Acta Crystallographica Section C
Crystal Structure
Communications
ISSN 0108-2701

Pentacarbonyl{tris[4-(methylsulfonyl)phenyl]stannyl}manganese(I): an unexpected tetragonal structure

Dharamdat Christendat, Ivor Wharf,* Anne-Marie Lebuis, Ian S. Butler and Denis F. R. Gilson

Chemistry Department, McGill University, 801 Sherbrooke Street West, Montréal, Québec, Canada H3A 2K6
Correspondence e-mail: ivor.wharf@mcgill.ca

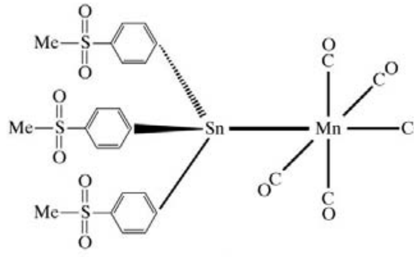
Received 18 December 2001
Accepted 7 March 2002
Online 19 April 2002

The title compound, [$MnSn(C_7H_7O_2S)_3(CO)_5$], is asymmetric but crystallizes in the highly symmetric tetragonal space group $I\overline{4}$. This is achieved without the need for any disorder, either around the Sn atom or in any of the methylsulfonyl groups. The environment around the Sn atom has the following geometry: Sn—Mn = 2.6564 (7) Å, mean Sn—C = 2.175 (5) Å, mean C—Sn—C = 103 (2)° and mean C—Sn—Mn = 115 (6)°. The crystal packing is assisted by weak Sn···O interactions between adjacent columns of molecules, with the resulting geometry at Sn approaching highly distorted trigonal–bipyramidal.

Comment

Group 14 tetraaryl molecules, $M\text{Ar}_4$, have been used extensively as model systems to test various paradigms for describing molecular packing and assessing the likelihood of a particular choice of space group (Lloyd & Brock, 1997). Often, as was predicted earlier by Kitaigorodskii (1961), such molecules crystallize in tetragonal space groups retaining molecular $\overline{4}$ (S_4) symmetry, which is the lowest energy configuration for these molecules (Hutchings *et al.*, 1975*a*,*b*). However, it is generally found that asymmetric molecules pack more effectively using only a few low-symmetry space groups, such as $P2_1/c$, $P\overline{1}$, $P2_12_12_1$, $P2_1$ or $C2/c$ (Kitaigorodskii, 1961).

Recently, we have reported the crystal structures of the series of compounds [$(p\text{-}XC_6H_4)_3SnMn(CO)_5$], with X = CH_3, CH_3O, CH_3S, F and Cl (Christendat *et al.*, 2002). These molecules are inherently asymmetric and, like [$Ph_3SnMn(CO)_5$] (Weber & Bryan, 1967), crystallize in one of the most frequently used space groups, *i.e.* $P2_1/c$ ($P2_1/n$) or $P\overline{1}$. We now report the structure of a sixth member of this set of bimetallic Sn–Mn compounds, [$\{p\text{-}CH_3S(O_2)C_6H_4\}_3SnMn(CO)_5$], (I). Although, in these compounds, the Sn and Mn atoms represent the two poles of spectroscopic and chemical interest, in fact, the $Mn(CO)_5$ moiety is of similar size to an aryl group so, structurally, Sn is the central atom in these molecules. Therefore, the structure of (I) will be compared with those of some related tetraaryltin compounds (Wharf & Lebuis, 2000), as well as with that of [$p\text{-}CH_3S(O_2)C_6H_4$]$_4$Sn (Wharf *et al.*, 1990).



(I)

The molecular structure and atomic numbering scheme for (I) are shown in Fig. 1. The overall geometry is the same as for the other members of the series, although the phenyl-ring torsion angles cover a much wider range (79.5, 11.8 and 34.1°) in (I) than in the compounds studied previously. Around Sn, the average Sn—C distance of 2.175 (5) Å is longer than the values found in analogous compounds (2.145–2.157 Å; Christendat *et al.*, 2002), but the Sn—Mn distance of 2.6564 (7) Å is not significantly less than that found in the structures of other members of this group of compounds. Like all other $Ar_3SnMn(CO)_5$ compounds, there is a quasi-mirror plane of symmetry in the central C_4MnSnC_3 skeleton of (I) [C3—Mn1—Sn1—C21 −0.7 (2)°]. Phenyl ring 2 (C21–C26) is almost coplanar with this quasi-mirror plane.

By far the most novel aspect of the crystal structure of (I) is its high symmetry (tetragonal), which is achieved without the need for disorder, notwithstanding the low molecular symmetry. However, the resulting space group ($I\overline{4}$), while noncentrosymmetric, is achiral (Jones, 1986), and no absolute chemical configuration is assigned to (I). Thus, the structure is not derived from that of [$p\text{-}CH_3S(O_2)C_6H_4$]$_4$Sn ($C2/c$, local symmetry 2), with one $p\text{-}CH_3S(O_2)C_6H_4$ moiety replaced by $Mn(CO)_5$ and subsequent disorder giving a molecule with pseudo-$\overline{4}$ symmetry. Indeed, it is noteworthy that the high crystal symmetry of (I) is achieved without the need for disordered $CH_3S(O_2)$– groups. Instead, molecules of (I) are assembled in columns parallel to the c axis, with one $p\text{-}CH_3S(O_2)C_6H_4$– (ring 3, C31–C36) acting as a spacer (Fig. 2). In each quadrant of the cell, two neighbouring columns of (I) related by a 2_1 axis are held together by a double embrace of $CH_3S(O_2)$– groups. Thus, two in one column attached to phenyl rings 1 (C11–C16) and 2, interlace with symmetry-related ($\frac{1}{2} - x, \frac{1}{2} - y, z + \frac{1}{2}$) $CH_3S(O_2)$– groups attached to rings 2 and 1, respectively, in the neighbouring column. These double chains are then parallel to the $\overline{4}$ axes, leaving $Mn(CO)_5$ groups from four adjacent double chains to pack around the other $\overline{4}$ axes in the unit cell.

The structure of (I) contradicts the general trend that unsymmetric molecules prefer to pack in lower symmetry space groups with the molecules packed in the most efficient way, the intermolecular interactions being much weaker than the covalent bonds of the molecule. With this model, Kitaigorodskii (1961) predicted that, as more obtrusive *para* substituents rendered an Ar$_4$Sn moiety less spherical, this molecule would distort from $\bar{4}$ symmetry so as to pack more efficiently in low-symmetry space groups. Examples of this are (p-C$_2$H$_5$OC$_6$H$_4$)$_4$Sn ($P2_1/c$; Wharf & Simard, 1991) and [p-CH$_3$S(O$_2$)C$_6$H$_4$]$_4$Sn ($C2/c$; Wharf *et al.*, 1990). However, [p-(CH$_3$)$_3$C$_6$H$_4$]$_4$Sn (Wharf & Lebuis, 2000) is tetragonal, the molecules having $\bar{4}$ symmetry.

The more recent approach of Desiraju & Sharma (1996) considers a crystal as a supramolecular entity formed by the mutual recognition of molecules. These networks may then be dissected into supramolecular synthons and molecular synthons, the former being the structural units which yield the supermolecular network of the crystal. In the case of (I), the crystal is constructed from two such quasi-tetrahedral supramolecular synthons, the first being the [–Mn(CO)$_5$]$_4$ cluster surrounding one $\bar{4}$ symmetry element, and the second being the two overlapping clusters formed by the coming together of four [phenyl(1)-S(O$_2$)CH$_3$] and four [phenyl(2)-S(O$_2$)CH$_3$] units from neighbouring molecules which surround the parallel $\bar{4}$ symmetry element. The four double chains which run through the unit cell are then pulled together by weak but significant Sn1$\cdots$O22$^{\rm i}$ interactions [3.498 (4) Å; symmetry code: (i) $y, 2-x, 2-z$]. The geometry at Sn (Fig. 1) may then be considered as highly distorted trigonal–bipyramidal, with the axial angle [O22$^{\rm i}\cdots$Sn1—C11] being 167.7 (1)°. Other intermolecular interactions that may be significant are O12$\cdots$H27$C^{\rm ii}$ of 2.59 Å and O32$\cdots$H16$^{\rm iii}$ of 2.86 Å [symmetry codes: (ii) $\frac{3}{2}-y, x-\frac{1}{2}, \frac{5}{2}-z$; (iii) $x, y, z-1$].

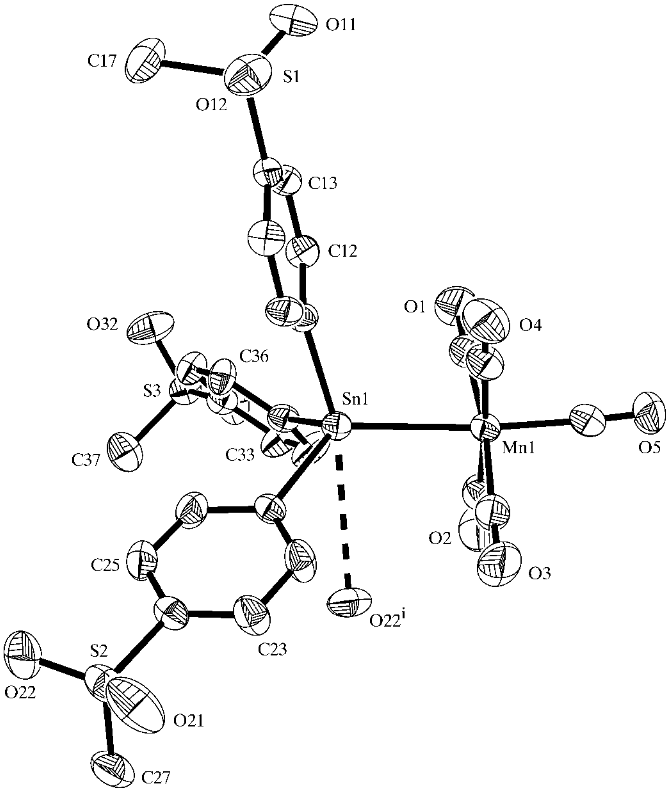


Figure 1
A view of the molecule of (I) showing the atom-labelling scheme and the coordination geometry around Sn. Atom O22$^{\rm i}$ is at ($y, 2-x, 2-z$). Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

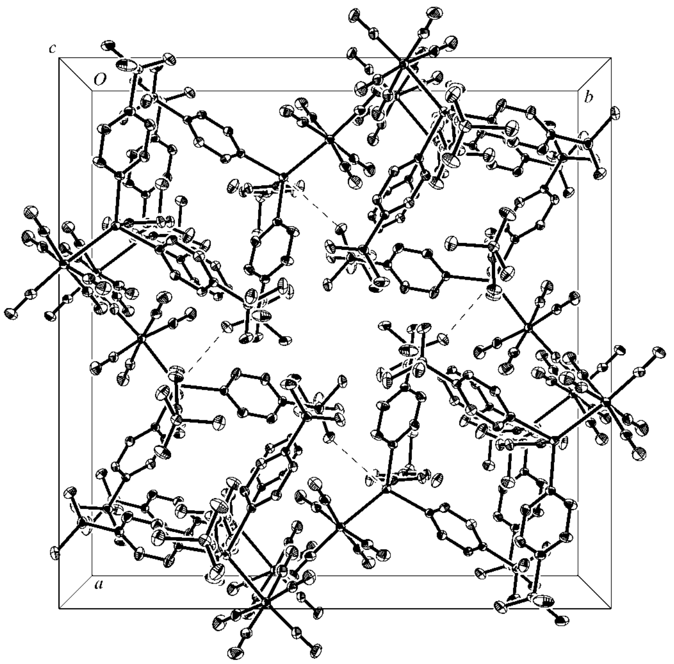


Figure 2
A packing diagram for (I) showing the intermolecular Sn1$\cdots$O22$^{\rm i}$ interactions [symmetry code: (i) $y, 2-x, 2-z$].

Experimental

Compound (I) was prepared previously by Christendat *et al.* (2002). Suitable crystals were obtained by slow evaporation of a CH$_2$Cl$_2$–benzene solution of (I).

Crystal data

[MnSn(C$_7$H$_7$O$_2$S)$_3$(CO)$_5$]
$M_r = 779.24$
Tetragonal, $I\bar{4}$
$a = 22.4188$ (1) Å
$c = 11.9764$ (1) Å
$V = 6019.37$ (6) Å^3
$Z = 8$
$D_x = 1.720$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 28 577 reflections
$\theta = 2.7$–73.3°
$\mu = 12.47$ mm^{-1}
$T = 279$ (2) K
Needle, colourless
0.70 × 0.08 × 0.05 mm

Data collection

Bruker SMART 2K/Platform diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\rm min} = 0.037$, $T_{\rm max} = 0.536$
34 825 measured reflections
5976 independent reflections
5643 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.072$
$\theta_{\rm max} = 73.3°$
$h = -27 \rightarrow 27$
$k = -27 \rightarrow 27$
$l = -14 \rightarrow 13$
316 standard reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.082$
$S = 0.99$
5976 reflections
382 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0544P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.002$
$\Delta\rho_{\rm max} = 0.69$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.37$ e Å^{-3}
Absolute structure: Flack (1983), 2802 Friedel pairs
Flack parameter = 0.009 (5)

m298 Dharamdat Christendat *et al.* • [MnSn(C$_7$H$_7$O$_2$S)$_3$(CO)$_5$] *Acta Cryst.* (2002). C**58**, m297–m299

Table 1
Selected geometric parameters (Å, °).

Sn1—C31	2.169 (4)	Mn1—C1	1.847 (5)
Sn1—C21	2.177 (4)	Mn1—C4	1.860 (5)
Sn1—C11	2.180 (4)	Mn1—C2	1.863 (6)
Sn1—Mn1	2.6564 (7)	Mn1—C3	1.877 (5)
Mn1—C5	1.836 (5)	Sn1···O22^{i}	3.498 (4)
C31—Sn1—C21	105.92 (16)	C4—Mn1—Sn1	85.23 (16)
C31—Sn1—C11	101.44 (16)	C2—Mn1—Sn1	90.64 (16)
C21—Sn1—C11	101.99 (15)	C3—Mn1—Sn1	91.22 (16)
C31—Sn1—Mn1	115.28 (12)	C31—Sn1···O22^{i}	75.93 (15)
C21—Sn1—Mn1	122.39 (11)	C21—Sn1···O22^{i}	67.74 (13)
C11—Sn1—Mn1	107.01 (11)	C11—Sn1···O22^{i}	167.65 (13)
C5—Mn1—Sn1	175.13 (15)	Mn1—Sn1···O22^{i}	84.79 (8)
C1—Mn1—Sn1	81.65 (16)		
C31—Sn1—Mn1—C3	−131.9 (2)	Mn1—Sn1—C11—C12	79.5 (4)
C21—Sn1—Mn1—C3	−0.7 (2)	Mn1—Sn1—C21—C22	11.8 (5)
C11—Sn1—Mn1—C3	116.1 (2)	Mn1—Sn1—C31—C32	34.1 (5)

Symmetry code: (i) $y, 2 - x, 2 - z$.

H atoms were allowed for as riding atoms, with C—H distances of 0.93 and 0.96 Å.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Financial assistance from the Fonds FCAR of the Gouvernement du Québec and from NSERC (Canada) is gratefully acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1638). Services for accessing these data are described at the back of the journal.

References

Bruker (1997). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (1999). *SMART* (Version 5.059) and *SAINT* (Version 6.06). Bruker AXS Inc., Madison, Wisconsin, USA.

Christendat, D., Wharf, I., Lebuis, A.-M., Butler, I. S. & Gilson, D. F. R. (2002). *Inorg. Chim. Acta*, **329**, 36–44.

Desiraju, G. R. & Sharma, C. V. K. (1996). *Perspectives in Supramolecular Chemistry: The Crystal as a Supramolecular Entity*, Vol. 2, edited by G. R. Desiraju, pp. 31–61. Chichester: Wiley.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Hutchings, M. G., Andose, J. D. & Mislow, K. (1975*a*). *J. Am. Chem. Soc.* **97**, 4553–4561.

Hutchings, M. G., Andose, J. D. & Mislow, K. (1975*b*). *J. Am. Chem. Soc.* **97**, 4562–4570.

Jones, P. G. (1986). *Acta Cryst.* A**42**, 57.

Kitaigorodskii, A. I. (1961). *Organic Chemical Crystallography*, pp. 94–105, 124–128. New York: Consultant's Bureau.

Lloyd, M. A. & Brock, C. P. (1997). *Acta Cryst.* B**53**, 780–786.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Weber, H. P. & Bryan, R. F. (1967). *Acta Cryst.* **22**, 822–836.

Wharf, I. & Lebuis, A.-M. (2000). *Main Group Met. Chem.* **23**, 497–503.

Wharf, I. & Simard, M. G. (1991). *Acta Cryst.* C**47**, 1314–1315.

Wharf, I., Simard, M. G. & Lamparski, H. (1990). *Can. J. Chem.* **68**, 1277–1282.

Acta Cryst. (2002). C**58**, m297–m299 Dharamdat Christendat *et al.* • [$MnSn(C_7H_7O_2S)_3(CO)_5$] **m299**