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The Crystal and Molecular Structure of Dichlorobis(2-pyridinethiolato)tin(IV)

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The crystal and molecular structures of dichlorobis(2-pyridinethiolato)tin(IV) have been determined by X-ray analysis. The crystal belongs to the triclinic system: $a=8.340(8)$, $b=12.456(7)$, $c=7.178(3)$ Å, $\alpha=86.46(4)$, $\beta=111.06(5)$, $\gamma=99.18(6)$°, space group $P\bar{1}$ with $Z=2$. The structure was determined by the heavy atom method and refined by the block-diagonal least-squares method ($R=0.058$). The complex is a distorted octahedral complex in which 2-pyridinethiolato ligands act as bidentate ligands, two four-membered (Sn, S, C, and N) chelate rings being present. Two Sn–Cl bonds are *cis*, two Sn–N bonds are *cis*, and two Sn–S bonds are *trans* configuration.

The synthesis of dichlorobis(2-pyridinethiolato)tin(IV) (**1**) and its possible structures were described in a previous report.1) Complex (**1**) is very stable. However, bis(benzenethiolato)dichlorotin(IV)1) or dichlorobis(4-pyridinethiolato)tin(IV)2) could not be isolated probably because of its instability. On the basis of IR spectral observation1) the stability of complex (**1**) is ascribed to the intramolecular four-membered chelate ring formation for the six-coordination of the tin atom.

2-Pyridinethiolato ligand acts as a uni- or bi-dentate or a bridging ligand in rhodium,3) iridium,4) and ruthenium(II)5,6) complexes.

This paper describes the crystal and moleuclar structures of **1** obtained by X-ray analysis: octahedral structure with four-membered chelate ring condensed with pyridine ring.

Experimental

Dichlorobis(2-pyridinethiolato)tin(IV) (**1**) was prepared by the reaction of di-2-pyridyl disulfide and tin(II) chloride in benzene in the presence of perhydroazepin-2-one.1) The crystal for the X-ray analysis was obtained by recrystallization from acetonitrile solution.

The crystal system was determined as triclinic from the oscillation and Weissenberg photographs. The density was measured by the flotation method in an aqueous solution of ZnI_2. The unit-cell parameters were determined by the least-squares method, using 20 reflections carefully measured on a Syntex model $P2_1$ four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda=0.71069$ Å). The intensity data were collected on a diffractometer with the 2θ-ω scanning mode ($2\theta\leqq 50°$). The variable-scan method was used, the minimum and maximum scan rates being 1° and 24° min^{-1}, respectively. Background was counted for half the scan time on each side of a reflection. The size of the crystal was $0.2\times0.1\times0.4$ mm. In order to confirm the stability of the crystal and the counting system, the intensities of three standard reflections were measured every 99 reflections. The standard reflections were stable to 1.0% from their mean values. Neither absorption nor extinction correction was made. This might reduce the accuracy of the structure obtained.

TABLE 1. CRYSTAL DATA

$C_{10}H_8Cl_2N_2S_2Sn$
M. W.: 409.91
Crystal system: $P\bar{1}$; $Z=2$
$a=8.340(8)$, $b=12.456(7)$, $c=7.178(3)$ Å,
$\alpha=86.46(4)$, $\beta=111.06(5)$, $\gamma=99.18(6)$°
$D_m=1.992$, $D_c=2.000$ $g\cdot cm^{-3}$

Determination and Refinement of the Structure

The structure was determined by the heavy atom method. The coordinates of the tin atom were obtained from the Patterson map. Other atoms were found by successive Fourier synthesis. Refinement of the structure was performed by the block-diagonal least-squares method with 2209 independent reflections of $|F_o|\geqq3\sigma$. The final refinement was carried out with anisotropic thermal parameters for all the atoms. The strongest reflections at low scattering angles were omitted from the refinement in order to exclude extinction effects. The R-index converged to 0.058 with an equal weight for each reflection. The atomic scattering factors were taken from the International Tables for X-Ray Crystallography.7) The program ORTEP coded by Johnson8) was used for drawing Figs. 1 and 2. The observed and calculated structure factors are given in Table 2.9)

Results and Discussion

The positional and thermal parameters with their standard deviations are given in Tables 3 and 4, respectively. The molecular structure for **1** and the numbering scheme of atoms are shown in Fig. 1. Bond lengths and bond angles with their standard deviations are given in Tables 5 and 6, respectively. The tin atom is six-coordinated and two 2-pyridinethiolato ligands act as bidentate ligands, forming two four-membered (Sn, S, C, and N) chelate rings. Two Sn–Cl bonds are of *cis* configuration as suggested by IR spectral data.1) Two Sn–N bonds are of *cis* and two Sn–S bonds are of *trans* configurations.

Deviations of ligand atoms from several least-squares planes are given in Table 7. Considerable deviations are observed from the mean plane (A) of five atoms (Sn, two Cl, and two N atoms), mean plane (B) of five atoms [Sn, Cl(1), N(1), and two S atoms], and mean plane (C) of five atoms [Sn, Cl(2), N(2), and two S atoms]. The angles of three pairs of *trans* bondings, Cl(1)–Sn–N(1), Cl(2)–Sn–N(2), and S(1)–Sn–S(2) are 161.1, 162.9, and 154.2°, respectively. The data show a distorted octahedral structure of **1**.

The lengths of C–S bonds of two 2-pyridinethiolato ligands in **1** are greater than the C–S bond of 2(1*H*)-pyridinethione (1.68 Å),[10] while the lengths of C–N bonds in the ligands are samller than the C–N bond length in 2(1*H*)-pyridinethione (1.39 Å).[10] This suggests that the ligands act as bidentate ligands forming four-membered chelate rings. The same phenomena have been observed for the corresponding ruthenium complex.[5a]

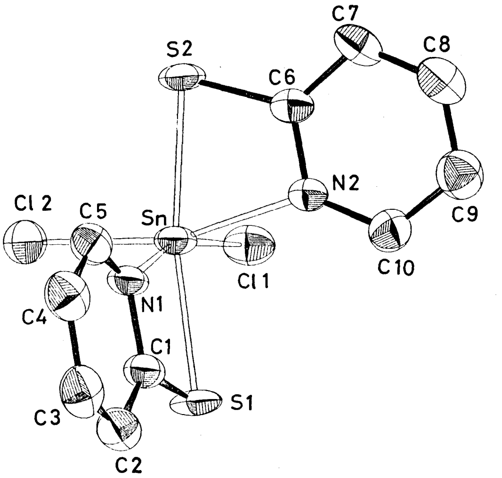

Fig. 1. The molecular structure for **1** and the numbering scheme of atoms. The ellipsoid encloses the region in which the center of the atom is found with probability 50%.

The bond lengths of two Sn–S bonds and two Sn–N bonds in **1** are nearly equal to the lengths of Sn–S bond [2.496(1) Å] and Sn–N bond [2.217(3) Å], respectively, in [2-[[(2-mercaptophenyl)imino]methyl]-phenolato]diphenyltin(IV), in which sulfur and nitrogen atoms are bonded to the tin atom forming five-membered chelate ring.[11] On the other hand, the lengths of two Sn–S bonds and two Sn–N bonds in **1** are smaller than those of the Sn–S bond [2.576(7) Å] and the Sn–N bond [2.62(2) Å], respectively, in triphenyl(4-pyridinethiolato)tin(IV), which has a polymeric structure formed by the intermolecular bridging through the nitrogen atom of the pyridine ring.[12] This suggests that two 2-pyridinethiolato ligands are bonded to the central tin atom through both nitrogen and sulfur atoms.

The deviation of S(1) atom from plane (D) of the pyridine ring [C(1—5) and N(1)] is 0.07 Å and that of S(2) from plane (E) of the pyridine ring [C(6—10) and N(2)] is 0.03 Å (Table 7). The sulfur atom lies practically on the same plane as the pyridine ring plane to which the atom is bonded. The deviations

Table 3. Atomic coordinates and their standard deviations

	x	*y*	*z*		*x*	*y*	*z*
Sn	0.2796(1)	0.2354(1)	0.0323(1)	C(3)	0.7090(16)	0.1216(10)	0.6520(18)
Cl(1)	0.2124(3)	0.3237(3)	−0.2869(4)	C(4)	0.5413(16)	0.1048(10)	0.6677(17)
Cl(2)	0.1955(4)	0.0560(3)	−0.1005(5)	C(5)	0.4064(15)	0.1344(9)	0.5063(16)
S(1)	0.5961(3)	0.2586(3)	0.1085(5)	C(6)	0.1265(12)	0.3752(9)	0.1894(16)
S(2)	0.0174(3)	0.2446(3)	0.1093(4)	C(7)	0.0605(15)	0.4546(10)	0.2573(17)
N(1)	0.4322(10)	0.1780(7)	0.3428(13)	C(8)	0.1648(17)	0.5528(11)	0.3098(19)
N(2)	0.2831(10)	0.3936(7)	0.1720(13)	C(9)	0.3311(17)	0.5739(11)	0.2932(19)
C(1)	0.5920(13)	0.1967(9)	0.3292(16)	C(10)	0.3873(14)	0.4906(10)	0.2245(18)
C(2)	0.7364(14)	0.1657(10)	0.4888(17)				

Table 4. Anisotropic thermal factors[a] ($\times 10^1$) and their standard deviations

	B_{11}	B_{22}	B_{33}	B_{12}	B_{23}	B_{31}
Sn	65(1)	55(1)	173(2)	24(1)	−21(1)	82(2)
Cl(1)	120(5)	78(3)	179(6)	48(5)	19(6)	87(9)
Cl(2)	148(5)	56(2)	244(8)	12(5)	−54(7)	141(10)
S(1)	60(4)	80(3)	240(8)	27(5)	14(7)	125(9)
S(2)	67(4)	65(3)	240(7)	7(5)	−55(7)	132(9)
N(1)	70(13)	51(7)	197(22)	26(15)	−36(19)	77(27)
N(2)	81(13)	46(7)	183(21)	24(15)	−10(18)	82(27)
C(1)	89(16)	51(9)	206(27)	19(18)	−52(24)	86(34)
C(2)	104(18)	59(10)	202(28)	30(21)	−48(25)	−11(36)
C(3)	168(23)	57(10)	198(29)	27(24)	−51(26)	−21(41)
C(4)	181(24)	61(10)	183(27)	38(24)	−49(26)	83(41)
C(5)	156(21)	52(9)	179(26)	30(21)	−37(23)	165(38)
C(6)	86(16)	56(9)	172(25)	31(19)	4(22)	78(32)
C(7)	149(21)	68(10)	187(27)	88(23)	−33(25)	104(38)
C(8)	180(24)	70(11)	246(33)	88(26)	−14(29)	126(46)
C(9)	181(25)	65(11)	228(31)	34(25)	−27(28)	116(45)
C(10)	125(20)	54(10)	235(30)	16(21)	−6(26)	88(39)

a) The anisotropic thermal factors are of the form $\exp\{-(h^2B_{11}+k^2B_{22}+l^2B_{33}+hkB_{12}+hlB_{31}+klB_{23})\}$.

TABLE 5. BOND LENGTHS AND THEIR STANDARD DEVIATIONS

Sn-Cl(1)	2.396(3) Å	Sn-Cl(2)	2.382(3) Å
Sn-S(1)	2.467(3)	Sn-S(2)	2.462(3)
Sn-N(1)	2.271(9)	Sn-N(2)	2.256(9)
S(1)-C(1)	1.729(12)	S(2)-C(6)	1.751(12)
N(1)-C(1)	1.352(15)	N(1)-C(5)	1.337(15)
N(2)-C(6)	1.340(15)	N(2)-C(10)	1.356(16)
C(1)-C(2)	1.420(17)	C(2)-C(3)	1.342(18)
C(3)-C(4)	1.425(19)	C(4)-C(5)	1.372(18)
C(6)-C(7)	1.394(17)	C(7)-C(8)	1.369(19)
C(8)-C(9)	1.416(20)	C(9)-C(10)	1.386(19)

TABLE 6. BOND ANGLES AND THEIR STANDARD DEVIATIONS

Cl(1)-Sn-Cl(2)	94.8(1)°	Cl(1)-Sn-S(1)	95.6(1)°
Cl(1)-Sn-S(2)	101.6(1)	Cl(1)-Sn-N(1)	161.1(3)
Cl(1)-Sn-N(2)	89.6(3)	Cl(2)-Sn-S(1)	100.7(1)
Cl(2)-Sn-S(2)	96.9(1)	Cl(2)-Sn-N(1)	93.2(3)
Cl(2)-Sn-N(2)	162.9(3)	S(1)-Sn-S(2)	154.2(1)
S(1)-Sn-N(1)	66.2(3)	S(1)-Sn-N(2)	95.3(3)
S(2)-Sn-N(1)	94.1(3)	S(2)-Sn-N(2)	66.0(3)
N(1)-Sn-N(2)	87.7(3)	Sn-S(1)-C(1)	81.8(4)
Sn-S(2)-C(6)	81.9(4)	Sn-N(1)-C(1)	98.1(7)
Sn-N(1)-C(5)	140.1(8)	C(1)-N(1)-C(5)	121.8(10)
Sn-N(2)-C(6)	100.0(7)	Sn-N(2)-C(10)	138.8(8)
C(6)-N(2)-C(10)	121.1(10)	S(1)-C(1)-N(1)	113.9(8)
S(1)-C(1)-C(2)	126.4(9)	N(1)-C(1)-C(2)	119.8(11)
C(1)-C(2)-C(3)	117.9(11)	C(2)-C(3)-C(4)	122.0(12)
C(3)-C(4)-C(5)	117.0(12)	N(1)-C(5)-C(4)	121.4(11)
S(2)-C(6)-N(2)	112.2(8)	S(2)-C(6)-C(7)	125.7(9)
N(2)-C(6)-C(7)	122.1(11)	C(6)-C(7)-C(8)	116.9(12)
C(7)-C(8)-C(9)	121.9(13)	C(8)-C(9)-C(10)	117.7(13)
N(2)-C(10)-C(9)	120.2(12)		

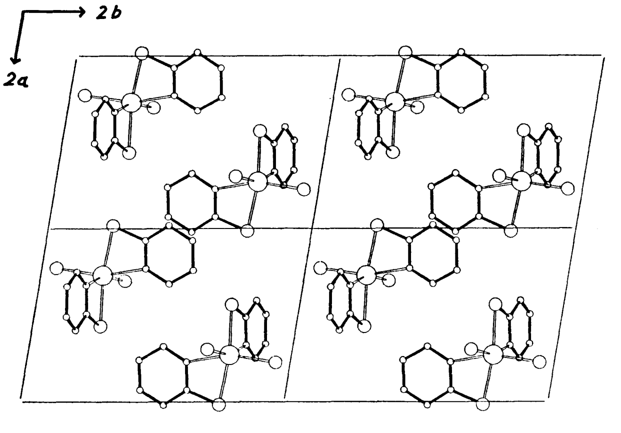

Fig. 2. The crystal structure of **1**.

of tin atom from planes (D) and (E) are 0.12 and 0.16 Å, respectively. The values of deviation seem to be comparatively small. This is supported by the fact that eight atoms [C(1—5), N(1), S(1), and Sn] are nearly on plane (F) within a deviation of 0.07 Å. The deviations of eight atoms [C(6—10), N(2), S(2), and Sn] from the mean plane (G) are also small (Table 7). This is in line with the IR spectral observation that the absorption bands due to pyridine ring vibrations and C–H out of plane bending vibrations in **1** appear in a higher spectral region than those in di-2-pyridyl disulfide, suggesting the depletion of π-electron density of the pyridine ring.¹⁾ The four-membered chelate ring condensed with the pyridine ring seems to be stabilized by mesomeric effect. The results support the assumption that the stability of **1** is based on the intramolecular chelation for six-coordination of the tin atom.¹⁾

The crystal structure is shown in Fig. 2. Intermolecular contacts are normal.

TABLE 7. DEVIATIONS OF LIGAND ATOMS FROM LEAST-SQUARES PLANE

Plane A: Sn, Cl(1), Cl(2), N(1), N(2) $0.9866X-0.0019Y-0.3939Z-2.2135=0$					
Sn	−0.009 Å	Cl(1)	0.339 Å	Cl(2)	−0.322 Å
N(1)	0.371	N(2)	−0.379		
Plane B: Sn, Cl(1), N(1), S(1), S(2) $-0.0281X+0.9179Y+0.3659Z-2.9247=0$					
Sn	−0.214	Cl(1)	−0.028	N(1)	−0.090
S(1)	0.177	S(2)	0.155		
Plane C: Sn, Cl(2), N(2), S(1), S(2) $0.0078X-0.4128Y+0.8442Z+0.8144=0$					
Sn	−0.183	Cl(2)	−0.070	N(2)	−0.149
S(1)	0.181	S(2)	0.220		
Plane D: C(1), C(2), C(3), C(4), C(5), N(1) $-0.1132X+0.9186Y+0.4109Z-2.6490=0$					
C(1)	0.014	C(2)	−0.007	C(3)	−0.004
C(4)	0.009	C(5)	−0.002	N(1)	−0.009
Sn[a]	−0.124	S(1)[a]	0.067		
Plane E: C(6), C(7), C(8), C(9), C(10), N(2) $0.1308X-0.3423Y+0.8259Z+0.3438=0$					
C(6)	0.005	C(7)	−0.003	C(8)	0.003
C(9)	−0.004	C(10)	0.005	N(2)	−0.006
Sn[a]	−0.164	S(2)[a]	−0.032		
Plane F: C(1), C(2), C(3), C(4), C(5), N(1), S(1), Sn $-0.1395X+0.9223Y+0.4134Z-2.5394=0$					
C(1)	0.009	C(2)	−0.042	C(3)	−0.032
C(4)	0.017	C(5)	0.034	N(1)	0.020
S(1)	0.060	Sn	−0.064	Cl(1)[a]	0.080
S(2)[a]	0.575				
Plane G: C(6), C(7), C(8), C(9), C(10), N(2), S(2), Sn $0.1492X-0.3651Y+0.8099Z+0.4770=0$					
C(6)	0.029	C(7)	−0.019	C(8)	−0.031
C(9)	−0.016	C(10)	0.033	N(2)	0.040
S(2)	0.022	Sn	−0.058	Cl(2)[a]	−0.118
S(1)[a]	0.674				

a) Omitted from the least-squares plane calculation.

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