Discussion. The current structure (Fig. 1) consists of the two differently substituted organophosphorus fragments $Ph_2P(Se)CH_2$— and $Ph_2P(AuCl)CH_2$—. The fragments are comparable to the known structures of [Se(dppm)] (Colton, Hoskins & Panagiotidou, 1987) and $[(AuCl_2)(dppm)]$ (Schmidbaur, Wohlleben, Wagner, Orama & Huttner, 1977), respectively [dppm = bis(diphenylphosphino)methane]. The two substituents are mutually *cis* [torsion angle Se—P(2)···P(1)—Au = 8°]. In the first fragment, the P—Se bond length is 2.104 (3) Å. This value is identical with the observed P—Se bond length in [Se(dppm)]. Similar values were found in the crystal structures of Ph_3PSe (Codding & Kerr, 1979) and Me_3PSe (Cogne, Grand, Langier, Robert & Wiesenfeld, 1980). They are typical of a P=Se bond length. The Au—Cl and Au—P bond lengths in the second fragment [2.311 (3) and 2.224 (3) Å] are comparable with those in $[AuCl_2(dppm)]$ [2.288 (1) and 2.238 (1) Å]. The Au—Cl bond is somewhat longer than the typical range 2.26–2.29 Å found in many chlorogold complexes (Jones, 1981, 1983, 1986). The Au atom displays the usual linear geometry with only slight deviations [175.2 (1)°]. The title molecule displays an intramolecular non-bonded Au–Se distance of 3.277 (1) Å. Comparable intermolecular non-bonded Au–Se distances are found in $[Ph_3PAuSePh]$ [3.460 (1) and 3.381 (1) Å (Jones & Thöne, 1990)], $[(Ph_3PAu)_2Se(p\text{-}C_6F_4Cl)]^+.SbF_6^-$ [3.516 (1) and 3.616 (1) Å (Jones & Thöne, 1992)] and $[Me_2PhPSeAuPPh_3]^+.SbF_6^-$ [3.353 (1) Å (Jones & Thöne, 1991*b*)]. These weak interactions probably play a significant role in the crystal packing.

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Structures of (L-Methionyl-L-methioninato)dimethyltin(IV) and (L-Alanyl-L-histidinato)dimethyltin(IV). A Class of Potential Antitumour Agents

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Abstract. $C_{12}H_{24}N_2O_3S_2Sn$ $[Me_2Sn(MetMet)]$, (I), $M_r = 427.17$, orthorhombic, $P2_12_12_1$, $a = 15.022$ (2), $b = 12.558$ (2), $c = 9.417$ (2) Å, $V = 1776.5$ (3) Å^3, $Z = 4$, $D_x = 1.60$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 15.44$ cm^{-1}, $F(000) = 864$, $T = 293$ K, $R = 0.032$ for 2243 unique reflections. $C_{11}H_{18}N_4O_3Sn.CH_3OH$ $[Me_2Sn(AlaHis)$ MeOH solvate], (II), $M_r = 405.02$, orthorhombic, $P2_12_12_1$, $a = 14.486$ (2), $b = 12.928$ (2), $c = 8.812$ (1) Å, $V = 1650.3$ (3) Å^3, $Z = 4$, $D_x = 1.63$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu =$

Table 1. *Data collection and refinement details*

	Me_2Sn(MetMet)	Me_2Sn(AlaHis)
Crystal size (mm)	0.4 × 0.2 × 0.4	0.4 × 0.4 × 0.6
Scan method	θ–2θ	θ–2θ
Data range, 2θ (°)	4–56	4–56
h, *k*, *l* maxima	19,16,12	19,17,11
Scan width (°)	1.2	1.5
Scan speed (° s^{-1})	0.03	0.03
No. of reflections used for lattice-parameter determination;	25	25
θ range (°)	2–28	2–28
Absorption correction	None	None
No. of standard reflections;	3	3
intensity variation (%)	± 10	± 10
No. of reflections measured	2457	2276
No. of unique reflections	2435	2253
No. of reflections with $F \geq 7\sigma(F)$	2243	2162
No. of variables	277	274
R	0.032	0.037
wR	0.037*	0.043†
S	1.396	1.078
Maximum shift/e.s.d.	0.195	0.097
Highest ΔF map residual (e Å^{-3})	0.717	0.825

* $w = 1/[\sigma^2 + 0.0008(F^2)]$.
† $w = 1/[\sigma^2 + 0.003(F^2)]$.

14.35 cm^{-1}, $F(000) = 816$, $T = 293$ K, $R = 0.037$ for 2162 unique reflections. In both complexes, dimethyltin(IV) is bound by the terminal amino N atom, the deprotonated peptide N atom and the terminal carboxylate of the dipeptides. The coordination around the Sn atom is distorted trigonal bipyramidal with Sn—(peptide N atom) distances of 2.108 (4) and 2.137 (5) Å, for (I) and (II) respectively; the imidazole and thioether groups are not involved in bonding.

Introduction. The antitumour activity of organotin compounds has been reviewed (Saxena & Huber, 1989), but their mode of action has not been fully established. During 1980–1982 alone, more than 1200 organotin compounds were screened at the National Cancer Institute in the USA (Sadler, 1982). Dibutyltin dichloride was found to be active *in vivo* towards animal tumours, *e.g.* adenocarcinoma 755 (Leiter, Abbot, Bourke, Schepartz & Wodinsky, 1963) and chemically induced pancreatic adenocarcinoma (Takahaschi, Furukawa, Kokubo, Kurata & Hayashi, 1983; Jang, Takahaschi, Furukawa, Toyoda, Hasegawa, Sato & Hayashi, 1986).

Pentacoordinated (organo)tin complexes with biological ligands, *e.g.* amino acids and dipeptides, also exhibit antitumour activity in animal systems. Di-*n*-butyltin glycylglycinate significantly increased the life span of mice bearing P388 leukemia (ILS 50%) and exhibited marginal activity against Lewis lung carcinoma (ILS 27%), mammary tumour CD8F$_1$ (50% inhibition) and MX-1 tumour (53% inhibition) (Ruisi, Silvestri, Lo Guidice, Barbieri, La Martina, Atassi, Huber & Graatz, 1985).

We have determined the crystal and molecular structure of [L-methionyl-L-methioninato(*N*−,*O*−)]-dimethyltin(IV) and [L-alanyl-L-histidinato-(*N*−,*O*−)]dimethyltin(IV) [henceforth abbreviated as Me_2Sn(MetMet) and Me_2Sn(AlaHis)] as representatives of dimethyltin(IV) dipeptides which, as in the case of Me_2Sn(AlaHis), bear an aromatic pendant arm which may be effective in DNA recognition (Sundquist & Lippard, 1990).

Table 2. *Fractional coordinates and equivalent isotropic thermal parameters* (Å^2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	*y*	*z*	U_{eq}
Compound (I)				
Sn	−0.02407 (2)	0.06961 (2)	−0.25675 (3)	0.0319 (1)
S(1)	−0.3820 (1)	0.2645 (1)	−0.2238 (2)	0.0649 (5)
S(2)	−0.3398 (1)	−0.3275 (1)	−0.3341 (2)	0.0713 (6)
O(1)	−0.0085 (2)	0.2389 (3)	−0.3058 (5)	0.047 (1)
O(2)	−0.0734 (4)	0.3815 (3)	−0.3989 (5)	0.064 (2)
O(3)	−0.2327 (3)	0.0354 (3)	−0.5484 (4)	0.048 (1)
N(1)	−0.1123 (2)	−0.0760 (3)	−0.2496 (4)	0.032 (1)
N(2)	−0.1335 (3)	0.1054 (3)	−0.3884 (4)	0.035 (1)
C(1)	−0.0699 (4)	0.2857 (4)	−0.3791 (6)	0.043 (1)
C(2)	−0.1451 (3)	0.2130 (4)	−0.4460 (5)	0.038 (1)
C(3)	−0.2377 (4)	0.2584 (4)	−0.4078 (6)	0.042 (2)
C(4)	−0.2634 (4)	0.2488 (5)	−0.2540 (7)	0.050 (2)
C(5)	−0.4174 (5)	0.1370 (7)	−0.298 (1)	0.085 (3)
C(6)	−0.1794 (3)	0.0266 (4)	−0.4496 (5)	0.033 (1)
C(7)	−0.1607 (3)	−0.0849 (4)	−0.3878 (5)	0.032 (1)
C(8)	−0.2472 (4)	−0.1482 (4)	−0.3748 (5)	0.040 (1)
C(9)	−0.2329 (4)	−0.2635 (4)	−0.3272 (7)	0.048 (2)
C(10)	−0.3153 (7)	−0.4531 (6)	−0.261 (1)	0.093 (3)
C(11)	−0.0258 (4)	0.1013 (5)	−0.0389 (6)	0.051 (2)
C(12)	0.0779 (4)	0.0156 (6)	−0.3936 (7)	0.066 (2)
Compound (II)				
Sn	−0.28432 (2)	−0.07515 (3)	0.03489 (4)	0.0272 (1)
O(1)	−0.2744 (3)	−0.0683 (4)	−0.2162 (5)	0.042 (1)
O(2)	−0.3041 (4)	−0.1449 (5)	−0.4337 (5)	0.048 (1)
O(3)	−0.3272 (4)	−0.3946 (4)	0.0028 (6)	0.050 (1)
N(1)	−0.3282 (4)	−0.1697 (4)	0.2406 (5)	0.034 (1)
N(2)	−0.3339 (3)	−0.2208 (4)	−0.0458 (4)	0.029 (1)
N(3)	−0.5533 (4)	−0.1378 (4)	−0.1196 (6)	0.038 (1)
N(4)	−0.5974 (4)	−0.0361 (5)	−0.3047 (9)	0.054 (2)
C(1)	−0.1409 (4)	−0.0960 (5)	0.0528 (8)	0.043 (2)
C(2)	−0.3901 (4)	0.0356 (5)	0.0409 (9)	0.044 (2)
C(3)	−0.3050 (4)	−0.1424 (5)	−0.2931 (6)	0.030 (1)
C(4)	−0.3437 (4)	−0.2366 (5)	−0.2090 (5)	0.029 (1)
C(5)	−0.3254 (3)	−0.3030 (4)	0.0428 (6)	0.029 (1)
C(6)	−0.3058 (4)	−0 2789 (5)	0.2097 (6)	0.035 (1)
C(7)	−0.3548 (7)	−0.3531 (6)	0.3183 (9)	0.062 (3)
C(8)	−0.4458 (4)	−0.2594 (4)	−0.2529 (6)	0.032 (1)
C(9)	−0.5101 (4)	−0.1659 (5)	−0.2500 (7)	0.033 (1)
C(10)	−0.6072 (5)	−0.0576 (6)	−0.1596 (9)	0.049 (2)
C(11)	−0.5368 (4)	−0.1069 (5)	−0.3626 (8)	0.047 (2)
C(1*M*)	−0.6129 (8)	−0.1792 (9)	0.244 (1)	0.079 (4)
O(1*M*)	−0.5255 (4)	−0.1755 (6)	0.1839 (7)	0.078 (3)

Experimental. (I) Me_2Sn(MetMet) was synthesized by dissolving methionylmethionine (0.200 g, 0.71 mmol) in 50 mL of anhydrous methanol. Freshly prepared Me_2SnO was added (0.118 g, 0.71 mmol) and the mixture was kept stirring under reflux. After 15 min, all solid dissolved. Stirring under reflux was continued for 4 h. The solution was concentrated to a small volume (*ca* 5 ml) with a rotatory evaporator, yielding a white solid which was filtered, washed with diethyl ether and dried *in vacuo* over P_4O_{10}. Analytical data: found C 33.80, H 5.56, N 6.56%; calculated (for $C_{12}H_{24}N_2O_3S_2Sn$) C 33.74, H 5.66, N 6.56%. Melting point 491–493 K. Colourless crystals of Me_2Sn(MetMet) were obtained by recrystallization of the solid from anhydrous methanol.

Table 3. *Selected bond distances* (Å) *and angles* (°)

Compound (I)			
Sn—O(1)	2.188 (4)	Sn—N(1)	2.259 (3)
Sn—N(2)	2.108 (4)	Sn—C(11)	2.089 (6)
Sn—C(12)	2.113 (7)	S(1)—C(4)	1.814 (6)
S(1)—C(5)	1.826 (9)	S(2)—C(9)	1.797 (6)
S(2)—C(10)	1.762 (8)	O(1)—C(1)	1.293 (7)
O(2)—C(1)	1.218 (6)	O(3)—C(6)	1.233 (6)
N(1)—C(7)	1.495 (6)	N(2)—C(2)	1.449 (6)
N(2)—C(6)	1.336 (6)	C(1)—C(2)	1.563 (7)
C(2)—C(3)	1.534 (8)	C(3)—C(4)	1.504 (8)
C(6)—C(7)	1.543 (6)	C(7)—C(8)	1.528 (7)
C(8)—C(9)	1.532 (8)		
C(11)—Sn—C(12)	132.0 (3)	N(2)—Sn—C(12)	106.0 (2)
N(2)—Sn—C(11)	121.8 (2)	N(1)—Sn—C(12)	100.6 (2)
N(1)—Sn—C(11)	96.7 (2)	N(1)—Sn—N(2)	74.5 (1)
O(1)—Sn—C(12)	96.1 (2)	O(1)—Sn—C(11)	91.4 (2)
O(1)—Sn—N(2)	75.6 (1)	O(1)—Sn—N(1)	148.8 (1)
C(4)—S(1)—C(5)	97.5 (3)	C(9)—S(2)—C(10)	101.5 (4)
Sn—O(1)—C(1)	118.5 (3)	Sn—N(1)—C(7)	108.7 (2)
Sn—N(2)—C(6)	119.9 (3)	Sn—N(2)—C(2)	119.5 (3)
C(2)—N(2)—C(6)	118.8 (4)	O(1)—C(1)—O(2)	124.1 (5)
O(2)—C(1)—C(2)	119.2 (5)	O(1)—C(1)—C(2)	116.6 (4)
N(2)—C(2)—C(1)	109.4 (4)	C(1)—C(2)—C(3)	111.4 (4)
N(2)—C(2)—C(3)	112.8 (4)	C(2)—C(3)—C(4)	113.3 (5)
S(1)—C(4)—C(3)	113.2 (4)	O(3)—C(6)—N(2)	126.5 (4)
N(2)—C(6)—C(7)	114.5 (4)	O(3)—C(6)—C(7)	119.0 (4)
N(1)—C(7)—C(6)	110.4 (4)	C(6)—C(7)—C(8)	110.3 (4)
N(1)—C(7)—C(8)	112.6 (4)	C(7)—C(8)—C(9)	113.3 (4)
S(2)—C(9)—C(8)	106.7 (4)		
Compound (II)			
Sn—O(1)	2.219 (4)	Sn—N(1)	2.276 (5)
Sn—N(2)	2.137 (5)	Sn—C(1)	2.101 (6)
Sn—C(2)	2.098 (6)	O(1)—C(3)	1.254 (7)
O(2)—C(3)	1.239 (7)	O(3)—C(5)	1.236 (7)
N(1)—C(6)	1.475 (8)	N(2)—C(4)	1.459 (6)
N(2)—C(5)	1.324 (7)	N(3)—C(9)	1.358 (8)
N(3)—C(10)	1.345 (9)	N(4)—C(10)	1.32 (1)
N(4)—C(11)	1.37 (1)	C(3)—C(4)	1.532 (8)
C(4)—C(8)	1.556 (8)	C(5)—C(6)	1.530 (8)
C(6)—C(7)	1.53 (1)	C(8)—C(9)	1.526 (8)
C(9)—C(11)	1.309 (9)	C(1*M*)—O(1*M*)	1.37 (1)
C(1)—Sn—C(2)	143.9 (3)	N(2)—Sn—C(2)	111.4 (2)
N(2)—Sn—C(1)	104.1 (2)	N(1)—Sn—C(2)	98.2 (2)
N(1)—Sn—C(1)	98.5 (2)	N(1)—Sn—N(2)	72.4 (2)
O(1)—Sn—C(2)	92.6 (2)	O(1)—Sn—C(1)	90.9 (2)
O(1)—Sn—N(2)	74.0 (2)	O(1)—Sn—N(1)	146.5 (2)
Sn—O(1)—C(3)	119.0 (4)	Sn—N(1)—C(6)	107.8 (3)
Sn—N(2)—C(5)	118.7 (4)	Sn—N(2)—C(4)	118.9 (3)
C(4)—N(2)—C(5)	118.5 (4)	C(9)—N(3)—C(10)	104.6 (5)
C(10)—N(4)—C(11)	106.8 (7)	O(1)—C(3)—O(2)	123.8 (6)
O(2)—C(3)—C(4)	117.8 (5)	O(1)—C(3)—C(4)	118.4 (5)
N(2)—C(4)—C(3)	109.3 (4)	C(3)—C(4)—C(8)	112.2 (4)
N(2)—C(4)—C(8)	111.4 (4)	O(3)—C(5)—N(2)	126.8 (5)
N(2)—C(5)—C(6)	114.9 (5)	O(3)—C(5)—C(6)	118.2 (5)
N(1)—C(6)—C(5)	109.4 (5)	C(5)—C(6)—C(7)	112.8 (5)
N(1)—C(6)—C(7)	112.5 (5)	C(4)—C(8)—C(9)	115.2 (5)
N(3)—C(9)—C(8)	120.5 (5)	C(8)—C(9)—C(11)	129.0 (6)
N(3)—C(9)—C(11)	110.4 (6)	N(3)—C(10)—N(4)	110.8 (6)
N(4)—C(11)—C(9)	107.3 (6)		

Table 4. *Possible hydrogen-bond geometry* (Å, °)

The second row of data for each hydrogen bond gives values normalized following Jeffrey & Lewis (1978) and Taylor & Kennard (1983).

D—H···*A*	*D*—H	*D*···A	H···*A*	*D*—H···*A*
Compound (I)				
N(1)—H(1N1)···O(3^{i})	0.882 (4)	3.045 (5)	2.233 (4)	152.88 (25)
	1.030		2.103	151.05
N(1)—H(2N1)···O(1^{ii})	1.050 (3)	2.995 (5)	2.011 (4)	154.70 (23)
	1.030		2.030	154.94
Compound (II)				
N(1)—H(1N1)···O($1M^{ii}$)	1.124 (5)	2.903 (8)	1.814 (6)	162.03 (36)
	1.030		1.903	162.90
O(1*M*)—H(10*M*)···N(2^{iii})	1.077 (6)	3.485 (7)	2.463 (4)	158.14 (45)
	0.938		2.592	159.28
O(1*M*)—H(1O*M*)···N(3^{iii})	1.077 (6)	2.748 (8)	2.453 (5)	94.08 (36)
	0.938		2.467	97.30
N(1)—H(2N1)···O(2^{iv})	1.032 (5)	2.909 (6)	1.887 (4)	170.43 (33)
	1.030		1.888	170.44
N(4)—H(1N4)···O(3^{v})	1.090 (7)	2.754 (9)	1.686 (5)	165.12 (43)
	1.030		1.744	165.62

Symmetry code: (i) $-x-\frac{1}{2}, -y, z+\frac{1}{2}$; (ii) $-x, y-\frac{1}{2}, -z-\frac{1}{2}$; (iii) x, y, z; (iv) $x, y, z+1$; (v) $-x-1, y+\frac{1}{2}, -z-\frac{1}{2}$.

(II) Me_2Sn(AlaHis) was prepared by the same synthetic procedure as that outlined above. Analytical data: found C 35.60, H 5.12, N 14.77%; calculated (for $C_{11}H_{18}N_4O_3Sn$) C 35.42, H 4.86, N 15.02%. Melting point 453–458 K. Clear colourless crystals of the solvate complex were obtained by redissolving the solid in anhydrous methanol and by slowly evaporating the solution in a vessel kept at 293 K.

Intensities were measured with a Philips PW1100 diffractometer, and the structures were solved by Patterson Fourier method and refined by full-matrix least squares based on *F* and with anisotropic thermal parameters for all non-H atoms. H atoms were partially located on a ΔF map but not refined. Scattering factors were contained in the computer program: *SHELX*76 (Sheldrick, 1976). Data collection details and results of the refinements are summarized in Table 1. Fractional coordinates with equivalent isotropic thermal parameters for the complexes are given in Table 2.* Selected bond distances and angles are given in Table 3. Hydrogen bonds are reported in Table 4.

Discussion. General views of the Me_2Sn(MetMet) and Me_2Sn(AlaHis).CH_3OH complexes are shown in Figs. 1 and 2, respectively. Stereoscopic views of partial crystal packing of the unit cells are presented in Figs. 3 and 4.

Molecular packing for the compound (I) (Fig. 3) shows two short intermolecular N(1)···O distances which are shorter than the sum of the van der Waals radii of 3.11 Å (Kitaigorodskii, 1979), which indicate hydrogen bonds with O(1) $(-x, y-\frac{1}{2}, -z-\frac{1}{2})$ and O(3) $(-x-\frac{1}{2}, -y, z+\frac{1}{2})$ atoms. For compound (II), molecular packing shows four hydrogen bonds: two involving atom N(1), one with methanol and one along the 001 direction with atom O(2) $(x, y, z+1)$; one hydrogen bond is present between atoms N(4) and O(3), and another between methanol and atom N(3) of the imidazole. Crystal packing shows contacts less than 3.2 Å for Sn···O(2) in (I), and Sn···O(1) and Sn···O(2) in (II).

In both complexes, tin(IV) is pentacoordinated by the terminal amino N atom, the deprotonated peptide N atom and the terminal carboxylate (in addi-

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters, as well as labelled partial packing diagrams, have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55276 (35 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

tion to the two σ-bonded methyl groups), forming a distorted trigonal bipyramidal arrangement around the metal ion. It is noteworthy that neither the imidazole ring of histidine nor the thioether group of methionine are bound to the metal. In an overall view, they are acting as pendant arms extending towards the outer part of the molecules.

For the alanylhistidine derivative, this is at variance with previously reported structures of closely related complexes of Cu^{2+} with β-alanylhistidine (carnosine) (Freeman & Szymanski, 1967) and glycylglycylhistidine-*N*-methylamide (Camerman, Camerman & Sarkar, 1976), where the imidazole groups coordinate to the cupric ions.

For the methionylmethionine complex, the structure is similar to that reported for Me_2Sn(GlyMet) (Preut, Mundus, Huber & Barbieri, 1986), and in contrast with the structure of the complex of glycylmethionine with Pt^{2+}, where a chelate complex *via* amino and deprotonated peptide N atoms and the thioether group is reported (Freeman & Golomb, 1970). This behaviour reflects the different nature of Pt^{2+} as a typical 'class B' (soft) metal ion, relative to $(CH_3)_2Sn^{2+}$, which is classified (Huheey, 1978) as a 'class A' (hard) ion.

With the exception of C(6) and C(7) in Me_2Sn(MetMet) and C(5) and C(6) in Me_2Sn(AlaHis), all atoms of the tridentate-donor skeleton are nearly planar.

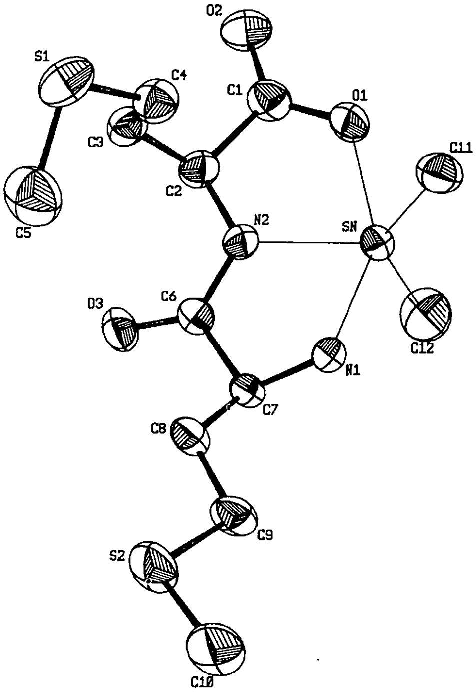

Fig. 1. General view of the Me_2Sn(MetMet) molecule.

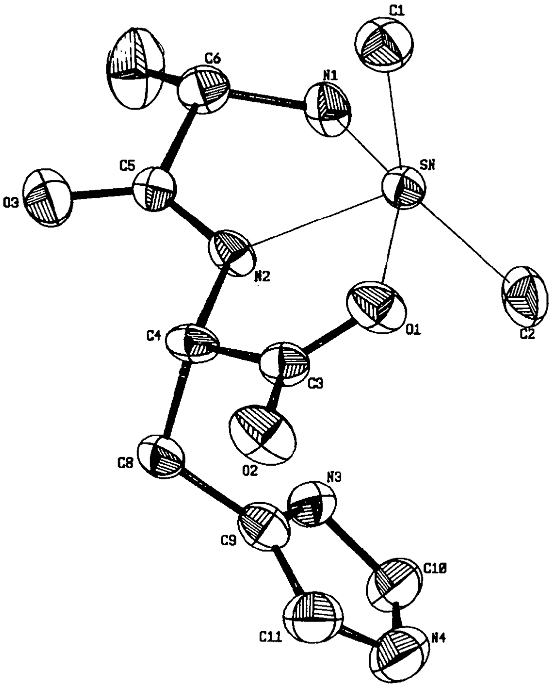

Fig. 2. General view of the Me_2Sn(AlaHis) molecule.

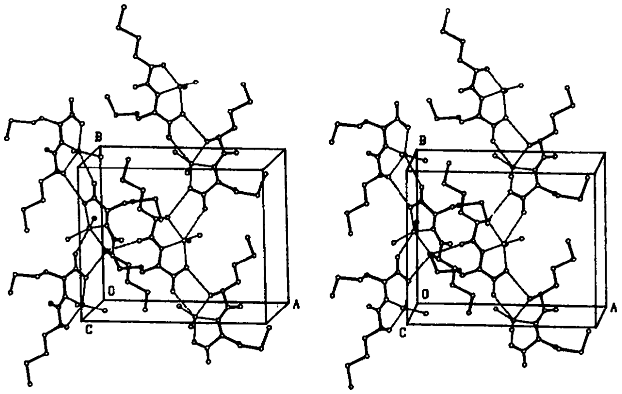

Fig. 3. Stereoscopic view of partial crystal packing of the unit cell of Me_2Sn(MetMet).

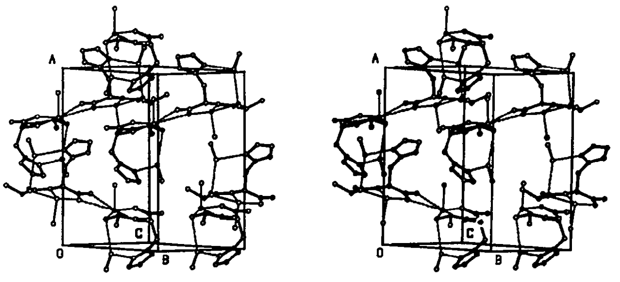

Fig. 4. Stereoscopic view of partial crystal packing of the unit cell of Me_2Sn(AlaHis).

Sn—(peptide N atom) distances are 2.108 (4) Å in (I) and 2.137 (5) Å in (II).

It is noteworthy that the C—Sn—C angle for the Me_2Sn(AlaHis) complex [143.9 (3)°] is the largest found among closely related R_2Sn(dipeptide) complexes (Preut, Mundus, Huber & Barbieri, 1986; Huber, Haupt, Preut, Barbieri & Lo Giudice, 1977).

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Structure of a Ring-Opened 2,5-Dimethylthiophene Complex, $(\eta^5\text{-}C_5Me_5)Ir(CO)(\textit{C,S}\text{-}Me_2C_4H_2S)$

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Abstract. Carbonyl(2,4-hexadiene-2-thiolato)(η^5-pentamethylcyclopentadienyl)iridium, $[Ir(C_6H_8S)(C_{10}H_{15})(CO)]$, $M_r = 467.6$, triclinic, $P\bar{1}$, $a = 13.694\ (4)$, $b = 16.519\ (5)$, $c = 7.740\ (2)$ Å, $\alpha = 102.51\ (2)$, $\beta = 103.43\ (2)$, $\gamma = 81.10\ (2)°$, $V = 1652.5\ (8)$ Å^3, $Z = 4$, $D_x = 1.880$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 81.64$ cm^{-1}, $F(000) = 904$, $T = 203$ K, $R = 0.0362$ ($wR = 0.0470$), 5822 unique reflections, 3843 with $F_o^2 \geq 3\sigma(|F_o|^2)$. In addition to the η^5-pentamethylcyclopentadienyl and CO ligands, the structure contains a non-planar six-membered ring made up of iridium, and the four C atoms and one S atom of the thiophene. The alternating short–long–short [1.33 (2), 1.48 (2), 1.34 (2) Å] pattern of the C—C bond distances indicates that the four-carbon section of the ring is a diene system.

Introduction. Previously we reported (Chen, Daniels & Angelici, 1990*a*) reactions of the isomeric 2,5-dimethylthiophene (2,5-Me_2T) complexes, Cp*Ir(η^4-2,5-Me_2T) and Cp*Ir(*C*,*S*-2,5-Me_2T), where Cp* = η^5-C_5Me_5, with CO to give the title complex Cp*Ir(CO)(*C*,*S*-2,5-Me_2T). Structures of the related Cp*Ir(PR_3)(*C*,*S*-2,5-Me_2T) complexes, where R = PMe_2Ph and $PMePh_2$, were described in that communication. The most interesting feature of these complexes was the six-membered ring which included the iridium and the four C atoms and one S atom of the thiophene. Of particular interest in the present structure was the effect of the CO ligand on the ring geometry.

Experimental. The title complex Cp*Ir(CO)(*C*,*S*-2,5-Me_2T) was isolated (Chen, Daniels & Angelici, 1991) as a by-product from the reaction of Cp*Ir(*C*,*S*-2,5-Me_2T) with $Fe(CO)_5$ and was identified by its IR and ^{1}H NMR spectra as being the same as that prepared previously (Chen, Daniels & Angelici, 1990*a*). Crystals were purified from CH_2Cl_2/hexane at 193 K. Orange–yellow crystal (0.12 × 0.19 × 0.11 mm).

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