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2,2':6',2''-Terpyridyl–Aquoisothiocyanatotriphenyltin(IV)(1:1)*

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Abstract. C₁₅H₁₁N₃·C₁₉H₁₇NOSSn, triclinic, $P\bar{1}$, $a = 10.326$ (2), $b = 10.739$ (2), $c = 15.880$ (2) Å, $\alpha = 105.04$ (1), $\beta = 97.14$ (1), $\gamma = 111.5$ (1)°, $Z = 2$, $D_c = 1.427$, $D_m = 1.432$ g cm⁻³. The final residual is $R_F = 0.026$ on 4581 observed reflections at 296 K. The Sn atom is coordinated to the NCS group, the three phenyl groups and the water-molecule O atom in a trigonal-bipyramidal arrangement. The terpyridyl group is hydrogen-bonded to the water-molecule O atom.

Introduction. Complex formation between neutral, planar tridentate ligands and tin tetrachloride, mono-organotin(IV) chlorides and diorganotin(IV) chlorides is well known (Fergusson, Roper & Wilkins, 1965; May & Curran, 1972; Pelizzi & Pelizzi, 1976; Einstein & Penfold, 1966). In particular, the chelating agent 2,2':6',2''-terpyridyl forms complexes with all these Sn^{IV} species, behaving as a tridentate in each case. Seven-coordination at the Sn atom has been proposed in several instances (May & Curran, 1972; Pelizzi & Pelizzi, 1976) and confirmed by crystal-structure analysis of the compound diisothiocyanatodimethyl-(terpyridyl)tin(IV) (Naik & Scheidt, 1973). However, no seven-coordinate Sn^{IV} complex with three Sn–C bonds has yet been characterized. Recently, the complex of triphenyltin chloride with 2,2':6',2''-terpyridyl was found to have a most unusual structure, in which the terpyridyl moiety was not bound directly to the Sn atom at all, but hydrogen-bonded to a coordinated water molecule (Prasad, Lee, Le Page & Smith, 1982).

Corresponding chloro and isothiocyanato organotin complexes often have different structures, e.g. the 2,2'-bipyridyl complexes of diphenyltin dichloride and diphenyltin diisothiocyanate both have approximately octahedral structures, but in the former, the phenyl groups are *trans* to each other (Harrison, King & Richards, 1974) whereas in the latter complex, the hydrocarbons are *cis* to each other (Gabe, Prasad, Le Page & Smith, 1982). Consequently, it was considered worthwhile to synthesize the isothiocyanato analogue of the complex between triphenyltin chloride and 2,2':6',2''-terpyridyl.

Triphenyltin chloride was a gift from M & T Chemicals. An ethanolic solution of triphenyltin isothiocyanate was prepared from the chloride by a metathetical reaction in ethanol and the precipitated potassium chloride was filtered off. The complex was obtained in good yield by mixing hot ethanolic solutions containing stoichiometric quantities of triphenyltin isothiocyanate and 2,2':6',2''-terpyridine. White crystals of the complex were obtained by recrystallization from ethanol (m.p. 391–393 K). Microanalyses were carried out by the Australian Micro-analytical service, CSIRO, Melbourne, Australia. Found (%): C 61.88, H 4.29, N 8.46, Sn 18.6; calculated (%) for C₃₄H₂₈N₄OSSn: C 61.93, H 4.28, N 8.50, Sn 18.0.

The diffraction intensities of a 0.35 × 0.35 × 0.35 mm crystal were measured at room temperature with graphite-monochromatized Mo K α radiation generated at 50 kV, 16 mA, using the $\theta/2\theta$ scan technique with line-profile analysis (Grant & Gabe, 1978). A total of

* NRC No. 20040.

Table 1. Atomic positional parameters and equivalent isotropic Debye-Waller parameters

E.s.d.'s refer to the last digit printed.

	x	y	z	B_{eq}^* (\AA^2)
Sn	0.169994 (24)	0.330684 (23)	0.281165 (14)	2.542 (5)
S	0.29557 (11)	-0.06979 (10)	0.16381 (7)	5.38 (3)
O	0.08553 (10)	0.49886 (18)	0.31409 (11)	2.84 (6)
N(1)	0.2444 (3)	0.1575 (3)	0.25183 (16)	4.01 (9)
N(2)	0.24991 (24)	0.74969 (23)	0.45756 (14)	2.83 (7)
N(3)	0.08538 (23)	0.77515 (22)	0.32114 (13)	2.53 (7)
N(4)	-0.0659 (3)	0.53355 (23)	0.17300 (14)	3.07 (7)
C(1)	0.2644 (3)	0.0624 (3)	0.21482 (17)	2.77 (8)
C(2)	0.2106 (3)	0.3569 (3)	0.42170 (17)	2.46 (8)
C(3)	0.3341 (3)	0.3518 (3)	0.46353 (18)	2.93 (9)
C(4)	0.3627 (3)	0.3711 (3)	0.55516 (19)	3.67 (10)
C(5)	0.2695 (4)	0.3941 (3)	0.60450 (19)	4.00 (11)
C(6)	0.1463 (3)	0.3979 (3)	0.56356 (19)	3.84 (11)
C(7)	0.1168 (3)	0.3804 (3)	0.47242 (18)	3.11 (9)
C(8)	0.3278 (3)	0.4524 (3)	0.22336 (17)	2.62 (8)
C(9)	0.3506 (3)	0.5904 (3)	0.22989 (18)	3.22 (9)
C(10)	0.4519 (3)	0.6667 (3)	0.19065 (20)	3.93 (10)
C(11)	0.5294 (3)	0.6061 (4)	0.14461 (21)	4.20 (11)
C(12)	0.5089 (4)	0.4704 (4)	0.13794 (22)	4.49 (12)
C(13)	0.4093 (3)	0.3941 (3)	0.17773 (20)	3.74 (10)
C(14)	-0.0404 (3)	0.1887 (3)	0.19894 (18)	2.91 (9)
C(15)	-0.0594 (3)	0.0945 (3)	0.11594 (19)	3.94 (11)
C(16)	-0.1955 (4)	0.0036 (4)	0.06181 (21)	5.33 (12)
C(17)	-0.3137 (4)	0.0034 (4)	0.09257 (24)	5.79 (13)
C(18)	-0.2981 (4)	0.0946 (4)	0.17577 (24)	5.65 (13)
C(19)	-0.1607 (4)	0.1870 (3)	0.22896 (20)	4.08 (10)
C(20)	0.3427 (3)	0.7400 (3)	0.51958 (19)	3.53 (10)
C(21)	0.4333 (4)	0.8547 (3)	0.59560 (20)	4.18 (11)
C(22)	0.4275 (4)	0.9818 (3)	0.60539 (20)	4.59 (11)
C(23)	0.3326 (3)	0.9947 (3)	0.54333 (19)	3.82 (10)
C(24)	0.2437 (3)	0.8756 (3)	0.46906 (17)	2.69 (8)
C(25)	0.1371 (3)	0.8824 (3)	0.40054 (17)	2.52 (8)
C(26)	0.0903 (3)	0.9897 (3)	0.41852 (18)	3.04 (9)
C(27)	-0.0155 (3)	0.9862 (3)	0.35417 (20)	3.44 (10)
C(28)	-0.0685 (3)	0.8778 (3)	0.27203 (18)	3.05 (9)
C(29)	-0.0142 (3)	0.7757 (3)	0.25811 (17)	2.56 (8)
C(30)	-0.0672 (3)	0.6568 (3)	0.17068 (17)	2.55 (8)
C(31)	-0.1168 (3)	0.6753 (3)	0.09127 (18)	3.18 (9)
C(32)	-0.1721 (3)	0.5607 (3)	0.01258 (19)	3.78 (10)
C(33)	-0.1751 (4)	0.4339 (3)	0.01427 (19)	4.02 (10)
C(34)	-0.1204 (4)	0.4241 (3)	0.09496 (20)	3.92 (10)
H(1)	0.146 (3)	0.586 (3)	0.3576 (17)	6.5 (8)
H(2)	0.045 (3)	0.520 (3)	0.2749 (16)	6.4 (8)
H(3)	0.402 (3)	0.3353 (23)	0.4277 (15)	4.5 (6)
H(4)	0.4441 (25)	0.3646 (24)	0.5807 (15)	4.6 (6)
H(5)	0.291 (3)	0.408 (3)	0.6695 (17)	6.6 (8)
H(6)	0.077 (3)	0.414 (3)	0.5987 (17)	6.8 (8)
H(7)	0.0270 (24)	0.3864 (22)	0.4423 (14)	4.0 (6)
H(9)	0.286 (3)	0.6362 (24)	0.2577 (15)	4.9 (7)
H(10)	0.463 (3)	0.7601 (24)	0.1930 (15)	5.0 (7)
H(11)	0.598 (3)	0.6567 (25)	0.1156 (16)	5.3 (7)
H(12)	0.561 (3)	0.421 (3)	0.1074 (17)	6.6 (8)
H(13)	0.396 (3)	0.2997 (24)	0.1768 (15)	5.0 (7)
H(15)	0.024 (3)	0.091 (3)	0.0963 (16)	6.1 (7)
H(16)	-0.200 (3)	-0.059 (3)	0.0020 (18)	7.6 (9)
H(17)	-0.413 (3)	-0.063 (3)	0.0525 (17)	7.5 (8)
H(18)	-0.379 (3)	0.102 (3)	0.2004 (17)	6.8 (8)
H(19)	-0.151 (3)	0.254 (3)	0.2842 (17)	6.4 (8)
H(20)	0.339 (3)	0.6402 (24)	0.5099 (15)	4.6 (6)
H(21)	0.497 (3)	0.8381 (24)	0.6388 (15)	5.0 (7)
H(22)	0.489 (3)	1.062 (3)	0.6550 (17)	6.6 (8)
H(23)	0.3230 (25)	1.0870 (23)	0.5501 (14)	4.3 (6)
H(26)	0.1349 (23)	1.0716 (22)	0.4767 (14)	3.5 (6)
H(27)	-0.0520 (25)	1.0600 (23)	0.3656 (14)	4.2 (6)
H(28)	-0.1433 (24)	0.8750 (23)	0.2256 (14)	4.0 (6)
H(31)	-0.1090 (23)	0.7698 (22)	0.0924 (14)	3.4 (6)
H(32)	-0.208 (3)	0.5701 (24)	-0.0450 (15)	5.3 (7)
H(33)	-0.213 (3)	0.345 (3)	-0.0423 (16)	5.8 (7)
H(34)	-0.121 (3)	0.3296 (24)	0.0972 (15)	4.8 (7)

* B_{eq} is the arithmetic mean of the principal axes of the thermal ellipsoid.

5615 measurements were made up to 50° in 2θ giving 5386 unique reflections of which 4581 had a net intensity larger than $3\sigma(I)$ based on counting statistics. The intensities were corrected for measured direct-beam polarization (Le Page, Gabe & Calvert, 1979). Absorption corrections were not applied ($\mu = 9.31 \text{ cm}^{-1}$). The cell parameters were obtained by least-squares refinement of the setting angles of 54 reflections with 2θ larger than 35° [$\lambda(\text{Mo } K\alpha_1) = 0.70932 \text{ \AA}$].

The Sn atom was found from a Patterson map. A heavy-atom-phased Fourier map revealed all the non-H atoms. After several cycles of refinement with isotropic thermal parameters, the structure was refined with anisotropic thermal parameters and the residual was lowered to $R_F = 0.03$. All the H atoms were then located in a difference map and their positional parameters were refined together with isotropic thermal parameters, while the other atoms were refined anisotropically by block-diagonal least squares minimizing the quantity $D = \sum w||F_o| - |F_c||^2$. Weights based on counting statistics were used throughout. In the final refinement cycle, the maximum value of the ratio between parameter shift and the corresponding e.s.d. was 0.3. The scattering curves for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974). The final residuals are $R_F = 0.026$ and $R_{wF} = 0.022$ for 4581 observed reflections. $R_F = 0.036$ and $R_{wF} = 0.022$ for a total of 5386 reflections. The atomic positional parameters and equivalent isotropic temperature factors are listed in Table 1.*

All calculations were performed using the NRC PDP8-e system of programs (Larson & Gabe, 1978).

Discussion. A stereoview of the molecule is shown in Fig. 1 and the atom names, distances and angles are shown in Fig. 2.

The molecular configuration is the same as that of the chloro complex (Prasad *et al.*, 1982). The Sn atom is coordinated to the three phenyl groups, the N atom of the NCS group and the water-molecule O atom. The

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36678 (37 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

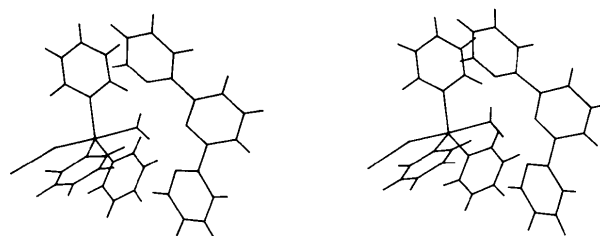


Fig. 1. Stereoscopic pair of the molecule seen approximately along the $[011]$ direction.

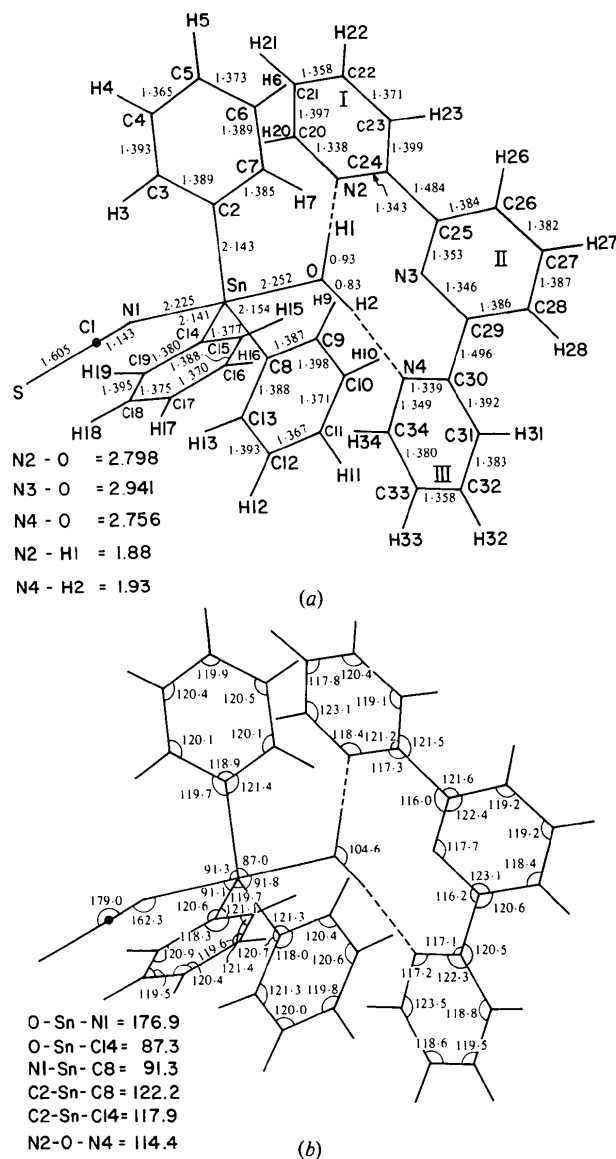


Fig. 2. (a) Atom names and bond distances (Å) (uncorrected for thermal motion). The e.s.d.'s on bond distances involving Sn are 0.002–0.003 Å and the others range from 0.003 to 0.005 Å. (b) Angles (°). The e.s.d.'s in angles involving Sn are 0.1° and the others range from 0.2 to 0.3°.

N atoms of the two outer rings of the terpyridyl group are hydrogen-bonded to the water-molecule O atom. It again shows that the Lewis acidity of the Sn atom with three phenyl groups attached is insufficient for more than one N atom of the terpyridyl group to be coordinated (Prasad *et al.*, 1982) and the terpyridyl group will coordinate as a tridentate ligand only or not at all (Einstein & Penfold, 1966).

The Sn atom and the three binding C atoms of the phenyl groups form the equatorial plane, while the NCS group and the O atom occupy the axial positions of a

trigonal bipyramid. The average Sn—C bond distance of 2.146 (3) Å is similar to the average Sn—C distance of 2.131 (2) Å in the chloro complex and the distances quoted in the literature (Harrison *et al.*, 1974) for five-coordinated complexes.

The Sn—O distance is 2.252 (2) Å and is comparable to the corresponding distance of 2.317 (2) Å in 2,2':6',2''-terpyridyl-aquachlorotriphenyltin(IV)(1:1).

The NCS group is linear, the angle N(1)—C(1)—S being 179.0 (3)°. The Sn—N distance of 2.225 (2) Å is shorter than the distance of 2.282 (4) Å found in the seven-coordinated complex, diisothiocyanatodimethyl(terpyridyl)tin(IV) (Naik & Scheidt, 1973). The C—S bond length of 1.605 (3) Å and the N—C bond length of 1.143 (4) Å are similar to the distances found in other metal isothiocyanato complexes (Domingos & Sheldrick, 1974; Chow, 1970; Forder & Sheldrick, 1970). The bending of the NCS group with respect to the Sn atom [Sn—N(1)—C(1) = 162.3 (2)°] is probably a steric effect.

The N atoms N(2) and N(4) of rings (I) and (III) of the terpyridyl group are strongly hydrogen-bonded to the water-molecule O atom; N(2)···H—O = 2.798 (3) Å and N(4)···H—O = 2.756 (3) Å. The terpyridyl group is not planar because of steric effects between N(3) and the water-molecule O atom. The dihedral angle between rings (I) and (II) is 19.6 (3)° and that between rings (II) and (III) is 29.5 (3)°. The dihedral angle between rings (III) and (I) is 22.2 (3)°. There are no other short intermolecular contacts and the molecules are held together in the crystal by van der Waals forces.

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Structure of Dichloro[*N,N,N',N'*-tetraethyl-3-diphenylphosphino-1,2-propanediamine-*N,N'*]zinc(II)

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Abstract. $\text{ZnCl}_2[(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CHN}(\text{C}_2\text{H}_5)_2\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2]$, $\text{C}_{23}\text{H}_{35}\text{Cl}_2\text{N}_2\text{PZn}$, triclinic, $P\bar{1}$ (at 138 K), $a = 11.206$ (6), $b = 12.436$ (5), $c = 10.005$ (4) Å, $\alpha = 106.55$ (3), $\beta = 97.80$ (3), $\gamma = 105.64$ (3)°, $Z = 2$, $V = 1252.46$ Å³, $D_c = 1.343$ g cm⁻³, $R = 0.029$ for 5160 reflections (Mo $K\alpha$ radiation). The environment about the zinc atom is a distorted tetrahedron with two chlorine atoms and two amino groups from the potentially tridentate ligand occupying the apices.

Introduction. The interaction of the Group IIb metal (zinc, cadmium, and mercury) halides with Lewis-base neutral ligands yields complexes $(MX_2)_n L_m$ that span a wide diversity of ligand-to-metal ratios (Evans, Mann, Peiser & Purdie, 1940; Houk & Dobson, 1968; Fawcett, Ou, Potenza & Schugar, 1978; DiVaira & Orioli, 1968). Although detailed X-ray crystallographic studies of several of these complexes reveal metal coordination numbers ranging from two to perhaps nine, an environment of two, four, or six ligands is most often encountered (Fawcett, Ou, Potenza & Schugar, 1978; Orioli & Ciampolini, 1972; Cameron & Forrest, 1971; DiVaira & Orioli, 1968). Very frequently the secondary valence is satisfied by additional weak or moderate bonds to the metal. While the numbers of crystallographic structural investigations of zinc and cadmium complexes are probably comparable, more extensive studies of mercury compounds are prevalent in the literature. Available data on

the structural chemistry of zinc-halide Lewis-base-ligand complexes indicate a preference for achieving four coordination and usually a distorted tetrahedral environment (Baenziger & Schultz, 1971).

In the recent past there has been widespread interest in the interaction of a variety of metal systems with potentially chelating 'mixed' multidentate ligands, species possessing at least two different Lewis-base centers strategically located along a chain or in *ortho* positions on a phenyl ring (Gatteschi, Ghilardi, Orlandini & Sacconi, 1978; Mealli, Midollini & Sacconi, 1978; Sacconi & DiVaira, 1978; DiVaira, Midollini & Sacconi, 1978). Because of this 'mixed' ligand interest and the multiplicity of coordination geometries exhibited by the Group IIb metals, an investigation of the crystal and molecular structures of $(MX_2)_n L_m$ species (where $M = \text{Zn, Cd, Hg}$; $X = \text{Cl, Br, I}$; and $L =$ 'mixed' ligand) has been initiated (Sen Gupta, Houk, van der Helm & Hossain, 1980; Houk, Sen Gupta, Hossain & van der Helm, 1982).

The interaction of an equal molar ratio of ZnCl_2 and the 'mixed' ligand $(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CHN}(\text{C}_2\text{H}_5)_2\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2$ (PNN) in ethanol yields white crystals of the 1:1 adduct $\text{ZnCl}_2(\text{PNN})$ (Houk & Dobson, 1968). The fairly well developed prismatic crystals were found to be unstable in the presence of air, moisture, and organic solvents. All X-ray measurements were carried out with a single crystal of dimensions $0.50 \times 0.50 \times 0.15$ mm on a Nonius CAD-4 automatic diffractometer, fitted with a low-temperature (cold N_2 gas stream) device.