(14) and 1.752 (15) Å, respectively. If phosphorus is a better π acceptor than chlorine, the Mn-C bond trans to phosphorus would be expected to be longer. However the standard deviations of the bonds in the manganese compound are rather large compared to the ones reported here.

The C-O bond lengths in $(PhO)_3PCr(CO)_5$ are less (cis average, 1.131 Å; trans, 1.136 Å) than in $Ph_3PCr(CO)_5$ (cis average, 1.14 Å; trans, 1.154 Å), which is the consistent expectation for less antibonding character of the CO multiple bond in the phosphite compound (resonance form II being less important).

The bond angles in the triphenylphosphine complex are normal with the C-P-C angles averaging 102.6° and the C-P-Cr angles averaging 115.6°.

Only a few crystal structures have been reported[26,29,41-45] for coordination compounds containing a triorganophosphite, and several of the reports are notes which do not describe the phosphite geometry. Its geometry is of interest because from models it has been suggested[46] that triphenyl phosphite would be less bulky than triphenylphosphine since the P-O-C bond angle allows more flexibility in relieving neighboring ring interactions. The O-P-O bond angles in $(PhO)_3PCr(CO)_5$ average 100.0° and the O-P-Cr angles average 117.8°. This does indeed indicate that the groups on phosphorus are collapsed together more in the case of the phosphite than in the case of the phosphine.

It follows that the Cr-P bond contains a larger amount of s character from the phosphorus hybrid in the case of the phosphite.[47]

The greater steric influence, if any, of triphenylphosphine is not evident from the distortion of the cis CO ligands from the plane of the chromium and cis carbons. The P-Cr-C(cis) bond angles are 87.5, 88.4, 94.3, and 96.2° (91.6° average) in the phosphine compared to 87.6, 90.6, 93.2, and 95.5° (91.7° average) in the phosphite.

The P-O-C angles of 123.5, 125.6, and 131.0° (126.7° average) in the phosphite are about the same as in the other triphenyl phosphite coordination compounds.[26,29,44,45]

Registry No. $(C_6H_5)_3PCr(CO)_5$, 14917-12-5; $(C_6H_5O)_3PCr(CO)_5$, 18461-39-7.

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Crystal and Molecular Structure of Dimethyldiisothiocyanato(terpyridyl)tin(IV)

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A three-dimensional X-ray crystal structure analysis of the compound of composition $(CH_3)_2Sn(NCS)_2(C_{15}H_{11}N_3)$ has established that it is a seven-coordinate compound with a pentagonal-bipyramidal configuration. The crystals are triclinic, space group $P\bar{1}$ with $a = 9.440$ (4), $b = 15.446$ (5), $c = 7.595$ (4) Å; $\alpha = 95.50$ (2), $\beta = 93.04$ (1), $\gamma = 71.30$ (2)°. There are two formula units per unit cell, observed and calculated densities are 1.59 and 1.588 g/cm³. The intensities of all independent reflections having $(\sin\theta)/\lambda \leq 0.648$ Å^{-1} were measured with graphite-monochromated Mo Kα radiation by θ-2θ scanning on a computer-controlled four-circle diffractometer; the 4395 data retained as statistically observable were employed for structure determination and refined by Patterson, Fourier, and anisotropic least-squares techniques to a conventional R of 0.029. Tin is bonded to three terpyridyl nitrogens and two isothiocyanato nitrogens so as to form a pentagonal plane. The methyl groups are trans at axial positions with a C-Sn-C angle of 173.7 (2)°. The average bond distances are Sn-C = 2.105 Å, Sn-N(NCS) = 2.283 Å, Sn-N(terpyridyl) = 2.515 Å. The terpyridyl group is distorted from planarity, although the individual pyridine rings are planar. Of the two isothiocyanate groups, one is essentially linear, while the other is bent with a SnNC angle of 155.1 (4)°. This bending is attributed to crystal packing.

Recently May and Curran[3] of our laboratory have reported the preparation and Mossbauer data of terpyridyl adducts with $R_2Sn(NCS)_2$ where R is an alkyl or aryl group. On the basis of infrared spectra and Mossbauer data they proposed that these complexes were seven-coordinate with axial carbon atoms and five nitrogen atoms in the equatorial plane of a pentagonal-bipyramidal coordination polyhedron. Seven-coordinate tin complexes are not uncommon; crystal structures of tris(tropolonato)monochlorotin(IV) and tris(tropolonato)-monohydroxytin(IV),[4] methyltris(nitrato)tin(IV),[5] and methyltris(diethyldithiocarbamato)tin(IV)[6] have established seven-coordination for tin in these complexes. However, seven-coordination has not been established for complexes having two carbon atoms bonded to tin. The possibility that these adducts were ionic six-coordinate complexes could not be ruled out since they show partial ionization in dimethylformamide and also react readily with sodium tetra-

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(2) (a) Peter C. Reilly Fellow, 1971-1972. (b) Taken in part from the dissertation submitted by D. V. N. to the Graduate School of the University of Notre Dame in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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phenylborate to give $[R_2Sn(NCS)terpy]^+[BPh_4]^-$ [7] (terpy = terpyridyl). These reactions are similar to those observed for the ionic compound $[(CH_3)_2SnCl(terpy)]^+[(CH_3)_2SnCl_3]^-$.[8] Therefore, the crystal and molecular structure of dimethyldiisothiocyanato(terpyridyl)tin(IV), a representative complex of this series, was determined.

Experimental Section

A sample of dimethyldiisothiocyanato(terpyridyl)tin(IV), furnished by Professor C. Curran, was recrystallized from absolute methanol to give single crystals. Precession photographs were employed to establish the space group as either $P1$ or $P\bar{1}$ and to determine preliminary lattice constants; the choice of the centrosymmetric space group[9] ($P\bar{1}$), supported by the negative result of sensitive tests for piezoelectricity (using a Giebe-Scheibe detector designed by H. Diamant), was confirmed by the subsequent refinement of structure. The experimental density of 1.59 g/cm^3, measured by flotation, compares well with the calculated density of 1.588 g/cm^3 for a cell content of 2 $[(CH_3)_2Sn(NCS)_2(C_{15}H_{11}N_3)]$.

The specimen crystal had dimensions of 0.23 × 0.16 × 0.24 mm and was mounted on a glass fiber with the 0.16-mm axis approximately parallel to the ϕ axis. Following the centering of the crystal on a computer-controlled four-circle Syntex diffractometer at ambient laboratory temperature of 20 ± 1°, 25 reflections representing a good sampling of reciprocal space and instrument settings were used to determine precise lattice constants using Mo Kα radiation (λ 0.71069 Å): $a = 9.440$ (4), $b = 15.446$ (5), and $c = 7.595$ (4) Å: $\cos\alpha = -0.0959$ or $\alpha = 95.50$ (2)°, $\cos\beta = -0.0530$ or $\beta = 93.04$ (1)°, and $\cos\gamma = 0.3206$ or $\gamma = 71.30$ (2)°. A Delaunay reduction using these cell parameters confirmed the triclinic description of the unit cell. The conventional reduced cell has $a' = 9.440$, $b' = 15.303$, $c' = 7.595$ Å; $\alpha' = 93.67$, $\beta' = 93.04$, $\gamma' = 107.05°$. The transformation matrix is

$$\begin{pmatrix} a' \\ b' \\ c' \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ -1 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix}$$

Intensity data were collected using graphite-monochromated Mo Kα radiation at a takeoff angle of ~4°. The axis of the monochromator was perpendicular to the θ-2θ axis of the diffractometer. All independent reflections for which $(\sin\theta)/\lambda \leq 0.648$ Å^{-1} were scanned by the θ-2θ technique at a variable rate, the slowest being 0.5°/min and the fastest being 12.0°/min. The slowest scan rate was used for reflections with intensities less than 75 counts/sec at the Kα_1 position, and the fastest scan rate for reflections with intensities greater than 750 counts/sec. The intermediate rates were selected automatically by the diffractometer based on a linear interpolation of the above limits. Background counts were taken at the extremes of the scan for a duration equal to that of the scanning time itself. Three standard reflections that were well distributed in reciprocal space were used for periodic (every 50 reflections) checking on the alignment and possible deterioration of the crystal; no significant alterations in the standard intensities were observed (≤±3% or 2σ from the mean) during the course of measurements. With a linear absorption coefficient of the crystal for Mo Kα radiation of only 14.16 cm^{-1}, maximum error from neglect of absorption corrections was calculated to be less than 4% in any intensity or less than 2% in any amplitude; consequently, no correction was applied. The intensity data were reduced to a set of relative squared amplitudes, $|F_o|^2$, by application of the Lorentz and polarization factor (Lp). The polarization correction used was $p = 0.5(\cos^2 2\theta_m + \cos^2 2\theta)$ where θ_m is the Bragg angle of the monochromator crystal and θ is the Bragg angle of the reflection being observed. Those data for which $|F_o| > 2\sigma_F$ were retained as objectively observed, σ_F being the standard deviation computed from $\sigma_F^2 = (Ct + K^2B)/(4|F_o|^2Lp^2)$, Ct being the total count from the scanning, K the ratio of scanning time to total background counting time (in the present case 1), B the total background count, and Lp the Lorentz-polarization correction. A total of 4395 independent reflections, 91% of the total geometrically possible, were thus retained and used for the determination and least-squares refinement of the structure.

Table I. Atomic Coordinates in Crystalline $(CH_3)_2Sn(NCS)_2(C_{15}H_{11}N_3)^a$

Atom	10^4x	10^4y	10^4z
S_1	4282 (2)	4222 (1)	8818 (2)
S_2	8108 (2)	1218 (1)	4909 (2)
N_1	3440 (5)	3094 (4)	6220 (7)
N_2	5108 (4)	1415 (3)	4395 (5)
N_{11}	2857 (3)	0792 (2)	2107 (4)
N_{22}	0323 (3)	2221 (2)	2314 (4)
N_{33}	0198 (4)	3445 (3)	5142 (5)
C_1	3814 (5)	3559 (3)	7299 (6)
C_2	6349 (5)	1355 (3)	4632 (5)
C_3	2032 (5)	1463 (4)	6071 (6)
C_4	2959 (7)	2907 (4)	2097 (8)
C_{11}	4011 (5)	0018 (3)	2241 (6)
C_{12}	4178 (5)	−0770 (3)	1119 (6)
C_{13}	3135 (5)	−0751 (3)	−0228 (6)
C_{14}	1925 (5)	0039 (3)	−0368 (5)
C_{15}	1800 (4)	0797 (3)	0841 (5)
C_{21}	0474 (4)	1637 (3)	0855 (5)
C_{22}	−0582 (5)	1802 (3)	−0534 (6)
C_{23}	−1798 (5)	2587 (4)	−0412 (7)
C_{24}	−1984 (5)	3178 (3)	1105 (7)
C_{25}	−0895 (5)	2968 (3)	2456 (6)
C_{31}	−1045 (5)	3540 (3)	4161 (6)
C_{32}	−2427 (6)	4122 (4)	4742 (8)
C_{33}	−2519 (7)	4597 (4)	6389 (9)
C_{34}	−1264 (7)	4503 (4)	7397 (8)
C_{35}	0082 (6)	3924 (4)	6727 (8)
	10^5x	10^5y	10^5z
Sn	26,074 (3)	21,757 (2)	41,662 (4)

[a] Figures in parentheses are the estimated standard deviations in the last significant figure.

A three-dimensional Patterson synthesis gave the positions of the tin and sulfur atoms in the asymmetric unit of structure, and the positions of the remaining atoms were developed from Fourier syntheses with initial phasing based on the contribution of the tin and sulfur atoms to the structure amplitudes. The structure was then refined by block-diagonal least-squares[10] techniques using all the data with individual isotropic thermal parameters for all atoms. The convergence of this refinement was followed by a Fourier difference synthesis from which approximate positions of all hydrogen atoms were found and included in the subsequent refinements, in fixed positions, with thermal parameters taken as one unit higher than those of the associated atom. The apparent C–H distances ranged from 0.82 to 1.2 Å. Block-diagonal least-squares minimization was then carried to convergence using individual anisotropic thermal parameters for all atoms (except hydrogen). A final cycle of full-matrix least-squares refinement[11] was carried out varying the positional parameters; the output of this refinement was used to obtain the elements of the inverse matrix for the calculation of standard deviations.[12] The final value of $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ was 0.029; that of $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o{}^2)]^{1/2}$ was 0.052. The estimated standard deviation of an observation of unit weight was 1.841. The final parameter shifts were less than 5% of their estimated standard deviation during the last cycle. Empirical weights ($w = 1/\sigma^2$) were calculated from $\sigma = \Sigma_{n=0}{}^3 a_n|F_o|^n$, the a_n's being the coefficients from the least-squares fitting of the curve $||F_o| - |F_c|| = \Sigma_{n=0}{}^3 a_n|F_o|^n$; the values of $|F_c|$ came from a

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Table II. Thermal Parameters (Å^2)^a

Atom type	Anisotropic parameters B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B^b
Sn	3.57 (1)	3.83 (1)	3.74 (1)	−1.299 (8)	−0.001 (8)	−0.356 (8)	3.68
S_1	6.29 (6)	5.12 (6)	5.42 (6)	−2.12 (5)	−1.51 (5)	−0.69 (5)	5.28
S_2	4.22 (5)	12.65 (1)	5.65 (7)	−4.16 (7)	−0.61 (5)	−0.92 (7)	5.98
N_1	5.7 (2)	7.4 (3)	8.6 (3)	−2.3 (2)	−0.5 (2)	−3.7 (2)	6.39
N_2	3.3 (1)	5.9 (2)	5.1 (2)	−1.6 (1)	−0.0 (1)	−0.5 (1)	4.57
N_{11}	3.4 (1)	3.3 (1)	3.3 (1)	−1.0 (1)	−0.0 (1)	−0.0 (1)	3.34
N_{22}	3.3 (1)	3.4 (1)	3.6 (1)	−0.8 (1)	−0.2 (1)	0.4 (1)	3.48
N_{33}	4.2 (2)	4.5 (2)	5.2 (2)	−0.4 (1)	0.4 (1)	−1.1 (1)	4.68
C_1	3.7 (2)	4.5 (2)	5.1 (2)	−1.1 (1)	−0.3 (1)	−0.8 (2)	4.38
C_2	4.0 (2)	5.0 (2)	3.3 (2)	−1.9 (2)	0.1 (1)	−0.4 (1)	3.96
C_3	4.2 (2)	6.3 (2)	3.8 (2)	−1.5 (2)	0.2 (1)	0.5 (2)	4.66
C_4	6.6 (3)	5.1 (2)	7.3 (3)	−2.4 (2)	0.7 (2)	1.2 (1)	5.96
C_{11}	3.9 (2)	3.9 (2)	4.1 (2)	−0.7 (1)	−0.1 (1)	0.1 (1)	4.08
C_{12}	4.9 (2)	3.5 (2)	4.3 (2)	−0.7 (1)	0.8 (2)	−0.2 (1)	4.30
C_{13}	5.4 (2)	3.8 (2)	3.9 (2)	−1.6 (2)	0.9 (2)	−0.7 (1)	4.23
C_{14}	4.9 (2)	4.6 (2)	3.3 (2)	−2.0 (2)	0.2 (1)	−0.3 (1)	4.09
C_{15}	3.5 (1)	3.6 (1)	2.9 (1)	−1.3 (1)	0.1 (1)	0.2 (1)	3.27
C_{21}	3.5 (1)	3.7 (2)	3.4 (1)	−1.4 (1)	−0.3 (1)	0.4 (1)	3.46
C_{22}	4.3 (2)	5.1 (2)	3.8 (2)	−1.8 (2)	−0.8 (2)	0.7 (1)	4.24
C_{23}	4.7 (2)	5.7 (2)	5.3 (2)	−1.3 (2)	−1.7 (2)	1.7 (2)	5.01
C_{24}	4.5 (2)	4.7 (2)	6.3 (3)	−0.5 (2)	−1.1 (2)	1.2 (2)	5.11
C_{25}	3.6 (2)	3.6 (2)	4.8 (2)	−0.6 (1)	−0.3 (1)	0.8 (1)	4.05
C_{31}	4.3 (2)	3.4 (2)	5.2 (2)	−0.4 (1)	0.5 (2)	0.4 (1)	4.36
C_{32}	4.6 (2)	5.0 (2)	7.8 (3)	0.3 (2)	0.4 (2)	−0.4 (2)	5.84
C_{33}	5.8 (3)	4.8 (2)	8.1 (3)	0.4 (2)	2.0 (3)	−0.8 (2)	6.09
C_{34}	6.6 (3)	5.1 (2)	6.7 (3)	−0.2 (2)	1.5 (2)	−1.2 (2)	6.09
C_{35}	5.7 (3)	6.3 (3)	5.9 (3)	−0.0 (2)	0.3 (2)	−2.0 (2)	6.00

^{a} The number in parentheses that follows each B_{ij} value is the estimated standard deviation in the last significant figure. The B_{ij} in Å^2 are related to the dimensionless β_{ij} employed during refinement as $B_{ij} = 4\beta_{ij}/a_i^*a_j^*$. ^{b} Isotropic thermal parameter calculated from $B = 4[V^2 \det(\beta_{ij})]^{1/2}$.

sensibly final description of the structure. These coefficients are $a_0 = 0.298$, $a_1 = 0.323 \times 10^{-1}$, $a_2 = -0.758 \times 10^{-3}$, and $a_3 = 0.738 \times 10^{-5}$. A final difference Fourier synthesis had no peaks greater than 0.44 e Å^{-3}.

The final values of $10F_o$ and $10F_c$ are available[13] for the 4395 reflections used in the refinement. The atomic coordinates within the asymmetric unit are given in Table I and the associated thermal parameters in Table II.

Results and Discussion

The crystal structure consists of well-separated discrete seven-coordinate $(CH_3)_2Sn(NCS)_2(C_{15}N_3H_{11})$ molecules. The coordination polyhedron around the tin(IV) atom is close to an idealized pentagonal bipyramid (D_{5h}) with five nitrogen donors in the equatorial plane and two carbon atoms in the axial positions as shown in Figure 1. This structure is entirely consistent with the Mossbauer data. The bond distances and angles of the coordination polyhedron are given in Table III and Table IV gives the detailed parameters of the isothiocyanate and terpyridyl ligands.

The five Sn–N distances in the equatorial plane are substantially longer than the corresponding Sn–N distances in complexes of lower coordination number. The Sn–N_{NCS} distances of 2.285 (4)[14] and 2.280 (4) Å are significantly longer than the 2.10-Å distance found in $(CH_3)_2Sn(NCS)_2$[15] and the 2.15-Å distance found in five-coordinate $(CH_3)_3SnNCS$.[16] The average Sn–N_t (N_t = terpyridyl nitrogen) distance of 2.52 Å is longer than the 2.36 Å average length in the six-coordinate complex $[(CH_3)_2SnCl(terpy)]^+$.[8] The Sn–N_t distances are comparable to the average M–N_t distances of 2.60 Å in nine-coordinate $[Eu(terpy)_3]^{3+}$[17] and 2.63 Å in $[PrCl(terpy)(H_2O)_5]^{2+}$.[18] The long Sn–N dis-

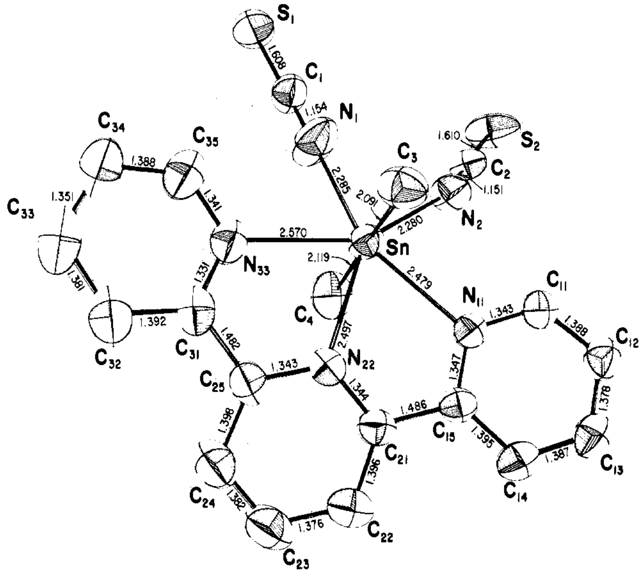

Figure 1. Model in perspective of $(CH_3)_2Sn(NCS)_2(C_{15}H_{11}N_3)$ carrying the pertinent bond distances in Å. Each atom is represented by an ellipsoid to include 50% of the probability distribution and having the shape, orientation, and relative size concomitant with the data of Table II.

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(13) A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-272.

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Table III. Parameters of the Coordination Polyhedron

A. Bond and Edge Lengths[a]

Type	Length, Å	Type	Length, Å
Sn-N_1	2.285 (4)	N_{33}-N_1	3.015 (6)
Sn-N_2	2.280 (4)	C_3-N_1	3.194 (7)
Sn-N_{11}	2.479 (3)	C_3-N_2	3.208 (6)
Sn-N_{22}	2.497 (3)	C_3-N_{11}	3.143 (6)
Sn-N_{33}	2.570 (4)	C_3-N_{22}	3.326 (6)
Sn-C_3	2.091 (5)	C_3-N_{33}	3.123 (6)
Sn-C_4	2.119 (5)	C_4-N_1	3.140 (8)
N_1-N_2	2.837 (6)	C_4-N_2	3.142 (7)
N_2-N_{11}	3.009 (5)	C_4-N_{11}	3.299 (6)
N_{11}-N_{22}	2.685 (4)	C_4-N_{22}	3.018 (7)
N_{22}-N_{33}	2.703 (5)	C_4-N_{33}	3.423 (7)

B. Bond Angles[a] Subtended at the Sn(IV) Atom

Type	Angle, deg	Type	Angle, deg
C_3-Sn-C_4	173.7 (2)	N_2-Sn-C_4	91.1 (2)
N_1-Sn-N_2	76.8 (2)	N_{11}-Sn-N_{22}	65.3 (1)
N_1-Sn-N_{11}	155.1 (1)	N_{11}-Sn-N_{33}	128.1 (1)
N_1-Sn-N_{22}	139.4 (1)	N_{11}-Sn-C_3	86.5 (2)
N_1-Sn-N_{33}	76.5 (2)	N_{11}-Sn-C_4	91.4 (2)
N_1-Sn-C_3	93.6 (2)	N_{22}-Sn-N_{33}	64.5 (1)
N_1-Sn-C_4	90.9 (2)	N_{22}-Sn-C_3	92.5 (2)
N_2-Sn-N_{11}	78.3 (1)	N_{22}-Sn-C_4	81.2 (2)
N_2-Sn-N_{22}	142.5 (1)	N_{33}-Sn-C_3	83.5 (2)
N_2-Sn-N_{33}	153.0 (1)	N_{33}-Sn-C_4	93.2 (2)
N_2-Sn-C_3	94.3 (2)		

[a] The estimated standard deviations are given in parentheses.

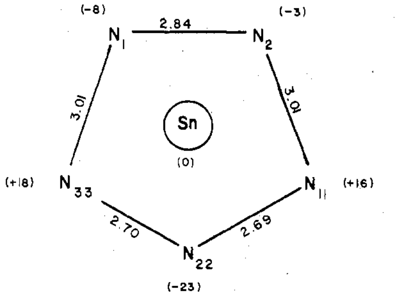

Figure 2. A diagram showing the perpendicular displacement of the atoms of the pentagonal plane (given in units of 0.01 Å) with respect to the calculated mean plane. The edge distances of the pentagon are given in Å.

tances in $(CH_3)_2Sn(NCS)_2$(terpy) are thus seen to be a direct consequence of the increased coordination number. The rather small values of the N_tSnN_t angles with values of 65.3 (1) and 64.5 (1)° directly result from the increased Sn-N_t distances.

The equatorial plane of the pentagonal bipyramid, consisting of the two isothiocyanate nitrogens, the three terpyridyl nitrogens, and the central tin atom is distorted from planarity as seen in Figure 2. The individual pyridine rings of the terpyridyl molecule are planar within the experimental error, but the entire molecule is distorted from planarity so that the two terminal nitrogen atoms are above the mean equatorial plane and the central nitrogen atom is below the mean equatorial plane. Both terminal rings are bent upward with respect to the central ring and rotated about the bonds connecting the terminal rings to the central ring. Figure 3 shows the displacement of the terminal rings with respect to the mean plane of the central ring. The angle between the normals to rings 1 and 2 is 14.8° and that between rings 2 and 3 is 22.3°. This distortion from planarity is common to the geometry of complexed terpyridyl ligands,[8,17-19] although the angles between the normals are generally smaller. The average value of the internal angles subtended at the carbon atoms (C_{15}, C_{21}, C_{25}, C_{31}) of the chelate rings is 116.3°, considerably smaller than the ideal value of 120°. The bending and rotation of the rings and the decrease in the angle at the carbon atoms of the chelate rings presumably represent the best compromise between bringing the terminal nitrogen atoms as close as possible to the tin atom and minimizing the van der Waals repulsion between the hydrogen atoms on C_{11} and C_{35} and the isothiocyanate nitrogen atoms. The nonbonded distances between these hydrogen atoms and the isothiocyanate nitrogens is ~2.4 Å.

Table IV. Bond Parameters of the Thiocyanate and Terpyridyl Molecule

A. Bond Lengths[a]

Type	Length, Å	Type	Length, Å
N_1-C_1	1.154 (6)	N_{22}-C_{25}	1.343 (5)
N_2-C_2	1.151 (5)	C_{21}-C_{22}	1.396 (5)
C_1-S_1	1.608 (4)	C_{22}-C_{23}	1.376 (7)
C_2-S_2	1.610 (4)	C_{23}-C_{24}	1.382 (7)
N_{11}-C_{11}	1.343 (5)	C_{24}-C_{25}	1.398 (6)
N_{11}-C_{15}	1.347 (5)	C_{25}-C_{31}	1.482 (6)
C_{11}-C_{12}	1.388 (6)	N_{33}-C_{31}	1.331 (6)
C_{12}-C_{13}	1.378 (6)	N_{33}-C_{35}	1.341 (6)
C_{13}-C_{14}	1.387 (6)	C_{31}-C_{32}	1.392 (6)
C_{14}-C_{15}	1.395 (5)	C_{32}-C_{33}	1.381 (8)
C_{15}-C_{21}	1.486 (5)	C_{33}-C_{34}	1.351 (8)
N_{22}-C_{21}	1.344 (5)	C_{34}-C_{35}	1.388 (7)

B. Bond Angles[a]

Type	Angle, deg	Type	Angle, deg
N_1-C_1-S_1	178.3 (4)	N_{22}-C_{21}-C_{22}	121.6 (4)
N_2-C_2-S_2	176.9 (4)	N_{22}-C_{25}-C_{31}	116.0 (4)
C_1-N_1-Sn	177.3 (5)	C_{21}-C_{22}-C_{23}	119.1 (4)
C_2-N_2-Sn	155.1 (4)	C_{22}-C_{23}-C_{24}	119.6 (4)
C_{11}-N_{11}-C_{15}	118.3 (3)	C_{23}-C_{24}-C_{25}	118.4 (4)
C_{11}-N_{11}-Sn	121.7 (3)	C_{24}-C_{25}-N_{22}	122.1 (4)
N_{11}-C_{11}-C_{12}	123.1 (4)	C_{24}-C_{25}-C_{31}	121.9 (4)
N_{11}-C_{15}-C_{21}	116.3 (3)	C_{25}-N_{22}-Sn	119.8 (3)
C_{11}-C_{12}-C_{13}	118.5 (4)	C_{25}-C_{31}-N_{33}	116.8 (4)
C_{12}-C_{13}-C_{14}	119.0 (4)	C_{25}-C_{31}-C_{32}	121.7 (4)
C_{13}-C_{14}-C_{15}	119.5 (4)	C_{31}-N_{33}-C_{35}	118.0 (4)
C_{14}-C_{15}-N_{11}	121.5 (4)	C_{31}-N_{33}-Sn	118.7 (3)
C_{14}-C_{15}-C_{21}	122.2 (4)	N_{33}-C_{31}-C_{32}	121.5 (5)
C_{15}-N_{11}-Sn	120.0 (2)	C_{31}-C_{32}-C_{33}	119.4 (5)
C_{15}-C_{21}-N_{22}	116.0 (3)	C_{32}-C_{33}-C_{34}	119.5 (5)
C_{15}-C_{21}-C_{22}	122.4 (4)	C_{33}-C_{34}-C_{35}	118.2 (5)
C_{21}-N_{22}-C_{25}	119.1 (3)	C_{34}-C_{35}-N_{33}	123.4 (5)
C_{21}-N_{22}-Sn	118.2 (2)	C_{35}-N_{33}-Sn	122.5 (3)

[a] The estimated standard deviations are given in parentheses.

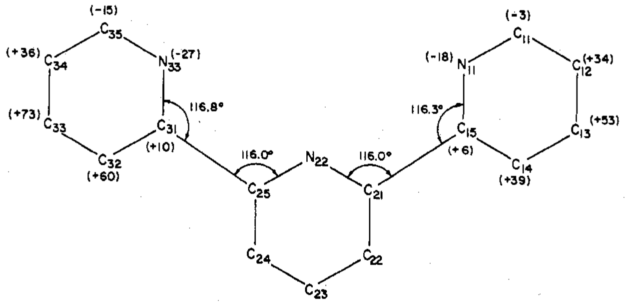

Figure 3. The displacement of the atoms in the terminal rings relative to the mean plane of the central ring of the terpyridyl molecule. Displacements are given in units of 0.01 Å.

One isothiocyanate group is bonded to the tin in a linear manner with a SnN_1C_1 angle of 177.3 (5)°; the other isothiocyanate ligand is bonded in a bent configuration with a SnN_2C_2 angle of 155.1 (4)°. The C-N and C-S bond lengths in both groups are equal within the experimental error and

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(19) D. E. C. Corbridge and E. G. Cox, *J. Chem. Soc.*, 594 (1956); F. W. B. Einstein and B. R. Penfold, *Acta Crystallogr.*, 20, 924 (1966).

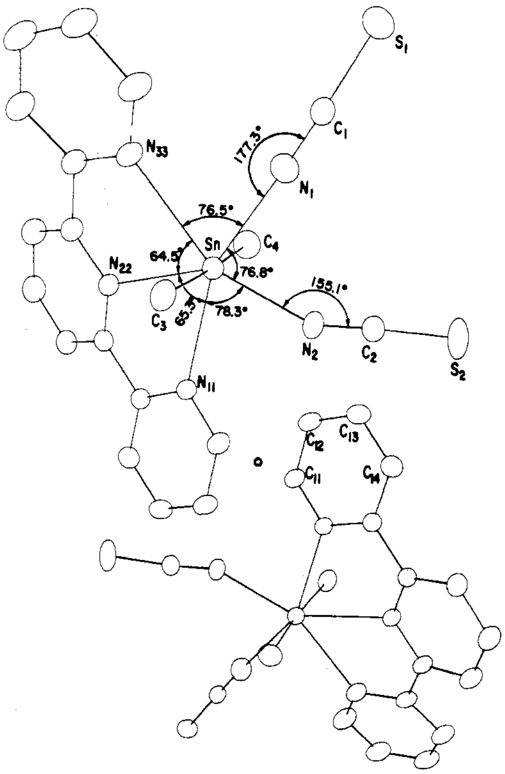

Figure 4. A perspective view of structure illustrating the molecular packing. The two molecules are related by a center of symmetry (o).

normal[15,20] with C-N = 1.152 (6) Å and C-S = 1.609 (4) Å. The two Sn-N_{NCS} distances are also equal; these data suggest that the bending of the SnN_2C_2 group is not a consequence of its bonding. An examination of the nonbonded distances between molecules reveals several close contacts between the bent isothiocyanate group and terpyridyl ring 1 of a neighboring molecule. Figure 4 shows this packing pattern which causes the bending of the isothiocyanate group. The close intermolecular distances in Figure 4 are $N_2 \cdots C_{11}$ = 3.43 Å, $N_2 \cdots C_{12}$ = 3.61 Å, $N_2 \cdots C_{13}$ = 3.56 Å, $C_2 \cdots C_{11}$ = 3.43 Å, $C_2 \cdots C_{12}$ = 3.54 Å, and $C_2 \cdots C_{13}$ = 3.40 Å. The only other close intermolecular contact is a 3.44-Å distance between two sulfur atoms related by a center of symmetry.

The Sn-C bond distances do not appear to have been lengthened as a consequence of the increased number of coordinated ligands about the tin, unlike the Sn-N bond lengths. The Sn-C lengths in the present study are 2.091 (5) and 2.119 (5) Å and are well within the range[21-23] of the Sn-C distances found in all the organotin complexes studied thus far. A comparison of the Sn-C lengths of this study with the Sn-C distances found in six-coordinate complexes suggests that if there is any variation in bond lengths with coordination number, it is in the direction of *shorter* bonds with increasing coordination number. Although the rather large estimated standard deviations in some of the reported studies make it difficult to assess trends, Sn-C bond distances appear to be relatively insensitive to changes in coordination number or the nature of the other ligands.

The C-Sn-C group is almost linear; the CSnC angle is 173.7 (2)°. Both methyl groups are slightly bent toward the central ring of the terpyridyl ligand to give nearly equivalent $C \cdots N$ edge distances (see Table IIIA). Presumably, this bending of the methyl groups averages the intramolecular repulsions among all donor atoms; if all the equatorial bonds were equivalent, a CSnC angle of 180° could be expected as is the case for polymeric six-coordinate $(CH_3)_2SnF_2$.[24]

Seven-coordinate complexes can have one of three idealized structures: the capped trigonal prism (C_{2v}), the capped octahedron (C_{3v}), or the pentagonal bipyramid (D_{5h}). In the present case, the apparent necessity of maintaining two short Sn-C bonds stabilizes the pentagonal bipyramid over the other possible structures.

Registry No. $(CH_3)_2Sn(NCS)_2(C_{15}H_{11}N_3)$, 37036-99-0.

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[20] A. Ferrari and A. Braibanti, *Acta Crystallogr.*, 18, 367 (1965); A. C. Hazell, *J. Chem. Soc.*, 5745 (1963); J. R. Knox and K. Eriks, *Inorg. Chem.*, 7, 84 (1968).

[21] The range of Sn-C lengths is 2.06-2.22 Å; *cf.* ref 5, 22, and 23.

[22] E. O. Schlemper, *Inorg. Chem.*, 6, 2012 (1967); see Table IV.

[23] A. G. Davies, H. J. Milledge, D. C. Puxley, and P. J. Smith, *J. Chem. Soc. A*, 2862 (1970); see Table 4.

[24] E. O. Schlemper and W. C. Hamilton, *Inorg. Chem.*, 5, 995 (1967).