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Influence of functionalities on the structure and luminescent properties of organotin(IV) dithiocarbamate complexes

Ajit N. Gupta [a], Vinod Kumar [a], Vikram Singh [a], Amit Rajput [b], Lal Bahadur Prasad [a], Michael G.B. Drew [c], Nanhai Singh [a, *]

[a] Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi 221005, India
[b] Department of Chemistry, Indian Institute of Technology, Kanpur 208016, India
[c] Department of Chemistry, University of Reading, Whiteknights, Reading, RG6 6AD UK

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ABSTRACT

Five new organotin(IV) dithiocarbamate complexes of the form R_2SnL_2 (R = ^{n}Bu, L = L1, (4-phenylpiperazine-1-dithiocarbamate) **1**, L2, (N-benzyl-N′-methyl-4-pyridyldithiocarbamate) **2**; Ph, L3, (N-benzyl-N′-methyl-3-pyridyldithiocarbamate) **3**) and Ph_3SnL (L = L4, (N,N′-di(methyl-3-pyridyldithiocarbamate)) **4**, L5, (4-ethoxycarbonylpiperidine-1-dithiocarbamate) **5**) have been synthesized and characterized by elemental analysis, spectroscopy (IR, UV–Vis., ^{1}H, ^{13}C and ^{119}Sn NMR) and their structures have been investigated by single crystal X-ray crystallography. In (**1**,**2**) the structure has C_2 symmetry with the tin atom in a highly distorted octahedral six-coordinate geometry in which the bidentate ligands are asymmetrically bonded and the two ^{n}Bu groups subtend an angle at the metal of 140.7(1), 141.4(3)°. By contrast **3**, also with C_2 symmetry, with phenyl substituents, is closely octahedral. In **3** the Py(N) on the dtc backbone interacts with the H37 on the adjacent molecule via unconventional C–H···N hydrogen bonding forming a six membered benzene like ($C_2H_2N_2$) structure. In **4** and **5** five coordinate TBP geometry is established; **4** contains two molecules in the asymmetric unit (**4A** and **4B**). In **4** the Py(N) on the dithiocarbamate unit uniquely interacts with the tin atom on the neighbouring molecule with Sn···N contacts at 3.11 Å. The C–H···π (CG) interactions between CG of **4A** and H34 of **4B** are also observed. These interactions have been supported by theoretical calculations. All the complexes luminesce in CH_2Cl_2 solution at room temperature except for **1**; the strongest luminescent behaviour is found in **4**. TGA analysis of **3** and **5** show a double and single step decomposition respectively.

Introduction

Transition and main group metal 1,1-dithiolates particularly that of dithiocarbamate ligands have been extensively studied because of their structural diversities, magnetic, optical and conducting properties and multifarious applications as sensitizers in solar energy conversion schemes, single source precursors for the formation of metal sulphides, flotation agents in metallurgy, oil additives, vulcanization accelerators in rubber technology, herbicides and pesticides etc [1–10].

The variety of structures and multifaceted chemistry of the monoanionic dithiocarbamate ligands may be viewed to the resonance structures (Fig. 1c) they exhibit in their complexes. The dithiocarbamate ligands are generally S,S- chelating due to dominant contribution of the resonance form c (Fig. 1) but less commonly they can bind to a metal in a chelating-bridging and monodentate fashion.

The growing interest in the dithiocarbamate complexes stems due to functionalization of the **R** groups on the nitrogen atom of the dithiocarbamate backbone which may result in more intriguing structures and may tune their physical properties. The resurgence of interest in hypervalent tin(IV)/organotin(IV) dithiocarbamate complexes in recent years is due to their rich variety of structures and applications in fields as diverse as agriculture, biology, catalysis and their use as single source precursors to tin sulphide materials (SnS, SnS_2, and Sn_2S_3) [8,11]. The design and development of dithiocarbamate ligands functionalized with additional donor groups enabling expanded bonding capabilities have not been a focus of research investigation for a long time. The majority of tin(IV)/organotin(IV) complexes reported until recently have been formed with the classical alkyl/aryl functionalized dithiocarbamate ligands [11].

Recently we modified the dithiocarbamate backbone by introducing the pyridyl group which resulted in the formation of both inter- and intramolecular M–N bonding/bonding interactions in

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* Corresponding author. Fax: +91 542 2386127.
E-mail addresses: nsinghbhu@gmail.com, nsingh@bhu.ac.in (N. Singh).

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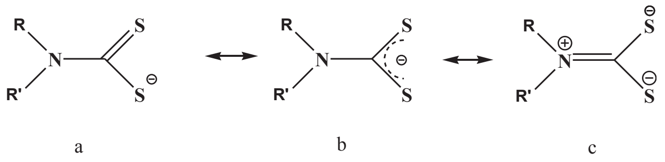

Fig. 1. Resonance structures of the dithiocarbamate ligands.

homo- and heteroleptic complexes which showed strong luminescent characteristics [12]. The pyridyl functionalized dithiocarbamate ligands manifest several features such as (i) the far apart Py(N) and dithiocarbamate (S,S) donor atoms may facilitate polymeric structures via M—N bonding/bonding interactions in homo- and heterometallic complexes (ii) the enhanced conjugation and conformational rigidity provided by the Py(N) may modify the luminescent behaviour of the complexes and (iii) the Py(N) makes available the bonding sites that may facilitate intra- and intermolecular hydrogen bonding to generate multidimensional arrays which are obviously not associated with the common alkyl/aryl dithiocarbamates. These modifications to the ligand environment can lead to significant changes in the structures (Fig. 2), luminescent properties and their uses as single source precursor for tin sulphides.

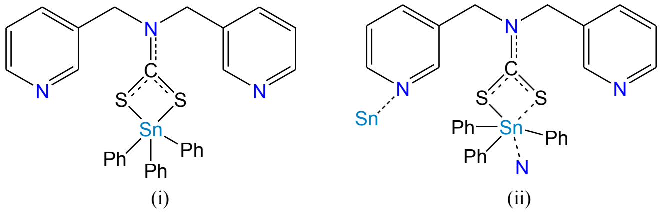

Fig. 2. The possible coordination modes for the pyridine functionalized ligand L4.

In order to establish possible changes in bonding behaviour/molecular architectures and luminescent characteristics it was considered worthwhile to make changes to the ligand frameworks and to undertake the synthesis, structural investigations, luminescent properties and TGA of five new organotin(IV) complexes utilizing the 4-phenylpiperazine-1-dithiocarbamate L1, N-benzyl-N′-methyl-4-pyridyldithiocarbamate L2, N-benzyl-N′-methyl-3-pyridyldithiocarbamate L3, N,N′-dimethyl-3-pyridyldithiocarbamate L4 and 4-ethoxycarbonylpiperidine-1-dithiocarbamate L5 ligands (Fig. 3). The results of these investigations are described in this presentation.

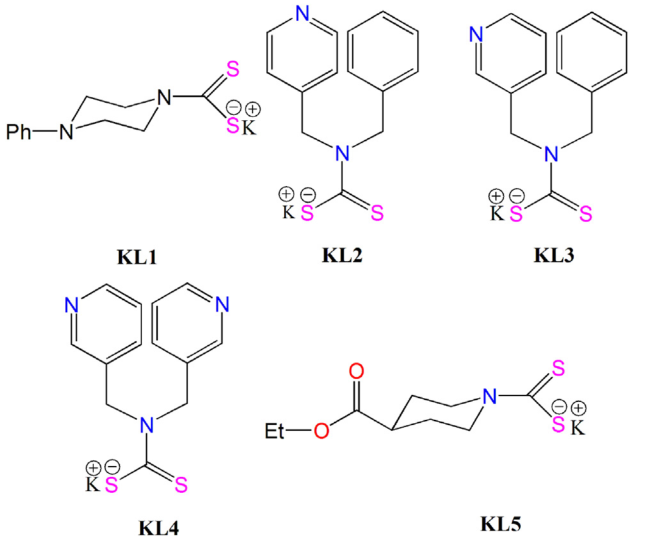

Fig. 3. Structure of the ligands (K**L1**-K**L5**) used in this work.

Experimental section

Materials and methods

All experiments were performed in open atmosphere. The chemicals 4-ethoxycarbonylpiperidine (Sigma–Aldrich), pyridine-4-aldehyde, pyridine-3-aldehyde, 3-picolylamine, benzyl amine and N-phenylpiperazine (all SPECTROCHEM) were used as received. Solvents were distilled prior to use. The potassium salt of the ligands (4-phenylpiperazine-1-dithiocarbamate) K**L1**, (N-benzyl-N′-methyl-4-pyridyldithiocarbamate) K**L2**, (N-benzyl-N′-methyl-3-pyridyldithiocarbamate) K**L3**, N, N′-di(methyl-3-lpyridyl)dithiocarbamate K**L4** and 4-ethoxycarbonylpiperidine-1-dithiocarbamate K**L5** were prepared by reaction of appropriate secondary amines with KOH and CS_2 in THF according to previously reported procedures [12] and characterized by IR, ^{1}H and ^{13}C NMR spectra. The experimental details pertaining to elemental (C, H, N) analyses, IR (KBr discs), NMR (^{1}H, ^{13}C and ^{119}Sn), UV–Vis. absorption and photoluminescent spectra are the same as described elsewhere [12]. TGA was recorded on a Perkin Elmer STV 6000 TG/DTA.

Syntheses of complexes

[R_2SnL_2] (R = ^{n}Bu, L = L1, **1**; L2, **2**; Ph, L3, **3**)
[R_3SnL] (R = Ph, L = L4, **4**; L5, **5**)

The complexes **1**–**3** were prepared by treating the one equivalent methanolic solution of the dibutyltin dichloride (0.303 g, 1 mmol)/diphenyltin dichloride (0.343 g, 1 mmol) with two equivalents of respective ligands while **4** and **5** were prepared by treating the triphenyltin chloride (0.385 g, 1 mmol) with the respective ligands in 1:1 ratio as given in Scheme 1b. The white precipitate was formed in a little while. In each case the reaction mixture was stirred for 6 h and the solid product was collected by filtration, washed with MeOH (2 × 5 ml) and ether (5 ml), and vacuum-dried. The crude products were recrystallized from dichloromethane/methanol mixture, yielding white crystals of the compounds **1**–**5**.

Characterization data

[(^{n}Bu)$_2$Sn(L1)$_2$] (1): Yield: (0.459 g, 75%), m. p. 140–142 °C. Anal. calc. for $C_{30}H_{44}N_4S_4Sn$ (707.62): C, 54.46; H, 6.57; N, 3.97%. Found: C, 54.35; H, 6.39; N, 3.78%. IR (KBr, cm^{-1}) $\nu = 1466$ ($\nu_{C\text{–}N}$), 1077 ($\nu_{C\text{–}S}$) cm^{-1}. ^{1}H NMR (300.40 MHz, $CDCl_3$): $\delta = 7.24\text{–}6.84$ (m, 10H, C_6H_5–), 4.19 (s, 8H, C_2H_4-NPh), 3.22 (s, 8H, C_2H_4–NCS_2), 1.99 (broad, 2H, –CH_2), 1.83 (broad, 2H, –CH_2), 1.40–1.33 (m, 2H, –CH_2), 0.86 (t, $J = 7.2$ Hz, 3H, –CH_3) ppm. ^{13}C NMR (75.45 MHz, $CDCl_3$): $\delta = 200.66$ (CS_2), 150.26 (1C, N–C_1 of C_6H_5–N), 129.29 (2C, C_3 & $C_{3'}$), 120.59 (1C, C_4), 116.43 (2C, C_2 & $C_{2'}$), 50.84, 48.80 (NC_4H_8-NPh), 29.66 (C-α), 28.42 (C-β), 26.37 (C-γ), 13.78 (C-δ) (C_4H_9Sn) ppm, (C_4H_9Sn) ppm. ^{119}Sn NMR (111.95 MHz, $CDCl_3$): $\delta = -330.66$ ppm. UV–vis. (CH_2Cl_2, λ_{max}/nm, ε/M^{-1} cm^{-1}): 258 (7.45×10^4), 290 (2.93×10^4).

[(^{n}Bu)$_2$Sn(L2)$_2$] (2): Yield: (0.537 g, 69%) m. p. 154–157 °C. Anal. calc. for $C_{36}H_{44}N_4S_4Sn$ (779.6): C, 55.45; H, 5.69; N, 7.19%. Found: C, 55.28; H, 5.51; N, 6.96%. IR (KBr, cm^{-1}) $\nu = 1483$ ($\nu_{C\text{–}N}$), 1080 ($\nu_{C\text{–}S}$) cm^{-1}. ^{1}H NMR (300.40 MHz, $CDCl_3$): δ 8.58 (s, 4H, Py-H), 7.32–7.11 (m, 14H, Py-H + Ar–H) 4.94 (s, 4H, Py-CH_2), 4.89 (s, 4H, Ar–CH_2–), 1.87 (broad, 2H, –CH_2), 1.73 (broad, 2H, –CH_2), 1.46–1.39 (m, 2H, –CH_2), 0.93 (t, $J = 7.2$ Hz, 3H, –CH_3) ppm. ^{13}C NMR (75.45 MHz, $CDCl_3$): $\delta = 201.82$ (CS_2), 150.19, 143.02, 133.32, 128.75, 122.12 (C_5H_5N + C_6H_5), 57.74 (Py-CH_2), 55.27 ($ArCH_2$), 29.33 (C-α), 27.82 (C-β), 26.14 (C-γ), 13.64 (C-δ) (C_4H_9Sn) ppm. ^{119}Sn NMR (111.95 MHz, $CDCl_3$): $\delta = -336.82$ ppm. UV–vis. (CH_2Cl_2, λ_{max}/nm, ε/M^{-1} cm^{-1}): 255 (5.11×10^4), 286 (2.0×10^4).

$[Ph_2Sn(L3)_2]$ (3): Yield: (0.622 g, 76%) m. p. 159–162 °C. Anal. calc. for $C_{40}H_{36}N_4S_4Sn$ (819.6): C, 58.61; H, 4.43; N 6.83%. Found: C, 58.46; H, 4.28; N 6.62%. IR (KBr, cm^{-1}) $\nu = 1469$ ($\nu_{C–N}$), 1069 ($\nu_{C–S}$) cm^{-1} .^{1}H NMR (300.40 MHz, $CDCl_3$): δ = 8.54–8.43 (m, 4H, Py), 7.65–7.19 (m, 14H, Ar–H + PyH), 4.98 (s, 4H,–CH_2–) ppm. ^{13}C NMR (75.45 MHz, $CDCl_3$): δ = 202.97 (CS_2), 150.24, 149.54, 135.48, 134.25, 133.60, 130.57, 128.65, 123.73 (C_5H_5N+$(C_6H_5)_2Sn$) ppm. ^{119}Sn NMR (111.95 MHz, $CDCl_3$): δ = −483.31 ppm. UV–vis. (CH_2Cl_2, λ_{max}/nm, ε/M^{-1} cm^{-1}): 258 (5.91×10^4), 295 (1.6×10^4).

$[Ph_3SnL4]$ (4): Yield (0.449 g, 72%) m. p. 176–178 °C. Anal. calc. for $C_{31}H_{27}N_3S_2Sn$ (624.3): C, 59.73; H, 4.36; N, 6.73%. Found: C, 59.58; H, 4.53; N, 6.58%. IR (KBr, cm^{-1}) $\nu = 1479$ ($\nu_{C–N}$), 1070 ($\nu_{C–S}$) cm^{-1}. ^{1}H NMR (300.40 MHz, $CDCl_3$): δ = 8.55–8.48 (d, 2H, C_5H_5N) 7.26–7.82 (m, 18H, Ar–H+3H, C_5H_5N), 5.07 (s, 4H, Py–CH_2–) ppm. ^{13}C NMR (75.45 MHz, $CDCl_3$): δ = 200.55 (CS_2), 149.54, 148.99, 141.24, 123.77 (C_5H_5N), 136.41, 135.45, 130.44, 129.38, 128.65, 128.45 (SnC_6H_5) ppm. ^{119}Sn NMR (111.95 MHz, $CDCl_3$): δ = −162.75 ppm. UV–vis. (CH_2Cl_2, λ_{max}/nm, ε/M^{-1} cm^{-1}): 256 (9.03×10^4), 300 (2.42×10^4).

$[Ph_3SnL5]$ (5): Yield: (0.500 g, 80%) m. p. 149–151 °C. Anal. calc. for $C_{27}H_{29}NO_2S_2Sn$ (582.3): C, 55.68; H, 5.02; N, 2.41%. Found: C, 55.52%, H, 4.83; N, 2.19%. IR (KBr, cm^{-1}) $\nu = 1477$ ($\nu_{C–N}$), 1069 ($\nu_{C–S}$) cm^{-1}. ^{1}H NMR (300.40 MHz, $CDCl_3$): δ 7.79–7.36 (15H, $(C_6H_5)_3Sn$), 4.18–4.11 (q, 2H, –O–CH_2–Me), 3.49–3.42 (t, 4H, –N$(CH_2)_2$–), 2.66 (s, 1H, CH–COOEt), 2.0–2.03 (m, 4H, CH$(CH_2)_2$), 1.27–1.22 (t, 3H, CH_3–) ppm. ^{13}C{^{1}H} (75.45 MHz, $CDCl_3$): δ 195.58 (CS_2), 173.72 (–COOEt), 142.15, 136.41, 135.45, 130.29, 129.64, 128.83, 128.45 (SnC_6H_5) 60.79 (–CH_2), 51.80, 50.55 (N$(CH_2)_4$), 39.31 (C$(CH_2)_2$), 27.69 (CH), 14.06 (CH_3–) ppm. ^{119}Sn NMR (111.95 MHz, $CDCl_3$): δ = −183.40 ppm. UV–vis. (CH_2Cl_2, λ_{max}/nm, ε/M^{-1} cm^{-1}): 250 (9.82×10^4), 300 (2.83×10^4).

Crystallography and theoretical calculations

X-ray crystal structure determinations

The X-ray diffraction data were collected by mounting single crystals of the samples on glass fibers. Single crystal X-ray data for **1**–**5** were collected on an Oxford Diffraction X-calibur CCD diffractometer at 293 K using Mo Kα radiation. The CRYSALIS program was used for data reduction [14a]. The crystal structures were solved by direct methods using the SHELXS-97 program [14b] and refined on F^2 by full matrix least-squares technique using SHELXL-97 [14c]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were geometrically fixed. In complex **4**, there are two molecules called **A** and **B** in the asymmetric unit. In **A**, nitrogen atom in a pyridine rings is disordered over two sites. Molecular structures were drawn using Diamond 3.0 and their weak interactions were shown using Mercury 2.2.

Theoretical calculations

Single point calculations were carried out using the Gaussian 03 program [15] Structures were optimized using the B3LYP density functional together with basis sets LANL2DZ for Sn, 6-31+G* for S and 6-31G for the remaining atoms. Starting models were taken from the crystal structures but with hydrogen atoms given theoretical positions.

Results and discussion

Synthetic procedure

The complexes **1**–**3** were synthesized by the reaction between the respective ligand (Fig. 3) and di-n-butyl/diphenyltin(IV) dichloride in 2:1 ratio while **4** and **5** by the reaction between KL4 or KL5 and triphenyltin(IV) chloride in 1:1 ratio (Scheme 1). All the complexes are isolated in quantitative yields, air stable, soluble in most common organic solvents and melt in temperature range 140–178 °C.

$$R_2SnCl_2 \,/\, Ph_3SnCl \xrightarrow[\text{rt,6 h, - KCl}]{\text{KL, MeOH}} R_2SnL_2 \,/\, Ph_3SnL$$

R=^{n}Bu, L1(**1**), L2 (**2**), Ph, L3 (**3**), L4 (**4**), L5 (**5**)

Scheme 1. General methodology for the synthesis of complexes **1**–**5**.

Spectroscopy

IR spectra of the complexes **1**–**5** show ν(C–N) and ν(CS_2) frequencies near 1466–1483, and 1069–1080 cm^{-1} diagnostic of dithiocarbamate ligand coordination. A significant enhancement in the ν(C–N) frequency of the dithiocarbamate complexes in comparison to the potassium salts of the ligands KL1-KL5 (1259–1348 cm^{-1}) concomitant with an increase in the C–N bond order (*vide infra*, X-ray crystallography) and dominant resonance structure (Fig. 1c).

In ^{1}H NMR spectra of the complexes (**1**–**5**), show characteristic resonances of the ligand functionalities and integrate well to the corresponding hydrogen atoms and there is no perceptible shift in the proton NMR spectra of complexes in comparison to the potassium salts of the ligands. In the ^{13}C NMR all the complexes showed a single low field resonance associated with the NCS_2 carbons of the dithiocarbamate moieties in the range δ 195.58–202.97 ppm. Notably because of the dominant contribution of $\mathbf{R_2N^+{=}CS_2^{2-}}$ resonance form in the dithiocarbamate complexes the NCS_2 carbon is more shielded than the free ligands hence the ^{13}C signal is shifted to higher field in the complexes as compared to free ligands (δ = 213.62–214.75 ppm).

^{119}Sn NMR spectroscopy is a very useful tool for investigating the coordination environment about the tin atom in organotin dithio complexes. As the coordination number around the tin increases, the ^{119}Sn chemical shift moves to lower frequency depending on the nature of substituents present on the dithio backbone. The ^{119}Sn NMR chemical shifts for the di-n-butyltin derivatives **1** and **2** are δ −330.66 and −336.82 ppm respectively are typical of six coordination of the tin atom while for diphenyltin derivative (**3**) δ −483.31 ppm is well within the range of diorganotin dithiocarbamates. The triphenyltin derivative **4** and **5** show chemical shifts −162.75 and −183.40 ppm respectively which is diagnostic of the five coordinate tin complexes [11b,h].

UV–Vis. and photoluminescent spectra

The UV–Vis. absorption spectra of **1**–**5** (Fig. 4a) in the dichloromethane solution display strong to medium bands near 260 nm (ε = 51,110–98,200 M^{-1} cm^{-1}) and 300 nm (ε = 16,000–29,300 M^{-1} cm^{-1}) which are assignable to π-π*intraligand charge transfer (ILCT) and ligand to metal charge transfer (LMCT) transitions respectively [11e].

In comparision to main group metal complexes, the luminescent properties of tin(IV)/organotin(IV) are extremely rare in the literature. Upon excitation at 285–300 nm the all the complexes except **1** exhibits a broad unstructured emission band at about 400 nm (Fig. 4b) which emanates from the LMCT state. It is worth mentioning that the lone pair of electrons on the pyridyl functionalities in **4** enhances conjugation, thus increasing the luminescent character in comparison to **2** and **3** with only one pyridyl

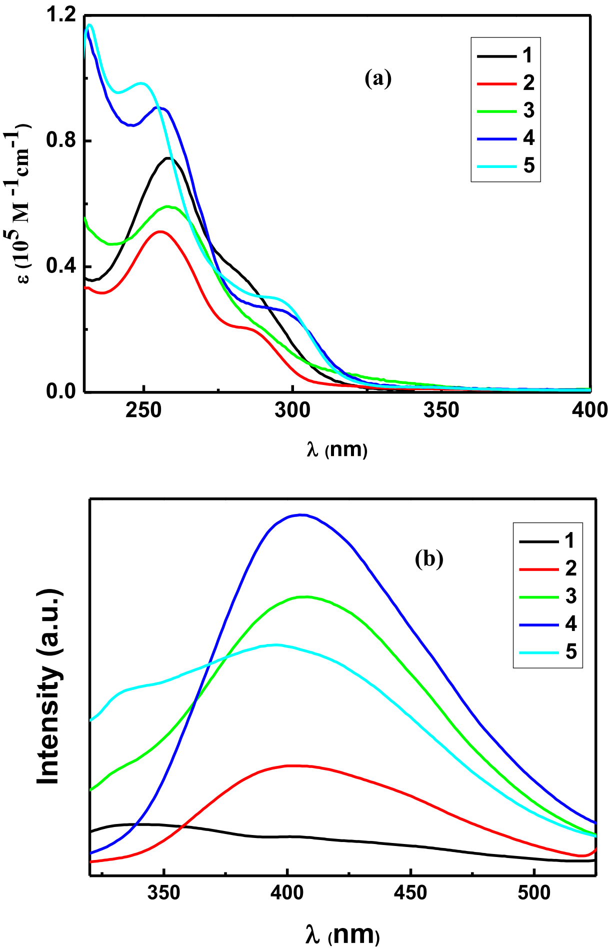

Fig. 4. (a) UV–Vis. absorption spectra of **1**–**5** in CH_2Cl_2 solution and (b) Photoluminescent spectra of **1**–**5** at room temperature.

Table 1
Selected bond lengths (Å) and bond angles° for **1**–**3**.

	1	2	3
Sn(1)–S(11)	2.9714(6)	2.8960(13)	2.5932(12)
Sn(1)–S(13)	2.5332(6)	2.5543(12)	2.6798(13)
Sn(1)-C(41)	2.140(2)	2.145(5)	2.139(4)
S(11)–C(12)	1.695(2)	1.705(5)	1.724(4)
S(13)–C(12)	1.731(2)	1.728(5)	1.713(4)
C(12)–N(14)	1.340(3)	1.356(6)	1.334(5)
S(13)–Sn(1)–C(41)	103.91(7)	104.27(14)	159.63(12)
C(41)–Sn(1)–C(41[a])	140.7(1)	141.4(3)	101.9(2)
S(13)–Sn(1)–S(13[a])	84.79(3)	87.81(6)	77.25(5)
C(41)-Sn(1)-S(13[a])	104.88(7)	103.30(13)	92.68(12)
C(41)-Sn(1)-S(11)	84.60(8)	81.44(13)	94.86(11)
C(41)-Sn(1)-S(11[a])	84.05(8)	85.69(14)	101.48(11)
S(11)-Sn(1)-S(13)	64.71(3)	65.95(4)	68.07(4)
S(13)-Sn(1)-S(11[a])	149.49(3)	153.58(4)	91.23(4)
S(11)-Sn(1)-S(11[a])	145.80(3)	140.41(5)	153.96(4)
S(11)–C(12)–S(13)	120.09(13)	120.5(3)	118.3(3)

[a] Symmetry elements **1** -x, y, 1.5-z; **2** 1-x, y, 1.5-z; **3** 1-x, y, 0.5-z.

group. Also, **5** shows somewhat strong luminescent behaviour due to two phenyl groups bonded to the tin thereby increasing the conjugation over the molecule in comparison to **1** having di-n-butyl fragment.

Crystal structures

Single crystals of **1**–**5** were grown by slow evaporation of the dichloromethane/methanol solution of the compounds. Selected bond distances, bond angles and crystallographic details are listed in Tables 1 and 2 and Table S1, ESI and molecular diagrams for **1**–**5** are shown in Figs. 5 and 7.

In the crystal structures of **1**, **2** and **3** the metal occupies a two-fold axis so that the asymmetric unit contains only half of the molecule. In each case, the metal is bonded to sulphur atoms from two dithiocarbamate ligands and two carbon atoms from c.a. di-n-butyl (in **1**, **2**) or phenyl ligands (in **3**). In **1** and **2**, the sulphur atoms of the dithiocarbamate ligands are bound unequally to the tin atom with S11 at distances 2.533(1)–2.554(1) Å and the S13 at somewhat longer distances of 2.896(1)–2.971(1) Å although these latter distances are still significantly less than the sum of the van der Waals radii of tin and sulphur (3.97 Å) and can be considered as bonds. The Sn–C distances of 2.140(2)–2.145(5) Å in these complexes are well within the range of reported diorganotin(IV) dithiocarbamate complexes [11a,b,d]. The two four-membered dithiocarbamate chelate rings are almost coplanar intersecting at angles of 1.95° in **1** and 4.05° in **2** so could be described as forming an equatorial plane. However the C41–Sn–C41 angles are far from axial being 140.7(1)° and 141.4(3)°. The coordination geometry around the tin atom is best considered as six-co-ordinate with a severely distorted octahedral geometry. In **3**, the geometry around the tin atom is very different. The two independent Sn–S distances are similar with Sn–S11, Sn–S13 2.593(1) and 2.680(1) Å. The Sn–C41 bond length is 2.139(4) Å. The two four-membered chelating dithiocarbamate rings intersect at 87.6(1)° and the geometry can be described as a distorted octahedral with three sulphur atoms and one carbon atom in the equatorial plane [11f]. The angle C41–Sn–C41 is 101.9(2)°, c.a. 40° less than the values in **1** and **2**.

The more intriguing feature of **3** is the supramolecular structure sustained by the intermolecular C–H···N non-classical hydrogen bonding interactions between N(36) and C(37)-H across the centre of symmetry at (1/4, −1/4, 0) which extends in 1-D chain and stabilized by the 6-membered cyclic structure analogue of benzene (Fig. 6) with dimensions N…H (2.63 Å), C···N (3.473 Å) and angle C–H···N (152°). DFT calculations on two molecules interacting in this way gave an energy of 8.54 kcalmol^{-1} less than the energy of two separated molecules showing that the interaction is a very significant part of the molecular packing.

Table 2
Selected bond lengths (Å) and bond angles° for **4A, 4B** and **5**.

	4A	4B	5
Sn(1)–S(11)	2.469(2)	2.516(2)	2.467(1)
Sn(1)–S(13)	3.040(2)	3.221(2)	3.021(1)
S(11)–C(12)	1.747(6)	1.756(6)	1.753(3)
S(13)–C(12)	1.696(6)	1.665(7)	1.685(3)
C(12)–N(14)	1.325(7)	1.352(7)	1.330(4)
Sn(1)-C(41)	2.152(7)	2.151(7)	2.170(3)
Sn(1)-C(51)	2.138(7)	2.120(6)	2.143(3)
Sn(1)-C(61)	2.129(6)	2.121(6)	2.149(3)
Sn(1)–S(11)–C(12)	97.5(2)	100.0(2)	96.64(11)
S(11)–C(12)–S(13)	118.7(4)	120.7(4)	118.87(18)
S(11)-Sn(1)-S(13)	61.0(1)	64.1(1)	64.38(6)
S(11)–Sn(1)–C(41)	91.5(2)	92.0(2)	93.7(1)
S(11)–Sn(1)–C(51)	117.1(2)	105.0(2)	116.7(1)
S(11)–Sn(1)–C(61)	116.1(2)	108.7(2)	117.4(1)
C(41)–Sn(1)–C(51)	104.1(3)	111.2(3)	105.7(1)
C(41)-Sn(1)-C(61)	107.2(3)	108.6(2)	104.7(1)
C(51)-Sn(1)-C(61)	116.1(3)	125.9(3)	114.6(1)
S(13)-Sn(1)-C(41)	155.6(2)	153.0(2)	157.8(1)
S(13)-Sn(1)-C(51)	87.9(2)	78.0(2)	88.4(1)
S(13)-Sn(1)-C(61)	85.5(2)	82.9(2)	83.9(1)

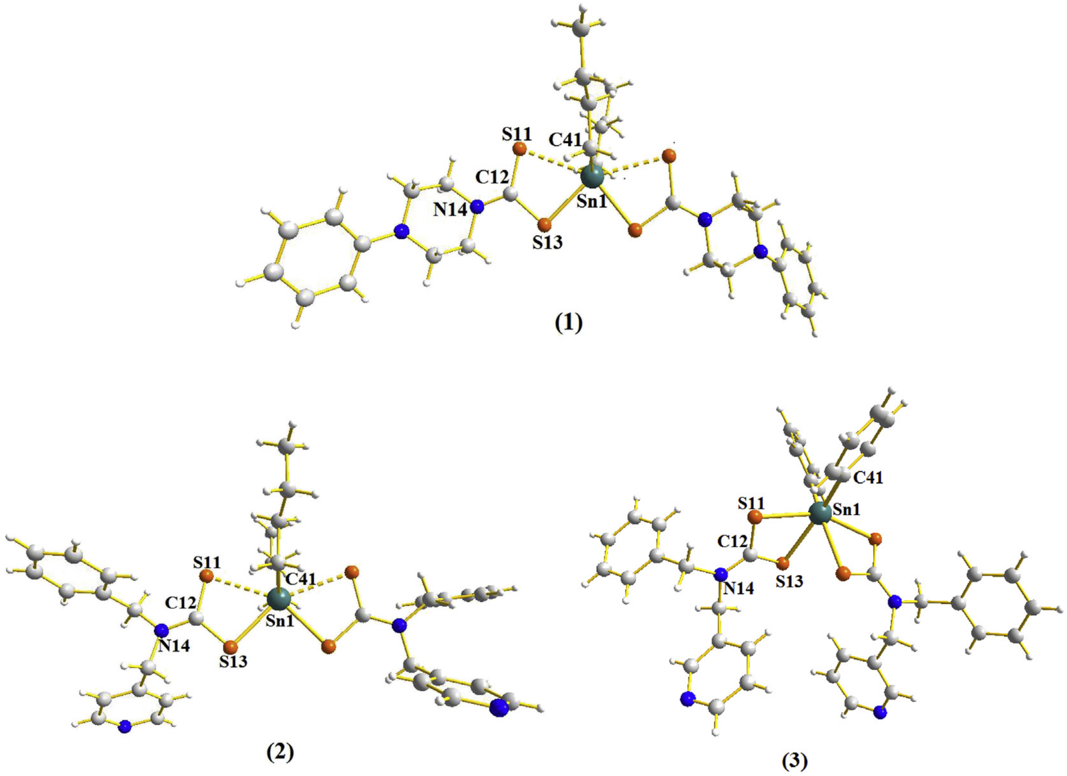

Fig. 5. Molecular structure and atom numbering scheme for **1**, **2** and **3**, Color code: Sn, Turquoise blue; S, Orange; N, Ink blue; C, Grey; H, Grey (Small). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The structures of **4** and **5** are similar with the tin atom is bonded asymmetrically to one bidentate dithiocarbamate ligand and three phenyl groups. The asymmetric unit of **4** contains two molecules **4A** and **4B**. In both structures the metal atom forms a short bond to S11 (2.469(2), 2.516(2), 2.467(1) Å) and a longer bond to S13 at 3.040(2), 3.221(2), 3.021(2) Å in **4A**, **4B**, **5** respectively. The Sn–C bonds range from 2.120(6)–2.170(3) Å which are well within the range of analogous triorganotin(IV) dithiocarbamate complexes [11a,h]. If the longer Sn–S13 bond is considered as a bond, then the overall coordination geometry around the tin atom is five-coordinate trigonal bipyramidal with a phenyl group C51 and S13 in axial positions. This is confirmed by the τ values which are 0.57, 0.58, 0.65 for **4A**, **4B** and **5** respectively.

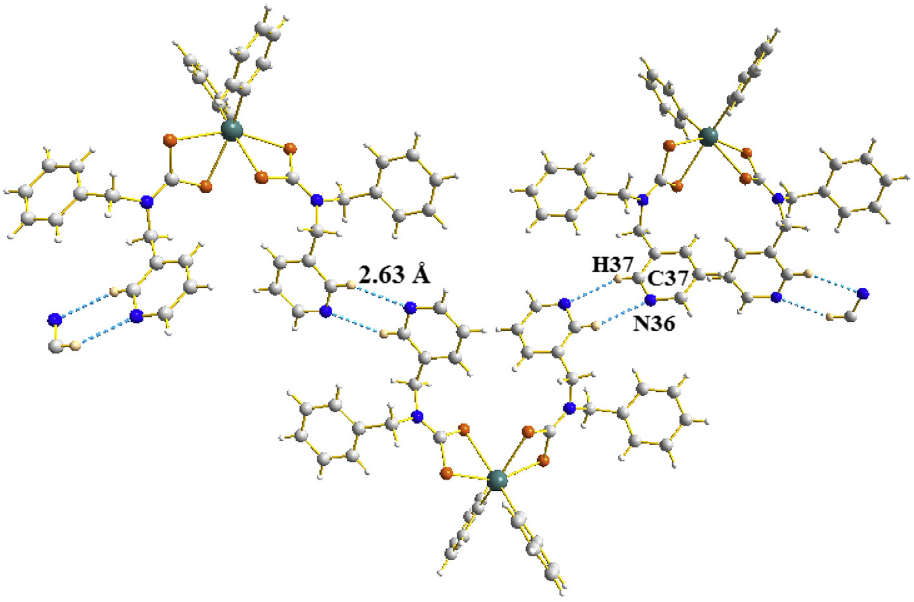

Fig. 6. N···H–C interactions forming a cyclic structure in 1-D chain motifs in **3**.

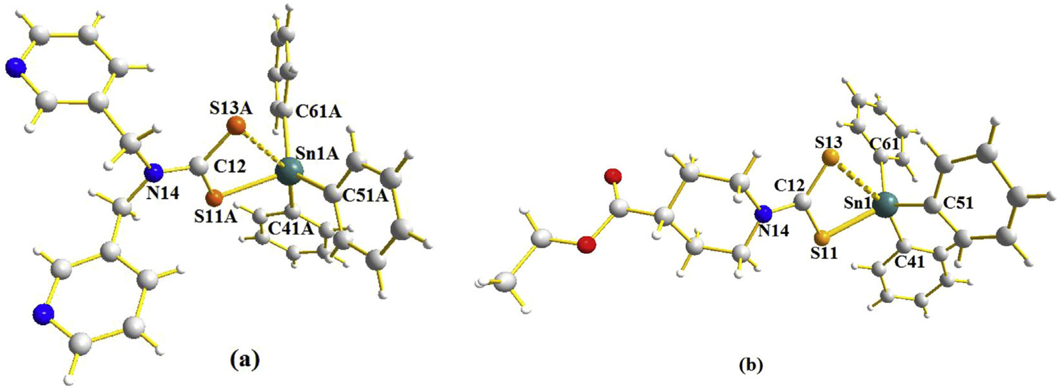

Fig. 7. Molecular structure and atom numbering scheme for (a) **4A** and (b) **5**. Color code: Sn, Turquoise blue; S, Orange; N, Ink blue; C, Grey; H, Grey (Small). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

More interestingly in **4B**, (but not in **4A**) the pyridyl(N) on an adjacent molecule is bonded to tin at somewhat longer distance of 3.116(8) Å which is less than sum of the van der Waals radii of tin and nitrogen which is 3.72 Å resulting in the formation of 1-D polymeric chain motif. It should be noted however that this distance is ca. 1.0 Å longer than the Sn—C (phenyl) distances. The overall geometry about the Sn atom can then be considered as distorted octahedral with rare coordination of (3C+2S+1N) (Fig. 8). Theoretical calculations were carried out on both molecules (**A** and **B**) in **4**, and it was found that **B** is more stable by 2.16 kcalmol^{-1}, when the additional Sn—N bond found in **B** is not considered. For molecule **B**, the dimer with two **B** molecules connected by the Sn—N36 (x, 1+y, z) bond at 3.116(8) Å is more stable than two separate monomers by 9.76 kcalmol^{-1}, thus confirming that the Sn—N interaction is significant.

Recently Tiekink and Zukerman-Schpector [13] evaluated the structural characteristics of C—H-π (chelate) interactions between C—H bonds and the centroid CG of four-membered MS$_2$C chelate ring in metal bis(1,1-dithiolates). For homoleptic bis—dithio complexes the values of $\alpha < 20$, β ranging from 110 to 180° and d between 2.4 and 3.6 Å were crucial to assesses the interactions where α is the angle between the perpendicular to the ring and the CG···H vector, β, the CG···H—C angle and d, the CG···H distance. The interaction between H34B (1+x, y, z) and the SnS$_2$C ring of molecule **A** is well within the usual limits. The H34B···CG distance is 2.85 Å, with α, 1.7 and β is 146.9° (Fig. 9) despite the asymmetric bonding of the dithio ligand. However the energy difference between the two molecules interacting in this way (A + B) and the separate molecules is negligible. Thus the energy gained by the H···CG interaction is cancelled out by poor steric effects involving the 3 phenyl rings. The calculation was then repeated but with the phenyl rings then replaced with methyl groups. Now the energy difference was −1.58 kcalmol^{-1} which supports the view that the interaction of the phenyl rings is repulsive and cancels out the effect of the interaction between H34B and the SnS$_2$C ring.

The closest S···S intermolecular distances between the coordinated dithiocarbamate ligands in **1**—**5** fall in the 4.14–6.76 Å range and are significantly larger than van der Waals radii so that there is

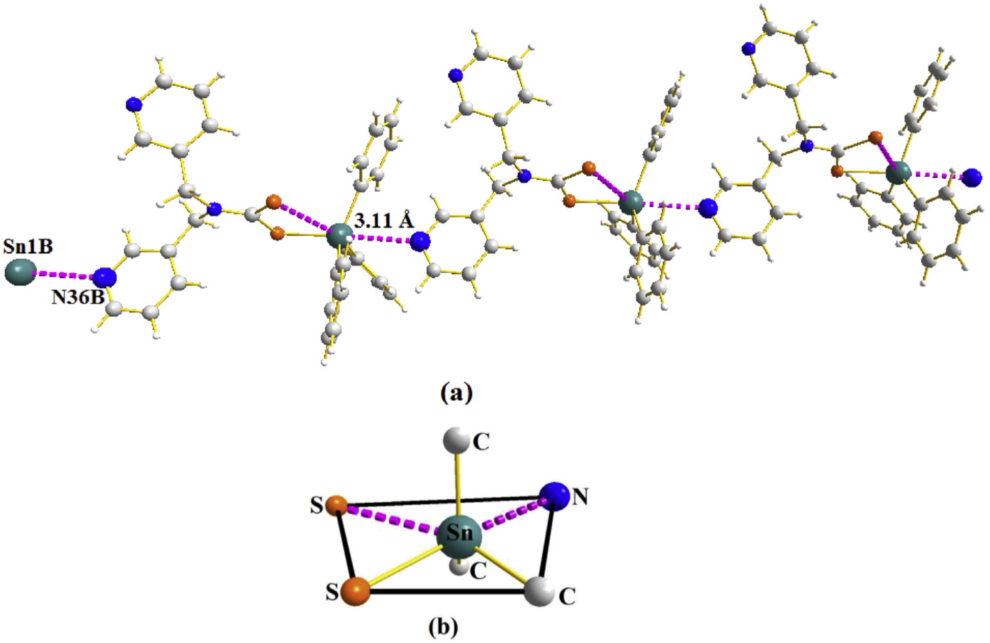

Fig. 8. (a) Polymeric 1-D chain motifs in **4** through intermolecular Sn···N secondary interactions (b) S$_2$C$_3$N coordination pattern around the tin centre.

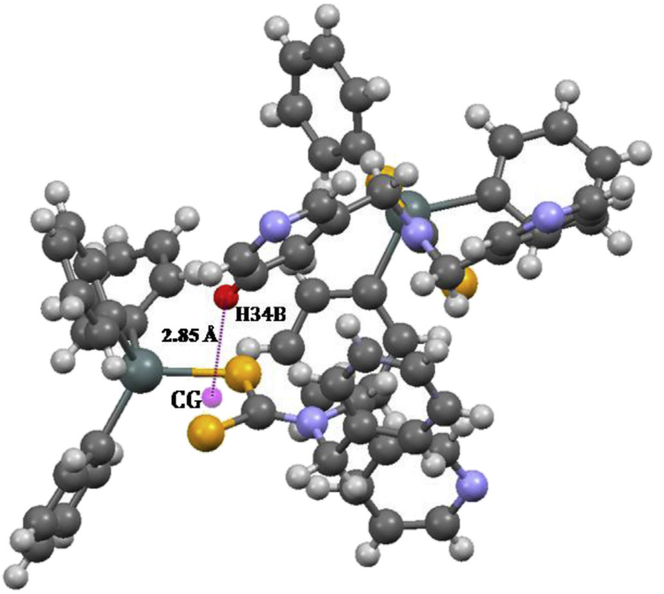

Fig. 9. Nearest intermolecular C–H···CG (SnS_2C) interactions between CG of unit **4A** and H34B of unit **4B**.

no significant S···S intermolecular associations in these complexes. In all the complexes the supramolecular architectures are stabilized via weaker S···H non-covalent interactions. The C(12)–N(14) distances of 1.325(7)–1.356(6) Å in **1**–**5** are concomitant with the resonance structure (Fig. 1). In all the complexes the length of the C–S bond is inversely correlated with the Sn–S bond, thus short S–C bonds of 1.665(7)–1.705(5) Å and long S–C bonds of 1.728(5)–1.756(6) Å correlate with long and short Sn–S bonds respectively. The exception is **3**, where the similar Sn–S bond lengths are accompanied by similar S–C bond lengths, 1.713(4), 1.723(4) Å though all are significantly shorter than the C–S single bond (ca.1.81 Å) due to π delocalization over the NCS_2 units.

Thermogravimetric analysis (TGA)

The thermogravimetric analysis of **3** and **5** carried out in the temperature range (upto 600 ^{O}C; heating rate 10 °C min^{-1} under nitrogen) and gives information about the decomposition pattern (Fig. S1). Complex **3** showed double step decomposition in the temperature range 200–410 °C and 410–560 °C with final residue of 24.9% which is in good agreement with calculated value of 22.3% for SnS_2 while **5** showed single step decomposition for **5** at 202–575 °C with final weight loss of 29.1% which correspond to the calculated values of 31.4% for SnS [8b].

Conclusions

The new pyridyl, phenylpiperazine and piperidine functionalized oragotin(IV) dithiocarbamate complexes **1**–**5** have been synthesized, fully characterized and their structures have been investigated by X-ray crystallography. **1**–**3** are 6-coordinate with severely distorted octahedral (**1**and **2**) and distorted octahedral geometry (**3**). In **3** the Py(N) interacts with the C–H hydrogen of the neighbouring molecule forming 6-membered benzene like ring ($C_2H_2N_2$) in the supramolecular architecture. In complex **4**, the Py(N) is uniquely connected to the tin atom (Sn···N = 3.11 Å) on the neighbouring molecule generating a 1-D polymeric chain structures and showed (3C+2S+1N) coordination around the tin centre. Also in this complex H34 of **4B** interacts to the CG of **4A** forming C–H···CG interactions between the two molecules. To our knowledge **3** and **4** are the examples of organotin dithiocarbamate complexes delineating these rare interactions. These have been supported by theoretical calculations. Except **1** all the complexes showed moderate to strong luminescent characteristics in CH_2Cl_2 solution at room temperature originating from the LMCT state. Complex **4** containing two pyridyl groups showed strong luminescent characteristics due to rich electron cloud on the molecules and providing overall conformational rigidity an important prerequisite for the higher luminescent behaviour of the molecules. TGA of **3** and **5** showed double and single step decomposition leaving residue corresponding to SnS_2 and SnS respectively. This study demonstrates that the organotin complexes with these underexploited dithiocarbamate ligands may be useful as functional materials.

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Appendix A. Supplementary data

CCDC 1017534 (**1**), 1017533 (**2**), 1017535 (**3**) 1017536 (**4**) and 1017532 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix B. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2015.03.034.

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