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The Crystal and Molecular Structures of Three (Acetylacetonato)organoantimony(V) Compounds, [(acac)R$_n$SbX$_{4-n}$]

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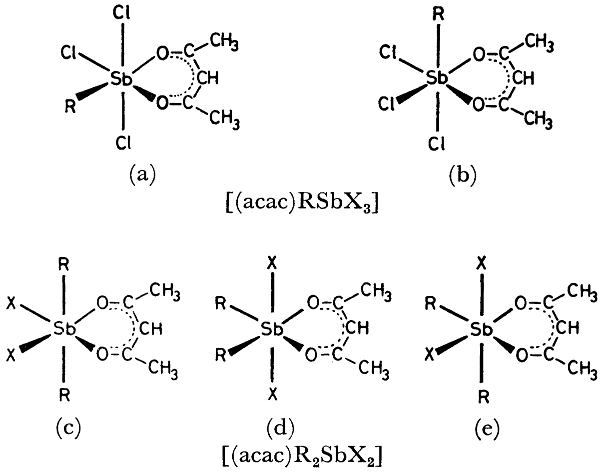
X-Ray crystal structure analyses of three (acetylacetonato)organoantimony(V) compounds have been conducted. Crystals of [(acac)MeSbCl$_3$] belong to the tetragonal system: a=13.865(1), c=24.935(5) Å, space group I4$_1$/a with Z=16. [(acac)Me$_2$SbBr$_2$] forms monoclinic crystals: a=9.247(1), b=7.695(1), c=9.104(1) Å, β=106.94(1)°, space group P2$_1$/m with Z=2. Crystals of [(acac)Ph$_2$SbCl$_2$] (high-melting point form) belong to the monoclinic system: a=14.733(11), b=7.541(1), c=16.014(13) Å, β=92.66(1)°, space group P2$_1$/c with Z=4. All structures have been elucidated by the heavy atom method and refined by the block-diagonal least-squares procedure. Through the three compounds, the antimony atoms have a slightly distorted octahedral geometry with substituents on apical positions, slightly bent towards the planar acetylacetonato groups.

The chemistry of (acetylacetonato)organoantimony(V) compounds of the type [(acac)R$_n$SbCl$_{4-n}$] (n=1 and R=Me, Et, or Ph; n=2 and R=Me, Et, or Ph; n=3 and R=Ph; and n=4 and R=Me, Et, or Ph)†† has been the subject of a number of recent papers.[1-6] Among them there are two possible configurations for [(acac)RSbCl$_3$], and three for [(acac)R$_2$SbCl$_2$] (Fig. 1). Spectroscopic studies of these two types of compound left some ambiguities on their molecular structures.[2,4,5,7] In order to determine the exact configuration of these molecules by X-ray diffraction, (acetylacetonato)methyltrichloroantimony(V) [(acac)MeSbCl$_3$], (acetylacetonato)dimethyldibromoantimony(V) [(acac)Me$_2$SbBr$_2$], and (acetylacetonato)diphenyldichloroantimony(V) [(acac)Ph$_2$SbCl$_2$] have been chosen as typical examples of [(acac)RSbCl$_3$] and [(acac)R$_2$SbCl$_2$]. As [(acac)Me$_2$SbCl$_2$] was untsable in the solid state, crystals of [(acac)Me$_2$SbBr$_2$] which were considered to have the same configuration as [(acac)Me$_2$SbCl$_2$] were subjected to X-ray structure analysis. Recrystallization of ([acac)Ph$_2$SbCl$_2$] from benzene gave two kinds of crystals in different forms: long prismatic (mp 192 °C) and rhombohedral (mp 184.5 °C) crystals (Table 1). This promoted the crystal structure analysis of two forms which may consist of molecules of different configurations. Kroon[8] determined the X-ray molecular structure of the low-melting point form, independently, which agrees well with the results obtained by the present authors.[9] Therefore, the crystal structure analysis of only the high-melting point form will be described. Brief accounts of the X-ray molecular structure of the above-mentioned compounds have been published.[10-12]



(a) (b)
[(acac)RSbX$_3$]

(c) (d) (e)
[(acac)R$_2$SbX$_2$]

Fig. 1. Possible configurations of [(acac)RSbX$_3$] ((a) and (b)) and [(acac)R$_2$SbX$_2$] ((c), (d), and (e)). X=Cl or Br.

Experimental

Crystal Data. Crystals were all supplied by Professor R. Okawara and co-workers of this university. The unit-cell dimensions of [(acac)MeSbCl$_3$] and [(acac)Me$_2$SbBr$_2$] were determined by the least-squares fit of 2θ values of high angle reflections measured on a G. E. Single Crystal Orienter equipped on a Rigaku SG-2 goniometer. Those of [(acac)Ph$_2$SbCl$_2$] were determined from Weissenberg photographs taken around the b and c axes, on which the Debye lines of tungsten were superimposed for calibration. In all cases nickel-filtered Cu $K\alpha$ radiation (λ=1.5418 Å) was used. Density measurements were carried out by the flotation method. Crystal data are given in Table 1.

Crystal structure analysis of [(acac)Me$_2$SbCl$_2$] instead of [(acac)Me$_2$SbBr$_2$] had been first intended, however, it was found during the preliminary X-ray work that all the [(acac)Me$_2$SbCl$_2$] single crystals examined readily decomposed at room temperature to give powder patterns. Approximate unit-cell parameters were determined from oscillation and Weissenberg photographs: a=9.00, b=7.59, c=9.05 Å, β=107.4°, U=590 Å^3, space group P2$_1$ or P2$_1$/m, D_c=1.82 g·cm^{-3} for Z=2. These facts suggest that [(acac)Me$_2$SbCl$_2$] is isomorphous or at least iso-structural with [(acac)Me$_2$SbBr$_2$].

Intensities. *[(acac)MeSbCl$_3$] and [(acac)Me$_2$SbBr$_2$]*: Intensities were measured on a Rigaku automated, four-circle-

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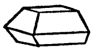
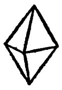
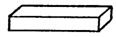
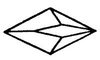
†† acac: acetylacetonato group, Me: methyl group, Et: ethyl group, and Ph: phenyl group.

Table 1. Crystal data

Compound	[(acac)MeSbCl$_3$]	[(acac)Me$_2$SbBr$_2$]	[(acac)Ph$_2$SbCl]	
			High-melting point form	Low-melting point form[8]
$F.W.$	342.5	410.74	445.98	445.98
Crystal	colorless polyhedral	colorless square bipyramidal	colorless long prismatic	colorless rhombohedral
				[a] 
Crystal system	tetragonal	monoclinic	monoclinic	monoclinic
Systematic absence of reflections	$h+k+l=2n$ $00l$, $l=4n$ $hk0$, $h=2n$ $k=2n$	$0k0$, $k=2n$	$00k$, $k=2n$ $h0l$, $l=2n$	$0k0$, $k=2n$ $h0l$, $l=2n$
Space group	I4$_1$/a	P2$_1$/m	P2$_1$/c	P2$_1$/c
a [Å]	13.685(1)	9.247(1)	14.733(11)	13.24
b [Å]		7.695(1)	7.541(1)	9.22
c [Å]	24.935(5)	9.104(1)	16.014(3)	15.49
β [°]		106.94 (1)	92.66 (1)	109.24
U [Å^3]	4669.8	619.7 (1)	1777.2	1785.3
D_m [g·cm^{-3}]	1.95 (ZnBr$_2$ aq solution)	2.21 (CH$_3$Br/C$_2$H$_5$OH)	1.66 (ZnI$_2$ aq solution)	—
Z	16	2	4	4
D_x [g·cm^{-3}]	1.95	2.20	1.67	1.66
μ [cm^{-1}]	30	91	156	161

a) Our observation.

diffractometer using zirconium-filtered Mo $K\alpha$ radiation. The θ-2θ scan technique was employed, scan rate being 4° min^{-1}. The scan width in 2θ was from $-1.0°$ from the $K\alpha_1$ to 1.0° from $K\alpha_2$ peak, where θ_c is the calculated value of the Bragg angle using λ(Mo $K\alpha_1$) (=0.70926 Å). Backgrounds were measured for 10 s before and after the scan of each peak. Totals of 2270(sin $\theta/\lambda \leqq 0.64$) and 1454(sin $\theta/\lambda \leqq 0.64$) independent reflections were collected, of which 206 and 72 reflections were classified as unobserved, respectively. Two and three standard reflections (004 and 080, and 400, 005, and 040) were measured after every 25 and 50 reflections for [(acac)MeSbCl$_3$] and [(acac)Me$_2$SbBr$_2$], respectively. Lorentz and polarization corrections were made by the AICOM-C$_2$ computer attached to the diffractometer. Absorption correction was made for the [(acac)Me$_2$SbBr$_2$] data.

[(acac)Ph$_2$SbCl$_2$]: Using nickel-filtered Cu $K\alpha$ radiation, layers from 0 through 4 around the b axis were recorded by the multiple-film Weissenberg technique. Reflections of the layers from 0 through 2 around the c axis were also collected mainly for the interlayer scaling. Intensities were estimated visually by using a calibrated standard scale. A total of 1720 (1453 non-zero) independent reflections were obtained. Lorentz and polarization effects were corrected but no absorption correction was made.

Elucidation of the Structure

All the structures of the three complexes have been elucidated by the heavy atom method.

[(acac)MeSbCl$_3$]: The position of the antimony atom was readily reduced from a three-dimensional Patterson map, and the positions of the non-hydrogen atoms by the successive Fourier syntheses.

[(acac)Me$_2$SbBr$_2$]: The systematic absence of reflection determined the corresponding space group as either P2$_1$/m or P2$_1$. Since the unit-cell contains two molecules, the following three possible cases have been examined: (1) P2$_1$/m, with the acac ligand positioned on the mirror plane, (2) P2$_1$/m, with the acac perpendicular to the mirror plane, or (3) P2$_1$, with the molecule itself having no symmetry. Approximate positions of the antimony and two bromine atoms obtained from the three-dimensional Patterson function excluded case (2). All the non-hydrogen atoms were located by the successive Fourier syntheses.

[(acac)Ph$_2$SbCl$_2$]: From the three-dimensional Patterson map, two sets of possible locations were obtained for the antimony and two chlorine atoms; (1) Sb (0.24, 0.25, 0.43), Cl (1) (0.30, 0.07, 0.53) and Cl(2) (0.14, 0.03, 0.39), or (2) Sb (0.24, 0.25, 0.43), Cl (1) (0.30, 0.43, 0.53), and Cl (2) (0.14, 0.03, 0.39). The successive two sets of Fourier syntheses favored the former parameters set, and located the non-hydrogen atoms.

Refinement

The structures determined were all refined by the block-diagonal least-squares procedure, the function minimized being $\Sigma w(\Delta F)^2$ using the HBLS V program.[13] Neutral atomic scattering factors used were taken from those of Hanson and co-workers.[14]

[(acac)MeSbCl$_3$]: The final $R_1=\sum||F_o|-|F_c||/\sum|F_o|=0.059$ and $R_2=\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2=0.059$ for 2064 non-zero reflections. The weighting scheme applied was: $w=(|F_{\max}|/|F_o|)^2$ for $|F_o|\geqq 40.0$, $w=1.0$ for $40.0\geqq|F_o|\geqq 15.0$, and $w=0.2$ for $|F_o|<15.0$.

[(acac)Me$_2$SbBr$_2$]: Two possible space group struc-

tures, $P2_1$ and $P2_1/m$ were refined isotropically, and a reasonable result obtained for $P2_1/m$. At the final stage of the refinement $F(020)$ was omitted from the calculation since it was largely affected by the extinction. Final anisotropic refinements with unit weight gave $R_1=0.076$ for 1381 non-zero reflections.

[(acac)Ph$_2$SbCl$_2$]: Anisotropic temperature factors were applied for the antimony and two chlorine atoms and w was taken as unity. The final $R_1=0.12$ for 1453 non-zero reflections.

The final positional and thermal parameters are given in Tables 2 and 3,[†††] respectively.

Table 2. The atomic fractional coordinates ($\times 10^4$) along with their estimated standard deviation in parentheses

Atom	x	y	z
[(acac)MeSbCl$_3$]			
Sb	2161 (4)	3193 (4)	188 (2)
Cl (1)	3089 (21)	3749 (19)	917 (10)
Cl (11)	1519 (21)	1870 (21)	688 (12)
Cl (21)	2978 (19)	4271 (21)	−411 (11)
O (1)	3328 (39)	2295 (46)	42 (24)
O (2)	1508 (45)	2570 (48)	−478 (23)
C (1)	4387 (66)	1166 (71)	−348 (46)
C (2)	3441 (61)	1687 (59)	−347 (34)
C (3)	2762 (74)	1487 (67)	−740 (37)
C (4)	1833 (65)	1919 (59)	−793 (33)
C (5)	1164 (81)	1634 (82)	−1237 (42)
C (6)	927 (69)	272 (43)	4134 (72)
[(acac)Me$_2$SbBr$_2$]			
Sb	5352 (1)	25	2618 (1)
Br (1)	7257 (2)	25	993 (2)
Br (2)	7388 (2)	25	5285 (2)
O (1)	3583 (15)	25	550 (15)
O (2)	3618 (16)	25	3759 (16)
C (1)	1136 (26)	25	−1333 (23)
C (2)	2158 (25)	25	381 (23)
C (3)	1480 (24)	25	1542 (26)
C (4)	2171 (22)	25	3060 (26)
C (5)	1235 (28)	25	4184 (28)
C (11)	5282 (21)	5285 (23)	2606 (18)
[(acac)Ph$_2$SbCl$_2$] (high-melting point form)			
Sb	2365 (1)	2417 (5)	4338 (1)
Cl (1)	3077 (8)	585 (15)	5431 (6)
Cl (2)	1198 (7)	345 (16)	3876 (7)
O (1)	3333 (17)	4413 (39)	4686 (16)
O (2)	1877 (14)	4273 (32)	3443 (12)
C (1)	4330 (27)	6905 (59)	4581 (24)
C (2)	3534 (26)	5750 (60)	4239 (24)
C (3)	3154 (27)	6389 (59)	3465 (25)
C (4)	2311 (19)	5597 (47)	3144 (18)
C (5)	1888 (27)	6469 (62)	2344 (25)
C (11)	3318 (21)	1527 (49)	3446 (20)
C (12)	2908 (25)	1149 (58)	2624 (23)
C (13)	3550 (27)	488 (60)	1970 (24)
C (14)	4481 (30)	245 (67)	2196 (27)
C (15)	4808 (27)	595 (61)	3077 (25)
C (16)	4216 (26)	1270 (58)	3668 (23)
C (21)	1483 (22)	3618 (52)	5247 (20)
C (22)	1394 (27)	5469 (62)	5194 (24)
C (23)	807 (26)	6277 (60)	5740 (24)
C (24)	362 (24)	5204 (57)	6336 (22)
C (25)	500 (30)	3418 (70)	6396 (27)
C (26)	1032 (23)	2547 (72)	5788 (21)

Results and Discussion

Molecular Structure. The atom numbering scheme is given in Fig. 2. A stereoscopic drawing of the molecules are shown in Fig. 3. Bond lengths and bond angles are listed in Table 4. Least-squares planes of various groups are presented in Table 5.

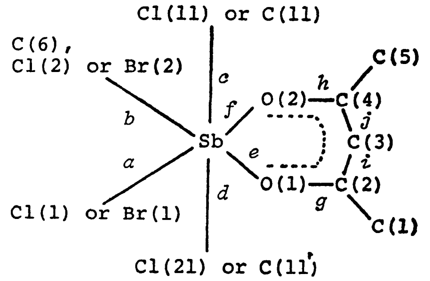


Fig. 2. The numbering scheme of atoms.

As seen in Fig. 3, the antimony atoms have slightly distorted octahedral geometries through the three compounds. In all cases the substituents are on apical positions, slightly bend towards the acetylacetonato groups.

In [(acac)MeSbCl$_3$] the methyl group has been located on the basal plane: of the two possible configurations in Fig. 1, (a) has been established. In [(acac)Me$_2$SbBr$_2$] and [(acac)Ph$_2$SbCl$_2$] the alkyl or aryl groups occupy the apical positions: the (c) configuration being found among the three possible ones in Fig. 1. From the PMR study[5] it has been concluded that both phenyl groups in [(acac)Ph$_2$SbCl$_2$] are approximately perpendicular to the bisector of the Cl–Sb–Cl angle. In the high-melting point form, one phenyl ring (C(11)–C(16)) is approximately perpendicular [89°] to the bisector, however, the other (C(21)–C(26)) is approximately parallel [3°]: the dihedral angle between two rings being 92° (Fig. 4). In the low-melting point form, both phenyl rings are neither perpendicular nor parallel to the bisector: each phenyl ring makes an angle of about 65 or 77° to the bisector, and the dihedral angle between them is about 38° (Fig. 4).[8] This appears to be the main difference between the molecular structures of the two isomers.

Among the three Sb–Cl bond lengths in [(acac)MeSbCl$_3$] those on apical positions [2.380(3) and 2.366(3) Å] are slightly longer than those on the basal plane [2.345(3) Å]. The Sb–Cl bond lengths in the high- and low-melting point forms are equal [av. 2.42 Å]. All of these Sb–Cl lengths are significantly longer than those in other antimony compounds.[15–20] The Sb–Br bond lengths in [(acac)MeSbBr$_2$] are 2.610(3) and 2.603(3) Å, which are slightly longer than those in SbBr$_3$ [2.52(3) Å].[21]

[†††] The observed and calculated structure factors are kept at the Chemical Society. Document No. 7824.

TABLE 3. THERMAL PARAMETERS ALONG WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES
Anisotropic thermal parameters ($\times 10^5$) are of the form: $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{23}kl+\beta_{13}hl)$, and isotropic ones are B (in Å^2).

Atom	β_{11} or B	β_{22}	β_{33}	β_{12}	β_{23}	β_{13}
[(acac)MeSbCl$_3$]						
Sb	399 (1)	482 (1)	136 (1)	144 (1)	−61 (1)	−45 (1)
Cl (1)	890 (2)	618 (2)	179 (4)	44 (3)	−130 (1)	−309 (2)
Cl (11)	709 (2)	742 (2)	287 (1)	−277 (3)	228 (2)	−2 (2)
Cl (21)	628 (2)	889 (2)	209 (1)	−51 (3)	299 (2)	22 (1)
O (1)	419 (3)	710 (4)	209 (1)	432 (7)	−106 (4)	−174 (3)
O (2)	592 (4)	712 (4)	193 (1)	257 (7)	−294 (4)	−230 (4)
C (1)	466 (5)	611 (6)	355 (3)	464 (10)	−144 (7)	−43 (6)
C (2)	466 (5)	408 (5)	178 (2)	112 (8)	15 (5)	69 (5)
C (3)	725 (7)	547 (6)	185 (2)	272 (10)	−103 (5)	−6 (6)
C (4)	608 (6)	401 (5)	155 (2)	−7 (9)	−47 (5)	−84 (5)
C (5)	866 (8)	876 (8)	224 (2)	159 (14)	−317 (7)	−457 (7)
C (6)	587 (6)	662 (7)	290 (2)	635 (11)	−151 (7)	95 (7)
[(acac)Me$_2$SbBr$_2$]						
Sb	988 (1)	1836 (2)	838 (1)	0	0	436 (2)
Br (1)	1195 (3)	3117 (6)	1230 (3)	0	0	959 (5)
Br (2)	1333 (3)	2767 (5)	996 (3)	0	0	133 (4)
O (1)	1096 (18)	3271 (41)	1037 (18)	0	0	734 (30)
O (2)	1141 (19)	4695 (56)	1040 (19)	0	0	947 (32)
C (1)	1333 (32)	4680 (88)	822 (26)	0	0	−377 (46)
C (2)	1525 (32)	2693 (54)	1035 (27)	0	0	585 (48)
C (3)	961 (27)	5118 (96)	1302 (32)	0	0	239 (48)
C (4)	798 (24)	4468 (82)	1470 (33)	0	0	836 (46)
C (5)	1572 (36)	4856 (94)	1574 (37)	0	0	2006 (62)
C (11)	2678 (33)	1933 (32)	1695 (25)	501 (56)	605 (49)	2704 (49)
[(acac)Ph$_2$SbCl$_2$] (high-melting point form)						
Sb	377 (10)	939 (48)	265 (8)	142 (69)	−43 (57)	−5 (12)
Cl (1)	780 (69)	1624 (262)	298 (38)	942 (228)	590 (177)	75 (81)
Cl (2)	567 (58)	1610 (256)	529 (52)	−628 (210)	−551 (209)	166 (87)
O (1)	4.3 (6)					
O (2)	2.7 (4)					
C (1)	4.7 (9)					
C (2)	4.1 (8)					
C (3)	4.3 (9)					
C (4)	2.2 (6)					
C (5)	4.6 (9)					
C (11)	2.6 (6)					
C (12)	3.9 (8)					
C (13)	4.4 (9)					
C (14)	5.4 (10)					
C (15)	4.5 (9)					
C (16)	4.0 (8)					
C (21)	2.9 (7)					
C (22)	4.3 (9)					
C (23)	4.2 (8)					
C (24)	3.5 (7)					
C (25)	5.3 (10)					
C (26)	4.2 (7)					

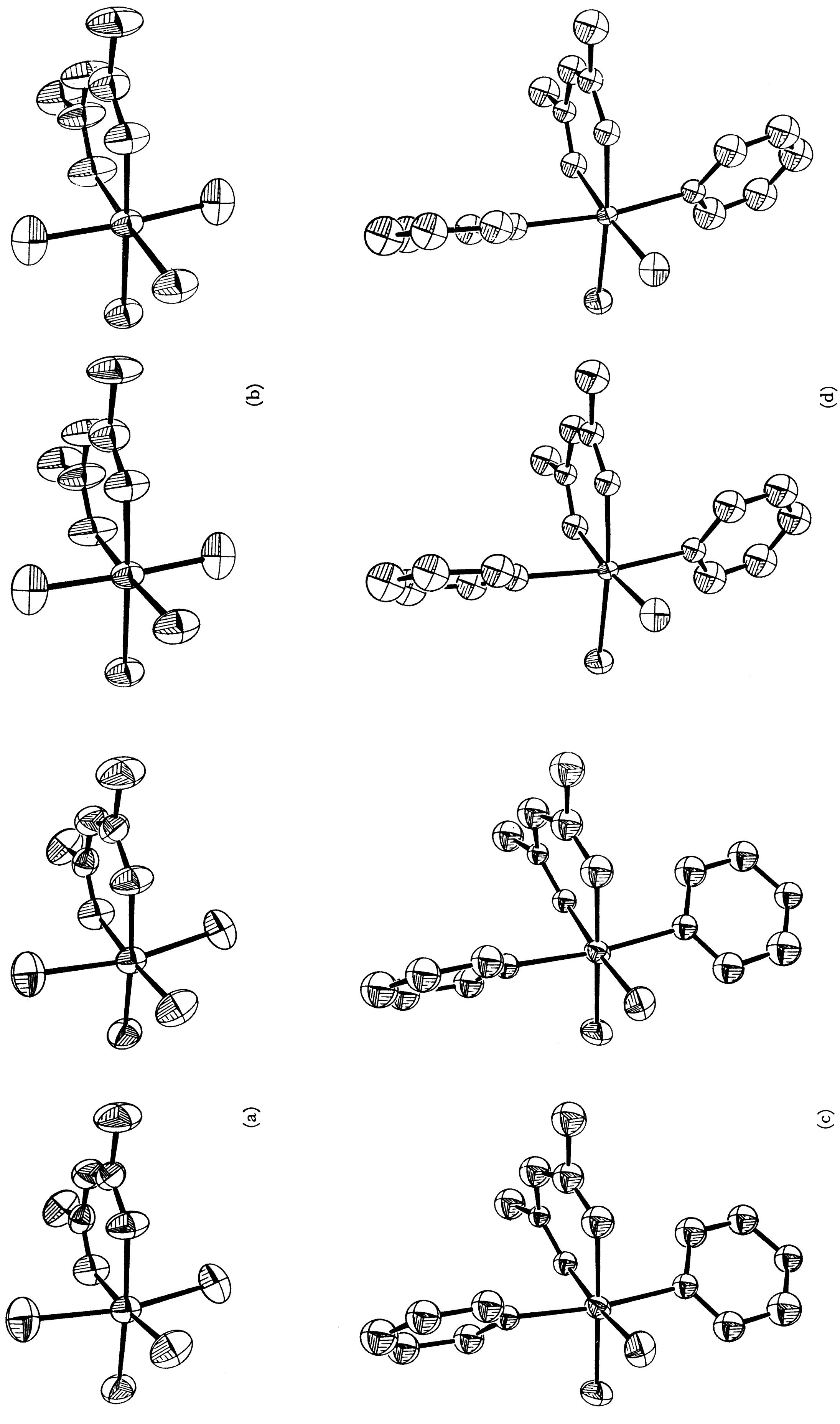


Fig. 3. The stereoscopic drawing of (a) [(acac)MeSbCl$_3$], (b) [(acac)Me$_2$SbBr$_2$], (c) [(acac)Ph$_2$SbCl$_2$](high-melting point form) and (d)[(acac)Ph$_2$SbCl$_2$] (low-melting point form).

Table 4. Bond lengths and bond angles (E.s.d.'s in parentheses)
The names of the bonds, *a*, *b*, *c*,...., and *l*, are the same as those given in Fig. 2.

	[(acac)·MeSbCl$_3$]	[(acac)·Me$_2$SbBr$_2$]	[(acac)Ph$_2$SbCl$_2$] High-melting point form	[(acac)Ph$_2$SbCl$_2$] Low-melting point form[8)
(a) Bond lengths (l/Å)				
Sb–X (X=Cl or Br)				
a	2.345(3)	2.610(3)	2.249(12)	2.415(3)
b		2.603(3)	2.414(12)	2.421(3)
c	2.366(3)			
d	2.380(3)			
Sb–C(R) (R=Me or Ph)				
b	2.134(11)			
c		2.144(20)	2.16 (4)	2.132(12)
d		2.144(20)	2.19 (4)	2.127(12)
Acetylacetonato group				
e	2.048(6)	2.104(14)	2.13 (3)	2.116(10)
f	2.069(7)	2.150(15)	2.11 (3)	2.117(10)
g	1.288(11)	1.28 (3)	1.28 (5)	1.26 (2)
h	1.269(11)	1.30 (3)	1.29 (4)	1.26 (2)
i	1.378(13)	1.38 (3)	1.42 (6)	1.38 (2)
j	1.408(13)	1.34 (3)	1.45 (6)	1.40 (2)
k	1.478(14)	1.57 (3)	1.54 (6)	1.50 (2)
l	1.489(14)	1.52 (4)	1.55 (6)	1.53 (2)
O(1)···O(2)	2.833 (9)	2.91 (2)	2.86 (4)	2.900[a)

	[(acac)·MeSbCl$_3$]	[(acac)·Me$_2$SbBr$_2$]	[(acac)Ph$_2$SbCl$_2$] High-melting point form	[(acac)Ph$_2$SbCl$_2$] Low-melting point form[8)
(b) Bond angles(ϕ/°)				
Around Sb				
a,b	99.0(3)	96.0(1)	97.5(4)	95.7(1)
a,c	92.4(1)	91.2(5)	91.6(10)	93.4(4)
a,d	91.8(1)	91.2(5)	90.5(11)	91.9(4)
a,e	84.8(2)	88.3(4)	87.3(8)	88.2(3)
a,f	171.8(2)	174.7(4)	172.2(7)	173.6(3)
b,c	96.7(3)	91.0(5)	94.1(10)	91.3(4)
b,d	93.4(3)	91.0(5)	92.0(11)	94.5(4)
b,e	175.4(3)	175.7(4)	175.1(9)	175.2(3)
b,f	89.2(3)	89.3(4)	90.3(7)	89.7(3)
c,d	168.4(1)	176.7(7)	173.3(14)	171.6(5)
c,e	85.7(2)	88.9(7)	86.8(13)	84.9(9)
c,f	87.0(2)	88.7(7)	88.2(12)	88.8(9)
d,e	83.9(2)	88.9(7)	86.9(13)	88.9(9)
d,f	87.4(2)	88.7(7)	88.9(12)	85.3(9)
Acetylacetonato group				
e,f	87.0(3)	86.4(5)	84.9(10)	86.5(4)
i,j	126.3(9)	127.1(23)	117.8(38)	120.7(15)
e,g	128.0(6)	127.7(14)	125.5(28)	127.9(9)
f,h	129.4(6)	124.7(14)	127.4(22)	126.5(9)
g,i	125.7(8)	126.2(21)	131.6(42)	125.2(15)
h,j	123.6(8)	128.0(22)	128.2(34)	126.7(15)
g,k	114.7(8)	114.8(19)	116.0(38)	114.1(15)
h,l	115.4(8)	112.1(20)	116.7(32)	113.5(15)
k,i	119.6(9)	119.0(21)	112.4(38)	120.8(15)
j,l	121.0(9)	119.9(22)	115.1(34)	119.7(15)

a) Calculated from the data of Kroon *et al.*[8)

Table 5. Least-squares planes and atom deviations

Plane equations are of the form $AX+BY+CZ+D=0$, where X, Y, Z, and D are measured in Å units: $X=ax$, $Y=by$, and $Z=cz$ for [(acac) MeSbCl$_3$] and $X=ax+cz\cos\beta$, $Y=by$, and $Z=cz\sin\beta$ for both [(acac)Me$_2$SbBr$_2$] and [(acac)Ph$_2$SbCl$_2$].

Acetylacetonato group

	O(1)	O(2)	C(1)	C(2)	C(3)	C(4)	C(5)
[(acac)MeSbCl$_3$] $-0.3954X+0.5724Y-0.7183Z+4.0109=0$	0.015	−0.014	−0.005	−0.004	−0.002	0.001	0.009
[(acac)Me$_2$SbBr$_2$] $Y=0.25$ (mirror plane)							
[(acac)Ph$_2$SbCl$_2$] (high-melting point form) $0.5973X-0.5924Y-0.5407Z+3.3379=0$	0.039	−0.050	−0.103	0.024	0.108	0.012	−0.022
[(acac)Ph$_2$SbCl$_2$] (low-melting point form)[a) $0.0263X-0.8640Y-0.5029Z+1.8036=0$	0.031	−0.039	−0.056	0.022	0.056	−0.001	−0.009

Phenyl rings

[(acac)Ph$_2$SbCl$_2$] (high-melting point form)

Ring(i)	$-0.2109X-0.9411Y+0.2643Z+0.5903=0$					
	C(11)	C(12)	C(13)	C(14)	C(15)	C(16)
	−0.014	0.022	0.004	−0.021	0.023	−0.012
Ring(ii)	$-0.0749X-0.1134Y-0.6520Z+7.1140=0$					
	C(21)	C(22)	C(23)	C(24)	C(25)	C(26)
	−0.008	−0.021	0.019	0.014	−0.045	0.042

a) Calculated from the data of Kroon *et al.*[8) The original numbering scheme of atoms are converted into as those given in Fig. 2.

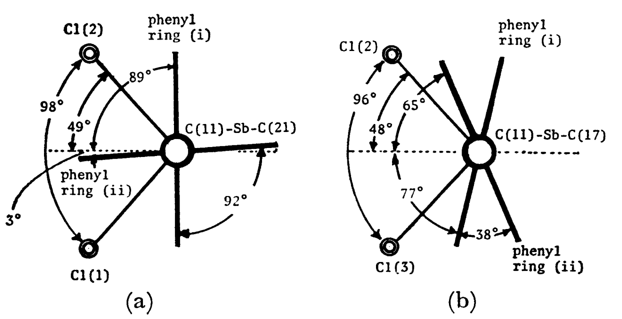


Fig. 4. The dihedral angles between the bisector(dotted line) of chloro substituents and phenyl groups in [(acac)-Ph_2SbCl_2]. (a) high-melting point form, and (b) low-melting point form.

The Sb–C(Me) bond lengths in [(acac)$MeSbCl_3$] and [(acac)Me_2SbBr_2] are standard values [2.134(11) and 2.144(20) Å, respectively] compared with those in hexa-coordinated antimony compounds: 2.10 and 2.14 Å in $Sb(CH_3)_3$[22] and 2.02(5) Å in $Me_3SbFe(CO)_4$.[23] The Sb–C(Ph) bond lengths in the high-melting point form of [(acac)Ph_2SbCl_2] are also standard values [2.16(4) and 2.19(4) Å] compared with those in the low-melting point form [2.132(12) and 2.127(12) Å] and also in $Ph_4Sb_2Cl_6$ [2.125(9) Å].[24]

The Sb–O bond lengths in [(acac)$MeSbCl_3$] [2.069(7) and 2.048(6) Å] are shorter than those in [(acac)Me_2SbBr_2] [2.104(14) and 2.150(15) Å] and [(acac)Ph_2SbCl_2] [2.13(3) and 2.11(3) Å].

The acetylacetonato groups are planar: in [(acac)Me_2SbBr_2] being exactly planar because it lies on a crystallographic mirror plane together with the antimony and two bromine atoms. In [(acac)$MeSbCl_3$] and [(acac)Ph_2SbCl_2] (low-melting point from) the acetylacetonato groups are also planar: maximum deviations of atoms from the plane, Δ_{max} being 0.02 and 0.06 Å, respectively. The mean planes are almost coplanar with the plane defined by Sb, O(1), and O(2) atoms, the dihedral angles between them being 1.2 and 1.4°, respectively. However, the planarity of the acetylacetonato group in [(acac)Ph_2SbCl_2] (high-melting point form) is not standard [$\Delta_{max}=0.11$ Å], the mean plane being bent by 15.0° away from the plane made by Sb, O(1), and O(2) atoms. This kind of bending has been found in other acetylacetonato compounds, [$Zr(acac)_4$][25] [22.6°] and [$Y(acac)_3 \cdot 3H_2O$][26] [18.9°]. In all cases the bond lengths and bond angles around the acetylacetonato ligands are standard compared with those of Lingafelter's standard data.[27]

The average bond length of the phenyl groups in [(acac)Ph_2SbCl_2] is 1.42 Å (high-melting point form)

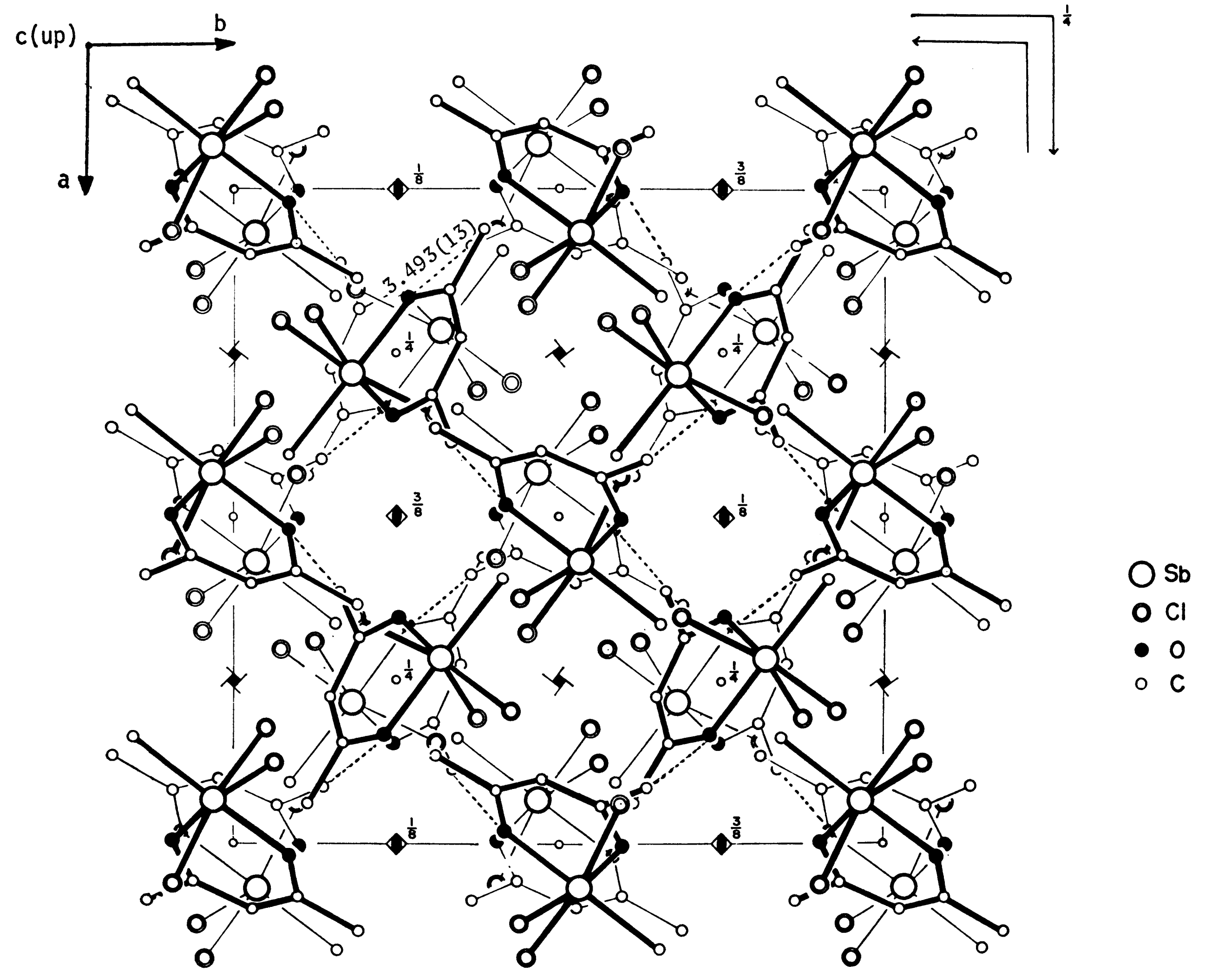


Fig. 5. The crystal structure of [(acac)$MeSbCl_3$] projected along the c axis.

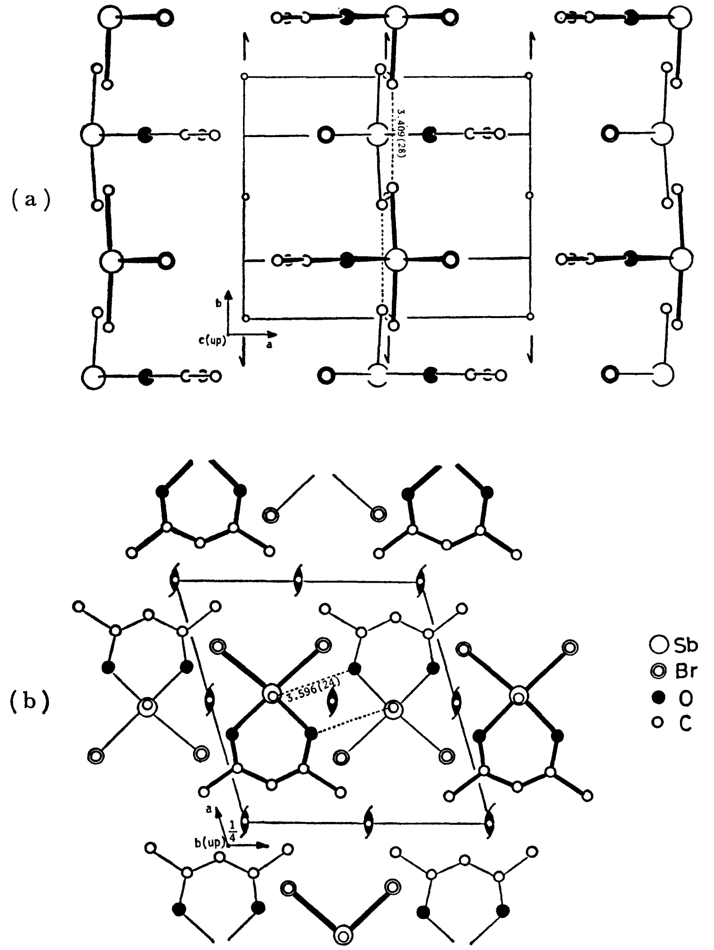


Fig. 6. (a) The crystal structure of [(acac)Me$_2$SbBr$_2$] projected along the c axis. (b) The crystal structure of [(acac)Me$_2$SbBr$_2$] projected along the b axis.

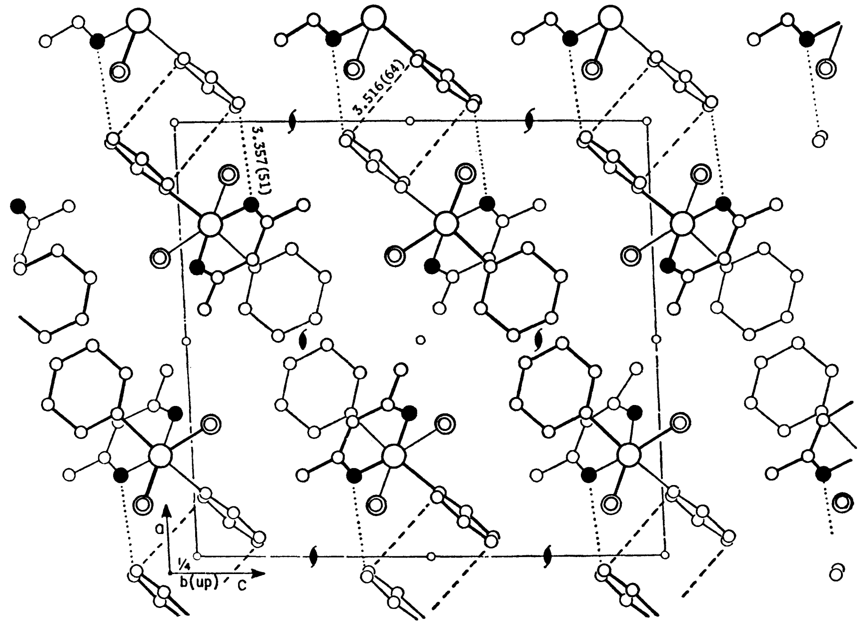


Fig. 7. The crystal structure of [(acac)Ph$_2$SbCl$_2$] (high-melting point form) projected along the b axis.

TABLE 6. SHORT INTERMOLECULAR ATOMIC CONTACTS LESS THAN 3.8 Å [l/Å] (E.s.d.'s in parentheses)

[(acac)MeSbCl$_3$]

Cl(1)···Cl(21)^{a}	3.764(4)	Cl(11)···C(6)^{e}	3.763(11)	key:			
Cl(1)···O(2)^{a}	3.750(7)	C(6)···Cl(11)^{e}	3.763(11)	a	$0.75-y$,	$0.25+x$,	$0.25+z$
Cl(21)···Cl(1)^{b}	3.764(4)	Cl(1)···C(1)^{f}	3.701(12)	b	$-0.25+y$,	$0.75-x$,	$-0.25+z$
O(2)···Cl(1)^{b}	3.750(7)	O(1)···C(5)^{f}	3.493(13)	e	$0.25-y$,	$-0.25+x$,	$-0.25+z$
C(1)···Cl(1)^{c}	3.701(12)			d	$-x$,	$1-y$,	$-z$
C(5)···O(1)^{c}	3.493(13)			c	$-x$,	$0.5-y$,	z
C(6)···C(6)^{d}	3.726(22)			f	$0.25+y$,	$0.25-x$,	$0.25+z$

[(acac)Me$_2$SbBr$_2$]

C(11)···C(11′)^{a}	3.409(28)	O(2)···C(11′)^{g}	3.596(24)	key:			
C(11′)···C(11)^{b}	3.409(28)	C(12)···O(2)^{h}	3.596(24)	a	x,	$1+y$,	z
C(3)···Br(1)^{c}	3.789(24)	O(2)···C(11)^{h}	3.596(24)	b	x,	$-1+y$,	z
Br(1)···C(3)^{d}	3.789(24)			c	$-1+x$,	y,	z
C(11)···O(1)^{e}	3.744(24)			d	$1+x$,	y,	z
O(1)···C(11′)^{e}	3.744(24)			e	$1-x$,	$0.5+y$,	$-z$
C(11,)···O(1)^{f}	3.744(24)			f	$1-x$,	$-0.5+y$,	$-z$
O(1)···C(11)^{f}	3.744(24)			g	$1-x$,	$0.5+y$,	$1-z$
C(11)···O(2)^{g}	3.596(24)			h	$1-x$,	$-0.5+y$,	$1-z$

[(acac)Ph$_2$SbCl$_2$] (high-melting point form)

O(1)···C(13)^{a}	3.657(54)	O(2)···C(24)^{h}	3.357(51)	key:			
C(1)···Cl(1)^{b}	3.632(46)	C(21)···C(23)^{h}	3.656(59)	a	x,	$0.5-y$,	$0.5+z$
C(1)···C(15)^{b}	3.769(64)	C(21)···C(24)^{h}	3.731(59)	b	x,	$1+y$,	z
C(1)···C(16)^{b}	3.603(62)	C(22)···C(23)^{h}	3.746(65)	c	x,	$-1+y$,	z
Cl(1)···C(1)^{c}	3.632(46)	C(22)···C(24)^{h}	3.516(64)	d	x,	$0.5-y$,	$-0.5+z$
C(15)···C(1)^{c}	3.769(64)	C(22)···C(25)^{h}	3.783(70)	e	$1-x$,	$0.5+y$,	$0.5-z$
C(16)···C(1)^{c}	3.603(62)	C(23)···C(21)^{h}	3.656(59)	f	$-x$,	$-y$,	$1-z$
C(13)···O(1)^{d}	3.657(54)	C(23)···C(22)^{h}	3.746(65)	g	$1-x$,	$1-y$,	$1-z$
C(1)···C(14)^{e}	3.630(67)	C(23)···C(26)^{h}	3.675(70)	h	$-x$,	$1-y$,	$1-z$
C(15)···C(14)^{e}	3.699(68)	C(24)···O(2)^{h}	3.357(51)	i	$1-x$,	$-0.5+y$,	$0.5-z$
C(3)···C(14)^{e}	3.786(67)	C(24)···C(21)^{h}	3.731(59)				
Cl(2)···C(25)^{f}	3.794(54)	C(24)···C(22)^{h}	3.516(64)				
C(25)···Cl(2)^{f}	3.794(54)	C(25)···C(22)^{h}	3.783(70)				
O(1)···C(1)^{g}	3.721(53)	C(26)···C(23)^{h}	3.675(70)				
C(1)···O(1)^{g}	3.721(53)	C(14)···C(1)^{i}	3.630(67)				
C(1)···C(1)^{g}	3.702(89)	C(14)···C(3)^{i}	3.786(67)				
C(1)···C(16)^{g}	3.713(62)	C(14)···C(15)^{i}	3.699(68)				
C(16)···C(1)^{g}	3.713(62)						

[(acac)Ph$_2$SbCl$_2$] (low-melting point form)[a]

O(1)···C(25)^{a}	3.673	C(3)···C(24)^{c}	3.673	key:			
O(1)···C(26)^{a}	3.572	C(14)···C(22)^{c}	3.780	a	$-x$,	$-y$,	$-z$
C(1)···C(26)^{a}	3.700	C(22)···C(14)^{d}	3.780	b	x,	$0.5-y$,	$0.5+z$
C(25)···O(1)^{a}	3.738	C(24)···C(1)^{d}	3.789	c	x,	$1+y$,	z
C(26)···O(1)^{a}	3.572	C(24)···C(3)^{d}	3.673	d	x,	$-1+y$,	z
C(26)···C(1)^{a}	3.700	C(1)···Cl(1)^{e}	3.756	e	x,	$0.5-y$,	$-0.5+z$
Cl(1)···C(1)^{b}	3.756	C(3)···C(12)^{e}	3.695	f	$1-x$,	$0.5+y$,	$0.5-z$
C(12)···C(3)^{b}	3.695	C(25)···C(14)^{e}	3.790	g	e$1-x$,	$-0.5+y$,	$0.5-z$
C(14)···C(25)^{b}	3.790	C(15)···O(2)^{f}	3.639				
C(1)···C(24)^{c}	3.789	O(2)···C(15)^{f}	3.639				

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[a] Calculated from the data of Kroon *et al.*,[8] in which e.s.d.'s are not given. The original numbering scheme of atoms are converted into as those given in Fig. 2.

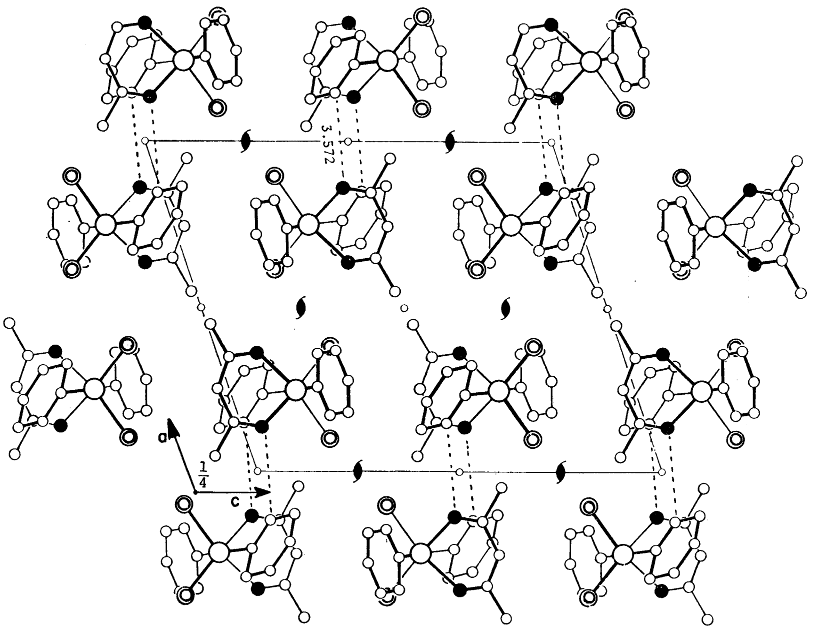

Fig. 8. The crystal structure of [(acac)Ph_2SbCl_2] (low-melting point form) projected along the b axis. (Drawn by using the data of the present authors.[9])

and 1.39 Å (low-melting point form[8]) respectively.

Crystal Structure. Crystal structures of the three compounds are respectively shown in Figs. 5, 6, and 7. In Fig. 8 the crystal structure of [(acac)Ph_2SbCl_2] (low-melting point form) is given using the data of Kroon *et al.*[8] Figures 9 shows a stereoscopic drawing of the packing of the former three crystals. Short intermolecular atomic contacts less than 3.8 Å are listed in Table 6.

[(acac)Me$SbCl_3$]: As seen in Fig. 5, in the tetragonal unit-cell molecules are arranged in helical manner along the crystallographic 4_1 screw axis, and each of these molecules is paired by the center of symmetry with a molecule to form a double helical arrangement along the c axis. In the four-fold helical arrangement of molecules, the closest atomic contacts occur between the methyl groups and the oxygen atoms of the acetylacetonato groups of the adjacent molecules of upper and lower steps [C(5)···O(1)=3.493(13) Å, Fig. 5].

[(acac)Me_2SbBr_2]: Along the b axis a pile of molecules forms a column, in which both methyl groups in apical positions of the molecule have the closest contacts with the other molecules above and below [C(11)···C(11′)^a =C(11′)···C(11)^b=3.409(28) Å, Fig. 6(a)]. Each molecule in the column has close contact with molecules in the adjacent column, related by the two-fold screw axis [C(11)···O(2)^g and O(2)···C(11′)^g, both 3.596 (24) Å, Fig. 6(b)], by which the two columns are tied. An infinite sheet parallel to the b and c axes is formed by rather close contacts with the adjacent tied columns along the c axis, and the parallel stack of these infinite sheets produces the crystal (Fig. 6(b)).

[(acac)Ph_2SbCl_2] (High-melting point form): Figure 7 shows that the molecules lie approximately parallel to the (101) plane. There are many close atomic contacts, the closest one being [O(2)···C(24)^h or C(24)···O(2)^h, 3.357(51) Å] between a pair of molecules related by the center of symmetry. Along the b axis each molecule has rather close contacts with the other molecules above and below: the shortest distance being 3.603(62) Å [C(1)···C(16)^b or C(16)···C(1)^c]. Molecules related by the center of symmetry have additional close contacts between the acetylacetonato and phenyl carbon atoms.

(Low-melting point form): Molecules lie approximately parallel to the (100) plane (Fig. 8). There are several close atomic contacts including the closest one [O(1)··· C(26)^a or C(26)···O(1)^a, 3.572 Å] between a pair of molecules related by the center of symmetry. Comparison of the crystal structures of the two forms indicates that the low-melting poing form has a looser packing and smaller number of short inter-atomic contacts than the high-melting point form (Table 6). These facts possibly contribute to the difference in melting point between the two forms.

Computations throughout the present study were carried out on a NEAC 2200-700 computer at Osaka University. Figures 3, and 9 were drawn on a NUMERICON 7000 system at Osaka University using a local version of ORTEP.[28]

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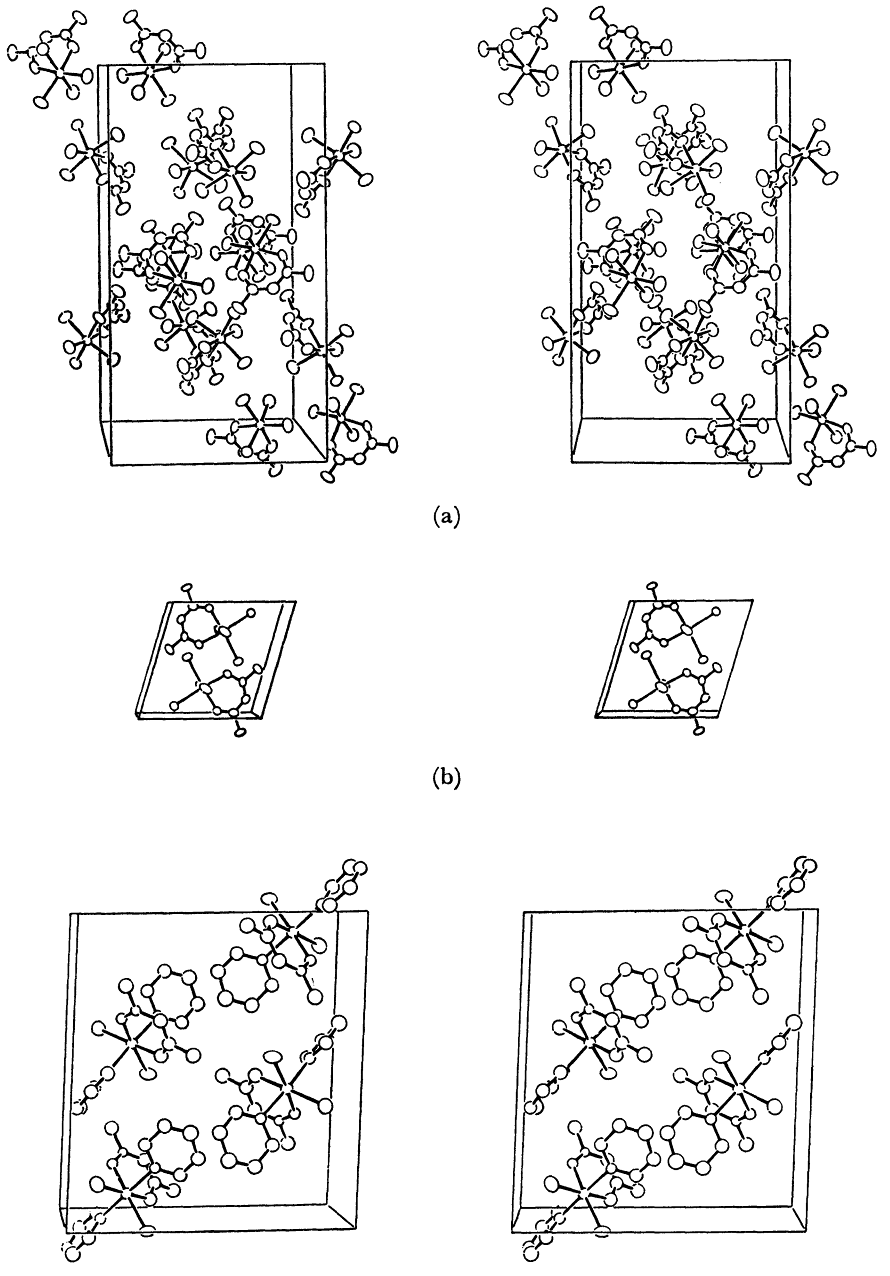

(a)

(b)

(c)

Fig. 9. Stereoscopic drawing of the molecular packings of (a) [(acac)MeSbCl$_3$], (b) [(acac)Me$_2$SbBr$_2$], and (c) [(acac)Ph$_2$SbCl$_2$] (high-melting point form).

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