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X-ray Structure of Tetrachloro(*N*-pyridoxylidene-*N'*-picolinoylhydrazine)tin(IV) Dihydrate

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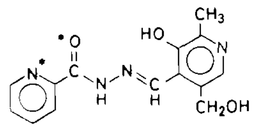
The synthesis and X-ray crystal structure of the title compound are described. Crystals are monoclinic, space group $P2_1/c$, *with unit cell dimensions:* a = *7.326(4),* b = *16.163(3),* c = *18.591(3)* Å, *β* = *94.6(2)°,* Z = *4. The structure was solved from diffractometer data by Patterson and Fourier techniques to* R = *3.8% for 2088 independent reflections. It consists of individual complex molecules, in which tin is six-co-ordinated by four chlorine atoms and the chelating system NCCO of the picolinoylhydrazide moiety of the organic ligand in a distorted octahedral configuration. The pyridoxal nitrogen is protonated at the expenses of the hydrazidic bridge. Packing is determined by a network of hydrogen bonds involving also the water molecules, one of them being disordered in two statistical positions.*

Introduction

Continuing our research program concerning the ligand behaviour of aroylhydrazones of aromatic aldehydes in metal complexes, we have recently synthesized and examined, by spectroscopic and diffraction techniques, some transition metal complexes of the salicyloylhydrazones of picolinaldehyde (H*sip*) [1–5] and of pyridoxal (H*sipox*) [6, 7]. Both these ligands contain the chelating group –C(O)–N(H)–N=C(H)– and act as terdentate.

In a previous paper in this journal [8], the probable structure of a number of tin complexes of these and other ligands of this kind was discussed on the basis of spectroscopic and conductometric measurements. The present work deals with the X-ray structure of one of these complexes, Sn(H*pipox*)$Cl_4 \cdot 2H_2O$, obtained from reaction of $SnCl_4$ and pyridoxal picolinoylhydrazone, (H*pipox*), (1)



(1)

The results of the structural analysis show that the ligand behaves as bidentate through the starred atoms and consequently the iminic nitrogen atom and the pyridoxal group are not involved in co-ordination.

Experimental

Preparation of Hpipox

The ethanol solution of picolinoylhydrazide and pyridoxal (1:1 molar ratio) was refluxed for 1 hour, until a yellow microcrystalline product was obtained, which, after recrystallization from ethanol, melts at 248 °C.

Preparation of Sn(Hpipox)$Cl_4 \cdot 2H_2O$

The tin(IV) complex was obtained by reacting at 80 °C an anhydrous ethanol solution containing equimolar amounts of $SnCl_4$ and of the ligand for twenty minutes under nitrogen atmosphere. After evaporation of the solvent, under reduced pressure, a microcrystalline orange product was separated. Crystals suitable for X-ray analysis were obtained by recrystallization from ethanol in *non*-anhydrous conditions. Analytical data are: Sn, 20.6; C, 29.2; H, 2.9; N, 9.7%. Calcd. for $C_{14}H_{18}Cl_4N_4O_5Sn$: Sn, 20.4; C, 28.9; H, 3.1; N, 9.6%.

Crystal Data

$C_{14}H_{18}Cl_4N_4O_5Sn$, M = 582.8, Monoclinic, a = 7.326(4), b = 16.163(3), c = 18.591(3) Å, β = 94.6(2)°, U = 2194(1) Å^3, D_m = 1.78 g cm^{-3}, Z = 4, D_c = 1.76 g cm^{-3}, $F(000)$ = 1152, λ(Cu-Kα) = 1.5418 Å, μ(Cu-Kα) = 143.9 cm^{-1}. Space group $P2_1/c$ (from systematic absences); crystal size 0.06 × 0.06 × 0.21 mm^3.

Crystallographic Measurements

Intensity data were collected on a on-line AED Siemens diffractometer, using the Ni-filtered Cu-Kα radiation and the ω–2θ ($2\theta_{max}$ = 120°) technique, a standard check reflection being measured every 20 reflections. In this way the intensities of 3182 inde-

TABLE I. Fractional Atomic Co-ordinates ($\times 10^4$ for Non-hydrogen Atoms, $\times 10^3$ for Hydrogen Atoms) with Estimated Standard Deviations in Parentheses.

	x/a	*y/b*	*z/c*
Sn	1610(1)	1719(0)	2036(0)
Cl(1)	3633(4)	696(1)	1659(1)
Cl(2)	4185(3)	2634(1)	2356(1)
Cl(3)	−1111(3)	876(2)	1827(1)
Cl(4)	960(3)	2399(2)	910(1)
O(1)	1826(7)	1234(3)	3085(3)
O(2)	2787(9)	−772(4)	4076(3)
O(3)	1204(10)	299(5)	6712(4)
N(1)	15(9)	2594(4)	2645(3)
N(2)	1045(10)	1461(4)	4258(3)
N(3)	1853(9)	691(4)	4411(3)
N(4)	4228(10)	−1800(5)	5701(4)
C(1)	−889(12)	3268(6)	2378(5)
C(2)	−1637(13)	3831(6)	2821(5)
C(3)	−1507(13)	3683(6)	3557(5)
C(4)	−617(13)	2981(5)	3820(4)
C(5)	123(11)	2437(5)	3362(4)
C(6)	1061(11)	1654(5)	3574(4)
C(7)	2121(12)	518(5)	5084(4)
C(8)	2874(11)	−279(5)	5302(4)
C(9)	3336(11)	−468(5)	6033(4)
C(10)	4012(11)	−1239(6)	6213(4)
C(11)	3824(11)	−1686(5)	4990(4)
C(12)	3147(11)	−897(5)	4789(4)
C(13)	3073(14)	147(6)	6644(4)
C(14)	4102(14)	−2355(6)	4478(5)
O(4)	4215(10)	3340(4)	3959(4)
O(51)	3323(24)	4787(11)	4676(9)
O(52)	−120(37)	351(15)	121(15)
H(O2)	225(14)	−23(7)	399(5)
H(O3)	89(16)	−12(8)	701(6)
H(N4)	466(16)	−241(7)	587(6)
H(1)	−84(12)	331(6)	191(5)
H(2)	−243(13)	437(6)	258(5)
H(3)	−219(13)	405(6)	377(5)
H(4)	−65(12)	289(6)	434(5)
H(7)	186(11)	88(5)	537(4)
H(10)	446(10)	−143(5)	671(4)
H(131)	383(8)	−1(4)	719(3)
H(132)	380(14)	64(6)	664(5)
H(141)	394	−226	390
H(142)	314	−282	463
H(143)	548	−256	463

pendent reflections were measured, of which 2088, having $I > 2\sigma(I)$, were considered observed and were employed in the analysis. After Lorentz and polarization corrections have been applied, the absolute scale was determined first by Wilson's method and then as a refinement parameter.

Structure Analysis

The structure was solved by the heavy-atom method, the initial set of coordinates for tin and the chlorine atoms being deduced from a three dimensional Patterson map. The non-hydrogen atoms were refined by isotropic and anisotropic least-squares, using unit weights, to $R = 0.042$; this refinement was successful assuming water O(5) distributed in two statistical positions, O(51) and O(52), with occupancy factors of 0.61 and 0.39 respectively. The contributions of the hydrogen atoms were considered as follows: (a) the hydrogen atoms from the O(4) water molecule gave recognizable peaks in the ΔF map, but, as their coordinates got worse in the least-squares refinement, they were not further considered; the location of the H atoms of the disordered O(5) water was not attempted; (b) the hydrogen atoms, from the C(14) methyl group were assumed in the calculated positions and all the group was refined as rigid body with free thermal parameters; (c) all the other hydrogen atoms were located in the ΔF map and isotropically refined. In such a way at the end of the refinement the following conventional residual R indexes were obtained: $R = 0.038$ and $R_w = 0.042$ for the observed reflections only; $R = 0.065$, $R_w = 0.043$ for all reflections ($w = 1/\sigma^2$).

The atomic scattering factors used in all calculations take into account the anomalous scattering effect following the *International Tables* [9]. Final co-ordinates and thermal parameters with their estimated standard deviations are given in Tables I and II. Observed and calculated structure factors can be obtained from the editor upon request.

All calculations were performed on the CYBER 76 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale (Bologna), using the SHELX-76 system of computer programs [10], with financial support from the University of Parma.

Results and Discussion

As can be seen from the projection along [100] of the structure (Fig. 1) and from the values of the bond distances and angles around tin (Table III), the environment of metal is octahedral elongated along Cl(2), Cl(3). The pyridine nitrogen, N(1), and the carbonyl oxygen, O(1), from the organic ligand, the chlorine atoms, Cl(1) and Cl(4) lie in the equatorial plane, while Cl(2) and Cl(3) are involved in the two apical interactions. Two types of distortions from regular octahedral symmetry are present: differences in bond lengths and angular distortions. The Sn–Cl (*eq*) distances, which are comparable with those found in other octahedral tin(IV) complexes containing the *cis*-$SnCl_4$ grouping [11–14], are significantly shorter than the Sn–Cl(*ax*) ones. The lengthening of the latter can be related to the hydrogen bond interactions in which the axial chlorines are involved. The

TABLE II. Thermal Parameters[a] with Estimated Standard Deviations in Parentheses; ($\times 10^4$ for the Sn Atom, $\times 10^2$ for the Hydrogen and O(51), O(52) Atoms, $\times 10^3$ for the Remaining Atoms).

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	Atom	U
Sn	556(4)	413(3)	295(3)	−11(3)	34(2)	61(3)	O(51)	15(1)
Cl(1)	80(2)	56(2)	62(1)	5(1)	17(1)	−4(1)	O(52)	8(2)
Cl(2)	68(2)	57(1)	47(1)	−14(1)	−2(1)	3(1)	H(O2)	10(4)
Cl(3)	69(2)	73(2)	56(1)	−22(1)	−2(1)	6(1)	H(O3)	7(5)
Cl(4)	77(2)	71(2)	34(1)	−2(1)	−1(1)	16(1)	H(N4)	5(5)
O(1)	58(4)	45(3)	35(3)	9(3)	8(3)	12(3)	H(1)	7(3)
O(2)	73(4)	55(4)	33(3)	6(3)	−1(3)	−1(3)	H(2)	11(3)
O(3)	90(6)	75(5)	52(4)	25(4)	15(4)	6(4)	H(3)	9(3)
N(1)	53(4)	38(4)	37(4)	−2(3)	5(3)	8(3)	H(4)	6(3)
N(2)	69(5)	34(4)	33(4)	1(3)	3(3)	4(3)	H(7)	2(2)
N(3)	59(5)	40(4)	28(3)	1(3)	−2(3)	4(3)	H(10)	5(2)
N(4)	47(4)	40(5)	59(5)	3(4)	3(3)	2(4)	H(131)	3(2)
C(1)	61(6)	49(5)	43(5)	13(5)	4(4)	12(5)	H(132)	9(4)
C(2)	62(6)	52(6)	52(6)	3(5)	5(5)	7(5)	H(141)	18(3)
C(3)	60(6)	41(5)	58(6)	11(5)	14(5)	5(4)	H(142)	18(3)
C(4)	64(6)	44(5)	40(5)	−9(5)	3(4)	5(4)	H(143)	18(3)
C(5)	51(5)	33(4)	36(4)	−2(4)	4(4)	4(3)		
C(6)	53(5)	43(5)	36(4)	−3(4)	1(4)	6(4)		
C(7)	59(6)	38(5)	31(4)	1(4)	0(4)	1(4)		
C(8)	51(5)	32(4)	32(4)	−3(4)	6(3)	2(3)		
C(9)	48(5)	48(5)	30(4)	2(4)	−5(4)	3(4)		
C(10)	40(5)	55(6)	39(5)	2(4)	−2(4)	8(4)		
C(11)	54(5)	43(5)	37(4)	6(5)	3(4)	5(4)		
C(12)	40(5)	47(5)	36(4)	−2(4)	−5(4)	1(4)		
C(13)	70(7)	60(6)	30(4)	2(5)	−4(4)	−3(4)		
C(14)	68(7)	53(6)	60(6)	14(5)	8(5)	−17(5)		
O(4)	104(6)	61(4)	70(5)	14(4)	6(4)	5(4)		

[a] Anisotropic thermal parameters are in the form $\exp[-2\pi^2(U_{11}a^{*2}h^2 + \ldots 2U_{23}b^*c^*kl)]$.

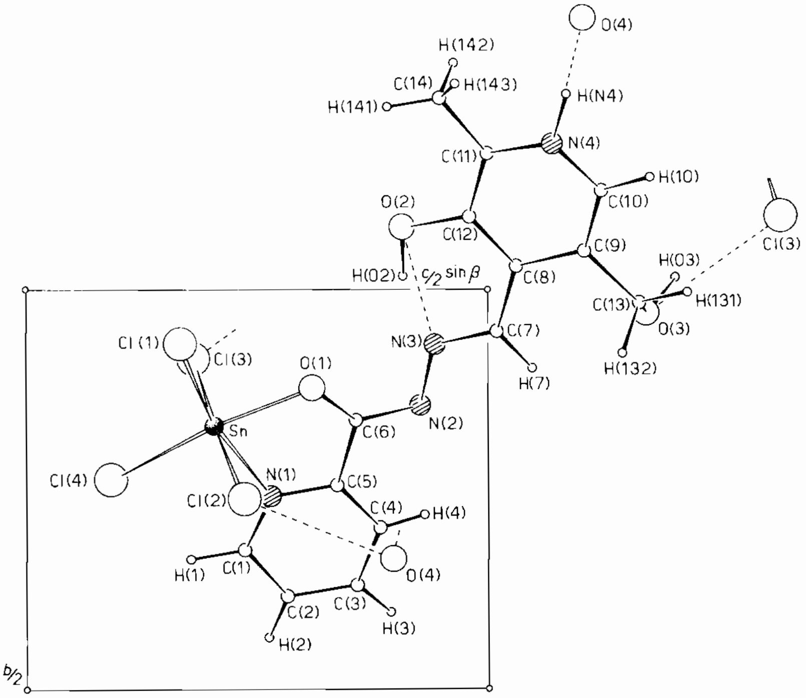


Fig. 1. Projection of the structure along [100].

TABLE III. Selected Interatomic Distances (Å) and Angles (°) with Estimated Standard Deviations in Parentheses.

(a) *Co-ordination polyhedron*			
Sn–Cl(1)	2.364(2)	Cl(2)–Sn–Cl(4)	91.8(1)
Sn–Cl(2)	2.433(2)	Cl(2)–Sn–O(1)	90.0(2)
Sn–Cl(3)	2.420(3)	Cl(2)–Sn–N(1)	85.2(2)
Sn–Cl(4)	2.378(2)	Cl(3)–Sn–Cl(4)	90.8(1)
Sn–O(1)	2.096(6)	Cl(3)–Sn–O(1)	86.5(2)
Sn–N(1)	2.204(6)	Cl(3)–Sn–N(1)	88.9(2)
Cl(1)–Sn–Cl(2)	90.3(1)	Cl(4)–Sn–O(1)	170.6(2)
Cl(1)–Sn–Cl(3)	95.0(1)	Cl(4)–Sn–N(1)	94.5(2)
Cl(1)–Sn–Cl(4)	98.5(1)	O(1)–Sn–N(1)	76.5(2)
Cl(1)–Sn–O(1)	90.7(2)	Sn–O(1)–C(6)	116.9(5)
Cl(1)–Sn–N(1)	166.4(2)	Sn–N(1)–C(5)	113.2(5)
Cl(2)–Sn–Cl(3)	173.7(1)	Sn–N(1)–C(1)	126.4(6)
(b) *Organic ligand*			
N(1)–C(5)	1.35(1)	C(3)–C(4)–C(5)	120.6(8)
N(1)–C(1)	1.35(1)	N(1)–C(5)–C(4)	119.9(7)
C(1)–C(2)	1.37(1)	C(4)–C(5)–C(6)	125.7(7)
C(2)–C(3)	1.38(1)	N(1)–C(5)–C(6)	114.3(7)
C(3)–C(4)	1.38(1)	N(2)–C(6)–C(5)	115.0(7)
C(4)–C(5)	1.37(1)	O(1)–C(6)–C(5)	118.6(7)
C(5)–C(6)	1.48(1)	O(1)–C(6)–N(2)	126.4(7)
O(1)–C(6)	1.30(1)	N(3)–N(2)–C(6)	111.9(6)
N(2)–C(6)	1.31(1)	N(2)–N(3)–C(7)	115.0(7)
N(2)–N(3)	1.40(1)	N(3)–C(7)–C(8)	119.5(8)
N(3)–C(7)	1.28(1)	C(7)–C(8)–C(12)	121.0(7)
C(7)–C(8)	1.45(1)	C(7)–C(8)–C(9)	121.4(7)
C(8)–C(9)	1.41(1)	C(9)–C(8)–C(12)	117.7(7)
C(9)–C(13)	1.53(1)	C(8)–C(9)–C(13)	122.7(8)
C(13)–O(3)	1.41(1)	C(9)–C(13)–O(3)	111.2(8)
C(9)–C(10)	1.37(1)	C(8)–C(9)–C(10)	119.1(8)
C(10)–N(4)	1.33(1)	C(10)–C(9)–C(13)	118.2(8)
N(4)–C(11)	1.34(1)	N(4)–C(10)–C(9)	120.3(8)
C(11)–C(14)	1.47(1)	C(10)–N(4)–C(11)	125.4(8)
C(11)–C(12)	1.41(1)	N(4)–C(11)–C(14)	120.4(8)
C(12)–O(2)	1.35(1)	N(4)–C(11)–C(12)	115.5(8)
C(12)–C(8)	1.41(1)	C(14)–C(11)–C(12)	124.1(8)
C(1)–N(1)–C(5)	120.2(7)	C(11)–C(12)–C(8)	122.0(8)
N(1)–C(1)–C(2)	121.6(8)	C(11)–C(12)–O(2)	115.8(7)
C(1)–C(2)–C(3)	118.7(9)	O(2)–C(12)–C(8)	122.3(7)
C(2)–C(3)–C(4)	119.1(9)		

Sn–Cl(*ax*) bond distances are close to those observed in *cis*-$[SnCl_4(OSeCl_2)]$ [11], in which the same distortion of the $SnCl_4$ group is observed, being probably due to the long co-ordinative interaction (Se–Cl = 3.01 Å) involving the axial chlorines from the tin environment. The angular distortions in the $SnCl_4$ moiety are shown by the values of the angles Cl(*ax*)–Sn–Cl(*ax*) = 173.7(1)° and Cl(*eq*)–Sn–Cl(*eq*) = 98.5(1)°. In the above mentioned complexes the same distortions have been systematically observed, but in the present compound they are less pronounced. The largest angular deviation from the regular octahedral geometry involves the O(1) and N(1) donor atoms of the organic ligand which, in co-ordinating to tin, form a roughly planar penta-atomic chelated ring; the angle O(1)–Sn–N(1) = 76.5(2)°, which is much narrower than 90°, is required by the relative rigidity of the chelated system, together with the large covalent radius of tin. The value of this angle is comparable with those found in other tin(IV) complexes, containing similar penta-atomic chelation rings with O and/or N as donor atoms [14, 15–21]. The 'bite' of the ligand (O(1)–N(1) = 2.66(1) Å) compares well with that observed for bipyridyl in tin complexes: N–N = 2.660(5) Å in $[SnF_4(\mathit{bipy})]$ [15] and 2.703(22) Å in $[Sn(CF_3COO)_2(C_2H_4)(\mathit{bipy})]$ [19]. As reported in Table IV the co-ordinating atoms in the equatorial plane show tetrahedral displacements, out of the weighted least-squares plane through them, which are most noticeable for N(1) and O(1). The value of the Sn–O bond distance ranks among the shortest ones found in the literature and agrees well with those observed in $[(C_6H_5)_3Sn(\mathit{bzbz}^*)]$ [22] (Sn–O(eq) = 2.094(7) Å), in $[(C_6H_5)_2Sn(\mathit{sat}^+)]$ [23] (Sn–O = 2.093(2) Å), and in $[(C_6H_5)_2Sn(\mathit{sab}^‡)]$ [17] (Sn–O = 2.085(8) Å). Among the tin(IV) complexes containing nitrogen as donor atoms, $[SnF_4(\mathit{bipy})]$ [15] and the *sat* and *sab* complexes show Sn–N distances which are comparable with that observed in the present work.

The ligand corresponds to a dipolar ion, owing to the shift of the proton from N(2) to N(4). As previously observed for complexed *sip* [3–5], *sipox* [7], free H*sip* [2] and H*pipox*•HCl [24], also the present ligand can be described as consisting of three planes (Table IV): the pyridine ring, (A), the pyridoxal ring, (B), and the chain, C(6)–N(2)–N(3)–C(7), (C), which bridges the two aromatic systems. The displacements from the coplanarity of these systems are indicated by the dihedral angles A, C = 4.8° and B, C = 13.2°. Considering the hydrazidic chain, the loss of the proton originally bound to N(2) produces a negative charge, which is mainly delocalized in the O(1)–C(6)–N(2) system as indicated by the values of the bond distances C(6)–O(1) = 1.30(1) and C(6)–N(2) = 1.31(1) Å, which are intermediate between single and double bond and ary closer to each other than in *sip* complexes. The values of the distance N(2)–N(3) is the longest among the corresponding ones observed in *sip* and H*sip* complexes. Such a situation in the chain is quite the same as that observed in a Cu complex of another aroyl hydrazone [25] in which the pyridine ring of H*sip* is replaced by an aliphatic group. In all these ligands (H*sip*, H*sipox*, H*pipox*) the N(3)–C(7) distances correspond fairly well to a double bond, while the two C–C distances adjacent to the aromatic rings show a preminent single bond character.

**bzbz* = 1,3-diphenylpropane-1,3-dionato.

+sat = dianion from 2-(*o*-hydroxyphenyl)benzothiazoline.

‡*sab* = dianion from 2-hydroxy-N-(2-hydroxybenzilidene)-aniline.

TABLE IV. Deviations (A) of Atoms from Average Planes in the Complex and Selected Dihedral Angles (°).

(1) *Main co-ordination plane:* O(1), N(1), Cl(4), Cl(1), Sn
O(1): 0.067, N(1): −0.133, Cl(4): 0.011, Cl(1): −0.020, Sn: 0.003.

(2) *Chelation ring:* O(1), C(6), C(5), N(1), Sn
O(1): 0.020, C(6): −0.007, C(5): −0.064, N(1): 0.049, Sn: −0.001.

(3) *Pyridine ring:* N(1), C(1)–C(5)
N(1): −0.011, C(1): 0.016, C(2): −0.004, C(3): −0.005, C(4): 0.000, C(5): 0.010, C(6): 0.055, O(1): −0.051.

(4) *Central chain:* C(6), O(1), N(2), N(3), C(7)
C(6): 0.000, O(1): −0.017, N(2): 0.002, N(3): 0.087, C(7): −0.100.

(5) *Central chain without O:* C(6), N(2), N(3), C(7)
C(6): −0.052, N(2): 0.040, N(3): 0.041, C(7): −0.066, O(1): −0.218.

(6) *Pyridoxal ring:* C(8), C(9), C(10), N(4), C(11), C(12)
C(8): −0.003, C(9): −0.001, C(10): 0.001, N(4): 0.002, C(11): −0.006, C(12): 0.007, O(2): 0.035, C(7): −0.034, C(13): −0.034, C(14): −0.020.

(1)–(2) = 5.4°
(3)–(4) = 5.7
(3)–(5) = 4.8
(2)–(4) = 2.4°
(4)–(6) = 19.7
(5)–(6) = 13.2

TABLE V. Possible Hydrogen Bonds in the Structure.

O(2)–H(O2)···N(3)	2.553(9) A	142.2°
O(3)–H(O3)···Cl(3)^{i}	3.319(8)	152.3
N(4)–H(N4)···O(4)^{ii}	2.789(10)	167.1
O(4)···Cl(2)	3.190(8)	
O(4)···O(51)	2.80(2)	
O(52)···Cl(3)	3.42(3)	
O(52)···O(51)^{iii}	2.73(3)	
O(52)···O(51)^{iv}	2.57(3)	

Roman numerals as superscripts refer to the following equivalent positions relative to the reference molecule at *x, y, z.*

i = −*x*, −*y*, 1 − *z*
ii = 1 − *x*, −*y*, 1 − *z*
iii = *x*, ½ − *y*, *z* − ½
iv = −*x*, *y* − ½, ½ − *z*

It is worthy to note that in the present complex H*pipox* shows quite a different conformation from that which it assumes in the hydrochloride derivative [24], where the pyridine moiety exhibits its nitrogen atom *anti* with respect to the oxygen atom of the CO group of the bridge. This behaviour, which is similar to that observed for the H*sip* ligand, can be explained by the co-ordination requirements imposed by the metal.

Another relevant aspect concerns the co-ordinating sites of the ligand which do not involve the pyridoxal moiety, and this could hardly be foreseen considering that the analogous *sipox* ligand in Cu(*sipox*)Cl·H_2O [7] has the same moiety involved in co-ordination to metal. The co-ordination in the H*pipox* complex is therefore the result of different effects: the tendency of Sn to assume an octahedral environment, the tendency of the ligand to maintain its planarity, the competitive effect of the pyridine nitrogen in coordinating and the complete protonation of the pyridoxal moiety which is now involved in hydrogen bonding.

Bond distances and angles in the pyridoxal ring are in agreement with those found in other compounds containing the same moiety [26–28].

As partially shown in Fig. 1, packing is determined by a network of hydrogen bonds which involves the axial chlorine atoms, the water molecules and the hetero-atoms from the pyridoxal moiety. The disordered water molecule, O(5), is not represented in the figure.

All possible hydrogen bonds are listed in Table V.

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