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A new general method for the preparation of bis(acetylacetonato)dihalogenotin(IV) by action of molecular oxygen on tin(II) halides in acetylacetone

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Abstract

A new general method for the preparation of bis(acetylacetonato)dihalogenotin (IV) by bubbling of oxygen through a solution (or suspension) of tin(II) halides in acetylacetone is described.

Up to now three different routes to bis(acetylacetonato)dihalogenotin(IV) have been reported. Substitution of the two halogen atoms in tetrahalide tin(IV) for acetylacetone was the first route:

$$SnX_4 + Hacac \rightarrow Sn(acac)_2X_2 + 2HX \qquad (1)$$

$Sn(acac)_2F_2$ [1], $Sn(acac)_2Cl_2$ [2–5] and $Sn(acac)_2Br_2$ [5] were obtained by this route. The second route entailed the replacement of phenyl in $SnPh_2X_2$ (X = Cl, Br, I) with acetylacetone [6–8] in the complexes $Sn(acac)_2X_2$ (X = Cl, Br, I):

$$SnPh_2Cl_2 + 2Hacac \rightarrow Sn(acac)_2Cl_2 + 2PhH \qquad (2)$$

$$Sn(Ph)_4 + SnX_4 + 4Hacac \rightarrow 2Sn(acac)_2X_2 + 4PhH \quad (X = Br, I) \qquad (3)$$

To make the complexes $Sn(acac)_2X_2$ (X = Br, I), the third and last method involving the following reactions [1,3,5] was used:

$$SnBr_4 + Cu(acac)_2 \rightarrow Sn(acac)_2Br_2 + CuBr_2 \qquad (4)$$

$$SnI_4 + Na(acac) \rightarrow Sn(acac)_2I_2 + 2NaI \qquad (5)$$

The characteristic feature of reactions 1–5 is that $Sn(acac)_2X_2$ is formed from the tin(IV), compounds by redistribution, and the oxidation state of tin atom remains unchanged.

We have found that complexes of the type $Sn(acac)_2X_2$ (X = F, Cl, Br, I) can be readily obtained (in contrast to previous methods [1–8]) by bubbling of molecular oxygen through a solution (or suspension) of tin(II) halide in acetylacetone according to the reaction:

$$\mathrm{SnX_2 + 1/2\ O_2 + 2Hacac \rightarrow Sn(acac)_2X_2 + H_2O} \qquad (6)$$

Tin(II) is oxidized to tin(IV) in reaction 6 under the action of molecular oxygen, with simultaneous formation of the dihalogenotin(IV)-bis-acetylacetonate) complexes.

Experimental

Reagents. SnF_2 and SnI_2 were synthesized by a procedure described previously [9]. $SnCl_2$ was obtained from reagent grade $SnCl_2 \cdot 2H_2O$ by dehydratation with acetic anhydride [10]. Reagent grade $SnBr_2$ was used without further purification. Commercial acetylacetone was distilled before use, b.p. 139 °C. Diethyl ether, hexane, chloroform were purified and dried by procedures, described previously [11].

Preparation of bis(acetylacetonato)difluorotin(IV). $Sn(acac)_2F_2$. Oxygen was bubbled for 1 h through a suspension of SnF_2 (6.25 g, 39.9 mmol) in 30 ml of hot acetylacetone (~ 70–90 °C). Acetylacetone was then removed under vacuum and $CHCl_3$ (50 ml) was added to the dry residue. The insoluble SnF_2 was then filtered off. After removal of $CHCl_3$, drying the product gave 4.6 g (33%) of white $Sn(acac)_2F_2$.

Preparation of bis(acetylacetonato)dichlorotin(IV). $Sn(acac)_2Cl_2$. Oxygen was bubbled for 1 h through a solution of 5.3 g (28 mmol) $SnCl_2$ in 30 ml of

Table 1

Identification of the $Sn(acac)_2X_2$ complexes obtained

Complex	Melting point (°C) [a]	Results of elemental analysis, (found/calcd.)(%))			Chemical shift, ppm, relative to TMS. [b]	
					CH_3 [c]	CH=
$Sn(acac)_2F_2$	not identified (225–226 [1])	3.58/3.98	33.55/33.84	11.47/10.71	2.14; 2.22 (2.18) [d]	5.72 (5.66) [d]
$Sn(acac)_2Cl_2$	204.5–205.5 (203–205[1]) (202 [2]) (202–203 [3,5]) (203–204 [8])	3.25/3.64	29.91/30.97	18.35/18.28	2.12; 2.21 (2.11; 2.20)	5.72 (5.69)
$Sn(acac)_2Br_2$	189.5–191.5 (183–185 [1,8]) (186–187 [3,5])	2.90/2.96	24.35/25.20	33.73/33.52	2.10; 2.20 (2.10; 2.19)	5.71 (5.72)
$Sn(acac)_2I_2$	179–181 (179–182 [1]) (179–180 [5]) (178–179 [8])	2.56/2.48	20.17/21.00	43.41/44.47	2.07; 2.17 (2.07; 2.17)	5.74 (5.73)

[a] Data in parentheses are given for comparison with the melting points obtained previously. [b] ^{1}H NMR spectra were recorded on a Bruker CXP-300 spectrometer (300.066 MHz) in $CDCl_3$, T 293 K. Chemical shifts were measured relative to an internal standard, hexamethyldisiloxane, HMDSO, taking into account that δ(HMDSO) 0.055 ppm. [c] Two signals from the CH_3 group are due to a *cis*-disposition of the acac ligands [1]. Chemical shifts in parentheses are those taken from refs. 1 and 8. [d] T 310 K.

acetylacetone for 10 min. The white precipitate that formed, was then filtered off, washed with dry ether (2 × 10 ml), and dried under vacuum. Yield 9.3 g (85%). It should be noted here that $Sn(acac)_2Cl_2$ is readily obtained from an acetylacetone solution of $SnCl_2$ (or $SnCl_2 \cdot 2H_2O$) quantitatively when left to stand in air for some days. The formation of $Sn(acac)_2Cl_2$ in degassed solutions was not observed.

Preparation of bis(acetylacetonato)dibromotin(IV). $Sn(acac)_2Br_2$. Oxygen was bubbled for 1 h through a suspension of 7.50 g (26.9 mmol) $SnBr_2$ in 30 ml of hot acetylacetone. The white precipitate that formed was filtered off, washed with dry ether (10 ml), and dried under vacuum to give 4.9 g $Sn(acac)_2Br_2$. Hexane was then added to the mother liquor, and more white product separated, which further was treated as in the previous case. An additional 5.7 g of the product was obtained. Total yield 82%.

Preparation of bis(acetylacetonato)diiodotin(IV). $Sn(acac)_2I_2$. Oxygen was bubbled through a suspension of 7.10 g (19.1 mmol) SnI_2 in 30 ml of warm (~ 40 °C) acetylacetone for 20 min until the red SnI_2 had entirely dissolved. The white precipitate, that formed during the bubbling of oxygen, was filtered off, washed with dry ether (10 ml) and dried under vacuum. A light yellow product (5.8 g) was obtained. Hexane was then added to the mother liquor and the white precipitate that resulted was filtered off, and washed with hexane and dry ether. This procedure gave more of the product (3.9 g). Total yield 89%.

Results of the elemental analysis of the isolated $Sn(acac)_2X_2$ complexes as well as melting points and ^1H NMR data as compared with those of previously known completes are given in Table 1. Our results are in good agreement with those obtained previously by others.

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