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The Preparation and Identification of Phases from the Tin(II) Chloride Glycylglycinate System

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Two new distinct products, $SnCl_2\cdot 2(C_4H_8N_2O_3)$ *and* $ClSn(C_4H_7N_2O_3)$ *can be obtained from the* $SnCl_2$: $C_4H_8N_2O_3$ *system. The IR,* ^{119}*Sn Mössbauer and thermal analytical data for the products are reported and discussed in terms of the bonding in these compounds.*

Introduction

Very few derivatives of tin(II) with biological molecules are known. A series of compounds prepared from some tin(II) halide: S-containing amino acid systems has recently been reported [1] but the only known derivative of an O-containing amino acid is diglycinatotin(II) [2].

We have studied the products obtained by reacting tin(II) chloride with the molecules glycylglycine, cytosine, adenine, inosine, adenosine and cytidine in methanol solution. The products of the reaction between $SnCl_2$ and all of the biological molecules (L) except glycylglycine under certain conditions are adducts with different values of n

$$SnCl_2 + nL \rightarrow SnCl_2\cdot Ln$$

and these compounds are described elsewhere [3]. Two different distinct products can be obtained from the $SnCl_2$:glycylglycine system. One of these is the adduct $SnCl_2\cdot 2(C_4H_8N_2O_3)$, but the other is a ternary compound of composition $ClSn(C_4H_7N_2O_3)$. The preparation and identification of these new compounds is described here.

Experimental

The products obtained from solutions of tin(II) chloride and glycylglycine in dry methanol were studied for different reaction times under oxygen-free nitrogen, and for different molar ratios of the reactants. The product obtained by refluxing a solution containing tin(II) chloride with either equimolar proportions or a two fold molar excess of glycylglycine for short periods of time (20–90 minutes) is always the adduct tin(II) chloride *bis* glycylglycine, $SnCl_2\cdot 2(C_4H_8N_2O_3)$.

The presence of glycylglycine in larger than two-fold excess leads to impure products and finally to the precipitation only of the excess of glycylglycine, at for example 4:1 excess. A two-fold molar excess of tin(II) chloride over glycylglycine leads, on refluxing, to an oil from which the only solid product obtained is also $SnCl_2\cdot 2(C_4H_8N_2O_3)$.

The product obtained by refluxing equimolar quantities of tin(II) chloride and glycylglycine under an oxygen-free nitrogen atmosphere in dry methanol for much longer periods (>10 hours) can however lead to the formation of either $SnCl_2\cdot 2(C_4H_8N_2O_3)$ or the ternary compound $ClSn(C_4H_7N_2O_3)$. The analytical data for these products are given in Table I.

TABLE I. Analytical Data for the Complexes (% calculated values in parentheses).

Compound	C%	H%	N%	Sm%	Cl%
$ClSnC_4H_7N_2O_3$	16.7 (16.83)	2.40 (2.45)	10.0 (9.82)	42.5 (41.63)	11.5 (12.45)
$SnCl_2\cdot 2C_4H_8N_2O_3$	20.5 (21.15)	3.51 (3.52)	11.6 (12.34)	26.6 (26.16)	15.7 (15.65)

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Elemental analyses for Sn were carried out by the method of Donaldson and Moser [4] ; chlorine was analysed by potentiometric titration with $AgNO_3$ solution. Carbon, hydrogen and nitrogen assays were carried out at the Department of Chemistry, The City University, (London) and the Laboratorio di Chimica Organica (Milano).

Ir spectra were obtained as mulls of Nujol and hexachlorobutadiene in the region 4000–250 cm^{-1}, using a Perkin Elmer 580 infrared spectrometer.

Thermal data were recorded using a Stanton Redcroft STA 780 simultaneous analyser by heating the sample in a furnace up to 600 °C, under a nitrogen atmosphere.

^{119}Sn Mössbauer data were measured using equipment previously described [5].

Results and Discussion

Infrared Spectra

The main features of the infrared spectra of $ClSn(C_4H_7N_2O_3)$ and $SnCl_2 \cdot 2(C_4H_8N_2O_3)$ are given in Table II. The spectrum for the chloride glycylglycinate shows changes in the regions of the -NH_2 and -CO_2 vibrations of glycylglycine on bond formation. The shifts in frequency and the appearance of new bands in the 3000–3400 cm^{-1} region of the spectrum are characteristic of the formation of a bond between the N of the -NH_2 group and the acceptor metal [3]. There are also significant changes in the symmetric and asymmetric vibrations of the -CO_2 group that are consistent with the formation of Sn–O bonds with the carboxylic acid moiety in an ester type bond [6]. There is very little difference in the frequencies of the peptide $\nu_{C=O}$ vibrations in the spectra of $ClSn(C_4H_7N_2O_3)$ and glycylglycine compared with those in the carboxylate CO region. This suggests that there is no bond formation between the peptide O atom and the tin. The appearance of new and broadened bands in the infrared spectra at 612 and 555 cm^{-1} are also in agreement with the formation of Sn–O and/or Sn–N bonds. The infrared data are thus consistent with tin(II), in $ClSn(C_4H_7N_2O_3)$, achieving its usual pyramidal three-co-ordination [7] with the formation of Sn–Cl, Sn–O and Sn–N bonds, perhaps in a polymeric structure of the type shown in Fig. 1.

TABLE II. Infrared Data for the Complexes.

$ClSnC_4H_7N_2O_3$ (cm^{-1})	$SnCl_2 \cdot 2(C_4H_8N_2O_3)$ (cm^{-1})	Assignment
3320	3360	ν_{NH_2}
3250	3295	
3100	3135	
1678	1678	$\nu_{C=O}$ (peptide)
1663	1662	
1622	1605	$\nu_{as}CO_2$
1557	1558	δNH (peptide)
1384	1410	ν_sCO_2

In contrast to the data for $ClSn(C_4H_7N_2O_3)$ the infrared spectrum for the adduct can only be consistent with the formation of Sn–N (amino) bonds. The significant difference between the spectra of the adduct and the free ligand are in the νNH_2 region in which $SnCl_2 \cdot 2(C_4H_8N_2O_3)$ shows peaks at 3360, 3295 and 3135 cm^{-1}. There are no differences between the spectrum of the adduct and the free ligand in the νCO (1678 and 1662 cm^{-1}), δNH (1558 cm^{-1}), $\nu_{as}CO_2$ (1605 cm^{-1}) and $\nu_{sym.}CO_2$ (1410 cm^{-1}) regions.

Thermal Decomposition

Tin(II) chloride glycylglycinate decomposes thermally, losing 37% of its total weight at 204 °C followed by slow loss of $SnCl_2$ at higher temperature. The weight loss of 37% leaves a residual product of $SnO + SnCl_2$. This residue of 53% is consistent with the formulation of the compound as $ClSn(C_4H_7N_2O_3)$.

The thermal decomposition process of the adduct $SnCl_2 \cdot 2(C_4H_8N_2O_3)$ is consistent with the existence of weak Sn–N interactions. The complex melts at 192 °C and this is immediately followed by two endothermic decompositions corresponding to a two-stage weight loss of 26%. The two weight losses occur at 204 (*ca.* 6%) and at 230 (*ca.* 20%), and can be attributed to loss of NH_3 and CO_2 respectively from both of the ligand molecules. This suggests that the Sn–N bonds are weak in that the complex melts and decomposes in a narrow temperature range by a process that is similar to the decomposition of glycylglycine itself but with the weight loss stages occurring at lower temperatures than for glycylglycine.

^{119}Sn Mössbauer Spectra

The ^{119}Sn Mössbauer data for $ClSn(C_4H_7N_2O_3)$ and $SnCl_2 \cdot 2(C_4H_8N_2O_3)$ are compared in Table III with those for other compounds with Sn–O, Sn–Cl and Sn–N bonds. The values of the chemical isomer shift and quadrupole splitting parameters for $ClSn(C_4H_7N_2O_3)$ are much closer to those of $Sn(CH_3$-

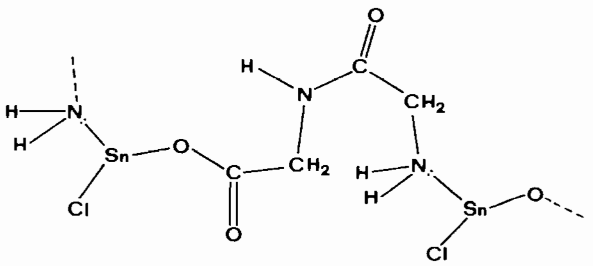


Fig. 1. The tin(II) chloride glycylglycinate.

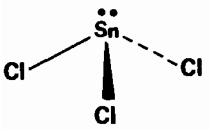
TABLE III. ^{119}Sn Mössbauer Data for the Complexes and Related Compounds, at Liquid N_2 Temperature.

Compound	δ mms^{-1}[a]	Δmms^{-1}	Ref.
$ClSn(C_4H_7N_2O_3)$	3.42	1.76	b
$SnCl_2 \cdot 2(C_4H_8N_2O_3)$	3.31	1.65	b
$SnCl_2$	4.12	0	8
$Sn(CH_3CO_2)_2$	3.21	1.77	9
$SnCl_2 \cdot 2$ morpholine	2.81	2.24	10

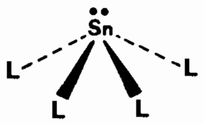
[a]Relative to $CaSnO_3$.
[b]This work.

$CO_2)_2$ than $SnCl_2$. This suggests that a strong Sn–O bond is formed when glycylglycine reacts with tin(II). This is consistent with the thermal decomposition data that suggest the residue of pyrolysis is a mixture of SnO and $SnCl_2$.

The shift for $SnCl_2 \cdot 2(C_4H_8N_2O_3)$ is lower than that for $SnCl_2$, and this is consistent with complex formation. Two main types of tin(II) chloride adduct are possible *viz.* (1) the formation of a trigonal pyramidal tin(II) moiety by co-ordination to only one donor atom of the ligand (A), or (2) the formation of a distorted four pyramidal moiety by co-ordination to two donor atoms of the ligand (B). There is no evidence from either thermal or ir data to suggest the presence of two different types of glycylglycine. This means that the two glycylglycine ligands must be in similar environments and that the tin adopts a four pyramidal co-ordination (B) with two strong Sn–Cl and two weak Sn–N interactions. The higher shift of 3.31 mms^{-1} in comparison to a typical $SnCl_2$ adduct with nitrogen donor molecules such as $SnCl_2 \cdot$2Morpholine is also consistent with the presence of only weak Sn–N interactions in $SnCl_2 \cdot 2(C_4H_8N_2O_3)$.



(A)



(B)

The relatively large quadrupole splittings found in $ClSn(C_4H_7N_2O_3)$ and $SnCl_2 \cdot 2(C_4H_8N_2O_3)$ are to be expected, in view of the low symmetry environments containing a lone pair, with bonds from Sn(II) to a mixture of different atoms.

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