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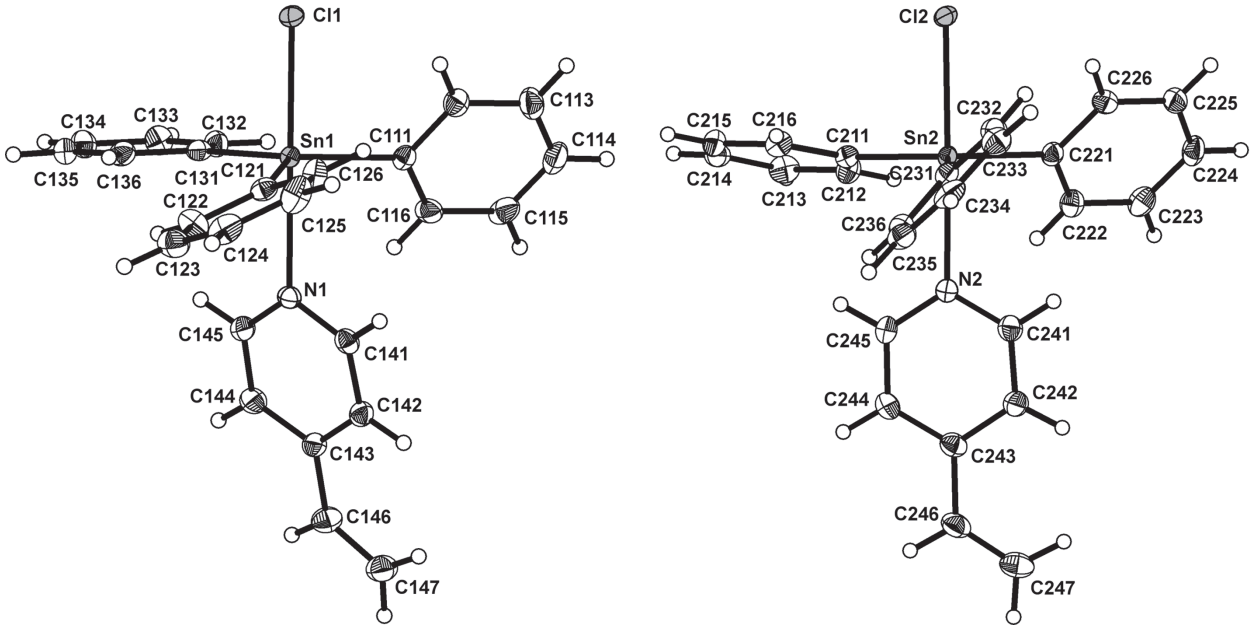
Hans Reuter* and Tobias Gieschen

Crystal structure of (4-vinylpyridine-κ*N*)triphenyl tin(IV) chloride, $C_{25}H_{22}ClNSn$



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Abstract

$C_{25}H_{22}ClNSn$, monoclinic, $P2_1/c$ (no. 14), $a = 17.8179(8)$ Å, $b = 15.6453(6)$ Å, $c = 17.4603(7)$ Å, $\beta = 116.588(2)°$, $V = 4352.6(3)$ Å^3, $Z = 8$, $R_{gt}(F) = 0.0297$, $wR_{ref}(F^2) = 0.0681$, $T = 100$ K.

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The two crystallographically independent molecules forming the asymmetric unit of the crystal structure are shown in the figure. Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colourless, Blocks Size 0.21 × 0.13 × 0.12 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	13.1 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$2\theta_{max}$, completeness::	56°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	209691, 10503, 0.067
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 9081
$N(param)_{refined}$:	512
Programs:	Bruker programs [12], SHELX [13, 14], DIAMOND [15]

Source of material

The title compound was obtained as a side product of the hydrostannylation of 4-vinylpyridine with triphenyltin(IV) hydride, Ph_3SnH, freshly prepared without purification from Ph_3SnCl and $Li[AlH_4]$.

Experimental details

All hydrogen atoms were identified in difference Fourier syntheses. All hydrogen atoms were included in the latest stages of the refinement by the use of a riding model. Common U_{iso}

***Corresponding author: Hans Reuter,** Institut für Chemie neuer Materialien, Universität Osnabrück, Barbarastr. 7, D-49069 Osnabrück, Germany, e-mail: hreuter@uos.de
Tobias Gieschen: Institut für Chemie neuer Materialien, Universität Osnabrück, Barbarastr. 7, D-49069 Osnabrück, Germany

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Sn1	0.54653(2)	0.65454(2)	0.24563(2)	0.01583(5)
Cl1	0.65677(4)	0.72810(4)	0.21916(4)	0.02173(12)
C111	0.56709(15)	0.73239(16)	0.35423(15)	0.0176(5)
C112	0.59856(16)	0.81499(16)	0.35912(17)	0.0223(5)
H112	0.6123	0.8350	0.3156	0.032(4)*
C113	0.60995(17)	0.86823(18)	0.42736(19)	0.0289(6)
H113	0.6311	0.9244	0.4299	0.032(4)*
C114	0.59065(17)	0.8398(2)	0.49150(18)	0.0303(6)
H114	0.5973	0.8768	0.5373	0.032(4)*
C115	0.56180(17)	0.7577(2)	0.48857(17)	0.0295(6)
H115	0.5497	0.7376	0.5332	0.032(4)*
C116	0.55017(16)	0.70392(18)	0.42060(16)	0.0232(5)
H116	0.5305	0.6473	0.4194	0.032(4)*
C121	0.44824(15)	0.68066(16)	0.12128(15)	0.0185(5)
C122	0.40999(17)	0.61406(18)	0.06424(17)	0.0250(6)
H122	0.4267	0.5568	0.0818	0.032(4)*
C123	0.34771(17)	0.6299(2)	−0.01805(18)	0.0286(6)
H123	0.3225	0.5837	−0.0564	0.032(4)*
C124	0.32246(17)	0.7129(2)	−0.04405(17)	0.0279(6)
H124	0.2796	0.7241	−0.1001	0.032(4)*
C125	0.36016(18)	0.7794(2)	0.01221(18)	0.0313(6)
H125	0.3431	0.8366	−0.0054	0.032(4)*
C126	0.42262(17)	0.76364(17)	0.09418(17)	0.0246(6)
H126	0.4481	0.8100	0.1321	0.032(4)*
C131	0.60506(15)	0.53290(16)	0.26762(16)	0.0185(5)
C132	0.65793(16)	0.50844(16)	0.35166(16)	0.0207(5)
H132	0.6674	0.5465	0.3975	0.029(2)*
C133	0.69679(16)	0.42900(17)	0.36884(17)	0.0244(5)
H133	0.7332	0.4133	0.4262	0.029(2)*
C134	0.68267(17)	0.37248(17)	0.30256(18)	0.0251(6)
H134	0.7091	0.3181	0.3144	0.029(2)*
C135	0.62967(17)	0.39587(17)	0.21883(18)	0.0243(5)
H135	0.6192	0.3571	0.1733	0.029(2)*
C136	0.59212(16)	0.47548(17)	0.20166(16)	0.0212(5)
H136	0.5569	0.4914	0.1440	0.029(2)*
N1	0.43663(13)	0.58054(13)	0.27428(13)	0.0174(4)
C141	0.37800(15)	0.62836(16)	0.28328(15)	0.0191(5)
H141	0.3714	0.6863	0.2651	0.029(2)*
C142	0.32724(15)	0.59712(16)	0.31765(16)	0.0200(5)
H142	0.2874	0.6334	0.3235	0.029(2)*
C143	0.33462(15)	0.51212(16)	0.34368(16)	0.0197(5)
C144	0.39198(17)	0.46202(17)	0.33018(18)	0.0244(5)
H143	0.3973	0.4030	0.3443	0.029(2)*
C145	0.44126(16)	0.49809(16)	0.29619(17)	0.0228(5)
H145	0.4803	0.4626	0.2880	0.029(2)*
C146	0.28546(17)	0.47389(19)	0.38371(17)	0.0261(6)
H146	0.2959	0.4154	0.3994	0.029(2)*
C147	0.22838(17)	0.5125(2)	0.40000(18)	0.0291(6)
H147	0.2156	0.5711	0.3855	0.029(2)*
H148	0.2000	0.4819	0.4262	0.029(2)*
Sn2	−0.04023(2)	0.31642(2)	0.23562(2)	0.01704(5)
Cl2	−0.14010(4)	0.24288(4)	0.28112(4)	0.02202(12)
C211	−0.05498(15)	0.21841(16)	0.14588(16)	0.0184(5)
C212	−0.10279(16)	0.23337(17)	0.05871(16)	0.0230(5)
H212	−0.1280	0.2878	0.0398	0.034(4)*
C213	−0.11414(17)	0.16992(18)	−0.00086(17)	0.0256(6)
H213	−0.1467	0.1810	−0.0602	0.034(4)*
C214	−0.07798(16)	0.09020(17)	0.02617(17)	0.0236(5)
H214	−0.0867	0.0463	−0.0145	0.034(4)*
C215	−0.02935(16)	0.07484(17)	0.11221(17)	0.0240(5)
H215	−0.0039	0.0205	0.1306	0.034(4)*
C216	−0.01739(16)	0.13841(16)	0.17216(16)	0.0210(5)
H216	0.0165	0.1274	0.2313	0.034(4)*
C221	−0.11600(15)	0.42929(16)	0.19948(16)	0.0184(5)
C222	−0.12648(16)	0.48043(16)	0.12965(16)	0.0219(5)
H222	−0.1015	0.4636	0.0940	0.027(4)*
C223	−0.17287(17)	0.55533(17)	0.11179(17)	0.0260(6)
H223	−0.1790	0.5896	0.0644	0.027(4)*
C224	−0.21023(16)	0.58040(17)	0.16263(18)	0.0257(6)
H224	−0.2417	0.6319	0.1505	0.027(4)*
C225	−0.20162(16)	0.52997(17)	0.23141(18)	0.0247(6)
H225	−0.2273	0.5468	0.2664	0.027(4)*
C226	−0.15554(15)	0.45497(17)	0.24894(17)	0.0217(5)
H226	−0.1508	0.4203	0.2956	0.027(4)*
C231	0.06231(15)	0.31343(16)	0.36052(16)	0.0186(5)
C232	0.04892(16)	0.33591(17)	0.43085(17)	0.0228(5)
H232	−0.0059	0.3515	0.4221	0.041(4)*
C233	0.11439(17)	0.33589(18)	0.51340(17)	0.0261(6)
H233	0.1045	0.3529	0.5603	0.041(4)*
C234	0.19365(17)	0.31114(17)	0.52708(18)	0.0261(6)
H234	0.2382	0.3102	0.5836	0.041(4)*
C235	0.20822(16)	0.28768(17)	0.45865(18)	0.0258(6)
H235	0.2627	0.2699	0.4681	0.041(4)*
C236	0.14315(16)	0.29007(17)	0.37580(17)	0.0231(5)
H236	0.1541	0.2755	0.3289	0.041(4)*
N2	0.05415(13)	0.38467(13)	0.18790(14)	0.0196(4)
C241	0.07108(16)	0.46843(17)	0.20368(16)	0.0225(5)
H241	0.0471	0.4981	0.2349	0.033(3)*
C242	0.12123(16)	0.51308(17)	0.17688(16)	0.0225(5)
H242	0.1302	0.5725	0.1884	0.033(3)*
C243	0.15901(16)	0.47129(17)	0.13283(16)	0.0221(5)
C244	0.1437(2)	0.38428(19)	0.1193(2)	0.0347(7)
H244	0.1697	0.3524	0.0913	0.033(3)*
C245	0.0907(2)	0.34378(18)	0.1462(2)	0.0328(7)
H245	0.0799	0.2845	0.1347	0.033(3)*
C246	0.21274(17)	0.51564(19)	0.10180(17)	0.0273(6)
H246	0.2447	0.4813	0.0823	0.033(3)*
C247	0.22021(18)	0.5995(2)	0.09884(17)	0.0292(6)
H247	0.1893	0.6361	0.1178	0.033(3)*
H248	0.2565	0.6232	0.0778	0.033(3)*

parameters were refined for all H-atoms of any phenyl and vinyl group.

Discussion

In contrast to the structural chemistry of coordination compounds 4-vinylpyridine (4-ViPy) undergoes with many transition metals, *i.e.* $ZnBr_2 \cdot 2$(4-ViPy) [1], $Ni(NCS)_2 \cdot 4$(4-ViPy) [2], $PtCl_2 \cdot 2$(4-ViPy) [3], $Ag(ClO_3) \cdot 2$(4-ViPy) [4], and $CuCl \cdot 4$(4-ViPy) [5], a research area strongly forced by the clathrate properties of $TM(NCS)_2 \cdot 4$(4-ViPy)-complexes [6]

of transition metals TM, no structural information are available on its inorganic or organic tin(IV) complexes. Even the parent compound, pyridine (py), plays a minor role in the coordination chemistry of organotin(IV) compounds. Most structural information are available from octahedral 1:2 complexes of diorganotin(IV) dihalides of general formula $R_2SnHal_2 \cdot 2py$, *i.e.* $Et_2SnCl_2 \cdot 2(4\text{-ViPy})$ [7], $Ph_2SnCl_2 \cdot 2(4\text{-ViPy})$ [8], and $(CF_3\text{-}(CH_2)_2)_2SnCl_2 \cdot 2(4\text{-ViPy})$ [9]. Moreover, only the structure of the 1:1 pyridine complex of the triorganotin(IV) monohalide, R_3SnHal with R = Methyl and Hal = Cl has been determined while from monoorganotin(IV) trihalides, $RSnHal_3$, no complexes with this Lewis base are documented. As the structure determination of $Me_3SnCl \cdot py$ was determined from intensity data visually estimated from Weissenberg photographs the *R*-value isn't very low (18.6%). Consequently, structural parameters like bond lengths [*i.e.* d(Sn—Cl) = 2.42(4) Å] and angles are very imprecise [10]. The overall structure – a trigonal-bipyramidally coordinated tin atom with chlorine and pyridine in axial and the three methyl groups in equatorial positions, however, seems to be correct. This structural feature is also realised in the title structure, $Ph_3SnCl \cdot 4\text{-ViPy}$. The asymmetric unit consists of two crystallographic independent molecules with the tin atoms trigonal-biypramidally coordinated from the three equatorally positioned phenyl groups and the chlorine atom and the 4-vinylpyridine molecule in axial positions. Within the equatorial plane, Sn—C bond lengths differ from 2.121(2)–2.143(2) Å in molecule 1 and from 2.123(2)–2.139(2) Å in molecule 2 with a mean value over all six Sn—C of 2.131(4) Å. The range of bond angles between the phenyl groups is somewhat larger, ranging from 118.0(1)°–122.0(1)° in molecule 1 and 117.4(1)°–121.7(1)° in molecule 2. C—C-bond lengths [mean value: 1.356(4) Å] and angles within the phenyl groups are as expected, especially the *ipso*-effect [11] is well pronounced [117.8(2)°–118.8(2)°]. Taking into account, that each of the two complexes exists as a pair of two enantiomers, the orientation of the three phenyl groups, defined by the angle between the normal vectors of the almost planar phenyl rings and the molecule axes, only slightly deviate from one molecule to another. Remarkable structural differences arise within the molecule axes, however. First of all, Sn—Cl bond lengths differ significantly in both molecules as do Sn—N bond lengths in opposite direction [d(Sn—Cl) = 2.4918(6) Å/2.5272(6) Å; d(Sn—N) = 2.510(2) Å/2.432(2) Å]. These values of Sn—Cl bond lengths are much more longer than in case of $Me_3SnCl \cdot py$ (see above). Moreover, the orientation of the 4-vinylpridine ligand in relation to the almost linear axis [179.28(5)°/178.28(5)°] as well as internal values for the rotation of the vinyl group around the C—C single bound to the pyridine moieties are strongly different. In molecule 1 the angle between the Sn—N bond and the least-squares plane of the pyridine ligand has a value of 1.2(2)°, while in molecule 2 this angle has a value of 22.7(2)°. On the other side, the pyridine group and the vinyl groups show a dihedral angle of 2.3(2)° in molecule 1, but 12.2(2)° in molecule 2. All other bond lengths and angles within the pyridine moieties are as expected including the bond angle at nitrogen [116.9(2)°/117.3(2)°] and the C—N bond lengths [1.338(3) and 135.0(3) Å/1.337(3) and 1.345(3) Å]. The vinyl groups attached to the pyridine moieties are characterized by a C—C single bond of 1.470(3)/1.458(4) Å, a C=C double bond of 1.319(4)/1.322(4) Å, and a bond angle of 126.6(3)°/125.3(3)°.

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