APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2003; **17**: 662–668
Environment, Biology and Toxicology
Published online in Wiley InterScience (www.interscience.wiley.com). DOI:10.1002/aoc.491

Synthesis, characterization and *in vitro* antitumor activity of some arylantimony ferrocenecarboxylates and crystal structures of $C_5H_5FeC_5H_4CO_2SbPh_4$ and $(C_5H_5FeC_5H_4CO_2)_2Sb(4\text{-}CH_3C_6H_4)_3$

Run-Chang Liu[1], Yong-Qiang Ma[1], Lin Yu[1], Jin-Shan Li[1]*, Jing-Rong Cui[2] and Rui-Qing Wang[2]

[1]State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, People's Republic of China
[2]National Research Laboratories of Natural and Biomimetic Drugs, Peking University, Beijing 100083, People's Republic of China

Received 15 July 2002; Revised 28 January 2003; Accepted 18 March 2003

A series of arylantimony ferrocenecarboxylates with the formula $(C_5H_5FeC_5H_4CO_2)_nSbAr_{(5-n)}$ ($n = 1$, 2; Ar = C_6H_5, 4-$CH_3C_6H_4$, 3-$CH_3C_6H_4$, 2-$CH_3C_6H_4$, 4-ClC_6H_4, 4-FC_6H_4) were synthesized and characterized by elemental analysis, IR, ^{1}H NMR and mass spectra. The crystal structures of $(C_5H_5FeC_5H_4CO_2)_2Sb(4\text{-}CH_3C_6H_4)_3$ and $C_5H_5FeC_5H_4CO_2SbPh_4$ were determined by X-ray diffraction. Four human neoplastic cell lines (HL-60, Bel-7402, KB and Hela) were used to screen these compounds. The results indicate that these compounds at 10 μM show certain *in vitro* antitumor activities. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: arylantimony; ferrocenecarboxylate; crystal structure; antitumor activity

INTRODUCTION

A large number of references describing synthesis, structures and biological activities of organoantimony carboxylates with the general formula R_nSbX_{5-n} (R = alkyl, aryl; $n = 3$, 4; X = carboxylate) have appeared in the literature.[1–19] The published data on the antitumor activity of these compounds, however, are relatively limited.[20,21] In recent years, the antitumor activity of some ferrocene derivatives has been reported.[22,23] In this paper we discuss the preparation of a series of arylantimony derivatives of ferrocenecarboxylic acid, which contain two or three active centers, namely the arylantimony(V) moiety and ferrocenecarboxylate group, in order to investigate the influence of the organic ligands at antimony on their antitumor activity. Furthermore, we are also interested in studying the nature of the bonding and the structural information of these compounds.

*Correspondence to: Jin-Shan Li, State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, People's Republic of China.
E-mail: jinshan_li2001@yahoo.com.cn

EXPERIMENTAL

General

All the reactions involving metal halides were carried out under anhydrous and oxygen-free argon atmosphere. Solvents were purified, dried, and stored using literature methods. Elemental analyses were determined on a Yanaco CHN Corder MT-3 elemental analyzer. IR spectra were recorded on a Bruker Equinox 55 spectrometer in KBr discs. ^{1}H NMR spectra were measured on a Bruker AC-200 spectrometer in $CDCl_3$ solution with tetramethylsilane as internal standard. Mass spectra electrospray ionization, (EI) were recorded on an HP-5988A at 70 eV; the ionization temperature was 200 °C.

Ferrocenecarboxylic acid was synthesized by the method reported by Benkeser.[24] Ar_3SbBr_2 was prepared by the method reported by Lice and Menzies.[25] Ar_4SbBr was prepared by the literature method.[20]

Synthesis of the title compounds

The ferrocenecarboxylic acid (1 mmol) and triethylamine (0.8 ml) was added to a stirred suspension of Ar_4SbBr (1 mmol) or Ar_3SbBr_2 (0.5 mmol) in toluene (40 ml) according to Eqn (1). The reaction mixture was stirred at room

Table 1. Yields and elemental analyses of the compounds

Compound	Yield (%)	M.p. (°C)	Elemental analysis: found (calc.) (%)		Formula
			C	H	
$\mathbf{I_1}$	62.3	219–221	63.25 (63.71)	4.65 (4.43)	$C_{35}H_{29}FeO_2Sb$
$\mathbf{I_2}$	75.4	246–247	52.74 (52.75)	3.36 (3.16)	$C_{35}H_{25}Cl_4FeO_2Sb$
$\mathbf{I_3}$	69.3	182–184	57.08 (57.49)	3.68 (3.45)	$C_{35}H_{25}F_4FeO_2Sb$
$\mathbf{II_1}$	50.6	248–250	59.16 (59.23)	4.38 (4.10)	$C_{40}H_{33}Fe_2O_4Sb$
$\mathbf{II_2}$	68.7	268 (dec.)	60.17 (60.53)	4.50 (4.60)	$C_{43}H_{39}Fe_2O_4Sb$
$\mathbf{II_3}$	73.0	228–230	60.31 (60.53)	5.07 (4.60)	$C_{43}H_{39}Fe_2O_4Sb$
$\mathbf{II_4}$	62.0	212–215	60.24 (60.53)	4.73 (4.60)	$C_{43}H_{39}Fe_2O_4Sb$
$\mathbf{II_5}$	68.3	254–256	55.92 (55.53)	3.89 (3.50)	$C_{40}H_{30}F_3Fe_2O_4Sb$

temperature for 24 h and filtered. The filtrate was evaporated *in vacuo*. The solid obtained was recrystallized from CH_2Cl_2–petroleum ether to afford the title compounds. The yields, melting points and elemental analysis of the compounds prepared are given in Table 1.

$$n C_5H_5FeC_5H_4CO_2H + Ar_{(5-n)}SbBr_n \xrightarrow{Et_3N} (C_5H_5FeC_5H_4CO_2)_nSbAr_{(5-n)} \quad (1)$$

$n = 1$: Ar = Ph ($\mathbf{I_1}$); 4-ClC_6H_4 ($\mathbf{I_2}$); 4-FC_6H_4 ($\mathbf{I_3}$)
$n = 2$: Ar = Ph ($\mathbf{II_1}$); 4-$CH_3C_6H_4$ ($\mathbf{II_2}$); 3-$CH_3C_6H_4$ ($\mathbf{II_3}$); 2-$CH_3C_6H_4$ ($\mathbf{II_4}$); 4-FC_6H_4 ($\mathbf{II_5}$)

Crystallography

Diffraction measurements of compounds $\mathbf{I_1}$ and $\mathbf{II_2}$ were carried out at 298 K on a Bruker Smart 1000 diffractometer (graphite-monochromatized Mo Kα radiation, λ = 0.71073 Å). The crystal class, orientation matrix and accurate unit-cell parameters were determined by standard procedures. The intensities were corrected for absorption using the SADABS program. The structure was solved by the heavy atom method and refined by a full-matrix least-squares procedure based on F^2. Non-hydrogen atoms were refined with anisotropic thermal parameters. Crystal data are summarized in Table 2.

Table 2. Crystallographic data for compounds $\mathbf{I_1}$ and $\mathbf{II_2}$

	$\mathbf{I_1}$	$\mathbf{II_2}$
Formula	$C_{35}H_{29}FeO_2Sb$	$C_{43}H_{39}Fe_2O_4Sb$
Temperature (K)	298	298
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/n$
Unit cell dimensions		
a (Å)	27.314	16.508
b (Å)	11.118	10.354
c (Å)	18.987	22.650
α (°)	90	90
β (°)	112.23	105.797
γ (°)	90	90
Volume (Å^3)	5635(3)	3722(4)
Z	8	4
Density (Mg mm^{-3})	1.554	1.512
Absorption coefficient (mm^{-1})	1.504	1.531
F(000)	2656	1704
Crystal size (mm^3)	0.35 × 0.25 × 0.10	0.35 × 0.25 × 0.20
θ range for data collection (°)	1.53–26.42	1.87–25.02
Reflections collected	12 993	14 534
Independent reflections	5769	6386
Completeness to $\theta = 25.02°$ (%)		97.1%
Goodness-of-fit on F^2	0.960	1.017
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0287$, $wR_2 = 0.0478$	$R_1 = 0.0981$, $wR_2 = 0.2092$
R indices (all data)	$R_1 = 0.0509$, $wR_2 = 0.0530$	$R_1 = 0.1462$, $wR_2 = 0.2366$
Large difference peak and hole (e Å^{-3})	0.457 and −0.515	1.196 and −2.126

Antitumor activity

The KB cell lines and Hela cell lines were obtained from the Institute of Cancer of Tianjin. Other cell lines were derived in the National Research Laboratories of Natural and Biomimetic Drugs of Peking University. All cell lines were grown in RPMI 1640 medium with 10% fetal bovine serum, in 5% CO_2 atmosphere.

The cytotoxic activity of these compounds was assayed by the 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl-2*H*-tetrazolium bromide (MTT, Thiazolyl blue) method.[26] The cell lines, human immature granulocyte leukemia (HL-60), human hepatocellular carcinoma (Bel-7402), human nasopharyngeal carcinoma (KB) and human cervical carcinoma (Hela) were used for screening. All cell lines were transferred into a 96-well culture plate. Aliquots of log-phase cells were incubated

for 72 h at 37 °C with four dose levels of each organoantimony complex in triplicate. 50 µl of 0.1% MTT (Sigma) was added to each well. After 4 h incubation, the culture medium was removed, and the blue formazan in the cells was dissolved with 150 µl of 2-propanol by vigorous shaking. The optical density of each well was measured at a wavelength of 570 nm. The cytotoxicity was determined by expressing the mean optical densities for drug-treated cells at each concentration as a percentage of that of untreated cells.

RESULTS AND DISCUSSION

The title compounds were prepared under mild conditions. All compounds are red crystalline solids and stable under ordinary conditions. They are soluble in organic solvents such as benzene, toluene, chloroform, and dimethyl sulfoxide, but are not soluble in water, ether, methanol, ethanol, or petroleum ether.

IR

The IR spectra of the title compounds were recorded in the range of 4000–400 cm^{-1}. The absorption bands can be assigned on the basis of the earlier publications and the important data are listed in Table 3.

The IR spectroscopic data provide further support for the molecular constitution of the title compounds. In the majority of organoantimony(V) compounds the antimony generally has a coordination number of five. Because the vacant 5d orbital of the antimony atom can accept a lone electron pair of ligands, in some cases the antimony may have a coordination number of six[5,6] or seven.[7,20] The IR stretching vibration frequencies of carbonyl groups in organoantimony carboxylates are very important for determining their structures. When there are interactions between the antimony atom and the carbonyl oxygen atoms of the carboxylate groups, the asymmetric absorption vibration frequencies [$\nu_{asy}(CO_2)$] of carbonyl groups decrease and the symmetric absorption vibration frequencies [$\nu_{sym}(CO_2)$] increase. Therefore, their differences [$\Delta\nu(CO_2)$] decrease.[3,8,9] In the IR spectra of the title compounds the carboxylate bands are observed in the characteristic regions: $\nu_{asy}(CO_2)$ between 1650 and 1624 cm^{-1} and $\nu_{sym}(CO_2)$ between 1395 and 1375 cm^{-1}. The $\Delta\nu(CO_2)$ values of these compounds are between 275 and 233 cm^{-1}. So we can assume that there are coordination interactions between the antimony atom and the carbonyl oxygen atom of the carboxylate group (see the crystal structures of compounds **I_1** and **II_2**). In addition, the frequencies ν_{asy}(Sb–C) appear between 503 and 462 cm^{-1}, which is consistent with the literature.[8]

Table 3. IR data of the compounds (cm^{-1})

Compound	ν_{asy} (CO_2)	ν_{sym} (CO_2)	$\Delta\nu$ (CO_2)	ν_{asy} (Sb–C)
I_1	1628	1395	233	465
I_2	1626	1383	243	490
I_3	1624	1387	237	462
II_1	1624	1379	235	463
II_2	1624	1379	245	486
II_3	1625	1377	248	503
II_4	1650	1375	275	472
II_5	1625	1378	247	482

^{1}H NMR

The ^{1}H NMR data of the title compounds are listed in Table 4. The protons of $C_5H_5FeC_5H_4$ appeared between 4.59 and 3.82 ppm. The protons of the aryl groups appeared between 7.94 and 7.21 ppm. All the protons in the compounds have been identified and the total number of protons calculated from the integration curve tallies with what was expected from the molecular formula.

Mass spectra

The main mass spectra data of compounds **I_2** and **II_1** are listed in Table 5. The molecular ion peak of compound **I_2** is observed. Although there is no molecular ion peak in compound **II_1**, the fragment ions found are in agreement with the expected structure of the compound. Decarboxylation and dearylation from the antimony atom are main breakdown patterns for the two compounds.

Antitumor activity

The antitumor activities of the title compounds are listed in Table 6. The results of preliminary bioassay show that

Table 4. ^{1}H NMR data of the compounds (ppm)

Compound	C_5H_4	C_5H_5	Ar
I_1	4.53 (2H, s); 4.25 (2H, s)	3.89 (5H, s)	7.24–7.78 (C_6H_5, 20H, m)
I_2	4.58 (2H, s); 4.18 (2H, s)	3.89 (5H, s)	7.25–7.83 (C_6H_4, 16H, m)
I_3	4.50 (2H, s); 4.23 (2H, s)	3.82 (5H, s)	7.24–7.93 (C_6H_4, 16H, m)
II_1	4.59 (4H, s); 4.21 (4H, s)	3.87 (10H, s)	7.21–7.73 (C_6H_5, 15H, m)
II_2	4.57 (4H, s); 4.23 (4H, s)	3.91 (10H, s)	7.23–7.91 (C_6H_4, 12H, m); 2.41 (CH_3, 9H, s)
II_3	4.53 (4H, s); 4.19 (4H, s)	3.85 (10H, s)	7.23–7.85 (C_6H_4, 12H, m); 2.40 (CH_3, 9H, s)
II_4	4.52 (4H, s); 4.25 (4H, s)	3.86 (10H, s)	7.24–7.90 (C_6H_4, 12H, m); 2.42 (CH_3, 9H, s)
II_5	4.58 (4H, s); 4.23 (4H, s)	3.95 (10H, s)	7.25–7.94 (C_6H_4, 12H, m)

Table 5. Fragment ions observed for compound I_2 and II_1

I_2			II_1		
m/z	Fragment	Intensity	*m/z*	Fragment	Intensity
795	$FcCO_2Sb(C_6H_4Cl)_4^+$	0.4	583	$FcCO_2SbPh_3^+$	21
683	$FcCO_2Sb(C_6H_4Cl)_3^+$	1	581	$FcCO_2SbPh_3^+$	26
567	$Sb(C_6H_4Cl)_4^+$	22	506	$FcCO_2SbPh_2^+$	30
565	$Sb(C_6H_4Cl)_4^+$	13	504	$FcCO_2SbPh_2^+$	41
345	$Sb(C_6H_4Cl)_2^+$	16	230	$FcCO_2H^+$	95
343	$Sb(C_6H_4Cl)_2^+$	20	200	$SbPh^+$	51
234	$Sb(C_6H_4Cl)^+$	100	198	$SbPh^+$	63
232	$Sb(C_6H_4Cl)^+$	95	185	Fc^+	8
229	$FcCO_2^+$	62	154	Ph_2^+	100
185	Fc^+	6	121	Sb^+	23
111	$(C_6H_4Cl)^+$	18	77	Ph^+	43

these compounds exhibit certain *in vitro* activities against the four tumor cell lines. The compounds that include the organoantimony moiety have relatively higher antitumor activities than ferrocenecarboxylic acid. The bioassay data indicate that the antitumor activities are affected by the nature of the aryl group: e.g. for compounds **I**, including monoferrocenecarboxylate, when Ar = 4-ClC_6H_4 or 4-FC_6H_4 the compounds $\mathbf{I_2}$ and $\mathbf{I_3}$ have a relatively higher antitumor activity; for compounds **II**, including diferrocenecarboxylate, when Ar = 4-$CH_3C_6H_4$ the compound $\mathbf{II_2}$ has a relatively higher antitumor activity.

Crystal structure

Structure of $C_5H_5FeC_5H_4CO_2SbPh_4$

A red crystal was recrystallized from CH_2Cl_2–petroleum ether solution. One crystal of approximate dimensions $0.35 \times 0.25 \times 0.10\ mm^3$ was mounted in a glass capillary and used for data collection. Figure 1 shows the molecular structure of compound $\mathbf{I_1}$ and gives the atom numbering scheme. The selected bond distances and angles are listed in Table 7. The crystal structure of compound $\mathbf{I_1}$ can be reported as a monomer. The most important feature in this structure is the strongest secondary interaction so far found between antimony and the formally non-bonded oxygen of the carboxylate group. This is the very interaction that makes the coordination geometry of antimony convert from a trigonal bipyramid (e.g. in $CH_3CO_2SbPh_4$[13] and $Ph_3GeCH(Ph)CH_2CO_2SbPh_4$[20]) to a distorted octahedron. The atoms Sb(1), O(1), O(2), C(24) and C(18) are coplanar within 0.0074 Å. The apical Sb(1)–C(12) and Sb(1)–C(30) distances [2.169(3) Å and 2.166(3) Å respectively] are almost equal, and the equatorial Sb(1)–C(18) and Sb(1)–C(24) distances [2.145(3) Å and 2.160(3) Å respectively] are different from each other. All these Sb–C distances are slightly different from those in $CH_3CO_2SbPh_4$ [2.142(6) Å, 2.136(7) Å, 2.135(5) Å and 2.175(6) Å respectively] and in $Ph_3GeCH(Ph)CH_2CO_2SbPh_4$ [2.123(4) Å, 2.121(5) Å, 2.122(5) Å and 2.170(5) Å respectively]. The almost equal Sb(1)–O(1) and Sb(1)–O(2) distances [2.3329(19) Å and 2.3381(18) Å respectively] are also different from those in $CH_3CO_2SbPh_4$ [2.235(4) Å and 2.585(5) Å respectively] and in $Ph_3GeCH(Ph)CH_2CO_2SbPh_4$ [2.289(3) Å and 3.233(3) Å respectively]. The almost equal C–O distances of the carboxyl group [1.267(3) Å and 1.274(3) Å] are between the typical bond lengths for C=O and C–O groups, and different from the corresponding C–O distances of $CH_3CO_2SbPh_4$ [1.289(8) Å and 1.258(8) Å respectively] and $Ph_3GeCH(Ph)CH_2CO_2SbPh_4$ [1.300(6) Å and 1.231(6) Å respectively]. The C(30)–Sb(1)–C(12) angle is 159.53(10)°, which is larger than the corresponding angle in $CH_3CO_2SbPh_4$ [152.6(2)°]. The Fe–C distances are consistent with the literature.[27]

Structure of $(C_5H_5FeC_5H_4CO_2)_2Sb(4\text{-}CH_3C_6H_4)_3$

The red crystal of $(C_5H_5FeC_5H_4CO_2)_2Sb(4\text{-}CH_3C_6H_4)_3$ was obtained from a CH_2Cl_2–petroleum ether solution. The

Table 6. Antitumor activity of the title compounds *in vitro*

Compound	Inhibition ratio (%)[a] (10 μM)			
	HL-60	Bel-7402	KB	Hela
$\mathbf{I_1}$	29.76	4.75	7.36	2.66
$\mathbf{I_2}$	59.00	70.15	80.43	1.52
$\mathbf{I_3}$	64.89	79.85	82.67	76.99
$\mathbf{II_1}$	21.21	−1.58	30.76	−7.22
$\mathbf{II_2}$	87.67	61.24	93.43	67.88
$\mathbf{II_3}$	24.73	10.23	20.80	0.44
$\mathbf{II_4}$	19.65	−0.14	13.58	1.58
$\mathbf{II_5}$	24.19	12.17	20.29	−1.77
A[b]	22.99	9.30	0.41	−15.12

[a] Inhibition ratio (%) = $(A_1 - A_2)/A_1 \times 100\%$. Drug is active when inhibition ratio at 10 μM concentration is ≥ 50%. A_1: the mean optical density of untreated cells. A_2: the mean optical density of drug-treated cells. Negative values indicate that the mean optical density of drug-treated cells (A_2) is greater than that of untreated cells (A_1), i.e. the drug promoted growth of some tumor cells.
[b] **A**: $C_5H_5FeC_5H_4CO_2H$.

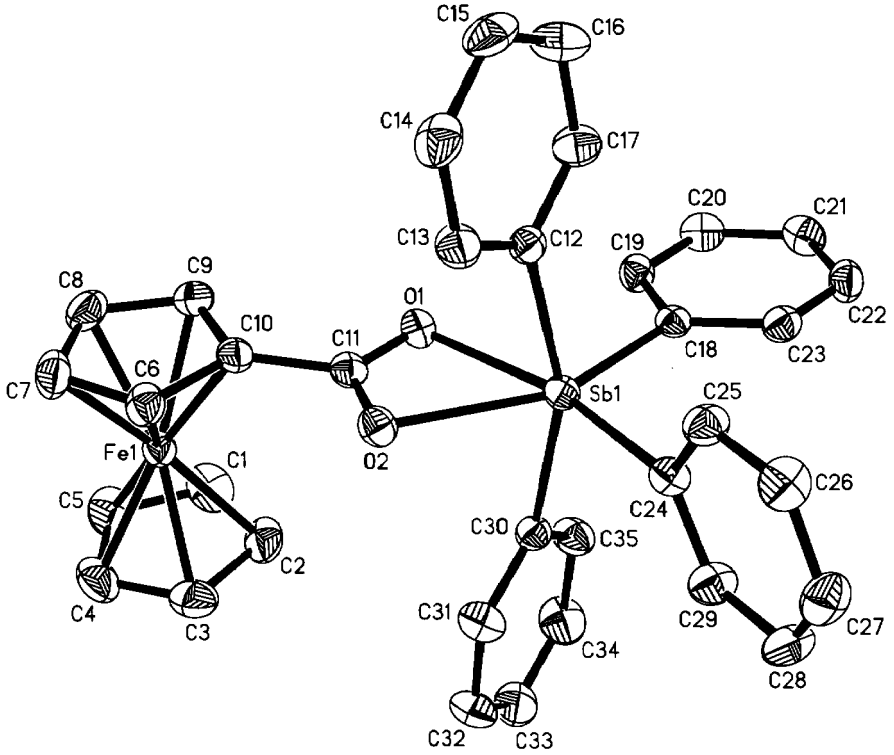

Figure 1. The molecular structure of $C_5H_5FeC_5H_4CO_2SbPh_4$ (**I_1**).

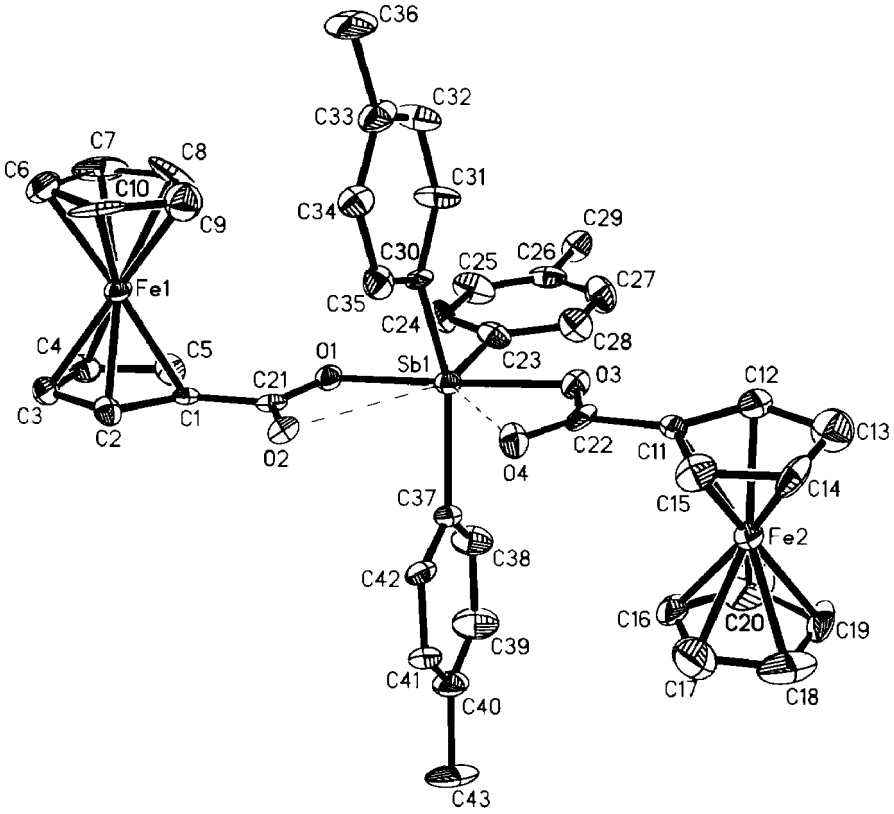

Figure 2. The molecular structure of $(C_5H_5FeC_5H_4CO_2)_2Sb(4\text{-}CH_3C_6H_4)_3$ (**II_2**).

Table 7. Selected bond distances and bond angles of compound $\mathbf{I_1}$

Bond	Distance (Å)	Bond	Angle (°)
Sb(1)–C(18)	2.145(3)	C(12)–Sb(1)–C(30)	159.53(10)
Sb(1)–C(24)	2.160(3)	C(12)–Sb(1)–C(18)	97.30(10)
Sb(1)–C(30)	2.166(3)	C(12)–Sb(1)–C(24)	95.20(10)
Sb(1)–C(12)	2.169(3)	C(12)–Sb(1)–O(1)	81.86(8)
Sb(1)–O(1)	2.3329(19)	C(12)–Sb(1)–O(2)	79.81(9)
Sb(1)–O(2)	2.3381(18)	C(30)–Sb(1)–C(18)	97.89(10)
O(1)–C(11)	1.267(3)	C(30)–Sb(1)–C(24)	94.52(10)
O(2)–C(11)	1.274(3)	C(30)–Sb(1)–O(1)	83.71(9)
C(10)–C(11)	1.467(4)	C(30)–Sb(1)–O(2)	80.12(9)
Fe(1)–C(1)	2.035(4)	C(18)–Sb(1)–C(24)	103.44(11)
Fe(1)–C(2)	2.042(3)	C(18)–Sb(1)–O(1)	93.04(9)
Fe(1)–C(3)	2.026(4)	O(1)–Sb(1)–O(2)	56.25(7)
Fe(1)–C(4)	2.028(4)	O(2)–Sb(1)–C(24)	107.26(9)
Fe(1)–C(5)	2.031(4)	O(1)–C(11)–O(2)	120.1(3)
Fe(1)–C(6)	2.041(3)	O(1)–C(11)–C(10)	120.7(3)
		O(2)–C(11)–C(10)	119.2(3)
		C(9)–Fe(1)–C(1)	107.22(16)

Table 8. Selected bond distances and bond angles of compound $\mathbf{II_2}$

Bond	Distance (Å)	Bond	Angle (°)
Sb(1)–C(30)	2.118(10)	O(3)–Sb(1)–O(1)	174.9(3)
Sb(1)–C(37)	2.147(12)	C(30)–Sb(1)–C(23)	109.5(5)
Sb(1)–C(23)	2.147(13)	C(30)–Sb(1)–C(37)	142.6(5)
Sb(1)–O(1)	2.133(8)	C(37)–Sb(1)–C(23)	107.9(5)
Sb(1)–O(3)	2.124(9)	O(1)–Sb(1)–C(23)	87.4(4)
Sb(1)–O(2)	2.859(16)	O(1)–Sb(1)–C(30)	92.4(4)
Sb(1)–O(4)	2.841(16)	O(1)–Sb(1)–C(37)	90.4(4)
O(1)–C(21)	1.271(14)	O(3)–Sb(1)–C(23)	87.5(4)
O(2)–C(21)	1.223(14)	O(3)–Sb(1)–C(30)	89.8(4)
O(3)–C(22)	1.327(15)	O(3)–Sb(1)–C(37)	90.7(4)
O(4)–C(22)	1.236(15)	O(2)–C(21)–O(1)	123.8(12)
C(1)–C(21)	1.496(17)	O(2)–C(21)–C(1)	121.8(11)
C(11)–C(22)	1.470(17)	O(1)–C(21)–C(1)	114.3(10)
Fe(1)–C(1)	2.025(11)	O(4)–C(22)–O(3)	121.4(11)
Fe(1)–C(2)	2.047(13)	O(4)–C(22)–C(11)	122.8(11)
Fe(1)–C(3)	2.036(13)	O(3)–C(22)–C(11)	115.8(11)
Fe(1)–C(4)	2.062(13)	C(1)–Fe(1)–C(6)	121.4(11)
Fe(1)–C(5)	2.042(13)	C(21)–C(1)–Fe(1)	122.4(8)
Fe(1)–C(6)	2.060(15)	C(22)–C(11)–Fe(2)	121.9(8)

molecular structure with the atom numbering scheme is depicted in Fig. 2. The selected bond distances and angles are listed in Table 8.

Carboxylates are versatile ligands, and can be either unidentate or bidentate. The molecule of compound $\mathbf{II_2}$ consists of a monomer with a seven-coordinated antimony atom surrounded by four oxygen atoms and three aryl groups. The coordination geometry of antimony can be described as a distorted pentagonal bipyramid with the plane being defined by four oxygen atoms from two asymmetrically chelating carboxylate groups and one carbon atom from one aryl group, with the other aryl groups occupying the axial positions. The atoms Sb(1), O(1), O(2), O(3), O(4) and C(23) are coplanar within 0.0108 Å. The Sb(1)–C(23) distance is 2.147(13) Å. The Sb(1)–O(1) and Sb(1)–O(3) distances are 2.133(8) Å and 2.124(9) Å respectively. The Sb(1)–O(2) and Sb(1)–O(4) distances are 2.859(16) and 2.841(16) Å respectively, which are considerably shorter than the sum (3.60 Å) of the van der Waals radii of antimony and oxygen atoms (2.2 Å and 1.40 Å respectively).[28] This indicates that there are weak coordination interactions between the carbonyl oxygen atoms of the two asymmetrical ferrocenecarboxylate groups and the antimony atom. The apical Sb(1)–C(30) and Sb(1)–C(37) distances are 2.118(10) Å and 2.147(12) Å respectively. The C(21)–O(1) and C(21)–O(2) distances [1.271(14) Å and 1.223(14) Å respectively] are slightly different from the C(22)–O(3) and C(22)–O(4) distances [1.327(15) Å and 1.236(15) Å respectively]. The C(30)–Sb(1)–C(37) angle is 142.6(5)°, which is smaller than the corresponding angle in $[Ph_3GeCH_2CH(CH_3)CO_2]_2Sb(4\text{-}ClC_6H_4)_3$ [149.86(19)°].[20]

SUPPLEMENTARY MATERIAL

Crystallographic data for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 186166 for compound $\mathbf{I_1}$ and CCDC no. 186165 for compound $\mathbf{II_2}$. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336 033; e-mail: deposit@ccdc.cam.ac.uk; Web: http://www.ccdc.cam.ac.uk).

Acknowledgements

We thank that Professor Linhong Wong and Assistant Professor Xuebin Leng for support of the crystallographic study. We are also grateful to Professor Kui Wang of National Research Laboratories of Natural and Biomimetic Drugs of Peking University for testing antitumor activity.

REFERENCES

1. Goddard AE. *J. Chem. Soc.* 1923; **123**: 2315.
2. Bajpai K, Singhal R, Strivastava RC. *Indian J. Chem. A* 1979; **18**: 73.
3. Singhal K, Rastogi R, Raj P. *Indian J. Chem. A* 1987; **26**: 146.
4. McEwen WE, Briles GH, Giddings BE. *J. Am. Chem. Soc.* 1969; **91**: 7079.
5. Hartke K, Wolff HM. *Chem. Ber.* 1980; **113**: 1394.
6. Millington PL, Sowerby DB. *J. Chem. Soc. Dalton Trans.* 1992; 1199.
7. Dogamala M, Huber F, Preut H. *Z. Anorg. Allg. Chem.* 1989; **571**: 130.
8. Doak GO, Long GG, Freedman LD. *J. Organometal Chem.* 1965; **4**: 82.

9. Glowacki A, Huber F, Preut H. *Recl. Trav. Chim. Pays-Bas* 1988; **107**: 278.
10. Beauchamp AL, Bennett MJ, Cotton FA. *J. Am. Chem. Soc.* 1969; **91**: 297.
11. Shen K, McEwen WE, LaPlaca LJ, Hamilton WC, Wolf AP. *J. Am. Chem. Soc.* 1968; **90**: 1718.
12. Bone SP, Sowerby DB. *J. Chem. Res.* 1979; **82**(S): 1029(M).
13. Bone SP, Sowerby DB. *Phosphorus, Sulfur, Silicon* 1989; **45**: 23.
14. Ruether R, Huber F, Preut H. *J. Organometal. Chem.* 1985; **295**: 21.
15. Brabant C, Blanck B, Beauchamp AL. *J. Organometal. Chem.* 1974; **82**: 231.
16. Lebedev VA, Bochkova RI, Kuzmin EA, Sharutin VV, Belov NV. *Dokl. Akad. Nauk SSSR* 1981; **260**: 1124.
17. Ferguson G, Glidewell C, Lloyd D, Metcalfe S. *J. Chem. Soc. Perkin Trans. 2* 1988; 731.
18. Li JS, Huang GQ, Wei YT, Xiong CH, Zhu DQ, Xie QL. *Appl. Organometal. Chem.* 1998; **12**: 31.
19. Gibbons MN, Sowerby DB. *J. Organometal. Chem.* 1998; **555**: 271.
20. Ma YQ, Li JS, Xuan ZA, Liu RC. *J. Organometal. Chem.* 2001; **620**: 235.
21. Li JS, Ma YQ, Cui JR, Wang RQ. *Appl. Organometal. Chem.* 2001; **15**: 639.
22. Lu WG, Tao JX, Li XY, Wang YZ. *Yingyong Huaxue* 2000; **17**: 126.
23. Snegur LV, Nekrasov YS, Gumenyuk VV, Zhilina ZV, Morozova NB, Skviridova IK, Rodina IA, Sergeeva NS, Shchitkov KG, Babin VN. *Ross. Khim. Zh.* 1998; **42**: 178 (in Russian).
24. Benkeser RA. *J. Am. Chem. Soc.* 1954; **76**: 4025.
25. Lice WJ, Menzies RS. *J. Chem. Soc.* 1950; 617.
26. Skehan P, Storeng R, Scudiero D, Monks A, McMahon J, Vistica D, Warren JT, Bokesch H, Kenney S, Boyd M. *J. Natl. Cancer Inst.* 1990; **24**: 1107.
27. Seiler P, Dunitz JD. *Acta Crystallogr. Sect. B* 1982; **38**: 1741.
28. Dean JA. *Lange's Handbook of Chemistry*, twelfth edition. McGraw-Hill: 1979; 3-120,3-123.

