ELSEVIER

Journal of Organometallic Chemistry 495 (1995) 177–184

Journal of Organo metallic Chemistry

Studies on the diorganotin(IV) complexes of some dihydroxamic acids

Mrinal K. Das *, Somnath De

Department of Chemistry, Jadavpur University, Calcutta 700 032, India

Received 7 December 1994

Abstract

Twenty-one diorganotin(IV) complexes of *N*, *N*-substituted dihydroxamic acids of the formula $\{R^1_2Sn[ON(R)CO]_2(CH_2)_n\}_2$ (R^1 = n-C_4H_9, C_6H_5; R = C_6H_5, 4-$CH_3C_6H_4$, 4-ClC_6H_4) were synthesized by the reaction of diorganotin(IV) dichlorides and dihydroxamic acids in the presence of triethylamine. Molecular weight determinations and electronic, IR, Raman and NMR spectroscopic techniques were utilized for the characterization and elucidation of the structural and bonding aspects of the compounds. The results suggest that all the compounds are dimeric and the di-n-butyltin(IV) dihydroxamates have *trans*-octahedral structures, whereas the diphenyltin(IV) dihydroxamates have *cis*-octahedral structures.

Keywords: Diphenyltin(IV); Dibutyltin(V); Dihydroxamic acids; Infrared spectroscopy; Raman spectroscopy; NMR spectroscopy

---

1. Introduction

Hydroxamic acids having the general formula $R^1CON(R)OH$ are weak organic acids of considerable biological importance [1–4]. Dihydroxamic acids having the general formula $(CH_2)_n[CON(R)OH]_2$ may be regarded as the synthetic analogues of the naturally occurring siderophore rhodotorulic acid [5], which has been put on clinical trial for the treatment of iron overload disease [6]. The importance of the organotin compounds in biology [7–10] and the environment [11,12] is now well established. Organotin compounds have also been found to exhibit antitumour activity [13,14]. The cytotoxicity of organotin compounds was studied in mice [15] and it was found that the functional groups attached to the tin atom in organotin compounds control the compounds' cytotoxicity towards the thymus gland. We have therefore been attracted by the idea of combining organotin species with monohydroxamic acids [16–18] and have now extended this study to dihydroxamic acids [19], in continuation of our work on iron [20,21] with dihydroxamic acids.

2. Experimental

2.1. Materials

All chemicals and reagents were of reagent-grade quality. Diphenyltin dichloride (Merck, Germany) and dibutyltin dichloride (Alfa, USA) were used as received. Chloroform (AR) was washed with concentrated H_2SO_4 and then with water and was kept over anhydrous $CaCl_2$ for 1 day and finally distilled over P_4O_{10} prior to use. Other solvents were dried by standard procedures.

2.2. Physical measurements

Infrared spectra were recorded on Perkin-Elmer 883 or 597 spectrophotometer as KBr discs. The spectra were calibrated with respect to the 1601 cm^{-1} band of a polystyrene film. Raman spectra were recorded with a Spex double monochromator model 1403 with 515.4 nm radiation from a Spectra-Physics Model 2020-5 argon ion laser as the excitation source. A Spex Datamate IB was used for monochromator control, data acquisition and analyses. ^1H NMR spectra were recorded on a Jeol JNM FX-100 (100 MHz), a Varian EM 390 (90 MHz), a Hitachi R-600 (60 MHz) or a Varian XL 200 MHz spectrometer in $CDCl_3$, using TMS as internal reference. UV spectra were recorded on a Pye-Unicam SP8-400 or a Hitachi U 2000 spectrophotometer.

---

* Corresponding author.

SSDI 0022-328X(95)05400-6

Molecular weights in chloroform were measured using a Knauer-11 vapour-pressure osmometer after calibration with benzil in the same solvent. Tin was determined gravimetrically as SnO_2 after decomposition with concentrated HNO_3. C, H and N analyses were carried out on a Perkin-Elmer 240C elemental analyzer. Melting points (uncorrected) were recorded on an electrical heating coil apparatus.

2.3. Preparation of dihydroxamic acids

The dihydroxamic acids used in this study were prepared by methods reported earlier [19].

2.4. Synthesis of organotin(IV) dihydroxamates

All the compounds were synthesized by the following general method.

Diorganotin(IV) dichloride, $R^1_2SnCl_2$ ($R^1 = C_6H_5$, n-C_4H_9) (0.86 g for $R^1 = C_6H_5$; 0.76 g for $R^1 =$ n-C_4H_9; 2.5 mmol) and the appropriate dihydroxamic acid $(CH_2)_n[CON(R)OH]_2$ ($R = C_6H_5$, 4-$CH_3C_6H_4$, 4-ClC_6H_4; $n = 2, 3, 4, 6, 8$) (2.5 mmol) were taken in dry chloroform (25 ml) in a two-necked flask (100 ml), fitted with a reflux condenser with a fused $CaCl_2$ drying tube at the top. To this, anhydrous triethylamine (0.56 g, 5.5 mmol) diluted with chloroform (5 ml) was added

Table 1
Analytical, physical and electronic spectral data for diorganotin(IV)dihydroxamates, $\{R^1_2Sn[ON(R)CO]_2(CH_2)_n\}_2$

Compound No.	$\{R^1_2Sn[ON(R)CO]_2(CH_2)_n\}_2$			M.p. (°C)	Yield [a] (%)	Elemental analysis: found (calcd.) (%)				λ_{max} (nm) (ligand)	Log ε_{max} [b]	Molecular weight: found (calcd.)
	R^1	R	n			Sn	C	H	N			
I	C_6H_5	C_6H_5	2	229–230	68	20.29	58.37	4.25	5.13	262.8 (257.5)	4.00	
						(20.78)	(56.87)	(4.24)	(4.91)	231.5 (224)	4.42	
II	C_6H_5	4-$CH_3C_6H_4$	2	224–226	89	19.31	60.09	4.68	4.60	259.5 (252)	3.97	1230
						(19.81)	(60.13)	(4.71)	(4.68)	229 (223.3)	4.37	(1198.46)
III	C_6H_5	4-ClC_6H_4	2	227–228	88	18.16	52.81	3.48	4.13	266.2 (259)	4.06	
						(18.34)	(52.34)	(3.46)	(4.38)	235 (224.4)	4.23	
IV	C_6H_5	C_6H_5	3	247–248	81	20.18	58.19	4.52	4.58	264 (256)	3.90	
						(20.26)	(59.52)	(4.48)	(4.79)	233 (224.3)	4.06	
V	C_6H_5	4-$CH_3C_6H_4$	3	249–250	73	19.50	60.67	5.17	4.49	262 (255)	3.97	1236.5
						(19.35)	(60.71)	(4.93)	(4.57)	244 (222)	3.94	(1226.52)
VI	C_6H_5	4-ClC_6H_4	3	176–178	52	17.98	53.34	4.01	4.64	270 (254.6)	4.03	
						(18.15)	(53.25)	(3.70)	(4.28)	244 (224.8)	3.98	
VII	C_6H_5	C_6H_5	4	179–180	69	19.73	60.32	4.55	4.34	263 (255)	4.06	
						(19.91)	(60.13)	(4.71)	(4.68)	234.5 (222.2)	4.51	
VIII	C_6H_5	4-$CH_3C_6H_4$	4	217–218	70	18.78	60.63	5.24	4.38	258 (254)	4.13	1289.5
						(18.92)	(60.27)	(5.14)	(4.47)			(1254.58)
IX	C_6H_5	4-ClC_6H_4	4	162–164	58	17.56	54.48	3.88	4.18	266 (252.5)	4.11	
						(17.76)	(53.95)	(3.92)	(4.19)	243 (223.5)	4.03	
X	C_6H_5	C_6H_5	6	138–140	84	19.04	60.20	5.32	4.37	264 (254.5)	3.89	
						(18.92)	(61.27)	(5.14)	(4.47)	244 (229)	3.89	
XI	C_6H_5	4-$CH_3C_6H_4$	6	133–134	79	17.89	62.03	5.74	4.20	263 (253.8)	3.87	1296.2
						(18.11)	(62.31)	(5.54)	(4.28)	246 (223)	3.05	(1310.68)
XII	C_6H_5	4-ClC_6H_4	6	110–112	83	17.18	56.04	4.25	4.30	257.5 (255.2)	4.00	
						(17.05)	(55.20)	(4.34)	(4.02)	238 (226)	4.62	
XIII	C_6H_5	C_6H_5	8	130–131	62	18.19	61.89	5.02	4.13	264 (253)	3.91	1276.9
						(18.11)	(62.31)	(5.54)	(4.28)	243 (222)	3.89	(1310.68)
XIV	C_6H_5	4-$CH_3C_6H_4$	8	114–116	65	17.10	62.48	5.54	3.92	259.2 (254.8)	3.99	
						(17.37)	(63.27)	(5.90)	(4.10)	232.6 (220.6)	4.18	
XV	C_6H_5	4-ClC_6H_4	8	142–144	55	16.23	56.74	4.53	3.78	264 (254.2)	3.97	
						(16.39)	(56.38)	(4.73)	(3.87)	231 (227.6)	4.27	
XVI	C_4H_9	C_6H_5	2	86–87	59	22.21	54.02	5.89	5.12	274 (257.5)	3.85	
						(22.34)	(54.26)	(6.07)	(5.27)	231 (224)	4.36	
XVII	C_4H_9	4-$CH_3C_6H_4$	2	196–198	64	20.89	56.14	6.11	4.57	258.4 (252)	4.03	1140.2
						(21.22)	(55.83)	(6.49)	(5.01)			(1118.52)
XVIII	C_4H_9	4-ClC_6H_4	2	90–92	61	19.94	48.43	5.21	4.75	275.5 (259)	3.92	
						(19.78)	(48.03)	(5.04)	(4.67)	230 (224.4)	4.32	
XIX	C_4H_9	C_6H_5	3	78–80	69	21.80	55.14	5.93	4.82	257.5 (256)	3.97	
						(21.77)	(55.07)	(6.29)	(5.14)	229.5 (224.5)	4.24	
XX	C_4H_9	4-$CH_3C_6H_4$	3	122–124	76	20.64	55.74	6.71	4.84	268 (255)	4.02	1170.5
						(20.70)	(56.56)	(6.60)	(4.89)	229.5 (222)	4.48	(1146.57)
XXI	C_4H_9	4-ClC_6H_4	3	82–84	73	19.34	48.85	4.83	4.64	281.5 (254.6)	3.89	
						(19.33)	(48.89)	(5.25)	(4.56)	229 (224.8)	4.21	

[a] Yields reported are of crude products.

[b] Log ε_{max} for the ligands could not be calculated as they are not completely soluble in chloroform, even in very dilute conditions.

dropwise with constant stirring from a pressure-equalizing dropping funnel. The mixture was refluxed on a water-bath for 5 h in order to ensure complete reaction. After cooling to room temperature, the solution was evaporated on a rotary evaporator to yield a sticky residue, which was dissolved in the minimum volume of dry benzene in warm conditions and the mixture was left overnight at room temperature. The precipitated silky white triethylamine hydrochloride was separated by suction filtration. The filtrate in each case was evaporated on a rotary evaporator to yield a pasty mass, which on trituration and washing several times with light petroleum (b.p. 40–60°C) yielded solid products. The crude products were then recrystallized from benzene–light petroleum ether (b.p. 40–60°C) mixture to yield crystalline solids.

3. Results and discussion

3.1. Synthesis

Diorganotin(IV) dichloride and an appropriate dihydroxamic acid were reacted in presence of a Lewis base,

Table 2
Infrared and Raman data for diorganotin(IV) dihydroxamates

Compound No.	ν(C=O)	Infrared data (cm^{-1})				Raman data	
		$-\Delta\nu$(C=O)	ν(N–O)	ν(Sn–C)	ν(Sn–O)	ν(Sn–C)	ν(Sn–O)
I	1561 vs,br	63	995 s	360 w	490 w		
			940 w		448 m		
II	1580 vs,br	44	1005 s	370 m	527 m	377	533
			930 m		455 s	259	
III	1562 vs,br	63	1000 s	350 w	500 m		
			927 w		455 s		
IV	1560 vs,br	82	995 s	380 m	470 w		
			920 m		458 m		
V	1560 vs,br	82	1000 s	415 m	484 m	410	520
			958 m		460 s	262	478
			948 m				455
VI	1548 vs,br	92	1005 s	400 m	490 w	410	531
			957 m,sh		452 s	263	491
							448
VII	1558 vs,br	67	1010 s	405 m	527 m		
			918 m		451 m		
VIII	1556 vs,br	64	970 m	385 sh	530 s	392	533
			933 sh		480 w	263	503
					455 s		460
IX	1560 vs,br	65	995 m	355 w	520 s		
			975 w		452 m		
X	1560 vs,br	68	995 s	385 m	520 s		
			922 m		450 s		
XI	1550 vs,br	70	1003 s	391 m	485 m		
			910 w		450 s		
XII	1540 vs,br	110	995 s	365 w	480 w		
			935 w		442 m		
XIII	1560 vs,br	70	998 m	405 w	528 m		
			918 m		452 m		
XIV	1558 vs,br	62	1005 s	390 m	520 m		
			920 w		455 s		
XV	1558 vs,br	72	990 s	355 w	490 w		
			940 m		442 ms		
XVI	1565 vs,br	59	990 s	576 m	480 m		
			930 m				
XVII	1530 vs,br	94	955 m	575 m	500 m		
			930 w				
XVIII	1565 vs,br	60	988 s	585 m	480 m		
			918 w				
XIX	1567 vs,br	75	955 m	600 w	478 m		
			912 m				
XX	1570 vs,br	72	970 m	586 m	495 m	590	548
			950 w				510
XXI	1565 vs,br	75	1000 s	606 m,sh	480 m		
			952 m				

Table 3
^{1}H NMR chemical shifts (δ in ppm) of diorganotin(IV) dihydroxamates, $\{R^1_2Sn[ON(R)CO]_2(CH_2)_n\}_2$

Compound No. [a–d]	Butyl-CH_3	$-(CH_2)_n-$	Aromatic protons	Ar–CH_3
I		2.04–2.56 m 2.80–3.12 m	7.04–7.44 m 7.48–7.80 m 7.88–8.08 br [g]	
II		2.04–2.6 m 2.80–3.2 m	7.04–7.54 m 7.56–7.84 m 7.92–8.08 br [g]	2.36 s Overlapped with CH_2, range 2.04–2.6
III		2.08–2.52 m 2.76–3.12 m	7.12–7.48 m 7.50–7.80 m 7.84–8.0 br [g]	
V		1.80–2.12 br [e] 2.16–2.64 br [e]	7.12–7.52 m 7.56–7.88 m 7.96–8.12 br [g]	2.42 s Overlapped with CH_2, range 2.16–2.64
VI		1.56 [a] 1.74–2.12 br [e] 2.16–2.64 br [e]	7.16–7.50 m 7.54–7.84 m 7.92–8.08 br [g]	
VII		1.44–2.0 br [e] 2.08–2.56 br [e]	7.12–7.60 m 7.68–7.92 m 8.0–8.20 br [g]	
VIII		1.36–1.86 br [e] 2.02–2.46 m	6.83–7.43 m 7.46–7.76 m 7.86–8.02 br [g]	2.36 s Overlapped with CH_2, range 2.02–2.46
IX		1.60–1.82 m 2.20–2.50 m	7.32–7.68 m 7.74–7.82 m 7.84–7.92 m	
X		1.20–1.95 m 2.10–2.50 br [e]	7.0–7.58 m 7.6–7.85 m	
XI		1.12–1.24 br [e] 1.40–1.70 br [f] 2.20–2.54 m	7.22–7.56 m 7.76–7.86 m 7.94–8.04 br [g]	2.44 s Overlapped with CH_2, range 2.20–2.54
XII		1.04–1.84 m,br 2.08–2.64 m	7.12–7.56 m 7.60–7.84 m 7.92–8.16 br [g]	
XIII		0.98–1.80 m,br 2.06–2.53 m	6.99–7.33 m 7.46–7.66 m 7.76–7.92 br [g]	
XIV		1.0–1.80 m,br 2.08–2.60 br [e]	7.08–7.56 m 7.60–7.92 m 8.0–8.12 br [g]	2.38 s Overlapped with CH_2, range 2.08–2.60
XV		1.0–1.88 m,br 2.08–2.60 br [e]	7.08–7.56 m 7.60–7.88 m 7.96–8.12 br [g]	
XVI	0.83 t [e]	1.03–1.83 m 2.12–2.92 m,br	7.20–7.79 m	
XVII	0.86 t	1.14–1.42 m 1.46–1.68 m 2.16–2.60 m	7.0–7.56 m	2.5 s Overlapped with CH_2, range 2.16–2.56
XVIII	0.85 t [e]	1.06–1.69 m 2.13–2.94 m,br	7.13–7.66 m	
XIX	0.88 t	1.0–1.12 m 1.20–1.44 m 1.48–1.68 m 1.80–2.0 br [e] 2.20–2.38 m	7.32–7.56 m	
XX	0.84 t	0.96–1.12 m 1.16–1.74 m 1.76–2.08 br [e] 2.12–2.60 m	7.04–7.44 m	2.42 s Overlapped with CH_2, range 2.12–2.60
XXI	0.92 t	1.16–1.80 m 1.84–2.08 br [e] 2.12–2.60 m	7.08–7.60 m	

such as triethylamine, in refluxing chloroform. Because of the insolubility of the ligands in benzene, the latter cannot be used as the solvent in this study. The HCl which is formed during the reaction is removed as triethylamine hydrochloride, the formation of which serves as the driving force for the forward reaction to completion. The reactants used were in 1 : 1 : 2 mole proportions, as shown in Eq. (1).

$$2R^1_2SnCl_2 + 2(CH_2)_n[CON(R)OH]_2 + 4B \rightarrow \{R^1_2Sn[ON(R)CO]_2(CH_2)_n\}_2 + 4B\cdot HCl \quad (1)$$

$R^1 = n-C_4H_9$, C_6H_5; $R = C_6H_5$, 4-$CH_3C_6H_4$, 4-ClC_6H_4; $B = (C_2H_5)_3N$; $n = 2, 3, 4, 6, 8$

The compounds prepared by this method are shown in Table 1, along with their yields and physical, analytical and electronic spectral data. IR and Raman data are given in Table 2 and ^1H NMR data in Table 3.

3.2. Molecular weights

Molecular weights of some representative compounds were determined by vapour pressure osmometry in chloroform and are given in Table 1. The data suggest that the compounds are dimeric. In principle, in addition to dimeric species, both monomeric and polymeric species having the same metal to ligand ratio may be formed. However, construction of molecular models (Theta Molecular Model; Wiley) shows that the formation of monomeric species with much strain is possible only with $n = 4$ acids; for $n \leqslant 3$ acid the –CONO– group cannot reach the octahedral sites on tin atom effectively, and for $n > 4$ acid, the –CONO– group can come within the binding sites of tin only with considerable strain.

3.3. Electronic spectra

The electronic absorption spectral data for diphenyltin(IV) and di-n-butyltin(IV) dihydroxamates are given in Table 1. A comparison of the electronic spectra of the compounds and the ligands in the range 200–400 nm in chloroform (against chloroform blank) shows that both the ligand bands which are found at 220.6–229 and 252–259 nm have undergone bathochromic shifts to 229–246 and 257.5–281.5 nm, respectively. These shifts indicate that the chromophoric systems have undergone perturbation due to coordination through the carbonyl group. In organotin bis(hydroxamates) [18,22] and organotin oxinates [23], such bathochromic shifts compared with those in the free ligands have also been reported; the results support our observations in the present systems. The coordination by the carbonyl group in the diorganotin(IV) dihydroxamates produces six-coordinated sp^3d^2-hybridized five-membered central tin species.

3.4. Vibrational spectra

The infrared spectra of both the ligands and the diorganotin(IV) dihydroxamates were recorded in the region 4000–300 cm^{-1} (as KBr discs) and the Raman spectra of some representative compounds were recorded in the region 900–200 cm^{-1} since the vibrations below 900 cm^{-1} associated with Sn–C and Sn–O modes are most useful in assessing the structures of the compounds.

The most prominent features of the infrared spectra are the absence of the ν(O–H) bands due to the N–OH group of the ligands occurring in the range 3230–3020 cm^{-1} [19]. This indicates that the reaction had taken place through the replacement of the N–OH hydrogen by the organotin moiety. The ν(N–O) modes in the ligands occur in the range 980–900 cm^{-1} [19] and therefore bands occurring at 1010–910 cm^{-1} in the diorganotin(IV) dihydroxamates are assigned to these modes in conformity with diorganotin(IV) bis(hydroxamates) [18]. For the ν(C = O) modes the most prominent bands in the ligands occur in the range 1650–1620 cm^{-1} [19] whereas for the compounds they occur in the range 1580–1530 cm^{-1}, with a decrease in ν(C = O) frequencies towards lower energy so that the individual decrease, $-\Delta\nu$(C = O), is in the range 110–44 cm^{-1}. This is indicative of coordination through the oxygen of a carbonyl group to tin. Therefore, the absence of ν(O–H) modes and the shifting of ν(C = O) modes towards lower energy support the tetradentate nature of dihydroxamic acids for diorganotin moieties.

The ν(Sn–C) and ν(Sn–O) stretching modes are found in the low-energy region along with the lower energy vibrational modes of the ligands. The asymmet-

---

Note to Table 3

[a] Measured as saturated solutions in $CDCl_3$ (99.8%).

[b] s = Singlet, t = triplet, m = multiplet, br = broad.

[c] **X**, **XVI**, **XVIII** measured at 60 MHz; **VIII**, **XIII** measured at 90 MHz; **I–VII**, **XII**, **XIV**, **XV**, **XVII**, **XX**, **XXI** measured at 100 MHz; **IX**, **XI**, **XIX** measured at 200 MHz.

[d] **IV** was to insoluble in $CDCl_3$ or DMSO-d_6 for NMR study.

[e] Unresolved.

[f] Two absorptions.

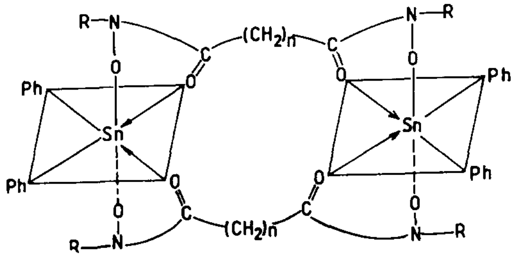
[g] Very small.

ric and symmetric ν(Sn–C) (phenyl) modes in phenyltin compounds have been assigned to the bands at 382–261 and 249–225 cm^{-1} [7,24]. Although we did not find bands in exactly the same region, the single bands occurring at 415–350 cm^{-1} in the diphenyltin(IV) dihydroxamates may be assigned to ν(Sn–C) asymmetric modes in consonance with those found for diphenyltin(IV) bis(hydroxamates) [18]. Any symmetric ν(Sn–C) (phenyl) modes occurring below 300 cm^{-1} are beyond the instrumental range used in this study, preventing us from identifying the low-frequency bands. In the dialkyltin bis(diketonates) (alkyl = CH_3, n-C_4H_9) [25–27] and dialkyltin bis(hydroxamates) (alkyl = CH_3, n-C_4H_9, n-C_3H_7) [28,29], a single ν(Sn–C) band found in the regions 590–556 and 620–566 cm^{-1}, respectively, has been assigned to ν(Sn–C) modes. In conformity with these, the single ν(Sn–C) (butyl) stretching modes are assigned to the absorptions at 606–575 cm^{-1} in di-n-butyltin(IV) dihydroxamates.

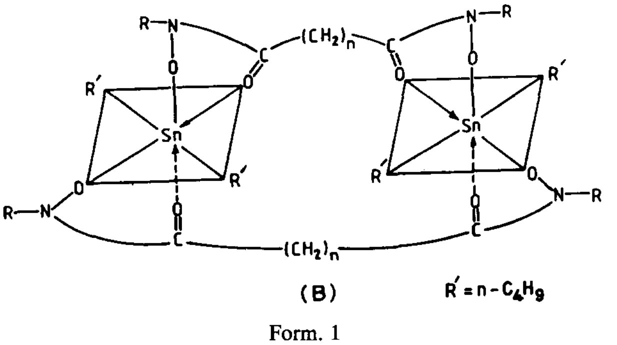
The ν(Sn–O) modes depend on the precise environment of the Sn–O group in the molecule. A range of 575–550 cm^{-1} has been suggested for various compounds [30]. In various acetylacetonates, the ν(Sn–O) modes occur at 461–404 cm^{-1} [23]. For L_2SnX_2 (X = Cl, Br, I, Ph, Bu; LH = hydroxamic acids), we have earlier reported the ν(Sn–O) modes in the range 525–400 cm^{-1} [16–18,31,32]. The nature of Sn–O bonds in the diorganotin(IV) dihydroxamates may be regarded as comparable to those of the bonds in acetylacetonates, oxinates and monohydroxamates and accordingly the absorptions appearing in the range 530–442 cm^{-1} for diorganotin(IV) dihydroxamates may be assigned to ν(Sn–O) modes.

In the Raman spectra, for triphenyltin(IV) dibenzoylmethanate and tropolonate three ν(Sn–C) (phenyl) have been reported in the ranges 385–220 and 538–221 cm^{-1}, respectively [33]. In this study, for four representative diphenyltin(IV) dihydroxamates two Sn–C stretching modes in each were found at 410–377 and 263–259 cm^{-1}, respectively, whereas for a representative di-n-butyltin(IV) dihydroxamate (compound **XX**) one Sn–C stretching mode was found at 590 cm^{-1}. For the same diphenyltin(IV) compounds, up to three ν(Sn–O) bands and for the same di-n-butyltin(IV) compound two ν(Sn–O) bands were found in the region 548–448 cm^{-1}.

The complexes $R^1_2Sn(L–L)$ (where $R^1 = C_6H_5$, n-C_4H_9; L–L = dihydroxamate ion) may exist as *cis* or *trans* octahedral structures in ideal cases. According to group theoretical predictions, *cis*-SnA_4R_2 should exhibit two Sn–C and four Sn–O stretching vibrations in both the infrared and Raman spectra. The *trans* isomer should exhibit one Sn–C and one Sn–O stretching vibrations in the infrared spectra and one Sn–C and two Sn–O vibrations in the Raman spectra [34]. We observed two ν(Sn–C) (phenyl) vibrations in the Raman spectra, one ν(Sn–C) (phenyl) vibration in the infrared spectra and one ν(Sn–C) (butyl) vibration in both the Raman and infrared spectra. For the diphenyltin(IV) dihydroxamates, two Sn–O stretching vibrations in the infrared spectra and up to three Sn–O stretching vibrations in the Raman spectra could be identified, others being somewhat obscure owing to ligand modes, mixing of normal modes and the appearance of overtones. For the di-n-butyltin(IV) compounds one Sn–O stretching mode could be identified in the infrared spectra and two Sn–O stretching modes in the Raman spectra. Therefore, on the basis of the above observations and in conjunction with the group theoretical predictions, a *cis*-octahedral configuration (**A**) is suggested for the diphenyltin(IV) compounds studied here, by analogy with other *cis*-diphenyltin(IV) compounds such as $(C_6H_5)_2Sn(acac)_2$ [35], $(C_6H_5)_2Sn(ox)_2$ [35] and $(C_6H_5)_2Sn$[bis(hydroxamates)] [18], and a *trans*-octahedral configuration (**B**) or a distorted *trans*-octahedral configuration may be suggested for di-n-butyltin(IV) dihydroxamates by analogy with other *trans*-dialkyltin(IV) compounds such as dimethyltin(IV) bis(acetylacetonate) [25,26], $(C_4H_9)_2Sn(CF_3COCHCOR)_2$ (R = Me, Et, ^{i}Bu, ^{i}Pr) [27], or di-n-butyltin(IV) bis(hydroxamates) [18]. Also, a three-dimensional X-ray diffraction study has suggested a *trans*-octahedral configuration of the butyl groups for di-n-butyltin(IV) bis(dibenzoylmethanate) [36].



(A)



(B) R′ = n-C_4H_9

Form. 1

3.5. ^1H NMR spectra

The ^{1}H NMR data are given in Table 3. For diphenyltin(IV) dihydroxamates, the $-CH_2-$ proton absorptions occur as multiplets or as broad unresolved signals in two groups in the regions δ 0.98–2.12 and 2.02–2.64 ppm, with the exceptions of compounds **I–III**, for which $-CH_2-$ proton absorptions occur as multiplets in the regions δ 2.04–2.6 and 2.76–3.2 ppm. For compounds **V–XV**, the absorptions at δ 0.98–2.12 and 2.02–2.64 ppm are assigned for the $(CH_2)_{n-2}$ group and $-CH_2-CO-$ group, respectively [37], whereas for compounds **I–III** the aforementioned two groups of absorptions arise from two $-CH_2-CO-$ groups and through mutual coupling of adjacent $-CH_2-$ protons. The CH_3 group protons on the aromatic rings of the dihydroxamate complexes which are derived from $(CH_2)_n[CON(4\text{-}CH_3C_6H_4)OH]_2$ ($n = 2$, 3, 4, 6, 8) ligands are observed at δ 2.36–2.44 ppm as singlets. The aromatic proton regions are very complex, because of the presence of phenyl groups both on tin and in the ligands. The aromatic proton absorptions are found in three groups, one at δ 6.83–7.68 ppm as multiplets (of strong intensity) and others at δ 7.46–7.92 ppm as multiplets (of low intensity) and δ 7.76–8.2 ppm as broad unresolved signals (of very weak intensity). The low and very weak intensity signals (corresponding to ca. four protons) which are observed at lower fields (mentioned above) in diphenyltin(IV) dihydroxamates, are found to be absent in the di-n-butyltin(IV) analogues and in the dihydroxamic acid ligands. Therefore, these signals must owe their origin to diphenyltin(IV) moiety and are most likely due to *ortho* hydrogens of the phenyl groups attached to tin. For the di-n-butyltin(IV) dihydroxamates, the aliphatic proton regions are very complex, because $-CH_2-$ groups are present both in the butyl group (attached to tin) and in the ligands. The $-(CH_2)-$ proton absorptions occur as two or more groups (as complex multiplets), one at δ 2.12–2.94 (for the $-CH_2-CO-$ group) and the others at δ 0.96–2.08 ppm (for both butyl and ligand $-(CH_2)-$ groups). The terminal CH_3 group protons of the butyl group are observed at δ 0.83–0.92 ppm [16,18] as triplets. The CH_3 group protons on the aromatic rings of the dihydroxamate complexes which are derived from $(CH_2)_n[CON(4\text{-}CH_3C_6H_4)OH]_2$ ($n = 2$, 3) ligands are observed at δ 2.42 and 2.5 ppm as singlets. Aromatic proton absorptions are found at δ 7.0–7.79 ppm as multiplets. The chemical shift values and the ratios of the total aromatic protons and aliphatic protons are consistent with the assigned formula.

Acknowledgements

This work was supported (in part) by DST, Government of India (Grant no. SP/S1/F-71/90). Thanks are due to Mr. M. Ghosh of the Indian Association for the Cultivation of Science for the Raman spectra.

References

[1] H. Kehl (ed.), *Chemistry and Biology of Hydroxamic Acids*, Karger, New York, 1982.
[2] S.R. Sandler and W. Karo, *Organic Functional Group Preparation*, Academic Press, New York, 1972, Chapter 12.
[3] P.A.S. Smith, *The Chemistry of Open-Chain Nitrogen Compounds*, Vol. 2, Benjamin, New York, 1966, Chapter 8.
[4] L. Bauer and O. Exner, *Angew. Chem., Int. Ed. Engl., 13* (1974), 376.
[5] C.J. Carrano and K.N. Raymond, *J. Am. Chem. Soc., 100* (1978) 5371.
[6] *Chem. Eng. News, 55* (1977) 24.
[7] R.C. Poller, *The Chemistry of Organotin Compounds*, Logos, London, 1970.
[8] W.P. Neuman, *The Organic Chemistry of Tin*, Wiley, New York, 1970.
[9] A.K. Sawyer, *Organotin Compounds*, Vol. 3, Dekker, New York, 1972.
[10] J.J. Zuckerman (ed.), *Organotin Compounds, New Chemistry and Applications*, Advances in Chemistry Series, No. 157, American Chemical Society, Washington, DC, 1976.
[11] J.J. Zuckerman, R.P. Reisdorf, H.V. Ellis, III, and R.R. Wilkinson, in J.M. Belama and F.E. Brinckman (eds.) *Chemical Problems in the Environment: Occurrence and Fate of the Organo-elements*, ACS Symposium Series, No. 82, American Chemical Society, Washington, DC, 1978, p. 338.
[12] F.E. Brinckman, *J. Organomet. Chem. Library, 12* (1981) 343.
[13] R. Barbieri, L. Pellerito, G. Ruisi, M.T. Lo Giudice, F. Huber and G. Atossi, *Inorg. Chim. Acta, 66* (1982) L39.
[14] A.J. Crowe and P.J. Smith, *Chem. Ind. (London)*, (1980) 200.
[15] L.R. Sherman and F. Huber, *Appl. Organomet. Chem.; Chem. Abstr., 109* (1988) 104156r.
[16] M.K. Das and M. Nath, *Indian J. Chem., Sect. A, 20* (1981) 1224.
[17] M.K. Das and M. Nath, *Z. Naturforsch., Teil B, 37* (1982) 889.
[18] M.K. Das, M. Nath and J.J. Zuckerman, *Inorg. Chim. Acta, 71* (1983) 49.
[19] M.K. Das, P. Bose and N. Roy, *J. Chem. Eng. Data, 29* (1984) 345.
[20] M.K. Das and N. Roy, *Indian J. Chem., Sect. A, 25* (1986) 246.
[21] M.K. Das, K. Chaudhury, N. Roy and P. Sarkar, *Transition Met. Chem., 15* (1990) 468.
[22] B. Pradhan and A.K. Ghosh, *J. Organomet. Chem., 131* (1977) 23.
[23] K. Kawasaki and R. Okawara, *J. Organomet. Chem., 6* (1966) 249.
[24] W.D. Honnick and J.J. Zuckerman, *J. Organomet. Chem., 178* (1979) 133.
[25] M.M. McGrady and R.S. Tobias, *J. Am. Chem. Soc., 87* (1965) 1909.
[26] Y. Kawasaki, T. Tanaka and R. Okawara, *Bull. Chem. Soc. Jpn., 37* (1964) 903.
[27] C. Sreelatha and V.D. Gupta, *Synth. React. Inorg. Met.-Org. Chem., 18* (1988) 29.
[28] G. Singh and V.D. Gupta, *Natl. Acad. Sci. Lett. India, 5* (1982) 423.
[29] G. Singh, C.K. Narula and V.D. Gupta, *Indian J. Chem., Sect. A, 21* (1982) 738.
[30] R.S. Tobias and C.E. Friedline, *Inorg. Chem., 4* (1965) 215.
[31] M.K. Das and M.R. Ghosh, *J. Indian Chem. Soc., 57* (1980) 678.

[32] M.K. Das and M.R. Ghosh, *Indian J. Chem., Sect. A, 20* (1981) 738.

[33] S.K. Brahma and W.H. Nelson, *J. Organomet. Chem., 273* (1984) 47.

[34] (a) F.A. Cotton, *Chemical Applications of Group Theory*, Wiley-Interscience, New York, 2nd edn., 1971; (b) M.K. Das, J. Buckle and P.G. Harrison, *Inorg. Chim. Acta, 6* (1972) 17.

[35] (a) B.W. Fitzsimmons, N.J. Seeley and A.W. Smith, *J. Chem. Soc., Chem. Commun.*, (1968) 390; (b) B.W. Fitzsimmons, N.J. Seeley and A.W. Smith, *J. Chem. Soc. A*, (1969) 143.

[36] G. Poli, C.J. Cheer and W.H. Nelson, *J. Organomet. Chem., 306* (1986) 347.

[37] S.J. Barclay, B.H. Huynh and K.N. Raymond, *Inorg. Chem., 23* (1984) 2011.