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Synthesis, Mössbauer and Infrared Studies of Inorganic Tin Derivatives of Amino Acids

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Although organotin derivatives of amino acids have been the subject of much interest recently [1–5], there has been little work on the corresponding inorganic tin compounds. The only previous reports are by Hall and Zuckerman [6], on diglycinatotin(II), $Sn(O{\cdot}CO{\cdot}CH_2{\cdot}NH_2)_2$, and by Sumarokova *et al.*, on a number of adducts of tin(IV) [7] or tin(II) [8] chloride with glycine, alanine and leucine.

The nature of the products obtained from the aqueous tin(II) chloride/sulphur-containing amino acid systems depend upon the conditions of the preparation. When concentrated aqueous solutions of tin(II) chloride and L-cysteine are mixed in an equimolar ratio, monochloro(S-cysteinato)tin(II) hydrate is precipitated as a pale yellow powder:

$$SnCl_2 + HS{\cdot}CH_2{\cdot}CH(NH_2){\cdot}COOH + H_2O \rightarrow Cl{\cdot}Sn{\cdot}S{\cdot}CH_2{\cdot}CH{\cdot}(NH_2){\cdot}COOH, H_2O + HCl$$

However, when dilute aqueous solutions of L-cysteine or DL-penicillamine hydrochloride (1 mol) are neutralised with sodium bicarbonate solution, followed by the addition of aqueous tin(II) chloride (1 mol), the cyclic tin(II) derivatives are formed as white and pale brown precipitates respectively:

$$Sn^{2+} + HS{\cdot}CH_2{\cdot}CH(NH_2){\cdot}COOH + 2HCO_3^- \rightarrow \overline{Sn{\cdot}S{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO{\cdot}O} + 2CO_2 + 2H_2O$$

$$Sn^{2+} + HS{\cdot}CH_2{\cdot}CH(\overset{+}{N}H_3){\cdot}COOH + 3HCO_3^- \rightarrow \overline{Sn{\cdot}S{\cdot}CMe_2{\cdot}CH(NH_2)CO{\cdot}O} + 3CO_2 + 3H_2O$$

When methanolic solutions of tin(II) chloride (1 mol) and L-cysteine methyl ester hydrochloride (2 mols) are mixed and allowed to stand for 2 days, colourless crystals of the tin(IV) complex, dichlorobis-S,S^1-(O-methylcysteinato)tin(IV), $Cl_2Sn(S{\cdot}CH_2{\cdot}CH(NH_2){\cdot}COOMe)_2$, are deposited in 20% yield. This product could result from oxidative addition of tin(II) chloride to the disulphide bond in L-cysteine methyl ester dihydrochloride (which may be formed by oxidation of the cysteine ester):

TABLE I. Analytical and Mössbauer Data for the Tin(II) and Tin(IV) Amino Acid Derivatives.

	Compound	Analysis: Found (Calcd.)					^{119m}Sn Mössbauer Data	
		C	H	N	S	Cl	δ[a] (mm/sec)	ΔE_Q (mm/sec)
1	$Cl{\cdot}Sn{\cdot}S{\cdot}CH_2{\cdot}CH(NH_2){\cdot}COOH, H_2O$	12.58 (12.33)	2.58 (2.76)	4.83 (4.79)	10.47 (10.97)	12.36 (12.13)	4.16	1.70
2	$\overline{Sn{\cdot}S{\cdot}CH_2CH(NH_2){\cdot}CO{\cdot}O}$	15.04 (15.15)	2.19 (2.12)	5.83 (5.89)	13.06 (13.48)	–	3.87	2.45
3	$\overline{Sn{\cdot}S{\cdot}CMe_2{\cdot}CH(NH_2){\cdot}CO{\cdot}O}$	22.36 (22.58)	3.62 (3.42)	5.15 (5.27)	11.32 (12.06)	–	3.70	2.71
4	$Sn{\cdot}(O{\cdot}CO{\cdot}CH(NH_2){\cdot}CH_2Ph)_2$	49.07 (48.35)	5.14 (4.52)	6.29 (6.27)	–	–	2.95	2.10
5	$Sn(O{\cdot}CO{\cdot}CH_2NH_2)_2$[b]	–	–	–	–	–	3.06	1.88
6	$Cl_2Sn{\cdot}(S{\cdot}CH_2{\cdot}CH(NH_2){\cdot}COOMe)_2$	20.83 (20.98)	3.40 (3.53)	6.41 (6.12)	14.00 (14.00)	15.55 (15.48)	0.85	1.34

[a]Relative to $CaSnO_3$ (error in δ and ΔE_Q = ± 0.05 mm/sec). [b]Reference 6.

$$SnCl_2 + (MeO{\cdot}CO{\cdot}CH(\overset{+}{N}H_3\bar{C}l){\cdot}CH_2S)_2 \rightarrow$$

$$Cl_2Sn(S{\cdot}CH_2{\cdot}CH(NH_2){\cdot}COOMe)_2 + 2HCl$$

The O-bonded derivative, bis(β-phenylalaninato)tin-(II), $Sn(O{\cdot}CO{\cdot}CH(NH_2){\cdot}CH_2{\cdot}Ph)_2$, was prepared for comparison with the derivatives of the S-containing amino acids. It is precipitated in 40% yield when a solution of tributyltin β-phenylalaninate [1] (2 mols) in toluene is added to tin(II) chloride (1 mol) in methanol:

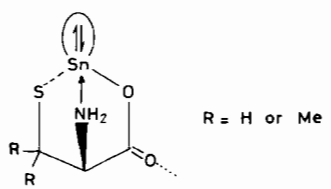
$$SnCl_2 + 2Bu_3SnO{\cdot}CO{\cdot}CH(NH_2){\cdot}CH_2Ph \rightarrow$$

$$Sn(O{\cdot}CO{\cdot}CH(NH_2){\cdot}CH_2Ph)_2 + 2Bu_3SnCl$$

The syntheses of these tin-amino acid derivatives were all carried out at room temperature and the analytical Mössbauer data for the new compounds are shown in Table I. The degree of hydration of the tin(II) aquo-complex was confirmed by thermogravimetric analysis (TGA). The tin(II)–sulphur bonded derivatives were found to be stable to oxidation, whereas bis(β-phenylalaninato)tin(II) slowly oxidised in air, as indicated by the appearance of a tin(IV) peak in the ^{119m}Sn Mössbauer spectrum.

The presence of tin–sulphur bonds in four of the complexes (*1–3, 6*) is confirmed by strong bands in their far infrared spectra at 365–376 cm^{-1} attributable to ν_{as} (Sn–S), (*c.f.* $Sn(SMe)_2$, which shows [9] ν_{as} (Sn–S) at 361 cm^{-1}). The crystalline tin(IV) complex (*6*) shows, in addition two bands at 277 cm^{-1} and 303 cm^{-1}, attributable to Sn–Cl stretching modes. In the near infrared region, the tin(IV) complex shows a doublet at 3067 cm^{-1} and 3125 cm^{-1}, indicative of a coordinated NH_2-residue, and a single band at 1724 cm^{-1}, due to a free carbonyl group, (*c.f.* $Me_2Sn(Cl)S{\cdot}CH_2{\cdot}CH(NH_2){\cdot}COOEt$, which is known [2] by X-ray crystallography to contain a chelating amino group and a free carbonyl moiety, and which shows [3] $\nu(NH_2)$ at 3243 cm^{-1} and 3309 cm^{-1} and ν(C=O) at 1733 cm^{-1}). This suggests that the tin(IV) complex has an octahedral structure with a *cis*-Cl_2Sn unit and two bidentate nitrogen-chelating amino acid residues.

The cyclic tin(II) esters of L-cysteine and DL-penicillamine (*2, 3*) show ν(C=O) bands at 1639 cm^{-1} and 1587 cm^{-1} respectively and may be weakly associated by intermolecular bridging carbonyl groups, as in the Pb(II) analogue, $\overline{Pb{\cdot}S{\cdot}CMe_2{\cdot}CH(NH_2){\cdot}CO{\cdot}O}$ (ν(CO) = 1587 cm^{-1}), which contains an intramolecularly coordinated NH_2-group [10]:



The compound $Cl{\cdot}Sn{\cdot}S{\cdot}CH_2{\cdot}CH(NH_2){\cdot}COOH$, H_2O (*1*), was also found to have a reduced ν(CO) frequency (1550 cm^{-1}) which may be due to weak intermolecular bridging.

An interesting feature of the ^{119m}Sn Mössbauer data (Table I) is that replacement of one or more Cl ligands in $SnCl_2$ (δ = 4.17 mm/sec; ΔE_Q = 0.00 mm/sec [11]), by sulphur containing amino acid groups (compounds *1–3*), results in only a slight drop in the values of the chemical isomer shift. This means that the total use of the tin bonding electrons in forming the bonds to the amino acid ligands must be very similar to that in $SnCl_2$ *i.e.* the tin is more likely to use *p*-electron density in bonding to the amino acid residue than *s*-electron density. It is significant, however, that the formation of Sn–O bonded derivatives (compounds *4, 5*), does result in a drop in the isomer shift, presumably because of greater use of Sn *s*-electron density in the Sn–O bond.

The appearance of a relatively large, resolvable, quadrupole splitting, ΔE_Q, for the amino acid derivatives, is indicative of an asymmetric environment about the tin atom. In compound *1*, replacement of one of the Cl atoms in $SnCl_2$ by an amino acid group, presumably results in the replacement of two of the short bonds in the tin(II) environment [12] by an Sn–S bond and, possibly, an N → Sn interaction. The greater asymmetry of the tin environment in $Cl{\cdot}Sn{\cdot}S{\cdot}CH_2{\cdot}CH(NH_2){\cdot}COOH$, H_2O results in the appearance of the resolvable quadrupole splitting. Replacement of the remaining Cl atom in compounds *2* and *3*, to give a tin environment containing one Sn–O bond, one Sn–S bond and, possibly, one N → Sn interaction, results in an increase in the quadrupole splitting. The smaller values of ΔE_Q for compounds *4* and *5*, in comparison with compounds *2* and *3*, again reflect the difference in Sn–S and Sn–O bond characteristics. The direction of the principal component of the electric field gradient, V_{zz}, in compounds *1–5* could lie either along the lone pair direction or, if the N → Sn interaction is weak, along the direction of that interaction. The ΔE_Q value for the tin(IV) derivative (*6*) is rather large for octahedral *cis*-Cl_2SnX_4 complexes [13] and probably arises from weak intermolecular N → Sn interactions.

This work indicates that, as with Pb(II) [10, 14] and organotin(IV) [2, 5, 15], inorganic Sn(II) and Sn(IV) appear to favour binding to a combination of S, O and N sites in amino acids. Further synthetic and spectroscopic work on these derivatives, together with details of the X-ray crystal structure of the tin-(IV) complex, will be published at a later date.

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