APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2003; **17**: 623–630
Published online in Wiley InterScience (www.interscience.wiley.com). DOI:10.1002/aoc.465

Synthesis, properties and crystal structural characterization of diorganotin(IV) derivatives of 2-mercapto-6-nitrobenzothiazole

Chunlin Ma[1,2]*, Qin Jiang[1] and Rufen Zhang[1]

[1]Department of Chemistry, Liaocheng University, Liaocheng 252059, People's Republic of China
[2]Department of Chemistry, Taishan University, Taian 271021, People's Republic of China

Received 5 November 2002; Revised 18 November 2002; Accepted 14 February 2003

The diorganotin(IV) dichlorides R_2SnCl_2 (R: Ph, $PhCH_2$ or *n*-Bu) react with 2-mercapto-6-nitrobenzothiazole (MNBT) in benzene to give $[Ph_2SnCl(MNBT)]$ (1), $[(PhCH_2)_2Sn(MNBT)_2]$ (2) and $[(n\text{-}Bu)_2Sn(MNBT)_2]$ (3). The three complexes have been characterized by elemental analysis and IR, ^1H, ^{13}C and ^{119}Sn NMR spectroscopies. X-ray studies of the crystal structures of 1, 2 and 3 show the following. The tin environment for complex 1 is distorted cis-trigonal bipyramid with chlorine and nitrogen atoms in apical positions. The structure of complex 2 is a distorted octahedron with two benzyl groups in the axial sites. The geometry at the tin atom of complex 3 is that of an irregular octahedron. Interestingly, intra-molecular non-bonded Cl···S interactions and S···S interaction were recognized in the crystallographic structures of 1 and 3 respectively. As a result, complex 1 is a polymer and complex 3 is a dimer. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: organotin; 2-mercapto-6-nitrobenzothiazole; crystal structure; non-bonded interaction; antitumour activity

INTRODUCTION

The environmental and biological chemistry of organotin(IV) complexes have been the subjects of interest for some time due to their increasingly widespread use.[1,2] In particular, a few diorganotin(IV) derivatives have been shown to exhibit *in vitro* antitumour properties against a wide panel of tumoral cell lines of human origin,[3–5] among which metallo-complexes of 2-mercaptobenzothiazole (HMBT) and the related 2-mercaptobenzoxazole (HMBO) have been extensively studied for both the diversity of their commercial application and the richness of their structural chemistry. Our interest in the structures and activity patterns for diorganotin(IV) complexes has recently prompted us to embark on a study of the ligand 2-mercapto-6-nitrobenzothiazole (MNBT). The ligand is interesting because of its potential dual bidentate coordinate possibilities, so that bonding takes place either from the heterocyclic nitrogen or from the thiol sulfur. And as literature reported, chelation by both sulfur and nitrogen atoms is commonly observed in dialkyltin compounds.[6] In this paper, we report in some detail the synthesis, structure and activity patterns of three diorganotin(IV) derivatives of MNBT.

*Correspondence to: Chunlin Ma, Department of Chemistry, Liaocheng University, Liaocheng 252059, People's Republic of China.
E-mail: macl@lctu.edu.cn
Contract/grant sponsor: National Natural Foundation; Contract/grant number: 20271025.
Contract/grant sponsor: Key Teachers Foundation from the State Education Ministry of China.
Contract/grant sponsor: Natural Foundation of Shandong Province.

EXPERIMENTAL

Materials and methods

Diphenyltin chloride, di-*n*-butyltin chloride and MNBT were commercially available, and they was used without further purification. Dibenzyltin chloride was prepared by a standard method reported in the literature.[7] The melting points were obtained with Kofler micro melting point apparatus and were uncorrected. IR spectra were recorded on a Nicolet-460 spectrophotometer using KBr discs and sodium chloride optics. ^1H, ^{13}C and ^{119}Sn NMR spectra were recorded on a Bruker AMX-300 spectrometer operating at 300 MHz, 75.3 MHz and 111.9 MHz respectively. The spectra were acquired at room temperature (298 K) unless specified otherwise; ^{13}C spectra are broadband proton decoupled. The chemical shifts are reported in parts per million with

respect to the references and are stated relative to external tetramethylsilane (TMS) for ^{1}H and ^{13}C NMR, and to neat tetramethyltin for ^{119}Sn NMR. Elemental analyses were performed with a PE-2400II apparatus.

Syntheses

*[$Ph_2SnCl(MNBT)$] (**1**)*

The reaction was carried out under nitrogen atmosphere. The MNBT thiazole (0.424 g, 2 mmol) and sodium ethoxide (0.136 g, 2 mmol) were added to a solution of absolute benzene (20 ml) in a Schlenk flask and stirred for 0.5 h. After the diphenyltin dichloride (0.343 g, 1 mmol) was added to the reactor, the reaction mixture was stirred for 12 h at 40 °C and then filtered. The filtered solution was gradually removed by evaporation under vacuum until solid product was obtained. The solid was then recrystallized from ether–dichloromethane. The buff crystal complex **1** was formed. Yield (pure product): 89%. M.p. 100–102 °C. Anal. Found: C, 43.86; H, 2.52; N, 5.29. Calc. for $C_{19}H_{13}ClN_2O_2S_2Sn$: C, 43.91; H, 2.52; N, 5.39%. ^{1}H NMR ($CDCl_3$): 7.46–7.79 (m, 13H, aromatic-H, $^3J_{SnH} = 89$ Hz). IR (KBr): ν_{as}(Sn–C), 278 cm^{-1}; ν_s(Sn–C), 232 cm^{-1}; ν(Sn–Cl), 266 cm^{-1}; ν(Sn–S), 290 cm^{-1}; ν(Sn–N), 448 cm^{-1}; ν(C–S), 748 cm^{-1}; ν(C=N), 1599 cm^{-1}. ^{13}C NMR ($CDCl_3$): 112.4(C(4)), 122.5(C(1)), 124.7 ($^3J_{SnC} = 50$ Hz, *m*-C), 129.6 ($^4J_{SnC} = 12$ Hz, *p*-C), 136.9 ($^2J_{SnC} = 36$ Hz, *o*-C), 142.2 (C(2)), 144.6 (C(5)), 145.1 (C(3)), 146.5 ($^1J_{SnC} = 489$ Hz, *i*-C). ^{119}Sn NMR ($CDCl_3$): −179.6.

*[$PhCH_2)_2Sn(MNBT)_2$] (**2**)*

The reaction mixture of the ligand MNBT (0.424 g, 2 mmol) and sodium ethoxide (0.136 g, 2 mmol) in benzene (20 ml) and dibenzyltin dichloride (0.371 g, 1 mmol) in a Schlenk flask was stirred for 12 h at 40 °C, cooled to room temperature and evaporated under vacuum. The solid was recrystallized from ether. Jade-green crystal complex **2** was formed. Yield: 92%. M.p. 196–198 °C. Anal. Found: C, 46.13; H, 2.70; N, 10.86. Calc. for $C_{28}H_{20}N_4O_4S_4Sn$: C, 46.50; H, 2.79; N, 10.62%. ^{1}H NMR ($CDCl_3$): 7.32–7.86 (m, 16H, aromatic-H), 3.26 ($^2J_{SnH} = 86$ Hz, 4H, CH_2–Ph). IR (KBr): ν(Sn–S), 265 and 271 cm^{-1}; ν_{as}(Sn–C), 468 cm^{-1}; ν_s(Sn–C), 426 cm^{-1}; ν(Sn–N), 455 cm^{-1}; ν(C–S), 750 cm^{-1}; ν(C=N), 1598 cm^{-1}. ^{13}C NMR ($CDCl_3$): 38.5 (CH_2–Ph, $^1J_{SnC} = 546$ Hz), 112.3 (C(4)), 121.4 (C(1)), 125.4 ($^4J_{SnC} = 30$ Hz, *m*-C), 127.0 ($^5J_{SnC} = 26$ Hz, *p*-C), 130.5 ($^3J_{SnC} = 44$ Hz, *o*-C), 139.0 ($^2J_{SnC} = 36$ Hz, *i*-C), 141.2 (C(2)), 142.9 (C(5)), 143.7 (C(3)). ^{119}Sn NMR ($CDCl_3$): −221.4.

*[(n-$Bu)_2Sn(MNBT)_2$] (**3**)*

The reaction mixture of the ligand MNBT (0.424 g, 2 mmol) and sodium ethoxide (0.136 g, 2 mmol) in benzene (20 ml) and di-*n*-butyltin dichloride (0.363 g, 1 mmol) in a Schlenk flask was stirred for 12 h at 50 °C, cooled to room temperature and evaporated under vacuum. The solid was recrystallized from ether. Yellow crystal complex **3** was formed. Yield: 90%. M.p. 146–148 °C. Anal. Found: C, 40.46; H, 3.52; N, 8.69. Calc. for $C_{22}H_{24}N_4O_4S_4Sn$: C, 40.33; H, 3.69; N, 8.55%. ^{1}H NMR ($CDCl_3$): 7.24–7.90 (m, 6H, aromatic-H), 0.90–1.10 m, 1.05–1.28 m (m, 18H, $^2J_{SnH} = 94$ Hz). IR (KBr): ν(Sn–S), 270 and 275 cm^{-1}; ν_{as}(Sn–C), 529 cm^{-1}; ν_s(Sn–C), 461 cm^{-1}; ν(Sn–N), 457 cm^{-1}; ν(C–S), 751 cm^{-1}; ν(C=N), 1597 cm^{-1}. ^{13}C NMR ($CDCl_3$): 113.5, 116.1, 125.8, 128.4, 129.7, 140.1, 142.2 (aromatic-C), 13.4, 26.0, 27.5, 29.4 (^{n}Bu, $^1J_{SnC} = 504.8$ Hz, $^2J_{SnC} = 36.6$ Hz, $^3J_{SnC} = 101.7$ Hz). ^{119}Sn NMR ($CDCl_3$): −120.5.

In vitro antitumour activity tests of complexes 1, 2 and 3

The samples for antitumour activity tests were prepared by dissolving the complexes **1**, **2** and **3** in dimethylsulfoxide, and by diluting the solution with water to a concentration of 10 μg ml^{-1}, then, according to the literature method, determining the inhibition rate of complexes **1**, **2** and **3** against culture cells of Ehrlich ascites carcinoma.[8]

X-ray crystallography

All X-ray crystallographic data were collected on a Bruker SMART CCD 1000 diffractometer. A criterion of observability was used for the solution and refinement. The structure was solved by direct methods and refined by a full-matrix least-squares procedure based on F^2 using the SHELXL-97 program system. All data were collected at 298(2) K using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and the $\omega/2\theta$ scan technique, and corrected for Lorentz and polarization effects but not for absorption. All non-hydrogen atoms were included in the model at their calculated positions. The positions of hydrogen atoms were calculated, and their contributions in structural factor calculations were included.

*Crystal data for complex **1***

Formula $C_{19}H_{13}ClN_2O_2S_2Sn$, $M = 519.57$, triclinic, space group $P\bar{1}$, $a = 12.961(6)$, $b = 13.835(7)$, $c = 16.412(8)$ Å, $\alpha = 69.184(8)°$, $\beta = 89.862(9)°$, $\gamma = 62.579(8)°$, $V = 2395(2)$ Å^3, $Z = 4$, $D_c = 1.441$ g cm^{-3}, $\mu = 1.367$ mm^{-1}, $F(000) = 1024$. GoF = 0.75, 13 476 reflections collected ($\theta = 1.80°$ to 26.63°) to give the all-data $R_1 = 0.209$ and $wR_2 = 0.118$, 9316 of which were used in the refinement to give the final $R_1 = 0.059$ and $wR_2 = 0.083$. Residual electron density: 0.60 and −0.64 e$^-$ Å^{-3}.

*Crystal data for complex **2***

Formula $C_{28}H_{20}N_4O_4S_4Sn$, $M = 723.41$, triclinic, space group $P\bar{1}$, $a = 8.625(2)$, $b = 12.842(3)$, $c = 14.093(3)$ Å, $\alpha = 91.895(3)°$, $\beta = 95.351(3)°$, $\gamma = 108.807(3)°$, $V = 1468.0(6)$ Å^3, $Z = 2$, $D_c = 1.637$ g cm^{-3}, $\mu = 1.196$ mm^{-1}, $F(000) = 724$. GoF = 1.01, 6531 reflections collected ($\theta = 1.45°$ to 24.78°) to give the all-data $R_1 = 0.048$ and $wR_2 = 0.070$, 4810 of which were used in the refinement to give the final $R_1 = 0.034$ and $wR_2 = 0.071$. Residual electron density: 0.50 and −0.43 e$^-$ Å^{-3}.

*Crystal data for complex **3***

Formula $C_{22}H_{24}N_4O_4S_4Sn$, $M = 655.38$, monoclinic, space group $P2(1)/c$, $a = 8.703(3)$, $b = 26.587(10)$, $c = 12.225(5)$ Å,

$\alpha = \gamma = 90°$, $\beta = 106.414(6)°$, $V = 2713.6(18)$ Å^3, $Z = 4$, $D_c = 1.604$ g cm^{-3}, $\mu = 1.285$ mm^{-1}, $F(000) = 1320$. GoF = 0.86, 14 091 reflections collected ($\theta = 1.53°$ to $24.79°$) to give the all-data $R_1 = 0.142$ and $wR_2 = 0.163$, 4668 of which were used in the refinement to give the final $R_1 = 0.056$ and $wR_2 = 0.131$. Residual electron density: 0.54 and -0.52 e$^-$ Å^{-3}.

RESULTS AND DISCUSSION

The synthesis procedure was as shown in Scheme 1.

IR data

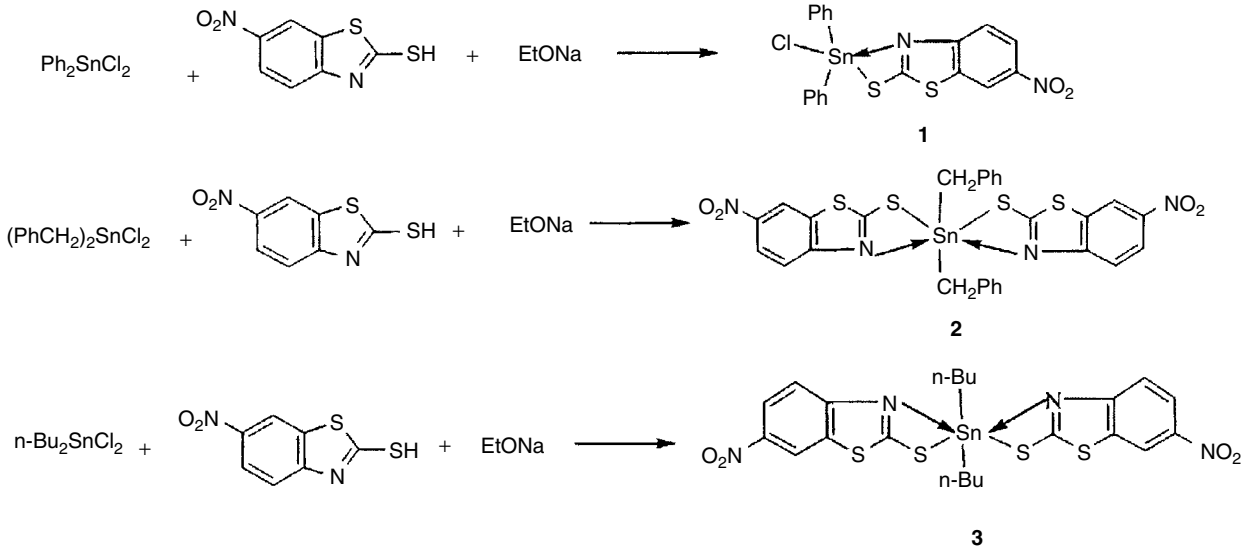
The explicit feature in the IR spectra of the three complexes is the absence of the band in the region 2550–2430 cm^{-1}, which appears in the free-ligand as the ν(S–H) vibration, thus indicating metal–ligand bond formation through this site. In the far-IR spectra, the strong absorption at 290 cm^{-1} for complex **1**, 265 and 271 cm^{-1} for complex **2** and 270 and 275 cm^{-1} for complex **3**, which is absent in the spectrum of the ligand, is assigned to the Sn–S stretching mode of vibration and all the values are consistent with those detected for a number of organotin(IV)–sulfur derivatives.[9] Medium-intensity bands at 278 and 232 cm^{-1} for complex **1**, 468 and 426 cm^{-1} for complex **2** and 529 and 461 cm^{-1} for complex **3** can be assigned to ν_{as}(Sn–C) and ν_s(Sn–C). The ν(C=N) band, occurring at about 1598 cm^{-1}, is considerably shifted towards lower frequencies with respect to that of the free ligand, confirming the coordination of the heterocyclic nitrogen to the tin. The stretching frequency is lowered owing to the displacement of electron density from the nitrogen to the tin atom, thus resulting in the weakening of the C=N bond as reported in the literature.[10] Thus, the weak- or medium-intensity bands at 448 cm^{-1} for complex **1**, 455 cm^{-1} for complex **2** and 457 cm^{-1} for complex **3** can be assigned to Sn–N stretching vibrations. The stretching frequency ν(C–S) in complex **1** is shifted to a lower value than those of complexes **2** and **3**.

NMR data

^{1}H NMR data showed that the signal of the –SH proton in the spectrum of the ligand is absent in all of the adducts, indicating the removal of the SH proton and the formation of Sn–S bonds. The information accords well with what the IR data have revealed. Moreover, the ^{1}H NMR spectra of complex **1** shows two multiplets attributable to the H(2,6) and H(3,4,5) of the phenyl protons. The resonance of H(2,6) has tin satellites with $^3J_{SnH}$ (89 Hz) greater than in uncomplexed Ph_2SnCl_2 (81.3 Hz).[11] The increase in the coupling constant indicates the higher coordination number of tin. The magnitudes of the tin(IV)–proton coupling constants for complexes **2** and **3** are different from those reported in the literature for the starting tetracoordinate diorganotin(IV) halides,[12,13] but they are smaller with respect to those indicated for hexacoordinate undissociated organotin(IV) complexes containing nitrogen-donor ligands;[14,15] this suggests a partial dissociation of our complexes in solution.

The ^{13}C NMR spectra of all three complexes show a significant downfield shift of all carbon resonances compared with the free ligand. The shift is a consequence of an electron density transfer from the ligand to the acceptor, which is consistent with that reported in the literature.[10,16]

The ^{119}Sn NMR value for **1** at -179.6 ppm in solution suggests that the Sn–N interaction probably survives in solution and that a five-coordinate species is maintained. Five-coordinate $ClPh_2SnXY$ compounds (X and Y are electronegative groups) in solution have an ^{119}Sn NMR value in the region -140 to -180 ppm, depending on the groups



Scheme 1.

present.[11,17,18] The chemical shift for complex **2** (−221.4 ppm) is somewhat different from the values (−300 to −500 ppm) expected for the six-coordinated tin(IV) compounds,[19] suggesting that the coordination is asymmetrical, with the two nitrogen atoms held more weakly than the two sulfur atoms. The chemical shift for complex **3** (−120.5 ppm) is not informative enough, as it can belong to penta- or weakly hexa-coordinated diorganotin(IV) complexes.[6]

Complementary information for the three complexes is given by the values of the coupling constant. The $^{1}J_{SnC}$ value for **1** is 489 Hz, and the calculated θ (C–Sn–C) according to the Lockhart equation[20] is 119°, corresponding to a geometry around the tin that can be classed as trigonal bipyramidal. The $^{n}J_{SnC}$ values ($^{4}J_{SnC} = 32$ Hz, $^{5}J_{SnC} = 26$ Hz, $^{3}J_{SnC} = 44$ Hz, $^{2}J_{SnC} = 38$ Hz) for **2** are in keeping with those usually found for weakly six-coordinate dibenzyltin compounds.[21] The $^{1}J_{SnC}$ value (504.8 Hz) for **3** is in agreement with those of penta-coordinate dibutyltin compounds (range 480–540 Hz).[15] So it can reasonably be assumed that the structure of complex **1** is likely similar to that observed in the solid state, whereas the distorted octahedral structure of complexes **2** and **3** observed in the solid state is not retained upon partial dissolution in solution.

From our NMR data for the three complexes, and following the structural studies, we conclude that the nitrogen ligand is labile, and hence that the mechanism of interaction of organotin complexes in biological systems differs from that of platinum complexes, which retain the Pt–N bonds when reacting with DNA. In organotin compounds, the Sn–N bonds are probably cleaved before the tin reaches its ultimate target.

Biologic activity measurement

The *in vitro* antitumour activity tests show that the inhibition rates (%) of complexes **1, 2** and**3** against culture cells of Ehrlich ascites carcinoma are 78%, 79% and 86% respectively. Thus, complexes **1, 2** and **3** have a certain biologic activity to Ehrlich ascites carcinoma compared with that of *cis*-$[Pt(NH_3)_2Cl_2]$(55). The butyl derivative **3** was the most active.

X-ray studies

The crystal structure and unit cell of complex **1** are shown in Figs 1 and 2 respectively, and those for complex **2** in Figs 3 and 4 respectively. The crystal structure and crystal packing of complex **3** are shown in Figs 5 and 6 respectively. All hydrogen atoms have been omitted for the purpose of clarity. Tables 1–3 respectively list selected bond lengths and angles for complexes **1**–**3**.

Structure of $[Ph_2SnCl(MNBT)]$ (1)

For complex **1**, the asymmetric unit contains two monomers A and B (Fig. 1), which are different from a crystallographic point of view. The conformations of the two independent molecules A and B are almost the same, with only small

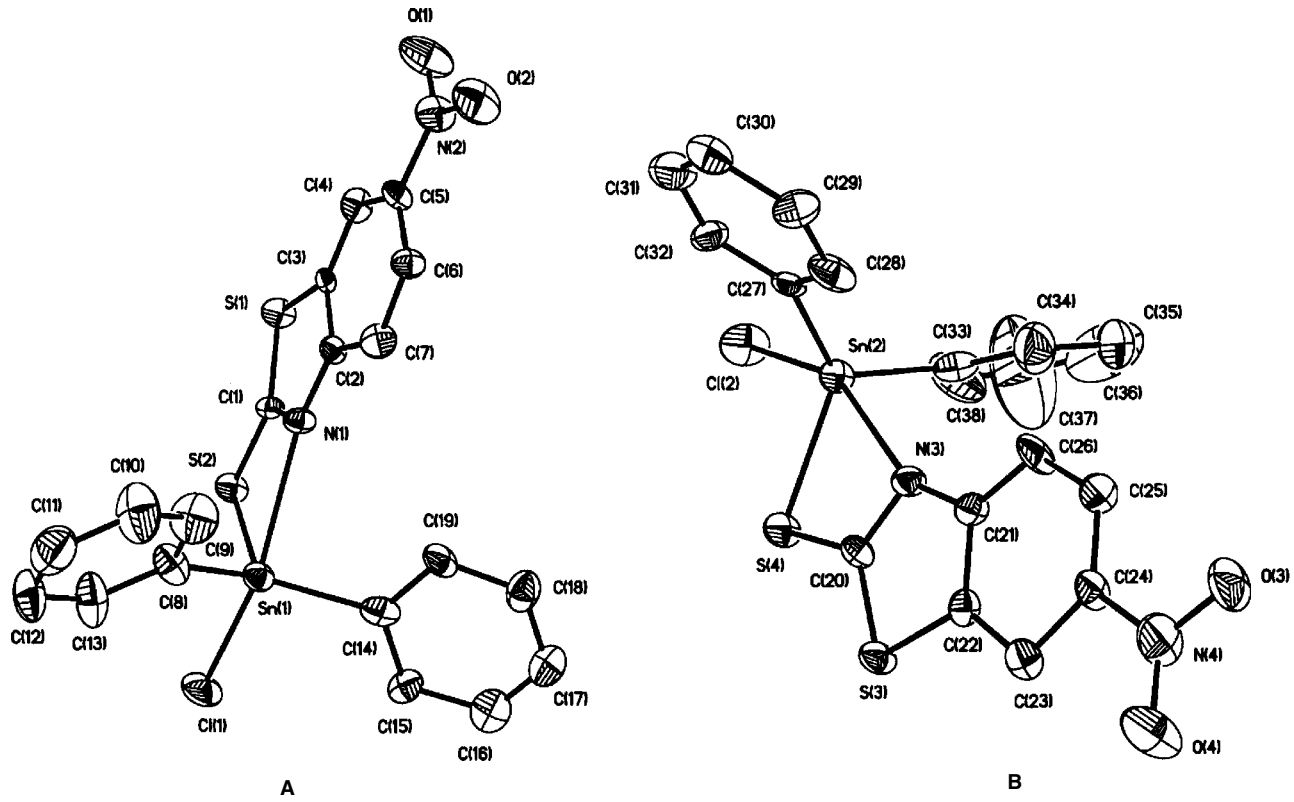


Figure 1. Molecular structure of complex **1**.

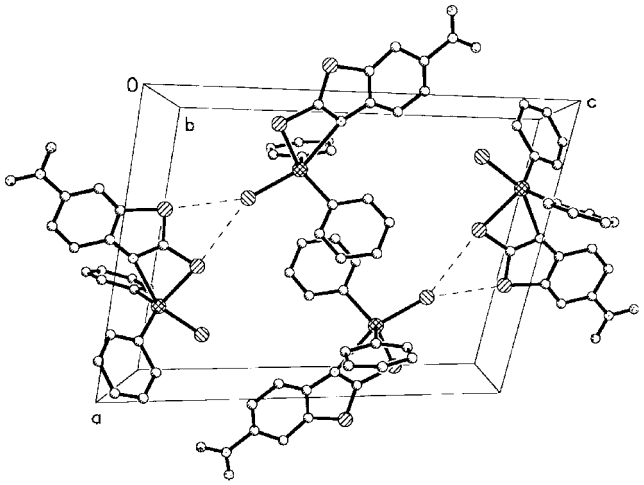


Figure 2. Unit cell of complex **1**.

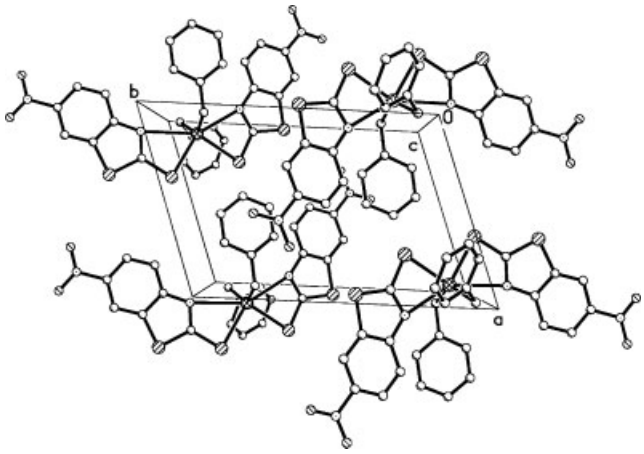


Figure 4. Unit cell of complex **2**.

differences in bond lengths and bond angles (see Table 1). Tin forms four primary bonds: two to the phenyl groups, and one each to sulfur and chlorine atoms. In addition, there exists a coordination interaction between tin and nitrogen atoms. The Sn–N bond length (Sn(1)–N(1), 2.595(7) Å and Sn(2)–N(3), 2.580(6) Å) is consistent with that of [2-(Me_2NCH_2)C_6H_4]$SnPh_2Cl$ (2.519(2) Å),[22] it is longer than that of Ph_2SnCl(MBT) (2.405(7) Å),[17] but it is much shorter than the sum of the van der Waals radii of tin and nitrogen, 3.74 Å,[23] thus providing four-membered chelate rings with bite angles of 62.90(16)° for N(1)–Sn(1)–S(2) and of 63.06(17)° for N(3)–Sn(2)–S(4). Including the tin–nitrogen interaction, the geometry at tin becomes distorted cis-trigonal bipyramidal with chlorine and nitrogen atoms in axial sites (Cl(1)–Sn(1)–N(1), 153.96(16)° and Cl(2)–Sn(2)–N(3), 154.78(18)°) and one sulfur and two phenyl carbon atoms occupying the equatorial plane (C(14)–Sn(1)–C(8), 123.6(4)° and C(33)–Sn(2)–C(27), 123.5(4)°). The sum of the angles subtended at the tin atom in the trigonal plane is 353.6° for A and 353.2° for B, so that the atoms Sn(1), C(8), C(14) and S(2) for A and Sn(2), C(27), C(33) and S(4) for B are almost in the same plane. The Sn–Cl bond length (Sn(1)–Cl(1), 2.367(3) Å and Sn(2)–Cl(2), 2.373(2) Å) lies in

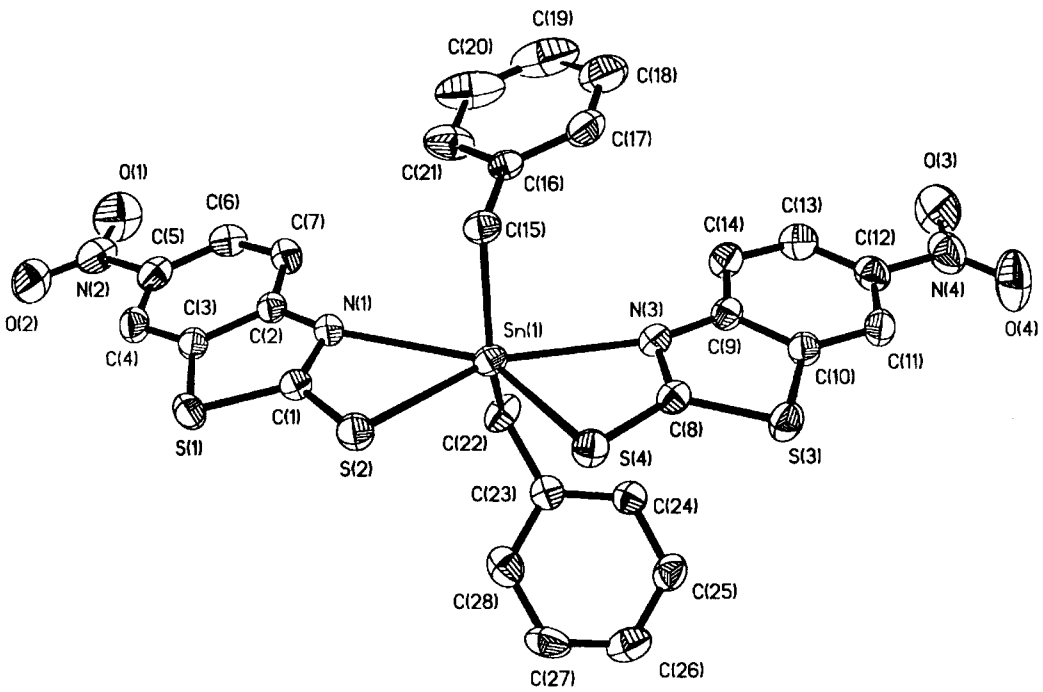


Figure 3. Molecular structure of complex **2**.

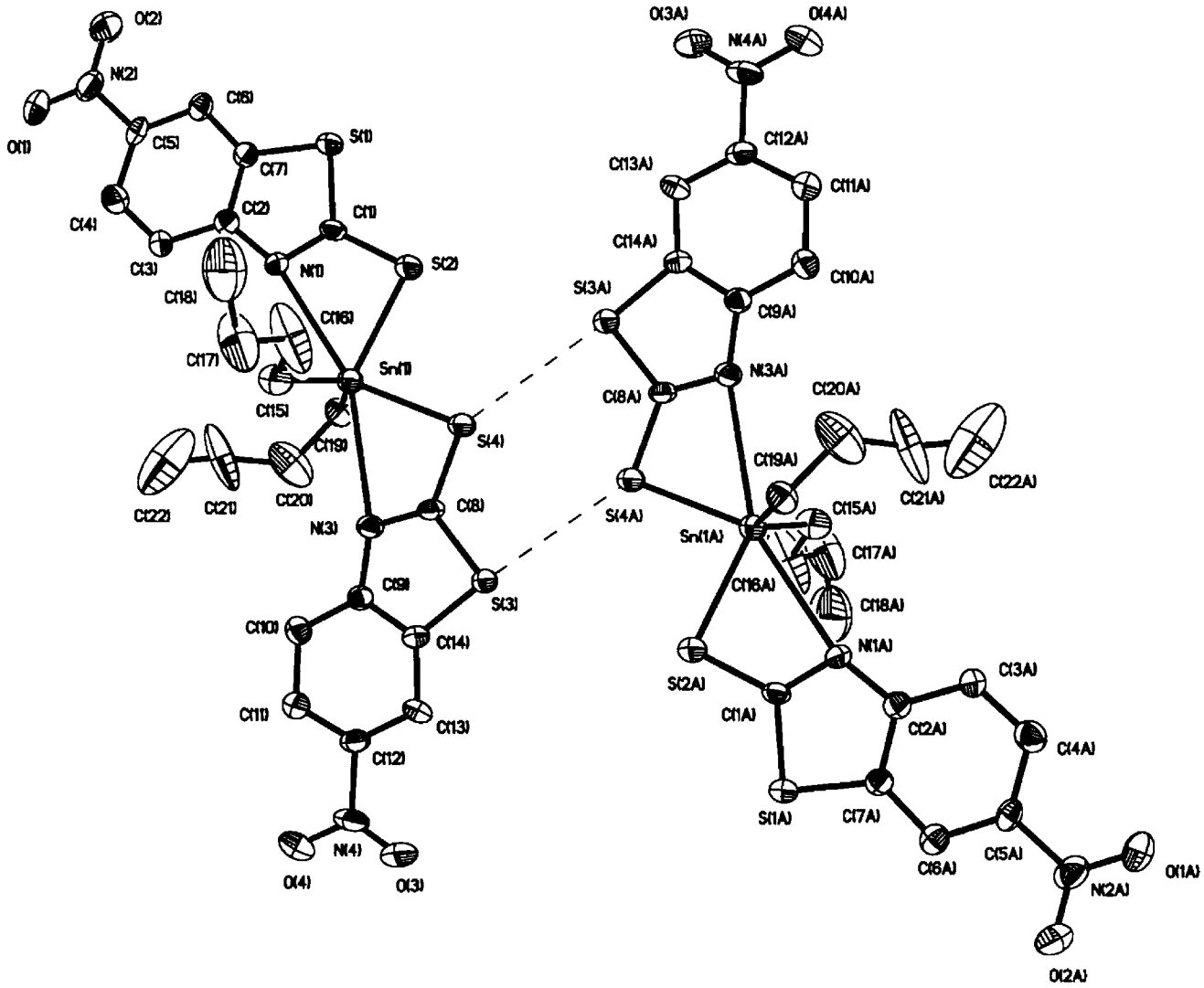


Figure 5. Molecular structure of complex **3**.

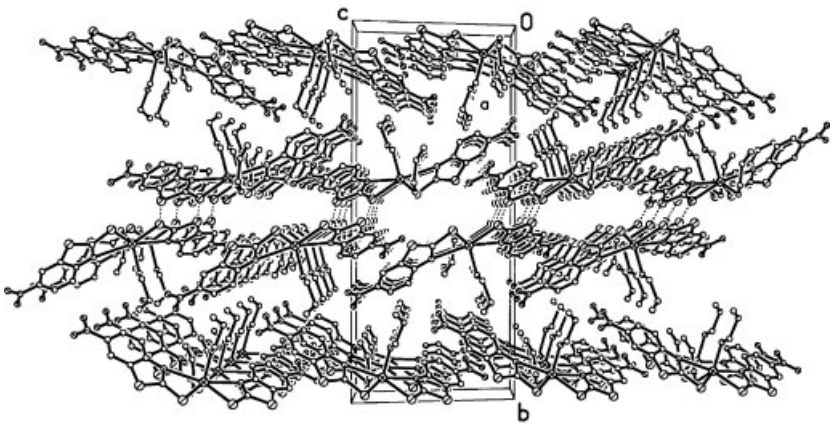


Figure 6. Crystal packing of complex **3**.

Table 1. Selected bond lengths (Å) and angles (°) for complex **1**

Molecule A		Molecule B	
Sn(1)–Cl(1)	2.367(3)	Sn(2)–Cl(2)	2.373(2)
Sn(1)–N(1)	2.595(7)	Sn(2)–N(3)	2.580(6)
Sn(1)–S(2)	2.444(2)	Sn(2)–S(4)	2.446(3)
Sn(1)–C(8)	2.102(12)	Sn(2)–C(27)	2.084(11)
Sn(1)–C(14)	2.066(10)	Sn(2)–C(33)	2.026(12)
Cl(1)···S(5)	3.42	Cl(2)···S(7)	3.44
Cl(1)···S(6)	3.51	Cl(2)···S(8)	3.56
Cl(1)–Sn(1)–N(1)	153.96(16)	Cl(2)–Sn(2)–N(3)	154.78(18)
S(2)–Sn(1)–N(1)	62.90(16)	S(4)–Sn(2)–N(3)	63.06(17)
C(8)–Sn(1)–S(2)	113.9(3)	C(27)–Sn(2)–S(4)	116.6(2)
C(14)–Sn(1)–S(2)	116.1(2)	C(33)–Sn(2)–S(4)	113.1(3)
C(14)–Sn(1)–C(8)	123.6(4)	C(33)–Sn(2)–C(27)	123.5(4)

Table 2. Selected bond lengths (Å) and angles (°) for complex **2**

Sn(1)–N(1)	2.82	Sn(1)–N(3)	2.596(3)
Sn(1)–S(2)	2.5358(12)	Sn(1)–S(4)	2.5239(11)
Sn(1)–C(15)	2.156(4)	Sn(1)–C(22)	2.153(4)
S(4)–Sn(1)–S(2)	89.82(4)	S(4)–Sn(1)–N(3)	62.17(8)
N(1)–Sn(1)–N(3)	148.1	S(2)–Sn(1)–N(1)	59.5
C(22)–Sn(1)–C(15)	133.96(18)		

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

Sn(1)–C(19)	2.139(10)	Sn(1)–C(15)	2.132(11)
Sn(1)–S(2)	2.494(3)	Sn(1)–S(4)	2.498(3)
Sn(1)–N(1)	2.82	Sn(1)–N(3)	2.86
S(3)···S(4)	3.51		
C(15)–Sn(1)–C(19)	131.0(5)	S(4)–Sn(1)–S(2)	86.74(9)
S(4)–Sn(1)–N(3)	58.8	S(2)–Sn(1)–N(1)	59.4
N(1)–Sn(1)–N(3)	155.7		

the range of the normal covalent radii (2.37–2.60 Å).[24] The Sn–S bond length (Sn(1)–S(2), 2.444(2) Å and Sn(2)–S(4), 2.446(3) Å) is well within the range of 2.41 to 2.48 Å reported of triphenyltin heteroarenethiolates,[25] it is shorter than that of $Ph_2SnCl(MBT)$ (2.485(22) Å)[17] and it is almost equal to that of $Ar_3Sn[S(C_5H_4N)]$.[22] Finally, the Sn–C bond lengths are approximately equal (from 2.026(12) and 2.102(12) Å), similar to the average value of 2.13 Å.[24]

Intra-molecular non-bonded S···X (X = O, S, N, etc.) interactions have been investigated for characterization of the molecular structures of a large number of organosulfur compounds,[26] but we have seen little discussion about the Cl···S interaction. In the represented crystalline structure of complex **1**, a relatively close contact (3.42, 3.51 Å for A and 3.44, 3.56 Å for B) between chlorine and sulfur atoms was recognized, which coincides well with that reported in $(Ph_2CH_2)_2SnClS_2CNC_4H_8O$[27] and is much shorter than the sum of the van der Waals radii (3.97 Å[28]) for these atoms. And it is the intra-molecular non-bonded Cl···S interaction that favoured the formation of the polymer of complex **1**.

It is worth noting that, despite using a 1 : 2 : 2 molar ratio of Ph_2SnCl_2 : MNBT : EtONa, we did not obtain the product with two chloride ligands replaced in Ph_2SnCl_2. This result suggests that the spatial resistances from the two phenyl groups are strong enough to prevent another ligand chelating to the central tin atom. The conclusion coincides well with the case of $Ph_2SnCl(MBT)$ reported in literature.[17]

Structures of $[(PhCH_2)_2Sn(MNBT)_2]$ (2) and $[(n\text{-}Bu)_2Sn(MNBT)_2]$ (3)

Both complexes **2** and **3** contain a six-coordinate tin atom. In each case, two carbon atoms and two sulfur atoms are covalently linked to the tin. The valence extension is performed via the nitrogen atoms. The two chelating nitrogen atoms occupy *trans* positions (N(1)–Sn(1)–N(3), 148.1° for **2**; N(1)–Sn(1)–N(3), 155.7° for **3**), whereas the cases for the sulfur bonding vary and they occupy *cis* positions S(2)–Sn(1)–S(4), 89.8(4)° for **2**; S(2)–Sn(1)–S(4), 86.74(9)° for **3**). In addition, on each side of the tin atom, the sulfur and nitrogen equatorial ligating atoms belong to the same moiety (S(2)–Sn(1)–N(1) 59.5° and S(4)–Sn(1)–N(3) 62.17(8)° for **2**; S(2)–Sn(1)–N(1) 59.4° and S(4)–Sn(1)–N(3) 58.8° for **3**), so their positions are fixed and the S–Sn–N angles can only admit very little deformation. In such structures, the sum of

angles between the tin atom and the equatorial ligating atoms (i.e. two nitrogen and two sulfur in each case) is 360.3° for **2** and 360.5° for **3**, compared with the ideal octahedral value of 360°.

The Sn–C bond lengths (2.153(4) Å and 2.156(4) Å in complex **2**; 2.132(11) and 2.139(10) Å in complex **3**) are quite close to those previously described in the literature.[24] It is worth noting that in complex **3** both the Sn–N bond lengths are markedly elongated (2.82 and 2.86 Å) compared with those reported in dibutyltin derivatives of 2-mercaptobenzothiaxazole and 5-chloro-2-mercaptobenzothiazole, with values ranging from 2.68 to 2.82 Å,[6] although they still lie within the sum of their respective van der Waals ratii (3.75 Å). This fact provides evidence of the large influence of the various substitutes in the phenyl group of the ligand. Owing to the effect of the nitryl in the opposite position, the trend of the heterocyclic nitrogen to coordinate to tin is weakened. For complex **2** the Sn–N bond lengths are 2.596(3) and 2.82 Å, which coincide well with the values referred to above[6] but which are still longer than those of the type '$SnCl_2N_2C_2$' recorded in the Cambridge Crystallographic Database,[24] (2.27 to 2.58 Å). Concerning the Sn–S bond lengths, we may note that in both complexes **2** and **3** they are slightly longer than the sum of the atomic radii (2.44 Å[29]): for **2** we have is 2.5239(11) and 2.5358(12) Å and for **3** we have 2.494(3) and 2.498(3) Å.

In addition, intra-molecular non-bonded S···S interactions were noted in the crystallographic analysis of complex **3**, which help in the construction of the dimer of complex **3**. The non-bonded S···S distance (3.51 Å) is longer than those reported in literature[26,27] but is shorter than the sum (3.70 Å) of the van der Waals radii (sulfur and sulfur).[30] There have been several papers that have discussed the non-bonded S···S interaction[31,32] and what we see in complex **3** can be regarded as a supplement to this kind of contact.

Acknowledgements

We thank the National Natural Foundation, People's Republic of China (20271025), the Key Teachers Foundation from the State Education Ministry of China and the National Natural Foundation of Shandong Province, People's Republic of China, for the financial support of this work.

REFERENCES

1. Casas JS, Castineiras A, Couce MD, Jorge ML, Russo U, Sanchez A, Seoane R, Sordo J, Varela JM. *Appl. Organometal. Chem.* 2000; **14**: 421.
2. Li J, Ma Y, Liu R, Li J. *Appl. Organometal. Chem.* 2001; **15**: 227.
3. Nath M, Yadav R, Eng G, Nguyen TT, Kumar A. *J. Organometal. Chem*. 1999; **577**: 1.
4. Kemmer M, Dalil H, Biesemans M, Martins JC, Mahieu B, Horn E, de Vos D, Tiekink ERT, Willem R, Gielen M. *J. Organometal. Chem*. 2000; **608**: 63.
5. Gielen M. *Appl. Organometal. Chem*. 2002; **16**: 481.
6. Susperregui J, Bayle M, Leger JM, Deleris G. *J. Organometal. Chem*. 1998; **556**: 105.
7. Koreschkow KA. *Berichte* 1935; **66**: 1961.
8. Gielen M, Khloufi A, Biesemans M, Willem R, Meunier-Piret J. *Polyhedron* 1992; **11**: 1861.
9. Moura CVR, de Sousa APG, Silva RM, Abras AR, Horner M, Bortoluzzi AJ, Filgueiras CAL, Wardell JL. *Polyhedron* 1999; **18**: 2961.
10. Pettinari C, Marchetti F, Pettinari R, Martini D, Drozdov A, Troyanov S. *Inorg. Chim. Acta* 2001; **325**: 103 and references cited therein.
11. Tarassoli A, Sedaghat T. *Inorg. Chem. Commun*. 2002; **645**: 105.
12. Harrison PG. Investigating tin using spectroscopy. In *Chemistry of Tin*, Harrison PG (ed.). Chapman and Hall: London, 1989; chapter 3, 61–115.
13. Casas JS, Martinez EG, Jorge ML, Russo U, Sanchez A, Gonzalez AS, Seoane R, Sordo J. *Appl. Organometal. Chem*. 2001; **15**: 204.
14. Honnick WD, Hughes MC, Schaeffer Jr CD, Zuckerman JJ. *Inorg. Chem.* 1976; **15**: 1391 and references cited therein.
15. Sousa PG, Silva RM, Cesar A, Wardell JL, Huffman JC, Abras A. *J. Organometal. Chem*. 2000; **605**: 82.
16. Aupers JH, Chohan ZH, Cox PJ, Doidge-Harrison SMSV, Howie A, Khan A, Spencer GM, Wardell JL. *Polyhedron* 1998; **17**: 4475.
17. Chohan ZH, Howie RA, Wardell JL. *J. Organometal. Chem.* 1999; **577**: 140.
18. Pettinari C, Pellei M, Santini C, Natali I, Accorroni F, Lorenzotti A. *Polyhedron* 1998; **17**: 4487.
19. Hadjikakou SK, Demertzis MA, Kubicki M, Kovala-Demertzi D. *Appl. Organometal. Chem*. 2000; **14**: 727.
20. Lockhart TP, Manders WF, Zuckerman JJ. *J. Am. Chem. Soc.* 1985; **107**: 4546.
21. Tarassoli A, Sedaghat T, Neumuller B, Ghassemzadeh M. *Inorg. Chim. Acta* 2001; **318**: 15.
22. Narga RA, Schuermann M, Silvestru C. *J. Organometal. Chem.* 2001; **623**: 161.
23. Bondi A. *J. Phys. Chem.* 1964; **68**: 441.
24. Allen FH, Bellard SA, Brice MD, Cartwright BA, Doubleday A, Higgs H, Hummelink T, Hummelink-Peters BG, Kennard O, Motherwell WDS, Rogers JR, Watson DG. *Acta Crystallogr. Sect. B* 1979; **35**: 2331.
25. Huheey JE, Keiter EA, Keiter RL. *Principles and Applications of Inorganic Chemistry*, 4th edn. Harper Collins: New York, 1993.
26. Nagao Y, Nishijima H, Iimori H, Ushirogochi H, Sano S, Shiro M. *J. Organometal. Chem*. 2000; **611**: 172.
27. Yin HD, Wang CH, Ma CL, Wang Y. *Chin. J. Chem*. 2002; **20**: 913.
28. Boere RT, Mook KH, Parvez MZ. *Anorg. Allg. Chem.* 1994; **620**: 1589.
29. Pauling L. *The Nature of the Chemical Bond*, 3rd edn. Cornell University Press: Ithaca, NY, 1960; 64.
30. Dai J, Munakata M, Wu LP, Kuroda-Sowa T, Suenaga Y. *Inorg. Chim. Acta* 1997; **258**: 65.
31. Glass RS, Adamowicz L, Broeker JL. *J. Am. Chem. Soc.* 1991; **113**: 1065.
32. Yasui M, Murata S, Iwasaki F, Furukawa N. *Bull. Chem. Soc. Jpn*. 1995; **68**: 744.

