



Structural and spectral studies of 3-(2-hydroxyphenylimino)-1-phenylbutan-1-one and its diorganotin(IV) complexes

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ABSTRACT

Two diorganotin(IV) complexes of the general formula R₂Sn[Ph(O)C=CH-C(Me)=N-C₆H₄(O)] (R = Ph, **1a**; R = Me, **1b**) have been synthesized from the corresponding diorganotin(IV) dichlorides and the ligand, 3-(2-hydroxyphenylimino)-1-phenylbutan-1-one (**1**) in methanol at room temperature in presence of triethylamine. Both compounds have been characterized by elemental analyses, IR and ¹H, ¹³C, ¹⁵N, ¹¹⁹Sn NMR spectra. The structures of the free ligand and the complexes have been confirmed by single crystal X-ray diffraction. There are three independent molecules in the crystal structure of the ligand **1** and in all three the O-bound proton is transferred to the imine nitrogen and makes an intramolecular N–H···O hydrogen bond with the carbonyl oxygen. In turn this makes an intermolecular hydrogen bond with the phenolic H atom. The crystal structure of **1** is trigonal and a new polymorph; triclinic and monoclinic forms have already been published. In **1a**, the central tin atom adopts distorted trigonal–bipyramidal coordination geometry whereas in dimeric **1b** it is distorted octahedral when including the intermolecular Sn–O(phenolic) bond [2.7998(20) Å]. The δ (¹¹⁹Sn) values for the complexes **1a** and **1b** are –306.6 and –127.9 ppm, respectively, thus indicating penta-coordinated Sn centres in solution.

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1. Introduction

The coordination chemistry of tridentate amino acid-derived Schiff bases [1–3] and related tridentate Schiff bases [4–8] with diorganotin(IV) centres has been discussed widely. Much interest arises from their pharmacological activity [6] where several organotin(IV) complexes have shown antitumour and antiviral activity [8]. Equilibrium and NMR studies on dimethyltin dipeptide complexes have investigated possible mechanisms for the toxic and antitumour activity of Sn complexes [9]. The coordination modes of the ONO donor tridentate *N*-(2-carboxyphenyl)salicylideneimine dianion and *N*-(2-carboxyphenyl)-5'-bromosalicylideneimine dianion towards diorganotin have been reported [10–12] whilst recently, chiral (salicylaldiminato)tin Schiff base complexes were reported with non-linear optical properties [12,13].

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The ligand, 3-(2-hydroxyphenylimino)-1-phenylbutan-1-one, used in this study has less conformational flexibility compared to 4-phenyl-2,4-butanedionebenzoylhydrazone(2-) used previously by us [14] because the former has an extra aromatic ring. We wanted to observe the change in spectral and structural properties arising from the this change in flexibility and ascertain the solid state structure of the ligand and its coordination mode with diorganotin(IV) dichlorides.

This study describes the syntheses and X-ray crystal structures of the ligand, 3-(2-hydroxyphenylimino)-1-phenylbutan-1-one (**1**) and its diorganotin(IV) complexes, Ph₂Sn[Ph(O)C=CH-C(Me)=N-C₆H₄(O)] (**1a**) and Me₂Sn[Ph(O)C=CH-C(Me)=N-C₆H₄(O)] (**1b**). Both the complexes have been structurally characterized in the solid and solution state by crystallography and NMR spectra.

2. Experimental

2.1. Materials

All chemicals and reagents were of reagent grade quality. Diphenyltin dichloride (Aldrich), dimethyltin dichloride (Fluka), benzoyl acetone (Aldrich), *o*-aminophenol and trimethylamine

(S.D. Fine Chemicals, India) were used as received. Methanol (Ranbaxy, India) was dried over CaO and distilled prior to use.

2.2. Physical measurements

Infrared spectra were recorded on a Perkin–Elmer 883 infrared spectrophotometer from 4000 to 200 cm^{-1} as KBr discs and were calibrated with respect to the 1601 cm^{-1} band of polystyrene film. Tin was estimated gravimetrically as SnO_2 after decomposition with concentrated HNO_3 . C, H and N analyses were carried out on a Perkin–Elmer 2400 II elemental analyser. Melting points (uncorrected) were recorded on an electrical heating-coil apparatus.

^1H (400.15 MHz), ^{13}C (100.61 MHz), NMR spectra of ligand **1** were recorded at 300 K in d_6 -DMSO on a Spect 400 spectrometer. ^1H (360.13 MHz), ^{13}C (90.566 MHz), ^{119}Sn (134.3 MHz) and ^{15}N (36.50 MHz) NMR spectra of the complexes (**1a** and **1b**) were recorded at 300 K on a Bruker AMX 360 spectrometer equipped with 5 mm broadband inverse probe and a Silicon Graphics Indy computer. The compounds studied were measured in CDCl_3 and ^1H and ^{13}C chemical shifts were referred to the central signal of the solvent [$\delta = 7.25$ (^1H) and $\delta = 77.00$ (^{13}C)]. The ^{15}N and ^{119}Sn chemical shifts were referred to external nitromethane and tetramethylstannane, respectively ($\delta = 0.0$) placed in a coaxial capillary. Positive values of the chemical shifts denote downfield shifts with respect to standards. Two-dimensional H,H-COSY, gs (gradient selected)-HMQC and gs-HMBC techniques were measured using the standard software provided by Bruker [15].

2.3. X-ray structure analyses of ligand (H_2L) (**1**), and complexes **1a** and **1b**

Single crystals of the ligand, 3-(2-hydroxyphenylimino)-1-phenylbutan-1-one (H_2L) (**1**) was grown from methanol. Crystals of **1a** were obtained from CHCl_3 /petroleum ether (40–60 °C) mixture and crystals of $\text{Me}_2\text{Sn}[\text{Ph}(\text{O})\text{C}=\text{CH}-\text{C}(\text{Me})=\text{N}-\text{C}_6\text{H}_4(\text{O})]$ (**1b**) were obtained from a methanol solution. Diffraction measurements of **1**, **1a** [100.0(2) K on a Bruker AXS X8 CCD] [16] and **1b** [160(2) K on a P4 four circle diffractometer] [17] using graphite-monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073$ Å) were corrected for absorption, however, there was a large peak ($11 \text{ e} \text{ \AA}^{-3}$) 1 Å from Sn for **1a**,

poor crystal quality probably contributed to this but if face indexing was possible this would have improved the absorption correction. The structures were solved and subsequently refined by full-matrix least-squares procedures on F^2 (SHELXTL) [18]. Hydrogen atom positions were calculated assuming ideal geometry and using appropriate riding models, but for **1**, H1A and H8C were located in the difference map and though the coordinates were refined the displacement parameter was treated as riding on the bound O or N atom, respectively. Further details are given in Table 1.

2.4. Synthesis and characterization of the ligand (H_2L) (**1**)

The ligand, 3-(2-hydroxyphenylimino)-1-phenylbutan-1-one (H_2L) has been prepared by refluxing a mixture of benzoyl acetone (1.23 g, 7.58 mmol) and *o*-aminophenol (0.827 g, 7.58 mmol) in methanol (20 ml) for 3 h. Orange crystalline solid appeared on cooling to room temperature. This was filtered, washed with methanol and dried. Single crystals suitable for X-ray crystallography were obtained by cooling a dilute methanolic solution of the compound. Yield: 1.54 g (80%); m.p. 169–170 °C. Anal. Calc. for $\text{C}_{16}\text{H}_{15}\text{NO}_2$ (formula weight 253.29): C, 75.87; H, 5.97; N, 5.53. Found: C, 75.66; H, 6.02; N, 5.57%. ^1H NMR, 400.15 MHz, d_6 -DMSO): 9.99 (s, 1H), 7.89 (t, 2H), 4.43–7.49 (m, 3H), 7.24 (t, 1H), 7.03–7.08 (m, 1H), 6.94 (t, 1H), 6.80–6.84 (m 1H), 6.02 (s, 1H), 3.32 (s, 1H), 2.13 (s, 3H); ^{13}C NMR, 100.61 MHz, d_6 -DMSO): 186.53, 162.57, 150.44, 139.64, 130.86, 128.33, 126.80, 126.48, 125.99, 125.11, 119.13, 115.86, 93.54, 20.08. Probable molecular structures of the ligand are given in Fig. 1.

2.5. Syntheses and characterization of diorganotin(IV) complexes **1a** and **1b**

2.5.1. $\text{Ph}_2\text{Sn}[\text{Ph}(\text{O})\text{C}=\text{CH}-\text{C}(\text{Me})=\text{N}-\text{C}_6\text{H}_4(\text{O})]$ (**1a**)

To a solution of ligand, 3-(2-hydroxyphenylimino)-1-phenylbutan-1-one, (H_2L) (0.633 g, 2.50 mmol) in dry methanol (25 ml) in a 100 ml beaker, triethylamine (0.558 g, 5.52 mmol) was added and the resulting yellow triethylammonium salt solution of the ligand was filtered to remove any insoluble impurities. To this solution, a solution of Ph_2SnCl_2 (0.859 g, 2.50 mmol) in 20 ml of dry methanol was added slowly at room temperature. After 30 min. shiny yellow crystals of compound **1a** appeared. This was filtered,

Table 1

Crystal refinement data for the free ligand (H_2L) (**1**), $\text{Ph}_2\text{Sn}[\text{Ph}(\text{O})\text{C}=\text{CH}-\text{C}(\text{Me})=\text{N}-\text{C}_6\text{H}_4(\text{O})]$ (**1a**) and $\text{Me}_2\text{Sn}[\text{Ph}(\text{O})\text{C}=\text{CH}-\text{C}(\text{Me})=\text{N}-\text{C}_6\text{H}_4(\text{O})]$ (**1b**).

	1	1a	1b
Empirical formula	$\text{C}_{16}\text{H}_{15}\text{NO}_2$	$\text{C}_{28}\text{H}_{23}\text{NO}_2\text{Sn}$	$\text{C}_{18}\text{H}_{19}\text{NO}_2\text{Sn}$
Formula weight	253.29	524.16	400.03
T (K)	100(2)	100(2)	160(2)
Crystal system	Trigonal	Monoclinic	Monoclinic
Space group	$P3_2$	$P2_1/c$	$P2_1/c$
a (Å)	15.8411(6)	13.8311(17)	10.7540(10)
b (Å)	15.8411(6)	15.8066(17)	8.550
c (Å)	14.1075(9)	11.4270(12)	18.5040(10)
α (°)	90	90	90
β (°)	90	113.617(5)	99.800(10)
γ (°)	120	90	90
V (Å ³)	3065.9(3)	2289.0(4)	1676.55(18)
Z	9	4	4
D_{calc} (g cm^{-3})	1.235	1.521	1.585
θ range for data collection (°)	1.48–21.77	2.33–34.35	2.23–25.00
Reflections collected	31931	19442	3934
Independent reflections [R_{int}]	4740 [0.0636]	7917 [0.0999]	2936 [0.0225]
Maximum and minimum transmission	0.9823 and 0.8762	0.796 and 0.582	0.8729 and 0.7083
Data/restraints/parameters	4740/49/525	7917/0/290	2936/0/201
Goodness-of-fit on F^2	1.160	1.054	1.117
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.1020$, $wR_2 = 0.2635$	$R_1 = 0.0874$, $wR_2 = 0.2387$	$R_1 = 0.0245$, $wR_2 = 0.0642$
R indices (all data)	$R_1 = 0.1056$, $wR_2 = 0.2662$	$R_1 = 0.1139$, $wR_2 = 0.2492$	$R_1 = 0.0266$, $wR_2 = 0.0654$
Largest difference peak and hole ($\text{e} \text{ \AA}^{-3}$)	0.442 and -0.467	11.44 (near Sn) and -1.441	0.408 and -0.521

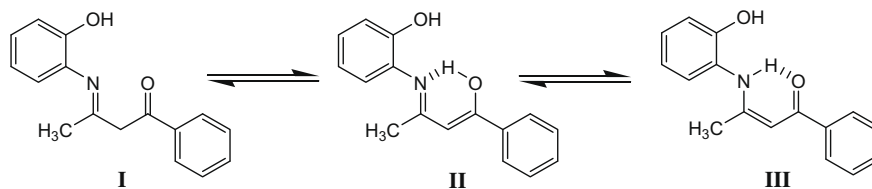


Fig. 1. Structure of ligand (H_2L) used in this study.

washed with petroleum ether (40–60 °C) and dried *in vacuo*. Single crystals suitable for X-ray crystallography were obtained from $CHCl_3$ /petroleum ether (40–60 °C) mixture. Yield: 1.85 g (84%); m.p. 186–187 °C. Anal. Calc. for $C_{28}H_{23}NO_2Sn$ (formula weight 524.16): C, 64.15; H, 4.42; N, 2.67; Sn, 22.64. Found: C, 64.32; H, 4.36; N, 2.73; Sn, 22.38%.

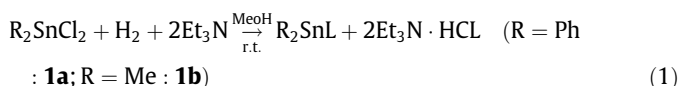
2.5.2. $Me_2Sn[Ph(O)C=CH-C(Me)=N-C_6H_4(O)]$ (**1b**)

To a solution of ligand, 3-(2-hydroxyphenylimino)-1-phenylbutan-1-one, (H_2L) (0.685 g, 2.704 mmol) in dry methanol (25 ml) in a 100 ml beaker, triethylamine (0.601 g, 5.95 mmol) was added and the resulting yellow triethylammonium salt solution of the ligand was filtered to remove any insoluble impurities. To this solution, a solution of Me_2SnCl_2 (0.593 g, 2.70 mmol) in 20 ml of dry methanol was added slowly at room temperature. After 30 min. shiny yellow crystals of compound **1b** appeared. This was filtered, washed with petroleum ether (40–60 °C) and dried *in vacuo*. Single crystals suitable for X-ray crystallography were also obtained from a methanol solution. Yield: 1.32 g (89%); m.p. 135–136 °C. Anal. Calc. for $C_{18}H_{19}NO_2Sn$ (formula weight 400.03): C, 54.04; H, 4.79; N, 3.50; Sn 29.67. Found: C, 53.91; H, 4.71; N, 3.55; Sn, 29.33%.

3. Results and discussion

3.1. Synthesis

The diorganotin(IV) complexes reported here, have been synthesized from diorganotin(IV) dichlorides (Ph_2SnCl_2 or Me_2SnCl_2) and 3-(2-hydroxyphenylimino)-1-phenylbutan-1-one (H_2L) in methanol at room temperature in presence of triethylamine (Eq. (1) below) in 1:1:2 ratio with slight excess of Et_3N . The complexes separated out from the reaction mixture



Although these two compounds have been prepared in methanol at room temperature, the compounds could also be prepared in other solvents such as benzene and toluene. Carrying out the reaction at higher temperature and/or using more concentrated solutions could further reduce reaction times. Both **1a** and **1b** are stable under atmospheric conditions.

3.2. Spectroscopic studies

In the infrared spectrum of the ligand, 3-(2-hydroxyphenylimino)-1-phenylbutan-1-one (H_2L) (**1**) there is one strong band at 1608 cm^{-1} which is assigned to $\nu(C=N)/\nu(C=C)$ stretching mode [19]. IR spectrum also indicates that there is no band corresponding to carbonyl $\nu(C=O)$ vibration. The stretching vibrations for phenolic proton and hydrogen bonded enolic $-OH$ (**II**)/ $N-H$ (**III**) protons (Fig. 1) appear as a strong envelope in the range $3496\text{--}2700\text{ cm}^{-1}$. The $O-H$ bending and $C-O$ stretching vibrations are found around 1138 cm^{-1} and 1330 cm^{-1} , respectively [20]. From infrared spectra, it is very difficult to conclude about its structure

in solid state. The ligand may exist either in imino-en-ol form (**II**) or in amino-en-one form (**III**) in the solid state (Fig. 1). There is a singlet signal at δ 9.99 ppm in 1H NMR spectra in d_6 -DMSO indicates the presence of enolic $-OH$ in solution. So the ligand exists in imino-en-ol form (**II**) in solution. To ascertain the structure of ligand in solid state we performed an X-ray crystallographic study which indicated that the ligand exists in amino-en-one form (**III**) in solid state (*vide infra*). The most significant difference emerges from a comparison of vibrational spectra of the ligand (H_2L) and its diorganotin(IV) complexes (**1a** and **1b**) is the disappearance of

Table 2

1H , ^{13}C , ^{119}Sn and ^{15}N NMR chemical shifts and $^J(^{119}Sn, ^1H)$ and $^J(^{119}Sn, ^{13}C)$ coupling constants for **1a** and **1b** in $CDCl_3$. Coupling constants values (Hz) are given in parentheses.

H/C no.	Compound 1a		Compound 1b	
	δ (1H)	δ (^{13}C)	δ (1H)	δ (^{13}C)
1	–	158.33 (13)	–	158.26 (13.9)
2	7.15	117.85 (12)	6.84	117.41 (7.6)
3	7.15	127.52	7.06	127.19
4	6.66	115.77	6.64	115.44
5	7.05	122.55 (24.1)	7.05	122.53 (22.2)
6	–	132.01 (45.1)	–	132.06 (42.2)
7	–	172.52 (10.9)	–	172.54 (11.8)
8	2.50	25.00 (15.6)	2.44	24.59 (13.2)
9	6.06	98.48 (33.1)	5.96	97.73 (31.6)
10	–	178.63 (22.1)	–	179.08 (20.8)
11	–	138.04	–	138.43
12	8.06	126.88	7.82	126.88
13	7.53	128.57	7.43	128.31
14	7.53	131.24	7.43	130.98
1'	–	138.66 (979.0)	0.73 (77.1)	–1.37 (648.5)
2'	7.94 (77.2)	136.37 (52.5)	–	–
3'	7.37	128.63 (84.9)	–	–
4'	7.37	130.23 (17.3)	–	–
Sn	–	–306.6 ^a	–	–127.9 ^a
N	–	–197.7 ^b	–	–199.5 ^b

^a δ (^{119}Sn).

^b δ (^{15}N).

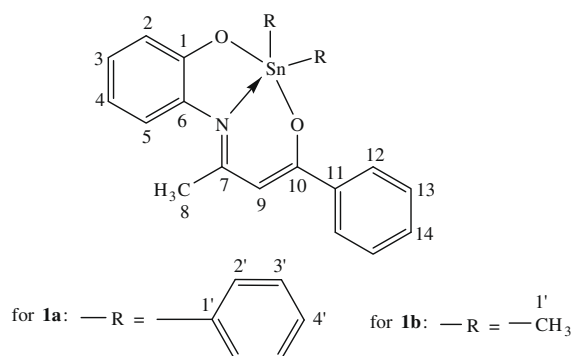


Fig. 2. Constitution of compounds **1a** and **1b** and numbering scheme for NMR assignments.

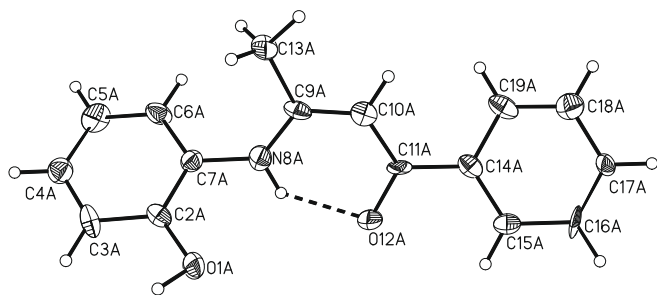


Fig. 3. Perspective view and atom numbering scheme of one of the three independent molecules of the ligand, 3-(2-hydroxyphenylimino)-1-phenylbutan-1-one (**1**) (labelling identical in other molecules apart from the suffix being B or C). Ellipsoids are drawn at the 50% probability level.

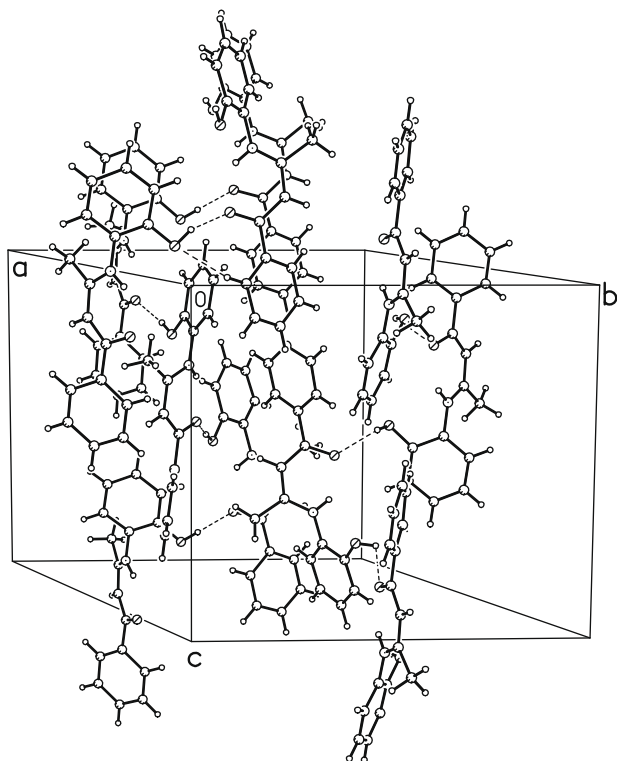


Fig. 4. View of the crystal packing of 3-(2-hydroxyphenylimino)-1-phenylbutan-1-one (**1**) showing intermolecular OH...O hydrogen bonds as dotted lines.

–O–H and N–H band. Strong bands at 1588 cm^{-1} for both **1a** and **1b** are assigned to $\nu(\text{C}=\text{N}=\text{C})$ stretching. This suggests the coordination of imino nitrogen, deprotonated phenolic and enolic oxygen to tin(IV), and therefore the tridentate dibasic nature of the coordinated ligand. X-ray crystallographic analyses of both complexes indicate that the ligand reacted with R_2SnCl_2 through its imino-en-ol form (**II**) (*vide infra*).

The NMR spectra (^1H , ^{13}C , ^{15}N , ^{119}Sn) for the compounds Ph_2SnL (**1a**) and Me_2SnL (**1b**) were measured and analyzed. Two-dimensional NMR spectra were used to assign proton and carbon chemical shifts unambiguously. H,H-COSY, gs(gradient selected)-HMQC and gs-HMBC techniques were also applied [21,22]. The ^{15}N NMR spectra were measured using the gs-HMBC technique (the experiment being optimised for $^nJ(^{15}\text{N}, ^1\text{H}) = 6\text{ Hz}$). The ^1H , ^{13}C , ^{15}N and ^{119}Sn chemical shifts are given in Table 2. We have been able to identify all proton and carbon signals separately for both compounds. For each compound the number of ^1H , ^{13}C and ^{15}N signals observed is in good agreement with the numbering shown in Fig. 2.

For the diphenyltin(IV) compound **1a** detection of $^2J(^{119}\text{Sn}, ^{13}\text{C})$ coupling (22.1 Hz and 10.9 Hz) with C(10) and C(7) carbons, and $^3J(^{119}\text{Sn}, ^{13}\text{C})$ coupling (33.1 Hz) with C(9) indicates the coordination of enolic oxygen and nitrogen atoms of the ligand with tin. The $^2J(^{119}\text{Sn}, ^{13}\text{C})$ coupling (13 Hz) with C(1) carbon and $^3J(^{119}\text{Sn}, ^{13}\text{C})$ coupling (12 Hz) with C(2) indicates the coordination of phenolic oxygen atom of the ligand with tin.

For the dimethyltin(IV) compound **1b** the $^2J(^{119}\text{Sn}, ^{13}\text{C})$ coupling (20.8 Hz and 11.8 Hz) with C(10) and C(7) and $^3J(^{119}\text{Sn}, ^{13}\text{C})$ coupling (31.6 Hz) with C(9) indicates the coordination of enolic oxygen and nitrogen atoms of the ligand with tin. The detection of $^2J(^{119}\text{Sn}, ^{13}\text{C})$ coupling (13.9 Hz) with C(1) and $^3J(^{119}\text{Sn}, ^{13}\text{C})$ coupling (7.6 Hz) with C(2) indicates coordination of the phenolic oxygen atom to tin.

The $^1J(^{119}\text{Sn}, ^{13}\text{C})$ coupling constant of 979.0 Hz with phenyl carbon for **1a** is comparable with reported values for phenyltin compounds [23–25] but lower than the value (993.2 Hz) seen in the hydrazone complex, $\text{Ph}_2\text{Sn}[2\text{-OC}_6\text{H}_4\text{CH}=\text{N}=\text{N}=\text{C}(\text{O})\text{C}_6\text{H}_5]$ [26]. The corresponding $^1J(^{119}\text{Sn}, ^{13}\text{C})$ coupling constant, 648.5 Hz with methyl carbon of **1b** is comparable with that seen for $\text{Me}_2\text{Sn}[2\text{-OC}_6\text{H}_4\text{CH}=\text{N}=\text{N}=\text{C}(\text{O})\text{C}_6\text{H}_5]$ [26].

The C–Sn–C angle in solution can be estimated from $^1J(^{119}\text{Sn}, ^{13}\text{C})$ coupling constants [24]. Using equation the $|^1J(^{119}\text{Sn}, ^{13}\text{C})| = (15.91 \pm 0.72)\theta - (1164 \pm 84)$, the $\text{C}_{\text{phenyl}}\text{-Sn-C}_{\text{phenyl}}$ angle was found to be 134.72° [cf. $120.1(2)^\circ$ in the X-ray study] for compound **1a**. For compound **1b**, the $\text{C}_{\text{methyl}}\text{-Sn-C}_{\text{methyl}}$ angle was calculated using the equation $|^1J(^{119}\text{Sn}, ^{13}\text{C})| = 10.7\theta - 778$ [27] with the $^1J(^{119}\text{Sn}, ^{13}\text{C})$ value of 649.9 Hz giving the angle as 133.31° [cf. 141.72° in the X-ray study]. The $^2J(\text{Sn-CH}_3)$ value of 77.1 Hz is in agreement with values reported (77–81 Hz) for the dimethyltin(IV) complexes with ONO donor tridentate ligands [10,13,26,28,29]. Using Lockhart's equation $[\text{Me-Sn-Me} = 0.0161(^2J(^{119}\text{Sn}, ^1\text{H}))^2 - 1.32(^2J(^{119}\text{Sn}, ^1\text{H})) + 133.4]$ [29], the C–Sn–C angle for **1b** is estimated to ca. 129° , yet this is lower from the value as obtained from X-ray structural study. X-ray structure of **1b** showed that it forms a dimeric structure through a long range coordination phenolic oxygen atom of second molecule. There is an expansion of $\text{C}_{\text{methyl}}\text{-Sn-C}_{\text{methyl}}$ (141.72°) angle to accommodate a sixth coordination site. However, in solution this dimeric structure dissociates to become a discrete five-coordinate tin complex. This contributes to the low $\text{C}_{\text{methyl}}\text{-Sn-C}_{\text{methyl}}$ angle as estimated from NMR in solution.

The ^{119}Sn NMR spectra were recorded in CDCl_3 . The $\delta(^{119}\text{Sn})$ values for **1a** and **1b** are -306.6 and -127.9 ppm, respectively.

Table 3
Selected bond lengths (Å) for the ligand, 3-(2-hydroxyphenylimino)-1-phenylbutan-1-one (H_2L) (**1**).

O(1A)–C(2A)	1.362(13)	O(1B)–C(2B)	1.351(12)	O(1C)–C(2C)	1.341(11)
O(1A)–H(1A)	0.89(13)	O(1B)–H(1B)	0.8400	O(1C)–H(1C)	0.8400
C(7A)–N(8A)	1.427(13)	C(7B)–N(8B)	1.426(12)	C(7C)–N(8C)	1.428(15)
N(8A)–C(9A)	1.324(13)	N(8B)–C(9B)	1.338(13)	N(8C)–C(9C)	1.344(14)
N(8A)–H(8A)	0.88	N(8B)–H(8B)	0.88	N(8C)–H(8C)	0.84(11)
C(9A)–C(10A)	1.348(15)	C(9B)–C(10B)	1.362(15)	C(9C)–C(10C)	1.396(15)
C(11A)–O(12A)	1.305(12)	C(11B)–O(12B)	1.308(12)	C(11C)–O(12C)	1.295(13)

Table 4

Intermolecular hydrogen bonding parameters for the ligand, 3-(2-hydroxyphenylimino)-1-phenylbutan-1-one (H₂L) (**1**) (Å and °).

D–H...A	d(D–H)	d(H...A)	d(D...A)	∠(DHA)
N(8A)–H(8A)...O(12A)	0.88	1.95	2.661(12)	136.3
O(1B)–H(1B)...O(12B)#1	0.84	2.32	2.625(9)	101.9
N(8B)–H(8B)...O(12B)	0.88	1.93	2.648(10)	137.7
O(1C)–H(1C)...O(12C)#2	0.84	1.81	2.643(10)	171.3
N(8C)–H(8C)...O(12C)	0.84(11)	1.97(11)	2.636(12)	135(10)
O(1A)–H(1A)...O(12A)#3	0.89(13)	1.81(13)	2.640(10)	153(11)

Symmetry transformations used to generate equivalent atoms: #1 $-x + y, -x + 1, z + 1/3$; #2 $-y + 1, x - y, z - 1/3$; #3 $-y + 1, x - y + 2, z - 1/3$.

These ¹¹⁹Sn chemical shifts are in the range reported (90–310 Hz) for five-coordinate tin compounds [23,26,27]. These δ (¹¹⁹Sn) values compare well with other diorganotin(IV) complexes containing ONO donor atoms [10,13,14,26]. It is well known that δ (¹¹⁹Sn) val-

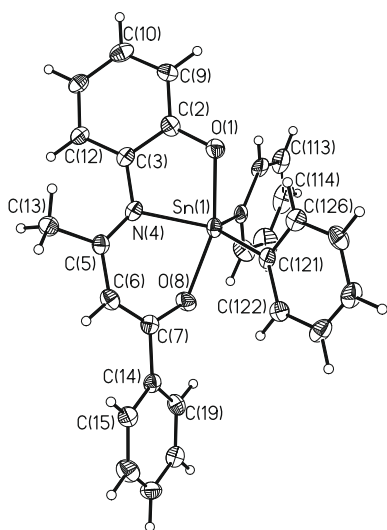


Fig. 5. Perspective view and atom numbering scheme of compound **1a**. Ellipsoids are drawn from 40% probability level.

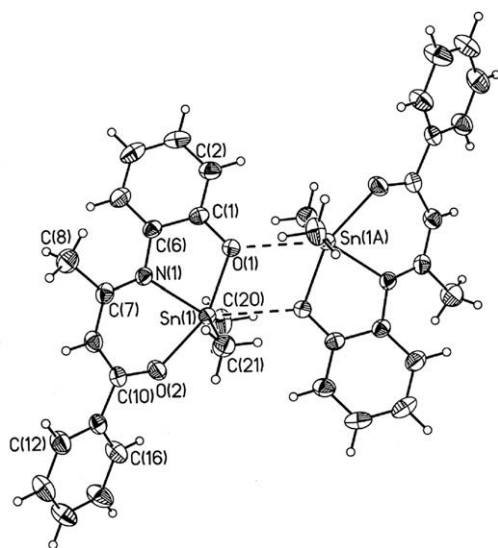


Fig. 6. Perspective view and atom numbering scheme of compound **1b**. Ellipsoids are drawn from 40% probability level. The suffix A denotes the symmetry operation $1 - x, 1 - y, -z$.

ues depend on the coordination number of the tin centre and the ligand bite [25]. This difference in δ (¹¹⁹Sn) value of 178.7 between Ph₂SnL (**1a**) and Me₂SnL (**1b**) is comparable with the differences found for Ph₂SnCl₂ and Me₂SnCl₂ [26] and other diorganotin(IV) complexes having a phenyl or methyl substituent on tin. This indicates that the ligand bite is comparable in both complexes. From ¹¹⁹Sn NMR spectra it is also evident that the five-coordinate solid state structure for **1a** (obtained from X-ray crystallography) is retained in solution. But in case of compound **1b**, the dimeric solid state structure dissociates in solution to form a five-coordinate tin complex.

4. Crystal structures of ligand **1**, Ph₂Sn[Ph(O)CCH-C(Me)N-C₆H₄(O)] (**1a**) and Me₂Sn[Ph(O)CCH-C(Me)N-C₆H₄(O)] (**1b**)

To confirm the actual structure of ligand, 3-(2-hydroxyphenylimino)-1-phenylbutan-1-one (H₂L) (**1**), single crystals X-ray structural study were performed. There are three crystallographically independent molecules in the asymmetric unit. The molecular structure of one molecule along with atom numbering scheme for the ligand is given in Fig. 3, and intermolecular hydrogen bonding and unit cell packing is given in Fig. 4. Selected bond lengths and angles are listed in Table 3. Intermolecular hydrogen bonding parameters are listed in Table 4.

Table 5

Selected bond lengths (Å) and angles (°) for **1a** and **1b**.

Compound 1a	Compound 1b	
Sn(1)–O(1)	2.110(4)	Sn(1)–O(1)
Sn(1)–O(8)	2.115(5)	Sn(1)–O(2)
Sn(1)–C(111)	2.130(6)	Sn(1)–C(20)
Sn(1)–C(121)	2.134(6)	Sn(1)–C(21)
Sn(1)–N(4)	2.140(5)	Sn(1)–N(1)
C(6)–C(7)	1.383(9)	C(7)–C(9)
C(5)–C(6)	1.417(8)	C(9)–C(10)
O(1)–C(2)	1.339(7)	O(1)–C(1)
O(8)–C(7)	1.329(7)	O(2)–C(10)
N(4)–C(5)	1.332(8)	N(1)–C(7)
N(4)–C(3)	1.421(7)	N(1)–C(6)
C(5)–C(13)	1.507(8)	C(7)–C(8)
C(7)–C(14)	1.486(8)	C(10)–C(11)
O(1)–Sn(1)–O(8)	159.31(17)	O(1)–Sn(1)–O(2)
O(1)–Sn(1)–C(111)	96.8(2)	O(1)–Sn(1)–C(20)
O(8)–Sn(1)–C(111)	94.5(2)	O(2)–Sn(1)–C(20)
O(1)–Sn(1)–C(121)	96.5(2)	O(1)–Sn(1)–C(21)
O(8)–Sn(1)–C(121)	92.7(2)	O(2)–Sn(1)–C(21)
C(111)–Sn(1)–C(121)	120.1(2)	C(20)–Sn(1)–C(21)
O(1)–Sn(1)–N(4)	76.85(18)	O(1)–Sn(1)–N(1)
O(8)–Sn(1)–N(4)	82.59(18)	O(2)–Sn(1)–N(1)
C(111)–Sn(1)–N(4)	116.8(2)	C(20)–Sn(1)–N(1)
C(121)–Sn(1)–N(4)	123.1(2)	C(21)–Sn(1)–N(1)
C(2)–O(1)–Sn(1)	110.2(4)	C(1)–O(1)–Sn(1)
O(1)–C(2)–C(3)	118.3(5)	O(1)–C(1)–C(6)
O(1)–C(2)–C(9)	122.6(6)	O(1)–C(1)–C(2)
C(3)–C(2)–C(9)	119.1(6)	O(1)–C(1)–C(6)
C(2)–C(3)–N(4)	114.5(5)	C(1)–C(6)–N(1)
C(12)–C(3)–N(4)	125.0(5)	C(9)–C(7)–N(1)
C(5)–N(4)–C(3)	125.9(5)	C(7)–N(1)–C(6)
C(5)–N(4)–Sn(1)	123.4(4)	C(7)–N(1)–Sn(1)
C(3)–N(4)–Sn(1)	108.8(4)	C(6)–N(1)–Sn(1)
C(7)–O(8)–Sn(1)	121.8(4)	C(10)–O(2)–Sn(1)
N(4)–C(5)–C(6)	122.5(5)	N(1)–C(6)–C(5)
N(4)–C(5)–C(13)	121.4(5)	N(1)–C(7)–C(8)
C(6)–C(5)–C(13)	116.1(5)	C(9)–C(7)–C(8)
C(7)–C(6)–C(5)	126.7(6)	C(10)–C(9)–C(7)
O(8)–C(7)–C(6)	123.6(5)	O(2)–C(10)–C(9)
O(8)–C(7)–C(14)	115.6(5)	O(2)–C(10)–C(11)
C(6)–C(7)–C(14)	120.7(6)	C(9)–C(10)–C(11)
		Sn(1)–O(1A)
		O(1)–Sn(1)–O(1A)
		Sn(1)–O(1A)–Sn(1A)

The X-ray structural investigation of ligand confirms that the enolic proton of imino-en-ol form (**II**, Fig. 1) is abstracted by the imine nitrogen and forms a hydrogen bond with a carbonyl oxygen so the ligand exists in amino-en-one form (**III**, Fig. 1). In all three independent molecules (where labels are given the suffix A, B or C) C11–O12 was chosen as a double bond and C1–O1 a single bond with O1 treated as a hydroxyl oxygen and O12 as a carbonyl O atom on the basis of the C–O bond lengths. The C(9A)–C(10A) distance of 1.348(15) Å is very close to C=C distance of 1.34 Å [30], thereby indicating a double bond. This is only possible if the ligand exist in amino-en-one form (**III** Fig. 1). The angles in the range 118.2(9)–125.6(10)° around C(9A) and C(10A) indicate that two carbons are sp^2 hybridised. The –NH–C(Me)=CH–C(=O)– portion of the ligand is planar in all three independent molecules. These differ in the relative orientations of the two aromatic rings. These are tilted in the range 10.5(7)–27.0(7)° with respect to each other, with molecule A having the largest twist. In comparison with the planar NH–C(Me)=CH–C(=O) bridge, it is the phenol ring which is twisted most of that plane [5.9(7)–64.9(7)°] when compared to the phenyl ring [26.4(7)–42.3(7)°]. In this case the greatest twist out of the plane containing the bridge is found in molecule C, for both rings. There is a chain parallel to the *c* axis propagated by OH...O hydrogen bonds involving the phenolic proton and the carbonyl oxygen atom. Despite the presence of aromatic rings, there is no sign of π - π stacking in the lattice.

A search of the August 2008 version of the Cambridge Structural Database [31,32] revealed that this is a new polymorph of **1**, tri-

clinic and monoclinic ($P2_1/n$) polymorphs have already been determined [33]. In contrast to the hydrogen bonded chain in **1**, the triclinic polymorph exists as centrosymmetric hydrogen bonded dimers, yet it also has more than one molecule in the asymmetric unit ($Z' = 2$). The monoclinic polymorph has only one molecule in the asymmetric unit but its hydrogen bonding motif is similar to **1**, such that it has chains propagated by OH...O hydrogen bonds. The ethanol solvate of **1** [34] retains the OH...O hydrogen bonded chain motif but propagation involves ethanol thereby increasing the chain length.

The molecular structures along with atom numbering schemes for **1a** and **1b** are given in Figs. 5 and 6, respectively. Selected bond lengths and angles for **1a** and **1b** are listed in Table 5.

The X-ray structural investigations of $\text{Ph}_2\text{Sn}[\text{Ph}(\text{O})\text{C}=\text{CH}-\text{C}(\text{Me})=\text{NC}_6\text{H}_4(\text{O})]$ (**1a**) and $\text{Me}_2\text{Sn}[\text{Ph}(\text{O})\text{C}=\text{CH}-\text{C}(\text{Me})=\text{NC}_6\text{H}_4(\text{O})]$ (**1b**) confirm that the ligand, 3-(2-hydroxyphenylimino)-1-phenylbutan-1-one (H_2L) behaves as a tridentate coordinating agent via imino nitrogen, enolic oxygen and phenolic oxygen atoms. The ligand forms six- and five-membered chelate rings. The electron density difference map indicates that no hydrogen is bonded to the nitrogen atoms and that extensive delocalisation takes place. The ligand, 3-(2-hydroxyphenylimino)-1-phenylbutan-1-one (H_2L) is not completely planar in either **1a** or **1b**.

$\text{Ph}_2\text{Sn}[\text{Ph}(\text{O})\text{C}=\text{CH}-\text{C}(\text{Me})=\text{NC}_6\text{H}_4(\text{O})]$ (**1a**) crystallises as discrete molecules whereas **1b** forms centrosymmetric dimers with weak Sn...O bonding interactions [2.7998(20) Å]. The index of trigonality, τ , for describing the continuum between square-pyramidal

Table 6

Comparison of C–Sn–C, O–Sn–O, C–Sn–N, O–Sn–N, O–Sn–C angles of **1a** and **1b** with those in some other diphenyltin(IV) and dimethyltin(IV) complexes derived from ONO donor tridentate Schiff bases.

Complexes	C–Sn–C	O–Sn–O	C–Sn–N	O–Sn–N	O–Sn–C	References
	127.09(8)	157.46(6)	121.70(8) 110.79(8)	84.02(7) 73.75(6)	94.54(8) 97.06(8) 94.01(8) 94.31(9)	Unpublished results
	121.26(15) 127.74(14)	157.19(10) 157.50(11)	114.36(14) 123.94(13) 112.46(12) 119.33(13)	84.38(11) 73.48(11) 84.16(11) 73.70(11)	97.59(15) 94.56(14) 97.38(14) 94.33(14)	[26]
	125.2(4) 122.7(3)	155.83(19) 155.89(19)	121.0(3) 113.2(3) 121.5(3) 115.1(3)	83.7(2) 72.55(19) 83.8(2) 72.66(19)	95.9(3) 97.4(3) 94.6(4) 99.2(3)	[26]
	119.9(3)	159.5(2)	116.7(3) 123.4(3)	76.7(3) 83.0(3)	96.3(3) 95.2(3) 96.9(3) 91.9(3)	This work
	141.72(14)	156.98(8)	111.32(12) 105.56(11)	76.49(18) 80.75(8)	99.76(12) 98.40(11) 85.23(11) 90.93(11)	This work
	120.81(12)	157.7(7)	121.17(11) 117.79(12)	83.84(10) 74.16(10)	93.63(11) 97.14(14) 95.93(13) 94.97(11)	[14]
	125.8(3) 126.9(3)	159.5(2) 158.7(2)	117.0(3) 117.2(3) 123.6(6) 109.2(3)	85.7(3) 73.8(2) 85.6(2) 74.2(2)	92.5(4) 96.9(3) 93.2(4) 96.0(3)	[14]

($\tau = 0$) and trigonal-bipyramidal ($\tau = 1$), defined by Addison and Reedijk [35] is 0.66 for **1a** but 0.25 for **1b** (when omitting the intermolecular Sn...O contact). Distorted trigonal-bipyramidal geometry is found in **1a**, where the source of the distortion is the chelating ligand [O(1)–Sn(1)–O(8), 159.31(17)°]. The trigonal angles involving the Ph groups do not differ significantly from 120° (see Table 5). However, square-pyramidal geometry is dominant over trigonal-bipyramidal geometry in **1b** which is to be expected with the extension of the tin coordination sphere to include a sixth atom, O(1A). This gives distorted octahedral coordination geometry containing a square plane defined by N(1), O(1), O(2) and O(1A) from which Sn(1) lies only 0.0609 (10) Å out of this plane towards N(1).

Owing to the geometric restraints of the ligand the coordination geometry around tin is not regular. The angles subtended at tin(IV) in **1a** by two oxygen atoms are significantly compressed to O(1)–Sn(1)–O(8), 159.31(17)° yet in dimeric **1b** it is compressed slightly more [O(1)–Sn(1)–O(2), 156.98(8)°]. The bite angles in **1a** N(4)–Sn(1)–O(1), 76.85(18)°, O(8)–Sn(1)–N(4), 82.59(18)° are distorted from 90° and are comparable with those found in **1b** (Table 5) and similar compounds [1–5,10–14,26,36–39]. These distortions arise from the rigidity of chelate rings, compounded by the large tin(IV) covalent radius.

The five-membered chelate rings in **1a** and **1b** are nearly planar but the six-membered chelate ring in **1a** possesses a half chair conformation, folded along the O...N vector by 35.5(3)° and the largest deviation from the plane defined by the six atoms is –0.305(5) Å by O(8) and Sn(1) deviates from the plane by the same magnitude. In **1b**, the six-membered chelate ring is very similar where the fold is 31.72(12)° and maximum deviation from this plane is 0.272(1) Å for Sn(1).

The Sn–O bond lengths [2.110(4), 2.115(5) Å] in **1a** and [2.110(2), 2.201(2) Å] **1b** compare well with the reported values for diorganotin(IV) complexes derived from ONO donor tridentate Schiff bases [1–5,10,11,14,26] but are shorter than diorganotin(IV) complexes derived from ONNO donor tetradentate Schiff bases 2.163–2.228 Å [38].

The Sn–N bond lengths of compound **1a** [2.140(5) Å] and compound **1b** [2.176(2) Å] are very close to Ph₂Sn(2-OC₁₀H₆CH=NCH₂COO) [2] and shorter than in Ph₂Sn(2-OC₆H₄CH=NC₆H₄O) [4], Me₂Sn(2-OC₆H₄CH=NC₆H₄O) [5], Me₂Sn(2-OC₆H₄CH=NC₆H₄COO) [10], R₂Sn[2-OC₆H₄CH=N–N=C(O)C₆H₅] (R = Ph, Me) [26] and much shorter than those found in regular six-coordinate diorganotin(IV) complexes [36–39] e.g. 2.266(2)–2.280(2) Å [36].

The Sn–C bond lengths [2.130(6), 2.134(6) Å] of **1a** are within the range of six-coordinate diorganotin(IV) complexes derived from ONNO donor tetradentate Schiff bases e.g. 2.126(8)–2.154(9) Å [37], five-coordinate [1,3,5] and six-coordinated [38] diorganotin(IV) complexes derived from ONO and ONNO donor Schiff bases, respectively. The Sn–C(methyl) bond lengths [2.100(3), 2.116(3) Å] in **1b** are comparable with other reported diorganotin(IV) complexes, [1–5,10–12,26,36–39].

The C–Sn–C and O–Sn–O angles [120.1(2) and 159.31(17)°] for the diphenyl complex **1a** are comparable with the diphenyltin(IV) complex derived from 4-phenyl-2,4-butanedionebenzoylhydrazone(2-) [14]. Although the O–Sn–O angle [156.98(8)°] in **1b** is comparable with dimethyltin(V) complex derived from 4-phenyl-2,4-butanedionebenzoylhydrazone(2-) [159.5(2); 158.7(2)°] [14] the C–Sn–C angle in **1b** is much higher [141.72(14)° cf. 125.8(3) and 126.9(3)°]. The C–Sn–C angle is much greater than that observed in **1a** as well as the value calculated on the basis of ¹J(¹¹⁹Sn, ¹³C) and ²J(¹¹⁹Sn, ¹H) coupling constant values (*vide supra*). A comparison of different angles around tin(IV) of compounds **1a** and **1b** with those other similar compounds having ONO donor atoms have been made in Table 6. It is clear that all angles are comparable except the C–Sn–C angle [141.72(14)°] in **1b** which en-

larges in the solid state to accommodate a phenoxy oxygen atom, thereby increasing the tin coordination number from five to six.

5. Conclusions

The ligand, 3-(2-hydroxyphenylimino)-1-phenylbutan-1-one, has reacted with diorganotin(IV) dichlorides to form two stable compounds **1a** and **1b**. The discrepancy in the C–Sn–C angle of **1a** between the X-ray data and estimation in solution by NMR of **1a** may be due to the relieving of some steric strain of the molecule in solution. The large discrepancy between C–Sn–C angle from X-ray data and estimation in solution of **1b** was due to dissociation of the dimeric structure to form a monomeric metal complex. However, ¹¹⁹Sn chemical shift values clearly indicate that the five-coordinate structure is retained in solution for both compounds.

6. Supplementary material

CCDC 686749, 634860 and 634861 contain the supplementary crystallographic data for **1**, **1a** and **1b**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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References

- [1] F.E. Smith, R.C. Hynes, T.T. Ang, L.E. Khoo, G. Eng, Can. J. Chem. 70 (1992) 1114.
- [2] L.E. Khoo, Y. Xu, N.K. Goh, L.S. Chia, L.L. Koh, Polyhedron 16 (1997) 573. and references therein.
- [3] D. Dakternieks, T.S. Basu Baul, S. Dutta, E.R.T. Tiekink, Organometallics 17 (1998) 3058.
- [4] H. Preut, F. Huber, R. Barbieri, N. Bertazzi, Z. Anorg. Allg. Chem. 423 (1976) 75.
- [5] H. Preut, F. Huber, H.J. Haupt, R. Cefalu, R. Barbieri, Z. Anorg. Allg. Chem. 410 (1974) 88.
- [6] M.F. Iskander, L. Labib, M.M.Z. Nour El-Din, M. Tawfik, Polyhedron 8 (1989) 2755.
- [7] T.E. Khalil, L. Labib, M.F. Iskander, L.S. Refaat, Polyhedron 13 (1994) 2569.
- [8] A.J. Crowe, M. Gielen (Eds.), Metal Based Antitumour Drugs, vol. 1, Freund, London, 1989, p. 103; L. Pellerito, L. Nagy, Coord. Chem. Rev. 224 (2002) 111.
- [9] K. Gajda-Schranz, A. Jancsó, C. Pettinari, T. Gajda, Dalton Trans. (2003) 2912.
- [10] D.K. Dey, M.K. Saha, M. Gielen, M. Kemmer, M. Biesemans, R. Willem, V. Gramlich, S. Mitra, J. Organomet. Chem. 590 (1999) 88.
- [11] G.M. Rosair, D.K. Dey, B. Samanta, S. Mitra, Acta Crystallogr. C 58 (2002) m266.
- [12] H.D. Yin, Q-B Wang, S-C Xue, J. Organomet. Chem. 690 (2005) 435.
- [13] J.M. Rivera, H. Reyes, A. Cortés, R. Santillan, P.G. Lacroix, C. Lepetit, K. Nakatani, N. Farfán, Chem. Mater. 18 (2006) 1174.
- [14] D.K. Dey, A. Lycka, S. Mitra, G.M. Rosair, J. Organomet. Chem. 689 (2004) 88.
- [15] XWINNMR, Version 3.5, Bruker-Biospin, Rheinstetten, Germany, 2004.
- [16] Bruker AXS APEX2 Version 2.1, Madison Wisconsin, USA 2006.
- [17] XSCANS Siemens, Madison Wisconsin, USA, 1995.
- [18] G.M. Sheldrick, SHELXL Program for the Refinement of Crystal Structures from Diffraction Data, Göttingen, Germany, 1997.
- [19] K. Nakamoto, Infrared Spectra of Inorganic and Co-ordination Compounds, 3rd ed., Wiley, New York, 1978.
- [20] L.J. Bellamy, Advances of Infrared Group Frequencies, Methuen and Co. Ltd., London, 1972.
- [21] W. Hull, in: W.R. Croasmun, R.M.K. Carlson (Eds.), Two-Dimensional NMR Spectroscopy. Application for Chemists and Biochemists, 2nd ed., VCH Publishers, New York, 1994 (Chapter 2).
- [22] S. Braun, H.-O. Kalinowski, S. Berger, 150 and More Basic NMR Experiments, 2nd ed., Wiley-VCH, Weinheim, 1998.
- [23] J. Holecěk, K. Handlír, M. Nádvořník, A. Lyčka, Z. Chem. 30 (1990) 265.
- [24] J. Holecěk, A. Lyčka, Inorg. Chim. Acta 118 (1986) L15.
- [25] J. Holecěk, M. Nádvořník, K. Handlír, A. Lyčka, J. Organomet. Chem. 241 (1983) 177.

- [26] D.K. Dey, B. Samanta, A. Lycka, L. Dahlenburg, Z. Naturforsch. 58b (2003) 336, and references therein.
- [27] T.P. Lockhart, F. Davidson, Organometallics 6 (1987) 2471.
- [28] K. Kawakami, T. Tanaka, J. Organomet. Chem. 49 (1973) 409.
- [29] T.P. Lockhart, W.F. Manders, Inorg. Chem. 25 (1986) 892.
- [30] F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen, R. Taylor, J. Chem. Soc., Perkin Trans. 2 (1987) S1.
- [31] D.A. Fletcher, R.F. McMeeking, D. Parkin, J. Chem. Inf. Comput. Sci. 36 (1996) 746.
- [32] F.H. Allen, Acta Crystallogr. B 58 (2002) 380.
- [33] T. Glowiak, J.M. Sobczak, J. Crystallogr. Spectrosc. Res. 22 (1992) 673.
- [34] Y.-C. Shi, Acta Crystallogr., Sect. E 61 (2005) 1130.
- [35] A.W. Addison, T.N. Rao, J. Reedijk, J. Van Rijn, G.C. Verschoor, J. Chem. Soc., Dalton Trans. (1984) 1349.
- [36] D.K. Dey, M.K. Saha, N. Bhartiya, R.K. Bansal, G. Rosair, S. Mitra, Polyhedron 18 (1999) 2687. and references therein.
- [37] D.K. Dey, M.K. Saha, S. Mitra, R.K. Bansal, L. Dahlenburg, Chem. Lett. 10 (2000) 1190.
- [38] S.G. Teoh, G.Y. Yeap, C.C. Loh, L.W. Foong, S.B. Teo, H.K. Fun, Polyhedron 16 (1997) 2213.
- [39] M. Calligaris, G. Nardin, L. Randaccio, J. Chem. Soc., Dalton Trans. (1972) 2003.
- [40] F.H. Allen, O. Kennard, Chem. Des. Autom. News 8 (1993) 1 and 31.