Synthesis, characterisation and thermal properties of Sn(II) pyrrolide complexes†

James D. Parish, a Michael W. Snook, a Andrew L. Johnson b,* a and Gabriele Kociok-Köhn b

SnO is a rare example of a stable p-type semiconductor material. Here, we describe the synthesis and characterisation of a family of Sn(II) pyrrolide complexes for future application in the MOCVD and ALD of tin containing thin films. Reaction of the Sn(II) amide complex, [(Me3Si)2N]Sn] with the N,N-bidentate pyrrole pro-ligand, L1H, forms the hetero- and homoleptic complexes [(L1)2Sn(NMe2)2] (1) and [(L1)2Sn] (2), respectively, bearing the 2-dimethylaminomethyl-pyrrolide ligand (L1). Reaction of [(Me3Si)2N]Sn] with the pyrrole-aldimine pro-ligands, L1H−L2H, results in the exclusive formation of the homoleptic bis-pyrrylide complexes [(L2)2Sn] (3–8). All complexes have been characterised by elemental analysis and NMR spectroscopy, and the molecular structures of complexes 1–5 and 8 are determined by single crystal X-ray diffraction. TG analysis and isothermal TG analysis have been used to evaluate the potential utility of these systems as MOCVD and ALD precursors.

Introduction

Transparent semiconducting oxide (TSO) thin films have attracted considerable interest due to their omnipresence in modern technology, finding wide-spread application in solar cells, light emitting diodes, flat panel displays, optical communicators, gas sensors and thin film transistors.1 The majority of commercially available semiconducting oxides are n-type, e.g., ZnO; many potential applications of TSOs are still limited by the scarcity of p-type counterparts.2 The development of suitable p-type TSOs is limited by the scarcity of p-type counterparts.2 The development of high performance p-type TSOs would leverage the inordinate potential of oxides for transparent electronics and optoelectronics by combining them with n-type TSOs in p–n heterojunctions.3 The recent rapid development of both photovoltaics and solar water splitting also calls for p-type electrodes towards oxygen, and formation of both Sn2O3 and SnO2 as phase impurities results in thin films with undesirable properties.10 Therefore, precise control over the oxidation state of the metal is paramount. Whilst a number of Sn-precursor/reactant combinations have been surveyed for the growth of SnO, the majority have focused on the utility of Sn(IV) precursor combinations, e.g., SnCl4/H2O11/H2O2,12 SnI4/O2,13 Sn(NMe2)4/H2O/H2O2,14 SnEt4/H2O2/O2-plasma and Bu4SnOEt/O3.15 Of the precursor/reactant combinations investigated, only three have utilised Sn(II) precursors (Fig. 1): in the case of the stannylene complex (A), reaction with H2O failed to produce SnO, and reaction with either H2O2,16 or NO17 resulted in the formation of a mixed phase of SnO/SnO2 (i.e. SnO2). Similarly, Sn(HMDS)2 (B) has also been used in conjunction with either

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H₂O or O₃ in an ALD process to deposit Sn(II) and Sn(IV) oxides and SiO₂ mixes between 80 and 250 °C.²⁻¹ To date, only the Sn(II) aminoalkoxide complex (C) has been found to produce phase pure SnO in an ALD process, with H₂O, between 90 °C and 210 °C, with crystallinity occurring above 150 °C.¹³ This dearth of suitable precursors for SnO production has prompted us, and others,²⁰ to investigate new Sn(II)-ligand combinations. In an attempt to optimise precursor reactivity and thermal stability, we chose to investigate the utility of the amino-pyrrolide (L₁) and pyrrolylaldiminato ligands (L₂)–¹⁸⁻¹⁹ ligands and are consistent with the formation of the bis-pyrrolylaldiminato Sn(II) compounds by a direct stoichiometric (1 : 1) reaction of [Sn{HMDS}₂] with the pyrrole ligands, L₁H. A comparable reaction of [Sn{HMDS}₂] in an equimolar reaction with L₈H results in the formation of the bis-pyrrole complexes, 2–8, in yields <50%, suggestive of a Schlenk equilibrium in which the putative mono-amide intermediates are unstable with respect to disproportionation, and formation of the bis-pyrrole complex. The ¹H NMR spectra of 2–8 clearly show the absence of resonances associated with the (HMDS) ligands and are consistent with the formation of the bis-pyrrole complexes. In the case of the sec-Bu derivative complex, 6, a racemic {±}sec-butyl amine was used for the synthesis of the proligand L₈H, resulting in the ¹H and ¹³C NMR spectra containing two sets of resonances corresponding to the presence of the associated (R,R), (R,S), (S,R) stereoisomers in solution. Elemental analysis confirms the formation of the bis-pyrrole complexes. The intrinsic C₂ symmetry of complexes 2–7 is negated somewhat in solution by a rapid, so-called, “flip-flop” equilibrium process in which the N↔Sn coordination bonds repeatedly open and close. In compound 8, however, the methyl and methine groups of the isopropyl substituents display a series of convoluted multiplets (δ = 0.89–1.36 ppm, 12H), alongside two broad resonances respectively (δ = 3.00 ppm, 1H; and 3.43 ppm, 1H) suggestive of a slow rotation, on the NMR timescale, about the N–C(phenyl) bond. The stoichiometric reaction (2 : 1) of the pro-ligands, L₁H and L₈H, with [Sn{HMDS}₂] produce the expected complexes cleanly in moderate to high yields (64–87%).

Solid state structures

X-ray diffraction studies of single crystals of complexes 1, 2, 3, 4, 5 and 8 unambiguously established their solid state structures. The structures of the heteroleptic and the homoleptic complexes [Sn{k²-N,N-NC₄H₄CH(NMe₂)}₂{N{SiMe₃}₂}](1) and [Sn{k²-N,N-NC₄H₄CH₂NMe₂}₂](2) are shown in Fig. 2. While compounds 1 and 2 are both chiral, the enantiomers co-crystallise in noncentrosymmetric space groups.
In the solid state, 1 crystallises in the monoclinic space group P21/c. The asymmetric unit cell contains a single monomorphic complex with a three-coordinate, pseudo-trigonal-pyramidal geometry about the Sn(II) centre, with the \( \{L^1\}^- \) ligand coordinated in a \( \kappa^2 \) fashion via the pyrrolide nitrogen and the pendant \( \{NMe_2\} \) group, as well as the nitrogen of the \( \{HMDS\} \) ligand, in a terminal bonding mode (Fig. 2).

The Sn(1)–N(1) (2.152) and Sn(1)–N(3) (2.127) bond lengths are comparable to those already reported for Sn-amide compounds,\(^{27} \) whereas the dative Sn(1)←NMe\(_2\) bond \([\text{Sn(1)}–\text{N(2)} \ (2.418)]\) is expectedly longer. Despite a constrained bite angle for the \( \{L^1\}^- \) ligand \([\text{N(1)}–\text{Sn(1)}–\text{N(2)} \ (74.52^\circ)]\), the N–Sn–N bond angles in 1 \([\text{N(1)}–\text{Sn(1)}–\text{N(3)} \ (96.36^\circ) \text{ and N(2)}–\text{Sn(1)}–\text{N(3)} \ (96.84^\circ)]\) suggest the absence of sp-hybridisation at the Sn(II) centre and that the tin–ligand bonds almost exclusively involve the p-orbitals; the nature of the electron lone pair in compound 1 can therefore be considered as essentially a 5s\(^2\) configuration and therefore non-directional.

Complex 2, which has intrinsic C\(_2\) symmetry, crystallises in the monoclinic space group P21/c and is shown in Fig. 2. Here the asymmetric unit cell contains a single molecule of the complex with a four-coordinate, pseudo-trigonal bipyramidal geometry \( (\tau = 0.83) \)\(^{28} \) in which the two \( \{L^1\}^- \) ligands are coordinated in the same \( \kappa^2 \) fashion observed in 1, with the N-atoms of the pyrrolide ligands occupying two equatorial, and the pendant \{NMe\(_2\}\} groups occupying the axial positions.

A cursory analysis of the bond angles about the Sn(II) centre in 2 \([\text{N(1)}–\text{Sn(1)}–\text{N(3)} \ (97.44^\circ) \text{ and N(2)}–\text{Sn(1)}–\text{N(3)} \ (147.21^\circ)]\) again suggests that the tin–ligand bonds almost exclusively involve the p-orbitals on Sn, and that the lone pair of electrons in 2 is therefore again essentially 5s\(^2\) based. The Sn–N\(_{py}\) \([\text{Sn(1)}–\text{N(1)} \ (2.179^\circ) \text{ and Sn(1)}–\text{N(3)} \ (2.165^\circ)]\) and Sn←NMe\(_2\) \([\text{Sn(1)}–\text{N(2)} \ (2.516^\circ) \text{ and Sn(1)}–\text{N(4)} \ (2.528^\circ)]\) bond lengths in 2 are commensurate with 1 and comparable complexes.

For the imine complexes 3, 4 and 5, which are structurally related to 2, the molecular structures are shown in Fig. 3. For complexes 3 and 5, which crystallise in the centrosymmetric space group P21/n, the asymmetric unit cell contains one full molecule of the bis-(pyrrolylaldiminate)Sn(II) complex. Complexes 3 and 5 are disordered such that all ligand atoms, with the exception of Sn(1), N(1) and N(3), exhibit 67 : 33 and 80 : 20 disorder, respectively, via a pseudo-mirror plane containing the three non-affected atoms. Complex 4 crystallises in the polar space group P21 with only one enantiomer of the chiral complex in the crystals, while in all three cases, the central Sn(II) atoms are four-coordinate; analysis of the bond angles about the tin centre suggests a trigonal bipyramidal

![Fig. 2](image1.png)\(\text{The molecular structures of complex 1 (top) and 2 (bottom) (50\% probability ellipsoids).}\)

![Fig. 3](image2.png)\(\text{The molecular structures of complex 3 (40\% probability ellipsoids), 4 (50\% probability ellipsoids) and 5 (50\% probability ellipsoids). Complexes 3 and 5 are disordered such that all ligand atoms, with the exception of Sn(1), N(1) and N(3), exhibited 67 : 33 and 80 : 20 disorder, respectively, via a pseudo-mirror plane containing the three non-affected atoms. The major component only is depicted for clarity.}\)
While the nitrogen atoms occupying the axial coordination sites and the those observed in \[\text{Sn(1)}\] possess molecular geometry \[^{28}\] \(\tau = 0.92\), \(4: \tau = 0.82\), \(5: \tau = 1.06\) with the imine nitrogen atoms occupying the axial coordination sites and the pyrrole nitrogen atoms the equatorial positions. While the \(N(\text{imine})=\text{Sn}–N(\text{py})\) bond angles increase from \(\sim 143^\circ\) to \(152^\circ\) as the imine substituent changes from methyl to ethyl and \(\tau\)-butyl, respectively, the \(N\text{py}=\text{Sn}–\text{py}\) angles \(\sim 92.17(10)^\circ\), \(4: 95.64(19)^\circ\), \(5: 88.33(15)^\circ\) are all around \(90^\circ\) suggesting that the \(\text{Sn}–\text{py}\) bonds involve mostly the \(\text{Sn}(\text{II})\) \(\text{p}\)-orbitals. The \(\text{Sn}–\text{py}\) and \(\text{Sn}–\text{NR}\) bond lengths (shown in Table 1) are all similar, \textit{ibid}.

Similarly to complexes 2–5, compound 8 is chiral (Fig. 4), possessing molecular \(C_2\) symmetry; the other enantiomer is also formed in the product, with 8 crystallising in the centro-symmetric monoclinic space group \(P2_1/\text{in}\). Exhibiting a 4-coordinate \(\text{Sn}(\text{II})\) centre, the geometry about the \(\text{Sn}(\text{II})\) atom is best described as square based pyramidal \(\tau = 0.15\). Interestingly, the \(\text{SN}–\text{py}\) bonds in 8 \([\text{SN}(1)=\text{SN}(1)=2.3138(16)\ \text{Å}, \text{SN}(1)=\text{SN}(3)=2.2871(16)\ \text{Å}\) are significantly longer than those reported for 1–5. Similarly, the \(\text{Sn}–\text{NR}\) bonds are also significantly longer \([\text{SN}(1)=\text{SN}(2)=2.3308(16)\ \text{Å}, \text{SN}(1)=\text{SN}(4)=2.3127(15)\ \text{Å}\) than those observed in 3–5. Consistent with this observation, the \(N\text{py}=\text{Sn}–\text{py}\) and \(N(\text{imine})=\text{Sn}–N(\text{imine})\) angles observed in 8 are both close to \(120^\circ\) \([127.03(6)^\circ\) and \(127.30(5)^\circ\) respectively], suggesting that the tin–ligand bonds almost exclusively involve \(\text{sp}^3\) hybridised orbitals on the tin, with the lone pair in 8 considered to be essentially based in a directional \(\text{sp}^3\) orbital.

### Thermal profiles

Two of the main precursor requirements for MOCVD and ALD applications are the need for volatility and thermal stability.\[^{29}\]

As the primary goal of synthesising compounds 1–8 was driven by our interest in their application as precursors for the MOCVD and ALD of \(\text{Sn}(\text{II})\) oxide films, melting point analysis, thermogravimetric analysis (TGA) and isothermal studies were employed to investigate the volatility and thermal stability of complexes 1–8. The melting points and analysis of compounds 1–8 were recorded with instruments housed in an argon filled glove-box in order to minimise reaction with atmospheric moisture/air. For the amino-pyrrolide complexes 1 and 2, results suggest that these materials are unsuitable for application as ALD precursors. Table 2 shows the melting and decomposition points for these complexes. Complex 1 displays a rather low decomposition temperature \((100\ ^\circ\text{C})\) quite close to...
its melting point (95 °C). Similarly for 2, a relatively low decomposition (50 °C) was observed before any phase transition could be detected, suggesting the possible lack of utility of these systems as ALD precursors. Despite this observation, the TGA of Sn(n)bis-(pyrrolide) 2–8 was performed in order to gain greater insight into the relative volatilities and thermal stabilities of the compounds.

As seen in Fig. 5, compounds 3–8 exhibit very similar thermal behaviour, consistent with single step evaporation. For all precursors, the onset of volatilisation (∼100 °C) and the temperature at which the evaporation is completed (between 220 and 255 °C for 3–7 and by 286 °C for 8) are similar.

Table 3 shows germane data, relating to the TG analysis of compounds 3–8, i.e. % residual mass and wt% of Sn in complexes. Fig. 4 clearly shows that compounds 3–8 exhibit very similar thermal behaviour, undergoing a clear, single mass loss event over a small temperature window to yield stable residues of between 4 and 16.5%, consistent with a single step evaporation process. In the case of complexes 6–8, the final mass residues are considerably lower than the expected mass residue for the production of the Sn metal, strongly suggestive of a high degree of volatility within these systems. For complexes 3–5, the mass residues are proportionately higher although still below the % mass residue expected if decomposition resulted in the formation of the Sn metal. Compound 2, which was also analysed, showed a complicated and shallow decomposition profile with mass loss starting at 36 °C. At 400 °C, the residual mass is ~67%, indicative of a non-volatile material with incomplete thermal decomposition (Fig. S1, ESI†).

Given the nature of the ligand systems involved in 3–8, it is unlikely that the TGA residues contain oxide products (i.e. SnO₃), and instead are more likely to be metallic Sn (with possible carbon impurities). This is consistent with the observation of metallic deposits (of Sn) in the TGA crucibles after decomposition studies, suggesting the possible application of these systems in the deposition of metallic tin under a non-oxidative atmosphere.

While the TGA data provide an indication of the volatility of the complexes, decomposition characteristics are less easy to discern for complexes with significant volatility. However, no stepwise decomposition processes are observed in the TGA profiles of 3–8, corresponding to the systematic breakdown of the pyrrolide ring systems, as postulated in other studies. More relevant investigations have suggested that pyrrolide complexes are susceptible to β-hydride elimination processes, in these cases most likely arising from hydride abstraction from the aldimine substituents. This is in contrast to complex 2, which possesses pendant {CH₃,NMe₂} groups, and as such does not share the same electronic delocalisation observed for the aldimine systems 3–8. Consequently, the thermal analysis of 2 (ESI†) shows a stepwise decomposition over a broad temperature range, consistent with the aforementioned decomposition pathway.

Remarkably, no discernible trends are observed between pyrrolide-aldimine substituents and volatilities/stabilities, with the ethyl (3) and t-butyl (4) substituted complexes showing the highest volatilities followed by the 2,6-diisopropyl-phenyl complex (8). However, it is noteworthy that the aryl containing system, 8, displays a strikingly high thermal stability, in contrast to the other systems investigated here.

We suggest that this high degree of thermal stability is in part due to the absence of a suitable hydride abstraction process, as discussed previously. This observation is the focus of further studies to enhance the thermal stability of selected precursor systems, and to expand the ALD window of selected compounds, whilst inhibiting CVD processes.

The thermal behaviour of complexes 3–8 was further investigated using isothermal TGA studies (Fig. 6). At a fixed temperature of 130 °C, the mass loss for each compound was measured over a period of 120 min (2 h). In all measurements, an approximate linear weight loss was observed, which could be indicative of sublimation, with limited signs of decomposition. However, for complexes 6 and 7, visual (m.p. studies) decomposition appears to begin at below 100 °C (Table 2). From the gradient of the corresponding plots, the evaporation rates at a set temperature of 130 °C were determined (Table 2). The evaporation rates were found to be in the range of 2.4–20 μg min⁻¹ cm⁻². From the thermal studies, one can conclude that among the Sn(n) pyrrolide complexes reported here,
Experimental

General procedures

Elemental analyses were performed using an Exeter Analytical CE 440 analyser. \(^1\)H, \(^{13}\)C and \(^{119}\)Sn NMR spectra were recorded on Bruker Advance 300 or 500 MHz FT-NMR spectrometers, as appropriate, in saturated solutions at room temperature. Chemical shifts are expressed in ppm with respect to Me\(_4\)Si \((\text{1}^\text{H} \text{ and } {^{13}\text{C}})\). TGA and PXRD analyses were performed using a PerkinElmer TGA7 and Bruker D8 instrument (Cu-K\(\alpha\) radiation), respectively.

All reactions were carried out under an inert atmosphere using standard Schlenk techniques. Solvents were dried and degassed under an argon atmosphere over activated alumina columns using an Innovative Technology solvent purification system (SPS). The Sn(II) amides, \([\text{Sn} \{\text{NMe}_2\}_2]\) and \([\text{Sn} \{\text{SiMe}_3\}_2]\), were prepared by literature methods.\(^{27,31}\) The precursors L\(^1\)-H–L\(^2\)-H were synthesized using literature methods.\(^{21}\)

Synthesis of \([\text{Sn}\{\kappa^2-\text{N},\kappa^\prime-\text{NC}_4\text{H}_3\text{CH}_2\text{NMe}_2\}\{\text{N(SiMe}_3\}_2]\)] \((1)\). A solution of \([\text{L}\text{H}(0.62 \text{ g, } 5 \text{ mmol}) \text{ in hexane (30 mL)}]\) was added to a cooled solution of \([\text{Sn(HMDS)}_2]\) \((2.20 \text{ g, } 5 \text{ mmol}) \text{ in hexane (30 mL)}\). The resulting clear, pale yellow solution was stirred for 3 h before \textit{in vacuo} removal of the volatiles and dissolution in fresh hexane. The solution was filtered through Celite\(\oplus\) and the volume reduction before storage at \(-28 \text{ °C} \text{ afforded colourless crystals.}

Yield: 1.13 g, 56%. Elemental analysis for \(\text{C}_1\text{H}_2\text{N}_3\text{Sn} \text{(expected): } \text{C} 38.92 \text{ (38.81)\%; H 7.26 (7.27)\%; N} 10.48 \text{ (10.45)\%}. \text{\(^1\)H NMR (500 MHz, } \text{C}_6\text{D}_6\): 6.96–7.04 \text{ (1H, Pyr, C4–H); 6.54–6.61 \text{ (1H, Pyr, C3–H); 6.32–6.38 \text{ (1H, Pyr, C2–H); 3.35 \text{ (br s, 6H, NMe}_2\}; 1.76 \text{(br s, } 6 \text{H, NMe}_2\); 0.25 \text{(s, 18H, SiMe}_3\}. \text{\(^{13}\)C NMR (125.7 MHz, } \text{C}_6\text{D}_6\): 135.5 \text{(1C, Pyr, C1); 125.5, 111.3, 107.5, 60.8 \text{(1C, CH}_2\}; 45.3 \text{(2C, NMe}_2\); 6.76 \text{(6C, SiMe}_3\); 119\text{Sn NMR (186.4 MHz, } \text{C}_6\text{D}_6\): 49.9].

Synthesis of \([\text{Sn}\{\kappa^2-\text{N},\kappa^\prime-\text{NC}_4\text{H}_3\text{CH}_2\text{NMe}_2\}\{\text{N(SiMe}_3\}_2\}] \((2)\). A solution of \([\text{L}\text{H}(1.25 \text{ g, } 10 \text{ mmol}) \text{ in hexane (30 mL)}]\) was added to a cooled solution of \([\text{Sn(HMDS)}_2]\) \((2.20 \text{ g, } 5 \text{ mmol}) \text{ in hexane (30 mL)}\). The resulting clear, pale yellow solution was stirred for 3 h before \textit{in vacuo} removal of the volatiles and dissolution in fresh hexane. The solution was filtered through Celite\(\oplus\) and the volume reduction before storage at \(-28 \text{ °C} \text{ afforded colourless crystals.}

Yield: 1.22 g, 67%. Elemental analysis for \(\text{C}_1\text{H}_2\text{N}_3\text{Sn} \text{(expected): } \text{C} 45.94 \text{ (46.06)\%; H 5.93 (6.07)\%; N} 15.22 \text{(15.33)\%}. \text{\(^1\)H NMR (300 MHz, } \text{C}_6\text{D}_6\): 6.99–7.01 \text{ (1H, Pyr, C4–H); 6.59–6.61 \text{ (1H, Pyr, C3–H); 6.36–6.39 \text{ (1H, Pyr, C2–H); 3.35 \text{ (s, 6H, CH}_2\); 1.86 \text{(s, } 6 \text{H, NMe}_2\). \text{\(^{13}\)C NMR (75.5 MHz, } \text{C}_6\text{D}_6\): 137.0 \text{(1C, Pyr, C1); 125.5 (1C, Pyr, C4); 109.5 \text{(1C, Pyr, C3); 108.0 (1C, Pyr, C2); 59.3 (1C, CH}_2\}; 44.8 \text{(2C, NMe}_2\); 119\text{Sn NMR (111.8 MHz, } \text{C}_6\text{D}_6\): \text{−275.0}.]

Synthesis of \([\text{Sn}\{\kappa^2-\text{N},\kappa^\prime-\text{NC}_4\text{H}_3\text{C(H)NMe}_2\}\}] \((3)\). A solution of \([\text{L}\text{H}(1.1 \text{ g, } 10 \text{ mmol}) \text{ in hexane (30 mL)}]\) was added to a cooled solution of \([\text{Sn(HMDS)}_2]\) \((2.20 \text{ g, } 5 \text{ mmol}) \text{ in hexane (30 mL)}\). The resulting clear, pale yellow solution was stirred for 3 h before \textit{in vacuo} removal of the volatiles and dissolution in fresh hexane. The solution was filtered through Celite\(\oplus\) and the volume reduction before storage at \(-28 \text{ °C} \text{ afforded colourless crystals.}

Yield: 1.45 g, 87%. Elemental analysis for

Conclusions

With the use of amine and aldimine substituted pyrroles as chelating ligands, a series of novel homoleptic Sn(n) complexes have been developed. All the compounds are monomorphic and volatile, showing variable sublimation behaviour. Given the limited choice of precursors available for MOCVD and ALD of Sn(n) oxide thin films, the ethyl and tert-butyl and 2,6-di-isopropylphenyl complexes of 4, 5 and 8, reported here, are promising precursor candidates for vapour deposition processes.

The work presented here primarily concerns precursor development and molecular characterisation. Detailed studies on the MOCVD and ALD of Sn(n) oxides using these precursors, and subsequent thin film characterisation, will be published separately.
C_{12}H_{14}N_{5}Sn (expected): C 42.96 (43.29)%, H 4.07 (4.24)%, N 16.63 (16.83)%. 1H NMR (500 MHz, C_{6}D_{6}): 7.35–7.41 (m, 1H, PyrCH{NMe}), 6.97–7.02 (m, 1H, Pyr, C4–H), 6.69–6.74 (m, 1H, Pyr, C3–H). 13C NMR (75.5 MHz, C_{6}D_{6}): 188.0 (1C, PyrCH{NMe}), 137.5 (1C, Pyr, C1), 133.3 (1C, Pyr, C4), 117.5 (1C, Pyr, C3), 112.9 (1C, Pyr, C2), 42.4 (1C, CH{3}). 119Sn NMR (111.8 MHz, C_{6}D_{6}): δ –402.3.

Synthesis of [Sn(κ–N,N′–NC6H4(C(=N)NH)2)] (4), [Sn(κ–N,N′–NC6H4(C(=N)NH)2)] (5), [Sn(κ–N,N′–NC6H4(C(=N)NH)2)] (6) [Sn(κ–N,N′–NC6H4(C(=N)NH)2)] (7) and [Sn(κ–N,N′–NC6H4(C(=N)NH)2)] (8). Complexes 4–8 were prepared in an analogous manner to 3 using 1.22 g (10 mmol) of L{1H}, 1.50 g (10 mmol) of L{7H}, 2.54 g (10 mmol) of L{7H}, respectively.

4: Storage at –28 °C afforded colourless crystals. Yield: 1.16 g, 64%. Elemental analysis for C_{14}H_{18}N_{4}Sn (expected): C 46.46 (46.58)%, H 4.87 (5.03)%, N 15.61 (15.52)%. 1H NMR (500 MHz, C_{6}D_{6}): 7.49–7.56 (m, 1H, PyrCH{NMe}), 7.04–7.07 (m, 1H, Pyr, C4–H), 6.73–6.77 (m, 1H, Pyr, C3–H), 6.50–6.53 (m, 1H, Pyr, C2–H), 3.18–3.25 (s, 2H, CH_{2}), 0.51 (t, 3H, CH_{3}). 13C NMR (75.5 MHz, C_{6}D_{6}): 159.3 (1C, PyrCH{NMe}), 137.5 (1C, Pyr, C1), 133.3 (1C, Pyr, C4), 117.5 (1C, Pyr, C3), 112.9 (1C, Pyr, C2), 41.9 (1C, CH{3}). 119Sn NMR (111.8 MHz, C_{6}D_{6}): δ –401.0.

Table 4 X-ray crystallographic data for compounds 1–5 and 8

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<td>96.431(3)</td>
<td>98.662(4)</td>
<td>104.193(3)</td>
<td>93.866(3)</td>
<td>95.487(2)</td>
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<td>γ/°</td>
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<td>1485.62(8)</td>
<td>3108.11(5)</td>
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<td>0.403 × 0.637 × 0.719</td>
<td>0.516 × 0.378 × 0.490</td>
<td>0.372 × 0.040 × 0.150</td>
<td>0.389 × 0.251 × 0.277</td>
<td>0.238 × 0.238 × 0.196</td>
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<td>150.00(10)</td>
<td>150.00(10)</td>
<td>150.00(10)</td>
<td>150.00(10)</td>
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<tr>
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<td>Cu-Kα</td>
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<td>Theta range (°)</td>
<td>6.54 to 54.958</td>
<td>6.586 to 54.958</td>
<td>3.797 to 72.307</td>
<td>4.423 to 73.010</td>
<td>4.375 to 73.438</td>
<td>6.732 to 145.674</td>
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<td>Absorption coefficient, μ/mm⁻²</td>
<td>1.451</td>
<td>1.627</td>
<td>15.833</td>
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<td>No. of reflections measured</td>
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<td>13015</td>
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<td>26377</td>
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<td>No. of independent reflections</td>
<td>4329</td>
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<td>2847</td>
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<td>R₁/₁₀</td>
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<td>0.0361</td>
<td>0.0405</td>
<td>0.0279</td>
<td>0.0598</td>
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<td>Final R₁ values (I &gt; 2σ(I))</td>
<td>0.0295</td>
<td>0.0291</td>
<td>0.0260</td>
<td>0.0336</td>
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<td>Final wR² values (I &gt; 2σ(I))</td>
<td>0.0561</td>
<td>0.0563</td>
<td>0.0631</td>
<td>0.0894</td>
<td>0.1407</td>
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<td>Final R₁ values (all data)</td>
<td>0.0372</td>
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<td>0.0291</td>
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<td>Final wR² values (all data)</td>
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<td>0.0896</td>
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<td>Goodness of fit on F²</td>
<td>1.068</td>
<td>1.061</td>
<td>1.128</td>
<td>1.077</td>
<td>1.090</td>
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<td>Largest diff. peak and hole (e Å⁻³)</td>
<td>0.42 and 0.35</td>
<td>0.33 and 0.51</td>
<td>1.008 and 0.401</td>
<td>1.203 and 0.788</td>
<td>1.728 and 0.965</td>
<td>0.73 and 0.70</td>
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<tr>
<td>CCDC number</td>
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Pyrr, C4), 118.2 (1C, Pyrr, C3), 112.7 (1C, Pyrr, C2), 64.3 (br, d, 1C, NC(CH3)2CH2CH3), 32.3 (d, 1C, NC(CH3)2CH2CH3), 22.6 (d, 1C, NC(CH3)2CH2CH3), 11.5 (d, 1C, NC(CH3)2CH2CH3). 119Sn NMR (186.4 MHz, C6D6): δ 385.7.

7: Storage at –28 °C afforded colourless crystals. Yield: 1.56 g, 75%. Elemental analysis for C19H32N4Sn (expected): C 75.5%, H 8.6%, N 13.0%. 1H NMR (500 MHz, C6D6): 7.56–7.61 (m, 1H, Pyrr, C4–H), 6.76–6.79 (m, 1H, Pyrr, C3–H), 6.33–6.35 (m, 1H, Pyrr, C2–H), 3.25–3.31 (t, J = 6.85 Hz, 2H, NCH3CH2CH2CH3), 1.47–1.54 (m, 2H, PyrrCHNCH2CH3), 1.12–1.20 (m, 2H, –NCH3CH2CH2CH3), 0.79 (t, J = 7.34 Hz 3H, NCH3CH2CH2CH3). 13C NMR (125.7 MHz, C6D6): δ 157.82 (s, 1C, PyrrCHN(=O)Bu), 137.6 (1C, Pyrr, C1), 133.5 (1C, Pyrr, C4), 117.8 (1C, Pyrr, C3), 112.9 (1C, Pyrr, C2), 57.4 (1C, NCH3CH2CH2CH3), 64.3 (br, d, 1C, NC(CH3)2CH2CH3), 21.1 (1C, NCH3CH2CH2CH3), 14.3 (1C, NCH3CH2CH2CH3). 119Sn NMR (186.4 MHz, C6D6): δ 401.5.

8: Storage at –28 °C afforded colourless crystals. Yield: 2.63 g, 84%. Elemental analysis for C30H40N4Sn (expected): C 65.37 (65.29%), H 6.83 (6.77%), N 8.91 (8.96%). 1H NMR (500 MHz, C6D6): 7.85–7.86 (m, 1H, PyrrCHN(Dipp)), 7.13–7.23 (m, 3H, ortho, meta-Dipp), 6.84–6.86 (m, 1H, Pyrr, C4–H), 6.62–6.64 (m, 1H, Pyrr, C3–H), 6.35–6.37 (m, 1H, Pyrr, C2–H), 3.43 (br s, 1H, CHMe2), 3.00 (br s, 1H, CHMe2), 0.89–1.36 (br, m, 12H, CHMe2). 13C NMR (125.7 MHz, C6D6): δ 158.6 (1C, PyrrCHN(Dipp)), 149.8 (1C, ipso-Dipp), 145.6 (1C, Pyrr, C1), 142.8 (1C, ortho-Dipp), 142.3 (1C, ortho-Dipp), 137.0 (s, 1C, Pyrr, C3), 126.7 (br, 2C, meta-Dipp), 124.6 (br, 1C, para-Dipp), 121.0 (1C, Pyrr, C4), 114.5 (1C, Pyrr, C2), 29.1 (br, 1C, CHMe2), 28.7 (br, 1C, CHMe2), 26.4 (br, CHMe2), 24.9 (br, CHMe2), 24.6 (br, CHMe2), 23.1 (br, CHMe2). 119Sn NMR (111.8 MHz, C6D6): δ 419.0.

Single crystal X-ray diffraction

Experimental details related to the single-crystal X-ray crystallographic studies of compounds 1–5 and 8 are summarised in Table 4. All crystallographic data were collected at 150(2) K either on a SuperNova (Dual, EosS2) diffractometer using radiation Cu-Kα (λ = 1.5418 Å) or Mo-Kα (λ = 0.71073 Å). All structures were solved by direct methods followed by full-matrix least squares refinement on F2 using the WINGX-2014 suite of programs or OLEX2. All hydrogen atoms were included in idealised positions and refined using the riding model. Crystals were isolated from an argon filled Schlenk flask and immersed in oil before being mounted onto the diffractometer.

The asymmetric unit cell of 3 comprises one molecule of the complex in which all ligand atoms, with the exception of Sn1, N3 and N1, exhibited 80:20 disorder via a pseudo-mirror plane containing the three non-affected atoms. Bond length restraints were included (for chemically equivalent bonds in both the major/minor components), in addition to ADP restraints.

Complex 5 suffers from similar disorder to that observed in 3, i.e. the asymmetric unit cell comprises one molecule of the complex in which all ligand atoms, with the exception of N3 and N1, exhibited 67:33 disorder via a pseudo-mirror plane containing the three non-affected atoms. Distance-similarity restraints were included for (chemically equivalent bonds in both the major/minor components), in addition to ADP restraints, to assist convergence. The Sn centre is disordered over two sites in the 9 : 1 ratio.

Thermogravimetric analysis (TGA)

TGA was performed using a TGA 4000 PerkinElmer system, housed in an argon filled glovebox. Samples were prepared air sensitively, and TGAs were performed under a flow of Ar at 20 ml min⁻¹ and heated from 30 °C to 400 °C at a ramp rate of 5 °C min⁻¹.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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References


