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Dichlorodialkyltin complexes with 4-bromopyrazole. The crystal structure of bis(4-bromopyrazole-N^2)dichlorodimethyltin(IV)

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Abstract

4-Bromopyrazole, which is much less basic than the corresponding pyrazole but with similar hydrogen-bonding acidity, gives stable solid hexacoordinate complexes with dimethyl- and divinyl-tindichloride. The crystal structure of the *trans*-octahedral compound $Sn(CH_3)_2Cl_2 \cdot 2C_3H_3BrN_2$ was determined by X-ray crystallography and refined to $R = 0.030$. Intra-molecular hydrogen bonds are probably responsible for the essentially coplanar orientation of the pyrazolic ring plane with the $SnCl_2N_2$ plane. The packing is stabilized by inter-molecular hydrogen bonding.

Keywords: Tin; Pyrazoles; X-ray structure

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1. Introduction

Complexes of diorganonotin dihalides with pyrazoles, $SnR_2X_2 \cdot 2L$ (R = organic group; L = ligand), have *trans*-octahedral structures with intra- and inter-molecular hydrogen bonds. The steric hindrance of R and L was shown to affect the Sn–N and N–H $\cdots$ Cl distances and the ring plane orientation with respect to the $SnCl_2N_2$ plane to some extent [1]. As a continuation of our interest in this field, we report here the synthesis of the complexes of 4-bromopyrazole with dimethyl- and divinyl-tin dichloride and the crystal structure of dichlorodimethylbis(4-bromopyrazole-N^2)tin(IV). The bromopyrazole is less basic than pyrazole (pK_a of $HL^+ = 0.63$ and 2.48 respectively [2]), but has similar hydrogen-bonding acidity, as defined by Kamlet and Taft [3] ($a_2^h = 0.63$ and 0.55, respectively [4]).

2. Experimental details

Dimethyltin dichloride and 4-bromopyrazole were commercial products, used as received. Divinyltin dichloride was prepared as previously described [5]. Solvents were purified by standard procedures. The IR and far-IR spectra were recorded on Nicolet 5SXC and a FAR 20F spectrometers, respectively, using Nujol mulls.

Bis(4-bromopyrazole) Dichlorodimethyl- and bis(4-bromopyrazole-N^2)dichlorodivinyl–tin(IV) were obtained as crystalline white solids on diffusion of cyclohexane into a dichloromethane solution of dialkyltin dichloride and the pyrazole in 1/2 molar ratio. Selected IR bands: methyl derivative, 3301 ν(NH), 570 ν(SnC), 242 ν(SnCl), 378 and 286 (pyrazole bands) cm^{-1}; vinyl derivative, 3326 ν(NH), 1584 ν(C=C), 555 ν(SnC), 228 ν(SnCl), 378 and 288 (pyrazole bands) cm^{-1}. The frequencies were attributed to the vibrations on the basis of previous assignments [1,6].

2.1. X-Ray data

A crystal of maximum dimension 0.2 mm was selected and used for the X-ray analysis. Data were collected using a Philips PW 1100 diffractometer with Mo Kα radiation. The crystal remained stable under irradiation. Cell dimensions were determined by least-squares refinement of 25 medium-angle settings. The structure was solved by Patterson and Fourier methods, alternated with cycles of least-squares refinement

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Table 1
Crystal and intensity data for [$Sn(CH_3)_2Cl_2(C_3H_3BrN_2)$]

Formula	$C_8H_{12}Cl_2Br_2N_4Sn$
M	513.6
System	Triclinic; $P\bar{1}$
Cell: a (Å)	8.045(3)
b(Å)	7.381(3)
c(Å)	8.045(3)
α(°)	107.12(4)
β(°)	108.05(4)
γ(°)	90.10(4)
D_c (g cm^{-3})	2.19
Z	2
μ (Mo Kα) (cm^{-1})	68.7
Scan mode	$\theta/2\theta$
Scan speed	2 deg/min
θ_{max} (deg)	25
Recorded reflections	1696
Observed reflections [$I > 3\sigma(I)$]	1661
Corrections	Lp, absorption [a] [8]
Residual (R)	0.030

[a] Maximum and minimum values of the absorption correction were 2.18 and 1.00 respectively.

of the atomic parameters. Hydrogen atoms were located on the Fourier-difference maps but were generally introduced in calculated positions with fixed C–H distances and isotropic temperature factors (C–H = 1.08 Å, U_{iso} = 0.08 Å^2). Anisotropy was introduced for all non-hydrogen atoms. Refinement of scale factor and positional and thermal parameters was performed minimizing the function $\Sigma w(\Delta F)^2$ with $w = 1$. At convergence, the largest parameter shift among the refined parameters of the non-hydrogen atoms was 0.2 times the standard deviation. No significant residual of electronic density was observed in the final electron density map. Form factors for the atoms were supplied internally by the SHELX program system [7]. Crystal and intensity data are reported in Table 1; final atomic parameters and bond distances and angles are listed in Tables 2 and 3, respectively. Full lists of atomic parameters have been deposited with the Cambridge Crystallographic Data Centre.

Table 2
Fractional coordinates with equivalent isotropic thermal parameters (Å^2)

Atom	x	y	z	U_{eq}
Sn(1)	0.000000	0.000000	0.000000	0.0351(1)
Br(1)	0.70985(8)	−0.42192(9)	0.31996(8)	0.0628(3)
Cl(1)	−0.1499(2)	0.0810(2)	0.2595(2)	0.0541(5)
N(1)	0.2503(6)	−0.1242(6)	0.1893(5)	0.047(1)
N(2)	0.2434(6)	−0.1450(6)	0.3487(5)	0.049(2)
C(1)	0.3880(7)	−0.2402(7)	0.4195(6)	0.048(2)
C(2)	0.4937(6)	−0.2830(6)	0.3002(6)	0.040(2)
C(3)	0.4028(6)	−0.2084(7)	0.1603(6)	0.045(2)
C(4)	0.1621(8)	0.2736(7)	0.1131(7)	0.060(2)

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

Table 3
Selected Bond lengths (Å) and angles (°)

Sn–Cl	2.563(2)	N(2)–C(1)	1.336(7)
Sn–C(4)	2.129(5)	C(1)–C(2)	1.373(8)
Sn–N(1)	2.359(4)	C(2)–C(3)	1.382(7)
N(1)–N(2)	1.351(6)	C(2)–Br	1.865(5)
N(1)–C(3)	1.319(6)		
Cl(1)–Sn–C(4)	90.2(2)	N(1)–N(2)–C(1)	111.8(4)
Cl(1)–Sn–N(1)	87.2(1)	N(2)–C(1)–C(2)	106.1(4)
N(1)–Sn–C(4)	90.8(2)	C(1)–C(2)–C(3)	106.0(4)
Sn–N(1)–N(2)	122.7(3)	C(2)–C(3)–N(1)	110.5(4)
Sn–N(1)–C(3)	131.2(3)	C(1)–C(2)–Br	126.6(4)
N(2)–N(1)–C(3)	105.6(4)	C(3)–C(2)–Br	127.3(4)
Hydrogen bonds			
Cl ··· H(N)	2.64	Cl ··· N(2)	3.297
Cl ··· H(N^i)	2.83	Cl ··· N(2^i)	3.327

i = x, 1 − y, z.

3. Discussion

4-Bromopyrazole affords stable hexacoordinate complexes with dimethyl- and divinyl-tin dichloride. The IR pattern is consistent with hydrogen bonding (N–H stretching region) and with a linear C–Sn–C (Sn–C stretching region), as shown previously for the corresponding pyrazole complexes [5,9]. In the far-IR the characteristic pyrazole bands at 364 and 257 cm^{-1}, attributed to C–Br deformations [6], shift to slightly higher frequencies, to the same extent for both complexes.

The molecular structure of bis(4-bromopyrazole-N^2)dichlorodimethyltin(IV) is shown in Fig. 1 with the numbering scheme used. The complex is *trans*-octahedral with molecular symmetry C_i, the Sn atom being located at the origin of the centrosymmetric cell. the coordination bond lengths are normal, and the Sn–N bond distance of 2.359(4) Å can be compared with the corresponding values in pyrazole and imidazole complexes *trans*-[$Sn(CH_3)_2Cl_2L_2$]: 2.379(6) Å (L = 3,5-dimethylpyrazole [10]); 2.338(6) Å (L = pyrazole

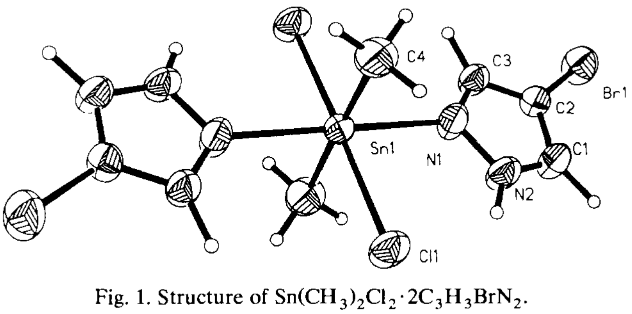

Fig. 1. Structure of $Sn(CH_3)_2Cl_2 \cdot 2C_3H_3BrN_2$.

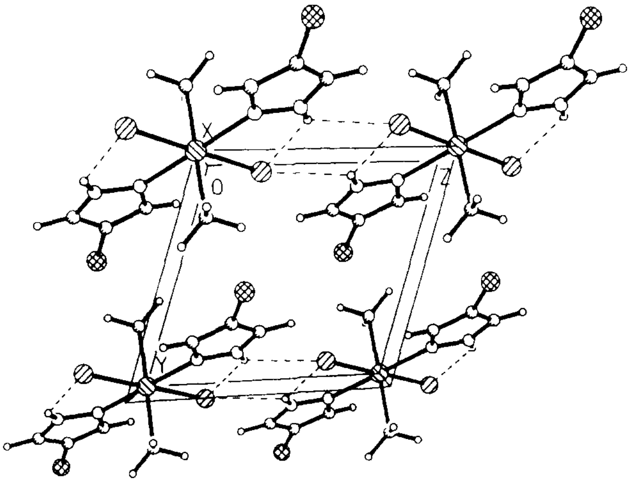

Fig. 2. Perspective view of the packing.

[9]); 2.329 Å (L = *N*-methylimidazole [11]); and 2.380(4) Å (L = 2-chloroimidazole [12]).

The Cl atoms are involved in a relatively strong intramolecular Cl ··· H–N hydrogen bond (see Table 3). This probably causes the small deviation of the Cl–Sn–N bond angle [87.2(1)°] from the ideal value, and the more pronounced asymmetry observed at N(1), where the Sn–N–N angle [122.7(3)°] is about 9° smaller than the corresponding Sn–N–C angle [131.2(3)°]. Intra-molecular hydrogen bonding is probably also responsible for the essential coplanarity of the pyrazole ring plane and the $SnCl_2N_2$ plane. The angle of 7.7° between the normals is much less than that found in dichlorodimethylbis(pyrazole)tin [9] and is comparable with those found in the dichlordivinyltin and dibromodicyclohexyltin bis(pyrazole) complexes [1].

As shown in Fig. 2, neighbouring molecules along the *c* axis are held together by intermolecular Cl ··· H–N hydrogen bonds, so that each Cl atom is involved in one intra and one inter-molecular H bond, with each pyrazole forming one intra- and one intermolecular bifurcated H bond. The intra- and intermolecular Cl ··· H–N distances are comparable, as are the Br ··· H–N distances in the cyclohexyl derivative [1], whereas they differ significantly in the corresponding pyrazole [9] and 3,5-dimethylpyrazole complexes [10].

In conclusion, the structure of dichlorodimethylbis-(4-bromopyrazole)tin(IV) shows that 4-bromopyrazole is as good a ligand as pyrazole, in spite of the different basicity, probably because of its hydrogen-bonding acidity.

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