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The crystal structure of dichlorodivinylbis(pyrazole-N^2)tin(IV)

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Abstract

The crystal structure of the complex $Sn(CH=CH_2)_2Cl_2 \cdot 2C_3H_4N_2$ has been determined. The compound crystallyzes in the monoclinic space group $C2/c$, with four molecules in a unit cell of dimensions a 13.634(2), b 8.960(2), c 13.482(2) Å, and β 115.0(1)°. The structure is centrosymmetric at the tin atom, with all *trans*-octahedral coordination geometry. The pyrazole ligands, bonded to the metal through their pyridine-like nitrogen atom, are intermolecularly hydrogen bonded to the chloride ligands.

Relevant features of the structure of the title compound are compared with those of the corresponding complexes of dimethyltin dichloride with pyrazoles.

In continuation of our studies of the complexation of diorganotin dihalides with heterocyclic ligands [1], we have prepared some dichlorodivinyltin derivatives. The interest in such compounds stems from the potential resonance interaction between the π-electron system of the organic group and the Sn(5d) orbitals [2–6], and the consequent effects upon the coordinating properties of the metal centre. We describe the crystal structure of the complex dichlorodivinylbis(pyrazole-N^2)tin(IV), and compare it with the known structure of the corresponding dichlorodimethylbis(pyrazole-N^2) [7].

Experimental

Divinylditinchloride was prepared by transmetallation between tetravinyltin and tin tetrachloride [8]. $Sn(CH=CH_2)_2Cl_2 \cdot 2C_3H_4N_2$ separated as a microcrystalline solid on mixing of divinyltin dichloride and pyrazole in 1/2 molar ratio in

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Table 1

Fractional atomic coordinates

Atom	x	y	z
Sn	0.0	0.0	0.0
Cl	0.0720(1)	0.1990(2)	−0.0891(2)
C(6)	−0.0550(9)	0.1650(10)	0.0755(9)
C(7)	−0.0909(23)	0.2725(36)	0.0646(21)
N(1)	0.1790(5)	−0.0625(8)	0.2498(5)
N(2)	0.1641(4)	−0.0030(7)	0.1540(4)
C(3)	0.2593(6)	0.0557(9)	0.1674(6)
C(4)	0.3359(6)	0.0323(10)	0.2753(7)
C(5)	0.2830(7)	−0.0450(12)	0.3272(6)

anhydrous dichloromethane. Suitable crystals for X-ray analysis were obtained by recrystallization from the same solvent. A well formed crystal of approximate dimensions 0.3 × 0.3 × 0.6 mm was sealed in a Lindemann capillary for determination of the cell dimensions and recording of the intensity data.

Crystal data. $C_{10}H_{14}N_4Cl_2Sn$, $M = 379.8$, monoclinic, space group $C2/c$ (no. 15), a 13.634(2), b 8.960(2), c 13.482(2) Å, β 115.0(1)°, U 1492.7 Å^3, $Z = 4$, $D_c = 1.70$ g/cm^3, $F(000) = 744$ μ(Mo-K_α) 19.0 cm^{-1}).

Data collection. 1870 (1800 independent, $R = 0.07$) reflections were collected on a Philips PW 1100 four-circle diffractometer in the range $4 < 2\theta < 56°$, θ–2θ step scan method, with Mo-K_α monochromatized radiation (λ 0.7107 Å). Reflections with $I \geq 2.5\sigma(I)$ were considered as observed (1468). The intensities were corrected for Lorentz and polarization effects, but not for absorption.

Determination and refinement of the structure. The structure was resolved by Fourier maps with Sn in the special position $\bar{1}$, and refined by full-matrix least-squares ($w = 1$) with anisotropic thermal parameters for all the non-hydrogen atoms. The hydrogen atoms were placed at calculated positions and not refined. The final conventional R factor was 0.0379. Scattering factors for all atoms were those incorporated in the program SHELX 76 [9]. Positional parameters for non-hydrogen atoms are listed in Table 1.

Infrared spectrum. The IR and far-IR spectrum of the title compound, recorded on a Nicolet 5SXC and a FAR 20F vacuum spectrometer respectively, shows the following relevant bands: 3308 s,br (N–H stretch), 1590 (C=C stretch), 554 s (Sn–C stretch), 223 s,br (Sn–Cl stretch) cm^{-1}.

Results and discussion

The most relevant features of the structure of $Sn(CH{=}CH_2)_2Cl_2 \cdot 2C_3H_4N_2$ compared with those of the corresponding complexes of the dichlorodimethyltin with pyrazole [7] and 3,5-dimethylpyrazole [10], are as follows:

(i) The structure (cf. Fig. 1) is centrosymmetric at the tin atom, with a quasi-regular all-*trans*-octahedral coordination geometry. The bond lengths and angles at the tin (cf. Tab. 2) are very close, within the standard deviations, to those reported for the corresponding dimethyltin complexes of pyrazoles.

(ii) The molecules are linked together in rows along the (0,0,1) direction by intermolecular hydrogen bonds to a chloride in a neighboring molecule at x, $-y$,

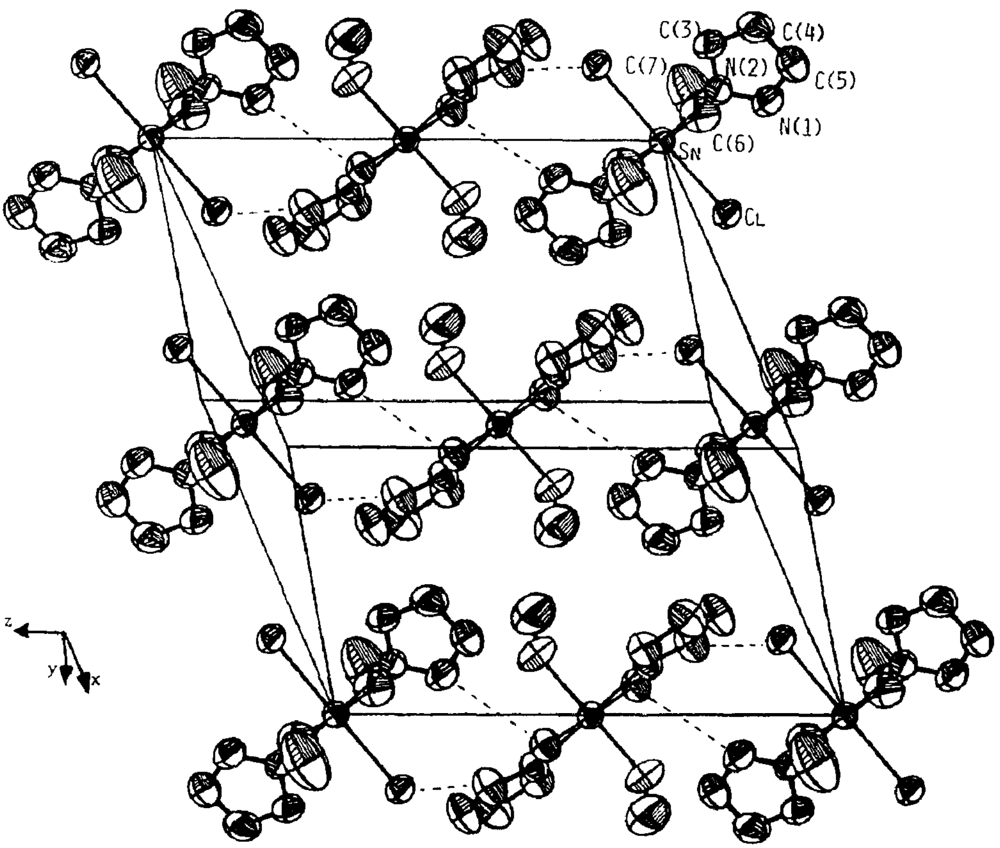

Fig. 1. A perspective view of the structure of dichlorodivinylbis(pyrazole-N^2)tin(IV).

$\frac{1}{2}+z$, the N···Cl distance for N(1)–H···Cl being 3.320(8) Å. Intramolecular N(1)–H···Cl contacts are longer (3.410(7) Å). This finding confirms that the observed shift to lower wavenumber, with broadening, of the N–N stretching band

Table 2

Bond distances (Å) and angles (°)

Sn–Cl	2.565(2)	C(3)–C(4)	1.402(10)
Sn–N(2)	2.322(5)	C(4)–C(5)	1.384(15)
Sn–C(6)	2.103(13)	C(5)–N(1)	1.369(9)
N(1)–N(2)	1.330(9)	C(6)–C(7)	1.063(33)
N(2)–C(3)	1.341(10)		
N(2)–Sn–Cl	90.7(2)	N(2)–C(3)–C(4)	109.5(7)
C(6)–Sn–Cl	91.3(3)	C(3)–C(4)–C(5)	106.3(8)
C(6)–Sn–N(2)	88.8(3)	C(4)–C(5)–N(1)	105.3(7)
Sn–N(2)–N(1)	124.5(5)	C(5)–N(1)–N(2)	112.2(7)
Sn–N(2)–C(3)	128.8(5)	Sn–C(6)–C(7)	143.9(17)
N(1)–N(2)–C(3)	106.5(6)		
Intermolecular hydrogen bond			
N(1)–H···Cl	distance	3.320(8) Å	
N(1)–H–Cl	angle	143°	

in the IR spectrum of the coordinated pyrazole when compared with that of the free pyrazole monomer, may be attributed to hydrogen bond formation.

(iii) The C(6)–C(7) bond distance (1.063(33) Å) appears to be extremely short relative to the normal length of a C=C bond, and is probably due to the large thermal motion. This large thermal motion may be caused by the partial decomposition of the crystal in the X-ray beam, but furthermore the peripheral situation of the vinyl groups in the row of molecules allows large librations, with consequent disorder in the position of these groups in the crystal. Because of this any discussion of the dimensions of the vinyl groups must be tentative. Severe limitations in the determination of the position of vinyl groups, arising from similar effects, have been observed previously in the determination of the structure of tetravinyl-1,3-bis(trifluoroacetoxy)distannoxane, for which the positions could not be determined [11]. To a lesser extent, analogous effects are present in the case of trivinyltintrichloroacetate [12], trivinyltinferrocenoate [13], and triphenylvinyltin [14].

The Sn–C bond length is in line with the values previously reported of vinyltin compounds. A modest shortening of the tin–vinyl bond is observed on going from tetra- to penta- or hexa-coordinate vinyltin derivatives: average values of 2.16 in triphenylvinyltin [14], 2.10 in trivinyltintrichloroacetate [12], and 2.09 Å in (2,2′-bipyridyl)bis(trifluoroacetato)divinyltin [11] may be calculated. The Sn–C bonds in organotin compounds are affected by inductive and resonance effects, mainly depending on the nature of the organic groups, and by orbital hybridization, which varies with the coordination number of the tin. This last effect seems to be responsible for the shortening of the Sn–C bond on going from tetra- to penta- or hexa-coordinate dimethyltin complexes, as a consequence of the preferential concentration of the *s*-electron density in this bond. The opposite trend is found for the phenyltin compounds because of the greater electron-withdrawal by this group [15]. The vinyl derivatives exhibit a shortening of the Sn–C bond in the same way as the methyl derivatives although the inductive effect should be similar to that of the phenyl group, as confirmed by Mössbauer isomeric shift measurements [2]. It thus seems reasonable to assume that this is not only influence of rehybridization of the inductive effect, which predominate for methyl and phenyl derivatives, respectively, but also of d_π–p_π interaction in the case of the vinyl derivatives.

The C–Sn–C angle is 180°, so that only one Sn–C stretching vibration can be IR active, and we tentatively attribute the band at 558 cm^{-1} to the asymmetric stretching mode. This value is consistent with those previously reported for *trans*-octahedral complexes [2].

The Sn–N bond length is about the same as that in the corresponding dimethyltin complex, and thus seems not to be affected by the inductive and conjugative effects of the vinyl group. These effects, as evidenced by NMR and Mössbauer studies [2,3], are responsible for the differences in Sn–O bond lengths between methyl- and vinyl-tin carboxylates with pentacoordinate structures [11,12]. The Sn–N distance in octahedral organotin complexes has been observed to be slightly dependent upon the basicity of the N-donor ligands and on whether there is a *cis* or a *trans* configuration [16]. The absence of any effect of the vinyl group may be attributed as due to the high degree of ionic character of the Sn–N bond.

The angle between the normals to the plane (Sn, Cl, N) and the plane of the pyrazole is 14°, whereas the corresponding angle in the complex of dimethyltin dichloride is 24° [7]. Similar orientations of the heterocyclic ligands have been calculated for the complexes with *N*-methylimidazole (24°) and pyridine (26°) [7]. Moreover the angle between the C(6)–C(7) axis and the normal to the plane (Sn, C(6), Cl) is 94°, thus indicating that the vinyl group is oriented towards the chlorine atom.

Both the orientation of the vinyl groups and the smaller tilting of the heterocyclic ligands from the plane (Sn, Cl, N) of the title compound with respect to that in the methyltin complexes can be attributed to minimization of the repulsive interactions between the π-electron systems of the ligands.

References

1 G. Valle, R. Ettorre, U. Vettori, V. Peruzzo and G. Plazzogna, J. Chem. Soc. Dalton Trans., (1987) 815.
2 D.V. Naik and C. Curran, J. Organomet. Chem., 81 (1974) 177.
3 E. Vincent, L. Verdonck, L. Naessens and G.P. Van Der Kelen, J. Organomet. Chem., 277 (1984) 235.
4 K. Handlir, J. Holecek, M. Navordnik, S.M. Teleb and A. Licka, Inorg. Chim. Acta, 150 (1988) 287.
5 V. Peruzzo, G. Plazzogna and G. Tagliavini, J. Organomet. Chem., 24 (1970) 347.
6 V. Peruzzo, G. Tagliavini and R.E. Hester, J. Organomet. Chem., 56 (1973) 185.
7 G. Valle, R. Ettorre, V. Peruzzo and G. Plazzogna, J. Organomet. Chem., 326 (1987) 169.
8 S.D. Rosemberg and A.J. Gibbons, J. Am. Chem. Soc., 79 (1957) 2139.
9 G.M. Sheldrick, SHELX 76 program for crystal structure determination. University of Cambridge, 1976.
10 R. Graziani, U. Casellato, R. Ettorre and G. Plazzogna, J. Chem. Soc. Dalton Trans., (1982) 805 and ref. therein.
11 C.D. Garner and B. Hughes, Inorg. Nucl. Chem. Lett., 12 (1976) 859.
12 S. Calogero, D.A. Clemente, V. Peruzzo and G. Tagliavini, J. Chem. Soc. Dalton Trans., (1979) 1172.
13 R. Graziani, U. Casellato and G. Plazzogna, J. Organomet. Chem., 187 (1980) 381.
14 F. Theobald and B. Trimaille, J. Organomet. Chem., 267 (1984) 143.
15 P.G. Harrison, T.J. King and J.A. Richards, J. Chem. Soc. Dalton Trans., (1974) 1723.
16 R. Bardi, A. Piazzesi, R. Ettorre and G. Plazzogna, J. Organomet. Chem., 270 (1984) 171.