Six-co-ordinate Tris(bidentate ligand) Tin(IV) Complexes

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New six-co-ordinate tris(bidentate ligand) complexes of tin(IV) with O,O′ ligands have been prepared and characterised by ^{1}H and ^{119}Sn NMR spectroscopy, elemental analysis and mass spectrometry. The ^{119}Sn NMR spectra of the symmetrical complexes reveal the interaction of the three ligands with the tin nuclei. Long range ^{4}J(Sn–H) and ^{5}J(Sn–H) coupling is observed. Comparison with the corresponding silicon complexes shows a linear relationship between the chemical shifts of the ^{119}Sn and ^{29}Si nuclei. Tin-119 NMR spectroscopy indicates that the tin(IV) complexes are six-co-ordinate species, except for the Sn(trop)$_3$X (Htrop = tropolone, X = Cl, Br or I) complexes which are seven-co-ordinate. Mixed mono- and di-basic bidentate ligand complexes form neutral six-co-ordinate complexes.

There has been considerable interest in the chemistry of the element silicon with particular emphasis on the biological aspects. However, the aqueous chemistry of the other Group IV elements has been largely neglected. Until now tin chelates, as models for the role of tin in biological systems, have been poorly investigated.

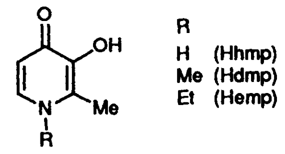
We have recently reported a series of six-co-ordinate bis(bidentate ligand)dihalogenotin complexes with monobasic ligands. The *cis–trans* isomerisation observed was analysed using ^{119}Sn NMR spectroscopy.[1] In 1931 Rosenheim *et al.*[2] proposed that $[Si(cat)_3]^{2-}$ (H_2cat = catechol) species may act as agents for solubilising silica in nature. We have previously reported[1] various tris(catecholato)silicon complexes which were studied by ^{29}Si NMR spectroscopy. Here we present NMR studies of the corresponding tin(IV) complexes. These complexes have been characterised by elemental analysis, fast atom bombardment (FAB), and electron impact (EI) mass spectrometry and liquid secondary ion mass spectroscopy (LSIMS) and multinuclear (^{1}H and ^{119}Sn) NMR spectroscopy.

Experimental

Materials.—Tin tetrachloride pentahydrate, tin tetrachloride, tin tetrabromide, tin tetraiodide, 4-nitrocatechol (H_2ncat) and 3,4-dihydroxynaphthalene [H_2(3,4-napdo)] were obtained commercially from Aldrich and were used without further purification. Catechol was purified by sublimation. Tropolone (Htrop) (2-hydroxycyclohepta-2,4,6-trien-1-one) was obtained from Lancaster.

4-Methylcatechol[3] (H_2mcat), 4-chlorocatechol[4,5] (H_2ccat), 4,5-dichlorocatechol[5] (H_2dccat), 4,5-dibromocatechol[6] (H_2dbcat), 4,5-dinitrocatechol[7] [H_2(4,5-dncat)], 3-hydroxy-2-methylpyridin-4-one[8] (Hhmp), 3-hydroxy-1,2-dimethylpyridin-4-one[9] (Hdmp) and 1-ethyl-3-hydroxy-2-methylpyridin-4-one[9] (Hemp) were prepared by literature methods.

Physical Measurements.—Proton and ^{119}Sn NMR spectra were recorded on JEOL GSX270 (270 MHz), JEOL EX270 (270 MHz) and Bruker WM250 (250 MHz) spectrometers and ^{119}Sn cross-polarisation magic-angle-spinning (CP MAS) NMR on a Bruker MSL 300 (300 MHz) spectrometer. Chemical shifts are quoted relative to tetramethylsilane for the ^{1}H nucleus and relative to tetramethyltin for the ^{119}Sn nucleus. Mass spectra were recorded on Micromass VG 7070E, VG Analytical 2AB-SE and VG Autospec Q spectrometers in the FAB, EI or LSIMS mode, with the sample suspended in either a *m*-nitrobenzyl alcohol or a dimethyl sulfoxide–glycerol matrix.



Preparation of the Tin(IV) *Complexes.*—The complexes derived from tropolone were prepared as described in the literature, by the addition of the free ligand to Sn(trop)$_2$X$_2$.[10] The catecholato complexes were prepared using a method analogous to that first described by Weinland and Maier[11] for the preparation of $Y_2[Sn(cat)_3]$.

[Sn(emp)$_3$]Cl. Tin tetrachloride pentahydrate (0.75 g, 2.1 mmol) in water (1 cm^3) was added to a hot solution of Hemp (1 g, 6.5 mmol) in water (10 cm^3). The solution was stirred until a white precipitate formed which was then centrifuged, washed with water and dried *in vacuo* at 50 °C. This method gave quantitative yields. The corresponding complexes derived from Hhmp and Hdmp and from $SnBr_4$ and SnI_4 were prepared in a similar manner.

Results and Discussion

Salts of the $[Sn(cat)_3]^{2-}$ anion were first reported in 1926 by Weinland and Maier.[11] We have prepared a series of tin(IV) complexes with a variety of dibasic catechol derivatives. These complexes are formed by reaction of the ligands with tin tetrahalides in alkaline solution [equation (1)], where X = Cl, Br or I and Y is a cation, *e.g.* K.

$$SnX_4 + 3H_2L + 2YOH \longrightarrow Y_2[SnL_3] + 4HX + 2H_2O \quad (1)$$

The corresponding tris complexes derived from the monobasic ligands were prepared by two methods. The complex Sn(trop)$_3$Cl was previously prepared by Muetterties and Wright[10] in 1964 by the stepwise formation of Sn(trop)$_2$Cl$_2$, followed by the addition of a further equivalent of tropolone [equation (2)]. They found that the bromide and iodide complexes could be prepared under similar conditions from the corresponding Sn(trop)$_2$X$_2$ (X = Cl, Br or I) complexes. The complexes formed with Hhmp, Hdmp and Hemp can be prepared as described above and also directly, by

$$Sn(trop)_2X_2 + Htrop \longrightarrow Sn(trop)_3X + HX \quad (2)$$

Table 1 Microanalyses (%) for the complexes[a]

Complex	C	H	N	X
$[NH_4]_2[Sn(cat)_3]$	45.00 (45.15)	4.05 (4.20)	5.75 (5.85)	—
$[NH_4]_2[Sn(ncat)_3]$	35.05 (35.20)	2.65 (2.80)	11.35 (11.40)	—
$[NH_4]_2[Sn(4,5\text{-}dncat)_3]\cdot 2H_2O$[b]	27.50 (27.55)	2.40 (2.30)	14.05 (14.25)	—
$[NH_4]_2[Sn(ccat)_3]$	36.90 (37.10)	4.70 (4.35)	4.80 (4.80)	18.15 (18.25)
$[NH_4]_2[Sn(dccat)_3]\cdot 2.5H_2O$[b]	29.65 (29.60)	2.70 (2.60)	3.80 (3.85)	28.95 (29.10)
$[NH_4]_2[Sn(cncat)_3]$[c]	45.55 (45.55)	2.95 (3.10)	2.40 (2.65)	—
$[NBu_4]_2[Sn(3,4\text{-}napdo)_3]$	68.15 (68.90)	8.35 (8.40)	2.55 (2.60)	—
$[Sn(emp)_3]Cl\cdot 2H_2O$	43.75 (44.55)	5.00 (5.30)	6.35 (6.50)	6.70 (5.50)
$[Sn(emp)_3]Br\cdot H_2O$	42.10 (42.80)	4.65 (4.80)	6.10 (6.25)	11.65 (11.85)
$[Sn(emp)_3]I\cdot 2H_2O$	39.80 (39.05)	4.15 (4.65)	5.70 (5.70)	18.15 (17.20)
$[Sn(dmp)_3]Cl\cdot 2H_2O$	41.05 (41.70)	4.65 (4.65)	6.70 (6.95)	5.80 (5.85)
$[Sn(dmp)_3]Br\cdot H_2O$	39.30 (39.95)	3.90 (4.15)	6.50 (6.65)	12.15 (12.65)
$[Sn(dmp)_3]I\cdot 2.5H_2O$	35.60 (35.75)	3.70 (4.15)	5.80 (5.95)	19.70 (18.00)
$[Sn(hmp)_3]Cl\cdot HCl$	38.75 (38.40)	3.70 (3.40)	7.50 (7.45)	14.00 (12.60)
$[Sn(hmp)_3]Br\cdot 5H_2O$	33.55 (33.60)	3.65 (3.75)	6.45 (6.55)	12.15 (12.40)
$[Sn(hmp)_3]I\cdot 3H_2O\cdot 0.3HI$	30.20 (30.45)	2.75 (3.45)	5.80 (5.20)	21.90 (23.20)
$Sn(trop)_3Cl\cdot H_2O$	48.20 (47.40)	3.20 (3.20)	—	6.15 (6.60)

[a] All samples dried at 50 or 70 °C *in vacuo*. Calculated values are in parentheses. [b] Not dried *in vacuo*. [c] H_2cncat = 4-Cyanocatechol.

Table 2 Proton NMR chemical shifts for the six-co-ordinate $[SnL_3]X$ complexes in $(CD_3)_2SO$ (270 MHz)

	δ				
Complex	H^6	H^5	CH_3	NR[a]	CH_2CH_3
$[Sn(emp)_3]Cl$[b]	8.07	6.97	2.50	4.27	1.36
$[Sn(emp)_3]Br$[c]	8.06	6.95	2.49	4.26	1.34
$[Sn(emp)_3]I$[b]	8.07	6.99	2.50	4.27	1.36
$[Sn(dmp)_3]Cl$[b]	8.03	6.92	2.45	3.92	—
$[Sn(dmp)_3]Br$[d]	8.01	6.90	2.44	3.91	—
$[Sn(dmp)_3]I$	7.93	6.83	2.46	3.93	—
$[Sn(hmp)_3]Cl$[e]	7.81	6.90	2.39	13.75	—
$[Sn(hmp)_3]Br$	7.82	6.90	2.30	13.47	—
$[Sn(hmp)_3]I$	7.75	6.82	2.29	13.36	—
Hemp	7.73	6.43	2.27	4.00	1.19
Hdmp	7.53	6.06	2.25	3.61	—
Hhmp	7.40	6.09	2.18	—	—
Hmal[f]	8.00	6.32	2.20	—	—

[a] R = H(hmp), Me(dmp) or Et(emp). [b] *J*(Sn–H) = 8.58 Hz. [c] *J*(Sn–H) = 8.25 Hz. [d] *J*(Sn–H) = 7.25 Hz. [e] *J*(Sn–H) = 7.92 Hz. [f] Hmal = malonic acid.

Table 3 FAB mass spectra results for the $Y_2[SnL_3]$ complexes

	m/z[b]		
Complex[a]	$[Sn^{IV}L_2(HL)]^-$	$[Sn^{IV}(HL)_3]^+$	$[Sn^{IV}L(HL)]^+$
$[NH_4]_2[Sn(cat)_3]$	445[c]	447 (47)	337 (100)[d]
$[NH_4]_2[Sn(dccat)_3]$	649[e]	650 (85)	473 (100)
$[NH_4]_2[Sn(dbcat)_3]$	917	917 (100)	652 (66)
$[NH_4]_2[Sn(ncat)_3]$	580[e]	—	—
$[NBu_4]_2[Sn(3,4\text{-}napdo)_3]$	595[d]	—	—

[a] Major isotope ^{120}Sn. [b] Figures in parentheses represent relative intensities. [c] Dimethyl sulfoxide–glycerol matrix. [d] *m*-Nitrobenzyl alcohol matrix. [e] LSIMS.

Table 4 Mass spectra results for the $[SnL_3]X$ (FAB^+) and SnL_3X (EI^+) complexes

	m/z[b]		
Complex[a]	$[Sn^{II}L]^+$	$[Sn^{IV}L_3]^+$	Matrix
$[Sn(hmp)_3]Cl$	244 (100)	492 (53)	*c*
$[Sn(hmp)_3]Br$	244 (100)	492 (57)	*c*
$[Sn(hmp)_3]I$	244 (100)	492 (69)	*d*
$[Sn(dmp)_3]Cl$	258 (24)	534 (100)	*d*
$[Sn(dmp)_3]Br$	258 (100)	534 (61)	*c*
$[Sn(dmp)_3]I$	258 (100)	534 (24)	*d*
$[Sn(emp)_3]Cl$	272 (65)	576 (100)	*d*
$[Sn(emp)_3]Br$	272 (100)	576 (76)	*c*
$[Sn(emp)_3]I$	272 (89)	576 (100)	*d*
$Sn(trop)_3Cl$[e]	241 (100)	483 (4)	
$Sn(trop)_3Br$[f]	241 (100)	483 (0)	
$Sn(trop)_3I$[g]	241 (100)	483 (0)	

[a] Major isotope ^{120}Sn. [b] Figures in parentheses represent relative intensities. [c] *m*-Nitrobenzyl alcohol matrix. [d] Dimethyl sulfoxide–glycerol matrix. [e] Also SnL_2Cl 397 (69) and $Sn^{II}Cl$ 155 (10). [f] Also SnL_2Br 441 (48) and $Sn^{II}Br$ 199 (90). [g] Also SnL_2I 489 (8) and $Sn^{II}I$ 247 (61).

the reaction of a tin tetrahalide with a stoichiometric amount of ligand in aqueous solution.

The results of the elemental analyses for the $[SnL_3]X$ complexes are presented in Table 1. They show good analytical purity for the chemical formulae proposed. The ^1H NMR spectroscopy results for these complexes are presented in Table 2. By comparison with the ^1H NMR spectra of the free ligands (Table 2) it is noted that, as for the SnL_2X_2 complexes described previously,[1] there is a downfield shift for both H^5 and H^6, indicating that the protons are more deshielded in the complexes.

Table 3 shows the mass spectrometry for the $Y_2[SnL_3]$ complexes. The parent ions are observed in both positive and negative FAB. The data for the SnL_3X complexes, which were obtained using either EI^+ or FAB^+ conditions as appropriate, are in Table 4. In all cases the parent $[SnL_3]^+$ ion is observed. Whereas hydrolysis products corresponding to $[ML_2(OH)]^+$ are observed for the analogous silicon and titanium complexes,[12] no such species are observed for the tin complexes demonstrating their greater stability to hydrolysis. For the tropolonato complexes the $[Sn(trop)_2X]^+$ ion is seen as a major fragment, suggesting that there is a stronger metal–halogen interaction (see below).

The ^{119}Sn NMR chemical-shift range observed for the catecholato complexes is δ −445 to −470 (Fig. 1) whereas for the complexes formed with the monobasic ligands (except Htrop) it is δ −452 to −458 (Table 5). These ranges are comparable to those found for the SnL_2Cl_2 (L = hmp, dmp or emp) complexes previously reported,[1] indicating that these are also six-co-ordinate tin(IV) species in solution. The crystal structure of a tris(catecholato)tin(IV) complex has recently been reported,[1] showing that the complex is six-co-ordinate in the solid state. The ^{119}Sn CP MAS NMR results shown in Table 5, for the $[Sn(dmp)_3]X$ (X = Cl, Br or I) complexes, are in agreement with the solution studies, indicating that the geometry remains essentially the same in both the solution and solid state.

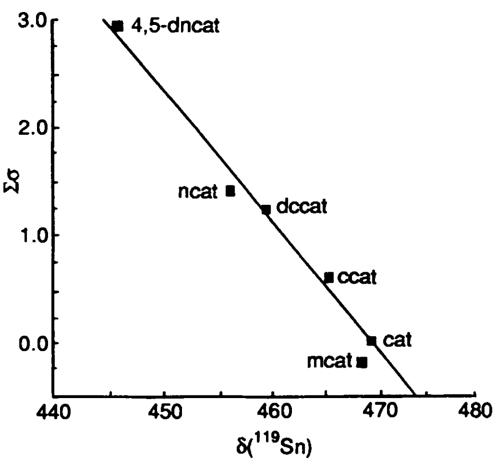


Fig. 1 Graph to show the Hammett factors *versus* $\delta(^{119}Sn)$

Table 5 Tin-119 NMR chemical shifts for the six-co-ordinate $[SnL_3]X$ and seven-co-ordinate SnL_3X complexes in Me_2SO (100.6 MHz)

Complex L	δ^a Cl	Br	I
hmp	−457.6	−457.6	−457.7
dmp	−453.4	−453.6	−451.7
dmp^b	−452.7	−452.6	−452.7
emp	−454.9	−454.4	−452.6
trop	−644.8	−727.3	—

[a] All values referenced to a secondary reference liquid $SnMe_4$ (at −150 ppm relative to neat $SnCl_4$). [b] CP MAS NMR [reference solid $C(SnMe_3)_4$ at 48.2 ppm].

As can be seen there is an appreciable overlap in the two ^{119}Sn NMR chemical-shift ranges, implying that the charge difference between the mono- and di-basic ligands has little effect on the shielding of the tin nuclei. The main factor affecting the chemical shift of the catecholato complexes appears to be associated with the electron density on the oxygens, ligands substituted with electron-withdrawing groups giving increased deshielding of the tin nucleus. For the 4- and 4,5-substituted catechols there is a reasonable correlation between δ and Σσ, where Σσ is the sum of the Hammett σ_m and σ_p values for the substituent, calculated with respect to the oxygens (Fig. 1). Similarly a correlation between $\delta(^{29}Si)$ and Σσ was found for the corresponding complexes,[13] thus a linear relationship was expected between the ^{119}Sn and ^{29}Si NMR chemical shifts (Fig. 2). The gradient found for this plot is *ca.* 3.5 which is somewhat smaller than that found[14] for organometallic complexes (5.6), indicating a relative reduction in sensitivity of the tin nucleus with respect to the silicon nucleus towards shielding effects.

For the complexes formed with the hydroxymethylpyridinones very little change is observed on changing from Hhmp to Hdmp to Hemp. Although theoretically the electron-donating ability of the alkyl groups is greater, the observed ionisation constants differ only slightly[15] and this is reflected in the similarity of the chemical shifts.

The crystal structures of $Sn(trop)_3Cl$ and $Sn(trop)_3(OH)$ show that this type of complex is seven-co-ordinate in the solid state.[16] The mass spectrometry for the complexes prepared in this work shows a strong interaction between the tin and halogen which could also indicate that these are seven-co-ordinate. This increase in the co-ordination number is reflected in the ^{119}Sn NMR spectra: $Sn(trop)_3Cl$ is *ca.* 200 ppm upfield from typical six-co-ordinate oxygen-donor complexes. Further, on changing to the bromo analogue a further upfield shift of *ca.* 80 ppm is observed. This correlates well with the results observed for the SnL_2X_2 complexes where the change in δ ($SnL_2Cl_2 \longrightarrow SnL_2Br_2$) is in the range δ 170–200.[1]

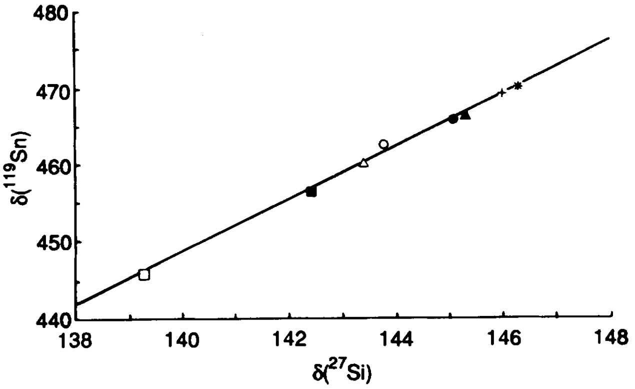


Fig. 2 Plot of $\delta(^{27}Si)$ *versus* $\delta(^{119}Sn)$ for □, $M(4,5\text{-dncat})_3$; ■, M(ncat); ○, $M(cat)(ncat)_2$; ●, $M(cat)_2(ncat)$; △, $M(dccat)_3$; ▲, $M(ccat)_3$; +, $M(mcat)_3$; and ✱, $M(cat)_3$

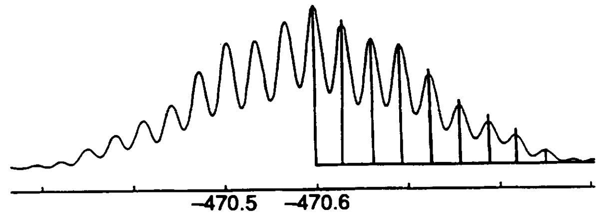


Fig. 3 Tin-119 NMR spectrum (D_2O, 93.28 MHz) of $[Sn(cat)_3]^{2-}$. Superimposed stick diagram shows the expected intensities for a heptuplet of heptuplets normalised to the central peak as unity

The complexes formed with the monobasic ligands Hhmp, Hdmp or Hemp do not appear to be seven-co-ordinate, even when their preparation is attempted in non-polar solvents. A possible explanation for this may be that the hmp^-, dmp^- and emp^- ions are more efficient electron donators than the $trop^-$ ion [pK_1 ≈3.7 *versus* pK_1(Htrop) = −0.52].[15,17] Thus the tendency for the tropolonato complexes to form an M–X bond seems to be greater. The different co-ordination numbers which may be observed for the tin(IV) nucleus are clearly reflected by the chemical-shift range in the ^{119}Sn NMR spectra.

The only complexes studied here with symmetrical ligands were those with catechol, the 4,5-disubstituted catechols and tropolone. Tin-119–proton interactions could be observed in both the ^{119}Sn and ^1H NMR spectra. Consequently, we have studied the proton-coupled ^{119}Sn NMR spectra of some 4,5-disubstituted catechols, where we would expect a heptuplet to arise due to coupling with the six equivalent protons in the three catechols. This was observed for H_2dcat, H_2dbcat, $H_2(4,5\text{-dncat})$ and $H_2(3,4\text{-napdo})$.

For the $[Sn(cat)_3]^{2-}$ complex a heptuplet of heptuplets would be expected to arise from ^4J(Sn–H) and ^5J(Sn–H) couplings. However experimentally a simpler spectrum is obtained (Fig. 3) which is attributed to overlap where $^4J \approx 3 \times {}^5J = 17.2$ Hz. A superimposed stick diagram is shown representing the predicted ratios, which is in accord with the experimental results.

Seven-fold co-ordination of the tropolonato complexes results in the loss of C_3 symmetry within the complexes and therefore the corresponding coupling constants are affected by the co-ordinated halogen and are no longer equivalent. Resolution of these couplings was not possible.

Equilibrium of an equimolar mixture of $[Sn(ncat)_3]^{2-}$ and $[Sn(cat)_3]^{2-}$ was achieved after 5 h. The ^{119}Sn NMR spectrum of the equilibrated solution shows a statistical distribution of all the expected species in the ratio 1:3:3:1. If the mixed complex distribution was dominated by overall

Table 6 Tin-119 NMR chemical shifts [$(CD_3)_2SO$, 100.6 MHz] and mass spectral values for the mixed ML_2L' complexes

		m/z*		
Complex	δ	$Sn^{II}L$	SnL_2L'	$SnL_2L'{\cdot}xNH_3$
$Sn(mal)_2$(3,4-napdo)	−460.0	245 (100)	582 (9)	371 (24)
$Sn(mal)_2$(cat)	−458.5	245 (29)	—	495 (67)
$Sn(mal)_2$(dccat)	−456.8	245 (100)	548 (12)	371 (100)
$Sn(dhp)_2$(dccat)	−474.3	230 (100)	518 (11)	586 (23)
$Sn(trop)_2$(dccat)	−461.8	241 (100)	573 (54)	—

* Figures in parentheses represent relative intensities.

electronic stability then the $[Sn(cat)(ncat)_2]^{2-}$ and $[Sn(ncat)(cat)_2]^{2-}$ resonances should dominate the spectrum as this would minimise the concentration of the 'weak' complex $[Sn(cat)_3]^{2-}$

Under the conditions described here tris(bidentate ligand) complexes with the softer ligands malonic acid (Hmal), 3-hydroxypyridin-2-one (Hdhp) or 5-hydroxy-2-hydroxymethyl-4*H*-pyran-4-one (Hkoj) could not be prepared. An attempt to prepare mixed $[ML'_2L'']^+$ complexes using a mixture of one of these ligands and Hhmp, Hdmp or Hemp was also unsuccessful. However mixed mono- and di-basic complexes were obtained in two ways. First by reaction of ML'_2I_2 (where L' = Hmal, Hkoj or Hdhp) with a stoichiometric equivalent of a catechol derivative in a polar solvent [equation (3)]. Secondly

$$SnL'_2I_2 + H_2L'' \longrightarrow SnL'_2L'' + 2HI \qquad (3)$$

by reaction of tin tetraiodide with stoichiometric amounts of the two ligands in a chloroform–ethanol mixture, as shown in equation (4). The ^{119}Sn NMR data and the results for the mass

$$SnI_4 + 2HL' + H_2L'' \longrightarrow SnL'_2L'' + 4HI \qquad (4)$$

spectrometry are presented in Table 6. As was observed for the tris(catecholato) complexes of tin an additive change in the ^{119}Sn chemical shift occurs {*cf.* $[Sn(cat)_3]^{2-}$, $\delta \approx -470$ and $[Sn(dccat)_3]^{2-}$, $\delta \approx -460$, see Fig. 1}.

These reactions do not proceed well for the hydroxymethylpyridinones. The major products appear to be the tris complexes $[ML'_3]^+$ and $[ML_3]^{2-}$. The preparation of complexes of this type with Hmal has recently been reported by the oxidative addition of quinones to $Sn^{II}L_2$.[18]

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