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Synthesis and molecular structure of dichlorodivinylbis[(3*H*)-imidazoline-2-thione]tin(IV)

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Abstract

The new complex $Sn(CH{=}CH_2)_2Cl_2 \cdot 2C_3H_4N_2S$ has been obtained as a crystalline solid. The crystal structure has been determined by an X-ray diffraction study, which reveals that the tin atom is hexa-coordinate *trans*-octahedral and the molecule is centrosymmetric. The imidazole ligands are bonded to the metal through the S atom. Each Cl atom is involved in intra- and inter-molecular hydrogen bonding with the N–H groups of heterocyclic rings.

Relevant structural details are consistent with values for related compounds.

Introduction

Interest in the coordination chemistry of heterocyclic thione donors stems from their wide range of applications [1], especially in possible interactions of metals and organometals with biological systems [2,3]. Studies with a variety of metals have shown that heterocyclic thioamides are commonly bound through sulfur for the neutral ligand and through both sulfur and nitrogen for the deprotonated species [5]. Previously we reported the crystal structure of the hexa-coordinate complex of dimethyltin dichloride with 2-(1*H*)pyridinethione, $Sn(CH_3)_2Cl_2 \cdot 2C_5H_5NS$ [6]. The configuration about tin resulted was *trans*-octahedral, with the heterocycle bonded through the sulfur. Recently the structure of the penta-coordinate dibromodimethyl[1-methyl-2(3*H*)-imidazoline-thione]tin(IV) was described as trigonal-bipyramidal. This complex was obtained when a 1/2 substrate/ligand molar ratio was used [7]. In continuation of our investigation of the coordination behaviour of diorganotin halides towards heterocyclic ligands N or S donors [4], we have made and determined the crystal structure of, dichlorodivinylbis(3*H*)imidazoline-2-thione]tin(IV): $Sn(CH{=}CH_2)_2Cl_2 \cdot 2C_3H_4N_2S$.

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Experimental

Divinyltindichloride was prepared by treating tetravinyltin with tin tetrachloride, as previously described [8]. All handling of the organotin derivatives were carried out under nitrogen to exclude moisture.

The complex $Sn(CH{=}CH_2)_2Cl_2 \cdot 2C_3H_4N_2S$ was prepared by mixing a chloroform solution of divinyltin dichloride with 1,3-imidazoline-2-thione (molar ratio 1 : 2) in chloroform-ethanol.

Infrared spectrum. The IR and Far-IR spectrum of the compounds, as a Nujol mull, was recorded on a Nicolet 5SXC spectrometer and that in KBr pellets on a Far 20 F vacuum spectrometer. Bands typical of the $Sn{-}CH{=}CH_2$ group (assigned as in refs. 4 and 13) appear at 976 and 947 cm^{-1} ($=CH_2$ bending) and 539 cm^{-1} (Sn–C stretch); the C=C stretch, expected to appear at 1580–1590 cm^{-1}, is probably obscured by the strong N–C=N stretching band (1579 cm^{-1}). Other ligands bands, assigned (cf. ref. 14) to the thioamide group, appear at 1472, 1273, 1067 and 730 cm^{-1}. The thioamide (IV) band [14] is very sensitive to coordination: its frequency changes from 775 cm^{-1} for the free ligand to 730 cm^{-1} for the complex. The N–H stretch, which is centred at 3237 cm^{-1}, although at higher frequency than that for the ligand, gives rise to a very broad band, indicative of hydrogen bonding.

X-ray analysis. Suitable crystals for the X-ray study were obtained by slow evaporation and cooling of the reaction mixture. A well formed crystal of maximum dimension 0.2 mm was selected. Data collection was performed on a Philips diffractometer. Cell dimensions were determined by least-square refinement of 25 medium-angle settings.

Crystal data. $C_{10}H_{14}Cl_2N_4S_2Sn$, $M = 444$, triclinic, space group $P\bar{1}$, $a = 8.275(5)$, $b = 8.235(5)$, $c = 7.431(5)$ Å, $\alpha = 124.88(3)$, $\beta = 99.08(3)$, $\gamma = 87.73(3)°$, $U = 409.4$ Å^3, $Z = 1$, $Dc = 1.809$ g cm^{-3}, $F(000) = 218$, $\mu(\text{Mo-}K_\alpha) = 20$ cm^{-1}.

Table 1

Fractional coordinates with isotropic thermal parameters (Å^2). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	x	y	z	U_{eq}
Sn(1)	0.000000	0.000000	0.000000	0.0303(1)
Cl(1)	−0.10691(9)	−0.3114(1)	−0.0421(2)	0.0469(5)
S(1)	0.31083(9)	−0.0276(1)	0.1664(1)	0.0392(4)
C(1)	−0.1349(8)	0.1522(8)	0.4306(9)	0.083(3)
C(2)	−0.0461(5)	0.1920(5)	0.3334(6)	0.045(1)
C(3)	0.3545(3)	−0.2649(4)	−0.0342(5)	0.033(1)
N(1)	0.2684(3)	−0.4331(4)	−0.1149(5)	0.041(1)
N(2)	0.4858(3)	−0.3194(4)	−0.1357(5)	0.044(1)
C(4)	0.3460(5)	−0.5938(5)	−0.2674(6)	0.045(2)
C(5)	0.4835(5)	−0.5240(5)	−0.2806(7)	0.049(2)
H(11)	−0.105(6)	0.255(7)	0.604(8)	–
H(12)	−0.225(6)	0.029(7)	0.305(8)	–
H(2)	−0.006(6)	0.293(7)	0.394(8)	–
$H(1)_N$	0.151(6)	−0.421(7)	−0.084(7)	–
H(4)	0.306(6)	−0.713(7)	−0.323(8)	–
H(5)	0.565(6)	−0.591(7)	−0.366(8)	–
$H(2)_N$	0.583(6)	−0.234(7)	−0.089(8)	–

Table 2

Bond distances (Å) and angles (°) with e.s.d.'s in parentheses [a]

Bond distances			
Sn–Cl(1)	2.575(1)	C(3)–N(1)	1.334(4)
Sn–C(2)	2.134(3)	N(1)–C(4)	1.377(4)
Sn–S(1)	2.733(1)	C(4)–C(5)	1.337(5)
C(1)–C(2)	1.275(6)	C(5)–N(2)	1.386(5)
S(1)–C(3)	1.719(3)	N(2)–C(3)	1.336(4)
Hydrogen bonds		*Contacts*	
Cl(1)···H(N1)	2.28	Cl(1)···N(1)	3.256
Cl(1)···H(N2^{I})	2.64	Cl(1)···N(2^{I})	3.327
Cl(1)···H(N1^{II})	2.89	Cl(1)···N(1^{II})	3.331
Bond angles			
Cl(1)–Sn–S(1)	92.1(0)	S(1)–C(3)–N(2)	126.8(2)
Cl(1)–Sn–C(2)	92.8(1)	C(3)–N(1)–C(4)	110.4(3)
S(1)–Sn–C(2)	88.4(1)	N(1)–C(4)–C(5)	107.3(3)
Sn–C(2)–C(1)	127.4(3)	C(4)–C(5)–N(2)	105.9(3)
Sn–S(1)–C(3)	102.9(1)	C(5)–N(2)–C(3)	110.7(3)
S(1)–C(3)–N(1)	127.5(2)		

[a] Superscripts: none = x, y, z; I = x, $1+y$, $1+z$; II = $1-x$, $-y$, $-z$.

A total of 2845 unique reflections were collected in the range $2° < 2\theta < 50°$ in the $\theta/2\theta$ scan mode using Mo-K_α radiation ($\lambda = 0.7107$ Å). Of these, 2673 with $I > 3\sigma(I)$ were considered as observed and used in subsequent calculations. The intensities were corrected for Lp and absorption [9]. The crystal was stable under irradiation.

The structure was solved by Fourier methods, alternated with cycles of least-squares refinement of the atomic parameters. All hydrogen atoms were located on the Fourier-difference maps and their coordinates were refined with fixed temperature factors ($U = 0.07$ Å^2). At convergence, the residual conventional R factor was 0.029. The function minimized was $\Sigma w(\Delta F)^2$ with $w = 1$. Scattering factors for the atoms were those incorporated in the SHELX program package [10]. Final atomic coordinates are listed in Table 1, and bond lengths and angles in Table 2. Lists of thermal parameters and structure factors are available from the author.

Results and discussion

Figure 1 shows the crystal structure of the compound, with the numbering scheme. The molecule is centrosymmetric, *trans*-octahedral.

The Sn–S bond distance of 2.733(1) Å is very close to that of 2.729(2) Å in dichlorodimethylbis[2(1*H*)-pyridinethione-*S*]tin(IV) [6], and the Sn–Cl distance of 2.575(1) Å agrees well with that of 2.571(3) Å in dichlorodimethylbis[*N*-methylimidazole]tin(IV) [11] and that of 2.565(2) Å in dichlorodivinylbis[pyrazole-N^2]tin(IV) [12]. The Sn–C bond length is consistent with values previously reported for vinyltin compounds [4]. As expected, the libration parameters of the terminal carbon atom of the vinyl group [C(1)] are higher (see the ORTEP diagram) than those of the other atoms. Nevertheless, there is no trace of disorder; the positions of this and of the

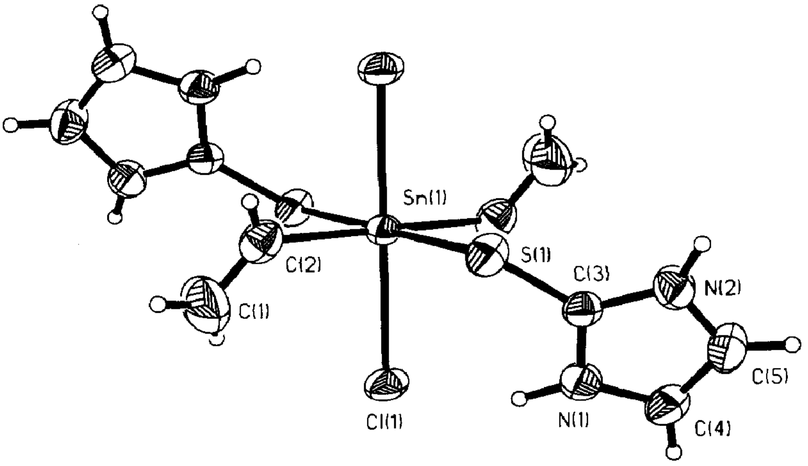

Fig. 1. Structure of dichlorodivinylbis[(3*H*)-imidazoline-2-thione]tin(IV).

attached hydrogens were easily determined from the Fourier map, and the C=C distance seems to be reliable.

The fact that the hydrogen atoms are directly bonded to the nitrogen atoms confirms the thione configuration of the heterocyclic ligand. Comparison of the structural details shows that the bond distances and angles in the cycle are very close to those in the free imidazole- and methylimidazole-thione [5,12]. There is slight lengthening in the C=S bond upon coordination [1.719(3) Å, compared with 1.698(2) and 1.685(2) Å, respectively]. These findings are out for the fact that the infrared frequencies of the N–C=N frequencies (1580, 1223, 1070 cm^{-1}) remain unchanged upon complexation, whereas the C–S bond is shifted by ca. 50 cm^{-1}. The presence of some Cl · · · N contact distances in the range 3.256–3.331 Å (Tab. 2) strongly suggests that the chlorine atoms form hydrogen bonds with the NH groups of the ligand. In particular the chlorine atom makes one intramolecular Cl · · · H–N bond to form an irregular, approximately planar, hexa-atomic metallacycle. The presence of this relatively strong hydrogen bond [Cl · · · H = 2.28 Å] seems to be crucial in determining the orientation of the imidazole ring. In addition, each chlorine atom is involved in two weaker intermolecular H bonds with the NH groups of adiacent molecules. The formation of similar, or even more complex networks of hydrogen bonds has often been observed, in the crystals of the above mentioned complexes and various related parent ligands.

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