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Tin-119 and Carbon-13 NMR Studies on Tin(IV) Xanthates

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Tin-119 NMR spectroscopy of solutions containing $Sn(exa)_4$ and $Sn(isopropxa)_4$ establishes the existence of the mixed xanthates $Sn(exa)_n(i\text{-}propxa)_{4-n}$. Furthermore, evidence is obtained for the existence of mono-, di-, and trihaloxanthates in solutions of appropriate mixtures of the tetraxanthates, dihaloxanthates and tetrahalides. The xanthate ligands undergo temperature dependent monodentate–bidentate exchange about the tin atom which determines the nature of the complexes observed in the various mixtures.

Introduction

Crystal structure determination of metal xanthate complexes have shown that the xanthate may act as a monodentate or a bidentate ligand [1]. In $Sn(exa)_4$ [2] both monodentate and bidentate ligands are present, giving an effective *cis*-octahedral environment about the tin atom (Fig. 1). Similarly, the corresponding dihalide complexes $Sn(exa)_2X_2$ (X = Cl, Br, I) are also *cis*-octahedral about the tin in the solid state [3]. The dihalide complexes are conveniently made by oxidative addition of the halogen to the tin (II) xanthate

$Sn(exa)_2 + X_2 \rightarrow Sn(exa)_2X_2$

or by metathesis

$Sn(exa)_4 + SnX_4 \rightarrow 2Sn(exa)_2X_2$

Attempts to isolate the monohalides $Sn(exa)_3X$ or the trihalides $Sn(exa)X_3$ have so far not been successful.

Recently tin-119 NMR spectroscopy has been used successfully in the elucidation of solution structures [4, 5] of a variety of octahedral tin (IV) complexes of general formula $SnCl_xBr_{4-x}L_2$ and $[SnCl_xBr_{5-x}L]^-$ (L = tributylphosphine, tributylphosphine oxide, acetone).

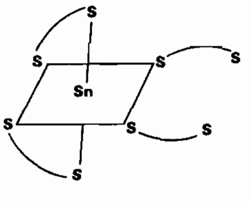

Fig. 1. The tin environment in $Sn(exa)_4$.

We now report tin-119 and carbon-13 NMR studies of a series of tin(IV) haloxanthate complexes in dichloromethane solution.

Experimental

NMR spectra were recorded on a JEOL FX 100 spectrometer, tin-119 at 37.06–37.08 MHz and carbon-13 at 25.0 MHz. Dichloromethane was the solvent. An external ^7Li lock was used and temperatures were maintained using a JEOL NM 5471 controller. Tin-119 NMR spectra were referenced against external $SnMe_4$ and carbon-13 against internal TMS. High frequency positive convention is used. Concentrations ranged between 0.1 *M* and 1.0 *M* and tris(acetylacetonato)chromium(III) was used as a paramagnetic relaxant.

The tin(IV) xanthates and the dihaloxanthates were prepared as previously described [3]. The compound $Sn(exa)_2ICl$ was made by the oxidative addition of ICl to $Sn(exa)_2$.

Results and Discussion

$Sn(mexa)_4$, $Sn(exa)_4$, $Sn(i\text{-}propxa)_4$, $Sn(exa)_n(i\text{-}propxa)_{4-n}$

The tin-119 NMR spectra of tetramethyl, tetraethyl and tetraisopropyl xanthates in dichloromethane solution at room temperature consisted of a sharp singlet (Table I) with half widths generally less than 25 Hz. Cooling solutions of $Sn(exa)_4$ or $Sn(i\text{-}propxa)_4$ to −90 °C causes little change to either the tin-119 or the carbon-13 spectra other than a small shift in the position of the resonances. These small changes in chemical shift are probably a result of increased viscosity at lower temperature.

The tin-119 NMR spectrum of a solution containing equimolar amounts of $Sn(exa)_4$ and $Sn(i\text{-}propxa)_4$ shows five resonances with intensities in proportion 1:4:6:4:1 as expected for a statistical distribution. The two outer resonances are identified by

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TABLE I. NMR Resonances for Tin Tetraxanthates in CH_2Cl_2.

Compound	$\delta(^{119}Sn)$ (ppm)	$\delta(^{13}C)^a$ (ppm)	Temperature (°C)
$Sn(mexa)_4$	−746	222.33	20
$Sn(exa)_4$	−739	221.07	20
	−746	220.87	−90
$Sn(i\text{-}propxa)_4$	−735	220.09	20
	−743	219.79	−90
$Sn(exa)(i\text{-}propxa)_3{}^b$	−736		20
$Sn(exa)_2(i\text{-}propxa)_2{}^b$	−737		20
$Sn(exa)_3(i\text{-}propxa)^b$	−738		20

[a] Chemical shift for the $O-C(S_2)$ carbon atom. [b] 1:1 mixture of $Sn(exa)_4$ and $Sn(i\text{-}propxa)_4$.

TABLE II. NMR Resonances for Tin Dihaloxanthates in CH_2Cl_2.

Compound	$\delta(^{119}Sn)$ (ppm)	$\delta(^{13}C)^a$ (ppm)	Temperature (°C)
$Sn(exa)_2Cl_2$	−762	226.80	20
	−759, −768,	225.84,	−80
	−778	226.50	
$Sn(exa)_2Br_2$	−1090	227.40	20
	−1068, −1092,	226.52	−80
	−1114		
$Sn(exa)_2I_2$	−1905,	229.16	20
	−1841, −1900,	228.08	−80
	−1955		
$Sn(exa)ClBr^b$	−921		20
	−910, −921,		−70
	−930, −940		
$Sn(exa)_2ClI^b$	−1311		20
	−1281, −1296,		−70
	−1331, −1341		
$Sn(exa)_2BrI^b$	−1495		20
	−1454, −1483,		−70
	−1455		
$Sn(i\text{-}propxa)_2Cl_2$	−758	225.1	20
	−754, −763,	224.30,	−80
	−772	224.96	
$Sn(exa)(i\text{-}propxa)Cl_2{}^c$	−760		20
	−756, −765		−80

[a] Chemical shift for the $O-C(S_2)$ carbon atom. [b] 1:1 mixtures of $Sn(exa)_2X_2$ where X = Cl, Br. [c] 1:1 mixtures of $Sn(exa)_2Cl_2$ and $Sn(i\text{-}propxa)_2Cl_2$.

their tin chemical shifts as being due to $Sn(exa)_4$ and $Sn(i\text{-}propxa)_4$.

The remaining resonances are assigned to the mixed ligand species $Sn(exa)(i\text{-}propxa)_3$, $Sn(exa)_2(i\text{-}propxa)_2$ and $Sn(exa)_3(i\text{-}propxa)$ (Table I). Cooling to −90 °C causes no change in the tin-119 spectrum other than a slight broadening of the resonances. Precipitation occurs below −90 °C. Observation of only five tin-119 resonances implies either that the xanthate ligands are monodentate or that there is rapid exchange between monodentate and bidentate xanthate groups even at low temperature.

$Sn(exa)_2X_2$ and $Sn(i\text{-}propxa)_2X_2$

The tin-119 NMR spectra of $Sn(exa)_2X_2$ (X = Cl, Br, I) and $Sn(i\text{-}propxa)_2Cl_2$ are readily observed in dichloromethane solution at room temperature and in each case comprises a single sharp resonance. Similarly only a single carbon-13 resonance due to the xanthate carbon is observed for each compound at room temperature (Table II).

Cooling solutions of these compounds to −80 °C causes the original tin-119 resonances to split into three new resonances of approximate relative intensities 16:8:1, the most intense resonance being at highest frequency. At −80 °C the carbon-13 spectra of $Sn(exa)_2Cl_2$ and $Sn(i\text{-}propxa)_2Cl_2$ each show two overlapping xanthate resonances with a relative intensity of approximately 2:1. The carbon-13 spectra of the other compounds contain only a single resonance attributable to the $O-C(S_2)$ carbon atom (Table II). We believe these tin-119 resonances are a manifestation of three different coordination modes of the

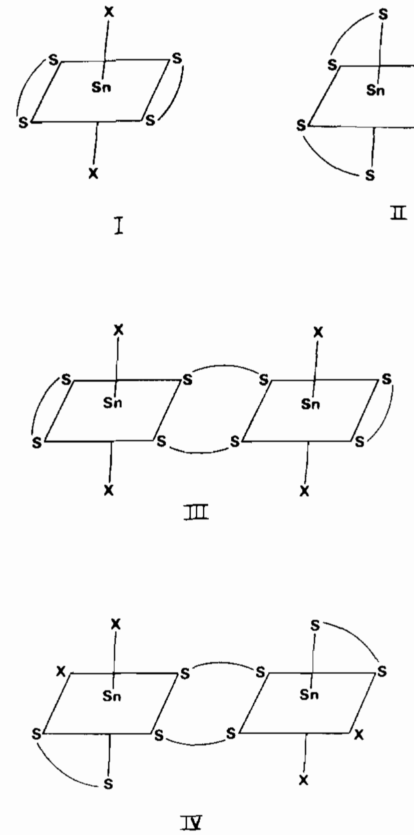

Fig. 2. Suggested structures of dihaloxanthates in solution at −80 °C.

xanthate ligand. The data are consistent with the existence of two isomeric and one polymeric form (Fig. 2), of $Sn(exa)_2Cl_2$. If the monodentate-bidentate exchange of the xanthate ligands in $Sn(exa)_2Cl_2$ is rapid at room temperature but slow at low temperature then the two most intense resonances in the tin-119 spectra may be assigned to *trans* and *cis* isomers (I and II in Fig. 2).

Earlier studies [4] have shown large differences in chemical shift between tin complexes with different coordination number. Since the tin-119 resonances for $Sn(exa)_2Cl_2$ are almost the same at room and low temperatures it must be assumed that there is no change in coordination number on cooling.

Assignment of the weakest resonance at low frequency is more tenuous but associated species containing bridging xanthate ligands (III and IV in Fig. 2) are consistent with the data.

Similar behaviour is noted for $Sn(exa)_2Br_2$ and $Sn(exa)_2I_2$. However in these cases only one carbon-13 resonance is observed at low temperature. A dichloromethane solution containing equimolar amounts of $Sn(exa)_2Cl_2$ and $Sn(exa)_2Br_2$ shows three tin-119 resonances of relative intensities 1:2:1 at room temperature. The two outer resonances are identified by their chemical shifts as due to the initial components whilst the central, most intense, resonance is assigned to the mixed halo species $Sn(exa)_2ClBr$. Similarly, appropriate 1:1 mixtures of $Sn(exa)_2X_2$ lead to the formation of $Sn(exa)_2BrI$ and $Sn(exa)_2ClI$. Interestingly, the tin-119 spectrum of $Sn(exa)_2ClI$ (which may be isolated as a pure solid) in dichloromethane is identical to that observed for the 1:1 mixture of $Sn(exa)_2Cl_2$ and $Sn(exa)_2I_2$. The positions of the resonances (Table II) are in good agreement with those expected for an average effect on $\delta(^{119}Sn)$ by different halogens. These experiments demonstrate not only the existence in solution of mixed halo species $Sn(exa)_2XX'$ but also show that halide exchange is slow on the NMR time scale although rapid on the preparative time scale. When the solutions are cooled to −80 °C the outer two resonances split as would be expected for the parent dihalocompounds (Fig. 3). The central resonances assigned to the mixed species $Sn(exa)_2XX'$ split into four signals for each of $Sn(exa)_2ClBr$ and $Sn(exa)_2ClI$ and into three signals for $Sn(exa)_2BrI$. These observations are consistent with rapid monodentate–bidentate ligand exchange slowing at room temperature and leading to formation of species of the type suggested in Fig. 2.

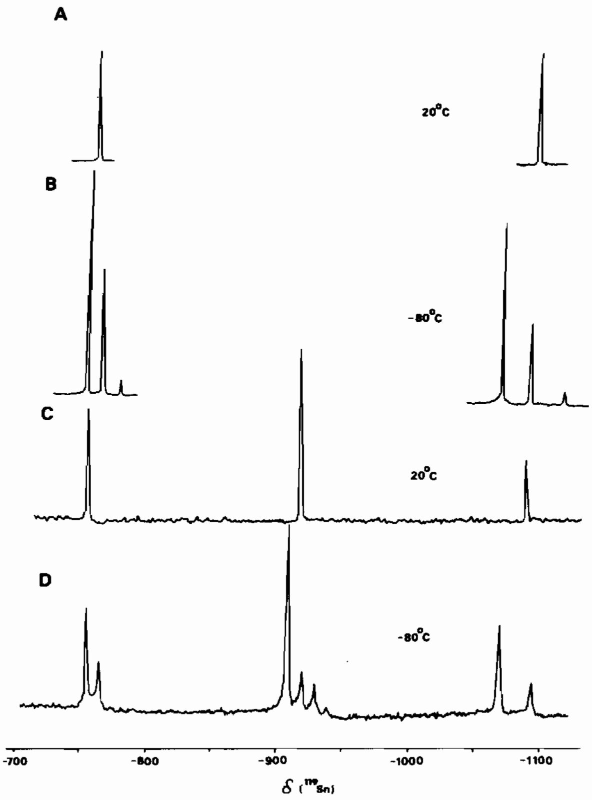

Fig. 3. A and B show tin-119 resonances for individual components $Sn(exa)_2Cl_2$ and $Sn(exa)_2Br_2$. C and D are tin-119 spectra for a 1:1 mixture of $Sn(exa)_2Cl_2$ and $Sn(exa)_2Br_2$.

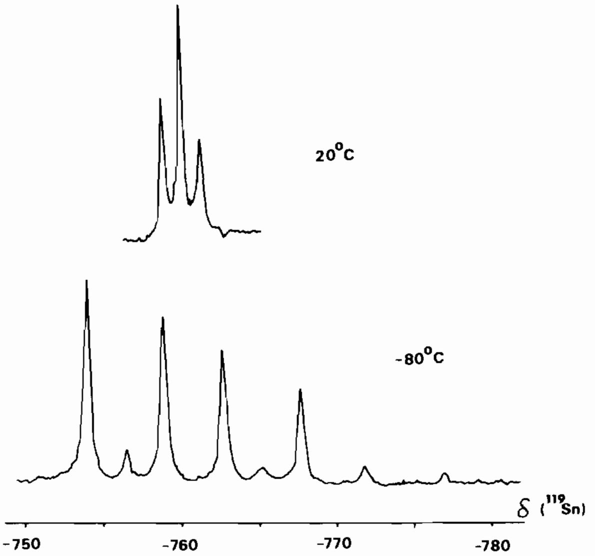

Fig. 4. Tin-119 spectra for a 1:1 mixture of $Sn(exa)_2Cl_2$ and $Sn(i\text{-}propxa)_2Cl_2$.

The tin-119 NMR spectrum of a dichloromethane solution containing equimolar quantities of $Sn(exa)_2Cl_2$ and $Sn(i\text{-}propxa)_2Cl_2$ (Table II) shows three resonances of relative intensities approximately 1:2:1. The outer two resonances are identified by their positions as due to the original components and the central resonance is assigned to the mixed xanthate ligand species $Sn(exa)(i\text{-}propxa)Cl_2$. Cooling this solution to −80 °C causes a dramatic change in the tin-119 spectrum (Fig. 4). Essentially resonances due to the original components are observed at this temperature with only very weak resonances attributed to the mixed species. Apparently formation of the mixed species Sn(exa)(i-propxa)Cl_2 is favoured at temperatures above which the monodentate–bidentate exchange of the xanthate ligands is rapid.

Sn(exa)$_3$X and Sn(exa)X$_3$

At room temperature the tin-119 spectrum of a dichloromethane solution containing equimolar quantities of $Sn(exa)_4$ and $Sn(exa)_2Cl_2$ shows three resonances of relative intensities 1:2:1. The two outer resonances are due to the original components and the central resonance is assigned to $Sn(exa)_3Cl$. Similarly, mixing the other dihalides with $Sn(exa)_4$ resulted in the formation of $Sn(exa)_3Br$ and $Sn(exa)_3I$. Tin-119 resonances for the $Sn(exa)_3X$ species remained essentially unchanged down to –70 °C (Table III) and it is assumed that these species are six coordinate with the xanthate ligands continuing the rapid exchange between monodentate and bidentate modes of coordination.

TABLE III. Tin-119 NMR Resonances for Mono- and Trihaloxanthates in CH_2Cl_2.

Compound	$\delta(^{119}Sn)$ (ppm)	Temperature (°C)
$Sn(exa)_3Cl^a$	–748	20
	–753	–70
$Sn(exa)_3Br^a$	–876	20
	–875	–70
$Sn(exa)_3I^a$	–1184	20
	–1176	–70
$Sn(exa)Cl_3{}^b$	–456	20
	–455	–70
$Sn(exa)Br_3{}^b$	–912	20

[a] 1:1 mixtures of $Sn(exa)_4$ and $Sn(exa)_2X_2$. [b] 1:1 mixtures of $Sn(exa)_2X_2$ and SnX_4.

The room temperature tin-119 NMR spectrum of a dichloromethane solution containing equimolar quantities of $SnCl_4$ and $Sn(exa)_2Cl_2$ comprises three resonances with approximate relative intensities 1:4:1. The resonance at lowest frequency (δ – 762 ppm) is due to $Sn(exa)_2Cl_2$ whilst the somewhat broader resonance ($W_{1/2}$ = 180 Hz) at highest frequency (δ – 192 ppm) is assigned to $SnCl_4$. The central resonance (δ – 456 ppm) is assigned to $Sn(exa)Cl_3$. The relative intensities of the signals suggest that formation of $Sn(exa)Cl_3$ is favoured above the statistical distribution.

At –70 °C the two higher frequency resonances sharpen only slightly whereas the resonance due to $Sn(exa)_2Cl_2$ splits into three signals similar to that observed for $Sn(exa)_2Cl_2$ at this temperature.

Substitution of a xanthate moiety by chlorine in the series $Sn(exa)_4$, $Sn(exa)_3Cl$, $Sn(exa)_2Cl_2$ causes only small shifts of $\delta(^{119}Sn)$ to lower frequency (δ – 739, –748, –762 ppm respectively) but on further substitution to $Sn(exa)Cl_3$ there is a drastic shift to high frequency (δ – 456 ppm). This is attributed to a change in coordination number from six to four so that chlorine bridged polymers in $Sn(exa)Cl_3$ solutions are unlikely.

The tin-119 NMR spectrum of a dichloromethane solution containing equimolar quantities of $SnBr_4$ and $Sn(exa)_2Br_2$ shows three resonances of relative intensities 1:1:1 at 20 °C. The outer resonances (δ – 655 ppm, –1190 ppm) are again identified as due to the initial components and the central resonance (–912 ppm) is assigned to $Sn(exa)Br_3$. The two resonances at higher frequency are somewhat broad ($W_{1/2}$ = 230 Hz). Cooling this solution to –40 °C causes the $Sn(exa)Br_3$ resonance to broaden ($W_{1/2}$ = 700 Hz) and at –80 °C it disappears with only the signals due to the initial components being present at this temperature (Table III). A possible explanation for these observations is that at room temperature the xanthate ligands are rapidly alternating between monodentate and bidentate coordination with the net result that the tin atom is essentially four coordinate in $SnBr_4$ and $Sn(exa)Br_3$. As the temperature is lowered the rate of monodentate–bidentate exchange becomes slower and at –80 °C the xanthate ligands act essentially as bidentate groups (as evidenced by the appearance of the $Sn(exa)_2Br_2$ spectrum at this temperature) which would require five coordination of the tin atom for the $Sn(exa)Br_3$. This appears to be unfavourable causing $Sn(exa)Br_3$ to disproportionate into the initial components $SnBr_4$ and $Sn(exa)_2Br_2$ which are four and six coordinate respectively. The different behaviour between $Sn(exa)Cl_3$ and $Sn(exa)Br_3$ is presumably due to the different size of the halogen atom. The corresponding iodo system could not be investigated because of the lower solubility of SnI_4 in dichloromethane.

References

1 G. Winter, *Rev. Inorg. Chem., 2,* 253 (1980).
2 C. L. Raston, P. R. Tennant, A. H. White and G. Winter, *Aust. J. Chem., 31,* 1493 (1978).
3 R. W. Gable, C. L. Raston, G. L. Rowbottom, A. H. White and G. Winter, *J. Chem. Soc. Dalton,* 1392 (1981).
4 R. Colton, D. Dakternieks and C. A. Harvey, *Inorg. Chim. Acta, 61,* 1 (1982).
5 R. Colton and D. Dakternieks, *Inorg. Chim. Acta, 71,* 101 (1983).