Journal of Organometallic Chemistry, 388 (1990) 63–70
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20615

Preparation, IR and ^{1}H NMR spectral studies of triorganotin(IV) complexes of *N*-benzoylglycine and *N*-benzoylglycylglycine

G.K. Sandhu and G. Kaur

Department of Chemistry, Guru Nanak Dev University, Amritsar–143005 (India)

(Received November 29th, 1989)

Abstract

The triorganotin(IV) derivatives of *N*-benzoylglycine (HAA); R_3SnAA and *N*-benzoylglycylglycine (HDP), R_3SnDP (R = methyl, n-propyl, n-butyl, phenyl, cyclohexyl, respectively) have been prepared from the triorganotin(IV) chlorides R_3SnCl and the appropriate sodium salts of the *N*-benzoylamino acids. *N*-Benzoylglycine complexes have penta-coordinate trigonal bipyramidal structure of tin(IV) with chelating bidentate carboxylate group in the solids and in chloroform solution. *N*-Benzoylglycylglycine complexes are penta-coordinate and are polymers in the solid state. The tin atom in triorganotin(IV) groups R_3Sn are coordinated by the unidentate carboxylic group and by the oxygen atoms of the amidocarbonyl group of the adjacent molecule. The complexes are monomers in non-coordinating solvents ($CHCl_3$, benzene and nitrobenzene). The HAA complexes retain the penta-coordinate geometry in solution, which is in contrast to the previously reported complexes with *N*-benzoyl-, *N*-acetyl- and *N*-formylamino acids and the corresponding dipeptides which are tetrahedral [1–3].

Introduction

Triorganotin(IV) complexes are biologically more active than diorgano- and monoorganotin(IV) complexes, owing to their ability to bind protein [4–6]. In cat haemoglobin, both cysteine and histidine residues are associated with the triorganotin(IV) moiety [6,7]. On the basis of the ambient temperature ^{119m}Sn Mössbauer spectrum the trimethyltin(IV) glycylglycinate was assigned a penta-coordinated, bridged polymeric trigonal bipyramidal geometry whereas tricyclohexyl tin(IV)-glycylglycinate has a hexa-coordinated arrangement with octahedral structure [8,9]. Up to now the only diorganotin(IV) derivatives of N-protected amino acids [10,11] and N-protected dipeptides [12] have previously been reported. Tributyl- and triphenyltin(IV) benzoyl glycinates with trigonal bipyramidal structures have also

been reported previously [13]. We report here the synthesis and characterization of triorganotin complexes of *N*-benzoylglycine and *N*-benzoylglycylglycine.

Experimental

Melting points were determined in open capillaries and are uncorrected. Elemental analysis were carried out by the Regional Sophisticated Instrumentation Centre, Punjab University, Chandigarh. Tin was estimated gravimetrically as SnO_2. Molecular weights were determined cryoscopically in benzene and nitrobenzene. IR spectra were recorded on a Pye-Unicam P321 instrument, in KBr discs and chloroform solutions. ^1H NMR spectra were recorded on JEOL PMX 6051 spectrometer using TMS as internal standard.

Published procedures were used to prepare tripropyltin(IV) [14], triphenyltin(IV) [15], *N*-benzoylglycine [14] and *N*-benzoylglycylglycine [16,17]. Trimethyltin(IV), tri-n-butyltin(IV) and tricyclohexyltin(IV) chlorides were obtained from Alfa Products U.S.A. and used as received.

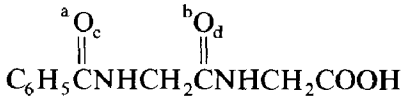
Preparation of complexes

To a solution of the sodium salt of *N*-benzoylglycine (5 mmol) in 95.50% ethyl alcohol (10 cm^3) and benzene (30 cm^3)(*N*-benzoylglycine is not soluble in absolute ethylalcohol) and that of *N*-benzoylglycylglycine (5 mmol) in a dry solvent mixture of benzene (30 cm^3) and absolute ethyl alcohol (10 cm^3) was added trialkyltin(IV) chloride (5 mmol). The reaction mixture was refluxed azeotropically over a water bath using Dean and Stark trap. Reflux was continued for 6–8 hours during which a white solid (sodium chloride) separated. The contents were then cooled and filtered under vacuum. To the filtrate was added benzene (30 cm^3) and the cycle of refluxing and filtration was repeated two or three times until all of the sodium chloride had separated. Then all the solvent was removed by distillation under reduced pressure to leave a solid/syrup. n-Tributyltin(IV), tri-n-propyltin(IV) complexes of the *N*-benzoylglycylglycine were syrups and washed with petroleum ether (40–60 °C). Tributyltin(IV) complexes solidify after about four months in a vacuum desiccator. Tripropyltin(IV) complex is a liquid. Trimethyltin(IV) derivative is a flocculent compound. Triphenyltin(IV) complex was recrystallized from absolute methyl alcohol whereas the tricyclohexyltin(IV) complex, was recrystallized from hot benzene. Tricyclohexyltin(IV) *N*-benzoylglycinate is recrystallized from absolute ethyl alcohol.

Results and discussion

The trialkyltin(IV) derivatives of *N*-benzoylglycine (HAA) and *N*-benzoylglycylglycine (HDP) listed in Table 1 have been prepared by the neutralization of the appropriate organotin(IV) chloride and the sodium salt of the ligand. In all the cases

(HAA)



(HDP)

(a denotes amido CO, c denotes amino NH,
b denotes peptide CO, d denotes peptide NH)

Table 1

Physical and analytical data of trialkyltin(IV) complexes with *N*-benzoylglycine and *N*-benzoylglycylglycine

Compound [a]	Yield (%)	m.p. (°C)	Solvent [x]	Analysis (Found (calcd) (%))				Molecular weight (Found (calcd))
				C	H	N	Sn	
$(CH_3)_3Sn(AA)$ (1)	62	s	[e]	–	–	–	35.00 (34.72)	310 [c] (341.6)
$(n\text{-}C_3H_7)_3SnAA$ (2)	60	s	[e]	–	–	–	27.50 (27.86)	420.6 [b] (425.6)
$(n\text{-}C_4H_9)_3SnAA$ (3) [12]	55	s	[e]	–	–	–	25.23 (25.36)	452 [c] (467.6)
$(C_6H_5)_3SnAA$ (4) [12]	58	163–164	[e]	60.58 (61.41)	4.07 (4.36)		22.32 (22.47)	(467.6) [d]
$(c\text{-}C_6H_{11})_3SnAA$ (5)	63	113–120	[f]	58.53 (59.38)	8.36 (7.51)	–	21.46 (21.73)	560 [c] (545.6)
$(CH_3)_3SnDP$ (6)	80	87– 90	[e]	41.44 (42.11)	5.05 (5.01)	6.44 (7.02)	29.83 (29.75)	380 [c] (398.6)
$(n\text{-}C_3H_7)_3SnDP$ (7)	95		[e]	49.54 (49.73)	6.50 (6.63)	5.73 (5.80)	24.68 (24.57)	455 [c] (482.6)
$(n\text{-}C_4H_9)_3SnDP$ (8)	70	90– 95	[e]	52.43 (52.61)	6.99 (7.24)	5.21 (5.33)	22.97 (22.60)	550 [b] (524.6)
$(C_6H_5)_3SnDP$ (9)	49	195–200	[h]	58.98 (59.52)	4.41 (4.45)	4.32 (4.78)	20.14 (20.28)	[d]
$(c\text{-}C_6H_{11})_3SnDP$ (10)	66	110–115	[j]	57.45 (57.75)	7.48 (7.30)	3.74 (4.64)	19.64 (19.68)	590 [c] (584.6)

[a] All compounds are white, HAA = *N*-benzoylglycine ($C_6H_5CONHCH_2COOH$), HDP = *N*-benzoylglycylglycine ($C_6H_5CONHCH_2CONHCH_2COOH$). [b] In benzene. [c] In nitrobenzene, [d] Separate at low temperature in nitrobenzene and insoluble in benzene and camphor. [e] Highly soluble in organic solvents. [f] Absolute ethyl alcohol. [h] CCl_4. [j] Benzene.

s = semisolid; [x] = solvent of crystallization.

Table 2

Infrared spectral data (cm^{-1})

Compound [a]	ν(N–H)	Amide I ν(CO)amide/peptide [b]	Amide II	$\nu(COO)_{asym}$	$\nu(COO)_{sym}$	$\Delta\nu$	$\nu(Sn-C)_{asym}$	$\nu(Sn-C)_{sym}$
EtAA [d]	3340s	1640s	1530s	1757s	1400m	357	–	–
EtAA [c]	3440m	1645s	1540m	1730s	1375m	375	–	–
NaAA [d]	3320b	1635s,b	1545m,b	1590s,b	1400s	190	–	–
1 [c]	3420m	1650s	1520m	1585m	1385s	190	–	–
2 [c]	3440m	1655s	1515m	1580m	1390s	190	545w	515w
3 [c]	3430m,b	1645s	1520m	1580m	1390s	190	550w	510w
4 [d]	3390m,b	1640s,b	1535m,b	1570m,b	11380m,b	190	260w	230w
4 [c]	3440m,b	1648s	1520m,b	1580m,b	1385 m,b	195	–	–
5 [d]	3340m,b	1648m	1545m,b	1600s	1410m	190	495m	425m
EtDP [d]	3360s	1660s 1635s	1535s	1735s	1375m	360	–	–
EtDP [c]	3420m 3320m,b	1650s	1520s	1740s	1375m	365	–	–
NaDP [d]	3360m,b 3280m,b	1675s 1650s	1542s	1600s	1390m	210	–	–
6 [d]	3360s,b	1640s,b	1542s,b	1650s,b	1390m,b	260	550m	520vw
6 [c]	3400m,b 3320m,b	1648s,b	1545s,b	1650s,b	1380m,b	270		
7 [c]	3405m,b 3310m,b	1645s,b	1510s	1650s,b	1380s	270	–	–
8 [d]	3280m,b	1635s,b	1545s,b	1635s,b	1375m	260	542m	505w
8 [c]	3405m,b 3340m,b	1645s,b	1518s,b	1650s,b	1380s	270	–	–
9 [d]	3350m,b	1615s	1540m,b	1640s,b	1385s	255	265m	225w
10 [d]	3290m,b	1640s,b	1530m,b	1640s,b	1390w	250	540m	505w
10 [c]	3410m,b 3320m,b	1650s,b	1515m,b	1650s,b	1385s,b	265	–	–

[a] For compounds see Table 1. [b] ν(CO)amide/peptide overlap. [c] Chloroform solution. [d] KBr disc.

studied, the composition showed a 1 : 1 molar ratio. R_3SnDP ($R = CH_3$, n-C_3H_7, n-C_4H_9, c-C_6H_{11}) and R_3SnAA ($R = CH_3$, n-C_3H_7, c-C_6H_{11}) are highly soluble in chloroform, whereas $(C_6H_5)_3SnDP$ is soluble in a (1 : 1) mixture of chloroform and dimethyl sulfoxide. Molecular weight measurements show (Table 1) that all the complexes are monomers at low temperature (by cryoscopy) in benzene and nitrobenzene. Structures have been assigned from their IR data (Table 2).

Infrared data

The vibrations due to CO(OH) of the free N-protected amino acid and dipeptide have disappeared from the spectra of the complexes, thus the MR_3 groups are bonded by the carboxylic group to the *N*-benzoylamino acid and the dipeptide moieties. The spectra of the organotin carboxylates with bridged structure show $\nu(COO)_{asym}$ bands at 1540–1560 cm^{-1}, but those of chelated carboxyl groups usually absorb at 1580–1600 cm^{-1} [18]. The presence of a medium-strong band at 1720–1750 cm^{-1} indicates unidentate bonding [3]. In the N-protected amino acid complexes **1–5**, the $\nu(COO)_{asym}$ and $\nu(COO)_{sym}$ occur in the 1570–1600 cm^{-1} and 1380–1400 cm^{-1} regions in the solid state as well as in chloroform solutions. The $\Delta\nu$, 190, for these complexes is similar to that for the sodium salt of the ligand, which indicates the presence of a bidentate chelating carboxylate group in these complexes. For the *N*-benzoylglycylglycine complexes **6–10**, the $\Delta\nu$, 265 ± 5, is higher than that for NaDP ($\Delta\nu = 210$) which shows either unidentate or asymmetric bonding of the carboxylate in the solid state and in solution. Evidence of metal-coordination by the basic atoms of the amide group is available from the infrared frequencies of the Amide I $\nu(C{=}O)$ and of Amide II [$(\nu(C{-}N) + \delta(N{-}H))$] as well as $\nu(NH)$ [19]. According to the literature, the following general pattern is observed upon coordination by oxygen (nitrogen) of the amido-group to a metal atom: (i) the frequency of the Amide I absorption band decreases (increases), and (ii) that of Amide II increases (decreases) compared with values observed for the free groups; (iii) $\nu(NH)$ bonds are nearly unchanged (in the absence of hydrogen bonding). For the solid complexes **1–5**, the amide I frequencies increase or remain the same; and those of amide II behave similarly or increase compared with those found in the AA, ester (Amide I at 1640, Amide II at 1330 cm^{-1}), which indicates the non-participation of C=O and NH in the coordination to tin(IV) and in addition indicates the presence of hydrogen bonding of the NH with the C=O group of the neighbouring molecules in the solid state. In the dipeptide complexes **6–10**, Amide I band frequencies decreased and Amide II increased with respect to ligand ester indicating the NHCO coordination to tin(IV). A marked shift of the $(\nu(CN) + \delta(NH))$ band towards higher frequencies and simultaneous shift of the $\nu(CO)$ amide band towards lower frequencies with change of state solid to one in solution are consistent with participation of the CONH group in the coordinate bonding with tin atom via donor oxygen atom in the solid state to form a NHCO–Sn donor–acceptor bond [1]. The above analysis of the N-protected dipeptide complexes showed that in chloroform solutions complexes **6–10** are present as simple molecules and having a tetrahedrally coordinated tin atom. In the solid state, the coordination number of tin atom increases owing to the formation of a NHCO–Sn donor–acceptor bond and tin becomes penta-coordinated. The tin atoms in the complexes **1–5** also have a coordination number of five. The presence of the stretching vibrations, $\nu(SnC)_{asym}$ and $\nu(SnC)_{sym}$, in the infrared spectra of all complexes excludes the exactly planar

Table 3

^{1}H NMR data (δ, $CDCl_3$)

Complex	C_6H_5	C–NH	CH_2	Sn–R	
				CH_2	CH_3
HAA [b]	8.01–7.07	[c]	4.23		
	(bm, 6H)		(d, 2H)		
$(n\text{-}C_3H_7)_3SnAA$ [a] (**2**)	7.47–6.63	8.01	4.06	1.83–1.20	1.26–0.80
	(bm, 5H)	(bm, 1H)	(d, 2H)	(bm, 12H)	(m, 9H)
$(n\text{-}C_4H_9)_3SnAA$ [a] (**3**)	8.27–7.27	[c]	4.23	2.00–1.23	1.13–0.57
	(bm, 6H)		(bd, 2H)	(bm, 18H)	(bm, 9H)
$(C_6H_5)_3SnAA$ [a] (**4**)	7.66–6.90	7.97–7.66	4.17	–	–
	(bm, 20H)	(m, 1H)	(d, 2H)		
HDP [b]	7.83–7.56	8.00	4.20	–	
	(bm, 5H)	(m, 2H)	(m, 4H)		
$(CH_3)_3SnDP$ [a] (**6**)	7.90–7.17		4.00		1.04–0.027
	(bm, 7H)		(bm, 4H)	–	(bm, 9H)
$(n\text{-}C_3H_7)_3SnDP$ [a] (**7**)	7.45–7.05	7.80–7.45	3.90	–	1.85–0.60
	(bm, 5H)	(bm, 2H)	(m, 4H)		(bm, 21H)
$(n\text{-}C_4H_9)_3SnDP$ [a] (**8**)	7.05–7.35	–	4.30–3.95	1.90–1.25	1.25–0.75
	(bm, 5H)		(bm, 4H)	(bm, 24H)	(bm, 9H)
$(c\text{-}C_6H_{11})_3SnDP$ [a] (**10**)	7.90–7.15	4.10			2.00–0.90
	(bm, 5H)	(m, 2H)			(bm, 35H)

[a] $CDCl_3$ (d: doublet, m: multiplet, bm: broad multiplet). [b] Trifluoroacetic acid. [c] Superimposed by phenyl protons.

arrangement of three Sn–C bonds around the tin atom present in a *trans*-trigonal bipyramid structure [20]. The ν(NH) bands indicate the formation of hydrogen bonds of NHCO $\cdots$ H in the solid complexes, and their disintegration upon dissolution of the complexes in chloroform. A weak to medium intensity band in the 470–490 cm^{-1} region has been assigned to Sn–O stretching vibrations for all the complexes [12].

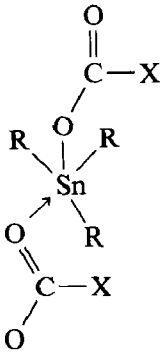
NMR Spectra

The ^{1}H NMR spectra of the soluble complexes and ethyl esters of HAA and HDP acids were recorded in deuteriochloroform and relevant data are given in Table 3. In the ^{1}H NMR spectra of the complexes studied, the CO(OH) signal of the free acid is missing and the NH signal is shifted towards higher field (if not obscured by superposition by phenyl protons). The N-H protons of the amide and peptide groups appear as a broad and weak signal, which is not visible in the spectra of some complexes. The resonances for the alkyl or aryl groups attached directly to tin(IV) appear as broad multiplets in the 1–2 ppm for -CH_2 and 0–1 ppm ranges for -CH_3 protons. The number of protons calculated from the integration curves is consistent with that calculated from the molecular formula of the complex.

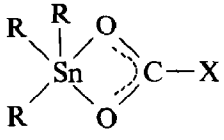
Conclusion

The infrared data of the *N*-benzoylglycine complexes R_3SnAA suggest a penta-coordinate trigonal bipyramidal structure [**A**] for tin(IV) with chelating bidentate carboxylate group in the solid as well as the solution states. This structure is supported by Mössbauer data (IS, 1.41, 1.22 mms^{-1}; QS, 3.61, 3.40 mms^{-1}) at 80 K

for the two complexes n-Bu_3SnAA and Ph_3SnAA (AA as in Table 1) [12]. The triorganotin(IV) derivatives of *N*-benzoylglycylglycine (**6–10**) in the solid state have a polymeric structure [**B**] having unidentate carboxylic groups. The molecules are linked by the weak intermolecular donor–acceptor NHCO–SnR_3 bond. The O–$Sn(R_3)O$ fragment has a slightly deformed *trans*-trigonal bipyramid geometry of atoms linked to the central tin atom with a slightly out-of-planar arrangement of the R_3Sn group. The complexes (**6–10**) are present in as simple molecules having tetrahedrally arranged R_3SnOCO groups in chloroform solution.



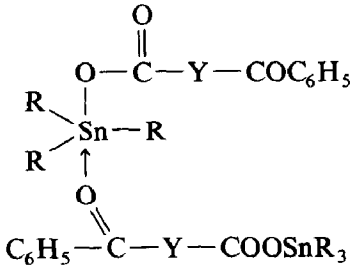
(solid)



(in solution)

$X = C_6H_5CONH_2CH_2$

[A]



(solid)

$Y = C_6H_5C(=O)-NHCH_2CONHCH_2COO$

[B]

Acknowledgements

Financial assistance from CSIR, New Delhi to G.K. is gratefully acknowledged.

References

1 G.K. Sandhu, G. Kaur, J. Holeček and A. Lyčka, J. Organomet. Chem., 332 (1987) 75.
2 G.K. Sandhu, G. Kaur, J. Holeček and A. Lyčka, J. Organomet. Chem., 345 (1988) 51.
3 G.K. Sandhu, G. Kaur, J. Holeček and A. Lyčka, J. Organomet. Chem., 365 (1989) 215.

4 A.G. Davies and P.J. Smith, Adv. Inorg. Chem. and Radiochem. 23 (1980) 1, C.A., 94 (1981) 84197w.
5 W.N. Aldridge, Organotin Compounds, New Chemistry and Applications, Ed. J.J. Zuckerman. Adv. Chem. Ser., Am. Chem. Soc. Washington, 157 (1976) 186, C.A., 86 (1977) 51129 g.
6 B.M. Elliot, W.N. Aldridge and J.M. Bridges. Biochem. J., 177, 461 (1979), C.A., 91 (1979) 70256r.
7 F. Taketa, K. Siebenlist, J. Kasten-Jolly and N. Polosaari, Arch. Biochem. Biophys., 203 (1980) 466, C.A., 93 (1980) 126546 w.
8 B.Y.K. Ho and J.J. Zuckerman, Abstr. 164th National meeting of Am. Chem. Soc., New York, (Fall 1972) 175.
9 B.Y.K. Ho and J.J. Zuckerman, Inorg. Chem., 12 (1973) 1552. C.A., 79 (1973) 32131r.
10 G.K. Sandhu, R. Gupta, S.S. Sandhu and R.V. Parish, Polyhedron, 4 (1985) 81.
11 G.K. Sandhu, R. Gupta, S.S. Sandhu, R.V. Parish and K. Brown, J. Organomet. Chem., 279 (1985) 373.
12 G.K. Sandhu, R. Gupta, S.S. Sandhu, L.S. Moore and R.V. Parish, J. Organomet. Chem., 311 (1986) 281.
13 V.G. Das, Y.C. Keong, N.G.S. Weng, C. Wei and T.C.W. Mak, J. Organomet. Chem., 311 (1986) 289.
14 A. Saitow, G.E. Rochow and D. Seyferth, J. Org. Chem., 23 (1958) 116. C.A., 52 (1958) 181 95.
15 D. Seyferth and F.G.A. Stone, J. Am. Chem. Soc., 79 (1957) 515.
16 B. Belleau and G. Malek, J. Am. Chem. Soc., 90 (1968) 1651.
17 E. Hoffman and I. Faiferman, J. Org, Chem., 29 (1964) 748.
18 W.D. Honnick and J.J. Zuckerman, J. Organomet. Chem., 178 (1979) 133.
19 G. Roge, F. Huber, H. Preut, A. Silvestri and R. Barbieri, J. Chem. Soc., Dalton Trans., (1983) 595.
20 G.K. Sandhu, S.P. Verma, L.S. Moore and R.V. Parish, J. Organomet. Chem., 321 (1987) 15.