Inorganica Chimica Acta, *71* (1983) 49–59

Di- and Triorganotin(IV) Derivatives of N,N-Substituted Hydroxylamines

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Received October 14, 1982

Twenty-four organotin(IV) N,N-disubstituted hydroxylamines of the formula R_2SnL_2 ($R = n\text{-}C_4H_9$ and C_6H_5; LH = N,N-disubstituted hydroxylamines) and $(C_6H_5)_3SnL$ (LH = as above) have been synthesized by the reaction of organotin(IV) chlorides and hydroxylamines in presence of triethylamine in benzene medium. UV, IR, NMR and Mössbauer spectroscopic techniques have been utilized for the characterization and elucidation of the structural and bonding aspects of the compounds. The results indicate that the di-n-butyltin(IV) bis(hydroxylaminates) have distorted trans-*octahedral structures, whereas the diphenyltin(IV) bis(hydroxylaminates) and triphenyltin(IV) hydroxylaminates are* cis-*octahedral and trigonal bipyramidal with equatorial triphenyltin groups, respectively.*

Introduction

The N-acyl derivatives of hydroxylamines, also known as hydroxamic acids, are weak organic acids with a wide variety of applications including use as commercial flotation reagents in extraction metallurgy, as antifungal agents, pharmaceuticals, etc. [1]. The hydroxamate group, -CON(OH), is also the active constituent of many siderophores – the microbial iron transport compounds [2]. On the other hand, organotin compounds play an important role in biology and the environment [3, 4]. The biocidal activity of organotin moieties is now well established [5–8] and such species have found extensive commercial application as fungicides, insecticides, bacteriocides and for the protection of surfaces (ship-hulls, pier pilings, etc.) from marine organisms [3]. Recently, diorganotin(IV) complexes of adenine and glycylglycine [9] and dibutyltin(IV) halide complexes with *ortho*-phenanthroline and bipyridyl [10] have been found to exhibit antitumor activity. We have, therefore, been attracted by the idea of combining the organotin species with ligands which themselves are biologically active with the potential for the enhanced activity in the compounds thus formed, and have earlier reported the synthesis of some di- and triorganotin(IV) hydroxylaminates [11, 12]. In this paper we report the synthesis, characterization and structural and bonding aspects of some diorganotin(IV) bis(hydroxylaminates), R_2SnL_2 ($R = n\text{-}C_4H_9$, C_6H_5; LH = N,N-substituted hydroxylamines) and triphenyltin(IV) hydroxylaminates, $(C_6H_5)_3SnL$ (LH = as above), with the help of UV, IR, NMR and Mössbauer spectroscopic techniques.

Experimental

Materials

All chemicals and reagents used were of reagent grade quality. Di-n-butyltin(IV) dichloride and diphenyltin(IV) dichloride (Alfa Products, MA, U.S.A.) and triphenyltin(IV) chloride (E. Merck, Germany) were used without further purification. Benzene, methanol, ethanol and petroleum ether (40–60 and 60–80 °C) were dried by the usual procedures and distilled prior to use. The following N-acyl, N-arylhydroxylamines were prepared by standard procedures reported earlier [11, 13–15]: N-benzoyl, N-phenylhydroxylamine (BPHA*H*), N-benzoyl, N-2-methylphenylhydroxylamine (B-2MePHA*H*), N-benzoyl, N-3-methylphenylhydroxylamine (B-3MePHA*H*), N-benzoyl, N-4-methylphenylhydroxylamine (B-4MePHA*H*), N-benzoyl, N-4-chlorophenylhydroxylamine (B-4ClPHA*H*), N-2-iodo-

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0020-1693/83/0000-0000/$03.00

benzoyl, N-phenylhydroxylamine (2-IBPHA*H*), N-3,5-dinitrobenzoyl, N-phenylhydroxylamine [3,5-$(NO_2)_2$BPHA*H*), N-cinnamoyl, N-phenylhydroxylamine (CPHA*H*) and N-acetyl, N-phenylhydroxylamine (APHA*H*).

Tin was determined gravimetrically as SnO_2 and nitrogen was determined by the microanalytical laboratory of Jadavpur University. Infrared spectra were recorded on Perkin-Elmer 621 or Beckman IR-20A instruments as Nujol mulls on KBr or as KBr discs and were calibrated with respect to the 1601 or 1028 cm^{-1} band of a polystyrene film. ^1H NMR spectra were recorded on a JEOL-JNM-MH-100 (at 100 MHz) and a Varian T-60A (at 60 MHz) spectrometers in $CDCl_3$ with TMS as internal standard. Electronic spectra were recorded in methanol with a Specord UV–VIS (Carl Zeiss) spectrophotometer. A Chenevard–Joumier Thermobalance (ADAMEL, Paris) was used for thermogravimetric analysis.

Tin-119m Mössbauer spectra were recorded on a cam-drive, constant-acceleration spectrometer [16] with the sample mounted in a cryostat at 77 K, or on a Ranger Engineering constant-acceleration spectrometer equipped with a NaI proportional counter using $Ca^{119m}SnO_3$ (New England Nuclear Corp.) as both source and standard reference material for zero velocity. Velocity calibration used both β-tin and natural iron foils. Data were fitted to Lorentzian curves by standard non-linear least-squares techniques.

Preparation of Organotin(IV) Hydroxylaminates

The organotin(IV) hydroxylaminates were prepared by the following general methods:

i) Diorganotin(IV) hydroxylaminates

Diorganotin(IV) dichloride, R_2SnCl_2, ($R = n\text{-}C_4H_9, C_6H_5$) (3.04 g for $R = n\text{-}C_4H_9$; 3.43 g for $R = C_6H_5$; 10.0 mmol) and the appropriate N-acyl, N-arylhydroxylamine (20.0 mmol) were taken in dry benzene (100 ml). Triethylamine (2.22 g, 22.0 mmol) diluted with benzene (10 ml) was added slowly and the mixture was refluxed for 4 h. After cooling the mixture was filtered to separate the precipitated triethylamine hydrochloride. The filtrate in each case was evaporated on a water bath to a pasty mass which on trituration and washing several times with petroleum ether (40–60 or 60–80 °C) and on refrigeration under a layer of petroleum ether for several days (sometimes 2–3 weeks) yielded crude solid products. These were then recrystallized from methanol, ethanol, benzene or petroleum ether or their binary mixtures. All compounds are colorless except III (pale brown), VI (light pink), VII (brown), XIII (greyish) and XVI (light yellow) (see Table I).

ii) Triphenyltin(IV) hydroxylaminates

Triphenyltin(IV) chloride (3.85 g, 10.0 mmol) and the appropriate N-acyl, N-aryl-hydroxylamine (10.0 mol) were taken in dry benzene (100 ml) to which triethylamine (1.11 g, 11.0 mmol) diluted with benzene (10 ml) was added, and the mixture was refluxed for 4 h. The remainder of the procedure was the same as in (i). The crude products were recrystallized from methanol or benzene-methanol mixture. All compounds were colorless except XXIII (light yellow) and XXIV (light yellow) (Table I).

Results and Discussion

Synthesis

The N-acyl, N-arylhydroxylamines react with diorganotin(IV) dichlorides and triphenyltin(IV) chloride according to the following reaction schemes:

$$R_2SnCl_2 + 2R'CONR''OH + 2(C_2H_5)_3N \rightarrow$$
$$R_2Sn(R'CONR''O)_2 + 2(C_2H_5)_3N{\cdot}HCl \qquad (1)$$

$$(C_6H_5)_3SnCl + R'CONR''OH + (C_2H_5)_3N \rightarrow$$
$$(C_6H_5)_3Sn(R'CONR''O) + (C_2H_5)_3N{\cdot}HCl \qquad (2)$$

$R = n\text{-}C_4H_9$, C_6H_5; $R' = C_6H_5$, $2\text{-}IC_6H_4$, $3,5\text{-}(NO_2)_2\text{-}C_6H_3$, $C_6H_4CH{=}CH$, CH_3; $R' = C_6H_5$; $R'' = 2\text{-}CH_3C_6H_4$, $3\text{-}CH_3C_6H_4$, $4\text{-}CH_3C_6H_4$, $4\text{-}ClC_6H_4$ (see Table I).

Triethylamine was added in order to remove the liberated HCl as the amine hydrochloride from the reaction mixture, which process also serves as the driving force for the reaction. The diorganotin(IV) and triphenyltin(IV) hydroxylaminates are solids stable to moisture and air. Analogous reactions with tributyltin(IV) chloride or acetate yielded only tarry products, presumably owing to decomposition and disproportionation reactions common in organotin compounds[17].

Thermogravimetric Study

The diorganotin bis(hydroxylaminates) have similar decomposition patterns in thermogravimetric analysis. The decompositions which begin at temperatures between 210 and 272 °C are complete at about 550–600 °C, the end products in all cases being tin(IV) oxide. No intermediates are found. The triphenyltin(IV) hydroxylaminates begin to decompose at 230–275 °C, and are finally converted to SnO_2 through some undefined intermediates at 345–500 °C.

TABLE I. Physical Properties and Analytical Data for Organotin(IV) Hydroxylaminates.

No.	Compounds	MP (°C)	λ_{max} (nm) Compound (ligand)	log ϵ_{max} compound (ligand)	Anal. Found % (Calcd)	
					Sn	N
I	$(n\text{-}C_4H_9)_2Sn(BPHA)_2$	107–108	266	4.09	18.02	4.14
			(265)	(3.89)	(18.06)	(4.26)
II	$(n\text{-}C_4H_9)_2Sn(B\text{-}2MePHA)_2$	83	256	4.26	17.30	3.80
			(255)	(3.85)	(17.32)	(4.09)
III	$(n\text{-}C_4H_9)_2Sn(B\text{-}3MePHA)_2$	65	261	4.38	17.37	4.08
			(260)	(3.80)	(17.32)	(4.09)
IV	$(n\text{-}C_4H_9)_2Sn(B\text{-}4MePHA)_2$	98	263	4.25	17.10	4.23
			(256)	(3.98)	(17.32)	(4.09)
V	$(n\text{-}C_4H_9)_2Sn(B\text{-}4ClPHA)_2$	100	273	4.29	16.28	4.04
			(270)	(3.96)	(16.34)	(3.86)
VI	$(n\text{-}C_4H_9)_2Sn(2\text{-}IBPHA)_2$	116	261	4.24	13.26	3.18
			(255)	(4.0)	(13.08)	(3.09)
VII	$(n\text{-}C_4H_9)_2Sn[3,5\text{-}(NO_2)_2BPHA]_2$	60–62	[a]	[a]	16.35	8.65
					(14.18)	(10.04)
VIII	$(n\text{-}C_4H_9)_2Sn(APHA)_2$	110–112	253	3.64	22.47	4.90
			(251)	(3.90)	(22.26)	(5.25)
IX	$(C_6H_5)_2Sn(BPHA)_2$	153–155	267	4.18	16.98	3.92
			(265)	(3.89)	(17.02)	(4.02)
X	$(C_6H_5)_2Sn(B\text{-}2MePHA)_2$	160–161	263	3.98	16.46	3.46
			(255)	(3.85)	(16.36)	(3.86)
XI	$(C_6H_5)_2Sn(B\text{-}3MePHA)_2$	126–127	262	4.13	16.53	3.67
			(260)	(3.80)	(16.36)	(3.86)
XII	$(C_6H_5)_2Sn(B\text{-}4MePHA)_2$	155–156	270	4.06	16.54	3.78
			(256)	(3.98)	(16.36)	(3.86)
XIII	$(C_6H_5)_2Sn(B\text{-}4ClPHA)_2$	80	272	4.16	15.39	3.59
			(270)	(3.96)	(15.49)	(3.66)
XIV	$(C_6H_5)_2Sn(2\text{-}IBPHA)_2$	190–192	256	4.07	12.70	3.03
			(255)	(4.0)	(12.51)	(2.95)
XV	$(C_6H_5)_2Sn(APHA)_2$	156	252	4.16	20.58	4.80
			(251)	(3.90)	(20.71)	(4.89)
XVI	$(C_6H_5)_2Sn(CPHA)_2$	202–204	300	4.53	15.46	3.80
			(278)	(4.29)	(15.84)	(3.74)
XVII	$(C_6H_5)_3Sn(BPHA)$	160	270	4.14	21.02	2.59
			(265)	(3.89)	(21.11)	(2.49)
XVIII	$(C_6H_5)_3Sn(B\text{-}2MePHA)$	62–64	257	3.92	20.49	2.60
			(255)	(3.85)	(20.60)	(2.43)
XIX	$(C_6H_5)_3Sn(B\text{-}3MePHA)$	132	263	4.08	20.23	2.44
			(260)	(3.80)	(20.60)	(2.43)
XX	$(C_6H_5)_3Sn(B\text{-}4MePHA)$	153–154	263	3.94	20.38	2.21
			(256)	(3.98)	(20.60)	(2.43)
XXI	$(C_6H_5)_3Sn(B\text{-}4ClPHA)$	80–82	273	4.02	20.09	2.43
			(270)	(3.96)	(19.89)	(2.35)
XXII	$(C_6H_5)_3Sn(2\text{-}IBPHA)$	193	258	3.88	16.94	1.91
			(255)	(4.0)	(17.25)	(2.03)
XXIII	$(C_6H_5)_3Sn(APHA)$	158	253	4.16	23.64	2.60
			(251)	(3.90)	(23.73)	(2.80)
XXIV	$(C_6H_5)_3Sn(CPHA)$	208–210	294	4.34	20.04	2.50
			(278)	(4.29)	(20.18)	(2.38)

[a] Not recorded since the sample was somewhat impure.

Electronic Spectra

UV spectra of both the ligands and compounds in the range 200–300 nm have been recorded in methanol in order to investigate whether the absorptions of the ligands are perturbed by the metal after complexation. The ligands have absorptions between 251 and 278 nm owing to π–π^* transitions of the carbonyl chloromophore. The organotin(IV) hydroxylates also have absorptions in the same range except that the λ_{max} values undergo slight bathochromic shifts as a result of coordination of the carbonyl group to the metal. The results are in conformity with those reported for phenyltin(IV) benzolhydroxylaminates [18] and organotin(IV) oximates [17].

TABLE II. Infrared Absorption Bands of Organotin(IV) Hydroxylaminates as KBr Discs, 1700–300 cm^{-1}.

Compounds	Absorption Bands (cm^{-1})
I	1602m sh, 1583s, 1562sh, 1552m, 1544vs, 1521m, 1492m, 1452m, 1442m, 1425m, 1420m, 1380m, 1147m, 1137m, 1005s, 990m, 922ms, 915ms, 897s, 767m, 752s, 712m, 690s, 670s, 650s, 629m, 602m, 592m, 522m, 475m, 416sh, 407m, 340w.
II	1602sh, 1582vs, 1572s, 1537vs, 1495m, 1457m, 1437m, 1427m, 1410m, 1372w, 1282w, 1262m, 1147s, 1107m, 1062m, 1037w, 1007vs, 977vw, 917s, 907vs, 857m, 830w, 787m, 767s, 751vs, 708s, 697m, 682vs, 667m, 640s, 607w, 594m, 567w, 551w, 525w, 517w, 489m, 457w, 445w, 421w, 399w, 317w.
III	1605m, 1590vs, 1550vs, 1545sh, 1502s, 1490m, 1468m, 1451s, 1420m, 1385m, 1353w, 1345w, 1320w, 1300m, 1285w, 1260w, 1190m, 1180m, 1155vs, 1090m, 1075s, 1040s, 1003s, 990m, 942vs, 930s sh, 920 m, 905s, 880m sh, 870m, 845vs, 796vs, 783vs, 722s, 703vs, 692s sh, 672 s, 625m, 620m, 595m sh, 535m, 510s, 474w, 460w, 435w, 380w, 345w br, 328w.
IV	1585m, 1542vs, 1538vs, 1509m, 1440m, 1398w, 1330m, 1300w, 1240w, 1145m, 1125m, 1075m, 1060w, 1028m sh, 1020m, 100s, 921m, sh, 915m, 921m sh, 810m, 803s, 766m, 700m, 688s, 680s, 665m, 605m, 586w, 540w, 508m, 480m, 400m.
V	1605m, 1600m, 1552vs, 1540s, 1510s, 1455m, 1440s, 1405m, 1270w, 1155m, 1105m, 1092s, 1080m, 1025s, 1010s, 930s, 925s, 920s, 835vs, 812w, 788m, 710s, 705s, 690s, 675s, 595m, 560m, 555m, 500m, 495s, 455m, 405w, 395m, 355w.
VI	1568s sh, 1558vs, 1540vs, 1520s, 1490m sh, 1485s, 1454m, 1438m, 1420m, 1411 s, 1405 m sh, 1369m, 1250m, 1170m, 1158m, 1060m, 1035s, 1022s, 1001 vs, 990m, 915s, 905 s sh, 895m sh, 865w, 760vs, 725m, 715m, 710m, 677vs, 660s, 620m, 590m, 537m sh, 530m, 490m sh, 480s, 470msh, 465w sh, 432m, 405s, 340w.
VII	1605s, 1585s, 1555s sh, 1545 s sh, 1522vs, 1472m sh, 1461m, 1435s, 1400m, 1368m sh, 1370m sh, 1355s sh, 1320vs, 1303s sh, 1270m, 1235w, 1205vs, 1165m, 1138m, 1095m, 1056s, 1021s, 1000m, 982m, 961m, 890s, 855w br, 830m, 770w sh, 750s, 733s, 705s, 686s, 675s, 664s, 650s sh, 595m br, 490w br, 318vw.
VIII	1590m, 1568vs, 1530m sh, 1488m, 1454s, 1438s, 1409m, 1365m, 1358m sh, 1330w, 1278w, 1250w, 1238rw, 1181w, 1165vs, 1145m, 1118w, 1075s sh, 1068s, 1060s sh, 1008m sh, 998s, 988m, 966m, 908m, 860m, 826w, 760s, 735vs, 712m, 682s, 661m, 640m, 600vs, 590vs, 510s, 483s, 450m br, 400 m br.
IX	1535m, 1340s sh, 1530s, 1510vs, 1495s sh, 1485s sh, 1455m, 1422s, 1285m, 1150m sh, 1142s, 1060m, 1052w sh, 1030s, 986m, 934vs, 910m, 905m, 760s, 755s sh, 715s, 680vs, 650s, 585m, 555m sh, 535m, 487m, 457w, 435m sh, 420s, 405m sh, 345w.
X	1585s, 1550s sh, 1530vs, 1520m sh, 1505m, 1435s sh, 1425s, 1370m, 1295w, 1151s, 1140m sh, 1110w, 1065m, 1035w sh, 1025m sh, 1010s, 985w, 922s, 915s sh, 855w, 786m, 765s, 750s, 715s, 685vs, 645s, 608w, 590m, 555m sh, 530m, 495w, 435s, 425m, 360w, 320vw, 310vw.
XI	1605m, 1590s, 1570m sh, 1550s sh, 1540vs, 1512s sh, 1505m, 1485s, 1470m sh, 1450s, 1435s, 1431s sh, 1390m, 1340w, 1322w, 1310m, 1285w, 1269w, 1200m, 1162s, 1098m, 1085s, 1052m, 1035m, 1009m, 970vs, 932m, 920m, 882m, 850s, 802s, 788s, 740s, 705vs, 678s, 625m, 551m sh, 542m, 520m sh, 512m, 410m br, 345w, 316w.
XII	1605m, 1590s, 1550s sh, 1530vs, 1505m sh, 1500s sh, 1482m, 1448s, 1434s, 1411m, 1337m, 1315m, 1300m, 1265w, 1215m, 1192m sh, 1180s, 1160s, 1115m, 1079s, 1045s, 1035s sh, 1020s, 1002m, 970w, 940s, 925s sh, 851m, 830vs, 805s, 783s, 738s, 725s, 700vs, 665m, 646w, 625s, 600m, 550m, 540m, 500m, 470m, 420m, 390w, 367w, 345w.
XIII	1588s, 1562m sh, 1530vs, 1490s, 1448s, 1432s, 1400s, 1335w, 1318w, 1300w, 1279m, 1265m, 1190w, 1172m sh, 1160s, 1095s, 1080s, 1040s, 1030s, 1016vs, 970w, 940vs, 925s sh, 840vs, 780s,

(continued on facing page)

TABLE II. *(continued)*

Compounds	Absorption Bands (cm^{-1})
	735s, 700vs, 690s sh, 678s sh, 667m sh, 636w, 610w, 598m, 555s, 540m sh, 495s, 445m, 400w, 350w, 320w.
XIV	1585m, 1555s, 1530vs, 1520s sh, 1450s, 1435s sh, 1424vs, 1329m, 1310m, 1296w, 1282w, 1255m, 1185m sh, 1166s, 1113w, 1072s, 1098vs, 1040s, 1020vs, 1000m, 988w, 968w, 937vs, 915m, 865m, 834w, 815vw, 760vs, 730vs, 695vs, 678s, 672s sh, 660m sh, 640m, 617w, 600s, 551s, 532w, 502m, 420m br, 390w, 345w, 320w.
XV	1585s sh, 1560vs, 1530m sh, 1480w, 1454s, 1438m sh, 1415m, 1380w, 1368s, 1330w, 1311m, 1300m, 1280w, 1260m, 1182w, 1170w, 1155m, 1090s, 1074s, 1030m sh, 1025m, 1010s, 998s, 980s, 920s, 850w, 835w, 818w, 775vs, 731vs, 695vs, 652s, 625m, 590m, 574s, 523s sh, 510s, 438w, 430w, 400w, 375w, 335w.
XVI	1621s, 1585m, 1563m, 1530vs, 1500m sh, 1481s, 1470m, 1440s, 1420s, 1320w, 1293m, 1270m, 1250m, 1192m, 1170m, 1150w, 1058s, 1040vs, 1024m, 1003s, 990m, 958s, 910m, 899w sh, 865m, 838w sh, 783s, 765m, 748s, 720s, 785vs, 760s, 650w sh, 583m, 560m, 527m, 480m, 430w br, 385vw, 340w.
XVII	1590w, 1573s, 1520vs, 1500s sh, 1490m sh, 1479m sh, 1465m, 1448m, 1430s sh, 1418s, 1330m, 1310m sh, 1291s, 1260m, 1178m, 1150vs, 1100w, 1070vs, 1060m sh, 1033vs, 1013vs, 997s, 966w, 932s, 912s, 880w, 852w, 840w, 770vs, 730vs, 720s, 695vs, 668s, 626m, 590s, 536s, 491m, 461w, 420s, 355w br, 315vw.
XVIII	1596w, 1579s, 1560m sh, 1555m sh, 1535vs, 1515w sh, 1490w, 1472s, 1455m, 1437s, 1422s, 1390w, 1377w, 1348vw, 1327w, 1292m, 1257w, 1185m, 1155s, 1114m, 1100vs, 1077s, 1045w, 1018s, 995m, 985w, 967w, 935vs, 928s, 920m sh, 913s sh, 902vw, 855w br, 800m, 770s, 730s, 699vs, 665m, 620vw, 597m, 535m, 503w, 498w, 475vw, 420m, 360w, 340w.
XIX	1590m, 1575s, 1520vs, 1500w, 1473m, 1450m sh, 1435s, 1420s, 1374w, 1325w, 1290m, 1205w, 1183m, 1150s, 1110m, 1090w, 1066s, 1037w, 1014s, 990m, 980w, 960w, 938s, 915m sh, 910w br, 795m, 763s, 720s, 690vs, 655m, 592m, 545m sh, 535m, 500m, 410m br, 340w.
XX	1596m, 1578s, 1560s, 1540vs, 1510m, 1472s, 1445s, 1420s, 1405w, 1375w, 1330m, 1288w, 1256w, 1208m, 1188m, 1172m, 1158s, 1107w, 1070s, 1033s, 1012s, 995m, 974vs, 950vw, 939s, 920m, 855vw, 845m, 834s, 800m, 774s, 737s, 730s, 700vs, 660w, 619m, 600m, 594m, 560vw, 535m, 494m, 425m, 405w, 385w, 340w, 315w.
XXI	1597w sh, 1580s, 1535s, sh, 1525vs, 1504s sh, 1483s, 1476m sh, 1441s, 1425s, 1397m, 1330w, 1310w, 1294w, 1270w, 1256w, 1186w, 1154s, 1100m sh, 1088s, 1071m, 1032s, 1024s, 1009s, 994w, 965w, 932s, 775s, 729s, 696vs, 680m, 658w, 630vs, 585m, 545s, 520w, 485m, 456w, 430m, 400m br, 365w, 338w, 310w.
XXII	1578s, 1558vs, 1530vs, 1500s sh, 1490m, 1473s, 1448m, 1430m sh, 1420vs, 1325w, 1304w, 1295w, 1277w, 1250m, 1182w, 1160s, 1117w, 1067s, 1040vs, 1030s, 1010vs, 990m, 960w, 930vs, 910s, 857w, 826w, 758vs, 724vs, 688vs, 673s, 669m sh, 655wsh, 635m, 610vw, 590m, 543s, 494s, 460w br, 420s, 385w, 338w. 310w.
XXIII	1592m, 1570vs, 1550s sh, 1535m sh, 1492m, 1457m, 1445m, 1415m, 1370m, 1332w, 1382w, 1260w, 1190w, 1175w, 1148m, 1130m sh, 1122m, 1102s, 992m, 970m, 913m, 865m, 838w, 762s, 716m, 687s, 666m, 645w, 590s, 567s, 515m, 485m, 450w, 380w, 350w br.
XXIV	1625s, 1585m, 1561m, 1532vs, 1484s, 1470m, 1443s, 1420vs, 1322w, 1295m, 1270w, 1250w, 1194m, 1170m, 1150w, 1060s, 1040vs, 1026s, 1005s, 992s, 960s, 910m, 868m, 840m, 785s, 768s, 761s, 750s, 687vs, 675s, 610w 580m, 558m, 530w sh, 525m, 475m br, 400w, 335w.

Infrared Spectra

The infrared spectra of both the ligands and the organotin(IV) hydroxylaminates (see Table II) have been recorded in the region 4000 to 300 cm^{-1}. The O–H stretching modes for free and hydrogen bonded N–O–H groups in the ligands occurring, respectively, in the regions 3240–3040 cm^{-1} and 2900–2700 cm^{-1} are absent in the spectra of the complexes indi-

TABLE III. Infrared Group Frequencies (cm^{-1}) in Di- and Triorganotin(IV) Hydroxylaminates.

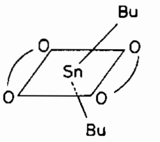
Compound No.	ν(C=O)	$\Delta\nu$(C=O)[a]	ν(N–O)	ν(Sn–C)	ν(Sn–O)
I	1544vs	71	922ms 915ms	592m 522m	475m 407m
II	1537vs	63	917s 907vs	594m 489m	445w 421w
III	1550vs	43	942vs 930ssh 920m	595msh 535m	510s 435w
IV	1538vs	59	921msh 915m 912msh	605m 508m	480m 400m
V	1552vs	40	930s 925s	595m 500m	455m 405w
VI	1540vs	71	915s 905ssh	590m 530m	480s 405s
VII	1522vs	93	961m 890s	595m 490wbr(?)	490wbr(?)
VIII	1568vs	102	966m 908m	600vs 590vs 510s	483s 400mbr
IX	1530s	85	934s 910m	345w	487m 457w
X	1530vs	70	922s 915ssh	360w	495w 435s
XI	1540vs	53	932m 920m	345w	512m 410mbr
XII	1530vs	67	940s 925ssh	345w	470m 420m
XIII	1530vs	62	940vs 925ssh	350w	445m 400w
XIV	1530vs	84	937vs 915m	320w	502m 420mbr
XV	1560vs	110	980s 920s	335w	510s 430w
XVI	1530vs	95	958s 910m	340w	480m 430wbr
XVII	1520vs	95	932s 912s	355wbr	491m 420s
XVIII	1535vs	65	928s 913ssh	360w 340w	498w 420m
XIX	1520vs	73	938s 910w	340w	500m 410mbr
XX	1540vs	57	939s 920m	385w 340w	494m 425m
XXI	1525vs	67	932s	365w 338w	485m 400mbr
XXII	1530vs br	84	930vs 910s	385w 338w	494s 420s
XXIII	1570vs	100	913m	380w 350w	515m 450w
XXIV	1532vs	93	910m	335w	525m 400w

[a] Red shift.

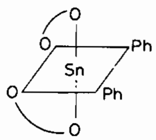
cating replacement of O–H hydrogen by tin during reaction. The ν(N–O) in the ligands occur in the range 920–873 cm^{-1} [19], and, therefore, bands occurring at 980–905 cm^{-1} in the organotin(IV) hydroxylaminates are assigned to these modes. The ν(C=O) modes which are observed at 1670–1590 cm^{-1} in the ligands occur at 1570–1520 cm^{-1} in the complexes, indicating a further shift of ν(C=O) by 110–40 cm^{-1} to lower energy (Table III). This suggests coordination of C=O to the metal through oxygen to give five-membered chelated rings at tin. 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 asymmetric and symmetric ν(Sn–C) stretching modes in $(n\text{-butyl})_nSnX_{4-n}$ (n = 2–4, X = halogen) occur at 602–592 and 522–503 cm^{-1}, respectively [20]. In conformity with these observations, we assign the asymmetric and symmetric ν(Sn–C)(butyl) stretching modes to the absorptions at 605–590 and 535–489 cm^{-1}, respectively, in the compounds studied here. The asymmetric and symmetric Sn–C (phenyl) stretching modes in phenyltin compounds have been assigned to the bands at 382–261 and 249–225 cm^{-1} [5, 21]. Thus the bands occurring at 360–320 cm^{-1} in the diphenyltin(IV) bis(hydroxylaminates) and those occurring at 385–335 cm^{-1} in the triphenyltin(IV)(hydroxylaminates) may be assigned to ν(Sn–C) (phenyl) asymmetric modes. The symmetric Sn–C (phenyl) modes occurring below 300 cm^{-1} are beyond the instrumental range used in this study.

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 [22]. However, for coordination complexes of the type $SnX_4 \cdot 2Ph_3EO$ (X = F, Cl, Br, I; E = P, As) the ν(Sn–O) modes are assigned to ~320 and 380 cm^{-1} bands, respectively [23], and at 470–400 cm^{-1} in $SnX_4 \cdot 2(CH_3)_3PO$ [24]. In pyridine N-oxide complexes, ν(Sn–O) appears at 400–300 cm^{-1} [25], whereas those in the DMSO complexes of tin(IV) appear at 500–400 cm^{-1} [26]. In various acetylacetonates, ν(Sn–O) occurs at 461–404 cm^{-1} [27]. For L_2SnX_2 (X = Cl, Br, I; LH = substituted hydroxylamines), we earlier reported ν(Sn–O) values in the range 455–400 cm^{-1} [13, 14]. The nature of the Sn–O bonds in the diorganotin(IV) bis(hydroxylaminates) and triphenyltin(IV) hydroxylaminates may be regarded as comparable to those in acetylacetonates or oxinates, rather than to the adducts, and accordingly we assign the absorptions at 525–400 cm^{-1} to ν(Sn–O) modes.

The complexes R_2SnL_2 (R = $n\text{-}C_4H_9$, C_6H_5; L = bidentate hydroxylamine ion) should exist as *cis*- or *trans*-octahedral structures through C=O coordination. According to group theoretical predictions these *cis*-SnA_4R_2 systems should exhibit two Sn–C and four Sn–O stretching vibrations and the *trans* isomer one Sn–C and one Sn–O stretching vibration in the IR spectra. The two ν(Sn–C)(butyl) stretching vibrations observed in each of the di-n-butyltin(IV) complexes indicate that they exist either in *cis*-octahedral or in highly distorted *trans*-octahedral configuration. This is consistent with the fact that the two methyl groups in dimethylbis(acetohydroxamato)tin(IV) are *cis* [28]. Thus a distorted *trans*-octahedral structure (*A*) is suggested for the di-n-butyltin(IV) bis(hydroxylaminates) by analogy with the observed C–Sn–C bond angle of 145.8° in $(CH_3)_2Sn[ON(CH_3)COCH_3]_2$ [29]. But a *cis*-octahedral configuration (*B*) has been suggested for all the diphenyltin(IV) compounds studied here by analogy with other *cis*-diphenyltin(IV) compounds such as $(C_6H_5)_2Sn(acac)_2$ and $(C_6H_5)_2Sn(ox)_2$ (acac = acetylacetonate ion, ox = oxinate ion) [30].

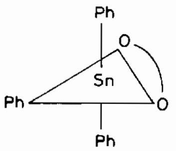


(A)

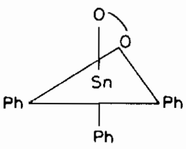


(B)

The shifting of ν(C=O) (~100–65 cm^{-1}) to lower frequencies in the triphenyltin(IV) hydroxylaminates is an indication of strong coordination of C=O to the metal to produce five-coordinated structures (*C* and *D*). The one containing a single phenyl group in an axial position (*D*) is suggested for the triphenyltin(IV) compounds by analogy with the structures of (1,3-diphenylpropane-1,3-dionato)triphenyltin(IV) [31] and (N-benzoyl, N-phenylhydroxylaminato)triphenyltin(IV) [32] where the bidentate chelated axial, equatorial attachment of the ligand oxygen atoms forces one of the phenyl groups into an axial position, contrary to the preferred axially-most-electronegative configuration [33] which would require the ligand to span the two axial sites or to form a bridge rather than chelate the tin atom.



(C)



(D)

^1H NMR Spectra

The ^1H NMR data are given in Table IV. For di-n-butyltin(IV) bis(hydroxylaminates) the n-butyl group resonates at δ = 1.43–1.80 ppm for the $-(CH_2)_3-$ group as complex patterns and at δ = 0.92–0.96 ppm for the terminal CH_3 as triplets. The absorptions owing to the aromatic protons of the ligands and phenyltin(IV) groups are complex. However, for the diphenyltin(IV) bis(hydroxylaminates), in addition to a large complex aromatic pattern, a multiplet of small intensity (equivalent to four protons) is also observed in each case at lower fields at δ = 7.83–7.90 ppm. Similarly, the aromatic proton absorptions for the triphenyltin(IV) hydroxylaminates are found in two groups; a weak signal (corresponding to approximately 6 protons) at δ = 7.72–8.0 ppm as a multiplet and a strong absorption centered at δ = 7.24–7.5 ppm as a complex pattern in each case. The methyl group protons on the aromatic rings of the hydroxylamine complexes are observed at δ =

TABLE IV. Chemical Shifts (δ in ppm) of Organotin(IV) Hydroxylaminates.[a,b]

Compound No.	Butyl Group		Aryl	Ar–CH_3/other protons
	–CH_3	–$(CH_2)_3$–		
I[c]	0.92t	1.55m	7.16m	
II[c]	0.92t	1.48m	7.10m	2.26s
		1.78m		
III[d]	0.93t[e]	1.64m	7.26m	2.23s
IV[c]	0.92t	1.60m	7.15m	2.28s
		1.80m		
V[c]	0.92t	1.64m	7.10m	
VI[c]	0.96t	1.85m	7.10m	
		1.80m	7.65s[f]	
			7.75s	
VII[d]	0.96t[e]		7.40s[g]	
			8.40d	
			8.90d	
			9.10s	
VIII[d]	0.96t	1.43m	7.4s	1.93s[h]
		1.70m		2.03s
IX[c]			7.35m	
			7.90m[i]	
X[c]			7.20m	2.25s
			7.85m[i]	
XI[d]			7.23m	2.23s
			7.85m[i]	
XII[d]			7.23m	2.26s
			7.83m[i]	
XIII[d]			7.25m	
			7.85m[i]	
XIV[d]			7.20m	
			7.83m[i]	
			7.56s[f]	
			7.76s	
XV[c]			7.40m	2.10s[g]
			7.88m[i]	
XVI[d]			7.40m	6.3s[j]
			7.86m[i]	6.6s[j]
XVII[c]			7.4m	
			8.0m[k]	
XVIII[c]			7.36m	2.24s
			7.96m[k]	
XIX[c]			7.24m	2.24s
			7.94m[k]	
XX[c]			7.50m	2.32s
			7.92m[k]	
XXI[c]			7.36m	
			7.96m[k]	
XXII[c]			7.4m	
			8.0m[k]	
			7.8s[e]	
			7.84s[f]	
XXIII[d]			7.36m	2.07s[h]
			7.72m[k]	
XXIV[d]			7.33m	6.56s[j]
			7.80m	6.30s[j]

[a] Measured as saturated solutions in $CDCl_3$ (99.8%). [b] s = singlet, t = triplet, m = multiplet. [c] Measured at 100 MHz. [d] Measured at 60 MHz. [e] A doublet or an unresolved triplet. [f] Absorptions owing to the *ortho*-hydrogens in the 2-iodobenzoyl group are found as two separate absorptions or a doublet. [g] Assignment was not possible owing to impurities. [h] Owing to the –$COCH_3$ group. [i] Absorptions owing to the *ortho*-hydrogens in the two *cis*-phenyl group on tin. [j] Two shifts owing to CH=CH, the lower field shifts being embedded within the aromatic absorptions. [k] Absorptions owing to the *ortho*-hydrogens in the two equatorial and one axial phenyl groups on tin (type *D*).

TABLE V. Tin-119m Mössbauer Data of Di- and Triorganotin(IV) Hydroxylaminates *vs.* $Ca^{119m}SnO_3$ at 77 K.

Compound No.	IS ($mm\ s^{-1}$) ±0.03	QS ($mm\ s^{-1}$) ±0.06	ρ (QS/IS)	<C–Sn–C (°) (see text)
$(n\text{-}C_4H_9)_2SnCl_2$[a]	1.60	3.25	2.03	134.8
I	1.31	3.29	2.51	136.0
II	1.32	3.34	2.53	137.5
III	1.31	3.24	2.47	134.5
IV	1.31	3.24	2.47	134.5
V	1.34	3.23	2.41	134.2
VI	1.37	3.33	2.43	137.2
VII	1.37[b]	3.53[c]	2.58	143.5
VIII	1.28	3.09	2.41	130.2
$(C_6H_5)_2SnCl_2$[d]	1.38	2.75	1.99	127.2
IX	0.83	1.86	2.24	[e]
X	0.84	1.68	2.00	[e]
XI	0.78	1.87	2.40	[e]
XII	0.82	1.95	2.38	97.7
XIII	0.82	1.94	2.37	96.8
XIV	0.86	1.92	2.23	94.9
XV	0.80	1.79	2.24	[e]
XVI	0.79	1.91	2.42	93.4
$(C_6H_5)_3SnCl$[f]	1.293	2.55	1.97	
XVII	0.78	1.87	2.39	
XVIII	0.98	1.90	1.94	
XIX	0.80	1.80	2.25	
XX	1.03	1.99	1.93	
XXI	0.81	1.96	2.42	
XXII	0.86	1.88	2.19	
XXIII	0.81	1.82	2.25	
XXIV	0.81	1.93	2.38	

[a] C. Yu. Aleksandrov, Ya. G. Dorfman, O. L. Lependina, K. P. Mitrofanov, M. V. Plotnikova, L. S. Polak, A. Yu. Temkin and V. S. Shpinel, *Russ. J. Phys. Chem. 38,* 1185 (1964) (Engl. Transl.), as quoted in ref. 31. [b] ±0.05. [c] ±0.10. [d] N. W. G. Debye, E. Rosenberg and J. J. Zuckerman, *J. Am. Chem. Soc., 90,* 3234 (1968). [e] Model fails. [f] B. W. Fitzsimmons, J. Ensling, P. Gutlich and K. M. Hasselbach, *J. Chem. Soc., A,* 1940 (1971).

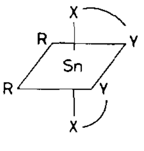
2.23–2.32 ppm, whereas the CH_3 protons of the acetyl group are found at $\delta = 2.07$ ppm in $(C_6H_5)_3Sn(APHA)$ (XXIII), $\delta = 1.93$ and 2.03 ppm in VIII and $\delta = 2.10$ ppm in XV as singlets. For the two diorganotin(IV) bis(N-2-iodobenzoyl-N-phenylhydroxylaminates), a pair of singlets (or a doublet) also appear at $\delta = 7.65$ and 7.75 ppm and $\delta = 7.56$ and 7.76 ppm downfield from the main aromatic signals which are centered at $\delta = 7.10$ ppm and $\delta = 7.20$ ppm for the di-n-butyl and di-phenyltin(IV) compounds, respectively. These absorptions are possibly due to the *ortho*-hydrogens of the ligands [11]. In the di-n-butyltin(IV) derivative of (N,N-3,5-dinitrobenzoyl)phenylhydroxylamine (VII), additional absorptions occur probably owing to further inequivalence of the *ortho*-hydrogens. The PMR studies indicate that the compounds are of the stoichiometry reported.

Mössbauer Spectra

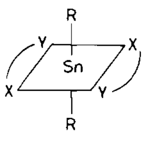
The Mössbauer spectral data are given in Table V. The isomer shifts (IS) reflect the tin(IV) state in all the compounds [34]. The observed IS values of di-n-butyl-, diphenyl- and triphenyltin(IV) hydroxylaminates are in the range 1.28–1.37, 0.78–0.86 and 0.78–1.03 mm s^{-1}, respectively. These IS values are smaller than those for the corresponding neutral precursors $(n\text{-}C_4H_9)_2SnCl_2$, $(C_6H_5)_2SnCl_2$ and $(C_6H_5)_3SnCl$. These observations are found to be general in going to 5- and 6-coordinated species whether charged or not, although there are exceptions [34].

The quadrupole splitting (QS) values for all the di-n-butyl-, diphenyl- and triphenyltin(IV) hydroxylaminates are 3.09–3.53, 1.68–1.95 and 1.80–1.99 mm s^{-1}, respectively.

Since the C=O donor site is strongly coordinating as indicated by IR spectra for the diorganotin(IV) hydroxylaminates, octahedral coordination about tin is formed; if the chelate bonds intramolecularly to form discrete molecular species, then two stereoisomers *cis*-$R_2Sn(X{-}Y)_2$ (*E*) and *trans*-$R_2Sn(X{-}Y)_2$ (*F*) (X–Y = bidentate ligand) are possible. But intermolecular bridging by the ligands can lead to the formation of dimeric (*G*) or oligomeric or polymeric

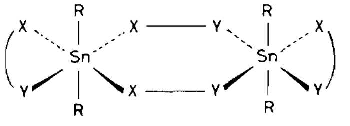


(E)

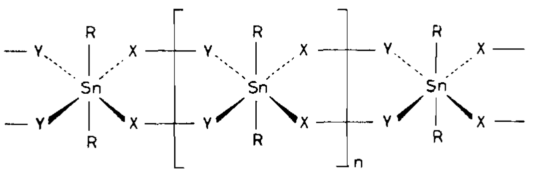


(F)

(*H*) structures which can also contain *cis-* or *trans-* R_2Sn moieties. However, polymeric structures (*H*) are less likely on the basis of the solubility of the compounds.



(G) (can also be cis-)



(H) (can also be cis-)

The *cis-* and *trans-*octahedral complexes of the type SnA_2B_4 can be differentiated by their QS values with the help of calculations from a point-charge model which predict the ratio of the QS values of the *trans-* and *cis-*isomers as equal to 2. The actual values for the complexes of the type R_2SnX_4 where the X atom is Cl or N or O as part of an organic ligand are approximately $|QS|_{cis} \sim 2$ and $|QS|_{trans} \sim 4$ mm s^{-1} [34].

The QS values of $(CH_3)_2Sn[ON(CH_3)COCH_3]_2$ which has a distorted *trans-*octahedral structure with C–Sn–C bond angle of 145.8° [28] is 3.31 mm s^{-1} [35]. A similar structure has been suggested for $(CH_3)_2Sn(BPHA)_2$ from its QS value of 3.07 mm s^{-1} [35]. Accordingly, distorted *trans-*octahedral structures (*A*) are suggested for all the di-n-butyltin(IV) bis(hydroxylaminates) studied here from their QS values of 3.09–3.53 mm s^{-1} (see Table V for the calculated C–Sn–C angles). The compound $(CH_3)_2Sn(ONHCOCH_3)_2$ has a QS value of 2.01 mm s^{-1} [28], indicating a *cis-*dimethyltin configuration which has also been confirmed by X-ray study [28].

The point charge model can be used to rationalize the changes in the magnitude of QS values as a function of the C–Sn–C angle in six-coordinated diorganotin(IV) compounds [36] as given by the following equation:

$$|QS| = 4\{R\}[1 - 3 \sin 2\theta \cos 2\theta]^{1/2} \qquad (3)$$

where R = the partial quadrupole splitting value for R, and C–Sn–C = $(180 - 2\theta)^\circ$. This observation is supported by abundant data on six-coordinated dimethyl [33, 36] and diphenyltin(IV) [37] compounds.

The QS values of 1.68–1.95 mm s^{-1} in the diphenyltin compounds are very close to 2. This indicates that these compounds possess *cis-*octahedral structure (*B*) (see Table V). This suggestion is in conformity with the QS values obtained for diphenyltin(IV) bis(acetylacetonates) (2.7–2.07 mm s^{-1}) [38], diphenyltin(IV) bis(oxinate) (1.78 mm s^{-1}) [30a], $(C_6H_5)_2Sn(BPHA)_2$ (1.80 mm s^{-1}) and $(C_6H_5)_2Sn\ [ON(CH_3)COCH_3]_2$ (1.61 mm s^{-1}) [35].

The triphenyltin(IV) hydroxylaminates may exist in either of the two possible trigonal bipyramidal structures, (*C*) and (*D*); in one, two equatorial and one axial position are occupied by phenyl groups (*D*); and in the other, one equatorial and two axial positions are occupied by phenyl groups (*C*). The QS values of 1.80–1.99 mm s^{-1} for the triphenyltin(IV) compounds cannot differentiate between the two stereoisomers. However, $(C_6H_5)_3Sn(BPHA)$ [32] possess a structure in which two equatorial and one axial positions are occupied by phenyl groups (type *D*).

The coordination number at tin is reflected in the ratio of QS to IS values (QS/IS = ρ); ρ values are greater than 2.1 when the coordination number of tin is greater than four, while values of 1.8 or lower are associated with four-coordination [34].

For the di-n-butyltin(IV) bis(hydroxylaminates), the ρ values are 2.41–2.53, suggesting greater than four-coordination. For the diphenyltin(IV) compounds, the ρ values are 2.23–2.62, with the exception of compound X for which a value of 2.0 is obtained. This is, however, possibly owing to the poor quality of the spectrum obtained from insufficient sample. For the triphenyltin(IV) hydroxyaminates, ρ values of greater than 2.1 (except XVIII and XX) suggest that the coordination number is greater than four. The ρ value for $(C_6H_5)_3Sn[ON(C_6H_5)COC_6H_5]$ is reported as 1.77 (IS = 1.26, QS = 1.94 mm s^{-1}) [39]. This value is much lower than that expected for pentacoordination, although X-ray data confirm the pentacoordinated structure [32]. However, for this compound we have obtained the ρ value of 2.39, which is in conformity with the known five-coordinated structure. Several triphenyltin(IV) derivatives of analogous ligands such as oxines [40, 41] and acetylacetones [31] have ρ values less than 1.8, but these have been suggested to be pentacoordinated [31, 40, 41]. The triphenyltin(IV) hydroxylaminates, except XVIII and XX, have ρ values between 2.19 and 2.42, suggesting that these are five-coordinated. Compounds XVIII and XX exhibit ρ values of 1.94 and 1.93, respectively, which are close to the value of 1.97 for triphenyltin(IV) chloride [40] which is monomeric and four-coordinated in the solid [42]. Therefore, these two compounds appear to be tetracoordinated without C=O coordination.

Acknowledgements

MKD wishes to express thanks to the UGC, India for financial assistance. Thanks are due to Prof. U. R. Ghatak and Mr. Ajoy Mukherjee, and Dr. N. Raychaudhuri, all of IACS, respectively, for ^1H NMR and IR spectra, and Dr. B. K. Nath of IICB for UV spectra. The work of the Oklahoma group is supported by the U.S. National Science Foundation through Grant No. CHE-78-26584 and the Office of Naval Research.

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