Synthesis, Structural and Physical Studies of Tin(IV) Complexes with 2-(2-Pyridyl)benzimidazole†

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The tin(IV) complexes $[SnX_4L]$ [L = 2-(2-pyridyl)benzimidazole; X = Cl, Br or I] and $[SnMe_2Cl_2L]$ were prepared by a dehydration reaction of *N*-(2-aminophenyl)pyridine-2-carboxamide L' with either SnX_4 (X = Cl, Br or I) or $SnMe_2Cl_2$ in chloroform solution. The X-ray crystal structures of $[SnMe_2Cl_2L]$ and $[SnBr_4L]\cdot0.5MeNO_2$ show a distorted octahedral geometry around the tin(IV) atom in both molecules. The ligand L acts as a bidentate chelate with ligated atoms being the pyridine-type nitrogens of the heterocyclic rings. The chlorine atoms in $[SnMe_2Cl_2L]$ are *cis* while the methyl groups are *trans* to each other. Infrared and Mössbauer spectra and a correlation of X-ray structural and anti-tumour (P388 lymphocytic leukaemia) data for the octahedral tin(IV) complexes are also reported. The X-ray structures are the first such reported for metal complexes containing 2-(2-pyridyl)benzimidazole.

There has been increased interest in the last few years in the synthesis of tin-based anti-tumour drugs.[1,2] The activity of many of these complexes is very closely linked to their structures.[3] The correlation between X-ray crystallographic data and anti-tumour activity allows a better understanding of the mode of action of the complexes and may facilitate the design and synthesis of even more active complexes.[3,4]

Herein we report the preparation, X-ray crystal structures, IR and Mössbauer spectra of octahedral tin(IV) complexes with the bidentate ligand 2-(2-pyridyl)benzimidazole (L). The preparation of one of the complexes, $[SnMe_2Cl_2L]$, has previously been reported *via* another route.[5] Furthermore, we have correlated the X-ray crystallographic data and anti-tumour activity for one of these complexes, $[SnMe_2Cl_2L]$, with literature data for some other octahedral tin(IV) complexes.

Experimental

Materials.—Tin(IV) chloride, tin(IV) bromide and dimethyltin(IV) chloride were bought from Aldrich and used without further purification. Tin(IV) iodide[6] and *N*-(2-aminophenyl)-pyridine-2-carboxamide[7] (L') were prepared by literature procedures. Reagent-grade chloroform and nitromethane were dried and distilled over powdered calcium hydride, while diethyl ether was dried and distilled over sodium wire. Synthesis, distillations, crystallization and spectroscopic characterization of the complexes were performed under high-purity argon using standard Schlenk techniques.

Carbon, H and N analyses were performed by the Imperial College, Microanalytical Service, London and tin was determined gravimetrically as tin dioxide.

Preparation of the Complexes.—Dichlorodimethyl[2-(2-pyridyl)benzimidazole]tin(IV), $[SnMe_2Cl_2L]\cdot0.2CHCl_3$. A solution of *N*-(2-aminophenyl)pyridine-2-carboxamide (0.30 g, 1.4 mmol) in chloroform (10 cm^3) was added to a solution of dimethyltin(IV) chloride (0.30 g, 1.4 mmol) in chloroform (10 cm^3). The solution was refluxed for 3 d and a yellow precipitate was formed. The solid was filtered off and washed with diethyl ether (3 × 10 cm^3) and dried *in vacuo*. Yield 0.50 g (85%).

Table 1 Elemental analyses (%) for tin(IV) complexes*

Compound	C	H	N	Sn
$[SnMe_2Cl_2L]\cdot$	40.45	3.45	10.05	28.60
$0.2CHCl_3$	(40.55)	(3.65)	(10.10)	(28.60)
$[SnCl_4L]\cdot$	29.20	1.90	8.20	22.90
$0.5CHCl_3$	(29.15)	(1.85)	(8.15)	(23.05)
$[SnBr_4L]$	22.65	1.35	6.70	18.70
	(22.75)	(1.45)	(6.65)	(14.00)
$[SnI_4L]$	17.70	1.10	4.95	14.00
	(17.55)	(1.10)	(5.10)	(14.45)

* Calculated values in parentheses.

The compounds $[SnCl_4L]\cdot0.5CHCl_3$, $[SnBr_4L]$ and $[SnI_4L]$ were prepared in a similar fashion except that the solutions were refluxed for 12 h and the yields were 75, 80 and 70% respectively. Elemental analyses for the tin(IV) complexes are summarized in Table 1.

Crystals of $[SnMe_2Cl_2L]$ and $[SnBr_4L]\cdot0.5MeNO_2$ suitable for X-ray structure analysis were obtained by slow cooling of hot concentrated solutions of the complexes in nitromethane.

X-Ray Analysis.—Collection and reduction of intensity data. Complete crystal data and parameters for data collection are reported in Table 2. Preliminary oscillation and Weissenberg photographs indicated the space group $P2_1/c$ for $[SnBr_4L]\cdot0.5MeNO_2$ and *Pbcm* or $Pbc2_1$ for $[SnMe_2Cl_2L]$. Unit-cell dimensions were derived from a least-squares refinement of the setting angles of 30 automatically centred reflections in the range $11 < 2\theta < 23°$ on a Syntex $P2_1$ diffractometer upgraded by CRYSTAL LOGIC with niobium filtered Mo-Kα radiation.

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 2 Summary of crystal and intensity collection data[a]

Compound	$[SnBr_4L]\cdot0.5MeNO_2$	$[SnMe_2Cl_2L]$
Formula	$C_{12.5}H_{10.5}Br_4N_{3.5}OSn$	$C_{14}H_{15}Cl_2N_3Sn$
M_w	666.07	414.89
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$Pbc2_1$
a/Å	8.0149(3)	9.1847(6)
b/Å	15.4026(6)	13.2358(9)
c/Å	14.9144(6)	13.163(1)
β/°	82.033(1)	
U/Å^3	1823.42(9)	1600.20(8)
D_c, D_m/Mg m^{-3}	2.418, 2.40	1.722, 1.70
Crystal size/mm	0.40 × 0.33 × 0.10	0.25 × 0.45 × 0.22
μ/cm^{-1}	98.89	17.79
Scan speed/° min^{-1}	3.0	4.5
Scan range/°	$2.2 + \alpha_1 - \alpha_2$	$1.9 + \alpha_1 - \alpha_2$
2θ limit/°	50.0	56.0
No. collected data	3608	4239
No. unique data	3214	3822
No. used data, N	2419 [$F_o > 6.5\sigma(F_o)$]	3399 [$F_o > 7.0\sigma(F_o)$]
R_{int}	0.0270	0.284
Range of h, k, l	0–9, 0–18, −17 to 17	0–12, 0–17, −17 to 17
g	0.000 15	0.0001
F(000)	1235	816
No. refined parameters, P	253	224
$\lvert\Delta/\sigma\rvert_{max}$	0.202	0.277
Δρ (min., max.)/e Å^{-3}	0.717, −0.521	0.747, −0.602
S[b]	1.30	1.35
R (obs., all data)[c]	0.0296, 0.0463	0.0198, 0.0252
R' (obs., all data)[d]	0.0351, 0.0412	0.0286, 0.0299

[a] Details in common: $Z = 4$, Mo-Kα radiation (λ = 0.710 69 Å); weighting scheme, $w^{-1} = \sigma^2(F_o) + g(F_o)^2$. [b] $S = [\Sigma w(\Delta F)^2/(N - P)]^{\frac{1}{2}}$. [c] $R = \Sigma|\Delta F|/\Sigma|F_o|$. [d] $R' = [\Sigma w(\Delta F)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$.

Three standard reflections measured every 97 reflections showed less than 3.0% intensity fluctuation. Lorentz, polarization and absorption corrections were applied. Scattering factors were taken from ref. 8.

Solution and refinement of the structure. The structures were solved by direct methods using the SHELX 86 program[9] and refined by full-matrix least squares, in which $\Sigma w\Delta^2$ was minimized using SHELX 76.[10] Attempts to refine $[SnMe_2Cl_2L]$ in the space group *Pbcm* failed but refinement proved successful in space group $Pbc2_1$. The hydrogen atoms of the methyl groups were placed riding on the carbon atoms with C–H 1.08 Å and the remaining H atoms were located from a Fourier difference map. Non-hydrogen atoms were refined anisotropically and H atoms isotropically. In $[SnBr_4L]\cdot0.5MeNO_2$ a solvent molecule ($MeNO_2$) positionally disordered around the centre of symmetry was found with a site occupation factor of 0.5. Eleven $\{[SnBr_4L]\cdot0.5MeNO_2\}$ and two $\{[SnMe_2Cl_2L]\}$ reflections showing poor agreement were given zero weighting during the last steps of refinement. Upon completion of the refinement of $[SnMe_2Cl_2L]$ a new least-squares calculation on the enantiomorphic molecule gave higher values for R and R' (0.0262 and 0.0390).

Fractional atomic coordinates for both compounds are listed in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

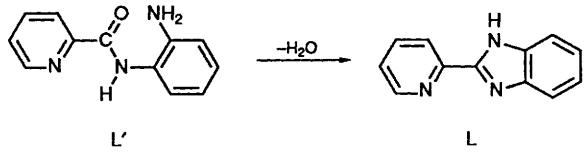
Other Physical Measurements.—Infrared spectra of the compounds dispersed in KBr pellets were recorded on a Perkin Elmer 577 spectrometer with polystyrene film used as calibrant. Mössbauer spectra were obtained at 77 K on a conventional constant-acceleration spectrometer that utilized a room-temperature $Ca^{119m}SnO_3$ source in conjunction with a liquid-nitrogen cryostat.

Results and Discussion

Synthesis and Characterization.—The tetrahalogeno complexes were prepared according to equation (1) (X = Cl, Br or I).

$$L' + SnX_4 \xrightarrow[\text{reflux}]{CHCl_3} [SnX_4L] + H_2O \qquad (1)$$

From this reaction it is evident that tin(IV) halide dehydrates N-(2-aminophenyl)pyridine-2-carboxamide (Scheme 1) and that the resulting ligand, 2-(2-pyridyl)benzimidazole, is co-ordinated to the tin(IV).



L′ L

Scheme 1

This dehydration reaction was unexpected, as our initial aim was to investigate the co-ordination properties of L′ through its amide functionality.[2,11–13] Ligands analogous to L′ have been known to possess anti-leukaemic activity.[14]

The complex $[SnMe_2Cl_2L]$ has previously been prepared[5] by mixing $[SnMe_2Cl_2]$ with L in hot anhydrous methanol or diethyl ether. It is interesting that the dehydration reaction for SnX_4 (X = Cl, Br or I) is much quicker and more efficient than for $[SnMeX_2]$.

The Mössbauer spectra of the three tetrahalogeno derivatives $[SnX_4L]$ (Table 4) present a well defined single line with a narrow linewidth. Attempts to fit these lines by quadrupole-split doublets gave only very small and unreliable values (*ca.* 0.24 mm s^{-1}) for the quadrupole interaction, without any

Table 3 Positional parameters ($\times 10^4$) of the non-hydrogen atoms

Atom	*x*	*y*	*z*
$[SnBr_4L]\cdot 0.5MeNO_2$			
Sn	8 332.1(4)	3 816.9(2)	2 243.1(2)
Br(1)	6 234.4(9)	4 015.6(4)	3 686.3(4)
Br(2)	9 860.6(8)	5 213.1(4)	2 478.1(4)
Br(3)	10 242.9(9)	2 823.4(4)	2 993.5(5)
Br(4)	31.8(7)	3 569.7(5)	654.7(4)
N(1)	6 714(5)	2 703(3)	1 862(3)
C(1)	7 065(8)	1 861(4)	1 916(4)
C(2)	6 031(8)	1 226(3)	1 663(4)
C(3)	4 564(8)	1 461(4)	1 365(4)
C(4)	4 160(7)	2 339(4)	1 303(4)
C(5)	5 265(6)	2 942(3)	1 548(3)
C(6)	5 108(6)	3 871(3)	1 438(3)
N(2)	3 806(6)	4 293(3)	1 170(3)
C(7)	4 211(6)	5 166(3)	1 085(3)
C(8)	3 327(7)	5 874(4)	818(4)
C(9)	4 112(8)	6 660(4)	796(4)
C(10)	5 748(9)	6 740(4)	1 022(4)
C(11)	6 630(8)	6 054(4)	1 285(4)
C(12)	5 836(6)	5 242(3)	1 321(3)
N(3)	6 630(5)	4 414(3)	1 542(3)
C	0(60)	−60(30)	−140(20)
N	840(30)	650(10)	35(9)
O(1)	2 190(30)	570(20)	−360(10)
O(2)	360(30)	1 230(10)	450(10)
$[SnMe_2Cl_2L]$			
Sn	794.5(1)	1 714.9(1)	2 500.0(0)
Cl(1)	−753.8(7)	2 970.4(7)	3 393.4(8)
Cl(2)	−1 182.6(9)	545.8(7)	1 816(1)
C(13)	1 028(4)	801(3)	3 807(3)
C(14)	838(4)	2 530(3)	1 125(3)
N(1)	2 968(3)	2 666(2)	2 992(2)
C(1)	2 913(3)	3 547(2)	3 500(2)
C(2)	4 148(3)	4 072(3)	3 766(3)
C(3)	5 490(4)	3 689(3)	3 500(3)
C(4)	5 563(3)	2 782(2)	2 965(2)
C(5)	4 268(2)	2 295(2)	2 724(2)
C(6)	4 229(2)	1 352(2)	2 151(2)
N(2)	5 419(3)	859(2)	1 790(2)
C(7)	4 917(3)	14(2)	1 283(2)
C(8)	5 658(3)	−762(2)	790(3)
C(9)	4 786(4)	−1 498(2)	352(2)
C(10)	3 266(4)	−1 477(3)	421(3)
C(11)	2 545(3)	−704(2)	916(3)
C(12)	3 396(3)	49(2)	1 358(2)
N(3)	2 994(2)	901(2)	1 899(2)

Table 4 119m-Tin Mössbauer effect spectral parameters (mm s^{-1})[a]

Compound	δ[b]	ΔE_Q	Γ
$[SnMe_2Cl_2L]\cdot 0.2CHCl_3$	1.45	4.18	0.85
$[SnCl_4L]\cdot 0.5CHCl_3$	0.41	—	0.88
$[SnBr_4L]$	0.65	—	0.90
$[SnI_4L]$	1.03	—	0.99

[a] Measured at 77 K. [b] Relative to room-temperature $CaSnO_3$.

improvement in the quality factors. Thus a zero ΔE value was used to calculate the Sn–Br bond length in $[SnBr_4L]$ according to equation (2)[15] (p.q.s. = partial quadrupole splitting). A

$$d(\text{Sn–Br})/\text{Å} = (-0.048 \pm 0.002)\ (4\ \text{p.q.s.}) + (2.589 \pm 0.003) \quad (2)$$

bond distance of 2.589 Å was obtained which compares very well with the experimental value of 2.552 Å (average distance). In a similar way, using equation (3),[16] a Sn–Cl bond distance of

$$d(\text{Sn–Cl})/\text{Å} = (-0.044 \pm 0.002)\ (4\ \text{p.q.s.}) + (2.420 \pm 0.003) \quad (3)$$

2.420 Å was obtained for $[SnCl_4L]$, which is in good agreement with Sn–Cl bond lengths reported in the literature.[17] Additionally isomer shift values for the tetrahalogeno derivatives lie well within the ranges typical for SnX_4N_2 octahedral compounds. All these results point to a nearly regular *cis*-octahedral structure for all these compounds.

The Mössbauer spectrum of the dichlorodimethyl derivative (Table 4) is characterized by a quadrupole-split doublet with a rather large value for the quadrupole interaction. The experimental value is typical for an octahedral co-ordination geometry with the two methyl groups in *trans* positions. Point-charge calculations give a ΔE_0 value of 4.00 mm s^{-1}, in good agreement with the experimental value of 4.18 mm s^{-1}, pointing to a nearly regular octahedral structure with a C–Sn–C bond angle close to 180°. The parameters are very close to those of similar compounds.[5,18]

The infrared spectra of the tin(IV) complexes are similar to those of other metal complexes with L.[19,20] The pyridine-ring bands at 996, 1046 and 1154 cm^{-1} are shifted upwards in the complexes, showing the involvement of the pyridine nitrogen in bonding to tin. In the free ligand there is a strong band at 1314 cm^{-1} which splits into a doublet on chelation.[19] In the tin complexes this doublet appears at *ca.* 1320 and 1300 cm^{-1}; strong evidence that the imidazole, pyridine-type, nitrogen atom is also involved in co-ordination.[19,20]

In the region 600–150 cm^{-1} the occurrence of ν(Sn–C), ν(Sn–X) (X = Cl, Br or I) and ν(Sn–N) vibrational modes is expected. These modes are difficult to assign unambiguously due to the presence of various ligand bands. Considering the band intensities and literature reports[21,22] it seems quite probable that the ν(Sn–C) mode is that at 540 cm^{-1} in the spectrum of $[SnMe_2Cl_2L]$; in the same spectrum a shoulder at 278 cm^{-1} and a very strong band at 250 cm^{-1} arises from the ν(Sn–Cl) vibrations of the *cis*-$SnCl_2$ group.[21] More complicated far-IR spectra are expected and indeed observed for $[SnX_4L]$ (X = Cl, Br or I) [for idealized C_{2v} symmetry; four ν(Sn–X) ($2A_1$, B_1, B_2) and two ν(Sn–N) (A_1, B_2) are IR active]. In accordance with the prediction of *cis* structure for $[SnCl_4L]\cdot 0.5CHCl_3$, we observed three strong bands (329, 320 and 313 cm^{-1}) close together and a band at 265 cm^{-1} of lower intensity. Since these bands are not observed for the bromide and iodide complexes, they are assigned to the Sn–Cl stretching modes. This observed intensity trend has been reported for *cis*-$[SnCl_4(bipy)]$[23] (bipy = 2,2′-bipyridine). The bromide complex also exhibits four halogen-sensitive bands at 250, 229, 218 and 209 cm^{-1} all of which can be assigned to the Sn–Br stretching modes.[23] The ν(Sn–I) and ν(Sn–N) vibrations are expected to appear below the lowest frequency limit (200 cm^{-1}) of the instrument used.

A selection of interatomic distances and bond angles in $[SnMe_2Cl_2L]$ and $[SnBr_4L]\cdot 0.5MeNO_2$ are listed in Table 5. The structures of the two tin(IV) complexes are shown in Figs. 1 and 2 respectively. The co-ordination environment of the tin atom in $[SnMe_2Cl_2L]$ is distorted octahedral. The chlorine atoms are *cis* to each other while the methyl groups are *trans*. The Sn–C distances of 2.114(3) and 2.107(4) Å and the Sn–Cl distances of 2.483(1) and 2.550(1) Å are in good agreement with those reported in the literature (Sn–C 2.07–2.22;[24,25] Sn–Cl 2.34–2.58 Å[17]). The difference in the Sn–Cl(1) and Sn–Cl(2) bond lengths is due to hydrogen bonding between the pyrrole nitrogen of the imidazole ring and Cl(2) (Table 5).

The ligand 2-(2-pyridyl)benzimidazole bears a close structural relationship to 1,10-phenanthroline (phen) and 2,2′-bipyridine and its co-ordination behaviour is expected to be similar to these ligands. Therefore it should be expected that L would act as a bidentate chelating agent with co-ordination occurring through the pyridine nitrogens of the heterocyclic rings[26] and indeed this was observed for both complexes. It is

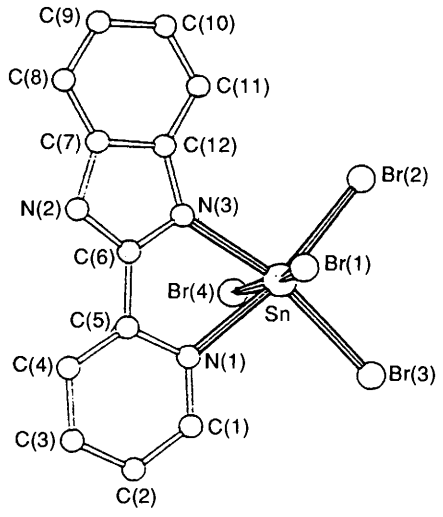


Fig. 1 An ORTEP diagram of $[SnBr_4L]\cdot 0.5MeNO_2$

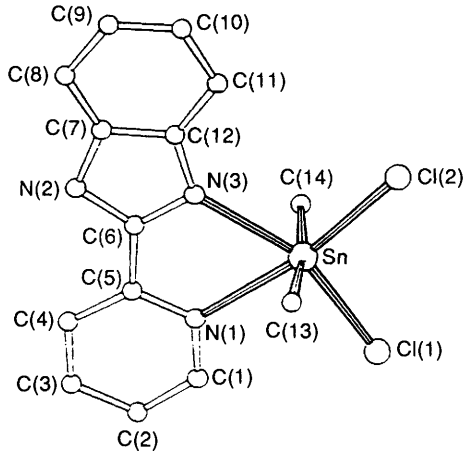


Fig. 2 An ORTEP diagram of $[SnMe_2Cl_2L]$

Table 5 Selected bond lengths (Å) and angles (°)

$[SnBr_4L]\cdot 0.5MeNO_2$		$[SnMe_2Cl_2L]$	
Sn–Br(1)	2.559(1)	Sn–Cl(1)	2.483(1)
Sn–Br(2)	2.523(1)	Sn–Cl(2)	2.550(1)
Sn–Br(3)	2.533(1)	Sn–C(13)	2.114(3)
Sn–Br(4)	2.592(1)	Sn–C(14)	2.107(4)
Sn–N(1)	2.271(4)	Sn–N(1)	2.447(2)
Sn–N(3)	2.212(4)	Sn–N(3)	2.422(2)
N(2)–H(N2)	0.75(4)	N(2)–H(N2)	0.74(4)
N(2)···Br(4)	3.410(5)	N(2)···Cl(2)	3.149(4)
H(N2)···Br(4)	2.66(4)	H(N2)···Cl(2)	2.54(4)
Br(1)–Sn–Br(2)	93.2(0)	Cl(1)–Sn–Cl(2)	99.5(0)
Br(1)–Sn–Br(3)	93.9(0)	Cl(1)–Sn–C(13)	93.2(1)
Br(2)–Sn–Br(3)	96.8(0)	Cl(2)–Sn–C(13)	90.7(1)
Br(1)–Sn–Br(4)	170.8(0)	Cl(1)–Sn–C(14)	94.3(1)
Br(2)–Sn–Br(4)	92.8(0)	Cl(2)–Sn–C(14)	91.2(1)
Br(3)–Sn–Br(4)	92.4(0)	C(13)–Sn–C(14)	171.9(1)
Br(1)–Sn–N(1)	88.2(1)	Cl(1)–Sn–N(1)	89.9(1)
Br(2)–Sn–N(1)	169.8(1)	Cl(2)–Sn–N(1)	170.6(1)
Br(3)–Sn–N(1)	93.2(1)	C(13)–Sn–N(1)	89.8(1)
Br(4)–Sn–N(1)	84.6(1)	C(14)–Sn–N(1)	87.0(1)
Br(1)–Sn–N(3)	85.3(1)	Cl(1)–Sn–N(3)	158.4(1)
Br(2)–Sn–N(3)	95.9(1)	Cl(2)–Sn–N(3)	102.0(1)
Br(3)–Sn–N(3)	167.2(1)	C(13)–Sn–N(3)	85.8(1)
Br(4)–Sn–N(3)	87.1(1)	C(14)–Sn–N(3)	86.0(1)
N(1)–Sn–N(3)	74.1(1)	N(1)–Sn–N(3)	68.6(1)
N(2)–H(N2)···Br(4)	179(4)	N(2)–H(N2)···Cl(2)	141(5)

Table 6 Crystallographic and anti-tumour activity (P388 lymphocytic leukaemia) data for octahedral tin(IV) complexes

Complex	X–Sn–X/°	Sn–N(av.)/Å	Best T/C (%)	Ref.
1 $[SnI_4(bipy)]$	95.8[a]	2.28	Inactive	28,[b] 29[c]
2 $[SnBr_4L]\cdot 0.5MeNO_2$	96.8[a]	2.24	—	This work[b]
3 $[SnMe_2Cl_2L]$	99.5	2.43	Inactive	This work,[b] 30[c]
4 $[SnEt_2Cl_2L]$	—	—	171	30[c]
5 $[SnEt_2Cl_2(bipy)]$	104.2	2.38	Inactive	31,[b] 30[c]
6 $[SnEt_2Cl_2(phen)]$	105.2	2.41	176	30[b,c]
7 $[SnEt_2Cl_2(pdt)]$[d]	103.2	2.50	144	32,[b] 33[c]
8 $[SnBu_2Cl_2(bipy)]$	104.3	2.40	131	33[b,c]
9 $[SnBu_2Cl_2(phen)]$	105	2.39	141	34,[b] 33[c]
10 $[SnPh_2Cl_2(bipy)]$	103.5	2.36	Inactive	17,[b] 33[c]

T/C (%) is the ratio of median survival time of treated animals to that of control animals multiplied by 100, indicating anticancer activity.
[a] X–Sn–X Angles *trans* to N–Sn–N angles. [b] Structural data only. [c] Anti-tumour data only. [d] pdt = 5,6-Diphenyl-3-(2-pyridyl)-1,2,4-triazine.

interesting that although ligand L has been known since 1954,[27] the present X-ray structures are the first of metal complexes containing this ligand to be reported.

The co-ordination environment of the tin atom in $[SnBr_4L]$ is also a distorted octahedron. The most interesting feature of this structure is the difference in the Sn–Br(4) bond length as compared to the other three Sn–Br bond lengths. This difference is due to hydrogen bonding between the pyrrole nitrogen of the imidazole ring and Br(4) (Table 5). The other remarkable aspect of this structure is the difference in bond lengths of the two Sn–N bonds (*ca.* 0.06 Å) {the corresponding difference in the structure of $[SnI_4(bipy)]$ is 0.02 Å}. The different Sn–N bond lengths may reflect the changes in donor strength of the respective nitrogen atoms.

Correlation of X-Ray Structural and Antitumour (P388 Lymphocytic Leukaemia) Data for Octahedral Tin(IV) Complexes.—The correlation of crystallographic and anti-tumour activity data for some diagnostic octahedral compounds (Table 6) appears to indicate that active complexes have average Sn–N bond lengths ≥2.39 Å and an angle X–Sn–X (X = halide) ranging from 103.2 to 105.2°. The highest activity is possessed by the compound $[SnEt_2Cl_2(phen)]$ with an average Sn–N bond length of 2.41 Å and an angle X–Sn–X 105.2°. Compounds **5**, **6**, **8** and **9** have almost identical Sn–N bond lengths but different X–Sn–X angles; the highest activity being observed in those complexes with higher X–Sn–X bond angles, *i.e.* compounds **6** and **9**. Compound **7** with the longest Sn–N bond length (2.50 Å) does not possess the highest anti-cancer activity possibly since it possesses the lowest X–Sn–X bond angle of all the active compounds referred to in Table 6). The same explanation could be given for the inactivity of the compound **3** for which the average Sn–N bond length (2.43 Å) is well above 2.39 Å but for which X–Sn–X is below 103°. On the basis of the above discussion we may propose that two criteria are required for an octahedral tin(IV) compound to possess antitumour activity: (*i*) that the Sn–N length must be ≥2.39 Å (the ideal possibly *ca.* 2.40 Å) and (*ii*) an X–Sn–X bond angle of at least 103°. Of course much more work is required in order to find the ideal Sn–N bond length and X–Sn–X bond angle to optimize antitumour activity. Efforts to characterize compound **4** (which shows exceptionally high anti-cancer activity) by X-ray analysis are underway.

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