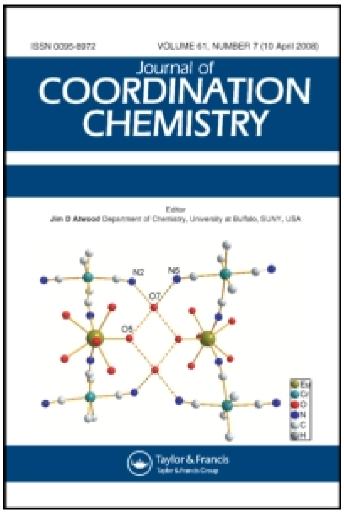

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Triorganotin(IV) esters of 2-{[<i>N</i>-(2-oxo-2H-naphthalene-1-yliden)hydrazo]}benzoic acid, instability of the cyclohexyl derivative

Jan Chalupa[a]; Libor Dušek[b]; Zdeňka Padělková[a]; Petr Švec[a]; Vladimír Pejchal[c]; Aleš Růžička[a]
[a] Department of General and Inorganic Chemistry, University of Pardubice, Pardubice, Czech Republic
[b] Institute of Environment Protection, University of Pardubice, Pardubice, Czech Republic [c] Institute of Organic Chemistry and Technology, University of Pardubice, Pardubice, Czech Republic

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Triorganotin(IV) esters of 2-{[*N*-(2-oxo-2H-naphthalene-1-yliden)hydrazo]}benzoic acid, instability of the cyclohexyl derivative

JAN CHALUPA†, LIBOR DUŠEK‡, ZDEŇKA PADĚLKOVÁ†, PETR ŠVEC†,
VLADIMÍR PEJCHAL§ and ALEŠ RŮŽIČKA*†

†Department of General and Inorganic Chemistry, University of Pardubice, Pardubice, Czech Republic
‡Institute of Environment Protection, University of Pardubice, Pardubice, Czech Republic
§Institute of Organic Chemistry and Technology, University of Pardubice, Pardubice, Czech Republic

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Three triorganotin(IV) esters of 2-{[*N*-(2-oxo-2H-naphthalene-1-yliden)hydrazo]}benzoic acid were prepared and studied by IR and NMR spectroscopy and X-ray crystallography for the tributyl- and triethyltin(IV)-2-{[*N*-(2-oxo-2H-naphthalene-1-yliden)hydrazo]}benzoates (**2**, **3**). These compounds are monomeric in solution with four-coordinate tin. The hydrazo tautomeric forms are present in chloroform solution as well as in the solid state. The coordination geometries of tin in **2** and **3** are trigonal bipyramidal with all three carbons in equatorial positions, one carboxylic oxygen and the quinone-type oxygen from adjacent molecules are in axial positions forming centrosymmetric dimers with the ring containing 20 members. The yield of the tricyclohexyltin(IV) derivative (**4**) is much lower than **2** or **3**, with instability towards moisture in solution. The product of the reaction with water is the *bis*(μ^2-hydroxo)-*bis*{2-{[*N*-(2-oxo-2H-naphthalene-1-yliden)hydrazo]}benzoato}tetracyclohexylditin (**4a**) dimer. The tin is five-coordinate in the solid state by two cyclohexyl and two hydroxy groups, the last coordination site is occupied by a monodentate carboxy group. The dimeric form of this compound remains in chloroform solution.

Keywords: Triorganotin(IV) esters; Azo dye; NMR; X-ray

1. Introduction

Triorganotin(IV) esters of carboxylic acids are catalysts and bioactive compounds [1, 2]. Structures of these compounds are well established by X-ray [3], Mössbauer, and CP MAS NMR in the solid state, and mainly by multinuclear NMR techniques in solution [1]. The tin in these compounds can be four-coordinate or five-coordinate with tin surrounded by three carbons from organo groups and two oxygens from an asymmetrically bidentate carboxylate (intramolecularly chelated) or two different carboxylate groups (intermolecularly bridging). Compounds with intermolecular

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*Corresponding author. Email: ales.ruzicka@upce.cz

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bridges form infinite polymeric networks in the solid state [3], which can be fragmented into oligomeric or monomeric particles in solution [4]. Another structural motif in polymeric and/or chelate arrangement occurs when another donor is present [3].

We reported previously [5] that organotin derivatives of simple azo dyes, methyl orange and *para*-methyl red (also used as acid-base indicators), when containing a C,N-chelating ligand, have different physico-chemical properties [5] from the free azo dyes; some organotin complexes of azo dyes were without an intramolecular Sn–N bond. More complicated azo dyes, which are involved in many industrial applications [6] and their triorganotin derivatives were also studied [7]. Some occur in two tautomeric forms, and there is also the possibility of increase in tin coordination via coordination of dye donor atoms. The products of reactions of triorganotin halides with azo dye silver salts are intensively colored and represent a special sort of metallacomplex dye that is extensively studied for its optical properties [6]. Organotin(IV) compounds have also been screened for *in vitro* and *in vivo* for antitumor activity [8] and biological activity against pathogenic fungi [4, 7, 9].

Now we report on simple trialkyltin derivatives of selected carboxylate ligands used in our previous study 2-{[*N*-(2-oxo-2H-naphthalene-1-yliden)hydrazo]}benzoate; 40 years ago this ligand was used for complexation of tributyl- and triphenyltin chloride [10]. The ligand makes interesting structures in solution and the solid state going from monomeric monodentate carboxylate, through bidentate forming polymers, through azo-hydrazone tautomerism where the formation of small (6 or 11), bigger 10-membered chelate rings, or even bigger cycles through an intermolecular connection can be formed, as we proposed for diesters of ketopimelic acid [11].

2. Experimental

2.1. *Materials and methods*

All syntheses were carried out in air. 2-{[*N*-(2-oxo-2H-naphthalene-1-yliden)hydrazo]}-benzoic acid (**1**) was a gift of Prof. Dr Antonín Lyčka (VÚOS a.s., Pardubice-Rybitví, Czech Republic); potassium butoxide, sodium hydroxide, isopropanol, tin halides, and dichloromethane were obtained from commercial sources (Sigma-Aldrich) and used without further purification.

2.2. *Triethyltin-2-{[N-(2-oxo-2H-naphthalene-1-yliden)hydrazo]}benzoate (2)*

Compound **2** was prepared by mixing triethyltin chloride (1 g, 4.14 mmol), 1.21 g of 2-{[*N*-(2-oxo-2H-naphthalene-1-yliden)hydrazo]}benzoic acid (4.14 mmol) and potassium tert-butoxide (0.4 g, 4.55 mmol) in dichloromethane (30 mL) for 12 h at reflux. The reaction mixture was filtered, solvent removed *in vacuo* and the solid residue crystallized from dichloromethane/hexane yielding 1.68 g (82%) of pure **2**. ^{1}H NMR ($CDCl_3$, 300 K, ppm): 16.48 (1H, s, Hα), 8.43 (1H, d, H15″), 8.26 (1H, d, H6″), 8.10 (1H, d, H3″), 7.59 (1H, d, H12″), 7.56 (1H, dd, H4″), 7.47 (1H, dd, H14″), 7.45 (1H, d, H10″), 7.36 (1H, dd, H13″), 7.18 (1H, dd, H5″), 6.67 (1H, d, H9″), 1.23 (6H, m, ethyl), 1.08 (9H, m, ethyl). ^{119}Sn {^{1}H} NMR ($CDCl_3$, 300 K, ppm): 160.75. Anal.– Found: C, 55.5%; H, 5.2%; N, 5.7%. Calcd: C, 55.57%; H, 5.27%; N, 5.63%. m.p. >350°C, λ_{max} (nm)/ε_{max} ($m^2 mol^{-1}$) in EtOH: 232/1260, 488/1002. $\nu_{as}(C=O)$ (cm^{-1})/$\nu_s(C=O)$ (cm^{-1}); 1647/1375.

2.3. *Tributyltin-2-{[N-(2-oxo-2H-naphthalene-1-yliden)hydrazo]}benzoate (3)*

Similar procedure as for **2** was applied for the tributyltin derivative. A 1 g of tributyltin chloride (3.07 mmol), 0.89 g of acid (3.07 mmol), and potassium butoxide (0.29 g, 3.37 mmol) yields 1.51 g (85%) of **3**. ^1H NMR ($CDCl_3$, 300 K, ppm): 16.48 (1H, s, Hα), 8.41 (1H, d, H15″), 8.26 (1H, d, H6″), 8.10 (1H, d, H3″), 7.57 (1H, d, H12″), 7.55 (1H, dd, H4″), 7.47 (1H, dd, H14″), 7.45 (1H, d, H10″), 7.34 (1H, dd, H13″), 7.17 (1H, dd, H5″), 6.65 (1H, d, H9″), 1.71 (6H, m, butyl), 1.48 (6H, m, butyl), 1.39 (6H, m, butyl), 0.93 (9H, m, butyl). $^{119}Sn\ \{^1H\}$ NMR ($CDCl_3$, 300 K, ppm): 127.16. Anal. Found: C, 59.8%; H, 6.5%; N, 4.7%. Calcd: C, 59.92%; H, 6.59%; N, 4.82%. m.p. 179–182°C, λ_{max} (nm)/ϵ_{max} ($m^2 mol^{-1}$) in EtOH: 204/29976, 228/24345, 312/5407, 486/11886. $\nu_{as}(C=O)$ (cm^{-1})/$\nu_s(C=O)$ (cm^{-1}); 1617/1345.

2.4. *Tricyclohexyltin-2-{[N-(2-oxo-2H-naphthalene-1-yliden)hydrazo]}benzoate (4)*

Similar procedure as for **2** was applied for the tricyclohexyltin derivative. A 1 g of tricyclohexyltin chloride (2.47 mmol), 0.72 g of acid (2.47 mmol), and potassium butoxide (0.24 g, 2.72 mmol) yields 0.34 g (21%) of **4**. ^1H NMR ($CDCl_3$, 300 K, ppm): 16.45 (1H, s, Hα), 8.42 (1H, d, H15″), 8.25 (1H, d, H6″), 8.08 (1H, d, H3″), 7.58 (1H, d, H12″), 7.55 (1H, dd, H4″), 7.49 (1H, dd, H14″), 7.47 (1H, d, H10″), 7.35 (1H, dd, H13″), 7.16 (1H, dd, H5″), 6.67 (1H, d, H9″), 2.02 (3H, m, cyclohexyl), 1.68 (24H, m, cyclohexyl), 1.31 (6H, m, cyclohexyl). $^{119}Sn\ \{^1H\}$ NMR ($CDCl_3$, 300K, ppm): 25.65. Anal. Found: C, 63.6%; H, 6.7%; N, 4.2%. Calcd: C, 63.75%; H, 6.73%; N, 4.25%. m.p. 164–166°C, λ_{max} (nm)/ε_{max} ($m^2 mol^{-1}$) in EtOH: 206/8208, 486/2639. $\nu_{as}(C=O)$ (cm^{-1})/$\nu_s(C=O)$ (cm^{-1}); 1622/1339.

Due to low yield of **4** an alternative procedure was applied [11]. Tricyclohexyltin chloride (1 g, 2.47 mmol), 0.72 g of free acid (2.47 mmol), and sodium hydroxide (0.24 g, 2.72 mmol) were refluxed in isopropanol (50 mL) for 10 h. Afterwards, the reaction mixture was filtered and solvent removed *in vacuo* giving only low yield of desired product.

2.5. *Bis(μ²-hydroxo)-bis{2-{[N-(2-oxo-2H-naphthalene-1-yliden)hydrazo]}-benzoato}-tetracyclohexylditin (4a)*

Compound **4** in dichloromethane in air for more than 5 days changes to **4a** essentially quantitatively. ^1H NMR ($CDCl_3$, 300 K, ppm): 16.68 (2H, s, Hα), 8.50 (2H, d, H15″), 8.35 (2H, d, H6″), 8.31 (2H, d, H3″), 7.72 (2H, d, H12″), 7.64 (2H, dd, H4″), 7.58 (2H, dd, H14″), 7.53 (2H, d, H10″), 7.41 (2H, dd, H13″), 7.30 (2H, dd, H5″), 6.63 (2H, d, H9″), 6.06 (2H, s, OH), 2.32 (4H, broad, cyclohexyl), 1.71 (32H, m, cyclohexyl), 1.31 (8H, m, cyclohexyl). $^{119}Sn\ \{^1H\}$ NMR ($CDCl_3$, 300 K, ppm): −273.5. Anal. Found: C, 58.7%; H, 5.5%; N, 4.7%. Calcd: C, 58.81%; H, 5.62%; N, 4.73%. m.p. 178–181°C.

2.6. *NMR spectroscopy*

The ^{1}H (500.13 MHz) and ^{119}Sn (186.50 MHz) NMR spectra of all compounds in $CDCl_3$ (30–50 mg in 0.6 mL) were recorded at ambient temperature on a Bruker Avance 500 spectrometer equipped with a 5 mm broadband probe with z-gradient. The ^{1}H chemical shifts were referred to the signal of residual $CHCl_3$ ($\delta(^1H) = 7.25$) and the ^{119}Sn chemical shifts were referred to external neat tetramethylstannane ($\delta(^{119}Sn) = 0.0$). Two-dimensional *gs*(gradient selected)-H,H-COSY and *gs*-^{1}H-^{13}C–HSQC [12, 13] spectra were recorded using standard programs provided by Bruker. ^{119}Sn NMR spectra were measured using the inverse gated-decoupling mode. ^{1}H and ^{13}C chemical shifts were assigned from 2-D NMR spectra (optimized for $^1J(^{13}C, ^1H)$ *ca.* 150 Hz and $^3J(^{13}C, ^1H)$ *ca.* 8 Hz, respectively).

2.7. *IR spectroscopy*

IR spectra were recorded on a Bruker Vector 22 mid-FTIR spectrophotometer with accessory MIRacle^{TM} in the solid state.

2.8. *UV-VIS spectroscopy*

UV-VIS spectra were measured in ethanol using a Biochrom Libra S22 UV-VIS spectrophotometer at 25°C.

2.9. *X-ray crystallography*

The single crystals of **2**, **3**, and **4a** were grown from *ca.* 5% CH_2Cl_2 solution into which hexane was charged *via* slow vapor diffusion on the air.

The X-ray data were collected on a Nonius KappaCCD diffractometer fitted with MoK_α radiation ($\lambda = 0.71073$ Å) at 150(1) K. The absorption correction was performed using a Gaussian procedure [14] and the structure was solved by direct methods (SIR92 [15]) with full-matrix least-squares refinements on F^2 using SHELXL97 [16]. There is an orientation disorder of organotin fragment (around 5%) in **2** caused by the thermal motion even at 150 K.

Crystallographic data for **2**; $C_{46}H_{52}N_4O_6Sn_2$, $M = 497.15$, triclinic, $P\bar{1}$, $a = 8.8010(5)$, $b = 10.8010(6)$, $c = 11.3580(6)$ Å, $\alpha = 97.260(5)$, $\beta = 95.077(5)$, $\gamma = 90.346(5)°$, $Z = 2$, $V = 1066.67(10)$ Å^3, $D_c = 1.548\ \mathrm{g\,cm^{-3}}$, $\mu = 1.224\ \mathrm{mm^{-1}}$, $T_{min} = 0.804$, $T_{max} = 0.855$; 18074 reflections measured ($\theta_{max} = 27.5°$), 4836 independent ($R_{int} = 0.0513$), 4318 with $I > 2\sigma(I)$, 262 parameters, $S = 1.186$, $R1$ (obs. data) $= 0.1291$, $wR2$ (all data) $= 0.3528$; max, min residual electron density $= 8.843$, -2.108 eÅ^{-3}. CCDC deposition number: 699215.

Crystallographic data for **3**; $C_{58}H_{76}N_4O_6Sn_2$, $M = 581.30$, triclinic, $P\bar{1}$, $a = 11.4890(7)$, $b = 11.6160(10)$, $c = 12.3240(7)$ Å, $\alpha = 70.900(5)$, $\beta = 65.178(5)$, $\gamma = 68.790(5)°$, $Z = 1$, $V = 1361.44(16)$ Å^3, $D_c = 1.418\ \mathrm{g\,cm^{-3}}$, $\mu = 0.970\ \mathrm{mm^{-1}}$, $T_{min} = 0.859$, $T_{max} = 0.926$; 26109 reflections measured ($\theta_{max} = 27.5°$), 6194 independent ($R_{int} = 0.049$), 5205 with $I > 2\sigma(I)$, 316 parameters, $S = 1.079$, $R1$ (obs. data) $= 0.042$, $wR2$ (all data) $= 0.089$; max, min residual electron density $= 1.505$, -0.674 eÅ^{-3}. CCDC deposition number: 699213.

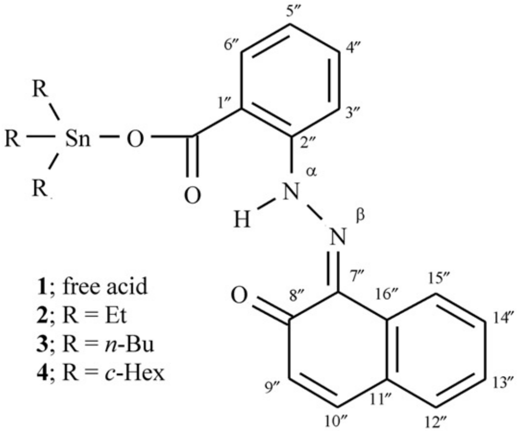

Figure 1. One structure and numbering scheme.

Crystallographic data for **4a**. CH_2Cl_2; $C_{60}H_{72}N_4O_8Cl_4Sn_2$, $M = 1356.40$, monoclinic, $P2_1/c$, $a = 12.1120(10)$, $b = 24.1140(12)$, $c = 10.5760(8)$ Å, $\beta = 101.680(7)°$, $Z = 2$, $V = 3029.2(4)$ Å^3, $D_c = 1.372\,\mathrm{g\,cm^{-3}}$, $\mu = 0.965\,\mathrm{mm^{-1}}$, $T_{\min} = 0.722$, $T_{\max} = 0.833$; 22006 reflections measured ($\theta_{\max} = 27.5°$), 6703 independent ($R_{\mathrm{int}} = 0.0453$), 5152 with $I > 2\sigma(I)$, 352 parameters, $S = 1.194$, $R1$ (obs. data) $= 0.0465$, $wR2$ (all data) $= 0.0918$; max, min residual electron density $= 0.739$, -0.656 eÅ^{-3}. CCDC deposition number: 699214.

3. Results and discussion

Triorganotin(IV) esters of 2-{[*N*-(2-oxo-2H-naphthalene-1-yliden)hydrazo]}benzoic acid (figure 1), **2**–**4**, were prepared by published methods [11, 21] from reaction of appropriate organotin(IV) chloride with one equivalent of 2-{[*N*-(2-oxo-2H-naphthalene-1-yliden)hydrazo]}benzoic acid and potassium butoxide in refluxing dichloromethane. All reactions gave satisfactory (85% of **3**) to moderate yields (21% for **4**) of analytically pure products after purification by crystallization and washing by chloroform/hexane. The purity of **2**–**4** was checked by elemental analysis and NMR measurements. All these compounds are stable in air for longer than 1 year except **4**, which changes to **4a** in dichloromethane in 5 days, probably by reaction with water to extrude cyclohexane.

3.1. *Structures of (1)–(4a)*

3.1.1. IR spectroscopy. The values of ν_{as} and ν_s for CO_2 [17] for **1**–**4** are collected in table 1; the range found for $\nu_{as}(CO_2)$ (1615–1647 cm^{-1}) and $\nu_s(CO_2)$ (1326–1375 cm^{-1}) clearly indicate monodentate carboxylate [11].

Table 1. Selected parameters of IR (neat) [cm^{-1}] and NMR [ppm] spectra for **1**–**4**.

Compd. (R)/Parameter	$\nu_{as}(CO_2)$	$\nu_s(CO_2)$	$\delta(^{119}Sn)$ in $CDCl_3$
1 (free acid)	1615	1326	–
2 (Et)	1647	1375	160.8
3 (n-Bu)	1617	1345	127.2
4 (c-Hex)	1622	1339	25.7

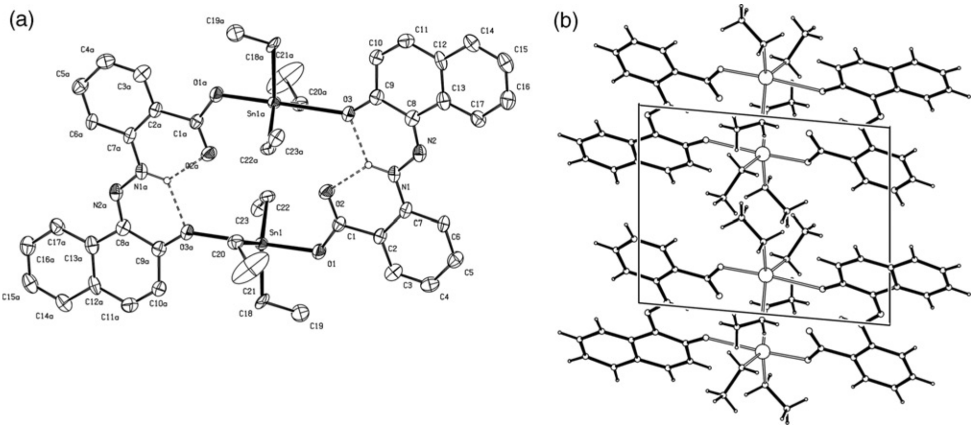

Figure 2. (a) Molecular structure of **2** with atom numbering scheme. (ORTEP 30% probability level), hydrogen atoms (except hydrazo) are omitted for clarity. Selected interatomic distances (Å) and angles (°): Sn1–O1 2.102(10), Sn1–C20 2.115(15), Sn1–C22 2.128(15), Sn1–C18 2.211(17), N1–N2 1.317(18), N1–C7 1.38(2), O1–C1 1.292(18), O3–C9 1.244(19), C1–O2 1.225(18), C1–C2 1.516(18), C2–C7 1.42(2), C2–C3 1.40(2), C7–C6 1.424(18), N2–C8 1.31(2), C13–C17 1.39(2), C13–C8 1.41(2), C13–C12 1.45(3), C6–C5 1.36(2), O1–Sn1–C20 98.6(6), O1–Sn1–C22 100.8(5), C20–Sn1–C22 127.6(6), O1–Sn1–C18 89.3(5), C20–Sn1–C18 114.3(6), C22–Sn1–C18 114.2(6), N2–N1–C7 117.3(12). H-bonding (D–H···A distances and angles): N1–H···O2 2.676(3), 127.82; N1–H···O3 2.645(2), 125.49; (b) Unit cell diagram for **2**.

3.1.2. NMR spectroscopy. NMR of **2**–**4a** in $CDCl_3$ reveal one sharp set of signals attributed to the ligand in ^1H NMR spectra, which corresponds with monomeric structure. Aliphatic parts of spectra are broadened indicating the geometrical nonequivalency of organotin moieties at room temperature (at least on the NMR time scale). One sharp signal was found in each ^1H NMR spectrum around 16.5 ppm indicating the presence of hydrazone tautomeric form of ligand in complexes. Only one signal was observed for **2**–**4a** in the ^{119}Sn NMR spectrum in $CDCl_3$ at room temperature. The chemical shift values (table 1) of these signals for **2**–**4** are in accord with values found for four-coordinate tin in noncoordinating solvent [12a, 18], but the same parameter for **4a** (−273.5 ppm) is in the range for five-coordinate organotin(IV) carboxylates [19]. Moreover, the sharp resonance in ^1H NMR spectrum at 6.06 ppm can be assigned to the bridging OH group.

3.1.3. X-ray diffraction studies. Crystals of **2** and **3** were grown by vapor diffusion in air; the same procedure was applied for **4** and only single crystals of **4a** were obtained. All attempts to crystallize **4** as single crystals suitable for X-ray analysis under

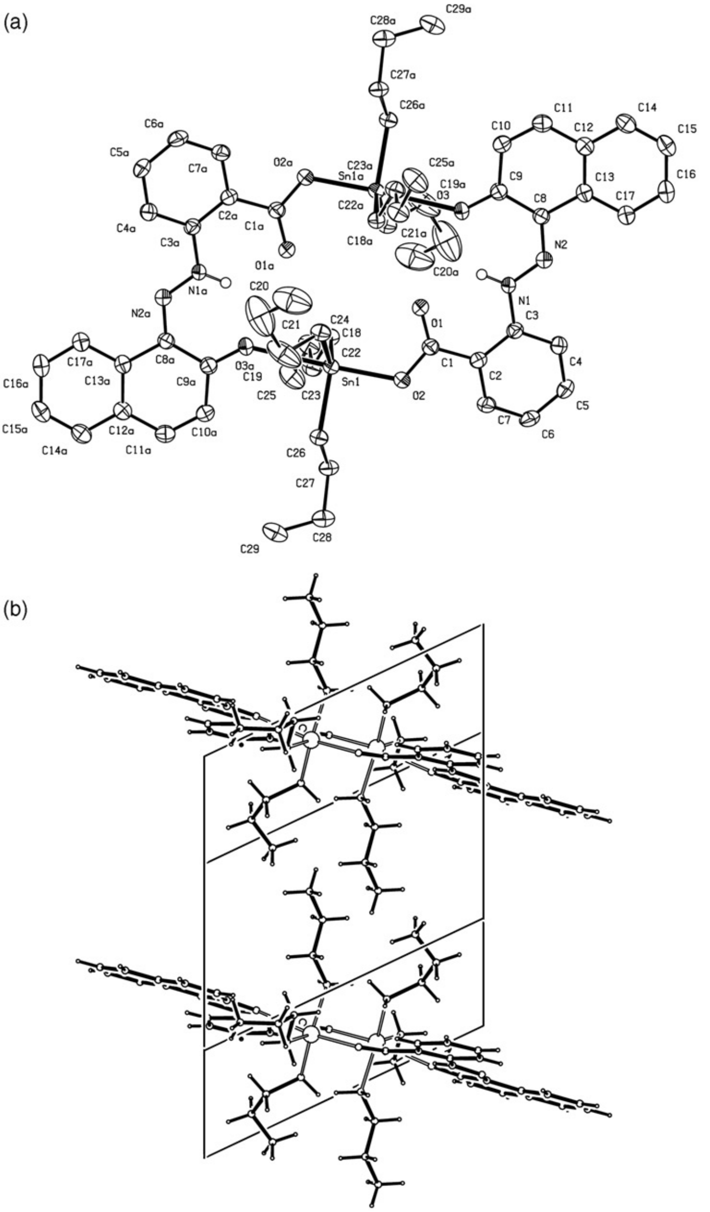

Figure 3. (a) Molecular structure of **3** with atom numbering scheme. (ORTEP 50% probability level), hydrogen atoms (except hydrazo) are omitted for clarity. Selected interatomic distances (Å) and angles (°): Sn1–C18 2.127(4), Sn1–O2 2.130(2), Sn1–O1 3.175(2), Sn1–O3 2.612(2), Sn1–Sn1a 5.3626(6), Sn1–C22 2.133(4), Sn1–C26 2.145(3), O1–C1 1.227(4), O3–C9 1.251(4), N1–N2 1.302(4), N1–C3 1.409(4), N1–H1 0.8600, N2–C8 1.327(4), O2–C1 1.292(4), C12–C13 1.406(5), C12–C11 1.439(5), C10–C11 1.343(5), C10–C9 1.445(5), C13–C8 1.459(5), C9–C8 1.458(5), O3–Sn1–O2 172.33(12), C18–Sn1–O2 102.87(13), C18–Sn1–C22 127.00(13), O2–Sn1–C22 94.96(12), C18–Sn1–C26 108.77(14), O2–Sn1–C26 88.78(12), C22–Sn1–C26 121.25(14). H–bonding (D–H ··· A distances and angles): N1–H ··· O1 2.682(3), 129.29; N1–H ··· O3 2.633(4), 129.99; (b) Unit cell diagram for **3**.

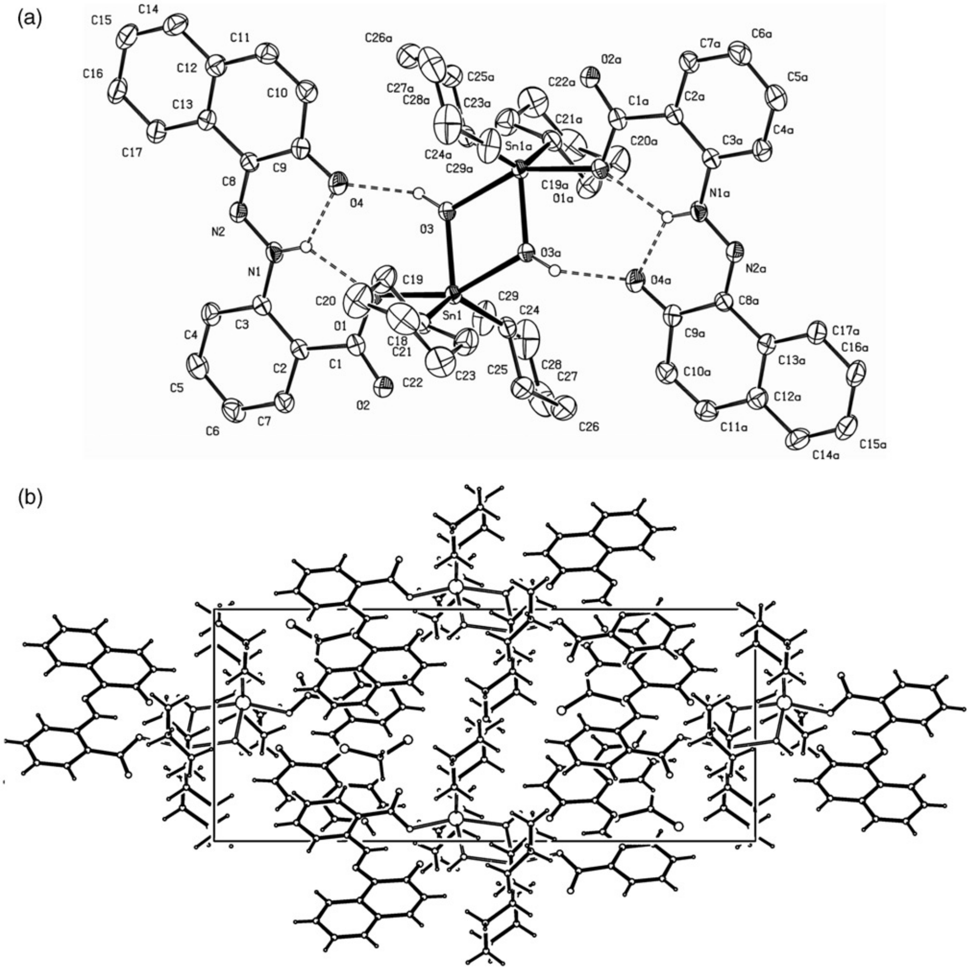

Figure 4. (a)Molecular structure of **4a** with atom numbering scheme (ORTEP 50% probability level); hydrogen atoms (except hydrazo and hydroxo) are omitted for clarity. Selected interatomic distances (Å) and angles (°): Sn1–O3 2.026(2), Sn1–C24 2.132(4), Sn1–C18 2.137(4), Sn1–O1 2.155(2), Sn1–O3a 2.252(2), O1–C1 1.295(4), O4–C9 1.246(5), N2–N1 1.306(4), N2–C8 1.322(5), O2–C1 1.232(5), O3–Sn1–C24 108.48(13), O3–Sn1–C18 114.04(13), C24–Sn1–C18 135.65(15), O3–Sn1–O1 82.98(10), C24–Sn1–O1 102.63(13), C18–Sn1–O1 94.56(13), O3–Sn1–O3a 70.85(11), C24–Sn1–O3 90.11(12), C18–Sn1–O3 92.19(13), O1–Sn1–O3 153.47(9), Sn1–O3–Sn1 109.15(11). H–bonding (D–H ⋯ A distances and angles): N1–H ⋯ O4 2.593(2), 133.25; N1–H ⋯ O1 2.642(3), 130.94; O3–H ⋯ O4 2.704(3), 130.54; (b) Unit cell diagram for **4a**.

anaerobic conditions failed. Solid-state structures of **2**, **3**, and **4a** were determined by X-ray diffraction.

A layered arrangement of dimeric **2** and **3** reveal connections through the quinoidal oxygens forming 20-membered rings (figures 2–4). In the structure of **4a**, there are two units connected by OH bridges. The planarity depends on the steric demands of aliphatic chains; **2** is almost planar, **4a** has an interplanar shift caused by H-bridging (figure 5), and **3** has planes of both ligands a bit twisted. The separation caused by Π–Π

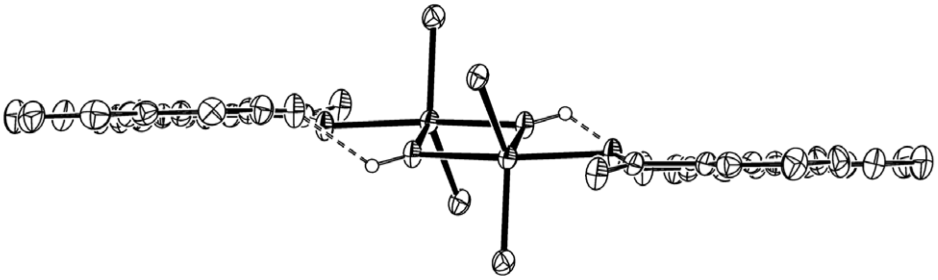

Figure 5. View of a planar arrangement of **4a**. Hydrogen atoms (except hydroxo) are omitted for clarity.

stacking between these planes in the crystal lattices is around 3.4 Å for all compounds [3.372(2) in **2**, 3.412(2) in **3**, and 3.389(2) Å in **4a**]. A nonclassical H-bridge is observed in **4a** for noncoordinated carboxylic oxygen and C–H of dichlormethane (D...H-A: 3.278(3) Å, 122.4°).

In all compounds, the hydrazone tautomeric form is observed with elongation of N1–N2 and appropriate distances in the naphthyl ring. Distances O3–C9 (for **2** and **3**) and O4–C9 (for **4a**) reveal significant double bond character.

The coordination geometry of tin in **2** and **3** can be described as distorted trigonal bipyramids (figures 2 and 3, for structural parameters see figure captions), where aliphatic carbons are equatorial and oxygens of ligands (one carboxylic and one quinoidal) axial. Angles C—Sn–C in the equatorial plane of **2** and **3** differ significantly from 107° to 128°, where the smallest were for carbon atoms lying in the direction to the center of the 20-membered rings and the bigger ones for angles for the outer carbon. The sum of angles in equatorial positions is 356.1° and 357.0°. Angles O–Sn–O in the tin coordination polyhedra are around 175°. Two ligands symmetrically bridge tins which are separated by 5.393(2) and 5.363(3) Å for **2** and **3**, respectively. The monodentate coordination (similar bonding distances as triphenyltin benzoate 2.073(2) Å and previously published organotin carboxylates containing C,N-chelating ligand) [5, 7, 11, 19, 20] of carboxylate is reflected in the disparate C–O bond distances (see figure 2 and 3 captions) and longer C–O separation associated with stronger Sn–O interaction. Second oxygens of carboxylic groups are out of the tin primary coordination sphere Sn–O2 3.203(3) Å for **2** and Sn–O1 3.175(2) Å for **3**. There is no interaction of tin with adjacent donor atoms. Possible hydrogen bridging between nitrogen of hydrazone and quinoidal or carboxylic oxygens was detected (see figure 2 and 3 captions).

The structure of **4a** has two diorganotin fragments bound to one ligand monodentate (disparate distances in carboxylic group are Sn1–O1 2.155(2) and 2.957(3) Å, similar to tricyclohexyltin acetate [21]) and bridged unsymmetrically by two OH groups. The coordination geometry of the tin is between trigonal bipyramidal and square pyramidal; based on the τ parameter (0.30) [22] it is more square pyramidal. Comparable structures were found for *bis*(μ^2-hydroxo)-*bis*(2,4,6-tris(trifluoromethyl)benzoato)tetraphenylditin, *bis*(μ^2-hydroxo)-*bis*[diphenyl(trichloroacetato-O)tin], and *bis*(μ^2-hydroxo)-tetrachloro-*bis*{2-[(-)-menthyloxycarbonyl)ethyl-C,O]}ditin [23–25]. Five-coordinate tin with cyclohexyl groups and isoleucinate or salicylidene ligands have trigonal bipyramidal geometry [26]. There is an extensive H-bridging network in **4a** connecting hydrazone, carboxylate, quinone, and hydroxo functional groups (figures 4 and 5).

In conclusion, three aliphatic tin derivatives of an azo dye ligand were prepared, two of them revealing good stability in air, but the tricyclohexyl derivative is instable giving dicyclohexyltin dihydroxo bridged derivative. Triorganotin compounds are monomeric in the solution and dimeric in solid state; the dicyclohexyl derivative retains dimeric structure in solution.

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