# Synthesis and characterisation of some tin(IV) and methyltin(IV) complexes with oximes and related Schiff's base ligands

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A variety of heteroleptic complexes of the type $[Sn(acac)_2Cl_{2-n}(L)_n]$ [where L = $\{O(CH_2)_3N{=}C(Me)Ar\}$ and $\{ON{=}C(R)Ar\}$; R = Me, H; Ar = 2–$C_5H_4N$, 2–$C_4H_3O$ or 2–$C_4H_3S$; $n$ = 1 or 2] have been synthesised in quantitative yields by the metathetical reaction of *cis*-$[Sn(acac)_2Cl_2]$ with the sodium salt of the ligands in anhydrous methanol–benzene mixture. Corresponding bis(acetylacetonato)methyloximatotin(IV) complexes have also been prepared by a similar reaction of *cis*-$[Sn(acac)_2IMe]$ with the potassium salt of the oximes. Absence of any significant shift in the hetero-aryl ring carbon/proton resonances of all the derivatives of internally functionalised ligands indicates non-participation of the hetero-atom of the ring on coordination to the tin atom. Spectroscopic data suggest retention of the *cis*-octahedral configuation for all these derivatives. Hydrolysis of $[Sn(acac)_2\{ON{=}C(Me)C_4H_3O\}Cl]$, followed by sintering at 650°C yielded pure $SnO_2$ microcrystals, which were characterised by XRD and SEM analyses.

**Keywords:** sodium/potassium salt, FAB Mass, $^{119}Sn$ NMR, *cis*-configuration

The $SnO_2$ thin films developed under low temperature conditions using metal alkoxides as precursors by sol-gel technique are being used in various optoelectronic devices, yet the high sensitivity of such precursors towards hydrolysis limits their use. This difficulty may be resolved by substitution of some of the alkoxy groups of metal alkoxides by modifiers such as acetylacetone which can provide control over the relative rates of hydrolysis/condensation processes.[1] There is also a great possibility of the application of such modified compounds in the related field of inorganic-organic hybrid materials (which allow introduction of organic molecules or even biomolecules inside an inorganic network) and these can be tailored for specific applications.[2,3]

Thus, monomeric complexes of the types, *cis*-$[Sn(acac)_2(OR)_2]$,[4] *cis*-$[Sn(acac)_2Cl_2]$[5] as well as *cis*-$[Sn(acac)_2IMe]$[6] may be used for making the desired specific precursors. Multidentate ligands such as Schiff's bases and oximes have also attracted considerable attention because of their remarkable structural diversity and biological implications.[7-10]

Our earlier studies on organotin(IV) complexes with functionalised oximes revealed quite interesting results with unique stannoxane networks.[11-15] In continuation to above we prepared some new heteroleptic derivatives of bis(acetylacetonato)tin(IV) and bis(acetylacetonato)methyltin(IV) with some internally functionalised Schiff's bases and with simple as well as internally functionalised oximes. Hydrolysis of a representative compound, $[Sn(acac)_2\{ON{=}C(Me)C_4H_3O\}Cl]$ has also been carried out and the results are reported herein.

## Results and discussion

Metathetical reactions of *cis*-$[Sn(acac)_2Cl_2]$ and *cis*-$[Sn(acac)_2IMe]$ with sodium/potassium salt of Schiff's bases/oximes under anhydrous conditions in refluxing methanol-benzene mixture yield complexes of the following types:

$$[Sn(acac)_2Cl_2] + n\,NaL \longrightarrow [Sn(acac)_2(Cl)_{2-n}L_n] + n\,NaCl\downarrow$$

**(1–9)**

(where L = $\{O(CH_2)_3N{=}C(Me)Ar\}$ and $\{ON{=}C(R)Ar\}$; R = Me, H; Ar = 2–$C_5H_4N$, 2-$C_4H_3O$ or 2-$C_4H_3S$; $n$ = 1 or 2)

$$[Sn(acac)_2IMe] + K[ON{=}C(R)R'] \longrightarrow [Sn(acac)_2\{ON{=}C(R)R'\}Me] + KI\downarrow$$

**(10–15)**

(where R = Me or Ph; R' = Me, Ph, $-CH_2CH_2Ph$, 2–$C_5H_4N$, 2–$C_4H_3O$ and 2–$C_4H_3S$)

All these derivatives are sharp melting coloured solids, soluble in common organic solvents particularly in polar solvents. Elemental analyses corresponded to the expected formula (Table 1). Molecular weight measurements indicated the monomeric nature of these complexes in solution. The FAB mass spectra of two of the compounds, **(5)** and **(6),** also supports the monomeric nature of these derivatives (Table 2).

*IR spectra*

IR spectra of all these derivatives have been recorded as KBr palates or as nujol mulls in the range 4000–400 $cm^{-1}$.

The absence of hydroxy group absorptions (which were present in the region 3100–3300 $cm^{-1}$ in the free ligands) indicates the deprotonation of the hydroxy group of the ligand and formation of an Sn–O bond. This was further supported by the appearance of new bands at 415 ± 10 $cm^{-1}$ assigned to $\nu_{Sn\text{-}O\ (schiff's\text{-}base)}$ and 405 ± 10 $cm^{-1}$ assigned to $\nu_{Sn\text{-}O\ (oxime)}$ mode in the corresponding derivatives. The appearance of $\nu_{C=N}$ stretching vibrations (1525–1580 $cm^{-1}$ in Schiff's base complexes and 1530–1590 $cm^{-1}$ in tinoximates) towards lower wave numbers (~ 20 $cm^{-1}$) in comparison to the free ligands, further supports the formation of an Sn–O bond through oxygen atom of the ligand moieties. In all these derivatives, the presence of strong $\nu_{C=O}$ stretching vibrations in the region 1595–1690 $cm^{-1}$ (1720 $cm^{-1}$ in the free acetylacetone), suggests the retention of bidentate nature of acetylacetonate moiety. Absorptions at 530–550 $cm^{-1}$ have been assigned to $\nu_{Sn\text{-}C}$ in monomethyltin(IV) complexes.

*NMR spectra*

NMR ($^1H$, $^{13}C$ and $^{119}Sn$) spectra of all these derivatives have been recorded in $CDCl_3/CHCl_3$ (using $D_2O$ lock) and the data are summarised in Table 3.

The hydroxyl proton resonances of the free Schiff's bases and oximes[16] (which were present in the region δ 4.89 to 5.50 ppm and δ 8.01–9.82 ppm, respectively) as well as of the free acetylacetone ligand (δ 15.0), were absent in the $^1H$ NMR spectra of the complexes indicating deprotonation of the ligand moieties and formation of an Sn–O bond through oxygen atom of the ligands.

In the case of mixed-ligand complexes derived from Schiff's bases, all ring protons and carbon resonances exhibited no appreciable shifts (0.01–0.13 ppm in $^1H$ and 0.6–1.3 ppm in $^{13}C$ NMR spectra) indicating non participation of heteroatom of the ring on coordination. However, a significant shift in $NCH_2$ protons and carbon resonances along with an up-field shift (~3.6 ppm) in the C=N carbon has been observed in case of compound **(1)**. The presence of only one single set of resonances for the methine proton and carbon atom of the acetylacetonate moiety in the NMR spectra of 1:2 derivatives **(2** and **3)** along with the appearance of double sets for these

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**Table 1** Physical and analytical data $[Sn(acac)_2\{O(CH_2)_3N=C(Me)Ar\}_nCl_{2-n}]$, $[Sn(acac)_2\{ON=C(R)R'\}_nCl_{2-n}]$ and for $[Sn(acac)_2\{ON=C(R)R'\}Me]$ complexes

| Compound | Recrystallisation solvent /% Yield[a] | M.p./°C | Elemental Analysis in % Found (Cald) | | | | |
|---|---|---|---|---|---|---|---|
| | | | Sn | C | H | N | S/Cl |
| $[Sn(acac)_2\{OC_4H_3C(Me)=N(CH_2)_3O\}Cl]$ | Hexane–Benzene (99) | 142 Dec. | 22.1 (22.8) | 43.9 (44.0) | 4.9 (5.0) | 2.6 (2.7) | 6.7 (6.8) |
| $[Sn(acac)_2\{OC_4H_3C(Me)=N(CH_2)_3O\}_2]$ | Hexane–Benzene (91) | 110 Dec. | 17.5 (18.2) | 51.5 (51.8) | 5.8 (5.9) | 4.1 (4.3) | – |
| $[Sn(acac)_2\{O(CH_2)_3N=C(Me)C_5H_4N\}]$ | Hexane–Benzene (99) | 125 Dec. | 17.0 (17.6) | – | – | 2.0[b] (2.0) | – |
| $[Sn(acac)_2\{ON=C(Me)C_4H_3O\}Cl]$ | Hexane–Benzene (83) | 98 | 24.4 (24.9) | 40.2 (40.3) | 4.1 (4.2) | 3.0 (2.9) | 6.3 (6.4) |
| $[Sn(acac)_2\{ON=C(Me)C_4H_3O\}_2]$ | Hexane–Benzene (85) | 185 | 20.8 (21.0) | 46.1 (46.7) | 4.2 (4.6) | 4.4 (4.9) | – |
| $[Sn(acac)_2\{ON=C(Me)C_5H_4N\}_2]$ | Hexane–Benzene (82) | 160 | 20.1 (20.2) | 48.8 (49.1) | 4.7 (4.8) | 9.0 (9.5) | – |
| $[Sn(acac)_2\{ON=C(Me)C_4H_3S\}_2]$ | Hexane–Benzene (82) | 75 | 19.8 (19.8) | 44.1 (44.2) | 4.3 (4.4) | 4.6 (4.7) | 10.6 (10.7) |
| $[Sn(acac)_2\{ON=C(H)C_4H_3O\}_2]$ | Hexane–Benzene (88) | 85 | 23.3 (23.4) | 44.6 (44.7) | 4.0 (4.1) | 5.0 (5.2) | – |
| $[Sn(acac)_2\{ON=C(H)C_4H_3S\}_2]$ | Hexane–Benzene (81) | 149 | 20.8 (20.8) | 42.1 (42.2) | 3.8 (3.9) | 4.6 (4.9) | 11.1 (11.2) |
| $[Sn(acac)_2\{ON=C(Me)_2\}Me]$ | Hexane–Benzene (90) | 70 | 29.4 (29.3) | – | – | 3.2[b] (3.4) | – |
| $[Sn(acac)_2\{ON=C(Me)CH_2CH_2Ph\}Me]$ | Hexane–Benzene (92) | 79 | 24.1 (24.0) | – | – | 2.7[b] (2.8) | – |
| $[Sn(acac)_2\{ON=C(Ph)_2\}Me]$ | Hexane–Benzene (87) | 75 | 22.5 (22.4) | – | – | 2.5[b] (2.6) | – |
| $[Sn(acac)_2\{ON=C(Me)C_5H_4N\}Me]$ | Hexane–Benzene (85) | 93 | 25.5 (25.4) | 46.0 (46.2) | 4.9 (5.2) | 5.6 (6.0) | – |
| $[Sn(acac)_2\{ON=C(Me)C_4H_3O\}Me]$ | Hexane–Benzene (80) | 81 | 26.1 (26.0) | 44.3 (44.7) | 4.9 (5.1) | 3.0 (3.1) | – |
| $[Sn(acac)_2\{ON=C(Me)C_4H_3S\}Me]$ | Hexane–Benzene (85) | 85 | 25.2 (25.1) | 43.0 (43.2) | 4.3 (4.9) | 2.8 (2.9) | – |

[a]Yield after recrystallisation.
[b]Estimated by Kjeldhal's method.

in the case of the 1:1 derivative **(1)**, suggest a distorted *cis*-octahedral geometry around tin in these complexes.

The corresponding bis(acetylacetonato)oximatotin(IV) derivatives **(4–9)** exhibit two sets of resonances for the CH proton and carbon atom of acetylacetonate moieties and only a single set of resonances for oximate moieties. Retention of the *cis*-configuration even after complexation with the functionalised ligands, was supported by the presence of multiple $^1H$ and $^{13}C$ NMR signals for $CH_3$ as well as for C=O carbons of the acetylacetone moieties, as has been reported for $[Sn(acac)_2Cl_2]$.[5] A similar kind of pattern has also been observed for the complexes of the type $[Sn(acac)_2\{ON=C(R)R'\}Me]$ **(10–15).** Appearance of only one signal for the methyl protons and for the C=O carbon atoms of the acetylacetonate moieties in some of these derivatives may be due to the presence of the fast exchange phenomenon on the NMR time scale. The oxime-methyl proton resonances exhibit a slight up-field shift (δ 0.01–0.13 ppm) on complexation. However, no appreciable shift has been observed in the ring protons and carbon resonances of the internally functionalised ligand moieties, thus ruling out the possibility of coordination through the heteroatom of the ring to the central tin atom. Similarly, no significant shift has been observed for the C=N carbon signals in all the oximato complexes.

Methyl–tin proton signals in monomethyltin(IV) complexes appeared as a singlet in the region δ 0.57–0.91 ppm [with $^2J(^{119}Sn–^1H)$ on an average of 118 Hz] indicating that there is no significant change in the *s*-character of the Sn–C bond on complexation with the oxime ligand ($^2J(^{119}Sn\text{-}^1H)$ = 117 Hz in $[Sn(acac)_2IMe]$).

The $^{119}Sn$ NMR spectra of some of the representative complexes displayed a single resonance in the regions δ –640 to –725 ppm for tin(IV) and δ –515 to –545 ppm for methyltin(IV) derivatives, which falls in the range of hexa-coordination around the tin atom in $SnO_6$[17] and $CSnO_5$[18] systems, respectively.

*Hydrolytic study*

Hydrolysis of one representative compound $[Sn(acac)_2\{ON=C(Me)C_4H_3O\}Cl]$ **(4)** was carried out using isopropanol as a solvent. On washing with a hot acetone–toluene mixture followed by air drying, pure $SnO_2$ powder was obtained. This sample ($SnO_2$) was then sintered at 300°C for 3 h. The XRD –pattern of the resultant powder showed it to be amorphous.

**Table 2** Important fragmentation ion peaks and their assignment

| Complex | Fragmented ions | *m/e* values |
|---|---|---|
| $[Sn(acac)_2\{ON=C(Me)C_4H_3O\}_2]$ **(5)** | $[Sn(acac)_2\{ONC(CH_3)C_4H_3O\}\{ONC(CH_3)C_3H_2\}]^+$ | 470 |
| | $[Sn\{OC(CH_3)CH(CH_3)CO\}\{ONC(CH)\}\{O\}]^+$ | 289 |
| | $[Sn\{OC(CH_3)CH(CH_3)CO\}\{H\}]^+$ | 219 |
| $[Sn(acac)_2\{ON=C(Me)C_5H_4N\}_2]$ **(6)** | $[Sn(acac)_2\{ONC(Me)C_5H_4N\}\{ONC(Me)CH_2\}]^+$ | 523 |
| | $[Sn\{ONC(CH_3)CH(CH_3)CO\}_2\{OC(Me)C_5H_4N\}(OH_2)]^+$ | 470 |
| | $[Sn\{OC(CH_3)CH(CH_3)CO\}\{ONC(Me)C_5H_4N\}(OH)]^+$ | 370 |
| | $[Sn\{OC(CH_3)CH(CH_3)CO\}\{ONC(Me)C_5H_4N\}]^+$ | 353 |
| | $[Sn\{OC(CH_3)CH(CH_3)CO\}\{H\}]^+$ | 219 |

**Table 3** NMR data in $CDCl_3$ for $[Sn(acac)_2\{O(CH_2)_3N=C(Me)Ar\}_nCl_{2-n}]$, $[Sn(acac)_2\{ON=C(R)R'\}_nCl_{2-n}]$ and $[Sn(acac)_2\{ON=C(R)R'\}Me]$ complexes

| S.no. | Compound | $^1$H NMR δ ppm | $^{13}C\{^1H\}$ NMR δ ppm | $^{119}Sn\{^1H\}$ NMR δ ppm |
|---|---|---|---|---|
| 1. | $[Sn(acac)_2\{O(CH_2)_3N=C(Me)C_4H_3O\text{-}2\}Cl]$ | 6.98 (H–5); 6.92 (H–3); 6.17 (H–4); 5.70, 5.50 (each s, *CH*–acac); 4.47 (–O*CH*$_2$); 3.53 (–N*CH*$_2$); 2.45{s, *CH*$_3$–C=N)}; 2.24, 2.21, 2.12, 2.05 {each s, *CH*$_3$–acac}; 1.98 {m, $CH_2$–*CH*$_2$–$CH_2$}. | 196.4, 191.2 (C=O); C=N (not observed); 130.7 (C–5); 120.8 (C–2); (C–4, not observed); 108.6 (C–3); 102.6, 100.4 {*CH*–acac}; 58.6 (–O*CH*$_2$); 45.3 (–N*CH*$_2$); 34.5 (*CH*$_3$–C=N), 27.9, 24.8 {*CH*$_3$–acac}; 27.3 ($CH_2$–*CH*$_2$–$CH_2$). | –646 |
| 2. | $[Sn(acac)_2\{O(CH_2)_3N=C(Me)C_4H_3O\text{-}2\}_2]$ | 6.99 (3.60 Hz (d) H–5); 6.92 (H–3); 6.16 {m, H–4}; 5.50 {s, *CH*–acac}; 4.46 (–O*CH*$_2$); 3.53 (–$NCH_2$); 2.45 {s, –*CH*$_3$–C=N–}; 2.05, 1.99 (s, *CH*$_3$–acac); 1.96 (m, $CH_2$–*CH*$_2$–$CH_2$). | 130.7 (C–5, C–2); 120.8 (C–4); 108.6 (C–3); 102.0 {*CH* (acac)}; 58.6 (–$OCH_2$); 45.4 (–$NCH_2$); 34.5 (*CH*$_3$–C=N); 27.3 ($CH_2$–*CH*$_2$–$CH_2$); 24.5 {$CH_3$ (acac)}; C=N, C=O (not observed). | –720 |
| 3. | $[Sn(acac)_2\{O(CH_2)_3N=C(Me)$ Py$\}_2]$ | 8.56 {14.71 Hz,d) H–6}; 7.82 {d, 7.50 Hz, H–3}; 7.63 {4.80 Hz, d, H–5}; 7.19 {27.61 Hz, 16.21 Hz, H–4 (dd); 4.94 {–CH (acac)}; 3.54 (–O*CH*$_2$); 3.37 (–$CH_2$–*CH*$_2$–$CH_2$); 2.64 (–N*CH*$_2$); 2.23 {s, *CH*$_3$–C=N}; 1.97, 1.91 {s, *CH*$_3$–acac}. | 194.5 (C=O); 163.5 (C=N); 155.9 (C–6); 148.8 (C–4); 136.2 (C–3); 121.8 (C–5); 95.1{*C*H–acac}; 60.0 (–O*CH*$_2$); 59.0 (–N*CH*$_2$); 32.7 ($CH_2$–*CH*$_2$–$CH_2$); 28.6, 22.5 {*CH*$_3$–acac); 13.9 (*CH*$_3$–C=N). | – |
| 4. | $[Sn(acac)_2\{ON=C(Me)C_4H_3O\}Cl]$ | 7.46 {d, 1.24 Hz (d) H–5}; 6.63 {dd, 3.65 Hz (d), 0.46 Hz (d) H–3}; 6.44 {m, H–4}; 5.70, 5.50 {s, *CH*–acac}; 2.21 (oxime–Me) 2.20 – 2.04 {multiple signals, *CH*$_3$–acac}. | 195.9, 191.2 (C=O); 150.1 (C=N); 148.1 (C–2); 143.6 (C–5); 111.2 (C–3); 110.0 (C–4); 102.6, 100.4 (*CH*–acac); 27.9, 24.8 (each s, *CH*$_3$–acac); 11.0 (oxime–Me). | – |
| 5. | $[Sn(acac)_2\{ON=C(Me)C_4H_3O\}_2]$ | 7.45 {d, 0.59 (d) Hz, H–5}, 6.62 (d, 3.27 Hz (d), H–3}; 6.43 {m, H–4}; 5.63, 5.49 (each s, *CH*–acac); 2.17(s, oxime–Me); 2.10, 2.04 (s, *CH*$_3$–acac). | 196.4, 195.8 (C=O); 152.7 (C=N); 149.7 (C–2); 143.6 (C–5); 111.3 (C–3); 110.9 (C–4); 102.5, 100.5 (*CH*–acac); 28.4, 24.8 (*CH*$_3$–acac); 11.1 (oxime–Me). | –715 |
| 6. | $[Sn(acac)_2\{ON=C(Me)$Py$\}_2]$ | 8.60 {d, 4.2 Hz, H–6}; 7.82 {d, 12.1 Hz, H–3}; 7.65 {td, 1.8 Hz (d), 7.7 Hz (t), H–5}; 7.25 {td, 1.2 Hz (d); 8.0 Hz (t), H–3}, 5.65, 5.50 (*CH*–acac); 2.34 (s, oxime–Me); 2.05, 2.04 (each s, *CH*$_3$–acac). | 195.1, 191.2 (C=O); 154.5 (C=N & C–2); 148.8 (C–6); 136.2 (C–4); 123.5 (C–3); 120.5 (C–5); 102.6, 100.4 (*CH*–acac); 27.8, 24.8 (*CH*$_3$–acac); 10.4 (oxime–Me). | – |
| 7. | $[Sn(acac)_2\{ON=C(Me)C_4H_3S\}_2]$ | 7.52 {d, 5.05 Hz (d) H–5}; 7.45 {d, 3.56 Hz (d), H–3}; 7.24 {m, H–4}; 5.69, 5.49 (s, *CH*–acac); 2.28 (s, oxime–Me); 2.18 – 2.03 (multiple signals, *CH*$_3$–acac}. | 195.7, 191.22 (C=O); 151.5 (C=N); 140.1 (C–2); 127.0 (C–5); 126.6 (C–3); 126.3 (C–4); 102.6, 100.4 (*CH*–acac); 28.0, 24.7 (s, *CH*$_3$–acac); 12.2 (oxime–Me). | – |
| 8. | $[Sn(acac)_2\{ON=C(H)C_4H_3O\}_2]$ | 7.72 {s, oxime–H}; 7.56 (m, H–5); 7.47{d, 0.89 Hz, H–3}; 6.74 {d, 3.27 Hz (d), H–4}; 5.76 (s, *CH*–acac); 2.37 – 2.18 {multiple signals, *CH*$_3$– acac}. | 191.3 (C=O); 142.9 (C–2); 141.5 (C–5); 112.1 (C–3); 111.8 (C–4); 102.7, 100.4 (*CH*–acac); 27.80, 24.80 (*CH*$_3$–acac). | –723 |
| 9. | $[Sn(acac)_2\{ON=C(H)C_4H_3S\}_2]$ | 7.67 {s, oxime–H}; 7.50 {d, 4.16 Hz (d), H–5}; 7.30 {d, 4.46 Hz (d), H–3}; 7.02 {t, 1.94 Hz (t), H–4}; 5.49, 5.28 (each s, *CH*–acac); 2.23 (s, oxime–Me); 2.04 (s, *CH*$_3$–acac). | 191.2 (C=O); 149.4 (C=N); 140.9 (C–2); 131.4 (C–3); 131.2 (C–5); 126.0 (C–4); 100.4 (*CH*–acac); 30.8, 24.8 (*CH*$_3$–acac). | –720 |
| 10. | $[Sn(acac)_2\{ON=CMe_2\}Me]$ | 5.48, 5.32 (s, *CH*–acac); 1.89 (s, *CH*$_3$–acac); 1.70 (s, oxime–Me); 0.57 (s, $^2J(^{119}Sn–^1H)$ = 118 Hz, Sn– *CH*$_3$). | 193.8, 190.0 (C=O); 101.0, 99.3 (*CH*–acac); 27.3, 23.7 (*CH*$_3$–acac); 20.6 (Sn–*CH*$_3$); 14.2 (oxime–Me). | –530 |
| 11. | $[Sn(acac)_2\{ON=C(Me)CH_2CH_2Ph\}Me]$ | 7.41 (m, Ph); 5.64, 5.40 (each s, *CH*–acac); 2.97 (m, Ph–C*CH*$_2$); 2.63 (m, Ph–*CH*$_2$); 2.21 (br, *CH*$_3$–acac); 0.76 {s, $^2J(^{119}Sn–^1H)$ = 120 Hz, Sn– *CH*$_3$}. | 194.0, 191.3, (C=O); 156.1 (C=N); 133.1, 129.7, 127.8 (Ph); 101.1, 100.0, (*CH*–acac); 26.6, 24.2, (*CH*$_3$–acac); 20.3 (Sn–*CH*$_3$); 19.5 {Ph–C*CH*$_2$}; 17.0 (Ph–*CH*$_2$); 12.1 (oxime–Me). | – |
| 12. | $[Sn(acac)_2\{ON=CPh_2\}Me]$ | 7.57 (m, Ph); 5.54, 5.31 (each s, *CH*–acac); 2.06 (br, *CH*$_3$–acac); 0.95 (s, $^2J(^{119}Sn–^1H)$ = 119 Hz, Sn– *CH*$_3$). | 194.1, 191.2 (C=O); 157.1 (C=N); 133.1, 129.3, 126.7, (Ph); 101.2, 99.9 (*CH*–acac); 26.9, 24.1 (*CH*$_3$–acac); 20.5 (Sn–$CH_3$). | –515 |
| 13. | $[Sn(acac)_2\{ON=C(Me)$Py$\}Me]$ | 8.52 (m, H–6); 7.57 (H–3); 7.25 (m, H–4); 7.16 (br, H–5); 5.57, 5.45 (each s, CH–acac); 2.31 (s, oxime–Me); 2.01 (s, *CH*$_3$–acac); 0.79 (s, $^2J(^{119}Sn–^1H)$ = 120 Hz, Sn– *CH*$_3$). | 193.9, 191.0 (C=O); 156.7 (C=N and C–2); 148.3 (C–6); 135.4 (C–4); 123.1 (C–3); 119.9 (C–5); 101.3, 100.3, (*CH*–acac); 27.6, 24.6 (*CH*$_3$–acac); 20.2 (Sn–$CH_3$); 10.0 (oxime–Me). | –539 |
| 14. | $[Sn(acac)_2\{ON=C(Me)C_4H_3O\}Me]$ | 7.30 (br, H–5); 6.29 (s, H–3); 6.25 (br, H–4); 5.50, 5.43 (each s, *CH*–acac); 2.09 (s, oxime–Me); 1.92 (br, *CH*$_3$–acac); 0.69 (s, $^2J(^{119}Sn–^1H)$ = 120 Hz, Sn– *CH*$_3$). | 194.0, 191.1 (C=O); 150.1 (C=N); 147.2 (C–2); 143.4 (C–5); 111.1 (C–3); 109.7 (C–4); 101.1, 100.3, (*CH*–acac); 27.6, 24.7 (*CH*$_3$–acac); 20.3 (Sn–$CH_3$); 11.0 (oxime–$CH_3$). | –541 |
| 15. | $[Sn(acac)_2\{ON=C(Me)C_4H_3S\}Me]$ | 7.60 (m, H–5); 7.44 (m, H–3); 7.10 (m, H–4); 5.43, 5.40 (each s, *CH*–acac); 2.37 (s, oxime–Me); 2.09 (m, acac–$CH_3$); 0.91 (s, $^2J(^{119}Sn–^1H)$ = 118 Hz, Sn– *CH*$_3$). | 193.9, 191.1 (C=O); 151.2 (C=N); 140.2 (C–2); 130.6 (C–5); 126.5 (C–3); 124.7 (C–4); 101.3, 100.3, (acac–CH); 27.5, 24.6, ($CH_3$–acac–); 20.2 (Sn–$CH_3$); 12.1 (oxime–Me). | –545 |

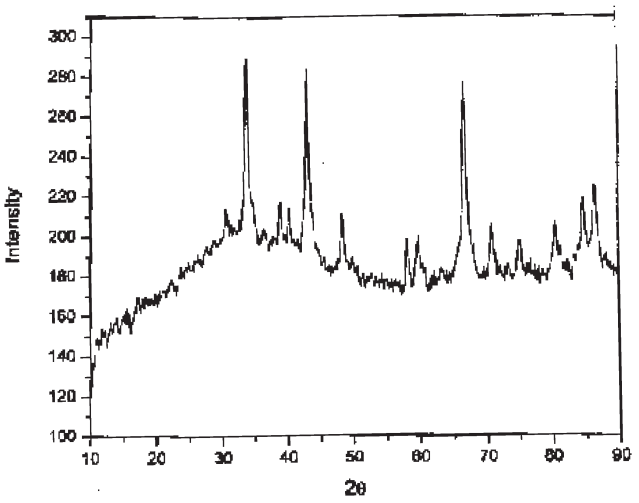


**Fig. 1** X-ray diffraction pattern of $SnO_2$ obtained from the hydrolysis of [Sn(acac)$_2${ON =C(Me)$C_4H_3O$}Cl] followed by sintering at 650 °C for 3 h.

However, on heating it again at 650°C for 3 h, crystalline $SnO_2$ was obtained[19] (Fig.1). Micro-analyses of the sample indicated formation of pure $SnO_2$ (C; 0.4% and H; 0.3%). The scanning electron micrographs[19] of the sample indicated the formation of microcrystals at the sintering temperature 650°C (Fig. 2).

*FAB mass spectra*

The assignment of some important fragmentation ion peaks (for which the isotopic pattern for tin was observed) for two compounds in their FAB Mass spectra have been made (Table 2) and the values for these indicated the monomeric nature of the complexes.

## Experimental

All manupilations were carried out under anhydrous conditions. Tin tetrachloride and acetylacetone were distilled before use. *Due precautions were taken while using hazardous solvents like benzene.* [Sn(acac)$_2$Cl$_2$][4,5] and [Sn(acac)$_2$IMe][6] were prepared according to the literature methods. Tin was estimated as tindioxide. Schiff's bases and oximes were prepared according to the literature methods.[7,16] $^1$H and $^{13}$C {$^1$H} NMR data for the newly synthesised Schiff's bases in $CDCl_3$ are as *[{2–$OC_4H_3C(Me)N(CH_2)_3OH$}]*, $^1$H NMR: 6.97{2.40 Hz (d) H–5 (d)}; 6.95 {2.10 Hz (d) H–3}; 6.10 {(m) H–4}; 4.9 (br.,OH); 4.40 {6.60 Hz, 6.90 Hz (t)–$OCH_2$}; 3.56 {3.60 Hz, 8.40 Hz, –$NCH_2$}; 2.4 {$CH_3$–C=N (S)}; 1.90 {(m) $CH_2$–*$CH_2$*–$CH_2$}, $^{13}$C{$^1$H} NMR: 178.0 (C=N); 129.4 (C–5); 120.1 (C–2); 116.1 (C–4); 107.8 (C–3); 58.7 (–$OCH_2$); 45.6 (–$NCH_2$); 36.0 (–$CH_3$–C=N–); 26.7 ($CH_2$–*$CH_2$*–$CH_2$–)] and for *[{2–$NC_5H_4C(Me)N(CH_2)_3OH$}]*, $^1$H NMR: 8.56 (d, 3.90 Hz, H–6); 7.95{d, 8.10 Hz, H–3}; 7.68{m, H–5}; 7.28 {dd, 5.40, 0.01 Hz, H–4}; 5.50 (br., OH); 3.86 {5.70, 0.90 Hz, 5.40 Hz, –$OCH_2$}; 3.67{m, $CH_2$–*$CH_2$*–$CH_2$}; 2.83 (–$NCH_2$); 2.35 {s, $CH_3$–C=N},$^{13}$C{$^1$H} NMR: 167.1 (C=N)]; 156.9 (C–6); 148.2 (C–4); 136.5 (C–3); 121.2 (C–5); 61.7 (–$OCH_2$); 50.6 (–$NCH_2$); 32.3 ($CH_2$–*$CH_2$*–$CH_2$); 13.8 ($CH_3$–C=N–)]. Molecular weight measurements were carried out by the elevation of boiling point in anhydrous chloroform **(10–15)** and by depression of freezing point in anhydrous benzene **(1–9)** using a Beckmann thermometer (Einstellthermometer *n*– Beckmann, Labertherm – N, Skalenwert, 0.01 k, made in GDR). C, H and N analyses were carried out on Elementar Vario EL III Carloerba 1108 elemental analyser. IR spectra were recorded as KBr plates/nujol mulls on Nicolet Magna-550 spectrophotometer in the range a 4000–400 cm$^{-1}$. $^1$H, $^{13}$C and $^{119}$Sn NMR spectra were recorded on a JEOL FX90Q spectrometer and on a AL 300 JEOL spectrometer in $CDCl_3$. FAB mass spectra were recorded on a JEOL SX 102/DA-6000 mass spectrometer/data system using argon/xenon (6 kv, 10 mA) as the FAB gas and m-nitrobenzyl alcohol as the matrix. Powder X-ray diffraction pattern was obtained on a Philips-1840 diffractometer (Fe$^{57}$; at λ1.937 Å).

*Preparation of [Sn(acac)$_2${ON=C($CH_3$)$C_4H_3O$}Cl]* **(4)**: To a methanolic solution of the sodium salt of the ligand, prepared *in situ* by the reaction of sodium (261 mg, 11.3 mmol) with 2–acetyl furan oxime (1.42 g, 11.3 mmol) in refluxing methanol, a benzene suspension of [Sn(acac)$_2$Cl$_2$] (4.40 g, 11.3 mmol) was added and the mixture refluxed for 5 h. The NaCl formed (662 mg) during the reaction was filtered off and the filtrate was concentrated *in vacuo* to give a creamish solid (5.40 g), which was recrystallised from benzene-*n*-hexane solution (4.48 g, 83%).

*Preparation of [Sn(acac)$_2${ON=C($CH_3$)$C_5H_4N$}$_2$]* **(6)**: To a methanolic solution of the sodium salt of the ligand, prepared in *situ* by the reaction of sodium (272 mg, 11.8 mmol) with 2–acetyl pyridine oxime (1.61 g, 11.8 mmol) in refluxing methanol, a benzene suspension of [Sn(acac)$_2$Cl$_2$] (2.30 g, 5.93 mmol) the mixture was added and refluxed for 5 h. The NaCl formed (691 mg) during the reaction was filtered off and the filtrate was concentrated *in vacuo* to give a pinkish solid (3.47 g), which was recrystallised from benzene-*n*-hexane solution (2.87 g, 82% yield).

*Preparation of [Sn(acac)$_2$[ON=C(Me)Py]Me]* **(13)**: To a methanolic solution of potassium salt of the ligand prepared in *situ* by the reaction of potassium (78 mg, 2.00 mmol) with 2–acetylpyridyl oxime (272 mg, 2.00 mmol) in refluxing methanol, a benzene solution of [Sn(acac)$_2$IMe] (918 mg, 2.00 mmol) was added and the mixture was refluxed for 3 h then dried *in vacuo*. The compound was extracted with benzene from the KI (320 mg, 1.93 mmol) formed during the reaction and the extract was concentrated *in vacuo* to give a pinkish yellow solid (926 mg), which was recrystallised from benzene-*n*-hexane mixture (801 mg, 86% yield).

*Hydrolysis of [Sn(acac)$_2${ON=C(Me)$C_4H_3O$}Cl]* **(4)**: Reaction of sodium (202 mg, 8.8 mmol) dissolved in isopropanol with [Sn(acac)$_2${ON=C(Me)$C_4H_3O$}Cl] (4193 mg, 8.8 mmol) also in isopropanol was carried out. NaCl was filtered off. To this clear solution 5–6 drops of distilled water was added and stirred for 2–days to give a gel. To ensure hydrolysis, the above mixture was refluxed for one hour. $SnO_2$ settled down, the supernatant liquid was decanted and the remaining $SnO_2$ was thoroughly washed with hot acetone–toluene mixture to remove all organic components. The resulting powdered $SnO_2$ was first air dried and then sintered at 300°C and at 650°C for 3 h, consecutively.

All other complexes were prepared by a similar route and the details are summarised in Table 1.

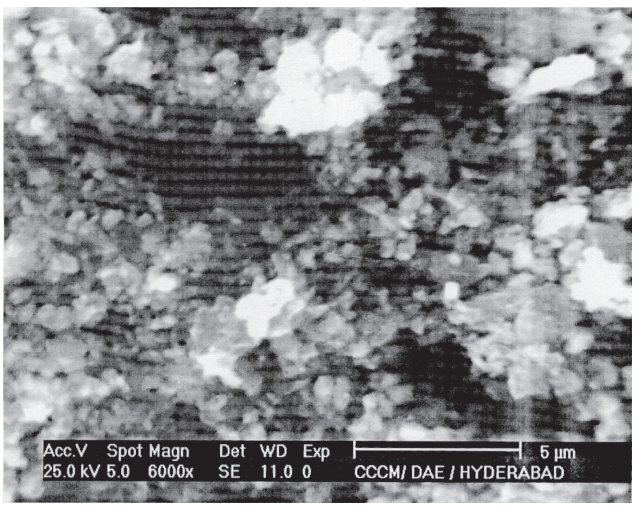


**Fig. 2** Scanning electron micrograph of $SnO_2$ sintered at 650°C temperature.

## Conclusion

In the absence of a single crystal X-ray diffraction analysis of at least one representative compound, it is difficult to comment on the structures of these derivatives, yet spectroscopic investigations together with molecular weight measurements and FAB Mass spectral studies of some of these complexes indicate non-participation of the heteroatom of the ring of the internally functionalised ligand moieties and retention of the *cis*-configuration around the tin atom in these monomeric complexes.

Presence of similar patterns for NMR chemical shifts for bis (acetylacetonato)Sn(L)$_n$Cl$_{2-n}$ (L = Schiff's bases and oximates) and for bis(acetylacetonato)methyloximatotin(IV) complexes, together with the value of the $^{119}$Sn NMR chemical shift in the range of hexa-coordination, suggest a distorted *cis*-octahedral environment in these complexes and the following tentative structure may be proposed for these derivatives:

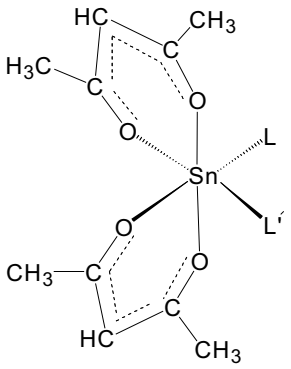


**Fig. 3** Proposed structure of [Sn(acac)$_2$LL′] [where L = L′ = {O(CH$_2$)$_3$N=C(Me)Ar}and {ON =C(R)Ar′}(1, 2, 5–9) and L′ = Cl (**3, 4**) or Me (**10–15**).

Formation of pure $SnO_2$ on complete hydrolysis of one of the compounds indicates the possibility of using these complexes as precursors for metal chalcogenide materials.

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