Stereochemistry and Crystal Structures of Triphenyltin Chloride Complexes with Bis(phenylsulfinyl)ethane

F. C. ZHU*, P. X. SHAO
Chemistry Department, Nankai University, Tianjin (China)
X. K. YAO, R. J. WANG and H. G. WANG
Test Center, Nankai University, Tianjin (China)

(Received July 10, 1989; revised November 27, 1989)

Abstract

2:1 Complexes of triphenyltin chloride (TPTC) with *meso*,*rac*-bis(phenylsulfinyl)ethane (*meso*,*rac*-BPSE) have been prepared in the form of crystals suitable for crystallography. The complex $(TPTC)_2\cdot$*meso*-BPSE is monoclinic with $a = 8.813(2)$, $b = 22.920(5)$, $c = 11.929(4)$ Å, $\beta = 104.16(2)°$, space group $P2_1/n$. $(TPTC)_2\cdot$*rac*-BPSE is an identical complex with $(TPTC)_2\cdot$*meso*-BPSE and configurational inversion of one sulfur atom in *rac*-BPSE happens when the ligand reacts with TPTC.

Introduction

Compounds of the type $RS(O)C_2H_4S(O)R$ exist as diastereoisomeric *rac* and *meso* forms which have different melting points. H^1 NMR has been used for the configurational assignment of a few ligands [1a–e]. X-ray crystal structure analyses prove that the higher melting isomer is of the *meso* form and the lower melting isomer is of the *rac* form when R groups are methyl, n-propyl and phenyl [2–5].

Synthetic transition metal complexes of disulfoxides are of recent interest [3, 5, 8–15]. Authors of refs. 3, 5 and 15 suggested that the correspondent noble metal complexes in which the ligands are bonded to metal ions via sulfur atoms have different molecular structures when the two ligands are diastereoisomers. It is worth studying a pair of crystal structures of oxygen bonded disulfoxide complexes. Several 1:1 adducts, TPTC·L (TPTC = triphenyltin chloride), have been reported [6, 7, 16]. In this paper, the preparation and crystal structures of 2:1 complexes of *meso*,*rac*-$PhS(O)C_2H_4S(O)Ph$ (*meso*,*rac*-BPSE), $(TPTC)_2\cdot L$, are reported.

Experimental

Preparation

meso, rac-BPSE

According to the method of Shao *et al.* [17] for the oxidation of disulfides to the corresponding disulfoxides, nitric acid was added dropwise to a solution of 1,2-bis(phenylthio)ethane in benzene cooled on a ice-bath. The solution was stirred for a suitable time. After neutralization and filtration, the *meso* and *rac* disulfoxides mixture was dried and dissolved in chloroform, petroleum ether (60–90 °C) was added to the solution to separate the mixture (*meso*-BPSE, melting point (m.p.) 166–167 °C; *rac*-BPSE, m.p. 120–122 °C).

$(TPTC)_2\cdot$meso-BPSE (I) and $(TPTC)_2\cdot$rac-BPSE (II)

TPTC and the corresponding ligand were dissolved in ethanol in the ratio of 2:1. The solution was stirred at 70 °C for 2 h. The reaction mixture, a colorless solution, was then allowed to stand at room temperature to evaporate the solvent and colorless crystals were separated manually.

Instrumentation

Solid-state IR spectra in the range from 400 to 4000 cm^{-1} were recorded on a Nicolet 5DX.FTIR spectrometer. Melting points and TGA data were recorded on a Du Pont 1090B thermometer.

X-ray Crystallography

Data collection were performed with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) on a Enraf-Nonius CAD4 four-circle diffractometer. Intensity data were collected in the range of $4° \leqslant 2\theta \leqslant 50°$ using a $\omega/2\theta$ scan technique. Lorentz and polarization corrections and an empirical absorption correction based on a series of Psi-scan were used.

---

*Author to whom correspondence should be addressed. Present address: Research Institute of Petroleum Processing, No. 15 Lab, P.O. Box 914, Beijing 100083, China.

0020-1693/90/$3.50

TABLE 1. Crystal data and structure determination parameters

	$(TPTC)_2$·*meso*-BPSE	$(TPTC)_2$·*rac*-BPSE
Formula	$C_{50}Cl_2H_{44}O_2S_2Sn_2$	$C_{50}Cl_2H_{44}O_2S_2Sn_2$
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a (Å)	8.813(2)	8.783(2)
b (Å)	22.920(5)	23.012(5)
c (Å)	11.929(4)	11.921(2)
β (°)	104.16(2)	103.89(2)
Z	2	2
Absorption coefficient (cm^{-1})	13.1	13.1
No. unique reflections	4442	4456
No. unique reflections with $I \geqslant 3\sigma(I)$	2485	3013
Refinement	full-matrix least-squares	full-matrix least-squares
R	0.063	0.052

Both structures were solved by using the Patterson heavy-atom method which revealed the position of the tin atom and all other non-hydrogen atoms were located from subsequent Fourier syntheses. The maximum final different Fourier peak was 1.6 e/Å^3 for **I** and 2.45 e/Å^3 for **II** respectively. All the peaks of more than 1 e/Å^3 were located in close proximity to the tin atom. The calculations were performed with the SDP-PLUS program system on a PDP11/44 computer. Crystal parameters and details of the data collection and structure solution are summarized in Table 1.

Results and Discussion

General Properties

Elementary analyses and crystal structures of the complexes clearly indicate the formation of $(TPTC)_2$·L. Infrared data are presented in Table 2. The fact that ν(SO) shifts to the lower frequencies after complexing in all instances is evidence that the ligands are bonded to the metal ions via the oxygen atoms. Sn–O absorbtion is at 453 cm^{-1}. **I** and **II** have identical composition, IR spectra, crystal data and melting points, suggesting that they may be one compound. They can easily dissolve in alcohol, acetone and chloroform and decompose around 170 °C.

Two complexes of TPTC·L with different properties have also been prepared when the ligands are *meso* and *rac* BPSE respectively [6, 16], so solvent and temperature are very important conditions for the preparation of the tin complexes.

Molecular Structure (Fig. 1)

I and **II** have been proved to be one complex by X-ray single crystal analyses. The complex molecule lies on a crystallographic center of symmetry situated at the center of the C–C′ single bond of the bidentate disulfoxide ligand. One ligand is bonded to two symmetry-related tin atoms to form a bridged species. The unique tin atom exhibits a trigonal bipyramidal environment and is bonded to three phenyl groups in the equatorial plane and to a chlorine and an oxygen atom in axial positions. Tin and chlorine atoms are on one side of the plane [formed by C(11), C(21), C(31)] while the oxygen atom is on the other side. Sulfur atoms in the complexes are chiral atoms with a distance of sulfur to plane [O, C and C(41)] about 0.72 Å. The S–O bond length is 1.53 Å [ν(SO) = 990 cm^{-1}], which

TABLE 2. Characterization of ligands and complexes

	Melting point (°C)	Boiling point[a] (°C)	ν(S=O) (cm^{-1})	ν(Sn–O) (cm^{-1})
$(SnPh_3Cl)_2$·*meso*-BPSE	140[b]	500	990	453
$(SnPh_3Cl)_2$·*rac*-BPSE	141[b]		990	453
$SnPh_3Cl$·*meso*-BPSE	134–137[c]		990[c]	450[c]
$SnPh_3Cl$·*rac*-BPSE	107–109[c]		989[c]	452, 425[c]
meso-BPSE	166–167		1036	
rac-BPSE	120–122		1036	

[a] Temperature at which the weight of TG is zero. [b] Temperature at the first peak of DTA. [c] Ref. 6.

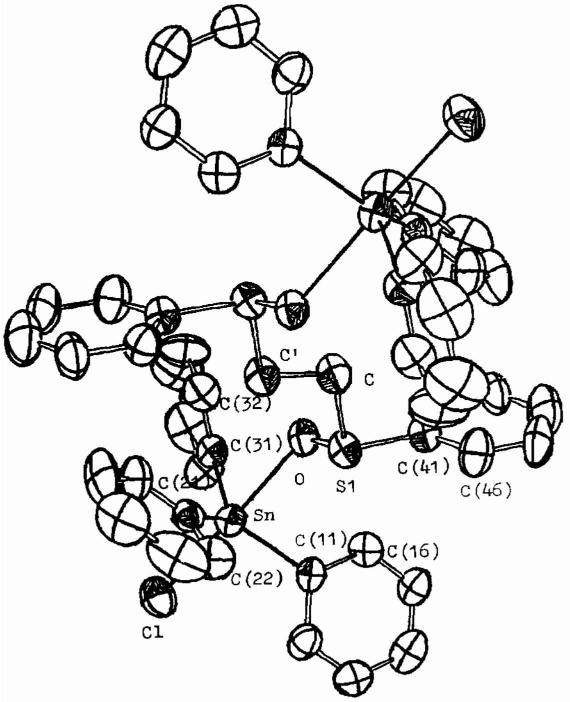
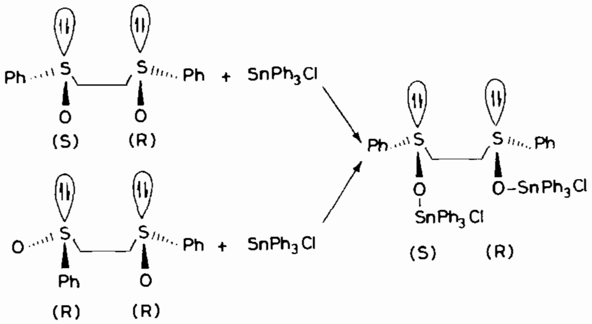


Fig. 1. Molecular structure of $(TPTC)_2 \cdot BPSE$.

TABLE 3. Atomic coordinates ($\times 10^4$, $\times 10^5$ for Sn) for $(SnPh_3Cl)_2 \cdot$*meso*-BPSE

	x/a	*y/b*	*z/c*	B_{eq}
Sn	41240(10)	38321(4)	23360(7)	3.17(1)
C(11)	5830(20)	4472(5)	3024(9)	3.0(2)
C(12)	7370(20)	4407(6)	2810(10)	4.4(3)
C(13)	8540(20)	4781(7)	3310(10)	5.3(4)
C(14)	8260(20)	5239(7)	3990(10)	5.2(4)
C(15)	6760(20)	5309(6)	4180(10)	4.2(3)
C(16)	5580(10)	4927(6)	3677(9)	3.6(3)
C(21)	3240(10)	3773(6)	0530(10)	3.5(3)
C(22)	3970(20)	4117(7)	−0220(10)	5.3(4)
C(23)	3410(20)	4046(9)	−1400(10)	7.3(5)
C(24)	2280(20)	3658(8)	−1870(10)	7.5(5)
C(25)	1570(20)	3337(7)	−1180(10)	7.1(4)
C(26)	2090(20)	3389(6)	0060(10)	4.9(3)
C(31)	2770(10)	3475(6)	3420(10)	3.4(3)
C(32)	1200(20)	3457(6)	3160(10)	4.7(3)
C(33)	0350(20)	3180(8)	3820(10)	6.4(4)
C(34)	1110(20)	2894(9)	4800(10)	7.5(4)
C(35)	2690(20)	2907(8)	5100(10)	6.9(4)
C(36)	3570(20)	3185(7)	4440(10)	5.0(3)
S(1)	2183(4)	5173(1)	1302(3)	3.47(7)
Cl	5962(5)	3025(2)	2468(3)	5.27(9)
O	2120(10)	4653(4)	2086(7)	3.6(2)
C	0170(10)	5260(6)	0420(10)	4.1(3)
C(41)	2240(10)	5806(5)	2150(10)	3.5(3)
C(42)	1940(20)	5767(6)	3240(10)	4.4(3)
C(43)	2030(20)	6260(6)	3920(20)	5.1(3)
C(44)	2380(20)	6781(7)	3500(20)	6.8(5)
C(45)	2690(20)	6833(6)	2430(20)	6.1(4)
C(46)	2620(20)	6335(6)	1760(10)	5.3(4)



Scheme 1. Reaction stereochemistry.

is longer than that in free ligands [1.487(2)–1.494(6) Å; ν(SO) = 1033–1037 cm^{-1}] and S-bonded complexes [1.40(2)–1.47(1) Å; ν(SO) = 1153 cm^{-1}] [3]. Atomic coordinates are given in Table 3; bond distances and angles for $(SnPh_3Cl)_2 \cdot$*meso*-BPSE in Tables 4 and 5 respectively.

Stereochemistry (Scheme 1)

There are two chiral sulfur atoms for every complex or ligand molecule. The absolute configurations of the atoms are *RS* for *meso*-BPSE; *RR* or *SS* for *rac*-BPSE; *RS* for $(TPTC)_2 \cdot BPSE$. Hence when *rac*-BPSE reacts with TPTC to form a 1:2 adduct configurational inversion happens for one sulfur atom. This phenomenon has not been reported for disulfoxides before.

Supplementary Material

Supplementary material including Tables of bond angles and bond distances for $(SnPh_3Cl)_2 \cdot$*rac*-BPSE may be obtained on request from one of the authors.

TABLE 4. Bond distances (Å) for $(SnPh_3Cl)_2 \cdot$*meso*-BPSE

Sn–C(11)	2.119(6)	C(31)–C(32)	1.340(9)
Sn–C(21)	2.113(6)	C(31)–C(36)	1.414(9)
Sn–C(31)	2.124(6)	C(32)–C(33)	1.364(9)
Sn–Cl	2.439(2)	C(33)–C(34)	1.363(12)
Sn–O	2.550(4)	C(34)–C(35)	1.351(13)
C(11)–C(12)	1.440(9)	C(35)–C(36)	1.393(11)
C(11)–C(16)	1.353(8)	S(1)–O	1.525(4)
C(12)–C(13)	1.366(10)	S(1)–C	1.837(6)
C(13)–C(14)	1.385(11)	S(1)–C(41)	1.760(7)
C(14)–C(15)	1.403(10)	C(41)–C(42)	1.402(9)
C(15)–C(16)	1.382(9)	C(41)–C(46)	1.364(9)
C(21)–C(22)	1.448(10)	C(42)–C(43)	1.382(9)
C(21)–C(26)	1.354(9)	C(43)–C(44)	1.361(12)
C(22)–C(23)	1.387(11)	C(44)–C(45)	1.385(13)
C(23)–C(24)	1.348(13)	C(45)–C(46)	1.383(11)
C(24)–C(25)	1.363(13)	C–C′	1.539
C(25)–C(26)	1.441(11)		

TABLE 5. Bond angles (°) for $(SnPh_3Cl)_2$·*meso*-BPSE

C(11)–Sn–C(21)	119.3(2)	C(23)–C(24)–C(25)	120.6(7)
C(11)–Sn–C(31)	118.9(2)	C(24)–C(25)–C(26)	119.6(8)
C(11)–Sn–Cl	95.9(2)	C(21)–C(26)–C(25)	119.6(8)
C(11)–Sn–O	86.7(2)	Sn–C(31)–C(32)	125.3(5)
C(21)–Sn–C(31)	118.3(2)	Sn–C(31)–C(36)	117.8(5)
C(21)–Sn–Cl	95.3(2)	C(32)–C(31)–C(36)	116.6(7)
C(21)–Sn–O	81.7(2)	C(31)–C(32)–C(33)	124.4(8)
C(31)–Sn–Cl	97.6(2)	C(32)–C(33)–C(34)	119.5(8)
C(31)–Sn–O	83.0(2)	C(33)–C(34)–C(35)	118.5(8)
Cl–Sn–O	176.7(1)	C(34)–C(35)–C(36)	122.4(8)
Sn–C(11)–C(12)	117.9(5)	C(31)–C(36)–C(35)	118.6(8)
Sn–C(11)–C(16)	123.5(5)	O–S(1)–C	105.1(3)
C(12)–C(11)–C(16)	118.6(6)	O–S(1)–C(41)	107.1(3)
C(11)–C(12)–C(13)	120.2(7)	C–S(1)–C(41)	97.3(3)
C(12)–C(13)–C(14)	120.3(8)	Sn–O–S(1)	121.2(5)
C(13)–C(14)–C(15)	119.5(7)	S(1)–C(41)–C(42)	119.7(5)
C(14)–C(15)–C(16)	119.9(7)	S(1)–C(41)–C(46)	121.5(5)
C(11)–C(16)–C(15)	121.5(6)	C(42)–C(41)–C(46)	119.2(7)
Sn–C(21)–C(22)	118.8(5)	C(41)–C(42)–C(43)	119.9(7)
Sn–C(21)–C(26)	120.9(5)	C(42)–C(43)–C(44)	119.2(8)
C(22)–C(21)–C(26)	120.1(6)	C(43)–C(44)–C(45)	122.2(8)
C(21)–C(22)–C(23)	117.2(8)	C(44)–C(45)–C(46)	117.9(8)
C(22)–C(23)–C(24)	122.8(9)	C(45)–C(46)–C(41)	121.6(8)
S–C–C′	107.4(9)		

Acknowledgement

The authors are grateful to the National Natural Science Foundation of China for support of their work.

References

1 (a) M. Cinquini and S. Colonna, *Int. J. Sulfur Chem.*, *4* (1976) 603; (b) H. Nieuwenhuyse and R. Louw, *J. Chem. Soc., Perkin Trans 1*, (1973) 839; (c) A. L. Ternay, Jr., *Q. Rep. Sulfur Chem.*, *3* (1968) 145; (d) H. Nieuwenhuyse and R. Louw, *Chem. Commun.*, (1968) 1561; (e) M. Cinquini, S. Colonna and F. Taddei, *Boll. Chim. Sci. Fac. Ind. Bologna, 27* (1969) 231.

2 T. Svinnig, F. Mo and T. Bruun, *Acta Crystallogr., Sect. B, 32* (1976) 759.

3 L. Cattalini, G. Michelon, G. Marangoni and G. Pelizzi, *J. Chem. Soc., Dalton Trans.*, (1976) 96.

4 G. Pelizzi, G. Michelon and M. Bonivento, *Cryst. Struct. Commun., 5* (1976) 617.

5 P. X. Shao, F. C. Zhu, X. K. Yao, H. G. Wang and R. J. Wang, *Chem. J. Chinese Univ., 9* (1989) 821.

6 C. A. L. Filgueiras, C. Celso, E. V. Marques and B. F. G. Johnson, *Inorg. Chim. Acta, 59* (1982) 71.

7 C. A. L. Filgueiras, P. R. Holland, B. F. G. Johnson and P. R. Raithby, *Acta Crystallogr., Sect. B, 38* (1982) 2684.

8 S. K. Madan, C. M. Hull and L. J. Herman, *Inorg. Chem., 7* (1968) 491.

9 T. R. Musgrave and G. D. Kent, *J. Coord. Chem., 2* (1972) 23.

10 A. P. Zipp and S. K. Madan, *Inorg. Chim. Acta, 22* (1977) 49.

11 C. A. L. Filgueiras and C. Celso, *Transition Met. Chem., 9* (1984) 158.

12 C. A. L. Filgueiras and E. V. Marques, *Transition Met. Chem., 10* (1985) 241.

13 (a) R. H. Zhang, Z. C. Huang and F. C. Zhu, *Acta Chim. Sin., 44* (1986) 513; (b) R. H. Zhang, F. C. Zhu, Q. S. Xue and Z. C. Huang, *J. Chin. Rare Earth Soc., 5*(3) (1987) 7.

14 A. P. Zipp and S. G. Zipp, *J. Inorg. Nucl. Chem., 42* (1980) 395.

15 G. Pelizzi, G. Michelon, G. Annibale and L. Cattalini, *Cryst. Struct. Commun., 5* (1976) 625.

16 A. Abras, F. J. Berry, J. G. Holden and C. A. L. Filgueiras, *Inorg. Chim. Acta, 74* (1983) 135.

17 P. X. Shao, M. D. Gui and J. T. Chen, *Chem. Reag., 1* (1983) 39.