O(2)	−0.0052 (8)	0.7926 (6)	0.2054 (5)	3.6 (3)
O(3)	0.0931 (9)	0.8203 (6)	0.0827 (5)	4.3 (3)
O(4)	0.5482 (9)	0.7433 (6)	0.1732 (5)	3.7 (3)
O(5)	0.4857 (9)	0.7874 (6)	0.0597 (5)	4.0 (3)
O(6)	0.2488 (10)	0.0679 (6)	0.5145 (5)	4.5 (4)
O(7)	0.4023 (9)	0.0891 (6)	0.6403 (5)	3.9 (3)
N(1)	0.2891 (9)	0.5610 (6)	0.2229 (5)	2.3 (3)
N(2)	0.2351 (9)	0.7227 (6)	0.3693 (5)	2.3 (3)
N(3)	0.3184 (11)	0.1392 (6)	0.5566 (6)	2.9 (3)
C(1)	0.3189 (13)	0.4850 (9)	0.1479 (7)	3.3 (5)
C(2)	0.3441 (15)	0.3367 (9)	0.1800 (8)	3.8 (5)
C(3)	0.3423 (14)	0.2680 (9)	0.2953 (7)	3.4 (5)
C(4)	0.3055 (12)	0.3447 (8)	0.3801 (6)	2.2 (4)
C(5)	0.2980 (12)	0.2912 (7)	0.5044 (7)	2.2 (4)
C(6)	0.2677 (12)	0.3725 (8)	0.5807 (7)	2.3 (4)
C(7)	0.2409 (12)	0.5217 (8)	0.5373 (6)	2.2 (4)
C(8)	0.2062 (12)	0.6113 (8)	0.6118 (6)	2.4 (4)
C(9)	0.1833 (13)	0.7542 (8)	0.5636 (7)	2.9 (4)
C(10)	0.1990 (12)	0.8066 (8)	0.4421 (7)	2.7 (4)
C(11)	0.2520 (11)	0.5809 (8)	0.4162 (6)	1.9 (4)
C(12)	0.2849 (12)	0.4922 (8)	0.3380 (7)	2.2 (4)
O(*W*1)	0.1207 (12)	0.8325 (7)	−0.1756 (6)	6.26 (18)
O(*W*2)†	0.1848 (22)	0.5085 (14)	0.8933 (11)	5.5 (3)
O(*W*2′)†	0.1076 (24)	0.4131 (15)	0.9188 (13)	6.5 (4)

† Disordered: an occupancy of 0.5 was assumed for each.

Table 2. *Selected geometric parameters* (Å, °)

V—O(1)	1.614 (6)	V—N(2)	2.142 (6)
V—O(2)	1.880 (6)	O(2)—O(3)	1.452 (8)
V—O(3)	1.875 (6)	O(4)—O(5)	1.460 (8)
V—O(4)	1.906 (6)	O(6)—N(3)	1.225 (9)
V—O(5)	1.878 (6)	O(7)—N(3)	1.219 (9)
V—N(1)	2.347 (6)		
O(1)—V—O(2)	102.0 (3)	O(5)—V—N(1)	86.10 (25)
O(1)—V—O(3)	104.4 (3)	O(5)—V—N(2)	131.7 (3)
O(1)—V—O(4)	99.5 (3)	N(1)—V—N(2)	72.18 (23)
O(1)—V—O(5)	102.1 (3)	V—O(2)—O(3)	67.0 (3)
O(1)—V—N(1)	166.2 (3)	V—O(3)—O(2)	67.4 (3)
O(1)—V—N(2)	94.2 (3)	V—O(4)—O(5)	66.3 (3)
O(2)—V—O(3)	45.51 (25)	V—O(5)—O(4)	68.3 (3)
O(2)—V—O(4)	157.8 (3)	V—N(1)—C(1)	127.7 (5)
O(2)—V—O(5)	132.9 (3)	V—N(1)—C(12)	114.3 (5)
O(2)—V—N(1)	79.68 (24)	C(1)—N(1)—C(12)	117.7 (7)
O(2)—V—N(2)	85.80 (24)	V—N(2)—C(10)	121.6 (5)
O(3)—V—O(4)	132.5 (3)	V—N(2)—C(11)	120.1 (5)
O(3)—V—O(5)	89.3 (3)	C(10)—N(2)—C(11)	118.3 (6)
O(3)—V—N(1)	86.7 (3)	O(6)—N(3)—O(7)	122.8 (6)
O(3)—V—N(2)	130.2 (3)	O(6)—N(3)—C(5)	118.3 (6)
O(4)—V—O(5)	45.39 (25)	O(7)—N(3)—C(5)	118.9 (7)
O(4)—V—N(1)	78.12 (24)	N(2)—C(11)—C(12)	118.0 (6)
O(4)—V—N(2)	87.39 (24)	N(1)—C(12)—C(11)	115.2 (6)

The structure was solved by direct methods and refined by a full-matrix least-squares method with all non-H atoms anisotropic except for the water O atoms. H-atom positions were calculated assuming a C—H distance of 1.08 Å. Solvent protons were omitted. All computing was performed using the *NRCVAX* system (Gabe, Le Page, Charland, Lee & White, 1989).

The authors wish to thank the Medical Research Council (MRC) of Canada, the Department of Education of Quebec (FCAR) and Nordic Merrell Dow Research Inc. of Montreal for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and least-squares-planes data have been deposited with the IUCr (Reference: BR1055). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1994). C**50**, 1046–1049

Tetrakis[*m*-(trifluoromethyl)phenyl]tin(IV)

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(*Received* 14 *September* 1992; *accepted* 25 *October* 1993)

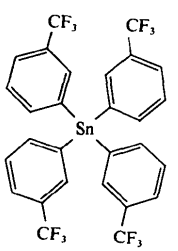
Abstract

The crystal structure of tetrakis[*m*-(trifluoromethyl)-phenyl]tin(IV), $[Sn(C_6H_4CF_3)_4]$, has been determined. The Mössbauer spectrum of the compound shows a single peak with an isomer shift of 1.20 mm s^{-1}. The molecule is tetrahedral with no short intermolecular contacts. The Sn atom is located at a special position and the four Sn—C bond lengths [2.143 (5) Å] are equal by symmetry.

Comment

Organotin compounds are known to possess a variety of biocidal properties. With this in mind, a range of organotin compounds have been screened (Eng, Coddington, Stockton & Acholonu, 1989; Eng & Acholonu, 1991; Eng, Khoo, Stockton & Coddington, 1992) against *Ceratacystis ulmi*, the fungus responsible for Dutch Elm Disease (DED), which has killed millions of elm trees in Europe and North America. Results from our earlier screening studies indicated that triphenyltin compounds are some of the more effective compounds of those tested (Eng, Coddington, Stockton & Acholonu, 1989; Eng & Acholonu, 1991; Eng, Khoo, Stockton & Coddington, 1992). This is not surprising since triphenyltin compounds are proven agricultural fungicides (Gitlitz, 1976; Smith, Okioga & Khoo, 1980; Sugavanam & Smith, 1970; Crowe, 1987).

In our efforts to develop a more effective fungicide against DED, we have introduced substituents into the phenyl rings of the triphenyltin compounds. The aim was to gain further insight into the effects of the structure of the organotin compounds on their inhibition of the fungus. Furthermore, the tetraaryltins are themselves of considerable structural interest in the solid state, and are known to crystallize in a variety of tetragonal space groups ($P42_1c$, $I\bar{4}$ or $I4_1/a$) depending on the type of packing in the crystal. The present paper reports the synthesis, Mössbauer data and the results of an X-ray crystal structure analysis for tetrakis[*m*-(trifluoromethyl)-phenyl]tin(IV), (I), which is a precursor for tris[*m*-(trifluoromethyl)phenyl]tin(IV) chloride.



(I)

Mössbauer spectroscopy provides a probe of the Sn atom that is sensitive to changes in the oxidation state and the configuration of the ligands around the Sn atom. The absence of any quadrupole splitting and the observation of only one peak in the Mössbauer spectrum of tetrakis[*m*-(trifluoromethyl)-phenyl]tin(IV) indicates that the stereochemistry of the compound is tetrahedral. The observed isomer shift of 1.20 mm s^{-1} is the same as the average of the values reported for tetraphenyltin(IV) [1.21 mm s^{-1} (Herber & Stoeckler, 1964), 1.15 mm s^{-1} (Gibb & Greenwood, 1966), 1.22 mm s^{-1} (Stoeckler & Sano, 1968) and 1.27 mm s^{-1} (Parish & Platt, 1968), giving a mean value of 1.21 mm s^{-1}]. For the title compound, the presence of the electronegative F atoms would be expected to cause some decrease in the electron density near the Sn nucleus, leading to a reduced isomer shift relative to tetraphenyltin(IV), but the wide range in reported isomer shifts for tetraphenyltin(IV) makes comparison difficult, and the expected decrease in the isomer shift is not detectable. The tetrahedral geometry of the molecule predicted by the Mössbauer spectrum is confirmed by the X-ray structural investigation.

An *ORTEP*II (Johnson, 1976) plot of the organotin complex is presented in Fig. 1. A stereo pair showing the packing arrangement of the molecules in the unit cell is shown in Fig. 2. As would be expected from symmetry considerations, the four Sn—C distances are constrained to be equal, with a bond length of 2.143 (5) Å, the same as those [2.143 (5) Å] in $(C_6H_5)_4Sn$ (Engelhardt, Leung, Raston & White, 1982) and similar to those [2.150 (3) Å] in $(m\text{-}CH_3C_6H_4)_4Sn$ (Karipides & Oertel, 1977). The phenyl rings show minimal distortion from ideal geometry, with the C—C distances very close to the expected value for aromatic rings [1.394 (5) Å (Sutton, 1965)]. Phenyl rings σ-bonded to metal atoms are expected to show marked deviations from D_{6h} symmetry with respect to the ring angles

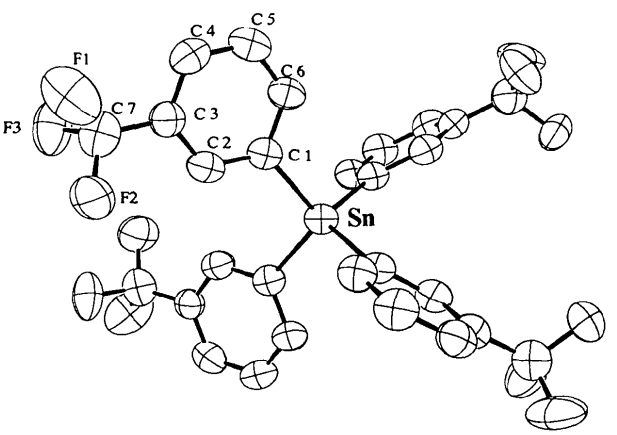


Fig. 1. *ORTEP*II (Johnson, 1976) plot of the molecule, showing the numbering scheme. Ellipsoids are drawn at the 50% probability level. Only the major orientation of the disordered CF_3 group is shown and H atoms have been omitted.

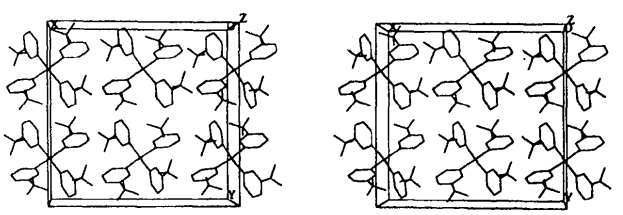


Fig. 2. Stereoview of the unit cell showing the packing arrangment. H atoms have been omitted for clarity.

(Churchill, Kalra & Veidis, 1973). Such marked deviation is reported for the compounds $[(p\text{-}SCH_3)\text{-}C_6H_4]_4Sn$ and $[(p\text{-}OCH_3)]C_6H_4]_4Sn$ (Wharf & Simard, 1987), for which the average ring angles are: $C_{ortho}—S_{Sn}—C_{ortho} = 116.5\ (5)$, $C_{Sn}—C_{ortho}—C_{meta} = 122.4\ (5)$, $C_{ortho}—C_{meta}—C_{para} = 119.8\ (5)$ and $C_{meta}—C_{para}—C_{meta} = 119.0\ (5)°$. For the title compound, $(m\text{-}CF_3C_6H_4)_4Sn$, such deviations in the average ring angles are not observed: $C_{ortho}—C_{Sn}—C_{ortho} = 119.0\ (5)$, $C_{Sn}—C_{ortho}—C_{meta} = 120.3\ (5)$, $C_{ortho}—C_{meta}—C_{para} = 120.1\ (5)$ and $C_{meta}—C_{para}—C_{meta} = 120.1\ (5)°$. It may be that the lower level of distortion is related to the more open packing present in the crystal of the title compound due to the bulk of the CF_3 groups.

Experimental

Tetrakis[*m*-(trifluoromethyl)phenyl]tin(IV) was prepared by the reaction of [*m*-(trifluoromethyl)phenyl]magnesium chloride in anhydrous ether with tin tetrachloride, resulting in an 81% yield of the product. The isolated product was washed with ether (280 K), air-dried and recrystallized from $CHCl_3$; m.p. 415-416 K [literature m.p. 415.7-417 K (Stern & Becker, 1964)]. Analysis for $C_{28}H_{16}F_{12}Sn$: calculated, C 48.10, H 2.31, Sn 16.98%; found, C 47.63, H 2.47, Sn 16.94%. The Mössbauer spectra were measured at 80 K on a Mössbauer spectrometer model MS-900 (Ranger Scientific Co., Burleson, TX, USA) in the acceleration mode with a moving source geometry and using a liquid nitrogen cryostat (CYRO Industries of America, Inc., Salem, NH, USA). The sample was mounted in a teflon holder. The source was 15 mCi $Ca^{119m}SnO_3$, and the velocity was calibrated at ambient temperature using a composition of $BaSnO_3$ and Sn foil (splitting = 2.52 mm s^{-1}). The resultant spectrum was analyzed by a least-squares fit to Lorentzian-shaped lines. All isomer shifts were calculated relative to $BaSnO_3$.

Crystal data

$[Sn(C_7H_4F_3)_4]$
$M_r = 699.10$
Tetragonal
$I4_1/a$
$a = 17.3167\ (13)$ Å
$c = 8.8439\ (5)$ Å
$V = 2652.0\ (2)$ Å^3
$Z = 4$
$D_x = 1.751$ Mg m^{-3}
Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 28 reflections
$\theta = 45\text{-}50°$
$\mu = 8.80$ mm^{-1}
$T = 293$ K
Thin flake
0.30 × 0.25 × 0.03 mm
White

Data collection

Enraf-Nonius diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{min} = 0.16$, $T_{max} = 0.37$
1628 measured reflections
676 independent reflections
638 observed reflections [$I > 2.5\sigma(I)$]
$R_{int} = 0.021$
$\theta_{max} = 49.9°$
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 8$
3 standard reflections (800, 0$\bar{8}$0, 004)
frequency: 60 min
intensity variation: 1.2%

Refinement

Refinement on F
$R = 0.031$
$wR = 0.042$
$S = 3.27$
638 reflections
148 parameters
H-atom parameters not refined
Weighting scheme based on counting statistics
$(\Delta/\sigma)_{max} = 0.071$
$\Delta\rho_{max} = 0.260$ e Å^{-3}
$\Delta\rho_{min} = -0.37$ e Å^{-3}
Extinction correction: secondary (Larson, 1970)
Extinction coefficient: 0.48 (5)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates, site occupancy factors and equivalent isotropic displacement parameters* (Å^2)

$B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	Occupancy	x	y	z	B_{eq}
Sn	1.0	1/2	3/4	1/8	4.226 (23)
C(1)	1.0	0.5599 (3)	0.6666 (3)	−0.0104 (6)	4.15 (24)
C(2)	1.0	0.5964 (3)	0.6854 (3)	−0.1458 (6)	4.5 (3)
C(3)	1.0	0.6356 (3)	0.6297 (3)	−0.2278 (6)	4.31 (24)
C(4)	1.0	0.6387 (3)	0.5545 (3)	−0.1756 (7)	5.1 (3)
C(5)	1.0	0.6035 (3)	0.5350 (3)	−0.0408 (7)	5.4 (3)
C(6)	1.0	0.5643 (3)	0.5910 (3)	0.0427 (6)	4.6 (3)
C(7)	1.0	0.6727 (4)	0.6498 (4)	−0.3722 (7)	6.3 (3)
F(1)	0.435	0.73139 (22)	0.60520 (19)	−0.4126 (6)	5.9 (4)
F(2)	0.435	0.6989 (3)	0.72462 (13)	−0.3779 (6)	7.3 (4)
F(3)	0.435	0.62258 (17)	0.6477 (3)	−0.4999 (6)	8.4 (5)
F(4)	0.391	0.62243 (19)	0.6795 (3)	−0.4612 (8)	9.4 (6)
F(5)	0.391	0.7334 (3)	0.6973 (3)	−0.3538 (7)	7.7 (5)
F(6)	0.391	0.7031 (4)	0.58451 (12)	−0.4413 (8)	7.7 (5)
F(7)	0.174	0.6495 (6)	0.6008 (4)	−0.4804 (15)	8.4 (13)
F(8)	0.174	0.7537 (3)	0.6429 (6)	−0.3733 (14)	5.3 (8)
F(9)	0.174	0.6581 (6)	0.7208 (3)	−0.4135 (14)	5.9 (9)

Table 2. *Selected geometric parameters* (Å, °)

Sn—C(1)	2.143 (5)	C(1)—C(2)	1.392 (7)
C(1)—C(6)	1.394 (7)	C(2)—C(3)	1.385 (7)
C(3)—C(4)	1.381 (7)	C(3)—C(7)	1.472 (8)
C(4)—C(5)	1.381 (8)	C(5)—C(6)	1.395 (8)
C(7)—F(1)	1.326 (8)	C(7)—F(2)	1.373 (7)
C(7)—F(3)	1.425 (8)	C(7)—F(4)	1.281 (8)
C(7)—F(5)	1.343 (8)	C(7)—F(6)	1.389 (8)
C(7)—F(7)	1.341 (12)	C(7)—F(8)	1.408 (8)
C(7)—F(9)	1.307 (9)		
C(1)—Sn—C(1^i)	108.19 (17)	C(1)—Sn—C(1^{ii})	112.06 (18)
Sn—C(1)—C(2)	122.8 (4)	Sn—C(1)—C(6)	118.1 (4)
C(2)—C(1)—C(6)	119.0 (5)	C(1)—C(2)—C(3)	120.6 (5)
C(2)—C(3)—C(4)	120.1 (5)	C(2)—C(3)—C(7)	120.2 (5)
C(4)—C(3)—C(7)	119.7 (5)	C(3)—C(4)—C(5)	120.1 (5)
C(4)—C(5)—C(6)	120.1 (5)	C(1)—C(6)—C(5)	120.0 (5)
C(3)—C(7)—F(1)	115.5 (5)	C(3)—C(7)—F(2)	113.6 (5)
C(3)—C(7)—F(3)	114.5 (5)	C(3)—C(7)—F(4)	109.3 (5)
C(3)—C(7)—F(5)	112.4 (5)	C(3)—C(7)—F(6)	110.7 (5)
C(3)—C(7)—F(7)	109.8 (7)	C(3)—C(7)—F(8)	114.9 (7)
C(3)—C(7)—F(9)	112.4 (7)	F(1)—C(7)—F(2)	106.7 (5)
F(1)—C(7)—F(3)	103.8 (5)	F(2)—C(7)—F(3)	101.4 (5)
F(4)—C(7)—F(5)	111.1 (6)	F(4)—C(7)—F(6)	108.3 (6)
F(5)—C(7)—F(6)	104.8 (5)	F(7)—C(7)—F(8)	103.9 (8)
F(7)—C(7)—F(9)	109.7 (8)	F(8)—C(7)—F(9)	105.7 (8)

Symmetry codes: (i) $-\frac{1}{4}+y, \frac{1}{4}-x, \frac{5}{4}-z$; (ii) $-x, \frac{1}{2}-y, z$.

Data were collected using the $\theta/2\theta$ scan mode and profile analysis (Grant & Gabe, 1978). The structure was solved by direct methods, followed by a difference Fourier synthesis. All non-

H atoms were refined with anisotropic displacement parameters. Refinement using all data (676) produced final residuals of $R = 0.033$, $wR = 0.042$. There is some disorder in the $-CF_3$ groups, which have three different orientations with occupancies of 0.453, 0.391 and 0.174. These were determined by fixing the displacement parameters to one value and allowing the occupancies to refine, then taking the average occupancy for the group, fixing it at that number then letting the displacement parameters refine. The *NRCCAD* diffractometer control program (Le Page, White & Gabe, 1986) was used for data collection and the *NRCVAX* system (Gabe, Le Page, Charland, Lee & White, 1989) was used for all computations.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71793 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD1031]

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Acta Cryst. (1994). C**50**, 1049–1052

Oxobis(*N*-oxopyridine-2-thiolato-*N*,*O*)vanadium(IV)

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(*Received* 22 *December* 1992; *accepted* 4 *January* 1994)

Abstract

The title compound, oxobis(pyridine-2-thiolato *N*-oxide-*N*,*O*)vanadium(IV), $[V(C_5H_4NOS)_2O]$, contains vanadium in a distorted square-pyramidal coordination geometry with a multiply bonded O atom at the apex and a basal plane defined by a *cis* S_2O_2 group of donor atoms from the organic ligands. The V—O basal distances are 1.952 (3) and 1.961 (3) Å, the V—S basal distances are 2.386 (2) and 2.361 (1) Å and the axial V=O distance is 1.593 (3) Å.

Comment

The conjugate base of 1-hydroxypyridine-2-thione (or its tautomer 2-pyridinethiol *N*-oxide) forms a variety of metal derivatives which have received extensive attention as a consequence of their antifungal and antibacterial activity (Pansy, Stander, Koerber & Donovick, 1953; Chandler & Segel, 1978; Box, Shanga, Sanghvi & Sugden, 1980; Bennett, Gannon & Onyekweln, 1982). The synthesis and characterization of several transition-metal and rare earth complexes with this ligand have been described (Robinson, 1964; Hodge, Nordquest & Blinn, 1972; West & Frank, 1979; Davidson, Preston & Russo, 1983). These authors have indicated that the formation of metal-ion complexes occurs with both the *N*-oxide O atom and the S atom serving as donors. The determination of the structures of the phenylbismuth, Zn and Ni complexes has confirmed these results (Curry & Jandacek, 1972; Barnett, Kretschmar & Hartman, 1977; Chen, Hu, Wu, Weng & Kang, 1991). Recently we reported the thermal behaviour of a number of first-row transition-metal complexes (Higes-Rolando, Pérez-Florindo &