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COORDINATION COMPOUNDS

# Synthesis and Spectral Characterization of Chloro-Organotin(IV) Complexes of S-Donor Ligand: Crystal Structure of Chloro-*t*-dibutyltin[4-methyl-1-piperidine]thiocarboxylate[1]

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**Abstract**—New chloromono- and diorganotin(IV) complexes of 4-methyl-1-piperidine dithiocarboxylic acid have been synthesized in anhydrous chloroform. The complexes were characterized by microanalysis, IR, $^{1}H$ and $^{13}C$ NMR, mass spectrometry and XRD. The FTIR spectra clearly demonstrate that organotin(IV) moieties react with [S,S] atoms of the ligand. Compound (**1**) and (**3**) exhibits the 5-coordinated while the compound (**2**) exhibit 6-coordinated geometry in solid state. Compound (**3**) shows distorted trigonal bipyramidal geometry which is confirmed by X-ray single-crystal diffraction.

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## INTRODUCTION

In recent years organotin complexes of sulphur donor ligands have been extensively studied because of variety of their structures and biological activities [1, 2]. Indeed, the increasing renewed attention paid nowadays to these species arises from their high stability, solvatochromic behaviour, 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]. These ligands are interesting because of their dual potential of bidentate nature as well as antifungal activity [6]. The bonding in metal complexes may takes place either from the amino nitrogen and the deprotonated thiol sulfur (N, S coordination) or from the dithiocarboxylic moiety (S, S coordination).

Sulfur containing molecules are currently under study as chemoprotectants in platinum-based chemotherapy. In particular, thiocarbonyl and thiol donors have shown promising properties for chemical use in modulating cisplatin nephrotoxicity [7, 8].

To our knowledge, no reports are available about coordination behaviour of chloromono organotin(IV) complexes of 4-methyl piperidine-1-dithiocarboxylic acid and as a continuation of our interest in synthesis, structural elucidation and antimicrobial activity of organotin(IV) complexes of dithiocarboxylic acids [9–11], we report here the synthesis, structural elucidation and antimicrobial activity of chloromono and diorganotin(IV) complexes of 4-methyl-1-piperidine dithiocarboxylic acid (Fig. 1).

## EXPERIMENTAL

### *Materials and Methods*

Melting points were determined in a capillary tube using electro thermal melting apparatus, model MPD Mitamura Riken Kogyo (Japan). FT-IR spectra were recorded as KBr discs/thin film in the range of 4000–250 $cm^{-1}$ with a Perkin-Elmer Spectrum 1000 FT-IR spectrophotometer. $^{1}H$ and $^{13}C$ NMR data were recorded on a Bruker 300 MHz FT-NMR Spectrometer. Elemental analyses were done on a CHNS analyzer 932 Leco, USA. Mass spectrometric data were collected on MAT-312 Mass spectrometer. The m/z values are computed according to H = 1, C = 12, N = 14, O = 16 and Sn = 120.

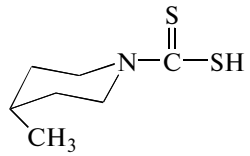



**Fig. 1.** Structure of 4-methyl-1-piperidine dithiocarboxylic acid (**HL**).

[1] The article is published in the original.

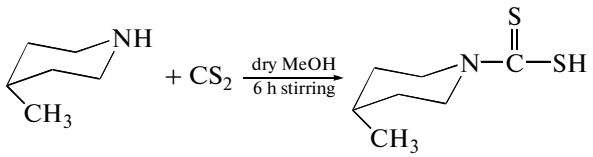
Organotin chlorides were purchased from Aldrich. The organic solvents like methanol, chloroform, DMSO, acetone and diethyl ether were purchased from Merck and dried by standard methods [12].

### *X-ray Crystallography*

X-ray crystallographic data with graphite-monochromated Mo$K_\alpha$ radiation ($\lambda = 0.71073$ Å) were collected on a Bruker Smart APEX CCD diffractometer, with cryocooling to 100 K using an Oxford Cryosystems 700 Series Cryostream Cooler. A semi-empirical absorption correction using equivalents was applied with SADABS (Bruker (2001). SADABS (Version 2.03a) and SHELXTL (Version 6.12). Bruker AXS Inc., Madison, Wisconsin, USA) and the structure was solved by direct methods and refined by a full-matrix least squares procedure based on $F^2$ using the SHELX97 [13]. All other calculations and graphics were performed with the SHELXTL package (Bruker (2001). SADABS (Version 2.03a) and SHELXTL (Version 6.12). Bruker AXS Inc., Madison, Wisconsin, USA) Program System.

### *Synthesis of 4-Methyl-1-piperidine Dithiocarboxylic Acid (HL)*

The ligand was synthesized by the reported method [11]. 4-Methyl-1-piperdine dithiocarboxylic acid was prepared by the reaction of 4-methylpiperdine and carbon disulfide as given below:




25.0 mL (1.0 mmol) of 4-methyl piperidine was added into 100 mL dried methanol, kept in 250 mL two necked round bottom flask equipped with condenser and magnetic stirrer. After stirring for 15 min, 15.2 mL (1.0 mmol) of carbon disulphide was added drop wise. This mixture was stirred at room temperature for 6 hours. The shining white precipitates formed were filtered through a whatman filter paper, washed with dried diethyl ether and were recrystallized from chloroform. Yield: 74%. m.p. 163–165°C. Solubility: acetone, chloroform, methanol and DMSO. Elemental analysis data for $C_7H_{13}NS_2$: Calcd., %C, 47.96; %H, 7.47; %N, 7.99; %S, 36.58. (Found) %C, 47.92; %H, 7.51; %N, 8.03; %S, 36.54. IR (KBr, $cm^{-1}$): 1282 (ν C=S), 2754 (ν S–H), 1410 (ν C–N), 2856 (ν $CH_2$), 2949 (ν $CH_3$). $^1$H NMR ($CDCl_3$, ppm), $^nJ(^1H, ^1H)$, 2.78 (t, 2,2', (12.0)), 1.56–1.81 (m, 3,3'), 1.16–1.28 (m, 4), 0.90 (d, $CH_3$, (6.6)), 1.58 (s, SH). $^{13}$C NMR ($CDCl_3$, ppm), 178.6 (CSS), 44.74 (C-2,2'), 30.01 (C-3,3'), 28.28 (C-4), 21.61 (C-5, $CH_3$).

### *Synthesis of $PhSnCl_2L$* (**1**)

The preparation of compound (**1**) was carried out at room temperature. 4-methyl-1-piperidine dithiocarboxylic acid (3.0 g, 17.1 mmol) and phenyltintrichloride (2.82 mL, 17.1 mmol) were added to 100 $cm^3$ of dry chloroform and stirred for 6 hours. The resulting solution was kept in open air at temperature for 4–5 days. After the evaporation of solvent the solid complex was well air dried and was recrystallized from acetone petroleum ether 4 : 1 (v/v) mixture. Yield: 72%. m.p. 194–196°C. Solubility: Acetone, methanol, THF and DMSO. Elemental analysis data for $C_{13}H_{17}NS_2Cl_2Sn$: Calcd., %C, 35.40; %H, 3.89; %N, 3.18; %S, 14.54. (Found) %C, 35.44; %H, 3.92; %N, 3.21; %S, 14.58. IR (KBr, $cm^{-1}$): 1218 (ν C=S), 427 (ν Sn–S), 315 (ν Sn–C), 237 (ν Sn–Cl), 1452 (ν C–N), 2875 (ν $CH_2$), 2961 (ν $CH_3$). $^1$H NMR ($CDCl_3$, ppm), $^nJ(^1H, ^1H)$, 2.79 (t, 4H, (10.5)), 1.55–1.64 (m, 4H), 1.20–1.34 (m, H), 0.90 (d, 3H, $CH_3$, (6.3)), [7.22–7.33 (m, 5H), SnPh].$^{13}$C NMR ($CDCl_3$, ppm), 193.57 (CSS), 54.12 (C-2,2'), 33.75 (C-3,3'), 28.78 (C-4), 21.22 (C-5, $CH_3$), [136.91, 133.72, 128.33, 129.76, SnPh].

### *Synthesis of $PhSnClL_2$* (**2**)

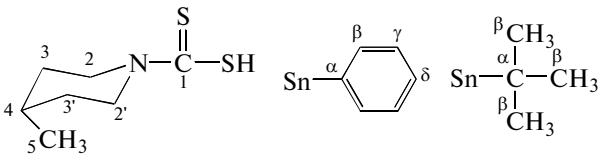
Compound (**2**) was synthesized in the same way as compound (**1**). For complexation, (3.0 g, 17.1 mmol) of 4-methyl-1-piperidine dithiocarboxylic acid and (1.41 mL, 8.5 mmol) of phenyltintrichloride were mixed. It was recrystallized from acetone: petroleum ether 4 : 1 (v/v) mixture. Yield: 69%. m.p. 148°C. Solubility: acetone, methanol, THF and DMSO. Elemental analysis data for $C_{20}H_{29}N_2S_4ClSn$: Calcd., %C, 41.42; %H, 5.04; %N, 4.83; %S, 22.12. (Found) %C, 41.46; %H, 5.08; %N, 4.87; %S, 22.08. IR (KBr, (KBr, $cm^{-1}$): 1237 (ν C=S), 432 (ν Sn–S), 323 (ν Sn–C), 232 (ν Sn–Cl), 1453 (ν C–N), 2868 (ν $CH_2$), 2965 (ν $CH_3$). $^1$H NMR ($CDCl_3$, ppm), $^nJ(^1H, ^1H)$, 2.78 (t, 8H, (10.8)), 1.56–1.64 (m, 8H), 1.21–1.35 (m, 2H), 0.90 (d, 6H, $CH_3$, (6.3)), [7.34–7.38 (m, 5H), SnPh].$^{13}$C NMR ($CDCl_3$, ppm), 196.04 (CSS), 53.36 (C-2,2'), 33.45 (C-3,3'), 29.08 (C-4), 21.84 (C-5, $CH_3$), [136.23, 133.45, 128.2, 129.49 $^4J$[14], SnPh],

### *Synthesis of $(^tBu)_2SnClL$* (**3**)

Compound (**3**) was synthesized by the same procedure used for synthesis of compound (**1**). Here (3.0 g, 17.1 mmol) of 4-methyl-1-piperidine dithiocarboxylic acid and (5.20 g, 17.1 mmol) of ditertiarybutyltin dichloride as starting materials. It was recrystallized from acetone: petroleum ether 4 : 1 (v/v) mixture. Yield: 65%. m.p. 123°C. Solubility: Acetone, methanol, THF and DMSO. Elemental analysis data for $C_{15}H_{30}NS_2ClSn$: Calcd., %C, 40.70; %H, 6.83; %N, 3.16; %S, 14.49. (Found) %C, 40.74; %H, 6.79; %N, 3.12; %S, 14.45. IR (KBr, $cm^{-1}$): 1228 (ν C=S), 428 (ν Sn–S), 529 (ν Sn–C), 262 (ν Sn–Cl), 1452 (ν C–N),

2847 (ν $CH_2$), 2936 (ν $CH_3$). $^1$H NMR ($CDCl_3$, ppm), $^nJ$($^1$H, $^1$H), 2.80 (t, 4H, (10.5)), 1.61–1.82 (m, 4H), 1.15–1.36 (m, H), 1.00 (d, 3H, $CH_3$, (6.6)), [1.48 (s, 9H), $SnC(CH_3)_3$]. $^{13}$C NMR ($CDCl_3$, ppm), 192.90 (CSS), 53.26 (C-2,2'), 33.93 (C-3,3'), 29.09 (C-4), 21.81 (C-5, $CH_3$), [8.45, 40.26 $SnC(CH_3)_3$].

NMR numbering is given in Scheme 1.



**Scheme 1.**

## RESULTS AND DISCUSSION

Chloromono- and diorganotin(IV) complexes (**1**)–(**3**) were prepared by mixing stochiometric amounts of 4-methyl-1-piperidine dithiocarboxylic acid with organotin(IV) chlorides. They are stable and are soluble in common organic solvents.

### *Infrared Spectroscopy*

Infrared spectra of the ligand and synthesized complexes were recorded in the range of 4000–250 $cm^{-1}$. In dithiocarbamates five peaks of primary importance are C=S, C–N, Sn–S, Sn–C and Sn–Cl.

For characterization of 4-methyl-1-piperidine dithiocarboxylic acid by infrared spectroscopy, comparison was made between the spectra of dithiocarboxylic acid and its precursors. The N–H band in secondary amine at 3200 $cm^{-1}$ disappeared when it react with carbon disulfide, indicating the formation of ligand. In chloromono- and diorganotin(IV) complexes comparison was made between the spectra of the complexes and their precursors. The disappearance of –SH band of free ligand in the region 2754 $cm^{-1}$ and appearance of Sn–S stretching bands in the range 427–432 $cm^{-1}$, Sn–C in the range of 529–315 $cm^{-1}$ and Sn-Cl in the range of 262–232 $cm^{-1}$ indicate the formation of complexes [14]. IR data is given in the Experimental section.

The ligand shows prominent aliphatic C–H symmetric and asymmetric bands in range of 2856 and 2949 $cm^{-1}$, respectively, while complexes show the same peaks in the range of 2875–2847 and 2961–2936 $cm^{-1}$. The vibrations due to ν(C=S) and ν(C–N) were found in range of 1282 and 1410 $cm^{-1}$ for ligand and from 1228–1218 and 1453–1452 $cm^{-1}$ for complexes, respectively. This decrease in the frequency of C=S and increase in frequency of C–N for the complexes indicate complexation. From infrared spectra of all complexes it is clear that there is no doublet peak in the region of 950 $cm^{-1}$ which indicate the bidentate nature of the ligand.

**Table 1.** Mass spectral data of 4-methyl-1-piperidine dithiocarboxylic acid and its chloro-organotin(IV) derivatives

| Fragment | (**HL**) | (**1**) | (**2**) | (**3**) |
|---|---|---|---|---|
| $[RCS_2Sn]^+$ | – | 294 (3) | – | 294 (29) |
| $[RCS_2]^+$ | 174 (25) | 174 (8) | – | – |
| $[PhSn]^+$ | – | 197 (2) | 197 (3) | – |
| $[ClSn]^+$ | – | 155 (50) | 155 (43) | 155 (7) |
| $[CS_2]^+$ | 76 (15) | 76 (56) | 76 (86) | 76 (2) |
| $[RCS]^+$ | 142 (33) | 142 (9) | 142 (2) | 142 (46) |
| $[R]^+$ | 98 (100) | 98 (48) | 98 (56) | 98 (8) |
| $[C_3H_6N]^+$ | 56 (48) | 56 (100) | 56 (100) | 56 (100) |
| $[C_4H_8N]^+$ | 70 (3) | 70 (6) | 70 (6) | 70 (38) |
| $[C_5H_9N]^+$ | 83 (21) | 83 (5) | 83 (19) | 83 (21) |
| $[Sn]^+$ | – | 120 (15) | 120 (22) | 120 (17) |

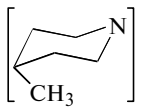
 = R.

**Table 2.** Crystal data and structure refinement parameters for complex (**3**)

| | |
|---|---|
| Empirical formula | $C_{15}H_{30}NS_2ClSn$ |
| Formula weight | 442.66 |
| Crystal system | Monoclinic |
| Space group | *C*2/*c* |
| Unit cell dimension | |
| *a* (Å) | 26.186 (6) |
| *b* (Å) | 13.604 (3) |
| *c* (Å) | 11.918 (3) |
| α (°) | 90.00 |
| β (°) | 111.785 (4) |
| γ (°) | 90.00 |
| *V* (Å$^3$) | 3942.5 (16) |
| *Z* | 8 |
| Dc (g $cm^{-3}$) | 1.492 |
| Crystal size (mm) | 0.40 × 0.40 × 0.40 |
| *F*(000) | 1808 |
| Total reflections | 4011 |
| Independent reflections | 3685 |
| All indices (all data) | $R_1 = 0.0239$, $WR_2 = 0.0474$ |
| Final *R* indices [$I > 2\sigma(I)$] | $R_1 = 0.0204$, $WR_2 = 0.0460$ |
| Goodness of fit | 1.058 |
| θ Range for data collection (°) | 4.04–24.39 |
| Date/restrains/parameters | 4011/0/188 |

### *$^1$H NMR*

$^1$H NMR spectra of the ligand (HL) and compounds (**1**)–(**3**) have been recorded on 300 MHz

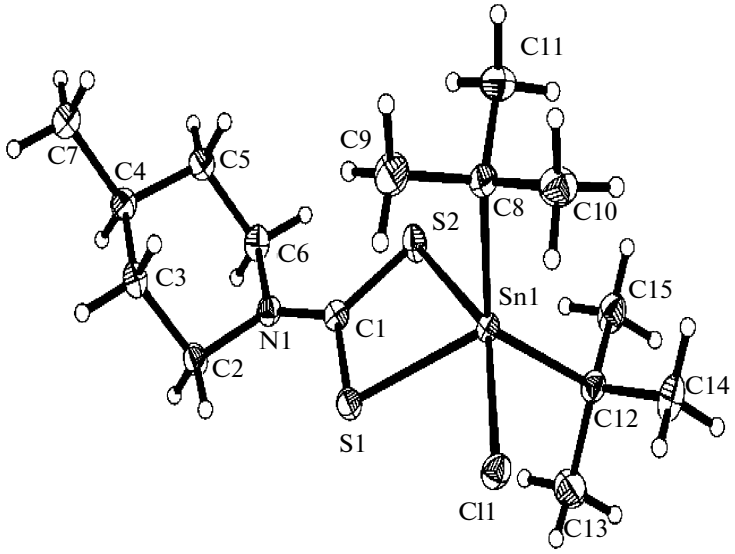



**Fig. 2.** ORTEP drawing of the X-ray structure of complex (**3**).

NMR spectrometer. The characteristic resonance peaks for the ligand and the complexes (**1**)–(**3**) are given in the Experimental section. The expected resonances are assigned by their peak multiplicity, intensity pattern, integration and tin satellites. The integration of spectra shows good agreement with the composition of the compounds.

The $^{1}$H NMR resonance signals of the protons attached to phenyl moieties of the tin have been assigned by their distinct multiplicity, *J*-values and comparison with the results obtained from the incremental method [15]. The protons of tertiary butyltin(IV) shows a sharp singlet at 1.48 ppm and of the phenyl moieties of the phenyltin(IV) derivatives mostly shows a complex pattern in the range 7.22–7.38 ppm.

The SH peak which appears as a singlet at 1.58 ppm in the ligand is absent in all the complexes which shows the deprotonation of the ligand. The methyl protons of the ligand give a sharp doublet at 0.90 ppm with coupling constant of 6.6 Hz. The protons of the 2,2' position appears as a triplet with coupling constant of 12 Hz at 2.78 ppm have moved down field in all the complexes. The rest of the protons which give a complex pattern, appear either with the same values of chemical shift or with a slight change which are non-significant.

### *$^{13}$C NMR*

The characteristic resonance peaks in the $^{13}$C NMR spectra of the ligand and complexes (**1**)–(**3**), are given in Experimental section.

The $^{13}$C NMR spectral data for the R groups attached to tin atom, where $R$ = Ph, $^{t}$Bu were assigned by comparison with related analogues as model compounds, combined with the $^{n}J[^{119}\mathrm{Sn}, ^{13}\mathrm{C}]$ coupling constant [16–18]. The carbon atoms of the phenyl group appear in the expected aromatic region ranging from 129.71–136.23 ppm.

The carbon labeled as (C-1) appears at 178.69 ppm in the ligand has shifted down field in the range of 196.04–192.90 ppm in the complexes, confirms the coordination of sulfur atom to the tin metal. The carbon atoms at 2,2' positions have also been shifted down field in the compounds (**1**)–(**3**). The other carbon atoms appear with slight change in their chemical shift values. This down field shift of carbon atoms labeled as carbon (C-1), carbon (C-2,2'), and appearance of signals for the carbon atoms of the R-groups attached to the tin metal in the $^{13}$C NMR spectra of the complexes indicate the formation of complexes.

### *Mass Spectrometry*

The fragment ions with their m/z (%) values for the ligand (HL) and compounds (**1**)–(**3**) are given in the Table 1.

As tin has ten naturally stable isotopes, each ion appears in the mass spectrum as a series of peaks close to each other due to isotopic effect. It has been observed that large organotin molecules suffer considerable fragmentation in the mass spectrometer, while small organotin molecules often show the molecular ion peaks [19]. In all complexes the base peak is due to the fragment $[C_3H_6N]^+$ with $m/z$ value of 56 which is obtained by the loss of $CS_2$ from the ligand, followed by the removal of $C_2H_4$ and $CH_3$ radicals. During the fragmentation of the complexes, first ligand is sepa-

rated, which is followed by the removal of $CS_2$ and several R groups.

### *Crystal Structure*

The crystal data and selected intramolecular bond distances and angles are given in Tables 2 and 3, respectively. The ORTEP diagram for the molecule of complex (**3**) together with the atom numbering scheme is shown in Fig. 2. The tin atom is five-coordinated by an asymmetrically coordinated dithiocarboxylate ligand, a chloride and two organic substituents. The coordination geometry is intermediate between square pyramidal and trigonal bipyramidal, with a $\tau$ value of 0.41 [20] showing that there is a slight bias towards square pyramidal geometry. The structure is similar to other diorganotin dithiocarbamate of general formula $R_2Sn(S_2CNR'_2)X$, (X is usually chloride), where the $\tau$ values range between 0.4–0.6, but are more often less than 0.5 [21]. The thiocarboxylate group is asymmetrically coordinated to the tin atom, with Sn–S1 and Sn–S2 bond lengths of 2.473(6) and 2.732(6) Å, respectively; the longer Sn-S2 bond length is approximately *trans* to the Cl substituent, with a Cl1Sn1S2 angle of 151.78(2)°. The C8SnlC12 angle is 127.06 (7)°, in keeping with other compounds of this type [21] and the S1Sn1S2 bite angle of the chelating dithiocarboxylate ligand is 68.69(2)°. The S–C bond lengths are the same within experimental error [S1–C1 = 1.747(19) Å and S2–C1 = 1.710(19) Å]. The Sn-Cl bond length [Sn1–Cl1 2.504 (7) Å] lies in the normal bond length range [2.37–2.60 Å] [22].

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

| | |
|---|---|
| Sn(1)–C(8) | 2.189 (2) |
| Sn(1)–C(12) | 2.190 (19) |
| Sn(1)–S(1) | 2.473 (6) |
| Sn(1)–Cl(1) | 2.504 (7) |
| Sn(1)–S(2) | 2.732 (6) |
| S(1)–C(1) | 1.747 (19) |
| S(2)–C(1) | 1.710 (19) |
| N(1)–C(1) | 1.319 (2) |
| N(1)–C(2) | 1.473 (2) |
| N(1)–C(6) | 1.474 (2) |
| C(8)Sn(1)C(12) | 127.06 (7) |
| C(8)Sn(1)S(1) | 112.06 (5) |
| C(12)Sn(1)S(1) | 120.41 (5) |
| S(1)Sn(1)Cl(1) | 83.24 (19) |
| C(8)Sn(1)S(2) | 96.01(5) |
| S(1)Sn(1)S(2) | 68.69 (2) |
| Cl(1)Sn(1)S(2) | 151.78(16) |
| C(1)S(1)Sn(1) | 90.77 (6) |
| C(1)S(2)Sn(1) | 83.22 (7) |
| N(1)C(1)S(2) | 123.32 (14) |
| N(1)C(1)S(1) | 119.91(14) |
| S(2)C(1)S(1) | 116.77(11) |
| C(12)Sn(1)S(2) | 96.36(5) |

## CONCLUSION

Organotin(IV) complexes are synthesized by mixing stoichiometric amounts of 4-methyl piperidine-1-dithiocarboxylic acid and organotin(IV) chlorides. In IR spectra of free ligand, the disappearance of –SH band in the region 2754 $cm^{-1}$ and appearance of Sn–S (432–427 $cm^{-1}$), Sn–C (529–315 $cm^{-1}$) and Sn–Cl (262–232 $cm^{-1}$) bands indicates the formation of complexes. The downfield shift of the carbon-5 in $^{13}C$ NMR spectra confirms the complexation. In most of the complexes the base peak is due to the fragment $[C_3H_6N]^+$ with $m/z$ value of (56). A molecular ion peak is only observed for the ligand (HL). The X-ray crystal structure of complex (**3**) shows the 5-coordinated geometry of the tin complex, which is intermediate between square pyramidal and trigonal bipyramidal, with a $\tau$ value of 0.41. The 4-methyl piperidine-1-dithiocarboxylic acid ligand is asymmetrically coordinated to tin.

## SUPPLEMENTARY MATERIAL

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 692448 for complex (**3**). 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, www.ccdc.cam.ac.uk).

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