

## INVESTIGATION INTO AROYLHYDRAZONES AS CHELATING AGENTS

### V \*. SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF TWO SEVEN-COORDINATE ORGANOTIN(IV) COMPLEXES WITH 2,6-DIACETILPYRIDINE BIS(2-AMINOBENZOYLHYDRAZONE)

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#### Summary

The chelating properties of the 2,6-diacetylpyridine bis(2-aminobenzoylhydrazone) ( $H_2dapa$ ) have been investigated in two new organotin(IV) complexes of stoichiometry  $SnBuCl(dapa)$  (**1**) and  $SnPh_2(dapa)$  (**2**). The structures of the two compounds have been determined by X-ray diffraction and refined by least-squares to  $R = 0.0416$  (1936 observed reflections) and 0.0706 (2653 observed reflections), respectively. Crystals of **1** are orthorhombic, space group  $Pnma$ , with  $a$  21.466(6),  $b$  17.286(5),  $c$  7.449(3) Å,  $U$  2764(2) Å<sup>3</sup> and  $Z = 4$ . Crystals of **2** are monoclinic, space group  $P2_1/a$ , with  $a$  23.389(9),  $b$  14.362(5),  $c$  9.388(4) Å,  $\beta$  87.14(5)°,  $U$  3150(2) Å<sup>3</sup> and  $Z = 4$ . Both complexes display distorted pentagonal bipyramidal structures with the deprotonated and quinquedentate  $H_2dapa$  ligand spanning the pentagonal plane. The IR spectra are also discussed.

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#### Introduction

Metal complexes of aroylhydrazones of general formula  $[R^1C(O)NHN=CR^2]_nR^3$  ( $n = 1$  or  $2$ ;  $R^1, R^3 = \text{aryl or heteroaryl}$ ;  $R^2 = H$  or  $CH_3$ ) have been the subjects of our recent structural investigations [1–5] carried out with the aim of examining the chelating properties of the hydrazone and the effects of the coordination on the conformation and geometry of the ligand in relation with the nature and size of both the metal ion and counterion.

Results of these studies have revealed that the chemistry of these complexes is governed largely by the versatile coordinating behaviour of the hydrazone as well as

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\* For Part IV see ref. 1.

by its ability to behave as a neutral or deprotonated ligand and by its tendency to function as an approximately planar quinquedentate ligand so producing seven-coordinate pentagonal-bipyramidal structures.

In the interest of extending our investigations in this research field, we now report the preparation and the crystal and molecular structure of two new seven-coordinate organotin(IV) compounds of stoichiometry  $\text{SnBuCl}(\text{dapa})$  (**1**) and  $\text{SnPh}_2(\text{dapa})$  (**2**) ( $\text{H}_2\text{dapa} = 2,6\text{-diacetylpyridine bis}(2\text{-aminobenzoylhydrazone})$ ).

The results presented here are of interest first because this is the first report of a metal complex of  $\text{H}_2\text{dapa}$  and secondly because the two structures provide much needed structural information about seven coordination for tin. In fact, from a search of the Cambridge Data Centre Files, only fourteen seven-coordinate species appear to be structurally characterized for tin(IV), five of which are from this laboratory.

## Experimental

*Materials and preparations.* Organic solvents were vacuum-degassed and distilled before use. Dibutyldichlorotin(IV) (Merck), dichlorodiphenyltin(IV) (Merck) and 2,6-diacetylpyridine (Aldrich) were obtained commercially. 2-Aminobenzohydrazide was prepared by treating hydrazine with ethyl 2-aminobenzoate using the published procedure [6]. 2,6-Diacetylpyridine bis(2-aminobenzoylhydrazone) ( $\text{H}_2\text{dapa}$ ) was obtained by mixing 2,6-diacetylpyridine and 2-aminobenzohydrazide (1:2 mol ratio) under reflux in absolute ethanol for about 3 h. A white-yellow product was obtained after cooling at room temperature, which melts at  $179^\circ\text{C}$ . The compound was identified by C, H, N elemental analysis (Anal. Found: C, 64.1; H, 5.6; N, 22.6  $\text{C}_{23}\text{H}_{23}\text{N}_7\text{O}_2$  calcd.: C, 64.3; H, 5.4; N, 22.8%. Mass:  $m/e = 429$  (6.3), 309 (12.5), 120 (100.0), 162 (12.5), 66 (15.6)).

The following procedure was used for the preparation of both tin complexes. The ethanol solution of the organotin(IV) derivative was added to the hot chloroform solution of  $\text{H}_2\text{dapa}$  in a 1/1 mol ratio. The mixture was refluxed for 1 h and then allowed to stand at room temperature. After several days of slow evaporation of solvents, crystals, which were suitable for the X-ray analysis, of the tin complexes were isolated.

Elemental C, H, N analyses were carried out on Perkin-Elmer model 240 automatic equipment. IR of KBr discs were obtained on a Perkin-Elmer model 283 B spectrophotometer in the range  $4000\text{--}200\text{ cm}^{-1}$ . The mass spectrum was determined with a Varian CH-5 spectrometer (70 eV).

*Collection and reduction of X-ray data.* Preliminary Weissenberg photographs taken of crystals of **1** indicated orthorhombic symmetry and showed the absence of  $0kl$  reflections for  $k + l$  odd and of  $hk0$  reflections for  $h$  odd, which imply that the space group is either  $Pn2_1a$  or  $Pnma$ . The ambiguity in the space group could not be resolved by analysis of the intensity statistics which were midway between the centric and the acentric distribution. The space group  $Pnma$  was therefore assigned on the basis of the complete structure determination. Examination by Weissenberg photography showed that the crystals of **2** belong to the monoclinic system and the systematic absences indicated the space group  $P2_1/a$ .

All subsequent measurements were performed on a Siemens AED single-crystal diffractometer under the control of a G.A. Jumbo 220 computer. The unit-cell

TABLE 1

## CRYSTALLOGRAPHICALLY IMPORTANT DATA COLLECTION AND DATA PROCESSING INFORMATION

Compound	SnBuCl(dapa)	SnPh <sub>2</sub> (dapa)
Formula	C <sub>27</sub> H <sub>30</sub> ClN <sub>7</sub> O <sub>2</sub> Sn	C <sub>35</sub> H <sub>31</sub> N <sub>7</sub> O <sub>2</sub> Sn
<i>M</i>	638.72	700.36
Crystal size (mm)	0.16 × 0.20 × 0.42	0.05 × 0.26 × 0.34
Crystal system	orthorhombic	monoclinic
Space group	<i>Pnma</i>	<i>P2<sub>1</sub>/a</i>
<i>a</i> (Å)	21.466(6)	23.389(9)
<i>b</i> (Å)	17.286(5)	14.362(5)
<i>c</i> (Å)	7.449(3)	9.388(4)
$\beta$ (°)	90	87.14(5)
<i>U</i> (Å <sup>3</sup> )	2764(2)	3150(2)
<i>Z</i>	4	4
<i>D<sub>c</sub></i> (g cm <sup>-3</sup> )	1.535	1.477
<i>F</i> (000)	1296	1424
Radiation $\lambda$ Cu-K $\alpha$ (Å)	1.54178	1.54178
$\mu$ (cm <sup>-1</sup> )	87.4	69.4
$2\theta$ limits, deg	7.0–130.0	6.0–120.0
Total reflections measured	2722	5235
Total unique reflections	2439	4676
Reflections with $I \geq 2\sigma(I)$	1396	2653
No. of variables	217	438
Final <i>R</i>	0.0416	0.0706

parameters were determined for both compounds by a least-squares fit to the diffractometer-measured  $\theta$  angles of 20 reflections, well separated in reciprocal space. A summary of the most significant crystallographic data and the experimental conditions for intensity data collection are given in Table 1 for the two compounds.

Intensities were recorded by the  $\theta$ – $2\theta$  scan method using Cu-K $\alpha$  radiation at a takeoff angle of 6°. The pulse height discriminator was set to accept 90% of the Cu-K $\alpha$  peak. For compound **1**, 1396 reflections, out of a total of 2722 collected in the range  $7.0^\circ < 2\theta < 130.0^\circ$ , with  $I \geq 2\sigma(I)$ , were considered observed and were used in the refinement procedure. For compound **2**, a total of 5235 reflections ( $hkl$  and  $\bar{h}kl$ ) were measured, with  $2\theta$  ranging from 6.0 to 120.0°. Symmetry-related reflections were averaged to give 4676 independent reflections, of which 2653 with  $I \geq 2\sigma(I)$  were available for use in the structure determination. No significant change in the intensity of a standard reflection measured at regular intervals was observed for **2**, while the check reflection for **1** showed a gradual variation of its intensity during data collection, maximum value 6%, which was found to be due to decomposition effects. The data were rescaled to correct for this. For each crystal, corrections were made for background intensity (peak-profile analysis according to Lehmann and Larsen [7]) and for Lorentz and polarization effects. Any attempt to apply an absorption correction failed due to difficulties in defining the crystal shape.

*Solution and refinement.* In both structures a three-dimensional Patterson function computed with all measured data was utilized to determine the positions of the tin atom, while the remaining non-hydrogen atoms were located by subsequent

(Continued on p. 14)

TABLE 2  
 SnBuCl(dapa). FRACTIONAL ATOMIC COORDINATES ( $\times 10^4$ ) (e.s.d.s in parentheses)

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Sn	4745(0)	2500(0)	2553(1)	C(11)	6651(5)	1800(6)	4511(16)
Cl	5268(2)	2500(0)	-365(4)	C(12)	6928(8)	2500(0)	4849(27)
O(1)	4102(2)	1682(3)	1435(9)	C(13)	4397(9)	2500(0)	5243(27)
N(1)	4350(5)	-758(4)	1844(11)	C(14) <sup>a</sup>	3982(16)	3049(20)	5905(51)
N(2)	4764(3)	683(3)	2296(8)	C(15) <sup>a</sup>	3368(20)	3050(23)	5764(60)
N(3)	5145(3)	1285(3)	2827(8)	C(16)	2986(14)	2500(0)	5837(43)
N(4)	5762(4)	2500(0)	3598(12)	H(1)N	4454(31)	-1218(44)	1489(97)
C(1)	3772(3)	395(4)	933(10)	H(2)N	4699(32)	-442(50)	1976(96)
C(2)	3854(4)	-421(4)	1044(11)	H(3)	3427(28)	-1506(37)	676(82)
C(3)	3391(5)	-885(5)	307(13)	H(4)	2560(29)	-882(39)	-1093(88)
C(4)	2882(5)	-587(6)	-477(15)	H(5)	2396(30)	422(38)	-1463(101)
C(5)	2795(4)	212(6)	-621(15)	H(6)	3144(28)	1080(37)	106(83)
C(6)	3255(4)	679(5)	82(13)	H(91)	5834(30)	31(39)	2543(96)
C(7)	4230(4)	956(4)	1590(11)	H(92)	6360(33)	307(35)	4056(83)
C(8)	5681(4)	1134(4)	3505(11)	H(93)	5646(31)	89(38)	4355(92)
C(9)	5925(4)	331(5)	3799(13)	H(11)	6809(28)	1321(36)	4566(87)
C(10)	6055(4)	1814(4)	3899(11)	H(12)	7365(58)	2500(0)	5317(151)

<sup>a</sup> Occupancy factor 0.5.

TABLE 3  
 SnPh<sub>2</sub> (dapa). FRACTIONAL ATOMIC COORDINATES ( $\times 10^4$ ) (e.s.d.s in parentheses)

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Sn	6827(0)	4624(1)	4323(1)	C(15)	7406(5)	6397(8)	2775(12)
O(1)	6479(3)	3323(5)	5269(8)	C(16)	7800(6)	6995(9)	1841(14)
O(2)	7522(3)	3756(5)	3416(8)	C(17)	7887(5)	4149(9)	2544(12)
N(1)	4804(5)	3163(9)	7314(13)	C(18)	8337(6)	3575(9)	1855(12)
N(2)	5691(4)	4156(7)	6113(10)	C(19)	8265(7)	2580(10)	1689(13)
N(3)	5996(4)	4898(7)	5998(10)	C(20)	8732(8)	2111(12)	1003(17)
N(4)	6585(4)	6182(6)	4333(10)	C(21)	9235(8)	2534(16)	572(18)
N(5)	7470(4)	5521(6)	2944(9)	C(22)	9309(8)	3497(14)	789(17)
N(6)	7908(4)	5050(7)	2232(9)	C(23)	8855(6)	3992(12)	1381(13)
N(7)	7790(6)	2148(9)	2131(17)	C(24)	7327(5)	4878(8)	6185(13)
C(1)	5680(5)	2467(8)	6151(12)	C(25)	7085(6)	4581(10)	7547(13)
C(2)	5126(5)	2390(9)	6840(13)	C(26)	7403(6)	4711(10)	8738(13)
C(3)	4915(6)	1499(10)	7083(14)	C(27)	7943(7)	5054(10)	8596(14)
C(4)	5203(7)	738(10)	6627(17)	C(28)	8170(6)	5318(10)	7279(15)
C(5)	5738(7)	802(11)	5965(18)	C(29)	7851(6)	5189(8)	6092(13)
C(6)	5962(6)	1687(9)	5754(15)	C(30)	6349(5)	4283(8)	2470(13)
C(7)	5970(5)	3362(9)	5830(12)	C(31)	6132(6)	4987(11)	1641(14)
C(8)	5785(5)	5748(9)	5838(12)	C(32)	5834(6)	4733(15)	444(15)
C(9)	5232(5)	5948(9)	6645(13)	C(33)	5782(8)	3838(14)	37(16)
C(10)	6126(5)	6476(8)	5179(12)	C(34)	6024(7)	3128(14)	839(19)
C(11)	6019(6)	7415(9)	5312(14)	C(35)	6312(6)	3378(12)	2043(16)
C(12)	6366(6)	8034(9)	4605(15)	H(1)N(1)	4971(50)	3770(90)	6964(130)
C(13)	6827(5)	7768(8)	3744(13)	H(2)N(1)	4379(50)	3197(90)	7376(130)
C(14)	6928(5)	6789(8)	3635(12)	H(1)N(7)	7359(60)	2466(60)	2550(170)

structure factor calculations and difference electron density maps. Preliminary density measurements for **1** indicated the presence of four molecules per unit cell. Thus, for the centric space group *Pnma* only half of the molecule is independent, with the molecule constrained to have either *m* or  $\bar{1}$  symmetry. To be consistent with the Patterson map the complex must have exact mirror symmetry, with Sn as well as Cl, N(4), C(12), C(13), C(16) and H(12) required to lie on mirror planes at  $b = \frac{1}{4}$  and  $\frac{3}{4}$ , with occupancy factors of 0.5.

Both the structures were refined by full-matrix least-squares procedures. The use of anisotropic thermal parameters for all non-hydrogen atoms except the butyl carbon atoms in **1**, and for all non-hydrogen atoms in **2** led to convergence with  $R = 0.0534$  (**1**) and  $0.0752$  (**2**). For compound **1** refinement in the alternative space group *Pn2<sub>1</sub>a* was also tried, but it was not successful in terms of  $U_{ij}$  (with thermal quadratic form of several atoms becoming non-positive definitive) and e.s.d.'s. Due to computational constraints the atomic parameters in **2** were partitioned into two blocks. A difference Fourier computed for compound **1** revealed all hydrogen atom positions except those bonded to the butyl chain, which appeared as highly diffuse peaks and therefore were neglected. The remaining hydrogen atoms were included in the final cycle of refinement with isotropic thermal parameters. For compound **2** the positions of only three hydrogen atoms, two bonded to N(1) and one to N(7), could be inferred from a difference map. Therefore the remaining hydrogens were obtained from geometrical considerations and constrained to ride on the corresponding non-hydrogen atom positions. Final  $R$  values were  $0.0416$  and  $0.0706$  for **1** and **2**, respectively. The quantity minimized was  $\sum w(|F_o| - |F_c|)^2$ . In the early stages of the refinement, unit weights were used, and in the final cycles  $w$  was derived from counting statistics. In each case, there were no significant features on the final difference synthesis. Complex neutral-atom scattering factors were employed throughout both structure solutions and refinements. All calculations were made with the use of the SHELX-76 system program [8] on the Cyber 76 computer of CINECA (Casalecchio, Bologna), with financial support from University of Parma. The final atomic coordinates are given in Tables 2 (**1**) and 3 (**2**) and selected bond distances and angles in Table 4 for both **1** and **2**. Tables of thermal parameters, coordinates for the hydrogen atoms and calculated and observed structure factor amplitudes are available from the authors.

## Results and discussion

Our previous studies on metal transition complexes of 2,6-diacetylpyridine aroylhydrazones have revealed in most cases a 1/1 metal/ligand ratio and have shown that the complexes with the metal chlorides contain the hydrazone in its neutral form. In complexes with metal acetates the hydrazone is bideprotonated [4,5]. With regards to complexes with organotin derivatives, only one compound,  $\text{SnPr}_2(\text{daps})$  ( $\text{H}_2\text{daps} = 2,6\text{-diacetylpyridine bis(salicyloylhydrazone)}$ ) [3] contains the hydrazone in its bideprotonated form. Such behaviour has now been found in the two title compounds.

It should be noted that, in spite of the identical experimental conditions used for the preparation, these two compounds have a different formula,  $\text{SnBuCl}(\text{dapa})$  and  $\text{SnPh}_2(\text{dapa})$ , which can be justified by the steric effects, as well as by the electronic factors, of the butyl and phenyl groups.

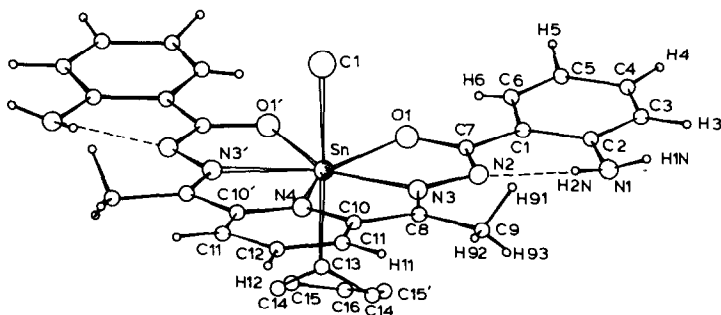


Fig. 1. Perspective view of the structure of  $\text{SnBuCl(dapa)}$  showing the atom labelling scheme (H-atoms from dapa are indicated).

Perspective views of each complex molecule, along with the adopted numbering scheme, are presented in Figs. 1 and 2. In both structures, despite the different formula,  $\text{H}_2\text{dapa}$  is found to function as a deprotonated and quinquedentate  $\text{N}_3\text{O}_2$  ligand and the tin atom has approximately pentagonal-bipyramidal coordination with the hydrazone forming the pentagon, and with the apices of the bipyramid occupied by the chloride ion and the butyl chain in **1** and by the two phenyl rings in **2**.

The IR spectra also agree with the similar ligand behaviour shown by the hydrazone in the coordination to tin. A comparison of the main vibrational bands of  $\text{H}_2\text{dapa}$  in its free state and in the coordinated form is reported in Table 5. Coordination mainly affects the amide I and  $\nu(\text{CN})$  bands, as observed in other metal complexes with *N*-acyl hydrazones [9–12].

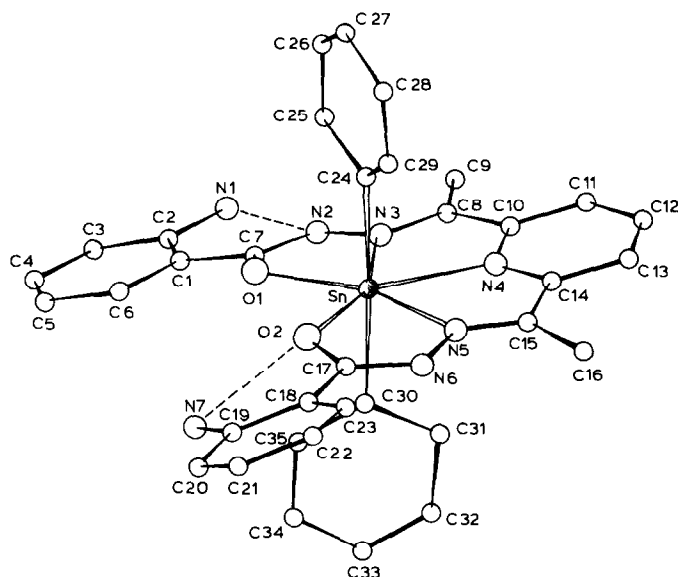


Fig. 2. Perspective view of the structure of  $\text{SnPh}_2(\text{dapa})$  showing the atom labelling scheme (H-atoms have been omitted for clarity).

TABLE 4  
 SELECTED BOND DISTANCES (Å) AND ANGLES (°) IN  $\text{SnBuCl}(\text{dapa})$  (1) AND  $\text{SnPh}_2(\text{dapa})$  (2)  
 (a) In the coordination polyhedron

Complex 1	Complex 2
Sn-O(1)	Sn-O(1)
Sn-N(3)	Sn-N(3)
Sn-N(4)	Sn-N(4)
Sn-Cl	Sn-N(5)
Sn-C(13)	Sn-O(2)
	Sn-C(24)
	Sn-C(30)
Cl-Sn-C(13)	C(24)-Sn-C(30)
O(1)-Sn-N(3)	O(1)-Sn-N(3)
N(3)-Sn-N(4)	N(3)-Sn-N(4)
O(1)-Sn-Cl	N(4)-Sn-N(5)
N(3)-Sn-Cl	N(5)-Sn-O(2)
N(4)-Sn-Cl	O(2)-Sn-O(1)
	2.144(5)
	2.278(5)
	2.318(9)
	2.446(3)
	2.138(20)
	173.1(5)
	70.7(2)
	67.3(2)
	87.1(2)
	84.6(2)
	82.3(2)
	2.207(7)
	2.266(9)
	2.308(9)
	2.324(9)
	2.187(7)
	2.182(12)
	2.170(12)
	176.4(4)
	69.2(3)
	68.0(3)
	67.5(3)
	69.6(3)
	85.8(3)



*(b) In the hydrazone moiety*

Complex 1		Complex 2	
O(1)-C(7)	1.290(9)	O(1)-C(7)	1.279(13)
C(7)-C(1)	1.465(10)	C(7)-C(1)	1.477(17)
C(7)-N(2)	1.347(10)	C(7)-N(2)	1.334(16)
N(2)-N(3)	1.381(8)	N(2)-N(3)	1.358(14)
N(3)-C(8)	1.283(11)	N(3)-C(8)	1.332(16)
C(8)-C(9)	1.500(11)	C(8)-C(9)	1.494(16)
C(8)-C(10)	1.453(11)	C(8)-C(10)	1.436(17)
C(10)-N(4)	1.361(8)	C(10)-N(4)	1.370(14)
N(1)-C(2)	1.352(13)	N(1)-C(2)	1.401(18)
Sn-O(1)-C(7)	118.0(5)	Sn-O(1)-C(7)	116.5(7)
O(1)-C(7)-N(2)	123.9(6)	O(1)-C(7)-N(2)	123.7(11)
C(7)-N(2)-N(3)	110.6(5)	C(7)-N(2)-N(3)	110.9(9)
N(2)-N(3)-Sn	116.5(4)	N(2)-N(3)-Sn	118.2(7)
N(2)-N(3)-C(8)	119.4(6)	N(2)-N(3)-C(8)	118.4(9)
Sn-N(3)-C(8)	124.1(5)	Sn-N(3)-C(8)	123.3(8)
N(3)-C(8)-C(9)	124.0(7)	N(3)-C(8)-C(9)	124.5(11)
N(3)-C(8)-C(10)	114.2(7)	N(3)-C(8)-C(10)	113.7(10)
C(9)-C(8)-C(10)	121.7(7)	C(9)-C(8)-C(10)	121.8(11)
C(8)-C(10)-N(4)	114.6(6)	C(8)-C(10)-N(4)	115.3(10)
C(10)-N(4)-Sn	119.4(3)	C(10)-N(4)-Sn	119.1(7)
		O(2)-C(17)	1.284(14)
		C(17)-C(18)	1.462(18)
		C(17)-N(6)	1.327(16)
		N(6)-N(5)	1.373(13)
		N(5)-C(15)	1.278(14)
		C(15)-C(16)	1.508(17)
		C(15)-C(14)	1.459(16)
		C(14)-N(4)	1.334(14)
		N(7)-C(19)	1.321(20)
		Sn-O(2)-C(17)	117.1(7)
		O(2)-C(17)-N(6)	125.8(10)
		C(17)-N(6)-N(5)	110.8(9)
		N(6)-N(5)-Sn	116.4(6)
		N(6)-N(5)-C(15)	120.9(9)
		Sn-N(5)-C(15)	122.6(8)
		N(5)-C(15)-C(16)	124.1(11)
		N(5)-C(15)-C(14)	113.7(10)
		C(16)-C(15)-C(14)	122.1(10)
		C(15)-C(14)-N(4)	116.4(10)
		C(14)-N(4)-Sn	119.3(7)

TABLE 5

COMPARISON OF THE MAIN IR BANDS ( $\text{cm}^{-1}$ ) IN  $\text{H}_2(\text{dapa})$  AND IN THE TWO TIN COMPLEXES

$\text{H}_2\text{dapa}$	$\text{SnBuCl}(\text{dapa})$	$\text{SnPh}_2(\text{dapa})$	Assignment
3510m			} $\nu(\text{NH})$
3450m	3400vs		
3340s		3340sh	
3210m	3280m	3305s	} $\nu(\text{CH})_{\text{aryl}}$
3060w	3060w	3060w	
3020w		3020w	} $\nu(\text{CH})_{\text{alkyl}}$
	2960m	2980w	
2920w	2920m	2920w	
	2860m		} amide I
1700s		1670sh	
1660vs, br	1620ms	1630vs, br	
1615sh		1610sh	$\delta(\text{NH})$
1600w	1590m		} ring
1580m	1565m	1570m	
1550sh	1545m	1550m	
1530vs	1500s	1510m	$\delta(\text{NH}) + \nu(\text{CN})$
1480m	1495sh	1485m	} ring
1450s	1460w	1450m	
1430m	1415m	1430m	
1355s	1375vs	1365m	$\delta(\text{CH})_{\text{alkyl}}$
	535m	270m	$\nu(\text{SnC})$

In both **1** and **2** the five hydrazone donor atoms are almost coplanar, as they do not deviate from the respective plane by more 0.02 Å in **1** and 0.04 Å in **2**. It is of interest to note that in **1** the tin atom rests 0.18 Å out of the equatorial plane, displaced towards the butyl carbon atom, while in **2** it lies in the plane. This is readily accounted for by the nature of the two axial groups, which are different in **1** and equivalent in **2**. In each case the pentagon is not regular, as one of the five sides, namely that corresponding to the O...O distance, is significantly longer (0.3–0.4 Å) than the other four. The sum of the five angles in the pentagon is 358.6° in **1** and 360.1° in **2**; the individual values ranging from 67.4 to 82.5° and from 67.5 to 85.8°, respectively. In **1** the axis of the bipyramid is approximately linear with a Cl–Sn–C(13) angle of 171.1(5)° and the tin atom is 0.20 Å from the straight line connecting the axial groups. In **2** the two Sn–C bonds are almost collinear, the C–Sn–C angle being 176.4(4)°, and the axis of the bipyramid is normal to the pentagonal plane, making an angle of 87.6° with the plane.

The distance of 2.144(5) Å for the unique crystallographically independent Sn–O bond in **1** is about 0.05 Å shorter than the two Sn–O bond distances in **2**, which are nearly equivalent at 2.207(7) and 2.187(7) Å. All of these bonds are appreciably shorter than those of 2.273(6) and 2.270(7) Å observed in the closely related  $\text{SnPr}_2(\text{daps})$  [3], which also involves a pentagonal-bipyramidal environment about tin with the quinquedentate daps ligand occupying the equatorial plane. The Sn–N distances, unlike the Sn–O distances, are almost identical in the two compounds (2.278(5) and 2.318(9) Å in **1**; 2.266(9), 2.308(9) and 2.324(9) Å in **2**) and slightly

shorter than the values found in the above daps derivative (2.326(8), 2.337(8), 2.315(9) Å). The Sn–Cl bond distance for **1** is 2.446(3) Å, which exceeds significantly that of 2.362(4) Å found in the tris(tropolonato)monochlorotin(IV) chloroform solvate [13], the only other structurally characterized seven-coordinate tin(IV) compound containing a similar type of bond. The Sn–C(butyl) bond distance in **1**, 2.14(2) Å, compares well with the value of 2.15(2) Å found for this bond in the seven-coordinate tris(*N,N*-diethyldithiocarbamato)-*n*-butyltin [14]. The Sn–C(phenyl)distances, 2.182(12) and 2.170(12) Å, for **2** are quite close to those found for other seven-coordinate pentagonal-bipyramidal diphenyltin(IV) complexes [15].

2,6-Diacetylpyridine hydrazone ligands, characterized structurally in our laboratories for Mn(H<sub>2</sub>dappc)Cl<sub>2</sub> · 5H<sub>2</sub>O [2], Mn(dappc) · 9H<sub>2</sub>O [4], Mn(H<sub>2</sub>dapb)Cl<sub>2</sub> · H<sub>2</sub>O [5] and SnPr<sub>2</sub>(daps) [3], all have an approximately planar quinquedentate behaviour and produce seven-membered stereochemistries, as found for H<sub>2</sub>dapa in the title compounds. The only two exceptions are Cu<sub>2</sub>(dappc)Cl<sub>2</sub> · H<sub>2</sub>O [16], in which the hydrazone has been found to act in an octadentate fashion towards two non-equivalent copper atoms which are both five-coordinate, and Zn<sub>2</sub>(dapt)<sub>2</sub> [1], in which the hydrazone behaves as a quinquedentate ligand with the pyridine nitrogen bridging two octahedrally-distorted zinc atoms. In the above situation the hydrazone is not planar, as its side arms are considerably twisted out of the plane of the central pyridine ring. The lack of structural data for any H<sub>2</sub>dapa metal complex precludes a more detailed analysis. However, it can be noted that there is a reasonable agreement between the corresponding bond distances and angles in the hydrazone moiety of the two title compounds (see Table 4).

In **1** two of the carbon atoms of the butyl chains, i.e. C(13) and C(16), actually lie in the mirror plane, while the other two atoms C(14) and C(15), are distributed below and above the plane, with occupancy of 0.5, giving rise to disorder in the structure. As a consequence of the disorder, the observed values for the C–C bond lengths are inaccurately determined. The torsion angle C(13)–C(14)–C(15)–C(16) is 38(7)°. The least-squares plane through the butyl carbon atoms makes an angle of 35.0° with the pentagonal plane.

The two phenyl groups in **2** are planar within experimental error and have normal distances and angles, the mean C–C bond length is 1.38(2) Å and all C–C–C angles are in the range 118–122°. The two rings are nearly normal to the pentagonal plane, the interplanar angle being 87.2° (C(24)–C(29)) and 91.9° (C(30)–C(35)), while the dihedral angle between them is 72.2°.

The crystal packing in the two compounds deserves special comment. In **1** both of the hydrogen atoms linked to the nitrogen atom of the amino group, N(1), are utilized in the formation of two hydrogen bonds, one intramolecular [N(1)...N(2) is 2.666(9) Å], the other intermolecular [N(1)...Cl at 1 – *x*,  $\bar{y}$ ,  $\bar{z}$ , 3.310(8) Å]. The extended crystal structure is stabilized by these hydrogen bonds and by Van der Waals interactions, the shortest of which is between N(1) and C(9) (1 – *x*,  $\bar{y}$ , 1 – *z*) at 3.38(1) Å. In contrast in **2**, in which a phenyl ring replaces the chlorine atom, the nitrogen atoms of the two amino groups, N(1) and N(7), exercise only a single donor function, as both participate only in intramolecular hydrogen bonding with adjacent atoms. Surprisingly, however, N(1) forms a hydrogen bond with a nitrogen atom, N(2), the separation distance being 2.72(1) Å, while N(7) is hydrogen-bonded to an oxygen atom, O(2), at a distance of 2.67(1) Å. This situation is a direct consequence of the two NH<sub>2</sub>-containing rings being rotated through different angles about the

C–C bonds linking them to the OCN moiety. This is expressed by the corresponding torsion angles: O(1)–C(7)–C(1)–C(2) is  $177(1)^\circ$  showing that N(1) and O(1) are *trans* to each other, while O(2)–C(17)–C(18)–C(19) is  $24(2)^\circ$  indicating that N(7) and O(2) are in the *cis* position. Moreover, the C(7)–C(1)–C(2)–N(1)–N(2) moiety is nearly planar with the deviation of any contributing atom from the least-squares plane being only 0.04 Å. The corresponding set of atoms C(17)–C(18)–C(19)–N(7)–O(2) shows a marked departure from planarity (maximum deviation 0.17 Å). It should be noted that this situation is different from that found in SnPr<sub>2</sub>(daps) [3], in which two OH groups replace the two amino groups in the hydrazone moiety and two n-propyl groups occupy the apical sites of the bipyramid. In this compound, in fact, the two phenolic oxygen atoms are both involved in intramolecular hydrogen bonds with adjacent nitrogen atoms and are *trans* to the coordinated oxygen atoms.

There are no unusually short intermolecular distances in the structure of **2**, so it would appear that the molecules are held together in the crystal by Van der Waals interactions only, the most significant are: N(1)...C(10) ( $1-x, 1-y, 1-z$ ) 3.31(2), N(1)...C(11) ( $1-x, 1-y, 1-z$ ) 3.31(2), C(19)...C(11) ( $3/2-x, y-\frac{1}{2}, 1-z$ ) 3.36(2) Å.

## References

- 1 C. Lorenzini, C. Pelizzi, G. Pelizzi and G. Predieri, *J. Chem. Soc., Dalton Trans.*, (1983) 2155.
- 2 M. Nardelli, C. Pelizzi and G. Pelizzi, *Transition Met. Chem.*, 2 (1977) 35.
- 3 C. Pelizzi and G. Pelizzi, *J. Chem. Soc., Dalton Trans.*, (1980) 1970.
- 4 C. Pelizzi, G. Pelizzi, G. Predieri and S. Resola, *J. Chem. Soc., Dalton Trans.*, (1982) 1349.
- 5 C. Lorenzini, C. Pelizzi, G. Pelizzi and G. Predieri, *J. Chem. Soc. Dalton Trans.*, (1983) 721.
- 6 E.H. Rodd (Ed.), *Chemistry of Carbon Compounds*, Vol. IIIA, Elsevier, Amsterdam, 1954, p. 577.
- 7 M.S. Lehmann and F.K. Larsen, *Acta Crystallogr. A*, 30 (1974) 580.
- 8 G.M. Sheldrick, SHELX-76, A Program for Crystal Structure Determination, Cambridge University, 1976.
- 9 K.K. Narang and A. Aggarwal, *Inorg. Chim. Acta*, 9 (1974) 137.
- 10 M.P. Teotia, J.N. Gurtu and V.B. Rana, *J. Inorg. Nucl. Chem.*, 42 (1980) 821.
- 11 M.F. Iskander, L. El-Sayed, S. Saddeck and M.A. Abno-Taleb, *Transition Met. Chem.*, 5 (1980) 168.
- 12 R.L. Dutta and A.K. Sarkar, *J. Inorg. Nucl. Chem.*, 43 (1981) 57.
- 13 J.J. Park, D.M. Collins and J.L. Hoard, *J. Am. Chem. Soc.*, 92 (1970) 3636.
- 14 J.S. Morris and E.O. Schlemper, *J. Cryst. Mol. Struct.*, 9 (1979) 1.
- 15 M. Nardelli, C. Pelizzi, G. Pelizzi and P. Tarasconi, *Inorg. Chim. Acta*, 30 (1978) 179.
- 16 A. Mangia, C. Pelizzi and G. Pelizzi, *Acta Crystallogr.*, B 30 (1974) 2146.