	2.15

TABLE IV. PMR Spectral Data for the Propionate β-Diketonate Derivative.

S. No.	Compound	$>$C–H τ	$>$C–CH$_3$ τ	O–C(=O)CH$_2$ τ	O–C(=O)CH$_2$–CH$_3$ τ
1.	$Sn(OOCCH_2CH_3)_4$	–	–	7.40	8.70
2.	$(acac)Sn(OOCCH_2CH_3)_3$	4.28	7.75	7.44	8.70
3.	$(acac)_2Sn(OOCCH_2CH_3)_2$	4.30	7.82	7.60	8.80

$$(RCOO)_3Sn(CH_3COCHCOCH_3) + 3R'COSH \longrightarrow (R'COS)_3Sn(CH_3COCHCOCH_3) + 3RCOOH\uparrow$$

$$(RCOO)_2Sn(CH_3COCHCOCH_3)_2 + 2R'COSH \longrightarrow (R'COS)_2Sn(CH_3COCHCOCH_3)_2 + 2RCOOH\uparrow$$

$R = CH_3$ or C_2H_5
$R' = CH_3, C_6H_5$

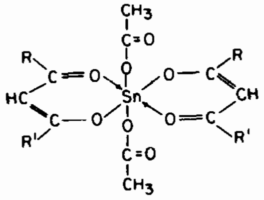
The insolubility of these mixed thioacetate and thiobenzoate acetylacetonates of tin in common organic solvents prevents further study on them.

The mixed carboxylate β-diketonate derivatives of tin being described here are quite interesting species from a structural point of view, as both carboxylate as well as β-diketonate moieties are capable of showing various modes of attachment to a metal centre.

Based on molecular weight and infrared spectral data, tin tetraacetate and tetrapropionate have been shown to exist as polymeric species [with two bridging (IR peaks at 1704 and 1262 cm^{-1}) and two free (IR peaks at 1560 and 1440 cm^{-1}) carboxylate groups] in the solid state and as monomeric species in solution with only free carboxylate groups [8].

The IR spectra of acetate β-diketonates of tin (I, III, IV, V, VII and VIII) show a strong absorption at 1685 ± 10 cm^{-1} and a medium intensity absorption at 1275 ± 10 cm^{-1}. The corresponding propionate β-diketonates (II and VI) also absorb at 1710 and 1290 ± 10 cm^{-1}. These peaks may be assigned to ν_{as} C=O and ν_s C=O, and their positions indicate the presence of free carbonyl group in all these compounds. Other peaks present in the region 1500–1700 cm^{-1} are strong intensity peaks at 1560 ± 10 cm^{-1} and 1530 cm^{-1}. The positions of these peaks are almost the same as reported for other β-diketonate complexes of tin(IV) [3] and therefore these peaks are probably due to C=C and chelated C=O groups of the β-diketonate moiety.

In comparison to the carboxylate group, the β-diketonate groups are expected to show stronger chelating behaviour and we believe that the free C=O group absorptions in the IR spectra of mixed carboxylate β-diketonates of tin are due to the carboxylate moieties. In view of the strong preference of tin(IV) to achieving coordination number six in various complexes, it seems reasonable to suggest that in dicarboxylate di-β-diketonate derivatives, the two β-diketonate moieties are chelating and the two carboxylate moieties are showing monodentate behaviour. The following tentative structure, having a *trans-* arrangement is proposed:



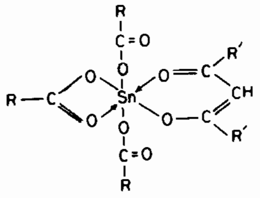
In the above context, the following points are worth mentioning:

(a) Tin diacetate di-β-diketonates (V, VII and VIII) have been found to be monomeric in refluxing chloroform.

(b) Tin dihalide di-β-diketonates [10] have been found to possess octahedral *trans*-structure on the basis of IR and PMR spectral analysis.

(c) The PMR spectrum of tin diacetate diacetylacetonate shows only three singlets at 4.25τ, 7.85τ and at 7.35τ, which are due to the methine proton $(\rangle C{-}H)$, the acetate methyl protons $(O{-}\overset{O}{\overset{\|}{C}}{-}CH_3)$ and the acetylatectone methyl protons $(C{\cdots}\overset{O}{\overset{\|}{C}}{-}CH_3)$ and this pattern again points towards a *trans*-structure. The PMR spectra of other tin dicarboxylate di-β-diketonates also show a similar pattern (Tables III and IV).

The tricarboxylate mono-β-diketonate derivatives of tin, which also show monomeric behaviour, may be represented by a number of possible structures, containing 5- or 6-coordinated tin atom. However, again it is reasonable to assume that tin would acquire a six coordination environment in these compounds also and we suggest the following tentative structure, having one chelating and two monodentate carboxylate groups arranged in a *trans*-fashion.



The carbonyl groups of the chelated carboxylate as well as the β-diketonate moieties absorb at the same position in the IR spectra and therefore cannot be distinguished. The PMR spectrum of triacetate mono-acetylacetonate derivative shows a single absorption for the acetylacetonate methyl groups at 7.80τ. However, the acetate methyl protons also appear as a singlet at 7.74τ, which may be due to the same chemical shift of methyl protons of both types of acetate groups or to fast exchange of the methyl groups of chelating and monodentate acetate groups. The close proximity of these two peaks makes a detailed PMR study difficult.

Acknowledgement

Financial help from P.L.-480 grant given to E.N. V. is gratefully acknowledged.

References

1 "Organotin Compounds", Ed. A. K. Sawyer, Vol. II, Marcel Dekker, New York (1971).
2 R. C. Mehrotra and V. D. Gupta, *J. Organometal. Chem.*, *4*, 237 (1965).
3 M. M. McGrady and R. S. Tobias, *J. Am. Chem. Soc.*, *87*, 1909 (1965).
4 W. H. Nelson and D. F. Martin, *J. Inorg. Nucl. Chem.*, *27*, 89 (1965).
5 D. P. Gaur, G. Srivastava and R. C. Mehrotra, *Indian J. Chem.*, *12*, 399 (1974).
6 R. C. Mehrotra and V. D. Gupta, *J. Indian Chem. Soc.*, *40*, 911 (1963).
7 A. L. Allred and D. W. Thompson, *Inorg. Chem.*, *7*, 1196 (1968).
8 A. Henderson and A. K. Holliday, *J. Organometal. Chem.*, *4*, 377 (1965).
9 E. N. Vasanta, G. Srivastava and R. C. Mehrotra, *Inorg. Chim. Acta*, *26*, 47 (1978).
10 Y. Kawasaki and T. Tanaka, *J. Chem. Phys.*, *43*, 3396 (1965).