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Synthesis, Spectral Studies and Antifungal Activity of β-Diketonate Complexes of Bimetallic Organotin(IV) aluminium(III)-μ-oxoalkoxides

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Organotin derivatives of the type PhMeSn(OAc)OAl (OPr^i)(L), PhMeSn(OAc)OAl$(L)_2$, $PhMeSnO_2Al_2(OPr^i)_3(L)$ and $PhMeSnO_2Al_2(OPr^i)_2(L)_2$ have been synthesized by the reaction of PhMeSn(OAc)OAl$(OPr^i)_2$ (**1**) and $PhMeSnO_2Al_2(OPr^i)_4$ (**2**) with β-diketones in 1:1 and 1:2 molar ratio in refluxing benzene. These complexes have been characterized by elemental analysis and spectral studies (IR, ^1H, ^{13}C, ^{27}Al and ^{119}Sn NMR). The results of antifungal activity of the complexes as well as precursors have also been recorded and discussed with the standard fungicide against *Colletotrichum falcatum*.

Key Words: Organotin, Bimetallic complexes, Spectral, Antifungal, β-Diketonate.

INTRODUCTION

Metal alkoxides have attracted a great deal of attention in recent years due to their wide range of application in various fields like high tech ceramics[1-5] as they have high heat resistance, biocompatibility, special electrical and optical properties, preparation of superconducting oxides[6,7], petrochemical industries[8], paints and textile industries[9-11] and in synthesis of number of industrially important polymers[12].

Bimetallic-μ-oxoalkoxides containing M–O–M' units could be of great interest in modeling the synergistic effect existing between the oxobridged metals[13]. A large number of bimetallic-μ-oxoalkoxides having transition metal have been synthesized[14,15]. These bimetallic-μ-oxoalkoxides are among the best catalyst for polymerization of heterocyclic monomers. Kapoor *et al.*[16-18] reported the synthesis of bimetallic-μ-oxoalkoxides containing a main group metal atom in place of transition metal. In recent years, lot of work has been done on bimetallic-μ-oxoalkoxides containing symmetrical tin but no work has been done on bimetallic-μ-oxoalkoxides containing unsymmetrical tin.

We report here the synthesis of two new bimetallic-μ-oxoalkoxides (**1**) and (**2**) containing unsymmetrical tin. In order to gain more information about the structures of these complexes, we have also synthesized their benzoylacetone [Hbzac], acetylacetone [Hacac] and hexafluoropentanedione [Hhfpd] derivatives.

EXPERIMENTAL

All manipulations were carried out in an inert atmosphere on a vacuum line by using Schlenk technique. During the course of synthesis, special precautions were taken to exclude moisture from the apparatus and chemicals. Special weighing bottles with standard joints were used for sampling of compounds for analytical purposes. Aluminium isopropoxide and phenylmethyltin chloride were prepared by reported methods[19]. Estimation of acetoxy group and isopropoxy group was done as described elsewhere[20]. Estimation of tin and aluminium was done as tin oxide and aluminium oxinate, respectively[21].

IR spectra were recorded as thin films on KBr plates using Schimadzu 8000 FTIR spectrophotometer. ^{1}H NMR spectra were recorded on Perkin-Elmer R-32, 90 MHz spectrometer. ^{13}C, ^{27}Al, ^{119}Sn NMR spectra were recorded on Bruker-300, 300 MHz instrument with TMS, $AlCl_3 \cdot 6H_2O$ and $(CH_3)_4Sn$, respectively at SAIF, Chandigarh.

Preparation of PhMeSn(OAc)OAl(OPr^i)$_2$: PhMeSn(OAc)OAl(OPr^i)$_2$ **(I)** was prepared[22] by refluxing phenylmethyltin diacetate (1.85 g, 5.62 mmol) and aluminium isopropoxide (1.15 g, 5.62 mmol) in xylene for 6 h on Dean Stark apparatus. The isopropyl acetate so formed was collected continuously from 80-139ºC. The excess of xylene was distilled off to give light yellow solid. The product was then recrystallized in benzene to give light yellow solid.

Preparation of PhMeSnO$_2$Al$_2$(OPr^i)$_4$: PhMeSnO$_2$Al$_2$(OPr^i)$_4$ **(II)** was prepared[22] by refluxing phenylmethyltin diacetate (3.36 g, 10.20 mmol) and aluminium isopropoxide (4.16 g, 20.40 mmol) in xylene for 8 h on Dean Stark apparatus. The isopropyl acetate so formed during the reaction was collected continuously from 80-139ºC. The reaction was continued further for 1 h to ensure the completion. The excess of xylene was distilled off at 40ºC/1 mmHg leaving behind yellow solid. The product was then recrystallized in benzene, which on slow evaporation of benzene gave yellow solid.

Reaction of PhMeSn(OAc)OAl(OPr^i)$_2$ with benzoylacetone in 1:1 molar ratio: Benzoylacetone (0.18 g, 1.14 mmol) was added to solution of PhMeSn(OAc)OAl(OPr^i)$_2$ (0.47 g, 1.14 mmol) in 50 mL benzene. The reaction mixture was refluxed for 6 h. The binary azeotrope of isopropanol-benzene was collected at 72-80ºC. Oxidimetric method was used to

determine the completion of reaction. Excess of solvent was distilled off at 40ºC/1 mmHg leaving behind creamish solid.

Reaction of PhMeSn(OAc)OAl(OPr^i)$_2$ with benzoylacetone in 1:2 molar ratio: To a solution of PhMeSn(OAc)OAl(OPr^i)$_2$ (0.51 g, 1.18 mmol) in 40 mL benzene, benzoylacetone (0.38 g, 2.36 mmol) was added. The reaction contents were refluxed for 8 h. At 72-80ºC, isopropanol was collected as binary azeotrope of isopropanol-benzene. The completion of the reaction was checked by oxidimetric method. Excess of solvent was distilled off under reduced pressure at 40ºC/1 mmHg. The creamish coloured product was obtained after crystallization.

Similar procedure was employed for the reactions of PhMeSn(OAc)OAl (OPr^i)$_2$ and PhMeSnO$_2$Al$_2$(OPr^i)$_4$ with other β-diketones in 1:1 and 1:2 molar ratios. Details along with the analytical data are given in Table-1.

The antifungal activity of the complexes was evaluated against *Colletotrichum falcatum*, a phytopathogenic fungus. Czepek's Dox agar medium[23] was used for growing culture of fungus. Two-fold serial dilution technique[24] was used to determine the minimum inhibitory concentration (MIC). Solution of different concentrations were prepared in DMSO. Then growth of fungus was measured after 72 h. Then percentage inhibition was calculated by the formula 100(C-T)/C (Where C = Diameter of the fungus in control and T = Diameter of the fungus in test)[25]. Bavistin was used as standard fungicide to compare the results with the other complexes.

RESULTS AND DISCUSSION

PhMeSn(OAc)OAl(OPr^i)$_2$ and PhMeSnO$_2$Al$_2$(OPr^i)$_4$ have been prepared by refluxing phenylmethyltin diacetate and aluminium isopropoxide in 1:1 and 1:2 molar ratios, respectively in xylene. The reactions can be depicted as follows:

$$PhMeSn(OAc)_2 + Al(OPr^i)_3 \xrightarrow{Xylene} PhMeSn(OAc)OAl(OPr^i)_2 + Pr^iOAc \quad (\mathbf{I})$$

$$PhMeSn(OAc)_2 + 2Al(OPr^i)_3 \xrightarrow{Xylene} PhMeSnO_2Al_2(OPr^i)_4 + 2Pr^iOAc \quad (\mathbf{II})$$

The above reaction involves stepwise replacement of the acetyl groups, as was confirmed by determining the isopropyl acetate liberated during the progress of the reaction. Compounds (**1** and **2**) were yellow solid, highly susceptible to hydrolysis and soluble in common organic solvents.

The reaction of (**1**) and (**2**) with β-diketones may be represented as follows:

$$PhMeSn(OAc)OAl(OPr^i)_2 + nHL \xrightarrow{Benzene/Reflux} PhMeSn(OAc)OAl(OPr^i)_{2-n}L_n + n\,Pr^iOH$$

$$PhMeSnO_2Al_2(OPr^i)_4 + nHL \xrightarrow{Benzene/Reflux} PhMeSnO_2Al_2(OPr^i)_{4-n}L_n + n\,Pr^iOH$$

(where n = 1-2 and L = bzac, acac and hfpd)

TABLE-1
ANALYTICAL DATA OF β-DIKETONATES OF (**I** AND **II**)

Compound g (mmol)	Ligand g (mmol)	Molar ratio	Refluxing time (h)	Product	Analysis Found (Calcd.)		
					Sn (%)	Al (%)	OPr^i (g)
$PhMeSn(OAc)OAl(OPr^i)_2$	Hbzac	1:1	6	$PhMeSn(OAc)OAl(OPr^i)(bzac)$	21.8	4.7	0.07
0.47 (1.14)	0.18 (1.14)				(22.3)	(5.0)	(0.07)
$PhMeSn(OAc)OAl(OPr^i)_2$	Hbzac	1:2	8	$PhMeSn(OAc)OAl(bzac)_2$	18.3	3.8	0.14
0.51 (1.18)	0.38 (2.36)				(18.7)	(4.2)	(0.14)
$PhMeSn(OAc)OAl(OPr^i)_2$	Hacac	1:1	6	$PhMeSn(OAc)OAl(OPr^i)(acac)$	24.7	5.2	0.07
0.50 (1.16)	0.12 (1.16)				(25.2)	(5.7)	(0.07)
$PhMeSn(OAc)OAl(OPr^i)_2$	Hacac	1:2	8	$PhMeSn(OAc)OAl(acac)_2$	22.8	4.9	0.19
0.68 (1.58)	0.32 (3.16)				(23.2)	(5.3)	(0.19)
$PhMeSn(OAc)OAl(OPr^i)_2$	Hhfpd	1:1	6	$PhMeSn(OAc)OAl(OPr^i)(hfpd)$	20.1	4.2	0.07
0.52 (1.20)	0.25 (1.20)				(20.5)	(4.7)	(0.07)
$PhMeSn(OAc)OAl(OPr^i)_2$	Hhfpd	1:2	8	$PhMeSn(OAc)OAl(hfpd)_2$	16.0	3.3	0.16
0.60 (1.39)	0.58 (2.78)				(16.3)	(3.7)	(0.16)
$PhMeSnO_2Al_2(OPr^i)_4$	Hbzac	1:1	6	$PhMeSnO_2Al_2(OPr^i)_3(bzac)$	18.3	7.9	0.04
0.40 (0.75)	0.12 (0.75)				(18.7)	(8.5)	(0.04)
$PhMeSnO_2Al_2(OPr^i)_4$	Hbzac	1:2	8	$PhMeSnO_2Al_2(OPr^i)_2(bzac)_2$	15.6	7.2	0.09
0.40 (0.75)	0.24 (1.50)				(16.1)	(7.3)	(0.09)
$PhMeSnO_2Al_2(OPr^i)_4$	Hacac	1:1	6	$PhMeSnO_2Al_2(OPr^i)_3(acac)$	20.1	9.3	0.06
0.52 (0.97)	0.09 (0.97)				(20.7)	(9.4)	(0.06)
$PhMeSnO_2Al_2(OPr^i)_4$	Hacac	1:2	8	$PhMeSnO_2Al_2(OPr^i)_2(acac)_2$	18.7	8.0	0.13
0.59 (1.10)	0. 22 (2.20)				(19.3)	(8.8)	(0.13)
$PhMeSnO_2Al_2(OPr^i)_4$	Hhfpd	1:1	6	$PhMeSnO_2Al_2(OPr^i)_3(hfpd)$	17.0	7.6	0.05
0.48 (0.90)	0.19 (0.90)				(17.4)	(7.9)	(0.05)
$PhMeSnO_2Al_2(OPr^i)_4$	Hhfpd	1:2	8	$PhMeSnO_2Al_2(OPr^i)_2(hfpd)_2$	14.0	5.8	0.01
0.44 (0.82)	0.34 (1.64)				(14.3)	(6.2)	(0.01)

The isopropanol liberated in the reaction was collected azeotropically as binary azeotrope of isopropanol-benzene and was estimated oxidimetrically.

The complexes thus obtained were pale yellow solid, soluble in benzene, chloroform, carbon tetrachloride, DMSO and hexane, susceptible to hydrolysis and tend to decompose on heating. The fact that further isopropoxy groups were not displaced even with an excess of ligand and increase in refluxing time indicate that two types of isopropoxy groups were present *i.e.* bridging and terminal. Bridging isopropoxy groups were not usually displaced.

IR Spectra: The IR spectra of (**1**) shows a strong band at 1595 and 1450 cm^{-1} due to ν_{asym}(C–O) and $\nu_{sym}(COO)^-$ stretching, respectively but these bands are found to be absent in (**2**), suggesting the presence of acetoxy group in the former compound.

In the IR spectra of β-diketonates the ν(O–H) band occurring at 3100 cm^{-1} disappears completely, thus indicating deprotonation of the β-diketone. The bands observed between 1620-1590 cm^{-1} are assigned to ν_{asym}(C=O) and ν_{sym}(C=O) of acetoxy and β-diketone. A band observed at 1520-1515 cm^{-1} is assigned to the ν_{sym}(C=C) vibration of the β-diketone moiety. The non-shifting of the ν_{sym}(C=C) band observed in the β-diketone confirms that both carbonyl groups are coordinating. The bands appearing at 1160 and 1100 cm^{-1} are due to ν(C–O + Pr^i–O) terminal and bridging groups, respectively. The band at 1080 cm^{-1} is due to ν(C–F). The band appearing at 950 cm^{-1} is due to the bridging isopropoxy groups and is absent in 1:2 derivatives of (**1**) indicating the complete replacement of the isopropoxy groups[26]. A number of bands observed in the region 575-420 cm^{-1} are due to ν(Sn–C) and ν(M–O) vibrations.

^{1}H NMR Spectra: ^{1}H NMR spectra of β-diketones display a signal at 13 ppm due to enolic –OH which is absent in the derivatives of (**I** and **II**) suggesting that the replacement of proton takes place in the enolic form. The signals observed in the region 7.6-6.9 ppm are assigned to the phenyl group attached to tin and phenyl ring protons of the ligand. A singlet at 6.4-6.2 ppm is assignable to methine proton of the ligand moiety. A multiplet in the range 4.0-3.8 ppm in some complexes is due to methine proton of the isopropoxy group. The proton integration area of methine protons of the isopropoxy groups to methyl of acetoxy is consistent with the replacement of one acetoxy group only in compound (**I**) and its derivatives. A broad signal centered at 2.1 ppm in the complexes is due to mixing of methyl protons of acetoxy and ligand. A broad overlapping multiplet in the region 1.3-0.7 ppm is due to the mixing of methyl protons of the bridging and terminal isopropoxy groups along with the protons of methyl group.

^{13}C NMR Spectra: ^{13}C NMR spectra of complexes of (**I** and **II**) display signals in the range 193.7-183.1 ppm due to carbonyl carbons. Phenyl ring carbons are observed in the range 145.6-126.9 ppm. The signal observed at 117.8 ppm is due to carbon of the $–CF_3$ group in hfpd derivatives. A sharp singlet observed at 95.1-93.2 ppm is due to methine carbon of the ligand moiety. Two signals at 63.0 ppm and two signals at 27 ppm are assigned to two different types of methine and methyl carbons of the isopropoxy groups[27]. The spectra of complexes of (**II**) exhibit two additional peaks at 28.0 and 64.0 ppm due to methyl and methine carbons of intramolecularly bridged isopropoxy moiety. No isopropoxy signals are observed in the 1:2 derivatives of (**I**), thus suggesting the complete substitution of the isopropoxy groups by β-diketone. Methyl carbon appears at its usual position *i.e.* at 5.8 ppm[28].

TABLE-2
FUNGICIDAL SCREENING DATA OF PRECURSORS AND β-DIKETONATES OF BIMETALLIC-μ-OXOALKOXIDES OF PHENYLMETHYLTIN DICHLORIDE
(% GROWTH INHIBITION AFTER THREE DAYS AT 30 ± 1ºC)

Complex	% Growth inhibition of Fungus conc. (ppm)		
	50	100	150
Hacac	6	12	18
Hbzac	5	12	16
Hhfpd	4	10	12
$PhMeSn(OAc)OAl(OPr^i)_2$	33	53	66
$PhMeSnO_2Al_2(OPr^i)_4$	26	37	51
$PhMeSn(OAc)OAl(OPr^i)(acac)$	30	42	56
$PhMeSn(OAc)OAl(acac)_2$	28	40	52
$PhMeSn(OAc)OAl(OPr^i)(bzac)$	28	42	50
$PhMeSn(OAc)OAl(bzac)_2$	22	38	48
$PhMeSn(OAc)OAl(OPr^i)(hfpd)$	24	32	45
$PhMeSn(OAc)OAl(hfpd)_2$	16	35	45
$PhMeSnO_2Al_2(OPr^i)_3(acac)$	26	32	46
$PhMeSnO_2Al_2(OPr^i)_2(acac)_2$	24	34	48
$PhMeSnO_2Al_2(OPr^i)_3(bzac)$	22	38	50
$PhMeSnO_2Al_2(OPr^i)_2(bzac)_2$	16	36	48
$PhMeSnO_2Al_2(OPr^i)_3(hfpd)$	18	32	44
$PhMeSnO_2Al_2(OPr^i)_2(hfpd)$	15	28	40
Bavistin ($C_{30}H_{24}N_2O_2$)	88	91	100

^{27}Al NMR Spectra: ^{27}Al NMR spectra of derivatives of (**I**) display a signal between 2.1-1.7 ppm which is due to the hexacoordinated Al atom. ^{27}Al NMR spectra of derivatives of (**II**) exhibit two signals at 71 and 2.0

ppm assignable to the tetrahedral and octahedral environment about the Al atom[29].

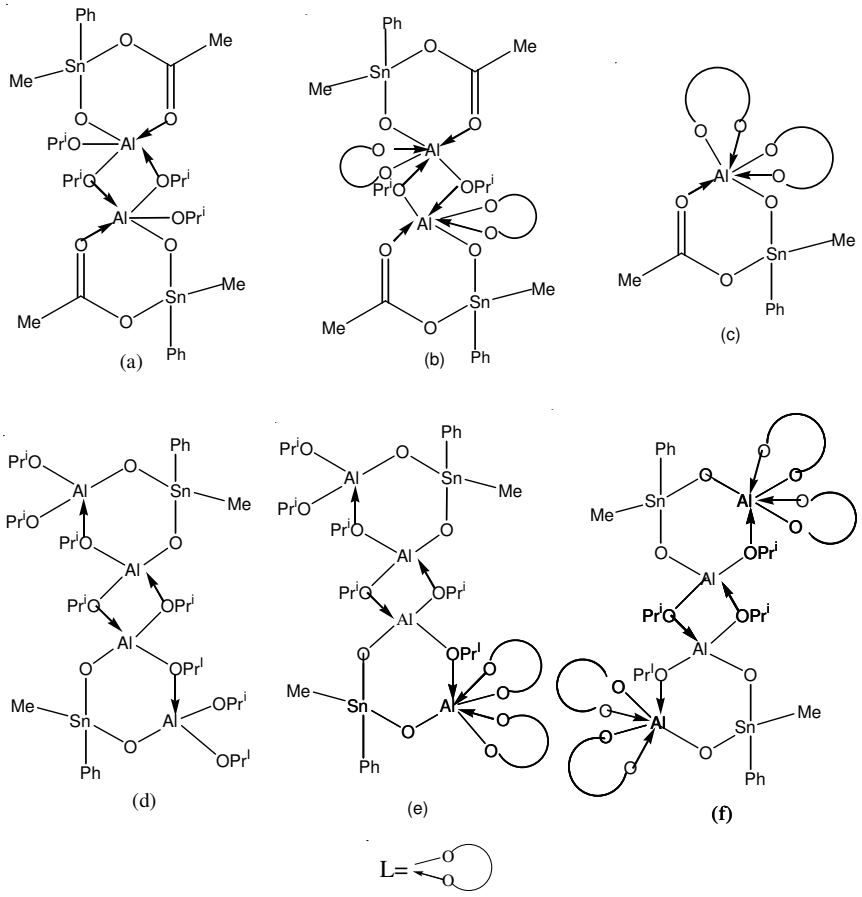

Fig. 1. Proposed structures of the complexes: (a) $PhMeSn(OAc)OAl(OPr^i)_2$, (b) $PhMeSn(OAc)OAl(OPr^i)(L)$, (c) $PhMeSn(OAc)OAl(L)_2$, (d) $PhMeSnO_2Al_2(OPr^i)_4$, (e) $PhMeSnO_2Al_2(OPr^i)_3(L)$ and (f) $PhMeSnO_2Al_2(OPr^i)_2(L)_2$

^{119}Sn NMR Spectra: ^{119}Sn NMR spectra of 1:1 and 1:2 derivatives of (**I** and **II**) produce signals at 79 ppm which are assignable to tetracoordinated[30] Sn atom.

Antifungal activity: Compound (**I**), (**II**) and their β-diketones show antifungal activity. After forming complex with β-diketones the activity was found to be increased. At 150 ppm, the complexes show 50 % growth inhibition. Further the complexes of acac show better antifungal activity then bzac and hfpd. The details are given in Table-2.

Conclusion

On the basis of above investigations the tentative structures (Fig. 1) have been assigned to these complexes and in all complexes, tin shows tetrahedral geometry. The antifungal activity of bimetallic-*m*-oxoalkoxides containing unsymmetrical tin was found to be increased after forming complexes as compared to β-diketones but slight decrease in activity was observed as compared to parent compound *i.e.* (**I** and **II**).

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