

Oxalyl-bis(N-phenyl/N-*p*-tolyl)hydroxamic Acids as Coordinating Ligands: Coordination Compounds with Organotins

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Two new ligands, viz. oxalyl-bis(N-phenyl/N-*p*-tolyl)hydroxamic acids (LH₂ and L'H₂) have been synthesised and characterised. These have been used to prepare some new types of organotin coordination compounds, (R₃Sn)₂L (R = phenyl), (R₃Sn)₂L' (R = phenyl, cyclohexyl), (R₂SnL)_n (R = phenyl, butyl, benzyl), [(R₂SnCl)₂L]₂ and [(R₂SnCl)₂L']₂ (R = *p*-tolyl). Some of these derivatives are found to be polymeric in nature.

Literature survey reveals that organotin hydroxamates such as (R₃Sn)₂L (where L = hydroxamic acid) have not been reported so far. The present study embodies the synthesis of two new ligands, viz. oxalyl-bis(N-phenyl/N-*p*-tolyl)hydroxamic acids (LH₂ and L'H₂ respectively) having two hydroxamic acid residues on both ends of dibasic acyl group. Involvement of both the coordination centres leads to the formation of novel coordination compounds of the type (R₃Sn)₂L.

Materials and Methods

Oxalyl-bis(N-phenyl) hydroxamic acid (LH₂)

It was synthesised by the slow addition of oxalyl chloride (8 g) to a solution of recrystallised and dried β-phenylhydroxylamine (16 g) in dry ether containing dry pyridine (8 g) at -10° to -15°C. The gummy mass so obtained was repeatedly extracted with 5N ammonia, washed with ether and acidified to pH 3 by

Table 1—Reaction Conditions and Characterisation Data of Organotin Compound of Oxalyl-bis(N-phenyl-*p*-tolyl) Hydroxamic Acids

Compound	Reactants		Ratio used (M:L)	m.p. °C	Found (Calc.) %				Mol. wt. found (Calc.)
	Organotin	Hydroxamic acid			N	C	H	Sn	
Bis(triphenyltin)-oxalyl-bis(N- <i>p</i> -tolyl) hydroxamate, [(Ph ₃ Sn) ₂ L'] (1)	(Ph ₃ Sn) ₂ O	L'H ₂	1.4:1	201-2	2.9 (2.8)	62.5 (63.1)	4.68 (4.4)	—	
Bis(tricyclohexyltin)-oxalyl-bis(N-tolyl) hydroxamate, [(R' ₃ Sn) ₂ L'] (2)	2R' ₃ SnBr (R' = cyclohexyl)	L'H ₂	2.2:1	248-50				23.2 (23.01)	
Dibenzyltin oxalyl-bis-(N- <i>p</i> -tolyl) hydroxamate, [Bz ₂ SnL'] ₂ (3)	(Bz ₃ Sn) ₂ O (Bz = benzyl)	L'H ₂	1:1	204-5	4.51 (4.67)	60.05 (60.1)	4.62 (4.67)	1118 (1198)	
Diphenyltin oxalyl-bis-N(- <i>p</i> -tolyl) hydroxamate, [Ph ₂ SnL'] (4)	Ph ₂ SnO	L'H ₂	1:1	240 (d)	4.45 (4.9)			20.9 20.8 1730 (1713)	
Dibutyltin oxalyl-bis-(N- <i>p</i> -tolyl) hydroxamate [Bu ₂ SnL'] ₄ (5)	Bu ₂ SnO	L'H ₂	1:1	205	51.33 54.2	6.19 (6.02)		23.2 22.4 2004 (2124)	
Bis[di(- <i>p</i> -tolyl)chlorotin]-oxalyl-bis(N- <i>p</i> -tolyl) hydroxamate [(R'' ₂ SnCl) ₂ L'] ₂ (6)	2R'' ₂ SnCl ₂ (R'' = <i>p</i> -tolyl)	L'H ₂	2:1	196-97	54.85 54.37	5.2 (4.3)		1953 (1942)	
Bis(triphenyltin) oxalyl-bis(N-phenyl) hydroxamate, [(Ph ₃ Sn) ₂ L] (7)	(Ph ₃ Sn) ₂ O	LH ₂	1.1:1	203-4	3.2 2.9			25.01 24.5 —	
Bis[di(- <i>p</i> -tolyl)chlorotin]-oxalyl-bis(N-phenyl) hydroxamate, [(R'' ₂ SnCl) ₂ L] ₂ (8)	2R'' ₂ SnCl ₂ (R'' = <i>p</i> -tolyl)	LH ₂	2:1	160(d)	2.8 3.0	50.0 (53.4)	4.02 (4.03)	24.8 (25.2) 1970 (1886)	

the addition of HCl when the compound precipitated. On decoloration with active charcoal and recrystallisation from rectified spirit, ash coloured compound (2.5 g) was obtained, m.p. 180° (Found: N, 9.7. $C_{14}H_{12}N_2O_4$ requires N, 10.3%); IR (nujol): 3170 (br, $\nu O-H$) 1625 (vs. $\nu C=O$), 900 cm^{-1} (m, $\nu N-O$); PMR (CH_3OD): δ 7.74 (2H, ring *ortho*); 7.23 (3H, ring *meta-para*).

Oxalyl-bis(N-p-tolyl) hydroxamic acid (L'H₂)

It was similarly prepared using recrystallised *p*-tolylhydroxylamine (17 g); yield 2.5 g (white); m.p. 194-95° (Found: C, 63.6; H, 5.5; N, 10.3. $C_{16}H_{16}N_2O_4$ requires C, 64.0; H, 5.5; N, 9.3%); IR (nujol): 3200 (br,

$\nu O-H$), 1640 (vs. $\nu C=O$), 901 cm^{-1} (m, $\nu N-O$); PMR (CH_3OD): δ 7.6 (2H, ring *ortho*), 7.05 (2H, ring *meta*), 2.2 (3H, tolyl methyl group).

Preparation of organotin (IV) derivatives

Organotin compounds of the types $[(R_3Sn)_2L]$ and $[R_2SnL']_n$ have been prepared by the azeotropic distillation of water from a mixture of bis(triorganotin) oxide and the ligand or from a mixture of diorganotin oxide and the ligand in appropriate proportions (Table I) respectively. Except for $[(Ph_3Sn)_2L]$, $[Bz_2SnL']_2$ and $[(Ph_3Sn)_2L]$ where the yields were about 80%, in other cases the yields varied from 50 to 65%. In the case of $[(R_2SnCl)_2L]_2$ and $[(R_2SnCl)_2L']_2$

Table 2—IR and PMR Data ($CDCl_3$) of Various Organotin Hydroxamates

Compd*	Ligand moiety			Organotin moiety			
	$\nu(C=O)$ (cm^{-1})	Band centre δ , ppm	Multiplicity	J	Band centre δ , ppm	Multiplicity	J
1	1595			—			—
	1570						
2	1570			—			—
3	1555	7.06 (<i>ortho</i> H of one ring & <i>meta</i> H of two rings)	Doublet ($J=9$ Hz)	—	6.77 (<i>ortho</i> H of one ring & <i>meta-para</i> H of two rings)	Complex multiplet	—
		6.35 (<i>ortho</i> H of another ring)	—do—	—	6.14 (<i>ortho</i> H of another ring)	Doublet ($J=9$ Hz)	—
		2.12 (CH_3-)	—do— ($J=20.7$ Hz)	—	2.56 ($-CH_2-$)	Quartet ($J=18, 11.7$ and 11.7 Hz)	—
4	1570	6.59 (<i>ortho</i> H of one ring & <i>meta</i> H of two rings)	—do— ($J=7.2$ Hz)	—	7.56 (<i>meta-para</i> H of one ring)	Quintuplet ($J=4.5, 4.5, 2.0$ and 4.5 Hz)	—
		6.36 (<i>ortho</i> H of another ring)	—do— ($J=9$ Hz)	—	7.22 (<i>ortho</i> H of two rings & <i>meta-para</i> H of another ring)	Doublet ($J=9$ Hz)	9 Hz
		1.93 (CH_3-)	—do— ($J=44$ Hz)	—			
5	1575	7.12 (one <i>ortho</i> H of one ring)	Singlet	—	2.25 (CH_3-)	Singlet	—
		6.85 (other <i>ortho</i> H of the former ring & four H of the other ring)	Complex multiplet	—	0.93 ($-CH_2-$)	Complex multiplet	—
		0.86 (CH_3-)	Singlet	—			
6	1570	7.36 (<i>ortho</i> H of one ring)	Doublet ($J=9$ Hz)	—	7.59 (<i>ortho</i> H of one ring)	Doublet ($J=10$ Hz)	—
		6.56 (<i>ortho</i> H of another ring & <i>meta</i> H of two rings)	—do— ($J=7$ Hz)	7 Hz	7.12 (<i>ortho</i> H of another ring & <i>meta</i> H of two rings)	—do— ($J=7$ Hz)	—
		2.15 (CH_3-)	Singlet	—	2.31 (CH_3-)	—do— ($J=4$ Hz)	—
7	1560		—	—			—
8	1570		—	—			—

*Sl. Nos. refer to compounds listed in Table 1.

(where R = *p*-tolyl), the liberated HCl was neutralised with 25% aq. ammonia and removed as NH₄Cl.

One typical procedure is described below.

Preparation of [(Ph₃Sn)₂L']

Bis(triphenyltin) oxide (1 g) and L'H₂ (0.3 g) in benzene (150 ml) were refluxed for 3 hr using a Dean and Stark water separator. The yellow coloured solution was filtered and concentrated. On adding petroleum ether white compound appeared which was purified from the same solvents and dried over anhydrous CaCl₂; yield 0.85 g.

Results and Discussion

As expected molecular weight data (osmometry in CHCl₃) indicate that in the case of diorganotin derivatives polymeric compounds like [Ph₂SnL']₃ and [Bu₂SnL']₄ are formed (Table 1). These compounds have been obtained using starting materials like Ph₂SnO, Bu₂SnO etc. which can supply only one organotin moiety to one ligand molecule when reacted in 1:1 molar ratio. [Bz₂SnL']₂, [(R₂SnCl)₂L']₂ and [(R₂SnCl)₂L']₂ (where R = *p*-tolyl) are also dimers. Unlike adipyl bis(*N*-phenyl) hydroxamic acid, where the two hydroxamic acid groups are separated by four CH₂ units thereby acting as a tetradentate ligand^{1,2}, the ligands under discussion have two such coordinating groups directly attached to each other.

The IR spectra of the two ligands LH₂ and L'H₂ exhibit peaks around 3170 and 3200 cm⁻¹, respectively assignable to νOH involved in strong intramolecular hydrogen bonding. As a result of this νC=O modes are also shifted to lower wavenumbers and appear around 1625 and 1640 cm⁻¹ respectively³. None of the organotin derivative of the two ligands (LH₂ and L'H₂) shows any band corresponding to νOH. Besides this, νC=O modes of the free ligands are shifted by 65-85 cm⁻¹ to lower wavenumbers in the

spectra of the organotin derivatives (Table 2). These results show that the ligands are strongly coordinated through both the hydroxamic acid groups³. As each hydroxamic acid residue occupies two coordination positions on the tin atom, for compounds of the type [(R₃Sn)₂L] and [(R₃Sn)₂L'] (R = phenyl) trigonal bipyramidal structures containing pentacoordinated tin cannot be ruled out⁴⁻⁶. For compounds of the type [R₂SnL']_n, a coordination number of six is assigned which indicates octahedral structure.

It is observed that for all the organotin derivatives of LH₂ and L'H₂ the ring protons are shielded as compared to those of the free ligands. This type of shielding arises possibly due to the presence of -O-N-CO-CO-N-O- skeleton^{5,6}. In the chelate molecule the two rings are possibly disposed in such a manner that the ring current effect of one aromatic ring shields the proton on the other ring and vice-versa. The observed shielding of the methyl protons (2.2 ppm) of L'H₂ in some of the organotin derivatives, may be due to the ring current effect or solvent effect.

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