Synthesis, Nuclear Magnetic Resonance and Crystallographic Studies of Six-co-ordinate bis(bidentate ligand)-dihalogenotin(IV) Complexes†

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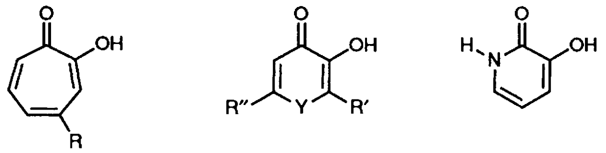
Six co-ordinate tin(IV) complexes of the type SnL_2X_2 have been prepared (where HL is a monobasic chelating ligand and X = Cl, Br or I). They have been characterised by elemental analysis, ^1H and ^{119}Sn NMR, positive-ion fast atom bombardment and electron-impact mass and vibrational spectroscopy. Three distinct ^{119}Sn NMR chemical shift ranges are observed depending on the halogen, demonstrating the relationship between the shielding of the tin nucleus and the electronegativity of the halogens. Geometrical isomerism was normally slow on the NMR time-scale and in some cases slow- and fast-exchange spectra were obtained by variable-temperature ^{119}Sn NMR spectroscopy. The crystal structures of two examples are reported. Both have non-crystallographic C_2 symmetry with the halides *cis*. The structures represent different configurational isomers further illustrating the facile interconversion between isomers in solution.

The toxicity and bioavailability of tin depends upon its speciation in the environment. As is well recognised for arsenic and mercury, biomethylation of tin, by metabolic methyl donors such as vitamin B_{12}, can also occur, even in cases where tin is in a stable form, *e.g.* SnO_2.[1] Although the oral toxicity of inorganic tin is considered to be low due to low absorption and rapid excretion,[2] complexation with chelates such as maltol (3-hydroxy-2-methyl-4*H*-pyran-4-one) (found in plants[3]) and 3-hydroxy-2-methylpyridin-4-one derivatives (shown to remove iron from the body[4]) may increase the solubility and hence the possibility of absorption.

There has been considerable research in the field of organotin chemistry; however in comparison, the co-ordination chemistry of tin(IV) in solution has been largely neglected. Complexes of the type SnL_2X_2 with tropolone (2-hydroxycyclohepta-2,4,6-trien-1-one) derivatives were first reported by Muetterties and Wright[5] in 1964. Similar complexes derived from kojic acid (5-hydroxy-2-hydroxymethyl-4*H*-pyran-4-one) were later reported by Tanaka and co-workers[6] and, more recently, the preparation of bis(maltolato)tin diiodide *via* the electrochemical oxidation of tin has been described.[7]

The present work describes the synthesis of a variety of six-co-ordinate bis(bidentate ligand)dihalogeno complexes of tin(IV), which have been characterised by elemental analysis, ^1H and ^{119}Sn NMR, mass and vibrational spectroscopy and by X-ray single-crystal studies of two representative examples. Complexes SnL_2X_2 derived from asymmetric chelates give rise to geometrical isomers which are non-rigid on the NMR time-scale. The different isomer distributions observed by multinuclear NMR spectroscopy have been used to aid our understanding of the solution structure of the complexes.

Experimental



R	
H	(Htrop)
Me	(Hmtrop)

Y	R′	R″	
NH	Me	H	(Hhmp)
NMe	Me	H	(Hdmp)
NEt	Me	H	(Hemp)
(collectively known as			(Hxmp)
O	Me	H	(Hmalt)
O	H	CH_2OH	(Hkoj)

Hdhp

Materials.—Tin tetrachloride pentahydrate, tin tetrachloride, tin tetrabromide, tin tetraiodide, 3-hydroxypyridin-2-one (2,3-dihydroxypyridine, Hdhp) and kojic acid (Hkoj) were obtained commercially from Aldrich and were used without further purification. Maltol (Hmalt) and tropolone (Htrop) were obtained from Lancaster. 3-Hydroxy-2-methylpyridin-4-one[8] (Hhmp), 3-hydroxy-1,2-dimethylpyridin-4-one[8] (Hdmp), 1-ethyl-3-hydroxy-2-methylpyridin-4-one[8] (Hemp) and 4-methyltropolone[9] (Hmtrop) were prepared by literature methods.

Physical Measurements.—Proton, $^{13}C-\{^1H\}$, and $^{119}Sn-\{^1H\}$ NMR spectra were recorded on JEOL GSX270 (270 MHz), EX270 (270 MHz) and Bruker WM250 (250 MHz) spectrometers, ^{119}Sn cross-polarisation magic angle spinning (CP MAS) NMR spectra on a University of London Bruker MSL300 (300 MHz) spectrometer. Chemical shifts are quoted relative to tetramethylsilane for ^1H, ^{13}C nuclei and to tetramethyltin for ^{119}Sn. Mass spectra were recorded on Micromass VG 7070E and VG Analytical 2AB-SE spectrometers in the positive-ion fast atom bombardment (FAB) or electron impact (EI) mode. Infrared spectra were recorded on a Perkin Elmer 1720X FT spectrometer as KBr or CsI discs. Microanalyses were by Medac, Imperial College and University College, London, laboratories.

Preparation of the Tin(IV) *Complexes.*—The complexes derived from Htrop and Hmtrop were prepared in a similar manner to that described for the the preparation of $Sn(trop)_2Cl_2$ by Muetterties and Wright.[5] However the solvent systems

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

used varied: $Sn(trop)_2Cl_2$, benzene–MeOH; $Sn(trop)_2Br_2$, toluene–MeCN; $Sn(trop)_2I_2$, toluene–MeCN; $Sn(mtrop)_2Cl_2$ and $Sn(mtrop)_2Br_2$, benzene. The compounds $Sn(koj)_2Cl_2$ and $Sn(koj)_2Br_2$ were prepared as described in the literature.[6]

$Sn(emp)_2Cl_2$. A stirred solution of Hemp (1.00 g, 6.52 mmol) in ethanol (10 cm^3) was treated with a solution of $SnCl_4{\cdot}5H_2O$ (1.14 g, 3.76 mmol) in ethanol (25 cm^3) under an argon atmosphere. The solution was refluxed with stirring for 12 h. The white crystals obtained were centrifuged, washed with ethanol, then diethyl ether and dried *in vacuo* at 50 °C. Yield 1.24 g, 71%. The corresponding complexes derived from Hdmp, Hhmp, Hmalt, and Hdhp were prepared in a similar manner. These complexes can also be prepared in solvents such as $CHCl_3$, CH_2Cl_2, $MeNO_2$, water and tetrahydrofuran under similar conditions.

$Sn(emp)_2Br_2$. A stirred solution of Hemp (0.5 g, 3.3 mmol) in hot chloroform (20 cm^3) was treated with a solution of $SnBr_4$ (0.71 g, 1.6 mmol) in chloroform (25 cm^3). The volume was reduced until the point of precipitation, the solution allowed to cool and then centrifuged. The pale yellow solid obtained was washed with diethyl ether and dried *in vacuo* at 50 °C. Yield 0.63 g, 68%. The corresponding complexes derived from Hdmp, Hhmp, Hmalt, and Hdhp were prepared in a similar manner. The last two can also be prepared from ethanol and water.

$Sn(malt)_2I_2$. A stirred solution of Hmalt (0.12 g, 0.96 mmol) in hot ethanol (5 cm^3) was treated with a solution of SnI_4 (0.3 g, 0.48 mmol) in ethanol (10 cm^3). The solution was allowed to cool and the yellow solid obtained was centrifuged and redissolved in chloroform. The yellow solution was then centrifuged and evaporated to dryness to give a yellow solid which was washed with diethyl ether and dried *in vacuo* at 50 °C. Yield 0.1 g, 38%. The corresponding complexes derived from Hdhp and Hkoj were prepared in a similar manner (although the solvent used for Hkoj was dichloromethane). These complexes can also be prepared from chloroform and water.

X-Ray Crystallography.—The complexes $Sn(malt)_2Cl_2{\cdot}CHCl_3$ and $Sn(trop)_2Cl_2$ were recrystallised from $CHCl_3$ and $MeNO_2$ respectively to yield crystals which were suitable for X-ray diffraction measurements.

Crystal data for $Sn(malt)_2Cl_2{\cdot}CHCl_3$. $C_{13}H_{11}Cl_5O_6Sn$, M = 559.2, orthorhombic, space group $Pbn2_1$, a = 9.216(10), b = 12.651(11), c = 16.538(24) Å, U = 1928(4) $Å^3$, Z = 4, D_c = 1.926 Mg m^{-3}. Clear prisms, dimensions 0.17 × 0.47 × 0.50 mm, μ(Mo-Kα) = 2.044 mm^{-1}, λ = 0.710 73 Å, $F(000)$ = 1088.

Data collection and processing. Siemens P4 diffractometer, room temperature, ω-scan method, (2θ range 3–45°), graphite monochromated Mo-Kα radiation; 1305 independent measured reflections, 1254 observed $[|F_o| > 3\sigma(|F_o|)]$, corrected for Lorentz and polarisation factors; numerical absorption correction (face indexed crystal). Maximum and minimum transmission factors 0.69 and 0.38 respectively.

Structure analysis and refinement. The structure was solved by direct methods and all the non-hydrogen atoms refined anisotropically. The hydrogen atoms were idealised (C–H 0.96 Å), assigned isotropic thermal parameters $U(H) = 1.2\ U_{eq}(C)$ and allowed to ride on their parent carbons. Refinement was by full-matrix least squares to $R = \Sigma[|F_o| - |F_c|]/\Sigma|F_o| = 0.034$, R' = 0.034 $[w^{-1} = \sigma^2(F) + 0.0003F^2]$. The polarity of the structure was determined both by an η refinement [η = 0.92(4)] and by an R factor test (R_g^{+} = 0.040, R_g^{-} = 0.041). The mean and maximum shift/error in the final refinement cycle were 0.001 and 0.004 respectively, maximum residual electron density 0.88 e $Å^{-3}$. Computations were carried out on an IBM 386/70 computer using the SHELXTL PC program.[10]

Crystal data for $Sn(trop)_2Cl_2$. $C_{14}H_{10}Cl_2O_4Sn$, M = 431.8, orthorhombic, space group $Pbca$, a = 7.146(3), b = 14.643(7), c = 28.373(12) Å, U = 2969(2) $Å^3$, Z = 8, D_c = 1.932 g cm^{-3}. Clear plates, dimensions 0.07 × 0.20 × 0.30 mm, μ(Mo-Kα) = 2.092 mm^{-1}, $F(000)$ = 1680. The unit-cell parameters were identical to those previously reported.[5]

Data collection and processing. Details as above except as follows. 1929 Independent measured reflections, 1316 observed $[|F_o| > 3\sigma(|F_o|)]$. Maximum and minimum transmission factors 0.87 and 0.63 respectively. The peak profiles were both asymmetric and diffuse, which coupled with the long c axial length probably result in partial overlap of some of the diffraction peaks.

Structure analysis and refinement. The structure was solved by direct methods. However, despite the low absorption coefficient, full anisotropic refinement (using absorption corrected data) resulted in several of the light atoms becoming non-positive definite. Thus only the tin and the halogens were refined anisotropically and the remaining atoms were refined isotropically. Hydrogen atoms were included in calculated positions with a common isotropic U and were allowed to ride on their parent carbons. There is no evidence for disorder within either tropolone unit. Refinement was by full-matrix least squares to R = 0.115. The details of the gross structure are however definitive. The mean and maximum shift/error in the final refinement were 0.000 and 0.000. The maximum residual electron density was 2.46 e $Å^{-3}$, in the region of the tin atom. Computations were carried out as above.

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

Results and Discussion

The ligands illustrated have obvious potential to act as chelating agents upon deprotonation, and we have found that this can be readily achieved by reaction with tin tetrahalides [equation (1)]

$$SnX_4 + 2HL \longrightarrow SnL_2X_2 + 2HX \qquad (1)$$

where HL are the ligands as shown and X = Cl, Br or I. The relative 'hardness' of the ligands appears to determine the stability of the complexes formed. The ligands Hmalt, Hkoj and Hdhp form SnL_2X_2 complexes in a variety of solvents (*e.g.* water, ethanol and chloroform). The preparation of the tropolonato complexes proceeds using solvents such as aqueous methanol, acetonitrile, toluene and chlorobenzene.[5] However, reactions involving Hhmp, Hdmp, and Hemp (the Hxmp ligands) are inclined to proceed further, leading to the formation of complexes of the type $[SnL_3]^+X^-$,[11] thus necessitating a more judicious choice of solvents (those with lower relative permittivities appear to inhibit the formation of the latter species). The trend is further exemplified as X changes from Cl to Br to I; indeed complexes of the type $Sn(xmp)_2I_2$ cannot be prepared in the solvents used here.

Table 1 shows the results of the mass spectrometry for the SnL_2X_2 complexes, which were obtained using both electron impact and fast atom bombardment conditions, where appropriate. The monomolecular nature of these complexes is indicated by the appearance of the fragments $[SnL_2X]^+$ and in some cases $[SnLX_2]^+$. The $[Sn^{II}L]^+$ species are presumably formed by reduction of the tin(IV) nucleus and the $[SnL_3]^+$ species are either contaminants or produced by reaction in the vapour phase. Further evidence that these types of complexes are monomolecular species was obtained by Muetterties *et al.*[12] who established by molecular weight studies that bis-(γ-isopropyltropolonato)tin dichloride is a monomer. The results of the ^1H NMR and elemental analyses are presented in Tables 2 and 3 respectively.

Vibrational Spectra.—Important infrared bands are shown in Table 4. The ν(Sn–O) frequencies are observed in the region 585–570 cm^{-1} and are easily distinguishable by their normally characteristic strong and broad bands,[6] which are much higher in frequency than those observed for the corresponding acetylacetonato complexes[7] (460–400 cm^{-1}), reflecting the difference between five- and six-membered chelate rings.[6] The

Table 1 Mass spectra of six-co-ordinate SnL$_2$X$_2$ complexes in the FAB mode unless otherwise stated

	m/z[b]			
Complex[a]	[Sn^{II}L]$^+$	Sn^{IV}L$_2$X]$^+$	[Sn^{IV}L$_3$]$^+$	Matrix
Sn(hmp)$_2$Cl$_2$	244 (100)	403 (46)	492 (7)	*c*
Sn(hmp)$_2$Br$_2$	244 (62)	447 (100)	492 (10)	*c*
Sn(dmp)$_2$Cl$_2$	258 (100)	431 (54)	534 (37)	*d*
Sn(dmp)$_2$Br$_2$	258 (100)	475 (8)	534 (7)	*c*
Sn(emp)$_2$Cl$_2$	272 (100)	459 (86)	576 (23)	*c*
Sn(emp)$_2$Br$_2$	272 (100)	503 (65)	576 (20)	*d*
Sn(dhp)$_2$Cl$_2$	230 (100)	375 (17)	450 (18)	*c*
Sn(dhp)$_2$Br$_2$	230 (100)	419 (27)	450 (18)	*c,e*
Sn(dhp)$_2$I$_2$	230 (100)	467 (7)	450 (22)	*c,e*
Sn(malt)$_2$Cl$_2$	245 (100)	405 (95)	495 (6)	*c*
Sn(malt)$_2$Br$_2$	245 (100)	449 (87)	495 (1)	*c,e*
Sn(malt)$_2$I$_2$	245 (100)	497 (47)	495 (22)	*c*
Sn(koj)$_2$Cl$_2$	261 (94)	437 (100)	543 (0)	*c,e*
Sn(koj)$_2$Br$_2$	261 (100)	481 (31)	543 (27)	*c,e*
Sn(koj)$_2$I$_2$	261 (100)	529 (17)	543 (3)	*c,e*
Sn(trop)$_2$Cl$_2$	241 (59)	397 (100)	483 (0)	*e,f*
Sn(trop)$_2$Br$_2$	241 (100)	441 (78)	483 (0)	*e,f*
Sn(trop)$_2$I$_2$	241 (100)	489 (40)	483 (0)	*e,f*

[a] Values with respect to isotopes ^{120}Sn and ^{79}Br. [b] Figures in parentheses represent relative intensities. [c] Dimethyl sulfoxide–glycerol matrix. [d] *m*-Nitrobenzyl alcohol matrix. [e] Value corresponding to [Sn^{IV}LX$_2$]$^+$ also observed. [f] Electron-impact mass spectrometry.

Table 2 Proton NMR chemical shifts for six-co-ordinate SnL$_2$X$_2$ complexes in (CD$_3$)$_2$SO unless otherwise stated, 270 MHz

Complex	Isomer	H^6 (d)	H^5 (d)	CH$_3$ (s)	NR	CH$_2$CH_3 (t)
Sn(emp)$_2$Cl$_2$	*trans*	7.95	6.96	2.37	4.25[a]	1.35
	cis	7.95	6.7	2.54	4.25[a]	1.35
Sn(emp)$_2$Br$_2$	*trans*	8.1	7.08	2.67	4.39[a]	1.49
	cis	8.1	6.83	2.62	4.39[a]	1.49
Sn(dmp)$_2$Cl$_2$	*trans*	7.92	6.92	2.44	3.91[b]	—
	cis	7.92	6.79	2.44	3.91[b]	—
Sn(dmp)$_2$Br$_2$	*trans*	8.07	7.07	2.61	4.06[b]	—
	cis	8.07	6.83	2.61	4.06[b]	—
Sn(hmp)$_2$Cl$_2$	*trans*	7.72	6.9	2.42	13.25[c]	—
	cis	7.72	6.66	2.26	13.14[c]	—
Sn(hmp)$_2$Br$_2$	*trans*	7.95	7.13	2.65	13.15[c]	—
	cis	7.95	6.9	2.65	13.15[c]	—
Sn(malt)$_2$Cl$_2$	*cis*	8.64	7.14	2.58	—	—
Sn(malt)$_2$Br$_2$	*cis*	8.66	7.16	2.60	—	—
Sn(malt)$_2$I$_2$[d]	*cis*	7.99	6.79	2.63	—	—

[a] R = CH$_2$ (q). [b] R = CH$_3$ (s). [c] R = H. [d] In CDCl$_3$.

Table 3 Microanalyses (%) for six-co-ordinate SnL$_2$X$_2$ complexes

Complex	C	H	N	X
Sn(emp)$_2$Cl$_2$	38.75 (38.90)	4.00 (4.10)	5.55 (5.65)	14.75 (14.35)
Sn(emp)$_2$Br$_2$	32.60 (32.95)	3.25 (3.45)	5.00 (4.80)	27.25 (27.40)
Sn(dmp)$_2$Cl$_2$	34.60 (33.45)	3.40 (3.40)	5.55 (5.60)	22.00 (21.15)
Sn(dmp)$_2$Br$_2$	29.95 (30.30)	2.60 (2.90)	5.25 (5.05)	28.60 (28.80)
Sn(hmp)$_2$Cl$_2$	33.65 (32.90)	2.90 (2.75)	6.45 (6.40)	18.20 (16.20)
Sn(dhp)$_2$Cl$_2$	28.25 (29.30)	1.85 (1.95)	6.45 (6.85)	17.80 (17.30)
Sn(dhp)$_2$Br$_2$	23.65 (24.10)	1.25 (1.60)	5.95 (5.60)	32.65 (32.05)
Sn(dhp)$_2$I$_2$	20.40 (20.25)	1.50 (1.35)	4.55 (4.75)	42.65 (42.80)
Sn(malt)$_2$Cl$_2$	32.65 (32.80)	2.10 (2.30)	—	18.75 (16.10)
Sn(malt)$_2$Br$_2$	26.30 (27.25)	1.75 (1.90)	—	32.05 (30.20)
Sn(malt)$_2$I$_2$	23.30 (23.15)	1.60 (1.60)	—	40.75 (40.75)
Sn(koj)$_2$Cl$_2$	30.10 (30.55)	2.05 (2.15)	—	15.35 (15.05)
Sn(koj)$_2$Br$_2$	25.50 (25.70)	1.65 (1.80)	—	28.55 (28.50)
Sn(trop)$_2$Cl$_2$	38.70 (38.95)	2.20 (2.35)	—	16.35 (16.40)

Satisfactory analyses could not be obtained for the complexes not listed above. Figures in parentheses represent expected values.

Table 4 Relevant features in the infrared spectra (cm^{-1}) obtained for SnL$_2$X$_2$ complexes

	ν(Sn–O)			
Complex	Cl	Br	I	ν(Sn–Cl)
Sn(emp)$_2$X$_2$	583	579	—	316, 300, 283
Sn(dmp)$_2$X$_2$	582	576	—	327, 313, 299
Sn(hmp)$_2$X$_2$	573	—	—	324, 311, 298 *
Sn(dhp)$_2$X$_2$	575	573	572	344, 330
Sn(malt)$_2$X$_2$	574	571	563	346, 330
Sn(koj)$_2$X$_2$	578	576	569	340, 334
Sn(trop)$_2$X$_2$	585	581	577	338, 328

* The band at 298 cm^{-1} is a shoulder.

Sn–O stretching frequency decreases in the order SnL$_2$Cl$_2$ > SnL$_2$Br$_2$ > SnL$_2$I$_2$.

The Sn–Cl stretches are in the region 290–350 cm^{-1}. When the halogen is substituted by either bromide or iodide these stretches disappear, but the rest of the spectrum remains essentially unchanged, indicating that direct co-ordination occurs between the tin and chloride, and that the Sn–Cl stretches have been correctly assigned. There are three Sn–Cl stretches observed for complexes with the Hxmp, two of these are assigned as ν_{sym} and ν_{asym} for the *cis* isomer and the third is tentatively assigned as ν_{asym} for the *trans* isomer.

Tin-199 *Nuclear Magnetic Resonance*.—The ^{119}Sn chemical shifts are affected by a number of parameters. The major factors appear to be the electronegativity of the substituents attached to the tin atom, the geometrical distortion they cause and the co-ordination number.[13,14] In general, an increase in co-ordination number from four to five to six leads to an increase in tin shielding of *ca.* 150 ppm each time, thus the approximate shift ranges are δ +200 to −60, −90 to −300 and −125 to − 525 respectively.[1] However, these ranges are a generalisation based upon mainly organotin compounds and it is interesting that the chemical shifts for [SnCl$_6$]$^{2-}$ and [SnBr$_6$]$^{2-}$ are at δ −732 and −2064 respectively.[14]

The chemical shifts (Table 5) for the SnL$_2$Cl$_2$ complexes lie in the range δ −400 to −500, whilst those for the bromo- and iodo-analogues are in the range δ −640 to −690 and δ −1120 to −1210 respectively showing clearly the increase in tin shielding concomitant with the reduction in the electronegativity and increase in size of the halogens.

The majority of the spectra were measured in dimethyl sulfoxide (dmso) due to the limited solubility of the complexes. We initially thought (as has previously been reported[15]) that direct co-ordination of the solvent might occur, either by halogen displacement or by an increase in the co-ordination number. The shifts in δ observed on changing from Cl to Br to I, however, preclude the possibility of halogen displacement.

Co-ordination numbers greater than six have been reported in the literature.[1,16] A shift of *ca.* 150 ppm in the ^{119}Sn NMR spectrum has been attributed to a change from six- to seven-co-ordination.[17] Elemental analysis results have shown the absence of solvents of crystallisation, and previous work[12] together with the mass spectroscopy data that we obtained indicate monomolecularity of these species. We have measured a number of ^{119}Sn CP MAS NMR spectra of these complexes. These show insignificant differences (Δδ < 10 ppm) from those obtained in the corresponding solution NMR spectra, indicating that the co-ordination number observed in the solid state is preserved in solution.

Isomerism.—Complexes of the type M(L–L′)$_2$X$_2$ can exist as five geometrical isomers (Fig. 1). All five isomers can be observed by NMR spectroscopy provided that slow exchange can be reached, and that the chemical shift differences between the inequivalent sites are resolvable. If this is the situation and

Table 5 Tin-119 NMR chemical shifts for six-co-ordinate SnL_2X_2 complexes in dmso unless otherwise stated, 100.6 MHz

Complex	δ^a		
L	X = Cl	Br	I
hmp	−475.5, −477.6, −479.6	−643.8, −650.3, −657.1[b]	
dmp	−472.9, −474.7, −476.7	−644.1, −650.3, −656.9	
emp	−473.3, −475.3, −477.4	−642.9, −649.1, −655.9	
dhp	−490.8, −495.6	−670.1, −689.4	−1147.6, −1209.9[c]
malt	−469.7, −474.9	−647.5, −666.1	−1139.6, −1194.9[d]
koj	−464.4, −469.9	−645.8, −666.4	−1123.2, −1183.1[b]
trop	−477.2	−672.6	
mtrop	−478.0	−672.8	

[a] All values referenced to a secondary reference $SnCl_4$ (−150 ppm with respect to $SnMe_4$). [b] Contamination by another tin-containing species was observed. [c] In $(CD_3)_2CO$. [d] In $CDCl_3$.

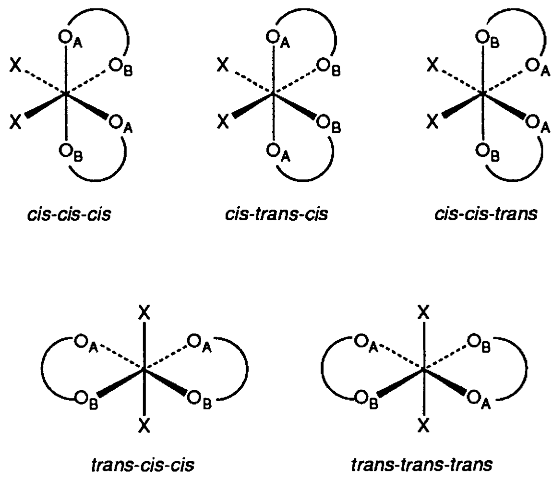

Fig. 1 Geometrical isomers of $M(L-L')_2X_2$

all five isomers are energetically equivalent one would expect to see a statistical distribution. However, in many cases this is not so, *e.g.* $Sn(acac)_2Me_2$ shows only the *trans* isomer and $Sn(acac)_2Cl_2$ (acac = acetylacetonate) and $Sn(trop)_2Me_2$ show only the *cis* isomers.[18–23]

The ^{119}Sn and ^1H NMR spectra of $Sn(trop)_2Cl_2$ are shown in Fig. 2(*a*). Although only one set of resonances is observed it is possible that the isomer resonances could be unresolved. In an attempt to observe three different *cis* isomers an asymmetric tropolone complex, $Sn(mtrop)_2Cl_2$, was prepared. The ^{119}Sn NMR spectrum showed only one resonance, although there was an increase in the linewidth.

On changing to a heavier halogen the increased steric bulk would be expected to reduce the rate of isomerism, thus, if the isomers are non-coincident, resolution becomes more probable. In a further attempt to separate the *cis* isomers the bromo analogue was prepared and although the expected shift in δ was seen, only one broad resonance was observed, indicating that either the resonances are coincident or that the isomerism is fast on the NMR time-scale.

The $Sn(L-L')_2X_2$ complexes formed with Hmalt, Hkoj and Hdhp all behave similarly to each other. Fig. 2(*b*) shows the ^{119}Sn and ^1H NMR spectra obtained for $Sn(malt)_2Cl_2$. Two sets of resonances are observed in the ^{119}Sn NMR spectrum, in the intensity ratio 2:1. These are attributed to the three possible *cis* isomers, where two of these isomer resonances are coincident. The complexes formed with the Hxmp show a more complicated phenomenon [see Fig. 2(*c*)(*i*)]. The intensity ratio of these three resonances is *ca.* 2:2:0.5 and we assign the extra resonance to the presence of the *trans* isomer, thus these complexes show a near-statistical distribution of all five isomers.

The presence of only one set of isomers in the ^1H NMR

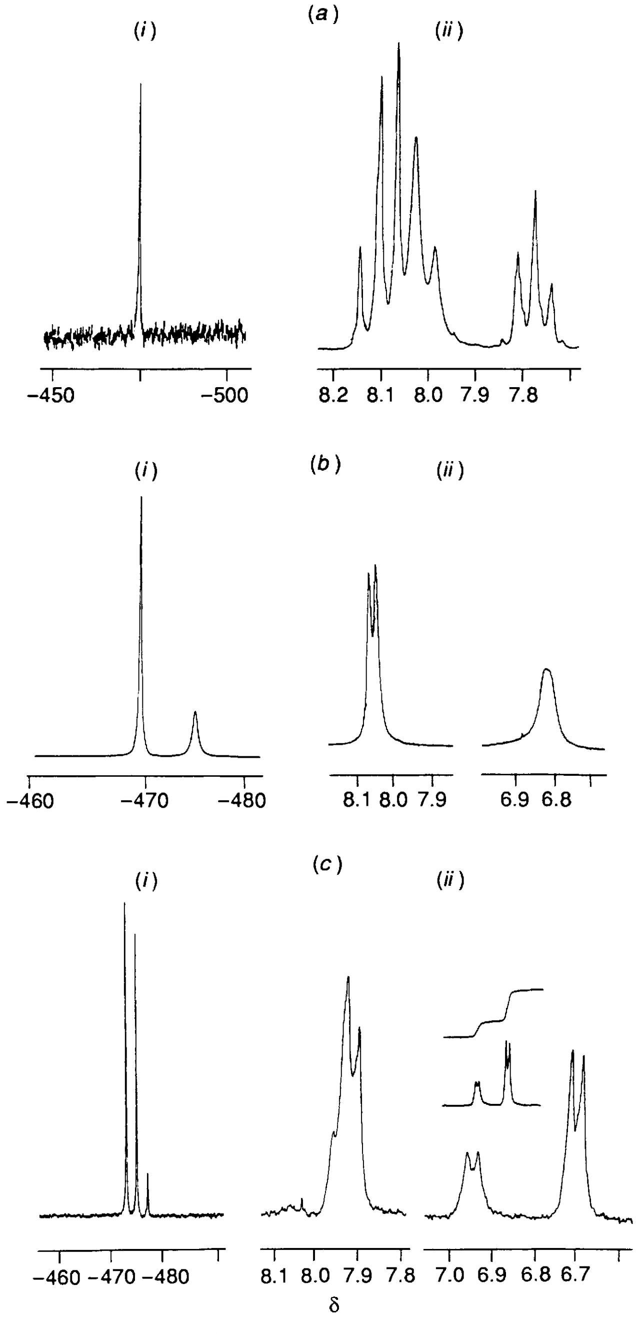

Fig. 2 Tin-119 (*i*) and ^1H NMR (*ii*) spectra of some ML_2X_2 complexes in $(CD_3)_2SO$: (*a*) $Sn(trop)_2Cl_2$, (*b*) $Sn(malt)_2Cl_2$, and (*c*) $Sn(emp)_2Cl_2$

Table 6 The observed isomer preferences for complexes of the type SnL_2Z_2 (where Z = Me, Cl, Br or I)

L^- *	Z	Isomer	Probable dominating electronic effect
acac,[20–22] O_2CMe,[19] dbzm,[22] koj[23]	Me	*trans*	Me σ donation
malt, dhp, trop,[18,22,23] mtrop	Me	*cis*	Sn–O d_π–p_π interaction
acac,[20–22] O_2CMe,[19] dbzm,[22] malt, koj,[23] dhp, trop,[18,22,23] mtrop	Cl, Br, I	*cis*	Sn–X d_π–p_π interaction
xmp	Cl, Br	*cis* and *trans*	Sn–O ≈ Sn–X d_π–p_π interaction

* dbzm = Dibenzoylmethanide.

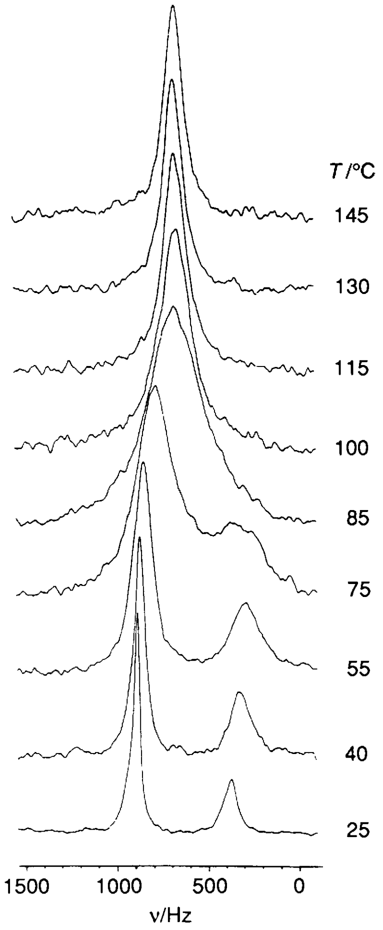

Fig. 3 The ^{119}Sn NMR spectra of $Sn(malt)_2Cl_2$ between 25 and 145 °C in $(CD_3)_2SO$, 100.6 MHz

spectrum of $Sn(malt)_2Cl_2$ [Fig. 2(*b*)(*ii*)] indicates that the *cis* isomers cannot be resolved by ^1H NMR spectroscopy (at ambient temperature). The appearance of a further set of resonances in the spectrum of $Sn(emp)_2Cl_2$ [Fig. 2(*c*)(*ii*)], suggests that only the *cis versus trans* isomers can be resolved. The observed ratio of *ca* 3:2 in the ^1H NMR spectrum is consistent with the ^{119} Sn NMR spectrum.

Complexes of the type $Sn(acac)_2Me_2$ with six-membered chelate rings have often been reported to *trans*,[19–22] although Lockhart *et al.*[20] recently reported that $Sn(acac)_2Me_2$ may also be in *cis–trans* equilibrium in solution. The preferred *trans* conformation is probably due to strong methyl σ donation, as the *cis* conformer would be less stable due to weakening of the Sn–O bond. It has been observed that complexes with five-membered rings show a preference for the *cis* isomer.[18,22,23] This could be due to increased Sn–O p_π–d_π interaction over the methyl σ donation. In contrast, the probable reason for the SnL_2X_2 (L = malt, dhp, koj, trop or mtrop) showing a preference for the *cis* isomer is the greater Sn-X p_π–d_π interaction over that of the Sn–O p_π–d_π interaction (Table 6).[24]

The only complexes reported here which appear to show both *cis* and *trans* isomerisation are those derived from the Hxmp ligand. Here the chelators are 'hard' ligands and it is postulated that the Sn–X and Sn–O p_π–d_π interactions are of similar importance, thus leading to the formation of all possible geometric isomers.

There is an increase in Δδ between the isomers, the heavier the halogen, as expected. The difference in δ between the *cis* isomers is *ca.* 5 and 20 ppm for Cl and Br respectively, for the malt, koj and dhp complexes. This difference decreases on changing the ligand to the Hxmp, to either *ca.* 2 and 7 or *ca.* 4 and 13 ppm depending on the assignment of the *trans* isomers. This reduction of Δδ for the xmp ligands indicates a reduction in the difference between the isomers, which supports the above rationalisation.

Individual assignment of the different resonances is difficult. The smaller of the ^{119}Sn resonances is broader than the others. Furthermore, it is generally observed that reduction of symmetry leads to an increase in linewidth and that for tin complexes the tin chemical shift is affected. The *cis-cis-cis* arrangement affords the greatest distortion, thus we attribute this isomer to the broader high-field resonance. We are unable unambiguously to assign the other two resonances to specific isomers.

In the ^{119}Sn NMR spectrum of $Sn(malt)_2I_2$ no change was seen down to −65 °C (in acetone), however on increasing the temperature, in the case of *cis*-$Sn(malt)_2Cl_2$ (Fig. 3) broadening of the two resonances, coalescence (T_c ≈ 75 °C) and ultimately sharpening of the final single resonance occurs. This clearly demonstrates the potential utility of variable-temperature ^{119}Sn NMR spectroscopy to evaluate kinetic parameters for this type of isomerism. In a parallel experiment with $Sn(emp)_2Cl_2$ (Fig. 4) broadening and coalescence are again observed, first for the different *cis* isomer resonances (T_c ≈ 60 °C) and at higher temperature for the *cis* and *trans* isomer resonances (T_c ≈ 80 °C), supporting the assignment of the *trans* isomer resonances at lowest field. Further evidence that leads to this assignment is given by Dillon and Marshall[25] who observed that for mixed-ligand hexahalogenotin complexes the ^{119}Sn NMR *cis* resonances occur at higher field than the corresponding *trans* resonances, however the assignment is far from conclusive.

There are many proposed mechanisms for this type of isomerisation, involving either bond-breaking or twist mechanisms.[26] The coalescence temperatures for these complexes are relatively low, indicating that bond cleavage is unlikely and that a twist mechanism is the most likely form of isomerisation.

X-Ray Studies.—The crystal structures of $Sn(malt)_2Cl_2 \cdot CHCl_3$ and $Sn(trop)_2Cl_2$ have been determined. Fractional atomic coordinates are listed in Tables 7 and 8, with selected bond lengths and angles in Tables 9 and 10. Both materials crystallise

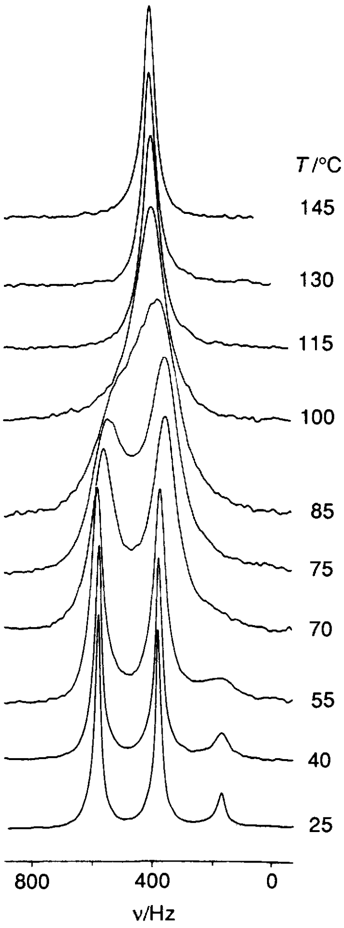

Fig. 4 The ^{119}Sn NMR spectra of Sn(emp)$_2$Cl$_2$ between 25 and 145 °C in (CD$_3$)$_2$SO, 100.6 MHz

Table 7 Atomic coordinates (× 10^4) for Sn(malt)$_2$Cl$_2$·CHCl$_3$

Atom	*x*	*y*	*z*
Sn	9 692(1)	6 273(1)	2 682
Cl(1)	8 261(3)	4 773(2)	2 967(2)
Cl(2)	8 902(3)	7 258(2)	3 804(2)
O(1)	15 197(8)	6 406(6)	3 196(6)
C(2)	14 017(10)	5 809(8)	3 307(6)
C(3)	12 697(11)	6 133(7)	3 046(6)
O(3)	11 491(6)	5 554(5)	3 160(5)
C(4)	12 584(8)	7 126(7)	2 641(6)
O(4)	11 322(7)	7 420(5)	2 416(4)
C(5)	13 856(10)	7 705(7)	2 528(7)
C(6)	15 114(10)	7 317(8)	2 805(10)
C(7)	14 310(11)	4 800(9)	3 747(10)
O(1′)	8 178(9)	6 980(6)	−273(5)
C(2′)	7 924(11)	7 251(8)	494(7)
C(3′)	8 625(9)	6 749(7)	1 124(6)
O(3′)	8 338(7)	7 034(5)	1 897(4)
C(4′)	9 648(10)	5 986(8)	954(7)
O(4′)	10 331(7)	5 574(6)	1 553(5)
C(5′)	9 894(12)	5 707(9)	150(8)
C(6′)	9 147(19)	6 201(11)	−419(8)
C(7′)	6 804(13)	8 120(8)	579(8)
C(10)	13 717(15)	4 874(11)	1 110(9)
Cl(3)	13 604(4)	6 099(3)	580(3)
Cl(4)	15 401(4)	4 744(3)	1 547(3)
Cl(5)	13 337(6)	3 857(3)	440(3)

Table 8 Atomic coordinates (× 10^4) for Sn(trop)$_2$Cl$_2$

Atom	*x*	*y*	*z*
Sn	1423(3)	2372(1)	1330(1)
Cl(1)	4329(10)	2367(4)	936(3)
Cl(2)	2678(11)	2101(4)	2082(2)
O(1)	−69(25)	2373(11)	693(6)
C(1)	−742(34)	1581(15)	562(8)
C(2)	−227(34)	821(15)	869(8)
O(2)	861(25)	994(11)	1248(6)
C(3)	−749(34)	−77(15)	805(8)
C(4)	−1879(38)	−463(19)	465(9)
C(5)	−2682(43)	−129(18)	94(9)
C(6)	−2714(43)	840(18)	−61(10)
C(7)	−1825(41)	1515(19)	198(10)
O(1′)	1323(24)	3778(10)	1342(6)
C(1′)	−121(35)	4101(15)	1568(8)
C(2′)	−1580(34)	3450(14)	1722(7)
O(2′)	−1151(21)	2566(10)	1646(5)
C(3′)	−3315(34)	3622(15)	1961(8)
C(4′)	−4026(39)	4464(16)	2096(9)
C(5′)	−3137(33)	5354(16)	2038(8)
C(6′)	−1652(39)	5595(18)	1833(9)
C(7′)	−245(36)	5045(16)	1639(8)

Table 9 Selected bond lengths (Å) and angles (°) for Sn(malt)$_2$Cl$_2$·CHCl$_3$

Sn–Cl(1)	2.358(4)	Sn–Cl(2)	2.351(4)
Sn–O(3)	2.050(7)	Sn–O(4)	2.135(7)
Sn–O(3′)	2.041(7)	Sn–O(4′)	2.149(9)
O(1)–C(2)	1.336(12)	O(1)–C(6)	1.324(14)
C(2)–C(3)	1.354(14)	C(2)–C(7)	1.493(16)
C(3)–O(3)	1.344(12)	C(3)–C(4)	1.428(13)
C(4)–O(4)	1.277(10)	C(4)–C(5)	1.395(12)
C(5)–C(6)	1.341(14)	O(1′)–C(2′)	1.334(13)
O(1′)–C(6′)	1.352(18)	C(2′)–C(3′)	1.381(14)
C(2′)–C(7′)	1.514(15)	C(3′)–O(3′)	1.355(12)
C(3′)–C(4′)	1.378(14)	C(4′)–O(4′)	1.284(13)
C(4′)–C(5′)	1.394(17)	C(5′)–C(6′)	1.322(20)
Cl(1)–Sn–Cl(2)	95.5(1)	Cl(1)–Sn–O(3)	91.0(2)
Cl(2)–Sn–O(3)	100.4(2)	Cl(1)–Sn–O(4)	169.0(2)
Cl(2)–Sn–O(4)	91.1(2)	O(3)–Sn–O(4)	79.2(3)
Cl(1)–Sn–O(3′)	99.5(2)	Cl(2)–Sn–O(3′)	93.6(2)
O(3)–Sn–O(3′)	161.6(3)	O(4)–Sn–O(3′)	88.8(3)
Cl(1)–Sn–O(4′)	89.8(2)	Cl(2)–Sn–O(4′)	171.6(2)
O(3)–Sn–O(4′)	86.0(3)	O(4)–Sn–O(4′)	84.7(3)
O(3′)–Sn–O(4′)	79.0(3)	C(2)–O(1)–C(6)	120.8(8)
O(1)–C(2)–C(3)	121.1(9)	O(1)–C(2)–C(7)	113.8(8)
C(3)–C(2)–C(7)	125.1(9)	C(2)–C(3)–O(3)	122.3(9)
C(2)–C(3)–C(4)	118.7(9)	O(3)–C(3)–C(4)	119.0(8)
Sn–O(3)–C(3)	111.9(6)	C(3)–C(4)–O(4)	117.4(8)
C(3)–C(4)–C(5)	117.7(8)	O(4)–C(4)–C(5)	124.9(8)
Sn–O(4)–C(4)	112.5(6)	C(4)–C(5)–C(6)	119.2(9)
O(1)–C(6)–C(5)	122.4(9)	C(2′)–O(1′)–C(6′)	118.2(9)
O(1′)–C(2′)–C(3′)	121.1(9)	O(1′)–C(2′)–C(7′)	113.3(10)
C(3′)–C(2′)–C(7′)	125.6(10)	C(2′)–C(3′)–O(3′)	119.9(8)
C(2′)–C(3′)–C(4′)	119.3(10)	O(3′)–C(3′)–C(4′)	120.7(9)
Sn–O(3′)–C(3′)	110.8(5)	C(3′)–C(4′)–O(4′)	117.6(10)
C(3′)–C(4′)–C(5′)	118.8(10)	O(4′)–C(4′)–C(5′)	123.6(10)
Sn–O(4′)–C(4′)	111.6(6)	C(4′)–C(5′)–C(6′)	118.3(11)
O(1′)–C(6′)–C(5′)	124.2(12)		

in space groups containing glide planes thus both Λ and Δ forms of each complex are present. In the Sn(malt)$_2$Cl$_2$ case, although different isomeric forms are observed by ^{119}Sn NMR spectroscopy in solution, the single crystal studied has the chlorines *cis* and the methyls *anti* (Fig. 5). Both molecules have non-crystallographic C_2 symmetry with the geometries of the two co-ordination spheres being essentially identical [the greatest deviation from the least squares fit = 0.07 Å for Cl(2)]. Despite the domination of the X-ray scattering by the Sn and Cl atoms (including the CHCl$_3$ solvent molecule), in the Sn(malt)$_2$Cl$_2$ structure the differences in the C–O bond lengths of the co-ordinated oxygens in both ligands are sufficiently large to permit assignment of the formal C=O [C(4)–O(4) and C(4′)–

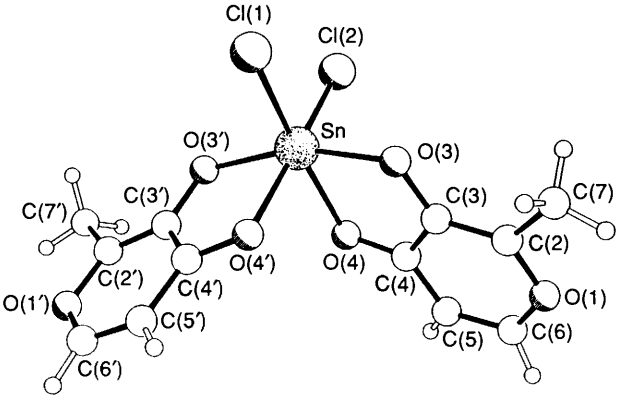

Fig. 5 The crystal structure of $Sn(malt)_2Cl_2 \cdot CHCl_3$ with the $CHCl_3$ omitted for clarity

Table 10 Selected bond lengths (Å) and angles (°) for $Sn(trop)_2Cl_2$

Sn–Cl(1)	2.359(8)	Sn–Cl(2)	2.347(7)
Sn–O(1)	2.101(17)	Sn–O(2)	2.071(16)
Sn–O(1′)	2.059(15)	Sn–O(2′)	2.065(15)
O(1)–C(1)	1.309(27)	C(1)–C(2)	1.461(31)
C(1)–C(7)	1.293(37)	C(2)–O(2)	1.350(28)
C(2)–C(3)	1.379(31)	C(3)–C(4)	1.380(35)
C(4)–C(5)	1.294(37)	C(5)–C(6)	1.485(38)
C(6)–C(7)	1.386(39)	O(1′)–C(1′)	1.303(29)
C(1′)–C(2′)	1.479(33)	C(1′)–C(7′)	1.400(31)
C(2′)–O(2′)	1.348(25)	C(2′)–C(3′)	1.436(33)
C(3′)–C(4′)	1.387(33)	C(4′)–C(5′)	1.459(34)
C(5′)–C(6′)	1.259(36)	C(6′)–C(7′)	1.401(36)
Cl(1)–Sn–Cl(2)	95.4(3)	Cl(1)–Sn–O(1)	92.2(5)
Cl(2)–Sn–O(1)	167.6(5)	Cl(1)–Sn–O(2)	96.5(5)
Cl(2)–Sn–O(2)	90.7(5)	O(1)–Sn–O(2)	78.7(6)
Cl(1)–Sn–O(1′)	92.4(5)	Cl(2)–Sn–O(1′)	99.7(5)
O(1)–Sn–O(1′)	89.8(6)	O(2)–Sn–O(1′)	165.7(7)
Cl(1)–Sn–O(2′)	171.9(4)	Cl(2)–Sn–O(2′)	88.3(4)
O(1)–Sn–O(2′)	85.5(6)	O(2)–Sn–O(2′)	90.6(6)
O(1′)–Sn–O(2′)	79.9(6)	Sn–O(1)–C(1)	115.5(14)
O(1)–C(1)–C(2)	114.3(20)	O(1)–C(1)–C(7)	120.8(22)
C(2)–C(1)–C(7)	124.8(22)	C(1)–C(2)–O(2)	118.6(19)
C(1)–C(2)–C(3)	125.4(21)	O(2)–C(2)–C(3)	116.1(20)
Sn–O(2)–C(2)	112.6(13)	C(2)–C(3)–C(4)	129.8(22)
C(3)–C(4)–C(5)	132.4(26)	C(4)–C(5)–C(6)	127.4(26)
C(5)–C(6)–C(7)	121.2(25)	C(1)–C(7)–C(6)	138.6(27)
Sn–O(1′)–C(1′)	113.5(14)	O(1′)–C(1′)–C(2′)	117.9(19)
O(1′)–C(1′)–C(7′)	118.7(21)	C(2′)–C(1′)–C(7′)	123.3(22)
C(1′)–C(2′)–O(2′)	114.3(19)	C(1′)–C(2′)–C(3′)	129.4(19)
O(2′)–C(2′)–C(3′)	116.2(19)	Sn–O(2′)–C(2′)	113.8(13)
C(2′)–C(3′)–C(4′)	127.1(22)	C(3′)–C(4′)–C(5′)	127.1(24)
C(4′)–C(5′)–C(6′)	131.9(24)	C(5′)–C(6′)–C(7′)	128.8(25)
C(1′)–C(7′)–C(6′)	132.0(24)		

O(4′)] and C–O$^-$ [C(3)–O(3) and C(3′)–O(3′)] groups [average 1.28(2) *versus* 1.35(2) Å respectively]. These are consistent with the expected resonance structure. Thus in this structure the C–O$^-$ groups are *trans* to each other the C=O groups are *cis* to each other and *trans* to Cl (*cis-cis-trans*, Fig. 1). The Sn–O bond lengths differ noticeably (Table 7). Those *trans* to O$^-$ are shorter than those *trans* to chlorine. In contrast, in the structure of $Sn(trop)_2Cl_2$ (Fig. 6) (despite the low accuracy of the determination) the trends in the four C–O bond lengths [(C(1)–O(1) 1.309(27), C(1′)–O(1′) 1.303(29), C(2)–O(2) 1.350(28), and C(2′)–O(2′) 1.348(25) Å] indicate that the equivalent bond types are now *cis* with respect to each other (*cis-cis-cis*, Fig.1), though the differences are not statistically significant. This observation reinforces the comments made above, *i.e.* that the energy differences between the alternative isomers are low. There are no significant intermolecular interactions in the structure of $Sn(trop)_2Cl_2$. However in $Sn(malt)_2Cl_2$ there are chains of weak C–H ··· O interactions involving the O$^-$ atoms of both ligands (Fig. 7).

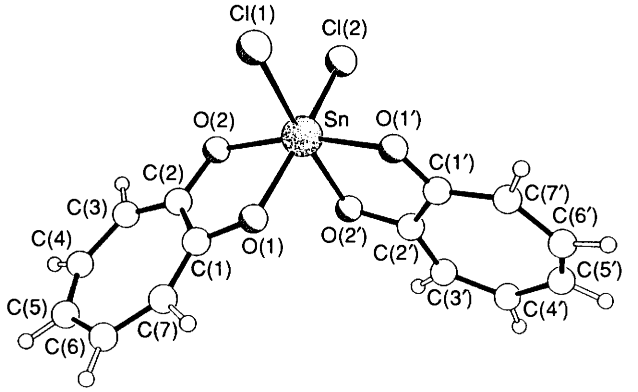

Fig. 6 The crystal structure of $Sn(trop)_2Cl_2$

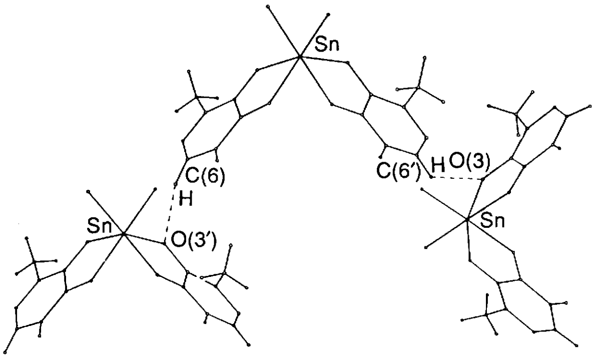

Fig. 7 Line drawing showing part of the loosely C–H ··· O linked molecules in the crystal of $Sn(malt)_2Cl_2 \cdot CHCl_3$. The C–H ··· O geometries are for: C(6)–H ··· O(3′), C ··· O 3.35, H ··· O 2.58 Å, C–H ··· O 138°; C(6′)–H ··· O(3), C ··· O 3.29, H ··· O 2.59 Å, C–H ··· O 129°

Conclusion

We have prepared a series of SnL_2X_2 complexes which all show *cis* isomerisation; for those complexes formed with the 'harder' chelates, xmp, we also observe the unusual *trans* isomers. The different *cis* isomers and the *trans* isomers are distinguishable by ^{119}Sn NMR spectroscopy. Variable-temperature ^{119}Sn NMR experiments indicate that isomerisation probably occurs *via* a twist mechanism. The crystal structures of two examples further confirm that the isomerisation is facile.

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