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Crystal structure of benzyltrichloridobis(1*H*-pyrazole- κ^2N)tin(IV), $C_{13}H_{15}Cl_3N_4Sn$

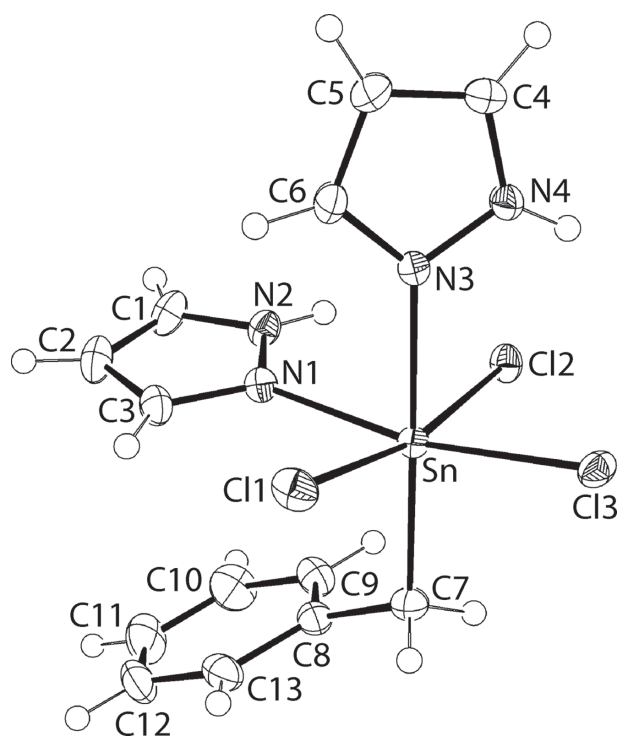


Table 1: Data collection and handling.

Crystal:	Prism, colorless
Size:	0.26 × 0.20 × 0.07 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	1.97 mm ⁻¹
Diffractometer, scan mode:	Bruker SMART, φ and ω -scans
θ_{\max} , completeness:	28.4°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	31378, 4198, 0.015
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 4051
$N(\text{param})_{\text{refined}}$:	196
Programs:	Bruker programs [1], SHELX [2–4], WinGX and ORTEP [5]

of the atoms including atomic coordinates and displacement parameters.

Source of material

The elemental analysis was performed on a Perkin-Elmer EA2400 CHN analyser. The IR spectrum was recorded using a Perkin-Elmer RX1 spectrophotometer in a Nujol mull between KBr plates. The ¹H NMR spectrum was recorded in CDCl₃ solution on a Bruker AVN FT-NMR spectrometer with chemical shifts relative to Me₄Si.

Dibenzyltin dichloride was prepared from direct synthesis using tin powder (Sigma-Aldrich) and benzyl chloride (Sigma-Aldrich) in toluene [6]. Pyrazole (Sigma-Aldrich; 0.14 g, 2.0 mmol) and dibenzyltin dichloride (0.37 g, 1 mmol) were heated in 95% ethanol (50 mL) for 30 min. After filtration, the filtrate was evaporated until colourless crystals were formed. Yield: 0.31 g (66%). *M.pt.*: 396–398 K. Calcd. for $C_{13}H_{15}Cl_3N_4Sn$: C 34.40; H 3.31; N 12.35%. Found: C 34.72; H 3.12; N 11.85%. IR (cm⁻¹) 569 (*m*) ν (Sn–N), 1516 (*s*) ν (C=N), 3311 (*m*) ν (N–H). ¹H NMR (CDCl₃, p.p.m.): δ 7.03–7.23 (5*H*, Ph–H), 2.97 (2*H*, Ph–CH₂), 6.25–7.60 (6*H*, pyrazole-H), 12.81 (2*H*, N–H).

Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.93–0.97 Å) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The N-bound H-atoms were located in difference Fourier maps but were refined with a distance restraint of N–H = 0.86 ± 0.01 Å, and with $U_{\text{iso}}(\text{H})$ set to $1.2U_{\text{equiv}}(\text{N})$. Owing to poor agreement, the (2 0 0) reflection was removed from the final cycles of refinement.

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Abstract

$C_{13}H_{15}Cl_3N_4Sn$, monoclinic, $C2/c$ (no. 15), $a = 32.4593(4)$ Å, $b = 7.43400(10)$ Å, $c = 14.7108(2)$ Å, $\beta = 106.084(1)^\circ$, $V = 3410.80(8)$ Å³, $Z = 8$, $R_{\text{gt}}(F) = 0.0151$, $wR_{\text{ref}}(F^2) = 0.0410$, $T = 293(2)$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
Sn	0.09953(2)	0.91211(2)	0.20525(2)	0.01493(4)
Cl1	0.13415(2)	0.69623(5)	0.32691(2)	0.02536(8)
Cl2	0.05745(2)	1.07713(4)	0.06465(2)	0.01991(7)
Cl3	0.05946(2)	1.06376(5)	0.30370(2)	0.02106(7)
N1	0.12381(4)	0.74538(16)	0.10400(8)	0.0180(2)
N2	0.10964(4)	0.76516(16)	0.00930(8)	0.0197(2)
H2N	0.0903(5)	0.844(2)	−0.0135(13)	0.024 [*]
N3	0.04611(4)	0.71723(15)	0.16662(8)	0.0169(2)
N4	0.00446(4)	0.76574(16)	0.14478(9)	0.0207(2)
H4N	−0.0023(6)	0.8760(14)	0.1455(14)	0.025 [*]
C1	0.13130(5)	0.6595(2)	−0.03484(11)	0.0263(3)
H1	0.127124	0.651259	−0.099846	0.032 [*]
C2	0.16086(5)	0.5655(2)	0.03346(12)	0.0273(3)
H2	0.180396	0.480662	0.024302	0.033 [*]
C3	0.15541(5)	0.6239(2)	0.11937(11)	0.0221(3)
H3	0.171368	0.584252	0.178631	0.027 [*]
C4	−0.02141(5)	0.6234(2)	0.12273(10)	0.0216(3)
H4	−0.051226	0.624823	0.105507	0.026 [*]
C5	0.00431(5)	0.4744(2)	0.13029(13)	0.0297(3)
H5	−0.004416	0.355301	0.119305	0.036 [*]
C6	0.04602(5)	0.5387(2)	0.15772(12)	0.0266(3)
H6	0.070454	0.467450	0.168390	0.032 [*]
C7	0.15224(5)	1.1026(2)	0.23733(11)	0.0229(3)
H7A	0.141057	1.222462	0.219750	0.027 [*]
H7B	0.165799	1.102152	0.304960	0.027 [*]
C8	0.18504(5)	1.06020(19)	0.18675(11)	0.0207(3)
C9	0.17840(5)	1.1089(2)	0.09221(12)	0.0250(3)
H9	0.153575	1.170627	0.061126	0.030 [*]
C10	0.20827(6)	1.0667(3)	0.04374(14)	0.0355(4)
H10	0.203451	1.100327	−0.019225	0.043 [*]
C11	0.24533(6)	0.9741(3)	0.08962(16)	0.0401(4)
H11	0.265425	0.945454	0.057488	0.048 [*]
C12	0.25226(5)	0.9245(2)	0.18325(16)	0.0355(4)
H12	0.277095	0.862431	0.213966	0.043 [*]
C13	0.22248(5)	0.9666(2)	0.23170(12)	0.0274(3)
H13	0.227454	0.932364	0.294623	0.033 [*]

Discussion

There are two crystal structures in the literature conforming to the general formula RSn(1*H*-pyrazole)₂X₃, namely for X = Cl and R = Ph [7] and R = 4-methylbenzyl [8]. The common feature of these structures is a facial arrangement of the three chlorido substituents and the presence of intra- and intermolecular N—H···Cl hydrogen bonding. Herein, the crystal and molecular structures of a third derivative, *i.e.* X = Cl and R = benzyl, are described.

The molecular structure (Figure, 50% displacement ellipsoids) features a six-coordinate tin centre defined by three chlorido atoms, a benzyl-C atom and two nitrogen atoms derived from the monodentate pyrazole molecules. The resultant CCl₃N₂ donor set has a *fac*-arrangement of the

chloride atoms. There are systematic variations in the Sn—N bond lengths with the Sn—N1 bond [2.2419(12) Å], having the N1 atom opposite the electronegative Cl3 atom, being significantly longer than the Sn—N3 bond [2.2096(12) Å], with the N3 atom opposite to the methylene-C atom. The Sn—Cl bond lengths span a relatively narrow range, *i.e.* 2.4345(3) Å [Sn—Cl1] to 2.4705(3) Å [Sn—Cl3]. An intramolecular N2—H2n···Cl2 hydrogen bond is noted [H2n···Cl2 = 2.478(16) Å, N2···Cl2 = 3.1106(13) Å with angle at H2n = 131.3(15)°]. The dihedral angle between the pyrazole rings is 77.85(9)°, indicating an almost orthogonal relationship, and the dihedral angles between each of the N1- and N3-pyrazole rings and the benzyl ring are 22.89(9) and 76.27(7)°, respectively.

In the crystal, pyrazole-N—H···Cl hydrogen bonds involving both acidic protons and symmetry-related Cl3 atoms are observed [N2—H2n···Cl3ⁱ: H2n···Cl3ⁱ = 2.686(18) Å, N2···Cl3ⁱ = 3.2694(12) Å with angle at H2n = 126.6(15)°; N4—H4n···Cl3ⁱⁱ: H4n···Cl3ⁱⁱ = 2.592(18) Å, N4···Cl3ⁱⁱ = 3.2648(14) Å with angle at H4n = 137.0(16)° for symmetry operations *i*: *x*, 2 − *y*, −1/2 + *z* and *ii*: −*x*, *y*, 1/2 − *z*]. The result of the hydrogen bonding is the formation of a chain along the *c* axis with a zigzag topology. Within the chain, there are close π(pyrazole)···π(pyrazole)ⁱⁱ contacts occurring between N3-pyrazole rings related by 2-fold symmetry [inter-centroid separation = 3.534(1) Å with an angle of inclination = 11.18(9)°]. The chains pack in the crystal without directional interactions between them.

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