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Synthesis of Stannic(IV) Complexes: Their Structural Elucidation in Solid and Solution State and Antimicrobial Activity

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ABSTRACT: *A series of organotin(IV) thiocarboxylates have been synthesized with the general formula R_2SnL_2 and R_3SnL ($R = Ph_2$(I), Me_3(II), n-Bu_3(III), Ph_3(IV), Cy_3(V), Me_2(VI), n-Bu_2(VII), and L = piperidine-1-thiocarboxylic acid) in anhydrous toluene under the reflux conditions. The complexes were characterized by microanalysis, IR, ^1H and ^{13}C NMR, mass spectrometry, and XRD. NMR data revealed that thiocarboxylic acid acts as bidentate, and complexes exhibit the four-coordinated geometry in solution state. In solid state, diorganotin complexes exhibit the hexa-coordinated geometry whereas the triorganotin(IV) compounds show the five-coordinated geometry. These complexes were also tested for their antimicrobial activity along with the ligand against different animals, plant pathogens, and* Artemia salina. *All complexes with few exceptions show high activity as compared to the ligand.* © 2007 Wiley Periodicals, Inc. Heteroatom Chem 18:664–674, 2007; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20380

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INTRODUCTION

Complexes containing 1,1-dithiolato ligands have been used as fungicides, pesticides, vulcanization accelerators, flotation agents, lubricant additives, and in deposition of ZnS or CdS thin film by metal organic chemical vapor deposition [1]. 1,1-Dithiolate ligands have recently attracted much attention mainly because of their interesting photophysical properties derived from their extensive electron delocalization onto all of the ligand atoms [2]. Indeed, the increasing renewed interest nowadays to these species is due to their high stability, solvatochromic behavior, room temperature luminescence in solution [3], and their status as excellent candidates for applications such as photocatalysis [4]. In addition, the variable coordination modes of 1,1-dithiolate ligands to metals make the structural studies more interesting [5]. The 1,1-dithiolate ligands have also been used to stabilize unusually high-oxidation states [6] or to facilitate the synthesis of clusters [5–7], and to the synthesis of inorganic–organic hybrid materials, which have potential in various applications such as electrical conductivity, magnetism [8], ion exchange separation, and catalysis [9].

Metal thiolato complexes have been extensively studied because of their ability to adopt

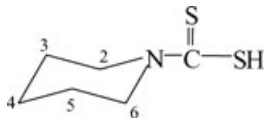


FIGURE 1 Structure of piperidine-1-thiocarboxylic acid.

various nuclearities and their relevance in biology, because they form the inorganic part of the biologically active centers of some metalloproteins and enzymes [10–13]. It has been well established that dithiocarbamates are a group of compounds that are active against fungi [14,15] and insects [14]. Extensive work has been done on dithiocarbamates to study their mode of bonding [16–20] and their biocidal activity [15,21]. Organotin compounds as well as dithiocarbamates ligands [22] are known for their antifungal [23], antibacterial [24], and antitumoral [25–28] activities. In the continuation of our interest in synthesis, structural elucidation, and antimicrobial activity of organotin(IV) complexes of thiocarboxylic acid [29–31], we report here the synthesis, structural elucidation, and antimicrobial activity of stannic(IV) complexes of piperidine-1-thiocarboxylic acid (Fig. 1).

RESULTS AND DISCUSSION

The complexes obtained in this investigation are solid. They are thermally stable, and their melting points with other physical data are listed in Table 1. The complexes are soluble in organic solvents. The complexes are characterized on the basis of a number of spectral techniques.

Infrared Spectral Studies

Infrared spectral studies of complexes (**I**)–(**VII**) were made to understand the nature of complexes in the solid state. The type of bonding between thiocarboxylic acid and the tin atom was deduced using the $\upsilon_{C—N}$ and $\upsilon_{C—S}$ vibrations.

It has been reported [14] that the observation of a single $\upsilon_{C—S}$ absorption in the region around 1000 cm^{-1} is indicative of dithiocarbamate groups that are bonded symmetrically or bidentate in nature. Splitting of this band around 1000 cm^{-1} has been reported for dithiocarbamate groups that act as a monodentate ligand or are unsymmetrically bonded [32–34]. As shown in Table 2, both di- and tri-thiocarboxylate compounds exhibit single $\upsilon_{C—S}$ vibrations between 971 and 979 cm^{-1} and $\upsilon_{C—N}$ vibrations between 1422 and 1482 cm^{-1}. The observed $\upsilon_{C—N}$ vibrations lie between the range for C—N single bonds (1250–1360 cm^{-1}) and C=N double bonds (1640–1690 cm^{-1}). This suggests that the C—N bonds in the complexes have some partial double bond character, which would result in some partial double bond character, for the C—S bonds. This type of bonding for the two C—S bonds can be achieved through the bonding of the two sulfur atoms with the tin atom. This interaction can be viewed as the coordination of one normal Sn—S bond and one weak Sn—S bond. The weak Sn—S bond is possible through π overlapping of the empty d-orbitals of the tin atom and the p-orbitals of sulfur. De Vries and Herber [19] have used the term "anisobidentate" to describe this type of bonding for a series of triphenyltin dithiocarbamates. This type of bonding would result in observing two Sn—S bond distances in the compound. In the present work, two different Sn—S bond distances were identified in the crystal structure of tricyclohexyltin *N*-*n*-butyldithiocarbamate [35]. One distance was 2.472 Å, and the another was 3.239 Å. Another example of this type of bonding can be found in $Ph_3SnS_2CN(CH_2)_5$ [18]. The crystal structure of this compound showed Sn—S bond lengths of 2.481 and 2.919 Å. Other examples are cited in a review by Tiekink [36]. The data show that the absorption at about 412–452 cm^{-1} for the complexes (**I–VII**) is assigned to the Sn—S stretching mode of vibration and Sn—C in the range 525–553 cm^{-1} indicates the formation of the complexes [37].

Mass Spectrometry

The conventional EI mass spectral data for the complexes **I–VII** are recorded, and different fragments obtained through various routes along with their *m/z* (%) are given in Table 3. In the mass spectral data, most fragment ions occur in a group of peaks as a result of tin isotopes. For simplicity, the mass spectral fragmentation data reported here are related to the principal isotope ^{120}Sn [38]. Molecular ion peak of low intensity was observed for the organotin(IV) derivatives. As the fragmentation pattern depends on the structure of the compounds, therefore, the base peak for organotin(IV) derivatives is derived by adopting a different fragmentation pattern. Base peak for complex **I, II, V**, and **VI** is due to fragment $[C_6H_{10}NS]^+$ at m/z (%) 128(100).

NMR Spectral Studies

^1H NMR spectral data of the synthesized thiocarboxylic acid and reported compounds (**I–VII**) are given in Table 4 along with their coupling values. The signals are assigned by their peak multiplicity,

TABLE 1 Physical Data of Organotin(**IV**) Thiocarboxylates

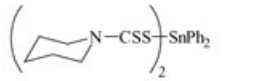
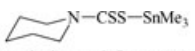
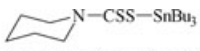
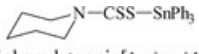
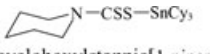
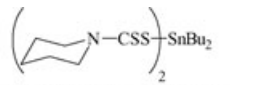
Compound	Quantity Used: First Reactant	Quantity Used: Second Reactant	Quantity Used: Third Reactant	MP (°C)	Yield (%)	Structure Formula with IUPAC Name	Elemental Analysis % Calculated (Found): C	H	N	S
I	HL 1 g (6.21 mmol)	Ph_2SnCl_2 1.06 g (3.10 mmol)	Et_3N 0.86 mL (6.21 mmol)	82–83	92	 Diphenylstannic-bis[1-piperidine] thiocarboxylate	48.56 (48.48)	5.05 (5.18)	4.72 (4.62)	21.58 (21.51)
II	HL 1 g (6.21 mmol)	Me_3SnCl 1.23 g (6.21 mmol)	Et_3N 0.86 mL (6.21 mmol)	121–122	95	 Trimethylstannic[1-piperidine] thiocarboxylate	33.33 (33.26)	5.86 (5.81)	4.32 (4.41)	19.75 (19.61)
III	HL 1 g (6.21 mmol)	Bu_3SnCl 1.68 g (6.21 mmol)	Et_3N 0.86 mL (6.21 mmol)	143–144	96	 Tributylstannic[1-piperidine] thiocarboxylate	48.00 (48.17)	8.22 (8.19)	3.11 (3.10)	14.22 (14.29)
IV	HL 1 g (6.21 mmol)	Ph_3SnCl 2.39 g (6.21 mmol)	Et_3N 0.86 mL (6.21 mmol)	182–183	90	 Triphenylstannic[1-piperidine] thiocarboxylate	56.47 (56.31)	4.90 (4.81)	2.74 (2.64)	12.54 (12.46)
V	HL 1 g (6.21 mmol)	Cy_3SnCl 2.98 g (6.21 mmol)	Et_3N 0.86 mL (6.21 mmol)	–	89	 Tricyclohexylstannic[1-piperidine] thiocarboxylate	54.85 (54.77)	7.61 (7.51)	2.66 (2.61)	12.19 (12.10)
VI	HL 1 g (6.21 mmol)	Me_2SnCl_2 0.68 g (3.10 mmol)	Et_3N 0.86 mL (6.21 mmol)	192–193	95	 Dimethylstannic-bis[1-piperidine] thiocarboxylate	35.82 (35.72)	4.54 (5.46)	5.97 (5.90)	27.29 (27.14)
VII	HL 1 g (6.21 mmol)	Bu_2SnCl_2 0.94 g (3.10 mmol)	Et_3N 0.86 mL (6.21 mmol)	95–96	97	 Dibutylstannic[1-piperidine] thiocarboxylate	43.39 (43.49)	6.87 (6.73)	5.06 (5.19)	23.14 (23.29)

TABLE 2 Assignments of Characteristic FT-IR Vibrations of 1-Piperidine Thiocarboxylic Acid and Their Organotin(IV) Complexes

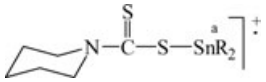
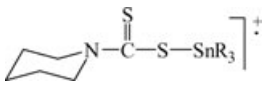
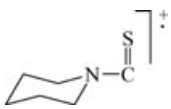
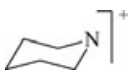
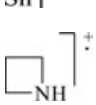
	IR Peak (cm^{-1})						
Compound	ν_{CH_2}	ν_{CN}	$\nu_{C=S}$	ν_{C-S}	ν_{SH}	ν_{Sn-C}	ν_{Sn-S}
HL	2862 m	1482 s	978 m	1045 m	2724 s	–	–
I	2870 m	1475 s	971 m	1072 m	–	232 s	420 m
II	2852 m	1470 s	976 m	1065 m	–	532 m	412 s
III	2835 m	1462 s	974 m	1060 m	–	525 m	429 w
IV	2823 m	1453 s	977 m	1043 m	–	252 s	432 w
V	2845 m	1445 s	979 m	1025 m	–	540 m	441 m
VI	2840 m	1422 s	973 m	1082 m	–	545 w	449 m
VII	2861 m	1432 s	974 m	1053 m	–	553 m	452 w

Abbreviations: s = strong, m = medium, w = weak.

intensity pattern, integration, and the satellites. The absence of the −SH proton resonance in the complexes is proposed as the formation of organotin(IV) dithiocarbamates by deprotonation. This information agrees with what the IR data have revealed. All the protons present in the synthesized compounds (**I–VII**) have been identified at position and number with the protons calculated from the incremental method [39].

The ^{1}H NMR spectra of the triphenyltin(IV) complex contained absorption in two regions. One region is assignable to the thiocarboxylate ligand

TABLE 3 Mass Spectral Data of Organotin(**IV**) Complexes of 1-Piperidine Thiocarboxylic Acid at 70 eV

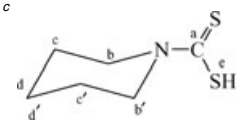
	m/z %						
Fragment Ion	***I***	***II***	***III***	***IV***	***V***	***VI***	***VII***
	433 (15.2)	–	–	–	–	309 (17.2)	393 (10.8)
	–	324 (16.1)	450 (20.5)	510 (12.6)	387 (20.1)	–	–
	128 (100)	128 (100)	128 (89.6)	128 (92.6)	128 (100)	128 (100)	128 (97.2)
	83 (130.2)	83 (25.2)	83 (100)	82 (100)	83 (85.6)	83 (77.9)	83 (100)
	55 (42.5)	55 (10.2)	55 (19.2)	55 (80.2)	55 (55.2)	55 (42.9)	55 (39.2)
$Sn]^+$	120 (12.2)	120 (8.9)	120 (12.5)	120 (7.6)	120 (20.1)	120 (16.2)	120 (17.3)
	56 (30.5)	56 (42.5)	56 (30.2)	56 (60.2)	56 (19.6)	56 (31.2)	56 (46.3)
$C_6H_5]^+$	77 (8.2)	77 (19.8)	77 (20.6)	77 (18.3)	77 (11.3)	77 (8.6)	77 (6.9)
$R_3Sn]^+$	–	164 (30.2)	290 (31.2)	347 (20.6)	324 (9.6)	–	–
$R_2Sn]^+$	271 (50.2)	149 (25.6)	233 (19.6)	271 (33.6)	216 (26.3)	149 (26.6)	233 (18.9)
$RSn]^+$	195 (26.4)	134 (16.3)	176 (12.3)	194 (17.8)	108 (7.6)	134 (15.6)	176 (16.3)

[a] R = CH_3, C_4H_9, C_6H_5, and C_6H_{12}.

TABLE 4 ^{1}H NMR Data[a–c] of 1-Piperidine Thiocarboxylic Acid and Their Organotin(**IV**) Complexes

	Chemical Shift (ppm)							
Proton	***HL***	***I***	***II***	***III***	***IV***	***V***	***VI***	***VII***
b,b′	3.82 m	3.70 m	3.80 m	3.76 m	3.72 m	3.65 m	3.60 m	3.58 m
c,c′	1.36 m	1.32 m	1.37 m	1.31 m	1.38 m	1.36 m	1.36 m	1.39 m
d,d′	1.72 m	1.74 m	1.77 m	1.75 m	1.73 m	1.78 m	1.76 m	1.79 m
e	1.12 s	–	–	–	–	–	–	–

[a]Compound **I**: Sn—C_6H_5, 7.91d ^{2}J[57.2], 7.50–7.53 m, 7.42–7.50 m. Compound **II**: Sn—CH_3, −0.01 ^{2}J[58.3]. Compound **III**: Sn—$CH_2CH_2CH_2CH_3$, 0.56–0.90 m, 0.20t(7.0). Compound **IV**: Sn—C_6H_5, 6.69–6.92 m, 6.86–7.30 m. Compound **V**: Sn—C_6H_{10}, 1.42–1.58 m. Compound **VI**: Sn—CH_3, 0.39t [77.8]. Compound **VII**: Sn—$CH_2CH_2CH_2CH_3$, 0.64–1.1 m, 0.23t (7.2).
[b]Chemical shifts (δ) in ppm. ^{2}J[^{119}Sn,^{1}H] and ^{3}J(^{1}H,^{1}H) in hertz are listed in square brackets and parenthesis, respectively. Multiplicity is given as: s = singlet, d = doublet, t = triplet, m = multiplet.
[c]



(1.12–3.82 ppm) and the other region to the triphenyltin moiety (6.69–6.92 ppm). Furthermore, the phenyl proton regions consisted of two groups of peaks. The ortho protons were observed at a lower field (6.86–7.30 ppm) and those for the meta and para protons at 6.69–6.92 ppm. These results are in agreement with values reported by Domazetis et al. [17] for a series of triphenyltin dithiocarbamate compounds. In addition, these authors reported that the difference in chemical shift resonances between the ortho and the meta and para protons (0.30–0.40 ppm) is an indication of anisobidentate bonding in the compounds. The difference in these resonances in the present study was in the range of 0.23 and 0.44 ppm, indicating that the dithiocarbamate compounds are also anisobidentate in solution. The ^{1}H NMR spectra of the tricyclohexyltin(IV) complex also contained absorption in two regions. The resonance in the region of 1.78–3.65 ppm was assigned to the thiocarboxylate ligand, and those in the range from 1.42 to 1.58 ppm was assigned to the tricyclohexyltin group. ^{2}J[^{119}Sn, ^{1}H] coupling values for compounds **I, II**, and **V** are 57.2, 58.3, and 77.8 Hz, respectively, indicating the four-coordinated geometry in the solution state [40]. Table 5 lists the chemical shifts of ^{13}C and tin–carbon coupling constants for the reported complexes (**I–VII**). The ^{13}C NMR chemical shifts owing to the phenyl and cyclohexyl groups are observed at positions comparable to other similar compounds [40,41]. The ^{13}C NMR chemical shift owing to $-CS_2$ carbon atom in the complexes was observed in the range from 195.9 to 195.1 ppm. Coordination of the tin atom in di- and triorganotin has been related to ^{n}J(^{119}Sn–^{13}C) coupling constants. The ^{n}J(^{119}Sn–^{13}C) coupling for complexes **VI** and **VII** is 378.6 and 578.6 Hz, respectively, which is indicative of four-coordinated geometry [41] in the solution state. These values are quite similar to the ^{1}J(^{119}Sn–^{13}C) coupling constant (335 Hz) for the four-coordinated tricyclohexyltin-2-[(*E*)-2-(2-hydroxy-5-methylphenyl)diazenyl]benzoate [42].

In order to gain further information about the possible coordination geometries in the solution, a close examination of ^{1}J[^{119}Sn–^{13}C] and ^{2}J[^{119}Sn–^{1}H] coupling constants was undertaken, as structural details, such as the determination of C—Sn—C bond angles, can be enumerated by use of the literature methods [43,44]. Data are summarized in Table 6. As indicated by Nadvornik and coworkers [44,45], ^{1}J[^{119}Sn–^{13}C] coupling constant is, instead,

TABLE 5 ^{13}C NMR Data[a–c] of 1-Piperdidine Carbodithioic Acids and Their Organotin(IV) Complexes

	Chemical Shift (ppm)							
Carbon	***HL***	***I***	***II***	***III***	***IV***	***V***	***VI***	***VII***
a	211.0	195.2	195.8	195.7	195.5	195.9	195.4	195.1
b,b′	52.4	52.8	52.5	52.6	52.2	52.1	52.9	52.3
c,c′	25.7	25.4	25.2	25.8	25.3	25.9	25.6	25.5
d,d′	24.0	24.4	24.1	24.7	24.5	24.8	24.3	24.6

[a]Compound **I**: Sn–C_6H_5, (C–α) 143.1, (C–β) 136.3 ^{2}J[46.2], (C–γ) 128.2 ^{3}J[65.9], (C–δ) 129.6 ^{4}J[14.6]. Compound **II**: Sn—CH_3, (C–α) −2.0 ^{1}J[395.6]. Compound **III**: Sn—$CH_2CH_2CH_2CH_3$, (C–α) 20.9 ^{1}J[558.3], (C–β) 28.6 ^{2}J[33.9], (C–γ) 27.6 ^{3}J[86.4], (C–δ) 14.0. Compound **IV**: Sn—C_6H_5, (C–α) 142.1 ^{1}J[638.1], (C–β) 136.0 ^{2}J[47.8], (C–γ) 135.9, (C–δ) 129.2. Compound **V**: Sn—C_6H_{10}, (C–α) 27.3, (C–β) 32.6, (C–γ) 30.8, (C–δ) 27.6. Compound **VI**: Sn—CH_3, 2.2 ^{1}J[378.6]. Compound **VII**: Sn—$CH_2CH_2CH_2CH_3$, (C–α) 22.6 ^{1}J[578.6], (C–β) 28.7 ^{2}J[34.29], (C–γ) 27.6 ^{3}J[87.2], (C–δ) 14.2
[b]Chemical shifts (δ) in ppm. ^{n}J[^{119}Sn,^{13}C] in hertz are listed in parenthesis.
[c]

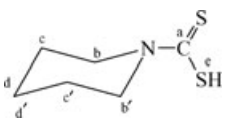


TABLE 6 C–Sn–C Angles Calculated from NMR

Compound	$^1J[^{119}Sn\text{-}^{13}C]$ *(Hz)*	*C—Sn—C Angles (°) Calculated*
VI	378.6	109.9
VII	578.6	127.5

quite amenable for making predictions about the geometry around the tin atom. For the diorganotin(IV) species, for which earlier results indicate five coordination geometries, the calculated C–Sn–C angles are consistent with the skew-trapezoidal bipyramidal geometries, with the lower apparent coordination number arising from the asymmetric coordination mode of the thiocarboxylate ligand.

X-ray Analysis

The atomic structure of piperidine-1-thiocarboxylic acid (**HL**) as an ion pair is given in Fig. 2. It crystallizes in monoclinic system with $P2_1$ space group. The structure shows that pairs are formed between piperidine dithiolate and piperidine in such a way that nitrogen atom of piperidine is directed toward the sulfur atoms of piperidine dithiolate. The ORTEP diagram reveals that four pairs are formed with almost equal C—S bond distances in the range 172.3(19)–171.1(2) Å and C—N bond distances in the range 147.3(3)–134.2(2) Å. Similarly, the angle between different bonds is almost equal. The crystal data and selected bond lengths and bond angles are given in Tables 7 and 8, respectively.

TABLE 7 Crystal Data and Structure Refinement Parameters for Compound (**HL**)

Empirical formula	$C_{11}H_{22}N_2S_2$
Formula weight	246
Crystal system	Monoclinic
Space group	$P2_1$
Unit cell dimensions	
a (Å)	12.346 (2)
b (Å)	15.369 (2)
c (Å)	14.258 (2)
α (°)	90.00
β (°)	93.01 (1)
γ (°)	90.00
V (Å^3)	2702.02 (7)
Z	8
D_c (g cm^{-3})	1.212
Crystal size (mm)	0.4 × 0.3 x 0.2
F (000)	1072
Total reflections	10919
Independent reflections	10049
R indices (all data)	$R_1 = 0.0361$, $wR_2 = 0.0739$
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0308$, $wR_2 = 0.0712$
Goodness-of-fit	1.060
Theta range for data collection (°)	1.0–23.5
Data/restraints/parameters	10919/9/574

The structure of compound **IV** is shown in Fig. 3, whereas the crystal data and selected bond lengths

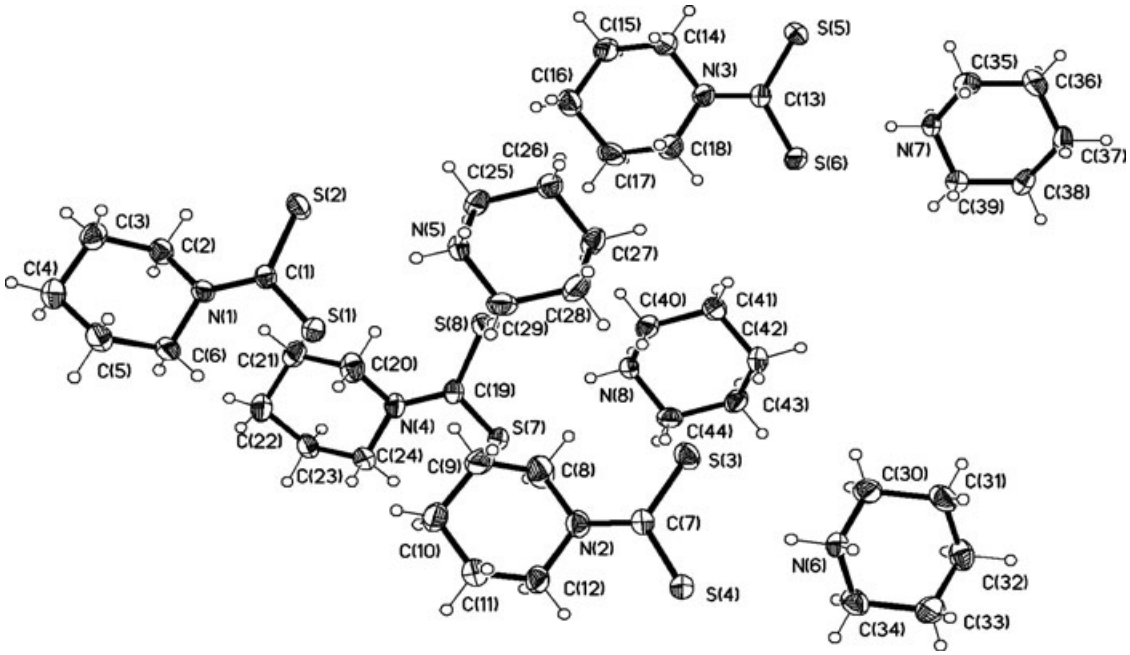


FIGURE 2 ORTEP drawing of ligand (**HL**) as ion pair with atomic numbering scheme.

TABLE 8 Selected Bond Lengths (Å) and Angles (°) of Compound (**HL)**

Bond Lengths (Å)	
S(1)–C(1)	172.3 (19)
S(2)–C(1)	171.1 (19)
S(3)–C(7)	171.1 (2)
S(4)–C(7)	171.3 (2)
S(5)–C(13)	172.3 (19)
S(6)–C(13)	170.8 (19)
S(7)–C(19)	172.1 (19)
S(8)–C(19)	171.1 (2)
N(1)–C(1)	134.0 (2)
N(1)–C(2)	146.6 (2)
N(1)–C(6)	146.6 (2)
N(2)–C(7)	134.2 (2)
N(2)–C(8)	147.0 (3)
N(2)–C(12)	147.3 (3)
N(3)–C(13)	134.0 (2)
N(3)–C(18)	145.9 (3)
N(4)–C(19)	134.3 (2)
Bond Angles (°)	
C(2)–N(1)–C(6)	111.8 (15)
C(7)–N(2)–C(8)	123.9 (19)
S(3)–C(7)–S(4)	119.4 (11)
N(4)–C(19)–S(8)	120.4 (15)

TABLE 9 Crystal Data and Structure Refinement Parameters for Compound (**IV)**

Empirical formula	$C_{24}H_{25}NS_2Sn$
Formula weight	510.26
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	9.984 (2)
b (Å)	15.878 (3)
c (Å)	14.541 (2)
α (°)	90.00
β (°)	102.412 (1)
γ (°)	90.00
V(Å^3)	2251.49 (7)
Z	2
D_c (g cm^{-3})	1.505
Crystal size (mm)	0.4 × 0.25 × 0.2
F (000)	1032
Total reflections	5150
Independent reflections	4840
R indices (all data)	$R_1 = 0.0203$, $wR_2 = 0.0431$
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0134$, $wR_2 = 0.0422$
Goodness-of-fit	1.085
Theta range for data collection (°)	1.0–27.5
Data/restraints/parameters	5150/0/254

and bond angles are given in Tables 9 and 10. The crystal structure shows that the tin atom is coordinated to two sulfur atoms of the ligand and three carbon atoms of the phenyl groups. The Sn—S bonds (Sn(1)–S(1) 2.47(4)Å and Sn(1)–S(2) 2.90(4)Å) lies closely to the analogues complex $Ph_3SnS_2CN(CH_2)_5$ [18]. Thus, shorter bond length is closed to the sum of the covalent radii of tin and sulfur (2.42 Å) but longer Sn—S bond length is much smaller than the van der Waals radii (4.0 Å) [46]. In this way, the ligand behaves as a bidentate ligand or more correctly as anisobidentate ligand and chelates the tin atom by means of sulfur atoms giving cis-trigonal bipyramid geometry around the tin atom similar to $Ph_3SnS_2CN(C_2H_5)(C_3H_7)$ [47]. The cis-trigonal bipyramid environment around tin is defined with

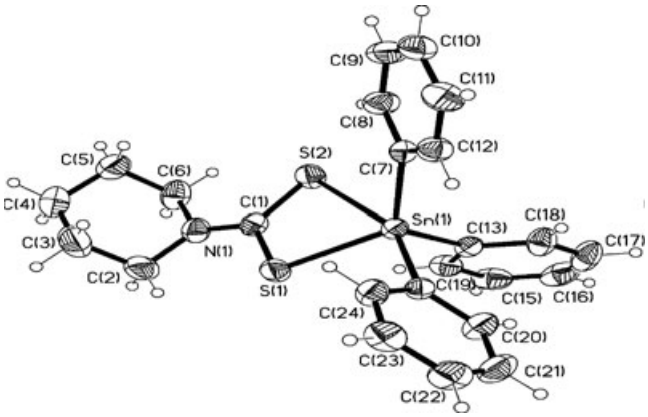


FIGURE 3 ORTEP drawing of compound **IV** with atomic numbering scheme.

TABLE 10 Selected Bond Lengths (Å) and Angles (°) of Compound (**IV)**

Bond Lengths (Å)	
Sn(1)–C(13)	2.13 (14)
Sn(1)–C(7)	2.14 (15)
Sn(1)–C(19)	2.17 (14)
Sn(1)–S(1)	2.47 (4)
Sn(1)–S(2)	2.90 (4)
S(1)–C(1)	1.75 (16)
S(2)–C(1)	1.69 (17)
Bond Angles (°)	
C(13)–Sn(1)–C(7)	120.17 (6)
C(13)–Sn(1)–C(19)	103.87 (6)
C(7)–Sn(1)–C(19)	101.60 (6)
C(13)–Sn(1)–S(1)	111.42 (5)
C(7)–Sn(1)–S(1)	121.19 (4)
C(19)–Sn(1)–S(1)	91.14 (4)
C(13)–Sn(1)–S(2)	88.89 (4)
C(19)–Sn(1)–S(2)	156.63 (4)
S(1)–Sn(1)–S(2)	65.79 (13)
C(1)–S(1)–Sn(1)	94.69 (5)
C(1)–S(2)–Sn(1)	81.95 (5)
C(12)–C(7)–Sn(1)	117.93 (11)
C(8)–C(7)–Sn(1)	124.64 (12)
C(14)–C(13)–Sn(1)	121.81 (12)
C(18)–C(13)–Sn(1)	119.57 (12)
C(24)–C(19)–Sn(1)	119.59 (11)
C(20)–C(19)–Sn(1)	122.35 (11)

TABLE 11 Antibacterial Activity[a–c] (Diameter of Inhibition Zone After 20 h) of 1-Piperidine Thiocarboxylic Acid and Their Organotin(IV) Complexes

	Inhibition Zone Diameter (mm)								
Bacterium (ATCC No.)	***HL***	***I***	***II***	***III***	***IV***	***V***	***VI***	***VII***	*Reference Drug*
Escherichia coli	15	20	–	16	–	12	24	–	–
Bacillus subtilis (11774)	15	40	24	40	25	49	40	22	22
Shigella flexenari (700390)	15	24	30	17	26	16	40	30	30
Stephlococcus aureus (25923)	20	20	20	16	12	17	21	22	22
Pseudomonas aeruginosa (10145)	20	22	15	38	24	22	12	30	30
Salmonella typhi (10749)	20	25	21	20	17	20	23	30	30

[a]In vitro, agar well diffusion method, conc. 3 mg/mL of DMSO.
[b]Reference drug, imipenum.
[c]Clinical implication: *Escherichia coli*, infection of wounds, urinary tract and dysentery; *Bacillus subtilis*, food poisoning; *Shigella flexenari*, blood diarrhea with fever and severe prostration; *Staphlococcus aureus*, food poisoning, scaled skin syndrome, endrocarditis; *Pseudomonas aeruginosa*, infection of wounds, eyes, septicemia; *Salmonella typhi*; typhoid fever, localized infection.

C(19) and S(2) at the apical position and S(1), C(13) and C(7) at the equatorial position. The sum of the equatorial angle, C(13)–Sn(1)–S(1) 111.42(5)°, C(7)–Sn(1)–C(13) 120.17(4)°, and C(7)–Sn(1)–S(1) 121.19(4)°, is 352.8° instead of the ideal 360° thus bipyramid is distorted. Being a part of chelate, the angle S(1)–Sn(1)–S(2) is not 90° but only 65.79(13)°, so the S(2) cannot occupy exactly the corresponding trans apical position of C(19) and the angle between the apical groups is 156.63(4)°, closely related to the value (156.50(6)°) found in $Ph_3SnS_2CN(C_2H_5)(C_3H_7)$ [47]. The Sn—C bond length, Sn(1)–C(7) 2.14(15) Å, is very similar to equatorial ones, Sn(1)–C(13) 2.139(14) Å, Sn(1)–C(7) 2.14(14) Å and is very close to the Sn—C distances in $Ph_3SnS_2CN(CH_3)(C_4H_9)$ [48]. Finally, the S—C bond lengths are characteristic of the dithiocarbamate group, as these distances are both intermediate between the values expected for single and double bonds [49].

Biological Activity

Antibacterial Activity. The synthesized complexes and free ligand are screened for antibacterial activity by the agar well-diffusion method [50], and the zone of inhibition is measured in millimeters. The antibacterial activity data are reported in Table 11. The complexes show high-antibacterial activity as compared to the free ligand. Some complexes also show high-antibacterial activity than the reference drug.

Antifungal Activity. The percent inhibition of the free ligand and their organotin(IV) complexes is reported in Table 12. Miconazole and amphotericin B were used as standard drugs. When the reported complexes (**I–VII**) were screened against different plant pathogens using the tube diffusion method [50], it was observed that the complexes show high-antifungal activity than the free ligands. It may be

TABLE 12 Antifungal Activity[a–c] (% Inhibition) of 1-Piperidine Thiocarboxylic Acid and Their Organotin(IV) Complexes

	Inhibition (%)								*MIC*
Fungus (ATCC No.)	***HL***	***I***	***II***	***III***	***IV***	***V***	***VI***	***VII***	*(μg/mL)*
Trichophyton longifusus (22397)	20	40	52	30	0	40	0	80	70.0
Candida albicans (2192)	10	20	30	40	0	50	70	60	110.8
Aspergillus flavis (1030)	0	10	20	0	40	55	70	60	20.0
Microsporum canis (9865)	20	60	0	50	55	60	80	0	98.4
Fusarium solani (11712)	28	0	30	70	0	40	60	90	73.2
Candida glaberata	30	0	70	60	40	80	60	95	110.8

[a]Concentration: 100 μg/mL of DMSO.
[b]MIC: Minimum inhibitory concentration.
[c]Percent inhibition (standard drug) = 100.

TABLE 13 Brine Shrimp (*Artemia salina*) Lethality Bioassay of 1-Piperidine Carbodithioic Acid and Their Organotin(IV) Complexes

Comp.	*Dose (μg/mL)*	*Number of Shrimps*	*Number of Survivors*	*LD_{50} (μg/mL)*	*Standard Drug*	*LD_{50} (μg/mL)*
HL	100	30	30	–	Etoposide	7.46
	10	30	30			
	1	30	30			
I	100	30	30	–	Etoposide	7.46
	10	30	30			
	1	30	30			
II	100	30	30	–	Etoposide	7.46
	10	30	30			
	1	30	30			
III	100	30	24	–	Etoposide	7.46
	10	30	30			
	1	30	30			
IV	100	30	0	1.12	Etoposide	7.46
	10	30	3			
	1	30	16			
V	100	30	0	3.72	Etoposide	7.46
	10	30	1			
	1	30	30			
VI	100	30	17	–	Etoposide	7.46
	10	30	30			
	1	30	30			
VII	100	30	20	–	Etoposide	7.46
	10	30	30			
	1	30	30			

concluded that metal coordination increases the activity as compared to free ligand.

Cytotoxicity. LD_{50} data have been determined for 1-piperidine carbodithioic acid and their organotin(IV) complexes (**I–VII**) by the brine shrimp bioassay method [51], and the results are summarized in Table 13. Highest toxicity was shown by compound **V** with LD_{50} value 3.78 μg/mL and minimum by compound **IV**, whereas the rest of the compounds do not show any cytotoxicity. Etoposide was used as a standard drug with LD_{50} value 7.46 μg/mL.

EXPERIMENTAL

Reagents

All the glass apparatus with standard quick fit joints were used throughout the work after cleaning and drying at 120°C. Carbon disulfide was purchased from Aldrich Chemical Company (USA) and was used as such. Piperidine was obtained from Merck Chemicals (Germany). Organotin(IV) chlorides were purchased from Aldrich Chemical Company (USA). Toluene, acetone, dichloromethane, diethyl ether, methanol, and chloroform were obtained from Merck Chemicals (Germany). All the solvents were purified and dried by the reported methods [52].

Spectroscopic Measurements

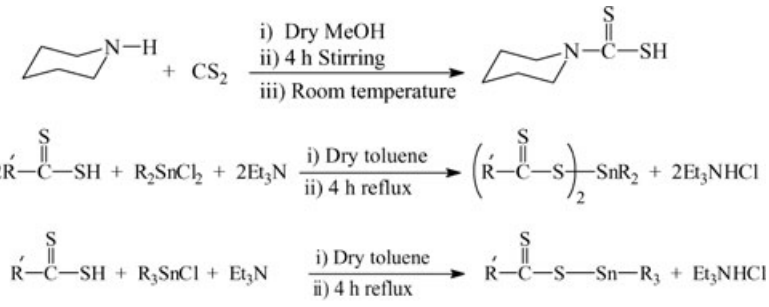
Elemental analysis was carried with a Perkin–Elmer 2400 series II instrument. Infrared spectra were recorded as KBr/CSI pellets or thin film on a Bio-Rad Elmer 16 FPC FT-IR instrument in the range 4000–400 cm^{-1}. Mass spectra were recorded on a MAT 8500 Finngin (Germany). The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-300 MHz using $CDCl_3$ as an internal reference.

Crystallography

X-ray single crystal analyses were made on Nonius Kappa CCD diffractometer with graphite monochromated Mo K_α radiation. The figures were plotted with the aid of ORTEPII [53]. The computing data collection was done by COLLECT [54], and computing cell refinement and data reduction were done by SCALEPACK [55] and DENZO [56] and SCALEPACK and SORTAV [55] method, respectively. The experimental absorption correction type was multiscan [55].

Procedure for the Synthesis of PipDTC (**HL**)

The stoichiometric amount of carbon disulfide was added dropwise to a solution of piperidine in methanol (100 cm^3) in a round bottom two-necked



where

R′ =				
R_2 =	Ph_2(I)	Me_2(VI)	Bu_2(VII)	–
R_3 =	Me_3(II)	Bu_3(III)	Ph_3(IV)	Cy_3(V)

SCHEME 1

flask, and the mixture was stirred at room temperature for 1 h. The solid product obtained was washed with diethyl ether and air-dried. Recrystallization (chloroform) of the solid gave piperidine-1-thiocarboxylic acid as white solid.

General Procedure for the Synthesis of the Complexes

Synthesized piperidine-1-thiocarboxylic acid (1 mmol) was suspended in dry toluene (100 cm^3) and was treated with triethylamine in a round bottom two-necked flask equipped with water condenser. The mixture was refluxed for 2–3 h. To a solution of triethyl ammonium salt of the ligand in dry toluene, diorganotin dichloride (2 mmol)/triorganotin chloride (1 mmol) was added as solid to a reaction flask with constant stirring and reaction mixture was refluxed for 4 h. After cooling the reaction mixture to room temperature, Et_3NHCl was filtered off and the solvent was evaporated by rotary apparatus under reduced pressure. Solid product was obtained. Recrystallization (chloroform) of the solid gave thiocarboxylates as white solid. The synthetic sequence for the preparation of the ligand and our target compounds is given in Scheme 1.

CONCLUSIONS

Di- and triorganotin(IV) complexes of piperidine-1-thicarboxylic acid have been synthesized and characterized. Detailed studies of the reported complexes indicate that triorganotin compounds exhibit the trigonal bipyramidal geometry whereas hexa-coordinated geometry was exhibited by diorganotin compounds in solid state. These complexes show four-coordinated geometry in the solution state. These complexes were also checked for their antimicrobial activity, and screening results show that reported compounds (**I–VII**) exhibit high-antimicrobial activity as compared to free ligand (piperidine-1-thiocarboxylic acid).

Supplementary Material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 296361 and 280266 for (**HL**) and complex **IV**, respectively. Copies of these information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CBZ 1EZ, UK (Fax: +44-1223-336033; email:deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

REFERENCES

[1] Coucouvanis, D. Prog Inorg Chem 1970, 11, 233–244.
[2] Vicente, J.; Chicote, M. T.; Huertas, S.; Jones, P. G. Inorg Chem 2003, 42, 4268–4274.
[3] Hong, M.; Cao, R.; Kawaguchi, H.; Tatsumi, K. Inorg Chem 2002, 41, 4824–4833.
[4] Noh, D. Y.; Seo, E. M.; Lee, H. L.; Jang, H. Y.; Choi, M. G.; Kim, Y. H.; Hong, J. Polyhedron 2001, 20, 1939–1945.
[5] Liu, C. W.; Liaw, B. J.; Wang, J. C.; Keng, T. C. Inorg Chem 2000, 39, 1329–1332.
[6] Coucouvanis, D.; Hollander, F. J.; Caffery, M. L. Inorg Chem 1976, 15, 1853–1860.

[7] Garland, M. T.; Halet, J. F.; Saillard, J. Y. Inorg Chem 2001, 40, 3342–3350.
[8] Su, W.; Hong, M.; Weng, J.; Liang, Y.; Zhao, Y.; Cao, R.; Zhou, Z.; Chan, A. S. C. Inorg Chim Acta 2002, 331, 8–15.
[9] Yaghi, O. M.; Li, H. J Am Chem Soc 1996, 117, 11600–11609.
[10] Stiefel, E. I.; Matsumoto, K. Transition Metal Sulfur Chemistry; ACS Sympoisum Series, 653; American Chemical Society: Washington, DC, 1995, Vol. 2.
[11] Raper, E. S. Coord Chem Rev 1996, 153, 199–255.
[12] Raper, E. S. Coord Chem Rev 1997, 165, 475–567.
[13] Kerbs, B.; Henkel, G. Angew Chem, Int Ed Engl 1991, 30, 769–772.
[14] Siddiqi, K. S.; Kureshy, R. I.; Khan, N. H.; Zaidi, S. A. A. Indian J Chem A 1985, 24, 578–584.
[15] Srivastava, T. N.; Kumar, V.; Srivastava, D. P. Nat Acad Sci Lett 1978, 1, 97–104.
[16] Srivastava, T. N.; Kumar, V.; J Organomet Chem 1976, 107, 55–61.
[17] Domazetis, G.; Magee, R. J.; James, B. D. J Organomet Chem 1977, 141, 57–69.
[18] Chandra, S.; James, B. D.; Magee, R. J.; Patalinghug, W. C.; Skelton, B. W.; White, A. H. J. Organomet. Chem 1988, 346, 7–15.
[19] De Vries, J. L. K. F.; Herber, R. H. Inorg Chem 1972, 11, 2458–2464.
[20] Bonati, F.; Ugo, R. J Organomet Chem 1967, 10, 257–268.
[21] Chauhan, H. P. S.; Shaik, M. N. J Inorg Biochem 2005, 99, 538–545.
[22] Thorn, G. D.; Ludwing, R. A. The Dithiocarbamates and Related Compounds; Elsevier, New York, 1962.
[23] Menzes, D. C.; Vieira, F. T.; de Lima, G. M.; Porto, A. O.; Cortes, M. E.; Ardisson, J. D.; Albrecht–Schmitt, T. E. Eur J Med Chem 2005, 40, 1277–1279.
[24] Bacchi, A.; Carcelli, M.; Pelagatti, P.; Pelizzi, G.; Rodriguez-arguelles, M. C.; Rongolino, D.; Solinas, C.; Zani, F. J. Inorg Biochem 2005, 99, 397–408.
[25] Memmer, M.; Gielen, M.; Biesemans, M.; DeVos, D.; Willem, R. Metal Based Drugs 1998, 5, 189–191.
[26] Gielen, M.; Dalil, H.; Mahieu, B.; De Vos, D.; Biesemans, M.; Willem, R. Metal Based Drugs 1998, 5, 527–529.
[27] Gielen, M.; Biesemans, M.; De Vos, D.; Willem, R. J Inorg Biochem 2000, 79, 139–145.
[28] Casini, A.; Messori, L.; Orioli, P.; Gielen, M.; Kemmer, M.; Willem, R. J Inorg Biochem 2001, 85, 297–301.
[29] Ali, S.; Ahmad, S. U.; Sadiq-ur-Rehman.; Shahzadi, S.; Parvez, M.; Mazhar, M. Appl Organomet Chem 2005, 19, 200.
[30] Ali, S.; Ahmad, S. U.; Shahzadi, S.; Sadiq–ur-Rehman.; Parvez, M.; Mazhar, M. Appl Organomet Chem 2005, 19, 201.
[31] Shahzadi, S.; Ali, S.; Bhatti, M. H.; Fettouhi, M.; Athar, M. J Organomet Chem 2006, 691, 1797–1802.
[32] Kupchi, E. J.; Calabretta, P. J. Inorg Chem 1965, 4, 973–978.
[33] Zaidi, A. A. Z.; Siddiqi, K. S.; Islam, N. Indian J Chem 1974, 12, 1197–1204.
[34] Honda, M.; Komura, M.; Kawaski, G.; Tanaka, T.; Okawara,K. J. Inorg Nucl Chem 1968, 30, 3231–3237.
[35] Song, X.; Cahill, C.; Eng, G. Main Group Met Chem 2002, 25, 13–21.
[36] Tiekink, E. R. T. Main Group Met Chem 1992, 15, 161–167.
[37] Molloy, K. C. In: The Chemistry of Metal-Carbon Bond; Hartley, F. (Ed) Wiley: New York, 1989.
[38] Shahzadi, S.; Shahid, K.; Ali, S.; Mazhar, M.; Khan, K. M. J Iran Chem Soc 2005, 2, 277–288.
[39] Kalinowski, H. O.; Berger S.; Brown, S. ^{13}C NMR Spectroskopie; Thieme: Stuttgart, 1984.
[40] Eng, G.; Song, X.; Duong, Q.; Strickman, D.; Glass, J.; May, L. Appl Organomet Chem 2003, 17, 218–225.
[41] Holecek, J.; Nadvornik, M.; Handlir, K.; Lycka, A. J Organomet Chem 1983, 258, 147–153.
[42] William, R.; Verbruggen, I.; Gielen, M.; Biesemans, M.; Mahieu, B.; Baul, T. S. B.; Tiekink, E. R. T. Organometallics 1998, 17, 5758–5766.
[43] Lockhart, T. P.; Manders, W. F. Inorg Chem 1986, 25, 892–895.
[44] Nadvornik, M.; Holecek, J.; Handlir, K.; Lycka. A. J Organomet Chem 1984, 275, 43–51.
[45] Holecek, J.; Nadvornik, M.; Handlir, K.; Lycka. A. J Organomet Chem 1986, 315, 299–308.
[46] Ma, C.; Zhang, J.; Zhang, R. Can J Chem 2003, 81, 107–116.
[47] Sanuddin, M.; Farina, Y.; Yamin, B. M. Acta Cryst 2004, E60, m1662–m1663.
[48] Kana, A. T.; Hibbert, T. G.; Mahon, M. F.; Molloy, K. C.; Parkin, I. P.; Price, L. S. Polyhedron 2001, 20, 2989–2995.
[49] Sheldrick, G. M.; Sheldrick, W. S. J. Chem. Soc A 1970, 490–497.
[50] Rehman, A.; Choudhary, M. I.; Thomsen, W. J. Bioassay Techniques for Drug Development; Harwood Academic Publishers: Amsterdam, The Netherlands, 2001.
[51] Meyer, B. N.; Ferrigni, N. R.; Putnam, J. E.; Jacobson, L. B.; Nichols, D. E.; McLaughlin, J. L. Planta Med 1982, 45, 31–34.
[52] Armarego, W. L. F.; Chai, C. L. L. Purification of Laboratory Chemical; Elsevier: New York, 2003.
[53] Johnson, C. K.; Bernett, M. N. ORTEP-3 for Windows; University of Glasgow, UK, 1996.
[54] Nonius. COLLECT, Nonius BV: Delft, The Netherlands, 1998.
[55] Blessing, R. H. Acta Cryst 1995, A51, 33–58.
[56] Otwinowski, Z.; Minor, W. Methods in Enzymology, Vol. 276; Macromolecular Crystallography, Part A; Carter, C. W. Jr; Sweet, R. M. (Eds.); Academic Press; New York, 1997.