

Structure of azo dye organotin(IV) compounds containing a C,N-chelating ligand†

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Two complexes derived from simple azo dyes (methyl orange and *para*-methyl red) and the [(2-dimethylaminomethyl)phenyl](diphenyl)tin(IV) moiety have been prepared and their NMR, MS, IR, Raman and UV-VIS spectra were measured and X-ray structures determined. Both compounds reveal the same structure in chloroform and in the solid state. The central tin atoms exist in a slightly distorted *trans*-trigonal bipyramidal geometry. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: organotin(IV) compounds; azo dyes; C,N-ligand; NMR; X-ray diffraction; electrospray ionization mass spectrometry

INTRODUCTION

Organometallic compounds with the possibility of hypercoordination play an important role in current research.^{1–3} Organotin(IV) compounds with the same type of coordination ability have been investigated for the last three decades,^{4,5} but the quantity of results in the field of additional ligand exchange reactions (halogens are commonly used as additional ligands) is rather rare.^{6,7} We have previously reported on the evaluation of intramolecular Sn–N interactions in these types of compound using NMR spectra parameters.^{8,9}

Organotin(IV) compounds have also been extensively studied and screened *in vitro* and *in vivo* for antitumour activity.^{10,11} Recently, considerable attention has been paid to triorganotin(IV) derivatives, owing to their high *in vitro* antifungal activities against some medically important fungi.^{7,12}

We report here on the synthesis and structural investigation of two complexes consisting of simple azo dyes (which are also used as acid–base indicators), namely methyl orange and *para*-methyl red, and a C,N-chelating ligand containing an organotin(IV) compound. These two substances represent a new type of compound containing, besides a C,N-chelating ligand, a bulky substituent instead of the halogen atom typically used in previous studies. The reaction products are intensively coloured and represent a special sort of metallo-complex dyestuff which are extensively studied for their special (mainly optical) properties.^{13–16} Theoretically, an intermolecular interaction between tin and the azo-group nitrogen(s) can exist. Our study is based on an application of X-ray data in the solid state and multinuclear magnetic resonance data in solution with the aim to characterize the coordination sphere of the tin(IV) atom. Electronic spectra were recorded to make a comparison of λ_{max} and extinction coefficients for **1** and **2** and their precursors (Fig. 1).

EXPERIMENTAL

General comments

All solvents were obtained from commercial sources (Acros). All reactions were carried out in air atmosphere and with commercially available solvents, without any drying or further purification. Aluminium foil was used for reaction

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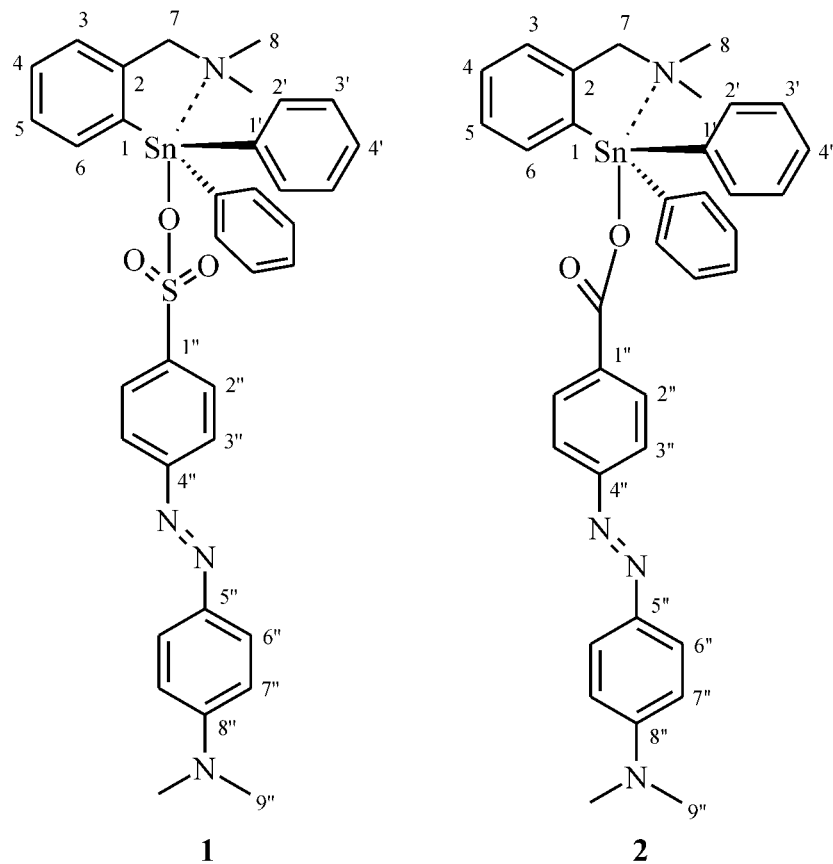


Figure 1. Structure and numbering scheme of compounds **1** and **2**.

flask light protection in the cases of reactions where silver(I) compounds were employed.

Synthesis

[[2-(Dimethylaminomethyl)phenyl](diphenyl)]tin(IV)-4-[[4'-(dimethylamino)phenyl]azo]benzenesulfonate (1)
To a warm (80 °C) solution of the sodium salt of 4-[[4'-(dimethylamino)phenyl]azo]benzenesulfonic acid (methyl orange, sodium salt; 1 g, 3.055 mmol) in 150 ml of water, an equimolar amount of AgNO₃ was added; the mixture was stirred at the elevated temperature for 2 h, then cooled to 10 °C and filtered. The crude product was washed twice with a small amount of cold water and twice with methanol. The dark-red precipitate was dried overnight *in vacuo* at room temperature. The resulting methyl orange silver(I) complex (1.2 g; 2.91 mmol; yield 96%) was suspended in toluene (200 ml) and added to solution of 1.29 g (2.91 mmol) [[2-(dimethylaminomethyl)phenyl](diphenyl)]tin chloride⁹ in toluene (100 ml). The mixture was refluxed for 3 h, then filtered; the filtrate was concentrated *in vacuo* to 15 ml and cooled to -50 °C. The resulting red crystals were crystallized from chloroform-hexane mixture (1:5) to give **1** as a pure deep-red solid. Yield: 1.49 g (72%); m.p. 217–218 °C. Found: C, 59.2; H, 5.2; N, 7.9. C₃₅H₃₆N₄O₃SSn requires C, 59.09; H, 5.20; N, 7.88. UV-VIS [λ (nm)/ ϵ (m² mol⁻¹)]: 420/3424. IR,

Raman (cm⁻¹): ν_a (N=N) 1443, ν (C=C) 1602, ν_a (S=O) 1280, ν_s (S=O) 1100.

[[2-(Dimethylaminomethyl)phenyl](diphenyl)]tin(IV)-4-(4'-dimethylaminophenylazo)benzoate (2)

Compound **2** was obtained analogously to **1** from 1 g (3.44 mmol) of the sodium salt of 4-(4'-dimethylaminophenylazo)benzoate (*para*-methyl red) and 1.39 g of the above-mentioned chloride⁹ (3.16 mmol – with respect to a 92% silver(I) complex yield) as an orange solid material, yield: 1.36 g (63.6%); m.p. 206–207 °C. Found: C, 63.9; H, 5.3; N, 8.4. C₃₆H₃₆N₄O₂Sn requires C, 64.02; H, 5.37; N, 8.30. UV-VIS [λ (nm)/ ϵ (m² mol⁻¹)]: 417/2630. IR, Raman (cm⁻¹): ν_a (N=N) 1445, ν (C=C) 1600, ν_a (C=O) 1636, ν_s (C=O) 1329.

NMR measurements

The ¹H (500.13 MHz), ¹³C (125.76 MHz), ¹¹⁹Sn (186.50 MHz) and ¹⁵N (50.65 MHz) NMR spectra of compounds **1** and **2** in deuteriochloroform were recorded at ambient temperature on a Bruker Avance 500 spectrometer equipped with a 5 mm broadband probe with z-gradient and an SGI O2 computer. The ¹³C and ¹H chemical shifts were referenced to the signal of CDCl₃ and residual CHCl₃ respectively (δ (¹³C) = 77.0, δ (¹H) = 7.25), the ¹¹⁹Sn chemical shifts were referenced to external neat tetramethylstannane (δ (¹¹⁹Sn) = 0.0), and the

^{15}N chemical shifts were referenced to external neat nitromethane ($\delta(^{15}\text{N}) = 0.0$).

Two-dimensional gradient-selected (gs)-H,H-COSY, gs- ^1H - ^{13}C -HSQC, gs- ^1H - ^{13}C -HMBC and gs- ^1H - ^{15}N -HMBC^{17,18} spectra were recorded using standard microprograms provided by Bruker. ^{119}Sn NMR spectra were measured using the inverse gated-decoupling mode. The ^1H and ^{13}C chemical shifts were assigned from gs-H,H-COSY, gs- ^1H - ^{13}C -HSQC and gs- ^1H - ^{13}C -HMBC^{17,18} spectra (with the latter two optimized for $^1J(^{13}\text{C},^1\text{H}) \approx 150$ Hz and $^3J(^{13}\text{C},^1\text{H}) \approx 8$ Hz respectively). The ^{15}N chemical shifts were assigned using gs- ^1H - ^{15}N HMBC spectra optimized for $^nJ(^{15}\text{N},^1\text{H}) = 4\text{--}5$ Hz. The assignment of ^{15}N chemical shifts of —N=N— moiety is in line with data published for ^{15}N selectively mono-enriched azobenzenes.¹⁹

Mass spectrometry

Electrospray ionization (ESI) mass spectra were measured on an Esquire3000 ion trap mass analyser (Bruker Daltonics, Bremen, Germany) within the mass range m/z 50–800. The mass spectrometer was tuned to give an optimum response for m/z 400. The samples were dissolved in acetonitrile and analysed by direct infusion at a flow rate of $2 \mu\text{l min}^{-1}$, both in the positive-ion and negative-ion modes. The ion source temperature was 300°C , and the flow rate and the pressure of nitrogen were 4 l min^{-1} and 10 psi respectively. For all MS/MS measurements, the isolation width was $m/z = 8$ and the collision amplitude was 0.7 V. Mass spectra were averaged over ten scans. Ions with relative abundances lower than 2% are neglected. 'Cat' means cationic and 'An' means anionic part of the molecule (see discussion below for the explanation).

Positive-ion ESI MS/MS of 408 for both compounds (mass-to-charge (m/z), proposed structure of the ion, the relative abundance): m/z 363, [Cat- CH_3NHCH_3]⁺, 91%; 330, [Cat- C_6H_6]⁺, 21%; 287, [Cat- $\text{C}_6\text{H}_6\text{—CH}_3\text{N=CH}_2$]⁺, 100%; 243, [Cat- $\text{CH}_3\text{NHCH}_3\text{—Sn}$]⁺, 51%; 210, [Cat- $\text{C}_6\text{H}_6\text{—Sn}$]⁺, 30%; 165, [Cat- $\text{C}_6\text{H}_6\text{—Sn—CH}_3\text{NHCH}_3$]⁺, 45%; 135, [Cat- $\text{C}_6\text{H}_5\text{—C}_6\text{H}_4\text{—Sn}$]⁺, 15%.

Negative-ion ESI MS/MS of 304 for compound **1** (mass-to-charge (m/z), proposed structure of the ion, the relative abundance): m/z 289, [An- CH_3][−], 38%; 260, [An- CH_3NCH_3][−], 3%; 240, [An- SO_2][−], 38%; 225, [An- $\text{SO}_2\text{—CH}_3$][−], 14%; 156, [C₆H₄SO₃][−], 100%.

Negative-ion ESI MS/MS of 268 for compound **2** (mass-to-charge (m/z), proposed structure of the ion, the relative abundance): m/z 224, [An- CO_2][−], 100%; 193, [An- $\text{CO}_2\text{—CH}_3\text{NH}_2$][−], 3%; 182, [An- $\text{CO}_2\text{—CH}_2\text{N=CH}_2$][−], 88%; 92, [C₆H₅NH][−], 5%.

Crystallography

Single crystals were obtained by vapour diffusion of hexane into *ca* 3% dichloromethane solution of **1** and by slow evaporation of CHCl_3 solution of **2**.

X-ray data for both structures were collected on a Nonius

KappaCCD diffractometer, Mo K_α radiation ($\lambda = 0.71073 \text{ \AA}$, graphite monochromator) at 150(2) K. The structures were solved by direct methods (SIR92²⁰); full-matrix least-squares refinements on F^2 were carried out by using the program SHELXL97.²¹

Both crystals suffered from positional disorder of some parts of the structure. In **1**, two ligands (phenyl- and (dimethylaminomethyl)phenyl-) exchange their positions, each with an occupancy close to 0.5. The disorder can be described as a result of the operation of mirror symmetry defined by the O1, Sn1 and C31 atoms (see Fig. 2); this preserves the trans-position of the nitrogen and oxygen atoms but displays the nitrogen atom slightly either on the left or on the right side of the O1—Sn1 axes. Two positions corresponding to disordered N18 and C17 atoms were clearly distinguished on a difference Fourier map; however, one pair of overlapping phenyl groups do not match exactly, causing a high correlation of atomic parameters and consequently instability in the refinement. Therefore, their geometry was fixed into idealized hexagons and refined under the assumption of rigid-body motion. Non-hydrogen atoms were refined anisotropically, except those with partial occupancy (last least-squared cycle gives $\Delta/\sigma_{\text{max}} = 0.001$). The positions of the hydrogen atoms were recalculated into idealized positions (riding model) and assigned temperature factors $H_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$ (pivot atom) and $1.5U_{\text{eq}}$ for the methyl moiety.

For **2**, one of two solvating CHCl_3 molecules is disordered into two positions as a result of rotation along a C—H bond. All non-hydrogen atoms are refined anisotropically; the hydrogen atoms were treated in the same way as the previous structure ($\Delta/\sigma_{\text{max}} = 0.001$). Absorption corrections were carried out for both data sets using a multiscan procedure (SORTAV²²). The crystallographic data for the individual structures are summarized in Table 1.

The full crystallographic data for compounds **1** and **2** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC-189176 and CCDC-189177 respectively. Copies of the data can be obtained free of charge on request (e-mail: deposit@ccdc.ca.ac.uk) and are also available in the form of standard CIF files as produced by SHELX by e-mail from the author (IC).

IR, Raman and UV-VIS spectroscopies

IR spectra were recorded on a Perkin-Elmer 684 spectrophotometer in Nujol mulls and in CHCl_3 (110 μm optical length) under laboratory conditions. Raman spectra were measured both in the solid state and in solution (CHCl_3) on Bruker IFS 55 apparatus using an FRA 106 adapter.

Electronic absorption spectra were recorded on a V-550 JASCO spectrophotometer in quartz cuvettes (optical length 1 cm) in UV and VIS region ($10000\text{--}35000 \text{ cm}^{-1}$) in CHCl_3 and in CH_3OH .

Table 1. Crystallographic parameters of the structures solved

	1	2
Formula	C ₃₅ H ₃₆ N ₄ O ₃ SSn	C ₃₆ H ₃₈ N ₄ O ₂ Sn·2(CHCl ₃)
<i>M</i>	711.43	914.11
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$ (no. 2)	<i>P</i> 2 ₁ / <i>c</i> (no. 14)
<i>a</i> (Å)	11.8300(2)	9.6271(1)
<i>b</i> (Å)	11.8540(2)	15.9260(4)
<i>c</i> (Å)	13.4070(2)	26.5390(3)
α (°)	65.757(1)	
β (°)	80.480(1)	97.0460(7)
γ (°)	70.207(1)	
<i>Z</i>	2	4
<i>V</i> (Å ³)	1612.26(5)	4038.22(8)
<i>D_c</i> (g cm ⁻³)	1.465	1.504
Dimensions (mm ³)	0.45 × 0.25 × 0.5	0.3 × 0.25 × 0.2
μ (mm ⁻¹)	0.898	1.068
<i>T_{min}</i> , <i>T_{max}</i>	0.819, 0.877	0.725, 0.811
<i>h</i> range	0, 15	0, 12
<i>k</i> range	-14, 15	-20, 20
<i>l</i> range	-16, 17	-34, 34
Reflections measured	27 681	66 755
independent (<i>R_{int}</i>) ^a	7285 (0.032)	9191 (0.047)
observed [<i>I</i> > 2 σ (<i>I</i>)]	6968	7480
Parameters refined	378	491
<i>S</i> value ^a	1.105	1.054
<i>R</i> (<i>F</i>) ^a	0.031	0.035
<i>wR</i> (<i>F</i> ²) ^a	0.078	0.089
$\Delta\rho_{\max}$; $\Delta\rho_{\min}$ (e ⁻ Å ⁻³)	1.02; -0.661	0.853; -0.748

^a $R_{\text{int}} = \sum |F_o^2 - F_{o,\text{mean}}^2| / \sum F_o^2$; $S = \{ \sum [w(F_o^2 - F_c^2)^2] / (N_{\text{diffrs}} - N_{\text{params}}) \}^{1/2}$; $R(F) = \sum |F_o| - |F_c| / \sum |F_o|$ for observed reflections; $wR(F^2) = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2 \}^{1/2}$ for all data.

RESULTS AND DISCUSSION

The compounds studied were prepared by the reaction of an azo-dye-silver(I) complex and [(2-dimethylaminomethyl)-phenyl](diphenyl)tin(IV) chloride in 1:1 ratio in warm toluene. Compounds **1** and **2** reveal satisfactory elemental analyses and the ¹H NMR spectra are in good conformity with the proposed composition. The ESI MS spectra of **1** and **2** can also be taken as proof of the compounds' identity and structure.

ESI mass spectrometry

The typical feature of the ESI mass spectra of the compounds studied is the cleavage of the Sn—O bond as the most labile one in both molecules. This cleavage primarily yields two complementary ions, which we call the cationic ('Cat') and anionic ('An') parts of the molecule (see observed ions in the Experimental). The cationic part (*m/z* 408) is identical for both molecules; therefore, the collision-induced dissociation

(CID) mass spectra of *m/z* 408 in MS/MS experiments are the same. The anionic parts differ by masses and also by fragmentation behaviour, and are therefore discussed separately.

Positive-ion ESI mass spectra

The first-stage mass spectrum of compound **1** exhibits only the ion *m/z* 408. In addition to this ion, the spectrum of compound **2** shows also the ion [M—C₆H₅]⁺ (*m/z* 599, relative abundance 29%). Owing to the characteristic isotopic distribution of the tin element, the presence or absence of tin atoms in individual fragment ions can be easily recognized.⁷ The structures of the observed ions are easily proposed by correlation with the known structure of the cationic part. Typical neutral losses are CH₃NHCH₃ ($\Delta m/z = 45$), CH₃N=CH₂ (43), C₆H₆ (78), C₆H₄ (76) and tin (120).

Negative-ion ESI mass spectra

The negative-ion ESI mass spectrum of compound **1** shows only the anionic part of the molecule (*m/z* 304) and the adduct ion with low abundance assigned as [An + An + Na]⁻ (*m/z* 631, 3%). The same adduct ion is observed in the first-stage mass spectrum of compound **2**: [An + An + Na]⁻ (*m/z* 559, 6%). The characteristic neutral losses for compound **1** are CH₃[·] ($\Delta m/z = 15$) followed by CH₃N[·] (29), SO₂ (64) and C₆H₄N₂ (104). In the case of compound **2**, the fragment ions (*m/z* 224, 43%, and *m/z* 182, 31%) are already present in the first-stage mass spectrum. The characteristic cleavage is the neutral loss of carbon dioxide ($\Delta m/z = 44$) followed by losses of CH₃NH₂ (31) or CH₂N=CH₂ (42).

ESI mass spectrometry in positive-ion and negative-ion modes gives complementary information for the structure confirmation of organotin complexes with a labile bond, where the cationic part of the molecule can be measured in the positive-ion mode and the anionic part in the negative-ion mode.

Solid-state study of compounds **1** and **2**

Crystallography

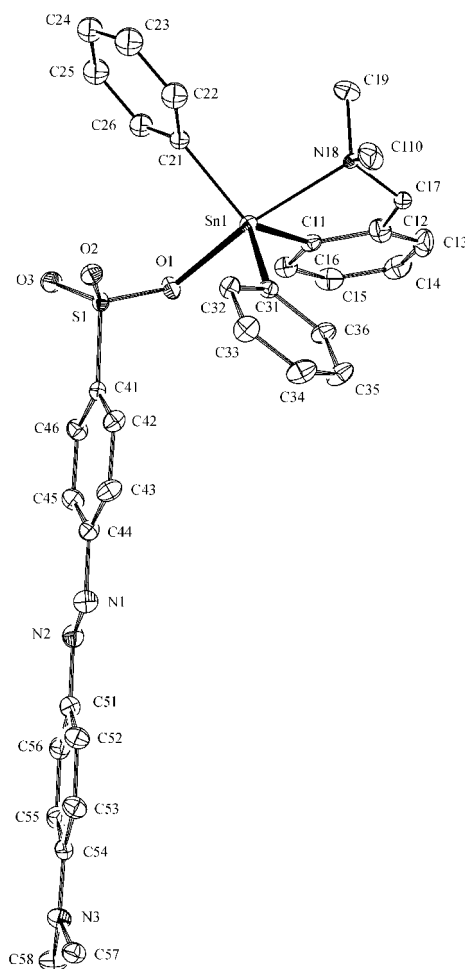
Selected parameters for the crystal structures of compounds **1** and **2** are collected in Table 2; the ORTEP drawing with the numbering scheme of compound **1** is depicted in Fig 2 and for compound **2** in Fig. 3. In both structures, the tin atoms exist in a slightly distorted *trans*-trigonal bipyramidal geometry defined by three *ipso*-carbon atoms of the phenyl groups in equatorial positions, with the intramolecularly bound nitrogen atom for the CH₂N(CH₃)₂ group and the oxygen atom of the sulfonate and carboxylate groups in apical positions (Sn1—O1 2.199(2) Å for **1** (2.37 Å for the analogous compound Me₃SnO₃SPh·H₂O)²³ and Sn1—O7 2.140(2) Å for **2** (2.073 Å for triphenyltin benzoate)²⁸). The remaining oxygen atoms (Sn1—O2 3.373(2) Å, Sn1—O3 4.298(2) Å for **1** and Sn1—O8 2.997(2) Å for **2**) are not involved in the first coordination sphere of the tin atom. The

Table 2. Selected bond lengths (Å) and angles (deg) for **1** and **2**

1		2	
Sn(1)—C(31)	2.130(2)	Sn(1)—C(31)	2.127(2)
Sn(1)—C(11)	2.131(2)	Sn(1)—C(11)	2.129(2)
Sn(1)—O(1)	2.199(2)	Sn(1)—O(7)	2.1400(16)
Sn(1)—C(21)	2.153(5)	Sn(1)—C(21)	2.145(2)
Sn(1)—N(18)	2.424(4)	Sn(1)—N(11)	2.5392(19)
N(18)—C(17)	1.445(6)	N(11)—C(17)	1.474(3)
N(1)—N(2)	1.257(3)	N(41)—N(42)	1.258(3)
N(1)—C(44)	1.436(3)	N(41)—C(45)	1.428(3)
N(2)—C(51)	1.420(3)	N(42)—C(51)	1.414(3)
N(3)—C(54)	1.371(3)	N(43)—C(54)	1.359(3)
N(3)—C(57)	1.450(3)	N(43)—C(57)	1.449(4)
N(3)—C(58)	1.441(3)	N(43)—C(58)	1.460(3)
S(1)—O(1)	1.503(2)	O(7)—C(41)	1.304(3)
S(1)—O(2)	1.441(2)	O(8)—C(41)	1.231(3)
S(1)—O(3)	1.439(2)	O(8)—Sn(1)	2.997(2)
C(31)—Sn(1)—C(11)	113.75(9)	C(31)—Sn(1)—C(11)	122.38(9)
C(31)—Sn(1)—O(1)	96.54(8)	C(31)—Sn(1)—O(7)	100.71(7)
C(11)—Sn(1)—O(1)	87.90(8)	C(11)—Sn(1)—O(7)	95.57(8)
C(31)—Sn(1)—C(21)	125.7(2)	C(31)—Sn(1)—C(21)	112.73(9)
C(11)—Sn(1)—C(21)	120.3(2)	C(11)—Sn(1)—C(21)	122.79(9)
O(1)—Sn(1)—C(21)	90.4(2)	O(7)—Sn(1)—C(21)	88.05(8)
C(31)—Sn(1)—N(18)	90.7(1)	C(31)—Sn(1)—N(11)	89.58(7)
C(11)—Sn(1)—N(18)	75.6(1)	C(11)—Sn(1)—N(11)	74.50(8)
O(1)—Sn(1)—N(18)	163.5(1)	O(7)—Sn(1)—N(11)	168.56(6)
C(21)—Sn(1)—N(18)	97.5(2)	C(21)—Sn(1)—N(11)	92.59(7)
N(2)—N(1)—C(44)	113.1(2)	N(42)—N(41)—C(45)	115.0(2)
N(1)—N(2)—C(51)	113.8(2)	N(41)—N(42)—C(51)	112.8(2)
C(54)—N(3)—C(57)	122.3(2)	C(54)—N(43)—C(57)	121.1(2)
C(54)—N(3)—C(58)	120.3(2)	C(54)—N(43)—C(58)	121.1(2)
C(57)—N(3)—C(58)	116.2(2)	C(57)—N(43)—C(58)	117.5(2)
S(1)—O(1)—Sn(1)	127.0(1)	C(41)—O(7)—Sn(1)	113.89(14)
O(1)—S(1)—O(2)	110.9(1)	O(8)—C(41)—O(7)	123.2(2)
O(1)—S(1)—O(3)	109.9(1)		
O(2)—S(1)—O(3)	116.6(1)		
O(1)—S(1)—C(41)	103.8(1)		

monodentate mode of coordination of the sulfonate and carboxylate is reflected in the disparate S—O1 1.503(2) Å, S—O2 1.441(2) Å, and S—O3 1.439(2) Å or C—O1 and C—O2 bond distances (see Table 2), with the longer separation between S—O (C—O) being associated with the stronger Sn—O interaction. The Sn—N1 distances (2.424(4) Å for **1**, 2.539(2) Å for **2**) are in the range of relatively strong intramolecular contacts, and these can be compared with the Sn—N distance values from 28 observations found in the Cambridge Structural Database²⁵ (the shortest distance for tin and nitrogen in the aminomethylphenyl moiety is 2.355 Å and its mean is 2.527 Å) as well as in [(2-dimethylaminomethyl)phenyl](diphenyl)tin(IV)-bromide (2.511 Å),²⁵ -chloride (2.4691 Å),²⁶ [Ph₂P(S)S][−] (2.548 Å)²⁶ and

[Ph₂P(S)O][−] (2.481 Å).²⁶ A further comparison can be made with the same molecules for the N—Sn—O and N—Sn—X (X = Br, Cl, S and O) angles (163.5(1)° for **1**, 168.56(6)° for **2**, the bromide (171.0°), the chloride (170.5°), [Ph₂P(S)S][−] (169.0°) and [Ph₂P(S)O][−] (168.6°). The same type of axial angle was found in Me₃SnO₃SPh·H₂O (O1—Sn—O4, 176.2°), the small differences probably being due to steric factors. The remaining donor groups of compounds **1** and **2** do not interact with the tin centre. Since only the solvent is affected by disorder, the structure of **2** (Fig. 3) affords the opportunity for a more detailed discussion of the molecular structure. The coordination polyhedron of tin is a distorted trigonal bipyramid, as the parameter²⁷ $\tau = 0.76$ ($\tau = 0$ and 1 for the square-pyramid and trigonal bipyramid respectively). As might be expected, the bond lengths and angles in the azo-dye moiety, as well as the planarity of its terminal —N(CH₃)₂ group, endorse the delocalization of electrons within the double bonds and aromatic system.

**Figure 2.** View of molecule **1** with atom numbering scheme. The second positions of disordered ligands as well as hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

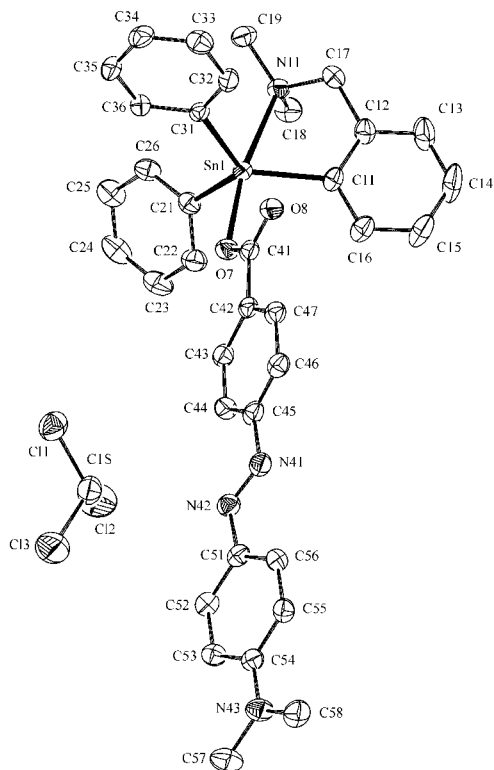


Figure 3. View of molecule **2** with atom numbering scheme. Hydrogen atoms and disordered molecule of CHCl_3 are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

The greater distances and angles are in agreement with a previously published study.²⁹

Solution-state study of compounds **1** and **2**

The ^1H , ^{13}C , ^{119}Sn and ^{15}N chemical shifts and $^nJ(^{119}\text{Sn}, ^{13}\text{C})$ coupling constants of compounds **1** and **2** measured in CDCl_3 are collected in Table 3. The solution structures of the triorganotin compounds **1** and **2** studied can be described on the basis of several NMR spectra parameters. The most important parameters for the direct evaluation of the structure arise from nuclei involved directly in the coordination polyhedra of the central tin atom.^{8,9} On the basis of this approach, we can consider both structures as *trans*-trigonal bipyramids with the more electronegative nitrogen and oxygen atoms in axial planes and carbon atoms in equatorial planes, with relatively strong intramolecular donor-acceptor Sn—N interactions. The NMR parameters used for the conclusions mentioned above are as follows. The values of $\delta(^{119}\text{Sn})$ of -190.4 ppm for **1**, -218.4 ppm for **2** are exactly in the range³⁰ for five-coordinated triorganotin sulfonates and carboxylates respectively, which is in line with the proposed structure. We compared the $\delta(^{119}\text{Sn})$ values of the compounds studied with the starting chloride and analogous bromide (-177.1 ppm for Cl, -180.8 ppm for Br).⁹ Both ^{119}Sn

chemical shifts for **1** and **2** are shifted moderately downfield in comparison with analogous compounds having distorted tetrahedral geometry (triphenyltin benzoate (-111.7 ppm)²⁴).

The C—Sn—C angle of the two phenyl *ipso*-carbon atoms is 125° for compound **1** and 124° for compound **2**, as calculated according to the procedure reported in Ref. 31 from $^1J(^{119}\text{Sn}, ^{13}\text{C})$ coupling constants values (818.1 Hz and 804.6 Hz).

It is also possible to compare these angles with those calculated for the starting chloride (average 123.0°), and those obtained from an X-ray solid state study (125.67° for **1** and 122.51° for **2**). The triphenyltin benzoate reveals a lower value for this coupling constant (650 Hz), which is typical for

Table 3. ^1H , ^{13}C , ^{15}N and ^{119}Sn chemical shifts (ppm) and $^nJ(^{119}\text{Sn}, ^{13}\text{C})$ coupling constants (± 0.5 Hz) of compounds **1** and **2** in CDCl_3

H/C no.	1			2		
	$\delta(^1\text{H})$	$\delta(^{13}\text{C})$	$^nJ(^{119}\text{Sn}, ^{13}\text{C})$	$\delta(^1\text{H})$	$\delta(^{13}\text{C})$	$^nJ(^{119}\text{Sn}, ^{13}\text{C})$
1	–	138.5	782.5	–	138.2	806.8
2	–	142.4	42.7	–	143.4	42.5
3	7.20	127.0	63.6	7.21	127.3	64.3
4	7.43	130.4	14.1	7.42	129.8	13.4
5	7.53	128.8	72.0	7.46	128.1	66.2
6	8.46 ^a	138.9	42.1	8.28 ^b	138.3	35.9
7	3.56	64.8	31.6	3.52	64.8	27.9
8	1.75	45.7	5.2	1.82	45.6	3.8
1'	–	138.5	818.1	–	140.8	804.6
2'	7.63 ^c	136.0	46.1	7.84 ^d	136.2	45.8
3'	7.34	128.9	71.3	7.41	128.6	70.4
4'	7.36	129.9	14.6	7.39	129.2	14.2
COO	–	–	–	–	170.4	–
1''	–	143.5	–	–	134.8	–
2''	7.38	126.9	–	8.13	130.8	–
3''	7.51	121.5	–	7.78	121.5	–
4''	–	152.6	–	–	152.5	–
5''	–	143.5	–	–	143.7	–
6''	7.84	125.1	–	7.87	125.1	–
7''	6.72	111.3	–	6.73	111.4	–
8''	–	153.7	–	–	154.9	–
9''	3.06	40.2	–	3.05	40.2	–
Sn	–	-190.4^e	–	–	-218.4^e	–
$\text{CH}_2\text{—N}$	–	-346.6^f	–	–	-347.9^f	–
$\text{C}(4'')\text{—N}=\text{C}$	–	91.5 ^f	–	–	94.0 ^f	–
$\text{C}(5'')\text{—N}=\text{C}$	–	121.2 ^f	–	–	120.5 ^f	–
$\text{C}(8'')\text{—N}=\text{C}$	–	-324.7^f	–	–	-325.6^f	–

^a $^3J(^{119}\text{Sn}, \text{H}) = 67.8$ Hz.

^b $^3J(^{119}\text{Sn}, \text{H}) = 64.7$ Hz.

^c $^3J(^{119}\text{Sn}, \text{H}) = 65.0$ Hz.

^d $^3J(^{119}\text{Sn}, \text{H}) = 65.3$ Hz.

^e $\delta(^{119}\text{Sn})$.

^f $\delta(^{15}\text{N})$.

triphenyltin compounds with distorted tetrahedral geometry. There are two additional types of coupling constant that can be used for intramolecular Sn—N interaction strength evaluation: ${}^nJ({}^{119}\text{Sn}, {}^{13}\text{C}(7))$ (31.6 Hz for **1** and 27.9 Hz for **2**) and ${}^3J({}^{119}\text{Sn}, {}^1\text{H}(6 \text{ or } 2))$ ³² (see Table 3). The magnitudes of these coupling constants show that the intramolecular connection is more consistent in **1** than in **2**. We can make the same conclusion on the basis of $\delta({}^{15}\text{N}(\text{CH}_2\text{N}(\text{CH}_3)_2))$ values⁸ (−346.6 ppm for **1** and −347.9 ppm for **2**) with respect to the chemical shift value of free amine (−353.0 ppm⁸) (the $\delta({}^{15}\text{N})$ values for all four nitrogen atoms present in compounds **1** and **2** were detected using $\text{gs-}^1\text{H-}^{15}\text{N}$ -HMBC spectra). The $\delta({}^{13}\text{C}(\text{COO}))$ value (170.4 ppm), which is comparable to values for four-coordinated triorganotin benzoates,³³ can be taken as additional information about the tin–carboxylate monodentate bond fashion.

Electronic and vibrational spectra

Electronic spectra were recorded with the idea of making a comparison of spectral parameters for **1** and **2** and their precursors (methyl orange, sodium salt for **1** and *para*-methyl red, sodium salt for **2**). Both carboxylate and sulfonate sodium salts have similar electronic spectra, with one maximum in the visible region at about 420 nm. When the sodium ion is replaced by the $[2-(\text{C}_6\text{H}_4)\text{CH}_2\text{N}(\text{CH}_3)_2\text{Ph}_2\text{Sn}]$ ligand, the energy and extinction coefficient of this band is only minimally changed. This fact suggests that there is no interaction between tin and the azo group.

The complexes prepared were investigated by IR and Raman spectroscopy in the solid state and in CHCl_3 solution. Bands characteristic for functional groups (carboxyl, sulfonyl, azo group and benzene ring) were found in all spectra measured (see Experimental section).

The very similar $\nu(\text{N}=\text{N})$ band frequencies in complexes **1** and **2** are associated with $\text{N}=\text{N}$ bond lengths obtained from X-ray analyses (1.257 Å for **1** and 1.260 Å for **2**). The difference between the asymmetric $\nu_a(\text{C}=\text{O})$ and symmetric $\nu_s(\text{C}=\text{O})$ band frequencies is characteristic for monodentate bonded carboxylic groups. For both complexes, the $\text{C}=\text{C}$ stretching vibrations of the phenyl ring were found at about 1600 cm^{-1} .

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REFERENCES

- Akiba K (ed.). *Chemistry of Hypervalent Compounds*. Wiley VCH: Weinheim, Germany, 1999; and references cited therein.
- Van Koten G, Albrecht M. *Angew. Chem. Int. Ed. Engl.* 2001; **40**: 3750.
- Holmes RR. *Chem. Rev.* 1990; **90**: 17.
- Jastrzebski JTBH, van Koten G. *Adv. Organomet. Chem.* 1993; **35**: 241.
- Smith PJ (ed.). *Chemistry of Tin*. Blackie Academic & Professional: Glasgow, UK, 1998.
- Jurkschat K, Pieper N, Seemeyer S, Schuermann M, Biesemans M, Verbruggen I, Willem R. *Organometallics* 2001; **20**: 686.
- Růžička A, Dostál L, Jambor R, Brus J, Císařová I, Holčapek M, Holeček J. *Appl. Organomet. Chem.* 2002; **16**: 315.
- Růžička A, Pejchal V, Holeček J, Lyčka A, Jacob K. *Collect. Czech. Chem. Commun.* 1998; **63**: 997.
- Růžička A, Jambor R, Brus J, Císařová I, Holeček J. *Inorg. Chim. Acta* 2001; **323**: 163.
- Crowe AJ. In *Metal Complexes in Cancer Chemotherapy*, Keppler BK (ed.). VCH: Weinheim, 1993; 369–379, and references cited therein.
- Gielen M. *Appl. Organomet. Chem.* 2002; **16**: 481 and references cited therein.
- Nath M, Yadav R, Eng G, Musingarimi P. *Appl. Organomet. Chem.* 1999; **13**: 29, and references cited therein.
- Price R. In *The Chemistry of Synthetic Dyes*, vol. **III**, Venkataraman K (ed.). Academic Press: New York, 1997; chapter VII.
- Baumann H. In *Ullmanns Encyclopaedie der Technischen Chemie*, vol. **16**. VCH: Weinheim, 1978.
- Beffa F, Back G. *Rev. Prog. Color Relat. Top.* 1984; **14**: 33.
- Zollinger H. In *Color Chemistry. Syntheses, Properties and Application of Organic Dyes and Pigments*, VCH: Weinheim, 1987.
- Hull W. In *Two-Dimensional NMR Spectroscopy. Application for Chemists and Biochemists*. Croasmun WR, Carlson RMK (eds). 2nd edition. VCH: New York, 1994.
- Braun S, Kalinowski H-O, Berger S. *150 and More Basic NMR Experiments*, 2nd edition. Wiley VCH: Weinheim, 1998.
- Lyčka A. *Collect. Czech. Chem. Commun.* 1982; **47**: 1112.
- Altomare A, Cascarone G, Giacovazzo C, Guagliardi A, Burla MC, Polidori G, Camalli M. *J. Appl. Crystallogr.* 1994; **27**: 435.
- Sheldrick GM. *SHELXL-97, A Program for Crystal Structure Refinement*. University of Göttingen, Germany, 1997.
- Blessing RH. *J. Appl. Crystallogr.* 1997; **30**: 421.
- Harrison PG, Phillips RC, Richards JA. *J. Organomet. Chem.* 1976; **114**: 47.
- Allen FH, Kennard O. *Chem. Des. Automat. News* 1993; **8**: 1, 31.
- van Koten G, Noltes JG, Spek AL. *J. Organomet. Chem.* 1976; **118**: 183.
- Varga RA, Schuerman M, Silvestru C. *J. Organomet. Chem.* 2001; **623**: 161.
- Addison AW, Rao TN, Reedijk J, Vanrijn J, Verschoor GC. *J. Chem. Soc. Dalton Trans.* 1984; 1349.
- Tiekink ERT. *Appl. Organomet. Chem.* 1991; **5**: 1; and references cited therein.
- Holeček J, Nádvořník M, Handlír K, Lyčka A. *J. Organomet. Chem.* 1983; **241**: 177.
- Willem R, Bouhdid A, Mahieu B, Ghys L, Biesemans M, Tiekink ERT, de Vos D, Gielen M. *J. Organomet. Chem.* 1997; **531**: 151.
- Holeček J, Handlír K, Nádvořník M, Lyčka A. *Z. Chem.* 1990; **30**: 265.
- Biesemans M, Martins J, Willem R, Lyčka A, Růžička A, Holeček J. *Magn. Reson. Chem.* 2002; **40**: 65.
- Lyčka A, Nádvořník M, Handlír K, Holeček J. *Collect. Czech. Chem. Commun.* 1984; **49**: 2903.