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PREPARATION AND PROPERTIES OF ORGANO(ACETYLACETONATO)-ANTIMONY(V) COMPOUNDS

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SUMMARY

Organo(acetylacetonato)antimony(V) compounds of the types R_2SbCl_2Acac, $R_4SbAcac$, $PhSbCl_3Acac$ and $Cl_4SbAcac$ have been synthesized. The compounds are monomeric in solution. IR and PMR data of these compounds, which contain a chelated Acac ligand have been discussed. Ph_2SbCl_2Acac shows abnormal behaviour, in that in chloroform solution a non-chelated configuration in which the Acac group is probably C-bonded, is also present.

INTRODUCTION

Recently the structure of pentavalent organoantimony compounds has received considerable attention[1]. The coordination behaviour of compounds R_n-$SbX_{(5-n)}$ ($n = 1$–4), in which X is a potentially bidentate ligand, is of special interest. Two groups have studied the IR spectra of trimethylantimony(V) derivatives Me_3-SbX_2 containing such ligands[2a,b]. Japanese workers have reported the synthesis and properties of tetrachloro(acetylacetonato)antimony $Cl_4SbAcac$ and of phenyltrichloro(acetylacetonato)antimony $PhSbCl_3Acac$[3,4].

The present paper deals with the preparation of some novel organo(acetylacetonato)antimony compounds of the type R_2SbCl_2Acac and $R_4SbAcac$*.

RESULTS AND DISCUSSION

Preparation

Organo(acetylacetonato)antimony(V) compounds R_2SbCl_2Acac (R = Me and Et) were prepared by dissolving the corresponding dialkylhydroxo(oxo)antimonies[5] in a mixture of concentrated hydrochloric acid and acetylacetone and extracting this solution with methylene chloride (*cf.* ref. 3b). The corresponding phenyl derivative was easily obtained by refluxing diphenyltrichloroantimony with acetylacetone in carbon tetrachloride.

Organo(acetylacetonato)antimony(V) compounds of the type $R_4SbAcac$ were obtained in quantitative yield by reacting acetylacetone with the corresponding R_4SbOMe derivatives (R = Ph[6a,b], Me, Et[7]).

* After this paper had been completed a recent study of $Ph_4SbAcac$ has come to our attention[15].

TABLE 1

ANALYTICAL AND PHYSICAL DATA FOR SOME ORGANO(ACETYLACETONATO)ANTIMONY(V) COMPOUNDS

Compound	M.p. (°C)	Molecular weight		Sb (%)		Cl (%)	
		Found	Calcd.	Found	Calcd.	Found	Calcd.
$Cl_4SbAcac$	131[a]	367	363	32.71	33.57	39.78	39.10
$PhSbCl_3Acac$	176–178(dec.)[b]	409	405	30.30	30.11	25.32	25.40
Ph_2SbCl_2Acac	180–190(dec.)	484	446	27.55	27.35	16.25	15.92
Me_2SbCl_2Acac	~ 150(dec.)	369[c]	322	38.21	37.88	22.85	22.05
Et_2SbCl_2Acac	102–104	364	350	34.99	34.85	20.87	20.20
$Ph_4SbAcac$	205–209(dec.)	522	529	22.32	23.06		
$Me_4SbAcac$	47–48[d]	291	281	43.68	43.32		
$Et_4SbAcac$	[e]	340	337	36.64	36.11		

[a] Reported[3b] 131°. [b] Reported[3b] 176–178°. [c] Difficult to determine because of limited solubility in benzene. [d] B.p. 102–103° (19 mm). [e] B.p. 84° (0.12 mm).

$Cl_4SbAcac$ and $PhSbCl_3Acac$ have been prepared as reported[3b].

Attempts to prepare compounds of the type $R_3SbClAcac$ were unsuccessful.

All organo(acetylacetonato)antimony(V) compounds, including the two reported by Okawara *et al.*[3b], were found to be monomeric in benzene solution at room temperature.

Melting points, analytical and molecular weight data for the various compounds prepared are given in Table 1.

Infrared spectra

Infrared spectral data in the region 2000–400 cm^{-1} for the various compounds are given in the experimental part. Table 2 shows the IR absorptions in the C=O, C=C stretching region.

For each of the organo(acetylacetonato)antimony(V) compounds described in this paper the position of the absorptions connected with the acetylacetonate ligand is very similar to the values reported for other metal acetylacetonates in which the

TABLE 2

INFRARED ABSORPTIONS OF SOME ORGANO(ACETYLACETONATO)ANTIMONY(V) COMPOUNDS IN THE 2000–1500 cm^{-1} REGION[a]

Compound	C=O	C=C
$Cl_4SbAcac$[b]	1548	1546
$PhSbCl_3Acac$[b]	1563, 1555	1546
Ph_2SbCl_2Acac[c]	1563	1537
Me_2SbCl_2Acac	1563	1527
Et_2SbCl_2Acac	1565	1527
$Ph_4SbAcac$	1587, 1575	1527
$Me_4SbAcac$	1587	1511, 1503
$Et_4SbAcac$	1585	1506, 1499

[a] The Sb–Acac absorptions have been tentatively assigned according to Behnke and Nakamoto[8]. [b] The IR data obtained for $Cl_4SbAcac$ and $PhSbCl_3Acac$ differ only slightly from the reported values[3a,4]. [c] An additional C=O absorption at 1715 cm^{-1} was observed in the chloroform solution spectrum.

acetylacetonate group acts as a bidentate ligand[9a,b]. These results indicate the presence of hexa-coordinated antimony in these compounds (*cf.* ref. 3a and 4).

One would expect the strength of the Sb–O coordinate bond to increase and ν(C=O) to decrease upon increasing the number of electron-withdrawing substituents at antimony. Indeed, as can be seen from Table 2 the C=O stretching frequency decreases when the organic ligands around antimony are successively replaced by chlorine. Okawara *et al.*[3a] observed the same phenomenon in their study of organotin acetylacetonates.

A rather interesting result is the difference between the spectrum of Ph_2SbCl_2-Acac in nujol and in chloroform solution. Whereas the nujol spectrum shows only one strong band at 1563 cm^{-1}, the $CHCl_3$ spectrum displays an additional weak band at 1715 cm^{-1}. This result indicates that whereas in the solid state Ph_2SbCl_2Acac occurs only in the hexa-coordinate form a penta-coordinate form with a non-chelating acetylacetonate group [ν(C=O) 1715 cm^{-1}] is also present to some extent in chloroform solution.

The assignments of the absorption bands in the region 600–400 cm^{-1} have to be tentative, as coupled vibrations will occur. In the spectra of the phenyl derivatives the strong phenyl absorptions at approximately 460 cm^{-1} (see also ref. 10) partly obscure the Sb–O stretching mode. The Sb–C stretching modes for Me_2SbCl_2Acac are most probably obscured by the strong acetylacetonate π-band[9a] at 564 cm^{-1}.

It seems reasonable to assume, that in the R_2SbCl_2Acac compounds, the R groups will occupy equatorial positions, whereas the two chlorine atoms occupy the axial positions. A structure with two phenyl groups occupying equatorial positions has been established for Ph_2SbCl_3 using X-ray spectroscopy[11]. The appearance of two absorption bands of weak intensity at 553 and 493 cm^{-1} in the nujol spectrum of Et_2SbCl_2Acac, which are assigned to the antisymmetric and the symmetric Sb–C stretching frequency respectively, further supports this assumption.

In $PhSbCl_3Acac$ it has been established that the phenyl group, together with one chlorine atom and the Acac group occupy the equatorial positions[4].

The tetramethyl- and tetraethyl(acetylacetonato)antimony compounds show a very broad band at about 520 cm^{-1}. This band, which could not be resolved, is assigned to the Sb–C stretching frequencies. The Sb–O stretching absorption for these compounds, which was not observed, probably occurs below 400 cm^{-1}.

PMR spectra

PMR spectral data for organo(acetylacetonato)antimony(V) compounds in deuterochloroform are tabulated in Table 3.

For the methyl- and ethylantimony derivatives single signals were observed for the methyl and methylene resonances.

With the exception of the spectra of $PhSbCl_3Acac$[3b,4] and Ph_2SbCl_2Acac, all compounds show one singlet due to the Acac methyl protons at δ 1.76–2.31 and one singlet due to the γ-H protons at δ 4.94–5.99 ppm.

The CH_3(Acac) and γ-H proton resonances appear at progressively lower field upon increasing the number of electron-withdrawing chlorine atoms at antimony. This reflects the increasing strength of the Sb–O coordinate bond in the order $R_4SbAcac < R_2SbCl_2Acac < RSbCl_3Acac < Cl_4SbAcac$ and agrees with the IR data.

At the magnet temperature (27°) the PMR spectrum of Ph_2SbCl_2Acac shows

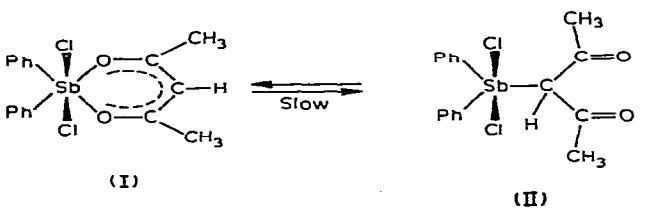
TABLE 3

PMR SPECTRAL DATA FOR SOME ORGANO(ACETYLACETONATO)ANTIMONY COMPOUNDS IN DEUTEROCHLOROFORM AT 27°

Compound	Chemical shifts (ppm[a])					
	$-CH=$	CH_3(Acac)	Ph(–Sb)	CH_3(–Sb)	$-CH_2$(–Sb)	$CH_3(-CH_2Sb)$
HAcac (enol form)	5.51[12]	2.01[12]				
$Cl_4SbAcac$[b]	5.99	2.31				
$PhSbCl_3Acac$[c]	5.91	2.23	7.51			
		2.28	8.06			
Ph_2SbCl_2Acac	5.35	1.96	7.38			
	5.79	2.13	7.90			
Me_2SbCl_2Acac	5.62	2.15		2.38		
Et_2SbCl_2Acac	5.63	2.15			2.81	1.51
$Ph_4SbAcac$	5.19	1.80	7.21			
			7.46			
$Me_4SbAcac$	5.09	1.76		1.09		
$Et_4SbAcac$	4.94	1.64			1.51	1.01

[a] Downfield from TMS, which is used as an internal standard. [b] Reported[3b,4] $-CH=$ at 6.06, CH_3(Acac) at 2.43 ppm. [c] Reported[3b,4] $-CH=$ at 5.85, CH_3(Acac) at 2.25 ppm (doublet).

two singlets at δ 1.96 and 2.13 ppm respectively, due to the Acac methyl protons and two singlets at δ 5.35 and 5.79 ppm due to the corresponding γ-H protons. The singlets at δ 1.96 and 5.35 ppm belong to one type of Acac group, while the singlets at δ 2.13 and 5.79 ppm belong to another, as for both sets an intensity ratio of 6/1 was observed. The two different Acac groups were observed to be present in a ratio 3/1. Heating the sample to 55° causes a change of this ratio to ~2.5/1, while no variation in chemical shift is observed. This change was shown to be reversible. Measurements at lower temperatures were prevented by the low solubility of Ph_2SbCl_2Acac in $CDCl_3$ or in other suitable solvents. These results combined with the observations from the IR spectrum, indicate that in $CHCl_3$ solution Ph_2SbCl_2Acac exists for about 75% in the chelated configuration (I) (Acac proton resonance signals at 1.96 and 5.35 ppm), which is in slow equilibrium with the non-chelated configuration (II) (signals at 2.13 and 5.79 ppm).



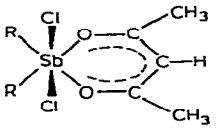
(I) (II)

The PMR data suggest, that for the non-chelated configuration, (II), the Acac group is symmetrically bonded to antimony by the γ-carbon atom, rather than by oxygen, because the methyl protons give rise to only one sharp singlet, which occurs at even lower field than the corresponding singlet of the chelated Acac group in (I) (*cf.* ref. 13 for a discussion of the PMR spectra of C-bonded platinum acetylacetonates). The two phenyl groups in (I) are either in equatorial or in axial positions, as an un-

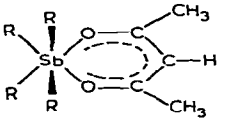
symmetrical arrangement of these groups around antimony would result in the appearance of two singlets for the two non-equivalent methyl groups of the chelated Acac group. Assuming that the chlorine atoms occupy axial positions[11] the structures (I) and (II) are proposed for the chelated and the non-chelated configuration.

Combined IR and PMR spectral evidence suggests a symmetrical structure (III) for R_2SbCl_2Acac (R = Me and Et).

The $R_4SbAcac$ derivatives (IV) (R = Me, Et, Ph) according to the IR and PMR data occur only in the chelated configuration.



(III)



(IV)

Non-equivalence of the equatorial and axial organic groups could not be observed. The PMR spectrum of $Me_4SbAcac$ in chloroform showed even at $-40°$ only one CH_3–Sb resonance indicating the presence of a non-rigid structure for this molecule in solution (*cf.* ref. 14).

EXPERIMENTAL PART

General

The IR spectra measured in the range 2000–400 cm^{-1} were run as mulls in nujol between KBr disks for the solid compounds [$Cl_4SbAcac$, $PhSbCl_3Acac$, R_2SbCl_2Acac (R = Me, Et and Ph) and $Ph_4SbAcac$] and as a liquid between AgCl disks for $R_4SbAcac$ (R = Me and Et). In order to obtain a better resolution in the range 1800–1400 cm^{-1} the spectra were also recorded as solutions in chloroform. All IR spectra were run on a Grubb–Parsons Spectromaster.

The PMR spectra were measured as solutions in deuterochloroform at 27° using a Varian Associates HA-100 spectrometer.

Molecular weights were measured on ~5% solutions in benzene, using a Mechrolab dynamic vapour pressure osmometer.

Analytical and physical data are given in Table 1.

Tetrachloro(acetylacetonato)antimony and phenyltrichloro(acetylacetonato)-antimony were prepared as reported in the literature[3b,4].

Preparation of organo(acetylacetonato)antimony(V) compounds

Diphenyldichloro(acetylacetonato)antimony

Diphenyltrichloroantimony 4.05 g (10.5 mmoles) was dissolved in a mixture of carbon tetrachloride (25 ml) and acetylacetone (1.05 g, 10.5 mmoles).

The reaction mixture was kept at reflux temperature for 15 min, after which the solvent was evaporated. The remaining yellow-brown solid afforded after repeated recrystallization from chloroform. 2.19 g of Ph_2SbCl_2Acac as a colourless crystalline solid. Yield 44.8%.

IR spectrum [s = strong, m = medium, w = weak, vw = very weak, (sh) =

shoulder, (br) = broad]: 1715* w, 1563 s, 1537 s, 1351 m, 1282 m, 1183 m, 1164 vw, 1160 vw, 1099 vw, 1070 vw, 1064 vw, 1058 vw, 1031 m, 1020 m, 999 m, 935 m, 917 (sh), 817 m, 736 s, 686 s, 655 vw, 649 vw, 574 m, 465 s, 462 (sh), 458 (sh), 421 m.

Dimethyldichloro(acetylacetonato)antimony

Dimethylhydroxo(oxo)antimony (1.3 g, 7.0 mmoles) was dissolved in a mixture of concentrated hydrochloric acid (25 ml) and acetylacetone (2 ml). The reaction mixture was extracted with methylenechloride. After evaporation of the solvent the remaining yellow-brown solid afforded after repeated recrystallization from chloroform/pentane, Me_2SbCl_2Acac (0.7 g) as a colourless crystalline solid. Yield 31.8%.

IR spectrum: 1563 s, 1527 s, 1429 w, 1351 s, 1282 m, 1022 s, 935 s, 859 m (br), 813 s, 770 vw, 722 vw, 670 m, 653 m, 584 w, 564 s, 431 m (br), 408 m (br).

Diethyldichloro(acetylacetonato)antimony

This compound was isolated in 38.4% yield as a colourless crystalline solid, by essentially the same procedure.

IR spectrum: 1565 s, 1527 s, 1410 w, 1340 s, 1282 m, 1190 m, 1031 m, 980 w, 961 w, 937 m, 813 m, 787 vw, 725 m, 669 m, 653 w, 566 m, 553 w, 495 w (br), 427 m (br), 409 m (br).

Tetraphenyl-, tetramethyl- and tetraethyl(acetylacetonato)antimony

These compounds were obtained in quantitative yield upon addition of acetylacetone in a 1/1 molar ratio to a benzene solution of the corresponding tetraphenyl- or tetraalkylmethoxoantimony compounds.

$Ph_4SbAcac$. IR spectrum: 1587 s, 1575 s, 1527 s, 1488 m, 1435 s, 1376 s, 1337 w, 1312 w, 1263 m, 1190 w, 1161 vw, 1099 vw, 1066 m, 1020 m, 999 w–m, 972 vw, 926 m, 857 vw, 795 m, 787 m, 740 (sh), 737 s, 733 s, 695 s, 664 w, 657 w, 643 w, 617 vw, 568 w, 537 w, 475 m, 465 m, 458 (sh), 454 m.

$Me_4SbAcac$. IR spectrum: 1587 s, 1503 s, 1449 s, 1375 s, 1299 w, 1235 m, 1199 m, 1163 w (sh), 1010 s, 970 m, 948 w (sh), 912 m, 836 vw, 810 w, 763 m, 704 m–s, 680 m (sh), 649 m, 621 vw, 602 vw, 534 m, 515 m (br).

$Et_4SbAcac$. IR spectrum: 1585 s, 1506 s (br), 1449 s (br), 1290 m, 1235 m, 1205 m, 1171 m, 1000 s (br), 948 m, 914 w, 823 vw, 775 m (br), 714 m–s (br), 680 w, 648 vw, 621 w (br), 531 m (br).

Attempts to prepare compounds of the type $R_3SbClAcac$

After keeping a mixture of R_3SbCl_2 (R = Me, Ph) and acetylacetone in carbon tetrachloride at reflux temperature for several hours R_3SbCl_2 was recovered almost quantitatively.

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* Only observed in a chloroform solution spectrum.

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