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Journal of Organometallic Chemistry 544 (1997) 29–35

Journal of Organometallic Chemistry

The behaviour of polydentate hydrazonic ligands derived from 2-acetylpyridine towards organotin compounds. Part I: the diorganotin(IV) complexes

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Received 29 January 1997

Abstract

The reactivity of the polydentate ligands bis(2-acetylpyridine) carbonohydrazone (H_2apc) and 2-acetylpyridine semicarbazone (Haps) as well as of their sulphur containing analogous bis(2-acetylpyridine) thiocarbonohydrazone (H_2apt) and 2-acetylpyridine thiosemicarbazone (Hapts) was investigated towards organotin compounds. An X-ray crystal structure determination carried out on $Ph_2Sn(Hapt)Cl \cdot H_2O$ (**1**) and $(n\text{-}Bu)_2Sn(apts)(OAc)$ (**5**) revealed that in both compounds the hydrazonic ligand is terdentate via a sulphur atom and two nitrogen atoms. The tin atom is six-coordinated in **1** and seven-coordinated in **5**. The similarities observed in the IR and ^1H NMR spectra are indicative of a similar behaviour of the ligand in all the complexes, thus suggesting a six-coordinated tin in the chloro derivatives and a seven-coordinated tin in the acetato ones. © 1997 Elsevier Science S.A.

Keywords: Polydentate ligands; Organotin compounds; Carbonohydrazone; Semicarbazone

1. Introduction

Organotins still have a lot of industrial applications, especially as antifouling agents, even if the recent disquiet regarding their toxicity and the environmental effect cannot be ignored.

The interest in the coordination chemistry and in the biological properties of organotin, recently led us to evaluate the in vitro antimicrobial and genotoxic properties of organotin complexes with the N_2O ligands di-2-pyridylketone and phenyl(2-pyridyl)ketone 2-aminobenzoylhydrazones [1] and di-2-pyridylketone 2-thenoylhydrazone [2]. As a continuation of these investigations, we report here the synthesis and characterisation of the compounds obtained by reacting Ph_2SnCl_2 and $(n\text{-}Bu)_2Sn(OAc)_2$ with the two N_2O ligands bis(2-acetylpyridine) carbonohydrazone (H_2apc) and 2-acetylpyridine semicarbazone (Haps) and with the analogous N_2S ligands bis(2-acetylpyridine) thiocarbonohydrazone (H_2apt) and 2-acetylpyridine thiosemicarbazone (Hapts) (Scheme 1). The X-ray crystal structures of $Ph_2Sn(Hapt)Cl \cdot H_2O$ and $(n\text{-}Bu)_2Sn(apts)(OAc)$ are also reported, together with that of the free ligand Hapts.

2. Experimental section

2.1. Materials and methods

All reactants and solvents were reagent grade. Elemental analyses (C, H, N and S) were carried out on a Carlo Erba CHNS-O EA1108 automatic equipment. Infrared spectra (4000–400 cm^{-1}) for KBr discs were recorded on a Nicolet 5PC FT-IR spectrometer, mass spectra on a Finnigan SSQ710 instrument, and ^1H NMR spectra on a Bruker AC 300 instrument; chemical shifts are given in ppm referred to tetramethylsilane. Melting points were obtained with a Gallenkamp MFB-595 apparatus in open capillaries.

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PII S0022-328X(97)00303-3

X = S, H_2apt X = O, H_2apc

X = S, Hapts X = O, Haps

Scheme 1.

2.2. Synthesis

The ligands were synthesised following published procedures [3,4].

$Ph_2Sn(Hapt)Cl \cdot H_2O$ (1). The ligand (0.30 g) was dissolved in absolute ethanol (50 ml) with an equimolar amount of Ph_2SnCl_2 (0.33 g). The solution was refluxed for 1 h; on cooling a deep yellow powder precipitated. Well formed crystals suitable for X-ray analysis were obtained by recrystallisation from absolute ethanol (yield 76%, m.p. 178–180°C (dec.)). Anal. Found: C 51.40, H 4.12, N 13.61, S 5.15; $C_{27}H_{27}ClN_6OSSn$ calc.: C 50.85, H 4.27, N 13.18, S 5.03%. ^1H NMR (d_6-DMSO) δ_H: 2.47 (s, 3H, CH_3), 2.81 (s, 3H, CH_3), 7.21–8.6 (18H, CH_{ar}), 11.34 (s, 1H, NH). IR main bands (cm^{-1}): 3470 br, ν(OH); 3293 m, ν(NH); 3080–3050 w, $\nu(CH_{ar})$; 1550 m, ν(CN); 1279 s; 789 and 733 m, $\delta(CH_{ar})$.

Compounds **2**, **3**, **4**, **5** and **6** were prepared by using a similar procedure.

$Ph_2Sn(Hapc)Cl$ (2). Amounts: H_2apc (0.10 g), Ph_2SnCl_2 (0.12 g), EtOH (20 ml). Yield 65%, m.p. 235°C (dec.). Anal. Found: C 53.50, H 4.18, N 13.60; $C_{27}H_{25}ClN_6OSn$ calc.: C 53.72, H 4.17, N 13.92%. ^1H NMR ($CDCl_3$) δ_H: 2.48 (s, 3H, CH_3), 2.73 (s, 3H, CH_3), 7.24–8.57 (18H, CH_{ar}), 8.72 (s, 1H, NH). IR main bands (cm^{-1}): 3290 m, ν(NH); 3080–3050 m, $\nu(CH_{ar})$; 2940 w, $\nu(CH_{alkyl})$; 1588 vs, ν(CN); 781 – 694 m, $\delta(CH_{ar})$.

$(n-Bu)_2Sn(Hapt)(OAc) \cdot H_2O$ (3). Amounts: H_2apt (0.10 g), $Bu_2Sn(OAc)_2$ (0.09 ml), EtOH (20 ml). Yield 52%, m.p. 148–152°C (dec.). Anal. Found: C 48.50, H 6.18, N 13.60, S 5.20; $C_{25}H_{38}N_6O_3SSn$ calc.: C 48.33, H 6.16, N 13.53, S 5.16%. ^1H NMR ($CDCl_3$) δ_H: 0.66 (t, 6H, $CH_{3(but)}$), 0.85–1.43 (m, 12H, CH_2), 2.06 (s, 3H, $CH_{3(acetate)}$), 2.42 and 2.68 (s, 3H, CH_3), 7.19–8.51 (8H, CH_{ar}), 9.03 (s, 1H, NH). IR main bands (cm^{-1}): 3335 w, ν(NH); 2956–2855 m, $\nu(CH_{alkyl})$; 1607 m, ν_{as}(COO); 1594 m, ν(CN); 1392 m, ν_{sym}(COO); 1271 s; 786 and 742 m, $\delta(CH_{ar})$.

$(n-Bu)_2Sn(Hapc)(OAc)$ (4). Amounts: H_2apc (0.10g), $Bu_2Sn(OAc)_2$ (0.09ml), toluene (35 ml). Yield 48%, m.p. 154–157°C (dec). Anal. Found: C 51.70, H 6.23, N 14.42; $C_{25}H_{36}N_6O_3Sn$ calc.: C 51.13, H 6.18, N 14.31%. ^1H NMR (d_6-DMSO) δ_H: 0.68 (t, 6H, $CH_{3(but)}$), 0.88–1.39 (m, 12H, CH_2), 2.07 (s, 3H, $CH_{3(acetate)}$), 2.40 and 2.66 (s, 3H, CH_3), 7.14–8.92 (8H, CH_{ar}), 8.12

Table 1
Summary of crystal data, intensity collection and refinement

Compound	1	5	Hapts
Formula	$C_{27}H_{27}ClN_6OSSn$	$C_{18}H_{30}N_4O_2SSn$	$C_8H_{11}N_4O_{0.5}S$
Molecular weight	637.75	485.21	203.26
Crystal system	triclinic	monoclinic	monoclinic
Space group	P$\bar{1}$	P2$_1$/c	P2$_1$/c
a (Å)	12.167(4)	14.126(3)	16.744(5)
b (Å)	13.969(5)	17.372(4)	9.480(3)
c (Å)	9.666(3)	18.791(5)	12.674(4)
α (°)	92.97(1)	90	90
β (°)	96.92(1)	96.67(2)	97.60(2)
γ (°)	113.14(2)	90	90
V (Å^3)	1490.8(9)	4580(2)	1994(1)
Z	2	8	8
D_c (g cm^{-3})	1.421	1.407	1.354
Diffractometer	Philips	Philips	Siemens
Radiation	MoKα	MoKα	MoKα
μ (cm^{-1})	10.46	12.25	2.91
Reflections measured	7192	14108	6379
Reflections unique	7192	13338	5819
Reflections observed ($F_0 > 4\sigma(F_0)$)	5195	7231	3135
Parameters varied	340	544	332
R1 for observed data	0.0475	0.0302	0.0465
wR2 for all data	0.2069	0.1467	0.1627

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^4$) (one third trace of the diagonalized matrix), with e.s.d.'s in parentheses for compound **1**

Atom	X/a	Y/b	Z/c	U(eq)
Sn	2294.1(4)	2032.7(3)	9123.2(4)	379(2)
S	2198(1)	3534(1)	7880(2)	412(6)
Cl	−58(2)	1227(2)	8756(2)	578(7)
N1	3711(6)	1346(5)	10388(7)	530(25)
N2	4323(5)	3126(4)	9169(5)	360(19)
N3	4651(5)	4023(4)	8500(5)	393(20)
N4	4122(5)	5100(5)	7224(6)	445(23)
N5	3286(5)	5417(4)	6546(6)	419(21)
N6	3048(7)	7032(6)	3971(7)	667(33)
C1	3387(9)	459(7)	11018(12)	799(45)
C2	4220(11)	159(9)	11745(14)	995(63)
C3	5434(11)	798(10)	11839(13)	1019(64)
C4	5794(9)	1708(8)	11228(10)	745(44)
C5	4895(7)	1959(6)	10486(7)	477(28)
C6	5212(6)	2924(5)	9769(6)	395(24)
C7	6502(6)	3609(6)	9718(9)	548(31)
C8	3752(6)	4216(5)	7901(6)	362(22)
C9	3678(6)	6179(5)	5789(7)	431(25)
C10	4965(8)	6754(8)	5594(11)	755(42)
C11	2732(7)	6478(5)	5042(7)	469(27)
C12	1618(9)	6178(9)	5435(13)	886(52)
C13	773(10)	6452(11)	4674(16)	1130(70)
C14	1069(10)	7005(9)	3544(13)	930(54)
C15	2178(10)	7269(8)	3245(11)	834(51)
C16	2283(7)	975(6)	7440(9)	582(31)
C17	3210(11)	1223(7)	6709(9)	864(48)
C18	3222(13)	596(8)	5546(10)	968(63)
C19	2317(15)	−267(13)	5087(19)	1608(94)
C20	1470(17)	−574(20)	5923(35)	3785(214)
C21	1429(14)	64(14)	7080(27)	2722(140)
C22	2257(5)	2553(5)	11221(6)	366(22)
C23	2747(6)	3619(5)	11609(6)	421(25)
C24	2695(7)	4033(7)	12933(7)	571(31)
C25	3164(7)	3368(7)	13895(8)	615(35)
C26	1704(8)	2297(8)	13545(8)	661(38)
C27	1727(7)	1874(6)	12190(8)	582(31)
O	8835(15)	2630(15)	595(18)	2614(142)

(s, 1H, NH). IR main bands (cm^{-1}): 3183 w, ν(NH); 3067 vw, $\nu(CH_{ar})$; 2956–2856 m, $\nu(CH_{alkyl})$; 1591 m, ν(CN); 1565 m, ν_{as}(COO); 1346 m, ν_{sym}(COO); 1271 s; 783, 742 and 671 m, $\delta(CH_{ar})$.

(n-Bu)₂Sn(apts)(OAc) (5). Amounts: Hapts (0.15 g), $Bu_2SnOAc)_2$ (0.21 ml), EtOH (20 ml). Yield 40%, m.p. 160–163°C. Anal. Found: C 44.59, H 6.20, N 11.57, S 6.65; $C_{18}H_{30}N_4O_2SSn$ calc.: C 44.56, H 6.23, N 11.55, S 6.61%. ^1H NMR ($CDCl_3$) δ_H: 0.70 (t, 6H, $CH_{3(but)}$), 0.88–1.14 (m, 12H, CH_2), 2.06 (S, 3H, $CH_{3(acetate)}$), 2.60 (s, 3H, CH_3), 5.45 (s, 2H, NH_2), 7.49 (t, 1H, CH_{ar}), 7.76 (d, 1H, CH_{ar}), 7.96 (t, 1H, CH_{ar}), 9.06 (d, 1H, CH_{ar}). IR main bands (cm^{-1}): 3281, 3176 m, $\nu(NH_2)$; 2957–2855 m, $\nu(CH_{alkyl})$; 1617 s, ν_{as}(COO); 1431 s, ν_{sym}(COO); 802 m, $\delta(CH_{ar})$. Crystals suitable for X-ray analysis were obtained by recrystallization from absolute ethanol.

$(n\text{-}Bu)_2Sn(aps)(OAc) \cdot C_2H_5OH \cdot 1.5H_2O$ (6). Amounts: Haps (0.20 g), $Bu_2Sn(OAc)_2$ (0.30 ml), EtOH (20 ml). Yield 61%, m.p. 150–152°C. Anal. Found: C 44.40, H 7.20, N 10.07; $C_{20}H_{39}N_4O_{5.5}Sn$ calc.: C 44.30, H 7.25, N 10.33%. ^1H NMR ($CDCl_3$) δ_H: 0.67 (t, 6H, $CH_{3(but)}$), 0.88–1.61 (m, 12H, CH_2), 2.04 (s, 3H,

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^4$) (one third trace of the diagonalized matrix), with e.s.d.'s in parentheses for compound **5**

Atom	X/a	Y/b	Z/c	U(eq)
Sn1	4171.8(2)	2195.7(2)	6150.2(2)	370(1)
Sn2	−800.1(3)	3850.4(2)	2646.2(2)	467(1)
S1	3511.6(11)	3330.5(8)	6830.4(7)	575(5)
S2	−463.7(10)	4424.8(8)	3952.3(7)	534(5)
O1	4442(3)	1683(2)	7306(2)	534(13)
O2	4899(3)	890(2)	6499(2)	613(14)
O3	−1860(3)	4096(3)	1574(2)	719(16)
O4	−1972(3)	4882(2)	2469(2)	588(14)
N1	4497(3)	1806(2)	4952(2)	406(13)
N2	3665(3)	3124(2)	5262(2)	369(12)
N3	3208(3)	3795(2)	5418(2)	426(13)
N4	2685(4)	4565(3)	6253(3)	541(18)
N5	−338(4)	2814(3)	1930(3)	671(19)
N6	494(3)	3152(2)	3245(2)	460(14)
N7	990(3)	3379(3)	3880(2)	505(15)
N8	1142(4)	4239(3)	4780(3)	606(19)
C1	4939(4)	1148(3)	4825(3)	480(18)
C2	5190(4)	961(3)	4157(3)	506(19)
C3	4976(4)	1477(3)	3606(3)	511(19)
C4	4527(4)	2157(3)	3733(3)	467(18)
C5	4289(3)	2313(3)	4413(2)	365(14)
C6	3809(3)	3033(3)	4596(2)	391(15)
C7	3529(4)	3635(3)	4041(3)	618(21)
C8	3129(3)	3908(3)	6107(3)	410(15)
C9	2881(4)	1553(4)	5982(3)	663(23)
C10	2156(5)	1725(6)	5404(4)	1115(39)
C11	1265(6)	1203(7)	5348(5)	1495(55)
C12	653(11)	1200(13)	4794(8)	3210(142)
C13	5638(4)	2554(3)	6288(3)	577(20)
C14	5917(5)	3237(5)	5840(5)	984(34)
C15	6914(7)	3425(6)	5903(6)	1470(56)
C16	7105(10)	4098(6)	5389(8)	2244(92)
C17	4842(4)	1063(3)	7141(3)	506(18)
C18	5265(5)	544(4)	7732(3)	840(28)
C19	−771(7)	2655(5)	1281(4)	982(35)
C20	−537(8)	2028(5)	892(5)	1142(40)
C21	152(7)	1547(5)	1196(5)	1077(40)
C22	617(6)	1701(4)	1856(4)	782(28)
C23	360(4)	2349(3)	2221(3)	563(20)
C24	838(4)	2566(3)	2930(3)	534(19)
C25	1699(5)	2129(4)	3244(4)	914(30)
C26	617(4)	3965(3)	4195(3)	453(17)
C27	129(5)	4630(5)	2183(4)	685(27)
C28	1181(5)	4632(4)	2452(4)	824(29)
C29	1738(6)	5278(5)	2165(5)	1072(39)
C30	2781(7)	5225(6)	2388(5)	1350(50)
C31	−1918(5)	3133(4)	2955(4)	742(25)
C32	−1678(5)	2574(5)	3556(4)	967(34)
C33	−2543(7)	2209(6)	3844(6)	1302(48)
C34	−2260(8)	1653(7)	4442(6)	1674(64)
C35	−2224(4)	4674(3)	1829(3)	532(19)
C36	−2977(6)	5126(6)	1378(6)	776(31)

Table 4
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^4$) (one third trace of the diagonalized matrix), with e.s.d.'s in parentheses for Hapts

Atom	*X/a*	*Y/b*	*Z/c*	*U*(eq)
S1	3618.6(3)	4560.3(7)	6698.6(5)	468(2)
N1	−441(1)	1673(2)	5577(2)	482(7)
N2	1607(1)	2416(2)	6327(2)	400(6)
N3	2221(1)	3291(2)	6117(2)	410(6)
N4	2876(1)	2663(3)	7751(2)	482(7)
C1	−1025(2)	909(3)	5947(3)	615(10)
C2	−885(2)	−73(4)	6743(3)	657(11)
C3	−102(2)	−318(3)	7181(3)	677(11)
C4	508(2)	452(3)	6819(2)	548(9)
C5	317(1)	1459(2)	6030(2)	376(6)
C6	944(1)	2403(2)	5688(2)	383(7)
C7	769(2)	3289(4)	4708(3)	614(11)
C8	2867(1)	3433(2)	6883(2)	377(6)
S2	7821.1(3)	4452.7(7)	6090.1(5)	464(2)
N5	3774(1)	1421(2)	4792(2)	420(6)
N6	5765(1)	2426(2)	5787(1)	381(6)
N7	6375(1)	3322(2)	5578(2)	414(6)
N8	7156(1)	2312(3)	7001(2)	468(7)
C9	3188(1)	575(3)	5064(2)	517(8)
C10	3262(2)	−247(3)	5960(2)	548(9)
C11	3987(2)	−231(3)	6623(2)	538(9)
C12	4596(1)	619(3)	6361(2)	460(8)
C13	4471(1)	1448(2)	5452(2)	355(6)
C14	5100(1)	2415(2)	5143(2)	401(7)
C15	4916(2)	3267(5)	4151(3)	759(13)
C16	7080(1)	3280(2)	6244(2)	376(6)
O	−1599(2)	3021(3)	3844(2)	754(9)

Table 6
Selected bond distances (Å) and angles (°) in compound **5**

Sn1–S1	2.582(2)	O1–C17	1.270(6)
Sn1–O1	2.337(3)	O2–C17	1.257(6)
Sn1–O2	2.545(4)	O3–C35	1.249(7)
Sn1–N1	2.445(4)	O4–C35	1.267(7)
Sn1–N2	2.370(4)	N2–N3	1.382(5)
Sn1–C9	2.130(6)	N2–C6	1.301(6)
Sn1–C13	2.149(5)	N3–C8	1.327(6)
Sn2–S2	2.641(2)	N4–C8	1.346(7)
Sn2–O3	2.404(4)	N6–N7	1.370(7)
Sn2–O4	2.436(4)	N6–C24	1.300(7)
Sn2–N5	2.383(5)	N7–C26	1.317(7)
Sn2–N6	2.367(4)	N8–C26	1.341(7)
Sn2–C27	2.140(8)	C5–C6	1.482(7)
Sn2–C31	2.144(7)	C17–C18	1.500(8)
S1–C8	1.725(5)	C23–C24	1.470(8)
S2–C26	1.737(5)	C35–C36	1.502(11)
C9–Sn1–C13	165.0(2)	Sn2–O4–C35	91.8(3)
N1–Sn1–N2	67.3(1)	Sn1–N1–C5	117.6(3)
O2–Sn1–N1	82.9(1)	Sn1–N1–C1	122.9(3)
O1–Sn1–O2	53.4(1)	C1–N1–C5	119.3(4)
S1–Sn1–N2	74.5(1)	Sn1–N2–C6	121.8(3)
S1–Sn1–O1	82.0(1)	Sn1–N2–N3	122.4(3)
C27–Sn2–C31	169.7(3)	N3–N2–C6	115.8(4)
N5–Sn2–N6	68.5(2)	N2–N3–C8	115.2(4)
O3–Sn2–N5	81.1(2)	Sn2–N5–C23	117.5(4)
O3–Sn2–O4	53.7(1)	Sn2–N5–C19	123.3(5)
S2–Sn2–N6	72.9(1)	C19–N5–C23	119.1(6)
S2–Sn2–O4	84.0(1)	Sn2–N6–C24	119.6(4)
Sn1–S1–C8	98.7(2)	Sn2–N6–N7	123.7(3)
Sn2–S2–C26	97.3(2)	N7–N6–C24	116.3(4)
Sn1–O1–C17	97.3(3)	N6–N7–C26	115.0(4)
Sn1–O2–C17	87.9(3)	O1–C17–O2	121.2(5)
Sn2–O3–C35	93.8(3)	O3–C35–O4	120.7(5)

$CH_{3(acetate)}$), 2.46 (s, 3H, CH_3), 3.40–3.49 (m, CH_3CH_2OH), 4.32 (t, CH_3CH_2OH), 5.11 (s, 2H, NH_2), 7.35 (t, 1H, CH_{ar}), 7.62 (d, 1H, CH_{ar}), 7.91 (t, 1H, CH_{ar}), 8.83 (d, 1H, CH_{ar}). IR main bands (cm^{-1}): 3380 br, ν(OH); 3317, 3197 m, $\nu(NH_2)$; 2955–2855 m, $\nu(CH_{alkyl})$; 1596 m, ν_{as}(COO); 1411 s, ν_{sym}(COO); 800–780 m, $\delta(CH_{ar})$.

Table 5
Selected bond distances (Å) and angles (°) in compound **1**

Sn–S	2.505(2)	N2–C6	1.300(10)
Sn–Cl	2.601(2)	N3–C8	1.304(9)
Sn–N1	2.509(8)	N4–N5	1.372(10)
Sn–N2	2.331(5)	N4–C8	1.369(9)
Sn–C16	2.135(9)	N5–C9	1.289(9)
Sn–C22	2.130(6)	C5–C6	1.483(10)
S–C8	1.748(6)	C9–C11	1.494(12)
N2–N3	1.379(8)		
C16–Sn–C22	156.9(3)	S–Sn–Cl	87.8(1)
N2–Sn–C22	94.1(2)	Sn–S–C8	97.5(2)
N2–Sn–C16	93.5(3)	Sn–N1–C5	115.6(5)
N1–Sn–C22	[illegible]1.0(2)	Sn–N1–C1	126.0(6)
N1–Sn–C16	81.9(3)	C1–N1–C5	118.3(7)
N1–Sn–N2	67.1(2)	Sn–N2–C6	123.3(5)
Cl–Sn–C22	87.8(2)	Sn–N2–N3	121.0(4)
Cl–Sn–C16	90.7(2)	N3–N2–C6	115.7(5)
Cl–Sn–N2	164.4(2)	N2–N3–C8	115.0(5)
Cl–Sn–N1	128.4(2)	N5–N4–C8	120.3(6)
S–Sn–C22	100.7(2)	N4–N5–C9	117.2(6)
S–Sn–C16	102.3(2)	N3–C8–N4	112.9(6)
S–Sn–N2	76.7(1)	S–C8–N4	117.5(5)
S–Sn–N1	143.8(2)	S–C8–N3	129.6(6)

2.3. X-ray data collection, structure determination and refinement of compounds 1, 5, and Hapts

Details of the X-ray experimental conditions, crystal data, data collection and structure refinement are given in Table 1. The data were processed with the peak-profile analysis procedure and corrected for Lorentz and polarization effects; for compounds **1** and **5** an absorption correction was also applied. No crystal decay was observed during the data collection period. All the structures were solved by combination of direct methods and Fourier difference techniques and refined by full-matrix least-squares based on F^2, with all non-hydrogen atoms allowing for anisotropic vibration. The hydrogen atoms were in part located in ΔF maps and in part included at their calculated positions and constrained to ride on their attached atoms. The hydrogen atoms from the solvent molecules were ignored. Com-

Table 7
Bond distances (Å) and angles (°) in Hapts

S1–C8	1.691(2)	S2–C16	1.697(2)
N1–C1	1.394(4)	N5–C9	1.347(3)
N1–C5	1.337(3)	N5–C13	1.343(3)
N2–N3	1.375(3)	N6–N7	1.380(3)
N2–C6	1.284(3)	N6–C14	1.290(3)
N3–C8	1.362(3)	N7–C16	1.358(3)
N4–C8	1.319(3)	N8–C16	1.322(3)
C5–C6	1.488(3)	C13–C14	1.488(3)
C6–C7	1.496(4)	C14–C15	1.492(5)
N3–N2–C6	119.3(2)	N7–N6–C14	118.8(2)
N2–N3–C8	117.8(2)	N6–N7–C16	117.8(2)
C4–C5–C6	121.2(2)	C12–C13–C14	122.2(2)
N1–C5–C6	116.8(2)	N5–C13–C14	115.8(2)
N2–C6–C5	114.0(2)	N6–C14–C13	114.9(2)
C5–C6–C7	120.7(2)	C13–C14–C15	118.7(2)
N2–C6–C7	125.2(2)	N6–C14–C15	126.4(2)
N3–C8–N4	117.4(2)	N7–C16–N8	117.7(2)
S1–C8–N4	122.7(2)	S2–C16–N8	122.4(2)
S1–C8–N3	119.9(2)	S2–C16–N7	119.9(2)

plex atom scattering factors were employed and anomalous dispersion corrections were applied to all non-hydrogen atoms. Calculations were performed on Gould POWER NODE 6040 and ENCORE91 computers, using the program packages SIR92 [5], SHELXL93 [6], PARST [7], and ZORTEP [8]. Final atomic coordinates are listed in Tables 2–4. Selected bond distances and angles are reported in Tables 5–7.

3. Results and discussion

Fig. 1 shows an ORTEP diagram of the complex molecule in $Ph_2Sn(Hapt)Cl \cdot H_2O$ (1) together with the atomic numbering scheme. The hydrazone ligand is monodeprotonated and acts as a terdentate N_2S donor giving rise to two five-membered chelate rings, one of which (SnNCCN) is strictly planar, while the other (SnSCNN) shows a slight degree of puckering. The coordination sphere of the metal is completed to highly distorted octahedral by a chlorine atom in the equatorial plane and two *trans*-positioned phenyl rings in the axial sites. The main distortion from the regular octahedral geometry comes from the stereochemical constraints of Hapt which cause the N1–Sn–N2 and N2–Sn–S angles to be 67.2(2) and 76.7(1)° and the N1–Sn–S angle to be 143.8(2)° instead of the expected 90 and 180°. Consequently, in the equatorial plane the N1–Sn–Cl angle is as large as 128.4(2)°. Even if to a lesser extent, also the axial C–Sn–C angle is far from linearity (156.9(3)°).

The four equatorial bonds at tin are slightly (Sn–S) or markedly (Sn–N, Sn–Cl) longer than the corresponding ones observed in $SnCl_3$(FPT) (HFPT = 2-formylpyridine thiosemicarbazone) [9], which also contains a six-coordinated tin atom bonded in the equatorial plane to a chlorine atom and an N_2S terdentate ligand. Unlike $SnCl_3$(FPT), in our compound the two Sn–N distances are considerably different. The Sn–C distances are unremarkable.

The hydrazone molecule has a non planar configuration, as shown by the dihedral angles of 5.1(3) and 25.6(3)° the central C5 through C11 moiety makes with the N1...C5 and N6...C15 pyridine rings, respectively.

As established by the X-ray analysis previously carried out on the free H_2apt [4], on complexation the hydrazone rearranges from the *E*–*Z* form to the more open *E*–*E* form. Moreover, the complexation effects are responsible for the thione-to-thiol evolution as indi-

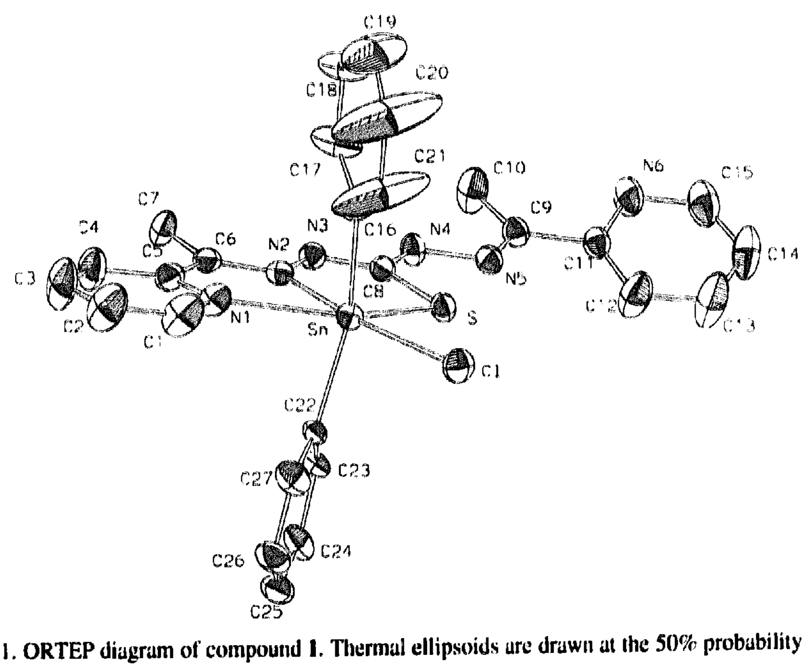

Fig. 1. ORTEP diagram of compound 1. Thermal ellipsoids are drawn at the 50% probability level.

cated by the lengthening of the S–C8 and C8–N4 bonds and the shortening of the C8–N3 bond.

Compound **1** crystallizes with a molecule of water which seems to play an important role in the packing as shown by the O ··· Cl intermolecular interaction of 3.33(2) Å, strongly indicative of hydrogen bonding.

In the ^{1}H NMR spectrum of the compound **1** there is a D_2O exchangeable peak at 11.34 ppm with unitary integration, that is attributable to a still present hydrazidic proton; the two methyl groups, as well as the corresponding protons of the two pyridinic rings, are not magnetically equivalent (see Section 2). In the IR spectrum the iminic band undergoes a negative shift compared to that in the free ligand (ν(CN): 1570 and 1550 cm^{-1}, respectively), as expected when the C=N group is involved in the coordination to a metal atom.

The main spectroscopic features of $Ph_2Sn(Hapc)Cl$ (**2**) resemble those of compound **1**: the ligand is monodeprotonated (δ_H (N–*H*) 8.72 ppm) and coordinates assuming the enolic form (as can be deduced from the disappearance of the ν(C=O) band which falls at 1695 cm^{-1} in the free ligand), thus the same structure as **1** can be proposed for **2** as well.

Dibutyltin diacetate reacts with H_2apt and H_2apc giving $(n\text{-}Bu)_2Sn(Hapt)(OAc) \cdot H_2O$ (**3**) and $(n\text{-}Bu)_2Sn(Hapc)(OAc)$ (**4**) respectively, independently of the ligand to metal *ratio* (1:1 or 1:2). The ^{1}H NMR data indicate that the ligands are again monodeprotonated and the complexes attain the electroneutrality by means of an acetato group. The carboxylate anion can coordinate in a number of ways (as unidentate, chelating or bridging bidentate) and can also be ionic. Predictions of the carboxylate bonding mode have frequently been

Fig. 2. ORTEP diagram of molecule A in compound **5**. Thermal ellipsoids are drawn at the 50% probability level.

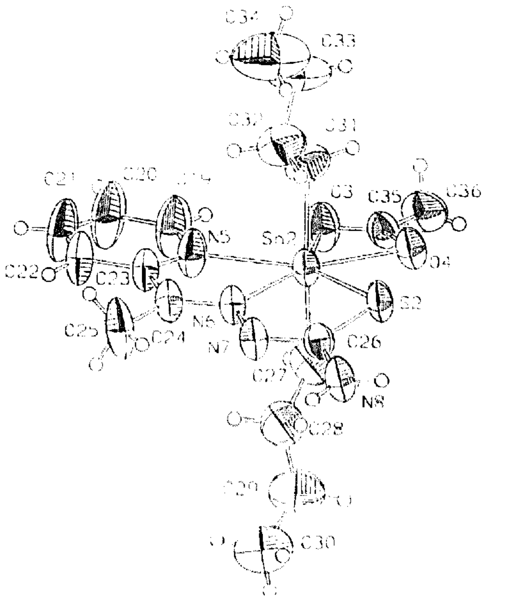

Fig. 3. ORTEP diagram of molecule B in compound **5**. Thermal ellipsoids are drawn at the 50% probability level.

based on IR data, the differences between the ν_{asym} and ν_{sym} C–O frequencies being considered particularly informative; in particular, $\Delta\nu$ values greater than 200–260 cm^{-1} are indicative of unidentate coordination [10], even if this assumption has to be taken with care [11]. $\Delta\nu$ for compounds **3** and **4** is 208 and 219 cm^{-1}, respectively, a value that does not permit to establish with certainty if the carboxylate anion is unidentate or chelating.

The X-ray analysis carried out on $(n\text{-}Bu)_2Sn(apts)(OAc)$ (**5**) has revealed the presence in the unit-cell of two crystallographically independent molecules in which the tin atom is coordinated in the form of a distorted pentagonal bipyramid with the pentagonal plane defined by the terdentate N_2S hydrazone and the bidentate acetato group, whereas the axial positions are occupied by the two organo groups. The ORTEP diagram of the two molecules is shown in Figs. 2 and 3. The compound which affords the best comparison with **5** is $[SnMe_2(PyTSC)(OAc)] \cdot HOAc$ (HPyTSC = pyridine-2-carbaldehyde thiosemicarbazone) [12] in which the tin atom is coordinated to a N_2S terdentate ligand, to a strongly asymmetric acetate ion and to two methyl groups in an approximately pentagonal bipyramidal environment. The Sn–S bond distance in this compound is significantly shorter than those in **5**, whereas the Sn–N bond distances are longer; and the lack of linearity in the C–Sn–C fragment is more marked.

The Sn–C distances, 2.130–2.149 Å, lie in the range of the bonds quoted in the literature for the few seven-coordinated diorganotin derivatives. The significant de-

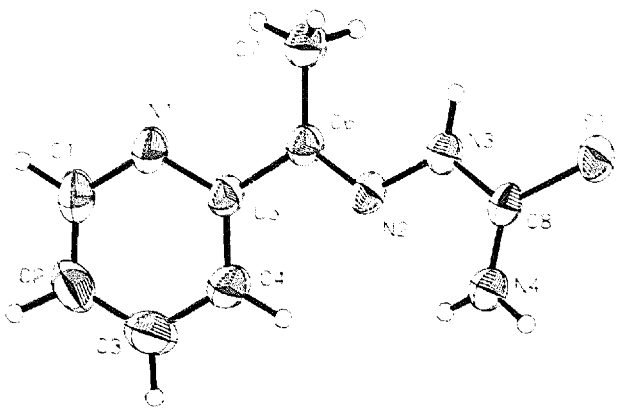

Fig. 4. ORTEP diagram of Hapts (molecule A). Thermal ellipsoids are drawn at the 50% probability level.

viations from a regular geometry are primarily due to the short bite of the acetato group which results in an O–Sn–O angle of 53.4(1)° (molecule A) and 53.7(1)° (molecule B) instead of the theoretical value of 72°. The other four angles subtended at tin in the girdle range from 67.3 to 82.9° in A and from 68.5 to 84.0° in B. The axial ligands also contribute to the observed distortion as the C–Sn–C angle is reduced from the expected value of 180° (165.0(2) and 169.7(3)° for A and B, respectively). None of the five equatorial atoms or tin lie more than 0.04 (A) and 0.12 Å (B) out of the least-squares plane. As in **1**, the chelating action of the hydrazone produces two five-membered chelate rings. An interesting difference between A and B regards the coordination mode of the acetato group which is asymmetric in A (Sn–O 2.337(3), 2.545(4) Å) and nearly symmetric in B (Sn–O 2.404(4), 2.436(4) Å). Unlike Hapt in compound **1**, apts has on the whole a nearly planar skeleton, the non-hydrogen atoms being displaced from the least-squares plane by not more than 0.13 Å in A and 0.29 Å in B. The molecules pack in the crystal in a polymeric way obtained by a net of intermolecular hydrogen bonds involving as donors the NH_2 hydrogens. As can be seen by comparing the structure of the monodeprotonated coordinated hydrazone ligand in **5** with that of the neutral free ligand (Fig. 4 shows the ORTEP diagram of one the two crystallographically independent molecules), the major difference consists in a 180° rotation about the C6–C5 and N3–C8 bonds which allows the pyridine nitrogen and the sulphur atom to participate in the coordination to tin. Significant differences occur in the planarity of the two free ligand molecules: the pyridine ring and the adjacent CCNN moiety make a dihedral angle of 16.4° in molecule A, whereas are practically coplanar (1.7°) in molecule B. As for the packing, the water molecule acts as donor towards A and as acceptor towards B, thus linking the molecules in chains.

Similarities are observed in the ^1H NMR spectra of **5** and $(n\text{-}Bu)_2Sn(aps)(OAc) \cdot C_2H_5OH \cdot 1.5H_2O$ (**6**) as for the following facts: (1) the hydrazidic N–H proton resonance disappears; (2) when the complexation stabilises the enolic tautomer of the deprotonated ligand, the two NH_2 protons become magnetically equivalent; (3) in the pyridinic ring involved in the coordination, the *para*-hydrogen is more deshielded than the *meta*-ones.

On the basis of the unequivocal X-ray structure of compound **5** and considering that the $\Delta\nu$ ($\nu(CH_3CO_2)_{asym} - \nu(CH_3CO_2)_{sym}$) value in the IR spectrum (186 cm^{-1}) as well as the signal observed for the acetate group in the ^1H NMR spectrum (2.06 ppm) are both similar to those observed in the other carboxylate complexes (208, 219 and 185 cm^{-1}, and 2.06, 2.07 and 2.04 ppm for **3**, **4** and **6** respectively), we can deduce a chelating behaviour of the acetate ion also in **3**, **4** and **6**, and, consequently the presence in all of them of a still fairly uncommon seven-coordinated tin.

Acknowledgements

Thanks are due to the Centro Interfacoltà Misure of the University of Parma for technical assistance.

References

[1] S. Ianelli, P. Mazza, M. Orcesi, C. Pelizzi, G. Pelizzi, F. Zani, J. Inorg. Biochem. 48 (1992) 253.
[2] M. Carcelli, C. Pelizzi, G. Pelizzi, P. Mazza, F. Zani, J. Organomet. Chem. 488 (1995) 55.
[3] F. Fuhkujiro, H. Kunio, N. Masukasu, T. Tsukuma, Yakugaku Zasshi 79 (1959) 1231.
[4] A. Bacchi, A. Bonini, M. Carcelli, F. Ferraro, E. Leporati, C. Pelizzi, G. Pelizzi, J. Chem. Soc. Dalton Trans. (1996) 2699.
[5] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polidori, M. Camalli, SIR 92, J. Appl. Crystallogr. 27 (1994) 435.
[6] G.M. Sheldrick, SHELXL93, Program for Structure Refinement, University of Göttingen, Germany, 1993.
[7] M. Nardelli, Comput. Chem. 7 (1983) 95.
[8] L. Zsolnai, H. Pritzkow, ZORTEP, ORTEP Original Program Modified for PC, University of Heidelberg, Germany, 1994.
[9] R.S. Barbieri, H.O. Beraldo, C.A.L. Filgueiras, A. Abras, J.F. Nixon, P.B. Hitchcock, Inorg. Chim. Acta 206 (1993) 169.
[10] G.B. Deacon, R.J. Phillips, Coord. Chem. Rev. 33 (1980) 227.
[11] N.W. Alcock, J. Culver, S.M. Roe, J. Chem. Soc. Dalton Trans. (1992) 1477.
[12] J.S. Casas, M.S. García-Tesende, C. Maichle-Mössmer, M.C. Rodríguez-Argüelles, A. Sánchez, J. Sordo, A. Vázquez-López, S. Pinelli, P. Lunghi, R. Albertini, J. Inorg. Biochem. 62 (1996) 41.