were carried out in the same manner described above for the reactions in $CDCl_3$ and CD_3OD. In some experiments (but not always) with **2**, a small triplet (with the coupling constant being less than 2 Hz) was observed at δ 9.50 *ca.* 2 hours after the reaction started and disappeared soon. Appearence and disappearence of this triplet could be observed several times in an experiment. The position, multiplicity and small coupling constant of the triplet unambiguously identify the triplet as the signal due to $-CH_2-CHO$.

Reaction with cis-DOCH$_2$CH=CHCH$_2$OD (1D) in CDCl$_3$ and CD$_3$COCD$_3$. This reaction was carried out with **2** in the same manner described above for reactions in $CDCl_3$ and CD_3COCD_3. Proton NMR of the final product showed signals only at δ1.89 (m), 3.80 (m) and 4.92 (m) with integration ratio being 3:2:1 which are in good agreement ith **4D**.

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Structure of Bis(triphenyltin(IV))piperazinebis(dithiocarbamate)

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Structural chemistry of organotin (IV) dithiocarbamate (dtc) complexes has been an interesting subject of study for a long time.[1-6] However, no accordant evidences are established for the bonding mode of the dtc ligand moiety for triphenyltin(IV) complexes although several physicochemical techniques have been attempted for its characterization.[7-11] Even though the X-ray data determined for a crystalline solid complex gave us decisive evidence on the position of the ligand atoms,[12,13] they could not be used with certainty for discerning the bonding fashion of the dtc ligand because of its ambiguous bond distance. For further understanding of this system, we report the crystal structure together with the ^{119}Sn NMR of the interesting complex, bis(triphenyltin(IV))piperazinebis(dithiocarbamate), $(Ph_3SnS_2CNC_2H_4)_2 \cdot 2CH_2Cl_2$.

The title complex was prepared by the literature procedure.[9] Recrystallization of the crude product in a dichloromethane-petroleum ether solvent pair (1:1) at 0 °C gave a colorless dichloromethane-solvated crystalline complex suitable for X-ray study. The dichloromethane-solvated crystals were unstable when removed from the mother liquor and, therefore, the crystal used for X-ray study was wedged, wet with mother liquor, into a glass capillary which was then sealed. All the crystallographic data[14] were obtained on an Enraf-Nonius CAD4 diffractometer with graphite monochromated molybdenum radiation ($\lambda(K_{\alpha 1}) = 0.70930$ Å, $\lambda(K_{\alpha 2}) = 0.71359$ Å) at an ambient temperature of 23(2) °C. The tin atom was located using MULTAN-80,[15] a system of computer program for direct method solution, and the remaining atoms were located in a series of difference Fourier maps and least-squares refinements[16] using SHELX-76.[17] All the hydrogen atoms, carbon atoms of phenyl group, and carbon and chlorine atoms of solvated dichloromethane were refined isotropically. The remaining atoms were refined anisotropically. The carbon atoms of phenyl group were fixed into a regular hexagon. The ^{119}Sn NMR spectrum[18] relative to external Me_4Sn was recorded on a Bruker AM-200 operating at 74.03 MHz(^{119}Sn) in pulse mode with Fourier transform at ambient temperature.

The molecular geometry and labeling scheme along with selected bond distances and angles for the title molecule is shown in Figure 1. The dichloromethane molecules solvated do not interact with the parent molecule and are not shown in the structure. The complex molecule is centrosymmetric. An interesting feature of the structure is the bonding mode of the dtc ligand. The Sn-S(1) distance of 2.473(3) Å is a normal value of Sn-S bond found in typical anisobidentate bonding complexes such as $Me_2Sn(S_2CNMe_2)_2$ (2.497(8) Å)[19] and $(t\text{-}Bu)_2Sn(S_2CNMe_2)_2$ (2.489(1) Å).[20] However, the Sn-S(2) distance of 3.065(3) Å in the present compound is considerably

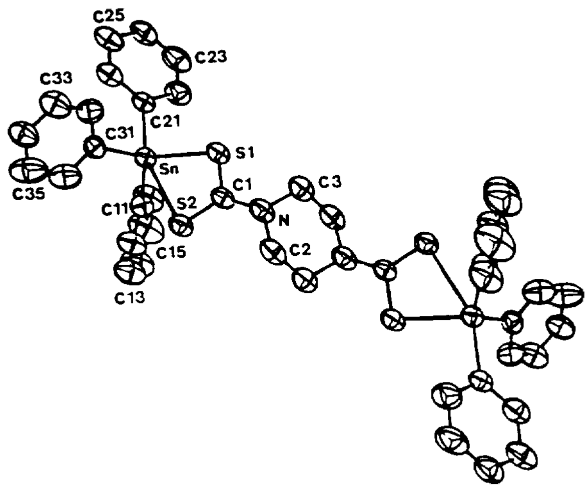

Figure 1. ORTEP drawing of bis(triphenyltin(IV))piperazinebis(dithiocarbamate). All hydrogens and solvated dichloromethane have been omitted for clarity. Relevant distances (Å) and angles (deg.): Sn-S(1), 2.473(3); Sn-S(2), 3.065(3); Sn-C(11), 2.131(6); Sn-C(21), 2.178(6); Sn-C(31), 2.134(6); C(1)-S(1), 1.749(9); C(1)-S(2), 1.673 (9), N-C(1), 1.336(11); N-C(2), 1.486(11); N-C(3), 1.474(12); S(1)-Sn-S(2), 63.6(1); S(1)-Sn-C(11), 114.0(2); S(2)-Sn-C(11), 85.7(3); S(1)-Sn-C(21), 93.2(2); S(2)-Sn-C(21), 156.8(2); C(11)-Sn-C(21), 108.6(2); S(1)-Sn-C(31), 114.8(2); S(2)-Sn-C(31), 81.7(2); C(11)-Sn-C(31), 116.0(2); C(21)-Sn-C(31), 107.2(2); S(1)-C(1)-S(2), 120.0 (5).

longer than the normal values (2.7-2.9 Å) of the corresponding Sn-S distance observed in the anisobidentate bonding mode,[4,6,20-22] although it is similar to the known Sn-S bond distance of 3.061(8) Å in $Me_2Sn(S_2CNMe_2)_2$.[19] Kumar Das *et al.*[23] regarded the distance of Sn-S (3.079(1) Å) in *n*-$BuPh_2Sn(S_2CNMe_2)$ as a weak coordinative interaction whereas Zuckerman *et al.*[12] did not count the distance of Sn-S (3.106(3) Å) in $Ph_3Sn(S_2CN(CH_2)_4)$ as a coordinative bond. Examination of the angular data around the Sn atom in the present one does neither yield decisive conclusion. Thus, the coordination number of tin atom in the present compound can hardly be determined solely by the crystal structural data. However, ^{119}Sn NMR[24] strongly suggests that the title molecule is pentacoordinate in solution, and as such the Sn-S(2) interaction should be regarded as a weak coordinative bond. A comparison of the $\delta(^{119}Sn)$ value (-167 ppm) of the present compound with that (-48 ppm) of its chlorine analogue Ph_3SnCl[24b] reveals an important information on the coordination number of its tin atom. In general, the chlorine atom bonded to tin is known to affect the $\delta(^{119}Sn)$ value to approximately the same degree as a monodentate dtc ligand. For example, the $\delta(^{119}Sn)$ value (-224 ppm) of the pentacoordinate $(t\text{-}Bu)_2SnCl(S_2CNMe_2)$[5] is approximately the same as that (-255 ppm) of $(t\text{-}Bu)_2Sn(S_2CNMe_2)_2$[5,20] in which one dtc acts as a monodentate thus affording the same pentacoordinate structure. On the other hand, the $\delta(^{119}Sn)$ value (-204 ppm) of the pentacoordinate $Me_2SnCl(S_2CNMe_2)$[5] moves remarkably upfield shift to -338 ppm in the hexacoordinate $Me_2Sn(S_2CNMe_2)_2$[5] in which both dtc ligands act as bidentate. Therefore, a drastic upfield shift of the present complex clearly indicates that the dtc ligand in the present compound acts as a bidentate even in solution similarly to our earlier result of coordinative Sn-S (3.093(1) Å) interaction in $CH_3OOCCH_2CH_2Sn(S_2CNMe_2)(SCH_2CH_2)_2O$.[25] The monodentate dtc ligands in $Sn(S_2CNMe_2)_4$[26] and $(t\text{-}Bu)_2Sn(S_2CNMe_2)_2$[20] have the second sulfur atom at 3.44-3.64 Å away from the tin atom. In conclusion, the title molecule seems to be predominantly pentacoordinate in crystalline state with S(1), C(11), and C(31) in equatorial and with C(21) and S(2) in axial positions (S(2)-Sn-C(21), 156.8(2)°), where the Sn atom is displaced by 0.505(1) Å toward C(21) from the S(1)-C(11)-C(13) plane. The axial Sn-C(21) and Sn-S(2) bond lengths are longer than the corresponding equational ones.

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