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X-ray Crystal Structure of Bis(4-benzoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-onato) Dibutyl Tin(IV), $C_{42}H_{44}N_4O_4Sn$, with *trans RR* Sn Configuration

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Abstract

A dialkyl tin complex of composition Bu_2SnL_2 (I) (L is a monofunctional bidentate ligand) has been made by reaction of $ClBu_2Sn{-}O{-}SnBu_2Cl$ with the substituted pyrazolone, $\text{PhCO}\overline{\text{C:C(OH)N(Ph)N:C}}\text{CH}_3$, in dry benzene. Crystals of I (M = 787.5) are monoclinic, space group $P2_1/C$, a = 9.714(6), b = 19.621(6), c = 22.68(1) Å, β = 114.00(4)°, V = 3949.2 Å^3, Z = 4, D_{calc} = 1.3240 cm^{-3}, λ(Mo Kα) = 0.71069 Å, μ = 6.960 cm^{-1}, T = 295 K, F(000) = 1624, R = 0.0628 for 2187 unique reflections. The molecule has a distorted octahedral geometry with Bu groups *trans* to each other. Four oxygen atoms of the pyrazolone moieties and the central Sn atom lie in the same plane.

Introduction

In marked contrast to the well-documented *cis*-R_2Sn structures of bis(quinolin-8-olato)dimethyl tin complexes, the crystal structure of the compound $[Sn(Et)(Pr)(C_{10}H_8NO)_2]$ shows that the octahedral geometry changes to a distorted *trans* configuration upon introducing a methyl substituent at the 2-position of the chelating ligand [1, 2]. In view of this, a study of the stereochemistry of the octahedral complex, formed by the interaction of the R_2Sn moiety with a bulky bidentate ligand, has been undertaken. Supporting evidence in favour of a *trans* geometry has now been obtained from a crystallographic study of the dialkyl title complex, bis(4-benzoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-onato) dibutyl tin(IV) (Fig. 1).

Experimental

The ligand was synthesized by the procedure reported by Jensen [3].

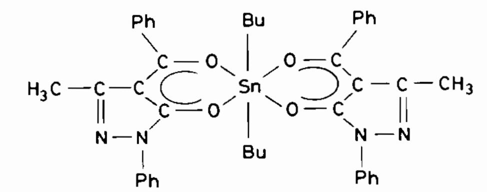

Fig. 1. The dialkyl title complex.

Synthesis of Complex

To a colourless solution of $ClBu_2Sn{-}O{-}SnBu_2Cl$ (1.39 g, 2.53 mmol) in dry benzene was added the yellowish ligand (4-benzoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-one) solution in dry benzene (1.40 g, 5.07 mmol) containing triethylamine (0.51 g, 5.06 mmol). The colour of the resultant solution changed to light yellowish from the original yellow. No heat change was observed. The reaction contents were stirred for ~3–4 h and the white precipitate of $Et_3N{\cdot}HCl$, so formed, was filtered off. On stripping off the excess solvent under reduced pressure, a yellowish sticky compound was obtained which became solid upon addition of petroleum ether. The compound was recrystallized from benzene petroleum ether mixture and characterized by single crystal X-ray analysis.

Crystal Data

Data were collected using a yellow crystal *c.* 0.25 × 0.15 × 0.10 mm, sealed in a capillary, on an Enraf-Nonius CAD 4 diffractometer in the $\omega/2\theta$ mode with $\Delta\theta = (0.8 + 0.35 \tan\theta)°$ and two standard reflections [049, 04$\bar{9}$] were measured every 1800 s exhibiting no significant change. Of the 5001 unique reflections, measured for $2 < \theta < 22°$ and $+h$ (10), $+k$ (20), $\pm l$ (21), 2187 with $|F^2| > \sigma(F^2)$ were used in the refinement where $(F^2) = \{\sigma^2(I) + (0.04I)^2\}^{1/2}/LP$.

There was no crystal decay and no absorption correction was made. $(\sin\theta/\lambda)_{max}$ = 0.5271 Å^{-1}. The structure was solved by heavy atom methods and refined by full matrix least-squares with anisotropic temperature factors. Hydrogen atoms were omitted. The weighing scheme was $\omega = 1/\sigma^2(F)$ and the

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final residuals were $R = 0.063$, $R' = 0.072$; the final difference map was < 0.6 e Å^{-3} throughout. A total of 451 parameters was refined for non-hydrogen atoms $(\Delta/\sigma)_{max} = 0.05$. Programs from the Enraf-Nonius structural determination package were run on a PDP 11/73 computer.

Results and Discussion

The reaction of 4-benzoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-one (LH) was carried out with $ClBu_2Sn{-}O{-}SnBu_2Cl$ in a 2:1 molar ratio in the presence of 2 mol of Et_3N in anhydrous benzene.

$$ClBu_2Sn{-}O{-}SnBu_2Cl + 2LH + 2Et_3N \xrightarrow{C_6H_6} Bu_2SnL_2 + Bu_2SnO + 2Et_3N{\cdot}HCl\downarrow$$

The resulting product was a yellow viscous mass which became solid upon addition of petroleum ether. On recrystallization from benzene petroleum ether, crystals of $Bu_2Sn[PhCO\overline{C:CON(Ph)N:C}Me]_2$, were obtained in ~50% yield. This product was characterized by single crystal X-ray analysis.

It is interesting to observe the fission of the Sn–O–Sn bond in these reactions resulting in the formation of the Bu_2SnL_2 type of product instead of the expected $LBu_2Sn{-}O{-}SnBu_2L$. This product has also been synthesized by the reaction of $Bu_2Sn(OPr^i)_2$ with pyrazolone or Bu_2SnCl_2 with pyrazolone in the presence of triethylamine as reported by us earlier [4].

The structure of the title compound is shown in Fig. 2 (PLUTO). Positional parameters of the non-H atoms and the equivalent values of the anisotropic temperature factors (B_{ij}) are given in Table 1. Bond lengths and angles are summarized in Tables 2 and 3, respectively. The crystal study of $Bu_2Sn[PhCO\overline{C:CON(Ph)N:C}Me]_2$ shows the coordination geometry around the tin atom to be nearly octahedral.

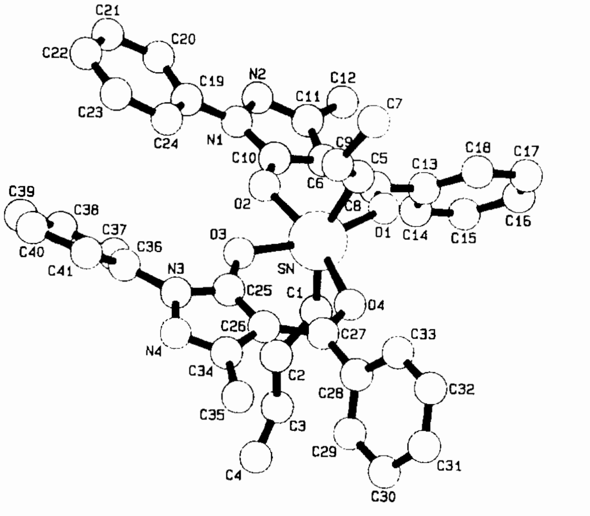

Fig. 2. Molecular structure of $Bu_2Sn[PhCO\overline{C:CON(Ph)N:C}CH_3]_2$ (PLUTO).

TABLE 1. Positional parameters and their e.s.d.s.

Atom	x	y	z	B (Å^2)
Sn	0.2474(2)	0.18743(6)	0.13988(5)	5.40(3)
O1	0.226(1)	0.0978(5)	0.0660(5)	7.6(4)
O2	0.209(1)	0.1048(5)	0.1907(4)	6.5(3)
O3	0.263(1)	0.2366(5)	0.2255(4)	5.5(3)
O4	0.286(1)	0.2992(5)	0.1123(5)	7.3(3)
N1	0.166(1)	−0.0050(6)	0.2132(5)	5.8(4)
N2	0.163(2)	−0.0702(7)	0.1894(6)	6.9(4)
N3	0.308(1)	0.3226(6)	0.2990(5)	5.4(3)
N4	0.343(2)	0.3937(7)	0.3043(6)	6.5(4)
C1	0.473(2)	0.1704(9)	0.1623(9)	8.0(6)
C2	0.577(2)	0.209(1)	0.215(1)	11.9(9)
C3	0.740(3)	0.196(1)	0.229(2)	18(1)
C4	0.847(3)	0.238(2)	0.262(2)	17(1)
C5	0.020(2)	0.206(1)	0.0766(8)	7.6(6)
C6	−0.068(3)	0.260(1)	0.091(1)	11.8(8)
C7	−0.234(3)	0.281(1)	0.038(2)	20(1)
C8	0.242(2)	0.0358(8)	0.0752(7)	5.6(4)
C9	0.225(2)	0.0042(7)	0.1275(7)	4.8(4)
C10	0.202(2)	0.0392(8)	0.1774(6)	5.1(4)
C11	0.199(2)	−0.0651(8)	0.1402(8)	6.5(6)
C12	0.205(2)	−0.1305(9)	0.1021(9)	8.2(6)
C13	0.269(2)	−0.0050(8)	0.0247(7)	5.1(4)
C14	0.391(2)	−0.0503(9)	0.0439(8)	7.1(6)
C15	0.417(2)	−0.0835(9)	−0.0051(9)	7.3(6)
C16	0.326(2)	−0.071(1)	−0.0702(8)	6.7(5)
C17	0.208(2)	−0.025(1)	−0.0877(8)	7.0(5)
C18	0.178(2)	0.0107(9)	−0.0391(7)	5.9(5)
C19	0.115(2)	0.0049(9)	0.2620(7)	5.2(5)
C20	0.074(2)	−0.053(1)	0.2869(8)	7.2(6)
C21	0.021(2)	−0.043(1)	0.3369(8)	7.9(6)
C22	0.013(2)	0.020(1)	0.3604(9)	8.3(7)
C23	0.051(2)	0.075(1)	0.3334(8)	8.4(6)
C24	0.104(2)	0.070(1)	0.2839(8)	8.0(6)
C25	0.298(2)	0.3020(8)	0.2415(6)	4.8(4)
C26	0.325(2)	0.3564(7)	0.2079(6)	4.2(4)
C27	0.322(2)	0.3517(8)	0.1455(7)	5.3(5)
C28	0.355(2)	0.4128(8)	0.1147(6)	5.2(5)
C29	0.499(2)	0.438(1)	0.1358(9)	8.3(6)
C30	0.529(3)	0.493(1)	0.104(1)	11.2(8)
C31	0.403(2)	0.522(1)	0.0508(9)	10.0(7)
C32	0.263(3)	0.495(1)	0.030(1)	10.1(8)
C33	0.239(2)	0.4398(9)	0.0610(8)	6.9(5)
C34	0.354(2)	0.4121(8)	0.2516(7)	5.0(4)
C35	0.388(2)	0.4872(8)	0.2446(9)	8.0(7)
C36	0.292(2)	0.2893(8)	0.3517(6)	5.4(5)
C37	0.345(2)	0.2211(9)	0.3657(8)	7.5(6)
C38	0.327(2)	0.193(1)	0.4198(7)	9.1(6)
C39	0.272(2)	0.226(1)	0.4566(8)	8.9(6)
C40	0.224(2)	0.292(1)	0.4417(8)	8.3(6)
C41	0.233(2)	0.3246(9)	0.3873(7)	7.4(5)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

TABLE 2. Bond distances (Å)

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Sn	O1	2.38(2)	C13	C14	1.40(2)
Sn	O2	2.11(1)	C13	C18	1.39(2)
Sn	O3	2.12(2)	C14	C15	1.40(3)
Sn	O4	2.35(2)	C15	C16	1.40(2)
Sn	C1	2.07(2)	C16	C17	1.38(3)
Sn	C5	2.12(2)	C17	C18	1.43(3)
O1	C8	1.24(2)	C19	C20	1.40(3)
O2	C10	1.32(2)	C19	C24	1.38(3)
O3	C25	1.35(2)	C20	C21	1.43(4)
O4	C27	1.24(2)	C21	C22	1.36(3)
N1	N2	1.38(2)	C22	C23	1.36(3)
N1	C10	1.33(2)	C23	C24	1.43(3)
N1	C19	1.40(2)	C25	C26	1.39(2)
N2	C11	1.30(3)	C26	C27	1.41(2)
N3	N4	1.43(2)	C26	C34	1.42(3)
N3	C25	1.33(2)	C27	C28	1.49(2)
N3	C36	1.43(3)	C28	C29	1.37(2)
N4	C34	1.29(2)	C28	C33	1.39(2)
C1	C2	1.43(3)	C29	C30	1.40(3)
C2	C3	1.51(4)	C30	C31	1.43(3)
C3	C4	1.30(4)	C31	C32	1.36(3)
C5	C6	1.49(3)	C32	C33	1.37(4)
C6	C7	1.63(3)	C34	C35	1.53(2)
C8	C9	1.41(2)	C36	C37	1.43(2)
C8	C13	1.50(2)	C36	C41	1.35(3)
C9	C10	1.42(2)	C37	C38	1.42(3)
C9	C11	1.43(2)	C38	C39	1.34(3)
C11	C12	1.56(3)	C39	C40	1.38(3)
C40	C41	1.43(3)			

Numbers in parentheses are e.s.d.s in the least significant digits.

The apparent propyl group is simply the butyl group with the final carbon atom of the chain so disordered that it is not visible in the electron density map. A glance at the temperature factors for the atoms C5, C6 and C7 reveals that by C7 the value has increased to $B = 20$ Å showing the evidence for disorder towards the end of the chain. Therefore, it was not possible to locate (DF) the terminal carbon on one butyl chain due to its high thermal motion. This is a relatively common phenomenon encountered with n-butyl groups. As a consequence of this, the diagram of the molecule does not show the terminal carbon on one butyl chain.

The two alkyl groups are approximately *trans* to each other [C1–Sn–C5 154.7(8)°] as has already been reported for the compound [Sn(Et)(Pr)($C_{10}H_8NO)_2$] [C–Sn–C 145.2(3)°] [2]. Even in bis(2,4-pentanedionato) dimethyl tin(IV), the two methyl groups occupy *trans* positions [C–Sn–C 180(0)°] [5].

The tin atom and the oxygen atoms of the pyrazolone moieties are essentially coplanar. It has been observed that of the four Sn–O bonds, two are strong [Sn–O2, 2.11(1); Sn–O3, 2.12(2)] and two are weak [Sn–O1, 2.38(2); Sn–O4, 2.35(2)]. It is reported that the Sn–O bond in complexes of the types bis(2-methylquinolin-8-olato)(ethyl) n-propyl tin(IV) [2] and bis(quinolin-8-olato) dimethyl tin [6] having *cis* arrangements of the methyl groups varies in length from 2.066(4) to 2.11 ± 0.01 Å, respectively. The short Sn–O bond distance 2.115 (av.) in the present compound is quite comparable with the reported value of 2.19 Å for the Sn–O bond in the

TABLE 3. Bond angles (°)

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
O1	Sn	O2	80.3(4)	C1	C2	C3	114(2)
O1	Sn	O3	159.3(4)	C2	C3	C4	122(3)
O1	Sn	O4	118.7(4)	Sn	C5	C6	121(1)
O1	Sn	C1	80.5(7)	C5	C6	C7	120(3)
O1	Sn	C5	83.4(7)	O1	C8	C9	122(2)
O2	Sn	O3	79.2(5)	O1	C8	C13	116(1)
O2	Sn	O4	160.9(4)	C9	C8	C13	122(1)
O2	Sn	C1	98.5(6)	C8	C9	C10	125(1)
O2	Sn	C5	97.9(6)	C8	C9	C11	133(1)
O3	Sn	O4	82.0(4)	C10	C9	C11	102(2)
O3	Sn	C1	100.1(7)	O2	C10	N1	121(1)
O3	Sn	C5	101.8(6)	O2	C10	C9	130(2)
O4	Sn	C1	87.0(6)	N1	C10	C9	110(1)
O4	Sn	C5	83.9(6)	N2	C11	C9	112(2)
C1	Sn	C5	154.7(8)	N2	C11	C12	120(2)
Sn	O1	C8	130(1)	C9	C11	C12	128(2)
Sn	O2	C10	129(2)	C8	C13	C14	119(1)
Sn	O3	C25	127(1)	C8	C13	C18	116(1)
Sn	O4	C27	131(2)	C14	C13	C18	124(2)
N2	N1	C10	109(1)	C13	C14	C15	117(1)

(continued)

TABLE 3. *(continued)*

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
N2	N1	C19	119(1)	C14	C15	C16	121(2)
C10	N1	C19	131(1)	C15	C16	C17	121(2)
N1	N2	C11	107(1)	C16	C17	C18	120(1)
N4	N3	C25	107(1)	C13	C18	C17	118(2)
N4	N3	C36	119(1)	N1	C19	C20	117(2)
C25	N3	C36	134(1)	N1	C19	C24	121(2)
N3	N4	C34	108(1)	C20	C19	C24	122(2)
Sn	C1	C2	116(2)	C19	C20	C21	117(2)
C20	C21	C22	123(3)	C28	C29	C30	120(2)
C21	C22	C23	119(2)	C29	C30	C31	117(3)
C22	C23	C24	123(3)	C30	C31	C32	123(2)
C19	C24	C23	118(2)	C31	C32	C33	119(2)
O3	C25	N3	118(1)	C28	C33	C32	121(2)
O3	C25	C26	132(1)	N4	C34	C26	111(1)
N3	C25	C26	110(1)	N4	C34	C35	118(1)
C25	C26	C27	125(1)	C26	C34	C35	131(2)
C25	C26	C34	104(1)	N3	C36	C37	118(2)
C27	C26	C34	132(1)	N3	C36	C41	119(1)
O4	C27	C26	123(2)	C37	C36	C41	123(2)
O4	C27	C28	117(1)	C36	C37	C38	114(2)
C26	C27	C28	120(1)	C37	C38	C39	125(3)
C27	C28	C29	121(1)	C38	C39	C40	119(2)
C27	C28	C33	118(1)	C39	C40	C41	120(2)
C29	C28	C33	121(2)	C36	C41	C40	118(2)

Numbers in parentheses are e.s.d.s. in the least significant digits.

case of *trans*-$(CH_3)_2Sn(acac)_2$ [5]. A slight distortion may stem from packing effects. However, the other long Sn–O average bond distance 2.365 Å appears to be quite weak. This may be due to the presence of a phenyl group in the vicinity. The Sn–C5 (Bu) bond length is 2.12(2) Å which is close to the reported value 2.089(8) Å^2. The shortest bond length present around tin atom is Sn–C1 (Bu) which is 2.07(2) Å.

It would be pertinent to note that the two donor oxygens O1 and O4 (the weak Sn–O bonds) are *cis* to each other and this leads to the fixation of the two phenyl groups attached to C8 and C27 on the same side of the pyrazolone moiety. Similarly, the other phenyl groups appended to N1 and N3 are *cis* to each other.

The *trans* preference of the Bu_2Sn moiety is the result of an overplay of electronic effects and unequal Sn–donor distances are better explained in an energetically favourable *trans* geometry than in *cis*.

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