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# Reactions of Tin Tetraacetate with Benzothiazolines

**E. N. Sakuntala** and **Rama Shanker***

Chemistry Department, College of Science, Udaipur, 313 001, India

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Tin tetraacetate with 2,2-disubstituted benzothiazolines yields mono and disubstituted derivatives, the latter being the final product even with excess of the ligand. In the products the benzothiazoline ring of the ligands is absent, but a new azomethine group is found, thus characterising the products as tin(IV) *Schiff* base complexes. The new compounds have been characterised by elemental analysis, IR, PMR, Molecular weight determination and a conductometric study.

*[Keywords: Benzothiazolines; Tin tetraacetate; Tin(IV) Schiff base complexes]*

*Reaktionen von Zinntetraacetat mit Benzothiazolinen*

Zinntetraacetat ergibt mit 2,2-disubstituierten Benzothiazolinen mono- und disubstituierte Verbindungen, wobei letztere auch mit Überschuß an Ligand die Endprodukte darstellen. In den Produkten fehlt der Benzothiazolinring, andererseits wird eine Azomethingruppe gefunden; damit sind die Produkte als Zinn(IV)-*Schiff*-Basen-Komplexe charakterisiert. Die neuen Verbindungen wurden mittels Elementaranalysen, IR, $^1$H-NMR, Molekulargewichtsbestimmungen und Leitfähigkeitsmessungen charakterisiert.

## Introduction

Recently benzostannathiazolines have been synthesised by refluxing 2,2-disubstituted benzothiazolines with trimethyltin hydroxide or trialkyltin ethoxide in benzene. During the reaction the benzothiazoline ring is opened and a new azomethine linkage is formed with nitrogen coordinating to the tin atom in these derivatives[1]. In view of the diverse behaviour of the carboxylic group reactions of tin tetraacetate with 2,2-disubstituted benzothiazolines have been carried out. The results are reported here.

## Experimental

Synthesis of tin tetraacetate and analysis of tin metal as well as that of the acetate group were carried out as mentioned in literature[2]. Benzothiazolines were synthesised according to reported methods[3—5]. Nitrogen and sulfur were estimated by *Kjeldahl*'s[6] and *Messenger*'s methods. Molecular weights in refluxing chloroform were determined with a semi-micro Gallenkamp ebulliometer employing a thermistor sensing device.

*Reaction of tin tetraacetate with 2-phenylbenzothiazoline in 1 : 1 molar ratio*

To a toluene solution of tintetraacetate (2.51 g; 7.06 mmol) 2-phenylbenzothiazoline (1.51 g; 7.06 mmol) in toluene was added. The solution was refluxed for 8–10 h at 130 °C. The liberated acetic acid [amount of acetic acid liberated, 0.42 g; for the removal of one mole of acetic acid (calcd. 0.42 g)] was collected as azeotrope of toluene (b. p. 106 °C) and estimated against a sodium hydroxide solution using phenolphthalein as the indicator. Excess of toluene was evaporated under reduced pressure (40–50 °C/2 mm), a dark yellow solid was obtained and crystallised from hot benzene (yield, 3.50 g; 98%).

The same procedure was followed for 1 : 2 ratio and with other 2,2-disubstituted benzothiazolines as well.

Infrared spectra were recorded in the region 4 000–200 cm$^{-1}$ on a Perkin-Elmer model 522 spectrometer. Proton magnetic resonance spectra were recorded in $CDCl_3$ solutions on a Perkin-Elmer R 12 B-Spectrometer, using *TMS* as an external standard.

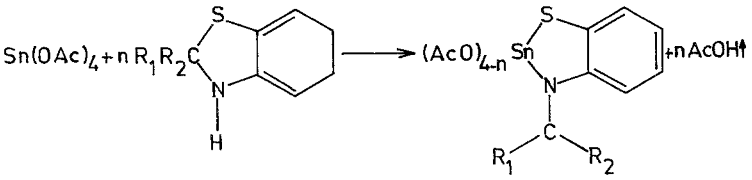
Table 1. *Reactions of tin tet*

| $Sn(OAc)_4$ (g) | $R_1R_2CNHC_6H_4S$ (g) | Acetic acid (g) found (calcd.) | Compd. formed (No.) |
|---|---|---|---|
| 2.30 | $R_1 = R_2 = Me$<br>1.07 | 0.33<br>(0.39) | $(AcO)_3SnSC_6H_4NCMe_2$ **(1)** |
| 2.10 | $R_1 = Me$, $R_2 = Et$<br>1.05 | 0.34<br>(0.35) | $(AcO)_3SnSC_6H_4NCMeEt$ **(2)** |
| 1.35 | $R_1 = Me$; $R_2 = i\text{-}Bu$<br>0.7861 | 0.23<br>(0.23) | $(AcO)_3SnSC_6H_4NCMe\ i\text{-}Bu$ **(3)** |
| 2.51 | $R_1 = H$; $R_2 = Ph$<br>1.51 | 0.42<br>(0.42) | $(AcO)_3SnSC_6H_4NCHC_6H_5$ **(5)** |
| 2.02 | $R_1 = Me$; $R_2 = Ph$<br>1.29 | 0.33<br>(0.34) | $(AcO)_3SnSC_6H_4NCMePh$ **(5)** |
| 0.79 | $R_1 = R_2 = Me$<br>0.73 | 0.26<br>(0.27) | $(AcO)_2Sn(SC_6H_4NCMe_2)_2$ **(6)** |
| 1.65 | $R_1 = Me$; $R_2 = Et$<br>1.66 | 0.55<br>(0.56) | $(AcO)_2Sn(SC_6H_4NCMeEt)_2$ **(7)** |
| 1.45 | $R_1 = Me$; $R_2 = i\text{-}Bu$<br>1.68 | 0.48<br>(0.49) | $(AcO)_2Sn(SC_6H_4NCMe\ i\text{-}Bu)_2$ **(8)** |
| 1.15 | $R_1 = H$; $R_2 = Ph$<br>1.38 | 0.37<br>(0.37) | $(AcO)_2Sn(SC_6H_4NCHC_6H_5)_2$ **(9)** |
| 1.08 | $R_1 = Me$; $R_2 = Ph$<br>1.38 | 0.35<br>(0.36) | $(AcO)_2Sn(SC_6H_4NCMePh)_2$ **(10)** |

## Results and Discussion

Reactions of tin tetraacetate with 2,2-disubstituted benzothiazolines can be represented as shown in Scheme 1.

*Scheme 1*



*$R_1 = Me$; $R_2 = Me$, $Et$, $i$-$Bu$, and $Ph$*

$R_1 = \mathrm{H}$, $R_2 = Ph$; $n = 1, 2$

*cetate with benzothiazolines*

| eld<br>%) | M.P.<br>°C | Mol. Wt.<br>found<br>(calcd.) | Analyses (%) found (calcd.) | | | |
|---|---|---|---|---|---|---|
| | | | Sn | *Ac*O | N | S |
| 2 | 261–262 | 438 | 25.64 | 38.23 | 3.13 | 6.82 |
| | | (460) | (25.80) | (39.13) | (3.04) | (6.96) |
| 7 | 272–274 | 452 | 24.92 | 12.52 | 3.01 | 6.82 |
| | | (474) | (25.03) | (12.66) | (2.95) | (6.76) |
| 5 | 284–286 | 520 | 23.78 | 12.34 | 2.64 | 6.31 |
| | | (501) | (23.65) | (11.97) | (2.79) | (6.38) |
| 8 | 240–242 | 530 | 23.01 | 33.32 | 2.72 | 6.15 |
| | | (508) | (23.36) | (35.42) | (2.75) | (6.30) |
| 7 | 208–209 | 518 | 23.01 | 10.82 | 2.91 | 6.02 |
| | | (522) | (22.74) | (11.50) | (2.68) | (6.14) |
| 8 | 226–228 | 538 | 21.13 | 20.32 | 4.84 | 11.41 |
| | | (565) | (21.01) | (21.24) | (4.96) | (11.31) |
| 8 | 258–260 | 560 | 19.98 | 20.11 | 4.64 | 9.82 |
| | | (593) | (20.01) | (20.24) | (4.72) | (10.80) |
| 6 | 268–270 | 630 | 18.02 | 18.67 | 4.01 | 9.78 |
| | | (649) | (18.29) | (18.51) | (4.32) | (9.88) |
| 8 | 210–212 | 701 | 18.20 | 16.21 | 4.32 | 9.82 |
| | | (661) | (17.95) | (18.14) | (4.23) | (9.69) |
| 8 | 188–190 | 650 | 16.89 | 17.38 | 3.98 | 9.21 |
| | | (689) | (17.22) | (17.42) | (4.06) | (9.30) |

The products are generally yellow crystalline solids, soluble in common organic solvents. They have sharp melting points. Molecular weight determination in refluxing chloroform indicated their monomeric nature. Conductivity measurements in nitrobenzene[7] indicated that these compounds are essentially covalent. The reactions of tin tetraacetate with the above benzothiazolines do not proceed beyond 1 : 2 ratios as indicated by the amounts of acetic acid evolved as well as by the analyses of the products obtained (Tab. 1).

Table 2. *IR frequencies (in $cm^{-1}$) and molar conductance (in $ohm^{-1}$ $cm^2$ $mol^{-1}$) of the complexes of tin tetraacetate with benzothiazolines*

| No. | $\nu$(C=O) | $\nu$(C=N) | $\nu$(Sn—S) | Molar conductance |
|---|---|---|---|---|
| **1** | 1 705 | 1 630 | 380 | 3.70 |
| **2** | 1 705 | 1 630 | 380 | 3.78 |
| **3** | 1 710 | 1 635 | 370 | 3.98 |
| **4** | 1 710 | 1 630 | 370 | 3.60 |
| **5** | 1 710 | 1 635 | 380 | 3.42 |
| **6** | 1 705 | 1 630 | 380 | 13.78 |
| **7** | 1 690 | 1 630 | 380 | 15.80 |
| **8** | 1 690 | 1 635 | 370 | 16.42 |
| **9** | 1 710 | 1 630 | 370 | 17.80 |
| **10** | 1 690 | 1 630 | 380 | 18.90 |

The IR spectra of the complexes as nujol mulls could not give much information since the resolution of the spectra was very poor. The solution spectra in carbon tetrachloride or chloroform were better resolved.

In the IR spectra of all the complexes (Tab. 2), bands due to stretching and deformation vibrations of NH group are not found in the region 3 320–3 370 $cm^{-1}$ and 1 675–1 700 $cm^{-1}$ regions[8—13]. This implies that the imino group is no longer present as such in the complexes. Instead a new peak is observed at 1 630 $cm^{-1}$ in both the types of derivatives. This peak is attributed to the stretching vibrations of the =CN-group[1,9,14,15]. This clearly indicates that during the reactions the benzothiazoline ring opens and the final products formed are the *Schiff* base complexes. The absorption due to $\nu_{as}$ (C=O) appears at 1 690–1 710 cm. The corresponding $\nu_s$ (C=O) expected at 1 330 $cm^{-1}$ appears to be masked by the ligand peaks in the same region in the 1 : 1 and 1 : 2 derivatives. The position of the carboxylic group indicates that the acetate groups remain uncoordinated[16, 17]. Sn—S stretching vibrations occur as a single peak at ~ 380 cm$^{-1}$ [18].

In the PMR spectra (Tab. 3) of all the 1 : 1 and 1 : 2 derivatives a sharp singlet observed at $\delta$ 4.4 ppm due to the proton attached to N of the benzothiazoline ring completely disappears. The acetate protons are observed as a sharp singlet in the region 2.1 and 1.8 ppm[2, 16] for 1 : 1 and 1 : 2 derivatives, respectively. The presence of only one peak even in case of 1 : 1 derivatives indicates probably a fast exchange amongst acetate groups at room temperature. The shift of the acetate peak in 1 : 2 derivatives shows that the acetate protons are more shielded by the presence of two ligand moieties. The aryl protons appear as a multiplet at 6.9–7.7 ppm. The azomethine proton in the 1 : 1 and 1 : 2 products of 2-phenylbenzothiazoline appears as a singlet at 8.0 ppm. This is a further confirmation of the presence of the azomethine group. —N = C*Me*$_2$ protons appear as a singlet at 2.8 ppm.

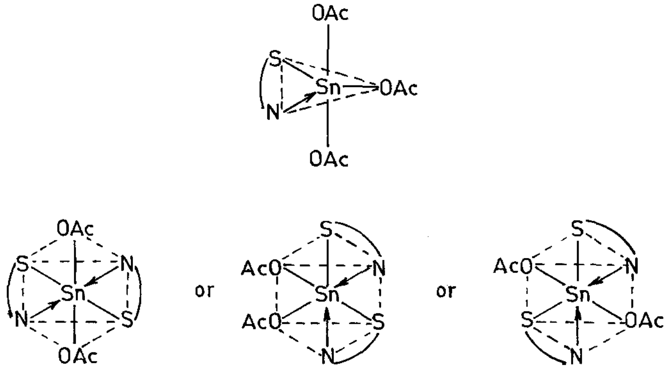
Table 3. *PMR data (in $\delta$ values) of the complexes of tin tetraacetate with benzothiazolines*

| No. | Phenyl protons | Acetate protons |
|---|---|---|
| **1** | 6.9–7.7 m | 2.1 s |
| **2** | 6.9–7.6 m | 2.3 s |
| **3** | 7.0–7.6 m | 2.1 s |
| **4** | 7.0–7.5 m | 2.1 s |
| **5** | 7.0–7.5 m | 2.2 s |
| **6** | 6.9–7.7 m | 1.8 s |
| **7** | 6.9–7.7 m | 1.9 s |
| **8** | 7.0–7.6 m | 1.8 s |
| **9** | 7.1–7.6 m | 1.8 s |
| **10** | 6.9–7.6 m | 1.8 s |

In the trialkyltin derivatives of 2,2-dimethylibenzothiazoline, the resonance due to = C*Me*$_2$ protons appear as two singlets of equal height at 1.8 ppm[1] while one singlet at 1.7 ppm is observed in the spectrum of the ligand; therefore both —N = C*Me*$_2$ methyls are magnetically nonequivalent in the trialkyltin(IV) complexes.

Based on IR and PMR spectra of 1 : 1 and 1 : 2 products, tin may be tentatively assigned coordination numbers 5 and 6, respectively. The structures shown in Scheme 2 may be tentatively proposed for the 1 : 1 and 1 : 2 derivatives.

*Scheme 2*



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