Tin(IV), Germanium(IV) and Silicon(IV) Complexes of the Dianion of 5,14-Dihydro-6,8,15,17- tetramethyldibenzo-[*b*,*i*][1,4,8,11]tetraazacyclotetradecine (H_2L): Crystal Structures of *trans*-Sn(L)Cl_2 and *trans*-Sn(L)$(NO_3)_2$·MeCN†

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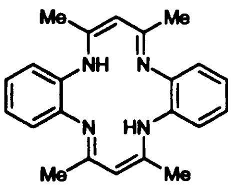
The macrocyclic complexes $M(L)X_2$ (H_2L = 5,14-dihydro-6,8,15,17-tetramethyldibenzo[*b*,*i*][1,4,8,11]-tetraazacyclotetradecine; M = Sn, X = Cl, Br or I; M = Ge, X = Cl; M = Si, X = Cl) have been prepared by the reaction of the tetrahalide MX_4 with H_2L (M = Sn or Ge) or Li_2L (M = Si) under mild conditions. Treatment of $Sn(L)Cl_2$ with $AgNO_3$ produces $Sn(L)(NO_3)_2$, which in turn gives $Sn(L)F_2$ upon reaction with $[NBu_4]F$. X-Ray crystal structures of $Sn(L)Cl_2$ and $Sn(L)(NO_3)_2$·MeCN reveal that the complexes retain the characteristic saddle-shaped configuration of the ligand but have adopted a *trans* geometry.

Complexes of the macrocyclic dianion L of 5,14-dihydro-6,8,-15,17-tetramethyldibenzo[*b*,*i*][1,4,8,11]tetrazacyclotetradecine (H_2L) have enjoyed a resurgence of interest. This derives in part from the superficial resemblance of this ligand to the porphyrin macrocycle, in the sense that L co-ordinates as a dianion through four nitrogen donor ligands in a square-planar arrangement. However there are some significant differences, in particular the smaller hole size of L relative to a porphyrin and the saddle-shaped conformation which is apparent in both the free ligand and its complexes.[1]

Until very recently, the chemistry of L had been almost entirely restricted to transition metals, with fully characterised examples of main group complexes limited to aluminium(III).[2] In general, the chemistry of main group elements with macrocyclic ligands has not been extensively developed, and we report here our investigations into the preparation and characterisation of complexes of L containing silicon, germanium and tin in the +4 oxidation state. While the preparation of this manuscript was in progress two other groups published examples of Groups 13 and 14 complexes of L. The first group prepared germanium(II), tin(II), gallium(III) and indium(III) complexes of L, with X-ray crystal structures of Ge(L), Sn(L) and Ga(L)Cl.[3] The second group claimed to have prepared the silicon(IV) and tin(IV) complexes $M(L)Me_2$ and $M(L)Cl_2$ (M = Si or Sn), although no structures were determined.[4] We had independently prepared $M(L)Cl_2$ (M = Sn, Ge or Si) by a different route and find that the chemical reactivity and ^1H and ^{13}C NMR spectroscopic data for the silicon and tin congeners are very different than those described in this recent report. We have established the composition and geometry of $Sn(L)Cl_2$ by an X-ray crystal-structure analysis. The preparation and characterisation of these tin, germanium and silicon complexes and a number of other tin derivatives, including a crystal structure of $Sn(L)(NO_3)_2$·MeCN are also described.

Results and Discussion

The reaction of free base H_2L with $SnCl_4$ and two equivalents of triethylamine in acetonitrile at 50 °C for 10 min resulted in the brick red complex $Sn(L)Cl_2$ **1** in 85% yield. Similar reactions of H_2L with $SnBr_4$ in acetonitrile or SnI_4 in toluene–acetonitrile produce $Sn(L)Br_2$ **2** (76% yield) or $Sn(L)I_2$ **3** (79% yield), respectively. These formulations are consistent with elemental analysis and ^1H and ^{13}C NMR spectroscopic data (Table 1). The aromatic protons, which appear as a broad singlet at δ 6.98 in the ^1H NMR spectrum of the free ligand in $CDCl_3$ solution, separate into two multiplets in the spectra of **1**–**3**. The methine peaks show satellites [*e.g.*, $^4J(SnH)$ = 5.27 Hz for **1**] due to coupling of the methine protons with tin in those molecules containing ^{117}Sn or ^{119}Sn (although individual ^{117}Sn and ^{119}Sn satellites are not resolved).



H_2L

Notable features of the structural chemistry of complexes of L are the saddle-shaped configuration adopted by the ligand, the marked displacement of the central metal from the N_4 plane and an apparent preference for *cis* geometry in six-co-ordinate complexes.[1] Certainly this last feature is observed for the structurally characterised Group 4 compounds $M(L)Cl_2$ (M = Ti or Zr) which exhibit *cis* chloro ligands.[5,6] The ^1H and ^{13}C NMR data did not allow assignment of the stereochemistry of complexes **1**–**3**, which by comparison with the analogous Group 4 compounds $M(L)Cl_2$ (M = Ti, Zr or Hf)[5,6] might be expected to adopt a *cis* configuration. However, the X-ray crystal structure of **1** (Fig. 1) shows approximately octahedral co-ordination geometry with the chloro substituents in the *trans* configuration. The saddle shape of the ligand is retained, and the tin atom is displaced from the N_4 plane towards the benzenoid face of the ligand by only 0.027 Å. This small displacement must be a steric consequence of the *trans* geometry, and contrasts with $Zr(L)Cl_2$[6] and Sn(L)[3] where marked displacements (1.071 and 1.15 Å, respectively) of the central metal from the N_4

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 ^1H (400 MHz) and ^{13}C-{^1H} (100 MHz) NMR spectroscopic data for complexes **1**–**7**[a]

	^1H NMR (δ)			^{13}C NMR (δ)					
Compound	C_6H_4 (m, m, 8 H)	CH (s, 2 H)	CH_3 (s, 12 H)	CH_3	CH	C_α	C_β	C_{ipso}	C=N
1 Sn(L)Cl_2	7.20, 7.07	5.13[b]	2.48	25.64	103.88	123.17	125.53	134.79	165.27
2 Sn(L)Br_2	7.21, 7.10	5.21[b]	2.48	25.69	104.24	123.35	125.70	—	165.5
3 Sn(L)I_2[c]	7.28, 7.18	5.42	2.49	25.73	—	123.91	126.05	—	—
4 Sn(L)$(NO_3)_2$	7.24, 7.13	5.20	2.52	25.54	103.15	123.12	125.85	134.80	167.01
5 Sn(L)F_2[d]	7.17, 7.05	5.01	2.47	25.81	103.18	123.34	125.48	136.28	165.73
6 Ge(L)Cl_2	7.16	5.38	2.51	24.53	103.44	122.07	125.48	134.35	163.62
7 Si(L)Cl_2	7.14	5.53	2.50	23.94	104.95	121.72	125.32	136.69	163.16

[a] All spectra recorded in $CDCl_3$ solution except where stated otherwise. Chemical shifts are reported downfield from internal $SiMe_4$; m = multiplet, s = singlet. [b] ^4J(SnH) = 5.27 (**1**), 5.54 (**2**) Hz for satellites arising from coupling to ^{117}Sn or ^{119}Sn. [c] Peaks in ^1H NMR spectrum broadened. Some peaks in ^{13}C NMR spectrum not observed. [d] ^{13}C NMR spectrum recorded in CD_2Cl_2.

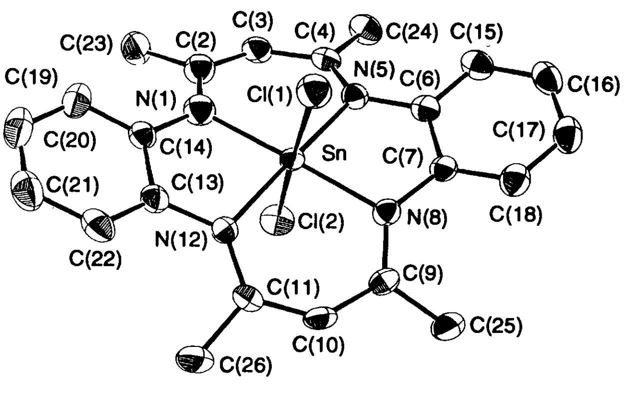

Fig. 1 Molecular structure of Sn(L)Cl_2 **1**. Important bond lengths (Å) and angles (°): Sn–Cl(1) 2.453(1), Sn–Cl(2) 2.521(1), Sn–N(1) 2.054(3), Sn–N(5) 2.066(3), Sn–N(8) 2.059(3), Sn–N(12) 2.067(3), Cl(1)–Sn–Cl(2) 178.0(0)

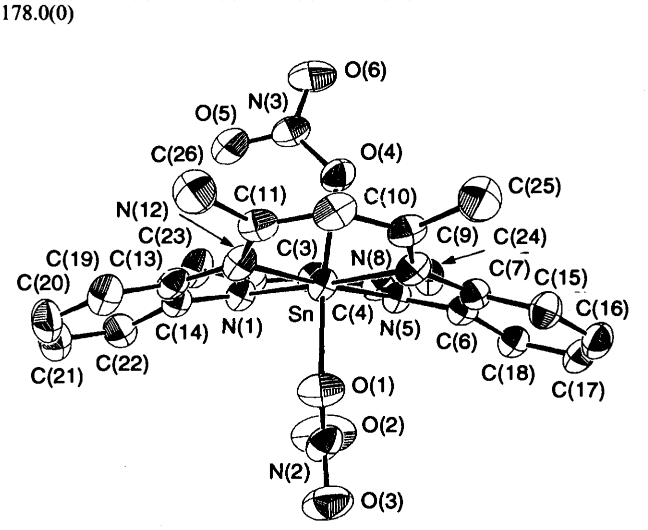

Fig. 2 Molecular structure of Sn(L)$(NO_3)_2$·MeCN **4**. Important bond lengths (Å) and angles (°): Sn–O(1) 2.149(4), Sn–O(4) 2.213(1), Sn–N(1) 2.051(3), Sn–N(5) 2.034(4), Sn–N(8) 2.070(4), Sn–N(12) 2.054(4), O(1)–Sn–O(4) 167.4(2), Sn–O(1)–N(1) 124.5(3), Sn–O(4)–N(3) 128.3(4)

plane are observed. The Sn–Cl(1) distance [2.453(1) Å] on the benzenoid face is shorter than the Sn–Cl(2) distance [2.521(1) Å] on the opposite face of the molecule. The Sn–N and Sn–Cl distances in **1** are comparable to those in the porphyrin complexes Sn(oep)Cl_2 (H_2oep = 2,3,7,8,12,13,17,18-octaethylporphyrin) and Sn(tpp)Cl_2 (H_2tpp = 5,10,15,20-tetraphenylporphyrin).[7,8]

The reaction of a $CHCl_3$ solution of Sn(L)Cl_2 **1** with two equivalents of $AgNO_3$ in MeCN yielded, after removal of AgCl(s) and work-up, a new complex. This was confirmed by elemental analysis and an X-ray crystal-structure determination to be Sn(L)$(NO_3)_2$·MeCN **4** (60% yield), containing *trans* monodentate nitrato ligands (Fig. 2) and one molecule of acetonitrile in the crystal lattice. Vibrations typical of monodentate NO_3^- ligands are observed in the IR spectrum of **4**.[9] The structure shows that the planes of the two nitrato ligands are approximately orthogonal, such that each ligand adopts the most stereochemically favourable orientation with respect to the saddle-shaped macrocycle. Displacement of the tin atom from the N_4 plane (0.062 Å) toward the shorter Sn–O bond distance on the benzenoid face is observed, just as in **1**.

Complexes **1**–**4** give identical ^1H NMR spectra in $(CD_3)_2SO$, suggesting that ionisation of the axial ligands may have taken place to give a common product, which was not isolated. The lability of the nitrato ligands in **4** is demonstrated by the preparation of the fourth complex in the halogeno series, Sn(L)F_2 **5** (76% yield), which precipitates from a chloroform solution of **4** to which $[NBu_4]F$ in acetonitrile has been added.

The orange germanium complex Ge(L)Cl_2 **6** is prepared in 85% yield from H_2L and $GeCl_4$ in acetonitrile at room temperature. This reaction proceeds smoothly without the addition of triethylamine, unlike the preparation of the tin congeners **1**–**3** for which this was required. The reaction of free base H_2L with $SiCl_4$, either with or without added NEt_3, did not produce the corresponding silicon analogue. However use of the lithium salt Li_2L[6] with $SiCl_4$ in tetrahydrofuran (thf) at −10 °C gave the bright orange silicon congener Si(L)Cl_2 **7** (76% yield). Unlike the tin and germanium complexes **1**–**6** which are air- and moisture-stable, the silicon complex **7** is too reactive towards moisture for satisfactory elemental analysis data to be obtained. Although the silicon and germanium complexes were not structurally characterised, the similarity of the spectroscopic data of M(L)Cl_2 (M = Sn, Ge or Si) suggests that the germanium and silicon complexes also adopt a *trans* geometry.

A key feature of the chemistry of the main-group elements is the availability of stable oxidation of states separated by two units. We have also prepared Sn(L)Cl_2 **1** by $C_6H_5ICl_2$ oxidation of Sn(L),[3] thus providing a chemical link between complexes of L containing the +II and +IV oxidation states of tin in the same co-ordination environment. The large displacement of the tin(II) atom from the N_4 plane in Sn(L)[3] relative to the almost in-plane arrangement of the tin(IV) complexes **1** and **4** is probably simply a consequence of the larger size of the tin(II) ion. The difference in geometry of the complexes M(L)Cl_2, which are *cis* where M is a Group 4 atom (Ti or Zr)[5,6] and *trans* for a Group 14 atom (Sn) can also be rationalised. A possible preference for *cis* geometry at the metal centre could be

Table 2 Crystal data and intensity collection parameters for $Sn(L)Cl_2$ **1** and $Sn(L)(NO_3)_2\cdot MeCN$ **4**

	1	**4**
Formula	$C_{22}H_{22}Cl_2N_4Sn$	$C_{24}H_{25}N_7O_6Sn$
M	531.76	625.89
Crystal size/mm	0.2 × 0.25 × 0.3	0.36 × 0.18 × 0.15
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/c$
a/Å	13.925(3)	8.852(1)
b/Å	10.683(1)	35.833(20)
c/Å	27.901(5)	7.946(2)
β/°	95.94(2)	95.30(2)
U/Å^3	4128.6	2509.4(1.5)
Z	8	4
D_m/g cm^{-3}	1.70	1.69
D_c/g cm^{-3}	1.704	1.656
F(000)	2112	1264
μ/cm^{-1}	15.1	10.4
λ(Mo-Kα)/Å	0.710 69	0.710 69
T/K	291	290
Min., max. 2θ/°	2, 50	2, 55
h, k, l range	$-16 < h < 16, 0 < k < 12, 0 < l < 32$	$-11 < h < 11, -45 < k < 0, 0 < l < 10$
No. of unique reflections	3228 (R_{int} = 0.029)	4852
No. of observed reflections [$I > 3\sigma(I)$]	2501	4033
Min., max. A	0.88, 1.00	0.77, 0.99
Least-squares weights	$1.0/[\sigma(F^2) + 0.001F^2]$	$1.0/[\sigma(F^2) + 0.002F^2]$
Function minimised	$\Sigma w[\lvert F_o\rvert - \lvert F_c\rvert]^2$	$\Sigma w[\lvert F_o\rvert - \lvert F_c\rvert]^2$
R, R'	0.0269, 0.0291	0.052, 0.056
Max. shift/error in final least-squares cycle	0.20	0.4
Max., min. peak heights in final electron density map/e Å^3	0.30, −0.49	1.4, −2.1

attributed to the steric requirements of the saddle-shaped ligand. However a comparison of related porphyrin complexes $M(por)Cl_2$ (M = Zr or Sn; por = porphyrin dianion) shows the same division in stereochemistry, *i.e. cis* geometry for the zirconium complexes[10,11] and *trans* geometry for the tin complexes.[7,8] This suggests that the preference of the Group 4 metals for *cis* geometry may be a characteristic of the metals themselves rather than a consequence of the steric demands of L. Much has been made in the literature of an apparent predilection of six-co-ordinate complexes of L for *cis* geometry.[1,3,4] While it is true that the four- and five-co-ordinate complexes do show marked displacement of the metal from the N_4 plane, probably for steric reasons related to the relatively small hole size of H_2L, there are few crystal structures of six-co-ordinate complexes and among these the *cis* geometry is confined to the Groups 4 and 5 metals.[1] Six-co-ordinate complexes of H_2L of the later transition elements, for example iron and ruthenium,[1] and the main-group element tin show the expected *trans* configuration, albeit distorted from idealised octahedral geometry. As noted above, this situation has a parallel in porphyrin chemistry where *trans* geometry is commonly observed for six-co-ordinate complexes of the later transition metals and main-group elements, while the early transition metals often exhibit the much less common out-of-plane *cis* arrangement.[12] In the case of the planar porphyrin macrocycle which is much less flexible than L, steric constraints imposed by the ligand can hardly be invoked as a reason for the preferred *cis* geometry of the Group 4 and 5 transition elements.

The preparations of the tin and silicon complexes **1** and **7** were recently claimed by Willey and Rudd.[4] However, their preparation and characterisation of these complexes differed from ours in almost every detail. We find complexes **1**–**7** to be air stable, and only **7** to be reactive towards moisture, whereas they report **1** and **7** to be extremely air- and moisture-sensitive. We prepared the compounds under mild conditions (H_2L with $SnCl_4$ at room temperature, Li_2L with $SiCl_4$ at −10 °C) in contrast to the harsh conditions (Li_2L with MCl_4 at 80 °C for 12 h) employed by Willey and Rudd.[4] We observe unique ^1H and ^{13}C NMR spectra in $CDCl_3$ for each of **1**–**7**. In particular, the resonances of the ligand protons in the ^1H NMR spectra of the four halogeno complexes (**1**–**3** and **5**) are progressively deshielded in the order F, Cl, Br, I. Remarkably, Willey and Rudd report identical ^1H and ^{13}C NMR data in $CDCl_3$ for the ligand in all four complexes $M(L)Cl_2$ and $M(L)Me_2$ (M = Si or Sn), and for the former pair this differs from the data we observe for **1** and **7** in $CDCl_3$. In fact the ^1H and ^{13}C NMR data they report for all these complexes, with the exception of high-field peaks attributed to the methyl groups, are identical to the NMR data for free H_2L in $CDCl_3$. Clearly, the compounds **1** and **7** prepared in our laboratory and those described by Willey and Rudd are different species. The structural characterisation of $Sn(L)Cl_2$ **1** reported here clearly establishes the formulation and geometry of this complex.

Experimental

General.—All solvents were dried and distilled prior to use. The compound H_2L was prepared by a modification of the literature method.[13] The syntheses of **1**–**6** were carried out under a nitrogen atmosphere, and subsequent isolation and purification procedures were carried out in air. Compound **7** was synthesised and manipulated under nitrogen in a Vacuum Atmospheres dry-box. Melting points were determined on a Riechert Kofler microscope hot stage and are uncorrected. UV/VIS absorption spectra were recorded on a Varian DMS 100 spectrophotometer. Proton and ^{13}C-{^1H} NMR spectra were recorded on a Bruker AM 400 spectrometer operating at 400 and 100 MHz, respectively. IR spectra were recorded as Nujol mulls between KBr plates on a Digilab FTS-7 FTIR spectrometer. Fast atom bombardment (FAB) mass spectra were recorded from a *m*-nitrobenzyl alcohol matrix on a VG 70-SE mass spectrometer using argon gas. Samples for elemental analysis were dried over P_2O_5 at room temperature. Elemental analyses were performed by Dr. R. G. Cunninghame and associates at the University of Otago and are gratefully acknowledged.

Table 3 Atomic coordinates for $Sn(L)Cl_2$ **1**

Atom	*X/a*	*Y/b*	*Z/c*
Sn	0.193 49(2)	0.047 11(3)	0.139 45(1)
Cl(1)	0.082 74(8)	0.041 37(11)	0.202 32(4)
Cl(2)	0.312 24(9)	0.052 29(13)	0.077 13(4)
N(1)	0.098 9(2)	0.155 3(3)	0.095 89(13)
C(2)	0.124 2(3)	0.275 8(4)	0.088 15(17)
C(3)	0.201 0(3)	0.335 7(4)	0.115 20(18)
C(4)	0.268 8(3)	0.303 5(4)	0.154 87(17)
N(5)	0.270 9(2)	0.190 1(3)	0.175 20(13)
C(6)	0.326 4(2)	0.142 6(4)	0.216 86(16)
C(7)	0.335 4(2)	0.009 3(4)	0.220 35(16)
N(8)	0.289 6(2)	−0.062 8(3)	0.181 85(13)
C(9)	0.308 5(3)	−0.177 3(3)	0.166 35(16)
C(10)	0.249 8(3)	−0.237 8(4)	0.128 97(18)
C(11)	0.164 3(3)	−0.207 9(4)	0.100 34(15)
N(12)	0.119 8(2)	−0.096 8(3)	0.102 28(14)
C(13)	0.032 3(3)	−0.051 7(4)	0.077 69(15)
C(14)	0.022 2(3)	0.081 3(4)	0.073 83(16)
C(15)	0.364 9(3)	0.214 6(5)	0.254 83(18)
C(16)	0.413 3(3)	0.160 2(5)	0.295 75(18)
C(17)	0.418 2(3)	0.032 4(5)	0.300 18(19)
C(18)	0.377 6(3)	−0.043 0(5)	0.262 87(17)
C(19)	−0.065 1(3)	0.128 7(5)	0.053 23(17)
C(20)	−0.137 3(3)	0.052 1(6)	0.033 48(18)
C(21)	−0.128 2(3)	−0.075 3(6)	0.037 8(2)
C(22)	−0.045 8(3)	−0.126 4(5)	0.061 52(17)
C(23)	0.074 1(4)	0.349 0(5)	0.047 1(2)
C(24)	0.341 0(4)	0.402 2(5)	0.171 7(2)
C(25)	0.396 0(4)	−0.247 7(5)	0.186 5(2)
C(26)	0.123 5(4)	−0.306 6(5)	0.066 0(2)

Table 4 Atomic coordinates for $Sn(L)(NO_3)_2\cdot MeCN$ **4**

Atom	*X/a*	*Y/b*	*Z/c*
Sn	0.413 10(4)	0.135 36(1)	0.106 24(4)
N(1)	0.241 0(4)	0.154 73(14)	0.238 7(5)
C(2)	0.239 9(6)	0.144 24(17)	0.403 1(6)
C(3)	0.331 0(6)	0.116 75(19)	0.478 2(6)
C(4)	0.434 9(5)	0.091 14(17)	0.417 3(6)
N(5)	0.467 2(4)	0.090 39(14)	0.256 1(5)
C(6)	0.565 6(5)	0.066 40(17)	0.179 6(6)
C(7)	0.638 0(5)	0.081 13(18)	0.039 3(6)
N(8)	0.598 2(4)	0.117 34(15)	−0.013 1(5)
C(9)	0.663 3(6)	0.142 70(18)	−0.111 5(6)
C(10)	0.600 1(6)	0.177 4(2)	−0.158 4(7)
C(11)	0.466 9(6)	0.196 64(18)	−0.128 9(6)
N(12)	0.361 1(5)	0.182 59(15)	−0.033 7(5)
C(13)	0.218 0(6)	0.196 76(16)	0.000 0(6)
C(14)	0.153 1(5)	0.180 96(17)	0.142 4(6)
C(15)	0.728 5(6)	0.057 0(2)	−0.047 9(7)
C(16)	0.750 1(7)	0.020 9(2)	0.002 7(9)
C(17)	0.675 9(8)	0.005 6(2)	0.136 2(8)
C(18)	0.583 3(7)	0.029 3(2)	0.219 0(7)
C(19)	0.128 6(6)	0.221 63(19)	−0.101 6(7)
C(20)	−0.016 7(6)	0.230 6(2)	−0.065 1(7)
C(21)	−0.079 4(6)	0.214 6(2)	0.066 9(7)
C(22)	0.005 0(6)	0.189 24(19)	0.170 6(6)
C(23)	0.142 7(8)	0.165 8(2)	0.516 2(7)
C(24)	0.512 0(8)	0.065 6(2)	0.546 5(7)
C(25)	0.812 8(8)	0.134 4(2)	−0.175 6(12)
C(26)	0.450 4(9)	0.235 4(2)	−0.202 7(12)
N(2)	0.165 9(5)	0.085 79(18)	−0.070 3(6)
O(1)	0.280 7(5)	0.106 04(15)	−0.092 1(4)
O(2)	0.130 7(7)	0.080 1(2)	0.072 5(6)
O(3)	0.095 3(6)	0.072 48(19)	−0.194 0(6)
N(3)	0.677 3(5)	0.168 77(17)	0.362 4(5)
O(4)	0.551 9(4)	0.175 17(14)	0.267 5(5)
O(5)	0.735 1(5)	0.138 20(16)	0.363 0(8)
O(6)	0.731 6(5)	0.195 08(17)	0.442 6(6)
C(27)	−0.022 8(9)	0.060 0(3)	0.403 7(11)
C(28)	0.101 6(10)	0.033 6(3)	0.405 8(9)
N(4)	0.200 3(9)	0.012 9(2)	0.408 6(11)

Syntheses.—$Sn(L)Cl_2$ **1**. A solution of $SnCl_4$ (1.94 g, 0.88 cm^3, 7.43 mmol) in acetonitrile (10 cm^3) was added dropwise to a suspension of H_2L (1.30 g, 3.77 mol) in acetonitrile (30 cm^3) to which triethylamine (1.05 cm^3, 7.50 mmol) had been added. During the addition process the H_2L dissolved to give a red solution which was then heated at 50 °C for 10 min. After cooling, the product precipitated as a purple microcrystalline solid (1.71 g, 85%), m.p. 305 °C (Found: C, 49.4; H, 4.15; N, 10.5. $C_{22}H_{22}Cl_2N_4Sn$ requires C, 49.65; H, 4.2; N, 10.5%); λ_{max}/nm (log ε) ($CHCl_3$) 286 (4.87), 390 (5.33), 432 (4.82); *m/z* (FAB) 495 (*M* − Cl), 459 (*M* − 2Cl).

$Sn(L)Br_2$ **2**. As described for **1** using $SnBr_4$ (1.51 g, 3.44 mmol) in acetonitrile (10 cm^3), and H_2L (1.19 g, 3.46 mmol) and triethylamine (0.96 cm^3, 6.83 mmol) in acetonitrile (40 cm^3). The product precipitated as a deep purple powder (1.67 g, 76%) which was recrystallised by slow diffusion of diethyl ether into a saturated chloroform solution, m.p. 252–254 °C (Found: C, 41.7; H, 3.5; N, 8.9. $C_{22}H_{22}Br_2N_4Sn\cdot H_2O$ requires C, 41.35; H, 3.8; N, 8.8%); λ_{max}/nm(log ε) ($CHCl_3$) 284 (4.38), 392 (4.82), 434 (4.32); *m/z* (FAB) 541 (*M* − Br).

$Sn(L)I_2$ **3**. As described for **1** using SnI_4 (0.91 g, 1.45 mmol) in toluene (20 cm^3), and H_2L (0.50 g, 1.45 mmol) and triethylamine (0.40 cm^3, 2.87 mmol) in acetonitrile (30 cm^3). The product precipitated as a dark purple powder (0.87 g, 79%) which was recrystallised from chloroform–ethanol to form red needles, m.p. 140 °C (decomp.) (Found: C, 37.8; H, 4.0; N, 7.1. $C_{22}H_{22}I_2N_4Sn\cdot C_2H_5OH$ requires C, 37.9; H, 3.7; N, 7.35%; one ethanol solvate molecule observed by ^1H NMR spectroscopy); λ_{max}/nm(log ε) ($CHCl_3$) 244 (4.49), 282 (4.47), 384 (4.71); *m/z* (FAB) 715 (M^+), 588 (*M* − I), 462 (*M* − 2I).

$Sn(L)(NO_3)_2$ **4**. A solution of $AgNO_3$ (0.18 g, 1.06 mmol) in acetonitrile (6 cm^3) was added to a solution of **1** (0.24 g, 0.45 mmol) in chloroform (100 cm^3). The resulting white precipitate of AgCl was removed by filtration. The volume was reduced by half and a further 50 cm^3 of acetonitrile was added. After concentrating the solution chunky red crystals of the product formed (0.17 g, 60%), m.p. > 350 °C (Found: C, 45.45; H, 4.15; N, 15.6. $C_{22}H_{22}N_6O_6Sn\cdot CH_3CN$ requires C, 46.0; H, 4.0; N, 15.65%; one acetonitrile solvate molecule observed by ^1H NMR spectroscopy and X-ray crystallography); λ_{max}/nm(log ε) ($CHCl_3$) 244 (4.54), 278 (4.57), 310 (4.36), 380 (4.99); ν(NO_3) 1485, 1285, 1003 cm^{-1} (Nujol).

$Sn(L)F_2$ **5**. A solution of $[NBu_4]F$ (0.11 g, 0.41 mmol) in acetonitrile (15 cm^3) was added dropwise to a stirred solution of **4** (0.09 g, 0.15 mmol) in chloroform (30 cm^3). The product precipitated as a mass of red crystals (0.053 g, 76%), m.p. 257–259 °C (decomp.) (Found: C, 44.6; H, 3.75; N, 9.1. $C_{22}H_{22}F_2N_4Sn$ requires C, 44.65; H, 3.75; N, 9.05%); λ_{max}/nm (log ε) ($CHCl_3$) 284 (3.83), 384 (4.37), 422 (3.78); ν(SnF) 489, 498 cm^{-1} (Nujol); *m/z* (FAB) 500 (M^+), 481 (*M* − F), 462 (*M* − 2F).

$Ge(L)Cl_2$ **6**. To a suspension of H_2L (0.50 g, 1.45 mmol) in MeCN (25 cm^3) was added $GeCl_4$ (0.34 g, 0.18 cm^3, 1.60 mmol). The mixture was stirred for 1 h during which time the yellow H_2L dissolved and a salmon pink solid formed. This was collected by filtration, dissolved in $CHCl_3$ to give an orange solution and filtered. Addition of hexane followed by reduction of the solvent volume gave the product as an orange solid (0.60 g, 85%) (Found: C, 53.8; H, 4.4; N, 11.7. $C_{22}H_{22}Cl_2GeN_4$ requires C, 53.3; H, 4.55; N, 11.5%); λ_{max}/nm($CHCl_3$) 356, 418.

$Si(L)Cl_2$ **7**. A solution of LiBu in hexane (1.18 cm^3 of a 2.59 mol dm^{-3} solution, 3.06 mmol) was added dropwise to a stirred solution of H_2L (0.500 g, 1.45 mol) in thf (25 cm^3) at −10 °C. The colour of the solution changed instantly from yellow to red-orange. Then $SiCl_4$ (0.27 g, 0.18 cm^3, 1.57 mmol) was added dropwise and the solution was allowed to warm slowly to room temperature over the course of 1 h. During this time a bright orange precipitate formed and the solution became orange. The solid was filtered off under nitrogen and recrystallised from CH_2Cl_2–hexane to give the product as a bright orange powder (0.52 g, 76%); λ_{max}/nm($CHCl_3$) 360, 400. This compound was characterised on the basis of a comparison of its spectral data with those of the tin and germanium analogues **1** and **6**, respectively.

X-Ray Crystal-structure Analyses of $Sn(L)Cl_2$ **1** *and* $Sn(L)(NO_3)_2{\cdot}MeCN$ **4**.—Unit-cell parameters were obtained from a least-squares fit to the four-circle coordinates of 25 reflections determined on a Enraf-Nonius CAD-4 diffractometer. Intensity data collection using graphite monochromated Mo-Kα radiation (λ = 0.710 69 Å) employed 2θ–ω scans with a peak to background count time of 2:1. The omega scan angle was 0.80 + 0.347 tan θ. Reflections were counted for 60 s or until $\sigma(I)/I$ was 0.02. Three reflections were monitored throughout data collection as a check on crystal alignment and decomposition, no systematic effects being observed. The data were corrected for Lorentz, polarisation and absorption[14] effects using locally written programs and equivalent reflections averaged. Details of crystal data and intensity collection parameters are given in Table 2.

The structures were solved by Patterson and difference Fourier techniques and refined by full-matrix least squares.[15] Atomic scattering factors were for neutral atoms.[16] After initial isotropic refinement all atoms were allowed to assume anisotropic motion. Hydrogen atoms were located from difference maps and allowed to refine with a common thermal parameter. At convergence final shifts were less than 15% of standard deviations and final peaks in difference maps were < 1 e Å^{-3}, randomly distributed. Final refinement details are given in Table 2 and atomic coordinates for **1** and **4** are given in Tables 3 and 4, respectively.

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

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