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Inorganic Chemistry Article

Synthesis, Characterization, and Hydrolytic Behavior of Mixed-Ligand Diorganotin Esters, $[R_2Sn(O_2CR')OSO_2Me]_2$ (R = n-Pr, n-Bu; R′ = C_9H_6N-2, 4-OMe-C_9H_5N-2, C_9H_6N-1)

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Reactions of the tin precursors, $R_2Sn(OMe)OSO_2Me$ (R = n-Pr, n-Bu), with an equimolar quantity of 2-quinoline/4-methoxy-2-quinoline/1-isoquinoline carboxylic acid in acetonitrile proceed under mild conditions (rt,12–15 h) via selective Sn–OMe bond cleavage to afford the corresponding mixed-ligand diorganotin derivatives $[R_2Sn(O_2CR')OSO_2Me]_2$ [R′ = C_9H_6N-2, R = n-Pr (**1**), n-Bu (**2**); R′ = 4-OMe-C_9H_5N-2, R = n-Pr (**3**), n-Bu (**4**); R′ = C_9H_6N-1, R = n-Pr (**5**), n-Bu (**6**)]. These have been characterized by FAB mass, IR, and multinuclear (^1H, ^{13}C, ^{119}Sn) NMR spectral data and X-ray crystallography (for **4** and **6**). The molecular structure of **4** ($C_{20}H_{29}NO_6SSn$, monoclinic, $P2_1/n$, $a = 14.1(13)$ Å, $b = 16.7(18)$ Å, $c = 20.3(19)$ Å, $\beta = 107(4)°$, $Z = 8$) comprises distorted octahedral geometry around each tin atom by virtue of weakly bridging methanesulfonate [Sn(1A)–O(3B) = 3.010, Sn(1B)–O(3A) = 2.984 Å] and {N,O} chelation of the carboxylate ligands. The spectral data of **1**–**4** suggest a similar structural motif in solution. The molecular structure of **6** ($C_{38}H_{53}N_2O_{10}S_2Sn_2$, monoclinic, $P2_1/c$, $a = 11.339(2)$ Å, $b = 14.806(3)$ Å, $c = 24.929(5)$ Å, $\beta = 100.537(3)°$, $Z = 4$) reveals varying bonding preferences with monomeric units being held together by a bridging methanesulfonate [Sn(2)–O(5) = 2.312(2) Å] and a carboxylate group bonded to Sn(1) and Sn(2) atoms, respectively. Slow hydrolysis of compound **2** derived from 2-quinoline carboxylic acid in moist CH_3CN affords the asymmetric distannoxane, $[Bu_2Sn(O_2CC_9H_6N\text{-}2)\text{-}O\text{-}Sn(OSO_2Me)Bu_2]_2$ (**7**) ($C_{27}H_{45}NO_6SSn_2$, monoclinic, $C2/c$, $a = 21.152(3)$ Å, $b = 13.307(2)$ Å, $c = 26.060(4)$ Å, $\beta = 110.02(10)°$, $Z = 8$) featuring ladder type structural motif by virtue of unique μ_2-coordination of covalently bonded oxygen atoms [O(6), O(6)#1] of the methanesulfonate groups.

Introduction

Diorganotin carboxylates derived from mono- and dicarboxylic acids are among the most extensively studied class of compounds owing to their rich structural chemistry[1] and potential applications such as PVC stabilizers, catalysts for transesterification reactions, polyurethane polymerization, and RTV silicone curing agents.[2] Recently, much attention has also been focused on their use as metal-based drugs.[3] The diverse structural motifs known in this family of compounds are primarily attributed to the ambidentate character of the carboxylate ligands and also the tendency of the tin atom to expand its coordination sphere from four to seven. Steric and electronic attributes of organic substit-

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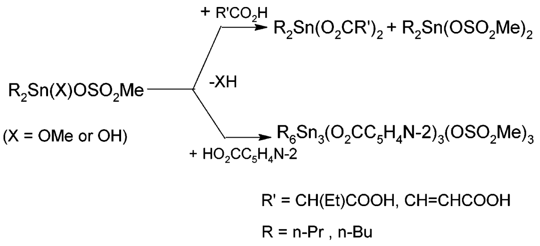
uents on tin and/or the carboxylate moiety impart significant influence on the structural characteristics in tin carboxylates. Recently, a number of carboxylate ligands bearing additional strategically placed functional group(s)/donor atom(s) capable of multidentate coordination have been used to derive a structurally interesting class of tin compounds.[4]

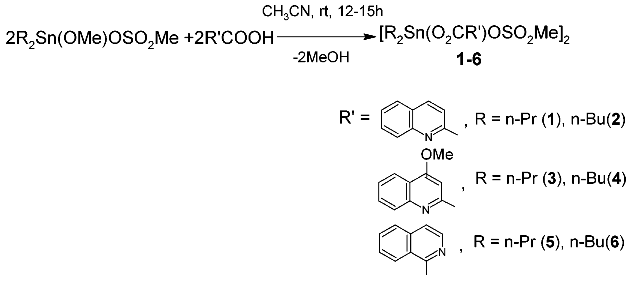
Mixed-ligand diorganotin(IV) carboxylates of the type $R_2Sn(X)O_2CR'$ (R, R′ = alkyl, aryl; X = Cl, OMe) represent an interesting family which have been the subject of interest in the past. These are generally prepared by a redistribution reaction[5] between symmetrical diorganotin precursors, R_2SnX_2 and $R_2Sn(O_2CR')_2$. Syntheses of (halo) diorganotin carboxylates have also been accomplished by a number of alternate methods which involve either Sn−O[6]/Sn−Sn[7]/Sn−C[8] bond cleavage with suitable reagents or addition of acyl halide on diorganotin oxide.[9] Although structural information for these compounds is largely derived from IR, multinuclear (^{1}H, ^{13}C, ^{119}Sn) NMR, and Mössbauer spectroscopy, only a few crystallographically authenticated examples such as $Me_2Sn(Cl)O_2CR'$ (R′ = CH_3, C_5H_4N-2) are known so far.[10] Generally, these compounds are known to form associated structures in the solid state.

It has been our endeavor to develop the chemistry of diorganotin carboxylates bearing co-ligands of ambidentate character. The primary impetus has been to comprehend competitive coordination modes of these ligands to the tin atom(s) and find a rationale related to the stability and structural motifs of this class of compounds. Toward this end, we have reported earlier on the synthesis[11] and reactivity behavior[12] of (methoxy/hydroxy)diorganotin methanesulfonates, $R_2Sn(X)OSO_2Me$ [R = n-Pr, n-Bu; X = OMe, OH] toward ethylmalonic/maleic/2-pyridine carboxylic acid. A significant feature of these studies is the formation of unstable mixed-ligand tin intermediates, $R_2Sn(O_2CR')OSO_2Me$, and their subsequent disproportionation to afford novel mono/trinuclear tin ester derivatives (Scheme 1).

Scheme 1



Scheme 2



To better understand the factors which influence the stability of such mixed-ligand tin derivatives toward disproportionation, we have extended analogous reactions of (methoxy)diorganotin methanesulfonates with 2-quinoline/4-methoxy-2-quinoline/1-isoquinoline carboxylic acid. This has resulted in the isolation of stable diorganotin esters, **1**−**6** (Scheme 2). X-ray crystal structures of **4** and **6** were determined to probe the bonding behavior of the ligands and its implications on the stability of these compounds. Preliminary studies on the hydrolytic behavior of **2** afforded the asymmetric distannoxane, $[Bu_2Sn(O_2CC_9H_6N\text{-}2)\text{-}O\text{-}Sn(OSO_2Me)Bu_2]_2$ (**7**), featuring the unprecedented μ_2-coordination mode of methanesulfonate groups. The details are reported herein.

Experimental Section

All operations were carried out using standard Schlenk line techniques under a dry nitrogen atmosphere. Solvents were freshly distilled over sodium benzophenone (toluene) or phosphorus pentaoxide (acetonitrile, hexane). Glasswares were dried in an oven at 110−120 °C and further flame dried under vacuum prior to use. The precursors, (methoxy)di-*n*-propyl/di-*n*-butyltin(IV) methanesulfonate, were prepared as reported earlier,[11] while 2-quinoline/4-methoxy-2-quinoline/1-isoquinoline carboxylic acid (Aldrich) were used as procured. ^{1}H, ^{13}C, and ^{119}Sn NMR spectra were recorded on BRUKER DPX-300 at 300, 75.46, and 111.88 MHz, respectively. ^{1}H and ^{13}C chemical shifts are quoted with respect to the residual protons of the solvent, while ^{119}Sn NMR data are given using tetramethyltin as internal standard. FAB mass spectra were recorded in 3-nitrobenzyl alcohol (NBA) matrix at room temperature on a JEOL SX 102/DA-6000 mass spectrometer/data system using argon/xenon (6 kV, 10 mA) as the FAB gas. IR spectra were recorded on Nicolet protégé 460 E.S.P. spectrophotometer using KBr optics. Elemental analysis (C, H, and N) was performed on a Perkin-Elmer model 2400CHN elemental analyzer.

Synthesis of $[R_2Sn(O_2CC_9H_6N\text{-}2)OSO_2Me]_2$ [R = n-Pr(1), n-Bu(2)]. To a stirred solution of $n\text{-}Pr_2Sn(OMe)OSO_2Me$ (0.52 g, 1.58 mmol) or $n\text{-}Bu_2Sn(OMe)OSO_2Me$ (0.75 g, 1.58 mmol) in acetonitrile (∼50 mL) was added 2-quinoline carboxylic acid (0.27 g, 1.58 mmol). The clear solution was stirred for 12−15 h at room temperature. Thereafter, the solvent was completely evaporated in a vacuum and the sticky residue washed with toluene to afford a

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white solid in each case. Recrystallization of these products from CH_2Cl_2/hexane mixture gave the desired compounds **1** and **2**, respectively.

Compound 1. Yield: 70%. IR (KBr, cm^{-1}): 1684 (ν_aCO_2), 1332 (ν_sCO_2), 1585 (ring vibrations), 1255, 1160, 1020 (νSO_3), 776 (νSMe). ^{1}H NMR ($CDCl_3$): δ 8.63 (d, $^3J_{H-H} = 7.3$ Hz, H-3, 2H), 8.53 (d, $^3J_{H-H} = 7.7$ Hz, H-4, 2H), 8.38 (br, H-8, 2H), 8.10 (t, $^3J_{H-H} = 9.0$ Hz, H-6, 2H), 8.06 (d, $^3J_{H-H} = 7.8$ Hz, H-5, 2H), 7.86 (t, $^3J_{H-H} = 7.4$ Hz, H-7, 2H), 3.03 (s, 6H, SMe), 1.92 (m, SnCH_2, 8H), 1.51 (m, SnCH$_2$CH_2, 8H), 0.85 (t, $^3J_{H-H} = 8.7$ Hz, Sn(CH$_2$)$_2$CH_3, 12H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ121.0, 125.9, 128.6, 129.0, 130.1, 132.2, 141.5, 143.1, 147.0 (aromatic carbons), 165.0 (CO_2), 39.7 (SMe), 17.4 (Cγ, $^3J_{Sn-C} = 136$ Hz), 18.4 (Cβ, $^2J_{Sn-C} = 43$ Hz), 32.7 (Cα). ^{119}Sn NMR ($CDCl_3$) δ −330. MS (FAB$^+$): *m/z* 847 (M − OSO$_2$Me − 4H]$^+$, 598 [M − 2(O$_2$CC$_9$H$_6$N-2) − 4H]$^+$, 378 [Pr$_2$Sn(O$_2$CC$_9$H$_6$N − 2)]$^+$. Anal. Calcd for $C_{34}H_{46}N_2O_{10}S_2Sn_2$ (946): C, 43.12; H, 4.86; N, 2.95. Found: C, 43.20; H, 4.79; N, 2.90.

Compound 2. Yield: 78%. IR (KBr, cm^{-1}): 1654 (ν_aCO_2), 1338 (ν_sCO_2), 1584 (ring vibrations), 1278, 1150, 1011 (νSO_3), 780 (νSMe). ^{1}H NMR ($CDCl_3$): δ 8.60 (d, $^3J_{H-H} = 7.2$ Hz, H-3, 2H), 8.44 (d, $^3J_{H-H} = 8.0$ Hz, H-4, 2H), 8.33 (br, H-8, 2H), 8.03 (t, $^3J_{H-H} = 9.0$ Hz, H-6, 2H), 7.98 (d, $^3J_{H-H} = 7.5$ Hz, H-5, 2H), 7.80 (t, $^3J_{H-H} = 7.5$ Hz, H-7, 2H), 2.96 (s, 6H, SMe), 1.91 (m, SnC$H_{2,}$ 8H), 1.37 (m, SnCH$_2$CH_2, 8H), 1.13 (m, Sn(CH$_2$)$_2$CH_2, 8H), 0.62 (t, $^3J_{H-H} = 6.7$ Hz, Sn (CH$_2$)$_3$CH_3, 12H). ^{13}C{^{1}H) NMR ($CDCl_3$): δ 121.2, 125.3, 128.9, 129.0, 130.1, 133.6, 141.0, 142.5, 147.0 (aromatic carbons), 165.1 (CO_2), 39.7 (SMe), 13.1 (Cδ), 25.7 (Cγ, $^3J_{Sn-C} = 140$ Hz), 25.7 (Cβ, $^2J_{Sn-C} = 40$ Hz), 30.0 (Cα). ^{119}Sn NMR ($CDCl_3$): δ −334. MS (FAB$^+$): *m/z* 908 (M + H − OSO$_2$Me]$^+$, 654 [M − 2OSO$_2$Me) − 2Bu − CO$_2$]$^+$, 406 [Bu$_2$Sn(O$_2$CC$_9$H$_6$N-2)]$^+$. Anal. Calcd for $C_{38}H_{54}N_2O_{10}S_2Sn_2$ (1002): C, 45.50; H, 5.38; N, 2.79. Found: C, 45.40; H, 5.30; N, 2.74.

Synthesis of [R$_2$Sn(4-OMe-O$_2$CC$_9$H$_5$N-2)OSO$_2$Me]$_2$ [R = n-Pr(3), n-Bu(4)]. The title compounds were prepared according to the procedure described for **1** and **2** by reacting n-Pr$_2$Sn(OMe)OSO$_2$Me (0.65 g, 1.95 mmol) or n-Bu$_2$Sn(OMe)OSO$_2$Me (0.7 g, 1.95 mmol) in acetonitrile (~50 mL) with 4-methoxy-2-quinoline carboxylic acid (0.39 g, 1.95 mmol).

Compound 3. Yield: 80%. IR(KBr, cm^{-1}): 1667 (ν_aCO_2), 1341 (ν_sCO_2), 1584 (ring vibrations), 1274, 1149, 990 (νSO_3), 773 (νSMe). ^{1}H NMR ($CDCl_3$): δ 8.41 (d, $^3J_{H-H} = 8.2$ Hz, H-5, 2H), 8.30 (br, H-8, 2H), 8.02 (t, $^3J_{H-H} = 7.4$ Hz, H-7, 2H), 7.89 (s, H-3, 2H), 7.78 (t, $^3J_{H-H} = 7.5$ Hz, H-6, 2H), 4.22 (s, OMe, 6H), 2.99 (s, SMe, 6H), 1.91 (m, SnCH_2, 8H), 1.54 (m, SnCH$_2$CH_2, 8H), 0.87 (t, $^3J_{H-H} = 8.0$ Hz, Sn(CH$_2$)$_2$CH_3, 12H). ^{13}C{^{1}H) NMR (DMSO-d_6): 121.1, 123.0, 125.6, 126.5, 128.8, 129.6, 132.1, 143.4, 149.0 (aromatic carbons), 165.3 (CO_2), 58.0 (OMe), 39.7 (SMe), 17.4 (Cγ, $^3J_{Sn-C} = 140$ Hz), 18.4 (Cβ, $^2J_{Sn-C} = 39$ Hz), 32.7 (Cα). ^{119}Sn NMR (DMSO-d_6): δ −304. MS (FAB$^+$): *m/z* 909 (M − OSO$_2$Me − 2H]$^+$, 408 [Pr$_2$Sn(4-OMe-O$_2$CC$_9$H$_6$N-2)]$^+$. Anal. Calcd for $C_{36}H_{50}N_2O_{12}S_2Sn_2$ (1006): C, 42.94; H, 4.97; N, 2.78. Found: C, 42.80; H, 4.85; N, 2.71

Compound 4. Yield: 75%. IR (KBr, cm^{-1}): 1686 (ν_aCO_2), 1338 (ν_sCO_2), 1583 (ring vibrations), 1270, 1145, 1011 (νSO_3), 776 (νSMe).^{1}H NMR ($CDCl_3$): δ 8.46 (d, $^3J_{H-H} = 8.1$ Hz, H-5, 2H), 8.38 (br, H-8, 2H), 7.96 (t, $^3J_{H-H} = 7.5$ Hz, H-7, 2H), 7.84 (s, H-3, 2H), 7.78 (t, $^3J_{H-H} = 7.5$ Hz, H-6, 2H), 4.28 (s, OMe, 6H), 2.81 (s, SMe, 6H), 1.95 (m, SnCH_2, 8H), 1.18 (m, SnCH$_2$(CH_2)$_2$, 16H), 0.69 (t, $^3J_{H-H} = 6.8$ Hz, Sn (CH$_2$)$_3$CH_3, 12H). ^{13}C{^{1}H) NMR (DMSO-d_6): 121.2, 122.6, 125.0, 126.1, 128.6, 129.4, 133.9, 143.2, 150.1 (aromatic carbons), 166.0(CO_2), 57.5 (OMe), 39.8(SMe), 13.3 (Cδ), 25.5 (Cγ, $^3J_{Sn-C} = 144$ Hz), 26.7 (Cβ, $^2J_{Sn-C} = 40$ Hz), 31.2 (Cα). ^{119}Sn (DMSO-d_6): δ −306. MS (FAB$^+$): *m/z* 965 (M − OSO$_2$Me − 2H]$^+$, 855 [M − 2Bu − OSO$_2$Me − 2H]$^+$, 436 [Bu$_2$Sn(4-OMe-O$_2$CC$_9$H$_6$N-2)]$^+$. Anal. Calcd for $C_{40}H_{58}N_2O_{12}S_2Sn_2$ (1062): C, 45.19; H, 5.46; N, 2.63. Found: C, 45.01; H, 5.55; N, 2.59.

Synthesis of [R$_2$Sn(O$_2$CC$_9$H$_6$N-1)OSO$_2$Me]$_2$ [R = n-Pr(5), n-Bu(6)]. The title compounds were obtained as pale yellow solids by following the similar procedure as described for **1** and **2** by reacting n-Pr$_2$Sn(OMe)OSO$_2$Me (0.74 g, 2.22 mmol) or n-Bu$_2$Sn(OMe)OSO$_2$Me (0.80 g, 2.22 mmol) with 1-quinoline carboxylic acid (0.38 g, 2.22 mmol).

Compound 5. Yield: 78%. IR (KBr, cm^{-1}): 1671, 1616 (ν_aCO_2), 1331 (ν_sCO_2), 1584 (ring vibrations), 1260, 1152, 1039 (νSO_3), 763 (νSMe). ^{1}H NMR ($CDCl_3$): δ 10.1 (d, $^3J_{H-H} = 7.2$ Hz, H-4, 2H), 9.29 (br, H-3, 2H), 8.15 (d, $^3J_{H-H} = 5.7$ Hz, H-8, 2H), 8.01 (t, $^3J_{H-H} = 7.7$ Hz, H-6, 2H), 7.92 (t, $^3J_{H-H} = 7.4$ Hz, H-7, 2H), 7.90 (d, $^3J_{H-H} = 6.3$ Hz, H-5, 2H), 3.01 (s, SMe, 6H), 1.80 (m, SnCH_2, 8H), 1.41 (m, SnCH$_2$CH_2, 8H), 0.79 (t, $^3J_{H-H} = 6.7$ Hz, Sn(CH$_2$)$_2$CH_3, 12H). ^{13}C{^{1}H) NMR ($CDCl_3$): δ 122.0, 124.2, 127.8, 129.1, 130.3, 131.5, 142.5, 144.2, 146.0 (aromatic carbons), 166.0(CO_2), 39.5(SMe), 18.0 (Cγ, $^3J_{Sn-C} = 140$ Hz), 19.2 (Cβ, $^2J_{Sn-C} = 45$ Hz), 33.1 (Cα). ^{119}Sn NMR ($CDCl_3$): δ −312. MS(FAB$^+$): *m/z* 849 [M − OSO$_2$Me − 2H]$^+$, 817 [M − 3Pr]$^+$, 378 [Pr$_2$Sn(O$_2$CC$_9$H$_6$N-1)]$^+$. Anal. Calcd for $C_{34}H_{46}N_2O_{10}S_2Sn_2$ (946): C, 43.12; H, 4.86; N, 2.95. Found: C, 42.91; H, 4.90; N, 2.84.

Compound 6. Yield: 74%. IR(KBr, cm^{-1}): 1676, 1620 (ν_aCO_2), 1330 (ν_sCO_2), 1590 (ring vibrations), 1260, 1155, 1044 (νSO_3), 763 (νSMe). ^{1}H NMR ($CDCl_3$): δ 10.1 (d, $^3J_{H-H} = 8.0$ Hz, H-4, 2H), 9.12 (br, H-3, 2H), 8.22 (d, $^3J_{H-H} = 6$ Hz, H-8, 2H), 8.06 (t, $^3J_{H-H} = 7.8$ Hz, H-6, 2H), 7.99 (t, $^3J_{H-H} = 8.7$ Hz, H-7, 2H), 7.95 (d, $^3J_{H-H} = 6.6$ Hz, H-5, 2H), 3.01 (s, SMe, 6H), 1.91 (t, $^3J_{H-H} = 9.0$ Hz, SnCH_2, 8H), 1.48 (m, SnCH$_2$CH_2, 8H), 1.25 (m, Sn(CH$_2$)$_2$CH_2, 8H), 0.76 (t, $^3J_{H-H} = 6.9$ Hz, Sn(CH$_2$)$_3$CH_3, 12H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 122.3, 125.0, 127.1, 129.2, 130.6, 133.2, 141.0, 143.5, 148.1 (aromatic carbons), 167.5 (CO_2), 39.4 (SMe), 13.1 (Cδ), 17.4 (Cγ, $^3J_{Sn-C} = 139$ Hz), 18.4 (Cβ, $^2J_{Sn-C} = 44$ Hz), 32.7 (Cα). ^{119}Sn NMR ($CDCl_3$): δ −312. MS(FAB$^+$): *m/z* 849 [M − OSO$_2$Me − 2H]$^+$, 406 [Bu$_2$Sn(O$_2$CC$_9$H$_6$N-1)]$^+$, 392 [Sn-(O$_2$CC$_9$H$_6$N-1)]$^+$. Anal. Calcd for $C_{38}H_{54}N_2O_{10}S_2Sn_2$ (1002): C, 45.50; H, 5.38; N, 2.79. Found: C, 45.34; H, 5.28; N, 2.65.

Synthesis of [Bu$_2$Sn(O$_2$CC$_9$H$_6$N-2)-O-Sn(OSO$_2$Me)Bu$_2$]$_2$ (7). [n-Bu$_2$Sn(O$_2$CC$_9$H$_6$N-2)OSO$_2$Me]$_2$ (**2**) (1.2 g, 1.19 mmol) was dissolved in ~50 mL of moist acetonitrile (95:5 v/v acetonitrile/water), and the clear solution was stirred at room temperature for 24 h. Thereafter, solvent was stripped off under vacuum. To the resulting viscous mass was added *n*-hexane with constant stirring. A white solid thus obtained was filtered and dried under vacuo. Recrystallization of the crude product from acetonitrile afforded **7** in analytically pure form.

Yield: 70%. IR(KBr, cm^{-1}): 1684 (ν_aCO_2), 1327 (ν_sCO_2), 1260, 1145, 1011 (νSO_3), 778 (SMe), 605 (νSn−O−Sn). ^{1}H NMR ($CDCl_3$): δ 8.58 (d, $^3J_{H-H} = 8.7$ Hz, H-3, 2H), 8.53 (d, $^3J_{H-H} = 7.2$ Hz, H-4, 2H), 8.42 (br, H-8, 2H), 8.02 (m, H-5 + H-6, 4H), 7.77 (t, $^3J_{H-H} = 7.5$ Hz, H-7, 2H), 2.96 (s, SMe, 6H), 1.80 (m, SnCH_2, 16H), 1.45 (m, SnCH$_2$CH_2, 16H), 1.12 (m, Sn(CH$_2$)$_2$CH_2, 16H), 0.94 (t, $^3J_{H-H} = 6.5$ Hz, Sn(CH$_2$)$_3$CH_3, 12H), 0.62 (t, $^3J_{H-H} = 6.7$ Hz, Sn(CH$_2$)$_3$CH_3, 12H). ^{119}Sn NMR ($CDCl_3$): δ −221, −278. Anal. Calcd for $C_{54}H_{90}N_2O_{12}S_2Sn_4$ (1502): C, 43.14; H, 5.99; N, 1.86. Found: C, 43.01; H, 5.90; N, 1.81.

X-ray Crystallography. The crystals of **4** and **6** were mounted along with the largest dimension in sealed capillaries and were used for data collection. The intensity data were collected on a Bruker

SMART APEX diffractometer equipped with molybdenum sealed tube and a highly oriented graphite monochromator at −100 °C. The systematic absences ($0k0$, $k = 2n + 1$; and $h01$, $h + 1 = 2n + 1$) (for **4**) and ($0k0$, $k = 2n + 1$; and $h01$, $1 = 2n + 1$) (for **6**) indicated the space groups $P2_1/n$ and $P2_1/c$, respectively. The structures were solved by direct methods using SHELXTL-PC.[13] Some atoms of the butyl groups (C1A−C4A, C8A, and C4B) (for **4**), C5−C8 and O(10) (for **6**) were found disordered and refined isotropically while other non-hydrogen atoms were refined anisotropically by the full-matrix least-squares method. The function minimized was $\sum w(||F_o| - |F_c||^2)$. Hydrogen atoms were included in the ideal position with fixed isotropic U values 1.2 times that of the atom they are attached to. A weighting scheme of the form $w = 1/[[\sigma^2(F_o)^2 + (aP)^2 + bP]$ with $a = 0.032$, $b = 0.00$ (for **4**), $a = 0.044$, $b = 0.00$ (for **6**) was used. The final difference map was devoid of significant features. All calculations were done on an IBM-compatible PC using programs Windows-NT operating system. The programs used were SMART,[14] SAINT+,[15] SADABS.[16]

The intensity data for **7** were collected on a Siemens P4 X-ray diffractometer by using scanning mode with graphite monochromatized Mo Kα radiation at 20 °C. A total of 9284 reflections were measured, 9033 were independent ($I_{int} = 0.0817$) and of which 4180 ($I > 2\sigma(I)$] were considered observed. The systematic absences hkl, $h + k = 2n + 1$, $h0l$, l odd and $0k0$, $k = 2n + 1$ indicated the space group $C2/c$. The structure was solved by direct method using SIR92[17] and refined by full-matrix least-squares refinement techniques on F^2 using SHELXTL.[18] Two methylene carbons of one butyl group and methyl group of the $MeSO_3$ ligand showed high thermal parameters and splitting. The disorder could be resolved for C24, C25, and C27 and these three atoms are refined isotropically with fixed C−C and C−S bond lengths. All other atoms were refined anisotropically. A weighting scheme of the form $w = 1/[[\sigma^2(F_o)^2 + (aP)^2 + bP]$ with $a = 0.6930$, $b = 6.94$ was used. The final difference map was devoid of significant features.

Results and Discussion

Synthesis of 1−6. The reactions between equimolar quantities of $R_2Sn(OMe)OSO_2Me$ (R = n-Pr, n-Bu) and 2-quinoline/4-methoxy-2-quinoline/1-isoquinoline carboxylic acid in acetonitrile proceed under mild conditions (rt, 12−15 h) to yield the corresponding mixed-ligand diorganotin complexes, $[R_2Sn(O_2CR')OSO_2Me]_2$ (**1**−**6**) in nearly 70−80% yield (Scheme 2). The chemoselective reactivity of Sn−OMe group in the precursor tin complexes toward the carboxylic acids is in accord with more basic character of methoxide group as compare to methanesulfonate.

Characterization. The compounds **1**−**6** are white to pale yellow crystalline solids and are stable up to 180 °C with decomposition being observed after this temperature. These are soluble in common organic solvents such as CH_3CN, CH_2Cl_2, $CHCl_3$, CH_3OH, and DMSO, etc. The identity of these compounds has been established by FAB mass, IR, and multinuclear (^1H, ^{13}C, ^{119}Sn) NMR spectral studies and structures for **4** and **6** further corroborated by single crystal diffraction. Although FAB mass spectra (3-nitrobenzylalcohol) do not show a molecular ion $[M]^+$ peak, structurally important fragment ions such as $[M - OSO_2Me]^+$ and $[M - R]^+$ are clearly discernible. IR spectra in both KBr and CH_2Cl_2 solution are quite similar and particularly useful in providing the bonding description of carboxylate and methanesulfonate groups in each compound. For **1**−**4**, the spectra exhibit a strong absorption at 1690−1650 cm^{-1} ($\nu_a CO_2$) similar to those previously reported for $Ph_2Sn(O_2CC_5H_4N\text{-}2)_2$[19] and $Bu_2Sn(O_2CC_5H_4N\text{-}2)_2 \cdot H_2O$[20] in which chelation through the {N,O}coordination mode has been observed. In contrast, two $\nu_a CO_2$ absorptions are observed at 1671, 1616 (for **5**) and 1676, 1620 cm^{-1} (for **6**). The former values are assigned to {N,O} chelation while lowering of IR frequency at 1610−1620 cm^{-1} suggests the possibility of tridentate coordination mode featuring {N,O} chelation and bridging carboxylate group.[21] The characteristic absorptions due to the νSO_3 mode appear in the region 1300−1000 cm^{-1} and apparently suggest bridging bidentate mode of methanesulfonate groups.[22] ^1H and $^{13}C\{^1H\}$ NMR spectra ($CDCl_3$) of **1**−**6** are in accord with the structural composition. In the ^1H NMR spectra, characteristic resonances due to Pr_2Sn/Bu_2Sn, SMe and aromatic ring protons appear in 1:1:1 integrated ratio. ^{119}Sn NMR spectrum of each compound in $CDCl_3$ or DMSO-d_6 (for **3** and **4**) shows a sharp resonance ($\nu_{1/2} = 10{-}14$ Hz) in a narrow chemical shift range of δ −304 to −340 typical of six coordinated polyhedra at each tin atom.[23] The presence of a single ^{119}Sn resonance in each compound strongly suggests that the tin atoms in the dimeric structures possess identical chemical environments. The structural similarities of **1**−**4** as well as **5** and **6** are thus evident from the above spectral data. These findings are further confirmed from X-ray crystal structure analysis of **4** and **6**.

X-ray Crystal Structures. The single crystals of **4** and **6** suitable for X-ray analysis were obtained by slow evaporation of acetonitrile solution. The molecular structures along with atomic labeling scheme are shown in Figures 1 and 2, respectively. The relevant crystal data are given in Table 1 while selected bond lengths and angles are listed in Tables 2 and 3, respectively. The crystal structure of each compound shows distinct coordination preferences of carboxylate and methanesulfonate ligands. The molecule **4** (monoclinic, $P2_1/n$) adopts a dimeric structure with the monomeric units held together by weakly coordinating methanesulfonate groups acting in a bridging bidentate mode [Sn(1A)−O(3B) = 3.010 Å, Sn(1B)−O(3A) = 2.984 Å]. These bond distances are much longer than normally observed in related diorganotin(IV) methanesulfonates (2.3−2.5 Å),[11,12] but shorter than the

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(13) *SMART (Ver 5.624). Software for data collection on CCD Detector system*; Bruker X-ray Analytical Instruments: Madison, WI, 1995.

(14) *SAINT+ (Ver 5.6). Software for data reduction on CCD Detector system*; Bruker X-ray Analytical Instruments: Madison, WI, 1995.

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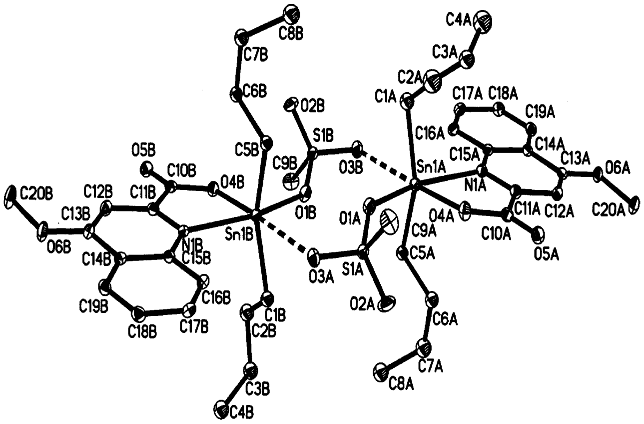

Figure 1. ORTEP view of **4**. The thermal ellipsoids are drawn at 30% probability level. Hydrogen atoms are omitted for clarity.

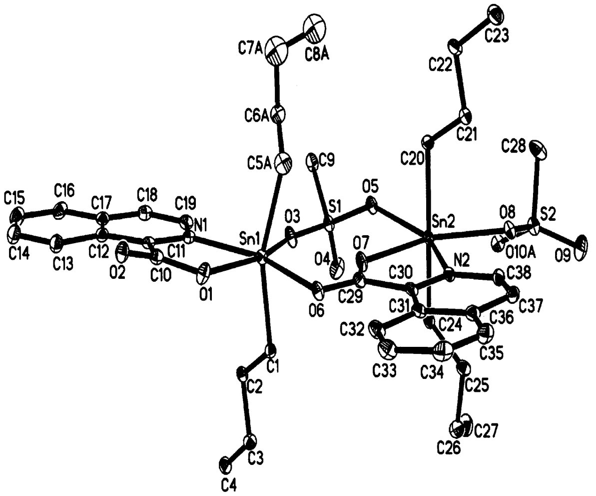

Figure 2. ORTEP view of **6**. The thermal ellipsoids are drawn at 30% probability level. Hydrogen atoms are omitted for clarity.

Table 1. Summary of Crystallographic Data for the Compounds **4**, **6**, and **7**[a]

	4	**6**	**7**
empirical formula	$C_{20}H_{29}NO_6SSn$	$C_{38}H_{53}N_2O_{10}S_2Sn_2$	$C_{27}H_{45}NO_6SSn2$
fw	530.19	999.32	749.07
T, K	173(2)	173(2)	293(2)
λ, Å	0.71073	0.71073	0.71073
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$C2/c$
a, Å	14.1(13)	11.339(2)	21.152(3)
b, Å	16.7(18)	14.806(3)	13.307(2)
c, Å	20.3(19)	24.929(5)	26.060(4)
α, deg	90	90	90
β, deg	107(4)	100.537(3)	110.020(10)
γ, deg	90	90	90
V, Å^3	4598(785)	4114.4(13)	6892(2)
Z	8	4	8
ρ_{calcd}, Mg m^{-3}	1.532	1.613	1.442
θ (deg)	1.56−28.02	1.61−25.00	1.66−30.01
μ, mm^{-1}	1.236	1.373	1.544
final R indices	R1 = 0.0347	R1 = 0.0354	R1 = 0.0668
[$I > 2\sigma(I)$]	wR2 = 0.0736	wR2 = 0.0805	wR2 = 0.1561
R indices (all data)	R1 = 0.0460	R1 = 0.0465	R1 = 0.1575
	wR2 = 0.0783	wR2 = 0.0850	wR2 = 0.2618

[a] $R1 = (\sum||F_o| - |F_c||/\sum|F_o|)$, $wR2 = \sum w(F_o^2 - F_c^2)^2/\sum[(F_o^2)^2]^{1/2}$, $s = [\sum w(F_o^2 - F_c^2)^2/n{-}p)]^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **4**

Bond Lengths			
Sn(1A)−C(1A)	2.07(15)	Sn(1A)−C(5A)	2.11(17)
Sn(1A)−O(1A)	2.2(2)	Sn(1A)−O(4A)	2.08(15)
Sn(1A)−O(3B)	3.010	Sn(1A)−N(1A)	2.32(19)
Sn(1B)−C(1B)	2.11(16)	Sn(1B)−C(5B)	2.11(17)
Sn(1B)−O(1B)	2.2(2)	Sn(1B)−O(4B)	2.08(15)
Sn(1B)−O(3A)	2.984	Sn(1B)−N(1B)	2.3(2)
Bond Angles			
C(1A)−Sn(1A)−C(5A)	151.4(10)	C(1B)−Sn(1B)−C(5B)	150.1(9)
O(3B)−Sn(1A)−O(1A)	103.1	O(3A)−Sn(1B)−O(1B)	103.5
O(4A)−Sn(1A)−O(1A)	83(4)	O(4B)−Sn(1B)−O(1B)	83(4)
O(4A)−Sn(1A)−N(1A)	74(4)	O(4B)−Sn(1B)−N(1B)	74(4)
O(3B)−Sn(1A)−N(1A)	100.1	O(3A)−Sn(1B)−N(1B)	99.4

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **6**

Bond Lengths			
Sn(1)−O(3)	2.366(2)	Sn(2)−O(5)	2.312(2)
Sn(1)−O(1)	2.112(2)	Sn(2)−O(8)	2.300(2)
Sn(1)−N(1)	2.291(3)	Sn(2)−N(2)	2.294(3)
Sn(1)−O(6)	2.507(2)	Sn(2)−O(7)	2.170(2)
Sn(1)−C(1)	2.104(3)	Sn(2)−C(20)	2.118(4)
Sn(1)−C(5A)	2.120(8)	Sn(2)−C(24)	2.113(3)
Bond Angles			
C(1)−Sn(1)−C(5A)	157.4(3)	C(24)−Sn(2)−C(20)	164.30(14)
O(1)−Sn(1)−O(6)	82.56(8)	O(8)−Sn(2)−O(5)	125.72(8)
O(3)−Sn(1)−O(6)	122.20(8)	O(7)−Sn(2)−O(5)	77.24(8)
N(1)−Sn(1)−O(3)	82.35(9)	O(7)−Sn(2)−N(2)	71.30(9)
O(1)−Sn(1)−N(1)	72.83(9)	N(2)−Sn(2)−O(8)	85.80(9)

sum of the van der Waals radii of Sn and O (3.68 Å).[24] The carboxylate ligand is bonded to each tin atom by {N,O} chelation forming five membered ring while the other carboxylic oxygen [O(5A) and O(5B)] remains free. Thus, the coordination geometry around each tin atom is a distorted octahedron with planar SnO_3N core occupying the equatorial position (360 ± 0.2°). The butyl groups adopt trans disposition with an average C−Sn−C angle of 150.7°. The metrical parameters of the carboxylate ligand involved in chelation [Sn(1A)−O(4A)/Sn(1B)−O(4B) = 2.08(15) Å, Sn(1A)−N(1A) = 2.32(19) Å, Sn(1B)−N(1B) = 2.3(2) Å] find a close analogy with those observed for previously known diorganotin carboxylates derived from 2-pyridine carboxylic acid.[12,25,26] The covalent Sn−O(methanesulfonate) bond distance [Sn(1A)−O(1A)/Sn(1B)−O(1B) = 2.2(2) Å] is comparable with the corresponding Sn−O distance reported earlier for $Bu_2Sn(OSO_2Me)_2$.[12]

The dimeric structure of **6** (monoclinic, $P2_1/c$) differs from **4** in respect of varying disposition of the ligands around the tin atoms. Particularly noteworthy is the structural variation due to different bonding behavior of carboxylate and methanesulfonate groups associated with each monomeric entity in the molecule. While {N,O} chelation of the carboxylate groups is evident, the ligand at Sn(2) atom behaves in a tridentate fashion with the O(6) atom forming a bridge between the two tin centers [Sn(1)−O(6) = 2.507(2) Å]. The methanesulfonate groups at Sn(1) and Sn(2) atoms display bridging bidentate and monodentate coordination modes, respectively [Sn(1)−O(3) = 2.366(2) Å, Sn(2)−O(5) = 2.312(2) Å, Sn(2)−O(8) = 2.300(2) Å]. Strong

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(26) (a) Gielen, M.; Boualam, M.; Tiekink, E. R. T. *Main Group Met. Chem.* **1993**, *16*, 251. (b) Jurkschat, K.; Tiekink, E. R. T. *Main Group Met. Chem.* **1994**, *17*, 659.

coordination of these ligands to the tin atoms results in a significant widening of the trans C−Sn−C angles [C(1)−Sn(1)−C(5A) = 157.4(3)°, C(24)−Sn(2)−C(20) = 164.30(14)°] as compared to the analogous parameters of **4** (150.7°). As a consequence, the tin atoms adopt a highly distorted octahedral geometry with the SnO_3N core (360 ± 0.1°) constituting the equatorial plane. Other metrical parameters associated with methanesulfonate and carboxylate ligands are similar to those observed for compound **4**.

Synthesis and Characterization of Asymmetric Distannoxane, $[Bu_2Sn(O_2CC_9H_6N\text{-}2)\text{-}O\text{-}Sn(OSO_2Me)Bu_2]_2$ (7). Attempts to crystallize the mixed-ligand tin compound, $[Bu_2Sn(O_2CC_9H_6N\text{-}2)OSO_2Me]_2$ (**2**), from acetonitrile solution did not yield the desired product. Instead, tetraorgano distannoxane (**7**) was obtained as colorless crystals presumably due to the hydrolysis of **2** in the presence of traces of moisture in the solvent. Treatment of **2** with moist acetonitrile (95:5 v/v CH_3CN/H_2O) also gave the distannoxane in ∼70% isolable yield. It is believed that $Bu_2Sn(OH)OSO_2Me$ and $Bu_2Sn(OH)O_2CC_9H_6N\text{-}2$ are the key intermediates during hydrolysis pathway of **2** and subsequently undergo condensation to afford the distannoxane. Although a similar mechanistic proposition has been suggested for the hydrolysis of diorganotin dihalides[27] and di-*tert*-butyltin diacetate,[28] hydrolytic behavior of mixed-ligand tin complexes with labile ligands as observed herein has not been reported so far. The identity of **7** has been established by elemental analysis, IR, NMR spectroscopy, and X-ray crystallography. In the ^1H NMR spectrum, resonances due to Bu_2Sn, SMe, and aromatic ring protons are discernible at the characteristic chemical shifts in the relative integral intensity ratio of 2:1:1. ^{119}Sn NMR spectrum ($CDCl_3$) shows two resonances of equal intensity at δ −221 and −278 due to endocyclic and exocyclic tin atoms, respectively, and suggests the retention of dimeric structure in solution. In this respect, **7** bears a close analogy with symmetric distannoxanes,[1a,29] in contrast to asymmetric analogues, $[Bu_2(O_2CR)Sn\text{-}O\text{-}Sn(X)Bu_2]_2$ (X = OMe, F, Cl; R = CF_3, CH_3), in which different oxo-tin species are known to exist in dynamic equilibrium in solution.[30] The stability of compound **7** may thus partly be attributed to strong {N,O} chelation of the carboxylate ligand. The IR spectrum of **7** both in solid and dichloromethane solution reveals a strong absorption at 1684 cm^{-1} due to ν_a-CO_2 mode suggesting {N,O} chelation. The characteristic absorption due to the νSn−O−Sn mode appears at 605 cm^{-1}.

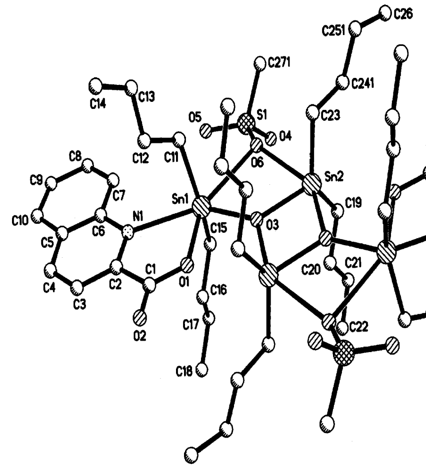

Figure 3. ORTEP view of **7**. The thermal ellipsoids are drawn at 30% probability level. Hydrogen atoms are omitted for clarity.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **7**

Bond Lengths			
Sn(1)−O(3)	2.066(5)	Sn(1)−C(11)	2.105(10)
Sn(1)−O(1)	2.110(6)	Sn(1)−C(15)	2.121(9)
Sn(1)−N(1)	2.498(6)	Sn(2)−C(19)	2.111(11)
Sn(1)−O(3)	2.048(11)	Sn(2)−C(23)	2.083(11)
Sn(2)−O(3)#1	2.068(5)	Sn(2)−Sn(2)#1	3.2495(12)
Sn(1)−O(6)	2.603(4)	Sn(2)−O(6)	2.632(4)
Bond Angles			
C(11)−Sn(1)−C(15)	145.2(4)	O(6)−Sn(2)−O(3)#1	145.88
O(3)−Sn(1)−O(1)	75.3(2)	C(23)−Sn(2)−C(19)	133.2(4)
O(1)−Sn(1)−N(1)	70.0(2)	O(3)−Sn(2)−C(19)	109.9(3)
O(3)−Sn(1)−O(6)	69.24	O(3)−Sn(2)−C(23)	109.7(3)
O(6)−Sn(1)−N(1)	145.39	O(3)−Sn(2)−O(3)#1	75.65
Sn(2)−O(3)−Sn(2)#1	104.3(2)	Sn(1)−O(6)−Sn(2)	90.65

The molecular structure of **7** is shown in Figure 3, and crystal data as well as selected bond lengths and angles are summarized in Tables 1 and 4, respectively. The molecule (monoclinic, *C*2/*c*) adopts a centrosymmetric dimeric structure by virtue of μ_3-oxo atoms [Sn(1)−O(3) = 2.066(5) Å; Sn(2)−O(3)#1 = 2.068(5) Å] which form the central $R_4Sn_2O_2$ core with planer Sn_2O_2 ring. The methanesulfonate groups associated with each endocyclic tin atom is uniquely coordinated to Sn(1) and Sn(1)#1 atoms (exocyclic) in a μ_2-fashion [Sn(2)−O(6) = 2.603(4) Å, Sn(1)−O(6) 2.632(4) Å] resulting in a ladder type structural motif. Each exocyclic tin atom is also bonded to the carboxylate ligand via a {N,O} chelation mode. The coordination geometry around the endocyclic tin atoms is distorted trigonal bipyramidal with the trigonal plane being defined by C_2O donor set in each case [C(23)−Sn(2)−C(19) = 133.2(4)°, O(3)−Sn(2)−C(23) = 109.7(3)°, O(3)−Sn(2)−C(19) = 109.9(3)°] with Sn(2) atom being deviated from the plane by 0.3099(5) Å. The axial position is occupied by O(6) and O(3)#1 atoms [O(6)−Sn(2)−O(3)#1 = 145.88°]. Each exocyclic tin atom adopts distorted octahedral geometry with the equatorial disposition of O(6), O(3), O(1), and N(1) atoms (sum of angles = 360 ± 0.2°) and the two butyl groups [C(11)−Sn(1)−C(15) = 145.2(4)°] occupying the trans position.

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In conclusion, mixed ligand diorganotin esters **1**−**6** are accessible from the reaction of precursor tin compounds, R_2-Sn(OMe)OSO_2Me, with the corresponding carboxylic acid. Although structural variations in **4** and **6** are evident due to ambidentate coordination of the ligands, strong {N,O} chelation of the carboxylate ligands forming a five membered ring is invariably observed in their structural motifs. The compounds **1**−**6** retain their structural identity in solution and are stable toward disproportionation unlike the related tin analogues derived from ethylmalonic/maleic/2-pyridine carboxylic acid.[12] The stability of **1**−**6** may thus partly be attributed to strong chelation effect of the carboxylate ligands as well as the ability of the co-ligand (methanesulfonate) to provide coordinative saturation around the tin atoms in the dimeric structural motif. The formation of stannoxane **7** represents the first example in which two different hemilabile functional groups bonded to the tin atom in the compound **2** undergo hydrolysis in a selective manner. Crystal structure of **7** features an unprecedented μ_2-coordination of methanesulfonate group.

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Supporting Information Available: X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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