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STEREOCHEMISTRY AND CRYSTAL STRUCTURE OF DIPHENYLTIN DICHLORIDE COMPLEXES WITH *MESO*- OR *RAC*-BIS(PHENYLSULPHINYL)ETHANE

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Abstract—1 : 1 Complexes of diphenyltin dichloride (DPTC) with *meso*- or *rac*-bis(phenylsulphinyl)ethane (*meso*- or *rac*-BPSE) were prepared. The results of X-ray crystal structure analysis revealed that DPTC·*meso*-BPSE (I) and DPTC·*rac*-BPSE (II) crystallized in different monoclinic space groups. For I, the space group is $P2_1/a$, whilst for II, the space group is $C2/c$. After the complexing reaction, *meso*-BPSE retains its configuration in crystal I, but one of the sulphur atoms of *rac*-BPSE in crystal II has dipositional disorder and the occupancies assigned to those positions are 0.5. Although environments of both positions can meet the demands of tetrahedral geometry for the sulphur atoms, their chirality is inverted with respect to each other, which means that about half of the *rac*-BPSE ligands invert their configuration in the complexing reaction with DPTC.

Owing to the fact that compounds of type RS(O) $CH_2CH_2S(O)R$ can exist as diastereoisomeric *rac* and *meso* forms, the metal complexes of these ligands have been extensively investigated in recent years.[1–12] However, few of these studies related to the stereochemistry of the complexes. The structure of the platinum complex of *meso*- or *rac*-bis(phenylsulphinyl)ethane (*meso*- or *rac*-BPSE) was determined by Cattalini *et al.*[1] and we reported the crystal structure of the palladium complex of *meso*-bis(n-propylsulphinyl)ethane (*meso*-BPrSE).[2] In these complexes, the ligands are bonded to metal ions via sulphur atoms and the chiral sulphur atoms remain in the original stereo-configuration. However, for the complex of triphenyltin chloride (TPTC) with *rac*-BPrSE, which was reported by Filgueiras *et al.*,[4] the ligand is coordinated to tin through oxygen atoms. More recently, we have further determined the crystal structure of the TPTC complexes of *meso*- or *rac*-BPSE and discovered that these two complexes had the same structure in which the ligand, BPSE, was the *meso*-isomer and the ratio of TPTC : BPSE was 2 : 1.[13] These results suggested that the configurational inversion occurred for one of the two chiral sulphur atoms in the *rac*-isomer when TPTC reacted with *rac*-BPSE to form a 2 : 1 complex. This is very interesting and has not been reported for disulphoxide complexes before. For further investigation of this phenomenon, in the present work we have prepared the 1 : 1 complexes of diphenyltin dichloride (DPTC) with

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meso- or *rac*-BPSE and determined their crystal structures by X-ray diffraction.

EXPERIMENTAL

Both *meso*- and *rac*-BPSE were prepared as described previously.[14] DPTC was prepared from tetraphenyltin by a standard procedure.[15]

IR spectra in the range of 4000–400 cm^{-1} were recorded on a Nicolet 5DX·FTIR spectrometer (KBr disc). Elemental analyses were performed using a Perkin–Elmer 240C instrument. Melting points were determined on a Du Pont 1090B thermal-meter (uncorrected).

DPTC and the corresponding ligand were dissolved in absolute alcohol at a ratio of 1 : 1. The solution was refluxed with stirring for 4 h. The resulting colourless solution was then allowed to stand at room temperature to evaporate the solvent slowly. After several days, colourless crystals of DPTC·*meso*-BPSE (**I**) and DPTC·*rac*-BPSE (**II**) were separated, respectively. Found (**I**) : C, 50.5; H, 3.9; Cl, 11.3; S, 10.1%. Found (**II**) : C, 50.6; H, 3.9; Cl, 11.7; S, 10.1%. Calc. for $C_{26}H_{24}Cl_2O_2S_2Sn$: C, 50.2; H, 3.9; Cl, 11.4; S, 10.3%.

Crystal data for complexes **I** and **II**, together with other experimental details, are summarized in Table 1. The diffraction experiments were carried out using an Enraf–Nonius CAD4 diffractometer with Mo-K_α radiation (λ = 0.71073 Å). The Lorentz polarization and empirical absorption corrections were applied to the intensity data. Both structures were solved by using Patterson analysis, which revealed the positions of the tin atoms, and all other non-hydrogen atoms were located from subsequent Fourier syntheses. The structures were refined by full-matrix least-squares with anisotropic thermal parameters for all non-hydrogen atoms. All the calculations were performed on a PDP 11/44 computer using the SDP-PLUS program package.

RESULTS AND DISCUSSION

The results of elemental analyses revealed that the products of the reactions of DPTC with *meso*- or *rac*-BPSE are the 1 : 1 complexes of DPTC with *meso*- or *rac*-BPSE. The fact that ν(S=O) shifts to lower frequency (see Table 2) after complexing in both instances suggests that the ligands are bonded to the tin atom via the oxygen atoms. However, the distinctly different melting points for these products (listed in Table 2) indicated that they are two different solids.

The X-ray structure analysis for both DPTC·

Table 1. Crystal data and structure determination parameters

Compound	DPTC·*meso*-BPSE	DPTC·*rac*-BPSE
Formula	$[C_{26}H_{24}Cl_2O_2S_2Sn]_n$	$[C_{26}H_{24}Cl_2O_2S_2Sn]_n$
Molecular weight	622.07	622.07
Unit cell parameters		
a (Å)	18.549(5)	20.548(4)
b (Å)	12.672(4)	12.726(1)
c (Å)	22.401(3)	20.230(5)
β (°)	90.15(2)	96.91(3)
V ($Å^3$)	5265.3	5251.4
Z	8	8
D_u (g cm^{-3})	1.57	1.57
Space group	$P2_1/a$	$C2/c$
Radiation	Graphite-monochromatized Mo-K_α(0.71073 Å)	
μ (cm^{-1})	13.51	13.51
Temperature (°C)	23	23
Scan mode	ω–2θ	ω–2θ
2θ range (°)	4–44	4–44
Unique data measured	7027	3510
Obs. data [$I > 3\sigma(I)$]	3364	2166
Weighting scheme	Unit weight	Unit weight
R factor	0.049	0.036
R_w factor	0.060	0.040
F (000)	2496	2496
Residual extrema in final difference map (e $Å^{-3}$)	0.85	0.54

Table 2. Melting points and IR data of ligands and complexes

Compound	m.p. (°C)	ν(S=O) (cm^{-1})	ν(Sn—O)(cm^{-1})
DPTC·*meso*-BPSE	139–140	966	457
DPTC·*rac*-BPSE	125–126	957	457
meso-BPSE	166–167	1036	
rac-BPSE	120–122	1036	

meso-BPSE (I) and DPTC·*rac*-BPSE (II) make it clear that they have crystallized in different monoclinic space groups, although they have identical stoichiometry. Perspective views with atomic labelling for I and II are shown in Figs 1 and 2, respectively. From the bond distances and angles for **I** and **II** listed in Tables 3 and 4, it can be seen that both crystals consist of the polymers of DPTC·*meso*-BPSE or DPTC·*rac*-BPSE. In each complex the bidentate ligand, either *meso*-BPSE or *rac*-BPSE, bridges between two tin atoms related by a 2_1 screw axis, via oxygen coordination, while each tin atom is bound to two oxygen atoms from different ligands, so that one-dimensional chains of $\left[\text{DPTC}\cdot\text{BPSE}\right]_n$ are formed.

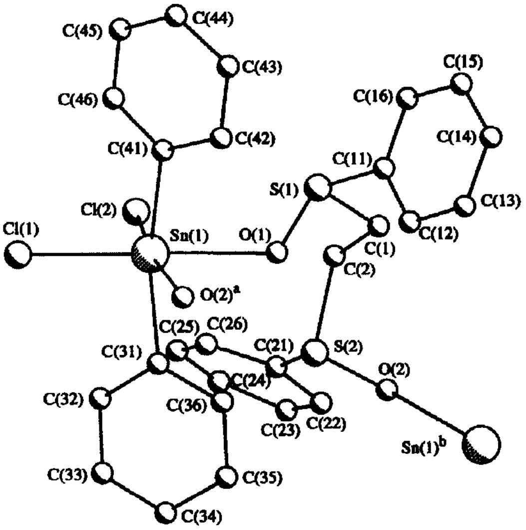

Fig. 1. A perspective view of complex **I**. The symmetrical transformation codes are the same as those in Table 3.

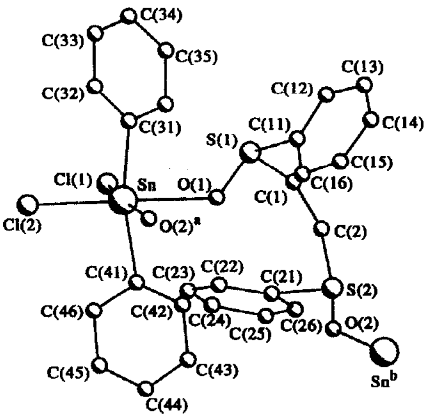

Fig. 2. A perspective view of complex **II**. The symmetrical transformation codes are the same as those in Table 4.

In each complex the tin atom has a distorted octahedral coordination, with two oxygen and two chlorine atoms occupying the equatorial positions. Around the tin atom, two axial phenyl groups give C—Sn—C angles of 162.5(2)° and 162.6(2)° in **I**, and 164.1(2)° in **II**, respectively. Comparing the corresponding bond distances and angles listed in Tables 3 and 4, it is found that the molecular structures of **I** and **II** are very similar to each other except for the Sn—O bonds. In complex **I**, four independent Sn—O bonds can be divided clearly into two groups. The shorter Sn—O bonds are 2.34(1) and 2.35(1) Å, and the longer Sn—O bonds are 2.47(2) and 2.49(2) Å, respectively. Each of the two independent chains present have one short and one long bond. In complex **II**, the two Sn—O bonds are very close to each other [2.376(6) and 2.372(6) Å].

It is worth pointing out that one of the two independent sulphur atoms in crystal **II** is dipositionally disordered and represented as S(2) and S(2)′ in Table 4. In the structural refinement, reasonable thermal parameters were derived from the least-squares method for S(2) and S(2)′ when each of them had been assigned the occupany of 0.5. The data listed in Table 4 show that both environments of S(2) and S(2)′ can meet the demands of tetrahedral geometry for the sulphur atom. Figure 3 shows the Newman projections along the sulphur → C(ethane) direction for S(1), S(2) and S(2)′ in crystal **II** according to the torsion angles in Table 5.

As the Newman projections show, the chirality of S(1) is the same as that of S(2), but the inverse of that of S(2)′, which means that about half of

Table 3. Selected bond distances (Å) and angles (°) for complex **I**

Chain 1			
Sn(1)—Cl(1)	2.465(4)	Sn(1)—Cl(2)	2.452(4)
Sn(1)—O(1)	2.34(1)	Sn(1)—O(2)[a]	2.47(2)
Sn(1)—C(31)	2.11(1)	Sn(1)—C(41)	2.15(1)
S(1)—O(1)	1.51(2)	S(1)—C(1)	1.82(2)
S(1)—C(11)	1.78(2)	S(2)—O(2)	1.50(1)
S(2)—C(2)	1.85(2)	S(2)—C(21)	1.79(2)
C(1)—C(2)	1.555(8)		
Cl(1)—Sn(1)—Cl(2)	92.6(1)	Cl(1)—Sn(1)—O(1)	179.1(3)
Cl(1)—Sn(1)—O(2)[a]	95.6(3)	Cl(1)—Sn(1)—C(31)	95.5(5)
Cl(1)—Sn(1)—C(41)	93.0(5)	Cl(2)—Sn(1)—O(1)	86.9(3)
Cl(2)—Sn(1)—O(2)[a]	171.9(3)	Cl(2)—Sn(1)—C(31)	98.6(5)
Cl(2)—Sn(1)—C(41)	96.4(4)	O(1)—Sn(1)—O(2)[a]	85.0(3)
O(1)—Sn(1)—C(31)	85.2(5)	O(1)—Sn(1)—C(41)	86.4(5)
O(2)[a]—Sn(1)—C(31)	80.0(5)	O(2)[a]—Sn(1)—C(41)	84.0(4)
C(31)—Sn(1)—C(41)	162.5(5)	O(1)—S(1)—C(1)	103.6(6)
O(1)—S(1)—C(11)	104.8(6)	C(1)—S(1)—C(11)	97.1(8)
O(2)—S(2)—C(2)	105.5(7)	O(2)—S(2)—C(21)	106.0(7)
C(2)—S(2)—C(21)	94.8(7)	Sn(1)—O(1)—S(1)	124.6(6)
Sn(1)[b]—O(2)—S(2)	143.7(6)	S(1)—C(1)—C(2)	109.9(4)
S(2)—C(2)—C(1)	108.7(4)		
Chain 2			
Sn(2)—Cl(3)	2.462(4)	Sn(2)—Cl(4)	2.457(4)
Sn(2)—O(3)[c]	2.35(1)	Sn(2)—O(4)	2.49(2)
Sn(2)—C(71)	2.11(1)	Sn(2)—C(81)	2.14(1)
S(3)—O(3)	1.53(2)	S(3)—C(3)	1.81(2)
S(3)—C(51)	1.79(2)	S(4)—O(4)	1.50(1)
S(4)—C(4)	1.86(2)	S(4)—C(61)	1.81(2)
C(3)—C(4)	1.54(2)		
Cl(3)—Sn(2)—Cl(4)	92.5(1)	Cl(3)—Sn(2)—O(3)[c]	179.5(2)
Cl(3)—Sn(2)—O(4)	95.9(3)	Cl(3)—Sn(2)—C(71)	95.2(4)
Cl(3)—Sn(2)—C(81)	93.2(5)	Cl(4)—Sn(2)—O(3)[c]	87.2(3)
Cl(4)—Sn(2)—O(4)	171.6(3)	Cl(4)—Sn(2)—C(71)	98.7(4)
Cl(4)—Sn(2)—C(81)	96.1(4)	O(3)[c]—Sn(2)—O(4)	84.6(3)
O(3)[c]—Sn(2)—C(71)	85.0(4)	O(3)[c]—Sn(2)—C(81)	86.8(5)
O(4)—Sn(2)—C(71)	79.4(4)	O(4)—Sn(2)—C(81)	84.5(5)
C(71)—Sn(2)—C(81)	162.6(5)	O(3)—S(3)—C(3)	103.5(6)
O(3)—S(3)—C(51)	105.1(6)	C(3)—S(3)—C(51)	97.1(7)
O(4)—S(4)—C(4)	104.6(7)	O(4)—S(4)—C(61)	104.2(7)
C(4)—S(4)—C(61)	95.2(7)	Sn(2)—O(3)—S(3)	123.2(5)
Sn(2)[d]—O(4)—S(4)	142.6(7)	S(3)—C(3)—C(4)	111(2)
S(4)—C(4)—C(3)	109(1)		

Numbers in parentheses are estimated standard deviations in the least significant digits.

Symmetrical transformation codes: [a] $(1.5-x, 0.5+y, 2-z)$; [b] $(1.5-x, -0.5+y, 2-z)$; [c] $(1.5-x, -0.5+y, 1-z)$; [d] $(1.5-x, 0.5+y, 1-z)$.

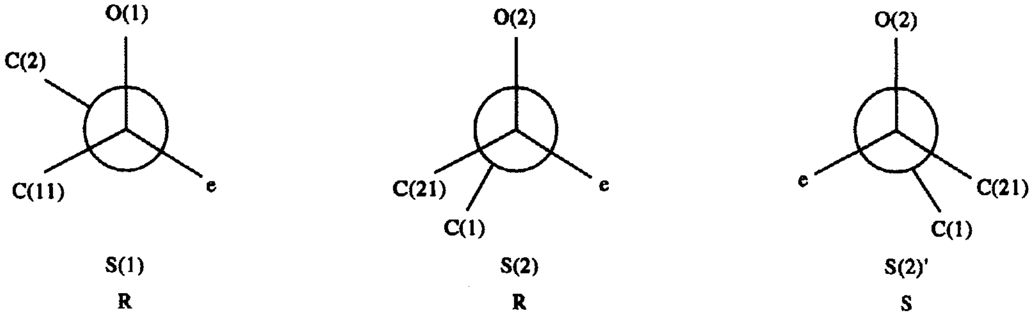

Fig. 3. Newman projections in the direction of sulphur → C(ethane) for complex **II**.

rac-BPSE ligands invert their configuration in the complexing reaction to become *meso*-BPSE. The result of checking the configuration of sulphur atoms in crystal **I** indicates that the ligands are still the *meso*-isomer after the complexing reaction. To sum up, the stereochemistry of the above two reactions can be expressed as in Scheme 1.

Supplementary material

Supplementary material, including coordinates, anisotropic thermal parameters, observed and calculated structure factors, for crystals **I** and **II** have been deposited with the Editor, and may also be obtained on request from the authors. Atomic coordinates have also been deposited at the Cambridge Crystallographic Data Centre.

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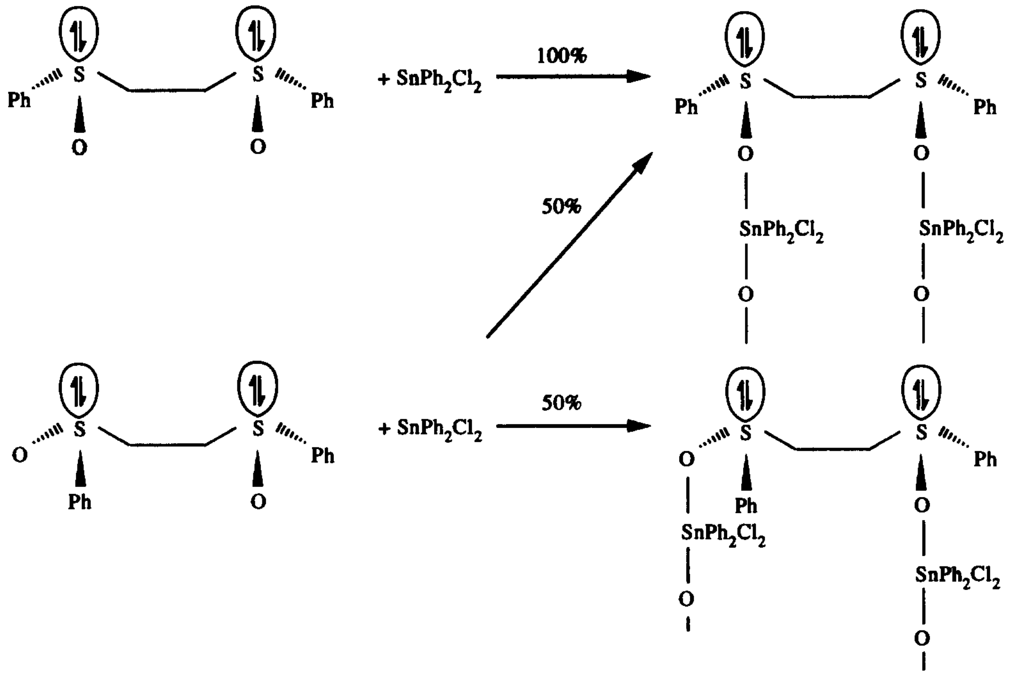

Scheme 1.

Table 4. Selected bond distances (Å) and angles (°) for complex **II**

Sn—Cl(1)	2.454(3)	Sn—Cl(2)	2.462(2)
Sn—O(1)	2.376(6)	Sn—O(2)^a	2.372(6)
Sn—C(31)	2.128(8)	Sn—C(41)	2.142(8)
S(1)—O(1)	1.515(6)	S(1)—C(1)	1.828(9)
S(1)—C(11)	1.794(9)	S(2)—O(2)	1.480(7)
S(2)—C(2)	1.80(2)	S(2)—C(21)	1.78(2)
S(2′)—O(2)	1.564(7)	S(2′)—C(2)	1.65(2)
S(2′)—C(21)	1.93(2)	C(1)—C(2)	1.51(1)
Cl(1)—Sn—Cl(2)	94.38(9)	Cl(1)—Sn—O(1)	89.8(2)
Cl(1)—Sn—O(2)^a	173.7(2)	Cl(1)—Sn—C(31)	95.1(2)
Cl(1)—Sn—C(41)	96.4(2)	Cl(2)—Sn—O(1)	175.8(2)
Cl(2)—Sn—O(2)^a	91.9(1)	Cl(2)—Sn—C(31)	93.3(2)
Cl(2)—Sn—C(41)	96.8(2)	O(1)—Sn—O(2)^a	83.9(3)
O(1)—Sn—C(31)	86.0(3)	O(1)—Sn—C(41)	83.2(3)
O(2)^a—Sn—C(31)	85.3(3)	O(2)^a—Sn—C(41)	82.2(3)
C(31)—Sn—C(41)	164.1(2)	O(1)—S(1)—C(1)	104.4(4)
O(1)—S(1)—C(11)	105.6(4)	C(1)—S(1)—C(11)	100.3(4)
O(2)—S(2)—C(2)	105.4(5)	O(2)—S(2)—C(21)	107.0(5)
C(2)—S(2)—C(21)	101.4(5)	O(2)—S(2′)—C(2)	108.5(5)
O(2)—S(2′)—C(21)	96.5(4)	C(2)—S(2′)—C(21)	100.4(5)
Sn—O(1)—S(1)	129.0(3)	Sn^b—O(2)—S(2)	138.6(4)
Sn^b—O(2)—S(2′)	124.9(3)	S(1)—C(1)—C(2)	112.0(7)
S(2)—C(2)—C(1)	125.5(7)	S(2′)—C(2)—C(1)	120.4(7)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Symmetrical transformation codes: $^a(1.5-x,\ -0.5+y,\ 0.5-z)$; $^b(1.5-x,\ 0.5+y,\ 0.5-z)$.

Table 5. Selected torsion angles (°) of complex **II**

Atom 1	Atom 2	Atom 3	Atom 4	Torsion angle
O(1)	S(1)	C(1)	C(2)	−50.7(7)
C(11)	S(1)	C(1)	C(2)	58.5(7)
e (S1)	S(1)	C(1)	C(2)	−175.4(6)
O(2)	S(2′)	C(2)	C(1)	158.4(7)
C(21)	S(2′)	C(2)	C(1)	57.8(9)
e (S2′)	S(2′)	C(2)	C(1)	−73.1(8)
O(2)	S(2)	C(2)	C(1)	−150.2(8)
C(21)	S(2)	C(2)	C(1)	−38.9(9)
e (S2)	S(2)	C(2)	C(1)	86.1(9)

e (S1), *e* (S2′) and *e* (S2) represent the direction of lone pair electrons in S(1), S(2′) and S(2) atoms respectively according to the tetrahedral geometry.

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