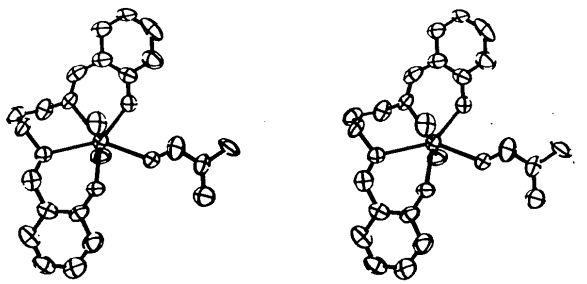

Fig. 2. An *ORTEP* (Johnson, 1976) drawing of the molecule.

deviation from the least-squares plane 0·141 (3) Å for O(4)]. The uranyl group is not considered linear, the U=O bonds deviating 5° from 180°, greater than that observed elsewhere (Lintredt *et al.* 1982; Bandoli, Clemente, Croato, Vidali & Vigato, 1973; Graziani, Casellato, Vigato, Rajan & Chakravorty, 1981). The U—N distances are found to be much longer than the U—O, more so than would be suggested by the difference in covalent radii between O and N. This is testimony to the 'hardness' (Pearson, 1963) of UO_2^{2+} which would be expected to be bonded less strongly to the 'softer' nitrogen. The U—O distance to the monodentate ligand (DMF) is the same as in the case of water (Bandoli, Cattalani, Clemento, Vidali & Vigato, 1972), also a polar ligand, and slightly shorter than in the case of methanol (Bandoli *et al.*, 1973) and ethanol (Bandoli, Clemente, Croato, Vidali & Vigato, 1971).

The propane chain that links the N(1) and N(2) imine atoms causes an increase of the N(1)—U—N(2) angle from a value of 62·4 (Bandoli *et al.*, 1972) or 66·4 (Lintredt *et al.*, 1982) to 71·2° and a decrease of the O(3)—U—O(5) and O(4)—U—O(5) angles from a mean value of 78·6 (Bandoli *et al.*, 1972, 1973) to 74·7°.

The C(9) atom of the propane group has a deviation of 0·15 (5) Å from the equatorial pentagon and defines with U and O(5) a twofold pseudosymmetry axis, so the molecule has the 'stepped' conformation (Casellato *et al.*, 1976; Bandoli *et al.*, 1972).

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Structure of a Seven-Coordinated Tin(IV)–Hydrazone Complex

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Abstract. Dichloro[2,6-diacetylpyridine bis(picolinoylhydrazonato)]tin(IV) monohydrate, $[Sn(C_{21}H_{17}N_7O_2)Cl_2].H_2O$, $M_r = 607{\cdot}02$, monoclinic, $P2_1/c$, $a = 8{\cdot}485$ (5), $b = 14{\cdot}476$ (6), $c = 19{\cdot}533$ (12) Å, $\beta = 95{\cdot}67$ (8)°, $V = 2387$ (2) Å^3, $Z = 4$, $D_x = 1{\cdot}689$ g cm^{-3}, D_m not measured, λ(Cu $K\alpha$) =

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1·54178 Å, $\mu = 111{\cdot}60\ cm^{-1}$, $F(000) = 1208$, $T = 298$ K, final $R = 0{\cdot}0604$ for 1066 observed reflections. The structure consists of discrete monomeric $Sn(dappc)Cl_2$ units [H_2dappc = 2,6-diacetylpyridine bis(picolinoylhydrazone)] and H_2O solvent molecules. The Sn atom has a slightly distorted seven-coordinate pentagonal bipyramidal environment, being bonded to two O and three N atoms of the hydrazone molecule in the pentagonal base and to two Cl atoms in the axial positions.

Introduction. This investigation is part of a research project, currently in progress in our laboratories, on synthetic and structural studies of metal complexes of 2,6-diacetylpyridine bis(acylhydrazones). Previous work on this subject has shown that these molecules have many interesting features, such as versatility for binding metal ions, flexibility in assuming different conformations and the possibility of coordinating either in the neutral or in the dianionic form (Lorenzini, Pelizzi, Pelizzi & Predieri, 1983; Pelizzi, Pelizzi & Predieri, 1984; Pelizzi, Pelizzi, Predieri & Vitali, 1985). In this paper, which also provides the opportunity to contribute to existing information on seven-coordinate tin, we present the X-ray crystal structure of [Sn(dappc)Cl_2].H_2O.

Experimental. Yellow crystals prepared by evaporating an MeOH/$CHCl_3$ (1:1 *v/v*) solution containing equimolar amounts of H_2dappc and $SnCl_2$. Tendency of crystals to occur as twins. Eventually, a marginally suitable crystal was located which, while being essentially single, yielded reflections of widely varying widths. The small prismatic crystal used for X-ray study was inadvertently lost before measurement of its dimensions. Siemens AED three-circle diffractometer on line to a General Automation Jumbo 220 computer, room temperature, Ni-filtered Cu $K\alpha$ radiation. Lattice parameters and their standard deviations obtained by least-squares refinement using setting angles for 15 well-centered reflections ($16{\cdot}4 \le \theta \le 29{\cdot}8°$) chosen from a variety of points in reciprocal space. Space group $P2_1/c$ assigned unambiguously on basis of systematic absences (l odd for $h0l$ and k odd for $0k0$). Intensity data collected by θ–2θ scans, θ range 3·0–60·0°; variable scan speed; index range h 0 to 8, k 0 to 14, l −18 to 18. A standard reflection (122) monitored every 75 measurements to check crystal alignment and stability: only random statistical fluctuations. 3694 reflections collected, 3299 unique and allowed by symmetry ($R_{int} = 0{\cdot}0379$), only 1066 observed [$I > 2\sigma(I)$] owing to the low reflecting power of the crystal and rapid intensity fall-off at high θ values. A second data collection with a somewhat larger crystal did not improve the intensity. Reflections were subjected to profile analysis following Lehmann & Larsen (1974). Intensity data corrected for Lorentz and polarization effects to give observed structure factors. Structure solved *via* usual heavy-atom methods; Sn atom obtained from a three-dimensional Patterson map and the other non-H atoms from electron-density syntheses. Full-matrix least-squares refinement based on F. $\sum w|\Delta F|^2$ minimized, unit weights. After isotropic refinement, corrections for absorption and extinction were applied using the method of Walker & Stuart (1983); transmission factors: absorption: 0·785–1·288; extinction: 0·850–1·138. Owing to the paucity of observed reflections and in order to reduce the number of variable parameters, only the Sn and Cl atoms were allowed to vibrate anisotropically. H atoms were excluded for the same reason, in spite of the presence in the final ΔF map of electron density at several of the expected H-atom positions. Convergence at $R = 0{\cdot}0604$ and $S = 4{\cdot}79$. 152 parameters varied in all; observations-to-variables ratio 7·0/1. $(\Delta/\sigma)_{max} = 0{\cdot}19$. Max. and min. peak heights in final ΔF map 0·38 and −0·58 e $Å^{-3}$ near heavy-atom positions. Scattering factors for neutral atoms and real and imaginary components of anomalous dispersion from *International Tables for X-ray Crystallography* (1974). Calculations carried out on a Gould SEL 32/77 computer. Programs employed in the structural determination: *SHELX*76 (Sheldrick, 1976), *ASSORB* (Ugozzoli, 1983), *PARST* (Nardelli, 1983) and *ORTEP*II (Johnson, 1976).

Final positional and equivalent isotropic thermal parameters are given in Table 1. Selected bond distances and angles are in Table 2.*

Discussion. The title compound crystallizes with four monomeric $Sn(dappc)Cl_2$ units and four H_2O solvent molecules in the unit cell. The oxidation of Sn^{II} to Sn^{IV}, caused by the air atmosphere, is noteworthy. As shown in Fig. 1, which also gives the atomic numbering scheme, the coordination polyhedron about the Sn atom has the shape of a pentagonal bipyramid; this is the most frequently observed seven-coordinate geometry. The pentagonal plane is made up of two O and three N atoms which belong to the hydrazone ligand, while the two Cl atoms are in the axial positions. The five equatorial donor atoms are almost coplanar, with a maximum displacement of 0·07 Å from the weighted mean plane.

The two Sn—Cl distances in the present study are nearly equivalent at 2·395 (7) and 2·387 (7) Å. These distances are similar to that of 2·362 (4) Å in tris(tropolonato)monochlorotin(IV) chloroform solvate (Park, Collins & Hoard, 1970), whereas a somewhat

* Lists of structure factors, anisotropic thermal parameters, and non-essential bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43884 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

longer value of 2·446 (3) Å has been found in SnBuCl(dapa) [H_2dapa = 2,6-diacetylpyridine bis(2-aminobenzoylhydrazone)] (Pelizzi, Pelizzi & Predieri, 1984). The Sn—O and Sn—N distances, which average 2·102 and 2·246 Å, respectively, are relatively short when compared to those observed in other seven-coordinate pentagonal bipyramidal Sn^{IV} compounds containing a quinquedentate hydrazone ligand in the pentagonal girdle, namely $SnPr^n_2$(daps) [H_2daps = 2,6-diacetylpyridine bis(2-hydroxybenzoylhydrazone)] (Pelizzi & Pelizzi, 1980), SnBuCl(dapa) and $SnPh_2$(dapa) (Pelizzi, Pelizzi & Predieri, 1984) [Sn—O 2·144 (5)–2·273 (6); Sn—N 2·266 (9)–2·337 (8) Å]. The angles subtended at Sn in the pentagonal plane range from 68·3 (7) to 78·0 (6)° with a mean value of 72·0°, exactly the same as that for a regular pentagonal-bipyramidal configuration. The bond angles between equatorial and axial positions show only small deviations from 90°, the range being 86·8 (5)–92·5 (4)°. The axial Cl—Sn—Cl angle is very nearly linear at 177·2 (3)° and the axis of the bipyramid is perpendicular to the pentagonal plane [at an angle of 89·7 (3)°].

Up to now, the structures of three metal complexes of H_2dappc have been investigated in our laboratories, namely Cu_2(dappc)$Cl_2.H_2O$ (Mangia, Pelizzi & Pelizzi, 1974), Mn(H_2dappc)$Cl_2.5H_2O$ (Nardelli, Pelizzi & Pelizzi, 1977) and Mn(dappc).$9H_2O$ (Pelizzi, Pelizzi, Predieri & Resola, 1982). The most evident difference between these structures concerns the deprotonation of the organic ligand, which occurs in the first and third structures as well as in the title compound, while in the pentahydrated Mn derivative the hydrazone was found to be in its neutral form. However, structurally the closest comparison is between the title compound and the two Mn derivatives in that both of them are characterized by the presence of a 1:1 molar ligand ratio, a seven-membered stereochemistry, and an N_3O_2 quinquedentate donor set. By contrast, in the Cu derivative the organic molecule is octadentate, coordinating to two non-equivalent Cu atoms, each of which is five-coordinate.

The solvating water molecule, O(3), shows a comparatively high thermal motion with respect to the other atoms. This suggests that it has some freedom in the structure, as it seems only to be involved in weak O···O and O···N bifurcated hydrogen bonds to the hydrazone atoms of the tin complex [range 3·12 (3)–3·22 (3) Å]. All other intermolecular contacts correspond to normal van der Waals interactions.

Table 1. *Fractional atomic coordinates* (×10⁴) *and equivalent isotropic thermal parameters* (Å² ×10⁴)

$U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}/U_{iso}
Sn	1397 (2)	4921 (1)	7000 (1)	612 (6)
Cl(1)	2150 (8)	6305 (5)	6446 (4)	789 (31)
Cl(2)	514 (8)	3564 (5)	7542 (4)	822 (29)
O(1)	3689 (17)	4733 (10)	7504 (8)	690 (49)
O(2)	2488 (19)	4125 (11)	6285 (9)	705 (54)
O(3)	5791 (25)	3172 (15)	6843 (11)	1245 (77)
N(1)	6323 (27)	4201 (15)	8297 (11)	877 (72)
N(2)	2914 (24)	5572 (14)	8456 (11)	720 (62)
N(3)	1445 (23)	5645 (13)	7988 (10)	663 (58)
N(4)	−990 (22)	5614 (13)	7120 (11)	638 (56)
N(5)	−414 (22)	4586 (12)	6113 (10)	602 (55)
N(6)	108 (24)	4017 (14)	5601 (10)	684 (60)
N(7)	3815 (27)	3031 (16)	5415 (12)	901 (72)
C(1)	7722 (35)	3916 (20)	8661 (16)	910 (94)
C(2)	8148 (37)	4312 (23)	9291 (17)	1046 (105)
C(3)	7289 (35)	5023 (26)	9565 (15)	1144 (95)
C(4)	5792 (33)	5303 (18)	9184 (14)	878 (94)
C(5)	5414 (27)	4840 (19)	8550 (12)	695 (72)
C(6)	3879 (26)	5062 (20)	8117 (12)	645 (63)
C(7)	374 (30)	6179 (18)	8223 (14)	700 (78)
C(8)	465 (33)	6747 (19)	8847 (15)	900 (93)
C(9)	−1060 (29)	6099 (17)	7676 (13)	642 (71)
C(10)	−2471 (29)	6602 (17)	7812 (12)	667 (71)
C(11)	−3812 (29)	6439 (18)	7296 (13)	718 (78)
C(12)	−3654 (30)	5883 (18)	6730 (13)	742 (80)
C(13)	−2132 (28)	5453 (16)	6673 (12)	596 (69)
C(14)	−1849 (25)	4897 (18)	6077 (11)	643 (62)
C(15)	−3078 (31)	4613 (18)	5493 (14)	857 (89)
C(16)	1615 (31)	3815 (17)	5779 (14)	674 (75)
C(17)	2312 (34)	3242 (19)	5240 (15)	801 (86)
C(18)	1395 (31)	2888 (19)	4697 (15)	814 (83)
C(19)	2126 (38)	2354 (21)	4201 (15)	1001 (99)
C(20)	3695 (38)	2146 (21)	4353 (16)	1019 (100)
C(21)	4520 (31)	2497 (20)	4931 (17)	930 (98)

Table 2. *Selected bond distances* (Å) *and angles* (°)

Sn—Cl(1)	2·395 (7)	O(1)—C(6)	1·28 (3)
Sn—Cl(2)	2·387 (7)	C(6)—N(2)	1·33 (3)
Sn—O(1)	2·109 (14)	N(2)—N(3)	1·47 (3)
Sn—O(2)	2·096 (17)	N(3)—C(7)	1·31 (3)
Sn—N(3)	2·193 (20)	O(2)—C(16)	1·26 (3)
Sn—N(4)	2·293 (19)	C(16)—N(6)	1·32 (3)
Sn—N(5)	2·252 (18)	N(6)—N(5)	1·40 (3)
		N(5)—C(14)	1·29 (3)

O(1)—Sn—N(3)	73·4 (7)	Sn—N(3)—N(2)	117 (1)
N(3)—Sn—N(4)	68·9 (7)	Sn—N(3)—C(7)	130 (2)
N(4)—Sn—N(5)	68·3 (7)	N(3)—C(7)—C(9)	104 (2)
N(5)—Sn—O(2)	71·4 (7)	Sn—O(2)—C(16)	117 (2)
O(2)—Sn—O(1)	78·0 (6)	O(2)—C(16)—N(6)	127 (2)
Cl(1)—Sn—Cl(2)	177·2 (3)	C(16)—N(6)—N(5)	108 (2)
Sn—O(1)—C(6)	114 (1)	N(6)—N(5)—C(14)	122 (2)
O(1)—C(6)—N(2)	130 (2)	Sn—N(5)—N(6)	116 (1)
C(6)—N(2)—N(3)	105 (2)	Sn—N(5)—C(14)	122 (1)
N(2)—N(3)—C(7)	113 (2)	N(5)—C(14)—C(13)	112 (2)

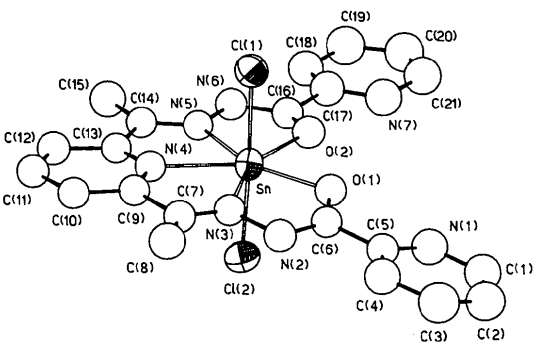

Fig. 1. A perspective view of the [Sn(dappc)Cl_2] complex. Thermal ellipsoids are shown at the 40% probability level.

The results of the present study support our earlier findings that this type of hydrazone prefers to maintain a nearly planar pentagonal configuration on coordination, leaving two vacant sites available for overall pentagonal bipyramidal coordination; these can be occupied by unidentate inorganic anions, σ-bonded organic groups or solvent molecules.

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Structures of Two Dibutyldichlorotin(IV) Adducts with Diarsine and Diphosphine Oxides

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Abstract. (1): [1,2-Bis(diphenylarsoryl)ethane]di-*n*-butyldichlorotin(IV), $[Sn(C_{26}H_{24}As_2O_2)Cl_2(C_4H_9)_2]$, $M_r = 822{\cdot}14$, monoclinic, $C2/c$, $a = 10{\cdot}879$ (4), $b = 20{\cdot}751$ (8), $c = 16{\cdot}014$ (6) Å, $\beta = 98{\cdot}45$ (5)°, $V = 3576$ (2) Å^3, $Z = 4$ (Sn on twofold axis), $D_x = 1{\cdot}527$ g cm^{-3}, D_m not measured, λ(Cu $K\alpha$) = 1·54178 Å, $\mu = 95{\cdot}17$ cm^{-1}, $F(000) = 1648$, $T = 298$ K, final $R = 0{\cdot}0407$ for 2114 unique observed reflections. (2): [Bis(diphenylphosphoryl)methane]di-*n*-butyldichlorotin(IV), $[Sn(C_{25}H_{22}O_2P_2)Cl_2(C_4H_9)_2]$, $M_r = 720{\cdot}22$, orthorhombic, *Pbca*, $a = 9{\cdot}80$ (1), $b = 19{\cdot}66$ (2), $c = 35{\cdot}36$ (3) Å, $V = 6813$ (11) Å^3, $Z = 8$, $D_x = 1{\cdot}404$ g cm^{-3}, D_m not measured, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 10{\cdot}29$ cm^{-1}, $F(000) = 2944$, $T = 298$ K, final $R = 0{\cdot}0822$ for 2716 unique observed reflections. Compound (1) has formula $SnBu^n_2Cl_2$(dpaoe)[dpaoe = 1,2-bis(diphenylarsoryl)ethane] and shows a polymeric nature as a result of the bridging action of the dpaoe ligand. The tin environment is that of a slightly distorted octahedron, the ligands being two Cl, two O and two butyl C atoms. The structure of (2) consists of discrete molecules of $SnBu^n_2Cl_2$(dppom) [dppom = bis(diphenylphosphoryl)methane] in which the metal atom is coordinated to two Cl and two butyl C groups and, more loosely to one than the other, to two O atoms from dppom. The coordination geometry about tin is highly distorted and does not exhibit the characteristics of an idealized polyhedron.

Introduction. Recent work in these laboratories has been directed towards an examination of organotin(IV) derivatives containing phosphorus or arsenic ligands (Harrison, Sharpe, Pelizzi, Pelizzi & Tarasconi, 1983*a*,*b*; Dondi, Nardelli, Pelizzi, Pelizzi & Predieri, 1985, 1986). Our interest in this research field arises from our awareness of the paucity of crystallographic studies on mixed organotin–organophosphorus and organotin–organoarsenic derivatives as revealed by a

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