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Synthesis, Characterization and Biological Activities of Some Triarylantimony Dichrysanthemates and Crystal Structure of $Ph_3Sb(O_2CCHCMe_2CMe_2)_2$

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A series of triarylantimony dichrysanthemate compounds of the type $Ar_3Sb(O_2CR)_2$ [$Ar = C_6H_5$, 4-$CH_3C_6H_4$, 3-$CH_3C_6H_4$, 2-$CH_3C_6H_4$, 4-ClC_6H_4; R = 4-ClC_6H_4CH(i-Pr), CMe_2CMe_2CH, *cis*-$Cl_2C{:}CHCHCMe_2CH$, *trans*-$Cl_2C{:}CHCHCMe_2CH$] have been synthesized and characterized by elemental analysis, infrared spectra, ^{1}H NMR spectra and mass spectra. Some activities of these compounds in plant growth regulation have been determined. Their results indicate that the derivatives of *cis*-dichlorochrysanthemic acid and *trans*-dichlorochrysanthemic acid significantly promote rooting of excised cucumber cotyledons at 10 ppm. An X ray structure determination has been carried out as follows for $Ph_3Sb(O_2CCHCMe_2CMe_2)_2$: orthorhombic, space group *Pbcn*, *Z* = 4, structure solution with 2385 independent reflections, *R* = 0.035. Lattice dimensions at 26 °C: *a* = 15.616(3) Å, *b* = 10.275(2) Å, *c* = 20.201(5) Å, *V* = 3241(2) Å^3, $\rho = 1.302$ g cm^{-3}. © 1997 John Wiley & Sons, Ltd.

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INTRODUCTION

Triorganoantimony dicarboxylates of the type $R_3Sb(O_2CR')_2$ have been known for a long time.[1–18] Their structures have been studied with the help of vibrational spectroscopy[4, 5, 13, 14, 19] and X-ray diffraction.[20–24] The biological activity of some triorganoantimony dicarboxylates has been reported.[11, 18] Bajpai and co-workers[11] considered that the activity was not significantly affected by the nature of the R or R′ group. However, Singhal and co-workers[18] found that the effect of the nature of the R or R′ group on the activity was relatively complex. In order to go further into the influence of the I-effect of the organic ligands R at Sb as well as the steric effect of the R or R′-group on the structure and the biological activity of $R_3Sb(O_2CR')_2$, we have synthesized a series of triarylantimony dichrysanthemates which contain two active centers, namely the triarylantimony(V) moiety and the chrysanthemate group.

EXPERIMENTAL

Elemental analyses were determined on a Yanaco CHN Corder MT-3 elemental analyzer. IR spectra in the region 4000–400 cm^{-1} were recorded in KBr disks on a Nicolet 5DX FT-IR spectrophotometer. ^{1}H NMR spectra were measured on a Bruker Ac-200 spectrometer in $CDCl_3$ solution with TMS as internal standard. Mass spectra were recorded on a VG ZAB-HS at 70 eV; the temperature of ionization was 200 °C.

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General method of preparation of triarylantimony dibromides

Triarylantimony was prepared by the method reported by De Ketellaere *et al.*,[25] using freshly distilled analytically pure-grade antimony trichloride and a Grignard reagent from dried redistilled ArX (X = Cl, Br) and magnesium turnings in sodium-dried ether, and was subsequently converted into the corresponding dibromide by direct bromination.[26] The solid product was recrystallized from toluene–petroleum ether (b. pt 60–90 °C) mixtures. A white crystalline solid, Ar_3SbBr_2 ($Ar = C_6H_5$, $4\text{-}CH_3C_6H_4$, $3\text{-}CH_3C_6H_4$, $2\text{-}CH_3C_6H_4$, $4\text{-}ClC_6H_4$), was obtained.

General method of preparation of triarylantimony dichrysanthemates

Triarylantimony dichrysanthemates were prepared by a more convenient method.[11] Recrystallized chrysanthemic acids (3 mmol) and potassium hydroxide (3 mmol) or triethylamine (1.5 ml) were stirred together in toluene (30 ml) at room temperature for 4 h, then triarylantimony dibromide (1.5 mmol) was added. The reaction mixture was stirred at room temperature for 6–8 h and filtered. The filtrate was evaporated to dryness by a rotary evaporator *in vacuo* to afford triarylantimony dichrysanthemates which were recrystallized from benzene–petroleum ether (60–90 °C) mixtures. Some data on the compounds are listed in Table 1.

Plant growth-regulating tests

The plant growth-regulating tests were carried out by the method reported by Zhao and Huang.[27] The concentrations of the aqueous solutions of 15 representative compounds were 10 ppm. For each compound being tested, 3 ml of its solution was placed by syringe in a Petri dish. Then 10 excised cucumber cotyledons were selected and put into the Petri dish. Finally the Petri dish was placed in a darkroom at 26 °C for five days. The number of roots on the 10 cotyledons was determined. Every test was repeated four times. Distilled water was used as the control and indole-3-acetic acid (10 ppm aqueous solution) was used for comparison.

RESULTS AND DISCUSSION

The reactions of triarylantimony dibromides with chrysanthemic acids in the presence of a base (potassium hydroxide or triethylamine) afford a

Table 1 Yields and elemental analyses of the compounds

				Elemental analysis: Found (calcd) (%)		
Compd	Yield (%)	State	M.pt (°C)	C	H	Formula for calculation
1	63	White crystals	158–159	64.40 (64.27)	6.49 (6.52)	$C_{34}H_{41}O_4Sb$
2	69	White crystals	157–159	65.05 (65.59)	6.67 (6.99)	$C_{37}H_{47}O_4Sb$
3	69	White crystals	110–111	65.52 (65.59)	6.86 (6.99)	$C_{37}H_{47}O_4Sb$
4	72	White crystals	174–177	65.42 (65.59)	7.17 (6.99)	$C_{37}H_{47}O_4Sb$
5	62	White crystals	159–161	55.07 (55.28)	5.37 (5.18)	$C_{34}H_{38}Cl_3O_4Sb$
6	65	White crystals	130–131	53.04 (53.09)	4.92 (4.32)	$C_{34}H_{33}Cl_4O_4Sb$
7	80	White crystals	39–42	54.70 (54.78)	5.02(4.85)	$C_{37}H_{39}Cl_4O_4Sb$
8	82	White crystals	42–46	54.78 (54.78)	4.46 (4.85)	$C_{37}H_{39}Cl_4O_4Sb$
9	58	White crystals	46–50	46.60 (46.80)	3.83 (3.47)	$C_{34}H_{30}Cl_7O_4Sb$
10	95	White crystals	38–42	52.96 (53.09)	4.40 (4.32)	$C_{34}H_{33}Cl_4O_4Sb$
11	68	White crystals	39–42	54.32 (54.78)	4.57 (4.85)	$C_{37}H_{39}Cl_4O_4Sb$
12	74	Yellow adhesive oil		55.22 (54.78)	4.57 (4.85)	$C_{37}H_{39}Cl_4O_4Sb$
13	82	Yellow adhesive oil		53.80 (54.78)	5.72 (4.85)	$C_{37}H_{39}Cl_4O_4Sb$
14	69	White crystals	44–48	47.12 (46.80)	3.94 (3.47)	$C_{34}H_{30}Cl_7O_4Sb$
15	77	White crystals	116–118	61.85 (61.88)	5.08 (5.06)	$C_{40}H_{39}Cl_2O_4Sb$
16	73	White crystals	120–122	63.03 (63.10)	5.60 (5.54)	$C_{43}H_{45}Cl_2O_4Sb$
17	73	White crystals	48–52	61.60 (63.10)	6.01 (5.54)	$C_{43}H_{45}Cl_2O_4Sb$
18	82	White crystals	155–157	54.84 (54.61)	4.42 (4.12)	$C_{40}H_{36}Cl_5O_4Sb$

series of triarylantimony dichrysanthemates (Eqn [1]):

$$\mathrm{Ar_3SbBr_2 + 2RCO_2H \longrightarrow Ar_3Sb(O_2CR)_2} \qquad [1]$$

$R = \overline{\mathrm{CMe_2CMe_2C}}\mathrm{H}$; Ar = C_6H_5 (**1**), 4-$CH_3C_6H_4$ (**2**), 3-$CH_3C_6H_4$ (**3**), 2-$CH_3C_6H_4$ (**4**), 4-ClC_6H_4 (**5**)
R = *cis*-$\mathrm{Cl_2C{:}CH}\overline{\mathrm{CHCMe_2C}}\mathrm{H}$; Ar = C_6H_5 (**6**), 4-$CH_3C_6H_4$ (**7**), 2-$CH_3C_6H_4$ (**8**), 4-ClC_6H_4 (**9**)
R = *trans*-$\mathrm{Cl_2C{:}CH}\overline{\mathrm{CHCMe_2C}}\mathrm{H}$; Ar = C_6H_5 (**10**), 4-$CH_3C_6H_4$ (**11**), 3-$CH_3C_6H_4$ (**12**), 2-$CH_3C_6H_4$ (**13**), 4-ClC_6H_4 (**14**)
R = 4-ClC_6H_4CH(i-Pr); Ar = C_6H_5 (**15**), 4-$CH_3C_6H_4$ (**16**), 2-$CH_3C_6H_4$ (**17**), 4-ClC_6H_4 (**18**)

The reactions proceed under mild conditions and the yields are generally high (58–95%). Most of the compounds are white crystals (only compounds **12** and **13** are yellow adhesive oils). They are unaffected by atmospheric moisture. They are easily soluble in various organic solvents, e.g. benzene, toluene, petroleum ether, ethanol, acetone or chloroform.

In the majority of organoantimony(V) compounds the antimony has generally a coordination number of five. Because the vacant 5d orbital of the antimony atom can accept lone electron pairs of ligands, in some cases the antimony may have a formal coordination number of six[28, 29] or seven.[24] For many organoantimony carboxylates there are interactions between the carbonyl oxygen atoms of the carboxylate groups and the antimony atom,[20, 24, 28, 29] but for some organoantimony carboxylates there is no interaction between the carbonyl oxygen atoms of the carboxylate groups and the antimony atom.[24] The IR stretching vibration frequencies of carboxylate groups in organoantimony carboxylates are very important for determining their structures: when there are interactions between the carbonyl oxygen atoms of the carboxylate groups and the antimony atom, the asymmetric absorption vibration frequencies [$\nu_{as}(CO_2)$] of the carboxylate groups decrease and the symmetric absorption vibration frequencies [$\nu_s(CO_2)$ increase. Their difference [$\Delta\nu(CO_2)$] therefore decreases.[4, 18, 30] In the IR spectra of the title compounds the carboxylate bands are observed in the characteristic regions: $\nu_{as}(CO_2)$ between 1660 and 1565 cm^{-1} and $\nu_s(CO_2)$ between 1381 and 1331 cm^{-1} (Table 2). On the basis of the difference $\Delta\nu(CO_2)$ these compounds can be divided in two classes: the compounds **2**, **4**, **8**, **12**, **13**, **15** and **17** show high $\Delta\nu$ values (between 291 and 328 cm^{-1}), while all other compounds show $\Delta\nu$ values between 216 and 280 cm^{-1} (Table 2). We can assume that the compounds **3**, **5**, **6**, **7**, **9**, **10**, **11**, **14**, **16** and **18** are analogous to compound **1**, in which there are interactions between the carbonyl oxygen atoms of the carboxylate groups and the antimony atom (see the crystal structure of **1**), while in all other compounds there are weaker interactions or no interaction between the carbonyl oxygen atoms of the carboxylate groups and the antimony atom. As contrasted with the +I effect of alkyl groups, the −I effect of the aryl groups enhances the Lewis acidity of Sb and leads to a stronger Sb···O=C coordination.[24] When Ar is 4-ClC_6H_4, the difference $\Delta\nu(CO_2)$ is relatively low; this means a relatively strong Sb···O=C coordination. When Ar is $CH_3C_6H_4$, the difference $\Delta\nu(CO_2)$ is relatively high; this means a relatively weak Sb···O=C coordination, or none. The former may be attributed to the −I effect of Cl, and the latter may be attributed to the +I effect of the methyl group. When Ar is 2-$CH_3C_6H_4$, the difference $\Delta\nu(CO_2)$ is very high; this may be attributed to the steric effect of the *ortho*-methyl group which weakens the Sb–C(Ph) bond and decreases the capacity of the antimony atom to accept lone electron pairs from the carbonyl oxygen atoms. In addition, the frequencies ν_{as}(Sb–C[Ph]) appear between 446 and 488 cm^{-1}; this is consistent with the literature [4].

Table 2 IR data of the compounds (cm^{-1})

Compound	$\nu_{as}(CO_2)$	$\nu_s(CO_2)$	$\Delta\nu(CO_2)$	ν_{as}(Sb–C[Ph])
1	1625	1346	278	460
2	1638	1335	303	483
3	1622	1342	280	446
4	1659	1331	328	486
5	1565	1349	216	488
6	1627	1364	263	458
7	1625	1372	253	483
8	1657	1360	297	485
9	1605	1380	225	487
10	1628	1348	280	454
11	1631	1357	274	485
12	1636	1344	292	476
13	1650	1338	312	485
14	1608	1381	227	487
15	1639	1348	291	456
16	1635	1359	276	485
17	1660	1340	320	460
18	1634	1358	276	486

The ^1H NMR spectra of the compound **1** has shown a multiplet at 7.41–7.90 ppm (due to Ph) and three singlets at 1.04 ppm (due to CH), 1.00 ppm (due to CH_3, in the *cis*-position) and 0.95 ppm (due to CH_3 in the *trans*-position) with an intensity ratio of 15:2:12:12 which suggests that both the chrysanthemate groups are equivalent. The ^1H NMR data of other compounds are listed in Table 3.

The mass spectra (MS) of compounds **1** and **6** are recorded and the main data are listed in Table 4. For both there is no molecular ion peak. Decarboxylation and dephenylation from the antimony atom are the two main breakdown patterns for the two compounds.

The data for plant growth-regulating activity of triarylantimony dichrysanthemates are listed in Table 5. Faucher[31] reported that *cis*/*trans*-2-(*N*,*N*,*N*-trimethylamino)ethyl chrysanthemate chloride caused stunting in corn, milo and cotton plants. Crammer and co-workers[32] reported that the products derived from *cis*/*trans*-chrysanthemic acid displayed potent inhibi-

Table 3 ^1H NMR data for compounds $Ar_3Sb(O_2CR)_2$ (ppm)

Compound	$Ar_3Sb(O_2\overline{CCHCMe_2C}Me_2)_2$ CH$_3$	CH	Ar
1	0.95 (12H, s), 1.00 (12H, s)	1.04 (2H, s)	7.41–7.90 (15H, m)
2	0.95 (12H, s), 1.00 (12H, s)	1.02 (2H, s)	7.20–7.82 (12H, m), 2.35 (9H, s)
3	0.97 (12H, s), 1.02 (12H, s)	1.07 (2H, s)	7.27–7.80 (12H, m), 2.34 (9H, s)
4	0.85 (12H, s), 0.97 (12H, s)	1.10 (2H, s)	7.33–8.27 (12H, m), 2.52 (9H, s)
5	0.98 (12H, s), 1.01 (12H, s)	1.09 (2H, s)	7.36–7.82 (12H, m)

$Ar_3Sb(O_2C\overline{CHCMe_2C}HCH{:}CCl_2)_2$

Compound	CH$_3$	O$_2$CCH	C:CCH	Cl$_2$C:CH	Ar
6	0.93 (6H, s), 1.07 (6H, s)	1.70 (2H, d)	1.75 (2H, m)	6.08 (2H, d)	7.47–7.93 (15H, m)
7	0.98 (6H, s), 1.08 (6H, s)	1.28 (2H, d)	1.70 (2H, m)	6.06 (2H, d)	7.28–7.88 (12H, m), 2.40 (9H, s)
8	0.98 (6H, s), 1.03 (6H, s)	1.57 (2H, d)	1.70 (2H, m)	5.96 (2H, d)	7.33–8.25 (12H, m), 2.51 (9H, s)
9	0.96 (6H, s), 1.08 (6H, s)	1.66 (2H, d)	1.86 (2H, m)	6.02 (2H, d)	7.42–7.82 (12H, m)
10	0.83 (6H, s), 1.00 (6H, s)	1.38 (2H, d)	2.00 (2H, m)	5.47 (2H, d)	7.46–7.95 (15H, m)
11	0.90 (6H, s), 1.01 (6H, s)	1.40 (2H, d)	1.98 (2H, m)	5.49 (2H, d)	7.26–7.86 (12H, m), 2.37 (9H, s)
12	0.88 (6H, s), 1.02 (6H, s)	1.42 (2H, d)	2.04 (2H, m)	5.48 (2H, d)	7.28–7.76 (12H, m), 2.36 (9H, s)
13	0.80 (6H, s), 0.93 (6H, s)	1.30 (2H, d)	1.86 (2H, m)	5.41 (2H, d)	7.36–8.13 (12H, m), 2.57 (9H, s)
14	0.86 (6H, s), 1.02 (6H, s)	1.29 (2H, d)	2.02 (2H, m)	5.52 (2H, d)	7.40–7.83 (12H, m)

$Ar_3Sb[O_2CCH(i\text{-}Pr)C_6H_4Cl\text{-}4]_2$

Compound	CH$_3$	CH	O$_2$CCH	C$_6$H$_4$	Ar
15	0.60 (12H, d)	2.09 (2H, m)	2.91 (2H, d)	6.95–7.07 (8H, m)	7.30–7.65 (15H, m)
16	0.65 (12H, d)	2.10 (2H, m)	2.92 (2H, d)	6.96–7.05 (8H, m)	7.05–7.53 (12H, m), 2.33 (9H, s)
17	0.58 (12H, d)	2.02 (2H, m)	2.77 (2H, d)	6.82–7.00 (8H, m)	7.22–7.92 (12H, m), 2.19 (9H, s)
18	0.61 (12H, d)	2.12 (2H, m)	2.92 (2H, d)	6.90–7.04 (8H, m)	7.23–7.55 (12H, m)

Table 4 Fragment ions observed for compounds **1** and **6**

Compound **1**			Compound **6**		
m/*z*	Fragment ion	Intensity	*m*/*z*	Fragment ion	intensity
557	$[Ph_2Sb(O_2C\overline{CHCMe_2C}Me_2)_2]^+$	11.3	691	$[Ph_2Sb(O_2C\overline{CHCMe_2C}HCH{:}CCl_2)_2]^+$	4.1
493	$[Ph_3Sb(O_2C\overline{CHCMe_2C}Me_2)]^+$	100.0	561	$[Ph_3Sb(O_2C\overline{CHCMe_2C}HCH{:}CCl_2)]^+$	100.0
352	Ph_3Sb^+	2.0	352	Ph_3Sb^+	9.5
275	Ph_2Sb^+	9.3	275	Ph_2Sb^+	4.6
198	$PhSb^+$	26.5	198	$PhSb^+$	91.0
121	Sb^+	1.2	121	Sb^+	5.3
77	Ph^+	7.8	77	Ph^+	61.0

tory effects on root elongation and lettuce seed germination at 10^{-4} and 10^{-5} M concentrations. From Table 5 we can see that compounds **4**, **5** and **15–18** inhibit rooting of excised cucumber cotyledons and **6–12** as well as **14** significantly promote rooting of excised cucumber cotyledons at 10 ppm concentration. The activity of compounds **6**, **9** and **10** is relatively high and approaching the activity of indole-3-acetic acid. The data in Table 5 indicate that the activity of triarylantimony dichrysanthemates is significantly affected by the nature of the aryl and

Table 5 Effect of triarylantimony dichrysanthemates on rooting of excised cucumber cotyledon (26 °C, in the dark)

Compound (10 ppm)	Number of roots on 10 cotyledons	Percentage over control (%)
3	9.0 ± 2.0	0.0
4	7.0 ± 1.0	− 22.2
5	7.3 ± 1.5	− 18.9
6	20.0 ± 2.0	122.2
7	16.3 ± 1.5	81.1
8	13.4 ± 1.6	48.9
9	21.3 ± 3.1	136.7
10	20.0 ± 3.5	122.2
11	14.0 ± 1.0	55.6
12	16.0 ± 5.6	77.8
14	16.7 ± 2.9	85.6
15	6.3 ± 3.1	− 30.0
16	5.7 ± 2.9	− 36.7
17	4.3 ± 0.6	− 52.2
18	2.7 ± 1.2	− 70.0
Distilled water	9.0 ± 1.4	
IAA[a]	24.4 ± 2.6	171.1

[a] IAA, Indole-3-acetic acid.

Table 6 Bond distances of compound **1** (Å)

Sb–O(1)	2.106(3)
Sb–O(2)	2.800(2)
Sb–C(11)	2.123(5)
Sb–C(21)	2.1898(5)
O(1)–C(1)	1.301(6)
O(2)–C(1)	1.229(6)
C(1)–C(2)	1.495(7)
C(2)–C(3)	1.547(8)
C(2)–C(4)	1.549(8)
C(3)–C(4)	1.523(9)
C(3)–C(7)	1.545(9)
C(3)–C(8)	1.523(9)
C(4)–C(5)	1.538(9)
C(4)–C(6)	1.53(1)
C(11)–C(12)	1.363(8)
C(11)–C(16)	1.398(9)
C(12)–C(13)	1.416(8)
C(13)–C(14)	1.38(1)
C(14)–C(15)	1.37(1)
C(15)–C(16)	1.417(9)
C(21)–C(22)	1.372(6)
C(22)–C(23)	1.407(8)
C(23)–C(24)	1.408(8)

Table 7 Bond angles (°) of compound **1**[a]

O(1)–Sb–O(1a)	177.6(2)	C(4)–C(3)–C(8)	121.8(6)
O(1)–Sb–O(2)	51.0(1)	C(7)–C(3)–C(8)	112.4(6)
O(1)–Sb–O(2a)	131.3(2)	C(2)–C(4)–C(3)	60.5(4)
O(2)–Sb–O(2a)	80.8(2)	C(2)–C(4)–C(5)	119.0(5)
O(1)–Sb–C(11)	92.1(2)	C(2)–C(4)–C(6)	113.7(7)
O(1)–Sb–C(11a)	88.7(2)	C(3)–C(4)–C(5)	119.4(6)
O(1)–Sb–C(21)	88.9(2)	C(3)–C(4)–C(6)	119.6(6)
C(11)–Sb–C(11a)	150.0(3)	C(5)–C(4)–C(6)	114.0(6)
C(11)–Sb–C(21)	105.1(2)	Sb–C(11)–C(12)	114.7(4)
C(11a)–Sb–C(21)	105.1(2)	Sb–C(11)–C(16)	122.8(5)
Sb–O(1)–C(1)	109.4(3)	C(12)–C(11)–C(16)	122.6(6)
O(1)–C(1)–O(2)	121.1(5)	C(11)–C(12)–C(13)	119.2(7)
O(1)–C(1)–C(2)	113.0(6)	C(12)–C(13)–C(14)	120.1(8)
O(2)–C(1)–C(2)	125.8(6)	C(13)–C(14)–C(15)	119.6(7)
C(1)–C(2)–C(3)	120.4(5)	C(14)–C(15)–C(16)	122.1(7)
C(1)–C(2)–C(4)	121.3(5)	C(11)–C(16)–C(15)	116.5(7)
C(3)–C(2)–C(4)	59.0(4)	Sb–C(21)–C(22)	116.8(3)
C(2)–C(3)–C(4)	60.6(4)	Sb–C(21)–C(22a)	116.8(3)
C(2)–C(3)–C(7)	111.8(6)	C(22)–C(21)–C(22a)	126.4(5)
C(2)–C(3)–C(8)	122.1(5)	C(21)–C(22)–C(23)	116.8(6)
C(4)–C(3)–C(7)	118.6(6)	C(22)–C(23)–C(24)	119.5(7)
		C(23)–C(24)–C(23a)	121.0(8)

[a] Symmetry operation: $a = 1 - x, y, 0.5 - z$.

chrysanthemate groups.

A colorless crystal of compound **1** was obtained from benzene–petroleum ether (60–90 °C) mixtures and was determined using MoKα radiation (λ=0.71073 Å) on an Enraf–Nonius CAD4 four-circle diffractometer. The structure of **1** was solved by means of direct methods using the SDP-PLUS program system. The crystallographic parameters and conditions of data collection are summarized as follows:

$C_{34}H_{41}O_4Sb$

Crystal data: orthorhombic, space group *Pbcn*, a=15.616(3) Å, b=10.275(2) Å, c=20.201(5) Å, V=3241(2) Å^3, mol. wt=635.45, density=1.302 g cm^{-3}, Z=4, F(000)=1312, μ=0.886 mm^{-1}, scan type ω–2 θ, 2°≤θ≤23°, crystal size 0.2 mm×0.3 mm×0.3 mm, number of independent reflections 2385, number of observed reflections 1202 [$I \geq 3\sigma(I)$].

Table 8 Least-squares planes and dihedral angle (°)

Atom	x	y	z	Distance±ESD
Orthonormal equation of plane 1:				
$0.9006x-0.0000y-0.4346z-4.8378=0$				
O(1)	8.6449	0.4227	6.9820	−0.0859±0.0057
O(2)	8.6851	−1.7540	6.6383	0.0997±0.0069
O(2a)	6.9312	−1.7540	3.4621	−0.0997±0.0000
O(1a)	6.9714	0.4227	3.1184	0.0859±0.0000
C(21)	7.8082	2.5687	5.0502	0.0000±0.0000
Sb	7.8082	0.3789	5.0502	0.0000±0.0000
C(11)	5.9024	−0.1708	5.8070	−2.0452±0.0086
C(11a)	9.7139	−0.1708	4.2934	2.0452±0.0000
Orthonormal equation of plane 2:				
$-0.1512x-0.5678y-0.0892z+5.4914=0$				
C(11)	5.9024	−0.1708	5.8070	−0.0028±0.0089
C(12)	4.8812	0.6455	5.4229	−0.0011±0.0110
C(13)	3.5660	0.3599	5.8637	0.0032±0.0128
C(14)	3.3306	−0.7291	6.6775	−0.0014±0.0129
C(15)	4.3784	−1.5363	7.0495	−0.0025±0.0134
C(16)	5.7059	−1.2905	6.6204	0.0045±0.0119
Orthonormal equation of plane 3:				
$-0.151(5)x+0.568(4)y-0.809(3)z+5.042(2)=0$				
C(11a)	9.7139	−0.1708	4.2934	0.0028±0.0000
C(12a)	10.7351	0.6455	4.6775	0.0011±0.0000
C(13a)	12.0503	0.3599	4.2368	−0.0032±0.0000
C(14a)	12.2858	−0.7291	3.4229	0.0014±0.0000
C(15a)	11.2379	−1.5363	3.0509	0.0025±0.0000
C(16a)	9.9104	−1.2905	3.4800	−0.0045±0.0000
Orthonormal equation of plane 4:				
$0.923(1)x-0.000(2)y-0.384(3)z-5.27(2)=0$				
C(21)	7.8082	2.5687	5.0502	0.0000±0.000
C(22)	8.2787	3.1867	6.1808	−0.0005±0.0096
C(23)	8.2795	4.5933	6.1802	0.0005±0.0108
C(24)	7.8082	5.2867	5.0502	0.0000±0.0000
C(22a)	7.3376	3.1867	3.9196	0.0005±0.0000
C(23a)	7.3368	4.5933	3.9202	−0.0005±0.0000

Plane no.	Plane no.	Dihedral angle (°)
1	2	77.56±0.27
2	3	69.19±0.21
2	4	80.12±0.30
3	4	80.12±0.14

Table 9 Fractional coordinates and thermal parameters of non-hydrogen atoms for compound **1**

Atom	x	y	z	B_{eq} (Å^2)
Sb	0.500	0.03688(7)	0.250	3.31(1)
O(1)	0.5536(4)	0.0411(6)	0.3456(3)	4.1(1)
O(2)	0.5562(5)	−0.1707(6)	0.3286(3)	5.5(2)
C(1)	0.5744(6)	−0.0765(9)	0.3633(4)	4.2(2)
C(2)	0.6225(6)	−0.0809(9)	0.4273(4)	4.3(2)
C(3)	0.6113(7)	−0.197(1)	0.4750(5)	5.5(3)
C(4)	0.6959(6)	−0.180(1)	0.4387(5)	5.8(3)
C(5)	0.7198(8)	−0.274(1)	0.3827(6)	8.0(3)
C(6)	0.7729(7)	−0.123(1)	0.4752(6)	9.2(4)
C(7)	0.6051(9)	−0.152(2)	0.5479(5)	8.9(4)
C(8)	0.5511(8)	−0.310(1)	0.4598(6)	7.6(3)
C(11)	0.3780(6)	−0.0166(9)	0.2875(4)	4.2(2)
C(12)	0.3126(6)	0.063(1)	0.2685(5)	6.9(3)
C(13)	0.2284(7)	0.035(1)	0.2903(6)	8.0(3)
C(14)	0.2133(7)	−0.071(1)	0.3306(6)	8.0(4)
C(15)	0.2804(8)	−0.150(1)	0.3490(7)	8.6(4)
C(16)	0.3654(7)	−0.126(1)	0.3277(6)	7.0(3)
C(21)	0.500	0.250	0.250	4.1(2)
C(22)	0.5301(6)	0.3101(9)	0.3060(5)	5.4(3)
C(23)	0.5302(7)	0.447(1)	0.3059(6)	7.0(3)
C(24)	0.500	0.515(1)	0.250	7.8(4)

The bond distances and angles are listed in Table 6 and Table 7, respectively. The least-squares planes and dihedral angles are listed in Table 8. The fractional coordinates and thermal parameters of non-hydrogen atoms are listed in Table 9. The molecular structure of **1** is shown in Fig. 1. The molecule can be considered as a greatly distorted trigonal bipyramid, the chrysanthemate groups occupy the axial positions and the carbon atoms of the three phenyl groups linked to the antimony atom occupy the equatorial position. The torsion angles of the equatorial phenyl groups are 69.19°, 80.12° and 80.12° respectively (see Table 8). Therefore the three equatorial phenyl groups can be considered as a ‘propellor blade’.

The distances Sb–O(1) and Sb–O(1a) [both 2.106(3) Å] are significantly different from the corresponding distances in $Me_3Sb(O_2C{-}2{-}C_4H_3S)_2$ [2.136(6), 2.124(6) Å][20] and in $Ph_3Sb(O_2C{-}2{-}C_4H_3S)_2$ [2.145(4), 2.095(4) Å].[24] The distances Sb–O(2) and Sb–O(2a) [both 2.800(2) Å] are also different from the corresponding distances in

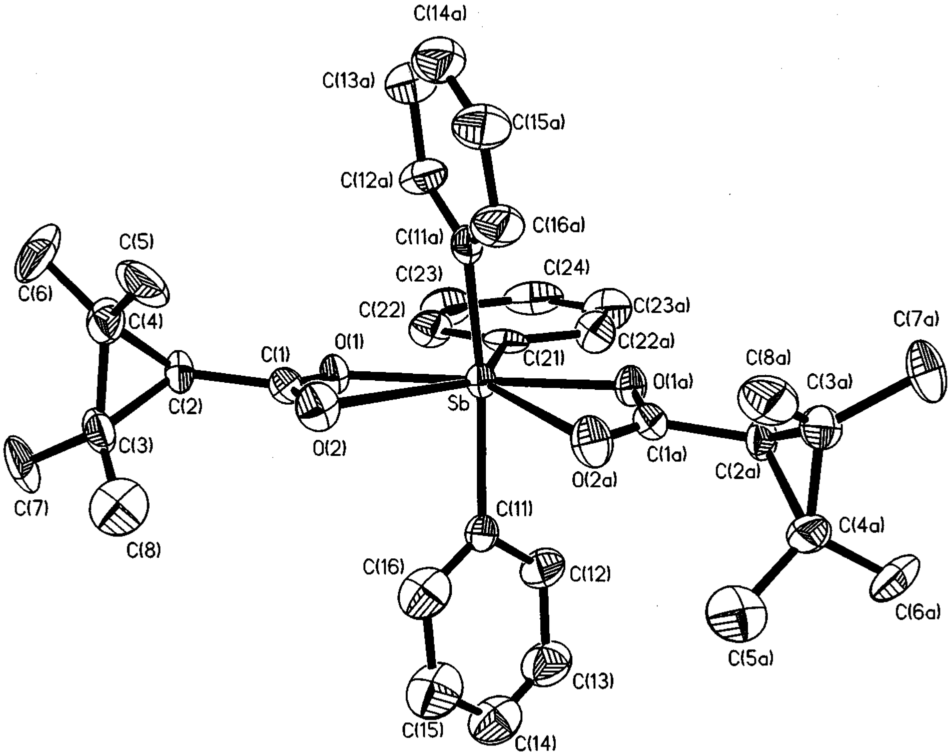

Figure 1 The molecular structure of $Ph_3Sb(O_2C\overline{CHCMe_2C}Me_2)_2$.

$Ph_3Sb(O_2C{-}2{-}C_4H_3S)_2$ [2.744(4), 2.949(4) Å][24] and considerably shorter than the sum of the covalent radii (3.60 Å).[23] This indicates that there are coordination interactions between the carbonyl oxygens of the chrysanthemate groups and the antimony atom. The equatorial C(11)–Sb–C(11a) angle, which is affected by adjacent O(2) and O(2a), is increased to 150.0(3)°, while the C(11)–Sb–C(21) angle and C(11a)–Sb–C(21) angle are all decreased to 105.1(3)°. The corresponding equatorial angles in $Ph_3Sb(O_2C{-}2{-}C_4H_3S)_2$ are 145.9(2)°, 104.4(2)° and 109.5(2)° respectively.[24] Compound **1** and $Ph_3Sb(O_2C{-}2{-}C_4H_3S)_2$ have the same Ph$_3$Sb(V) moiety; they differ in their 2,2,3,3-tetramethylcyclopropyl and 2-thienyl groups. The structural differences between compound **1** and $Ph_3Sb(O_2C{-}2{-}C_4H_3S)_2$ are mainly caused by the steric effect of 2,2,3,3-tetramethylcyclopropyl. It is clear that the steric effect of 2,2,3,3-tetramethylcyclopropyl is greater than that of 2-thienyl. From Table 8 and Fig. 1 we can see that the atoms O(1), O(2), O(2a), O(1a), C(21) and Sb are virtually coplanar. The structure of the molecule of compound **1** thus tends towards a distorted pentagonal bipyramid with four oxygen atoms and C(21) in equatorial positions and two carbon atoms, C(11) and C(11a), in axial positions. The antimony atom has a formal coordination number of seven.[24]

CONCLUSIONS

Triorganoantimony dichrysanthemates with the general formula $R_3Sb(O_2CR')_2$ have plant growth-regulating activity. The nature of the R or R' group affects significantly both biological activities and structures of these compounds. The molecular structure of compound **1** tends towards a distorted pentagonal bipyrimid. The antimony atom has a formal coordination number of seven.

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