APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 7, 39-43 (1993)

Diorganotin(IV) complexes of indole 3-acetic acid

G K Sandhu and N Sharma
Department of Chemistry, Guru Nanak Dev University, Amritsar 143 005, India

Alkyl derivatives of indole 3-acetic acid (IAA) have been prepared and are suitable for investigating steric substituent effects on hormonal activity without major interference from electronic effects. Triorganotin(IV) derivatives of indole 3-acetic acid and *N*-methylindole 3-acetic acid have been reported to act as insecticidal, fungicidal and bactericidal agents. Me_3SnIAA is more active as a biocide than Cy_3SnIAA. The activity of these two compounds may be due to the fact that four-coordinated tin monomers or five-coordinated tin polymers are often more active than chelated five-coordinated tin species because these readily undergo hydrolysis to give $R_3Sn(H_2O^+)_2$ species. The ligand affects the rate of formation of the ligand-free active organotin entity. Biocidal activity is expected from diorganotin(IV) pentacoordinated complexes of indole 3-acetic acid in the present case due to (i) the activity of pentacoordinated organotin species, (ii) the presence of an —NH moiety in the complexes, which is an active site for binding. The NH moiety may be deprotonated and nitrogen may coordinate with metal ions present in the physiological systems and thus destroy the activity of enzymes.

Keywords: Diorganotin(IV), indole 3-acetic acid, biocidal activity

INTRODUCTION

Only a few studies on triorganotin(IV) derivatives of indole 3-acetic acid (Fig. 1) and their biocidal activity have been reported.[1-4] A few indole thiocarbamates of diorganotin and triorganotin(IV) have also been synthesized and characterized.[5]

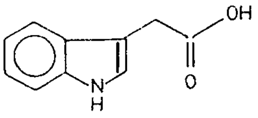


Figure 1 Indole 3-acetic cid (IAA).

Our interest in the present work is mainly in the synthesis and mode of bonding of functional groups such as COO and ring NH present in indole 3-acetic acid (IAA).

EXPERIMENTAL

Materials

Dimethyl, di-n-butyl and di-n-octyltin oxides were obtained from Alpha Products (USA). Diethyl- and di-n-propyl-tin oxides were prepared by a reported method.[6] Indole 3-acetic acid was obtained from Aldrich Chemicals and used without further purification.

Preparation of sodium salt

Indole 3-acetic acid (0.1 mol) and sodium hydroxide (0.1 mol) were dissolved in distilled ethanol (95%, 50 cm^3) and refluxed until a clear solution was obtained (pH 7–7.2). After removing the excess of ethanol by distillation, dry benzene (20 cm^3) was added to remove water azeotropically using a Dean and Stark trap. The sodium salt separated, was filtered and was washed several times with dry acetone and ether and dried in vacuum.

Preparation of ethyl ester

The ester of indole 3-acetic acid was prepared by refluxing 0.1 mol of the acid in absolute ethanol (20 cm^3) and 2–3 drops of sulphuric acid for 3 h. The solution was filtered and poured into excess water. Finally the ester was extracted with ether and dried over anhydrous sodium sulphate.

Preparation of complexes

Indole 3-acetic acid (0.1 mol) was dissolved in a mixture of dry benzene (30 cm^3) and absolute ethanol (10 cm^3) and dialkyltin(IV) oxide (0.1 mol) was added to it. The reaction mixture was then refluxed azeotropically over a water bath. Dialkyltin(IV) oxide went into solution within 10–15 min to give a clear solution.

0268-2605/93/010039-05 $07.50

Received 29 June 1992
Accepted 29 June 1992

Table 1 Physical and analytical data of diorganotin(IV) complexes of indole 3-acetic acid

No.	Complex[a]	Colour	Yield (%)	M.p. (°C)	Analysis (%): Found (Calcd) C	H	N	Sn
1	$[Me_2SnIAA]_2O$	Light pink	87	250–252	37.21 (37.40)	4.39 (4.23)	3.50 (4.23)	34.81 (35.89)
2	$[Et_2SnIAA]_2O$	Brown	90	235–237	45.62 (45.62)	5.05 (5.01)	3.61 (3.90)	32.55 (33.09)
3	$[nPr_2SnIAA]_2O$	Brown	85	229–230	48.75 (49.65)	5.94 (5.68)	3.47 (3.62)	30.12 (30.69)
4	$[nBu_2SnIAA]_2O$	Brown	96	220–222	50.32 (52.00)	6.41 (6.26)	2.69 (3.37)	27.23 (28.62)
5	$[nOct_2SnIAA]_2O$	Brown	94	180–181	57.62 (59.31)	8.23 (7.98)	2.21 (2.66)	21.75 (22.86)

[a] Abbreviation: IAA, Indole 3-acetic acid. Complexes are crystallysed from absolute ethanol.

Refluxing was further continued for 3–4 h and the contents were then cooled and solvent was removed under reduced pressure. A light pink solid was obtained in the case of dimethyl complex, whereas all the other complexes were brown in colour. Complexes were recrystallized from absolute ethanol.

Physical measurements

Elemental analyses of complexes were carried out by the Microanalytical Service, R.S.I.C., Panjab University, Chandigarh. Tin was estimated as SnO_2. Infrared spectra of compounds were recorded on a Perkin–Elmer 1430 spectrophotometer in the 4000–400 cm^{-1} range as Nujol mulls. The ^1H and ^{13}C NMR spectra were recorded on a Bruker AC 200 MHz spectrometer using TMS as an internal standard.

RESULTS AND DISCUSSION

Diorganotin(IV) derivatives of indole 3-acetic acid have been synthesized by reacting IAA with organotin oxide in a 1:1 molar ratio (Eqn [1]).

$$2R_2SnO + 2IAA \rightarrow (R_2SnIAA)_2O + H_2O \quad [1]$$

Reactions were also performed in a 1:2 (metal: ligand) molar ratio using dibutyl- and dioctyl-tin oxides but the complexes formed in a 1:1 stoichiometry; this was confirmed by elemental analysis, IR, ^1H and ^{13}C NMR spectroscopy. All the complexes have been recrystallized from absolute ethanol. The dioctyltin(IV) complex (**5**) is more soluble in benzene, chloroform, carbontetrachloride, and ethylacetate than the other complexes, **1–4**, which are partially soluble in most of these solvents (Table 1)).

Table 2 Infrared spectral data (Nujol, 4000–400 cm^{-1}) of diorganotin(IV) complexes of indole 3-acetic acid

No.	Complex[a]	ν(NH)	$\nu(COO)_{asym}$	$\nu(COO)_{sym}$	$\Delta\nu$	ν(Sn—O—Sn)	ν(Sn—C)	ν(Sn—O)
	IAA	3270m	1700vs	1230s	470	—	—	—
	IAA, Na	3395s	1570s	1385s	185	—	—	—
	IAAEt	3415s	1725s	1175s	550	—	—	—
1	$[Me_2SnIAA]_2O$	3405s	1570s	1380s	190	645m	605sh 570m	500m
2	$[Et_2SnIAA]_2O$	3300b, s	1625s, 1560s	1225s 1380vs	400 180	645m	605sh 540w	490s 450w
3	$[nPr_2SnIAA]_2O$	3340s	1625s 1580sh	1225s 1380s	400 200	625m	605w 555m	480w 460w
4	$[nBu_2SnIAA]_2O$	3340s	1620s 1580sh	1230s 1380s	390 200	625s	605m 550m	485w 460w
5	$[nOct_2SnIAA]_2O$	3250b	1665s 1560sh	1240s 1375s	365 185	630s	600w 570sh	465m

[a] Abbreviations: IAANa, sodium salt; IAAEt, ester.

Table 3 ^{1}H NMR data (scale, δ ppm) of diorganotin(IV) complexes of indole 3-acetic acid

No.	Complex	Indole protons	—NH—	—CH$_2$—	Sn—R	
					—CH$_2$—	CH$_3$
	IAA[a]	7.57–7.02 (m, 10H)	6.24 (s, 1H)	3.72 (s, 2H)	—	—
	IAAEt[b]	8.35–7.21 (m, 10H)	6.93 (s, 1H)	3.91 (s, 2H)	—	—
1	[Me$_2$SnIAA]$_2$O[a]	7.67–7.32 (m, 10H)	6.79 (s, 2H)	3.52 (s, 4H)	—	0.32 (s, 6H) 0.53 (s, 6H)
2	[Et$_2$SnIAA]$_2$O[a]	7.65–7.00 (m, 12H)	—[c]	3.60 (s, 4H)	1.19–0.83 (m, 8H)	0.81–0.74 (t, 12H)
3	[nPr$_2$SnIAA]$_2$O[a]	7.53–7.02 (m, 12H)	—[c]	3.58 (s, 4H)	1.55–1.21 (m, 16H)	0.88–0.73 (t, 12H)
4	[nBu$_2$SnIAA]$_2$O[b]	7.52–7.01 (m, 10H)	6.89 (s, 2H)	3.56 (s, 4H)	1.50–1.00 (m, 24H)	0.84–0.74 (t, 12H)
5	[nOct$_2$SnIAA]$_2$O[b]	7.56–7.11 (m, 10H)	6.66 (s, 2H)	3.54 (s, 4H)	1.51–1.23 (m, 56H)	0.81–0.71 (t, 12H)

Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet. Coupling constants not recorded.
[a] Spectra recorded in CDCl$_3$ + 2 drops DMSO-d$_6$. [b] Spectra recorded in CDCl$_3$. [c] NH protons overlapped by indole protons.

Infrared spectra

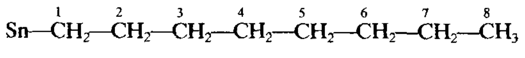
Infrared data for the ligand (IAA), the sodium salt of the ligand (IAANa), the ligand ester (IAAEt) and the complexes have been recorded in 4000–400 cm^{-1} as Nujol mulls (Table 2). A broad band in the range 2900–2600 cm^{-1} present in the IAA and IAAEt spectra is absent in the case of the complexes, indicating deprotonation of the carboxyl group. The spectra of complexes **2–5** show ν(NH) at a lower position compared with that in IAAEt. This ν(NH) lowering may be the result of (1) coordination of the amino group to tin(IV) to form Sn–N, (2) intramolecular or weak intermolecular N—H···O=C bonding. Coordination of nitrogen to tin is ruled out because the nitrogen atom binds to metal only when nitrogen is deprotonated on complex formation. Intramolecular or weak intermolecular N—H···O=C bonding is supported by the ν(NH) lowering[7] which is accompanied by a lowering of $\nu(\mathrm{COO})_{\mathrm{asym}}$ since both the NH and O=C moieties are involved in weak intramolecular hydrogen bonding whereas in complex **1**, ν(NH) in the IAAEt range reveals that the amino nitrogen neither coordinates to tin nor is involved in hydrogen bonding.

The COO modes provide a reasonably good indication to ascertain the nature of the bonding patterns of carboxylates. The $\Delta\nu$ value, $[\Delta\nu = \nu(\mathrm{COO})_{\mathrm{asym}} - \nu(\mathrm{COO})_{\mathrm{sym}}]$ is lower in the spectra of complexes **1–5** compared with that in IAANa and IAAEt. The presence of two values for $\nu(\mathrm{COO})_{\mathrm{asym}}$ and $\nu(\mathrm{COO})_{\mathrm{sym}}$ in complexes **2–5** indicates that the two carboxylates are bonded asymmetrically to tin.[8] The $\Delta\nu$ values, being in the range of IAANa and IAAEt, clearly indicate that one carboxylate is bidentate in nature while the other carboxylate is bonded to tin(IV) in a unidentate manner.[8] Symmetric bidentate bonding of carboxylate groups in complex **1** is confirmed by the presence of only one value of $\nu(\mathrm{COO})_{\mathrm{asym}}$ and $\nu(\mathrm{COO})_{\mathrm{sym}}$ in the IAANa range.[8] The presence of two Sn–C absorption bands in the 600–500 cm^{-1} region reveals a non-linear configuration of the R$_2$Sn moiety.[7] A medium-intensity band in the 650–625 cm^{-1} region is attributed to ν(Sn—O—Sn), which indicates a Sn—O—Sn bridged structure for these complexes.[8] Absorption bands in the 500–400 cm^{-1} region are assigned to stretching frequencies of Sn–O bonds.[8]

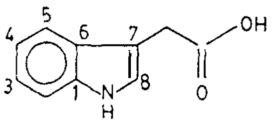
^{1}H NMR spectra

The ^{1}H NMR spectra of soluble complex **1** and IAAEt have been recorded in CDCl$_3$ and those of complexes **1–4** and IAA have been recorded in CDCl$_3$ plus two drops of DMSO-d$_6$ (Table 3, δ ppm). In the spectra of IAA, the acidic proton is not detectable, probably due to the formation of a complex DMSO-d$_6$–HIAA. The N-H signal in complexes **1**, **4** and **5**) is shifted upfield compared with that in IAAEt whereas in complexes **2**

Table 4 ^{13}C NMR chemical shift ($CDCl_3$, DMSO; δ, ppm) of diorganotin(IV) complexes of indole-3-acetic acid



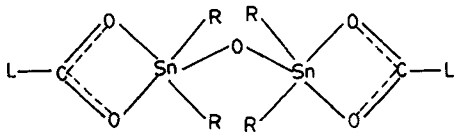
$$\mathrm{Sn{-}\overset{1}{C}H_2{-}\overset{2}{C}H_2{-}\overset{3}{C}H_2{-}\overset{4}{C}H_2{-}\overset{5}{C}H_2{-}\overset{6}{C}H_2{-}\overset{7}{C}H_2{-}\overset{8}{C}H_3}$$



IAA

No.	Complex	Indole carbons										Sn—R							
		C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	COO	CH_2	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8
	IAAH	136.00	118.82	118.46	111.15	107.85	123.25	127.04	121.35	174.23	31.02	—	—	—	—	—	—	—	—
	IAAEt	136.07	119.42	118.69	111.35	107.83	123.39	127.05	121.92	172.52	31.40	—	—	—	—	—	—	—	—
1	$[(Me_2SnIAA]_2O^a$	135.23	117.52	—	110.28	108.12	122.16	126.33	120.10	176.36	32.32	4.73 6.44	—	—	—	—	—	—	—
2	$[Et_2SnIAA]_2O^a$	135.45	117.78	—	110.51	108.32	122.44	126.58	120.43	177.12	32.27	19.48	8.65	—	—	—	—	—	—
3	$[nPr_2SnIAA]_2O^a$	135.78	118.18	—	110.81	108.81	122.68	126.87	120.83	177.00	32.38	29.05	18.20	17.67	—	—	—	—	—
4	$[nBu_2SnIAA]_2O^a$	135.69	118.19	118.07	110.75	108.74	122.62	126.77	120.80	177.10	32.87	27.33	26.46	25.91	12.91	—	—	—	—
5	$[nOct_2SnIAA]_2O^b$	136.09	119.42	118.93	111.29	110.19	123.00	127.39	122.00	177.62	33.96	32.02	31.98	29.30	28.57	27.09	25.59	22.76	14.12

[a] Spectra were recorded in $CDCl_3$ + 2 drops DMSO-d_6; [b] Spectra were recorded in $CDCl_3$.



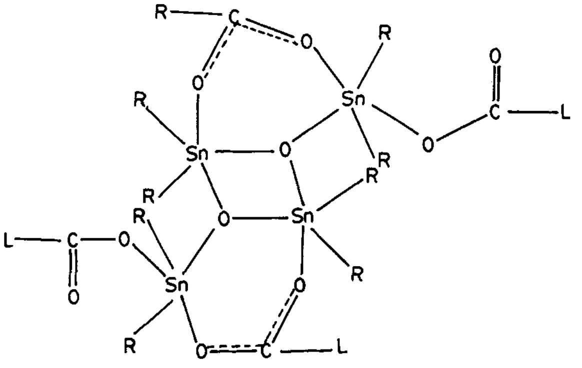
Complex **1**: R = CH_3

Figure 2

and **3** it is obscured by indole protons. This observation clearly indicates the non-participation of amino nitrogen in bonding to tin(IV). Indole protons remain in the same position in the complexes compared with those in IAA which again suggests that an amino nitrogen is not involved in bonding to tin(IV). The —CH_2— protons next to the carboxylate group in the complexes undergo a downfield shift which reveals the participation of carboxylate in bonding to tin(IV). Two singlets are observed in complex **1** due to methyl groups, indicating the non-linear or non-equivalent nature of methyl groups. A triplet is observed due to methyl protons and a multiplet is seen due to the alkyl group —CH_2— attached directly to tin(IV) in complexes **2**–**5**. However, the number of protons calculated from the integration curve are equal to those calculated from the molecular formula of the complexes, which confirms the complexation.

^{13}C NMR spectra

The ^{13}C NMR spectra of soluble complex **1** and IAAEt have been recorded in $CDCl_3$ and those of complexes **1**–**4** and ligand (IAA) have been recorded in $CDCl_3$ plus two drops of DMSO-d_6 (Table 4; δ ppm).



Complex **2**: R = Et
3: R = n-Pr
4: R = n-Bu
5: R = n-C_8H_{17}

Figure 3

The number of signals found corresponds with the presence of magnetically non-equivalent carbon atoms. The position of the indole moiety carbon signals, especially the carbons directly bonded to amino nitrogen (C_1 and C_8, Table 4), remains unperturbed as compared with that in IAA, clearly indicating that NH nitrogen is not involved in bonding to tin(IV). The downfield shift of carboxylate carbon in the complexes as compared with that in IAA and IAAEt indicates the participation of the carboxylate group in coordination to tin(IV). The position of the CH_2 carbon signal directly bonded to carboxylate also undergoes a downfield shift which further confirms the participation of a carboxylate group in coordination to tin(IV). The identification of alkyl carbons in all the complexes confirms complexation.

CONCLUSIONS

Five-coordinated trigonal bipyramidal geometry is assigned to complex **1** with bidentate carboxylate groups and a Sn—O—Sn bridge (Fig. 2). The structure of complexes **2**–**5** features two bidentate bridging and two monodentate carboxylate ligands and both tin atoms are in trigonal bipyramidal geometries (Fig. 3).[8] These structures, with one bridging tricoordinated oxygen and two axial R groups, have recently been confirmed by X-ray structure determination of $(^nR_2SnO_2C\,CH_2SC_6H_5)_2O$ (R = n-Pr, n-Bu).[8]

Acknowledgement One of us (NS) is grateful to the Council of Scientific and Industrial Research, India, for financial assistance.

REFERENCES

1. Nebojsa, I, Branimir, K, Volker, M, Drazen, V T and Eszter, G B *Croat. Chem. Acta*, 1991, 64(1): 79
2. Molloy, K C, Purcell, T G, Hann, E, Schumann, H and Zuckerman, J J *Organometallics*, 1986, 5(1): 85
3. Molloy, K C, Purcell, T G, Mahon, M F and Minshall, E *Appl. Organomet. Chem.*, 1987, 1(6): 507
4. Blunden, S J, Smith, P J and Sugavanam, B *Pestic. Sci.*, 1984, 15: 253
5. Gupta, V D, Gupta, V K and Srivastava, D K *Indian J. Chem.* 1986, 25A(2): 162
6. Zakharkin, L I, Okhobystin, O Y and Strunin, B N *Zh. Prikl. Khim.* 1963, 36(9): 2034 and 1964, 60: 3002
7. Sandhu, G K and Kaur, G *Main Group Met. Chem.*, 1990, 13(3): 149
8. Sandhu, G K, Sharma, N and Tiekink, E R T *J. Organomet. Chem.*, 1989, 371: C_1–C_3 and 1991, 403: 119