DALTON
FULL PAPER

Reactions of diorganotin(IV) oxides with isatin 3- and 2-thiosemicarbazones and with isatin 2,3-bis(thiosemicarbazone): influence of diphenyldithiophosphinic acid (isatin = 1*H*-indole-2,3-dione)

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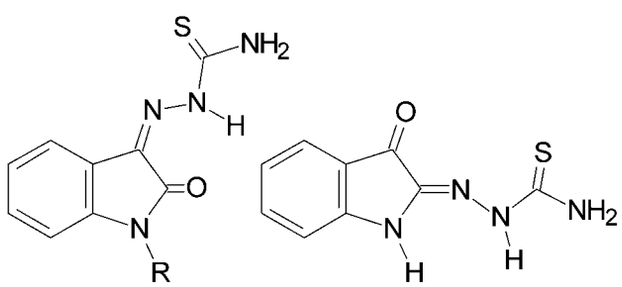
Reaction between $SnMe_2O$ and isatin 3-thiosemicarbazone (HL^I) in the presence of diphenyldithiophosphinic acid (HS_2PPh_2) afforded $[SnMe_2(S_2PPh_2)_2]$ and $[SnMe_2L^I\{O(S)PPh_2\}]\cdot EtOH$, which were studied by X-ray diffraction and IR spectroscopy in the solid state and by multinuclear (^1H, ^{13}C, ^{31}P and ^{119}Sn) NMR spectroscopy in $CDCl_3$ or dmso-d_6 solution (isatin = 1*H*-indole-2,3-dione). In the bis(dithiophosphinate) derivative the tin atom is bound to two strongly anisobidentate ligands both in the solid state and in solution in chloroform. In the mixed-ligand complex the monothiophosphinate ligand is O-co-ordinated and the thiosemicarbazone (TSC) is bound primarily through its sulfur atom and the nitrogen atom of the azomethine group, although there is an additional weak bond with the remaining isatin oxygen atom [O(1)]. The NMR spectrum in dmso-d_6 suggests weakening of the Sn–S bond and reinforcement of the Sn–O(1) bond. For comparison, the structure of HL^I was also studied by X-ray diffraction. Reaction of $SnMe_2O$ with isatin 2,3-bis(thiosemicarbazone) (H_2LL) afforded $[SnMe_2(LL)]$. X-Ray diffraction shows that one TSC chain is bound to the metal through the sulfur atom and the azomethine nitrogen atom, forming a five-membered metallacycle. The other chain co-ordinates through the nitrogen of the hydrazine group following its deprotonation. The co-ordination sphere changes in dmso-d_6 solution, in which a molecule of solvent probably occupies a co-ordination position to make the co-ordination number of the metal center up to six. The spectra of the other $[SnR_2(LL)]$ complexes prepared (R = Et or Bu) suggest that both have structures similar to that of the methyl derivative. Reaction of $SnMe_2O$ with isatin 2-thiosemicarbazone (H_2L^{II}) gave $[SnMe_2L^{II}]$, the NMR spectra of which indicate a five-co-ordinated tin atom and an O,N,S-tridentate TSC ligand.

Introduction

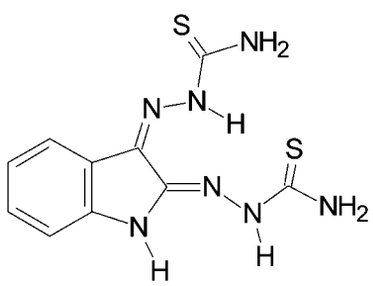
In previous work[1] we explored the synergic coupling between diorganotin(IV) compounds and thiosemicarbazones (TSCs) in order to obtain new metal compounds able to inhibit the proliferation of leukemia cells. The TSCs used were derivatives of pyridine-2-carbaldehyde thiosemicarbazone, because this compound itself has a degree of antileukemic activity.[2] They included H_2DAPTSC [2,6-diacetylpyridine bis(thiosemicarbazone)],[3] which afforded complexes with significant biological activity.[1]

Looking for greater carcinostatic activity, we have now turned our attention to TSCs derived from isatin (1*H*-indole-2,3-dione) which was recently found to be endogenous in mammalian tissues and body fluids.[4] 1-Methylisatin 3-thiosemicarbazone (methisazone, **Ia**) is used clinically as an antiviral agent,[5] and several derivatives of **Ia** possess significant anticancer activity.[6] There is nevertheless surprisingly little published information on the co-ordination behaviour of this type of ligand. The only metal complexes of isatin derivatives to have been studied by X-ray diffraction appear to be two of Ni^{II} and one $TlMe_2^+$ complex of isatin 3-thiosemicarbazone (HL^I, **Ib**),[7] although several more of HL^I with transition or non-transition metal ions have been studied spectroscopically.[8] There are also reports of complexes of Cu^I and Cu^{II} with isatin 2-thiosemicarbazone (H_2L^{II}, **II**) and isatin 2,3-bis(thiosemicarbazone) (H_2LL, **III**), respectively.[8c] For the copper(I) derivative, $Cu(H_2L^{II})Cl$, co-ordination through the thioamide N of a



(**Ia**, R= Me) (**Ib**,R= H, HL^I)

II (H_2L^{II})



III (H_2LL)

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neutral TSC chain was hypothesized on the basis of changes in the IR, Raman and ^{1}H NMR spectra;[8c] for the H_2LL derivative, $Cu(H_2LL)Cl_2$, IR and conductivity data suggest that the actual complex is the ion $[Cu(H_2LL)Cl]^+$ and that one TSC chain coordinates *via* the S atom of the thioamide group and N atom of the azomethine group while the other binds only through the N atom of the hydrazine group.[8c]

In the course of our work on pyridine-based TSCs and others it became evident that the ease with which diorganotin(IV) thiosemicarbazonates can be synthesized depends on the charge of the anion. Dianionic ligands readily afford good yields of neutral 1:1 complexes such as $[SnR_2(STSC)]$ (H_2STSC = salicylaldehyde thiosemicarbazone),[9] $[SnR_2(PxTSC)]$ (H_2-PxTSC = pyridoxal thiosemicarbazone; pyridoxal = 3-hydroxy-5-hydroxymethyl-2-methylpyridine-4-carbaldehyde)[10] and $[SnR_2(DAPTSC)]$,[3] but the isolation of complexes of monoanions with $[SnR_2(TSC)_2]$ stoichiometry is in our experience very difficult, although cases have been reported.[11] It is easier to obtain mixed complexes such as $[SnR_2(PyTSC)(OAc)]$[1] and $[SnR_2(PyTSC)(S_2PPh_2)]$ (PyTSC = pyridine 2-carbaldehyde thiosemicarbazone),[12] in which a single TSC^- ligand is accompanied by a second monoanion with less stringent steric demands.

The foregoing experience was borne in mind in the work on the reactions of diorganotin(IV) cations with isatin thiosemicarbazones that is now reported: H_2L^{II} and H_2LL were used alone but, following a single attempt at similar use of HL^I, this latter was employed in the presence of diphenyldithiophosphinato ion as a second ligand. Here we describe the syntheses of the new compounds isolated, their structures and spectroscopic properties and those of HL^I.

Experimental

Materials and methods

Diorganotin(IV) dihalides, dibutyltin(IV) oxide, diphenyldithiophosphinic acid, isatin and the other chemicals employed in the preparation of the TSCs were used as supplied by commercial sources. $SnMe_2O$ and $SnEt_2O$ were obtained by hydrolysis of $SnMe_2Cl_2$ and $SnEt_2Cl_2$, respectively.[13] Solvents were purified by the usual methods. Elemental analyses (C, H, N and S) were performed in a Carlo-Erba 1108 analyzer. IR spectra were recorded on a Bruker IFS-66V spectrometer, NMR spectra on Bruker AMX 300 and AMX 500 spectrometers in dmso-d_6 or $CDCl_3$. ^{1}H and ^{13}C signals were referred to TMS *via* the solvent signals (δ 2.50 and 39.50 respectively for dmso-d_6, 7.27 for ^{1}H in $CDCl_3$), ^{31}P to an external 85% H_3PO_4 solution, and ^{119}Sn to external neat $Sn(CH_3)_4$.

Synthesis of HL^I, H_2L^{II} and H_2LL

HL^I was prepared from isatin and thiosemicarbazide in ethanol–water (*ca.* 1:1 ratio) following the general procedure outlined by Anderson *et al.*[14] The yellow solid isolated was recrystallized from ethanol as orange single crystals suitable for X-ray diffraction studies. IR (KBr, cm^{-1}): 3424s, 3327s, 3277m, $\nu(NH_2)$; 3158s, br, ν[N(2)–H], ν[N(4)–H]; 1699s, ν(C=O); 1622s, 1595s, ν(C=N); 890m, ν(C=S). NMR data were recorded in dmso-d_6 (see Fig. 1 for numbering scheme). ^{1}H: δ[N(1)H_2] 8.84s(1), 8.49s(1); δ[N(2)H] 12.46(1); δ[N(4)H] 11.03s; δ[C(4)H] 6.88d(1); δ[C(5)H] 7.30t(1); δ[C(6)H] 7.03t(1); and δ[C(7)H] 7.61d(1). ^{13}C: δ[C(1)] 178.9; δ[C(2)] 132.2; δ[C(3)] 162.6; δ[C(4)–C(7)] 111.1, 131.3, 127.3, 120.9; δ[C(8)] 119.9; δ[C(9)] 142.3.

H_2L^{II} cannot be obtained by direct condensation because, unlike other α-dicarbonyl compounds, isatin only condenses with one molecule of thiosemicarbazide at position 3, so H_2L^{II} was synthesized by a method similar to that used by Dmitrukha and Pel'kis[15] for isatin 2-arylhydrazones. A solution of thiosemicarbazide (0.7 g, 0.01 mol) in 100 mL of absolute ethanol was added to a solution of 1.2 g (0.01 mol) of previously prepared[16] 2-methoxy-3*H*-3-indolone in 70 mL of dry benzene. After 1 h stirring the red solid formed was filtered off, washed with ethanol and vacuum dried. mp 225 °C. Found: C, 48.0; H, 3.3; N, 25.5. Calc. for H_2L^{II} ($C_9H_8N_4OS$): C, 49.1; H, 3.6; N, 25.5%. IR (KBr, cm^{-1}): 3439m, 3368s, 3262s, $\nu(NH_2)$; 3178s, br, ν[N(2)–H], ν[N(4)–H]; 1694, ν(C=O); 1620s, 1604s, ν(C=N); 890, ν(C=S). NMR data were recorded in dmso-d_6 (see Fig. 1 for numbering scheme). ^{1}H: δ[N(1)H_2] 8.60s(1), 7.82s(1); δ[N(2)H] 10.45s,br; δ[N(4)H] 10.44s,br; δ[C(4)H] 7.06d(1); δ[C(5)H] 7.60td(1); δ[C(6)H] 7.02td(1); and δ[C(7)H] 7.56d(1). ^{13}C: δ[C(1)] 183.3; δ[C(2)] 179.0; δ[C(3)] 150.8; δ[C(4)–C(7)] 112.2, 124.2, 135.0, 121.3; δ[C(8)] 119.5; δ[C(9)] 137.5.

H_2LL was prepared by Tomchin *et al.*'s[17] procedure **a** using H_2L^{II} and thiosemicarbazide in anhydrous dmf. IR (KBr, cm^{-1}): 3442s, 3276s, 3244s, $\nu(NH_2)$; 3162s, br, ν(NH); 1624m, 1599s, ν(C=N); 906m, ν(C=S). NMR data were recorded in dmso-d_6 (see Fig. 4 for numbering scheme). ^{1}H: δ[N(1)H_2] 8.88s(1), 8.52s(1); δ[N(7)H_2] 8.68s(1), 7.02s(1); δ[N(2)H] 12.19s(1); δ[N(4)H] 10.62s(1); δ[N(6)H] 10.45s(1); δ[C(4)H] 7.01d(1); δ[C(5)H] 7.35t(1); δ[C(6)H] 7.02t(1); and δ[C(7)H] 7.71d(1). ^{13}C: δ[C(1)] 178.2; δ[C(10)] 177.6; δ[C(2)] 133.8; δ[C(3)] 143.6; δ[C(4)–C(7)] 110.7, 131.2, 121.1, 120.7; δ[C(8)] 121.4; δ[C(9)] 139.3.

Synthesis of the complexes

Reaction of SnR_2O, HS_2PPh_2 and HL^I. To a suspension of 0.15 g (0.9 mmol) of $SnMe_2O$ in 15 mL of ethanol was added 0.23 g (0.9 mmol) of HS_2PPh_2 suspended in 20 mL of the same solvent. After 15 min of stirring a suspension of 0.20 g (0.9 mmol) of HL^I in 30 mL of ethanol was added and stirring continued for 7 days. The solid remaining after this time was filtered off and discarded and the resulting clear solution stored at 0 °C. The pale yellow solid formed was filtered off, vacuum dried and identified as $[SnMe_2(S_2PPh_2)_2]$. mp 182 °C. Found: C, 48.3; H, 4.1; S, 19.2. $C_{26}H_{26}P_2S_4Sn$ requires: C, 48.2; H, 4.1; S, 19.8.% IR (KBr, cm^{-1}): 644s, $\nu_{asym}(PS_2)$; 538s, $\nu_{sym}(PS_2)$ + ν_{asym}(Sn–C); 474m, ν_{sym}(Sn–C). NMR data were recorded in $CDCl_3$. ^{1}H: $\delta(CH_3Sn)$ 1.51s(6), $^2J(^1H–^{119}Sn) = 79$ Hz, $\delta(CH_o)$ 7.90m(8), $\delta(CH_m,CH_p)$ 7.44m(12). ^{13}C: δ(CSn) 17.91; $\delta(C_i)$ 138.8d; $\delta(C_o)$ 131.0d; $\delta(C_m)$ 128.4d; $\delta(C_p)$ 131.3d. ^{31}P: δ 56.9s. ^{119}Sn: δ −139.3.

Concentration of the remaining mother liquor in air afforded red crystals that were suitable for X-ray diffraction studies and later identified as $[SnMe_2L^I\{O(S)PPh_2\}]\cdot EtOH$. mp 238 °C. Found: C, 47.3; H, 4.8; N, 8.7. $C_{25}H_{29}N_4O_3PS_2Sn$ requires: C, 46.4; H, 4.5; N, 8.7. IR (KBr, cm^{-1}): 3424m, 3290m,br, $\nu(NH_2)$; 3135m, ν(N(4)–H); 1683s, ν(C=O); 1613s, 1592s, ν(C=N); 1020s, ν(P–O); 798sh, ν(C=S); 611s, ν(P=S); 565m, ν_{asym}(Sn–C); 470w, ν_{sym}(Sn–C). NMR spectra were recorded in dmso-d_6. ^{1}H: δ[N(1)H_2] 8.93s(1), 8.88s(1); δ[N(4)H] 11.16s(1); δ[C(4)H] 6.97d(1); δ[C(5)H] 7.38 (overlapping monothiophosphinato signals); δ[C(6)H] 7.08t(1); δ[C(7)H] 8.34d(1); $\delta(CH_3Sn)$ 0.94s(6), $^2J(^1H–^{119}Sn) = 92$ Hz; δ(CH of PhP) 8.09m(2), 7.75m(4), 7.40. ^{13}C: δ(CSn) 12.1s; δ[C(1)] 178.3s; δ[C(2)] 132.1s; δ[C(3)] 165.6s; δ[C(4)] 110.9s; δ[C(5)] 130.1s; δ[C(6)] 122.3s; δ[C(7)] 126.7s; δ[C(8)] 117.3s; δ[C(9)] 142.7s; $\delta(C_i)$ 141.4d; $\delta(C_o)$ 129.9d; $\delta(C_m)$ 127.5d; $\delta(C_i)$ 127.3s. ^{31}P: δ 61.6s; ^{119}Sn: δ −138.0.

When the above reaction was performed with Sn^nBu_2O only the complex $[SnBu_2(S_2PPh_2)_2]$ was obtained. mp 135 °C. Found: C, 52.6; H, 5.4; S, 16.6. $C_{32}H_{38}P_2S_4Sn$ requires: C, 52.5; H, 5.2; S, 17.5%. IR (KBr, cm^{-1}): 650s, $\nu_{asym}(PS_2)$; 547s, $\nu_{sym}(PS_2)$; 690s, ν_{asym}(Sn–C) + ligand vibration. NMR spectra were recorded in $CDCl_3$. ^{1}H: butyl fragment, $\delta(H_\alpha)$ 1.69m(4), $\delta(H_\beta)$ 2.06t(4), $\delta(H_\gamma)$ 1.12tt(4), $\delta(H_\delta)$ 0.67t(6); PhP fragment, $\delta(H_o)$ 7.92m(8), $\delta(H_{m,p})$ 7.42m(12). ^{13}C: butyl fragment, $\delta(C_\alpha)$ 26.3, $\delta(C_\beta)$ 36.4s, $\delta(C_\gamma)$ 28.3s, $\delta(C_\delta)$ 13.9s. ^{31}P: δ 57.5s. ^{119}Sn: δ −142.2.

$[SnMe_2L^{II}]$. To a suspension of 0.12 g (1.2 mmol) of H_2L^{II} in 100 mL of anhydrous benzene (**CAUTION**) was added 0.10 g

(1.6 mmol) of $SnMe_2O$, and the mixture refluxed for 10 days. After removal of the benzene/water azeotrope in a Dean–Stark funnel the reaction mixture was left to cool to room temperature and the red solid formed filtered off and vacuum dried. mp 222 °C (decomposition). Found: C, 35.7; H, 3.6; N, 15.6. $C_{11}H_{12}N_4OSSn$ requires: C, 36.1; H, 3.3; N, 15.3%. IR (KBr, cm^{-1}): 3391m, 3315m,br, $\nu(NH_2)$; 1684s, ν(C=O); 1608s, br, ν(C=N); 890m, ν(C=S), 550m, ν_{asym} (Sn–C); 500m, ν_{sym}(Sn–C). NMR spectra were recorded in dmso-d_6. ^{1}H: δ[N(1)H_2] 8.07s(1), 7.56s(1); δ[C(4)H] 7.36d(1); δ[C(5)H] 6.77td(1); δ[C(6)H] 7.40td(1); δ[C(7)H] 7.48d(1); δ[CH_3Sn] 1.02s(6); $^2J(^1H–^{119}Sn)$ = 87 Hz. ^{13}C: δ[C(1)] 179.9; δ[C(2)] 173.8; δ[C(3)] 158.0; δ[C(4)–C(7)] 114.1, 125.2, 130.0, 123.3; δ[C(8)] 120.0; δ[C(9)] 137.0; δ(CSn) 9.8. ^{119}Sn: δ −187.0.

[$SnMe_2$(LL)]. To 0.23 g (1.4 mmol) of $SnMe_2O$ suspended in 25 mL of ethanol was added 0.41 g (1.4 mmol) of H_2LL dissolved in 125 mL of hot ethanol. The mixture was refluxed for 3 days and filtered, the solid discarded, and the filtrate vacuum concentrated. After a few days at room temperature this liquor afforded red single crystals suitable for X-ray diffraction. mp 182 °C. Found: C, 32.5; H, 3.0; N, 21.8. $C_{12}H_{15}N_7S_2Sn$ requires: C, 32.8; H, 3.4; N, 22.3%. IR (KBr, cm^{-1}): 3479m, 3432w, 3352m, 3302m,br, $\nu(NH_2)$; 3171w, ν[N(4)–H]; 1622s, 1600s, ν(C=N); 903m, 789w, ν(C=S); 565m, ν_{asym}(Sn–C); 489m, ν_{sym}(Sn–C). NMR spectra were recorded in dmso-d_6. ^{1}H: δ[N(1)H_2] 8.17s(2); δ[N(7)H_2] 6.11s(2); δ[N(4)H] 10.36s(1); δ[C(4)H] 7.03d(1); δ[C(5)H] 6.96td(1); δ[C(6)H] 7.25d(1); δ[C(7)H] 7.83d(1); δ[CH_3Sn] 1.11s(6), $^2J(^1H–^{119}Sn)$ = 104 Hz. ^{13}C: δ[C(1)] 183.6; δ[C(10)] 169.7; δ[C(2)] 131.7; δ[C(3)] 145.6; δ[C(4)–C(7)] 110.5, 129.6, 120.9, 120.4; δ[C(8)] 123.1; δ[C(9)] 142.0; δ[C–Sn] 23.4. ^{119}Sn: δ −315.4.

[$SnEt_2$(LL)] and [$SnBu_2$(LL)] were prepared similarly.

[$SnEt_2$(LL)]. mp 189 °C. Found: C, 36.2; H, 4.2; N, 20.7. $C_{14}H_{19}N_7S_2Sn$ requires: C, 35.9; H, 4.1; N, 20.5%. IR (KBr, cm^{-1}): 3474m, 3430sh, 3350m, 3280m,br, $\nu(NH_2)$; 3176m, ν[N(4)–H]; 1618s, 1580s, ν(C=N); 903m, 800w, ν(C=S); 523m, ν_{asym} (Sn–C); 497m, ν_{sym}(Sn–C). NMR spectra were recorded in dmso-d_6. ^{1}H: δ [N(1)H_2] 8.13s(2); δ [N(7)H_2] 6.04s(2); δ[N(4)H] 10.28s(1); δ[C(4)H] 7.00d(1); δ[C(5)H] 6.93td(1); δ[C(6)H] 7.22td(1); δ[C(7)H] 7.79d(1); δ[CH(α)–Sn] 1.51q(2), 1.75q(2); δ[CH(β)–Sn] 1.10t(6). ^{13}C: δ[C(1)] 183.6; δ[C(10)] 170.3; δ[C(2)] 131.5; δ[C(3)] 145.5; δ[C(4)–C(7)] 110.0, 128.8, 120.4, 120.0; δ[C(8)] 122.7; δ[C(9)] 141.6; δ[C(α)–Sn] 33.6; δ[C(β)–Sn] 10.2. ^{119}Sn: δ −300.4.

[$SnBu_2$(LL)]. mp 90 °C. Found: C, 41.3; H, 4.9; N, 18.3. $C_{18}H_{27}N_7S_2Sn$ requires: C, 41.2; H, 5.2; N, 18.7%. IR (KBr, cm^{-1}): 3450sh, 3428m, 3282m,br, $\nu(NH_2)$; 3176m, ν[N(4)–H]; 1616s, 1586s,br, ν(C=N); 905m, 811w, ν(C=S); 600w, ν_{sym}(Sn–C). NMR spectra were recorded in dmso-d_6. ^{1}H: δ[N(1)H_2] 8.19s(2); δ[N(7)H_2] 6.11s(2); δ[N(4)H] 10.38s(1); δ[C(4)H] 7.01d(1); δ[C(5)H] 6.95td(1); δ[C(6)H] 7.21td(1); δ[C(7)H] 7.81d(1); δ[C(α)–Sn] 1.56m(4); δ[C(β)–Sn] 1.78m(4); δ[C(γ)–Sn] 1.17sex(4); δ[C(δ)–Sn] 0.41t(6). ^{13}C: δ[C(1)] 183.8; δ[C(10)] 170.0; δ[C(2)] 130.0; δ[C(4)–C(7)] 110.5, 129.4, 120.9, 120.5; δ[C(8)] 123.0; δ[C(9)] 141.9; δ[C(α)–Sn] 25.6; δ[C(β)–Sn] 27.4; δ[C(γ)–Sn] 27.3; δ[C(δ)–Sn] 13.7. ^{119}Sn: δ −285.5.

X-Ray crystallography

X-Ray diffraction was performed on an Enraf-Nonius CAD4 diffractometer for HL^I, [$SnMe_2(S_2PPh_2)_2$] and [$SnMe_2L^I${O(S)-PPh_2}]·EtOH and an Enraf-Nonius MACH3 for [$SnMe_2$(LL)]. Crystal data and data collection[18a,b] and refinement details are listed in Table 1. The models were refined on F^2 by full matrix least squares.[18c] In HL^I the hydrogen atoms were located in Fourier difference maps and refined isotropically, while in [$SnMe_2(S_2PPh_2)_2$] and [$SnMe_2$(LL)] they were included in the model at ideal geometrical positions. This latter treatment was also applied to [$SnMe_2L^I${O(S)PPh_2}]·EtOH, except for N(1)–H, N(4)–H and O(3)–H, which were refined isotropically.

Since the Flack parameter[18d] for HL^I [0.2(3)] is rather high but all attempts to solve the structure in the centrosymmetric space group failed, refinement was eventually performed assuming the presence of a racemic twin. Molecular graphics were obtained with ZORTEP.[18e]

CCDC reference number 186/2183.

See http://www.rsc.org/suppdata/dt/b0/b005103i/ for crystallographic files in .cif format.

Results and discussion

Synthesis of the complexes

Direct reaction between SnR_2O and HL^I gave no identifiable products other than the reactants themselves. Although this ligand has two potentially deprotonable N–H groups, one in the thiosemicarbazone chain and the other in the indole moiety, usually only the former is deprotonated (although some exceptions are known[8]). Thus in the absence of other anions, two L^{I-} anions are needed to make neutral complexes with SnR_2^{2+}. This is probably too demanding sterically, especially if the O(1), N(2) and S(1) atoms of each thiosemicarbazonato must enter the co-ordination sphere (see below).

In view of the above results we proceeded to prepare mixed ligand complexes with one L^{I-} anion and one sterically less demanding monoanion (see Introduction). The ternary system formed by $SnMe_2O$, HL^I and HS_2PPh_2 initially afforded the corresponding bis(dithiophosphinato) complex but the mother liquor, after long standing in contact with air, surprisingly yielded the complex [$SnMe_2L^I${O(S)PPh_2}], which contains a monothiophosphinato anion formed by partial oxidation of $Ph_2PS_2^-$. When Sn^nBu_2O was used instead of $SnMe_2O$ the only product identified was [$Sn^nBu_2(S_2PPh_2)_2$]; this suggests that the mixed-ligand complex is less stable with dibutyl- than with dimethyl-tin(IV), in keeping with the previously observed relative stabilities of [SnR_2(PyTSC)(S_2PPh_2)] (R = Me, Et or ^{n}Bu) in solution.[12]

To our best knowledge, this is the first reported case of a sulfur being replaced by an oxygen in a phosphorus 1,1-dithiolato complex. Note that [$SnMe_2(S_2PPh_2)_2$] (and [$Sn^nBu_2(S_2PPh_2)_2$]), like most other organotin(IV) diorganodithiophosphinates,[19] appear to be resistant to atmospheric moisture and oxygen. Also, the reactions of SnR_2O or $SnRO_{1.5}$ with dithiophosphoric acids in 1:1 mole ratio afford tetraorganodistannoxanes or hydroxo-bridged complexes [SnR_2-(μ-OH)($S_2P(OR')_2$)]$_2$ without any appreciable alteration of the S–P bonds.[20,21] Nor have we observed any such change in [SnR_2(PyTSC)(S_2PPh_2)].[12] Thus the formation of the monothiophosphinato complex may be due to some influence of the TSC^- ligand, although further experiments are necessary to establish the source of the oxygen and the reaction mechanism.

It is noteworthy that whereas [$SnR_2(OSPR'_2)_2$] complexes are hydrolyzed by atmospheric moisture to [SnR_2(μ-OH)-{O(S)PR'_2}]$_2$ or [(SnR_2{O(S)PR'_2})$_2$O]$_2$,[22,23] [$SnMe_2L^I${O(S)-PPh_2}], once isolated, seems to be chemically stable in air, the only alteration observed being progressive degradation of the crystals due to loss of ethanol.

The reactions of H_2L^{II} and H_2LL with dialkyltin(IV) oxides were straightforward, giving complexes of the dideprotonated ligand. Thus isatin 2-thiosemicarbazone, unlike HL^I, loses both its N–H protons under the reaction conditions.

Crystal structures

Fig. 1 shows a ZORTEP[18e] drawing of HL^I. Selected bond lengths and angles are listed in Table 2. Both the isatin and the TSC moieties are planar (rms = 0.0152 and 0.0346 Å respectively) and their planes form a dihedral angle of 11.8°. In

Table 1 Crystal data, data collection and refinement

	HL^I	$[SnMe_2(S_2PPh_2)_2]$	$[SnMe_2L^I\{O(S)PPh_2\}]\cdot EtOH$	$[SnMe_2(LL)]$
Chemical formula	$C_9H_8N_4OS$	$C_{26}H_{26}P_2S_4Sn$	$C_{25}H_{29}N_4O_3PS_2Sn$	$C_{12}H_{15}N_7S_2Sn$
Formula weight	220.25	647.34	647.30	440.12
Crystal system	Orthorhombic	Triclinic	Triclinic	Monoclinic
Space group (no.)	$P2_12_12_1$ (19)	$P\bar{1}$(2)	$P\bar{1}$(2)	$P2_1/n$(14)
a/Å	15.007(2)	10.607(2)	10.658(2)	14.913(3)
b/Å	15.250(2)	11.2736(9)	10.958(2)	7.341(1)
c/Å	4.3768(5)	13.764(1)	13.978(3)	15.188(3)
α/°		112.017(7)	88.72(1)	
β/°		99.50(1)	77.83(1)	102.93(1)
γ/°		104.36(9)	62.28(2)	
V/Å^3	1001.7(2)	1415.9(3)	1394.1(5)	1620.5(6)
Z	4	2	2	4
T/K	293	293	213	293
μ/mm^{-1}	0.300	1.324	9.510	1.841
Reflections measured	2196	5509	5408	4871
Independent reflections (R_{int})	2196 (0.000)	5200 (0.0292)	4594 (0.0896)	4707 (0.0722)
$R1$ ($I > 2\sigma(I)$)/$wR2$	0.0526/0.1472	0.0342/0.0969	0.0508/0.1465	0.0634/0.1193

Table 2 Bond lengths (Å) and angles (°) for HL^I[a]

S(1)–C(1)	1.663(4)	C(6)–C(7)	1.395(7)
O(1)–C(3)	1.235(6)	C(7)–C(8)	1.380(7)
N(4)–C(3)	1.350(6)	C(8)–C(2)	1.456(6)
N(4)–C(9)	1.398(7)	N(4)–H(41)	0.96(4)
N(3)–C(2)	1.286(5)	H(41)···S(1)^{i}	2.40(4)
N(3)–N(2)	1.356(5)	N(4)···S(1)^{i}	3.348(4)
N(2)–C(1)	1.366(5)	N(2)–H(2)	0.83(4)
N(1)–C(1)	1.321(5)	H(2)···O(1)	2.09(4)
C(3)–C(2)	1.495(6)	N(2)···O(1)	2.730(5)
C(9)–C(4)	1.381(7)	N(1)–H(12)	1.02(5)
C(9)–C(8)	1.395(6)	H(12)···O(1)^{ii}	1.90(5)
C(4)–C(5)	1.371(9)	N(1)···O(1)^{ii}	2.899(5)
C(5)–C(6)	1.369(8)		
C(3)–N(4)–C(9)	111.7(4)	C(7)–C(8)–C(9)	119.9(5)
C(2)–N(3)–N(2)	117.3(4)	C(7)–C(8)–C(2)	133.5(4)
N(3)–N(2)–C(1)	120.7(4)	C(9)–C(8)–C(2)	106.5(4)
O(1)–C(3)–N(4)	127.3(4)	N(3)–C(2)–C(8)	126.4(4)
O(1)–C(3)–C(2)	126.6(4)	N(3)–C(2)–C(3)	127.1(4)
N(4)–C(3)–C(2)	106.0(4)	C(8)–C(2)–C(3)	106.3(4)
C(4)–C(9)–C(8)	122.1(5)	N(1)–C(1)–N(2)	115.6(4)
C(4)–C(9)–N(4)	128.5(4)	N(1)–C(1)–S(1)	126.1(4)
C(8)–C(9)–N(4)	109.4(5)	N(2)–C(1)–S(1)	118.3(3)
C(5)–C(4)–C(9)	116.3(5)	N(4)–H(41)···S(1)^{i}	171(4)
C(6)–C(5)–C(4)	123.5(6)	N(2)–H(2)···O(1)	134(4)
C(5)–C(6)–C(7)	119.6(6)	N(1)–H(12)···O(1)^{ii}	165(4)
C(8)–C(7)–C(6)	118.5(5)		

[a] Symmetry transformations used to generate equivalent atoms: i $-x$, $y+\frac{1}{2}$, $-z+\frac{3}{2}$; ii $-x$, $y-\frac{1}{2}$, $-z+\frac{3}{2}$.

fulfilment of a prediction based on spectroscopic data,[24] the molecule adopts the Z configuration about the C(2)–N(3) bond, which allows stabilization by an N(2)–H···O(1) intramolecular hydrogen bond (see Fig. 1, Table 2). The bond lengths and angles in the TSC chain are similar to those of N(1)-substituted isatin thiosemicarbazones,[8j,25] especially the N(1)-monosubstituted species, although longer N(2)–N(3) and shorter N(2)–C(1) distances in HL^I appear to reflect the differences in intermolecular interactions (see below). In the pentagonal isatin ring the C(2)–C(3) bond is shorter than in free isatin [1.495(6) Å as against 1.555(3)[26] Å], supporting the argument that in the latter compound this bond is lengthened by repulsion between the lone pairs of the two oxygens in *cis* position.[26] The remaining C=O bond is slightly longer than in isatin due to condensation at the position 3 with the thiosemicarbazide.

In addition to the N(2)–H···O(1) bond mentioned above there is another intramolecular hydrogen bond N(1)–H···N(3) [not shown in Fig. 1; N(1)–H 0.93(6), H···N(3) 2.22(5) Å, N(1)···N(3) 2.633(6) Å, N(1)–H···N(3) 105(4)°]; this helps stabilize the molecule in *E* configuration with respect

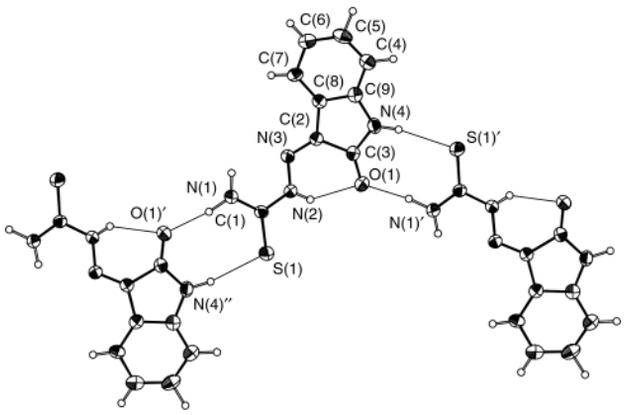

Fig. 1 Zortep plot showing the intra- and inter-molecular hydrogen bonds in crystals of the ligand HL^I.

to the C(1)–N(2) bond, the configuration usually found in uncomplexed TSCs with no N(1) substituents. Unlike N(1)-substituted TSCs,[27] HL^I also has two intermolecular hydrogen bonds, one in which the second amino hydrogen bridges between N(1) and the oxygen of a neighboring molecule [O(1) thus participates in two hydrogen bonds] and the other between the sulfur atom and the N(4)–H group of the same neighbor. These two bonds link the molecules in chains along the *b* axis which stack and cross with others.

The structure of $[SnMe_2(S_2PPh_2)_2]$ was studied using a crystal obtained by recrystallization from ethanol. Fig. 2 shows a ZORTEP plot of the molecular structure, and Table 3 lists selected bond lengths and angles. In this molecule the tin atom is bound to two strongly anisobidentate dithiophosphinato ligands. The Sn–S(12) and Sn–S(22) distances are close to those found in other diorganotin(IV) complexes with phosphorus 1,1-dithiolato ligands,[19] but the Sn–S(11) and Sn–S(21) distances, though shorter than the sum of the van der Waals radii (4.0 Å),[28] must be considered as indicating secondary interactions. If these weak bonds are taken into account, the co-ordination polyhedron around the tin atom can be described as a bicapped tetrahedron.

X-Ray analysis of a crystal of the orange product isolated from the mother liquor of the ternary system $SnMe_2O$–HL^I–HS_2PPh_2 after prolonged contact with air showed the unexpected formation of the mixed-ligand complex $[SnMe_2L^I\{O(S)PPh_2\}]\cdot EtOH$. In this complex (Fig. 3; the main bond lengths and angles are listed in Table 4), the monothiophosphinato anion is O-monodentate. The co-ordination polyhedron can be described as a highly distorted trigonal bipyramid if the L^{I-} ligand is considered as S,N-bidentate, or as a distorted octahedron if the weak Sn–O(1) interaction

Table 3 Selected bond distances (Å) and angles (°) in [$SnMe_2(S_2PPh_2)_2$]

Sn–C(1)	2.100(5)	Sn–S(11)	3.325(1)
Sn–C(2)	2.103(4)	S(11)–P(1)	1.958(2)
Sn–S(22)	2.482(1)	S(12)–P(1)	2.060(2)
Sn–S(12)	2.499(1)	S(21)–P(2)	1.958(2)
Sn–S(21)	3.199(1)	S(22)–P(2)	2.058(1)
C(1)–Sn–C(2)	129.6(2)	S(21)–Sn–S(11)	136.56(3)
C(1)–Sn–S(22)	105.2(2)	C(9)–P(1)–C(3)	105.5(2)
C(2)–Sn–S(22)	112.4(1)	C(9)–P(1)–S(11)	111.8(1)
C(1)–Sn–S(12)	110.4(2)	C(3)–P(1)–S(11)	113.9(1)
C(2)–Sn–S(12)	105.1(1)	C(9)–P(1)–S(12)	107.6(1)
S(22)–Sn–S(12)	85.4(1)	C(3)–P(1)–S(12)	105.0(1)
C(1)–Sn–S(21)	84.2(2)	S(11)–P(1)–S(12)	112.41(7)
C(2)–Sn–S(21)	78.0(1)	C(21)–P(2)–C(15)	106.5(2)
S(22)–Sn–S(21)	70.77(3)	C(21)–P(2)–S(21)	113.6(2)
S(12)–Sn–S(21)	154.87(3)	C(15)–P(2)–S(21)	111.9(1)
C(1)–Sn–S(11)	76.0(1)	C(21)–P(2)–S(22)	105.8(2)
C(2)–Sn–S(11)	85.5(1)	C(15)–P(2)–S(22)	105.9(2)
S(22)–Sn–S(11)	151.66(3)	S(21)–P(2)–S(22)	112.60(6)
S(12)–Sn–S(11)	68.30(3)		

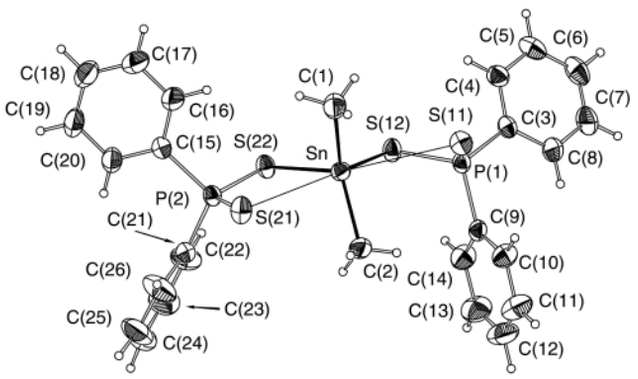

Fig. 2 Molecular structure of [$SnMe_2(S_2PPh_2)_2$].

is also taken into account. However, the short Sn–O(1) distance {2.822(5) Å, shorter than the sum of the van der Waals radii (3.7 Å[28]) but longer than the 2.111(2) Å found in [$SnMe_2$(STSC)][9]} is probably mainly imposed by the rigidity of the ligand backbone, the C(3)–O(1) bond length [1.229(7) Å] being almost the same as in uncomplexed HL^I [1.235(6) Å] whereas in [NiL^I_2]·EtOH[7a] a long but undeniable Ni–O bond lengthens the C(3)–O(1) distance to 1.253(5) Å and shortens the C(2)–C(3) distance to 1.464(7) Å [from 1.495(6) Å in HL^I]. The large esds of the bond lengths in [$TlMe_2L^I$(dmso)],[7b] which also has an O(1)–Tl bond, prevent comparison with [$SnMe_2L^I$-{O(S)PPh_2}]·EtOH. The N(3)–C(2)–C(3) angle narrows from 127.1(4)° in HL^I to 119.3(5)° in [$SnMe_2L^I${O(S)PPh_2}]·EtOH, to 114.0(6) and 116.7(6)° in the nickel(II) complexes[7a] and to 118.5(12)° in the $TlMe_2^+$ complex,[7b] but the C(2)–C(3)–O(1) angle is hardly changed in any of these complexes.

The configuration of the TSC chain about the C(1)–N(2) bond (*E* in uncomplexed HL^I) changes to *Z* to facilitate S,N(3) co-ordination. The Sn–S(1) and Sn–N(3) distances [2.456(2) and 2.371(5) Å, respectively] are both, especially the former, shorter than in [$SnMe_2$(PyTSC)(S_2PPh_2)], in which Sn–S 2.519(1) and Sn–N(3) 2.364(4) Å.[12] Furthermore, S(1)–C(1) is slightly longer than in the PyTSC derivative, suggesting a greater contribution of the thiol form in the L^{I-} ligand. In fact, in [$SnMe_2L^I${O(S)PPh_2}]·EtOH L^{I-} is more thiolic, and exhibits a greater apparent C(1)–N(1) bond multiplicity, than in its nickel(II) and $TlMe_2^+$ complexes[7] {C(1)–N(1) 1.315(9) Å, as against 1.333(8) Å in [NiL^I_2]·EtOH and 1.35(2) Å in [$TlMe_2L^I$-(dmso)]}.[7] The dihedral angle of 19.4(1)° between the plane of the TSC chain (rms = 0.0450 Å) and that of the isatin rings (rms = 0.0114 Å) is wider than in the uncomplexed ligand (see above), presumably because of the influence of the

Table 4 Selected bond distances (Å) and angles (°) for [$SnMe_2L^I$-{O(S)PPh_2}]·EtOH[a]

Sn–C(1Me)	2.121(7)	C(2)–C(3)	1.479(8)
Sn–C(2Me)	2.111(6)	O(1)–C(3)	1.229(7)
Sn–O(2)	2.151(5)	O(3)–H(3)	0.9(2)
Sn–N(3)	2.371(5)	H(3)···O(1)^{i}	1.9(2)
Sn–S(1)	2.456(2)	O(3)···O(1)^{i}	2.780(8)
Sn–O(1)	2.822(5)	N(1)–H(2N1)	0.77(9)
Sn–S(2)	4.310(2)	H(2N1)···O(3)	2.07(9)
S(1)–C(1)	1.741(6)	N(1)···O(3)	2.84(1)
S(2)–P	1.974(2)	N(4)–H(4)	0.78(7)
P–O(2)	1.527(5)	H(4)···S(2)^{ii}	2.76(8)
N(1)–C(1)	1.315(9)	N(4)···S(2)^{ii}	3.484(7)
N(2)–C(1)	1.340(9)	N(1)–H(1N1)	0.86(9)
N(2)–N(3)	1.354(7)	H(1N1)···S(2)^{iii}	2.73(9)
N(3)–C(2)	1.301(8)	N(1)···S(2)^{iii}	3.439(7)
C(2Me)–Sn–C(1Me)	142.0(3)	C(2Me)–Sn–O(1)	75.4(2)
C(2Me)–Sn–O(2)	94.8(2)	C(1Me)–Sn–O(1)	76.0(2)
C(1Me)–Sn–O(2)	87.3(2)	O(2)–Sn–O(1)	134.1(2)
C(2Me)–Sn–N(3)	97.2(2)	S(1)–Sn–O(1)	141.7(1)
C(1Me)–Sn–N(3)	93.7(2)	N(3)–C(2)–C(3)	119.3(5)
O(2)–Sn–N(3)	159.0(2)	C(2)–C(3)–O(1)	126.7(6)
C(2Me)–Sn–S(1)	109.8(2)	O(3)–H(3)···O(1)^{i}	170(14)
N(3)–Sn–O(1)	66.0(2)	N(1)–H(2N1)···O(3)	173(9)
C(1Me)–Sn–S(1)	108.2(2)	N(4)–H(4)···S(2)^{ii}	156(7)
O(2)–Sn–S(1)	84.0(2)	N(1)–H(1N1)···S(2)^{iii}	141(7)
N(3)–Sn–S(1)	75.7(1)		

[a] Symmetry transformations used to generate equivalent atoms: i *x*, *y* + 1, *z*; ii *x* + 1, *y* − 1, *z*; iii *x* + 1, *y*, *z*.

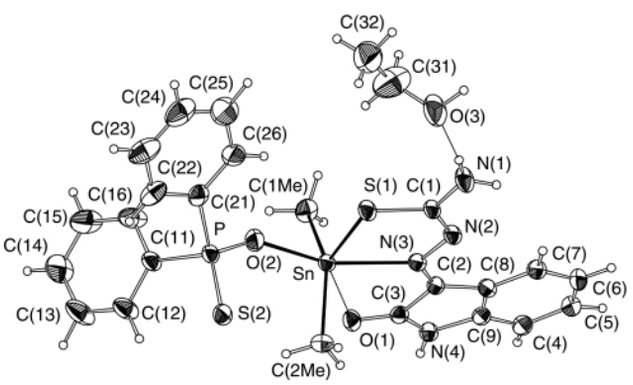

Fig. 3 Molecular structure of [$SnMe_2(L^I)${O(S)PPh_2}]·EtOH, showing intermolecular interactions.

co-ordination bonds. The monothiophosphinato ligand is O-monodentate, the Sn–S(2) distance being longer than the sum of the van der Waals radii (4.0 Å).[28] The Sn–O(2) distance [2.151(5) Å] is slightly longer than those found in [$SnMe_2$-{O(S)PPh_2}$_2$] [2.041(8) and 2.081(8) Å][29a] but shorter than in the mixed-ligand complex [$SnMe_2$(PyTSC)(OAc)]·HOAc [2.220(3) Å].[1]

The molecule of EtOH is bound to one molecule of the complex through a hydrogen bond that involves the O atom of the hydroxyl group and one of the amino hydrogens of the TSC chain (see Table 4), and to another by a hydrogen bond involving its own hydroxyl hydrogen and the isatin oxygen. Thus each O(3) bridges between two molecules, creating a chain running along the *b* axis. The hydrogen bond network is completed by two interactions of the S atom: one with the N(4)–H group of one neighbor (as in the "free" ligand), the other with the amino group of another *via* the amino H atom not involved in binding the ethanol (see Table 4).

[$SnMe_2$(LL)] (Fig. 4) is the first H_2LL complex to have had its structure characterized by X-ray diffraction. Note that simultaneous S,N(3) chelation by the two LL^{2-} TSC chains appears to be prevented by their proximity on the isatin framework: if both adopted the more usual configuration of the chain [*Z* configuration with respect to both C(3)–N(30) and N(20)–

Table 5 Selected bond lengths [Å] and angles [°] for $[SnMe_2(LL)]$[a]

Sn–C(1Me)	2.107(7)	C(3)–C(2)	1.478(9)
Sn–C(2Me)	2.113(7)	C(2)–C(8)	1.457(9)
Sn–N(30)	2.203(5)	C(8)–C(7)	1.385(8)
Sn–N(2)	2.256(5)	C(8)–C(9)	1.396(9)
Sn–S(10)	2.656(2)	C(7)–C(6)	1.384(9)
Sn···S(1)	3.161(2)	C(6)–C(5)	1.384(9)
S(10)–C(10)	1.731(8)	C(5)–C(4)	1.381(9)
S(1)–C(1)	1.686(8)	C(4)–C(9)	1.37(1)
N(4)–C(3)	1.368(9)	N(4)–H(4)	0.86
N(4)–C(9)	1.414(8)	H(4)···S(1)[i]	2.65
N(30)–C(3)	1.289(8)	N(4)···S(1)[i]	3.471(6)
N(30)–N(20)	1.408(7)	N(10)–H(10B)	0.86
N(20)–C(10)	1.312(8)	H(10B)···N(20)[ii]	2.40
N(10)–C(10)	1.352(8)	N(10)···N(20)[ii]	3.103(8)
N(3)–C(2)	1.287(8)	N(1)–H(1B)	0.86
N(3)–N(2)	1.383(7)	H(1B)···N(3)[iii]	2.47
N(2)–C(1)	1.348(8)	N(1)···N(3)[iii]	3.145(7)
N(1)–C(1)	1.338(8)		
C(1Me)–Sn–C(2Me)	140.6(3)	N(30)–C(3)–C(2)	127.2(7)
C(1Me)–Sn–N(30)	97.0(2)	N(3)–C(2)–C(8)	123.2(6)
C(2Me)–Sn–N(30)	121.5(3)	N(3)–C(2)–C(3)	130.0(7)
C(1Me)–Sn–N(2)	102.9(2)	C(8)–C(2)–C(3)	106.3(6)
C(2Me)–Sn–N(2)	92.3(2)	C(7)–C(8)–C(9)	120.0(7)
N(30)–Sn–N(2)	80.2(2)	C(7)–C(8)–C(2)	132.8(7)
C(1Me)–Sn–S(10)	92.7(2)	C(9)–C(8)–C(2)	107.2(6)
C(2Me)–Sn–S(10)	90.5(2)	C(6)–C(7)–C(8)	118.3(7)
N(30)–Sn–S(10)	74.0(2)	C(7)–C(6)–C(5)	120.7(7)
N(2)–Sn–S(10)	151.2(2)	C(4)–C(5)–C(6)	121.5(7)
C(10)–S(10)–Sn	92.1(2)	C(9)–C(4)–C(5)	117.6(7)
C(3)–N(4)–C(9)	110.6(6)	C(4)–C(9)–C(8)	121.9(6)
C(3)–N(30)–N(20)	112.4(6)	C(4)–C(9)–N(4)	129.2(7)
C(3)–N(30)–Sn	127.1(5)	C(8)–C(9)–N(4)	109.0(6)
N(20)–N(30)–Sn	120.5(4)	N(10)–C(10)–S(10)	118.2(6)
C(10)–N(20)–N(30)	114.5(6)	N(1)–C(1)–N(2)	118.6(7)
C(2)–N(3)–N(2)	118.1(6)	N(1)–C(1)–S(1)	122.4(6)
C(1)–N(2)–N(3)	113.5(6)	N(2)–C(1)–S(1)	119.1(6)
C(1)–N(2)–Sn	114.7(5)	N(4)–H(4)···S(1)[i]	159.7
N(3)–N(2)–Sn	131.5(4)	N(10)–H(10B)···N(20)[ii]	139.2
N(30)–C(3)–N(4)	126.0(6)	N(1)–H(1B)···N(3)[iii]	136.1

[a] Symmetry transformations used to generate equivalent atoms: i $x-\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$; ii $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; iii $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$.

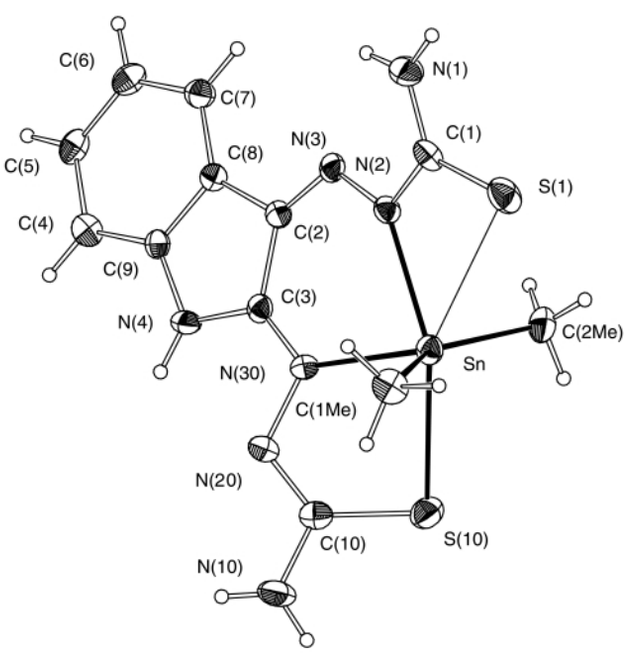

Fig. 4 Molecular structure of $[SnMe_2(LL)]$.

C(10)], then co-ordination of both N(3) and N(30) to the tin atom would probably place the sulfur atoms too far from the metal center for effective co-ordination. One of the TSC chains therefore retains the *E* configuration of free HL^I about the C(1)–N(2) bond (see above) and co-ordinates through the deprotonated N(2). The Sn···S(1) distance [3.161(2) Å], though shorter than the sum of the van der Waals radii (4.0 Å), indicates only a secondary bond. The configuration of the other arm makes S(10),N(30) chelation possible; the Sn–N(30) bond is very short [2.203(5) Å], shorter than the equivalent bond in the mixed-ligand complex [2.371(5) Å], but the Sn–S(10) distance is longer than Sn–S(1) in $[SnMe_2L^I\{O(S)PPh_2\}]\cdot EtOH$. Thus $(LL)^{2-}$ forms three strong bonds (two Sn–N and one Sn–S) and one weak Sn···S bond; a similar co-ordination mode has been proposed on the basis of spectroscopic and conductivity data[8c] for the undeprotonated H_2LL ligand of the copper(II) complex $[CuCl(H_2LL)]Cl$. Together with the two Sn–C bonds, the Sn–$(LL)^{2-}$ bonds define a very distorted octahedral co-ordination polyhedron with the methyl groups apical and an equatorial plane in which one position can be regarded either as vacant (if only the strong Sn–$(LL)^{2-}$ bonds are considered) or as occupied by S(1). The distortion of the octahedron is most evident in the C(1Me)–Sn–C(2Me) angle of 140.6(3)° (Table 5), very different from the ideal value of 180°. Also, the equatorial angles imposed by the rigidity of the ligand differ widely from 90°, especially those involving S(1) if this atom is included. Roughly three planes can be defined in $(LL)^{2-}$: one through the isatin ring system (rms = 0.0168 Å), and one through each TSC chain (rms = 0.0688 Å for the C(2) chain, 0.1356 Å for the other). The more planar TSC arm forms a dihedral angle of 22.9(3)° with the isatin plane, while the chain that is more strongly chelated to the metal is tilted 31.9(1)° in the opposite direction, placing S(1) and S(10) on opposite sides of the isatin plane. The $SnMe_2$ moiety is practically orthogonal to the best plane through the equatorial kernel [Sn, N(2), N(30), S(1), S(10), rms = 0.2072 Å], the dihedral angle being 89.8(2)°, and accordingly forms a dihedral angle of 64.5(2)° with the isatin plane.

Intermolecular association in $[SnMe_2(LL)]$ is mediated by a network of hydrogen bonds between the N(4)–H group and S(1), and between each amino group and the unco-ordinated nitrogen of the other chain [N(3) or N(20); see Table 5].

IR spectra (see Experimental section)

For $[SnMe_2(S_2PPh_2)_2]$ the value of $\Delta = \nu_{asym}(PS_2) - \nu_{sym}(PS_2)$ is 106 cm^{-1}, a value typical of diphenyldithiophosphinato complexes in which, as was shown by X-ray diffraction in this case, the ligand is essentially monodentate but is also bound by a weak secondary bond *via* the second S atom.[30] The similar value found for $[SnBu_2(S_2PPh_2)_2]$ suggests a similar structure for the latter compound.

The IR spectrum of HL^I shows bands at 3424, 3327 and 3277 cm^{-1} attributed to $\nu(NH_2)$; the positions of these bands for the complex $[SnMe_2L^I\{O(S)PPh_2\}]\cdot EtOH$, at 3424 and 3290 cm^{-1} [the latter reinforced by the ethanol ν(OH) band], are in keeping with the non-co-ordination of N(1), whereas the deprotonation of N(2) narrows and slightly shifts a broad band located at 3158 cm^{-1} in the spectrum of HL^I. The weak oxygen-co-ordination of the isatin and the nitrogen-co-ordination of the TSC chain shift ν(C=O) and ν(C=N) respectively to just slightly lower wavenumbers, but ν(C=S) (at 890 cm^{-1} for free HL^I) undergoes a larger shift. The monothiophosphinato bands are close to their positions for other complexes in which, as in this case, this ligand is O-monodentate.[29]

The spectrum of $[SnMe_2L^{II}]$ does not show the "free" ligand band at 3178 cm^{-1} indicating deprotonation of both N–H groups. Neither the sulfur nor the amino N seems to be co-ordinated (the slight shift of $\nu(NH_2)$ from its position in the spectrum of the "free" ligand is probably due to differences as regards involvement in hydrogen bonds), and neither does the shift of ν(C=O) seem large enough to suggest co-ordination *via* this group (even the weak Sn–O bond in $[SnMe_2L^I\{O(S)PPh_2\}]\cdot EtOH$ shifts ν(C=O) 16 cm^{-1}, as against 10 cm^{-1} in this

case). In the range 1650–1450 cm^{-1} there are only two strong bands, a very broad one at 1608 cm^{-1} and a strong band at 1466 cm^{-1}, making a clearer pattern than present in the IR spectra of the "free" ligand or the L^{I-} derivative. This region of the spectrum resembles that of the N(2)-co-ordinated (*p*-anisaldehyde thiosemicarbazonato)dimethylthallium(III),[31] which shows strong bands at 1550 and 1470 cm^{-1}; this suggests that $(L^{II})^{2-}$ may be N(2)-co-ordinated in $[SnMe_2L^{II}]$. If this were so the isatin nitrogen would be well placed to complete chelation, and co-ordination *via* this latter atom might explain the breadth and location of the band at 1608 cm^{-1}, which may include stretching vibrations of the isatin ring as well as ν(C=N).

In the IR spectrum of H_2LL the $\nu(NH_2)$ bands lie at 3442, 3276 and 3244 cm^{-1}. The slight shift to higher wavenumbers for $[SnMe_2(LL)]$ is probably a consequence of changes in hydrogen bonding. The ν(N–H) band at 3162 cm^{-1} in the "free" ligand spectrum loses intensity and narrows for $[SnMe_2(LL)]$ as a result of deprotonation of two of the three nitrogens that are protonated in H_2LL, N(2) and N(20). The 1624 and 1599 cm^{-1} bands of H_2LL do not change significantly upon co-ordination, but in the 1575–1375 cm^{-1} range the two bands present in the spectrum of the "free" ligand (at 1528 and 1471 cm^{-1}) split into five bands at 1553, 1494, 1468, 1391 and 1378 cm^{-1} for $[SnMe_2(LL)]$; the first and third probably reflect the co-ordination of one TSC chain *via* N(2), corresponding to the (*p*-anisaldehyde thiosemicarbazonato)dimethylthallium(III) bands at 1550 and 1470 cm^{-1},[31] and the other three the N(3)-co-ordination of the other chain. The two distinct C=S bands in the spectrum of $[SnMe_2(LL)]$ reflect the presence of both co-ordinated and unco-ordinated sulfurs. The spectrum of the ethyl derivative is practically identical to that of $[SnMe_2(LL)]$, suggesting a similar structure. However, the spectrum of $[SnBu_2(LL)]$ is slightly different, making inference of its co-ordination mode impossible.

NMR spectra (see Experimental section)

The spectra of $[SnMe_2(S_2PPh_2)_2]$ and $[SnBu_2(S_2PPh_2)_2]$ were recorded in $CDCl_3$. Substitution of the $^2J(^1H–^{119}Sn)$ value of the methyl derivative (79 Hz) in the Lockhart and Manders equation 2[32] affords a value of 130° for the C–Sn–C angle, almost exactly the angle found in the solid state (see Table 3). The co-ordination polyhedron present in the solid state therefore probably persists in chloroform. The ^{119}Sn chemical shifts (δ −139.3 and −142.2 for the methyl and butyl derivatives, respectively) clearly differ from those of five- and six-co-ordinated dithiocarbamates (*e.g.* $[SnMe_2Cl(S_2CNEt_2)]$, co-ordination number five, δ −204; $[SnMe_2(S_2CNEt_2)_2]$, co-ordination number six, δ −336; both measurements in CH_2Cl_2[33]), suggesting co-ordination number four as found in the solid state. The ^{31}P chemical shift is practically the same for the methyl and butyl derivatives; although this parameter depends on a complex set of factors,[34] this equality suggests that in both complexes the dithiophosphinato ligand has the same co-ordination mode.

The mixed-ligand complex $[SnMe_2L^I\{O(S)PPh_2\}]\cdot EtOH$ is very insoluble in chloroform, and its NMR spectra were accordingly recorded in dmso-d_6 or dmso solution. The HL^I signals were identified as previously.[7a] As might be expected, deprotonation of this ligand leads to loss of the singlet for N(2)H at δ 12.46 in the ^1H NMR spectrum of HL^I. Co-ordination also deshields all the protons of the six membered isatin ring, especially C(7)H, and slightly deshields N(4)H. The singlets for $N(1)H_2$ shift downfield from δ 8.84 and 8.49 for the "free" ligand to δ 8.93 and 8.88 for the complex [whereas they shift upfield for other complexes of L^{I-}[7] or similar ligands (see below)]. Furthermore, these signals do not merge as they usually do when TSCs co-ordinate, possibly because significant C(1)–N(1) bond multiplicity (see the X-ray discussion) prevents free rotation about this bond from making the two H nuclei magnetically equivalent. The two multiplets at δ 8.09 and 7.75, and a singlet at δ 7.40, are all due to the $Ph_2P(S)O^-$ ligand, while the ethanol molecule has signals at δ 4.33 (t), 3.42 (c) and 1.04 (t). Substitution of the $^2J(^1H–^{119}Sn)$ coupling constant (92 Hz) in Lockhart and Manders' equation 2[32] affords a value of 148° for the C–Sn–C angle, in good agreement with the X-ray value (142.0°).

In the ^{13}C NMR spectrum of $[SnMe_2L^I\{O(S)PPh_2\}]\cdot EtOH$ the C(1) signal lies almost at the same position as for the "free" ligand {whereas in $[NiL^I_2]\cdot EtOH$[7a] and $[TlMe_2L^I(dmso)]$[7b] S(1) co-ordination shifts this signal downfield by 9 and 10 ppm respectively}. The C(3) atom is deshielded, a change that in the case of the above mentioned complexes of Ni and Tl was related to the presence of a metal–oxygen bond.[7] Thus dissolution in dmso appears to weaken the Sn–S(1) bond while making the Sn–O(1) bond stronger than in the solid state. The $\delta(^{119}Sn)$ value, −138.0, shows less shielding than in any of the other diorganotin(IV) thiosemicarbazonates studied in this work, suggesting a low co-ordination number, but even so is probably compatible with five-co-ordination.[35]

Partial analyses of the ^1H NMR spectrum of H_2L^{II} suggest that this molecule is in imino-hydrazine form in dmso solution[8c] [that is, with the "N(4)" H atom bound to N(3)]. The ^1H NMR spectrum of $[SnMe_2(L^{II})]$ shows signals for neither of these groups, indicating bideprotonation of the ligand, and as for $[SnMe_2L^I\{O(S)PPh_2\}]\cdot EtOH$ the $N(1)H_2$ protons appear as two broad singlets, although the separation between them (156 Hz) is smaller than for the "free" ligand (236.1 Hz). Substitution of the $^2J(^1H–^{119}Sn)$ value (87 Hz) in Lockhart and Manders' equation 2[32] gives a value of 141° for the C–Sn–C angle.

To our best knowledge there has been no previous ^{13}C NMR study of H_2L^{II}. The signals reported in the Experimental part have been assigned by analogy with those of HL^I and H_2LL. In the complex C(1) and C(2) are shielded and C(3) is deshielded. These changes are compatible with chelation through the O, N(2) [or N(3)] and S atoms, although any Sn–S bond is probably weak, causing little evolution of the thioamide group toward the thiol form. The ^{119}Sn signal appears at δ −187, well inside the range for five-co-ordinated dimethyltin(IV) complexes.[35]

The ^1H NMR data of H_2LL in dmso-d_6 distinguish between the two TSC chains (see Experimental part). The protons on the C(2) chain are more deshielded than those of the C(3) chain, probably because the former is in *E* configuration while the latter adopts *Z* configuration.[36] Both NH_2 groups have different signals for each proton (as usual in free TSCs), but the separation is 110 Hz for $N(1)H_2$ and 498 Hz for $N(7)H_2$. The deprotonation of both TSC chains upon co-ordination is indicated by loss of the N(2)H and N(6)H signals in the spectra of the complexes, and co-ordination also merges each pair of amino group signals into a new signal that integrates to two protons. Substitution in Lockhart and Manders' equation 2[32] of the $^2J(^1H–^{119}Sn)$ value for $[SnMe_2(LL)]$, 104 Hz, gives the C–Sn–C angle as 170°. The significant difference from the angle found in the X-ray study, 141°, implies marked changes in co-ordination upon dissolution.

The ^{13}C NMR spectra in dmso-d_6 are similar for all three complexes, indicating similar structural arrangements in this solvent. The data are consistent with the two TSC chains having different co-ordination modes. Thus the C(10) signal shifts upfield from *ca.* δ 178 to *ca.* 170 as a consequence of thione-to-thiol evolution, while the C(1) signal shifts downfield from *ca.* δ 178 to *ca.* 184, showing that the C(2) chain retains the thione form. Deprotonation and metallation slightly deshield C(3) (from *ca.* δ 144 to *ca.* 146) but slightly shield C(2) (from *ca.* δ 134 to *ca.* 131). The $\delta(^{119}Sn)$ values (*e.g.* −315.4 for $[SnMe_2(LL)]$) are indicative of six-co-ordination and suggest that the very weakly bound S(1) atom in the solid state is

probably replaced by a molecule of solvent. This would explain the widening of the C–Sn–C angle indicated by the $^{2}J(^{1}H–^{119}Sn)$ value (see above), and would place the methyl groups in the apical positions of an octahedral co-ordination polyhedron.

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