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# (2,2′-Bipyridyl)diisothiocyanatodiphenyltin(IV)*

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**Abstract.** $C_{24}H_{18}N_4S_2Sn$, monoclinic, $P2_1/n$, $a$ = 10·722 (3), $b$ = 15·752 (4), $c$ = 14·131 (2) Å, $\beta$ = 92·32 (2)°, $Z$ = 4, $D_c$ = 1·52 Mg m$^{-3}$. The final residual is $R_F$ = 0·043 for 2438 observed reflections at 299 K. The Sn atom is coordinated to the two N atoms of the bipyridyl molecule, the two phenyl groups and to the N atoms of each of the two NCS groups in a distorted octahedral configuration.

**Introduction.** The 1:1 complexes formed between diorganotin dihalides (or diisothiocyanates) and bidentate ligands of the $\alpha$-diimine type are almost invariably octahedral, with *trans* hydrocarbon groups and *cis* halo (or isothiocyanato) groups (Smith, Grant & Gray, 1979, and references therein). This has been confirmed in one instance by a structure analysis performed on the compound (2,2′-bipyridyl)dichlorodiphenyltin(IV) (Harrison, King & Richards, 1974). The only exceptions so far reported are the complexes formed by diphenyltin diisothiocyanate with 1,10-phenanthroline or 2,2′-bipyridyl (Mullins & Curran, 1967, 1968) and 5,6-diphenyl-3-(2-pyridyl)-1,2,4-triazine (Smith *et al.*, 1979). These have all been assigned approximately octahedral structures with *cis* phenyl groups and *trans* isothiocyanato groups. The assignments of these exceptional structures have been made on the basis of dipole moment and Mössbauer measurements. The purpose of the present investigation was to confirm unequivocally one of the latter structures, having *cis* phenyl groups. Since it readily formed suitable crystals, the compound (2,2′-bipyridyl)diisothiocyanatodiphenyltin(IV) was chosen to be the subject of the study.

Diphenyltin dichloride was obtained from Alpha Inorganics, Inc., and 2,2′-bipyridyl was obtained from the Aldrich Chemical Company, Inc. An ethanolic solution of diphenyltin diisothiocyanate was obtained from the chloride by a metathetical reaction with potassium thiocyanate in ethanol. The precipitated potassium chloride was filtered off, and the stoichiometric quantity of 2,2′-bipyridyl in ethanol solution was added. The white crystals which formed readily were filtered off, and later recrystallized from ethanol (m.p. 470 K) (Mullins & Curran, 1968). A microanalysis was performed by the Australian Microanalytical Service, CSIRO, Melbourne, Australia. Found (%): C 52·65, H 3·26, N 10·21, Sn 22·00; calculated for $C_{24}H_{18}N_4S_2Sn$: C 52·87, H 3·33, N 10·28, Sn 21·77.

The diffraction intensities of a 0·3 × 0·3 × 0·3 mm crystal were measured at room temperature with graphite-monochromatized Mo $K\alpha$ radiation generated at 50 kV, 16 mA, using the $\theta/2\theta$ scan technique with line-profile analysis (Grant & Gabe, 1978). A total of 3270 measurements were made up to 45° in $2\theta$ giving 3123 valid unique reflections of which 2438 had a net intensity larger than $3\sigma(I)$ based on counting statistics, while 139 of the 147 measurements of systematic absences had intensities less than $3\sigma(I)$. The intensities were corrected for measured direct-beam polarization (Le Page, Gabe & Calvert, 1979). Absorption corrections were not applied ($\mu$ = 1·26 mm$^{-1}$). The cell parameters were obtained by least-squares refinement of the setting angles of 39 reflections with $2\theta$ larger than 35° [$\lambda$(Mo $K\alpha_1$) = 0·70932 Å].

The Sn atom was found from an $E$ map based on phases derived by *MULTAN* (Germain, Main & Woolfson, 1971) for the 228 largest $E$ values. A heavy-atom-phased Fourier map revealed all the other non-H atoms and isotropic refinement followed by anisotropic refinement lowered the residual to $R_F$ = 0·11. The H atoms were then located on 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 using counting-statistics' weights. An extinction correction was included (Larson, 1970). The scattering curves for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974). The atoms H(4), H(20), H(21) and H(23) refined to unreasonable positions and were returned to their calculated positions. The final residuals are $R_F$ =

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0·043 and $R_{wF}$ = 0·036. The atomic positional parameters and equivalent isotropic temperature parameters are listed in Table 1.*

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

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$^2$) |
|---|---|---|---|---|
| Sn | 0·03331 (5) | 0·35621 (3) | 0·25713 (4) | 4·838 (23) |
| S(1) | 0·41502 (22) | 0·34724 (18) | 0·08710 (18) | 9·28 (17) |
| S(2) | −0·3239 (3) | 0·34537 (22) | 0·4428 (3) | 16·1 (3) |
| N(1) | 0·1873 (5) | 0·3637 (4) | 0·1596 (4) | 5·9 (3) |
| N(2) | −0·1420 (5) | 0·3789 (4) | 0·3198 (4) | 6·5 (4) |
| N(3) | 0·0201 (5) | 0·5012 (3) | 0·2227 (4) | 6·4 (4) |
| N(4) | −0·0965 (5) | 0·3787 (3) | 0·1234 (4) | 5·4 (3) |
| C(1) | 0·2802 (6) | 0·3561 (4) | 0·1301 (4) | 5·3 (4) |
| C(2) | −0·2157 (6) | 0·3643 (5) | 0·3671 (5) | 6·2 (4) |
| C(3) | 0·0863 (8) | 0·5583 (5) | 0·2751 (7) | 9·6 (6) |
| C(4) | 0·0696 (9) | 0·6445 (5) | 0·2575 (8) | 12·5 (7) |
| C(5) | −0·0088 (8) | 0·6686 (5) | 0·1855 (8) | 11·4 (7) |
| C(6) | −0·0717 (8) | 0·6124 (5) | 0·1310 (6) | 9·0 (6) |
| C(7) | −0·0552 (6) | 0·5264 (4) | 0·1508 (5) | 6·2 (5) |
| C(8) | −0·1201 (6) | 0·4591 (4) | 0·0960 (5) | 5·4 (4) |
| C(9) | −0·2033 (7) | 0·4746 (5) | 0·0214 (5) | 7·5 (5) |
| C(10) | −0·2630 (8) | 0·4087 (6) | −0·0226 (6) | 8·8 (6) |
| C(11) | −0·2371 (8) | 0·3265 (5) | 0·0062 (6) | 8·7 (6) |
| C(12) | −0·1527 (7) | 0·3134 (5) | 0·0808 (5) | 7·1 (5) |
| C(13) | 0·0150 (6) | 0·2198 (4) | 0·2497 (5) | 4·9 (4) |
| C(14) | 0·0816 (7) | 0·1742 (4) | 0·1873 (6) | 6·7 (5) |
| C(15) | 0·0784 (7) | 0·0847 (5) | 0·1890 (6) | 7·9 (5) |
| C(16) | 0·0109 (7) | 0·0443 (4) | 0·2512 (6) | 7·2 (5) |
| C(17) | −0·0522 (8) | 0·0889 (5) | 0·3128 (6) | 8·0 (5) |
| C(18) | −0·0512 (7) | 0·1763 (5) | 0·3125 (5) | 7·2 (5) |
| C(19) | 0·1457 (7) | 0·3832 (4) | 0·3858 (5) | 5·9 (4) |
| C(20) | 0·2726 (7) | 0·3817 (5) | 0·3841 (6) | 7·4 (5) |
| C(21) | 0·3417 (7) | 0·3978 (5) | 0·4710 (6) | 9·2 (6) |
| C(22) | 0·2827 (9) | 0·4109 (5) | 0·5484 (7) | 10·5 (7) |
| C(23) | 0·1586 (9) | 0·4092 (7) | 0·5514 (7) | 13·9 (8) |
| C(24) | 0·0874 (8) | 0·3946 (7) | 0·4677 (6) | 11·7 (7) |
| H(3) | 0·152 (5) | 0·537 (4) | 0·330 (4) | 9·7 (20) |
| H(4) | 0·103 (7) | 0·689 (5) | 0·301 (5) | 15·5 (27) |
| H(5) | −0·030 (6) | 0·719 (5) | 0·185 (5) | 12·9 (25) |
| H(6) | −0·108 (5) | 0·624 (4) | 0·081 (4) | 8·8 (19) |
| H(9) | −0·224 (5) | 0·532 (4) | 0·003 (4) | 8·7 (19) |
| H(10) | −0·329 (6) | 0·419 (4) | −0·079 (4) | 11·2 (21) |
| H(11) | −0·294 (6) | 0·272 (4) | −0·016 (5) | 10·8 (22) |
| H(12) | −0·140 (5) | 0·258 (4) | 0·105 (4) | 9·0 (19) |
| H(14) | 0·132 (5) | 0·204 (4) | 0·136 (4) | 10·0 (20) |
| H(15) | 0·131 (5) | 0·049 (4) | 0·139 (4) | 10·7 (18) |
| H(16) | 0·007 (6) | −0·024 (5) | 0·252 (5) | 7·9 (24) |
| H(17) | −0·104 (5) | 0·065 (4) | 0·364 (4) | 9·0 (19) |
| H(18) | −0·097 (6) | 0·213 (4) | 0·358 (5) | 12·0 (22) |
| H(20) | 0·323 (5) | 0·368 (4) | 0·315 (4) | 9·0 (18) |
| H(21) | 0·434 (5) | 0·401 (4) | 0·464 (4) | 10·1 (20) |
| H(22) | 0·334 (6) | 0·429 (5) | 0·611 (5) | 13·4 (25) |
| H(23) | 0·106 (7) | 0·415 (5) | 0·624 (5) | 17·9 (29) |
| H(24) | −0·008 (6) | 0·388 (4) | 0·467 (5) | 13·3 (23) |

**Discussion.** A stereoscopic view of the molecule is shown in Fig. 1. The atom names, distances and angles are indicated in Fig. 2.

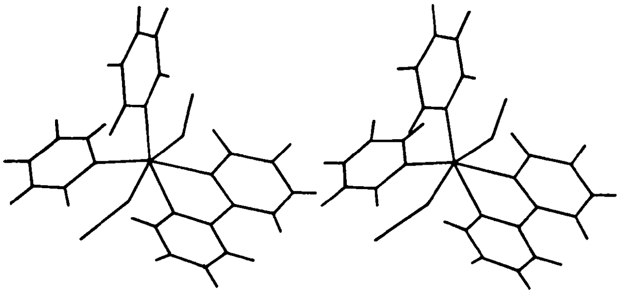

Fig. 1. Stereoscopic pair of the molecule seen approximately along the [100] direction.

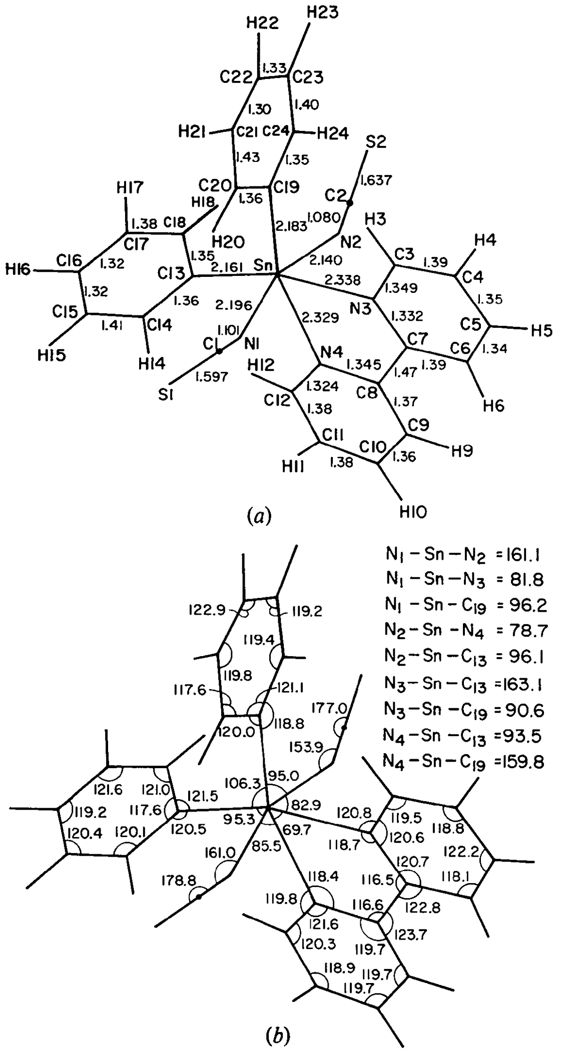

Fig. 2. (*a*) Atom names and bond distances (Å) (uncorrected for thermal motion). The e.s.d.'s on bond distances involving Sn are ~0·005 Å, involving H are ~0·07 Å and for the other atoms range from 0·005–0·01 Å. (*b*) Angles (°) in the molecule. The e.s.d.'s on angles involving Sn are ~0·2° and for the others ~0·8°.

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* Lists of anisotropic thermal parameters and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36265 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The coordination around Sn is a distorted octahedron. The Sn atom is coordinated to the two N atoms of the bipyridyl molecule, to the two phenyl groups and to the N atoms of each of the two NCS groups. In contrast to the structure of (2,2′-bipyridyl)dichlorodiphenyltin(IV) (Harrison *et al.*, 1974), the two phenyl groups are in the *cis* configuration rather than the *trans* arrangement found for the dichloro complex. The average Sn—C distance of 2·172 (6) Å is not significantly longer than the average Sn—C distance of 2·152 (8) Å found in the chloro complex, but is probably significantly longer than the average Sn—C distances of 2·09 (3) Å in triphenyltin isothiocyanate (Domingos & Sheldrick, 1974), 2·133 (6) Å in (iodomethyl)triphenyltin(IV) (Harrison & Molloy, 1978) and 2·125 (4) Å in triphenyltin(IV) isocyanate (Tarkhova, Chuprunov, Simonov & Belov, 1977), possibly due to the increased coordination number. The C—C distances in the phenyl rings are all normal.

The bipyridyl group is essentially planar, the dihedral angle between the two rings being only 1·7 (7)°. The associated average Sn—N distance of 2·333 (5) Å appears to be shorter than the average Sn—N distance of 2·359 (6) Å in (2,2′-bipyridyl)dichlorodiphenyltin(IV). The difference may not be significant, however, as the C—C bond lengths and the N—C bond lengths in the bipyridyl group are the same in both complexes. The planes of the two phenyl rings are almost perpendicular to each other and to the plane of the bipyridyl group.

Each NCS group is almost linear; N(1)—C(1)—S(1) = 178·8 (7); N(2)—C(2)—S(2) = 177·0 (7)°. The Sn—N distances of 2·196 (5) and 2·140 (6) Å are longer than the average Sn—N distance of 2·10 (2) Å in diisothiocyanatodimethyltin(IV) (Chow, 1970) which is a tetrahedral complex, but shorter than the 2·282 (4) Å length found in diisothiocyanatodimethylterpyridyltin(IV) (Naik & Scheidt, 1973) which is a seven-coordinated complex, confirming the increase in bond length with increasing coordination number. The C—S bond lengths of 1·597 (7) and 1·637 (7) Å are similar to the C—S distances found in other metal isothiocyanato complexes (Domingos & Sheldrick, 1974; Naik & Scheidt, 1973; Chow, 1970; Forder & Sheldrick, 1970). The two N—C distances of 1·101(8) and 1·080 (9) Å are marginally shorter than the N—C distance of 1·15 (5) Å found in diisothiocyanatodimethyltin(IV) (Chow, 1970). This may be a consequence of the stronger Sn—NCS bonding present in the tetrahedral complex, but in view of the larger e.s.d.'s in the latter structure no firm conclusion may be drawn. The bonding mechanism of NCS groups in metal isothiocyanate complexes is not well understood and observed N—C distances range from 1·07 to 1·31 Å (Hazell, 1963; Knox & Eriks, 1968). The bent configuration of the NCS groups with respect to the Sn atom [Sn—N(1)—C(1) = 161·0 (5); Sn—N(2)—C(2) = 153·9 (6)°] is probably a steric effect. This may, in turn, be related to the observed differences in the two Sn—NCS distances.

The structure confirms the earlier assignment made on the basis of Mössbauer and dipole-moment data, that the phenyl groups are *cis* and the isothiocyanato groups are *trans* to each other (Mullins & Curran, 1968).

There are no short contacts with neighboring molecules and the structure is held together by van der Waals forces. This is probably the reason for the rather large thermal motion exhibited by the S atoms and some of the C atoms.

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