Inorganica Chimica Acta, 71 (1983) 101–107

Tin-119 NMR Studies on some Adducts of Tin(IV) Halides

RAY COLTON and DAINIS DAKTERNIEKS

Department of Inorganic Chemistry, University of Melbourne, Parkville, Vic. 3052, Australia

Received September 30, 1982

Tin-119 and phosphorus-31 NMR spectra have been recorded for $SnCl_4L_2$, $SnBr_4L_2$ (L = tributylphosphine oxide) and mixtures thereof. The compound $SnCl_4L_2$ exists predominantly as the trans *L_2 isomer with a small proportion of the* cis *L_2 isomer also present in solution whereas $SnBr_4L_2$ appears to be present only as the* trans *L_2 isomer. In the mixed solution all the* trans *$SnCl_xBr_{4-x}L_2$ species are observed. The anionic complexes $[SnCl_5L]^-$ and $[SnBr_5L]^-$ both show slight dissociation in solution to SnX_4L_2 and $[SnX_6]^{2-}$ (X = Cl, Br). The tin-119 NMR spectrum of an equimolar mixture of $[SnCl_5L]^-$ and $[SnBr_5L]^-$ shows ten of the possible twelve $[SnCl_xBr_{5-x}L]^-$ species.*

In contrast, SnX_4L_2 (L' = acetone; X = Cl, Br) exist predominantly as cis *L'_2 isomers. A 1:1 mixture of the complexes in dichloromethane solution at –50 °C shows average tin-119 resonances for each stoichiometry of mixed halo species* cis *$SnCl_xBr_{4-x}L'_2$. Subsequent cooling to –100 °C slows intramolecular processes sufficiently to enable observation and identification of most of the individual geometric isomers of each stoichiometry. The anionic complexes $[SnCl_5L']^-$ and $[SnBr_5L']^-$ show no appreciable dissociation in dichloromethane solution and the tin-119 spectrum of a 1:1 mixture of these compounds at –100 °C shows only six resonances corresponding to various $[SnCl_xBr_{5-x}L']^-$ species without distinguishing between individual isomers of each stoichiometry. Cooling to –110 °C enables identification of some of these isomers.*

The pairwise additivity model, using previously established interaction parameters, was used to assign all isomeric species observed in the tin-119 spectra of these systems.

Introduction

Adducts of tin(IV) halides SnX_4L_2 involving neutral oxygen, sulphur, selenium or nitrogen donors (L) have been well characterised by Raman, infrared and Mössbauer spectroscopy [1, 2]. Ruzicka and Merbach have studied *cis–trans* equilibria for various SnX_4L_2 adducts in solution using vibrational [3] as well as ^1H, ^{19}F and ^{31}P NMR spectroscopy [4]. More recently the $SnX_4(PBu_3)_2$ and $[SnX_5(PBu_3)]^-$ systems (X = Cl, Br) were examined for which *trans* $SnCl_xBr_{4-x}(PBu_3)_2$ (6 species) and $[SnCl_xBr_{5-x}(PBu_3)]^-$ (12 species) were identified [5]. It was also shown that the pairwise additivity model for calculating chemical shifts of the central atom [6] was very useful in enabling identification of individual tin species.

In this paper we extend the applicability of the additivity model and now report studies for two other ligands, tributylphosphine oxide and acetone, which show rather different behaviour to the PBu_3 system and to each other.

Experimental

All NMR spectra were recorded on a JEOL FX100 spectrometer, tin-119 at 37.06–37.08 MHz and phosphorus-31 at 40.26 MHz, using external ^7Li lock. Tin-119 NMR spectra were referenced against external $SnMe_4$ and phosphorus-31 spectra against external 85% H_3PO_4. High frequency positive convention is used. Temperatures were maintained using a JEOL NM 5471 controller.

All solutions were prepared under a dry nitrogen atmosphere using A.R. dichloromethane as solvent. The pentahalo anions $[SnCl_5]^-$ and $[SnBr_5]^-$ were prepared by interaction of tin(IV) halide and one mol of NBu_4X in dichloromethane. Other compounds were from commercial sources.

Results and Discussion

Tributylphosphine Oxide Adducts

At 30 °C the phosphorus-31 and tin-119 NMR spectra of $SnCl_4L_2$ (L = tributylphosphine oxide) show coupling $^2J_{Sn-P}$ and the presence of *cis* and *trans* L_2 isomers, the *cis* L_2 isomer being present in

0020-1693/83/0000-0000/$03.00

TABLE I. NMR Data[a] for $SnCl_xBr_{4-x}L_2$ (L = tributylphosphine oxide) Compounds in Dichloromethane Solution at –30 °C.

Compound	$\delta(^{119}Sn)$ rel. $SnMe_4$ (ppm)	$\delta(^{119}Sn)$ rel. $SnCl_4$ (ppm)		$^2J(Sn-P)$ (Hz)
		Expt.	Calc.[b]	
trans L_2 *Compounds*				
1 $SnCl_4L_2$	–700	–550	–550	137
2 $SnCl_3BrL_2$	–871	–721	–723	130
3 $SnCl_2Br_2L_2$ (*t* Cl, Cl)	–1048	–898	–897	137
4 $SnCl_2Br_2L_2$ (*c* Cl, Cl)	–1053	–903	–918	150
5 $SnClBr_3L_2$	–1260	–1110	–1113	163
6 $SnBr_4L_2$	–1479	–1329	–1329	185
cis L_2 *Compounds*[c]				
7 $SnCl_4L_2$	–707	–557	–557	176
8 $SnCl_3BrL_2$ (Cl, Cl)	–881	–731	–731	180
9 $SnCl_3BrL_2$ (Cl, Br)	–887	–737	–737	189
10 $SnCl_2Br_2L_2$ (Cl, Cl)	–1040	–890	–905	172
11 $SnCl_2Br_2L_2$ (Cl, Br)			–932	
12 $SnCl_2Br_2L_2$ (Br, Br)			–937	
13 $SnClBr_3L_2$(Cl, Br)	–1248	–1098	–1126	185
14 $SnClBr_3L_2$(Br, Br)			–1153	
15 $SnBr_4L_2$			–1370	

[a] Estimated error in $\delta(^{119}Sn)$ ±2 ppm; estimated error in $^2J(Sn-P)$ ±5 Hz. [b] Interaction parameters in ppm: Cl–Cl = 0, Cl–Br = –46.2, Br–Br = –113.3, Cl–L = –68.7, Br–L = –109.4, L–L = –144.9. [c] The group *trans* to the L groups is indicated after the formula.

only about 5% abundance (the identification of the isomers is discussed below). Dichloromethane solutions of $SnBr_4L_2$ require cooling to –20 °C before coupling $^2J_{Sn-P}$ is observed and at this temperature only the *trans* L_2 isomer is observed in the phosphorus-31 and tin-119 NMR spectra. The phosphorus-31 chemical shifts for the two *trans* L_2 compounds ($SnCl_4L_2$ $\delta(^{31}P)$ = 68.8 ppm; $SnBr_4L_2$ $\delta(^{31}P)$ = 67.9 ppm) differ by only 1 ppm, since coordination is through oxygen and not phosphorus, with the result that phosphorus-31 NMR is not a good probe with which to study this system. However, the tin-119 resonances for the two adducts are separated by almost 800 ppm and consequently are more informative. Tin-119 spectra for this system were subsequently recorded at –30 °C so that interaction parameters derived from the $SnCl_6^{2-}/SnBr_6^{2-}$ system [5] could be directly used.

A 1:1 mixture of $SnCl_4L_2$ and $SnBr_4L_2$ in dichloromethane solution gives complex tin-119 and phosphorus-31 NMR spectra. Identification of the species present was not possible from the phosphorus-31 spectrum because of overlapping resonances. However, the tin-119 spectrum consists of five major groups of resonances which are well separated, each group being dominated by an intense triplet (Fig. 1). The outermost triplets are identified as *trans*-$SnCl_4L_2$ and *trans*-$SnBr_4L_2$ respectively and the intermediate region corresponds to various isomers of $SnCl_xBr_{4-x}L_2$, whose identification was possible by use of the pairwise additivity model first proposed by Vladimiroff and Malinowski [6].

In the pairwise additivity model the chemical shift of the central atom is estimated by summing the interactions of the ligand along the edges of the coordination polyhedron, there being twelve such interactions in an octahedral molecule [7]. Taking $SnCl_4$ as the reference we have established [5] values of the interaction parameters for octahedral tin(IV) as Cl–Cl = 0, Cl–Br = –46.2 and Br–Br = –113.3 ppm at –30 °C and these values appear independent of other substituents in the coordination sphere of the tin atom. The additional interaction parametrs Cl–L = –68.7, Br–L = –109.4 ppm were calculated from the tin-119 resonances for each of the respective *trans*-SnX_4L_2 compounds. Subsequent calculation of expected tin chemical shifts for the remaining *trans*-$SnCl_xBr_{4-x}L_2$ species

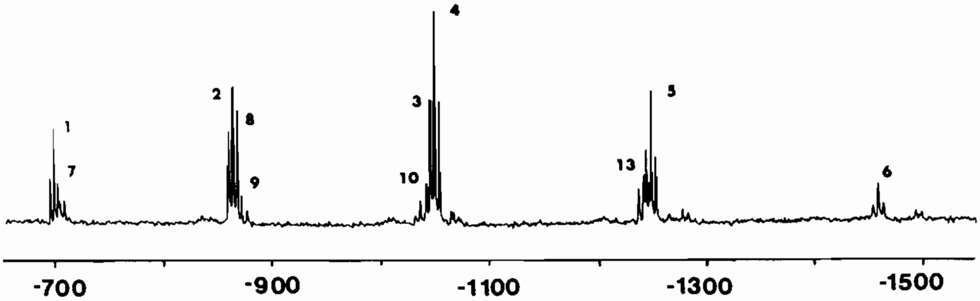

Fig. 1. Tin-119 NMR spectrum of an equimolar mixture of $SnCl_4L_2$ and $SnBr_4L_2$ in dichloromethane solution at –30 °C. For species numbering see Table I.

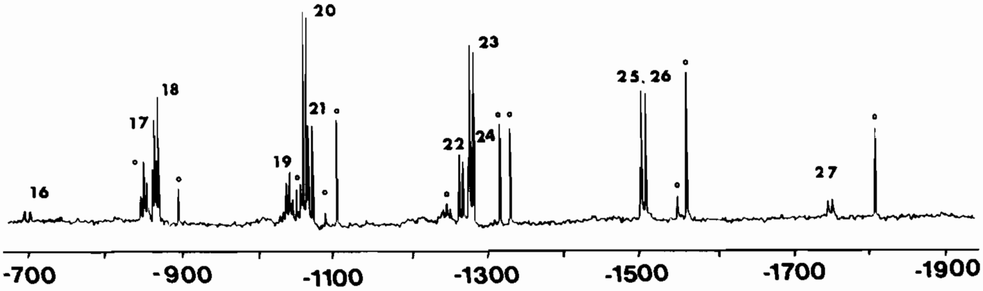

Fig. 2. Tin-119 NMR spectrum of an equimolar mixture of $[SnCl_5L]^-$ and $[SnBr_5L]^-$ in dichloromethane solution at –50 °C. For species numbering see Table II. ° Denotes species $SnCl_xBr_{4-x}L_2$ and $[SnCl_xBr_{6-x}]^{2-}$ formed according to equation 1.

give values very close to those observed for the main triplets in the tin-119 spectrum (Table I). The *trans*-$SnCl_xBr_{4-x}L_2$ isomers are present in concentrations close to a statistical distribution.

Additionally there are also some weaker resonances present in the tin-119 spectrum of the mixture. These resonances were identified as *cis*-$SnCl_xBr_{4-x}L_2$ isomers. If it is assumed that the less intense resonance (at lower frequency) observed in the spectrum of $SnCl_4L_2$ is due to the *cis*-$SnCl_4L_2$ isomer, this then allows a value of L–L = –144.9 ppm to be calculated. Using this value of L–L gives the calculated tin chemical shifts expected for various *cis*-$SnCl_xBr_{4-x}L_2$ isomers which are reasonably close to the extra resonances observed (Table I). Not all the possible *cis*-$SnCl_xBr_{4-x}L_2$ isomers are observed and this may be related to the fact that *cis*-$SnBr_4L_2$ does not appear in the spectrum of $SnBr_4L_2$ itself.

The compounds $[SnX_5L]^-$ (L = tributylphosphine oxide; X = Cl, Br) were generated in dichloromethane solution by mixing equimolar quantities of SnX_4, NBu_4X and tributylphosphine oxide. Although both phosphorus-31 and tin-119 spectra indicate some disproportionation of the type:

$$2[SnX_5L]^- \rightleftarrows SnX_4L_2 + [SnX_6]^{2-} \qquad (1)$$

(for $[SnCl_5L]^-$ $\delta(^{31}P)$ = 67.3 and for $[SnBr_5L]^-$ $\delta(^{31}P)$ = 65.8 ppm) this disproportionation is most clearly seen in the tin-119 spectra which show the presence of $[SnX_6]^{2-}$. Spectra were recorded at –50 °C to avoid ligand exchange.

A 1:1 mixture of $[SnCl_5L]^-$ and $[SnBr_5L]^-$ gave a variety of tin species at –50 °C. These species could not be identified for the phosphorus-31 spectrum but the tin-119 spectrum was more informative (Fig. 2) where ten of the twelve possible species (including isomers) of the series $[SnCl_xBr_{5-x}L]^-$ were identified. Significant quantities of $SnCl_xBr_{4-x}L_2$ and $[SnCl_xBr_{6-x}]^{2-}$ resulting from disproportionation of the pentahalo complexes were also obvious in the tin-119 spectrum.

Since the tin-119 spectrum of this mixture was recorded at –50 °C the appropriate halo interaction parameters were determined from the $[SnCl_6]^{2-}$/$[SnBr_6]^{2-}$ system at –50 °C. These new values for –50 °C are Cl–Cl = 0, Br–Cl = –47.5, Br–Br = –110.7 ppm. The interaction parameters Cl–L = –68.5, Br–L = –108.5 ppm were obtained from values of *trans*-$SnCl_4L_2$ and *trans*-$SnBr_4L_2$ measured at –50 °C. The pairwise additivity model allows prediction of tin chemical shifts for the singly charged species once a value of the chemical shift

TABLE II. NMR Data[a] for $[SnCl_xBr_{5-x}L]^-$ Species (L = tributylphosphine oxide) in Dichloromethane at −50 °C.

Compound[c]		$\delta(^{119}Sn)$ rel. $SnMe_4$ (ppm)	$\delta(^{119}Sn)$ rel. $SnCl_4$ (ppm)		$^2J(Sn-P)$ (Hz)
			Expt.	Calc.[b]	
16 $[SnCl_5L]^-$		−700	−550	−546	160
17 $[SnCl_4BrL]^-$	(Cl)	−880	−730	−729	160
18 $[SnCl_4BrL]^-$	(Br)	−883	−733	−736	185
19 $[SnCl_3Br_2L]^-$	(Cl, *t*)	−1053	−903	−911	160
20 $[SnCl_3Br_2L]^-$	(Cl, *c*)	−1073	−923	−927	170
21 $[SnCl_3Br_2L]^-$	(Br)	−1080	−930	−934	195
22 $[SnCl_2Br_3L]^-$	(Cl)	−1270	−1120	−1125	185
23 $[SnCl_2Br_3L]^-$	(Br, *t*)	−1283	−1133	−1132	185
24 $[SnCl_2Br_3L]^-$	(Br, *c*)	−1284	−1134	−1148	185
25 $[SnClBr_4L]^-$	(Cl)	−1501	−1351	−1339	210
26 $[SnClBr_4L]^-$	(Br)			−1362	
27 $[SnBr_5L]^-$		−1737	−1587	−1592	230

[a] Estimated errors as in Table I. [b] Interaction parameters in ppm: Cl–Cl = 0, Br–Cl = −47.5, Br–Br = −110.7 (calculated from $[SnCl_6]^{2-}/[SnBr_6]^{2-}$ system at −50 °C), Cl–L = −68.5, Br–L = −108.5, δ charge = −272. [c] The halide *trans* to L is indicated after the formula.

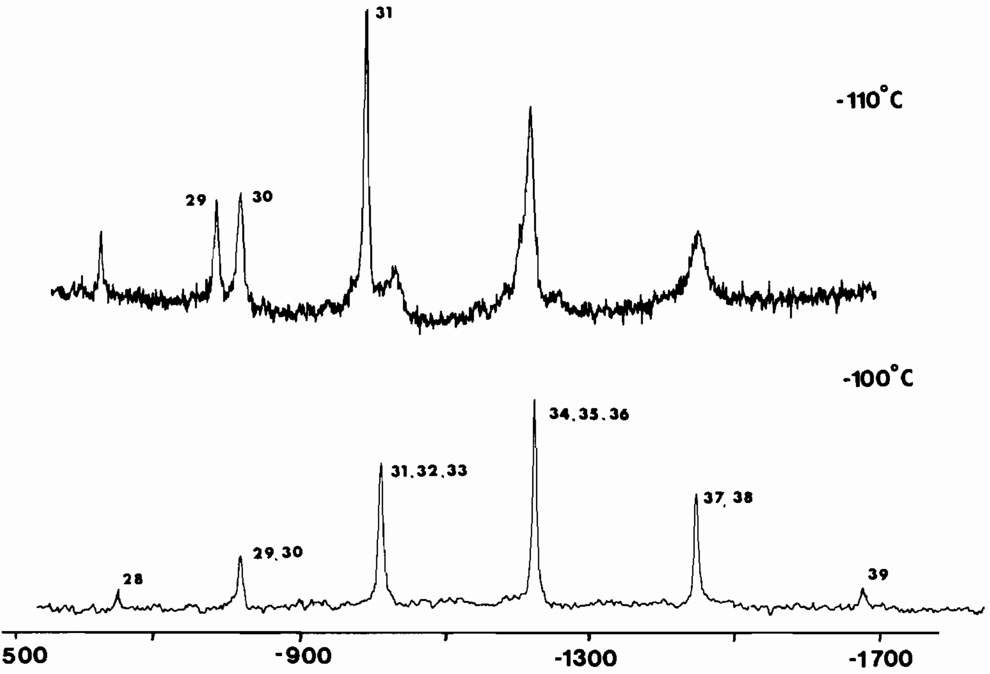

Fig. 3. Tin-119 NMR spectra of an equimolar solution on $[SnCl_5L']^-$ and $[SnBr_5L']^-$ in dichloromethane. For species numbering see Table III.

due to charge has been assigned. This correction for charge is assigned as before [5] by first calculating a provisional value based on the difference between the chemical shift of $[SnX_5L]^-$, calculated using the appropriate pairwise interaction parameters and the experimentally observed chemical shift for $[SnX_5L]^-$. These difference values (δ charge = −274 ppm for $[SnCl_5L]^-$, δ charge = −267 ppm for

TABLE III. Tin-119 NMR Data for $[SnCl_xBr_{5-x}L']^-$ Species (L' = acetone) in Dichloromethane at –100 °C.

Compound[a]		$\delta(^{119}Sn)$ rel. $SnMe_4$	$\delta(^{119}Sn)$ rel. $SnCl_4$ (ppm)	
			Expt.	Calc.[b]
28 $[SnCl_5L']^-$		–668	–518	–518
29 $[SnCl_4BrL']^-$	(Cl)	–841	–691[c]	–692
30 $[SnCl_4BrL']^-$	(Br)			–705
31 $[SnCl_3Br_2L']^-$	(Cl, *t*)	–1033	–883[d]	–866
32 $[SnCl_3Br_2L']^-$	(Cl, *c*)			–882
33 $[SnCl_3Br_2L']^-$	(Br)			–895
34 $[SnCl_2Br_3L']^-$	(Cl)	–1236	–1086[e]	–1072
35 $[SnCl_2Br_3L']^-$	(Br, *t*)			–1085
36 $[SnCl_2Br_3L']^-$	(Br, *c*)			–1101
37 $[SnClBr_4L']^-$	(Cl)	–1451	–1301	–1278
38 $[SnClBr_4L']^-$	(Br)			–1307
39 $[SnBr_5L']^-$		–1679	–1529	–1529

[a] The halide *trans* to L' is indicated after the formula. [b] Interaction parameters in ppm: Cl–Cl = 0, Br–Cl = –46.8, Br–Br = –109.5 (calculated from $[SnCl_6]^{2-}/[SnBr_6]^{2-}$ system at –100 °C),Cl–L = –61.5, Br–L = –95.3, δ charge = –272. [c] At –110 °C becomes two resonances at –666 and –697 ppm (rel. $SnCl_4$). [d] Split into two resonances at –865 and –904 ppm (rel. $SnCl_4$) at –110 °C. [e] Partially resolved into resonances at –1068 and –1081 ppm (rel. $SnCl_4$) at –110 °C.

$[SnBr_5L]^-$) were used to calculate the chemical shift of all members of the $[SnCl_xBr_{5-x}L]^-$ series. Errors were then minimised over all species and a value of δ charge = –272 ppm was found to give the best fit. Calculated and experimental tin-119 shifts are given in Table II.

Acetone Adducts

The complexes $[SnX_5L']^-$ (L' = acetone; X = Cl, Br) were prepared in dichloromethane solution from the appropriate pentahalo tin(IV) salt and acetone. The tin-119 NMR spectrum of $[SnCl_5L']^-$ at –100 °C shows only a small degree of dissociation (eqn. 1), but $[SnBr_5L']^-$ precipitates from solution at about –50 °C. A 1:1 mixture of $[SnCl_5L']^-$ and $[SnBr_5L']^-$ is soluble at –100 °C and the tin-119 NMR spectrum of this solution is shown in Fig. 3. The six observed resonances correspond to the various halide combinations $[SnCl_xBr_{5-x}L']^-$ but individual isomers are not resolved. The assumption of a chemical shift effect due to charge, δ charge = –272 ppm and using pairwise halo interaction parameters appropriate to –100 °C (Cl–Cl = 0, Br–Cl = –46.8, Br–Br = –109.5 ppm; as determined from the $[SnCl_6]^{2-}/[SnBr_6]^{2-}$ system at –100 °C) gives the additional interaction parameters Cl–L' = –61.5 and Br–L' = –95.3 ppm. Calculated chemical shifts obtained by using these interaction parameters are shown in Table III and are compared to observed tin-119 shifts. Although individual isomers are not seen, the position of the observed resonance for each stoichiometry is reasonable for rapid exchange between the isomers for each stoichiometry.

Cooling this mixture to –110 °C leads to marked changes in the tin-119 spectrum. The previous average resonance for the compound $[SnCl_4BrL']^-$ is now split into two signals, one for each of the possible isomers of this stoichiometry, *i.e.* species 29 and 30. The relative intensities of these resonances is not 1:4, thus suggesting that there is still some exchange process operative. At –110 °C the signal for $[SnCl_3Br_2L']^-$ is now partially resolved into a fairly sharp singlet and a fairly broad signal suggesting that one of the possible isomeric forms (*i.e.* species 31) is now 'frozen out' while the other two isomers (species 32 and 33) are still undergoing fairly rapid exchange. The remaining resonances, due to bromo rich species, are considerably broadened and, in fact, the resonance due to $[SnBr_5L']^-$ is too broad to be detected at –110 °C. These results are consistent with an intermolecular exchange process involving L' where exchange is more rapid for bromo rich species than for chloro rich species [8].

The complexes $SnX_4L'_2$ (L' = acetone; X = Cl, Br) were prepared in dichloromethane solution by adding slightly more than two mole equivalents of acetone to the appropriate tin(IV) tetrahalide. The tin-119 NMR spectrum of $SnCl_4L'_2$ at –100 °C shows two resonances (–622 ppm, –632 ppm), the one at higher frequency having only about 5–8% the intensity of the stronger resonance. Similarly $SnBr_4L'_2$ also gave a weak and a strong resonance (–1367

TABLE IV. Tin-119 NMR Data[a] for $SnCl_xBr_{4-x}L'_2$ Species (L' = acetone) in Dichloromethane at −100 °C.

Compound		$\delta(^{119}Sn)$ rel. $SnMe_4$ (ppm)	$\delta(^{119}Sn)$ rel. $SnCl_4$ (ppm)	
			Expt.	Calc.[b]
cis L'_2 *species*[c]				
40 $SnCl_4L'_2$		−632	−482	−482
41 $SnCl_3BrL'_2$	(Cl, Cl)	−790	−640	−643
42 $SnCl_3BrL'_2$	(Cl, Br)	−813	−663	−656
43 $SnCl_2Br_2L'_2$	(Cl, Cl)	−958	−808	−804
44 $SnCl_2Br_2L'_2$	(Cl, Br)	−988	−838	−833
45 $SnCl_2Br_2L'_2$	(Br, Br)		not resolved	−846
46 $SnClBr_3L'_2$	(Cl, Br)	−1170	−1020	−1010
47 $SnClBr_3L'_2$	(Br, Br)	−1190[d]	−1040	−1040
48 $SnBr_4L'_2$		−1383	−1233	−1232
trans L'_2 *species*				
49 $SnCl_4L'_2$		−1367	−1217	−1200
50 $SnBr_4L'_2$		−622	−472	−492

[a] Estimated errors as in Table I. [b] L'−L' = −113 ppm. Other interaction parameters as in Table III. [c] The halide *trans* to L' is indicated after the formula. [d] Peak broad.

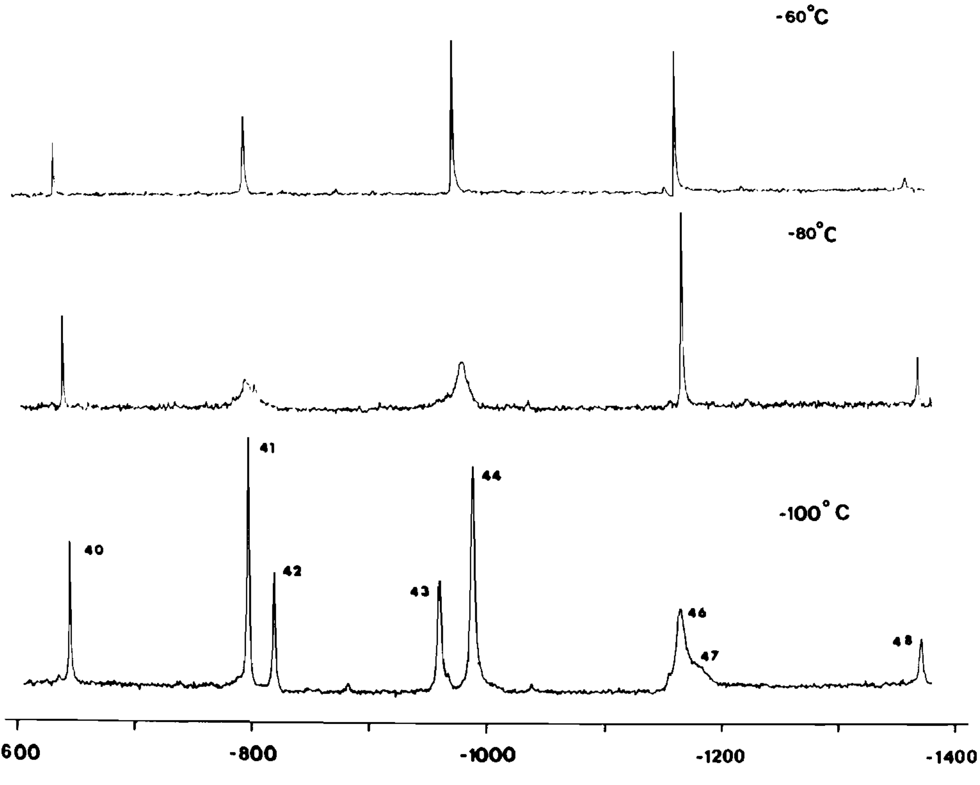

Fig. 4. Tin-119 NMR spectra of an equimolar solution of $SnCl_4L'_2$ and $SnBr_4L'_2$, containing a slight excess of L', in dichloromethane.

ppm, −1382 ppm) at −100 °C. It was previously shown that the adduct $SnCl_4L'_2$ exists predominantly as the *cis* isomer [3, 4] but the structure of $SnBr_4L'_2$ does not appear to have been determined. It is now assumed (and justified below) that the more intense resonance is in each case due to the *cis*-$SnX_4L'_2$ isomer and that the weaker resonance is in each case due to the *trans*-$SnX_4L'_2$ isomer.

The tin-119 NMR spectrum for a 1:1 mixture of $SnCl_4L'_2$ and $SnBr_4L'_2$ at −100 °C is shown in Fig. 4. Use of the interaction parameters derived for the $[SnX_5L']^-$ system gives the interaction parameter $L'-L' = -113$ ppm (identical values are obtained from $SnCl_4L'_2$ and $SnBr_4L'_2$). These interaction parameters were used to calculate expected chemical shifts for all the *cis* L'_2 isomers of $SnCl_xBr_{4-x}L'_2$ and give reasonable assignments for the observed tin-119 resonances (Table IV).

Tin-119 NMR spectra for the $SnCl_4L'_2/SnBr_4L'_2$ mixture recorded at various temperatures are also shown in Fig. 4. At temperatures above −40 °C only an extremely broad resonance, indicative of rapid intermolecular exchange, is observed. Cooling to −60 °C clearly shows the five resonances due to the various stoichiometries $SnCl_xBr_{4-x}L'_2$ without distinguishing between individual isomers. The resonance due to $SnBr_4L'_2$ is still a little broad at this temperature which is consistent with the acetone ligand still exchanging at a moderate rate. At −80 °C the resonance due to $SnBr_4L'_2$ has sharpened considerably while the resonances due to species of composition $SnCl_3BrL'_2$ and $SnCl_2Br_2L'_2$ have broadened, presumably due to slowing of acetone exchange with these species [8]. At −100 °C the isomers of $SnCl_3BrL'_2$ and $SnCl_2Br_2L'_2$ are clearly resolved indicating that intermolecular acetone exchange is now slow on the NMR time-scale at this temperature. The resonances due to the isomeric forms of $SnClBr_3L'_2$ are distinguishable though still fairly broad at −100 °C. Further cooling to −115 °C gives broader resonances, due probably to viscosity effects. These results are consistent with those observed for the anionic $[SnCl_xBr_{5-x}L']^-$ system and with the previous observation that dissociation of a ligand, in this case acetone, becomes easier from $SnCl_4$ to $SnBr_4$ adducts due to a reduction of effective charge on the tin atom [8].

Conclusions

The pairwise additivity model [6] may be successfully applied to enable identification of tin-119 resonances for a large range of octahedral adducts of tin(IV) halides with both *cis* and *trans* stereochemistry. The interaction parameters are essentially constant over a large temperature range for the series of tin(IV) adducts investigated and imply an essentially constant stereochemistry about the tin atom. The correction δ charge also appears fairly constant, the value for singly charged anions being half that found for doubly charged anions.

References

1 J. D. Dumas and M. Gomel, *Bull. Soc. Chim. France,* 1885 (1974).

2 R. Barbieri and A. Silvestri, *Inorg. Chim. Acta, 47,* 201 (1981).

3 S. J. Ruzicka and A. E. Merbach, *Inorg. Chim Acta, 20,* 221 (1976).

4 S. J. Ruzicka and A. E. Merbach, *Inorg. Chim. Acta, 22,* 191 (1977).

5 R. Colton, D. Dakternieks and C-A. Harvey, *Inorg. Chim. Acta, 61,* 1 (1982).

6 T. Vladimiroff and E. R. Malinowski, *J. Chem. Phys.,* 46, 1830 (1967).

7 R. G. Kidd and H. G. Spinney, *Inorg. Chem., 12,* 1967 (1973).

8 S. J. Ruzicka, C. M. P. Favez and A. E. Merbach, *Inorg. Chim. Acta, 23,* 239 (1977).