



dithiophosphorus ligands, *i.e.* a strong coordination ability of such ligands for tin, only seldom intermolecular associations by bridging dithiocarbamate units were observed, *e.g.* a *bimetallic triconnective* pattern of the 1,1-dithio ligand resulting in dimeric  $[(H_2C=CH)_2Sn\{S_2CN(cyclo-Hexyl)_2\}_2]_2$  via secondary  $Sn\cdots S$  [3.662(5) Å] intermolecular interactions and a distorted pentagonal bipyramidal  $C_2SnS_5$  core,<sup>6,15</sup> or the polymeric  $[Me_2Sn\{S_2CN(CH_2)_5\}Cl]_n$  built through secondary  $Sn\cdots S$  [3.750(1) Å] intermolecular interactions and a distorted octahedral  $C_2SnS_3Cl$  core.<sup>6,16</sup> On the other hand, even if the sulfur atoms in species as  $RR'Sn(dtc)_2$  and  $RR'Sn(dtc)X$  ( $X =$  halogen,  $dtc =$  dithiocarbamate ligand) are usually not involved in intermolecular secondary bonding, the use of 1,1-dithio ligands bearing functionalities with O or N donor atoms, capable for further intermolecular hydrogen bonding, resulted in extended supramolecular networks.<sup>4</sup>

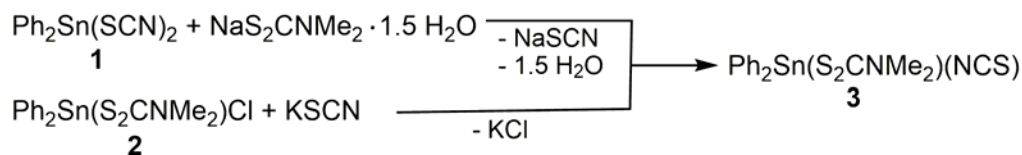
We have extended our studies on complexes with dithiocarbamate ligands in order to investigate their structural features and we reported recently on several diorganotin(IV) compounds of type  $RR'Sn(S_2CNR''_2)_2$  [ $R = Me, Bu^n, Ph; R' = 2-(Me_2NCH_2)C_6H_4, R'' = Me, Et$ ], as well as on

species of type  $R_2Sn(S_2CNR'_2)Cl$  [ $R = Me, Bu^n, Ph, 2-(Me_2NCH_2)C_6H_4, R' = Me, Et$ ] or  $R_2Sn(S_2CNR'_2)(NCS)$  [ $R = Me, Bu^n, 2-(Me_2NCH_2)C_6H_4, R' = Me, Et$ ].<sup>17,18</sup> It should be mentioned here that in contrast with the large number of diorganotin(IV) compounds containing both a dithiocarbamate group and a halido ligand on tin, only few reports were dedicated to related mixed diorganotin(IV) complexes with dithiocarbamate/pseudohalido ligands.

As a continuation of our studies, we report here on the new compound  $Ph_2Sn(S_2CNMe_2)(NCS)$ , emphasizing the structural characteristics at molecular and supramolecular level.

## RESULTS

The diorganotin(IV) compound **3** was prepared by two methods based on salt metathesis reactions between either (i)  $Ph_2Sn(SCN)_2$  (**1**) and sodium dimethyldithiocarbamate, or (ii)  $Ph_2Sn(S_2CNMe_2)Cl$  (**2**) and KSCN, respectively, in 1:1 molar ratio, as depicted in Scheme 1, using a solvent mixture of methanol/dichloromethane.



Scheme 1

$Ph_2Sn(S_2CNMe_2)(NCS)$  (**3**) was isolated as a microcrystalline, colourless solid. The identity and the purity of this compound were confirmed by elemental analysis and multinuclear ( $^1H, ^{13}C, ^{119}Sn$ ) NMR spectroscopy. The ESI+ mass spectrum shows as base peak the  $[Ph_2Sn(S_2CNMe_2)^+]$  cation.

The FT-IR spectrum of **3** displays bands of strong intensity at  $2035\text{ cm}^{-1}$  [ $\nu(CN)$ ] and at  $731\text{ cm}^{-1}$  [ $\nu(CS)$ ], which support an isothiocyanato behavior of the NCS ligand.<sup>19</sup> Bands of strong or medium intensity in the range  $1240\text{--}1550\text{ cm}^{-1}$  suggest a C-N bond of a strength intermediate between single C-N and double C=N bonds, while the bands at  $970$  and at  $1244\text{ cm}^{-1}$  were assigned to  $\nu_s(CS_2)$  and to  $\nu_{as}(CS_2)$ , respectively.<sup>20</sup>

The crystal and molecular structure of **3** was determined by single-crystal X-ray diffraction.

## DISCUSSION

### Spectroscopic characterization in solution

The multinuclear NMR spectra, recorded in  $CDCl_3$  solution at room temperature, are consistent with the formulation of compound **3**. According to the  $^1H$  and  $^{13}C$  NMR spectra, the two phenyl groups attached to tin are equivalent in solution, as are the two methyl groups attached to nitrogen also. The  $^1H$  NMR multiplet resonance characteristic for the  $C_6H_5$ -*ortho* protons is accompanied by 117/119 tin satellites ( $^3J_{119SnH} = 96.2, ^3J_{117SnH} = 80.8$  Hz) and the  $^{13}C$  NMR singlet resonances given by the  $C_6H_5$ -*ortho*, *meta* and *para* carbons are accompanied by tin satellites, as well. In the  $^{13}C$  NMR spectra of  $Ph_2Sn(SCN)_2$  used as starting material, as well as in that one of **3**, a

characteristic resonance for the NCS carbon was not observed. At low field, the  $^{13}\text{C}$  NMR spectrum of **3** displays only one resonance ( $\delta = 196.1$  ppm) assigned to the  $\text{S}_2\text{C}$  in the dimethyldithiocarbamate ligand. The  $^{119}\text{Sn}$  NMR spectrum shows only a singlet, broad resonance, at  $\delta = -387.5$  ppm. The broad aspect of this resonance might be determined by an isothiocyanato behaviour of the NCS ligand

in solution, as it was observed also in other related tin(IV) complexes.<sup>21</sup>

### X-Ray diffraction studies

The molecular structure of **3** is depicted in Figure 1 and relevant interatomic distances and angles are given in Table 1.

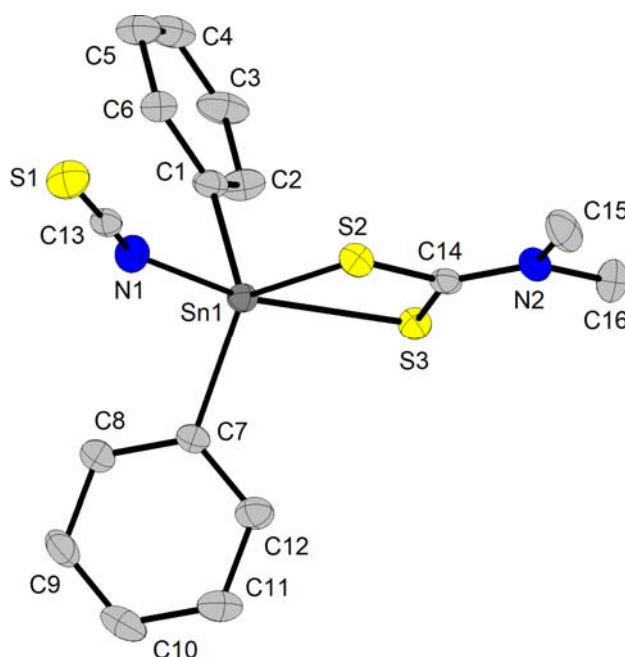


Fig. 1 – Molecular structure of  $\text{Ph}_2\text{Sn}(\text{S}_2\text{CNMe}_2)(\text{NCS})$  (**3**). Thermal ellipsoids are drawn at 50% probability (hydrogen atoms are omitted for clarity).

Table 1

Selected interatomic distances (Å) and angles (°) for $\text{Ph}_2\text{Sn}(\text{S}_2\text{CNMe}_2)(\text{NCS})$ ( <b>3</b> )			
Sn(1)-C(1)	2.138(4)	N(1)-Sn(1)-S(3)	157.51(11)
Sn(1)-C(7)	2.123(4)	C(1)-Sn(1)-C(7)	129.20(16)
Sn(1)-N(1)	2.199(4)	C(1)-Sn(1)-S(2)	115.18(11)
		C(7)-Sn(1)-S(2)	115.60(11)
		N(1)-Sn(1)-C(1)	92.06(16)
		N(1)-Sn(1)-C(7)	92.41(15)
		N(1)-Sn(1)-S(2)	86.57(11)
Sn(1)-S(2)	2.4582(12)	S(3)-Sn(1)-S(2)	71.12(4)
Sn(1)-S(3)	2.6347(11)	S(3)-Sn(1)-C(1)	94.86(12)
		S(3)-Sn(1)-C(7)	99.64(11)
		Sn(1)-S(2)-C(14)	87.65(16)
		Sn(1)-S(3)-C(14)	82.59(16)
C(14)-N(2)	1.321(6)	C(14)-N(2)-C(15)	123.0(4)
C(15)-N(2)	1.464(7)	C(14)-N(2)-C(16)	121.4(4)
C(16)-N(2)	1.466(7)	C(15)-N(2)-C(16)	115.5(4)
C(14)-S(2)	1.739(5)	S(2)-C(14)-S(3)	118.3(3)
C(14)-S(3)	1.715(4)	S(2)-C(14)-N(2)	120.0(3)
		S(3)-C(14)-N(2)	121.8(4)
N(1)-C(13)	1.179(7)	Sn(1)-N(1)-C(13)	152.9(3)
C(13)-S(1)	1.604(5)	N(1)-C(13)-S(1)	178.5(4)

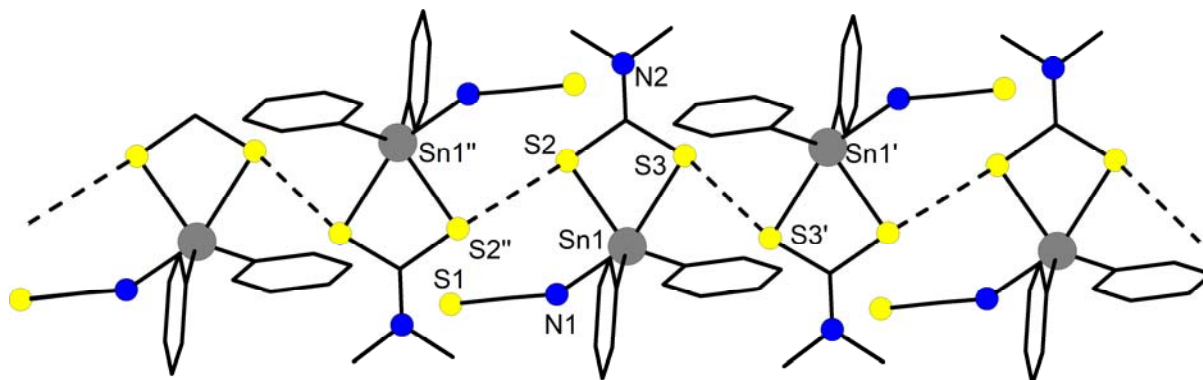


Fig. 2 – View of a polymeric chain built through intermolecular S...S interactions in the crystal of **3**. Hydrogen atoms are omitted for clarity [symmetry equivalent atoms  $(-x, 1-y, -z)$  and  $(1-x, 1-y, 1-z)$  are given by “prime” and “double prime”, respectively].

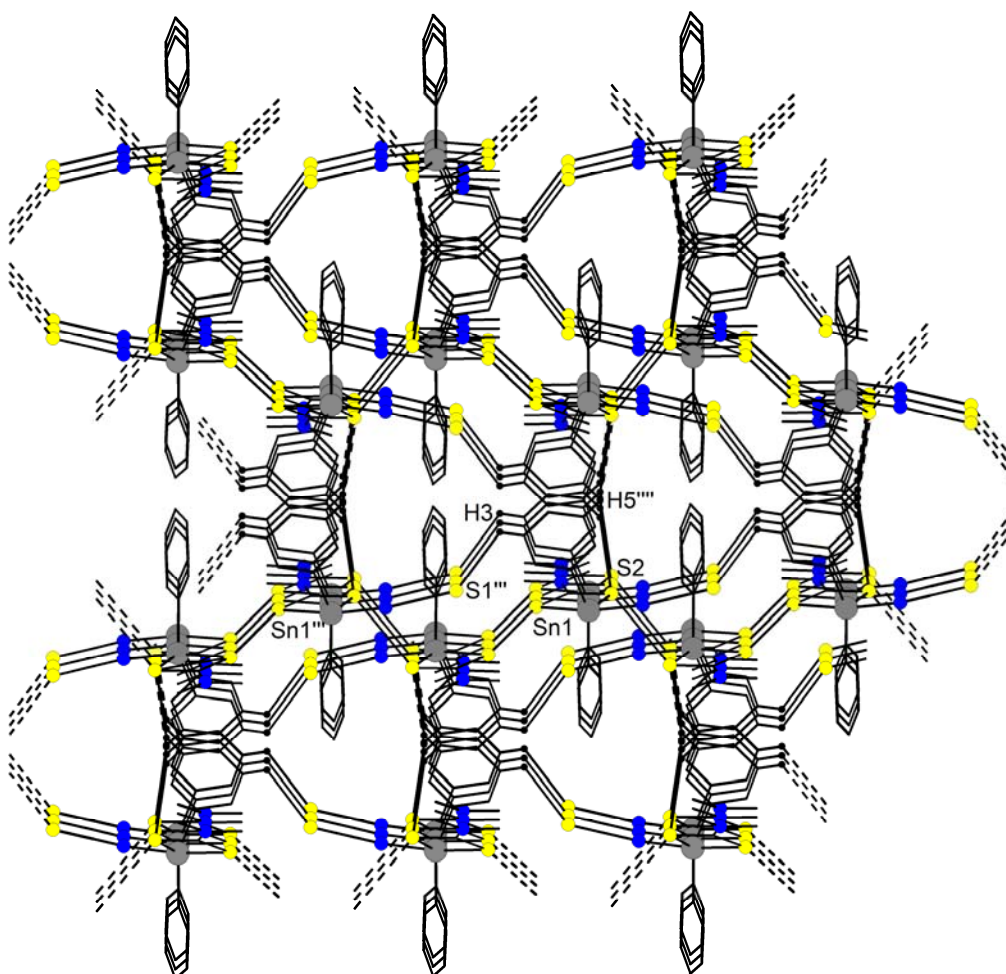


Fig. 3 – View along axis *c* of the 3D supramolecular network in the crystal of **3** (only hydrogens involved in intermolecular contacts are shown) [symmetry equivalent atoms  $(-1+x, y, z)$  and  $(x, 1.5-y, -0.5+z)$  are given by “triple prime” and “quadruple prime”, respectively].

The dimethyldithiocarbamate ligand behaves as an asymmetric bidentate, chelating moiety with slightly different Sn–S bonds [Sn1–S2 2.4582(12) Å, Sn1–S3 2.6347(11) Å; *c.f.*  $\Sigma r_{\text{cov}}(\text{Sn}, \text{S}) = 2.44$  Å,<sup>22</sup>  $\Sigma r_{\text{vdw}}(\text{Sn}, \text{S}) = 4.31$  Å<sup>23</sup>], while the second anionic ligand acts as an isothiocyanato NCS group, being coordinated to tin through the nitrogen atom [Sn1–N1 2.199(4) Å, *c.f.*

$\Sigma r_{\text{cov}}(\text{Sn}, \text{N}) = 2.10$  Å<sup>22</sup>]. In this way a distorted trigonal bipyramidal coordination geometry is realized about tin ( $\text{C}_2\text{SnS}_2\text{N}$  core), with the nitrogen atom and the sulfur atom weaker bonded to tin in axial positions [N1–Sn1–S3 157.51(11)°]. The distortion of the coordination geometry is reflected by a  $\tau$  value of 0.82, where  $\tau$  is a parameter which characterizes the pentacoordinated



complexes, *i.e.*  $\tau = 0$  for an ideal square pyramid (SP) and  $\tau = 1$  for an ideal trigonal bipyramid (TBP).<sup>24</sup> The observed Sn–S interatomic distances are similar to those observed in the related  $\text{Ph}_2\text{Sn}(\text{S}_2\text{CNMe}_2)\text{Cl}$  [2.4718(10)/ 2.6834(10) Å]<sup>17</sup> or  $\text{Me}_2\text{Sn}(\text{S}_2\text{CNMe}_2)$  (NCS) [2.4596(13)/ 2.6688(13) Å],<sup>18</sup> which also exhibit a distorted trigonal bipyramidal coordination geometry with  $\tau$  values of 0.85 and 0.77, respectively. The two carbon-sulfur interatomic distances in the dithiocarbamate ligand of **3** are of similar length and they correspond to intermediate values between single C–S and double C=S bonds, as was found in the related species  $\text{Me}_2\text{Sn}(\text{S}_2\text{CNMe}_2)\text{X}$  (X = Cl,<sup>25</sup> NCS<sup>18</sup>),  $\text{Me}_2\text{Sn}(\text{S}_2\text{CNEt}_2)\text{Cl}$ ,<sup>26</sup> or  $\text{Ph}_2\text{Sn}(\text{S}_2\text{CNMe}_2)\text{Cl}$ .<sup>17</sup> The NCS ligand is almost linear in **3** [N1–C13–S1 178.5(4)°] and the magnitude of the N1–C13 and the S1–C13 interatomic distances suggest a N=C=S structure for this ligand.

A closer look to the crystal revealed no Sn $\cdots$ SCN intermolecular interactions, as was observed in the related  $\text{Me}_2\text{Sn}(\text{S}_2\text{CNR}_2)(\text{NCS})$  (R = Me, Et),<sup>18</sup> but intermolecular S $\cdots$ S contacts between the sulfur atoms of the  $\text{Me}_2\text{NCS}_2$  ligands in neighbour molecules [S2 $\cdots$ S2'' 3.54, S3 $\cdots$ S3' 3.27 Å, *c.f.*  $\Sigma r_{\text{vdW}}(\text{S},\text{S}) = 3.78$  Å<sup>22</sup>] result in polymeric chains (Fig. 2). Such intermolecular S $\cdots$ S secondary interactions (S $\cdots$ S 3.64 Å), weaker than in **3**, were observed previously in the hypercoordinated mercury(II) complex [2-( $\text{Me}_2\text{NCH}_2$ ) $\text{C}_6\text{H}_4$ ] $\text{HgS}(\text{S})\text{CNMe}_2$ .<sup>27</sup>

Further weak H $\cdots$ S intermolecular contacts S1'' $\cdots$ H3 2.93 Å and S2'''' $\cdots$ H5 2.95 Å, *c.f.*  $\Sigma r_{\text{vdW}}(\text{H},\text{S}) = 3.09$  Å<sup>22</sup>] between the  $\text{C}_6\text{H}_5$ -*meta* hydrogens in one phenyl group and the sulfur atoms of the isothiocyanate and the 1,1-dithio ligands of neighbouring molecules of **3**, respectively, connect the polymeric chains in a 3D supramolecular network (Fig. 3).

## EXPERIMENTAL

The starting materials  $\text{Ph}_2\text{Sn}(\text{SCN})_2$  (**1**),<sup>28</sup> and  $\text{Ph}_2\text{Sn}(\text{S}_2\text{CNMe}_2)\text{Cl}$  (**2**),<sup>17</sup> were prepared according to literature procedures, while  $\text{NaS}_2\text{CNMe}_2 \cdot 1.5 \text{H}_2\text{O}$  and KSCN were commercially available and used as received from Aldrich. The melting point was measured on an Electrothermal 9200 apparatus. The ESI+ mass spectrum was recorded on a Thermo Scientific LTQ-Orbitrap XL spectrometer equipped with a standard ESI/APCI source. The <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H} and <sup>119</sup>Sn{<sup>1</sup>H} NMR spectra were recorded on a BRUKER Avance III 400 instrument. The <sup>1</sup>H and <sup>13</sup>C chemical shifts are reported in  $\delta$  units (ppm) relative to the

residual peak of solvent ( $\text{CHCl}_3$ , 7.26 ppm) in the <sup>1</sup>H NMR spectra and to the peak of the deuterated solvent ( $\text{CDCl}_3$ , 77.16 ppm) in <sup>13</sup>C{<sup>1</sup>H} NMR spectra.<sup>29</sup> The <sup>119</sup>Sn{<sup>1</sup>H} NMR resonance is reported in  $\delta$  units (ppm) relative to  $\text{Me}_4\text{Sn}$ . The NMR spectra were processed using the MestReNova software,<sup>30</sup> and the mass spectrum was processed with the Thermo Xcalibur software.<sup>31</sup> Elemental analysis was performed on a Flash EA 1112 analyzer and FT-IR spectra were recorded on a Jasco FTIR-610 machine in the range 4000–500  $\text{cm}^{-1}$ .

### Synthesis of $\text{Ph}_2\text{Sn}(\text{S}_2\text{CNMe}_2)(\text{NCS})$ (**3**)

*Method a:* A solution of  $\text{NaS}_2\text{CNMe}_2 \cdot 1.5 \text{H}_2\text{O}$  (0.22 g, 1.28 mmol) in methanol (10 mL) was added dropwise, under stirring, to a solution of  $\text{Ph}_2\text{Sn}(\text{SCN})_2$  (0.498 g, 1.28 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL). After 3 hours of stirring, the solvents were removed in vacuum and  $\text{CH}_2\text{Cl}_2$  (15 mL) was added to the reaction mixture. NaSCN was filtered off and, after removing  $\text{CH}_2\text{Cl}_2$  from the remained clear solution, the title compound resulted as a colourless microcrystalline solid. The product was washed with n-hexane (5 mL) and dried under reduced pressure. Yield: 0.48 g (83%).

*Method b:* A solution of KSCN (0.13 g, 1.35 mmol) in methanol (10 mL) was added dropwise, under stirring, to a solution of  $\text{Ph}_2\text{Sn}(\text{S}_2\text{CNMe}_2)\text{Cl}$  (0.578 g, 1.35 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL). After 2 hours of stirring, the solvents were removed in vacuum and  $\text{CH}_2\text{Cl}_2$  (15 mL) was added to the reaction mixture. KCl was filtered off and the solvent was removed from the remained clear solution, affording isolation of **3** as a solid which was worked-up as above. Yield: 0.47 g (78%). M.p. 139–140 °C. Anal. Found: C, 42.48; H, 3.66; N, 6.33%. Calc. for  $\text{C}_{16}\text{H}_{16}\text{N}_2\text{S}_3\text{Sn}$  (Mw = 451.21): C, 42.59; H, 3.57; N, 6.21%; <sup>1</sup>H NMR ( $\text{CDCl}_3$ , 400.131 MHz),  $\delta$  [ppm]: 3.43 [s, N( $\text{CH}_3$ )<sub>2</sub>], 7.45–7.54 (m, 6H,  $\text{SnC}_6\text{H}_5$ -*meta+para*), 7.96 (dd, 4H,  $\text{SnC}_6\text{H}_5$ -*ortho*), <sup>3</sup> $J_{\text{HH}} = 7.6$ , <sup>4</sup> $J_{\text{HH}} = 2.2$ , <sup>3</sup> $J_{119\text{SnH}} = 96.2$ , <sup>3</sup> $J_{117\text{SnH}} = 80.8$  Hz); <sup>13</sup>C NMR ( $\text{CDCl}_3$ , 100.61 MHz),  $\delta$  [ppm]: 46.13 [s, N( $\text{CH}_3$ )<sub>2</sub>], 129.17 (s,  $\text{SnC}_6\text{H}_5$ -*meta*), <sup>3</sup> $J_{\text{SnC}} = 87.9$  Hz), 130.72 (s,  $\text{SnC}_6\text{H}_5$ -*para*), <sup>4</sup> $J_{\text{SnC}} = 18.1$  Hz), 135.64 (s,  $\text{SnC}_6\text{H}_5$ -*ortho*), <sup>2</sup> $J_{\text{SnC}} = 60.4$  Hz), 139.63 (s,  $\text{SnC}_6\text{H}_5$ -*ipso*), 196.1 (s, S2C); <sup>119</sup>Sn NMR ( $\text{CDCl}_3$ , 149.2 MHz):  $\delta = -387.5$  (s, br). MS (ESI+, MeOH), *m/z* (%): 393.95 (100) [M – NCS]<sup>+</sup>. FT-IR (v,  $\text{cm}^{-1}$ ): 731s, 970m, 1157m, 1244m, 1394s, 1543s, 2035s.

### Crystal structure determination

Single-crystals of **3**, suitable for X-ray diffraction were obtained from a mixture of chloroform/n-hexane (1:3, v:v). Details of the crystal structure determination and refinement are given in Table 2. Data were collected at room temperature on a Bruker D-8 Venture diffractometer, using graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) from a  $\text{I}\mu\text{S}$  3.0 microfocus source with multilayer optics, at low temperature (100 K). The structure was refined with anisotropic thermal parameters for non-H atoms. Hydrogen atoms were placed in fixed, idealized positions and refined with a riding model and a mutual isotropic thermal parameter. For structure solving and refinement the Bruker APEX3 Software Package was used.<sup>32</sup> Intermolecular secondary bonding interactions were found with PLATON.<sup>33</sup> The drawings were created using the Diamond program.<sup>34</sup>

Table 2

Crystal data and structure refinement for Ph<sub>2</sub>Sn(S<sub>2</sub>CNMe<sub>2</sub>)(NCS) (**3**)

Empirical formula	C <sub>16</sub> H <sub>16</sub> N <sub>2</sub> S <sub>3</sub> Sn
Formula weight, g/mol	451.20
Temperature, K	100(2)
Wavelength, Å	0.71073
Crystal system	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> , Å	10.2097(8)
<i>b</i> , Å	18.7988(13)
<i>c</i> , Å	10.0744(8)
$\alpha$ , °	90
$\beta$ , °	105.937(2)
$\gamma$ , °	90
Volume, Å <sup>3</sup>	1859.3(2)
<i>Z</i>	4
Density (calculated), g/cm <sup>3</sup>	1.612
Absorption coefficient, mm <sup>-1</sup>	1.708
F(000)	896
Crystal size, mm	0.08 x 0.09 x 0.13
Theta range for data collection, °	2.1 to 28.3
Reflections collected / unique data	38266 / 4630
R(int)	0.104
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	4630 / 0 / 204
Goodness-of-fit on F <sup>2</sup>	1.04
Final R indices [I > 2σ(I)]	R1 = 0.0444, wR2 = 0.0700
R indices (all data)	R1 = 0.0861, wR2 = 0.0834
Largest diff. peak and hole, e/Å <sup>3</sup>	0.80 and -0.90

## CONCLUSIONS

The diorganotin(IV) complex Ph<sub>2</sub>Sn(S<sub>2</sub>CNMe<sub>2</sub>)(NCS) (**3**) was prepared and structurally characterized, both in solution and in solid state. The <sup>1</sup>H and <sup>13</sup>C NMR spectra suggest the equivalence of the phenyl groups attached to tin and the methyl groups attached to nitrogen, respectively. The single-crystal X-ray diffraction determination of its molecular structure revealed a distorted trigonal bipyramidal C<sub>2</sub>SnS<sub>2</sub>N core. In the crystal weak S⋯S and H⋯S intermolecular contacts resulted in a 3D supramolecular architecture.

## Supplementary material

CCDC 2046959 contains the supplementary crystallographic data for compound **3**. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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## REFERENCES

1. "Tin Chemistry – Fundamentals, Frontiers and Applications", A. G. Davies, M. Gielen, K. Pannell and E. R. T. Tiekink (Eds.), Wiley, Chichester, 2008.
2. M. Gielen and E. R. T. Tiekink, "Tin compounds and their therapeutic potential", in "Metallotherapeutic Drugs and Metal-based Diagnostic Agents: The Use of Metals in Medicine", M. Gielen and E. R. T. Tiekink (Eds.), Wiley, Chichester, 2005, p. 421.
3. V. K. Jain, *Coord. Chem. Rev.*, **1994**, *135/136*, 809.
4. C. Silvestru and J. E. Drake, *Coord. Chem. Rev.*, **2001**, *223*, 117, and references cited therein.
5. M. Gielen, *Appl. Organomet. Chem.*, **2002**, *16*, 481.
6. E. R. T. Tiekink, *Appl. Organomet. Chem.*, **2008**, *22*, 533, and references therein.
7. J. O. Adeyemi and D. C. Onwudiwe, *Molecules*, **2018**, *23*, 2571.
8. H.-D. Yin and S. C. Xue, *Appl. Organomet. Chem.*, **2006**, *20*, 283.
9. P. K. Gogoi, D. P. Phukan and D. K. Das, *Asian J. Chem.*, **1999**, *11*, 1291.
10. D. C. Menezes, F. T. Vieira, G. M. de Lima, A. O. Porto, M. E. Cortes, J. D. Ardisson and T. E. Albrecht-Schmitt, *Eur. J. Med. Chem.*, **2005**, *40*, 1277.
11. D. C. Menezes, G. M. de Lima, A. O. Porto, C. L. Donnici, J. D. Ardisson, A. C. Doriguetto and J. Ellena, *Polyhedron*, **2004**, *23*, 2103.
12. K. Ramasamy, V. L. Kuznetsov, K. Gopal, M. A. Malik, J. Raftery, P. P. Edwards and P. O'Brien, *Chem. Mater.*, **2013**, *25*, 266.

13. (a) I. Haiduc, "1,1-Dithiolato Ligands", in "Comprehensive Coordination Chemistry II. From Biology to Nanotechnology", J. A. McCleverty and T. J. Meyer (Editors-in-Chief); Vol. 1, "Fundamentals", A. B. P. Lever (Ed.), Elsevier, Amsterdam, 2003, p. 349, and references cited therein. (b) I. Haiduc, "1,1-Dithiolato Ligands", in "Reference Module in Chemistry, Molecular Sciences and Chemical Engineering" (on line publication), Elsevier, Amsterdam, 2013, p. 1-15, <http://dx.doi.org/10.1016/B978-0-12-409547-2.00884-2> (update of ref. 13a).
14. (a) I. Haiduc, "Dichalcogenoimidodiphosph(in)ate Ligands", in "Comprehensive Coordination Chemistry II. From Biology to Nanotechnology", J. A. McCleverty, T. J. Meyer (Editors-in-Chief); Vol. 1, "Fundamentals", A. B. P. Lever (Ed.), Elsevier, Amsterdam, 2003, p. 323, and references cited therein. (b) I. Haiduc, "Dichalcogenoimidodiphosph(in)ate Ligands", in "Reference Module in Chemistry, Molecular Sciences and Chemical Engineering" (online publication), Elsevier, Amsterdam, 2013, p. 1-9, <http://dx.doi.org/10.1016/B978-0-12-409547-2.00928-8> (update of ref. 14a).
15. V. J. Hall and E. R. T. Tiekink, *Main Group Met. Chem.*, **1998**, *21*, 245.
16. S. Ali, S. U. Ahmad, S. Shahzadi, Sadiq-ur-Rehman, M. Parvez and M. Mazhar, *Appl. Organomet. Chem.*, **2005**, *19*, 201.
17. C. Comşa, A. Cristea, A. Silvestru and C. Silvestru, *Studia Univ. Babeş-Bolyai, Chem.*, **2006**, *51*, 41.
18. N. Chiorean, C. Coza, A. Pop and A. Silvestru, *J. Organomet. Chem.*, **2019**, *880*, 83.
19. K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds", sixth edition, Part B, Wiley, New Jersey, 2008, p. 120.
20. (a) H. Nabipour, S. Ghammamy, S. Ashuri and Z. S. Aghbolagh, *Org. Chem. J.*, **2010**, *2*, 75; (b) G. Eng, X. Song, Q. Duong, D. Strickman, J. Glass and L. May, *Appl. Organomet. Chem.*, **2003**, *17*, 218.
21. C. Coza, A. Stegărescu, R. Şuteu and A. Silvestru, *J. Organomet. Chem.*, **2015**, *777*, 71.
22. J. Emsley, "Die Elemente", Walter de Gruyter, Berlin, Germany, 1994.
23. S. Alvarez, *Dalton Trans.*, **2013**, *42*, 8617.
24. A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn and C. Verschoor, *J. Chem. Soc., Dalton Trans.*, **1984**, 1349.
25. K. Furue, T. Kimura, N. Yasuoka, N. Kasai and M. Kakudo, *Bull. Chem. Soc. Jpn.*, **1970**, *43*, 1661.
26. E. R. T. Tiekink, V. J. Hall and M. A. Buntine, *Z. Kristallogr.*, **1999**, *214*, 124.
27. O. Cadar, A. Pöllnitz, D. Mărgineanu and C. Silvestru, *Inorg. Chim. Acta*, **2018**, *475*, 90.
28. P. R. Shukla and A. Sattar, *Asian J. Chem.*, **1997**, *9*, 598.
29. G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, **2010**, *29*, 2176.
30. MestReNova, version 10.0.1-14719. Mestrelab Research S.L., Feliciano Barrera 9B, Santiago de Compostela, 15706 (Spain), **2015**.
31. Qual Browser, Thermo Xcalibur, version 2.1.0 SP1.1160. Thermo Fischer Scientific Inc., Waltham, MA, 02454 (USA), **2011**.
32. G. M. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.*, **2015**, *71*, 3.
33. A. L. Spek, *Acta Crystallogr., Sect. D: Biol. Crystallogr.*, **2009**, *65*, 148.
34. DIAMOND-Visual Crystal Structure Information System, Crystal Impact, Postfach 1251, D-53002 Bonn (Germany), **2015**.

