Structural flexibility in octahedral tin(IV) bischelates: electronic and hybridization effects

J. Chem. Research (S), 2001, 93–96
J. Chem. Research (M), 2001, 0354–0388

Parthasarathi Laavanya, Radhakrishnan Selvaraju, Swaminathan Thenmozhi and Krishnaswamy Panchanatheswaran*

Department of Chemistry, Bharathidasan University, Tiruchirappalli – 620 024, Tamil Nadu, India

PM3 calculations on the bis chelates containing acetylacetonato and dithiocarbamato groups with two monodentate ligands reveal the existence of *cis* and skew trapezoidal bipyramid(*STB*) octahedral geometry for these complexes. The calculations also show that the nitrato complexes assume bicapped tetrahedral geometry. Crystallographic investigation on the complex, $Br_2Sn[S_2CN(C_2H_5)_2]_2$ confirms the *cis* orientation of the bromine atoms, as predicted by the calculations.

Keywords: octahedral tin(iv) bischelates

Theoretical calculations had been used as a diagnostic tool successfully to probe into the molecular structures of organotin complexes.[10] The geometry of bisdithiocarbamates(dtc) containing two monodentate ligands had been probed by us theoretically using PM3 calculations.[11] Electron rich groups prefer *cis* orientation. In order to elucidate the influence of other effects *viz*., hybridization of tin and weak interactions between the ligands, PM3 calculations with two sets of complexes containing acetylacetonate(acac) and nitrate ligands have been made in this study. The results are compared with the analogous dithiocarbamates.

The PM3 optimized structures of some selected $XYSn[S_2CN(C_2H_5)_2]_2$, $XYSn(acac)_2$ and $XYSn(NO_3)_2$ [X, Y = monodentate ligands] complexes are given in Figs 1–3, respectively. In the dithiocarbamate complexes,[23,27,28] the variation of Sn–S bond lengths within the tin-diethyldithiocarbamate indicates anisobidentate bonding for the chelating group. In contrast, the variation of Sn–O bond lengths within one $Sn–NO_3$ entity, in the nitrato complexes is high and indicates strong and weak bonding of the oxygens of each of the nitrato groups. All the nitrato complexes can exist in two forms and exhibit weak Sn...O interactions with bite angles around 50° although nitrate ion can bind to the metals in bidentate fashion with bite angles around 70°.[31] The nitrato complexes are unstable compared to the acetylacetonato complexes but more stable than the dithiocarbamato complexes as expected from the strength of Sn–O bonds. It must be noted

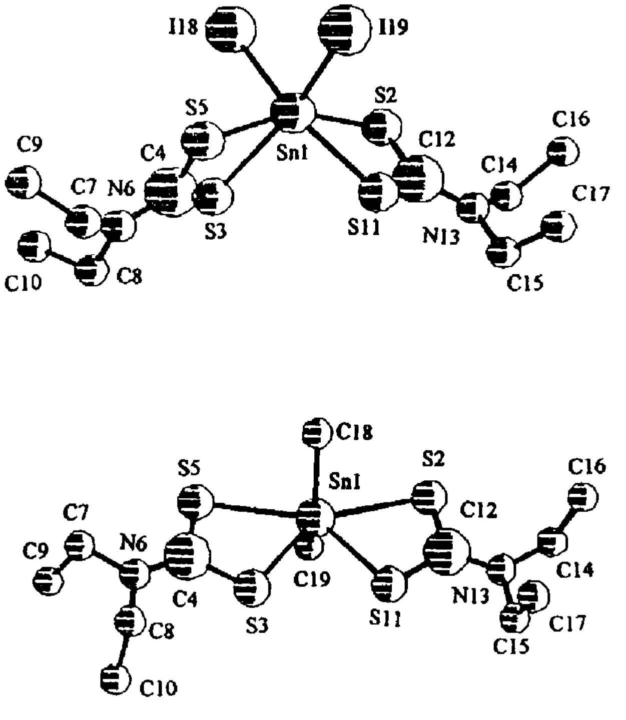

Fig. 1 PM3 optimized structure of $XYSn[S_2CN(C_2H_5)_2]_2$; (i) X = Y = I; (ii) X = Y = Me

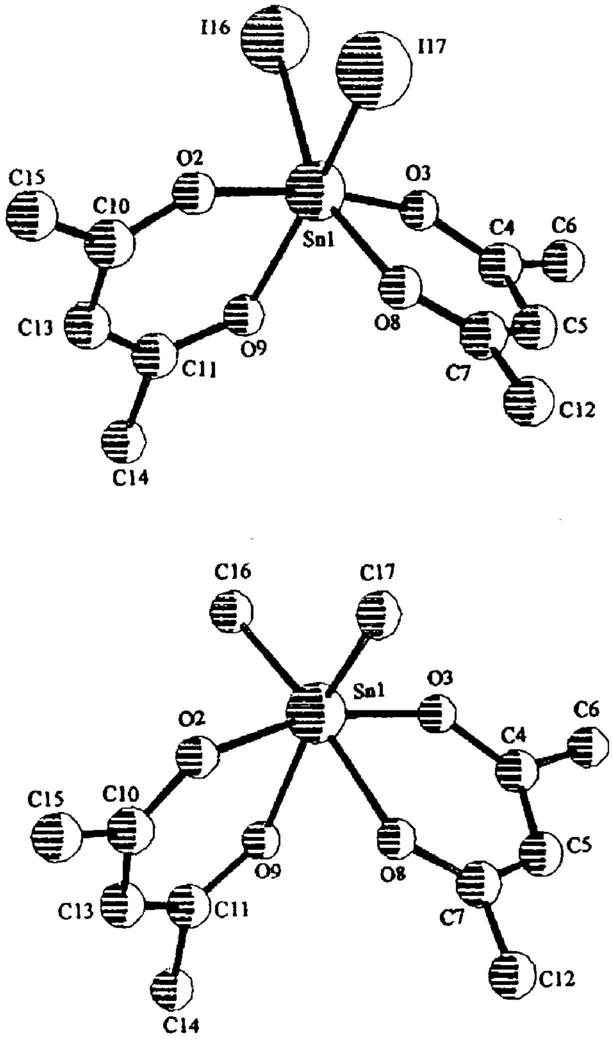

Fig. 2 PM3 optimized structure of $XYSn(acac)_2$

---

* To receive any correspondence. E-mail:pan@bdu.ernet.in

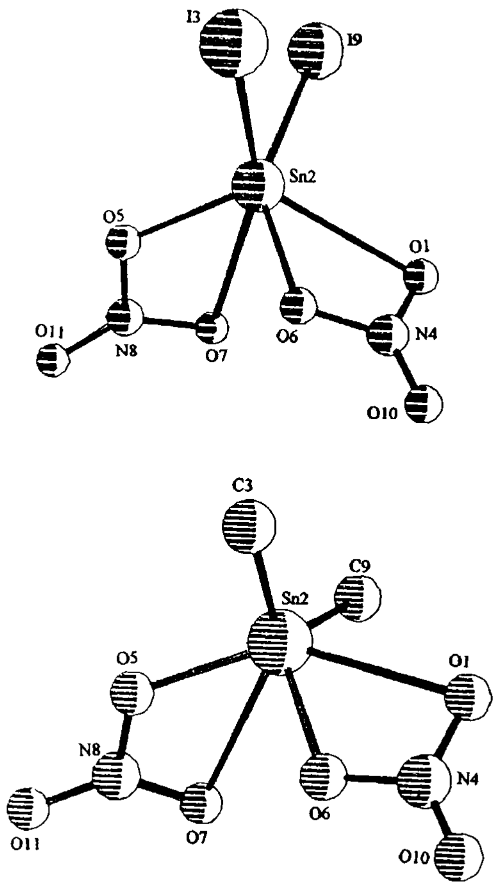

Fig. 3 PM3 optimized structure of $XYSn(NO_3)_2$

Table 1 Crystal data and structure refinement parameters for *cis*-$Br_2Sn[S_2CN(C_2H_5)_2]_2$

Empirical formula	$C_{10}H_{20}Br_2N_2S_4Sn$
Formula weight	575.03
Temperature	293(2) K
Wavelength	0.71069 Å
Crystal system	Triclinic
Space group	Pbar1
Unit cell dimensions	*a* = 7.179(6) Å α = 93.82(3)° *b* = 9.354(4) Å β = 99.00(4)° *c* = 15.563(4) Å γ = 109.11(5)°
Volume	967.6(9) Å^3
Z	2
R(int)	0.0358
Density (calculated)	1.974 Mg/m^3
Absorption coefficient	5.871 mm^{-1}
F(000)	556
Crystal size	0.06 x 0.11 x 0.11 mm
Theta range for data collection	2.32 to 24.98°
Index ranges	$-8 \le h \le 8, -11 \le k \le 11, 0 \le l \le 18$
Reflections collected	3391
Independent reflections	3391
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3391 / 0 / 178
Goodness-of-fit on F^2	1.195
Final R indices [I ≥ 2sigma(I)]	R_1 = 0.0538, wR_2 = 0.1060
R indices (all data)	R_1 = 0.0888, wR_2 = 0.1173
Largest diff. peak and hole	0.694 and -0.691 e Å^{-3}
No. of reflections [I≥ 2sigma(I)]	2615
T_{min} & T_{max}	0.8069 and 0.9989

Table 2 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	*x*	*y*	*z*	U(eq)
Sn	2531 (1)	2332 (1)	7523(1)	41(1)
Br1	2613 (2)	4996 (1)	7203(1)	62(1)
Br2	5753 (2)	2619 (1)	6954(1)	66(1)
S1	142 (4)	2230 (3)	8605(2)	53(1)
S2	−223 (3)	1236 (3)	6206(2)	45(1)
S3	1435 (4)	−614 (3)	7351(2)	57(1)
S4	4494 (4)	2784 (3)	9062(2)	54(1)
N1	−1847(11)	−1802 (8)	6078(5)	45(2)
N2	2110(12)	2470 (9)	10240(5)	52(2)
C1	2226(13)	2487(10)	9405(6)	43(2)
C2	−395(13)	−574(10)	6495(6)	42(2)
C3	−3463(14)	−1717(11)	5383(6)	55(3)
C4	3909(16)	2768(12)	10933(7)	63(3)
C5	−1994(16)	−3328(10)	6291(7)	55(3)
C6	−5241(15)	−1642(13)	5727(8)	67(3)
C7	228(16)	2195(14)	10562(7)	72(3)
C8	−1357(18)	−4184(13)	5612(8)	77(3)
C9	13(21)	3628(16)	10935(9)	99(5)
C10	4252(20)	1343(15)	11161(10)	101(5)

that the nitrato complexes are assumed to be monomeric but they can exist in the polymeric form enhancing their stability.

The C–Sn–C angles in $Me_2Sn(acac)_2$ is calculated to be 104.2° and 138.9°, for the two forms, respectively whose heats of formation differ by 5.1 kcal/mol. The same angle was found to be 180° by single crystal X-ray diffraction analysis.[37] Further the compound, $Me_2Sn(dtc)_2$ had been shown to crystallise in triclinic, monoclinic and orthorhombic polymorphic forms with C–Sn–C angles, 142.3(2)°; 142.8(3)°, 136.9(3)° [2 molecules]; 135.6(6)°, 136[2 molecules], respectively.[38] Calculations also indicate that the C–Sn–C angle is variable and can assume 105.5° and 131.9° in the above complex without affecting its stability as evident from their heats of formation values[14.8 and 14.0 kcal/mol].[11] We conclude that crystal packing effects as well as the intramolecular electronic effects contribute and decide the structural flexibility and preferential geometry adopted by the tin(IV) chelates.

In all the complexes, the tin atom is positively charged and all the ligating atoms are negatively charged ; strong bonds are formed by alkyl groups due to the involvement of sp^3 hybrid orbitals of carbon. The bond order decreases in the order, CH_3 > Cl > Br > I in all the series expected for the sizes of the ligating atoms. There is no evidence for π-donation of electrons by the ligating atoms or three centre bonds involving tin from the PM3 calculations. The latter model had been used to explain the geometry of five and six coordinate tin complexes.

In *STB*-$Me_2Sn[S_2CN(C_2H_5)_2]_2$, the electrons are filled in three degenerate sets of orbitals. The first set may be conceived as "sp" hybrid orbitals involving s and p_z orbital of tin(–14.9 eV) which are used to bond to two carbon atoms of the methyl group. The second set of degenerate orbitals (–12.9 eV) with 19.2% of tin character accomodates the electrons of the sulfur of the dithiocarbamato group. The third set of degenerate orbitals(–11.7 eV) with 9.2% of tin character contributes to the weaker interaction with sulfur. While the bond order of Sn–C(Me) bond is close to one, the bond order for other bonds are lower than one making a total bond order of four around tin. As expected for hypervalent molecules,[41] the average bond order around tin is much less than one, being equal to 0.58 for $Me_2Sn(dtc)_2$. The tin and the carbon orbital contributions are almost equal leading to a normal two electron bond between tin and carbon(CH_3) atoms. The deviation of C–Sn–C angle from 180° is attributed to intramolecular van der Waals interactions between the ligating atoms. In

Table 3 Bond lengths [Å] and angles [°] for *cis*-$Br_2Sn[S_2CN(C_2H_5)_2]_2$

Sn–S2	2.508(3)	N1–C2	1.316(11)
Sn–S4	2.513(3)	N1–C5	1.461(11)
Sn–Br2	2.545(2)	N1–C3	1.483(11)
Sn–Br1	2.557(2)	N2–C1	1.316(11)
Sn–S1	2.570(3)	N2–C7	1.464(12)
Sn–S3	2.588(3)	N2–C4	1.483(12)
S1–C1	1.728(9)	C3–C6	1.480(13)
S2–C2	1.751(9)	C4–C10	1.49 (2)
S3–C2	1.730(9)	C5–C8	1.498(13)
S4–C1	1.735(9)	C7–C9	1.49 (2)

S2–Sn–S4	161.28 (9)	C1–S4–Sn	86.6 (3)
C2–N1–C5	121.8 (8)	C2–N1–C5	121.8 (8)
C2–N1–C3	122.1 (7)	C2–N1–C3	122.1 (7)
S2–Sn–Br2	104.85 (8)	C5–N1–C3	116.0 (7)
S4–Sn–Br2	88.92 (8)	C1–N2–C7	123.3 (8)
S2–Sn–Br1	88.61 (8)	C1–N2–C4	121.9 (8)
S4–Sn–Br1	103.61 (8)	C7–N2–C4	114.7 (8)
Br2–Sn–Br1	92.64 (6)	N2–C1–S1	121.7 (7)
S2–Sn–S1	94.72(10)	N2–C1–S4	121.2 (7)
S4–Sn–S1	71.09 (9)	S1–C1–S4	117.1 (5)
Br2–Sn–S1	160.01 (7)	N1–C2–S3	123.6 (7)
Br1–Sn–S1	91.84 (8)	N1–C2–S2	120.8 (7)
S2–Sn–S3	70.64 (9)	S3–C2–S2	115.7 (5)
S4–Sn–S3	96.47(10)	C6–C3–N1	112.8 (8)
Br2–Sn–S3	92.91 (8)	N2–C4–C10	112.5 (9)
Br1–Sn–S3	159.25 (7)	N1–C5–C8	111.6 (8)
S1–Sn–S3	89.73(10)	N2–C7–C9	112.5(10)
C1–S1–Sn	85.0 (3)	C2–S2–Sn	87.6 (3)
C2–S3–Sn	85.5 (3)		

cis-$X_2Sn[S_2CN(C_2H_5)_2]_2$ (X=Cl, Br, I), the first Sn–X bond is formed by the overlap of the p_x orbital of tin with the s orbital of X. The second Sn–X bond is formed by the overlap of the p_y orbital of tin with the s orbital of X. The contribution of tin orbitals to Sn–X bond is lowest(27%) in *cis*-$Br_2Sn[S_2CN(C_2H_5)_2]_2$ and highest(37%) in *cis*-$I_2Sn[S_2CN(C_2H_5)_2]_2$. In all the cases the bonding electrons are present in the molecular orbital which draws contribution from p_x and p_y orbitals of halogens accounting for the X–Sn–Y bond angle of 90°. The strong Sn–S bonds are formed by the degenerate orbitals containing 21.7% tin character. The weak Sn-S bonds are formed by utilizing the orbitals of only 19.4% of tin character. In the case of the acetylacetonato complexes, the X–Sn–Y angle is 98.9° for $I_2Sn(acac)_2$, 103.6° for $Br_2Sn(acac)_2$, 101.2° for $Cl_2Sn(acac)_2$ and 104.2° for $Me_2Sn(acac)_2$. Calculations reveal that in $Cl_2Sn(acac)_2$, the quadruply degenerate orbitals(≅21 eV) are used for the formation of Sn–O bonds whose bond orders are almost similar. The other two Sn–X bonds are formed by the overlap of ligand orbitals(≅ 70%) with the high energy orbitals of tin(≅28%). As expected the X–Sn–Y angles do not show much variation. The bonding path in the nitrato complexes is

Table 4 Anisotropic displacement parameters ($Å^2 \times 10^3$). The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

Atom	U11	U22	U33	U23	U13	U12
Sn	36 (1)	41 (1)	41 (1)	5 (1)	9 (1)	17 (1)
Br1	66 (1)	45 (1)	67 (1)	11 (1)	6 (1)	21 (1)
Br2	46 (1)	86 (1)	67 (1)	10 (1)	21 (1)	29 (1)
S1	39 (2)	64 (2)	54 (2)	10 (2)	11 (2)	25 (2)
S2	41 (2)	42 (2)	46 (2)	4 (2)	2 (2)	17 (2)
S3	53 (2)	60 (2)	57 (2)	14 (2)	4 (2)	33 (2)
S4	39 (2)	68 (2)	49 (2)	8 (2)	7 (2)	21 (2)
N1	44 (6)	37 (6)	52 (7)	9 (5)	15 (5)	19 (5)
N2	56 (7)	52 (7)	39 (7)	0 (5)	5 (6)	14 (6)
C1	38 (7)	33 (7)	45 (8)	2 (6)	4 (6)	15 (6)
C2	44 (7)	43 (8)	40 (7)	3 (6)	12 (6)	25 (6)
C3	52 (9)	48 (9)	48 (8)	6 (7)	–3 (7)	15 (7)
C4	60(10)	55 (10)	53 (9)	2 (7)	4 (8)	11 (8)
C5	67(10)	4 2(8)	55 (9)	17 (7)	18 (8)	22 (7)
C6	42 (8)	66 (11)	96(13)	26 (9)	18 (8)	26 (8)
C7	57(10)	97 (13)	60(10)	18 (9)	28 (8)	38 (9)
C8	82(12)	68 (11)	82(12)	9 (9)	30(10)	47(10)
C9	107(16)	113(17)	100(15)	22(13)	61(13)	68(14)
C10	80(13)	82 (14)	106(16)	27(12)	–17(12)	31(11)

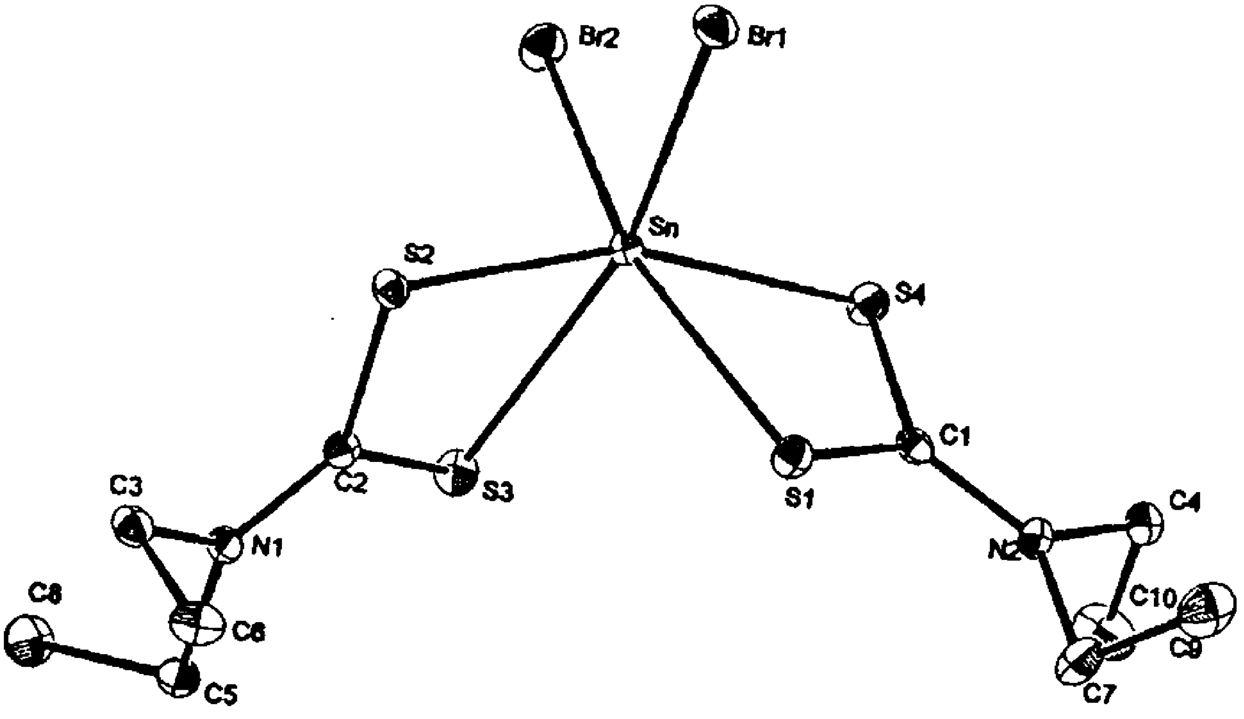

Fig. 4 Thermal ellipsoidal plot of cis-$Br_2Sn[S_2CN(C_2H_5)_2]_2$

Table 5 Hydrogen atom coordinates (× 10^4) and isotropic displacement parameters (Å^2 × 10^3)

Atom	x	y	z	Ueq
H3A	–2965 (21)	–808 (17)	5105 (9)	73(18)
H3B	–3879 (21)	–2591 (17)	4947 (9)	73(18)
H4A	5075 (23)	3410 (18)	10737(10)	73(18)
H4B	3736 (23)	3293 (18)	11452(10)	73(18)
H5A	–3336 (24)	–3883 (16)	6355(10)	73(18)
H5B	–1103 (24)	–3223 (16)	6857(10)	73(18)
H6A	–6223 (85)	–1572(157)	5245(20)	112(21)
H6B	–4872 (42)	–790 (89)	6157(64)	112(21)
H6C	–5815(120)	–2573 (70)	5972(81)	112(21)
H7A	–897 (24)	1712 (21)	10091(11)	73(18)
H7B	172 (24)	1526 (21)	11013(11)	73(18)
H8A	–2114(145)	–4210(129)	5045(16)	112(21)
H8B	–1642(186)	–5241 (44)	5741(51)	112(21)
H8C	43 (48)	–3746 (90)	5617(60)	112(21)
H9A	–1130(115)	3366 (26)	11220(75)	112(21)
H9B	–144(194)	4228 (72)	10486(18)	112(21)
H9C	1204 (87)	4174 (74)	11371(61)	112(21)
H10A	5206(146)	1554 (36)	11687(45)	112(21)
H10B	4732(180)	935 (79)	10688(40)	112(21)
H10C	2997 (50)	603 (56)	11226(83)	112(21)

consistent with the separation of sp^3 orbitals of tin into a set of doubly degenerate orbitals(≅22 eV) with two other higher energy orbitals whose energies differ considerably. These two different higher energy orbitals are used for the formation of Sn–X bonds which are essentially non-equivalent in contrast to the bonding of similar ligands to tin in dithiocarbamato and acetylacetonato complexes. The other "two ligand orbitals" differ in energy in the complexes (–14.8 to –17.4 eV) and contribute for the formation of weak Sn–O bonds. The resulting overall geometry of the nitrato complexes can best be described as bicapped tetrahedron in which the weakly bonded oxygens occupy the capped positions, as reported for $Ph_2Sn(O_2N_2Ph)_2$.[43]

In order to test the validity of the above structural predictions, the X-ray crystallographic investigation on dibromobis(N,N-diethyldithio carbamato)tin(IV) was carried out. The above complex was prepared by the reported method.[11] Slow evaporation of the tetrahydrofuran solution of the above compound gave rise to pale yellow diffraction quality crystals. The formation of the product had been accounted by the oxidative addition of the initially formed tetraethylthiuram disulfide to tin(II) bromide.[23] A distorted octahedral arrangement of the two dithiocarbamato groups and the two bromine atoms around tin(IV) is indicated by the X-ray investigation (Fig. 4). The structural parameters of $Br_2Sn[S_2CN(C_2H_5)_2]_2$ closely resemble those of the chloro analogue,[23] the most striking similarity being the *cis* dispositions of the halogens in both the cases. In contrast, the C–Sn–C angle in $^nBu_2Sn[S_2CN(C_2H_5)_2]_2$ had been observed to be 140.8(2)° and 132.6(2)°(two molecules).[24]

The structural flexibility originates from the flexibility in the hybridization involved in the formation of the three sets of complexes. While the nitrato complexes are formed by using the sp^3 hybrid orbitals, the formation of the dithiocarbamato complexes is best explained on the basis of "sp" hybridization scheme. The distortion from the ideal geometry in all the cases are not traced to steric effects but may arise due to inter-bond repulsions or intramolecular close contacts between atoms.

Crystal data for cis-$Br_2Sn[S_2CN(C_2H_5)_2]_2$: $C_{10}H_{20}Br_2N_2S_4Sn$; M_r = 575.03; crystal colour/habit, pale yellow/needle ; crystal system, triclinic; space group and Z, P-1 and 2, a = 7.179(6) A°, b = 9.354(4) Å, c = 15.563(4) Å, α = 93.82(3)°, β = 99.00(4)°, γ = 109.11(5) °, Volume, 967.6(9) A^{o3}, Scan method, 2θ; D_c = 1.974 Mg/m^3, μ (MoKα) = 5.871 mm^{-1}, T_{min} and T_{max} = 0.8069 and 0.9989; F(000), 556; θ range for data collection, 2.32–24.98° ; Crystal size 0.06 × 0.11 × 0.11 mm; Index ranges, $-8 \leq h \leq 8$, $-11 \leq k \leq 11$, $0 \leq l \leq 18$; Reflections collected 3739; Independent reflections 3391; Refinement method, Full-matrix least-squares on F^2, Goodness-of-fit on F^2, 1.195; Final R indices [I ≥ 2sigma(I)] R_1 = 0.0538, wR_2 = 0.1060; R indices (all data) R_1 = 0.0888, wR_2 = 0.1173; Largest diff. peak and hole 0.694 and –0.691 e Å^{-3}.

Tables of structure factors and hydrogen atom coordinates as well as the complete list of the bond parameters have been deposited at the Cambridge Crystallographic Data Centre.

PL thanks the Council of Scientific and Industrial Research, Government of India for the award of Senior Research Fellowship[9/475(92)/99- EMRI]. KP thanks the University Grants Commission, Government of India for the award of a Major Research Project[F12-108/90(RBBII) dt., 23.04.91].

Techniques used : X-ray diffraction and PM3 calculations

References : 44

Figures : 4

Tables : 15

Received 26 June 2000; accepted 21 October 2000
Paper 00/417

References cited in this synopsis

10 M.A. Buntine, V.J. Hall, F.J. Kosovel, E. R. T. Tiekink, *J. Phys. Chem. A*, 1998, **102**, 2472.
11 R. Selvaraju, M. Manoharan, P. Laavanya, K. Panchanatheswaran, P. Venuvanalingam, *J. Chem. Res.(S)*, 1999, 82; *J. Chem. Res.(M)*, 1999, 419.
23 R. Selvaraju, K. Panchanatheswaran, K. Venkatasubramanian, *Polyhedron*, 1994, **13**, 903.
24 V. Vrabel, J. Lokaj, E. Kello, J. Garaj, A.C. Batsanov, Y.T. Struchkov, *Acta Cryst.*, 1992, **C48**, 633.
27 V. Vrabel, E. Kello, *Acta Cryst.*, 1993, **C49**, 873.
28 S.W. Ng, C. Wei, V.G. Kumar Das, T.C.W. Mak, *J. Organomet. Chem.*, 1987, **334**, 295.
31 A.F. Wells, Structural Inorganic Chemistry, V edn., Clarendon Press, Oxford, 1984, p. 823.
37 G.A. Miller, E.O. Schlemper, *Inorg. Chem.*, 1973, **12**, 677.
38 T.P. Lockhart, W. F. Manders, E.O. Schlemper, J.J. Zuckerman, *J. Am. Chem. Soc.*, 1986, **108**, 4074.
43 U. Kolb, M. Beuter, M. Druger, *Inorg. Chem.*, 1994, **33**, 4522.