

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

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Abstract. $C_{15}H_{11}N_3 \cdot C_{18}H_{17}ClOSn$, monoclinic, $P2_1/n$; at room temperature (299 K): $a = 10.752$ (2), $b = 9.560$ (2), $c = 28.307$ (6) Å, $\beta = 95.42$ (2)°; at 115 K: $a = 10.6644$ (6), $b = 9.4819$ (4), $c = 28.338$ (2) Å, $\beta = 95.922$ (5)°; $Z = 4$, $D_c = 1.45$ Mg m⁻³. The final residual (R_F) is 0.020 on 3333 observed reflections at 115 K and 0.027 on 2986 observed reflections at room temperature. The Sn atom is coordinated to the Cl atom, 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 which in turn is coordinated to the Sn atom.

Introduction. Complex formation between triorganotin chlorides and neutral tridentate chelating agents is rare (Smith & Liengme, 1975). However, complex formation between neutral, planar tridentates and tin tetrachloride, monoorganotin(IV) chlorides and diorganotin(IV) chlorides is well known (Fergusson, Roper & Wilkins, 1965; May & Curran, 1972; Pelizzi & Pelizzi, 1976; Einstein & Penfold, 1968). 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 for the compound diisothiocyanatodimethyl(terpyridyl)tin(IV) (Naik & Scheidt, 1973).

Consequently, when a stable, 1:1 complex between 2,2':6',2''-terpyridyl and triphenyltin chloride was isolated, it was considered entirely possible that the complex might contain seven-coordinate Sn. Since no seven-coordinate Sn^{IV} complex containing three Sn–C bonds has yet been confirmed, a crystal-structure analysis of the title compound was undertaken.

Triphenyltin chloride was obtained from M & T Chemicals Inc., and 2,2':6',2''-terpyridyl was obtained from the Aldrich Chemical Company. The complex was obtained in good yield by mixing stoichiometric

quantities of hot, ethanolic solutions of triphenyltin chloride and 2,2':6',2''-terpyridyl. The complex was recrystallized from ethanol and obtained as white needles (m.p. 371 K). A microanalysis was performed by the Australian Microanalytical Service, CSIRO, Melbourne, Australia. Found (%): C 62.20, H 4.40, Cl 5.80, N 6.57, Sn 19.10; calculated (%) for $C_{33}H_{28}ClN_3OSn$, C 62.25, H 4.43, Cl 5.57, N 6.60, Sn 18.64.

The diffraction intensities of a $0.3 \times 0.3 \times 0.3$ mm crystal of the title compound were first measured at room temperature (299 K). Graphite-monochromatized Mo $K\alpha$ radiation, generated at 50 kV and 16 mA, was used in a $\theta/2\theta$ scan with line-profile analysis (Grant & Gabe, 1978). The crystals deteriorated on exposure to X-rays, as shown by a decrease in the intensities of the reference reflections, and the complete data set was collected from two crystals of approximately equal size.

Reflections were measured up to $2\theta = 45^\circ$, giving a total of 3825 unique reflections of which 2986 had a net intensity larger than $3\sigma(I)$ (based on counting statistics) and were considered to be observed, while 280 of the 282 measurements of systematic absences were found to be unobserved. The intensities were corrected for measured direct-beam polarization (Le Page, Gabe & Calvert, 1979) but not for absorption ($\mu = 1.02$ mm⁻¹). The cell parameters were obtained by least-squares refinement of the setting angles of 42 reflections with 2θ greater than 42° [$\lambda(\text{Mo } K\alpha_1) = 0.70932$ Å].

The diffraction intensities were remeasured at 115 K; all other experimental conditions were the same. No decay of the reference reflections was observed at this temperature. A total of 3761 unique reflections were measured of which 3333 had a net intensity larger than $3\sigma(I)$. The cell parameters at this temperature were obtained in the same way as at room temperature.

The structure was first solved using the intensity data measured at room temperature by the application of *MULTAN* (Germain, Main & Woolfson, 1971) to the 356 largest E values. The resulting E map revealed the

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Table 1. Atomic positional parameters and equivalent isotropic thermal parameters

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

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

	x	y	z	B_{eq} (Å ²)
Cl	0.38882 (7)	0.34354 (8)	0.423810 (24)	2.56 (3)
Sn	0.221846 (17)	0.496618 (19)	0.380399 (6)	1.426 (7)
O	0.06658 (16)	0.62216 (17)	0.33510 (5)	1.60 (7)
N(1)	-0.13159 (20)	0.68224 (22)	0.38755 (7)	1.86 (10)
N(2)	-0.19219 (19)	0.51710 (21)	0.31063 (7)	1.65 (9)
N(3)	-0.01186 (20)	0.49474 (22)	0.24760 (7)	1.75 (9)
C(1)	0.26511 (23)	0.6840 (3)	0.42066 (8)	1.57 (11)
C(2)	0.3414 (3)	0.6793 (3)	0.46419 (9)	2.35 (13)
C(3)	0.3728 (3)	0.8029 (3)	0.48870 (9)	3.16 (14)
C(4)	0.3321 (3)	0.9309 (3)	0.47129 (10)	2.94 (14)
C(5)	0.2566 (3)	0.9380 (3)	0.42878 (10)	2.53 (13)
C(6)	0.2243 (3)	0.8155 (3)	0.40383 (9)	1.95 (12)
C(7)	0.07514 (24)	0.3610 (3)	0.39800 (8)	1.57 (11)
C(8)	0.0250 (3)	0.3737 (3)	0.44070 (9)	2.84 (14)
C(9)	-0.0718 (3)	0.2888 (3)	0.45272 (10)	3.36 (15)
C(10)	-0.1204 (3)	0.1871 (3)	0.42154 (10)	3.06 (14)
C(11)	-0.0732 (3)	0.1728 (3)	0.37886 (10)	3.36 (15)
C(12)	0.0232 (3)	0.2585 (3)	0.36711 (9)	2.83 (14)
C(13)	0.30878 (23)	0.4836 (3)	0.31612 (8)	1.50 (10)
C(14)	0.30019 (25)	0.3653 (3)	0.28703 (9)	1.83 (12)
C(15)	0.3570 (3)	0.3625 (3)	0.24546 (9)	2.15 (12)
C(16)	0.4247 (3)	0.4763 (3)	0.23238 (9)	2.29 (12)
C(17)	0.4364 (3)	0.5941 (3)	0.26098 (9)	2.39 (13)
C(18)	0.3779 (3)	0.5975 (3)	0.30253 (9)	1.95 (12)
C(19)	-0.1072 (3)	0.7746 (3)	0.42314 (9)	2.49 (13)
C(20)	-0.1835 (3)	0.7916 (3)	0.45933 (9)	2.91 (14)
C(21)	-0.2897 (3)	0.7112 (3)	0.45855 (9)	3.09 (15)
C(22)	-0.3174 (3)	0.6167 (3)	0.42219 (10)	2.65 (13)
C(23)	-0.2360 (3)	0.6039 (3)	0.38704 (9)	1.79 (12)
C(24)	-0.26048 (24)	0.5008 (3)	0.34736 (8)	1.78 (11)
C(25)	-0.3478 (3)	0.3921 (3)	0.34925 (10)	2.39 (13)
C(26)	-0.3645 (3)	0.2990 (3)	0.31246 (10)	2.77 (13)
C(27)	-0.2949 (3)	0.3126 (3)	0.27455 (9)	2.50 (13)
C(28)	-0.20914 (25)	0.4229 (3)	0.27483 (9)	1.82 (11)
C(29)	-0.1278 (3)	0.4410 (3)	0.23593 (9)	1.86 (11)
C(30)	-0.1687 (3)	0.4020 (3)	0.18918 (9)	2.69 (13)
C(31)	-0.0886 (3)	0.4198 (3)	0.15477 (9)	3.31 (15)
C(32)	0.0310 (3)	0.4733 (3)	0.16656 (9)	2.85 (14)
C(33)	0.0645 (3)	0.5086 (3)	0.21341 (9)	2.23 (12)
H(2)	0.3721 (21)	0.5836 (24)	0.4761 (7)	2.1 (5)
H(3)	0.4183 (24)	0.795 (3)	0.5156 (8)	3.6 (6)
H(4)	0.3531 (25)	1.0192 (24)	0.4875 (8)	3.5 (6)
H(5)	0.2325 (22)	1.0269 (22)	0.4156 (7)	2.2 (5)
H(6)	0.1750 (21)	0.8245 (22)	0.3767 (7)	1.6 (5)
H(8)	0.0536 (23)	0.4368 (25)	0.4616 (8)	3.3 (6)
H(9)	-0.104 (3)	0.303 (3)	0.4815 (8)	4.5 (7)
H(10)	-0.1822 (23)	0.1318 (24)	0.4298 (8)	3.0 (6)
H(11)	-0.0971 (25)	0.107 (3)	0.3593 (8)	4.2 (7)
H(12)	0.0509 (24)	0.248 (3)	0.3377 (8)	3.7 (6)
H(14)	0.2584 (21)	0.2866 (22)	0.2957 (7)	1.8 (5)
H(15)	0.3471 (22)	0.2835 (24)	0.2271 (7)	2.4 (6)
H(16)	0.4656 (22)	0.4722 (23)	0.2042 (8)	2.5 (6)
H(17)	0.4825 (22)	0.6733 (24)	0.2524 (7)	2.5 (6)
H(18)	0.3838 (21)	0.6803 (22)	0.3215 (7)	1.8 (5)
H(19)	-0.0320 (21)	0.8255 (23)	0.4210 (7)	2.1 (5)
H(20)	-0.1568 (24)	0.859 (3)	0.4822 (8)	3.8 (7)
H(21)	-0.3392 (24)	0.723 (3)	0.4811 (8)	3.6 (6)
H(22)	-0.3828 (22)	0.5654 (23)	0.4203 (7)	2.3 (6)
H(25)	-0.3933 (20)	0.3872 (22)	0.3755 (7)	1.7 (5)
H(26)	-0.4250 (23)	0.2241 (25)	0.3130 (8)	3.0 (6)
H(27)	-0.3066 (21)	0.2449 (24)	0.2490 (7)	2.7 (6)
H(30)	-0.2493 (23)	0.3645 (24)	0.1832 (8)	3.1 (6)
H(31)	-0.125 (3)	0.396 (3)	0.1219 (9)	5.6 (8)
H(32)	0.0883 (22)	0.4897 (22)	0.1449 (7)	2.3 (5)
H(33)	0.1436 (21)	0.5477 (21)	0.2222 (7)	1.7 (5)
OH(1)	0.0045 (23)	0.641 (3)	0.3492 (8)	3.7 (7)
OH(2)	0.0392 (25)	0.578 (3)	0.3096 (9)	4.5 (7)

positions of the Sn atom and all but one of the other 38 non-H atoms, which was subsequently located on a difference map.

The R_F factor was lowered to 0.044 with least squares at which point the H atoms were located in a difference map. Further refinement of positional and anisotropic thermal parameters (isotropic for H atoms) with counting-statistics' weights gave a final $R_F = 0.027$ and $R_{wF} = 0.039$. An extinction correction was included (Larson, 1970). The scattering curves for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974).

The atomic positions obtained above were further refined using the intensity data measured at 115 K. The final residuals obtained using the low-temperature data are $R_F = 0.020$ and $R_{wF} = 0.021$ and the corresponding atomic positional and equivalent isotropic temperature parameters are listed in Table 1.*

All the calculations were performed using the NRC PDP8-e program system (Larson & Gabe, 1978) and the same system on a PDP-11.

Discussion. A stereoview of the molecule is shown in Fig. 1 and the atom names, distances and angles are shown in Fig. 2. While the structures obtained at the two temperatures were essentially the same, the e.s.d.'s for bond lengths and angles for the low-temperature data are approximately half the e.s.d.'s for the room-temperature data.

It was expected that the Sn atom would be found to be seven-coordinate, being bound to the three phenyl groups, the Cl atom and the three N atoms of the terpyridyl group. However, the terpyridyl is not directly coordinated to the Sn atom at all, and the complex involves five-coordinate Sn. The Sn atom is coordinated to the three phenyl groups, the Cl atom, and the O atom of a water molecule. The terpyridyl group is held

* Lists of anisotropic thermal parameters and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36266 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

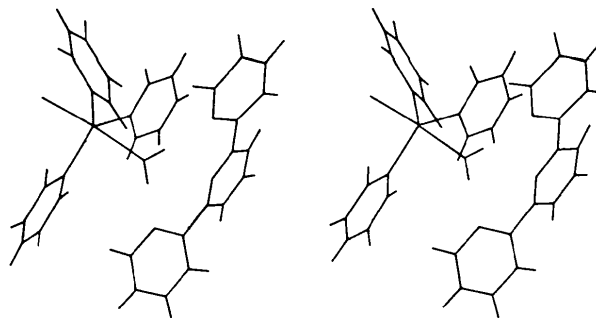


Fig. 1. Stereoscopic pair of the molecule seen approximately along the $|100|$ direction.

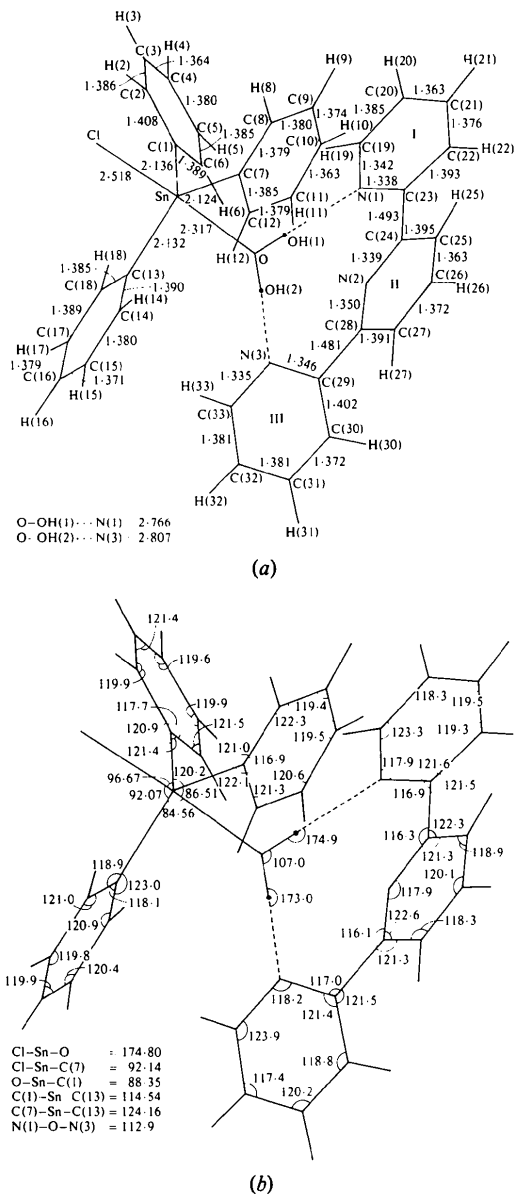


Fig. 2. (a) Atom names and bond distances (Å) (uncorrected for thermal motion). The e.s.d.'s on bond distances involving Sn are ~ 0.002 Å; involving H ~ 0.02 Å, and for the other atoms ~ 0.004 Å. (b) Angles ($^{\circ}$) in the molecule. The e.s.d.'s on angles involving Sn are $\sim 0.08^{\circ}$ and the others $\sim 0.2^{\circ}$.

in the crystal only by hydrogen bonds, between the water molecule O and N atoms of the two outer rings of the terpyridyl group. It appears that the Lewis acidity of the Sn atom, with three phenyl groups and a Cl atom attached, is not sufficient for two or three N atoms of the terpyridyl group to be coordinated, and the terpyridyl group is so bulky that steric restraints make it unfavourable for only one N atom to be coordinated. This is in accordance with the observation made by Einstein & Penfold (1966) that the terpyridyl will coordinate either as a tridentate ligand or not at all.

The Sn atom and the three bonding C atoms of the phenyl groups form the equatorial plane, while the Cl and O atoms occupy the axial positions of a trigonal-bipyramidal configuration. The average Sn—C bond distance of $2.131(2)$ Å between Sn and the phenyl rings is shorter than the average Sn—C distances of $2.152(7)$ Å in (2,2'-bipyridyl)dichlorodiphenyltin(IV) (Harrison, King & Richards, 1974) and $2.173(6)$ Å in (2,2'-bipyridyl)diisothiocyanatodiphenyltin(IV) (Gabe, Prasad, Le Page & Smith, 1982), both six-coordinated complexes, whereas it is larger than the average Sn—C distance of $2.09(3)$ Å in the tetrahedral complex triphenyltin isothiocyanate (Domingos & Sheldrick, 1974). However, it is similar to the average Sn—C distance of $2.125(4)$ Å in the five-coordinated complex triphenyltin isocyanate (Tarkhova, Chuprunov, Simonov & Belov, 1977). The C—C distances in the phenyl rings are all normal.

The Sn—Cl distance of $2.518(1)$ Å is within the range of Sn—Cl distances (2.32 – 2.58 Å) quoted by Harrison *et al.* (1974).

The Sn—O distance is $2.317(2)$ Å and is larger than the Sn—O distance of $2.25(2)$ Å in dichlorodimethylbis(pyridine *N*-oxide)tin(IV) (Blom, Penfold & Robinson, 1969). However, the elongation of the Sn—O bond is not surprising as the O atom is very strongly hydrogen-bonded to the N atoms of rings (I) and (III) of the terpyridyl group; the relevant N—O distances are N(1)···O $2.766(2)$ and N(3)···O $2.807(2)$ Å. These N—O distances are all well within the range of those (2.73 – 3.22 Å) quoted (*International Tables for X-ray Crystallography*, 1962) for O—H···N type hydrogen bonds. The N(2)···O distance [$2.949(3)$ Å] is probably not a hydrogen bond and steric effects between N(2) and the water O atom may be the reason that the terpyridyl group is not planar. Ring (II) is twisted away from the plane of rings (I) and (III). The dihedral angle between rings (I) and (II) is $14.3(3)^{\circ}$, and between rings (II) and (III) is $32.0(2)^{\circ}$. The N—C and C—C bond distances in the terpyridyl group are similar to the distances quoted for terpyridyl-zinc chloride (Einstein & Penfold, 1966). There are no short intermolecular contacts and presumably the crystal is held together by weak van der Waals forces.

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References

- BLOM, E. A., PENFOLD, B. R. & ROBINSON, W. T. (1969). *J. Chem. Soc. A*, pp. 913–917.
 DOMINGOS, A. M. & SHELDICK, G. M. (1974). *J. Organomet. Chem.* **67**, 257–263.
 EINSTEIN, F. W. B. & PENFOLD, B. R. (1966). *Acta Cryst.* **20**, 924–926.

- EINSTEIN, F. W. B. & PENFOLD, B. R. (1968). *J. Chem. Soc. A*, pp. 3019–3024.
- FERGUSON, J. E., ROPER, W. R. & WILKINS, C. J. (1965). *J. Chem. Soc.* pp. 3716–3720.
- GABE, E. J., PRASAD, L., LE PAGE, Y. & SMITH, F. E. (1982). *Acta Cryst.* B38, 256–258.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A27, 368–376.
- GRANT, D. F. & GABE, E. J. (1978). *J. Appl. Cryst.* 11, 114–120.
- HARRISON, P. G., KING, T. J. & RICHARDS, J. A. (1974). *J. Chem. Soc. Dalton Trans.* pp. 1723–1726.
- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- LARSON, A. C. (1970). *Crystallographic Computing*, edited by F. R. AHMED, pp. 291–294. Copenhagen: Munksgaard.
- LARSON, A. C. & GABE, E. J. (1978). *Computing in Crystallography*, edited by H. SCHENK, R. OLTHOFF-HAZEKAMP, H. VAN KONINGSVELD & G. C. BASSI, p. 81. Delft Univ. Press.
- LE PAGE, Y., GABE, E. J. & CALVERT, L. D. (1979). *J. Appl. Cryst.* 12, 25–26.
- MAY, J. C. & CURRAN, C. (1972). *J. Organomet. Chem.* 39, 289–294.
- NAIK, D. V. & SCHEIDT, W. R. (1973). *Inorg. Chem.* 12, 272–276.
- PELIZZI, C. & PELIZZI, G. (1976). *Inorg. Chim. Acta*, 18, 139–144.
- SMITH, F. E. & LIENGME, B. V. (1975). *J. Organomet. Chem.* 91, C31–C32.
- TARKHOVA, T. N., CHUPRUNOV, E. V., SIMONOV, M. A. & BELOV, N. V. (1977). *Kristallografiya*, 22, 1004–1008.

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Structure of Diaquasuccinatocadmium(II) Hemihydrate

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Abstract. $C_4H_8CdO_6 \cdot \frac{1}{2}H_2O$, $M_r = 273.5$, monoclinic, $P2_1/a$, $Z = 8$, $a = 8.405(2)$, $b = 12.719(4)$, $c = 15.295(7)$ Å, $\beta = 96.20(1)^\circ$, $V = 1625$ Å³, $D_x = 2.23$, $D_m = 2.17(2)$ Mg m⁻³, $\mu = 2.66$ mm⁻¹, $\lambda = 0.71073$ Å; final $R = 0.040$ with 3966 observations. The structure consists of two crystallographically independent seven-coordinate Cd atoms in an approximately pentagonal-bipyramidal arrangement. These are then bridged by succinate ions to form a three-dimensional polymer.

Introduction. ¹¹³Cd NMR spectroscopy with a chemical-shift range of ~850 p.p.m. has been shown in recent years to offer potential as a sensitive probe of metal-ion sites in a variety of compounds (Rodesiler, Griffith, Ellis & Amma, 1980, and references therein). However, there is a lack of single-crystal X-ray structure data to correlate with NMR data deemed necessary to place the ¹¹³Cd NMR on a solid base as a probe of metal sites. As part of a comprehensive program involved in the synthesis, crystal structure

analysis and ¹¹³Cd NMR measurement, we synthesized the title compound and determined its crystal structure.

The title compound was prepared by mixing 30 ml of a 0.1 M aqueous solution of Cd(NO₃)₂ and 60 ml of 0.1 M succinic acid and adjusting to a pH of 6.5 with NaOH. Crystals grew by slow evaporation of the resulting solution over a period of days. The crystalline compound was not soluble in the solvents we have used on other Cd complexes and we were not able to obtain a solution ¹¹³Cd Fourier transform (FT) NMR. However, efforts are underway to make ¹¹³Cd FT NMR measurements on solids in the near future. Hence, although the data presented herein are not immediately useful for the crystal structure/¹¹³Cd NMR correlations, they will be useful in the future. In addition, the coordination polyhedron presented here is similar to that of bis(*o*-hydroxybenzoato)cadmium(II) dihydrate and bis(*p*-aminobenzoato)cadmium(II) monohydrate for which we have ¹¹³Cd NMR solution data.

A single crystal ~0.2 × 0.3 × 0.3 mm was mounted on a CAD-4 diffractometer interfaced to a PDP-11/40 computer and the crystal was aligned and intensity data collected by standard techniques (Enraf–Nonius, 1980). Details are found in Table 1.

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